Journal of Electroanalytical Chemistry 660 (2011) 50–56

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Preparation and electrochemical properties of modified electrodes with Keggin-type silicotungstates and PEDOT

Diana M. Fernandes [a], Christopher M.A. Brett [b], Ana M.V. Cavaleiro [a,*]

[a] *Department of Chemistry/CICECO, University of Aveiro, 3810-193 Aveiro, Portugal*
[b] *Department of Chemistry, Faculty of Science and Technology, University of Coimbra, 3004-535 Coimbra, Portugal*

ARTICLE INFO

Article history:
Received 5 August 2010
Received in revised form 9 May 2011
Accepted 3 June 2011
Available online 7 June 2011

This article is dedicated to the memory of Professor Helena Maria Carapuça

Keywords:
Keggin-type polyoxotungstates
Silicotungstates
PEDOT
Electropolymerisation
Electrochemical behaviour
Polyoxometalates

ABSTRACT

Hybrid organic/inorganic films composed of the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT), with Keggin type polyoxotungstates $[SiW_{12}O_{40}]^{4-}$, $[SiW_{11}O_{39}]^{8-}$, $[SiW_{11}Fe^{III}(H_2O)O_{39}]^{5-}$ or $[SiW_{11}Co^{II}(H_2O)O_{39}]^{6-}$ were synthesized by electrochemical polymerization in aqueous solution on the surface of glassy carbon electrodes. Cyclic voltammetry showed that the electrochemical behaviour of the polyoxometalates in the films was very similar to those in solution, and gave evidence of high electrochemical stability. Electrochemical impedance spectroscopy revealed that the charge transfer resistance increased with increasing pH and with more negative potentials. These modified electrodes were found to be very stable and could be used for at least 1 month without significant alterations.

1. Introduction

Polyoxometalates (POMs) are polyionic metal oxide clusters that have attracted the interest of scientists for many decades. These compounds have applications in fields such as materials science [1,2], analytical chemistry [3] and medicine [4] due to their interesting properties which may include high thermal stability, rich redox chemistry, photochemical properties and catalytic activity towards a number of industrially and biologically significant reactions [5–9].

One of the most important characteristics of many polyoxometalates (e.g. Keggin-, Dawson- and Finke-type POM anions [5]) is their ability to accept a large number of electrons, giving rise to mixed-valence species, which makes them very attractive for use in the preparation of modified electrodes and in electrocatalysis [6,7]. Thus, the production of new devices using polyoxometalates, that maintain and enhance their beneficial properties, is of great interest.

There are several procedures for the modification of electrodes by POMs, based on electrostatic interactions, namely electrochemical deposition, entrapment into polymeric matrices and layer-by-layer self-assembly methods [10–14]. Over the last several years there has been growing interest in conducting and redox polymer films due to the prospect of their application in different fields such as sensors, molecular electronics, corrosion protection, and displays and light emitting diodes [15–17]. The most commonly studied conducting polymers used in electrode modification are of the polyaniline or polypyrrole types, which can be doped with anionic species such as redox-active Keggin-type polyoxometalates [18–27]. Polythiophene and poly(3-methylthiophene) have also been studied as hosts for heteropolyanions, incorporating phosphometalates and silicometalates [28–30].

Poly(3,4-ethylenedioxythiophene) (PEDOT), a derivative of polythiophene with dioxyethylene groups [31], has the advantage of being one of the most stable conducting polymers compared with polymers like polyaniline or polypyrrole, arising from dioxy-ring electron donation and a favourable geometry [32–34]. The 3,4-disubstituted thiophene ring, unlike other unsubstituted polyheterocycles, leaves no sites free for carbonyl formation. This stability has led to multiple applications such as in light emitting diodes, solar cells and electrochemical capacitors, amongst others [35–37]. In addition, it participates to a small extent in side reactions with oxygen and hydrogen ions, which can be beneficial from the point of view of interference elimination [38]. PEDOT has excellent electrical conductivity and optoelectronic properties [33,39–41], which is useful for different applications, and also has an excellent environmental stability [42].

---

* Corresponding author. Tel.: +351 234 370734; fax: +351 234 370084.
E-mail address: anacavaleiro@ua.pt (A.M.V. Cavaleiro).

1572-6657/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jelechem.2011.06.004

PEDOT is frequently prepared by electropolymerization of 3,4-ethylenedioxythiophene (EDOT) by potential cycling in aqueous or nonaqueous solvents. It is commonly accepted that PEDOT is very stable in its doped oxidized state [43]. The exact nature of electrochemical processes occurring in PEDOT films is fairly complex [44]. The system is believed to undergo several overlapping fast redox transitions characterized by high diffusion coefficients for charge propagation [45]. The above properties make PEDOT attractive as a potential material for fabrication of composite matrices. Some work has already been done using PEDOT and Keggin anions. Kulesza and collaborators prepared electrodes containing $[PMo_{12}O_{40}]^{3-}$ and carbon nanoparticles [13], platinum nanoparticles [46] or nanotubes [47,48] dispersed in PEDOT films. They also produced hybrid films of PEDOT and $[PMo_{12}O_{40}]^{3-}$ or $[PW_{12}O_{40}]^{3-}$ by electrodeposition [14]. White et al. have used PEDOT and polyoxometalates to prepare electrodes using the vapour transport method [49].

The majority of the reported work on electrode modification using hybrid POM salts involves the parent Keggin and Dawson structures. However, transition metal-substituted POMs have proved to be extremely attractive as catalysts in homogeneous solution [8,9,50–53] and, in some cases, immobilized into polymer modified electrodes, where the transition metals may play an important role as active sites [6,7]. Thus, investigation of the potentialities of electrode modification by metal-substituted silicotungstates is important in the electrochemical and materials chemistry fields.

We have been studying electrode modification by transition metal-substituted Keggin-type phospho- and silicotungstates by different methods, namely by the droplet evaporation method, layer-by-layer self-assembly methodology and incorporation into carbon paste electrodes [11,12,54,55]. The present work concerns the preparation and electrochemical characterization of PEDOT-modified electrodes doped with $[SiW_{11}Fe^{III}(H_2O)O_{39}]^{5-}$ ($SiW_{11}Fe$), $[SiW_{11}Co^{II}(H_2O)O_{39}]^{6-}$ ($SiW_{11}Co$), and, for comparison, $[SiW_{11}O_{39}]^{8-}$ (SiW_{11}) and $[SiW_{12}O_{40}]^{4-}$ (SiW_{12}). These modified electrodes are prepared by controlled electrodeposition of composite (hybrid) films of PEDOT with the Keggin-type silicotungstates. The electrochemical behaviour of the immobilized POMs was examined by cyclic voltammetry and the effect of solution pH and scan rate on the voltammetric behaviour of the modified electrodes was evaluated. Furthermore, the modified electrodes were studied by electrochemical impedance spectroscopy.

