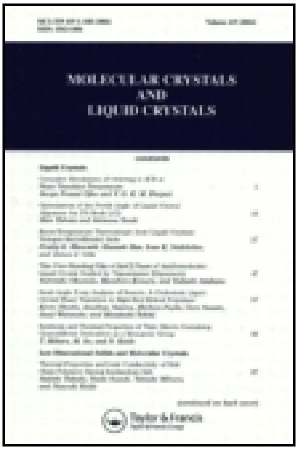

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Computer Modelling of Lithium and Proton Intercalation in Spinel Lithium Manganates: Effect of Octahedral Vacancies

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The effect of octahedral Mn vacancies on lithium and proton intercalation in the spinel structure of lithium manganate is investigated by means of atomistic simulation techniques. Prefered insertion sites and migration pathways for Li ions in the interstitial space of the lattice are calculated. The computations indicate an energetic preference for both Li ions and protons to cluster around the octahedral defects to compensate the local charge.

Keywords: lithium manganate; spinel; lithium insertion; proton insertion; computer modelling

INTRODUCTION

Insertion reactions of lithium ions or protons in spinel-structured lithium manganates are of fundamental importance to the applications of these materials in advanced batteries and as selective lithium sorbents[1-13]. In recent work we have used atomistic simulation methods to model lithium extraction-insertion and migration in spinel manganates[14]. A key feature of the technique is the treatment of lattice relaxation around interstitial ions and vacancies introduced into the crystal by intercalation reactions, through explicit calculations of the long-range and short-range interactions among the surrounding ions of the lattice. In this way local perturbations are effectively modelled and the crystal is not considered simply a rigid lattice through which ion species diffuse. The energies associated with inserting lithium ions into different lattice sites can then be calculated and compared, and the key energetic and structural contributions which drive and modify the intercalation reactions can be identified.

In the work presented here, we have used this methodology to investigate intercalation processes in spinels of composition $Li_{1+x}Mn_{2-x}O_4$ ($0\leq x<0.33$). The replacement of x Mn with Li has two important effects on the properties of the materials. Firstly, an increase in the tetravalent Mn content of the compounds occurs with increasing x, lowering the amount of Li that can be extracted from the lattice by oxidation[4,10,12], but in acid solution the Li is readily removed by exchange with protons to give protonated Mn(IV) oxide spinels[10-13]. Secondly, the x Li is generally considered to replace Mn in octahedral sites of the spinel structure (16d in Fd3m)[5]. This introduces local structural and electronic changes in the lattice which modify the lithium intercalation behaviour[7]. Our objectives were therefore to specifically probe at the atomic level the effects of Mn deficiency in 16d sites on both Li ions and protons inserted into the interstitial space of the host structure.

ATOMISTIC SIMULATION METHODS

Calculations were performed using lattice energy minimisation techniques (embodied in the codes GULP[15] and CASCADE[16]) which are described in detail elsewhere[17]. The basis of the simulations is the specification of a potential model, which describes the energy of the system as a function of the atomic coordinates and allows the evaluation of the lattice energy. The interatomic interactions within the lattice are described by ionic two-body potentials which include both long-range Coulombic interactions and short-range modifications due to electron charge cloud overlap-repulsions and van der Waals forces. Ionic polarisability is incorporated by the shell model in which each ion is treated in terms of a core (representing the nucleus and core electrons) connected via a harmonic spring to a shell (representing the valence electrons). The potential parameters for each ion-ion interaction and shell model parameters used in this study are described in our previous work[14].

The calculations of energies associated with interstitial species and lattice vacancies are based on Mott-Littleton methodology[18]. The crystal lattice is divided into two concentric regions, so that ions in a spherical inner region (1) surrounding the defect are treated explicitly, while the ions in the remainder of the crystal are relaxed by quasi-continuum methods. Hydroxyl groups were modelled with the O-H interaction described by an attractive

Morse potential[19], in an approach recently applied to investigate protons in perovskite-type oxides[20].

RESULTS AND DISCUSSION

Lithium Insertion Sites and Migration

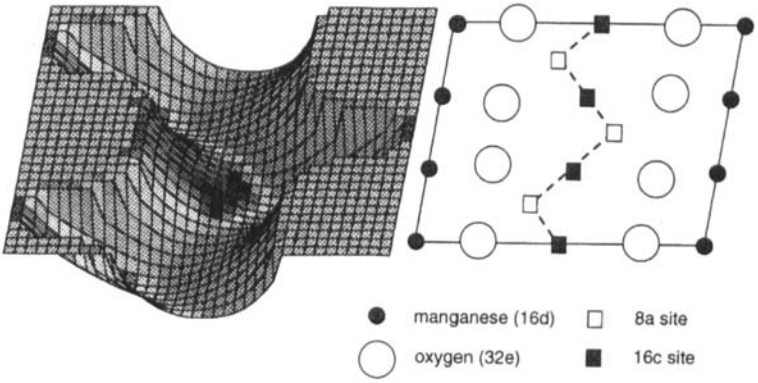

FIGURE 1 Energy surface for an isolated Li ion in the [110] plane of delithiated spinel manganese oxide.

