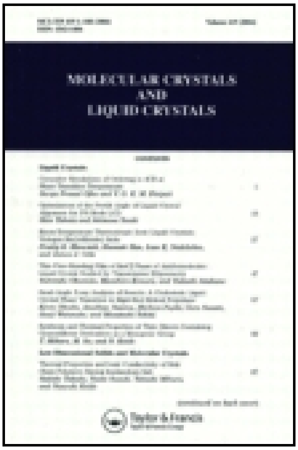

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ELECTROCHEMICAL SPECTROSCOPY AND STRUCTURAL STUDY OF THE Na:C_{60} SYSTEM

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Abstract Electrochemical intercalation of Na in solid C_{60} has been performed using polymer electrolytes and very slow rate stepwise voltamperometry. Five reduction steps are observed as on the Li_xC_{60} system we studied previously, but with appearance of solubility of the compound beyond the first one. That paper focus on that first step which presents the same hysteresis and X-rays diffraction pattern as in Li_xC_{60} where it was shown to correspond to $Li_{0.5}C_{60}$ formation. The fact that the polymer electrolyte could play a role is discussed.

INTRODUCTION

Chemical intercalation of sodium into the interstitial sites of solid C_{60} has been shown to yield a range of compounds from Na_2C_{60} to Na_6C_{60} [1] and then to $Na_{11}C_{60}$ [2]. These two latter compounds retain the fcc structure of the pristine C_{60} with formation of a cluster of 4 to 9 partly ionized sodium in the octahedral site, on the contrary to heavy alkali metals intercalation compounds which turn from fcc to bct and bcc structures beyond the A_3C_{60} composition [3]. The Na intercalation was carried out using either sodium-containing compounds [1] or metallic vessels [1,2] to be able to operate at much higher temperature than for heavy alkali metals, to overcome the low vapor pressure of Na.

We previously succeeded to prepare intercalation compounds of lithium for which the same difficulties occur, in an electrochemical way with the use of $P(EO)_8LiClO_4$ polymer electrolyte [4]. Polymer electrolytes present a much larger electrochemical stability window than liquid ones, particularly at negative potential [5] making able to work at potential close to that of Li. Moreover neutral or ionized C_{60} appeared to have a very limited solubility in the electrolyte we used, on the contrary to what is observed with liquid electrolytes [6,7]. We obtained in that way composition limits of 0.5, 1, 2, 3, 4 or 6 and finally 12, the latter probably being no more an intercalation compound but a new molecular entity resulting from a displacement reaction, as supported by molecular dynamic calculations of its stability [8]. The 0.5 composition was unexpected but we did not succeed to characterize its structure, due to the low contribution of the Li to the X-ray diffraction pattern [9].

We undertook the same study for the Na:C_{60} system to compare to its vapor transport high temperature synthesis, with also the prospect to characterize structurally the low contents compounds, taking advantage of a larger contribution from Na than Li to the X-ray diffraction.

EXPERIMENTAL

For the electrochemical intercalation studies, coin-type cells are used, with metallic sodium as negative electrode, a $(PEO)_nNaX$ polymer membrane as electrolyte and a composite positive electrode. Such electrode is prepared from a suspension of C_{60} in a solution of the polymer electrolyte in acetonitrile, cast on a stainless steel disc, evaporated and dried at 80°C under dynamic vacuum; it contains ca. 60% C_{60} powder and 40% electrolyte by volume. C_{60} powders with more than 99.5% purity were used, from several sources. Possible solvent residues were evacuated by heat treatment, in the 150-180°C range under dynamic secondary vacuum.

The cells are operated at 80°C to be in the amorphous ion-conducting phase of the electrolyte and driven in a step-potential controlled mode, recording the chronoamperogram at each potential level with a system we have specially designed for electrochemical studies of slow rate solid-state redox processes [10]. The potential scanning can be performed either with regular time duration of the potential plateau or with automatic stepwise increment when the redox current has decreased below a predetermined value. Typical conditions are 10mV potential step every few hours to account for equilibration time related to low values of the diffusion coefficients in solids. That step potential electrochemical spectroscopy [11] enables to determine if the observed redox processes do correspond to single-phase solid-solution domains or to phase transformations with two-phase equilibria composition range [12].
For in-situ XRD studies, special cells with a beryllium window are used whose detailed description can be found in reference 12.

