Reversible Electrochemical Insertion of Lithium Ions into Graphite in $LiClO_4$–Propylene Carbonate Electrolyte

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For the first time, reversible electrochemical insertion of unsolvated lithium into graphite previously treated in $LiClO_4$–ethylene carbonate solution is carried out in a $LiClO_4$–propylene carbonate electrolyte.

Recently the most important development in the field of secondary batteries has been the rocking chair type lithium ion system with lithium-graphitized anodes and transition metal oxides, *e.g.* Mn_2O_4 and CoO_2, as cathodes.[1,2] The capacity of the carbonaceous electrodes is dependent on the electrolyte and on the nature of the carbon used. For pure graphite, the maximum electrochemical capacity expected in standard conditions is 372 mAh g^{-1}, corresponding to the stage 1 LiC_6 compound.

However, it was shown that Li-graphite insertion compounds are unstable in many solvents like propylene carbonate (PC) in which graphite exfoliation occurs with the irreversible destruction of the electrode.[3–5] In our laboratory, we showed that reversible electrochemical insertion of unsolvated lithium could be obtained in an $LiClO_4$–ethylene carbonate (EC) electrolyte. The formation of pure LiC_6 compound was shown by X-ray diffraction studies.[6,7] According to previous reports, some charge current is irreversibly consumed during the first insertion reaction which forms an Li^+–conducting protective layer at the carbon surface.[8,9] This layer, impervious to the solvent molecules, allows only the Li^+ ion to be inserted. In the case of the insertion in $LiClO_4$–EC electrolyte, this protective layer was observed and characterized by TEM studies.[10]

Here we present, for the first time, the reversible electrochemical insertion of unsolvated Li^+ ion in a pure $LiClO_4$–PC electrolyte. The graphite electrode was previously treated in EC–$LiClO_4$ electrolyte to form the protective layer.

The insertion reactions are carried out in three-electrode cells without electrolyte stirring. The working electrode is composed of natural milled graphite (UF4 Le Carbone Lorraine, outgassed under vacuum at 430 °C, 10 m^2 g^{-1}, grain size lower than 20 μm) and of PVDF as binder. This mixture, UF_4 and PVDF, is first stirred in PC and then spread on a titanium collector. This sytem is dried at 140 °C under vacuum for 1 h. The auxiliary and reference electrodes are metallic lithium ribbons. $LiClO_4$ (Aldrich) is vacuum dried at 150 °C for 4 h. EC and PC (Aldrich) are outgassed under vacuum. The electrolytes used are EC–$LiClO_4$ (1.5 mol kg^{-1} EC) and PC–$LiClO_4$ (1 mol dm^{-3}).

Fig. 1 shows the first and the second galvanostatic charge–discharge curves of the composite electrode UF_4–PVDF (10 mass%) in EC–$LiClO_4$ electrolyte. The potentials are given *vs.* Li^+/Li.

In the case of the first insertion, the initial potential close to 3.2 V decreases sharply to 1 V. Below this value, the presence of a shoulder is attributed to electrolyte decomposition and to the formation of the protective layer. The plateaux at 0.20, 0.12 and 0.085 mV are related to lithium insertion with stage transformations as previously described.[8,11] Between 3 and 0.020 V, the electrochemical capacity x in the graphite reduction process is equal to 1.56 (x refers to Li_xC_6). This excess of capacity (0.56 in comparison to the richest insertion compound) is mainly due to reactions leading to the formation of the protective layer. A possible partial reduction of PVDF cannot be excluded.[12]

The shoulder below 1 V is missing in the second reduction process which means that the protective layer is mainly formed during the first reduction of graphite in the EC–$LiClO_4$ electrolyte.

Fig. 2 shows a charge–discharge cycle of a composite UF_4–PVDF (2 mass%) electrode carried out at 10 μA mg^{-1} carbon in PC–$LiClO_4$ (1 mol dm^{-3}) electrolyte. The long horizontal plateau at 0.95 V in the reduction curve, up to x = 0.35, corresponds to the insertion of solvated lithium ions and to the concomitant decomposition of the coinserted solvent molecules which leads to graphite exfoliation. In fact, the reduction of PC results in the formation of propylene and lithium carbonate.[13] Above x = 0.35, the potential tends rapidly to 0 V. During the oxidation (deinsertion) process, the electrochemical capacity recovered is negligible.

These results show that unsolvated lithium ion insertion into graphite in the EC–$LiClO_4$ electrolyte is made possible by the formation of the protective carbonated layer which is a lithium ion conductor.[10] On the contrary, in PC–$LiClO_4$ electrolyte,

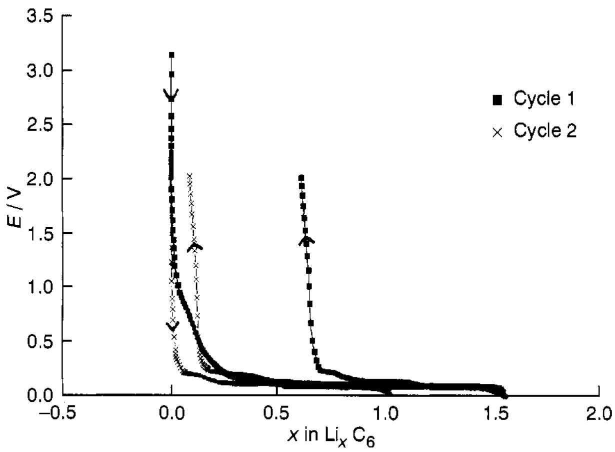

Fig. 1 First and second galvanostatic charge–discharge cycles of a UF_4–PVDF (10 mass%) composite electrode in EC–$LiClO_4$ (1.5 mole kg^{-1} EC). (Specific current = 10 μA mg^{-1} carbon; T = 20 °C; Time required for insertion up to x = 1.5 : 56 h).

