Reseña Tesis. Advanced nanostructured carbon materials for electrochemical energy storage devices: Supercapacitors and micro-capacitors

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OBJECTIVES AND NOVELTY

The main objective of the work developed is the synthesis and characterization of advanced nanostructured carbon materials for energy storage applications. Four different topics have been studied: (i) electrochemical hydrogen storage on superporous activated carbons (ACs); (ii) electrochemical quartz crystal microbalance (EQCM) and in situ Raman characterization of a zeolite-templated carbon (ZTC); (iii) ordered mesoporous carbon thin film as electrodes for micro-capators; and (iv) superporous AC as electrodes for supercapacitors in ionic liquids. Porous carbon materials have been intensely investigated as electrodes for energy storage applications because of their low-cost, versatility of structure/texture, good conductivity and high cycling life. A relevant electrochemical application of carbon materials is hydrogen storage by electro-reduction of water in alkaline and neutral media. To investigate the mechanism of electrochemical hydrogen storage, two ACs, with different porosity and surface chemistry were electrochemically characterized in two different electrolytes (6 M KOH and 0.5 M Na_2SO_4).

Currently, templated carbons have attracted much attention because the combination of both tailored and ordered porous network with a nano-sized structure could result in the development of unique features for their potential applications. The ZTC synthesized in the nanochannels of zeolite Y is a promising candidate as electrode for electric double-layer capacitors because of its unique structure consisting of buckybowl-like nanographenes assembled into a three-dimensional regular network with a well-defined pore size of 1.2 nm and large surface area. The electrochemical behaviour of the ZTC, focusing on both the surface chemistry and structural changes produced under different electrochemical conditions in 1M H_2SO_4 medium, was studied using the EQCM that allows the simultaneous monitoring of the voltammetric and gravimetric responses of ZTC.

The recent technological trend towards portable electronic devices has leaded a strong interest in small-scale energy storage devices. Thin film capacitors have great potential to be used as power source in small-scale energy storage devices. A silica-templated ordered mesoporous carbon thin film was directly synthesized on a graphite current collector using an ordered mesoporous silica thin film as hard-template. The nanostructure of the silica, the composite silica/carbon and the mesoporous carbon thin films was characterized by microscopy and spectroscopy techniques. Electrochemical behaviour of both the mesoporous carbon and the composite silica/carbon thin films was analyzed in 1 M H_2SO_4 solution.

The use of ionic liquid and organic-based electrolytes for supercapacitors is being widely studied in recent years, because they allow increasing the operating voltage with respect to the aqueous electrolytes that leads to an increase of the energy density of the device. The electrochemical behaviour of a superporous AC with a tailored porosity (high apparent specific surface area and a high volume of micropores with an average pore size of around 1.4 nm) was analysed in PYR_{14} TFSI at different temperatures (20, 40 and 60 ºC) as well as in 1M Et_4N BF_4/PC, 1M PYR_{14} BF_4/PC and 1M PYR_{14} TFSI/PC at 20 ºC.

RESULTS

Regarding the electrochemical hydrogen storage in nanoporous carbons, Figure 1 shows, as example, the Raman spectra acquired for the ANK3 sample in 6 M KOH solution. The D (1350 cm^{-1}) and G (1585 cm^{-1}) bands, which are characteristic of graphene based carbons, are observed in all the experiments. When decreasing the potential, two bands at around 1110 and 1500 cm^{-1} are observed, which are related to electrochemical hydrogen storage and have been assigned to Csp^2–H and C=C stretching vibration, respectively, in amorphous carbon-hydrogen bonds. These two bands appear simultaneously when the potential decreases, and disappear simultaneously when the potential goes to more positive values. This indicates that hydrogen chemisorption is reversible. It was shown that weakly bonded hydrogen was the dominant form in basic medium, while strongly bonded hydrogen dominated in neutral medium [1].

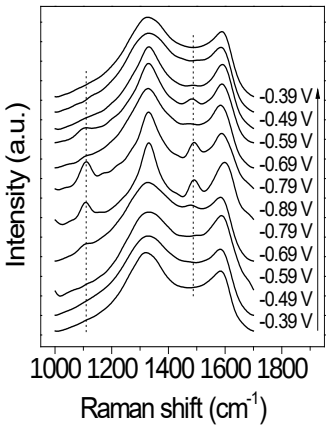

Figure 1. Raman spectra for the sample ANK3 at different potentials referred to NHE in 6 M KOH solution. Spectra normalized versus the D band.

