# Electrochemical properties of C60 thin film

N. Yoshiyama[a], H. Endo[a], H. Yamamoto[a], Y. Tanaka[b] and M. Tokumoto[b]

[a]College of Sci. & Technol., Nihon University
Narashinodai, Funabashi-shi, Chiba 274, Japan

[b]Electrotechnical Laboratory
Umezono, Tsukuba-shi, Ibaragi 305, Japan

Fundamental electrochemical properties of the evaporated $C_{60}$ film were studied by the voltammentry in the organic electrolyte solution. The reversible four reduction waves were observed corresponding to the formation of alkali metal-salts of fullerene, $A_xC_{60}$ (A: Li, K, Rb, x=1,2,3,4). Also the two reduction waves were found in the electrolyte solution with $NH_4^+$ ion. The voltammograms observed for each cation specy were compared and discussed in relation to the cation radius. The change of optical density spectrum by the redox reactions was measured in the wavelength range of visible light. The rapid decrease of the resistivity of the $C_{60}$ film was observed after the doping of potassium through the protective polyimide overlayer.

## 1. INTRODUCTION

Fullerenes have been attracted many attentions as a new class of functional materials.[1,2] Since Hebard et al.[3] reported that the potassium-doped fullerene $K_3C_{60}$ shows a superconductive critical temperature Tc of 18 K, the value of Tc in a series of the alkali metal-doped fullerene increases as increasing the radius of the alkali ion. Such the doping has been done by exposure of the alkali metal vapor in a vacuum tube. Then the doping is controled by the nominal composition of the specimen or by monitoring the resistivity of the doped fullerene film. Since the doping procedure is really not easy, a noble doping technique is needed for the material research of a doped fullerene.

An electrochemical process is expected to be a candidate for a new doping technique. Electrochemical properties of a solvated fullerene molecule were investigated in a supporting organic salt by many groups[4-7]. In those works, the reversible redox waves were discussed in relation to the formation of $C_{60}$ cations with multi-valences. On the other hand, electrochemical properties of the fullerene film has been also examined in the voltammetry using a solid polymer electrolyte[8-10] or an organic electrolyte solution[11].

The purposes of this work are to study a fundamental process of electrochemical reactions of the C60 thin film by a voltammetry in organic electrolyte solution and to develop an electrochemical doping process of alkali metals ions or ammonium ions into the C60 thin film. The

redox potentials of the film observed were substantially in agreement with those of the solvated C60 ion. The dependences of the reducing potentials were investigated with respect to the kind of the electrolyte solution or the cation species. After the cation doping the characteristic color changes or the drastic decrease of the electric resistivity were observed. As a result it was confirmed that the electrochemical doping is a useful process to obtain various cation-doped fullerenes.

## 2. EXPERIMENTAL

The $C_{60}$ thin film was prepared from purified $C_{60}$ powder (Texas Fullerenes Corp.) by a thermal vacuum evaporation. The distance between the substrate and the crucible was about 10 cm. The background pressure of the chamber was $2.0 \times 10^{-6}$ Torr and the pressure increased up to about $1.0 \times 10^{-5}$ Torr during the evaporation. The substrate was at ambient temperature. The crucible was heated very slowly at first to remove organic remanents.

The prepared C60 thin film on the Au film was a polycrystal with a fcc phase. The estimated lattice constant was about 1.43 nm of which the value was slightly larger than the reported value, about 1.42 nm[12].

At first the Au film of few tens nm thick was deposited as an electrode for electrochemical measurements on fused quartz. The C60 film of about 500 nm thick was evaporated. Furthermore Au electrode films were prepared for some of the specimen films in order to measure the electrical

resistivity of the doped C₆₀ film. Finally a protective overlayer of polyimide (Hitachi Chemical Co. Ltd., HL-1305) was formed by a spin coating.

