Atomic-Scale Structure of Intercalated/De-intercalated Electrode Materials in Lithium/Sodium ion Batteries

Lin Gu1*, Yong-Sheng Hu1, Yu-Guo Guo2, Xue-Jie Huang1, Hong Li1, Li-Quan Chen1
1. Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China.
2. Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.
*E-mail: l.gu@aphy.iphy.ac.cn

To satisfy ever-demanding inquires upon energy storage for applications in portable electronics, electric vehicles and smart grid etc., lithium-ion batteries have been proved to be one of the ideal candidates in terms of energy density and power density. However, limited understanding for the structural evolution of electrode materials at atomic scale amid electrochemical processes substantially hinders their further performance optimization. The recent success of annular-bright-field (ABF) imaging method erected on aberration-corrected scanning transmission electron microscopy (STEM) has been demonstrated to be a powerful technique to directly visualize individual light atoms, in particular, the lithium ions, probing the nearly-equilibrated local structure of lithiated/delithiated electrodes under electrochemical cycling at atomic resolution.

**Figure 1** (a) shows the schematic of the ABF imaging geometry with a convergent beam and an annular-shaped bright-field detector. A sub-angstrom-sized probe scans across the specimen with the annular detector defining a collection semi-angle at given camera lengths. HAADF and ABF images of LiFePO4 viewed along [010] zone axes are displayed in **Figure 1(b)** and **Figure 1(c)**, respectively. Compared to the HAADF image, it is clearly demonstrated that not only Fe and P are revealed in ABF image, but also the atomic columns of O and Li. The ABF contrast tends to minimize the variance of the atomic number (Z) by following a $Z^{1/3}$ dependency. With the unique ABF method, we have further studied possible electrochemical reaction mechanisms and detailed microstructure for (partially) lithiated/delithiated 1D-LiFePO4, 2D-LiCoO2, Li2MnO3, and 3D-Li4Ti5O12 and other lithium-based active materials with atomic resolution, which are essential for basic understanding and further performance optimization. These achievements provide new insight into the lithium/sodium storage mechanism in important cathode materials for lithium/sodium ion batteries.