

# Electrochemical formation and properties of two-component films of transition metal complexes and C<sub>60</sub> or C<sub>70</sub>

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**Abstract** The electrochemically active polymers have been formed during electro-reduction carried out in solution containing fullerenes, C<sub>60</sub> or C<sub>70</sub>, and transition metal complexes of Pd(II), Pt(II), Rh(III), and Ir(I). In these films, fullerene moieties are covalently bounded to transition metal atoms (Pd and Pt) or their complexes (Rh and Ir) to form a polymeric network. All films exhibit electrochemical activity at negative potentials due to the fullerene cages reduction process. For all studied metal complexes, yields of formation of films containing C<sub>70</sub> are higher than yields of electrodeposition of their C<sub>60</sub> analogs. C<sub>70</sub>/M films also exhibit higher porosity in comparison to C<sub>60</sub>/M layers. The differences in film morphology and efficiency of polymer formation are responsible for differences in electrochemical responses of these films in acetonitrile containing supporting electrolyte only. C<sub>70</sub>/M films shows more reversible voltammetric behavior in negative potential range. They also show higher potential range of electrochemical stability. Processes of film formation and electrochemical properties of polymers depend on the transition metal ions or atoms bonding fullerene cages into polymeric network. The highest efficiency of polymerization was observed for fullerene/Pd and fullerene/Rh films. In the case of fullerene/Pd films, the charge transfer processes related to the fullerene moieties reduction in negative potential range exhibit the best reversibility among all of the studied systems. Capacitance performances of C<sub>60</sub>/Pd and C<sub>70</sub>/Pd films deposited on the porous Au/quartz electrode were also compared. Capacitance properties of both films are signifi-

cantly affected by the conditions of electropolymerization. Only a fraction of the film having a direct contact with solution contributes to pseudocapacitance. Capacitance properties of these films also depend on the size of cations of supporting electrolyte. The C<sub>70</sub>/Pd film exhibits much better capacitance performance comparison to C<sub>60</sub>/Pd polymer.

**Keywords** Fullerenes · Fullerene polymers · Electropolymerization · Transition metal complexes

## Introduction

The new electrochemically active materials have been of considerable interest in recent years due to their potential application as electroactive materials in batteries [1], supercapacitors [2], sensors [3, 4], or electrochromic devices [5]. Recently, considerable attention has been paid to the preparation and properties of polymers containing fullerenes [6–12]. The incorporation of the pseudo-spherical  $\pi$ -electron cages of fullerenes into solid-phase can significantly modify electronic, magnetic, and optical properties of materials.

Fullerenes can form homopolymers through [2+2] cycloaddition [13–18]. These systems are relatively unstable. Fullerenes can be also incorporated into main polymeric chain to form a “pearl necklace” structure [19–22] or to the side chains of polymers as pendant substituents [23–26]. So far, chemical polymerization is mostly used for the preparation of fullerene-containing polymers. However, the rate of chemical polymerization is difficult to control. Moreover, the structure of the resulting systems is poorly defined in many cases. Using electrochemical polymerization instead can remove some of these disadvantages.

Recently, we have focused on the development of novel electroactive polymers based on fullerenes [27–37]. The

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electrochemical reduction of fullerene epoxides,  $C_{60}O$  and  $C_{70}O$ , results in deposition of polymeric films onto electrode surfaces [27–29]. Two-component films of fullerenes or their derivatives and transition metal complexes are formed on the electrode during reduction carried out in solution containing fullerenes and complexes of such transition metals as palladium [30–33], platinum [34], rhodium [30], or iridium [30]. In the resulting films, the fullerene moieties are believed to be bonded to the metal centers in  $\eta^2$  fashion to form a polymeric network. Polymers of  $C_{60}$  and transition metal complexes,  $C_{60}/M$ , exhibit electrochemical activity in the negative potential range due to the reduction of the fullerene moieties present. The process of film reduction is accompanied by the transport of cations from the supporting electrolyte into the film [31]. Therefore, these films exhibit *n*-doped properties. Redox-active films of transition metals and fullerene derivatives containing electron-donating groups, 2'-ferrocenylpyrrolidino-[3',4';1,2][ $C_{60}$ ]fullerene and  $C_{60}$  with a covalently linked zinc *meso*-tetraphenylporphyrin, can be also synthesized under electrochemical conditions [35–37]. These films can undergo both *p*- and *n*-doping. At negative potentials, reduction of fullerene moieties occurs. In positive potential range, the processes of ferrocene or zinc *meso*-tetraphenylporphyrin oxidation take place.

Recently, it was also shown that  $C_{60}/Pd$  polymer exhibits very good capacitance performance [38]. Capacitance properties of this polymer depend on the condition of polymer deposition, solvent, and supporting electrolyte.

So far, most of the work was focused on the study of formation and properties of [ $C_{60}$ ]fullerene-based electroactive materials. In this paper, the processes of electropolymerization of two component films of transition metal complexes and [ $C_{60}$ ]fullerene,  $C_{60}/M$ , and [ $C_{70}$ ]fullerene,  $C_{70}/M$ , are compared. The electrochemical properties of these films are also investigated. A special attention is paid to comparison of capacitance properties of  $C_{60}/Pd$  and  $C_{70}/Pd$  films.

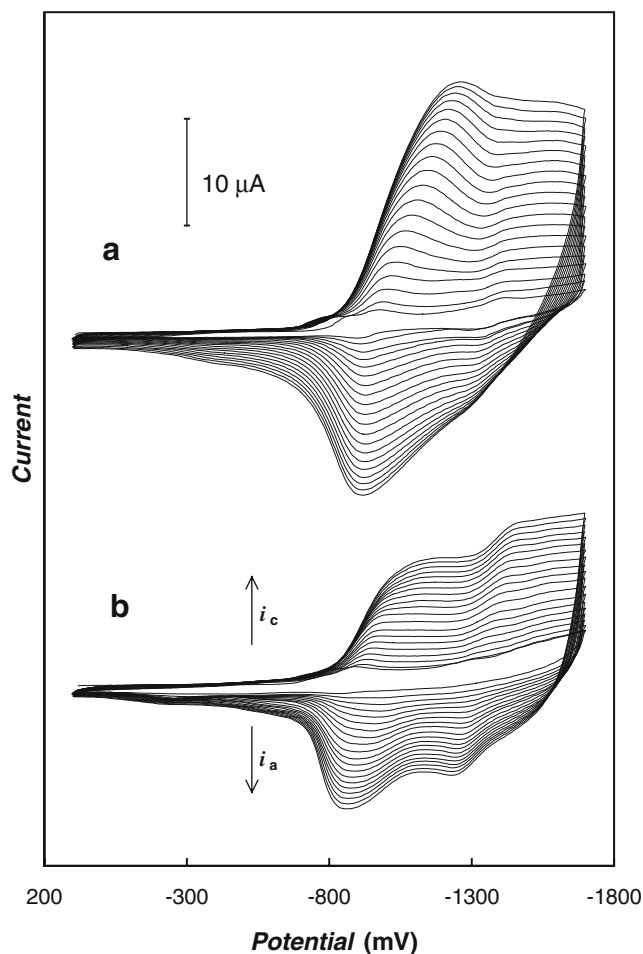
## Experimental

Palladium(II) acetate (98%),  $Pd(ac)_2$ , (Aldrich), di- $\mu$ -chlorodichlorobis(ethylene)-diplatinum(II) (97%),  $[Pt(\mu-Cl)Cl(C_2H_4)]_2$ , (ABCR GmbH, Karlsruhe, Germany), rhodium(II) trifluoroacetate dimer,  $[Rh(CF_3COO)_2]_2$ , (Aldrich), [ $C_{60}$ ]fullerene (99.5+%; MER Corporation, Tuscon, Arizona) and [ $C_{70}$ ]fullerene (98.5%; Southern Chemical Group) were used as received. Iridium complex,  $IrCl(CO)_2(p\text{-toluidine})$ , was synthesized according to procedure described elsewhere [39]. The supporting electrolytes, tetra(ethyl)ammonium perchlorate (Acros Organics), tetra(*n*-butyl)ammonium perchlorate (Fluka) and tetra(*n*-hexyl)ammonium perchlorate (Alfa Aesar), were dried under vacuum for 24 h before use.

Acetonitrile (99.9%) and toluene (99.8%) were used as received from Aldrich Chemical.

