

Preparation, physical-chemical and electrochemical characterization of ZrO₂ aerogels modified with H₃[PW₁₂O₄₀]

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This work presents the synthesis of ZrO₂ aerogels modified with H₃[PW₁₂O₄₀] by different methods, namely: by adding the heteropolyacid during the sol-gel synthesis of ZrO₂ gel (method A) or by immersing ZrO₂ gel (method B) / aerogel (method C) in H₃[PW₁₂O₄₀] solution followed by low temperature supercritical drying / drying at 80°C. The resulted zirconia based aerogels (ZrO₂-H₃[PW₁₂O₄₀]) were morpho-structurally analyzed by using BET method, X-ray diffraction, Raman and FT-IR spectroscopy. Concentration of Zr, W in ZrO₂-H₃[PW₁₂O₄₀] aerogels was determined by using inductively coupled plasma atomic emission spectroscopy (ICP-AES). Electrochemical behavior of ZrO₂ aerogels modified with H₃[PW₁₂O₄₀] as well as of the unmodified ZrO₂ aerogel was studied using cyclic voltammetry. All carbon paste electrodes based on zirconia aerogels exhibited a favorable redox activity. Carbon paste electrodes modified with ZrO₂-H₃[PW₁₂O₄₀] obtained by methods A and B exhibited a better electrochemical stability and a better electrochemical behavior than that prepared using method C.

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1. Introduction

Aerogels are unique materials which are characterized by a very low density, wide open pores and a high specific surface area, fact which impresses the interesting physical properties, as very low thermal conductivity and low rate of sound combined with a high optical transparency [1]. Zirconium dioxide is one of the most studied ceramic materials. ZrO₂ adopts a monoclinic crystal structure at room temperature and transitions to tetragonal and cubic at higher temperatures. The high ionic conductivity makes it one of the most useful electroceramics [2].

ZrO₂ aerogels are generally obtained by a sol-gel process followed by supercritical drying using liquid CO₂. The morphology of ZrO₂ aerogel and its physical-chemical properties depend on preparation and drying conditions of ZrO₂ gel, as well as on the thermal treatment of formed aerogel.

The sol-gel process represents, pointedly, the synthesis of an amorphous inorganic network (at least in the first steps) by chemical reactions in solution, at room temperature. By suitable thermal treatments, the amorphous inorganic polymers can be transformed in glassies, at more inferior temperatures than melting point (around the vitreous transition temperature) or in oxidic crystallized materials. The specific step of the process, transition from liquid phase (solution or colloidal solution)

to solid (bi- or multiphased gel) determines the name of the whole process [3]. In the present step, as results from the definition proposed by Schmidt [3], two principal variants of sol-gel process are distinguished, function on precursor nature: “alkoxide” method using molecular solutions (of organometallic compounds) and colloidal method (using colloidal solutions – aqueous solutions of some inorganic salts) [4].

Most of the works in the sol-gel area, in fact the first ones, were done using alkoxides as precursors. The use of inorganic salts – nitrates and chlorides – or organic salts (acetates, carboxylates or acetyl-acetonates compounds instead of alkoxides) involves a different chemistry and introduces different problems, as is that of anions removing from system. Generally, their use determines the chemical and physical properties, different structure and microstructure [4].

Polyoxometalates (POMs) have shown properties in several domains, including luminescence, photochromism, magnetism, electrics, catalysis and medicine, due to their many possibilities of composition and to their rich redox chemistry [5]. Therefore, the structural and functional characteristics of POMs have prompted their transition from inorganic chemistry to materials science as functional electroactive materials. Their small size and solubility normally requires them to be adsorbed or

anchored to a given substrate for a variety of applications [6].

Heteropolyacids (HPAs) present considerable interest as proton conducting electrolytes in low temperature fuel cells. It has been shown that the oxygen reduction reaction is strongly promoted in the presence of phosphotungstic acid (PWA), with respect to other liquid fuel cell electrolytes, e.g. phosphoric acid. Generally HPAs are characterized by a high-protonic activity and suitable oxygen affinity properties [7].

There are many applications to exploit the redox activity of POMs, some examples being supercapacitors, conducting polymers, oxygen-enriched carbons, decorated carbon materials, solid electrolyte based zirconia [6].

