A REVERSIBLE GRAPHITE–LITHIUM NEGATIVE ELECTRODE FOR ELECTROCHEMICAL GENERATORS

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Summary

Lithium intercalation compounds in graphite have been obtained by electrochemical methods using a solid organic electrolyte (polyethylene oxide with lithium perchlorate). Intermittent electrochemical techniques have enabled the kinetic (diffusion coefficient) and thermodynamic (enthalpy) values to be calculated. Some secondary battery cycling tests using lithium–graphite as a negative electrode are reported.

1. Introduction

Lithium is still considered to be the most promising alkali metal for electrochemical applications in high energy density batteries. In the last ten years technical developments have produced a spectacular increase in its use as a negative electrode [1], because, in addition to its thermodynamical potential (one of the lowest), it has a remarkable coulombic capacity. However, when metallic lithium is used in a normal temperature secondary battery, some cyclability problems appear due to the dendritic electrodeposition of the metal. This considerably affects the electrode geometry and increases the chemical attack of the electrolyte, leading to the passivation of the electrode by an insulating layer [2, 3].

To avoid this situation, the use of metal–lithium alloys, such as lithium–aluminium [4, 5], which dissolve/redeposit lithium reversibly, or non-stoichiometric compounds such as $Li_x WO_2$ [6] have been recommended.
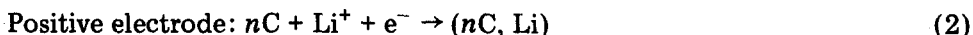
To prevent dendritic deposition on pure lithium and to attain an overall efficiency of over 90% during cycling in a secondary battery, the current density must be limited to 1 mA/cm² [2]. The aluminium electrode increases the cycling efficiency and a coulombic density of 5 C/cm² is reached, but for practical industrial purposes a minimum value of 20 C/cm² must be obtained.

Graphite is well known for its ideal lamellar structure. The van der Waals type forces between the planes are weak and so, under certain conditions, different molecules, atoms or ions can penetrate into the host structure, increasing the c-axis periodicity I_c and so form a graphite intercalated compound (G.I.C.). This G.I.C. can be characterized by its stage, which is defined as the number of host layers between two successive guest layers, so that a first stage compound in which every interlayer void is filled is the most concentrated, as with lithium, where the first stage formula is LiC_6 (gold coloured) and the second stage is LiC_{12-18} (blue coloured) [7]. Other stages are black.

The electrochemical intercalation of lithium into graphite has been made possible by the use of a solid electrolyte based on polyethylene oxide and lithium perchlorate (formula $P(OE)_8-LiClO_4$) [8]. The all solid cell is as follows:

$$Li(-)/P(OE)_8LiClO_4/G(HOPG)(+)$$

(HOPG: Highly Oriented Pyrographite), and the electrode reactions can be described as:

Negative electrode: $Li \rightarrow Li^+ + e^-$ (1)

Positive electrode: $nC + Li^+ + e^- \rightarrow (nC, Li)$ (2)

followed by: $(nC, Li) \rightarrow LiCn$ (3)

where (1) represents oxidation and dissolution of metallic lithium in the electrolyte; (2) the reduction and deposition of lithium on the HOPG; and (3) the intercalation of lithium into graphite.

Potentiometric and galvanometric intermittent titration techniques [9] (PITT and GITT) have been used in this study to determine the diffusion coefficient of lithium into graphite.

Reversibility tests of the $LiC_6-P(OE)_8LiClO_4$ electrode have also been carried out in an all solid battery using an $NiCl_2$ G.I.C. as a reversible positive electrode [10].

2. Experimental

Figure 1 shows the type of electrochemical cell used. The lithium disc of 12 mm dia. is separated from the HOPG electrode by the solid electrolyte that had been first dried and degassed under vacuum.

X-ray analysis was carried out with a Philips apparatus using Cu Kα ($\lambda = 1.5415$ Å) radiation.
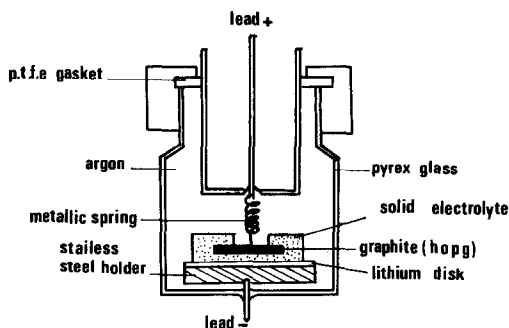
Fig. 1. Electrochemical cell schematic diagram.

