

Available online at www.sciencedirect.com



ELECTROCHIMICA

Electrochimica Acta 53 (2008) 4550-4556

www.elsevier.com/locate/electacta

Electrochemical studies of osmium-(pyrrole-methyl) pyridine-co-polymers deposited using the membrane template method

Susan Warren¹, Rodica Doaga¹, Timothy McCormac¹, Eithne Dempsey^{*,1}

Centre for Research in Electroanalytical Technologies (CREATE), Department of Science, Institute of Technology Tallaght, Tallaght, Dublin 24, Ireland

Received 6 July 2007; received in revised form 3 October 2007; accepted 12 January 2008

Available online 31 January 2008

Abstract

The electrochemical characterisation of films formed by co-polymerisation of $[Os(2,2'-bipyridine)_2XCI]$ (Os–PMP) where *X* is 3-(pyrrole-1yl-methyl)pyridine with 3-methyl thiophene or 1,2-diaminobenzene was carried out. The use of the membrane template method, which allowed growth of tubules of redox co-polymer was employed in the case of 1,2-diaminobenzene. Cyclic voltammetry allowed formation of the most stable 3-methylthiophene/Os–PMP films while chronocoulometry was used to co-polymerise Os–PMP with 1,2-diaminobenzene, resulting in stable films of co-polymer micro-tubules with thin-film behaviour up to 0.5 V s^{-1} ($r^2 = 0.9997$). Surface analysis was carried out using SEM. © 2008 Elsevier Ltd. All rights reserved.

Keywords: Osmium complex; Co-polymer; Membrane template method

1. Introduction

A polymer/co-polymer may play a highly varied role as a membrane component of chemical and/or biological sensor devices. It may serve as a catalytic layer, a redox mediator, or it may provide for molecular recognition and/or pre-concentration of analyte [1]. Possibly the most important advantage of polymer coatings is that they provide a three-dimensional reaction zone at the electrode surface, which generates an increase in the flux of reactions that occur there, in turn augmenting sensitivity.

For many years the electron acceptor properties of osmium complexes have resulted in their use as electron transfer mediators for a number of flavoproteins. Osmium bipyridine complexes have been attached to various conducting polymer backbones [2,3] which in turn were cross-linked to enzymes, forming electrically wired reagentless enzyme systems. The incorporation of the biocatalyst together with a long chain osmium complex-modified pyrrole derivative with a long flexible spacer arm during the electropolymerisation process was described by Habermuller et al. [4]. Co-polymerisation of this new mediator-modified pyrrole monomer with pyrrole was examined. The co-polymerisation of an osmium bipyridine complex modified with a pyrrole unit connected via a long spacer arm in the presence of pyrrole-3-carboxylic acid and the enzyme, glucose oxidase, also resulted in a stable reagentless biosensor [5].

The electrochemical homopolymerisation of the short chain $[Os(2,2'-bipyridine)_2(3-(pyrrole-1yl-methyl)pyridine)Cl⁻]$ (Os–PMP) has not been possible to date, to the best of our knowledge, but may be co-polymerised with other monomers such as pyrrole and *N*-methylpyrrole [6]. The ruthenium analogue $[Ru(2,2'-bipyridine)_2(PMP)Cl]^+$ has been used to generate electronically conducting co-polymer films of pyrrole [7] and 3-methyl thiophene [8] and their ionic and electronic conductivity examined.

In this work, co-polymer films of Os–PMP with poly-3methylthiophene and 1,2-diaminobenzene co-polymers were formed, the latter grown using the membrane-templated method. This procedure entails synthesis or deposition of the desired material within the pores of nano/micropore membranes resulting in polymeric nano/micro-tubules, the size of which depends on the membrane pore size. The membranetemplated method has been used for synthesis of polymers such as 3-methylthiophene [9], poly-aniline and its derivatives [10–13], poly-acetylene [14] diaminobenzene derivatives [15] and polypyrrole [16–19]. The electronic conductivity of polymers synthesised by the templated method was found to be

^{*} Corresponding author. Tel.: +353 1 4042862; fax: +353 1 4042700.

