Articles

Electrochemical Reactions of C$_{60}$ Films in the Presence of Water: An Electrochemical Quartz Crystal Microbalance Study

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Mass transport behavior of C$_{60}$ films on electrodes with different thicknesses has been studied by an Electrochemical Quartz Crystal Microbalance (EQCM) during electrochemical reduction-oxidation processes in the presence of water. C$_{60}$ films were found to be reduced in the presence of water and they remains quite stable. In thin films, the mass on electrode decreased after a complete cycle while X-ray Photoelectron Spectroscopy (XPS) study does not support the existence or formation of C$_{60}$-epoxides during electrochemical reduction processes in the presence of water or oxygen.

Introduction

Thin films of C$_{60}$ are of great interest because of its possibility for photovoltaic sensors and electrochemical ones as well.[1~11] As studies related to thin films, Langmuir-Blodgett films of C$_{60}$ and its derivatives were attempted for the study of charge-transfer membranes by several researchers.[1,5,12] Self-assembled monolayers of C$_{60}$ with its derivatives as thiols and silanes were studied.[13~15] Electrochemistry is one of valuable methods for characterization of thin films. Electrochemistry of C$_{60}$ films on electrodes in aprotic media has been studied by groups of Bard,[2,5] Kadish,[6,7] and Oyama[9] using Electrochemical Quartz Crystal Microbalance (EQCM) technique, Scanning Tunneling Microscopy (STM), and Scanning Electrochemical Microscopy (SECM). It is known that reduced C$_{60}$, *i.e.*, C$_{60}^{-}$, C$_{60}^{2-}$, and C$_{60}^{3-}$ are relatively stable in aprotic media, but lose activity rapidly resulting in decomposition of C$_{60}$ if water or oxygen is present in the media. Kalsbeck and Thorp[16] addressed that electrolytic reduction in the presence of oxygen or water leads to disruption of C$_{60}$ framework yielding decomposition. Microgravimetry using an EQCM could be a good tool to elucidate their claim. Here we report EQCM results on reaction of C$_{60}$ in the presence of water in this regard.

Experimental

Materials. Acetonitrile (HPLC grade, Merck) and dichloromethane (HPLC grade, Aldrich) were used as received. Benzene (GR grade, Fischer) was used after distillation. Deionized water (>18 MΩ) was used throughout the experiment. As a supporting electrolyte, tetrabutylammonium hexafluorophosphate, TBAPF$_6$ (Aldrich), was used as received.

Apparatus and Procedures. C$_{60}$ (Hoechst AG, Frankfurt, Germany) films were prepared by drying a benzene solution of C$_{60}$ on electrode surfaces and the average thick-

nesses were estimated as *ca.* 40, 160, and 215 monolayers of C$_{60}$. C$_{60}$ films from a dilute but saturated dichloromethane solution prepared by sonicating a dichloromethane solution containing little C$_{60}$ was used for comparison.[17] C$_{60}$ films prepared in this way are expected to have the minimum quantity of solvent molecules in the coating because C$_{60}$ does not show good affinity to dichloromethane.

An EQCM used was a home-made one[18,19] equipped with AT-cut quartz crystals using Ag/AgCl and a Pt wire as a reference electrode and a counter electrode, respectively, and measurements were carried out on a benchtop with bubbling of Ar throughout the experiments. A commercial potentiostat (BAS 100B/W) and XPS (VSW TA10) were used. As working electrodes, gold-coated quartz crystals of 10.000 MHz (International Crystal Manufacturing, Co.) were used mainly, however, platinum-coated ones of 9.000 MHz (Seiko, EG&G) were used for comparison.

Results and Discussion

There were many reports on the electrochemistry of C$_{60}$ films, however, they are not considered to be matched with each other well. The previous electrochemical microgravimetry results performed in non-aqueous solvents also were in the similar situations. In order to study the mass change response of C$_{60}$ films in the presence of water, it was needed for us to be able to reproduce the previous results.

Among the several attempts was found a work Tatsuma *et al.* performed to be most reasonable. They showed in acetonitrile that the net mass increased at C$_{60}$ films prepared on platinum electrodes after the first cycle, which are estimated *ca.* 160 monolayer thick.[9] Their measurements using platinum electrodes were carried out in a glove box free from oxygen and water and they stressed that their rigorous atmospheric condition during experiment was critical in obtaining the results.

