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Formation of Redox-Active, Two-Component Films by Electrochemical Reduction of C_{60} and Transition Metal Complexes

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Abstract: Electrochemical reduction of C_{60} in 4:1 toluene/acetonitrile solution in the presence of $(PhCN)_2PdCl_2$, $Ir(CO)_2Cl$(*p*-toluidine), or $(CF_3CO_2)_4Rh_2$ produces three different, redox-active, black films that coat the electrode. These films are insoluble in common organic solvents and adhere strongly to the electrode surface. Film formation has been monitored by multiscan cyclic voltammetry, which gives information about the requirements for film growth. The three different films (on the original electrodes) can be transferred to a solution of acetonitrile that contains only the supporting electrolyte, tetra(*n*-butyl)ammonium perchlorate, where the films retain their redox activity. Each film displays a significant decrease in resistivity (*i.e.* a window of conductivity) in the potential region in which it is grown and in which it displays redox activity. The films have been examined by scanning electron microscopy, which shows variations in the nature of the three films' morphologies with the film formed from $(PhCN)_2PdCl_2$ displaying the greatest uniformity and smoothest surface. Analysis of the films by infrared spectroscopy and laser desorption mass spectrometry reveals that intact C_{60} units are present within each film. Treatment of the palladium/C_{60} film with triphenylphosphine results in film dissolution and the formation of the previously characterized complex, $(\eta^2\text{-}C_{60})Pd(PPh_3)_2$. The rhodium/$C_{60}$ film dissolves in pyridine and $^{19}F\{^1H\}$ NMR spectroscopy reveals that $(CF_3CO_2)_4Rh_2$ is extracted intact from the film. The structure of the films is discussed in terms of covalent bonding between the fullerenes and the metal atoms or complexes within the film.

Introduction

Although the process of fullerene polymerization has proven to be challenging, significant progress has also been made in the polymerization of fullerenes through high pressure,[1] photochemical,[2] and chemical[3] methods. Fullerenes have also been chemically modified to facilitate the formation of charm bracelet polymers.[4] Recently, this laboratory has shown that redox active, fullerene-based films, which are believed to be polymers based on their insolubility in common solvents, can be formed by the electrochemical reduction of either the fullerene epoxide, $C_{60}O$,[5,6] or of a mixture of C_{60} and dioxygen[7] in toluene/acetonitrile solution. These films appear to be related to the conducting polymers such as polyaniline, polypyrrole, and polythiophene, that are generally obtained by oxidation of corresponding monomers.[8] The film produced by electroreduction of $C_{60}O$ has been shown to have the ability to store up to eight electrons per fullerene unit, and thus has potential as a component in an energy storage battery.[9] 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. The electrochemistry of C_{60}, both in solution and as thin films on electrodes, has received considerable study.[10] Six reversible, one-electron reduction waves are seen in solution. These processes involve filling of the triply degenerate LUMO of C_{60}. Additionally, a reversible, one-electron oxidation is observed at relatively high potential.

Our initial work began with the development of an electrochemical procedure for the formation of the previously known polymer, $C_{60}Pd_n$, where *n* can range from 1 to 7.[11,12] This black material has been prepared in amorphous form by the chemical reaction between C_{60} and a palladium(0) complex such as tris(dibenzylideneacetone)dipalladium(0). The $C_{60}Pd_n$ polymer, which is a heterogeneous catalyst for hydrogenation reactions,[13] is insoluble in common organic solvents but dissolves in the

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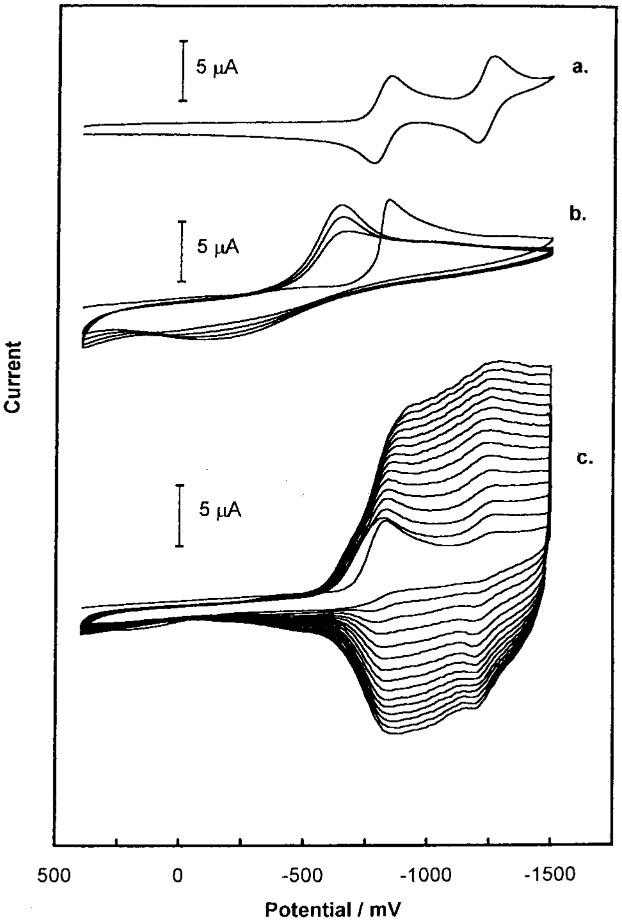

Figure 1. Cyclic voltammograms obtained for (a) 0.65 mM C_{60}, (b) 0.5 mM $(PhCN)_2PdCl_2$, and (c) 0.3 mM C_{60} and 0.5 mM $(PhCN)_2PdCl_2$ at a gold electrode in an acetonitrile−toluene mixture (1:4) containing 0.1 M tetra(*n*-butyl)ammonium perchlorate. Sweep rate was 100 mV/s.

