Electrochemical Properties of Buckminster-fullerene (C$_{60}$) in Acetonitrile Containing Quarternary Ammonium Electrolytes

Il Kwang Kim*, Hyun Jin Kim, Gi Su Oh
Il Chol Jeon⁺, Byoung Joon Ahn⁺

*Department of Chemistry, Wonkwang University., Iksan City,
570-749, Korea
⁺Department of Chemistry, Chŏnbuk National University., Chŏnju
City, 560-756, Korea
(Received August 20, 1995)

Abstract : Thin films of buckminsterfullerene(C$_{60}$) formed by solution drop casting on Pt foil electrode surfaces were studied by cyclic voltammetry(CV) in acetonitrile(MeCN) containing quaternary ammonium or alkali-metal salts as supporting electrolyte. The electrochemical behaviors of C$_{60}$ films are found to be strongly dependent on the nature of the supporting electrolytes, especially with tetrabutyl ammonium perchlorate (TBAP, NBu$_4$ClO$_4$), and tetrabutyl ammonium tetrafluoroborate (TBABF$_4$, NBu$_4$BF$_4$). Reasonably stable films are formed into which electrons can be injected. The interaction of C$_{60}$ film with the quaternary ammonium cation may produce the fulleride salts (TBA$^+$)(C$_{60}^-$) and (TBA$^+$)$_2$(C$_{60}^{2-}$). The bulk electroreduction with a controlled potential to generate the soluble C$_{60}^{3-}$ anions(dark red-brown color) is followed by electrooxidative deposition to produce a neutral C$_{60}$ film on the surface. The peak currents(I$_{pc}$ and I$_{pa}$) of these thin film were dramatically decreased with repetitive potential scanning. These results could be explained by the adsorption-desorption phenomena and ion pairing interaction of reduced species(C$_{60}^-$, and C$_{60}^{2-}$) onto the electrode surface. The peak current changes and peak potential shifts of the thin C$_{60}$ film in cyclic voltammograms formed from solution were observed by varying scan rates.

Keywords : Buckminsterfullerene(C$_{60}$), Fulleride salts, Electrochemical reduction.

1. Introduction

Fullerenes, pure carbon molecules with closed-cage structure consisting of five and six membered rings, have been intensely studied both experimentally and theoretically since their discovery in 1985[1]. The study of fullerene chemistry has grown rapidly since the method for preparing fullerenes in gram quantities was reported[2]. Studies of fullerene's reactivities have revealed very special properties, such as the photoelectrochemical behavior of C_{60} and C_{70} [3], the conductivity and superconductivity of alkali-metal-doped C_{60}(where the alkali metals are K, Rb, Cs, etc.)[4], and the reductive electrochemistry of C_{60} and C_{70}[5]. C_{60} films, casted on an electrode surface by evaporation of C_{60} solutions, were doped with alkali metals or quaternary ammonium cations upon electroreduction in acetonitrile[6]. While the electroreductions of fullerenes have been studied in various solvents and electrolyte systems, the stoichiometry of electrogenerated $C_{60}{}^{3-}$ films has not been fully elucidated nor have the solubility and stability of these fulleride films have been characterized. At low temperature, Echegoyen *et. al* all. determined the C_{60} and C_{70} accept six electrons to generate $C_{60}{}^{6-}$ and $C_{70}{}^{6-}$ anions[7]. Also, kinetics and thermodynamics for the electroreduction of buckminsterfullerene were studied[8] and using EQCM and CV, the ion pairing of electrogenerated C_{60} anions($C_{60}{}^{-}$, $C_{60}{}^{2-}$) with quaternary ammonium cations was observed[9].

In the present paper, we report a study on the electrochemical properties of the thin films of fullerene C_{60} formed by solution drop casting on the Pt foil electrode in MeCN. And the bulk electroreduction under a controlled potential sufficiently negative to generate the soluble $C_{60}{}^{3-}$ anion (dark red-brown color in MeCN) is followed by electrooxidative deposition to form a neutral C_{60} film on the surface of Pt foil electrode.