Figure 1(A) shows the frequency response from a C$_{60}$ film (*ca.* 160 monolayer thick) on a platinum electrode in acetonit-
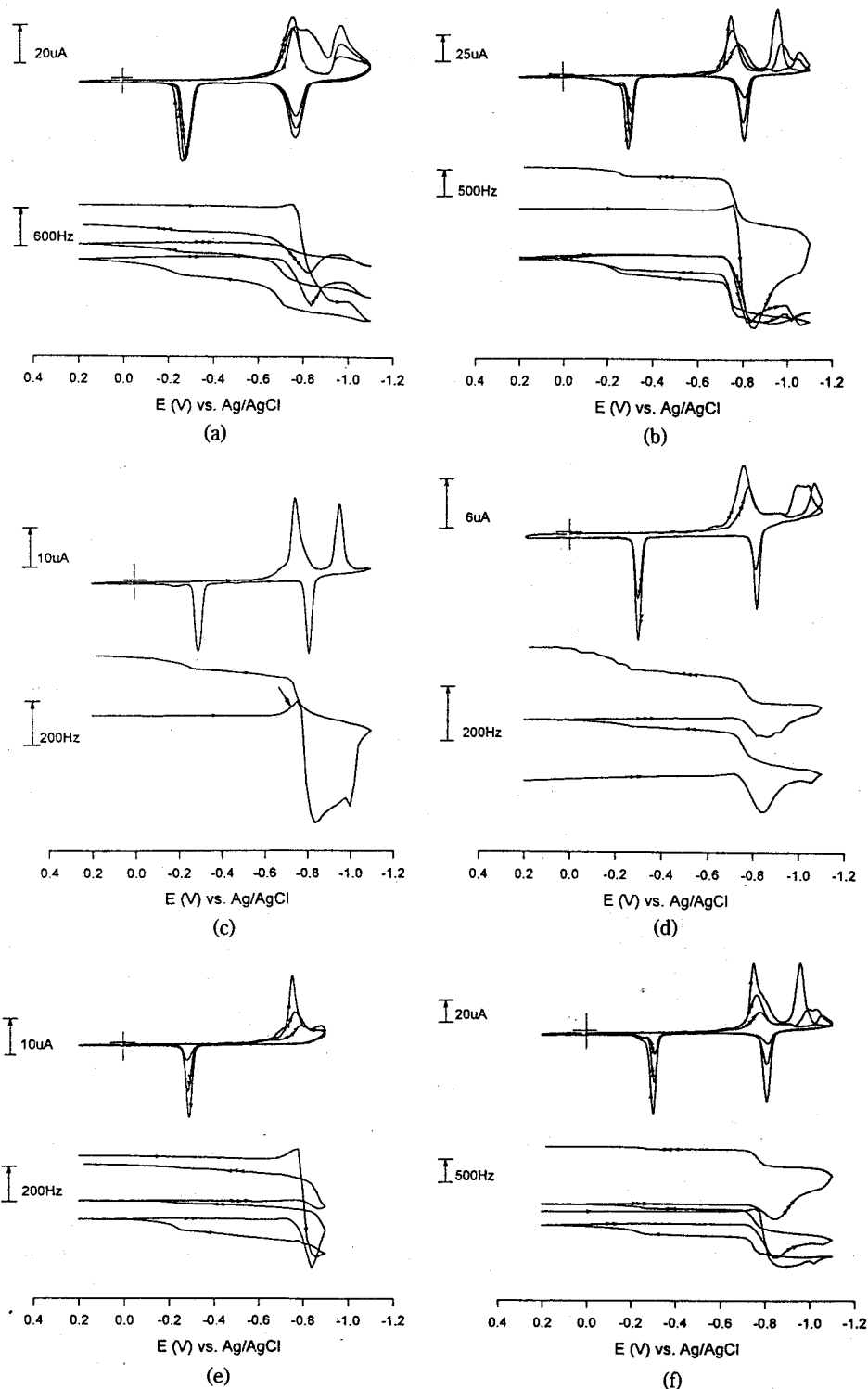
Figure 1. (A) A frequency response of a C_{60} film of *ca.* 160 monolayer thick on a platinum electrode. It shows that almost the same result as Tatsumas. (B) CV and the frequency response for much thicker (*ca.* 215 monolayers) film on a gold electrode. A similar mass change pattern to (F) is observed except the net mass increase after a complete potential cycle. (C) CV of a C_{60} film on a gold electrode and the corresponding frequency response curves recorded during the first potential cycle initiated at −0.2 V. A 5-mm-diameter gold electrode prepared on an AT-cut quartz oscillator was used as a working electrode. (D) Subsequent CV and the frequency response with potential cycling. (E) A frequency response curve covered between 0.2 and −0.9 V showing that an increase in mass is a major process near reduction peaks. (F) A frequency response of a thicker (*ca.* 160 monolayers of C_{60}) film on a gold electrode. A mass increase after the first reduction peak and an additional increase are observed during the cathodic scan and the mass decreased in two steps during the reverse scan. The resultant mass increased after a complete cycle. Supporting electrolyte: 0.1 M TBAPF₆. Scan rate: 10 mV/s.

