A Model for the Charge Capacity of $1T$–TiS$_2$ Intercalated with Li

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ABSTRACT ■

The variation of the charge capacity of a double-layer $1T$–TiS$_2$ model system upon increasing intercalation with lithium is examined at a molecular level. The charge capacity is modeled through the global hardness index of density functional theory. The results obtained qualitatively reproduce the experimental trend observed in the voltage–composition variation curve in this system. Comparison with previous theoretical models show that the present approach may give a more complete information about the double-layer capacitance, since it takes into account the lithium ionicity and the host–guest specific interactions. © 1995 John Wiley & Sons, Inc.

Introduction

The layered compounds $1T$–TiX$_2$(X = S, Se, Te), intercalated with Li, are used as cathodes in intercalation batteries [1, 2]. In particular, the TiS$_2$ system is a good electronic and ionic conductor which may be used as a reversible battery when intercalated with an electron donor such as Li [3]. Most of the theoretical and experimental work in this field has been devoted to the study of the voltage (V)–composition (x) curves for Li intercalation at the cathode [4–6]. The voltage–composition variation may be used to represent the charge capacity of the system upon the increasing concentration of the impurity.

Theoretical models for the charge capacity variation upon increasing intercalation may be obtained by combining the derivatives $-dx/dV$ with suitable models of surface charge densities [7] or by application of the lattice gas (LG) model which directly relates the composition x with the thermodynamic chemical potential μ [8]. However, both theoretical models only partially reproduce the potential–composition variation experimental

curves. For instance, Wang [7] proposed a simplified model in which the Li^+ ions in the van der Waals gap and the induced electronic charges in the two neighboring TiS_2 layers are replaced by a double-layer capacitor. The double-layer capacitance is then obtained from the ratio of a surface charge to the potential calculated from the image potential model. Several factors are neglected in this model: For example, the filling of the conduction bands as the electrons are supplied to the S—Ti—S layers during the intercalation [9] and the ionicity [10] and ordering of the Li^+ ions in the van der Waals gap [11].

On the other hand, within the LG model, the derivative of the composition with respect to the thermodynamic chemical potential (μ) is used to represent the charge capacity variation as a function of the amount of Li intercalated. In this model, the changes in the chemical potential due to the electronic contributions μ_{el} are neglected, so that the charge transfer characteristic of the intercalation process is not taken into account [8, 12].

In this work, we present a molecular model to discuss the double-layer capacitance data observed in the Li_xTiS_2 system, which explicitly includes the electronic contribution of the chemical potential.

Model and Calculations

THE CLUSTER MODEL

When Li is intercalated in $1T$—TiS_2, a charge transfer occurs from the guest to the conducting band of the host, leaving a Li^+ species in the van der Waals gap [13]. Within a rigid band (RB) approach, it is assumed that a complete charge transfer (one electron/lithium atom) occurs upon intercalation [14]. However, some experimental evidence from NMR studies indicates that a partial electron transfer may be involved in this process [15].

The methods of quantum chemistry (molecular orbital [MO] and density functional theory [DFT]) may be helpful to discuss this problem beyond the RB approximation, since the major features of the electronic structure of the lattice are determined by a local environment formed by a reduced arrangement of atoms [16]. These specific interactions are best described by quantum chemistry methods. The major problem here is, however, the determination of a *minimal* molecular structure

(*cluster* model) that describes the local interactions correctly, while retaining the major features of the electronic structure of the solid coming from its periodical properties [17].

Within a microscopic model of the system, the Fermi level may be represented as the electronic chemical potential μ_{el}. This basic quantity is defined, in the context of density functional theory, as [18]

$$\mu_{el} = \left[\frac{\partial E}{\partial N}\right]_v \approx -\frac{I + A}{2}, \qquad (1)$$

where E is the electronic energy; N, number of electrons; v, the external potential; I, the ionization potential; and A, the electron affinity. Working definitions of the quantities I and A are possible within MO theory [19].