RESULTS

Electrochemical Spectroscopy

In fig.1a below is reported the result of a first reduction/intercalation performed at intermediate potential scanning rate, in the form of a voltammogram. Five successive reduction peaks are observed, the first three beeing at almost the same potential position as on the Li_xC_{60} system and with similar kinetics [4, 9, 12].

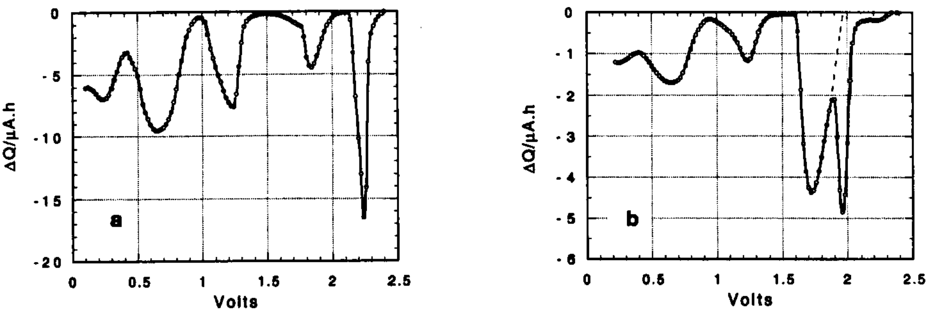

FIGURE 1 Voltammograms of first reduction in Na:C_{60} cells operated at 80°C using $P(EO)_{12}NaCF_3SO_3$. a) with -20 mV/1h potential steps. b) with -20mV /0.2h steps. Each dot is the charge increment during a potential plateau.

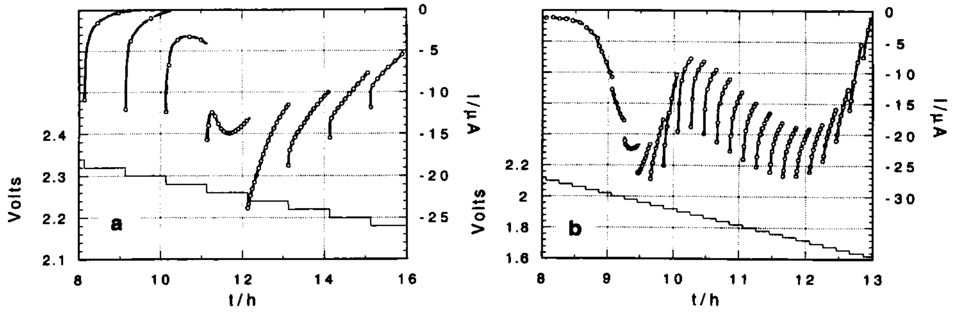

FIGURE 2 Time dependence of the current on first reduction:
a) during the first peak of fig 1a, from 2.32 V to 2.18 V at -20mV/1h
b) during the first two peaks of fig 1b, from 2.12 V to 1.62 V at -20mV/0.2h

The first reduction step starts at potential between 2.4 V and 2.1V vs. Na^+/Na^0, depending on the potential scan rate and on both the composite electrode composition and its mode of preparation. It corresponds to a first order transition which usually needs an over-potential to be initiated, ie. which occurs with hysteresis. This is indicated by a shift of the peak position to a lower potential value when increasing the potential scan rate (from 2.25V to 1.95 V in Fig.1b vs. 1a when the average potential scan rate was increased by a factor of 5). As for Li [9,12] it can also be seen from the time dependence of the reduction current which increases at constant potential once reduction/intercalation is initiated (Fig. 2a and 2b, from 2.28 V and 2.10 V respectively). Moreover, after that step, the equilibrium open circuit potential is close to 2.4 V. This hysteresis was not observed with a composite electrode containing a small amount of graphite to increase its electronic conductivity . In that case intercalation initiated at 2.4 V.

The second step (peaks at about 1.8 V in fig 1a and 1b) also appears to be a first-order transition: it has an unsymmetrical shape whose initial slope depends on the scan rate and with a zero-current intercept at about 1.95 V corresponding to its OCV equilibrium value.

The third reduction step extends from 1.4V to 1V, with a shape and time dependences of the current at each potential which are not characteristic of a two-phase process but those of a solid solution intercalation.

