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FINAL REPORT

FOR CRADA NO. C-06-02

BETWEEN

BROOKHAVEN SCIENCE ASSOCIATES

AND

LG CHEMICAL

Project Entitled: Characterization of Cathode Materials for Rechargeable Lithium Batteries using Synchrotron Based In Situ X-ray Techniques

Brookhaven PI: Xiao-Qing Yang

Submitted by: Michael J. Furey
Manager, Research Partnerships
Brookhaven National Laboratory

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Report for CRADA with LG Chemical, Ltd. (CRADA No. BNL-C-06-02)

Proposal Title: Characterization of Cathode Materials for Rechargeable Lithium Batteries using Synchrotron based in situ X-ray technique.

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Budget $60,000

Project Duration: One year.

Technical Abstract:

The emergence of portable telecommunication, computer equipment and ultimately hybrid electric vehicles has created a substantial interest in manufacturing rechargeable batteries that are less expensive, non-toxic, operate for longer time, small in size and weigh less. Li-ion batteries are taking an increasing share of the rechargeable battery market. The present commercial battery is based on a layered $LiCoO_2$ cathode and a graphitized carbon anode. $LiCoO_2$ is expensive but it has the advantage being easily manufactured in a reproducible manner. Other low cost layered compounds such as $LiNiO_2$, $LiNi_{0.85}Co_{0.15}O_2$ or cubic spinels such as $LiMn_2O_4$ have been considered. However, these suffer from cycle life and thermal stability problems. Recently, some battery companies have demonstrated a new concept of mixing two different types of insertion compounds to make a composite cathode, aimed at reducing cost and improving self-discharge. Reports clearly showed that this blending technique can prevent the decline in capacity caused by cycling or storage at elevated temperatures. However, not much work has been reported on the charge-discharge characteristics and phase transitions for these composite cathodes.

Understanding the structure and structural changes of electrode materials during the electrochemical cycling is the key to develop better lithium ion batteries. The successful commercialization of the lithium-ion battery is mainly built on the advances in solid state chemistry of the intercalation compounds. Most of the progress in understanding the lithium ion battery materials has been obtained from x-ray diffraction studies. Up to now, most XRD studies on lithium-ion battery materials have been done ex situ. Although these ex situ XRD studies have provided important information about the structures of battery materials, they do face three major problems. First of all, the pre-selected charge (discharge) states may not be representative for the full picture of the structural changes during charge (discharge). In other words, the important information might be missed for those charge (discharge) states which were not selected for ex situ XRD studies. Secondly, the structure of the sample may have changed after removed from the cell. Finally, it is impossible to use the ex situ XRD to study the dynamic

effects during high rate charge-discharge, which is crucial for the application of lithium-ion batteries for electric vehicle. A few in situ studies have been done using conventional x-ray tube sources. All of the in situ XRD studies using conventional x-ray tube sources have been done in the reflection mode in cells with beryllium windows. Because of the weak signals, data collection takes a long time, often several hundred hours for a single charge-discharge cycle. This long time data collection is not suitable for dynamic studies at all. Furthermore, in the reflection mode, the x-ray beam probes mainly the surface layer of the cathode materials.

In collaboration with LG Chemical Ltd., BNL group designed and constructed the cells for *in situ* studies. LG Chemical provided several blended samples and pouch cells to BNL for preliminary *in situ* study. The LG Chemical provided help on integrate the blended cathode into these cells. The BNL team carried out *in situ* XAS and XRD studies on the samples and pouch cells provided by LG Chemical under normal charge-discharge conditions at elevated temperature. Major finding are reported below.

