Shedding Light on the Entropy Change Found for the Transition Stage II → Stage I of Li-Ion Storage in Graphite

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In order to examine the controversial hypothesis put forward to explain the entropy step experimentally observed for the stage II to stage I transition for lithium intercalation in graphite, a transparent statistical mechanical model is developed. The results obtained show that the entropy increase can be explained by the change of configurational entropy occurring at occupation of half of the lattice. Comparison with experimental data shows that attractive interactions between intercalated particles in the same lattice contribute to the entropy increase, and that for the stage II to stage I transition the entropy contribution due to the lattice 2 is predominant. A currently used strategy for measuring the intercalation entropy is also discussed in this paper.

In statistical mechanics, all the thermodynamic properties of a system can be obtained from its partition function once it is determined. Different partition functions may be formulated in different ensembles (microcanonical, canonical, grand canonical, etc.), depending on the boundary conditions chosen to describe the related thermodynamic systems. However, it can be shown that all the ensembles are thermodynamically equivalent as long as the systems are large enough so that their fluctuations may be ignored. Thus, a currently used strategy

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Model and Statistical Mechanical Background

The Monte Carlo simulations performed in Reference 20, based on a semiempirical hamiltonian, showed the sequential filling of a hexagonal lattice in a two-step sequence. Voltammetric experiments also have shown that the occurrence of Stages I and II is related to two well-defined energy states, which become evident as voltammetric peaks. For this reason, and seeking the simplest model that allows the experimental features to be understood, we propose the model described in Figure 1. We show there two lattices, defined as 1 and 2, which we will assume that may be occupied by particles (the Li ions), and we will denote the interaction energies of the particles with the lattices as \( E_1 \) and \( E_2 \) respectively (\( E_1 < E_2 \)). We will neglect the interactions between particles in different lattices, so that the interaction of the particles coming into lattice 2 with the particles in lattice 1 is included in its energy \( E_2 \). Thus, the present formulation corresponds to a two-level lattice gas. It will be assumed that each lattice has \( M \) sites where the incoming ions may be located, thus giving a total of \( 2M \) sites that may be occupied.

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![Figure 1. Schematic representation of the present model for Li intercalation in graphite. The upper part shows the two empty lattices (empty symbols), say lattice 1(squares) and lattice 2(circles), which may be progressively occupied by Li ions. The lower part of the figure shows on the left the representation of Stage II (X = 0.5), where filled squares represent filled sites for lattice 1; and on the right, the representation of Stage I (X = 1), where filled circles denote that lattice 2 has also been filled.](image-url)

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is to choose the ensemble where the calculations are less demanding, then calculate the thermodynamic properties within it, and assume the results to be valid for thermodynamic systems under other boundary conditions. This is the approach we have applied here. On this basis, our calculations will be made within the canonical ensemble, where the partition function $Q$ is given by:

$$Q(N, 2M) = \sum_{(i(\text{states})} e^{-E_i/kT} = \sum_{j(\text{levels})} \Omega_j e^{-E_j/kT} \tag{1}$$

where $\Omega_j$ labels the degeneracy of the $j$th energy level $E_j$ and $N$ the number of inserted ions. The term $2M$ indicates the total number of sites where the ions may be inserted and $kT$ is the Boltzmann constant multiplied by the absolute temperature.

The degeneracy $\Omega_j$ may be straightforwardly calculated by counting the number of ways of distributing $N$ particles among $M$ sites with energy $E_j$ and $M$ sites with energy $E_2$. Two cases may be distinguished, for $N < M$ and for $N \geq M$. For $N < M$ we obtain:

$$\Omega_j = \frac{(M!)^2}{(N - j)!((N - M) - j)!} \tag{2}$$

where $j$ is an index running between 0 and $N$ in Equation 1.

For the case where $N \geq M$ we have:

$$\Omega_j = \frac{(M!)^2}{(2M - N - j)!((N - M + j)!((M - j))!} \tag{3}$$

where $j$ is an index running between 0 and $2M - N$ in Equation 1.

