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 delihiation and lithiation process are greatly needed. Recently, new *in situ* synchrotron x-ray diffraction and absorption techniques to study crystalline structural changes of $LiFePO_4$ 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 $Li_{1.2}Ni_{0.15}Co_{0.10}Mn_{0.55}O_2$ (i.e., $0.5Li_2MnO_3$ • $0.5LiNi_{0.37}Co_{0.24}Mn_{0.39}O_2$) 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 $Li_4Ti_5O_{12}$ 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.

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References

[1] Xiaojian Wang, Hai-Yan Chen, Xiqian Yu, Lijun Wu, Kyung-Wan Nam, Jianming Bai, Hong Li, Xuejie Huang and Xiao-Qing Yang, Chem. Commun. 47 (2011) 7170.

[2] Xiqian Yu, Qi Wang, Yongning Zhou, Hong Li, Xiao-Qing Yang, Kyung-Wan Nam, Steven N. Ehrlich, Syed Khalid and Ying Shirley Meng, Chem. Commun., 48 (2012), 11537.