

## CRYSTAL CHEMICAL MODELING OF THE LI ION DISTRIBUTION IN $\text{Li}_x\text{Mn}_2\text{O}_4$

C. Lane Rohrer  
Alcoa Technical Center  
Aluminum Company of America, Alcoa Center, PA 15069

Gregory S. Rohrer  
Department of Materials Science and Engineering  
Carnegie Mellon University, Pittsburgh, PA 15213

### ABSTRACT

The Monte Carlo bond valence method was used to model the local atomic structure of  $\text{Li}_x\text{Mn}_2\text{O}_4$  ( $x = 0.25$  and  $x = 1.0$ ). The results predict that  $\text{Mn}^{+3}$  and  $\text{Mn}^{+4}$  are randomly distributed at the octahedral positions and that the  $\text{Mn}^{+3}\text{-O}$  bond distance is 2.02 Å while the  $\text{Mn}^{+4}\text{-O}$  distance is 1.91 Å. As the Li content decreases, the cell contracts due to the higher concentration of shorter bonds. Based on maps that show the distribution of crystal chemically equivalent sites, we conclude that the Li ion diffusion paths go through 48f sites, that Li might be more mobile for the case of  $x = 1.0$  than for  $x = 0.25$  (due to the expanded cell volume), and that for  $x > 1$ , the 16c position is the most likely Li site.

### INTRODUCTION

The cathode materials used in most secondary Li-ion battery designs are transition metal compounds that can reversibly vary their Li content as the battery charges and discharges. Transition metal oxides that are currently in use or being considered for use as cathodes in commercial cells include:  $\text{Li}_x\text{Mn}_2\text{O}_4$  ( $0.25 \leq x \leq 1.0$ ) [1],  $\text{Li}_x\text{NiO}_2$  ( $0.3 \leq x \leq 0.75$ ) [2], and  $\text{Li}_x\text{CoO}_2$  ( $0.55 \leq x \leq 0.93$ ) [3]. Determining the atomistic details of the crystal structures of these compounds is

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complicated by several issues. First, as nonstoichiometric materials, they exhibit both occupation disorder on the Li sites and valence disorder on the transition metal sites. Changes in the distribution of metal atom valences and Li occupations locally distort the bond distances and the detailed arrangement of the O sublattice. If the distortions do not have long range order, conventional scattering experiments offer little insight. Furthermore, since the X-ray scattering power of Li is very small, locating the positions of the Li ions by X-ray diffraction is, at best, challenging.

In this paper, we describe the local atomic structure of  $\text{Li}_x\text{Mn}_2\text{O}_4$  that is predicted by a crystal chemical model. The model, which we call the Monte Carlo Bond Valence (MCBV) method, is a computational procedure for finding the atomic configurations of partially disordered systems which most nearly satisfy a set of quantitative crystal chemical rules established by the work of Pauling [4], Brown [5], and O'Keeffe [6]. The computational strategy and implementation of our algorithm has been described in an earlier paper [7]. In this paper, we present the results of calculations that specify the local bond lengths in the  $\text{Li}_x\text{Mn}_2\text{O}_4$  system, the extent to which the Li occupancies and Mn valences are ordered, the Li ion diffusion paths, and how these paths are affected by changes in Li stoichiometry.

#### DETAILS OF THE CALCULATIONS

$\text{Li}_x\text{Mn}_2\text{O}_4$  crystallizes in the spinel structure when  $0.25 \leq x \leq 1.0$ . Using the Wykoff notation for space group  $\text{Fd}\bar{3}\text{m}$  (no. 227, origin choice 1), O occupies the 32e sites completely, Mn(III) and Mn(IV) occupy the octahedral 16d sites, and Li is thought to be distributed on the 8a tetrahedral sites [8]. Two compositions were simulated:  $\text{Li}_{0.25}(\text{Mn}^{+3}_{0.25}\text{Mn}^{+4}_{1.75})\text{O}_4$  and  $\text{Li}_{1.0}(\text{Mn}^{+3}_1\text{Mn}^{+4}_1)\text{O}_4$ . In both cases, the atoms were initially placed in the ideal spinel positions with the two Mn valences distributed randomly over the 16d sites and the Li ions distributed randomly (for the substoichiometric case) over the 8a sites.