With respect to the characterization of a ZTC by using the EQCM and *in situ* Raman spectroscopy techniques, it was shown that under electrochemical oxidation conditions, a high anodic current and a net mass increase were recorded, resulting in the increase of the specific capacitance owing to the contribution of the pseudocapacitance, mainly derived from the hydroquinone-quinone redox couple (see Figure 2 as example). Under more severe electrochemical conditions, ZTC suffered a remarkable degradation that involves a noticeable loss of conductivity and of the porous structure. Both the EQCM and the temperature programmed desorption results obtained suggested that that the electrochemical oxidation and gasification of the ZTC takes place simultaneously [2].

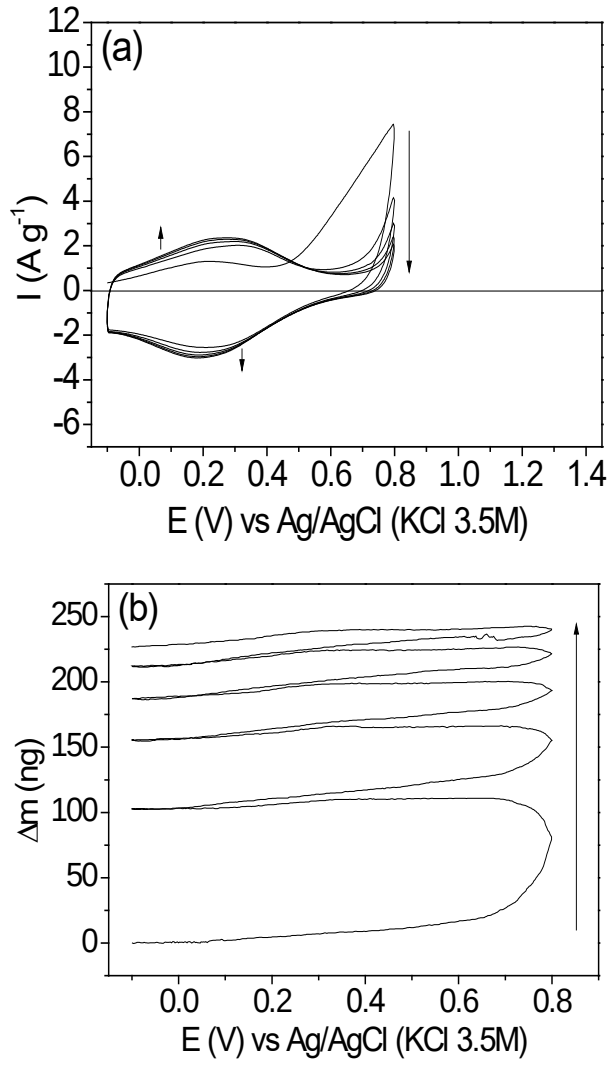

Figure 2. Cyclic voltammograms (a) and gravimetric response (b) simultaneously obtained between -0.10 V and 0.80 V of ZTC at 5 mV s^{-1} in 1M H_2SO_4 solution.

Concerning the synthesis and characterization of silica-templated ordered mesoporous carbon thin films, very high capacitance values were recorded for the mesoporous carbon and the composite silica/carbon thin films symmetric capacitors, thus improving the values reported for other carbon-based devices. The very similar electrochemical results obtained for both thin films demonstrated that the uniform carbon coating makes the composite to have excellent electrical conductivity. Furthermore, the durability test performed demonstrated that the thin films synthesized showed low degradation, even after a high number of cycles are applied (Figure 3) [3].

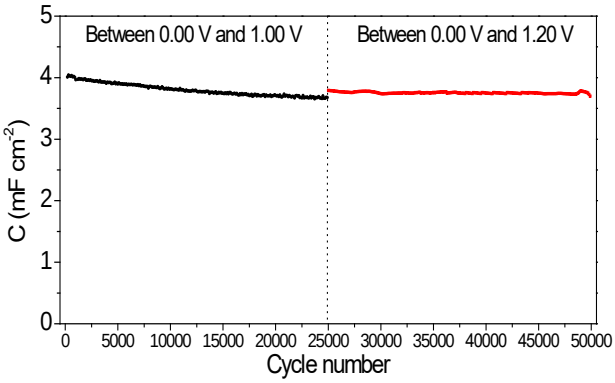

Figure 3. Specific capacitance versus cycle number plot for the symmetric electrochemical capacitor made from the mesoporous carbon thin film: between 0.00 V and 1.00 V (-■- black square symbols) and between 0.00 V and 1.20 V (-■- red square symbols). Current density: 10 mA cm^{-2}.