rile. It looks in good agreement with the previous work[9] that showed the net mass increase during the first cycle using a platinum electrode covered with *ca*. 160 monolayers of C_{60}. In Figure 1(B) is shown a mass change response in acetonitrile obtained from a gold electrode with a C_{60} film of *ca*. 215 monolayer thick. It also shows a similar mass change response to the one described above. These results confirm that it is possible to reproduce a mass change response same as a previous report has been done. In addition, it is not inevitable to carry out experiments in a strict condition as Tatsuma stated to get these results and it is enough to perform in a condition stated in the Experimental section. Regarding the experimental condition of the present study, it is obvious that the amount of O_2 in acetonitrile is low enough that the direct O_2 reduction usually observed near -0.5 V is not apparent in voltammograms in the subsequent figures. The effect of electrode material seems to be important in the mass change of C_{60} coatings as well as the thickness of the films during electrochemical reactions.[20] The thickness effect will be discussed briefly later.

Mass change responses of C₆₀ films of various thickness in acetonitrile. In Figure 1(C), a cyclic voltammogram (CV) of C_{60} film, recorded during the first potential cycle using a C_{60} film of 40 monolayer thick on a gold-coated crystal, with an Ar-degassed acetonitrile solution shows reduction-oxidation peaks matching well the previously published results.[2,4~7,9] The corresponding frequency response (Δf *vs. E* curve) shows that there is a small mass decrease at -0.7 V, which is followed by a large increase near the first reduction. In Figure 1(D) which illustrates the subsequent CV and frequency response of the following two cycles, it is obvious that reduction-oxidation current decreased gradually and the mass change rate has been attenuated with potential cycling.

In the present case, the decrease of current has been explained as loss of activity of C_{60} films, that is, it is attributed to reduction of active area on C_{60} films due to reconstruction of C_{60} microcrystals and merge of crystals to bigger ones losing porosity due to repeated dissolution-redeposition cycles and consequently results in smaller current and little dissolution.[2] By the way, the mass decrease near -0.7 V is interpreted in terms of the dissolution of C_{60}^- or the ejection of residual solvent occluded in the casting procedure and a mass increase reflects incorporation of electrolyte forming salts such as $TBA^+C_{60}^-$. Regarding this possibility, Bard *et al.* have used the SECM technique detecting significant quantity of oxidation current due to C_{60}^- detected at the tip electrode during the first potential cycle. Essentially no tip current was registered after extended potential cycles, suggesting that a less soluble $TBA^+C_{60}^-$ is formed or that the initial material contained residual solvent affecting film solubility.[2]

Especially during the first negative scan, it is highly likely that residual solvent is released from the film yielding a mass decrease because C_{60} films have not ever experienced any rearrangement to egress solvent molecules. Some nonpolar solvents such as benzene and toluene is known to show strong affinity to C_{60} molecules. The crystals grown in benzene or toluene occlude solvent molecules in few mass % of the crystal and these solvent molecules could be removed in high vacuum over 400 °C.[21] In respect to release of solvent,

a series of experiments was performed by changing film drying-time. Though it is not shown here, a film which was dried for 30 s by blowing hot air was found to show almost no mass decrease due to release of solvent near the first reduction wave.[20] Consequently, egress of residual solvent was believed to be the main factor on a mass decrease near -0.7 V in Figure 1(C) rather than dissolution of C_{60}^- since dissolution was not considered to be affected by blowing hot air. In addition, fluctuations of mass near reduction waves are found to be negligible with repeated potential cycles. It is reasonable because trapped solvent molecules near the solution/film interface would be depleted upon repeated cycles.

