

OPINION

Cathode materials for next generation lithium ion batteries



Jiantie Xu^{a,b}, Shixue Dou^{b,*}, Huakun Liu^b, Liming Dai^{a,**}

^aDepartment of Macromolecular Science and Engineering, School of Engineering, Case Western Reserve University, Cleveland, OH 44106, USA

^bInstitute for Superconducting and Electronic Materials, University of Wollongong, Wollongong, NSW 2522, Australia

Received 22 May 2013; accepted 23 May 2013

Available online 28 June 2013

KEYWORDS

Greenhouse gas emissions;
Energy conversion and storage;
Cathode materials;
Lithium ion batteries;
Electric vehicles

Abstract

The recent progress and future development of cathode materials for lithium ion batteries have been critically reviewed in this article. We have given some critical opinions and rational ideas regarding the development of cathode materials to dramatically reduce the cost and increase the efficiency of future lithium ion batteries, which will revolutionize the way for transportation and affect many aspects of our lives.

© 2013 Elsevier Ltd. All rights reserved.

The world energy consumption, along with CO₂ emission, has been increasing exponentially during the past 50 years or so. As we become more aware of greenhouse gas emissions (GHG, such as CO₂ and CH₄) and their detrimental effects on our planet, it has become more important than ever to develop clean and renewable energy systems, such as solar cells, fuel cells, batteries, and wind power generators. Being powered largely by burning fossil fuels, transportation vehicles, including automobiles, ships, airplanes, and spacecrafts, are among the primary sources for the GHG [1]. The inevitably increasing fuel shortage, along with the public awareness of ‘greenhouse’ effects, has

made it highly desirable to develop electric vehicles (EVs, hybrid electric vehicles (HEVs) and/or plug-in hybrid electric vehicles (PHEVs)), instead of fossil fuel vehicles, with a low GHG emission. However, commercial applications of EVs will not be realized if advanced energy storage systems with an efficient energy saving and emission reduction cannot be successfully developed [2].

With no moving parts or noise and virtually without any pollution, batteries can convert chemical energy directly into electricity. They require little upkeep for potential large-scale applications. Among the entire battery family, several battery types, including lead acid (LA) batteries, nickel metal hydride (NiMH) batteries, and lithium ion batteries (LIBs), have great potential for EV applications. Although the current vehicle market is dominated by LA and NiMH batteries, the LIBs have received intensive research and development focus because of their high energy density, long cycle life, and superior environmental friendliness [3].

*Corresponding author.

**Corresponding author. Tel.: +1 216 368 4176;
fax: +1 216 368 4204.

E-mail addresses: shi_dou@uow.edu.au (S. Dou),
liming.dai@case.edu (L. Dai).

So far, LIBs have been widely used in various portable and smart devices (e.g., cell phones, MP3 devices, cameras, and laptops). For EV applications, however, the performance of LIBs, particularly their energy density, safety, and cost, still need to be significantly improved. Therefore, further development of the LIB technology is urgently needed.

Figure 1 shows the basic working principles for a LIB. As can be seen, a lithium ion battery is composed of three essential components, namely the Li^+ intercalation anode, cathode, and the electrolyte/separator. Li^+ ions move from the cathode to the anode through the electrolyte/separator during charging and back when discharging, and simultaneously, the electrons flow out of the external circuit to provide the electrical power (Figure 1). Although the efficiency of energy conversion for LIBs depends on a variety of factors, their overall performance strongly relies on the structure and property of the materials used. The key to success in the development of advanced LIBs to meet the emerging EV market demands is the electrode materials, especially the cathode. Indeed, the recently-released Argonne National Laboratory Battery Performance and Cost Model (BatPac) [4] shows that the cost of electrode materials accounts for ~44% (~30% for the $\text{Li}_{1.05}(\text{Ni}_{4/9}\text{Mn}_{4/9}\text{Co}_{1/9})_{0.95}\text{O}_2$ cathode and ~14% for the graphite anode) in a typical battery design involving cathode and anode electrodes, current collector, electrolyte, binders, cell/battery modules, and battery jacket. The cathode costs nearly twice as much as the anode. This could be attributed to the fact that the working voltage, energy density, and rate capability of a LIB are mainly determined by the limited theoretical capacity and thermodynamics of the cathode material in the present LIB technology. As discussed in more details below, therefore, it is critical to develop promising cathode materials for the current LIB technology.