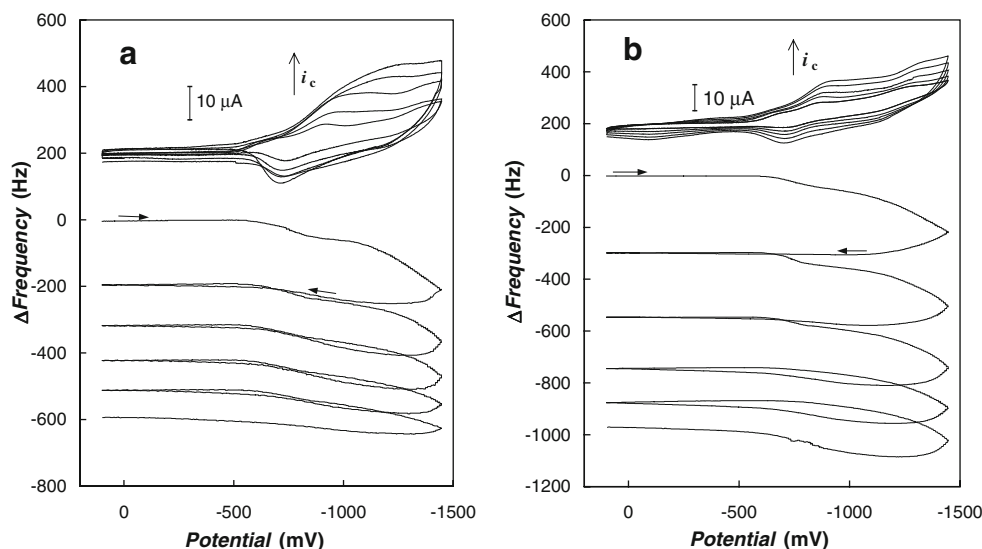
Voltammetric experiments were performed on a potentiostat/galvanostat Model 283 (EG&G Instruments) with a three-electrode cell. A gold disk with a diameter of 1.5 mm (Bioanalytical Systems) was used as the working electrode. Before the experiment, the electrode was polished with fine carborundum paper and then with a 0.5- $\mu m$  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  $cm^2$ .

Simultaneous voltammetric and piezoelectric microgravimetry experiments were carried out with a home-built potentiostat and an electrochemical quartz crystal microbal-



**Fig. 1** Multicyclic voltammograms for **a** 0.25 mM  $C_{60}$  and 0.85 mM  $Pd(ac)_2$ , and **b** 0.25 mM  $C_{70}$  and 0.85 mM  $Pd(ac)_2$  in acetonitrile/toluene (1:4, v:v) containing 0.1 M tetra(*n*-butyl)ammonium perchlorate recorded at gold disk Au (1.5 mm diameter). The sweep rate was 100  $mV s^{-1}$

**Fig. 2** Multicyclic voltammograms and curves of the frequency changes vs potential simultaneously recorded at the same Au/quartz electrode in acetonitrile/toluene (1:4, v:v) containing 0.1 M tetra(*n*-butyl) ammonium perchlorate and **a** 0.25 mM  $C_{60}$  and 0.85 mM Pd(ac) $_2$ , and **b** 0.25 mM  $C_{70}$  and 0.85 mM Pd(ac) $_2$ . The sweep rate was 25 mV s $^{-1}$

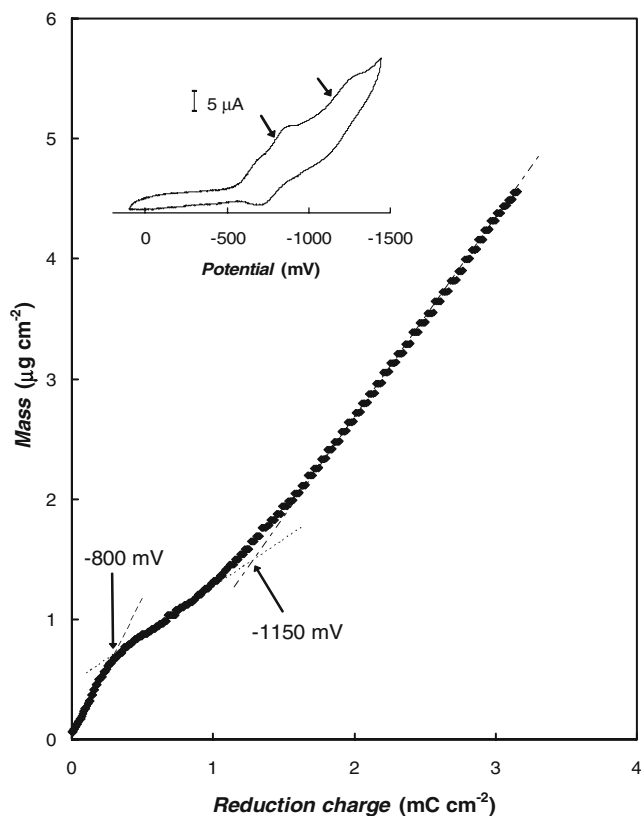


ance, EQCM 5510 (Institute of Physical Chemistry, Warsaw, Poland). Plano-convex quartz crystals were used. The 14 mm diameter AT-cut, plano-convex quartz crystals with a 5-MHz resonant frequency were obtained from Omig (Warsaw, Poland). A 100-nm gold film, which was vacuum deposited on the quartz crystal, 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 cm $^2$ . Unpolished quartz crystals were used for better adherence of the film. The sensitivity of the mass measurement calculated from the Sauerbrey equation was 17.7 ng Hz $^{-1}$  cm $^{-2}$ . A mass range within which Sauerbrey equation is valid has been determined using the process of polypyrrole electrodeposition. Polypyrrole was formed under potentiostatic conditions. A linear relationship between the charge of pyrrole oxidation and mass of polymer deposited on the electrode surface was observed for mass as large as 100 μg cm $^{-2}$ . The Au/quartz electrode with surface area of 0.24 cm $^2$  was used for study of capacitance properties of polymers.

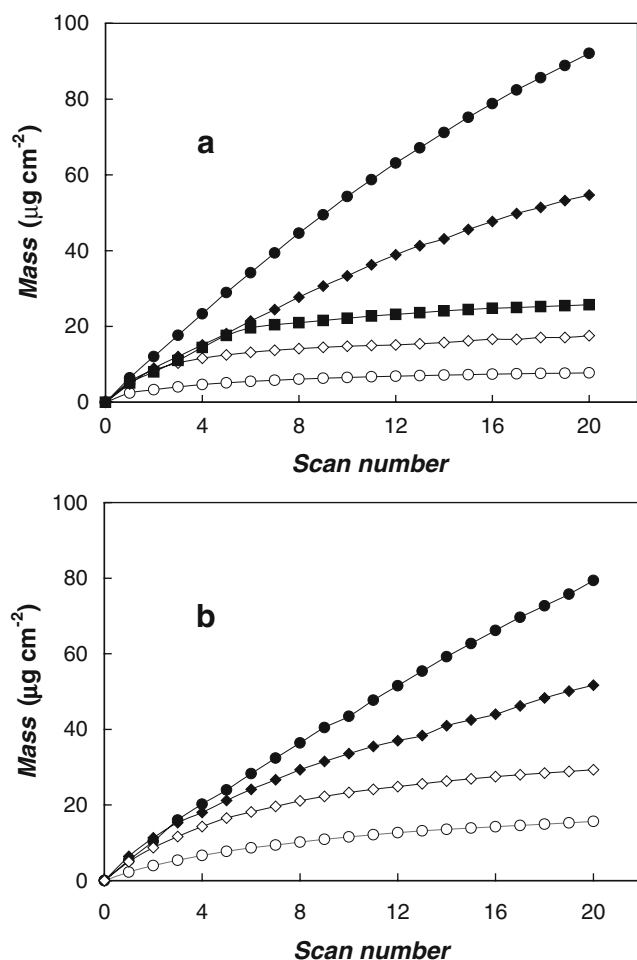
Secondary electron scanning electron microscopy images were obtained with the use of an S-3000N instrument of Hitachi. The accelerating voltages for the electron beam were 10 and 20 keV, and the average working distance was 5 mm.

The  $C_{60}/M$  and  $C_{70}/M$  films were prepared by electroreduction of an acetonitrile/toluene (1:4, v:v) solution that contained the fullerene and transition metal complexes, and 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 in the potential range from 100 to -1,450 mV. 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

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.



**Fig. 3** Dependences of the mass of  $C_{70}/Pd$  ( $\Delta m$ ) deposited on the Au/quartz electrode under EQCM conditions on the charge of reduction ( $Q$ ). The grown acetonitrile/toluene (1:4, v:v) solution contained 0.25 mM  $C_{70}$ , 0.85 mM Pd(ac) $_2$  and 0.1 M tetra(*n*-butyl)ammonium perchlorate. The sweep rate was 25 mV s $^{-1}$ . Reduction charge was calculated by integration of voltammetric curve shown inset. Arrows indicate potentials corresponding to the charges of the change of  $Q-\Delta m$  slope



