LITHIUM ION RECHARGEABLE SYSTEMS STUDIES

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Introduction

Lithium ion systems, although relatively new, have attracted much interest worldwide. Their high energy density, long cycle life and relative safety, compared with metallic lithium rechargeable systems, make them prime candidates for powering portable electronic equipment. Although lithium ion cells are presently used in a few consumer devices, e.g., portable phones, camcorders, and laptop computers, there is room for considerable improvement in their performance. Specific areas that need to be addressed include:

- Carbon anode - a) increase reversible capacity
  b) minimize passivation

- Cathode - a) extend cycle life
  b) improve rate capability
  c) increase capacity

There are several programs ongoing at Sandia National Laboratories which are investigating means of achieving the stated objectives in these specific areas. This paper will review these programs.

Sandia Programs in Lithium Ion Systems

1. *Battery Technology Initiative*. This is a Cooperative Research and Development Agreement (CRADA) with four industrial partners; AT&T Bell Laboratories, Eveready Battery Co., Rayovac Corp., and Wilson Greatbatch Ltd. The goal of this program is to develop a carbon, based on prior Sandia technology, that is suitable as an anode in lithium ion rechargeable cells. Certain carbon foams, developed for military applications, have been shown to intercalate lithium ions very efficiently. Processing variables are being studied in a controlled fashion, and the resulting carbonaceous materials are then physically characterized. Electrochemical screening is then carried out on the samples, i.e., intercalation efficiency and irreversible passivation; materials that pass the test are sent to the industrial partners for evaluation in their electrode configurations. Thus the research and development steps are performed in parallel, shortening the time to commercialization. Results to date have been encouraging, with some carbon samples achieving a reversible capacity of > 600 mAh/g. However, the irreversible passivation is high. Work is now focusing on reducing the passivation, while maintaining the high reversible capacity.

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2. *Flexible Carbon Anode.* Typical intercalation anodes in lithium ion rechargeable batteries consist of a powdered carbon mixed with a binder which is pasted onto a collector. The presence of an inert binder within the anode structure leads to lower capacity and energy density in the battery. Under certain circumstances, the binder might block some active sites on the carbon, lowering the capacity and energy density even further, or hinder the movement of lithium ions into and out of the carbon, adversely affecting its rate capability.

To minimize these effects, we have developed a thin, flexible carbon fiber that intercalates lithium ions to the same level as many powdered carbons. This fiber can be woven, knitted or matted into a cloth for use as an anode in a lithium ion rechargeable battery. The absence of binder and current collector grid should maximize the capacity and energy density of batteries using this anode material.

A commercial grade of poly(acrylonitrile) (PAN) used for producing high strength carbon fibers was used to prepare the flexible carbon fibers. It was used either as a continuous filament yarn or a non-woven fabric, having individual filaments with a diameter of ~13μm. The yarns and cloths were carbonized by first oxidizing in air at temperatures ranging from 230° to 290° C, then pyrolyzing in argon at temperatures ranging from 900° to 1400° C. The resulting carbon yarns and fabrics were flexible enough to be wound around a 0.25 inch diameter mandrel.

Potentiostatic, galvanostatic, and potentiodynamic tests were conducted on these materials in flooded half-cells, in which lithium foil was used for both the counter and reference electrodes. To determine the optimum pre-oxidation and carbonization temperatures, a test matrix was run using PAN yarn. The reversible capacity and passivation were measured potentiostatically in $LiCF_3SO_3$/PC electrolyte. The results are summarized in Table I.

Table I. Reversible capacity (passivation in parentheses), mAh/g, of carbon fibers as a function of oxidation temperature and carbonization temperature.

Ox. Temp.	Carbonization Temperature		
	900°C	1100°C	1400°C
230°C	365 (89)	465 (126)	208 (15)
270°C	272 (82)	274 (91)	205 (19)
290°C	246 (71)	472 (74)	212 (7)

Within the temperature range tested, 1100° C is the optimum carbonization temperature to achieve maximum reversible capacity. Passivation can be seen to decrease as the pre-oxidation temperature is raised.

