

BRIEF COMMUNICATION

Electrochemical Intercalation of Lithium Ions into Polyparaphenylene in LiClO₄-Carbonates Electrolytes

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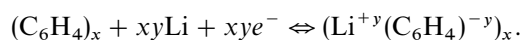
The electrochemical intercalation of unsolvated lithium cations into polyparaphenylene (PPP) has been carried out in a EC/PC (1/1 volume) mixture using LiClO₄ as lithium salt. It leads to formation of saturated materials with composition Li_{0.5}(C₆H₄). Cyclic voltammetry and galvanostatic measurements reveal three successive phase transformations in the intercalation–deintercalation process. The irreversible side reactions which occur during the first PPP reduction, like decomposition of the electrolytes (EC and PC) and reduction of the binder (PVDF), are responsible for an important capacity loss that decreases rapidly in the following cycles. The cells exhibit finally a good reversibility. © 1997 Academic Press

INTRODUCTION

Extensive efforts have been carried out for preparing suitable carbon materials as anode in lithium-ion secondary batteries. In the wide family of carbonaceous materials graphite was investigated first because it reversibly intercalates and deintercalates lithium at a low flat voltage, yielding a theoretical capacity of 372 mAh/g corresponding to a Li₁C₆ composition (1, 2).

More recently other disordered carbon-based materials such as hard and soft carbons or so-called “house of cards” carbon have been shown to exhibit capacities higher than 600 mAh/g with, however, some hysteresis in the intercalation–deintercalation process (3, 5). The presence of hydrogen in such carbons must also be considered for determining the capacity values.

Polyparaphenylene (C₆H₄)_x or PPP is a fairly crystalline conjugated polymer presenting redox properties. In particular it can be reduced chemically or electrochemically in liquid or solid electrolyte (6, 8). Such a redox reaction occurs simultaneously with an intercalation process according to the equation:



Previously intercalation of Li⁺ into PPP was carried out by Shacklette *et al.* (9) using complex lithium organoborate electrolytes in ether. In the present research we have investigated the electrochemical properties of PPP in more practical electrolytes consisting of a solution of LiClO₄ in a mixture of ethylene carbonate (EC) and propylene carbonate (PC), which allows an unsolvated lithium intercalation.

EXPERIMENTAL

Poly(paraphenylene) was prepared according to the method of Kovacic *et al.* (10), which gives a brown powder of high surface area (about 50 m²/g). This powder was carefully washed out with hot hydrochloric acid and water, then annealed at 400°C under vacuum during 36 hours to remove the catalyst residues.

A two-electrode cell was used for electrochemical measurements, where lithium was both reference and counter-electrode. Polyparaphenylene-based electrodes were formed by PPP (about 83% by weight (w/w)), carbon black (CB, 8% w/w) to assure electronic conductivity, and polyvinylidene difluoride (PVDF, 9% w/w). This composite material was deposited on a titanium collector.

The electrolyte was a solution of LiClO₄ dissolved in a mixture of propylene carbonate (PC) and ethylene carbonate (EC) with a volumic ratio of 1/1. Lithium perchlorate LiClO₄ (Aldrich, purity 99%) and EC (Fluka, purity > 99%) were outgassed under dynamic vacuum at 150 and 20°C, respectively. PC was heated at 80°C under vacuum to remove traces of water.

Ten discharge (reduction)/charge (oxidation) cycles were systematically performed at constant specific current (galvanostatic mode) or with potentials sweeping with steps of –10.0 mV every 0.5 hour in the discharge process and +10.0 mV every 0.5 hour in the charge process (cyclic voltammetry). The scan starts from the equilibrium value

reached at the end of the preceding relaxation. A multichannel microprocessor-controlled Mac Pile potentiostat/galvanostat was used to perform the electrochemical experiments. The potentials referred to a Li^+/Li electrode.

