



## Novel poly(hexylmethacrylate) composite carbon electrodes modified with Keggin-type tungstophosphate-tetrabutylammonium salts

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### ABSTRACT

Novel poly(hexylmethacrylate) carbon composite electrodes have been prepared from graphite powder and poly(hexylmethacrylate) binder, and modified with Keggin-type polyoxotungstate anions in the form of tetra-*n*-butylammonium (TBA) hybrid salts. The salts used were the lacunary anion compound, [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>4</sub>H<sub>3</sub>[PW<sub>11</sub>O<sub>39</sub>], and the metal substituted [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>4</sub>H[PW<sub>11</sub>Co<sup>II</sup>(H<sub>2</sub>O)<sub>39</sub>].H<sub>2</sub>O. Carbon composite electrodes without poly(hexylmethacrylate) were also prepared for comparison. The electrochemical features of the polyoxoanions were maintained after immobilization. The influence of scan rate and pH on the voltammetric characteristics of the first tungsten reduction process of the immobilized polyoxometalates led to the conclusion that the process was diffusion-controlled, depending on the uptake of protons from solution. The chemically modified electrodes were stable and their preparation was easy to perform, their good stability being related to the insolubility of the hybrid salts in aqueous solution, and to the affinity of TBA towards the pasting liquid. This new modification using poly(hexylmethacrylate) also slightly improves the current sensitivity. In the absence of polyoxometalates, the peak current for the hexacyanoferrate redox couple is significantly higher when poly(hexylmethacrylate) binder is used.

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### 1. Introduction

Interest in polyoxometalates (POMs) is increasing worldwide due to their enormous variety of structures and often unexpected properties in catalysis, medicine, electrochemistry, analytical chemistry, materials science, energy storage and optical properties [1–13]. Their interesting properties include high thermal stability, rich redox chemistry, photochemical and catalytic features towards a number of industrially and biologically significant reactions [1,2,10–13]. Among these properties, the ability to undergo reversible multi-electron redox processes makes them very attractive for chemically modified electrodes and electrocatalysis [1,10]. Attaching redox active POMs onto electrodes simplifies the study of their electrochemistry and facilitates their application in many fields. A number of strategies have been developed to prepare chemically modified electrodes with a variety of POMs. Several groups have immobilized POMs using procedures such as electrochemical deposition [14,15], entrapment into polymeric matrices [16,17] and adsorption of a POM anion mono-layer from an aqueous solution generally followed by the adsorption of a second layer of a counter-cation (e.g. [NH<sub>3</sub>(CH<sub>2</sub>)<sub>x</sub>NH<sub>3</sub>]<sup>2+</sup> or [Os(bpy)<sub>3</sub>]<sup>2+</sup>)

[1,18–20]. However, often these electrodes have a limited stability because electrode surfaces cannot be renewed in the case of leakage, contamination or passivation.

Other approaches have been the immobilization of organic–inorganic hybrids, e.g., POM salts of large organic cations incorporated into gel films on pyrolytic graphite [21] or by surface deposition of POM salts onto carbon electrodes [22–24]. Recently, interest has focused on the design and preparation of novel POM based hybrid materials, as well as application to three dimensional bulk-modified carbon-paste electrodes by direct mixing [25].

Carbon-paste electrodes (CPE) are composite electrodes because they result from the combination of two or more materials. They consist of a mixture of, at least, an electrically conducting carbon powder and an organic liquid and they have been widely applied in electrochemistry owing to their many advantages: they are inexpensive, easy to prepare, easy to handle, have low background currents and surface renewal is rapid [26]. Among the advantageous properties and characteristics listed above, CPEs allow the preparation of electrodes with a desired composition and, hence, with pre-determined properties. The choice of carbon paste components (carbon powder and pasting liquid), their ratio in the mixture and the way in which the CPEs are prepared (homogenization of the paste, packing of the paste in the electrode body, etc.) are important aspects that determine the properties,

