IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent of:	Clive P. Bosnyak, et al.	
U.S. Patent No.:	10,153,483	Attorney Docket No. 18768-0210IP6
Issue Date:	Dec. 11, 2018	
Appl. Serial No.:	13/529,797	
Filing Date:	June 21, 2012	
Title:	LITHIUM ION BATTERIES USING DISCRETE CARBON NANOTUBES, METHODS FOR PRODUCTION THEREOF AND PRODUCTS OBTAINED THEREFROM	

SUPPLEMENTAL DECLARATION OF DR. YU ZHU

LGES 1056
LGES v. MRD
IPR2024-01013

TABLE OF CONTENTS

I. "Discrete carbon nanotubes"....2

II. OHATA-KAVAN....4

A. PO's assertions that the electrode active material is not in contact with the nanotubes in the Ohata-Kavan composition are inconsistent with Ohata's disclosure....4

1. PO's theory that there is no contact between nanotubes and electrode active material is illogical and technically inaccurate....5
2. The solubility of Ohata's binder in NMP belies PO's argument that Ohata's nanotubes remain fully embedded in the binder matrix....11
3. PO's own corroborating references refute its theory of complete embedding of Ohata's nanotubes in the binder material....12

B. The nanotubes in the Ohata-Kavan composition are discrete....16

C. PO fails to refute my earlier opinion regarding several distinct motivations for the Ohata-Kavan combination....17

1. PO's objections to my earlier opinion regarding motivations to combine Ohata and Kavan are premised on its incorrect theory that nanotubes are fully embedded in the binder....17

III. ADDITIONAL REMARKS....19

I, Yu Zhu, declare the following:

1. I am submitting this declaration (my "Second Declaration") in support of the Petitioner's Reply to Patent Owner's Response ("POR") to the Petition for *inter partes* review of the '483 Patent. This Second Declaration supplements certain portions of my prior declaration in support of the Petition for this IPR Proceeding (LGES-1003, "my First Declaration"). In my First Declaration, I address many topics, including (but not limited to) my background and qualifications, the level of skill in art, an overview of the '483 Patent, a POSITA's background knowledge, certain legal standards explained to me by counsel, legal principles applied for the purposes of my analysis and this declaration, and a detailed analysis of the prior art against the claim elements of the '483 Patent.

2. I maintain all of my earlier analysis and continue to hold the opinions expressed in my First Declaration. This Second Declaration does not replace my First Declaration. These declarations are complementary and should be read in tandem. Accordingly, this Second Declaration does not cover every topic addressed in my First Declaration.

3. In forming this Second Declaration, I have considered, among various documents, the following:

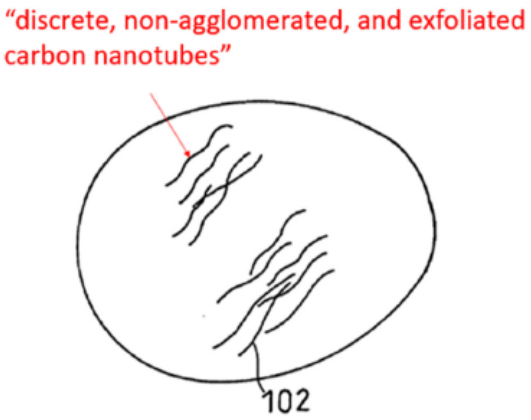
- MRD's Patent Owner Response ("POR") and documents cited therein
- LGES-1054 Deposition Transcript of Dr. Deborah Chung in IPR2024-01006 ('909 Patent)
- LGES-1059 "Increase the Mechanical Performance of Polyvinylidene Fluoride (PVDF)." M. Hou. Cheng. Advanced Materials Research Vols. 393-395 (2012).
- LGES-1061 U.S. Patent Pub. No. 2007/0060708 ("Wang")
- LGES-1062 "Alternative solvents for Lithium-Nickel-Cobalt-Manganese-Oxide electrode fabrication for lithium-ion-cells." F. Heim. Journal of Power Sources 558 (2023) 232546 ("Heim")
- LGES-1063 US Patent No. 8,540,902 ("Xing")

4. I have no financial interest in the parties or in the outcome of this proceeding. I am being compensated for my work as an expert on an hourly basis. My compensation is not dependent on the outcome of these proceedings or the content of my opinions.

