In situ/operando characterization of batteries using X-ray diffraction and X-ray absorption spectroscopy

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Abstract

Li-ion batteries (LIBs) have been explored in recent years because of their high energy densities. In our study, various advanced metal oxides such as polyoxometalates (POMs) and high-entropy oxides (HEOs) were utilized as electrode materials for LIBs. They exhibit different behaviors from the traditional binary or ternary metal oxides. POMs are transition metal oxide clusters with specified structures, and they can provide multi-electron-transfer processes during charging/discharging processes. HEOs are a class of metal oxides which contains at least five cations in the crystal structure thus exhibits high entropy of the system. Those metal oxides exhibit high capacity (could up to 1000 mA h g^{-1} as anode for LIBs) and well cycling stability (without significant capacity fading up to 100 cycles). In order to figure out the charge storage mechanism of those advanced metal oxides, we employed several *in operando* synchrotron X-ray techniques including X-ray diffraction, X-ray absorption spectroscopy, as well as transmission X-ray microscopy. Based on the observations from above techniques, we could identify the changes of crystal structures, oxidation states, and the morphologies of those metal oxide electrodes during charging and discharging processes.

Aqueous sodium ion battery (ASIB) is a promising energy storage device with the advantages of high safety and low cost. In this study, a Prussian blue analogue, copper hexacyanoferrates is modified with addition of two different functional groups. The modified cathode material was carefully analyzed by in operando XRD measurements, X-ray photoelectron spectroscopy, cyclic voltammetry (CV), and charge-discharge measurement to reveal their electrochemical performances. Various electrolytes were tested in this ASIB system to optimize the electrochemical performance, including capacity, energy density, rate capability, as well as cycling stability. The ASIB with the optimized electrolyte showed a great rate capacity for more than 80% from 1 C to 20 C and an outstanding cycle stability (~ 100% after 1000 cycle at 20 C). The high discharge plateau at about 0.7 V (vs Ag/AgCl) indicates that it is a promising electrode material for high-energy ASIB applications. This Prussian blue analogue cathode material was further assembled in a full cell system with $NaTi_2(PO_4)_3$ as anode material to demonstrate the potential for practical applications.

Keywords – lithium ion battery, sodium ion battery, in operando X-ray diffraction, in operando X-ray absorption spectroscopy