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Capacitance Improvement of Carbon Aerogels by the immobilization of Polyoxometalates Nanoparticles

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ABSTRACT

A Hybrid material was prepared by the immobilization of H₃PMo₁₂O₄₀ polyoxometalate nanoparticles (POM) on to the surface of a carbon aerogel (CA) matrix, in order to determine its potential application as electrode material for a supercapacitor cell. Several aerogels matrices with different microstructure properties and activation degree were exposed to a POM solution 1.15mM to determine the key properties for the immobilization of POM nanoparticles. All matrices and hybrid materials were characterized by ATR, nitrogen isotherms. For the electrochemical characterization our materials were grounded with 10% of Teflon and 20% conducting carbon to make a film that was pressed onto a stainless steel grid and cyclic voltammetry was used as the electrochemical technique, using 0.5 M H₂SO₄ as electrolyte. The highest degree of activation and smaller pore size of the aerogel matrix were the key factors influencing the immobilization and dispersion of POM nanoparticles, which improved the capacitance behavior making this material suitable for its application as supercapacitor electrode material.

1. Introduction

Carbon aerogels are porous materials where their porosity and pore size distribution can be controlled by modifying the synthesis parameters. In these materials the electrolyte can access almost all pores and is for this reason that they are promising electrode materials for their application as supercapacitors [1].

As we can find in many reports, some factors influencing the electrochemical performance of carbon aerogels and many others carbonaceous materials used as electrode materials for electrochemical devices have been identified. Some of these factors are surface area, pore size, and surface functional groups concentrations, among others[2]. These factors can be modified by the synthesis parameters and the material activation methodology. The activation of carbon materials can be carried out by a chemical or a thermal route. In the first activation route some surface active groups can be added to the matrix (OH functional group), while the thermal activation increases the surface area, probably due to the mass loss in the material. [3]

Oxygen based functional groups are required to incorporate polyoxometalate particles (POM) on to a carbon matrix. Therefore, an activation process such as the chemical route has to be carried out in order to obtain a POM-based hybrid material with a carbon aerogel matrix. POM particles are of great interest in energy storage applications such as in electrode materials for supercapacitors [4], [5], [6], due to their reversible multielectron redox reactions.

In the present study, a porous carbon material aerogel-type was prepared by using a molar ratio of resorcinol (R)/formaldehyde (F) of 0.5 and a resorcinol (R)/Na₂CO₃ catalyst (C) of 100, in order to obtain an aerogel matrix with pores in the range of 2-5nm and high surface area. The novelty of this work is the incorporation of molecular oxides polyoxometalate-type (POMs) on to the surface of chemically activated aerogel, in order to improve capacitance.

2. Experimental

2.1 Synthesis of carbon aerogel and incorporation of POMs

Carbon aerogels (CAs) were produced using a R/F molar ratio of 0.5 and a molar ratio of R/C of 100. All reagents were used as purchased: Resorcinol (99% purity) from Reasol, formaldehyde from Fermont (37.4%; methanol stabilized), and sodium carbonate by Fermont (99.7% purity). All solutions were prepared with deionized water. First, all reagents in solution were stirred and placed on a cylindrical crystal jar in an oven at 85 °C for 96 hours to obtain the corresponding precursor gel. Then the solvent exchange was carried out by adding acetone in order to prepare the RF gel for the supercritical drying. This solvent exchange was carried out during three days by multiple replacement of residual water with fresh acetone. Subsequently the CO₂ supercritical drying was carried out by keeping the RF gel at 30 °C and under 7.4 MPa, using a SFT-100 equipment. This process was followed by carbonization during 30 min at 850 °C in order to obtain the carbon aerogels (CA) with high surface area, as previously reported [7], [8], [9].

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Activated carbon aerogel was prepared according to the following procedure: the chemical activation [10] of carbon aerogel was performed by the dissolution of KOH in ethanol and mixing with CA using a KOH/CA mass ratio of 0.5/1 and 5/1. The mixture was dried at 110 °C and then carbonized in a tubular furnace at 850°C for 3 hours using a heating rate of 5°C/min. After the mixture cooled down to room temperature, the resultant materials were taken out and washed with 10% HCl and deionized water. Finally, the materials were dried at 110°C for 6h.

