Electrochemistry of Fullerene C_{60} Embedded in a Gel-like Membrane of Tetraoctylphosphonium Bromide on an Electrode in Aqueous Solution

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In this communication, we describe the first finding that fullerene C_{60} embedded in a gel-like membrane formed from tetraoctylphosphonium bromide on an electrode in an aqueous system gives stable electrochemistry leading to the formation of C_{60}^{-}, C_{60}^{2-} and C_{60}^{3-}.

Electrochemistry of fullerenes is forefront in the study of fullerene science, since multiply-charged anions of fullerene lead to a variety of unique functions.[1] Therefore controlled production of the multiply-charged anions of fullerenes in a variety of environments is important. On the other hand, the chemistry and physics of organic gels that have potential applications in the construction of “intelligent” material systems are also of an exciting area.[2] Organic gels are known to provide suitable microenvironments for the electrochemistry and regulated electrochemistry of some redox active molecules.[3] To our knowledge, however, no report has been published thus far describing the electrochemistry of fullerenes in a gel membrane system.

Although well-defined cyclic voltammograms leading to the formation of C_{60}^{6-} are observed for C_{60} in organic solvents,[4] electrochemistry of fullerene thin films on electrode surfaces is rather complicated and unstable both in organic[5] and aqueous media[6]. We have recently described that stable electrochemistry is possible at C_{60}/cationic lipid-modified electrode systems.[7] We describe here the electrochemical behavior of C_{60} in a gel-like membrane on an electrode surface.

Six hundreds mg of tetraoctylphosphonium bromide (TOPB) or 200 mg of tetraoctylammonium bromide (TOAB) was placed on a 0.5 mol dm^{-3} (2 mL) tetraethylammonium chloride aqueous solution phase. It was found that TOPB forms, within a minute, a phase-separated gel-like viscous phase on the underlying electrolyte solution phase (Figure 1A). On the contrary, TOAB did not form such a phase, instead, it remained being of solid structure even after a month, although it was gradually hydrated (Figure 1B). Addition of 5 mol% of C_{60} to TOPB or TOAB gave similar result.

A typical procedure for the preparation of a gel-like membrane of C_{60}/TOPB (molar ratio, 1/19) on an electrode is as follows. A fifteen microliter portion of C_{60} (Bucky USA, 99.95%)/TOPB in toluene ([TOPB] = 9.50 mmol dm^{-3}, [C_{60}] = 0.50 mmol dm^{-3}) was placed on a homemade basal plane pyrolytic graphite (BPG) electrode surface (geometric area, 0.36 cm^2), then air-dried. A C_{60}/TOAB (molar ratio, 1/19)-modified electrode was prepared by the similar manner. The modified electrodes thus obtained were immersed in a 0.5 mol dm^{-3} tetraethylammonium chloride aqueous solution (pH = 10) [8], followed by the measurements of electrochemistry at 25 ˚C using cyclic voltammetry (BAS-100BW Electrochemical Analyzer, Bioanalytical Systems) under an argon atmosphere (99.998% purity). A saturated calomel electrode (SCE) and a Pt plate electrode were used as the reference and the counter electrode, respectively.

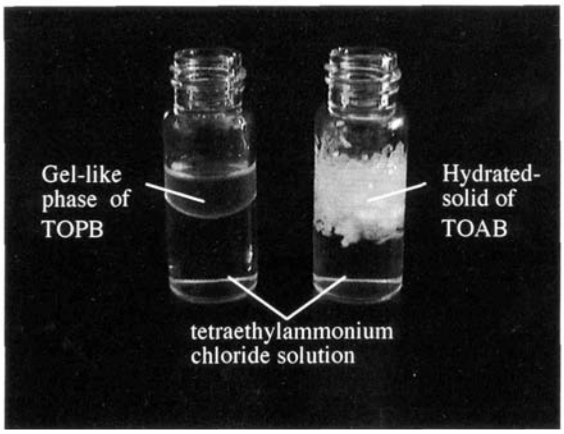

Figure 1. A photograph showing a gel-like phase of TOPB and a hydrated-solid of TOAB on water containing 0.5 mol dm^{-3} tetraethylammonium chloride at 25 ˚C.

Figure 2 shows typical cyclic voltammograms (CVs) for a gel-like membrane of C_{60}/TOPB on a BPG electrode. Three redox couples corresponding to C_{60}/C_{60}^{-}, C_{60}^{-}/C_{60}^{2-} and C_{60}^{2-}/C_{60}^{3-} are clearly seen in the potential window in the aqueous medium. This is the first example showing the electrochemistry of fullerene C_{60} incorporated in a gel-like membrane on an electrode. The formal potentials for electrochemistry of C_{60} in the membrane were: –0.17, –0.66, and –1.23 V for E_1^{0}’, E_2^{0}’ and E_3^{0}’, respectively (average for eight modified electrodes). The stability of the modified electrode was estimated by continuous potential cycling at a scan rate of 0.1 V/s. A gradual increase in the peak current was observed for first five potential cycling and then reached maximum after 6-10 cycles, followed by a gradual decrease in the current because of the instability of C_{60}^{3-}, since only slight decrease in the current was observed for the cycling over the first two redox waves leading to the generation of C_{60}^{2-}. The reduction charge decreased for the second and the third reduction processes, as compared with that for the first redox process. Expected smaller diffusion coefficients and instability of the redox species may explain the behavior.