The importance of POMs in obtaining chemically modified electrodes has been recognized in the recent years owing to their excellent electrochemical properties. There are three main strategies for POMs immobilization: (i) electrochemical deposition on metal electrodes; (ii) immobilization as a dopant in conductive polymeric matrices; (iii) adsorption. POMs are able to adsorb on the surface of carbon-based materials [5].

Carbon paste is one of the convenient conductive matrices to prepare the chemically modified electrodes by simple mixing of graphite / binder paste and modifier. These types of electrodes are inexpensive and present many advantages, such as low background current, wide range of used potential, easy fabrication and rapid renewal [8].

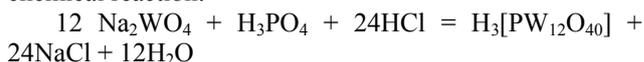
In this context, this work presents the synthesis of ZrO₂ aerogels modified with H₃[PW₁₂O₄₀] by using three methods, namely by adding the phosphododecawolframic acid (PWA) during the sol-gel synthesis of ZrO₂ gel (method A), or by immersion of ZrO₂ gel (method B) / ZrO₂ aerogel (method C) in PWA solution. The resulted aerogels were morpho-structurally analyzed by using BET method, X-ray diffraction, Raman and FT-IR spectroscopy. Concentration of Zr and W in ZrO₂-H₃PW₁₂O₄₀ aerogels was determined by using inductively coupled plasma atomic emission spectroscopy. Also, the electrochemical behavior of ZrO₂ aerogels modified with H₃PW₁₂O₄₀, as well as of the unmodified ZrO₂ aerogel was

studied using cyclic voltammetry, these materials being incorporated in carbon paste electrodes.

2. Experimental

2.1. Synthesis of H₃[PW₁₂O₄₀].x H₂O (PWA)

Synthesis of phosphododecawolframic acid H₃[PW₁₂O₄₀] x H₂O takes place according to the following chemical reaction:



To a solution obtained by dissolving Na₂WO₄·2H₂O in 500 ml distilled water, at room temperature, 85% H₃PO₄ (ρ = 1.71 g/ml) and 36% HCl solution (ρ=1.17 g/ml) were added under continuous stirring, in the molar ratios of 12.12/1.00/67.20. Obtaining of PWA in solid state is realized by liquid - liquid extraction with ethyl ether in strong acid medium followed by filtration in vacuum, washing with cold water and drying at room temperature [9].

2.2. Obtaining of ZrO₂ - H₃[PW₁₂O₄₀] aerogels

For the preparation of ZrO₂ gels, Zr (IV) propoxide-ZrPr (70%, Fluka) was used as precursor, propanol-PrOH (Aldrich), acetylacetone-AcAc (>99%, Merck) and deionized water as solvent / reactant, and HNO₃ (70%, Aldrich) as catalyst.

In the first step, by mixing HNO₃, H₂O and PrOH (half of required volume) in the molar ratios presented in Table 1, solution I was obtained. Then, in another glass, solution II was prepared by mixing, under continuously stirring, Zr tetrapropoxide with the rest of PrOH (1/2 vol). To solution II, being under continuously stirring, solution I was added in drops and the gel was obtained. The resulted ZrO₂ gels were kept for maturation in tight polyethylene box, during 1-2 months, then were three times washed with propanol and were dried in supercritical conditions with liquid CO₂ using a SAMDRI PVT 3D dryer.

Table 1. Synthesis conditions, specific surface BET and elemental analysis results (concentration of Zr, W, P) of ZrO₂-H₃[PW₁₂O₄₀] aerogels obtained by method B

No. of sample	Modification method	Molar ratios					S _{BET} [m ² /g]	Concentration [%]		
		ZrPr	PrOH	H ₂ O	HNO ₃	AcAc		Zr	W	P
1	A	1	10.199	2.784	-	0.239	102	26.1	0.51	0.02
2	B	1	10.102	5.667	0.992	-	12	15.8	3.84	0.07
3	C	1	9.635	4.999	0.990	-	0.73	19.7	7.86	0.19

The following supercritical conditions were used: scavenging of autoclave with liquid CO₂ at T = 0 -10⁰C and p ≥ 54 atm, during 4 hours followed by heating of autoclave to supercritical conditions of liquid CO₂

(T>35°C, p>82 atm), during 30 minutes, and depressurization of autoclave at atmospheric pressure, maintaining the temperature at 37-40°C during 60 minutes.