The incorporation of POM particles onto this CA matrix to obtain a hybrid material was performed by mixing in an ultrasonic bath for 3h, 0.04 g of CA in a 1.7 mM $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (Fermont) solution. The obtained suspension was filtered off and washed with a pH=2 solution, and finally the material was dried at 100°C for 1h.

2.3 Structure and physical properties

The materials were degassed at 120 °C under vacuum to remove all the adsorbed species before nitrogen adsorption and desorption isotherms were taken, using an *Nova 1200e* (Quantachrome). The BET surface area (S_{BET}) was analyzed by BET (Brunauer-Emmett-Teller) theory, and ATR analyses were performed directly over the sample to detect the vibration frequency changes for each functional groups present in the carbon aerogels, as well for the confirmation of the polyoxometalates presence.

2.4 Electrochemical characterization

To determinate the electrochemical performance of the prepared electro-active materials, cyclic voltammetry (CV) technique was used in an Arbin SuperCap model SCTS8 potentiostat using a 3-electrode cell with 0.5 M H_2SO_4 solutions as the electrolyte. A Pt gauze was used as the counter electrode, sulfate saturated electrode (SSE) as the reference electrode, and our electro-active materials as the working electrode. The working electrodes were prepared by mixing our electro-active materials (CA and Hybrids) (60%) with Teflon (10%) and conducting carbon (30%) in ethanol, this mixture was stirred under heat until alcohol evaporation (≈ 1.5 h) to obtain a paste that was pressed on to a stainless steel grid (316L, chemically resistant to acidic media) used as the current collector. The CV current was normalized by the electro-active material weight of the composite electrode and all characterizations were made after purging with nitrogen.

3. Results and discussion

The S_{BET} was calculated in a relative pressure range between 0 and 0.3, these results are presented in Table 1. The surface area of the carbon aerogel matrix (ACPQ2-100) decreased when incorporating the polyoxometalate (ACPQ2-100/POM) from 334m²/g to 274m²/g, probably due to the pore obstruction by POM particles. This phenomenon has being observed in some others carbon matrices in the presence of POM's [11], [12], [13], [14], [15], [16], [17], [18]



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and other functional groups like anthraquinone [19]. The mesoporosity of the materials are confirmed by the hysteresis observed on the isotherms (not shown here).

Table 1. Surface area of samples ACPQ2-100 and ACPQ2-100/POM.

Sample	S_{BET} (m^2/g)
ACPQ2-100	334
ACPQ2-100/POM	274

Carbon aerogel (ACPQ2-100) ATR spectrum is shown in Figure 1, where a peak at 3340 cm^{-1} is detected and is related mainly to OH functional group as expected, and in less degree to absorbed water due to the hydrophilic nature of this matrix. The peaks at 2850 and 2918 cm^{-1} are related to the stretching vibrational mode of $-\text{CH}_2$ group, at 1055 cm^{-1} and 1220 cm^{-1} region is related with CH-O-CH linkage between the two resorcinol molecules as expected in the poly-condensation reaction between resorcinol and formaldehyde. The peak at 1475 cm^{-1} corresponds to the scissors vibration of CH_2 group, and the peak at 1614 cm^{-1} region is related with the stretching vibrational mode of aromatic rings. [20], [21], [22]. The absorption bands at 800 , 876 , 955 and 1060 cm^{-1} region can be considered as an evidence of the diluted presence of POM particles [23].

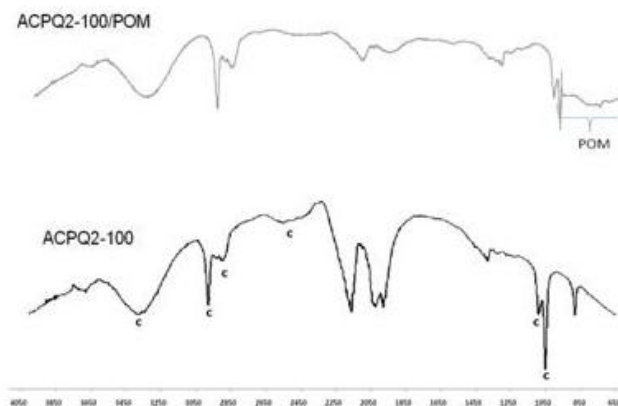
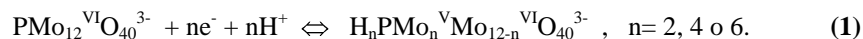


Figure 1. ATR spectra from ACPQ2-100 and ACPQ2-100/POM samples with the vibrational modes correspond to carbon aerogels and polyoxometalate.

