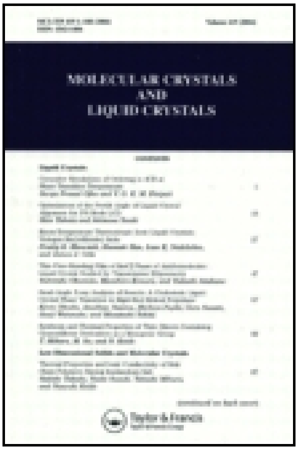

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Lithium Electrochemical Intercalation into HOPG : Kinetics Analysis of One- and Two-Phases Domains

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Electrochemical intercalation of lithium ions into HOPG has been followed using the Galvanostatic Intermittent Titration Technique. The kinetics analysis presented discriminates one- and two-phases domains, taking also into account the observation of transient lithium deposition ensuing LiC_6 appearance.

Keywords: graphite; lithium ions batteries; electrochemical intercalation

INTRODUCTION

The recent outstanding outbreak of secondary lithium batteries is related to the use of graphite or carbon intercalation compounds as negative electrode in so-called lithium-ion or rocking-chair batteries. Despite this success the kinetic aspects of the electrochemical intercalation process, a key factor for the power output, remains fundamentally poorly understood, as it appears when considering the discrepancies on published lithium diffusion coefficients[1-3]. Practically, fine graphite powders or porous carbons composite electrodes are used in order to improve this kinetic in commercially available batteries, but also in most fundamental studies, increasing modelling difficulties. Another complication lies in the occurrence of phase transitions due to the staging phenomena and therefore moving boundaries which theoretically forbid the use of Fick's diffusive equations. Taking these problems into account we analyse GITT (Galvanostatic Intermittent Titration Technique) results obtained on well ordered and geometrically defined HOPG samples, trying to discriminate one and two-phases behaviours.

EXPERIMENTAL

Electrochemical intercalation of Li^+ ions into HOPG from aprotic solutions is known to be excessively slow. This speed has been increased by regularly piercing the sample ($2*6*0.4$ mm^3, m : 4.1 mg, holes : 0.2 mm of diameter, centre to centre 0.4 mm), in order to lower diffusion lengths. The electrochemical cell involved two electrodes : HOPG as the working one and a lithium ribbon (with an area twice the sample one) as both the counter and reference ones. A PC driven galvanostat Mac-Pile II (Bio-Logic, France) was used as power source and for potential measurements. GITT intercalation was performed in a 1 M solution of $LiCF_3SO_3$ in EC/DMC, using current pulses of 10 µA during 0.5 hour followed by 0.5 hours relaxation times, so that x = 1 (in Li_xC_6) was theoretically obtained in 300 hours (150 charging hrs). DMC was distilled under vacuum, $LiCF_3SO_3$ and EC dehydrated under vacuum at 80°C and 20°C. The reported results correspond to the 4th charge cycle.

RESULTS AND DISCUSSION

The complete curve of Fig. 1 (15,000 measurements) has been decomposed for clarity's sake into four *curves a, b, c, d* corresponding to the potential values at critical steps of the current or relaxation pulses, according to the insert.

As a pseudo equilibrium one, the *curve a* agrees rather well with published works[4-6]. Therefore phases domains can be identified without new XRD investigation. Two pure stage domains appear at the x values of about 0.2 and 0.3, corresponding to the grey stage III and the blue "poor" stage IIp.

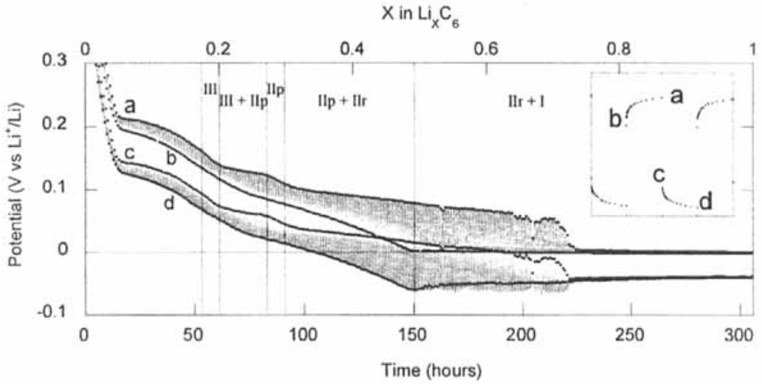

Fig 1 : GITT Potential-Time complete curve : HOPG / 1M $LiCF_3SO_3$. Potential at ends of relaxation times (a), following instantaneously current interruption (b), current establishments (c), pseudo-stationary potential at end of current pulses (d).

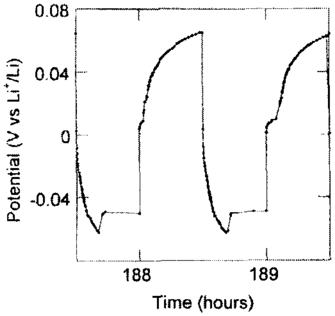

Fig 2 : Selected GITT Potential-Time curves evidencing transient Li deposition

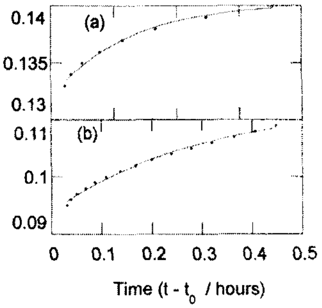

Fig 4 : Selected Potential-Time curves
(a) stage III (b) stage IIp
Experimental values : dots, Fitting : solid lines