E-mail address: eithne.dempsey@ittdublin.ie (E. Dempsey).

¹ ISE members.

^{0013-4686/\$ –} see front matter © 2008 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2008.01.049

greater by an order of magnitude than that of the bulk samples (powders and thin films) of the same polymers [20]. When polymers are synthesised within the pores of the track-etched polycarbonate membranes, the polymer preferentially nucleates and grows on the pore walls, resulting in polymeric tubules at short polymerisation times [18]. Due to their finite small size, high surface area, and porosity, polymer nanotubes have wide applications ranging from chemical, biological to microelectronics, energetics, optics, and medical sensing [11]. The thickness and length of the polymer nanostructures depends on polymerisation/co-polymerisation parameters such as polymerisation time, temperature, pH, dopant counterion, etc. [16].

In this research, the synthesis, characterisation and application of Os–PMP, co-polymerised with 3-methyl thiophene or 1,2-diaminobenzene was evaluated electrochemically and the use of polymeric tubules grown using the membrane template method was employed as a possible method to enhance surface area and electron transfer capabilities of the film.

2. Materials and methods

2.1. Materials

Potassium hexachloroosmate-K2OsCl₆ (Aldrich), 97% 3-(pyrrol-1yl-methyl)pyridine/PMP (Aldrich), 99+% ethylene glycol (Aldrich), 95+% ammonium hexafluorophosphate NH_4PF_6 (Aldrich), $[Os(bpy)_2PMP(Cl)]PF_6$ was synthesised as described below, tetrabutylammonium perchlorate-TBAP (Sigma), 99+% 3-methylthiophene (Acros Organics), HPLC Grade Acetonitrile-CH3CN (Aldrich) used for electrochemical experiments was previously dried using magnesium sulphate and then 4 Å molecular sieves, 8-12 mesh (Aldrich), HPLC Grade dichloromethane (Labscan), deuterated acetonitrile- d_2 99.5 atom% D, phosphate-buffered saline tablets-PBS (Aldrich), sodium dihydrogen phosphate ACS (Merck), potassium chloride-KCl (Fluka), dimethylformamide/DMF (Aldrich). 1,2-Phenylenediamine (Sigma-Aldrich) was purified three times by recrystallisation from water and polycarbonate track etch membranes with pores of 1 µm PCM (polycarbonate membrane) were obtained from Sterlitech Corporation.

2.2. Procedures

2.2.1. Co-polymerisation of $[Os(bpy)_2PMP(Cl)]PF_6$ and 3-methylthiophene

The optimum ratio for co-polymerisation was found to be 3.5 mM [Os(bpy)₂PMP(Cl)]PF₆ and 20 mM 3-methylthiophene. The osmium complex was dissolved in 0.1 M TBAP/acetonitrile, before adding the 3-methylthiophene and all solutions were made up to a final volume of 3 cm^3 . Solutions were degassed prior to co-polymerisation. Co-polymer films formed using cyclic voltammetry at a glassy carbon electrode, were cycled between $-0.2 \rightarrow +1.4 \text{ V}$ vs. Ag | Ag⁺ using a scan rate of 0.1 V s⁻¹. Films formed by chronocoulometry were formed by holding the potential at +1.4 V vs. Ag | Ag⁺. A fresh solution was used for each film to minimise errors. After formation of each film the modified electrode was rinsed carefully with the electrolyte in which the film was to be examined prior to analysis.

2.2.2. Co-polymerisation of $[Os(bpy)_2PMP(Cl)]PF_6$ and 1,2-diaminobenzene (DAB) using the membrane template method

The co-polymerisation was carried out using chronocoulometry, holding the potential at 1.0 V for 500 s. A polycarbonate membrane (PCM) was held on the GCE using an *O* rubber ring and the electrode was then placed in a solution of 3.5 mM [Os(bpy)₂PMP(Cl)]PF₆ and 5 mM 1,2diaminobenzene, made up in 0.1 M TBAP/CH₃CN. Following polymerisation, the template membrane was dissolved by soaking the electrode for 10 min, under continuous stirring, in dichloromethane, leaving the co-polymer nanostructures on the surface of the electrode. The [Os(bpy)₂PMP(Cl)]PF₆-1,2diaminobenzene (Os–PMP–DAB) co-polymer was stabilised by scanning for 10 cycles at a scan rate of 5 mV s^{-1} .