2. Experimental

2.1 Reagents and Instruments

Buckminsterfullerene(C_{60}) was purchased from TCI and used as received. The C_{60} sample appears ~95 % pure from chromatography studies. Tetrabutyl ammonium perchlorate(TBAClO₄ : Alfa Co.), tetrabutyl ammonium tetrafluoroborate (TBABF₄ : Aldrich), lithium perchlorate(LiClO₄ : Aldrich), and sodium perchlorate(NaClO₄ : Sigma) were used as supporting electrolyte. Toluene (Fisher), acetonitrile(MeCN : Merck), and benzene (Aldrich) were used as solvents to prepare the C_{60} sample solutions. Acetonitrile (CH_3CN) was purified by distilling over anhydrous $AlCl_3$ (15 g/L), over Li_2CO_3 (10 g/L), and redistilled over CaH_2 (2 g/L) prior to use. Purified solvents were reserved in 5 Å molecular sieves (8~12 mesh). Tetrabutyl ammonium perchlorate was twice recrystallized from absolute ethanol and dried in vacuum at 40 ℃ prior to use.

Electrochemical measurements were carried out using a Model 273 Potentiostat/Galvanostat, M270 software and the M303A electrode system. The working cell was purged by nitrogen gas(N_2) to remove the residual oxygen (O_2). In cyclic voltammetry, the working electrode was a Pt foil electrode(area: 0.14 cm², thickness : 0.05 mm), and the auxiliary electrode was a Pt wire. All potentials were recorded against a Ag/AgCl reference electrode. Controlled potential electrolysis was performed with EG&G PAR 173 potentiostat coupled with an EG&G PAR 179 digital coulometer.

2.2 Preparation of the Thin Films

The thin films on the Pt foil electrode were prepared by solution drop casting[10] of 2~5 μL of a C_{60} solution in benzene, toluene, and acetonitrile (1 mM). The color of solution was dark red-purple indicating $C_{60}{}^{-}$ anions in benzene and toluene[11] and dark red-brown colored colloidal solution indicating neutral C_{60} and almost did not dissolve in acetonitrile.

2.3. Preparation of the C_{60}^{3-} solutions

Typically, a few mg of solid C_{60} present as a fine suspension in $20\sim25$ mL of acetonitrile (MeCN), 0.1 M $TBA(ClO_4)$, was bulk electroreduced while stirring at a mercury pool electrode polarized at -1.6 V $vs.$ Ag/AgCl. After the transfer of 3.0 electrons per C_{60} molecule, all of the solid eventually dissolved as the electrolysis current decayed to zero. The resulting C_{60}^{3-} solution was dark red-brown color.

3. Results and Discussion

3.1 Cyclic Voltammetry of C_{60} films upon the quaternary ammonium salt and different electrolytes

$Fig.$ 1 shows that the cyclic voltammetric behaviors of C_{60} films formed by solution drop csating in acetonitrile solution containing 0.1 M $TBAClO_4$. As seen in the figure, the peak currents were decreased upon the scan number.
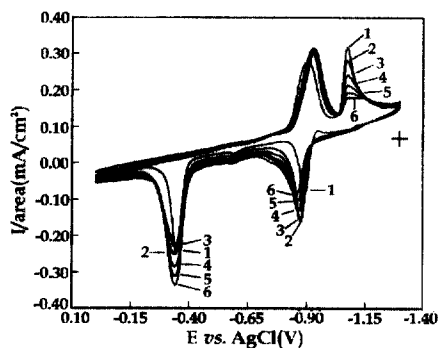

$Fig.$ $1.$ Cyclic voltammogram of the C_{60} coated Pt electrode in 0.1M $TBAClO_4$, MeCN solution. Scan rate $=$ 50 mV/sec. The area of the Pt electrode is $0.15cm^2$. The C_{60} coated electrode was prepared by casting $5\mu L$ of the C_{60} solution in toluene. The numbers in peak is representing the scan number. + : The start point of the scanning.

