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Charging Processes in Electroactive C_{60}/Pd Films: Effect of Solvent and Supporting Electrolyte

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The electrochemical properties of solid films deposited on an electrode surface by simultaneous electrochemical reduction of C_{60} and palladium(II) acetate trimer in an acetonitrile/toluene mixture have been studied using cyclic voltammetry. The electrochemical switching between the doped (conducting) and undoped (nonconducting) states involves both electron and ion transport within the film. The overall control of charge percolation through the C_{60}/Pd electroactive material is governed by the transport of cations. The ion transport depends both on the nature of solvent and supporting electrolyte. The size of solvent molecule is the major factor determining the degree of solvent swelling of the layer. In the case of small solvent molecules, the C_{60}/Pd film exhibits a reversible redox behavior. For larger molecule solvents, the voltammograms show a departure from reversibility. The reduction of the layer is accompanied by changes in its morphology allowing for the solvent swelling of the film also in the case of large molecule solvents. The electrochemical response of the layer is not affected by the anions of the supporting electrolyte. However, a strong influence of both nature and concentration of supporting electrolyte cations on the redox properties of the layer is observed, since these cations are incorporated into the C_{60}/Pd layer. The redox ability in solutions containing large cations is considerably reduced. The activation of the film at negative potentials results in an increase of the doping level. The stability of the films is affected by the potential range over which they are examined. Scanning to highly negative potentials results in the loss of redox activity due to removal of the film from the electrode surface.

Introduction

Polymerization of fullerenes is expected to lead to a range of new materials with interesting and useful properties, some of which can be readily anticipated on the basis of the extensive redox chemistry that these carbon allotropes exhibit. Fullerenes may be polymerized through high pressure,[1] photochemical,[2,3] and chemical[4] methods.[5] Fullerenes can also be chemically modified to facilitate polymerization.[6] Electrochemical methods are also an attractive route for forming fullerene-based polymers. The electrochemistry of C_{60}, both in solution and as thin films on electrodes, has received considerable study.[7] In solution, up to six reversible, one-electron reduction waves can be observed for C_{60}.[8] These electrode processes result from the sequential filling of the triply degenerate LUMO of C_{60}. Additionally, for C_{60} a reversible, one-electron oxidation is observed at relatively high potential.

Redox active, fullerene-based films can be formed by the electrochemical reduction of either the fullerene epoxide, $C_{60}O$,[9,10] or of a mixture of C_{60} and dioxygen[11] in toluene/acetonitrile solution. These films are believed to be polymeric since they display essentially no solubility in common organic solvents. The electrochemical responses of these films have some features in common with conducting polymers such as polyaniline, polypyrrole, and polythiophene, which are generally obtained by oxidation of corresponding monomers.[12−14] The film obtained via the electroreduction of $C_{60}O$ has the ability to store up to eight electrons per C_{60} component.[15]

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Consequently such films have potential utility as an energy storage battery. Here we describe a new electrochemical approach to the formation of fullerene-based polymers through a two-component polymerization that utilizes the formation of covalent bonds between transition metal complexes and fullerenes to form the polymeric network.

Recently, this laboratory has developed an electrochemical procedure for the formation of new redox-active films through the reduction of C_{60} in the presence of selected transition metal complexes.[16,17] The resulting films form tough, insoluble coatings on a variety of electrode surfaces. Thus, it has been demonstrated that C_{60} forms films when reduced in the presence of $Pd(PhCN)_2Cl_2$, $Pt(py)_2Cl_2$, $Ir(CO)_2Cl(p\text{-}NH_2C_6H_4Me)$, or $Rh_2(O_2CCF_3)_4$ and that the metal (along with some of its ligands in the case of the rhodium and iridium precursors) is incorporated into the material. That work showed that neither prior coordination of the fullerene to the metal complex nor redox activity of the metal complex itself was necessary to obtain film formation. The development of these films began with attempts to form an electroactive material based on the prior work of Nagashima and co-workers, who demonstrated that amorphous, black materials could be prepared through the chemical reaction between C_{60} and a palladium(0) complex such as tris(dibenzylideneacetone)dipalladium(0).[18,19] These materials, which have compositions $C_{60}Pd_n$, where n can range from 1 to 7, are believed to consist of repeating $\cdots C_{60}PdC_{60}PdC_{60}Pd\cdots$ units that are cross-linked by additional palladium atoms. The $C_{60}Pd_n$ materials are insoluble in common organic solvents but dissolve in the presence of triphenylphosphine to form $(\eta^2\text{-}C_{60})Pd(PPh_3)_2$, a well-characterized complex whose structure has been determined by X-ray crystallography.[20−22] Since $(\eta^2\text{-}C_{60})Pd(PPh_3)_2$ can be extracted from the chemically generated $C_{60}Pd_n$ material and also from the films that are prepared by electroreduction of C_{60} and $Pd(PhCN)_2Cl_2$ after treatment with triphenylphosphine, it is likely that the palladium atoms are η^2-bonded to the fullerene in both types of materials. Additionally, $C_{60}Pd_6$ subunits with a local octahedral structure appear to be likely components in the material with composition $C_{60}Pd_3$.[19] Here we describe studies of the effects of solvent and supporting electrolyte on the redox characteristics of the electrochemically generated Pd/C_{60} film. The influence of structural changes within the C_{60}/Pd film during doping reactions is also studied.