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characteristics and behaviour of CPEs [27]. Generally, the organic liquid used as the binder component of pastes is a non-conductive mineral oil, such as Nujol or liquid paraffin. Owing to their chemical inertness as well as good adhesive ability, these viscous liquids have been widely used in the process of fabricating traditional CPEs. However, since these binders are not conductive, which to some extent weakens the electrochemical response, other pasting binders have been used to improve the carbon-paste electrode response. Much has been published about CPEs using ionic liquids mixed with organic binders or as their substitutes [28–30]. Other carbon composite electrodes based on graphite and cellulose acetate [31] or graphite and poly(vinyl chloride) [32,33] have also been developed. Graphite–epoxy composite electrodes have been used as biosensors [34].

Four preparative methods can be used to modify the surface or composition of the CPE, namely adsorption, covalent binding, dissolution and direct mixing, among which direct mixing is the most common [26]. In general, the modifiers used with direct mixing should be insoluble in the analyte solution, or they should at least strongly adsorb to the paste components in order to avoid dissolution of the modifier from the electrode surface during measurements. Therefore, for studies in aqueous solutions, the traditional salts of POMs and alkali metals like  $\text{Na}^+$  or  $\text{K}^+$  cannot be directly used as bulk modifiers of CPEs owing to their good solubility in water. However, organic–inorganic hybrids of POMs such as tetrabutylammonium (TBA) salts of the lacunary and transition-metal monosubstituted Keggin-type anions are insoluble in aqueous solutions [35].

The present work concerns novel carbon composite electrodes modified with tetrabutylammonium (TBA) salts of the  $\alpha$ -isomers of  $[\text{PW}_{11}\text{O}_{39}]^{7-}$  ( $\text{PW}_{11}$ ) and  $[\text{PW}_{11}\text{Co}^{\text{II}}(\text{H}_2\text{O})\text{O}_{39}]^{5-}$  ( $\text{PW}_{11}\text{Co}$ ), and a new easy way to immobilize these POMs by surface film or bulk modification. For surface modification, a drop of a mixture of graphite and poly(hexylmethacrylate), with or without tetrabutylammonium salts of lacunary and monosubstituted POM anions is deposited on the top of the surface of a normal carbon-paste electrode (graphite/mineral oil). These modified electrodes were characterised using  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  model electroactive species in aqueous solution by cyclic voltammetry and the influence of the solution pH and the voltammetric scan rate evaluated. Bulk modification was done by mixing the same POM salts directly with the carbon paste without using the poly(hexylmethacrylate) binder. Comparison with the electrochemical behaviour of the polyoxoanion deposited on the surface of the electrodes and in aqueous solution was also carried out. To our knowledge, this is the first report of fabrication of a carbon composite electrode using poly(hexylmethacrylate) binder.

## 2. Experimental

### 2.1. Reagents and solutions

Sulfuric acid (Fluka), acetic acid (Pronalab), sodium acetate (Carlo Erba), poly(hexylmethacrylate) solution (MW 400,000 in toluene – Aldrich), mineral oil (Fluka), potassium ferricyanide (Merck), potassium chloride (Merck) and graphite powder (< 20 micron, Sigma Aldrich) were used as received. The tetrabutylammonium salts of the  $\alpha$ -Keggin phosphotungstates  $[(\text{C}_4\text{H}_9)_4\text{N}]_4\text{H}_3[\text{PW}_{11}\text{O}_{39}]$  (TBA- $\text{PW}_{11}$ ) and  $[(\text{C}_4\text{H}_9)_4\text{N}]_4\text{H}[\text{PW}_{11}\text{Co}^{\text{II}}(\text{H}_2\text{O})\text{O}_{39}]\cdot\text{H}_2\text{O}$ , (TBA- $\text{PW}_{11}\text{Co}$ ) were prepared by a previously-published procedure [36]. All the compounds were characterized by thermal and elemental analysis, thermogravimetry, infrared spectroscopy and powder X-ray diffraction and the results were in agreement with previously-published values [37].

