CHARACTERIZATION OF SUPERCAPACITORS BASED ON ACTIVATED CARBON FIBRES/CONDUCTING POLYMERS BY POSITION-RESOLVED µSAXS

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Introduction

Porous carbon/conducting polymers composites seem to be 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 concluded 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 fibers (ACF) as porous carbon and polyaniline (PANI) as conducting polymer to prepare composites. In order to optimize the composite performance as supercapacitor, it is very convenient the characterization of these materials by a position resolved technique. Our research group has successfully used Small Angle X-ray Scattering with a microbeam (µSAXS) to characterize the porosity of ACF across the fiber diameter [2-5].

The objective of the present work is to analyze by µSAXS the effect of the polymerization method (chemical and electrochemical polymerization methods) in the properties of the PANI coating (penetration of PANI into the microporosity and inside the core of the starting ACF).

Experimental

ACF/PANI composites electrodes were prepared using a commercial ACF (A20; Osaka Gas Co. Ltd) and carrying out a polymerization of aniline. Two different polymerization methods were used :

(i) chemical polymerization (sample *A20_C*): composite electrodes were prepared by introducing the ACF and aniline in the polymerization reactor at 0 ∘C containing ammonium persulphate dissolved in 1MHCl solution. The aniline:ammonium persulphate molar ratio was 1:1 and the polymerization time was 1h. A polyaniline coating is then obtained over the carbon material. The composites were then washed with 1M HCl, followed by washing with 1M NH_4OH. The material was dried in dynamic vacuum for 24 h.

(ii) electrochemical polymerization (sample *A20_E*): A paste of the ACF mixed (~1mg) with the binder polytetrafluoroethylene (PTFE, 20 wt. %) was spread and pressed uniformly and thinly with a spatula onto a graphite disk electrode (0.6 cm diam.). No conductivity promoter, such as acetylene black was used. After drying, the electrode was placed as the working electrode in a solution of 0.15 M aniline + 1.0 M HCl + 0.5 M KCl and subjected to electro-polymerization. This electro-polymerization was carried out using a single potential step from the lower potential of 0.3 V, where no electrode reaction occurred, to an upper potential of 1.0 V, where the polymerization took place for a time until the total charge passed was 0.5 C·mg_{ACF}^{-1}. The reference electrode was Ag/AgCl.

Surface area characterization of the samples was carried out by physical adsorption (N_2 at 77 K and CO_2 at 273 K) using an automatic adsorption system (Autosorb-6, Quantrachrome). The µSAXS measurements were done at the microfocus beamline (ID13) in the "European Synchrotron Radiation Facility" (Grenoble). The experiments 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 samples were previously embedded in a resin for facilitating the posterior cut for the analysis. The experiments were done on thin microtome cross-sections (films of 10 µm thickness). Each sample was scanned horizontally and vertically.

Results and Discussion

Figure 1 includes the scattering curves corresponding to the measurements at the center of the fiber for the commercial ACF (*A20*) and two ACF/PANI composites prepared using the sample *A20* and the two different processes: chemical and electrochemical methods. 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 (results not shown here), which seems to indicate that, for both methods, the deposition of polyaniline takes place inside the microporosity existing in the starting ACF.
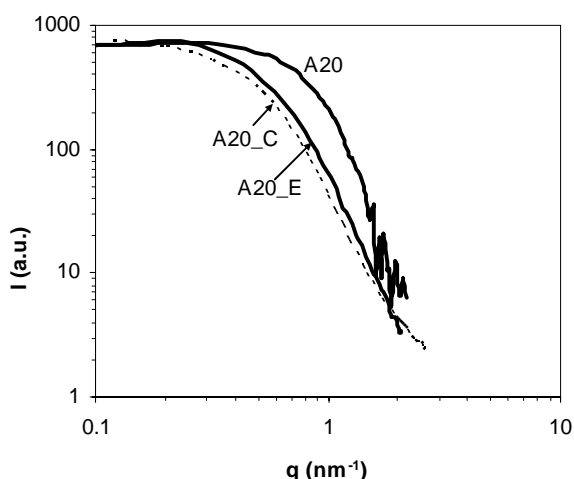
Fig. 1 Scattering curves corresponding to measurements at the center of the fiber for the ACF *A20* and two ACF/PANI composites prepared from *A20* and using two different methods (chemical (sample *A20_C*) and electrochemical (sample *A20_E*)).

In order to analyze if the deposition of the PANI is similar in all the regions across the fiber diameter, scattering measurements across the fiber diameter have been done. Figure 2 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*)).
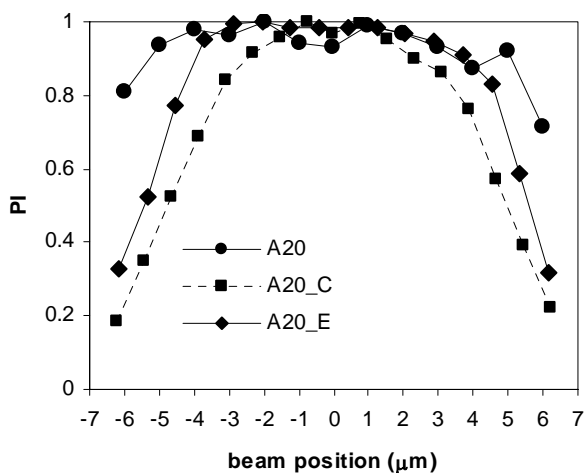
Fig. 2 Normalized Porod Invariant (PI) values estimated for the different measurements carried out across the fiber diameters of the starting ACF (*A20*) and two ACF/PANI composites (chemical method (sample *A20_C*) and electrochemical method (sample *A20_E*)).

In the plot of Figure 2, beam position equal to zero corresponds to the center of the fiber. Interestingly, the figure shows that the fiber diameter does not change in the composites compared to the original ACF, indicating that the PANI film is deposited inside the micropores. Additionally, the 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.

Conclusions

Preliminary experiments carried out by position-resolved microbeam small angle X-ray scattering (µSAXS) on ACF/PANI composites reveal that, for both preparation methods (chemical and electrochemical), the coating of PANI takes place inside the microporosity and is higher in the external regions of the ACF than in the core. The fiber diameter is not changed, and it seems that the penetration of PANI inside the fibers occurs in a larger extent for the chemical polymerization.

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