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Influence of texture in hybrid carbon-phosphomolybdic acid materials on their performance as electrodes in supercapacitors

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ABSTRACT

In this paper, phosphomolybdic acid $H_3PMo_{12}O_{40}$ (PMo_{12}) was anchored to four synthetic micro-mesoporous carbons and a commercial one to analyse the relationship between the porous texture of the support, the PMo_{12} adsorption and the performance of the resulting hybrid materials as electrodes in supercapacitors. The uptake of PMo_{12} on carbon supports follows a clear correlation with the micropore volume, which implies that PMo_{12} is mainly adsorbed in microporosity as a consequence of a greater confinement in this kind of pores instead of mesopores. Transmission electron microscopy indicates that the PMo_{12} adsorbed is homogeneously dispersed in the carbon texture. Finally, the addition of PMo_{12} to the original carbon electrodes provided capacitances up to 293 F per gram of electrode, substantially larger than the 206–240 F g^{-1} of the unmodified activated carbon. This result represented an increase of up to 35% in terms of gravimetric energy density and 160% in terms of volumetric energy density, after PMo_{12} integration into the carbon matrix.

1. Introduction

The depletion of fossil fuels and concerns about climate change are leading towards a new and sustainable model of generation and management of energy [1], promoting the use of sustainable energy sources to satisfy our energy demand [2]. This urgent need to improve efficiency and sustainability of the current energy model has turned electrical energy storage into an issue of great importance, thus boosting research on new energy storage systems and on the improvement of existing ones [3].

In this context, supercapacitors, also called electrochemical capacitors, appear as a real alternative in the electrochemical energy storage field [4] capable of meeting some specific requirements of high-power energy applications such as hybrid electric vehicles or other electric appliances. There are two main types of supercapacitors [5]: (i) Double-Layer Capacitors based on the electrophysical mechanism derived from charge polarization at the electric double layer and (ii) Pseudocapacitors based on certain redox processes taking place al variable potentials energy [1].

Porous carbon materials belong to the first type and feature large surfaces that favour energy storage at the double layer. Transition metal oxides and conducting polymers belong to the second type since they may undergo faradaic processes allowing for redox charge storage; making them all fundamental candidates for supercapacitor electrode materials [4]. Specifically, carbon materials have been playing a significant role in the development of alternative clean and sustainable energy technologies due to their good conductivity, high surface area, controlled bulk and surface chemistry, tunable porous structure, low cost, and availability [6,7]. On the other hand, their energy storage mechanism (electric double layer) limits their energy density. Therefore, methods to enhance the electrochemical performance of these carbon materials have been widely investigated by incorporating other materials such as

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conducting polymers or metal oxides, which present a significant high redox activity [1].

Metal oxides, represent an attractive alternative as electrode materials for supercapacitors due to their high gravimetric capacitance, which results in devices of high energy and power density. Among the available metal oxides, hydrated RuO_2 has been one of the most studied due to its good performance [8], but it is too expensive for practical application. Other oxides, such as MnO_2, Co_3O_4, NiO, Fe_3O_4, or V_2O_5 have been proposed [9], but most of them are poor electronic conductors [10,11], which does not allow to reach the theoretical capacitances of these metal oxides, limiting the rate capability for high power performance.

Alternatively, a whole family of molecular metal oxide clusters known as polyoxometalates (POMs), are arising great interest in the field of energy storage systems as faradaic electrode materials. Indeed, POMs are nanometric clusters of vanadium, molybdenum or tungsten oxides with well-defined molecular structures with reversible redox activity [12,13]. These clusters were initially proposed by our group combined with conducting organic polymers [14–17] and subsequently with carbon materials [18–20] as building blocks for energy storage applications, and in particular for supercapacitors.

The choice of POMs to introduce faradaic processes in the carbon matrices was based on their higher reversibility, compared to other metal oxides, and their nanometric size (1 nm) resulting in the greatest degree of dispersion [21]. These dispersed nanoparticulate electroactive clusters provide maximal active surface, faster electrode reactions and reversible multielectron electrochemical activity [22], as required in the case of electrochemical supercapacitors.

Since carbon substrates showed a strong affinity for POMs [18, 23, 24], a growing number of papers studying hybrid materials composed of POMs and carbon materials as matrices have been reported, aiming at the development of electrode materials and energy storage devices with improved power and energy densities. Despite these increasing interest on this type of hybrid materials, only a very few examples made with POMs and carbon supports can be found to date. Among the carbon substrates available to produce these composites, carbon nanotubes [25–29], and graphene [20, 30–32] are the most popular matrices to fabricate carbon-POMs electrodes.