With the intercalation being an electron transfer reaction, a natural property to describe this process is the electronic chemical potential. Then, we make the ansatz that the minimal cluster structure corresponds to the one where the electronic chemical potential remains approximately unchanged upon increasing the cluster size. In this way, the μ_{el} value associated to the minimal structure will describe reasonably well the electronic chemical potential of the solid.

Calculations for different clusters were performed using the extended Hückel code. The basic unit composed of two hexagonal unit cells shown in Figure 1(a) was considered. This unit considers a van der Waals (VDW) gap to mimic the interlaminar spacing and keeps the right octahedral symmetry around the Ti atoms. Bigger clusters are built by adding successive units, maintaining the octahedral symmetry.

Figure 2 displays the results obtained for the electronic chemical potential variation with increasing cluster size. It may be seen that for a four-unit structure μ_{el} reaches a critical value that remains almost constant upon addition of new basic unities. Then, the representative cluster corresponds to a Ti_8S_{32} displayed in Figure 1(b). The Ti atom was taken in its d^0 configuration.

THE CHARGE CAPACITY MODEL

At a molecular level, the *charge capacity* concept introduced by Huheey, $\kappa = 1/I - A$ [20], measures the ability of an atom or group of atoms to absorb additional electronic charge. Recently, Politzer proposed a simple relationship between
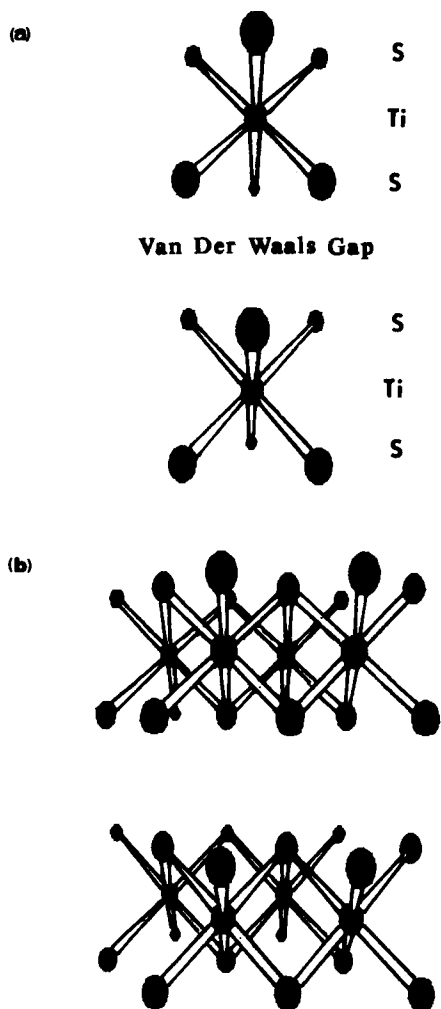
FIGURE 1. Cluster model for 1T–TiS$_2$: (a) basic unit composed of two hexagonal unit cells; (b) cluster model composed of four basic units (Ti$_8$S$_{32}$).

the charge capacity and the hardness concept of density functional theory [21]. Within this model, the electronegativity of a system in the presence of electron transfer, $\chi(Q)$, is a function of the acquired charge Q, which up to first order is given by

$$\chi(Q) = \chi^0 + Q\left[\frac{\partial\chi}{\partial Q}\right]_{Q=0},\qquad(2)$$

where the first term of Eq. (2) represents, in the present case, the electronegativity of the lattice in the absence of lithium (intrinsic electronegativity).