ZrO₂-H₃[PW₁₂O₄₀] aerogels were obtained by three methods: (A) adding of 0.01 M of PWA in ethanol solution during the sol-gel synthesis of ZrO₂ gel; (B) immersion of ZrO₂ gel (16 g) in 20 ml ethanol solution of PWA (10⁻² M) followed by supercritical drying; (C) immersion of ZrO₂ aerogel (1g) in 10 ml ethanol solution of PWA (10⁻² M), followed by drying of aerogels at 70^o C (8h).

Determination of specific surface area of ZrO₂ - H₃[PW₁₂O₄₀] aerogels by using Kr adsorption isotherm (BET method)

In order to measure the specific surface area, home-made equipment was used. Kr was used as adsorbate because it allows a good precision of specific surface area determination. Determinations were made at the temperature of liquid nitrogen, at $p/p_0 = 0.05-0.35$ (where $p = 0.013 - 0.394$ atm). Before recording the Kr adsorption isotherm, the sample was degassed in vacuum for removing the water and cooled at liquid nitrogen temperature.

X-ray diffraction of ZrO₂ - H₃[PW₁₂O₄₀] aerogels

The X-ray diffraction (XRD) analysis (XRD) was carried out on a Shimadzu XRD 6000 diffractometer using CuK α radiation ($\lambda=1.54$ Å), with Ni-filter. The diffractograms were recorded in 2 θ range from 10^o to 80^o with a speed of 1^o/min.

Raman and FT-IR spectroscopy of ZrO₂ - H₃[PW₁₂O₄₀] aerogels

Micro-Raman spectra of investigated samples were recorded on a Dilor Labram system equipped with a microscope objective of Leica PL FLUOTAR x100/0.75, a diffraction network of 600 lines/mm and an external laser with the wavelength of 532 nm. The laser power incident on the samples was of 5 mW, and the spectral resolution was of 6 cm⁻¹.

FT-IR spectra of investigated samples were recorded with a spectral resolution of 4 cm⁻¹ by using a Jasco spectrometer.

Elemental analysis using inductively coupled plasma atomic emission spectroscopy (ICP-AES)

Determination of percent concentration of Zr and W in ZrO₂ based aerogels was realized using a computer-controlled Spectro Flame-D type spectrometer (Spectroanalytical Instruments –USA).

Electrochemical measurements

Materials: Graphite powder and paraffin oil from Fluka - Buchs (Switzerland) were used. Buffer solutions were prepared using K₂HPO₄·2H₂O and KH₂PO₄·H₂O from Merck (Darmstadt, Germany).

Carbon paste electrodes were obtained by mixing of zirconia based aerogel with graphite powder, 1:1 (w/w) ratio, and then with paraffin oil. Surface coverage (Γ , mol cm⁻²) for every electrode was estimated by integration of peak area recorded using cyclic voltammetry at low scan rate ($v < 10$ mV s⁻¹) and considering the surface redox valence being equal to 1 [10]. The presented results are average values of at least three electrodes prepared in same experimental conditions.

Electrochemical measurements of cyclic voltammetry were performed in a conventional electrochemical cell with three electrodes. Carbon paste was used as working electrode, a saturated calomel electrode (SCE) as reference electrode and a Pt wire as counter electrode.

The cell was connected to a computer-controlled voltammetric analyzer Autolab-PGSTAT10 (Eco Chemie, Utrecht, Netherlands). A 0.1 M phosphate buffer solution (pH 7) was used as supporting electrolyte.

3. Results and discussions

3.1. Determination of specific surface area of ZrO₂ - H₃[PW₁₂O₄₀] samples

Using the obtained Kr adsorption isotherm, the specific surface areas of the above samples were calculated by employing the BET method [11] taking into account that a Kr atom in monostrate has a section of 19.5 Å. The BET specific surfaces area are presented in Table 2 for ZrO₂ aerogel and ZrO₂ -H₃[PW₁₂O₄₀] samples. As one can see after modifying the ZrO₂ aerogel with PWA a dramatic decrease of the BET specific surface area occurred.