The MCBV simulations included 5x5x5 unit cells (3584 and 3200 atoms for the stoichiometric and substoichiometric cases, respectively) with periodic boundary conditions. Scaling factors in the code [7] were adjusted so that simulation results for the better characterized  $\text{MgAl}_2\text{O}_4$  reproduced accepted structural parameters. One MCBV cycle comprised a sequential random shift in the position of each atom within a 1 Å radius, together with an attempted atom species exchange with another atom (or vacancy) in the same sublattice (i.e. a  $\text{Mn}^{+3}$  could exchange with a  $\text{Mn}^{+4}$  or a Li could exchange with a vacancy in the 8a sublattice). The cycle was concluded with an attempted change in the system volume. Each attempted change in atom position or volume was accepted or rejected based upon whether the change improved the overall fit to the guiding crystal chemical rules described in [7]. Each composition was run for over 30000 MCBV cycles. The effective "temperature" was decreased at 10000 cycles in an attempt to "anneal in" the most favorable structure. All properties discussed in the following section were averaged over the final 15000 cycles, during which both systems were in equilibrated states.

## RESULTS AND DISCUSSION

The average lattice parameters for the stoichiometric case were insignificantly anisotropic with values of 8.25 Å, 8.26 Å, and 8.28 Å for a, b, and c, respectively, in reasonable agreement with the experimental isotropic value of 8.239 Å [8]. Decreasing the Li content from  $x=1$  to  $x=0.25$  resulted in a decrease in the lattice parameters to 8.11 Å, 8.12 Å, and 8.12 Å. This result differs from experimentally determined values (8.045 Å for  $x=0.27$ ) by less than 1% [8].

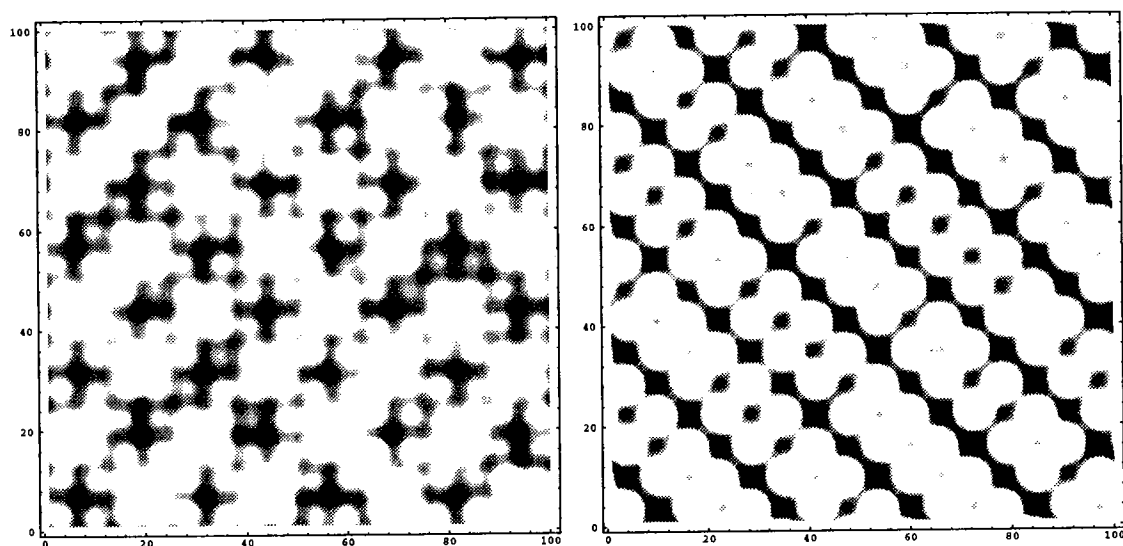
Average cation-oxygen bond lengths were nearly the same for both compositions. The Li-O average bond length was 1.99 Å. The calculated  $\text{Mn}^{+4}$ -O average bond length (1.91 Å) was shorter than the  $\text{Mn}^{+3}$ -O bond length (2.02 Å), in agreement with the expected stronger bond between the higher valence cation and the oxygen ion. The higher proportion of shorter  $\text{Mn}^{+4}$ -O bonds in

the Li depleted system accounts for the decrease in lattice parameter noted above.

