

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE PATENT TRIAL AND APPEAL BOARD

AMPEREX TECHNOLOGY LTD.
Petitioner,

v.

SEMICONDUCTOR ENERGY LABORATORY CO., LTD.
Patent Owner

U.S. Patent No. 10,741,828
Case IPR2023-01016

DECLARATION OF JAMES MULLINS, PH.D.

I, Dr. James L. Mullins, declare as follows:

1. My name is Dr. James L. Mullins.
2. I have been retained by petitioner Amperex Technology Limited (“ATL”) in the above-captioned *inter partes* review relating to U.S. Patent 10,741,828 to provide opinions on various documents.

I. INTRODUCTION

3. My career as a professional and academic/research librarian spanned more than 44 years including library positions at Indiana University, Villanova University, Massachusetts Institute of Technology, and Purdue University. Appendix A is a true and correct copy of my curriculum vitae describing my background and experience.

4. In 2018, I founded the firm Prior Art Documentation Librarian Services, LLC, located at 106 Berrow, Williamsburg, VA 23188 after purchasing the intellectual property of and successor to Prior Art Documentation, LLC located at 711 South Race Street, Urbana, IL 61801. Further information about my firm, Prior Art Documentation Librarian Services, LLC (PADLS), is available at www.priorartdoclib.com.

5. I have been retained by ATL to offer my opinion on the authenticity and dates of public accessibility of various documents. For this service, I am being paid my usual hourly fee of \$275.00. I have no stake in the outcome of this

proceeding or any related litigation or administrative proceedings, and my compensation in no way depends on the substance of my testimony or the outcome of this proceeding.

II. QUALIFICATIONS

6. I received a Bachelor of Arts degree in History, Religion and Political Science in 1972 as well as a Master of Arts degree in Library Science in 1973 from the University of Iowa. I received my Ph.D. in Academic Library Management in 1984 from Indiana University. Over the past forty-four years, I have held various positions in the field of library and information sciences.

7. I am presently Dean of Libraries Emeritus and Esther Ellis Norton Professor Emeritus at Purdue University, and have been since January 1, 2018. I have been previously employed as follows:

- Dean of Libraries and Professor and Esther Ellis Norton Professor, Purdue University, West Lafayette, IN (2004-2017)
- Assistant/Associate Director for Administration, Massachusetts Institute of Technology (MIT) Libraries, Cambridge, MA (2000-2004)
- University Librarian and Director, Falvey Memorial Library, Villanova University, Villanova, PA (1996-2000)

- Director of Library Services, Indiana University South Bend, South Bend, IN (1978-1996)
- Part-time Instructor, School of Library and Information Science, Indiana University, Bloomington, IN (1979-1996)
- Associate Law Librarian, and associated titles, Indiana University School of Law, Bloomington, IN (1974-1978)
- Catalog Librarian, Assistant Professor, Georgia Southern College (now University), Statesboro, GA (1973-1974)

8. I am a member of the American Library Association (“ALA”), where I served as the chair of the Research Committee of the Association of College and Research Libraries (“ACRL”). My service to ALA included service on the editorial board of the most prominent library journal, *College and Research Libraries*. I also served on the Standards Committee, College Section of the Association of College and Research Libraries, where I was instrumental in developing a re-issue of the *Standards for College Libraries* in 2000.

9. I am an author of numerous publications in the field of library science, and have given presentations in library sciences at national and international conferences. During more than 44 years as an academic librarian and library science scholar, I have gained extensive experience with catalog records and online library management systems (LMS) built using Machine-Readable Cataloging (“MARC”)

standards. As an academic library administrator, I have had responsibility to ensure that students were educated to identify, locate, assess, and integrate information garnered from research library resources. I have also facilitated the research of faculty colleagues either directly or through the provision of and access to the requisite print and/or digital materials and services at the universities where I worked.

10. Based on my experience identified above and detailed in my curriculum vitae, which is attached hereto as Appendix A, I consider myself to be an expert in the field of library science and academic library administration. I have previously offered my opinions on the public availability and authenticity of documents in over 40 cases. I have been deposed in one case.

III. BACKGROUND ON PUBLIC ACCESSIBILITY

A. Scope of This Declaration

11. I am not a lawyer, and I am not rendering an opinion on the legal question of whether a particular document is, or is not, a “printed publication” under the law. I am, however, rendering my expert opinion on the authenticity of the document referenced herein and when and how this document was disseminated or otherwise made available to the extent that persons interested and ordinarily skilled in the subject matter or art, exercising reasonable diligence, could have located the document.

12. I am informed by counsel that an item is considered authentic if there is sufficient evidence to support a finding that the item is what it is claimed to be. I am also informed that authenticity can be established based on the contents of the document itself, such as the appearance, content, substance, internal patterns, or other distinctive characteristics of the item.

13. I am informed by counsel that a given reference qualifies as “publicly accessible” if it was disseminated or otherwise made available such that a person interested in and ordinarily skilled in the relevant subject matter could locate it through the exercise of ordinary diligence.

14. While I understand that the determination of public accessibility under the foregoing standard rests on a case-by-case analysis of the facts particular to an individual publication, I also understand that a publication is rendered “publicly accessible” if it is cataloged and indexed by a library such that a person interested in the relevant subject matter could locate it (*i.e.*, I understand that cataloging and indexing by a library is sufficient, though there are other ways that a printed publication may qualify as “publicly accessible”). One manner of sufficient indexing is indexing according to subject matter. I understand that it is not necessary to prove someone actually looked at the publication in order to show it was publicly accessible by virtue of a library’s cataloging and indexing thereof. I understand that cataloging and indexing by a single library of a single instance of a particular

publication is sufficient. I understand that, even if access to a library is restricted, a publication that has been cataloged and indexed therein is publicly accessible so long as a presumption is raised that the portion of the public concerned with the relevant subject matter would know of the publication. I also understand that the cataloging and indexing of information that would guide a person interested in the relevant subject matter to the publication, such as the cataloging and indexing of an abstract for the publication, is sufficient to render the publication publicly accessible.

15. I understand that evidence showing the specific date when a publication became publicly accessible is not necessary. Rather, routine business practices, such as general library cataloging and indexing practices, can be used to establish an approximate date on which a publication became publicly accessible.

16. Around 2010, many journals ceased to publish print copies in favor of being published only online. Verification of the online publication and the public accessibility is shown the toward the top of articles published in such journals, often showing date of submission, revision, and acceptance before publication within a specific issue of the digital journal.

B. Person of Ordinary Skill in the Art

17. In forming the opinions expressed in this declaration, I have reviewed the documents and appendices referenced herein. These materials are records created in the ordinary course of business by publishers, libraries, indexing services, and

others. From my years of experience, I am familiar with the process for creating many of these records, and I know that these records are created by people with knowledge of the information contained within the record. Further, these records are created with the expectation that researchers and other members of the public will use them. All materials cited in this declaration and its appendices are of a type that experts in my field would reasonably rely upon and refer to in forming their opinions.

18. I have been informed by counsel that the subject matter of this proceeding relates to lithium-ion batteries, including positive electrode active materials (PEAMs) for use in such batteries.

19. I have been informed by counsel that a “person of ordinary skill in the art at the time of the inventions” (POSITA) is a hypothetical person who is presumed to be familiar with the relevant field and its literature at the time of the inventions. This hypothetical person is also a person of ordinary creativity, capable of understanding the scientific principles applicable to the pertinent field.

20. I have been informed by counsel that persons of ordinary skill in this subject matter or art would have included someone that possesses at least a bachelor’s degree in chemistry, chemical engineering, or materials science and at least five years of experience in the field of batteries and battery materials. I understand that individuals with different education and additional experience could

still be of ordinary skill in the art if that additional experience compensates for a deficit in their education and experience.

21. It is my opinion that such a person would have been actively engaged in academic research and learning through study and practice in the field, and possibly through formal instruction through the bibliographic resources relevant to his or her research. By 2015, such a person would have had access to a vast array of online resources.

C. OCLC and *WorldCat*

22. Online Computer Library Center (OCLC) is a not-for-profit worldwide consortium of libraries. OCLC's practices have been consistent since the 1970s through the present. Accordingly, the OCLC practices discussed below were in place during the time frame discussed in my opinions section. OCLC was created "to establish, maintain and operate a computerized library network and to promote the evolution of library use, of libraries themselves, and of librarianship, and to provide processes and products for the benefit of library users and libraries, including such objectives as increasing availability of library resources to individual library patrons. and reducing the rate of rise of library per-unit costs, all for the fundamental public purpose of furthering ease of access to and use of the ever-expanding body of

worldwide scientific, literary and educational knowledge and information.”¹ Among other services, OCLC and its members are responsible for maintaining the *WorldCat* database (<http://www.worldcat.org/>), used by libraries throughout the world.

23. *WorldCat* is the world’s largest public online catalog, maintained by the OCLC, a not-for-profit international library consortium, and built with the records created by the thousands of libraries that are members of OCLC. OCLC provides bibliographic and abstract information to the public based on these records. *WorldCat* requires no knowledge of MARC tags and code and does not require a login or password. *WorldCat* is easily accessible through the World Wide Web to all who wish to search it; there are no restrictions to be a member of a particular community, etc.

D. Periodicals

24. A library typically creates a catalog record for a periodical publication when the library receives its first issue. When the institution receives subsequent issues/volumes of the print periodical, the issues/volumes are checked in (often using

¹ OCLC Online Computer Library Center, Inc., *Amended Articles of Incorporation of OCLC Online Computer Library Center, Inc.*, Third Article (OCLC, Dublin, Ohio, Revised November 30, 2016),

<https://www.oclc.org/content/dam/oclc/membership/articles-of-incorporation.pdf>.

a date stamp), added to the institution's holding records, and made available very soon thereafter—normally within a few days of receipt or (at most) within a few weeks of receipt. However, once a journal transitions to an online, digital, copy only the record is no longer updated except to state that access is available “online.”

25. The initial periodicals record will sometimes not reflect all subsequent changes in publication details (including minor variations in title, frequency, etc.).

E. Indexing

26. Indexing services use a wide variety of controlled vocabularies to provide subject access and other means of discovering the content of documents. The formats in which these access terms are presented vary from service to service.

27. Online indexing services commonly provide bibliographic information, abstracts, and full-text copies of the indexed publications, along with a list of the documents cited in the indexed publication. These services also often provide lists of publications that cite a given document. A citation of a document is evidence that the document was publicly available and in use by researchers no later than the publication date of the citing document.

28. *Science Direct* is a website which provides subscription-based access to a large database of scientific and medical research. It hosts over 18 million pieces of content from 4,000 academic journals and 30,000 e-books. The journals are grouped into four main sections: *Physical Sciences and Engineering*, *Life Sciences*,

Health Sciences, and *Social Sciences and Humanities*. Article abstracts are freely available, but access to their full texts (in PDF and, for newer publications, also HTML) generally requires a subscription or pay-per-view purchase.

IV. OPINION REGARDING AUTHENTICITY AND PUBLIC ACCESSIBILITY

Document A: Ex. 1005: Shim, Jae-Hyun, Jaehan Lee, Sang Yun Han, and Sanghun Lee. “Synergistic Effects of Coating and Doping for Lithium Ion Battery Cathode Materials: Synthesis and Characterization of Lithium Titanate-coated LiCoO₂ with Mg Doping.” *Electrochimica Acta* 186 (December, 2015): 201-208. (“Shim”)

36. I have been asked to opine on the authenticity and public access of an article written by Jae-Hyun Shim, et al., with the title: “Synergistic Effects of Coating and Doping for Lithium Ion Battery Cathode Materials: Synthesis and Characterization of Lithium Titanate-coated LiCoO₂ with Mg Doping” published in, *Electrochimica Acta*, 186, December 2015, pages 201-208. (“Shim”). Shim is submitted as Ex. 1005.

1. Authentication

29. Ex. 1005 (Shim) is a research paper titled “Synergistic Effects of Coating and Doping for Lithium Ion Battery Cathode Materials: Synthesis and Characterization of Lithium Titanate-coated LiCoO₂ with Mg Doping” published in *Electrochimica Acta*, volume 186 in its December, 2015 issue on pages 201-208.

30. For the purpose of my analysis, I refer to the article by Shim and the journal, *Electrochimica Acta*, in which the article is found as “Shim,” it being understood that cataloging information applies to the journal as a whole.

31. Ex. 1005 (Shim) was assessed by me for authenticity. Attachment A-1 was the search I completed on October 5, 2023 through the Purdue University Libraries (PUL) Online Catalog (OPAC) by entering the title of the article: “Synergistic Effects of Coating and Doping for Lithium Ion Battery Cathode Materials: Synthesis and Characterization of Lithium Titanate-coated LiCoO₂ with Mg Doping.” This search retrieved Shim through *Science Direct* the proprietary database of Elsevier, Inc., a major publisher in the science and engineering fields.

32. I downloaded Attachment A-2 at this URL: <https://www.sciencedirect.com/science/article/pii/S0013468615307180>.

33. When published in 2015, Shim would have been behind a ‘wall’ limited to subscribers of *Science Direct*, which nearly all university and research libraries would have been at that time. Consistent with the scientific publishing world as a whole, older articles once limited only to subscribers to *Science Direct* are now made accessible through ‘open access,’ which is now the case for Shim. The URL link above provides open access to Shim.

34. Based on my experience at Purdue University Libraries, I affirm that a search through the PUL online catalog would only provide access to published

material that meets the standard of authenticity. Therefore, since I was able to retrieve Shim by a search on the PUL online-catalog that provided a link to Shim as an open access document in the *Science Direct* database, I have no doubt that Shim is an authentic document published in *Electrochimica Acta*, volume 186, December 2015, on pages 201-208.

2. Public Accessibility

35. Attachment A-3 is a true and correct copy of the *WorldCat* entry for the journal in which Shim was published: *Electrochimica Acta*.

36. I obtained Attachment A-3 by completing a search for the journal *Electrochimica Acta* on *WorldCat* on October 5, 2023.

37. Attachment A-3 shows that *Electrochimica Acta* (Shim) is the title associated with this *WorldCat* entry, as verified by title: *Electrochimica Acta* by publisher: Elsevier Ltd; and by ISSN: 0013-4686.

38. *Electrochimica Acta* (Shim) could have been located by searching for the title: *Electrochimica Acta*; or by searching the subject headings *Analytical* and/or *Chemistry*; *Electrochemistry*.

39. When I searched *WorldCat* for holdings of *Electrochimica Acta* in Indiana, the Purdue University Libraries was among the 880 libraries shown as holding *Electrochimica Acta* worldwide.

40. The search discussed above could have been performed anywhere in the world by anyone with access to the internet in 2015.

41. *Electrochimica Acta* began publication in 1959 in print format and continues to be published in print as well as online in digital format. To document public access to Shim in digital format by the research community, shown below is evidence of access to Shim prior to July 5, 2016.

42. Attachment A-4 is from the first page, page 201, of the Shim article as published in *Electrochimica Acta*, volume 186. At the middle of the page is a record of that indicates publication record from receipt through availability online as shown below:

ARTICLE INFO

Article history:

Received 8 June 2015

Received in revised form 8 October 2015

Accepted 23 October 2015

Available online 11 November 2015

43. Publication online occurred on November 11, 2015, therefore, from that date, Shim was available to the research community who had access to *Science Direct*. In addition, *Science Direct* could have been searched through the keywords: *Lithium Ion Battery*; *Lithium titanate*; *Synergistic Effect*; and/or *Lithium Cobalt Oxide*, to retrieve Shim as shown below:

Keywords:
lithium ion battery
lithium titanate
synergistic effect
lithium cobalt oxide

44. To determine the public accessibility of Shim, I researched articles that cite Shim prior to July 5, 2016. Attachment A-5 is an article by Bikash Mandal, I. Basumallick, and Susanta Ghosh titled “Synthesis, Characterization And Electrochemical Studies On Novel Li₂MZrO₄ (M= Fe, Mn) Cathode Material For Lithium-ion Battery” published *Advanced Materials Letters*, volume 7, number 2 (February, 2016) on pages 150-155 (“Mandal”).

45. I downloaded Mandal on October 4th 2023 at this open access URL: https://aml.iaamonline.org/article_14806_c172ac04a0e591c5729dd39033d9e408.pdf.

46. Attachment A-5, which is a true and correct copy of Mandal, lists Shim as reference number 13 on page 154, as shown below:

13. Shim, J.-H.; Lee, J.; Han, S. Y.; Lee, S.; *Electrochimica Acta*, **2015**, 186, 201.

47. Based on this, I conclude that Mandal is evidence that Shim was known and accepted as a scholarly reference when Mandal was published in *Advanced Materials Letters*, volume 7, number 2 (February 2016) on pages 150-155.

3. Conclusion

48. Based on the evidence presented here—publication in the widely held periodical, *Electrochimica Acta*, online indexing, *Science Direct*, and publication, and library processing, *WorldCat* and Purdue University Library—it is my opinion that Ex. 1005, Shim, is an authentic document that was publicly available online to researchers no later than November 11, 2015. Citation to Shim occurred in a journal article, Mandal, published in February 2016—evidence that Shim was known and considered authentic as of February 2016, prior to July 5, 2016.

V. AVAILABILITY FOR CROSS-EXAMINATION

49. In signing this Declaration, I recognize that this Declaration will be filed as evidence in a contested case before the Patent Trial and Appeal Board of the U.S. Patent and Trademark Office. I also recognize that I may be subject to cross-examination in the case and that cross-examination will take place within the United States. If cross-examination is required of me, I will appear for cross-examination within the United States during the time allotted for cross-examination.

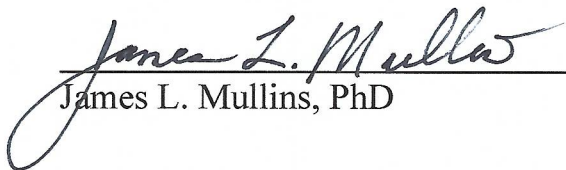
VI. RIGHT TO SUPPLEMENT

50. I reserve the right to supplement my opinions in the future to respond to any arguments that the Patent Owner raises and to take into account new information as it becomes available to me.

