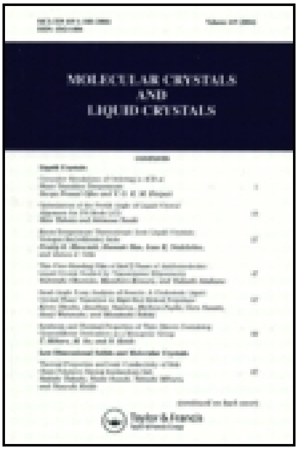

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The Electrochemical Behaviour of Fullerenes in Liquid Electrolyte

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THE ELECTROCHEMICAL BEHAVIOR OF FULLERENES IN LIQUID ELECTROLYTE.

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Abstract. The electrochemical behavior of a C_{60} and C_{70} mixture based composite electrode is examined in propylene carbonate solutions in which C_{60}/C_{70} is not notably soluble . A wide variety of salts based on Li^+ or quaternary ammonium (NR_4^+) where (R= C_4H_9, C_3H_7, and C_2H_5) were investigated.We show that when a C_{60}/C_{70} electrode is first polarized towards cathodic potentials, electrochemical intercalation is observed with a step-by-step formation of fullerites salts. The relative amounts of reacted species depends on the nature of both the cation and the anion employed in the salt.

INTRODUCTION

The electrochemical reduction of C_{60} (or C_{70}) was carried out using different experimental conditions:

- A solution of C_{60} into CH_2Cl_2 [1] and benzonitrile or toluene [2,3] .
- Thin film of C_{60} in contact with a liquid solvent which does not dissolve it [4].
- Composite electrode in solid polyethylene oxide (POE) electrolyte [5] using a technique described elswhere [6].

However, the stoichiometry of electrogenerated C_{60}^{x-} has not been fully elucidated nor have the solubility and stability of these fullerides been characterized.

In this paper, we used bulky electrodes containing in a addition to C_{60}/C_{70} mixture an electron conductors and POE used only as binder . The electrolyte is a liquid solution of lithium salt LiX or tetraalkylammonium iodide (NR_4I) in propylene carbonate. The purpose of this study is to examine by voltammetric technique the modification of electrochemical behavior of C_{60}/C_{70} electrode when subjected to cationic intercalation (charge) /de-intercalation (discharge) operations, following the general equation (1).

$$C_{60}/C_{70} + xA^+ + xe^- \rightleftarrows A_xC_{60}/C_{70} \qquad (1)$$

The current peaks potentials are analyzed and discussed with respect to the effect of different parameters such as the nature of anions and the size of the cations.

MATERIALS AND SAMPLE PREPARATION

Since C_{60} and C_{70} have close electrochemical behaviors, we have used C_{60} and C_{70} mixture (approximative composition 85% C_{60} and 15% C_{70}) supplied by MGP/ISAR (France). The sample was evacuated under vacuum at 180°C for 24 hours to full dehydratation . The dissolved salts consisted of LiX with X= ClO_4^-, BF_4^-, AsF_6^-, $CF_3SO_3^-$and I^- or quaternary ammonium iodides: NR_4I with R= C_4H_9 , C_3H_7, and C_2H_5. The tetraethylammonium (TEA) and tetrapropylammonium (TPA) iodides were used as received where as the tetrabutylammonium (TBA) one was recrystallized twice from absolute ethanol and dried in vacuum at 40°C. The other salts were purified following the procedures reported elsewhere [7]. The electrochemical test were carried out on cells with the C_{60} /C_{70} compound as the working electrode and metallic lithium as both reference and counter electrodes. The electrolyte consisted of a molar solution of lithium salts (except LiI) and TBAI in purified propylene carbonate, and 0.1M for less soluble salts: LiI, TPAI, and TEAI. Even with lower concentration, the cations available in the electrolyte are in a large excess to fully achieve the reaction (1).

The fullerite based electrode was composed of vol. 50% C_{60} /C_{70}, 33% acetylene black and 17% polyethylene oxide (POE) used as binder. After stirring it into acetonitrile and drying, the mixture was pressed to c.a. 2t/cm^2 to form a pellet of 8 mm in diameter. The total weight was in the 5-20 mg range, (theoritical capacity (Q_{th}) = 63.4 µAh/mg/F). The pellet was dried under primary vacuum at 120°C for several hours and mounted into button type cell (CR2430). The cells were assembled into a dry box filled with argon which was cycled through a column capable of removing O_2 and H_2O and maintaining their concentrations lower than 1ppm. We used slow scan voltammetry as investigation technique (1mV/mn) in the voltage limits of (1.5-3V), with a first electrode polarization to reduction potential. Only the first cyclic voltammogram will be given here. The electrochemical tests were performed at the room temperature.