Electrolyte solutions for voltammetry were prepared using ultra-pure water (resistivity 18.2 M $\Omega$  cm at 25 °C, Direct-Q 3 UV sys-

tem, Millipore). Solutions within the pH range 2.0–3.0 were prepared by mixing appropriate amounts of a 0.01 M  $\text{H}_2\text{SO}_4$  solution with a 0.10 M  $\text{CH}_3\text{COOH}/\text{NaCH}_3\text{COO}$  buffer (pH = 4.6). Potassium ferricyanide solutions (1.0 mM) were prepared dissolving the proper amount of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  in 1.0 M KCl.

### 2.2. Apparatus

Electrochemical experiments were carried out on 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 a platinum wire (7.5 cm length) (BAS, MW-1032) and Ag/AgCl (sat. KCl) (BAS, MF-2052), respectively. The working electrode was a carbon-paste electrode, CPE, inserted into a CPE cavity of diameter 3 mm (BAS, MF-2010). A combined glass electrode (Hanna Instruments HI 1230) connected to an Inolab pH level 1 pH meter was used for pH measurements.

### 2.3. Preparation of the unmodified and modified CPEs

The carbon-paste electrode without bulk modification ( $\text{CPE}_1$ ) was fabricated as follows. A mass of 1.0 g of graphite powder and 0.5 mL of mineral oil were mixed in an agate mortar and pestle to achieve a homogeneous mixture. A portion of this paste was then packed into the cavity of the carbon-paste electrode body and the surface was smoothed on a piece of a weighing paper. POM bulk-modified carbon-paste electrodes were prepared by substituting a corresponding amount of the graphite powder (10% mass ratio of the modifier relative to the carbon powder) by TBA- $\text{PW}_{11}$  ( $\text{PW}_{11}\text{-CPE}_1$ ) or TBA- $\text{PW}_{11}\text{Co}$  ( $\text{PW}_{11}\text{Co-CPE}_1$ ).

For the poly(hexylmethacrylate) carbon composite electrodes ( $\text{CPE}_2$ ), two mixtures were prepared: (a) 0.75 g of graphite powder and 1.50 g of poly(hexylmethacrylate) solution and (b) 0.75 g of graphite powder, 0.10 g of POM and 1.50 g of poly(hexylmethacrylate) solution. A drop of 5  $\mu\text{L}$  of the slurry was placed onto the surface of an unmodified CPE prepared as described above and the solvent was allowed to evaporate for about 20 min. If the drop spread outside the circular area of the carbon paste the electrode assembly was rejected; thus, all electrodes employed had the same surface area. Electrodes with film composition (a), abbreviated as  $\text{CPE}_2$ , were used for the characterization of the electrode in the absence of POMs. The POMs used for case (b) were TBA- $\text{PW}_{11}$  ( $\text{PW}_{11}\text{-CPE}_2$ ) or TBA- $\text{PW}_{11}\text{Co}$  ( $\text{PW}_{11}\text{Co-CPE}_2$ ).

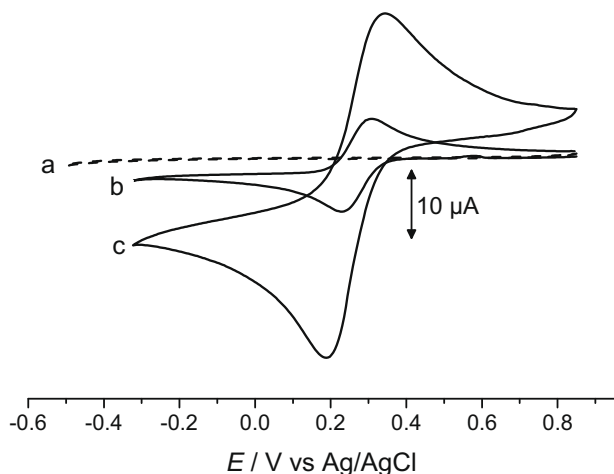
An electrode surface activation step was done by cycling the potential 60 times, between 0.0 V and  $-0.85$  V, in 0.01 M  $\text{H}_2\text{SO}_4$  at a scan rate of 100 mV  $\text{s}^{-1}$ . This step was needed to stabilise the electrodes and to obtain reproducible results, after which they were ready to use.