Figure 1 shows *in situ* XRD patterns of the $LiMO_x$ composite cathode collected during charge. Bragg peaks corresponding to both cubic $Li_{1-x}Mn_2O_4$ spinel and hexagonal $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ layered phases were clearly observed in the *in situ* XRD patterns of the $LiMO_x$ composite cathode. All peaks can be indexed as $(111)_C$, $(511)_C$, $(440)_C$ and $(531)_C$ for cubic spinel phase, and $(003)_H$, $(107)_H$, $(108)_H$, $(110)_H$ and $(113)_H$ for hexagonal layered phase. In general, the variations of *in situ* XRD peaks for both cubic spinel and hexagonal layered components during charge show similar trends as observed in the *in situ* XRD patterns of each component during charge. However, there are some interesting features to be pointed out in the *in situ* XRD patterns of the $LiMO_x$ composite cathode during charge. At the beginning of charge (scan 1 to 13), only the Bragg peaks corresponding to $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ phase started to move while the Bragg peaks corresponding to $Li_{1-x}Mn_2O_4$ phase remained unchanged until the cell voltage reaches ~ 3.9V *vs.* Li/Li^+. Once the Bragg peaks for the cubic spinel phase started to move to higher angles (scan 17), the structure change of the $Li_{1-x}Mn_2O_4$ component came to dominate the structure change of the $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ component until the cell voltage reaches at ~ 4.3V *vs.* Li/Li^+ (scan 37). During this region (scan 17 to 37), the XRD peaks corresponding to hexagonal cell do not seem to shift their 2θ positions, which can be observed at the $(003)_H$ peaks. (scan 17 to 37) After the cubic spinel phase dominant region, the Bragg peaks for the hexagonal layered phase only keep moving (scan 41 to 84) until the end of charge. Compared with the (003) peak of the single $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cathode at the end of charge, (003) peak feature at the end of charge (scan 84) indicates that the phase transformation from H2 to H3 is much more promoted in the $LiMO_x$ composite cathode.

In order to provide clearer understandings on the structure changes of the $Li_{1-x}Mn_2O_4$, $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$, and $LiMO_x$ composite cathodes during the first charge, the lattice parameters of three cells which were calculated by the least-square refinements using the *in situ* XRD data are plotted as a function of x in lithium metal oxide cathodes ($Li_{1-x}MO_x$) in Fig. 2. Standard deviation of the least squire fitting of the lattice parameters is plotted using error bars. The lattice parameters for the $Li_{1-x}Mn_2O_4$ during charge show continuous contraction of the cubic spinel unit cell. On the other hand, the lattice parameters of the $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ show an initial expansion along the c-axis and a simultaneous contraction along the a- and b-axis during early stage of charge. Towards the end of charge there is a major contraction along the c-axis and a slight expansion along the a- and b-axis. The lattice parameter changes of the $Li_{1-x}Mn_2O_4$ and $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ during charge agrees well with the previous results.

The lattice parameter changes of $Li_{1-x}Mn_2O_4$ and $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ components in the $LiMO_x$ composite cathode were coincident well with the observed *in situ* XRD patterns of

the mixed cathode shown in Fig. 1. Based on the features of the lattice parameters of each component, the lattice parameter changes of the $LiMO_x$ composite cathode can be divided into 4 regions as depicted in Fig. 2. In the region I (x = 0.0 to ~ 0.1), it is clearly seen that the lattice parameter of $Li_{1-x}Mn_2O_4$ in the $LiMO_x$ composite cathode remains uncharged at the beginning of the charge while the a- and c- axes of the $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ in the $LiMO_x$ composite cathode continuously changes. Region II (x = ~ 0.1 to ~ 0.4) shows a rapid and significant contraction of the cubic spinel lattice parameters as much as that of lattice parameters for the single $Li_{1-x}Mn_2O_4$ cathode. On the other hand, in this region II, the a- and c- axes of the $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ in the $LiMO_x$ composite cathode show only slight changes in their lattice parameters, which are different from the lattice parameter changes of the single $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cathode having continuous contraction along the a-axis and expansion along the c-axis during charge. In region III (x = ~ 0.4 to ~ 0.8), the lattice parameter changes were observed only in the $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ in the $LiMO_x$ composite cathode, indicating slight expansion along the a-axis and major contraction along the c-axis. At the end of the charge, slight further lattice contraction of the spinel unit cell was observed in region IV (x= ~0.8 to 1.0), whereas the lattice parameters for the $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ in the $LiMO_x$ composite cathode remained unchanged. The lattice parameter changes in region IV reveals that a high voltage capacity in the $LiMO_x$ composite cathode at ~ 5.1V *vs.* Li/Li^+ would be attributed to the additional Li^+ extraction from the spinel phase in the $LiMO_x$ composite cathode not to the electrolyte decomposition. It should be noted that the slight further lattice contraction of the cubic spinel phase in the $LiMO_x$ composite cathode at the end of charge (~ 5.1V *vs.* Li/Li^+) was not observed in the single $Li_{1-x}Mn_2O_4$ cathode. The addition of the layered $LiNi_{0.8}Co_{0.2}O_2$ to manganese spinel was reported to prevent Mn dissolution as well as electrolyte decomposition. Therefore, the mixing of the $Li_{1-x}Mn_2O_4$ and $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ might result in the suppression of the electrolyte decomposition at high voltages. This is also supported by the promoted phase transformation from H2 to H3 in the $LiMO_x$ composite cathode at the end of charge.