I. "Discrete carbon nanotubes"

5. As an initial matter, PO's reference to my statements at deposition regarding the term "discrete" omits critical context. *See* POR, 52. My agreement that I was "identifying that nanotube [marked with the red arrow

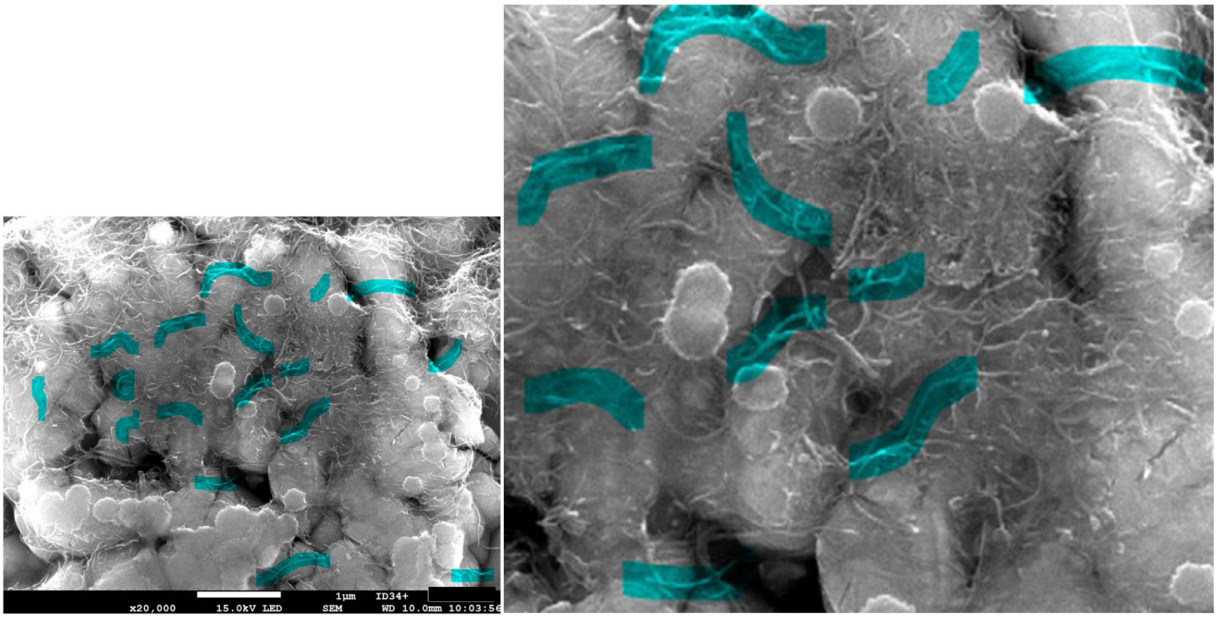
in the figure *infra*] as discrete because it's fully isolated from the other nanotubes" (MRD-2024, 10:21-11:12) was not intended to be a definition requiring that a nanotube necessarily must be isolated to be discrete. Instead, it is a description of the particular illustrated example, as described below. *See* LGES-1003, 50. As I explain in the next section, while "discrete" surely encompasses individually isolated nanotubes, it is not limited to only individually isolated nanotubes.



LGES-1003, 50

6. I understand that PO asserted infringement of its "discrete" carbon nanotubes in a related proceeding in district court. In particular, I have reviewed the SEMs images below that PO provided as alleged evidence of such assertion, and I understand that PO provided the blue highlighting to indicate what it regards as discrete nanotubes in the accused products.

However, it can be clearly seen that most if not all of the nanotubes that PO highlighted are touching another nanotube at some point along its length.



LGES-1050, 33 (original) *Id.* (cropped, magnified)

7. To be sure, a fully isolated carbon nanotube that is not touching any other nanotube is likely "discrete." However, this is a description, not a definition. Just as a carbon nanotube is undeniably a nanotube without all nanotubes needing to be carbon nanotubes, a fully isolated nanotube can be discrete without all discrete nanotubes needing to be fully isolated.

II. OHATA-KAVAN

A. PO's assertions that the electrode active material is not in contact with the nanotubes in the Ohata-Kavan composition are inconsistent with Ohata's disclosure

8. PO's interpretation of Ohata as producing a morphology having nanotubes fully embedded in the final electrode material formulation would preclude

there from being attachment between nanotubes and active material particles. This conflicts with Ohata's goal of using nanotubes to provide "an excellent conductive path in an electrode." LGES-1004, [0016]. In fact, contact between nanotubes and active material is necessary in order to have a functional electrode material.

