Electrochemical Studies of C_{60}/Pd Films Formed by the Reduction of C_{60} in the Presence of Palladium(II) Acetate Trimer. Effects of Varying C_{60}/Pd(II) Ratios in the Precursor Solutions

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Cyclic voltammetric studies of the electrochemical formation and redox properties of C_{60}/Pd films are reported. Films used in this work are generated under multicyclic scans in an acetonitrile/toluene (1:4, v/v) mixture containing fullerene C_{60} and palladium(II) acetate trimer as the film precursors and tetra(*n*-butyl)ammonium perchlorate as supporting electrolyte. The structure and electrochemical properties of the deposited layers depend on the relative concentrations of the precursors (C_{60} and $\{Pd(OAc)_2\}_3$) present in the growth solution. In the presence of excess palladium(II) acetate trimer, palladium, as well as the redox active film, is deposited, as shown by electrochemical studies of the behavior of the modified electrodes toward hydrogen evolution and palladium oxidation in aqueous acidic solution. At very negative potentials, all of the films decompose which is presumed to be due to the repulsive interaction between negatively charged C_{60} centers and mechanical strain induced by the incorporation of cations from the supporting electrolyte in the film. However, the stability of the films depends on the C_{60} to Pd(II) ratio in the solution from which the film was prepared. The presence of deposits of palladium within the film changes the mechanical and electrochemical stability of the films and also alters the reversibility of the charging processes.

Introduction

In recent years considerable effort has been expended to developing techniques for polymerization of fullerenes.[1−3] Because of the high stability of the fullerene cage, the direct polymerization of fullerene monomers requires the use of forcing conditions. Rao et al.[4] and Ito et al.[5] described the photoinduced polymerization of C_{60} films. The polymerization of C_{60} and C_{70} can also be accomplished under high-frequency plasma[6] and high-pressure[7] conditions. However, the resulting films are very unstable, and they decompose easily with formation of the precursor units.

Fullerene molecules can be introduced into the main chain of organic polymers to form "pearl necklace" polymers[8−19] or into the side chains as pendant groups to form "charm bracelet" polymers.[20−22] The "charm necklace" polymer developed from C_{60}-modified poly(*N*-vinylcarbazole) can be used as a photoconductor.[14,16,17] Benicori et al. prepared a conjugated, redox active, polythiophene-based polymer with covalently appended

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fullerene moieties.[18] Dendritic C_{60}-based macromolecules are a new and very interesting area of fullerene macromolecular chemistry. Several methods have been utilized to functionalize the fullerene surface with a controlled number of dendritic macromolecules[23−28] and to form novel starlike copolymers.[29−34]

This laboratory has been involved in formation of redox active films based on C_{60} and produced by electrochemical reactions.[35−41] The initial work began with the development of an electrochemical procedure for the formation of redox-active films with the epoxide, $C_{60}O$, as the precursor.[35,36] The film obtained via the electroreduction of $C_{60}O$ strongly adheres to a variety of electrodes,[35] and has the ability to store up to eight electrons per C_{60} component.[42] Subsequent work showed that a related film is readily prepared by the reduction of C_{60} or C_{70} in the presence of limited amounts of dioxygen in a toluene/acetonitrile mixture. This process has the advantage that it eliminates the need to prepare $C_{60}O$.

Recently, a two-component electroreductive process that involves the reduction of C_{60} in the presence of transition metal complexes of Pd, Pt, Ir, and Rh has been developed.[38,40] This process produces films that are electroactive and display windows of conductivity. The structure and properties of the films formed by electroreduction of C_{60} and palladium complexes such as palladium(II)acetate trimer, $\{Pd(OAc)_2\}_3$, or bis(benzonitrile)palladium(II)dichloride have received the most study.[38,39] Previously, a series of studies were conducted on films that were obtained by a preparative procedure that utilized fixed concentrations of C_{60} (0.25 mM) and palladium(II) acetate trimer (0.60 mM).[39] The electrochemical switching between the doped (conducting) and undoped (nonconducting) states of such films involves both electron and ion transport within the film. Charge percolation through the C_{60}/Pd electroactive material is accomplished by the transport of cations, and ion transport depends both on the solvent and on the nature of cation (but not the anion) present in the supporting electrolyte. The doping level of the film can be increased by activation at negative potentials. The stability of the film is affected by the potential range over which it is examined. Scanning to highly negative potentials results in the loss of redox activity due to removal of the film from the electrode surface.

Related C_{60}/Pd materials can be prepared chemically through the reaction of C_{60} and $Pd_2(dba)_3$ (dba is dibenzylideneacetone) in chloroform.[43] The properties of the chemically formed C_{60}/Pd material depend on the relative concentration of palladium complex and fullerene in the solution used for the chemical preparation. Samples of $C_{60}Pd_n$ ($n > 3$) are catalytically active for hydrogenation of alkenes.[44]

In this paper we examined the effect of the solution composition on the structure and properties of electrochemically formed C_{60}/Pd films. Because of the similar potential windows for the C_{60} reduction and palladium(II) complex reduction, the processes of C_{60}/Pd film formation and palladium phase deposition can take place at the electrode surface simultaneously. By changing the ratio of palladium(II) complex concentration to the concentration of C_{60} we were able to manipulate some of the electrochemical properties of the films.