$Table$ 1 shows both the change of the peak potential and the peak area upon the scan number. Plotting the change of the peak current and the peak area $vs.$ the scan number was shown in $Fig.$ $2.$ We obtained the two pair of peaks from the cyclic voltammogram of $Fig.$ $1.$ We could predict the electron transfers with two-steps to generate the fullerene anions(C_{60}^{-}, C_{60}^{2-}) during reduction-oxidation process of the adsorbed C_{60} on the electrode surfaces from the decrease of the current and peak area of the $Fig.$ $1, 2$ and $Table$ $1, 2.$
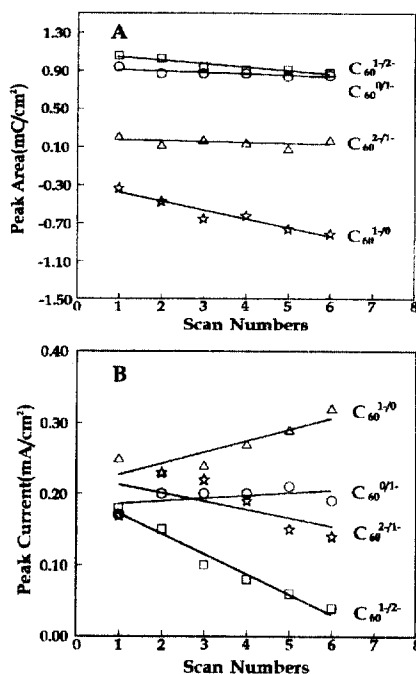

$Fig.$ $2.$ Plot of the peak area and peak current $vs.$ cycle numbers from $Fig.$ $1.$

The cyclic voltammograms have shown that the peak currents and areas are reduced with increase of the scan number. It could be suggested that the salt $(TBA^+)(C_{60}^-)$ or $(TBA^+)_2(C_{60}^{2-})$ was produced by the interaction between the fullerene anions and supporting electrolyte cations. Decreasing in the peak current of $C_{60}^{1-/2-}$ (at -1.09 V) was larger than that of $C_{60}^{0/1-}$(-0.94 V) in $Fig.$ $1.$

Table 1. The peak potenitals values from Fig. 1.

Cycles (Peak No.)	$-E_{pc}$ ($C_{60}^{0/1-}$)	$-E_{pc}$ ($C_{60}^{1-/2-}$)	$-E_{pa}$ ($C_{60}^{1-/0}$)	$-E_{pa}$ ($C_{60}^{2-/1-}$)
1	0.9073	1.0760	0.3470	0.8931
2	0.9250	1.0760	0.3400	0.8760
3	0.9280	1.0780	0.3400	0.8740
4	0.9320	1.0780	0.3400	0.8660
5	0.9317	1.0780	0.3441	0.8604
6	0.9358	1.0800	0.3401	0.8545

Table 2. The peak current values from Fig. 1.

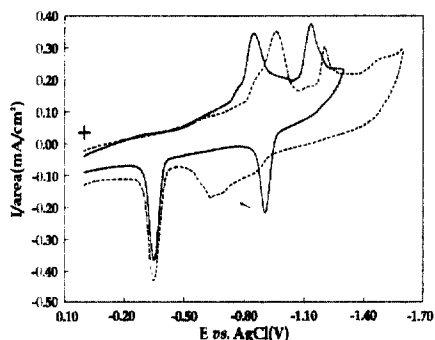| Cycles (Peak No.)	I_{pc} ($C_{60}^{0/1-}$)	I_{pc} ($C_{60}^{1-/2-}$)	I_{pa} ($C_{60}^{1-/0}$)	I_{pa} ($C_{60}^{2-/1-}$)
1	0.1736	0.1839	0.2535	0.1707
2	0.1974	0.1503	0.2282	0.2262
3	0.2004	0.1019	0.2419	0.2202
4	0.2042	0.0770	0.2684	0.1858
5	0.2063	0.0584	0.2903	0.0519
6	0.1968	0.0390	0.3172	0.1382

Fig. 3. Cyclic voltammograms of the C_{60} coated Pt electrode in 0.1M TBABF6, MeCN solution. Scan rate = 50 mV/sec. The C_{60} coated electrode was prepared by casting 5μL of the C_{60} solution in toluene. The area of the Pt electrode is 0.14cm^2. 1 : Potential window : 0.0V ~ −1.3V. 2 : Potential window : 0.0V ~ −1.6V.

