Science Bulletin 64 (2019) 149–150

Contents lists available at ScienceDirect

Science Bulletin

journal homepage: www.elsevier.com/locate/scib

Research Highlight

High-energy Mn-based layered cathodes for sodium-ion batteries

Shaohua Guo *, Haoshen Zhou *

College of Engineering and Applied Sciences, National Laboratory of Solid State Microstructures, Collaborative Innovation Center of Advanced Microstructures, Jiangsu Key Laboratory of Artificial Functional Materials, Nanjing University, Nanjing 210093, China

Sodium-ion batteries (SIBs) have great potential in large-scale energy storage applications due to the low cost and abundance of sodium resources [1,2]. However, some critical issues, such as low energy density and inferior cycling performance, definitely hinder the practical application of SIBs, in part because of the bigger and heavier Na ion in contrast with the Li ion as an energy carrier [3]. Recently, a surge of attention has been paid to the Mn-based materials due to the earth abundant and environmentally friendly manganese element [4,5]. However, Jahn-Teller lattice distortion in Na_xMnO_2, which frequently results from high-spin six-coordinated Mn^{3+} electronic structure, is supposed to go against its structural and electrochemical stability [6,7]. Moreover, the complex host rearrangement accompanied by a transition metal layers shift often occurs during the electrochemical reaction, unavoidably leading to the large volume expansion/contraction and the resulted deteriorated electrochemical performance [8,9]. Therefore, the rational design of high-performance Mn-based hosts for SIBs remains a great challenge.

Recently, Hu and co-workers [10] reported P2-type $Na_{0.72}[Li_{0.24}Mn_{0.76}]O_2$ materials as a cathode for SIBs, which could deliver a superhigh energy density of ~700 Wh/kg with the potential region of 1.5–4.5 V on the basis of the cathode mass. The results demonstrated that the large reversible capacity derived from both anionic and cationic redox. More importantly, no distinct phase transition of $Na_{0.72}[Li_{0.24}Mn_{0.76}]O_2$ was observed during the charge and discharge process. The material delivered an initial charge capacity of ~210 mAh/g on basis of only oxygen anionic redox. On subsequent cycling, the reversible capacity of ~270 mAh/g derived from both anionic and cationic Mn^{3+}/Mn^{4+} redox (Fig. 1a). The partial O^{2-} ions could be oxidized to O^- at the high voltage region, which could not only supply a large capacity, but also effectively decrease the repulsions between the adjacent oxygen layers. And the induction effect of anion redox partially eliminated the change of interslab distance (Fig. 1b), thus resulting in a small volume change. The average repulsions between the adjacent oxygen layers fail to meet the requirement of P2-O2 phase transition, assuring the homogeneous reaction and the stability of material during electrochemical reaction. In this case, the reversible anionic redox reaction could not only help improve the specific capacity, but also make positive contribution to stabilizing structure during the Na ion deintercalation/intercalation.

This work may provide new insights for rational design of high-performance layered oxides for promoting the practical application of SIBs. The finding that the anionic redox reaction induced low strain in this work can be extended to other material systems for both Li-ion and Na-ion batteries.

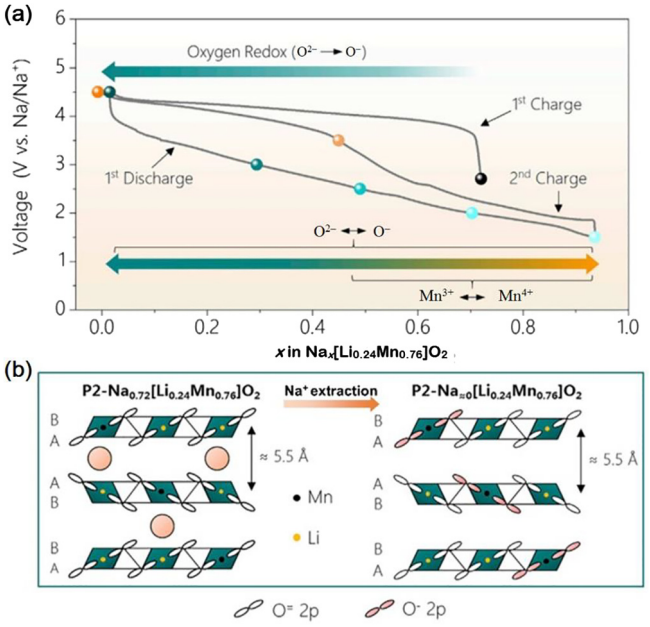


Fig. 1. (Color online) (a) Function of sodium content and voltage. (b) Interaction between the slabs when oxygen oxidation is involved. The oxygen 2p orbital of oxidized oxygen is colored pink. This figure is adapted from Ref. [10].

* Corresponding authors.
E-mail addresses: shguo@nju.edu.cn (S. Guo), hszhou@nju.edu.cn (H. Zhou).

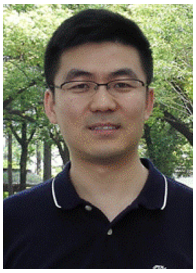
https://doi.org/10.1016/j.scib.2019.01.004

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] Hwang JY, Myung ST, Sun YK. Sodium-ion batteries: present and future. Chem Soc Rev 2017;46:3529–614.
[2] Vaalma C, Buchholz D, Weil M, et al. A cost and resource analysis of sodium-ion batteries. Nat Rev Mater 2018;3:18013.
[3] Yabuuchi N, Kubota K, Dahbi M, et al. Research development on sodium-ion batteries. Chem Rev 2014;114:11636–82.
[4] Ortiz-Vitoriano N, Drewett NE, Gonzalo E, et al. High performance manganese-based layered oxide cathodes: overcoming the challenges of sodium ion batteries. Energy Environ Sci 2017;10:1051–74.
[5] You Y, Xin S, Asl HY, et al. Insights into the improved high-voltage performance of Li-incorporated layered oxide cathodes for sodium-ion batteries. Chem 2018;4:2124–39.
[6] Li X, Ma X, Su D, et al. Direct visualization of the Jahn-Teller effect coupled to Na ordering in $Na_{5/8}MnO_2$. Nat Mater 2014;13:586–92.
[7] Guo S, Li Q, Liu P, et al. Environmentally stable interface of layered oxide cathodes for sodium-ion batteries. Nat Commun 2017;8:135.
[8] Yabuuchi N, Kajiyama M, Iwatate J, et al. P2-type $Na_xFe_{1/2}Mn_{1/2}O_2$ made from earth-abundant elements for rechargeable Na batteries. Nat Mater 2012;11:512–7.
[9] Lu ZH, Dahn JR. In situ X-ray diffraction study of P2-$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$. J Electrochem Soc 2001;148:A1225–9.
[10] Rong X, Hu E, Lu Y, et al. Anionic redox reaction-induced high-capacity and low-strain cathode with suppressed phase transition. Joule 2018. https://doi.org/10.1016/j.joule.2018.10.022.



Shaohua Guo obtained his Ph.D. degree from University of Tsukuba in 2015, and then worked as a postdoctoral researcher in National Institute of Advanced Industrial Science and Technology (AIST). He currently is an associate professor in Nanjing University. His research interests focus on functional materials for lithium-ion batteries, sodium-ion batteries, solid-state batteries, and other energy storage devices.

Haoshen Zhou obtained his B.S. degree from Nanjing University in 1985, and received his Ph.D. degree from the University of Tokyo in 1994. He is a professor in Nanjing University. His research interests include the synthesis of energy active materials and their applications in Li-ion batteries, Na-ion batteries, Li-redox flow batteries, metal–air batteries, and new type batteries/cells.