## The effect of mixed Mn valences on Li migration in LiMn<sub>2</sub>O<sub>4</sub> spinel: A molecular dynamics study

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Previous molecular dynamics (MD) simulations have shown that, with good choice of potential shapes and parameters, the structure and properties of stoichiometric  $LiMn_2O_4$  can be reproduced to good accuracy. In particular, the experimentally observed self-diffusion of Li ions was shown to occur only for a discrete, mixed Mn valence model. Here, those MD studies have been extended, demonstrating that periodically switching the Mn valence states, reflecting an electron hopping model, greatly facilitates the Li ion self-diffusion. The interaction is mediated by the O atoms, which coordinate both cations and temporarily adopt local distortions based on the three coordinating Mn valences. Although the O atoms continue to vibrate harmonically about a displaced mean, permitting the Li atoms to migrate, the time and spatial average remains that of the ideal spinel with distributed Li. © 2004 American Institute of Physics. [DOI: 10.1063/1.1644320]

Lithium manganese spinels are attractive candidates for cathode materials of rechargeable lithium ion batteries and have the advantage of low cost and low toxicity over cobaltor nickel-containing oxides. LiMn<sub>2</sub>O<sub>4</sub> presents a first-order structural phase transition at 290 K,<sup>1-5</sup> adopting a hightemperature (HT) ideal spinel phase (cubic a=8.2468 Å,  $Fd\bar{3}m)^6$  above the transition and a low-temperature (LT) orthorhombic phase  $(3a \times 3a \times a; Fddd)^7$  below. This material is believed to be a mixed valence compound comprised of distinct Mn<sup>III</sup> and Mn<sup>IV</sup> ions,<sup>5,8</sup> and the phase transition is considered to arise from partial charge ordering of the Mn ions.<sup>7</sup> In the HT phase, a single site of Wychoff 16d symmetry is populated by Mn in the ratio Mn<sup>III</sup>:Mn<sup>IV</sup>=1:1, whereas there are five independent Mn sites in the LT phase, two having Mn<sup>IV</sup> character with three other Mn<sup>III</sup>-like sites. Li ion dynamics in the HT and LT phases are also different. Self-diffusion of Li ions is only observed in the HT phase, where Li ions diffuse along 8a-16c-8a diffusion pathways, changing from tetrahedral to octahedral O atom coordinations.<sup>9</sup> Molecular dynamics (MD) simulations have also suggested that Li and O atoms adopt harmonic distributions about mean positions displaced from the HT phase ideal, and that the local structural disorder is strongly dependent on the local distribution of  $Mn^{III}/Mn^{IV}$  at 16d sites.<sup>10</sup> In this work, additional MD simulations were performed to examine the correlations between local structural disorder and Li ion migration in stoichiometric  $LiMn_2O_4$ .

MD simulations were carried out using the MXDORTO program developed by Kawamura.<sup>11</sup> A Gilbert-Ida-type pair potential function<sup>12</sup> was used:

$$U(r_{ij}) = Z_i Z_j e^{2/r_{ij}} + f_0(b_i + b_j) \\ \times \exp[(a_i + a_j - r_{ij})/(b_i + b_j)],$$
(1)

where  $Z_i$  is the effective charge, e is the elementary electric charge,  $r_{ij}$  is the interatomic distance,  $f_0$  is a constant (4.1868 kJ mol<sup>-1</sup> Å<sup>-1</sup>), and  $a_i$  and  $b_i$  represent the size and stiffness parameters, respectively. The potential parameters derived by Suzuki et al.<sup>13</sup> were also used in this study. Those parameters reproduce the unit cell parameters, mean atomic coordinates, and other experimental observations very well.<sup>10,13</sup>

In the current simulations, three distinct models were assumed: (I) A model in which the arrangement of Mn valences were invariant; (II) a model in which the arrangement of Mn valences were changed with time, preserving overall charge neutrality; and (III) a model in which Mn valences were charge-ordered in the same manner as in the LT phase.

