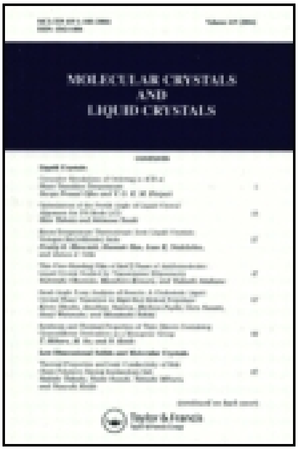

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ELECTROCHEMICAL REDUCTION OF GRAPHITE AND FULLERENES FROM SOLID LITHIUM SALT/POLYMER ELECTROLYTES

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Abstract Electrochemical reduction of graphite and fullerenes has been carried out in solid state cells operating with solid polymer electrolytes based on poly(ethyleneoxide), (PEO), complexed with lithium perchlorate. Low speed cyclic voltammetry, galvanostatic reduction and oxidation experiments give evidence for different successive redox states which appear during the cycling of both carbon materials. Preliminary electron diffraction studies have been performed on selected intercalated fullerenes.

INTRODUCTION

Solid state batteries are suitable to carry out the intercalation in host structures of unsolvated cations in contrast with cells operating with liquid electrolytes[1,2]. For example, the intercalation of Li^+ into graphite from liquid electrolytes leads usually either to the formation of low intercalant content compounds or to the decomposition of the intercalated solvent which degrades irreversibly the host material[3]. Only few specific salt and solvent liquid associations allow the obtention of binary unsolvated Li^+-graphite phases[4,5]. The use of solid electrolytes can also prevent the dissolution of the host electrodes which can occur before or during the intercalation process as already reported for certain fullerides[6]. We have studied the electrochemical intercalation of Li^+ ions into large specific area carbon materials (CM) such as divided graphite or fullerene C_{60}/C_{70}(90/10) by using a solid electrolyte based on polyethylene oxide (PEO) and lithium perchlorate $LiClO_4$. The button cell used is as follows : (CM)/$P(EO)_8LiClO_4$/Li.

Low speed cyclic voltammetry, galvanostatic reduction and oxidation experiments have been performed to study the reversibility of the intercalation process. Some preliminary electron diffraction studies have been carried out on selected intercalated fullerenes. Finally, our results will be discussed as regards to other previously published works.

EXPERIMENTAL

Button-type cells were composed of metallic Li negative electrode, $P(EO)_8LiClO_4$ polymer electrolyte film and a composite positive electrode containing active material and electrolyte, cast from acetonitrile dispersion onto a stainless steel current collector[1,2,12]. The cells were operated under an argon flow at 83°C to insure a high ionic conductivity of the electrolyte[7]. Divided natural graphite (UF4 from Le Carbone Lorraine, average diameter = 7 µm) and fullerene C_{60}/C_{70} from MGP-ISAR were vacuum heated at 300°C and 180°C respectively before utilization. For transmission electron microscopy (TEM) studies, fullerene was dissolved in acetonitrile. The solution thus obtained was cast on the amorphous carbon of a copper TEM specimen grid. This grid was heated at around 120°C under vacuum to remove the solvent residus and then placed in the composite electrode of the cell.

RESULTS AND DISCUSSION

Figure 1 gives the cell voltage recorded during the galvanostatic reduction and oxidation of a composite electrode containing ca. 55 weight % divided UF4 graphite and 45 w % $P(EO)_8$ $LiClO_4$. Both curves present voltage plateaus corresponding to stage transformations and slopes related to the stoichiometric domains of pure stages. During the reduction, the initial potential close to 2.9 V decreases sharply up to about 200 mV which corresponds to a first short plateau. Then, the potential decreases again to a second plateau at 105 mV. A shoulder appears however at ca. 130 mV. Finally, a third long plateau starting at 80 mV is followed by a decrease of the voltage up to 0 V corresponding to the metal lithium deposition. The oxidation curve which is 31 % shorter than the former reduction curve presents 4 plateaus at ca. 50, 100, 125 and 230 mV. The reduction curve is very similar in shape to that obtained recently with a pyrographite electrochemically reduced in an ethylene carbonate (EC) based electrolyte allowing only unsolvated Li^+ ions to be intercalated[4] : in this case, the different slopes have been related to the composition domains of pure stages identified by X-ray diffraction studies : thus, stage I LiC_6, stage II LiC_{12}, stage II LiC_{18} and stage III are certainly responsible for the slopes of the reduction curve presented in figure 1. In contrast with the similarity observed between the shapes of the reduction curves obtained in solid state cells or with the EC based electrolytes, the oxidation curves are somewhat different. The first oxidation plateau appearing in figure 1 at the average potential value of 50 mV is clearly extended over a large amount of coulombic charges in contrast with what is observed in the oxidation obtained in EC electrolytes where this first plateau is only marked by a short shoulder. Thus, the extraction of Li^+ from graphite in solid cells occurs via the same successive processes observed during the reduction, ie, $LiC_6 \rightarrow LiC_{12} \rightarrow LiC_{18}$... stage transformations whereas in EC based electrolytes, simultaneous transformations of LiC_6, LiC_{12} and LiC_{18} into a stage III are observed and characterized by a unique long plateau at ca. 150 mV. These differences are probably related to the balance between the solvation energy of Li^+ and the interactive energy between intercalated Li^+ and graphite, the last one being dependent on the Li/C ratio. Kinetic effects should also be taken into account due to differences in Li^+ mobility through the electrode/electrolyte interface.