2. Experimental

2.1. Reagents and solutions

Sulphuric acid (Fluka), sodium sulphate (Sigma–Aldrich) and 3,4-ethylenedioxythiophene (Aldrich) were used as received. The potassium salts of the α-Keggin silicotungstates $K_8[SiW_{11}O_{39}]\cdot 13H_2O$, $K_5[SiW_{11}Fe^{III}(H_2O)O_{39}]\cdot 13H_2O$ and $K_6[SiW_{11}Co^{II}(H_2O)O_{39}]\cdot 12H_2O$ were prepared by previously-published procedures [56,57]. Silicotungstic acid, $H_4[SiW_{12}O_{40}]\cdot xH_2O$ (Merck), was used as received. All compounds were characterized by thermal and elemental analysis, and infrared spectroscopy and the results were in agreement with previously-published values [57].

Electrolyte solutions for voltammetry were prepared using ultra-pure water (resistivity 18.2 MΩ cm at 25 °C, Direct-Q 3 UV system, Millipore). Buffer solutions within the pH range 1.5–3.0 were prepared by mixing appropriate amounts of a 0.2 M H_2SO_4 solution with a 0.5 M Na_2SO_4 solution.

The solutions used for the film preparation were used immediately after their preparation and degassed with pure nitrogen for at least 10 min to remove dissolved oxygen. Solutions used for electrochemical characterization were also degassed with nitrogen for 10 min before use.

2.2. Instrumentation and methods

Cyclic voltammetry experiments were carried out using a computer-controlled potentiostat (PGSTAT-12/GPES software from Autolab/Ecochemie, Netherlands). A conventional three-electrode compartment cell was used. The auxiliary and reference electrodes were platinum wire (7.5 cm, BAS, MW-1032) and Ag/AgCl (sat. KCl) (BAS, MF-2052), respectively. The working electrode was a glassy carbon electrode, GCE, (3 mm diameter, BAS, MF-2012), bare or surface-modified with the POM doped PEDOT films.

Electrochemical impedance measurements were carried out using a Solartron 1250 Frequency Response Analyser, coupled to a Solartron 1286 Electrochemical Interface (UK) controlled by ZPlot 4.1 Software. The voltage perturbation was 10 mV rms over a frequency range from 65 kHz to 0.1 Hz with 10 frequencies per decade, and integration time 60 s. Impedance spectra were analysed by fitting equivalent electrical circuits using ZView 3.2 Software (Scribner Associates, USA).

A combined glass electrode (Hanna Instruments HI 1230) connected to an Inolab pH level 1 pH meter was used for the pH measurements.

2.3. Preparation of POM doped PEDOT films

Prior to coating, the GCE was conditioned by a polishing/cleaning procedure. The GCE was successively polished with 1.0 μm diamond polishing compound (Metadi II, Buehler) and aluminium oxide of particle size 0.3 μm (Buehler-Masterprep) on a microcloth polishing pad (BAS Bioanalytical Systems Inc.), then the electrode was rinsed with ultra-pure water and finally sonicated for 5 min in an ultrasonic bath (Branson 2510). Electrochemical pre-treatment of the electrode was performed by applying 20 consecutive potential scans, between −0.8 V and 0.8 V, at a scan rate of $0.1\ V\ s^{-1}$ in NH_4Ac/HCl (pH 3.4; 1.0 M NH_4Ac/0.5 M HCl) buffer solution.

Unless otherwise stated, the POM-doped PEDOT films were prepared by potential cycling (five cycles) at $100\ mV\ s^{-1}$ from −0.75 to 1.1 V vs. Ag/AgCl in 0.25 mM SiW_{12}, SiW_{11}, $SiW_{11}Fe$ or $SiW_{11}Co$/5 mM EDOT/0.2 M H_2SO_4 solutions. All measurements were made at room temperature (∼25 °C).

3. Results and discussion

The electrodeposition of PEDOT films doped with Keggin-type polyoxotungstates on glassy carbon electrodes, was carried out by potential cycling in aqueous solutions containing the chosen POM ($SiW_{11}Fe$, $SiW_{11}Co$, SiW_{12} or SiW_{11}) and EDOT in 0.2 M H_2SO_4. A set of experiments was initially performed in order to choose the POM and EDOT concentrations as well as the scan rate, range of potentials and number of cycles for electrodeposition. Three concentrations of POM (0.5, 0.4 and 0.25 mM) and EDOT (10, 7.5 and 5 mM) were used and the best results were obtained for 0.25 mM of POM and 5 mM of EDOT. Scan rates of 50 and $100\ mV\ s^{-1}$ were employed and electropolymerization was performed during 5 or 10 cycles; better results were obtained using $100\ mV\ s^{-1}$ and 5 cycles.

PEDOT's electronic structure (Fig. 1) is controlled by the applied potential, switching between the conductive (oxidized) and the insulating (reduced) states. Oxidized PEDOT has a transparent sky blue colour that turns dark purple upon reduction [58]. The polymer and POM are expected to interact electrostatically with

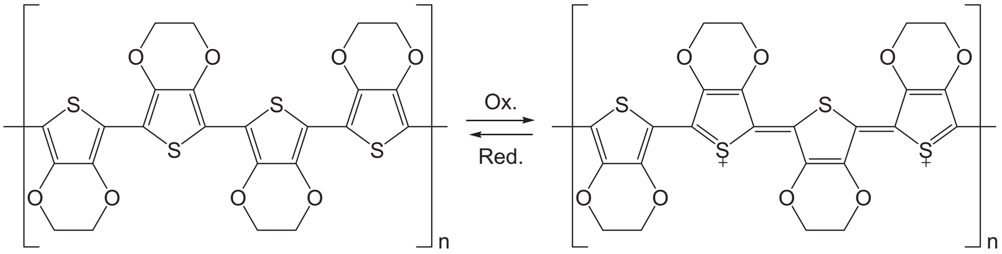

Fig. 1. Neutral PEDOT (left) is oxidized to form a conducting polycation (right) in the presence of charge-balancing anions.

each other during the deposition process, because oxidized PEDOT is positively charged and the polyoxometalate is anionic.

3.1. Cyclic voltammetry of the POM doped PEDOT films

3.1.1. Film formation and stability

Fig. 2 shows cyclic voltammograms that demonstrate the growth of $SiW_{11}Fe$-doped PEDOT films. PEDOT is generated on the electrode surface during positive scans [14,16], with simultaneous attraction of compensating anions during the potential cycling and film growth, which leads to increased stability of the composite film. The fact that all voltammetric peak currents increase almost linearly with each cycle in Fig. 2 implies a linear growth of the film. The cyclic voltammograms for the other three silicotungstates were similar.