1. PO's theory that there is no contact between nanotubes and electrode active material is illogical and technically inaccurate

9. PO argues that the nanotubes of the Ohata-Kavan combination are "fully embedded within and coated by the resin matrix," which "prevent[s] the active material from attaching to the surface of the CNTs." POR, 34-35, 42-44. I find this position illogical. A composition in which there was no contact between nanotubes and active material, as PO proposes, would be non-functional as a battery electrode material.

10. It is well-established that in a battery electrode material, there must be electrical contact between the active material and the conductive additive, due to the relatively low intrinsic electrical conductivity of the active material itself, to enable current flow through the electrode. MRD-2017, [0094] (CNTs "provide for the delivery of the electrons to the active material particles" and "form electrical bridges between the active material particles"); MRD-2018, [0092] (CNTs "ensure the distribution of electrons

to the particles of active material and . . . form electrical bridges between the particles of active material"). In other words, without contact between the conductive additive (*e.g.*, nanotubes) and the active material, the electrode material would be inoperable in a battery.

11. Given this basic physical understanding of the operation of a battery electrode, the PO's position is clearly flawed. PO argues that a "resin layer separat[es] the active material from the surface of the CNTs" such that "it is impossible for the active material to attach to the surface of the CNTs." POR, 45. This does not make sense. PVDF is non-conductive. A configuration in which CNTs are fully embedded within an insulating resin and thus electrically isolated from the active material is not viable and is inconsistent with battery fabrication practices that are specifically intended to enhance conductivity. LGES-1001: 2:4-5; MRD-2008, 2:63-65; MRD-2017, [0005], [0094]; MRD-2018, [0092]; LGES-1005, 1-2 ("Introduction" section generally explaining conductivity in the context of electrode fabrication, CNTs, and active materials); LGES-1004, Abstract, [0004]. Moreover, as I further explain below, PO's theory is incompatible with Ohata's stated goal of improving conductivity and with the actual electrochemical results disclosed in his data.

12. PO's position is inconsistent with the teachings of Ohata. Ohata aims to use nanotubes to "form an excellent conductive path in an electrode." LGES-1004, [0016]. This could not happen in PO's hypothetical structure. Indeed, Ohata's Table 3 reports good electrochemical performance that aligns with Ohata's objective, which would be impossible when all the CNTs are entirely embedded in PVDF, an electrically insulating material. *See* LGES-1004, Table 3. Again, nanotubes that are "fully embedded" within a non-conductive PVDF binder and thus not able to contact the active material particles, as PO proposes (*see* POR, 19), would be unable to provide such a conductive path. It is my opinion that an electrode material without contact between conductive additive (*e.g.*, nanotubes) and active material simply would be non-functional in practical use.

13. Dr. Chung offers no evidence that PVDF fails to dissolve under the relevant processing conditions. On the contrary, it is well known that PVDF is highly soluble in NMP. For instance, PVDF is fully dissolvable in NMP at concentrations greater than or equal to 10% by weight, indicating that all the example conditions disclosed in Ohata are within a fully dissolved range. *See, e.g.,* LGES-1062, 2; LGES-1004, [0032] (describing that "positive electrode material mixture paste was prepared by mixing 3.3 parts by weight of the resultant masterbatch, 100 parts by weight of lithium cobalt oxide

(LiCoO2) as an active material and 45 parts by weight of N-methyl-2-pyrrolidone with a mixer"); *see also id.*, [0040], [0044], [0046].

14. The dissolution of PVDF usually takes some time, a POSITA would have understood the dissolution of the polymer is necessary step and may require some time to dissolve it. If not given enough time and not using the right approach, PVDF may not be completely dissolved and will lead to the aggregated undissolved particles in NMP solution. This is a strict condition that a POSITA would try to avoid. Therefore, the dissolution of PVDF in the solvent, followed by mixing with insoluble electrode active materials (cathode/anode) to form a slurry, is a general procedure and an established practice in the battery manufacturing industry. There are also dedicated procedures developed specifically for dissolving PVDF in NMP.

15. Binder, conductive filler, and active materials are inseparable components in the battery slurry, and they interact collectively to form optimized electrode during casting process. Therefore, it is essential to consider the interactions between all components, even when the focus is on just one. Again, it is unreasonable to suggest that Ohata discusses the binder in isolation, without regard to the distribution of the conductive filler or its interaction with the active materials.

