A theoretical study of lithium ion interaction with tin oxide

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Abstract

Semiempirical MNDO calculations were used to calculate the interaction between Li+ and (SnO₂)₁₅ clusters. Our calculations predicted that Li+ adsorbs preferentially on mono-coordinate oxygen (A-type sites). The higher energy barrier to intercalation (~ 7.41 eV) suggests that the ion remains adsorbed at the oxide surface, but that the presence of oxygen vacancies probably decreases this barrier, favouring the Li+ intercalation. © 1997 Elsevier Science B.V.

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1. Introduction

Due to their technological importance, an increasing amount of work has been done on SnO₂ films. Extensive reviews by Jarzembki and Marton [1–3] describe the synthesis, structure, and optical and electrical properties of tin oxide. SnO₂ films have been used as resistors, transparent electrodes, sensors, and more recently as counter-electrodes for a transmissive electrochromic device [4,5]. For the latter purpose the SnO₂ films were deposited by the dip-coating technique onto tin oxide-coated glass. The electrochemical response of these electrodes in acetonitrile solutions containing 0.1 M LiClO₄ as the supporting electrolyte exhibits a cathodic current peak that is related to the electroreduction of Sn(IV), followed by the insertion of lithium ions [4]. The anodic response is characteristic of the deintercalation process, indicating the oxidation of the reduced tin oxide.

The electrochemical behaviour of different oxides during the electroreduction indicates that the ions as Li⁺ or H⁺ diffuse through the films in order to maintain the charge compensation on the films.

The simulation of the interaction between adsorbates and active sites demands consistent models, including information about the surface of the oxide.

Several papers have described the structure and mechanism associated with the interaction between SnO₂ and different molecules [6–8], and theoretical studies using different models have investigated the interaction between several adsorbates and SnO₂ [9–11]. Skafidas et al. [9] used the Monte Carlo technique to model the behaviour of SnO₂ as a carbon monoxide sensor. Using semiempirical calculations Martins et al. [10] investigated the interaction between H₂ and the SnO₂ (110) surface in order to analyse the gas–solid adsorption process. Munnix and Schmeits [11] calculated the electronic structure of ideal single crystal surfaces (110), (001) and (100) using the scattering theoretical method. Their results
show that the surface characteristics are governed by the coordination of the atoms on the surface.

Gercher and Cox [6,7] determined the correlation between the surface state and the catalytic reaction rate between water, methanol and formic acid and SnO$_2$ (110). The authors concluded that the local composition plays a considerable role in the dissociation of these molecules on the SnO$_2$ (110) surface.

Lithium insertion in metal oxides is a process of interest for many electrochemical applications, including rechargeable batteries and electrochromic displays. It is well known that electrochemical insertion processes modify the bulk properties of the host materials. Semiempirical methods such as MNDO have been used to investigate intercalation phenomena. Pershin and Overchuk [12] used the cluster approach on the basis of the MNDO method to ascertain the optimal position of the LiNH$_2$ molecule relative to the lattice points of graphite, as well as the electronic properties for the intercalant-host (LiNH$_2$–graphite matrix) system. For C$_{60}$ molecules the energy barriers calculated with the MNDO method indicate that the Li$^+$ remains stable at the reduced molecule surface (C$_{60}$) due to strong interaction and the presence of a barrier to the diffusion process [13].

SnO$_2$ (110) surface has been described recently in the literature and can be obtained experimentally under different atomic compositions as reduced, oxidized and defective surfaces [6–8].

In this paper we simulated the interaction between lithium ions and the oxidized SnO$_2$ (110) surface. This surface is described as an ideal surface which exposes five-coordinate Sn$^{4+}$ cations in the second atomic layer and three-coordinate O$^{2-}$ anions. The outer atomic layer is composed of two-coordinate O$^{2-}$, and the presence of mono-coordinate O$^{2-}$ is also considered.

![Fig. 1. Cluster model representation of Sn$_{10}$O$_{20}$.](image-url)
2. Models and methods

We used the semiempirical MNDO method [14] for the calculation of the interaction between Li$^+$ and a tin oxide crystal, taking the Sn and Li standard parameters for MNDO from the MOPAC 6.0 [15] program. The calculations were performed using the cluster model (SnO$_2$)$_{15}$, represented in Fig. 1, derived from the crystallographic data from Baur [16] and optimized by Martins et al. [10] who investigated the influence of cluster size on geometry and electrical properties using the MNDO, AM1 and PM3 semiempirical methods to reproduce the possible active sites in the (110) surface direction of the crystal. The interaction between two different sites, A and B, was analyzed as presented in Fig. 1. The interaction sites were optimized according to the following criteria: the distance and angle of mono-coordinate O$^2^-$ was optimized in the interactions between the lithium and type A sites, the distance between the two-coordinate O$^-$ and tin was optimized in the interactions between the lithium and type B sites, and the spatial distribution of lithium was completely optimized.