It is known that the silicotungstates used in this work are unstable in neutral and basic aqueous solution and undergo a series of hydrolysis processes, so the electrochemical characterisation experiments were carried out in acidic aqueous solutions. Voltammetric studies in aqueous solution (pH range of 2.0–4.5) with the lacunary and metal-substituted polyoxometalates used in this work were performed by us previously [54] and the main features are indicated here for a better understanding of the results obtained with POM-doped PEDOT. In aqueous acidic solution, all compounds presented two reversible or quasi-reversible two-electron consecutive waves at negative potentials, corresponding to the reduction of W^{VI} atoms [54,55]. Most of these reductions involved the uptake of protons to prevent build-up of negative charge. The redox process of the $Fe^{III/II}$ metal centre was clearly seen as a quasi-reversible one-electron process. For the cobalt-substituted species no Co-metal reduction/oxidation peaks were seen within the potential range employed.

Fig. 3 shows cyclic voltammograms in the potential range from −0.75 to 0.0 V vs. Ag/AgCl for $SiW_{11}Fe$ doped PEDOT films at three different times after film preparation. Shortly after the films were prepared, the voltammetric response was characterized by three pairs of peaks. Scans were recorded every day during 6 days at the beginning and at the end of the day; at the end of each day, the electrode was left to rest in its protecting case. It can be observed that the pair of peaks at less negative potential, corresponding to the $Fe^{III/II}$, process did not change, but there were significant changes in the cyclic voltammograms, corresponding to the tungsten (VI) reduction peaks. After deposition, these peaks corresponded to two reduction processes of one and three electrons, respectively, at less and more negative potentials. At the end of the first day (~6–8 h after electrode preparation), these peaks were altered and the cyclic voltammograms showed the typical two two-electron reductions, inferred from the changes in the peak heights. The observed change in the peak positions and heights corresponding to tungsten reduction suggests some reorganization of the structure. After 6 days this behaviour was maintained and after longer time periods no further significant changes were observed in the cyclic voltammograms. According to these results, it appears that the prepared modified electrodes should be left to rest for at least 1 day in order to attain reproducible cyclic voltammograms. For the other POM-doped PEDOT films a similar electrochemical behaviour, with alteration during the first 24 h after preparation, was observed.

After modified electrode stabilization, the redox processes may be described by the following equations:

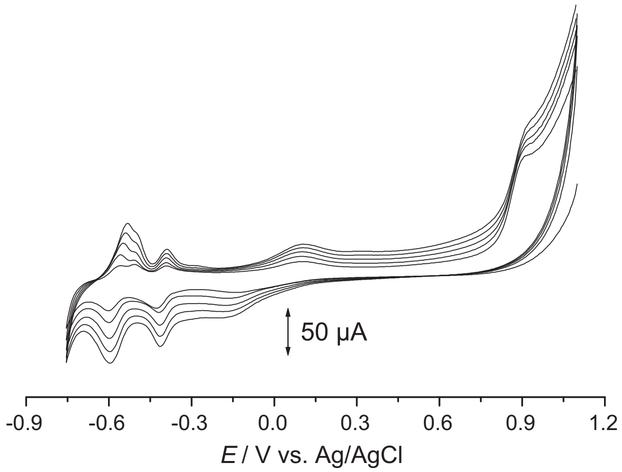

Fig. 2. Electropolymerisation and formation of hybrid films by potential cycling in 5 mM EDOT/0.25 mM $SiW_{11}Fe$/0.2 M H_2SO_4 solution. Potential range −0.75 to 1.1 V; scan rate 100 mV s^{-1}.

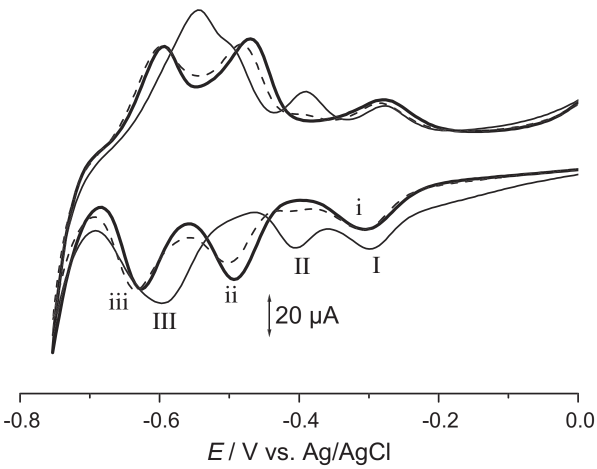

Fig. 3. Cyclic voltammograms for $SiW_{11}Fe$-doped PEDOT obtained in 0.2 M H_2SO_4 solution, v = 100 mV s^{-1}: (–) after deposition; (- - -) end of the first day; (thick line) 6 days later.

$$\mathrm{SiW_{11}^{VI}Fe^{III}(H_2O)O_{39}^{5-} + e^- \leftrightharpoons SiW_{11}^{VI}Fe^{II}(H_2O)O_{39}^{6-}} \quad \text{(peak i)}$$

$$\mathrm{SiW_{11}^{VI}Fe^{II}(H_2O)O_{39}^{6-} + 2e^- + 2H^+ \leftrightharpoons H_2SiW_2^{V}W_9^{VI}Fe^{II}(H_2O)O_{39}^{6-}} \quad \text{(peak ii)}$$

$$\mathrm{H_2SiW_2^{V}W_9^{VI}Fe^{II}(H_2O)O_{39}^{6-} + 2e^- + 2H^+ \leftrightharpoons H_4SiW_4^{V}W_7^{VI}Fe^{II}(H_2O)O_{39}^{6-}} \quad \text{(peak iii)}$$

Fig. 4 shows cyclic voltammograms, in the same potential range, of a $\mathrm{SiW_{11}Fe}$-doped PEDOT modified electrode (6 days after preparation) and, for comparison, the cyclic voltammogram of a PEDOT film prepared by the same procedure, but without POM. The results demonstrate that the contribution of PEDOT to the overall electrochemical response of the POM-doped films is relatively low, the voltammetric behaviour of these films being dominated by the redox characteristics of the polyoxometalates. In the cyclic voltammogram of $\mathrm{SiW_{11}Fe}$ in Fig. 4, two reduction waves can be observed, at −496 and −628 mV, corresponding to the reduction of tungsten atoms. Another reduction peak is observed at −305 mV, which corresponds to the reduction of $\mathrm{Fe^{III}}$.

