

LETTERS

Interplay of Configurational and Structural Transitions in the Course of Intercalation

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On the basis of a combination of the lattice gas and the linear elasticity theories, we argue that the major features of the intercalation isotherms can be well understood in terms of a coupling between the configurational and the structural transitions. Competitive effects of the internal and loading stresses are discussed. A simple model, operating with the hydrostatic parts of the stress and strain fields, is shown to be applicable to a quantitative description of experimental data on electrochemical intercalation into crystalline and layered host matrixes.

I. Introduction

Intercalation of guest particles into host matrixes is a basic problem related to the design of hydrogen storage systems,¹ rechargeable high-energy batteries, electrochromic devices, (see ref 2 for a review), and superconductors.³

The insertion process can be viewed as an adsorption of guest particles on the host lattice. For charged particles, the ionic charge inside the matrix is compensated by the electrons. For that reason, the electrochemical intercalation is also similar (at least in some aspects) to a 3D adsorption of neutral species. On the basis of this analogy, the intercalation is traditionally described within the lattice gas (LG) model. In this approach, all the properties (the intercalation isotherm or capacity—concentration dependence) are connected with an ordering of the guest on different adsorption sites of a rigid host lattice—the configurational transitions.

However, the insertion of the guest species induces stress in the host matrix, which may lead to segregation effects⁴ or even to instabilities⁵ of the host—guest system. Also, a loading path

is shown⁶ to influence the guest uptake efficiency. Therefore, the host may undergo an expansion or local distortion. Typical examples are the hydrogen sorption by metals,^{6–9} or the intercalation of Li ions into layered materials.^{10,11} Quite often the host undergoes structural transformations^{12–15} due to intercalation. These are the structural transitions. In such cases, the standard LG approach also operates with several sublattices^{10,15} corresponding to each configuration of the host. However, such a restructuring suggests that the elastic effects should be taken into account. A general thermomechanical theory of the stress—composition interaction was developed by Larche and Cahn.¹⁶ This theory implies the existence of coupling between the elastic properties of the host material and the structure or the dynamics associated with the guest species. In other words, the configurational and structural transitions should be considered to be coupled. In our previous papers, we investigated such a coupling for 2D systems¹⁷ and, semi-empirically, for 3D systems.^{18,19} In terms of application to the intercalation, the theory agrees well with experimental data on layered Li_xTiS_2 and crystalline Li_xWO_3 and Na_xWO_3 compounds at equilibrium conditions.

In this study, we introduce a simple approach to the description of different intercalation systems in the framework

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of a scheme that combines the LG and the linear elasticity theories. This approach allows us to obtain a quantitative description of various insertion process on the basis of a reliable approximation for the strain and stress fields. These account for the loading mechanism and the volume dilatation during different types of transitions (expansion, staging, or restructuring).

II. Model

The host material is described as a 3D lattice of adsorbing sites with their positions given by a set vectors (\mathbf{r}_i). Because of the elastic properties of the real host, each site of this “auxiliary” lattice may deviate from its equilibrium position \mathbf{r}_i^0 such that we deal with the displacements $\mathbf{u}_i = \mathbf{r}_i - \mathbf{r}_i^0$. Therefore, the host properties are described by the Hamiltonian $H_H[\{\mathbf{u}_i\}]$.

The distribution of the intercalants on the host sites is given by a set of occupation numbers $\{t_i\}$, with $t_i = 0$ or $t_i = 1$. The guest subsystem is characterized by the chemical potential μ and the nearest-neighbor interaction parameter W (at equilibrium positions). For electrochemical insertion, the chemical potential μ gives a deviation of the electrode potential $-eV$ from its standard value E_0 . In this way, an arrangement of the intercalants on a rigid host lattice is governed by the LG Hamiltonian

$$H_G = W \sum_{ij} t_i t_j - \mu \sum_i t_i \quad (1)$$

that describes the configurational transitions of the intercalated species. These could consist of droplet formation for attractive interactions ($W < 0$) or the order–disorder transition for repulsive interactions ($W > 0$). In the latter case, one introduces²⁰ the sublattice concentrations as appropriate for the symmetry of a given system.