Table 2. Synthesis conditions, BET area of specific surface and results of elemental analysis (concentration of Zr, W, P) of ZrO₂ - H₃[PW₁₂O₄₀] aerogels obtained by method C

No. sample	Modification method	Molar ratios						S _{BET} [m ² /g]	Concentration [%]	
		ZrPr	H ₃ [PW ₁₂ O ₄₀] × 10 ⁴ M	PrOH	H ₂ O	HNO ₃	AcAc		Zr	W
1	-	1	-	10.102	5.66	0.99	-	260	-	-
2	A	1	0.125	10.202	2.784	-	0.239	46	14.0	0.31
3	B	1	2	10.102	5.667	0.992	-	8.8	12.8	0.32
4	C	1	1	10.102	5.667	0.990	-	1.85	21.5	16.4

3.2. XRD analysis

XRD diffractograms illustrated in Fig. 1 shows the presence of preponderantly amorphous structure of all samples, although the signature of the crystalline structure, which could be associated with monoclinic and cubic zirconia, is evidenced. By following the mentioned assumption regarding the presence of these two crystalline phases, one can remark that the sample A contains preponderantly cubic crystalline structures, whereas the blank aerogel sample (M) together with the samples obtained by immersion of the ZrO₂ gel (B) and aerogel (C) into the PWA solution preponderantly contains monoclinic crystalline structures.

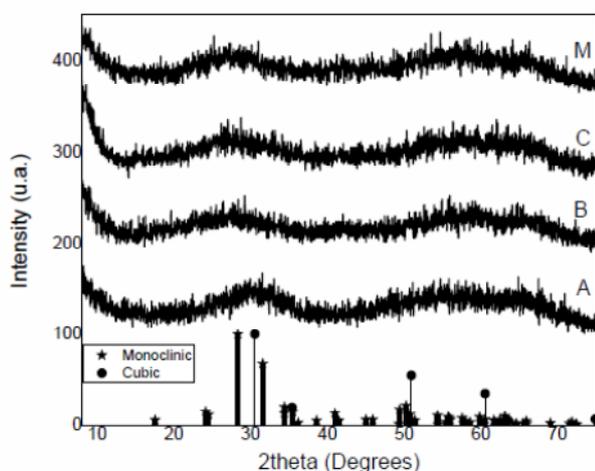


Fig. 1. XRD patterns of ZrO₂-H₃PW₁₂O₄₀ aerogels obtained by different preparation methods together with the pattern of the blank ZrO₂ aerogel sample

3.3. Raman and FT-IR spectroscopy of ZrO₂-H₃[PW₁₂O₄₀] samples

Raman and FT-IR spectroscopy were employed in order to determine the H₃[PW₁₂O₄₀] influence on ZrO₂ aerogel structure. Raman and FT-IR spectra of ZrO₂ aerogel samples modified with H₃PW₁₂O₄₀ by different preparation methods are illustrated in Fig. 2a and 2b (A-C) together with the spectrum of the unmodified ZrO₂ aerogel (Figs. 2a and 2b M).

First of all the Raman spectrum of the blank ZrO₂ aerogel was analysed and the assignment of the vibrational bands was performed by using the Raman data of the crystalline monoclinic, tetragonal or cubic ZrO₂ structures [3, 4, 12]. Thus, the bands situated in the spectral range up to 250 cm⁻¹ can be preponderantly attributed to vibrations in which Zr-Zr motions are involved, those observed between 340 and 385 cm⁻¹ to Zr-O vibrations, whereas the Raman bands located in the 385- 780 cm⁻¹ spectral region can be associated to O-O vibrations [12]. It is worth mentioning that the anionic or/and cationic character of the investigated structure was taken into consideration for the assignment of these bands.

By comparing the spectra recorded on the modified samples with that of the blank ZrO₂ aerogel sample the H₃PW₁₂O₄₀ influence on the ZrO₂ network can be observed. Thus, from Fig. 2a one can see that the Raman spectrum of porous samples prepared by method A shows less spectral modifications compared with those recorded on the samples obtained by methods B and C. The most intense bands are due to the ZrO₂ network vibration, whereas the bands due to the H₃PW₁₂O₄₀ structure are very weak. The close analysis of the spectrum reveals that the bands assigned to the ZrO₂ network vibrations are shifted to lower wavenumber values and broader as compared to those of the unmodified ZrO₂ sample as a consequence of the H₃PW₁₂O₄₀ presence.

