

ELECTROCHEMICAL INTERCALATION OF FLUORIDES INTO PYROGRAPHITE

DENIS BILLAUD and ABDELLATIF CHÉNITE

Laboratoire de Chimie du Solide Minéral, Associé au CNRS N° 158, Service de Chimie Minérale Appliquée, Université de Nancy I, B P 239, 54506 Vandoeuvre-les-Nancy Cédex (France)

(Received August 10, 1983)

Summary

BF_4^- , PF_6^- and AsF_6^- ions have been intercalated, from their lithium salts dissolved in dry nitromethane, into pyrographite by electrochemical techniques. The synthesised intercalation compounds, of ideal formula $\text{C}_{24n}^+ \text{X}^- (\text{CH}_3\text{NO}_2)_2$ where n is the stage, were studied and electrochemical intercalation of PF_6^- and AsF_6^- is described in detail. During galvanostatic charging of the system $\text{Li}/\text{LiX}-\text{CH}_3\text{NO}_2/\text{pyrographite}$ the existence of a plateau at about 4.7 V with respect to lithium, corresponding to the transformation of a stage 2 compound to a stage 1 compound, was observed. As the charge of stage 1 varies from about C_{25}^+ to about C_{20}^+ , the potential varies from about 4.7 V to about 5 V. The galvanostatic discharge curve is similar, with the same stage transformation potentials, but with a shorter discharge duration.

Low speed cyclic voltammetry has been used to study the reversibility of the reactions and the results obtained agree with the galvanostatic measurements.

These Group V fluoride compounds synthesised in nitromethane may be compared with similar compounds produced in other solvents. They could be utilised for cathodic materials in high energy density batteries because of their high potential (about 5 V) with respect to lithium. The high basal plane conductivity (approaching $3 \mu\Omega \text{ cm}$) shows the strong metallic character of these electronic conductors.

Introduction

The feasibility of using graphite intercalation compounds as electrode materials for high energy density batteries has already been reported [1]. Among the acceptor compounds, the fluoride anions (BF_4^- and Group V fluorides) show a very high basal plane conductivity (ρ_a) especially for stages 4 and 5 (for example, ρ_a is approximately $2.2 \mu\Omega \text{ cm}$ for PF_6^-) [2]. The

compounds obtained have, in the past, been studied using various techniques X-ray diffraction and dilatometry to monitor the stage (n) and the inter-planar distance (I_c), weight uptake and elemental analysis to give the ideal formula $C_{24n}^+X^-(CH_3NO_2)_2$. Basal plane conductivities have been measured *in situ* at room temperature by a contactless method [3], and physical techniques such as nuclear magnetic resonance of ^{19}F and ^{31}P have confirmed the nature of the intercalated species [4] The electrochemical properties of these compounds have not been studied, however, and the work reported here was undertaken to obtain more information on the reversibility of the stage transformation The data obtained are compared with other published results concerning the electrochemical intercalation of fluorides in solvents other than nitromethane [5, 6]

Experimental

Highly Oriented Pyrolytic Graphite from Union Carbide (HOPG) was cut and cleaved into standard squares, 0.5 cm \times 0.5 cm \times 0.25 mm thick for X-ray characterisation and the resistivity measurements $LiPF_6$ and $LiAsF_6$ were heated to about 100 °C under vacuum to remove traces of moisture but the nitromethane, CH_3NO_2 , had to be initially dried over calcium chloride, $CaCl_2$, then over phosphorus pentoxide, P_2O_5 , and finally distilled under $CaCl_2$

The working electrode was a piece of pyrographite connected to a platinum wire, the counterelectrode a 0.5 mm dia platinum wire, and the reference electrode was a lithium ribbon in contact with the solution through a Luggin capillary The electrolyte used was the fluoride salt dissolved in CH_3NO_2 (0.5M) Galvanostatic and cyclic voltammetry experiments were performed under an inert atmosphere

Results

Figure 1 shows the charging curve of a graphite anode in 0.4M $LiAsF_6$ dissolved in CH_3NO_2 at a current of $9.57 \mu A mg^{-1}$ The potential is relative to a lithium reference electrode The plateau at 4.64 V corresponds to the transformation of stage 2 to stage 1, as seen by X-ray diffraction The charge of the carbon atoms varies from C_{25}^+ to C_{20}^+ and the potential from 4.64 V to 4.92 V for the stage 1 compound while for stage 2 the corresponding values are C_{57}^+ - C_{45}^+ and 4.4 - 4.64 V

