Doped carbon material electrodes for energy applications

A.C. Ramírez-Pérez

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SUPERVISORS: Diego Cazorla Amorós and Emilia Morallón Núñez.

**Corresponding autor:* anacristina.ramirez@ua.es

OBJECTIVES AND NOVELTY

Carbon materials have many advantages such as lightweight, chemical stability, electrical conductivity and both porosity and surface chemistry that can be tailored. These materials play an important role in devices for generation and storage of energy, like fuel cells and supercapacitors. However, in these fields the performance of the carbon materials depends on the porosity and the surface chemistry. In order to improve their properties, the use of N-doped carbon materials has been proposed; these N-doped carbon materials can be obtained by different methods. In this work, we have selected a nitrogen-rich polymer (polypyrrole, PPy) as precursor of N-doped carbon materials. PPy-based materials were obtained by adsorption from different concentrations of Py monomer on commercial activated carbon fibers (ACF). After the chemical polymerization was performed, the N-doped activated carbon samples were prepared by carbonization at different temperatures.

Additionally, the use of electrochemically active metal oxides can improve the capacitance of porous carbon materials by the incorporation of pseudocapacitance. Then, the mixture of a superporous activated carbon (AC) obtained from Spanish anthracite and metal oxides (Co_3O_4 and $CuCo_2O_4$) at different percentages have been prepared. Six different composite materials were prepared in order to evaluate their electrochemical performance and the influence of the metal oxides in the electrochemical properties of the AC.

All the samples (N-doped carbon materials and composites AC/metal oxides materials were characterized using different techniques: XPS, SEM, elemental analysis, XRD, physical adsorption of N_2, cyclic voltammetry. The most relevant were selected to be used as electrodes in supercapacitors and as catalysts in the oxygen reduction reaction (ORR).

RESULTS

PPy-based materials

Table 1 shows (as an example) the textural properties of selected carbon materials. Then, it can be observed an important decrease in the adsorption capacity after polymerization of PPy into the porosity of the activated carbon fibers (*F*). This decrease could be due to the presence of the PPy film over the surface of the fibers, as observed with PANI[1]. After carbonization, the small increase in the adsorption capacity observed is a consequence of the PPy carbonization.

The analysis of XPS N 1s spectra for *FP5* indicates the presence of 2 peaks in the sample. The main signal appear at 400.1eV which is characteristic of pyrrolic-nitrogen[2][3]. The second signal at lower binding energy can be assigned to the iminic nitrogen (BE=398.6eV)[2]. After carbonization, important changes occur in the XPS. The heat treatment at 500 ºC results in two XPS peaks that appear at different binding energies. One of them is associated to pyridine groups (398eV) and the second one with positively charged N functionalities such as pyrrole and/or pyridone groups (400.7eV)[3][4]. After heat treatment at 800 ºC the second peak shifts to higher binding energies and can be attributed to quaternary N (400.7eV). These functionalities appear due to the condensation reactions that take place at these temperatures

The electrochemical properties of the samples were investigated by cyclic voltammetry (CV) at a relatively slow scan rate ($5mV.s^{-1}$) and galvanostatic charge-discharge cycles at different current densities. The results indicate that the main contribution to capacitance is the charge and discharge of the double layer.

Durability tests were made by the evolution of the capacitance during 2000 charge-discharge cycles in two electrodes cell configuration (Table 1) at 1.4 V and at 0.5 A/g. The results show that the heat treated samples present the highest initial capacitance and capacitance retention in comparison to the original material. This result is attributed to the presence of positively charged nitrogen species and pyridinic groups on the carbon material surface. Moreover, these N-functional groups increase the wettability of the electrode which facilitates interactions with the electrolyte. Nonetheless the presence of the polypyrrole does not imply a better performance of the carbon materials.

Table 1. Porous texture characterization. Quantification of Nitrogen containing. Values of capacitance and its retention after 2000cycles of charge-discharge at 0.5 A/g in 1M H_2SO_4. Onset potential obtained in RRDE configuration for ORR

Sample	A_{BET} [m²/g]	V_{DR} (N_2) [cm³/g]	V_{DR} (CO_2) [cm³/g]	N%	C_0 [F/g]	C_f [F/g]	C/C_0 [%]
F	1919	0.8	0.4	--	47	46	97
FP5	1125	0.5	0.3	2.2	30	4	13
FP55	1366	0.6	0.6	2.1	54	52	96
FP58	1435	0.6	0.6	1.4	50	48	96

AC-Metal oxides materials

Two kinds of spinel nanoparticles were synthesized, Co_3O_4 and $CuCo_2O_4$; both of them were characterized by different physicochemical techniques. The characterization by cyclic voltammetry is in agreement with the structural data obtained by XRD and XPS. The typical cyclic voltammetry of this kind of oxides is obtained; it contains two peaks corresponding to the two redox processes of these spinel electrodes. An activated carbon was prepared by activation with KOH of Spanish anthracite, showing high micropore volume and a narrow micropore size distribution. The combination of these two kinds of materials (activated carbon and metal oxides nanoparticles) was used to prepare composite materials by physical mixing. These composite materials have been used as electrodes in supercapacitors in alkaline conditions and in the reaction of oxygen reduction.

All the samples where used as catalysts in ORR being the carbon materials obtained up to 800ºC the ones that have the higher catalytic activity due to the higher concentration in pyridine and quaternary N functionalities[5][6].

The catalytic activity of the AC stands out with respect to the rest of the materials studied in this Thesis. This seems to be related with the higher porosity development in this material which can increase the residence time of the oxygen molecules and the peroxide species improving the electrochemical activity towards the complete reduction of the oxygen molecule. The addition of cobalt based metal oxides in the superporous activated carbon does not imply an increase in the electrochemical activity, which seems to be due to the decrease in porosity of the composite material. However, an increase in the selectivity of the reaction towards the complete reduction of oxygen molecule is observed.

CONCLUSIONS

The results obtained in this Ph.D. Thesis support that carbon materials are among the most suitable for supercapacitor and catalysis applications due to their physicochemical properties, such as high surface area and possibility of tailoring both the surface chemistry and porosity. These characteristics can be selected in order to improve both the performance of carbon-based supercapacitors and their catalytic properties. The use of conducting polymers and metal oxides provides an interesting alternative for improving the properties of the typical activated carbon materials. Thus, two kinds of carbon materials based on polypyrrole were synthesized by heat treatment in inert atmosphere at two different temperatures, showing the presence of nitrogen surface groups. At high temperatures, quaternary and pyridinic groups predominate. Composite materials based on PPy and activated carbon fibers containing nitrogen species between 1 and 4wt% are prepared. The capacitors built with the N-doped activated carbon fibers materials after carbonization, have a better performance in terms of capacitance and durability than the pristine activated carbon fibers. This confirms the beneficial contribution of nitrogen functional groups. The capacitors show a high durability at a voltage of 1.4V in comparison to the capacitor prepared with the activated carbon fibers. The supercapacitors based on the metal oxide/activated carbon materials show that small quantities of oxides nanoparticles (*Co5_A95* and *CuCo5_A95*) increase the capacitance and stability of the capacitor. The addition of cobalt based metal oxides in the superporous activated carbon does not imply an increase in the activity in the ORR, which seems to be due to the decrease in porosity of the composite material. However, an increase in the selectivity of the reaction towards the complete reduction of oxygen molecule is observed.

RELATED PUBLICATIONS

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