A series of tests have been initiated on carbon cloths, prepared from PAN yarn. The non-woven fabric was prepared from 37 mm long staple fiber that had been crimped, using a hydroentaglement procedure. All samples were oxidized at 230° C and carbonized at 1100° C. Typical results from a carbon cloth test are shown in Figure 1. The first 20 cycles are potentiodynamic scans between 3.0 V and 10 mV at 1 mV/sec. The final 5 cycles were run galvanostatically at 0.64 mA, with a potential hold at the end of each charge and discharge cycle, until the current reached 50 $\mu A/cm^2$ (1). These results are preliminary and tests are continuing.

3. *Lithium Manganese Oxide Doping*. The purpose of this DOE/Basic Energy Sciences (BES) funded program is to understand the influence that doping of lithium manganese oxide spinel has on the fundamental properties that control its performance as a cathode. Specifically, by modifying the spinel lattice we should be able to impact three critical areas: 1) minimize lattice expansion on lithiation - to extend cycle life, 2) modify the lattice to improve the kinetics of lithium insertion/deinsertion - to increase rate capability, and 3) provide additional sites where lithium can reside - to enhance capacity. The program consists of three phases: solid state molecular modeling of doped $Li_xMn_2O_4$ using Biosym software, synthesis of materials based on predictions of the model, and electrochemical evaluation of the newly synthesized materials.

We have examined the crystal structure of pyrolusite (β-MnO_2), ramsdellite (γ-MnO_2), $LiMn_2O_4$ spinel, and a lithium-deficient spinel $\square_{1.0}Mn_2O_4$ (λ-MnO_2). We have also modeled several spinels with intermediate compositions based on the amount of lithium inserted into the tetrahedral site. Three dimensional representations of the structures provide a basis for identifying site occupancies, coordinations, manganese valence, order-disorder, and potentially new dopants for enhanced cathode behavior. X-ray diffraction and neutron diffraction simulations of the crystal structures provide good agreement with observed patterns for synthesized samples. Ionic modeling of these materials consists of an energy minimization approach using Coulombic, short-range, and van der Waals interactions (2). Results from rigid ion and shell models allow a systematic analysis of changes in lattice energy, cell volume, strain, and the relative stability of doped structures using ions such as aluminum, cobalt, nickel, and titanium.

Constant pressure minimizations, while maintaining isometric symmetry, suggest a stabilization of the lithium manganese spinel structure with decreasing lithium content. Minimized cell parameters are typically within two percent of the observed values; minimized crystal structures provide X-ray diffraction patterns that are in agreement with experimental patterns. Our simulations of the doped $LiMn_2O_4$ materials indicates substantial stabilization of the spinel structure with either Ni^{+2} or Co^{+2} substitution for Mn^{+3} and accompanied by oxidation of some Mn^{+3} to Mn^{+4}. We observe about a 1.5% reduction in the unit cell parameters for the Ni^{+2} and Co^{+2} $LiMn_2O_4$ spinels for dopant concentrations up to 20%. Substitution of Ti^{+4} in $LiMn_2O_4$ provided a significantly destabilized spinel structure with an expanded unit cell. Calculated X-ray diffraction

patterns for these doped spinels provide a convenient method for identifying the new materials and the extent of doping associated with the laboratory synthesis work.

We have developed a solution method for preparing controlled stoichiometry lithium manganese oxide precursors. The process involves nonaqueous coprecipitation of a mixed lithium manganese oxalate. The oxalate coprecipitate is thermally decomposed at moderate temperatures ($\sim 600°$ C) to form the desired oxide phase. For example, very fine particle size, phase pure (as determined by X-ray diffraction) $LiMn_2O_4$ and $Li_2Mn_2O_4$ have been prepared using this process. Currently we are preparing a variety of transition metal doped powders by this technique and are in the initial stages of characterizing their electrical properties in laboratory test cells.

4. *Electric Vehicle Research and Development.* Sandia National Laboratories is participating in a CRADA with the U.S. Advanced Battery Consortium (USABC) to develop lithium ion battery technology for electric vehicles. The tasks include materials development for lithium polymer batteries. Sandia also provides technical support for tasks that range from modeling cells and cell components (e.g., electrode shape effects on cell performance), recycling and reclamation studies on rechargeable batteries and preparing a safety test plan. Finally, Sandia provides testing and performance evaluation for our research and development projects as well as for other USABC contractors. This testing is performed with complete confidentiality and is reported to USABC and its contractors.

