Electrochemistry of C_{60} Films: Quartz Crystal Microbalance and Mass Spectrometric Studies

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The incorporation of tetra-*n*-butylammonium (TBA^+) upon electroreduction of films of C_{60} on an electrode in MeCN solutions was studied by electrochemical quartz crystal microbalance (EQCM) and laser desorption mass spectrometry (LDMS) methods. EQCM allowed estimation of the extent of dissolution of the films upon reduction to the C_{60}^- and C_{60}^{2-} forms and the increase in mass caused by incorporation of TBA^+. LDMS analysis also indicated the presence of TBA^+ after reduction. Both methods suggested that TBA^+ remains in the lattice after reoxidation of the reduced forms to C_{60}, indicating a new type of "ionic charge trapping" in these films.

Introduction

We describe how studies of solvent cast films of the fullerene, C_{60}, by laser desorption mass spectrometry (LDMS) and electrochemical quartz crystal microbalance (EQCM) measurements provide information about their doping by tetra-*n*-butylammonium (TBA^+) ions during electrochemical redox processes. Previous reports from this laboratory[1,2] described the electrochemistry of multilayer films of C_{60} formed on electrode surfaces by evaporation of benzene solutions. The cyclic voltammetric (CV) behavior of such films in MeCN differed significantly from that found for solutions of C_{60}, e.g., in benzene or CH_2Cl_2.[3-7] The large potential difference observed between the reduction and reoxidation waves in the film (e.g., for the C_{60}/C_{60}^- couple) was ascribed to large structural changes that occur upon charge compensation (doping) of the films by cations such as TBA^+, Na^+, and K^+. Confirmatory results have appeared in recent photoelectrochemical[8] and Raman spectroscopic[9] investigations. In addition, scanning electrochemical microscopy (SECM) studies[2] showed that there was partial solubility of the C_{60} films during initial reduction cycles, while scanning tunneling microscopy (STM) showed structural changes of the film (i.e., compaction) on reduction. Additional information about these films obtained in the work reported here confirms the importance of TBA^+ doping and suggests that the TBA^+ that enters the film on reduction is retained on reoxidation in a novel, *charge trapping*, phenomenon.

Experimental Section

The preparation of the films on the electrodes, by drop coating of a few microliters of a C_{60} solution in benzene (2-3 mM), and the CV studies followed previous reports.[1,2] Electrochemistry was carried out in MeCN containing 0.1 M $(TBA)PF_6$ as supporting electrolyte in single-compartment cells with a Pt counter electrode and a Ag wire quasi-reference electrode (Ag QRE). Solutions were prepared in a drybox under a He atmosphere and added to the electrochemical cell. Electrochemical studies and preparation of samples for LDMS were carried out in the drybox. The cell was sealed and removed from the drybox for the EQCM measurements.

The working electrode used in the EQCM experiments was a gold-coated quartz crystal (0.24-cm^2 active area) (Leybold Inficon Inc., East Syracuse, NY) that oscillated at a fundamental frequency, f_0, of 6 MHz. For LDMS studies a gold-plated stainless steel rod was employed as an electrode and then introduced as a probe into the mass spectrometer. This was accomplished by removing the electrode from the cell, rinsing carefully with dry MeCN, and sealing it in a vial with parafilm inside the drybox. The probe was removed from the drybox and transferred into the mass spectrometer via a glovebag purged with Ar to prevent contact with the air and possible reactions with water vapor and oxygen.

In the EQCM measurements, frequency changes were measured with a Leybold oscillator and a Philips Model PM6654 frequency counter (John Fluke Manufacturing Co., San Antonio, TX). The Teflon EQCM cell was designed for studies in nonaqueous solvents and was similar to that previously reported.[10] The Fourier-transform ion cyclotron resonance mass spectrometer, based on an Extrel FTMS-2000 instrument equipped with a 3.0-T superconducting magnet and differentially pumped dual cubic trapped ion cells, was described in detail.[11] A Spectra Physics DCR-11 Nd:YAG laser operated at 1064 nm in the Q-switch mode with a 8-ns pulse width was used for laser desorption. Laser light was transmitted through a fiber optic which terminated about 0.5 mm from the sample surface. A 1-mm^2 area of the electrode was subjected to a laser irradiance of up to 3×10^8 W/cm^2. A more detailed description of the laser desorption technique is available.[12]