Results and Discussion

Cyclic Voltammetric Studies of Films and Film Formation from Solutions with Varying $\{Pd(OAc)_2\}_3/C_{60}\}$ Ratios. Under the conditions used in this article C_{60} alone in toluene/acetonitrile solution (4/1, v/v) with 0.10 M tetra(*n*-butyl)ammonium perchlorate as supporting electrolyte undergoes three reversible reductions with peak reduction potentials at −800, −1250, and −1750 mV. Under the same conditions, the irreversible electrochemical reduction of $\{Pd(OAc)_2\}_3$ occurs with a peak reduction potential of −700 mV on the first cycle as seen in trace a of Figure 1. This wave shifts to −600 mV on subsequent cycles. Figure 1 also shows the multicyclic voltammograms in traces b to e that were recorded for solutions containing 0.31 mM C_{60} and concentrations of $\{Pd(OAc)_2\}_3$ that range from 0.45 mM to 2.21 mM. Alteration of the $\{Pd(OAc)_2\}_3/C_{60}$ ratio affects both the growth of the films on the electrode surface and the electrochemical properties of the layers. Under these conditions, film growth is most effective with $\{Pd(OAc)_2\}_3$ concentrations less than 1 mM as see in traces b and c.

The electrodes coated with C_{60}/Pd films were transferred to solutions of acetonitrile that contained only supporting electrolyte (0.10 M tetra(*n*-butyl)ammonium perchlorate), and multicyclic voltammograms were recorded. Relevant data are shown in Figure 2. The voltammetric responses of the films depend on the

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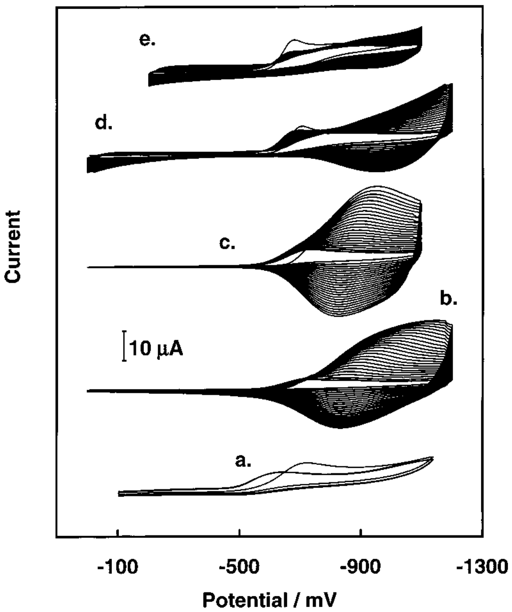

Figure 1. Multicyclic voltammograms obtained for (a) 2.21 mM $\{Pd(OAc)_2\}_3$ without any C_{60}, (b) 0.31 mM C_{60} and 0.45 mM $\{Pd(OAc)_2\}_3$, (c) 0.31 mM C_{60} and 0.86 mM $\{Pd(OAc)_2\}_3$, (d) 0.31 mM C_{60} and 1.48 mM $\{Pd(OAc)_2\}_3$, and (e) 0.31 mM C_{60} and 2.21 mM $\{Pd(OAc)_2\}_3$ at a gold electrode in acetonitrile/toluene mixture (1:4 v/v) containing 0.10 M TBAP. In traces b−e, 26 cycles are shown. The sweep rate was 100 mV/s.

composition of the solution from which it was prepared. Moreover, each film retains its distinctive electrochemical behavior throughout repeated cyclic polarization in the potential range from 0 to −1600 mV with no significant change in the shape of the voltammetric features. The ratio of oxidation to reduction charge is independent of the conditions of film formation and is 0.96 ± 0.02. The films formed in solutions with lower $\{Pd(OAc)_2\}_3/C_{60}$ ratios are more easily reduced. Cyclic voltammograms show peaks of reduction and reoxidation of the layer at −780 mV (trace a). These peaks disappear for the layers formed in solutions with higher $\{Pd(OAc)_2\}_3/C_{60}$ ratios, and the processes of reduction and oxidation shift toward more negative potentials (traces b and c) for these films.

As expected for redox processes of materials that are localized on the electrode surface, the current intensity changes linearly with the sweep rate in the range from 10 to 500 mV/s for samples of the C_{60}/Pd film immersed in an acetonitrile solution that contains only the supporting electrolyte, 0.10 M tetra(*n*-butyl)ammonium perchlorate. Figure 3 shows the results obtained for two different films formed with different $\{Pd(OAc)_2\}_3/C_{60}$ ratios. In both cases the shape of the cyclic voltammograms remains independent of the sweep rate, while the magnitude of the current decreases as the sweep rate slows. Additionally, we observed that the voltammograms do not change when the solutions are stirred. This behavior is consistent with a surface reaction as the rate-limiting step.

