

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.


Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- 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.



	Experiment title: Simultaneous position resolved microSAXS and microfluorescence measurements of chemically activated carbon fibres. [#]	Experiment number: MA-165
Beamline: ID21	Date of experiment: from: 10-NOV-2006 8:00 to: 13-NOV-2006 8:00	Date of report: 11 th July 2007 <i>Received at ESRF:</i>
Shifts: 9	Local contact(s): Dr. Murielle SALOME	
Names and affiliations of applicants (* indicates experimentalists): Prof. Diego CAZORLA-AMOROS (UNIVERSITY OF ALICANTE, SPAIN) Dr. Dolores LOZANO-DOLORES (UNIVERSITY OF ALICANTE, SPAIN)* Mr. Juan Antonio MACIA-AGULLO (UNIVERSITY OF ALICANTE, SPAIN)* Mrs. Sonia DOMINGUEZ-DOMINGUEZ (UNIVERSITY OF ALICANTE, SPAIN)* Prof. Dr. Martin MUELLER (UNIVERSITY OF KIEL, GERMANY)*		

[#] In the application for beam time in this experiment we asked for 6 shifts of beam time on ID13 and 3 shifts of beam time on ID21. However, we got 9 allocated shifts on ID21. Thus, only microfluorescence measurements of activated carbon fibres were carried out.

Report:

1. Introduction

Activated carbon fibres (ACFs) are porous materials, which can be prepared with a high surface area and controlled pore size distribution. Their porous texture depends strongly on both, the activation process and the nature of the precursor. Chemical activation is a very interesting method to prepare porous carbon materials, which are used in many applications, such as gas storage (i.e., hydrogen and methane), supercapacitors, technologies related to pollution abatement, and so on. The chemical activation process consists of contacting a carbonaceous precursor with a chemical activating agent (KOH and NaOH among others), followed by a heat treatment stage, and finally by a washing step to remove the chemical agent and the inorganic reaction products. A detailed description of this process has been published elsewhere [1,2]. The carbonaceous precursors used for the preparation of ACFs are carbon fibres (CF), which can be obtained from different precursors. In our case, we have used two types of carbon fibres to prepare the ACFs: i) isotropic pitch-based carbon fibres (Kureha) and, ii) anisotropic PAN-based carbon fibres (consisting of an oriented external ring and a more isotropic fibre core) (Hexcel).

In our last experiment carried out at the beamline ID13 at ESRF (ME-366), the characterisation of chemically ACFs prepared from these two different precursors and using KOH and NaOH as activating agents was done using μ SAXS technique. The results showed that depending on the precursor, the chemical activation process produces isotropic or anisotropic development of porosity for the Kureha and Hexcel carbon fibres, respectively. In addition, it was demonstrated that the porosity development reaches the fibre core [3].

Considering that the distribution of the porosity across the fibre diameter in the ACFs is important because it affects to their final performance in a given application, further research is needed to understand more about the chemical activation process. The distribution of the porosity across the fibre diameter must be directly related to the distribution of the activating agent inside the fibre during the heat treatment step and also to the efficiency of removing the activating agent after the heat treatment stage by washing. Thus, in order to understand more about the chemical activation process and to optimise the properties of ACFs, the aim of this experiment is to try to visualise the location of the potassium and sodium of the used activating agents (KOH and NaOH, respectively) during the different stages of the chemical activation process by position-

resolved microfluorescence (ID21, ESRF). ACFs with different levels of washing (without washing, simple water washing and hydrochloric acid plus water washing) were prepared for these measurements.

2. Experimental

As previously mentioned, two carbon fibres were used as precursors for the preparation of ACFs: commercial petroleum pitch-based carbon fibres (Kureha Chemical Industry) and commercial high performance PAN-based carbon fibres (Hexcel). Chemically ACF were prepared by chemical activation with KOH or NaOH of both precursors. After the heat treatment stage, samples with different levels of washing were prepared: i) without washing; ii) simple water washing and; iii) hydrochloric acid plus water washing. 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, Quantachrome).