This means that a part of C_{60}^{2-} in the salt was not oxidized to C_{60}^{1-} during the oxidation process after forming the salts (TBA$^+$)(C$_{60}^-$) and (TBA$^+$)$_2$(C$_{60}^{2-}$) produced by interaction between C_{60}^{2-} anions and tetrabutyl ammonium cations. Fig. 3 shows that the cyclic voltammogram of the C_{60} film using TBABF4 as supporting electrolyte. The peak shapes changed and the peak potential shifted with the expansion of the potential window in Fig. 3. When the potential

window is fixed from 0.00 V to −1.30 V, the first and second peak in cathodic direction appeared at −0.93 and −1.20 volts with their corresponding anodic peaks. This shows that electrochemical reaction of C_{60} was reversible process on the electrode surface. When the switching potential expended to −1.60 volts, the cathodic peaks shifted to anodic direction that the anodic peak at −0.90 volts was shifted to more positive(−0.60 volts) and broadened. And the peak for the production of the C_{60}^{3-} anion at near −1.50 V was appeared. As results, we proposed that the peak shift and broadening occurred by the effect of the generated C_{60}^{3-} anion.
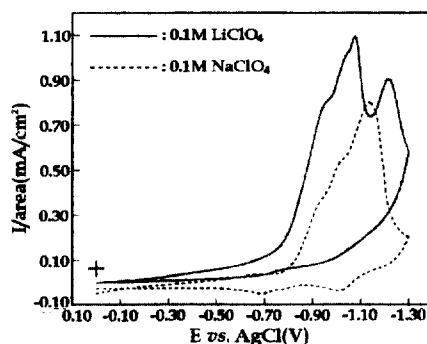

Fig. 4. Cyclic voltammogram of the C_{60} coated Pt electrode in 0.1M LiClO$_4$, and NaClO$_4$, MeCN solution. Scan rate = 50 mV/sec. The areas of the Pt electrode in using LiClO$_4$, and NaClO$_4$ were 0.105cm^2, and 0.14cm^2, respectively. The C_{60} coated electrode was prepared by casting 5μL of the C_{60} solution in toluene.

Fig. 4 shows the cyclic voltammogram of C_{60} film using LiClO$_4$ and NaClO$_4$ as a supporting electrolyte. These results differed from case of quaternary ammonium salts, the separated two cathodic peaks were merged to one peak and anodic peaks were diminished.

3.2 Cyclic voltammetry with the different casting solvents

Fig. 5 shows the cyclic voltammogram of C_{60}

film on electrode surface formed by drop casting with toluene solution. All the peak potentials were shifted to anodic direction and peak currents were decreased then *Fig. 3*.
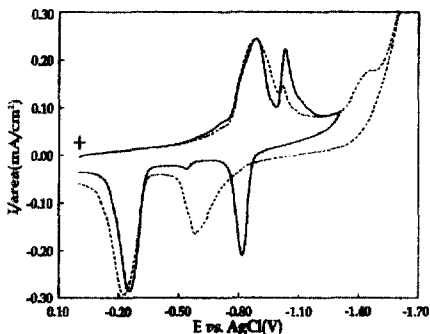

