

Stability studies of an electrochemically formed [C₆₀] fullerene-palladium two-component film

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Abstract The stability of C₆₀ and palladium two-component films, C₆₀/Pd, has been investigated. The effect of different polymerization conditions on the electrochemical stability of the film upon prolonged potential cycling has been studied. Stable voltammetric behavior was observed for polymers formed at potentials less negative than the potential of third C₆₀ reduction step. The incorporation of palladium particles into the structure of C₆₀/Pd polymers increases the polymer stability. The C₆₀/Pd films are doped with supporting electrolyte cations during reduction. The size of these cations is a crucial factor in determining the stability of the film. A strong solvent effect on the potential stability of the film was also observed. The widest range of stable voltammetric properties was found for acetonitrile and *N,N*-dimethylformamide. No effect of the temperature on the film stability was observed. The results reported in this work allow for the determination of the optimal conditions for the formation of stable C₆₀/Pd films.

Keywords Fullerenes · Fullerene polymer films · Electropolymerization · Polymer stability

Introduction

Since the first electrosynthesis of polypyrrole [1], a lot of attention has been paid to the synthesis of electroactive polymers and investigation of their properties. The potential applications of conducting polymers have given rise to

considerable research efforts in developing new materials for electronics, optics, and energy conversion. The possibility of reversible switching of conducting polymers between two redox states makes them particularly suitable for rechargeable batteries [2]. In the first prototypes of commercial batteries with conductive polymers, Li/polypyrrole and Li/polyaniline systems were used [3]. The application of polythiophene and their derivatives in rechargeable batteries was also investigated [4–7].

The main requirements for a useful electroactive polymer are (1) high ambient conductivity, (2) good electrochemical stability, (3) mechanical strength and processability, (4) fast current response to potential changes, and (5) high capacitance. Polypyrrole, polyaniline, their derivatives, and composite materials containing these polymers are the most studied materials for application as polymeric electroactive materials in batteries [8–18]. These polymers, which are synthesized through electropolymerization of their monomers, show improved conductivity, coulombic efficiency, rate capability, and the cycle life over conventional electrode materials. They exhibit *p*-doped properties and serve as the negative electrode materials in lithium batteries.

Electrochemical procedures for the formation of redox-active fullerene-based materials have been developed [19–41]. Polymeric films can be deposited on the electrode surface during reduction of fullerene epoxides, C₆₀O and C₇₀O [19, 20]. Related films can readily be prepared by electroreduction of C₆₀ or C₇₀ in the presence of small amounts of dioxygen in a mixed toluene/acetonitrile solution [20, 21]. Fullerenes can be also introduced as pendant substituents into side chains of polymers to form “charm bracelet” polymers. In this case, the methanefullerenes and pyrrolidino fullerene derivatives have been used as precursors for electropolymerization [23–28]. A large group of electroactive materials comprised of alternating fullerenes

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and metal ions or complexes of metal ions has also been synthesized [29–41]. The fullerene moieties are believed to be bonded to the metal centers in η^2 fashion to form a polymeric network. Due to the presence of electron-accepting fullerene cages, these materials exhibit *n*-doped properties.

Two component polymers of C_{60} and palladium have been studied the most intensively [34–37, 41]. These polymers are deposited at the electrode surface during reduction carried out in an acetonitrile/toluene mixture containing the fullerene and a palladium(II) complex. The reduced film shows high conductivity [32] and exhibit high specific capacitance [41]. It has become clear that variations of supporting electrolyte, solvent, and concentrations of polymerization precursors in the growth solution are of crucial importance to the properties of the resulting polymer [35–37]. Likewise, we have found that the structure and composition of three C_{60}/Pd film depend on the concentration of precursors of the polymerization, fullerene and palladium(II) complex, in the growth solution. By changing the conditions of polymerization, it is possible to obtain a material that consists of short $-Pd-C_{60}-Pd-C_{60}-Pd-C_{60}-$ chains or to form a highly cross-linked network. A polymeric material containing palladium particles can be also electrosynthesized.

The key requirement for commercial application of C_{60}/Pd films, for example, in electronics, energy storage, or batteries, is their electrochemical stability. In this paper, we report the results of a systematical study of the influence of different parameters on the electrochemical stability of C_{60}/Pd polymer. The effects of the composition of growth solution, potential range, and the rate of polymer formation were investigated. The influence of cation doping and solvent swelling during the polymer reduction under cyclic voltammetric conditions was also studied. These results allow for the determination of the optimal conditions for the stable electrochemical behavior of C_{60}/Pd films.

Experimental

Palladium acetate, $Pd(ac)_2$ (Aldrich) and C_{60} (Southern Chemical Group) were used as received. The supporting electrolytes tetra(ethyl)ammonium perchlorate, tetra(*n*-butyl)ammonium perchlorate, and tetra(*n*-hexyl)ammonium perchlorate (Sigma Chemical) were dried under vacuum for 24 h before use. Acetonitrile (99.9%), *N,N*-dimethylformamide (99.9%), dimethylsulphoxide (anhydrous 99.9%) were used as received from Aldrich Chemical. Toluene (Aldrich Chemical) was purified by distillation over sodium under a nitrogen atmosphere.

Voltammetric experiments were performed on a potentiostat/galvanostat Model 283 (EG&G Instruments) with a three-electrode cell. A gold disk with a diameter of 1.5 mm (Bioanalytical Systems) was used as the working electrode.

Before the experiment, the electrode was polished with fine carborundum paper and then with a 0.5- μ m alumina slurry. Subsequently, the electrode was sonicated in water to remove traces of alumina from the gold surface, washed with water, and dried. A silver wire immersed in 0.010 M silver perchlorate and 0.09 M tetra(*n*-butyl)ammonium perchlorate in acetonitrile that was separated from the working electrode by a ceramic tip (Bioanalytical Systems) served as the reference electrode. The counter electrode was a platinum tab with an area of about 0.5 cm².

