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**Development of new electrolyte and cathode materials
for rechargeable lithium batteries**

FINAL ABSTRACT

ON CRADA WITH GOULD, INC.
CRADA No. BNL C-95-20
(April 1995----April 1996)

Xiao-Qing Yang

July 1997

DEPARTMENT OF APPLIED SCIENCE
BROOKHAVEN NATIONAL LABORATORY

Under contract No. DE-AC02-76CH00016 with the
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Project #: BNL C-95-20

Project Status: Completed

Title: Development of new electrolyte and cathode materials for rechargeable lithium batteries

Abstract:

Gould Inc., in their effort of developing lithium ion batteries, are facing two important problems: The performance of the electrolyte and the reliability of the cathode materials. For the electrolyte, new additives are needed to improve the conductivity and the lithium transference number. For the cathode material, LiMn_2O_4 spinel was chosen by Gould as cathode material because of its low cost and toxicity. However, it is an irreproducible product with unpredictable failure modes. Therefore, the fundamental understanding of the failure mechanism of LiMn_2O_4 spinel is very important for quality controls.. These two problems have been addressed through this completed CRADA by BNL and Gould teams. Several additives, which increase the ionic conductivity and lithium transference number of the electrolyte, were synthesized at BNL and delivered to Gould. The evaluation of these additives was not fully completed by Gould team, since the additives are made for liquid electrolytes while Gould will be using gel electrolytes in their battery cells. BNL will be working on new additives which are suitable for gel electrolytes in the CRADA works. The unique facilities of BNL at National Synchrotron Light Source (NSLS) was used to do *in situ* x-ray diffraction and x-ray absorption studies on LiMn_2O_4 in operating cells that was delivered by Gould. Preliminary data shows that the relationships between the performance and structural changes of the cathode materials can be studied by these *in situ* techniques. The significant problem is The short period of this one year CRADA forced us to truncate several long term goals. This is the most significant problem. The results obtained so far point to very promising future collaboration. Towards this endeavor, a new one year CRADA between BNL and Gould Electronics, Inc.(BNL-C-97-08), has been executed. Both BNL and Gould team would like to see this new CRADA to be converted to a multiyear CRADA.

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Significant accomplishments:

The tasks defined in our proposal were successfully completed by both BNL and Gould. BNL teams.

In the task of developing new electrolytes, the use of aza-ether anion acceptors is a key part of our approach to improve electrolyte conductivity, decrease ion pairing and enhance lithium ion transport. Although studies of crown ether, such as 18-crown-6, and 12-crown-4, for cation coordination have been reported previously, there is little work on anion coordination due to the lack of suitable anion receptors. However, anion coordination is much more important than cation coordination in lithium battery electrolytes since the goal is to increase the concentration of free lithium cations. The achievement of anion coordination would therefore open a new approach for lithium battery electrolyte development. We have synthesized a family of aza-ether based compounds for anion receptors. The molecular structures of these compounds are shown in figure 1. The ion complexation of these new anion receptors was studied by ionic conductivity and x-ray absorption spectroscopy [1,2]. A more recent study has shown that the ionic conductivity can be increased by two orders of magnitude when these anion receptors are used as additives in Poly(ethylene oxide) (PEO) based polymer electrolytes [3]. Representative results are given in figure 2. Both x-ray absorption studies of halide ions and ^{51}Cr NMR have confirmed anion complexation by the anion receptors. Gould team has done some work on studying the electrochemical stability and ion transference number of electrolytes using these anion receptors. Unfortunately, this work was not fully completed because Gould team had to focus on their studies of gel electrolytes.

