Atomic-Scale Characterization of Electrode Materials in Lithium/Sodium-ion Batteries by STEM

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The rapid development of portable electronics and hybrid electric vehicle (HEV) markets promotes the research of electric energy storage systems. Among them, lithium-ion batteries (LIBs) and sodium-ion batteries (NIBs) have attracted intense attention, due to their high energy density and long cycle lifetime. The demand for higher energy density LIBs and NIBs facilitate the study of various electrode materials. Performance optimization of electrode materials necessitates information about structural evolution of electrode materials at an atomic scale. However, limited understanding for the structural evolution of electrode materials at atomic resolution, especially the Li/Na ions distribution and arrangement at the atomic level, underlying electrochemical process substantially hinders our exploration of reaction mechanism and further performance optimization.

The annular-bright-field (ABF) imaging in aberration-corrected scanning transmission electron microscopy (STEM) allows simultaneous imaging of light and heavy elements, providing an unprecedented opportunity to probe the nearly equilibrated local structure of electrode materials after electrochemical cycling at atomic resolution. A JEM-ARM200F STEM operated at 200 kV and equipped with double aberration-correctors for both probe-forming and imaging lenses was used to perform HAADF and ABF imaging. To observe Li directly using ABF collection geometry, the acceptance semiangle in this study was fixed between 12 and 25 mrad. The STEM ABF and HAADF images were taken simultaneously at the optimal defocus value of the HAADF imaging condition, which was more defocused than the optimal ABF imaging condition on this instrument. Thus, the contrast in the ABF image was reversed with the bright area corresponding to the atomic positions.

There are many problems in the practical operations of these batteries, including poor cycling stability and rate performance. Sodium-based layered oxides with a P2-type layered framework have been considered as one of the most promising cathode materials for SIBs. However, they suffer from the undesired P2–O2 phase transition, which leads to rapid capacity decay and limited reversible capacities. Accordingly, many issues in the structural evolution of electrode materials during the different charge/discharge process are needed to be clarified. The phase transition behavior of the electrode materials at high rate cycling is quite different from that at the low rate. Here we present structural evolutions of several electrode materials at the atomic scale [1,2]: i) Mg-substituted P2-$Na_{0.67}Mn_{0.67}Ni_{0.33-x}Mg_xO_2$ (x < 0.33) (a cathode materials for SIBs), where both the reversible capacity and the capacity retention of the P2-type cathode material were remarkably improved as the P2–O2 phase transition was thus suppressed during cycling (Figure 1); ii) $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (a cathode material for LIBs), which shows Li-rich and Li-poor phases' coexistence with tetrahedral occupation of Li in Li-poor phase during high-rate charging; The high rate induced overpotential is thought to be the driving force for the formation of this intermediate Li-poor phase (Figure 2) [3].

References:

[1] Wang *et al,* Angew. Chem. Int. Ed. **55** (2016), p. 7445.
[2] Zhou *et al,* Adv. Energy Mater. **6** (2016), p. 1600579.
[3] The authors acknowledge funding from the National Natural Science Foundation of China. Prof. Y.G. Guo and X.Q. Yang are thanked for many useful discussions and contributions to this work.
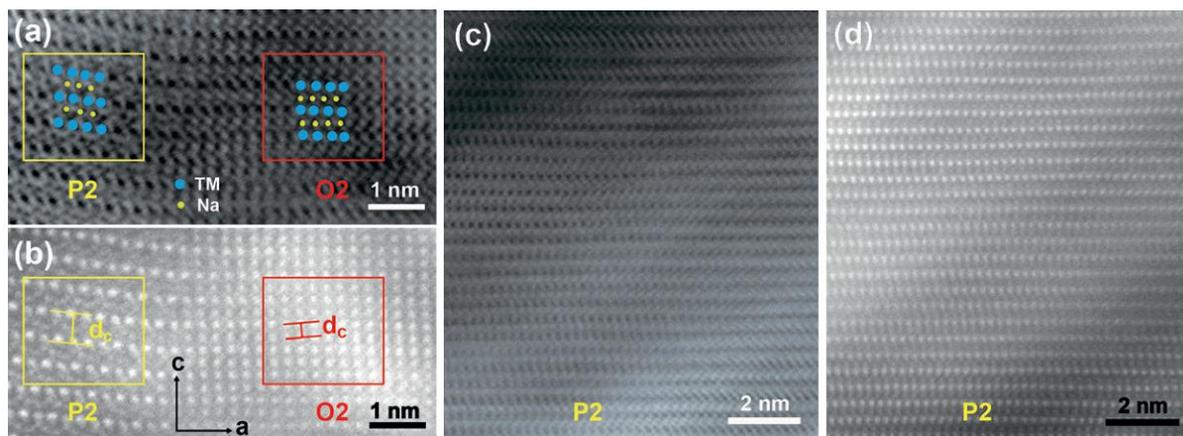

Figure 1. a) ABF- and b) HAADF-STEM images of a P2-type $Na_{0.67}Mn_{0.67}Ni_{0.33}$-$xMg_xO_2$ (x= 0) electrode when charging to 4.22 V at the [010] zone axis; the yellow and red rectangles indicate areas with the P2 and O2 structure. c) ABF- and d) HAADF-STEM images of a P2-type $Na_{0.67}Mn_{0.67}Ni_{0.33-x}Mg_xO_2$ (x= 0.05) electrode when charging to 4.22 V.
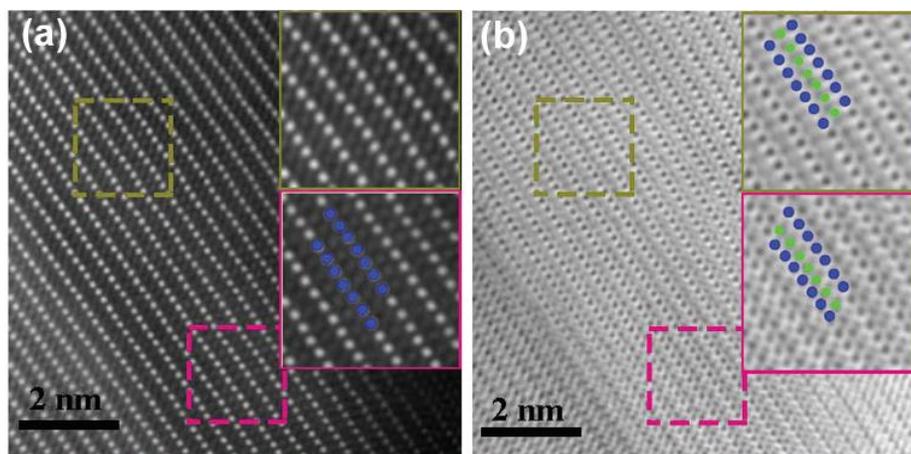

Figure 2. Structure of half charged NMC at 30C rate. a) Typical HAADF image taken along the [110] zone axis of the NMC electrode after 55 s charging at the current rate of 30C. The zoom-in image of the areas marked with orange and pink squares, respectively. b) Corresponding ABF images of NMC electrode after 55 s charging. The zoom-in image of the areas marked with orange and pink squares, respectively. The blue and green dots indicate the TM ions and Li ions, respectively.