On the other hand, a large mass increase following the mass decrease near the reduction wave is considered to reflect incorporation of electrolyte forming $TBA^+C_{60}^-$ salt, since incorporation is the only possibility for a mass increase in this case. In order to make the effect of possible dissolution of C_{60}^- and C_{60}^{2-} explicit, a frequency response curve which covered between 0.2 and -0.9 V was recorded in Figure 1(E). This figure with a CV displaying just the first reduction-oxidation waves shows that the overall rate of mass decrease is much slow compared with the one in Figure 1(C) and the mass increase is predominant near a reduction peak. Consequently, it is evident that dissolution of reduced species of C_{60} is the primary factor to determine the declination of baseline and a mass increase following a mass decrease near a reduction wave reflects the incorporation of electrolyte. Thus, a fluctuation of frequency change, a peak-like change in frequency, is considered to show a combined process of a mass decrease due to release of solvent and a succeeding mass increase due to incorporation of electrolytes.

Upon reversal of the scan direction, the mass response curve in Figure 1(C) showed a large decrease occurred after oxidation to $TBA^+C_{60}^-$ on a baseline showing a steady decrease in mass. It represents the ejection of TBA^+ during the oxidation of $(TBA^+)_2C_{60}^{2-}$ to $TBA^+C_{60}^-$. After this, the mass change is not large until the upper limit and the net change in mass is negative. A similar mass change pattern in the subsequent scans shown in Figure 1(D) is repeated with successive potential cycles except reduced change rate. It is interesting that the mass change reflecting the oxidation of $TBA^+C_{60}^-$ to C_{60} is smaller than the mass change in oxidation of $(TBA^+)_2C_{60}^{2-}$ to $TBA^+C_{60}^-$, while the corresponding current is observed. It means that significant amount of TBA^+ is trapped in C_{60} crystals after $TBA^+C_{60}^-$ is oxidized.