The coupling between the host and the guest is given by the Hamiltonian $H_C[\{\mathbf{u}_i\}, \{t_i\}]$ which takes into account a dependence of the binding energy on the site displacement and also the pairwise interaction between the guest particles through the host lattice. The overall Hamiltonian is now written as

$$H = H_H[\{\mathbf{u}_i\}] + H_G[\{t_i\}] + H_C[\{\mathbf{u}_i\}, \{t_i\}] \quad (2)$$

The free energy F corresponding to the above Hamiltonian is given by

$$F = F_H + F_G(x) + F_C(x) \quad (3)$$

where x is the intercalant concentration. Here, F_H is the host free energy in the absence of intercalation, and F_G is the guest free energy for the rigid host lattice. The latter term can be calculated using the mean field approximation to obtain the well-known relation^{2,10} for the chemical potential

$$\mu_0(x) = -eV - E_0 = qWx + \frac{1}{\beta} \ln\left(\frac{x}{1-x}\right) \quad (4)$$

where q is the coordination number of the host lattice and $\beta = 1/kT$. The coupling term $\beta F_C = -\ln(\langle e^{-\beta H_C} \rangle_{(\mathbf{u}_i)} \rangle_{(t_i)})$ requires averaging over the displacements and the occupation numbers and is calculated with the reference terms H_H and H_G . In fact, this is an infinite series including the correlations of all orders in the reference state. The main problem is to specify $H_C[\{\mathbf{u}_i\}, \{t_i\}]$ coherently with the host symmetry and elastic properties. It is known that real host materials have rather complicated elastic properties (e.g., strong anisotropy). Therefore, only some simplified model calculations are expected to give tractable results. However, such predictions (e.g., a rigid

plane model²¹) do not exhibit quantitative agreement with experimental data. An approximate perturbative scheme developed previously^{18,19} has shown that the coupling term is concerned with the concentration dependence of the host response to the intercalation. The most evident host response is the change in volume upon insertion of the guest species. Depending on the nature of the host, a stress field may result if the lattice is not totally free to relax. In this situation, it seems reasonable to estimate the coupling term on the basis of the continuum theory of elasticity with the concentration-dependent stress and strain fields. Then, the host–guest free energy is the sum of the lattice gas and elastic part:

$$F(x) = F_G(x) + F_{el}(x) \quad (5)$$

$F_G(x)$ is the configurational (lattice gas) part, in which the pairwise interaction is renormalized^{2,20} as a result of the interaction through the matrix. The elastic part is approximated by the free energy of a strained isotropic body under a loading stress $\sigma(x)$. Because the strain is assumed to be purely dilatational, we operate with traces ϵ and σ of the corresponding tensors:

$$F_{el}(x) = \frac{\Lambda}{2} \epsilon(x)^2 - \sigma(x) \epsilon(x) \quad (6)$$

Λ is the effective elastic constant, which is independent of the concentration. The total stress $S = S(x)$ is given by

$$S(x) = \frac{dF_{el}}{d\epsilon(x)} = \Lambda \epsilon(x) - \sigma(x) \quad (7)$$

Therefore, we have two stress contributions. The internal, or self-stress, $\Lambda \epsilon(x)$ corresponds to the host reaction to the guest insertion. The second term $\sigma(x)$ describes a loading procedure that may include sample clamping or other effects that are not directly related to the strain. It is important that, in general, $\sigma(x)$ is a function of x (not a function of $\epsilon(x)$). For instance, if the sample is clamped such that $\epsilon(x) = 0$, then we have stress accumulation proportional to the concentration, $\sigma(x) \propto x$.

The guest chemical potential $\mu(x)$ is given by the concentration derivative of the total free energy,

$$\mu(x) = \mu_0(x) + S(x) \frac{d\epsilon(x)}{dx} - \frac{d\sigma(x)}{dx} \epsilon(x) \quad (8)$$

Here, the second term involves the so-called chemical expansion coefficient $d\epsilon(x)/dx$, whereas the last term is associated with the loading path. We see that the intercalation level depends on the interplay of the internal stress and the loading stress. The latter could be small, but its concentration derivative is not necessary small; therefore, there may be serious consequences for the loading path.⁶ In particular, for a given material (Λ) and a suitable loading path $\sigma(x)$, there may be a cancellation of the last two terms in eq 8 in a given domain of x . This explains why in some cases the purely configurational description ($\mu(x) = \mu_0(x)$) works well. If the host–guest system forms a solid solution, then the guest partial molar volume $V_m(x)$ is related to the total volume $V(x) = xV_m(x) + V_0$, where V_0 is the initial host volume (at $x = 0$). However, the strain is also related to the volume variation $\epsilon(x) = (V(x) - V_0)/V_0 = xV_m(x)/V_0$.

