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Electrochemical characterization of glassy carbon electrodes modified with hybrid inorganic-organic single-layer of α -Keggin type polyoxotungstates

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Abstract It has been demonstrated, for the first time, that an adsorbed single-layer of the hybrid salts $(\text{TBA})_4\text{H}_3\text{PW}_{11}\text{O}_{39}$, $(\text{TBA})_4\text{PW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39}$, $(\text{TBA})_4\text{PW}_{11}\text{Mn}(\text{H}_2\text{O})\text{O}_{39}$ and $(\text{TBA})_4\text{HPW}_{11}\text{Co}(\text{H}_2\text{O})\text{O}_{39}$ can be fabricated on the surface of a glassy carbon electrode by the droplet evaporation methodology. These chemically modified electrodes were stable and their preparation was reproducible and easy to perform. The electrochemical features of the immobilized polyanions were different from those of the corresponding soluble species, namely in what concerns the peak potential values. The effect of the scan rate and of pH on the voltammetric features led to the conclusion that the first W reduction process for all immobilized polyanions was diffusion-controlled. For TBA-PW₁₁, TBA-PW₁₁Fe and TBA-PW₁₁Co the two-electron reductions at the first W waves are accompanied by the uptake of protons (2 H⁺ for the PW₁₁ anion and 4 H⁺ for the Fe-substituted and Co-substituted species). For the PW₁₁Mn-modified electrode, the reduction at the first W wave was a 1 e/2 H⁺ process. Additionally, the results obtained in the presence of Na₂SO₄ in the solution highlighted the role of the ions in the supporting electrolyte in the redox features of the immobilized hybrid phosphotungstates.

Keywords α -Keggin-type polyoxotungstates · Metal-substituted polyoxotungstates · Glassy carbon-modified electrodes · Inorganic-organic hybrids · Electrochemical behaviour

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Introduction

Polyoxometalates (POMs) are polyionic metal oxide clusters that have attracted much attention in different domains including catalysis [1–4], materials science [5, 6] and medicine [7] owing to their having various possibilities of composition, high thermal stability and very rich redox chemistry [3, 8, 9]. POMs are composed primarily of an early transition metal, M (e.g., W^{VI}, Mo^{VI})—the addenda atom—oxygen and at least one heteroatom, X (Si, P, Ge, etc). This large class of polyoxoanions include the Keggin anions, having general formula $[\text{XM}_{12}\text{O}_{40}]^{m-}$, and the Dawson anions, $[\text{X}_2\text{M}_{18}\text{O}_{62}]^{p-}$, amongst others [8]. The α -Keggin polyanions contain four corner-shared M_3O_{13} groups and a central XO_4^{n-} group. This class of POM has been intensively studied by electrochemical methods in aqueous [3] and non-aqueous solution [10, 11]. These heteropolyanions can be further modified by substitution of at least one of the addenda atoms by another *d*-block metal, M' , giving complexes of general formula α - $[\text{XM}_{11}\text{M}'(\text{H}_2\text{O})\text{O}_{39}]^{p-}$, which hold for additional redox features [3, 8, 12, 13]. The outstanding electrochemical and electrocatalytic properties of this type of POMs, including the transition-metal-substituted α -Keggin-type structures, made this class of compounds very attractive as modifiers for electrodes.

There are several procedures for the modification of electrodes by POMs: electrochemical deposition [14, 15], entrapment in polymeric matrices [16–20] and adsorption of single layers [21–23] or multi-layers [21, 22, 24] by dip-coating the electrode in an aqueous POM solution. However, the high solubility of many POM compounds in aqueous media limits the stability of those modified electrodes leading to leaching of the polyanion from the electrode, and to the consequent drop of their electrochemical features [25, 26]. Further, for the polymer entrapped POM modification, the electrochemical

behaviour of the polyanion depends on the polymer used and on the preparation procedure [3, 19, 20]. Therefore, sol-gel methods [23, 25, 26] have been used to provide mechanically stable composite electrodes. However, these methods are somewhat time-consuming owing to the successive chemical procedures needed for their fabrication, and the maintenance of the electrochemical features of the incorporated POM anions may depend on the silicate matrix preparation procedure [27]. Another recent approach is the immobilization of inorganic-organic hybrids, e.g. POM salts of large organic cations such as quaternary ammonium salts in the form of carbon paste electrodes [26, 28, 29] or incorporated in a gel film on pyrolytic graphite [30], by ionic binding of the POM to a 4-aminophenyl derivatized glassy carbon electrode [31], or by physical adsorption of hexadecylpyridinium POM salts onto spectroscopic graphite rods [32].