However, the mass change pattern is variant with the film conditions such as thickness of film,[20] solvents used to prepare films, and film drying time. To investigate the effect of thickness of films, frequency responses were studied using thicker films. In Figure 1(F) is shown the frequency response of a thicker (*ca*. 160 monolayers of C_{60}) film on a gold electrode. It shows almost the same mass changing pattern in a thin film that a mass increase after the first reduction peak and an additional increase with a slight decrease between the two increases are observed in the cathodic scan and the mass decreased in two steps during the reverse scan. Upon completion of the first cycle, however, the resultant mass was increased not like the thin film case shown in Figure 1(C). The current and frequency response for a much thicker (*ca*. 215 monolayers) film is shown in Figure
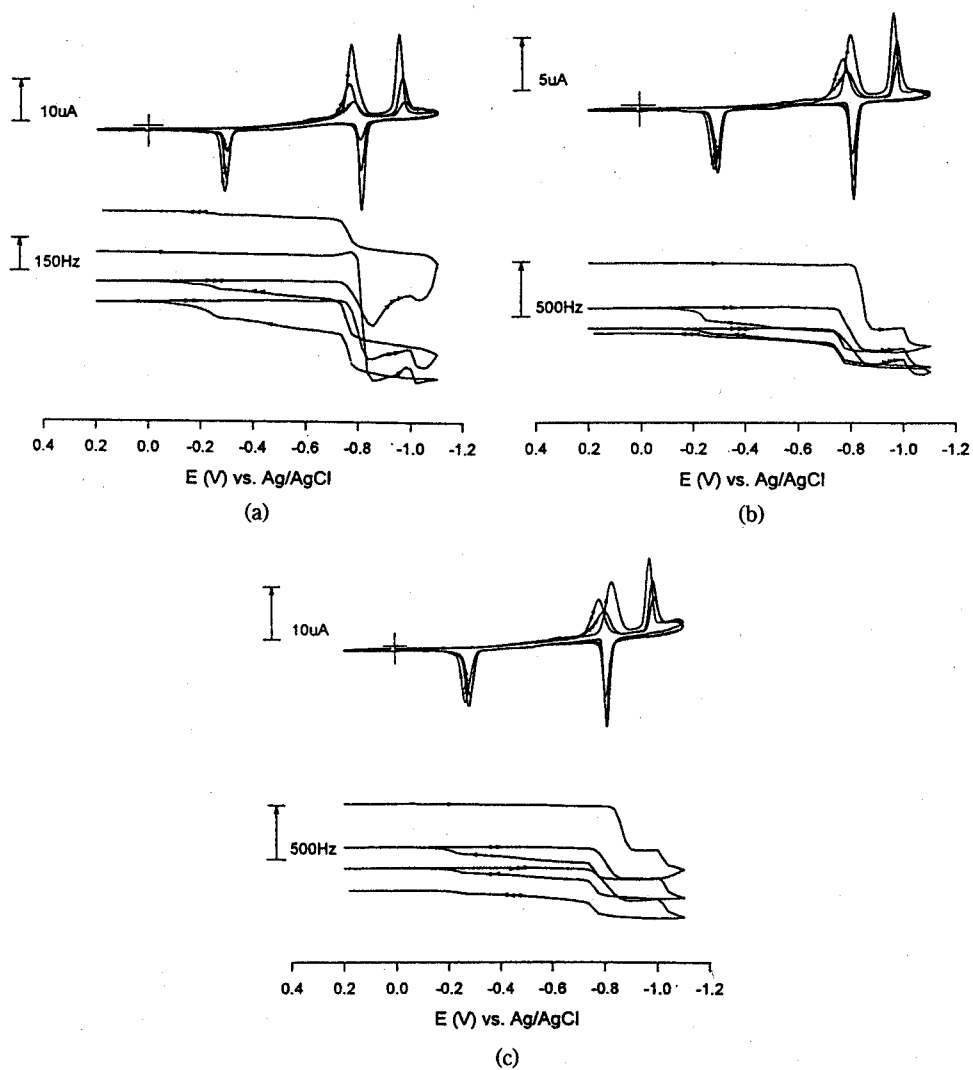
Figure 2. (A) CV and the corresponding frequency response of a C_{60} film in 4%, (B) 8%, and (C) 10% water solution in acetonitrile. Supporting electrolyte: 0.1 M TBAPF$_6$. Scan rate: 10 mV/s.

1(B). Similar mass change pattern to Figure 1(F) is observed except the net mass increase after a complete potential cycle.

Mass change responses of C_{60} films in the presence of water. The reaction of reduced C_{60} forming multiple epoxides on the C_{60} cage with oxygen and/or water and the subsequent decomposition into small pieces have been proposed and it might be a possible reason for the mass decrease while C_{60} is reduced.[16] Electrochemistry and microgravimetry of C_{60} in the presence of water were performed since it was considered worthy to confirm this possibility. Cyclic voltammograms and the corresponding frequency responses recorded in the presence of water are shown in Figures 2(A) to (C). Figure 2(A), recorded in a solution of 4% water in acetonitrile, shows that the first reduction wave is as large as the one of Figure 1(C) and potential cycling did not affect the peak currents unlike the case of pure acetonitrile. It seems that C_{60} can be reduced in the presence of small amount of water and C_{60} films are rather stable upon repeated reduction-oxidation cycling. The reason to retain activity in the presence of water is attributed to the fact that water and benzene released from the C_{60} film is

