

PHASE CHANGES AND DIFFUSIVITY IN THE CARBON-LITHIUM ELECTRODE

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Summary

Using a coulometric technique, the phase and diffusivity changes during lithium intercalation in graphite have been studied. A carbon-lithium intercalation cell using molten LiCl-KCl (Eut.) electrolyte was prepared and used under an argon atmosphere. An approximate solution to the cylindrical Fick's diffusion problem was applied to calculate the lithium diffusivity values in graphite. Phase and diffusivity variations in the higher, and lower, stage lithium intercalation regions have been obtained for spectroscopic graphite at 476 - 482 °C.

Introduction

Graphites having varying degrees of crystalline lamellar structure react with lithium to form multiple stoichiometries or the stage intercalation compounds, $C_{6n}Li$ or more generally C_nLi [1 - 6]. The intercalation mechanism has been defined [7] to occur in two dimensions; *i.e.*, transport and orientation of intercalants occur between the weakly bonded planes of the lamellar host materials. Such properties may provide new advantages when devising unique carbon-lithium electrodes for high energy secondary batteries at ambient and high temperatures. The work presented here forms the first systematic study [8] of phase changes and diffusivity in the carbon-lithium system. A pulse coulometric method, the "Galvanostatic Intermittent Titration Technique" [9 - 12], was applied to intercalate lithium in graphite from molten LiCl-KCl eutectic.

In the GIT technique, a constant current is applied intermittently across the solid working electrode and electrolyte interface. Under GITT conditions, the diffusion of electroactive species into the solid working electrode controls its electrochemical potential. The transient potential response and resulting steady-state potentials are recorded. These can then be used in activity and single phase diffusivity calculations of the electroactive species in the solid working electrode.

Theoretical

An electrochemical carbon–lithium intercalation cell described by

Ta, LiAl(2-phase)/LiCl–KCl (Eut.)/C_(1-x)Li_x, Ta

was used. The equilibrium potential, E , of such a cell varies with the activity of lithium in carbon, in accordance with the Nernst equation. Hence, phase changes in the carbon–lithium electrode together with changes in the weight fraction, x , can be studied by applying GITT in succession.

The unsteady state diffusion in a cylinder (geometry used) with prescribed flux is described by the following equations

$$\frac{\partial C}{\partial t} = \frac{\bar{D}}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C}{\partial r} \right) \quad (1)$$

$$C(r, t) = C(r, 0) \quad 0 \ll r \ll a, t = 0 \quad (2)$$

$$\bar{D} \left(\frac{\partial C}{\partial r} \right) = \frac{I}{zFS} \quad r = a, 0 < t \ll \tau \quad (3)$$

$$\frac{\partial C}{\partial r} = 0 \quad r = 0, t > 0 \quad (4)$$

where $S (=2\pi aL)$ is the surface area, \bar{D} the average diffusion coefficient, I the applied constant current, τ the current pulse time period, z the charge number of electroactive species, and F Faraday's constant. The complete solution [13] and a more rapidly converging solution [14] for this problem are known. In the case of small values of time ($t \ll a^2/\bar{D}$), the appropriate solution [14] at the electrode and electrolyte interface ($r = a$) becomes

$$C(a, t) - C(r, 0) = \frac{I}{\pi z Fa L \bar{D}} \left[(\bar{D}t)^{1/2} i \operatorname{erfc}(0) + \frac{\bar{D}t}{a} i^2 \operatorname{erfc}(0) + \frac{3(\bar{D}t)^{3/2}}{2a^2} i^3 \operatorname{erfc}(0) + \frac{3(\bar{D}t)^2}{a^3} i^3 \operatorname{erfc}(0) + \dots \right] \quad (5)$$

