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Noteworthy electroanalytical features of the stage 4 to stage 3 phase transition in lithiated graphite

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Abstract A careful study of electrochemical lithiation of a composite graphite electrode at elevated temperatures was performed using a potentiostatic intermittent titration technique. Special emphasis was placed on the stage 4 to stage 3 phase transition, occurring in the range of x (in Li_xC_6) between 0.12 and 0.22 (this corresponds to the partial dimensionless intercalation level θ ranging from 0 to 1). An abrupt increase in the Li chemical diffusion coefficient, D_{chem} , when approaching the relative coverage level $\theta = 1/3$, and a specific non-Arrhenius shape of the plot of D_{chem} vs. the inverse of the absolute temperature were observed. These two features of the phase transition seem to be in agreement with a recent thermodynamic model for adatoms diffusing on a surface with two considerably different barrier energy sites.

Keywords Electrochemical lithiation · Graphite electrode · Potentiostatic intermittent titration

Introduction

The phase diagram of lithiated graphite, Li_xC_6 , has been reported and discussed in full detail [1]. The most prominent feature on this diagram is the two-phase coexistence regions evidenced by direct in-situ XRD studies. This was proved for the stages 1 and 2 ($0.5 < x < 1.0$), 2 and 3 ($0.21 < x < 0.5$) and, finally, stage 4

and the dilute phase 1' ($0.04-0.07 < x < 0.12$), where x denotes here the intercalation level of Li_xC_6 . However, no indication of two-phase coexistence has been obtained within the relatively sloping portion of the chronopotammetric curve of a graphite electrode in the range of x between 0.12 and 0.21 [2, 3, 4]. A gradual shift in the position of the (002) peak on the XRD pattern of a graphite electrode in the above range of x was observed. This was incompatible with two-phase coexistence; thus a kind of solid solution for stages 4 and 3 was proposed to explain the above phase transition. However, this assumption hardly complied with the mechanisms of the staging process [5]. Moreover, it basically failed to explain the appearance of a small peak of the differential intercalation capacity, C_{int} , in the related range of x . The majority of researchers routinely reproduced this peak but its nature has still remained a mystery.

The concept of a “solid solution” implies a random mixing of the stage 4 packets, of fraction θ , with the stage 3 packets, of the rest of the fraction, $1-\theta$ [1]. In contrast, here we assume that the stage 3 is regularly distributed among the stage 4, in a specific way, similar to the distribution of adatoms on a surface with two sites of different energy barriers [6, 7]. Our consideration partly overlaps with that of McKinnon et al. [8], who treated theoretically the break of the $\theta = 1/2$ symmetry in the case of a triangular gas. These authors, however, did not extend their thermodynamic analysis to a very peculiar behavior of the potential and temperature dependencies of the chemical diffusion coefficients.

In this work we used a theoretical model, recently developed by Chvoj et al. [6, 7], which predicts a new type of diffuse phase transition. The model was adapted to describe the equilibrium characteristics of Li insertion and the related chemical diffusion coefficients as functions of both the potential and temperature. We summarize here our findings related to the experimental evidence of such a phase transition in Li_xC_6 . A more detailed paper considering this and an alternative approach to Li-insertion into graphite will be presented elsewhere [9].

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Experimental

The preparation of thin composite graphite electrodes based on synthetic graphite powder (KS-15, Lonza) has been described previously [10, 11]. Each electrode (10–15 μm thick) contained approximately from 1 to 2 mg of the active mass. The coin-type cell assembly was performed in a glove box filled with pure, dry Ar. The working graphite electrode was placed versus a similar sized Li counter-electrode, separated by a thin Cellgard membrane; a thin foil of Li (the reference electrode) was pressed onto a Ni wire and carefully isolated from both the electrodes and the stainless steel cell's framework by a thin Teflon tape. The cell was closed in a clamping device and the borders were, in addition, isolated with an epoxy glue. After drying overnight at room temperature, the cell was ready for measurements. This cell construction allowed us to reversibly cycle the graphite electrode for several hundred cycles without any appreciable deterioration of the reversible capacity. This test is especially important for measurements at elevated temperatures, since the latter were often reported as a major reason for the fast capacity fading. The temperature of the aqueous bath was automatically controlled. The accuracy of the temperature measurements was not worse than 1 $^{\circ}\text{C}$.

The electrolyte solution was 1 M LiPF_6 (Merck) in an ethylene carbonate (EC)+dimethyl carbonate (DMC) 1:1 mixture (Merck ultra-pure solvents) in the presence of 5% of dimethyl pyrocarbonate.