The most significant accomplishments were made in the field of cathode materials studies. We used *in situ* synchrotron based X-ray Absorption (XAS) and X-Ray Diffraction (XRD) techniques for studies of the cathode materials. The near edge XAS results show clear edge position shifts during charge-discharge cycling which corresponds to the intercalation and de-intercalation of lithium ions from the cathode materials. Some of the spectra obtained in these studies are plotted in figure 3 and figure 4. For the XAS studies special battery cells were designed and constructed by the BNL group. The thin film lithium ion cells developed by Gould team were directly used in the XRD studies without any modification. These studies provided us very useful information about the structural changes of the cathode materials during charge-discharge cycles. An example of the experimental data is shown in figure 5. This data set shows transmission geometry x-ray diffraction 2θ scans done on a Gould Li-ion cell ~ 0.5 mm in thickness. The evolution of the $\text{Li}_x\text{Mn}_2\text{O}_4$ (511), (333), and (531) peaks as the cell was discharged from 3.90 to 2.94 volts are shown. Analysis of the peak positions shows that the $\text{Li}_x\text{Mn}_2\text{O}_4$ lattice constant expands from 8.03 to 8.18 Å as the cell voltage dropped from 3.90 to 2.94 volts. More importantly, over part of the discharge voltage range, the individual $\text{Li}_x\text{Mn}_2\text{O}_4$ peaks are all split into two peaks, which is a signature of two phase coexistence. In this particular batch of $\text{Li}_x\text{Mn}_2\text{O}_4$, a first order structural transition occurs where single phase cubic material converts into two cubic phases with different densities. This structural transition has implications on battery performance which will be

further studied in our next CRADA. Because of the high resolution of a synchrotron-based diffractometer, it is possible to detect secondary phase(s) which have subtle structural modifications from the primary phase. An example is shown in Fig. 6. This particular cell did not perform well and had a voltage plateau at 1.5 V. The bottom scan in figure 6 shows x-ray diffraction scans of the (333), (511), (440), and (531) peaks of $\text{Li}_x\text{Mn}_2\text{O}_4$ cathode material in its initial state. For a cubic structure, the (333) and (511) peaks are at the same value of 2θ , so they should appear as a single peak. In this material, however, the (333) and (511) peaks are split into at least three separate peaks, and the (440) and (531) peaks are considerably broadened as well. These features all indicate that two or more phases exist in this material. The series of scans shown in figure 6 also suggest that the 1.5 V plateau is related to a structural transition within the cathode material. As the cell voltage was raised through the plateau, the $\text{Li}_x\text{Mn}_2\text{O}_4$ peaks, which were initially split or broadened, became narrower and more intense until there was no evidence of the secondary phase. This example shows how structural features observed in the *in situ* x-ray diffraction experiments can be *directly* correlated with electrochemical behavior. In this particular case, the x-ray experiments also provide a simple test for assessing the quality of $\text{Li}_x\text{Mn}_2\text{O}_4$ starting material, since the splitting of the LiMn_2O_4 (333) and (511) peaks can be observed before the starting material is placed in battery cells. Figure 7 shows plots of the lattice constants found from *in situ* x-ray diffraction studies of three different batches of LiMn_2O_4 throughout a charge interval. Dramatically different structural behavior can be seen in these different batches of material. Two of the batches (batch-2 and batch-3) exhibit two phase coexistence behavior (see figure 5 above), while the third (batch-1) does not. Since the structural transition between single phase and two phase coexistence is first order, it is likely that grains of $\text{Li}_x\text{Mn}_2\text{O}_4$ are fractured during each transition, which in turn would cause cell performance to deteriorate. Another readily observable feature of the data in figure 7 is that the lattice constant of the batch-3 material does not change nearly as much at lower capacities as the batch-1 and batch-2 materials. This behavior suggests that the Li is being removed from different sites in this material. The differences in these materials are not obvious on examination of the initially processed materials. However, the differences in structural behavior can be readily seen in the *in situ* x-ray diffraction data of figure 7. This is one of the major strengths of the *in situ* x-ray scattering technique; structural properties which actually affect the electrochemical behavior are readily seen. An article describing this work in detail has been submitted to *Journal of the Electrochemical Society* [4]. Another paper based on these studies was published on *Appl. Phys. Lett.*[5].

Significant problems:

As mentioned before, the most significant problem of this CRADA was, we were working on a long term project which was funded by a short term CRADA. It was difficult to make long term planning for both BNL and Gould teams. We hope the new multiyear CRADA will be funded. The other problem was we did not go far enough on the electrolyte studies. The new additives developed at BNL were not fully evaluated by Gould team. Gould team was focused on their studies on the gel electrolyte systems. BNL team is planning to increase their

development effort on additives which are suitable for gel electrolytes, These new additives will be evaluated by the Gould team in future CRADA works.