Models I and II contained 512 Li, 512 Mn<sup>III</sup>, 512 Mn<sup>IV</sup>, and 2048 O atoms in a pseudocubic MD cell of dimension 33.004 Å, being four times larger than the ideal  $LiMn_2O_4$ spinel lattice parameter. The  $Z_i$  values were assumed to be 1.0 for Li<sup>I</sup>, 1.4 for Mn<sup>III</sup>, 2.4 for Mn<sup>IV</sup>, and -1.2 for O<sup>II</sup>.<sup>13</sup> The Mn<sup>III</sup> and Mn<sup>IV</sup> atoms were randomly assigned to the  $Fd\overline{3}m$  16d sites as initial configurations. Periodic boundary conditions were applied in all directions. Atomic motions and Coulomb interactions were calculated using the Verlet algorithm<sup>14</sup> and Ewald method,<sup>15</sup> respectively. A temperature of 300 K was simulated by controlling the atomic velocities and lattice parameters of an NTP ensemble calculated at 2 fs intervals for 320 ps. The model II simulation was identical, except that, after stabilizing for 100 ps, the Mn charges were then randomly redistributed at 40 ps intervals, preserving overall charge neutrality. Model III contained 216 Li, 240 Mn<sup>III</sup>-like, 192 Mn<sup>IV</sup>, and 864 O atoms in a rectangular MD cell of dimensions 24.7435×24.8402×24.5967 Å<sup>3</sup> corresponding to  $1 \times 1 \times 3$  units of the LT phase *Fddd* cell. The effective charges of Mn<sup>III</sup>-like atoms were modified from +1.4 (Mn<sup>III</sup>) to +1.5 to maintain charge neutrality.

The distribution of Li atoms along the 8a-16c-8a dif-

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FIG. 1. Two-dimensional frequency distribution map of all Li atoms obtained from the model I MD simulation with an inset of residual electron density distribution (see Ref. 16) in the  $(\overline{1}10)$  plane obtained from synchrotron x-ray powder diffraction.

fusion pathway for model I is shown in Fig. 1. It represents the superposition of all Li atom positions after applying appropriate rotational and translational operations to bring the HT phase equivalent sites into coincidence. The experimentally observed charge or difference electron density distribution, as revealed by powder x-ray diffraction and the independent atom model with all Li contributions omitted, is also inset for comparison.<sup>16</sup> The two important features of the residual electron density distribution along the diffusion pathway are peaks around 1.40 Å away from 8a (denoted A in Fig. 1) and the aspherical distribution around 8a extending lobes towards 16c (denoted B). The model I simulation was previously analyzed elsewhere.<sup>10</sup> The results showed that the Li-omitted independent atom model difference electron density distribution at B could be interpreted as a superposition of harmonically vibrating Li atoms displaced by around 0.16 Å from their ideal 8a sites, while the density accumulating at A, 1.40 Å away from 8a site, reflected a diffuse distribution of Li atoms located outside their ideal tetrahedral bonding environment. This information is also contained in the radial frequency distribution of all Li atoms as a function of distance r from initial positions (8a) shown in Fig. 2.

Figure 3 shows the mean square displacements (MSDs) of Li atoms as a function of time in three models. According



FIG. 3. MSD of Li atoms.

to the random walk theory,<sup>17</sup> the MSDs of diffusing atoms should increase linearly with time. The Li MSD in model I becomes constant within about 30 ps as structural relaxation is attained. This suggests that Li atoms barely diffuse at 300 K in model I. On the other hand, the Li MSD in model II increases with every Mn valence reshuffle, indicating substantial Li self-diffusion can occur at 300 K. Figure 2 shows that the radial distribution of Li atom displacements in model II extends much further than in model I, with some Li displaced by up to 6.0 Å from their initial positions, covering the second-nearest-neighbor 16c octahedral interstices. This is more clearly seen by comparing the two-dimensional distributions in Figs. 1 and 4. In model III, the Li MSD shown in Fig. 3 is even smaller than for model I, suggesting that almost no Li diffusion occurs in the LT phase. This agrees well with experiment.9