In the electrochemical measurement the working electrode was the specimen film. The counter and the reference electrode was a stainless steel and AgCl/Ag through a salt bridge, respectively. The electrolyte solutions investigated were 0.1N-LiClO₄/DMSO, 0.1N-KClO₄/(CH₃)₂SO (DMSO), 0.1N-KClO₄/ HCON (CH₃)₂ (DMF),0.1N-KClO₄/CH₃CON(CH₃)₂ (DMAC), and 0.1N-RbClO₄/DMSO. The cyclic voltammogram (CV) was measured by the function generator (Hokuto Denko, HB-104) and the potentiostat (Hokuto Denko, HA-301). Before the measurement bubling by nitrogen gas was done for about 30 minutes to remove oxygen gas from the electrolyte solution.

When the voltammetry was measured, the optical absorbance was simultaniously monitored by the spectrometer (Shimazu Corp. UV-3100) through the electrolyte cell at the several fixed wavelength from 410 nm to 810 nm.

## 3. ELECTROCHEMICAL ACTIVITY OF C₆₀ THIN FILM

### 3-1 Voltammetry

Figure 1 shows the typical voltammograms of the C₆₀ film without the protective overlayer in the DMSO solution including the alkali metal cations (Li⁺, K⁺, and Rb⁺) and NH₄⁺ ion. Four reduction waves were clearly observed for the alkali metals cations, while only two waves were obtained for

NH₄⁺. Then the Au film was not electrochemically active in the reduction region from 0 V to -2 V vs. AgCl/Ag.
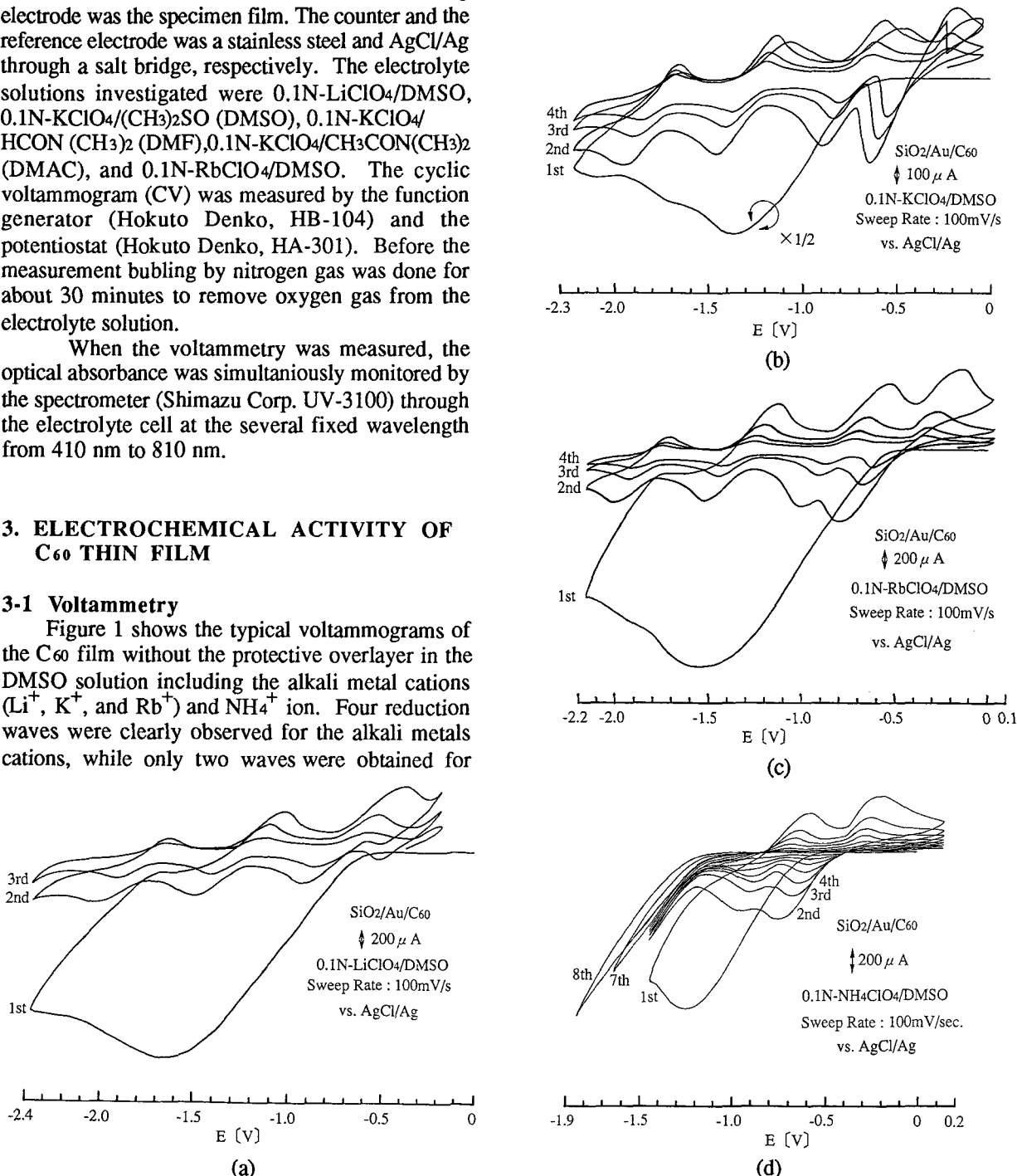