The steady-state change in solute concentration is given by Faraday's Laws

$$C(r, \infty) - C(r, 0) = \frac{I\tau}{\pi z Fa^2 L} \quad (6)$$

Considering only the first three terms and replacing these by the $i^n \operatorname{erfc}(0)$ values in eqn. (5), for $t \ll a^2/\bar{D}$ one obtains

$$C(a, t) - C(r, 0) = \frac{I}{\pi z Fa L \bar{D}} \left[\left(\frac{\bar{D}t}{\pi} \right)^{1/2} + \frac{\bar{D}t}{4a} + \frac{(\bar{D}t)^{3/2}}{4\pi^{1/2}a^2} \right] \quad (7)$$

In GITT, for small currents and short polarization times the potential and concentration changes in single phase follow an approximate linear form. At

$t = \tau$ dividing eqn. (7) by eqn. (6) and using this approximation for $\tau \ll a^2/\bar{D}$ gives

$$\frac{\Delta E_\tau}{\Delta E_s} = \frac{a}{\bar{D}\tau} \left[\left(\frac{\bar{D}\tau}{\pi} \right)^{1/2} + \frac{\bar{D}\tau}{4a} + \frac{(\bar{D}\tau)^{3/2}}{4\pi^{1/2}a^2} \right] \quad (8)$$

On opening the brackets and rearranging terms in eqn. (8) one obtains

$$(\pi\tau\bar{D})^{1/2} \left(\frac{\Delta E_\tau}{\Delta E_s} - \frac{1}{4} \right) = \left(a + \frac{\bar{D}\tau}{4a} \right) \quad (9)$$

Finally, on squaring both sides of eqn. (9) and neglecting terms $O(\bar{D}^2)$, the expression for the diffusion coefficients \bar{D} for $\tau \ll a^2/\bar{D}$ becomes

$$\bar{D} = \frac{2a^2}{\tau \left[2\pi \left(\frac{\Delta E_\tau}{\Delta E_s} - \frac{1}{4} \right)^2 - 1 \right]} \quad (10)$$

where ΔE_τ and ΔE_s are the transient and steady-state potential changes, respectively. The above eqn. (10) is useful for calculating diffusivity values, \bar{D} , under GITT conditions for a cylindrical geometry [8].

Experimental

The experimental work and preparation of the electrochemical cell were carried out under argon in an inert-atmosphere system (Vac/Atmosphere Co., Hawthorne, CA). The experimental objective was to record the cell transient potentials, as well as the currents at constant cell temperature, as the concentration of lithium in graphite was increased using GITT. The magnitude of the current through the electrochemical cell and its pulse time were adjusted using a potentiostat (PAR 371) and a universal programmer (PAR 175) in the electrical circuit. A digital oscilloscope (Nicolet Explorer 2090-II) was used to record the cell transient potentials during each polarization and relaxation period. The oscilloscope and programmer were preset and manually triggered. Each cell transient potential response was recorded, with the desired magnification, on an X-Y recorder (HP 7040A). Potential changes were thus recorded with sufficient clarity and the electrolyte potential drop (IR drop) was directly measurable. A strip-chart recorder was used to record the applied current.

The cell configuration and the construction of its electrodes are shown in Figs. 1 and 2, respectively. The cell electrolyte was a purified, molten (in mol%) 42 LiCl-58 KCl eutectic (m.p. 352 °C). A two-phase, ($\alpha + \beta$), lithium-aluminum alloy was used as the reference and counter electrode material. The working electrode was a high purity (99.9995%) spectroscopic graphite rod (dia., 3 mm; density, 1.9 g cm⁻³, Ultra F/U-7). A chromel-alumel

