

UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE PATENT TRIAL AND APPEAL BOARD

ZHUHAI COSMX BATTERY CO., LTD.,
Petitioner

v.

NINGDE AMPEREX TECHNOLOGY LIMITED,
Patent Owner

Case IPR2023-00587
Patent No. 10,964,987

DECLARATION OF SAMUEL P. GIDO, PhD

CosMX Exhibit 1003, Page 1 of 512

TABLE OF CONTENTS

I.	INTRODUCTION	1
II.	BACKGROUND AND QUALIFICATIONS	2
III.	LEVEL OF ORDINARY SKILL IN THE ART	7
IV.	MATERIALS CONSIDERED AND RELIED UPON	8
V.	LEGAL STANDARDS	9
	A. Claim Construction	9
	B. Anticipation	10
	C. Obviousness	10
VI.	STATE OF THE ART	12
VII.	OVERVIEW OF PRIOR ART	38
	A. Nishikawa	38
	B. Iwai	39
	C. Honda	45
VIII.	THE '987 PATENT	46
IX.	CLAIM CONSTRUCTION	47
X.	THE CHALLENGED CLAIMS ARE UNPATENTABLE	48
	A. Ground 1: <i>Nishikawa</i> Would Have Anticipated Claims 1-2 and 4-9	48
	1. Claim 1	48
	2. Claim 2: The separator according to claim 1, wherein the porous layer has a thickness of 0.2 μm to 10 μm .	54

3. Claim 4: The separator according to claim 1, wherein a volume ratio of the inorganic particles to the binder is in a range from 0.2 to 3.0. 54
4. Claim 5: The separator according to claim 1, wherein the porous layer has a porosity of 20% to 90%. 60
5. Claim 6: The separator according to claim 1, wherein the inorganic particles are one or more selected from the group consisting of alumina, silica, magnesia, titanium oxide, hafnium dioxide, tin oxide, zirconia, cerium dioxide, nickel oxide, zinc oxide, calcium oxide, boehmite, aluminum hydroxide, magnesium hydroxide, calcium hydroxide, and barium sulfate. 60
6. Claim 7: The separator according to claim 1, wherein the binder is one or more selected from the group consisting of polyvinylidene fluoride, vinylidene fluoride-hexafluoropropylene copolymer, polyamide, polyacrylonitrile, polyacrylate, polyacrylic acid, polyacrylates, sodium carboxymethylcellulose, polyvinylpyrrolidone, polyvinyl ether, polymethyl methacrylate, polytetrafluoroethylene and polyhexafluoropropylene. 61
7. Claim 8: An energy storage device, comprising the separator according to claim 1. 62
8. Claim 9: The energy storage device according to claim 8, wherein the energy storage device is a lithium-ion battery. 62
- B. Ground 2: *Nishikawa* Would Have Rendered Obvious Claims 10-16 63
 1. Claim 10 63
 2. Claim 11: The method according to claim 10, wherein the solid content in the coating solution is in a range from 7% to 25%. 72

3. Claim 12: The method according to claim 10, wherein the coagulating solution comprises a second solvent and a third solvent, and the second solvent has a mass percentage of 20% to 60%. 72
4. Claim 13: The method according to claim 10, wherein the first solvent is one or more independently selected from the group consisting of N-methylpyrrolidone, dimethylacetamide and dimethylformamide. 73
5. Claim 14: The method according to claim 10, wherein the porous substrate comprises a polymer film, a multilayer polymer film, or a non-woven fabric formed by any one or more of the following polymers: polyethylene, polypropylene, polyethylene terephthalate, polyphthaloyl diamine, polybutylene terephthalate, polyester, polyacetal, polyamide, polyimide, polyetheretherketone, polyaryletherketone, polyetherimide, polyamide imide, polybenzimidazole, polyethersulfone, polyphenylene oxide, cycloolefin copolymer, polyphenylene sulfide, and polyethylene naphthalene. 74
6. Claim 15: The method according to claim 14, wherein the polyethylene is at least one selected from the group consisting of high density polyethylene, low density polyethylene, and ultrahigh molecular weight polyethylene. 74
7. Claim 16: The method according to claim 12, wherein the second solvent is one or more independently selected from the group consisting of N-methylpyrrolidone, dimethylacetamide and dimethylformamide, and the third solvent is one or more selected from the group consisting of deionized water, ethanol, propanol, acetone, dimethyl carbonate and diethyl carbonate. 75
- C. Ground 3: *Nishikawa* and *Honda* Would Have Rendered Obvious Claim 17 76

1.	Claim 17: The separator according to claim 1, wherein the porous layer has pores formed by the binder, at least a part of the inorganic particles are embedded in the pores.	76
D.	Ground 4: <i>Iwai</i> Anticipates Claims 1-2 and 4-9	78
1.	Claim 1	78
2.	Claim 2: The separator according to claim 1, wherein the porous layer has a thickness of 0.2 μm to 10 μm .	88
3.	Claim 4: The separator according to claim 1, wherein a volume ratio of the inorganic particles to the binder is in a range from 0.2 to 3.0.	88
4.	Claim 5: The separator according to claim 1, wherein the porous layer has a porosity of 20% to 90%.	92
5.	Claim 6: The separator according to claim 1, wherein the inorganic particles are one or more selected from the group consisting of alumina, silica, magnesia, titanium oxide, hafnium dioxide, tin oxide, zirconia, cerium dioxide, nickel oxide, zinc oxide, calcium oxide, boehmite, aluminum hydroxide, magnesium hydroxide, calcium hydroxide, and barium sulfate.	93
6.	Claim 7: The separator according to claim 1, wherein the binder is one or more selected from the group consisting of polyvinylidene fluoride, vinylidene fluoride-hexafluoropropylene copolymer, polyamide, polyacrylonitrile, polyacrylate, polyacrylic acid, polyacrylates, sodium carboxymethylcellulose, polyvinylpyrrolidone, polyvinyl ether, polymethyl methacrylate, polytetrafluoroethylene and polyhexafluoropropylene.	93
7.	Claim 8: An energy storage device, comprising the separator according to claim 1.	94

8.	Claim 9: The energy storage device according to claim 8, wherein the energy storage device is a lithium-ion battery.	95
E.	Ground 5: <i>Iwai</i> Would Have Rendered Obvious Claim 3	95
1.	Claim 3: The separator according to claim 1, wherein the pores have an average pore size of 0.3 μm to 20 μm .	95
XI.	CONCLUSION	1

LIST OF EXHIBITS

Exhibit	Description
Ex. 1001	U.S. Patent No. 10,964,987
Ex. 1002	Prosecution History of U.S. Patent No. 10,964,987
Ex. 1003	Declaration of Dr. Samuel Gido
Ex. 1004	Curriculum Vitae of Dr. Samuel Gido
Ex. 1005	Nishikawa et al., U.S. Patent No. 7,976,987
Ex. 1006	Iwai et al., U.S. Patent App. Pub. No. 2014/0248525
Ex. 1007	Honda et al., U.S. Patent App. Pub. No. 2015/0263325
Ex. 1008	Jurgen O. Besenhard (ed.), Handbook of Battery Materials (1999)
Ex. 1009	Seo et al., U.S. Patent No. 8,318,360
Ex. 1010	Lee et al., U.S. Patent No. 7,662,517
Ex. 1011	Sigma-Aldrich Safety Data Sheet for Aluminum hydroxide fine powder pure, hydrargillite
Ex. 1013	Sigma-Aldrich Safety Data Sheet for Poly [N,N'-(1,3-phenylene) isophthalamide]
Ex. 1017	Patnaik, Handbook of Inorganic Chemicals (2002)
Ex. 1018	Ahmad et al., Synthesis of Polyvinylidene Fluoride (PVDF) Membranes for Protein Binding: Effect of Casting Thickness, Journal of Applied Polymer Science (2013)
Ex. 1019	Katayama et al., U.S. Patent App. Pub. No. 2010/0221965

LIST OF APPENDICES

Appendix	Description
A	Showa Denko Webpage on HIGILITE® (Machine Translation)
B	Lin et al., Poly(m-phenylene isophthalamide) (PMIA): A potential polymer for breaking through the selectivity-permeability trade-off for ultrafiltration membranes, <i>Journal of Membrane Science</i> 518 (2016) 72-78.
C	Huang et al., Ionic Conductivity of Microporous PVDF-HFP/PS Polymer Blends, <i>Journal of The Electrochemical Society</i> , 148 (3) A279-A283 (2001).
D	Kynar Flex 2801 Technical Data Sheet
E	Kynar Flex 2751 Technical Data Sheet
F	U.S. National Transportation Safety Board, Incident Report NTSB/AIR-14/01, PB2014-108867. Auxiliary Power Unit Battery Fire, Japan Airlines Boeing 787-8, JA829J, Boston, Massachusetts January 7, 2013.
G	Prosini et al., A novel intrinsically porous separator for self-standing lithium-ion batteries, <i>Electrochimica Acta</i> 48 (2002) 227-233.
H	Hotza et al., Review: aqueous tape casting of ceramic powders, <i>Materials Science and Engineering A</i> 202 (1995) 206-217.
I	Huang, Separator technologies for lithium-ion batteries, <i>J. Solid State Electrochem.</i> (2011) 15:649–662.
J	Arora et al., “Battery Separators” <i>Chem. Rev.</i> 2004, 104, 4419-4462.
K	Venugopal et al., Characterization of microporous separators for lithium-ion batteries, <i>J. Power Sources</i> 1999, 77, 34.
L	Kim et al., U.S. Patent No. 7,709,152
M	Park et al., U.S. Patent No. 7,695,870
N	Lee et al., U.S. Patent No. 7,638,241
O	“A basic guide to particle characterization,” published by Malvern Instruments Ltd. (2015)
P	Choi et al., Enhancement of thermal stability and cycle performance in lithium-ion cells through the use of ceramic coated separators, <i>Journal of Power Sources</i> , Vol. 195, pp. 6192-6196, 2010.
Q	Shinohara et al., U.S. Patent No. 6,447,958
R	Zhang, A review on the separators of liquid electrolyte Li-ion batteries, <i>Journal of Power Sources</i> 164 (2007) 351–364
S	Isaacson et al., U.S. Patent No. 3,558,764

T	Larsen et al., U.S. Patent No. 3,351,495
U	Lundquist et al., U.S. Patent No. 4,650,730
V	Yu et al., U.S. Patent No. 5,565,281
W	Yu et al., U.S. Patent No. 5,952,120
X	Carlson et al., U.S. Patent No. 6,306,545
Y	Kim et al., Characteristics of PVdF-HFP/TiO ₂ composite membrane electrolytes prepared by phase inversion and conventional casting methods, <i>Electrochimica Acta</i> 51 (2006) 5636–5644.

I, Samuel Gido, of Amherst, Massachusetts, declare that:

I. INTRODUCTION

1. My name is Samuel Gido, and I have been retained by counsel for Petitioner Zhuhai CosMX Battery Co., Ltd. (“Petitioner”) as an expert witness to provide assistance regarding U.S. Patent No. 10,964,987 (“the ’987 Patent”). Specifically, I have been asked to consider the validity of claims 1-17 of the ’987 Patent (the “challenged claims”) in view of prior art, anticipation and obviousness considerations, and the understanding of a person of ordinary skill in the art at the time of the invention (“POSA”) as it relates to the ’987 Patent. I have personal knowledge of the facts and opinions set forth in this declaration and believe them to be true. If called upon to do so, I would testify competently thereto.

2. I am being compensated for my time at my standard consulting rate. I am also being reimbursed for expenses that I incur during the course of this work. My compensation is not contingent upon the results of my study, the substance of my opinions, or the outcome of any proceeding involving the challenged claims. I have no financial interest in the outcome of this matter or on the pending litigation between Petitioner and Patent Owner.

3. My analysis here is based on my years of education, research and experience, as well as my investigation and study of relevant materials, including those cited herein.

4. I may rely upon these materials, my knowledge and experience, and/or additional materials to rebut arguments raised by the Patent Owner. Further, I may also consider additional documents and information in forming any necessary opinions, including documents that may not yet have been provided to me.

5. My analysis of the materials in this proceeding is ongoing and I will continue to review any new material as it is provided. This declaration represents only those opinions I have formed to date. I reserve the right to revise, supplement, and/or amend my opinions stated herein based on new information and on my continuing analysis of the materials already provided.

II. BACKGROUND AND QUALIFICATIONS

6. I have been on the faculty at the University of Massachusetts at Amherst since 1993. I am currently Associate Professor of Polymer Science and Engineering. I have broad expertise across the fields of polymers (plastics), polymer-nanoparticle composites, fluorinated polymers, polyolefins, porous materials, phase separations, and coating processes. I am an expert in and experienced user of a range of materials characterization techniques including scattering, and spectroscopies, but with a particular emphasis on microscopy, especially electron microscopy. Over the years I have studied materials for a broad range of applications including: batteries, fuels cells, adhesives, non-stick coatings, elastomers, composites and nanostructures. In addition to academic research, I have done research for, and/or consulted for a

range of companies including: W.L. Gore, Boston Scientific, FujiFilm (Japan), Kureha Chemical Industry (Japan), Loctite Corp. (now Henkle), Rexam Graphics, St. Gobain, and Scapa Tape.

7. I studied for my bachelor's degree in Chemical Engineering at Princeton University, and graduated *Magna Cum Laude* in 1988. While at Princeton I did research at the nearby Textile Research Institute (<https://www.triprinceton.org/what-we-offer>) ("TRI"), where I focused on applying foamed coatings to porous substrates. I completed a bachelor's thesis on this topic; the title of my thesis was: "Foam Flow Through Porous Media: Image Analysis Development & Investigation of Microscopic Flow Mechanism." TRI also provided my first involvement in using scanning electron microscopy (SEM) to coatings and porous materials.

8. After graduating from Princeton in 1988, I moved on to a doctoral program at the Massachusetts Institute of Technology (MIT). My home department at MIT was Chemical Engineering, but I also was part of the interdisciplinary Program in Polymer Science and Technology (PPST, <http://polymerscience.mit.edu/>). I did my research and doctoral thesis under the direction of Prof. Edwin L. Thomas, who was in the Materials Science and Engineering Department at MIT. Prof. Thomas is a world-renowned expert in the study of polymer structure using electron microscopy. Therefore, my training and

research at MIT focused on the use of electron microscopy, including SEM and transmission electron microscopy (TEM), to study a range of different topics including plastics, rubbers, copolymers, polymer-ceramic composites, phase behavior, and phase separations. After receiving my Ph.D. in 1993, I moved on to begin my career as an Assistant Professor in the Polymer Science and Engineering Department at the University of Massachusetts at Amherst. Over my academic career I have received millions of dollars of research funding from government (U.S. Army, National Science Foundation, U.S. Department of Education), foundations (Bill and Melinda Gates Foundation, W. M. Keck Foundation), and industry.

9. I have focused on a bottom-up concept of new materials design for advanced applications. In particular, I have worked on development of new molecular structures for the control of nanometer and micrometer length scale structure and morphology, directed toward improving properties such as: mechanical strength, transport (diffusion) of gases and liquids in porous materials, electrical properties, and adhesion. A large part of this research is on controlling the phase separation behavior (coagulation) of material to form unique, functional structures. One particular published study was on using phase separation to produce porous structures in high density polyethylene. *See* Ex. 1004 (Peer-Reviewed Publication 65).

10. I have numerous publications and a U.S. Patent on fluorinated polymers

for a range of applications, including in separators for batteries and fuel cells. I have done research on materials for batteries and fuel cells, including fluorinated polymers and polymer particle composites, with funding from Kureaha (Japan), and the U.S. Army. In these studies, we developed polymer chemistries, nanometer and micrometer scale composite structures and porous structures, and coating processes to enhance ion conductivity in the separator layers. Additionally, I have worked and continue to work as a consultant for W. L. Gore, a leading company in fluorinated polymers. I have consulted for industry on the topic of coating processes, particularly for Rexam Graphics and Scapa Tape. I was also a co-founder of a startup company, Smart Surfaces LLC, that developed environmentally friendly, non-stick coatings for boats (and other structures in a marine environment) to prevent fouling with marine organisms. Smart Surfaces was sold to FujiFilm in 2006, and I continued to consult for the resultant company: FujiFilm Smart Surfaces LLC. These coatings, were silicone based, contained ceramic filler particles, and cured by a coagulation (phase separation) process.

11. I did a research project for Loctite Corporation in which I used electron microscopy to study adhesive polymer layers filled with inorganic reinforcing particles. And I did research for Boston Scientific, which resulted in a U.S. Patent, on polymer coatings for heart stents, using a number of techniques including electron microscopy. These coatings contained filler particles, a particulate drug, and we

studied the diffusion of this drug through the coating layer.

12. One of the best ways to really understand a topic is to teach it to someone else. I have taught and continue to teach topics, relevant to this matter, to our advanced graduate students (doctoral candidates) in the Polymer Science and Engineering Department at the University of Massachusetts at Amherst. In past years I have taught PSE 608 Introduction to Polymer Engineering, which includes topics such as mechanical properties, coatings processes, and diffusion of ions in materials. I have also taught in the past and am currently teaching PSE 602 Polymer Characterization Laboratory, in which the students gain practical laboratory experience with techniques of importance in this matter including SEM, and static laser light scattering (aka laser diffraction) for size determination. I teach PSE 608 Physical Chemistry of Polymers I and PSE 789 Physical Chemistry of Polymers II. In this sequence of classes, I cover, among other things, phase behavior and phase separations (coagulation), and the theory of laser light scattering. I also teach PSE 721 Polymer Morphology. This class focuses on nanometer and micrometer size structure in polymers and composites, as well as the use of electron microscopy to study materials structure. In PSE 608 and also in PSE 721, polyethylene is repeatedly used as an example for in depth discussion of polymer structure, and characterization methods. I also teach a seminar class for freshman, FFYS 191POLY The Polymer Age, which focuses on popular and societal impacts of polymers. In this class, I

present a seminar on lithium ion batteries with a particular focus on the materials used in their construction and the safety issues related to separators.

III. LEVEL OF ORDINARY SKILL IN THE ART

13. In rendering the opinions set forth in this declaration, I was asked to consider the patent claims and the prior art through the eyes of a person of ordinary skill in the art (“POSA”) at the time of the alleged invention, which I understand is asserted to be as early as April 11, 2018. I understand that determining the ordinary skill in the art includes looking, among other considerations, at (i) the type of problems encountered in the art; (ii) prior art solutions to those problems; (iii) rapidity with which innovations are made; (iv) sophistication of the technology; and (v) educational level of active workers in the field. I understand that a POSA is not a specific real individual, but rather is a hypothetical individual having the qualities reflected by the factors above. I understand that a POSA would also have knowledge from the teachings of the prior art, including the art cited below.

14. Taking these factors into consideration, on or before April 11, 2018, a POSA of the ’987 Patent would have had at least a bachelor’s degree or equivalent degree from an accredited institution in chemistry, chemical engineering, materials science, or a similar discipline covering relevant principles of organic and inorganic chemistry, polymer processing, ceramic materials, and ceramic processing, as well as three or more years of experience in electrochemical energy storage devices,

lithium-ion battery technology, separators, characterizations and analyses of particle size, film thickness, and/or materials compositions, battery performance characterization, or other applications of polymer chemistry, ceramic chemistry, and ceramic processing. More education could substitute for less experience, and vice versa.

15. With bachelors and PhD degrees in Chemical Engineering, and years of experience working in the fields of polymers, polymer-filler composites, polymer processing, coatings, batteries and other energy storage devices, electron microscopy and laser diffraction, I meet and surpass the definition of a POSA in this matter. Before April 11, 2018, my level of skill in the art was at least that of a POSA. I am qualified to provide opinions concerning what a POSA would have known and understood at that time, and my analysis and conclusions herein are from the perspective of a POSA as of that date.

IV. MATERIALS CONSIDERED AND RELIED UPON

16. In reaching the conclusions described in this declaration, I have relied on the documents and materials cited herein as well as those identified in this declaration, including the '987 Patent, the prosecution history of the '987 Patent, and prior art references cited herein. These materials comprise patents, related documents, and printed publications. Each of these materials is a type of document that experts in my field would have reasonably relied upon when forming their

opinions.

17. In quoting the cited references, all emphasis is added unless otherwise noted.

18. I have also relied on my education, training, research, knowledge, and personal and professional experience in the relevant technologies and systems that were already in use prior to, and within the timeframe of the earliest asserted invention date of the claimed subject matter in the '987 Patent, which is April 11, 2018.

V. LEGAL STANDARDS

19. I am not a lawyer. My understanding of the legal standards to apply in reaching the conclusions in this declaration is based on discussions with counsel for Petitioner and my reading of the documents submitted in this proceeding. In preparing this declaration, I have tried to faithfully apply these legal standards to the challenged claims.

A. Claim Construction

20. I have been instructed that the terms appearing in the '987 patent should be interpreted in view of the claim language itself, the specification, the prosecution history of the patent, and any relevant extrinsic evidence. The words of a claim are generally given their ordinary and customary meaning, which is the meaning that the term would have to a POSA at the time of the invention, which I have assumed

here is April 11, 2018. While claim limitations cannot be read in from the specification, the specification is the single best guide to the meaning of a disputed term. I have followed these principles in reviewing the claims of the '987 patent and forming the opinions set forth in this declaration.

B. Anticipation

21. I have been told that under 35 U.S.C. § 102, a patent claim is invalid if its subject matter was patented or described in a printed publication before the effective filing date of the claimed invention. I have been told that this is referred to as invalidity by anticipation. I have been told that a patent claim is anticipated under § 102 if a single prior art reference discloses, either expressly or inherently, all limitations of the claimed invention.

C. Obviousness

22. I understand that the existence of each and every element of the claimed invention in a prior art does not necessarily prove obviousness and that most, if not all, inventions rely on building blocks of prior art. But I have been told that under 35 U.S.C. § 103, a patent claim may be obvious if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a POSA to which said subject matter pertains. I have been told that a proper obviousness analysis requires the following:

- a. Determine the scope and content of the prior art;
- b. Ascertain the differences between the prior art and the claims at issue;
- c. Resolve the level of ordinary skill in the pertinent art; and
- d. Consider evidence of secondary indicia of non-obviousness (if available).

23. I have been told that the relevant time for considering whether a claim would have been obvious to a POSA is the time of invention. For my obviousness analysis, counsel for Petitioner instructed me to assume that the date of invention for the challenged claims is April 11, 2018. My opinions would not change if I assumed a later date of invention.

24. I have been told that a reference may be modified or combined with other references, or with a POSA's own knowledge, if the person would have found the modification or combination obvious. I have also been told that a POSA is presumed to know all the relevant prior art, and the obviousness analysis may take into account the inferences and creative steps that a POSA would employ.

25. I have been told that whether a prior art reference renders a patent claim obvious is determined from the perspective of a POSA. I have also been told that, while there is no requirement that the prior art contain an express suggestion to combine known elements to achieve the claimed invention, and while a suggestion to combine known elements to achieve the claimed invention may come from the prior art as a whole or individually and may consider the inferences and creative

steps a POSA would employ, as filtered through the knowledge of one skilled in the art, obviousness grounds cannot be sustained by mere conclusory statements and must include some articulated reasoning with some rational underpinning to support the legal conclusion of obviousness.

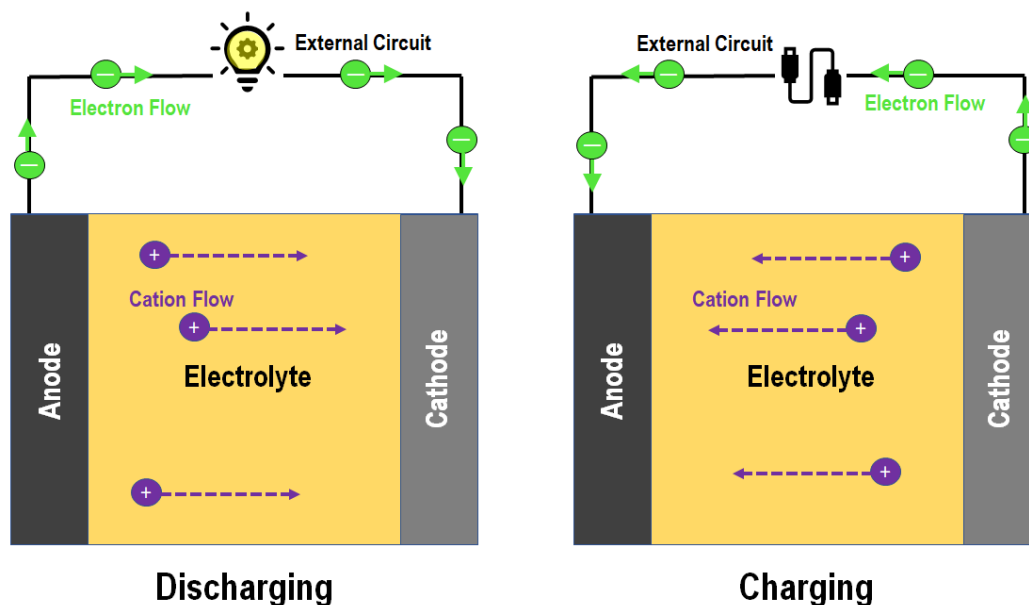
26. I have been told that there is no rigid rule that a reference or combination of references must contain a “teaching, suggestion, or motivation” to combine references. However, I also have been told that the “teaching, suggestion, or motivation” test can be used in establishing a rationale for combining elements of the prior art. I have also been told to be aware of distortions caused by hindsight bias, and that reading into the prior art the teachings of the invention at issue is improper.

VI. STATE OF THE ART

27. The most basic structure of any battery is illustrated below, in which an anode (negative electrode) and a cathode (positive electrode) are separated from one another and immersed in an electrolyte (medium capable of transporting ions). On discharging, positive ions, known as cations (atoms missing one or more electrons), diffuse through the electrolyte, from the anode across the gap to the cathode. In order to maintain electrical neutrality, electrons move separately through an external circuit from the anode to the cathode, where they are recombined with the cations to reform atoms. As the electrons make this journey through the external circuit they comprise an electrical current, which can be used to perform work, such as lighting

a lightbulb (as shown), or running an electric vehicle, computer, or smart phone. Charging the battery is the reverse process, in which an external voltage is used to push electrons through the external circuit back to the anode, creating cations at the cathode that migrate through the electrolyte to meet the electrons and reform the atoms at the anode.

General Battery Schematic



28. The term “battery” was coined by Benjamin Franklin in 1749 to refer to a rechargeable electrical power storage device he had built, which was actually an array of capacitors. Around 1799-1800, Italian scientist Alessandro Volta demonstrated the first true battery, consisting of alternating stacks of copper and zinc (the electrodes), separated by layers of cloth or cardboard soaked in brine or weak

acid (electrolyte). The rechargeable, or secondary, battery was invented in 1859 by Gaston Plante. This was a lead-acid battery similar to those still used today to start internal-combustion-powered vehicles. Plante also pioneered the spiral-rolled arrangement of electrodes and separator, still used in cylindrical batteries.

29. The first mass-produced and widely marketed battery was the Columbia Dry Cell, introduced by the National Carbon Company in 1896. It had a cylindrical shape, larger but recognizable to modern eyes. It also featured a cylindrically coiled cardboard separator between the anode and cathode. Alkaline batteries, the common disposable batteries still in common use, were invented in the 1950s and commercialized in 1959 by Union Carbide, the descendant of the National Carbon Company.

30. Lithium primary batteries (single use) were first conceived and studied in the 1960s. The 1970s and 1980s saw extensive development of lithium-ion secondary (rechargeable) batteries, culminating in the commercialization of the first lithium-ion battery by Sony in 1991. The 2019 Nobel Prize in Chemistry was awarded to three scientists who were instrumental in this work to develop practical lithium-ion batteries.

31. In a battery, the two electrodes, anode and cathode, must never touch. If they do, an electrical short circuit will result, discharging the battery so quickly that resistive heating from the high current inside the battery may cause a fire or

explosion, especially if the electrolyte fluid is combustible.

32. There are workable battery designs in which electrodes (for instance plates of metal and metal oxides) are suspended, apart from each another, in a bath of electrolyte fluid. A lead acid car battery is like this. But this is inefficient. The energy density of a battery (energy stored divided by the weight) is increased if the electrodes can be placed very close together, bearing in mind that they must also be prevented from ever actually contacting. Modern and emerging applications like electric vehicles and handheld electronics require high battery energy density.

33. To make batteries more energy dense, and thus more portable, separators are employed to act as a physical barrier as the electrodes are brought very close together. The production of modern battery configurations involves rolling long strips of electrodes into jellyroll structures to fit into cylindrical or prismatic cans, or squeezing multilayered sandwiches of electrodes into flat pouches. These processes force anode and cathode layers against one another and would cause them to touch if it were not for separator layers inserted between the electrodes.

34. The separators must be electrically insulating with respect to current flow carried by electrons. They must be chemically stable in the strong oxidizing and reducing environment of battery electrochemistry. And they must facilitate the transport of cations (positively charged atoms). The separation function and the ion conduction function are usually accomplished by separate materials. For instance,

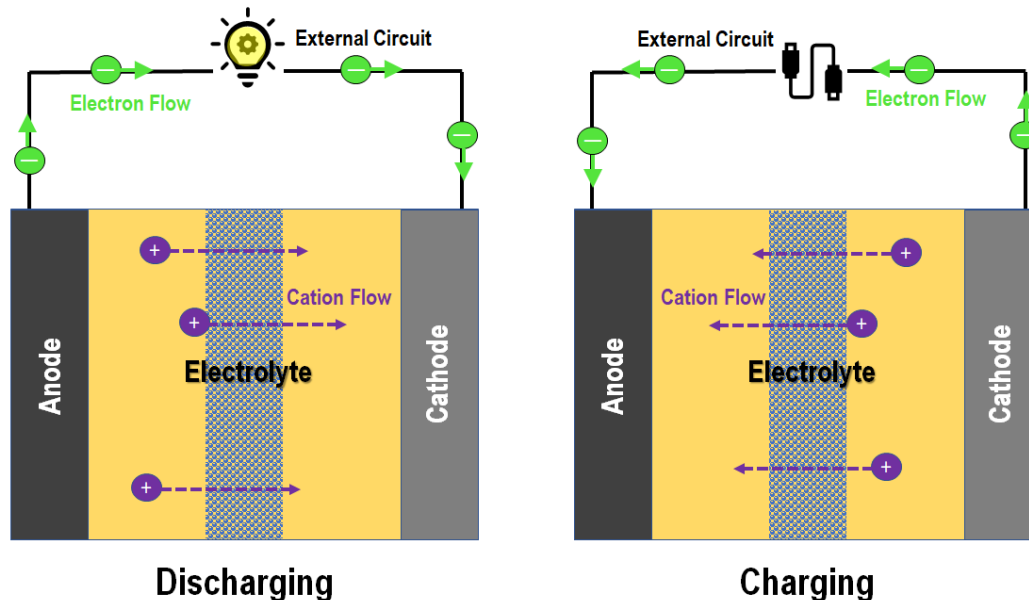
Volta's battery "pile" used cardboard separators soaked in a brine solution electrolyte.

35. Because of their high energy density and ability to withstand many discharging and charging cycles with little loss of capacity, lithium-ion batteries have become ubiquitous in the modern world. They power our smart phones, laptop computers, electric cars, and myriad other devices. They are beginning to be used to balance and back up our power grids to allow greater integration of green energy sources such as wind and solar. The rapid rise of these applications has led to a strong push over the past two decades, by industrial and academic researchers, to optimize lithium-ion batteries by, for example, improving energy density, charge and discharge rates, reliability and safety.

36. A schematic of the most common embodiment of the modern lithium-ion battery is shown below. A typical anode is formed of, for instance, a lithium carbon (graphite) intercalation compound coated onto a copper foil current collector. A typical cathode is formed of, for instance, lithium metal oxide dispersed in a polymer binder, coated onto an aluminum foil current collector. The anode and cathode are separated by a separator, which is typically a porous structure impregnated with a fluid electrolyte. The electrolyte fluid is generally a polar organic solvent, such as an organic carbonate liquid. Lithium cations are solubilized in this electrolyte solvent and can move between the electrodes by passing through the

separator.

Li-Ion Battery with Separator



37. In the 2000s, as lithium-ion batteries became ever more ubiquitous in portable devices, rare battery fires and explosions started to become a problem. With billions of these batteries being used in the world, even a rare problem produced a significant number of incidents. A famous case was the 2013 grounding of the Boeing 787 due to battery fires in Boston and Japan. *See, e.g.*, Appendix F. These fires in lithium-ion batteries result from short circuits in which the separator is breached. This can occur upon overcharging of the battery, in which lithium metal dendrites (sharp pointy structures) grow from the anode, pierce the separator, and contact the cathode. Short circuits can also result from damage to the battery such as

a puncture. Short circuits lead to thermal runaway, which is a feedback cascade of structural damage due to heating, from high current, producing even more damage, which leads to more current and more damage, rapidly escalating to a fire or explosion of the organic liquid electrolyte, which has combustibility similar to gasoline. Additionally: “Both shrinking and melting of the separator could result in physical contact of the electrodes so that direct chemical reactions between the strongly oxidative cathode material and the strongly reductive anode material occur, and the generated heat causes thermal runaway.” Appendix R, 359.

38. Thus, over the last two decades, increasing the safety of battery separators has been a focus of extensive effort by those of skill in the art. One approach is to increase the mechanical robustness and high temperature stability of separators. For instance, the Evonik-Degussa SEPARION separator uses a porous non-woven fabric of polyethylene terephthalate (PET) fibers coated with ceramic particles, using a sol-gel process that does not use a polymer binder. PET has better high temperature stability than, for instance, polyolefins. Adding the ceramic coating further increases heat resistance. Appendix J, 4427.

39. It had been known for a long time (about a century) that adding inorganic particles to a polymer material can increase the strength and high temperature performance of the polymer. This was not a discovery of people working on battery separators, but rather comes from related, broader fields of

polymer processing, polymer compounding, and composite materials. For instance, car tires are black because the rubber (which is inherently white or slightly yellowish) is mixed with carbon black, an inorganic, particulate form of carbon. Without carbon black the rubber tires would be too soft and weak and would fail easily, especially at high temperatures experienced on a hot road in summer and exacerbated by repetitive, high-rate mechanical flexing. The inorganic filler particles improve the strength of the rubber and allow it to maintain its strength to higher temperatures. This is because the inorganic particles are themselves stable to very high temperature and because they reinforce the polymer molecules such that they are less likely to be degraded by high temperature, and to the degree that some degradation of the polymer occurs the presence of the inorganic filler mitigates the effect on properties.

40. Other high temperature resistant separators were produced in which inorganic, ceramic, particles were mixed with a polymer and cast to produce a free-standing film (*see, e.g.*, Appendix G, Appendix Q) or coated directly onto electrodes. The investigators who worked on these approaches in the 2000s and 2010s were importing, into the field of batteries, longstanding knowledge about polymer and ceramic properties and processing, especially knowledge of coating processes to produce thin films or tapes of polymer-ceramic slurries or mixtures. *See, e.g.*, Appendix H. This had already been used for a broad range of disparate applications, from porous coatings on specialty inkjet paper to capacitors.

41. Besides making battery separators stronger and more heat resistant, another approach to lithium-ion battery safety was to give separators a thermal shut-off functionality. This is achieved using uniaxially or biaxially stretched (oriented) porous, polyolefin separator films. The two polyolefin materials most often used in this capacity are polyethylene (PE) and polypropylene (PP). Different grades of PE are available and used in these applications, including low density polyethylene, high density PE (HDPE), and ultrahigh molecular weight PE (UHMWPE). In a dry process, solid films of polyolefin are mechanically stretched in one direction (uniaxial) or two directions (biaxial). This opens up voids or pores in the film. There is also a wet process for making polyolefin separators, based on a phase separation or a coagulation (phase inversion) process of the polyolefin from solvents, which also often incorporates stretching of the separator film.

42. The images below are scanning electron microscope (SEM) images of polyolefin separators produced by the dry (a) and wet (b) processes. Appendix I, Appendix J. Separator (a) has been uniaxially stretched (vertical direction) creating pores that are elongated in the direction of stretch, and separator (b) has more of a biaxial (in plane) orientation.

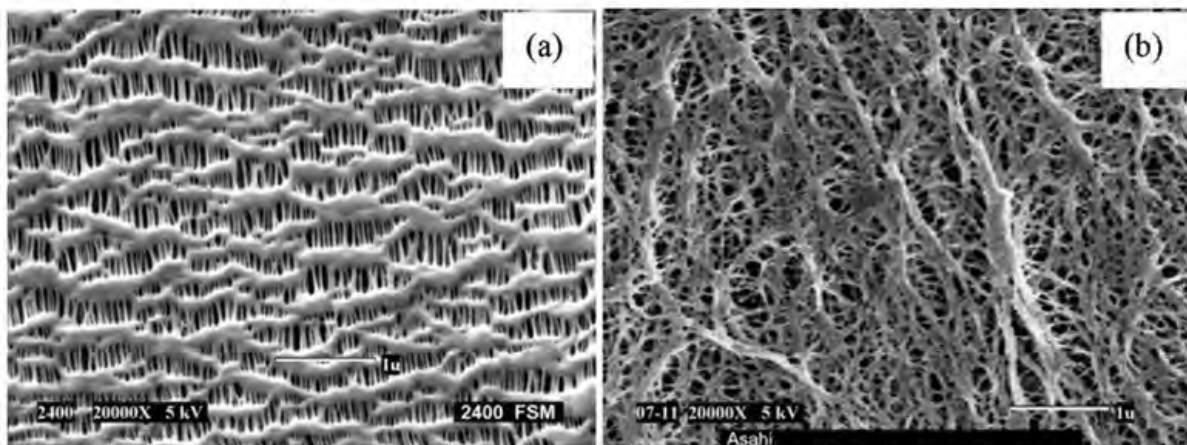


Fig. 4 Separators fabricated by the dry (a) and the wet (b) processes [7]

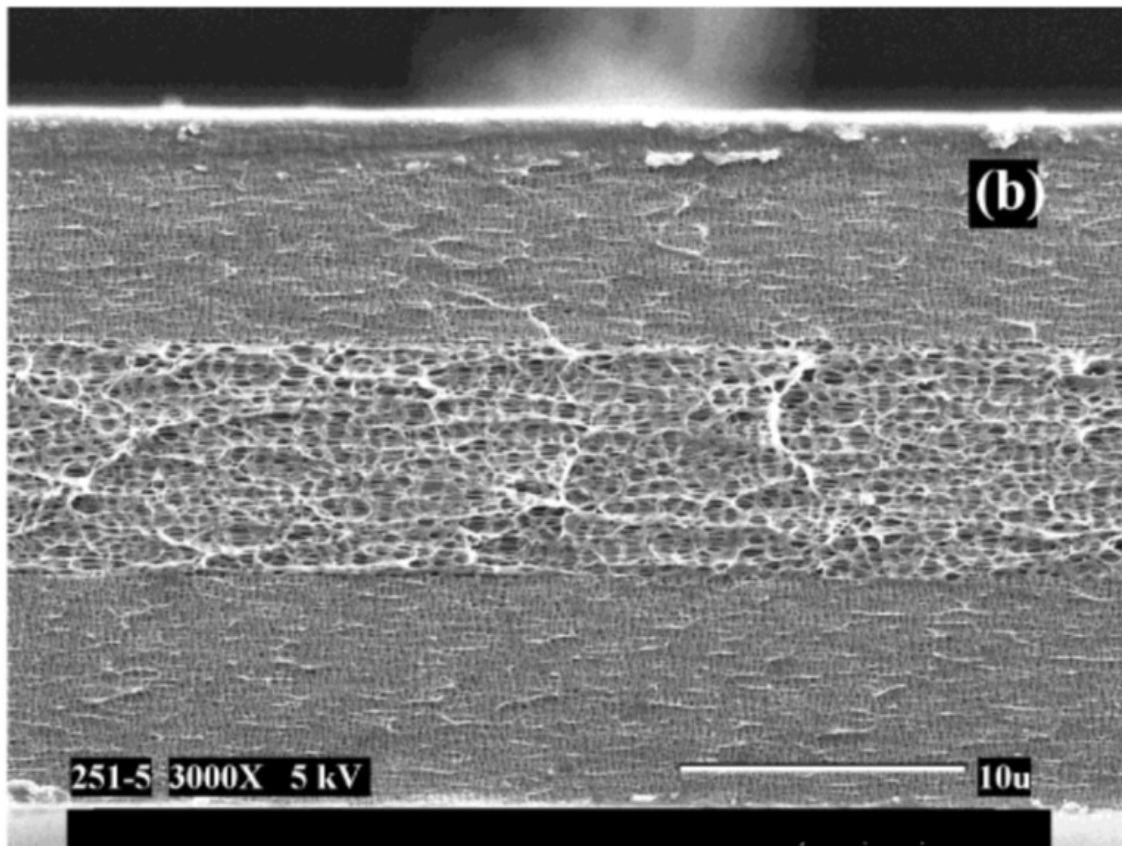
43. The melting point of HDPE and UHMWPE varies slightly with different resins and different processing histories, but is generally in the range of 120°C to 130°C. In the event of a short circuit or a puncture, a battery with a PE separator is resistant to a thermal runaway because the PE melts and as it does it shrinks to close off the pores. This converts the porous layer into a layer which is impermeable and electrically insulating. This restricts ion flow and short circuited electron current, and shuts down or at least slows the process to the point where the battery is less likely to burst into flames. Appendix I, Appendix J.

44. Although a PE separator can perform this shutoff function, the heat shrinkage of the PE tends to be more than is required to simply close off the pores and shut down the short circuit. A PE separator can shrink and distort to such a high degree that it loses its mechanical integrity, pulls the wider battery structure apart,

and bigger holes are opened up in the separator, exacerbating the thermal runaway. To address this shortcoming, multi-layer polyolefin separators were developed that have both PE and PP layers.

45. The image below is a cross-sectional SEM image of a three-layer separator (Celgard 2325) with two PP outer layers and an inner PE layer. Appendix J. PP has a higher melting point in the range of 160°C to 170°C. In the event of a short circuit and temperature increase, the PE layer of this separator melts around 130°C, closing off the pore structure. But the PP, which is well below its melting temperature, maintains its structural integrity. Only above the higher melting point of PP is this separator in danger of shrinking and distorting to the point where it fails catastrophically. This multilayer design, where one layer (PE) performs the shut off function, and the other (PP) holds the separator together, was an improvement in battery safety. *See, e.g.*, Appendix I, Appendix J, Appendix K. The technology for the production of microporous polyolefins films by mechanical stretching was developed in the 1960s and 1970s. *See, e.g.*, Appendix S (Isaacson et al., U.S. Patent No. 3,558,764 titled “Process for Preparing Microporous Film” (issued Jan 26, 1971). Microporous, polyolefin battery separators were also developed in the 1960s. *See, e.g.*, Appendix T (Larsen et al., U.S. Patent No. 3,351,495 titled “Battery Separator” (issued Nov. 7, 1967). The use of multilayer polyolefin separators for a thermal shut-off function in lithium ion batteries goes back to the 1980s. *See, e.g.*, Appendix U

(Lundquist et al., U.S. Patent No. 4,650,730 titled “Battery Separator” (issued Mar. 17, 1987). Research and development activity on these multilayer, thermal shutdown, polyolefin separators followed through the 1990s. *See, e.g.*, Appendix V (U.S. Patent No. 5,565,281 titled “Shutdown, Bilayer Battery Separator” (issued Oct. 15, 1996). And the three-layer PP-PE-PP separator of the type shown in the SEM image below was patented by Celgard in 1999. *See, e.g.*, Appendix W (Yu et al., U.S. Patent No. 5,952,120 titled “Method of Making a Trilayer Battery Separator” (issued Sept. 14, 1999).



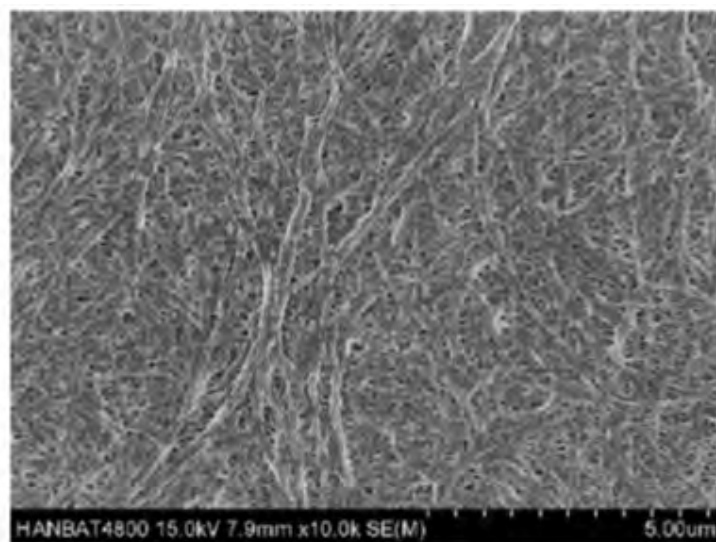
46. With the success of this multilayer composite structure for improved thermal shutoff in separators, it became logical to look for other even more temperature-stable material layers—beyond PP—to couple with the melting and shut-off function of the PE. For this POSAs turned to ceramic particle containing layers that were already known in the art to provide high temperature stable Li-ion battery separators as single free-standing layers or layers coated directly onto electrodes. These included porous ceramic layers, produced by sol-gel processes without polymer binder used as Li-ion battery separators. *See, e.g.*, Appendix X

(Carlson et al., U.S. Patent No. 6,306,545 titled “Separators for Electrochemical Cells” (issued Oct. 23, 2001). Single layer separator materials consisting of composites of ceramic particles and polymer binder were also used, including layers of metal oxide (titanium oxide) particles in a resin binder of polyvinylidene fluoride-hexafluoropropylene copolymer, in which porosity is created by a phase inversion process (addition of a non-solvent). *See, e.g.*, Appendix Y (Kim et al., “Characteristics of PVdF-HFP/TiO₂ composite membrane electrolytes prepared by phase inversion and conventional casting methods,” *Electrochimica Acta* 51 (2006) 5636–5644). This 2006 publication describes a stand-alone separator layer which has the same composition, similar structure and morphology, and is produced by a similar method as the porous layer in the ’987 patent. And as noted above, coating a separator layer onto a porous polyolefin substrate was known from roughly the 1990s.

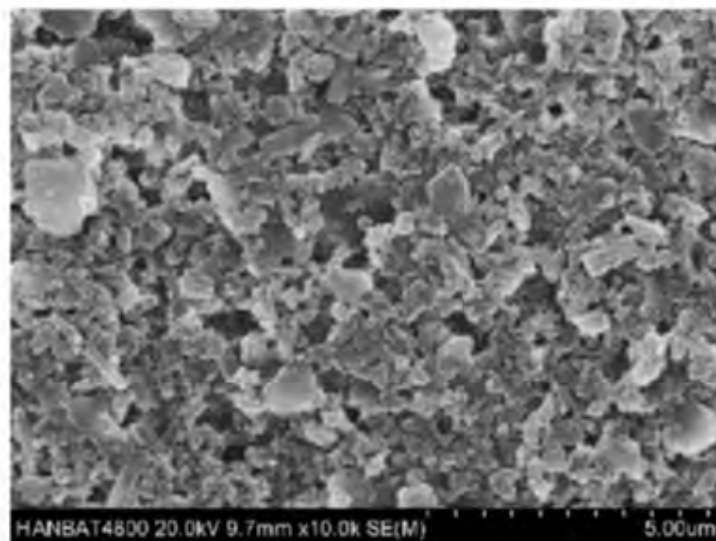
47. The approach of coating porous layers of ceramic particles and binder onto polyolefin separators was patented in 2009 and 2010 by LG Chem (“LG”). *See, e.g.*, Appendix L, Appendix M, Appendix N, Ex. 1009. LG’s separators use a stretched, porous PE separator (for its thermal shutoff qualities) coated on one or both sides with a slurry of ceramic particles in polymer binder, with a solvent. Upon drying of the solvent, a porous layer of ceramic particles in polymer binder is left on the PE. This adds high-temperature structural integrity to the separator, above the

melting point of PE and exceeding the temperature limit of the PE-PP composite separators.

48. The images below are SEM images of the surface of an uncoated PE separator (a), and then the same separator with a ceramic-binder layer coated onto it (b). Appendix P. The surface is completely coated with the ceramic particles, which are bonded together by a binder polymer. The porosity of this separator layer comes from the pore space between the jagged ceramic particles. It is well understood that packings of particulate materials such as these ceramic particles generally only fill about half the volume. The interstitial space between the particles is connected into tortuous pores, which span the layer. Other examples of ceramic coated polyolefin separators soon followed.



(a) PE separator



(b) Ceramic-coated separator

Fig. 1. Scanning electron micrographs of the surface of a porous PE membrane and ceramic-coated separator (ACS-3).

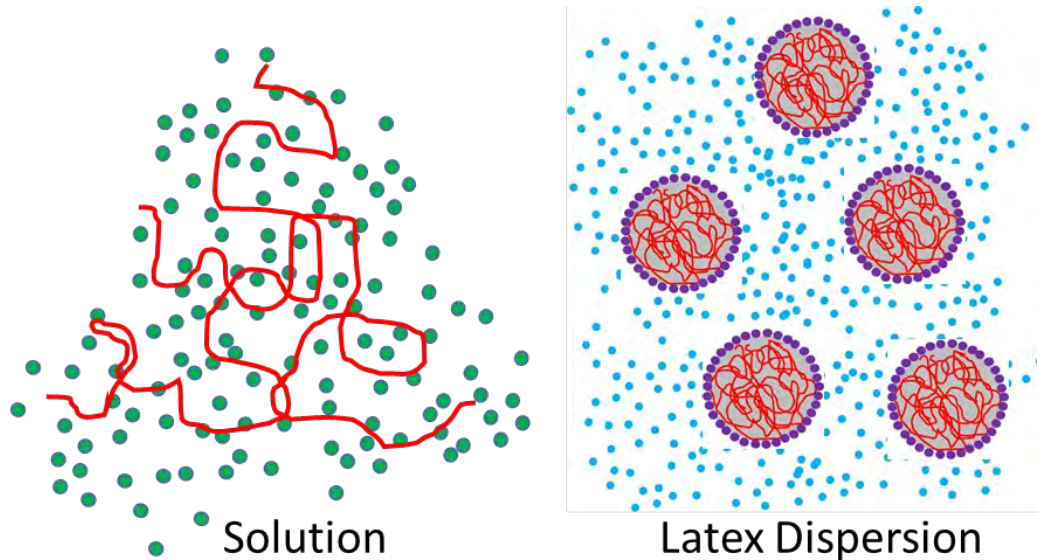
49. The properties of these ceramic particle and binder layers are influenced by the properties of the particles used, as well as the type of polymer binder. The main requirements for the particles are that they be stable at high

temperatures; chemically inert in the electrochemical environment of the battery cell; and able, through their packing, to enable a porous structure. To achieve these requirements, the particles are often some form of metal oxide, metal hydroxide, or other ceramic such as silica, silicon carbide, or a sulfate, such as barium sulfate. The particle size is also important to give the separator the required porosity and mechanical properties, such as handling properties during battery assembly and adhesion to adjacent electrodes.

50. Typically, the ceramic particles on ceramic coated battery separators are held together in a binder, which is a polymer, or more typically a mixture of polymers, along with smaller amounts of other components such as dispersing aids, or stabilizers, typically surfactants, or possibly chemical additives to adjust pH or other conditions. The ceramic particles and binder are generally mixed into a slurry—that is, a liquid containing dissolved components as well as dispersed particulate components—by adding the dry ingredients (binder polymer plus particles) into a solvent. The solvents used must be compatible with both the binder polymers and the inorganic particles. The solvent(s) is (are) often a polar organic solvent, or water, or mixtures of polar organic solvents, or mixtures of water with polar organic solvents.

51. Depending on the solvent used, the binder polymers are polymers that are soluble in polar organic solvents or in water. It is also possible to disperse binder

polymers that are not water soluble in water by using these polymers in the form of latex particles. The figure below illustrates the difference between a polymer in solution, on the left, and a polymer latex suspended in a solvent (often water), on the right. Here the polymer is shown as a red coil. In the solution, it is intimately mixed on a molecular scale with organic solvent molecules, shown in green. In the latex dispersion, by contrast, the polymer is compacted into nanometer sized balls or particles, which are essentially pure polymer in their interiors. These particles are surrounded by surfactant molecules, shown in purple, which stabilize the latex particles and compatibilize their interaction with an aqueous solvent (water or mostly water), shown in blue, which does not usually dissolve the particular type of polymer. The use of a latex polymer binder is not inherently different from the use of a dissolved polymer binder. Both methods disperse the binder in the coating slurry and both allow the binder to perform its function of forming a solid layer that embeds the ceramic particles.

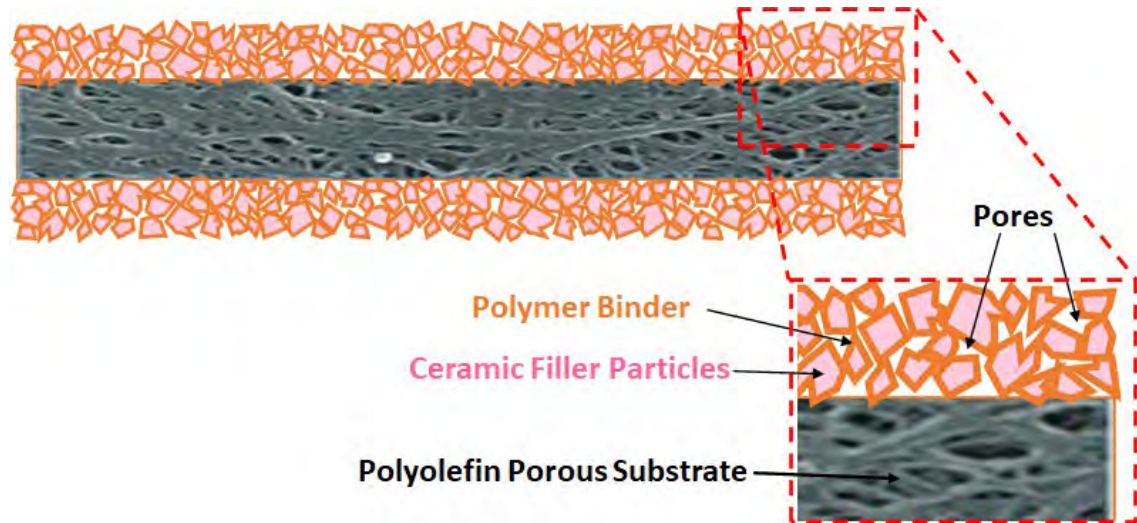


52. Some separators, such as those described in the patents in Appendices L-N and Exhibit 1009, use high particle loadings up to as much as 90% by weight, or more. In these ceramic coated separator layers, the binder is there as a glue to hold the particles together, but the structure of the layer is dominated by the particles, and the porosity is a result of the interstitial cavities between the relatively tightly packed particles. Other separators have been developed in which the amount of polymer binder in the ceramic particle containing layer is significantly greater, perhaps more than 50%. In these cases the particles are generally separated from one another and surrounded by binder. The ability of interstitial spaces in the particle packing to create porosity is greatly reduced. In these cases, it is necessary to generate porosity in the binder polymer itself. This is typically done by a solvent/non-solvent

coagulation, also known as a phase inversion processing method. Phase inversion is a generally known and widely used processing technique for polymers in general, and is the wet process used to make polyolefin separator layers, as discussed above. It has also been used to create porosity in ceramic-binder polymer layers on coated separators. From the 2000s, when polymer binder-ceramic particle composite separator layers were being developed, investigators understood that there was an interplay between parameters such as particle size, pore size, percent porosity, and layer thickness. In some approaches, like that of LG [Appendix L, Appendix M, Appendix N, Ex. 1009], the pore size and porosity are created by interstitial spaces between the pores, so the design choices made about particle size distribution influence pore size and porosity. In approaches based on phase inversion or coagulation of the binder to form pores, the choice of particle type and particle size also influences pore size and porosity, because the particles can act as nucleating sites for the phase separation that creates the pores.

53. Thus, well before 2018, separators regularly included a porous substrate, such as a polyolefin porous substrate, and a porous layer formed on one or both sides of the porous substrate, as illustrated below. It was likewise known to form the porous layer of a **polymer binder**, such as polyvinylidene fluoride, and **inorganic particles**, such as ceramic filler particles, as illustrated. As explained above, those in the art recognized that a polymer **binder** is non-conducting and can be

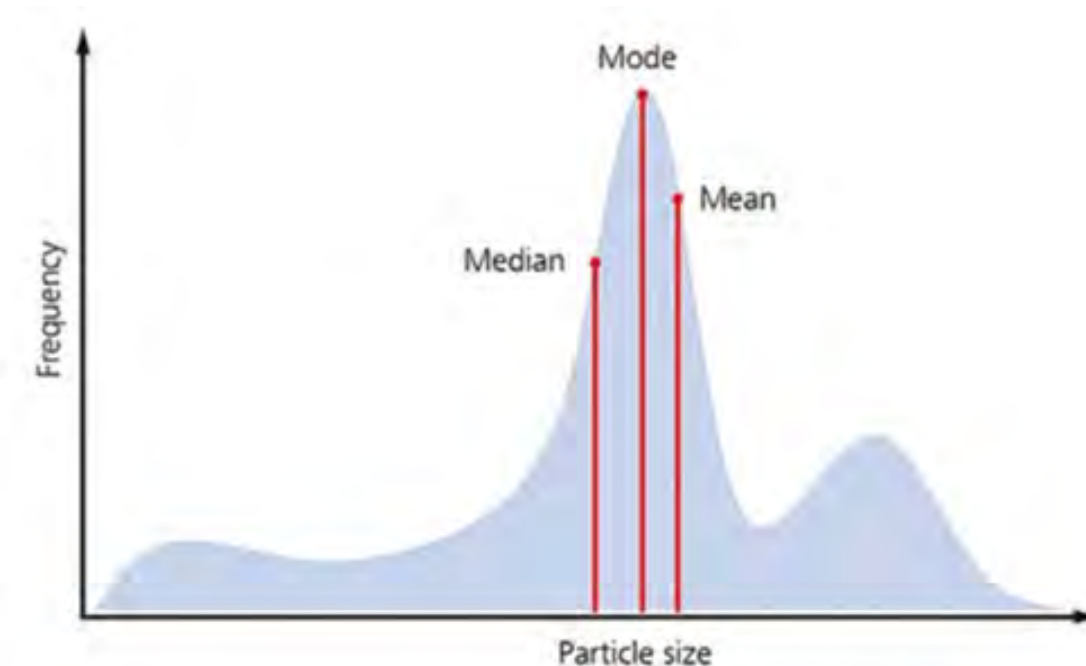
formed to be porous, while the addition of **inorganic particles** improves both mechanical strength and high-temperature stability.



54. The particles in any batch of ceramic particles come in a distribution of sizes, resulting from the process of making the particles, which typically involves pulverizing, grinding, or milling larger pieces of the materials. The figure below illustrates what a general particle size distribution might look like. Appendix O. The frequency of occurrence (*i.e.*, the relative number of particles) in the powder is plotted against size. As illustrated, it is possible that the distribution of sizes (typically diameter or radius) is multimodal, meaning there is more than one peak in

the distribution.

55. The distribution represents a large amount of complex information, and



POSAs often want, or need, to summarize this information in a more compact form, which typically involves averages. These averages are attempts to capture the essence of the distribution in a single number or a few numbers. The figure above illustrates a few such numbers, the median (middle point of distribution), mode (peak of the distribution), and mean (arithmetic average). Clearly, any one or all of these values, given in the absence of the graph of the distribution, does not really convey the complexity of the distribution.

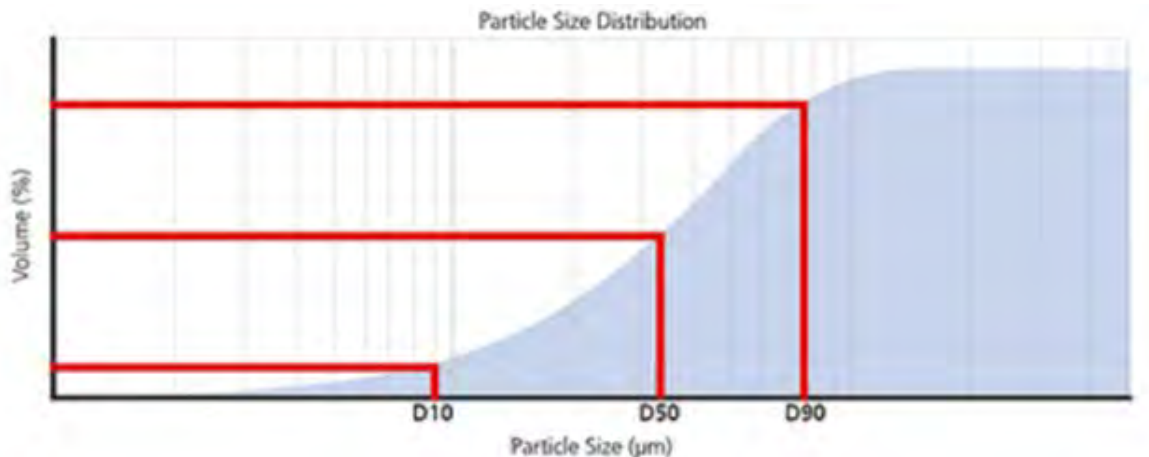
56. Another complicating factor for distributions of particle sizes is the fact that averages of distributions can be calculated by weighting (counting) the

contributions of various particles differently, according to different properties. The simplest average is a number weighted average in which each particle, no matter how big or small, is given the same importance in the average. But this type of number average tends to give too much weight to the smallest particles. There may be many of these small particles, but since they are small, their contribution to the total mass or volume of particles (and thus to material properties) may be less significant than a smaller number of large particles. Thus, practitioners in the field often use other types of averages, such as a surface area average, a mass average, or a volume average.

57. A mass average is calculated from the distribution above by multiplying (weighting) the frequency (number) of particles at each size by their mass. The smaller, less massive, particles now contribute less to the average than larger particles. The mass average size is generally larger than the number average size. For a distribution of particles that are all of the same material, the masses of the various particles are directly proportional to the volumes of the particles (because the mass is simply obtained by multiplying volume by the common density of all the particles). Thus, in such a distribution, the volume average of the distribution and the mass average of the distribution are the same. Light scattering, a technique commonly used to measure particle size, gives volume-weighted results. For this and other reasons, practitioners in the field are accustomed to using volume-weighted

averages to discuss particle size.

58. A common way to convey a bit more about the distribution of particle



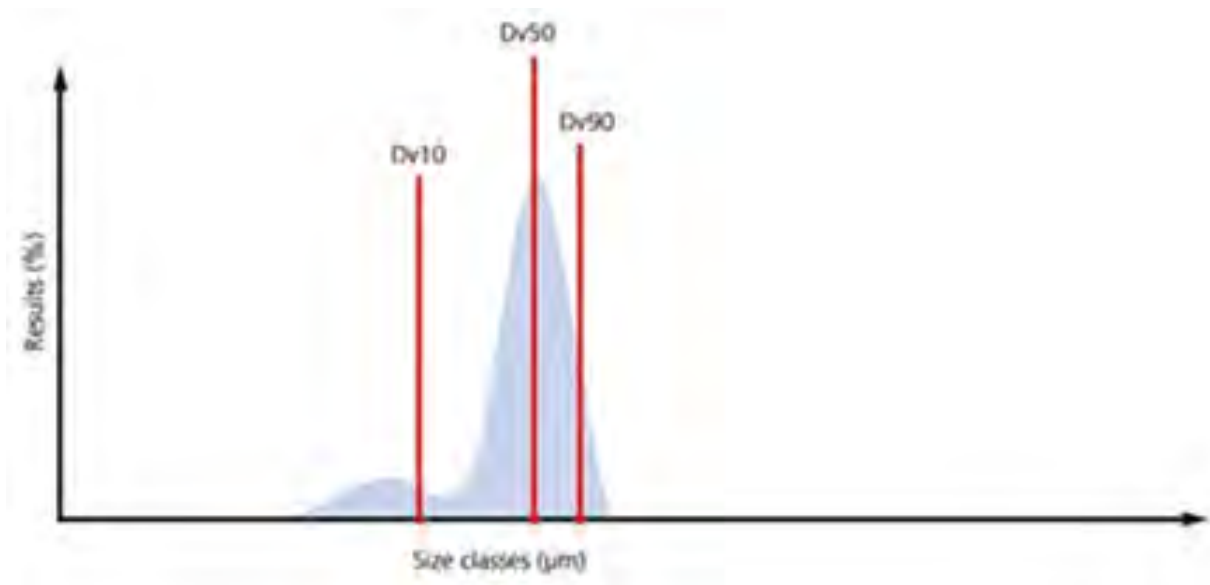
sizes than is conveyed by simple averages is to look at the properties of a cumulative size distribution. A volume-weighted cumulative particle size distribution is illustrated in the figure above. Appendix O. As shown, as particle size (here, particle diameter in microns (μm)) increases, a running total is plotted of the volume (as a percentage of the total volume of all the particles) of the particles up to that particle size. Eventually, at a large particle size, the cumulative distribution reaches a plateau (100%) because all the particles in the distribution are accounted for. Typically, such a cumulative distribution is characterized by the particle sizes at which the cumulative volume reaches particular percentages of the total. Shown in the figure are those most commonly used, namely, D10, D50, and D90.

59. D10 is the particle size (in an appropriate unit such as μm) at which

10% of the total particle volume is reached. D50 is the particle size at which 50% of the total particle volume is reached. And D90 is the particle size at which 90% of the total particle volume is reached.

60. It is actually possible to do this type of analysis of a cumulative size distribution on the different bases mentioned previously: number (frequency) basis, surface area basis, mass basis and volume basis. These different values are differentiated as follows (for the D50 case): Dn50, Ds50, Dm50, and Dv50. However, it is also common for POSAs to define D10, D50, and D90 in a particular context as being on one of these bases and simply use D10, D50, and D90.