The film stability also depends on the composition of the solution that was used to prepare the film. Relevant data for films grown with concentrations of $\{Pd(OAc)_2\}_3$ in the optimal range for film growth (as demonstrated in Figure 1) are shown in Figure 4. As seen in trace c, very stable voltammetric behavior is observed for the

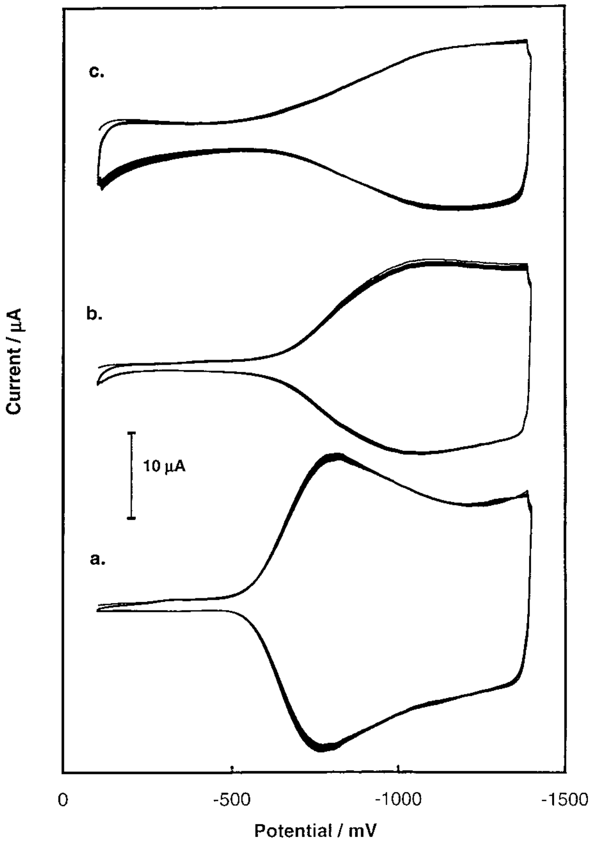

Figure 2. Multicyclic voltammograms of electrochemically formed C_{60}/Pd films obtained in acetonitrile containing 0.10 M TBAP with no electroactive solute. Twenty cycles are shown in each case. The sweep rate was 100 mV/s. The C_{60}/Pd films were grown under cyclic voltammetry conditions in an acetonitrile/toluene mixture (1:4 v/v) containing 0.10 M TBAP as supporting electrolyte and (a) 0.31 mM C_{60} and 0.45 mM $\{Pd(OAc)_2\}_3$, (b) 0.31 mM C_{60} and 0.86 mM $\{Pd(OAc)_2\}_3$, and (c) 0.31 mM C_{60} and 1.48 mM $\{Pd(OAc)_2\}_3$.

layer grown in the solution containing the largest concentration of $\{Pd(OAc)_2\}_3$ (0.90 mM) used in this part of the study. This film retains its redox activity upon cyclic polarization in the whole cathodic potential window available in acetonitrile with almost no change in the shape of the voltammetric features. The sequence of three pairs of peaks (P_{C1}/P_{A1}, P_{C2}/P_{A2}, and P_{C3}/P_{A3}) can be seen in the voltammograms. These three peaks are probably related to the consecutive transfer of three electrons onto each C_{60} unit. Much less stable behavior is observed for films grown with lower concentrations of the palladium precursor. Trace b of Figure 4 shows the cyclic voltammogram of the layer grown in a solution with a lower concentration of $\{Pd(OAc)_2\}_3$·(0.60 mM). This layer is partially decomposed at potentials more negative than −2100 mV. For the first few voltammetric cycles, the decrease of both reduction and oxidation charges is observed which indicates the loss of electroactive material from the electrode surface. Eventually, the voltammetric response reaches a steady-state behavior. For the layer formed from a solution with the lowest $\{Pd(OAc)_2\}_3$ concentration (0.30 mM), total decomposition of the C_{60}/Pd layer is observed if the switching potential in the cathodic cycle is more negative than −1800 mV (trace a in Figure 4). At a large platinum foil electrode, visual observation reveals that the loss of redox activity of the electrode is accompanied