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.[14−16] The structure of polymeric $C_{60}Pd_n$ is believed to consist of linear chains made up of $\cdots C_{60}Pd(C_{60}Pd)_nC_{60}Pd\cdots$ units that are cross linked through $C_{60}PdC_{60}$ units to create a three-dimensional grid. Evidence has been reported to suggest that $C_{60}Pd_6$ subunits with a local octahedral structure are present within the polymer.[12] Since $(\eta^2\text{-}C_{60})Pd(PPh_3)_2$ can be extracted from the polymer by treatment with triphenylphosphine, it is likely that the palladium atoms are η^2-bonded to the fullerene in $C_{60}Pd_n$ itself.

Results

Formation of Film from a Solution of $(PhCN)_2PdCl_2$ and C_{60}. Figure 1 shows representative electrochemical data for the formation of a film from a solution of $(PhCN)_2PdCl_2$ and C_{60}. Trace a shows the cyclic voltammogram of a solution of C_{60} alone in toluene/acetonitrile (4/1 v/v) at a gold electrode. In this potential range the first two reversible, one-electron reductions of C_{60} are seen. Trace b shows the electrochemical behavior of $(PhCN)_2PdCl_2$ under similar conditions. Note that in the initial scan the reductive peak occurs at nearly the same potentials as that for the first reduction of C_{60}, and that on successive scans, the reduction peak moves to a more positive value. Examination of the electrode after reduction of $(PhCN)_2PdCl_2$ reveals the presence of a dark film of palladium metal on the surface. Trace c shows the multiscan cyclic voltammograms of a solution of 0.3 mM C_{60} and 0.5 mM $(PhCN)_2PdCl_2$. The steady increase in current with increasing cycling is indicative of the deposition of a redox active film and indeed visual observation of the electrode surface after electrolysis reveals the presence of a black coating on the electrode. Formation of this black film inhibits the electrodeposition of metallic palladium as shown by the absence of the low potential peak at −700 mV which is seen in trace b.

Scheme 1

$$C_{60} + e^- \longrightarrow [C_{60}]^-$$

$$[C_{60}]^- + (PhCN)_2Pd^{II}Cl_2 \longrightarrow (PhCN)_2Pd^{II}Cl(C_{60}^-) + Cl^-$$

$$(PhCN)_2Pd^{II}Cl(C_{60}^-) + [C_{60}]^- \longrightarrow Pd^{II}(C_{60}^-)_2 + 2\ PhCN + Cl^-$$

$$Pd^{II}(C_{60}^-)_2 \quad = \quad Pd^0(C_{60}^0)_2$$

$$n\ Pd(C_{60})_2 \longrightarrow Pd_n(C_{60}) + 2n\ \text{-}1\ C_{60}$$

Film formation can proceed via the steps shown in Scheme 1. The initial electrochemical step is reduction of C_{60} to $[C_{60}]^-$. The $[C_{60}]^-$ anion that is produced can then replace the chloride ions on the palladium complex. It is important to realize that the product, $Pd^{II}(C_{60}^-)_2$, is equivalent to $Pd^0(C_{60}^\circ)_2$, and that the fullerene/metal complexes can be formulated with a variety of assignments of ligand and metal oxidation states. Once $Pd^0(C_{60}^\circ)_2$ is formed it can go on to deposit the insoluble film. This scheme suggests that electropolymerization should proceed at any potential sufficient to generate $[C_{60}]^-$. Thus, it should not be necessary to have the switching potential reach −1500 mV as it does in trace c of Figure 1, and indeed reducing the switching potential to −800 mV still allows electroreductive film formation to occur.

The electrode coated with the black film retains its redox activity when it is transferred to a solution of acetonitrile that contains only the supporting electrolyte, 0.10 M tetra(*n*-butyl)ammonium perchlorate. Relevant data are shown in trace a of Figure 2.

The $C_{60}Pd_n$ film has been deposited across an interdigitated microelectrode array. Figure 3 shows that the resistance of the $C_{60}Pd_n$ film drops by over 4 orders of magnitude in the potential range used for the electrodeposition. This behavior is analogous with the discrete windows of conductivity found for conducting polymers.[17]

The black film, which is insoluble in common organic solvents and in water, has been examined by spectroscopic and chemical means. Analysis of the film (on the electrode after removal from solution and washing with acetonitrile and methanol) by energy-dispersive X-ray spectroscopy reveals that carbon and palladium occur in similar regions of the deposit while chlorine is absent.