Electroanalytical measurements (slow scan cyclic voltammetry, SSCV, and potentiostatic intermittent titration, PITT) were carried out using Schlumberger's 1286 electrochemical interface driven by Corrware software from Scribner Associates (486 IBM PC). Highly resolved PITT data were analyzed with the use of finite-space diffusion models [12]. In the vicinity of the incremental capacity peaks, the potential step height was as small as 5 mV. Each subsequent step was applied after complete equilibration during the preceding step. The residual (background) time-independent current varied between 2 and 15 $\mu\text{A mg}^{-1}$, depending on the potential, step height and temperature. Careful subtraction of this current from the measured one is required to increase the accuracy of the calculated values of D_{chem} .

Results and discussion

The chemical diffusion coefficient related to the intercalation of ions into an electrode bulk can be determined by using of one of the small-amplitude electrochemical relaxation techniques, e.g. PITT [12]. A small potential step, typically of 5–10 mV, is applied to the electrode to change its equilibrium intercalation level by a small increment, Δx . The current passing through the electrode is measured as a function of time and treated according to a finite-space diffusion model [12]. The kinetic (so-called Cottrell) parameter, $I t^{1/2}$, is found as a slope of the I vs. $t^{-1/2}$ plot, whereas the corresponding equilibrium incremental charge is calculated by numerical integration of the current with respect to time. Then the chemical diffusion coefficient D is calculated according to Eq. 1 [11, 12]:

$$\begin{aligned} D_{\text{chem}} &= \left[\frac{\pi^{1/2}/I t^{1/2}}{Q_m \Delta x} \right]^2 \\ &= \left[\frac{\left(\frac{\pi^{1/2}/I t^{1/2}}{\Delta \Phi} \right) / Q_m (\Delta x / \Delta \Phi)}{C_{\text{int}}} \right]^2 \\ &= \left[\frac{\left(\frac{\pi^{1/2}/I t^{1/2}}{\Delta \Phi} \right) / C_{\text{int}}}{1} \right]^2 \quad \text{at } t < \tau \end{aligned} \quad (1)$$

where $\Delta Q = Q_m \Delta x$ accounts for the change in the charge during a potential step, l is the characteristic diffusion length approximated here as one half of the average particle size ($l = 7 \mu\text{m}$), τ is the characteristic diffusion time constant, and Q_m is the maximal intercalation charge at full intercalation ($\Delta x = 1$). In the range of potentials corresponding to the abrupt change of the intercalation isotherm (i.e. in the vicinity of the C_{int} peaks) the potential step was as small as 5 mV; in other cases the step was varied from 10 to 50 mV. The choice of the required potential step was a compromise between the required high resolution of the data with respect to the potential (i.e. exploiting the maximum number of points in the potential region under consideration) and the accuracy of the background current subtraction. When titrations were performed in the vicinity of a slowly changing intercalation isotherm, the step chosen should not be too small, otherwise the parasitic charging current, which is not related to the solid-state diffusion, will be mistakenly encountered in the current response under consideration.

Figure 1 shows the dependence of $\log D_{\text{chem}}$ vs. potential Φ measured at 60 $^{\circ}\text{C}$ (the related phase composition of the system is indicated at the top of the figure). At the bottom, close to the phase boundaries (depicted as dotted lines), the values of the intercalation level x are indicated. Within the two-phase regions there is a strict correspondence between the cyclic voltammetric peaks (not shown in this paper) and the minima on the $\log D_{\text{chem}}$ vs. Φ plot [9]. This was first observed for lithiation of graphite at room temperature [11] and interpreted in terms of a lattice-gas model with strong attractive interactions between the intercalation sites. Here we concentrate on the temperature dependence of D_{chem} measured at different potentials. In order to describe this transition by a lattice-gas model, the portion of the intercalation isotherm related to the stage 4 to stage 3 transition ($0.12 < x < 0.22$) was rescaled with respect to the partial dimensionless intercalation level θ (ranged from 0 to 1). First proof of the model consisted in comparison between the theoretical and experimental potential dependences of $\log D_{\text{chem}}$. In brief, it is seen from Fig. 1 that in the vicinity of the potential at 0.19 V ($\theta = 0.3$) the $\log D_{\text{chem}}$ vs. Φ curve increases abruptly, approaching, at higher values of θ , a constant value designated by a straight line. Generally, the shape of the curve corresponds well with that predicted by the model [6, 7].

