

Comparative Study of Two Types of Iron Doped Carbon Aerogels for Electrochemical Applications

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Abstract: Iron doped carbon aerogels have been prepared by sol-gel polymerization of potassium salt of 2,4-dihydroxybenzoic acid with formaldehyde followed by an ion-exchange process between K^+ doped wet gel and Fe(II) or Fe(III) ion aqueous solutions. The resulted Fe(II) or Fe(III) doped gels have been dried in supercritical conditions with liquid CO_2 and then pyrolyzed in high temperature resulting two types of iron doped carbon aerogels. These aerogels were morpho-structural investigated by using BET method, transmission electron microscopy, X-ray diffraction and elemental analysis. Also, these iron doped carbon aerogels (CAD-Fe⁽²⁺⁾ and CAD-Fe⁽³⁺⁾) were tested for realization of modified carbon paste electrodes. CAD-Fe⁽²⁺⁾ aerogel showed better electrochemical activity than CAD-Fe⁽³⁺⁾ and also a good electrocatalytic activity towards H_2O_2 reduction (expressed by an electrocatalytic efficiency of 404% measured at – 500 mV vs. SCE).

Keywords: carbon aerogel, modified electrode, electrocatalytic efficiency, hydrogen peroxide.

1. INTRODUCTION

The development of carbon materials with controlled porosity is an attractive research field favoring their use as electrode materials, adsorbents or catalyst supports in specific applications [1]. In this context, carbon aerogels still present a high potential for application fields. These aerogels are special monolithic carbon materials which consist of interconnected carbon nanospheres forming a three-dimensional network that is characterized by: high surface area, high porosity and good mechanical properties, depending on the synthesis parameters and conditions [1,2]. These materials, undoped or doped with different metallic species, were obtained by sol-gel process followed by drying in supercritical conditions of CO_2 , and pyrolysis in inert atmosphere [3,4].

Carbon aerogels have controllable morpho-structural properties by the choice of synthesis parameters and are clean and recyclable. For that they are widely used in electrochemical [5-9] and, catalytic applications [8-18] or as adsorbent materials [10,19-21].

The use of carbon aerogels for electrochemical applications have seen a development aiming to increase both the electrocatalytic efficiency, time of life, renewable capacity and to reduce the

losses of metal from aerogel structure during the electrocatalytic act [22-25]. The using of carbon aerogels as electrode materials has received increasing attention during last years, these have been extensively used in electrochemical supercapacitor [26,27].

For our study, Fe doped carbon aerogels have been prepared by sol-gel polymerization of potassium salt of 2,4-dihydroxybenzoic acid with formaldehyde followed by an ion-exchange process between K^+ doped wet gel and Fe(II) or Fe(III) ion aqueous solutions [4]. The resulted Fe(II) or Fe(III) doped gels were dried in supercritical conditions of CO_2 and then pyrolyzed in high temperature and inert atmosphere. The resulted iron doped carbon aerogels, termed CAD-Fe⁽²⁺⁾ and CAD-Fe⁽³⁺⁾, were morpho-structural investigated by BET method, transmission electron microscopy (TEM), X-ray diffraction and elemental analysis.

Prepared iron doped carbon aerogels were used for realization of modified carbon paste electrodes (CPEs). These electrodes were investigated using cyclic voltammetry measurements (CV), technique which was used to identify the mechanisms of electrochemical reactions and to analyze the electrode process kinetics.

