Observation of Electrochemical C_{60} Reduction of a Diamond Thin Film Electrode at Room Temperature

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Highly conductive boron-doped diamond thin film electrodes were used for the first time to examine the cyclic voltammetric behavior of C_{60} reduction at room temperature as a demonstration of the relatively wide potential window in nonaqueous media. Five reduction peaks were observable on diamond electrodes at room temperature, while four reduction peaks were observed on Pt.

Highly conductive boron-doped diamond thin films have recently been of great interest due to their unique properties, e.g., wide potential window in aqueous media,[1,2] and fast electron transfer kinetics for outer-sphere type redox couples.[3-5] However, in nonaqueous media, there have been very few reports.[3] In the present work, we have chosen to examine the multiple reduction steps of C_{60} in nonaqueous solution in order to more fully exploit the wide potential window.

C_{60}, due to its unique geometry and electronic properties, has attracted wide interest.[6] Since it is a highly extended aromatic system, C_{60} is able to delocalize excess charge very effectively, so that its radical anions are relatively stable, making it possible to observe multiple one-electron reduction steps.[7-13] The LUMO of C_{60} is triply degenerate, and thus the molecule is able to accept up to six electrons to form diamagnetic C_{60}^{6-}.[14-16] However, it has been difficult to observe all of the reduction peaks due to the very negative potentials involved, so that special measures must be employed. For example, in order to observe the sixth reduction peak using Pt and glassy carbon electrodes, low temperatures have usually been employed.[12, 13] As for boron-doped diamond thin film electrodes, their wide potential window could be expected to be highly advantageous for observing the more negative reduction peaks for C_{60}. In the present work, diamond thin film electrodes were used to study the electrochemical behavior for C_{60} reduction in nonaqueous media at room temperature.

Boron-doped polycrystalline diamond thin films were grown on an n-Si (100) substrate using a high-pressure microwave plasma-assisted chemical vapor deposition system (ASTeX Corp., Woburn, MA). Detailed conditions have been described elsewhere.[17] Acetone/methanol (9 : 1 by volume) was used as the carbon source, and B_2O_3 was used as the boron source. The B/C weight ratio in the feedstock was approximately 10^4 ppm. The film thickness was approximately 40 μm. The apparent electrode area was ca. 0.25 cm^2. For comparison, a platinum electrode was used (electrode area, ~ 0.1 cm^2). C_{60} (Tokyo Kasei Kogyo Co., Ltd.) was used, without further purification at a concentration of ca. 5×10^{-4} M. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) (Tokyo Kasei Kogyo Co., Ltd.). The vacuum-type electrochemical cell used was designed and constructed in-house. Highly purified acetonitrile and toluene (Wako Pure Chemical Industries, Ltd.) were dried over CaH_2, deaerated by repeated freeze-pump-thaw cycles, and vapor-transferred directly into the electrochemical cell. The ratio of acetonitrile to toluene was 1:5 by volume. All of the voltammograms (cyclic and differential pulse) were recorded using an HZ-3000 automatic polarization system (Hokuto Denko Co., Ltd., Japan), with a platinum counter electrode. A silver wire was used as a quasireference (Ag QRE), and the ferrocene/ferrocenium redox couple (Fc/Fc^+) was used as an internal potential reference. All measurements were carried out under vacuum at room temperature (22±2 °C).

Figure 1 shows cyclic voltammograms (CV) for C_{60}, both on Pt and a diamond thin film electrode at room temperature. For the Pt electrode (Figure 1 a), four reduction peaks for C_{60} were clearly observed in the CV curve. The measured $E_{1/2}$ values (midpoint potentials, i.e., the average of the anodic and cathodic CV peak potentials), relative to Fc/Fc^+, for the four reduction steps were -1.13, -1.57, -2.06, and -2.53 V, although others have observed five peaks under different experimental conditions.[18] The CV obtained for the diamond electrode yielded five clear peaks (excluding the first small peak, as discussed below) due to the wider potential window. It should also be pointed out that the appearance of the CV for diamond (Fig. 1b) is similar to that expected for a microelectrode array. This may be due to the fact that sp^2-type carbon impurities on the diamond surface are acting as microelectrodes. Moreover, the smaller current densities observed in Fig. 1 (b) indicate that only a portion of the surface was electrochemically active. Comparing the $E_{1/2}$ values for the Pt and diamond electrodes, as well as those reported in the literature for glassy carbon (GC)[19] and Hg[20] electrodes (see Table 1), it is apparent that the first peak (-0.69 V) observed on the diamond electrode must be due to a process other than the reduction of solution-phase C_{60}. It may be due to reduction of adsorbed C_{60}. In the case of GC, the sixth reduction peak also could not be observed due to a steep increase in the background current.[19] In addition, on mercury ultramicroelectrodes, at slow potential sweep rates (5 mV s^{-1}) the sixth peak was unclear. However, at fast sweep rates (1.6 V s^{-1}), it was observed more clearly[20], probably due to the increased peak current. It may also be possible to observe all six reduction peaks using diamond with further optimization of the experimental conditions, for example, the use of diamond microelectrodes and ultrapurification of the electrolyte.

