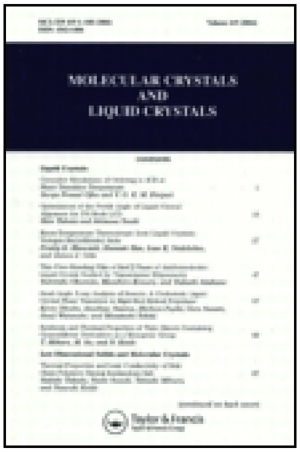

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Electrointercalation of Lithium into Graphite : Effects of the Electrolyte Composition and the Graphite Surface Treatment

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Electrointercalation of lithium into graphite : effects of the electrolyte composition and the graphite surface treatment

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The graphite surface was modified in order to obtain the reversible lithium intercalation upon cycling in electrolytes containing only PC as a solvent species. Such surface modifications were obtained (i) by wetting graphite in chloro ethylene carbonate, or (ii) by forming previously a passivating layer by reducting graphite in EC or Cl-EC based electrolytes or finally (iii) by cycling in mixed PC+Cl-EC electrolytes. In all cases, high reversibility and high electrochemical capacities were obtained.

Keywords: Graphite; lithium; passivating layer; propylene carbonate; intercalation

INTRODUCTION

During the past years, large effort has been dedicated to the development of secondary "lithium ion" batteries using carbonaceous materials as anodes. Such materials must display the following properties: high specific capacity, low potential vs Li^+/Li of the intercalation and deintercalation processes and compatibility with electrolytes. These properties are partially fulfilled by graphite which displays a theoretical capacity of 372 Ah/Kg, corresponding to the compound LiC_6. However, the electrochemical intercalation of lithium into graphite, which occurs at potentials below 0.3 V in selected electrolytes, is not possible when propylene carbonate (PC) is used as a unique solvent [1,2,3]. In that case, graphite exfoliation and an electrical disconnection of the particles have been observed. The destruction of the graphite structure is due to the co-intercalation of the PC molecules which are reduced liberating propylene which exfoliates the graphene sheets. The prevention of such a graphite exfoliation can be obtained if a passivating film is formed on the surface graphite before the lithium intercalation.

In the present research, different ways were investigated to allow reversible lithium intercalation to occur in electrolytes containing only PC as solvent species.

EXPERIMENTAL

Electrochemical studies were carried out in a two-electrode cell: the counter electrode is a lithium ribbon acting also as a reference electrode, the working composite electrode is composed of 96% (w/w) of graphite (UF4 le Carbone Lorraine) and of 4% (w/w) of a binder PVDF (Aldrich). Ethylene carbonate (EC) and propylene carbonate were outgassed under vacuum while chloro ethylene carbonate (Cl-EC) is used as received. $LiClO_4$, $LiBF_4$ and $LiAsF_6$ are heated under vacuum at 150, 80 and 120°C respectively. The galvanostatic cycling measurements were carried out using a multi-channel microprocessor-controlled Mac Pile potentiostat/galvanostat. The electrochemical capacity X is referred to the Li_xC_6 composition.

RESULTS AND DISCUSSION

Fig. 1 shows the first galvanostatic charge-discharge cycles of graphite UF4 in the following electrolytes: PC/$LiClO_4$ (1mol.dm^{-3}), EC/$LiClO_4$ (1.5mol.kg^{-1}) and Cl-EC/$LiClO_4$ (1mol.dm^{-3}). During the first reduction of graphite, an irreversible process occurs. It is characterized by the presence of potential plateaux at 0.9, 0.8 and 1.7 V vs Li^+/Li respectively. In the presence of EC and Cl-EC, the curves exhibit a succession of plateaux between 0.25 and 0 V. These plateaux are characteristic of a multiphase system corresponding to the well known formation of graphite intercalation compounds of lithium [4,5]. On the contrary, in the presence of PC, such a reversible intercalation does not occur and

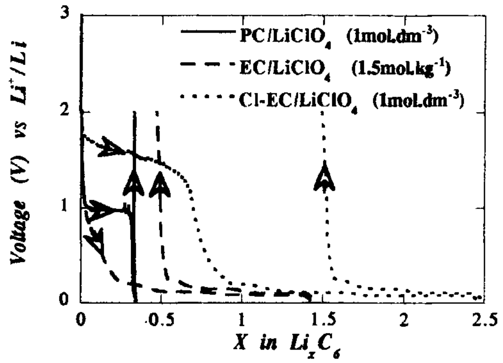

FIGURE 1 First galvanostatic cycle of the UF4-PVDF composite electrode in PC/LiClO4, EC/LiClO4 and Cl-EC/LiClO4.