2. EXPERIMENTAL

2.1. Sample preparation

Practically, K_2CO_3 was added to a 2,4-dihydroxybenzoic acid

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(DHBA) demineralised water suspension (DHBA/K₂CO₃ = 0.5; DHBA/H₂O = 0.0446 g/cm³), under vigorous stirring. After 30 min, when all the acid was neutralized, the solution became clear and after another 30 min, 37% formaldehyde (F) and then K₂CO₃ (C) (DHBA/F = 2; DHBA/C = 50) were added to the solution. The resulting solution was placed into tightly closed glass moulds (7 cm-length x 1 cm-internal diameter) and cured for a period of time: 1 day at room temperature and 4 days at 70°C. The resulting K⁺-doped gel rods were cut into 0.5-1 cm pellets and washed with fresh acetone for 1 day. The K⁺-loaded wet gels were then soaked for 3 days in 0.1 M aqueous solutions of Fe(NO₃)₃·9H₂O or Fe(OAc)₂ [4]. The metal solutions were renewed daily. Finally, samples were washed once more with fresh acetone and they were subsequently dried with CO₂ in supercritical conditions. The resulting Fe doped organic aerogels were pyrolysed at 750°C for 3h in an Ar atmosphere, obtaining iron and iron oxide particles-doped carbon aerogel. The Fe doped carbon aerogels prepared using Fe (II) and Fe (III) salts were labelled CAD-Fe⁽²⁺⁾ and CAD-Fe⁽³⁺⁾, respectively. By drying and pyrolysis of K⁺-doped gels the blank carbon aerogel sample (CAD-K) was obtained.

2.2. Morpho-structural characterization

Surface area determinations were performed by the Brunauer-Emmett-Teller (BET) method, using an ASAP 2000 surface area analyzer (Micrometrics Instruments Corp). Transmission electron microscopy of the iron doped carbon aerogels was performed with a Hitachi H-7000 microscope operating at 125 keV. The X-ray diffraction patterns were recorded in a θ -2 θ Bragg-Bretano geometry with a Siemens D5000 powder diffractometer with Cu-K α incident radiation (λ =1.5406 Å) and a graphite monochromator. Elemental analyses were performed with an inductively coupled plasma-mass spectroscope (ICP-MS).

2.3. Electrochemical measurements

All cyclic voltammetric measurements were realized in an electrochemical cell equipped with three electrodes: working electrode (WE)–carbon paste electrode (geometrical area, 0.071 cm²), reference electrode (RE)–saturated calomel electrode (SCE) and a counter electrode (CE)–platinum wire. Cyclic voltammetry studies were performed using a voltammetric analyzer Autolab (Autolab-PGSTAT 10, Eco Chemie, Utrecht, Netherlands) connected to a PC computer for potential control and data acquisition.

For every electrode, the surface coverage (Γ , mol cm⁻²) was evaluated from the integrated anodic peak of the cyclic voltammograms, at a slow scan rate (10 mV s⁻¹) [28,29]. All presented results are the average of obtained values with at least three electrodes prepared in identically way.

Supporting electrolyte was a 0.1 M phosphate buffer solution and the pH was adjusted at desired value, using H₃PO₄ or NaOH solutions (Merck - Darmstadt, Germany).

Carbon paste electrodes modified with carbon aerogel doped with iron were prepared by thoroughly mixing 50 mg graphite powder (Fluka - Buchs, Switzerland) with 50 mg of aerogel and 20 μ L paraffin oil (Fluka). The final pastes were put into a cavity of an in-house made Teflon holder using pyrolytic graphite in the bottom for electric contact.

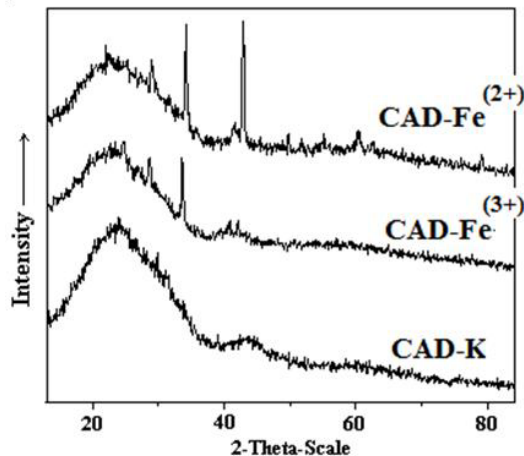


Figure 1. XRD patterns of K and Fe doped carbon aerogels.