61. Of course, even D10, D50, and D90 fail to fully convey the details of some distributions, such as the bimodal distribution shown below. Appendix O. But the fact that the D10 is shifted further to the small size than the D90 is to the large, for example, provides a clue to the asymmetry of the distribution. The value D90-D10 gives a rough indication of the breadth of the distribution and is often referred to as the span. The span may also be represented on relative or percentage basis as $(D90-D10)/D50$.



62. Prior to 2018, it was known in the art to adjust particle size—including as indicated through cumulative particle size values D10, D50, and D90—of the inorganic particles to achieve desirable separator properties. Another parameter those in the art knew to adjust was thickness of the porous layer. Moreover, it was recognized by those in the art that particle size and porous layer thickness were related parameters that were to be adjusted together. Finally, it was known in the art to adjust pore size and porosity of the porous layer. For instance, LG’s series of patents, granted around 2010, on ceramic coated separators includes extensive teachings on particle size and how it relates to layer thickness: “In the organic/inorganic composite separator... the size of inorganic particles in the porous coating layer... is **preferably in the range from 0.001 to 10um, if possible, in order to form a coating layer in a uniform thickness** and ensure suitable porosity. If the

particle size is less than 0.001 um, a dispersing property is deteriorated, so it is not easy to control properties of the organic/inorganic composite separator. **If the particle size exceeds 10um, the thickness of the porous coating layer is increased, which may deteriorate mechanical properties.**” Appendix M, 5:66-67, 6:1-9. Additionally, LG’s patents taught that the pore size and porosity were important parameters for battery performance that were also influenced by particle size. “The pore size and porosity are mainly dependent on the size of inorganic particles... In case the pore size and porosity are respectively less than 0.001 um and 10%, the porous active layer may act as a resistance layer. In case the pore size and porosity are respectively greater than 10 um and 90%, mechanical properties may be deteriorated.” Appendix L, 6:67, 7:1-9.

VII. OVERVIEW OF PRIOR ART

A. Nishikawa

63. U.S. Patent No. 7,976,987 (Ex. 1005) (“*Nishikawa*”) issued July 12, 2011, and constitutes prior art under at least 35 U.S.C. §§ 102(a)(1) and (2).

64. *Nishikawa* describes a separator for use in a lithium-ion battery. *Nishikawa*, 1:8-18. *Nishikawa*’s separator includes an “microporous membrane” that is “laminated with a heat resistant porous layer.” *Id.*, 2:47-52. *Nishikawa*’s porous layer includes both “inorganic filler” and a “resin.” *Id.*

65. As shown below, *Nishikawa* describes Example 4 and Example 5

separators in which the porous layer has a D90 of the inorganic particles that is 1.05 μ m and 1.07 μ m, respectively. In *Nishikawa*'s Example 4 and 5 separators, the porous layer has a thickness of 3.15 μ m. *Id.*, Table 1, 16:25-29, 16:37-38. Thus, in *Nishikawa*'s Example 4 and 5 separators a ratio of the D90 of the inorganic filler to the thickness of the porous layer is 0.33 and 0.34, respectively—both of which are within a range from 0.3 to 3.0.

TABLE 2

	d10	d50	d90	α	Sliding property	Coating property
Example 4	0.38	0.75	1.05	0.89	good	good
Example 5	0.50	1.02	1.07	0.56	good	good
Example 6	1.50	8.0	22.0	2.56	good	poor
Example 7	5.10	23.0	58.0	2.30	good	poor

B. Iwai

66. U.S. Patent App. Pub. No. 2014/0248525 (Ex. 1006) ("*Iwai*") has a 35 U.S.C. § 371(c) date of April 17, 2014, and constitutes prior art under at least 35 U.S.C. §§ 102(a)(1) and (2).

67. *Iwai* describes a separator for use in a lithium-ion battery. *Iwai*, [0001]. *Iwai*'s separator includes a "porous substrate" and an "adhesive porous layer" that is "appl[ied] on one or both sides of the porous substrate." *Iwai*, [0021]. *Iwai*'s adhesive porous layer includes both "inorganic particles" and a "polyvinylidene-

fluoride resin.” *Id.*, [0022]. *Iwai*, like others in the art, recognized that desirable properties of a separator could be achieved by adjusting particle size—as indicated through cumulative particle size values D10, D50, and D90—of the inorganic particles. In particular, *Iwai* taught that desirable adhesion of the separator could be achieved by keeping a “ratio a/r between an average thickness ‘ a ’ (μm) of the adhesive porous layer on one of the sides of the porous substrate and a volume average particle diameter ‘ r ’ (μm) of the” inorganic particles within a prescribed range. *Id.*, [0043]. While a POSA may typically understand the term “volume average particle diameter” to refer to the mean (arithmetic average) diameter of particles in the particle distribution, *Iwai* equates the “volume average particle diameter ‘ r ’ (μm)” with D50, stating “the volume average particle diameter (μm) of the filler is a particle diameter at 50% cumulative volume calculated from a smaller side in a volume particle size distribution.” *Id.*, [0038]; *see also* [0160].

68. As shown in Table 1 below, *Iwai* describes an example separator, the Example 7 separator, in which the adhesive porous layer has a D50 of $1.2\mu\text{m}$ and a D90-D10 of $1.6\mu\text{m}$. *Iwai*, [0039].

TABLE 1

	Average		Filler				
	thickness a (μm) of adhesive porous layer	Resin type	Type	Volume average particle diameter r (μm)	D90 – D10 (μm)	Content (% by mass)	a/r
Example 1	2.1	Resin A	Organic filler A	1.8	1.3	5	1.2
Example 2	1.1	Resin A	Organic filler A	1.8	1.3	20	0.6
Example 3	1.5	Resin A	Organic filler A	1.8	1.3	25	0.8
Example 4	3.5	Resin A	Organic filler A	1.8	1.3	1	1.9
Example 5	4.7	Resin A	Organic filler A	1.8	1.3	0.3	2.6
Example 6	3.0	Resin A	Organic filler B	3.0	2.0	20	1.0
Example 7	2.2	Resin A	Inorganic fillers C, D	1.2	1.6	10	1.8
Example 8	2.1	Resins A, B	Organic filler A	1.8	1.3	30	1.2
Comparative Example 1	1.3	Resin A	—	—	—	0	—
Comparative Example 2	3.1	Resin A	Inorganic filler D	0.8	1.1	40	3.9
Comparative Example 3	5.5	Resin A	Organic filler A	1.8	1.3	20	3.1
Comparative Example 4	2.0	Resin A	Organic filler E	5.0	3.6	1	0.4
Comparative Example 5	0.7	Resin A	Organic filler A	1.8	1.3	5	0.4
Comparative Example 6	5.0	Resin A	Organic filler E	5.0	3.6	5	1.0
Comparative Example 7	2.1	Resin A	Organic filler F	4.0	2.5	30	0.5

***Iwai*, Table 1 (cropped and annotated)**

69. From *Iwai*'s Table 1, a POSA would have recognized that D90 of the inorganic filler in *Iwai*'s Example 7 separator must be between 1.6μm and 2.8μm. In particular, a POSA would have recognized from the provided span, D90-D10, that D10 must be related to the D90 value as follows. Because Table 1 shows that, for Example 7, D90-D10 is 1.6, a POSA would have known that:

$$D90 - D10 = 1.6\mu\text{m}$$

70. Further, a POSA could have solved for D10 as follows:

$$D90 = 1.6\mu\text{m} + D10$$

$$D90 - 1.6\mu\text{m} = D10 \text{ (Equation 1)}$$

71. A POSA would also have recognized that D10 for *Iwai*'s Example 7 separator must be greater than 0μm. This is because D10 is “a particle diameter at which a cumulative volume of particles reaches 10% from a smaller side in a volume

particle size distribution.” *Iwai*, [0039]. A POSA would have recognized that, because the particles at 10% of the cumulative volume cannot have a particle diameter less than $0\mu\text{m}$, D10 must be greater than $0\mu\text{m}$.

72. A POSA would likewise have recognized that D10 for *Iwai*’s Example 7 separator cannot be equal to or more than D50 for *Iwai*’s Example 7 separator. This is because D50 in *Iwai* is “a particle diameter at 50% cumulative volume calculated from a smaller side in a volume particle distribution.” *Id.*, [0038]. A POSA would have recognized that the particle size at 10% of the cumulative volume cannot have a particle diameter that is equal to or more than the particle diameter at 50% of the cumulative volume. Therefore, D10 for *Iwai*’s Example 7 separator must be less than D50 for *Iwai*’s Example 7 separator. Because Table 1 shows that, for Example 7, D50 is $1.2\mu\text{m}$, a POSA would have known that:

$$0\mu\text{m} < D10 < 1.2\mu\text{m} \text{ (Equation 2)}$$

73. Replacing D10 in Equation 2 per Equation 1, a POSA would have recognized:

$$0 < D90 - 1.6\mu\text{m} < 1.2\mu\text{m}$$

$$1.6\mu\text{m} < D90 < 2.8\mu\text{m}$$

74. Thus, a POSA would have recognized, D90 for *Iwai*’s Example 7 separator must be greater than $1.6\mu\text{m}$ and less than $2.8\mu\text{m}$.

75. In *Iwai*’s Example 7 separator, the adhesive porous layer has a

thickness of 2.2 μ m. *Id.*, Table 1. Thus, a POSA would have understood, in *Iwai*'s Example 7 separator, a ratio of the D90 of the inorganic particles to the thickness of the porous membrane ($\frac{D90}{Thickness}$) must have a value in a range from $\frac{1.6\mu m}{2.2\mu m} = 0.72$ to $\frac{2.8\mu m}{2.2\mu m} = 1.27$, a value which falls within a range from 0.3 to 3.0.

76. Also from *Iwai*'s Table 1, a POSA would have recognized that D90 of the inorganic filler in *Iwai*'s Comparative Example 2 separator must be between 1.1 μ m and 1.9 μ m. In particular, a POSA would have recognized from the provided span, D90-D10, that D10 must be related to the D90 value as follows. Because Table 1 shows that, for Comparative Example 2, D90-D10 is 1.1, a POSA would have known that:

$$D90 - D10 = 1.1$$

77. Further, a POSA could have solved for D10 as follows:

$$D90 = 1.1 + D10$$

$$D90 - 1.1 = D10 \text{ (Equation 6)}$$

78. A POSA would also have recognized that D10 for *Iwai*'s Comparative Example 2 separator must be greater than 0. This is because D10 is "a particle diameter at which a cumulative volume of particles reaches 10% from a smaller side in a volume particle size distribution." *Iwai*, [0039]. A POSA would have recognized that, because the particles at 10% of the cumulative volume cannot have a particle

diameter less than 0, D10 must be greater than 0.

79. A POSA would likewise have recognized that D10 for *Iwai*'s Comparative Example 2 separator cannot be equal to or more than D50 for *Iwai*'s Comparative Example 2 separator. This is because D50 is "a particle diameter at 50% cumulative volume calculated from a smaller side in a volume particle distribution." *Id.*, [0038]. A POSA would have recognized that, because the particles at 10% of the cumulative volume cannot have a particle diameter that is equal to or more than the particle diameter of the particles at 50% of the cumulative volume, D10 for *Iwai*'s Comparative Example 2 separator must be less than D50 for *Iwai*'s Comparative Example 2 separator. Because Table 1 shows that, for Comparative Example 2, D50 is 0.8, a POSA would have known that:

$$0 < D10 < 0.8 \text{ (Equation 7)}$$

80. Replacing D10 in Equation 7 per Equation 6, a POSA would have recognized:

$$0 < D90 - 1.1 < 0.8$$

$$1.1 < D90 < 1.9$$

81. Thus, a POSA would have recognized, D90 for *Iwai*'s Comparative Example 2 separator must be greater than 1.1 μ m and less than 1.9 μ m.

82. In *Iwai*'s Comparative Example 2 separator, the adhesive porous layer has a thickness of 3.1 μ m. *Id.*, Table 1. Thus, a POSA would have understood, in

Iwai's Comparative Example 2 separator, a ratio of the D90 of the inorganic particles to the thickness of the porous membrane ($\frac{D90}{Thickness}$) must have a value in a range from 0.35 to 0.61. This is because, as shown below, a ratio of the lowest possible D90 value (1.1 μ m) to the thickness (3.1 μ m) is 0.35, while a ratio of the highest possible D90 value (1.9 μ m) to the thickness (3.1 μ m) is 0.61. The ratio thus has a value between 0.35 and 0.61, and thus a value which falls within the claimed range from 0.3 to 3.0.

$$\frac{1.1\mu\text{m}}{3.1\mu\text{m}} = 0.35$$

$$\frac{1.9\mu\text{m}}{3.1\mu\text{m}} = 0.61$$

C. Honda

83. U.S. Patent App. Pub. No. 2015/0263325 (Ex. 1007) ("*Honda*") has a 35 U.S.C. § 371(c) date of May 6, 2015, and constitutes prior art under at least 35 U.S.C. §§ 102(a)(1) and (2).

84. *Honda* describes a separator that includes a "porous substrate" and a "porous layer that is provided on one side or both sides of the porous substrate." *Honda*, [0021]-[003]. *Honda*'s porous layer, like *Nishikawa*'s and *Iwai*'s, includes a resin and inorganic filler. *Honda*, [0023], [0033]; *see also id.*, [0229]. *Honda* teaches an embodiment of the porous layer in which "a resin has a fibril shape to form a three-dimensional network structure, by which a filler is trapped by the

network structure.” Honda, [0164] *see also id.*, [0228]. Honda states such a structure is “preferable.” Honda, [0164]; *see also id.*, [0228].

85. I would consider *Nishikawa*, *Iwai*, and *Honda* to be from the same field of endeavor as the ’987 patent, namely, separators for lithium-ion batteries. *See, e.g.*, ’987 patent, 1:14-34; *Nishikawa*, Abstract; *Iwai*, [0001]-[0002]; *Honda*, [0001]-[0002]. Moreover, each is addressing a problem discussed in the ’987 patent, such as improving adhesion, heat resistance, and cycle performance of a battery. ’987 patent, Abstract, 4:57-62; *Nishikawa*, 2:35-41; *Iwai*, [0017]-[0018]; *Honda*, [0016].

VIII. THE ’987 PATENT

86. Like *Nishikawa*, *Iwai*, and *Honda*, the ’987 patent describes a “separator” for use in an “energy storage device,” such as a lithium-ion battery. ’987 patent, 1:14-24. Like the separators in *Nishikawa*, *Iwai*, and *Honda*, the claimed separator includes a porous substrate and a porous layer arranged on a surface of the porous substrate. *Id.*, 1:48-50. And like the porous layers in *Nishikawa*, *Iwai*, and *Honda*, the claimed porous layer includes both inorganic particles and a binder. *Id.*, 1:50-51.

87. The ’987 patent requires that a ratio of Dv90 of the inorganic particles to the thickness of the porous layer be in a range from 0.3 to 3.0. *Id.*, 1:51-53. “[B]y controlling the ratio of Dv90 of the inorganic particles to the thickness of the porous

layer,” the ’987 patent states, “pores having a larger average pore size can be obtained.” *Id.*, 5:13-16. When the ratio is in this range, the patent states, “the mechanical strength of the porous layer is increased, and the porous layer is prevented from undergoing pore blockage due to compression in the preparation or cycle process of the energy storage device.” *Id.*, 5:28-35. As explained below, both *Nishikawa* and *Iwai* describe example separators for which a ratio of Dv90 of the inorganic particles to the thickness of the porous layer is in the range required by the ’987 patent.

88. Claim 1, the sole independent claim, recites:

A **separator**, comprising:

a porous substrate; and

a **porous layer** arranged on a surface of the **porous substrate**,

wherein the **porous layer** comprises **inorganic particles** and a **binder**,
and

a ratio of Dv90 of the **inorganic particles** to the thickness of the
porous layer is in a range from 0.3 to 3.0.

IX. CLAIM CONSTRUCTION

89. I have applied the above-mentioned legal standard of claim construction here.

X. THE CHALLENGED CLAIMS ARE UNPATENTABLE

90. As described below, it is my opinion that each of the challenged claims is anticipated by or would have been rendered obvious by either *Nishikawa*, alone or in combination with *Honda*, and/or *Iwai* alone.

A. Ground 1: *Nishikawa* Would Have Anticipated Claims 1-2 and 4-9

1. Claim 1

91. *Nishikawa* anticipates claim 1.

a. 1[p] A separator, comprising:

92. *Nishikawa* describes “[a] separator.” For example, *Nishikawa* describes a “separator for a nonaqueous secondary battery” and two example separators in Examples 4 and 5. *Nishikawa*, 2:47-52, 15:51-16:44, 22:10-52.

b. 1[a] a porous substrate; and

93. *Nishikawa* discloses “a porous substrate.” In *Nishikawa*, the separator includes a “microporous membrane.” *Nishikawa*, 2:47-52; *see also id.*, 8:57-67, 15:51-16:6¹. A POSA would have understood *Nishikawa*’s microporous membrane

¹ *Nishikawa*’s Example 4 separator is “produced in the same manner as in Example 1, except that” the coating slurry is modified. *Nishikawa*, 22:37-40. *Nishikawa*’s Example 5 separator is “produced in the same manner as in Example 4 except that the inorganic filler was changed” from H-43M to H-42M,

to be a “porous substrate” for at least three reasons. First, this is because *Nishikawa* describes the microporous membrane as having “pores inside,” which indicates it is “porous.” Second, like embodiments of the porous substrate in the ’987 patent, *Nishikawa*’s microporous membrane is formed of polyethylene and/or polypropylene, compare *Nishikawa*, 8:62-67 with ’987 patent, 2:9-52. Third, just as the ’987 patent describes a porous layer being “coat[ed] ... onto a surface of [the] porous substrate,” ’987 patent, 2:25-26, *Nishikawa* describes a heat resistant porous layer being “coat[ed] ... on both the surfaces of the microporous membrane,” *Nishikawa*, 16:24-29. *Nishikawa*’s Example 4 and Example 5 separators each include a polyethylene microporous membrane onto which a heat resistant porous layer is coated. *Nishikawa*, 15:51-16:14, 22:37-38.

c. 1[b] a porous layer arranged on a surface of the porous substrate,

94. *Nishikawa* discloses “a porous layer arranged on a surface of the porous

where H-42M and H-43M are both commercially available aluminum hydroxide organic fillers having different particle size distribution as shown in Table 2.

Nishikawa, 22:26-33, 22:46-51. Accordingly, throughout my declaration, citations to discussions of Example 1 are provided where they apply equally to Example 4 and Example 5.

substrate.” In *Nishikawa*, the separator includes a “heat resistant porous layer” that is “laminated” onto both sides of the microporous membrane. *Nishikawa*, 2:47-52. *Nishikawa*’s Example 4 and Example 5 separators each include a heat resistant porous layer that is “coat[ed] ... onto both the surfaces of the polyethylene microporous membrane.” *Id.*, 16:25-35.

d. 1[c] wherein the porous layer comprises inorganic particles and a binder,

95. *Nishikawa* discloses “wherein the porous layer comprises inorganic particles and a binder.”

96. Regarding inorganic particles, in *Nishikawa*, the heat resistant porous layer includes “inorganic filler.” *Nishikawa*, 2:47-52. The heat resistant porous layer in each of *Nishikawa*’s Example 4 and Example 5 separators includes inorganic filler of aluminum hydroxide, like embodiments of the claimed “inorganic particles” described in the ’987 patent. Compare *Nishikawa*, 22:26-33, 22:46-51 with ’987 patent, 2:1-6. Compare also *Nishikawa*, 2:53-56 (listing materials for *Nishikawa*’s inorganic filler) with ’987 patent claim 6 (listing materials for claimed “inorganic particles”).

97. Regarding a binder, in *Nishikawa* the heat resistant porous layer includes a “heat resistant resin.” *Nishikawa*, 2:47-52. A POSA would have understood *Nishikawa*’s heat resistant resin to be a “binder” for at least two reasons.

First, just as the '987 patent describes “pores formed by the **binder**” through which “diffusion” takes place, *Nishikawa*’s **heat resistant resin** has “pores inside ... through which a gas or a liquid can pass,” *compare* '987 patent, 3:59-61, 4:10-14 *with Nishikawa*, 7:41-45. Second, like embodiments of the **binder** in the '987 patent, *Nishikawa*’s **heat resistant resin** is formed of polyamide, *compare Nishikawa*, 3:5-9 *with* '987 patent, 2:9-52. *Compare also Nishikawa*, 7:49-57 (listing materials for *Nishikawa*’s **heat resistant resin**, including polyamide and carboxymethylcellulose (a form of cellulose)) *with* '987 patent claim 7 (listing materials for claimed “**binder**,” including polyamide and cellulose). *Nishikawa*’s Example 4 and Example 5 **separators** each include polyamide **heat resistant resin**. *Nishikawa*, 22:26-35.

- e. **1[d] a ratio of Dv90 of the **inorganic particles** to the thickness of the **porous layer** is in a range from 0.3 to 3.0.**

98. *Nishikawa* discloses that “a ratio of Dv90 of the **inorganic particles** to the thickness of the **porous layer** is in a range from 0.3 to 3.0” because in each of *Nishikawa*’s Example 4 and Example 5 **separators** a ratio of a D90 of the **inorganic filler** to the thickness of the **heat resistant porous layer** is within the claimed range.

99. As shown below in Table 2, in *Nishikawa*’s Example 4 and Example 5 **separators** the **heat resistant porous layer** has a D90 of the **inorganic filler** that is 1.05µm and 1.07µm, respectively. A POSA would have understood “D90,” as used by *Nishikawa* in Examples 4 and 5, to disclose the claimed “Dv90.” As explained in

the State of the Art, it is possible for a cumulative size distribution to be on any of a number (frequency) basis, surface area basis, mass (i.e., weight) basis and volume basis, and these may be differentiated as (for the D50 case): Dn50, Ds50, Dm50, and Dv50, respectively. The '987 patent uses a cumulative volume distribution (hence the “v” in “Dv90”). *Nishikawa* actually defines its D90 with reference to a cumulative weight distribution, *see Nishikawa*, 3:52-55. But a POSA would have recognized that where, as in *Nishikawa*’s Examples 4 and 5, the **inorganic filler** is of a single material (here, aluminum hydroxide, *see Nishikawa*, 22:26-35, 22:46-51), a cumulative volume distribution and a cumulative weight distribution will have the same D90 value. This is because, as a POSA would have known, volume is directly proportional to weight—in particular, mass is equivalent to volume multiplied with density. Where the **inorganic filler** is of a single material, the density relating each particle’s mass to each particle’s volume will be the same, such that Dm90 and Dv90 will have the same value. *Compare also Nishikawa*, 3:52-55 (defining “D90” as “an average **particle** diameter (μm) of weight accumulation of 90% by weight calculated from a smaller particle side in a particle size distribution”) *with* '987 patent, 1:53-56 (defining “Dv90” as “a **particle** size which reaches 90% the cumulative volume from the side of small particle size in the granularity distribution on a volume basis.”).

TABLE 2

	d10	d50	d90	α	Sliding property	Coating property
Example 4	0.38	0.75	1.05	0.89	good	good
Example 5	0.50	1.02	1.07	0.56	good	good
Example 6	1.50	8.0	22.0	2.56	good	poor
Example 7	5.10	23.0	58.0	2.30	good	poor

100. In each of *Nishikawa*'s Example 4 and Example 5 separators, the heat resistant porous layer has a thickness of 3.15 μ m on each side of the microporous membrane. *Nishikawa*, Table 1, 16:24-44. I note that Table 1, shown below, lists the thickness of the heat resistant porous layer in Example 1 (which is, in this aspect, the same as Examples 4 and 5) as 6.3 μ m. In Example 1 (and Examples 4 and 5), there are heat resistant porous layers formed on both sides of the microporous membrane, *id.*, 16:24-44, and 6.3 μ m is the total thickness of both heat resistant porous layers. I know this because *Nishikawa* provides a total thickness of the separator as 17.8 μ m (*id.*, Table 1, 16:36-38) and provides a thickness of the microporous membrane as 11.5 (*id.*, Table 1, 16:6-8). Subtracting the thickness of the microporous membrane from the total thickness of the separator leaves 6.3 μ m, which must account for a thickness of both heat resistant porous layers. Thus, each of both heat resistant porous layers has half that thickness, namely, 3.15 μ m.

101. Thus, as summarized in *Nishikawa*'s Ratios Table below, in each of

Nishikawa's Example 4 and Example 5 **separators** a ratio of the D90 of the **inorganic filler** to the thickness of the **heat resistant porous layer** is any of 0.33 and 0.34, respectively.

<i>Nishikawa's</i> Example	D90 (μm)	Thickness (μm)	Ratio ($\frac{D90}{Thickness}$)
4	1.05	3.15	0.33
5	1.07	3.15	0.34

Nishikawa's Ratios Table

102. Thus, *Nishikawa* discloses two example **separators** in which a ratio of D90 of the **inorganic filler** to the thickness of the **heat resistant porous layer** “is in a range from 0.3 to 3.0.”

2. **Claim 2: The **separator** according to claim 1, wherein the **porous layer** has a thickness of 0.2 μm to 10 μm.**

103. *Nishikawa* discloses “wherein the **porous layer** has a thickness of 0.2 μm to 10 μm.” As explained above for claim element 1[d], in each of *Nishikawa's* Example 4 and Example 5 **separators**, the **heat resistant porous layer** has a thickness of 3.15μm on each side of the **microporous membrane**. *Nishikawa*, Table 1, 16:24-44. This 3.15μm thickness is within the claimed range of 0.2 μm to 10 μm.

3. **Claim 4: The **separator** according to claim 1, wherein a volume ratio of the **inorganic particles** to the **binder** is in a range from 0.2 to 3.0.**

104. *Nishikawa* discloses “wherein a volume ratio of the **inorganic particles**

to the binder is in a range from 0.2 to 3.0,” because a POSA would have understood from *Nishikawa* that each of the Example 4 and Example 5 separators has a “volume ratio of the inorganic particles to the binder” of 1.71, as explained below.

105. *Nishikawa* provides a mass ratio of the inorganic filler to the resin for the Example 4 and Example 5 separators, stating the poly-m-phenylene isophthalamide resin and the inorganic filler containing aluminum hydroxide “were mixed at a weight ratio of 25/75.” *Nishikawa*, 22:26-29. From this, a POSA would have recognized the mass ratio of the inorganic filler to the resin is as follows:

$$\frac{M_{\text{resin}}}{M_{\text{filler}}} = \frac{25}{75}$$

106. Or, equivalently:

$$\frac{M_{\text{filler}}}{M_{\text{resin}}} = \frac{75}{25}$$

$$\frac{M_{\text{filler}}}{M_{\text{resin}}} = 3 \text{ (Equation 3)}$$

107. While Equation 3 provides a mass ratio, a POSA would have known how to determine a volume ratio from a mass ratio. In particular, a POSA would have known that a mass ratio is convertible to a volume ratio by multiplying the masses by a reciprocal of the densities, ρ , of the materials. This is shown in Equation 4, where “ ρ_{filler} ” refers to a density of the inorganic filler and “ ρ_{resin} ” refers to a mass of the resin, and “ V_{filler} ” refers to a density of the inorganic filler and “ V_{resin} ”

refers to a mass of the resin:

$$\frac{V_{\text{filler}}}{V_{\text{resin}}} = \frac{M_{\text{filler}}}{M_{\text{resin}}} \times \frac{\rho_{\text{resin}}}{\rho_{\text{filler}}} \text{ (Equation 4)}$$

108. Replacing $\frac{M_{\text{filler}}}{M_{\text{resin}}}$ in Equation 4 per Equation 3 provides Equation 5

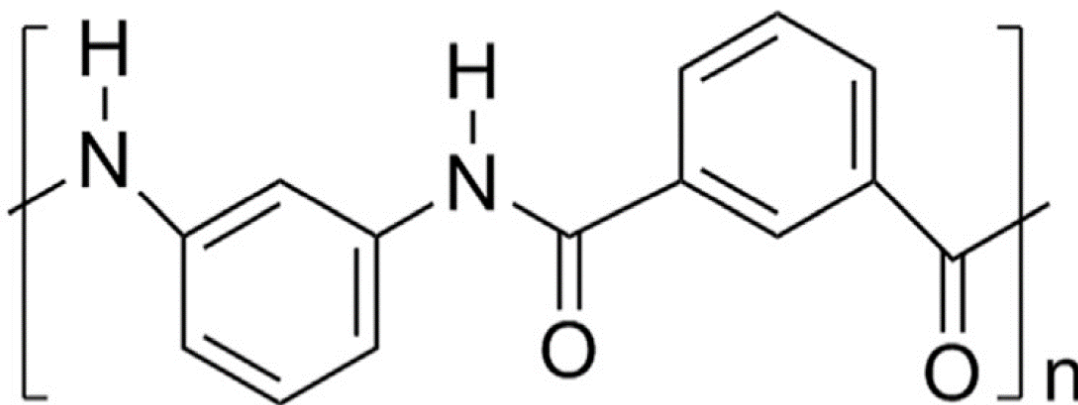
below:

$$\frac{V_{\text{filler}}}{V_{\text{resin}}} = 3 \times \frac{\rho_{\text{resin}}}{\rho_{\text{filler}}} \text{ (Equation 5)}$$

109. The separator of Example 4 in *Nishikawa* uses as an inorganic filler “aluminum hydroxide (H-43M, produced by Showa Denko K.K.).” *Nishikawa*, 22:28-29. The product information for Showa Denko’s H-43M (obtained from http://www.sdsh-showadenko.com/product_03.php) indicates H-43M has a CAS Registry Number of 21645-51-2. See Appendix A. Using this CAS Registry Number, I obtained the Sigma-Aldrich Material Safety Data Sheet for CAS No. 21645-51-2 shown in Exhibit 1011. Exhibit 1011 is a true and accurate copy of a Material Safety Data Sheet for “Aluminum hydroxide fine powder pure, hydrargillite” from Sigma-Aldrich. Exhibit 1011 was downloaded by me from Sigma-Aldrich’s website on February 17, 2023. Exhibit 1011 has a file name <https://www.sigmaaldrich.com/US/en/sds/mm/1.01093>. POSAs regularly employ CAS Registry Numbers and regularly rely on Material Safety Data Sheets as a reliable authority on the physical properties of a given material. Having determined that the H-43M product identified in *Nishikawa* is CAS No. 21645-51-2, a POSA

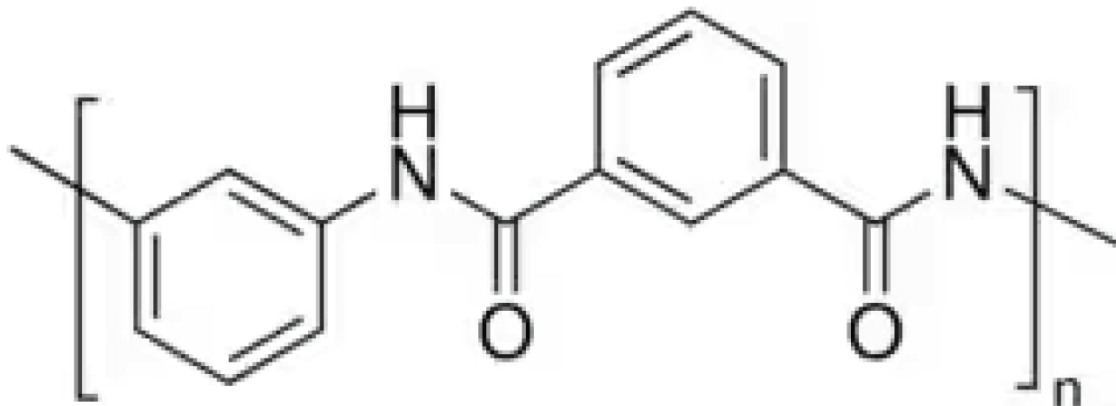
would have known that the H-43M product has a density ρ_{filler} of 2.42 g/cm³, as listed in the Sigma-Aldrich Material Safety Data Sheet for CAS No. 21645-51-2. Ex. 1011, 5.

110. The **separator** of Example 4 in *Nishikawa* uses a poly-m-phenylene isophthalamide **resin**. *Nishikawa*, 22:26-27. As a POSA would have known, sometimes chemical compounds can be referred to by different names. Poly-m-phenylene isophthalamide is such a compound. As relevant here, poly-m-phenylene isophthalamide can also be referred to as poly [N,N'-(1,3-phenylene) isophthalamide]. This can be shown by, for example, comparing the chemical structures given these names. In an article by Lin et al. from the Journal of Membrane Science, for example, poly-m-phenylene isophthalamide is shown to have the chemical compound below. Appendix B, Figure 1.



111. And the Sigma-Aldrich Material Safety Data Sheet for poly [N,N'-(1,3-phenylene) isophthalamide].

(1,3-phenylene) isophthalamide] (CAS Registry No. 25765-47-3) provides the chemical compound below. Exhibit 1013, 1.



112. As a POSA would recognize, these chemical compounds are identical. The brackets indicate a repeating unit of the structure which is repeated n times. This repeat unit can be specified in any way, so long as it includes everything that needs to be repeated. From the top structure to the lower structure, the brackets have been shifted so that the NH that appears on the far left (top), is instead accounted for on the far right (bottom). Both schematics show the same atoms connected in the same way. This indicates that poly-m-phenylene isophthalamide and poly [N,N'-(1,3-phenylene) isophthalamide] are alternative names for the same chemical compound. Having determined that the poly-m-phenylene isophthalamide identified in *Nishikawa* is the same chemical compound as poly [N,N'-(1,3-phenylene) isophthalamide], a POSA would have known that poly-m-phenylene isophthalamide has a density ρ_{resin} of 1.38 g/cm³, as listed in the Sigma-Aldrich Material Safety Data

Sheet for poly [N,N'-(1,3-phenylene) isophthalamide] (CAS Registry No. 25765-47-3). Ex. 1013, 3.

113. So, plugging the values of ρ_{filler} and ρ_{resin} into Equation 5, a POSA would have arrived at a volume ratio for *Nishikawa's* Example 4 separator of:

$$\frac{V_{\text{filler}}}{V_{\text{resin}}} = 3 \times \frac{\rho_{\text{resin}}}{\rho_{\text{filler}}} \text{ (Equation 5)}$$

$$\frac{V_{\text{filler}}}{V_{\text{resin}}} = 3 \times \frac{1.38}{2.42}$$

$$\frac{V_{\text{filler}}}{V_{\text{resin}}} = 1.71$$

114. Thus, *Nishikawa's* Example 4 separator has a volume ratio of 1.71. This volume ratio of 1.71 is “in a range from 0.2 to 3.0,” as claim 4 recites.

115. *Nishikawa's* Example 5 separator has the same volume ratio of 1.71. This is because the only difference between Examples 4 and 5 is that the H-43M aluminum hydroxide of Example 4 has been switched to H-42M aluminum hydroxide, which has different particle size characteristics but is likewise the chemical compound have CAS Registry No. 21645-51-2. See Appendix A. Accordingly, a POSA would have known that the H-42M product likewise has a density ρ_{filler} of 2.42 g/cm³, as listed in the Sigma-Aldrich Material Safety Data Sheet for CAS No. 21645-51-2. Ex. 1011, 5. Plugging the same density ρ_{filler} of 2.42 g/cm³ into Equation 5 above yields the same volume ratio, namely, 1.71. This volume ratio

of 1.71 is “in a range from 0.2 to 3.0,” as claim 4 recites.

116. Thus, a POSA would have understood *Nishikawa* to disclose that, in each of the **separators** of Examples 4 and 5, a volume ratio of the **inorganic particles** to the **binder** is 1.71, a value that is “in a range from 0.2 to 3.0.”

4. Claim 5: The **separator according to claim 1, wherein the **porous layer** has a porosity of 20% to 90%.**

117. *Nishikawa* discloses “wherein the porous layer has a porosity of 20% to 90%.” *Nishikawa* states “[t]he heat resistant porous layer preferably has a porosity of 60 to 90%.” *Nishikawa*, 8:49-50.

5. Claim 6: The **separator according to claim 1, wherein the **inorganic particles** are one or more selected from the group consisting of alumina, silica, magnesia, titanium oxide, hafnium dioxide, tin oxide, zirconia, cerium dioxide, nickel oxide, zinc oxide, calcium oxide, boehmite, aluminum hydroxide, magnesium hydroxide, calcium hydroxide, and barium sulfate.**

118. *Nishikawa* discloses “wherein the **inorganic particles** are one or more selected from the group consisting of ... aluminum hydroxide [and] magnesium hydroxide.” The **heat resistant porous layer** in each of *Nishikawa*’s Example 4 and Example 5 **separators** includes **inorganic filler** of aluminum hydroxide. *Nishikawa*, 22:26-35, 22:46-52. *Nishikawa* additionally envisions that the **inorganic filler** may be magnesium hydroxide. *Id.*, 5:48-50.

6. **Claim 7: The separator according to claim 1, wherein the binder is one or more selected from the group consisting of polyvinylidene fluoride, vinylidene fluoride-hexafluoropropylene copolymer, polyamide, polyacrylonitrile, polyacrylate, polyacrylic acid, polyacrylates, sodium carboxymethylcellulose, polyvinylpyrrolidone, polyvinyl ether, polymethyl methacrylate, polytetrafluoroethylene and polyhexafluoropropylene.**

119. *Nishikawa* discloses “wherein the binder is one or more selected from the group consisting of ... polyamide.” The heat resistant porous layer in each of *Nishikawa*’s Example 4 and Example 5 separators includes a resin of poly-m-phenylene isophthalamide, which a POSA would have understood to be a polyamide. *Nishikawa*, 22:10-35, 22:46-51; *see also Nishikawa*, 7:49-55 (recommending a resin of polyamide). This is because, as shown in the chemical structure of poly-m-phenylene isophthalamide reproduced and annotated below, this polymer is linked together by amide linkages in its backbone. Appendix B. This is also reflected in the ending of the chemical name, poly-m-phenylene isophthal**amide**. Chemical names are constructed to tell the reader what kind of chemical functionality the compounds contain. *Compare also Nishikawa*, 7:49-57 (listing materials for *Nishikawa*’s heat resistant resin, including polyamide and cellulose, which is a category of chemical compounds that a POSA would have understood to encompass sodium carboxymethylcellulose) with ’987 patent claim 7 (listing materials for claimed “binder,” including polyamide and sodium carboxymethylcellulose).

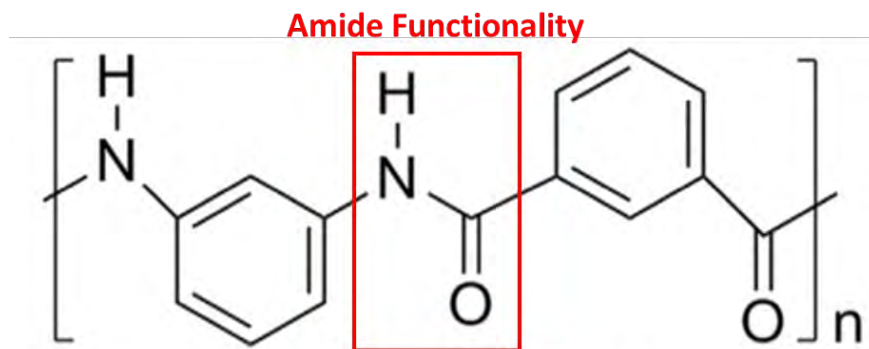


Fig. 1. Chemical structure of PMIA.

7. Claim 8: An energy storage device, comprising the separator according to claim 1.

120. *Nishikawa* discloses “[a]n energy storage device, comprising the separator according to claim 1.” As explained above for claim 1, each of *Nishikawa*’s Example 4 and Example 5 separators discloses “the separator according to claim 1.” And *Nishikawa* discloses using the example separators “for a nonaqueous secondary battery,” which is one “energy storage device” described in the ’987 patent. *Nishikawa*, 22:37-40, 22:46-51; ’987 patent, 1:20-21 (describing “[n]on-aqueous secondary batteries”).

8. Claim 9: The energy storage device according to claim 8, wherein the energy storage device is a lithium-ion battery.

121. *Nishikawa* discloses “wherein the energy storage device is a lithium-ion battery.” As explained for claim 8, *Nishikawa*’s Example 4 and Example 5 separators are for a nonaqueous secondary battery, which *Nishikawa* states “is represented by a lithium ion secondary battery.” *Nishikawa*, 1:14-18. A POSA would

likewise have known that a lithium-ion battery is a typical nonaqueous secondary battery.

B. Ground 2: *Nishikawa* Would Have Rendered Obvious Claims 10-16

1. Claim 10

122. *Nishikawa* would have rendered obvious claim 10.

a. 10[p] A method for preparing the separator of claim 1, wherein the method comprises steps of:

123. As explained above for claim 1, each of *Nishikawa*'s Example 4 and Example 5 separators discloses "the separator of claim 1." *Nishikawa* further discloses "[a] method for preparing" each of *Nishikawa*'s Example 4 and Example 5 separators. *Nishikawa*, 15:51-16:44 (Example 1), 22:10-42 (Example 4, same as Example 1 in some aspects), 22:46-52 (Example 5, same as Examples 1 and 4 in some aspects).

b. 10[a] mixing inorganic particles with a binder to generate a mixture; and 10[b] adding a first solvent into the mixture;

124. *Nishikawa* teaches "mixing inorganic particles with a binder to generate a mixture" and "adding a first solvent into the mixture." In particular, *Nishikawa* teaches that, to prepare each of the Example 4 and Example 5 separators, a poly-m-phenylene isophthalamide resin and an inorganic filler containing aluminum hydroxide "were mixed at a weight ratio of 25/75." *Nishikawa*, 22:26-29. A POSA

would have understood this to teach mixing the **inorganic filler** containing aluminum hydroxide with the poly-m-phenylene isophthalamide **resin** to generate a mixture.

125. *Nishikawa* further teaches that the **resin** and **inorganic filler**, once mixed together into the mixture, were “mixed [at a particular concentration] with a mixed **solvent** containing dimethylacetamide (DMAc) and tripropylene glycol (TPG) [in a particular weight ratio], thereby providing a coating slurry.” *Nishikawa*, 22:26-33 (Example 4), 22:46-51 (Example 5 same as Example 4 in relevant aspects). The **solvent** *Nishikawa* describes, dimethylacetamide, is one embodiment of the claimed “**first solvent**” described in the ’987 patent. *Compare Nishikawa*, 22:26-33 with ’987 patent, 2:35-38. A POSA would have understood this to teach adding a **solvent**, the dimethylacetamide, to the mixture of the **inorganic filler** containing aluminum hydroxide with the poly-m-phenylene isophthalamide **resin**.

c. 10[c] stirring the mixture with the first solvent to obtain a uniform coating solution;

126. *Nishikawa* would have rendered obvious “stirring the mixture with the **first solvent** to obtain a **uniform coating solution**.” *Nishikawa* teaches that the **resin** and **inorganic filler**, once mixed together, were “mixed [at a particular concentration] with a mixed **solvent** containing dimethylacetamide (DMAc) and tripropylene glycol (TPG) [in a particular weight ratio], thereby providing a **coating slurry**.” *Nishikawa*, 22:26-33 (Example 4), 22:46-51 (Example 5 same as Example 4 in relevant aspects).

A POSA would have understood *Nishikawa*'s "mix[ing]" to be synonymous with—or at least to have rendered obvious—the claimed "stirring." This is so at least because stirring was a typical and widespread technique known to a POSA for mixing dry ingredients, like the **resin** and **inorganic filler**, into a solvent like the **first solvent**. For this reason, mixing by stirring would have been nothing more than the use of a known technique and would have yielded nothing more than predictable results.

127. A POSA would also have been motivated and found it obvious to make the "**coating slurry**" taught by *Nishikawa* "uniform." As *Nishikawa* explains, it is "favorable" for the **heat resistant porous layer** formed from the **coating slurry** to "hav[e] uniform minute pores," and a POSA would have recognized that uniformity in the **coating slurry** would lead to *Nishikawa*'s desired uniformity in the **heat resistant porous layer** formed from the **coating slurry**. Moreover, such uniformity was known to be desirable in the art, and a POSA would have known how to achieve such uniformity. As just one example, *Honda* recommends "enhancing the dispersibilities of the resin particles and inorganic filler" in a **coating liquid**, which a POSA would have recognized leads to greater uniformity. See also Ex. 1010, 10:50-53 (recommending a solvent that "facilitates uniform mixing"). Still further, a POSA would have known how to achieve such uniformity. POSAs producing coatings have long recognized the importance of a uniform coating solution, which

can also be referred to as a coating slurry or coating mixture. For instance, *Katayama* discusses the need for uniformity in the coating slurry: “[T]he inorganic fine particles ... are likely to be settled in the slurry. In particular, if the particle size is 1 μm or less, the fine particles are likely to be agglomerated together. Thus, it may be difficult to maintain a stable dispersion state of the fine particles in the slurry. ... When the slurry in which the fine particles are agglomerated or settled is applied to the base or the like, the application tends to be not uniform. The non-uniform application of the slurry reduces the evenness of the separator produced. Consequently, in the lithium secondary battery, the ionic conduction is not uniform within the separator, which may cause a deficiency such as a deposition of lithium during charging of the battery particularly at a high current density.” Exhibit 1019, [0011]-[0013]. *Katayama* then teaches how to achieve this desired uniformity using mixing techniques, including **stirring**: “... a method of using a slurry that is prepared by dispersing the insulating fine particles in a solvent with various types of mixing and **stirring** devices such as a disperser, an agitator, a homogenizer, a ball mill, an attritor, and a jet mill” *Id.*, [0113]. More generally, a POSA would have known, for example, that dispersion is achievable through commercially available dispersing devices in which desirable dispersion is achieved by controlling dispersion conditions such as a number of rotations, dispersion energy, and dispersion time.

128. As a POSA would have recognized in general, a uniform coating slurry

is fundamental to a successful coating process. This is true for at least three reasons. First, a POSA would have known, a non-uniform slurry will result in non-uniform coverage on the surface being coated. There may be bare patches, or bare streaks in the coating direction, and other places with too much (too thick) material. Since producing the coating slurry requires mixing dry powder ingredients with a liquid solvent, incomplete mixing may result in clumps of dry material suspended in the liquid. These would result in patches or streaks of dry powder in places on the coated surface. If the coating slurry is non-uniform, then the coating thickness may vary widely and there may be bare patches with no coating at all, or places covered with dry powder that falls off and leaves a bare patch. Second, a POSA would have recognized that a non-uniform coating slurry may gum up the coating equipment. This may cause the coating process to fail, and it may damage the coating equipment. Third, a POSA would have known that he or she should not even attempt to start a coating process until he or she is sure that the coating slurry is well mixed and uniformly dispersed. To do otherwise would risk failure of the coating process and potential damage to expensive equipment. Accordingly, for at least these reasons, a POSA would have been motivated and found it obvious to prepare a uniform coating slurry.

d. 10[d] coating the uniform coating solution onto a surface of a porous substrate to form a wet film;

129. *Nishikawa* teaches “coating the uniform coating solution onto a surface of a porous substrate to form a wet film.” In *Nishikawa*, the coating slurry is “coat[ed] ... on both the surfaces of the polyethylene microporous membrane.” *Nishikawa*, 16:25-29 (Example 1); 22:37-40 (Example 4 same as Example 1 in relevant aspects), 22:46-51 (Example 5 same as Example 4 in relevant aspects). A POSA would have understood the coating slurry thus coated in *Nishikawa* to be “a wet film” because the term “slurry” used by *Nishikawa*, like the term “solution” used in the ‘987 patent, always refers to a wet fluid. And any coating process using a wet fluid (slurry or solution) necessarily produces a wet coating or wet film, at least before it is dried. (*Nishikawa* does disclose a drying step, but this is later in the process. *Nishikawa*, 16:31-32.) Finally, *Nishikawa* describes its own process as a “wet coating method.” *Id.*, 7:58-63.

e. 10[e] [wherein the solid content in] the coating solution is in a range from 7% to 25%²;

130. *Nishikawa* teaches “[wherein the solid content in] the coating solution

² This claim limitation reads only “the coating solution is in a range from 7% to 25%,” but does not specify what aspect of the coating solution falls within this

is in a range from 7% to 25%” because a POSA would have recognized that each of *Nishikawa*’s Example 4 and Example 5 **separators** is prepared with a solid content in the **coating slurry** that “is in a range from 7% to 25%.”

131. A POSA would have understood the “solid content” in claim 10 to refer to the solids composition of the **coating solution**. That would be the total amount of solids—i.e., the **inorganic particles** plus **binder** (and any other non-solvent, non-volatile components such as surfactants, viscosity modifiers, etc.) Put another way, the solid content in a coating solution (aka a coating slurry) is all the material that is left when the coating solution is completely dried, that is when all volatile components (solvents) are removed by drying. The solid content is then expressed as a percentage of the total amount of **coating solution**, which would include the total amount of solids as well as the solvent.

percentage range. I have been told that, for purposes of this IPR, Petitioner reads “the **coating solution** is in a range from 7% to 25%” as “wherein the solid content in the **coating solution** is in a range from 7% to 25%.” *See, e.g.*, 2:30-31, 6:14-15, claim 11. Based on my knowledge of how a POSA would understand this claim language, I agree this is the best reading of claim 10. Accordingly, I have provided my opinions as to whether *Nishikawa* would have rendered obvious “wherein the solid content in the **coating solution** is in a range from 7% to 25%.”

132. Claim 10 does not specify the basis on which this percentage is calculated. In theory, the solid content could be calculated based on weight (mass) or based on volume. A POSA would have understood claim 10 to refer to—or at least to include—a solid content calculated based on mass. This is because, in preparing such a coating solution, it is natural to weight out amounts of different components to be added. Measuring out amounts to be added on a volume basis, on the other hand, would be impractical as there are no simple ways to quickly determine volumes of materials, such as the powdered ingredients being mixed. The nominal volume of a powder, when packed into a container, is much higher than the actual volume occupied by the material since packed particles only fill, very roughly, about half the space that the powder occupies (the balance being air). Were volumes to be needed for these components, a POSA would have to (i) weigh the ingredients to determine a mass of each ingredient and (ii) determine a volume for each ingredient by dividing the mass by the ingredient’s density (e.g., as described above in connection with claim 4). For this reason, mass is the usual basis on which formulating and mixing these types of ingredients is done, and for this reason it is my opinion that a POSA would have understood claim 10 to refer to—or at least to include—a solid content calculated based on mass.

133. Each of *Nishikawa*’s Example 4 and Example 5 **separators** is prepared with a solid content in the **coating slurry** that “is in a range from 7% to 25%.” For

Example 4, *Nishikawa* states that, in the **coating slurry**, the poly-m-phenylene isophthalamide **resin** has a concentration “of 5.5% by weight.” *Nishikawa*, 22:26-35. *Nishikawa* also states that the poly-m-phenylene isophthalamide **resin** and the **inorganic filler** containing aluminum hydroxide “were mixed at a weight ratio of 25/75,” meaning there is three times as much (by weight) **inorganic filler** as **resin** in the **coating slurry**. *Id.* From this, a POSA would have recognized that, in the **coating slurry**, the **inorganic filler** has a concentration of 16.5% by weight, as this is three times the 5.5% concentration by weight of the **resin**. As noted above, the “solid content” of the **coating slurry**, a POSA would have known, is simply the sum of the concentrations by weight of any solid content in the **coating slurry**—here in *Nishikawa*’s Example 4, the **resin** and the **inorganic filler**. Accordingly, a POSA would have understood that the solid content” of the **coating slurry** in Example 4 is the sum of the 5.5% concentration by weight of the **resin** and the 16.5% concentration by weight of the **inorganic filler**, namely, 22%. *Nishikawa*’s Example 5 has the same solid content, as it is the same as Example 4 in the relevant aspects. *Nishikawa*, 22:46-51. Thus, a POSA would have understood that each of *Nishikawa*’s Example 4 and Example 5 **separators** has a solid content of 22%, which is within the claimed range.

- f. **10[f] wherein a ratio of Dv90 of the inorganic particles to the thickness of the porous layer is in a range from 0.3 to 3.0.**

134. As explained above for claim element 1[d], *Nishikawa* discloses “wherein a ratio of Dv90 of the inorganic particles to the thickness of the porous layer is in a range from 0.3 to 3.0.”

2. **Claim 11: The method according to claim 10, wherein the solid content in the coating solution is in a range from 7% to 25%.**

135. As explained above for claim element 10[e], *Nishikawa* teaches “wherein the solid content in the coating solution is in a range from 7% to 25%.”

3. **Claim 12: The method according to claim 10, wherein the coagulating solution comprises a second solvent and a third solvent, and the second solvent has a mass percentage of 20% to 60%.**

136. *Nishikawa* teaches “wherein the coagulating solution comprises a second solvent and a third solvent, and the second solvent has a mass percentage of 20% to 60%.”

137. *Nishikawa* describes a “coagulation bath,” used in both Examples 4 and 5, in which the microporous membrane, coated with the coating slurry, is “immersed.” *Nishikawa*, 16:29-31, 22:37-40 (Example 4 same as Example 1 in relevant aspects), 22:46-51 (Example 5 same as Example 4 in relevant aspects). *Nishikawa*’s coagulation bath, a POSA would have recognized, teaches the claimed “coagulating solution,” in which the ’987 patent likewise states the porous substrate, coated with

the **coating solution**, is “immers[ed].” ’987 patent, 2:27-28.

138. *Nishikawa*’s **coagulation bath** includes **dimethylacetamide**, which is one of the embodiments of the “**second solvent**” in the ’987 patent. *Compare Nishikawa*, 16:29-31 with ’987 patent, 6:40-43. *Nishikawa*’s **coagulation bath** also includes **water**, which is one of the embodiments of the “**third solvent**” in the ’987 patent. *Compare Nishikawa*, 16:29-31 with ’987 patent, 6:43-46.

139. *Nishikawa* also teaches that the **dimethylacetamide** “has a mass percentage of 20% to 60%.” This is because *Nishikawa*’s **coagulation bath** is described as having “a weight ratio of water / **DMAc** [**dimethylacetamide**] / TPG [tripropylene glycol] of 50/**25**/25,” from which a POSA would understand the **dimethylacetamide** has a mass percentage of 25%. Thus, in each of *Nishikawa*’s Example 4 and Example 5 **separators**, the **dimethylacetamide** has a mass percentage of 25%, which is within the claimed range.

4. Claim 13: The method according to claim 10, wherein the **first solvent is one or more independently selected from the group consisting of N-methylpyrrolidone, dimethylacetamide and dimethylformamide.**

140. *Nishikawa* teaches “wherein the **first solvent** is one or more independently selected from the group consisting of ... dimethylacetamide.” In preparing each of the Example 4 and Example 5 **separators**, *Nishikawa* uses a **solvent** containing dimethylacetamide. *Nishikawa*, 22:26-33 (Example 4), 22:46-51

(Example 5 same as Example 4 in relevant aspects).

5. **Claim 14: The method according to claim 10, wherein the porous substrate comprises a polymer film, a multilayer polymer film, or a non-woven fabric formed by any one or more of the following polymers: polyethylene, polypropylene, polyethylene terephthalate, polyphthaloyl diamine, polybutylene terephthalate, polyester, polyacetal, polyamide, polyimide, polyetheretherketone, polyaryletherketone, polyetherimide, polyamide imide, polybenzimidazole, polyethersulfone, polyphenylene oxide, cycloolefin copolymer, polyphenylene sulfide, and polyethylene naphthalene.**

141. *Nishikawa* teaches “wherein the porous substrate comprises a polymer film ... formed by ... polyethylene.” In each of *Nishikawa*’s Example 4 and Example 5 separators, the microporous membrane is a “polyethylene microporous membrane,” formed of polyethylene. *Nishikawa*, 15:51-16:14 (Example 1), 22:36-37 (Example 4 uses “polyethylene microporous membrane” of Example 1), 22:46-51 (Example 5 same as Example 4 in relevant aspects). A POSA would have understood a “polyethylene microporous membrane” to be an example of a polymer film, polyethylene being a polymer and a membrane being a thin layer which is synonymous with a film.

6. **Claim 15: The method according to claim 14, wherein the polyethylene is at least one selected from the group consisting of high density polyethylene, low density polyethylene, and ultrahigh molecular weight polyethylene.**

142. *Nishikawa* teaches “wherein the polyethylene is at least one selected

from the group consisting of high density polyethylene, ... and ultrahigh molecular weight polyethylene.” This is because *Nishikawa* states that “preferred examples of polyethylene” for the microporous membrane “include high density polyethylene and a mixture of high density polyethylene and ultrahigh molecular weight polyethylene.” *Nishikawa*, 8:63-67.

7. **Claim 16: The method according to claim 12, wherein the second solvent is one or more independently selected from the group consisting of N-methylpyrrolidone, dimethylacetamide and dimethylformamide, and the third solvent is one or more selected from the group consisting of deionized water, ethanol, propanol, acetone, dimethyl carbonate and diethyl carbonate.**

143. *Nishikawa* teaches that “the second solvent is ... dimethylacetamide” and “the third solvent is ... deionized water.” In preparing each of the Example 4 and Example 5 separators, *Nishikawa*’s coagulation bath includes dimethylacetamide and water. *Nishikawa*, 16:29-31. A POSA would have understood *Nishikawa*’s use of water to teach “deionized water” at least because a POSA would have known it would be desirable to use pure water in *Nishikawa*, to avoid any complications from impurities, and deionized water would have been the most likely source of pure water for a POSA.

C. Ground 3: *Nishikawa* and *Honda* Would Have Rendered Obvious Claim 17

- 1. Claim 17: The separator according to claim 1, wherein the porous layer has pores formed by the binder, at least a part of the inorganic particles are embedded in the pores.**

144. *Nishikawa* and *Honda* would have rendered obvious “wherein the porous layer has pores formed by the binder, at least a part of the inorganic particles are embedded in the pores.”

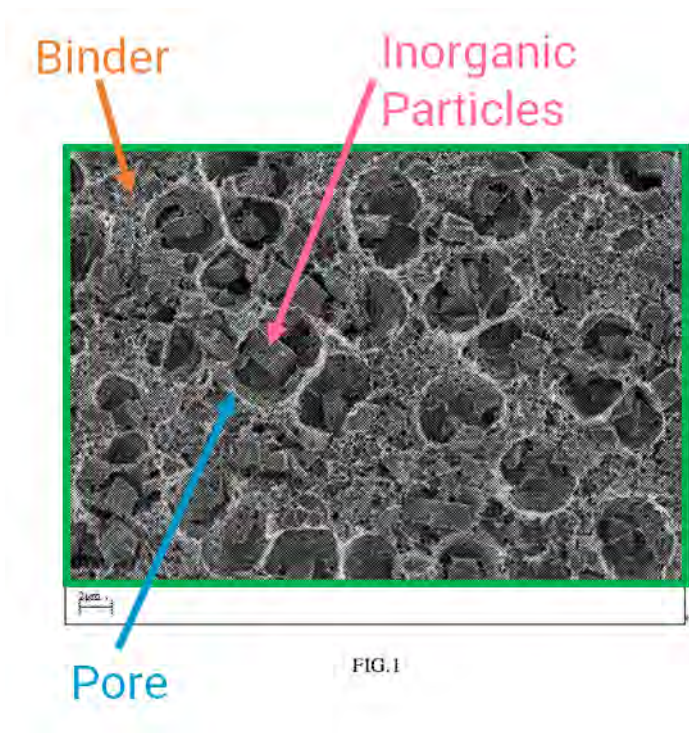
145. *Nishikawa* describes “pores in the heat resistant porous layer,” *Nishikawa*, 7:26-30. *Nishikawa* explains that “[t]he heat resistant porous layer of the invention contains the heat resistant resin, has numerous minute pores inside, and has a such a structure that the minute pores are connected to each other, thereby providing a porous layer, through which a gas or a liquid can pass from one surface to the other surface.” *Id.*, 7:41-45. *Nishikawa* also explains that the “inorganic filler contribut[es] to the formation of pores” in the heat resistant porous layer, but does not explain how. *Nishikawa* does not further describe the structure of those pores.

146. *Honda* explains how inorganic filler can contribute to the formation of pores. In particular, *Honda* recommends a porous layer in which “a resin has a fibril shape to form a three-dimensional network structure, by which a filler is trapped by the network structure.” *Honda*, [0164] *see also id.*, [0228]. A POSA would have recognized from *Honda* that such “a three-dimensional network structure” of the

resin would include “pores formed by the” resin. In particular, the pores are formed in the voids of the “three-dimensional network structure” *Honda* describes.

147. Thus, from *Honda*, a POSA would have recognized that one way for the “inorganic filler [to] contribut[e] to the formation of pores” in the resin of heat resistant porous layer—as *Nishikawa* envisions—is for the inorganic filler to be “trapped by” the pores in the resin, as *Honda* describes. Accordingly, from *Nishikawa* and *Honda*, a POSA would have been motivated and found it obvious for the inorganic filler to be “trapped by” the pores in the resin.

148. Thus, from *Nishikawa* and *Honda*, a POSA would have been motivated and found it obvious to implement *Nishikawa*’s heat resistant porous layer to have pores formed by the resin, with at least a part of the inorganic filler trapped in the pores, as *Honda* describes. A POSA would have understood such inorganic filler trapped in the pores to be “embedded in” the pores, at least because the ’987 patent shows such “embedded” inorganic particles are trapped in the pores, as annotated Figure 1 of the ’987 patent, below, shows.



D. Ground 4: *Iwai* Anticipates Claims 1-2 and 4-9

1. Claim 1

149. *Iwai* anticipates claim 1.

a. 1[p] A separator, comprising:

150. To the extent this preamble is limiting, *Iwai* describes “[a] separator.”

Iwai describes a “separator for a non-aqueous secondary battery” and example separators in Example 7 and Comparative Example 2. *Iwai*, [0001], [0206]-[0208], [0215]-[0217].

b. 1[a] a porous substrate; and

151. *Iwai* discloses “a porous substrate.” In *Iwai*, the separator includes a

“porous substrate.” *Iwai*, [0020]; *see also id.*, [0046]-[0047]. Each of *Iwai*’s Example 7 and Comparative Example 2 **separators** includes a porous substrate. *Id.*, [0157] (Example 1 includes a “porous substrate”); [0206]-[0208] (Example 7 same as Example 1); [0215]-[0217] (Comparative Example 2 same as Example 1)³.

c. 1[b] a porous layer arranged on a surface of the porous substrate,

152. *Iwai* discloses “a porous layer arranged on a surface of the porous

³ *Iwai*’s Example 7 is “obtained in the same manner as in Example 1, except that” the “organic filler A” used in Example 1 is replaced with a mixture of “inorganic filler C,” which is “a magnesium hydroxide filler having a volume average particle diameter of 1.6 μm,” and “inorganic filler D” which is “a magnesium hydroxide filler having a volume average particle diameter of 0.8 μm,” and “the average thickness a of the adhesive porous layer” was changed as shown in Table 1. *Iwai*, [0206]. *Iwai*’s Comparative Example 2 is “obtained in the same manner as in Example 1, except that the inorganic filler D was used instead of the organic filler A and that the average thickness of the adhesive porous layer” was changed as shown in Table 1. *Id.*, [0215]. Accordingly, throughout my discussion of Ground 4, citations to discussions of Example 1 are provided where they equally apply to Example 7 and Comparative Example 2.

substrate.” In *Iwai*, the separator includes an “adhesive porous layer” that is “provided on one or both sides of the porous substrate.” *Iwai*, [0021]; *see also id.*, [0063]. Each of *Iwai*’s Example 7 and Comparative Example 2 separators includes an adhesive porous layer that is “applied ... to both sides of” the porous substrate. *Iwai*, [0189].

d. 1[c] wherein the porous layer comprises inorganic particles and a binder,

153. *Iwai* discloses “wherein the porous layer comprises inorganic particles and a binder.”

154. Regarding inorganic particles, in *Iwai* the adhesive porous layer includes “filler” such as “inorganic filler.” *Iwai*, [0087]-[0088]. The adhesive porous layer in each of *Iwai*’s Example 7 and Comparative Example 2 separators includes inorganic filler of magnesium hydroxide, which is one embodiment of the claimed “inorganic particles” described in the ’987 patent. *Id.*, [0206] (Example 7), [0215] (Comparative Example 2), Table 1; ’987 patent, 2:1-6. *Compare also Iwai*, [0092] (listing materials for *Iwai*’s inorganic filler) with ’987 patent claim 6 (listing materials for claimed “inorganic particles”).

155. Regarding a binder, in *Iwai* the adhesive porous layer includes a “resin” of “polyvinylidene-fluoride,” which is one embodiment of the claimed “binder” described in the ’987 patent. *Iwai*, [0022]; ’987 patent, 2:7-13 The adhesive porous

layer in each of *Iwai*'s Example 7 and Comparative Example 2 separators includes the polyvinylidene-fluoride resin. *Id.*, [0187], Table 1. Compare also *Iwai*, [0074]-[0075] (listing materials for *Iwai*'s polyvinylidene-fluoride resin) with '987 patent claim 7 (listing materials for claimed "binder").

- e. 1[d] a ratio of Dv90 of the inorganic particles to the thickness of the porous layer is in a range from 0.3 to 3.0.

156. *Iwai* discloses that "a ratio of Dv90 of the inorganic particles to the thickness of the porous layer is in a range from 0.3 to 3.0" because a POSA would have recognized that, in each of *Iwai*'s Example 7 and Comparative Example 2 separators, a ratio of a D90 of the inorganic filler to the thickness of the porous membrane must have a value that falls within the claimed range.

157. Table 1, below, shows *Iwai*'s Example 7 separator includes inorganic filler having a volume average particle diameter of 1.2µm. Table 1 also shows that D90-D10 for the inorganic filler—that is, a difference between the D90 of the inorganic filler and the D10 of the inorganic filler—in *Iwai*'s Example 7 separator is 1.6µm.