VII. JURAT

51. 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 full 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 U.S. Code.

Dated: October 6, 2023


James L. Mullins, PhD

JAMES L. MULLINS, PhD

Prior Art Documentation Librarian Services, LLC

205 Saint Cuthbert, Williamsburg, VA 23188

jlmullins@priorartdoclib.com

ph. 765 479 4956

Prior Art Documentation Librarian Services, LLC. (PADLS). Founded January 2018. As of July, 2023, 1 have completed 123 declarations for 39 law firms; five depositions were scheduled, three cancelled a few days prior, one was held in February, 2019 and a second was held in June 2023.

Library Experience:

2018-present Dean Emeritus, Libraries & Norton Professor Emeritus, Purdue University
2011 - 2017 Dean of Libraries & Esther Ellis Norton Professor, Purdue University
2004 - 2011 Dean of Libraries & Professor, Purdue University, West Lafayette, IN
2000-2004 Assistant/Associate Director for Administration, MIT Libraries, Massachusetts Institute of Technology, Cambridge, MA.
1996-2000 University Librarian & Director, Falvey Memorial Library. Villanova University, Villanova, PA.
1978-1996 Director of Library Services, Indiana University South Bend.
1974-1978 Associate Librarian, Indiana University Bloomington, School of Law.
1973-1974 Instructor/Catalog Librarian. Georgia Southern College (now University).

Teaching Experience:

1977-1996 Associate Professor (part-time), School of Library and Information Science, Indiana University. Subjects taught: Cataloging, Management, and Academic Librarianship.

Education:

1972 - University of Iowa. Honors Bachelor of Arts, History, Religion & Political Science.
1973 - University of Iowa. Master of Arts in Library Science.
1984 - Indiana University. Doctor of Philosophy. Concentration: Academic Library Administration. Emphasis: Law Librarianship.

Awards and Recognition:

2017 Wilmeth Active Learning Center/Library of Engineering and Science, Grand Reading Room, was announced by President Mitch Daniels, Purdue University, that it would be re-named the James L. Mullins Reading Room to honor his leadership and reputation in the academic library profession. September 2017. Portrait unveiled December 2017.

2017 Distinguished Alumnus Award by the School of Informatics and Computing, Indiana University, Bloomington. Given June 25, 2017.

2016 Hugh C. Atkinson Memorial Award, jointly sponsored by the four divisions of the American Library Association (ALA), June 27, 2016.

2015 ACRL Excellence in University Libraries Award, April 23, 2015.

Named Esther Ellis Norton Professor of Library Science by Purdue Trustees, December 11, 2011.

International Review Panel to evaluate the University of Pretoria Library, February 20 – 24, 2011. Pretoria, South Africa.

Publications: (selected)

Designing the Academic Library, Chapter Contributor. Association of College and Research Libraries, American Library Association, 2022.

A Purdue Icon: Creation, Life, and Legacy, edited by James L. Mullins, Founder's Series, Purdue University Press, 138pp., August 2017.

"The policy and institutional framework." In *Research Data Management, Practical Strategies for Information Professionals*, edited by Ray, J M. Purdue University Press, pp.25-44, 2014.

"DataCite: linking research to data sets and content." In Benson, P and Silver, S. *What Editors Want: An Author's Guide to Scientific Journal Publishing*. University of Chicago Press, pp. 21-23, December 2012.

"Library Publishing Services: Strategies for Success," with R. Crow, O. Ivins, A. Mower, C. Murray-Rust, J. Ogburn, D Nesdill, M. Newton, J. Speer, C. Watkinson. *Scholarly Publishing and Academic Resources Coalition (SPARC)*, version 2.0, March 2012.

"The Changing Definition and Role of Collections and Services in the University Research Library." *Indiana Libraries*, Vol 31, Number 1 (2012), pp.18-24.

"Are MLS Graduates Being Prepared for the Changing and Emerging Roles that Librarians must now assume within Research Libraries?" *Journal of Library Administration*. Volume 52, Issue 1, 2012, p. 124-132

Baykoucheva, Svetla. What Do Libraries Have to Do with e-Science?: An Interview with James L. Mullins, Dean of Purdue University Libraries. *Chem. Inf. Bull.* [Online] 2011, 63 (1), 45-49. <http://www.acscinf.org/publications/bulletin/63-1/mullins.php> (accessed Mar 16, 2011).

“The Challenges of e-Science Data-set Management and Scholarly Communication for Domain Sciences and Technology: a Role for Academic Libraries and Librarians,” chapter in, *The Digital Deluge: Can Libraries Cope with e-Science?*” Deanna B. Marcum and Gerald George, editors, Libraries Unlimited/Teacher Ideas Press, 2009. (a monograph publication of the combined proceedings of the KIT/CLIR proceedings).

“Bringing Librarianship to e-Science,” *College and Research Libraries*. vol. 70, no. 3, May 2009, editorial.

“The Librarian’s Role in e-Science” *Joho Kanri (Journal on Information Processing and Management)*, Japan Science and Technology Agency (formerly Japan Information Center of Science and Technology), Tokyo, Japan. Translated into Japanese by Taeko Kato. March 2008.

The Challenge of e-Science Data-set Management to Domain Sciences and Engineering: a Role for Academic Libraries and Librarians,” KIT (Kanazawa Institute of Technology)/CLIR (Council of Library and Information Resources) International Roundtable for Library and Information Science, July 5-6, 2007. Developments in e-science status quo and the challenge, The Japan Foundation, 2007.

“An Administrative Perspective,” Chapter 14, *Proven Strategies for Building an Information Literacy Program*, Susan Curzon and Lynn Lampert, editors, Neal-Schuman Publishers, Inc., New York, 2007. pp. 229-237.

Library Management and Marketing in a Multicultural World, proceedings of the IFLA Management and Marketing (M&M) Section, Shanghai, China, August 16-17, 2006, edited. K.G. Saur, Munchen, Germany, June 2007. 390 pp.

Top Ten Assumptions for the Future of Academic Libraries and Librarians: a report from the ACRL Research Committee, with Frank R. Allen and Jon R. Hufford. *College & Research Libraries*, April 2007, vol.68, no.4. pp.240-241, 246.

To Stand the Test of Time: Long-term Stewardship of Digital Data Sets in Science and Engineering. A report to the National Science Foundation from the ARL Workshop on New Collaborative Relationships: the Role of Academic Libraries in the Digital Data Universe. September 26-27, 2006, Arlington, VA. p.141. <http://www.arl.org/bm~doc/digdatarpt.pdf>

“Enabling Interaction and Quality in a Distributed Data DRIS,” *Enabling Interaction and Quality: Beyond the Hanseatic League*. 8th International Conference on Current Research Information Systems, with D. Scott Brandt and Michael Witt. Promoted by euro CRIS. Leuven University Press, 2006. pp.55-62. Editors: Anne Garns Steine Asserson and Eduard J. Simons.

"Standards for College Libraries, the final version approved January 2000," prepared by the ACRL College Libraries Standards Committee (member), *C&RL News*, March 2000, p.175-182.

"Standards for College Libraries: a draft," prepared by the ACRL College Libraries Section, Standards Committee (member), *C&RL News*, May 1999, p. 375-381.

"Statistical Measures of Usage of Web-based Resources," *The Serials Librarian*, vol. 36, no. 1-2 (1999) p. 207-10.

"An Opportunity: Cooperation between the Library and Computer Services," in *Building Partnerships: Computing and Library Professionals*. Edited by Anne G. Lipow and Sheila D. Creth. Berkeley and San Carlos, CA, Library Solutions Press, 1995. p. 69-70.

"Faculty Status of Librarians: A Comparative Study of Two Universities in the United Kingdom and How They Compare to the Association of College and Research Libraries Standards," in *Academic Librarianship, Past, Present, and Future: a Festschrift in Honor of David Kaser*. Englewood, Colorado; Libraries Unlimited, 1989. p. 67-78. Review in: *College & Research Libraries*, vol. 51, no. 6. November 1990, p. 573-574.

Presentations: (Representative)

“How Long the Odyssey? Transitioning the Library and Librarians to Meet the Needs and Expectations of the 21st Century University,” David Kaser Lecture, School of Informatics & Computing, Indiana University, Bloomington, IN, November 16, 2015.

Presentation at University of Cape Town, Cape Town, South Africa, August 20, 2015.

“The Challenge of Discovering Science and Technology Information,” Moderator, International Federation of Library Associations (IFLA) Science and Technological Libraries Section Program, Cape Town, South Africa, August 18, 2015.

“An Odyssey in Data Management: Purdue University,” International Federation of Library Associations (IFLA) Research Data Management: Finding Our Role – A program of the Research Data Alliance, Cape Town, South Africa, August 17, 2015.

Presentation at University of Pretoria, Pretoria, South Africa, August 11, 2015.

Co-Convener with Sarah Thomas, Harvard University, at the Harvard Purdue Symposium on Data Management, Harvard University, Cambridge, MA, June 15-18, 2015.

“Strategic Communication,” panel discussion on the Director's role and perspective on library communications at Committee on Institutional Cooperation (CIC) Center for Library Initiatives (CLI) Annual Conference, University of Illinois Urbana-Champaign, May 20, 2015.

“Issues in Data Management,” panel discussion moderated by Catherine Woteki, United States Undersecretary for Research, Education & Economics at 20th Agriculture Network Information Collaborative (AgNIC) Annual Meeting in the National Agricultural Library, Beltsville, MD, May 6, 2015.

“Active learning/IMPACT & the Active Learning Center at Purdue University,” Florida Institute of Technology, Melbourne, FL, February 11, 2015.

“Science+art=creativity: libraries and the new collaborative thinking,” panel moderator, International Federation of Library Associations (IFLA) 80th General Conference and Assembly, Lyon, France, August 19, 2014.

“Purdue University The Active Learning Center—A new concept for a library,” Association of University Architects 59th Annual National Conference, University of Notre Dame, South Bend, IN, June 23, 2014.

“Big Data & Implications for Academic Libraries,” keynote speaker, Greater Western Library Alliance (GWLA) Cyber-infrastructure Conference, Kansas City, MO, May 28, 2014.

“Research Infrastructure,” panel moderator, Association of Research Libraries (ARL) 164th Membership Meeting, Ohio State University, Columbus, OH, May 7, 2014.

“An Eight Year Odyssey in Data Management: Purdue University,” International Association of Scientific and Technological University Libraries (IATUL) 2013 Workshop Research Data Management: Finding Our Role, University of Oxford, UK, December 2013.

“Purdue University Libraries & Press: from collaboration to integration,” Ithaka Sustainable Scholarship, The Evolving Digital Landscape: New Roles and Responsibilities in Higher Education, libraries as publishers, New York, New York, October 2013.

“Tsinghua and Purdue: Research Libraries for the 21st Century,” Tsinghua University, Tsinghua, China, August 2013.

“Purdue Publishing Experience in the Libraries Publishing Coalition,” Association of American University Presses Annual Meeting, Press-Library Coalition Panel, Boston, Massachusetts, June 21, 2013.

“Indiana University Librarians Day: Purdue University Libraries Ready for the 21st Century,” Indiana University Purdue University Indianapolis (IUPUI), June 7, 2013.

“Purdue University Libraries and Open Access; CNI Project Update,” Coalition for Networked Information, San Antonio, TX, April 5, 2013.

Memorial Resolution, honoring Joseph Brannon, to the Board of the Association of College & Research Libraries, Seattle, WA, January 2013.

“An overview of sustaining e-Science collaboration in an Academic Research Library—the Purdue experience,” Duraspace e-Science Institute webcast, October 17, 2012.

“The Role of Libraries in Data Curation, Access, and Preservation: an International Perspective,” Panel Moderator, 78th General Conference and Assembly, International Federation of Library Associations, Helsinki, Finland, August 15, 2012.

“21st Century Libraries,” moderator of First Plenary Session, International Association of Technological University Libraries 33rd Annual Conference, Singapore, June 4, 2012.

“Planning for New Buildings on Campus,” panel presenter, University of Calgary Building Symposium on Designing Libraries for the 21st Century, Calgary, Alberta, Canada, May 17, 2012.

“Data Management and e-Science, the Purdue Response.” Wiley-Blackwell Executive Seminar-2012, Washington, DC, March 23, 2012.

“An overview of Sustaining e-Science Collaboration in Academic Research Libraries and the Purdue Experience.” Leadership & Career Development Program Institute, Association of Research Libraries (ARL). Houston, TX, March 21, 2012.

“An overview of Data Activities at Purdue University in response to Data Management Requirements.” Coalition for Academic Scientific Computation (CASC). Arlington, VA, September 8, 2011.

“Getting on Track with Tenure,” Association of College and Research Libraries (ACRL) Research Program Committee. Washington, DC, June 26, 2011.

“Integration of the Press and Libraries Collaboration to Promote Scholarly Communication,” Association of Library Collections & Technical Services (ALCTS) Scholarly Communication Interest Group – American Library Association, New Orleans, Louisiana, June 25, 2011.

“Cooperation for improving access to scholarly communication,” with N. Lossau (Germany), C. Mazurek (Poland), J. Stokker (Australia), panel moderator and presenter, Second Plenary Session, International Association of Scientific and Technological University Libraries (IATUL) 32nd Conference 2011, Warsaw, Poland. May 29-June 2, 2011.

“Riding the Wave of Data,” STM Annual Spring Conference 2011. Trailblazing & transforming scholarly publishing 2011. Washington, D.C., April 28, 2011.

“Confronting old assumptions to assume new roles: physical and operational integration of the Press and Libraries at Purdue University,” keynote speaker, 2011 BioOne Publishers & Partners Meeting. Washington, D. C., April 22, 2011.

“Are MLS Graduates Being Prepared for the Changing and Emerging Roles that Librarians must now assume within Research Libraries?” University of Oklahoma Libraries Seminar, March 4, 2011, Oklahoma City, Oklahoma.

“The Future Role of University Librarians,” the University of Cape Town, South Africa, February 25, 2011.

“New Roles for Librarians: the Application of Library Science to Scientific/Technical Research – Purdue University – a case study. International Council for Science and Technology (ICSTI); Ottawa, Canada. June 9, 2009.

“Reinventing Science Librarianship: Models for the Future,” Association of Research Libraries / Coalition for Networked Information. October 16-17th, 2008, Arlington, VA. Moderator and convener of Data Curation: Issues and Challenges.

“Practical Implementation and Opportunities Created at Purdue University,” African Digital Curation Conference, Pretoria, South Africa, (live video transmission), February 12, 2008.

Keynote speaker. “*Scholarly Communication & Academe: The Winter of Our Discontent*,” XXVII Charleston Conference on Issues in Book and Serial Acquisition, Charleston, South Carolina. November 8, 2007.

Keynote speaker. “*Enabling Access to Scientific & Technical Data-sets in e-Science: a role for Library and Archival Sciences*,” Greater Western Library Alliance (GWLA), Tucson, Arizona. September 17, 2007. A meeting of library directors and vice presidents for research of member institutions.

“*The Challenge of e-Science Data-set Management to Domain Sciences and Engineering: a Role for Academic Libraries and Librarians*,” KIT (Kanazawa Institute of Technology)/CLIR (Council of

Library and Information Resources) International Roundtable for Library and Information Science, July 5-6, 2007. Invited to participate by the Deputy Librarian of Congress.

International Association of Technological University Libraries (IATUL), Stockholm, Sweden. June 8, 2007. Invited paper, *Enabling International Access to Scientific Data-sets: creation of the Distributed Data Curation Center (D2C2)*.

“A New Collaboration for Librarians: The Principles of Library and Archival Sciences Applied to the Curation of Datasets,” Symposium of the Libraries and the College of Engineering, University of Louisville, April 6, 2007.

“Purdue University Libraries: Through Pre-eminent Innovation and Creativity, Meeting the Challenges of the Information Age,” Board of Trustees, Purdue University, February 15, 2007.

ARL Workshop on New Collaborative Relationships: The Role of Academic Libraries in the Digital Data Universe, September 26-27, 2006, Arlington, VA. Invited participant.

NARA and SDSC: A partnership. A panel before the National Science Foundation, June 27, 2006. Arlington, VA. Invited participant.

“Kaleidoscope of Scientific Literacy: fusing new connections,” with Diane Rein, American Library Association, Association of College and Research Libraries, Science & Technology Section, Annual Conference, New Orleans, June 26th, 2006.

“Leadership for Learning: Building a Culture of Teaching in Academic Libraries – an administrative perspective,” American Library Association, Association of College and Research Libraries, Instruction Section, Annual Conference, New Orleans, June 25th, 2006.

“Building an interdisciplinary research program in an academic library:

how the Libraries’ associate dean for research makes a difference at Purdue University,” International Association of Technological University Libraries (IATUL), Porto, Portugal, May 23rd, 2006.

“Enabling Interaction and Quality in a Distributed Data DRIS,” *Enabling Interaction and Quality: Beyond the Hanseatic League*. 8th International Conference on Current Research Information Systems, with D. Scott Brandt and Michael Witt. Promoted by euro CRIS, Bergen, Norway, May 12th, 2006, Brandt, and Witt presented in person

“Interdisciplinary Research,” with D. Scott Brandt, Coalition for Networked Information (CNI) Spring Meeting: Project Briefing, Washington, D.C., April 3rd, 2006.

“An Interview with Purdue’s James Mullins,” a podcast submitted by Matt Pasiewicz, on *Educause Connect*, http://connect.educause.edu/James_L_Mullins_Interview_CNI_2005

“Managing Long-Lived Digital Data-sets and their Curation: Interdisciplinary Policy Issues,” Managing Digital Assets Forum, Association of Research Libraries (ARL), Washington, D.C., October 28th, 2005.

“The Odyssey of a Librarian.” Indiana Library Federation (ILF), District 2 Meeting, South Bend, Indiana. October 4th, 2005.