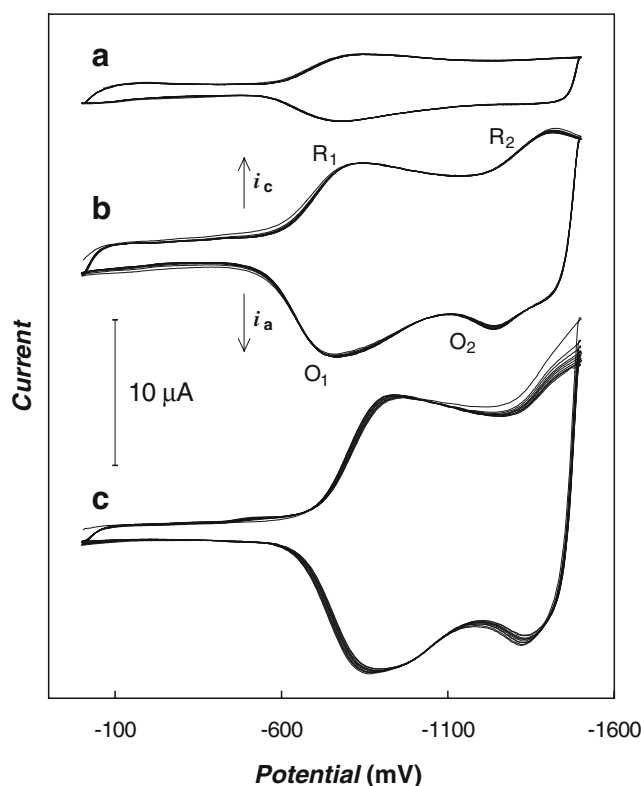
**Fig. 4** Dependences of the mass of Au/quartz electrode on the cycle number during  $C_{60}/Pd$  (a) and  $C_{70}/Pd$  (b) film deposition in acetonitrile/toluene (1:4, v:v) containing 0.1 M tetra(*n*-butyl)ammonium perchlorate, a 0.25 mM  $C_{60}$  and b 0.25 mM  $C_{70}$ . Concentration of  $Pd(ac)_2$  was 1 mM (empty circles), 2 mM (empty diamonds), 2.5 mM (filled squares), 3 mM (filled diamonds), and 4 mM (filled circles)

## Results and discussion

**$C_{60}/Pd$  and  $C_{70}/Pd$  polymers** The  $C_{60}/Pd$  and  $C_{70}/Pd$  polymeric thin films are formed during reduction carried out in acetonitrile/toluene (1:4, v:v) mixture containing  $Pd(ac)_2$  and fullerene. Voltammograms of  $C_{60}/Pd$  and  $C_{70}/Pd$  polymer formation are compared in Fig. 1. Upon repeated scanning of the potential between 100 and  $-1,700$  mV with a scan rate 100 mV/s, an increase of the current in the potential range for fullerene moiety reduction is seen for two systems. For the processes of both polymer deposition, qualitative and quantitative differences are observed. Peak currents related to the reduction of fullerene moieties are much better defined for the process of  $C_{70}/Pd$  deposition. However, currents observed for the process of  $C_{60}/Pd$  formation are higher than currents recorded in the solution containing  $C_{70}$ .

Figure 2 shows results of electrochemical quartz crystal microbalance (EQCM) studies of the processes of  $C_{60}/Pd$  and  $C_{70}/Pd$  film electrodeposition on Au/quartz electrode. The frequency decreases in the cathodic cycle in the potential range of palladium cation reduction due to the polymer deposition process. Three ranges with different slopes corresponding to the reduction of  $Pd(II)$  and two fullerene reduction steps are observed on  $E-\Delta f$  curves. A small decrease of frequency in the positive scan direction is related to the film oxidation followed by egress of the supporting electrolyte cations from the polymer to the solution. Frequency changes observed during  $C_{70}/Pd$  deposition are higher than the frequency changes obtained for the process of  $C_{60}/Pd$  electropolymerization. These results are rather puzzled in respect to voltammograms of films formation which are shown in Fig. 1 as multicyclic voltammograms of polymer electrodeposition indicate higher efficiency of  $C_{60}/Pd$  film formation.

Figure 3 shows dependences of the mass of  $C_{70}/Pd$  polymer,  $\Delta m$ , deposition at the electrode surface on the charge of reduction,  $Q$ , obtained on the base of results presented in Fig. 2. Reduction charge was obtained by integration of voltammogram. This graph can be divided into



**Fig. 5** Cyclic voltammograms of  $C_{60}/Pd$  (a) and  $C_{70}/Pd$  film (b and c) in acetonitrile containing 0.10 M tetra(*n*-butyl)ammonium perchlorate (a and b) and 0.10 M tetra(ethyl)ammonium perchlorate (c) recorded at Au (1.5 mm). The sweep rate was 100 mV s<sup>-1</sup>. The  $C_{60}/Pd$  and  $C_{70}/Pd$  films were grown under cyclic voltammetry conditions in acetonitrile/toluene (1:4, v:v) containing 0.10 M tetra(*n*-butyl)ammonium perchlorate, 0.25 mM  $C_{60}$  or  $C_{70}$ , and 0.85 mM  $Pd(ac)_2$

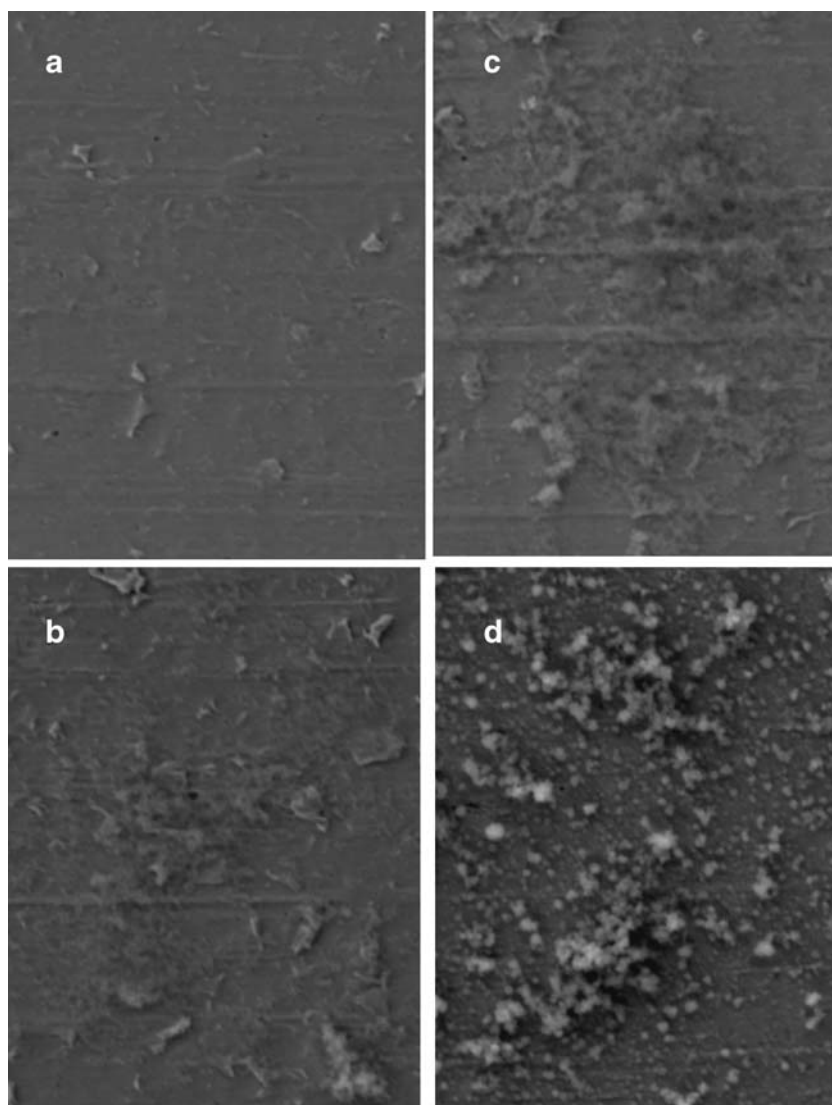
three parts. Initially, for the low charges, a linear  $Q-\Delta m$  relation with a high slope equal to  $2.36 \mu\text{g}/\text{mC}$  is observed. This slope is very close to the slope of  $Q-\Delta m$  relation obtained for the process of palladium deposition from acetonitrile/toluene (1:4, v:v) mixture containing palladium acetate and supporting electrolyte only. Potential of  $\text{Pd}(\text{ac})_2$  reduction process is about 50 mV less negative than the potential of  $\text{C}_{70}$  reduction. In the range of higher reduction charges, corresponding to the fullerene first reduction step, the slope of  $Q-\Delta m$  relation becomes low and equal to  $0.76 \mu\text{g}/\text{mC}$ . It is obvious that formation of  $\text{C}_{70}/\text{Pd}$  polymer on the electrode surface inhibits the process of palladium deposition and decrease of slope of  $Q-\Delta m$  relation occurs. At higher charges corresponding to the second fullerene reduction step, a very significant increase of slope of  $Q-\Delta m$  relation to  $1.65 \mu\text{g}/\text{mC}$  is observed. These large changes in slope cannot be explained by higher doping of the polymer with supporting electrolyte cations. They indicate that the

rate of polymerization is also influenced by the charge of fullerene cage. Probably, increase of negative charge on  $\text{C}_{60}$  and  $\text{C}_{70}$  during their reduction favors the bonding of palladium to fullerene and rate of polymerization increases.

Similar behavior was observed for the process of  $\text{C}_{60}/\text{Pd}$  electropolymerization. The slope of initial part of  $Q-\Delta m$  relation is  $2.38 \mu\text{g}/\text{mC}$ . Next, the polymer is deposited, and the slope drops to  $0.51 \mu\text{g}/\text{mC}$ . A lower value of the slope of this linear part of the graph in comparison to the value obtained for  $\text{C}_{70}/\text{Pd}$  system indicates lower efficiency of  $\text{C}_{60}/\text{Pd}$  film formation. In the potential range of second  $\text{C}_{60}$  reduction step, the slope of  $Q-\Delta m$  relationship increases to  $1.91 \mu\text{g}/\text{mC}$ .