3. Electrochemical intercalation of lithium

(a) PITT

A -50 mV *vs.* Li pulse was intermittently imposed on the HOPG electrode while the variation of current intensity was recorded. As Fig. 2 shows, during this first step (about 100 s) the current decreases very rapidly, and consideration of Fick's two diffusion equations under limiting conditions gives the expression for the variation of i as a function of $t^{1/2}$:

$$i(t) = \frac{2Q\tilde{D}^{1/2}}{(L+l)\pi^{1/2}} \frac{1}{t^{1/2}} \qquad \text{if} \quad t \ll \frac{(L+l)^2}{4\tilde{D}}$$

where Q is the total coulombic capacity of the guest structure, $\tilde{D}$ the diffusion coefficient of lithium, and L, l are the geometrical characteristics of the HOPG electrode.
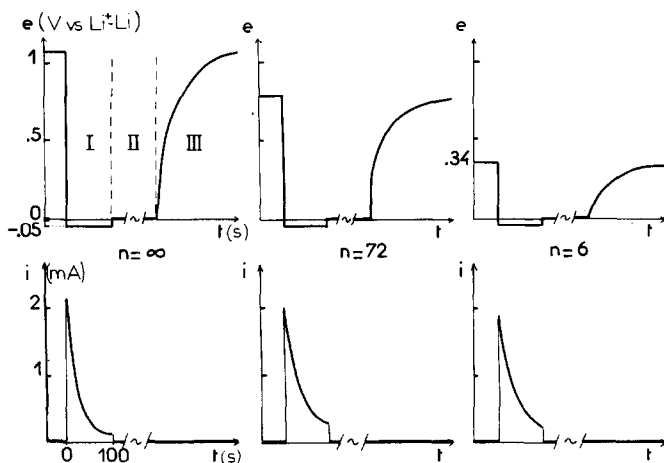

Fig. 2. PITT tests.

The linear behaviour of i as a function of $t^{1/2}$ permits the value of $\tilde{D}$ to be found:

$$\tilde{D} = 6 \pm 1 \times 10^{-8} \text{ cm}^2/\text{s}.$$

Two other successive steps then follow, the second in which the cell potential reaches zero, proving that metallic lithium has been deposited on the graphite and its intercalation is continuing until the beginning of the third step where the potential rises to a new equilibrium value which depends on the chemical activity of lithium in the GIC.

(b) GITT

In this method a current of 200 μA is imposed on the cell for about 100 s and the variation of potential is recorded (Fig. 3). Similar behaviour of the GIC electrode is found to that described above. The potential turns to a negative value (I'') when lithium deposits on the graphite. In this case, we can also calculate the $\tilde{D}$ value when we consider the variations of potential in the first step (I). We find $\tilde{D} = 4 \pm 1 \times 10^{-8}$ cm^2/s at a low level of intercalation, which is very close to the value calculated from the PITT.
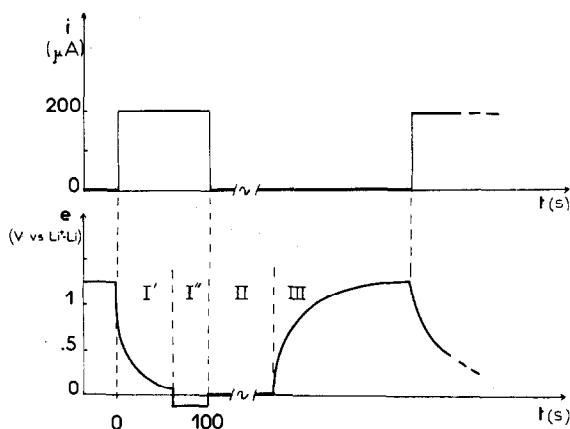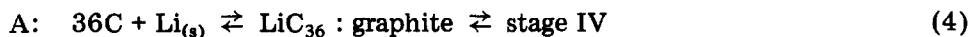

Fig. 3. GITT tests.

(c) Titration curve: OCV = f(Q)

In Fig. 4 we report the thermodynamic curve of the OCV of the Li/LiC$_n$ system as a function of Q the total coulombic quantity (proportional to $1/n$). This shows three important steps (which are in reality a succession of smaller steps), corresponding to the transitions of the graphite electrode from pure graphite ($n = \infty$) to the first stage ($n = 6$) according to the main reactions:
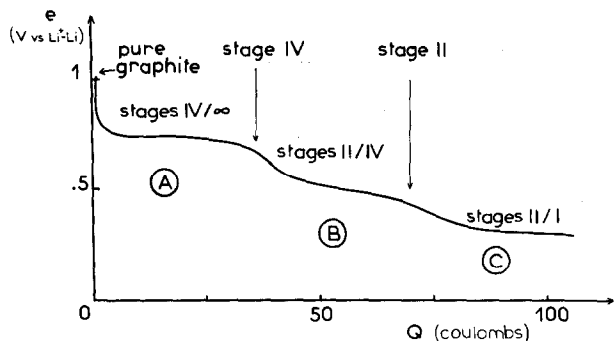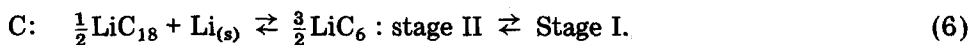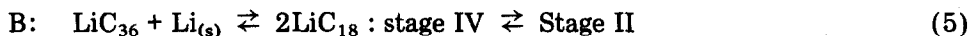
A: $36C + \text{Li}_{(s)} \rightleftarrows \text{LiC}_{36}$: graphite $\rightleftarrows$ stage IV   (4)

Fig. 4. OCV of the G.I.C./Li system.