16. Ohata specifically describes how the binder interacts with the carbon filler and how these interactions are optimized during electrode formation in lithium-ion batteries, as reflected in the title of the patent: "ELECTRODE FOR A BATTERY AND PRODUCTION METHOD THEREOF." LGES-1004, Title.

17. In asserting that CNTs remain embedded within PVDF so as to prevent active ion material from contacting the CNTs, Dr. Chung fails to account for the weak interaction between PVDF and oxidized CNTs. PVDF is highly hydrophobic, while oxidized CNTs carry many hydrophilic functional groups, leading to poor interfacial adhesion. Hou (LGES-1059) is one of references that report this weak interaction between PVDF and CNTs. *See* LGES-1059, 5 ("[t]his result indicates that even though good dispersion of CNTs among the PVDF has been achieved, the interaction between CNTs and PVDF was relative weak").

18. Regarding pristine CNTs, although they have better interaction with PVDF than ox-CNTs, they (pristine CNTs) still have weak interaction with PVDF. Therefore, when NMP, PVDF, and CNTs are mixed, NMP will dissolve PVDF and substantially remove PVDF from CNT even if they were previously mixed. Again, as I explained above, a POSITA would understand the importance of dissolving PVDF for making good electrode

slurry and this will be the pursuit for any regular handling of battery electrode preparation.

19. Moreover, while PO uses field emission scanning electron micrograph (FESEM) images to show that CNT is fully embedded within PVDF, this is logically wrong in this context. *See, e.g.,* MRD-2006, ¶106 (citing MRD-2010, FIGS. 2(c) and 2(d)). In solution, the PVDF molecules will be dissolved in NMP and removed from the CNT. However, FESEM samples were carried out in vacuum, where all the solvent are dried. If all the solvent (liquid) is dried, all the solute (solid state contents like CNT and PVDF) will inevitably attached together. This experiment does not prove anything regarding the status of PVDF and CNT interaction because any polymer in solution dried together with CNT will yield same status. This is a logically false/misleading argument.

20. Further, MRD-2010 includes FESEM image of "a composite of 2% by weight functionalized multi-wall CNTs ('f-CNT) to 98% by weight PVDF)." This also does not equate to the state of the ox-CNT-resin paste after NMP dissolution. Accordingly, MRD-2010 cannot be properly used to tell the state of the Ohata-Kavan ox-CNTs after mixing with the NMP.

2. The solubility of Ohata's binder in NMP belies PO's argument that Ohata's nanotubes remain fully embedded in the binder matrix

21. Even if Ohata's nanotubes are fully embedded within the PVDF binder (which is not true as the conductive paths have been established in the masterbatch) of the masterbatch formulation, that embedding would not withstand the further processing of the masterbatch to prepare the electrode material mixture paste. Ohata's masterbatch is mixed with active material particles and NMP, such that "[t]he masterbatch ***was easily dissolved*** in [NMP]." LGES-1004, [0032]. Moreover, it was well-known that PVDF (the binder of the Ohata-Kavan masterbatch) is readily soluble in NMP. *See* LGES-1061, [0004] ("Typically, a combination of polyvinylidene fluoride (PVDF) and N-methyl-2-pyrrolidone (NMP) is used for the binder and the solvent. Polyvinylidene fluoride is soluble in NMP and allows for the preparation of a paste having a proper viscosity"); LGES-1062, 2.

22. The high solubility of PVDF in NMP directly refutes PO's allegation that even after processing with NMP, the nanotubes remain "fully embedded within and coated by the resin matrix," thus "preventing the active material from attaching to the surface of the CNTs." POR, 44. And in fact, extensive dissolution of PVDF make sense given the need for physical contact between the nanotubes and active material discussed *supra*.

23. Moreover, PO's position that "the PVDF coating would be more strongly bound to the oxidized CNTs" is inconsistent with literature reports of a weak interaction between functionalized nanotubes and PVDF. In fact, the weak interaction between PVDF and CNT were well-documented. As shown in Hou's paper (LGES-1059), it was known in the art that while CNTs disperse well among PVDF, interaction between CNTs and PVDF is relatively weak. LGES-1059, 5 ("[t]his result indicates that even though good dispersion of CNTs among the PVDF has been achieved, the interaction between CNTs and PVDF was relative weak." A POSITA would recognize that a solvent capable of dissolving g PVDF—such as NMP—can substantially (most, if not all) remove it from the CNT surface in solution, enabling direct interaction between the CNT and the active material particles to form strong bonding in solution.