2.3. Apparatus

Cyclic voltammetry, chronocoulometry and amperometric experiments were conducted using a CH Instrument 750 potentiostat. A single-compartment electrochemical cell was used with a platinum counter electrode and Ag | AgCl | KCl (3 M) reference for aqueous solutions. For non-aqueous solutions the reference employed was a silver wire in contact with an acetonitrile solution of AgNO₃ (0.01 M) and 0.1 M of the same supporting electrolyte as that employed in the cell (referred to as Ag | Ag⁺ throughout the text). All films were prepared using glassy carbon electrodes which were polished through three grades of alumina and sonicated in deionised water prior to use. NMR studies were carried out on a Joel 300 MHz spectrometer, and UV studies were done using UV-160A (Shimadzu). SEM studies were performed using a Hitachi S-2400N system.

2.4. Synthesis

 $Os(bpy)_2Cl_2$ was prepared as described previously [21]. Preparation of Os(bpy)₂PMP(Cl)]PF₆ was adapted from synthetic methods previously described by Warren et al. [22] and Serroni et al. [23]. Os(bpy)₂Cl₂ (0.175 mmol/100 mg) and 3-(pyrrol-1yl-methyl) pyridine (0.185 mmol/29.23 mg) were stirred in the dark in ethylene glycol (16 cm³) for 20 min to ensure the solids had dissolved. The solution was then heated to reflux temperature for 30 min. The solution was allowed to cool to room temperature before addition of deionised water (16 cm^3) and filtration to remove any unreacted starting materials. Excess NH₄PF₆ was added to the filtrate and this solution was then placed at 4 °C for 30-60 min prior to filtration of the product to ensure that complete precipitation had occurred. The product was dried under vacuum and then recrystallised from a 2:1 acetone/water mixture. The purified product was filtered, washed with copious amounts of water and dried overnight in a vacuum oven at 60 °C, 200 mbar pressure. Percentage yield of product obtained was 93% (136.9 mg).



Fig. 1. $[Os(bpy)_2PMP(Cl)]PF_6$ at GCE. in 0.1 M tetrabutylammonium perchlorate/acetonitrile at scan rate of 0.1 V s⁻¹, vs. Ag | Ag⁺.

¹H NMR: (300 MHz, acetonitrile- d_2) values given in ppm relative to SiMe₄ (see Fig. 1 inset).

3-(Pyrrole-1-yl-methyl) pyridine unit

- Ring A: δ, 6.45 (s, H₂, H₅), 6.04 (d, H₃, H₄).
- Ring B: δ, 4.93 (s).
- Ring C: δ, 8.47 (d, H₂), 8.32 (t, H₆), 7.47 (dd, H₄), and 7.27 (m, H₅).
- Bipyridine ring D: δ, 8.45 (d, H₂), 8.33 (t, H₄), 7.85 (m, H₅), and 7.38 (m, H₄).
- Bipyridine ring E: δ, 7.61 (t, H₂), 7.27 (m, H₅), 7.85 (m, H₄), and 6.93 (m, H₃).
- Bipyridine ring F: δ, 7.61 (t, H₂), 7.85 (m, H₅), 7.85 (m, H₄), and 6.93 (m, H₃).
- Bipyridine ring G: δ: 8.33 (t, H₂), 7.85 (m, H₄), 7.22 (m, H₅), and 6.93 (m, H₃).

2.5. Electrochemical characterisation

Characterisation of starting materials and the $[Os(bpy)_2 PMP(Cl)]PF_6$ (Os–PMP) product was carried out in 0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile. $[Os(bpy)_2PMP(Cl)]Cl$ was analysed in a 0.1 M KCl/PBS solution vs. Ag | AgCl | KCl (3 M). All solutions were degassed for a minimum of 10 min prior to analysis.