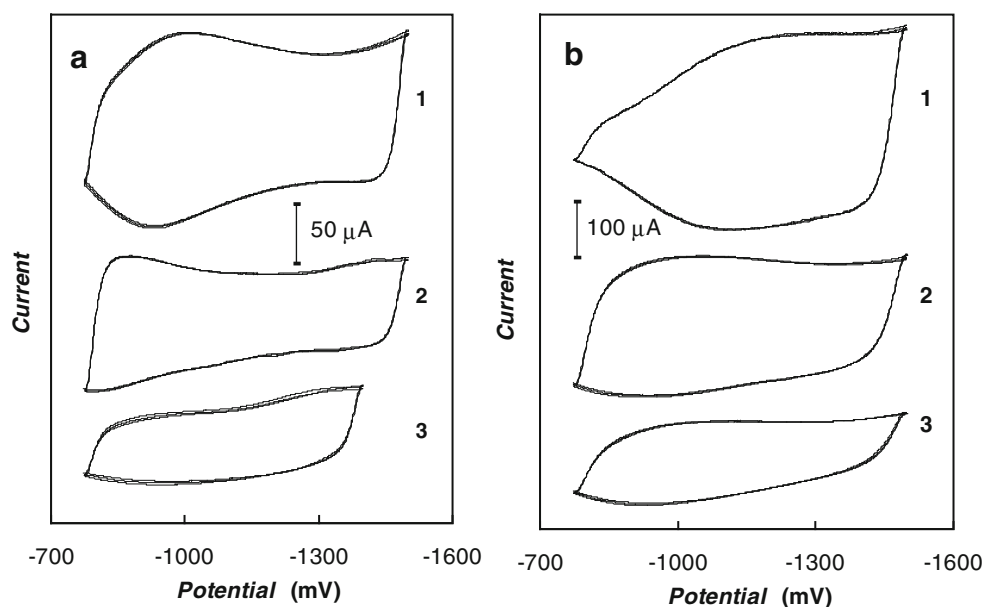
In Fig. 4, the changes of mass of the electrode as a function of a scan number are shown for solutions containing different concentration of  $\text{Pd}(\text{ac})_2$  and the same concentration of  $\text{C}_{60}$  and  $\text{C}_{70}$ . The mass of the polymer deposited in single voltammetric cycle was calculated from

**Fig. 6** SEM images of films formed on gold foil during 20 (a and c) or 40 (b and d) voltammetric cycle in the potential range +100 to -1,450 mV in acetonitrile/toluene (1:4, v:v) containing 0.1 M tetra(*n*-butyl) ammonium perchlorate and a and b 0.25 mM  $\text{C}_{60}$  and 2.00 mM  $\text{Pd}(\text{ac})_2$ , and c and d 0.25 mM  $\text{C}_{70}$  and 2.00 mM  $\text{Pd}(\text{ac})_2$





**Fig. 7** Cyclic voltammograms of **a**  $C_{60}/Pd$  and **b**  $C_{70}/Pd$  films in acetonitrile containing 1 0.10 M tetra(ethyl)ammonium perchlorate, 2 0.10 M tetra(*n*-butyl)ammonium perchlorate, and 3 0.10 M tetra(*n*-hexyl) ammonium perchlorate in the potential range of fullerene cage reduction recorded at Au/quartz electrode. The sweep rate was  $100 \text{ mV s}^{-1}$ . The  $C_{60}/Pd$  and  $C_{70}/Pd$  films were grown under cyclic voltammetry conditions in acetonitrile/toluene (1:4, v:v) containing 0.10 M tetra(*n*-butyl) ammonium perchlorate, 0.25 mM  $C_{60}$  or  $C_{70}$  and 2.0 mM  $Pd(ac)_2$



a difference in frequency on the beginning of negatively going scan and at the end of positively going scan. For low concentration of  $Pd(ac)_2$  (lower than about 2 mM for a solution containing  $C_{60}$  and 2.5 mM for a solution containing  $C_{70}$ ), the amount of  $C_{60}/Pd$  and  $C_{70}/Pd$  film deposited on the electrode surface in each cycle decreases with the increase in the scan number and becomes very small for scan number higher than 10. It indicates that the process of polymer deposition under these conditions becomes inhibited by the polymeric layer deposited on the electrode surface. For low concentration of  $Pd(ac)_2$ , the mass of polymer deposited in a solution containing  $C_{70}$  is about 1.5 times higher than the mass of  $C_{60}/Pd$  polymer deposited from a solution containing fullerene  $C_{60}$ . In a solution containing a higher concentration of palladium acetate, an almost linear increase of the mass of the electrode with the scan number is observed even for higher scan numbers. This effect is probably related to simultaneous deposition of fullerene polymer and of metallic particles of palladium [40].

Results presented in Fig. 4 were obtained assuming that according to the Saurbrey equation, only the mass changes of the electrode are responsible for frequency changes of the quartz crystal. In the case of polymeric material, also other factors, like roughness and porosity of polymer and their viscosity and viscoelasticity may contribute to the frequency changes of the crystal [41]. These effects are more significant and can contribute to the mass changes presented in Fig. 4 for porous fullerene/ $Pd$  films formed in solutions containing a low concentration of  $Pd(ac)_2$ .

The voltammetric behavior of  $C_{60}/Pd$  and  $C_{70}/Pd$  films in potential range 0 to  $-1,500 \text{ mV}$  in acetonitrile solution containing only supporting electrolyte is compared in Fig. 5. For  $C_{70}/Pd$  film, voltammograms were recorded in solution

containing tetra(ethyl)ammonium and tetra(*n*-butyl)ammonium perchlorate. In this potential range, two pairs of voltammetric peaks,  $R_1/O_1$  and  $R_2/O_2$ , corresponding to the two consecutive one-electro reduction steps of  $C_{60}$  and  $C_{70}$  cages are observed. The voltammetric current recorded for  $C_{70}/Pd$  film is much higher than current of  $C_{60}/Pd$  film formation. Also, the voltammetric peaks of  $C_{70}$  cage reduction are much better pronounced. The  $C_{70}/Pd$  film reduction current depends on the size of cation of supporting electrolyte indicating that the process of film reduction is accompanied by the transport of cations from solution into

**Table 1** Specific capacitance of the  $C_{60}/Pd$  and  $C_{70}/Pd$  films in acetonitrile solutions containing different tetra(*n*-alkyl)ammonium perchlorates

Concentration of precursors	Supporting electrolyte (0.1 M)	Specific capacitance ( $F \text{ g}^{-1}$ )
1.0 mM $Pd(ac)_2$ + 0.25 mM $C_{60}$	( <i>n</i> -Bu) $_4$ NCIO $_4$	240 <sup>a</sup>
2.0 mM $Pd(ac)_2$ + 0.25 mM $C_{60}$	(Et) $_4$ NCIO $_4$	145 <sup>a</sup>
2.0 mM $Pd(ac)_2$ + 0.25 mM $C_{60}$	( <i>n</i> -Bu) $_4$ NCIO $_4$	105 <sup>a</sup> 130 <sup>b</sup> 195 <sup>c</sup>
2.0 mM $Pd(ac)_2$ + 0.25 mM $C_{60}$	( <i>n</i> -Hx) $_4$ NCIO $_4$	70 <sup>a</sup>
3.0 mM $Pd(ac)_2$ + 0.25 mM $C_{60}$	( <i>n</i> -Bu) $_4$ NCIO $_4$	85 <sup>a</sup>
1.0 mM $Pd(ac)_2$ + 0.25 mM $C_{70}$	( <i>n</i> -Bu) $_4$ NCIO $_4$	270 <sup>a</sup>
2.0 mM $Pd(ac)_2$ + 0.25 mM $C_{70}$	(Et) $_4$ NCIO $_4$	185 <sup>a</sup>
2.0 mM $Pd(ac)_2$ + 0.25 mM $C_{70}$	( <i>n</i> -Bu) $_4$ NCIO $_4$	125 <sup>a</sup> 160 <sup>b</sup>
2.0 mM $Pd(ac)_2$ + 0.25 mM $C_{70}$	( <i>n</i> -Hx) $_4$ NCIO $_4$	80 <sup>a</sup>
3.0 mM $Pd(ac)_2$ + 0.25 mM $C_{70}$	( <i>n</i> -Bu) $_4$ NCIO $_4$	125 <sup>a</sup>