RESULTS AND DISCUSSION

Figure 1 shows the cyclic voltammograms obtained with LiClO$_4$(a), LiI(b), LiAsF$_6$(c), LiCF$_3$SO$_3$(d), and LiBF$_4$(e), and figure 2 corresponds to that obtained with TBAI(a), TPAI(b), and TEAI(c). Several reduction peaks appear followed by re-oxidation peaks when the potential sweeping was reversed. The current peak position are given in Table 1. The comparative tests which were carried out with electrodes containing only acetylene black did not show any reduction peaks in the voltage limits of 1.5-3V. Therefore, the observed peaks are characteristic of C_{60}/C_{70} mixture. The shape of voltammograms in both figures 1 and 2 differ from each others which emphasizes the role of the counter ion in the first series and of the cation (NR_4^+) in the second ones. Though all experiments described above where carried out using the same lot of the C_{60}/C_{70} mixture, we observed some slight differences in the cyclic voltammograms obtained with an other sample lots.

TABLE1: Peaks potentials of C_{60}/C_{70} based composite electrode in propylene carbonate.

	E, V vs Li/Li$^+$						
Salts	Reduction				Reoxidation		
	1st	2nd	3rd	4th	1st	2nd	3rd
LiClO$_4$	2.40	2.08	1.72		2.21	2.48	
LiI^a	2.06	1.72^b	1.66		2.68		
LiAsF$_6$	2.10	1.92^b			2.08	2.44	
LiCF$_3$SO$_3$	2.28	2.04	1.74^b	1.68	2.40	2.64	
LiBF$_4$	2.12^b	2.04	1.6		2.12^b	2.4	2.72
(TBAI)	2.36	1.92			2.21	2.62	
(TPAI)^a	2.32	2.16	1.8		2.52		
(TEAI)^a	2.12	1.8			2.76		

a) 0.1 M ; b (Shoulder)