3.1.2. Film characterisation

Cyclic voltammograms of the $\mathrm{SiW_{12}}$ and $\mathrm{SiW_{11}}$ doped films reveal two clearly resolved 2-e^- reduction waves, as can be seen for the $\mathrm{SiW_{12}}$ anion in Fig. 5a. The peak potentials do not differ much from each other (Table 1), but the voltammograms are better defined for the parent anion than those of the lacunary anion where the peaks are broader. Cyclic voltammograms of $\mathrm{SiW_{12}}$ in $\mathrm{H_2SO_4}$ aqueous solution usually show three redox couples corresponding to two one-electron waves followed by one two-electron wave [5]. However, Keita and Nadjo reported that in strong acid aqueous solutions ($\mathrm{HClO_4}$ and HCl) and in DMF, with stepwise addition of perchloric acid [59], significant changes of the waves are observed; in particular, the first voltammetric wave changes from a one-electron, diffusion-controlled process to an overall, apparently direct, two-electron transfer. So it is possible that the PEDOT environment where the $\mathrm{SiW_{12}}$ is immobilized may favour similar changes to the number of reduction waves.

For the $\mathrm{SiW_{11}Co}$ anion in aqueous solution or immobilized on electrodes [54,55], the cyclic voltammograms usually have two 2-electron reduction peaks, both due to the reduction of tungsten atoms, and no peaks corresponding to cobalt redox processes, within the potential window used. However, cyclic voltammograms of $\mathrm{SiW_{11}Co}$-doped PEDOT on the modified electrode revealed a third reduction peak at approximately −350 mV vs. Ag/AgCl, in addition to those corresponding to reduction of tungsten (Fig. 5b). Because the cyclic voltammograms of $\mathrm{SiW_{12}}$ and $\mathrm{SiW_{11}}$ have only two reduction waves of almost equal height (Fig. 5a), the possibility of formation of another reduced tungsten species was ruled out. Also, the fact that a third peak is not observed in the cyclic voltammograms of $\mathrm{SiW_{12}}$ or $\mathrm{SiW_{11}}$ shows that this peak cannot be attributed to the polymer. Thus, this third reduction peak is attributed to a process occurring at the substituting metal, cobalt. A much higher redox po-

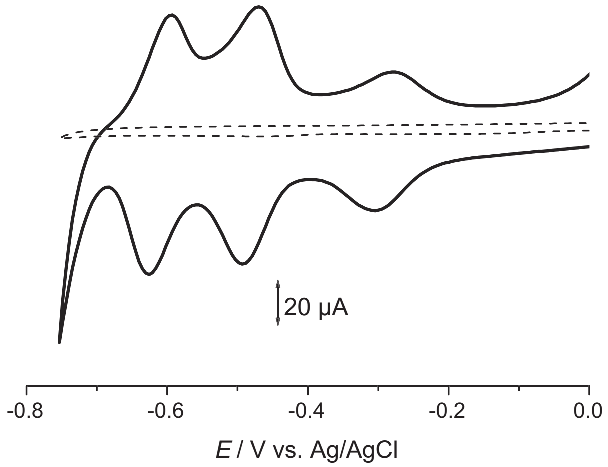

Fig. 4. Cyclic voltammograms for: (full line) $\mathrm{SiW_{11}Fe}$-doped PEDOT and (dashed line) PEDOT film. Electrolyte: 0.2 M $\mathrm{H_2SO_4}$ solution, v = 100 mV s^{-1}.

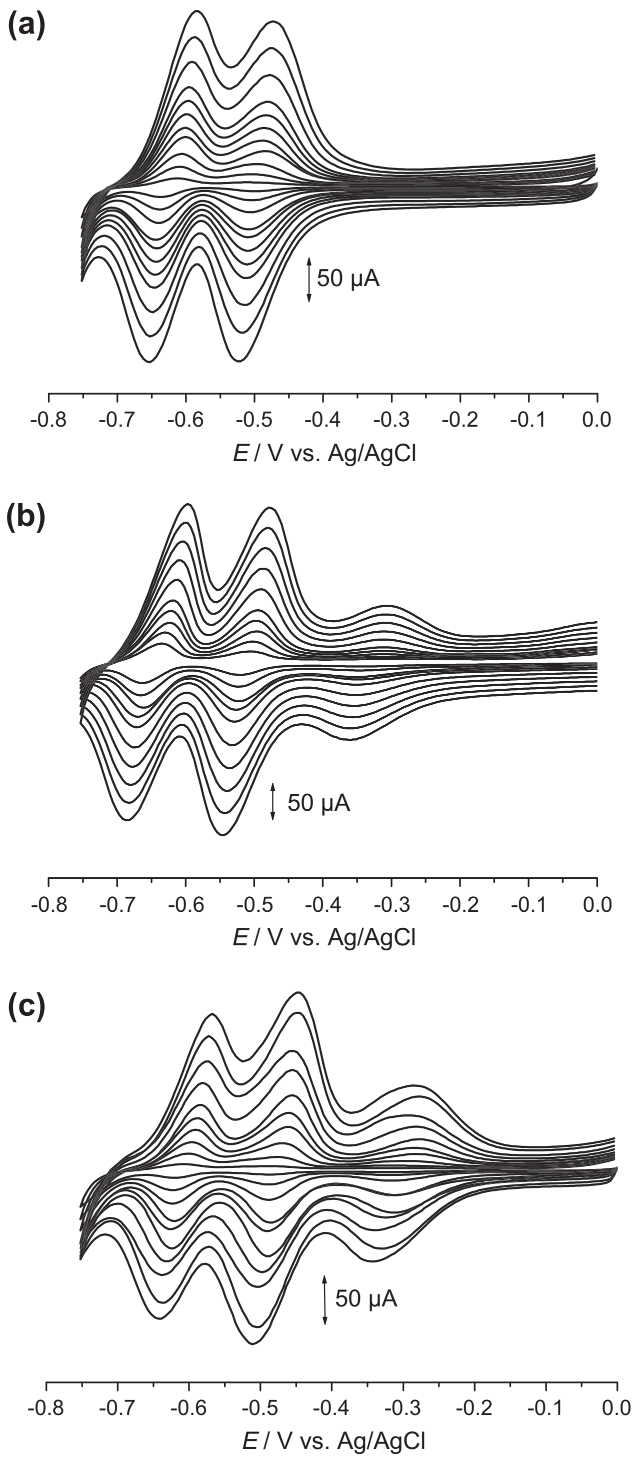

Fig. 5. Cyclic voltammograms of (a) $\mathrm{SiW_{12}}$, (b) $\mathrm{SiW_{11}Co}$ and (c) $\mathrm{SiW_{11}Fe}$ doped PEDOT modified electrodes 0.2 M $\mathrm{H_2SO_4}$ solution at scan rates of 25, 50, 75, 100, 125, 150, 175, 200, 250, 300, 350 and 400 mV s^{-1}.

Table 1
Cyclic voltammetric data for the 1st tungsten reduction process for the silicotungstate doped PEDOT modified electrodes at 100 mV/s in 0.2 M H_2SO_4 (values within an experimental uncertainty of ±4 mV).