Simultaneous voltammetric and piezoelectric microgravimetry experiments were carried out with a home-built potentiostat and an electrochemical quartz crystal microbalance, EQCM 5510 (Institute of Physical Chemistry, Warsaw, Poland). Plano-convex quartz crystals were used. The 14-mm-diameter, AT-cut plano-convex quartz crystals with a 5-MHz resonant frequency were obtained from Omig (Warsaw, Poland). A 100-nm gold film, which was vacuum-deposited on the quartz crystal, served as the working electrode. The projected region of this Au electrode was 5 mm in diameter. The area of the circuit center spot and two contacting radial strips was 0.24 cm². Unpolished quartz crystals were used for better adherence of the film. The sensitivity of the mass measurement calculated from the Saurbrey equation was 17.7 ng Hz⁻¹ cm⁻².

Secondary electron scanning electron microscopy images were obtained with the use of an S-3000N instrument of Hitachi. The accelerating voltages for the electron beam were 10 and 20 keV and the average working distance was 5 mm.

The C_{60}/Pd film was prepared by electro-reduction of an acetonitrile/toluene (1:4, *v/v*) solution that contained the fullerene and palladium acetate as well as the supporting electrolyte, 0.10 M tetra(*n*-butyl)ammonium perchlorate. Films were grown under cyclic voltammetric conditions mostly at a potential sweep rate of 100 mV/s. The electrochemical properties of the film were studied in a solution of the chosen solvent containing only the supporting electrolyte. In this case, the electrode covered with the film was removed from the growth solution, rinsed several times with an acetonitrile/toluene (1:4, *v/v*) solution, and then placed in a solution containing 0.10 M of supporting electrolyte. The modified electrode was allowed to equilibrate for 10 min while degassing with argon in a fresh solution before electrochemical measurements were performed.

Results and discussion

Effect of the potential range of C_{60}/Pd polymer formation
The C_{60}/Pd polymer was formed during reduction carried out in acetonitrile/toluene (1:4, *v/v*) mixture containing C_{60} , palladium acetate, and supporting electrolyte. Voltammo-

grams of the film formation obtained for different potential ranges are shown in Fig. 1. In the same figure, the voltammetric behaviors of obtained polymeric films recorded in acetonitrile containing tetra(*n*-butyl)ammonium perchlorate are shown. Upon repeated scanning of the potential in solution containing C_{60} , palladium acetate, tetra(*n*-butyl)ammonium perchlorate, an increase of the current in the potential range for fullerene moiety reduction is seen. Such behavior indicates formation of electrochemically active film on the electrode surface. For potential less negative than about $-1,300$ mV, both multivoltammograms of film formation and voltammograms of the films recorded in acetonitrile solutions are very similar.

However, if the negative range of film formation potential becomes more negative than $-1,300$ mV, the decrease of the yield of polymer formation is observed. Voltammograms of

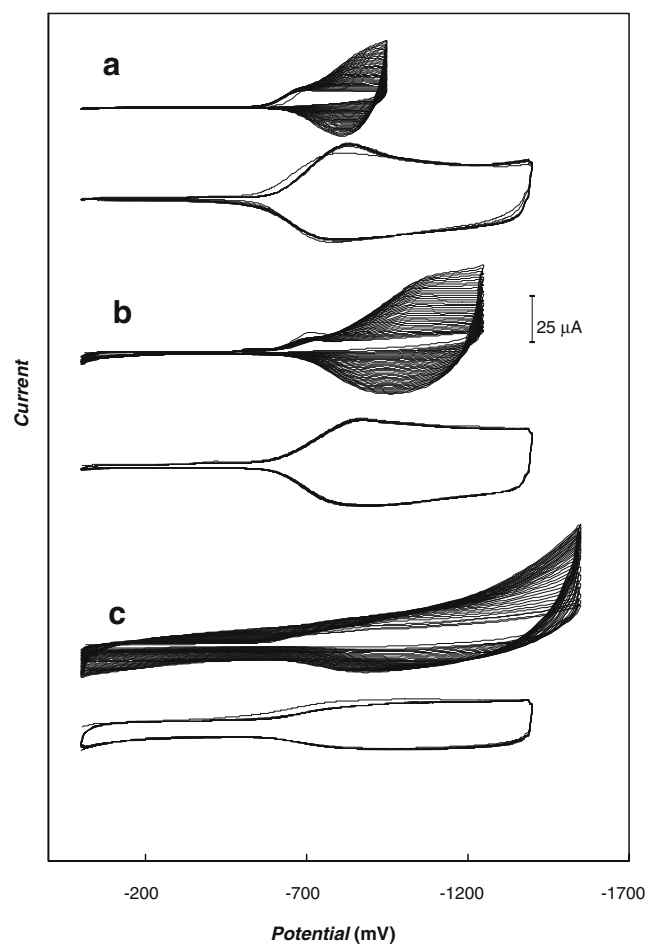


Fig. 1 Multicyclic voltammograms recorded at a gold (1.5-mm diameter) electrode in acetonitrile/toluene (1:4, *v/v*) containing 0.27 mM C_{60} , 2.70 mM $Pd(ac)_2$, and 0.10 M tetra(*n*-butyl)ammonium perchlorate, and cyclic voltammograms recorded at a gold (1.5-mm diameter) electrode covered with C_{60}/Pd film in acetonitrile containing 0.10 M tetra(*n*-butyl)ammonium perchlorate. The potential range of polymer deposition was: **a** from 0 to -950 mV, **b** from 0 to $-1,250$ mV, and **c** from 0 to $-1,550$ mV. The sweep rate was 100 mV s^{-1}

the film recorded in acetonitrile solution containing only the supporting electrolyte exhibit low currents of film reduction at negative potentials. Also, significant increase of the capacitance current in the potential range less negative than potentials of film reduction is observed.