the long horizontal plateau present at 0.95 V is attributed to the graphite exfoliation resulting from the decomposition of PC and the simultaneous evolution of propylene between the graphene layers. Since PC exhibits more attractive properties than most other electrolytes, we investigated the possibility of cycling graphite in a PC based electrolyte, employing various methods. One is to use a mixture of solvents like PC+Cl-EC since Cl-EC is able to form a passivating layer at a potential higher than that corresponding to the PC decomposition and to graphite exfoliation [6,7]. The second one is to cover the graphite with a wetting solvent to modify its surface properties and therefore the interactions with PC and graphite. Finally, the third one is to use graphite electrodes previously covered by a protective layer formed in a selected electrolyte. Fig. 2 shows the first and fourth charge-discharge curve of graphite in PC(95% v/v)+Cl-EC(5% v/v)/LiClO4 (1mol.dm^{-3}). The shape of the first cycle is comparable to that obtained in Cl-EC/LiClO4 electrolyte. The irreversible capacity decreases upon cycling as seen in the fourth cycle while the reversible capacity remains constant around the LiC$_6$ composition. The influence of the concentration of Cl-EC in PC on the value of the irreversible capacity is negligeable as shown in fig. 3. Thus, when a small amount of Cl-EC is added to PC, the reversible cycling of graphite can be achieved with a high capacity. The influence of the nature of the lithium salt contained in the Cl-EC+PC mixture was also investigated. Fig. 4 displays the evolution of the reversible capacity X as a

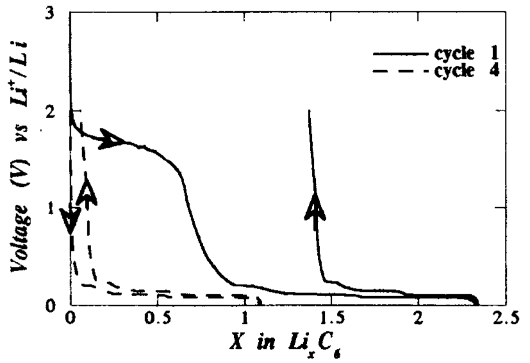

FIGURE 2 Charge and discharge curves of the composite electrode UF4-PVDF in PC(95% v/v)+Cl-EC(5% v/v)/LiClO$_4$ (1mol.dm^{-3}).

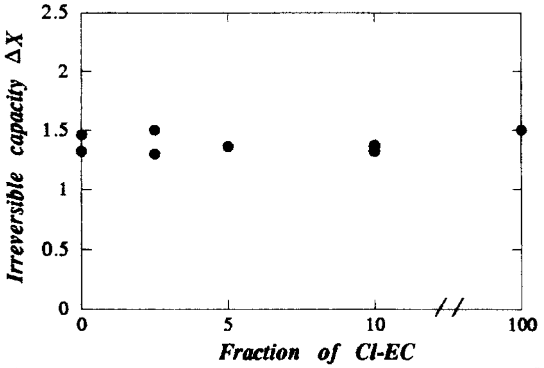

FIGURE 3 Irreversible capacity ΔX versus volumic ratio Cl-EC/PC+Cl-EC.

function both of the type of lithium salt (LiClO$_4$, LiBF$_4$ and LiAsF$_6$) and of the cycle number. It appears that the best cycleability and the highest capacity are obtained when LiClO$_4$ and LiAsF$_6$ are used. In the presence of LiBF$_4$, the capacity decreases as the cycle number increases. In fact, the layer formed in these conditions on the graphite surface is dense and exhibits a low ionic conductivity. This layer is mainly composed of LiF characterized by TEM and EELS. With LiAsF$_6$, the passivating layer contains C, O and F evidenced by EELS measurements, but oxygen content is higher than that of fluorine. A more comprehensive study of the reduction mechanisms of these electrolytes needs further investigations which are now in progress [8]. Since Cl-EC is a strong wetting agent of graphite, a composite graphite electrode was previously immersed several minutes in pure Cl-EC and then placed, without rincing, in a

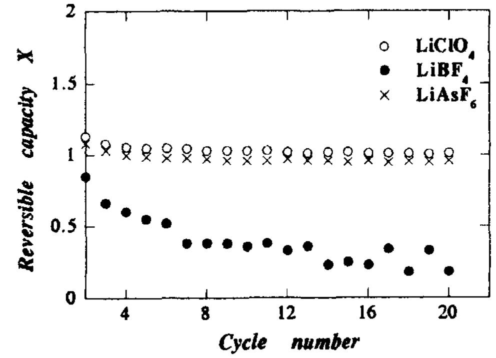

FIGURE 4 Cycleability of the graphite electrode in electrolytes containing different salts $LiClO_4$, $LiBF_4$ or $LiAsF_6$ in PC(90% v/v)+Cl-EC(10% v/v).