POM	E_{pc}[a]	$\lvert\Delta E_p\rvert$[a]	$\lvert E_{pc}-E_{p/2}\rvert$[a]	E_{pc} (M′)[a]	$E_{pc(aq)}$[b]
SiW_{12}	−509	15	35	–	–
SiW_{11}	−521	29	33	–	−501
$SiW_{11}Fe$	−495	28	34	−305	−563
$SiW_{11}Co$	−522	26	32	−350	−566

[a] mV vs. Ag/AgCl.

[b] E_{pc} values for the polyoxoanions in aqueous solution (mV vs. Ag/AgCl) at pH 2.0, v = 50 mV s^{-1} [55].

tential was determined for the $SiW_{11}Co^{III/II}$ couple (+1.10 V vs. NHE) in [60]. It is thus most probable that the observed peak, with $E_{1/2}$ near −340 mV, corresponds to the $Co^{II/I}$ redox couple. For cobalt, oxidation states lower than +2 usually need the stabilizing effects of π-acceptor ligands. Some type of interaction may be established between cobalt and the thiophene rings, that could stabilise Co(I). Many examples may be found of electrochemical studies involving $Co^{II/I}$ redox couples, namely cobalt complexes with bipyridine [61,62], porphyrins [63,64], phthalocyanines [64,65], and Schiff bases [66]. The observed redox potentials vary over a large range, depending on the ligands.

The effect of scan rate was investigated for SiW_{12}, $SiW_{11}Fe$ and $SiW_{11}Co$ in 0.2 M H_2SO_4 solution (Fig. 5). The cathodic and anodic peak currents are directly proportional to scan rate with $0.999 \geqslant r \geqslant 0.996$ (figures in supplementary data), which indicates a surface-confined process, and the ratio of magnitude of oxidation to reduction peak currents is in the range 0.97–0.99. The anodic/cathodic peak-to-peak separation (ΔE_p) increased with scan rate up to 50 mV at 400 mV s^{-1}, characteristic of a quasi-reversible surface-confined process.

Table 1 presents the voltammetric data for the four silicotungstates studied at 100 mV s^{-1} scan rate and, for comparison, the values in aqueous solution. The values of $\lvert E_p-E_{p/2}\rvert$, between 28 and 35 mV, suggest a 2-electron reduction process as referred to previously, since a minimum value of 45/n mV would be obtained for a reversible process [67]. Also, as a consequence of immobilization, there were no significant differences between the potential of the first tungsten reduction process upon metal substitution, in contrast to aqueous solutions. A similar behaviour was observed for these POMs immobilized on modified electrodes prepared by other methods, namely by the droplet evaporation [54] or by the layer-by-layer method [11,12].

Since the peak separation is small, the surface coverage can be estimated approximately from cyclic voltammetry by the equation for reversible surface-confined species $\Gamma = (4I_{pa}RT)/(n^2F^2vA)$, where I_{pa} is the anodic peak current (amperes), n is the number of electrons transferred (2 in this case), v is the scan rate (V s^{-1}), A is the geometric area of the electrode (0.0725 cm^2), R is the gas constant, T is the temperature (298 K) and F is the Faraday constant [67]. Peak currents were plotted against scan rate (25–300 mV s^{-1}) and the value of I_{pa}/v obtained was used to calculate the surface coverage. This led to a value of 1.2×10^{-9} mol cm^{-2} for SiW_{12}, 9.6×10^{-10} mol cm^{-2} for $SiW_{11}Fe$ and 1.3×10^{-9} mol cm^{-2} for $SiW_{11}Co$. Comparing these values to those obtained by Wang et al. (1.0×10^{-10} mol cm^{-2}) for monolayer coverage [68], ours correspond to coverage by more than one monolayer.

The pH of the electrolyte solution has a marked effect on the voltammetric behaviour of POM-doped PEDOT modified electrodes. With increasing pH, from 1.5 to 3.0, the peak potentials shift to more negative values while the peak currents gradually decrease. An increase in pH also leads to a change in the slopes of plots of lg(I_p) vs. lg(v). Above 125 mV s^{-1}, for the higher pH values used (2.5 and 3.0), the process ceases to be surface-confined (i.e. I_p is directly proportional to v) and begins the transition to diffusion control (slope of I_p vs. v is 0.80 ± 0.02). With increasing scan rate, the diffusion rate of the solvated protons into the immobilized polyoxometalates begins to determine the rate of electrochemical reduction. Also with an increase of pH there is an increase in the concentration of Na^+ in the buffer (with replacement of H^+ by Na^+), and, thus, slower penetration of the bulkier cations to the active centres, which explains the decrease of current.