There are two possible explanations for this effect. The decrease in the efficiency of film formation can be related to the increase of the amount of film formed during the negatively going voltammetry scan. The amount of the material deposited on the electrode surface increases with the shift of the potential limit toward more negative values. It was shown that the material buried deeply in the film is not oxidized during the positively going scan [34]. This can influence the properties of the polymer and process of film formation. The amount of material, which is not re-oxidized in positively going scan, increases with the increase of the amount of polymer deposited at the electrode surface in the negatively going scan.

The other effect responsible for the dependence of the yield of polymer formation with the potential range of deposition can be related to the structural changes of the film. The C_{60}/Pd film is formed by reductive electropolymerization. Consequently, the cations of supporting electrolyte are incorporated into the film structure during the polymer formation [35]. The degree of film doping with cations depends on the fullerene oxidation state and therefore on the potential. The repulsive interaction between negatively charged fullerene centers and the presence of large cations of supporting electrolyte in the polymeric structure can result in the lower yield of the polymer formation.

To probe dependence of the yield of C_{60}/Pd polymer formation on the potential range of electropolymerization, the effect of the sweep rate on the properties of formed film was investigated. The relevant data are shown in Fig. 2. In all cases, the potential range of polymerization was the same. The negative limit of potential range, equal to $-1,100$ mV, corresponds to the C_{60}^- oxidation state. The amount of polymer deposited on the electrode surface in negatively going cycle increases with the decrease in the sweep rate. However, the increasing amount of C_{60}/Pd does not affect the yield of the polymer formation.

Voltammograms presented in Fig. 2e show the increase of fullerene-related reduction and oxidation current in negative potential range with the decrease in the sweep rate of the film formation under voltammetric conditions. In conclusion, the structural changes of the film due to the fullerene cages reduction and cations doping are more likely responsible for the changes of yield of polymer formation with potential range of electropolymerization. Moreover, the negative limit of this potential should not be more negative than the potential corresponding to the second reduction step of fullerene.

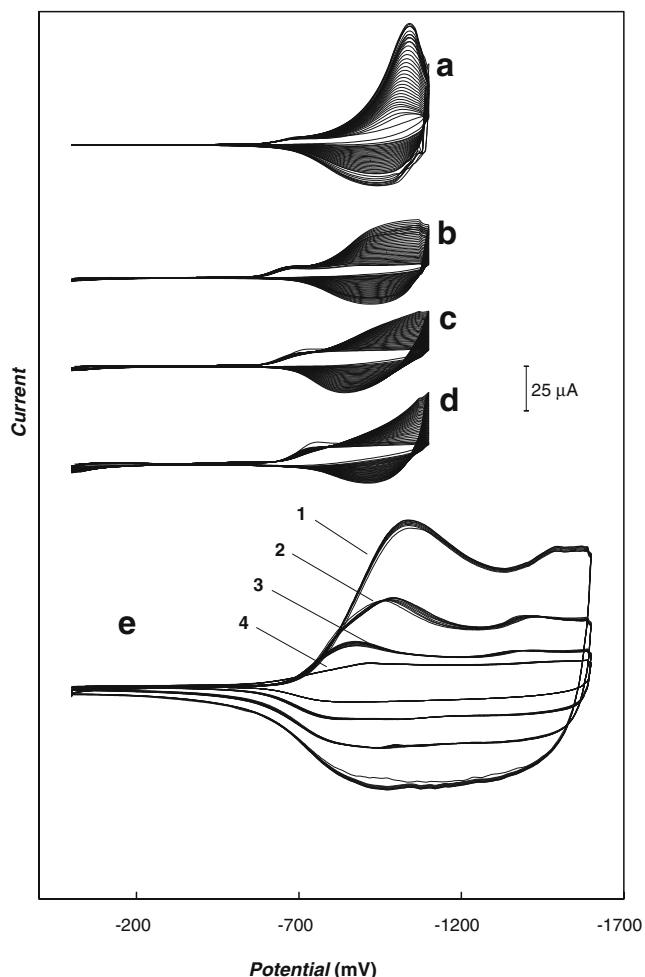


Fig. 2 Multicyclic voltammograms recorded at a gold (1.5-mm diameter) electrode in acetonitrile/toluene (1:4, *v/v*) containing 0.27 mM C_{60} , 2.70 mM $Pd(ac)_2$, and 0.10 M tetra(*n*-butyl)ammonium perchlorate in the potential range from 0 to $-1,000$ mV. The sweep rate was: **a** 20 $mV s^{-1}$, **b** 50 $mV s^{-1}$, **c** 100 $mV s^{-1}$, and **d** 200 $mV s^{-1}$. Panel **e** shows cyclic voltammograms recorded at a gold (1.5-mm diameter) electrode covered with C_{60}/Pd film in acetonitrile containing 0.10 M tetra(*n*-butyl)ammonium perchlorate at sweep rate 100 $mV s^{-1}$. The scan rate of C_{60}/Pd film formation was: (1) 20 $mV s^{-1}$, (2) 50 $mV s^{-1}$, (3) 100 $mV s^{-1}$, and (4) 200 $mV s^{-1}$

Effect of the supporting electrolyte The C_{60}/Pd film is electrochemically active in negative potential range due to the reduction of fullerene cage. Switching between oxidation states at negative potentials involves cation transport between the film and the solution [35]. Therefore, the voltammetric response of the film is strongly affected by the nature of the cation of supporting electrolyte. Figures 3, 4, and 5 show cyclic voltammograms recorded for gold electrode covered with C_{60}/Pd in acetonitrile containing different tetra(alkyl)ammonium perchlorates. The voltammetric curves were recorded for different potential ranges. The cation of supporting electrolyte influences both the magnitude of the current of film reduction and the potential range of the film's electrochemically stable response. The

size of tetra(alkyl)ammonium cation is the factor responsible for observed differences.