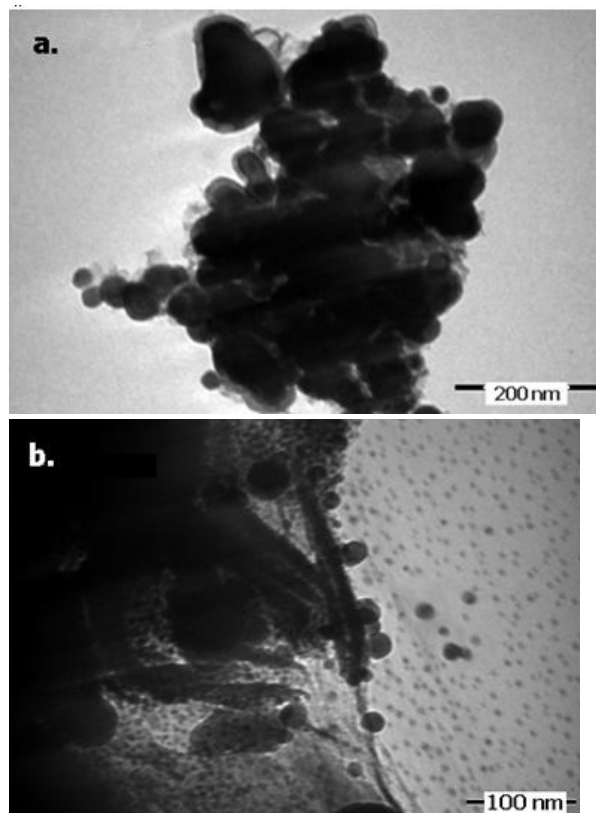


Figure 2. TEM images of CAD-Fe⁽²⁺⁾ (a) and CAD-Fe⁽³⁺⁾ (b).

Table 1. Physical and chemical characteristics of K and Fe doped carbon aerogels

Sample	Density (g/cm ³) ± 0.01	S _{BET} (m ² /g) ± 30	% Fe ± 2
CAD-K	0.65	550	-
CAD-Fe ⁽²⁺⁾	0.62	430	10
CAD-Fe ⁽³⁺⁾	0.64	720	18

3. RESULTS AND DISCUSSIONS

3.1. Morphological and structural characterization

BET analysis shows that CAD-Fe⁽³⁺⁾ has the highest surface area (Table 1). CAD-Fe⁽²⁺⁾ presents the highest iron amount (~ 18% wt). The mass density is between 0.62-0.65 g/cm³. The XRD patterns of iron doped carbon aerogels (Figure 1) show both large peak specific for amorphous carbon structure (around 2θ = 23°) and thin peaks specific for graphene-like structure (less visible at around 2θ = 26.5°) and metallic structures (Fe⁰, Fe₃O₄) [4]. For blank sample (CAD-K) only two large peaks (around 2θ = 23° and 44°) proper to amorphous carbon are evidenced (Figure 1).

The TEM images (Figure 2) demonstrate the presence of both isolated and agglomerated iron nanoparticles in the carbon aerogel matrix. The formation of various nanographitic carbon forms (nanoribbons, nanosheets, nanotubes) were already evidenced in previous works [4,30] by using TEM and Raman spectroscopy. The growing of these pseudo-graphitic forms and the decreasing of BET surface area (Table 1) observed in the case of CAD-Fe⁽²⁺⁾ sample are probably due to the presence of higher iron amount in the carbon framework [4].

3.2. Electrochemical applications

Figure 3 presents cyclic voltammograms recorded in 0.1 M phosphate buffer solutions (pH 7) for carbon paste electrodes modified with K doped carbon aerogel, CAD-K-CPEs (blank sample, Figure 3A), Fe²⁺ doped carbon aerogels, CAD-Fe⁽²⁺⁾-CPEs, and Fe³⁺ doped carbon aerogels, CAD-Fe⁽³⁺⁾-CPEs (Figure 3B).

