In situ monitoring of fast delithiation (sodiation) process in electrode materials for Li- and Na-ion batteries by using time-resolved X-ray techniques

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The high charge and discharge rate for electrical energy storage devices is an important technological issue for hybrid electric vehicle (HEV) and plug-in hybrid electric vehicle (PHEV) applications. For the development of advanced electrode materials with high power density, the in-depth understanding of the relationship between the structural changes and the electrochemical performance upon fast charging and discharging is critical. Therefore, time-resolved spectroscopic techniques, especially under operando conditions, to monitor and study the structural changes during the fast delithiation and lithiation process are greatly needed. Recently, new in situ synchrotron x-ray diffraction and absorption techniques to study crystalline structural changes of LiFePO₄ during chemical and electrochemical delithiation have been developed and reported by our group, with excellent time resolving ability for dynamic studies [1,2].

Here, we employed these newly developed time-resolved X-rays to the Li rich layered oxides with a specific chemistry of Li₁.₂Ni₀.₁₅Co₀.₁₀Mn₀.₅₅O₂ (i.e., 0.₅Li₂MnO₃ • 0.₅LiNi₀.₃₇Co₀.₂₄Mn₀.₃₉O₂) which can deliver the specific capacity over 250 mAh g⁻¹ at high operating voltage (>3.5V vs. Li/Li⁺ in average). Electronic and local structural changes that occur during a constant voltage charging of 5.₀V vs. Li/Li⁺ were monitored by using in situ quick X-ray absorption spectroscopy (QXAS) at Mn, Co and Ni K-edges with fast time resolution (a few seconds). The charge transfer rate and local structural changes at/around each element upon the fact delithiation will be discussed in comparison with the results obtained from normal in situ XAS during the slow rate charge (~C/12 rate).

Crystal structure changes of the spinel Li₄Ti₅O₁₂ material during the chemical sodiation using in situ time-resolved XRD will also be covered as an example of the kinetic study of Na-ion battery chemistry.

Acknowledgement
The work was supported by the U.S. Department of Energy, the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies, under the program of Vehicle Technology Program, under Contract Number DEAC02-98CH10886. Work at Institute of Physics of CAS was supported by NSFC (50672122, 50730005), “973” project (2007CB936501) of China.

References