The highest reduction currents for the C_{60}/Pd film were obtained for small tetra(ethyl)ammonium cations. For these ions, the largest potential range of stability was also observed. In this case, the film shows stable voltammetric response at potentials less negative than $-2,200$ mV. The increase in the size of supporting electrolyte cation results in the decrease of the charge related to the polymer reduction and in the shifting of the negative limit of the potential range of film stability toward less negative values. In the case of tetra(*n*-hexyl)ammonium perchlorate, the C_{60}/Pd film is slowly decomposed at potential $-1,500$ mV.

Results presented in Figs. 3, 4, and 5 show that even for prolonged potential scanning to very negative potentials the film is not completely removed from the surface of the electrode (Figs. 3c, 4c, and 5b). The stationary background current is observed in voltammograms recorded for prolonged

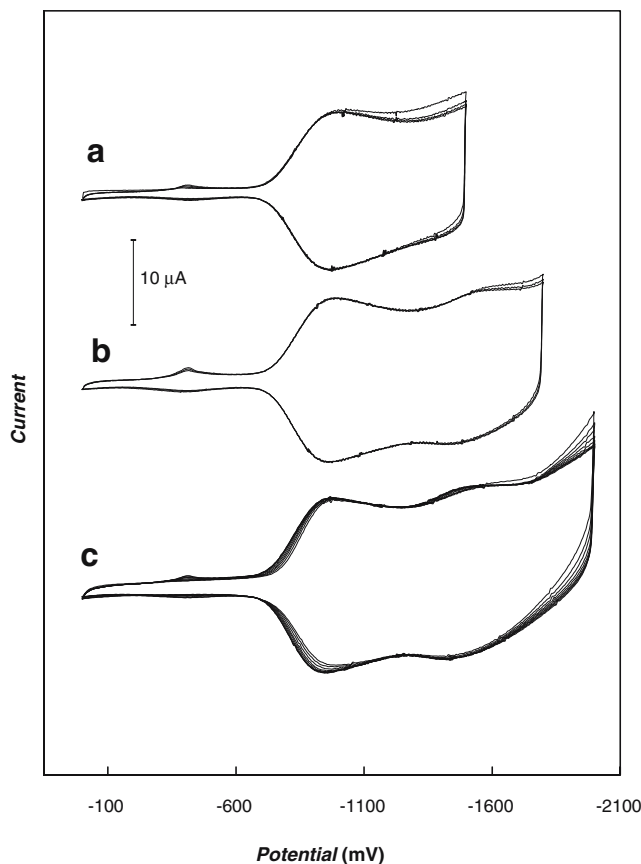


Fig. 3 Multicyclic voltammograms recorded at a gold (1.5-mm diameter) electrode covered with C_{60}/Pd film in acetonitrile containing 0.10 M tetra(ethyl)ammonium perchlorate at sweep rate 100 $mV s^{-1}$. The potential range was: **a** from 0 to $-1,500$ mV, **b** from 0 to $-1,800$ mV, and **c** from 0 to $-2,000$ mV. The C_{60}/Pd film was deposited under cyclic voltammetric conditions in acetonitrile/toluene (1:4, *v/v*) containing 0.27 mM C_{60} , 3.56 mM $Pd(ac)_2$, and 0.10 M tetra(*n*-butyl)ammonium perchlorate in the potential range from -200 to $-1,050$ mV. The sweep rate was 100 $mV s^{-1}$

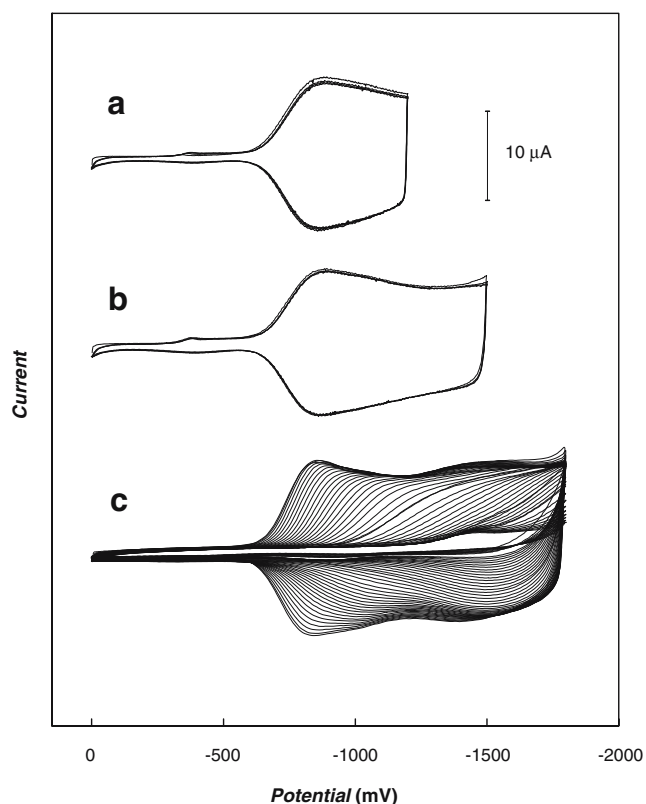


Fig. 4 Multicyclic voltammograms recorded at a gold (1.5-mm diameter) electrode covered with C_{60}/Pd film in acetonitrile containing 0.10 M tetra (*n*-butyl)ammonium perchlorate at sweep rate 100 mV s^{-1} . The potential range was: **a** from 0 to $-1,200 \text{ mV}$, **b** from 0 to $-1,500 \text{ mV}$, and **c** from 0 to $-1,800 \text{ mV}$. The C_{60}/Pd film was deposited under cyclic voltammetric conditions in acetonitrile/toluene (1:4, v/v) containing 0.27 mM C_{60} , 3.56 mM $Pd(ac)_2$, and 0.10 M tetra(*n*-butyl)ammonium perchlorate in the potential range from -200 to $-1,050 \text{ mV}$. The sweep rate was 100 mV s^{-1}