Figure 2 shows the cyclic voltammograms of samples ACPQ2-100 (CA matrix) and ACPQ2-100/POM (hybrid material) in $0.5\text{ M H}_2\text{SO}_4$. The most relevant difference between the voltammograms of these samples is their profile change. The CA matrix (ACPQ2-100) voltammogram shows a profile deviated in the negative voltage range from the typical rectangular shape characteristic of a capacitive behavior, which is indicative of the resistive nature of this material. On the other hand, the hybrid material voltammogram shows a more evident rectangular profile, confirming its capacitive behavior and less resistive contribution. In addition, three redox pairs at $-0.13\text{V}/-0.1\text{V}$ (a), $-0.27\text{V}/-$

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0.24V (b) and -0.5V/-0.47V (c) are detected and correspond to the six electron transfer of polyoxometalate particles confirming its presence [23]. In equation 1 we show these multiple reversible redox reactions.



These results suggest that functional groups (OH) generated during the chemical activation of the matrix ACPQ2-100 are responsible for its resistive nature, since in the hybrid material this phenomena is considerably reduced probably due to the bonding of these OH groups with POM particles.

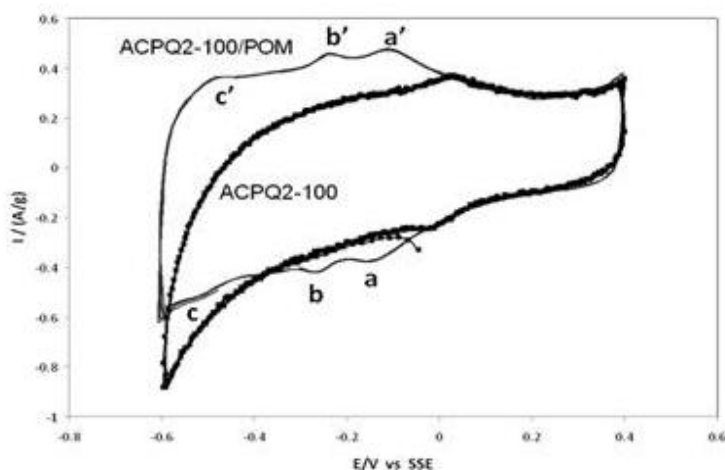


Figure 2. Cyclic voltammetry carried out at a scan rate of 10 mV/s for the hybrid material ACPQ2-100/POM and its corresponding array ACPQ2-100. The sweep potential was started in the negative direction.

From these voltammograms, capacitance values were calculated to eq. (2).

$$C = I \left(\frac{t}{\Delta V} \right) \quad (2)$$

Where C is the capacitance I is the applied current, t is the discharge time and ΔV is the potential change as a function of discharge process. Capacitance values of 156 F/g for ACPQ2-100 CA matrix and of 188 F/g for ACPQ2-100/POM hybrid material were obtained, confirming the capacitance improvement in the hybrid material due to the incorporation of POM particles through their bonding with OH functional groups of the activated CA matrix.

4. Conclusions

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Incorporation of POM particles on to the surface of CA matrix (ACPQ2-100) with a BET surface area of 334 m²/g was confirmed by a decrease in BET surface area (274 m²/g) due to pore obstruction, by ATR, and by the presence of three reversible redox processes characteristic of POM ACPQ2-100/POM hybrid material showed an improved electrochemical behavior, with a rectangular shape voltammogram profile indicative of a capacitive behavior with a smaller resistive nature compared to its AC matrix, aside from the faradic contribution of the three redox process of the POM particles. These results are reflected in the improved capacitance value from 156F/g for the CA matrix to 188F/g for the hybrid material.

5. Acknowledgements

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