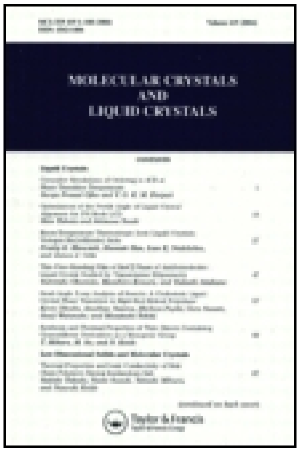

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Electroreduction of polyparaphenylene in $LiClO_4$-ethylene carbonate electrolyte

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Polyparaphenylene powders are electrochemically reduced in $LiClO_4$-ethylene carbonate electrolyte. Intercalation of Li^+ ions occurs and leads to the formation of $Li_{0.5}(C_6H_4)$ compounds. Side reactions due to the electrolyte decomposition are responsible for the important irreversible electrochemical capacity observed during the first charge-discharge cycles. The degradation products were analyzed by TEM and EELS between 2.85 and 0.75 V.

Keywords: Polyparaphenylene; lithium; electrochemical intercalation

INTRODUCTION

Polyparaphenylene (PPP) is a conjugated polymer which can react with electron donating species to give, in the intercalated state, compounds of high electrical conductivity. The intercalation of alkali metal can be achieved either by chemical or by electrochemical ways[1,2]. Previously, intercalation of lithium cations was carried out in complex electrolytes composed of ether solvents and of organic salts like lithium organoborates. In such media, Li^+ ions and solvent molecules are generally cointercalated[3]. In this research, we used ethylene carbonate (EC) and lithium perchlorate as electrolytic solutions for unsolvated Li^+ intercalation into PPP.

EXPERIMENTAL

Polyparaphenylene was prepared according to the method of KOVACIC[4]. The brown insoluble powder was washed out with hot hydrochloric acid to remove the catalyst residues and then heated at 400°C under vacuum for further purification.

The PPP electrodes were composed of PPP (about 83 % by weight w/w), carbon black (CB, 8% w/w) and polyvinylidene difluoride (PVDF, 9% w/w). This composite material was deposited on a titanium collector. The electrochemical measurements were performed using a two-electrode test glass cell. Lithium metal was used both as a counter-electrode and a reference electrode. The electrolyte was $LiClO_4$ (1.5 $mol.kg^{-1}$ EC) in ethylene carbonate (EC).Ten discharge (reduction)/charge (oxidation) cycles were systematically performed at constant specific current (galvanostatic mode) or with potentials sweeping with step of +/- 10.0 mV every 0.5 hour (cyclic voltammetry) using a computer controlled potentiostat/galvanostat Mac Pile (Biologic). The potentials referred to a Li^+/Li electrode.

EELS measurements were conducted on a transmission electron microscope Philips CM20 operating at 200 keV with an unsaturated LaB_6 cathode. The electron energy loss spectra (EELS) spectra were recorded in the diffraction mode coupling by means of a Gatan 666 parallel spectrometer.

RESULTS AND DISCUSSIONS

Fig. 1 shows the voltage profiles of the first and second discharge-charge for the composite electrode PPP/PVDF/CB (83/9/8 % w/w) in EC/$LiClO_4$ at 20 °C between 2.85 and 0.05 V. A low specific current (5.6 μA/mg) was chosen for a good observation of the potential slope changes : the open-circuit cell voltage initially drops rapidly until it reaches 0.9 V where begins a plateau around 0.8 V. Below 0.8 V, a smooth potential decrease was observed between up to 0.3 V. Finally a second plateau, attributed to the intercalation of Li^+ into PPP, takes place at potentials lower than 0.3 V. An important irreversible capacity ($\Delta x \sim 5.2$) is consumed by side reactions like principally the decomposition reactions of the electrolyte[5,6]. Our PPP powder exhibits an appreciable internal porosity (some tens %) and an important internal surface, higher than 250 $m^2.g^{-1}$ in agreement with previous data[7]. That could explain partly the considerable amount of irreversible capacity observed during the first reduction process[8]. Other