Less obvious is the "rich" copper-coloured stage IIr domain at about x = 0.5. Pure yellow stage I was not attained but its colour clearly appeared for x above 0.5. Deformed two phases plateaux are devoted to equilibrium between these phases. For a x value of about 0.73 the potential drops suddenly near 0 V vs Li,

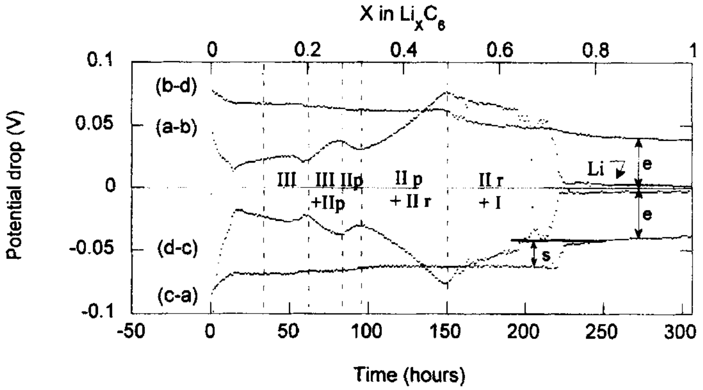

Fig 3 : Evolution of potential differences vs time deduced from Fig 1

suggesting the deposition of a permanent lithium layer onto the sample. Examination of the *curve b* reveals that this zero potential had indeed been transiently reached before, since x = 0.5, i. e. at the very beginning of the stages II/I plateau. Our interpretation is that true lithium deposition begins locally at this time, together with on going intercalation. Nevertheless the metal gets enough time to "dissolve" during the relaxation together through its oxidation by the solvent (i. e. formation of the Solid Electrolyte Interface, SEI) and through its chemical intercalation onto the sample. Indeed lithium would appear under the SEI on the graphite surface (the electron collector) in the form of aggregates which grow through the SEI until they contact the electrolyte solution. As a proof the corresponding voltage profiles (Fig 2) show for each current pulse a typical germination overvoltage followed by a plateau and for each relaxation a small plateau at about 0 V, which is significant for the presence of a lithium deposit, followed by the usual inner ionic rearrangement. Transient metal deposition may be due to difficulty for Li$^+$ ions to diffuse through the incipient saturated LiC_6 phase. Later, at the experimental dependant value x = 0.73, the excess of lithium has not enough time anymore to react entirely during the relaxation period, therefore permanent deposition ensues (in another experiment with 2 hours 5 μA current/relaxation pulses x increased to 0.83). The *curve d* itself presents also a fair minimum for x = 0.5 corroborating overvoltage lithium germination. Finally, pursuing lithium intercalation is demonstrated by XRD showing about 80% first stage at x ~ 1.

Fig. 3 reports curves obtained by subtraction between *curves a, b, c* and *d*. Obviously *(b–d)* and *(c–a)* appear as ohmic drops while *(d–c)* and *(a–b)* represent the potential sweep during the "diffusive" phenomena of relaxation or current establishment. These last curves are quite symmetric, at least until x = 0.5. The difference between the *curves (b–d)* and *(c–a)* for x above 0.5 are again explained when considering the sample as partially covered by lithium on the *curve d*, but uncovered on the *curve a*. For x < 0.5 both curves *(b–d)* and *(c–a)* cumulate ohmic drops in the sample (negligible), in the SEI (about 2 kΩ, **s** on the figure) and in the electrolyte (about 4 kΩ, **e**), while for x > 0.73 **s** is short-circuited by the lithium deposit. For 0.5 < x < 0.73 **s** appears on the *curve (c–a)* but disappears progressively on the *curve (b–d)* as result of the increasing number of emerging lithium aggregates.

Meanwhile the *curves (d–c)* or *(a–b)* can be viewed as a first qualitative preview of the evolution of diffusion coefficients D, at least before x = 0.5. The largest the potential deviations during constant time increments, the lowest the D values. So D minima seem to appear at the end of two-phases plateaux (x about 0.2 and 0.3). Indeed to our point of view D has not the same meaning in one and two phases domains, this last case being primarily relevant of boundary mobilities u[7]. In one hand apparent diffusion coefficients D_a may be inferred from boundaries moving, which involve time square root laws through the relation $D_a = u.\Delta E$ where ΔE is the experimental overvoltage. In the other hand, the use of small perturbations on two-phases plateaux often exalts one phase overcharge or over concentration aspects[8-9]. In this last case D_a appears as the average value of the two phases. A deeper analysis is in progress.

More significant is the apparent decrease of D for pure stages when the stage number decreases, which may be due to repulsive forces. Thus selected *potential-time curves* related to the stages III and IIp (Fig. 4) have been analysed. These curves are relatively symmetric after establishment or interruption of the current. Fitting them to finite diffusion exponential laws, i. e

$$E = E^{\infty} - \Delta E \exp((t_0 - t)/\tau),$$

allows to calculate time constants τ for each stage : τ (st.III) = 0.12 hr, τ (st.IIp) = 0.29 hr and therefore to evaluate D according to $\tau = l^2/D$, with l = 0.1 mm (half distance between two holes) :

$$D\,(\text{st.III}) = 2.3\ 10^{-7}\ \text{cm}^2/\text{s} \qquad D(\text{st. IIp}) = 9.6\ 10^{-8}\ \text{cm}^2/\text{s}$$

A decrease of D is effectively observed with decreasing stage number.

To conclude, GITT analysis has allowed to discriminate interfering processes. Of course more work is needed to ascertain our interpretations.

Acknowledgments

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