The film has been examined by scanning electron microscopy (SEM). Parts a and b of Figure 4 show SEM images of the

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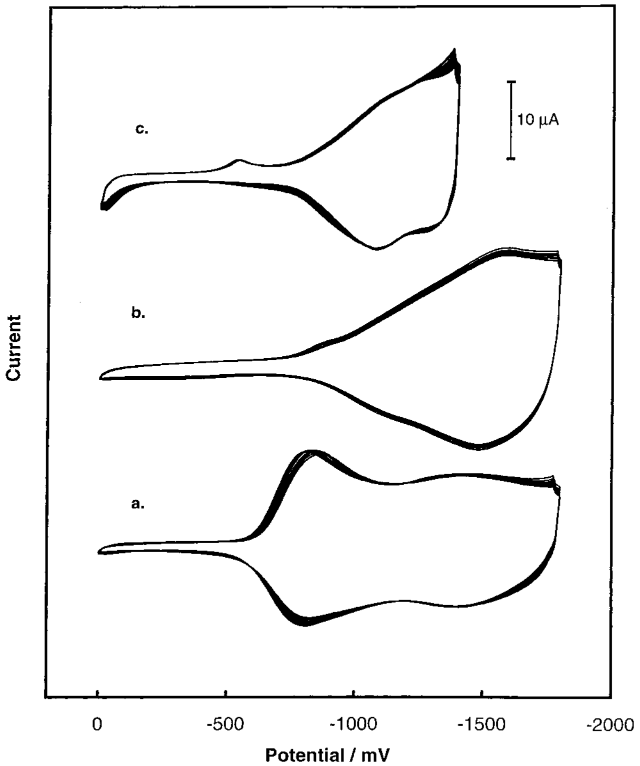

Figure 2. Multicyclic voltammograms of electropolymerized films from (a) $(PhCN)_2PdCl_2/C_{60}$, (b) $Ir^I(CO)_2Cl$(*p*-toluidine)/C_{60}, and (c) $(CF_3CO_2)_4Rh_2/C_{60}$ obtained in acetonitrile containing 0.1 M tetra(*n*-butyl)ammonium perchlorate with no electroactive solute. Fifteen cycles are shown in each case.

$C_{60}Pd_n$ film grown on a platinum electrode. Part a shows a cross section of the film with the platinum electrode at the bottom, while part b shows a view perpendicular to the electrode surface. As seen in part a, the film grows to a uniform thickness of 30 μm. As the view onto the surface in part b shows, the film is relatively flat with a few outcroppings.

The infrared spectrum of the black deposit taken 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} that are due to tetra(*n*-butyl)ammonium ions that are entrapped in the polymer. A strong band at 1091 cm^{-1} is due to the polymeric fullerene framework, since similar features are seen in the other electrolytically produced fullerene films.

The black deposit of $C_{60}Pd_n$ can be removed from the electrode surface by treatment with a dichloromethane solution of triphenylphosphine. As the deposit dissolves, the solution becomes green. Analysis of the solution by $^{31}P\{^1H\}$ NMR spectroscopy reveals a strong resonance at 25.5 ppm, which is indicative of the formation of $(\eta^2\text{-}C_{60})Pd(PPh_3)_2$, a green compound of known structure.[13] These data suggest that the electrode deposit consists of a polymeric material with C_{60} units bonded to palladium atoms in an η^2-fashion. Each palladium atom coordinates to two C_{60} units as in the model described by Nagashima for chemically prepared $C_{60}Pd_n$.[11]

Formation of Film from a Solution of $Ir(CO)_2Cl$(*p*-toluidine) and C_{60}. This electrochemical procedure has been extended to form new materials. The following example demonstrates that the transition metal component need not be reducible electrochemically for polymerization to occur. Figure 5 shows cyclic voltammograms for the $Ir(CO)_2Cl$(*p*-toluidine)/C_{60} system. Trace a shows that $Ir(CO)_2Cl$(*p*-toluidine) is redox inactive in the region where the first two reductions of C_{60} occur. In contrast when C_{60} and $Ir(CO)_2Cl$(*p*-toluidine) are present in solution during electrolysis, film growth occurs as shown in trace b of Figure 3. Again a black film can be observed on the electrode surface after electrolysis and that film is not soluble in common organic solvents.