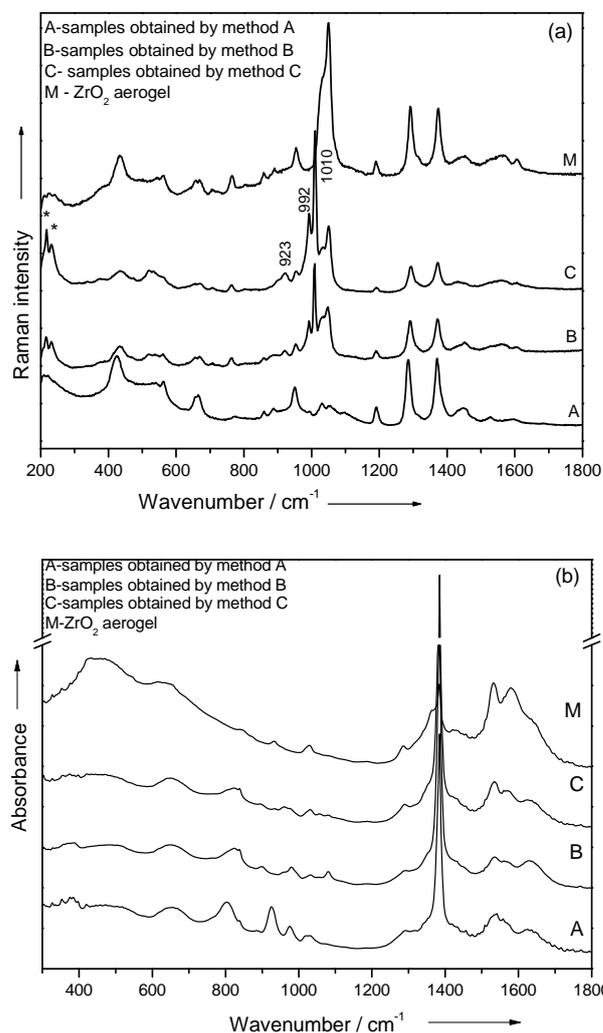


Fig. 2. Raman (a) and FT-IR (b) spectra of ZrO₂-H₃PW₁₂O₄₀ aerogels obtained by different preparation methods together with the spectrum of the blank ZrO₂ aerogel sample

Furthermore, the attention was focused on the spectra recorded from the samples prepared by methods B and C. The spectrum of the ZrO₂ aerogels impregnated with H₃PW₁₂O₄₀ (Fig. 2aC) clearly shows the H₃PW₁₂O₄₀ influence on the ZrO₂ network. Well defined bands

(denoted by *) can be observed in the small wavenumbers domain (200-260 cm^{-1}), their bandwidth being smaller even than that of the bands recorded for the blank sample. This result indicates that the structure containing Zr cations (involved in vibrations that give rise to these bands) is a more orderly one. The presence of W is more clearly evidenced in the 920-1015 cm^{-1} spectral range. The existence of these bands proves the formation of structural units of WO_6 octahedra or WO_4 tetrahedra type. More precisely, the bands from 992 and 1010 cm^{-1} and 923 cm^{-1} are given by W=O and W-O-W vibrations, respectively [13].

The Raman spectrum of the ZrO_2 gel impregnated with $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (Fig. 2aB) shows the same spectral fingerprints as in the case of impregnated zirconia aerogels. Though, there are a few important spectral changes that will be further presented. Thus, the bands observed in the 920-1015 cm^{-1} spectral range, that originate from vibrations of the structural units in which tungsten is involved, are less intense than those recorded for the samples synthesized by impregnating the aerogels. This shows that, when using the preparation method B, tungsten seems to be included in the porous network of ZrO_2 , so it doesn't form its own structural units.

By following the elemental analysis results (Table 2) one can observe that by aerogel impregnation W content increases. This result is further supported by the analysis of the Raman spectra, since the intensity of the Raman bands is related to the concentration and thus, one can conclude that more $\text{H}_3\text{PW}_{12}\text{O}_{40}$ amount entered into the aerogel and less $\text{H}_3\text{PW}_{12}\text{O}_{40}$ entered into the gel.