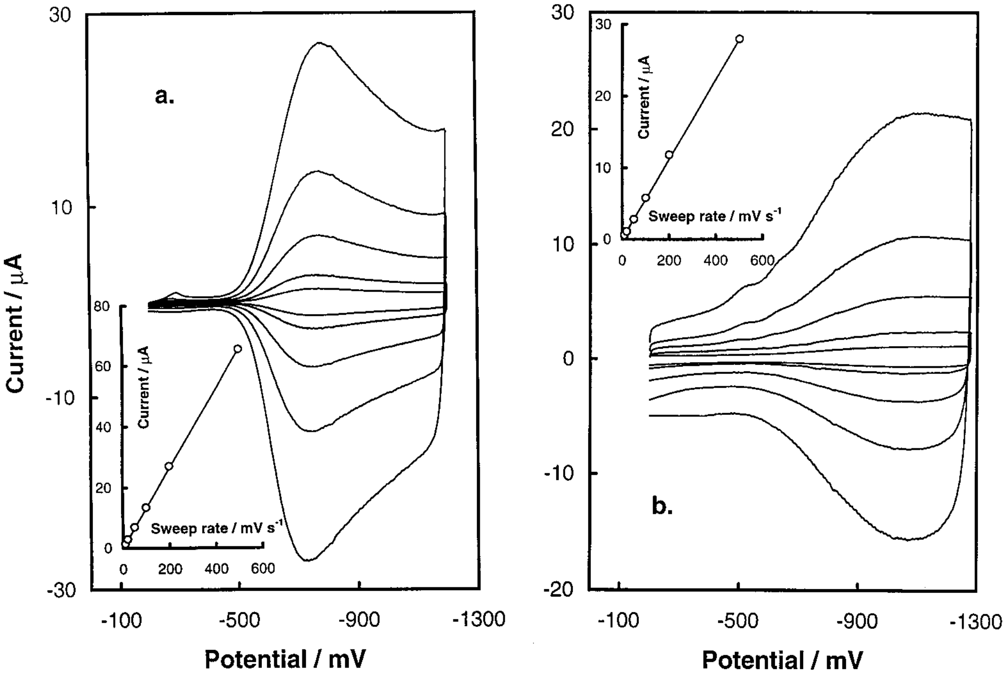

Figure 3. Voltammograms of electrochemically formed C_{60}/Pd films obtained in acetonitrile containing 0.10 M TBAP with no electroactive solute for different sweep rates: 10 (innermost), 20, 50, 100, and 200 mV/s (outermost) and the dependence of the reduction peak current on the sweep rate (insert graph). The C_{60}/Pd films were grown under cyclic voltammetry conditions in an acetonitrile/toluene mixture (1:4 v/v) containing 0.10 M TBAP as supporting electrolyte and (a) 0.31 mM C_{60} and 0.86 mM $\{Pd(OAc)_2\}_3$ and (b) 0.31 mM C_{60} and 2.08 mM $\{Pd(OAc)_2\}_3$.

by the appearance of dark clouds of material falling from the electrode. After complete loss of electrochemical activity, the surface of the electrode is clean and shiny. This indicates removal of the layer from the electrode surface at negative potentials. This observation is very useful for the cleaning of electrodes, particularly the very fragile interdigitated microsensor electrodes, on which C_{60}/Pd film has been deposited. The strong repulsion interaction between the multiply negatively charged C_{60} units and mechanical strain caused by the influx of cations are likely causes of the film decomposition.

By depositing the C_{60}/Pd films across an interdigitated microelectrode array it is possible to examine the resistance of the film as a function of applied potential. Figure 5 shows the dependence of the resistance on the potential for two films prepared in solutions with different [Pd]/[C_{60}] ratios. In both cases the resistance drops in the potential range where the film undergoes reduction. The magnitude of the potential drop is larger for the electrode covered by the layer grown in solution containing larger excess of the palladium complex (trace b). In both cases hysteresis is observed in the dependence of the resistance on the potential. This hysteresis is probably caused by changes in the structure of the layer due to the doping/undoping process in which tetra(*n*-butyl)ammonium cations enter and leave the film. The lower resistance of the layer shown in trace b may be due to the presence of palladium particles deposited along with the redox active film.

Cyclic Voltammetric Studies of the C_{60}/Pd Films in Acidic Aqueous Solutions. The processes of film formation and reduction of the palladium complex occur in the same potential range. Therefore, it is very likely that palladium is also deposited along with the polymeric C_{60}/Pd film. Additionally, it is likely that the amount of palladium deposited depends on the ratio of $\{Pd(OAc)_2\}_3/C_{60}$ concentrations in the solutions used to form the films.

The voltammetric behavior of a palladium electrode in acidic water solution is well characterized.[36-38] Therefore, the changes of voltammograms of C_{60}/Pd layers formed under different conditions recorded in acidic aqueous solution may be a good indicator for changes in structure and composition of the layers.