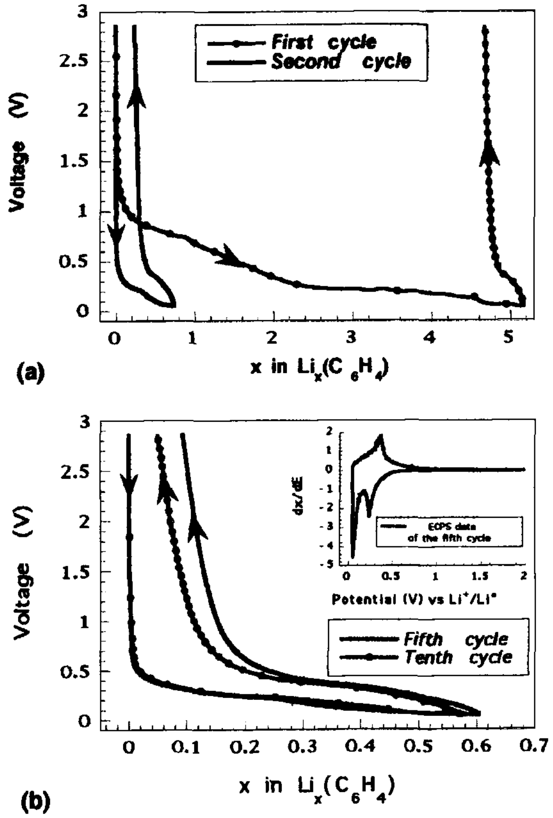

FIGURE 1 Charge-discharge curves of the composite electrode PPP / PVDF/ CB (83/9/8 % w/w) correspond to (a) the first and second cycles (b) the fifth and tenth cycles and ECPS data of the fifth cycle in EC - $LiClO_4$ (1.5 mol.kg^{-1} EC) with a specific current equal to 5.6 μA.mg^{-1}(T = 20 °C)

irreversible reactions could be considered like the reduction of the binder (PVDF) with probably formation of LiF cristallites, the reaction of lithium with active sites such as -Cl, -OH, or carbon radical which are present in the pristine polymer. Moreover, lithium perchlorate is thermodynamically unstable in the presence of carbon, and can be reduced to LiCl[5,6]. During the second cycle, the irreversible capacity decreases drastically but remains still important (Δx~0.24). This decrease continued in the following cycles, but the plateau around 0.8 V is no more apparent. Then, up to the fifth cycle (fig. 1b displayed the fifth and tenth cells exhibit a good reversibility. The reversible capacity is stable near 0.50, corresponding to the stoichiometry $Li_{0.5}$ (C_6H_4).

The curves exhibit potential slope changes which are attributed to a reordering of the polymer structure, like in other multiphase systems like polyacetylene[1]. The potential values of these transformations can be observed clearly in the electrochemical potential spectroscopy (ECPS) data of the fifth cycle displayed in fig. 1b : two peaks in the discharge process were present at 0.21 V and 0.06 V, associated with only one peak, at 0.32 V, in the charge process. That indicates that the second transformation of phase is only partially reversible. Nearly the same transformation potentials were observed in the cyclic voltammetry experiments. Fig. 2 displays the first and second cyclic voltammograms between 2.85 and 0.01 V of the PPP electrode. The irreversible decomposition of the electrolyte appears clearly in the first reduction wave with a strong peak centred at 0.7 V which disappears in the second cycle. The irreversible capacities Δx, calculated from the cyclic voltammogramms, appeared to be Δx~4.51 and Δx~0.75 respectively for the first and second cycle. The sum of the Δx corresponding to the first and second cycle are comparable whatever the techniques used, galvanostatic or voltammetric methods. The curves show two well-defined peaks at 0.20 and 0.02 V in the reduction process, which can be associated respectively with those appearing at 0.32 and 0.05 V in the oxidation process.

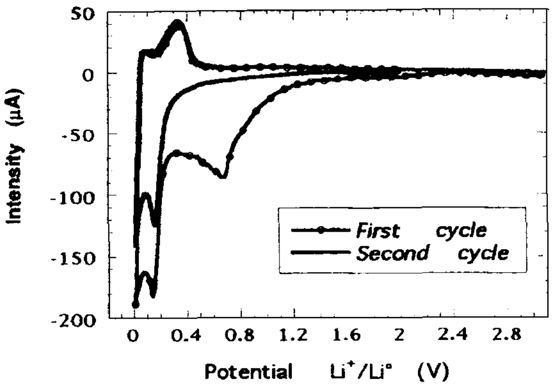

FIGURE 2 The first and second voltammograms of the composite electrode PPP / PVDF/ CB (83/9/8 % w/w) in EC - $LiClO_4$ (1.5 $mol.kg^{-1}$ EC) recorded with a 10.0 mV/0.5 h scan rate (T = 20 °C)