"New College Library Standards," Standards Committee Presentation, ALA, Chicago, July 7, 2000. SUNY Library Directors, Lake George, New York. *“The College Library Standards: a Tool for Assessment.”* April 5, 2000.

Tri-State College Library Association, *Finding You Have Talents You Never Knew You Had*, Penn State Great Valley, March 25, 2000.

Using Web Statistics, American Library Association, New Orleans, June 24, 1999.

Keynote speaker at the JSTOR Workshop, January 29, 30, 1999. University of Pennsylvania, Philadelphia, PA.

"The New Standards for Electronic Resources Statistics," Society of Scholarly Publishers, Washington, D.C., September 17, 1998.

"Evaluating Online Resources: Now that you've got them what do you do?," joint presenter with Chuck Hamaker, LSU, at the NASIG Conference, Boulder, Colorado. June 1998.

"What Employers Are Looking for in New Librarians?" Pennsylvania Library Association, Philadelphia. September 26, 1997.

"The Theory of Matrix Management" panel presentation of the Comparative Library Organization Committee of the Library Organization and Management Section of the Library Administration and Management Association, a division of the American Library Association, Annual Meeting, Chicago, June 24, 1990.

Professional Involvement: (summary of recent emphasis)

The focus for my professional involvement and research has moved recently toward managing massive data-sets. This has resulted in working with faculty in the sciences and technology to determine how librarians can collaborate in managing, curating, and preserving data-sets for future access and documentation. This has included various speaking opportunities as well as participation in planning with the National Science Foundation (NSF) on ways in which librarians can be integrated more completely into the funded research process. Participation in the Kanazawa Institute of Technology/Council of Library Resources Roundtable was particularly rewarding and provided new opportunities to share with international colleagues the issues surrounding data-set management. I was

the champion for the creation of the Distributed Data Curation Center (D2C2) at Purdue University (<http://d2c2.lib.purdue.edu/>)

Throughout my career, beginning with my dissertation, I have been actively involved with assessing and evaluating libraries. In the fall of 1999, I contacted twenty-two academic library directors to determine whether the need was also felt by others. The response was overwhelmingly affirmative. This resulted in a meeting at ALA Midwinter, January 2000. A formal meeting followed at Villanova University in April 2000. As convener, I helped to form the University Libraries Group (ULG), modeled after the Oberlin Group for college libraries. The ULG is made up of university libraries that support diverse wide-ranging programs through doctoral level and have a level of support that places them in the top tier of academic institutions. A few of the member libraries, along with Villanova, are William and Mary, Wake Forest, Lehigh, Carnegie-Mellon, Tufts, Marquette, Miami of Ohio, and Southern Methodist. In 1994 appointed to the Standards Committee, College Section, Association of College and Research Libraries. During the next six years, the Committee concentrated on changing the focus of the standards from quantitative analysis of input and output factors to emphasis on assessment of the outcome. Culmination of the work was a re-issue of the *Standards for College Libraries* in 2000. The knowledge gained through my work experience enabled me to formulate the changes needed in the standards. This work allowed for close collaboration with accrediting agencies, both professional and regional. During this same time another focus emerged, the impact of digital resources. Through my work on the JSTOR Statistics Task Force, standards were developed on the collection of use of electronic databases. This Standard was later adopted in 1998 by the International Consortium of Library Consortia (ICOLC). In 2002, the American Library Association appointed me to serve as the liaison to the Marketing and Management Section of the International Federation of Library Associations (IFLA).

Professional Service: (representative list)

Nominations Committee, Association of Research Libraries (ARL), 2016.

Steering Committee, Scholarly Publishing and Academic Resources Coalition (SPARC), 2016 – 2017.
“Excellence in Library Services,” Chair, Review Team, University of Hong Kong, Hong Kong, August 24-27, 2015.

Chair, Management Advisory Board, 2015-2017; Member, Scientific Advisory Board, arXiv, Cornell University, 1/1/2013 – present.

Advisory Board for the Wayne State University School of Library and Information Science, July 2012 – present.

Advisory Board for Microsoft Academic Search, 2012 – 2015. Redmond, WA.

Transforming Research Libraries, a Strategic Direction Steering Committee of the Association of Research Libraries (ARL), 2012-2015.

Science and Technology section, representing ARL, International Federation of Library Associations (IFLA), Chair, 2013 – 2017; Member, 2011 to present.

Member of University of Pretoria, South Africa, Library Review Committee. August 2013.

Co-chair, Local Arrangements Planning Committee for 2013 Conference, Association of College and Research Libraries (ACRL), a division of the American Library Association (ALA).

Association of Research Libraries Leadership & Career Development Program Mentor, 2011-2017.

e-Science Task Force, Association of Research Libraries. July 2006 – present. Chair, October 2011 – October 2012.

Board of Directors, International Association of Technological University Libraries (IATUL). January 2008 – December 2014.

Midwest Collaborative for Library Services (MCLS); Board Member, October 2010 – December 2012.

Chair, Library Directors, Committee on Institutional Cooperation (CIC), July 2010 – June 2012.

Board of Directors, Association of Research Libraries (ARL); October 2008 – October 2011.

Scholarly Communication Steering Committee, Association of Research Libraries (ARL) 2008-2011.

Editorial Board, *College and Research Libraries*, Association of College and Research Libraries, American Library Association. January 2008 – December 2014.

Chair, Organizing Committee for IATUL Conference 2010, June 21-24, 2010, Purdue University, West Lafayette, Indiana/Chicago, Illinois.

Conference Planning Committee for National Conference of the Association of College and Research Libraries, 2009, Seattle, Washington.

Research Committee, Association of College and Research Libraries, ACRL, division of ALA. 2002-2007, chair, 2005-2007.

Association of Research Libraries, Search and Screen Committee, Executive Director. March – January 2008.

Center for Research Libraries, Board of Directors. April 2006 – April 2012.

Academic Libraries of Indiana, Board of Directors, 2004 – present. Vice-president, 2005-2007.

President, 2007- 2009.

ALA Representative to the International Federation of Library Associations (IFLA), Marketing and Management (M&M) Section, initial term 2003-2007, re-appointed for second term, 2007-2011.

Invited to represent Research Libraries at the ACRL/3M Wonewok Retreat to assess Marketing of Academic Libraries, October 2002.

Hugh A. Atkinson Award Committee, LAMA Representative, ALA, 2001-2005.

Program Committee, Library Administrators and Management Association (LAMA), a division of ALA. 1996-2001.

ACRL, Standards and Accreditation Committee, a division of ALA. Liaison to RBMS Section of ACRL. 1997-2002.

Elected to the Executive Committee of LAMA, LOMS, a division of the American Library Association, 1998-2000. Nominated as Chair/Elect for 2003 – 2005.

Columbia University Press Advisory Committee. 1996 - 2000.

LITA/LAMA Conference Evaluation Committee, Pittsburgh, Pennsylvania, October 1996.

"New Learning Communities," Coalition for Networked Information, Indianapolis. November 19-21, 1995. Facilitator for invitational, national conference committed to developing collaborative learning and teaching techniques, involving librarians.

Planning Committee-Evaluation. LITA/LAMA 1996 Conference, Pittsburgh. This first conference, to be held jointly between two divisions of ALA, will focus on new technologies within libraries.

Indiana Cooperative Library Services Authority (InCoLSA), elected to Executive Committee, April 1991, served as President in 1993-94. InCoLSA is a statewide network of academic, public, school, and special libraries that supports library cooperation for cataloging, interlibrary loan, collection development and application of new technologies.

Governor's Conference on Libraries and Information Services. Served on Planning Committee, Academic Libraries Representative, appointed by the Governor to represent academic libraries in Indiana, Chair, Finance Committee, April 1989-July 1991.

Indiana Library Endowment Foundation Board, 1984-92. Charter Member, 1984, President, 1988-1992. 2004-2005.

University Service: (Summary)

Served on search and screen committees for senior positions including chancellor, dean, and directors; most recently I have been asked to serve on the search committee for the provost of Purdue University. At MIT service included the Library Council & appointment to the Administrative Council by President

Vest, 2001-2003 & Member of the Faculty Committee on the Library System. At Purdue appointed by the President to the Search Committee for the Provost, October 2007 to May 2008; member of the Capital Projects Committee, and IT Operational Oversight Committee as senior academic dean, 2008-2014.

Global Council, Global Policy Institute, 2012 – 2016.

Academic Program Excellence and Rankings (APER) project team, 2014.

Representative of the Academic Deans on the Re-engineering Business Operations, Purdue University, 2016 –

Academic Deans Council chaired by Provost – 2004 – 2017.

University Promotion and Tenure Committee – 2006 – 2017.

"Outstanding Team Award, Electronic Reserve Project," served as Chair, recognition awarded by the President of Villanova University to one team who made an outstanding contribution to the operations of the University, selected by a committee of administrators, faculty, and staff. Awarded September 9, 1999.

Nominated for the IUSB Lundquist Award, 1995 & 1996. The Lundquist award is given to faculty who have "exhibited excellence in teaching, scholarly or artistic achievement, and diversified relevant service..."

ATTACHMENT

A-1

ARTICLE

Synergistic effects of coating and doping for lithium ion battery cathode materials: synthesis and characterization of lithium titanate-coated LiCoO₂ with Mg doping

Shim, Jae-Hyun ; Lee, Jaehan ; Han, Sang Yun ; Lee, Sanghun

Electrochimica acta, 2015, Vol.186, p.201-208

“Lithium titanates are introduced as coating materials on the surface of Mg-doped LiCoO₂ in which the residual Li₂CO₃ after synthesis of the active materials is used as a lithium source...”



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Title	Synergistic effects of coating and doping for lithium ion battery cathode materials: synthesis and characterization of lithium titanate-coated LiCoO ₂ with Mg doping
Author	Shim, Jae-Hyun > Lee, Jaehan > Han, Sang Yun > Lee, Sanghun >
Is Part Of	Electrochimica acta, 2015, Vol.186, p.201-208
Subjects	lithium cobalt oxide > lithium ion battery > lithium titanate > synergistic effect >
Description	Lithium titanates are introduced as coating materials on the surface of Mg-doped LiCoO ₂ in which the residual Li ₂ CO ₃ after synthesis of the active materials is used as a lithium source. It is revealed that two completely different lithium titanate phases (monoclinic Li ₂ TiO ₃ and spinel Li ₄ Ti ₅ O ₁₂) can be obtained as the coating materials depending on the concentration of a titanium source. Characterization of the coating materials is performed with various experimental techniques including XRD, nano SIMS, TEM, EELS and current measurement using nano probe. The Li ₄ Ti ₅ O ₁₂ coating layer from the high concentration of titanium source secures better electrochemical performances than the Li ₂ TiO ₃ one from the low concentration of titanium source due to its “zero-strain” characteristic. In addition, it is shown that the doped ions (Mg ²⁺) from the active materials move to the coating layer and strongly enhance the conductivity of Li ₄ Ti ₅ O ₁₂ . Consequently, synergistic effects on the cell performances of cyclability and rate capability from coating and doping for the LiCoO ₂ cathode materials are rigorously investigated.
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ATTACHMENT

A-2



Synergistic effects of coating and doping for lithium ion battery cathode materials: synthesis and characterization of lithium titanate-coated LiCoO_2 with Mg doping

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ABSTRACT

Lithium titanates are introduced as coating materials on the surface of Mg-doped LiCoO_2 in which the residual Li_2CO_3 after synthesis of the active materials is used as a lithium source. It is revealed that two completely different lithium titanate phases (monoclinic Li_2TiO_3 and spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$) can be obtained as the coating materials depending on the concentration of a titanium source. Characterization of the coating materials is performed with various experimental techniques including XRD, nano SIMS, TEM, EELS and current measurement using nano probe. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coating layer from the high concentration of titanium source secures better electrochemical performances than the Li_2TiO_3 one from the low concentration of titanium source due to its “zero-strain” characteristic. In addition, it is shown that the doped ions (Mg^{2+}) from the active materials move to the coating layer and strongly enhance the conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Consequently, synergistic effects on the cell performances of cyclability and rate capability from coating and doping for the LiCoO_2 cathode materials are rigorously investigated.

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1. Introduction

Since the first commercialization of lithium ion battery (LIB), the layered lithium transition metal oxides (LiMO_2 , M: Co, Ni, Mn, and so forth) have been one of the most predominant cathode materials in LIBs, particularly, for portable electronics. However, as the usage of LIBs has increased in other area, such as, transport applications (electric vehicles and hybrid electric vehicles) and massive energy storage facilities, demands for better electrochemical performances of LIBs are drastically increasing. From various experimental evidences, several degradation mechanisms of the layered cathode materials have been proposed [1–4]. One is the dissolution of transition metal ions into the electrolytes when the electrode is delithiated. Another mechanism is that the MO_2 layer at the delithiated state shears from the electrode surface, which results in the capacity fade. In addition, the mechanically vulnerable charged form of the materials with the expanded lattice suffers from oxygen loss and side reaction with electrolytes at the highly oxidized surfaces. None of these mechanisms are

mutually exclusive, and conceivably multiple mechanisms are concurrently involved in a cathode degradation.

Coating is one of the simplest as well as most effective methods to be considered for minimization of the degradation and consequent capacity fade during cycling. The primary role of the coating layer is physical protection from chemical reaction with the electrolytes. The common feature of successful coating materials, such as, ZrO_2 , SiO_2 , ZnO , Al_2O_3 , $\text{Al}(\text{OH})_3$, AlPO_4 , and AlF_3 , is that the metal ion in the coating layer has only one stable valence state at ambient condition [5], therefore, the active materials can obtain much enhanced stability. However, because the coating materials generally exhibit poor lithium ion conduction, recently, inorganic materials containing lithium ions have been proposed. For example, Lu et al. suggested that monoclinic Li_2TiO_3 , a Li-rich layered material similar to Li_2MnO_3 , would be a good candidate [6]. They showed that the Li_2TiO_3 -coated LiMO_2 nanobelts strongly improved rate capability and cycling ability as cathode materials. The effect of Li_2TiO_3 is not limited only to the layered materials. Deng et al. reported that this material worked well for the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel cathode [7]. They showed that the Li_2TiO_3 -coated samples delivered excellent discharge capacities even at a very high charging/discharging rate of 5C. Meanwhile, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is another example of lithium ion conductor

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being used as a coating material. In fact, it has been extensively used as an anode material for a long time because it rarely suffers from volume change, which is so called a “zero-strain” material, during ion insertion and extraction [8–10]. However, because $\text{Li}_4\text{Ti}_5\text{O}_{12}$ shares the same structure of spinel ($\text{Fd}\bar{3}m$) with LiMn_2O_4 and the crystallographic mismatch between them (lattice parameter a of $\text{Li}_4\text{Ti}_5\text{O}_{12}$: 8.248 Å and that of LiMn_2O_4 : 8.357 Å) is not significant, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ or its similar derivatives have been suggested as a coating material on the spinel cathodes [11–14]. Meanwhile, even though a few studies reported that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can be applied to the layered materials, for example, LiCoO_2 [15–18], it has not been so successful in industry, probably because it does not produce acceptable electrochemical performances, such as, cycling lifetime and high rate capability. This disqualification is mainly ascribed to its low electrical conductivity ($\sigma < 10^{-13} \text{ S cm}^{-1}$) [19].

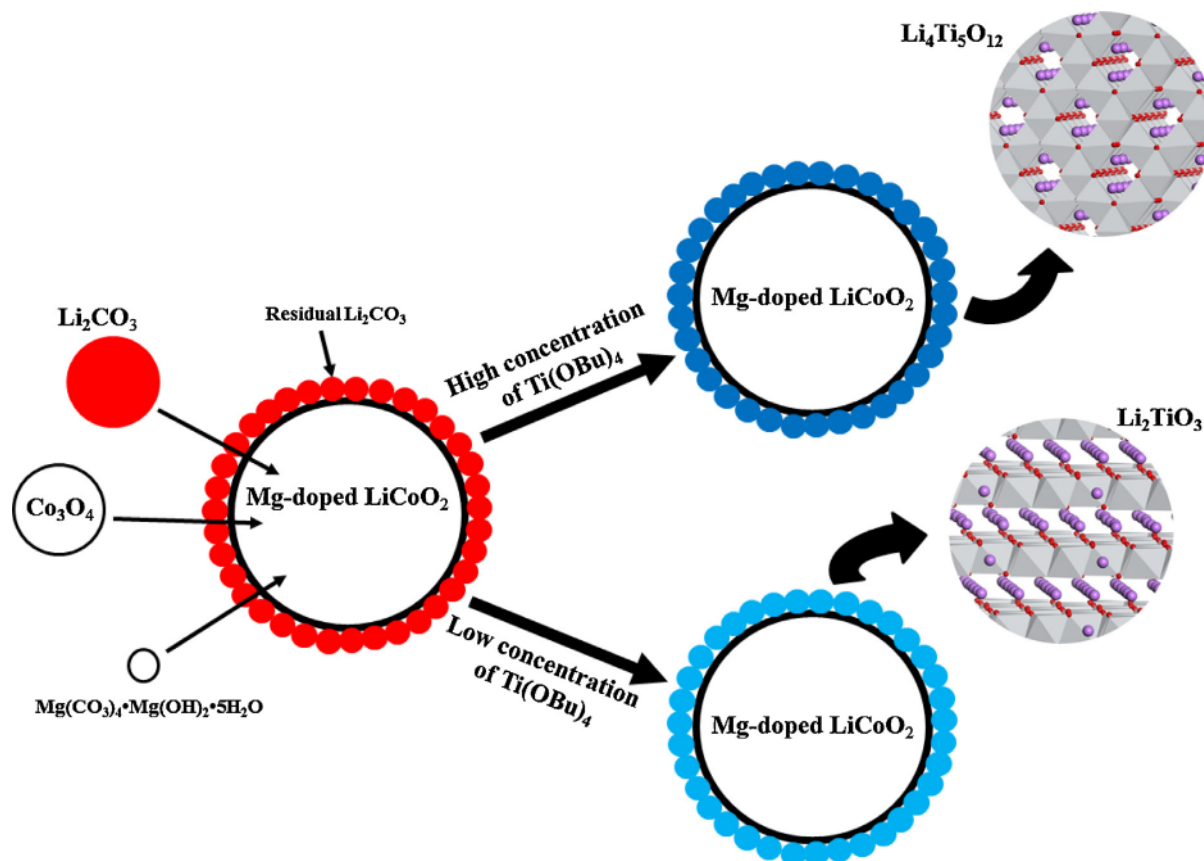
By modifying electronic structure of original active materials, doping is a simple method to efficiently improve cell performances. For example, because Mg has a valence state of 2^+ rather than Co (3^+) or Li (1^+), the Mg-doped LiCoO_2 exhibits strong electrical conductivity compared to the bare LiCoO_2 and, therefore, it shows excellent cell performances [20–24]. Besides Mg, various dopants for LiCoO_2 , such as, Al [25], Zr [26], Sn [27], B [28], and so forth [29], have also been explored. In this study, with combination of the above-mentioned coating of lithium titanate and doping of Mg, we investigate their synergistic effects on the LiCoO_2 cathode materials. From various experimental works including X-ray diffraction (XRD), nano secondary ion mass spectrometry (nano SIMS), transmission electron microscopy (TEM), electron energy-loss spectroscopy (EELS), current measurement by nano probe, and electrochemical characterization, it is revealed that the doped ions (Mg^{2+}) have an effect not only on the active materials themselves but also on the coating layer. In addition, utilizing limited amounts

of residual lithium ions, it is shown that the phase of lithium titanate is varied with the contents of Ti source. Because the phases are very different in several respects, the electrochemical performances of the cells employing them are also consequently different.