Fig. 5. Cyclic voltammogram of the C_{60} coated Pt electrode in 0.1M TBAClO$_4$, MeCN solution. Scan rate = 100 mV/sec. The area of the Pt electrode is 0.16cm^2. The C_{60} coated electrode was prepared by casting 5 μL of the C_{60} solution in toluene. 1 : Potential window : 0.0V ~ −1.3V. 2 : Potential window: 0.0V ~ − 1.6V.
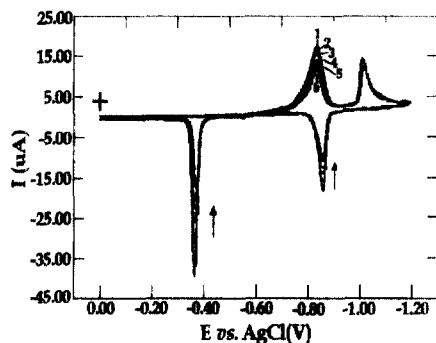

Fig. 6. Cyclic voltammograms of the C_{60} coated Pt electrode according to scan numbers in 0.1M TBAClO$_4$, MeCN solution. Scan rate = 10 mV/sec. The C_{60} coated electrode was prepared by casting 5 μL of the C_{60} solution in MeCN.

Fig. 6 is the cyclic voltammogram of C_{60} film formed by drop casting with acetonitrile solution. Before dropping the C_{60} sample solution the sample was sonicated for 5min. because the C_{60} was insoluble and colloidal suspension in this solvent. *Fig 6* showed that the peaks was

sharp and the intensity was relatively small. The sharpness of peaks was shown that the film was monolayed thin surface and molecular packed structure. The peak currents were depended upon the C_{60} quantity adsorbed on electrode surface and the interaction of fullerene anions. The decreasing of peak currents with scan number means that the adsorbed C_{60} was decreas of last from electrode surface by interacting with TBA anion.

3.3 Scan rate effects

Fig. 7 shows the cyclic voltammogram from the C_{60} film in 0.1M TBAClO$_4$ acetonitrile with the scan rate from 5 to 100 mV/sec. The peak potential and peak current values from *Fig. 7* were shown in *Table 3*, it was shown that the current contained both of diffusion and chemical reaction current from the $I_{pc}/\nu^{1/2}$ values were increased with increase of scan rate.
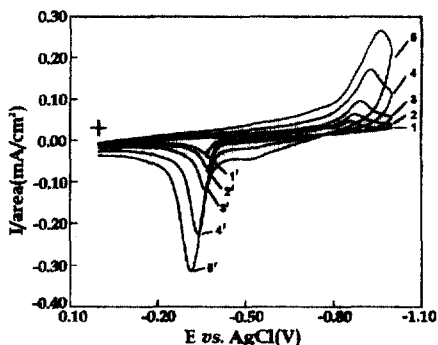

Fig. 7. Cyclic voltammogram of the C_{60} coated Pt electrode in 0.1M TBAClO$_4$, MeCN solution. The area of the Pt electrode is 0.14cm^2. The C_{60} coated electrode was prepared by casting 5μL of the C_{60} solution in toluene. 1 : 5mV/sec., 2 : 10mV/sec., 3 : 20mV/sec., 4 : 50mV/sec., 5 : 100mV/sec.

Fig. 8 is the cyclic voltammogram with the scan rate 100, 50, and 20 mV/sec., at same condition with *Fig. 7*, only except potential window; 0.0~−1.6 volts. All peak currents in *Fig. 7, 8* are increased with the scan rate and the cathodic peak was shifted to negative

potential and the anodic peak was shifted to positive potential. Therefore, We can suggest that the electro- chemical reaction is proceeded as CE process from the data of *Table 3.*