Moreover, it must be noticed that the experimental yield in solid state cells is much lower than that obtained in liquid electrolyte cells. In fact, the actual experimental composition in the solid state cell of the stage I is LiC_{23} instead of the theoretical LiC_6 composition.It mean that only 26 % of graphite is intercalated assuming a LiC_6 composition This low yield is depending on the quality of the contact between the solid electrolyte and the electrode. It is also related to the intergranular diffusion and therefore to the particule size, the binder /active material ratio and the pressure needed to obtain the pressed electrode as described elsewhere (13).

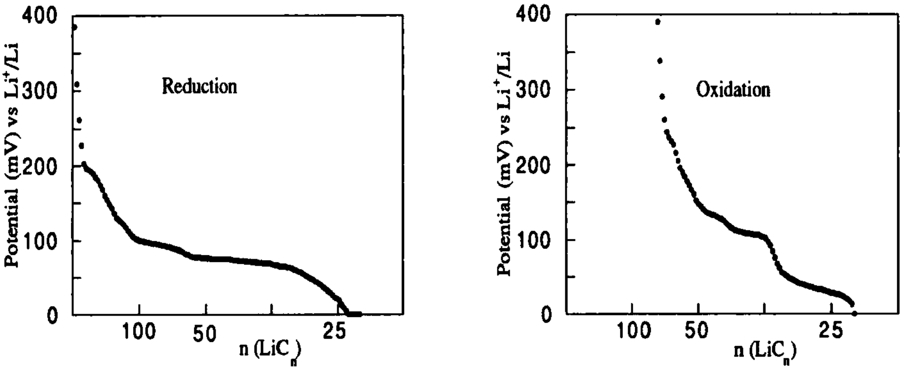

Fig. 1 Constant current reduction and oxidation curves at 1.55 µA/mg and 83 °C of the system Li/ $P(EO)_8$-$LiClO_4$ / Graphite (UF4)- $P(EO)_8$-$LiClO_4$ composite in the weight ratio 55/45, (graphite weight : 2.43mg).

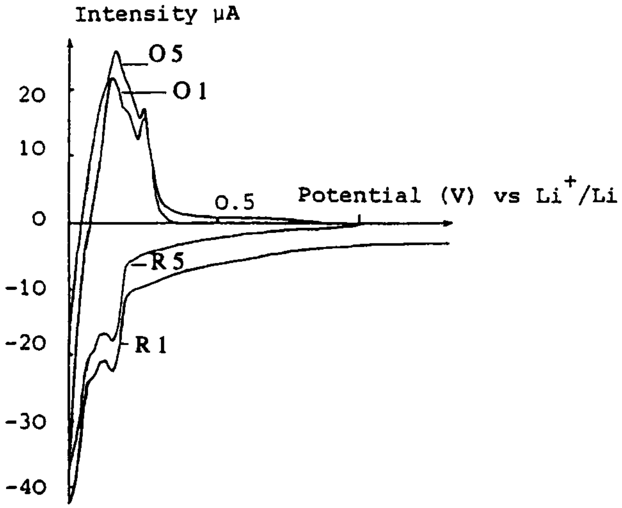

Fig. 2 Cyclic voltammograms of the system of the figure 1 recorded for a 1.5 mV/mn sweep rate. R1 (O1) and R5 (O5) represent the first and fith voltammograms obtained in reduction (R) and oxidation (O) processes.

Figure 2 shows the 1st and 5th voltammograms performed using the same solid cell. The first reduction wave R1 is characterized by a noticeable negative current appearing from the reduction beginning up to 198 mV. Beyond this value, a peak at 154 mV, a shoulder at 77 mV and an unachieved peak at 0 mV are observed. Corresponding transformations appear during the oxidation wave at 148, 184 and 255 mV. The 5th cycle presents the same transformations but the initial negative current probably due to side reactions is strongly diminished.