2. Experimental Section

2.1. Synthesis of materials

The Mg-doped LiCoO_2 ($\text{LiMg}_{0.01}\text{Co}_{0.99}\text{O}_2$) was prepared by solid-state reaction. Starting materials of Li_2CO_3 , Co_3O_4 and $\text{Mg}(\text{CO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ were mixed by a mechanical mixer with a rotating speed of 80 rpm for 1 h. The ratio of Li: Co: Mg was adjusted to 1.04: 0.99: 0.01 considering that unreacted Li_2CO_3 remains on the surface of Mg-doped LiCoO_2 particles after synthesis. Then, the powder mixtures were heated at 1000°C for 5 h in air to produce the Mg-doped LiCoO_2 . The sol-gel technique was employed for the lithium titanate coating. For this purpose, various amounts of $\text{Ti}(\text{O}i\text{Bu})_4$ (0.457 g, 1.372 g, and 2.286 g) were, respectively, dissolved in 100 g of ethanol with 3 h stirring at room temperature. Then, 50 g of the synthesized active materials was added into each of the solutions with 4 h stirring at 80°C . The residual Li_2CO_3 on the surface of the active materials was used as a lithium source for the coating. Utilization of the residual Li_2CO_3 has a benefit because impurities such as LiOH or Li_2CO_3 usually impede the Li ion diffusion and charge transfer reactions at the interfaces and promote the formation of HF [30]. Moreover, Li_2CO_3 has been considered as a main source of CO_2 gas at high temperatures. Then, each of the solutions was heated at 950°C for 6 h and then naturally cooled down to room temperature. As described in Scheme 1, the structure of lithium titanate coating layer is



Scheme 1. Synthesis and Coating Process of Lithium Titanate-Coated LiCoO_2 .

dependent on the concentration of Ti source, which will be thoroughly examined and discussed in the section of Results and Discussion. For comparison, uncoated but Mg-doped LiCoO_2 and lithium titanate-coated with high concentration of $\text{Ti}(\text{OBU})_4$ (2.230 g in ethanol 100 g) but Mg-undoped LiCoO_2 were also prepared through similar processes. The denotation of each material is summarized in Table 1.

2.2. Characterization of materials

To study structures of the materials, XRD measurements were employed using a Philips X'PERT PRO diffractometer with $\text{Cu K}\alpha$ radiation. Diffraction patterns were obtained for $2\theta = 10^\circ \sim 130^\circ$ with step size of 0.013° and scan rate of $0.67^\circ/\text{min}$. Silicon powder (Aldrich, 99 %) was used as an internal standard to calculate cell parameters. The spatial distributions of elements on the cross section of the particles were analyzed by nano SIMS (Cameca Nano-SIMS 50, France), the resolution of which was 50 nm. The data were obtained in multi-collection detector mode by sputtering the sample with a $\sim 0.4 \text{ pA}$ Cs primary ion beam (impact energy: 16 keV) focused to a spot of $\sim 100 \text{ nm}$ diameter. The primary ion beam was rastered over $15 \times 15 \mu\text{m}^2$. The samples were mounted using epoxy resin and then polished with SiC paper. In the negative mode, the detected ions were $^{7}\text{Li}^{16}\text{O}^-$, $^{24}\text{Mg}^{16}\text{O}^-$, $^{48}\text{Ti}^{16}\text{O}^-$, and $^{59}\text{Co}^{16}\text{O}^-$. The scanning TEM (STEM) observations were performed using a Cs-corrected STEM (JEM-2100F, JEOL Co., Japan) at 200 kV, which is equipped with a spherical aberration corrector (CEOS GmbH, Germany) at the Korea Advanced Nano Fab Center (KANC). The size of minimum probe is $\sim 1 \text{ \AA}$ in diameter. The samples for the STEM measurements were prepared by Focused Ion Beam (FIB, Hellios FEI, USA). The EELS was performed using a spectrum-image scheme based on the STEM observation (Gatan GIF 200 spectrometer). The energy resolution estimated by the full width at half maximum of the zero loss peaks was about 0.8 eV and the energy dispersion was 0.05 eV/ch. The current-voltage characteristics of the active materials and the lithium titanate coating layers were measured by nano probe (Nanostation, KLEINDIEK, Germany) with a scanning electron microscope (SEM). To acquire the current-voltage curves, the voltage was applied from -4 V to 4 V .

2.3. Measurement of electrochemical performances

To study the electrochemical performances, 2032 coin-type cells were prepared. First, the active materials, conducting materials (Super-P carbon black) and binders (polyvinylidene fluoride) were blended with a ratio of 96: 2:2 (in wt%) in N-methyl-2-pyrrolidone. Then, the slurry was cast on aluminum foil and dried at 110°C for 10 h in a vacuum oven. The electrolyte for the cells was 1.15 M LiPF_6 in ethylene carbonate/diethyl carbonate/ethyl methyl carbonate (30: 30: 40 in vol%) + fluoroethylene carbonate 5% (Panax etec Co., Ltd, Korea). The lithium foil was used as the negative electrode and the capacity of the manufactured cells was 1.5 mAh/cm^2 . The reversible discharge capacities were

measured between 3.0 and 4.5 V. The AC-impedance measurements were performed using a Biologic VMP3 impedance analyzer over the frequency range of 500 kHz $\sim$ 5 mHz with amplitude of 10 mV.

3. Results and Discussion

Fig. 1 shows lattice parameters of the samples obtained from the Rietveld refinement of the XRD data. Compared to the pristine (undoped) LiCoO_2 , the Mg-doped ones including uncoated- LCO_{Mg} , $\text{LT0-LCO}_{\text{Mg}}$, $\text{LT1-LCO}_{\text{Mg}}$, and $\text{LT2-LCO}_{\text{Mg}}$ have larger a and c parameters, which is caused by larger ionic size of Mg^{2+} (0.72 Å) than Co^{3+} (0.545 Å). This observation is consistent with the previous studies [22,26,31]. Interestingly, the lattice parameters are slightly reduced with lithium titanate coating. This indicates that the concentration of Mg^{2+} ions in the active materials has decreased when they are coated with lithium titanates, in other words, a small amount of Mg^{2+} ions in the Mg-doped LiCoO_2 has diffused to the coating layer. This migration of Mg^{2+} ions is clearly evidenced by nano SIMS analysis. As shown in Fig. 2, the Mg^{2+} ions are homogeneously distributed over the entire particle of uncoated- LCO_{Mg} whereas the Mg map of the $\text{LT2-LCO}_{\text{Mg}}$ particle exhibits slightly larger population at the edges of particle (yellow arrows) than in the bulk (inner area), which is in accord with the Ti map even though its intensity is much smaller. A few studies have reported that metal ions from coating layer, for example, MgO , diffuse into the interlayers of LiCoO_2 active materials during electrochemical processes, and advance the cell performances [32–34], however, the diffusion in the reverse direction (from active materials to coating layer) either before or during electrochemical processes has never been noted previously. The diffused Mg^{2+} ions enhance a role of the coating layer to improve electrochemical performances, which will be discussed in the later part. Thickness of the coating layer is too thin ($\sim 200 \text{ nm}$) to characterize its detailed structure by XRD (Fig. S1 in Supplementary Data).

In order to characterize the structural features of the cathode materials in the nm scale, a spherical aberration-corrected STEM was employed. The contrast of the high-angle annular-dark-field (HAADF) image shows the $Z^{1.7}$ dependency, instead of $Z^{1/3}$ for annular-bright-field (ABF) image, where Z is the atomic number [35]. Fig. 3 shows HAADF STEM images of lithium titanate-coated and Mg-doped LiCoO_2 with different coating levels. $\text{LT0-LCO}_{\text{Mg}}$, that is, the sample coated by the low concentration of $\text{Ti}(\text{OBU})_4$ seems to be divided into two regions (L and M in Fig. 3a) with respect to their contrast. From the fast Fourier transform (FFT)

Table 1
Notation of the Materials in This Study.

Name	Amount of $\text{Ti}(\text{OBU})_4$ for lithium titanate coating (g/100 g of ethanol)	Mg doping (Co: Mg = 0.99: 0.01)
$\text{LT0-LCO}_{\text{Mg}}$	0.457	O
$\text{LT1-LCO}_{\text{Mg}}$	1.372	O
$\text{LT2-LCO}_{\text{Mg}}$	2.286	O
Uncoated- LCO_{Mg}	None	O
LT2-LCO	2.230	X

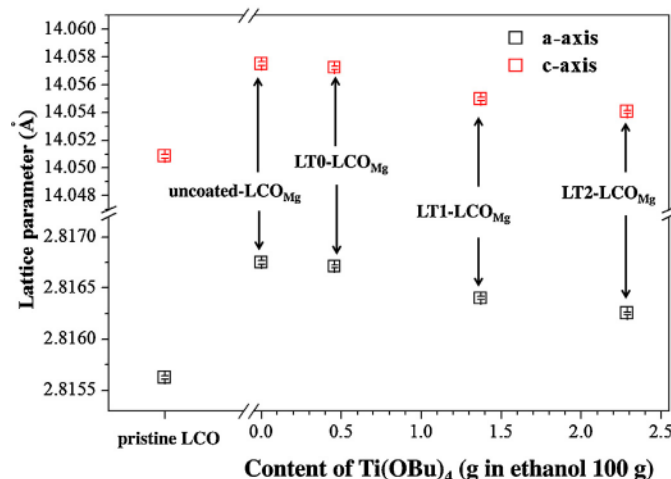


Fig. 1. Lattice parameter vs content of $\text{Ti}(\text{OBU})_4$ for LiCoO_2 .

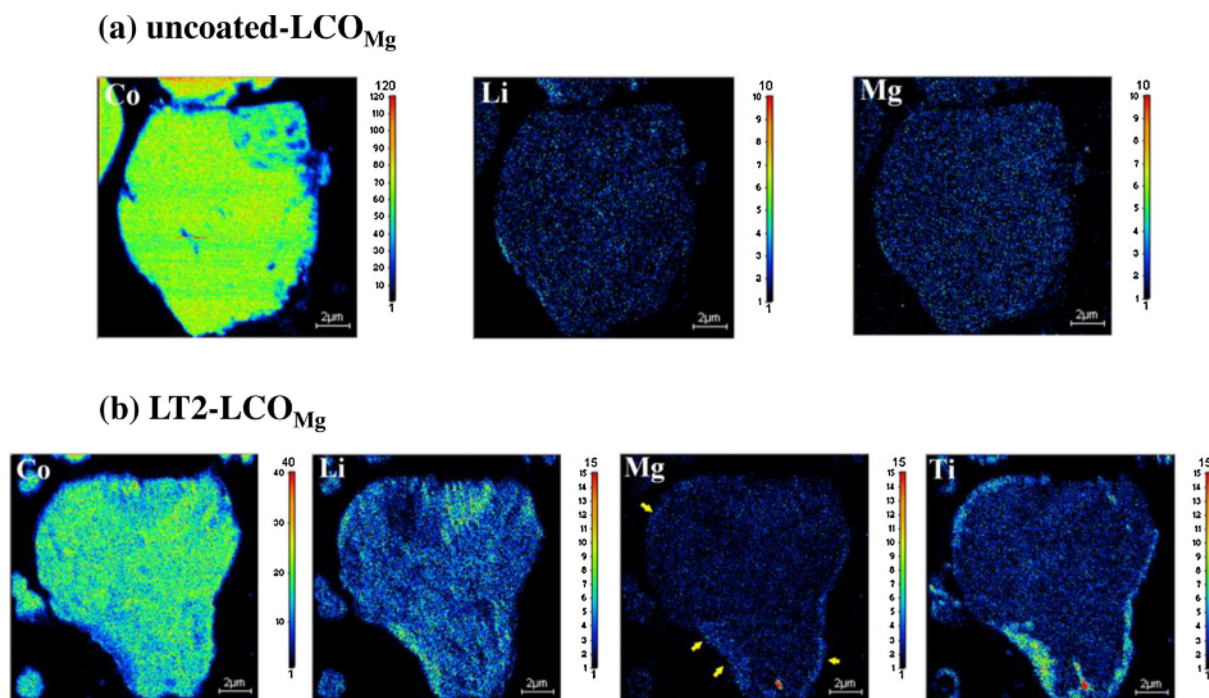


Fig. 2. Elemental distributions of metals on the cross sections of (a) uncoated-LCO_{Mg} and (b) LT2-LCO_{Mg} particles obtained by nano SIMS. (For interpretation of the references to color in text, the reader is referred to the web version of this article.)

patterns, regions L and M were identified as LiCoO₂ ($R\bar{3}m$) and Li₂TiO₃ (C2/c), respectively. It is noteworthy that the Li₂TiO₃ crystal was epitaxially grown on the surface of LiCoO₂ as a coating layer. The [0 0 1] direction of LiCoO₂ (*c*-axis) was completely parallel to the [0 0 1] direction of Li₂TiO₃. Meanwhile, LT2-LCO_{Mg}, that is, the sample coated by the high concentration of Ti(OBu)₄ is also divided into two regions (L and N in Fig. 3c), however, the structure of coating layer (region N) is distinct from that of LT0-LCO_{Mg}. From the FFT analysis, it was determined as the spinel structure of Li₄Ti₅O₁₂ ($Fd\bar{3}m$). In more detail, the enlarged STEM image inserted in region N shows that the lattice spacing is ~ 0.48 nm, which is corresponding to that of the (111) or ($1\bar{1}\bar{1}$) planes of spinel Li₄Ti₅O₁₂. For LT1-LCO_{Mg}, that is, the sample coated by the moderate concentration of Ti(OBu)₄, differently with the previous cases, three discriminable regions (L, M, and N) are shown in the STEM image (Fig. 3b). In this case, from the FFT analysis, it was revealed that the monoclinic Li₂TiO₃ phase is grown on the LiCoO₂

surface, and then, the spinel phase of Li₄Ti₅O₁₂ is developed on top of the monoclinic one. This dependence of coating layer structure on the concentration of Ti source is caused by the ratio of Li and Ti for the stable states of lithium titanates. According to the phase diagram of Li₂O-TiO₂ binary system [36], Li₄Ti₅O₁₂ is the stable phase under the condition of more than 71 mol% of TiO₂ whereas Li₂TiO₃ is the stable one when TiO₂ is less than 51 mol%. Between the two concentration limits, solid solutions of Li₄Ti₅O₁₂ and Li₂TiO₃ are favored. In our study, only the contents of Ti source are varied while those of Li source (residual lithium on the surface of LiCoO₂ particles) are fixed, therefore, it is considered that the structural variation of the coating layer in this work complies with the phase diagram. Additional TEM images and diffraction patterns from different zone-axes are included in Supplementary Data to clearly distinguish the structures (Fig. S2).

To evaluate the electrochemical performances of lithium titanate-coated and Mg-doped LiCoO₂ (LT0-LCO_{Mg}, LT1-LCO_{Mg},

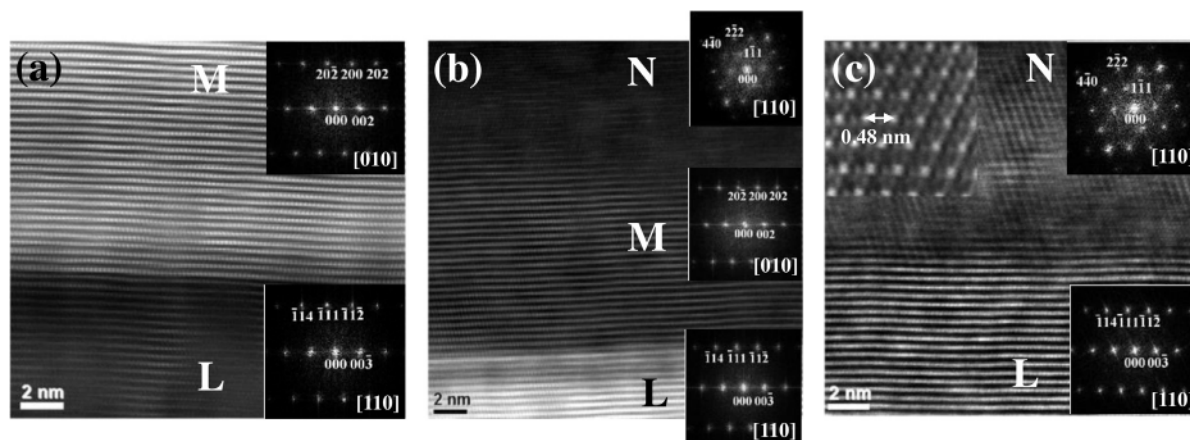


Fig. 3. HAADF STEM images of (a) LT0-LCO_{Mg}, (b) LT1-LCO_{Mg}, and (c) LT2-LCO_{Mg}. The insets on right side of each image are the FFT patterns of corresponding regions. The inset on left side of (c) is enlarged image of region N.