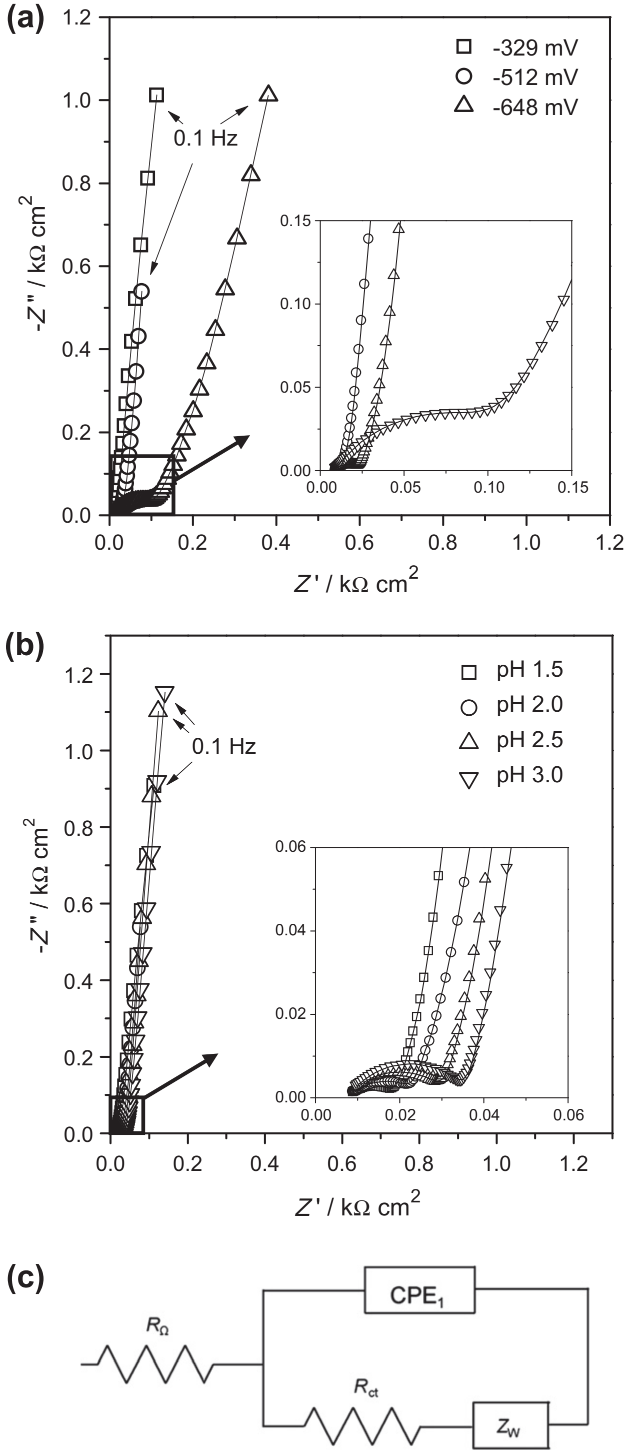

Fig. 6. Complex plane impedance spectra of PEDOT/$SiW_{11}Fe$ modified electrode in H_2SO_4/Na_2SO_4 buffer solution (a) pH 2.0, at different applied potentials, (b) at −512 mV vs. Ag/AgCl at different values of pH and (c) equivalent circuit used to fit the spectra.

Table 2
Parameters obtained from impedance spectra of the POM-doped PEDOT modified electrode in pH 2.0 H_2SO_4/Na_2SO_4 buffer solution by fitting to the equivalent circuit in Fig. 6c.

POM	Potential (mV)	$R_{ct}/\Omega\ cm^2$	$C/\mu F\ cm^{-2}\ s^{n-1}$	n	$R_{dif}/\Omega\ cm^2$	$\alpha(W_o)$
$SiW_{11}Fe$	−329	–[a]	–[a]	–[a]	11.8	0.46
	−512	12.2	56.5	0.71	16.2	0.46
	−648	87.5	107.1	0.72	81.5	0.46
$SiW_{11}Co$	−329	–[a]	–[a]	–[a]	8.1	0.48
	−512	19.9	7.2	0.82	89.1	0.46
	−648	50.9	27.0	0.70	153	0.47
SiW_{12}	−329	–[a]	–[a]	–[a]	34.9	0.45
	−512	229	6.7	0.70	135	0.47
	−648	313	15.1	0.68	195	0.46

[a] Element not included.

Table 3
Parameters obtained from impedance spectra of the POM-doped PEDOT modified electrodes at −512 mV in H_2SO_4/Na_2SO_4 buffer solutions with different pH values by fitting to the equivalent circuit in Fig. 6c.

POM	pH	$R_{ct}/\Omega\ cm^2$	$C/\mu F\ cm^{-2}\ s^{n-1}$	n	$R_{dif}/\Omega\ cm^2$	$\alpha(W_o)$
$SiW_{11}Fe$	1.5	8.1	60.7	0.73	14.2	0.46
	2.0	12.2	56.5	0.71	16.2	0.46
	2.5	19.5	50.0	0.72	18.4	0.47
	3.0	25.5	34.7	0.71	20.4	0.47
$SiW_{11}Co$	1.5	18.2	15.6	0.77	73.3	0.46
	2.0	19.9	7.2	0.82	89.1	0.46
	2.5	57.1	6.4	0.74	86.0	0.47
	3.0	81.1	5.3	0.69	117	0.48
SiW_{12}	1.5	130	22.1	0.67	104	0.46
	2.0	229	6.7	0.70	135	0.47
	2.5	240	7.4	0.69	162	0.46
	3.0	273	8.9	0.68	195	0.46

Plots of peak potential vs. pH gave a slope of −70 mV/pH unit for SiW_{12} (r = 0.999 and SD = 2.93), −89 mV/pH unit for $SiW_{11}Fe$ (r = 0.999 and SD = 3.11) and −86 mV/pH unit for $SiW_{11}Co$ (r = 0.998 and SD = 3.46). The effect of pH at SiW_{11}-doped PEDOT modified electrodes could not be evaluated because with increasing pH the reduction waves of this anion tend to overlap and the potentials of the individual peaks are difficult to determine accurately. The slopes show that the redox mechanism at the tungsten atoms immobilized on the PEDOT film requires the involvement of protons. So, in the present experimental conditions, assuming Nernstian behaviour, the first W reduction in SiW_{12} is a two-electron/two-proton process. For the metal-substituted anions the slopes are slightly higher (more by 19 mV for $SiW_{11}Fe$ and 16 mV for $SiW_{11}Co$, in comparison with the parent anion), indicating that the two-electron reduction is probably accompanied by addition of two to three protons [54].

The stability of POM-doped PEDOT modified electrodes was studied, by cycling 100 times in 0.2 M H_2SO_4 solution between −0.75 and 0.0 V at 100 mV s^{-1}. The peak currents for $SiW_{11}Fe$ decreased by only 0.9% after 50 cycles and 5.0% after 100 cycles. The values for $SiW_{11}Co$ were 2.0% (50 cycles) and 4.9% (100 cycles), and for SiW_{12} 1.7% (50 cycles) and 2.5% (100 cycles). After this, the electrodes were left immersed in this solution for 1 month: there was no decrease in peak current but the peak potentials shifted approximately 11 mV to more positive values. The reason for this high stability may be the strong electrostatic interaction between the polyoxometalate and the conductive PEDOT polymer.

3.2. Electrochemical impedance spectroscopy of the POM-doped PEDOT films

Electrochemical impedance spectroscopy (EIS) is an extremely powerful and sensitive characterization technique for probing the charge transfer and charge separation processes occurring at electrode/solution or modified electrode/solution interfaces as well as their variation in time. EIS was used to examine the interfacial properties of the PEDOT/POM modified electrodes. To our knowledge no previous impedance studies have been carried out at POM-doped PEDOT modified electrodes.

Two series of experiments were performed: first, measurements were carried out in pH 2.0 H_2SO_4/Na_2SO_4 buffer solution at three different potentials (−329, −512 and −648 mV vs. Ag/AgCl) chosen to encompass the redox reactions of the silicotungstate. Secondly, measurements were carried out at four different pH values at −512 mV vs. Ag/AgCl.

Complex plane impedance spectra in pH 2.0 H_2SO_4/Na_2SO_4 buffer solution are illustrated in Fig. 6a for $SiW_{11}Fe$ as an example. There are clear differences between the spectra obtained at the three potentials. The spectrum recorded at −329 mV was a straight line and, for the other two potentials, the spectra included a semicircle in the high frequency range that corresponds to kinetic control of the charge-transfer process and a linear part characteristic of the lower frequency attributed to a diffusion process. The diameter of the semicircle is greater for spectra recorded at −648 mV. This increase in the diameter can be due to the interfacial charge transfer process becoming slower with increasing negative potentials.