If the loading is composition-independent, $\sigma(x) = \sigma$, and the sample volume changes linearly ($V_m = \text{const}$, $\epsilon(x) = xV_m/V_0$, as in the PdH_x α -phase), then we recover the well-known result⁹ $\mu(x) = \mu_0(x) - (\sigma - \Lambda xV_m/V_0)V_m/V_0$. In our previous work,^{18,19} we analyzed another extreme case of vanishing total stress, $S(x)$

$\rightarrow 0$, and the loading stress that is proportional to the concentration, $\sigma(x) = \sigma_0 x$. In that case,

$$\mu(x) = \mu_0(x) - \gamma p(x) \quad (9)$$

where $\gamma = (V(1) - V_0)/V_0\sigma_0$ and $p(x) = (V(x) - V_0)/(V(1) - V_0) = \epsilon(x)V_0/(V(1) - V_0)$. Note, however, that the above result is valid only for linear behavior of $p(x) = px$. For an arbitrary $p(x)$, eq 9 is an approximation whose validity can be tested by comparison to the experimental or computer simulation data. Therefore, for non-Vegard's behavior and the linear loading $\sigma(x) = \sigma_0 x$, we deal with a modified LG (MLG) description.

$$\mu(x) = \mu_0(x) + [\bar{\Lambda}p(x) - \gamma x] \frac{dp(x)}{dx} - \gamma p(x) \quad (10)$$

where $\bar{\Lambda} = \Lambda\gamma^2/\sigma_0^2$.

The strain can be measured as a volume dilatation or as a change of the interlayer spacing during the transitions between different phases (staging in graphite, restructuring in Li_xWO_3 , α - β transition in PdH_x , etc). In any case, the lattice parameters do not obey the linear Vegard law²² but instead exhibit a sharp change near the transition compositions x_n^0 . This behavior is described by the following approximation (an absolute value is considered).

$$p(x) = \frac{1}{2} \left[1 + \sum_n p_n \tanh[\alpha_n(x - x_n^0)] \right] \quad (11)$$

where n represents the number of phase boundaries. In Li_xWO_3 , $n = 1, 2$ corresponds to monoclinic-tetragonal and tetragonal-cubic transitions, respectively. Although the staging is suppressed for Li_xTiS_2 ,²³ the interlayer spacing exhibits a non-Vegard variation, and an inflection point near $x = 0.09$ becomes more pronounced with decreasing temperature.¹¹ This behavior implies a hidden tendency toward staging (with $n = 1, 2$ marking the boundaries), which becomes real when, for instance, Li is substituted by Ag ions.²⁴ The set of rigidity parameters α_n controls the local slope, and p_n are the weights corresponding to each phase such that $\sum_n p_n = 1$. This is consistent with experimental observations¹² indicating that the structures are not pure but contain some features that indicate a mixing of phases. The present form of $p(x)$ corresponds to continuous structural transitions but can be easily modified to take into account the jumplike behavior (as for the staging^{2,25}). Note, however, that the experimental dependencies are usually smoothed because of a finite concentration resolution. Then it is difficult to distinguish between the stepwise variation and a sharp (but continuous) transition. For that reason, the criticality criteria, determined on the grounds of rigorous statistical mechanical arguments ($\mu(x)$ loops or a divergent $dx/d\mu$), only approximately conform to the experimental data.

III. Results

For layered matrixes (such as TiS_2), the volume dilatation is mainly due to the c -axis expansion, so $p(x)$ is associated with the normalized layer spacing. The values of the parameters p_n , α_n , and x_n^0 were chosen to provide a good fit (Figure 1a) to the experimental data.²⁶ On the basis of this fit, we analyze the intercalation isotherm $\mu(x)$ (Figure 1b) and the capacity $C(x)$, which is given by^{10,11} $C(x) = dx/d\mu$ (see Figure 1c), which refines our previous results.¹⁸ We see that the purely configurational behavior (pure LG-dotted lines) takes place only at low (or high) intercalant concentrations. At intermediate x