Measurements were made at room temperature ( $\sim 20$  °C). Solutions were degassed with pure nitrogen for 5 min before the measurements and nitrogen-blanketed during the measurements.

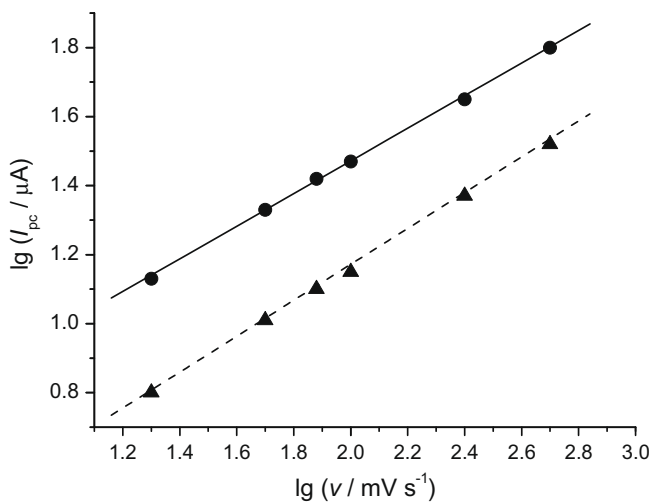
## 3. Results and discussion

### 3.1. Characterization of carbon-paste electrodes $\text{CPE}_1$ and $\text{CPE}_2$

Hexacyanoferrate electroactive species were selected to evaluate the performance of  $\text{CPE}_1$  and  $\text{CPE}_2$ . A more reversible voltammogram indicates faster electrode kinetics and better access to the electrode and a greater available surface area should result in higher peak currents. Fig. 1 shows the electrochemical response of  $\text{CPE}_1$  and  $\text{CPE}_2$  in 1.0 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$  + 1.0 M KCl solution: a slight increase in the background current response at  $\text{CPE}_2$  is visible with respect to  $\text{CPE}_1$ . On the other hand, the peak current for the



**Fig. 1.** Cyclic voltammograms of (a) CPE<sub>1</sub> and CPE<sub>2</sub> in 1 M KCl electrolyte, and (b) CPE<sub>1</sub> and (c) CPE<sub>2</sub> in a solution of 1 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>] + 1 M KCl. Scan rate 20 mV s<sup>-1</sup>.



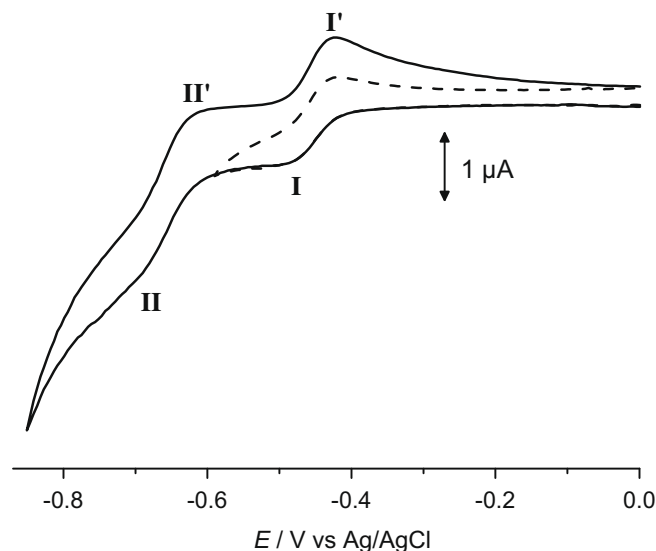
**Fig. 2.** Plot of  $\lg I_{pc}$  vs.  $\lg v$  for (▲) CPE<sub>1</sub> and (●) CPE<sub>2</sub> in a solution of 1 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>] + 1 M KCl.

[Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> redox couple is significantly higher (increase >115%) at CPE<sub>2</sub>. The poly(hexylmethacrylate)-graphite electrode surface may have more exposed graphite particles, and possibly additional porosity or roughness, leading to a higher available area for electrode reaction. The peak-to-peak separations ( $\Delta E_p$ ) were 76 mV for the CPE<sub>1</sub> and 170 mV for CPE<sub>2</sub>, indicating quasi-reversible electron transfer processes, the increase for CPE<sub>2</sub> attributed to slower kinetics. As reported previously, the reaction kinetics of electroactive species in concentrated interfacial solution in such systems may be slowed down due to lower mobility of molecules [38].

The relationship between  $I_p$  and  $v$ , seen in Fig. 2 as  $\lg(I_p, A)$  vs.  $\lg(v, mV s^{-1})$ , gave slopes close to 0.50 for both CPE<sub>1</sub> and CPE<sub>2</sub>, the square root relationship between cathodic peak currents and scan rate indicating that the redox processes at CPE<sub>1</sub> and CPE<sub>2</sub> are diffusion-controlled. In the timescale used (scan rates between 20 and 1000 mV s<sup>-1</sup>) the values of  $E_{1/2}$  did not change significantly (<10%) with scan rate and the ratio of anodic and cathodic peak currents was ca. 1.

### 3.2. Voltammetric behaviour of POM-CPE<sub>1</sub> and POM-CPE<sub>2</sub>

Generally,  $\alpha$ -Keggin phosphotungstates are unstable in neutral and basic solutions [2]. Therefore, all studies with the electrodes



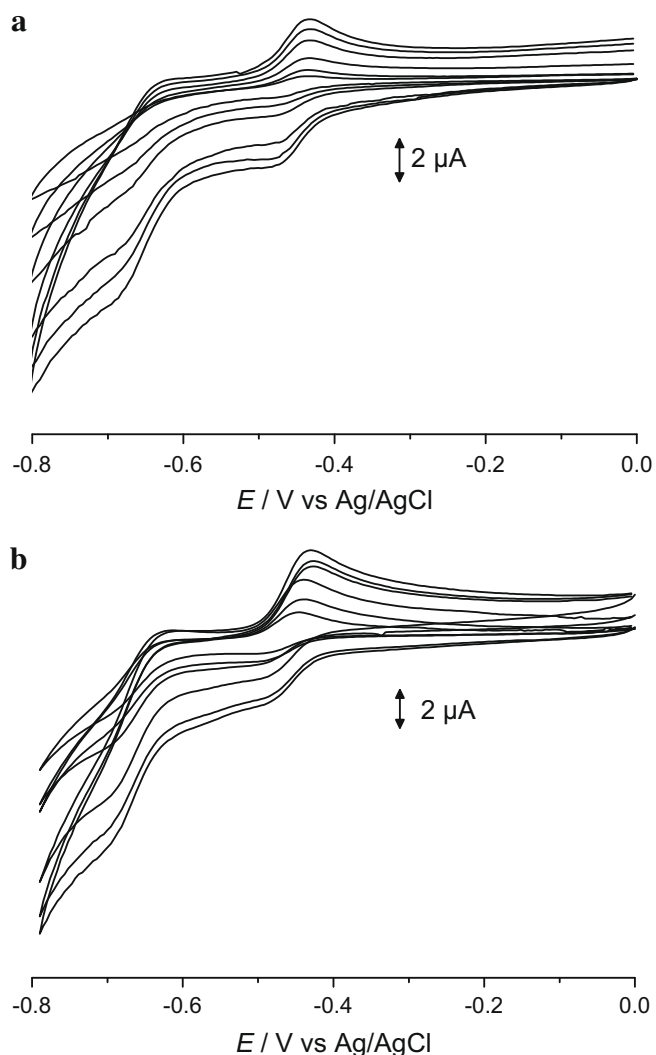
**Fig. 3.** Cyclic voltammograms for PW<sub>11</sub>Co-CPE<sub>2</sub> immersed in pH 2.0 H<sub>2</sub>SO<sub>4</sub>/HOAc/NaOAc aqueous solution at  $v = 50 mV s^{-1}$ , inverting the scan direction after the first reduction peak (- -) and after the second reduction peak (-).

modified with the TBA salts of the phosphotungstates PW<sub>11</sub> and PW<sub>11</sub>Co were performed in an acidic aqueous solution.