TABLE 1

	Average		Filler				
	thickness a (μm) of adhesive porous layer	Resin type	Type	Volume average particle diameter r (μm)	D90 – D10 (μm)	Content (% by mass)	a/r
Example 1	2.1	Resin A	Organic filler A	1.8	1.3	5	1.2
Example 2	1.1	Resin A	Organic filler A	1.8	1.3	20	0.6
Example 3	1.5	Resin A	Organic filler A	1.8	1.3	25	0.8
Example 4	3.5	Resin A	Organic filler A	1.8	1.3	1	1.9
Example 5	4.7	Resin A	Organic filler A	1.8	1.3	0.3	2.6
Example 6	3.0	Resin A	Organic filler B	3.0	2.0	20	1.0
Example 7	2.2	Resin A	Inorganic fillers C, D	1.2	1.6	10	1.8
Example 8	2.1	Resins A, B	Organic filler A	1.8	1.3	30	1.2
Comparative Example 1	1.3	Resin A	—	—	—	0	—
Comparative Example 2	3.1	Resin A	Inorganic filler D	0.8	1.1	40	3.9
Comparative Example 3	5.5	Resin A	Organic filler A	1.8	1.3	20	3.1
Comparative Example 4	2.0	Resin A	Organic filler E	5.0	3.6	1	0.4
Comparative Example 5	0.7	Resin A	Organic filler A	1.8	1.3	5	0.4
Comparative Example 6	5.0	Resin A	Organic filler E	5.0	3.6	5	1.0
Comparative Example 7	2.1	Resin A	Organic filler F	4.0	2.5	30	0.5

***Iwai*, Table 1 (cropped and annotated)**

158. From *Iwai*'s Table 1, a POSA would have recognized that D90 of the inorganic filler in *Iwai*'s Example 7 separator must be between 1.6μm and 2.8μm, as explained below.

159. **Volume average particle diameter.** *Iwai* defines “volume average particle diameter” as “a particle diameter at 50% cumulative volume calculated from a smaller side in a volume particle size distribution.” *Iwai*, [0038]. As noted above, while a POSA may typically understand the term “volume average particle diameter” to refer to the mean (arithmetic average) diameter of particles in the particle distribution, by defining “the volume average particle diameter (μm) of the filler” as “a particle diameter at 50% cumulative volume calculated from a smaller side in a volume particle size distribution.,” *Iwai* equates the “volume average particle

diameter ‘r’ (μm)” with D50, stating *Id.*, [0038]; *see also* [0160]. For *Iwai*’s Example 7 **separator**, the volume average particle diameter—that is, the D50—of the **inorganic filler** is 1.2μm.

160. **D10.** *Iwai* defines D10 as “a particle diameter at which a cumulative volume of particles reaches 10% from a smaller side in a volume particle size distribution.” *Iwai*, [0039]. A POSA would have recognized that D10 for *Iwai*’s Example 7 **separator** must be greater than 0, because it would not be possible for particles at 10% of the **inorganic filler** volume to have a particle diameter of 0. Further, a POSA would have recognized that D10 for *Iwai*’s Example 7 **separator** must be less than the volume average particle diameter of the **inorganic filler** for *Iwai*’s Example 7 **separator**, because it would not be possible for the particle diameter at 10% cumulative volume to be more than the particle diameter at 50% cumulative volume. Thus, a POSA would have recognized that D10 for *Iwai*’s Example 7 **separator** must be less than 1.2μm.

161. **D90.** *Iwai*’s Table 1 shows D90-D10 for *Iwai*’s Example 7 **separator** as 1.6μm, as shown above. Thus, a POSA would have recognized:

$$D90 - D10 = 1.6$$

$$D90 = 1.6 + D10$$

$$D90 - 1.6 = D10 \text{ (Equation 1)}$$

162. Further, as explained above, a POSA would have recognized that D10

for *Iwai*'s Example 7 **separator** must be greater than 0 and less than 1.2µm:

$$0 < D10 < 1.2 \text{ (Equation 2)}$$

163. Replacing D10 in Equation 2 per Equation 1, a POSA would have recognized:

$$0 < D90 - 1.6 < 1.2$$

$$1.6 < D90 < 2.8$$

164. Thus, a POSA would have recognized, D90 for *Iwai*'s Example 7 **separator** must be greater than 1.6µm and less than 2.8µm. A POSA would have recognized that "D90," as used by *Iwai*, is synonymous with "Dv90," as used in the '987 patent, at least because *Iwai* and the '987 patent define them synonymously. *Compare Iwai*, [0040] (defining "D90" as "particle diameter at which a cumulative volume of particles reaches 90% from a smaller side in a volume particle size distribution") with '987 patent, 1:53-56 (defining "Dv90" as "a particle size which reaches 90% the cumulative volume from the side of small particle size in the granularity distribution on a volume basis.").

165. Thus, a POSA would have understood that, in *Iwai*'s Example 7 **separator**, the D90 of the **inorganic particles** must be greater than 1.6µm and less than 2.8µm. Further, Table 1 shows that the thickness of the **adhesive porous layer** in *Iwai*'s Example 7 **separator** is 2.2µm. Thus, as summarized in *Iwai*'s Ratios Table below, in *Iwai*'s Example 7 **separator** the ratio of the D90 of the **inorganic particles**

to the thickness of the porous membrane must be greater than 0.72 and less than 1.27.

166. Similar calculations show that, in *Iwai's* Comparative Example 2 separator, the ratio of D90 of the inorganic filler to the thickness of the porous membrane must also have a value that falls within the claimed range.

167. Table 1, above, shows *Iwai's* Comparative Example 2 separator includes inorganic filler having a volume average particle diameter of 0.8 μ m. Table 1 also shows that D90-D10 for the inorganic filler—that is, a difference between the D90 of the inorganic filler and the D10 of the inorganic filler—in *Iwai's* Comparative Example 2 separator is 1.1 μ m.

168. From *Iwai's* Table 1, a POSA would have recognized that D90 of the inorganic filler in *Iwai's* Comparative Example 2 separator must be between 1.6 μ m and 2.8 μ m, as explained below.

169. **Volume average particle diameter.** For *Iwai's* Comparative Example 2 separator, the volume average particle diameter of the inorganic filler is 0.8 μ m.

170. **D10.** A POSA would have recognized that D10 for *Iwai's* Comparative Example 2 separator must be greater than 0, because it would not be possible for particles at 10% of the cumulative volume of inorganic filler particles to have a particle diameter of 0. Further, a POSA would have recognized that D10 for *Iwai's* Comparative Example 2 separator must be less than the volume average particle

diameter of the **inorganic filler** for *Iwai*'s Comparative Example 2 **separator**, because it would not be possible for the particle diameter at 10% cumulative volume to be more than the particle diameter at 50% cumulative volume. Thus, a POSA would have recognized, D10 for *Iwai*'s Comparative Example 2 **separator** must be less than 0.8µm.

171. **D90.** *Iwai*'s Table 1 shows D90-D10 for *Iwai*'s Comparative Example 2 **separator** as 1.1µm, as shown above. Thus, a POSA would have recognized:

$$D90 - D10 = 1.1$$

$$D90 = 1.1 + D10$$

$$D90 - 1.1 = D10 \text{ (Equation 6)}$$

172. Further, as explained, a POSA would have recognized that D10 for *Iwai*'s Comparative Example 2 **separator** must be greater than 0 and less than 0.8µm:

$$0 < D10 < 0.8 \text{ (Equation 7)}$$

173. Replacing D10 in Equation 7 per Equation 6, a POSA would have recognized:

$$0 < D90 - 1.1 < 0.8$$

$$1.1 < D90 < 1.9$$

174. Thus, a POSA would have understood that, in *Iwai*'s Comparative Example 2 **separator**, a D90 of the **inorganic particles** must be greater than 1.1µm

and less than 1.9µm. Further, Table 1 shows that a thickness of the **adhesive porous layer** in *Iwai*'s Comparative Example 2 **separator** is 3.1µm. Thus, as summarized in the *Iwai*'s Ratios Table below, in *Iwai*'s Comparative Example 2 **separator** a ratio of the D90 of the **inorganic particles** to the thickness of the **porous membrane** must be greater than 0.35 and less than 0.61.

<i>Iwai</i> 's Example	D90 (µm)	Thickness (µm)	Ratio ($\frac{D90}{Thickness}$)
Example 7	1.6 < D90 < 2.8	2.2	0.72 < Ratio < 1.27
Comparative Example 2	1.1 < D90 < 1.9	3.1	0.35 < Ratio < 0.61

***Iwai*'s Ratios Table**

175. Thus, *Iwai* discloses an example **separator** (Example 7) in which a ratio of D90 of the **inorganic particles** to the thickness of the **porous membrane** must have a value that falls between 0.72 and 1.27, and *Iwai* discloses an example **separator** (Comparative Example 2) in which a ratio of D90 of the **inorganic particles** to the thickness of the **porous membrane** must have a value that falls between 0.35 and 0.61. Put differently, inherent in *Iwai* is that each of *Iwai*'s Example 7 and Comparative Example 2 **separators** has a ratio of D90 of the **inorganic particles** to the thickness of the **porous membrane** having a value "in a range from 0.3 to 3.0." A POSA would have understood each of *Iwai*'s Example 7 and Comparative Example 2 **separators** to thus disclose, as claim 1 requires, a **separator** in which "a

ratio of Dv90 of the **inorganic particles** to the thickness of the **porous layer** is in a range from 0.3 to 3.0.”

2. Claim 2: The **separator according to claim 1, wherein the **porous layer** has a thickness of 0.2 μm to 10 μm .**

176. *Iwai* discloses “wherein the **porous layer** has a thickness of 0.2 μm to 10 μm .” As Table 1 shows, in *Iwai*’s Example 7 **separator**, the **adhesive porous layer** has a thickness of 2.2 μm , and in *Iwai*’s Comparative Example 2 **separator**, the **adhesive porous layer** has a thickness of 3.1 μm . *Iwai*, Table 1.

3. Claim 4: The **separator according to claim 1, wherein a volume ratio of the **inorganic particles** to the **binder** is in a range from 0.2 to 3.0.**

177. *Iwai* discloses “wherein a volume ratio of the **inorganic particles** to the **binder** is in a range from 0.2 to 3.0,” because a POSA would have understood from *Iwai* that the **separator** of Comparative Example 2 has a volume ratio of 0.51, as explained below.

178. As Table 1 shows, the **separator** of Comparative Example 2 has “Filler” with “Content (% by mass)” of 40%. *Iwai*, Table 1. As *Iwai* explains, this “Content (% by mass)” refers to “[a] content of the **filler** in the coating liquid ... with respect to a total mass of the **polyvinylidene-fluoride resin** and the **filler**.” *Iwai*, [0189]. Thus, a POSA would have understood from *Iwai* that, in the **separator** of Comparative Example 2, the **inorganic filler** accounts for 40% of the total mass of the

polyvinylidene-fluoride resin and the inorganic filler. This is reflected in Equation 8 below, where “M_{filler}” refers to the mass of the inorganic filler and “M_{resin}” refers to the mass of the polyvinylidene-fluoride resin:

$$\frac{M_{\text{filler}}}{M_{\text{filler}} + M_{\text{resin}}} = 0.4 \text{ (Equation 8)}$$

179. Taking the reciprocal of Equation 8 provides Equation 9:

$$\frac{M_{\text{filler}} + M_{\text{resin}}}{M_{\text{filler}}} = 2.5$$

$$M_{\text{filler}} + M_{\text{resin}} = 2.5M_{\text{filler}}$$

$$M_{\text{resin}} = 1.5M_{\text{filler}}$$

$$\frac{M_{\text{resin}}}{M_{\text{filler}}} = 1.5 \text{ (Equation 9)}$$

180. And taking the reciprocal of Equation 9 provides Equation 10:

$$\frac{M_{\text{filler}}}{M_{\text{resin}}} = 0.67 \text{ (Equation 10)}$$

181. While Equation 10 provides a mass ratio, a POSA would have known how to determine a volume ratio from a mass ratio. In particular, a POSA would have known that a mass is convertible to a volume by dividing the mass by the density, ρ , of the material. In general: V [volume] = M [mass] / ρ [mass/volume]. So, a ratio of the masses of two materials can be converted into the ratio of volumes by multiplying this mass ratio by the reciprocal density ratio. This is shown in Equation 11, where “ ρ_{filler} ” refers to the density of the inorganic filler and “ ρ_{resin} ”

refers to a density of the polyvinylidene-fluoride resin, and “V_{filler}” refers to the volume of the inorganic filler and “V_{resin}” refers to the volume of the polyvinylidene-fluoride resin:

$$\frac{V_{\text{filler}}}{V_{\text{resin}}} = \frac{M_{\text{filler}}}{M_{\text{resin}}} \times \frac{\rho_{\text{resin}}}{\rho_{\text{filler}}} \text{ (Equation 11)}$$

182. Replacing $M_{\text{filler}}/M_{\text{resin}}$ in Equation 11 per Equation 10 provides Equation 12 below:

$$\frac{V_{\text{filler}}}{V_{\text{resin}}} = 0.67 \frac{\rho_{\text{resin}}}{\rho_{\text{filler}}} \text{ (Equation 12)}$$

183. The separator of Comparative Example 2 in *Iwai* uses an inorganic filler of magnesium hydroxide, which has a density ρ_{filler} of 2.36 g/cm³. Ex. 1017, 525. The separator of Comparative Example 2 in *Iwai* uses a polyvinylidene-fluoride resin that is a vinylidene fluoride (VDF) / hexafluoropropylene (HFP) copolymer in which the VDF and HFP monomers are provided in a molar ratio of 98.9 to 1.1. *Iwai*, [0187] (Example 1), [0215] (Comparative Example 2 same as Example 1). A POSA would have known how to convert this molar ratio into a weight ratio or weight percentage based on the facts that (i) VDF has a molar mass of 64.034 g/mol and (ii) HFP has a molar mass of 150.021 g/mol. (VDF has the chemical formula C₂H₂F₂, and HFP has the chemical formula C₃F₆. The atomic weights of the constituent atoms are: C (12.011 g/mol), F (18.998 g/mol), and H (1.008 g/mol). Therefore, the molar mass of VDF is 2×12.011 + 2×18.998 + 2×1.008 = 64.034 g/mol. And the molar

mass of HFP is $3 \times 12.011 + 6 \times 18.998 = 150.021$ g/mol) From this, it can be determined that there is 2.54% by weight of HFP and 97.46% by weight of VDF in the Comparative Example 2 binder copolymer.

184. From these percentages by weight, a POSA would have recognized that the **polyvinylidene-fluoride resin** in *Iwai's* Comparative Example 2 has a density that is effectively the same as the density of pure polyvinylidene-fluoride. Polyvinylidene-fluoride hexafluoropropylene copolymer is a common material, and there are numerous examples of this material, with similar compositions to those used in *Iwai's* examples, that are cited in the academic literature or available commercially. Densities for these copolymers are widely reported. The density of pure polyvinylidene fluoride is 1.78 g/cm^3 . *See, e.g.*, Ex. 1018, 3440. Commercially available PVDF-HFP copolymers with 10% and 15% HFP by weight—much higher than the 2.54% HFP by weight of *Iwai's* Comparative Example 2—are reported to have densities in the range of 1.7 to 1.8 g/cm^3 , which is effectively the same as pure polyvinylidene-fluoride. *See, e.g.*, Appendix C, A280 (stating Kynar Flex 2801 has 10% by weight HFP and Kynar Flex 2751 has 15% by weight HFP); Appendix D (Kynar Flex 2801 Technical Data Sheet giving density as 1.78 g/cm^3); Appendix E (Kynar Flex 2751 Technical Data Sheet giving specific gravity as 1.7 - 1.8. A POSA knows that specific gravity is defined as the density of a material divided by the density of water, which is 1.0 g/cm^3 . Thus this data sheet is telling a POSA that this

VDF-HFP copolymer with 15% HFP has a density of 1.7 to 1.8 g/cm³, which again is no different from pure polyvinylidene chloride. From this, a POSA would have been able to identify a density ρ_{resin} of the **resin** in *Iwai*'s Comparative Example 2 to be effectively the same as the density of pure polyvinylidene fluoride, namely, 1.78 g/cm³. See, e.g., Appendix 1018, 3440.

185. Finally, plugging the values of ρ_{filler} and ρ_{resin} into Equation 13, a POSA would have arrived at a volume ratio for *Iwai*'s Comparative Example 2 separator of:

$$\frac{V_{\text{filler}}}{V_{\text{resin}}} = 0.67 \frac{\rho_{\text{resin}}}{\rho_{\text{filler}}} \text{ (Equation 13)}$$

$$\frac{V_{\text{filler}}}{V_{\text{resin}}} = 0.67 \frac{1.78}{2.36}$$

$$\frac{V_{\text{filler}}}{V_{\text{resin}}} = 0.51$$

186. Thus, a POSA would have understood *Iwai* to disclose that, in the **separator** of Comparative Example 2, a volume ratio of the **inorganic particles** to the **binder** is 0.51—a value that is “in a range from 0.2 to 3.0.”

4. Claim 5: The **separator according to claim 1, wherein the **porous layer** has a porosity of 20% to 90%.**

187. *Iwai* discloses “wherein the **porous layer** has a porosity of 20% to 90%.” *Iwai* discloses that “it is preferable that the **adhesive porous layer** has a porosity of from 30% to 60%.” *Iwai*, [0066]. As *Iwai* explains, “in a case in which the porosity

is 30% or more, good ion permeability can be obtained.” *Id.* See also Ex. 1008, 246 (“High porosity is desirable for unhindered ionic current flow.”).

5. **Claim 6: The separator according to claim 1, wherein the inorganic particles are one or more selected from the group consisting of alumina, silica, magnesia, titanium oxide, hafnium dioxide, tin oxide, zirconia, cerium dioxide, nickel oxide, zinc oxide, calcium oxide, boehmite, aluminum hydroxide, magnesium hydroxide, calcium hydroxide, and barium sulfate.**

188. *Iwai* discloses “wherein the inorganic particles are one or more selected from the group consisting of alumina, ... titanium oxide, hafnium dioxide, tin oxide, zirconia, ... aluminum hydroxide, magnesium hydroxide, ... and barium sulfate.” The adhesive porous layer in each of *Iwai*’s Example 7 and Comparative Example 2 separators includes inorganic filler of magnesium hydroxide. *Iwai*, [0206], [0215]. *Iwai* additionally envisions that the inorganic filler may be alumina, zirconia, and other metal oxides; aluminum hydroxide and other metal hydroxides; and barium sulfate. *Iwai*, [0092].

6. **Claim 7: The separator according to claim 1, wherein the binder is one or more selected from the group consisting of polyvinylidene fluoride, vinylidene fluoride-hexafluoropropylene copolymer, polyamide, polyacrylonitrile, polyacrylate, polyacrylic acid, polyacrylates, sodium carboxymethylcellulose, polyvinylpyrrolidone, polyvinyl ether, polymethyl methacrylate, polytetrafluoroethylene and polyhexafluoropropylene.**

189. *Iwai* discloses “wherein the binder is one or more selected from the

group consisting of polyvinylidene fluoride [and] vinylidene fluoride-hexafluoropropylene copolymer.” The porous membrane in each of *Iwai*’s Example 7 and Comparative Example 2 separators includes as the polyvinylidene-fluoride resin a vinylidene fluoride-hexafluoropropylene copolymer. *Iwai*, [0187] (Example 1), [0206] (same as Example 1), [0215] (same as Example 1). *Iwai* additionally envisions that the polyvinylidene-fluoride resin may be polyvinylidene fluoride. *Iwai*, [0074].

7. Claim 8: An energy storage device, comprising the separator according to claim 1.

190. *Iwai* discloses “[a]n energy storage device, comprising the separator according to claim 1.” Each of *Iwai*’s Example 7 and Comparative Example 2 separators discloses “the separator according to claim 1,” as explained above for claim 1, and *Iwai* discloses using each of the Example 7 and Comparative Example 2 separators in a “lithium ion secondary battery,” which is one “energy storage device” described in the ’987 patent. *Iwai*, [0002]-[0003] (describing “a separator for non-aqueous secondary batter[ies] ... which are represented by lithium-ion secondary batteries”), [0187]-[0199] (describing production of “test battery” in Example 1), [0207] (same for Example 7), [0216] (same for Comparative Example 2); ’987 patent, 1:20-21 (describing “[n]on-aqueous secondary batteries, particularly lithium-ion batteries”), 2:17-18 (“the energy storage device is a lithium-

ion battery”).

8. Claim 9: The energy storage device according to claim 8, wherein the energy storage device is a lithium-ion battery.

191. *Iwai* discloses “wherein the energy storage device is a lithium-ion battery.” As explained for claim 8, *Iwai* discloses using each of the Example 7 and Comparative Example 2 separators in a “lithium ion secondary battery.”

E. Ground 5: *Iwai* Would Have Rendered Obvious Claim 3

1. Claim 3: The separator according to claim 1, wherein the pores have an average pore size of 0.3 μm to 20 μm .

192. *Iwai* would have rendered obvious “wherein the pores have an average pore size of 0.3 μm to 20 μm .” *Iwai* teaches that “the adhesive porous layer is a layer having a structure in which a large number of micropores are present inside thereof and the micropores connect to one another, which allows gas or liquid to pass therethrough from one side to the other side.” *Iwai*, [0062]. From *Iwai*, a POSA would have been motivated and found it obvious to implement *Iwai*’s separator to have “an average pore size” within the claimed range for at least two reasons.

193. First, *Iwai* recognizes, like the ’987 patent, that pore size must be adjusted to accommodate two competing concerns: the pores must be large enough to suppress “the blockage of pores.” But the pores also need to be small enough to promote uniformity of ion flow, and to prevent “non-uniformity of the pores at the surface,” which can undermine adhesion. *Iwai*, [0067]; compare with ’987 patent,

5:28-35 (“pore blockage”), 5:43-49 (“non-uniform surface of the porous layer”). From these competing concerns described in *Iwai*, a POSA would have been motivated and found it obvious to implement each of *Iwai*’s Example 7 and Comparative Example 2 **separators** to address these concerns. And a POSA would have understood how to adjust pore size, as it was understood by 2018 that “pore size and the porosity are very important factors for the control of ion conductivity in a battery thus, are directly related to the quality of the battery.” Ex. 1009, 4:34-37. *See also* Ex. 1010, 5:47-50 (“[T]he present inventors have recognized that controlling the porosity and pore size” of a porous layer “is one of the factors affecting the quality of a battery.”). Thus, because *Iwai* teaches that pore size is a parameter to be adjusted to address these competing concerns, and adjustment of pore size would have been within a POSA’s skill, a pore size within the claimed range would have been obvious to a POSA.

194. Second, while *Iwai* recommends a specific range of pore diameters—“from 20 nm to 100 nm,” that is, from .02 μ m to .1 μ m—a POSA would still have found it obvious to adjust *Iwai*’s pore size outside this range, as pore size adjustment was widely understood, as explained in the State of the Art, and a POSA would not have found *Iwai*’s recommended range to be limiting. Rather, a POSA would have recognized that “micropore,” as used by *Iwai* to describe the pores of its porous layer, was a term used in the art to refer to a broader range of pores, namely, those having

any size less than approximately 1 μ m. *See, e.g.*, Ex. 1008, 247 (“One distinguishes between microporous and microporous separators, the latter having to show pore diameters below 1 micron (μ m), i.e., below one-thousandth of a millimeter.”). Accordingly, a POSA would have found it obvious to adjust pore size for each of *Iwai*’s Example 7 and Comparative Example 2 **separators** within a broader micropore range up to at least 1 μ m, provided *Iwai*’s identified competing concerns of pore blockage and non-uniformity were addressed. As noted above, because *Iwai* teaches that pore size is a parameter to be adjusted to address these competing concerns, and adjustment of pore size would have been within a POSA’s skill, adjusting *Iwai*’s pore size would have been obvious to a POSA.

XI. CONCLUSION

I declare that all statements made herein of my knowledge are true, that all statements made on information and belief are believed to be true, and that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

Dated: February 22, 2023

By:



Samuel P. Gido
Amherst, Massachusetts

Appendix A

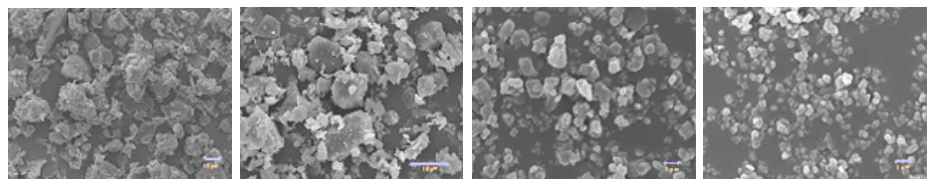
CosMX Exhibit 1003, Page 108 of 512

HIGILITE® (fine particles, particles)

Petrochemical Division	English name	HIGILITE®
Functional Chemicals Division	Product nickname	• Aluminum hydroxide (fine particles, particles) / aluminum hydroxide
Ceramics Division		• H-21 / H-21
Graphite Division		• H-31 / H-31
Aluminum Functional		• H-32 / H-32 • H-42
Components Division		/ H-42
High-tech Battery Materials		• H-42M / H-42M
Division		• H-43 / H-43
Basic Chemicals Division		• H-43M / H-43M
レゾナック Optical		• aluminum hydroxide <chemical name>
Semiconductor Co., Ltd.		
Original Electronic Functional		
Materials Division		
レゾナック・パッケージング		
original packaging business		
promotion department		

Product Description

Under the condition of 200 ~ 350°C, HIGILITE® will undergo violent dehydration reaction and absorb a lot of heat at the same time. Therefore, when HIGILITE® is used as a filler for rubber, plastic, and paper materials, even if heated, the temperature rise of the material is suppressed, the self-extinguishing property is improved, and the generation of smoke is suppressed at the same time. During this process, HIGILITE® will not produce toxic gas, and it can exert its excellent performance as a flame retardant filler. In addition, it improves the arc and creepage resistance of plastics. The main products that can meet the requirements of the above-mentioned applications are H-42M and H-43M of fine particles and particles.



HW H-32 H-42 H-43M

[Main application]

1. Polyaluminum chloride, sodium aluminate, various aluminum salts.
2. Flame retardant filler for latex compound and synthetic rubber.
3. Flame retardant filler for vinyl chloride, epoxy resin, polyester resin, polyurethane resin, polyolefin resin.
4. Catalysts and catalyst supports.
5. Internal filler for coated paper and flame retardant paper.

品名		细 粒			微 粒			
品质项目		H-21	H-31	H-32	H-42	H-42M	H-43	H-43M
化学组成	附着水分 (%)	0.07	0.08	0.20	0.25	0.23	0.30	0.30
	Al(OH) ₃ (%)	99.8	99.8	99.8	99.6	99.6	99.6	99.6
	Fe ₂ O ₃ (%)	0.01	0.01	0.01	0.01	0.01	0.01	0.01
	SiO ₂ (%)	0.01	0.01	0.01	0.01	0.01	0.01	0.01
	Na ₂ O (%)	0.17	0.17	0.17	0.34	0.33	0.40	0.34
	w-Na ₂ O (%)	0.02	0.02	0.02	0.10	0.05	0.13	0.07
	+75 μm量 (%)	0.20	0.04	—	—	—	—	—
	+45 μm量 (%)	—	—	0.10	0.02	0.01	0.02	0.02
	平均粒径 (μm)	27	18	8	1.0	1.0	0.75	0.75
	—30 μm (%)	56	76	96	100	100	100	100
粒度分布	—20 μm (%)	40	54	85	100	100	100	100
	—10 μm (%)	23	31	58	100	100	100	100
	—5 μm (%)	8	12	34	100	100	100	100
	—2 μm (%)	2	4	12	98	98	100	100
	—1 μm (%)	0	1	3	47	46	78	78
	堆积密度 (g/cm ³)	1.0	0.9	0.7	0.2	0.2	0.2	0.2
	白度	1.4	1.2	1.1	0.5	0.5	0.4	0.4
	BET比表面积 (m ² /g)	13	14	20	5.0	5.0	6.7	6.7

Product related information

Properties

White powder

storage conditions, etc.

Keep dry

packaging

25kg paper bag, ton bag, etc.

Chemical Examination Law Number

(1)-17

CAS Reg#

CAS21645-51-2

Relevant laws and regulations (Japanese domestic law)

Dust damage prevention rules

Company Profile

Domestic Group

Japan headquarters

Group products

contact us

Subsidiaries

▲ 回页首

[Sitemap](#) [Regarding website use](#) [Personal Information Protection Policy](#)

Copyright (C) SHOWA DENKO (SHANGHAI) CO.,LTD. All rights reserved.

Appendix B

CosMX Exhibit 1003, Page 111 of 512



Poly(m-phenylene isophthalamide) (PMIA): A potential polymer for breaking through the selectivity-permeability trade-off for ultrafiltration membranes

Chun-Er Lin^a, Jun Wang^a, Ming-Yong Zhou^a, Bao-Ku Zhu^{a,b,*}, Li-Ping Zhu^a, Cong-Jie Gao^{a,b}

^a Key Laboratory of Macromolecule Synthesis and Functionalization (MOE), ERC of Membrane and Water Treatment (MOE), Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

^b CIC-Zj on Membrane and Water Treatment Technology, Zhejiang University of Technology, Hangzhou 310014, China

ARTICLE INFO

Article history:

Received 27 March 2016

Received in revised form

25 June 2016

Accepted 28 June 2016

Available online 30 June 2016

Keywords:

Poly(m-phenylene isophthalamide)

Ultrafiltration membrane

Permeability

Selectivity

Trade-off

ABSTRACT

The selectivity-permeability trade-off represents a limitation to the performance of ultrafiltration (UF) membranes. Theoretically, this trade-off is mainly determined by the pore structure, including the porosity, pore radius distribution and skin layer thickness. Benefiting from its high rigidity and high surface free energy, poly(m-phenylene isophthalamide) (PMIA) is proposed for preparing a high-performance UF membrane. In this work, PMIA membranes with various effective pore radii (6.58 nm, 6.84 nm and 9.28 nm) were fabricated via nonsolvent-induced phase separation (NIPS). Through selectivity-permeability analysis, the PMIA membrane was found to break through the trade-off between selectivity and permeability. Compared with other UF membranes, the PMIA membrane exhibited a high porosity, narrow pore radius distribution and excellent hydrophilicity, leading to its high performance in the filtration process. This phenomenon could probably be attributed to the high rigidity, which confined the motion of the PMIA chain to suppressing pore collapse during pore formation, as well as to the high surface free energy that caused the hydrophilicity. All of these results clearly indicated that PMIA might be the most appropriate polymer for fabricating the UF membrane.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Ultrafiltration (UF) membranes are widely used in water purification [1], wastewater treatment [2], protein product concentration [3], hemodialysis [4], and more. Currently, commercial UF membranes are mostly made from polysulfone (PSf), celluloses, polycarbonate (PC), polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), polyvinyl chloride (PVC) and other inorganic materials. Each series contains membranes that have a range of pore size or molecular weight cut-off. Generally, the performance characteristics of UF membranes mainly contain permeability and selectivity that are inversely related. Because the steric (size exclusion) effect acts as the main separate mechanism [5], the selectivity of UF membrane is determined by pore radius (R) and pore radius distribution (σ) [6], while the permeability is governed mainly by the pore radius (R), porosity (ϵ) and skin layer thickness (δ_m). To identify the underlying relationship between the selectivity and permeability, Mehta and Zydney [7] developed a

trade-off that known UF membranes cannot permeate.

Structurally, an ideal UF membrane should have a high porosity, narrow pore radius distribution and thin skin layer. Additionally, taking the surface property into consideration, hydrophilicity endows the UF membrane with excellent wettability, which effectively improves the water permeation in the filtration process [8,9]. The block copolymer (BCP) membrane, which is supposed to possess high selectivity due to its uniform pore size, has attracted substantial attention in recent years. Nevertheless, limited by their relatively low permeability, the benefits did not outweigh the limitations [10]. Additionally, the synthesis complexity and high cost of BCP make it difficult to produce on a large scale. Therefore, it is important to seek a suitable material for preparing a high-performance UF membrane.

Poly(m-phenylene isophthalamide) (PMIA), due to its hydrogen bond network, has excellent mechanical properties and an outstanding thermal stability [11]. The glass transition temperature (T_g) of PMIA is up to 558 K (shown in Table 1), resulting in a broad range of temperature and high rigidity, which is necessary for membranes with high porosity. Meanwhile, the PMIA membrane is supposed to be hydrophilic due to the high surface free energy provided by the amide bond. Additionally, its high solubility in a common organic solvent (such as DMF and DMAc) makes it

* Corresponding author at: Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China.

E-mail address: zhubk@zju.edu.cn (B.-K. Zhu).

<http://dx.doi.org/10.1016/j.memsci.2016.06.042>

0376-7388/© 2016 Elsevier B.V. All rights reserved.

Table 1
Glass transition temperature and surface free energy of polymers.

Polymer	Glass transition temperature (K)	Surface free energy (mN m ⁻¹)	Δ (mN m ⁻¹)	Ref.
PMIA	558	50.5 ^a	22.3	[13]
PSf	458	42.3	30.5	[14,15]
PP	~260	29	43.8	[14]
PAN	398	38.6	34.2	[14,16]
PTFE	303–399	19.5	53.3	[14,17]
PVC	344–371	41	31.8	[14,17]
PVDF	238	25	47.8	[14,17]
Nylon	320–330	44	28.8	[14,17]
Cellulose	503	56.7	16.1	[14,18]
Cellulose acetate	243–473	45.9	26.9	[14]
H ₂ O	/	72.8	/	[18]

Δ, the difference value of the surface free energy between polymers and water.

^a 50.5, the surface free energy for PMIA, which was obtained from measurements using the two liquid method.

possible to prepare the PMIA membrane by nonsolvent-induced phase separation (NIPS), which is favorable for developing large scale UF membranes [12]. Therefore, PMIA may be a promising material for preparing UF membranes because of these prominent physiochemical properties. However, to the best of our knowledge, there are few (if any) reports about PMIA ultrafiltration membranes via NIPS.

In this work, PMIA ultrafiltration membranes with various effective pore radii (6.58 nm, 6.84 nm, and 9.28 nm) were prepared by varying the temperature of the coagulation bath during the NIPS process. As expected, the prepared PMIA membrane achieves remarkable performance, breaking through the selectivity-permeability trade-off, which can be ascribed to their excellent pore structure and surface hydrophilicity.

2. Materials and methods

2.1. Materials

Poly(m-phenylene isophthalamide) (PMIA) fiber was provided by DuPont Co., Ltd. (USA) and dried at 100 °C for 12 h before use. Its chemical structure is shown in Fig. 1. Dimethyl acetamide (DMAC), dimethyl formamide (DMF), glycerin and bovine serum albumin (BSA) were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). A series of polyethylene glycols (PEGs, MW 10,000–100,000) were purchased from Sigma-Aldrich (USA). All solvents and chemicals were reagent grade and used as received. Ultrapure water (18 MΩ cm⁻¹, Millipore Milli-Q) was used in all aqueous solutions.

2.2. Membrane fabrication

The PMIA membranes were fabricated by the traditional phase inversion method. The casting solution was prepared by dissolving 12 g of PMIA in 88 g of mixed solution (DMAC/DMF/glycerin 1/1/0.8 wt/wt/wt) at 80 °C for 6 h. After filtration and removal of air

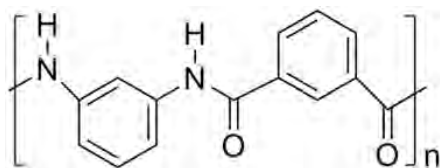


Fig. 1. Chemical structure of PMIA.

bubbles by vacuum deaeration, the solution was cast on a glass substrate with a steel knife; then, the liquid film was immersed into a water coagulation bath at 30 °C, 50 °C or 70 °C. The formed membrane was peeled off and subsequently washed in water at 60 °C for 3 d to extract the residual solvent. The as-prepared PMIA membranes were designated M30, M50 and M70, with the digits indicating the temperature of coagulation baths. Before testing, PMIA membranes were stored in 10 mM phosphate buffer solution (PBS, pH = 7.4) and 5 g/L BSA/PBS solution at 4 °C. For convenience, the PMIA membrane soaked in PBS is referred to as a PMIA/PBS membrane, while that in BSA/PBS solution is referred to as a PMIA/BSA membrane. To ensure equilibrium adsorption, the PMIA/BSA membrane was soaked for 24 h before use.

2.3. Membrane characterization

2.3.1. Membrane surface properties

The surface and cross-section morphology of the membrane was characterized by field emission scanning electronic microscopy (FE-SEM, Hitachi, S-4800, Japan). Images captured at a chosen magnification (50 k) were used to measure the membrane surface pore structure characteristics. With the help of ImageJ software (National Institutes of Health, NIH), binary images were acquired with the pores in black and surface in white at a chosen threshold level [19]. In this method, the pores on the surface should be disconnected from each other and were supposed to be circular. Thus, the porosity (ϵ_{sp}) and pore area can be directly obtained from the software. Then, based on these data, the average pore radius (R_{sa}) and pore density (N_{sp}) can be calculated.

The membrane surface zeta potential was determined from the streaming potential measurement with a SurPass Electrokinetic Analyser (Anton Paar, GmbH, Austria). This measurement was performed at 20 °C in 1 mM KCl solution with the solution pH values ranging from 2 to 10, and the zeta potential was calculated using the Helmholtz-Smoluchowski equation. The water contact angle of the membrane was measured with a contact angle meter system (OCA20, Dataphysics, Germany) in the sessile-drop mode at room temperature.

2.3.2. Pore structure characterization

Polyethylene glycols (PEGs, MW 10,000–100,000) were used as solutes in the feed solution with the solute concentration kept at 200 ppm by weight. The membrane was placed at the bottom of the stirred cell and compacted for 30 min at 0.015 MPa to reach a stable flux. After the stirred cell was filled with PEG solution, the experiment was conducted under 0.01 MPa at room temperature (20 ± 3 °C).

The rejection data for the PEG solution were plotted versus the solute radius on log-probability paper (shown in Fig. S1 in Supplementary information), showing straight lines fit with high correlation coefficients ($R^2 > 0.95$). By ignoring the concentration polarization as well as the steric and hydrodynamic interaction between pores and solutes, the average pore radius (R_a) and geometric standard deviation (GSD, σ_p) were determined. Then, the pore density (N) and porosity (ϵ) were calculated as described in Ref. [20]. Meanwhile, the effective pore radius (R_e) can be approximated using the Hagen-Poiseuille equation:

$$J_v = \frac{\epsilon R_e^2 \Delta P}{8 \eta \delta_m} \quad (1)$$

where J_v is the flux, ΔP is the pressure (Pa), η is the water viscosity (0.001 Pa s), δ_m is the skin layer thickness and ϵ is the porosity. The most probable pore radius (R_m) can be directly acquired from the probability density function curve, which was determined by the average pore radius and geometric standard deviation [6,20].

2.4. Filtration performance

All filtration experiments were conducted on a 47-mm-diameter Amicon UF cell (XFUF04701 Millipore) connected with a 500-mL reservoir containing and a N₂ gas cylinder at room temperature (20 ± 3 °C). The pressure in the stirred cell was controlled by the pressure regulator, which was connected to the N₂ gas cylinder. Each membrane was initially compacted for 30 min at 0.07 MPa to reach a stable flux.

The permeability (L_p , m s⁻¹ Pa⁻¹) was evaluated by measuring the water (pH=6.5) flow rate via timed collection over a range of pressures from 0.01 to 0.05 MPa and calculated directly from the slope of the flux versus pressure data as:

$$L_p = \frac{J_v}{\Delta P} \quad (2)$$

where J_v is the volumetric filtrate flux (m s⁻¹).

After water filtration, the stirred cell was then filled with 5 g/L BSA/PBS solution, and the stirring speed was set to 600 rpm using a magnetic stirrer. After removing 2 mL of the sample to wash out the dead volume beneath the membrane, the filtrate samples were obtained for subsequent analysis. Meanwhile, the feed samples were collected directly from the stirred cell immediately before and after the experiment. The filtrate flow rates were evaluated using a digital balance and the protein concentration was determined by a UV/vis spectrophotometer (Shimadzu, UV-1601, Japan) at 280 nm.

Because the states for PMIA/PBS and PMIA/BSA were different, two methods were adopted for the rejection measurement. By adjusting the pressure in the stirred cell, the filtrate flow rate for the PMIA/PBS membrane was fixed to 1.5×10^{-5} m s⁻¹ where the actual sieving coefficient (S_a) was close to the asymptotic sieving coefficient (S_∞) and a highly polarized condition was avoided [7]. As for the PMIA/BSA membrane, to minimize protein deposition, data were gained by monotonically increasing the flux (by increasing the applied pressure).

The observed sieving coefficient (S_o) was defined as:

$$S_o = \frac{C_f}{C_b} \quad (3)$$

where C_f and C_b are the solute concentrations in filtrate and bulk solution, respectively. Combined with the mass transfer coefficient (k), the actual sieving coefficient (S_a) can be calculated from the observed sieving coefficient (S_o) using a stagnant film model [5]:

$$S_a = \frac{S_o}{(1-S_o)\exp(J_v/k) + S_o} \quad (4)$$

The separation factor (α), which represented the selectivity of the membrane, was obtained from the asymptotic sieving

coefficient (S_∞) by the following equation [7]:

$$\alpha = \frac{1}{S_\infty} \quad (5)$$

3. Results and discussion

3.1. Pore structure of the PMIA membrane

The surface morphology of the PMIA membrane (PMIA/PBS membrane) was observed by scanning electronic microscopy (SEM). As shown in Fig. 2(a), M30 was a typical ultrafiltration membrane with an estimated pore radius of approximately 10 nm. According to the binary image (Fig. 2(b)) transformed from the original SEM image, the surface pore structure parameters of M30 were obtained and are listed in Table 2. Moreover, the results also show that the PMIA membrane features a typical asymmetric structure consisting of a dense selective skin (approximately 0.1 μm) and finger-like macrovoids (see Fig. 2(c)) with a membrane thickness of approximately 130 μm. Because the skin layer thickness (δ_m) was equal to the dense selective skin thickness multiplied by the tortuosity factor (τ), the skin layer thickness for the PMIA membrane was calculated as 0.2 μm with a tortuosity factor (τ) of 2 [21], which was within the range of the skin layer thickness for UF membranes [20,22,23]. Additionally, as shown in Supplementary Fig. S2, both M50 and M70 have a similar structure, and their surface pore structure parameters are also presented in Table 2. In addition, the pore structure parameters of the PMIA membrane were calculated from the transport data with PEG solutes, as summarized in Table 2.

Clearly, as the temperature of the coagulating bath increased from 30 to 70 °C, the average pore radius of the PMIA membranes increased from approximately 5 to 9 nm and the porosity increased from approximately 5% to 10%. This observation can be attributed to the fact that a high temperature will enhance the mutual diffusivity between the non-solvent and casting solution to form large pores. By comparing the results obtained from the two different methods mentioned above, some differences can be found in the pore radius and porosity, which can be explained by the following reasons. First, because SEM sample preparation requires serial dehydration, capillary forces at the liquid-solid interface will cause the pore to shrink, which accounts for the slight reduction in the pore radius and porosity. Second, the surface pore measured by SEM is probably not the “sieve pore”, which has a decisive effect on the membrane filtration performance. Therefore, the pore structure, characterized by PEG filtration, can exactly reflect the actual structure of the PMIA membrane in the filtration process. Hence, on the basis of the average pore radius (R_a) and GSD (σ_p) acquired from PEG filtration, the pore radius distribution

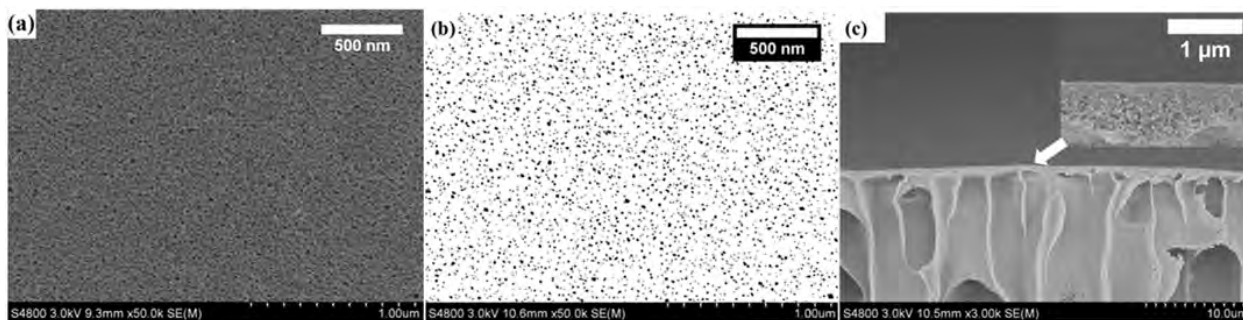


Fig. 2. SEM images of the (a) surface and (c) cross section for M30. (b) Binary image transformed from the SEM image of the surface of M30.

Table 2
Pore structure parameters of the PMIA membranes.

Name	R_{sa} (nm)	R_a (nm)	N_{sp} (μm^{-2})	N (μm^{-2})	ε_{sp} (%)	ε (%)
M30	5.46	6.26	686	632	5.15	5.65
M50	6.42	7.57	620	642	6.42	6.88
M70	7.15	8.73	605	644	8.97	9.23

R_{sa} , N_{sp} and ε_{sp} were obtained from SEM images, while R_a , N and ε were measured from PEG filtration.

and corresponding cumulative curves are shown in Fig. 3. The pore radius of the PMIA membrane is in the range of 3–15 nm, showing a narrow distribution.

3.2. Surface properties of the PMIA membrane

With a state water contact angle of approximately 65° , the PMIA membrane (PMIA/PBS membrane) demonstrated excellent hydrophilicity due to the high surface free energy of PMIA, implying an improvement in the permeability compared to hydrophobic UF membranes. Conversely, as shown in Fig. 4, the streaming potential measurement illustrated that the PMIA membrane has an isoelectric point around pH 4.5. This observation is common for polymeric UF membranes, such as PES and PVDF membranes, owing to the adsorption of hydroxide ions in aqueous electrolyte solution [24].

3.3. Selectivity-permeability analysis for the PMIA membrane

Here, the selectivity-permeability analysis developed by Mehta and Zydney is applied, as it is considered an effective method to analyze the performance of new ultrafiltration membranes [7]. The PMIA/PBS and PMIA/BSA membranes, which were in the same physical “state” [7], were both carefully evaluated.

As shown in Fig. 5, the permeability was obtained from the slope of flux versus pressure data. The value increased from approximately 2 to $4 \times 10^{-9} \text{ m s}^{-1} \text{ Pa}^{-1}$ for the PMIA/BSA membranes, while that of the PMIA/PBS membranes improved from approximately 3 to $8 \times 10^{-9} \text{ m s}^{-1} \text{ Pa}^{-1}$ as the temperature of the coagulation bath increased from 30°C to 70°C . This observation can mainly be attributed to the increase in the pore radius, as mentioned above. Moreover, the permeability for the PMIA/BSA membrane was much lower than that of the PMIA/PBS membrane, as the BSA adsorption greatly reduced the pore radius.

The relationships between the observed sieving coefficients (S_o) and filtrate flux of the PMIA/BSA membranes are shown in Fig. 6. Considering the effect of the concentration polarization, the

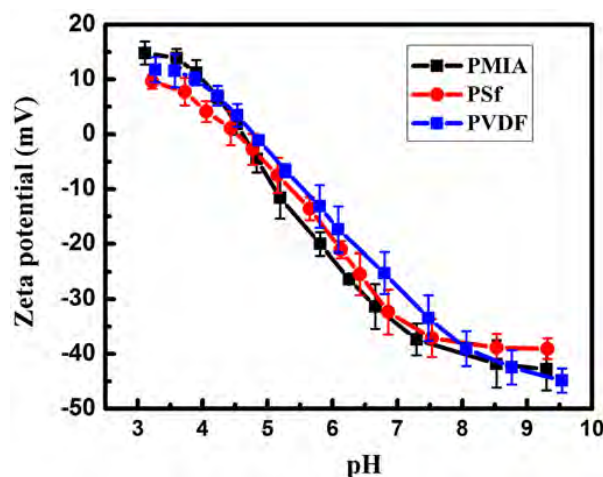


Fig. 4. Surface zeta potential for PMIA, PES and PVDF membranes at different pH values.

actual sieving coefficients (S_a) were obtained from the observed sieving coefficients using Eq. (4). Thus, the asymptotic sieving coefficients (S_∞) can be determined by fitting the sieving coefficients to the hydrodynamic model using an optimization procedure [25,26] (Solver, Microsoft Excel). According to Eq. (5), the separation factors (α) of M30, M50 and M70 were calculated as 384, 139 and 114, respectively. As for the PMIA/PBS membranes, the sieving coefficients and separation factors are presented in Fig. 7. It can be seen that the separation factors for the PMIA/PBS membranes (10–200) were much lower than those of the PMIA/BSA membranes, as the BSA adsorption greatly reduced the pore radius. Nevertheless, both membranes show a similar decrease in the selectivity with increasing pore radius.

Fig. 8 shows two different selectivity-permeability trade-offs, respectively, for PMIA and other UF membranes [25,27–33]. Obviously, the PMIA membranes break through the original trade-off; the permeability at a given separation factor increases twofold while the separation factors at a given permeability are improved nearly 10 times. Therefore, based on theoretical calculation [7], a new upper bound (dashed curve) is plotted with $\varepsilon/\delta_m=2.5$ and $\sigma/r=0.18$, suggesting a high porosity and narrow pore radius distribution compared to the original parameter ($\varepsilon/\delta_m=1$ and $\sigma/r=0.2$, solid line). In spite of the different temperatures of the coagulation bath, all PMIA membranes show a similar trade-off between selectivity and permeability with the data clustering

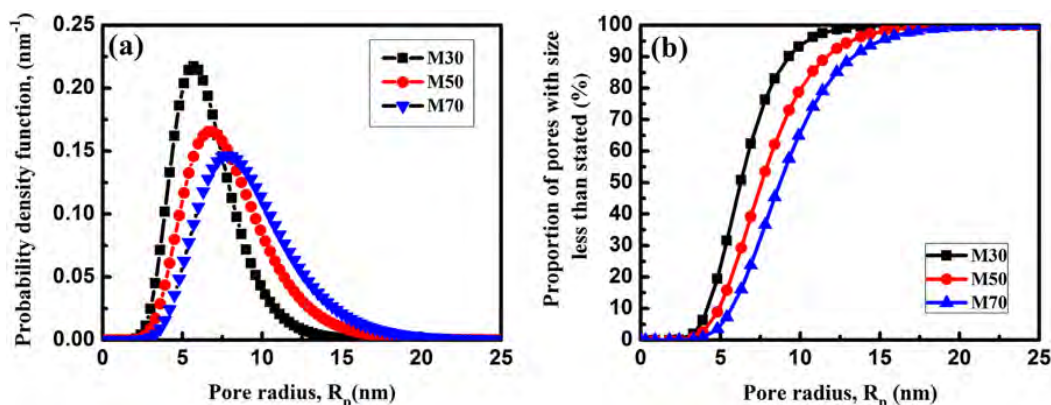


Fig. 3. (a) Pore radius distribution curves and (b) cumulative curves of PMIA membranes.

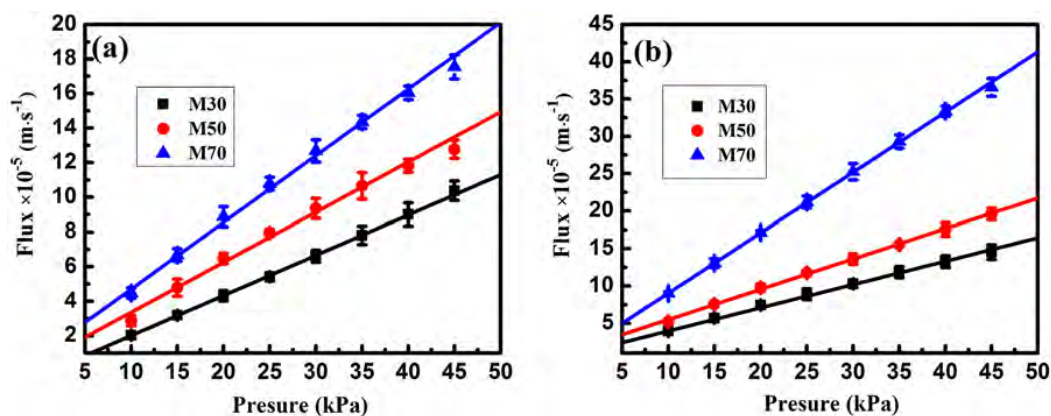


Fig. 5. Flux dependence of the applied pressure for the (a) PMIA/BSA membranes and (b) PMIA/PBS membranes.

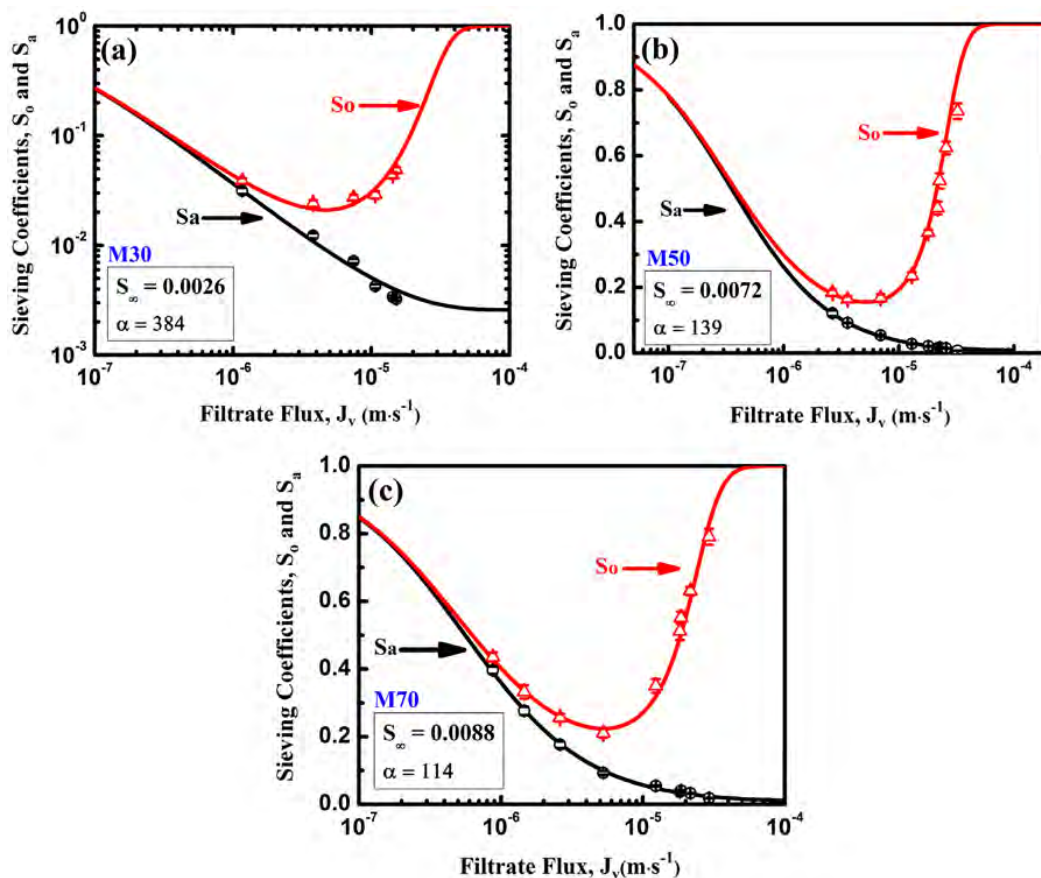


Fig. 6. Sieving coefficients as a function of the filtrate flux for the PMIA/BSA membranes. The solid lines represent the hydrodynamic model predictions with the optimized parameters.

along the dash curve regardless of whether they were adsorbed with BSA. Because the data of the other UF membranes are far from the new upper bound, the new selectivity-permeability trade-off is only suitable for PMIA membranes.

3.4. Comparisons between PMIA and other UF membranes

In this study, more attention is paid to the reasons for the excellent performance of the PMIA membrane. Therefore, six UF

membrane types were chosen for comparison based on the original upper bound (solid line in Fig. 8). Their permeability and separation factors, as well as MWCO, were observed in previous studies, as shown in Table 3. The other parameters of the pore structure could be calculated from the MWCO and GSD (σ_p), with the GSD for the pore radius distribution appropriately valued as 2 [6,34,35].

As shown in Table 3, the effective pore radius (R_e) of the PMIA

CosMX Exhibit 1003, Page 116 of 512

Ningde Amperex Tech. Exhibit No. 2031
Zhuhai CosMX Battery Co. Ltd. v. Ningde Amperex Tech.
IPR2025-00432, U.S. Patent No. 11,575,148
Page 116 of 512

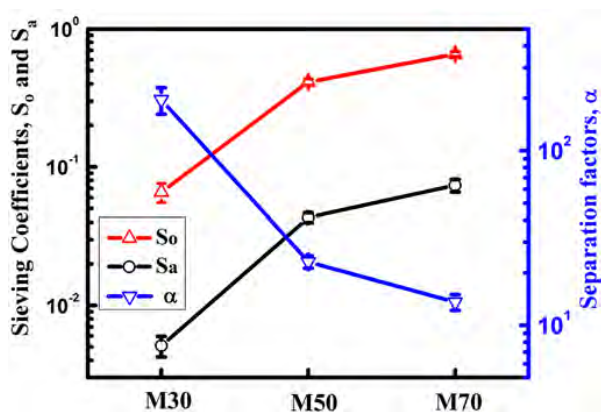


Fig. 7. Sieving coefficients and separation factors for the PMIA/PBS membranes.

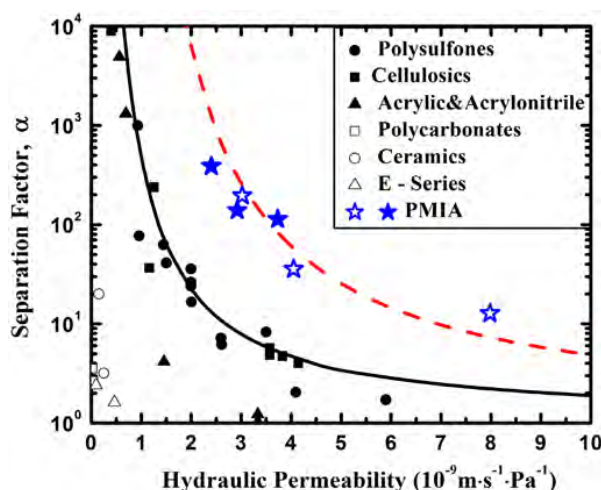


Fig. 8. Selectivity-permeability trade-off for ultrafiltration membranes, including PMIA and other UF membranes [7]. The curves represent the model calculations using a log-normal pore radius distribution with different parameters. The filled blue stars represent the PMIA/BSA membranes, while the hollow blue stars represent the PMIA/PBS membranes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

membrane (6–9 nm) was smaller than that of the other UF membranes (10–24 nm); however, the porosity (6–10%) was much higher. Hence, depending on the Hagen-Poiseuille equation (Eq. (1)), the high porosity results in the large permeability of the PMIA membrane. Conversely, the selectivity is related to the most probable pore radius (R_m) and pore radius distribution (GSD, σ_p).

Generally, a large R_m leads to a relatively small separation factor, while a small σ_p results in a large separation factor [6]. Therefore, the narrow pore radius distribution ($\sigma_p=1.3$ –1.4) improves the separation factor for the PMIA membrane.

Compared with the other polymeric UF membranes, the high porosity and narrow pore radius distribution of the PMIA membrane were possibly generated from the rigid chain of PMIA. The high rigidity can confine the motion of the chain, containing the movement and rearrangement of the chain segment as well as the change in the conformation, during the membrane formation process. Furthermore, this effect could be effectively reinforced by the hydrogen bonding between the polymeric chains. Therefore, the pore collapse will be suppressed and membrane will have a higher porosity and narrower pore radius distribution compared to those of the membranes fabricated by polymer with a flexible chain, such as PVC and PVDF. As for the surface property, compared with the hydrophobic membrane prepared by PSf and PES whose chains are rigid, the hydrophilicity of the PMIA membrane undoubtedly improves its permeability. Hence, cellulose seems to be a suitable material for UF membranes due to its high glass transition temperature (rigid chain) and high surface free energy (hydrophilicity), as shown in Table 1. However, the insolubility in common organic solvents is one of its biggest disadvantages [38].

Accordingly, as a result of its rigid chain and high surface free energy, PMIA appears to be the most suitable polymer for UF membrane fabrication, which has been manifested by the breakthrough in the selectivity-permeability trade-off for the PMIA membrane.

4. Conclusions

In this work, PMIA was chosen to fabricate the ultrafiltration membrane due to its rigidity, high surface free energy and processability. Through selectivity-permeability analysis, the PMIA membrane was found to break through the selectivity-permeability trade-off, with permeability and separation factors ranging from 2.5 to $8 \times 10^{-9} \text{ m s}^{-1} \text{ Pa}^{-1}$ and from 400 to 10, respectively. Compared with the other UF membranes, the high performance of the PMIA membrane was confirmed in terms of the high porosity, narrow pore radius distribution and excellent hydrophilicity. These superior properties could probably be attributed to the high rigidity, which confined the motion of the chain to suppress the pore collapse during membrane formation, as well as to the high surface free energy, which resulted in hydrophilicity.

Therefore, the PMIA membrane could be operated at a lower pressure than other UF membranes, decreasing the energy consumption. This membrane also has a broad range of temperatures available due to the high glass transition temperature. Furthermore, compared with the hydrophobic membrane, the PMIA

Table 3
Characteristic parameters of the pore structure and performance for different membranes.

Polymer	Name	R_m (nm)	R_e (nm)	σ_p	ϵ (%)	L_p ($10^{-9} \text{ m s}^{-1} \text{ Pa}^{-1}$)	α	Ref.
PMIA	M30	5.66	6.58	1.36	5.65	3.06 (2.4)	196 (389)	This work
	M50	6.81	6.84	1.40	6.88	4.02 (2.92)	36 (139)	
	M70	7.83	9.28	1.39	9.23	7.92 (3.73)	13 (113)	
PSf	PTHK	2.55	12.25	~2	0.73	1.38	< 90	[7,29]
Polyacrylonitrile	MX100	2.55	12.25	~2	0.78	1.46	< 70	[7,29]
Cellulose	YM100	2.55	12.25	~2	1.14	2.15	< 20	[7,29]
PES	OMEGA 100-K	2.55	12.25	~2	1.50	2.0	27	[25,36]
PES	OMEGA 50-K	2.10	10.21	~2	1.05	0.93	1000	[25,37]
PES	OMEGA 300-K	4.89	23.55	~2	2.95	4.1	2	[25,37]

The data for the PMIA membrane, in parentheses, were obtained from the PMIA/BSA membrane. The MWCO for PTHK, MX100, YM100, and OMEGA 100-K were 100 kDa, while those for OMEGA 50-k and OMEGA 300-k were, respectively, 50 and 300 kDa.

membrane, with hydrophilicity, is supposed to exhibit good anti-fouling properties. All of these great properties of the PMIA membranes demonstrate their potential for excellent performance in industrial applications. Hence, PMIA is probably the most suitable polymer for preparing ultrafiltration membranes.

Acknowledgments

The National 863 Program of China (grant number 2012AA03A602), the National 973 Program of China (grant number 2009CB623402) and the Nature Science Foundation Committee of China (grant number 20974094) are thanked for supporting this work.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.memsci.2016.06.042>.

Nomenclature

L_p	permeability of membranes ($\text{m s}^{-1} \text{Pa}^{-1}$)
J_v	volumetric filtrate flux (m s^{-1})
ΔP	pressure (Pa)
k	mass transfer coefficient
S_o	observed sieving coefficient
S_a	actual sieving coefficient
S_∞	asymptotic sieving coefficients
C_f	solute concentration in filtrate (mol m^{-3})
C_b	solute concentration in bulk (mol m^{-3})
α	separation factor
R_a	average pore radius (nm)
R_{sa}	surface average pore radius (nm)
R_m	most probable pore radius (nm)
R_e	effective pore radius (nm)
R_s	solute radius (nm)
σ_p	geometric standard deviation
n	pore density
N_{sp}	pore density
ε	porosity
ε_{sp}	surface porosity
η	water viscosity (0.001 Pa s)
δ_m	skin layer thickness (μm)

References

- [1] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Marinas, A. M. Mayes, Science and technology for water purification in the coming decades, *Nature* 452 (2008) 301–310.
- [2] M. Marcucci, G. Nosenzo, G. Capannelli, I. Ciabatti, D. Corrieri, G. Ciardelli, Treatment and reuse of textile effluents based on new ultrafiltration and other membrane technologies, *Desalination* 138 (2001) 75–82.
- [3] A.L. Zydney, Protein separations using membrane filtration: new opportunities for whey fractionation, *Int. Dairy J.* 8 (1998) 243–250.
- [4] A.L. Zydney, Bulk Mass, Transport limitations during high-flux hemodialysis, *Artif. Organs* 17 (1993) 919–924.
- [5] L.J. Zeman, A.L. Zydney, *Microfiltration and Ultrafiltration: Principles and Applications*, Marcel Dekker Inc., New York, 1996.
- [6] S. Mochizuki, A.L. Zydney, Theoretical analysis of pore size distribution effects on membrane transport, *J. Membr. Sci.* 82 (1993) 211–227.
- [7] A. Mehta, A.L. Zydney, Permeability and selectivity analysis for ultrafiltration membranes, *J. Membr. Sci.* 249 (2005) 245–249.