Figure 2 shows a suggested road map for the research and development of LIB electrode materials in terms of the achievable voltage and capacity. Most of the current and future promising cathode materials shown in Figure 2 can be classified into four groups: $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, lithium-excess $\text{Li}[\text{Li}, \text{Mn}, \text{Ni}, \text{Co}]\text{O}_2$, lithium metal polyoxyanion $\text{Li}_3\text{V}_2\text{PO}_4$, LiMPO_4 and LiMSiO_4 ($\text{M}=\text{Mn}, \text{Fe}, \text{Co}$, and combinations of thereof), and (O_2 , S, Li_2S). As can be seen, there are rather limited number of cathode materials of significant promise. Below, we list major pros and cons for each of the material groups.

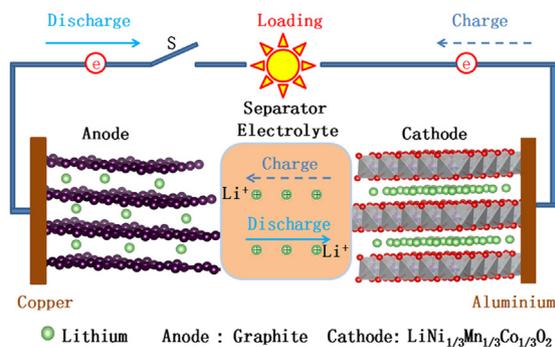


Figure 1 Schematic representation of a typical lithium ion battery.

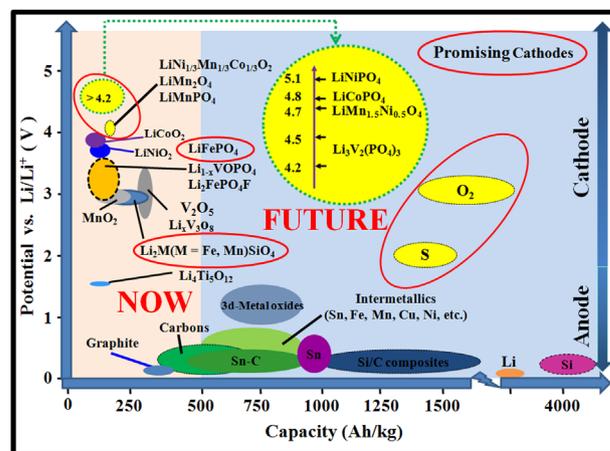


Figure 2 Electrode materials and corresponding electrochemical performances in the current LIB technologies (adapted from Reference [16]).