Spectra for $SiW_{11}Fe$ obtained at −512 mV in H_2SO_4/Na_2SO_4 buffer solutions of different pH values also presented the same profile, Fig. 6b. The diameter of the semicircle increases with increase of pH, due to electron transfer becoming more difficult because of the consumption of protons as already seen by cyclic voltammetry. This behaviour was observed for the other two POMs studied, $SiW_{11}Co$ and SiW_{12}.

All spectra were fitted to the equivalent circuit shown in Fig. 6c. The circuit comprises a cell resistance, R_Ω, in series with a parallel combination of a constant phase element, CPE, and a charge transfer resistance, R_{ct}, plus Warburg element, Z_W. The CPE was modelled as a non-ideal capacitor, given by CPE = $-1/(Ci\omega)^n$, where C is the capacitance, which describes the charge separation at the double layer interface, ω is the frequency in rad s^{-1} and the n exponent is due to the heterogeneity of the surface. The Warburg element was modelled as an open circuit finite Warburg element, W_0, where $Z_W(W_o) = R_{dif}$ ctnh $([i\tau\omega]^{\alpha})/(i\tau\omega)^{\alpha}$, R_{dif} being a diffusion resistance.

Tables 2 and 3 show the values of the parameters obtained. The circuit elements R_{ct} and R_{dif} relate directly to the accessibility of the electrode substrate and the flow of species at the electrode substrate and though the film, respectively. Both of these depend on the applied potential and on the pH of electrolyte used. The values are significantly larger for SiW_{12} than for the other two POMs with substituted metal ions although the capacitance values are correspondingly smaller; the presence of the transition metal substituent appears to facilitate charge transfer and diffusion. In all cases $\alpha(W_o)$ is between 0.45 and 0.48 which is close to the value of 0.50 for perfectly uniform diffusion although the CPE exponent is lower, suggesting a greater non-uniformity at the film/electrode interface.

The impedance results are in agreement with those from cyclic voltammetry. In particular, the shift of peak potentials in cyclic voltammetry to more negative values together with a decrease in current as the pH of the electrolyte solution increases is in agreement with the increase of the charge transfer resistance in the impedance spectra.

4. Conclusions

The present work demonstrates the feasibility of preparation of hybrid films of $[SiW_{12}O_{40}]^{4-}$, $[SiW_{11}O_{39}]^{8-}$, $[SiW_{11}Fe^{III}(H_2O)O_{39}]^{5-}$ or $[SiW_{11}Co^{II}(H_2O)O_{39}]^{6-}$ and PEDOT, under aqueous conditions, on the surface of glassy carbon electrodes. The electrochemical behaviour of these modified electrodes was studied by cyclic voltammetry and electrochemical impedance spectroscopy. Cyclic voltammograms of the films showed, in all cases, two well-resolved 2-electron waves attributable to tungsten redox processes and one 1-electron wave attributable to the substituting metal, when present. The effect of scan rate in cyclic voltammetry leads to the conclusion that the first tungsten reduction process is surface-confined when buffer solutions of pH 1.5 and 2.0 are used. However, when buffer solutions of pH 2.5 and 3.0 are used, for scan rates higher than 125 mV s^{-1} the reaction mechanism begins to change from surface control to diffusion control. The studies at different pH indicate that the reductions are proton dependent. Electrochemical impedance spectroscopy is in agreement with these observations and clearly shows the marked effect of the introduction of a transition metal substituent in SiW_{12} in POM-doped PEDOT films. The impedance results showed that the charge transfer resistance increased with increasing pH and for higher values of potential. The POM-doped PEDOT modified electrodes have high stability, which can be attributed to strong electrostatic interaction between the polyoxometalate and the conducting PEDOT polymer.

Acknowledgments

The authors thank Fundação para a Ciência e a Tecnologia (FCT) for financial support (Project POCI 2010-Feder-POCI/QUI/56534/2004). D. Fernandes acknowledges FCT for her PhD grant SFRH/BD/30797/2006. Thanks are also due to CICECO and the University of Aveiro, and CEMUC® (Research Unit 285) University of Coimbra.