2.6. SEM

Following film preparation electrodes were mounted and stabilised using parafilm. A strip of aluminum foil, with a hole pierced in the centre to allow access to the sample surface, was placed over the electrode to minimise charging effects of the electron beam on the electrode surface. Alternatively sputtering of a nanometer thick layer of gold was performed in order to minimise or avoid effects of electron beam onto the electrode surface and charging of the sample.

3. Results and discussion

3.1. Characterisation of [Os(bpy)₂PMP(Cl)]⁺

Spectroscopic characterisation using UV–visible spectroscopy of $[Os(bpy)_2PMP(Cl)]PF_6$ (in acetonitrile) resulted in $\lambda_{max} = 294$ nm ($\varepsilon = 8,185$ M⁻¹ cm⁻¹). A cyclic voltammogram of the $[Os(bpy)_2PMP(Cl)]PF_6$ complex (Fig. 1) shows the reversible Os^{2+/3+} couple at +0.035 V vs. Ag | Ag⁺, an irreversible oxidation wave at +1.092 V vs. Ag | Ag⁺ attributed to the pyrrole ligand, and two reversible peaks at –1.790 and –2.088 V vs. Ag | Ag⁺ pertaining to the successive reductions of the bipyridine ligands, bpy^{0/-1} and bpy^{-1/-2}, respectively. The third bipyridine reduction was expected but not observed as it occurred outside the electrochemical window of our system.

3.1.1. Co-polymer film studies of $[Os(bpy)_2PMP(Cl)]PF_6$ and 3-methylthiophene

All films were grown as described above both by cyclic voltammetry and chronocoulometry, and analysed in 0.1 M TBAP/acetonitrile or 0.1 M LiClO₄/H₂O. Table 1 shows the electrochemical data for films formed using chronocoulometry. Films analysed in 0.1 M TBAP/MeCN showed a consistent $E_{1/2}$ value of + 0.059 V vs. Ag | Ag⁺ for films with charges below 1×10^{-4} C. Films analysed in 0.1 M LiClO₄/H₂O showed a higher $E_{1/2}$ of +0.312 V vs. Ag | AgCl, and much larger ΔE_p and FWHM values, indicating that it was more difficult to oxidise the film in aqueous electrolytes. The increase in ΔE_p and FWHM values with increasing film thickness could be related to the increasing hydrophobicity of the film as its thickness increases, resulting in an increasing resistive effect within the film towards the hydrophilic electrolyte and solvent.

Table 2 shows the electrochemical data for films formed by cyclic voltammetry and analysed in organic and aqueous electrolytes. Once again the films studied in aqueous electrolyte

Table 1

Electrochemical data for the Os^{2+/3+} osmium/3-methylthiophene films formed by chronocoulometry analysed in 0.1 M TBAP/acetonitrile or 0.1 M LiClO₄/H₂O

Charge passed (mC)	Film $Q \times 10^5$ (C)		$E_{1/2}$ (V)	$E_{1/2}$ (V)		$\Delta E_{\rm p} ({\rm mV})$		FWHM _{OX} (mV)		FWHM _{RED} (mV)	
	MeCN	H ₂ O	MeCN	H ₂ O	MeCN	H ₂ O	MeCN	H ₂ O	MeCN	H ₂ O	
2.5	0.987	0.317	0.059	0.310	27	75	122	180	-102	-148	
5.0	1.276	0.429	0.059	0.314	27	87	120	204	-104	-146	
10.0	1.470	0.608	0.059	0.313	32	86	130	220	-108	-144	
15.0	2.491	_ ^a	0.070	_ ^a	33	_ ^a	136	_a	-100	_ ^a	

^a Films formed for greater than 10 mC showed no electrochemistry in aqueous electrolyte.