The majority of the published work on chemically modified electrodes involves modification with the parent Keggin-type and Dawson-type structures. Surprisingly, few studies have been performed with metal-substituted POMs. In spite of their large variety of composition [33]: for example, iron-substituted species have been immobilized by entrapment into polymeric matrices, e.g. Fe^{III} Keggin-phosphotungstate [16, 20], Fe^{III} Keggin-silicotungstate [34] and Fe^{III} Dawson-phosphotungstate [17]. Electrode modification with electrodeposited Pd^{II} Keggin-phosphotungstate and Dawson-phosphotungstate [35, 36], and with Cu^{II} Dawson-phosphotungstate in a polymeric matrix [17], was also tested. In particular, the above-mentioned studies using hybrid POM salts were restricted to modification of electrodes with the parent Keggin-anions or Dawson-anions, $\text{PMo}_{12}\text{O}_{40}^{3-}$ [26, 28], $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ [30] and $\text{SiW}_{12}\text{O}_{40}^{4-}$ [29, 32]. However, transition-metal-substituted POMs have proven to be extremely attractive as electrocatalysts in homogeneous solution and, in some cases, immobilized into polymer modified electrodes, where the transition metals may play an important role as active sites [3]. So, the exploitation of the potentialities of electrode modification with metal-substituted POMs, particularly of metal-substituted phosphotungstates, is an enthusiastic approach in the electrochemical and inorganic chemistry fields.

The aim of this work is to explore the fabrication of new chemically modified electrodes based on the immobilization of the water-insoluble tetrabutylammonium (TBA) salts of phosphotungstates of the Keggin-type, $\alpha\text{-}[\text{PW}_{11}\text{M}'(\text{H}_2\text{O})\text{O}_{39}]^{p-}$, $\text{M}' = \text{Fe}^{\text{III}}$, Mn^{III} and Co^{II} ($\text{PW}_{11}\text{M}'$) and the related structure, $\alpha\text{-}[\text{PW}_{11}\text{O}_{39}]^{7-}$ (PW_{11}), the lacunary precursor, as adsorbed single-layers onto glassy carbon electrodes. An adsorbed single-layer shall be established as a non-organized and relatively thick deposit, opposite to self-assembled-monolayer structures or to layer-by-layer assemblies. The present adsorbed single-layer methodology allows the deposition of the TBA-polyanions salts by a relatively simple procedure. Hence, the electrochemical behaviour of the immobilized polyanions in the TBA inorganic-organic

hybrid microenvironment was examined. Also, the effects of pH and Na_2SO_4 in the cell solution on the voltammetric behaviour of the modified electrodes were evaluated. Comparisons were made with the redox behaviour of these Keggin-type anions in homogeneous solution. As far as we know, this is the first attempt to immobilize the Mn^{III} -substituted and Co^{II} -substituted phosphotungstate anions. Also, the present electrode modification methodology is applied, for the first time, to the immobilization of the hybrid salts TBA-phosphotungstates on glassy carbon.

Experimental

Reagents and solutions

All the reagents were used as received. Tetrabutylammonium salts of the following compounds were prepared by known procedures [12, 37]: $(\text{TBA})_4\text{H}_3\text{PW}_{11}\text{O}_{39}$, $(\text{TBA})_4\text{PW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39}$, $(\text{TBA})_4\text{PW}_{11}\text{Mn}(\text{H}_2\text{O})\text{O}_{39}$ and $(\text{TBA})_4\text{HPW}_{11}\text{Co}(\text{H}_2\text{O})\text{O}_{39}$. Sodium sulphate (Riedel de Haen), sulphuric acid (Fluka), acetic acid (Pronalab), sodium acetate (Carlo Erba) and acetonitrile (Panreac, for instrumental analysis, HPLC grade) were used as received. Electrolyte solutions for voltammetry were prepared using water purified in a Milli-Q System. Solutions within the pH region 2.2–3.7 were prepared by mixing the 0.1 M $\text{CH}_3\text{COOH}/\text{NaCH}_3\text{COO}$ aqueous solution (buffer with pH = 4.6) with appropriate amounts of 0.01 M H_2SO_4 . Solutions of pH 1.0 and 1.9 were prepared with H_2SO_4 .

Apparatus

Cyclic voltammetry measurements were carried out on a BAS 100B/W electrochemical analyser using a conventional three-electrode single-compartment cell supplied by BAS Inc. The working electrode was a modified glassy carbon disc. The auxiliary electrode was a Pt wire. The reference electrode was Ag/AgCl (saturated with KCl). Measurements were made at room temperature, within the potential window +1,000 mV to –700 mV. The solutions were degassed with pure nitrogen for 5 min before the measurements and blanketed with nitrogen gas during the voltammetric experiments. pH measurements were performed with a Cole-Parmer pH-meter and a Orion 9104S glass electrode. UV-vis spectra were obtained at a Jasco V-560 spectrometer, with 1-cm-path quartz cells.