immiscible and thus dissolution-redeposition is difficult to occur since C_{60} is not soluble in both acetonitrile and water. Therefore, incorporation of electrolyte is the only possible consequence after reduction if decomposition does not occur, because reduced species is hard to be dissolved into solution. As a result, a mass of C_{60} film increases upon reduction process and it is retrieved to a certain extent after oxidation steps. As described before, the net mass change is negative with a pure acetonitrile solution. On the other hand, the net mass change in the presence of water after the first cycle is positive. The mass change is getting negative with successive cycling and the mass after the third cycle decreases. This trend is more distinct in concentrated water solution of acetonitrile as shown in Figures 2(B) and (C), which are obtained in 8% and 10% water solutions, respectively. Every frequency curve which shows negative net frequency change after a complete cycle illustrates solvent release peaks near the reduction potentials. The net mass change becomes more positive with the concentration of water in the solution as shown in Figure 3. It seems that this change is closely associated with the amount of electrolytes incorpo-
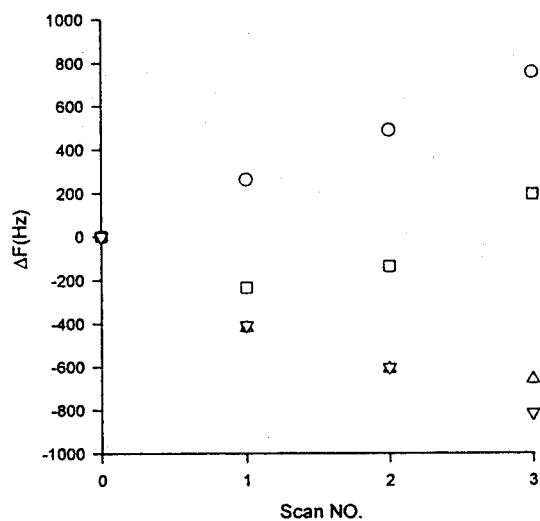
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Figure 3. The net frequency change of C_{60} films for the initial three potential cycles obtained at after each cycle in various concentration of water in acetonitrile. Supporting electrolyte: 0.1 M TBAPF₆. Scan rate: 10 mV/s.
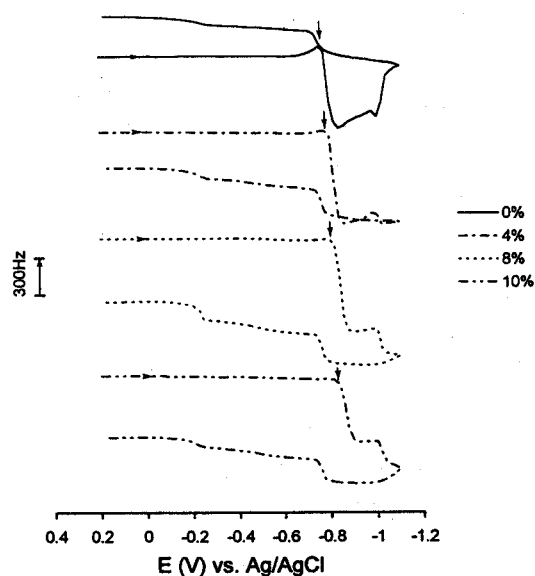

Figure 5. CV and the corresponding frequency response of a C_{60} film prepared from a dichloromethane solution in acetonitrile. Supporting electrolyte: 0.1 M TBAPF₆. Scan rate: 10 mV/s.

Figure 4. Frequency responses of C_{60} films recorded in various concentration of water in acetonitrile showing shifts in potential of ingress and egress of electrolytes into C_{60} films. Supporting electrolyte: 0.1 M TBAPF₆. Scan rate: 10 mV/s.

the benzene-acetonitrile mixed phase.

XPS measurements on C₆₀ films. The generation of C_{60}-epoxides during reduction-oxidation cycles in a solution containing oxygen and/or water has been reported previously.[16] Electrochemistry of $C_{60}O$, one of C_{60}-epoxides, was studied recently in several solvents such as o-dichlorobenzene and dichloromethane.[22] In order to explicate the mass change in this regard, C_{60} films subject to potential cycling were examined by XPS. A bare gold-electrode on quartz crystal, a C_{60} film prepared on a gold-electrode, and a C_{60} film after extended potential cycling in a 10% water solution were examined. If epoxides were generated, C_{60} is believed to be decomposed and mass on electrode should be decreased.[16] However, any enhancement of oxygen signals that may support the presence or generation of epoxides was not detected. It is considered that XPS data go with the result of microgravimetry since EQCM measurements showed an increase in mass. It is believed that C_{60} can be undergone electrochemical reduction and reduced species are quite stable in the presence of water. The generation of epoxides during electrochemical potential cycling can be clarified by further studies such as high resolution mass spectrometric measurement.