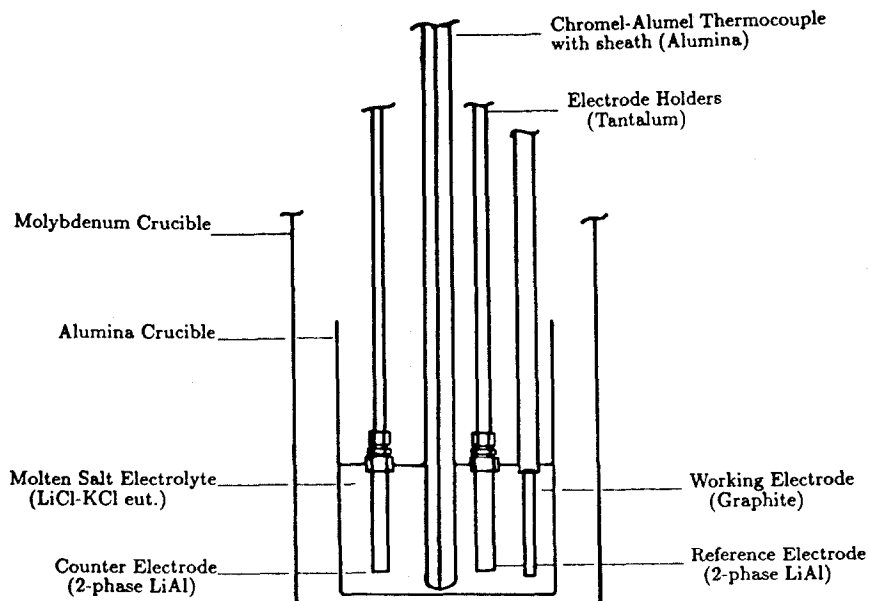


Fig. 1. Electrochemical cell configuration for the carbon-lithium intercalation experiments in molten LiCl-KCl (Eut).

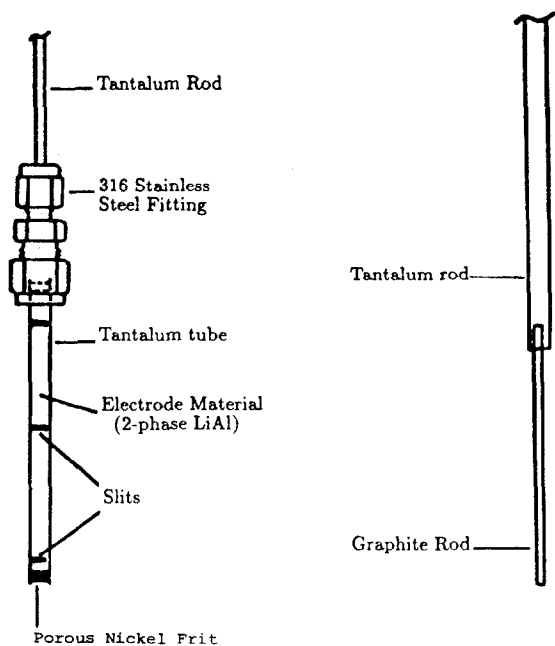


Fig. 2. Electrode construction for the carbon-lithium intercalation experiments: (a) two-phase LiAl alloy reference and counter electrodes; (b) spectroscopic graphite working electrode.

thermocouple with an alumina sheath was used to measure the electrolyte temperature. The cell vessel consisted of a 500 ml cylindrical alumina crucible (Coors/AD-998).

Ultrapure-grade lithium chloride and potassium chloride salts (Alfa, Danvers, MA) were dried under vacuum at 100 °C and 500 °C. Next, stoichiometric quantities of the dried salts were weighed and transferred into a clean alumina crucible. This was lowered to the bottom of the glove box furnace-well. The mixture melted at approximately 454 °C, after which the temperature of the molten electrolyte could be lowered if desired. The electrolyte was then purified by applying 2 V across aluminum (cathode) and graphite (anode) electrodes until the background current dropped below 0.03 mA cm⁻². The temperature of the melt was adjusted to a desired value, and the electrodes were lowered into this purified melt.