Cycles	< 10 ⁵ (C)		$E_{1/2}$ (V)		$\Delta E_{\rm p} ({ m mV})$		FWHM _{OX} (mV)		FWHM _{RED} (mV)	
0. H2	M LiClO4/ 0	0.1 M TBAP/ acetonitrile	0.1 M LiClO ₄ / H ₂ O	0.1 M TBAP/ acetonitrile	0.1 M LiClO ₄ / H ₂ O	0.1 M TBAP/ acetonitrile	0.1 M LiClO ₄ / H ₂ O	0.1 M TBAP/ acetonitrile	0.1 M LiClO ₄ / H ₂ O	0.1 M TBAP/ acetonitrile
1 0.8	02	0.409	0.315	0.082	70	21	168	113	-139	
2 1.	13	0.860	0.319	0.077	73	25	166	117	-141	-103
3 2.	17	1.277	0.317	0.078	71	29	169	120	-143	-101
4 2.4	58	1.842	0.309	0.079	68	27	174	117	-148	-103
5 2.:	39	2.772	0.318	0.074	74	35	169	121	-151	-111
6 2.	84	4.528	0.307	0.080	68	34	168	126	-151	-105
7 2.	68	5.020	0.310	0.079	82	40	172	126	-146	-109

Table 2

resulted in larger ΔE_p and FWHM values in comparison to films studied in organic media. All films were prepared using 0.1 M TBAP/MeCN, and analysed in that same solvent system for organic film studies and in 0.1 M LiClO₄/H₂O for aqueous film studies. It would be assumed that the film would have improved behaviour in a solvent and electrolyte system from which it was formed, considering that both were employed in the polymerisation process and become an integral part of the resulting polymer film [24]. ΔE_p and FWHM values were again observed to increase with film thickness. The E_{1/2} values appeared to be independent of film thickness for both electrolytes and it was observed that the film was more difficult to oxidise in aqueous electrolyte.

Films formed using both methods with similar charge values were evaluated using cyclic voltammetry and it was noticeable that the film formed by chronocoulometry had a much larger background current (data not shown), which was accredited to the conducting polymer backbone. This could be due to the differing timescales of the two techniques employed. In chronocoulometry, the potential was stepped just once from -0.2 V vs. $Ag \mid Ag^{+}$ to the oxidation potential of the 3-methylthiophene, +1.4 V vs. Ag | Ag⁺ and held there until the appropriate charge has passed. The timescale of this experiment was in the region of seconds, e.g. 15 mC film takes 25 s. In the case of cyclic voltammetry the potential was continually swept from -0.2 to 1.4 V vs. Ag | Ag⁺, a process that took minutes. From this perspective it is possible that films formed by CV contained less conductive polymer backbone as the timescale of the experiment leads to degradation of the conductive properties of the polymer. When cyclic voltammograms of films prepared using each method were compared in aqueous electrolyte there was a much smaller Faradaic current when compared to the films studied in acetonitrile. This phenomenon may be attributed to the known hydrophobicity of polythiophenes, which can result in less efficient electrochemical behaviour in aqueous media [1].

Fig. 2 shows cyclic voltammograms for two films, one studied in organic electrolyte and the other studied in an aqueous electrolyte. Firstly the film in aqueous media has a more positive $E_{1/2}$, indicating that this film is more difficult to oxidise/reduce



Fig. 2. Cyclic voltammograms for a film formed by CV and analysed in 0.1 M TBAP/MeCN (—) and 0.1 M LiClO₄/H₂O (_____) at v = 0.010 V s⁻¹.

in aqueous media. Secondly, although the charge for both films is somewhat similar $\sim 2 \times 10^{-5}$ C, the shapes and current responses of the two CVs are quite different. The film studied in organic media was more typical of a thin film with $\Delta E_p = 32$ mV. The aqueous film however, showed a larger $\Delta E_p = 72$ mV and the oxidation and reduction peaks appeared broader than those of the organic film—suggesting slower charge transport properties. Plots of ΔE_p vs. scan rate (υ) for a thin (one cycle) and a thick (seven cycles) film were carried out in 0.1 M TBAP/MeCN. The thin film showed little dependence on scan rate (data not shown).