By analysing the FT-IR spectra (Fig. 2b) of the pure aerogel sample one can observe in the low wavenumber range bands due to ZrO_2 structures vibrations. Thus, the absorption signals that can be associated to O-O vibrations can be clearly observed in the spectrum around 460 and 630 cm^{-1} . Moreover, the absorption bands assigned to vibrations of organic groups present in the structure of ZrO_2 aerogel can be also observed in the 1400-1700 cm^{-1} spectral region.

The comparison of the FT-IR spectra recorded on the modified samples with that of the blank ZrO_2 aerogel sample reveals the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ influence on the ZrO_2 network. Thus, one can remark the presence of the bands given by the PWA vibrations, whereas the intensity of the bands due to ZrO_2 network decreased. The fingerprint band of the PWA can be observed around 808 and 980 cm^{-1} (W-O-W vibrations) in the spectra of all modified aerogels, while the other specific band around 1080 cm^{-1} (P-O vibration) can be noticed only in the spectrum of the sample B [14]. Other two specific bands assigned to Lewis acid sites can be observed in the spectra around 1400 and 1600 cm^{-1} . Other specific band corresponding to Lewis acid sites can be observed in the spectra of modified aerogels around 1635 cm^{-1} [15]. The analysis of the FT-IR spectra further supports the assumption derived from Raman spectra analysis according to that greater $\text{H}_3\text{PW}_{12}\text{O}_{40}$ amount entered into the aerogel as compared to the gel.

3.4. Electrochemical behavior of carbon paste electrode modified with aerogels

Fig. 3 (A-D) presents the voltammetric response of carbon paste electrodes (CPEs) with modified and unmodified ZrO_2 aerogels, using a phosphate buffer solution (pH 7) as an electrolyte. It can be observed that the recorded voltammograms on CPEs with ZrO_2 modified with $\text{H}_3\text{PW}_{12}\text{O}_{40}$ present a well-defined one peak pair in the case of samples obtained by methods A and B and well-defined two peak pairs for the sample prepared by method C.

The electrochemical behavior of investigated aerogels, characterized by the electrochemical parameters presented in Table 3, proves the presence of an irreversible process ($\Delta E_p > 59 \text{ mV}$), excepting the ZrO_2 aerogel modified with $\text{H}_3\text{PW}_{12}\text{O}_{40}$ by method A. It can be also observed that the ZrO_2 - $\text{H}_3\text{PW}_{12}\text{O}_{40}$ samples present an increase of ΔE_p , the second peak pair being characterized by a ratio $I_{pa}/I_{pc} \sim 1$, which is specific to adsorption conditions [16].

Table 3. Electrochemical parameters corresponding to voltammetric response of CPEs with ZrO_2 - $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ aerogels obtained by method C. Experimental conditions: see figures 2 A-D

Electrode	$E^{0'}$ (mV vs. SCE)	ΔE_{peak} (mV)	I_{pa}/I_{pc}	Surface coverage, Γ (10^9 mol cm^{-2})
1	-143	74	0.74	41.7
2	-199	103	0.79	38.1
3	-11.8	5.3	1.33	0.13
4	-233	62	0.51	39.3
5	I	34.5	1.41	9.7
	II	-213.5	239	1.15

The formal standard potentials ($E^{0'}$), estimated as the average of cathodic and anodic peak potentials, have values in the range of -233 and +34.5 mV vs. SCE. This fact suggest an easier oxidation for CPEs modified with zirconia by method B and a more difficult oxidation for CPEs modified with zirconia by method A, excepting the first peak of CPEs modified with zirconia by method C, which appear to more positive potentials.

The electrochemical/electrocatalytic stability of modified electrodes represents an important parameter for long-time usage, especially when they are used as electrochemical interfaces.

In order to check the electrochemical stability of modified CPEs, cyclic voltammograms were recorded by continuously cycling of electrode potential in a potential range which covers the peak potentials. It can be observed from Fig. 4 that the surface coverage progressively decreases and the shape of voltammograms remain unchanged. Time dependence of surface coverage, observed in Figs. 5A and 5B shows the presence of an electrochemical deactivation process during cycling process of modified electrodes.