- (1) In the past two decades, the layered oxide LiCoO_2 cathode has been widely used in portable electronics [3]. The high cost, toxicity, chemical instability in the deep charged state, safety concern, and limited capacity (only ~135 Ah/kg) associated with LiCoO_2 , however, have prevented its large-scale applications in transportation and stationary storage. Having a similar capacity of ~140 Ah/kg as that of LiCoO_2 , but a relatively high working voltage of ~4.7 V (~4.1 V for LiCoO_2), $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ is becoming an attractive candidate for high-energy applications. Furthermore, the cycle life and rate capability of doped $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (spinel structure) could be enhanced significantly by cationic substitutions (Co, Cr, Fe, Ga, or Zn) [5] and surface modification (AlPO_4 , ZnO , Al_2O_3 and Bi_2O_3) [6]. In order to obtain a uniform surface modification and/or strong cationic coating, however, a complicated and high-cost post-chemical process is necessary [7]. To make the matter even worse, the currently used standard electrolytes (LiPF_6 in EC/DEC/DMC) are not appropriate for $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode, which requires the high working voltage (~4.7 V).
- (2) Lithium-excess layered oxides, $\text{Li}[\text{Li}, \text{Mn}, \text{Ni}, \text{Co}]\text{O}_2$, such as $(\text{Li}_2\text{MnO}_3)_x(\text{LiMO}_2 (\text{M}=\text{Ni}, \text{Co}, \text{Mn}))_{1-x}$, offer a ~4.0 V working voltage with much higher capacity values of ~250 Ah/kg than those of LiCoO_2 and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_2$ [8]. However, there is often a huge irreversible capacity loss associated with the oxygen and lithium loss from the host structure of the lithium-excess layered oxides ($\text{Li}[\text{Li}, \text{Mn}, \text{Ni}, \text{Co}]\text{O}_2$) at the end of the first charging process. Although the irreversible capacity loss can be significantly reduced by coating with insulating materials (e.g., Al_2O_3 , AlPO_4 , MgO , RuO_2) [9], the high surface area associated with the nanostructured lithium-excess layered oxides ($\text{Li}[\text{Li}, \text{Mn}, \text{Ni}, \text{Co}]\text{O}_2$) could have a high surface reactivity to induce side reactions between the electrodes and the electrolyte. This could lead to destabilization of the active materials and an increase in impeding passivation. Therefore, the electrolyte safety, together with the relatively high cost of the electrode materials, is the major concern for lithium-excess layered oxides to be used as the cathode in LIBs.

- (3) Among the LiMPO_4 ($M=\text{Fe, Mn, Ni, Co}$, or combinations of thereof) compounds (specific capacity ~ 170 Ah/kg), LiFePO_4 has been recently developed for commercial applications because of its low cost, low toxicity, high safety, and excellent cycling performance. Unlike LiFePO_4 , the much higher voltages seen in Figure 2 for LiMPO_4 ($M=\text{Mn, Ni}$ and Co) (~ 170 Ah/kg) and $\text{Li}_3\text{V}_2\text{PO}_4$ (~ 197 Ah/kg) ensure a higher theoretical energy density. However, it is a big challenge to secure a high rate capability, cycling stability, and highly compatible electrolyte for LiMPO_4 ($M=\text{Mn, Ni}$ and Co) or $\text{Li}_3\text{V}_2\text{PO}_4$ due to their low electronic/ionic conductivity and high working voltage (>4.6 V) [10,11]. The success of LiFePO_4 has also spurred growing interest in Li_2MSiO_4 ($M=\text{Mn, Fe, Co}$, and Ni). Because of the possibility of having two lithium ions to be reversibly extracted from the host structure, the Li_2MSiO_4 cathode could offer a high theoretical capacity of ~ 330 Ah/kg. However, its rate capability and cycling performance are still far from satisfying the requirements for commercialization, though some positive results for Li_2MSiO_4 ($M=\text{Mn, Fe, Co}$, and Ni) have been recently reported [12].
- (4) Compared with the cathode materials described above, Li-O_2 , Li-S/C , and $\text{Li}_2\text{S-Si}$ can offer a much higher energy density (Figure 2) [13-15], which is a distinguished advantage that could make them the most promising cathode material. For the Li-O_2 battery, however, the reversibility and compatibility are still big problems, as well as the catalysts for the O_2 cathode. For the Li-S/C and $\text{Li}_2\text{S-Si}$ battery systems, the cycling life and polarization of the nanostructured sulfur also need to be further improved.