potential scanning. The morphology of the C_{60}/Pd polymer before and after prolonged potential cycling in the range from 0 to $-1,800 \text{ mV}$ is compared in Fig. 6. Film that remains at the electrode surface after prolonged potential cycling exhibits a different morphology than a freshly prepared layer. It is relatively flat and less porous. This C_{60}/Pd thin layer initially grown on the electrode surface exhibit higher stability over potential cycling in negative potential range.

Effect of the solvent It was shown that solvent significantly influences the voltammetric response of electrodes coated with C_{60}/Pd polymer [36, 41]. Results of EQCM studies provide more evidence that solvent is directly involved in the process of film reduction. Figure 7a, b shows simultaneously recorded voltammograms and frequency changes as a function of potential for an electrode covered with C_{60}/Pd in acetonitrile and *N,N*-dimethylformamide containing tetra (ethyl)ammonium perchlorate. In both solvents, the decrease of frequency in the potential range of film reduction is related to the mass increase due to counterion incorporation into the film to maintain charge neutrality. Figure 7c shows

the dependence of mass changes on the charge of the film reduction.

Despite the fact that the same counterion is transferred from the solution to the film, the changes of the mass of the electrode are significantly higher in the case of *N,N*-dimethylformamide than acetonitrile for the same charge of polymer reduction. It indicates that the swelling of the polymer due to solvent incorporation takes place during the polymer reduction. The nature of the solvent incorporated into the film during its reduction significantly influences the film stability. Figure 8 shows the exemplary voltammograms recorded in potential range from 0 to $-1,500 \text{ mV}$ for three different solvents containing the same supporting electrolyte, tetra(*n*-butyl) ammonium perchlorate. The most stable voltammetric behavior is observed for acetonitrile solution. In large polar solvents, for example, dimethylsulphoxide, the film is quickly removed from the electrode surface. In this solvent, decomposition of the film starts at about $-1,500 \text{ mV}$.

Effect of the concentration of precursors for polymerization in the growth solution The composition and structure of the

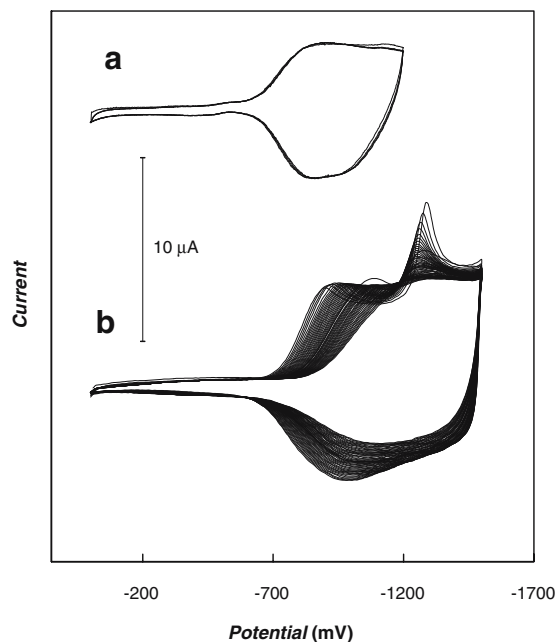


Fig. 5 Multicyclic voltammograms recorded at a gold (1.5-mm diameter) electrode covered with C_{60}/Pd film in acetonitrile containing 0.10 M tetra (*n*-hexyl)ammonium perchlorate at sweep rate 100 mV s^{-1} . The potential range was: **a** from 0 to $-1,200 \text{ mV}$, and **b** from 0 to $-1,500 \text{ mV}$. The C_{60}/Pd film was deposited under cyclic voltammetric conditions in acetonitrile/toluene (1:4, v/v) containing 0.27 mM C_{60} , 3.56 mM $Pd(ac)_2$, and 0.10 M tetra(*n*-butyl)ammonium perchlorate in the potential range from -200 to $-1,050 \text{ mV}$. The sweep rate was 100 mV s^{-1}