Table 3. The peak potential and peak currents upon the scan rates in *Fig. 7.*

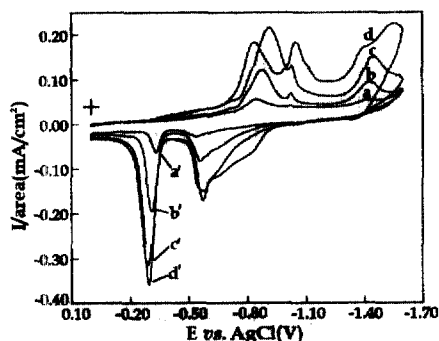| Scan Rate (mV/sec.)	Peak No.	$-E_{pc}$ (Volts)	$-E_{pa}$ (Volts)	I_{pc} (uA/cm²)	I_{pa} (uA/cm²)	I_{pa}/I_{pc}	$I_p/V^{1/2}$
5	1	0.8550	0.3630	24.700	29.093	1.1779	11.0462
10	2	0.8708	0.3691	34.810	63.762	1.8317	11.0079
20	3	0.8937	0.3599	58.600	110.40	1.8840	13.1034
50	4	0.9287	0.3386	118.00	203.10	1.7212	16.6878
100	5	0.9623	0.3127	180.80	274.70	1.5194	18.0800

Fig. 8. Cyclic voltammogram of the C_{60} coated Pt electrode in 0.1M TBAClO₄, MeCN solution. The area of the Pt electrode is 0.14cm². The C_{60} coated electrode was prepared by casting 5μL of the C_{60} solution in toluene. 4 : the 1st scan with 100 mV/sec., 3 : the 2nd scan with 100 mV/sec., 2 : the 3rd scan with 50 mV/sec., 1 : the 5th scan with 20 mV/sec.

3.4 The cyclic voltammogram of the C_{60}^{3-} solutions from the controlled potential electrolysis

Fig. 9 shows the cyclic voltammogram of C_{60}^{3-}(dark red-brown color) solution obtained by the controlled potential electrolysis at -1.50 volts in acetonitrile containing 0.1 M TBAClO₄. The peak currents were very weak, and the delay time (20 sec.) were applied to the switching potential.
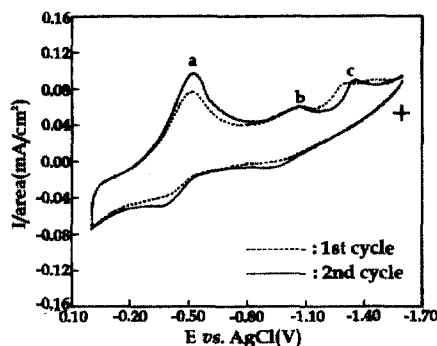

Fig. 9. Cyclic voltammogram from C_{60}^{3-} solution in 0.1M TBAClO₄, MeCN. Scan rate = 50 mV/sec.

As seen, the cyclic voltammogram was shown that all of the cathodic peaks were almost reduced and the corresponding anodic peaks were almost disappeared due to formation of fulleride anion-quarternary ammonium cation complex.

3.5 The evidence on the interaction of the fullerride anions and the amine
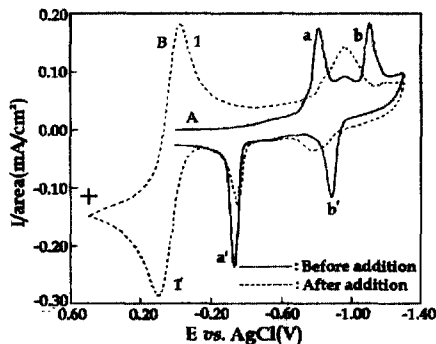
Fig. 10 shows that the cylic voltammograms

Fig. 10. Cyclic voltammogram of the C_{60} coated Pt electrode and the effect of TPA addtion in 0.1M TBABF₆, MeCN solution. Scan rate = 50 mV/sec. The area of the Pt electrode is 0.14cm². The C_{60} coated electrode was prepared by casting 5μL of the C_{60} solution on toluene. A : Cyclic voltammogram with only the C_{60} coated electrode, B : After addition of 100μL of 0.1M TPA(N,N,N',N'-tetramethyl-p-phenylenediamine) in MeCN.