Results and discussion

An initial rest period, usually 18 h or less, was required to obtain a steady potential between the working and reference electrodes. At steady-state the potential changes were fairly small ($\leq 1 - 2$ mV h⁻¹). Lithium is known to dissolve in molten chlorides, therefore each coulometry experiment was completed within 12 - 18 h after initial steady-state was achieved. Usually an experiment was subdivided into 120 - 180 polarization and relaxation periods. A typical current pulse time of 10 s and a relaxation time of approximately 5 min were used. The current density used was 30 mA cm⁻² (values between 20 and 140 mA cm⁻² were used in one experiment).

The steady-state potentials, obtained at the end of each relaxation period, were plotted directly against the total coulombs passed during the GITT experiment. Figure 3 shows one such experimental steady-state potential variation over calculated lithium concentrations in graphite at 482 °C. This steady-state potential plot is seen to consist of regions of continuous solubility, small plateaux, and large plateaux. Not shown here, the initial steady-state potential and the small plateaux were difficult to reproduce. All of these aspects indicate that lithium intercalation in graphite proceeds to form both stoichiometric and non-stoichiometric compositions. In the higher stages region a continuous solubility of lithium in graphite (or fractional filling of host graphite) occurs. Further lithium intercalation tends towards formation of the stoichiometric compounds in the lower stages region. Hence, both single and multi-phase regions exist for the lithium intercalation compositions in graphite.

The diffusivity data were calculated from the transient and steady-state potential changes, using these values in eqn. (10). Figure 4 shows the resulting diffusivity values of lithium in graphite in a second experiment (with different stoichiometry) at 476 °C. These values show a very rapid diffusion of lithium in graphite. This is not completely unexpected [15, 16].

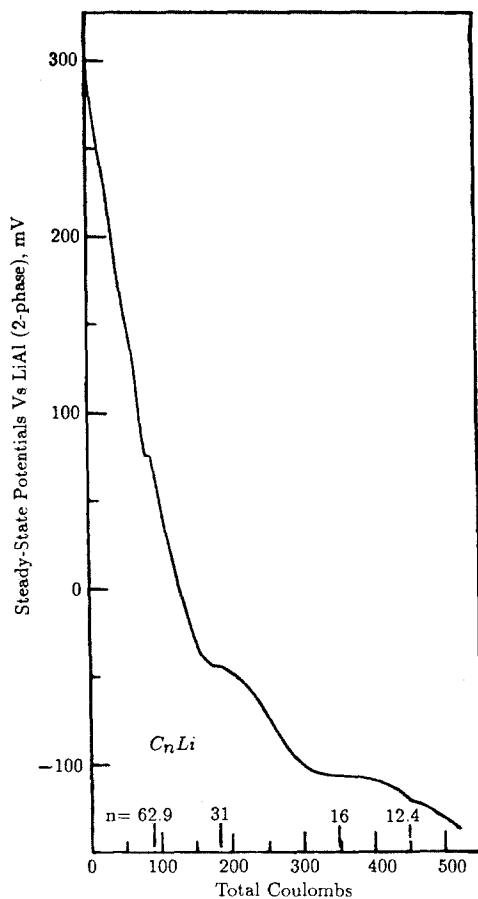


Fig. 3. Steady-state potentials *vs.* total coulombs passed in the carbon–lithium system at 482 °C, using an LiAl reference electrode. Also shown are the stoichiometric compositions formed.

Furthermore, these values are comparable with lithium diffusivities in selective three-dimensional solids, for example, those shown in Table 1. In the higher stages region these diffusivity values are less dependent on composition. In the lower stages region, the diffusivity values show fluctuations. This is clearly a region where the stoichiometric compounds can coexist with liquid-like disorder of the intercalant [19]. Hence, the fluctuations observed in the lower stages region may be sensitive to structural changes and filling in host graphite.