References

[1] J.M. Clemente-Juan, E. Coronado, Coord. Chem. Rev. 193 (195) (1999) 361.
[2] P. Gomez-Romero, Adv. Mater. 13 (2001) 163.
[3] D.E. Katsoulis, Chem. Rev. 98 (1998) 359.
[4] J.T. Rhule, C.L. Hill, D.A. Judd, Chem. Rev. 98 (1998) 327.
[5] M.T. Pope, Heteropoly and Isopoly Oxometalates, Springer Verlag, 1983.
[6] M. Sadakane M, E. Steckhan, Chem. Rev. 98 (1998) 219.
[7] B. Keita, L. Nadjo, J. Mol. Catal. A – Chem. 262 (2007) 190.
[8] C.L. Hill, C.M. Prosser-McCartha, Coord. Chem. Rev. 143 (1995) 407.
[9] R. Neumann, Prog. Inorg. Chem. 47 (1998) 317.
[10] S. Liu, Z. Tang, Nano Today 5 (2010) 267.
[11] D.M. Fernandes, H.M. Carapuça, C.M.A. Brett, A.M.V. Cavaleiro, Thin Solid Films 518 (2010) 5881.
[12] D.M. Fernandes, H.M. Carapuça, C.M.A. Brett, A.M.V. Cavaleiro, J. Solid State Eletrochem. 15 (2011) 811.
[13] M. Skunik, B. Baranowska, D. Fattakhova, K. Miecznikowski, M. Chojak, A. Kuhn, P.J. Kulesza, J. Solid State Electrochem. 10 (2006) 168.
[14] L. Adamczyk, P.J. Kulesza, K. Miecznikowski, B. Palys, M. Chojak, D. Krawczyk, J. Electrochem. Soc. 152 (2005) E98.
[15] C. Barbero, M.C. Miras, B. Schnyder, O. Haas, R. Kotz, J. Mater. Chem. 4 (1994) 1775.
[16] G. Inzelt, M. Pineri, J.W. Schultze, M.A. Vorotyntsev, Electrochim. Acta 45 (2000) 2403.
[17] J.F. Rubinson, H.B. Mark Jr., Interfacial Electrochemistry, Conducting Polymer Films as Electrodes, New York, 1999, p. 689.
[18] A.M. White, R.C.T. Slade, Electrochim. Acta 48 (2003) 2583.
[19] A.M. White, R.C.T. Slade, Synth. Metals 139 (2003) 123.
[20] A. Balamurugan, S.M. Chen, J. Solid State Electrochem. 11 (2007) 1679.
[21] P.C. Lekha, S. Subramanian, D.P. Padiyan, J. Mater. Sci. 44 (2009) 6040.
[22] P. Gomez-Romero, M. Chojak, K. Cuentas-Gallegos, J.A. Arsensio, P.J. Kulesza, N. Casan-Pastor, M. Lira-Cantu, Electrochem. Commun. 5 (2003) 149.
[23] P. Gomez-Romero, M. Lira-Cantu, Adv. Mater. 9 (1997) 144.
[24] E.F.C. Chimamkpam, F. Hussain, A. Engel, A. Schilling, G.R. Patzke, Z. Anorg. Allg. Chem. 635 (2009) 624.
[25] T.F. Otero, S.A. Cheng, F. Huerta, J. Phys. Chem. B 104 (2000) 10522.
[26] T.F. Otero, S.A. Cheng, D. Alonso, F. Huerta, J. Phys. Chem. B 104 (2000) 10528.
[27] S. Cheng, T.F. Otero, E. Coronado, C.J.G. García, E.M. Ferrero, C.G. Saiz, J. Phys. Chem. B 106 (2002) 7585.
[28] B. Fabre, G. Bidan, D. Fichou, J. Chim. Phys. Phys.-Chim. Biol. 89 (1992) 1053.
[29] M. Lapkowski, G. Bidan, M. Fournier, Synth. Metals 41 (1991) 407.
[30] J.L. Sauvajol, J.P. Lereporte, C. Chorro, G. Poussigue, J. Phys. -Condes. Matter 4 (1992) 3179.
[31] F. Petraki, S. Kennou, S. Nespurek, J. Appl. Phys. 103 (2008) 033710.
[32] G. Heywang, F. Jonas, Adv. Mater. 4 (1992) 116.
[33] M. Dietrich, J. Heinze, G. Heywang, F. Jonas, J. Electroanal. Chem. 369 (1994) 87.
[34] H. Yamoto, O. Ohwa, W. Wernet, J. Electroanal. Chem. 397 (1995) 63.
[35] F. Jonas, G. Heywang, Electrochim. Acta 39 (1994) 1345.
[36] P.M. Beaujuge, J.R. Reynolds, Chem. Rev. 110 (2010) 268.
[37] J. Vaillant, M. Lira-Cantu, K. Cuentas-Gallegos, N. Casan-Pastor, P. Gómez-Romero, Prog. Solid State Chem. 34 (2006) 147.
[38] Y. Yang, Y. Jiang, J. Xu, J. Yu, Thin Solid Films 516 (2008) 1191.
[39] M. Granstrom, M. Berggren, O. Inganas, Science 267 (1995) 1479.
[40] M. Mastragostino, C. Arbizzani, A. Bongini, G. Barbarella, M. Zambianchi, Electrochim. Acta 38 (1992) 135.
[41] C. Kvarnstrom, H. Neugebauer, S. Blomquist, H.J. Ahonen, J. Kankare, A. Ivaska, Electrochim. Acta 44 (1999) 2739.
[42] A. Kumar, J.R. Reynolds, Macromolecules 29 (1996) 7629.
[43] J.C. Lacroix, K.K. Kanazawa, A.D. Diaz, J. Electrochem. Soc. 136 (1989) 1308.
[44] X. Chen, O. Inganas, J. Phys. Chem. 100 (1996) 15202.
[45] J. Bobacka, A. Lewenstam, A. Ivaska, J. Electroanal. Chem. 89 (2004) 17.
[46] K. Karnicka, M. Chojak, K. Miecznikowska, M. Skunik, B. Baranowska, A. Kolary, A. Piranska, B. Palys, L. Adamczyk, P.J. Kulesza, Bioelectrochemistry 66 (2005) 79.
[47] M. Skunik, P.J. Kulesza, Anal. Chim. Acta 631 (2009) 153.
[48] P.J. Kulesza, M. Skunik, B. Baranowska, K. Miecznikowski, M. Chojak, K. Karnicka, E. Frackowiak, F. Béguin, A. Kuhn, M.H. Delville, B. Starobrzynska, A. Ernst, Electrochim. Acta 51 (2006) 2373.
[49] M. White, R.C.T. Slade, Electrochim. Acta 49 (2004) 861.
[50] I.V. Kozhevnikov, Chem. Rev. 98 (1998) 171.
[51] L.E. Briand, G.T. Baronetti, H.J. Thomas, Appl. Catal. 256 (2003) 37.
[52] N. Mizuno, K. Yamaguchi, K. Kamata, Coord. Chem. Rev. 249 (2005) 1944.
[53] C.L. Hill, J. Mol. Catal. A – Chem. 262 (2007) 2.
[54] D.M. Fernandes, S.M.N. Simões, H.M. Carapuça, A.M.V. Cavaleiro, Electrochim. Acta 53 (2008) 6580.
[55] F.A.R.S. Couto, A.M.V. Cavaleiro, J.D. Pedrosa de Jesus, J.E.J. Simão, Inorg. Chim. Acta 281 (1998) 225.
[56] C.M. Tourne, G.F. Tourne, S.A. Malik, T.J.R. Weakly, J. Inorg. Nucl. Chem. 32 (1970) 3875.
[57] F. Zonnevijlle, C.M. Tourne, G.F. Tourne, Inorg. Chem. 21 (1982) 2751.
[58] J.P. Lock, J.L. Lutkenhaus, N.S. Zacharia, S.G. Im, P.T. Hammond, K.K. Gleason, Synth. Met. 157 (2007) 894.
[59] B. Keita, L. Nadjo, J. Electroanal. Chem. 227 (1987) 77.
[60] S.A. Malik, T.J.R. Weakley, J. Chem. Soc. A (1968) 2647.
[61] D.A. Buttry, F.C. Anson, J. Am. Chem. Soc. 105 (1983) 685.
[62] S.A. Richert, P.K.S. Tsang, D.T. Sawyer, Inorg. Chem. 28 (1989) 2471.
[63] W. Zhu, M. Sintic, Z. Ou, P.J. Sintic, J.A. McDonald, P.R. Brotherhood, M.J. Crossley, K.M. Kadish, Inorg. Chem. 49 (2010) 1027.
[64] J.A. Claussen, G. Ochoa, M. Páez, J. Costamagna, M. Gulppi, T. Nyokong, F. Bedioui, J.H. Zagal, J. Solid State Electrochem. 12 (2008) 473.
[65] M.N. Yarasir, M. Kandaz, B.F. Senkal, A. Koca, B. Salih, Dyes Pigm. 77 (2008) 7.
[66] P.C. Gach, J.A. Karty, D.G. Peters, J. Electroanal. Chem. 612 (2008) 22.
[67] A.T. Hubbard, F.C. Anson, Anal. Chem. 38 (1966) 58.
[68] B. Wang, R.N. Vyas, S. Shaik, Langmuir 23 (2007) 11120.