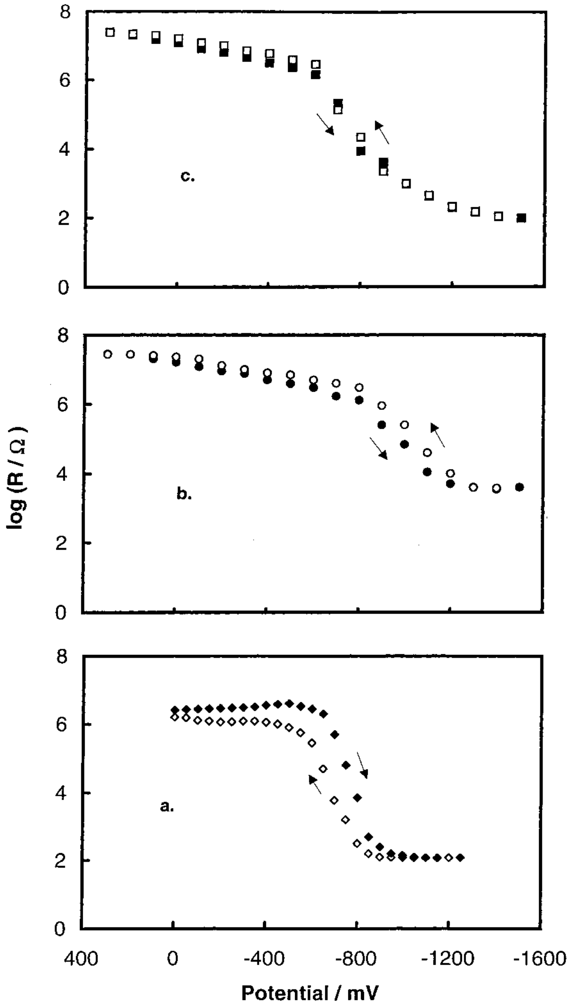

Figure 3. The dependence of the steady-state resistance of electropolymerized films from (a) $(PhCN)_2PdCl_2/C_{60}$, (b) $Ir^I(CO)_2Cl$(*p*-toluidine)/C_{60}, and (c) $(CF_3CO_2)_4Rh_2/C_{60}$ on the potential. The data were obtained with platinum interdigitated microelectrode arrays in acetonitrile/toluene (1:4) containing 0.1 M tetra(*n*-butyl)ammonium perchlorate. Array fingers were ~1 cm long, 5 μm high, and separated from each other by 5 μm.

The infrared spectrum of the film reveals very strong bands at 2035 and 1970 cm^{-1} that are due to ligating carbon monoxide. Thus, a *cis*-$Ir(CO)_2$ unit is present in the film. Infrared bands at 1446, 1423, 1158, 581, and 524 cm^{-1} are indicative of the presence of C_{60} moieties in the film. The infrared spectrum also shows bands at 2950, 2925, and 2870 cm^{-1} that are consistent with the presence of tetra(*n*-butyl)ammonium ions within the film and bands at 3456 and 1642 cm^{-1} that are assigned to water. Strong broad bands at 1084 and 1020 cm^{-1} are also present. Previous studies of fullerene films prepared from $C_{60}O$ or from C_{60} plus dioxygen have revealed infrared bands due to the adsorption of moisture from the environment and strong bands in the 1000−1100 cm^{-1} region which appear to be characteristic of the film.[5−7]

Trace b of Figure 2 shows the multiscan cyclic voltammetry of the $C_{60}\{Ir(CO)_2\}_n$ film after transfer of the coated electrode into a solution of 0.10 M tetra(*n*-butyl)ammonium perchlorate in acetonitrile. The film retains its redox activity throughout 15 cycles of reduction and oxidation. This behavior is analogous