Electroactive polymers can be classified into three major types: redox polymers, electrochemically conducting polymers, and loaded ionomers. The first class of materials is especially interesting. Usually, depending on the electronic structure and doping level the electrochemically formed redox polymer layers show a discrete window of conductivity.[23−26] The electrochemical switching between the doped (conducting) and undoped (non conducting) states involves both electron and ion transport within the film. The electron transport can be described by the hopping model.[27,28] According to this model the electron is successively transferred between neighboring acceptor and donor redox sites. This process is accompanied by the transport of charge-compensating counterions within the matrix. Usually, the overall control of charge percolation through the electroactive material is governed by the transport of counterions.[29−40] Different factors can influence the rate of counterion transport through the redox active layer. The degree of solvent swelling,[40−44] size of supporting electrolyte ions,[18,19,24−28] and morphology of the film [44,45] are the most important factors that determine the redox properties of the layer. In the case of a sufficiently porous layer, the ion-transport limitation may be due to either interaction with the material itself or with the solution within the pores. The doping of the layer by cations can be described by one of the following processes:[39]

$$\{C_{60}/Pd, (C^+A^-)_m\} + ne^- + nC^+ \rightarrow \{C_{60}{}^{n-}/Pd/nC^+, (C^+A^-)_m\} \quad (1)$$

$$\{C_{60}/Pd, (C^+A^-)_m\} + ne^- \rightarrow \{C_{60}{}^{n-}/Pd/nC^+, (C^+A^-)_{m-n}\} + nA^- \quad (2)$$

In the cation charge-transfer process (eq 1) the cations, C^+, move from the bulk electrolyte to the vicinity of the reduced chain site. In the second process (eq 2) anions,

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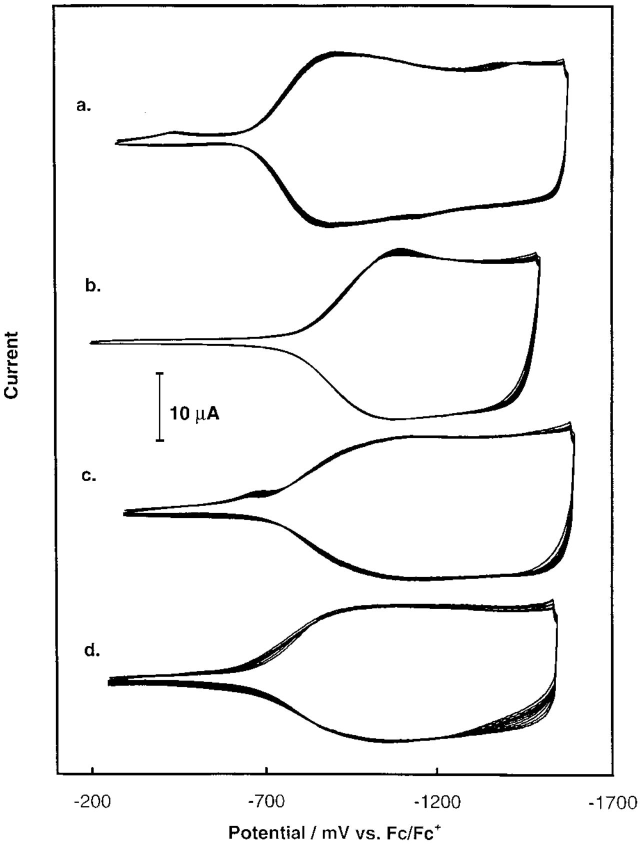

Figure 1. Multicyclic voltammograms of electrochemically generated C_{60}/Pd films obtained in (a) acetonitrile, (b) dichloromethane, (c) acetone, and (d) *N,N*-dimethylformamide containing 0.1 M tetra(*n*-butyl)ammonium perchlorate. Sweep rate was 100 mV/s. The C_{60}/Pd films were grown under cyclic voltammetry conditions in acetonitrile/toluene mixture (1:4, v/v) containing 0.10 M tetra(*n*-butyl)ammonium perchlorate as a supporting electrolyte.

A^-, which are already present in the film-covered electrode, depart from the film.

Results

Film Formation. Films were obtained as described previously[16] through electroreduction of a solution containing both C_{60} (0.25 mM) and palladium(II) acetate trimer (0.60 mM). The solvent was acetonitrile/toluene (1:4 v/v). Films were grown by repeated cycling through the potential range: −100 to −1150 mV. Because of the low dielectric constant of the acetonitrile/toluene mixture, the supporting electrolyte was limited to either tetra(*n*-butyl)ammonium perchlorate or tetra(*n*-hexyl)ammonium perchlorate. The reduction peak observed in the first cathodic cycle for both salts corresponds to the simultaneous reduction of Pd(II) acetate trimer and C_{60}.

The thickness of the films can be controlled by the number of voltammetric cycles. Films prepared using 30 redox cycles were routinely employed in this study. After the film was formed, the resulting electrode was rinsed several times with a fresh acetonitrile/toluene (1:4 v/v) mixture and then placed in the chosen solvent and supporting electrolyte. The electrodes were allowed to equilibrate for 10 min in their new environment before electrochemical measurement of their redox properties.

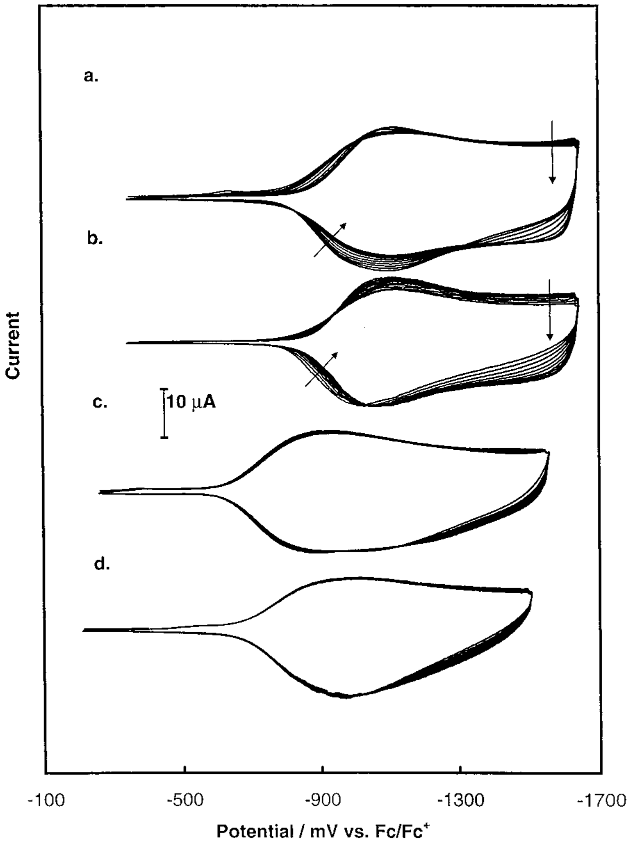

Figure 2. Multicyclic voltammograms of electrochemically generated C_{60}/Pd films obtained in (a) benzonitrile, (b) *o*-dichlorobenzene, (c) dimethyl sulfoxide, and (d) propylene carbonate containing 0.10 M tetra(*n*-butyl)ammonium perchlorate. Sweep rate was 100 mV/s.