Preparation of the modified electrodes and voltammetric procedures

Acetonitrile solutions with a concentration of ca. 3 mM for TBA salts of PW_{11} and PW_{11}M ($\text{M} = \text{Fe}^{\text{III}}$, Mn^{III} and Co^{II}) were prepared. The surface of the glassy carbon

working electrode was polished with 0.3 μm alumina and washed with distilled water. The condition of the bare glassy carbon electrode (GCE) was calibrated regularly using $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple (1 mM) as the reference probe. In 0.01 M H_2SO_4 aqueous solution, $[\text{Fe}(\text{CN})_6]^{3-/4-}$ presented $E_{1/2} = +270$ mV versus Ag/AgCl, with a peak separation, ΔE_p , (anodic to cathodic) of 69 mV. Then, a micro-drop of 3 μL of the acetonitrile solutions of the selected POM was placed onto the surface of the glassy carbon electrode and the solvent was allowed to evaporate for about 15 min at room temperature. After this, the modified working electrode was ready to use. The corresponding surface concentration of the TBA-phosphotungstate salts was ca. 1.3×10^{-7} mol/cm². To this surface concentration corresponds an estimated value of 2 μm for the thickness of the adsorbed hybrid layers (based on the calculated volume of the $(\text{TBA})_4\text{PW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39}$ and $(\text{TBA})_4\text{HPW}_{11}\text{Co}(\text{H}_2\text{O})\text{O}_{39}$; respectively 2,726 and 2,772 \AA^3). Different experimental conditions were tested for the preparation of the adsorbed TBA-phosphotungstate salts. The concentration of TBA-phosphotungstate acetonitrile solution was varied between 1 mM and 6 mM and higher micro drop volumes (6 μL and 9 μL) were also tested. However, it was for the above mentioned conditions (3 μL of a 3 mM TBA-phosphotungstate acetonitrile solution) that the definition of the cyclic voltammograms was the best. For these modified electrodes, an electrochemical activation step was performed in a 0.01 M H_2SO_4 solution, consisting of a 60 multi-cycle runs regime, between -0.7 V and $+0.4$ V (or $+1.0$ V for the PW_{11}Mn -modified electrode). Half-wave potentials were calculated from the cyclic voltammetric peaks as the average of the cathodic (E_{pc}) and anodic peak potentials (E_{pa}).

UV-vis spectroscopy measurements

The UV-vis spectra of the hybrid single-layers of TBA- PW_{11}M ($\text{M} = \text{Mn}^{\text{III}}$ and Co^{II}) were obtained as follows: the hybrid single-layers were prepared as described in the previous section, the modified electrode was immersed in the acidic electrolyte solution and the multi-cycle regime was applied. Then the modified electrode was removed from the solution, washed with water and immersed in 10 mL of acetonitrile until complete dissolution is deposited. For achieving a solution with a suitable polyanion concentration for the UV-vis spectra acquisition, ten deposits had to be collected.

The UV-vis spectra of the initial TBA-phosphotungstates in acetonitrile were also recorded.

Results and discussion

General voltammetric behaviour of the TBA-phosphotungstate-modified electrodes

Generally, the soluble α -Keggin phosphotungstates are unstable in neutral and basic solutions [8]. Therefore, all

studies with the electrodes modified with immobilized TBA salts of the phosphotungstates PW_{11} , PW_{11}Fe , PW_{11}Mn and PW_{11}Co were performed in acidic aqueous solution.

The cyclic voltammograms (CV) of acidic solutions of the dissolved lacunary PW_{11} anion and of the metal-substituted anion PW_{11}Fe and PW_{11}Co show two reversible or quasi-reversible two-electron waves at negative potentials, corresponding to the reduction of the tungsten atoms [14, 38]. For all these polyanions, the W reduction processes are accompanied by the addition of protons to counterbalance the increase in the negative charge upon reduction and, therefore, the half-wave potentials of the W waves are pH-dependent. For the metal-substituted species, the half-wave potentials, $E_{1/2}$, of the W waves are shifted towards more negative values compared with the lacunary anion [38]. Additionally, for the PW_{11}Fe anion, the redox process associated to the substituted metal is observed, at more positive potentials (eg. $E_{1/2}$ of $+84$ mV at 10 mV/s, pH 2 [20]). For the PW_{11}Co anion, the oxidation of the Co^{II} was not observed within the aqueous working potential window. For the PW_{11}Mn anion in aqueous solution, as far as we know, there is no available information about the redox processes of the W atoms. Nevertheless, the related species SiW_{11}Mn presents a first W reduction peak of two electrons [39, 40] whereas the similar anion ZnW_{11}Mn exhibits only one electron for the first reduction of the tungsten-oxide cage structure [41]. The redox process of the $\text{Mn}^{\text{III/II}}$ pair in PW_{11}Mn anion was studied by Pope and collaborators [42] but no comments were made about the W redox processes.