Cyclic voltammograms of the dissolved lacunary PW<sub>11</sub> anion and of the metal-substituted PW<sub>11</sub>Co in acidic solutions show two reversible or quasi-reversible two-electron waves at negative potentials, corresponding to the reduction of the tungsten atoms [14,39]. In these anions, the tungsten reduction processes are accompanied by the addition of protons to counterbalance the increase in the negative charge and, therefore, the half-wave potentials of the W waves are pH-dependent.

The voltammetric features of the TBA-phosphotungstates immobilized in the carbon-paste electrode were similar to those observed in aqueous solution for the corresponding anions in terms of the numbers of electrons transferred. However, the shape of the cyclic voltammograms is a little different from those obtained for aqueous dissolved POMs, but similar to those obtained for the TBA-silicotungstates immobilized by the droplet methodology [24]. Fig. 3 shows cyclic voltammograms for PW<sub>11</sub>Co-CPE<sub>2</sub> immersed in pH 2.0 aqueous solution (H<sub>2</sub>SO<sub>4</sub>/HOAc/NaOAc). In the conditions used two reversible or quasi-reversible two-electron waves were observed with reduction peak potentials at -482 and -685 mV vs. Ag/AgCl for PW<sub>11</sub>Co. In the same conditions PW<sub>11</sub> presented peaks at -487 and -685 mV. Redox peaks I-I' and II-II' are attributed to two consecutive two-electron reduction processes of the tungsten atoms, i.e. corresponding to the expected four-electron global reduction process, as was obtained for the corresponding silicotungstates in previous work [14,24,40]. The first pair was always well-defined but the resolution of the second couple was worse for higher pH values. The reduction/oxidation peak of the substituting metal (Co<sup>III/II</sup>) was not observed because Co(II) is not electroactive within the potential window used from -0.85 to 0.0 V. Electrochemical pre-treatment, consisting of scanning for 60 cycles, led to a better definition of the cyclic voltammograms. This suggests that cycling leads to reorganization and/or wetting of the layer containing the TBA-phosphotungstate salts, resulting in an increase of the electron transfer rate from the electrode surface to the redox sites of the polyanion.

Cyclic voltammograms at PW<sub>11</sub>-CPE<sub>1</sub> and PW<sub>11</sub>-CPE<sub>2</sub> in pH 2.0 H<sub>2</sub>SO<sub>4</sub>/HOAc/NaOAc aqueous solution at scan rates from 20 to 1000 mV s<sup>-1</sup> are shown in Fig. 4. Cathodic and anodic peak currents were proportional to the square root of scan rate which



**Fig. 4.** Cyclic voltammograms for (a)  $PW_{11}$ -CPE<sub>1</sub> and (b)  $PW_{11}$ -CPE<sub>2</sub> immersed in pH 2.0 buffer solution ( $H_2SO_4/HOAc/NaOAc$ ) at scan rates 20, 50, 100, 500, 750, and 1000  $mV s^{-1}$ .

means that the process is controlled by counter-ion diffusion (see below). The expected behaviour ( $I_p$  proportional to  $v$ ) for a surface-confined redox process was not observed for any of the immobilized TBA-phosphotungstates. The same occurred for other electrodes modified with Keggin-type anions, such as with  $H_3[PMo_{12}O_{40}] \cdot nH_2O$  for higher scan rates ( $v \geq 100 mV s^{-1}$ ) [41] in a ceramic-carbon electrode, for hexadecylpyridium phosphomolybdate hybrid material in a carbon-paste electrode [20], and for lacunary and Fe and Co metal substituted phospho- and silicotungstate TBA salts adsorbed on GCE by droplet evaporation [23,24].

