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- fill in a separate form for each project or series of measurements.
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- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** **Characterisation of supercapacitors based on activated carbon fibres/conducting polymers by position-resolved microSAXS and microRaman**	**Experiment number**: **MA 365**
Beamline: ID13	**Date of experiment**: from: 25 November 2007 to: 29 November 2007	**Date of report**: 14th April 2008
Shifts: 9	**Local contact(s)**: Dr. Richard DAVIES	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Prof. Diego CAZORLA-AMOROS[a]
Mrs. MARIA JESUS BLEDA MARTINEZ [a]
Dr. Dolores LOZANO-DOLORES [a]
Dr. Emilia MORALLON NUÑEZ* [b]
Prof. Dr. Martin MUELLER [c]
Mr. Juan Antonio MACIÁ AGULLÓ* [a]
Mr. Antonio Luís TOMÁS GARCÍA* [a]
Dr. Joaquín ARIAS PARDILLA* [b]

[a] Departamento de Química Inorgánica; Universidad de Alicante; E-03080, Alicante, SPAIN

[b] Departamento de Química Física; Universidad de Alicante; E-03080, Alicante, SPAIN

[c] Institut fuer Exp. Und Angewandte Physik; Universitaet Kiel; D-24118 Kiel, GERMANY

Report:

1. Introduction

Porous carbon/conducting polymers composites seem to be very interesting materials to be used as electrodes for supercapacitors, because they take the advantage from both, the double layer mechanism provided by porous carbon materials and the pseudocapacitative contribution from conducting polymers. From our research about preparation and characterization of porous carbon/conducting polymers composites, we conclude that the final performance of the composites as supercapacitors depends on the properties of the starting porous material and also on the polymerization process [1].

In the present work we have used activated carbon fibres (ACF) as porous carbon and polyaniline (PANI) as conducting polymer. In order to understand the effect of the different properties and preparation methods and to optimize the composite performance in this application, the characterization of these materials by a position resolved technique, sensitive to both the porous texture and the polymer, is very interesting. μSAXS has been successfully used by our research group to characterize the porosity of ACF across the fibre diameter (experiments ME-93 and ME-366) [2-5]. Thus, the aim of the present experiments was to do a simultaneous characterization of the porous carbon/polymer composite by using position resolved μSAXS and *in situ* microfocus Raman Spectroscopy at beamline ID13. Unfortunately, it was not possible to do the *in situ* microfocus Raman Spectroscopy measurements because the set-up was not suitable to work with the type of samples we prepared. Thus, in this report we present only μSAXS results which, as shown below are of great interest.

2. Experimental

A series of ACF/PANI composites have been prepared in our laboratory. For the preparation of ACF, different precursors (essentially PAN and pitch based carbon fibres) and different activating agents (essentially CO_2 and KOH) have been used. ACF with different degrees of porosity, different fibre diameters

(between 6 and 20 μm) and with different surface chemistry have been obtained. Moreover, a commercial ACF has been also used as starting material. To prepare ACF/PANI composites, two different methods have been selected for the preparation of PANI: i) chemical method ; and ii) electrochemical method.

Porous texture characterisation of all the samples was carried out by physical adsorption (N_2 at 77 K and CO_2 at 273 K; Autosorb-6, Quantrachrome). The μSAXS measurements done at ID13 consist of scans across the diameters of the ACF and ACF/PANI composites using a beam size of about 0.5 μm with a step size of around 1 μm and with an accuracy between 0.1-0.5 μm (the distance of the area detector (MAR-CCD) to the samples was 470 mm). The experiments were done on thin microtome cross-sections made in the Chemistry and Microimaging Laboratory (ESRF). The samples were previously embedded in a resin for facilitating the posterior cut for the analysis. The investigated samples were films of 10 μm thickness. Each sample was scanned horizontally and vertically.

3. Results

Figure 1 includes the scattering curves corresponding to the measurements at the center of the fiber for a commercial ACF (*A20*) and two ACF/PANI composites prepared using the sample *A20*, one prepared by a chemical method (*A20_C*) and another one prepared by an electrochemical method (*A20_E*). It is seen that the shape of the curves is characteristic of microporous materials, and that the intensity decreases for the samples ACF/PANI composites compared to the starting ACF (sample *A20*) in the scattering region corresponding to micropores. This decrease of scattering intensity for the ACF/PANI composites agrees with the reduction of porosity obtained for these materials by gas adsorption characterization, which seems to indicate that, for both methods, the deposition of polyaniline takes place inside the microporosity existing in the starting ACF. Table 1 contains the porous texture characterization results corresponding to the ACF and one of the ACF/PANI composites.