3. PO's own corroborating references refute its theory of complete embedding of Ohata's nanotubes in the binder material

24. PO's explanation for why Ohata's nanotubes purportedly remain embedded in the binder is also refuted by PO's own corroborating references.

25. For instance, PO cites MRD-2017's Figure 2 to argue that carbon nanotubes remain embedded in PVDF "domains," even after NMP dissolution, thereby preventing contact with active material. MRD-2006, ¶123. But PO's

interpretation of this figure is speculative and contradicted by MRD-2017's own disclosure. MRD-2017 states that "[o]bservations with an SEM (see FIG. 2) showed that the CNTs are well dispersed around the micrometric $LiFePO_4$/C particles," and that the resulting electrode achieves a reasonable conductivity of "2.8 μS/cm"—performance that would be impossible if the CNTs were completely electrically isolated. MRD-2017, [0123]; *see also id.* [0125] (describing conductivity of comparative example). MRD-2017 further explains that CNTs "provide for the delivery of the electrons to the active material particles" and "form electrical bridges between the active material particles." *Id,* [0094]. These disclosures confirm that CNTs physically contact the active material, rather than being insulated from the active material. Figure 2 of MRD-2017 is thus consistent with, not contrary to, the well-established understanding (discussed *supra*) that CNTs must contact the active material to form a functional electrode. PO's suggestion that CNTs remain buried in PVDF after NMP dissolution finds no support in either Fig. 2 or the text of MRD-2017.

26. MRD-2018, another reference PO attempts, but fails, to use as corroborating its embedded nanotubes theory, is an application from the same inventors as MRD-2017 and discloses a similar composition for electrode manufacture, although with different proportions of constituent components. MRD-2018,

[0121]-[0131]. Like MRD-2017, MRD-2018 states that "CNTs are well dispersed around the micron-sized particles of $LiFePO_4$/C (FIGS. 2A and 2B)," and that the CNTs "ensure the distribution of electrons to the particles of active material and . . . form electrical bridges between the particles of active material." MRD-2018, [0092], [0131]. This disclosure further undermines PO's assertion that the CNTs become embedded or isolated within the PVDF matrix.

27. PO's reliance on MRD-2008 is likewise misplaced and contradicted by the reference itself. PO cites MRD-2008 as describing a "glue-like" process in which carbon black is "embedded in PVDF resin," analogizing it to the Ohata-Kavan structure. POR, 22. In particular, the flaw in PO's argument lies in that carbon black becomes embedded in a way that electrically isolates it from the active material. However, MRD-2008 directly refutes that interpretation.

28. MRD-2008 clearly describes PVDF as an electrically insulating material. MRD-2008, 10:10, 5:28-32. If the conductive carbon black were truly embedded or encapsulated within PVDF to the point of being isolated from the active material—as PO suggests—the resulting structure would lack the necessary conductivity to function as an electrode. Indeed, MRD-2008 makes clear that conductivity improvements come not from embedding or

insulating the conductive additive (carbon black), but from preserving carbon black's contact with the active material and maintaining conductive pathways.

29. Specifically, MRD-2008 discloses that: (i) "It is believed that this behavior ['unexpected improvement in performance realized when using greater amounts of binder relative to CB'] may be attributed to the improved interface electronic conductivity between the active material particles and the acetylene black conductive additives"; and (ii) "The branch structure of the acetylene black is clearly preserved from the original acetylene black powder . . . PVDF coatings integrate these conductive branches to form continuous electronic pathways." MRD-2008, 10:21-32, 11:13-17. These statements confirm that PVDF functions to support the conductive network of acetylene black and acetylene black's binding to active materials, but not to encapsulate or isolate acetylene black within the PVDF.

30. Moreover, MRD-2008 contains no testing involving carbon nanotubes. Its findings are based entirely on carbon black, making PO's attempt to apply those findings to CNT-containing systems speculative at best. Even so, as discussed above, MRD-2008 directly contradicts PO's assertions that conductive additives become embedded and electrically isolated.

