SAND96-1145C
CONF-9606212--1

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY STUDIES OF LITHIUM DIFFUSION IN DOPED MANGANESE OXIDE.

B. J. Johnson, D. H. Doughty, J. A. Voigt, T. J. Boyle
*Sandia National Laboratories, P. O. Box 5800, Albuquerque, NM 87185-0614

Cathode performance is critical to overall lithium ion rechargeable battery performance and impacts some of the most important challenges in the development of commercial lithium ion rechargeable batteries, namely energy density, cycle life, and rate capability. We are investigating the influence of doping lithium manganese oxide cathode materials on the fundamental properties that control cathode performance.

The goal of our studies was to develop improved understanding of the chemical and physical properties that determine the performance of manganese oxide cathodes as well as to produce improved materials and preparation techniques for cathodes. We have developed an atomistic model of structures of various manganese oxide and lithium manganese oxide compounds.[1] 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.

To compliment our modeling effort, we have developed a non-aqueous co-precipitation process to prepare controlled stoichiometry lithium manganese oxalate precipitates which when calcined form high purity $Li_xMn_yO_z$ powders.[2] The process involves mixing a $LiNO_3$ and $Mn(NO_3)_2$ methanolic solution with dehydrated tetramethylammonium oxalate forming an off-white precipitate. A variety of transition metal dopants have been incorporated into this process. The resulting precipitated oxalates were readily converted to a number of phase pure lithium manganese oxides at moderate temperatures ($\leq 600°C$) with the phase formed being dependent on the initial Li/Mn ratio in the starting solution. Our results are in general agreement with recent publications by Bito,[3] and Tarascon.[4]

This communication continues the electrochemical characterization and demonstrates that lithium diffusion rates in manganese oxide can be controlled by the quantity of dopant. This result is attributed to the dopant effecting the lattice parameter of the lithium manganese oxide unit cell. Lithium diffusion in bulk $LiMn_2O_4$ is thought to occur through the one dimensional channels in the spinel structure. We took a representative dopant, aluminum, which decreases the lattice parameter on increasing levels of dopant, and studied the effect on electrode diffusion characteristics. The electrochemical testing has consisted of galvanostatic cycling from 3.5 V to 4.3 V with select impedance measurements at OCV, 4.05, 4.15 Volts. These voltages were chosen to probe the materials characteristics during multiple cycles, and during charge and discharge of the 4 volt plateau. We employed a standard three electrode configuration with lithium counter and reference electrodes. Cathodes were manufactured using 82% $LiMn_2O_4$, 10 % conductive carbon and 8% Teflon. The electrolyte was a 50:50 EC/DMC 1 M $LiPF_6$ solution. Electrochemical cycling was conducted at 0.5 mA/cm^2. Electrochemical impedance spectroscopy measurements were conducted at open circuit potential (OCV). Impedance measurements were taken at frequencies between 65 kHz to 0.01 Hz.

The electrochemical impedance spectroscopy (EIS) response for the Sandia designed aluminum-doped manganese oxide is shown in figure 1. The inset figure shows the OCV impedance response. This response was modeled by a simple resistor in series with a capacitor, simulating the solution resistance in series with the porous electrode response, i.e. double layer capacitance. As the electrode potential was increased to 4.05 V, the impedance response was controlled by a charge transfer region and a diffusion controlled region. The diffusion response was modeled by a simple Warburg-type response.

It was previously shown in our modeling studies that as the level of dopant atoms is increased in the manganese oxide material the lattice parameter of the unit cell is varied. Depending on the dopant atom, the lattice parameter, which is directly related to the size of the diffusion channels, can be either increased, as in the case of titanium doping, or decreased, as in the case of nickel, cobalt and aluminum.[1] We measured the EIS response for a series of aluminum dopant levels. By plotting the low frequency reactance or resistance versus $\omega^{-1/2}$, where ω is the applied frequency in radians, and plotting the slope of this line versus the dopant level, one obtains figure 2. This slope is inversely proportional to the lithium diffusion constant. Therefore, as the level of aluminum dopant was increased, a concurrent decrease in diffusion rate was observed. This effect on the diffusion rate was attributed to the decrease in the lattice parameter of the doped oxide.