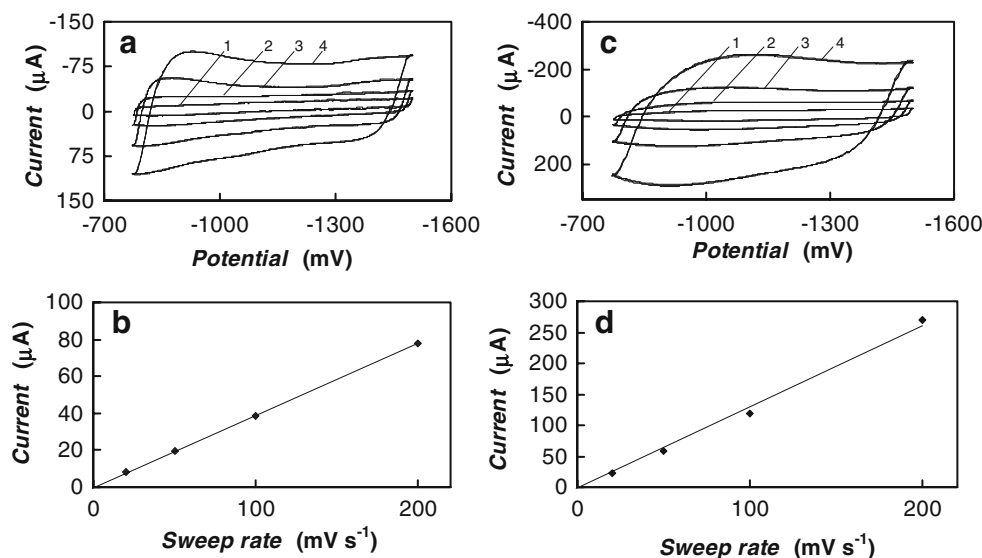
Conditions of polymer deposition:

<sup>a</sup> Twenty cycles in the potential range from 100 to  $-1,450 \text{ mV}$ ; sweep rate was  $100 \text{ mVs}^{-1}$

<sup>b</sup> Ten cycles in the potential range from 100 to  $-1,450 \text{ mV}$ ; sweep rate was  $100 \text{ mVs}^{-1}$

<sup>c</sup> Five cycles in the potential range from 100 to  $-1,450 \text{ mV}$ ; sweep rate was  $100 \text{ mVs}^{-1}$

**Fig. 8** Cyclic voltammograms of **a**  $C_{60}/Pd$  and **c**  $C_{70}/Pd$  film in acetonitrile containing 0.10 M tetra(*n*-butyl)ammonium perchlorate recorded at Au/quartz electrode. The sweep rate was 1, 2, 5, 10, 20, 50, 100, and 200  $mV s^{-1}$ . Dependence of the pseudo-capacitive current on the sweep rate for **(b)**  $C_{60}/Pd$  and **(d)**  $C_{70}/Pd$ . Films were grown under cyclic voltammetry conditions in acetonitrile/toluene (1:4, v:v) containing 0.10 M tetra(*n*-butyl)ammonium perchlorate, 0.25 mM  $C_{60}$  or  $C_{70}$ , and 2.0 mM  $Pd(ac)_2$



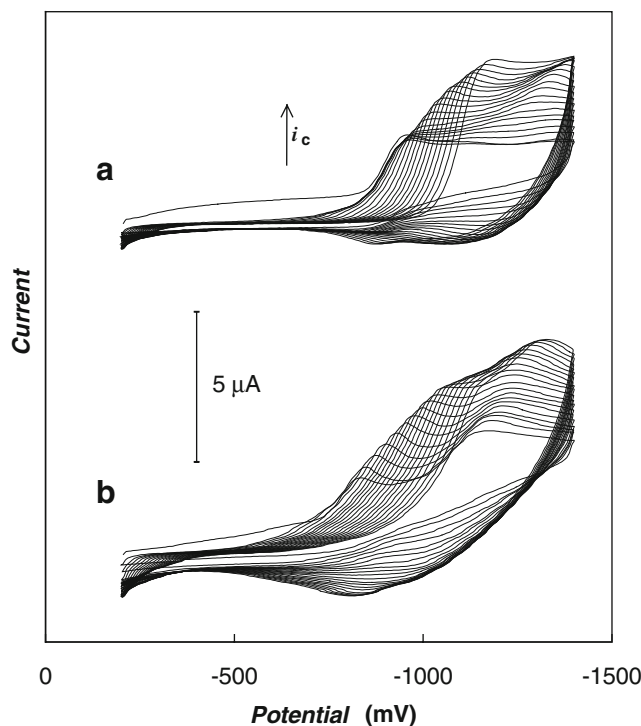
the film. The charge related to the film reduction process is much higher in acetonitrile containing tetra(ethyl)ammonium perchlorate than the charge of  $C_{70}/Pd$  electroreduction in the presence of bigger tetra(*n*-butyl)ammonium cations. A similar behavior was observed for  $C_{60}/Pd$  film [31].

Current recorded in the potential range of fullerene cage reduction is much higher in the case of  $C_{70}/Pd$  film than this one observed for  $C_{60}/Pd$ . This effect can be related to the higher efficiency of  $C_{70}/Pd$  film formation (Fig. 2). Structural differences of both films may be another reason of such behavior. The morphology of  $C_{70}/Pd$  and  $C_{60}/Pd$  films are compared in Fig. 6. The  $C_{70}/Pd$  film shows higher porosity. Such structure may be easier penetrated by solvent and supporting electrolyte ions during the film reduction leading to higher current.

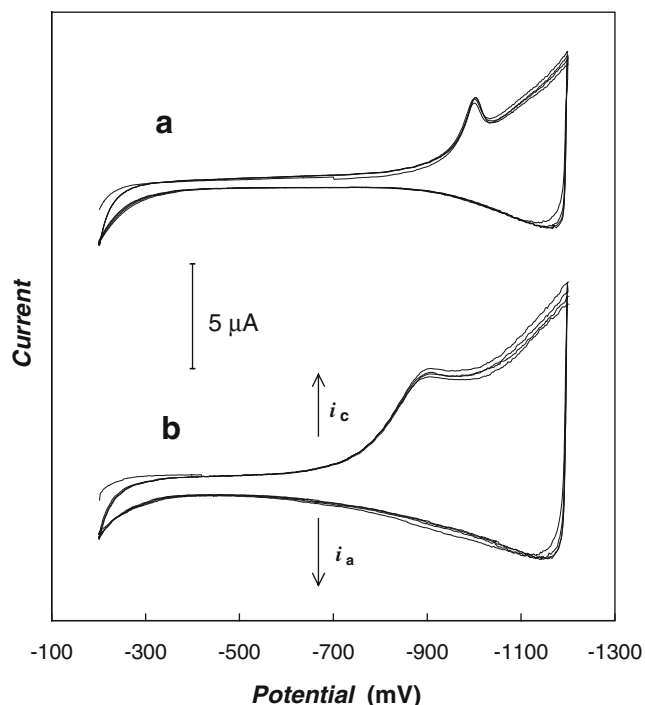
It was shown that  $C_{60}/Pd$  film is a very good electrochemical supercapacitor [38]. The comparison of voltammetric responses of  $C_{60}/Pd$  and  $C_{70}/Pd$  film (Fig. 5) indicate that capacitance properties of  $C_{70}/Pd$  should even be a better electrochemical capacitor. A comparison of capacitance properties of  $C_{70}/Pd$  and  $C_{60}/Pd$  films were done for films deposited on the rough surface of gold deposited on unpolished quartz crystal. In this case, the polymer sticks better to the surface of the electrode allowing for an easy transfer of the electrode covered with polymer from one solution to the other. It was also observed that increase of the potential range of formation toward the potential of fullerene second reduction step leads to better mechanical and electrochemical stability of the film, particularly for polymers formed in solution containing low concentration of  $Pd(ac)_2$ . Therefore, in this paper, capacitance properties were investigated for films deposited under voltammetric conditions in potential range 100  $\div$  -1,450 mV.

Voltammograms obtained for  $C_{70}/Pd$  and  $C_{60}/Pd$  polymeric films in acetonitrile containing different tetra(*n*-alkyl)

ammonium perchlorates are shown in Fig. 7. Voltammograms recorded in the potential range of films reduction show pseudorectangular cathodic and anodic profile that are the mirror image of one another. Such behavior is typical for ideal capacitor. The departure from the ideal rectangular shape is related to the faradaic process of film reduction and reoxidation. The voltammetric behavior in the potential range



**Fig. 9** Multicyclic voltammograms for **a** 0.27 mM  $C_{60}$  and 1.10 mM  $[Pt(\mu-Cl)Cl(C_2H_4)]_2$  and **b** 0.27 mM  $C_{70}$  and 1.10 mM  $[Pt(\mu-Cl)Cl(C_2H_4)]_2$  in acetonitrile/toluene (1:4, v:v) containing 0.1 M tetra(*n*-butyl)ammonium perchlorate recorded at Au (1.5 mm). The sweep rate was 50  $mV s^{-1}$



**Fig. 10** Cyclic voltammograms of **a**  $C_{60}/Pt$  and **b**  $C_{70}/Pt$  film in acetonitrile containing 0.10 M tetra(ethyl)ammonium perchlorate recorded at Au (1.5 mm). The sweep rate was  $50 \text{ mV s}^{-1}$ . The  $C_{60}/Pt$  and  $C_{70}/Pt$  films were grown under cyclic voltammetry conditions in acetonitrile/toluene (1:4, v:v) containing 0.10 M tetra(*n*-butyl) ammonium perchlorate, 0.27 mM  $C_{60}$  or  $C_{70}$ , and 1.05 mM  $[Pt(\mu-Cl)Cl(C_2H_4)_2]$

