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Electrochemistry of C_{60} and C_{70} Incorporated in Polymer Films and Reversible Electrochemical Transformation of C_{60}

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Multilayer fullerene films have exhibited interesting electrochemical, photochemical, and optical properties. We report here the first electrochemical study of fullerenes C_x (x = 60 and 70) trapped in polymer films on platinum and carbon electrodes. The cyclic voltammetry (CV) of poly-**1**–C_{60} and poly-**1**–C_{70} films in MeCN electrolyte is close to that of dissolved C_x and differs markedly from the CV of solid C_x. The results also provide evidence for a reversible electrochemical transformation of C_{60} in this media upon its fifth reduction stage.

C_{60} and C_{70} can be reduced in solution at low temperature in a stepwise manner up to their hexaanions.[1-3] Their first three and four reversible one-electron reductions have also been examined as Langmuir films[4,5] and as solid films[4,6-14] in MeCN electrolyte. However, scanning the potential over the third or the fourth reduction irreversibly damaged the solid films,[4,6,14] since the electrogenerated C_x^{n-} anions are more soluble in polar solvents than neutral C_x.

The poly-**1**–C_x films were prepared according to an easy and rapid procedure developed in our laboratory,[15] namely by the evaporation on Pt or C disk electrodes (5-mm diameter) of a drop (20–40 μL) of CH_2Cl_2, 0.25 mM in C_x[16] and 2.5 mM in **1a** or **1b**. The water-insoluble monomeric coating was electropolymerized at 0.76 V *vs* SCE in 0.1 M $LiClO_4$ aqueous electrolyte. As already demonstrated with the electropolymerization of layers of **1** containing various anions[15] or enzymes,[17] this procedure allows irreversible trapping of C_x molecules in a polymer film coated on the electrode surface.[18] The modified electrodes were then thoroughly rinsed with MeCN, dried under vacuum, and studied by CV in tetra-*n*-butylammonium perchlorate (TBAP)–MeCN electrolyte.[20]

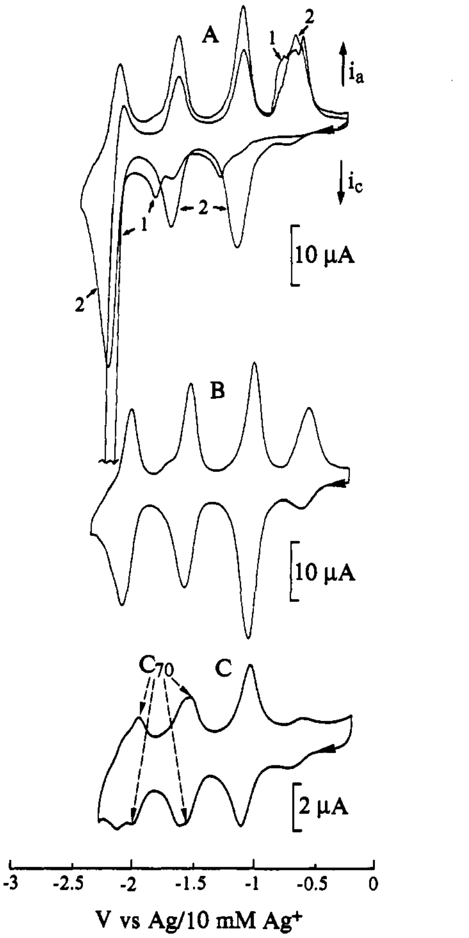
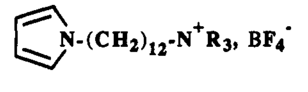


Figure 1. Cyclic voltammograms in 0.1 M TBAP in MeCN for (A) a C/poly-**1b**–C_{60} modified electrode, (1) first cycle, (2) second cycle, and (B) fourth cycle, ν = 100 mV s^{-1}. (C) C/poly-**1b**–C_{70} (contaminated with C_{60}) modified electrode, fifth cycle, ν = 20 mV s^{-1}.



1a R = CH_2CH_3

1b R = $(CH_2)_3CH_3$

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[16] C_{60} (99.9%) and C_{70} (97%) were purshased from Syncom, Groningen, The Netherlands, and used as obtained.

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[18] The resulting modified electrode exhibited the quasireversible redox peak system ($E_{1/2}$ = 0.6 V vs SCE) typical of a N-substituted polypyrrole.[19] Apparent surface concentrations of alkylammonium units, Γ_{N^+}, were calculated from the integrated charge under the polypyrrole oxidation wave, assuming that one in three pyrrole units is oxidized.[19] Thin films with Γ_{N^+} of 1 to 2 × 10^{-8} mol cm^{-2} were obtained under these experimental conditions (electropolymerization yield, 5–10%).

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[20] Electrochemical experiments were conducted in a glove box under an argon atmosphere at 20 °C. The Ag/10 mM $AgNO_3$ + 0.1 M TBAP in MeCN system was used as a reference electrode. The $AgNO_3$ solution was separated from the working compartment by a salt bridge. Potentiels were also referenced to the Fc/Fc^+ couple (where Fc is ferrocene), which was used as an internal standard. Electrochemical experiments followed the procedures described in the following: Cosnier, S.; Deronzier, A.; Moutet, J.-C. *J. Mol. Catal.* **1988**, *45*, 381. MeCN (Rathburn, HPLC grade S) was used without further purification. TBAP (Fluka puriss) was recrystallized from ethyl acetate/cyclohexane and dried under vacuum at 80 °C for 3 days.