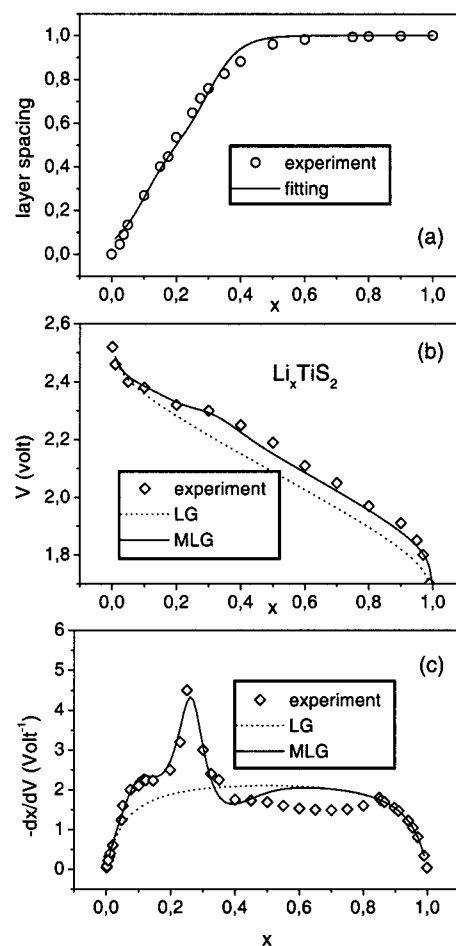


Figure 1. Normalized layer spacing (a), voltage (b), and capacity (c) for Li_xTiS_2 as functions of Li concentration. The symbols correspond to the experimental data.^{26,11} The parameters are $p_1 = p_2 = 1/2$, $\alpha_1 = 10$, $\alpha_2 = 12$, $x_1^0 = 0.09$, $x_2^0 = 0.27$, $\beta\gamma = 2$, $\beta\bar{\Lambda} = 0.4$, and $\beta W = 2.5$; β corresponds to room temperature.

values, the structural changes ($p(x)$) are important. For instance, the hole-particle symmetry of the LG description is broken by elastic effects. Similar agreement is reached for Li_xWO_3 (Figure 2). In this case, the peaks in $C(x)$ mark the boundaries between different symmetry phases.¹² Note that the theory exhibits surprisingly good agreement with the experimental data, even without explicit treatment of the lattice symmetry, by taking into account only the volume dilatation. Indeed, Li_xTiS_2 is a layered compound whose response to the insertion is physically different from that of crystalline Li_xWO_3 (e.g., the former increases whereas the latter decreases the volume). This result suggests that the information about the strain field is important in reproducing the equilibrium features of various intercalation compounds.

In summary, our approach implies that the main equilibrium features of various insertion systems (which differ in their microscopic details) can be well understood in terms of coupling between the structural and configurational transitions. In a simple approximation, this coupling is concerned with the concentration dependence of the hydrostatic parts of the stress and strain fields, which are associated with internal and loading effects.⁶ The theory gives a quantitative description of different insertion processes involving volume expansion (Li_xTiS_2 , α - PdH_x) or restructuring (Li_xWO_3). Our results may have implications in various domains such as hydrogen sorption,¹ electrochemical intercalation supplemented by staging (e.g., Li-

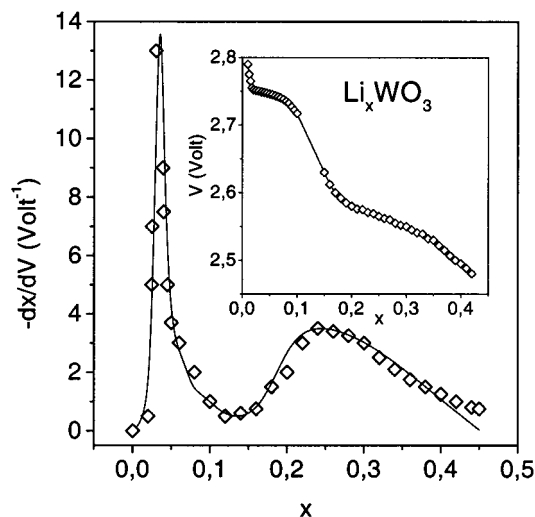


Figure 2. Differential capacity and voltage (inset) for crystalline Li_xWO_3 . The symbols correspond to experimental data.¹² The parameters are $p_1 = 0.7$, $p_2 = 0.3$, $\alpha_1 = \alpha_2 = 15$, $x_1^0 = 0.05$, $x_2^0 = 0.27$, $\beta\gamma = 1.8$, $\beta\Lambda = 0.01$, and $\beta W = 2.2$.

graphite), impurities in alloys, layered superconductors,³ volume transitions in hydrated gels,²⁷ etcetera.

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