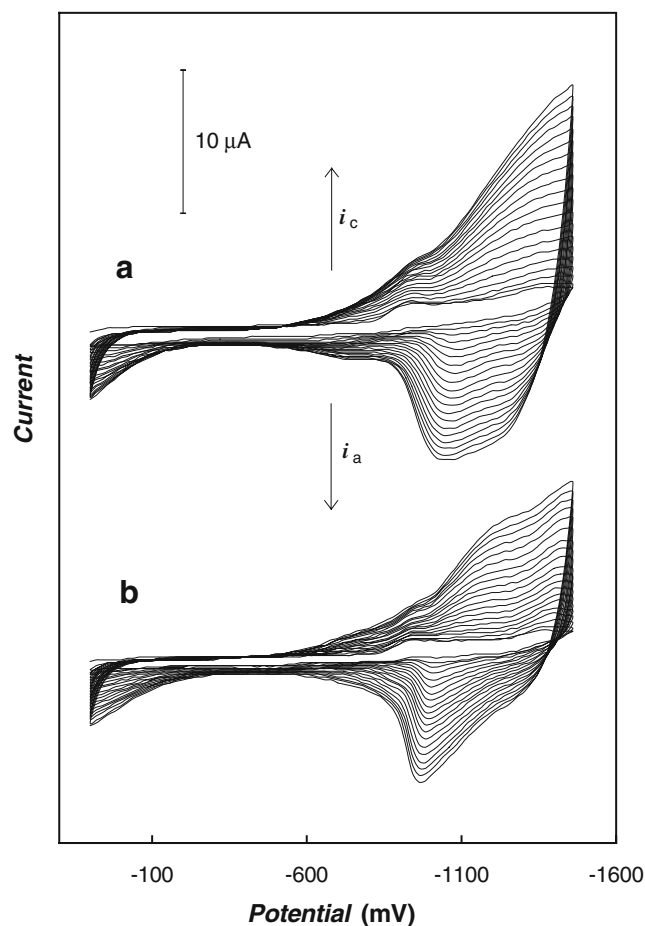
of pseudocapacitance is less reversible for  $C_{70}/Pd$  film. Specific capacitance,  $C_s$ , can be calculated by the integration of cyclic voltammograms according to the equation:

$$C_s = \frac{\int i dt}{\Delta E m} \quad (1)$$

where  $i$  is the pseudocapacitance current,  $\Delta E$  is the potential range of integration, and  $m$  mass of the polymer deposited on the electrode surface. Values of specific capacitances obtained this way are collected in Table 1. Relatively large values of specific capacitance were obtained for both films. It locates them among good supercapacitors. However, specific capacitances of the  $C_{60}/Pd$  films are significantly lower than reported in earlier paper [38]. This effect is related to the different conditions of film formation. In this paper, polymers were deposited in relatively high potential range. Therefore, the amount of polymer deposited on the electrode surface in each cycle is relatively large. The mass of  $C_{60}/Pd$  film deposited in 20 voltammetric cycles from solution containing 3.5 mM  $Pd(ac)_2$  and 0.25 mM  $C_{60}$  is about  $75 \mu\text{g cm}^{-2}$ . For comparison, the limiting mass of  $C_{60}/Pd$  layers studied earlier [38] was about  $25 \mu\text{g cm}^{-2}$ . It was shown, that at negative potentials, only a fraction of the polymer is reduced [33]. Therefore, for thicker films, the fraction of electrochemically inactive film increases, and

decrease in the specific capacitance is observed. This conclusion is supported by results presented in Table 1. A decrease of number of voltammetric cycles of polymer formation results in increase of film specific capacitance. Also, a very strong effect of grown solution composition on the film specific capacitance is observed. Both effects are related to the changes of the amount of polymer deposited on the electrode surface. For thinner  $C_{60}/Pd$  and  $C_{70}/Pd$  films obtained during deposition from solution with low concentration of  $Pd(ac)_2$  or for low number of voltammetric scans, values of specific capacitance are close to earlier published data.

Both, faradaic and capacitance components of the current depend linearly on the sweep rate. Therefore, a linear dependence of pseudocapacitance current on the sweep rate should be expected. Exemplary voltammograms recorded for different sweep rates and relation of current as a function of sweep rate are shown in Fig. 8 for  $C_{60}/Pd$  and  $C_{70}/Pd$  film. The specific capacitance,  $C_s$ , calculated from the slope of  $i-v$  linear relation was found to be equal to 155 and  $85 \text{ F g}^{-1}$  for



**Fig. 11** Multicyclic voltammograms for **a** 0.25 mM  $C_{60}$  and 0.85 mM  $[Rh(CF_3COO)_2]_2$ , and **b** 0.25 mM  $C_{70}$  and 0.85 mM  $[Rh(CF_3COO)_2]_2$  in acetonitrile/toluene (1:4, v:v) containing 0.1 M tetra(*n*-butyl) ammonium perchlorate recorded at Au (1.5 mm). The sweep rate was  $100 \text{ mV s}^{-1}$



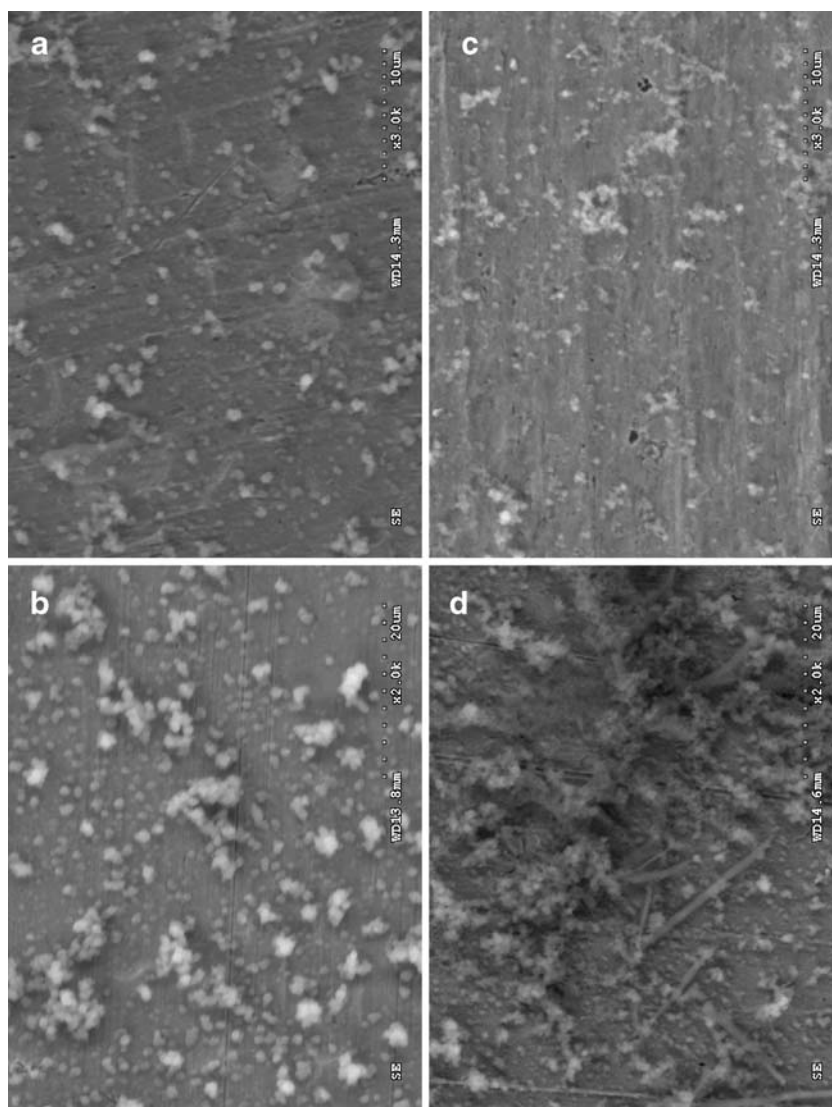
$C_{70}/Pd$  and  $C_{60}/Pd$  film, respectively. In the case of  $C_{70}/Pd$  film, a departure from the reversible capacitance behavior is observed for higher sweep rates.