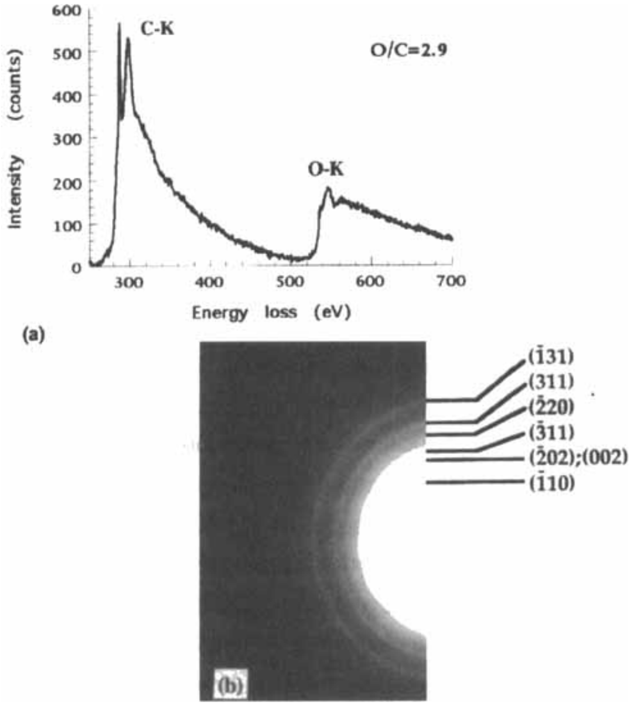

FIGURE 3 EELS spectrum (a) and ED diagram (b) of carbonates found on PPP electrode between 2.85 and 0.75 V

Transmission electron microscope study of the composite electrode after complete first discharge-charge between 2.85 and 0.75 V in EC/$LiClO_4$ reveals the existence of a spongy layer at the PPP surface. Analysis by EELS indicates that the layer is composed mainly of carbon, oxygen and lithium. To fully characterize this layer, we examined the fine structure of the threshold level of the carbon. The two peaks present at 288 and 298 eV are related to the electronic transitions of the (1s) atomic carbon orbitals towards the vacant antibonding molecular π^* and σ^* orbitals corresponding respectively to the C = 0 and C-0 bonds (Fig. 3a). The atomic 0/C ratio of 2.9 suggests that the layer which formed at potentials higher than 0.75 V consists of lithium carbonate As a matter of fact, a deeper analysis in the low energy loss zone shows the presence of lithium. Moreover, the ED diagram of this layer (fig. 3b) formed during the first reduction process in the range of potentials 2.85-0.75 V displayed diffraction rings which are typical of monoclinic Li_2CO_3. Then we attributed the voltage plateau around 0.8 V observed in the electrochemical curve to the reduction of ethylene carbonate into Li_2CO_3. By analogy with the graphite and carbons reduction in EC/$LiClO_4$ electrolyte[5,6], we believe that lithium alkylcarbonates and LiCl cristallites were formed below 0.75 V. As a matter of fact, in EC/$NaClO_4$ electrolyte, during the first reduction of PPP, T.E.M. studies reveal that the electrolyte decomposition occurs with formation of Na_2CO_3 at potentials higher than 0.75 V and sodium alkylcarbonates at potentials lower than 0.75 V[9]. A similar behaviour can be expected with EC/$LiClO_4$ electrolytes.

CONCLUSION

The electrochemical intercalation of lithium ions into PPP using ethylene carbonate electrolytes allows the formation of compounds of stoichiometry $Li_{0.5}(C_6H_4)$. Such compositions are comparable to those related in ether solvents [2,3], in solid state electrolyte using electrochemically synthetised PPP[10] and to those obtained by direct reaction of gaseous heavy metal with PPP[11]. In EC-$LiClO_4$ electrolyte, the coinsertion of the solvent molecules is prevented by the formation of a passivating layer formed onto the polymer surface and resulting of the decomposition of the electrolyte. A good electrochemical reversibility is observed after five charge-discharge cycles. However, the excessive irreversible capacities observed during the first cycles restrict the use of PPP as anodic material in secondary rocking chair batteries. Extra investigations are needed to reduced the effects of such side irreversible reactions

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