Figure 6 shows voltammograms from a variety of coated electrodes that have been transferred to a 1.0 M H_2SO_4 aqueous solution. The layers were deposited on the surface of glassy carbon electrode (GCE) in solutions with various $\{Pd(OAc)_2\}_3/[C_{60}]$ ratios. After the electrode was washed with a toluene/acetonitrile (4:1, v/v) mixture and then with water, the electrodes were transferred to the 1.0 M H_2SO_4 aqueous solution and cyclic voltammograms were recorded. In the potential range used for these studies the C_{60}/Pd film itself is electrochemically inactive. Trace a of Figure 6 shows the background current obtained on bare GCE electrode. As seen in trace b, the metallic palladium phase formed during reduction of the $\{Pd(OAc)_2\}_3$ complex in the absence of fullerene exhibits characteristic voltammetric features with underpotential hydrogen adsorption/desorption peaks ($P_C^{H,ad}/P_A^{H,ad}$) and oxide layer formation (P_A^{PdO}) and reduction (P_C^{PdO}) clearly visible. The large current recorded at potentials more negative than -100 mV is related to the bulk evolution of H_2. This behavior is consistent with the previous results obtained for palladium electrodes.[45-47] Traces c−e show voltammograms of C_{60}/Pd layers formed in solutions with varied $\{Pd(OAc)_2\}_3/[C_{60}]$ ratios. For the film formed with the

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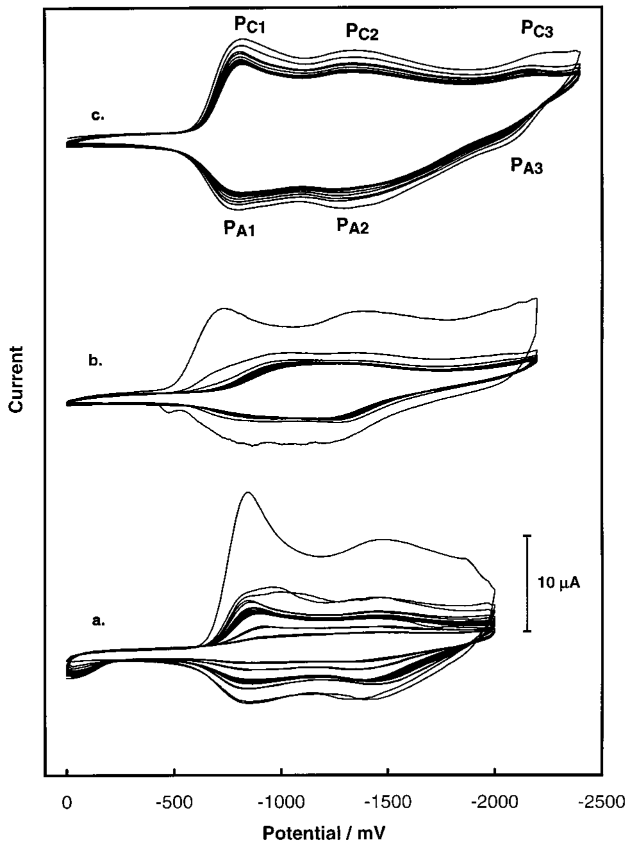

Figure 4. Multicyclic voltammograms of electrochemically formed C_{60}/Pd films obtained in acetonitrile containing 0.10 M TBAP with no electroactive solute. Fifteen cycles are shown in each case. The sweep rate was 100 mV/s. The C_{60}/Pd films were grown under cyclic voltammetry conditions in an acetonitrile/toluene mixture (1:4 v/v) containing 0.10 M TBAP as supporting electrolyte, 0.25 mM C_{60}, and (a) 0.30 mM $\{Pd(OAc)_2\}_3$, (b) 0.60 mM $\{Pd(OAc)_2\}_3$, and (c) 0.90 mM $\{Pd(OAc)_2\}_3$.

highest $\{Pd(OAc)_2\}_3$/[C_{60}] ratios, peaks resulting from the hydrogen underpotential adsorption/desorption process and palladium oxide layer formation are clearly present as seen in trace c. These observations indicate that palladium has formed on the electrode surface. For films prepared with lower $\{Pd(OAc)_2\}_3$/[C_{60}] ratios there is a shift in the potential for oxide layer formation toward more positive potentials, and the potential of the reduction of the palladium oxide component shifts toward less positive values as seen in traces d and e. A similar effect is observed for the hydrogen adsorption/desorption process. Moreover, the changes observed in the currents for the palladium oxidation and hydrogen evolution change in such a manner that less metallic palladium is present in the film form with low $\{Pd(OAc)_2\}_3$/[C_{60}] ratios. These observations suggest that intermixing of the palladium and polymeric C_{60}/Pd materials results in increasing irreversibility for hydrogen evolution and oxide formation.