Since the absolute electronegativity is the negative of the electronic chemical potential in the DFT

scheme [18], it is possible to rewrite the Politzer expression as

$$\mu_{el}(Q) = \mu_{el}^0 - \frac{Q}{\kappa},\qquad(3)$$

with

$$\kappa = -\left[\frac{\partial Q}{\partial \mu_{el}}\right] = \frac{1}{2\eta},\qquad(4)$$

where the finite variation expression for the global hardness $\eta = 0.5\ (I - A)$, given by Parr and Pearson [22], was used. Combination of Eqs. (3) and (4) gives the desired expression for the charge capacity, in terms of the electronic chemical potential, namely,

$$\kappa = \frac{1}{2\eta} = \frac{Q}{\left[\mu_{el}^0 - \mu_{el}(Q)\right]}.\qquad(5)$$

CALCULATIONS AND DISCUSSION

First of all, we focused our attention on the successive intercalation of Li in the available octahedrical sites, formed by the sulfur bilayers in line with the Ti atoms. A correction for the VDW gap expansion was included by increasing it in 0.5 Å, which corresponds to the experimentally observed expansion [15].

Figure 3 summarizes the result obtained. It may be observed that after the intercalation of the first Li atom in our model cluster, having four vacant octahedrical (Oh) sites, the charge capacity reaches a maximum value for $x = 0.25$, which is equivalent to the maximum peak observed in the experimental voltage–composition variation curve reported by Thompson [4]. Beyond this point, a decrease of the charge capacity is observed, until a stationary regime is attained.

Within our model, this result may be explained as follows: In the region $0 < x < 0.25$, the increase in the charge capacity may be exclusively accounted for by the first term of Eq. (2) (i.e., the *intrinsic* electronegativity of the undoped lattice). After addition of the first lithium atom, the variation of $\chi(Q)$ given by the second term of Eq. (2), causes the electronegativity of the dopped system to dramatically diminish (with respect to the undoped lattice) to a constant *equilibrium* value, generating a decrease in the tendency of acquiring more charge. The succesive intercalation of additional lithium is exclusively governed by the second term of Eq. (2), which allows a change in χ
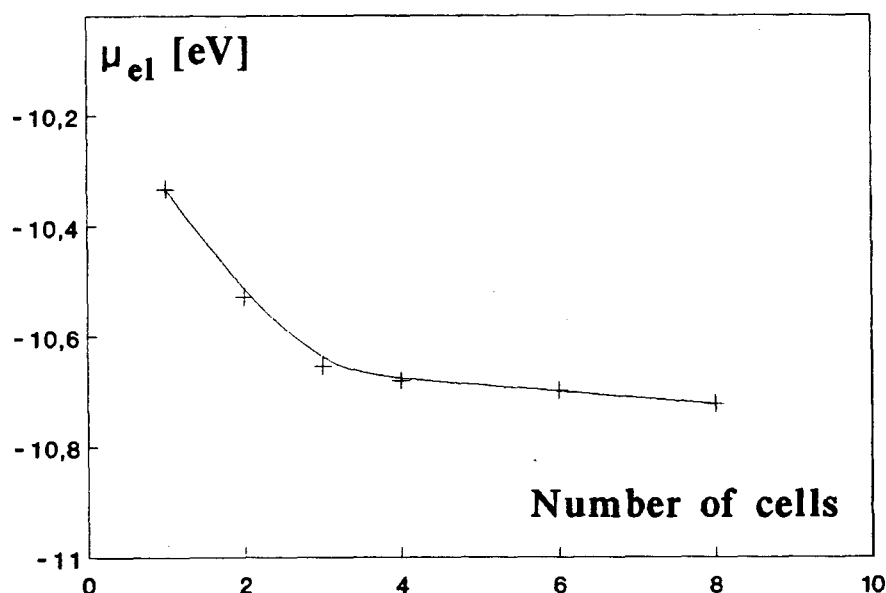
FIGURE 2. Variation of the electronic chemical potential with increasing cluster size.

that probably permits the equalization of the electronegativity of the system, in the region $0.3 < x < 0.80$. The discrepancy with the experimental curve near $x = 1$ is naturally associated to the cluster model adopted to represent the solid.