With further variations on materials properties that are accessible with our synthesis technique we plan to quantify the diffusion rates and better correlate the effect on diffusion rate on varying the materials characteristics.

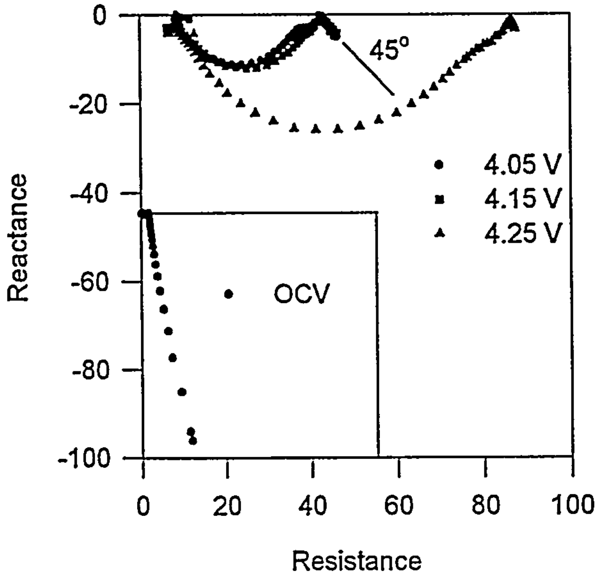

Figure 1. Impedance response of $Li_xAl_{0.125}Mn_{1.875}O_4$, (i.e.y = 0.125) at OCV, 4.05, 4.15, and 4.25 V v. Li^+/Li.

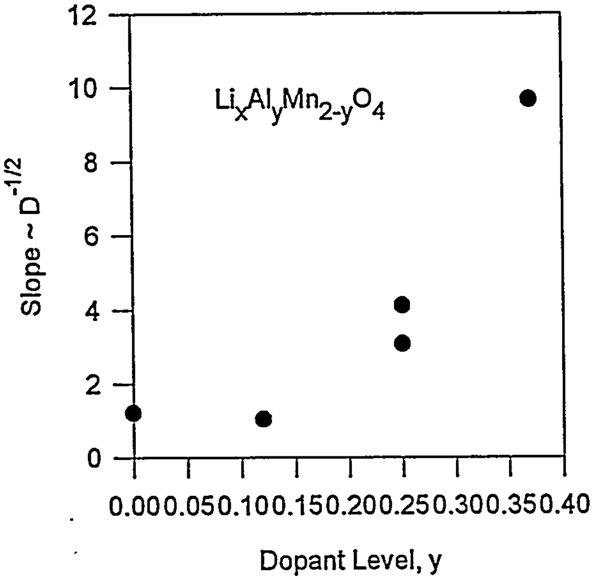

Figure 2. Resultant plot of the slope (of the reactance versus $\omega^{-1/2}$ plot) versus increasing levels of Al^{3+} dopant.

References:

1. R. T. Cygan, H. R. Westrich, and D. H. Doughty; *Mat. Res. Soc. Symp. Proc.*, **393**, 113 (1995).
2. J. A. Voigt, T. J. Boyle, D. H. Doughty, B. A. Hernandez, B. J. Johnson, S. C. Levy, C. J. Tafoya, and M. Rosay; *Mat. Res. Soc. Symp. Proc.*, **393**, 101 (1995).
3. Y. Bito, H. Murai, S. Ito, M. Hasegawa, and Y. Toyoguchi, *ECSProceedings*, **93-23**, 461 (1993).
4. J. M. Tarascon, E. Wang, F. K. Shokoohi, W.R. McKinnon and S. Colson, *J. Electrochem. Soc.*, **138**, 2859 (1991).

---

* This work was performed at Sandia National Laboratories, supported by the U.S. Department of Energy under Contract #DE-ACO4-94-AL85000.

DISCLAIMER