The influence of scan rate on current response was analysed for films grown using CV. A general trend that occurred between all films studied in organic electrolyte was that the slope for $I_{p,c}$ was slightly less than that obtained for $I_{p,a}$. This suggests that the insertion of the ClO₄⁻ anion into the film occurred faster than expulsion of the anion from the film. As the co-polymer film was polymerised from 0.1 M TBAP/MeCN, this electrolyte and solvent are an integral part of the co-polymer matrix, and thus would have an affinity for that particular electrolyte. For films studied in aqueous electrolytes, this trend was seen to reverse, whereby the $I_{p,c}$ slopes were found to be larger than those for the $I_{p,a}$ values. Once again this can be explained in terms of anion affinity of the film, the larger $I_{p,c}$ values indicating that the anion expulsion process required less time to occur relative to the anion inclusion step. In terms of the anion expulsion, as the co-polymer film has a poor affinity for the aqueous anion it will repel it with more ease relative to that of the anion which partially consists of its makeup, resulting in a larger slope and $\sqrt{D_{\rm CT}C_{\rm M}}$ value (where D_{CT} = charge transport diffusion co-efficient and $C_{\rm M}$ = concentration of redox sites) for $I_{\rm p,c}$ relative to the $I_{\rm p,a}$.

For films analysed in both organic and aqueous media, thinfilm behaviour was observed up to four formation cycles, up to a scan rate of 0.3 V s^{-1} . Fig. 3(a) and (b) is graphical representations of the Randles–Sevcik plots for thick and thin films in organic and aqueous electrolytes, respectively. It was observed that $\sqrt{D_{\text{CT}}C_{\text{M}}}$ values increased (from 2×10^{-9} to $15 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-0.5}$) with increasing cycle number (one to five cycles) as expected. Values are given for films formed up to five cycles as in the case of greater loadings a large shift in $E_{1/2}$ and ΔE_{p} with respect to scan rate was observed. As film thickness was unknown it was not possible to isolate individual D_{CT} and C_{M} values.

Films grown using two cycles were analysed for 100 cycles at a scan rate of 0.1 V s^{-1} , and stability described as the % decrease in anodic current. It was observed as expected that Os/3-MT copolymer films were more stable in the organic electrolyte (1.3%) than the aqueous system (2.8%).

3.1.2. Co-polymerisation of $[Os(bpy)_2PMP(Cl)]PF_6$ and 1,2-diaminobenzene (DAB) using the membrane template method

The electrochemical co-polymerisation of $Os(bpy)_2$ PMP(Cl)]PF₆ with 1,2-diaminobenzene was carried out using chronocoulometry in 0.1 M TBAP/CH₃CN, holding the potential at 1.0 V for 500 s, using the membrane tem-



Fig. 3. (a) Randles–Sevcik plots for thin and thick films studied in 0.1 M TBAP/MeCN. (b) Randles–Sevcik plots for thin and thick films studied in 0.1 M $LiClO_4/H_2O$.

plate method. The co-polymerisation was performed in the presence of the polycarbonate membrane (PCM) with pores of $\theta \approx 1 \,\mu$ m. Following dissolution of the membrane the GCE/Os(bpy)₂PMP(Cl)]PF₆–DAB nanostructures system were examined electrochemically and using SEM.

This technique allows formation of microrods of polymer grown in the pores of a polycarbonate membrane. The copolymer films formed with and without the membranes were analysed at different scan rates in the 0.1 M KCI/PBS pH 7.00. The Os couple had a more positive potential in an aqueous electrolyte, indicating that this film was more difficult to oxidise/reduce in aqueous media (similar to Os–PMP/3-MT films). This was the case for films prepared normally and for those where the polycarbonate membrane (PCM) was employed to generate redox co-polymer tubules.

Table 3 shows a comparison of electrochemical data for Os–PMP–DAB films grown normally (i) and using the membrane templating method (ii). In terms of surface coverage (Γ) (measured at 5 mV s⁻¹), the co-polymer films showed similar values 2.5×10^{-10} mol cm⁻² and 2.9×10^{-10} mol, respectively. The % decrease in current intensity (I_{pa} and I_{pc} % loss), were 9.7% and 5.9% for the film grown normally and 3.7% and 2.9%