RESULTS AND DISCUSSION

Figure 1 shows the typical voltage profiles of the first galvanostatic discharge (reduction) and charge (oxidation) of PPP. A low specific current ($8.82 \mu\text{A}/\text{mg}$) between 2.9 and 0.05 V was chosen for allowing a good observation of the potential slope changes. The initial open-circuit cell voltage is typically above 2.9 V. Upon discharge the cell voltage drops rapidly until it reaches a plateau value around 0.8 V. As previously reported, such a plateau was also present during the reduction of graphite or petroleum coke in a lithium carbonate electrolyte (11, 13). At those potentials the decomposition of the electrolyte takes place on the surface of the polymer with production of a solid film of Li_2CO_3 . Below 0.8 V, the potential decreases slowly down to a second potential plateau at around 0.2 V. During this process one may assume, by analogy with graphite, that the reduction of the electrolyte still continues with formation of lithium alkylcarbonates (12). The second plateau observed near 0.2 V was attributed to the intercalation of Li^+ into PPP. The total reversible capacity between 0.05 and 2.9 V during the first charge led to a $\text{Li}_{0.52}(\text{C}_6\text{H}_4)$ formulation.

The important irreversible capacity loss observed during the first cycle ($\Delta y \approx 3.8$) can be explained by side reactions. First, the formation of the passivating layer is related to the specific area of the carbonaceous electrode as shown by Fong *et al.* (11). The high specific area (about $50 \text{ m}^2/\text{g}$) of PPP is responsible partly for the irreversible capacity. Second, an irreversible reduction of the binder (PVDF) occurs also during the electrochemical process with prob-

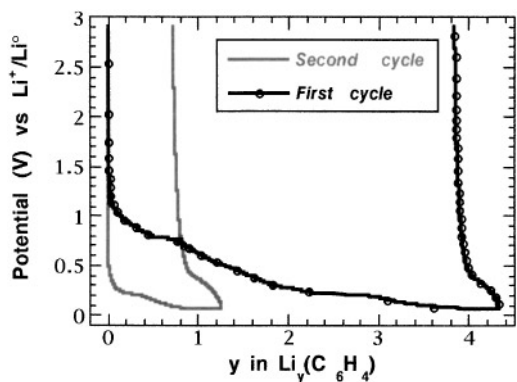


FIG. 1. Potential profiles of first and second cycles in a Li/EC-PC (1–1 vol. mixture)/ LiClO_4 1 M/PPP-PVDF-CB (83–9–8) system cycled with a constant specific current ($8.82 \mu\text{A}/\text{mg}$).

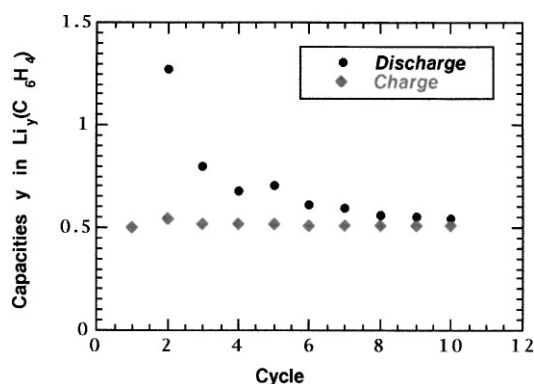


FIG. 2. Evolution of charge and discharge capacities during 10 cycles at constant specific current ($8.82 \mu\text{A}/\text{mg}$). The first discharge capacity ($y = 4.34$) is not represented.

ably formation of LiF crystallites (12, 15). Lithium perchlorate is thermodynamically unstable in the presence of carbon and may be reduced to LiCl ; as a matter of fact the presence of LiCl was previously observed at the lithium and aluminium–lithium surface (14) during the reduction process respectively in an EC/ LiClO_4 (12) and in a PC/ LiClO_4 electrolyte. Moreover, Li can react with active sites such as $-\text{Cl}$, $-\text{OH}$, and carbon radicals in the bulk of the polymer electrode. Elemental analyses of the pristine polymer reveals the presence of chlorine (0.3% w/w) and oxygen (0.3% w/w).

In the second cycle (Fig. 1) the irreversible capacity is still important ($\Delta y \approx 0.7$) but the plateau and the following slow potential decrease can be attributed to formation of lithium carbonate as alkylcarbonate has disappeared.

In the following cycles the irreversible capacity decreases upon cycling (Fig. 2). The reversible capacity is stable near 0.52. Such a value corresponds also to that obtained when gaseous heavy alkali metals react directly with PPP (16). After the fifth cycle, we can consider that the side reactions no longer occur and that the cells are exhibiting a good reversibility.