- [8] Z. Yi, L.-P. Zhu, Y.-Y. Xu, Y.-F. Zhao, X.-T. Ma, B.-K. Zhu, Polysulfone-based amphiphilic polymer for hydrophilicity and fouling-resistant modification of polyethersulfone membranes, *J. Membr. Sci.* 365 (2010) 25–33.
- [9] J.-H. Jiang, L.-P. Zhu, H.-T. Zhang, B.-K. Zhu, Y.-Y. Xu, Improved hydrodynamic permeability and antifouling properties of poly (vinylidene fluoride) membranes using polydopamine nanoparticles as additives, *J. Membr. Sci.* 457 (2014) 73–81.
- [10] S.E. Querelle, E.A. Jackson, E.L. Cussler, M.A. Hillmyer, Ultrafiltration membranes with a thin poly styrene-*b*-poly isoprene selective layer, *ACS Appl. Mater. Interfaces* 5 (2013) 5044–5050.
- [11] P. Nimmanpipug, K. Tashiro, O. Rangsiman, Factors governing the three-dimensional hydrogen-bond network structure of poly (m-phenylene isophthalamide) and a series of its model compounds (4): similarity in local conformation and packing structure between a complicated three-arm model compound and the linear model compounds, *J. Phys. Chem. B* 110 (2006) 20858–20864.
- [12] J. Huang, K. Zhang, The high flux poly (m-phenylene isophthalamide) nano-filtration membrane for dye purification and desalination, *Desalination* 282 (2011) 19–26.
- [13] M. Keating, High glass transitions of high-performance thermoplastics, *Thermochim. Acta* 319 (1998) 201–212.
- [14] A. Kuo, Z. Pu, *Polymer data handbook*, Polymer Data Handbook, 1999.
- [15] L. De Bartolo, A. Gugliuzza, S. Morelli, B. Cirillo, A. Gordano, E. Drioli, Novel PEEK-WC membranes with low plasma protein affinity related to surface free energy parameters, *J. Mater. Sci.: Mater. Med.* 15 (2004) 877–883.
- [16] X. Zhao, Y. Su, W. Chen, J. Peng, Z. Jiang, Grafting perfluoroalkyl groups onto polyacrylonitrile membrane surface for improved fouling release property, *J. Membr. Sci.* 415 (2012) 824–834.
- [17] A. Zosel, Adhesion and tack of polymers: influence of mechanical properties and surface tensions, *Colloid Polym. Sci.* 263 (1985) 541–553.
- [18] P.E. Luner, E. Oh, Characterization of the surface free energy of cellulose ether films, *Colloids Surf.: Physicochem. Eng. Asp.* 181 (2001) 31–48.
- [19] W. Sun, T. Chen, C. Chen, J. Li, A study on membrane morphology by digital image processing, *J. Membr. Sci.* 305 (2007) 93–102.
- [20] S. Singh, K. Khulbe, T. Matsuura, P. Ramamurthy, Membrane characterization by solute transport and atomic force microscopy, *J. Membr. Sci.* 142 (1998) 111–127.
- [21] F.P. Cuperus, *Characterization of Ultrafiltration Membranes: Pore Structure and Top Layer Thickness*, PhD Thesis, University of Twente, Enschede, The Netherlands, 1990.
- [22] A. Kakuta, M. Kuramoto, M. Ohno, H. Kushida, A. Tanioka, K. Ishikawa, Freeze-dried cellulose acetate membrane fine structure observation, *J. Polym. Sci.: Polym. Chem. Ed.* 18 (1980) 3229–3243.
- [23] A. Fane, C. Fell, A. Waters, The relationship between membrane surface pore characteristics and flux for ultrafiltration membranes, *J. Membr. Sci.* 9 (1981) 245–262.
- [24] D.B. Burns, A.L. Zydney, Buffer effects on the zeta potential of ultrafiltration membranes, *J. Membr. Sci.* 172 (2000) 39–48.
- [25] W.S. Opong, A.L. Zydney, Diffusive and convective protein transport through asymmetric membranes, *AIChE J.* 37 (1991) 1497–1510.
- [26] L.D. Nghiem, A.I. Schäfer, M. Elimelech, Removal of natural hormones by nanofiltration membranes: measurement, modeling, and mechanisms, *Environ. Sci. Technol.* 38 (2004) 1888–1896.
- [27] K.D. Miller, S. Weitzel, V. Rodgers, Reduction of membrane fouling in the presence of high polarization resistance, *J. Membr. Sci.* 76 (1993) 77–83.
- [28] S. Nakatsuka, A.S. Michaels, Transport and separation of proteins by ultrafiltration through sorptive and non-sorptive membranes, *J. Membr. Sci.* 69 (1992) 189–211.
- [29] R. Shukla, M. Balakrishnan, G.P. Agarwal, Bovine serum albumin-hemoglobin fractionation: significance of ultrafiltration system and feed solution characteristics, *Bioseparation* 9 (2000) 7–19.
- [30] N.S. Pujar, A.L. Zydney, Electrostatic and electrokinetic interactions during protein transport through narrow pore membranes, *Ind. Eng. Chem. Res.* 33 (1994) 2473–2482.
- [31] A. Fane, C. Fell, A. Waters, Ultrafiltration of protein solutions through partially permeable membranes—the effect of adsorption and solution environment, *J. Membr. Sci.* 16 (1983) 211–224.
- [32] P. Prádanos, A. Hernández, Cross-flow ultrafiltration of proteins through asymmetric polysulfonic membranes: I. retention curves and pore size distributions, *Biotechnol. Bioeng.* 47 (1995) 617–625.
- [33] L. Millesime, J. Dulieu, B. Chaufer, Fractionation of proteins with modified membranes, *Bioseparation* 6 (1996) 135–145.
- [34] K.H. Youm, W.S. Kim, Prediction of intrinsic pore properties of ultrafiltration membrane by solute rejection curves: effects of operating conditions on pore properties, *J. Chem. Eng. Jpn.* 24 (1991) 1–7.
- [35] T. Horiuchi, P. Malchesky, M. Emura, M. Usami, Y. Nose, Solute/pore changes in plasma filtration, *Prog. Artif. Organs* (1986) 877–882.
- [36] S. Mochizuki, A.L. Zydney, Effect of protein adsorption on the transport characteristics of asymmetric ultrafiltration membranes, *Biotechnol. Prog.* 8 (1992) 553–561.
- [37] B.C. Robertson, A.L. Zydney, Protein adsorption in asymmetric ultrafiltration membranes with highly constricted pores, *J. Colloid Interface Sci.* 134 (1990) 563–575.
- [38] V.K. Thakur, S.I. Voicu, Recent advances in cellulose and chitosan based membranes for water purification: a concise review, *Carbohydr. Polym.* 146 (2016) 148–165.

CosMX Exhibit 1003, Page 118 of 512

Ningde Amperex Tech. Exhibit No. 2031
Zhuhai CosMX Battery Co. Ltd. v. Ningde Amperex Tech.
IPR2025-00432, U.S. Patent No. 11,575,148
Page 118 of 512

Appendix C

CosMX Exhibit 1003, Page 119 of 512

Ionic Conductivity of Microporous PVDF-HFP/PS Polymer Blends

To cite this article: Haitao Huang and Stephanie L. Wunder 2001 *J. Electrochem. Soc.* **148** A279

View the [article online](#) for updates and enhancements.



 **244th Electrochemical Society Meeting**
October 8 – 12, 2023 • Gothenburg, Sweden
50 symposia in electrochemistry & solid
state science
Abstract submission deadline:
April 7, 2023

Read the call for
papers &
submit your abstract!

This content was downloaded from IP address 128.119.168.112 on 20/02/2023 at 16:27

CosMX Exhibit 1003, Page 120 of 512

Ningde Amperex Tech. Exhibit No. 2031
Zhuhai CosMX Battery Co. Ltd. v. Ningde Amperex Tech.
IPR2025-00432, U.S. Patent No. 11,575,148
Page 120 of 512



Ionic Conductivity of Microporous PVDF-HFP/PS Polymer Blends

Haitao Huang* and Stephanie L. Wunder[‡]

Department of Chemistry, Temple University, Philadelphia, Pennsylvania, 19122 USA

Separators made from blends of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and polystyrene (PS) were microporous when cast from solvent/nonsolvent mixtures of acetone/dimethylcarbonate(DMC)/butanol(BuOH), where BuOH was the nonsolvent for both polymers. The ionic conductivities of these separators reached 2 mS cm^{-1} and could be increased to 4 mS cm^{-1} with addition of fumed silica. The morphology of the separators was characterized by scanning electron microscopy, nonsolvent (BuOH) and solvent (propylene carbonate, PC) uptake, and differential scanning calorimetry, and correlated with ionic conductivity measurements using 1 M LiPF_6 in ethylene carbonate(DMC)/diethyl carbonate, in the ratio 4:5:1 by weight. The solvent filled the microporous network and caused the pore walls to swell. The greater the former contribution, which increased with increasing PS content, the higher the ionic conductivity. Passing two identical microporous films through a double-roll laminator at a temperature above the glass transition temperature, T_g , of PS ($T_g = 95^\circ\text{C}$) and below the melt temperature, T_m , of PVDF-HFP ($T_m = 133^\circ\text{C}$) preserved the microporous structure, with a conductivity decrease of only 20% compared with un-laminated films.

© 2001 The Electrochemical Society. [DOI: 10.1149/1.1346897] All rights reserved.

Manuscript submitted September 16, 2000; revised manuscript received November 26, 2000.

Hybrid or plasticized polymer electrolytes can be made from a polymer and solutions of lithium salts in organic solvents. Investigated polymers which incorporate liquid electrolytes include poly(vinylidene fluoride) (PVDF),¹⁻²¹ poly(methyl methacrylate) (PMMA),²⁰⁻²⁶ polyacrylonitrile (PAN),^{20,21,27,28} poly(vinyl chloride) (PVC),²⁰ poly(vinyl sulfone) (PVS),²⁹ poly(ethylene oxide) (PEO),^{20,30,31} or their blends. Compared with “dry” polymer electrolytes (so-called solid polymer electrolytes), *e.g.*, PEO/lithium salt solid complexes, these plasticized, or gelled, polymer electrolytes possess higher ionic conductivity, about $10^{-3} \text{ S cm}^{-1}$ at room temperature, and therefore may be useful for lithium or lithium-ion battery applications. Polymer electrolytes based on PVDF or its copolymer, poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), have received much attention, particularly since Gozdz *et al.*,^{5,6} at Bellcore proposed a technique in which the PVDF-HFP film matrix is prepared first and then reswollen in Li salt electrolyte solution at the last stage. In this so-called Bellcore technology, most of the processes of preparing the polymer electrolytes and cells do not require a moisture-free environment. This makes PVDF-based polymer electrolytes of practical interest and promising in near-term applications for lithium-ion batteries.

The ionic conductivity of PVDF-based polymers was first reported by Feuillade and Perche¹ in 1975, and then by Tsuchida *et al.*,^{2,3} in the early 1980s. The ionic conductivity of PVDF-based polymer electrolytes was initially 10^{-5} to $10^{-6} \text{ S cm}^{-1}$ at room temperature,² while conductivities of over $10^{-3} \text{ S cm}^{-1}$ are now obtained.^{4-7,10,12-16} In the earlier studies, the PVDF-HFP copolymer was directly plasticized with liquid Li salt electrolytes. The polymer was dissolved in a low-boiling solvent (tetrahydrofuran, acetone, etc.) together with a nonaqueous lithium salt solution, *e.g.*, LiClO_4 in propylene carbonate (PC), to form a homogeneous gel after evaporation of the low-boiling solvent. At liquid electrolyte concentrations of over 60%, the ionic conductivity of the polymer gel exceeds $10^{-3} \text{ S cm}^{-1}$ at room temperature.^{4,6,10,11} Some gel polymer-liquid electrolyte systems have been described as single-phase homogeneous systems.¹⁹ Alternatively, a mechanism of conduction in these gel systems has been suggested, in which there are two conduction domains, a swollen polymer phase of lower conductivity and a Li salt electrolyte solution phase of higher ionic conductivity.^{17,18,22,23} At low polymer content, the gel electrolytes can be considered as consisting of a liquid electrolyte dispersed in a polymer matrix, with the lithium and counter ions migrating through

the solvent. With increasing polymer content the contribution or volume fraction of the high conduction path decreases.¹¹ Strong interactions may exist between the polymer chains and the Li^+ ions or solvent molecules, leading to a decrease in the number of charge carriers and an increase in the activation energy of conduction.²²

A two-phase structure has been proposed for PVDF-type polymers prepared according to the Bellcore process. The heterogeneous phase-separated polymer electrolyte²⁰ PVDF-HFP films were prepared by film casting using dibutyl phthalate (DBP) as a plasticizer. The DBP is removed with methanol, leaving a nanoporous structure in the polymer,²⁰ before the films are soaked in liquid electrolyte.^{5,6} In addition, nanoparticle fumed silica (SiO_2) has been added into the composite film and it has been suggested that the interfacial regions around the nanoparticle filler²⁰ enhance electrolyte uptake. In our previous work, we demonstrated that when DBP was replaced with PEO oligomers, which were incompatible with the PVDF-HFP, the pore size increased from the nanometer to the micron size range, and as a result the conductivity of the films increased.¹⁵ Microporous structures in PVDF or PVDF-HFP films using solvent/nonsolvent casting solutions have also been formed in our laboratory¹⁶ as well as elsewhere.^{7,12-14}

In porous polymer separators the amount of electrolyte uptake, the pore volume, size, interconnectivity, and the type of polymer that forms the pore walls are important factors in determining the ionic conductivity of the films. For polyolefin separators such as Celgard, where minimal swelling of the hydrophobic polymer occurs, the liquid electrolyte forms a one-phase system in the porous polymer network. In the polymer matrices that are more compatible with the polar solvents used as liquid electrolytes, there is also swelling of the polymer by the solvent.

In polymers such as polyacrylonitrile (PAN) and poly(methyl methacrylate) (PMMA), uptake of the polar solvents may result in their dissolution. In porous PVDF-type polymers, the semicrystalline nature of PVDF results in equilibrium swelling rather than dissolution. Desirable properties of these separators include the ability to bond to the electrode materials and to be wetted by the polar solvents used in lithium battery applications.

In this paper, the morphology and conductivity of films composed of PVDF-HFP blended with a second polymer, polystyrene (PS), are examined. PS was chosen because it was expected to be relatively nonadsorbing for the electrolyte solvent and would contribute to the mechanical stability of the separators. A solvent/nonsolvent casting process is used to produce microporous films. Correlation of pore structure with solvent uptake indicates that increased conductivity is obtained for separators containing increased PS content. A mechanism of conductivity in the microporous struc-

* Electrochemical Society Active Member.

[‡] E-mail: slwunder@unix.temple.edu

CosMX Exhibit 1003, Page 121 of 512

tures is proposed, in which the more liquidlike electrolyte phase in the pores has higher conductivity than that of the swollen pore walls.

The ability of the PVDF-HFP/PS films to preserve their microporous structure after a simulated lamination step at elevated temperatures and pressure was investigated. When films were self-laminated in a temperature region above the glass transition temperature, T_g , of PS but below the melting temperature, T_m , of PVDF-HFP copolymers, the microporous morphology was preserved. To achieve bonding to the anode or cathode, PS would therefore have to be incorporated as part of the binder in the electrodes.

Experimental

Preparation of films from PVDF-HFP/PS polymer blends.—The PVDF-HFP copolymers used in this work were Kynar 2801 and 2751 from ELF Atochem, and contained, respectively, 10 and 15% by weight HFP. The PS used was purchased from Aldrich (Merck Index 14). Since the PS was not very soluble in acetone, it was dissolved in dimethyl carbonate (DMC, Aldrich) at elevated temperature (50–60°C) prior to mixing it, by slow dropwise addition, with the solution of PVDF-HFP in acetone. The solution became cloudy, and was kept in suspension by constant agitation using a Vortex Genie (Fisher). Subsequently, BuOH was added (or not as a control), the resulting blend slurry was doctor-bladed onto a polyester sheet and strong and self-supporting thin films were formed after solvent evaporation. The polymer in the casting slurry was between 14–16 wt%. Further drying of the films was carried out at room temperature under vacuum. The film thickness varied from 0.10 to 0.18 mm, although thinner films (60 μm) could be prepared. A Laminex model LX4 double-roll table-top laminator was used for self-lamination of the separators, using a speed of 1 cm s^{-1} ; temperature was measured using a thermocouple. The residence time of the film in the heated zone was 20 s, and the pressure was estimated to be less than 100 psi.

Conductivity measurements.—The polymer blend films were soaked in an electrolyte containing 1 M LiPF_6 dissolved in ethylene carbonate/DMC/diethyl carbonate (EC/DMC/DEC) in the weight ratio 4:5:1 (Grant Chemical). The soaked films were sandwiched between two stainless steel blocking electrodes in a dry box. Ionic conductivity was measured on the sealed films outside the dry box using an ac impedance technique, in which a Schlumberger SI 1255 frequency response analyzer was coupled with an EG&G potentiostat/galvanostat model 273A. The amplitude of the ac voltage was 5 mV and the frequency ranged from 100 KHz to 100 Hz. Cole-Cole plots were characterized by slanted straight lines intercepting the real axis on the high-frequency side, from which the resistance was calculated, assuming an equivalent circuit in which a resistor is in series with a double layer capacitor. No effects due to interfacial resistance between the separator and the stainless steel electrodes were observed.

Characterization of microporous structure.—Cross-sectional views of the PVDF-HFP/PS blend films were observed using scanning electron microscopy (SEM, Philips model 501B). Solvent up-

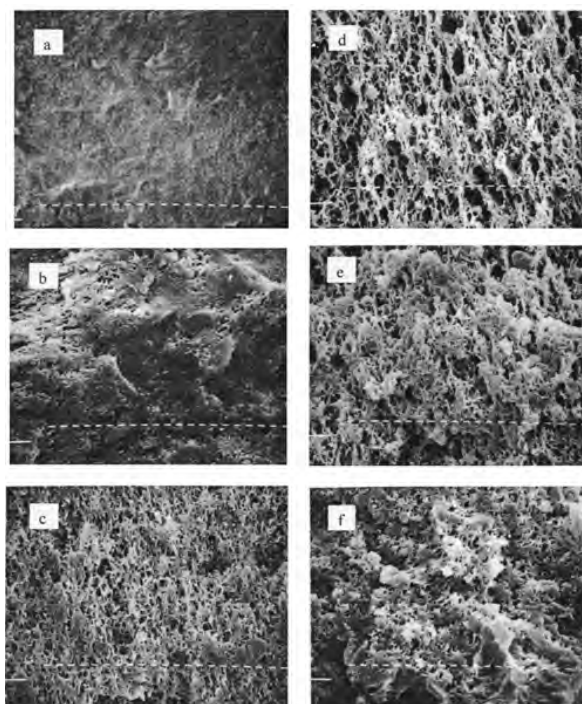


Figure 1. SEMs of the cross-sectional views of PVDF-HFP/PS films cast from solvent/nonsolvent mixtures: (a) 0% PS (sample #2); (b) 10% PS (sample #5); (c) 20% PS (sample #6); (d) 30% PS (sample #7); (e) 40% PS (sample #8); and (f) film made from 20% PS (sample #6) laminated at 120°C.

take was obtained by measurement of weight gain using thermogravimetric analysis (TGA) (TA Instruments, Hi-Res TGA 2950). TGA scans were run to 180°C. Although the boiling point of PC is 242°C, TGA scans showed that the PC was completely removed by 180°C; polymers without solvent uptake exhibited no weight loss over this temperature range, but decomposed at higher temperatures. Differential scanning calorimetry (DSC) measurements (TA Instruments DSC 2920) were obtained at a scan speed of 10°C/min. Specific surface area measurements were made using a single point BET technique (MONOSORS Surface Area Analyzer, model MS-12, Quantachrome Co.) with N_2/He as the adsorbing gas.

Results and Discussion

Formation of microporous structure.—The compositions of the PVDF-HFP/PS blend polymer films prepared with or without addition of BuOH are listed in Table I. The appearance of the pure PVDF-HFP films was transparent when cast without BuOH, and the transparency was reduced with the addition of BuOH in the casting solvent. The films became translucent when PVDF-HFP was blended with PS (tested up to 30% PS) and cast from acetone/DMC. The addition of BuOH resulted in PVDF-HFP/PS films that were opaque. The changes in transparency reflected a variation in the morphology of the polymer films, as observed by scanning electron microscopy (SEM). SEMs of the cross-sectional views of samples 2 and 5–8 are shown in Fig. 1.

Samples cast from the pure PVDF-HFP copolymers (with either 10% or 15% HFP) or their mixtures from acetone or from (by weight) 75% acetone/25% butanol (samples 1 and 2, respectively) are not microporous, as shown in Fig. 1a for sample 2; nanopores would not be observable at this magnification. Boudin *et al.*¹³ observed a microporous morphology when PVDF homopolymer (Kynar 741) was cast from a solvent/nonsolvent (acetone/butanol) mixture. Michot *et al.*¹⁴ found that the porosity of PVDF homopolymer

Table I. Composition of PVDF-HFP/PS blends.

Blend	%KYNAR 2801 (PVDF-10% HFP)	%KYNAR 2751 (PVDF-15% HFP)	%Polystyrene	Addition of butanol
1	60	40	0	No
2	60	40	0	Yes
3	80	0	20	No
4	80	0	20	Yes
5	50	40	10	Yes
6	40	40	20	Yes
7	30	40	30	Yes
8	20	40	40	Yes

CosMX Exhibit 1003, Page 122 of 512

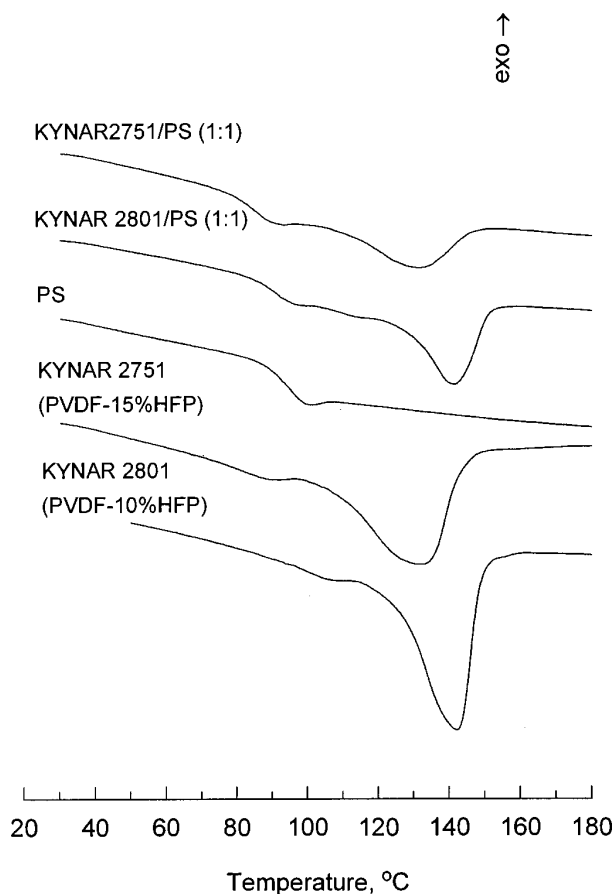


Figure 2. DSC curves of PVDF-HFP, PS, and PVDF-HFP/PS (1:1 by weight) polymer blends. Scan rate: $10^{\circ}\text{C min}^{-1}$.

was greater than for the copolymer PVDF-HFP (Kynar 2801) when both were cast from a single solvent [either acetone, tetrahydrofuran (THF) or methyl ethyl ketone (MEK)]. Pore formation in the polymer matrix is a result of phase separation between the polymer and solvent during the evaporation of solvent, and is driven by poor solubility of the polymer in the solvent. Crystallinity decreases polymer solubility and thus phase separation is enhanced with increased crystallinity of the polymer. Because HFP is known to reduce the crystallinity of PVDF, it is reasonable that no micro-sized pores formed in samples 1 and 2, whereas the PVDF homopolymer films^{13,14} were microporous.

Comparison of PVDF-HFP(80%)/PS(20%) cast from acetone/DMC (sample 3) or from (by weight) 50%acetone/33.3%DMC/16.7%BuOH (No. 4 and No. 6) shows that only the samples cast from the solvent/nonsolvent mixtures exhibit a microporous morphology. The micrograph of sample 6 is shown in Fig. 1c, and is similar to that of sample 4 (not shown); small differences in the amount of HFP in the copolymer did not affect the results. All of the films containing PS and cast from acetone/DMC/BuOH mixtures exhibited a microporous morphology as shown in Fig. 1b-e. The porosity and pore volume of the films varied with the PS content, with pore sizes greater than $0.5\text{ }\mu\text{m}$.

In our previous work,¹⁶ we discussed the formation of porous structures from solvent/nonsolvent mixtures. BuOH is a nonsolvent for both PVDF-HFP and PS. Polymer precipitation in a nonsolvent is associated with phase inversion that creates pores. In addition, PS is not miscible with PVDF-HFP, as shown by the DSC results in Fig. 2. The PVDF-HFP/PS blends were made in weight ratios of 1:1.

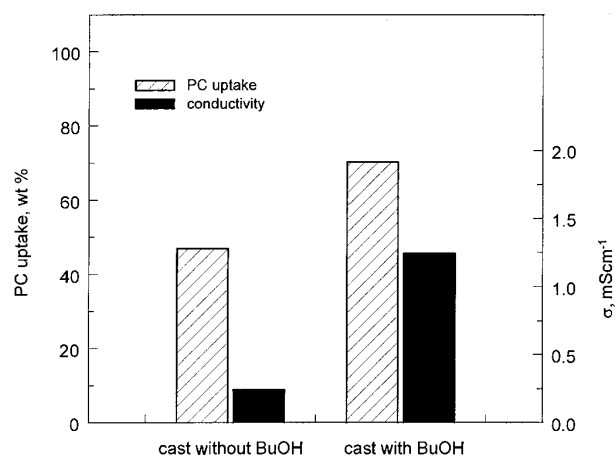


Figure 3. PC uptake and ionic conductivity of PVDF-HFP/PS (80:20 by weight) films prepared with and without BuOH added into casting solvent.

The temperature of the glass transition, T_g , of a PS film that was cast from cyclohexane/dimethyl carbonate (DMC) is 95.3°C , and the temperature of the melting points, T_m , of Kynar 2801 and 2751 are 142.4 and 132.9°C , respectively. For the Kynar 2801/PS blend, T_g appears at 91.6°C and T_m at 141.7°C . The Kynar 2751/PS blend exhibits a T_g and T_m , of 86.6°C and 131.6°C , respectively. While the slight lowering of T_g for the PS may indicate a small degree of mixing of PS with the PVDF-HFP amorphous segments, the blends are essentially incompatible. Therefore, complete phase separation of the polymers occurs in the blends. Phase separation between PS and PVDF-HFP and their co-precipitation in the nonsolvent BuOH both contribute to the formation of microporous structures in the PVDF-HFP/PS blend matrices.

Characterization of pore volume and solvent uptake.—The conductivity of plasticized polymer electrolytes is dominated mainly by the uptake of electrolyte solution by the polymer matrix. The liquid electrolyte is trapped in the pores,¹³ and the pore walls can also be swollen by the electrolyte. In our previous work¹⁶ we obtained the pore volume through a measurement of nonsolvent uptake. Since PVDF-HFP and PS do not swell in BuOH, as confirmed by TGA measurements of nonporous films, any increase in weight of the films after immersion in BuOH is a measure of the solvent trapped in the pores, and thus is related to the pore volume of the films. On the other hand, propylene carbonate (PC) uptake measures both pore volume and the swelling of the polymer matrix. TGA measurements confirm that PVDF-HFP can be swollen by PC, but that PS swelling in this solvent is minimal. Measurements of BuOH and PC uptake provide a means of separating the amount of electrolyte solution trapped by the pores and absorbed by the polymer. PC is used instead of the EC/DMC/DEC mixture because it has much lower volatility, thus making the weight uptake measurements more accurate.

To measure PC absorption, films were immersed in PC for 10 min and the TGA weight loss corresponding to the PC uptake was obtained using $(W_{\text{PC+film}} - W_{\text{film}})/(W_{\text{PC+film}})$; PC uptake increased with increasing time as discussed below. Figure 3 compares the PC uptake of PVDF-HFP/PS films cast with (sample 4, microporous) and without (sample 3, nonporous) butanol. There is a 50% increase in PC uptake for the porous film cast using nonsolvent. These two samples were composed of the same chemical components and differ only in their morphology. The results in Fig. 3 indicate that the solvent uptake depends on more than just the nature of the polymer. The increase in the amount of PC absorbed by sample 4 (microporous) is due to the liquid trapped in the pores.

To measure pore volume, films were immersed in butanol for 1 h, after which no further weight gain was observed, and uptake was

CosMX Exhibit 1003, Page 123 of 512

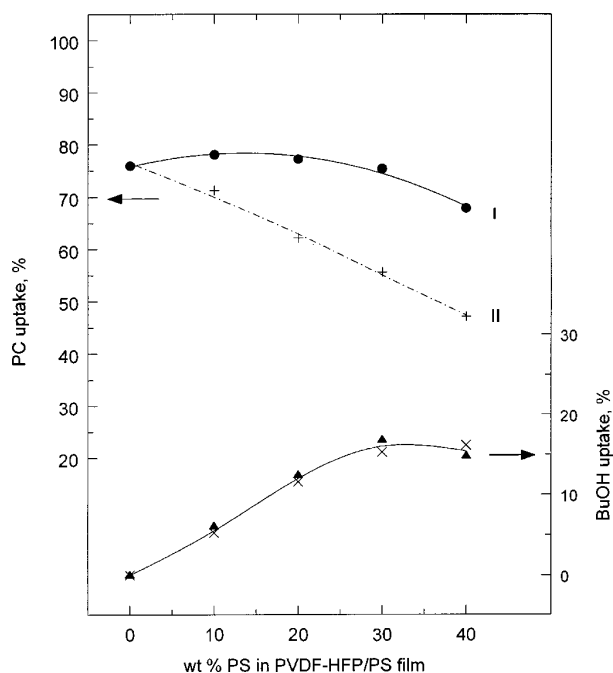


Figure 4. Solvent (BuOH or PC) uptake of PVDF-HFP/PS as a function of weight percent PS: PC-I: (●) experimental; II: +, calculated; BuOH, (▲) experimental; X calculated.

calculated from $(W_{\text{BuOH+film}} - W_{\text{film}})/(W_{\text{BuOH+film}})$. The results for a series of PVDF-HFP blends with increasing amounts of PS [sample 2, no PS, and samples 5-8 (▲)], are presented in Fig. 4, and show that pore volume increased with increased PS of the films, consistent with the SEM observations of Fig. 1.

The amount of PC uptake obtained from the same series of PVDF-HFP/PS blends with increasing PS content is shown in Fig. 4 [sample 2 (no PS) and samples 5-8 (●, connected with solid line I as guide)]. PC uptake decreased, although the porosity increased with increasing PS content for these films. Although this may appear contradictory to the results shown in Fig. 3, PC uptake in the blends is due to both the swelling of the polymer films and their porosity. Since PC uptake by PS is negligible, the decrease in PC uptake shown in line I reflects the increasing amount of PS in the blends.

The swelling of nonporous PVDF-HFP films by PC was measured for films cast without PS from acetone/butanol (75%/25% by weight) mixtures in the same ratios of Kynar 2801/Kynar 2751 as for samples 5-8. There was a slight increase in PC uptake as the ratio of PVDF-HFP 15%/PVDF-HFP 10% increased. As was the case for sample 2 (SEM Fig. 1a), these films exhibited no microporous morphology, so it is reasonable to assume that the PC uptake was due to PVDF-HFP swelling.

The contribution from swelling expected in PVDF-HFP/PS films (samples 5-8) was estimated by multiplying the value of PC uptake from PVDF-HFP by the weight percent of PVDF-HFP. Blends composed of nonporous PVDF-HFP/PS would then be expected to have PC uptakes given by line II in Fig. 4, that is PC uptake would decrease with increasing PS content. Because the uptake represented by line II is the amount of PC that swells the PVDF-HFP phase, the amount of PC trapped in the micropores can then be calculated from the differences between the PC uptake of lines I and II. The results of this calculation were converted into the expected amount of butanol uptake in the pores using the ratio of the densities between BuOH and PC, and presented in Fig. 3 (cross-hatched). The calculated values very closely match those directly measured from BuOH uptake (▲), and suggest that the model in which solvent uptake both

fills the pores and swells the surrounding pore walls, depending on the nature of the solvent, is reasonable. The amount of PC uptake increased with increased soaking time, but contributed only to the swelling of the PVDF-HFP.

Self-lamination of microporous separators.—In order to determine whether the pore structure is preserved during a lamination step, two identical microporous films, composed of either 20%PS (sample 6) or 40%PS (sample 8), were self-laminated at three temperatures, between 90-100°C, between 120-125°C, and between 160-180°C, at pressures below 100 psi. Microporous films were opaque (white), as discussed above, whereas they appeared clear when no microporous structure existed. When the films were laminated at temperatures above ~160°C, they became transparent, and SEMs confirmed the lack of a microporous structure. At temperatures below about 90°C-100°C, the laminated films remained opaque, but did not adhere to each other. In the temperature range between 120 and 125°C, the laminated films remained opaque and did not come apart even after soaking in electrolyte solution at room temperature. SEMs confirmed the presence of the microporous morphology, as shown at the interface region in Fig. 1f for the sample prepared with 20%PS (sample 6). The temperature region in which the lamination produced self-adherent films that remained microporous was above the T_g of the PS component, but below the T_m of the PVDF-HFP component. Although the PS could dissolve in DMC at 60°C, it did not dissolve in the electrolyte solution at that temperature.

Ionic conductivity and conduction path.—Figure 3 also compares the conductivity between films with (sample 4) and without (sample 3) a microporous structure. For the latter, the conductivity is $\sim 0.3 \text{ mS cm}^{-1}$, similar to a PVDF-12% HFP film swollen with 50% 1 M $\text{LiPF}_6/\text{EC}/\text{PC}$.⁴ The microporous film exhibits a conductivity nearly five times higher, suggesting that it is the existence of micropores in the polymer matrix that enhances the conductivity. The ionic conductivity measurements for the polymer films discussed in Fig. 4 (samples 2 and 5-8) are presented in Fig. 5a, and verify the importance of the microporous structure. Ionic conductivity increases with increasing pore volume.

A mechanism in which two conduction paths exist has been proposed for gel polymer electrolytes,^{22,23} and this mechanism is perhaps more appropriate for microporous polymer electrolytes. The simplest model is one in which the interconnected pores form a conduction path filled with pure liquid electrolyte, which has a higher conductivity than that of the liquid electrolyte that swells the surrounding pore walls. The ratio between the PC stored in the pores (the difference between lines II and I in Fig. 4) and the total PC uptake (line I in Fig. 4) is plotted against the content of PS in Fig. 5b. This ratio is a measure of how much of the absorbed liquid is in the higher conduction free liquid electrolyte path, and demonstrates that the greater this amount, the higher the conductivity of the films (Fig. 5a).

Figure 5c is a plot of the surface area of the pores measured by a single point Brunner-Emmett-Teller (BET) technique vs. the content of PS in samples 2 and samples 5-8. However, the surface area of the pores does not correlate as well as pore volume measurements with the variation in conductivity shown in Fig. 5a. This suggests that pore size and shape may need to be taken into account when using surface area as a measure of porosity, and more detailed, multipoint measurements are necessary.

Addition of fumed silica (SiO_2) to the films further increased their conductivity and improved their mechanical properties. For example, for films prepared based on the same polymer composition and casting solvents as for sample 6, a conductivity of nearly 4 mS cm^{-1} was obtained with the addition of 35% SiO_2 , and tough solid films less than $60 \mu\text{m}$ thick could be prepared. BuOH uptake and BET data obtained for films containing fumed SiO_2 were not straightforwardly related to pore volume or surface area, because fumed SiO_2 itself has very high surface area.

CosMX Exhibit 1003, Page 124 of 512

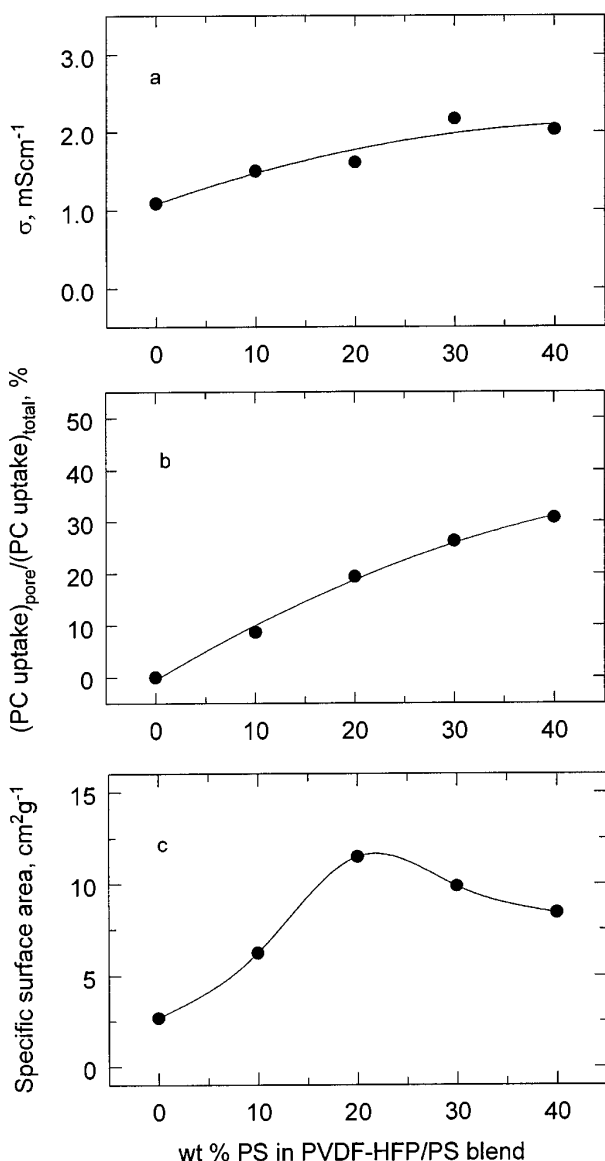


Figure 5. (a) Conductivity, (b) $(\text{PC uptake})_{\text{pore}}/(\text{PC uptake})_{\text{total}}$, and (c) specific surface area of PVDF-HFP/PS films as a function of weight percent PS.

The ionic conductivities of self-laminated separators that remained microporous were compared with the unlaminated films. The separator prepared with 20%PS (sample 6) had an initial conductivity of 1.62 mS cm^{-1} , which decreased 20% to 1.28 mS cm^{-1} after lamination. The separator prepared with 40%PS (sample 8) had an initial conductivity of 2.03 mS cm^{-1} , which also decreased 20% to 1.62 mS cm^{-1} after lamination. These results demonstrate that high conductivity separators can be prepared whose morphology and therefore high conductivity pathway can be maintained during the lamination procedure. This is in contrast to the published Bellcore

process,^{5,6} in which bonding via lamination of the anode, cathode, and polymer separator takes place before extraction of the plasticizer to avoid collapse of the pore structure.

Conclusions

High conductivity microporous separators can be prepared from PVDF-HFP/PS when cast from solvent/nonsolvent mixtures for the polymers. Film conductivity increased with increasing PS content. A two-phase model, with a higher conductivity path consisting of the liquid electrolyte in the interconnected pore structure and a lower conductivity path consisting of the swollen PVDF-HFP phase, was used to account for the conductivity trends. When the films were laminated in a temperature region above the T_g of PS but below the T_m of PVDF-HFP, they remained microporous, with conductivity decreases of only 20%. These results have ramifications for lithium-ion battery manufacturing technology. Microporous separators can be manufactured separately and post-laminated to anodes and cathodes while maintaining the microporous structure necessary for high conductivity. This is a departure from Bellcore technology,^{5,6} where the plasticizer must be kept in the separator during the lamination step to avoid collapse of the pores.

Temple University assisted in meeting the publication costs of this article.

References

- G. Feuillade and Ph. Perche, *J. Appl. Electrochem.*, **5**, 63 (1975).
- E. Tsuchida, H. Ohno, and K. Tsunemi, *Electrochim. Acta*, **28**, 591 (1983).
- E. Tsuchida, H. Ohno, and K. Tsunemi, *Electrochim. Acta*, **28**, 833 (1983).
- A. S. Gozdz, C. N. Schmutz, J. M. Tarascon, and P. C. Warren, U.S. Pat. 5,418,091 (1995).
- A. S. Gozdz, C. N. Schmutz, J. M. Tarascon, and P. C. Warren, U.S. Pat. 5,540,741 (1996).
- J. M. Tarascon, A. S. Gozdz, C. Schmutz, F. Shokoohi, and P. C. Warren, *Solid State Ionics*, **86-88**, 49 (1996).
- A. Du Pasquier, P. C. Warren, D. Culver, A. S. Gozdz, G. G. Amatucci, and J. M. Tarascon, Abstract 116, The Electrochemical Society Meeting Abstracts, Vol. 99-2, Honolulu, HI, Oct. 17-22, 1999.
- K. M. Abraham, Z. Jiang, and B. Carroll, *Chem. Mater.*, **9**, 1978 (1997).
- Z. Jiang, B. Carroll, and K. M. Abraham, *Electrochim. Acta*, **42**, 2667 (1997).
- W. Huang and J. R. Akridge, *Mater. Res. Soc. Symp. Proc.*, **548**, 325 (1999).
- A. M. Christie, L. Christie, and C. A. Vincent, *J. Power Sources*, **74**, 77 (1998).
- X. Andrieu, C. Jehoulet, and F. Boudin, in Proceedings of the 38th Power Sources Conference, p. 266, Atlantic City, NJ (1998).
- F. Boudin, X. Andrieu, C. Jehoulet, and I. I. Olsen, *J. Power Sources*, **81-82**, 804 (1999).
- T. Michot, A. Nishimoto, and M. Watanabe, *Electrochim. Acta*, **45**, 1347 (2000).
- H. Wang, H. Huang, and S. L. Wunder, *J. Electrochem. Soc.*, **147**, 2853 (2000).
- H. Huang and S. L. Wunder, *J. Power Sources*, Submitted.
- P. Mustarelli, E. Quartarone, C. Capiglia, C. Tomasi, and A. Magistris, *Solid State Ionics*, **122**, 285 (1999).
- C. Capiglia, Y. Saito, H. Yamamoto, H. Kageyama, and P. Mustarelli, *Electrochim. Acta*, **45**, 1341 (2000).
- M. Forsyth, P. M. Meakin, and D. R. MacFarlane, *Electrochim. Acta*, **40**, 2339 (1995).
- J. Y. Sing, Y. Y. Wang, and C. C. Wan, *J. Power Sources*, **77**, 183 (1999).
- K. Murata, S. Izuchi, and Y. Yoshihisa, *Electrochim. Acta*, **45**, 1501 (2000).
- O. Bohnke, G. Frand, M. Rezzazzi, C. Rousselot, and C. Truche, *Solid State Ionics*, **66**, 97 (1993).
- O. Bohnke, G. Frand, M. Rezzazzi, C. Rousselot, and C. Truche, *Solid State Ionics*, **66**, 105 (1993).
- G. B. Appetecchi, F. Croce, and B. Scrosati, *Electrochim. Acta*, **40**, 99 (1995).
- T. Iijima, Y. Toyoguchi, and N. Eda, *Denki Kagaku oyobi Kogyo Butsuri Kagaku*, **53**, 619 (1985).
- Y. K. Yarovsky, H. P. Wang, and S. L. Wunder, *Solid State Ionics*, **118**, 301 (1999).
- K. M. Abraham and M. Alamgir, *J. Electrochem. Soc.*, **137**, 1657 (1990).
- K. M. Abraham and M. Alamgir, U.S. Pat. 5,219,679 (1993).
- H. S. Choe, J. Giaccai, M. Alamgir, and K. M. Abraham, *Electrochim. Acta*, **40**, 2289 (1995).
- G. B. Appetecchi, G. Dautzenberg, and B. Scrosati, *J. Electrochem. Soc.*, **143**, 6 (1996).
- G. B. Appetecchi, F. Croce, and B. Scrosati, *J. Power Sources*, **66**, 77 (1997).

Appendix D

CosMX Exhibit 1003, Page 126 of 512

KYNAR FLEX®

2801-00

Kynar Flex® resins are fluorinated thermoplastic copolymers.

Outstanding characteristics: chemical resistance, imperviousness to UV, high barrier properties, high purity, good mechanical and thermo-mechanical properties. This product is **NSF/ANSI/CAN 61** certified.

Kynar Flex® 2801 resin is the powder form of the **Kynar Flex® 2800-00 resin**. To be used as an additive in LLDPE to improve the extrusion rate.

PROPERTIES	VALUE	UNIT	TEST STANDARD
RHEOLOGICAL PROPERTIES			
Melt Volume-Flow Rate	0.5	cm ³ /10min	ISO 1133
Temperature	230	°C	-
	446	°F	-
Load	5	kg	-
	11	lb	-
Melt Flow Rate	3 - 8	g/10min	ASTM D1238
Temperature	230	°C	-
Load	12.5	kg	-
Melt Viscosity, 230°C, 100 s ⁻¹	23 - 27	kPoise	ASTM D3835
MECHANICAL PROPERTIES			
Tensile Modulus	700	MPa	ISO 527-1/-2
	102000	psi	
Tensile Modulus, 73 °F	552 - 896	MPa	ASTM D638
	80000 - 130000	psi	
Yield stress	27	MPa	ISO 527-1/-2
	3920	psi	
Tensile Strength at Yield, 73 °F	20 - 34.5	MPa	ASTM D638
	2900 - 5000	psi	
Yield strain	15	%	ISO 527-1/-2
Elongation at Yield, 73 °F	10 - 20	%	ASTM D638
Nominal Strain at Break	>50	%	ISO 527-1/-2
Tensile Strength at Break, 73 °F	17.2 - 34.5	MPa	ASTM D638
	2500 - 5000	psi	
Elongation at Break, 73 °F	100 - 300	%	ASTM D638
Taber Abrasion, CS 17 1000g:pad	16 - 19	mg/1000 cycles	ASTM-G195-13A
Hardness, Shore D, 73 °F	60 - 70	-	ASTM D2240
Flexural Modulus, 73 °F	483 - 758	MPa	ASTM D790
	70000 - 110000	psi	

arkema.com

ARKEMA

CosMX Exhibit 1003, Page 127 of 512

KYNAR FLEX®

2801-00

Flexural Strength @ 5% Strain, 73 °F	20.7 - 34.5	MPa	ASTM D790
	3000 - 5000	psi	
Compressive Strength, 73 °F	31 - 41.4	MPa	ASTM D695
	4500 - 6000	psi	
Unnotched Impact Strength, 73 °F	No Break	kJ/m	ASTM D256
Notched Impact Strength, 73 °F	0.534 - 1.07	kJ/m	ASTM D256
	10 - 20	ftlb/in	
Coefficient of Friction, Static vs. Steel, 73 °F	0.33	-	ASTM D1894
Coefficient of Friction, Dynamic vs. Steel, 73 °F	0.33	-	ASTM D1894
THERMAL PROPERTIES			
Melting Temperature, 10°C/min	143	°C	ISO 11357-1/-3
Melting Point, 73 °F	140 - 145	°C	ASTM D3418
Glass Transition Temperature, 10°C/min	-40	°C	ISO 11357-1/-2
Glass Transition Temperature (Tg)	-41.1 - -39.4	°C	ASTM D7028
	-42 - -39	°F	
Temperature Rating	130	°C	UL RTI
	266	°F	
Temp. of Deflection Under Load, 1.80 MPa	48	°C	ISO 75-1/-2
	118	°F	
Heat Deflection Temperature, 264 Psi, 248 °F/hr	40 - 55	°C	ASTM D648
	104 - 131	°F	
Heat Deflection Temperature, 66 Psi, 248 °F/hr	60 - 75	°C	ASTM D648
	140 - 167	°F	
Vicat Softening Temperature, 50°C/h 50N	79	°C	ISO 306
	174	°F	
Coeff. of Linear Thermal Expansion, parallel	160	E-6/K	ISO 11359-1/-2
Coefficient of Thermal Expansion, 73 °F	12.6 - 18.5	10E-5/°C	ASTM D696
	7 - 10.3	10E-5/°F	
Burning Behav. at 1.5 mm Nominal Thickness	V-0	class	IEC 60695-11-10
Thickness Tested	1.5	mm	-
	0.0591	in	
Yellow Card available	yes	-	-
Burning Behav. at Thickness h	V-0	class	IEC 60695-11-10
Thickness Tested	0.8	mm	-
	0.0315	in	

arkema.com

ARKEMA

CosMX Exhibit 1003, Page 128 of 512

Ningde Amperex Tech. Exhibit No. 2031
Zhuhai CosMX Battery Co. Ltd. v. Ningde Amperex Tech.
IPR2025-00432, U.S. Patent No. 11,575,148
Page 128 of 512

Arkema France - A French "société anonyme", registered in the Nanterre (France) Trade and Companies Register under the number 319 632 790 SDC/11-2018
Source: automatically generated TDS from Material Database on 17-11-2022

KYNAR FLEX®

2801-00

Oxygen Index	43	%	ISO 4589-1/-2
Limiting Oxygen Index, 73 °F	42	%	ASTM D2863
Thermal Conductivity	0.144 - 0.18	W/(m K)	ASTM D433
	1 - 1.25	BTU in /(hr ft2 F)	
Specific Heat	745 - 958	J/(kg K)	DSC
	0.28 - 0.36	BTU/(lb·°F)	
Thermal Decomposition TGA, in air	375	°C	1% wt. loss
	707	°F	
Thermal Decomposition TGA, in nitrogen	410	°C	1% wt. loss
	770	°F	
Relative Thermal Index, Mechanical	130	°C	UL 746B
	266	°F	
Relative Thermal Index, Electrical	130	°C	UL 746B
	266	°F	
ELECTRICAL PROPERTIES			
Relative Permittivity, 1MHz	7	-	IEC 60250
Dielectric Constant, 1 kHz	3.5 - 10.6	-	ASTM D150
Dissipation Factor, 1MHz	2330	E-4	IEC 60250
Dissipation Factor, 100 kHz	0.02 - 0.21	-	ASTM D150
Volume Resistivity	2E12	Ohm*m	IEC 60093
Volume Resistivity, DC 68 °F, 65% R.H.	2E14	Ohm*cm	ASTM D257
Dielectric (Electric) Strength, 73°F	1.3 - 1.5	kV/mil	ASTM D149
OTHER PROPERTIES			
Water Absorption	0.03	%	Sim. to ISO 62
Density	1780	kg/m³	ISO 1183
	1.78	g/cm³	
Specific Gravity, 73 °F	1.77 - 1.8	-	ASTM D792
OPTICAL PROPERTIES			
Refractive Index @ sodium D line	1.41	-	ASTM D542

MAIN APPLICATIONS:

- corrosion protection in the chemical industry
- wire and cable
- coating (painting, co-extrusion)
- off shore

arkema.com

ARKEMA

CosMX Exhibit 1003, Page 129 of 512

Ningde Amperex Tech. Exhibit No. 2031
Zhuhai CosMX Battery Co. Ltd. v. Ningde Amperex Tech.
IPR2025-00432, U.S. Patent No. 11,575,148
Page 129 of 512

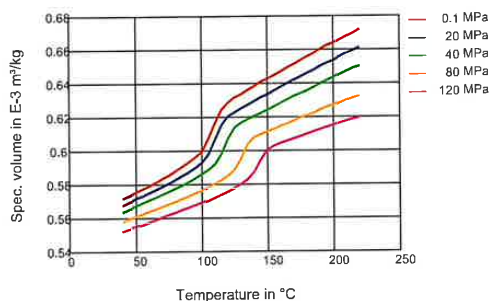
Arkema France - A French "société anonyme", registered in the Nanterre (France) Trade and Companies Register under the number 319 632 790 SDC/11-2018
Source: automatically generated TDS from Material Database on 17-11-2022

KYNAR FLEX[®]

2801-00

DIAGRAMS

SPECIFIC VOLUME-TEMPERATURE (PVT)



DELIVERY FORM	Headquarters: Arkema France 420 rue d'Estienne d'Orves 92705 Colombes Cedex France T +33 (0)1 49 00 80 80 arkema.com Arkema Inc. – High Performance Polymers 900 First Avenue King of Prussia, PA 19406 Tel.: +1 610 205 7000 hpp.arkema.com
Powder	
SPECIAL CHARACTERISTICS	
Heat Stabilized, Light Stabilized	
REGIONAL AVAILABILITY	
North America, Europe, Asia Pacific, South and Central America, Near East/Africa	

The statements, technical information and recommendations contained herein are believed to be accurate as of the date hereof. Since the conditions and methods of use of the product and of the information referred to herein are beyond our control, ARKEMA expressly disclaims any and all liability as to any results obtained or arising from any use of the product or reliance on such information; NO WARRANTY OF FITNESS FOR ANY PARTICULAR PURPOSE, WARRANTY OF MERCHANTABILITY OR ANY OTHER WARRANTY, EXPRESSED OR IMPLIED, IS MADE CONCERNING THE GOODS DESCRIBED OR THE INFORMATION PROVIDED HEREIN. The information provided herein relates only to the specific product designated and may not be applicable when such product is used in combination with other materials or in any process. The user should thoroughly test any application before commercialization. Nothing contained herein constitutes a license to practice under any patent and it should not be construed as an inducement to infringe any patent and the user is advised to take appropriate steps to be sure that any proposed use of the product will not result in patent infringement.

arkema.com

ARKEMA

CosMX Exhibit 1003, Page 130 of 512

Appendix E

CosMX Exhibit 1003, Page 131 of 512

KYNAR FLEX®

2751-00

Kynar Flex® resins are fluorinated thermoplastic copolymers.

Outstanding characteristics: chemical resistance, imperviousness to UV, barrier properties and high purity.
Kynar Flex® 2751-00 resin is a powder grade where maximum flexibility or impact strength is required.

PROPERTIES	VALUE	UNIT	TEST STANDARD
RHEOLOGICAL PROPERTIES			
Melt Volume-Flow Rate	1.9	cm ³ /10min	ISO 1133
Temperature	230	°C	-
	446	°F	-
Load	5	kg	-
	11	lb	-
Melt Flow Rate	4 - 14	g/10min	ASTM D1238
Temperature	230	°C	-
Load	12.5	kg	-
Melt Viscosity, 230°C, 100 s ⁻¹	20 - 25	kPoise	ASTM D3835
MECHANICAL PROPERTIES			
Tensile Modulus	450	MPa	ISO 527-1/-2
	65300	psi	
Tensile Modulus, 73 °F	552 - 896	MPa	ASTM D638
	80000 - 130000	psi	
Yield stress	21	MPa	ISO 527-1/-2
	3050	psi	
Tensile Strength at Yield, 73 °F	20 - 34.5	MPa	ASTM D638
	2900 - 5000	psi	
Yield strain	15	%	ISO 527-1/-2
Elongation at Yield, 73 °F	10 - 20	%	ASTM D638
Nominal Strain at Break	>50	%	ISO 527-1/-2
Tensile Strength at Break, 73 °F	17.2 - 34.5	MPa	ASTM D638
	2500 - 5000	psi	
Elongation at Break, 73 °F	100 - 300	%	ASTM D638
Taber Abrasion, CS 17 1000g:pad	16 - 19	mg/1000 cycles	ASTM-G195-13A
Hardness, Shore D, 73 °F	60 - 70	-	ASTM D2240
Flexural Modulus, 73 °F	483 - 758	MPa	ASTM D790
	70000 - 110000	psi	

Arkema France - A French "société anonyme", registered in the Nanterre (France) Trade and Companies Register under the number 319 632 790 SDC/11-2018
Source: automatically generated TDS from Material Database on 17-11-2022

arkema.com

ARKEMA

CosMX Exhibit 1003, Page 132 of 512

Ningde Amperex Tech. Exhibit No. 2031
Zhuhai CosMX Battery Co. Ltd. v. Ningde Amperex Tech.
IPR2025-00432, U.S. Patent No. 11,575,148
Page 132 of 512

KYNAR FLEX®

2751-00

Flexural Strength @ 5% Strain, 73 °F	20.7 - 34.5	MPa	ASTM D790
	3000 - 5000	psi	
Compressive Strength, 73 °F	31 - 41.4	MPa	ASTM D695
	4500 - 6000	psi	
Charpy Notched Impact Strength, +23°C	No Break	kJ/m²	ISO 179/1eA
Unnotched Impact Strength, 73 °F	No Break	kJ/m	ASTM D256
Notched Impact Strength, 73 °F	0.534 - 1.07	kJ/m	ASTM D256
	10 - 20	ftlb/in	
Coefficient of Friction, Static vs. Steel, 73 °F	0.33	-	ASTM D1894
Coefficient of Friction, Dynamic vs. Steel, 73 °F	0.33	-	ASTM D1894
THERMAL PROPERTIES			
Melting Temperature, 10°C/min	134	°C	ISO 11357-1/-3
Melting Point, 73 °F	140 - 145	°C	ASTM D3418
Glass Transition Temperature, 10°C/min	-40	°C	ISO 11357-1/-2
Glass Transition Temperature (Tg)	-41.1 - -39.4	°C	ASTM D7028
	-42 - -39	°F	
Temp. of Deflection Under Load, 1.80 MPa	40	°C	ISO 75-1/-2
	104	°F	
Heat Deflection Temperature, 264 Psi, 248 °F/hr	40 - 55	°C	ASTM D648
	104 - 131	°F	
Heat Deflection Temperature, 66 Psi, 248 °F/hr	60 - 75	°C	ASTM D648
	140 - 167	°F	
Coefficient of Thermal Expansion, 73 °F	12.6 - 18.5	10E-5/°C	ASTM D696
	7 - 10.3	10E-5/°F	
Burning Behav. at Thickness h	V-0	class	IEC 60695-11-10
Thickness Tested	0.8	mm	-
	0.0315	in	
Oxygen Index	43	%	ISO 4589-1/-2
Limiting Oxygen Index, 73 °F	42	%	ASTM D2863
Thermal Conductivity	0.144 - 0.18	W/(m K)	ASTM D433
	1 - 1.25	BTU in /(hr ft² F)	
Specific Heat	745 - 958	J/(kg K)	DSC
	0.28 - 0.36	BTU/(lb·°F)	
Thermal Decomposition TGA, in air	375	°C	1% wt. loss
	707	°F	

Arkema France - A French "société anonyme", registered in the Nanterre (France) Trade and Companies Register under the number 319 632 790 SDC/11-2018
Source: automatically generated TDS from Material Database on 17-11-2022

arkema.com

ARKEMA

CosMX Exhibit 1003, Page 133 of 512

Ningde Amperex Tech. Exhibit No. 2031
Zhuhai CosMX Battery Co. Ltd. v. Ningde Amperex Tech.
IPR2025-00432, U.S. Patent No. 11,575,148
Page 133 of 512

KYNAR FLEX®

2751-00

Thermal Decomposition TGA, in nitrogen	410	°C	1% wt. loss
	770	°F	
ELECTRICAL PROPERTIES			
Dielectric Constant, 1 kHz	3.5 - 10.6	-	ASTM D150
Dissipation Factor, 100 kHz	0.02 - 0.21	-	ASTM D150
Volume Resistivity	2E12	Ohm*m	IEC 60093
Volume Resistivity, DC 68 °F, 65% R.H.	2E14	Ohm*cm	ASTM D257
Surface Resistivity, 73 °F	5.1E11 - 5.3E11	Ohm per square	ASTM D257
Dielectric (Electric) Strength, 73°F	1.3 - 1.5	kV/mil	ASTM D149
OTHER PROPERTIES			
Water Absorption	0.03 - 0.05	%	ASTM D570
Specific Gravity, 73 °F	1.7 - 1.8	-	ASTM D792
OPTICAL PROPERTIES			
Refractive Index @ sodium D line	1.41	-	ASTM D542

MAIN APPLICATIONS:

- flexible tubing
- corrosion protection in the chemical industry
- off-shore
- wire and cable

DELIVERY FORM	Headquarters: Arkema France 420 rue d'Estienne d'Orves 92705 Colombes Cedex France T +33 (0)1 49 00 80 80 arkema.com Arkema Inc. – High Performance Polymers 900 First Avenue King of Prussia, PA 19406 Tel.: +1 610 205 7000 hpp.arkema.com
Powder	
REGIONAL AVAILABILITY	
North America, Europe, Asia Pacific, South and Central America, Near East/Africa	

The statements, technical information and recommendations contained herein are believed to be accurate as of the date hereof. Since the conditions and methods of use of the product and of the information referred to herein are beyond our control, ARKEMA expressly disclaims any and all liability as to any results obtained or arising from any use of the product or reliance on such information; NO WARRANTY OF FITNESS FOR ANY PARTICULAR PURPOSE, WARRANTY OF MERCHANTABILITY OR ANY OTHER WARRANTY, EXPRESSED OR IMPLIED, IS MADE CONCERNING THE GOODS DESCRIBED OR THE INFORMATION PROVIDED HEREIN. The information provided herein relates only to the specific product designated and may not be applicable when such product is used in combination with other materials or in any process. The user should thoroughly test any application before commercialization. Nothing contained herein constitutes a license to practice under any patent and it should not be construed as an inducement to infringe any patent and the user is advised to take appropriate steps to be sure that any proposed use of the product will not result in patent infringement.

arkema.com

ARKEMA

CosMX Exhibit 1003, Page 134 of 512

Appendix F

CosMX Exhibit 1003, Page 135 of 512

Auxiliary Power Unit Battery Fire
Japan Airlines Boeing 787-8, JA829J
Boston, Massachusetts
January 7, 2013



Incident Report

NTSB/AIR-14/01
PB2014-108867



**National
Transportation
Safety Board**

CosMX Exhibit 1003, Page 136 of 512

Ningde Amperex Tech. Exhibit No. 2031
Zhuhai CosMX Battery Co. Ltd. v. Ningde Amperex Tech.
IPR2025-00432, U.S. Patent No. 11,575,148
Page 136 of 512

Aircraft Incident Report

Auxiliary Power Unit Battery Fire
Japan Airlines Boeing 787-8, JA829J
Boston, Massachusetts
January 7, 2013



**National
Transportation
Safety Board**

490 L'Enfant Plaza, S.W.
Washington, D.C. 20594

CosMX Exhibit 1003, Page 137 of 512

National Transportation Safety Board. 2014. *Auxiliary Power Unit Battery Fire, Japan Airlines Boeing 787-8, JA829J, Boston, Massachusetts, January 7, 2013*. NTSB/AIR-14/01. Washington, DC.

Abstract: This report discusses the January 7, 2013, incident involving a Japan Airlines Boeing 787-8, JA829J, which was parked at a gate at General Edward Lawrence Logan International Airport, Boston, Massachusetts, when maintenance personnel observed smoke coming from the lid of the auxiliary power unit battery case, as well as a fire with two distinct flames at the electrical connector on the front of the case. No passengers or crewmembers were aboard the airplane at the time, and none of the maintenance or cleaning personnel aboard the airplane was injured. Safety issues relate to cell internal short circuiting and the potential for thermal runaway of one or more battery cells, fire, explosion, and flammable electrolyte release; cell manufacturing defects and oversight of cell manufacturing processes; thermal management of large-format lithium-ion batteries; insufficient guidance for manufacturers to use in determining and justifying key assumptions in safety assessments; insufficient guidance for Federal Aviation Administration (FAA) certification engineers to use during the type certification process to ensure compliance with applicable requirements; and stale flight data and poor-quality audio recording of the 787 enhanced airborne flight recorder. Safety recommendations are addressed to the FAA, The Boeing Company, and GS Yuasa Corporation.

The National Transportation Safety Board (NTSB) is an independent federal agency dedicated to promoting aviation, railroad, highway, marine, and pipeline safety. Established in 1967, the agency is mandated by Congress through the Independent Safety Board Act of 1974 to investigate transportation accidents, determine the probable causes of the accidents, issue safety recommendations, study transportation safety issues, and evaluate the safety effectiveness of government agencies involved in transportation. The NTSB makes public its actions and decisions through accident reports, safety studies, special investigation reports, safety recommendations, and statistical reviews.

The NTSB does not assign fault or blame for an accident or incident; rather, as specified by NTSB regulation, "accident/incident investigations are fact-finding proceedings with no formal issues and no adverse parties ... and are not conducted for the purpose of determining the rights or liabilities of any person." 49 C.F.R. § 831.4. Assignment of fault or legal liability is not relevant to the NTSB's statutory mission to improve transportation safety by investigating accidents and incidents and issuing safety recommendations. In addition, statutory language prohibits the admission into evidence or use of any part of an NTSB report related to an accident in a civil action for damages resulting from a matter mentioned in the report. 49 U.S.C. § 1154(b).