Industry benefits realized:

For the Gould team, by collaborating with BNL team, the unique facility such as National Synchrotron Light Source at BNL was utilized for important battery material studies. Very useful information about the relationship between performance and structural changes of the LiMn_2O_4 cathode materials was obtained through the *in situ* X-ray absorption and diffraction studies. The results were used for their development efforts on new thin film lithium ion batteries.

BNL benefits realized:

For the BNL team, the thin film rechargeable lithium battery cells designed and constructed by Gould team is one of the most important factors for their success of *in situ* x-ray absorption and diffraction studies. The knowledge gained is not only valuable to industry for developing their commercial lithium batteries, but also very important to BNL for the fundamental understanding of Li intercalation process in cathode materials and the effects of the anion receptors in the new generation of electrolytes.

Future works:

More *in situ* x-ray absorption and diffraction studies have been planned by both BNL and Gould teams. The relation between the synthesis conditions and structural changes of LiMn_2O_4 cathode materials during charge-discharge cycles, the effects of overcharge and over discharge, the structural changes related to cycle life, the structural changes during charge-discharge at high and low temperatures will be studied. These studies will be very important to Gould for their thin film lithium battery design, as well as material testing and quality control.

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Chemical Structure of New Anion Receptors

Figure 1. Chemical structure of new anion receptors.

$\text{R} = \text{CF}_3\text{SO}_2$ is an electron withdrawing group. L_xR are linear compounds, C_xR are cyclic compounds.

Conductivity of $\text{PEO}_{16}(\text{LiCl})$ and $\text{PEO}_{16}(\text{LiCl}+\text{L6R})$

Figure 2. Conductivity of $\text{PEO}_{16}(\text{LiCl})$ and $\text{PEO}_{16}(\text{LiCl}+\text{L6R})$. When anion receptor L6R was added in the polymer electrolyte, the ionic conductivity is increased by two orders of magnitude.

***In situ* Ni K edge XANES for Li_xNiO_2 during charge**
 $x = 1.0, 0.88, 0.77, 0.66, 0.54, 0.18, 0.01$

Figure 3. *In situ* Ni K edge XANES for Li_xNiO_2 during charge. During the charging, Li is reduced from 1.0 to 0.88, 0.77, 0.66, 0.54, 0.18, 0.01. The absorption peak above the Ni K edge shifted to higher energy because of the change in Ni oxidation state.

***In situ* Mn K edge XANES for $\text{Li}_x\text{Mn}_2\text{O}_4$ during charge
 $x = 1.0, 0.75, 0.5, 0.25$ and 0.0**

Figure 4. *In situ* Mn K edge XANES for $\text{Li}_x\text{Mn}_2\text{O}_4$ during charge. During the charging, Li is reduced from 1 to 0.75, 0.5, 0.25, 0.0. The absorption peak above Mn K edge shifted to higher energy because of the change in Mn oxidation state.

Figure 5. *In situ* x-ray diffraction 2θ scans showing the evolution of $\text{Li}_x\text{Mn}_2\text{O}_4$ (511), (333), and (531) peaks as a lithium ion cell is discharged from 3.90 to 2.94 V. The (440) peak at $2\theta \sim 20.3^\circ$ also evolves, but it is obscured by an aluminum peak.

Figure 6. *In situ* x-ray diffraction 2θ scans showing the evolution of the $\text{Li}_x\text{Mn}_2\text{O}_4$ (511), (333), (440) and (531) peaks as a lithium ion cell is charged from 1.37 to 2.92 V. This data is from the initial charge of the cell; the satellite peaks at the (511) and (333) peak position and the broadening of the (440) and (531) peaks at 1.37 V arise from a secondary phase present in the cathode material. This secondary phase converts into the primary phase as the cell is charged.

Figure 7. Evolution of the $\text{Li}_x\text{Mn}_2\text{O}_4$ lattice constant in three different batches of cathode material during cell charging. Both the structural and the electrochemical behavior in the three batches of material are different. For example, the batch-1 material remains single phase throughout the charging procedure, but the batch-2 and batch-3 materials both undergo first order phase transitions to two phase coexistence behavior.