Solvent Effects on the Electrochemical Response of the Film. The voltammetric behavior of the C_{60}/Pd film in a variety of solvents containing 0.10 M tetra(*n*-butyl)ammonium perchlorate is shown in Figures 1 and 2. These data show that the C_{60}/Pd film is essentially insoluble and stable in a range of potential solvents including *o*-dichlorobenzene, which is an excellent solvent for neutral C_{60}, and acetonitrile and dimethyl sulfoxide, which could provide a good ligating environment for palladium.

In the anodic and cathodic cycle the voltammograms show broad peaks that appear near −1000 mV for the redox reaction of the electroactive film. With the solutions used to generate Figure 1, the anodic and cathodic parts of the voltammograms are nearly symmetrical. The peak potentials associated with the reduction and oxidation waves are very close to one another, and the integrated charge under the reduction wave approaches that under the oxidation wave. These results indicate that charge transfer through the C_{60}/Pd film has a good degree of reversibility in these solutions.

The voltammograms presented in Figure 1 are similar to those reported in the literature for redox active films obtained by electropolymerization of polypyrrole[30,46,47,48]

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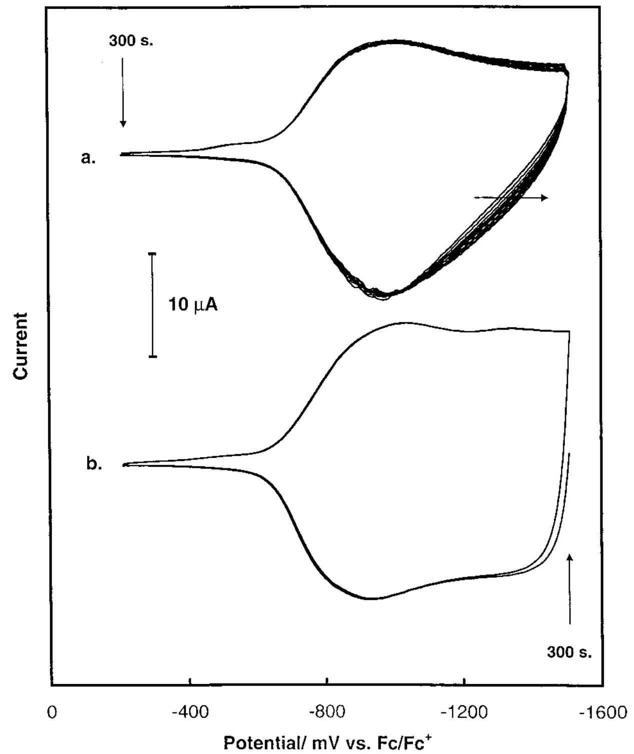

Figure 3. Multicyclic voltammograms of electrochemically generated C_{60}/Pd films obtained in propylene carbonate containing 0.1 M tetra(*n*-butyl)ammonium perchlorate. Sweep rate was 100 mV/s. Before recording the electrode was kept for 300 s at potential (a) −200 mV and (b) −1500 mV.

polyaniline,[49,50,51] or polythiophene.[52,53,54,55] A characteristic large, nonfaradaic residual current is observed at the end of the doping wave for these films as well as for the C_{60}/Pd film. This effect is associated with a high limiting capacitance, C_L. At high doping levels, double layers of static charge, which involve molecular distances between weakly trapped ions and the surface of molecular chains, are formed in the polymer matrixes. Those are responsible for the large residual current.[56,57] In the case of the C_{60}/Pd polymer this effect may also be related to the overlapping of the successive reduction processes for the C_{60} centers.

The electrochemical behavior of the film is somewhat different in the four solvents used to create the data in Figure 2. A pronounced tailing of the $i - E$ curves is observed. These observations indicate that the electrochemical reactions in the film take place rather slowly.[58] The voltammetric response of the Pd/C_{60} layer changes during redox cycling in benzonitrile and *o*-dichlorobenzene (traces a and b of Figure 2). In these solutions, the voltammograms become more symmetrical and the peak-to-peak separation decreases during successive cycles.

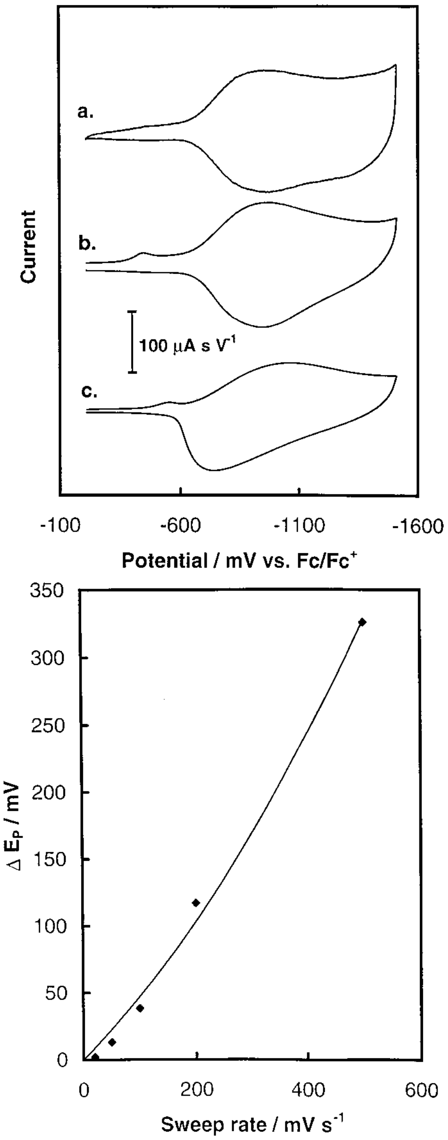

Figure 4. Influence of sweep rate on voltammetric response of C_{60}/Pd film. Sweep rate was (a) 20 mV/s, (b) 100 mV/s, and (c) 500 mV/s (upper panel). Lower panel presents the difference between cathodic and anodic peak potential as a function of sweep rate.