For more detailed background information on this report, visit <http://www.nts.gov/investigations/dms.html> and search for NTSB accident ID DCA13IA037. Recent publications are available in their entirety on the Internet at <http://www.nts.gov>. Other information about available publications also may be obtained from the website or by contacting:

**National Transportation Safety Board
Records Management Division, CIO-40
490 L'Enfant Plaza, SW
Washington, DC 20594
(800) 877-6799 or (202) 314-6551**

NTSB publications may be purchased from the National Technical Information Service. To purchase this publication, order product number PB2014-108867 from:

**National Technical Information Service
5301 Shawnee Rd.
Alexandria, VA 22312
(800) 553-6847 or (703) 605-6000
<http://www.ntis.gov/>**

Contents

Figures.....	iii
Tables	iv
Abbreviations	v
Executive Summary	vii
1. Factual Information	1
1.1 Event History	1
1.2 Airplane Information	4
1.2.1 Battery Information	4
1.2.2 Battery and Related Component Information	10
1.2.3 Postincident Airplane Examination	11
1.2.4 Additional Airplane-Related Information	12
1.3 Flight Recorders	13
1.4 Incident Battery Examinations	15
1.4.1 External Observations	15
1.4.2 Radiographic Examinations of Incident Battery and Cells	17
1.4.3 Disassembly of Incident Battery	20
1.4.4 Battery Case Protrusion and Corresponding Cell Case Damage	23
1.4.5 Disassembly of Incident Battery Cells	24
1.5 Exemplar Battery Examinations and Testing	30
1.5.1 Radiographic Examinations of Exemplar Battery Cells	30
1.5.2 Cell Soft-Short Tests	31
1.5.3 Examinations of Cells From the Incident Airplane Main Battery	32
1.5.4 Cell-Level Abuse Tests	34
1.5.5 Rivet Observations During Cell- and Battery-Level Testing	37
1.5.6 Cold Temperature Cell- and Battery-Level Testing	39
1.5.7 Battery-Level Nail Penetration Tests	40
1.5.8 Additional Testing	41
1.6 Battery Manufacturing Information	42
1.6.1 Main and Auxiliary Power Unit Battery Development	42
1.6.2 Cell Manufacturing Process	45
1.7 System Safety and Certification	47
1.7.1 Type Certification Overview and Battery Special Conditions	47
1.7.2 Certification Plan	48
1.7.3 System Safety Assessment	49
1.8 Additional Information	52
1.8.1 Federal Aviation Administration Actions After Battery Incidents	52
1.8.2 Previously Issued Safety Recommendations	54

2. Analysis	56
2.1 Failure Sequence	56
2.2 Emergency Response	58
2.3 Cell Manufacturing Concerns	58
2.4 Thermal Management of Large-Format Lithium-Ion Batteries	62
2.4.1 Battery Internal Heating During High-Current Discharge	62
2.4.2 Cell-Level Temperature and Voltage Monitoring	65
2.4.3 Thermal Safety Limits for Cells	66
2.5 Certification Process	67
2.5.1 Validation of Assumptions and Data Used in Safety Assessments Involving New Technology	68
2.5.2 Validating Methods of Compliance for Designs Involving New Technology	72
2.5.3 Certification of Lithium-ion Batteries and Certification of New Technology	74
2.6 Flight Recorder Issues	75
2.6.1 Stale Flight Data	75
2.6.2 Poor-Quality Cockpit Voice Recording	76
3. Conclusions	78
3.1 Findings	78
3.2 Probable Cause	79
4. Recommendations	80
4.1 New Recommendations	80
4.2 Previously Issued Safety Recommendations Classified in This Report	82
5. Appendixes	84
Appendix A: Investigation and Hearing	84
Appendix B: Boeing 787 Type Certification Special Conditions 25-359-SC	86
Appendix C: Comments From the Bureau d'Enquêtes et d'Analyses pour la Sécurité de l'Aviation Civile	88
References	95

Figures

Figure 1. Photograph of smoke emanating from the incident airplane's aft E/E bay.	3
Figure 2. Main and APU exemplar battery.	6
Figure 3. Electrode winding layout.	7
Figure 4. Exploded-view diagram of LVP65 lithium-ion cell construction.	8
Figure 5. Riveted header assembly.	9
Figure 6. Right aft corner of the battery lid and side 4 of the battery case.	16
Figure 7. Cross-sectional view of the APU battery.	18
Figure 8. Cross-sectional view of cell 5 aluminum current collectors.	19
Figure 9. Cross-sectional view of cell 6 aluminum current collectors.	20
Figure 10. Thermal damage to battery.	22
Figure 11. Lower and upper fixation trays.	23
Figure 12. Protrusion on the lower left of battery case side 3.	24
Figure 13. Cell 5 winding closest to cell 6.	27
Figure 14. Cell 6 winding closest to cell 5.	28
Figure 15. Results of cell-level internal short circuit abuse test.	36
Figure 16. Winding flattening process.	46

Tables

Table 1. Specifications for the main and APU battery and cells.....	5
Table 2. Events surrounding APU shutdown.	14

Abbreviations

AC	advisory circular
ACO	aircraft certification office
AD	airworthiness directive
APSIF	UTC Aerospace Systems' Airplane Power Systems Integration Facility
APU	auxiliary power unit
ARAC	aviation rulemaking advisory committee
ARC	accelerating rate calorimetry
ARFF	aircraft rescue and firefighting
ARP	Aerospace Recommended Practice
ATP	acceptance test procedure
BCU	battery charger unit
BEA	Bureau d'Enquêtes et d'Analyses pour la Sécurité de l'Aviation Civile
BMU	battery monitoring unit
BOS	General Edward Lawrence Logan International Airport
CFR	<i>Code of Federal Regulations</i>
CT	computed tomography
CVR	cockpit voice recorder
DPA	destructive physical analysis
EAFR	enhanced airborne flight recorder
EASA	European Aviation Safety Agency
ECS	environmental control system
EDS	energy dispersive x-ray spectroscopy
E/E bay	electronic equipment bay

EICAS	engine indicating and crew alerting system
EPS	electrical power system
EUROCAE	European Organization for Civil Aviation Equipment
FAA	Federal Aviation Administration
FAI	first article inspection
FDR	flight data recorder
FHA	functional hazard assessment
FMEA	failure modes and effects analysis
FOD	foreign object debris
JAL	Japan Airlines
JTSB	Japan Transport Safety Board
KAI	Kanto Aircraft Instrument Company
NASA	National Aeronautics and Space Administration
NRT	Narita International Airport
NTSB	National Transportation Safety Board
ODA	organization designation authorization
SAE	Society of Automotive Engineers
SCD	specification control drawing
SEI	solid electrolyte interphase
SEM	scanning electron microscope
SPU	start power unit
TAK	Takamatsu Airport
TSO	technical standard order
UL	Underwriters Laboratories

Executive Summary

On January 7, 2013, about 1021 eastern standard time, smoke was discovered by cleaning personnel in the aft cabin of a Japan Airlines (JAL) Boeing 787-8, JA829J, which was parked at a gate at General Edward Lawrence Logan International Airport (BOS), Boston, Massachusetts. About the same time, a maintenance manager in the cockpit observed that the auxiliary power unit (APU) had automatically shut down. Shortly afterward, a mechanic opened the aft electronic equipment bay and found heavy smoke coming from the lid of the APU battery case and a fire with two distinct flames at the electrical connector on the front of the case. None of the 183 passengers and 11 crewmembers were aboard the airplane at the time, and none of the maintenance or cleaning personnel aboard the airplane was injured. Aircraft rescue and firefighting personnel responded, and one firefighter received minor injuries. The airplane had arrived from Narita International Airport, Narita, Japan, as a regularly scheduled passenger flight operated as JAL flight 008 and conducted under the provisions of 14 *Code of Federal Regulations* (CFR) Part 129.

The APU battery model is the same model used for the 787 main battery. On January 16, 2013, an incident involving the main battery occurred aboard a 787 airplane operated by All Nippon Airways during a flight from Yamaguchi to Tokyo, Japan. The airplane made an emergency landing at Takamatsu Airport (TAK), Takamatsu, Japan, shortly after takeoff. The Japan Transport Safety Board investigated this incident with support from the National Transportation Safety Board (NTSB).

Boeing was responsible for the overall integration and certification of the equipment in the 787's electrical power conversion subsystem, which is part of the airplane's electrical power system (EPS). Boeing contracted with Thales Avionics Electrical Systems to design the 787 electrical power conversion subsystem, which includes the main and APU batteries. Thales then subcontracted with various manufacturers for the main and APU battery system components, including GS Yuasa Corporation, which developed, designed, and manufactured the main and APU batteries.

Boeing was required to demonstrate that the 787's design complied with the Federal Aviation Administration's (FAA) Special Conditions 25-359-SC, "Boeing Model 787-8 Airplane; Lithium-Ion Battery Installation," which detailed nine specific requirements regarding the use of these batteries on the airplane. As part of the compliance demonstration with these requirements and 14 CFR Part 25 airworthiness standards, Boeing performed a safety assessment to determine the potential hazards that various failure conditions of EPS components could introduce to the airplane and its occupants. Boeing determined that the rate of occurrence of cell venting for the 787 battery would be about 1 in 10 million flight hours. However, at the time of the BOS and TAK incidents (both of which involved cell venting), the in-service 787 fleet had accumulated less than 52,000 flight hours.

After the BOS and TAK events and the FAA's subsequent grounding of the US 787 fleet, Boeing modified the 787 main and APU battery design and its installation configuration to include, among other things, a stainless steel enclosure for the battery case and a duct that vents

from the interior of the enclosure to the exterior of the airplane to prevent smoke from entering the occupiable space of the airplane. In April 2013, the FAA issued an airworthiness directive mandating the installation of the modified battery aboard US 787 airplanes before they could return to service.

The 787 main and APU battery design was also modified to mitigate the most severe effects of an internal short circuit (that is, cascading, cell-to-cell thermal runaway of other cells within the battery; excessive heat; flammable electrolyte release; and fire). The recommendations resulting from the safety issues identified during this investigation could help prevent such effects from occurring in future battery designs.

The NTSB identified the following safety issues as a result of this incident investigation:

- **Cell internal short circuiting and the potential for thermal runaway of one or more battery cells, fire, explosion, and flammable electrolyte release.** This incident involved an uncontrollable increase in temperature and pressure (thermal runaway) of a single APU battery cell as a result of an internal short circuit and the cascading thermal runaway of the other seven cells within the battery. This type of failure was not expected based on the testing and analysis of the main and APU battery that Boeing performed as part of the 787 certification program. However, GS Yuasa did not test the battery under the most severe conditions possible in service, and the test battery was different than the final battery design certified for installation on the airplane. Also, Boeing's analysis of the main and APU battery did not consider the possibility that cascading thermal runaway of the battery could occur as a result of a cell internal short circuit.
- **Cell manufacturing defects and oversight of cell manufacturing processes.** After the incident, the NTSB visited GS Yuasa's production facility to observe the cell manufacturing process. During the visit, the NTSB identified several concerns, including foreign object debris (FOD) generation during cell welding operations and a postassembly inspection process that could not reliably detect manufacturing defects, such as FOD and perturbations (wrinkles) in the cell windings, which could lead to internal short circuiting. In addition, the FAA's oversight of Boeing, Boeing's oversight of Thales, and Thales' oversight of GS Yuasa did not ensure that the cell manufacturing process was consistent with established industry practices.
- **Thermal management of large-format lithium-ion batteries.** Testing performed during the investigation showed that localized heat generated inside a 787 main and APU battery during maximum current discharging exposed a cell to high-temperature conditions. Such conditions could lead to an internal short circuit and cell thermal runaway. As a result, thermal protections incorporated in large-format lithium-ion battery designs need to account for all sources of heating in the battery during the most extreme charge and discharge current conditions. Thermal protections include (1) recording and monitoring cell-level temperatures and voltages to ensure that exceedances resulting from localized or other sources of heating can be detected and addressed before cell damage occurs and (2) establishing thermal safety limits for

cells to ensure that self-heating does not occur at a temperature that is less than the battery's maximum operating temperature.

- **Insufficient guidance for manufacturers to use in determining and justifying key assumptions in safety assessments.** Boeing's EPS safety assessment for the 787 main and APU battery included an underlying assumption that the effect of an internal short circuit within a cell would be limited to venting of only that cell without fire. However, the assessment did not explicitly discuss this key assumption or provide the engineering rationale and justifications to support the assumption. Also, as demonstrated by the circumstances of this incident, Boeing's assumption was incorrect, and Boeing's assessment did not consider the consequences if the assumption were incorrect or incorporate design mitigations to limit the safety effects that could result in such a case. Boeing indicated in certification documents that it used a version of FAA Advisory Circular (AC) 25.1309, "System Design and Analysis" (referred to as the Arsenal draft), as guidance during the 787 certification program. However, the analysis that Boeing presented in its EPS safety assessment did not appear to be consistent with the guidance in the AC. In addition, Boeing and FAA reviews of the EPS safety assessment did not reveal that the assessment had not (1) considered the most severe effects of a cell internal short circuit and (2) included requirements to mitigate related risks.
- **Insufficient guidance for FAA certification engineers to use during the type certification process to ensure compliance with applicable requirements.** During the 787 certification process, the FAA did not recognize that cascading thermal runaway of the battery could occur as a result of a cell internal short circuit. As a result, FAA certification engineers did not require a thermal runaway test as part of the compliance demonstration (with applicable airworthiness regulations and lithium-ion battery special conditions) for certification of the main and APU battery. Guidance to FAA certification staff at the time that Boeing submitted its application for the 787 type certificate, including FAA Order 8110.4, "Type Certification," did not clearly indicate how individual special conditions should be traced to compliance deliverables (such as test procedures, test reports, and safety assessments) in a certification plan.
- **Stale flight data and poor-quality audio recording of the 787 enhanced airborne flight recorder (EAFR).** The incident airplane was equipped with forward and aft EAFRs, which recorded cockpit audio data and flight parametric data. The EAFRs recorded stale flight data for some parameters (that is, data that appeared to be valid and continued to be recorded after a parameter source stopped providing valid data), which delayed the NTSB's complete understanding of the recorded data. In addition, the audio recordings from both EAFRs during the airborne portion of the flight were poor quality. The signal levels of the three radio/hot microphone channels were very low, and the recording from the cockpit area microphone channel was completely obscured by the ambient cockpit noise. These issues did not impact the NTSB's investigation because the conversations and sounds related to the circumstances of the

incident occurred after the airplane arrived at the gate and the engines were shut down, at which point the quality of the audio recordings was excellent.

The NTSB determines that the probable cause of this incident was an internal short circuit within a cell of the APU lithium-ion battery, which led to thermal runaway that cascaded to adjacent cells, resulting in the release of smoke and fire. The incident resulted from Boeing's failure to incorporate design requirements to mitigate the most severe effects of an internal short circuit within an APU battery cell and the FAA's failure to identify this design deficiency during the type design certification process.

As a result of this investigation, the NTSB makes safety recommendations to the FAA, Boeing, and GS Yuasa. The NTSB previously issued safety recommendations to the FAA regarding (1) insufficient testing methods and guidance for addressing the safety risks of internal short circuits and thermal runaway and (2) the need for outside technical knowledge and expertise to help the FAA ensure the safe introduction of new technology into aircraft designs.

x

CosMX Exhibit 1003, Page 148 of 512

1. Factual Information

1.1 Event History

On January 7, 2013, about 1021 eastern standard time,¹ smoke was discovered by cleaning personnel in the aft cabin of a Japan Airlines (JAL) Boeing 787-8, JA829J, which was parked at a gate at General Edward Lawrence Logan International Airport (BOS), Boston, Massachusetts. About the same time, a maintenance manager in the cockpit observed that the auxiliary power unit (APU) had automatically shut down.² Shortly afterward, a mechanic opened the aft electronic equipment bay (E/E bay) and found heavy smoke coming from the lid of the APU battery case and a fire with two distinct flames at the electrical connector on the front of the case.³ None of the 183 passengers and 11 crewmembers were aboard the airplane at the time, and none of the maintenance or cleaning personnel aboard the airplane was injured. Aircraft rescue and firefighting (ARFF) personnel responded, and one firefighter received minor injuries. The airplane had arrived from Narita International Airport (NRT), Narita, Japan, as a regularly scheduled passenger flight operated as JAL flight 008 and conducted under the provisions of 14 *Code of Federal Regulations* (CFR) Part 129.

The captain of JAL flight 008 reported that the APU was turned on about 30 to 40 min before the airplane left the gate at NRT (about 0247Z) and was shut down after the engines started.⁴ He stated that the flight, which departed NRT about 0304Z, was uneventful except for occasional moderate turbulence about 6.5 to 7 hours into the flight. Flight data recorder (FDR) data showed that the airplane touched down at BOS at 1000:24 and that the APU was started at 1004:10 while the airplane was taxied to the gate. The captain indicated that the APU operated normally. FDR data also showed that the airplane was parked at the gate with the parking brake set and both engines shut down by 1006:54.

The maintenance manager (the JAL director of aircraft maintenance and engineering at BOS) reported that the passengers had deplaned by 1015 and that the flight and cabin crewmembers had deplaned by 1020, at which time he and the cabin cleaning crew had entered

¹ All times in this report are eastern standard time unless otherwise noted.

² The APU battery provides power to start the APU during ground and flight operations. The APU controller monitors the parameters that are needed to operate the APU. The APU controller is powered by the APU battery bus, which receives its power from the APU battery. If the APU battery were to fail, then the APU battery bus would no longer receive power, and the APU would shut down.

³ The mechanic provided a written statement to the National Transportation Safety Board (NTSB) describing his observations. The mechanic's statement indicated that, after he checked the aft E/E bay, he saw "heavy smoke in the compartment." He reported that he "saw [a] small flame around [the] APU batt[ery]." He added that he "decided [to] discharge [the hand-held dry chemical fire] extinguisher" but could not "discharge continuously" because he believed that there was a "dangerous environment in the compartment." Further, he stated that he "tried fire extinguishing, but [the] smoke and flame (flame size about 3 inch[es]) did not stop." In addition, the mechanic gave the NTSB a drawing that showed two 3-in flames at the electrical connector on the front of the battery case. (The front of the battery case is oriented toward the front of the airplane.) The maintenance manager also provided a written statement to the NTSB, which indicated that the mechanic had seen "flames around the APU battery."

⁴ Eastern standard time is 5 hours behind coordinated universal time (also referred to as UTC or Zulu time).

the airplane. Shortly afterward, a member of the cleaning crew told the maintenance manager, who was in the cockpit, about “an electrical burning smell and smoke in the aft cabin.” The maintenance manager then observed a loss of power to systems powered by the APU and realized that the APU had automatically shut down. After confirming that the airplane’s electrical power systems were off, the maintenance manager turned the main and APU battery switches to the “off” position. FDR data showed that the APU battery failed at 1021:15 and that the APU shut down at 1021:37, which was also when the APU controller lost power.

A JAL mechanic in the aft cabin at the time reported that, when the airplane lost power, he went to the cockpit and learned that the APU had shut down. The mechanic then went back to the aft cabin and saw and smelled smoke. A JAL station manager arrived at the airplane and reported that, when he went into the cabin (through the door where the passenger boarding bridge is attached), he saw “intense” smoke that was concentrated 10 ft aft of the door. The turnaround coordinator for JAL flights 008 and 007,⁵ who had also entered the aft cabin and observed the smoke, described the smoke as “caustic smelling.” The mechanic notified the maintenance manager about the smoke, and the maintenance manager asked the mechanic to check the aft E/E bay. The mechanic found heavy smoke and flames in the compartment coming from the lid of the APU battery case. The mechanic reported that he used a dry chemical fire extinguisher (located at the base of the passenger boarding bridge) to attempt to put out the fire but that the smoke and flames did not stop.

About 1037, ARFF personnel at BOS were notified about smoke in the cabin of a JAL airplane.⁶ Review of a time-stamped airport security camera video showed that the first of five ARFF trucks arrived on scene within 1 min (at 1037:50).⁷ The other four ARFF trucks arrived on scene about 2.5 min after initial notification. A ladder truck, a rescue truck, an airstair truck, a hazardous materials truck, and a fire command vehicle also responded to the incident.

The JAL mechanic advised ARFF personnel that the fire was in the aft E/E bay and led a firefighter to the aft E/E bay door.⁸ The firefighter reported that, after entering the compartment, he could see “a white glow about the size of a softball” on a hand-held thermal imaging camera.⁹ The firefighter also reported that he applied “a shot” of Halotron (a clean fire-extinguishing agent) to knock down the fire.¹⁰ The thermal imaging camera showed that the white glow was

⁵ JAL flight 007 had been scheduled to depart BOS later that morning using the incident airplane.

⁶ The JAL station manager stated that he asked a gate agent to call ARFF. The gate agent then called her supervisor, who called ARFF from a telephone at the passenger check-in counter.

⁷ The airplane was located at gate 8A in terminal E. The first ARFF truck to reach the scene (after incident notification) was already in terminal E for terminal familiarization training. The airport security camera recording times were correlated to the FDR times (within 3 seconds).

⁸ The term “fire” is commonly used by ARFF personnel in reference to an ARFF response or event. Although the JAL mechanic reported that flames were coming from the front of the APU battery case, none of the ARFF personnel who responded to this incident reported seeing flames.

⁹ The hand-held thermal imaging cameras that ARFF personnel at BOS used had a heat-density scale portrayed as brightness and/or coloring of an object (that is, the whiter and brighter the object, the higher the heat intensity).

¹⁰ According to the Halotron website, “Halotron is a rapidly evaporating liquid...that leaves no residue, thereby minimizing or eliminating potential agent-related damage to...assets like electronic equipment, machinery, motors

still present but was less intense than before. The airport security camera video showed smoke coming out of the airplane, as shown in figure 1, at 1040:26.



Source: *Boston Herald*.

Figure 1. Photograph of smoke emanating from the incident airplane's aft E/E bay.

An ARFF captain went into the aft E/E bay with the thermal imaging camera, which showed a heat signature near the APU battery. After he exited the E/E bay, another firefighter entered it. This firefighter reported no visibility because of the smoke. He did not know where the battery was located within the E/E bay, but he knew of a "hot spot" about 6 to 8 in ahead of him, so he discharged a "quick burst" of Halotron for 10 to 20 seconds. The firefighter exited and reentered the E/E bay with the thermal imaging camera. He reported that the battery case was visible and that he saw "a white glow with radiant heat waves" but no flames. An ARFF lieutenant who entered the aft E/E bay reported that the battery appeared to be rekindling.

The ARFF captain reentered the E/E bay and saw heavy white smoke (which he had seen earlier billowing through the floor of the aft cabin) but no flames. The captain applied shots of Halotron to the fire for 5 min, which he believed had knocked down the fire. He reported that the battery was emitting white smoke, creating heavy smoke conditions. The ARFF captain also reported that the battery was hissing loudly and that liquid was flowing down the sides of the battery case. A firefighter (outside the airplane) reported that he heard a "pop" sound and saw

and construction materials." Halotron is dispersed at a rate of 5 lbs per second. A "shot" of Halotron was estimated to last between 15 and 20 seconds, corresponding to between 75 and 100 lbs of the fire-extinguishing agent dispersed. ARFF personnel are trained to use a clean agent, such as Halotron, in electrical and avionics compartments because water would ruin electrical and avionics components.

smoke “pouring out of” the aft E/E bay. The ARFF captain received a minor burn on his neck when the battery, in his words, “exploded.”

After additional firefighting efforts and the placement of a ventilation fan by the E/E bay door to clear smoke, the incident commander decided to remove the APU battery.¹¹ (The airport security camera video showed that, at 1105:58, smoke was no longer visible from the exterior of the airplane.) Firefighters reported that removing the battery was difficult because a metal kick shield installed in front of the battery prevented them from accessing the battery’s quarter-turn quick disconnect knob. Also, the quick disconnect knob could not be turned because it was charred and had melted away. The airport security camera video showed that the battery was removed from the aft E/E bay at 1157:20, about 80 min after the initial notification of the event.¹² The ARFF incident report showed that the event was “controlled” about 1219 (about 1 hour 40 min after the initial notification).

1.2 Airplane Information

The Boeing 787 “Dreamliner” is a twin-engine, wide-body commercial airplane. The 787 program began in April 2004, with the 787’s first flight in December 2009, certification in August 2011, and first delivery in September 2011. The incident airplane, JA829J, was delivered new to JAL on December 20, 2012. At the time of the incident, the airplane had logged 169 flight hours and 22 flight cycles. There were no abnormal indications or maintenance messages related to issues with the incident battery between the date of delivery and the date of the incident.

Boeing was responsible for the overall integration and certification of the equipment in the 787’s electrical power conversion subsystem, which is part of the airplane’s electrical power system. Boeing contracted with Thales Avionics Electrical Systems of Neuilly-sur-Seine, France, to design the 787 electrical power conversion subsystem, which includes the main and APU batteries. Thales subcontracted with various manufacturers for the main and APU battery system components.

1.2.1 Battery Information

The APU battery, part number LVP65-8-402, was developed, designed, and manufactured by GS Yuasa Corporation of Kyoto, Japan.¹³ The battery had eight individual lithium-ion cells, all of which were from the same manufacturing lot that GS Yuasa produced in July 2012. The APU battery installed on the incident airplane, serial number 394, was manufactured in September 2012 and was delivered new to Boeing. The battery was installed in

¹¹ In addition, the incident commander asked a JAL mechanic and a firefighter to disconnect the main battery as a precaution in case it was feeding the APU battery fire.

¹² ARFF personnel had to cut the kick shield installed in front of the battery case to access the battery and then cut the connectors to the battery to remove it.

¹³ GS Yuasa assigned this part number to the battery model at the time of the incident. Boeing’s part number for the battery model at the time of the incident was B3856-901.

the incident airplane on October 15, 2012, and was initially charged by the airplane on or about October 19, 2012. Boeing records showed no installation issues associated with the APU battery. Boeing records also showed that, on December 6, 2012, the battery electrical connector was removed (to facilitate a routine inspection of a nearby power panel) and reinstalled the same day.

As previously stated, the APU battery (installed in the aft E/E bay) provides power to start the APU (installed in the tail of the airplane) during ground and flight operations. The aft E/E bay is an electrical equipment compartment located aft of the main landing gear and beneath approximately the third set of cabin doors (L3 and R3). The compartment is only accessible from the ground by a door in the aft cargo compartment and a set of doors in the airplane belly. The APU battery is located at floor level within the aft E/E bay.

Unique to the 787, the LVP65-8-402 battery model is also used for the 787 main battery, which is located in the forward E/E bay. The main battery, which also has eight individual lithium-ion cells, provides power to selected electrical/electronic equipment during ground and flight operations for normal and failure conditions. Table 1 shows the specifications for the LVP65-8-402 battery and LVP65 cells.

Table 1. Specifications for the main and APU battery and cells.

Specification	Battery	Cell
Nominal capacity (ampere-hours)	75	75
Nominal voltage (volts)	29.6	3.7
Operational voltage range (volts)	20 to 32.2	2.5 to 4.025
Weight (lbs)	61.8	6
Dimensions (in)		
Width	10.9	5.2
Depth	14.2	2.0
Height	8.5	7.7

Note: Battery specification information was based on information from a Thales document. Cell specification information was provided by GS Yuasa.

The 787 main and APU lithium-ion battery has primarily nonflammable components, but the electrolyte in the battery cells is flammable. The eight cells are connected in series and assembled in two rows of four cells, as shown in figure 2. Thermoplastic insulation sheets provide electrical isolation and physical separation between each cell and between the cells and the aluminum battery case, which is electrically grounded. Plastic upper and lower fixation trays secure the position and orientation of the cells in the battery case, and forward and center brace bars hold the fixation trays in place.

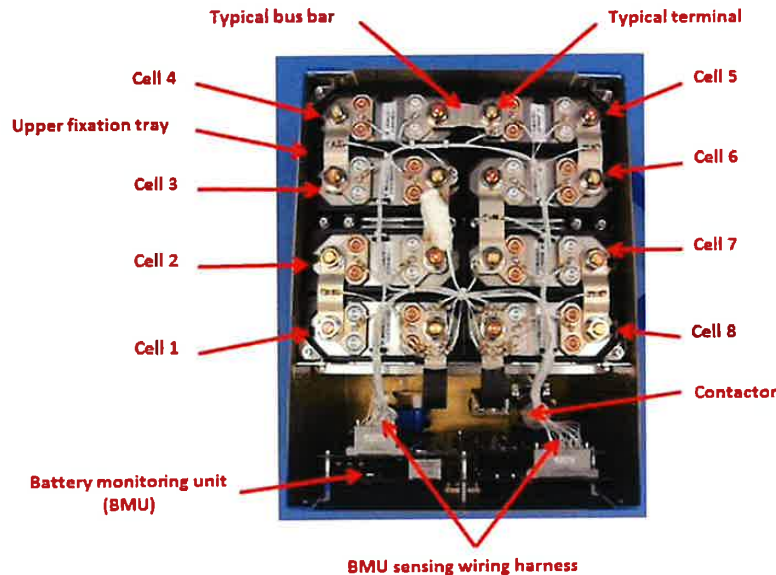


Figure 2. Main and APU exemplar battery.

In addition to the eight individual battery cells, the battery case includes two circuit boards that comprise the battery monitoring unit (BMU); cell voltage sensing wires between battery internal components and the BMU; a Hall effect current sensor for current monitoring; a contactor; bus bars for the main current pathways between the cells and to the J3 connector, which connects to the outside of the battery case; and the J1 connector, which leads outside of the battery case.¹⁴

Each cell has three internal electrode winding assemblies. Each winding assembly is about 30 ft long and is configured with an electrode, then a separator, then another electrode, and then another separator. One electrode—the anode—is a copper foil coated in a carbon active material; the other electrode—the cathode—is an aluminum foil coated in a lithium-cobalt-oxide compound active material. The separator material is made of polyolefin.

The three internal cell windings have been described as flattened “jelly rolls.” The innermost (last) wrap of the sandwiched electrode layers is the coated copper anode layer wrapped around a thermoplastic mandrel core. The coated aluminum cathode layer begins on the

¹⁴ A Hall effect current sensor detects and measures electrical current in a wire and generates a signal proportional to the current measured. The plastic J3 connector provides battery power to the airplane, and the aluminum J1 connector provides signal information used by the BMU and the battery charger unit.

second-to-last wrap and ends on the second wrap. The outermost wrap, the first wrap, is an extra layer of anode and separator. The separator extends beyond the outermost wrap of anode and winds several more times around the exterior of the winding. Figure 3 shows the electrode winding layout. Two layers of thermoplastic electrical insulation surround the electrode winding assemblies. Sheets of thermoplastic insulation (held together with thermoplastic tape) electrically isolate the stainless steel cell cases (which are not grounded) from the windings.

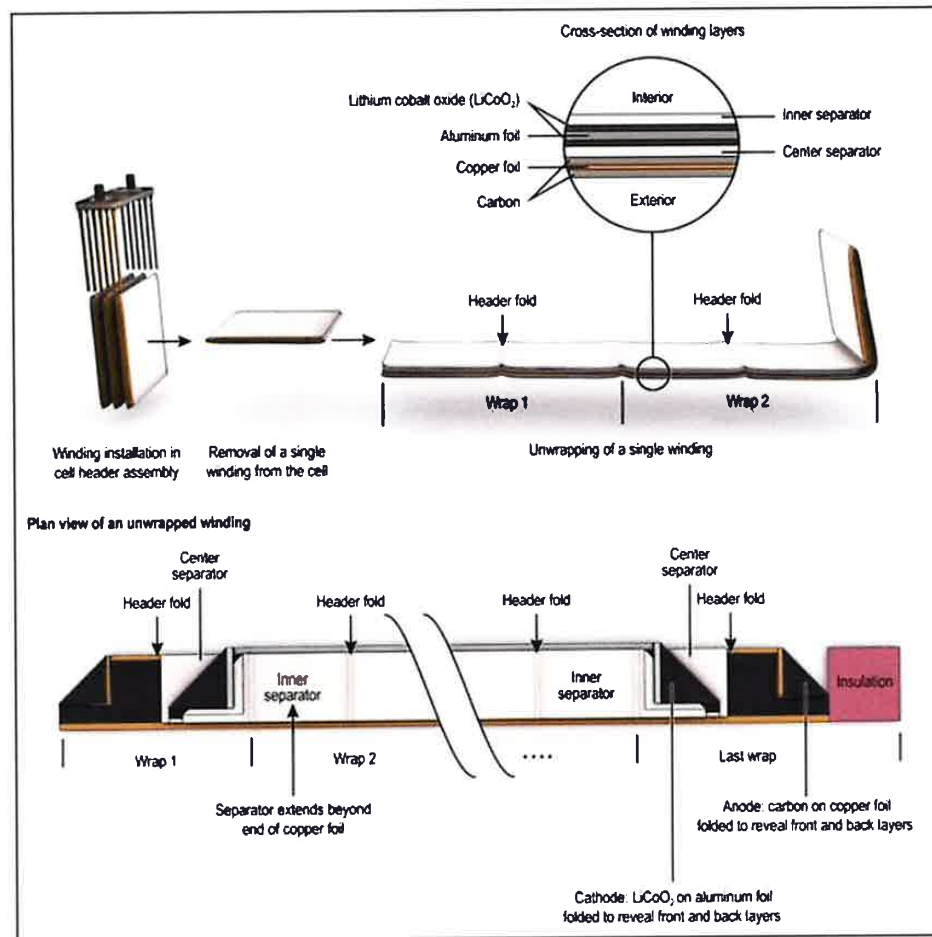


Figure 3. Electrode winding layout.

Two sets of current collectors—one set for the anode and one set for the cathode—are attached on their respective side of each winding assembly to conduct electrical current to and from the positive (cathode) and the negative (anode) terminal assemblies, which are connected to adjacent cells by bus bars. (The electrode edges, where the current collectors attach, are not coated with an active material.) Current collector “fingers” provide the electrical path between

the windings and the terminal plates on the exterior of each cell. According to GS Yuasa, the aluminum current collector fingers were designed to melt open under high current conditions, thereby functioning as an electrical fuse. Three pairs of copper current collector fingers are used for the anode, and three pairs of aluminum current collector fingers are used for the cathode. The fingers extend about one-half of the way down the left (anode) and right (cathode) sides of the cell. At the top of the cell's interior, the current collector fingers connect together into either copper (anode) or aluminum (cathode) bars, which connect with their respective terminal plates on the cell's exterior. Thermoplastic electrical insulating material is used between the cell case and the current collector bars and terminal plates. Figure 4 shows a diagram of the cell construction. Section 1.4 discusses the postincident examination of the APU battery and cells involved in the BOS event.

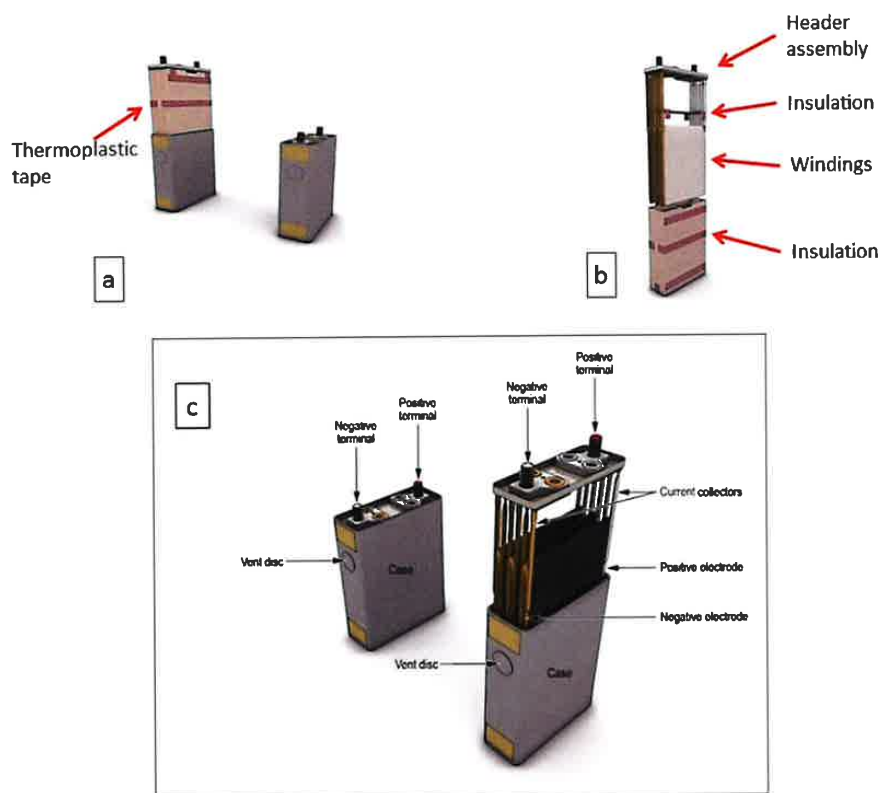


Figure 4. Exploded-view diagram of LVP65 lithium-ion cell construction.

Note: Figures 4a and 4b show the cell construction with the insulation (held together with thermoplastic tape) as installed in the cell. Figure 4c shows the cell construction without the insulation.

Each current collector attaches to two rivets that connect a collector plate with the respective terminal plate on a cell's exterior. Two aluminum rivets are installed at the positive terminal, and two copper rivets are installed at the negative terminal. The rivets provide electrical

continuity between the cell's exterior and interior. Figure 5 shows a photograph of a riveted header assembly. Section 1.5.5 discusses the postincident examination of riveted assemblies.



Source: Underwriters Laboratories.

Figure 5. Riveted header assembly.

Boeing's requirements for the battery, as specified in a proprietary Thales/GS Yuasa report, included the following:

- a 5-year service life under any combination of operating conditions specified within the Thales/GS Yuasa report,
- an operating temperature range of -0.4°F to 158°F,
- a specific charge acceptance capability with an internal temperature between -0.4°F to 32°F,

- a specific current capacity from a fully discharged state within 75 min at an ambient temperature of $77^{\circ}\text{F} \pm 18^{\circ}\text{F}$ for 30,000 flight hours, and
- a specific current end-of-life rated capacity or greater.¹⁵

1.2.2 Battery and Related Component Information

The BMU is mounted inside the battery case (see figure 2). The BMU includes a main circuit card and a subcircuit card, each of which contains two independent monitoring systems: BMU1 and BMU2 (main circuit card) and BMU3 and BMU4 (subcircuit card). Each of the four BMU systems has an initiated built-in test function. BMU1 monitors for cell overcharge, overdischarge, overheating, and imbalance; controls the cell balancing function when any cell reaches a predetermined threshold; and provides voltage measurement to the battery charger unit (BCU). BMU2 provides redundant monitoring for cell overcharge. BMU3 controls the contactor and provides additional monitoring for battery and cell overcharge. BMU4 monitors for cell overdischarge and high current charge. The BMU was designed to send a signal to the BCU to discontinue charging if any of the battery monitoring thresholds were exceeded. The incident main circuit card and subcircuit card were manufactured by Kanto Aircraft Instrument Company (KAI) Ltd. The main circuit card and subcircuit card do not contain nonvolatile memory, and none of the BMU data were recorded on the FDR. Examination and testing of the BMU components, which were thermally damaged, revealed no pre-failure anomalies.¹⁶

The contactor is a device that can electrically isolate the battery cells from the BCU and battery bus. The contactor, which is mounted in the bottom of the battery case near the BMU (see figure 2), is normally closed during battery operations. The contactor can only be commanded to open by BMU3 if a cell overvoltage or high battery voltage is detected. The incident contactor was manufactured by Zodiac Aerospace. The damage to the contactor precluded a full functional test from being performed. X-rays and disassembly of the contactor revealed no pre-failure anomalies.

The BCU includes an electric connector for communication (among the BCU, battery, and airplane), a ground wire stud, and power terminals for the two large battery cables. The BCU of the incident APU battery was manufactured by Securaplane Technologies. At Securaplane, the National Transportation Safety Board (NTSB) performed visual examinations, preliminary electrical tests, and acceptance test procedure (ATP) functional testing of the BCU. The ATP testing revealed a previously unknown electrical oscillation in the output charge voltage, which was later determined (through additional testing at Boeing and Underwriters Laboratories [UL]) not to be related to the circumstances of the incident, as discussed in section 1.5.8.¹⁷

¹⁵ The actual charge acceptance capability, current capacity, and current end-of-life rated capacity are proprietary.

¹⁶ The damage to the BMU was too extensive to perform testing as a complete assembly; as a result, the testing was conducted at the component level.

¹⁷ The NTSB contracted with UL to perform testing as part of this incident investigation. UL performed testing in its laboratories in Northbrook, Illinois; Melville, New York; and Taipei, Taiwan.

The APU controller operates the valves, motors, and sensors that control the operation of the APU and contains nonvolatile memory to record various APU parameters, including battery voltage. The APU controller in the 787 airplane is located near the bulk cargo door on the right side of the aft fuselage (where it is separated from the APU battery and the BCU). The incident APU controller was manufactured by Hamilton Sundstrand.¹⁸ Examination and testing (as part of obtaining the nonvolatile memory) showed that the APU controller operated normally and that the APU's function did not affect the battery's operation at the time of the failure.

The start power unit (SPU) converts DC battery power to AC power for starting the APU and provides excitation power for the APU during startup. The SPU of the incident airplane was manufactured by Securaplane Technologies. ATP testing of the SPU found no anomalies, and the SPU's function did not affect the battery's operation at the time of the failure.

1.2.3 Postincident Airplane Examination

The aft E/E bay (the APU battery installation location) showed damage consistent with heat generated from the APU battery and smoke, hot gases, and electrolyte discharged from the battery. Evidence of material expelled from the battery (in the form of residue and thermal damage) was observed in an area that extended about 20 in from the battery installation. No primary structures (that is, those associated with airplane flight loads) exhibited damage; secondary structures—specifically, the avionics rack and the floor panel—exhibited thermal damage near the APU battery's installation location.¹⁹

The wires that connected to the battery case had been thermally damaged, and the front of the battery case showed thermal damage near the J1 and J3 connectors, where the mechanic's drawing indicated two small flames. The shielded bundle of signal wires, which were the circuits between the BMU and BCU, had burned away from the J1 connector. The copper conductors and shield braiding were melted, which was consistent with resistive heating due to high levels of electrical current (beyond the level that the wires were capable of carrying). The single wire designed to be the battery case ground wire (an intended electrical ground path) remained connected at each end, with the wire insulation partially melted and slightly blackened on the interior surface, which was also consistent with resistive heating due to high levels of electrical current.

The aft E/E bay contains electrical cabinets (referred to as panels) that house components used to distribute electrical power from each engine and the APU. The panel labeled P49 is the source of electrical power distribution for the APU battery bus. No physical damage was noted to the P49 panel. When the circuit breakers on the P49 panel were disengaged, continuity checks of the circuit breakers, contactors, and battery cables to the BCU and battery bus revealed no faults.

The environmental control system (ECS) on the incident airplane was designed to provide pressurized and heated or cooled air to the 787 passenger cabin and E/E bays. The ECS

¹⁸ Hamilton Sundstrand later merged with Goodrich Corporation to form UTC Aerospace Systems.

¹⁹ The avionics rack separated the APU battery from the BCU.

avionics cooling function was designed to remove smoke overboard through fans in the cooling ducts by changing supply valve positions (and using differential pressure when the airplane is in flight).²⁰ During this incident, the supply valves (which were electrically driven) lost electrical power after the APU shut down because the APU was the only source of electrical power being used at the time. As a result, smoke generated by the APU battery could not be effectively directed outside the cabin and aft E/E bay.

1.2.4 Additional Airplane-Related Information

According to the Japan Transport Safety Board (JTSB), on January 16, 2013, a “serious incident” involving the main battery occurred aboard a 787 airplane operated by All Nippon Airways during a flight from Yamaguchi to Tokyo, Japan.²¹ The pilots received a smoke warning in the cockpit after the airplane climbed above an altitude of 32,000 ft. The airplane made an emergency landing at Takamatsu Airport (TAK), Takamatsu, Japan. Of the 137 airplane occupants, 4 passengers received minor injuries during evacuation via the emergency slides. The JTSB investigated this incident with the NTSB’s support and issued its final report on the incident in September 2014 (JTSB 2014).²²

Boeing reported that, as of the date of the TAK battery event (which occurred 9 days after the BOS battery event), the 787 fleet comprised 50 in-service airplanes that had accumulated 51,662 flight hours and 18,665 cycles.²³ After the BOS and TAK events, Boeing modified the 787 battery design and its installation configuration to include (1) additional insulation between the battery cells, (2) vents in the side of the battery case, (3) a stainless steel enclosure for the battery case, and (4) an ECS duct that vents from the interior of the stainless steel enclosure to the exterior of the airplane to prevent smoke from entering the occupiable space of the airplane. Section 1.8.1 discusses the Federal Aviation Administration (FAA) airworthiness directive (AD) mandating the installation of the new battery (part number LVP65-8-403) aboard US airplanes.²⁴

²⁰ The aft E/E bay contains two smoke detectors.

²¹ Chapter 1 of Annex 13, “Aircraft Accident and Incident Investigation,” to the Convention on International Civil Aviation defines a serious incident as “an incident involving circumstances indicating that there was a high probability of an accident and associated with the operation of an aircraft which, in the case of a manned aircraft, takes place between the time any person boards the aircraft with the intention of flight until such time as all such persons have disembarked.”

²² The JTSB’s report on the TAK incident stated that heat generation in a single cell “was probably caused by [an] internal short circuit” which developed into “thermal propagation to other cells, [which] consequently damaged the whole battery.” The report also stated that possible contributing factors to the thermal propagation were that “the test conducted during the developmental phase did not appropriately simulate the on-board [battery] configuration, and the effects of internal short circuit were underestimated.”

²³ One cycle comprises a complete engine startup and shutdown. The number of 787 flight hours indicated does not include about 6,000 flight test hours.

²⁴ GS Yuasa assigned this part number to the redesigned battery. The Boeing part number for the redesigned battery is B3856-902.

On January 14, 2014, an LVP65-8-403 main battery failed on a JAL 787 airplane that was parked at a gate at NRT. (The airplane was being prepared for scheduled flight.) The Japan Civil Aviation Bureau is investigating this incident with assistance from the JTSB and the NTSB. Maintenance personnel reported seeing smoke outside the cockpit window. Preliminary information indicated that one cell had overheated and vented electrolyte and that the enclosure for the battery case contained the vented electrolyte.

1.3 Flight Recorders

The BOS incident airplane was equipped with forward and aft General Electric model EAFR 2100 enhanced airborne flight recorders (EAFR), which recorded cockpit voice recorder (CVR) audio data and FDR parametric data.²⁵ The forward and aft recorders, which were powered by the left and right 28-volt DC buses, respectively, recorded the same set of flight data independently of each other. The forward recorder had an independent power supply to provide backup power to the recorder for about 10 min if the left 28-volt DC bus lost power.²⁶ (The aft recorder had no backup power supply.)

The CVR portion of the EAFR recorded 2 hours of audio data from the cockpit area microphone, the captain's audio selector panel/hot microphone, the first officer's audio selector panel/hot microphone, and the jumpseat/observer's position. The audio information from the forward recorder was used to produce a transcription summary for this incident. The summary began at 0828:21, when the airplane was level in cruise flight at 39,000 ft, and ended at 1031:35, when the forward EAFR stopped recording.

According to the transcription summary, at 1021:41, the CVR recorded sounds associated with the APU shutting down. Conversations among maintenance personnel and the turnaround coordinator about the APU shutdown began about 9 seconds later. At 1024:10, the turnaround coordinator reported smoke in the cabin. No voices were heard on the CVR from 1024:22 to the end of the recording (1031:35).

FDR data before 1021:01 showed no abnormal voltage or current indications. At 1021:01, the voltage of the APU battery decreased from 32 to 31 volts. Three seconds later, the data showed a change in current flow from 3 amperes out of the battery to between 44 and 45 amperes into the battery.²⁷ The current flow into the battery occurred for about 4 seconds; the remainder of the recording showed either no current flow or current flow out of the battery. Between 1021:07 and 1021:09, the battery voltage continued to decrease. At 1021:10, the battery voltage returned to 31 volts. At 1021:27, the battery voltage began decreasing again, reaching

²⁵ Specifically, the EAFR is a multifunction recorder that records flight (FDR) data; audio (CVR) data; and communication, navigation, and surveillance air traffic management messages. The EAFR is a new recording system with a new flight data recording format that allows multiple predefined frames of data that can vary in length and structure. This format provides more flexibility for storing data than older formats that use a single fixed-frame length and structure. The EAFR is currently installed only on 787 airplanes.

²⁶ A lithium-ion battery was used for the recorder independent power supply.

²⁷ This behavior was consistent with the BCU attempting to charge the battery.

28 volts at 1021:30, and the APU shut down 7 seconds later.²⁸ Table 2 shows selected events recorded before and after the APU shutdown. The FDR did not record any data indicating that the APU battery voltage had exceeded 32 volts.

Table 2. Events surrounding APU shutdown.

Time	Event
1000:24	Airplane touched down.
1004:10	APU started.
1006:15	Airplane completed turn into parking location.
1006:48	Parking brake set.
1006:52	Engine 1 shut down.
1006:54	Engine 2 shut down.
1021:01	APU battery bus voltage decreased from 32 to 31 volts.
1021:04	APU battery current increased from 3 amperes out of the battery to between 44 and 45 amperes into the battery.
1021:07	APU battery bus voltage decreased to 30 volts.
1021:08	APU battery current flow returned to 3 amperes out of the battery.
1021:09	APU battery bus voltage decreased to 29 volts.
1021:10	APU battery bus voltage increased to 31 volts.
1021:15	Engine indicating and crew alerting system (EICAS) message discrete indicated that the APU battery failed.
1021:27	APU battery bus voltage began decreasing 1 volt per second during the next 3 seconds.
1021:30	APU battery bus voltage reached 28 volts.
1021:37	APU battery bus voltage decreased to zero volts and returned to 28 volts three times, and APU battery current began to move between zero and 4 to 5 amperes out of the battery.
1021:37	APU controller went offline, and APU had shut down.
1021:37	Aft EAFR stopped recording. Forward EAFR continued recording for about 9 min 58 seconds.
1021:40	EICAS message discretes indicated that the left and right 1 and 2 AC buses became unpowered.
1021:41	EICAS message discrete showed that the APU battery failure was no longer indicated.
1022:00	EICAS message discrete indicated that the main battery was discharging.
1022:10	APU controller went back online.
1022:53	EICAS message discrete indicated that the main battery power switch was off.
1023:16	Airplane systems providing data to the EAFR had shut down.
1031:35	Forward EAFR stopped recording.

Note: The APU controller is the source of 32 recorded parameters, including APU shaft speed and APU battery bus voltage.

The EAFR has an integral flight data acquisition function, which receives data from various sources and then transmits those data to the FDR function according to a predetermined schedule for storage into crash-protected memory. If no new value has been received since the last time that a parameter's value was sent to the FDR function, the flight data acquisition function continues to transmit the last value received from the source. These data are referred to as "stale data."

For some parameters, the flight data acquisition function has multiple prioritized data sources from which it receives parameter values. For these parameters, a separate source index

²⁸ Key parameters that showed the APU battery failure and APU shutdown are presented in figure 2 of the FDR Group Chairman's Factual Report, which is available at www.nts.gov in the public docket for this incident (DCA13IA037). The EAFR records two parameters that indicate the APU battery voltage. Details about the sources of these parameters (APU_Batt_VDC_A and DCBus_APU_Battery_Volts) are included in addendum 1 of the FDR Group Chairman's Factual Report.

parameter that indicates the source being used is generated by the flight data acquisition function and then recorded.²⁹ For parameters with a source index, stale data are indicated by the source index being set to “no source available.” Parameters that have only a single source do not have a source index parameter and thus do not have a recorded indication that the data could be stale.³⁰ This recording methodology can lead to cases in which apparently valid data continue to be recorded after a parameter source stops providing valid data. This problem delayed the NTSB’s complete understanding of the recorded data during the initial stages of this investigation. Section 2.6.1 discusses issues associated with stale data in analyzing accidents, incidents, and maintenance events.

1.4 Incident Battery Examinations

1.4.1 External Observations

The APU battery was examined at the NTSB’s materials laboratory in Washington, DC. Observations were documented using a numbering system designating the front of the battery (facing the external power connectors) as side 1, the left side as side 2, the back of the battery (facing the back wall of the aft E/E bay) as side 3, and the right side as side 4.³¹

Side 1 (forward face) of the battery case exhibited black residue and white powdery material on the exterior surface, which were consistent with thermal damage from the flames reported at the front of the case and the application of a dry chemical fire-extinguishing agent by the JAL mechanic, respectively. Side 2 (left side) of the battery case appeared to have the least visible damage of the four battery sides, with some soot residue and an area of buckling observed.

Side 3 (aft face) of the battery case appeared to be more damaged near side 4 than near side 2. Vertical black streaks, which were consistent with residue from dripping liquid, were observed toward side 4 in a location that corresponded to the right aft corner of the battery lid. A roughly oval deposit of black residue appeared on the side 3 upper portion near the side 4 edge. Side 3 had a mostly circular distortion near the lower corner adjoining sides 3 and 4. This distortion was a paint discoloration with about a 1-in diameter and a 0.25-in-wide nodular protrusion in the middle. The protrusion, which is discussed in more detail in section 1.4.4, was located about 1.5 in from the bottom and left edge of the battery case.

Side 4 (right side) of the battery case appeared to have the most extensive damage of the four battery sides. The exterior was heavily coated with black residue that was concentrated near side 3. Thicker black deposits were visible on the right side near the battery lid. Large, mostly

²⁹ In many cases, a source index parameter defines the source of a group of parameters that are transmitted to the EAFR from the same group of sources.

³⁰ Left and right radio altitude are among the mandatory parameters that do not have a recorded indication that the data could be stale.

³¹ When facing aft in the airplane, the left and right sides of the battery correspond with the left and right sides of the airplane.

circular areas of thermal damage to the paint were located at the same elevation as the battery cell vent discs (as viewed from the exterior).³² An area of thermal damage to the paint was adjacent to and opposite from the cell 6 vent disc. A distortion and an area of missing paint and soot were adjacent to and opposite from the cell 7 vent disc. Paint discolorations were visible at the cell 5 and 8 vent locations.

The lid on the battery case was bulged and creased. The right aft lid corner (as viewed from the front of the battery case) exhibited more soot, charring, and residue than the rest of the lid and the most damage to the lid fastening points.³³ Figure 6 shows the bulged battery case lid and side 4 of the battery case.



Figure 6. Right aft corner of the battery lid and side 4 of the battery case.

In addition, the NTSB's examination of the battery found no external fire or heat source that would have caused the battery to overheat (thermal abuse), no impact or other forces imposed on the battery from external sources (mechanical abuse), and no external shorting of wires (electrical abuse) associated with the battery system.

³² A vent disc is a scored plate that ruptures when the internal pressure in a cell reaches a predetermined level. The battery was configured with the vent disc for each cell oriented toward the exterior of the battery.

³³ Eight mounting tabs were used to attach the battery lid to the battery case, and screws were used to fasten the mounting tabs. The two mounting tabs on side 1 remained engaged with the screws. The mounting tabs on sides 2 through 4 had torn from the screws by gross deformation and overstress. The torn mounting tabs and their fracture surfaces exhibited deposits consistent with breakage during the battery failure.

1.4.2 Radiographic Examinations of Incident Battery and Cells

The NTSB conducted radiographic examinations at Chesapeake Testing in Belcamp, Maryland, to examine and document the internal configuration of the incident airplane's main and APU batteries before disassembly and six of the eight APU battery cells after removal from the battery.³⁴ The batteries were documented using x-ray computed tomography (CT) scans and digital radiography, and the battery cells were documented using CT scans. The images of the components were examined for signs of missing or damaged parts, contamination, or other anomalies.

The CT scans of the main battery showed no anomalies outside the cells. (The main battery cells were subsequently examined for internal anomalies, as discussed in section 1.5.1.) The CT scans of the APU battery showed a breach of the battery case that corresponded with a breach of the cell 5 wall. The CT scans of the APU battery also showed that several cells were distorted with an expanded or a contracted profile, as shown in figure 7; several current collectors inside the cells had separated from their header assemblies; and some current collector fingers were out of their designed parallel alignment.

³⁴ Cells 2 and 8 were not included in the radiographic examinations because those cells were used to validate the cutting procedure that would be employed during the NTSB's internal examinations of all of the cells (see section 1.4.5). Cell 2 was chosen for the procedure because the cell exhibited relatively less thermal damage and cell case deformation than other cells in the battery. Cell 8 was also chosen for the procedure because, on the basis of available external cell evidence, that cell was the least likely of the more heavily damaged cells on the right side of the battery (cells 5 through 8) to have been the origination point for the event. In addition to the radiographic examinations of the batteries and cells, neutron computed tomography studies were conducted at the National Institute of Standards and Technology in Gaithersburg, Maryland, to examine and document the material distribution on the header assembly of each cell in the incident battery.

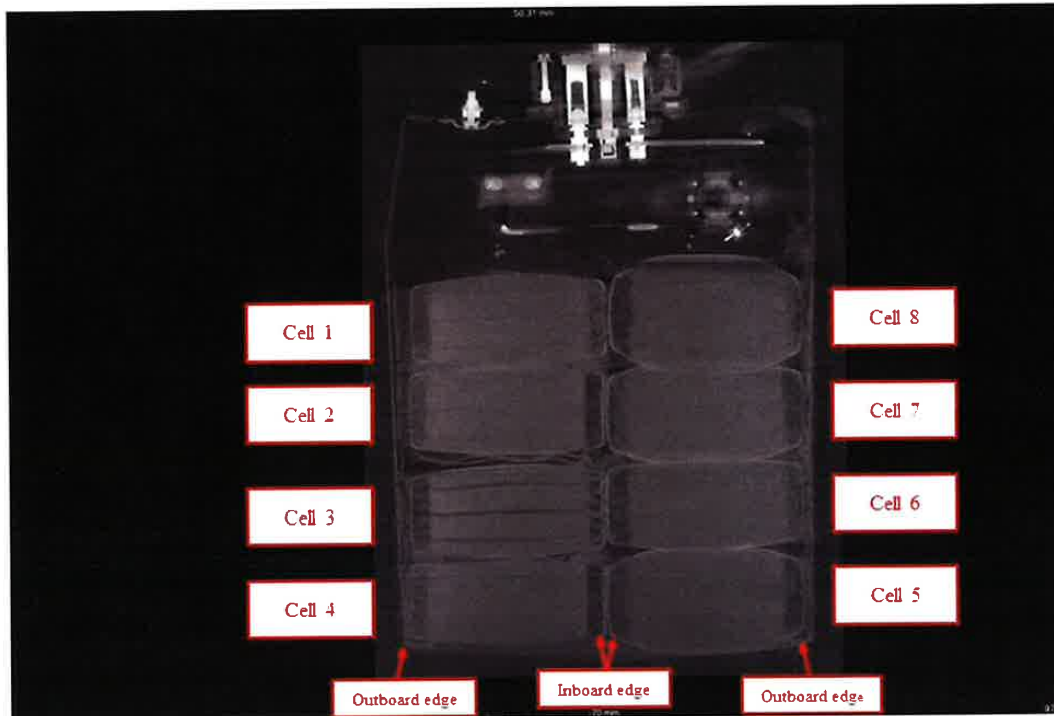


Figure 7. Cross-sectional view of the APU battery.

Note: This image was taken at the approximate midpoint of the cells. Due to the orientation of the incident APU battery during CT scanning, the resulting images appeared as mirror images of the battery. Thus, the orientation of the cells in this figure is different than the orientation of cells in other figures showing the APU battery.

The six individual APU battery cells that were examined were cells 1 and 3 through 7. The CT scans for cells 1 and 3 showed that the cells' current collectors were intact and that the windings were not uniform in some areas due to ripples and separations. The CT scans for cell 4 showed that the cell had no separations within the winding layers and that the current collectors were intact. Findings from the CT scans for cells 5, 6, and 7 included the following:

- Cell 5: Two cell wall breaches in separate locations were identified. The larger of the two breaches appeared to consist of separate smaller holes. The smaller breach appeared to consist of a single hole with some material missing from the outer cell wall around the hole. The areas inside the cell near the breaches differed from the general appearance of the cell. Also, two of the six aluminum (cathode) current collector fingers had breaks with rounded material on the ends. These breaks, as shown in figure 8, appeared as complete separations through the fingers. The current collector finger breaks occurred in the center winding. The other four aluminum current collectors and all of the copper (anode) current collectors were intact.

- Cell 6: Four of the six aluminum current collector fingers had breaks, as shown in figure 9, including one with breaks at multiple locations and another that was missing more material at the breakage location than the other current collector fingers with breaks. The current collector finger breaks occurred in the winding closest to cell 5 and the center winding. The other two aluminum current collectors and all of the copper current collectors were intact.
- Cell 7: Four of the six aluminum current collector fingers had breaks, including one with multiple breaks. All six current collector fingers appeared to be displaced from their original positions. The current collector finger breaks occurred in the winding closest to cell 6 and the center winding. The other two aluminum current collectors and all of the copper current collectors were intact.

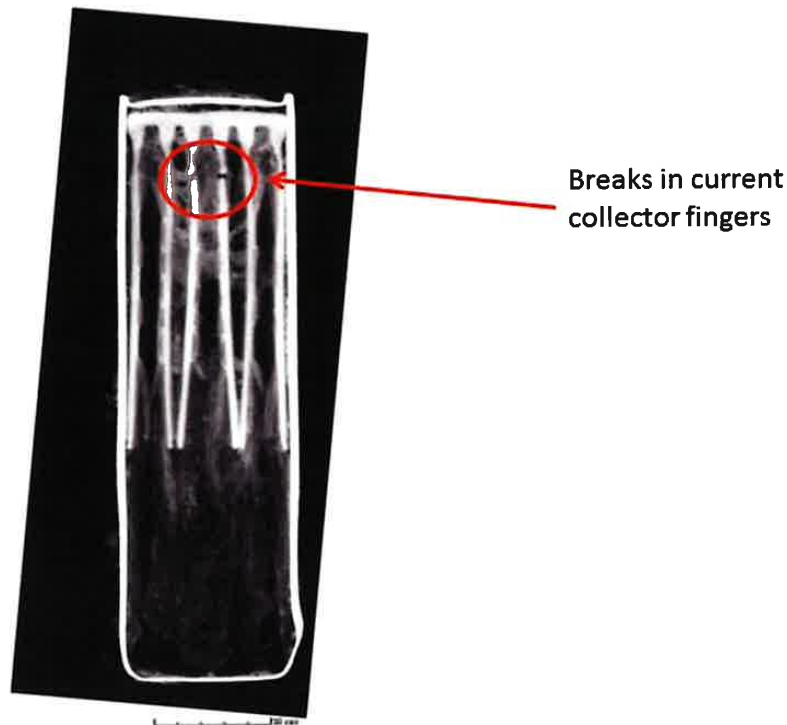


Figure 8. Cross-sectional view of cell 5 aluminum current collectors.

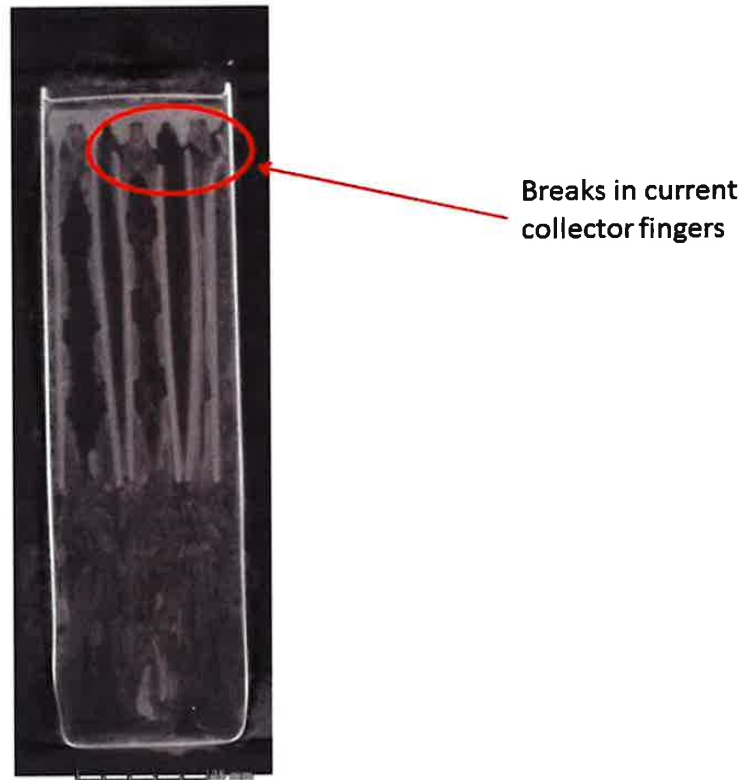


Figure 9. Cross-sectional view of cell 6 aluminum current collectors.

1.4.3 Disassembly of Incident Battery

After charred debris from the top of the battery case was removed, the physical condition of the BMU's sensing wiring harness was examined and was found to have damage consistent with exposure to a high-temperature environment. The damage to the wire insulation degraded progressively from the left side of the battery (cells 1 through 4), where the insulation was thermally discolored, to the right side of the battery (cells 5 through 8), where the insulation was missing for cells 5 and 6 (mostly in the position of cell 5), charred for cell 7, and thermally discolored for cell 8. Also, the wires above cells 5 and 6 were bare, indicating that the area of the most severe thermal damage to the wiring harness was located above cells 5 and 6.

Side 2 of the battery case was folded down to reveal cells 1 through 4. The insulation sheet adjacent to the battery cells remained in place. Behind this insulation sheet, a portion of the other insulation sheet was visible but was missing some sections. Although the insulation

between cells 1 through 4 was damaged, the material could be distinguished from other thermally damaged material in the battery case. The interior surface of side 2 had a clean area with a similar outline to that of an insulation sheet. The rest of the interior surface of side 2 was coated with residue.

Battery case side 4 was folded down to reveal cells 5 through 8. The cells exhibited a darkened, charred appearance. The insulation sheets were completely charred and could not be distinguished from each other and other thermally damaged material in the battery case, and portions of the charred insulation adhered to the cells. The interior surface of side 4 had portions of the charred insulation adhering to areas where the insulation sheets contacted the interior surface. The rest of the interior surface of side 4 was coated with residue.

Side 3 of the battery case was folded down to reveal the sides of cells 4 and 5. The side of cell 4 had staining that resembled a flowing residue. The side of cell 5 had similar staining but also had a cleaner area on the cell case without staining, combustion products, and fire-extinguishing residue. The corresponding area on the interior surface of side 3 was similarly clean and had large portions of insulation that had adhered to the case. The insulation on side 3 was thermally degraded and fragmented, and the portions of the insulation adhering to the battery case directly behind cell 5 exhibited some thinning.

The battery case contained no foreign object debris (FOD). There was no evidence of cell-to-battery case shorting before the thermal event, bus bar shorting, or resistive heating of the bus bars (including those leading to the J1 connector through the contactor and Hall effect current sensor) within the battery case. There were no loose electrical connections at terminals or on BMU wires. There was also no visible evidence of water (resulting from condensation) within the battery case or external surfaces of the battery cells.

Cells 1 through 4 exhibited the least thermal and mechanical damage. Of these cells, cell 3 appeared to be the most thermally damaged. Cells 1 through 3 had vented (with their vent discs opened slightly), and the cell 4 vent disc remained intact.³⁵ Even though the cell 4 vent disc did not rupture, weight measurements for the cell were lower than specifications.

Cells 5 through 8 exhibited the most thermal and mechanical damage, as shown by the thermal decomposition and degradation of the materials in contact with these cells. These materials included bisphenol A thermoplastic polyester and crystalline thermoplastic; the lowest decomposition temperature of these materials is 550°F. Thermal damage was the most severe near cells 5 and 6, as shown in figure 10. The vent discs on cells 5 through 8 had ruptured in a manner indicative of a rapid pressure release.³⁶ Cells 5 through 8 sustained gross mechanical plastic deformation with cells pressing into adjacent cells.

³⁵ The vent discs are scored with an "x" pattern, which enables preferential tearing when the disc ruptures, creating four independent petals. For the vent discs on cells 1 through 3, the four petals had parted slightly but remained in the same plane.