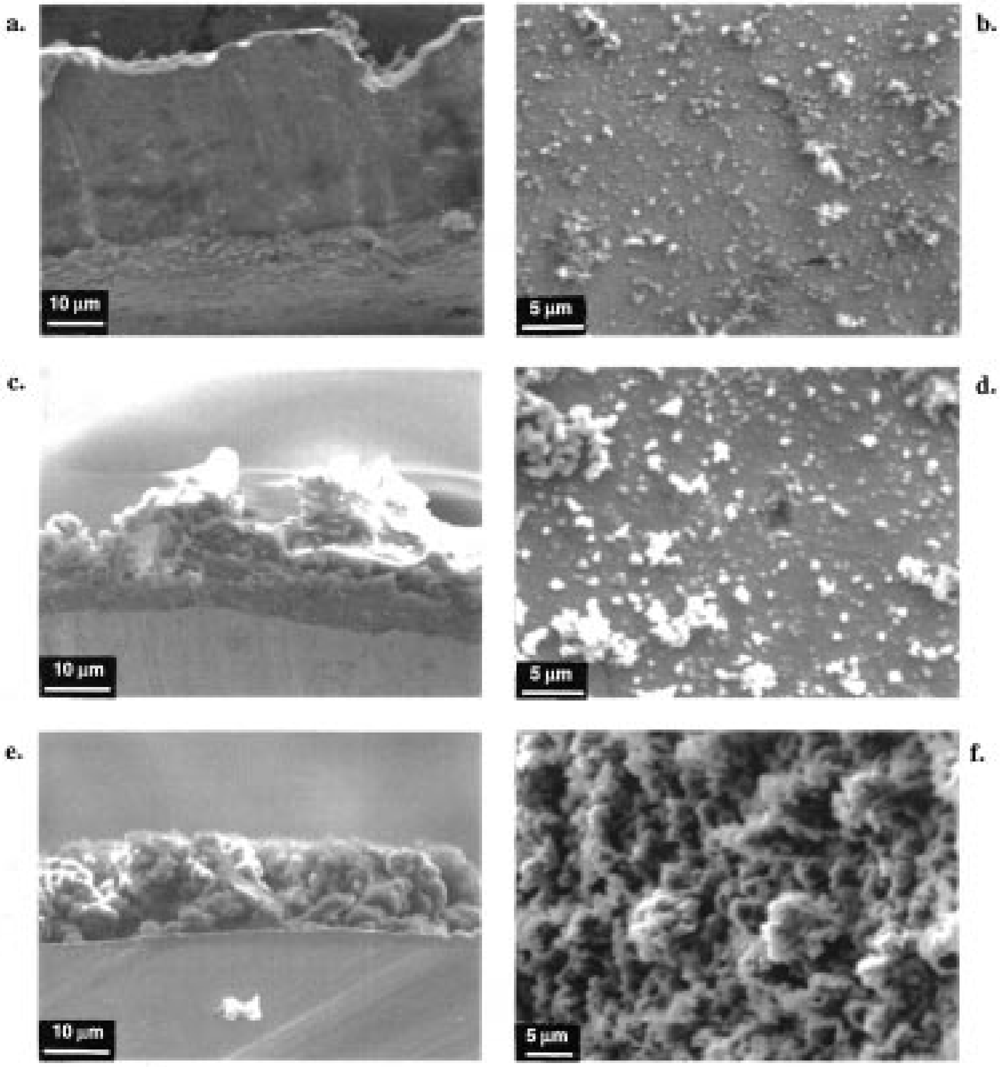

Figure 4. Scanning electron microscopic images of electropolymerized films from (a and b) $(PhCN)_2PdCl_2/C_{60}$; (c and d) $Ir^I(CO)_2Cl$(*p*-toluidine)/C_{60}, and (d and e) $(CF_3CO_2)_4Rh_2/C_{60}$. Views a, c, and e are cross sections of the film on the electrode with the platinum electrode at the bottom, while views b, d, and f look down on the surface of the film.

to that seen with the $C_{60}Pd_n$ film, but there are distinct differences in the cyclic voltammograms that are observed.

Trace b of Figure 3 shows that the resistance of the $C_{60}\{Ir(CO)_2\}_n$ film drops significantly in the potential range used for the electrodeposition.

Parts c and d of Figure 4 show SEM images of the $C_{60}\{Ir(CO)_2\}_n$ film grown on a platinum electrode. Part c shows a cross section of the film with the platinum electrode at the bottom, while part d shows a view perpendicular to the electrode surface. Comparison of these images with those in parts a and b of Figure 4 reveals that the $C_{60}\{Ir(CO)_2\}_n$ film is less uniform and that its surface is more uneven than the $C_{60}Pd_n$ film. Examination of the film by energy-dispersive X-ray analysis indicates that iridium is present in the film but that chlorine is not.

Electrochemical and spectroscopic studies reveal that reduction beyond that necessary to form $[C_{60}]^-$ is required to form the film. Trace c of Figure 5 shows that when the multiscan cyclic voltammetry is switched at −900 mV so that only the first C_{60} reduction process is involved, no film deposition occurs. Additionally, reaction of chemically generated $[C_{60}]^-$ with $Ir(CO)_2Cl$(*p*-toluidine) does not result in film deposition, rather a soluble species with ν(CO) at 2050 and 2030 cm^{-1} is formed. The characteristic low-energy absorptions at 910 and 1080 nm of $[C_{60}]^-$ are lost in this reaction, and we postulate that $[C_{60}]^-$ displaces chloride ion from the iridium complex to yield $Ir(CO)_2(\eta^2\text{-}C_{60}^-)$(*p*-toluidine), which remains in solution. Further reduction of this soluble species in the presence of C_{60} generates the film.

Laser desorption mass spectrometry in the negative ion mode of the film reveals a strong peak at 720 amu which indicates that C_{60} molecules are present in the film.

Formation of Film from a Solution of $(CF_3CO_2)_4Rh_2$ and C_{60}. Figure 6 shows cyclic voltammograms for the $(CF_3CO_2)_4Rh_2/C_{60}$ system. Trace a shows that $(CF_3CO_2)_4Rh_2$, like $Ir(CO)_2Cl$(*p*-toluidine), is redox inactive in the region where the first two reductions of C_{60} occur. However, when $(CF_3CO_2)_4Rh_2$ and C_{60} are both present in solution during electrolysis, film growth occurs as shown in trace b of Figure 6. Again a black film can be observed on the electrode surface after electrolysis. The film is not soluble in acetonitrile, toluene, or dichloromethane. Unlike the case with the $Ir(CO)_2Cl$(*p*-toluidine)/C_{60} system, it is not necessary to have the electrode potential reach that necessary for reduction of C_{60} to $[C_{60}]^{2-}$ before film formation occurs. Film growth also occurs when the switching potential is reduced to 900 mV and only the first one-electron reduction of C_{60} is scanned. Film growth is inhibited when pyridine, which is known to coordinate to the two axial sites in