The geometry optimization of the cluster models and lithium interaction with the surface by gradients and energy minimization has been previously carried out using the BFGS [17] algorithm which makes use of the first and second derivatives. The geometry minimization of the bare cluster model was done by maintaining the symmetry of the crystal. The geometry optimization of the lithium–tin oxide surface system was done with the bare cluster geometry frozen. The molecular geometry was optimized using the Precise Keyword, which improves the tolerance in geometry optimization by increasing the self-consistent field (SCF) convergence criteria by a factor of 100.

The interaction energy ($\Delta E$) between (SnO$_2$)$_{15}$ and lithium is calculated as follows:

$$\Delta E = E_T(SnO_2)_{15} \cdots nLi - E_T(SnO_2)_{15} - E_{TnLi}$$

(1)

Fig. 2. Interaction between three Li$^+$ and a type A site in O(8), O(23) and O(24).
3. Results and discussion

The electrochemical process occurring during the tin oxide electroreduction and lithium insertion is represented by the reaction:

\[(SnO_2)_{15} + n e^- + nLi^+ \rightarrow (SnO_2)_{15} \cdots nLi\]  \hspace{1cm} (2)

In order to observe synergetic effects, interactions between one, two and three Li$^+$ ions with similar sites were calculated (mono-coordinate sites O(8), O(23) and O(24), and two-coordinate sites O(3) O(6) and O(21)).

The following relations show the interaction energies between the lithium ion and A sites.

\[(SnO_2)_{15} + 1e^- + 1Li^+ \rightarrow (SnO_2)_{15} \cdots Li\]
\[\Delta E = -6.92 \text{ eV/Li} \] \hspace{1cm} (3)

\[(SnO_2)_{15} + 2e^- + 2Li^+ \rightarrow (SnO_2)_{15} \cdots 2Li\]
\[\Delta E = -6.50 \text{ eV/Li} \] \hspace{1cm} (4)

\[(SnO_2)_{15} + 3e^- + 3Li^+ \rightarrow (SnO_2)_{15} \cdots 3Li\]
\[\Delta E = -6.56 \text{ eV/Li} \] \hspace{1cm} (5)

Eqs. (6)-(8) show the interaction energies between lithium ions and B sites.

\[(SnO_2)_{15} + 1e^- + 1Li^+ \rightarrow (SnO_2)_{15} \cdots Li\]
\[\Delta E = -5.70 \text{ eV/Li} \] \hspace{1cm} (6)

\[(SnO_2)_{15} + 2e^- + 2Li^+ \rightarrow (SnO_2)_{15} \cdots 2Li\]
\[\Delta E = -4.85 \text{ eV/Li} \] \hspace{1cm} (7)

\[(SnO_2)_{15} + 3e^- + 3Li^+ \rightarrow (SnO_2)_{15} \cdots 3Li\]
\[\Delta E = -4.74 \text{ eV/Li} \] \hspace{1cm} (8)

Figs. 2 and 3 show the optimized values for charge, order and interatomic distance between three Li$^+$ ions and the A and B sites.

These results indicate the existence of a preferential interaction between the Li$^+$ and the type A sites (mono-coordinate oxygen). Comparing the interaction energy in both cases, a saturation effect with the increase of Li$^+$ ions can be observed. The stability of the interaction decreases with the saturation.

Comparing Figs. 1 and 2 no change in the distance between the oxygen in the surface and tin as the Li$^+$ approaches the interaction site is observed. However, the angle of the subsequent oxygen changes in order to produce multi-coordinate bonding between the lithium and oxygen at the surface.

Fig. 3 shows that the interatomic distance between

![Fig. 3. Interaction between three Li$^+$ and a type B site in O(3), O(6) and O(2).]
the two-coordinate oxygen at the surface and the tin is still unchanged as the Li⁺ approaches.

The Li/MNDO method has been applied successfully to many systems and it is useful in order to obtain properties for lithium compounds. Kaufmann et al. [18] demonstrated that the MNDO method successfully predicted the structure and energy for compounds where the lithium is bound to oxygen or nitrogen.