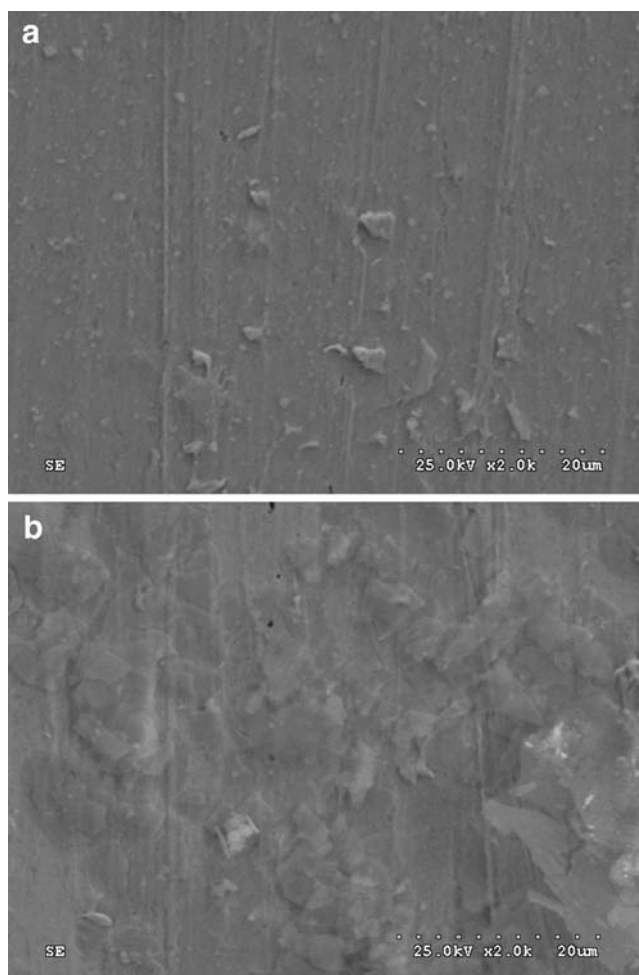


Fig. 6 SEM images of films formed on gold foil under cyclic voltammetric conditions (20 cycles) from 0.27 mM C_{60} , 3.56 mM $Pd(ac)_2$, and 0.10 M tetra(*n*-butyl)ammonium perchlorate in acetonitrile/toluene (1:4, *v/v*) after (a) and before (b) prolonged potential cycling in acetonitrile containing only 0.10 M tetra(*n*-butyl)ammonium perchlorate

C_{60}/Pd film depend upon the concentration of palladium complex and C_{60} in the growth solution [36, 37]. In the potential range of the polymer formation, a palladium metallic phase is deposited simultaneously. The size of metallic particles, which is changed in the range from 5 to 20 nm, and their amount depend on the ratio of $Pd(ac)_2$ concentration to the concentration of C_{60} . The presence of metallic palladium incorporated into the polymer also affects the film stability.

Figure 9 shows the effect of $Pd(ac)_2$ concentration in solution from which films are grown on the voltammetric response of the C_{60}/Pd films in acetonitrile containing tetra(*n*-butyl)ammonium perchlorate. The concentration of fullerene in growth solution was constant. Films formed in solution containing 3.12 mM $Pd(ac)_2$ are quickly removed from the electrode surface when the potential is cycled in the range from 0 to 1,800 mV. Current related to

the fullerene moieties reduction/re-oxidation decreases steadily with prolonged potential cycling. After about 20 cycles, a small steady-state current is reached. The increase of palladium complex concentration in the grown solution results in films that exhibit much better electrochemical stability. Film formed in acetonitrile/toluene (1:4, *v/v*) containing 7.13 mM $Pd(ac)_2$ exhibits stability over much longer potential range. The negative potential limit of film stability reaches a value of about $-2,500$ mV as is seen on the voltammogram of Fig. 9c. In addition to the stability increasing, films containing palladium nanoparticles are also more mechanically stable. The electrode covered with this film can be easily transferred from one solution to another without film damage.

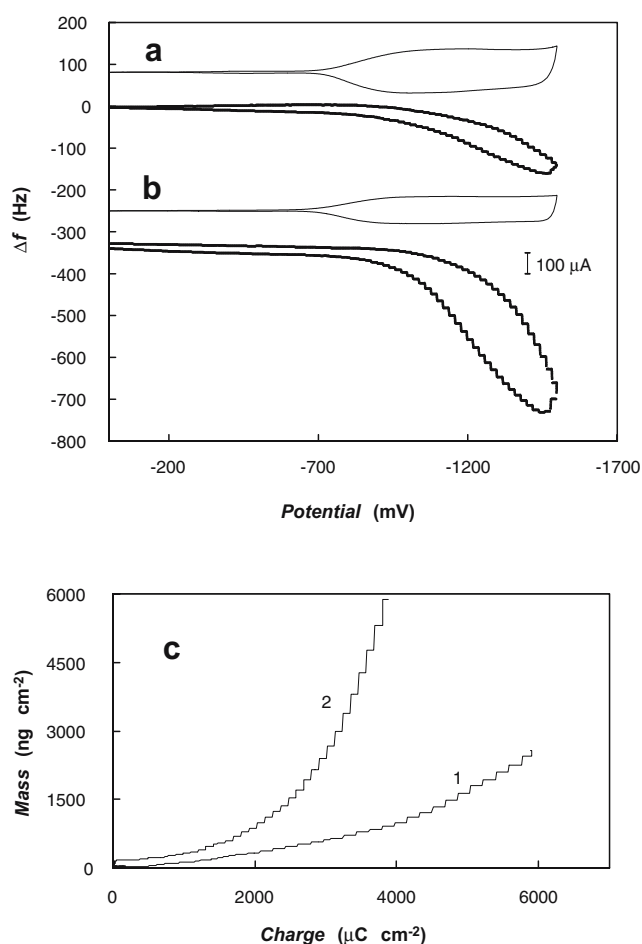


Fig. 7 Multicyclic voltammograms and curves of the frequency change vs potential simultaneously recorded at the same Au/quartz electrode coated with C_{60}/Pd in a acetonitrile and b *N,N*-dimethylformamide containing 0.10 M tetra(ethyl)ammonium perchlorate. The sweep rate was 50 mV/s. c Dependence of the mass change on the charge of film reduction for (1) acetonitrile and (2) *N,N*-dimethylformamide solution. The C_{60}/Pd film was deposited under cyclic voltammetric conditions in acetonitrile/toluene (1:4, *v/v*) containing 0.27 mM C_{60} , 3.56 mM $Pd(ac)_2$, and 0.10 M tetra(*n*-butyl)ammonium perchlorate in the potential range from -200 to $-1,050$ mV. The sweep rate was 50 mV s^{-1}