Comparison of the results obtained from our molecular model with those reported by Wang [7] are especially significant because our model explicitly introduces the charge-transfer effect from Li to the lowest unoccupied molecular orbital (LUMO) of the model cluster, which corresponds to the T_{2g} level of the Ti atoms. On the other hand, as recognized in [7], this effect of the filling of the conduction bands as electrons that are supplied to the S—Ti—S layers during intercalation is neglected. Furthermore, while the double-layer capacitor model assumes a *complete* electron transfer from Li to the lattice, our molecular model
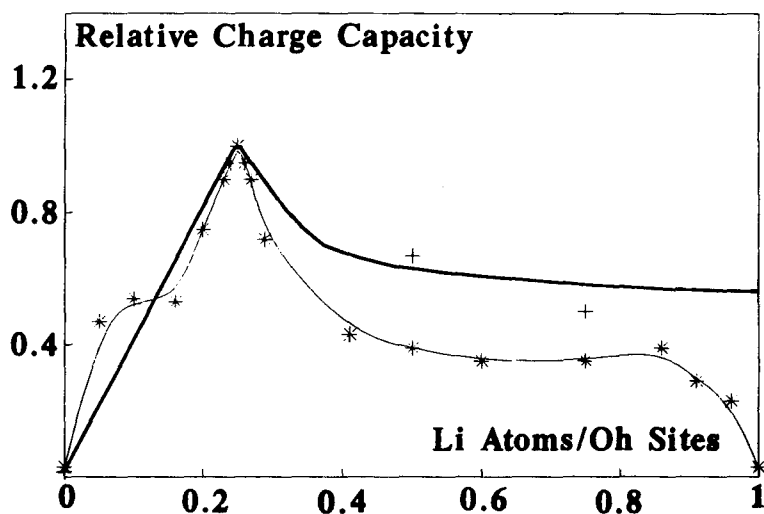

FIGURE 3. Comparison between (∗) experimental charge capacity taken from [4] and solid line + predicted charge capacity from our molecular model. A relative scale was used for comparison.

predicts a Li ionicity of about 75%. This result is consistent with NMR experimental data, showing that as the intercalation proceeds the electron donation becomes progressively less complete [15].

Additionally, our results show that the electron density around the sulfur atoms decreases upon successive intercalation of Li: It seems then possible that in a first step lithium donates charge to the titanium atoms and a fraction of electronic charge is recovered by Li via a polarization of the sulfur atoms around it. This explanation is consistent with band structure calculations on these systems [23].

Concluding Remarks

A *cluster*-like approach was used to represent the extended bidimensional lattice 1T–TiS$_2$. The choice of the minimal molecular unity to represent the layered dichalcogenide was performed on the basis of the variation of the electronic chemical potential upon addition of *hexagonal unit cells* into the system. Our calculations showed that for a cluster composed of four units the electronic chemical potential reaches an almost constant value. The electronic structure of the resulting model system reproduced qualitatively well the relevant aspects of the band structure of the solid obtained from a tight-binding calculation. The model cluster was used to study the charge-capacity variation of the lattice upon intercalation with Li in this system. The following results were obtained:

(i) The intercalation of Li into the 1T–TiS$_2$ lattice may be analyzed as an electron-transfer reaction. Within this model, the process may be discussed in terms of the variation of the electronegativity of the system upon successive intercalation with lithium. In particular, the charge-capacity variation may be qualitatively explained in terms of a simple model introducing the concept of *intrinsic* electronegativity of the undoped lattice and the principle of electronegativity equalization.

(ii) Our model also permits the analysis of specific host/guest interactions. For instance, it permits the introduction of lithium ionicity, which has been always neglected in previous theoretical studies in this system. The presence of partially ionized Li in the lattice induces polarization in the adjacent sulfur atoms, producing a *backdonation*-like effect toward the intercalated lithium.

Finally, it is worth mentioning that the present approach allows the intercalation process to be discussed in molecular terms, avoiding the use of empirical parameters and eliminating fitting procedures to experimental data.

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