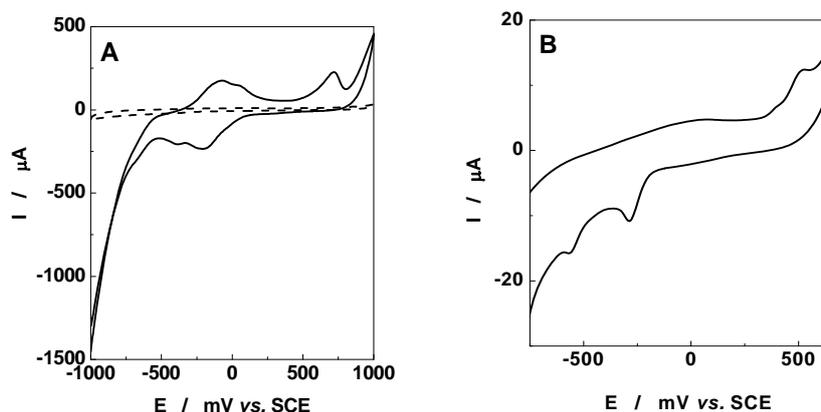


Fig. 3. Cyclic voltammograms corresponding to unmodified carbon paste electrode (---) and ZrO_2 aerogel (—) (A); ZrO_2 - $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ aerogels obtained by method A (B) and B (C,D). Experimental conditions: starting potential, -1000 mV vs. SCE (A,B,D) and -750 mV vs. SCE (C); potential scan rate, 50 mV s^{-1} ; supporting electrolyte, 0.1 M phosphate buffer (pH 7)

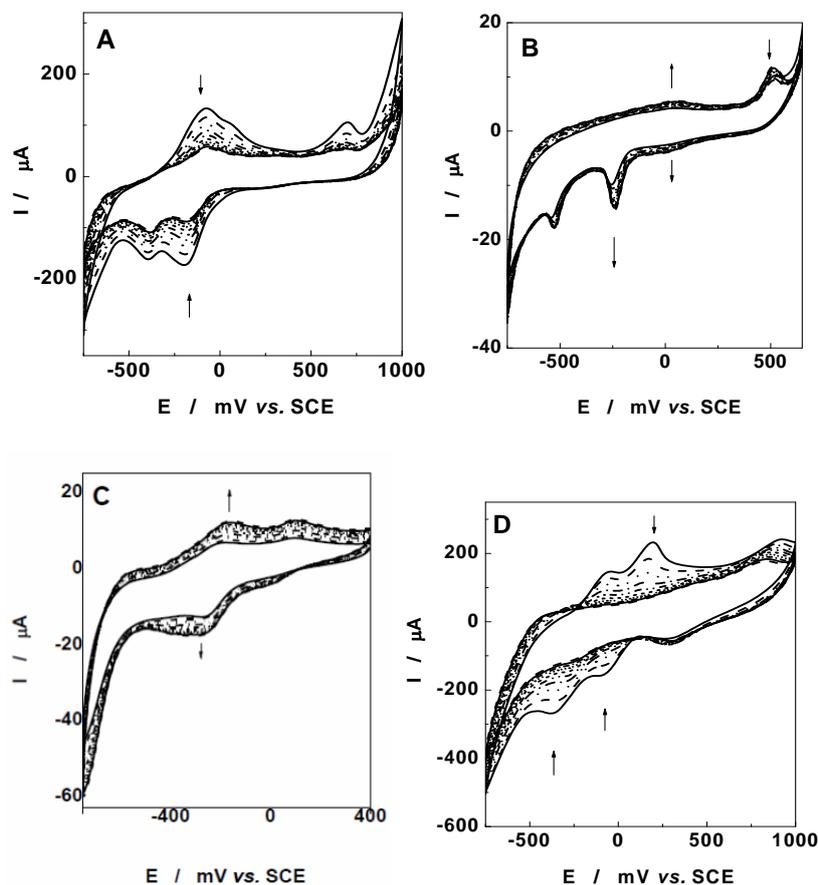


Fig. 4. Cyclic voltammograms corresponding to CPEs with zirconia aerogel (A); ZrO_2 - $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ aerogels obtained by method A (B), B (C) and C (D). Experimental conditions: starting potential, -750 mV vs. SCE; potential scan rate, 50 mV s^{-1} ; cycling time, 1400 s (A), 1200 s (B,D), 920 s (C); supporting electrolyte, 0.1 M phosphate buffer (pH 7.0)

Contrarily, in the case of CPEs for zirconia based samples obtained using methods A and B an increase of surface coverage took place, corresponding to peak pairs, excepting the surface coverage of supplementary peak pair

of electrode modified by using method A, which decreases (Figs. 4B and 4C). This fact proves the presence of an electrochemical activation process of both electrodes. Probably, this behavior is due to the polioxometalate

diffusion in solution, which leads to the appearance of a good redox activity. In the case of CPEs modified with ZrO_2 - $H_3PW_{12}O_{40}$ obtained by method C, a decrease of the electrode surface took place, corresponding to both peaks, fact which indicates a deactivation process of both electrodes. The obtained results prove the importance of modification method on the electrochemical stability of modified CPEs.

