X-ray Absorption Spectroscopic Studies of Layered Lithium Nickel Manganese Oxides for Li Rechargeable Batteries

Won-Sub Yoon,[a,b] Clare P. Grey,[a]
Xiao-Qing Yang,[b] Mahalingam Balasubramanian,[b] and James McBreen[b]

[a]Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794, USA
[b]Brookhaven National Laboratory, Upton, New York 11973, USA

$LiCoO_2$ is the most widely used cathode material in commercial secondary lithium batteries due to its many advantages, which include easy preparation and high theoretical specific capacity. However, the toxicity and high cost of cobalt represent some of the problems of this material. Thus, extensive research has been carried out over past 10 years to find alternative cathode materials. Layered lithium nickel manganese oxides have recently been shown to be promising cathode materials for use in lithium-ion batteries.[1,2] Ohzuku et al. showed that lithium nickel manganese oxide represents a possible alternative to $LiCoO_2$ for advanced lithium batteries, in terms of its operating voltage, capacity, cycleability, safety, and materials economy.[1] Lu et al. reported that $Li[Ni_xLi_{(1/3-2x/3)}Mn_{(2/3-x/3)}]O_2$ with x = 1/3, 5/12, or 1/2 can be cycled between 2.0 and 4.6 V and a stable capacity of about 200, 180, or 160 mAh/g, can be obtained respectively. Their DSC results showed good safety characteristics.[2] Kim et al. showed in their $xLiNi_{0.5}Mn_{0.5}O_2{\bullet}(1-x)Li_2TiO_3$ systems that the electrochemically inactive Li_2TiO_3 component contributes to the stabilization of $LiMn_{0.5}Ni_{0.5}O_2$ electrodes.[3] However, the detailed studies on the local electronic and atomic structures of these materials during charge and discharge has not been reported.

Numerous studies on the electronic structure of cathode materials for Li Rechargeable batteries have been made extensively. X-ray absorption spectroscopy (XAS) has been used to examine the electronic and local structure of the cathode materials.[4-7] Most of the XAS studies reported in the literature are focused on the K-edge of the transition metals in the cathode materials. The absorption peak features of the metal K-edge XAS include the useful structural information such as oxidation state of chemical species, their site symmetries, and covalent bond strength. In some compounds, the small pre-edge peak was used to infer the electronic structure of the central atom since the transition is very sensitive to chemical environments in spite of the electric dipole-forbidden transition. However, the metal K-edge XAS could not give any direct information for participation of oxygen in the charge compensation process. Only indirect inference for the contribution of oxygen atom was obtained from the peak intensity for electronic transition of 1s electron to 4p orbital with shakedown process. In contrast, using soft x-ray absorption spectroscopy, the direct information about oxygen can be obtained by oxygen K-edge study.

In this paper, we apply both soft and hard X-ray absorption spectroscopy to examine the lithium nickel manganese oxide electrode systems. The electronic and local structure changes around the Mn/Ni metal and oxygen sites during the first charge and discharge processes were studied. The major charge compensation mechanisms in the lithium nickel manganese oxides electrode system during electrochemical cycling has been established.

Lithium nickel manganese oxides were synthesized by a solid state reaction using lithium hydroxide and nickel manganese hydroxide. The Ni and Mn K-edge XAS measurements were performed in the transmission mode at beamline 18B of the National Synchrotron Light Source (NSLS). The *in situ* Mn and Ni K-edge XAS data were obtained in two separate cells. Energy calibration was carried out by using the first inflection point of the spectrum of Mn and Ni metal foil as a reference (*i.e.*, Mn K-edge = 6539 eV and Ni K-edge = 8333 eV). Reference spectra were simultaneously collected for each *in situ* spectrum by using Mn or Ni metal foils. Soft-XAS measurements were performed at beamline U7A of the NSLS. The beam size was 1 mm in diameter. The estimated incident X-ray energy resolution was ~0.2 eV. Data were obtained both in total electron yield (TEY) and fluorescence yield (FY) modes. The TEY data were recorded using a channel electron multiplier while the FY data were recorded using a windowless energy dispersive Si (Li) detector.

From the observation of hard-XAS results, we can conclude that the charge compensation, when charging between 2 and 4.6 V, is achieved mainly by the oxidation of Ni^{2+} to Ni^{4+} ions, while the manganese ions remain mostly unchanged in the Mn^{4+} state. The EXAFS results are consistent with these conclusions. When discharging at low voltage plateau (~1 V), however, the charge compensation for the Li-ion electrochemical process is achieved via reduction of Mn^{4+}. Soft-XAS results show that the TEY data are completely different from the FY data for during the charge process. This indicate that there are substantial differences between the surface and bulk of the electrode material during charge process. More detailed discussion will be presented at the meeting.

Acknowledgment

The work done at SUNY Stony Brook was supported by the National Science Foundation (DMR 9901308). The work done at BNL was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, Electric and Hybrid Propulsion Division, USDOE under Contract Number DE-AC02-98CH10886.

References

1. T. Ohzuku and Y. Makimura, *Chemistry Letters*, 744 (2001).
2. Z. Lu, D. D. MacNeil, and J. R. Dahn, *Electrochem. Solid-State Lett.*, **4**, A191 (2001).
3. J.-S. Kim, C. S. Johnson, and M. M. Thackeray, *Electrochem. Commun*. **4**, 205 (2002).
4. C. Delmas, J.P. Peres, A. Rougier, A. Demourgues, F. Weill, A. Chadwick, M. Broussely, F. Perton, Ph. Biensan, and P. Willmann, *J. Power Sources*, **68**, 120 (1997).
5. I. Nakai and T. Nakagome, *Electrochem. Solid-State Lett.*, **1**, 259 (1998).
6. W.-S. Yoon, K.-K. Lee, and K.-B. Kim, *J. Electrochem. Soc.*, **147**, 2023 (2000).
7. M. Balasubramanian, S. Sun, X. Q. Yang, and J. McBreen, *J. Electrochem. Soc.*, **147**, 2903 (2000).