In these simulations, Li diffusion occurred purely as a consequence of the lattice dynamics. It arose only when the spinel lattice was undergoing significant local distortion, such as during the initial 30 ps of structural relaxation, or following every reshuffle of the Mn<sup>III</sup>/Mn<sup>IV</sup> valences in model II. This correlation supports a model in which Li migration is induced via a mechanism involving  $Mn e_{g}$  electron hopping and is mediated by resultant distortion modes of the mutually coordinating O atoms. It is also consistent with observations of electrical transport properties in LiMn<sub>2</sub>O<sub>4</sub> that are dominated by nonadiabatic small polaron hopping.<sup>18</sup>

Distortions of the LiO<sub>4</sub> tetrahedral faces that form bottlenecks along the 8a-16c-8a diffusion pathway can be char-



FIG. 2. Frequency distributions of the radial displacement of all Li atoms as a function of distance r from initial positions. Downloaded 30 Jan 2004 to 133.68.126.131. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp



FIG. 4. Two-dimensional frequency distribution of all lithium obtained from the model II MD simulation.



FIG. 5. A cage of twelve Mn atoms around the 8a tetrahedral site with six coplanar Mn atoms coordinating the 16c octahedral vacancies.

acterized by the radius of a circle circumscribed through the vertices of each face and centered at their midpoint. There are three relevant configurations. Faces of tetrahedra occupied by Li adopt a mean circumscribed radius of 1.903(2) Å. Immediately prior to Li migration, the three faces through which the Li does not pass adopt a mean radius of 1.895(7) Å, whereas the face through which Li does pass takes a mean radius of 1.987(14) Å. The latter is slightly larger than the sum (1.97 Å) of conventional ionic radii<sup>19</sup> (O<sup>II</sup>: 1.38 Å,Li<sup>I</sup>: 0.59 Å), while the adjacent and average face dimensions are clearly smaller.

The MD simulation provides additional statistics about the 16*c* octahedral vacancy sites. Prior to Li migration the 16*c* sites are coordinated by a second shell of 6 Mn atoms at 2.92 Å, with an average oxidation state of +3.5 (3 Mn<sup>III</sup> +3 Mn<sup>IV</sup>), as shown in Fig. 5. In instances in which Li migrated into these sites, the mean Mn oxidation state had reduced to +3.3, reflecting a second shell comprised of 4 Mn<sup>III</sup> and 2 Mn<sup>IV</sup> atoms. For the 8*a* tetrahedral sites occupied by Li, the first shell of four O atoms is surrounded by a second shell of twelve O atoms at 3.45 Å, four Li atoms at 3.57 Å, and twelve Mn atoms at 3.42 Å. The mean valence of Mn in the second shell of 8*a* site scarcely changed from 3.5 before and after the Li diffusion into the adjacent 16*c* site.

The MD simulations reported here suggest a consistent picture of the Li diffusion mechanism observed in real LiMn<sub>2</sub>O<sub>4</sub>. Under the influence of an applied electrochemical potential, the hopping of Mn atom  $e_g$  electrons could serve to lower the Coulomb repulsive potential at the 16*c* sites, while causing less pronounced effects at the 8*a* sites. The mutually coordinated O atoms are transiently displaced, opening the tetrahedral face bottlenecks beyond the critical radius and permitting Li to pass. The converse should also occur in order for Li to migrate forwards into subsequent 8*a* sites. We therefore feel confident in stating that Mn atom  $e_g$  orbital electron hopping is the trigger of the Li atom diffusion mechanism but it is dependent on the transient distribution of the Mn<sup>III</sup> and Mn<sup>IV</sup> species and mediated by accompanying O atom displacements.

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