The results presented in Figure 3 suggest that activation of the Pd/C_{60} layer takes place at negative potentials, where the film is reduced. The film was cycled in a propylene carbonate solution with 0.10 M tetra(*n*-butyl)ammonium perchlorate as supporting electrolyte. As seen in trace a when the electrode is held at a potential of −200 mV for 300 s before recording the cyclic voltammograms, the resulting curves show poorly reversible behavior and significant tailing. However, the layer is partially activated during multicyclic polarization. In contrast, when the electrode is held at −1500 mV for 300 s before recording the cyclic voltammogram, nearly reversible voltammetric behavior is observed, as seen in Trace b of Figure 3.

Figure 4 shows the effect of the sweep rate on the voltammetric response of the C_{60}/Pd film in propylene carbonate solution containing tetra(*n*-butyl)ammonium

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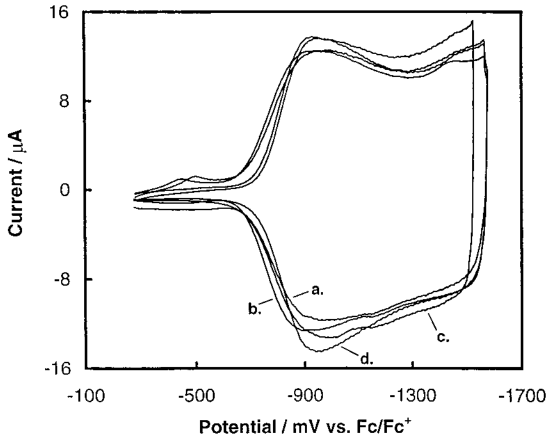

Figure 5. Cyclic voltammograms of electrochemically generated C_{60}/Pd films obtained in acetonitrile containing (a) 0.1 M tetra(*n*-butyl)ammonium perchlorate, (b) 0.1 M tetra(*n*-butyl)ammonium tetraphenylborate, (c) 0.1 M tetra(*n*-butyl)ammonium hexafluorophosphate, and (d) 0.10 M tetra(*n*-butyl)ammonium bromide. Sweep rate was 100 mV/s.

perchlorate as the supporting electrolyte. For low sweep rates the charge transfer through the layer is almost reversible (trace a in upper panel). The increase of the sweep rate results in a certain degree of irreversibility. The separation between cathodic and anodic peak potentials increases (lower panel of Figure 4) and a pronounced tailing of the $i - E$ curves is observed (traces b and c in upper panel).

Effects of Supporting Electrolytes on the Electrochemical Response of the C_{60}/Pd Film. To examine the effect of the supporting electrolyte on the redox properties of the C_{60}/Pd films, voltammograms in acetonitrile solution containing different supporting electrolytes were recorded. The effect of different anions in the supporting electrolyte on the $i - E$ curves of the C_{60}/Pd film is shown in Figure 5. The four supporting electrolytes, tetra(*n*-butyl)ammonium perchlorate, tetra(*n*-butyl)ammonium tetraphenylborate, tetra(*n*-butyl)ammonium hexafluorophosphate, and tetra(*n*-butyl)ammonium bromide involve a common cation but anions that differ significantly in size and shape. Nevertheless, the $i - E$ response obtained with the small inorganic bromide ion is almost the same as the one recorded for the large tetraphenylborate ion. The similarity of the cyclic voltammograms in Figure 5 suggests that the process of C_{60}/Pd electroreduction is not accomplished by transport of anions through the film.

However, the voltammetric response of the C_{60}/Pd layer strongly depends on the nature of the cation in the supporting electrolyte. Figure 6 shows the size effect of tetra(alkyl)ammonium cations on the cyclic voltammograms of the C_{60}/Pd film. The charge involved in the reduction and reoxidation of the film increases with a decrease in the size of cation. This effect suggests that small cations migrate more easily through the pores of the polymer. The reversibility of charge-transfer processes in the C_{60}/Pd layer depends on the other hand only slightly on the size of the cations. For tetra(ethyl)ammonium and tetra(*n*-butyl)ammonium cations, the cathodic and anodic wave are perfectly symmetrical. Some departure from the reversibility is observed for the larger tetra(*n*-hexyl)ammonium cations.

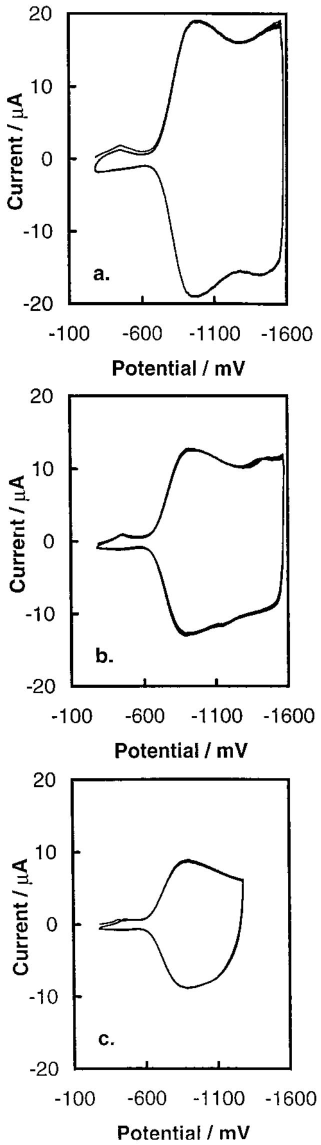

Figure 6. Multicyclic voltammograms of electrochemically generated C_{60}/Pd films obtained in acetonitrile containing (a) 0.1 M tetra(ethyl)ammonium perchlorate, (b) 0.1 M tetra(*n*-butyl)ammonium perchlorate, and (c) 0.1 M tetra(*n*-hexyl)ammonium perchlorate. Sweep rate was 100 mV/s.