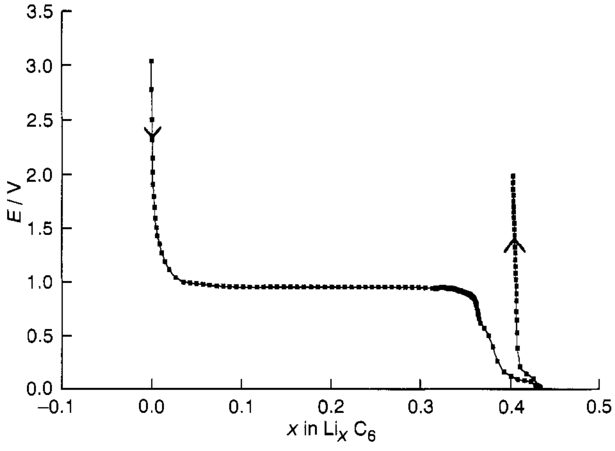

Fig. 2 Galvanostatic first reduction–oxidation cycle of a UF_4–PVDF (2 mass%) composite electrode in PC–$LiClO_4$ (1 mol dm^{-3}) electrolyte (Specific current = 10 μA mg^{-1} carbon; T = 20 °C)

reversible insertion is not possible due to the irreversible degradation (exfoliation) of graphite.

Since PC exhibits more attractive properties than EC (higher salt solubility and melting point), we investigated the possibility of cycling in a PC–$LiClO_4$ electrolyte, employing graphite electrodes previously covered by a protective layer formed in a EC–$LiClO_4$ solution.

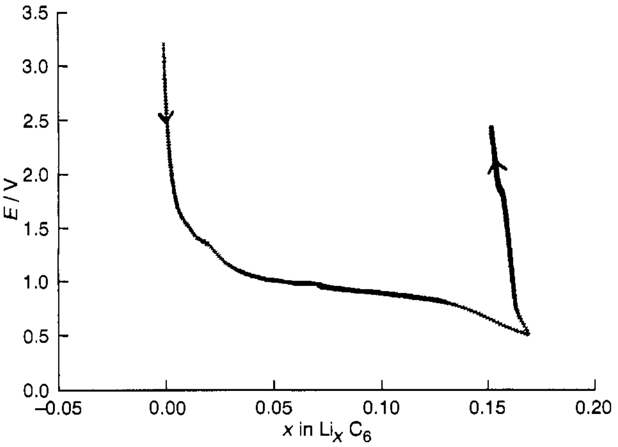

Fig. 3 First galvanostatic cathodic and anodic treatment of a UF_4–PVDF (10 mass%) composite electrode in EC–$LiClO_4$ (1.5 mole kg^{-1} EC) (Specific current = 3 μA mg^{-1} carbon; T = 20 °C)

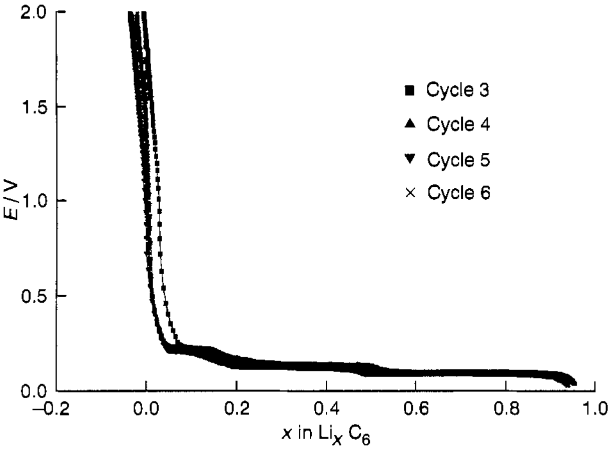

Fig. 4 Galvanostatic charge–discharge cycles of the treated electrode in Fig. 3 in PC–$LiClO_4$ (1 mol dm^{-3}) electrolyte. Cycles 3–6 are shown (Specific current = 10 μA mg^{-1} carbon; T = 20 °C; time required for insertion up to x = 0.95 for cycle 3 = 35.5 h)

Fig. 3 presents a first electrochemical cycle of a UF_4–PVDF (10 mass%) electrode in EC–$LiClO_4$ electrolyte. The reduction potential was limited to 0.48 V in order to allow the formation of the protective layer characterized by the shoulder at around 0.9 V[8,9] and to avoid lithium insertion.[6]

Fig. 4 presents four charge–discharge cycles of such a treated electrode in pure PC–$LiClO_4$ electrolyte, between 2 and 0.02 V and at 10 μA mg^{-1} carbon.

The shape of these curves and the position and length of the plateaux are comparable to those obtained with the EC–$LiClO_4$ electrolyte.[14] The yellow compound obtained at 0.02 V was identified as LiC_6 by X-ray diffraction studies. The reversible capacity x is equal to 0.95.

Reversible unsolvated lithium insertion into graphite can be performed in PC–$LiClO_4$ electrolyte if graphite has been previously covered by an adequate and adhesive protective lithium ionic conducting layer. In these conditions, the maximum capacity x attainable is comparable to the theoretical values corresponding to the formation of LiC_6.

The use of such a protected graphite electrode may offer several advantages for practical batteries: with no irreversible loss of capacity at the first cycle and the possibility to operate at low temperature due to the higher conductivity of the electrolyte.

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