It can be observed that voltammetric response of CAD-K-CPEs doesn't present peaks; the observed current is due to double layer capacitance. In contrast, for CAD-Fe⁽³⁺⁾-CPEs weak outlined peaks corresponding to Fe³⁺/Fe²⁺ couple were obtained. In the case of CAD-Fe⁽²⁺⁾-CPEs it can be observed a voltammetric response as well outlined peak pairs. Explanation for this difference in electrochemical behavior is probably due to the higher percent of metal and higher quantity of pseudo-graphene structure in CAD-Fe⁽²⁺⁾ which is better electrically conductor [4,18].

It can be concluded from the analysis of obtained cyclic voltammograms that the redox process is monoelectronic quasi-reversible ($\Delta E_p > 59$ mV and $I_{pa} / I_{pc} \cong 1$). The values of formal standard potential $E^{0'}$ of iron species from adsorbed aerogels (evaluated as average of anodic and cathodic potentials and presented in Table 2 together with surface coverages) are situated in the potential negative ranges. High differences between the peak potentials, ΔE_p , (see Table 2), confirm the irreversibility of electrode process and suggest an important contribution of diffusion process.

The voltammetric response of CAD-Fe⁽³⁺⁾-CPEs was investigated as a function of pH. The voltammograms recorded in phosphate buffer solution (pH 5) show more pronounced peaks (Figure 4),

Table 2. Electrochemical parameters corresponding to voltammetric response of carbon paste electrodes modified with iron doped carbon aerogels. Experimental conditions: see Figure 3B.

Electrode	$E^{0'}$ (mV vs. SCE)	ΔE_{peak} (mV)	I_{pa}/I_{pc}	Surface coverage, Γ (mol cm ⁻²)
Fe ⁽²⁺⁾ -CAD-CPEs	-341	380	1.31	2.2×10^{-6}
Fe ⁽³⁺⁾ -CAD-CPEs	-231	151	1.63	1.6×10^{-9}

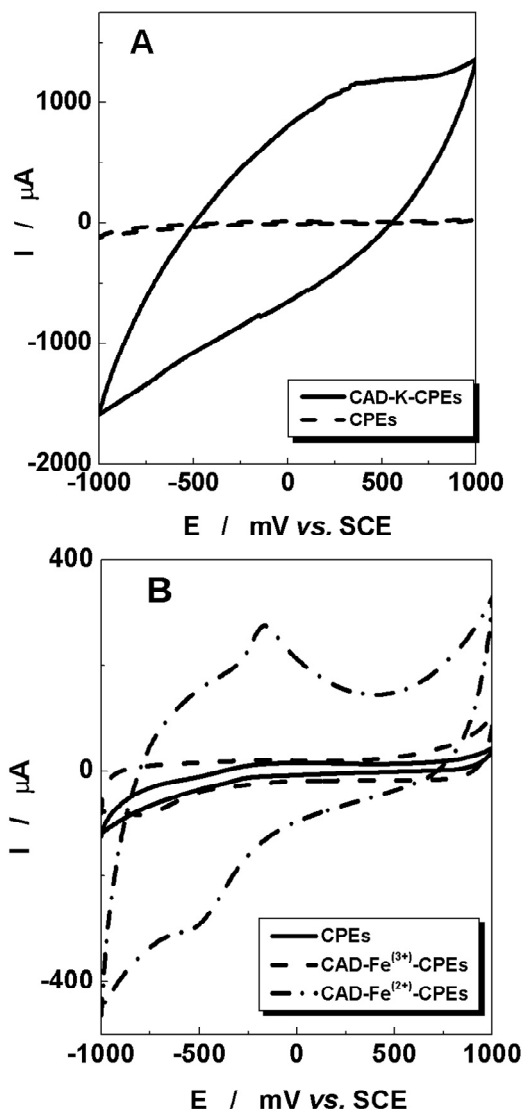


Figure 3. Cyclic voltammograms corresponding to CAD-K-CPEs (A) and CAD-Fe-CPEs (B). Experimental conditions: starting potential, -1000 mV vs. SCE; potential scan rate, 50 mV s⁻¹; supporting electrolyte, 0.1 M phosphate buffer solution (pH 7.0).

which suggest a beneficial effect of supporting electrolyte acidity on Fe³⁺/Fe²⁺ redox couple. It is known that acidic media enhances the response of Fe³⁺ [31].