Conclusions

Phase changes and diffusivity in the carbon–lithium system have been studied by step-wise electrochemical intercalation in molten LiCl–KCl

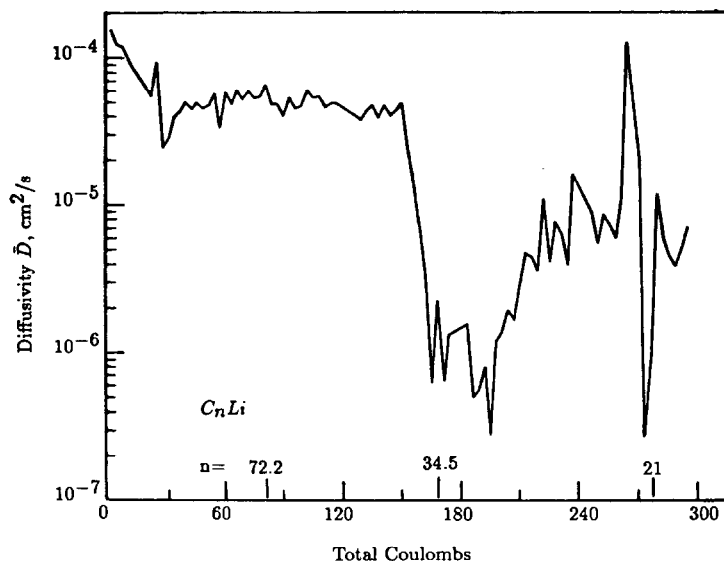


Fig. 4. Lithium diffusivity values in the carbon-lithium system at 476 °C. Also shown are stoichiometric compositions noted in the experiment at 476 °C.

TABLE 1

Comparison of lithium diffusivity in graphite and lithium alloys

Lithium alloy (single phase)	Diffusivity of lithium ($\text{cm}^2 \text{s}^{-1}$)	Temperature (°C)	Reference
Lithium-aluminum			12
$\text{Li}_{1+\delta}\text{Al}$	2.4×10^{-6}	415	
$0 \leq \delta \leq 0.25$	1.8×10^{-5}	600	
Lithium-gallium			17
$\text{Li}_{1+\delta}\text{Ga}$	$1.6 \times 10^{-6} - 6.8 \times 10^{-5}$	415	
$-0.15 \leq \delta \leq 0.20$			
Lithium-tin			18
$\text{Li}_{1+\delta}\text{Sn}$	$2.24 \times 10^{-6} - 4.1 \times 10^{-6}$	415	
$-0.8 \leq \delta \times 10^2 \leq 0.8$			
$\text{Li}_{13+\delta}\text{Sn}$	$5.01 \times 10^{-5} - 7.59 \times 10^{-4}$	415	
$-2 \leq \delta \times 10^2 \leq 2$			
Lithium-antimony			9
$\text{Li}_{3+\delta}\text{Sb}$	$2.93 \times 10^{-5} - 10^{-4}$	400	
$-7.5 \times 10^{-4} \leq \delta \leq$ 7.5×10^{-4}	$8.91 \times 10^{-5} - 2.11 \times 10^{-4}$	600	
Lithium-bismuth			9
$\text{Li}_{3+\delta}\text{Bi}$	$8.57 \times 10^{-5} - 2.51 \times 10^{-4}$	400	
$-0.15 \leq \delta \leq 0$	$1.45 \times 10^{-4} - 3.16 \times 10^{-4}$	600	
Lithium-graphite up to C_{21}Li	$10^{-4} - 4 \times 10^{-7}$	476	Fig. 4

eutectic. The Galvanostatic Intermittent Titration Technique was applied to spectroscopic-grade, cylindrical graphite electrodes. In the higher stages region, lithium shows a continuous solubility in graphite. Also lithium diffusivity values in this region are very rapid and relatively independent of composition. In the lower stages (higher lithium concentration) region, lithium solubility in graphite shows plateaux that indicate the formation of stoichiometric compositions. Lithium diffusivity values in this lower stages region show fluctuations that may be related to changes occurring within the host graphite.

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