Fig. 1. Typical cyclic voltammograms of the C₆₀ thin film in the electrolyte solution of (a) 0.1N-LiClO₄/DMSO, (b) 0.1N-KClO₄/DMSO, (c) 0.1N-RbClO₄/DMSO , and (d) NH₄ClO₄/DMSO with the sweep rate of 100 mV/sec.

Table 1
Half-cell potentials of the C60 thin film in the KClO4 system

| Scan Rate | 20 (vs. AgCl/Ag) | | | | 100 (vs. AgCl/Ag) | | | |
|---|---|---|---|---|---|---|---|---|
| | E1 | E2 | E3 | E4 | E1 | E2 | E3 | E4 |
| 0.1N-KClO4/DMF | -0.33 | -0.58 | -0.93 | | -0.32 | -0.76 | -1.08 | |
| 0.1N-KClO4/DMAC | | | | | -0.25 | -0.50 | -0.97 | -1.60 |
| 0.1N-KClO4/DMSO | -0.30 | -0.71 | -0.12 | | -0.42 | -0.75 | -1.30 | -1.82 |

E1,E2,E3 and E4 are half-cell potentials ; e.q.,E1=1/2(E1red+E1ox)

As a general tendancy the voltammogram of the first sweep was deformed. The reversible few cycles of the voltammogram were, however, obtained with the almost same size of several waves. From the point of a coulometry the result reveals that the same number of electrons concern with each redox reaction. So the observed reduction waves correspond to the formation of alkali metal-salts of fullerenes, $A_xC_{60}$ (A: Li, K, Rb, x=1,2,3,4). Since the C60 film dissolved into the solution, the swelling of the CV gradually decreased during the measurement.

As results the electrochemical activity of the alkali metals cations were confirmed and the new finding of the ammonium ion was reported here. Recently Zhou et al.[13] reported that the reaction of ammonia with $Na_2CsC_{60}$ resulted in the high Tc of the compound $(NH_3)_4Na_2CsC_{60}$. So it is also interesting to investigate the fullerene compounds with NH4.

## 3-2 Dependence on Condition of Voltammetry

The half-cell potential (HCP) was defined as the mean value of the potentials corresponding to the couple of redox waves. For the potassium salts the several kinds of solution were investigated. Also the dependence of HCP's on the sweep rate in the voltammetry was studied. The results are summarized in Table 1. The solution of DMSO resulted in the most stable CV. The results dependen on the speed of the dissolve of the film. So only three redox waves were observed in the case of the low sweep rate, while the high speed sweep resulted in four redox waves.

## 3-3 Dependence on Cation Species

The values of the reductive HCP's observed are summarized in Fig. 2. The value of the HCP increased slightly as increasing the radius of the cation with the exception of $NH_4^+$. This result
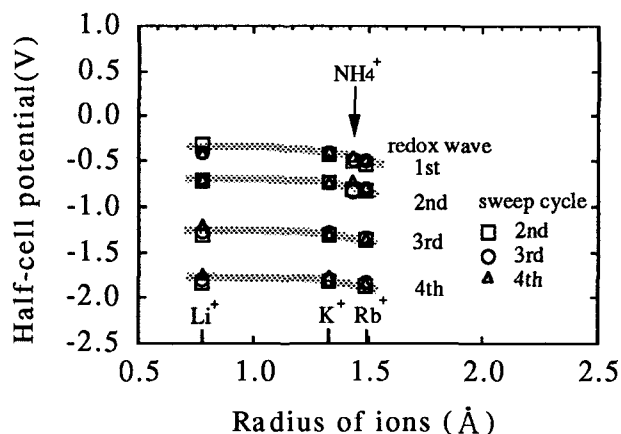