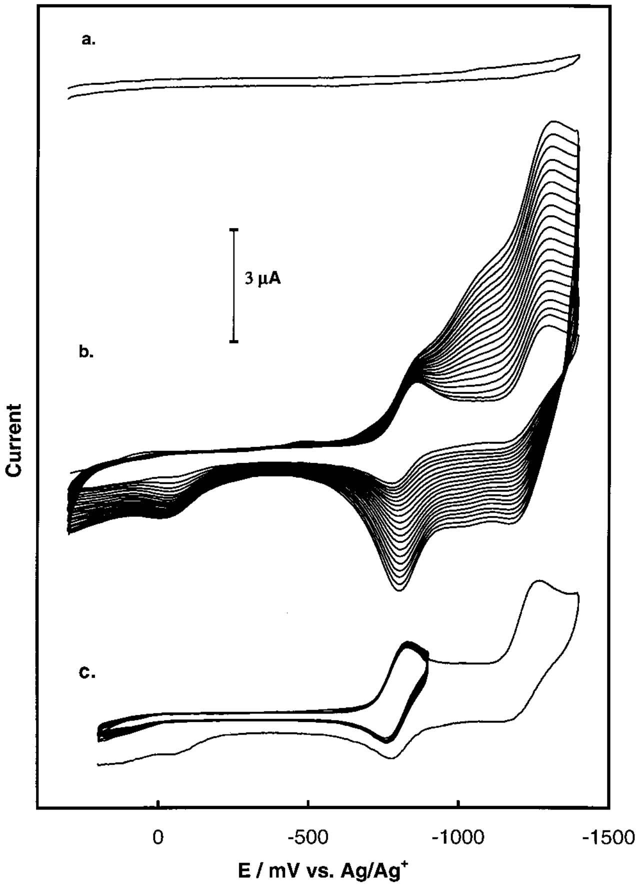

Figure 5. (a) Cyclic voltammogram obtained for 0.9 mM $Ir^I(CO)_2Cl$(*p*-toluidine) over the potential region from +250 to −1400 mV. (b) Multicyclic voltammograms (20 cycles) for 0.25 mM C_{60} + 0.85 mM $Ir^I(CO)_2Cl$(*p*-toluidine) in the potential region from +250 to −1400 mV. (c) Multicyclic voltammograms (45 cycles) for 0.25 mM C_{60} + 0.85 mM $Ir^I(CO)_2Cl$(*p*-toluidine) in the potential region from +250 to −900 mV, but on the 46th cycle the switching potential was altered to −1400 mV to include the second reduction of C_{60}. Data were gathered at a gold electrode in acetonitrile/toluene mixture (4:1) containing 0.1 M tetra(*n*-butyl)ammonium perchlorate. The sweep rate was 100 mV/s.

$(CF_3CO_2)_4Rh_2$,[18] is present during the electrolysis as shown in trace c of Figure 6. Only the first two reversible reduction waves of C_{60} are observed in the potential window utilized.

The infrared spectrum of the $C_{60}\{(CF_3CO_2)_4Rh_2\}_n$ film reveals bands at 1658, 1632, 1562, 1454, 1150, 733, and 701 cm^{-1} that are due to $(CF_3CO_2)_4Rh_2$ units in the film. (The infrared spectrum of $(CF_3CO_2)_4Rh_2$ itself contains strong, broad bands at 1661, 1640, 1458, 1198, 1160, 762, and 695 cm^{-1}.) Absorptions at 1454, 1419, 1160, 582, and 525 cm^{-1} are indicative of the presence of fullerene cages within the polymer. The infrared spectrum also shows bands at 2956, 2924, and 2868 cm^{-1} that are consistent with the presence of tetra(*n*-butyl)ammonium ions within the film as well as a weak feature at 3440 cm^{-1} that is due to adsorbed water.

Trace c of Figure 2 shows the multiscan cyclic voltammetry of the $C_{60}\{(CF_3CO_2)_4Rh_2\}_n$ film after transfer of the coated electrode into a solution of 0.10 M tetra(*n*-butyl)ammonium perchlorate in acetonitrile. The film retains its redox activity throughout 15 cycles of reduction and oxidation.

Trace c of Figure 3 shows that the resistance of the $C_{60}\{(CF_3CO_2)_4Rh_2\}_n$ film drops significantly in the potential range used for the electro-deposition.

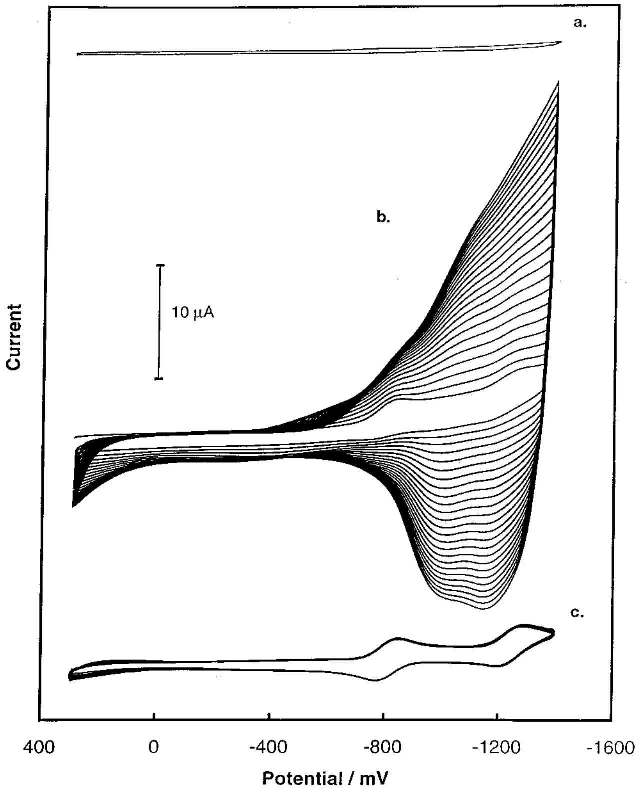

Figure 6. (a) Cyclic voltammogram obtained for 0.9 mM $(CF_3CO_2)_4Rh_2$. (b) Multicyclic voltammograms (24 cycles) for 0.25 mM C_{60} and 0.85 mM $(CF_3CO_2)_4Rh_2$. (c) Multicyclic voltammograms (20 cycles) for 0.25 mM C_{60}, 0.85 mM $(CF_3CO_2)_4Rh_2$, and 60 mM pyridine. Data were gathered at a gold electrode in acetonitrile/toluene mixture (4:1) containing 0.1 M tetra(*n*-butyl)ammonium perchlorate. The sweep rate was 100 mV/s.

