

In Situ X-ray Diffraction Studies of Cathode Materials in Lithium Batteries

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ABSTRACT

There is an increasing interest in lithiated transition metal oxides because of their use as cathodes in lithium batteries. LiCoO_2 , LiNiO_2 and LiMn_2O_4 are the three most widely used and studied materials. At present, although it is relative expensive and toxic, LiCoO_2 is the material of choice in commercial lithium ion batteries because of its ease of manufacture, better thermal stability and cycle life. However, the potential use of lithium ion batteries with larger capacity for power tools and electric vehicles in the future will demand new cathode materials with higher energy density, lower cost and better thermal stability. LiNiO_2 is isostructural with LiCoO_2 . It offers lower cost and high energy density than LiCoO_2 . However, it has much poorer thermal stability than LiCoO_2 , in the charged (delithiated) state. Co, Al, and other elements have been used to partially replace Ni in LiNiO_2 system in order to increase the thermal stability. LiMn_2O_4 has the highest thermal stability and lowest cost and toxicity. However, the low energy density and poor cycle life at elevated temperature are the major obstacles for this material.

In order to develop safer, cheaper, and better performance cathode materials, the in-depth understanding of the relationships between the thermal stability and structure, performance and structure are very important. The performance here includes energy density and cycle life of the cathode materials. X-ray diffraction (XRD) is one of the most powerful tools to study these relationships. The pioneer ex situ XRD work on cathode materials for lithium batteries was done by Ohzuku¹⁻⁴. His XRD studies on LiMn_2O_4 , LiCoO_2 , LiNiO_2 , $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$, and $\text{LiAl}_x\text{Ni}_{1-x}\text{O}_2$ cathodes at different states of charge have provided important guidelines for the development of these new materials. However, the kinetic nature of the battery system definitely requires an in situ XRD technique to study the detail structural changes of the system during charge and discharge. The in situ XRD technique was used by Reimers, Li, and Dahn⁵⁻⁷ to study the LiCoO_2 , LiNiO_2 , and LiMn_2O_4 systems. Their results of these studies have demonstrated that in situ XRD can provide more detailed information about the cathode material structural changes during charge-discharge. Conventional x-ray sources were used in these studies and the beryllium windows were used in the in situ cells. Provisions were made to prevent corrosion of the beryllium windows during charge-discharge. For this reason, the in situ cells were often designed quite differently than a real battery. More seriously, the problem of beryllium corrosion restricted the voltage range of the cell below 4.5 V. This limited the use of this technique to study the effects of overcharge which is very important to the thermal stability of the cathodes. Using the plastic lithium battery technology, Amatucci, Tarascon, and Klein⁸ constructed an in situ XRD cell, which allows structural investigations at voltages greater than 5 V without any beryllium window corrosion. However, all of these in situ XRD studies using conventional x-ray sources probe the cell in reflection geometry. Therefore, the observed structural changes are predominantly from the top few microns of the electrode coating, which might not be representative for the whole coating during charge-discharge especially when the rate is high.

A new in situ XRD lithium battery cell was designed for using the strong x-ray source from synchrotron light source. The beryllium windows were replaced by Mylar

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windows. The electrodes were incorporated into the cells with a Li foil negative electrode, a Celgard separator, and 1M LiPF₆ electrolyte in 1:1 EC:DMC solvent. Taking the advantage of the strong beam, the experiments were carried out in the transmission mode and the cell configuration is similar to the real battery cells. Two cathode material systems, the LiMn₂O₄ and a family of LiM_xNiO₂ (x=Co, Al, Mg, Ti) were studied using this synchrotron based in situ XRD. The in situ XRD measurements were made at Beam Line X18A at National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The beam line was operated at an energy of 10.375 keV ($\lambda=1.195$ Å) which also offered the advantage of increased penetration depth over the conventional Cu α x-ray source.

In the studies of Li_xMn₂O₄ system, lithium rich (x=1.03-1.06) spinel materials, obtained from two different sources, were studied. Three cubic phases with different lattice constants were observed during charge-discharge cycles in all the samples when a sufficiently low charge-discharge rate ($\leq C/10$) was used. For the first time, two regions of two-phase coexistence were observed, indicating that both phase transitions are first order. The separation of the Bragg peaks representing these three phases varies from sample to sample and also depends on the charge-discharge rate. These results show that the de-intercalation of lithium in lithium rich spinel cathode materials proceeds through a series of phase transitions from a high-lithium-content phase to a low-lithium-content phase and finally to a λ -MnO₂ like cubic phase, rather than through a continuous lattice constant contraction in a single phase.

In the studies of the LiM_xNi_{1-x}O₂ (x=Co, Al, Mg, Ti) system, the relationship between the structural changes during charge-discharge and the thermal stability was investigated. Since the thermal stability problem mainly occurred at fully charged or over-charged state for cathodes, the discussion of structural changes in this presentation will be focused on the voltage range from 4.1V to 5.1V. The results for four materials will be discussed: LiNiO₂, LiCo_{0.2}Ni_{0.8}O₂, LiCo_{0.175}Al_{0.025}Ni_{0.8}O₂, and LiMg_{0.125}Ti_{0.125}Ni_{0.75}O₂. The LiMg_{0.125}Ti_{0.125}Ni_{0.75}O₂ cathode is a newly synthesized material by FMC Corp. Gao has presented the superior thermal stability and cyclebility of this new material in a recently published paper⁹. In this paper, evidence was given that the thermal stability of these materials is in the order of LiMg_{0.125}Ti_{0.125}Ni_{0.75}, LiCo_{0.2}Ni_{0.8}O₂, LiNiO₂ with LiNiO₂ as the least stable material. Clear evidence of the correlation between the thermal stability and the characteristic structural change behavior of these materials during over-charge will be given in this presentation. These changes include the number of phase transitions and the varying ranges of the lattice constants during charge and over-charge based on the in situ XRD studies.

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