We consider first Li in a model spinel manganate in which the 16d octahedral sites of the Mn-O framework structure are fully occupied by Mn. Figure 1 shows the energy surface calculated for an isolated Li ion migrating in the [110] plane. In this case Li ions are restricted to the channels between the chains of edge-sharing [MnO_6] octahedra. In the interstitial space the 8a tetrahedral sites appear as energy minima for insertion of the Li ion at this site. This agrees with experimental results which show that Li ions initially return to 8a sites when reintercalated in λ-MnO_2 derived from stoichiometric $LiMn_2O_4$[2]. The lowest energy pathway for a Li ion to hop between two 8a sites is through an intermediate 16c interstice where the energy barrier is 1.1 eV. This value represents a relatively high activation energy for lithium migration, but the energy becomes lower as more Li is intercalated[14]. It is worth noting that in the energy profile for Li in the delithiated manganate the 16c interstice appears as a saddle point, and not as a local minimum. However, as continued intercalation introduces increased quantities of lithium into the the interstitial space, the energy surface will be modified by Li-Li interactions and changes in the oxidation state of the Mn-O host[14]. 16c interstices will then become more favourable for Li as 8a sites are filled[3].

For $x>0$, the $Li_{1+x}Mn_{2-x}O_4$ compound may be modelled as a "defect" manganese dioxide in which x Mn^{4+} octahedral sites are vacant. Charge compensation is achieved by the distribution of four Li^+ ions in and around the vacancy, in octahedral and tetrahedral interstices. Neutron diffraction studies have indicated that the 16d sites are occupied by the excess lithium[5], although at least one report has suggested that lithium associated with the 16d defect may be disordered with some lithium appearing in 16c sites[21]. Our calculations suggest that, for $0 \leq x \leq 0.33$, 8a and 16d sites are more likely to be occupied by Li ions in preference to 16c interstices. The overall Mn oxidation state of the lithium manganate increases with x according to the formula $Li_{1+x}Mn^{3+}_{1-3x}Mn^{4+}_{1+2x}O_4$, so that each 16d site unoccupied by Mn results in four Li ions which cannot be deintercalated by oxidation. We have calculated vacancy energies for a model $Li_{1+x}Mn_{2-x}O_4$ lattice and found that Li in 8a sites neighbouring a 16d Mn vacancy require *ca.* 0.3 eV greater energy to be removed than a 8a Li ion isolated from the 16d defect. This suggests that Li remaining in the lattice after complete oxidation to Mn^{4+} will be localised around the defect. The result agrees with a model in which 8a Li surrounding a 16d vacancy are partially "pinned"[7].

Calculations on four residual Li ions in the defect spinel system confirmed that there is also an energetic preference for remaining Li to be localised around the 16d vacancy after a deintercalation step. However, in this case we found no significant difference between two configurations: (i) one Li in the 16d vacancy and the other Li ions at neighbouring 8a tetrahedral sites, and (ii) all four Li ions at 8a sites.

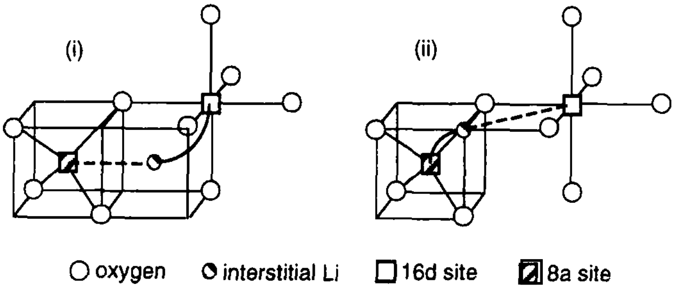

FIGURE 2 Li migration paths between 8a and 16d sites.

Activation energies were calculated for two possible Li migration pathways between 16d and 8a sites in $Li_{1+x}Mn_{2-x}O_4$. The saddlepoints are schematically represented in Figure 2. In case (i) the Li ion migrates through a 48f tetrahedral site which face-shares with the 16d octahedron and edge-shares with the 8a tetrahedron. The calculated activation energy when all neighbouring 8a sites were unoccupied was 1.24 eV. In case (ii) the saddlepoint is a 16c octahedral interstice face-sharing with the 8a tetrahedron and edge-sharing with the 16d octahedron. The activation energy in this case is 1.12 eV, indicating a small energetic preference for this pathway. However, introducing Li ions into neighbouring 8a sites increased the activation energies to 1.84 and 2.35 eV for the 48f and 16c interstitial paths respectively. This suggests that Li migration between 8a and 16d sites will become increasingly less favourable as Li is intercalated into the lattice, and that the prefered path will become that by the 48f interstice.

Proton Insertion

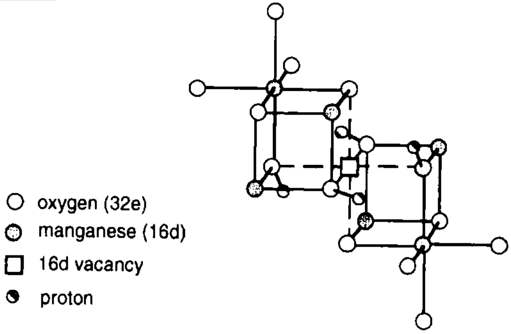

FIGURE 3 Configuration for four hydroxyls at an octahedral vacancy.

Although the four Li associated with 16d defects cannot be deintercalated by oxidation of the host matrix, these Li ions readily exchange with protons in acid solution. Vibrational spectroscopy indicates that the inserted protons form hydroxyl groups by bonding to lattice oxygen ions[11,13]. Our computations indicate that the most energetically stable configuration for hydroxyl ions in the lattice is that in which each 16d defect is coordinated by four hydroxyls distributed symmetrically around the vacant octahedron, as illustrated in Figure 3. In the fully relaxed (energy-minimised) configuration calculated, each hydroxyl proton is orientated into the interstitial channels of the spinel defined by the 8a and 16c sites. The result is in good agreement with the proton site determined from recently obtained neutron data[22].

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