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Short communication

A theoretical model to determine intercalation entropy and enthalpy: Application to lithium/graphite

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ABSTRACT

Intercalation compounds play a fundamental role to increase the capabilities of electrochemical cells to store energy. A new computational model is developed to calculate the intercalation entropy and enthalpy in electrochemical intercalation compounds. The new methodology is applied to the intercalation of lithium ions into graphite, finding a good agreement with experimental measurements. The main features of the experimental data are correctly reproduced, including the step in the intercalation entropy and enthalpy for the stage II to stage I transition.

1. Introduction

In recent years, measurements of open-circuit voltage (OCV) at different temperatures of an electrochemical cell upon energy storage have been used to characterize the intercalation entropy and enthalpy of the cell [1,2,3,4]. These measurements are performed by changing the temperature of the cell and measuring the equilibrium value of the OCV for the new temperature. The OCV vs. temperature measurements are collected for different states of charge of the electrodes of the cell. Since the OCV vs. temperature measurements are time-consuming as it is necessary to reach the equilibrium value of the OCV, different methods to measure the intercalation entropy have been recently developed [5,6].

The continuing and increasing new developments of batteries of electrochemical cells to store energy require of new and more sophisticated parameters to characterize and optimize their performance. The intercalation entropy is one of them and constitutes a very important thermodynamic value as it allows us to analyze the reversible heat generation in the electrode materials of a battery. When the battery size increases the area-to-volume ratio decreases and the heat transfer away from the battery becomes more inefficient [7,8]. The total heat generation rate can be divided into reversible and irreversible parts. The irreversible part depends on the internal resistance of the cells whereas the reversible one is a function of the intercalation entropy [9,8]. It was found that the reversible heat generation rate is a significant portion of the total heat generation rate and that it can contribute to more than 50% of the total generated heat at the C/1 discharge rate [10,11,8]. Therefore, it is very important to determine the intercalation entropy of an electrochemical cell to prevent high temperature excursions of their electrode materials.

In the last years and accompanying the developing of cells to store energy, different theoretical approaches have been applied to understand and improve the performance of anodic and cathodic materials. In this sense, insertion and intercalation potentials for different electrode materials were determined by means of *ab initio* methods [12, 13,13,14,15]. Diffusion barriers were obtained from *ab initio* and quantum Monte Carlo [16,17,18] calculations. Molecular dynamic simulations have been used in diffusion studies [19,20,21]. Intercalation studies of ions were performed by mean of a lattice-gas model by using the mean-field approximation and Monte Carlo simulations [22, 23]. In recent times multiscale physical models have emerged, spanning scales from few atoms to the device level that can predict the behavior of the materials and their time evolution. These methods, subject of different extensive reviews [24,25,26] may profit from the previous fine grained methods, using some of their results as input.

Here we show how the intercalation entropy and enthalpy can be theoretically determined. As previously stated some of the outputs of the present theoretical model like the intercalation entropy may be useful for multiscale models [26]. Particularly, we study the *Li*_graphite intercalation compound by modeling it as a lattice-gas and performing grand

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canonical Monte Carlo simulations. The main features of the experimental intercalation entropy and enthalpy are correctly reproduced.

2. Material and methods

Reynier et al. have experimentally studied the intercalation entropy and enthalpy of *Li*-ions into graphite by using test half-cells with metallic lithium as counter and reference electrodes and a composite graphite working electrode [1]. The theoretical results of the present work are compared below with experimental data of OCV, intercalation entropy and enthalpy vs. lithium concentration (x), which were picked up from the work of Reynier et al. [1].

3. Theory and computational methods

To calculate the intercalation entropy of intercalation compounds, a lattice gas model is considered within a grand canonical ensemble, where the volume of the system is constant and the particle number may change. The total energy of the system is given by:

$$U(S, V, N) \tag{1}$$

where S is the entropy, V is the volume and N the number of particles of the system. An increment of the energy is given by:

$$dU = TdS + PdV + \mu \mathrm{dN} \tag{2}$$

where T is the temperature and μ is the chemical potential. The constant volume condition in our model yields:

$$dU = TdS + \mu \mathrm{dN} \tag{3}$$

Therefore, the intercalation entropy is given by:

$$\frac{dS}{dN} = \frac{1}{T}\left(\frac{dU}{dN} - \mu\right) \tag{4}$$

For a given T and μ a Monte Carlo grand canonical simulation is performed and the energy change ΔU is calculated and saved for each accepted particle insertion or deletion in the simulation. In this way the following mean value is obtained:

$$<\frac{dU}{dN}> = \frac{\Sigma_i^{N_i} \Delta U_i - \Sigma_d^{N_d} \Delta U_d}{N_i + N_d} \tag{5}$$

where i and d denote insertion and deletion moves respectively. Finally, the mean value of the intercalation entropy is obtained from:

$$\frac{dS}{dN} = \frac{1}{T}\left(<\frac{dU}{dN}> - \mu\right) \tag{6}$$

Seeking for a particular application of the above formalism, a lattice-gas model is employed to study the insertion of *Li*-ions into graphite. The centers of the carbon hexagons in a graphite with AA stacking [27,28,29] are used to define the lattice for the *Li*-ion gas. The sites of the lattice are located at a distance d from these centers. This distance corresponds to half of the distance between the (0001) graphite basal planes. Fig. 1a shows a top view of a *Li*-ion (green) on a lattice site and Fig. 1b shows a lateral view of this *Li*-ion.