The voltammetric features of the TBA-phosphotungstate salts immobilized at the GCE surface were similar, in terms of the number of voltammetric waves, to those observed in aqueous solution for the corresponding soluble polyanions, at identical pH. It must be noted that the electrochemical pre-treatment consisting of the multi-cycling scanning (cf. Experimental) led to a better definition of the CVs (Fig. 1). This is indicative of reorganization and/or wetting of the adsorbed layer of the TBA-phosphotungstate salts (which is relatively thick) leading to an increase of the electron transfer rate from the electrode surface to the redox sites at the polyanion, which is in a TBA microenvironment. In fact, for TBA-polyanion layers of lower thickness (ca. 0.7 μm , produced from a 1 mM solution) the number of multi-cycles needed in the electrochemical pre-treatment was much lower (ten cycles), indicating a faster reorganization and/or wetting of the adsorbed layer. For these thinner layers the peak currents were ca. 1/3 the values for the thicker deposits, and the W half-wave potentials were ca. 10 mV more negative. As the voltammetric features did not improve in these thinner TBA-polyanion layers, namely the overall definition of the peaks, further results were obtained using the thicker (2 μm) TBA-phosphotungstate-modified GCEs. Figure 2 shows representative CVs of the TBA-phosphotungstate elec-

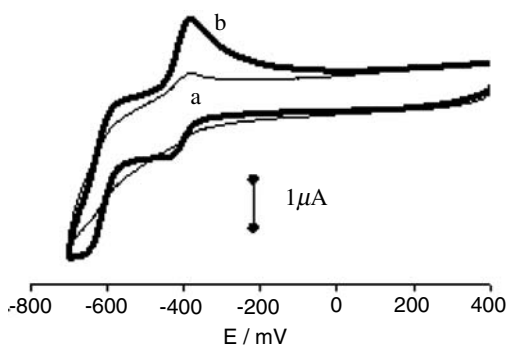


Fig. 1 Effect of the multi-cycling scanning on the cyclic voltammograms for a TBA-PW₁₁Co modified electrode: **a** first scan and **b** 60th scan. Test solution: sulphuric acid (pH 1.9). Scan rate: 100 mV/s

trodes immersed in aqueous sulphuric acid solution of pH 1.9. All polyanions in the adsorbed TBA-phosphotungstate layer presented two reduction waves for the W atoms, with the corresponding re-oxidation counterparts. The cyclic voltammograms recorded at a potential window including only the first W redox process are also included in Fig. 2. For the TBA-PW₁₁Fe-modified and TBA-PW₁₁Mn-modified electrodes the pair of peaks for the one-electron reduction/oxidation of the first row transition metal is also observed. Table 1 presents the voltammetric data for the immobilized TBA-phosphotungstates, in which the peak currents for the first W redox process were extracted from the corresponding voltammograms (curves b in Fig. 2). The values for the Fe^{III/II} and Mn^{III/II} one-electron processes were also included. As a consequence of the immobilization, the

potentials of the first W process for all polyanions were 50–100 mV less negative than the corresponding values in aqueous solution (see Table 1) showing evidence of the fact that the electron transfer at the tungsten-oxide cage structure is thermodynamically favourable for the adsorbed TBA-phosphotungstate layers. This can be explained considering the effect of ion-pairing, which is certainly occurring within the TBA-phosphotungstate hybrid environment. Interestingly, there were no substantial differences between the potentials of the first W process upon metal substitution, opposite to what occurs for the dissolved polyanions. The eventual demetalation of the M-substituted phosphotungstates within the adsorbed layer owing to the effect of the acidic medium cannot be advanced as a cause of the proximity of the W potentials to those of the lacunary anion. The structural and chemical integrity of the immobilized M-substituted phosphotungstates was preserved; this was checked by analysing the visible spectra of the deposited layers. For instance, for the TBA-PW₁₁Mn and TBA-PW₁₁Co salts re-collected from the corresponding electrodes into acetonitrile (see Experimental), the bands for the Mn^{III} and Co^{II} were clearly observed (for PW₁₁Mn: a band at 489 nm with a shoulder at 523 nm and for PW₁₁Co: a band at 478 nm with a shoulder at 510 nm) and were identical to those of the corresponding polyanion salts in acetonitrile.

At a first glance, the shapes of all the voltammetric waves resemble those for a common solution process, i.e. in which there is diffusion control. In fact, recording the CVs at different scan rates (between 5 mV/s and 150 mV/s) in the potential range from 0 V to -0.7 V (Fig. 3) allows concluding that, for the first W reduction

Fig. 2 Cyclic voltammograms for **A** TBA-PW₁₁, **B** TBA-PW₁₁Fe, **C** TBA-PW₁₁Co and **D** TBA-PW₁₁Mn modified electrodes: **a** large potential window and **b** potential window for the first W reduction. Test solution: sulphuric acid (pH 1.9). Scan rate: 50 mV/s