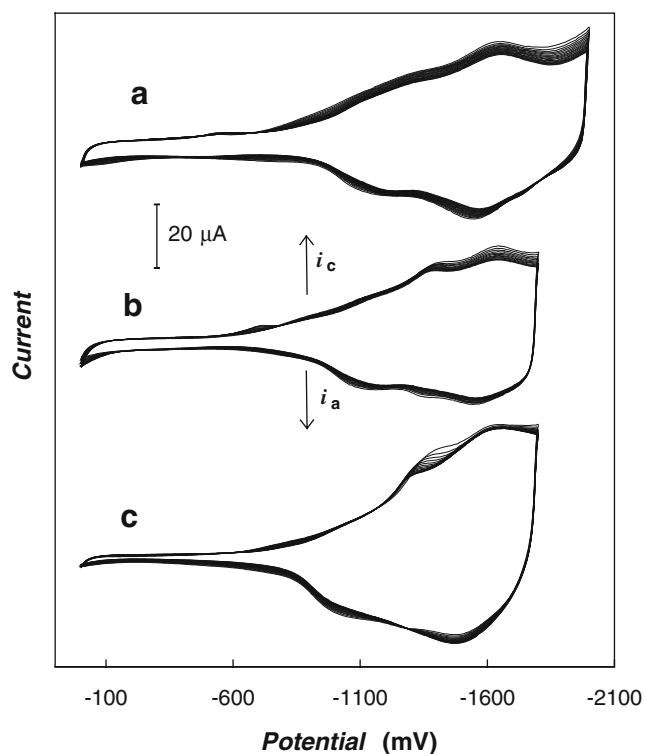
**$C_{60}/Pt$  and  $C_{70}/Pt$  polymers** Multicyclic voltammograms recorded in acetonitrile/toluene (1:4, v:v) solution containing  $[Pt(\mu-Cl)Cl(C_2H_4)]_2$  and  $C_{60}$  or  $C_{70}$  are shown in Fig. 9. Also in this case, the increase of the current in the following cycles, due to the redox-active film formation is observed. Similar to the  $C_{60}/Pd$  and  $C_{70}/Pd$  films, fullerene cages are bounded through platinum atoms in  $\eta^2$  fashion [34]. However, the addition effect, a shift of reduction potential toward values that are more negative with the increase of scan number is observed. This effect is stronger for  $C_{60}/Pt$  film. Such behavior indicates that the polymeric phase deposited on the electrode surface inhibits the process of platinum complex and fullerene reduction.

Figure 10 shows voltammograms recorded for electrode covered with  $C_{60}/Pt$  and  $C_{70}/Pt$  in solution acetonitrile containing only a supporting electrolyte. Similar to palladium-containing polymers, both films are electrochemically active at negative potentials due to the fullerene cages reduction. The shape of voltammograms and slope of current–potential relation at potentials of the film reduction indicate that electrode processes of  $C_{60}/Pt$  and  $C_{70}/Pt$  films are less reversible than their palladium analogs. These films are also much less stable in comparison to their palladium polymers. At potentials more negative than about  $-1,500$  mV, a slow decomposition of films is observed upon cyclic potential scanning.

**$C_{60}/Rh$  and  $C_{70}/Rh$  polymers** Multicyclic voltammograms of both fullerene and rhodium film formation are shown in Fig. 11. These voltammograms and results of EQCM study

**Fig. 12** SEM images of films formed on gold foil during 20 (a and c) or 40 (b and d) voltammetric cycle in the potential range  $+100$  to  $-1,450$  mV in acetonitrile/toluene (1:4, v:v) containing 0.1 M tetra(*n*-butyl) ammonium perchlorate and a and b 0.25 mM  $C_{60}$  and 0.85 mM  $[Rh(CF_3COO)_2]_2$ , and c and d 0.25 mM  $C_{70}$  and 0.85 mM  $[Rh(CF_3COO)_2]_2$

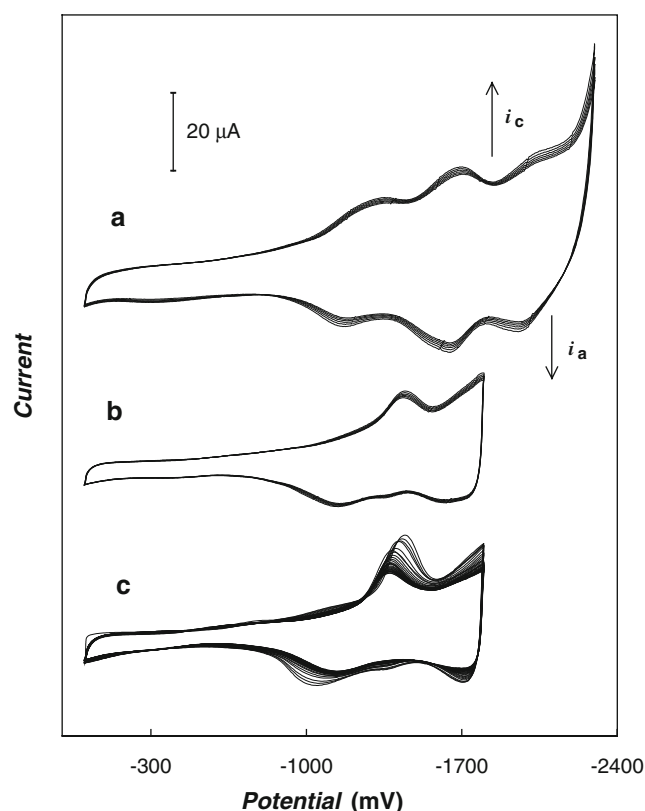




**Fig. 13** Cyclic voltammograms of  $C_{60}/Rh$  film in acetonitrile containing **a** 0.10 M tetra(ethyl)ammonium perchlorate, **b** 0.10 M tetra(*n*-butyl)ammonium perchlorate, and **c** 0.10 M tetra(*n*-hexyl)ammonium perchlorate recorded at Au (1.5 mm). The sweep rate was  $100 \text{ mV s}^{-1}$ . The  $C_{60}/Rh$  film was grown under cyclic voltammetry conditions in acetonitrile/toluene (1:4, v:v) containing 0.10 M tetra(*n*-butyl)ammonium perchlorate, 0.25 mM  $C_{60}$  and 0.85 mM  $[Rh(\text{CF}_3\text{COO})_2]_2$

show that the efficiency of  $C_{60}/Rh$  film formation is higher. Both films exhibit similar surface morphology (Fig. 12). Thin films are relatively flat with numerous small outcroppings on the surface. Thicker films are much more porous. However, the porosity of  $C_{70}/Rh$  is bigger than the porosity observed for  $C_{60}/Rh$  film. The structure of the polymer is a very important factor that determines the redox properties of the film. In the case of a sufficiently porous layer, the solid phase is easily penetrated by the solvent. Also, a transport of ions from the solution into the polymer takes place more easily.

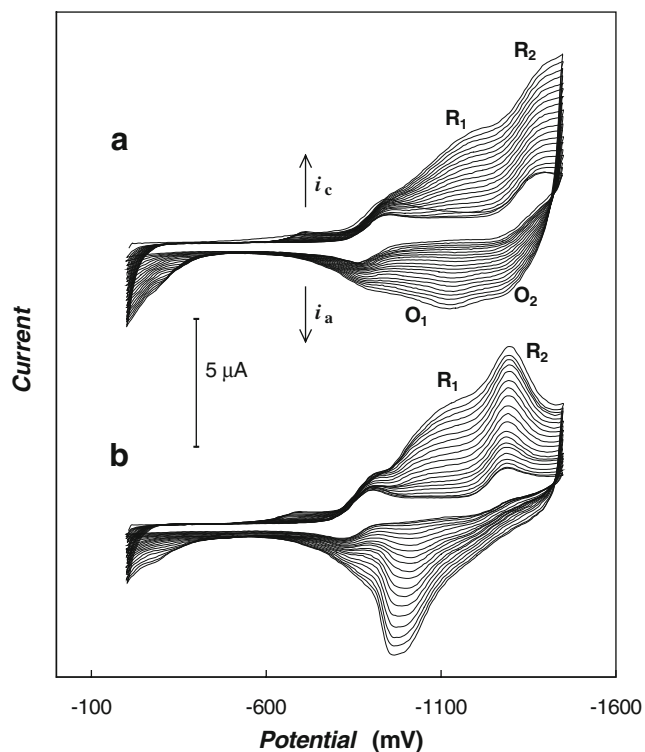
The porosity factor is probably responsible for the differences in voltammetric responses of  $C_{60}/Rh$  and  $C_{70}/Rh$  films in acetonitrile containing different supporting electrolytes. Voltammograms presented in Figs. 13 and 14 show electrochemical properties of  $C_{60}/Rh$  and  $C_{70}/Rh$ , respectively. Voltammetric response of both films depends on the size of supporting electrolyte cations indicating that the process of film reduction is accompanied by the transport of cations from solution into the film. Supporting electrolyte cations affect the charge of film reduction, reversibility of the polymer redox processes, and film



**Fig. 14** Cyclic voltammograms of  $C_{70}/Rh$  film in acetonitrile containing **a** 0.10 M tetra(ethyl)ammonium perchlorate, **b** 0.10 M tetra(*n*-butyl)ammonium perchlorate, and **c** 0.10 M tetra(*n*-hexyl)ammonium perchlorate recorded at Au (1.5 mm). The sweep rate was  $100 \text{ mV s}^{-1}$ . The  $C_{70}/Rh$  film was grown under cyclic voltammetry conditions in acetonitrile/toluene (1:4, v:v) containing 0.10 M tetra(*n*-butyl)ammonium perchlorate, 0.25 mM  $C_{70}$ , and 0.85 mM  $[Rh(\text{CF}_3\text{COO})_2]_2$

stability. Both films exhibit higher stability in solution containing small tetra(ethyl)ammonium cation. Under cyclic voltammetric conditions,  $C_{70}/Rh$  film is stable up to  $-2.3 \text{ V}$ . The potential range of this polymer stable voltammetric behavior is relatively broad compared to the stability of  $C_{60}/Pd$  film [42]. The decomposition of  $C_{60}/Rh$  film starts at potentials more negative than about  $-2.0 \text{ V}$ . In a solution containing bigger tetra(*n*-butyl)ammonium and tetra(*n*-hexyl)ammonium cations, both polymers are less stable and decompose at potentials more negative than about  $-1.8 \text{ V}$ . It was postulated that unstable behavior of fullerene polymers at negative potential is related to the structural changes of the film during cation incorporation and repulsion between negatively charged fullerene cages [31, 32].