The last two steps appear well resolved, below 0.9V and 0.5V, by contrast from what was observed in the Li:C_{60} system where both occured close to 1V. Their kinetics is much slower than that of the previous ones. They seem to correspond to single phase process but this has to be confirmed.

Reproducible quantitative determinations of all these steps (surface of the peaks) have not yet been obtained, due to the onset of a self-discharge process once the second reduction step is reached. This is due to a slight solubility of the reduced $C_{60}{}^{n-}$ species in this Na^+ conducting P(EO) based electrolyte, which then act as redox shuttles between the two electrodes and induce internal electrical losses. This solubility is observed when opening the cell: the black tint of the composite positive electrode has extended to the whole electrolyte membrane. That was not observed when studying Li:C_{60} in $P(EO)_8LiClO_4$ electrolyte.

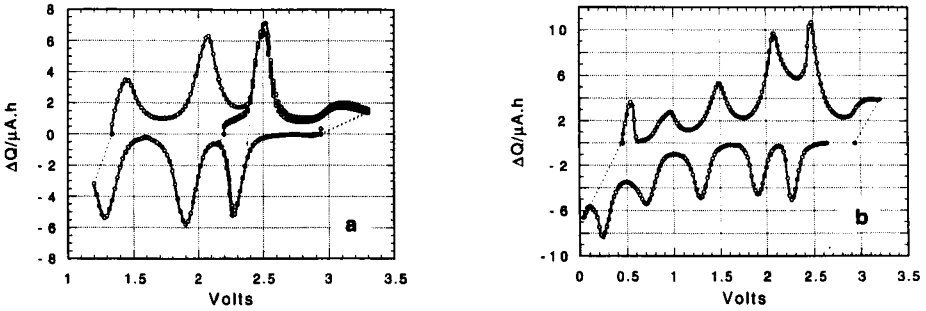

FIGURE 3 Cycling at 20mV/1h, increasing the potential windows:
a) on the first redox state and then on the first and second one, from the 5th to the 7th oxidation, with limits: 2.2V → 3.3V → 2.2V → 3.3V→ 1.2V → 3.3V
b) 8th cycle from 2.7V open circuit value to 20mV and back to 3.2V

Experiments with $P(EO)_{20}NaI$ have been performed in an attempt to find an electrolyte with less solubility and to get quantitative determinations of the successive steps. With -20mV/2h potential scanning and final currents at each potential level corresponding at least to a nominal C/200 rate (1 Na intercalation within 200h), we observed quantitative ratios of 0.5, 2 and 3 for the first three reduction steps, as in the Li_xC_{60} system.

Upon cycling the cells while setting the limits to progressively lower potential (more reducing), waves of equivalent coulombic area are observed (Fig. 3), out of the first step which remains characteristic of a first order transition close to 2.4 V with no hysteresis (the initial slopes of the reduction and oxidation peaks are aligned).

In-situ X-ray diffraction measurements

When the first reduction step is performed by decreasing the potential of the cell down to 2.2V, new Bragg peaks are observed while those of pristine C_{60} decrease in amplitude but do not significantly shift in position. These broad new peaks are listed in Table 1, for Na and also for Li from experiments in which the same behaviour was observed [9]. Then, as soon as potential lower than that of C_{60}^{2-} formation are imposed or is the cell is let to self discharge in OCV mode, there is a rapid disappearance of the whole XRD pattern. The pattern observed at 2.2 volt appeared to be stable if the potential is kept constant and it is reversible: upon reoxidation at 2.6V the new lines disappears and their intensities are recovered in the peaks of pristine C_{60} as can be seen in Fig 4.

TABLE 1 2Θ positions ($CuK\alpha_1$) of recorded Bragg peaks on systems reduced at 2.2V. **Bold** characters indicate new peaks compared to that of pure C_{60}.
For $Li:C_{60}$, positions are calculated from previous experiment using $FeK\alpha_1$ radiation [9]

C_{60}	<111>			<220>			<311>		<222>
$Na:C_{60}$	10.78	**11.70**	**14.70**	17.69	**18.94**	**19.52**	20.76	**21.08**	21.69
$Li:C_{60}$	10.83	**11.79**	**14.67**	17.73	**19.03**	**19.77**	20.79	**21.22**	21.67