Parts e and f of Figure 4 show SEM images of the $C_{60}\{(CF_3CO_2)_4Rh_2\}_n$ film grown on a platinum electrode. Part e shows a cross section of the film with the platinum electrode at the bottom, while part f shows a view perpendicular to the electrode surface. Comparison of these images with those of the $C_{60}Pd_n$ and $C_{60}\{Ir(CO)_2\}_n$ films shows that the $C_{60}\{(CF_3CO_2)_4Rh_2\}_n$ film is considerably rougher and less uniform than the other two films.

The $C_{60}\{(CF_3CO_2)_4Rh_2\}_n$ film dissolves partially in pyridine. The $^{19}F\{^1H\}$ NMR spectrum of the resulting solution reveals the presence of a single resonance at −73 ppm (relative to $CFCl_3$), which is consistent with the presence of $(CF_3CO_2)_4Rh_2$ in the extracted solution, since $(CF_3CO_2)_4Rh_2$ in pyridine solution also shows a ^{19}F resonance at −73 ppm.

Laser desorption mass spectrometry in the negative ion mode of the film reveals a strong peak at 720 amu which confirms that C_{60} moieties are present in the film.

Discussion

Three new electroactive films have been prepared by electroreduction of mixtures of C_{60} with $(PhCN)_2PdCl_2$, $Ir(CO)_2Cl$(*p*-toluidine), or $(CF_3CO_2)_4Rh_2$ in toluene/acetonitrile solution. This method differs from most methods of electropolymerization in that two different components are utilized in the processes described here. The films that are produced adhere to the electrode surface and are generally quite robust. As shown in Figure 2, all three films can be transferred in air to a solution that contains only supporting electrolyte, and each film retains its distinctive electrochemical activity in that solution.

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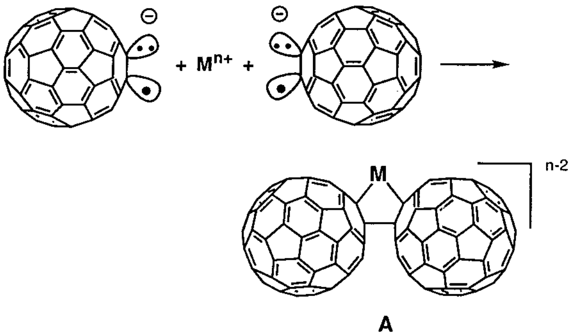
The films undergo marked drop in their resistivities in the potential region in which they are grown as shown in Figure 3. Such a drop in resistivity is consistent with the presence of a window of conductivity, which is a characteristic of a number of conducting polymers such as polypyrrole and polythiophene. In such conventional redox polymers, the charge transport occurs via self-exchange from one redox site to another.[19,20] The redox layer is conductive when both oxidized and reduced sites are present. Therefore, for redox-active polymers the potential dependence of resistance very often shows a peak with the maximum corresponding to the situation where there are equal concentrations of oxidized and reduced sites in the layer.[17,21] For the C_{60} polymeric layers studied in this paper, the resistance reaches almost a constant value at negative potentials. This behavior can be related to the different redox states of each C_{60} moiety within the network present in the film. The overlapping of energy bands corresponding to different fullerene redox states may be responsible for the fact that no decreases in resistance of the films are observed at negative potentials.

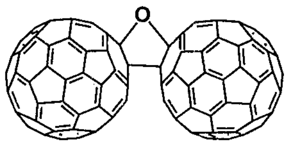
The films are generally insoluble in common organic solvents, and this insolubility is suggestive of the presence of a polymeric network within the film. However, by treatment with suitable ligands it is possible to extract components from the films. Thus treatment of $C_{60}Pd_n$ with triphenylphosphine produces $(\eta^2\text{-}C_{60})Pd(PPh_3)_2$, and it is thus likely that $(\eta^2\text{-}C_{60})Pd$ units are present in the film. Similarly, dissolution of the $C_{60}\{(CF_3CO_2)_4Rh_2\}_n$ film in pyridine extracts $(CF_3CO_2)_4Rh_2$ intact from the solid, and consequently $(CF_3CO_2)_4Rh_2$ units are present in the film.

The available evidence indicates that the films have polymeric structures that consist of a covalent network composed of intact fullerene cages and metal atoms or complexes. The model devised by Nakashima and co-workers[11] for $C_{60}Pd_n$ seems appropriate for the film created by electroreduction of C_{60} and $(PhCN)_2PdCl_2$. The film obtained from $Ir(CO)_2Cl$(*p*-toluidine) and C_{60} may have a similar structure with $Ir(CO)_2$ units, rather than simple palladium atoms, that bridge two fullerene cages. Similarly, the film made from $(CF_3CO_2)_4Rh_2$ and C_{60} may contain linear chains made up of alternating C_{60} and $(CF_3CO_2)_4Rh_2$ units with the fullerene component axially coordinated in η^2-fashion to the rhodium dimer. The presence of tetra(*n*-butyl)ammonium ions in these films suggests that some of the fullerene units within the films are present as fulleride ions. Such a possibility is especially likely since the films are deposited under reducing conditions at potentials where fulleride ions are present. An additional possibility for a structural component of the films is the metal-bridged difullerene unit **A** shown in eq 1. It is well established that fulleride ions undergo polymerization with carbon−carbon bond formation in solids such as KC_{60}.[22,23] As shown in eq 1, addition of two fulleride monoanions to a metal center could create the bridging unit **A**. Alternatively, such a unit could also be formed from a combination of M^{n+}, neutral C_{60}, and $[C_{60}]^{2-}$. The structural unit **A** would be expected to retain the electrochemical activity found in fullerenes, just as the similarly constructed $C_{120}O$, structure **B**, does.[24] Further efforts are underway to synthesize molecules that contain the unit **A** or to extract such units from electrochemically generated films.