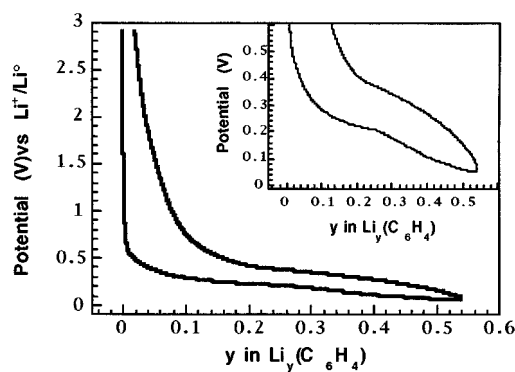


FIG. 3. Potential profiles of the 10th cycle in a Li/EC-PC (1–1 vol. mixture)/ LiClO_4 1 M/PPP-PVDF-CB (83–9–8) system cycled with a constant specific current ($8.82 \mu\text{A}/\text{mg}$).

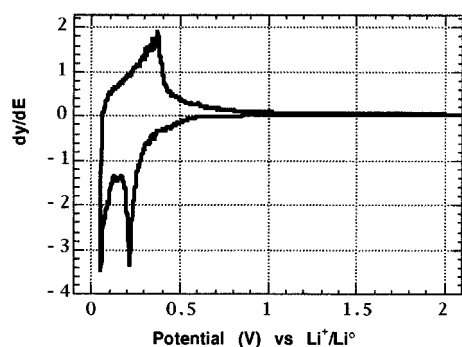


FIG. 4. ECPS data of the 10th cycle in a Li/EC-PC (1-1 vol. mixture)/LiClO₄ 1 M/PPP-PVDF-CB (83-9-8) system cycled with a constant specific current (8.82 μ A/mg).

Figure 3 shows the 10th cycle. Intercalation and deintercalation take place at potentials lower than 0.6 V vs Li⁺/Li. The curve exhibits potential slope changes which as a rule can be attributed to appearance of multiphase systems. These transformations are more apparent in the electrochemical potential spectroscopy (ECPS) curve given in Fig. 4. The 10th cycle shows two peaks in the discharge process at 0.20 and 0.05 V associated with only one peak in the charge process at 0.32 V. Such a phenomenon indicates that the second phase transformation is only partially reversible. This spectroscopy method is equivalent to linear sweep voltammetry at a nearly infinitesimal effective sweep rate. As a matter of fact, the voltammogram of the 10th cycle performed with a 10 mV/0.5 hour scan rate (Fig. 5b) is quite similar to the ECPS curve (Fig. 4).

Cyclic voltammograms of the system Li/EC-PC/LiClO₄/PPP-PVDF-CB (83-9-8) were recorded with low potential steps of 10.0 mV every 0.5 hour between 2.0 V and 0.01 V. Both first and second cyclic voltammograms were characterized by two peaks at 0.19 and 0.02 V in the reduction process. These peaks can be associated respectively to those

appearing at 0.32 and 0.05 V in the oxidation process. A broad reduction peak, starting at nearly 1 V and presenting a maximum at 0.6 V, is observed in the first cycle; it disappears almost totally in the second cycle. This peak can be associated partly with the irreversible decomposition of the electrolyte on the polymer surface, which was described above for the first cycles on the galvanostatic curves.

The definition of the peaks has been improved in the following cyclic voltammograms. Thus, in the 10th cycle (Fig. 5b), sharp well-separated peaks appear. The two reversible peaks are also present. We have calculated the amount of current for each reversible peak (Q_{d1} , Q_{d2} , Q_{c1} , Q_{c2} for the peaks at 0.20, 0.01 during the discharge, 0.32 and 0.05 V during the charge). The obtained $Q_{c1}/Q_{d1} \approx 0.9$ and $Q_{c2}/Q_{d2} \approx 0.4$ ratios indicate that the second transformation, at low potential, is partially reversible.

A careful observation of the cyclic voltammograms shows an additional reversible transformation characterized by a hump present in every cycle in the oxidation process at 0.65 V (Fig. 5b) associated with a shoulder at discharge at 0.52 V. This shoulder is quite difficult to observe because it is included in the main peak centered at 0.19 V. The intensities of such peaks are low and their contribution to the electrochemical capacity is minor. The potential values of the three transformations are given in Table 1 as well as the corresponding free enthalpies $\Delta G = -FE$.