Such an unusual behavior of the electrode can be easily understood in the framework of the model with two different energy barrier sites. The model deals with the occupation of sites on a (100) surface of a fcc crystal [6, 7]. Two kinds of sites are present on the surface: through a bridge position A (a shallow site) the particle moves to either a two-fold nearest-neighbor site A, or to a four-fold hollow site B. Thus two distinct single-jump hopping rates W_1 and W_2 appear in the model. Interactions between the sites are neglected at this stage of the analysis (for details see the original papers [6, 7]). The

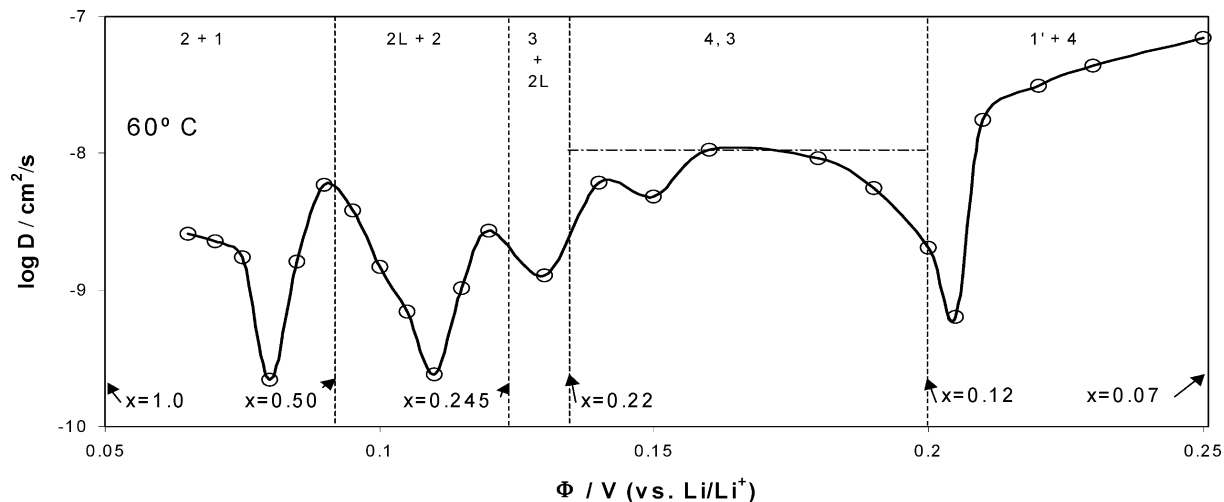


Fig. 1 A plot of the logarithm of the chemical diffusion coefficient D_{chem} vs. potential Φ measured with a graphite electrode at 60 °C. The borders of the phase boundaries are indicated

hollow sites of the stage 4 sublattice with an energy barrier E_2 are first occupied. Owing to the geometrical properties of the lattice, this occupation is completed at $\theta = 1/3$. The first peak of C_{int} at $\theta = 0.17$ signifies a half-occupation of the sublattice. In this limit, the result coincides with that expected for a lattice-gas model with one kind of energy site [8]. When $\Delta E = E_2 - E_1$ is large enough (E_1 and E_2 are the energy barriers, characterizing the diffusion from the shallow and the hollow sites, respectively), the partial occupations of both the energetically non-equivalent sites, c and y , approach to 1 and 0, respectively, despite the fact that the total θ seems to be continuous around the critical point, $\theta = 1/3$; thus full occupation of the hollow sites is attained [6, 7]. The related drastic changes in the entropy will result in a minimum of C_{int} (zero at zero absolute temperature), as opposed to the case of strong inter-particle interactions (note that the conventional first-order phase transitions in electrochemically intercalated materials occur due to highly attractive short-range interactions).

The model with two different adsorption (intercalation) sites predicts a drastic increase in D_{chem} at $\theta > 1/3$ when the shallow sites start to be occupied (these sites are characterized by a lower energy barrier, $E_1 < E_2$). The absence of inter-particle interactions should result in a constant, potential-independent D_{chem} within the whole domain $0.33 < \theta < 1$.

Another important consequence of the model is a characteristic, non-Arrhenius shape of the plots of $\ln D_{\text{chem}}$ vs. $1/T$, which originates from a specific dependence of the effective diffusion barrier on temperature in the vicinity of the critical coverage. In fact, increase in the temperature at $\theta > 1/3$ will force the particles to leave the hollow sites of the sublattice in order to occupy the shallow sites. In this case, the unoccupied hollow sites become traps for the particles moving between the shallow sites. This means that the effective energy barrier E_a^A becomes temperature dependent at θ equal to or higher

than $1/3$ [7]. Our model calculations fully support this conclusion.

