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MODELING, SYNTHESIS AND CHARACTERIZATION OF $LiMn_2O_4$ SPINELS.

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OBJECTIVE

We will report on an integrated program to understand the fundamentals of $LiMn_2O_4$ performance as a cathode for lithium ion rechargeable batteries. Specifically, our program is designed to address the effects of doping on the crystal chemistry, lattice constants, and electrochemical performance. Our work is being expanded to include studies on $LiCoO_2$ and $LiNiO_2$.

APPROACH

In order to evaluate potentially new cathode materials based on the $LiMn_2O_4$ spinel structure, we have used an atomistic theoretical approach. The atomic simulations employ an energy optimization of the crystal structure based on the summation of Coulombic, short-range repulsive, and van der Waals interactions. A minimum energy structure is obtained under the constraint of P1 symmetry and constant pressure conditions, thereby allowing all 56 atoms of the spinel unit cell and the cell parameters to relax while maintaining an isometric crystal. A shell model that accounts for electronic polarization is used to refine the model. Pure $LiMn_2O_4$ and various doped spinels were examined in this study in order to determine the lattice energy, unit cell volume, and the relative stability of the doped structures. The theoretical model provides results as a function of the ionic radii of the substituted metal ion and dopant amount. The cations included as dopants in this initial evaluation include Ti^{4+}, Nb^{5+}, Al^{3+}, Co^{2+}, Ni^{2+}, B^{3+}, Cr^{3+}, Sc^{3+}, Y^{3+}.

ACCOMPLISHMENTS

It is generally well recognized that battery performance is intimately linked to lattice expansion and contraction upon lithiation and delithiation of the spinel. It was found that Ti^{4+} and Nb^{5+} doped spinels exhibit significant unit cell expansion (and energy destabilization), typically on the order of about 1%. Whereas Al^{3+} and Co^{2+} doped compounds exhibit only slight unit cell contraction of 0.4%. The model predicts limited and similar unit cell changes with lithium content for Al^{3+} and Co^{2+} compared to the undoped material. Calculations also indicate that the spinel structures are stable for 10% excess Li (i.e. $Li_{1.1}Mn_2O_4$) for both the undoped or Al^{3+} doped material.

Molecular dynamics simulations are also used to compare the relative diffusion rates of lithium ion in these various structures. The mechanism of lithium ion diffusion along the (110) pathways

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involving tetrahedral vacancies has been examined. Absolute diffusion rates at relatively high temperatures indicate less than an order of magnitude difference between 12 % Li (i.e. $Li_{0.12}Mn_2O_4$) and 88 % Li (i.e. $Li_{0.88}Mn_2O_4$) spinel compositions based on the number of vacancies. Activation energies for lithium ion diffusion are similar at approximately 95 kJ/mole.

Comparisons between actual and predicted behavior are necessary in order to validate the model performance. Toward this end we have developed an innovative process (U.S. Patent # 5,630,994) to prepare doped $LiMn_2O_4$ which uses a non-aqueous solution processing technique. This process allows us to prepare uniformly doped precursors that can be sintered at low temperature (600 to 800°C) to produce phase pure target compositions. Additionally, we have developed an electrochemical cell for *in-situ* X-ray diffraction that allows for fast, accurate, and precise characterization of the lattice parameters of the spinel.

The cell is designed to reduce attenuation of the diffracted beam by the current collector and deliver a more reliable diffraction spectrum. The oxide is pressed into the grid in such a way so that the electrode and metal are at the same height on the sample stage. This is done so that in the event the sample moves out of the plane of focus of the X-ray source, such as might happen when the electrode expands and contracts on charge and discharge, any shift in the diffraction pattern can be correctly attributed to a change in the lattice parameter rather than to this physical displacement of the sample.

In addition, the cell housing is highly transparent to the X-ray and has a relatively high background in only one area of the range. Consequently, an X-ray pattern can be collected over a 2Ω range of over 80° in as little as 10 minutes. Over a smaller 2Ω range, significantly shorter acquisition times are required. These considerations allow for real time characterization of the lattice parameters as the cell is cycled. Finally, the cell design allows for use of electrodes similar in composition to those found in commercial cells. This ensures characterization of materials in a form expected to be encountered in the intended application. We have completed initial evaluation of this cell using the undoped spinel at varying states of charge.

FUTURE DIRECTIONS

We are extending this approach to other cathode materials, notably LiCoO2, since this is the cathode material of choice in most commercial cells. We have performed an initial characterization of the $LiCoO_2$ system. In the case of the undoped spinel a lattice parameter expansion and contraction on the order of approximately 8% is observed, while in the case of the cobalt oxide a phase transition can be monitored as the oxide is charged to levels in excess of approximately 0.5 mole percent.

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