

Electrochemical polymerization of fullerene C₆₀

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Cyclic voltammetry data show that fullerene C₆₀ films on the Pt electrode surface in MeCN are electropolymerized to form polymeric C₆₀.

Key words: fullerenes, electropolymerization, cyclic voltammetry.

As known,¹ the voltammetric behavior of C₆₀ in solution is described by six redox transitions C₆₀^{0/-}/2⁻/3⁻/4⁻/5⁻/6⁻. The electrochemistry of thin C₆₀ films has been studied by many researchers (see, e.g., Ref. 2). All authors observed in the voltammograms of C₆₀ films the same two peaks in the region of potentials of the first two redox transitions of fullerene in solution, corresponding to the redox pairs C₆₀^{0/-} and C₆₀^{-/2-}, although the electrochemistry of the films have several specific features.²

We have shown (Fig. 1, a) that along with these peaks (E² and E³), one more peak (E¹) is observed in the cyclic voltammograms of MeCN/0.05 M Bu₄NPF₆ of the C₆₀ films deposited by sublimation *in vacuo* on a mesh Pt electrode. The potentials of all peaks are presented in Table 1 (entry 1). It is noteworthy that the E¹ peak has been detected previously,² but has not been thoroughly considered because of its very low intensity. Under the present conditions, the E¹ peak increases from cycle to cycle with the cyclic variation of the electrode potential in the potential region of the first two redox potentials of C₆₀ (see Fig. 1, a), while the E² and E³ peaks identified previously change in a more complicated manner: they first increase and then decrease. The latter effect for the E² and E³ peaks is caused, in particular, by the fact² that the film first swells and its permeability for counter ions increases (an increase in the signals) and then falls down and is dissolved due to the solubility of the reduced forms of C₆₀ (decrease in the signals). At the same time, the height of the E¹ peak (and this is extremely important to note) monotonically increases with time (until C₆₀ substantially falls down from the electrode), i.e., the substance and/or a new phase responsible for the appearance of this peak is insoluble and remains on the electrode.

To reveal the nature of the E¹ peak, let us consider Fig. 1, b, which presents the voltammogram of the C₆₀ films pretreated under a pressure of 1.5 GPa at 330 °C. In this thermobaric treatment, as has been shown previ-

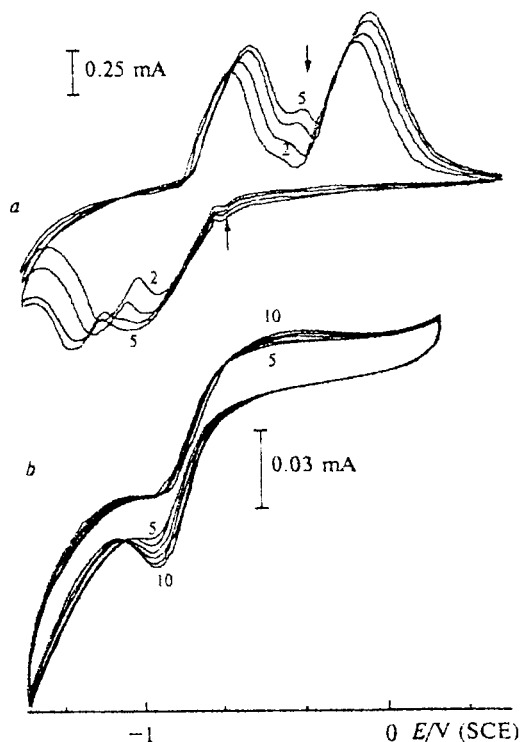


Fig. 1. Evolution of cyclic voltammograms of C₆₀ (a) and poly-C₆₀ films (b) on the mesh Pt electrode in MeCN/0.05 M Bu₄NPF₆ with potential scanning rate 10 (a) and 50 (b) mV s⁻¹. Figures designate numbers of cycles, arrows show the E¹ peak.

ously,³ fullerene is transformed to polyfullerene in which C₆₀ molecules are linked by covalent C—C bonds to form a cyclobutane fragment. The voltammograms of this film exhibit only the E¹ peak. Thus, the E¹ peak detected after both the thermobaric treatment of the initial monomer and its electrochemical treatment corresponds to the redox transition related to the appearance of a new phase, polyfullerene.