Through the CRADA with LG Chemical, we could identify the relationship between structural changes during charge-discharge of the blended cathode materials and the performance of the lithium batteries using these blended cathode materials. The results were provided to LG to help them develop better performance Li-ion batteries. This CRADA also helped BNL Li-ion battery research group to develop the in situ X-ray techniques for Li batteries. Recommended follow-on work would be further collaboration between BNL group and LG Chemical to investigate various Li battery cells at different cycling conditions, which will make BNL group even stronger in state-of-art Li battery research field.

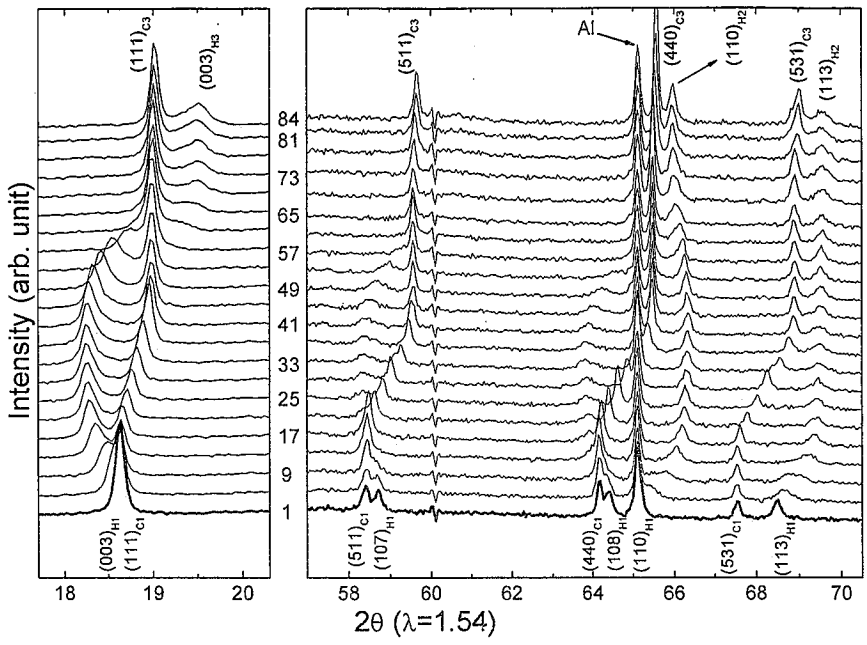

Figure 1. In situ XRD patterns of a mixed $LiMn_2O_4$ + $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cathode during the first charge at C/7 rate. The 2θ angles have been converted to those corresponding to the Cu Kα radiation. (λ=1.54 Å)

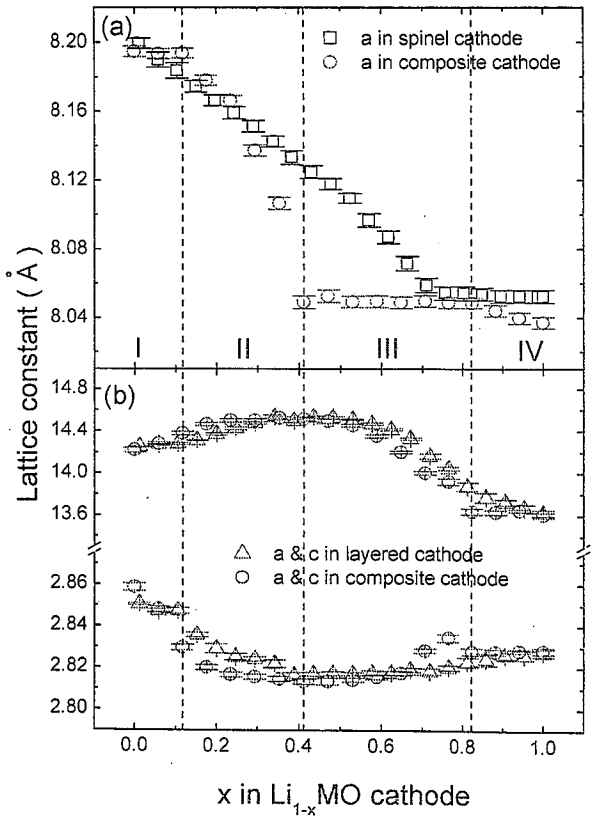

Figure 2. Variations of the lattice parameters of $Li_{1-x}Mn_2O_4$, $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ and mixed $Li_{1-x}Mn_2O_4$ + $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cathodes as a function of x during first charge.