MAGNETIC RESONANCE AND X-RAY ABSORPTION STUDIES
OF MATERIALS FOR ADVANCED BATTERIES

Progress Report

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Although only five months have elapsed since the official award date for this new grant, there is considerable progress to report. One manuscript has been submitted and several other projects are in various stages of completion. A brief description of each project, categorized by materials appears below. This is followed by a short account of work in progress and projects planned for the near future.

1. Transition Metal Cathodes

a. $\text{Li}_x\text{V}_6\text{O}_{13}$:

A collaborative study with Uppsala University (Sweden), begun before this DOE grant was awarded, has recently been completed. A revised approach was undertaken recently in order to obtain a better understanding of the multiphase behavior of the lithium vanadate system as a function of Li content. With our new x-ray absorption model, conceived of partly under this DOE grant, we have successfully fit both the near edge (NEXAFS) and the extended edge (EXAFS) x-ray absorption data acquired at the Brookhaven National Lab National Synchrotron Light Source (NSLS). In addition, ^7Li NMR spectra were shown to be consistent with the presence of mixtures of distinct phases, corresponding to $x = 2$ and higher values. A manuscript describing this work has been submitted to the *Journal of Applied Physics*.

b. Li_xFeS_2

In a collaboration with Tel Aviv University, *in situ* synchrotron x-ray absorption measurements were made on thin Li/polymer electrolyte/iron pyrite cells. The total cell thickness was typically less than 80 μm , so that x-ray transmission measurements at the iron k-edge were found to yield good absorption edge spectra. We have obtained both Fe k-edge NEXAFS and EXAFS data on six cells in various states of charge or discharge. Analysis of the data is underway, with special emphasis on correlating structural changes with Li content, and checking for the presence of intermediate iron-sulfur compounds in partially discharged cells.

2. Polymer Electrolytes

As part of a second collaboration with Tel Aviv University, we are characterizing the Li ion environment in poly(ethylene oxide) (PEO) - based composite electrolytes. Of current interest to us are compounds with very high salt (typically LiI) concentrations and also containing nano-sized (~ 100 nm) particles. Though these electrolytes show little promise for ambient temperature applications, they have sufficient electrical conductivity at only moderately high temperatures (~ 90 $^\circ\text{C}$) to be considered in electric vehicle (EV) applications. The low cost of PEO and LiI, compared to the more "exotic" polymers and electrolyte salts, makes these materials particularly attractive for scaled up applications such as EV's. Using solid state NMR methods, we have determined that an abrupt increase in electrical conductivity, which occurs at about 80 $^\circ\text{C}$, is correlated with a change in lithium environment from polymer-coordinated to more nearly ionic. A manuscript is in preparation,

for submission during the next two months.

3. *Lithiated Carbon*

Our collaborators at Tel Aviv University have also provided us with samples of high-capacity carbon (nearly 600 mA-hr/g, some 80 % higher than in LiC_6 graphite), based on relatively low temperature ($< 1500^\circ\text{C}$) decomposition of cotton. A preliminary ^7Li NMR result is most revealing. With high resolution methods (magic angle spinning and proton decoupling), we have observed three distinct Li environments: (i) intercalated graphite-like; (ii) ionic - which is most likely contained in the irreversible surface layer formed by electrochemical reduction of the solvent; (iii) a new species of relatively mobile Li (as judged from line widths) that is apparently correlated with hydrogen-containing regions of the disordered carbon. A manuscript is in preparation, intended for submission during the next two months.

Plans for the next six months

1. Analysis of the Fe k-edge x-ray absorption data for the Li_xFeS_2 system will be completed during the next two months.
2. A project on $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ cathodes, prepared by collaborators at Carnegie Mellon University, will be undertaken. NMR of both lithium isotopes (^6Li and ^7Li) and x-ray absorption measurements will be used to attempt to correlate structure with electrical properties of these cathodes.
3. We will begin studying a series of gel electrolytes based on poly(vinylidene difluoride) (Pvdf), prepared by collaborators at the U.S. Army Communications and Electronics Command (CECOM). Of particular interest in this project are: (a) the effect of new electrolyte salts, such as Li superacids, on low temperature conductivity; (b) the effect of inorganic nanoscale particles, such as Al_2O_3 or TiO_2 , on electrical properties. Variable temperature NMR will be utilized in conjunction with differential scanning calorimetry to characterize ionic mobility and polymer motions above the glass transition.
4. We will study the high capacity carbon anodes described above with infra-red absorption. We hope to confirm the presence of different Li environments by measuring the distinct vibrational modes associated with each.

No significant changes in budget expenditure rate are anticipated at this time.