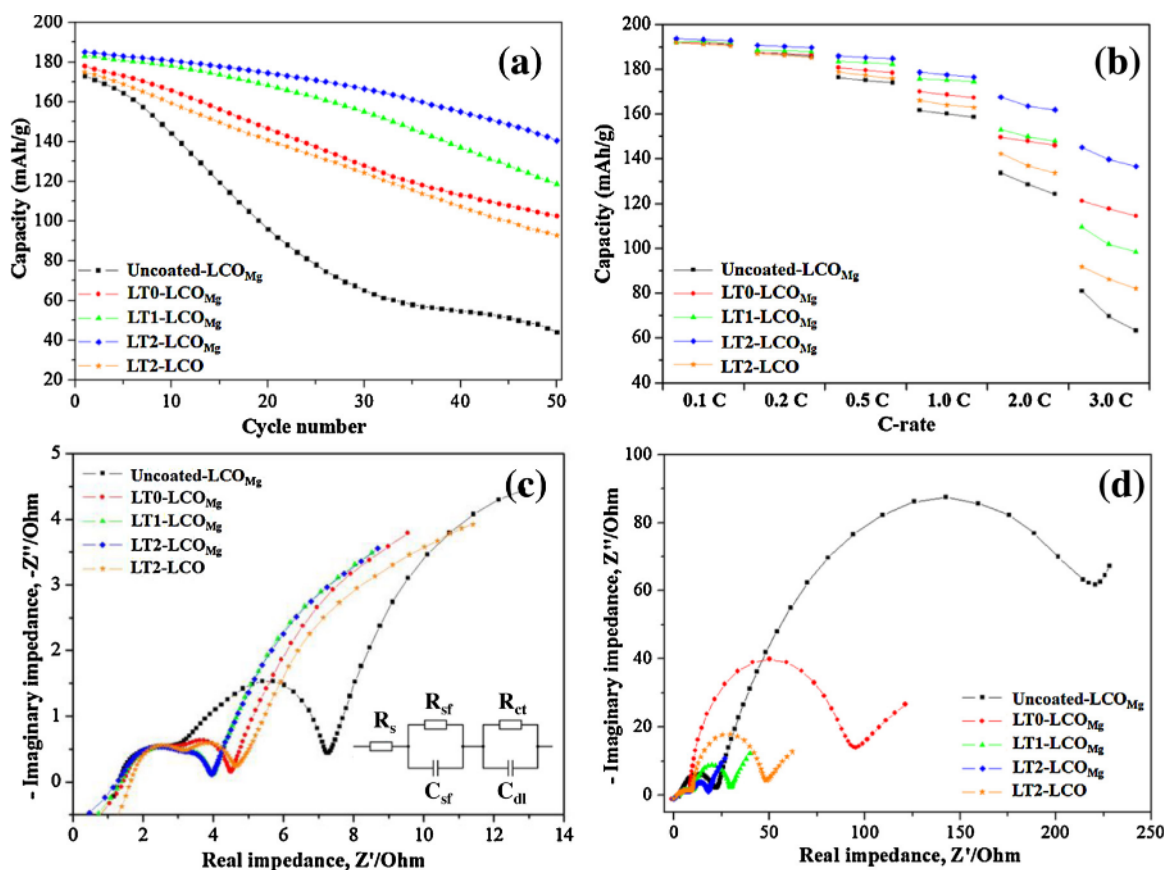


Fig. 4. Cycling performances of various cathode materials with different coatings measured at (a) 1C-rate and (b) incremental charging/discharging rates from 0.1C to 3C in the range of 3.0–4.5 V. Nyquist plots measured at (c) 2nd and (d) 50th cycle. The inset diagram in (c) is an equivalent circuit. (R_s , R_{sf} , and R_{ct} are the resistances of electrolyte solution, solid electrolyte interface, and charge transfer at the interface of cathode/electrolyte, respectively. C_{sf} and C_{dl} are the capacitances of solid electrolyte and double layer, respectively.)

and LT2-LCO_{Mg}), 2032 coin-type cells were assembled with Li metal as an anode. For comparison, uncoated-LCO_{Mg} and LT2-LCO (without Mg doping) were also tested. The cycling abilities at a rate of 0.5C (=160 mAh/g) are compared in Fig. 4a, where the capacities were measured within a range of 3.0–4.5 V. LT2-LCO_{Mg} exhibits not only the highest discharge capacity at the first cycle (184.9 mAh/g) but also the best capacity retention of higher than 76% after 50 cycles (140.6 mAh/g). Compared to uncoated-LCO_{Mg} (172.2 mAh/g), the improvement in the initial capacity of LT2-LCO_{Mg} is considerable (higher by 7%). However, even more remarkable is the enhancement in the cycling ability. After 50 cycles, the capacity retention of uncoated-LCO_{Mg} is just 25% (44.0 mAh/g) of the initial capacity. Even though somewhat advancement of the electrochemical performances is also managed by the coatings with low or moderate concentrations of Ti source, the significance is not so much as LT2-LCO_{Mg}. Therefore, it is considered that the coating layer of LT2-LCO_{Mg} (spinel Li₄Ti₅O₁₂) provides better performances for LiCoO₂ cathode than that of LT0-LCO_{Mg} (monoclinic Li₂TiO₃). In fact, this discrepancy in effectiveness of the coatings comes not only from the volume (or area) of the coating layer but also from the structural or phase stability during cycling, which will be shown and discussed further in the later part. In addition, Mg doping assists in improving the cell performances. As shown in Fig. 4a, the coating effect without the Mg doping is fairly limited, which is probably related to the low electronic conductivity of the coating materials. Fig. 4b shows a cycling result at incremental charging/discharging rates from 0.1C to 3C. At 0.1C, the discharge capacities of the samples are almost the same, however, at the high C-rates, the capacity of LT2-LCO_{Mg} is

strongly improved compared to that of uncoated-LCO_{Mg}. In this rate capability experiment, a synergistic effect of coating and doping is observed as well. We obtained useful information of charge transfer property from electrochemical impedance spectroscopy (EIS) measurements. In Fig. 4c and d, the Nyquist plots of the cells from the differently treated cathode materials at the 2nd and the 50th cycle are compared. An equivalent circuit is presented in the figure inset. The intercept at real impedance (Z') axis at the high frequency corresponds to the solution resistance (R_s), which is the impedance related to ion diffusion in the electrolyte solution. The high and low frequency semicircles are attributed to the solid electrolyte interface resistance (R_{sf}) and the charge transfer resistance at the interface of cathode/electrolyte (R_{ct}), respectively. All the impedance components (R_s , R_{sf} , and R_{ct}) are listed in Table 2. At the 2nd cycle, LT2-LCO_{Mg} shows the smallest resistances, but the differences are insignificant. Meanwhile, at the 50th cycle, all the resistances become large as a result of cycling degradation. In particular, R_{ct} is most significantly increased, which means that the charge transfer at the interface of cathode/electrode becomes hard

Table 2
Resistances Obtained from Equivalent Circuit Fitting of EIS Experimental Data.

Samples	2nd cycle			50th cycle		
	R_s (Ω)	R_{sf} (Ω)	R_{ct} (Ω)	R_s (Ω)	R_{sf} (Ω)	R_{ct} (Ω)
Uncoated-LCO _{Mg}	1.33	5.23	16.21	3.00	19.58	247.0
LT0-LCO _{Mg}	1.43	3.74	11.79	1.45	7.46	89.38
LT1-LCO _{Mg}	1.41	2.65	11.66	2.00	7.30	22.60
LT2-LCO _{Mg}	1.27	2.56	10.99	2.20	6.69	9.98
LT2-LCO	1.66	3.12	12.05	1.92	7.80	41.36

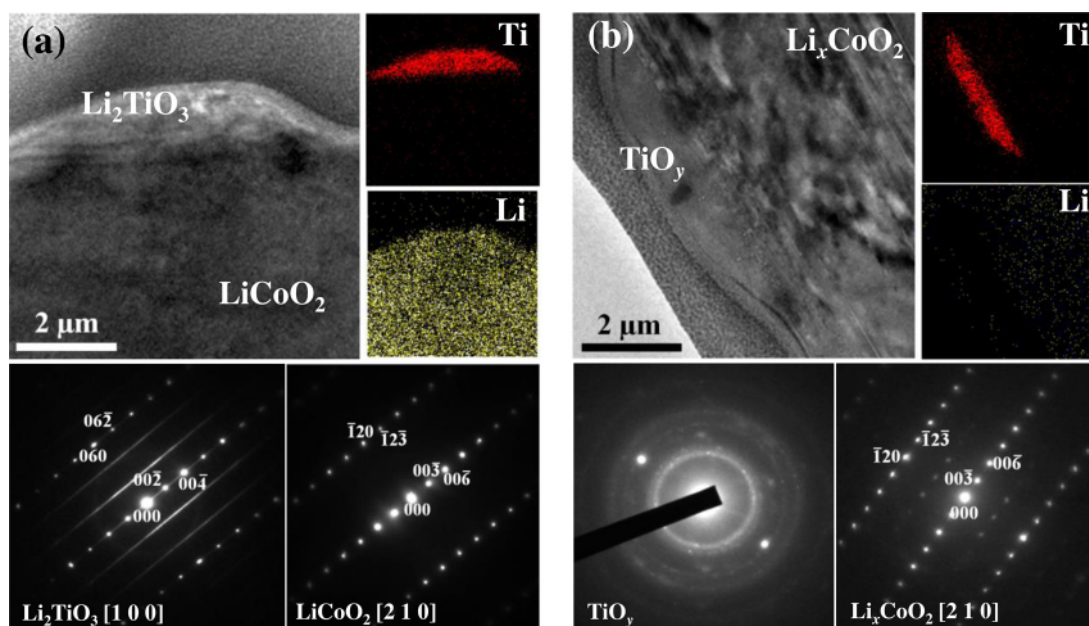


Fig. 5. Bright-field TEM images (main figures), SAED patterns of coating layers (bottom left figures) and active materials (bottom right figures), and Ti/Li maps from EELS (right figures) of (a) fresh (uncycled) and (b) first-charged state of LT0-LCO_{Mg}.

to occur. The smaller R_{ct} of LT2-LCO_{Mg} than LT0-LCO_{Mg} is in agreement with the experimental results of lithium conductivities of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [37] and Li_2TiO_3 [38]. The relatively high ionic conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ possibly alleviates the cycling deterioration and consequential rapid rise of R_{ct} .

In order to trace an origin of the different effectiveness of monoclinic Li_2TiO_3 and spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as coating materials, the structural changes of the materials after charging (delithiating) were investigated by TEM. Fig. 5a shows a TEM image, selected area electron diffraction (SAED) patterns, and EELS maps of Ti and Li of fresh (uncycled) LT0-LCO_{Mg}. The electron incidence was along the [1 0 0] zone-axis of Li_2TiO_3 , which is parallel to [2 1 0] zone-axis of LiCoO_2 . The typical diffraction spots of monoclinic phase of Li_2TiO_3 and hexagonal phase of LiCoO_2 are respectively observed in their

SAED patterns. It has been known that the lines between the main reflections of the Li_2TiO_3 phase are from the stacking faults of LiTi_2 metal layers [39]. Meanwhile, Fig. 5b exhibits the same analysis of LT0-LCO_{Mg} after the first charge. For the LiCoO_2 phase, in addition to the original diffraction spots of the hexagonal phase, weak but new diffraction spots are appeared in the middle of them. The additional spots are attributed to the characteristics of the charged (partially delithiated) state of lithium cobalt oxide (Li_xCoO_2). As shown in the EELS maps, the Li ions in the Li_2TiO_3 coating layer are completely extracted after charging, which means that they are electrochemically active in the range of operating voltages, while the Ti ions still remain in that layer. The SAED pattern of the TiO_y layer shows diffused diffraction rings, which indicates that a substantial amount of the delithiated coating layer loses its

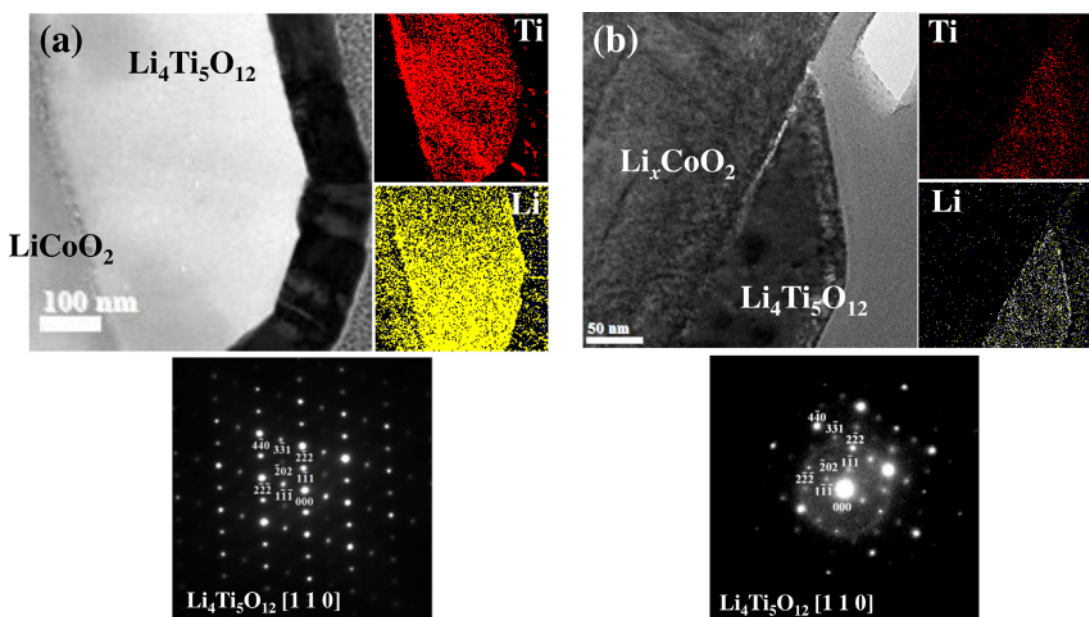


Fig. 6. Bright-field TEM images (main figures), SAED patterns of coating layer (bottom figures), and Ti/Li maps from EELS (right figures) of (a) fresh (uncycled) and (b) first-charged state of LT2-LCO_{Mg}. The SAED patterns of active materials are the same as those of LT0-LCO_{Mg} in Fig. 5.

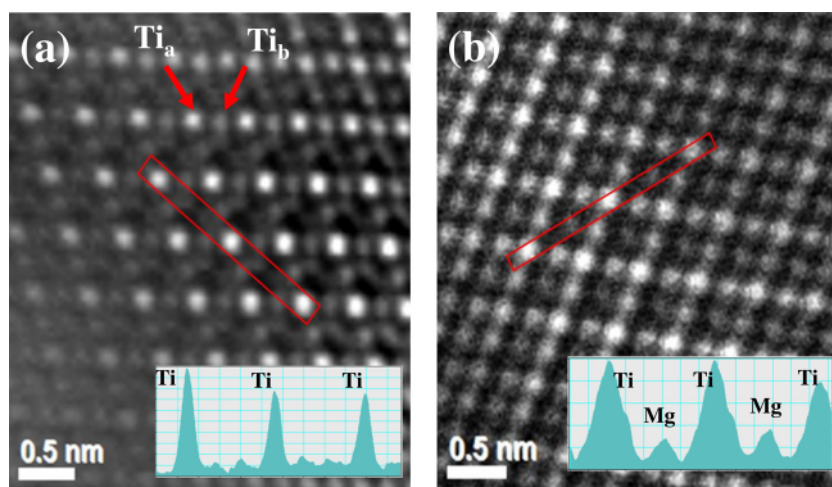


Fig. 7. HAADF STEM images of first charged state of (a) (undoped) LT2-LCO and (b) LT2-LCO_{Mg}. The insets are the contrast line profiles in red rectangles. For explanation of Ti_a and Ti_b with different brightness in (a), see the text.

monoclinic crystalline structure. The same analysis was done on LT2-LCO_{Mg} (Fig. 6). The EELS map of Li shows that Li ions in Li₄Ti₅O₁₂ do not leave from the coating layer during the first charge while the majority of Li ions in LiCoO₂ are extracted. In addition, the SAED pattern of Li₄Ti₅O₁₂ phase, in which the electron incidence was along with [110] zone-axis, after the first charge is almost the same as that of the fresh sample except the diffraction spots in the former become slightly more diffused than those in the latter. This observation indicates that the Li₄Ti₅O₁₂ coating layer still maintain the crystalline structure after charge, that is, the “zero strain” characteristic, unlike the Li₂TiO₃ coating layer. In conclusion, the most crucial difference between the two coating layers is the electrochemical activity of the Li ions that they carry inside themselves. If the Li ion cycling of a material is sufficiently reversible, the electrochemical activity itself might not be a matter. However, the lithiation/delithiation of Li₂TiO₃ is catastrophically irreversible, therefore, the coating layer of Li₂TiO₃ phase possibly acts as a resistance after some cycling (large R_{ct}) as shown by the EIS experiment. This is reminiscent of the relatively poor cyclability of layered-layered composite cathode materials, one component of which is lithium-rich metal oxide, for example, Li₂MnO₃ [40]. TEM images and SAED patterns obtained after 50 cycles (Fig. S3 in Supplementary Data) demonstrate the irreversible transformation of Li₂TiO₃ and the structure consistency of Li₄Ti₅O₁₂ with cycling.

