# First Electrochemical Reductions of $C_{84}$ Films on Electrodes

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The higher fullerene $C_{84}$ embedded in cast films of molecular-bilayer-forming cationic lipids on electrodes was found to exhibit evident electron transfer reactions leading to the generation of $C_{84}$ multi-charged anions.

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The chemistry of fulleride anions is among the most fundamental in the field of fullerene science.[1] However, reports[1b,c] describing the electrochemical properties of higher fullerenes have been limited due to their low abundance compared with the more readily available $C_{60}$ and $C_{70}$. From the aspects of both fundamentals and applications, the electrochemistry of fullerene films is important;[2] however, to our knowledge, no reports have thus far described the electrochemistry of films of higher fullerenes on electrode surfaces. Recently we described the stable aqueous electrochemistry of $C_{60}$ incorporated in films of cationic artificial lipids.[3a,b] We also found that the electrochemistry of a $C_{60}$-lipid composite film on an electrode was tunable by inducing a phase transition of the lipid bilayer film.[3c] In organic solution, the higher fullerene $C_{84}$ with molecular symmetry $D_2$ and $D_{2d}$ has been reported to show multiple reduction processes,[4] of which the first three reduction processes are stable and the last two being unstable. Separation of $D_2$ and $D_{2d}$ isomers of $C_{84}$ has been described in the literatures[5], though their separation is extremely difficult. In this paper, we report the first finding of the electrochemical production of multiple $C_{84}$ anions in films on electrodes.

In this work, $C_{84}$ is embedded in thin films of cationic amphiphiles on electrode surfaces. The cationic amphiphiles used in this study were tetraoctylammonium bromide (**1**) and didodecyldimethylammonium bromide (**2**)[6]. Aqueous solutions of **2** prepared by ultrasonication form a bilayer structure like liposomes and biological cell membranes. X-ray diffraction diagrams of cast films of **1** and **2** gave rise to ordered reflection peaks that indicate the existence of well-organized multilayer structures. Molecular-bilayer formation for cast films of double-chain lipids are well-known. As the higher fullerene $C_{84}$, isomers of molecular symmetry $D_2$ and $D_{2d}$ (a 2:1 abundance ratio) were used in this experiment.[7]

The procedure for preparing a modified electrode is as follows. A fifteen-microliter portion of $C_{84}$/amphiphile (molar ratio, 1/19) or $C_{84}$ solely in *o*-dichlorobenzene ($[C_{84}]$ = 0.50 mM, 1 M = 1 mol $dm^{-3}$) was placed on a homemade basal plane pyrolytic graphite (BPG) disk electrode (geometric area, 0.20 $cm^2$),[3] followed by hot-air drying (approximately 40 °C) for 1.5 h and then drying in vacuum at ambient temperature for 4 h. The cyclic voltammetry and differential pulse voltammetry (BAS-100BW Electrochemical Analyzer, Bioanalytical Systems) for the modified electrodes were examined in water[8] containing 0.5 M tetraethylammonium chloride (TEAC) as the electrolyte at 25 °C in an argon atmosphere. A saturated calomel electrode (SCE) and a Pt plate electrode were used as the reference and the counter electrodes, respectively.

We first measured cyclic voltammograms (CVs) for a film containing only $C_{84}$ cast on a BPG electrode in water. It was

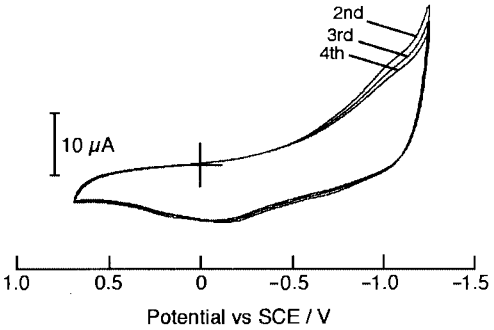

**Figure 1.** CVs of $C_{84}$-coated electrode in water containing 0.5 M TEAC at 25 °C. Scan rate, 100 mV/s.

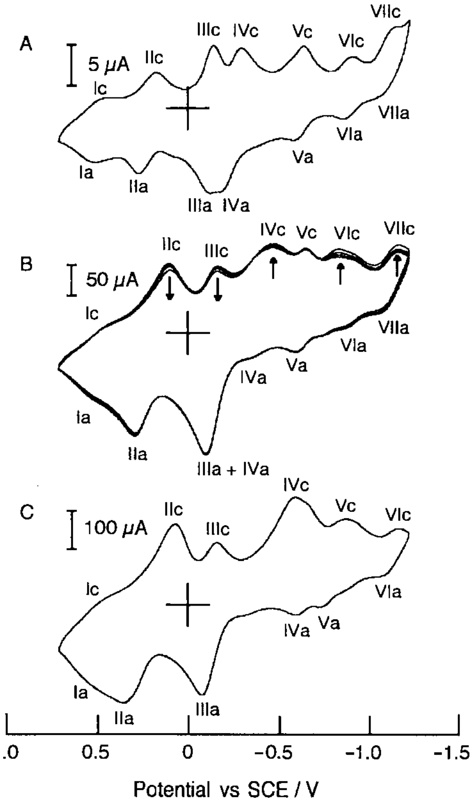

**Figure 2.** CVs of a $C_{84}$/**1**(molar ratio, 1/19)-coated electrode in water containing 0.5 M TEAC at 25 °C. Scan rates are: (A) 5 mV/s, (B) 100 mV/s (2nd −5th scans indicated by arrows) and (C) 300 mV/s. Ic–VIIc and Ia–VIIa denote cathodic and anodic peaks in the CVs, respectively.