It can be seen from Table 1 (entries 1 and 2) that the E¹_{pc} values for the C₆₀ films treated thermobarically and electrochemically differ substantially. However, it should be kept in mind that the degree of polymerization of the electrochemically generated poly-C₆₀ is evidently lower. In addition, the amount of the new phase obtained electrochemically is much less than that of the phase obtained thermobarically, the latter being equal to 100%. In the latter case, the dense, adhesion, and insoluble poly-C₆₀ film is considerably less permeable. These reasons along with a strong superposition of the cathodic peaks in Fig. 1, *a* result in a noticeable difference in the E¹_{pc} values measured in entries 1 and 2. For thinner polyfullerene films, the differentiation of the potential is not so significant.

It should be mentioned in conclusion that heating of the poly-C₆₀ film to 200 °C for 1.5 h is accompanied by the complete conversion of the polymer into the monomer, which is evidenced by the data of entries 3 and 1 in Table 1. The voltammograms of the C₆₀ and thermally treated poly-C₆₀ films are almost identical.

Thus, poly-C₆₀ can be prepared not only thermobarically,³ photochemically,⁴ or due to the charge transfer from alkali metals (M) to a C₆₀ molecule in compounds M₁C₆₀,⁵ but electrochemically as well. It is most probable that the solid-phase polymerization occurs at the stage of electrogeneration of the C₆₀²⁻ dianion via the reaction of [2+2]-cycloaddition.⁶

Experimental

Fullerene was synthesized and purified by a known procedure.³ Fullerene films were deposited on a mesh Pt electrode (surface area 0.6–0.7 cm²) by sublimation of C₆₀ *in vacuo* (10⁻⁵ Torr) for 1 h. The films thus obtained were treated for 15 min at 1.5 GPa and 330 °C as described previously.³

Voltammetric measurements were performed at -20 °C in a dry inert atmosphere in MeCN (Aldrich). Acetonitrile was purified by refluxing over P₂O₅ and distilled directly to an electrochemical cell filled with argon.⁷ An 0.05 M solution of Bu₄NPF₆ (Aldrich) was used as the supporting electrolyte; the salt was preliminarily dehydrated by melting *in vacuo*.

All potentials were determined relative to the aqueous saturated calomel electrode (SCE) by referring the potential of the reference electrode (Ag/AgCl/4 M aqueous solution of LiCl), which was separated from the solution studied in the

Table 1. Potentials of peaks* (V, SCE) of C₆₀ films deposited on the Pt electrode before (1) and after (2) thermobaric treatment and poly-C₆₀ films after heating to 200 °C for 1.5 h (3)

Entry	Number of cycle	-E ¹ _{pc}	-E ¹ _{pa}	-E ² _{pc}	-E ² _{pa}	-E ³ _{pc}	-E ³ _{pa}
1	2	0.55	0.35	1.00	0.15	1.20	0.60
	4	0.55	0.37	0.97	0.15	1.15	0.60
2	5	0.92	0.41	—	—	—	—
	10	0.92	0.41	—	—	—	—
3	2	0.55	0.32	0.95	0.13	1.10	0.50
	4	0.55	0.35	0.92	0.15	1.10	0.50

Note. Medium MeCN/0.05 M Bu₄NPF₆, 20±2 °C, potential scanning rate 10 mV s⁻¹ (1, 3) and 50 mV s⁻¹ (2).

*E_{pc} and E_{pa} are potentials of cathodic and anodic peaks, respectively.

cell by a bridge filled with a solution of the supporting electrolyte, to the potential of the redox transition of ferrocene^{0/+} (E⁰ = 0.42 V, SCE).

A mesh Pt electrode with the deposited C₆₀ film or poly-C₆₀ was used as the working electrode (see above). Voltammetric measurements were performed by a PR-8 programmer and a PI-50-1 potentiostat without compensation of ohmic losses. Voltammograms were recorded on an N307/1 two-coordinate recorder.

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