Results and Discussion

LDMS Experiments. Mass spectrometry studies of the C_{60} films before and after electrochemical treatment were conducted to identify ions incorporated into the film. For reference, the cyclic voltammogram showing the first two reduction and subsequent reoxidation waves of a C_{60} film in MeCN is shown in Figure 1a. When a probe coated with C_{60} was immersed in MeCN containing 0.1 M $(TBA)PF_6$ for 1 h and then rinsed thoroughly with dry

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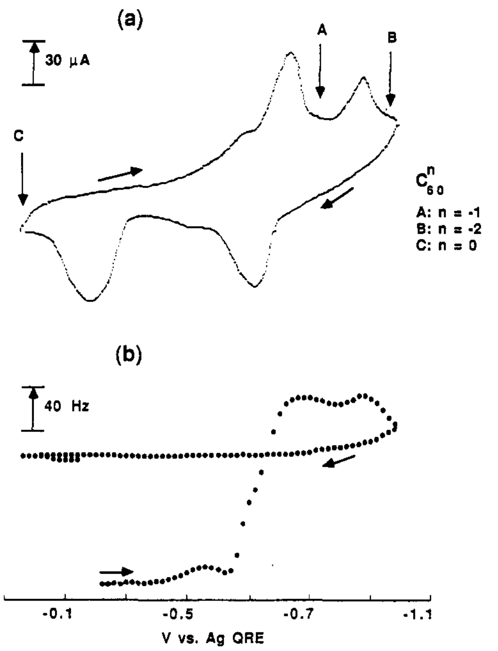

Figure 1. (a) Cyclic voltammogram of a 6.84-µg C_{60} film on a 0.24-cm^2 gold-coated quartz crystal at a scan rate of 200 mV/s. (b) Frequency response measured simultaneously during the potential sweep.

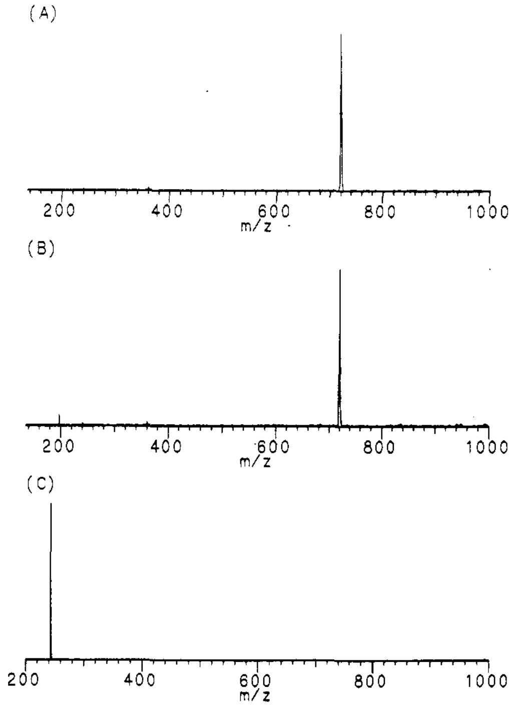

Figure 2. Mass spectra of a C_{60} film in (A) positive ion mode and (B) negative ion mode. (C) is the spectrum in positive ion mode after holding the film at a potential of −0.75 V vs Ag QRE for 50 min in an acetonitrile solution containing 0.1 M (TBA)PF_6.

MeCN and transferred to the mass spectrometer, the spectra shown in Figure 2A,B were obtained. Note that these show only the presence of C_{60}^- (negative mode) and C_{60}^+ (positive mode) ($m/z = 720$). If the same experiment was carried out without rinsing with fresh MeCN, the positive ion spectrum also showed the presence of TBA^+ ($m/z = 242$) while the negative ion spectrum showed PF_6^- ($m/z = 145$) because of carryover of some electrolyte with the C_{60} film.

The LDMS behavior of the film upon complete reduction to C_{60}^- at −0.75 V vs Ag QRE for about 50 min (Figure 1a, point A) followed by rinsing with MeCN is shown in Figure 2C. This positive ion spectrum shows TBA^+ as the only positive ion present, suggesting that C_{60}^- will not ionize during the laser pulse to form a cation. The negative ion spectrum, obtained by applying the laser pulse to a different spot on the probe, is similar to Figure 2B and shows only C_{60}^-. These results are consistent with formation of the $TBA^+C_{60}^-$ structure, as proposed from the previous electrochemical studies.