Reporting on these activities is outside the scope of this paper but can be obtained from other sources. (3).

Conclusions

Lithium ion is an exciting new technology that promises to bring high energy, long life power sources, having a reduced environmental impact, to the consumer electronics industry. However, this emerging technology still requires improvement in several areas before its use becomes widespread. These areas include improving the capacity of the anode while reducing its passivation, and increasing the capacity, cycle life and rate capability of the cathode. Several programs are underway at Sandia National Laboratories that address these critical issues.

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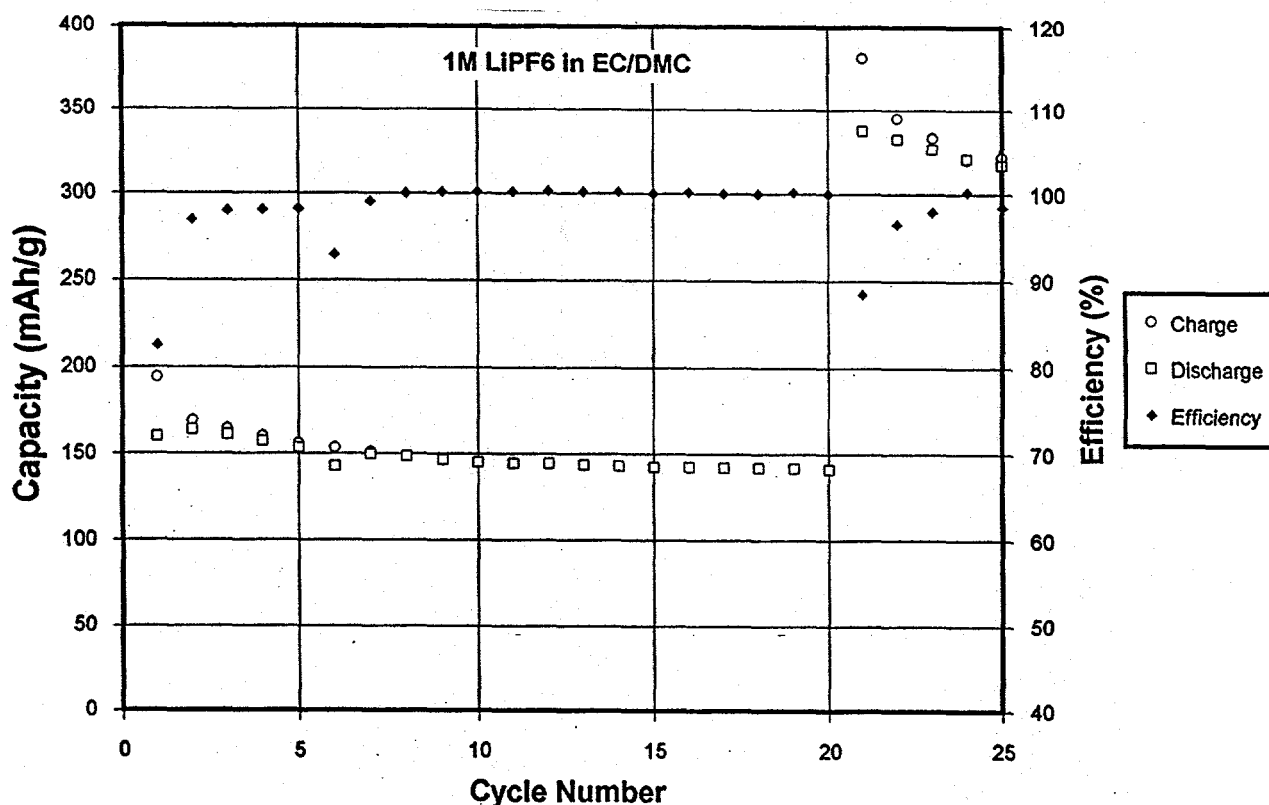
Figure 1. PAN carbon cloth test. Cycles 1-20 are potentiodynamic scans between 3.0 V and 10 mV at 1 mV/sec. Cycles 20-25 are galvanostatic at 0.64 mA with a potential hold at the end of each cycle until current density reaches 50 $\mu A/cm^2$.