The voltammetric response of the C_{60}/Pd layer also depends on the concentration of the supporting electrolyte. The shape of the voltammograms and the charge corresponding to cathodic and anodic processes obtained with varying concentrations (ranging from 0.05 to 0.50 M) of tetra(*n*-alkyl)ammonium perchlorate salts were almost identical. However, the electrolyte concentration had a demonstrable effect on the peak potentials. Figure 7 shows a plot of E_f versus the logarithm of the supporting electrolyte concentration. The formal potential, E_f, was calculated as the average of the cathodic and anodic peak potentials.

The two mechanisms for charge transfer in the C_{60}/Pd layer lead to opposite effects for the dependence of E_f upon concentration of the supporting electrolyte.[39] Assuming that the charge-transfer process is reversible and described by the Nernst equation, the dependence of reversible formal potential for the processes 1 and 2 on the supporting electrolyte concentration is expressed by the following equations:

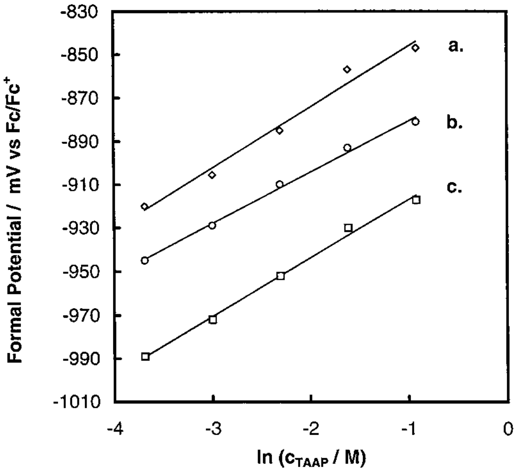

Figure 7. Plot of formal potential versus supporting electrolyte concentration for (a) tetra(*n*-hexyl)ammonium perchlorate, (b) tetra(*n*-butyl)ammonium perchlorate, and (c) tetra(ethyl)-ammonium perchlorate. Sweep rate was 100 mV/s.

$$E_f = E_f{}^{\circ} + \frac{RT}{nF} \ln \frac{[C_{60}/Pd,(C^+A^-)_m]}{[C_{60}{}^{n-}/Pd/nC^+,(C^+A^-)_m]} + \frac{RT}{F} \ln[C^+] \quad (3)$$

$$E_f = E_f{}^{\circ} + \frac{RT}{nF} \ln \frac{[C_{60}/Pd,(C^+A^-)_m]}{[C_{60}{}^{n-}/Pd/nC^+,(C^+A^-)_{m-n}]} - \frac{RT}{F} \ln[A^-] \quad (4)$$

Equation 3 for process 1 predicts a negative shift of the formal potential with increase of the ion concentration in the solution. For the anion exchange process 2 the opposite effect can be expected as seen from eq 4.

According to eq 3, the theoretical slope of the E_f versus log c relation at 20 °C should be equal to 25 mV/log unit.[39] The values obtained for tetra(ethyl)-, tetra(*n*-butyl)-, and tetra(*n*-hexyl)ammonium cations are equal to 22, 26, and 28 mV/log unit, respectively. These values are very close to the ones predicted by eq 3. These results show also that the processes of doping and undoping of the C_{60}/Pd layer in the presence of tetra(*n*-alkyl)ammonium cations are very close to reversibility and can be described by the Nernst equation.

Figure 8 shows that similar changes in the voltammetric response of the C_{60}/Pd layer were also observed in solutions containing different alkali metal cations. Completely reversible redox behavior was observed in the presence of Li^+, K^+, and Cs^+ ions in acetonitrile. However, the charges associated with the doping and undoping processes decrease significantly in order: $Li^+ > K^+ \gg Cs^+$. This effect is consistent with the increase of cation size and with the observations presented in Figure 6 where different sizes of tetra(alkyl)ammonium cations also affect the charge transfer in a similar fashion.

Figure 9 presents multicyclic voltammograms recorded for a C_{60}/Pd layer in acetonitrile solution containing large cations: tetra(phenyl)arsonium (traces a and b) and bis(triphenylphosphine)imminium (trace c). For comparison, the voltammogram obtained in the presence of tetra(*n*-butyl)ammonium cations in solution is shown as the dashed line in trace a. In traces a and c, there are large decreases in the doping and undoping charges and decreases of degree of reversibility for the large cations. As seen in trace b, electrochemical pretreatment of the layer at negative potentials (−1500 mV for 300 s) results in an increase in the charging and discharging currents. In this case, we suggest that the electrochemical pretreatment results in a change in the layer structure. The voltammetric response in the following cycles remains the same, which indicates that the structural changes in the activated layer are irreversible. After activation, the first anodic cycle clearly shows two well-separated peaks which are probably related to stepwise oxidation of $C_{60}{}^{2-}$ centers in the film.