As was expected for active redox species immobilized on electrode surface [17], cyclic voltammograms recorded at potential scan rates in the range of 10 - 100 $mV s^{-1}$, for CPEs modified with ZrO_2 aerogel impregnated with ethanol solution of $H_3PW_{12}O_{40}$, present a linear dependence of peak current (I_p) on the potential scan rate (v) (results not shown). The slope of $\log I$ vs. $\log v$ graph is close to the theoretical value (1), fact which confirms the existence of adsorbed redox species and of a kinetic control.

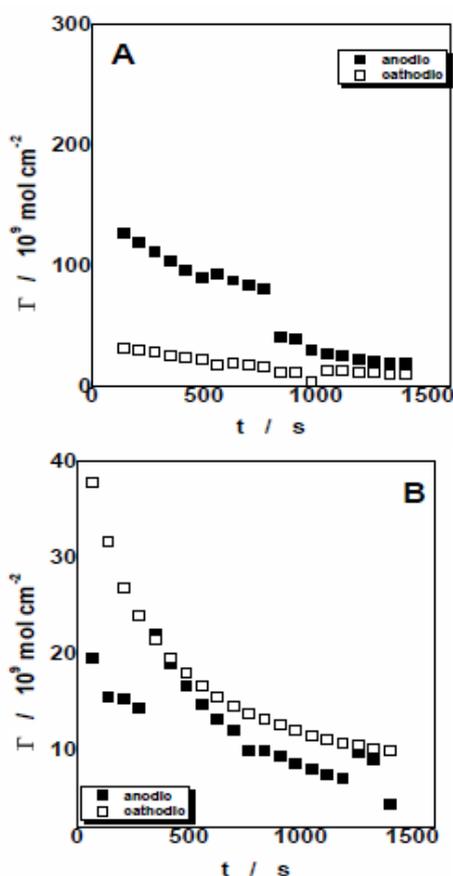


Fig. 5. Time dependence of surface coverage of CPEs with ZrO_2 aerogel (A) and ZrO_2 - $H_3[PW_{12}O_{40}]$ obtained by method C (B). Experimental conditions: the same as for Fig. 3

4. Conclusions

Unmodified ZrO_2 aerogel, prepared using the molar ratio $ZrPr / H_2O = 1 / 4.999$ is 2 times less stable compared with that prepared with a molar ratio $ZrPr / H_2O = 1/5.667$,

losing up to 400°C 90% of weight. By modifying the ZrO_2 aerogel with PWA a dramatic decrease of the BET specific surface area took place.

XRD diffractograms shows the presence of preponderantly amorphous structure of all samples.

Raman spectra recorded on the ZrO_2 - $H_3[PW_{12}O_{40}]$ samples revealed that, when preparing the samples by impregnation of the ZrO_2 gel with $H_3[PW_{12}O_{40}]$, tungsten seems to be included in the porous network of ZrO_2 , and it doesn't form its own structural units, as in the case of the samples obtained by impregnating the ZrO_2 aerogel. Moreover, the analysis of the Raman spectra was in agreement with the results of elemental analysis and FT-IR spectra, that more $H_3PW_{12}O_{40}$ amount entered into the aerogel and less was incorporated into the gel.

Four types of carbon paste electrodes were obtained through incorporation of zirconia and ZrO_2 - $H_3PW_{12}O_{40}$ in carbon paste. By using cyclic voltammetric measurements, all obtained modified electrodes presented redox activity. The electrochemical behavior of studied electrodes proved the importance of modification method of ZrO_2 with $H_3PW_{12}O_{40}$. The modified electrodes with ZrO_2 - $H_3PW_{12}O_{40}$ obtained by method B present an activation electrochemical process in contrast to those obtained by method C.

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