³⁶ For the vent discs on cells 5 through 8, the four petals were generally splayed out and positioned out of plane with each disc's original position, which was indicative of a more forceful opening than that for the vent discs for cells 1 through 4. For cell 5, the petal closest to side 1 of the cell was completely missing.

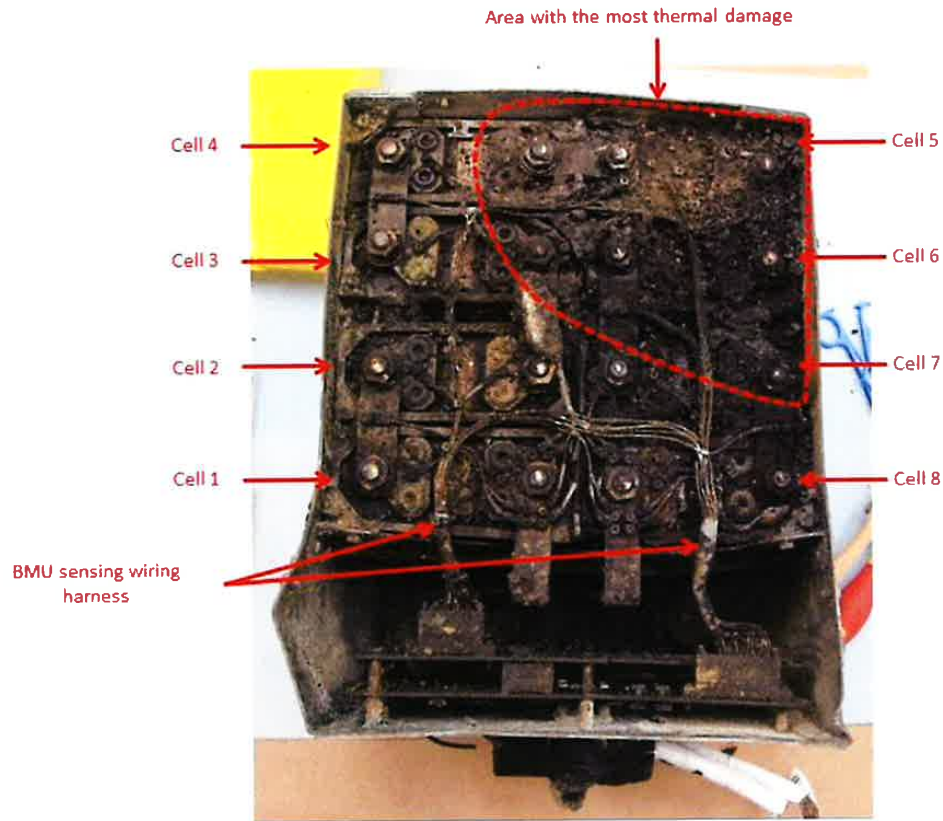


Figure 10. Thermal damage to battery.

The bus bars were removed from the cell terminal assemblies to allow extraction of the battery cells. The electrical contact surfaces of the bus bars showed no indications of localized resistive heating or arcing.

Debris and discoloration consistent with thermal damage were present on the cell 1 through 4 footprints on the lower fixation tray. The footprints of cells 5 through 8 were thermally decomposed, as shown in figure 11. Portions of the lower fixation tray under cells 5 and 6 could not be readily distinguished from other thermally damaged materials in the battery case. The portions of the upper fixation tray that contacted cells 1 through 4 sustained less damage than the portions that contacted cells 5 through 8. The cell 4 upper fixation tray imprint remained mostly intact, but the imprints for cells 1 through 3 showed progressively more damage. Minimal material remained from the portions of the upper fixation tray that contacted cells 5 through 8, which is also shown in figure 11.

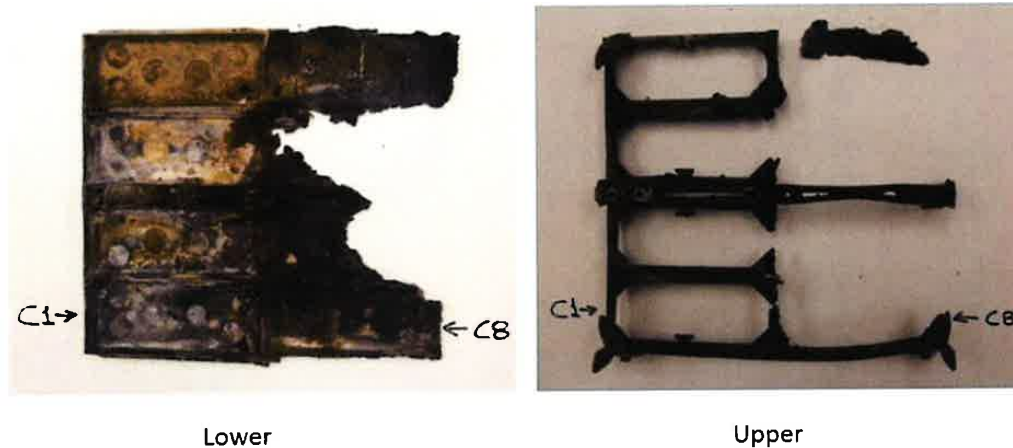


Figure 11. Lower and upper fixation trays.

The J3 connector and receptacle were also examined. The J3 connector had dark deposits on one of the blades on the positive terminal. Analysis of the dark deposits revealed the presence of a hydrocarbon. The other blades on the positive terminal and the blades on the negative terminal of the connector appeared clean with no deposits, stains, or discoloration. The J3 receptacle had thermally induced deformation in one corner. The terminals on the receptacle showed no indications of deposits, stains, or discoloration.

1.4.4 Battery Case Protrusion and Corresponding Cell Case Damage

As stated in section 1.4.1, the battery case exhibited a 0.25-in-wide nodular protrusion on the lower left of side 3, as shown in figure 12. The protrusion extended about 0.12 in from the case. The protrusion appeared metallic and had no paint. Two concentric rings surrounding the protrusion corresponded with the discoloration of exterior paint. Deposits consistent with thermally degraded materials were observed on and near the protrusion. Three holes on the periphery of the protrusion were identified. The largest of these holes was elliptical in shape, with its longest dimension measuring 0.080 in. The two other holes, which were similar in size, measured about 0.004 in. Most of the interior side of the protrusion contained dull gray flaky material consistent with spatter, as well as shiny black material consistent with charred plastics and tars.

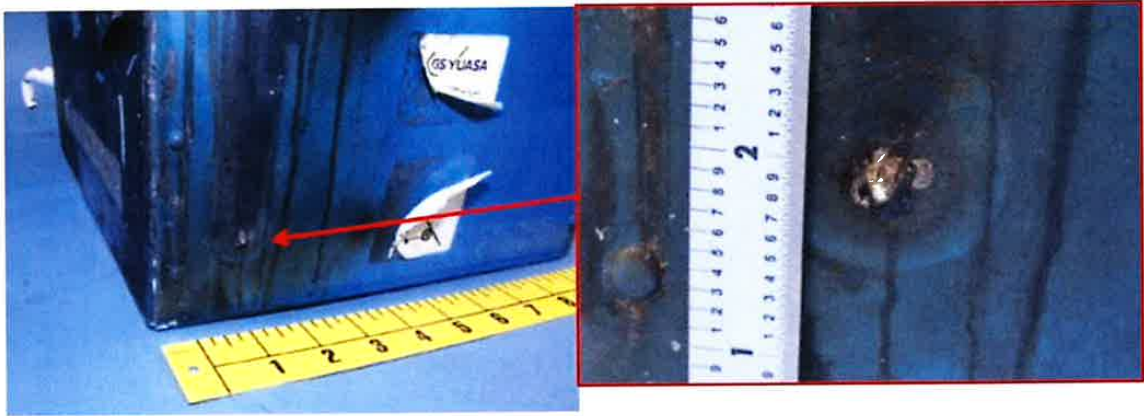


Figure 12. Protrusion on the lower left of battery case side 3.

The side of the cell 5 case that faced side 3 of the battery case had been heavily damaged, especially toward its edges and corners. Four holes were identified on the lower portions of this side of the cell case, all of which exhibited large amounts of dark, rough-appearing features consistent with decomposition products. The largest hole (in terms of size and amount of decomposition products) was about 0.2 in; this hole corresponded with the location of the protrusion on the battery case.

The battery case protrusion was examined using a scanning electron microscope (SEM) and energy dispersive x-ray spectroscopy (EDS). The examinations found that the observed damage was consistent with electrical arcing and contact between the cell 5 case and the battery case.³⁷ (Before contact, the cell 5 case was located about 0.2 in from the battery case with a plastic insulator in the space.) Specifically, evidence of material transfer between the cases was found on the interior surface of the battery case and the exterior surface of the cell case. Also, the battery case exhibited no inward deformation at the protrusion, but the cell case exhibited outward expansion. SEM and EDS examinations further showed that all the holes on the cell 5 case contained various compounds and alloys that were not consistent with the cell case material (a stainless steel) but were instead consistent with the battery case material (an aluminum alloy).

1.4.5 Disassembly of Incident Battery Cells

The NTSB conducted a teardown of each individual battery cell to determine whether the cells contained any anomalies.³⁸ The teardown, which was conducted in the NTSB's materials

³⁷ The other seven cells did not exhibit any evidence of electrical arcing on the exterior of the cell cases.

³⁸ Cell observations were documented using a numbering system that was similar to that for the battery. The front of the cell (facing the J1 and J3 power connectors) was designated as side 1, the left side was designated as side 2, the back of the cell (facing the back wall of the aft E/E bay) was designated as side 3, and the right side was designated as side 4.

laboratory, consisted of disassembling the cell cases, removing the electrode windings, separating the individual windings from the header assembly and current collectors, and unrolling the individual windings. Internal evaluations of each cell consisted of visual, chemical, electrical, and other observations about the overall condition of the internal cell components, the internal surface of the cell case, the current collectors, the header assembly, and the windings.

The windings had been heavily damaged as a result of the incident. The internal evaluations of the cells found no evidence of preexisting defects in, or internal damage to, the copper anode, aluminum cathode, or polyolefin separator. There was also no evidence of preexisting current collector separation, FOD of sufficient size within the cells to cause an internal failure that could lead to thermal runaway, and lithium deposits within the cell windings.

As stated in section 1.4.3, external observations of the cells showed that cells 5 through 8 were more thermally damaged than cells 1 through 4. In particular, the thermal damage to the materials near cells 5 through 8 and the opened vent discs of those cells (with the vent disc petals either missing or peeled outward from the cell cases) were consistent with a higher pressure, more energetic event in cells 5 through 8 compared with cells 1 through 4. The internal examination of the cells showed differences in the degradation of materials that were also consistent with higher temperature exposure in cells 5 through 8.

Cells 1 through 4, when opened, were generally wet and had a smell consistent with liquid electrolyte. The components of cells 1 through 4, including the anode, separator, and cathode, were found intact with most damage limited to a change in opacity in portions of the separator, which was consistent with the activation of the shutdown properties of the separator.³⁹ Damage patterns in cells 1 through 4 were consistent with greater external thermal exposure on battery side 4, which was closest to cells 5 through 8. The damage patterns were also consistent with less external thermal exposure on side 2, which faced the exterior of the battery case. In general, the windings for cells 1 through 4 exhibited damage consistent with greater thermal exposure on the exterior of the cells and the sides that were closer to other cells compared with the interior of the cells and the sides that were exposed to open areas within the battery case. There was no visual evidence of electrical short circuits found in the windings of cells 1 through 4.

Cells 5 through 8, when opened, were dry and did not have a smell consistent with liquid electrolyte. The components of cells 5 through 8 exhibited evidence of damage consistent with high heat exposure and localized high current, including several aluminum current collector fingers that had separated from their header assemblies. For each cell, the aluminum cathode was heavily damaged and was missing large sections of the foil. The copper anode was generally intact but contained pinholes and discolorations with areas of missing active coating material. The separator was missing, which was consistent with thermal exposure above the melting

³⁹ The separator is opaque but becomes more transparent as it thermally degrades. When this degradation occurs, the pores in the separator close, shutting down the lithium-ion transport between the anode and cathode. The shutdown properties of the separator activate just before melting begins.

temperature of the separator material. Sections 1.4.5.1 through 1.4.5.4 provide additional details about the teardown of cells 5 through 8, respectively.⁴⁰

1.4.5.1 Cell 5

The cell 5 examination found evidence of arcing damage on the cell case interior and relatively minor damage to the winding adjacent to the protrusion in the battery case. The cell case was mostly intact. The lower half of the winding closest to battery case side 3 and adjacent to the protrusion in the battery case had adhered to the cell case. The appearance of the cell case and the adherence of the electrodes were consistent with localized heating, melting, separation, and solidification from electrical arcing. No visible portion of the thermoplastic insulation in the cell case remained. Black residue was present on the interior surfaces of the cell case and the exterior of the windings. SEM/EDS analysis found that the chemical composition of the residue was consistent with that of the thermoplastic insulation.

The condition of the aluminum cathode and the copper anode in each winding was consistent with high heat exposure. Most of the cathode material was present but was brittle. Most of the uncoated aluminum foil (at the edges of the windings) remained intact, but portions were missing. The coated aluminum foil was discolored and fractured with areas of the foil missing generally near the header (top) or footer (bottom) fold. Most of the missing aluminum foil had melted and solidified into oblong-shaped globules. The copper foil was intact but had discolorations and small pinholes that propagated through several wraps. The coating on the copper foil had mostly flaked off. The separator was not found during the examination.

For the winding that was closest to battery case side 3, the copper foil was discolored at the header fold with small ripples. The copper foil also exhibited a band of darker color adjacent to the nodular protrusion, which was consistent with high heat exposure. This band of color propagated from the exterior to interior wraps of the winding. The center winding copper foil had ripples along the header fold. This winding appeared to have more overall damage than the other two windings. The winding closest to cell 6 showed the most fragmentation of the aluminum foil and the coated material. The first and second wraps of the winding had thermally adhered to the interior of the cell case, and portions of the first wrap had also thermally adhered to subsequent wraps of the winding. One of the innermost wraps showed folds in the copper foil on the side facing cell 6, which were present through several layers of the winding, as shown in figure 13. Other notable features found during the winding examination were the lack of any sizeable repeating rifts in the windings and the greater amount of damage to the exterior wraps of the windings compared with the interior wraps.

⁴⁰ For additional information about the teardown of cells 1 through 4, see Materials Laboratory Factual Report 13-060, which is available at www.nts.gov in the public docket for this incident. Also, during the teardown of the eight cells, numerous specimens were excised to examine, using SEM and EDS, the physical and chemical characteristics of various internal components. Materials Laboratory Factual Report 13-060 also includes information from these examinations.



Figure 13. Cell 5 winding closest to cell 6.

The pair of aluminum current collectors for the center winding (which in this cell were adjacent to the vent disc) were no longer connected to the header assembly. The detachment of the current collectors occurred at the top of the current collector fingers where the collectors were designed to act as a fusible link. SEM examinations found that the breaks were consistent with thermal fracture associated with high current, as shown by the CT scans of the rounded features at the fracture surfaces (see figure 8). The two other pairs of aluminum current collectors and the three pairs of copper current collectors were intact.

1.4.5.2 Cell 6

The interior of the cell 6 case exhibited a blackened appearance. Portions of the windings and other charred materials were stuck to the bottom of the case on sides 1 and 3. There was no evidence of electrical arcing or short circuits between the windings and the cell case.

The windings exhibited varying degrees of thermal damage based on the amount of aluminum cathode material remaining and the thermal discoloration of the copper anode foil. The winding closest to cell 5 had the least cathode material remaining, and the winding closest to cell 7 had the most cathode material remaining, which was consistent with higher temperatures on side 3 of the cell that tapered off toward side 1. The separator material had melted and could not be identified in all three windings.

For the winding closest to cell 5 and the center winding, the aluminum foil was mostly missing, with the active material coating remaining. Remnants of the aluminum foil were visible as specks or small blobs of solidified aluminum. For the winding closest to cell 7, the aluminum foil was intact but was brittle. The second wrap included an area where the aluminum foil had fused to the copper foil.

For all three windings, large portions of the active material coating for the copper foil had delaminated, exposing large areas of the foil. Pinholes and localized areas of thermal discoloration, which were consistent with localized hot spots, were observed near the edges of the copper foil. The winding closest to cell 5 showed areas of concentrated thermal discoloration that appeared in a repeating pattern on the copper foil, as shown in figure 14. One area of thermal discoloration began on multiple exterior wraps and became lighter toward the interior wraps. Another area of thermal discoloration began about midway through the wraps and continued all of the way to the interior wraps. This pattern of thermal discoloration, which was concentrated on the side of the foil closest to the copper current collectors, exhibited a radiating pattern of wrinkles. The center winding showed an area of thermal discoloration that began at one of the outermost wraps and continued into the winding. The winding closest to cell 7 showed a repeating area of thermal discoloration at one of the outermost wraps.



Figure 14. Cell 6 winding closest to cell 5.

The current collector sides of the winding assemblies (cell sides 2 and 4) appeared blackened and charred and had no remaining insulation material. The copper current collectors were intact and attached to the windings. The aluminum current collectors exhibited fractures with areas of missing material, and two of the three pairs of aluminum current collectors (those in the winding closest to cell 5 and the center winding) had fused and were disconnected from the header assembly. The other pair of aluminum current collectors were intact.

1.4.5.3 Cell 7

The condition of the cell 7 electrodes was consistent with high heat exposure. The three windings had varying amounts of the aluminum cathode foil remaining. The winding closest to cell 8 had more aluminum foil and active material remaining than the two windings that were closer to cell 6. In each of the windings, the coated aluminum was discolored and fractured with areas of aluminum missing generally near the header or footer fold.

The copper anode foil in the winding closest to cell 6 was discolored at the header fold and had small ripples. The copper foil in the center winding was missing a section adjacent to the vent disc, which was consistent with high thermal exposure. The missing section propagated through the winding, with the most material missing from the exterior of an outermost wrap. The

copper foil in the winding closest to cell 8 was discolored at the header fold and contained small ripples in a radiating pattern. The separator was not found.

The pair of aluminum current collectors for the center winding and the pair for the winding closest to cell 6 were no longer connected to the header assembly. The separation in these current collectors occurred at the top of the current collector fingers where the collectors were designed to act as a fusible link. The center winding current collector fingers were separated in one location, and the current collector fingers closest to cell 6 were separated in several locations. The other pair of aluminum current collectors and the three pairs of copper current collectors were intact.

1.4.5.4 Cell 8

For cell 8, there was no discernible difference in the amount of thermal damage between the cathode and anode sides of the winding assemblies. All of the current collectors were intact and showed no readily identifiable abnormalities.

Portions of copper anode windings adhered to the side 1 and side 3 surfaces of the cell case and exhibited hues of purple and blue, consistent with exposure to high temperatures in an oxidizing environment. The cell case surfaces did not reveal any evidence of electrical arcing. The side 2 and side 4 surfaces exhibited a blackened appearance, and charred thermoplastic insulation had adhered to the surfaces. The bottom of the cell case also exhibited a blackened appearance with pieces of charred material adhering to the bottom surface.

The aluminum cathode foil in all three windings was found melted and discontinuous, but the winding closest to cell 7 appeared to be exposed to the highest temperatures because the aluminum foil in the center winding and the winding closest to the BMU had more intact aluminum remaining. (More aluminum remained on the winding closest to the BMU than on the center winding.) For each winding, the copper anode foil could be seen in the areas where the aluminum foil was missing. Small globules of solidified aluminum were interspersed throughout the remaining carbon active material. The separator material had completely melted and could not be identified.

For the winding closest to cell 7, most of the copper foil exhibited discoloration consistent with severe thermal exposure, particularly along the edge where the electrode attached to the current collector near the header fold of the winding. This discoloration continued throughout the winding. The center winding and the winding closest to the BMU showed concentrated thermal discoloration along the edge of the copper foils where they had been attached to the current collector near the header fold of the windings. This discoloration also continued throughout the windings. Areas speckled with small holes appeared throughout the copper foils, some of which continued through several wraps of the windings.

1.4.5.5 TIAX Examination of Cell Teardown Samples

The NTSB contracted with TIAX LLC of Lexington, Massachusetts, to independently examine and analyze cell 6 samples (which included remnants from all three cell windings) to determine if any internal short circuit indicators were present. TIAX's examination of the cell 6

evidence confirmed the findings of the NTSB's cell 6 examination (TIAX *Review* 2013). For example, TIAX determined that the winding closest to cell 5 was more thermally and physically damaged than the other two windings, with almost no aluminum cathode foil remaining; the winding closest to cell 7 had the least damage. TIAX found that most of the aluminum current collectors and all of the separators had melted and that a major portion of the copper (anode) current collectors remained.⁴¹ TIAX also found that most of the copper current collectors had small holes, especially near wrinkled and folded areas of the copper foil. TIAX found no evidence of foreign metal.

TIAX's examination of the winding closest to cell 5 showed regions of thermal discoloration on the copper current collector. TIAX indicated that such areas could be consistent with the presence of an internal short but that it was not possible to determine whether a short could have occurred locally or developed from an external source.

TIAX's examination of the remaining copper current collectors showed that, in the winding closest to cell 7 and the center winding (which, as previously stated, were less damaged than the winding closest to cell 5), the windings' outer regions appeared more damaged thermally than the inner regions. TIAX indicated that this observation was consistent with "an origin of thermal stress" outside these windings with elevated temperatures that decreased toward the windings' inner regions.

Some abnormalities were observed in multiple regions of the windings. For example, a significant amount of beaded metal was observed around the edge of an irregularly shaped hole in a copper current collector in the winding closest to cell 5. TIAX noted that this type of formation could indicate the highest temperatures reached during the incident. The NTSB analyzed the ridges using EDS and found that the beads at the edge of the irregularly shaped hole were copper, which indicated that the hole had resulted from the melting of copper.

1.5 Exemplar Battery Examinations and Testing

1.5.1 Radiographic Examinations of Exemplar Battery Cells

Additional radiographic studies were conducted to examine and document the internal configuration of individual battery cells from five batteries. One of the batteries was the main battery installed on the incident airplane (referred to as battery 412); the other four batteries (referred to as batteries 149, 305, 344, and 376) were provided by Boeing.⁴² These batteries had been installed on 787 airplanes being assembled at Boeing but were removed before any flight

⁴¹ TIAX referred to the current collector fingers and the foils of the electrode winding assemblies as current collectors.

⁴² The battery numbers reflect the battery serial numbers.

time because the batteries overdischarged and latched.⁴³ The CT scans of these cells were examined for indications of missing or damaged parts, contamination, or other anomalies.⁴⁴

The CT scans showed that all of the cells from all five batteries contained areas of wrinkled and/or separated windings. Three batteries (149, 376, and 412) showed an anomaly (specifically, a small protrusion from the insulator) in the aluminum terminal plate for one cell; one battery (305) showed this anomaly for two cells. Battery 305 showed a measureable angle between the aluminum current collectors and the cell header in one cell; battery 149 showed this condition for two cells. (The measured angles ranged from about 1.0° to 1.7°.) Battery 149 also showed a localized bulge in one cell's wall. In addition, battery 305 showed copper current collectors that had out-of-alignment clips in two cells.

1.5.2 Cell Soft-Short Tests

A soft short can occur when the electrical isolation between the positive and negative electrodes of a cell is compromised. TIAX indicated that features creating soft shorts could reside undetected within a cell and develop slowly over time. TIAX further indicated that some soft shorts could dissipate over time, whereas others could become severe enough to result in the early failure of a battery (a loss of capacity and failure to hold a charge) or progress to "a more serious, higher-magnitude short" that could cause "catastrophic failure of the cell" (TIAX Report 2013).

The Naval Surface Warfare Center, Carderock Division, and TIAX performed two different types of nondestructive soft-short testing. A total of 40 cells from the incident airplane main battery and the four batteries that Boeing provided were used for the soft-short testing. The test results were used along with the radiographic examination results (discussed in section 1.5.1) to identify possible cells for TIAX's destructive physical analysis (DPA) of an exemplar battery cell, as discussed in section 1.5.3.

The Carderock soft-short testing involved a procedure that monitored cell self-discharge rate decays, which, for lithium-ion cells, occur from current leakage across the separator.⁴⁵ The test procedure discharged cells to a low state of charge, removed the discharge load, and observed the cells during a 1- to 2-week period to determine whether any anomalous decays in cell voltage occurred.⁴⁶ (Voltage decay is an indicator of a potential soft-short formation within

⁴³ Overdischarging of the battery occurs when the battery or any cell is below a predetermined voltage. If a cell's voltage drops below the predetermined level, the BMU latches a fault and prevents the battery from recharging.

⁴⁴ Before CT scanning began, the five exemplar batteries were disassembled at the Naval Surface Warfare Center, Carderock Division, US Department of the Navy. During disassembly, the batteries were evaluated for construction consistency and the presence of FOD. No anomalies were found.

⁴⁵ The Carderock soft-short testing was based on the Darcy test method, which was developed by the battery group lead for projects and integration at the National Aeronautics and Space Administration's (NASA) Johnson Space Center in Houston, Texas.

⁴⁶ State of charge is the percent of electrical potential between the designed minimum and maximum voltage potentials.

the cell.) None of the eight cells from the five batteries exhibited anomalous decays in cell voltage during the observation period.

The TIAX soft-short testing involved (1) charging each cell individually to the nominal voltage of 3.7 volts, (2) placing each cell test group in a pre-test configuration for 12 hours to equalize any variations in the state of charge, and (3) connecting each cell group to soft-short test instrumentation and monitoring the response of each cell for 24 hours to measure the level of self-discharge of each battery cell.⁴⁷ (According to TIAX, an internal short could have “an anomalously higher level of self-discharge” compared with other cells in the test group.) TIAX’s report on the testing indicated that “all [40] cells showed normal (short-free) response characteristics.”

UL conducted additional soft-short-related tests, referred to as aging sorting tests. UL conducted these tests to identify cells with possible internal anomalies because, according to UL, cells with such anomalies could exhibit higher self-discharging rates than cells without internal anomalies (Tabaddor and others 2014). The testing, which was conducted at temperatures of 77°F, 32°F, and -0.4°F, produced generally consistent results among the cells in each battery. The testing found all but one cell to be within acceptable limits. (At -0.4°F, a cell in one battery displayed a performance change in the discharge rate that differed from the other cells; this characteristic had not been displayed at other temperatures, and the specific cause of the difference was not determined.)

1.5.3 Examinations of Cells From the Incident Airplane Main Battery

TIAX and UL performed separate DPAs of cells from battery 412 to note any abnormalities in the cells. The laboratories used different methods to conduct the DPAs, but both laboratories’ DPAs found areas in the cell windings that were susceptible to lithium deposits.

TIAX conducted coin cell tests before its DPA to determine the anode-to-cathode ratio in the cells and the tolerance of the electrodes to the specific charging conditions likely to lead to lithium deposits.⁴⁸ The coin cells were built from samples of electrodes and electrolyte harvested from cell 4 in battery 344. According to TIAX, the tests showed that (1) the anode-to-cathode ratio had “a large anode capacity excess,” which would be consistent with a cell designed to avoid lithium deposits on the anode, and (2) voltage, charging current, and temperature extremes (within allowed operational ranges for the cell) did not produce visual evidence of lithium deposits (TIAX 2014).⁴⁹ Thus, according to the results of the coin cell tests, the LVP65 cell chemistry was not susceptible to lithium deposits under high-current or low-temperature conditions.

⁴⁷ The TIAX soft-short testing, which was based on a proprietary test method, was quicker and more sensitive than the Carderock soft-short testing.

⁴⁸ Coin cells are small specimens extracted from battery cells that are used to examine the electrochemical properties of the anode and cathode, excluding cell- and battery-level effects.

⁴⁹ According to GS Yuasa, the 787 battery cells were designed so that the capacity of the anode was greater than that in previous cell designs.

Before TIAX's DPA, cell 1 in battery 412 was charged to the maximum voltage allowed by the BMU (4.2 volts) at the maximum normal charging current (46 amperes) at 32°F to simulate the worst-case conditions for potential lithium deposits (within the airplane's specified operating envelope).⁵⁰ A fully charged cell, in which the anode appears bright gold in color, facilitated the identification of potential abnormalities. This process was repeated 20 times (with rest periods in between each charging cycle) before the DPA was performed. According to TIAX's report, the following abnormalities were observed during the DPA:

- More than 100 areas of "ingressed under-lithiation" of the anode (that is, areas of the anode that were incompletely charged) were found in each winding.
- More than 90 full creases spanning the width of the electrodes and several hundred partial creases (that is, those that did not run from one side of an electrode to its other side) were found in all three windings.⁵¹ The full creases in the anodes were located generally where the connection to the current collectors (along the edges) ended. Many of the full and partial creases showed features consistent with underlithiation of the anode.
- A total of 61 clusters of silver-colored deposits were located in the outer two windings, with fewer clusters located in the center winding.⁵² These deposits were generally adjacent to underlithiated areas on the anode. According to TIAX, these areas indicated that mechanical abnormalities in the windings resulted in uneven charging of the anode, which might have caused lithium to deposit adjacent to underlithiated areas.

Samples of the silver-colored deposits observed during TIAX's DPA were analyzed at the Naval Surface Warfare Center, Carderock Division, using x-ray photoelectron spectroscopy. The analysis showed that the deposits contained lithium along with the constituents of the electrolyte (Mansour and others 2014). No metallic elements besides lithium were found.

The DPAs that UL performed were conducted as part of testing to determine whether potential risks of cell degradation, failure, or loss of performance under specific applications, such as low temperature, existed for LVP65 cells. The DPAs involved three cells from battery 412 (cells 3, 5, and 6). All of the test cells were at 100% state of charge (4.025 volts). Cell 3 was subjected to pulse charging at -0.4°F, cell 5 was subjected to normal constant-current constant-voltage charging at 32°F, and cell 6 was subjected to pulse charging at 77°F.⁵³ The pulse

⁵⁰ The DPA could not be performed at the battery's minimum operating temperature (-0.4°F) because, upon charging at this temperature, the voltage reached 4.025 volts rapidly, causing the current to spike and drop. Thus, high current could not be sustained long enough to produce lithium deposits.

⁵¹ The normal folds at the top and bottom of the windings were not considered to be creases.

⁵² Each cluster represented an entire feature area and not the number of individual deposits.

⁵³ Pulse charging involves applying current in rapid short repetitive intervals. During the UL tests, the intervals ranged from about 0.25 to 0.50 second.

charging tests revealed no lithium deposits in the cell tested at 77°F and a progressive decrease in charge transfer (cell capacity) as the temperature decreased to -0.4°F.⁵⁴

Visual examinations of the windings from cells 5 and 6 revealed features consistent with lithium deposits. (UL referred to these deposits as lithium dendrites).⁵⁵ No features consistent with lithium deposits were observed in the cell 3 windings. All observed features were found adjacent to wrinkled regions of the windings. According to UL, wrinkles can form dendrites by creating “non-uniform current density distributions” within the windings due to the “uneven contact between the electrodes and separator in a wrinkled region” (Tabaddor and others 2014).

A normal electrode assembly with consistent uniform spacing between the anode and cathode allows uniform lithium-ion transport via the shortest pathway. Thus, an assembly with wrinkled or creased regions could result in non-uniform lithium-ion transport. According to UL, non-uniform lithium-ion transport could also occur from following causes:

- localized deformations of the windings during manufacturing, such as those that occur when flattening the assemblies to the “jelly roll” shape or by stresses resulting from welding the current collectors to the electrodes;
- poor quality control of the coating and winding processes during manufacturing; and
- cell swelling during charge and contracting during discharge, which creates movement of the current collector fingers attached to the windings.

1.5.4 Cell-Level Abuse Tests

UL conducted testing to understand and compare the energy level of a thermal runaway in response to three different methods of simulating an internal short circuit within a single cell from exemplar battery assemblies.⁵⁶ The internal short circuits were initiated in a single cell winding using the indentation, nail penetration, or hot pad methods.⁵⁷ The tests were conducted at temperatures of 77°F and 158°F. Cell temperatures were measured by thermocouples at

⁵⁴ In its submission to the NTSB for this investigation, GS Yuasa stated that, after the incident, it conducted more than 100 cold charge cycle tests, all of which revealed a loss of capacity when charging repeatedly at -9.4°F.

⁵⁵ A lithium dendrite is a lithium metal deposit that can form on a coated anode surface. Lithium dendrites can grow over time and cause internal short circuiting. The lithium metal can react exothermically with electrolyte. In addition, lithium dendrites can cause the electrodes to become unstable and thus result in an exothermic reaction. Such reactions at both the anode and cathode, as well internal short circuits from lithium dendrite formation, can result in a thermal runaway (Belov and Yang 2008, 885-894).

⁵⁶ Cells 1 through 8 from batteries 149 and 241 were used for the indentation, nail penetration, and hot pad tests; cell 8 from battery 171 was also used for a hot pad test. (Boeing provided batteries 241 and 171, in addition to the previously provided battery 149, for the cell-level abuse tests). A total of 17 cells were tested.

⁵⁷ The indentation method, which UL developed, creates a localized, small-scale internal short circuit condition by stressing the electrodes without breaching the cell case. The nail penetration method involves inserting a nail through a cell case to penetrate the electrodes and induce an internal short circuit condition within the cell. The hot pad method involves placing a small electric heating pad on a cell to heat the cell to a desired temperature to induce an internal short circuit condition.

various locations on the cell cases, and cell voltage responses were measured by probes attached to the cell terminals.

During all tests, when the internal short circuit was induced in a single winding of a cell, the cell voltage decreased immediately.⁵⁸ The cell voltage then recovered but, within 30 seconds, decreased again and remained at a level consistent with the failure of all three windings (Wang and Wu 2014). The most significant effects observed from the tests included the temperature increase and venting as the cell entered thermal runaway, the decrease and recovery in cell voltage that occurred immediately after the induced internal short circuit, and the fused aluminum current collectors in response to the internal short circuit.⁵⁹

Figure 15 shows the cell voltage output measured during an internal short circuit test. The test was conducted at 77°F, and the internal short circuit was induced using the indentation method. Region A in the figure shows the fully charged cell before the introduction of the simulated internal short circuit in a single winding of the cell. Region B shows the cell voltage output immediately after the initiation of the internal short circuit but before the failed winding's current collector fused open. The cell's temperature reached about 150°F at this point in the test (about 5 seconds after the initiation of the internal short circuit). Region C shows the voltage output after the failed winding's current collector fused open and the subsequent recovery of the cell with the voltage output from the two remaining windings. Region D shows the decreasing cell voltage output as the remaining two windings fail due to the heat generated by the first failed winding.⁶⁰ The cell's temperature reached about 500°F at that point in the test (about 27 seconds after the initiation of the internal short circuit). The cell's maximum temperature, about 610°F, occurred about 90 seconds after the initiation of the internal short circuit.

⁵⁸ For the 158°F tests, the voltage drop was between 0.50 to 0.75 VDC; for the 77°F tests, the voltage drop was between 1.00 and 1.25 VDC.

⁵⁹ Excessive current flow through the current collector finger causes the fuse portion of the finger to heat to the point of melting and open the electrical circuit between the winding and the other windings in a cell. Postincident discussions with GS Yuasa revealed that the current collector fingers were sized to allow for required power loads that the cell would encounter in service without fusing open.

⁶⁰ The three electrode windings in the 787 main and APU battery cell design are electrically connected in parallel. When the voltage of a single winding arranged in parallel with other windings drops below that of the adjacent windings, the remaining windings will attempt to charge the lower voltage winding to equalize the voltage across the parallel circuit. The charging currents that result could discharge the remaining windings, causing an overall drop in cell voltage or a rupture of the cell assembly. (Reddy and Linden, 2011).

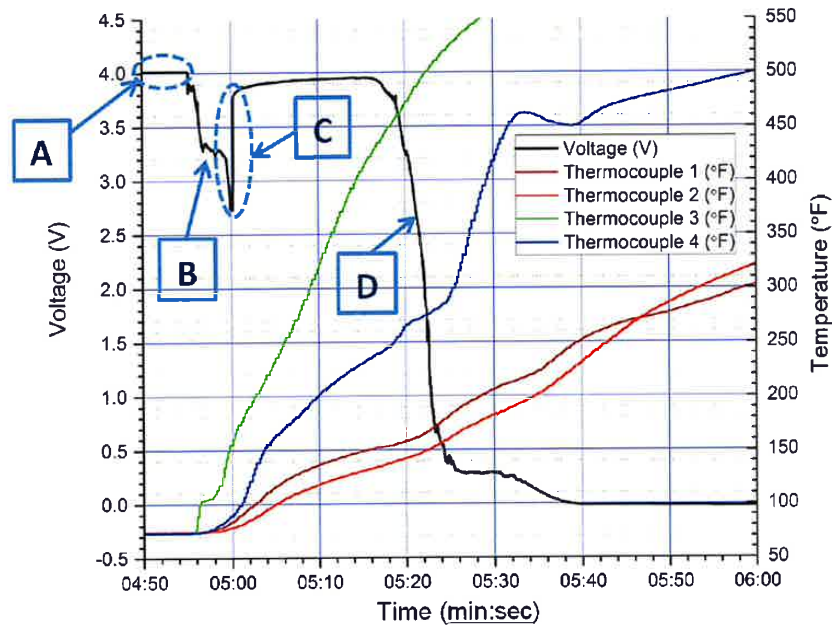


Figure 15. Results of cell-level internal short circuit abuse test.

Note: The preceding paragraph describes each region depicted in this figure. The thermocouples used to measure cell temperature were typically placed at the cell's copper (negative) rivet (thermocouple 1), the aluminum (positive) rivet (thermocouple 2), 0.2 in from the internal short circuit initiation point (thermocouple 3), and 0.1 in from the vent disc (thermocouple 4).

During all indentation and nail penetration tests conducted at 77°F and 158°F, the current collector fingers in the initiating outer winding fused open. During some of the indentation and nail penetration testing at 158°F, the current collector fingers in the center winding also fused open. During all hot pad testing conducted at 77°F and 158°F, only the current collector fingers in the initiating outer winding directly adjacent to the hot pad fused open. None of the center or far outer windings had fused current collectors.

When nail penetration testing was conducted at 158°F on two separate cells with a nail that entered the top of the cells (rather than the side of the cells) and shorted only the center winding, the center winding current collector fingers fused open, and the current collector fingers in the outer windings remained intact.⁶¹ Data recorded during these tests showed that, after the internal short circuit was induced, the cell voltage dropped immediately, abruptly recovered, and then dropped to zero volts. For the tests in which the current collector fingers fused open in the

⁶¹ A similar behavior involving only the center current collector fingers fusing open in the initiating cell was observed during the 158°F full-scale battery nail penetration test described in section 1.5.7. Also, as stated in section 1.4.2, CT scans of the incident battery showed that, for cell 5, the current collector fingers in only the center winding fused open as a result of the battery thermal event.

outer winding and the center winding, the recorded data showed two separate voltage decreases with two recoveries.

UL's testing showed that, with a significant internal short circuit, the current flow through a winding could reach a level sufficient to open the winding's fusible link. In addition, the testing showed that conduction of the heat generated by an internal short circuit in one winding of a parallel arrangement to adjacent windings could cause thermal damage in those windings and lead to thermal runaway of the entire cell.

Thermal abuse testing performed using accelerating rate calorimetry (ARC) showed that the cells, at zero and 100% state of charge, started to generate internal heat at temperatures as low as 144°F, which is below the maximum operational temperature of the battery (158°F).⁶² When the ambient condition of a fully charged cell was increased beyond 176°F, the self-heating rate exceeded 0.04°F per minute. When the temperature of the cell was raised to about 266°F, the separator melted, and the cell entered thermal runaway and vented. None of the current collectors fused during the abuse testing using ARC.

1.5.5 Rivet Observations During Cell- and Battery-Level Testing

The aluminum and copper rivets on 787 main and APU battery cells clamp together the electrical components at the top of each cell, including a copper top plate, external and internal thermoplastic seals, and a current collector, to conduct current flow into and out of the cells.⁶³ The rivets also provide a hermetic seal intended to prevent leakage of electrolyte from the cell case and protect the electrolyte from external moisture. Evidence of rivet seal leakage was found in cell 4 of the incident APU battery, which had melted seals and weighed less than specifications despite the vent disc remaining intact.

During tests to determine the effects of simulated APU starts on individual cells and a complete battery assembly, UL made observations about the aluminum rivets (Wang, Chiang, and Wu 2014).⁶⁴ The APU start simulations on a full battery were performed using battery 459 at temperatures of 77°F and 32°F after the individual battery cells underwent the same levels of charge and discharge.⁶⁵ After a normal battery-level first charge/discharge cycle at 77°F, the

⁶² The cells were slowly heated in an ARC chamber so that an adiabatic condition existed (that is, no heat was transferred between the cells and the surrounding environment) until the cells began to self-heat to the point that they eventually failed.

⁶³ The aluminum rivets conduct energy from the aluminum current collector, and the copper rivets conduct energy from the copper current collector.

⁶⁴ UL disassembled the battery before the battery-level tests to examine and test the individual cells and reassembled the battery afterward using GS Yuasa documentation provided to UL by the NTSB. (The battery could be disassembled and reassembled outside of GS Yuasa.)

⁶⁵ The APU start profile is similar to two failed starts followed by a successful start during a short time period using the APU battery as the only starting power source. An APU start discharge attempt at -0.4°F was not completed because the battery voltage dropped and the test was stopped to prevent battery damage. As shown in UL's test plan (which was distributed to the parties to the investigation before testing began), the discharge rate used during UL's testing was based on the design requirement at the time of certification, and a post-test review found that this discharge rate was not exceeded.

temperature of the aluminum rivets on the positive terminal of cell 5 increased progressively through 14 cycles to a maximum temperature of 315°F, which exceeded the melting temperature of the separator and the temperature at which the thermoplastic seals begin to soften.⁶⁶

An infrared thermal image taken at 32°F during the last of the 14 battery-level test cycles showed that the aluminum rivets on cell 5 were sources of heat in addition to heat from the electrode windings. The image also showed that heat was conducted from the cell 5 aluminum rivets through the copper bus bar to the copper rivets on cell 6. Further, strain gauges placed on the sides and tops of the cell cases showed that the stresses in the cells increased during discharge, with cell 5 exhibiting the highest strain during a test at 32°F. In addition, the efficiency of the cells decreased as temperatures decreased such that 30% of the discharge energy heated the cell when the temperature was reduced to 0°F.

UL performed subsequent examinations and testing on cell 5 from battery 459, including CT scans; DC resistance measurements; cell leakage tests; and a cell DPA, which included visual inspection of the separator and compositional analysis of the electrolyte. The testing showed that the aluminum rivet seals leaked and that the DC resistance between the aluminum current collectors and the riveted joint was significantly higher (three orders of magnitude) than that of the same joint in other cells. The CT scans revealed visible gaps between the rivet and the current collector (internally) and the rivet and the copper top plate (externally). During the DPA examination, plastic seals were found deformed, and the separator material showed localized melting between the anode and cathode adjacent to the aluminum center winding current collector finger. Separator melting was not observed elsewhere in the windings.

The 787 battery was designed to measure temperature only on two cell bus bars and not at or within each cell. Infrared thermal images and thermocouple data from the UL battery-level testing showed that (1) temperatures were not even across the surfaces of individual cells, (2) the cell temperatures differed from each other, and (3) the bus bar temperatures were lower than the cell temperatures and substantially lower than the temperature at the rivets, and (4) the changes in bus bar temperatures lagged behind the changes in cell temperatures. As a result, UL conducted heat flow tests on a header assembly that had been removed from a cell to determine the internal temperatures of a cell. The interior portion of one of the aluminum rivets was heated until the exterior of the rivet reached the 315°F maximum temperature measured during the APU start simulations. At that temperature, the interior portion of the rivet measured 332°F, and the top of the internal aluminum current collector measured 277°F, which was higher than the melting temperature of the separator.⁶⁷

The NTSB's CT scans of the rivet assemblies in cells from the main battery on the incident airplane (battery 412) revealed gaps and voids between the rivets and assembly components. After the rivet assembly in cell 5 was cross-sectioned, rinsed, and dried, water

⁶⁶ During the testing, the temperature of both aluminum rivets was measured using an infrared camera. A thermocouple was also placed on one of the rivets to further measure temperature.

⁶⁷ The interior portion of the rivet and the current collector had been within the cell before it was disassembled for the heat flow test.

seeped out of gaps at the edges of the plastic seals in the assembly. The water revealed gaps that were not initially seen under magnification.

Further examination of cell 5 in battery 412 revealed brown deposits that were consistent with dried electrolyte. These deposits were found around a rivet hole of the internal current collector, which had been in contact with an aluminum rivet. Closer examination of the current collector's surface showed evidence of material consistent with oxidation products under the rivet head. The current collector was bent and skewed out from the rivets, and the exterior plastic seal was deformed, diminishing the sealing surface. The deformation caused the plastic sealing surfaces to separate from the top of the stainless steel cell case. Multiple gaps between the contact surfaces were found between the rivet and copper top plate and between the rivet and current collector. The copper plate had a nickel finish, and the shoulder of the rivet had an impressed circular pattern (consistent with machining ridges) that had not been transferred into the nickel plating, which was consistent with a lack of compressive force in this area. The rest of the plating around the rivet hole showed no indications of contact with the rivet.

1.5.6 Cold Temperature Cell- and Battery-Level Testing

The airplanes involved in the BOS, TAK, and NRT events were based in Tokyo and were exposed to below-freezing temperatures during the winter months. At the time of the NRT event, the 787s based in Japan represented less than one-third of the worldwide 787 fleet. Even though other 787 airplanes had occasionally been exposed to below-freezing temperatures while at their base location, the winter temperatures in Tokyo were the coldest of the cities where 787 airplanes were based. The NTSB was concerned that cold weather exposure could be a significant risk factor for the 787 main and APU lithium-ion battery.⁶⁸ As a result, UL conducted cold temperature testing at the cell and battery levels to determine the effect that cold temperature charging could have on the battery's performance. During the cell-level testing, the cells heated significantly more when discharged at temperatures between 0°F and 32°F than at temperatures above 32°F.

As previously stated, during battery-level testing at 32°F, the aluminum rivets on a cell increased in temperature to a maximum of 315°F, which exceeded the melting temperature of the separator material. Cell disassembly found melting at the edges of the separator layers that had been adjacent to the aluminum current collector fingers. (Such melting was not found during the cell-level tests.) Measurement of the electrical resistance across rivet-to-collector joints after cell disassembly showed that the resistance in a cell that heated (cell 5 of battery 459) was 74.5 milliohms; the resistance of other cells was typically 0.03 milliohm. In its submission for this investigation, Boeing stated that it was revising the low temperature charging limit for the main and APU battery and BCU to "reduce the likelihood of an internal short circuit and improve cell and battery reliability."

⁶⁸ In its report on the TAK incident, the JTSB noted the cold temperatures that existed at the time of the three battery events and indicated that cold temperature could be related to the cause of the failures.

1.5.7 Battery-Level Nail Penetration Tests

UL conducted nail penetration tests on LVP65-8-402 batteries to determine the effects of a simulated short circuit within a single cell. The nail penetration tests were conducted with battery numbers 436 and 445, which Boeing provided in addition to the other 787 exemplar batteries.⁶⁹ A specially designed nail with an embedded thermocouple (which provided a single temperature within the nail-penetrated cell) was used during the tests.

In one test, the battery was electrically grounded using a single ground wire that was representative of the ground wire installed on the 787 airplane (Chapin and others, *NTSB Battery Tests [Asset 445]*, 2014).⁷⁰ The battery temperature at the start of this test was between 52°F and 57°F, which was consistent with temperatures in the E/E bay during a typical flight, as measured by Boeing.⁷¹ In another test, the battery was not electrically grounded (similar to the test setup used by GS Yuasa in a 2006 battery development test, as described in section 1.7.3), and the test was conducted at the battery's maximum operating temperature of 158°F (Chapin and others, *NTSB Battery Tests [Asset 436]*, 2014).⁷²

The test with the electrically grounded battery showed that thermal runaway occurred when a short circuit was induced into a single cell inside the battery, resulting in cell swelling and venting of the nail-penetrated cell. None of the other cells in the battery underwent thermal runaway or vented. This test also showed that the initiating cell and other cells within the battery case began to electrically discharge at an uncontrolled rate, causing a high electrical current to discharge through the ground wire circuit.⁷³ Within 30 seconds of the initiation of cell venting of the nail-penetrated cell, the ground wire fused open, and the current flow through the grounding path ceased. The post-test examination of the battery found evidence of arcing between the nail-penetrated cell (cell 6) and the battery case, including welding of the cell case and the center brace bar of the battery case.

The test with the ungrounded battery showed that thermal runaway of a single cell propagated to all other cells inside the battery case. This result (propagation to and venting of all cells) differed from the results of GS Yuasa's battery development test (venting of the

⁶⁹ Before the testing, the batteries were disassembled so that nondestructive tests could be performed. Cells 1 and 2 from battery 445 were damaged during disassembly, so they were replaced with identical cells from battery 271, which Boeing also provided.

⁷⁰ The battery case, when installed in the airplane, is grounded via the 787 common return network. The battery test setup did not include all electrical ground paths to the battery case as installed on the airplane (that is, the ground wire, shielded signal wires, and a physical connection between the battery case mounting rails and ground).

⁷¹ APU battery temperature was not recorded on the incident EAFR. After the incident, Boeing monitored E/E bay temperatures during several flights and reported average values of 50°F to 59°F during a typical flight.

⁷² UL's reports on these tests included detailed information about the test facility, test fixture, instrumentation, data acquisition, test procedures, and results.

⁷³ As previously stated, the incident battery ground wire was found intact with the wire insulation exhibiting an undamaged exterior surface but a slightly blackened interior surface, which was consistent with resistive heating associated with the flow of high levels of electrical current. Also, the shielded signal wires exhibited signs of internal heating that were consistent with resistive heating by high levels of electrical current.

nail-penetrated cell and no propagation to and venting of other cells), but the NTSB notes that GS Yuasa performed its battery test at a temperature that did not represent the battery's maximum operating temperature under normal conditions (158°F). The post-test examination of the ungrounded battery used for the UL test found no evidence of arcing between the nail-penetrated cell (or other vented cells) and the battery case.

The findings of these tests were part of the basis for Safety Recommendations A-14-32 through -36, which were issued in May 2014 (see section 1.8.2).

1.5.8 Additional Testing

Early in the investigation of the BOS incident, the NTSB performed ATP functional testing of the BCU of the incident airplane's APU battery at Securaplane's facility. At the request of the JTSB, the NTSB also performed ATP testing on both BCUs from the airplane involved in the TAK incident. As stated in section 1.2.2, the ATP testing revealed a previously unknown electrical oscillation in the output charge voltage of each BCU. Boeing and UL conducted separate detailed examinations of the BCU from the APU battery that had been installed on the BOS airplane and integrated system testing of a battery, the BCU, and battery-related components. The testing at Boeing and UL found that the oscillation could slightly diminish the battery's life but was unrelated to thermal runaway.⁷⁴ As a result of its testing, Boeing changed the BCU design to minimize the oscillation. GS Yuasa conducted testing as part of the JTSB's investigation of the TAK incident and similarly found that the BCU oscillation could shorten a cell's life.

During the investigation of the BOS and TAK incidents, Boeing developed and conducted (along with its contractors) more than 40 different laboratory and airplane tests to understand various battery failure modes. Boeing also performed tests to learn information that would support the redesign of the main and APU battery systems.⁷⁵

Boeing performed a laboratory test to understand the effects of moisture condensing on the battery. This test subjected the battery case and internal battery components to simulated flight cycles in an environmental chamber with varying temperature, pressure, and humidity conditions.⁷⁶ After the testing was completed, small amounts of condensation were noted on the top of the cells. The condensation created an electrical short path between the cell case and the battery case. Boeing performed a subsequent laboratory test in which a single cell was placed in a container with saline solution and voltage was provided to represent the other cells of a battery.

⁷⁴ One of the reports that UL developed as part of this investigation refers to the BCU oscillation testing as part of the "Noisy Test Procedure" (Tabaddor and others 2014). "Noisy" electrical power refers to the lack of continuous voltage; current; and, if AC power, frequency. UL's report includes specific details about the frequency and current characteristics used for the testing.

⁷⁵ For additional information about the testing that Boeing performed, see the testing addendum to the Airworthiness Group Chairman's Factual Report, which is available at www.nts.gov in the public docket for this incident.

⁷⁶ The battery assembly used during this test did not use actual cells; thermally equivalent representative cells were instead used for the testing.

The single cell vented, and post-test examination revealed damage internal to the cell header, including evidence of arcing, shorting, and heat damage.

Another laboratory test examined the vibration environment of the battery. This test subjected the battery to vibration levels in the pitch, roll, and yaw axes in excess of the levels occurring during in-service operations. The battery's performance was monitored, and the battery was examined, before and after each vibration series. Slight changes in cell case voltages were noted, but no changes in the battery's performance were observed. Post-test examinations of the battery revealed areas of slight abrasions to battery components and one failed BMU sensing wire.⁷⁷

In addition to the previously mentioned integrated battery/BCU system component testing, Boeing conducted flight and ground tests with an instrumented 787 airplane to determine the atmospheric and electrical environment of the system installation. During the flight and ground tests, the battery and charger performed with no anomalies, and no thermal or vibration data exceeded the design requirements. Temperatures for the main and APU battery and the forward and aft E/E bays during the flight tests were comparable with in-service temperatures. Examination of the flight test data showed oscillations during the constant-voltage charging cycle at low-current loading, which were similar to the oscillations observed during the BCU testing at Securaplane. No other abnormal electrical transients were observed in the flight and ground test data.

1.6 Battery Manufacturing Information

1.6.1 Main and Auxiliary Power Unit Battery Development

In 2003, Boeing created a statement of work to outsource the design and manufacture of the 787 power conversion subsystem and awarded this contract to Thales in May 2004. Thales then subcontracted (with concurrence from Boeing) the design and manufacture of the 787 main and APU battery to GS Yuasa and the design and manufacture of the 787 battery charging system to Securaplane Technologies.⁷⁸

Boeing, with participation from Thales, created the specification control drawing (SCD) and interface control drawing to be used during the development and manufacture of the 787 battery and battery charging system.⁷⁹ Thales was responsible for providing these specifications to GS Yuasa and Securaplane, managing these subtier suppliers, and meeting all of the

⁷⁷ The LVP65-8-403 battery design incorporated improvements to the BMU sensing wiring installation.

⁷⁸ Outsourcing is an industry practice that can be practical and effective when all aspects of the design, manufacture, and certification of a component or system have been verified to ensure an airplane's safety of flight. Postincident interviews revealed that all of the companies involved with the design and manufacture of the 787 power conversion subsystem agreed that each would retain ownership of their associated intellectual properties.

⁷⁹ According to Boeing, the SCD depicts the performance and design requirements, functional and physical interfaces, and quality assurance requirements for the development, procurement, and configuration control of an item or assembly. The interface control drawing is a formal engineering document that defines, among other things, the interface between mating parts, connections, and signals.

specification requirements for the battery and battery charger system. Thales, along with its subtier suppliers, was also responsible for providing Boeing with required testing and analysis results.

The basic design of the battery began in 2005. As part of the design, GS Yuasa contracted with KAI to design and manufacture the BMU. As the battery design matured, preliminary design reviews and critical design reviews were conducted by Boeing along with Thales and GS Yuasa. Qualification testing was witnessed by delegated representatives from Boeing.⁸⁰

In early 2007, GS Yuasa and Thales redesigned the battery (with Boeing's approval) after a November 2006 fire at Securaplane during the development of the BCU.⁸¹ The redesigned battery included a contactor and a BMU subcircuit card to interrupt charging in an abnormal situation. Qualification testing of this redesigned battery was completed in June 2007. In October 2009, GS Yuasa and Thales redesigned the battery again (with Boeing's approval) after a July 2009 cell venting event at UTC Aerospace Systems' Airplane Power Systems Integration Facility (APSIF), where 787 power conversion subsystem components were tested as an integrated electrical system.⁸² The redesigned battery included a modified BMU4 subcircuit card to avoid the subsequent recharging of the battery after overdischarge and a battery diode module (added to the electrical system) so that the main battery could be charged only by the dedicated charger and not be inadvertently charged by the airplane's electrical system. The critical design review for this battery redesign was completed in January 2010, and qualification testing was completed in June 2010.⁸³ (The FAA was aware of both battery events.)

Boeing required its suppliers and subtier suppliers to perform first article inspections (FAI), according to industry standards, on first production runs of any component. The FAI was the primary method for inspecting and testing vendor components and was considered to be an essential step in approving an order or a contract. The intent of the FAI was to determine if a vendor's product met acceptance and quality control requirements to ensure that all engineering, design, and specification requirements were correctly understood, accounted for, verified, and

⁸⁰ Qualification tests are performed to demonstrate that a design conforms to a set of requirements, such as the requirements defined in Boeing's main and APU battery SCD.

⁸¹ On November 6, 2006, a fire occurred at the main Securaplane building when a 787 development battery was being charged for a test. The battery had been in use for about 14 months. Investigation of the incident found that thermal runaway of the battery occurred and that the BMU was not connected directly to the BCU. The cause of battery failure was unknown but was surmised to be a cell internal short circuit followed by overcharge of at least one other cell.

⁸² On July 7, 2009, an APU battery experienced a loss of voltage and vented electrolyte during integrated system testing at UTC Aerospace Systems' APSIF. An investigation of the incident by Boeing, Thales, and GS Yuasa determined that the failure of the battery most likely resulted from thermal runaway of a single cell due to an internal short circuit created by repetitive overdischarge and subsequent high-rate charging operations. During the NTSB's April 2013 investigative hearing on the BOS incident, Boeing representatives testified that integrated system testing was conducted on the entire electrical system, including the APU and its grounding system, and that a number of protective (non-abuse) tests were conducted to ensure that the APU system would meet its design requirements.

⁸³ The changes to the battery that were made after the BOS and TAK incidents are discussed in sections 1.2.4 and 1.8.1.

recorded. GS Yuasa accomplished the FAI for the main and APU battery in November 2008, and Thales approved the FAI results in January 2009. GS Yuasa performed another FAI of the battery after its redesign resulting from the APSIF event. Further, in November 2010, Boeing performed an FAI on an LVP65-8-402 battery at GS Yuasa and found that the battery complied with acceptance and quality control requirements.

Boeing's surveillance of Thales was conducted in accordance with contractual specifications and requirements. Boeing also relied on the Bureau Veritas Certification to perform surveillance assessments of Thales twice a year.⁸⁴

Thales conducted two audits of GS Yuasa between the time that battery production began and the incident. These audits, which were conducted in June 2011 and September 2012, found 11 discrepancies, all of which were subsequently closed. None of the discrepancies were directly related to battery or cell manufacturing. Thales reported the results of these audits to Boeing.

Boeing did not conduct any audits of GS Yuasa before the incident and relied on Thales to audit its subtier suppliers.⁸⁵ After the incident, Boeing sent an audit team to Thales and GS Yuasa (and KAI) to review the management of subtier suppliers, quality of manufacturing and business processes, and adherence to Boeing standards. The audit found 17 items of noncompliance with Boeing requirements. Most of the noncompliance items at GS Yuasa involved adherence to written procedures and communication with Thales and Boeing regarding authorization for proposed procedural and testing changes for the battery. The noncompliance items at Thales involved adherence to contractual requirements for Boeing's approval on drawing or procedural changes. Corrective actions for all of the noncompliance items have been completed by Thales and verified by Boeing.

The FAA did not conduct any audits of GS Yuasa before the incident.⁸⁶ In late January 2013, the FAA conducted an audit of GS Yuasa (and KAI) and found several items of noncompliance, including (1) noncompliance with component/assembly part markings and no traceability to assembly drawings and instructions and (2) noncompliance with assembly and installation instructions of battery components.⁸⁷ Corrective actions for these and other items of noncompliance have been completed by GS Yuasa and verified by the FAA.

⁸⁴ The Bureau Veritas Certification is an international certification organization that Boeing used to help ensure that its suppliers had an accredited quality management system in place.

⁸⁵ Boeing had a source inspector at GS Yuasa, but the inspector was contractually limited to determining whether specific inspection and checklist items, as detailed in agreements among Boeing, Thales, and GS Yuasa, met minimum quality standards. Any issues that the inspector found had to be routed to a US Boeing representative to coordinate through Thales.

⁸⁶ The FAA did not consider the 787 battery to be a critical component because the Seattle Aircraft Certification Office (which was responsible for the airplane's certification) regarded the battery as a redundant system. As a result, the FAA's automated supplier selection process, which identifies suppliers for evaluation, did not select GS Yuasa.

⁸⁷ Other items of noncompliance involved storage procedures for returned batteries and the root cause and analysis for returned batteries.

1.6.2 Cell Manufacturing Process

After the BOS incident, the NTSB visited GS Yuasa's production facility for the 787 main and APU battery to observe the LVP65 cell manufacturing process, including the electrode coating, winding, flattening, assembly, and postassembly inspection stages.⁸⁸ The coating process involved placing a foil roll on a reel in an enclosed case, unrolling the foil, and coating the foil (except its edges) with anode or cathode active material.⁸⁹ The machine operator checked the thickness of the coating periodically using a hand-held micrometer. The uncoated area on the edge of the foil material was monitored visually and measured periodically by the operator.⁹⁰ During operations in which the foils were unwound, the machine operator also monitored the foil roll for defects such as wrinkles.⁹¹ After one side of the foil roll was coated, dried, and rewound, the roll was inverted, unwound, coated on the opposite side, dried, and rewound. Winding sensors in the machinery were in place to prevent misalignment of the foil roll. The machine operator visually inspected the winding edges for burrs. If defects were found during the coating process, an engineering-level review board would be convened to determine the disposition of the foil material.

Another machine used a cylindrical winding mandrel to wind the cathode and anode foils together with the separator sheets to create the cell windings. Afterward, the machine operator measured the alignment and weight of each winding. The machine operator then partially flattened each winding by hand compression, as shown in figure 16a, and positioned the three windings for final flattening. The final flattening process was accomplished using a compression jig with two flat plates facing the three windings. After final flattening, the machine operator attached heat-resistant plastic tape to the ends of the cell where the curves of the windings were located, as shown in figure 16b. Figures 16a and 16b also show perturbations of the electrode foil that were created during the flattening process.⁹²

⁸⁸ At the time of the NTSB's visit, GS Yuasa was manufacturing LVP65-8-403 batteries.

⁸⁹ As previously stated, the current collectors are attached to the uncoated edges of the electrode winding assembly.

⁹⁰ At the time of the NTSB's visit, operators involved with cell manufacturing were working either 0800 to 2000 or 2000 to 0800 (local time) Monday through Friday unless production demands required more work hours. Operators involved in the postassembly CT inspection process received two 15-min breaks and one 45-min meal break during each shift.

⁹¹ GS Yuasa defined "wrinkles" as visible longitudinal or diagonal surface creases in the electrode coating on the foil that occur before the winding and flattening processes.

⁹² In this report, a perturbation is defined as a change in the electrode foil nominal form due to compressive buckling.

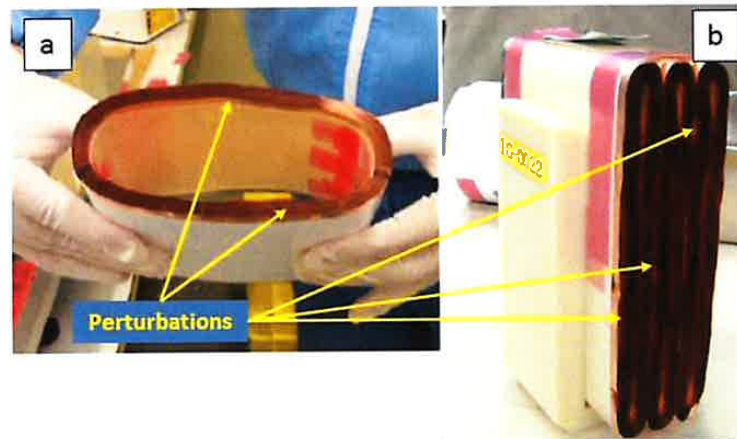


Figure 16. Winding flattening process.

Note: Figure 16a shows an electrode being hand flattened after winding and removal from the mandrel, and figure 16b shows the three-electrode assembly after final flattening and taping.

The flattened three-winding assembly was then manually attached to a prefabricated cell header assembly, which consisted of the cell header cover, two sets of current collectors attached to the cover with insulators in between, and two threaded terminals. Metallic tweezers were used to align the windings with the cell header assembly before manual ultrasonic welding.⁹³ A vacuum and vacuum brush on the ultrasonic welding machine (operated by a foot pedal) were in place to remove FOD generated from welding. Afterward, the cell was wrapped with an insulating polymer film and heat-resistant tape and placed inside a prismatic (rectangular-shaped) stainless steel cell case.

The next process involved manual tungsten inert gas welding of the header cover to the cell case. During this process, the welded cell was examined visually by an inspector using a magnifying glass to identify potential weld deposit defects. If a defect was identified, the cell case header cover would be welded again. The cell was also inspected for potential damage to the insulating film, excessive heat, and other defects. If such damage was found, an engineering-level review board would determine the disposition of the cell. A prefabricated small hole in the side of the cell case was used to manually fill the battery cell with liquid electrolyte. The electrolyte filling process was performed using three separate steps to prevent overflow, and the cell was precharged to low voltages in between each filling step.⁹⁴

The postassembly inspection process involved examining a cell's interior using CT scans. An inspector viewed the CT image to identify any potential ultrasonic weld defects on the current collectors and any enclosed FOD. (The CT resolution settings were unknown because

⁹³ Metallic tweezers were used for processes in which precision was needed to assemble parts.

⁹⁴ The NTSB did not observe the electrolyte filling process during its visit to GS Yuasa.

they were not supplied to the NTSB.) If a defect was identified, the cell would be subject to further assessment.⁹⁵ GS Yuasa stated that less than 1% of manufactured cells were rejected.

