Investigation of the Charge Compensation Mechanism on the Lithium Transition Metal Oxide Electrode during Li-ion deintercalation by Soft X-ray Absorption Spectroscopy

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Soft XAS (200 eV to 1000 eV), using synchrotron radiation, has been applied to investigate the electronic structure of specific ions in the electrode materials for Li rechargeable batteries, especially, low z elements like oxygen and fluorine that cannot be directly investigated by hard XAS (above 1000 eV). Recent theoretical calculations on electrode materials for Li batteries indicate that electron exchange in cathode materials (i.e., oxidation and reduction) may involve the participation of the oxygen 2p band, in addition to charge compensation by the metal ions. Soft XAS at O K-edge could provide crucial experimental evidence for the oxygen contribution to charge compensation in the Li-ion intercalation-deintercalation process.

Soft XAS spectra can be obtained in both the electron yield (EY) and fluorescence yield (FY) modes. The electron yield mode is surface sensitive (within ~ 50 Å) while the fluorescence yield mode is suitable for probing the bulk (more than ~ 2000 Å). Unfortunately, most of the soft XAS results reported in the literature on lithium battery materials have been obtained by the electron yield method only. Although soft XAS, using electron yield method, gives useful information about the electronic structure of the transition metal and oxygen ions, the results are limited only to probing the surface or near surface, which may not reflect what is happening in the bulk. In contrast, our previous soft XAS study using both the FY and PEY modes clearly showed that the surface of nickel-based compounds has a different electronic structure from the bulk. Therefore, both FY and PEY detection modes were used simultaneously in this paper in order to obtain more complete information about the electronic structure.

Although studies on the charge compensation mechanism for the cathode materials of lithium batteries have been reported in literature, the techniques used in most those studies are limited in hard XAS only. The lack of systematic study of the charge compensation mechanism for the cathode materials of lithium batteries during Li\textsuperscript{+} intercalation/de-intercalation left many important questions unanswered, such as what is the role of oxygen, what are the correlations between transition metal ions and the surrounding oxygen ions. These are the issues we are trying to address in this paper, by using the combination of hard and soft XAS techniques, together with the simultaneous data collection with both PEY and FY modes in soft XAS.

Soft XAS measurements were performed in both fluorescence yield (FY) and partial electron yield (PEY) modes at beamline U7A of the NSLS. The beam size was 1 mm in diameter. The estimated incident X-ray energy resolution was ~ 0.15 eV at the oxygen K-edge (E/ΔE ~ 3500). Monochromator absorption features and beam instabilities were normalized out by dividing the detected FY and PEY signals by the photoemission current of a clean gold mesh placed in the incident beam. Energy calibration was carried out by initially calibrating the principal monochromator Io oxygen absorption feature to 531.2 eV using an oxygen gas phase absorption cell. An additional Io mesh of Ni was also placed in the incident beam to insure energy calibration (based on the oxygen calibration above) and energy scale reproducibility of the many PEY or FY spectra presented. The PEY data were recorded using a channel electron multiplier while the FY data were recorded using a windowless energy dispersive Si (Li) detector. A linear background fit to the pre-edge region was subtracted from the spectra. The O K-edge spectra are normalized between 585 and 630 eV. The cells were first charged to the desired value of deintercalated Li-ion content (x value) at a C/50 rate and then relaxed for a day. The electrochemical cells were disassembled in an argon-filled glove box, and the Li\textsubscript{1-x}Co\textsubscript{1/3}Ni\textsubscript{1/3}Mn\textsubscript{1/3}O\textsubscript{2} electrodes were taken out from the cell. The electrodes were then washed with tetrahydrofuran (THF) and dried thoroughly in vacuum. All soft XAS sample preparations were carried out in an inert atmosphere, except during the insertion in the experimental XAS chamber, when the samples were exposed to air for a few minutes.

The electronic structure and local environment of transition metals and oxygen in the electrochemically Li-ion deintercalated Li\textsubscript{1-x}MO\textsubscript{2} (M = Mn, Co, and Ni) electrode system were studied. The major charge compensation mechanisms in the Li\textsubscript{1-x}MO\textsubscript{2} (M = Mn, Co, and Ni) electrode system on Li-ion deintercalation are established. This combination of hard and soft XAS analysis gives a better understanding of the charge compensation mechanism of lithium transition metal oxides during Li intercalation/deintercalation. More detailed discussion will be presented at the meeting.

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References