Charging in 0.4M $LiPF_6-CH_3NO_2$ results in a characteristic of similar shape, as shown in Fig 2. The plateau, however, is at 4.75 V, the charge of the stage 1 compound varies from C_{26}^+ to C_{21}^+ , equivalent to potentials of 4.75 - 4.95 V, and with the corresponding values for the stage 2 compound being about C_{58}^+ - C_{48}^+ and 4.5 - 4.75 V, respectively

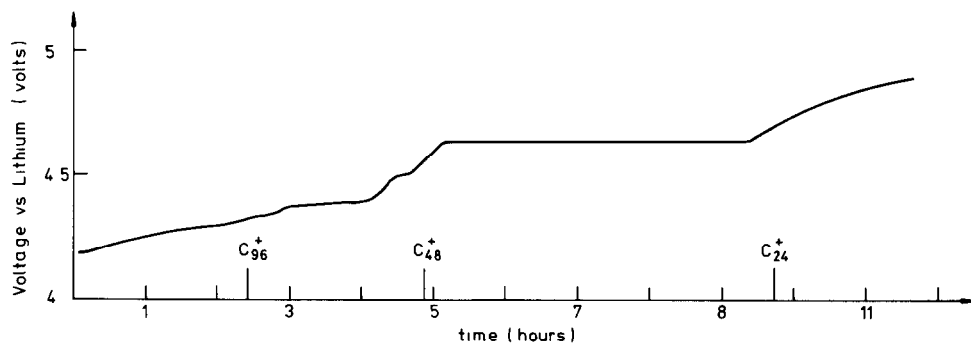


Fig 1 Constant current charge of the system $\text{Li/LiAsF}_6\text{-CH}_3\text{NO}_2$ 0.4M/graphite (electrolysis current $9.57 \mu\text{A/mg}$)

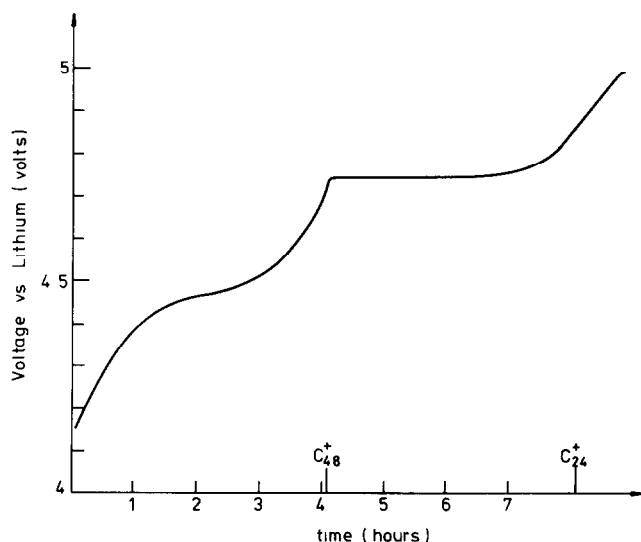


Fig 2 Constant current charge of the system $\text{Li/LiPF}_6\text{-CH}_3\text{NO}_2$ 0.4M/graphite (electrolysis current $11.3 \mu\text{A/mg}$)

A typical discharge curve at constant current, corresponding to the charge curve shown in Fig. 1, is shown in Fig. 3. Although the stage transformations occur at the same potential, the shorter length of the plateau in the discharge curve indicates non-reversibility of the intercalation process. The transformation of stage 2 to stage 1 (charge) requires 143 C g^{-1} whereas stage 1 to stage 2 (discharge) delivers only 100 C g^{-1} .

Figure 4 shows a typical cyclic voltammetry curve. Using an LiAsF_6 electrolyte dissolved in $0.4\text{M CH}_3\text{NO}_2$, the potential of the graphite (20.9 mg) with respect to lithium was varied from 3.8 to 5 V at 5 mV min^{-1} and two peaks (A and B) appear in both oxidation and reduction cycles. The potentials where the stage transformations appear (4.35 V for peak A, and 4.62 V for peak B) are in close agreement with the values observed in Fig. 1. This implies