1.7 System Safety and Certification

As part of its investigation of this incident, the NTSB reviewed the *Federal Aviation Regulations* and special conditions applicable to the 787 main and APU battery and battery charger system. The NTSB also reviewed the corresponding certification plan, which Boeing developed and the FAA approved. The plan defined the agreed-upon methods to be used to demonstrate that the battery and its charger system met applicable FAA and European Aviation Safety Agency (EASA) requirements.⁹⁶ In addition, the NTSB reviewed sections of Boeing's 787-8 electrical power system (EPS) safety assessment that pertained to the main and APU battery, which Boeing developed to evaluate the EPS design for compliance with safety requirements defined by the FAA and EASA.

1.7.1 Type Certification Overview and Battery Special Conditions

On March 28, 2003, Boeing applied for a type certificate for the 787-8 airplane. The FAA's aircraft certification office (ACO) in Seattle, Washington, conducted the certification oversight process. In September 2004, Boeing met with representatives from the ACO to indicate the company's intent to use lithium-ion technology for the main and APU battery on the 787 airplane.⁹⁷ At that time, the 787 was expected to be the first transport-category airplane to have permanently installed, rechargeable lithium-ion batteries.⁹⁸ In response, the FAA reviewed the adequacy of the existing regulations governing the installation of batteries in large transport-category airplanes and determined that the regulations did not sufficiently address several failure, operational, and maintenance characteristics of lithium-ion batteries that could affect the safety of the battery installations.⁹⁹

Title 14 CFR 21.16, "Special Conditions," states that, if the FAA finds that airworthiness regulations do not contain adequate or appropriate safety standards for an aircraft because of a "novel" or an "unusual" design feature, special conditions should be issued to prescribe safety standards that establish a level of safety equivalent to that established in the regulations. Special conditions are developed by the appropriate ACO with the applicant's full participation. The ACOs use issue papers to review the adequacy of existing regulations; determine the special

⁹⁵ Information about other steps in the cell assembly process (and information about the battery assembly process) is detailed in the Manufacturing Data and Manufacturing Cell Group Factual Report, which is available at www.nts.gov in the public docket for this incident.

⁹⁶ The 787-8 FAA certification was also validated by EASA.

⁹⁷ Boeing also intended to use lithium-ion batteries in the 787's flight control electronics, emergency lighting system, and recorder independent power supply.

⁹⁸ After the incident, the FAA stated that the Cessna Citation CJ4 was the first civil airplane certificated with a lithium-ion main battery. The Citation CJ4 is not a transport-category airplane.

⁹⁹ The battery regulations that existed at the time were in 14 CFR 25.1353, "Electrical Equipment and Installations," paragraphs (c)(1) through (4).

conditions that would be proposed to address any inadequacies; and track the relevant technical, regulatory, and administrative issues that could arise in certifying the new technology.

In a March 31, 2006, issue paper, “Special Condition: Lithium-Ion Battery Installations” (referred to as Issue Paper SE-9), the FAA stated that, despite limited experience with the use of lithium-ion batteries in commercial aviation applications, other users of lithium-ion batteries, including wireless telephone manufacturers and electric vehicle manufacturers, had experienced safety problems with this technology. These problems included overcharging; overdischarging; and flammability of cell components as a result of the liquid electrolyte, which could serve as a source of fuel for an external fire if the battery case were breached. The FAA also noted that, in general, lithium-ion batteries are “significantly more susceptible to internal failures that can result in self-sustaining increases in temperature and pressure (thermal runaway)” than nickel-cadmium or lead-acid batteries.

On April 23, 2007, the FAA issued a notice of proposed special conditions (*Federal Register* 2007, 21162), which proposed nine safety requirements regarding the use of lithium-ion batteries for the 787 to ensure that these battery installations would not be “hazardous or unreliable.” On September 28, 2007, the FAA issued Final Special Conditions 25-359-SC, “Boeing Model 787-8 Airplane; Lithium-Ion Battery Installation” (*Federal Register* 2007, 57842), which became effective on November 13, 2007. The intent of the final special conditions, which are shown in appendix B, was to establish additional safety standards that the FAA considered necessary to provide a level of safety equivalent to the existing standards for aircraft batteries.

According to the 787-8 type certificate data sheet, the airplane received transport-category approval on August 26, 2011. The type certification basis included the 14 CFR Part 25 airworthiness standards and the special conditions for the lithium-ion battery installation.¹⁰⁰

1.7.2 Certification Plan

FAA Order 8110.4, “Type Certification,” described the responsibilities and procedures for the FAA and the type certificate applicant to follow when evaluating and approving design data for new civil aircraft, such as the 787-8.¹⁰¹ In accordance with paragraph 2-11d(1)(d) of the order, Boeing’s 787 EPS certification plan presented a high-level system description of the EPS, which included the main and APU battery and battery charger system; defined the methods (for example, tests and analyses) to show compliance with applicable FAA and EASA requirements;

¹⁰⁰ The applicable regulations were 14 CFR Part 25 through amendment 25-119 and amendments 25-120, 25-124, 25-125, and 25-128 (with exceptions). Other applicable regulations were 14 CFR Part 26, “Continued Airworthiness and Safety Improvements for Transport Category Airplanes”; 14 CFR Part 34, “Fuel Venting and Exhaust Emission Requirements for Turbine Engine Powered Airplanes”; 14 CFR Part 36, “Noise Standards: Aircraft Type and Airworthiness Certification”; equivalent level of safety references; and special conditions for 13 other subjects.

¹⁰¹ When Boeing submitted its application for the 787-8 type certificate, revision B of FAA Order 8110.4, dated April 24, 2000, was in effect. Revision C of the order was issued on October 12, 2005.

and defined the compliance submittals (that is, certification deliverables) to be provided to the agencies. The FAA approved the initial certification plan on December 22, 2005. Boeing was required to ensure that the certification plan was kept current throughout the 787's design, development, and certification phases, and any revisions to the certification plan were required to be approved by the FAA.

According to Boeing, on January 8, 2007, the FAA approved revision C of the certification plan and indicated that Boeing could proceed with the implementation of the proposed certification activities. Boeing conducted tests and analyses to demonstrate, among other things, that the main and APU battery and battery charger system complied with relevant 14 CFR Part 25 requirements, including sections 25.863, "Flammable Fluid Fire Protection," paragraphs (a) and (b)(3); 25.1309, "Equipment, Systems, and Installations," paragraphs (a), (b)(1), (b)(2), and (c) through (g); and Special Conditions 25-359-SC.

1.7.3 System Safety Assessment

Safety assessments are a primary means of compliance for systems that are critical to safe flight and operation. These assessments are performed by the manufacturer and its suppliers and are reviewed and accepted by the FAA. Safety assessments proceed in a stepwise, data-driven manner to ensure that all significant single-failure conditions have been identified and all combinations of failures that could lead to hazardous or catastrophic airplane-level effects have been considered and appropriately mitigated. The safety assessment process, which is outlined in FAA Advisory Circular (AC) 25.1309-1A, "System Design and Analysis," is not mandatory, but manufacturers that do not conduct safety assessments must demonstrate compliance in another manner, such as ground or flight tests. Boeing indicated in certification documents that it used a version of AC 25.1309 (referred to as the Arsenal draft) as guidance during the 787 type design certification program.¹⁰²

Overall compliance with the applicable 787-8 main and APU lithium-ion battery safety requirements was shown through formal analyses and qualification tests. Thales and GS Yuasa performed these analyses and tests, and Boeing reviewed and approved the results.

Boeing's 787-8 EPS safety assessment, dated September 16, 2009, presented the overall safety analysis of the EPS. This analysis evaluated the design of the EPS for compliance with safety requirements derived from 14 CFR Part 25, EASA certification specifications, Special Conditions 25-359-SC, and accompanying advisory material. For the main and APU lithium-ion battery and battery charger systems, the safety assessment included a failure modes and effects analysis (FMEA) to provide a bottom-up qualitative and quantitative way to identify the effects

¹⁰² In 1996, an FAA aviation rulemaking advisory committee (ARAC) was chartered to harmonize the FAA's practices related to 14 CFR 25.1309 with those of Europe and Canada. The committee released its final report to the FAA in August 2002, but the revised AC 25.1309, referred to as the Arsenal draft, has not yet been issued. On April 29, 2003, the FAA published a notice of availability of the ARAC-recommended proposed changes to the airworthiness standards for transport-category airplanes regarding equipment, systems, and installations as well as the current AC 25.1309 (version 1A). This notice of availability indicated that the ARAC-recommended proposed changes could be used for airplane certification programs through a request for an equivalent level of safety finding.

of a failure at the next (higher) level of a system; a functional hazard assessment (FHA) to determine the potential hazards that various failures of electrical system components could introduce to the airplane and its occupants; and a fault tree analysis for the hazards identified in the FHA.¹⁰³

The FHA identified and classified two hazards associated with the main and APU lithium-ion battery: “battery vents smoke/fire,” which was classified as catastrophic, and “battery vent and/or smoke (without fire),” which was classified as hazardous.¹⁰⁴ On the basis of the FHA’s results, Boeing defined failure detection and mitigation requirements for the main and APU battery, including the following three requirements related to smoke, gas, and electrolyte release:

- The battery shall have a probability of less than 1×10^{-7} for gas emission.
- The battery shall have a probability of less than 1×10^{-7} for smoke emission.
- The battery shall be designed to prevent spilling flammable fluid, a hazardous event with a probability of less than 1×10^{-9} .

This analysis determined that overcharging was the only known failure mode that could result in cell venting with smoke and fire. As a result, Boeing established additional design requirements to ensure that the likelihood of occurrence of an overcharge event would be extremely improbable (one in 1 billion flight hours or a probability of 1×10^{-9}).¹⁰⁵ Boeing further determined that cell venting without fire could be initiated by several different failure modes, including external overheating, external short circuiting, internal short circuiting, recharging a battery that has been overdischarged, a high rate of charging, or charging at cold temperatures.

¹⁰³ A FMEA is an analytical process that postulates all known and reasonable failure modes. The FMEA assesses the effects of those failures and documents the effects that the failures could have at the airplane level. The FMEA also supports the development of fault tree basic events. An FHA examines a system’s functions and purpose, identifies failure conditions that could occur with a loss or malfunction of the system, and classifies those conditions by severity (at the airplane and system levels). After the hazard classification for a system is established, the manufacturer conducts system-specific safety analyses to identify ways to mitigate the adverse effects of a failure condition. A fault tree analysis is a structured, deductive, top-down qualitative and quantitative analysis that depicts the relationship(s) between each failure condition and its primary cause(s).

¹⁰⁴ The harmonized requirements for 14 CFR 25.1309 define a catastrophic event as one that normally involves a hull loss with multiple fatalities. This event is assigned an allowable qualitative probability of being extremely improbable and an average quantitative probability of less than 1×10^{-9} per flight hour. The harmonized requirements for section 25.1309 define a hazardous event as one that normally involves a large reduction in functional capability or safety margins of the airplane with serious or fatal injury to a small number of passengers or cabin crew along with physical distress or excessive workload impairing the flight crew’s ability. This event is assigned an allowable qualitative probability of being extremely remote and an average quantitative probability of less than 1×10^{-7} per flight hour.

¹⁰⁵ The risk of fire was addressed through overcharge protections. For example, Boeing required that “the battery monitoring unit when combined with the overall battery protection subsystem shall prevent undetected over-charge (over-voltage).”

One of the objectives of a FMEA is to support safety analyses by documenting that there are no known single-point failures that would result in catastrophic failure conditions. Boeing's 787 EPS safety assessment identified no single-point-failure catastrophic effects for the main and APU lithium-ion battery.

Boeing's FMEA was based on information contained within GS Yuasa's FMEA, which GS Yuasa developed with assistance from Boeing and Thales. GS Yuasa's FMEA included a calculation of a representative failure rate for the LVP65 cell. This calculation was based on in-service data from about 14,000 existing large-scale industrial lithium-ion cells manufactured by GS Yuasa, which had a similar design and manufacturing process as the LVP65 cell.¹⁰⁶ GS Yuasa's FMEA indicated that none of the industrial cells had experienced any failures, including venting, electrolyte release, or rupture of a vent disc. (GS Yuasa's FMEA did not include an analysis of usage and environmental similarities between the industrial cells and the LVP65 cells or a discussion of the hazardous effects of a lithium-ion cell failure, including overheating or venting.) On the basis of this information, Boeing determined that the rate of occurrence of cell venting for the 787 battery would be about 1 in 10 million flight hours.

Boeing's 787 EPS safety assessment also included Boeing's analysis of the results of a single development (noncertification) nail penetration test that GS Yuasa performed in November 2006.¹⁰⁷ This test involved driving a steel nail through a cell case to penetrate the electrodes of a fully charged single cell within a fully charged, nongrounded, preproduction battery to induce an internal short circuit within the cell. The purpose of the test, which was conducted at a temperature representative of the E/E bay operating temperature during a typical flight, was to observe the behavior of the cells near the nail-penetrated cell, observe any release of smoke or initiation of fire, and document any damage to the battery case.¹⁰⁸

The nail penetration test results showed that the surface temperature of the nail-penetrated cell increased, smoke vented from the cell and the battery case, and the surface temperature of the adjacent cells increased with no venting.¹⁰⁹ On the basis of this development test and the in-service data of the industrial cell that GS Yuasa designed and manufactured, Boeing determined that the effects of a cell internal short circuit would be limited to (1) the

¹⁰⁶ According to GS Yuasa, failure rate data from industrial cells were used because, at that time, there were no available in-service failure history data for the LVP65 cells. According to GS Yuasa, a cell's failure rate was related more to the cell's manufacturing process and mechanical design rather than the materials used in the construction of the cell. GS Yuasa noted that some variation in chemistry existed between the LVP65 cell and the industrial cell but indicated that the difference in chemistry could impact the effect of the failure and not the probability of occurrence.

¹⁰⁷ Boeing collaborated with GS Yuasa and Thales about the development tests to be performed on cells and batteries. Results from this testing helped Boeing determine what types of abuse (thermal, physical, and/or electrical) certification testing and/or safety analyses needed to be performed to show compliance with the applicable battery regulations, including the special conditions. The development tests were not required by the FAA.

¹⁰⁸ As previously stated, Boeing reported that E/E bay temperatures during a typical flight ranged from 50°F to 59°F.

¹⁰⁹ Tests and analyses that GS Yuasa performed were reviewed by Boeing project engineers, safety reliability and maintainability engineers, and authorized representatives (who acted on behalf of the FAA during certification tasks).

release of smoke from the battery, which could be effectively handled by the airplane's ventilation system, and (2) an increase in surface temperature of the short-circuited cell with no propagation of thermal runaway to adjacent cells, damage to the battery case, fire, or explosion.

At the conclusion of the 787 testing and safety assessment process, Boeing prepared documentation for the FAA showing Boeing's proposed methods for demonstrating compliance with 14 CFR 25.1309 and each of the nine special conditions in 25-359-SC. The FAA used this information to make findings of compliance. Title 49 CFR 44702(d) allows the FAA to delegate to a qualified individual a matter related to issuing a certificate or a matter related to the examination, testing, and inspection necessary to issue a certificate. In October 2005, the FAA established the organization designation authorization (ODA) program to address delegations to organizations and standardize its oversight of organizational designees.¹¹⁰ With an ODA, FAA-approved engineering designees in various technical areas act on behalf of the FAA during certification tasks. Boeing, which received ODA approval in August 2009, refers to its engineering designees as authorized representatives. They can make findings, as authorized by the FAA, for certain reports or tests in support of type certification programs, but only the FAA can issue a type certificate. Boeing's and the FAA's roles in the certification of the 787 main and APU battery are further discussed in section 2.5.

1.8 Additional Information

1.8.1 Federal Aviation Administration Actions After Battery Incidents

On January 11, 2013, 4 days after the BOS incident, the FAA announced that it would undertake a comprehensive review of the 787's critical systems with the possibility of further action pending new data and information. The FAA stated that, in addition to a review of the 787's design, manufacture, and assembly, it would verify that the 787 battery system complied with the special conditions that were part of the 787's certification (as discussed in section 1.7 and appendix B).

On January 16, 2013, after the TAK incident, the FAA issued emergency AD 2013-02-51 to address a potential battery fire risk in the 787.¹¹¹ The emergency AD "was prompted by recent incidents involving lithium-ion battery failures that resulted in release of flammable electrolytes, heat damage, and smoke on two Model 787-8 airplanes." The emergency AD indicated that these conditions "could result in damage to critical systems and structures, and the potential for fire in the electrical compartment." The emergency AD instructed owners and operators of Boeing 787-8 airplanes to, "before further flight, modify the battery system, or take other

¹¹⁰ Before that time, designated engineering representatives performed certification activities that the FAA delegated.

¹¹¹ Earlier that day, JAL and All Nippon Airways had voluntarily decided to stop 787 operations as a result of the TAK battery event. On January 17, 2013, the Japan Civil Aviation Bureau issued a directive with the same content as FAA emergency AD 2013-02-51. Civil aviation authorities in other countries also required operators of 787 airplanes to temporarily cease operations.

actions, in accordance with a method approved by the Manager, Seattle Aircraft Certification Office.”¹¹²

On March 12, 2013, the FAA announced that it had approved Boeing’s certification plan for a redesigned 787 battery system. The FAA stated that the certification plan required Boeing to conduct “extensive testing and analysis” to demonstrate compliance with the applicable safety regulations and special conditions. Also, the FAA stated that the improvements to the battery system included “a redesign of the internal battery components to minimize initiation of a short circuit within the battery, better insulation of the cells and the addition of a new containment and venting system.”

On April 19, 2013, the FAA announced that it had approved Boeing’s modifications to the 787 battery system, which were designed “to address risks at the battery cell level, the battery level and the aircraft level.” The FAA stated that a team of agency certification specialists observed “rigorous tests” that Boeing was required to perform and reviewed a “detailed analysis” of the design changes. The FAA also stated that it would monitor the modifications of the affected airplanes in the US fleet to ensure proper installation of the new design.

On April 22, 2013, the FAA superseded AD 2013-02-51 with AD 2013-08-12, which became effective on April 26, 2013 (*Federal Register* 2013, 24673). AD 2013-08-12 required 787 operators to (1) install main and APU battery enclosures and ECS ducts; (2) replace the main battery, the APU battery, and their respective battery chargers; and (3) revise the maintenance program to include a requirement for replacement of the main and APU battery enclosure vent burst discs.¹¹³ The AD was intended to “allow the aircraft to return to service as soon as possible by mandating a modification that will address the unsafe condition.” The AD noted that, for all future 787 airplanes, the replacement batteries, their respective chargers and enclosures, and duct installations would be incorporated before delivery.

AD-2013-08-12 detailed Boeing’s measures to improve the reliability of the battery and prevent any hazardous effects on the airplane from a battery failure. According to the AD, those measures are as follows:

- Minimize the Probability of a Single Battery Cell Failure—Each main and APU battery consists of a set of individual cells within a battery case. Each battery cell will be encapsulated to isolate the cell electrically. Locking nuts with specific torque values will be used on every cell terminal to prevent overheating of the terminal due to a loose electrical connection. Drainage within the battery case will be improved to remove any condensation within the battery. The battery monitoring and charging unit will be changed to

¹¹² One US operator had six 787s in service when the emergency AD was issued. On February 1, 2013, the FAA issued AD 2013-02-51, which stated that emergency AD 2013-02-51 had previously been sent to all known US owners and operators of 787-8 airplanes but that “this AD is effective February 22, 2013 to all persons except those persons to whom it was made immediately effective by Emergency AD 2013-02-51” (*Federal Register* 2013, 12231).

¹¹³ The vent burst discs are frangible discs on the battery enclosures.

reduce the operational voltage range to lessen electrical stress on the battery cell and to enhance overdischarge protection. Boeing has also made mandatory changes to the battery manufacturing and acceptance testing processes to improve the overall quality of the battery.

- Minimize the Probability of Multiple Cell Failure Propagation—Additional insulation will be provided between each battery cell and between each cell and the battery case to thermally and electrically isolate the individual battery cells. High temperature sleeving will also be added to the battery internal wiring harness to protect against short circuits. In addition, cell venting will be added to the battery case to allow any cell [gases], including electrolytes, to escape into the battery enclosure to minimize heat build-up within the battery case.
- Preclude Hazardous Airplane-Level Safety Effects of a Battery Failure That Might Occur—As stated previously, each main and APU battery consists of a set of individual cells within a battery case. The case containing the cells will be secured within a stainless steel, sealed enclosure. This enclosure will be connected to a titanium ECS duct that vents to the outside of the airplane. Should a battery failure occur, and generate significant heat, pressure, and [gases], a metallic frangible disc (also referred to as a vent burst disc) at the interface of the enclosure and vent duct will open and allow the heat, pressure, and [gases] to safely vent overboard through the ECS duct. This will prevent the introduction of any heat, pressure, or [gases] in the electronics equipment bays or any occupied area of the airplane.

On March 19, 2014, the FAA announced the findings of a joint FAA-Boeing team that was formed in January 2013 to review the Boeing 787's design, manufacture, and assembly processes. The team found that the 787 "was soundly designed" and "met its intended safety level" and that Boeing and the FAA had "effective processes in place to identify and correct issues that emerged before and after certification."

In the team's report on its findings, the team made recommendations to further improve Boeing processes and FAA oversight (FAA 2014). The team recommended that Boeing (1) continue to implement gated design and production processes, (2) ensure that suppliers are fully aware of their responsibilities, (3) ensure that suppliers identify realistic program risks, and (4) require suppliers to follow industry standards for personnel performing Boeing-required inspections. The team recommended that the FAA revise its orders on (1) certificate management of manufacturers to recognize new aircraft manufacturing business models; (2) production approval procedures to better address complex, large-scale manufacturers with extended supply chains; and (3) engineering conformity inspections to ensure that they are based on risk. The FAA indicated that it was taking actions to address these three recommendations.

1.8.2 Previously Issued Safety Recommendations

In response to the circumstances leading to this incident, on May 22, 2014, the NTSB issued Safety Recommendations A-14-32 through -36 to the FAA. In its letter to the FAA, the

NTSB stated that the type of failure that occurred during this incident—thermal runaway of a single cell as a result of an internal short circuit and the cascading thermal runaway of other cells within the battery—was not expected based on the testing and analysis of the APU battery system that Boeing performed as part of the 787 certification program (see section 1.7.3). The recommendations asked the FAA to take the following actions to (1) account for internal short circuits and thermal runaway during lithium-ion battery certification tests and (2) ensure the safe introduction of new technology into aircraft designs:

Develop abuse tests that subject a single cell within a permanently installed, rechargeable lithium-ion battery to thermal runaway and demonstrate that the battery installation mitigates all hazardous effects of propagation to other cells and the release of electrolyte, fire, or explosive debris outside the battery case. The tests should replicate the battery installation on the aircraft and be conducted under conditions that produce the most severe outcome. (A-14-32)

After Safety Recommendation A-14-32 has been completed, require aircraft manufacturers to perform the tests and demonstrate acceptable performance as part of the certification of any new aircraft design that incorporates a permanently installed, rechargeable lithium-ion battery. (A-14-33)

Work with lithium-ion battery technology experts from government and test standards organizations, including US national laboratories, to develop guidance on acceptable methods to induce thermal runaway that most reliably simulate cell internal short-circuiting hazards at the cell, battery, and aircraft levels. (A-14-34)

Review the methods of compliance used to certify permanently installed, rechargeable lithium-ion batteries on in-service aircraft and require additional testing, if needed, to ensure that the battery design and installation adequately protects against all adverse effects of a cell thermal runaway. (A-14-35)

Develop a policy to establish, when practicable, a panel of independent technical experts to advise on methods of compliance and best practices for certifying the safety of new technology to be used on new or existing aircraft. The panel should be established as early as possible in the certification program to ensure that the most current research and information related to the technology could be incorporated during the program. (A-14-36)

Boeing's description of the certification testing performed on the redesigned battery model (LVP-8-403) before the 787 returned to service was consistent with the NTSB's certification recommendations. On August 19, 2014, the FAA responded to Safety Recommendations A-14-32 through -36. Section 2.5.3 discusses the FAA's response and the NTSB's classifications of the recommendations.

2. Analysis

2.1 Failure Sequence

According to the available evidence from this incident investigation, the NTSB concludes that the battery failure did not result from overcharging, overdischarging, external short circuiting, external heating, installation factors, or environmental conditions of the airplane. Specifically, EAFR data before the event did not show any evidence of the battery being charged to a level above the designed operating voltage, the battery being discharged to a level below the overdischarge threshold, or any high-current discharges that could be associated with an external short circuit. The EAFR data showed no preexisting battery failure messages indicating that the overdischarge protection circuit had activated. In addition, examination of the aft E/E bay (where the APU battery was installed) showed no evidence of external short circuits, such as chafing on the battery cables, or external sources of heat, mechanical damage, or electrical abuse that could have initiated the battery failure.

Individual component tests (including those for the BCU, SPU, and APU controller) and integrated system tests, which included a BCU and other battery-related components, found no evidence indicating that external components were related to the battery failure. Vibration testing was performed at levels that exceeded in-service levels without damage that could lead to battery failure. A battery-level test showed that condensation could occur within the battery and result in a shorting path between the cell and battery cases, and a cell-level test with moisture showed that a cell failure could occur and result in arcing, shorting, and heat damage internal to the cell header. However, the damage observed during the cell-level test was not found in the cell header from the incident APU battery. In addition, airplane flight test data did not show any abnormal electrical transients that could lead to battery failure.

External observations of the battery case showed more thermal damage on the right side of the case than the left side. The right aft corner of the battery case showed the most thermal damage and the most damage to the case lid and its fastening points. The right aft area corresponded to the positions of cells 5 and 6.

The inside of the battery case, the BMU sensing wiring harness, and the lower and upper fixation trays showed the most thermal damage in the areas near cells 5, 6, and 7. The insulating material between the cells was the most damaged in the areas adjacent to cells 5 through 8. Further, cells 5 through 8 vented, and the petals of their vent discs were splayed out, indicating that the cells vented under high pressure. Cells 1 through 3 also had ruptured vent discs, but they remained mostly in the same plane as the vent opening, indicating that the venting occurred with less force than the venting for cells 5 through 8. This evidence showed that the initiating thermal event and subsequent thermal runaway of additional cells began on the right side of the battery where cells 5 through 8 were located.

CT scans of the battery showed that the aft side of cell 8 had expanded into cell 7 and that cell 7 appeared to have expanded into cell 6, indicating that cell 8 vented after cell 7 and that cell 7 vented after cell 6. CT scans and examinations showed that side 3 of cell 6 (which was closest to cell 5) was slightly convex with a flat area in the middle of the cell. CT scans and

examinations also showed that side 1 of cell 5 (which was closest to cell 6) was convex with a concave-to-flat area in approximately the middle of the cell. Although the sequence of whether cell 5 or cell 6 expanded first could not be determined due to the complexity of these features, the NTSB was able to determine that the thermal event initiated in a single cell.

Cells 5 and 6 exhibited comparable internal thermal damage, including the melting of the aluminum cathode, no remaining separator or other insulating materials, and fused current collector fingers. Cells 5 and 6 also showed evidence of internal short circuiting, including pinholes, radiating patterns, and thermal discoloration. The lower and upper fixation trays were more thermally damaged in the position of cell 6, and cell 3 (across from cell 6) exhibited the most thermal damage of the cells on the left side of the battery. Cell 7 also sustained internal thermal damage similar to cells 5 and 6, including two pairs of fused current collector fingers. This thermal damage pattern, centered about the position of cell 6 and extending to cells 5, 7, and 3, is consistent with the battery thermal event originating in cell 6.

The NTSB and UL's postincident testing on individual cells showed that an internal short circuit could cause current collector fingers to fuse open and lead to failure of a cell.¹¹⁴ Data recorded during these tests showed a distinctive trace in which the cell voltage initially decreased, abruptly recovered, and then decreased to zero volts. The incident EAFR recorded a decrease in battery voltage followed by a single recovery in voltage and then a drop in voltage to a level consistent with one failed cell in the battery. Visual examinations and CT scans showed that one set of cell 5 aluminum current collector fingers (in the center winding) had fused open and that two sets of cell 6 aluminum current collector fingers (in the winding closest to cell 5 and the center winding) had also fused open.

During the individual cell tests in which two sets of aluminum current collector fingers fused open as a result of an internal short circuit, the recorded data showed two separate voltage decreases with two recoveries, which were not seen in the incident EAFR data. In addition, a full battery test that simulated an internal short circuit (via nail penetration) in cell 6 showed arcing between cell 6 and the center brace bar, which was not found in the incident battery. The similarity between the voltage drop behavior observed during testing for a single pair of fused current collector fingers and the EAFR data from the incident and the lack of welding between cell 6 and the center brace bar are consistent with an internal short circuit originating in cell 5.

The NTSB concludes that the battery failure resulted from an internal short circuit that occurred in cell 5 or cell 6 and led to thermal runaway that propagated to adjacent cells. The thermal damage to the battery cells precluded a determination of the cause of the internal short circuit, and postincident laboratory testing and subsequent engineering analysis of potential failure modes were unable to determine the precise cause of the internal short circuit. Possible causes for cell internal short circuits are discussed in sections 2.3 and 2.4.

¹¹⁴ The NTSB and UL's testing showed that, when current collector fingers fused open only in the center winding, that winding had to be the initiation point of the internal short circuit rather than initiation due to heat from an adjacent cell or winding.

2.2 Emergency Response

The response to the incident was timely. According to airport security camera video, the five BOS ARFF vehicles that responded to the incident did not experience any delay from initial notification to arrival at the scene. The ARFF truck that was positioned near the incident airplane responded to the event within 1 min of initial notification, and the four other ARFF vehicles arrived on scene within 2.5 min of initial notification. The firefighting procedures used during the incident, including the use of Halotron, were appropriate and consistent with guidance in effect at the time.¹¹⁵

The incident commander decided to have the APU battery removed from the airplane once the intensity of the battery fire diminished. ARFF personnel encountered difficulties in removing the battery from its installation location, especially given that they could not readily access the battery's quick disconnect knob. One of Boeing's postincident changes to the battery and its installation involved placing the redesigned battery into a sealed stainless steel enclosure connected to a duct that was intended to allow heat, pressure, and gases resulting from a battery failure to vent outside of the airplane. As a result of this change, Boeing created and distributed firefighting procedures for events involving the main and APU lithium-ion battery. These procedures advise ARFF personnel to allow a battery undergoing thermal runaway to vent overboard and then stand by to monitor for additional fire. Thus, during active venting of the 787 main or APU battery, it is no longer necessary for ARFF personnel to enter the E/E bay.¹¹⁶

2.3 Cell Manufacturing Concerns

GS Yuasa stated that it manufactured the incident battery according to drawing specifications provided by Thales and Boeing, and GS Yuasa's and Boeing's FAI processes showed that the battery complied with Boeing's acceptance and quality control requirements. However, the NTSB's observations of GS Yuasa's cell manufacturing process identified several concerns.

First, the manual cell winding flattening process can create perturbations (that is, electrode foil buckling) in the windings. Such perturbations (see figure 16) were visually consistent with the wrinkles found in the CT scans of LVP65-8-402 exemplar batteries and those

¹¹⁵ On June 12, 1995, the FAA issued CertAlert 95-03, which described the approved use of Halotron in airport firefighting operations. Also, Safety Alert for Operators 09013, "Fighting Fires Caused By Lithium Type Batteries in Portable Electronic Devices," which was issued on June 23, 2009, stated that a Halon replacement (Halotron) could be used to prevent the spread of such fires to other flammable materials. At commercial airports, Halotron has been effectively used to fight fires in areas with sensitive electrical equipment, such as that in the aft E/E bay. In January 2014, the FAA issued a report indicating that, for consumer electronic devices, water was "the most effective" in suppressing lithium-ion battery fires and preventing thermal runaway propagation (FAA 2014). The report did not address the use of water for suppressing fires involving large, permanently installed, rechargeable lithium-ion batteries, such as the 787 main and APU battery.

¹¹⁶ According to Boeing, if the battery is not venting or when active venting is complete, firefighters should enter the E/E bay to ensure that no visible fire source exists. If a visible flame is present, Halon (or Halotron) is the recommended agent for suppressing the fire. Boeing procedures indicated that the battery pack should not be disconnected from the airplane's electrical system by using the quick disconnect knob or cutting the battery cables.

observed during DPAs of the main battery on the incident airplane (as discussed later in this section). The windings are predisposed to such defects because flattening a round cylindrical object into an oval cylindrical object can cause uneven deformation and distortion due to the non-uniform distribution of stress, which results in buckling in areas of compressive stress. Also, subsequent swelling and contracting of the electrodes during charging and discharging can further exacerbate perturbations within the winding layers.

Second, two of the welding operations—ultrasonic welding of the current collectors to the winding and tungsten inert gas welding of the cell header to the cell case—occur in an area where internal cell components are also assembled. Welding can generate FOD in the form of weld spatter and small metallic particles that become airborne. No physical shielding was used at the tungsten inert gas weld station to isolate this FOD-generating process from adjacent FOD-sensitive processes, such as those involving internal components of nearby open cells. Even though the ultrasonic welding machine incorporated a vacuum system to mitigate the amount of FOD generated, this process was observed generating airborne FOD.

Third, some of the cell manufacturing processes were not consistent with industry practices.¹¹⁷ For example, production of wound prismatic (rectangular-shaped) battery cells is typically performed on a flattened elliptical or rectangular mandrel, which reduces the chance for perturbations and folds during winding, but GS Yuasa used a cylindrical mandrel during the winding process.

The cell electrolyte filling process was also inconsistent with industry practices. The electrolyte was filled in three iterative steps to prevent overflow followed by a precharge to low voltages after each step. GS Yuasa stated that the cell's solid electrolyte interphase (SEI) layer does not form during the precharging process because the final precharge brings the battery to 20% state of charge.¹¹⁸ Industry practices for electrolyte filling include one-step filling followed by a full charging sequence to develop the SEI layer. Developing the SEI layer is important because it allows safe cell operation during normal charging and discharging, and disruption of the SEI layer could lead to internal short circuiting. It is unknown whether GS Yuasa's precharging process affects the development of the SEI layer or the chemical properties or performance aspects of the cell. GS Yuasa representatives stated that the company has not studied the effect of its iterative electrolyte filling process on battery safety. Thus, the safety effect of GS Yuasa's precharging process during the electrolyte filling process is unknown.¹¹⁹

Last, GS Yuasa used CT equipment during the postassembly inspection process to ensure that the current collectors were properly welded to the winding edges and that FOD was not

¹¹⁷ The industry practices discussed in this section were based on information from (1) discussions with industry personnel, including those from the Naval Surface Warfare Center, Carderock Division; the US Department of Energy; and TIAX; and (2) site visits to other battery manufacturer plants.

¹¹⁸ During the full initial charge and discharge of a cell, the surface of the anode forms the SEI layer.

¹¹⁹ Although the NTSB did not observe the electrolyte filling process during its visit to GS Yuasa, the NTSB did observe dried material consistent with solid electrolyte residue on the electrolyte filling container and tube, which was not consistent with industry practices because superfluous solid material introduced into a battery cell could interfere with the battery charging and discharging processes.

enclosed in a cell. However, the resolution settings of GS Yuasa's CT equipment was such that many internal cell features, including individual winding layers, could not be identified during the NTSB's visit to GS Yuasa's facility. As a result, perturbations in the windings and small-sized FOD and burrs might not be recognized with the CT equipment used at the time of the NTSB's visit. GS Yuasa stated that it was not aware that FOD might not be visible on the company's CT scans.

GS Yuasa's CT scans also did not detect features that the NTSB, TIAX, and UL identified during this investigation. For example, TIAX's and UL's DPAs of cells from the main battery on the incident airplane found cell windings with numerous wrinkles, folds, and creases.¹²⁰ Also, the NTSB's CT scans of the eight cells in each of the five exemplar batteries (including the main battery from the incident airplane) revealed wrinkled windings, cell-to-cell inconsistencies in the clearances between the current collector fingers and the cell case sides, and variances between the rivet heads of the terminals and the top of the cell windings. GS Yuasa indicated that it did not know whether such features could result from its LVP65 cell manufacturing process and that it did not have a process to inspect for the features.

Manufacturing defects, including FOD, burrs on component edges, and perturbations in windings (which were visually consistent with the wrinkles found in postincident CT scans and cell teardowns), are known to lead to local lithium deposits, perforation of the separator layer, or shorting between electrodes (Mikolajczak and others 2011). During the UL and TIAX DPAs of battery cells from the main battery on the incident airplane, silver-colored deposits consistent with lithium metal were observed adjacent to wrinkles (that is, those features that were visually consistent with perturbations). According to GS Yuasa representatives, the company has not studied the effects of folds and wrinkles on battery safety, performance, and reliability.

GS Yuasa monitors for "wrinkles" (that is, visible longitudinal or diagonal surface creases) in the anode and cathode foils before the winding process but does not monitor for features such as perturbations formed during the winding, flattening, and assembly processes. Further, although GS Yuasa stated that it had a formal process for actively monitoring for and controlling burrs, GS Yuasa's process for monitoring for FOD was not a formal standardized quality control process for locating, reducing, and preventing FOD generation during the cell assembly process.

GS Yuasa performed most of its quality control inspections after a cell was fully manufactured and indicated that less than 1 percent of manufactured cells were rejected. This low rejection rate could be the result of few defects to detect; however, most of the evidence (that is, poor internal manufacturing steps along with the lack of a formal inspection for manufactured defects) indicated that GS Yuasa's inspection process did not adequately screen for defects that developed during the manufacturing process. GS Yuasa's checks during the manufacturing process relied on visual inspection rather than formal sampling processes that included rejection or acceptance criteria.

¹²⁰ The wrinkles and folds can modify the anode-to-cathode ratio locally, resulting in lithium deposits on the anode surface.

Vigilance decrements might also have played a role in the inadequate inspection process. GS Yuasa indicated that personnel involved with cell manufacturing for LVP-8-402 batteries worked 8-hour shifts. The visual inspection tasks performed by these personnel were vigilance tasks.¹²¹ Human factors research on inspection indicates that, as time on task increases, defects are more likely to be missed, especially if they seem to rarely occur (Fisher and others 2006, 997-1024).¹²²

Industry research on lithium-ion battery hazards showed that, about the time that the LVP65 cells were being manufactured, cell failures in various industries had been caused by, among other things, internal faults resulting from manufacturing defects (Mikolajczak and others 2011). However, GS Yuasa did not establish its cell manufacturing process to minimize the potential for manufacturing defects or develop formal inspection criteria of the cells that would reliably identify any defects that were introduced during the process.

Although GS Yuasa was responsible for manufacturing the 787 main and APU battery and cells, Thales was responsible for providing Boeing with consistent and safe power conversion subsystems (which included the main and APU battery systems) for 787 airplanes. Thales audited GS Yuasa in June 2011 and September 2012, and all of the discrepancies noted in the audits were subsequently addressed. However, none of the discrepancies were related to cell features, such as perturbations created and FOD generated, from GS Yuasa's cell manufacturing process. Postincident interviews revealed that Thales did not recognize that such features could result from the cell manufacturing process or that GS Yuasa's quality controls were not established to detect these features.

Boeing and FAA personnel did not conduct any audits of GS Yuasa before the incident. (Boeing stated that it relied on Thales to audit its subtier suppliers.) Boeing, as the production approval holder (that is, the holder of a production certificate), provided oversight to ensure that its contracted suppliers of the 787 power conversion subsystem adhered to their approved quality control system for the manufacturing of subsystem components. The FAA provided oversight of Boeing to ensure that (1) its contracted suppliers followed approved procedures for the production of products, articles, and parts that conformed to Boeing's approved type design and (2) such products, articles, and parts were airworthy and safe for operations. However, given the observations discussed above about GS Yuasa's cell manufacturing process, Boeing's and the FAA's oversight of suppliers manufacturing the 787 power conversion subsystem components could have been more effective.

The NTSB concludes that GS Yuasa's cell manufacturing process allowed defects that could lead to internal short circuiting, including wrinkles and FOD, to be introduced into the

¹²¹ The NTSB notes that visual inspection tasks performed during 8-hour workdays can lead to vigilance decrements. At the time of the NTSB's visit to GS Yuasa, personnel involved with cell manufacturing were working 12-hour shifts because of the demand for new LVP65-8-403 batteries after the 787 returned to flight.

¹²² The greatest performance decrements are expected within the first 30 minutes of time on task; during that time, performance can be reduced as much as 30% but is typically reduced no more than 10% (Teichner 1974, 339-353). A 30% performance decrement is more likely for a highly detectable signal (defect) during a 3-hour period.

Boeing 787 main and APU battery. Therefore, the NTSB recommends that GS Yuasa (1) review its cell manufacturing processes to minimize or prevent defects that could affect cell safety and (2) ensure that its employees are properly trained to identify and eliminate these defects. The NTSB also recommends that Boeing develop or revise processes to establish more effective oversight of its suppliers (including subtier suppliers) to ensure that the product being manufactured adheres to established industry standards. Further, the NTSB recommends that the FAA develop or revise processes to establish more effective oversight of production approval holders and their suppliers (including subtier suppliers) to ensure that they adhere to established manufacturing industry standards.

2.4 Thermal Management of Large-Format Lithium-Ion Batteries

Testing performed during the investigation showed that a cell in a 787 battery assembly generated localized high-temperature conditions during maximum current discharge. This measured high temperature was above the allowable design maximum temperature, which could lead to an internal short circuit and cell thermal runaway. This section describes those test results and discusses the importance of ensuring that large-format lithium-ion battery and cells are sufficiently designed and monitored to prevent degradation that can lead to cell thermal runaway.

2.4.1 Battery Internal Heating During High-Current Discharge

The NTSB and UL performed testing on an exemplar 787 battery to evaluate the battery's performance during discharge under the highest currents that the battery was rated to carry. The testing included simulated APU starts at 77°F and 32°F with a high-current load. The battery cell design used riveted joints (part of the terminal assembly in the cell headers) as part of the current conduction path into and out of the cells. The simulated APU start tests revealed significant localized heating near the aluminum rivets of one of the test battery's cells. The temperature change was the greatest during the discharge phase of repeated battery charge and discharge cycles at lower temperatures.¹²³ The affected cell, located in position 5 of the test battery, began to exhibit a more substantial temperature rise in the area of the aluminum riveted joint compared with the temperature rise in other cells in the battery after the first full charge/discharge cycle of the test. During the subsequent test cycles, the affected cell's temperature increased progressively to a maximum temperature of 315°F near this joint.

Post-test measurement of the riveted joint of the affected cell showed a significant increase in contact resistance (three orders of magnitude) between the aluminum rivet and the current collector compared with the contact resistance of cells from another 787 battery.¹²⁴ Because the heating occurred during periods of maximum current draw on the

¹²³ In this context, a cycle comprises three high-current discharges followed by one charge. The battery was allowed to stabilize after each cycle.

¹²⁴ The affected cell's post-test contact resistance measured between the aluminum rivet and the current collector was 74.5 milliohms, whereas the resistance in the same location for a cell from another battery was 0.030 milliohm. The Boeing battery SCD required contact resistance for new components to be less than 0.025 milliohm.

battery and was localized to the area of the riveted joint, the NTSB and UL determined that the source was resistive heating resulting from current through the area of high contact resistance.¹²⁵ The cell's windings were also a source of resistive heating during the simulated APU start testing, with the most significant heating occurring at 32°F.¹²⁶ Although all of the battery cells would have been affected by this heating, only cell 5 showed excessive localized heating near the cell's aluminum riveted joint.

This testing also showed that the heat generated inside the battery during the heaviest current loading condition of a full APU start could expose a cell to temperatures exceeding the maximum approved operating temperature of the battery (158°F) without detection by the battery's monitoring system. Post-test disassembly and examination of the affected cell showed thermal degradation (melting) along the edges of the cell's separator in the location where the aluminum current collectors attached to the cell windings, indicating that the cell's maximum temperature (at the aluminum riveted joint) exceeded the melting temperature of the separator.¹²⁷ The post-test examination of the affected cell also showed that the excessive temperature of the cell caused (1) softening and deformation of the plastic insulator material positioned between the aluminum rivet, the aluminum current collector, and the cell case to provide a hermetic seal at each rivet and (2) electrolyte leakage through the riveted joint.¹²⁸ Moisture entering the cell and electrolyte exiting the cell due to the softening and deformation of the seal could degrade internal cell chemistry and lead to cell failure, including thermal runaway.

The NTSB reviewed the design of the 787 main and APU battery cells to determine potential causes of the resistive heating observed near the aluminum rivets. The Boeing SCD for the battery stated that "connector contacts shall be designed to carry the same or better electrical current as the equivalent wire size." However, the aluminum rivet used in the 787 main and APU battery cell had a smaller cross-sectional area than would be required, according to the American Wire Gauge standard, for a wire rated to carry an equivalent current. Further, the Boeing SCD for the battery required terminal attachments to have "a complete metal-to-metal compression system." Examination of the rivet assemblies showed that the riveted joint had no springs or

¹²⁵ The electrical contact resistance between mated components (such as an aluminum rivet and a current collector) is a function of the real contact surface area between interfacing parts of a joint, contact pressure between mating surfaces, surface topography, and the presence of an oxide on mating surfaces, among other factors. The smaller the contact area between interfacing parts of the joint, the higher the resistance to current flow, and the more heat generated. The heat generated when a current is passing through a conduction path is directly proportional to the square of the current multiplied by the resistance of the conduction path.

¹²⁶ Testing performed by the NTSB and UL showed that, as the 787 main and APU battery approached temperatures below 32°F, the battery's efficiency decreased such that 30% of the discharge energy was released as heat instead of usable electrical energy at 0°F. This heat loss was the result of both electrochemical and resistive heating losses in the cell windings, which increased at colder temperatures. (Lithium-ion cells normally heat during discharge as a result of the electrochemical reaction that occurs within the battery cells. Heat is also produced as a result of resistance in electrical current conduction paths within the battery and cells.)

¹²⁷ Boeing's EPS safety assessment indicated that heat-induced shrinkage of a cell separator, such as that observed after the NTSB and UL's testing, is a potential cause of cell internal short circuiting and could lead to thermal runaway.

¹²⁸ According to UL, the thermoplastic seals used between the rivets, the cell case, and the current collector can permanently deform when exposed to temperatures between about 176°F and 230°F under load.

other compression devices.¹²⁹ Thus, the aluminum riveted joint assembly could be a significant source of resistive heating during maximum current discharge conditions for the 787 main and APU battery. Proper sizing of electrical components and positive retention of pressure in a joint are essential in preventing resistive heating, particularly during the most severe discharge current levels for the battery (that is, those that occur during a full APU start).

Another potential cause of the resistive heating was the poor electrical connection between the rivet and current collector components in the riveted joint. During the APU start tests, the excessive heating in the joint became evident only after the affected cell had successfully completed earlier cell- and battery-level simulated APU starts, indicating that the electrical connection between the rivet and current collector components degraded with continued usage. Proper design, manufacture, and damage tolerance of electrical connections among the components of a joint intended to transmit current through the cells is critical to minimize resistive heating inside the battery under the most severe operating conditions during repeated charge and discharge cycles. Testing of large-format lithium-ion batteries designed to carry large currents (similar to the 787 main and APU battery) for other applications showed that heat generated by poorly formed joints can flow toward the internal battery and cell structure, resulting in a considerable temperature increase that can lead to thermal runaway (Taheri and others 2011, 6525-6533).

After the BOS and TAK battery incidents, Boeing modified and recertified the 787 main and APU battery design to prevent a full battery thermal runaway resulting from a cell internal short circuit. The redesign also included a stainless steel enclosure designed to mitigate the effects of a full battery thermal runaway if it were to occur, even though FAA Special Conditions 25-359-SC did not require this enhanced level of mitigation.¹³⁰ Preventing cell thermal runaway by minimizing sources of heating is critical to the safety of future lithium-ion battery designs. However, current industry standards for the design and qualification of permanently installed, large-format, rechargeable lithium-ion batteries used on civil aircraft do not include guidance on industry best practices to minimize internally generated sources of heating, such as resistive and electrochemical heating, in the design and manufacture of these batteries.

Identifying and minimizing all sources of heating generated within a large-format lithium-ion battery during operation (particularly heating that can be localized to a cell as a result of electrical current flow through components, connections, and cell windings at lower temperatures) are important parts of the battery's design and manufacturing processes. These

¹²⁹ Without such devices, additional causes of joint degradation could include thermal shock, torque applied to the terminal during assembly, bending of the current collectors during the manufacturing of the cell header assembly, manufacturing errors, or the stress created within various cells when the battery is subjected to temperature extremes. A NASA technical standard requires that clamping pressure across semipermanent joints (such as those containing rivets) be consistent with applicable mechanical engineering assembly and installation requirements (NASA 2013).

¹³⁰ According to Boeing, the redesigned battery system included changes to prevent and isolate a fault if one were to occur. The redesign incorporated multiple layers of protection, including the new enclosure, to ensure that there would be no impact to the airplane and no possibility of fire if a battery failed. The enclosure was designed to keep any amount of battery overheating from affecting the airplane.

actions are necessary to account for the cumulative effects of electrochemical and resistive heating within a cell or in other locations within the battery to minimize the possibility that a cell (or cells) could be exposed to temperatures above allowed operational limits during high-current, low-temperature discharging that could cause permanent damage to a cell and lead to thermal runaway.

The NTSB concludes that the thermal protections incorporated in large-format lithium-ion battery designs need to account for all sources of heating in the battery during the most extreme charge and discharge current conditions and protect cells from damage that could lead to thermal runaway. Therefore, the NTSB recommends that the FAA work with aviation industry experts to develop or modify design safety standards for large-format lithium-ion batteries to require that sources of excessive heating, including electrical contact resistance from components and connections, be identified, minimized, and documented as part of the design. The standards should include measures for identifying and minimizing potential sources of heating that consider the range of operating temperatures and the most extreme electrical currents that the battery could be expected to experience during repeated charge and discharge cycles.

2.4.2 Cell-Level Temperature and Voltage Monitoring

FAA special condition 1 (see appendix B) required the 787 main and APU battery to maintain safe cell temperatures during any foreseeable charging or discharging condition and any failure of the charging or battery monitoring system not shown to be extremely remote. Maintaining safe cell temperature is critical because, once a cell heats to the point that the SEI layer degrades or the separator becomes thermally damaged, an internal short circuit and thermal runaway can occur. Further, as shown by the affected cell in the NTSB and UL's simulated APU start tests, localized heating of the cell to excessive temperatures occurred rapidly and went undetected by the BMU when the battery was discharged at its maximum current rating. Thus, the thermal management protections incorporated into the battery did not detect the developing temperature exceedance and prevent the cell from reaching an unsafe temperature.

The 787 main and APU battery was designed to measure temperature only on two cell bus bars and not at each cell. The NTSB and UL's simulated APU start tests showed that the temperature sensors on the bus bars recorded a peak value that was less than the cell temperature at the aluminum riveted joint. Thus, the temperature measured on the bus bars did not accurately reflect actual cell temperatures. In addition, the temperatures measured on the bus bars are not recorded by the BMU or at another location in the airplane. Accurate temperature data at the cell level, when monitored and recorded, could allow the battery monitoring system to (1) detect a rise in cell temperature and take actions before the temperature exceeded safe limits and caused damage and (2) provide timely notification to the flight crew or maintenance personnel if required.

Special condition 7 addressed voltage monitoring to prevent overcharging that could lead to thermal runaway. During the NTSB and UL's simulated APU start testing on individual cells, cell voltages (in millivolts) were found to be an important indicator of battery health and could

thus be used to mitigate failures. Also, during cell abuse testing, a drop in voltage of an individual cell preceded thermal runaway and venting.¹³¹ The 787 main and APU battery design incorporated provisions to monitor each cell's voltage and inhibit discharging of the battery below a specified voltage to protect the cells against overdischarge. Comparing the voltage drops of various cells during discharge could allow the BMU to inhibit subsequent charging or electrically isolate the cell to minimize further damage to the battery. The voltages measured by the sensors on the 787 cell bus bars were not recorded, and design standards do not require voltage data to be recorded. These data, if recorded, could provide maintenance or engineering personnel with trend data or other important information that could be used to determine the cause of a cell failure.

The NTSB concludes that more accurate cell temperature measurements and enhanced temperature and voltage monitoring and recording could help ensure that excessive cell temperatures resulting from localized or other sources of heating could be detected and addressed in a timely manner to minimize cell damage. Therefore, the NTSB recommends that the FAA work with aviation industry experts to develop or modify existing safety standards related to the design of permanently installed lithium-ion batteries to require monitoring of individual cell temperature and voltage and recording of exceedances to prevent internal cell damage during operations under the most extreme operating temperatures and currents. The NTSB also recommends that, once the guidance requested in Safety Recommendation A-14-115 has been issued, the FAA require type certification applicants to demonstrate that the battery monitoring system maintains each individual cell within safe temperature limits at the most extreme battery operating temperatures and the heaviest electrical current loads approved for operation. In addition, the NTSB recommends that the FAA work with lithium-ion industry experts to (1) conduct research into battery monitoring system technologies that could improve the recognition of conditions leading to thermal runaway, (2) develop active mitigation of such conditions to minimize damage, and (3) update design and safety standards accordingly.

2.4.3 Thermal Safety Limits for Cells

Boeing established the 787 main and APU battery's maximum operating temperature (158°F) at the same maximum operating temperature as that for nickel-cadmium batteries installed in other airplane models. The NTSB and UL's ARC testing on 787 main and APU lithium-ion battery cells determined that the cell began to self-heat at 144°F.¹³² Maintaining cell temperature at or just above a cell's self-heating threshold for an extended period of time could

¹³¹ For example, the testing found that about 0.8 second elapsed between the time that an initial failure in a cell (as indicated by a 20-millivolt voltage drop) was detected and the time when the cell went into thermal runaway and vented.

¹³² Different types of cell-level testing are available to determine the onset of cell damage and objectively establish limits for the battery monitoring system to provide a margin of safety. The ARC test is a well-documented technique that slowly heats cells in adiabatic conditions to document the heat absorbed or generated by the cells.

result in thermal runaway.¹³³ Thus, the upper temperature limit of the 787 battery was inappropriate for the cell materials.

GS Yuasa did not use the self-heating threshold to determine the safe temperature limit for the 787 battery. Instead, GS Yuasa determined the safe cell temperature by conducting a test in which cell temperatures were elevated until cell venting occurred; in another set of tests, the cells were exposed to reduced temperatures for varying durations, and no cell venting occurred. These test methods were inadequate because the cells might not have been at elevated temperatures long enough to go into thermal runaway from the breakdown of cell materials. The temperature at which cell self-heating begins can be an objective measure for establishing a battery's margin of safety.

Thermal runaway due to overheating can occur either rapidly when a cell is exposed to temperatures that are high enough to melt the separator or slowly as the cell's SEI layer degrades when above the self-heating temperature. Research showed that SEI layer damage is cumulative and that the thermal degradation of some commercial cells, when maintained at their self-heating temperature, continued for 2 days before thermal runaway occurred (Mikolajczak and others 2011).

As previously stated, FAA special condition 1 required the 787 main and APU battery to maintain safe cell temperatures during any foreseeable charging or discharging condition and any failure of the charging or battery monitoring system not shown to be extremely remote. However, current aviation industry standards do not define methods to determine safe cell temperature limits. Such standards exist for non-aviation-related applications.¹³⁴

The NTSB concludes that determining the initial point of self-heating in a lithium-ion cell is important in establishing thermal safety limits. Therefore, the NTSB recommends that the FAA work with industry experts to develop appropriate test methods for determining the initial point of self-heating in a lithium-ion cell to establish objective margins of thermal safety for future battery designs.

2.5 Certification Process

Type certification is a regulatory process that the FAA uses to ensure that aircraft product designs comply with applicable *Federal Aviation Regulations* and, as in this case, applicable special conditions. The 787 main and APU lithium-ion battery design was evaluated and approved as part of the Boeing 787 type design certification program. Although the investigation of this incident found that thermal runaway of a cell (due to an internal short circuit within a

¹³³ According to a NASA technical memorandum, "above a threshold temperature, a 'self-heating' condition could occur due to exothermic reactions occurring internally within the cell. Such reactions may include reactions between lithium and electrolyte and the thermal decomposition of internal cell components. If the internal heat generation is allowed to continue, a catastrophic cell 'thermal runaway' condition could occur, which would be a serious safety concern for a manned application" (Baldwin and others, 2010).

¹³⁴ For example, see Sandia National Laboratories' electrical energy storage system abuse test manual for electric and hybrid electric vehicles (Doughty and Crafts, 2006).

single cell of the APU battery) propagated to other cells and resulted in thermal runaway of the battery and fire, this design vulnerability was not identified during the certification of the 787 battery installation.

The NTSB's investigation of this incident found that more effective implementation of the certification process for designs incorporating new technology could be achieved through improvements in several focused areas. These areas include validation of the assumptions made and the data used in preliminary and final safety assessments developed during certification programs and the manner in which the FAA evaluates methods of compliance with special conditions during the certification process, as discussed in sections 2.5.1 and 2.5.2, respectively. Improvements in these areas could help foster better interactions between type design applicants and the FAA to ensure the completeness of data used by the applicant to demonstrate compliance with FAA requirements.

2.5.1 Validation of Assumptions and Data Used in Safety Assessments Involving New Technology

To effectively show compliance with FAA requirements during the certification process, Boeing needed to identify all foreseeable ways that 787 main and APU battery failures could cause the identified airplane-level hazards of venting with smoke and fire (classified by Boeing as a catastrophic event) or venting with or without smoke (classified by Boeing as a hazardous event). Boeing recognized that the propagation of cell-to-cell thermal runaway was a failure condition that could result from an internal short circuit in a single battery cell and evaluated this failure condition using the results of GS Yuasa's November 2006 development nail penetration test.¹³⁵ As stated in section 1.7.3, the nail penetration test results showed that the surface temperature of the nail-penetrated cell increased, smoke vented from the cell and the battery case, and the surface temperature of the adjacent cells increased with no venting. As a result of this test, Boeing, Thales, and GS Yuasa determined that an internal short circuit in a single cell that resulted in thermal runaway would not propagate to other cells within the battery case or generate a fire.

Boeing and Thales performed preliminary and final EPS safety assessments, which included fault tree analyses, FMEAs, and failure rate data provided by GS Yuasa. These assessments considered internal short circuit failures but were developed with the underlying assumption that the most severe effect of an internal short circuit within a cell would be limited to venting of only that cell without fire and propagation to other cells. Thus, the potential for an internal short circuit to lead to multiple-cell or battery thermal runaway with venting, electrolyte leakage, excessive heat, and fire was not analyzed in the safety assessment.

As shown by the circumstances of the BOS incident, the assumption that thermal runaway of a cell would not propagate to other cells within the battery case was incorrect.

¹³⁵ Boeing, Thales, and GS Yuasa indicated that other battery-level development nail penetration tests were performed, but no documentation of those tests and their results was available for the NTSB's review. For information about these tests, see the addendum to the System Safety and Certification Group Chairman's Factual Report, which is available at www.nts.gov in the public docket for this incident.

Validation of assumptions related to failure conditions that can impact safety is a critical step in the development and certification of an aircraft. The validation process must employ a level of rigor that is consistent with the potential hazard to the aircraft in case an assumption is incorrect. Society of Automotive Engineers (SAE) Aerospace Recommended Practice (ARP) 4754 provides a structured process for managing and validating assumptions with steps that include ensuring that assumptions are explicitly stated, appropriately disseminated, and justified by supporting data (SAE 2010).¹³⁶ The ARP notes that validating assumptions can be accomplished using reviews, analyses, and tests.

Development testing is often necessary to validate important design assumptions, but the nail penetration test performed by GS Yuasa did not adequately account for a number of factors that were relevant to propagation risk. For example, the test was not conducted at the battery's maximum operating temperature of 158°F, and the test setup did not fully represent the battery installation on the 787 airplane.¹³⁷ Also, the test did not include repeated trials of inducing thermal runaway of a cell in multiple batteries to understand how the repeatability of these tests could impact the validity of the test results. Further, the test was performed using a development unit that did not incorporate the final battery design certified as part the 787 type design.¹³⁸

Other development tests were performed to evaluate various aspects of the 787 battery's performance, including the July 2009 integrated system test at UTC Aerospace Systems' APSIF. This test was not designed to evaluate internal short circuiting effects or the cell-to-cell propagation risk. During the test, the battery was unintentionally charged at an excessive rate, which resulted in the venting of a single cell. Although the thermal runaway of that cell did not propagate to other cells within the battery case, the results of this test should not have been considered to be confirmation of the results of GS Yuasa's 2006 nail penetration test because the APSIF test was not designed to examine engineering factors that could likely influence whether

¹³⁶ SAE ARP 4754 is an industry guideline that addresses design development for civil aircraft systems with failure modes that could affect the safety of aircraft on which the systems are installed. SAE ARP 4754 defines validation as "the determination that the requirements for a product are correct and complete." The original version of the ARP, "Certification Considerations for Highly-Integrated or Complex Aircraft Systems," was issued in November 1996 and was in use at the time of the 787 certification program. The current version of the ARP, revision A, was issued in December 2010 and was retitled, "Guidelines for Development of Civil Aircraft and Systems." The revised guideline was expanded to include all types of aircraft certification programs and not just those incorporating highly integrated or complex systems.

¹³⁷ The NTSB and UL's postincident nail penetration testing with an ungrounded battery at the battery's maximum operating temperature showed that thermal runaway of a single cell propagated to all other cells inside the battery case. Also, the JTSB conducted a heat propagation test on three 787 main and APU batteries. During all three tests, an internal short circuit was initiated in a single cell of each test battery using the nail penetration method. According to the JTSB's final report on the TAK incident, propagation of thermal runaway to multiple cells within the battery occurred during two of the three tests. For both of these tests, the battery was connected to the BCU, and the battery case was grounded, simulating the actual configuration as installed on the airplane. One of these tests was conducted at 158°F, and the other test was conducted at 86°F. The test involving the ungrounded battery case (during which no propagation occurred) was conducted at 86°F.

¹³⁸ According to Boeing, Thales, and GS Yuasa, electrolyte leakage was observed during two engineering (noncertification) cell vent tests in September 2009; as a result, the battery case design was modified to incorporate additional sealing to prevent electrolyte leakage. Also, the preproduction battery design used during GS Yuasa's testing had a different vent disc arrangement than the arrangement in the final battery design.

an internal short circuit would lead to propagation. As a result, the repeatability of the test result under all operating environments and usage conditions was not ensured.

Further, GS Yuasa's qualification abuse tests, which were intended to demonstrate that the battery design met the criteria established in the 787 main and APU battery SCD, did not provide adequate evidence to discount the possibility of propagation in the event of cell thermal runaway resulting from an internal short circuit.¹³⁹ Specifically, none of these tests drove a cell into thermal runaway to demonstrate that propagation would not occur or that the battery case could contain the effects of multiple-cell venting. Also, the batteries used during the tests were not grounded as installed on the airplane. Thus, the results of these tests were not relevant or sufficient for making assumptions about propagation with a grounded battery and for the full range of operating conditions.¹⁴⁰

In addition to underestimating the most severe effects of a cell internal short circuit, Boeing, Thales, and GS Yuasa also underestimated the rate of occurrence for this failure mode. Boeing indicated in its EPS safety assessment that the rate of occurrence of cell venting would be about one in 10 million flight hours. However, this predicted failure rate was significantly lower than the actual failure rate observed for the 787's first 52,000 hours of service, during which time both the BOS and TAK incidents occurred.

Boeing used data from GS Yuasa to determine the rate of occurrence of cell venting. These data were based on GS Yuasa's experience with a lithium-ion battery with a similar mechanical design, which GS Yuasa manufactured for use in an industrial application. Of the more than 14,000 similarly designed lithium-ion battery cells in service at the time, GS Yuasa found that none had experienced thermal runaway or venting. Because no failures had occurred, GS Yuasa used probabilistic methods to estimate a failure rate for the industrial battery cells.¹⁴¹ After accounting for capacity differences between the two battery applications and establishing that the environmental and usage conditions and the manufacturing processes for the 787 and industrial applications would be similar, GS Yuasa determined that the 787 main and APU battery cells would have a failure rate similar to that of the industrial cells.

The method that GS Yuasa used in estimating the failure rate for 787 main and APU battery cells was consistent with industry practices for components manufactured with controlled processes and subjected to similar stress conditions during normal use over time. However, the NTSB found no documented analysis comparing the duty cycle and environment expected in the

¹³⁹ The qualification abuse testing included two external short circuit tests (low and high impedance shorts at battery terminals), one overcharge test (charge battery to 36 volts for 25 hours), and one overdischarge test (discharge battery to zero volts). These qualification tests were conducted at the battery's maximum operating temperature of 158°F, and no thermal runaway occurred. A qualification test involving high-temperature storage (185°F for 18 hours) also resulted in no thermal runaway.

¹⁴⁰ During the NTSB's April 2013 investigative hearing on the BOS incident, a Boeing representative testified that Boeing used "state of the art in testing" and that no propagation of cells occurred during qualification abuse testing, nail penetration testing, and the venting event at APSIF.

¹⁴¹ Probabilistic methods model and describe the random variations in systems. Probabilistic methods demonstrate compliance in the certification process using probabilistic risk analysis techniques.

787 application with that experienced in the industrial application. If the 787 application had higher mechanical and/or electrical stress levels than the industrial application due to differences in duty cycle and environment, the onset of certain failure modes could be accelerated, or failure modes not previously exhibited in the industrial cells, such as internal short circuiting and cell venting, could be manifested in the 787 battery cells.¹⁴² Given the potential safety consequences of cell venting and the lack of historical data on cell and battery performance in an airplane application, Boeing, Thales, and GS Yuasa should have performed a structured engineering analysis, supplemented by testing, to compare the differences in duty cycle and environment between the two applications and measure the impact on battery and cell features that drive safety-related failure modes, effects, and rates. This level of rigor was needed to determine whether the use of the industrial cell failure rate was appropriate for the 787 application.

