

## Electrochemistry of a Fullerene / Ammonium Lipid Composite Film on an Electrode in Water. Generation of $C_{60}^{3-}$

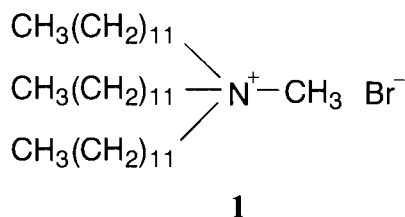
Naotoshi Nakashima,\* Takuto Kuriyama, Takeshi Tokunaga, Hiroto Murakami, and Takamasa Sagara  
*Department of Applied Chemistry, Faculty of Engineering, Nagasaki University, Bunkyo-cho, Nagasaki 852-8521*

(Received March 6, 1998; CL-980165)

We describe for the first time the finding that  $C_{60}$  embedded in a cast film of triple-chain ammonium lipid, tridodecylmethylammonium bromide, on an electrode shows three-consecutive one-electron transfer processes leading to  $C_{60}^{3-}$  in aqueous solution.

The preparation, characterization and functionalization of fullerene thin films are also of interest from both a fundamental and a practical point of view.<sup>1-2</sup> Our interest is focused on the combination of fullerene chemistry and the chemistry of lipid bilayer membranes.<sup>3</sup> Despite much interest in the electrochemistry of fullerenes,<sup>4</sup> aqueous solution electrochemistry of fullerenes has been very limited.<sup>5-8</sup> Hill and co-workers<sup>8</sup> described that two reduction and reoxidation peaks on the cyclic voltammograms (CVs) of  $C_{60}$  film-modified electrodes disappeared by continuous potential cycling. On the contrary, we have discovered, very recently, that in an aqueous system,  $C_{60}$  embedded in a cast film of ditetradecyldimethylammonium poly(styrene sulfonate) on an electrode undergoes two-consecutive reversible one-electron transfer reaction with the electrode with the formal potential of -0.290 and -0.910 V vs. Ag/AgCl/saturated KCl and that the generated radical monoanion and dianion are unusually stable.<sup>9</sup> Here we describe, for the first time, three-consecutive one electron transfer reactions of  $C_{60}$  embedded in lipid films of tridodecylmethylammonium bromide (**1**; see Chart 1) on an electrode in the aqueous system.

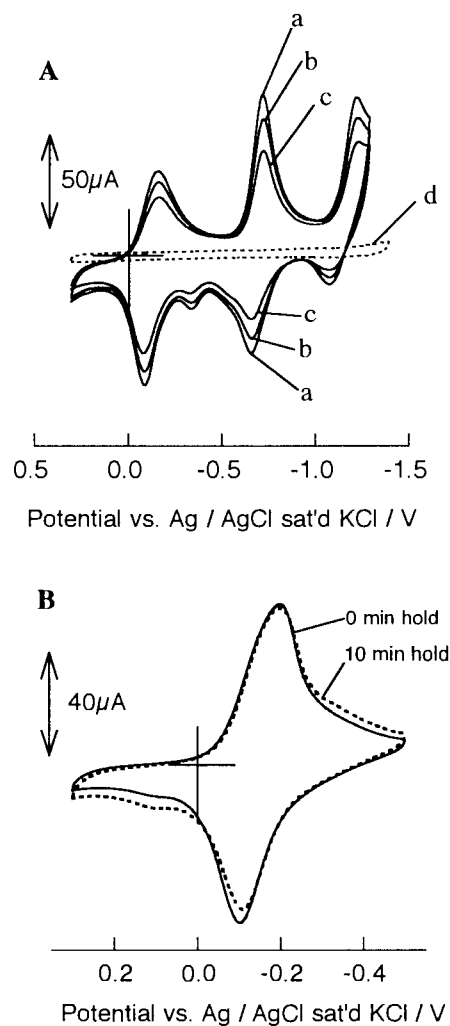
Chart 1.



Artificial lipid, **1**, is known to form molecular-bilayer structure.<sup>10</sup> This compound is readily soluble in benzene and forms, by the conventional solvent evaporation method, water-insoluble multibilayer films. Typical procedure for the preparation of modified electrodes is as follows. A ten microliter portion of  $C_{60}$  (Bucky USA, 99.995%) / **1** in benzene ( $[\mathbf{1}] = 15.2 \text{ mmol/dm}^3$ ,  $[C_{60}] = 0.80 \text{ mmol/dm}^3$ ) was placed on a homemade basal plane pyrolytic graphite (BPG) disk electrode<sup>11</sup> (geometric area,  $0.25 \text{ cm}^2$ ), then air-dried. The electrochemistry for the cast films of  $C_{60}$ / **1** on the BPG electrodes was examined using cyclic voltammetry (equipment, BAS-100BW Electrochemical Analyzer, Bioanalytical Systems) under an argon atmosphere. A

Ag/AgCl/saturated KCl electrode and a Pt plate electrode were used as the reference and the counter electrodes, respectively.

Figure 1 shows typical cyclic voltammograms (CVs) for cast films of  $C_{60}$ / **1** on BPG electrodes in water (pH = 10)<sup>12</sup> at 25 °C. We can see evident three redox couples corresponding to  $C_{60} / C_{60}^-$ ,  $C_{60}^- / C_{60}^{2-}$  and  $C_{60}^{2-} / C_{60}^{3-}$ , respectively (Figure 1A).