To overcome the above-mentioned limitations associated with cathode materials and to facilitate the commercialization of LIBs for the EV market, some further research efforts to be taken include: (1) development of proper electrolytes with a wide electrochemical window, high anodic stability, low volatility, low flammability, and good environmental friendliness (e.g., the optimized organic ethylene carbonate/diethyl carbonate electrolyte (EC: DEC) and ionic liquids (ILs)) especially for high voltage cathode materials (>4.5 V) [16-18]; (2) development of ideal binders (e.g., carboxymethyl cellulose (CMC) and alginate [19,20]) to make an intimate adherence between the current collector and electrode materials in LIBs for improved electrochemical performance and enhanced stability during electrochemical cycling; (3) establishment of a combined computational and experimental approach for material screening to identify cathode materials with high capacity, high energy density, and low cost [21]; and (4) construction of various prototype LIBs with different promising cathode materials (Figure 2) assisted by tradeoff analyses on the gravimetric energy density, volumetric energy density, cost and environmental friendliness for different applications [22,23].

In conclusion, the limited dynamics and theoretical capacity of the current cathode materials discussed above have been shown to be the bottleneck for the development of low-cost LIBs with excellent cycling stability, high rate

capability, large gravimetric and volumetric energy densities, and improved safety characteristics. This article provides some critical opinions and rational ideas regarding the development of cathode materials with optimized structures and properties to take up a spot at the top-right corner of the road map shown in Figure 2. Continued research and development efforts in this exciting field will surely revolutionize the way for transportation that can affect many aspects of our lives.

Acknowledgments

The authors are grateful for financial support from AFOSR (FA9550-12-1-0037, FA-9550-12-1-0069, FA 9550-10-1-0546), NSF (NSF-CMMI-1000768, NSF-DMR-1106160, and Automotive CRC-2020.).

References

- [1] M. Meinshausen, N. Meinshausen, W. Hare, S.C.B. Raper, K. Frieler, R. Knutti, D.J. Frame, M.R. Allen, *Nature* 458 (2009) 1158-1162.
- [2] O. van Vliet, A.S. Brouwer, T. Kuramochi, M. van den Broek, A. Faaij, *Journal of Power Sources* 196 (2011) 2298-2310.
- [3] J.B. Goodenough, Y. Kim, *Chemistry of Materials* 22 (2010) 587-603.
- [4] (<http://www.epa.gov/oms/climate/documents/bat-pa-c-v2-beta.xlsx>).
- [5] Y. Xie, M.-F. Ye, L.-J. Jiang, R.-S. Zhu, *Ionics* 17 (2011) 383-389.
- [6] J. Liu, A. Manthiram, *Chemistry of Materials* 21 (2009) 1695-1707.
- [7] D. Kovacheva, B. Markovsky, G. Salitra, Y. Talyosef, M. Gorova, E. Levi, M. Riboch, H.-J. Kim, D. Aurbach, *Electrochimica Acta* 50 (2005) 5553-5560.
- [8] Z. Lu, L.Y. Beaulieu, R.A. Donaberger, C.L. Thomas, J.R. Dahn, *Journal of The Electrochemical Society* 149 (2002) A778-A791.
- [9] A. Manthiram, *The Journal of Physical Chemistry Letters* 2 (2011) 176-184.
- [10] K. Zaghbi, A. Guerfi, P. Hovington, A. Vijh, M. Trudeau, A. Mauger, J.B. Goodenough, C.M. Julien, *Journal of Power Sources* 232 (2013) 357-369.
- [11] H. Huang, S.C. Yin, T. Kerr, N. Taylor, L.F. Nazar, *Advanced Materials* 14 (2002) 1525-1528.
- [12] D. Rangappa, K.D. Murukanahally, T. Tomai, A. Unemoto, I. Honma, *Nano Letters* 12 (2012) 1146-1151.
- [13] P.G. Bruce, S.A. Freunberger, L.J. Hardwick, J.-M. Tarascon, *Nature Materials* 11 (2012) 19-29.
- [14] X. Ji, K.T. Lee, L.F. Nazar, *Nature Materials* 8 (2009) 500-506.
- [15] Y. Yang, G. Zheng, Y. Cui, *Chemical Society Reviews* 42 (2013) 3018-3032.
- [16] J.M. Tarascon, M. Armand, *Nature* 414 (2001) 359-367.
- [17] J. Xu, S.-L. Chou, M. Avdeev, M. Sale, H.-K. Liu, S.-X. Dou, *Electrochimica Acta* 88 (2013) 865-870.
- [18] W. Lu, A. Goering, L. Qu, L. Dai, *Physical Chemistry Chemical Physics* 14 (2012) 12099-12104.
- [19] J. Xu, S.-L. Chou, Q.-f. Gu, H.-K. Liu, S.-X. Dou, *Journal of Power Sources* 225 (2013) 172-178.
- [20] I. Kovalenko, B. Zdyrko, A. Magasinski, B. Hertzberg, Z. Milicev, R. Burtovyy, I. Luzinov, G. Yushin, *Science* 334 (2011) 75-79.
- [21] H. Chen, G. Hautier, A. Jain, C. Moore, B. Kang, R. Doe, L. Wu, Y. Zhu, Y. Tang, G. Ceder, *Chemistry of Materials* 24 (2012) 2009-2016.