The I_p - $v^{1/2}$ dependence is linear in a wide range of potential scan rates (0.01 – 0.64 V s⁻¹) for CAD-Fe⁽²⁺⁾-CPEs (Figure 5) and proves the participation of dissolved specie of iron at redox process. Slopes of log I vs. log v dependencies (0.68 ± 0.05 , R/N = 0.9767 / 10 for oxidation process and 0.65 ± 0.047 , R/N = 0.9794 / 10 for reduction process) are closed to theoretical value (0.5), confirming the existence of active redox specie in solution and the diffusion control.

The stability of obtained modified electrodes was tested in potentiodynamic conditions: the potential of modified electrodes was scanning in the redox activity range of mediator (± 120 mV to

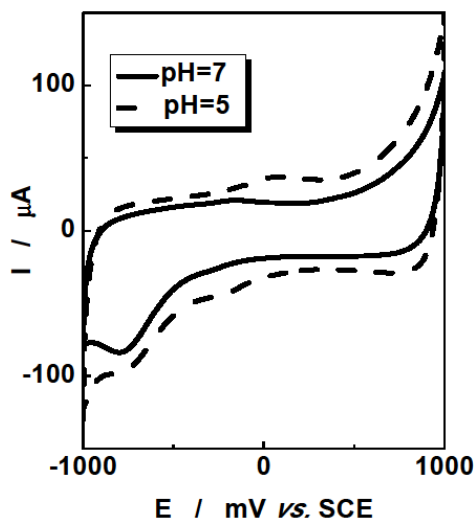


Figure 4. Cyclic voltammograms corresponding to CAD-Fe⁽³⁺⁾-CPEs. Experimental conditions: starting potential, -1000 mV vs. SCE; potential scan rate, 50 mV s⁻¹; supporting electrolyte, 0.1 M phosphate buffer.

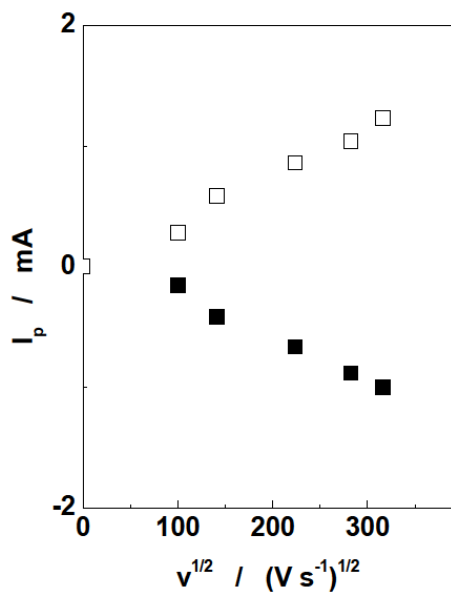


Figure 5. Potential scan rate influence on electrochemical behavior of CAD-Fe⁽²⁺⁾-CPEs. Experimental conditions: see Figure 4.

wards formal standard potential), with the scan rate of 50 mV s⁻¹, during 25 cycles, in phosphate buffer solution pH 7 (Figure 6). An increase in the surface coverage can be observed, while the shape of voltammogram is unchanged, which proves the electrochemical activation of electrode during cycling. Probably, this is due to Fe diffusion in solution, which leads to a better redox activity.

For carbon paste electrodes modified with CAD-Fe⁽²⁺⁾ aerogel, the electrocatalytic activity for H₂O₂ reduction was investigated using cyclic voltammetric measurements, knowing the electrocatalytic activity of Fe²⁺/Fe³⁺ couple.