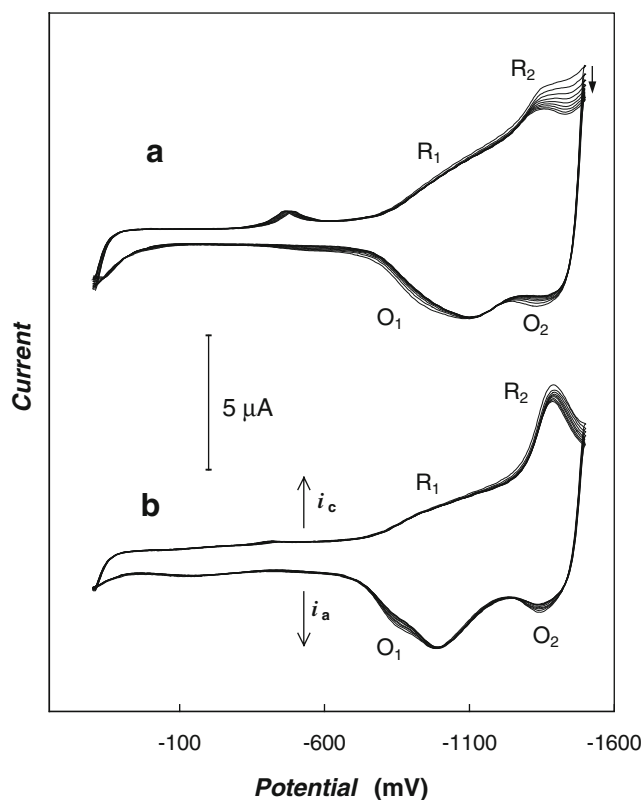
The  $C_{70}/Rh$  film exhibits also much better reversibility of electrochemical reduction processes, particularly in solution containing tetra(ethyl)ammonium cations (Fig. 14a). In the studied potential range, the reduction peaks related to the first three reduction steps of fullerene cage become better pronounced in comparison to the reduction peaks recorded for  $C_{60}/Rh$  film (Fig. 13a).



**Fig. 15** Multicyclic voltammograms for **a** 0.25 mM  $C_{60}$  and 0.85 mM  $\text{IrCl}(\text{CO})_2(p\text{-toluidine})$ , and **b** 0.25 mM  $C_{70}$  and 0.85 mM  $\text{IrCl}(\text{CO})_2(p\text{-toluidine})$  in acetonitrile/toluene (1:4, v:v) containing 0.1 M tetra(*n*-butyl)ammonium perchlorate recorded at Au (1.5 mm). The sweep rate was  $100 \text{ mV s}^{-1}$

*C<sub>60</sub>/Ir* and *C<sub>70</sub>/Ir* polymers Voltammograms of *C<sub>60</sub>/Ir* and *C<sub>70</sub>/Ir* film formation are shown in Fig. 15. In the potential range of polymer formation, iridium complex,  $\text{Ir}(\text{CO})_2\text{Cl}(p\text{-toluidine})$ , is redox inactive [30]. Currents recorded at negative potentials are related to the reduction of fullerenes from solution and film reduction processes. Voltammograms of film deposition show significant differences. In the studied potential range, two reduction steps of the films formed on the electrode surface are observed. Currents corresponding to the first reduction step of fullerene involved in polymeric network,  $R_1$ , are similar for both polymers. The broad reduction peak  $R_2$ , observed on the voltammograms of *C<sub>60</sub>/Ir* film formation, is responsible for the second reduction step of *C<sub>60</sub>*. In the case of *C<sub>70</sub>/Ir* film, this peak is much sharper and better pronounced. The second *C<sub>70</sub>/Ir* reduction step occurs at less negative potentials than the second step of *C<sub>60</sub>/Ir* reduction. In anodic cycle, currents related to two oxidation steps,  $O_1$  and  $O_2$ , are observed.

A similar behavior is observed for *C<sub>60</sub>/Ir* and *C<sub>70</sub>/Ir* films in acetonitrile solution containing only supporting electrolyte (Fig. 16). Also in this case, peaks related to the fullerene cage reduction steps are better separated and pronounced for *C<sub>70</sub>/Ir* film.



**Fig. 16** Cyclic voltammograms of **a**  $C_{60}/\text{Ir}$  and **b**  $C_{70}/\text{Ir}$  films in acetonitrile containing 0.10 M tetra(*n*-butyl)ammonium perchlorate recorded at Au (1.5 mm). The sweep rate was  $100 \text{ mV s}^{-2}$ . The  $C_{60}/\text{Ir}$  and  $C_{70}/\text{Ir}$  films were grown under cyclic voltammetry conditions in acetonitrile/toluene (1:4, v:v) containing 0.10 M tetra(*n*-butyl)ammonium perchlorate, 0.25 mM  $C_{60}$  or  $C_{70}$ , and 0.85 mM  $\text{IrCl}(\text{CO})_2(p\text{-toluidine})$

## Conclusions

So far, studies of formation and properties of co-polymers of fullerenes and transition metal complexes were focused on *C<sub>60</sub>*-containing materials. In this paper, processes of formation and properties of *C<sub>60</sub>/M* and *C<sub>70</sub>/M* ( $M = \text{Pt}, \text{Pd}, \text{Ir}, \text{Rh}$ ) are compared. For the same condition of electropolymerization, efficiency of *C<sub>70</sub>/M* film formation is higher than the yield of *C<sub>60</sub>/M* deposition. Also, processes related to the reduction of fullerene cage are more reversible for *C<sub>70</sub>* containing-films in comparison to the *C<sub>60</sub>/M* layers. Voltammograms of *C<sub>70</sub>/M* films in acetonitrile containing supporting electrolyte exhibit reduction peaks that are better defined and separated. Both differences in yield of electropolymerization and redox properties of *C<sub>60</sub>/M* and *C<sub>70</sub>/M* are probably related to structural differences of these films. Films containing *C<sub>70</sub>* exhibit higher porosity in comparison to *C<sub>60</sub>* analogs. Therefore, transport of counterions during the electrode processes and solvent swelling are easier for *C<sub>70</sub>/M*.

In fullerene/Pd and fullerene/Pt films, *C<sub>60</sub>* or *C<sub>70</sub>* cages are bounded through palladium or platinum atoms to form a polymeric network. These films are formed in potential

range of metal complex reduction [31, 34]. Despite the similarity in the mechanism of film formation and film structure, both polymers exhibit different electrochemical properties. In the case of C<sub>60</sub>/Pt and C<sub>70</sub>/Pt systems, the polymeric phase deposited on the electrode surface inhibits the reduction processes at negative potentials. Also, charge transfer processes related to the reduction of fullerene cages in fullerene/Pt films are much slower and less reversible in comparison to the fullerene/Pd films.

In the case of fullerene/Rh and fullerene/Ir films, the fullerene cages are bridged by Rh(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> or Ir(CO)<sub>2</sub> moieties [30]. The voltammetric responses of these polymers in acetonitrile solution indicate a lower rate of charge transfer processes in comparison to fullerene/Pd films.

The spacer bridging fullerene cages also influences the yield of polymer formation. The highest yield of polymer formation was observed for fullerene/Rh systems. Yields of fullerene/Pt and fullerene/Ir electropolymerization were much lower in comparison to the two other studied systems.

A comparison of voltammograms of investigated films recorded in acetonitrile solution containing supporting electrolyte only indicates that fullerene/Pd and fullerene/Rh can be considered as good electrochemical capacitors. In the case of rhodium films, a typical capacitance behavior, pseudorectangular cathodic profile of voltammograms, is observed only in low potential range, limiting its application for capacitors. Therefore, in this paper, capacitance studies were focused on C<sub>60</sub>/Pd and C<sub>70</sub>/Pd films. Studied polymers exhibit high pseudocapacitance. Specific capacitance of polymers increase with decrease in size of supporting electrolyte cations. C<sub>70</sub>/Pd films exhibit better capacitance performance than films of C<sub>60</sub>/Pd.

Values of specific capacitance reported in this paper are generally lower than what were given previously [38] for films deposited on smooth gold electrode. This effect is related to the differences in conditions of film formation. Results presented in this paper indicate that capacitance performance of the polymer depends on the amount of polymeric material deposited on the electrode surface. However, only a fraction of the film having direct contact with the solution takes place in electrode processes. Therefore, the fraction of electrochemically inactive material becomes bigger for thicker films, and specific capacitance decreases.

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