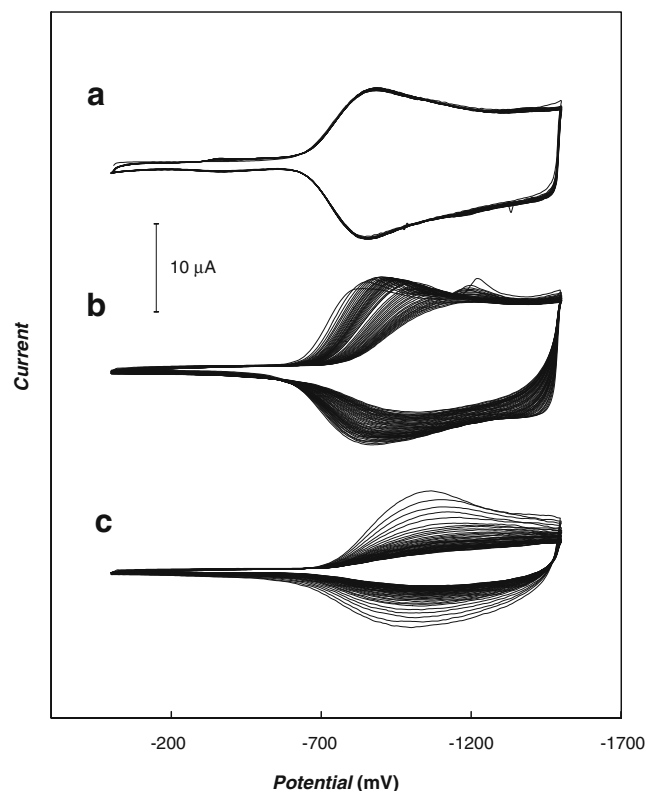


Fig. 8 Multicyclic voltammograms recorded at a gold (1.5-mm diameter) electrode covered with C_{60}/Pd film in **a** acetonitrile, **b** N,N -dimethylformamide, and **c** dimethylsulphoxide containing 0.10 M tetra(n -butyl)ammonium perchlorate at sweep rate 100 mV s^{-1} . The C_{60}/Pd film was deposited under cyclic voltammetric conditions in acetonitrile/toluene (1:4, v/v) containing 0.27 mM C_{60} , 3.56 mM Pd(ac) $_2$, and 0.10 M tetra(n -butyl)ammonium perchlorate in the potential range from -200 to $-1,050$ mV. The sweep rate was 100 mV s^{-1}

Temperature effect The effect of temperature on the stability of C_{60}/Pd films was investigated in dimethylformamide solution. In this case, the temperature range available for the study (up to 130°C) was much larger than the temperature range available for acetonitrile. The film was formed in acetonitrile/toluene (1:4, v/v) mixture containing 0.25 mM C_{60} and 3.55 mM Pd(ac) $_2$. Temperature practically

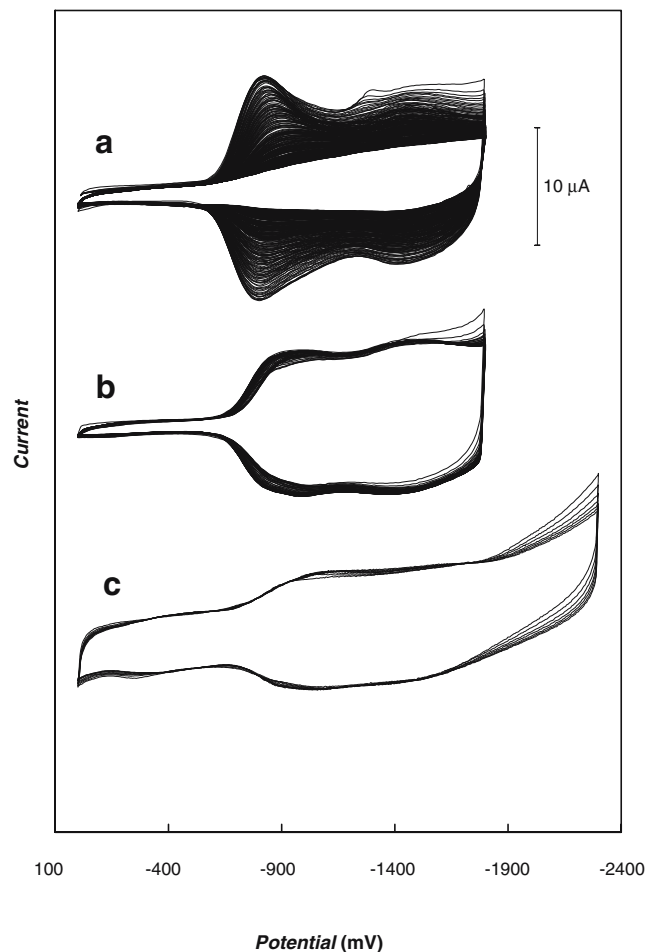


Fig. 9 Multicyclic voltammograms recorded at a gold (1.5-mm diameter) electrode covered with C_{60}/Pd film in acetonitrile containing 0.10 M tetra(n -butyl)ammonium perchlorate at sweep rate 100 mV s^{-1} . The C_{60}/Pd film was deposited under cyclic voltammetric conditions in acetonitrile/toluene (1:4, v/v) containing 0.27 mM C_{60} , 0.10 M tetra(n -butyl)ammonium perchlorate, and **a** 3.12 mM Pd(ac) $_2$, **b** 5.34 mM Pd(ac) $_2$, and **c** 7.13 mM Pd(ac) $_2$ in the potential range from -200 to $-1,050$ mV. The sweep rate was 100 mV s^{-1}