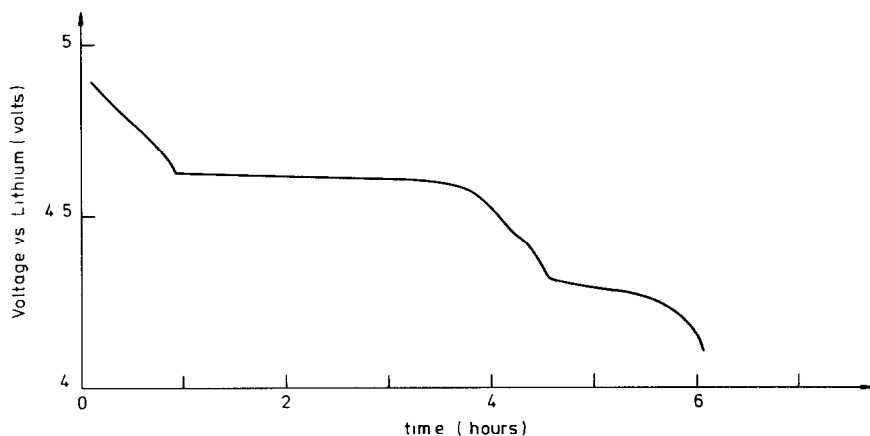


Fig 3 Constant current discharge of the system $\text{Li}/\text{LiAsF}_6\text{-CH}_3\text{NO}_2$ 0.4M/graphite (electrolysis current $9.57 \mu\text{A}/\text{mg}$)

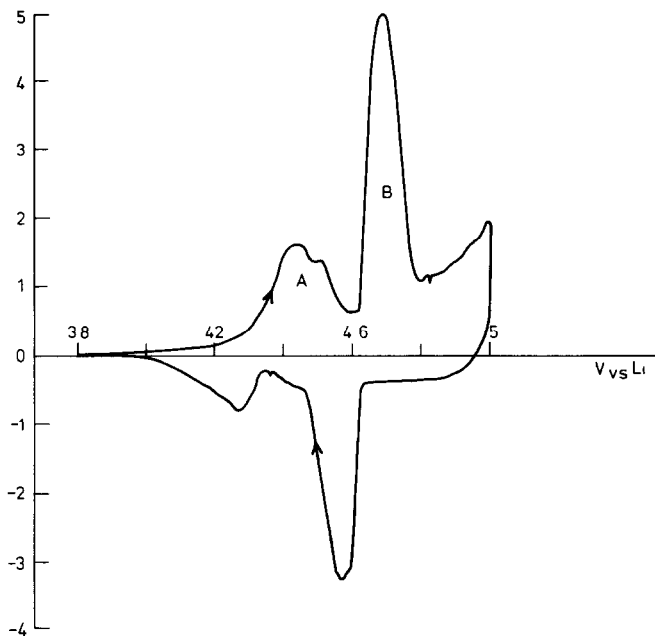


Fig 4 Cyclic voltammogram on $\text{C}_{24n}\text{AsF}_6(\text{CH}_3\text{NO}_2)_2$ at $5 \text{ mV}/\text{min}$ between 3.8 and 5 V vs Li . Peaks A and B correspond to the transformations stage $3 \leftrightarrow$ stage 2 and stage $2 \leftrightarrow$ stage 1, respectively

that peaks A and B correspond to the transformations stage $3 \rightarrow$ stage 2 and stage $2 \rightarrow$ stage 1, respectively. A significant decrease in the areas of the peaks occurs over successive cycles (Table 1)

A cyclic voltammetry curve obtained using $\text{LiPF}_6\text{-CH}_3\text{NO}_2$ (0.4M) is shown in Fig. 5. This is in agreement with the charging curve of Fig 2.

TABLE 1

| Cycle | Peak B (C g^{-1}) |
|---------------|------------------------------|
| 1 (oxidation) | 143 |
| 2 (oxidation) | 130 |
| 2 (reduction) | 121 |
| 5 (oxidation) | 114 |
| 5 (reduction) | 95 |