The faradic yield of the first reduction is fairly low since only 14 w % of graphite is intercalated assuming a LiC_6 composition. It is clear that solid state intercalation leads to inhomogeneous materials, even at low current densities or low potential sweep rates contrary to the intercalation in liquid electrolyte where the active host material is in permanent contact with the intercalant.

Figure 3 presents the first cyclovoltammogram of the system :
C_{60}-P(EO)$_8$LiClO$_4$ (30/70)/P(EO)$_8$LiClO$_4$/Li recorded at 1.5 mV/mn between 2.58 and 1.10 V. Three well defined peaks are apparent during the reduction wave (A, B,C) and during the oxidation cycle (A', B', C'). The potentials corresponding to these transformations are respectively 2.44, 2.05 and 1.58 V. This curve is very similar to the one recently proposed by Chabre et al.[8] who used the step-potential electrochemical spectroscopy (SPES)[9]. This technique has allowed these authors to achieve the obtention of Li_xC_{60} in quasi-equilibrium conditions and to propose for the three A, B and C redox transformations, x values equal to 0.5, 2 and 3 respectively. They found also two other transformations in the reduction wave as a shoulder at 1.0 V on a broad peak at 0.8 V and corresponding to x values equal to 4 and 12 respectively. The related reoxidation peaks do not appear on the voltammogram probably due to an extensive reorganization of the solid C_{60}.

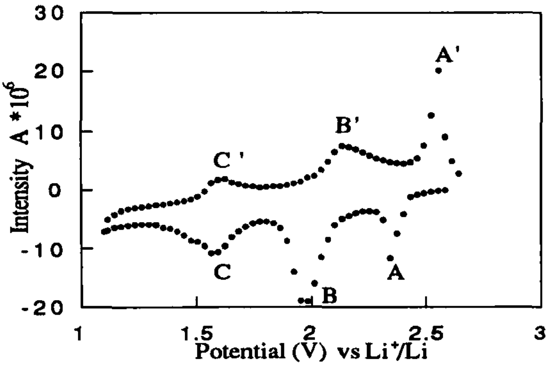

Fig. 3 Cyclic voltammogram of the system Li/ P(EO)$_8$-LiClO$_4$ /C_{60}P(EO)$_8$-LiClO$_4$ composite in the weight ratio 30/70, sweep rate =1.5 mV/mn (active weight : 2.9 mg)

The reduction and oxidation curves of C_{60}-P(EO)$_8$ LiClO$_4$ composite (weight ratio 68/32) are reported in figure 4. The 23.5 μA constant current reduction curve exhibits five plateaus at 2.35, 1.99, 1.6, 0.90 and 0.65 V in agreement with the redox transformation values presented in the voltammogram of figure 3 and in reference[8].

However, the 5.55 μA oxidation carried out on the same sample and after a potential relaxation up to 0.59 V shows only three plateaus at 2.45, 2.1 (shoulder) and 1.1 V.

The two first plateaus are related to the A' and B' transformations presented in figure 3. No plateau at 1.6 V corresponds to the C' peak while the plateau at 1.1 V could be related to each or both transformations described in the voltammogram given in reference[8]. More studies in these potential ranges are needed to interpret these events.

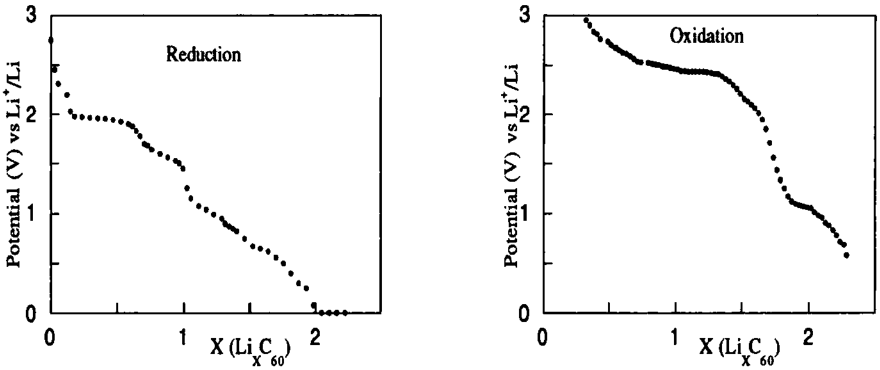

Fig 4 Constant current reduction (electrolysis current = 23.5 μA) and oxidation (electrolysis current = 5.55 μA) at 83°C of the system Li/P(EO)$_8$-LiClO$_4$/C60-P(EO)$_8$-LiClO$_4$ composite in the weight ratio 68/32 (C_{60} weight : 3.58 mg).