B. The nanotubes in the Ohata-Kavan composition are discrete

31. PO's argument that the Ohata-Kavan composition would not include discrete nanotubes because of the presence of a continuous network of nanotubes is unsustainable because of its reliance on an overly restrictive construction for "discrete." The term "discrete" does not preclude a network of nanotubes, *e.g.*, in point-to-point contact, to provide a conductive pathway through the electrode material, as is the case in the Ohata-Kavan composition. Indeed, the '483 Patent itself indicates that discrete nanotubes enhance conductivity, which is well-aligned with the purpose of the nanotubes in the Ohata-Kavan combination. *See* LGES-1001, 1:44-50, 2:24-28, 2:4-11, 2:12-17. For instance, as shown in Table 1 of the '483 Patent, the '483 Patent focuses on the conductivity improvement, with Table 1 comparing conductivity/resistance.

32. PO's further attempts to argue against the discreteness of the Ohata-Kavan nanotubes fail in their reliance on Gan—an entirely different reference. For instance, in addressing the Petition's explanation that oxidation further promotes that the nanotubes are discrete, PO cites to Gan, which, it alleges, "teaches that functionalized CNTs within a polymer will be drawn closer together … facilitating the formation of a continuous network." POR, 58-59. Yet as noted *supra*, a continuous, conductive network of nanotubes is

consistent with a population of discrete nanotubes, *e.g.*, nanotubes in point-to-point contact. Even to the extent that Gan is relevant to the structure of the Ohata-Kavan composition (which PO has not established), the morphology of Gan's nanotube network does not demonstrate absence of discrete nanotubes in Ohata-Kavan.

33. Separately, PO also appears to argue that the Ohata-Kavan nanotubes would be arranged as shown in Gan's SEM images. *See* POR, 54-55. But PO's reliance on Gan's FIG. 5, which illustrates networks of non-oxidized nanotubes, is irrelevant to the Ohata-Kavan composition including oxidized nanotubes. MRD-2019, [0014]. A POSITA would not have been able to draw any conclusions about the arrangement of the Ohata-Kavan nanotubes from this image of an entirely different material, fabricated in an entirely different way.

C. PO fails to refute my earlier opinion regarding several distinct motivations for the Ohata-Kavan combination

1. PO's objections to my earlier opinion regarding motivations to combine Ohata and Kavan are premised on its incorrect theory that nanotubes are fully embedded in the binder

34. I previously explained that oxidized nanotubes would promote dispersion of the nanotubes in the composite. I note that PO asserts that this improved dispersibility is because the functional groups "enhance[] the CNTs'

interaction with water," while in the Ohata-Kavan composition, "the naked oxidized CNTs are not exposed to water, but instead are first covered in resin," and thus that "Kavan does not support the assertion that oxidizing the resin-covered CNTs of Ohata-Kavan would improve dispersibility." POR, 47.

35. PO's argument is technically and factually wrong. First, as I already explained, the Ohata-Kavan nanotubes are not embedded in resin. Second, PO is factually wrong in explaining that Kavan uses only water as the dispersion medium. In fact, Kavan uses NMP as the solvent for PVDF and for slurry formation during electrode fabrication. *See* LGES-1005, 2 (Experimental Section describing that "The electrodes were prepared as follows: powder precursor material . . . was mixed with 5 wt% of polyvinylidene fluoride (PVDF) dissolved in N-methyl-2-pyrrolidone [NMP]. The resulting slurry was diluted with N-methyl-2-pyrrolidone until a consistence of viscous paste"). Third, in the Ohata-Kavan combination, the masterbatch is mixed with NMP and active material, as taught by Ohata. *See* LGES-1004, [0032]. Moreover, both NMP and water are polar solvents. Functionalized nanotubes would be expected to have improved dispersibility not only in water, but also in other polar solvents such as NMP.

36. With regard to the dispersion of nanotubes, MRD also argues that "Ohata alone already achieves uniform dispersal without oxidation," and thus "there would have been no motivation to oxidize to improve dispersion." POR, 47-48. But PO cites to Ohata's description of uniform dispersion of nanotubes in its masterbatch. Even if there were no room for improvement in the dispersion of nanotubes in the masterbatch (which is not necessarily true), PO ignores that the presence of oxidative functionalities on the nanotubes would still promote dispersion of the nanotubes in the later-formed NMP slurry.

III. ADDITIONAL REMARKS

37. I currently hold the opinions set expressed in this declaration. But my analysis may continue, and I may acquire additional information and/or attain supplemental insights that may result in added observations.

I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further 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: 7/14/2025 By: Yu Zhu