of before and after adding 100 μL 0.1M TPA in

acetonitrile. In this figure, "A" was shown the cyclic voltammogram of C_{60} film in 0.1 M TBAClO$_4$ of acetonitrile. "B" was shown the cyclic voltammogram of C_{60} film after adding 0.1 M TPA at the same condition. All the peaks (1, 2 and 1', 2' in A) were decreased, broadened or merged and new reversible peaks (1 and 1' in B) were appeared by addition TPA. These have shown that the amine compound was easily interacted with fulleride anion and this interaction may be applicable to surface modification with amine compound or electrochemical reaction.

$$C_{60} + \rho\,(TBA^{+})$$
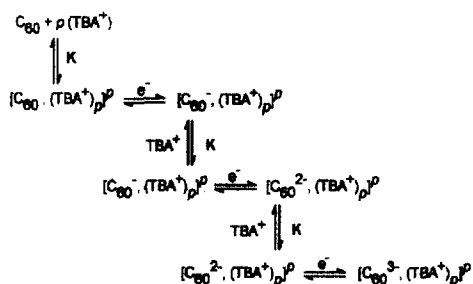
Scheme 1. The proposed EC mechanism.

p : The number of the electrolyte cation.

K_{as} : The association constant.

Conclusion

In this report, we have studied the electrochemical behaviors of the C_{60} thin film casted on the electrode surfaces by the cyclic voltammetry in acetonitrile solution. The behaviors of the C_{60} film casted on electrode surface; i) the peak currents were decreased with the scan number, ii) From this result, it was predicted that the fulleride complex, $(TBA^{+})(C_{60}^{-})$, and $(TBA^{+})_2(C_{60}^{2-})$ were generated by the interaction between the fullerene anions and the supporting electrolyte cations, iii) In final, the CE mechanism of the electrode process was proposed as the following *scheme 1*.

References

1. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature*, **318**, 162(1985).
2. W. Kröschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, *Nature*, **347**, 354(1990).
3. P. V. Kamet, I. Bedha, and S. Hotchandani, *J. Phys. Chem.*, **98**, 9137(1994).
4. A. F. Hebard, M. J. Roseinsky, C. R. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Plastra, A. P. Ramirez, and A. P. Krotan, *Nature*, **350**, 600(1991).
5. J. P. McCauley Jr., Q. Zhu, N. Coustel, O. Zhou, G. Baughan, S. H. J. Idziak, J. E. Fischer, S. W. Tozer, D. M. Groski, N. Bykovetz, C. L. Lin, A. R. McGhie, B. H. Allen, W. J. Romanow, A. M. Denenstein, and A. B. Smith III, *J. Am. Chem. Soc.*, **113**, 8537(1991).
6. X. Liu, W. C. Wan, S. M. Owens, and W. E. Broderick, *J. Am. Chem. Soc.*, **116**, 5489(1994).
7. W. Koh, D. Dubois, W. Kutner, M. T. Jones, and K. M. Kadish, *J. Phys. Chem.*, **96**(11), 4163(1992).
8. C. Jehoulet, A. J. Bard, and F. Wudl, *J. Am. Chem. Soc.*, **113**, 5456(1991).
9. Q. Xie, E. Pérez-Cordero, and L. Echegoyen, *J. Am. Chem. Soc.*, **114**, 3978(1992).
10. M. V. Mirkin, L. O. S. Bulhões, and A. J. Bard, *J. Am. Chem. Soc.*, **115**, 201(1993).
11. F. Zhou, S. L. Yau, C. Jehoulet, D. A. laude, Z. Guan, and A. J. Bard, *J. Phys. Chem.*, **96**(11), 4160(1992).
12. R. G. Compton, R. A. Spackman, and R. G. Wellington, *J. Electroanal. Chem.*, **327**, 337 (1992).

13. R. G. Compton, R. A. Spackman, D. J. Riley, R. G. Wellington, J. C. Eklund, and A. C. Fusher, *J. Electroanal. Chem.*, **344**, 235(1993).

14. K. Chopra and I. Kaur, "Thin Film Device Applications", New York, Plenum Press, p.42(1983).

15. A. Hirsch, "The Chemistry of the Fullerenes", New York, p.40(1994).