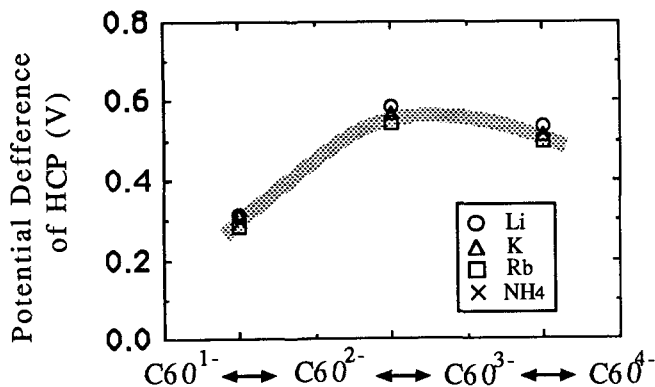Fig. 2. Half-cell potentials of the redox waves for the Li, K, and Rb cation.



Fig. 3. Potential difference between each HCP for the Li, K, Rb, and NH4 cation.

reveals that the large cation more hardly diffuses and the $NH_4^+$ behaves as an effectively large cation in the C60 film. On the other hand, the difference of

the half-cell potential $\Delta$HCP almost does not depend on the cation species as shown in Fig. 3, since the energy level of the lowest unoccupied molecular orbital in the $C_{60}$ cation is reflected in the each reducing potential.

In Table 2 the results of the CV in the potassium system are compared with the results that were obtained by several groups for the solvated fullerene molecule ion in supporting organic salts[4-6] and for the fullerene film with the solid polymer electrolyte[10]. Generally the obtained voltammograms of the film were substantially in good agreement with the results of the solvated fullerene ion.

It should be, however, noticed that the value of $\Delta$HCP12 of this work is smaller than that of the solvated fullerene molecule ion. This result may be caused by the structural deformation of the film when the valence of the fullerene changes between $C_{60}$ and $C_{60}^-$. From the same reason the splitting of the first couple of redox waves is comparatively large as already shown in Fig. 1. These results indicate that the comparatively large structural change of the $C_{60}$ thin film takes place at the first redox reaction accompanying with the first cation doping and dedoping. This is the feature of the electrochemical property of the $C_{60}$ film which is not observed in the case of solvated fullerenes.

## 4. PROPERTIES OF DOPED $C_{60}$ THIN FILM

### 4-1 Spectrum of Optical Density

The normalized changes of the optical density $\Delta$O.D./O.D. induced by the redox reactions were studied for the alkali metals system with the simultanious observation of the voltammogram. Figure 4 shows the differential coefficient of the $\Delta$O.D./O.D. to the applied potential measured at several wavelength of 410, 510, 610, 710, and 810 nm. Since the half sweep of the first voltammogram was irregular, the oxidation process of the latter half of the cycle should be reliable. In the wavelength range above ca. 600 nm $\Delta$O.D./O.D. increased at the reduced states, while $\Delta$O.D./O.D. decreased at the reduced states in the wavelength region less than ca. 500 nm. These characteristic change of the optical density typically appeared in the $Li^+$ system.

The obtained results qualitatively agreed with the change of the optical absorbance reported by Kaneto et al.[10]. As the result the reduced $C_{60}$ thin film revealed a greenish color being contrast to a brownish color of the pristine $C_{60}$ film.