4555

Scan rate (mV s^{-1})	$E_{1/2}$ (V)		$\Delta E_{\rm p}$ (V)		FWHM _{OX} (mV)		FWHM _{RED} (mV)	
	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)
10	0.346	0.338	0.052	0.044	192	178	166	162
50	0.343	0.335	0.050	0.041	194	176	170	166
100	0.342	0.335	0.048	0.038	196	178	172	166
500	0.343	0.335	0.063	0.052	222	184	174	178

Electrochemical characterisation for the osmium co-polymer Os-PMP-DAB films in 0.1 M KCl/PBS (pH 7.00) following formation by chronocoulometry in the absence (i) of and in the presence of (ii) polycarbonate membrane

for film grown in the presence of the polycarbonate membrane, demonstrating an increase in stability for the nanostructured film. ΔE , $E_{1/2}$ and full width at half-maximum both for oxidation and reduction peaks (FWHM) were evaluated and films formed in the presence of polycarbonate membrane had slightly lower values for each parameter demonstrating that films were thinner and easier to oxidise.

Table 3

Fig. 4 shows the dependence of current vs. scan rate for the Os(bpy)₂PMP(Cl)]PF₆–DAB co-polymer analysed in 0.1 M TBAP/CH₃CN, after the membrane was dissolved in CH₂Cl₂, demonstrating thin-film behaviour with linearity up to 0.5 V s⁻¹ ($r^2 = 0.9992$ and 0.9997 for $i_{p(c)}$ and $i_{p(a)}$, respectively).

SEM images of 1,2-DAB alone growth through the pores of PCM (Fig. 5(A)) showed the rod like structures of dimensions approximately $5-10 \,\mu\text{m}$. The image shown in Fig. 5(B) was obtained upon dissolution of the template membrane showing the aggregation of co-polymer nanostructures into structures with dimensions ranging from 20 μ m to approximately 80 μ m spaced at regular intervals across the surface of the electrode.

Hulteen and Martin [25] reported that in developing template synthetic methods two typical concerns need to be taken into consideration, a solvophobic component (because the polycarbonate membranes are more hydrophobic than hydrophilic) to the interaction between the co-polymer and the pore wall or/and an electrostatic component if the polymer is cationic because there are anionic sites on the pore walls of the polycarbonate membranes. The fact that the individual nanostructures aggregated forming clusters (Fig. 5(B)) may be due to the advent of capillary forces between the nanotubes upon dissolution of the



Fig. 4. Effect of scan rate, between 5 and 500 mV s^{-1} , for GCE/Os(bpy)₂ PMP(Cl)]PF₆-DAB sensor in 0.1 M TBAP/CH₃CN.

template membrane. The prevention of the aggregation process may be possible by applying an ultrasonication step in the presence of a surfactant solution, but this phenomenon could damage the larger nanotubes and would also remove the nanostructures from the electrode resulting in formation of a suspension [16]. A future approach could be based on the application of templated method in order to synthesise polymers using the polycarbonate membranes by firstly converting one side of the membrane into a working electrode. This has been accomplished by electroplating the membrane using Au or Pt solutions, resulting in Au or Pt microelectrodes at the base of each of the pores [17]



Fig. 5. (A) SEM image of GCE/polydiaminobenzene tubule network, magnification $3000\times$, accelerating voltage 10 kV, resolution $10 \,\mu\text{m}$; (B) SEM image of Os(bpy)₂PMP(Cl)]PF₆-diaminobenzene fibrilar co-polymer aggregate, magnification $2000\times$, accelerating voltage of 10 kV, resolution $20 \,\mu\text{m}$.

which were then employed to electrochemically synthesise the polymer tubules into each pore.

4. Conclusions

Successful synthesis and characterisation of a pyrrole modified osmium complex, [Os(bpy)₂PMP(Cl)]PF was performed. To the best of our knowledge the research presented here is the first report based on Os–PMP immobilisation by polymerisation with 3-methylthiophene and 1,2-diaminobenzene. Further novelty lies in the use of the membrane template method to form redox tubules of Os–PMP and DAB on the electrode surface.