In order to be consistent with application of the model to the experimental results, and to avoid complications arising from the overlap of the selected domain of x with neighboring two-phase domains, the model was fitted to the quantity D_{chem} obtained for eight different temperatures at a potential close to the middle of the selected interval of x (or θ) [9]. This was a potential step from 0.18 to 0.16 V (vs. Li/Li^+). The currents were carefully measured and treated as explained above. The related values of D_{chem} are shown as closed circles in Fig. 2, together with the estimated error bars. The solid curve represents the best fit of the theoretical curve to the experimental one. The parameters used were as follows: $E_1 = 0.122$ eV, $\Delta E = 0.437$ eV, $\theta = 0.47$, $W_2/W_1 = 6 \times 10^4$. Agreement between both curves is quite good. From the limiting low-temperature Arrhenius-shaped portion of the curve, we estimated the energy barrier between the shallow–shallow and shallow–hollow sites as $E_1 = 0.122$ eV or 1.92×10^{-20} J (11.6 kJ/mol). Correlation of these values with real crystallography of a lithiated graphite electrode is an important issue, and is currently under study in our laboratory. However, the estimated values for the energy barriers of Li diffusion related to the lithiated graphite stages 4 and 3 are in good agreement with some theoretical and experimental data on Li diffusion in a number of lithiated inorganic hosts. An ab initio study of Li diffusion paths in $\text{Li}_x\text{-CoO}_2$ results in a diffusion activation energy of 0.13 eV for the octahedral \rightarrow tetrahedral \rightarrow octahedral sites path vs. 0.27 eV for the octahedral \rightarrow octahedral sites path [13]. Using a pulsed NMR technique, the Li diffusion energy barrier both for $\text{Li}_{0.33}\text{TiS}_2$ and $\text{Li}_{0.94}\text{TiS}_2$ was found to be 6.7 kcal/mol (0.29 eV) [14].

Conclusion

A careful analysis of slow-scan rate cyclic voltammetric curves (SSCV) and chronoamperometric curves (PITT)

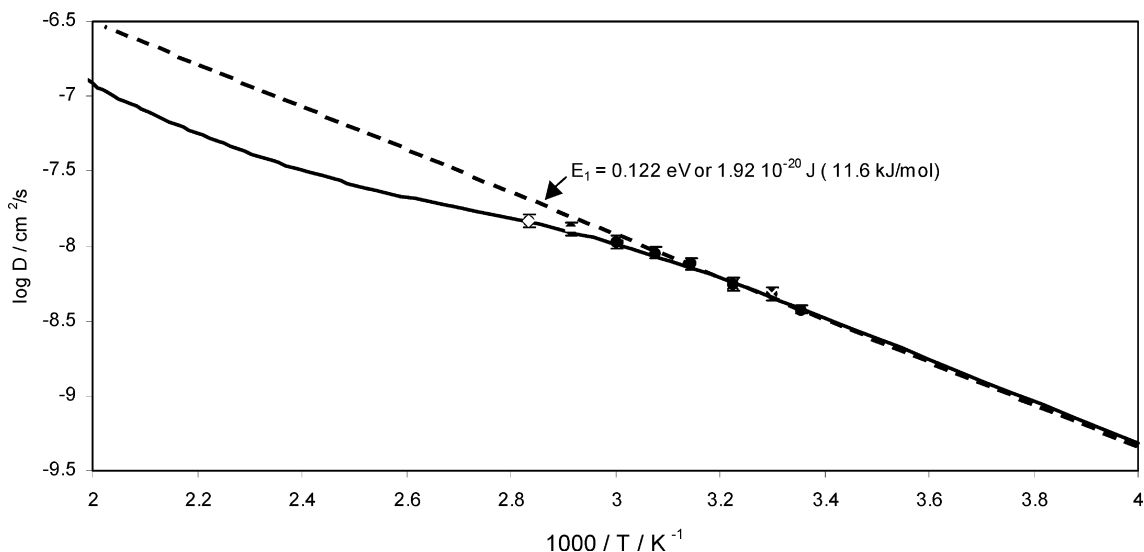


Fig. 2 Comparison between the theoretical (solid line) and the experimentally determined D_{chem} (solid circles with error bars) as functions of the inverse temperature. The values of the parameters have been found by a best fit of the calculated theoretical curve to the experimental points

related to a composite graphite electrode in a wide range of temperatures, from 25 to 80 °C, has been performed. The concept of a solid solution between the lithiated graphite stages 4 and 3 was reconsidered by adopting a thermodynamic model first proposed for description of adatoms diffusing on a surface with two different site energies. This model predicted a new type of first-order phase transition related to an abrupt increase in D_{chem} when approaching the coverage level $\theta=1/3$, and a specific non-Arrhenius shape of the D_{chem} vs. temperature plot. Both these two characteristic features have been observed experimentally in the selected domain of the stage 4 to stage 3 transition. The estimated values for the energy barriers of the Li diffusion related to the Li_xC_6 stages 4 and 3 seem to be in good agreement with the theoretical and experimental data obtained with a number of lithiated inorganic hosts.

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