B: $\quad LiC_{36} + Li_{(s)} \rightleftarrows 2LiC_{18}$: stage IV $\rightleftarrows$ Stage II $\qquad$ (5)

C: $\quad \frac{1}{2}LiC_{18} + Li_{(s)} \rightleftarrows \frac{3}{2}LiC_6$: stage II $\rightleftarrows$ Stage I. $\qquad$ (6)

Calculations of free energy variations for these three chemical equilibria are given by the relation $\Delta G = -eF$, where e is the corresponding step potential. So, at 60 °C, $\Delta G_4 = -16.6$ kcal/Li, $\Delta G_5 = -11.5$ kcal/Li and $\Delta G_6 = -7.7$ kcal/Li. Linear combination of the ΔG values gives the ΔG of the final reaction:

$6C + Li \rightleftarrows LiC_6$ $\qquad$ (7)

$\Delta G_7 = -9 \pm 1$ kcal/Li in a HOPG.
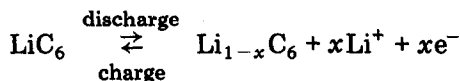
(d) X-rays and chemical analysis

The X-ray diffractogram of the final G.I.C., shows, beside characteristic rays of pure graphite, different stages (from IV to I), Table 1. Note that the presence of stage III has not been clearly observed in the thermodynamic OCV curve (Fig. 4).

The fact that we have found higher stages than the predicted first one (Q value) proves that the electro-intercalation reaction is not 100% efficient. This is confirmed by the acidimetric chemical analysis which gives LiC_{15} as the average formula of the final compound.

4. $LiC_6/P(OE)_8LiClO_4$ reversible electrode

Reversibility tests have been carried out with a chemically prepared LiC_6 compound [7] using an $LiC_6/P(OE)_8LiClO_4/Li$ electrochemical cell.
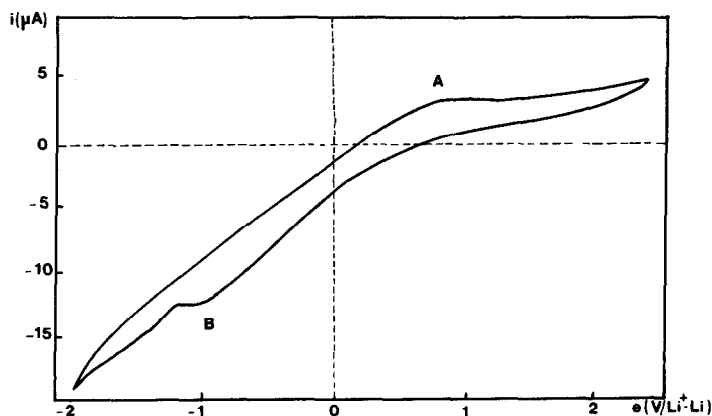
For this cell the electrode reactions can be predicted as follows:

$$LiC_6 \overset{\text{discharge}}{\underset{\text{charge}}{\rightleftarrows}} Li_{1-x}C_6 + xLi^+ + xe^-$$

and

TABLE 1

Int.	$d_{exp.}$ (Å)	Indexations (00l)				
		Stage				Graphite
		I	II	III	IV	
m	7.25		001			
m⁻	4.7					
m⁻	4.15					
m	4.03					
m⁺	3.707	001				
f	3.5		002			
m⁺	3.466			003	004	
F	3.35					002
f	2.75				005	
f	2.67			004		
m	2.35		003			
m	2.25				006	
f	2.075			005		
m	1.855	002				
f	1.77					
F	1.675					004

Fig. 5. Cyclovoltamogram of the LiC$_6$/Li system.

$$x\text{Li}^+ + x\text{e}^- \overset{\text{discharge}}{\underset{\text{charge}}{\rightleftarrows}} \text{Li}.$$
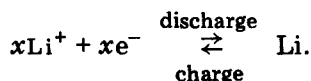
The cyclovoltamogram in Fig. 5 shows two peaks, A and B, corresponding to the de-intercalation and intercalation of lithium from/into the GIC. The kinetic conditions of de-intercalation (A) are satisfactory up to a current of 3 μA (corresponding to 50 μA/cm^2 current density), so LiC$_6$ is a good lithium electrode. The intercalation of lithium (B) occurs more easily as a current density of 200 μA/cm^2 has been achieved.

5. Conclusions

The electrochemical intercalation of lithium into graphite has been achieved by the use of a solid polymer electrolyte [8] which does not solvate the Li^+ ions as is the case with the liquid propylene carbonate/graphite system. This intercalation can lead to the first stage G.I.C. which is richest in lithium.

The use of $LiC_6/P(OE)_8LiClO_4$ as a replacement negative electrode in lithium secondary batteries can be envisaged as its mechanical properties are interesting. We can summarise these as:

— good chemical stability;
— good thermal stability (limited by the electrolyte to 120 °C);
— good mechanical behaviour (maximum expansion parallel to the c axis is 10%);
— electrochemical reversibility;
— good Faradaic capacity (340 A h/kg for LiC_6, capacity >20 C/cm^2);
— small loss of potential $vs.$ Li (300 - 400 mV).

Acknowledgments

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