In order to study the synergistic effects of coating and doping for the cathode materials, the Li₄Ti₅O₁₂ coating layers of LT2-LCO_{Mg} and LT2-LCO were compared. Fig. 7 shows enlarged HAADF STEM images, which were viewed along the [110] direction, of the two samples. In Fig. 7a, the different atomic columns of Li₄Ti₅O₁₂ in the charged state of LT2-LCO (without Mg doping) are revealed based on the contrast, where the 16d Ti sites are clearly identified as shown in the contrast line profile. The strong and weak spots indicate that there are two different Ti columns (Ti_a and Ti_b in Fig. 7a) and the population of Ti in the Ti_a columns is greater than that in the Ti_b columns. This observation on spinel Li₄Ti₅O₁₂ by STEM was previously reported by Lu et al. [41], and is reproduced here. In their study, the 8a Li sites were also successfully visualized using the ABF images, which is not possible by the HAADF images due to the low atomic number of Li ions. Meanwhile, a notable change in the contrast was observed in the Li₄Ti₅O₁₂ coating layer of the Mg-doped sample (LT2-LCO_{Mg}). As shown in Fig. 7b, bright

white spots are appeared in the centers of diamond patterns of Ti ions. The new spots obviously come from the Mg ions. It is considered that the excellent electrochemical performances of LT2-LCO_{Mg} are originated by the high electrical conductivity of Mg-doped Li₄Ti₅O₁₂. Chen et al. reported that the Mg-doped Li₄Ti₅O₁₂ exhibits a completely different electrical behavior ($\sigma = 10^{-2} \text{ S cm}^{-1}$) from the nearly insulating undoped Li₄Ti₅O₁₂ [19]. The current-voltage (IV) curves in Fig. 8 provide supporting evidences of these different electrical characteristics. In this experiment, one probe contacts the active materials of LiCoO₂ while the other probe is placed on the Li₄Ti₅O₁₂ coating layer as demonstrated in the figure inset. Because the fully lithiated LiCoO₂ is an insulator [42], the current at the discharged state of LT2-LCO_{Mg} is almost zero. Meanwhile, the significant current is detected at its charged state, which indicates that both the delithiated LiCoO₂ and Mg-doped Li₄Ti₅O₁₂ are electrically conductive. However, the conductivity of the coating layer of LT2-LCO, that is, the undoped Li₄Ti₅O₁₂, is not as good as that of the Mg-doped Li₄Ti₅O₁₂. Hence, the formation of a conductive coating material, that is, Mg-doped Li₄Ti₅O₁₂, is an

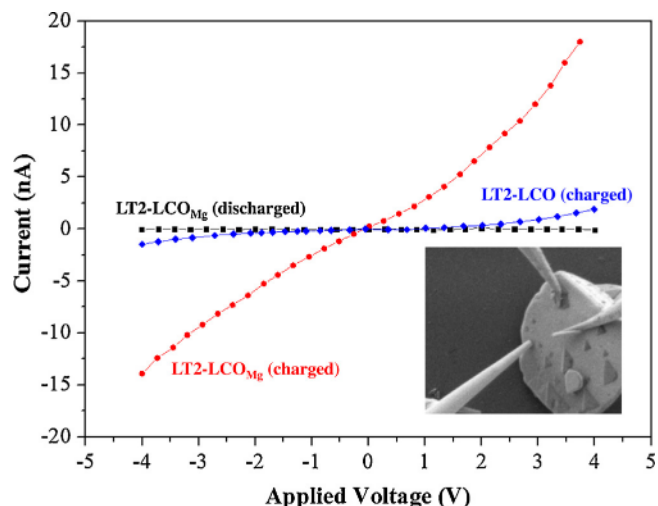


Fig. 8. Current-voltage plot of discharged/charged LT2-LCO_{Mg} and charged LT2-LCO. The inset is an SEM image of measuring by nano probe.

origin of synergistic effects of coating and doping for the cathode materials in this study.

4. Conclusion

We synthesized and characterized lithium titanate-coated LiCoO_2 with Mg doping in which the remaining lithium carbonates after synthesis of the active materials were reused as a lithium source for the coating materials. Due to its excellent stability during charging/discharging, the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which was obtained from the high concentration of Ti source, showed much better electrochemical performances as a coating material than the monoclinic Li_2TiO_3 , which was from the low concentration of Ti source. In addition, it was observed that the dopant ions (Mg^{2+}) in the active materials diffused to the coating layer, and efficiently improved the cell performances by formation of highly conductive Mg-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which is considered as a mechanism of synergistic effects of coating and doping for the cathode materials in LIB.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2015.10.135>.

References

- [1] J. Vetter, P. Novák, M.R. Wagner, C. Veit, K.-C. Möller, J.O. Besenhard, M. Winter, M. Wohlfahrt-Mehrens, C. Vogler, A. Hammouche, *J. Power Sources* 147 (2005) 269–281.
- [2] M.M. Thackeray, *J. Electrochem. Soc.* 142 (1995) 2558–2563.
- [3] G. Ceder, M.K. Aydinol, *Solid State Ionics* 109 (1998) 151–157.
- [4] P. Arora, R.E. White, M. Doyle, *J. Electrochem. Soc.* 145 (1998) 3647–3667.
- [5] Z. Chen, Y. Qin, K. Amine, Y.-K. Sun, *J. Mater. Chem.* 20 (2010) 7606–7612.
- [6] J. Lu, Q. Peng, W. Wang, C. Nan, L. Li, Y. Li, *J. Am. Chem. Soc.* 135 (2013) 1649–1652.
- [7] H. Deng, P. Nie, H. Luo, Y. Zhang, J. Wang, X. Zhang, *J. Mater. Chem. A* 2 (2014) 18256–18262.
- [8] E. Ferg, R.J. Gummow, A. Dekock, M.M. Thackeray, *J. Electrochem. Soc.* 141 (1994) L147–L150.
- [9] T. Ohzuku, A. Ueda, N. Yamamoto, *J. Electrochem. Soc.* 142 (1995) 1431–1435.
- [10] C.P. Sandhya, B. John, C. Couri, *Ionics* 20 (2014) 601–620 and references therein.
- [11] D.-Q. Liu, X.Q. Liu, Z.-Z. He, *Mater. Chem. Phys.* 105 (2007) 362–366.
- [12] T.-F. Yi, J. Shu, Y.-R. Zhu, A.-N. Zhu, R.-S. Zhu, *Electrochem. Commun.* 11 (2009) 91–94.
- [13] Y.-R. Zhu, T.-F. Yi, R.-S. Zhu, A.-N. Zhou, *Ceram. Int.* 39 (2013) 3087–3094.
- [14] J. Li, Y. Zhu, L. Wang, C. Cao, *ACS Appl. Mater. Interfaces* 6 (2014) 18742–18750.
- [15] N. Ohta, K. Takada, L. Zhang, R. Ma, M. Osada, T. Sasaki, *Adv. Mater.* 18 (2006) 2226–2229.
- [16] T.-F. Yi, J. Shu, C.-B. Yue, X.-D. Zhu, A.-N. Zhou, Y.-R. Zhu, R.-S. Zhu, *Mater. Res. Bull.* 45 (2010) 456–459.
- [17] T.-F. Yi, J. Shu, Y. Wang, J. Xue, J. Meng, C.-B. Yue, R.-S. Zhu, *Surf. Coat. Tech.* 205 (2011) 3885–3889.
- [18] G.T.-K. Fey, C.-F. Huang, P. Muralidharan, E.S.-S. Chang, *J. Power Sources* 174 (2007) 1147–1151.
- [19] C.H. Chen, J.T. Vaughey, A.N. Jansen, D.W. Dees, *J. Electrochem. Soc.* 148 (2001) A102–A104.
- [20] S. Levasseur, M. Menetrier, C. Delmas, *Chem. Mater.* 14 (2002) 3584–3590.
- [21] H.-J. Kim, Y.U. Jeong, J.-H. Lee, J.-J. Kim, *J. Power Sources* 159 (2006) 233–236.
- [22] H. Tukamoto, A.R. West, *J. Electrochem. Soc.* 144 (1997) 3164–3168.
- [23] F. Nobili, S. Dsoke, F. Croce, R. Marassi, *Electrochim. Acta* 50 (2005) 2307–2313.
- [24] F. Nobili, F. Croce, R. Tossici, I. Meschini, P. Reale, R. Marassi, *J. Power Sources* 197 (2012) 276–284.
- [25] F. Zhou, W. Luo, X. Zhao, J.R. Dahn, *J. Electrochem. Soc.* 156 (2009) A917–A920.
- [26] H.-S. Kim, T.-K. Ko, B.-K. Na, W.I. Cho, B.W. Chao, *J. Power Sources* 138 (2004) 232–239.
- [27] S. Valanarasu, R. Chandramohan, *Cryst. Res. Technol.* 45 (2010) 835–839.
- [28] R. Alcántara, P. Lavela, J.L. Tirado, R. Stoyanova, E. Zhecheva, *J. Solid State Chem.* 134 (1997) 265–273.
- [29] M. Zhou, M. Yoshio, S. Gopukumar, J. Yamaki, *Chem. Mater.* 15 (2003) 4699–4702.
- [30] M.-H. Park, M. Noh, S. Lee, M. Ko, S. Chae, S. Sim, S. Choi, H. Kim, H. Nam, S. Park, J. Cho, *Nano Lett.* 14 (2014) 4083–4089.
- [31] M. Mladenov, R. Stoyanova, E. Zhecheva, S. Vassilev, *Electrochem. Commun.* 3 (2001) 410–416.
- [32] Z. Wang, L. Liu, L. Chen, X. Huang, *Solid State Ionics* 148 (2002) 335–342.
- [33] H. Zhao, L. Gao, W. Qui, X. Zhang, *J. Power Sources* 132 (2004) 195–200.
- [34] J.-H. Shim, S. Lee, S.S. Park, *Chem. Mater.* 26 (2014) 2537–2543.
- [35] S.D. Findlay, N. Shibata, H. Sawada, E. Okunishi, Y. Kondo, T. Yamamoto, Y. Ikuhara, *Appl. Phys. Lett.* 95 (2009) 191913.
- [36] G. Izquierdo, A.R. West, *Mater. Res. Bull.* 15 (1980) 1655–1660.
- [37] S. Takai, M. Kamata, S. Fujine, K. Yoneda, K. Kanda, T. Esaka, *Solid State Ionics* 123 (1999) 165–172.
- [38] B. Ruprecht, M. Wilkening, R. Uecker, P. Heitjans, *Phys. Chem. Chem. Phys.* 14 (2012) 11974–11980.
- [39] N.V. Tarakina, R.B. Neder, T.A. Denisova, L.G. Maksimova, Y.V. Baklanova, A.P. Tyutyunnik, V.G. Zubkov, *Dalton Trans.* 39 (2010) 8168–8176.
- [40] P. He, H. Yu, D. Li, H. Zhou, *J. Mater. Chem.* 22 (2012) .
- [41] X. Lu, L. Zhao, X. He, R. Xiao, L. Gu, Y.-S. Hu, H. Li, Z. Wang, X. Duan, L. Chen, J. Maier, Y. Ikuhara, *Adv. Mater.* 24 (2012) 3233–3238.
- [42] F. Sauvage, J.-M. Tarascon, E. Baudrin, *J. Phys. Chem. C* 111 (2007) 9624–9630.

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Synergistic effects of coating and doping for lithium ion battery cathode materials: synthesis and characterization of lithium titanate-coated LiCoO₂ with Mg doping



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ABSTRACT

Lithium titanates are introduced as coating materials on the surface of Mg-doped LiCoO₂ in which the residual Li₂CO₃ after synthesis of the active materials is used as a lithium source. It is revealed that two completely different lithium titanate phases (monoclinic Li₂TiO₃ and spinel Li₄Ti₅O₁₂) can be obtained as the coating materials depending on the concentration of a titanium source. Characterization of the coating materials is performed with various experimental techniques including XRD, nano SIMS, TEM, EELS and current measurement using nano probe. The Li₄Ti₅O₁₂ coating layer from the high concentration of titanium source secures better electrochemical performances than the Li₂TiO₃ one from the low concentration of titanium source due to its “zero-strain” characteristic. In addition, it is shown that the doped ions (Mg²⁺) from the active materials move to the coating layer and strongly enhance the conductivity of Li₄Ti₅O₁₂. Consequently, synergistic effects on the cell performances of cyclability and rate capability from coating and doping for the LiCoO₂ cathode materials are rigorously investigated.

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ATTACHMENT

A-5

Synthesis, characterization and electrochemical studies on novel Li_2MZrO_4 ($\text{M} = \text{Fe}, \text{Mn}$) cathode material for lithium-ion battery

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ABSTRACT

We report a novel cathode of the molecular formula, Li_2MZrO_4 ($\text{M} = \text{Fe}, \text{Mn}$), based on an inexpensive, earth-abundant, and eco-friendly materials, which have theoretical capacities within $119 - 238 \text{ mAh.g}^{-1}$ depending on the number of lithium ions extracted from material, suitable for high power rechargeable lithium-ion battery. X-ray diffraction (XRD) revealed tetragonal crystal structure of the synthesized material. SEM images illustrate the formation of porous material with large surface area. The cyclic voltammograms of Li_2MZrO_4 ($\text{M}=\text{Fe}, \text{Mn}$) showed only one pair of redox peak corresponding to the anodic and cathodic reactions within a potential window of $2.2 - 4.5$ volts vs. Li/Li^+ . The first discharge capacities were 89 mAhg^{-1} for $\text{Li}_2\text{FeZrO}_4$, whereas in case of $\text{Li}_2\text{MnZrO}_4$ it was 94 mAhg^{-1} at 0.1 C rates, which are equivalent to removal of one lithium ion from the compounds. Copyright © 2016 VBRI Press.

Keywords: SEM; Li_2MZrO_4 (M = Fe, Mn) new cathode; powder XRD; cyclic voltammetry; lithium-ion battery.

Introduction

Lithium-ion batteries have found to be the most popular energy storage system over the last two decades [1-3], providing solutions to environmental issues and the growing demand for portable electronic devices as well as hybrid electric vehicles (HEVs) [4, 5].

Several lithium transition metal oxides have been functioned as the competitive intercalation cathode materials for their applications in rechargeable lithium-ion batteries (LIBs) [6-9]. Among them, layered rock-salt compound LiCoO_2 is established appropriate and efficient for commercial application in accordance with its higher theoretical capacity (274 mAhg^{-1}), high operating potential ($\sim 3.9 \text{ Volt}$), flat charge-discharge plateau, ease of synthesis, high electronic conductivity and excellent cycling ability [10-13]. However, certain limitations still persist with LiCoO_2 material, as extraction of more than fifty percent Li^+ ions from the material always destroy the crystal structure and thus capacity not more than 140 mAhg^{-1} are achievable under reversible condition. Besides this, the cobalt oxide material suffers from elevated cost and environmental incompatibility [9,14,15]. Therefore, for large-scale application, such as EVs and backup power system, alternating low cost cathode materials, having large faradic capacity and environmental compatibility, are highly desired.

Iron-based cathode materials are thus the ideal candidates for future LIBs taking into account of

manufacturing cost and environmental safety issues [16-18]. Among iron-based compounds, LiFePO_4 cathode material is regarded as the potential and promising candidate for future LIBs and thus intensively studied during last century [19-26]. However, limitation lies with this material due to its deprived electronic conductivity and sluggish Li^+ ion transport [27-31]. Electrical conductivity as well as transport properties of this material has been improved by proper doping with higher valent metal cations [32-37] or coating with conducting carbon additives in the cost of its intrinsic capacity [38-43]. Hence, searching for an alternate iron based cathode material having higher faradic capacity is urgently needed for high power lithium ion batteries.

In this paper, we report a promising and inexpensive cathode material of the formula, Li_2MZrO_4 ($\text{M} = \text{Fe}, \text{Mn}$) having theoretical capacity 238 mAhg^{-1} suitable for next generation high power rechargeable LIBs [44-49].

Experimental

Material synthesis procedure

Li_2MZrO_4 (M = Fe or Mn) materials were synthesized applying modified solid-state synthesis method [19, 50]. In order to synthesize 1.5 g of $\text{Li}_2\text{FeZrO}_4$, the stoichiometric amounts i.e.; 0.4927 g Li_2CO_3 (Sigma-Aldrich, USA, 99.9 %), 1.1995 g $\text{Fe}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$ (Aldrich, USA, 99.9 %) and 0.8217 g ZrO_2 (Aldrich, USA, 99.9 %) were weighted. For

1.5 g of $\text{Li}_2\text{MnZrO}_4$, 1.025 g Li_2ZrO_3 (Aldrich, USA, 99.9 %) and 1.6491 g $\text{Mn(II)(CH}_3\text{COO)}_2 \cdot 4\text{H}_2\text{O}$ (Merck, USA, 99.5 %) were weighted. Before weighing and mixing, all the reagents were ground individually to make fine powder. After taking the stoichiometric amount of the reagents as mentioned above in a mortar pestle, small amount of pure acetone (Merck, USA, GR grade) was added to the mixture and ground them further to prepare a homogeneous mixture. The acetone was slowly evaporated out during grinding and the residual mixture was then taken in a highly crystallized alumina boat, placed inside a horizontal tubular furnace and calcined at 500 °C for 4 hours under nitrogen atmosphere. After cooling down to room temperature, the powder was ground again and sintered at 800 °C for 8 hours under nitrogen atmosphere for crystalline particle growth. Finally, the sintered materials ($\text{Li}_2\text{FeZrO}_4$ and $\text{Li}_2\text{MnZrO}_4$) were cool down to room temperature very slowly and preserved to reach out of moisture for further use.

Characterization

TGA (Thermal Gravimetric Analysis) of the precursor mixture was recorded with a Thermo Balance (Perkin Elmer, Sweden model number STA 6000) to establish the decomposition temperature. A curve, representing the percentage of weight loss versus temperature, was obtained after thermal treatment in the temperature region of 42 °C-933 °C at the rate of 20 °Cmin⁻¹ under continuous nitrogen gas flow.