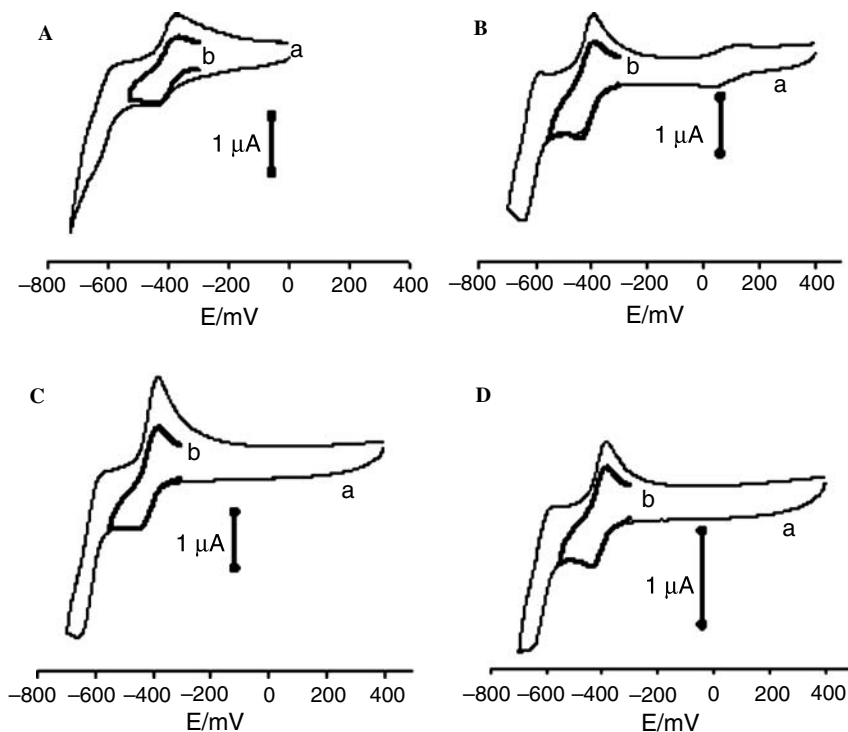


Table 1 Cyclic voltammetric data for the immobilized TBA-phosphotungstate salts ^a (E_{pc} values for dissolved polyanions also included for the W wave ^b)

Anion	First W wave					$M^{III/II}$ wave		
	$E_{pc}(mV)$	$E_{1/2}(mV)$	$ \Delta E_p (mV)$	$I_{pc}(\mu A)$	$E_{pc}(aq)^b (mV)$	$E_{1/2}(mV)$	$ \Delta E_p (mV)$	$I_{pc}(\mu A)$
PW ₁₁	-433	-404	57	-0.43	-486			
PW ₁₁ Fe	-438	-414	47	-0.54	-550	+78 ^c	83	-0.20
PW ₁₁ Co	-448	-415	65	-0.43	-548			
PW ₁₁ Mn	-437	-411	52	-0.26		+649 ^d	211	-0.19

^aTest solution: sulphuric acid, pH 1.9; scan rate 50 mV/s

^b E_{pc} values for dissolved polyanions in aqueous solution of pH 2.2, scan rate 100 mV/s [38]

^c $E_{1/2} = +84$ mV ($\Delta E_p = 69$ mV) for the dissolved PW₁₁Fe at pH 2, 10 mV/s [20]

^d $E_{1/2} = +720$ mV (ΔE_p in the range 80–170 mV) for the dissolved PW₁₁Mn at pH 3.5–6.5, 20 mV/s [42]

wave the peak current intensity was proportional to the square root of the scan rate, ν , which is a characteristic of a diffusion-controlled process. For all immobilized polyanions, the log–log plot of the cathodic peak current (I_{pc}) of the first W reduction peak versus ν gave slopes within the interval [0.4–0.6], which indicates that I_{pc} shall be proportional to the square root of the scan rate. The same holds for the Fe^{III/II} redox processes in TBA-PW₁₁Fe. The data for the second W reduction wave was not included, owing to difficult baseline assignment. The expected behaviour (of I_p being proportional to ν) for a surface-confined redox process was not observed for any of the immobilized TBA-phosphotungstates. In addition, the anodic/cathodic peak-to-peak separation (ΔE_p) of the first W processes was ca. 50–60 mV (50 mV/s) instead of zero, as would be expected for a reversible surface process. For the TBA-PW₁₁Mn-modified and TBA-PW₁₁Co-modified electrodes those values increased slightly with increasing scan rates, evidencing more critical kinetic restrictions. All these data are indicative of either a slow electron transfer within the TBA-phosphotungstate layer or to a relatively slow diffusion of protons into the wetted adsorbed layer. On

the other hand, for the thinner (0.7 μ m) TBA-phosphotungstate-modified electrodes, the ΔE_p for the first W process decreased slightly to 40–50 mV, compared with the thicker electrodes. This may indicate that the first W electrode-process is becoming less constrained by the diffusion of protons because the deposited layer is thinner. Nevertheless, the I_p versus ν behaviour was, again, typical of diffusion-controlled processes (log–log slopes of 0.5–0.6).