Table 2
Half-cell potentials and the potential difference between each half-cell potential

| | Potential(V) | HCP1 [a) | HCP2 | HCP3 | HCP4 | HCP5 | HCP6 |
| | | $\Delta$HCP12 [b) | $\Delta$HCP23 | $\Delta$HCP34 | $\Delta$HCP45 | $\Delta$HCP56 | |
|---|---|---|---|---|---|---|---|
| Xie [c) | vs. Fc/Fc$^+$ | -1.06 | -1.44 | -1.92 | -2.41 | -2.89 | -3.25 |
| | | 0.38 | 0.48 | 0.49 | 0.48 | 0.36 | |
| Haufler [d) | vs. N.H.E. | -0.61 | -1.00 | | | | |
| | | 0.39 | | | | | |
| Allemand [e) | vs. AgCl/Ag | -0.33 | -0.73 | -1.22 | | | |
| | | 0.40 | 0.49 | | | | |
| K.Kaneto [f) | vs. Li | 2.29 | 2.75 | | | | |
| | | 0.46 | | | | | |
| This work | vs. AgCl/Ag | -0.42 | -0.74 | -1.31 | -1.82 | | |
| | | 0.32 | 0.57 | 0.52 | | | |

a) HCP1,HCP2,HCP3,HCP4,HCP5, and HCP6 are half-cell potentials; e.q., HCP1=1/2(E1red+E1ox)

b) $\Delta$HCP12,$\Delta$HCP23,$\Delta$HCP34,$\Delta$HCP45, and $\Delta$HCP56 are difference between each half-cell potential; e.q., $\Delta$HCPij=HCPi-HCPj

c) HCP of $C_{60}$ in CH3CN/toluene at a 100mV/s scan rate [6)

d) HCP of $C_{60}$ in CH2Cl2(0.05M[(n-Bu)4N]BF4) at a 100mV/s scan rate [4)

e) HCP of $C_{60}$ in CH2Cl2 at a 100mV/s scan rate [5)

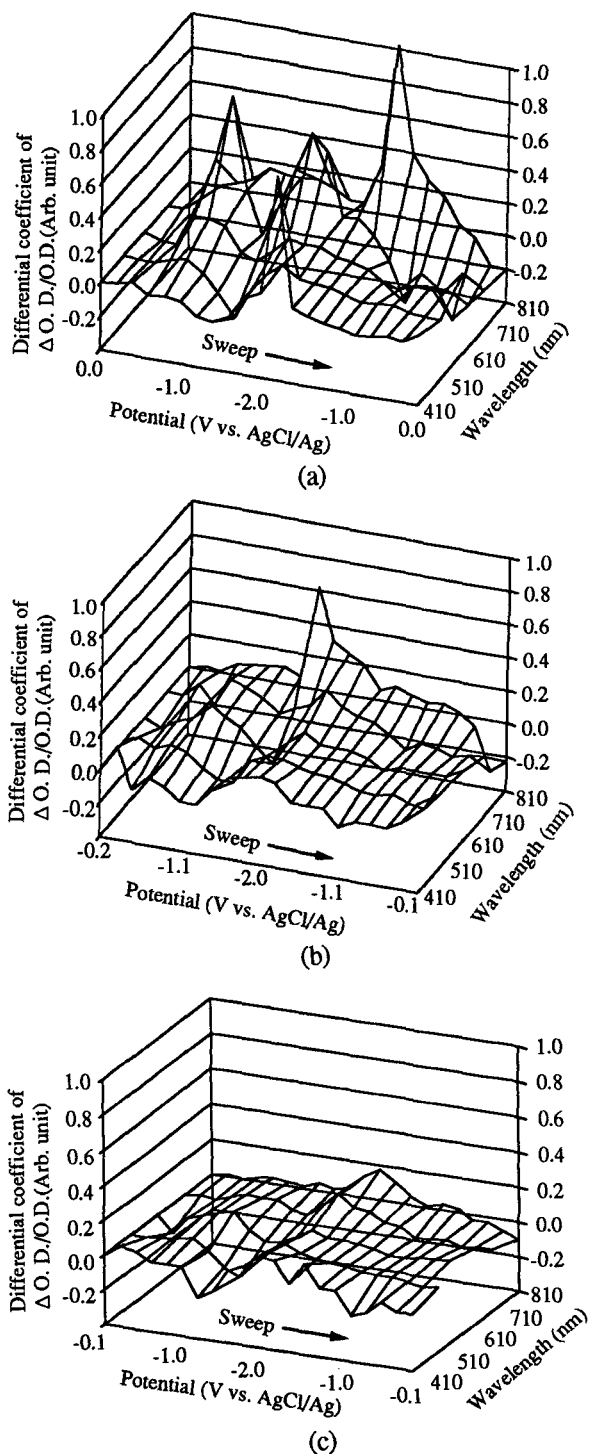f) HCP of $C_{60}$ film whih a solid polymer electrolyte of ca. 0.05M LiClO4/THF at a 3mV/s scan rate [10)