The voltammetric peak separations, ΔE_p, were seen to vary between 0.11 and 0.17 V, which is greater than that observed for GC (80 mV).[19] There was no correlation between these values and the $E_{1/2}$ values for the five redox steps for C_{60}, indicating that the electrode kinetics do not vary with potential, as expected for a degenerate semiconductor electrode. The reason for the ΔE_p values being larger than those observed for other electrodes most likely involves depressed electrode kinetics and uncompensated ohmic resistance.

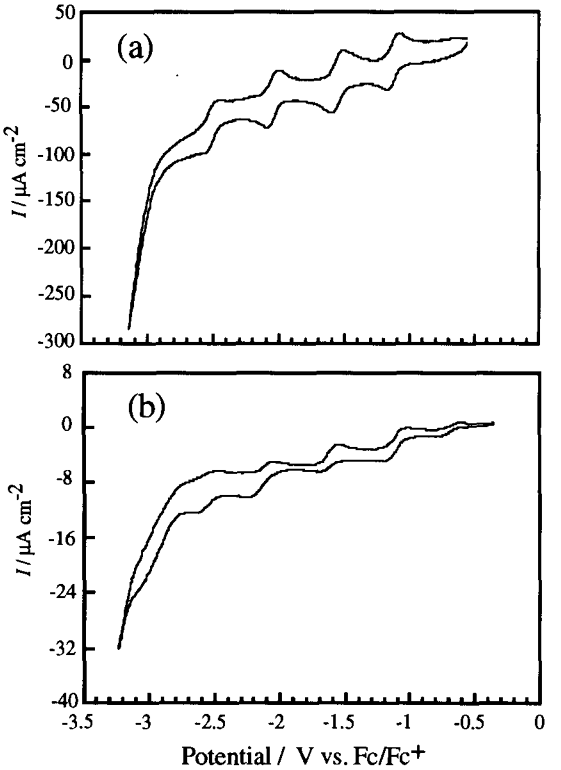

Figure 1. Electrochemical behavior for C_{60} (0.5 mM) using cyclic voltammetry at 10 mV s^{-1} on (a) platinum and (b) highly boron-doped diamond in CH_3CN/toluene (1:5 v/v) at room temperature.

Table 1. $E_{1/2}$ and ΔE_p values for the successive reduction steps for C_{60} on various types of electrode materials

Electrode [Method]		$E_{1/2}$ / V vs. Fc/Fc$^+$ (ΔE_p / V)					
		0/1-	1-/2-	2-/3-	3-/4-	4-/5-	5-/6-
glassy carbon[a]	[CV]	-0.99 (0.08)	-1.41 (0.08)	-1.90 (0.07)	-2.38 (0.07)	-2.89 (0.08)	-3.26[b]
mercury[c]	[CV]	-1.03	-1.45	-1.93	-2.42	-2.90	-3.27
platinum[d]	[CV]	-1.13 (0.08)	-1.57 (0.09)	-2.06 (0.07)	-2.53 (0.08)		
diamond[e]	[CV]	-1.12 (0.14)	-1.61 (0.11)	-2.14 (0.16)	-2.56 (0.12)	-2.97[f] (0.17[f])	

[a] At 25°C.[19] [b] Estimated from Osteryoung square wave voltammetry. [c] At 21°C.[20] [d] $E_{1/2}$ of Fc/Fc$^+$ is 0.86 V vs. Ag QRE. [e] $E_{1/2}$ of Fc/Fc$^+$ is 0.64 V vs. Ag QRE. [f] Estimated from differential pulse voltammetry.

In summary, the diamond film electrode was used for the first time in an organic solvent system to study the electrochemical reduction for C_{60}. At room temperature, five electrochemical reduction peaks of C_{60} were clearly observed. We have noted that the electrochemical behavior in this case appears to be mediated by sp^2 carbon impurities. We have examined a number of redox couples in aqueous solution, and, in almost every case, there is little influence of these impurities, which we estimate to be present at less than 1 % of the total surface area.[21] One notable exception is O_2 reduction in acid solution.[22] The possible reasons for the observations in nonaqueous electrolyte in the present work are under investigation. In any case, diamond film electrodes appear to have promise in the study of electrochemical behavior at very negative potentials in nonaqueous solutions.

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