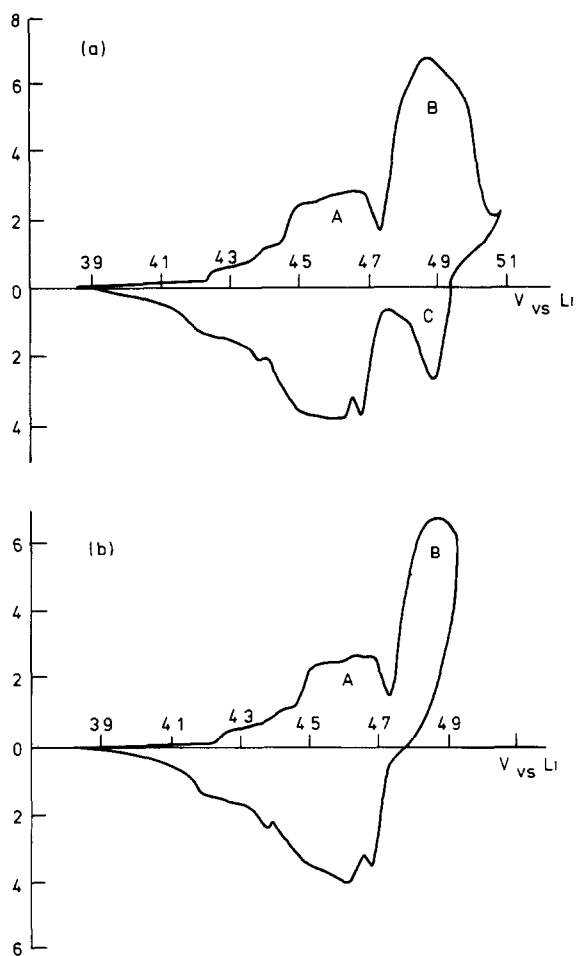


Fig 5 Cyclic voltammograms on $\text{C}_{24n}\text{PF}_6(\text{CH}_3\text{NO}_2)_2$ (a) At 5 mV/min between 3.85 and 5.1 V, (b) between 3.85 and 4.95 V. Peak C corresponds to the reversible over oxidation of the system

Compared with Fig 4, however, an additional peak, C, appears at about 5 V in the reduction cycle. This might have been due to a reversible over oxidation of the intercalation compound. A corresponding peak in the oxidation cycle cannot be resolved; it is probably contained in peak B which would, therefore, be the sum of the stage 2 \rightarrow stage 1 transformation and the reversible over oxidation. Peak C disappears when the final potential is stopped at around 4.9 V (Fig 5(b)). This behaviour of $C_{24n}^+PF_6^-(CH_3NO_2)_2$ was completely different from that of $C_{24n}^+AsF_6^-(CH_3NO_2)_2$, when no such reversible over oxidation was observed.

Discussion

Intercalation of PF_6^- and AsF_6^- into pyrographite has been obtained by electrochemical techniques using fluoride salts dissolved in nitromethane. The synthesized intercalation compounds are similar in nature with the ideal formula $C_{24n}X^+(CH_3NO_2)_2$ (where n is the stage), but each has different interplanar distances (7.8 Å and 8 Å in $C_{24n}PF_6(CH_3NO_2)_2$ and $C_{24n}AsF_6(CH_3NO_2)_2$, respectively) due to the different sizes of the intercalated anions. The electrochemical behaviour observed during galvanostatic charge and discharge is similar in both cases with a well defined plateau corresponding to the stage 1 \leftrightarrow stage 2 transformation at comparable potentials.

The cyclic voltammograms, however, do differ. The extra transformation peak of the graphite/ PF_6^- system is at a higher potential than the stage 2 \leftrightarrow stage 1 transformation, and might be due to over oxidation of the carbon with the formation of covalent C-F bonds. It is known that AsF_6^- and SbF_6^- are more powerful fluorinating agents than BF_4^- and PF_6^- ions. Thus, it can be assumed that over oxidation with the graphite- AsF_6^- system leads to strong covalent bonds and, hence, cannot be seen in the cyclic voltammogram during the reduction process.

The formation of such C-F bonds remains to be checked by direct characterization methods (^{13}C nuclear magnetic resonance, electron spectroscopy for chemical analysis or ^{19}F nuclear magnetic resonance). Differences between normal and over oxidised compounds, however, have already been observed in terms of the basal plane resistivity, infra-red reflectivity, and X-ray diffraction [7]. Compounds synthesised from fluorides dissolved in propylene carbonate (PC) [6] have a different formula, $C_{24n}X^-(PC)_4$. These compounds give curves similar to our findings although there is no information on the reversibility of the reactions appearing after the formation of stage 1. It would be interesting to see if the reversible over oxidation observed in the compounds studied here also appears with solvents different from nitromethane. Because of their high potential against lithium and because of the reversibility of the over oxidation observed, certain of these fluoride intercalation compounds are interesting materials for use in high energy density batteries.

References

- 1 M Armand and P Touzain, *Mater Sci Eng*, 31 (1977) 319
- 2 D Billaud, A Pron, F L Vogel and A Hérold, *Mater Res Bull*, 15 (11) (1980) 1627
- 3 E J McRae, J F Maréché and A Hérold, *J Phys E Sci Instrum*, 13 (1980) 241
- 4 G R Miller, H A Resing, F L Vogel, A Pron, T C Wu and D Billaud, *J Phys Chem*, 84 (1980) 3333
- 5 J Besenhard, *Thesis*, Munich, 1973
- 6 A Jobert, P Touzain and L Bonnetain, *Carbon*, 19 (1981) 193
- 7 D Billaud, Ph Flanders, A Pron and J E Fischer, *Mater Sci Eng*, 54 (1982) 31