Further Deposition of Palladium on the C_{60}/Pd Films. The electrochemically deposited films can be further modified by transferring the film to a second solution and observing the electrochemical behavior in

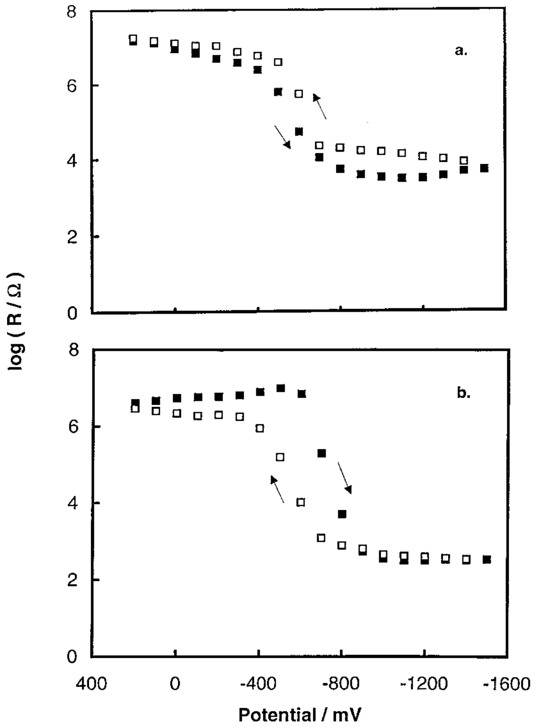

Figure 5. Dependence of the steady-state resistance of electrochemically formed C_{60}/Pd films on the potential. The C_{60}/Pd films were grown under cyclic voltammetry conditions in an acetonitrile/toluene mixture (1:4 v/v) containing 0.10 M TBAP as supporting electrolyte and (a) 0.25 mM C_{60} and 0.80 mM $\{Pd(OAc)_2\}_3$ and (b) 0.25 mM C_{60} and 1.2 mM $\{Pd(OAc)_2\}_3$ at an interdigitated microarrays electrode. Array fingers were ~1 cm long, 5 μm high, and separated from each other by 5 μm.

the presence of either C_{60} alone or $\{Pd(OAc)_2\}_3$ alone. No further film growth occurs when the modified electrode is transferred to a solution containing just C_{60} and supporting electrolyte. Thus, both components, C_{60} and $\{Pd(OAc)_2\}_3$, must be present to electrochemically deposit the film. However, with $\{Pd(OAc)_2\}_3$ present it is possible to modify the film by further deposition of palladium. Figure 7 shows cyclic voltammograms of the film in the presence of varying concentrations of $\{Pd(OAc)_2\}_3$. The inner trace shows the film in a toluene/acetonitrile (4:1 v/v) solution with only 0.10 M TBAP as supporting electrolyte. The other three traces show that there is an increase in current as the concentration of $\{Pd(OAc)_2\}_3$ increases. Under these conditions palladium deposition onto the film occurs and that deposition results in further modification of the film.

Figure 8 shows the effects of palladium deposition on the electrochemical behavior of the C_{60}/Pd film. Trace a shows the electrochemical behavior of an unmodified film directly after preparation and transfer to a toluene/acetonitrile (4:1 v/v) solution with 0.10 M TBAP as supporting electrolyte. Trace b shows behavior after palladium was deposited during five redox cycles in an acetonitrile solution containing 1.5 mM $\{Pd(OAc)_2\}_3$ and 0.1 M TBAP in the potential range from 0 to −1000 mV. Trace c shows the behavior after 25 cycles of palladium deposition. Comparison of traces b and c with trace a reveals that palladium deposition results in reduction of the current and a shift in the redox wave to more negative potentials which are comparable to the voltammograms seen in traces a and b of Figure 2. These

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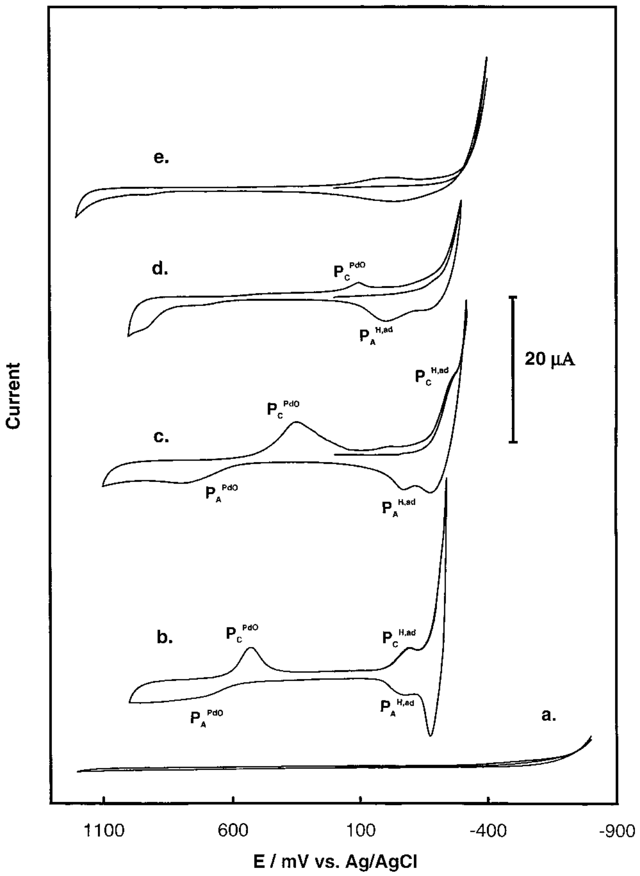