The interactions between the ions of the gas are divided into two parts, the in-plane interactions and the out-of-plane interactions. The in-plane interactions are the interactions between ions in the same layer of graphite. These interactions are assumed to be given by a Lennard-Jones potential [30,31]:

$$V_{ij} = c_i c_j \in \left[\left(\frac{r_m}{r_{ij}}\right)^{12} - 2\left(\frac{r_m}{r_{ij}}\right)^{6}\right] \tag{7}$$

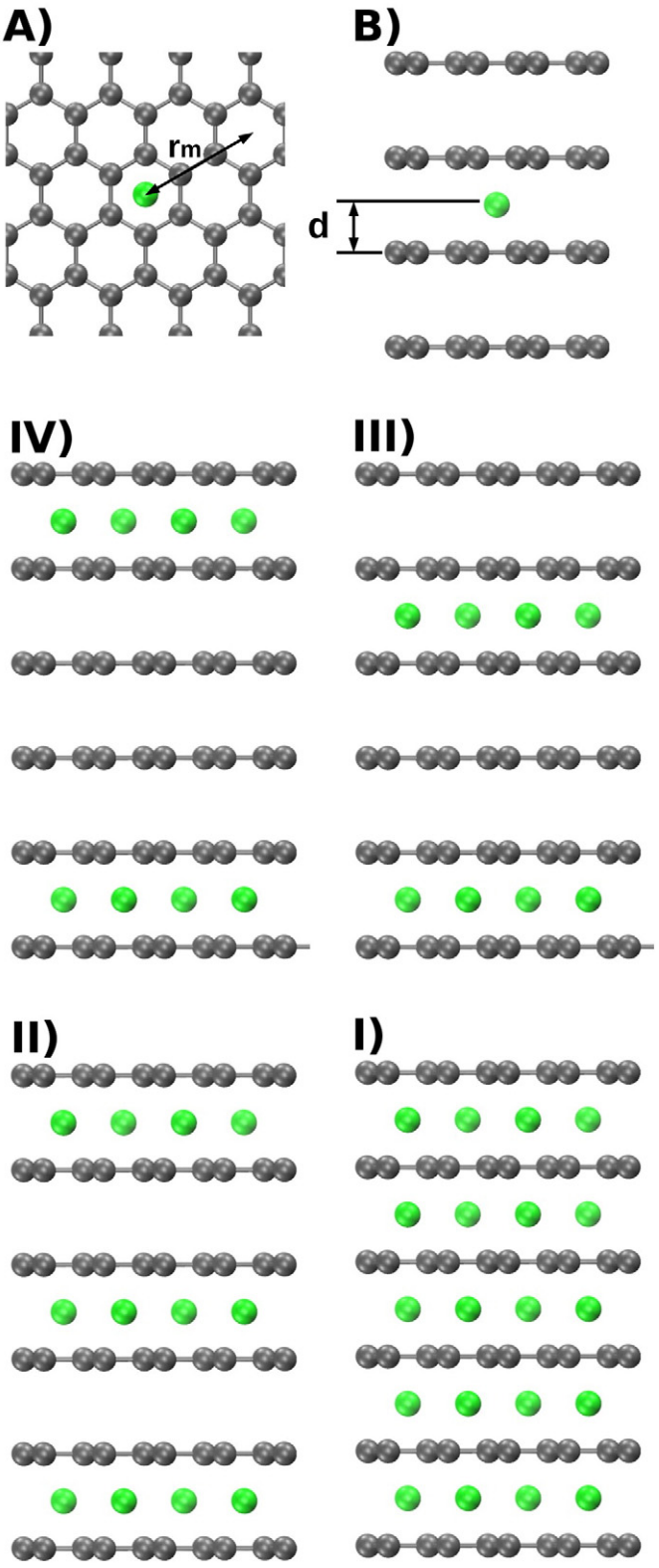

Fig. 1. A) Scheme of a top view of a *Li*-ion (green) on a lattice site. The distance to the second neighbor r_m is also indicated. B) A lateral view of the *Li*-ion on the lattice site. IV-I) Schemes of four known stages of the *Li*-graphite intercalation compound.

where c takes the value 1 if there is a *Li*-ion on the lattice-site and 0 if not, r_{ij} is the distance between sites i and j lying on the same plane, r_m is the distance to the second neighbor (Fig. 1a) and $\in$ is the value of the attractive interaction at r_m. The out-of-plane interactions are the