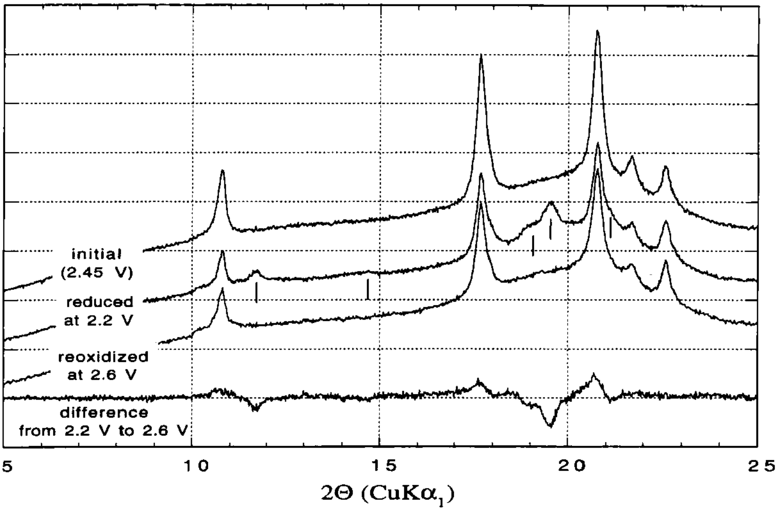

FIGURE 4 in-situX-rays diffraction patterns of the Na:C_{60} system, initial, reduced at 2.2 V and reoxidized at 2.6 V. Extra Bragg peaks of the reduced phase are indicated by |

DISCUSSION

Although the limitation due to solubility of the reduced species prevents quantitative electrochemical spectroscopy as previously obtained with Li, the shape of the first reduction voltamperogram (fig. 1) is different from that of the waves observed in cycling experiments once a large amount of C_{60} has dissolved (fig. 2). That last shapes can be compared to what was observed by other groups in similar experiments with liquid electrolytes [7,13-15]. They correspond to redox waves of C_{60}^{n-} anions into solution, out of dissolution and recrystallization of C_{60} around 2.4V vs. Na [14,15].

Thus we think that the variance in shape and amplitude of peaks of the voltammogram observed upon the first reduction is a qualitative observation of a set of intercalated phases. Taking into account results of the high temperature vapour phase synthesis [1, 2], we propose the following scheme for the attribution of that set of first reduction peaks: the two first steps at 2.3V and 1.95V have to be attributed to formation of new phases $Na_{0.5}C_{60}$ and Na_2C_{60}. The third one from 1.4 to 1V would be Na_3C_{60} formation in an homogeneous solid solution process from Na_2C_{60}. The last two steps would correspond to Na_6C_{60} and $Na_{11}C_{60}$ formation, with cluster of partly ionized sodium [1,2] . We have not yet been able to get evidence of a possible Na_1C_{60} composition as was obtained in the Li:C_{60} system by deintercalation of Li_2C_{60} [16].

As to the X-ray diffraction study of the first step, which apparently leads to $Na_{0.5}C_{60}$ formation, we can make the following observations: i) a superlattice of C_{60} (fcc with a ≈ 14.17Å at room temperature) would not give rise to such intense new lines, ii) we do not clearly see shifts or broadenings of the C_{60} lines which would be due to a distortion of the lattice towards a less symmetrical unit cell and moreover, in such a case, there is no reason for the extra peaks to be broader than the peaks from the C_{60} lattice and finally iii) when setting the potential at 2.2V constant value, the extra peaks appear and stabilize in intensity rapidly whereas the C_{60} lines are still decreasing for a while before stabilizing. That directly suggests a two-phase system and one cannot not rule out that part of the C_{60} has not been reduced and that the new broad Bragg peaks would correspond to the formation at the surface of the C_{60} of a solid compound involving reduced species C_{60}, Na and P(EO).

The reversibility of this step, which was previously observed both electrochemically and in X-ray diffraction for $Li_{0.5}C_{60}$ [4, 9] has been confirmed for the Na:C_{60} system. Thus if such a complex involving PEO does exist that means that it could be oxidized with recrystallisation of C_{60} on the working electrode. However in such a scheme it is difficult to understand the stoichiometries reached upon further reduction as obtained for the Li:C_{60} system. Experiments with new cross-linked P(EO) based Na electrolytes and with crystalline ones are in progress to overcome the solubility problem and confirm these attributions.

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