Figure 6. Cyclic voltammograms of (a) a bare glassy carbon electrode, (b) a glassy carbon electrode covered by palladium film, and (c−e) glassy carbon electrodes covered by C_{60}/Pd films recorded in 1.0 M H_2SO_4 aqueous solution. Sweep rate was 100 mV/s. The C_{60}/Pd films were grown under cyclic voltammetry conditions in acetonitrile/toluene mixture (1:4 v/v) containing 0.10 M TBAP as supporting electrolyte and (c) 0.25 mM C_{60} and 1.20 mM $\{Pd(OAc)_2\}_3$, (d) 0.25 mM C_{60} and 0.70 mM $\{Pd(OAc)_2\}_3$, and (e) 0.25 mM C_{60} and 0.30 mM $\{Pd(OAc)_2\}_3$. The metallic palladium layer was formed in an acetonitrile/toluene mixture (1:4 v/v) containing 0.10 M TBAP and 1.50 mM $\{Pd(OAc)_2\}_3$.

changes suggest that the reversibility of the redox process is lessened by the deposition of palladium which limits access of the supporting electrolyte into the film.

Conclusions

The present studies show that the redox properties of C_{60}/Pd films are modified by changes in the composition of the solution from which the films are grown. The available evidence suggests that these films consist of covalently bonded PdC_{60} moieties that are organized into chains, $\cdots C_{60}Pd(C_{60}Pd)_nC_{60}Pd\cdots$. Variations in the $\{Pd(OAc)_2\}_3/C_{60}\}$ ratios in the solutions used to prepare the redox active films can result in creation of cross-linking between these $\cdots C_{60}Pd(C_{60}Pd)_nC_{60}Pd\cdots$ chains through $C_{60}PdC_{60}$ units and to the deposition of palladium. The results shown in Figure 6 indicate that palladium as well as the redox active C_{60}/Pd film can be deposited on the electrode surface. The presence of cross-linking and deposits of palladium within the film changes the mechanical and electrochemical stability of the films and also alters the reversibility of the charging processes as seen in Figures 2 and 8.

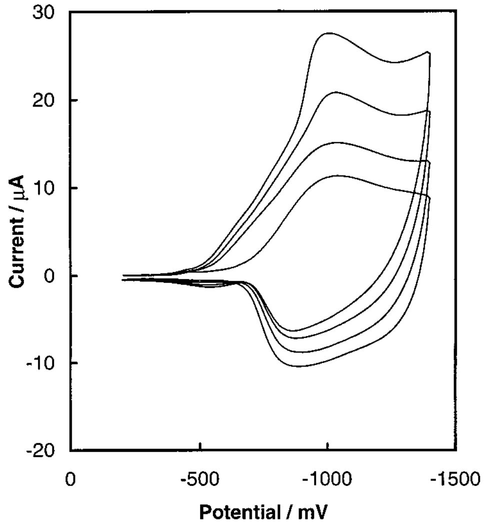

Figure 7. Voltammograms of electrochemically formed C_{60}/Pd film in the presence of $\{Pd(OAc)_2\}_3$. The initial layer was formed by 25 cycles of electroreduction of a solution of 0.30 mM C_{60} and 0.82 mM of $\{Pd(OAc)_2\}_3$ in toluene/acetonitrile (4:1 v/v) with 0.10 M TBAP as supporting electrolyte. This layer was then transferred into a toluene/acetonitrile (4:1 v/v) solution with 0.10 M TBAP as supporting electrolyte and (a) 0 mM $\{Pd(OAc)_2\}_3$ (innermost trace); (b) 0.76 mM $\{Pd(OAc)_2\}_3$; (c) 1.51 mM $\{Pd(OAc)_2\}_3$; and (d) 2.26 mM $\{Pd(OAc)_2\}_3$ (outermost trace).