Finally, in responding to a reviewer's suggestion, an experiment for which C_{60} films were prepared from a dichloromethane solution[17] was devised. The solubility of C_{60} in dichloromethane is not high enough to prepare C_{60} films as we did using benzene solution. When C_{60} is sonicated for a long time in dichloromethane, a dilute solution could be obtained. It is used as a casting solution for C_{60} films. Since dichloromethane is not volatile enough compared with benzene, evenly coated C_{60} films can be prepared. This film is expected not to include solvent molecules as much as a benzene solution case due to poor affinity between C_{60} and dichloromethane and consequently no mass decrease near the first reduction wave is anticipated. The electrochemistry of this film is reported recently and it is quite different from the previous ones. Figure 5 illustrates the frequency response of

rated and release of solvent as well. In this case, a mass decrease near reduction peaks is considered to represent solvent release. It is prominent especially in the case of reduction of C_{60} to C_{60}^-.

It is worthy to note that electrolyte ejection potential moves to positive direction and incorporation potential shifts to negative direction with the content of water in the solution as marked in Figure 4. This trend is especially remarkable in reduction of C_{60} to C_{60}^- and oxidation of C_{60}^{2-} to C_{60}^-. It is considered that reduction of C_{60} in an acetonitrile solution is more favorable than reduction in the presence of water because ejected solvent molecules and acetonitrile are easy to be mixed together and C_{60} could be dissolved in
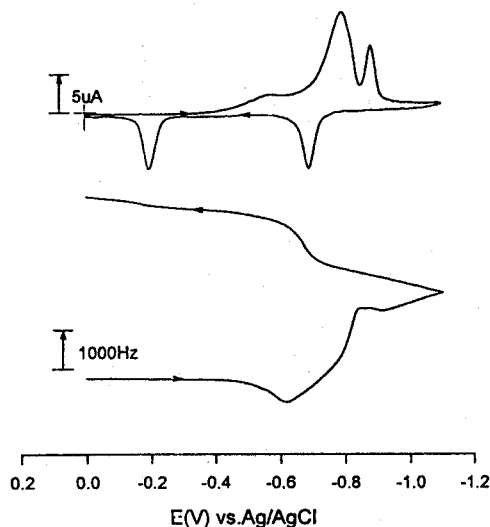
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the film on a gold electrode in acetonitrile showing no mass decrease near the first reduction wave as expected. It is worthy to stress that the net mass change is very large compared with previous results. It is due to predominant dissolution of C_{60}^- or C_{60}^{2-} over incorporation of electrolytes as mentioned in a previous paragraph. Accordingly, it supports that the mass decrease near reduction waves in Figure 1(C) is due to the release of solvent molecules.

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Cobalt(III) Complexes of N,N'-Bis(2(S)-aminopropyl)-1(R),2(R)-*trans*-1,2-diaminocyclohexane

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A novel optically active tetraamine ligand possessing four asymmetric centers, N,N'-bis(2(S)-aminopropyl)-1(R),2(R)-*trans*-1,2-diaminocyclohexane (SRRS-apchxn) and its cobalt(III) complexes, [Co(SRRS-apchxn)X$_2$]$^{n+}$ (X=Cl$^-$, H$_2$O, X$_2$ =CO$_3^{2-}$) have been synthesized. This ligand has coordinated stereospecifically to the cobalt(III) ion to give only the Λ-*uns-cis*-(SS) isomer. A trans dichloro complex has been obtained *via* the stereospecific isomerization of Λ-*uns-cis*-(SS)-[Co(SRRS-apchxn)Cl$_2$]$^+$ to *trans*-(SS)-[Co(SRRS-apchxn)Cl$_2$]$^+$ in CH$_3$OH-HCl medium. Ligand and complexes have been characterized by electronic absorption, ^{1}H NMR, CD spectra, and also by elemental analysis. It is of interest that this is one of the few Co^{III}(N$_4$)X$_2$ type complex preparations, which produces such an *uns-cis* isomer with stereospecificity.

Introduction

The stereochemistry of the metal chelates containing mul-

tidentate ligands is an interesting field of study because various chelating modes of those ligands are able to firm a variety of geometrical and optical isomers. The stability of