- [22] S.J. Dillon, K. Sun, *Current Opinion in Solid State and Materials Science* 16 (2012) 153-162.
- [23] B.L. Ellis, K.T. Lee, L.F. Nazar, *Chemistry of Materials* 22 (2010) 691-714.



Jiantie (Kenny) Xu is a Ph.D. student in the Institute for Superconducting and Electronic Materials, University of Wollongong, under the supervision of Prof. Shi Xue Dou and Prof. Hua Kun Liu. Currently, he is a visiting student in the Department of Macromolecular Science and Engineering, Case Western Reserve University, under the supervision of Prof. Liming Dai. His current research is focused on nanomaterials for lithium ion batteries and sodium ion batteries.



Shi Xue Dou is a Professor and Director of the Institute for Superconducting and Electronic Materials (ISEM) at UOW. He received his Ph.D. in chemistry in 1984 at Dalhousie University, Canada. He was elected as a Fellow of the Australian Academy of Technological Science and Engineering in 1994. He was awarded a D.Sc. by the University of New South Wales in 1998 and three Australian Professorial Fellowship by Australian

Research Council in 1993, 2002 and 2007. He is responsible for a number of breakthroughs in development of superconductors and energy materials. He is program leader for ongoing Automotive CRC 2020. He has supervised 65 Ph.D. students and more than 50 postdoctoral and visiting fellows.



Hua Kun Liu is a leader of energy materials research program at Institute for Superconducting and Electronic Materials, University of Wollongong, Australia since 1994. She has been awarded the ARC Australian Professorial Fellowships in 1994-1998, 1999-2003, 2003-2005 and 2006-2010. She has supervised 45 Ph.D. and 15 Masters to completion and 20 postdoctoral and visiting fellows. She has published 500 refereed

journal papers, cited 13,000 times, h-index=52 (on 03/2013), 1 USA patent and 10 Australian Innovation provisional Patents applications. Her research has been focused on clean energy materials. The research topics cover the materials science and engineering and electrochemistry and applications.



Liming Dai joined Case Western Reserve University (CWRU) in fall 2009 as the Kent Hale Smith Professor in the Department of Macromolecular Science and Engineering. He is also the director of the Center of Advanced Science and Engineering for Carbon (CASE4Carbon). He received a B.Sc. degree from Zhejiang University in 1983 and a Ph.D. from the Australian National University under the supervision of Professor

John White in 1991. He accepted a postdoctoral fellowship from the Cavendish Laboratory at the University of Cambridge, and two years later became a visiting fellow at the University of Illinois at Urbana-Champaign. He spent 10 years with the Commonwealth Scientific and Industrial Research Organization (CSIRO) in Australia. Before joining the CWRU, he was an associate professor of polymer engineering at the University of Akron and the Wright Brothers Institute Endowed Chair Professor of Nanomaterials at the University of Dayton. He is a Fellow of the Royal Society of Chemistry and Fellow of the American Institute for Medical and Biological Engineering (AIMBE). His expertise lies across the synthesis, chemical modification and device fabrication of conjugated polymers and carbon nanomaterials for energy-related and biomedical applications.