**Figure 1.** Typical cyclic voltammograms at the scan rate of 0.1 V/s for cast films of  $C_{60}$ / **1** (molar ratio, 1/19) (a - c in A, and B) and **1** only (d) on a BPG electrode in water (pH = 10) containing  $0.5 \text{ mol/dm}^3$  tetraethylammonium chloride as the supporting electrolyte; (A): 2nd (a), 5th (b) and 10th (c) scans, (B): voltammograms for the first redox couple after potential hold for given time at -0.5 V.

The obtained formal potentials (average for three modified electrodes) were -0.12, -0.74 and -1.21 V for  $E_1^{0'}$ ,  $E_2^{0'}$  and  $E_3^{0'}$ , respectively; both  $E_1^{0'}$  and  $E_2^{0'}$  for the modified electrode shifted less-negative by ca. 0.17 V relative to those of  $C_{60}$ /ditetradecyldimethylammonium poly(styrene sulfonate)<sup>9</sup> on BPG. This positive shift would come from the strong binding between the fullerene anions and tridodecylmethylammonium cations and make possible the detection of three reduction peaks within the potential window in the aqueous solution. The radical trianion generated in this system is not so stable; that is, continuous potential cycling at the scan rate of 0.1 V/s caused gradual decrease in the currents. On the contrary, only slight decrease in the current was observed for potential cycling over the first two redox couples. The radical monoanion of  $C_{60}$  in this system was found to be stable, that is, virtually no change in the CVs for the first redox wave was observed even after a 10 min hold at -0.5 V (Figure 1B). A small anodic peak appeared near -0.34 V, suggesting the generation of a subproduct<sup>13</sup> through the chemical reaction of the fullerene anions and water. The peak was not observed when the CV was cycled back from -0.5 V.

The cathodic and anodic currents for the first redox couple in the cyclic voltammograms of the  $C_{60}/\mathbf{1}$  film on BPG increased in proportion to the square root of the scan rate in the range of 0.1 - 1.0 V/s, indicating that the electrochemistry is diffusion-controlled. The amount of reacted  $C_{60}$  calculated from the CV at the very low scan rate (2 mV/s) was  $1.5 \times 10^{-8}$  mol/cm<sup>2</sup> (values are averages for three films). Supporting electrolytes are known to influence the voltammograms for cast films of  $C_{60}$  on the electrodes because the electrode reactions involve incorporation of cations from the bulk solution.<sup>14, 15</sup> In the present system, however, the CVs for cast films of  $C_{60}/\mathbf{1}$  on BPG were essentially the same in tetraethylammonium chloride, NaCl and KCl aqueous solution (data not shown), suggesting that tridodecylmethylammonium ion in **1** acts as the counter cation during the reduction of the fullerene.

In conclusion, we have discovered that in an aqueous system,  $C_{60}$  embedded in cast films of **1** on BPG shows evident three-consecutive one-electron transfer processes leading to  $C_{60}^{3-}$ . This finding would be applicable to a variety of fullerene derivatives, higher fullerenes and metallofullerenes. Greater detail about the characterization of the present system are currently under investigation in our laboratory.

This work was supported, in part, by the Grant-in-Aids from the Ministry of Education, Science, Sports, and Culture, Japan, Ogasawara Science and Technology Foundation and Iketani Science and Technology Foundation. We would like to thank Professor T. Kunitake for kindly providing compound **1**.

## References and Notes

- 1 "Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials: Vol.5," ed by K. M. Kadish and R. S. Ruoff, The Electrochemical Soc., Pennington (1997).
- 2 For a review, see: J. Chlistunoff, D. Cliffler, and A. J. Bard, *Thin Solid Films*, **257**, 166 (1995).
- 3 H. Murakami, Y. Watanabe, and N. Nakashima, *J. Am. Chem. Soc.*, **118**, 4484 (1996).
- 4 J. Chlistunoff, and A. J. Bard, in "Handbook of Organic Conductive Molecules and Polymers," ed by H. S. Nalwa, John Wiley & Sons, Chichester (1997), pp. 333-412.
- 5 A. Szucs, A. Loix, J. B. Nagy, and L. Lamberts, *J. Electroanal. Chem.*, **397**, 191 (1995).
- 6 P. Boulas, W. Kutner, M. T. Jones, and K. M. Kadish, *J. Phys. Chem.*, **98**, 1282 (1994).
- 7 W. A. Kalsbeck and H. H. Thorp, *J. Electroanal. Chem.*, **314**, 363 (1991).
- 8 J. J. Davis, H. A. O. Hill, A. Kurz, A. D. Leighton, and A. Y. Safronov, *J. Electroanal. Chem.*, **429**, 7 (1997).
- 9 N. Nakashima, T. Tokunaga, Y. Nonaka, T. Nakanishi, H. Murakami, and T. Sagara, submitted for publication.
- 10 T. Kunitake, N. Kimizuka, N. Higashi, and N. Nakashima, *J. Am. Chem. Soc.*, **106**, 1978 (1984).
- 11 A-E. F. Nassar, Y. Narikiyo, T. Sagara, N. Nakashima, and J. F. Rusling, *J. Chem. Soc. Faraday Trans.*, **91**, 1775 (1995).
- 12 Tetraethylammonium hydroxide aqueous solution was used to adjust pH. The peak top of the cathodic current was not detected at neutral and acidic solutions because of the narrow potential window.
- 13 T. F. Guarr, M. S. Meier, V. K. Vance, and M. Clayton, *J. Am. Chem. Soc.*, **115**, 9862 (1993).
- 14 In Ref. 4, pp.386-390.
- 15 A. Szucs, A. Loix, J. B. Nagy, and L. Lamberts, *J. Electroanal. Chem.*, **402**, 137 (1996).