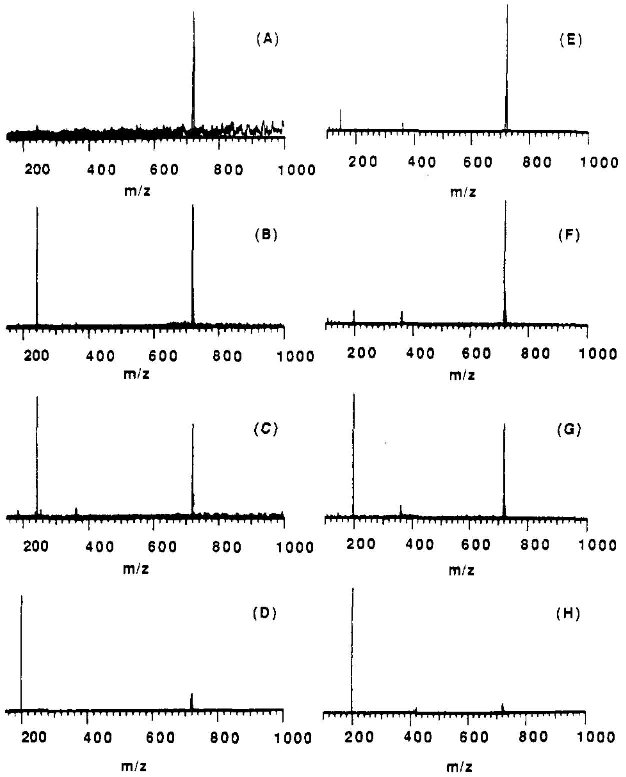

Figure 3. Mass spectra of a C_{60} film. (A–D) Four consecutive laser pulses applied to the C_{60} film with mapping of positive ions. (E–H) Four consecutive laser pulses applied to a different position on the same film with mapping of negative ions. A potential of −0.75 V vs Ag QRE was held for 50 min, and then a potential of 0.35 V vs Ag QRE was applied and held for 50 min to produce the film.

In another study a fresh C_{60} film was fully reduced, as described above, and then completely reoxidized by applying a potential of 0.35 V (Figure 1a, more positive than point C). LDMS results for four laser pulses to the same spot on the probe are shown in Figure 3. The first pulse (Figure 3A) showed only C_{60}^+ in the positive ion spectrum. However, the next pulses (Figure 3B,C) showed both C_{60}^+ and TBA^+. The fourth pulse (Figure 3D) showed only a small peak for residual C_{60} and a larger peak from the Au substrate ($m/z = 197$), suggesting that the first three pulses removed essentially all of the C_{60} film from that spot. The presence of TBA^+ in the spectra following reoxidation suggests that this ion is trapped inside the C_{60} matrix upon oxidation of the $TBA^+C_{60}^-$. It is absent from the first pulse spectrum, because the TBA^+ can be lost from the topmost layer of C_{60}, with fresh C_{60} forming on the surface via deposition by oxidation of a small amount of C_{60}^- that dissolves in the solution during reduction.[2] The negative ion spectra taken by subjecting a different spot on the same film to four laser pulses (Figure 3E–H) show a C_{60}^- peak with a small peak for PF_6^-. A substrate peak (Au^-) appears on the spectra of the third and fourth laser pulses.

EQCM Studies. Information about the extent of doping and dissolution of the films was obtained by monitoring the changes in mass during reduction and reoxidation. These mass changes are determined by monitoring shifts in the frequency of the film/Au/quartz crystal during a potential scan or step, as described in a number of previous studies.[13-16] The mass change,

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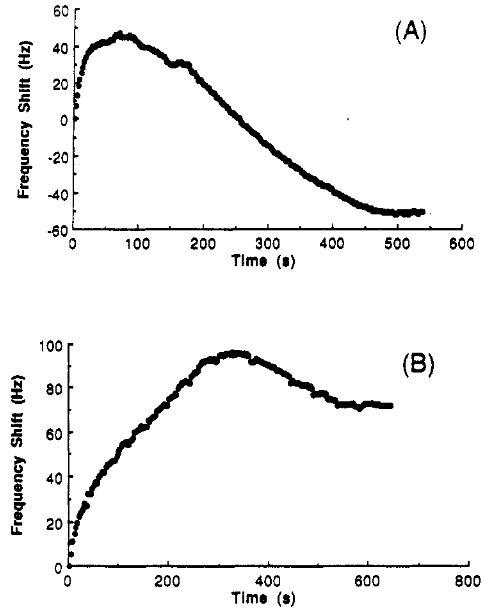

Figure 4. Frequency shift versus time observed for two 4.3-μg C_{60} films after applying potentials of −0.75 V vs Ag QRE (A) and −1.00 V vs Ag QRE (B).