TOAB was used to compare with TOPB. Typical CVs for a C_{60}/TOAB-modified electrode are shown in Figure 3. It is evident that the modified-electrode gives well-defined voltammograms leading to the formation of C_{60}^{3-} as well as that for the C_{60}/TOPB-modified electrode. The formal potentials for the C_{60}/TOAB electrode were –0.11, –0.64 and –1.28 V vs. SCE for E_1^{0}’, E_2^{0}’ and E_3^{0}’, respectively (average for seven-modified electrodes), which are almost comparable to those of the C_{60}/TOPB-modified electrodes.

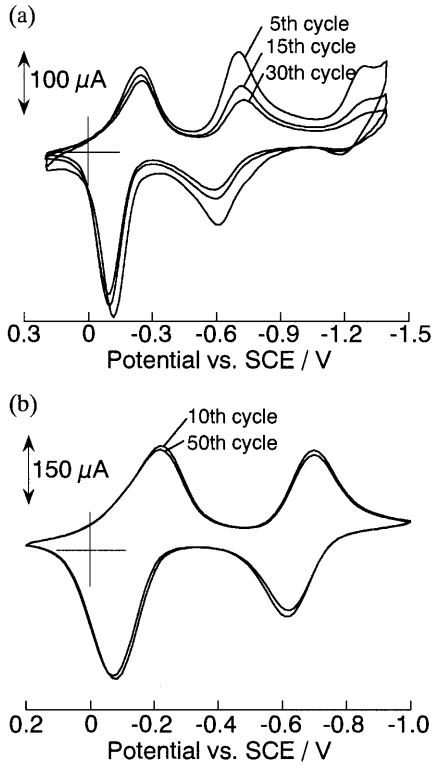

Figure 2. Typical cyclic voltammograms showing three redox couples (a) and two redox couples (b) of a C_{60}/TOPB(molar ratio, 1/19)-modified BPG electrode in water (pH 10) containing 0.5 mol dm^{-3} tetraethylammonium chloride. Scanrate, 0.1 V/s .

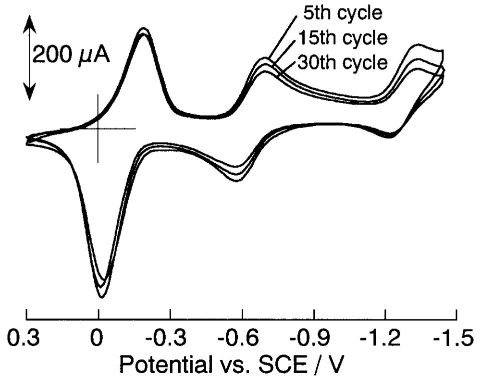

Figure 3. Typical cyclic voltammograms at the scan rate of 0.1 V/s for a cast film of C_{60}/TOAB (molar ratio, 1/19) on a BPG electrode in water (pH 10) containing 0.5 mol dm^{-3} tetraethylammonium chloride.

The cathodic current for the first and second redox couples in the CVs for C_{60}/TOPB- and C_{60}/TOAB-modified electrodes increased in proportion to the square root of scan rate in the range of 0.05 – 1.0 V/s, suggesting that the electrochemistry is controlled by diffusion process. In contrast, the peak current at the electrodes at scan rates below 0.01V/s was proportional to the scan rates (data not shown), as expected for the thin-layer electrochemical behavior[9].

The amounts of reacted C_{60} calculated from the cathodic current (1st reduction) in the CVs at the very low scan rate (0.002 V/s) of C_{60}/TOPB-modified electrodes and of C_{60}/TOAB-modified electrodes were 1.3×10^{-8} and 2.1×10^{-8} mol cm^{-2}, respectively (the values are the average for six films), indicating that about 63 and 97% of C_{60} in the membranes of TOPB and TOAB, respectively, are electroactive.

In conclusion, we have discovered that the organic gel-like membrane film of TOPB on an electrode provides suitable microenvironments for the electrochemistry of fullerene C_{60} leading to $C_{60}{}^{3-}$. Details including the structure of the gel-like membrane of C_{60}/TOPB as well as the electron transfer mechanisms of fullerene C_{60} and higher fullerenes at the gel-like and non-gel membrane systems are now in progress in our laboratory. The finding affords the opportunity to undergo electrochemical communication of fullerenes and related materials at gel-modified electrode systems that possess many possible applications in a variety of areas in science.

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References and Notes

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