found that the electrode gave no cathodic peak current in aqueous solution (Figure 1). In sharp contrast with this result, well-defined multiple electron transfer reactions for a composite film of $C_{84}$/**1** cast on a BPG electrode occur as shown in Figure 2. The electrode gives multiple cathodic peaks together with their corresponding anodic peaks. This is the first demonstration of the redox behavior of $C_{84}$ in a film on an electrode. The formal potentials for the six redox couples estimated from the CV at 5 mV/s are: + 477, + 204, – 145, – 254, – 636, – 900 and – 1110 mV. Up to scan rates of 100 mV/s, the peak potential of the fourth reduction process of the electrode shifted to the negative and at the scan rate of 300 mV/s, this cathodic peak merged into the reduction peak appeared at – 600 mV (see Figure 2C). This behavior was not observed for the other reduction processes. This may be due to a lower electron transfer rate for the fourth reduction process.

The CVs of **1**/$C_{84}$-coated electrode were stable for potential cycling at the higher scan rates than 300 mV/s, while lower scans than 100 mV/s caused gradual decrease in the current (data not shown). The results indicate that the electrochemically generated $C_{84}$ anions in the cationic lipid films were not sensitive toward water. As shown in Figure 3, the differential pulse voltammograms (DPVs) of $C_{84}$/**1** and $C_{84}$/**2**-coated electrodes are found to give eight and six reduction peaks, respectively, leading to the generation of multi-charged $C_{84}$ anions.

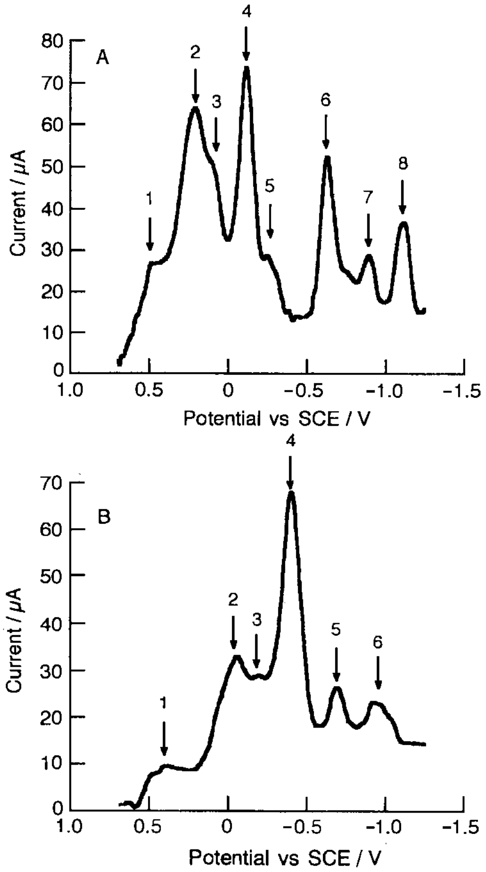

**Figure 3.** DPVs (25 mV/s scan rate, 50 mV pulse amplitude, 50 ms pulse width, 200 ms pulse interval) for electrodes modified with a cast film of (A) $C_{84}$/**1**(molar ratio, 1/19) or (B) $C_{84}$/**2** (molar ratio, 1/19) in water containing 0.5 M TEAC at 25 °C.

Because $C_{84}$ used in this study exists as the two isomers, the assignment of their multiple redox processes at the modified electrode system is complex. The accurate assignment of the voltammograms is now in progress in our laboratory.

To be emphasized is the observation of large positive shift of the half-wave potentials in the DPV of $C_{84}$ embedded in the films of **1** compared to those in organic solution[4]. This shift suggests the strong binding of $C_{84}$ anions with tetraoctylammonium cation in the film.[9] Hydrophobic microenvironments afforded by the tetraoctylammonium matrix contribute to the generation and stability of $C_{84}$ anions.

In conclusion, this is the initial report describing multiple electron transfer reactions of the higher fullerene $C_{84}$, when embedded in films on electrodes containing cationic amphiphiles. This exciting result has both fundamental and applied implications that are under continuing study in this laboratory. Of particular interest is the characterization of the structure and electron transfer properties of other higher fullerenes and metallofullerenes in lipid films on electrodes.

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