(1)

A



B

Prior coordination of the fullerene to metal complexes used in the film-forming reactions described here does not appear to be necessary. Efforts to form a palladium complex with C_{60} from reaction of $(PhCN)_2PdCl_2$ and C_{60} in benzene yielded crystalline $Pd_6Cl_{12}\cdot 0.5C_{60}\cdot 1.5C_6H_6$ in which the three components are cocrystallized without any covalent bonding between them.[25] Additionally, no reaction has been observed between C_{60} and either $Ir(CO)_2Cl$(*p*-toluidine) or $(CF_3CO_2)_4Rh_2$ when these are mixed in a suitable solvent.

The films described here have considerable potential in a number of applications. The ability of the fullerene moiety to undergo multiple redox reactions makes any fullerene containing material a potential battery material. The ability to utilize a range of different transition metal precursors for film formation suggests that the film characteristics including electrical conductivity, voltammetric behavior, magnetism, and chemical reactivity can be altered over a wide range. In the cases described here the metal component can be a simple metal atom, as is the case with the $C_{60}Pd_n$ film, a metal center with other ligands appended, as is the case with the $C_{60}\{Ir(CO)_2\}_n$ film, or a polynuclear metal complex, as is the case with the $C_{60}\{(CF_3CO_2)_4Rh_2\}_n$ film. The metal centers in these films may also have the ability to react with added ligands. Such reactions can be expected to alter the electrochemical characteristics of these films and may result in the development of new sensors of ligating species.

Other transition metal complexes including substitutionally inert $RhCl_3(pyridine)_3$ and *cis*-$Pt(pyridine)_2Cl_2$ also produce films that adhere to electrode surface upon electroreduction in the presence of C_{60}. The structures and physical, chemical, and catalytic properties of this family of electrochemically produced films are under investigation. This electrochemical synthesis of redox active films from two distinctly different monomers represents a significant new approach to polymer generation. The ability to incorporate a variety of different metals and accompanying ligands into these films and the likelihood that the metal ligation within the films can be altered after the films synthesis suggest that the properties of these films can be readily manipulated by chemical means.

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Experimental Section

The film precursors, $(PhCN)_2PdCl_2$[26] and $Ir(CO)_2Cl$(*p*-toluidine),[27] were prepared by standard routes, while $(CF_3CO_2)_4Rh_2$ was purchased from Alfa. The C_{60} was purchased from MER Corp., Tucson, AZ, and used without additional purification. Tetra(*n*-butyl)ammonium perchlorate (TBAP) (Sigma Chemical Co.) was dried under reduced pressure at 70 °C for 24 h. Acetonitrile (99.8%) was used as received from Aldrich. Toluene (Aldrich Chemical Co.) was purified by distillation over sodium under argon atmosphere.

Voltammetry. Voltammetric experiments were performed on a BAS CV50-W Electroanalytical System with a three-electrode cell. The working electrode was a gold wire (Bioanalytical System Inc.) with a diameter of 1.5 mm. Prior to the experiment, the electrode was polished with a fine carborundum paper and then with a 0.5 μm alumina slurry. Next the electrode was sonicated in water to remove the traces of alumina from the gold surface, washed with water, and dried. A silver wire that was 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 System Inc.) served as the reference electrode. With this solvent system and reference electrode, the ferrocene/ferrocinium redox potential was +161 mV. All potentials are expressed with respect to this electrode. The counter electrode was a platinum tab with an area of $\sim$0.5 cm^2.

Film Growth. Film growth can be achieved under multicyclic scans similar to those shown in Figures 1, 5, and 6 or under potentiostatic conditions at suitably negative potentials. All films used in this work were generated under multicyclic scans.

Microscopy. Scanning electron micrograph images were obtained with the use of an ISI (Topcon) DS 130 microscope with a LaB_6 crystal filament cathode. The accelerating voltage of the electron beam was 10 kV.

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 gold array fingers which are about 1 cm long and 5 μm high. Individual fingers are separated from each other by 5 μm. Prior to use, interdigitated microelectrodes were tested with an ohmmeter to make sure that there was no short circuit between two sets of fingers. The appropriate film was deposited on the microelectrode array under multicyclic scans in the potential range from 0 to −1200 mV for the $C_{60}Pd_n$ film or from 0 to −1400 mV for $C_{60}\{Ir(CO)_2\}_n$ and $C_{60}\{(CF_3CO_2)_4Rh_2\}_n$ films. 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 a connection between them, voltammograms were recorded for set A and set B of fingers driven alone or together. Identical $i-E$ responses for both cases indicated that the fingers were connected by the film. For measurements of the change in resistance with potential, a triode-type device circuit was used.[28] 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 (ΔE_2) was applied between the A and B set 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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