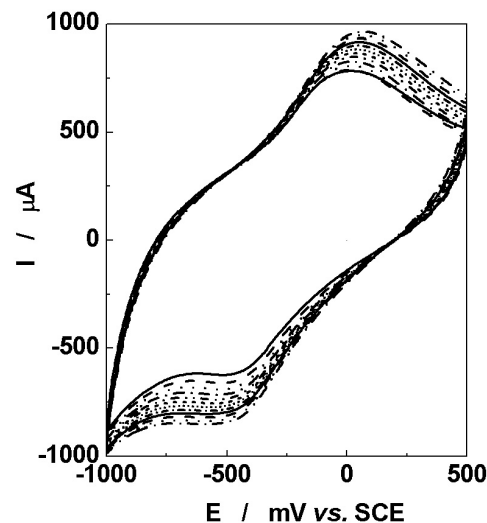


Figure 6. Cyclic voltammograms corresponding to cycling the CAD-Fe⁽²⁺⁾-CPEs. Experimental conditions: starting potential, -1000 mV vs. SCE; potential scan rate, 50 mV s⁻¹; supporting electrolyte, 0.1 M phosphate buffer (pH 7.0).

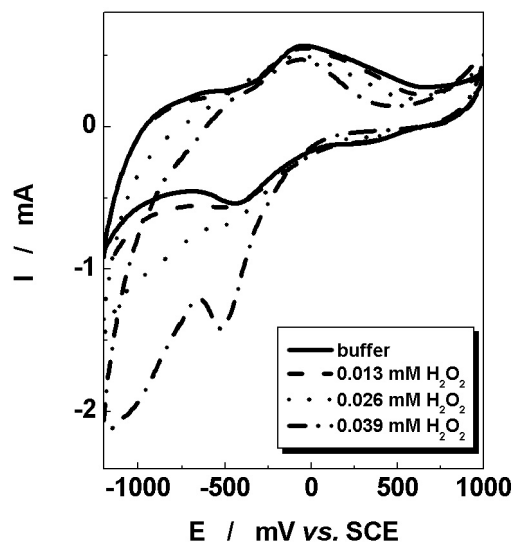


Figure 7. Cyclic voltammograms corresponding to CAD-Fe⁽²⁺⁾-CPEs, in the absence and in the presence of H₂O₂. Experimental conditions: starting potential, -1200 mV vs. SCE; potential scan rate, 10 mV s⁻¹; supporting electrolyte, 0.1 M phosphate buffer (pH 7.0).

Figure 7 presents the cyclic voltammograms corresponding to CAD-Fe⁽²⁺⁾-CPEs, in phosphate buffer solution pH 7, in the absence and in the presence of H₂O₂ solutions with different concentrations. As can be observed, in the presence of H₂O₂, the reduction peak increases significantly and the oxidation one decreases, which suggests a good electrocatalytic effect in the case of studied modified electrodes. The electrocatalytic efficiency estimated with relation:

$$E_f = \frac{I_{[H_2O_2]_{\neq 0}} - I_{[H_2O_2]_{=0}}}{I_{[H_2O_2]_{=0}}} \quad (1)$$

and measured at the potential of -500 mV vs. SCE (39 mM H₂O₂) had the value of 404% for CAD-Fe⁽²⁺⁾-CPES.

Thus, it can be concluded that CAD-Fe⁽²⁺⁾ can be used to obtain electroactive composite materials with improved electrochemical and electrocatalytic characteristics. These electrodes can be also used for obtaining amperometric sensors for H₂O₂, with high detection limits, or biosensors for determination of many compounds of biomedical and biotechnological interest.

4. CONCLUSIONS

Two types of iron doped carbon aerogels (with 10 and 18% wt Fe respectively) were synthesized using Fe(NO₃)₃·9H₂O and Fe(OAc)₂ aqueous solutions as precursors. By physical-chemical characterization, Fe (18%) doped carbon aerogel presented a higher pseudo-graphene content and a lower surface area than Fe (10%) doped carbon aerogel.

By incorporation in carbon paste of the Fe doped carbon aerogels, modified carbon electrodes with electrocatalytic activity towards H₂O₂ reduction were obtained. From cyclic voltammetric measurements, it was observed that the voltammetric response of these electrodes correspond to a diffusion process, and in the case of Fe (18%) doped carbon aerogel-CPEs, by cycling of electrode potentials, the electrochemical activation took place.

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