On the other hand, activated carbon have not had the same success on this topic despite patented methods to anchor POMs onto activated carbon were known many years ago [33]. Since only few recent work had been reported on the application of polyoxometalate-activated carbon system as active materials in supercapacitors, our group explored the study of these composites materials and its electrochemical performance during the last years [18,19]. The results showed that adsorbed POMs on activated carbons supports allows enhancing the performance of the hybrid electrode. Thereby they achieve to combine the double-layer capacitance of the carbon and the redox activity of the metallic oxide, leading to a higher energy and power, as well as much improved cycling stability.

Taking into account all these considerations, we have developed materials composed of a porous carbon matrix with POMs, where a synthetic carbon and three activated carbons derived from it as well as a commercial one (Norit) were used to support PMo_{12}. The purpose was to study the influence of the carbon texture on the adsorption of PMo_{12} trying to analyse where and how they are adsorbed, and the further use of these hybrid materials as electrodes in supercapacitors.

2. Experimental

2.1. Materials

The original starting carbon material was prepared following the procedure of resorcinol-formaldehyde polycondensation, described originally by Pekala [34], with some modifications. To that effect, resorcinol (R) was diluted in deionized water (W) in a molar ratio R/W of 0.04, and then NaOH solution was added as catalyst (C) being the R/C molar ratio of 250. The mixture was stirred for 30 min. Formaldehyde was then added at a molar ratio R/F = 0.5, and after 10 min stirring the samples were introduced sealed in an oven at 84 °C for 72 h. The resulting wet resin was dried for two days at 80 °C at ambient pressure and then carbonized to obtain the starting carbon. This carbonization was carried out in a horizontal tubular furnace under a flowing nitrogen atmosphere at 900 °C for 1 h after a temperature ramp of 3 °C min^{-1}. Then the sample was allowed to cool down to room temperature under a constant nitrogen flow rate, obtaining a carbon monolith.

In addition to this carbon, three activated carbons were produced through chemical activation from the latter. Activation of the resorcinol-formaldehyde hydrogel obtained in the previous step allowed increasing porosity and porous surface [35,36]. This activation process consisted in the carbonization of the material in the presence of KOH. Specifically, a known amount of carbon monolith, obtained previously, was physically mixed with KOH in ratios of 0.5:1, 1:1 and 3:1 (w/w). The mixture was then carbonized using a heating rate of 3 °C min^{-1} up to 900 °C, followed by a 1 h temperature plateau, under a nitrogen atmosphere. After cooling down, the remaining KOH that did not react was removed by washing the dry product, obtained after the carbonization, with HCl solution. To prevent the an initial vigorous reaction the samples were firstly infiltrated with water under vacuum and subsequently 1 M HCl solution was added during 24 h. After checking that the solution has acidic pH, successive washes with water were carried out until the acid was completely removed.

The final step was the infiltration of the different carbons with phosphomolybdic acid, $H_3PMo_{12}O_{40}\cdot 6H_2O$ (PMo_{12}) (Sigma-Aldrich) based on the procedure developed by Alcañiz et al. [37] with some modifications. The three activated carbons and one carbon xerogel have been used as supports for PMo_{12} impregnation. For the impregnation, six solutions of PMo_{12} with concentrations of 0.25, 1, 2, 5, 10, y 20 mM were prepared. Then 50 mg of dried carbon were infiltrated with 7 mL of aqueous solutions firstly under vacuum until no bubbles are observed and then for 24 h at room temperature at ambient pressure. Next, the obtained infiltrated carbon was washed with water and dried in a muffle at 100 °C overnight. The amount of PMo_{12} impregnated was determined by the difference between the initial weight of AC and the final weight of the impregnated sample.

The resulting electrodes were labelled as C250-x PMo_{12}y, where C250 corresponds to the original R/C ratio of the starting carbon xerogel, x represents the mass ratio of activating agent and carbon (w/w) used and y indicates the initial concentration of the PMo_{12} aqueous solution used to infiltrate the samples.

In order to compare with monolith C250, a powdered commercial activated carbon (AC) DLC Super 30, kindly supplied by Norit Chemicals®, were mixed for 24 h with different concentrations of PMo_{12} solutions (0.25, 0.5, 1, 2, 5, 10 and 20 mM), then washed with deionized water, filtered off and dried in a muffle at 80 °C. The labelling of this material was Norit-PMo_{12}y, where y has the same meaning as in the C250 series.