The complex was firstly co-polymerised with 3-methylthiophene, using cyclic voltammetry and chronocoulometry resulting in a stable redox active film. Secondly, a co-polymer based on Os(bpy)₂PMP(Cl)]PF₆ and 1,2diaminobenzene, was formed using the membrane templating method. Electrochemical evaluation was carried out and it was found that the Os-PMP/DAB film had similar characteristics to that of the Os-3MT co-polymer film, showing improved characteristics in organic electrolytes (thin-film behaviour was demonstrated up to 0.5 V s^{-1}). Those Os–PMP/DAB films formed using the membrane template method had improved stability and were easier to oxidise relative to those examined in the absence of the tubule structure on the surface. It was expected that an enhanced surface area would be evident with increased surface coverage, however, due to apparent aggregation of the tubules into regularly spaced clusters on the surface the coverage was not significantly improved. Future work will examine further this process and will also extend the method to include immobilisation of glucose oxidase with subsequent evaluation of the mediating properties of the redox system.

References

- G.G. Wallace, G.M. Spinks, L.A.P. Kane-Maguire, P.R. Teasdale, Conductive Electroactive Polymers, Intelligent Materials Systems, CRC Press, 2003, p. 179.
- [2] Y. Degani, A. Heller, J. Am. Chem. Soc. 111 (1989) 2357.
- [3] A. Heller, Acc. Chem. Res. 23 (1990) 128.
- [4] K. Habermuller, A. Ramanavicius, V. Laurinavicius, W. Schuhmann, Electroanalysis 12 (2000) 1383.
- [5] S. Reiter, K. Habermuller, W. Schuhmann, Sens. Actuators B 79 (2001) 150.
- [6] W. Schuhmann, C. Kranz, J. Huber, H. Wohlschläger, Synth. Met. 61 (1993) 31.
- [7] J. Ochmanska, P.G. Pickup, J. Electroanal. Chem. 271 (1989) 83.
- [8] J. Ochmanska, P.G. Pickup, J. Electroanal. Chem. 297 (1991) 197.
- [9] M.A. Sato, S. Tanaka, K. Kaeriyama, Synth. Met. 14 (1986) 279.
- [10] S. Mu, Electrochim. Acta 51 (2006) 3434.
- [11] L.Y. Xin, X.G. Zhang, G.Q. Zhang, C.M. Shen, J. Appl. Polym. Sci. 96 (2005) 1539.
- [12] R.V. Parthasarathy, C.R. Martin, Chem. Mater. 6 (1994) 1627.
- [13] L.D. Pra, S.D. Champagne, Thin Solid Films 479 (2005) 321.
- [14] W. Liang, C.R. Martin, J. Am. Chem. Soc. 112 (1990) 9666.
- [15] F. Curulli, F. Valentini, S. Orlanducci, M.L. Terranova, C. Paoletti, G. Palleschi, Sens. Actuators B 100 (2004) 65.
- [16] S. De Vito, C.R. Martin, Chem. Mater. 10 (1998) 1738.
- [17] L.S. Van Dyke, C.R. Martin, Langmuir 6 (1990) 1118.
- [18] V.M. Cepak, J.C. Hulteen, G. Che, K.B. Jirage, B.B. Lakshmi, E.R. Fisher, C.R. Martin, J. Mater. Res. 13 (1998) 3070.
- [19] R.M. Penner, C.R. Martin, J. Electrochem. Soc. 133 (1986) 310.
- [20] M. Steinhart, S. Senz, R.B. Wehrspohn, U. Gösele, J.H. Wendorff, Macromolecules 36 (2003) 3646.
- [21] S. Warren, T. McCormac, E. Mitkova Mihaylova, E. Dempsey, Electroanalysis 18 (2006) 1778.
- [22] S. Warren, T. McCormac, E. Dempsey, Bioelectrochemistry 67 (2005) 23.
- [23] S. Serroni, S. Campagna, G. Denti, T.E. Keyes, J.G. Vos, Inorg. Chem. 35 (1996) 4513.
- [24] M. Omastova, S. Kosima, B. Shakalova, D. Jancula, Synth. Met. 53 (1993) 227.
- [25] J.C. Hulteen, C.R. Martin, J. Mater. Chem. 7 (1997) 1075.