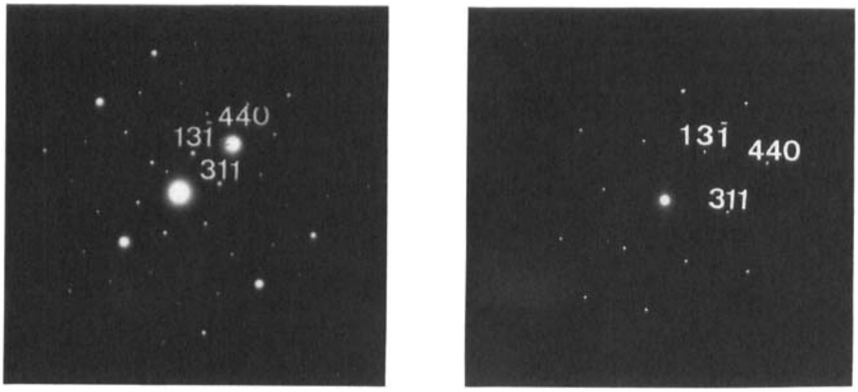

Fig. 5 Transmission electron diffraction diagrams for Li/C_{60} selected phases. The selected electron diffraction pattern can be indexed as the [-1 1 2] zone axis from a fcc crystal.

Preliminary electron diffraction studies have been carried out on samples of C_{60} deposited on the TEM grids and intercalated galvanostatically up to 1.99, 1.00 and 0.45 V with current densities equal to 0.85, 0.76 and 1.55 μA/mg. It appears that the samples are very inhomogeneous and present mixtures of amorphous and cristalline phases. In these conditions, it is not possible to make a suitable correspondence between a phase observed and the potential reached for the intercalation. However, besides the previously described undoped C_{60} phase (fcc, a = 1.42 nm[10,11]) we found two different phases corresponding to fcc systems with parameters a equal to 1.436 nm and 1.469 nm (figure 5A and 5B). These studies are still currently in progress in order to correlate these phase to the electrochemical events.

CONCLUSION

Solid state cells are suitable to obtain the intercalation of unsolvated cations into host structures such as graphite and fullerenes. However, their design leads usually to inhomogeneous materials due to the growth of an intercalation front from the surface of the host structure in contact with the solid electrolyte towards the electron collector. The intercalation process is thus limited both by the cation diffusion through the solid electrolyte/carbon electrode interface and through the electrode. In this case, the use of composites made of host materials and ionic conducting electrolyte can prevent partially these diffusion problems which are more or less important depending on the sign and the value of the electrolysis current or on the direction of the potential sweep.

Studies of optimal synthesis equilibrium conditions are in progress and will therefore lead to a better characterization of the phases obtained at a given potential. TEM studies appear to be suitable for identifying these intercalated phases.

REFERENCES

1. M.B. Armand, Material for Advanced Batteries, p. 145.
   D.W. Murphy, J. Broadhead and B.C. Steele Eds., Plenum, NY (1980)
2. R. Yazami and P. Touzain, J. Power Sources, 9, 365 (1983)
3. P. Willmann, Thesis, Nancy (1979)
4. D. Billaud, F.X. Henry and P. Willmann, Mat. Res. Bull., vol 28, 5, 477 (1993)
5. D. Guyomard and J.M. Tarascon, J. Electrochem. Soc., 4, 139, 937 (1992)
6. C. Jehoulet, A.J. Bard and R. Wudl, J. Am. Chem. Soc., 113, 5446 (1991)
7. M.B. Armand, Polymer Electrolyte Reviews, J.R. Mac Callum, C.A. Vincent Eds (Elsevier Applied Science, London, 1987) vol. 1, 1 (1987)
8. Y. Chabre, D. Djurado, M. Armand, W.R. Romanov, N. Coustel, J.P. Mc Cauley, J.E. Fischer and A. Smith, J. Am.Chem.Soc., 114, 764 (1992)
9. C. Mouget and Y. Chabre, in Multichannel Potentiostat Galvanostat "Mac Pile", licensed from CNRS & UJF Grenoble to Bio-Logic Co., 1, av. de l'Europe, 38640 Claix, France
10. H.W. Kroto, J.R. Heath, S.C. O' Brien, R.F. Curl and R.E. Smalley, Nature, 318, 162 (1985)
11. N. Troullier and J.L. Martins, Phys. Rev. B. 46, 3, 1754, (1992)
12. D. Billaud and S. Lemont, Electrochemica Acta, 37, 9, 1675 (1992)
13. S. Lemont and D Billaud, to be published.