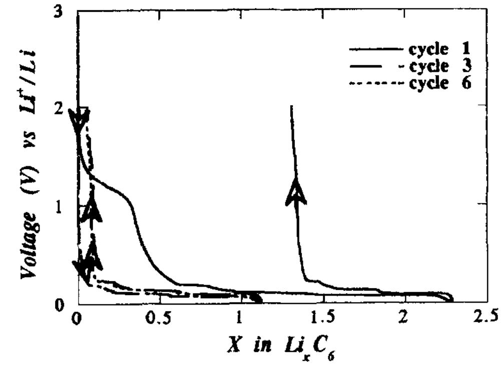

FIGURE 5 Galvanostatic charge-discharge cycles of the treated electrode in PC/$LiClO_4$ (specific current=7μA/mg, T=20°C). The electrode is initially immersed in a solution of Cl-EC for some minutes.

cell containing PC/$LiClO_4$ as electrolyte. Fig. 5 shows several charge-discharge cycles obtained in these conditions. Cl-EC adsorbed on graphite is reduced at around 1.2 V to form a passivating layer allowing graphite to be cycled reversibly with a high capacity in the PC/$LiCLO_4$ solution. At low potentials, the presence of plateaux shows that the reversible intercalation occured. The irreversible capacity observed during the first cycles is comparable to the values obtained with Cl-EC/$LiClO_4$ and PC+Cl-EC/$LiClO_4$ electrolytes as shown in fig. 3 for the Cl-EC fraction equal to zero. Finally, cycling in PC/$LiClO_4$ is also possible when graphite is previously reduced in EC/$LiClO_4$ or Cl-EC/$LiClO_4$ electrolytes to form a passivating layer. Such data were previously described elsewhere [9]. The efficiency of the Cl-EC based electrolytes containing $LiClO_4$ was also shown by cycling at 60°C without reversible capacity loss.

CONCLUSION

Intercalation of lithium into graphite is not possible in electrolytes containing only PC as solvent. However, the substitution of the methyl group of the PC molecule by hydrogen or an halogen leads to solvents which can be reduced to form passivating layers allowing reversible lithium intercalation to occur. Intercalation of lithium can be obtained however in PC when the surface of graphite is previously treated. One way is to form a passivating layer by reducting graphite in EC or Cl-EC based electrolytes, the other way is to wet graphite with pure Cl-EC, which can be strongly adsorbed on graphite. In all these cases, the cycleability in PC is achieved with a good reversibility and a high capacity. The identification of the reduction products of the Cl-EC based electrolytes is currently under investigations in order to understand the reduction mechanisms of Cl-EC in the presence of PC.

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References

[1.] A. N. Dey and B. P. Sullivan, J. Electrochem. Soc., **117**, 222 (1970)
[2.] M. Arakawa and J. I. Yamaki, J. Electroanal. Chem., **219**, 273 (1987).
[3.] D. Aurbach and Y. Ein-Eli, J. Electrochem. Soc., **142**, 1746 (1995).
[4.] D. Billaud, F. X. Henry and P. Willmann, Mater. Res. Bull., **28**, 477 (1993).
[5.] T. Zheng and J. R. Dahn, Synth. Metals, **73**, 1 (1995).
[6.] Z. X. Shu, R. S. McMillan, J. J. Murray and I. J. Davidson, J. Electrochem. Soc., **142**, L161 (1995).
[7.] Z. X. Shu, R. S. McMillan, J. J. Murray and I. J. Davidson, J. Electrochem. Soc., **143**, 2230 (1996).
[8.] A. Naji, J. Ghanbaja, P. Willmann and D. Billaud, to be published.
[9.] D. Billaud, A. Naji and P. Willmann, J. Chem. Soc., Chem. Commun., 1867 (1995).