The synthesized solid materials were characterized using powder X-ray Diffractometer (XRD) and Scanning Electron Microscopy (SEM). Powder XRD pattern were recorded from a Ultima III Rigaku machine using Cu-K α ($\lambda=1.5406$ Å) as the radiation source in the range of $2\theta=10^{\circ}$ - 70° with scan rate $5^{\circ} \text{ min}^{-1}$. The particle size distribution and surface morphology was examined using a Scanning Electron Microscope (JEOL, Model-JSM-6360, UK).

In order to evaluate the electrochemical characteristics of the synthesized materials, the working electrode (cathode) was prepared as follows: first a slurry was made by mixing 80wt % of active material ($\text{Li}_2\text{MZR}_2\text{O}_4$, $\text{M} = \text{Fe}$ or Mn), 8wt % carbon black (Alfa Aesar, USA, 99.9 %), 8wt % graphite powder (Alfa Aesar, USA, 99.99 %) and 4wt % binder polyvinylidene fluoride (PVDF, Aldrich, USA, 99.9 %) in a solvent of N-methyl pyrrolidone (NMP) (Merck, USA, 99.5 %) [51-53]. The uniform slurry, as obtained, was then coated on an aluminum foil (1 cm^2) and dried inside a vacuum oven at 60°C . The coated foil was then pressed by a hydraulic press at $8\text{-}10 \text{ Tcm}^{-2}$ to attain better contact between the active material and the aluminum foil current collector [54-56]. Finally, the coated foil was dried overnight at 80°C under vacuum to eliminate NMP completely in order to get the loading mass of the active materials, which was $\sim 2.5 \text{ mg cm}^{-2}$. The dried electrode was used as cathode to fabricate a coin type cell, which is composed of lithium metal foil (Aldrich, USA, 99.9 %) as anode, 1M LiPF_6 (Alfa Aesar, 98 %) solution, prepared in ethylene carbonate (EC) (Aldrich, 99.9 %) and dimethyl carbonate (DMC) (Aldrich, 99.9 %) in 1:1 ratio as an electrolyte and a porous polypropylene (PP) film soaked with this electrolyte as the separator [57-59]. The coin type

cell was assembled inside a glove bag under argon atmosphere after complete replacement of air and moisture by pure argon gas. A computer controlled potentiostat/galvanostat, model VersaStat TMII (Princeton Applied Research) was used for electrochemical studies. The cyclic voltammograms (CVs) were recorded at a scan rate of 0.2 mVs⁻¹ with a cut-off limit 2 – 4.5 V vs. Li/Li⁺. The charge-discharge measurements were carried out with a current rate 0.1C.

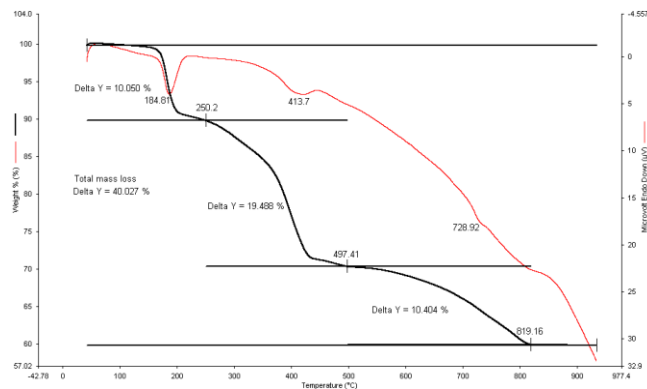


Fig. 1. TGA-DTA curve of the precursor mixture for synthesis of $\text{Li}_2\text{FeZrO}_4$.

Results and discussion

TGA-DTA analysis

Fig. 1 demonstrates the TGA-DTA curve of the precursor materials recorded under nitrogen environment. It is noticed from the illustration that the major weight loss has occurred mainly in three steps. In the first step within the temperature range between room temperature (RT) to 250 °C, 10 % weight loss was observed that is attributed owing to the elimination of humidity and water of crystallization from $\text{Fe}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$ crystals. In the second step, within the temperature range 250 °C-500 °C another 19.5 % weight loss has occurred, which is attributed due to the decomposition of $\text{Fe}(\text{C}_2\text{O}_4)$ and Li_2CO_3 . It is clear from the literature that pure Li_2CO_3 decomposes above 720 °C, but herein, it starts to disintegrate well below 720 °C within the above temperature range for being a eutectic mixture [60]. In the final step, within 800 °C the decomposition of carbonate and oxalate are accomplished and thereby a new material was produced. Based on the DTA-TGA study, the calcinations and sintering temperatures for the synthesis of zirconate materials are set at 500 °C for 4 hours and at 800 °C for 8 hours, respectively.

Powder XRD analysis

Powder XRD pattern of $\text{Li}_2\text{FeZrO}_4$ and $\text{Li}_2\text{MnZrO}_4$, illustrated in **Fig. 2** and **Fig. 3**, are recorded within the range, $2\theta = 10^\circ\text{--}70^\circ$ at scan rate of 5°min^{-1} employing Cu-K_α ($\lambda = 1.5406 \text{ \AA}$) as the radiation source. The peak location and pattern were evaluated in comparison with the reported JCPDS data, file number 38-0281 for $\text{Li}_2\text{FeZrO}_4$ and 40-0360 for $\text{Li}_2\text{MnZrO}_4$, where an entire matching of peak positions was observed. However, a careful and systematic analysis of the XRD data using a software, called POWDIN, revealed that the present material ($\text{Li}_2\text{FeZrO}_4$)

belongs to tetragonal crystal structure with space lattice *P*-type and lattice parameters, $a = 4.1988 \text{ \AA}$ and $c = 9.0607 \text{ \AA}$ in contrast to the literature report of *I*-type lattice with lattice parameters, $a = 4.193 \text{ \AA}$ and $c = 9.003 \text{ \AA}$. Likewise, $\text{Li}_2\text{MnZrO}_4$ has tetragonal crystal structure with space lattice *P*-type and lattice parameters, $a = 4.2470 \text{ \AA}$ and $c = 9.2410 \text{ \AA}$, which exactly matches with the literature data.

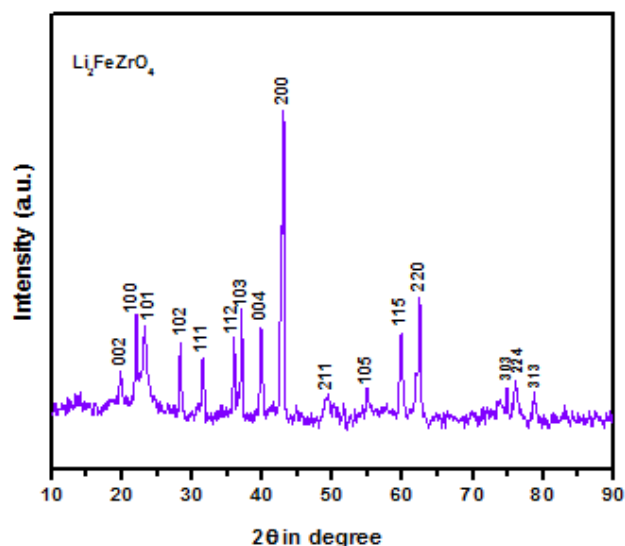


Fig. 2. Powder XRD pattern of $\text{Li}_2\text{FeZrO}_4$ sintered at 800°C .

Careful assessment of the XRD pattern reveals that the peaks for $\text{Li}_2\text{FeZrO}_4$ are very sharp, intense and the crystals are highly oriented along 200 planes, whereas peaks for $\text{Li}_2\text{MnZrO}_4$ are broaden and no specific orientation of the crystals are observed. The high-intense peaks are in favor of highly crystalline particle growth, whereas peak-broadening supports the formation of nano material.

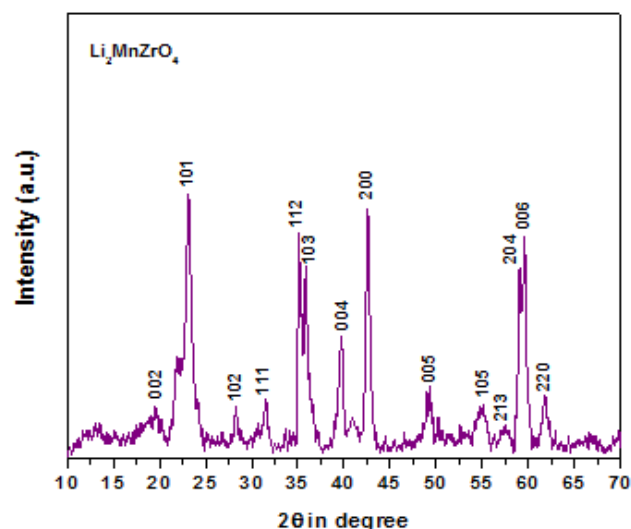


Fig. 3. Powder XRD pattern of $\text{Li}_2\text{MnZrO}_4$ sintered at 800°C .

SEM analysis

Scanning Electron Microscopy (SEM) was performed to investigate the particle size distribution and surface morphology of the synthesized materials. The SEM images,

presented in Fig. 4, clearly illustrate the arrangement of porous smaller size grains with large surface area, which ultimately influence the performance of the material. Moreover, SEM images clearly indicate that the particles are composed of nano and micron sizes, and their sizes lie between 200 nm to $1 \mu\text{m}$. Further it is evident from the SEM images that $\text{Li}_2\text{MnZrO}_4$ particles are more evenly distributed and particle size distributions are more even and homogeneous, whereas, it is uneven and agglomerations among the particles are observed in case of $\text{Li}_2\text{FeZrO}_4$ material.

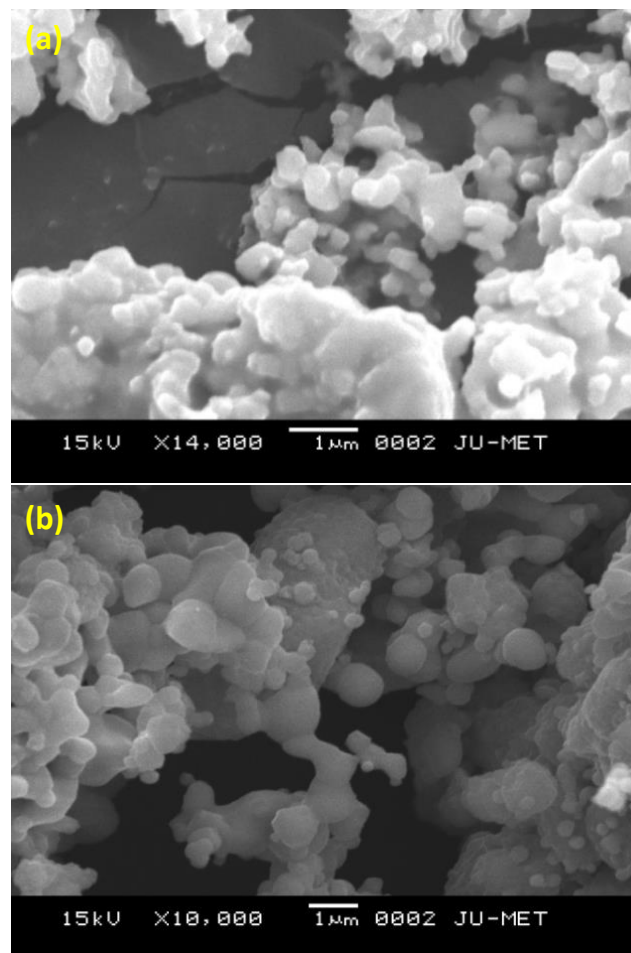


Fig. 4. SEM images of $\text{Li}_2\text{FeZrO}_4$ (a); and $\text{Li}_2\text{MnZrO}_4$ (b).

CV and charge-discharge study

For the potential application of Li_2MZrO_4 ($M = \text{Fe}$ or Mn) material, the cyclic voltammograms (CVs) were used to evaluate the electrochemical performance. The CVs were recorded with the aforementioned fabricated laboratory model cells within the potential window of 2.2–4.5 volts vs. Li/Li^+ , at a scan rate of 0.2 mVs^{-1} and the corresponding i - v graphs for $\text{Li}_2\text{FeZrO}_4$ and $\text{Li}_2\text{MnZrO}_4$ were in Fig. 5, respectively. The cyclic voltammograms clearly showed one pair of redox peaks within the specified window corresponding to the cathodic and anodic reactions. In principle, the reversibility of a redox system can be justified from the ratio of $i_{p,r}/i_{p,f}$, where, $i_{p,r}$ and $i_{p,f}$ are the backward and forward peak current, respectively; which is unity for a reversible process. Since the measurement of

cathodic peak current, in case of $\text{Li}_2\text{MnZrO}_4$, is difficult due to complexity in locating the proper baseline from which the peak current to be measured, the current ratios of the present systems are calculated using the empirical method of Nicholson [61] (Equation 1),

$$\frac{i_{p,r}}{i_{p,f}} = \frac{(i_{p,r})_0}{i_{p,f}} + 0.48 \frac{i_L}{i_{p,f}} + 0.086 \quad (1)$$

where, $(i_{p,f})$ is forward peak current, and $(i_{p,r})$ is reverse peak current and (i_L) is the measured current at the switching potential of the forward peak from the same baseline. The measured current values for both the systems are included in **Table 1**. From the ratio of backward and forward peak current, it is clear that both the systems are highly reversible.

Table 1. Ratio of the reverse and forward peak currents for reversibility test.

Cathode	$i_{p,f}$ ($\mu\text{A.cm}^{-2}$)	$(i_{p,r})_0$ ($\mu\text{A.cm}^{-2}$)	i_L ($\mu\text{A.cm}^{-2}$)	$(i_{p,r})/(i_{p,f})$
$\text{Li}_2\text{FeZrO}_4$	114	109	49	1.24
$\text{Li}_2\text{MnZrO}_4$	131	63	116	1.00

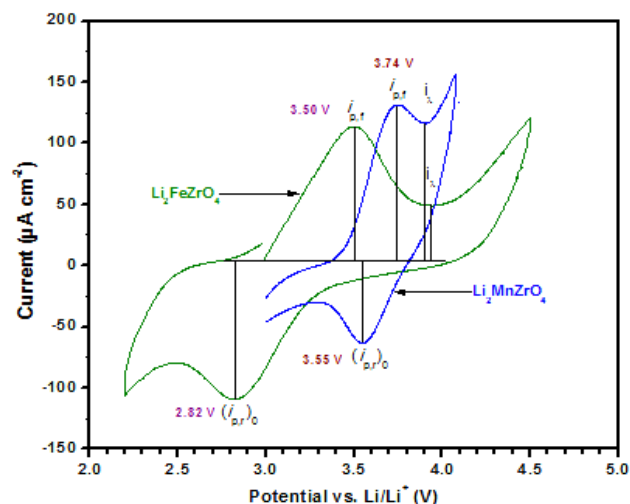


Fig. 5. Cyclic voltammograms of $\text{Li}_2\text{FeZrO}_4$ & $\text{Li}_2\text{MnZrO}_4$ vs. Li at the scan rate of 0.2 mVs^{-1} .

The peaks in the anodic scan are due to removal of first lithium ion from the compound, whereas, peaks in the reverse scan are due to insertion of first lithium ion in the matrix. Careful scrutiny of the CVs revealed that the redox peaks in case of iron substituted zirconium are very sharp compared to manganese substituted zirconium material. This clearly suggests that electronic conductivity of iron substituted zirconium is higher than that of manganese substituted zirconium material and thus the reaction kinetics is faster in case of $\text{Li}_2\text{FeZrO}_4$. On the other hand, the separation between anodic and cathodic peaks (ΔV) for both the materials are quite large, 0.70 V for $\text{Li}_2\text{FeZrO}_4$, whereas it is about 0.50 V for $\text{Li}_2\text{MnZrO}_4$, which indicates that the electrochemical behavior is controlled by diffusion steps. It is well known that the maximum rate of reaction (i_p) in a reversible diffusion controlled reaction will only be achieved if the sweeping potential cross beyond the formal potential and thus large peak potential difference is

expected. Again if the reaction is slow and the rate of electron transfer rather than the diffusion is the rate determining step, the sweep will continue further before the maximum reaction rate is observed. In the present study, large ΔV indicates that kinetics for both the materials are diffusion controlled and in case of $\text{Li}_2\text{FeZrO}_4$ having highest ΔV indicates that electron transfer rate rather than diffusion is the rate determining step. Therefore it may be concluded from the CVs that electron transfer reaction in $\text{Li}_2\text{MnZrO}_4$ is faster than $\text{Li}_2\text{FeZrO}_4$, which may reflect in the faradic capacity.

Coin cells using Li_2MZrO_4 ($M = \text{Fe or Mn}$) cathode and lithium anode were galvanostatically charged and discharged between 2.2 to 4.5 volts vs. Li/Li^+ at room temperature. **Fig. 6** represents the charge and discharge profiles for 1st cycle at 0.1 C rates. The $\text{Li}_2\text{FeZrO}_4$ compound delivers a first cycle charge and discharge capacity of 93 and 89 mAhg^{-1} , respectively, whereas the $\text{Li}_2\text{MnZrO}_4$ compound delivers a first cycle charge and discharge capacity of 99 and 94 mAhg^{-1} , respectively. Both the compounds deliver a first cycle discharge capacity around 90 mAhg^{-1} , which is $\sim 76 \%$ of their theoretical capacity based on one lithium ion extraction. The discharge capacity can further be enhanced towards theoretical value by the formation of nano sized particles. It should be mentioned here that the discharge potential for both the compounds is similar, but the charging potential in case of $\text{Li}_2\text{MnZrO}_4$ compound is higher than $\text{Li}_2\text{FeZrO}_4$ and this might be due to higher interfacial resistance of the cell made out of $\text{Li}_2\text{MnZrO}_4$ compound.