Δm (μg/cm^2), is related to the frequency change, Δf (Hz), by the Sauerbrey equation[16]

$$\Delta f = -(f_0^2/N\rho_q)\Delta m = -81.5\Delta m \qquad (1)$$

where f_0 is the fundamental frequency mode of the crystal (6 MHz), N is the frequency constant (1.67×10^5 Hz cm), and ρ_q is the density of the crystal.

The result of the reduction of a C_{60} film by stepping the potential to −0.75 V vs Ag QRE and recording Δf at 3-s intervals is shown in Figure 4A. The frequency first increased, showing a loss of mass from the film, and then decreased to a final value, after cessation of the current flow, that was lower than the initial frequency. This result can be interpreted as an initial dissolution, consistent with previous SECM measurements,[2] which showed production of some dissolved C_{60}^- during initial reductive scans and related to residual casting solvent (benzene) in the film. The rate of dissolution decreases after about 100 s, and the mass increases as $TBA^+C_{60}^-$ is formed. Although nonrigidity of the C_{60} film and uncorrected temperature effects affect the accuracy of measurements of Δm via eq 1, an estimate of mass changes during reduction is possible. The net mass increase in Figure 4A, m_g, is 0.13 μg and is a combination of mass gain from TBA^+ incorporation, m_{TBA^+}, and the loss of C_{60}^-, $m_{C_{60}^-}$ (ignoring solvent gains or losses):

$$m_g = m_{TBA^+} - m_{C_{60}^-} \qquad (2)$$

The amount of C_{60} initially on the electrode, m_t (4.3 μg), is the total of dissolved C_{60} ($m_{C_{60}^-}$) and the reduced form that remained on the electrode, $m'_{C_{60}^-}$:

$$m_t = m_{C_{60}^-} + m'_{C_{60}^-} \qquad (3)$$

Finally, when the film is fully reduced, the number of moles of C_{60}^- and TBA^+ are equal:

$$m_{TBA^+}/242 = m'_{C_{60}^-}/720 \qquad (4)$$

Simultaneous solution of eqs 2–4 yields $m_{TBA^+} = 1.1$ μg and $m_{C_{60}^-} = 0.98$ μg (equivalent to about 23% of the mass of the original film). Thus, only a small amount of the film dissolves on reduction, in agreement with the previous study.[2] When the fully reduced film was stepped to 0.35 V vs Ag QRE, beyond the oxidation wave (Figure 1a) no frequency shift was seen for up to 10 min. At more positive potentials the mass of the film actually increased slightly. This lack of loss of the TBA^+ on reoxidation again suggests trapping of this dopant within the C_{60} film, with the slight increase seen perhaps due to some incorporation of PF_6^-.

A similar experiment was performed by stepping past the second reduction wave to −1.00 V vs Ag QRE with a fresh film (Figure 4B). The shape of the Δf vs time curve is similar to that for the first reduction but indicates a greater amount of dissolution on forming C_{60}^{2-}. Kadish and co-workers[17] have shown that the C_{60}^{3-} form is very soluble in MeCN. The final frequency decrease again indicates doping of the film with TBA^+. A calculation similar to that given above indicates that about 43% of the film dissolves during this reduction step.

Similar weight changes and evidence for doping with TBA^+ on reduction and trapping of the TBA^+ on reoxidation were also seen in EQCM measurements made during a potential sweep experiment (Figure 1b). Consistent with the early stages of the potential step experiments, frequency increases are seen for both reduction waves, with a small frequency decrease following the second wave. However, no frequency changes are seen on the anodic sweep during either reoxidation step.

Conclusions

The work reported here adds to our picture of the behavior of thin films of C_{60} in MeCN upon reduction and reoxidation. C_{60} is highly insoluble in MeCN, with the solubility increasing upon reduction. Solubility of the −1 and −2 forms of C_{60} is only partial in the presence of TBA^+ and appears to depend upon the amount of residual solvent, e.g., benzene, left in the film after casting. Upon reduction of C_{60}, TBA^+ enters the lattice with a considerable structural change. The EQCM and LDMS results suggest that this TBA^+ is incorporated in the lattice in a way that after oxidation the C_{60} film still contains incorporated TBA^+ as "trapped ions". We do not know of another example of such ion trapping in films, although there is no reason it would not occur in other films. This trapping phenomenon perhaps accounts for the large splitting seen in the CV waves of C_{60} films.

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