The voltammographic behavior of a C_{60}/Pd film that was formed in a acetonitrile/toluene (1:4 v/v) mixture with tetra(*n*-hexyl)ammonium perchlorate as supporting electrolyte was also examined. Figure 10 shows a comparison of the electrochemical behavior of this film with a film formed in the presence of tetra(*n*-butyl)-ammonium perchlorate. The data in Figure 10 were gathered with a simple acetonitrile solution with tetra(*n*-butyl)ammonium perchlorate as supporting electrolyte. The film formed in the presence of tetra(*n*-hexyl)-ammonium perchlorate is stable to the solvent and retains reversible electrochemical activity. The layer formed in the presence of tetra(*n*-hexyl)ammonium perchlorate exhibits higher charging and discharging currents than the layer produced in the presence of the smaller tetra(*n*-butyl)ammonium cations. Therefore, the conditions of film formation influence the morphology of the layer. The one produced in the presence of large tetra(*n*-hexyl)ammonium cations is likely to be more porous and better able to accept and discharge cations.

Effect of Switching Potential on the Film Stability. The C_{60}/Pd layer is destabilized at negative potentials. Figure 11 shows that the film grown in solutions containing tetra(*n*-butyl)ammonium perchlorate is stable and shows reversible electrochemical behavior with switching of the final cathodic potential at −1600, −1800, and −2000 mV as seen in traces a, b, and c, respectively. However, when the switching potential is −2200 mV as seen in trace d, the current decreases from one cycle to the next. This current diminution is accompanied by a visible loss of a black plume of material from the electrode surface.

The film formed in the presence of the larger tetra(*n*-hexyl)ammonium cations shows a more limited potential window of stability. Figure 12 indicates that the electroactive material is completely removed from the electrode surface when the switching potential is set at only −1500 mV. For the first three cycles the reduction potential of the layer is shifted toward more negative values, and the charge corresponding to the doping and undoping processes dramatically decreases. For the following cycles nearly only the background current of the gold electrode is recorded.

Conclusions

The results presented here show that the C_{60}/Pd films show remarkably reversible electrochemical charging and discharging in a variety of different solvents. These include several solvents that are capable of dissolving one of the two film components, the fullerene and the

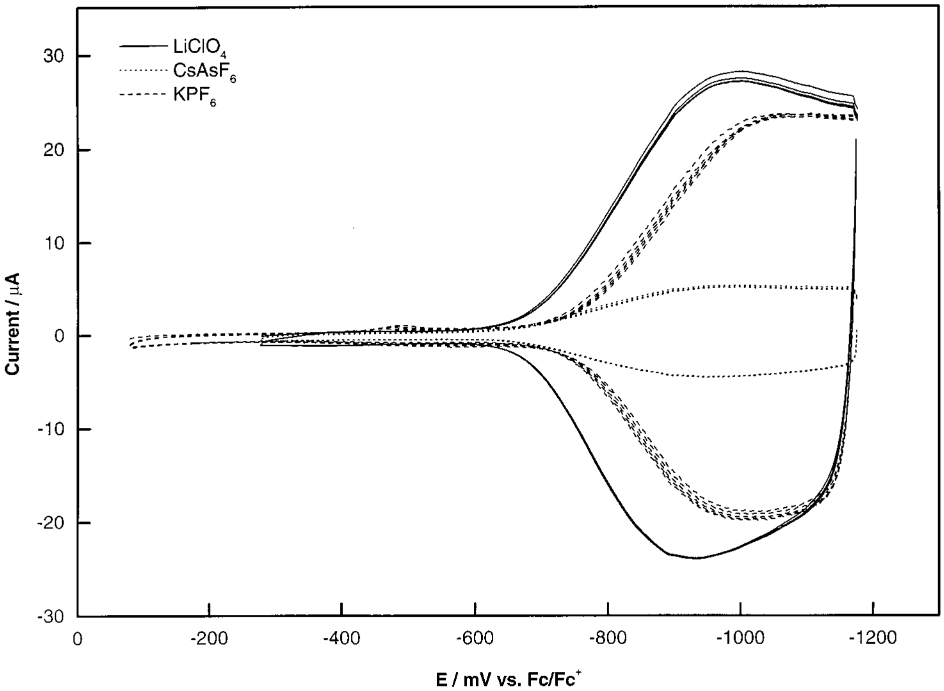

Figure 8. Multicyclic voltammograms of electrochemically generated C_{60}/Pd films obtained in acetonitrile containing (a) 0.1 M lithium perchlorate, (b) 0.1 M potassium hexafluorophosphate, and (c) 0.1 M cesium hexafluoroarsenate. Sweep rate was 100 mV/s.

palladium center. Nevertheless, the films retain their electrochemical activity on repeated cycling in all eight solvents used to generate Figures 1 and 2. The charging/discharging process shows a dependence on the size of the cation in the supporting electrolyte as seen in Figures 6, 8, and 9, but is relatively insensitive to the size and nature of the anion as noted in Figure 5. These observations coupled with the data shown in Figure 7, which relates the peak potential to the concentration of three supporting electrolytes, indicate that the doping of the film is best described by the incorporation of cations into the film as shown in eq 1. Consequently, the structure of the C_{60}/Pd film must be capable of accepting transport of these cations in and out of the film. It is likely that the electrochemically generated films have a more porous structure than the chemically prepared material, which is proposed to have extensive cross linking by palladium atoms.[18] The effect of the incorporation of cations into the film is also seen in the data in Figure 10, which shows that the size of the cation in the supporting electrolyte used to prepare the film has a notable effect on the subsequent redox characteristics of that film. Additionally, pretreating the films by polarization at negative potentials effects their subsequent redox activity as seen in Figure 3 and in trace b of Figure 9. This activation of the film appears to occur via slow migration of cations into the film during the initial polarization process.