Therefore, it may be assumed that the rate-determining step in the electron transfer processes is the transportation of protons from the solution to the TBA-phosphotungstate within the immobilized layer, considering the fact that the initial pre-treatment led to an activation of the modified electrodes in terms of the electron transfers between the glassy carbon surface and the active redox sites at the polyanions. This phenomenon occurred also for other electrodes modified with Keggin anions in which the peak current values were found to be diffusion-controlled, e.g. for phosphotungstic acid [43] and silicotungstic acid [44] immobilized in a tetramethoxysilane-derived gel, for phosphotungstic acid [27] in a ceramic-carbon electrode and for 12-molybdophosphate hybrid material in a carbon paste electrode [26].

Another interesting consideration about the adsorbed TBA-phosphotungstates concerns the number of electrons transferred in the W-redox processes. For the TBA-PW₁₁Fe electrode (Fig. 2B) by comparison of the peak currents (Table 1) for the Fe^{III/II} couple with that of the first W reduction process, it appears that this W wave corresponds to a two-electron process (i.e. to two coincident one-electron W^{VI}/W^V reductions) as occurs for the dissolved PW₁₁Fe anion [20, 38]. Note that the peak currents for the Fe^{III/II} couple shall be influenced by the lower reversibility of this process (the peak-to-peak separation is substantially higher than for the first W wave), thus the I_p for the Fe^{III/II} reduction is certainly lower than for a fully reversible process. The same holds for the Mn^{III/II} couple, and the observed reduction current was identical to that of the iron couple, as expected for the transfer of one-electron. This allows further comparisons: surprisingly, for the immobilized PW₁₁Mn, (Fig. 2D and Table 1) the first W wave appears to correspond to a one-electron process. On the

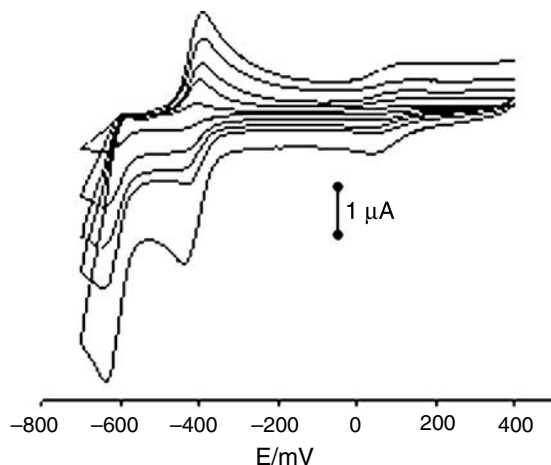


Fig. 3 Cyclic voltammograms for TBA-PW₁₁Fe modified electrode in 0.01 M sulphuric acid solution (pH 1.9) at different scan rates (between 5 mV/s and 150 mV/s)

other hand, for the immobilized PW_{11} and $PW_{11}Co$ salts, (Fig. 2A, C and Table 1) the first W wave correspond to a two-electron process, accordingly to the behaviour of the soluble anions. These comparisons of peak currents are possible because the reproducibility of the electrode preparation procedure is good (relative standard deviations, RSD, of less than 5% for four different electrodes, prepared in different occasions).

Additionally, the present electrode modification scheme, producing adsorbed single-layers of the TBA salts of the phosphotungstates, although having a relatively low robustness when compared with bulk-modified electrodes (sol-gel or carbon paste methods), the preparation procedure is reproducible and easy to perform. Also, the short-time stability is very good: a single modified electrode maintains its voltammetric features for a 12-h period of continuous work in acidic solution, with very small peak current variations (RSD values smaller than 5%) for the first W reduction process for all polyanions. This shows that the present adsorbed TBA-phosphotungstate layers are stable, i.e. no leaching or chemical degradation occurred. The polyanions modified electrodes maintained their electrochemical activity for a 4-day period being stored overnight in a dry atmosphere. However, after 7 days the voltammetric signals decreased to about 50–60% of the original values.

Effect of the solution pH on the electrochemical behaviour of the TBA-phosphotungstate-modified electrodes

As mentioned in the previous section, the voltammetric features of the phosphotungstates immobilized as TBA salts at the GCE were typical of diffusion-controlled processes. In addition, although the W reduction processes were apparently thermodynamically favourable, eventual kinetic restrictions were occurring, leading to unexpected high values for ΔE_p and the diffusion of protons was advanced as a possible rate-determining step. Therefore, CV experiments in solutions of different pH values were performed (pH interval 1.0–3.7). With increasing pH, the peak potential of all the first W waves shifted monotonously towards more negative values. The slopes of the E_{pc} versus pH were 66 mV/pH unit for TBA- PW_{11} , and 111–113 mV/pH unit for the metal-substituted anions. Also, lower peak currents were detected as pH increased. The obtained values, assuming a Nernstian behaviour, indicate that the two-electron reductions at the first W waves for the immobilized PW_{11} , $PW_{11}Fe$ and $PW_{11}Co$ are accompanied by the uptake of protons ($2 H^+$ for the PW_{11} anion and $4 H^+$ for the metal-substituted species) which diffuse from the solution to the wetted layer of the TBA-phosphotungstate. These values are different from those obtained in aqueous solutions where the first W wave corresponded to a $3 H^+ / 2e$ process for both soluble anions PW_{11} and $PW_{11}Fe$ [20, 38]. For the $PW_{11}Mn$ -modified electrode, assuming that only one electron is transferred at the first