The reversible electrochemical capacities calculated from the cyclic voltammograms appeared to be close to 0.5, corresponding to the composition Li_{0.5}(C₆H₄); the theoretical value of 0.5 can be reached by electrochemical experiments in liquid electrolyte, with both galvanostatic conditions and cyclic voltammetry. The values are similar to those previously reported for intercalation of Li⁺ into PPP in liquid electrolytes such as lithium tetraphenylborate/tetrahydrofuran (THF) (9).

Previous experiments carried out with solid electrolytes (8) show nearly the same potential profiles. Under such

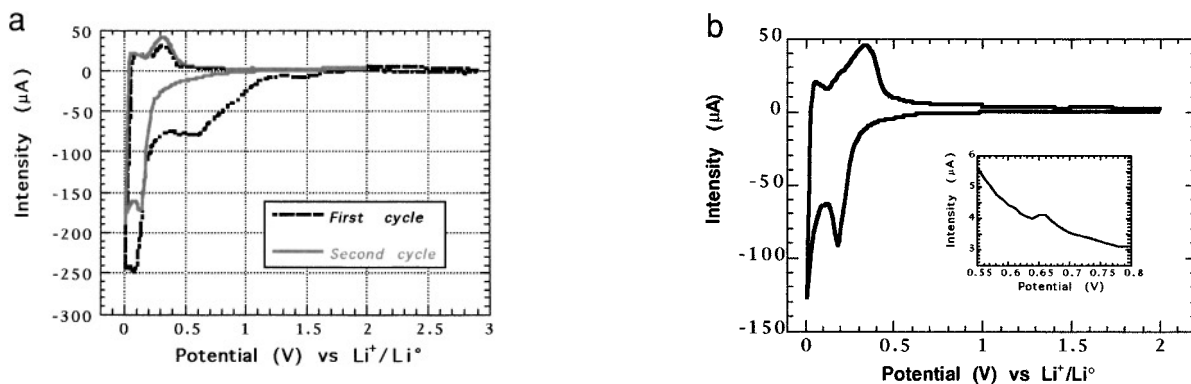


FIG. 5. (a) Voltammograms of first and second cycles for a Li/EC-PC (1-1 vol. mixture)/LiClO₄ 1 M/PPP-PVDF-CB (83-9-8) system with 10 mV/0.5 h scan rate. (b) Voltammogram of the 10th cycle for a Li/EC-PC (1-1 vol. mixture)/LiClO₄ 1 M/PPP-PVDF-CB (83-9-8) system with 10 mV/0.5 h scan rate.

TABLE 1
Potentials Corresponding to the Intensity Maxima, Equilibrium Potentials, and Free Energies G for the PPP-Li system

	Potential (V) vs $\text{Li}^+/\text{Li}^\circ$			$-\Delta G$ (kJ/mol·Li)
	Reduction	Oxidation	Equilibrium potential	
Liquid electrolyte	0.01	0.05	0.03	2.9
	0.20	0.32	0.26	25.1
	0.52	0.65	0.53	51.1
Solid electrolyte (8)	0.01	0.05	0.03	2.9
	0.18	0.38	0.28	27.0
	0.45	0.71	0.57	55.5

conditions the potentials are slightly shifted to lower values during discharge and to higher values during charge as seen in Table 1. These potential shifts can be related to kinetic effects resulting from the intrinsic properties of the solid electrolytes which have at the same temperature electrical conductivities much lower than those of the liquid electrolytes.

CONCLUSIONS

The intercalation of Li^+ ions into PPP using liquid or solid electrolytes give similar results. Our experiments for carbonate electrolytes lead to intercalation of unsolvated lithium ions. The richest metal composition corresponds to stoichiometric $\text{Li}_{0.5}(\text{C}_6\text{H}_4)$. In contrast the electrochemical insertion of Li^+ THF or other ether solvents (such as 2-methyltetrahydrofuran, MTHF), with strong cation solvation for Li^+ , for instance, leads usually to formation of ternary intercalation compounds in which various amounts

of solvent molecules are cointercalated with Li^+ . The formation of a stable passivation film on the polymer surface is believed to be the reason for the absence of co-insertion of the solvent. Excessive irreversible capacities are observed in the first cycles. Further investigations will be necessary to reduce such capacity losses before using the concerned compounds as anode materials for secondary batteries.

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