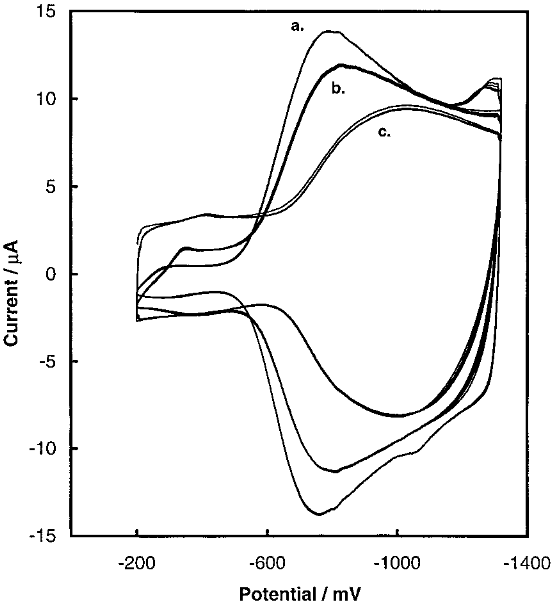

Figure 8. Voltammograms of electrochemically formed C_{60}/Pd film (a) and C_{60}/Pd film covered by a metallic palladium layer (b and (c) obtained in acetonitrile containing 0.10 M TBAP with no electroactive solute. The C_{60}/Pd films were grown under cyclic voltammetry conditions in an acetonitrile/toluene mixture (1:4 v/v) containing 0.10 M TBAP as supporting electrolyte and (a) 0.30 mM C_{60}/Pd and 0.86 mM $\{Pd(OAc)_2\}_3$. The deposition of palladium was done in acetonitrile solution containing 1.50 mM $\{Pd(OAc)_2\}_3$ and 0.10 M TBAP under multicyclic scans in the potential range from 0 to −1000 mV. Number of scans were 5 for the modified film responsible for trace (b) and 25 for the film responsible for trace (c). The sweep rate was always 100 mV/s.

Metal microparticles deposited into polymer-modified electrodes have received considerable attention for a variety of uses as catalysts, electrocatalysts, and sensors.[48−57] For example, deposition of metallic particles into porous matrices can lead to an increase in the specific area of the catalytic material and thus can improve its catalytic efficiency. Further study of the properties of the palladium particles deposited on or co-deposited with the C_{60}/Pd films is warranted.

Experimental Section

Materials. Palladium(II) acetate trimer ($\{Pd(OAc)_2\}_3$) was purchased from Alfa, C_{60} from Southern Chemical Group, and both used without additional purification. The supporting electrolyte, tetra(*n*-butyl)ammonium perchlorate (TBAP) (Sigma Chemical Co.), was used as received. Anhydrous acetonitrile (99.9%) was used as received from Aldrich. Toluene (Aldrich Chemical Co.) was purified by distillation over sodium under argon atmosphere. Water was purified with a Millipore Milli-Q system.

Voltammetry. Voltammetric experiments were performed on a BAS CV50−W Electroanalytical System with a three-electrode cell. Gold with a diameter of 1.5 mm (Bioanalytical Systems Inc.), palladium with a diameter of 0.5 mm (Goodfellow Cambridge Lmt.), and glassy carbon with a diameter of 4 mm (Bioanalytical Systems Inc.) were used as working disk electrodes. Prior to the experiment the electrodes were polished with a fine carborundum paper and then with a 0.5 μm alumina slurry. Next the electrodes were sonicated in water to remove the traces of alumina from the gold surface, washed with water and dried. A silver wire immersed in 0.01 M silver perchlorate and 0.09 M TBAP in acetonitrile and separated from the working electrode by a ceramic tip (Bioanalytical Systems Inc.) served as the reference electrode for the experiments performed in nonaqueous solutions. For this reference electrode, the ferrocene/ferrocinium redox potential was +161 mV. In experiments carried out in 1 M H_2SO_4, an aqueous 1.0 M KCl solution Ag/AgCl electrode, which was separated from the working electrode by a ceramic tip (Bioanalytical Systems Inc.), was used as the reference electrode. The counter electrode was a platinum tab with an area of about 0.5 cm^2.

Resistance Measurements. Interdigitated microsensor electrodes manufactured by AAI-ABTECH were used for the measurements of the film resistance. These assemblies consist of two sets (A and B) of fingers which are about 1 cm long and 5 mm high. Individual fingers are separated from each other by 5 mm. Prior to use, the interdigitated microelectrodes were tested with an ohmmeter to make sure that there was no short circuit between two sets of fingers. The C_{60}/Pd films were deposited on the microelectrode array under multicyclic scans in the potential range from 0 to −1100 mV. The film-covered electrodes were washed with an acetonitrile/toluene (1:4 v/v) mixture and transferred to a solution of 0.1 M tetra(*n*-butyl)ammonium perchlorate in acetonitrile/toluene (1:4 v/v). To determine whether the film that coated the fingers of the microarray electrode resulted in connection between them, voltammograms were recorded for set A and set B of the fingers driven alone or together. Identical voltammetric responses for both cases indicated that the polymer film connected the fingers. For measurements of the change in resistance with potential, a triode-type device circuit was used.[58] One set of electrode fingers was connected to the potentiostat and a variable potential (E_1) was applied. The potential E_1 was measured with respect to a silver/silver ion electrode. A second, small potential difference (DE_2) was applied between the A and B sets of gold fingers. Under these conditions, the current flowing between the fingers depends on the resistance of the polymer layer. The potential E_1 was changed by steps of 50 mV and the steady-state resistance of the polymer layer was measured.

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