W wave, the slope of 113 mV/pH unit points to the uptake of two protons. No data for the soluble polyanion is available. In addition, the different behaviour observed upon variation of pH for the immobilized TBA- PW_{11} and for the metal-substituted species supports the fact that no de-metallation occurs for the immobilized polyanions, i.e. the hybrid TBA-phosphotungstate layers are chemically stable within the pH region under consideration.

The present results highlight the fact that the environment where the phosphotungstates are held in (consisting of a layer where the TBA counterions and, eventually, the protons from the molecular formula are interacting with the polyanions) have an important impact on the electrochemical redox processes at the W atoms.

Effect of Na_2SO_4 in solution on the electrochemical behaviour of the TBA-phosphotungstate-modified electrodes

Some electrochemical studies of soluble polyoxometalates have demonstrated that redox features may be influenced by the presence of different supporting electrolytes [11, 45–48]. For example, in non-aqueous media, the presence of H^+ , Li^+ or Na^+ caused one-electron waves to change into two-electron waves for $SiMo_{12}O_{40}^{4-}$ and $PtMo_{12}O_{40}^{3-}$ [11]. Thus, it seems possible to control the redox potentials and the number of electrons introduced at each W reduction step by changing cations in the supporting electrolytes [11]. Nevertheless, for electrodes modified with POMs, similar studies have been made only with $P_2W_{18}O_{62}^{6-}$ immobilized within a gel on the surface of wax-impregnated graphite electrode; the results led to the conclusion that there were no effects on the cyclic voltammograms owing to the presence of Na_2SO_4 in solution, i.e. Na^+ cations were unnecessary to the charge compensation process and did not interfere in the number of transferred electrons [49].

In the present work, we studied the effect of Na_2SO_4 in solution on the voltammetric features of the electrodes modified with the adsorbed single-layers of TBA- PW_{11} , TBA- $PW_{11}Fe$ and TBA- $PW_{11}Co$. Different amounts of Na_2SO_4 (0.1 M and 0.3 M) were added to the initial supporting electrolyte (0.1 M H_2SO_4). It is worth mentioning that the solution pH varied as a result of the addition of Na_2SO_4 , from 1.0 to 1.8 and to 2.1, respectively for the 0.1 M and 0.3 M Na_2SO_4 solutions.

For the TBA- $PW_{11}Fe$ electrode, the presence of 0.1 M Na_2SO_4 in the solution produced an increment of the peak currents for the W processes (Fig. 4). For the initial experimental conditions (0.1 M H_2SO_4), the first and second W redox processes were located at -360 mV and -575 mV. These values, as well as the peak-to-peak separation, were unchanged upon the addition of the sodium sulphate. Additionally, the log-log plot of the cathodic peak current (I_{pc}) of the first W reduction peak versus ν gave a slope of 0.54 indicating that I_{pc} is still

diffusion-controlled. The peaks for the $\text{Fe}^{\text{III/II}}$ couple also increased in height in the presence of 0.1 M Na_2SO_4 . Therefore, an increase in the number of transferred electrons in each W wave is not likely to occur in the present immobilized phosphotungstate salts. When the amount of Na_2SO_4 in solution was increased to 0.3 M, the cathodic and anodic peak currents stabilised and a slight potential shift to more negative values was observed (Fig. 4). Furthermore, after the modified electrode being used in the solutions containing 0.1 or 0.3 M Na_2SO_4 , the original cyclic voltammograms (0.1 M H_2SO_4 , without Na^+) could not be obtained. The same general behaviour was observed also for PW_{11}Co .

For the TBA- PW_{11} -modified electrode in the 0.1 M H_2SO_4 solution the two W redox processes occurred at -352 mV and -564 mV. The presence of 0.1 M Na_2SO_4 did not change the voltammetric behaviour of this modified electrode, opposite to what happened for the TBA- PW_{11}Fe and TBA- PW_{11}Co electrodes.