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Figure 1A shows the first and second CV scans of a C/poly-**1b**–C_{60} electrode recorded within the window encompassing the first four reductions of the fullerene. On the first scan, several small reduction waves are followed by a large reduction peak located around −2.2 V. Four well-behaved pairs of peaks are visible on the second scan, suggesting that a rearrangement occurring during the first cyclic scan improves the permeation of the tetrabutylammonium cations in the film and thus the associated charge transfer in the polymer. After a few cycles, a stable voltammogram is obtained (Figure 1B), with four reversible CV reductions at −0.69, −1.12, −1.65, and −2.14 V vs Ag/10 mM Ag^+ (−0.76, −1.19, −1.72, and −2.21 vs Fc/Fc^+). These values are close to those reported for dissolved C_{60}.[1-3,21,22] Potential separation between cathodic and anodic peaks varies from 20 mV (second wave) to 50 mV (first and fourth waves) at a scan rate (ν) of 100 mV s^{-1}, as expected for a multilayer film.

The pair of peaks corresponding to the first C_{60} reduction remains abnormally low, as compared with those for other redox processes. The cathodic peak is very weak, while its corresponding anodic peak is more or less pronounced, according to the modified electrode studied. This feature is independant of ν in the 10–200 mV s^{-1} range. However, the charge measured under the first two reduction peaks is equal to that recorded under the two reoxidation peaks, indicating that part of the $C_{60}{}^{0/-}$ reduction is mediated through the $C_{60}{}^{-/2-}$ redox system. Obviously, reorganization of the film structure takes place during the formation of the $C_{60}{}^-$ species.

The apparent surface concentration of C_{60}($\Gamma_{C_{60}}$) was determined from the integrated current recorded at a low scan rate (ν = 20 mV s^{-1}) under the four reduction waves. We found that the charge measured is independant of ν in the 5–50 mV s^{-1} range. Typically, Γ_{C60} values of approximatively 3×10^{-9} mol cm^{-2} were obtained. This corresponds to coats of ca. 20 monolayers.[4] The stability of the modified electrodes was estimated by scanning repeatedly at ν = 100 mV s^{-1} over both the first and second pairs of waves. A slow decrease in peak currents was observed, with a 20% drop in electroactivity after 40 cycles.

If the CV scan is continued beyond the fourth reduction of C_{60} (Figure 2), a fifth reduction occurs at $E_{1/2}$ = −2.59 V vs Ag/10 mM Ag^+ (−2.66 V vs Fc/Fc^+). This poorly reversible wave can be attributed to the formation of $C_{60}{}^{5-}$. This species is very reactive under these experimental conditions, as demonstrated by the appearance on the reverse scan of two new anodic peaks (labeled with an asterisk in Figure 2) at E_p = −2.25 and −1.82 V vs Ag/10 mM Ag^+ (−2.32 V and −1.89 V vs Fc/Fc^+). These peaks are 140–180 mV more negative than the $C_{60}{}^{n-}$ reoxidation ones. They are tentatively attributed to the formation of $C_{60}H_2$ in the polymer film, which is formed through the reaction of $C_{60}{}^{5-}$ with protons from residual water. These peak potentials are in good agreement with literature values.[23,24] It is noteworthy that the $C_{60}H_2{}^{3-/2-}$ peak is smaller than that of $C_{60}H_2{}^{4-/3-}$. In addition, no wave attributable to the $C_{60}H_2{}^{2-/-}$ and $C_{60}H_2{}^{-/0}$ redox couples can be seen on the CV curve. Furthermore, on a second scan down to the four C_{60} reductions, the initial voltammogram features are fully restored without additional peaks. Indeed, it is known that the products of the third and fourth $C_{60}H_2$ reductions are unstable and decompose rapidly to give the parent C_{60}.[23,24]

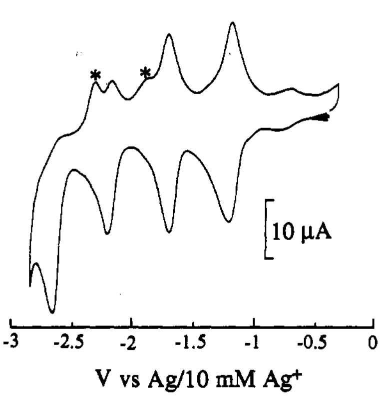

Figure 2. Cyclic voltammogram for a C/poly-**1b**–C_{60} modified electrode in 0.1 M TBAP + MeCN. Scan extended down to the fifth reduction process; ν = 50 mV s^{-1}.

The first two reduction potentials for C_{60} and C_{70} are virtually identical; in contrast, the potentials for the $C_{70}H_2{}^{2-/3-}$ and $C_{70}H_2{}^{3-/4-}$ redox couples diverge from the C_{60} ones as the potential becomes more negative.[2,25] Thus, on the CV of a poly-**1b**–C_{70} (contaminated with C_{60}[16]) film electrode (Figure 1C), the two pairs of peaks that appear at $E_{1/2}$ = −1.58 and −2.02 V vs Ag/10 mM Ag^+ (−1.65 and −2.09 V vs Fc/Fc^+) in front of the tri- and tetraanion steps of C_{60} can unambiguously be attributed to the third and fourth one-electron reductions of C_{70}.

In summary, this work presents a straightforward procedure requiring only a few micrograms of fullerene for producing C_x-containing polymer films on electrodes that will permit their electrochemical properties in common electrolytes and under typical experimental conditions to be studied. Cyclic voltammetry experiments strongly suggest the transformation of C_{60} to $C_{60}H_2$ through electrogenerated $C_{60}{}^{5-}$. The clear voltammetric data indicate that it will probably be possible to use this electrode modification procedure to study higher or substituted fullerenes that are either not available in adequate amounts or not sufficiently soluble for regular electrochemical studies. Ongoing investigations will also include the study of the photoelectrochemical properties of these fullerene films.

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