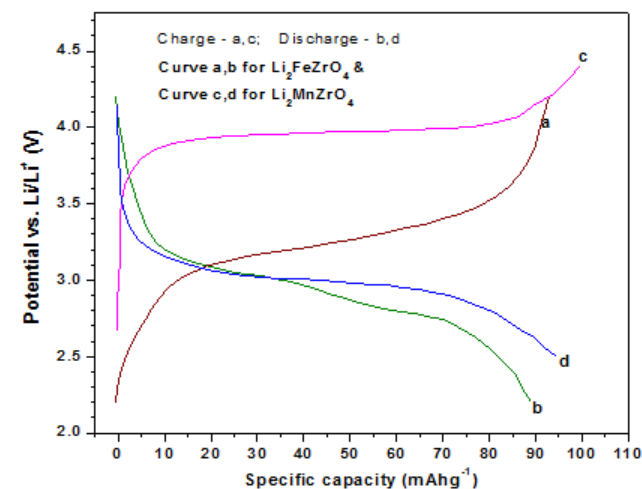


Fig. 6. Charge-discharge curve of $\text{Li}_2\text{FeZrO}_4$ & $\text{Li}_2\text{MnZrO}_4$ cathodes vs. Li anode at 0.1 C rates.

Conclusion

A new and novel cathode of the formula, Li_2MZrO_4 ($M = \text{Fe or Mn}$), has been successfully synthesized by solid-state method based on cheaper and environment friendly precursors. Powder XRD pattern matches with the literature data and thus support the formation of pure crystalline material. SEM images revealed the formation of particles within nano to micron range. Cyclic voltammograms of the assembled cells using these materials as cathode display high reversibility and the electrochemical processes are controlled by diffusion step. The first cycle discharge

capacity delivered by these compounds is $\sim 90 \text{ mAhg}^{-1}$, which is 75 % of their theoretical capacity based on one lithium ion extraction and this can further be enhanced by synthesizing nano sized material. The discharge capacity of these materials can be further enhanced by extracting both the lithium ions in a large potential window by choosing a suitable electrolytic solution. Finally, cost effective, environment friendly lithium ion batteries are proposed out of these materials, as these compounds are non-toxic and inexpensive.

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Reference

- Patil, A.; Patil, V.; Wook Shin, D.; Choi, J.-W.; Paik, D.-S.; Yoon, S.-J.; *Materials Research Bulletin*, **2008**, *43*, 1913.
DOI: [10.1016/j.materresbull.2007.08.031](https://doi.org/10.1016/j.materresbull.2007.08.031)
- Scrosati, B.; Garche, J.; *Journal of Power Sources*, **2010**, *195*, 2419.
DOI: [10.1016/j.jpowsour.2009.11.048](https://doi.org/10.1016/j.jpowsour.2009.11.048)
- Ye, L.; Lv, W.; Zhang, K. H. L.; Wang, X.; Yan, P.; Dickerson, J. H.; He, W.; *Energy*, **2015**, *83*, 669.
DOI: [10.1016/j.energy.2015.02.072](https://doi.org/10.1016/j.energy.2015.02.072)
- Goodenough, J. B.; Kim, Y.; *Chemistry of Materials*, **2010**, *22*, 587.
DOI: [10.1021/cm901452z](https://doi.org/10.1021/cm901452z)
- Lu, L.; Han, X.; Li, J.; Hua, J.; Ouyang, M.; *Journal of Power Sources*, **2013**, *226*, 272.
DOI: [10.1016/j.jpowsour.2012.10.060](https://doi.org/10.1016/j.jpowsour.2012.10.060)
- Chikkannanavar, S. B.; Bernardi, D. M.; Liu, L.; *Journal of Power Sources*, **2014**, *248*, 91.
DOI: [10.1016/j.jpowsour.2013.09.052](https://doi.org/10.1016/j.jpowsour.2013.09.052)
- Erickson, E. M.; Ghanty, C.; Aurbach, D.; *The Journal of Physical Chemistry Letters*, **2014**, *5*, 3313.
DOI: [10.1021/jz501387m](https://doi.org/10.1021/jz501387m)
- Song, H. K.; Lee, K. T.; Kim, M. G.; Nazar, L. F.; Cho, J.; *Advanced Functional Materials*, **2010**, *20*, 3818.
DOI: [10.1002/adfm.201000231](https://doi.org/10.1002/adfm.201000231)
- Xu, B.; Qian, D.; Wang, Z.; Meng, Y. S.; *Materials Science and Engineering R*, **2012**, *73*, 51.
DOI: [10.1016/j.mser.2012.05.003](https://doi.org/10.1016/j.mser.2012.05.003)
- Shim, J.-H.; Lee, K.-S.; Missyul, A.; Lee, J.; Linn, B.; Lee, E. C.; Lee, S.; *Chemistry of Materials*, **2015**, *27*, 3273.
DOI: [10.1021/acs.chemmater.5b00159](https://doi.org/10.1021/acs.chemmater.5b00159)
- Smekens, J.; Paulsen, J.; Yang, W.; Omar, N.; Deconinck, J.; Hubin, A.; Van Mierlo, J.; *Electrochimica Acta*, **2015**, *174*, 615.
DOI: [10.1016/j.electacta.2015.06.015](https://doi.org/10.1016/j.electacta.2015.06.015)
- Park, J. S.; Mane, A. U.; Elam, J. W.; Croy, J. R.; *Chemistry of Materials*, **2015**, *27*, 1917.
DOI: [10.1021/acs.chemmater.5b00603](https://doi.org/10.1021/acs.chemmater.5b00603)
- Shim, J.-H.; Lee, J.; Han, S. Y.; Lee, S.; *Electrochimica Acta*, **2015**, *186*, 201.
DOI: [10.1016/j.electacta.2015.10.135](https://doi.org/10.1016/j.electacta.2015.10.135)
- Islam, M. S.; Driscoll, D. J.; Fisher, C. A. J.; Slater, P. R.; *Chemistry of Materials*, **2005**, *17*, 5085.
DOI: [10.1021/cm050999v](https://doi.org/10.1021/cm050999v)
- Meng, Y. S.; Whittingham, M. S.; *Journal of The Electrochemical Society*, **2013**, *160*, Y2.
DOI: [10.1149/2.028305jes](https://doi.org/10.1149/2.028305jes)
- Mandal, B.; Basumallick, I.; Ghosh, S.; *British Journal of Applied Science and Technology*, **2014**, *4*, 1509.
DOI: [10.9734/BJAST/2014/7959](https://doi.org/10.9734/BJAST/2014/7959)
- Mandal, B.; Basumallick, I.; Ghosh, S.; *Journal of Chemical Sciences*, **2015**, *127*, 141.
DOI: [10.1007/s12039-014-0759-9](https://doi.org/10.1007/s12039-014-0759-9)
- Mandal, B.; Basumallick, I.; Ghosh, S.; *International Research Journal of Pure and Applied Chemistry*, **2015**, *5*, 30.
DOI: [10.9734/IRJPAC/2015/10924](https://doi.org/10.9734/IRJPAC/2015/10924)
- Beninati, S.; Damen, L.; Mastragostino, M.; *Journal of Power Sources*, **2008**, *180*, 875.
DOI: [10.1016/j.jpowsour.2008.02.066](https://doi.org/10.1016/j.jpowsour.2008.02.066)
- Huang, Y. H.; Park, K. S.; Goodenough, J. B.; *Journal of the Electrochemical Society*, **2006**, *153*, A2282.
DOI: [10.1149/1.2360769](https://doi.org/10.1149/1.2360769)
- Murugan, A. V.; Muraliganth, T.; Manthiram, A.; *Electrochemistry Communications*, **2008**, *10*, 903.
DOI: [10.1016/j.elecom.2008.04.004](https://doi.org/10.1016/j.elecom.2008.04.004)
- Padhi, A. K.; Nanjundaswamy, K. S.; Goodenough, J. B.; *Journal of The Electrochemical Society*, **1997**, *144*, 1188.
DOI: [10.1149/1.1837571](https://doi.org/10.1149/1.1837571)
- Yang, H.; Wu, X. L.; Cao, M. H.; Guo, Y. G.; *The Journal of Physical Chemistry C*, **2009**, *113*, 3345.
DOI: [10.1021/jp808080t](https://doi.org/10.1021/jp808080t)
- Yang, J.; Xu, J. J.; *Journal of The Electrochemical Society*, **2006**, *153*, A716.
DOI: [10.1149/1.2168410](https://doi.org/10.1149/1.2168410)
- Ding, B.; Ji, G.; Sha, Z.; Wu, J.; Lu, L.; Lee, J. Y.; *Energy Technology*, **2015**, *3*, 63.
DOI: [10.1002/ente.201402117](https://doi.org/10.1002/ente.201402117)
- Ma, X.; Chen, G.; Liu, Q.; Zeng, G.; Wu, T.; *Journal of Nanomaterials*, **2015**, *2015*.
DOI: [10.1155/2015/301731](https://doi.org/10.1155/2015/301731)
- Park, M.; Zhang, X.; Chung, M.; Less, G. B.; Sastry, A. M.; *Journal of Power Sources*, **2010**, *195*, 7904.
DOI: [10.1016/j.jpowsour.2010.06.060](https://doi.org/10.1016/j.jpowsour.2010.06.060)
- Yuan, L.-X.; Wang, Z.-H.; Zhang, W.-X.; Hu, X.-L.; Chen, J.-T.; Huang, Y.-H.; Goodenough, J. B.; *Energy & Environmental Science*, **2011**, *4*, 269.
DOI: [10.1039/C0EE00029A](https://doi.org/10.1039/C0EE00029A)
- Gu, H. B.; Jun, D. K.; Park, G. C.; Jin, B.; Jin, E. M.; *Journal of nanoscience and nanotechnology*, **2007**, *7*, 3980.
DOI: [10.1166/jnn.2007.079](https://doi.org/10.1166/jnn.2007.079)
- Nan, C.; Lu, J.; Li, L.; Li, L.; Peng, Q.; Li, Y.; *Nano Res.*, **2013**, *6*, 469.
DOI: [10.1007/s12274-013-0324-8](https://doi.org/10.1007/s12274-013-0324-8)
- Pei, B.; Yao, H.; Zhang, W.; Yang, Z.; *Journal of Power Sources*, **2012**, *220*, 317.
DOI: [10.1016/j.jpowsour.2012.07.128](https://doi.org/10.1016/j.jpowsour.2012.07.128)
- Chung, S.-Y.; Bloking, J. T.; Chiang, Y.-M.; *Nature Materials*, **2002**, *1*, 123.
DOI: [10.1038/nmat732](https://doi.org/10.1038/nmat732)
- Wang, G. X.; Bewlay, S.; Yao, J.; Ahn, J. H.; Dou, S. X.; Liu, H. K.; *Electrochemical and Solid-State Letters*, **2004**, *7*, A503.
DOI: [10.1149/1.1819867](https://doi.org/10.1149/1.1819867)
- Jayaprakash, N.; Kalaiselvi, N.; Periasamy, P.; *International Journal of Electrochemical Science*, **2008**, *3*, 476.
DOI: <http://pdf.easechem.com/pdf/07/3040476.pdf>
- Mandal, B.; Basumallick, I.; Ghosh, S.; *British Journal of Applied Science and Technology*, **2014**, *4*, 1509.
DOI: [10.9734/BJAST/2014/7959](https://doi.org/10.9734/BJAST/2014/7959)
- Yang, Z.; Xia, J.; Zhi, L.; Zhang, W.; Pei, B.; *Ionics*, **2014**, *20*, 169.
DOI: [10.1007/s11581-013-0974-2](https://doi.org/10.1007/s11581-013-0974-2)
- Lv, X.-Y.; Cui, X.-R.; Long, Y.-F.; Su, J.; Wen, Y.-X.; *Ionics*, **2015**, *1*.
DOI: [10.1007/s11581-015-1440-0](https://doi.org/10.1007/s11581-015-1440-0)
- Chen, Z.; Dahn, J. R.; *Journal of The Electrochemical Society*, **2002**, *149*, A1184.
DOI: [10.1149/1.1498255](https://doi.org/10.1149/1.1498255)
- Wang, J.; Sun, X.; *Energy & Environmental Science*, **2012**, *5*, 5163.
DOI: [10.1039/C1EE01263K](https://doi.org/10.1039/C1EE01263K)
- Gao, F.; Tang, Z.; *Electrochimica Acta*, **2008**, *53*, 5071.
DOI: [10.1016/j.electacta.2007.10.069](https://doi.org/10.1016/j.electacta.2007.10.069)
- Vu, A.; Stein, A.; *Chemistry of Materials*, **2011**, *23*, 3237.
DOI: [10.1021/cm201197j](https://doi.org/10.1021/cm201197j)
- Zhang, W.-J.; *Journal of The Electrochemical Society*, **2010**, *157*, A1040.
DOI: [10.1149/1.3460840](https://doi.org/10.1149/1.3460840)
- Ma, Z.; Fan, Y.; Shao, G.; Wang, G.; Song, J.; Liu, T.; *ACS applied materials & interfaces*, **2015**, *7*, 2937.
DOI: [10.1021/am5084368](https://doi.org/10.1021/am5084368)
- Fana, X. Y.; Li, Y.; Wang, J. J.; Gou, L.; Zhao, P.; Li, D. L.; Huang, L.; Sun, S. G.; *Journal of Alloys and Compounds*, **2010**, *493*, 77.
DOI: [10.1016/j.jallcom.2009.12.179](https://doi.org/10.1016/j.jallcom.2009.12.179)
- Kuzma, M.; Dominko, R.; Meden, A.; Makovec, D.; Bele, M.; Jamnik, J.; Gaberšček, M.; *Journal of Power Sources*, **2009**, *189*, 81.
DOI: [10.1016/j.jpowsour.2008.11.015](https://doi.org/10.1016/j.jpowsour.2008.11.015)

46. Nyte'n, A.; Abouimrane, A.; Armand, M.; Gustafsson, T.; Thomas, J. O.; *Electrochemistry Communications*, **2005**, 7, 156.
DOI:[10.1016/j.elecom.2004.11.008](https://doi.org/10.1016/j.elecom.2004.11.008)
47. Zhua, H.; Wua, X.; Zana, L.; Zhanga, Y.; *Electrochimica Acta*, **2014**, 117, 34.
DOI:[10.1016/j.electacta.2013.11.089](https://doi.org/10.1016/j.electacta.2013.11.089)
48. Zhang, Z.; Liu, X.; Wu, Y.; Zhao, H.; *Journal of Solid State Electrochemistry*, **2015**, 19, 469.
DOI:[10.1007/s10008-014-2624-7](https://doi.org/10.1007/s10008-014-2624-7)
49. Wagner, N. P.; Dalod, A. R.; Svensson, A. M.; Vullum-Bruer, F.; *ECS Transactions*, **2015**, 64, 33.
DOI:[10.1149/06422.0033ecst](https://doi.org/10.1149/06422.0033ecst)
50. Maccario, M.; Croguennec, L.; Cras, F. L.; Delmas, C.; *Journal of Power Sources*, **2008**, 183, 411.
DOI:[10.1016/j.jpowsour.2008.05.045](https://doi.org/10.1016/j.jpowsour.2008.05.045)
51. Kam, K. C.; Gustafsson, T.; Thomas, J. O.; *Solid State Ionics*, **2011**, 192, 356.
DOI:[10.1016/j.ssi.2010.03.030](https://doi.org/10.1016/j.ssi.2010.03.030)
52. Li, L.; Guo, H.; Li, X.; Wang, Z.; Peng, W.; Xiang, K.; Cao, X.; *Journal of Power Sources*, **2009**, 189, 45.
DOI:[10.1016/j.jpowsour.2008.12.017](https://doi.org/10.1016/j.jpowsour.2008.12.017)
53. Nyten, A.; Kamali, S.; Haggstrom, L.; Gustafsson, T.; Thomas, J. O.; *Journal of Materials Chemistry*, **2006**, 16, 2266.
DOI:[10.1039/b601184e](https://doi.org/10.1039/b601184e)
54. Doherty, M.; Caruso, R. A.; Smarsly, B. M.; Adelhelm, P.; Drummond, C. J.; *Chemistry of Materials*, **2009**, 21, 5300.
DOI:[10.1021/cm9024167](https://doi.org/10.1021/cm9024167)
55. Lee, S. B.; Cho, S. H.; Cho, S. J.; Park, G. J.; Park, S. H.; Lee, Y. S.; *Electrochemistry Communications*, **2008**, 10, 1219.
DOI:[10.1016/j.elecom.2008.06.007](https://doi.org/10.1016/j.elecom.2008.06.007)
56. Lim, S.; Yoon, C. S.; Cho, J.; *Chemistry of Materials*, **2008**, 20, 4560.
DOI:[10.1021/cm8006364](https://doi.org/10.1021/cm8006364)
57. Shang, H.; Chu, W.; Cheng, J.; Pan, F.; Cheng, D.; Xia, D.; Wang, W.; Wu, Z.; *Journal of Materials Chemistry A*, **2013**, 1, 6635.
DOI:[10.1039/C3TA10390K](https://doi.org/10.1039/C3TA10390K)
58. Tan, G.; Wu, F.; Li, L.; Chen, R.; Chen, S.; *The Journal of Physical Chemistry C*, **2013**, 117, 6013.
DOI:[10.1021/jp309724q](https://doi.org/10.1021/jp309724q)
59. Zhang, Y.; Chen, L.; Ou, J.; Wang, J.; Zheng, B.; Yuan, H.; Guo, Y.; Xiao, D.; *Journal of Materials Chemistry A*, **2013**, 1, 7933.
60. Kim, J.-W.; Lee, H.-G.; *Metallurgical and Materials Transactions B*, **2001**, 32, 17.
DOI:[10.1007/s11663-001-0003-0](https://doi.org/10.1007/s11663-001-0003-0)
61. Nicholson, R. S.; Shain, I.; *Analytical Chemistry*, **1964**, 36, 706.
DOI:[10.1021/ac60221a002](https://doi.org/10.1021/ac60221a002)

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