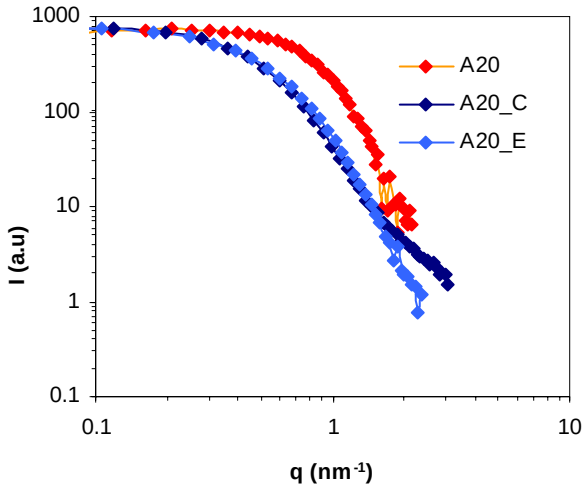

Figure 1.- Scattering curves corresponding to measurements at the center of the fiber for the ACF *A20* and two ACF/PANI composites prepared from *A20* and using two different methods (chemical (sample *A20_C*) and electrochemical (sample *A20_E*)

Table 1.- Porous texture characterization results corresponding to a commercial ACF (*A20*) and the ACF/PANI composite prepared from *A20* and using the chemical method (sample *A20_C*)

Sample	BET (m^2/g)	$V_{DR}(N_2)$ (cm^3/g)	$V_{DR}(CO_2)$ (cm^3/g)
A20	1628	0.77	0.38
A20_C	1002	0.43	0.29

In order to analyze if the deposit of the PANI is similar on all the regions across the fibre diameter, scattering measurements across the fiber diameter have been done. As an example, Figure 2 presents the scattering curves corresponding to the ACF/PANI composite prepared by the chemical method (*A20_C*). Each curve includes a number, which corresponds to the measurement number (starting from the external zone of the fiber and ending in the opposite zone across the fibre diameter). The maximum scattering corresponds to the measurement carried out at the center of the fiber. These results indicate a higher concentration of pores in the center of the fiber than in the external areas.

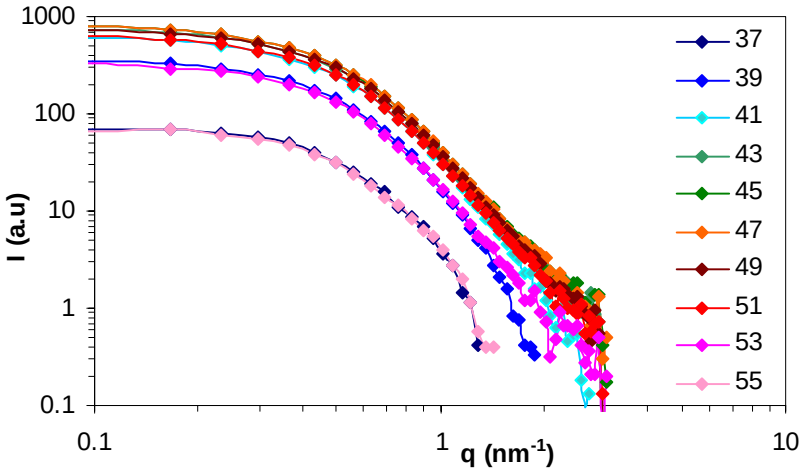

Figure 2.- Scattering curves corresponding to some measurements across the fiber diameter for the sample *A20_C* (right).

For a better observation of pore distribution across the fiber diameter, Figure 3 includes the normalized Porod Invariant (PI) values estimated for the different measurements carried out across the fiber diameter versus the beam position for the starting ACF (*A20*) and for the two ACF/PANI composites (chemical method (*A20_C*) and electrochemical method (*A20_E*)). In this plot, beam position equal to zero corresponds to the center of the fiber. This figure shows that the scattering profiles, as a function of the position of the fibers, are different for the two ACF/PANI composites and the starting ACF. In the case of the starting ACF, the scattering is similar for all the regions, indicating a homogeneous distribution of porosity within the fibers. However, for the ACF/PANI composites the scattering intensity is much higher at the internal zones than at the external parts of the composites, which seems to point out that, for both methods (chemical and electrochemical methods) the deposit of PANI is higher in the external regions of the ACF than in the core. Additionally, it seems that the penetration of PANI inside the fibers occurs in a larger extent for the chemical polymerization.

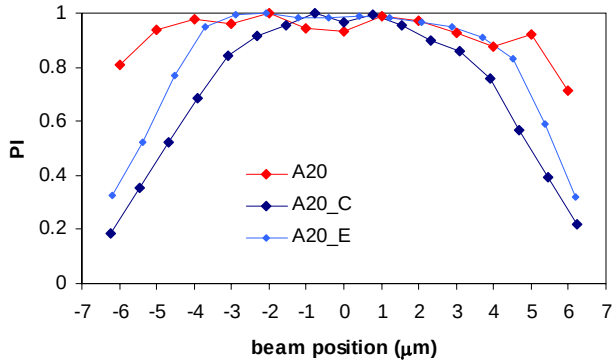

Figure 3.- Normalized Porod Invariant values estimated for the different measurements carried out across the fiber diameters of the starting ACF (*A20*) and two ACF/PANI composites (chemical method (sample *A20_C*) and electrochemical method (sample *A20_E*)).

4. References

[1] Bleda-Martinez MJ, Morallon E, Cazorla-Amorós D. Polyaniline/porous carbon electrodes by chemical polymerization: effect of carbon surface chemistry. Electrochimica Acta 52 (2007) 4962-4968

[2] Lozano-Castelló D, Raymundo-Piñero E, Cazorla-Amorós D, Linares-Solano A, Müller M, Riekel C. Characterization of pore distribution in activated carbon fibres by microbeam small angle X-ray scattering. Carbon 2002;40:2727-2735.

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