The energy for $E_j$ is in turn given by:

$$E_j = \begin{cases} 
(N - j)E_1 + jE_2 & \text{for } N < M \\
(N - j)E_1 + (N - M + j)E_2 & \text{for } N \geq M \tag{4}
\end{cases}$$

We have used a numerical procedure to evaluate the partition function $Q$ for different situations, and found that results with $M = 100$ are converged with respect to the size of the system. Once $Q$ was obtained for different $N$, different properties were obtained according to following equations:

$$A = -kT \ln Q \tag{5}$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_{M,N} = k \sum_{j(\text{levels})} \frac{\Omega_j}{Q} e^{-E_j/kT} + k \ln Q \tag{6}$$

$$\mu = -kT \left(\frac{\partial \ln Q}{\partial N}\right)_{T,M} \tag{7}$$

$$\left(\frac{\partial N}{\partial \mu}\right)_{T,M} = -\frac{1}{kT} \left(\frac{\partial \ln Q}{\partial N}\right)_{T,M} \tag{8}$$

where $A$ denotes the Helmholz free energy, $S$ the entropy and $\mu$ the chemical potential. The last two equations may be useful to simulate voltamograms under quasi-equilibrium conditions, since $\mu$ is linearly related to the electrode potential, and the derivative in Equation 8 is proportional to the current in a linear voltammetric sweep.

**Results and Discussion**

To proceed with the discussion, instead of using the number of particles as the independent variable, we define the fractional occupation $X$ of the lattices as:

$$X = N/(2M) \tag{9}$$

and all thermodynamic properties will be discussed in terms of this quantity.

Figure 2 shows the entropy of the present system as a function of the occupation, for different energy differences $\Delta E = E_2 - E_1$, which are indicated in the figure.

Let us discuss first the case $\Delta E = 0$. In this case, the particles distribute over all sites with the same probability, and the entropy reflects the following conditions: for $X \to 0$, we have that $S \to 0$, since there are no particles in the system. In the discrete system, $S(1)/(2MkT) = \ln(2M)$, which comes close to zero for very large systems. For $X \to 1$, we have similarly that $S \to 0$, since the system becomes completely ordered. The entropy maximum occurs at $X = 0.5$, a condition that delivers the maximum number of configurations. It is interesting to see what happens for larger $\Delta E$ values. The entropy curve becomes progressively flat at the maximum, and finally develops a local minimum between two local maxima, located at $X \approx 0.25$ and $X \approx 0.75$ (See Figure 2). The derivatives of the curves shown in Figure 2, which are indicated in Figure 3, show the entropy values measured in the literature, and are illustrated in Figure 3. We will from now on denote this quantity as $S'(N) = (\frac{\partial S}{\partial N})_{T,M}$. It is evident from this Figure that a step develops in $S'(N)$ for increasing $\Delta E/kT$ values. The origin of this
step can be understood by considering the occupancy of the two energy levels, \( E_1 \) and \( E_2 \), which are shown in Figure 4.

It becomes evident that as the energy difference \( \Delta E/kT \) increases, the occupancy of the two energy levels becomes progressively differentiated, until a point is reached where the occupation is close to being sequential. Thus, the situation for \( \Delta E/kT = 8 \) is such that lattice 1 is practically complete as lattice 2 starts to fill. Under this condition, the step in \( S'(N) \) is quite large, since the change in the physical situation is from one where the entropy of the system is rapidly decreasing, as lattice 1 is completely filled, to another one where entropy increases because an empty lattice is starting to be filled. Thus, up to now, the present model is able to account qualitatively for the entropy step found in experiments at \( X = 0.5 \). However, a close comparison with experiments shows that some improvements are necessary to be able to obtain a quantitative agreement.

If we look, for example, at the voltammograms of Levi et al.,\textsuperscript{22} we can see that the peaks attributed to the occurrence of stages I and II are separated by about 37 mV, which in terms of the thermal energy at room temperature (0.0257 eV) amounts to 1.44 kT. Thus, 1.44 is the value that corresponds to \( \Delta E/kT \) in the present modeling. Figures 2 and 3 clearly show that such a small value of \( \Delta E/kT \) could not account for the step in \( S' \) in References 12, 13. In order to come close experimental results, an important conclusion drawn by Levi and Aurbach must be born in mind: The effective interaction of the particles leading to the peaks labeled as e) and d) in Reference 20 is attractive, leading to a half-width of peaks close to 18 mV, instead of the 90 mV for the Langmuirian-Nerstian relationship. These attractive interactions are absent in our model so far, but this can be remediated straightforwardly, by modifying Equation 4 to account for the interaction among particles in an average way. This can be easily done by replacing \( E_1 \) and \( E_2 \) by \( E_1^* \) and \( E_2^* \), which are defined as:

\[
E_1^* = E_1 + g_1N_1^n n_1^2/2 \tag{10}
\]

\[
E_2^* = E_2 + g_2N_2^n n_2^2/2 \tag{11}
\]

where \( g_1 \) and \( g_2 \) are interaction parameters, \( N_1^n = N_2^n = 6 \) is the number of neighbors in each of the lattices, \( n_1 \) and \( n_2 \) are the occupancies of the layers, and the factor 1/2 is to account for the double summation in the average interaction. The set of Equations 10 and 11 is the Bragg-Williams approximation applied to each of the lattices.\textsuperscript{23} Assuming a value of \( \Delta E/kT = 1.44 \), as suggested by experiments, we can simulate voltammograms using Equations 7 and 8. Voltammograms simulated with different values of \( g_1 = g_2 \) are shown in Figure 5, where we can appreciate how the half-width peak is strongly sensitive to the interaction parameter \( g_1 \).

According to these results, one possible approach to come closer to experimental findings would be to fit the half-width peak of the experimental voltammograms (18 mV) and calculate with these parameters the \( S'(N) \) plots. Calculations with \( g_1(kT) = -0.40 \) deliver a half peak width of this order, and the corresponding \( S'(N) \) vs \( N \) plot is shown in Figure 6. While the general behavior of the \( S'(N) - N \) resembles the experiment, the entropy increases at the transition between stages, say \( \Delta S'(I \rightarrow I) \) yields a value 5.8 J/(mol-K), which strongly underestimates the experimental value (14 J/(mol-K)).

While this disagreement may be attributed to the approximate nature of the present model, a number of considerations must be made concerning the experimental results. On the one hand, although the voltammetric experiments have been made at very low sweep rates (4 μV.s\(^{-1}\)), it is possible that quasi-equilibrium conditions have not been reached. The potential difference between the anodic and cathodic peaks, as well as their different widths may be an indication of this. Also, it is intrinsic from experiments that the graphite electrodes are not perfect, and a number of other technical features, such as
contact resistances between grains may be widened the voltammetric profiles. Another consideration that should be taken into account is: the occurrence of borders of the growing phases, suggesting nucleation with the conjecture of Yazami and Reynier concerning the occurrence of a dilute lithium layer between adjacent complete lithium hexagonal layers.

Another important result is that the interaction between intercalated ions can be inferred to be strongly attractive, as was assumed by Levi et al. when simulating voltammetric profiles.

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References

1. D. In Choi, G.-B. Han, D. Jin Lee, J.-K. Park, and J. Wook Choi, Journal of The Electrochemical Society, 158, A1150 (2011).
2. O. Jankovský, J. Kováč, J. Leitner, K. Rika, and D. Sedmidubský, Thermochimica Acta, 634, 26 (2016).
3. Y. Reynier, R. Yazami, and B. Fultz, Journal of Power Sources, 298, 349 (2015).

Table I. Entropy increase at the transition between stages, ΔS(II → I), for the different values of the interaction parameters g. The predicted voltammetric half peak is also included.

| Interaction parameter g/(kT) | Entropy change at the stage II→stage I transition S/ mol K−1 | Voltammetric Half peak width mV |
|-----------------------------|---------------|-----------------|
| −0.5 | 7.2 | 14.1 |
| −0.6 | 12.6 | 3.51 |
| −0.65 | 15.1 | 0.26 |
| −2/3 (Briggs) | 15.9 | 0 |

Figure 7. Derivative of the configurational entropy according to the double lattice model presented in Figure 1, as a function of the fraction of occupied sites X for ΔE/kT = 1.44 and g/(kT) = −0.666.

Conclusions

In the present work, we have shown using a very simple model, based on statistical mechanics, that the controversial origin of the entropy step between stage II and stage I for lithium intercalation in graphite may be explained on a configurational basis, in agreement with the conjecture of Yazami and Reynier concerning the occurrence of a dilute lithium layer between adjacent complete lithium hexagonal layers.

Another important result is that the interaction between intercalated ions can be inferred to be strongly attractive, as was assumed by Levi et al. when simulating voltammetric profiles.