By examining partial radial distribution functions, we explored the possibility that the  $Mn^{+3}$  and  $Mn^{+4}$  site occupancies might be ordered and that the Mn ordering would influence the distribution of occupied Li positions in the substoichiometric crystal. However, neither long range nor short range ordering was observed in either simulation. Because this result seems counterintuitive, some additional consideration is appropriate. First, the complete absence of order can not be attributed to a weakness of the model; its ability to reproduce short range order effects (strong solute-vacancy correlations) in supersaturated Mg(Al)O solutions has already been demonstrated [7]. It is possible, however, that the selection of scaling parameters affected the outcome. Also, observations of longer range structural ordering in atomistic simulations are strongly dependent on the chosen periodic repeat unit. Unless the repeat unit reproduces the symmetry of the expected ordering behavior, the long range ordering will be frustrated by the restrictions of the periodic boundary conditions [9]. It is possible that the 5x5x5 unit cell repeat unit was an inappropriate choice for the observation of long range ordering amongst the cations.

The most interesting results arising from the present model concern the placement of the Li cations. While the average Li positions were found to be at the 8a sites, it is possible to map the spatial distribution of crystal chemically equivalent sites by removing all of the cations from the averaged structure and then progressing a single Li cation across specified planes normal to the z direction. The goodness of crystal chemical fit for Li (calculated bond valence at a given site close to the formal valence of +1) was found to be spatially extended into 48f sites. The paths of good bond valence fit for the stoichiometric system are shown in Fig. 1a for the  $z = .25$  lattice units plane. The dark centers of the crosses are the occupied 8a sites, while the more numerous ends of the crosses are the 48f sites. Because the dark areas represent a continuum of positions that Li can occupy without significantly changing its crystal chemical environment,

they were interpreted as demarcating the likely diffusion paths. Of particular interest was that a simple calculation of the area in the plane where the bond valence was within  $\pm 0.5$  of the correct valence indicated a higher average percent "good" area for the stoichiometric case ( $\sim 11.5\%$ ) than for the Li depleted case ( $\sim 8.0\%$ ). This seems to imply greater Li mobility in the stoichiometric system, a prediction which seems counterintuitive but is probably an effect of the decreasing cell volume (and interstitial volume) that accompanies the Li depletion. It is also important to remember that the changing fraction of vacant sites will have the opposite effect on the diffusivity. Experimental ionic conductivity measurements as a function of Li content will be necessary to verify or contradict this prediction.



**Figure 1** (a) Contour map indicating goodness of bond valence fit for Li in the  $z=0.25$  lattice units plane in the stoichiometric system. The gray scale ranges from black (perfect bond valence fit of +1) to white (calculated bond valence different from perfect by greater than 1). (b) Same as (a), but for  $z=0.375$  lattice units.

To determine which sites excess Li might occupy, a Li ion was also progressed across a Mn-O plane at  $z=0.375$  lattice units (see Fig. 1b). The white circular sites

arranged in clover patterns are occupied by oxygen. The pale gray centers of these clovers are the Mn sites. The dark rows of octahedral sites separating the rows of clovers indicate a very good bond valence fit for Li cations in these planes. It is suggested that these 16c sites may serve to accommodate excess Li. Note that the random appearance of darker Mn sites corresponds with Li diffusion paths in planes above and below the plane shown.

## CONCLUSIONS

The Monte Carlo Bond Valence method was used to predict the relaxed bond lengths in  $\text{Li}_x\text{Mn}_2\text{O}_4$  as a function of Li content. Li was observed to occupy 8a sites for  $x = 1$  and  $x = .25$  and 16c sites are predicted to accommodate excess Li for  $x > 1$ . Li diffuses through paths between 8a and 48f sites. The simulation results implied that Li should be more mobile in the stoichiometric case, possibly due to the greater lattice volume, but this prediction needs experimental verification. Such experimentation could also explore the possibility of increasing the Li diffusivity by the addition of dopants which increase the lattice parameter.

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