Table 1 presents voltammetric data for the immobilized TBA-phosphotungstates. The potentials for the first tungsten process at the  $PW_{11}Co$  carbon-paste electrodes were almost 70 mV less negative than the corresponding polyoxoanion in aqueous solution. This may demonstrate that the electron transfer at the tung-

sten-oxide cage structure is thermodynamically favoured for this POM when it is immobilized in the carbon paste. For the  $PW_{11}$  no significant changes were observed. Also, as a consequence of immobilization, there were no substantial differences between the potential of the first tungsten process upon metal substitution, in contrast to aqueous solutions [39]. A similar behaviour was observed for these POMs immobilized by the droplet evaporation method [23].

The cathodic peak potentials shifted slightly in the negative direction and the corresponding anodic peak potentials to the positive direction with increasing scan rates, leading to an increase of peak-to-peak separation ( $\Delta E_p$ ). The fact that  $\Delta E_p$  for the first W reduction wave has a value of 29 mV for CPE<sub>1</sub> (see Table 1), together with the linear relation between peak currents and square root of scan rate alluded to above indicates a 2-electron counterion diffusion-controlled process ( $57/n mV$  for a reversible process). The values of  $|E_p - E_{p/2}|$  are in agreement with this hypothesis. The values of  $\Delta E_p$  for CPE<sub>2</sub> are larger which suggests kinetic constraints in the presence of the polymer in the matrix. This could be due to a very thin film of the polymer remaining on top of parts of the exposed graphite particles, which reduces the ease of reduction or oxidation [31]. The mechanism will involve successive additions of electrons and protons (for reduction), as has been observed in non-aqueous solution and where it was also pointed out that there are pronounced medium effects on the observed voltammetry [42].

Initial pre-treatment led to activation of the modified electrode in terms of electron transfer between the electrode and the active redox sites of the TBA-phosphotungstates, so it may be assumed that diffusion of  $H^+(aq)$  from the solution to the immobilized phosphotungstates is rate-determining.

The pH of the supporting electrolyte has an influence on the electrochemical behaviour of POM-CPE. With increasing pH, the cathodic and anodic peak potentials are shifted in the negative direction by 99 mV for  $PW_{11}Co$  and by 62 mV per pH unit for  $PW_{11}$ , suggesting  $2e^-/3H^+$  (as noted before in [24]), and  $2e^-/2H^+$  processes, respectively, the protons diffusing from the solution to the surface of the electrode to maintain charge neutrality. For surface-confined processes, the amount of POM that is accessible for reaction at an electrode surface can be determined, as in [43], but to do so in this case would require knowledge of the diffusion coefficient of the counterion which it is not feasible to ascertain with meaningful accuracy particularly given the non-uniformity of composite electrode surfaces.