Boeing indicated in certification documents that it used a version of AC 25.1309 (referred to as the Arsenal draft) as guidance in preparing the EPS safety assessment for the 787 type design certification program. The draft AC addressed the treatment of assumptions and data, stating that the underlying assumptions, data sources, and analytical techniques used in safety analyses should be identified and justified to ensure the validity of the conclusions made in safety assessments. However, the analysis that Boeing presented in its EPS safety assessment did not appear to be consistent with the guidance provided in the draft AC. Specifically, the analysis did not (1) identify Boeing's assumption that thermal runaway of a cell would not propagate to other cells and (2) provide the engineering rationale needed to justify broad use of this assumption under all operating conditions. Also, the analysis did not sufficiently evaluate and justify the use of the industrial battery failure rate data in predicting the risk of a cell venting occurrence for the 787 battery. Further, even if this information had been included in the EPS safety assessment, the validity of the supporting safety analyses would have been difficult to justify given the limited data available. For example, the assumption that propagation would not occur was based on the result of GS Yuasa's single 2006 nail penetration test, and the failure rate prediction for cell venting was developed without a rigorous comparison of the most severe environmental and usage conditions between the industrial and 787 battery applications.

AC 25.1309 (Arsenal draft) also stated, "where it is not possible to fully justify the adequacy of the safety analysis and where data or assumptions are critical to the acceptability of the failure condition, extra conservatism should be built into either the analysis or the design." The assumption that the design of the main and APU battery prevented thermal runaway of a single cell from propagating to other cells inside the battery case was critical to accepting the risk of an internal short circuit in a cell because, if the assumption were incorrect, thermal runaway of the battery could occur. As a result, Boeing should have taken a more conservative approach in its safety analyses by including the possibility that propagation of thermal runaway from cell to cell could result from an internal short circuit and considering the potential effects if this failure condition were to occur. If such an approach had been taken, Boeing authorized representatives

¹⁴² For example, stresses on the cells introduced by altitude changes would only be present in the 787 application, and these stresses applied over time in service could change the failure modes, the severity of failure effects, and increase the rates of failure for the cells and the entire battery installation. Deterministic methods that involve accelerated stress testing are commonly used to evaluate the influence of engineering factors, such as stress, design, and environment, on item reliability (Condra 1993).

and/or FAA certification engineers independently reviewing the EPS safety assessment would likely have required Boeing, Thales, and GS Yuasa design engineers to (1) perform more exhaustive test and analysis to properly validate claims about propagation and cell failure rate or (2) incorporate design features to safely accommodate cascading thermal runaway of all cells inside the battery case.¹⁴³

Critical assumptions and conclusions made in GS Yuasa's and Thales' safety analyses and used in Boeing's EPS safety assessment were not fully delineated and justified with appropriate data and engineering rationale. However, multiple independent reviews of the EPS safety assessment by Boeing authorized representatives and FAA certification engineers did not reveal these deficiencies. The review process for safety assessments should be designed to closely examine the data used to support conclusions and challenge assumptions, particularly those that could result in significant safety consequences if incorrect. Also, the review process should be designed to ensure a conservative approach when available engineering data and experience are limited.

The NTSB concludes that Boeing's EPS safety assessment did not consider the most severe effects of a cell internal short circuit and include requirements to mitigate related risks and that the review of the assessment by Boeing authorized representatives and FAA certification engineers did not reveal this deficiency. Therefore, the NTSB recommends that Boeing modify its process for developing safety assessments for designs incorporating new technology to ensure that the conclusions made are validated and that any identified deficiencies are corrected. The NTSB also recommends that the FAA provide its certification engineers with written guidance and training to ensure that (1) assumptions, data sources, and analytical techniques are fully identified and justified in applicants' safety assessments for designs incorporating new technology and (2) an appropriate level of conservatism is included in the analysis or design, consistent with the intent of AC 25.1309 (Arsenal draft). Further, the NTSB recommends that, during annual recurrent training for engineering designees, the FAA discuss the need for applicants to identify, validate, and justify key assumptions and supporting engineering rationale used in safety assessments addressing new technology.

2.5.2 Validating Methods of Compliance for Designs Involving New Technology

The FAA was responsible for approving Boeing's methods of compliance and the data produced from various analyses and tests. The FAA approved Boeing's qualification test program (which was outlined in Boeing's EPS certification plan) and Boeing's EPS safety assessment as methods of demonstrating that the battery complied with the FAA's special conditions. Boeing's safety assessment was an important method of compliance because it identified the battery failure modes that could produce conditions prohibited by the FAA's special conditions and defined the safety requirements needed to mitigate the potential risks to a

¹⁴³ Regarding the process for validating assumptions, ARP 4754 stated, "where the consequences of an erroneous assumption appear to have significant potential to reduce safety, one possible validation strategy consists of showing how the system design, in fact, limits or bounds the achievable consequences of an assumption error."

level deemed acceptable by the FAA.¹⁴⁴ However, because Boeing's safety assessment did not consider the potential for cell-to-cell propagation with fire as a result of an internal short circuit, Boeing did not identify, in the 787 main and APU battery SCD or elsewhere, safety requirements directly addressing battery performance with a single cell in thermal runaway. Also, because the battery SCD did not contain a specific requirement for battery performance with a cell in thermal runaway, the need for a thermal runaway qualification test or other related verification activity as part of the battery's certification would have been less visible to Boeing authorized representatives and FAA certification engineers.¹⁴⁵

Although GS Yuasa's battery design included features intended to prevent cell-to-cell propagation, such as cell spacing and thermal insulation materials between cells, these provisions were insufficient, as demonstrated by the BOS and the TAK incidents. These battery design features were not fully linked to defined, measurable performance criteria in Boeing's battery SCD, so the effectiveness of the design features in preventing propagation was not verified during battery qualification testing. The NTSB concludes that Boeing failed to incorporate design requirements in the 787 main and APU battery SCD to mitigate the most severe effects of a cell internal short circuit and that the FAA failed to uncover this design vulnerability as part of its review and approval of Boeing's EPS certification plan and proposed methods of compliance.

AC 25.1309 (Arsenal draft) noted that a safety assessment should trace the work leading to conclusions (including the basis for classification of the severity of hazards, the assumptions made, and supporting rationale for assumptions) as part of certification. However, none of the certification deliverables to which the FAA and Boeing agreed established the relationships among each individual special condition, related hazards and assumptions from the EPS safety assessment, safety requirements in the main and APU battery SCD, and the resulting data used to show compliance.¹⁴⁶ Thus, the FAA could not effectively use traceability principles to evaluate the completeness of Boeing's proposed methods of compliance, particularly for special condition 2, which addressed battery thermal runaway.¹⁴⁷ As a result, the FAA approved Boeing's proposed EPS certification plan, including qualification tests, for the 787 main and APU battery without the details necessary to demonstrate compliance with the individual special conditions.

If these relationships had been fully discussed in certification documentation or through other communications between Boeing and the FAA as part of the certification process, Boeing authorized representatives and FAA certification engineers would have had a better understanding of how the assumption regarding the propagation of thermal runaway as a result of

¹⁴⁴ AC 25.1309 (Arsenal draft) provided guidance on the acceptable failure probability per flight hour of equipment and systems installed on an airplane as a function of the severity of the resulting failure condition.

¹⁴⁵ ARP 4754 defines verification as "the evaluation of an implementation of requirements to determine that they have been met."

¹⁴⁶ Traceability is defined in revision A of ARP 4754 as "the recorded relationship established between two or more elements of the development process."

¹⁴⁷ Special condition 2 indicated that the "design of the lithium-ion batteries must preclude the occurrence of self-sustaining, uncontrolled increases in temperature or pressure."

a cell internal short circuit related to special condition 2.¹⁴⁸ In addition, traceability would likely have revealed the absence of safety requirements addressing cell thermal runaway and propagation in the battery SCD and the need for a thermal runaway test as part of planned qualification tests to demonstrate that the design met the requirements of special condition 2 for the internal short circuit failure condition. However, guidance used by FAA certification staff at the time of Boeing's application for the 787-8 type certificate, including FAA Order 8110.4, "Type Certification," revision B, did not include the use of traceability principles that relate each special condition to design data and compliance deliverables (such as test procedures, test reports, and safety assessments) as part of certification planning to ensure that the methods of compliance were correct and complete.

The NTSB concludes that unclear traceability among the individual special conditions, safety assessment assumptions and rationale, requirements, and proposed methods of compliance for the 787 main and APU battery likely contributed to the FAA's failure to identify the need for a thermal runaway certification test. Therefore, the NTSB recommends that the FAA develop written guidance for its certification engineers and engineering designees about the use of traceability principles to verify that the methods of compliance proposed by type certification applicants for special conditions involving new technology are correct and complete. The NTSB also recommends that, once the guidance requested in Safety Recommendation A-14-121 has been issued, the FAA provide training to its certification engineers and engineering designees on the subjects discussed in the guidance. The NTSB further recommends that the FAA require applicants to discuss key assumptions related to safety-significant failure conditions, their validation, and their traceability to requirements and proposed methods of compliance during certification planning meetings for type designs involving special conditions.

2.5.3 Certification of Lithium-ion Batteries and Certification of New Technology

As stated in section 1.8.2, the NTSB issued Safety Recommendations A-14-32 through -36 to the FAA regarding (1) insufficient testing methods and guidance for addressing the safety risks of internal short circuits and thermal runaway and (2) the need for outside technical knowledge and expertise to help the FAA ensure the safe introduction of new technology into aircraft designs. On August 19, 2014, the FAA responded to these recommendations.

In its response letter, the FAA stated that it has been working with RTCA Special Committee SC-211 to revise RTCA document DO-311, "Minimum Operational Performance Standards for Rechargeable Lithium Battery Systems," to "capture all the enhancements and lessons learned" from the BOS incident, including the need for a test that subject a single cell

¹⁴⁸ A review of available minutes from monthly meetings between the FAA and Boeing during the planning and implementation phases of the 787 certification program did not reveal any communications related to Boeing's assumption or proposed qualification test plan for the main and APU battery as it related to the thermal runaway propagation failure condition due to cell internal short circuiting.

within a lithium-ion battery to thermal runaway as a result of an internal short circuit.¹⁴⁹ The FAA also stated that, until these revisions are completed, it would use the issue paper process to provide new design applicants with acceptable methods of compliance for conducting tests and analyses to address the potential failure effects of permanently installed, rechargeable lithium-ion batteries. The FAA further stated that it was surveying previous approvals of rechargeable lithium battery systems to determine those existing approved designs that require additional testing and/or analysis to ensure that they can mitigate all adverse effects of a cell thermal runaway. In addition, the FAA stated that it was setting up meetings with internal stakeholders to determine how best to implement Safety Recommendation A-14-36.

The NTSB is encouraged that the FAA is taking steps to enhance RTCA document DO-311 but is concerned that aircraft installation factors might not be addressed in the document given that DO-311 is a battery-level standard. On the basis of the FAA's actions, the NTSB classifies Safety Recommendations A-14-32 through -36 "Open—Acceptable Response" pending review of future updates regarding the FAA's progress in completing the recommended actions.

2.6 Flight Recorder Issues

2.6.1 Stale Flight Data

The EAFR is a new recording system with a new flight data recording format, and the 787 is currently the only airplane that uses the EAFR to record CVR, FDR, and other data. The investigation of this incident found that the EAFR recorded stale data for some parameters (see section 1.3). The recording of stale data impacted the early stages of this investigation because significant additional effort was required to identify stale data when possible as well as those parameters for which it was not possible to determine whether the data samples were stale. This process delayed the NTSB's complete understanding of the recorded data.

Stale EAFR data could impact future investigations as well. The recording of stale data could lead to cases in which apparently valid data continued to be recorded after a parameter source stopped providing valid data, which could result in latent faults in the recording system for mandatory parameters.¹⁵⁰ These mandatory parameters would thus be unavailable because an EAFR's source would no longer be providing the data. In addition, the safe operation of an aircraft could be impacted if stale EAFR data were unintentionally used by an operator to assess and resolve maintenance issues.

¹⁴⁹ In 2006, the FAA chartered a federal advisory committee, known as RTCA Special Committee SC-211, to develop a standard for the design, certification, production, and use of permanently installed, rechargeable lithium-ion battery systems. The committee included representatives from the FAA, US Air Force, US Navy, US Army, commercial air carriers, and battery and aircraft manufacturers. Boeing, Thales, and GS Yuasa were also members of the RTCA special committee. The resulting standard, DO-311, which was issued in 2008, is currently considered by the FAA to be an acceptable means of compliance to the special conditions for rechargeable lithium-ion batteries and battery systems.

¹⁵⁰ Title 14 CFR 121.344, "Digital Flight Data Recorders for Transport Category Airplanes," details mandatory parameter requirements. Title 14 CFR Part 121 Appendix M provides supplemental information to 14 CFR 121.344.

The NTSB concludes that stale EAFR data could impede future accident and incident investigations by delaying the full understanding of the recorded data; stale data could also impact aircraft safety if an operator's maintenance activities were based on these data. At this time, the NTSB is concerned with the EAFR stale data recording issue on 787 airplanes because future EAFR installations might take greater advantage of the flexibility of the new recording format, which could mitigate the stale data issue. Therefore, the NTSB recommends that the FAA require Boeing 787 operators to incorporate guidance about the EAFR stale data issue in their maintenance manuals to prevent stale data from being used for maintenance activities or flight recorder maintenance. In addition, the NTSB recommends that the FAA (1) evaluate whether the recording of stale data by the Boeing 787 EAFR, including whether the data are specifically identified as stale, impacts the certification of the recording system regarding the ranges, accuracies, and sampling intervals specified in 14 CFR Part 121 Appendix M and (2) take appropriate measures to correct any problems found.

2.6.2 Poor-Quality Cockpit Voice Recording

The investigation of this incident found that the audio recording obtained from both EAFRs was poor quality. The signal levels of the three radio/hot microphone channels of the audio recording (the captain's audio selector panel, the first officer's audio selector panel, and the jumpseat/observer's position) were very low and used only about 25% of the available total dynamic range of the recorder. Further, throughout the recording, random full-deflection noise spikes could be heard. These random noise spikes were very short in duration but used the full dynamic range of the radio/hot microphone channel recording.

The recording from the cockpit area microphone channel of the EAFR was also poor quality. During the airborne portion of the flight that was captured on the recording, almost all of the individual crew conversations were completely obscured by the ambient cockpit noise. After the airplane landed, the cockpit noise was reduced, so the crew conversations became clearer. Once the airplane arrived at the gate and the engines were shut down, the crew conversations could easily be heard, and the overall quality of the recording was excellent. Thus, the issues with the EAFR audio recording did not impact this investigation because the conversations and sounds related to the circumstances of the incident occurred during the portion of the recording that was excellent quality.

The EAFR was certified under FAA Technical Standard Order (TSO) C123B, "Cockpit Voice Recorder Equipment," which was based on the European Organization for Civil Aviation Equipment (EUROCAE) ED-112A document, "Minimum Operational Performance Specification for Crash Protected Airborne Recording Systems." The installation and performance requirements in chapter I-6 of the EUROCAE document also include guidance to determine if a CVR installation would be acceptable. This guidance stated that the CVR should use all available dynamic ranges of the recorder and mitigate cockpit area background noise. The FAA took exception to this chapter of the EUROCAE ED-112A document and removed the chapter's requirements from the final TSO C123B language. As a result, the CVR certifier and installer can determine what constitutes an acceptable recording without the use of any industry-approved standard regarding specific installation guidance.

The NTSB concludes that the poor audio recording quality of the EAFR could impede future aircraft investigations because the recorded conversations and other cockpit sounds might be obscured. Therefore, the NTSB recommends that the FAA require Boeing to improve the quality of (1) the EAFR radio/hot microphone channels by using the maximum available dynamic range of the individual channels and (2) the cockpit area microphone airborne recordings by increasing the crew conversation signals over the ambient background noise. In addition, the NTSB recommends that the FAA either remove the current exception to ED-112A chapter I-6 in TSO 123B or provide installers and certifiers with specific guidance to determine whether a CVR installation would be acceptable.

3. Conclusions

3.1 Findings

1. The battery failure did not result from overcharging, overdischarging, external short circuiting, external heating, installation factors, or environmental conditions of the airplane.
2. The battery failure resulted from an internal short circuit that occurred in cell 5 or cell 6 and led to thermal runaway that propagated to adjacent cells.
3. GS Yuasa's cell manufacturing process allowed defects that could lead to internal short circuiting, including wrinkles and foreign object debris, to be introduced into the Boeing 787 main and auxiliary power unit battery.
4. The thermal protections incorporated in large-format lithium-ion battery designs need to account for all sources of heating in the battery during the most extreme charge and discharge current conditions and protect cells from damage that could lead to thermal runaway.
5. More accurate cell temperature measurements and enhanced temperature and voltage monitoring and recording could help ensure that excessive cell temperatures resulting from localized or other sources of heating could be detected and addressed in a timely manner to minimize cell damage.
6. Determining the initial point of self-heating in a lithium-ion cell is important in establishing thermal safety limits.
7. Boeing's electrical power system safety assessment did not consider the most severe effects of a cell internal short circuit and include requirements to mitigate related risks, and the review of the assessment by Boeing authorized representatives and Federal Aviation Administration certification engineers did not reveal this deficiency.
8. Boeing failed to incorporate design requirements in the 787 main and auxiliary power unit battery specification control drawing to mitigate the most severe effects of a cell internal short circuit, and the Federal Aviation Administration failed to uncover this design vulnerability as part of its review and approval of Boeing's electrical power system certification plan and proposed methods of compliance.
9. Unclear traceability among the individual special conditions, safety assessment assumptions and rationale, requirements, and proposed methods of compliance for the 787 main and auxiliary power unit battery likely contributed to the Federal Aviation Administration's failure to identify the need for a thermal runaway certification test.
10. Stale enhanced airborne flight recorder data could impede future accident and incident investigations by delaying the full understanding of the recorded data; stale data could

also impact aircraft safety if an operator's maintenance activities were based on these data.

11. The poor audio recording quality of the enhanced airborne flight recorder could impede future aircraft investigations because the recorded conversations and other cockpit sounds might be obscured.

3.2 Probable Cause

The National Transportation Safety Board determines that the probable cause of this incident was an internal short circuit within a cell of the auxiliary power unit (APU) lithium-ion battery, which led to thermal runaway that cascaded to adjacent cells, resulting in the release of smoke and fire. The incident resulted from Boeing's failure to incorporate design requirements to mitigate the most severe effects of an internal short circuit within an APU battery cell and the Federal Aviation Administration's failure to identify this design deficiency during the type design certification process.

4. Recommendations

4.1 New Recommendations

As a result of this investigation, the National Transportation Safety Board makes the following new safety recommendations:

To the Federal Aviation Administration:

Develop or revise processes to establish more effective oversight of production approval holders and their suppliers (including sub-tier suppliers) to ensure that they adhere to established manufacturing industry standards. (A-14-113)

Work with aviation industry experts to develop or modify design safety standards for large-format lithium-ion batteries to require that sources of excessive heating, including electrical contact resistance from components and connections, be identified, minimized, and documented as part of the design. The standards should include measures for identifying and minimizing potential sources of heating that consider the range of operating temperatures and the most extreme electrical currents that the battery could be expected to experience during repeated charge and discharge cycles. (A-14-114)

Work with aviation industry experts to develop or modify existing safety standards related to the design of permanently installed lithium-ion batteries to require monitoring of individual cell temperature and voltage and recording of exceedances to prevent internal cell damage during operations under the most extreme operating temperatures and currents. (A-14-115)

Once the guidance requested in Safety Recommendation A-14-115 has been issued, require type certification applicants to demonstrate that the battery monitoring system maintains each individual cell within safe temperature limits at the most extreme battery operating temperatures and the heaviest electrical current loads approved for operation. (A-14-116)

Work with lithium-ion industry experts to (1) conduct research into battery monitoring system technologies that could improve the recognition of conditions leading to thermal runaway, (2) develop active mitigation of such conditions to minimize damage, and (3) update design and safety standards accordingly. (A-14-117)

Work with industry experts to develop appropriate test methods for determining the initial point of self-heating in a lithium-ion cell to establish objective margins of thermal safety for future battery designs. (A-14-118)

Provide your certification engineers with written guidance and training to ensure that (1) assumptions, data sources, and analytical techniques are fully identified

and justified in applicants' safety assessments for designs incorporating new technology and (2) an appropriate level of conservatism is included in the analysis or design, consistent with the intent of Advisory Circular 25.1309 (Arsenal draft). (A-14-119)

During annual recurrent training for engineering designees, discuss the need for applicants to identify, validate, and justify key assumptions and supporting engineering rationale used in safety assessments addressing new technology. (A-14-120)

Develop written guidance for your certification engineers and engineering designees about the use of traceability principles to verify that the methods of compliance proposed by type certification applicants for special conditions involving new technology are correct and complete. (A-14-121)

Once the guidance requested in Safety Recommendation A-14-121 has been issued, provide training to your certification engineers and engineering designees on the subjects discussed in the guidance. (A-14-122)

Require applicants to discuss key assumptions related to safety-significant failure conditions, their validation, and their traceability to requirements and proposed methods of compliance during certification planning meetings for type designs involving special conditions. (A-14-123)

Require Boeing 787 operators to incorporate guidance about the enhanced airborne flight recorder stale data issue in their maintenance manuals to prevent stale data from being used for maintenance activities or flight recorder maintenance. (A-14-124)

Evaluate whether the recording of stale data by the Boeing 787 enhanced airborne flight recorder, including whether the data are specifically identified as stale, impacts the certification of the recording system regarding the ranges, accuracies, and sampling intervals specified in 14 *Code of Federal Regulations* Part 121 Appendix M, and take appropriate measures to correct any problems found. (A-14-125)

Require Boeing to improve the quality of (1) the enhanced airborne flight recorder radio/hot microphone channels by using the maximum available dynamic range of the individual channels and (2) the cockpit area microphone airborne recordings by increasing the crew conversation signals over the ambient background noise. (A-14-126)

Either remove the current exception to European Organization for Civil Aviation Equipment ED-112A, "Minimum Operational Performance Specification for Crash Protected Airborne Recording Systems," chapter I-6 in Technical Standard Order 123B, "Cockpit Voice Recorder Equipment," or provide installers and certifiers with specific guidance to determine whether a cockpit voice recorder installation would be acceptable. (A-14-127)

To the Boeing Company:

Develop or revise processes to establish more effective oversight of your suppliers (including sub-tier suppliers) to ensure that the product being manufactured adheres to established industry standards. (A-14-128)

Modify your process for developing safety assessments for designs incorporating new technology to ensure that the conclusions made are validated and that any identified deficiencies are corrected. (A-14-129)

To GS Yuasa Corporation:

Review your cell manufacturing processes to minimize or prevent defects that could affect cell safety, and ensure that your employees are properly trained to identify and eliminate these defects. (A-14-130)

4.2 Previously Issued Safety Recommendations Classified in This Report

Safety Recommendations A-14-32 through -36 are classified “Open—Acceptable Response” in section 2.5.3 of this report.

Develop abuse tests that subject a single cell within a permanently installed, rechargeable lithium-ion battery to thermal runaway and demonstrate that the battery installation mitigates all hazardous effects of propagation to other cells and the release of electrolyte, fire, or explosive debris outside the battery case. The tests should replicate the battery installation on the aircraft and be conducted under conditions that produce the most severe outcome. (A-14-32)

After Safety Recommendation A-14-32 has been completed, require aircraft manufacturers to perform the tests and demonstrate acceptable performance as part of the certification of any new aircraft design that incorporates a permanently installed, rechargeable lithium-ion battery. (A-14-33)

Work with lithium-ion battery technology experts from government and test standards organizations, including US national laboratories, to develop guidance on acceptable methods to induce thermal runaway that most reliably simulate cell internal short-circuiting hazards at the cell, battery, and aircraft levels. (A-14-34)

Review the methods of compliance used to certify permanently installed, rechargeable lithium-ion batteries on in-service aircraft and require additional testing, if needed, to ensure that the battery design and installation adequately protects against all adverse effects of a cell thermal runaway. (A-14-35)

Develop a policy to establish, when practicable, a panel of independent technical experts to advise on methods of compliance and best practices for certifying the safety of new technology to be used on new or existing aircraft. The panel should

be established as early as possible in the certification program to ensure that the most current research and information related to the technology could be incorporated during the program. (A 14-36)

BY THE NATIONAL TRANSPORTATION SAFETY BOARD

CHRISTOPHER A. HART
Acting Chairman

ROBERT L. SUMWALT
Member

MARK R. ROSEKIND
Member

EARL F. WEENER
Member

Adopted: November 21, 2014

5. Appendixes

Appendix A: Investigation and Hearing

The National Transportation Safety Board (NTSB) was notified of this incident on January 7, 2013, and sent an investigator to the scene the same day and two investigators to the scene the next day. The following investigative groups were formed: airworthiness, airport emergency response, battery and fire, manufacturing, and systems safety and certification. Also, specialists were assigned to conduct the readout of the flight data recorder and transcribe the cockpit voice recorder at the NTSB's laboratory in Washington, DC. In addition, a specialist was assigned to conduct radiographic studies of 787 batteries and cells.

The following organizations provided technical assistance to the NTSB during this investigation:

- Naval Surface Warfare Center, Carderock Division, US Department of the Navy, West Bethesda, Maryland;
- TIAX LLC, Lexington, Massachusetts;
- Underwriters Laboratories LLC, Northbrook, Illinois; Melville, New York; and Taipei, Taiwan
- US Department of Energy, Washington, DC;
- Chesapeake Testing, Belcamp, Maryland;
- National Institute of Standards and Technology, Gaithersburg, Maryland; and
- Naval Research Laboratory, Washington, DC.

Parties to the investigation were the Federal Aviation Administration (FAA) and Boeing Commercial Airplanes. In accordance with the provisions of Annex 13 to the Convention on International Civil Aviation, the Japan Transport Safety Board (JTSB) and the Bureau d'Enquêtes et d'Analyses pour la Sécurité de l'Aviation Civile (BEA) participated in this investigation. Japan Airlines and GS Yuasa Corporation participated in the investigation as technical advisors to the JTSB, and Thales Avionics Electrical Systems and the European Aviation Safety Agency participated in the investigation as technical advisors to the BEA, as provided for in Annex 13.

On April 23 and 24, 2013, the NTSB held an investigative hearing regarding the Boeing 787 battery's design and certification. The safety issues discussed were the battery system's (1) selection and certification requirements, (2) design and development, (3) design verification and validation, and (4) certification and the FAA's findings of compliance. Parties to the investigative hearing were the FAA, Boeing, Thales, and GS Yuasa.

Between the date of the incident and the investigative hearing, the NTSB issued an interim factual report on this incident (March 7, 2013) and held a forum on lithium-ion batteries in transportation (April 11 and 12, 2013). The interim factual report and presentations from the forum are available at www.nts.gov.

Appendix B: Boeing 787 Type Certification Special Conditions 25-359-SC

The FAA issued the following nine special conditions, in place of the electrical equipment and installation requirements of 14 *Code of Federal Regulations* (CFR) 25.1353(c)(1) through (c)(4), for the design and installation of lithium-ion batteries as part of the type certification basis for the Boeing 787-8:

- (1) Safe cell temperatures and pressures must be maintained during any foreseeable charging or discharging condition and during any failure of the charging or battery monitoring system not shown to be extremely remote. The lithium-ion battery installation must preclude explosion in the event of those failures.
- (2) Design of the lithium-ion batteries must preclude the occurrence of self-sustaining, uncontrolled increases in temperature or pressure.
- (3) No explosive or toxic gases emitted by any lithium-ion battery in normal operation, or as the result of any failure of the battery charging system, monitoring system, or battery installation not shown to be extremely remote, may accumulate in hazardous quantities within the airplane.
- (4) Installations of lithium-ion batteries must meet the requirements of 14 CFR 25.863(a) through (d).
- (5) No corrosive fluids or gases that may escape from any lithium-ion battery may damage surrounding structure or any adjacent systems, equipment, or electrical wiring of the airplane in such a way as to cause a major or more severe failure condition, in accordance with 14 CFR 25.1309(b) and applicable regulatory guidance.
- (6) Each lithium-ion battery installation must have provisions to prevent any hazardous effect on structure or essential systems caused by the maximum amount of heat the battery can generate during a short circuit of the battery or of its individual cells.
- (7) Lithium-ion battery installations must have a system to control the charging rate of the battery automatically, so as to prevent battery overheating or overcharging, and,
 - (i) A battery temperature sensing and over-temperature warning system with a means for automatically disconnecting the battery from its charging source in the event of an over-temperature condition, or,

(ii) A battery failure sensing and warning system with a means for automatically disconnecting the battery from its charging source in the event of battery failure.

(8) Any lithium-ion battery installation whose function is required for safe operation of the airplane must incorporate a monitoring and warning feature that will provide an indication to the appropriate flight crewmembers whenever the state-of-charge of the batteries has fallen below levels considered acceptable for dispatch of the airplane.

(9) The Instructions for Continued Airworthiness required by 14 CFR 25.1529 must contain maintenance requirements for measurements of battery capacity at appropriate intervals to ensure that batteries whose function is required for safe operation of the airplane will perform their intended function as long as the battery is installed in the airplane. The Instructions for Continued Airworthiness must also contain procedures for the maintenance of lithium-ion batteries in spares storage to prevent the replacement of batteries whose function is required for safe operation of the airplane with batteries that have experienced degraded charge retention ability or other damage due to prolonged storage at a low state of charge.

The FAA noted that these special conditions were “not intended to replace 14 CFR 25.1353(c) in the certification basis of the Boeing 787-8 airplane” and that the special conditions applied “only to lithium-ion batteries and their installations.” The FAA also noted that the requirements of 14 CFR 25.1353(c) remained in effect “for batteries and battery installations of the Boeing 787-8 airplane that do not use lithium-ion batteries.”

Appendix C: Comments From the Bureau d'Enquêtes et d'Analyses pour la Sécurité de l'Aviation Civile



BEA
Bureau d'Enquêtes et d'Analyses
pour la sécurité de l'aviation civile

Le Bourget, le 28 octobre 2014

To : David Helson
NTSB investigator

Subject : BEA comments to append to the NTSB draft report for the serious incident to the Boeing 787-8 registered JA829J

Dear David,

Thank you for having associated the BEA (Bureau d'Enquêtes et d'Analyses pour la sécurité de l'Aviation Civile) with the investigation into the serious incident to B 787-8, registered JA 829J, and for giving us the opportunity to make comments on the Draft Final Report. We hereby present you with the comments that we would like to be appended to the final report in accordance with the provisions of Annex 13.

We are also proposing safety actions to be taken in the light of the investigation done.

The BEA remains at your disposal for any further information that you may wish to obtain.

Yours sincerely,

Emmanuel DELBARRE
BEA Accredited representative

Aéroport du Bourget
Zone Sud - Bâtiment 153
200 rue de Paris
93350 Le Bourget Cedex
France
Tel : +33 1 49 92 72 00
Fax : +33 1 49 92 72 03
www.bea.aero

BEA proposed comments to append to the report.

The BEA agrees that an internal short circuit within a cell of the APU battery led to thermal runaway that cascaded to thermo-mechanical propagation to surrounding cells.

However, the initiating phenomenon of the internal short circuit has not been identified during the investigation and it was impossible to conclusively determine the origin of the internal short circuit. Indeed, the internal short circuit is not a root cause by itself but a "way point" in the chain of events. The reason of the development of the short circuit inside the first cell could not be determined from post incident laboratory testing and subsequent engineering analysis of potential failure modes.

The fact that the root cause couldn't be determined should also be included in the section 3.1 Findings and also in the section 3.2 Probable Causes.

In addition, the NTSB report also lists some concerns that have been observed during the investigation (refer to sections 2.3 and 2.4), namely:

- The **presence of wrinkles** generated by the manufacturing process or influenced by the manufacturing process and developed during charge and discharge due to swelling/deswelling. The report considers that "wrinkles and folds can modify anode-to-cathode ratio locally, resulting in lithium deposits at the anode surface". The BEA states that although wrinkles were observed during DPA of the incident batteries, their effect on lithium deposition hasn't been proved (no Li-metal was found by XPS analysis). The various tests performed by GSY, on LVP 65 cells didn't reveal neither Li metal dendrites nor internal short with heat generation and venting.
- The **presence of FOD** related to the manufacturing process : no FOD was identified during the teardown of the incident battery and during post incident investigation on exemplar batteries.
- The **propensity of cells to generate self-heating** below the upper operational specified temperature (70°C) (section 2.4.3): Lab in charge assessed self-heating rate in cell at 100%SOC and stated that cells self-heat at temperature as low as 60°C with a self-heating rate near 0.01°C.min-1. However the sensitivity threshold of this equipment is as high as at 0.02°C.min-1. Values below the sensitivity threshold are not relevant. The sensitivity threshold is reached at 85°C for 100%SOC cell1 which is consistent with the current state of the art on lithium-ion battery.
- The **seal assembly and rivets integrity**. Thales testing shows that when the battery is used within its specified power and temperature ranges then no anomaly occurs².

Proposed safety actions to be taken

The BEA suggests to take into account of the various reports and the Thales testings and to consider the following safety actions to be taken :

¹ UL report entitled "Multi-Level Forensic and Functional Analysis of the 787 Main/APU Lithium Ion Battery" Doc. ref. NTSBC130004 2014, p 120-123.

² THALES Submission to the National Transportation Safety Board For the DCA13IA037 page 17 & 18

- “As the investigation could not identify the mechanism of the internal short circuit, the aircraft manufacturer and the equipment manufacturers should :
- continue studies of internal short circuit mechanism considering the effects of internal and external phenomenon that potentially impacts the Li-ion batteries in operational conditions, such as the aircraft electrical environment and particularly the risk associated to potential transient current and voltage ;
 - continue studies on the impact of other environmental parameters such as humidity and vibrations ;
 - continue efforts to improve Li-ion batteries quality and its reliability.

BEA detailed comments on the NTSB draft report on the serious incident to the Boeing 787-8 registered JA829J.

Page/Section:	Sentence/Comment:
	§ 1.4.3 Disassembly of the incident Battery Existing sentence: “There was no evidence of cell-to-battery case shorting before the thermal event, bus bar shorting or resistive heating of bus bar ...”.
Comment:	APU battery has demonstrate the presence of a protrusion on side 3 facing Cell 5. At the place of the protrusion the cell 5 exhibits a small hole. The Cell 5 windings also demonstrate holes that are consistent with materials that had penetrated into the cell 5 and its windings. The material found in the cell 5 and its winding were chemically analyzed and confirmed to be Battery aluminum alloy. This was interpreted by the investigation team as resulted from an arcing phenomenon between the cell 5 casing and Battery case. At this stage there is no evidence to say that arcing occurs before or during the thermal event. Modification proposal “There was evidence of cell 5-to-battery case shorting during the JAL event. The exact time, at which the shorting between cell 5 and battery case occurs, is not determined. In addition there is no evidence of bus bar shorting or resistive heating of bus bar”

Page/Section:	Sentence/Comment:
	§ 1.4.3 Disassembly of the incident Battery Existing sentence: There was also no visible evidence of water (resulting from condensation) within the battery case or external surfaces of the battery cells.
Comment:	APU battery has undergone a very significant heating during the thermal runaway. Therefore, if water, for instance from condensation, had been present, it has been vaporized during thermal runaway. Consequently, it was impossible to find any evidence of water inside the battery after the event. In order not to rule out this parameter, the following wording is proposed.

	Modification proposal “Due to high heat exposure of the APU battery during the incident event, it was obviously not possible to conclude on water presence resulting from condensation within the battery before or during the incident event.”
--	--

Page/Section:	Sentence/Comment:
	§ 1.5.3 Examinations of main battery cells from incident airplane Existing sentence: “More than 100 areas of “ingressed underlithiation” of the anode (that is, areas of the anode than are incompletely charged) were found”
Comment:	Color variations in full charge carbon anode are known to be due to underlithiation. However, color is only a semi-quantitative and subjective measure of Li state of charge [1], [2]. Additionally XPS analysis from Carderock don't show any obvious difference in lithium concentration between “blue or purple areas”, called “underlithiated” and gold areas, called “fully lithiated” Modification proposal More than 100 areas of “ingressed” underlithiation of the anode were found (that is, areas of the anode than are incompletely charged. However Carderock XPS analysis doesn't show any significant concentration difference of lithium element between blue/purple area, called underlithiated area, and gold area, called fully lithiated area) [1] Direct in situ measurements of Li transport in Li-ion battery negative electrodes, Harris et al, Chemical Physics Letters 485 (2010) 265–274 [2] Revisited structures of dense and dilute stage II lithium-graphite intercalation compounds, D. Billaud et al, J. Phys. Chem. Solids 57 (1996) 775.

Page/Section:	Sentence/Comment:
	§ 1.5.3 Examinations of main battery cells from incident airplane Existing sentence: “According to TIAX, these areas indicate that mechanical abnormalities in the windings results in uneven charging of the anode and might have caused lithium to deposit adjacent to underlithiated area.”
Comment:	This explanation, representing TIAX' interpretation, is only based on a phenomenal description and is not supported by any technical and scientific demonstration, simulation, calculation and complete testing. Modification proposal “According to TIAX, these areas indicate that, in theory, mechanical abnormalities in the windings might result in uneven charging of the anode and might have caused lithium to depose adjacent to underlithiated area. However TIAX didn't perform

	chemical analysis, simulation, calculation and appropriate testing to validate this scenario. At the opposite, Carderock showed through deep chemical analysis (XPS) that the observed silver colored deposits didn't contain any lithium metal, invalidating the explanation proposed by TIAX"
--	---

Page/Section:	Sentence/Comment:
	§ 1.5.3 Examinations of main battery cells from incident airplane Existing sentence: "In its submission to the NTSB for this incident, GS YUASA stated that, after the incident, it conducted more than 100 cold charge cycle tests, and all of the tests revealed a loss of capacity when charging repeatedly at -9.4°F."
Comment:	The reader would surely be interested not only by the loss of capacity during charge/discharge cycles which is normal behavior of this battery technology in these specific test conditions, but it would be of greater interest to learn there from those tests that no dendrite was created during those cold charge cycles. For information, the 105 cycles of tests widely cover the time period that the incident battery was exposed onboard airplane. Such important and relevant information needs to be provided to the reader in order to have better understanding of potential dendrite presence or not according to the operating conditions specified on this airplane. Modification proposal "In its submission to the NTSB for this incident, GS YUASA stated that, after the incident, it conducted more than 100 cold charge cycle tests, and all of the tests revealed a loss of capacity when charging repeatedly at -9.4°F and no lithium plating was observed".

Page/ Section:	Sentence/Comment:
	§1.5.4 Cell-level abuse tests Existing sentence: "... cells started to generate internal heat at temperatures as low as 144°F, which is below the allowable operational temperature of the battery"
comment	As written by BEA/Thales comments on the airworthiness group report, UL used an ARC equipment to assess self-heating rate in cell at 100%SOC and 0%SOC. The sensitivity threshold of this equipment is given at $0.02^{\circ}\text{C}\cdot\text{min}^{-1}$ by the equipment manufacturer (cf UL report p121 and 122). However UL states that cells self-heat at temperature as low as 60°C (self-heating rate near $0.01^{\circ}\text{C}\cdot\text{min}^{-1}$, but the self-heating rate at this temperature is below the sensitivity threshold of

	the equipment. Values below the sensitivity threshold are not relevant. The sensitivity threshold is reached at 110 °C for 0%SOC cell (cf p 121, UL report) and 85°C for 100%SOC cell (cf UL report 122). Modification proposal "...cells started to generate internal heat at temperatures as low as 85°C (100%SOC) and 110°C (0%SOC) (and remove the last part of the sentence as the battery is qualified for temperatures comprised between -18°C and 70°C).
--	--

Page/Section:	Sentence/Comment:
	§ 1.5.5 Rivet observations during cell- and battery-level testing Existing sentence: "the aluminum rivets on the positive terminal of cell 5 increased progressively through 14 cycles to a maximum of 157°C/315°F"
Comment:	Some precision need to be added: - In some case, the UL tests were performed with an average current of 940A. - The worst case with a battery voltage at 20Vdc corresponds to a power of 18.8KW during the simulation of APU start. - With a battery fully charged before the APU start simulation, the battery voltage is between 25 and 26Vdc the power was comprise between 23.5KW and 24.4KW. - Thales tests have demonstrated that the rivets are designed to withstand APU start with a maximum power of 18KW in all the temperature range in compliance with Boeing SCD. - In the case of APU start out of Boeing SCD (> 18KW) the rivets are damaged and this damage are irreversible. Modification proposal Taking into account of Thales testing and submission, this paragraph should be amended by adding that in the operating range this phenomenon does not occur.

Page/Section:	Sentence/Comment:
	§ 1.5.5 Rivet observations during cell- and battery-level testing Existing sentence: "<i>The cell leakage test showed that the seal of the cell was damaged</i>"
Comment:	Note that all the tests performed by UL and reported in the section refer to battery that was tested outside of the power specified domain over 18 kW as mentioned in the previous comment. Thales tests exactly showed the same results after abnormal APU start (>18KW) BEA suggests taking into account the THALES results in this chapter or clearly indicates that tests were performed out of power specified domain.

Page/Section:	Sentence/Comment:
	§ 2.1 Failure sequence Existing sentence: <i>"A battery-level test showed that condensation could occur within the battery and result in shorting path between the cell and the battery cases, and cell-level test with moisture showed that a cell failure could occur and result in arcing, shorting, and heat damage internal to cell header. However the damage observed during the cell-level test was not found in the cell header from the incident APU battery. In addition, airplane flight test data did not show any abnormal electrical transients that could lead to battery failure."</i>
Comment:	<i>During the investigation, it was not possible to show that the JAL Boston Cells, and specifically cell 5 and cell 6, had experienced or not shortings as described in the Thales submission. In addition based on information provided by NTSB, the flight test recording system was capable of recording signals that had frequency up to hundreds of Khz. The Transient phenomena that are seen as a potential contributing factor by BEA and Thales are in a range of 2 to 4 Mhz. That means that such phenomenon couldn't be captured by the aircraft flight test installation.</i> The BEA suggests taking into account the THALES results in this chapter and to modify it as follows : <i>The information collected during the investigation does not allow to determine if the damages observed during the cell-level test on the cell headers were similar to the incident APU battery. In addition, during the airplane flight test, the system used to collect the electrical data had limited electrical transients recording capabilities (in the range of hundreds Kilo Hertz) and did not make it possible to capture electrical transient phenomenon that occurs with High Frequency range (Mhz).</i>

References

- Airworthiness Directives; The Boeing Company Airplanes. *Federal Register*. Vol. 78. No. 36. February 22, 2013. 12231.
- Airworthiness Directives; The Boeing Company Airplanes. *Federal Register*. Vol. 78. No. 81. April 26, 2013. 24673.
- Baldwin, Richard S., William R. Bennett, Eunice K. Wong, MaryBeth R. Lewton, and Megan K. Harris. "Battery Separator Characterization and Evaluation Procedures for NASA's [National Aeronautics and Space Administration] Advanced Lithium-Ion Batteries." NASA Technical Memorandum NASA/TM-2010-216099. NASA, Washington, DC, 2010.
- Belov, D. and M.H. Yang. "Failure Mechanism of Li-ion Battery at Overcharge Conditions." *Journal of Solid State Electrochemistry* 12 (2008): 885-894.
- Chapin, J. Thomas, Pravinray D. Gandhi, and Paul W. Brazis, Jr. "NTSB Battery Tests—Final Report for 787 Battery (Asset 436) Tested at 70°C, Ungrounded." Underwriters Laboratories LLC, Northbrook, IL, 2014.
- Chapin, J. Thomas, Pravinray D. Gandhi, and Paul W. Brazis, Jr. "NTSB Battery Tests—Final Report for 787 Battery (Asset 445) Tested at 15°C, Grounded." Underwriters Laboratories LLC, Northbrook, IL, 2014.
- Condra, Lloyd W. *Reliability Improvement With Design of Experiments*. New York, NY: Marcel Dekker Inc., 1993.
- Doughty, Daniel H. and Chris C. Crafts. *FreedomCAR Electrical Energy Storage System Abuse Test Manual for Electric and Hybrid Electric Vehicle Applications*. SAND2005-3123, Sandia National Laboratories, Albuquerque, New Mexico, 2006.
- FAA (Federal Aviation Administration), Boeing 787-8 Critical Systems Review Team. *Boeing 787-8 Design, Certification, and Manufacturing System Review*. Washington, DC: FAA, 2014. www.faa.gov/about/plans_reports/media/787_Report_Final.pdf
- FAA, William J. Hughes Technical Center. *Extinguishment of Lithium-Ion and Lithium-Metal Battery Fires*. DOT/FAA/TC-13/53, Atlantic City, NJ: FAA, 2014.
- Fisher, D.L., R. Schweickert, and C.G. Drury. "Mathematical Models in Engineering Psychology: Optimizing Performance." In *Handbook of Human Factors and Ergonomics*, by ed. G. Salvendy, 997-1024. Hoboken, NJ: John Wiley and Sons, 2006.

Japan Transport Safety Board. *Emergency Evacuation Using Slides, All Nippon Airways Co., Ltd., Boeing 787-8, JA804A, Takamatsu Airport, At 08:49 JST, January 16, 2013.* Aircraft Serious Incident Investigation Report AI2014-4, Tokyo, Japan: JTSB, 2014. www.mlit.go.jp/jtsb/english.html

Mansour, Azzam N., D. Fuentevilla, and Jim A. Zaykoski. *XPS [x-ray photoelectron spectroscopy] Investigation of a Carbon Anode, Separator from a Cold Charged Li-Ion Cell and a Lithium Foil Control Sample, Factual Report.* West Bethesda, MD: Naval Surface Warfare Center, Carderock Division, 2014.

Mikolajczak, C., M. Kahn, K. White, and R.T. Long. *Lithium-Ion Batteries Hazard and Use Assessment Final Report.* Quincy, MA: The Fire Protection Research Foundation, 2011.

NASA Technical Standard, "Electrical Bonding for NASA Launch Vehicles, Spacecraft, Payloads, and Flight Equipment." NASA-STD-4003A, Washington, DC, 2013.

Reddy, Thomas B. and David Linden. *Linden's Handbook of Batteries.* Fourth edition. New York, NY: McGraw-Hill, 2011.

SAE International. "Guidelines for Development of Civil Aircraft and Systems." *SAE Aerospace Recommended Practice 4754A.* Warrendale, PA: SAE, 2010.

Special Conditions: Boeing Model 787-8 Airplane; Lithium Ion Battery Installation. *Federal Register.* Vol. 72. No. 82. April 30, 2007. 21162.

Special Conditions: Boeing Model 787-8 Airplane; Lithium Ion Battery Installation. *Federal Register.* Vol. 72. No. 196. October 11, 2007. 57842.

Tabaddor, Mahmood, Helena Chiang, Dennis Grzic, and Alvin Wu. *Multi-Level Forensic and Functional Analysis of the 787 Main/APU Lithium-Ion Battery.* Northbrook, IL: Underwriters Laboratories LLC, 2014.

Taheri, Peyman, Scott Hsieh, and Majid Bahrami. "Investigating Electrical Contact Resistance Losses in Lithium-Ion Battery Assemblies for Hybrid and Electric Vehicles." *Journal of Power Sources* 196 (2011): 6525-6533.

Teichner, W.H. "The Detection of a Simple Visual Signal as a Function of Time of Watch." *Human Factors* 16 (1974): 339-353.

TIAX LLC. *Report on Soft-Short Testing of Batteries 149, 305, 344, 376, and 412.* Lexington, MA: TIAX, 2013.

—. *Review of Cell 6 Tear Down Samples of Incident APU Battery.* Lexington, MA: TIAX, 2013.

—. *Teardown of LVP65 Li-Ion Cell 1 from Battery 412.* Lexington, MA: TIAX, 2014.

Wang, Carl and Alvin Wu. *Cell-Level IIISC [indentation-induced internal short circuit], Nail Penetration, Hot Pad and ARC Tests for LVP65*. Northbrook, IL: Underwriters Laboratories LLC, 2014.

Wang, Carl, Helena Chiang, and Alvin Wu. *Analysis of Asset 459 Cell 5*. Northbrook, IL: Underwriters Laboratories LLC, 2014.

Appendix G

CosMX Exhibit 1003, Page 246 of 512



A novel intrinsically porous separator for self-standing lithium-ion batteries

Pier Paolo Prosini*, Paola Villano, Maria Carewska

ENEA, IDROCOMB, C.R. Casaccia, S.P. 89, Via Anguillarese 301, 00060-Rome, Italy

Received 27 August 2002

Abstract

γ -LiAlO₂, Al₂O₃ and MgO were used as fillers in a PVdF-HFP polymer matrix to form self-standing, intrinsically porous separators for lithium-ion batteries. These separators can be hot-laminated onto the electrodes without losing their ability to adsorb liquid electrolyte. The electrochemical stability of the separators was tested by constructing half-cells with the configuration: Li/fibre-glass/filler-based separator/electrode. MgO-based separators were found to work well with both positive and negative electrodes. An ionic conductivity of about 4×10^{-4} S cm⁻¹ was calculated for the MgO-based separator containing 40% 1 M solution of LiPF₆ in an EC/DMC 1:1 solvent. Self-standing, lithium-ion cells were constructed using the MgO-based separator and the resulting battery performance evaluated in terms of cyclability, power and energy density.

© 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Lithium-ion batteries; PVdF-HFP; Polymer electrolyte

1. Introduction

Lithium-ion rechargeable batteries with LiCoO₂ cathodes and carbon anodes are rapidly replacing other battery systems due to their high energy and power densities. Since the introduction of lithium-ion batteries by SONY in 1991 [1], the market for these has grown to around 400 million cells per year by 2000 [2]. Energy densities of about 120–130 Wh kg⁻¹ are now available in cell using metal cans, with higher values of 160–170 Wh kg⁻¹ estimated for cells with light weight packaging [3]. The concept suggested by Bellcore [4,5] to construct a light weight battery is based on the preparation of a free-standing battery stack that needs no external pressure to maintain contact between the electrodes. The electrodes and separator in the Bellcore system contain a plasticizer that can be extracted after lamination, leaving a porous structure, which is subsequently activated by filling the cell with a liquid electrolyte.

Recently, PEO based composite polymer electrolyte prepared using nano-scale ceramic fillers such as SiO₂, Al₂O₃, TiO₂ and MgO [6–8] have shown enhanced ionic conductivities and improved mechanical and thermal stability. The effect of inorganic oxides such as SiO₂ [9], Al₂O₃ [10], CeO₂ [11] and TiO₂ [12] on the electrochemical properties of plasticized polymer electrolytes have been also studied. It has been shown that ceramic fillers may greatly influence the characteristic and the properties of polymer electrolyte enhancing the mechanical stability and the conductivity. Furthermore, the liquid-phylic tendency of these particles may help in holding the liquid component within the membrane structure.

Abraham et al. [13] prepared ceramic-polymer composite electrolytes from Li-ion conducting ceramic PVdF gel electrolytes. They found that the nature of the ceramic did not influence the conductivity significantly.

A new concept for obtaining a porous separator that can be laminated to the electrodes in a solvent-extraction-free process to produce a battery stack was described recently [14]. The separator was produced by casting a dispersion of inert particles of Li_{0.35}La_{0.55}TiO₃ in a solution of high molecular weight polyethylene

* Corresponding author. Tel.: +39-6-3048-6768; fax: +39-6-3048-6357

E-mail address: prosini@casaccia.enea.it (P.P. Prosini).

(UHMWPE) in decaline: 1 wt.% UHMWPE was sufficient to give free-standing anodes and cathodes. In paper [14], it was stated that $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$, which is known as a solid-state ion conductor, does not contribute to the conductivity of the system. The particles only help to create the porous structure. Therefore, other particles such as Al_2O_3 or SiO_2 can also be used for this purpose.

In this paper we describe our results concerning the construction of self-standing plastic lithium-ion batteries based on the intrinsically porous separator concept [15]. $\gamma\text{-LiAlO}_2$, Al_2O_3 and MgO were used as fillers in a PVdF-HFP polymer matrix to form self-standing, intrinsically porous separators that can be laminated under heat and pressure without losing their ability to swell on the addition of liquid electrolyte. Lithium-ion battery cells were assembled, hot laminated and activated by soaking in liquid electrolyte; battery performance was then evaluated as a function of the discharge rate and cycle number.

2. Experimental

2.1. Preparation of electrodes, separators and cells

2.1.1. Cathode

LiMn_2O_4 powder (Merck, battery grade) was used as the cathode active material. Carbon black (Super P, MMM carbon, Belgium) was used as a conductive agent. PVdF-HFP copolymer (Aldrich) was used as a binder and cyclohexanone (Fluka) was used as a solvent to prepare the electrode slurry. The active electrode material and the conductive agent were mixed in a weight ratio of 18:1. The polymer was dissolved in the solvent in a weight ratio of 1:19 and heated at 70 °C to facilitate dissolution. The blend of powders was added to the polymer solution in a weight ratio of 1:1. Approximately 20% by weight of cyclohexanone was added to the mixture to regulate the viscosity. The mixture was mixed for 20 h. The paste so-obtained was spread over a glass using calibrated slits. The weight after drying of the electrode was 16 mg cm^{-2} with a thickness of 110–150 μm . The electrode was cold-calendered to reduce the thickness.

2.1.2. Anode

MCMB graphite (Osaka Gas, Japan) was used as the active anode material. Carbon black (Super P, MMM carbon, Belgium) was used as a conductive agent. PVdF-HFP copolymer (Aldrich) was used as a binder and cyclohexanone (Fluka) was used as a solvent to prepare the electrode paste. The graphite and the carbon were mixed intimately in a weight ratio of 18:1. The blend of powders was added to the polymer solution, prepared as described above, in a weight ratio of 1:1.

About 30% by weight of cyclohexanone was added to the mixture to obtain the correct viscosity. The mixture was then mixed for 20 h, and the paste spread over a glass using calibrated slits. The weight after drying the electrode was 2–4 mg cm^{-2} with a final thickness of 40–80 μm .

Both the electrodes were dried in an oven at 110 °C for 1 day prior to use. The porosity of the electrodes was calculated using the formula:

$$\text{porosity} = 100 \times \frac{\text{true density of the active electrode material} - \text{density of the coating}}{\text{true density of the active electrode material}}$$

The resulting electrode porosities were 54 and 38% for the positive and the negative electrode, respectively.

2.1.3. Separators

Three inorganic oxide were used as the filler to make the separator. $\gamma\text{-LiAlO}_2$ (Cyprus Foote Mineral Co, HAS10), MgO (BDH), Al_2O_3 (Aldrich) were dried and sieved to remove larger aggregates. The polymer was dissolved in the solvent in a weight ratio of 1:19, and heated at 70 °C to facilitate dissolution. The selected powder was added to the polymer solution in a weight ratio of 1:2. The mixture was mixed for 48 h. The paste so-obtained was spread over a glass using a calibrated slit of 100 μm , to give a thickness after drying of 30–50 μm .

2.1.4. Battery cells

The electrode (positive or negative) and the selected separator were layered and hot laminated at 80 °C. A fibre-glass disk was used as an additional separator, and lithium metal was used both as counter and reference electrode. The cells were assembled in T-shaped hydraulic connectors. The cells were soaked in a 1 M solution of LiPF_6 (Merck, battery grade) in EC/DMC 1:1. Stainless Steel (SS) cylinders were used as current-collectors. Hereafter, we refer to these cells as ‘half-cells’.

To create lithium-ion battery cells, the layered cathode/separator/anode were hot laminated at 80 °C. The cells were soaked in a 1 M solution of LiPF_6 in EC/DMC 1:1, dried on blotting-paper and assembled in a T-shaped hydraulic connector. Metallic lithium, which has been considered as a suitable reference electrode for Li-based redox system [16,17] was used as reference electrode. SS cylinders were used as current-collectors. The cells were assembled in a dry-room (R.H. < 0.1% at 20 °C).

2.2. Electrochemical tests

2.2.1. Ionic conductivity

Ionic conductivities were determined from complex impedance spectra measured using a frequency response

analyzer (FRA Solartron, model 1260). The separator was soaked in a 1 M solution of LiPF_6 in EC/DMC 1:1, dried on blotting paper and sandwiched in a T-shaped hydraulic connector between two SS cylinders. The cell was assembled in a dry-room (R.H. < 0.1% at 20 °C).

2.2.2. Electrochemical compatibility

The electrochemical compatibility of the separators with the electrodes was tested by cycling the half-cells. Charge/discharge tests were performed using a Maccor Battery Cycler (Maccor 4000). Graphite/Li half-cells were discharged at C/2 rate to 5 mV and then trickle discharged at 5 mV until the current flow decreased to a C/20 rate. The cell was charged at C/2 rate to 2.5 V. $\text{LiMn}_2\text{O}_4/\text{Li}$ half-cells were charged at C/6 rate and discharged at C/4 rate between 4.4 and 3.6 V. The compatibility was considered good when the half-cell cycled well with high capacity and unitary charge/discharge ratio. Alternatively, to evaluate anodic stability, a cell was prepared by sandwiching the separator, filled with the electrolyte solution, between a SS electrode and a lithium foil. The electrochemical stability was tested by slowly increasing the cell voltage until the onset of current flow. The voltage was swept from OCV towards a more anodic potential with a scan rate of 0.5 mV s^{-1} by means of an AMEL voltammetric set-up.

2.2.3. Battery performance

Lithium-ion cells were charged at C/2 rate at a constant capacity of 0.28 mAh g^{-1} based on the weight of the active anode material, and discharged at C/2 rate to 1.5 V.

To test the effect of different discharge rates, the cell was subjected to various discharge rates: C/4, C/2, 1C and 3C. The cell was always charged using the same procedure to insure identical initial conditions: a constant current step at 1C rate until the voltage reached 4.2 V, followed by a constant voltage step until the current fell below C/10 rate.

3. Results and discussion

3.1. Electrochemical compatibility

The search for the best filler to realize a self-standing plastic lithium-ion battery was quite difficult; we found that some inorganic filler are not inert with respect to the electrodes. When we started to select an appropriate filler for the separator, we concentrate our efforts on the compatibility of the filler with the anode, because we assumed that the major instability would be at the negative electrode/separator interface rather than on the positive side. This arose from the fact that the metal ions of the inorganic oxides that we selected are in a very

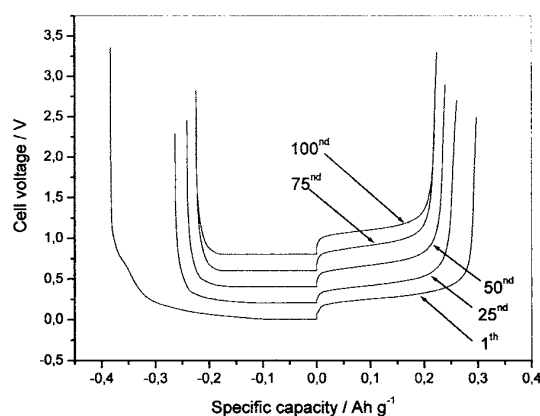


Fig. 1. Selected voltage profiles for a Li/fibre-glass/ γ - LiAlO_2 -based separator/anode cell. Discharge current was 1.27 mA cm^{-2} to 5 mV vs. Li, then the cell was left to equilibrate until the current density was less than 0.127 mA cm^{-2} . Charge current density was 1.27 mA cm^{-2} . The anode loading of graphite was 5.4 mg cm^{-2} .

high oxidation state, and can therefore take part in a reduction reaction when in contact with the anode, especially in its fully lithiated state. For this same reason, we assumed that the oxides could exhibit higher anodic stability. γ - LiAlO_2 was demonstrated to have a good stability towards a lithium metal anode in poly(ethylene oxide)-based electrolytes [18] and was selected as the first filler for the intrinsically porous separator. We made a half-cell battery by coupling a graphite electrode to the γ - LiAlO_2 -based separator. Fig. 1 shows the voltage profile for selected cycles. The charge/discharge ratio during the initial cycles was influenced by the formation of the solid electrolyte interface [19]. After a few cycles, the charge/discharge ratio approached unit. Its value after the 20th cycle was greater than 0.992. About 50% of the total capacity was accumulated during the galvanostatic discharge at C/2 rate. The cell was cycled for 100 full cycles with good capacity retention.

This result was very encouraging and showed that γ - LiAlO_2 has good stability in contact with a graphite electrode. Anodic stability of γ - LiAlO_2 -based separator was tested by sandwiching the separator between a lithium metal electrode and a blocking electrode, and slowly increasing the cell voltage until onset of current flow was observed. In Fig. 2 the current–voltage profile is reported for a γ - LiAlO_2 -based separator containing 40 wt.% liquid electrolyte. A very low current ($1.5 \text{ } \mu\text{A cm}^{-2}$) was observed in the system at the start of the experiment, becoming approximately $3 \text{ } \mu\text{A cm}^{-2}$ at 4.2 V. On further increase cell voltage, a current began to flow, indicating the onset of some electrolyte decomposition process. From this we concluded that the electrochemical stability of the separator was good enough for it to be used with high-voltage cathode materials. The cathode compatibility of the separator

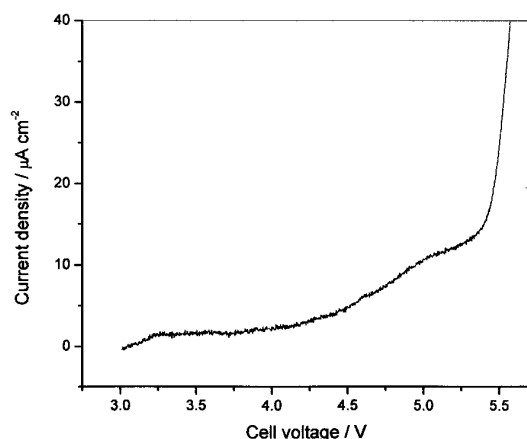


Fig. 2. Current–voltage profile for a LiAlO_2 -based separator containing a 40 wt.% of 1 M solution of LiPF_6 in EC/DMC 1:1 liquid electrolyte sandwiched between lithium metal and SS electrodes. Scan rate 0.5 mV s^{-1} .

was also tested by cycling the half-cell formed by coupling the separator with a LiMn_2O_4 -based electrode. Surprisingly, the half-cell did not cycle. During the first charge, the cell voltage increased initially, but then decreased after a short time, clearly indicating an electrolyte decomposition process. We conclude that the stability is strongly influenced by the nature of the separator/electrode interface, with high stability found for SS and poor stability for the composite cathode. A catalytic interaction between the electrolyte, the γ - LiAlO_2 particle and the cathode materials (LiMn_2O_4 and carbon black) at the separator/electrode interface could be responsible of the poor stability of the γ - LiAlO_2 -based separator in contact with the cathode. On the basis of our previously reported result on PEO-based electrolyte [20], we must therefore conclude that the voltammetry test between two SS current collectors is not adequate to evaluate the stability of electrolytes, since it does not reproduce the actual cell environment.

Our interest thus shifted to other fillers with good cathode stability. Fig. 3 shows the cycling behaviour of half-cells assembled using separator membranes based on MgO and Al_2O_3 . Both the membranes were found to have good stability when in contact with the high voltage cathode, with specific capacities around 120 mAh g^{-1} and good capacity retention upon cycling. Fig. 4 shows a selected charge/discharge cycle for a LiMn_2O_4 -based cathode/ MgO -based separator/fibre-glass/ Li cell. It is possible to observe two well resolved lithium intercalation plateaus at 4.08 and 4.20 V vs. Li, and corresponding de-intercalation plateaus at 4.02 and 3.86 V vs. Li, in good agreement with the data reported in literature [21] and related to a two-phases intercalation/de-intercalation process.

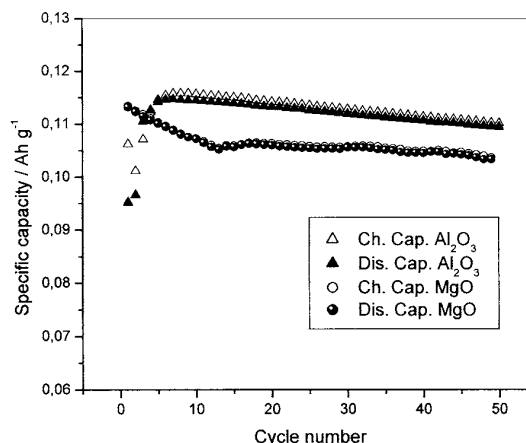


Fig. 3. Specific capacity for two half-cells realized with different separators, the fillers used to prepare the separators are reported in the figure. The insertion/release process was driven at a current density of 0.5 mA cm^{-2} in charge and 0.76 mA cm^{-2} in discharge. The cathode loading of LiMn_2O_4 was 15.3 mg cm^{-2} .

Testing the anode compatibility for these inorganic oxides, we found that only MgO exhibited good stability upon cycling. Fig. 5 shows the voltage profile recorded for a selected cycle. The cell cycled better than for the γ - LiAlO_2 -based separator in terms of larger reversible capacity and smaller voltage hysteresis between the charge and discharge half-cycles. About 94% of the charge was accumulated during the galvanostatic step. After a few cycles, the charge/discharge ratio approached unit. Its value after the 20th cycle was greater than 0.992.

On the other hand, the half-cells prepared with separator based on Al_2O_3 never reached the end of their first cycle (5 mV vs. Li).

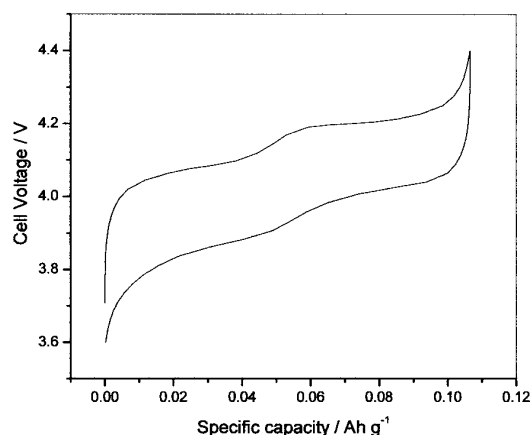


Fig. 4. Voltage profile for a Li /fibre-glass/ MgO -based separator/cathode cell. The cathode loading of LiMn_2O_4 was 15.3 mg cm^{-2} . Discharge current was 0.76 mA cm^{-2} . Charge current density was 0.5 mA cm^{-2} .