Table 1 Conditions of the stable voltammetric behavior of C_{60}/Pd film

Solvent	Supporting electrolyte	Negative potential limit of stable voltammetric behavior (mV)	Difference between potentials of reduction and oxidation peak (mV)	Q_{Ox} / Q_{Red}
Acetonitrile ^a	(Et_4N)ClO $_4$	$-2,200$	17.24	0.95
Acetonitrile ^a	(n -Bt $_4N$)ClO $_4$	$-1,800$	30.30	0.94
Acetonitrile ^a	(n -Hx $_4N$)ClO $_4$	$-1,500$	90.10	0.65
N,N -Dimethylformamide ^a	(n -Bt $_4N$)ClO $_4$	$-1,500$	57.14	0.92
Dimethylsulphoxide ^a	(n -Bt $_4N$)ClO $_4$	$-1,500$	71.43	0.71
Acetonitrile ^b	(Et_4N)ClO $_4$	$-2,800$	–	0.94

^a C_{60}/Pd film was deposited under cyclic voltammetric conditions in acetonitrile/toluene (1:4, v/v) containing 0.27 mM C_{60} , 0.10 M tetra(n -butyl)ammonium perchlorate, and 3.56 mM Pd(ac) $_2$ in the potential range from -200 to $-1,050$ mV. The sweep rate during film deposition was 100 mV s^{-1} .

^b C_{60}/Pd film was deposited under cyclic voltammetric conditions in acetonitrile/toluene (1:4, v/v) containing 0.27 mM C_{60} , 0.10 M tetra(n -butyl)ammonium perchlorate, and 7.50 mM Pd(ac) $_2$ in the potential range from -200 to $-1,050$ mV. The sweep rate during film deposition was 100 mV s^{-1} .

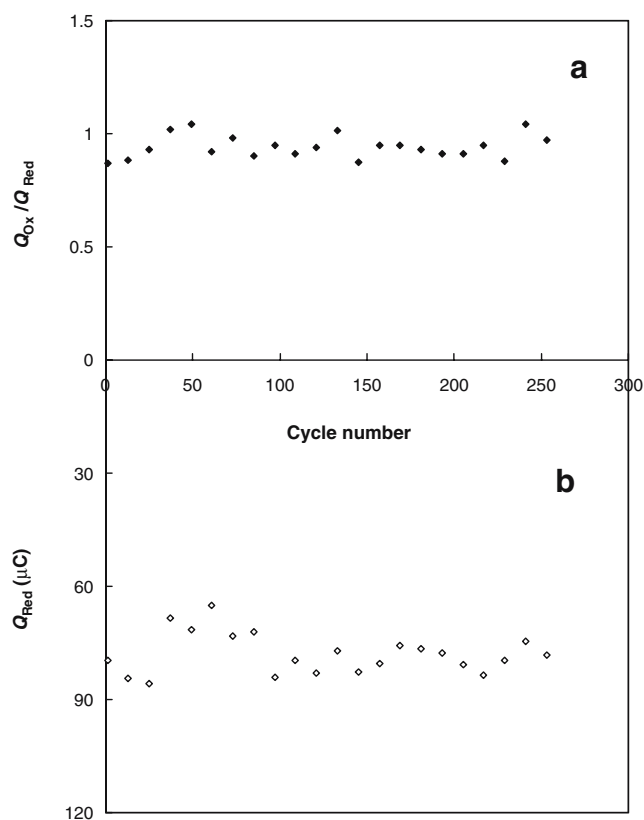


Fig. 10 Dependences of charge related to reduction, Q_{Red} , and the ratio of the charge of film oxidation to the charge of film reduction, Q_{Ox} / Q_{Red} , on the cycle number obtained under prolonged potential cycling of gold electrode covered with C_{60}/Pd film in the potential range from 400 to 1,400 mV. The sweep rate was 20 mV s^{-1} . C_{60}/Pd film was deposited under cyclic voltammetric conditions in acetonitrile/toluene (1:4, v/v) containing 0.27 mM C_{60} , 0.10 M tetra(*n*-butyl)ammonium perchlorate, and 3.56 mM $Pd(ac)_2$ in the potential range from -200 to $-1,050$ mV. The sweep rate during film deposition was 100 mV s^{-1}

does not influence the film stability. The film was stable in the potential range from 0 to $-1,500$ mV for whole temperature range (from 20 to 130°C) studied. Only, the increase of the charge of film reduction by about 20% is observed when temperature is changed from 20 to 130°C . A similar study was done in acetonitrile in the temperature range from 20 to 75°C . In this case, no effect of temperature on the film stability was also observed.

Conclusions

C_{60}/Pd films show a relatively stable electrochemical behavior. The potential range of film stability depends on the (1) conditions of film formation, particularly the ratio of $Pd(ac)_2$ to C_{60} concentration, (2) solvent, and (3) supporting electrolyte used for polymer doping. Results of the studies described above are collected in Table 1. Values given in this table are obtained mainly for films formed in solution containing low concentration of $Pd(ac)_2$. Films

formed in solution containing a large concentration of palladium acetate are much more stable (the last line in Table 1). However, they exhibit much lower capacitance and are therefore less likely candidates for successful use in batteries. Temperature change in the range from 20 to 130°C does not significantly affect stability of the film.

The most stable behavior for C_{60}/Pd films was found in acetonitrile solutions containing small cation electrolytes, for example, tetra(ethyl)ammonium cations. In solution containing tetra(*n*-butyl)ammonium perchlorate, the stability of C_{60}/Pd films over prolonged potential cycling (~ 250 cycles) was studied. Figure 10 shows the dependence of charge related to reduction, Q_{Red} , and the ratio of the charge of film oxidation to the charge of film reduction, Q_{Ox} / Q_{Red} , on the cycle number. Reduction charge is almost constant. The ratio Q_{Ox} / Q_{Red} is also constant and close to unity. Therefore, the C_{60}/Pd films can be used as an electroactive material in rechargeable batteries.

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