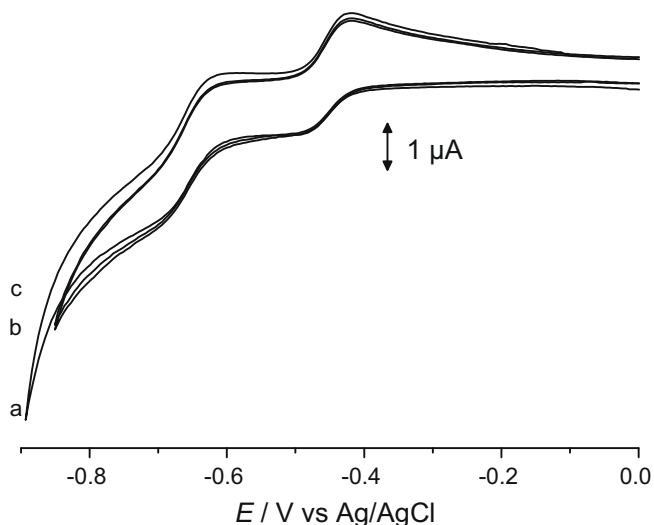
### 3.3. Stability of POM modified CPEs

Compared with polyoxometalate-modified electrodes fabricated by other methods, POM-CPEs have certain advantages. One of the main attractions of using CPEs is that the surface of the electrodes can be renewed after each use. Another is that the resulting carbon-paste electrode possesses high stability. Fig. 5 shows, as an example, the cyclic voltammograms for the  $PW_{11}$ -CPE<sub>2</sub> electrodes. When the potential range is maintained in the range 0.0 to  $-0.9 V$ , POM-CPEs were stable for over 150 cycles at a scan rate of  $100 mV s^{-1}$  and the current response remains almost unchanged. After use during a full working day, these modified CPEs were kept overnight in a protecting case and were stored at room temperature

**Table 1**  
Cyclic voltammetric data for the first W reduction processes in pH 2.0 buffer solution ( $H_2SO_4/HOAc/NaOAc$ ) at  $50 mV s^{-1}$ .

| Electrode                     | $E_{pc}$ (mV vs. Ag/AgCl) | $E_{pa}$ (mV vs. Ag/AgCl) | $ \Delta E_p $ (mV) | $ E_{pc} - E_{p/2} $ (mV) | $I_{pc}$ ( $\mu A$ ) | $E_{pc}^*$ (mV vs. Ag/AgCl) |
|-------------------------------|---------------------------|---------------------------|---------------------|---------------------------|----------------------|-----------------------------|
| $PW_{11}$ -CPE <sub>1</sub>   | -470                      | -441                      | 29                  | 28                        | -0.40                | -486                        |
| $PW_{11}Co$ -CPE <sub>1</sub> | -487                      | -458                      | 29                  | 29                        | -0.45                | -548                        |
| $PW_{11}$ -CPE <sub>2</sub>   | -487                      | -449                      | 38                  | 32                        | -0.72                | -486                        |
| $PW_{11}Co$ -CPE <sub>2</sub> | -482                      | -425                      | 57                  | 34                        | -0.53                | -548                        |

\*  $E_{pc}$  values for the polyoxoanions in aqueous solution of pH 2.2,  $v = 100 mV s^{-1}$  [39].



**Fig. 5.** Cyclic voltammograms for  $PW_{11}$ -CPE<sub>2</sub> immersed in pH 2.0 buffer solution ( $H_2SO_4/HOAc/NaOAc$ ),  $v = 50 \text{ mV s}^{-1}$ : (a) first, (b) second working day, and (c) after one week.

( $\sim 20^\circ\text{C}$ ); on testing the next day the results were practically identical. After storing again for one week at room temperature there was negligible change in the shape and height of the redox waves. The decrease of peak current values compared with the original ones was less than 5%. Peak potentials were constant throughout.

#### 4. Conclusions

A new chemically modified carbon-paste electrode (CPE<sub>2</sub>) has been developed, modifying the surface of a traditional carbon-paste electrode with a coating of a mixture of graphite, poly(hexylmethacrylate) and the polyoxometalates (TBA- $PW_{11}$  and TBA- $PW_{11}Co$ ). The electrochemical behaviour of the modified electrodes was studied by cyclic voltammetry. For the two immobilized TBA-phosphotungstates, the first tungsten redox processes were diffusion-controlled, and were accompanied by the uptake of protons diffusing from the acidic solution into the mixture containing the POMs. Compared with other types of POM-modified electrode, CPEs present the advantages of high stability due to the insolubility of the organic-inorganic hybrid salts of POMs in aqueous solution and the affinity of the organic part ( $(C_4H_9)_4N^+$ ) toward the paste which is important for practical applications. Modification using poly(hexylmethacrylate) also slightly improves the electrode sensitivity for the same amount of POMs.

This is the first report of fabrication of a composite carbon electrode using poly(hexylmethacrylate) and this work demonstrated that these new electrodes are stable and that they have the necessary characteristics for application as electrochemical sensors for detection of analytes such as bromate, nitrite or hydrogen peroxide, depending on the POMs immobilized.

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