As seen in Figures 11 and 12, the C_{60}/Pd films are not indefinitely stable to cycling through very negative potentials. The film grown in the presence of tetra(*n*-butyl)ammonium perchlorate undergoes disruption after the negative switching potential reaches −2200 mV. The film obtained from a solution containing tetra(*n*-hexyl)-ammonium perchlorate is less stable and is lost from the electrode when the switching potential reaches −1600 mV. The instability at negative potentials can

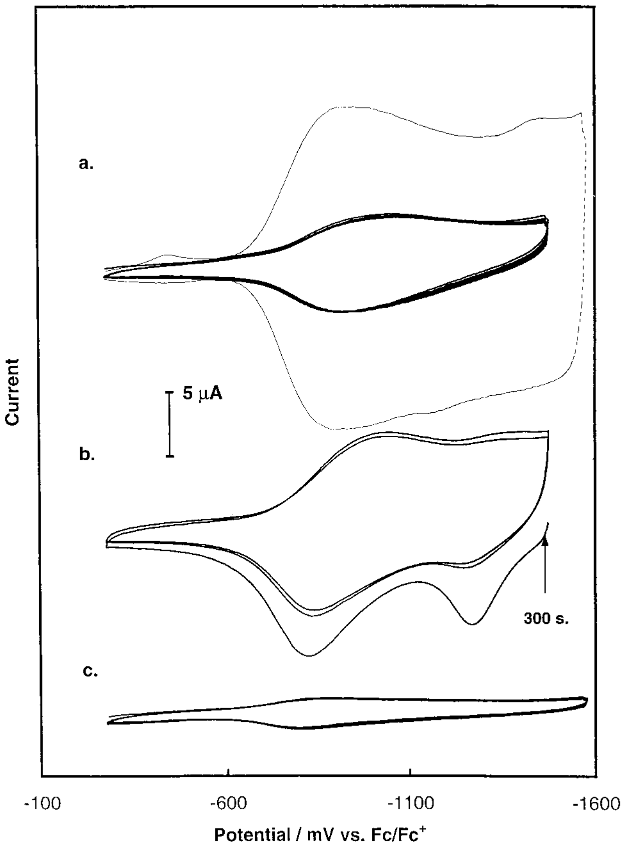

Figure 9. Multicyclic voltammograms of electrochemically generated C_{60}/Pd films obtained in acetonitrile containing: (a, b) 0.10 M tetraphenylarsonium chloride, and (c) 0.10 M bis-(triphenylphosphine)imminim chloride. Trace b was obtained for electrode activated at −1500 mV for 300 s. In trace a the voltammogram recorded in acetonitrile containing 0.10 M tetra(*n*-butyl)ammonium perchlorate is shown for comparison (broken line).

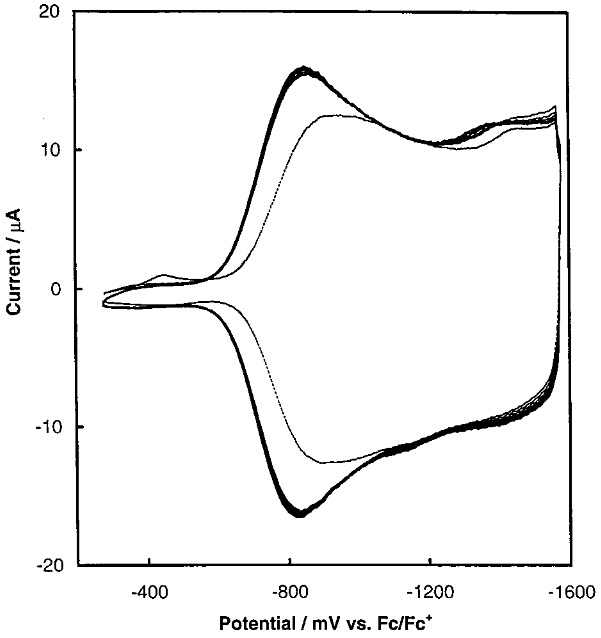

Figure 10. Multicyclic voltammograms of electrochemically generated C_{60}/Pd films obtained in acetonitrile containing 0.10 M tetra(*n*-butyl)ammonium perchlorate. The C_{60}/Pd films were grown under cyclic voltammetry conditions in acetonitrile/toluene mixture (1:1 v/v) containing 0.10 M tetra(*n*-butyl)ammonium perchlorate (broken line) or 0.10 M tetra(*n*-hexyl)ammonium perchlorate (solid line) as supporting electrolyte. Sweep rate was 100 mV/s.

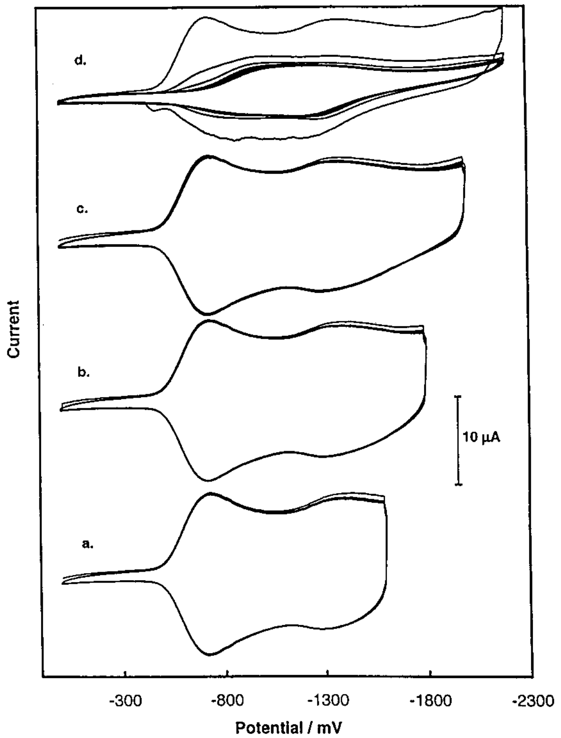

Figure 11. Multicyclic (10 cycles) voltammograms of electrochemically generated C_{60}/Pd films obtained in acetonitrile containing 0.10 M tetra(*n*-butyl)ammonium perchlorate as a function of the switching potential which is moved stepwise from 1600 to 2200 mV in traces a−d. The sweep rate was 100 mV/s.