Fig. 5. The resistivity of the potassium doped $C_{60}$ thin film protected by the polyimide layer vs. time after the doping. The inserted voltammogram is obtained from the $C_{60}$ thin film with the protective overlayer.

## 4-2 Electrical Resistivity

The alkali metal-doped $A_xC_{60}$ film was stable even in the air by the protective layer, though the bare $A_xC_{60}$ was quite unstable. When the $C_{60}$ thin film protected by the polyimide overlayer was measured, the observed voltammogram is deformed like as shown in Fig. 5. Since the cation diffused slowly in the protective layer, the shape of the first and second redox pair waves were deformed.

After the applied voltage was held at about -0.8 V vs. AgCl/Ag for about 10 sec, the specimen was taken out from the electrolyte cell and the resistivity of the film was measured. As shown in Fig. 5 the resistivity of the film decreased rapidly from the initial value of ca. $6 \times 10^9$ $\Omega$ cm to ca. $4 \times 10^5$ $\Omega$ cm. The successive decrease of the resistivity was caused by thermal diffusion of potassium atoms stored in the polyimide layer, not by the direct electrochemical doping. Though the amount of the doping atoms was still small in this work, it was demonstrated that the electrochemical doping was available to get the doped $A_xC_{60}$.

## 5. SUMMARY

The electrochemical properties of the evaporated $C_{60}$ thin film were studied by the voltammetry in



Fig. 4. Differential coefficient of the normalized change of the optical density $\Delta$O.D./O.D. to the sweeped potential vs. wavelength observed in the solution of (a) 0.1N-LiKClO4/DMSO, (b) 0.1N-KClO4/DMSO, and (c) 0.1N-RbClO4/DMSO.
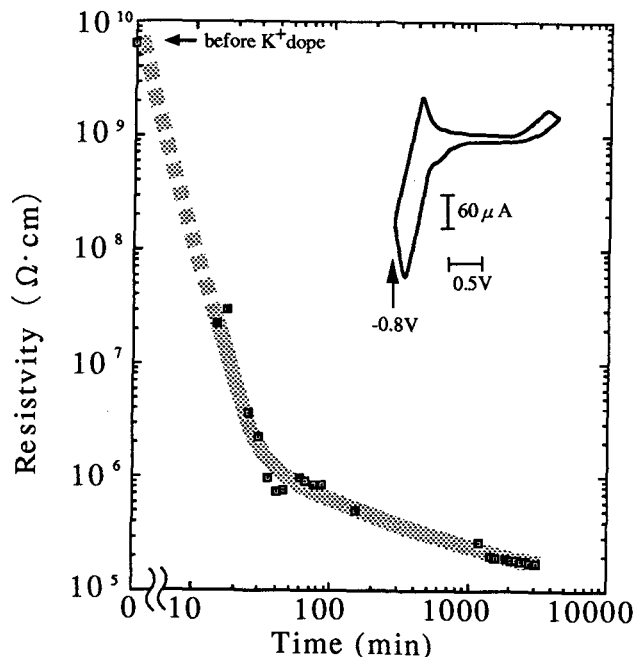
the organic electrolyte solution including alkali metals cations and $NH_4^+$. The reductive HCP's of the film were substantially in agreement with those of the solvated $C_{60}$ ion. However, the first redox potential changed because of the large structural deformation of the film.

The change of the optical density induced by the cation doping characteristically depends on the wavelength. Also the possibility of the electrochemical alkali metals-doping into the $C_{60}$ film even through the protective overlayer was confirmed. Conclusively a noble doping technique for the $C_{60}$ will be opened by the electrochemical process.

The accurate control of the highly doping of alkali metals into the film or the application of this electrochemical process for other various cations are the subjects for a future study.

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