All these phenomena highlight the role of the ions in the supporting electrolyte in the redox features of the immobilized hybrid phosphotungstates. Some possible effects can be envisaged: (1) the extent of ion-pairing of the Na^+ cation, assuming a facilitated transportation all through the adsorbed layer, with the immobilized phosphotungstates which have neighbouring TBA⁺ (and protons) as structural counter-cations; (2) the effects of raising pH as a consequence of the addition of Na_2SO_4 and (3) the effect of an increase of the conductivity of the adsorbed thick layer as a consequence of an eventual incorporation of the added ions from the new Na_2SO_4 electrolyte inside the TBA-phosphotungstate single-layer. For the electrodes modified with TBA- PW_{11}Fe and TBA- PW_{11}Co , the initial increase in the peaks current in the presence of 0.1 M Na_2SO_4 , may be, in fact, a consequence of an increase in the conductivity of the adsorbed thick layer. If additional ion-pairing with Na^+ would prevail, a variation of the peak potentials towards more positive values could be expected. Though, the peaks position remained unchanged. These results point to the occurrence of an effective incorporation of the Na_2SO_4 electrolyte within the TBA-phosphotungstate layer. This process may occur by exchanging a rather loose structural proton (initially present in PW_{11}Co and added to the PW_{11}Fe as a

consequence of the electrochemical reduction of Fe^{III} to Fe^{II}) by Na^+ . It must be pointed out that for these electrodes the original voltammograms in 0.1 M H_2SO_4 could not be restored after the contact with the Na_2SO_4 electrolyte. For the TBA- PW_{11} electrode, considering that it contains three protons, presumably strongly bonded to the PW_{11} anion (which holds per se a (-7) charge and is known to have protonable oxygen atoms at the vacancy [45]), the interchange with Na^+ from the added electrolyte would be difficult. Therefore, no observable effects were detected by adding 0.1 M Na_2SO_4 . Though, all these considerations have to be further examined and work on these effects is still in progress.

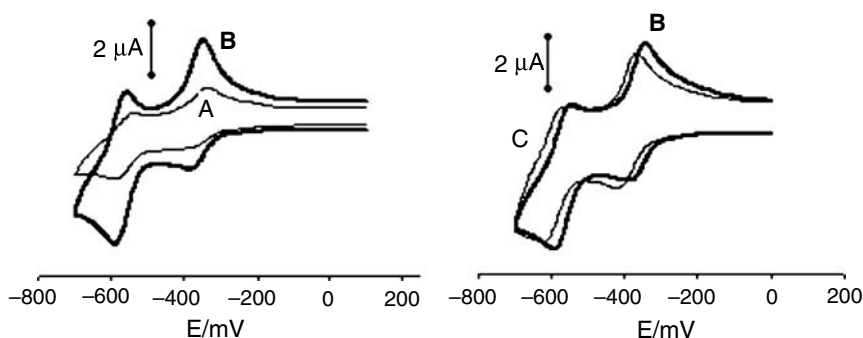
Conclusions

It has been demonstrated, for the first time, that an adsorbed single-layer of the hybrid salts, TBA-phosphotungstates can be fabricated on the surface of a glassy carbon electrode by the droplet evaporation methodology. These chemically modified electrodes were mechanically and chemically stable and their preparation was reproducible and easy to perform.

The main objective of the present work was to attain the immobilization of the TBA salts of the lacunary PW_{11} polyanion and of its analogues substituted with Fe, Co and Mn by a simple methodology, in order to allow the study of their electrochemical properties. This was successfully achieved, and in fact, this work provides the first example of adsorbed hybrid-phosphotungstate-modified GC electrodes.

For all the modified electrodes, consisting of a rather thick layer of the TBA-phosphotungstate, the W redox processes were diffusion-dependent, and in fact the first W reduction process was accompanied by the uptake of protons diffusing from the acidic solution into the immobilized TBA-phosphotungstate layer. Further, the first W reduction process for all modified electrodes was thermodynamically favoured compared with what occurs with the corresponding soluble polyanions. Additionally, the effect of other ions in the test solution (from the Na_2SO_4 electrolyte) leads to interesting observations: for the metal-substituted anions, the addition of Na_2SO_4 changed the voltammetric features, namely the peak currents.

Fig. 4 Comparative cyclic voltammograms of TBA- PW_{11}Fe modified electrode in different medium: **A** 0.1 M H_2SO_4 (pH = 1.0), **B** 0.1 M H_2SO_4 + 0.1 M Na_2SO_4 and **C** 0.1 M H_2SO_4 + 0.3 M Na_2SO_4 . Scan rate: 100 mV/s



Therefore, considering future applications of the single-layer TBA-phosphotungstate-modified electrodes, namely in the electrocatalysis field, two aspects may be of relevance: firstly, the relatively high chemical and mechanical stability of the modified electrodes and, secondly, the specific voltammetric features of the adsorbed TBA-phosphotungstates, especially the effect of the presence of the lacunary metal upon the W waves potential which may lead to electrocatalysts with a active metal centre ($\text{Fe}^{\text{III/II}}$ and $\text{Mn}^{\text{III/II}}$) and simultaneously with a W framework of reversible and relatively facile redox behaviour.

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