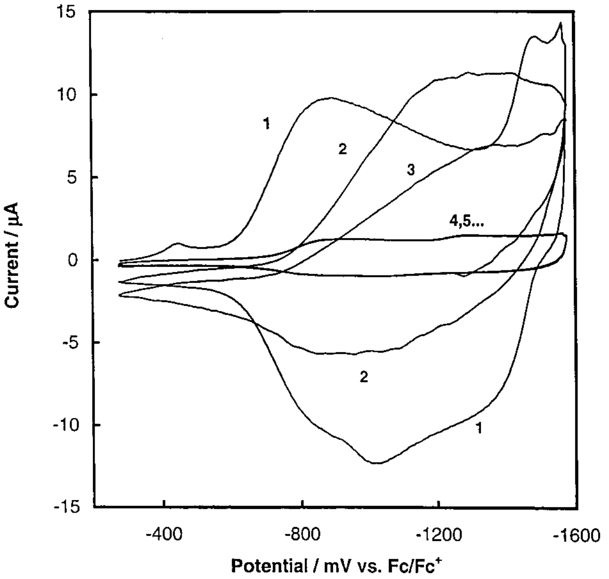

Figure 12. Multicyclic voltammograms of electrochemically generated C_{60}/Pd films obtained in acetonitrile containing 0.1 M tetra(*n*-butyl)ammonium perchlorate. The C_{60}/Pd films were grown under cyclic voltammetry conditions in acetonitrile/toluene mixture (1:4 v/v) containing 0.1 M tetra(*n*-hexyl)ammonium perchlorate as a supporting electrolyte. Sweep rate was 100 mV/s.

be attributed to several factors. The high degree of charging that occurs at these potentials requires significant incorporation of cations into the structure to balance the negative charge within the C_{60}/Pd portion of the film. Thus the structure of the film must swell to accommodate these ions. This swelling induces stress within the film. Additionally, the increasingly high negative charge on the C_{60}/Pd portion of the film increases the Coulombic repulsion in this part of the film. Finally, earlier electrochemical work on isolated, molecular transition metal complexes of C_{60} like $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ indicated that dissociation of the fullerene from the complex was facilitated by the stepwise reduction of the complex.[59] Thus reduction of the fullerene component to the formally di- and trianionic forms is expected to labilize the $(\eta^2\text{-}C_{60})Pd$ bonds in the film. Indeed, given the instability of $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ toward electrochemical reduction and the general observation that palladium complexes are more prone to ligand dissociation that are their platinum counterparts, it is surprising that the C_{60}/Pd films show the general stability that is seen in the results presented here.

Experimental Section

Materials. Palladium(II) acetate trimer (Alfa), C_{60} (Southern Chemical Group), tetra(ethyl)ammonium perchlorate, tetra(*n*-butyl)ammonium perchlorate, tetra(*n*-hexyl)ammonium perchlorate, tetra(phenyl)arsonium chloride, and bis(triphenylphosphine)imminium chloride (Sigma Chemical Co.) were obtained commercially and used as received. Lithium perchlorate and potassium hexafluorophosphate (Aldrich) were dried under reduced pressure at 90 °C for 24 h. Cesium hexafluoroarsenate was prepared by precipitation from an aqueous solution containing an equimolar mixture of nearly saturated CsBr (Aldrich) and $LiAsF_6$ (Aldrich). The $CsAsF_6$ was recrystallized from methanol and then dried under reduced pressure at 90 °C. Anhydrous solvents, acetonitrile (99.9%), acetone (99.9%), dichloromethane (99+%), dimethyl sulfoxide (99+%), propylene carbonate (99+%), *N*,*N*-dimeth-

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(59) Lerke, S. A.; Parkinson, B. A.; Evans, D. H.; Fagan, P. J. *J. Am. Chem. Soc.* **1992**, *114*, 7807.

ylformamide (99+%), benzonitrile (99.9%) and *o*-dichlorobenzene (99%) were used as received from Aldrich. Toluene (Aldrich Chemical Co.) was purified by distillation over sodium under argon atmosphere.

Instrumentation. Voltammetric experiments were performed on a BAS CV-50W Electroanalytical System with a three-electrode cell. Gold disks with a diameter of 1.5 mm (Bioanalytical Systems Inc.) were used as working electrodes. Prior to the experiment the electrodes were polished with fine carborundum paper and then with a 0.5 μm alumina slurry. Subsequently, 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 tetra(*n*-butyl)ammonium perchlorate 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. All potentials are reported with the potential of ferrocene/ferrocinium redox couple as the standard reference potential. The counter electrode was a platinum tab with an area of about 0.5 cm^2. All experiments were performed with 50−80% iR compensation.

Film Growth Procedure. Films were prepared through electroreduction of an acetonitrile/toluene (1:4 v/v) solution that contained both C_{60} (0.25 mM) and palladium(II) acetate trimer (0.60 mM) and the supporting electrolyte, which was either 0.10 M tetra(*n*-butyl)ammonium perchlorate or 0.10 M tetra(*n*-hexyl)ammonium perchlorate as described previously.[15] Films were grown by repeated cycling (uniformly 30 cycles in this work) through the potential range of −100 to −1150 mV. After the film was formed, the film-covered electrode was rinsed several times with a fresh acetonitrile/toluene (1:4 v/v) mixture and then placed in the chosen solvent and supporting electrolyte. The transfer of the electrodes from one solvent to another was accomplished in air without protection from normal atmospheric conditions. The electrodes were allowed to equilibrate for 10 min in the new solution before electrochemical measurements were conducted.

The infrared spectrum of the film taken from the electrode surface in a KBr pellet reveals the presence of fullerene absorptions at 1421, 1182, 580, and 522 cm^{-1} as well as bands at 2957, 2940, and 2870 cm^{-1}. The latter are due to tetra(*n*-butyl)ammonium ions entrapped in the film. A strong band at 1091 cm^{-1} is assigned to the polymeric fullerene framework.

The film has also been examined by xps spectroscopy. Photoelectrons detected at binding energies of 287.3 eV and of 339.3, 344.8, 535.5, and 563.6 eV are indicative of the presence of carbon and palladium, respectively, in the film.

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