The Li–O interatomic distances obtained in our calculations are in good agreement with the experimental results. Comparisons between the experimental Li–O interatomic distance, using LiOH as the reference compound, and calculations using PM3 and MNDO indicate differences less than 1% [19]. However, Koch and Anders [20] reported that, in general, the calculation of Li–O and Li–C interatomic distances of monolithiated organosulphur compounds are more accurate with the PM3 than with the MNDO method in comparison to ab initio methods or X-ray diffraction data. The values for the interatomic distance between the two-coordinate Li⁺ and oxygen are similar to those obtained in the literature for the homodimer of 1-lithiouracil (1.96 Å) [21]. The ability of lithium, a monovalent electropositive element, to form three-coordinate bonding is well known [22].

From the analysis of Figs. 2 and 3 a charge transfer from the lithium to the (SnO₂)₁₅ cluster can be observed. This becomes understandable when the potentials of the cluster and the Li atom are compared. According to our calculations, the ionization potential of the (SnO₂)₁₅ cluster is 9.6 eV. The energy of the lithium 2s level (HOMO – 1.47 eV) is higher than the Fermi energy of the (SnO₂)₁₅ cluster; therefore, the lithium atom should be strongly ionized.

In order for the simulation to be consistent with the electrochemical process represented by Eq. (2), the calculations were performed with the system electrically neutral. The results indicate that the electrical charge injected into the system (SnO₂)₁₅/Li⁺ by an external electron source could be distributed in the system. The optimization of the (SnO₂)₁₅/Li⁺ geometry was done with the cluster geometry frozen and an interaction energy of –0.08 eV was determined. In order to investigate the relaxation effects on the structure promoted by the insertion of Li⁺, we performed the geometry minimization of the interatomic distances Sn(34)–O(12), Sn(19)–O(41), Sn(43)–O(36), Sn(40)–O(33), Sn(13)–O(20), Sn(10)–O(17), and the Li⁺ position in the relaxed structure. Table 1 shows the changes in these parameters. According to these data on lithium insertion, the oxide tends to change its volume to accommodate the guest ions. The relaxation leads to an interaction energy of –0.66 eV.

The energy barrier for the intercalation process was obtained using the dummy atom methodology implemented in the MOPAC program, that is a pure mathematical tool useful in defining the geometry. The minimized spatial coordinates for the Li⁺ intercalated in the frozen cluster structure was attributed to the dummy atom. The distance from the Li⁺ to the dummy atom was kept fixed for each point in the approximation coordinate, and the angle and dihedral angle between the lithium atom and the neighbour- hood atoms were optimized in order to obtain the most energetically favourable insertion–ejection route. Fig. 4 exhibits the relative change in energy of the system for the distance of Li⁺ to the geometric position inside the frozen cluster. From these data we observe that 7.5 eV are necessary for the Li⁺ intercalation in tin oxide. In the lower energy intercalation route (–7.41 eV) the Li⁺ is located at 1.95 Å from O(14), and at 2.26 Å from O(23) (Fig. 4). This suggests that the presence of oxygen vacancies at the tin oxide surface decreases the barrier to intercalation. This probably occurs once the SnO₂ in its undoped form is an n-type semiconductor.

The optimized charge for the intercalated Li⁺ in the frozen cluster structure was 0.04, indicating that most of the injected charge is allocated to the lithium, and that the tin oxide cluster remains in its original oxidation state.

### Table 1

<table>
<thead>
<tr>
<th>Bond</th>
<th>Frozen distance/Å</th>
<th>Optimized distance  Å</th>
</tr>
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<tbody>
<tr>
<td>Sn(34)–O(12)</td>
<td>2.10</td>
<td>2.24</td>
</tr>
<tr>
<td>Sn(19)–O(41)</td>
<td>2.05</td>
<td>2.12</td>
</tr>
<tr>
<td>Sn(43)–O(36)</td>
<td>2.08</td>
<td>2.09</td>
</tr>
<tr>
<td>Sn(40)–O(33)</td>
<td>2.13</td>
<td>2.21</td>
</tr>
<tr>
<td>Sn(13)–O(20)</td>
<td>2.13</td>
<td>2.22</td>
</tr>
<tr>
<td>Sn(10)–O(17)</td>
<td>2.21</td>
<td>2.27</td>
</tr>
</tbody>
</table>
4. Conclusion

We have presented a theoretical description of geometric properties for the interaction between the Li$^+$ and the (SnO$_2$)$_{13}$ cluster using the MNDO semiempirical method.

In conclusion, Li$^+$ adsors preferentially on mono-coordinate oxygen (A-type sites). The higher energy barrier to intercalation suggests that the ion remains adsorbed at the oxide surface, but the presence of oxygen vacancies decreases this barrier favouring the Li$^+$ intercalation. Stable multi-coordinate bonds between the lithium and oxygen at the surface were determined which are probably associated with the characteristic electrochemical behaviour of these materials.

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References