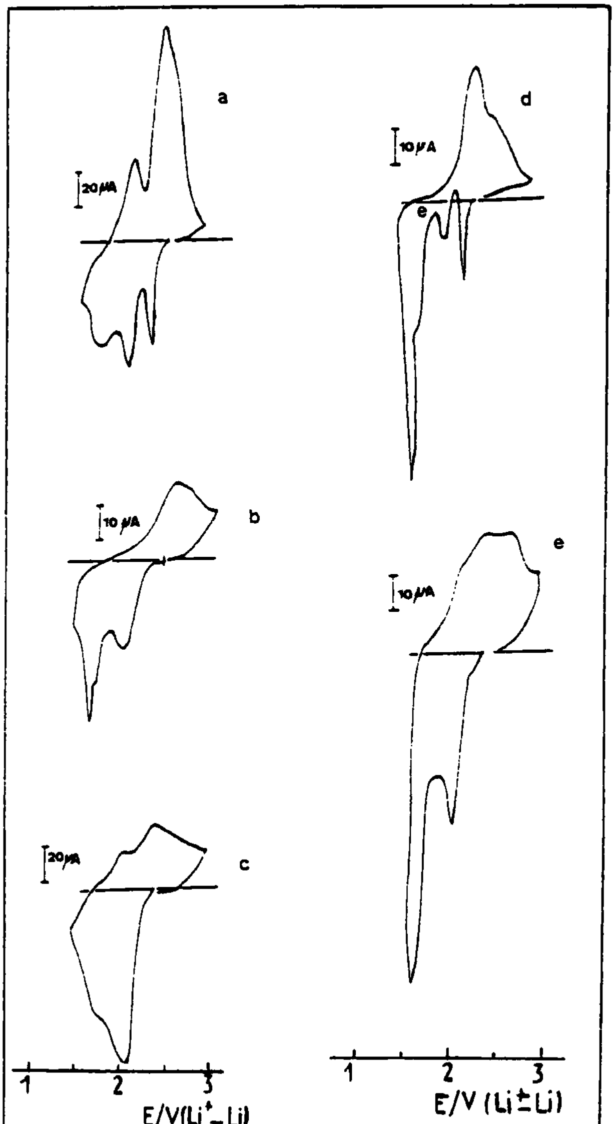

Figure-1

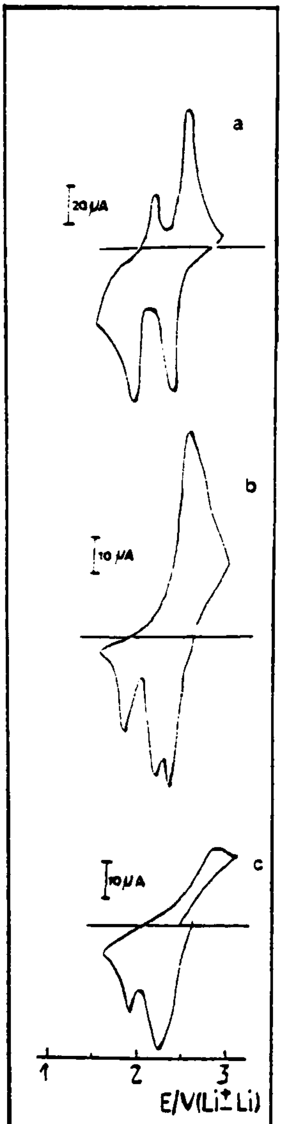

Figure -2

FIGURE 1: Cyclic voltammograms of C_{60}/C_{70} mixture based composite electrode using various salts in propylene carbonate .$LiClO_4$(a), LiI(b), $LiAsF_6$(c), $LiCF_3SO_3$(d), and $LiBF_4$(e), Scan rate 1mV/mn

FIGURE 2: Cyclic voltammograms of C_{60}/C_{70} mixture (theoritical capacity (Q_{th}) = 255 μAh/F) with NR_4I /CP solution at V= 1mV/mn 1M TBAI (a), 0.1M TPAI (b), and 0.1M TEAI (c).

TABLE II: Cation intercalation and deintercalation relative amounts x.

salts	x_i	x_d	$\Delta x = x_i - x_d$
$LiClO_4$	7	8	- 1
LiI	4.7 ~ 5	4	0.7 ~ 1
$LiAsF_6$	1.7 ~ 2	1.2 ~1	0.5 ~ 1
$LiCF_3SO_3$	7	7.23 ~ 7	- 0.23~ 0
$LiBF_4$	2	2 .2 ~ 2	- 0.2 ~ 0
TBAI	1.5	0.6	0.9
TPAI	1	1.5	- 0.5
TEAI	1	0.7	0.3

Since the first experiments [1-5], it was showed that the electrochemical reduction of the C_{60}/C_{70} occurs in successive steps which have been attributed to a step by-step one-electron transfert andthe formation of fullerite anions such as C_{60}^{x-} (x=1, 2, 3...). Each step can be schematically represented by the equation:

$$A_x^{x+}C_{60}^{x-} + A^+ + e^- \rightleftharpoons A_{x+1}^{(x+1)+}C_{60}^{(x+1)-} \qquad (2)$$

In our results, the amount of electricity passed after each reduction peak is difficult to evaluate with a good occuracy due to the peaks overlaps. However, one can roughly determine the total amount x at the end of the reduction and the re-oxidation operations. Table II gives the estimated values (within 10 % of occuracy) of intercalated (x_i) and de-intercalated (x_d) lithium. It leads as to the following comments:

With lithium salts, x_i increases in the order $AsF_6 < BF_4 < I < CF_3SO_3 = ClO_4$. Since the anions polarizability should vary in the same order, we attribute this result to the polarizability effect.

With tetra-alkylammonium iodides, x_i is much more lower than that obtained with lithium. However, despite its larger size, TBA gives higher x_i than TPA and TEA. In this case, the cation polarizability may have a more dominent effect compared with the size effect which should favor TPA and TEA. In some cases $\Delta x = x_i - x_d$ has negative values.This surprising result can be attributed to the possible anion intercalation during the re-oxidation of the C_{60}/C_{70} electrode.This should contribute to the excess charge observed. We previousely reported the possible electrochemical oxidation of the C_{60}/C_{70} mixture by the anion intercalation or electrosorption at the electrode surface [8].

The differences in the reduction peaks potential can result from :

i) the differences in the electrolyte conductivity (ohmic drop).

ii) the cation-anion electrostatic interaction (Debye-Hückel theory) especially in the Helmholtz double layer .

iii) the inter and intra granular ion diffusion (size effect especially in bulky electrodes).

CONCLUSION

Li_xC_{60}/C_{70} and $(NR_4^+)_xC_{60}/C_{70}$ compouds can be obtained by electrochemical reduction in liquid electrolyte with bulky electrodes eventhought their preparation is hindred by their partial dissolution into the solvent . For the Li_xC_{60}/C_{70} phases, the reversibility of the intercalation reaction depends on the nature of counter ion and on the lowest potential reached during the reduction. It is also hindered by the possible intercalation or electroadsorption of the anion . Partially reduced solid state material $(NR_4^+)_xC_{60}/C_{70}$, where $0<x<1.5$ can be obtained.

The nature of the cation is important in the redox process, and different behavior is found with Li^+ and NR_4^+.

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