From the study of the electrochemical performance of a superporous activated in ionic liquid-based electrolytes it was shown that very high capacitance values in the pure PYR_{14} TFSI at three different temperatures (20, 40 and 60 ºC) as well as in 1M Et_4N BF_4/PC, 1M PYR_{14} BF_4/PC and 1M PYR_{14} TFSI/PC at 20 ºC were shown by the AC using a three-electrode configuration. Furthermore, excellent electrochemical behaviour (in terms of capacitance and retained capacitance) was also shown by AC-based supercapacitors in 1M Et_4N BF_4/PC, 1M PYR_{14} BF_4/PC and 1M PYR_{14} TFSI/PC at 20 ºC as shown in Figure 4 [4].

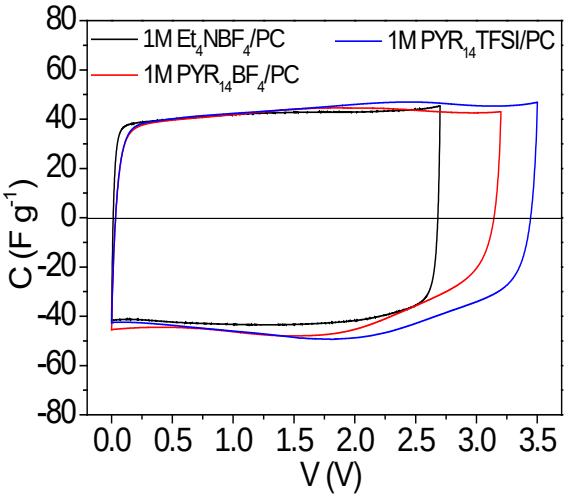

Figure 4. Cyclic voltammograms at 5 mV s^{-1} in two-electrode configuration in: 1M Et_4N BF_4/PC, 1M PYR_{14} BF_4/PC and 1M PYR_{14} TFSI/PC. 20 ºC.

CONCLUSIONS

Carbon materials with tailored porosity were revealed as promising candidates to be used as electrodes for electrochemical capacitors.

In situ Raman spectroscopy confirmed that chemical carbon-hydrogen bonds are formed during the charge process and that this hydrogen chemisorption is reversible.

The electrochemical oxidation of ZTC under

anodic conditions produced structural changes that involved the degradation of the three-dimensional regular network. The results suggested that the electrochemical oxidation and gasification of the ZTC takes place simultaneously.

It was shown that both the mesoporous carbon thin film and the composite silica/carbon thin film showed exceptional electrochemical properties, in terms of capacitance, rate performance and stability, making them promising candidates as electrodes for micro-capacitors.

It was demonstrated that the tailored porosity of the AC makes it an excellent candidate to be used as electrode for the design of high voltage, high energy supercapacitors containing non-conventional electrolytes.

RELATED PUBLICATIONS

[1] Leyva-García S, Morallón E, Cazorla-Amorós D, Béguin F, Lozano-Castelló D, New insights on electrochemical hydrogen storage in nanoporous carbons by in situ Raman spectroscopy, Carbon, 2014; 69, 401–408.

[2] Leyva-García S, Nueangnoraj K, Lozano-Castelló D, Nishihara H, Kyotani T, Morallón E, Cazorla-Amorós D, Characterization of a zeolite-templated carbon by electrochemical quartz crystal microbalance and in situ Raman spectroscopy, Carbon, 2015; 89, 63–73.

[3] Leyva-García S, Lozano-Castelló S, Morallón E and Cazorla-Amorós D, Silica-templated ordered mesoporous carbon thin films as electrodes for micro-capacitors. J. Mater. Chem. A, 2016; 4, 4570–4579.

[4] Leyva-García S, Lozano-Castelló D, Morallón E, Vogl T, Schütter C, Passerini S, Balducci A and Cazorla-Amorós, Electrochemical performance of a superporous activated carbon in ionic liquid-based electrolytes, J. Power Sources, 2016; 336, 419-426.

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