Position-resolved microfluorescence experiments were carried out with the scanning X-ray microscope (SXM) in the fluorescence mode at the ID21 beamline at the ESRF (Grenoble, France). The SXM is a sensitive technique for visualising the location of the potassium and sodium of the used activating agents during the different stages of the chemical activation and the following washes of the prepared ACFs. The beam energy was set to 3.7 keV, and we used the K absorption edges of Na, K, Cl, O and S, which are the important elements for our study. The samples were previously embedded in a resin for facilitating the posterior cut for the analysis. The sections were made in the Chemistry and Microimaging Laboratory (ESRF), using the microtome. The investigated samples were films of 5 μm thickness. Each sample was scanned horizontally and vertically using a piezoelectric stage, and both the transmission signal and the fluorescence spectra were recorded to produce a set of images.

3. Results and discussion

As an example, Figure 1 contains the two-dimensional potassium patterns corresponding to the PAN-based carbon fibres (anisotropic fibres) activated with KOH (4/1 KOH/C ratio) at 750 °C during 1 h under nitrogen atmosphere (500 ml/min) (Sample 1). The different images have been taken from sections of ACFs after different levels of washing: without washing (Sample 1); simple water washes (Sample 1_H) and; hydrochloric acid plus water washing (Sample 1_Cl). It should be remarked that the scales for the images presented in Figures 1 are not comparable. In Figure 1 left it can be observed that the activating agent (KOH) and/or other potassium compounds formed during the reaction (carbonate, oxides, metallic potassium, ..) reach the core of the carbon fibre. These potassium compounds seem to remain inside the fibre after several washes with water (sample 1_H) (see Figure 1 middle) and even after several washes with hydrochloric acid followed by several washes with water (sample 1_Cl) (see Figure 1 right). For all the cases, the core seems to have more potassium compounds than the outer region.

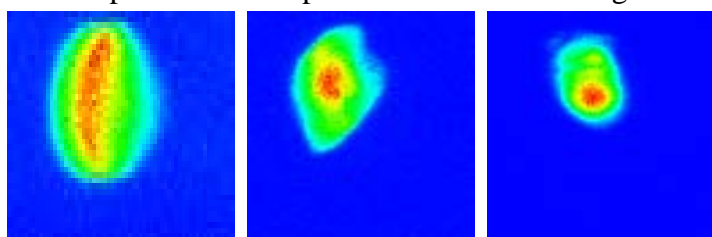


Figure 1. Two-dimensional potassium patterns corresponding to the cross-sections of Sample 1 after different levels of washing. From left to right: without washing (sample 1); simple water washing (sample 1_H) and; hydrochloric acid plus water washing (sample 1_Cl).

Figure 2 contains the two-dimensional potassium patterns corresponding to Sample 2, which is ACFs prepared from pitch-based carbon fibres (isotropic fibres) activated with KOH under the same conditions than Sample 1. Similarly to Sample 1, the different images have been taken from sections of ACFs after different levels of washing. Again, it should be noted that the scales for the images presented in Figures 2 are not comparable. For this type of carbon fibre, the maximum potassium compounds concentration just after the activation (Sample 2) is located in the outer part of the fiber (see Figure 2 left). However, it can be said that potassium compounds also reach the core of the carbon fibre and they still remain after washing with only water (Sample 2_H), as it is seen in Figure 2 middle. Contrary to the anisotropic PAN-based ACFs, in the case of isotropic pitch-based ACFs, KOH concentration in the inner part of the fibre decreases considerably after washing with hydrochloric acid and water (Sample 2_Cl) (see Figure 2 right).

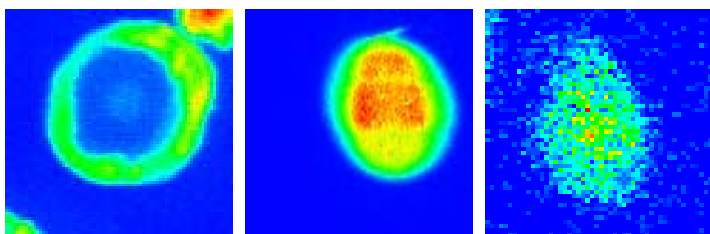


Figure 2. Two-dimensional potassium patterns corresponding to the cross-sections of Sample 2 after different levels of washing. From left to right: without washing (Sample 2); simple water washing (Sample 2_H) and; hydrochloric acid plus water washing (Sample 2_Cl).

For a better comparison between samples, profiles of potassium concentration (Intensity of the potassium signal) versus the distance across the fibre diameter have been obtained from images presented in Figure 1 and 2, and they have been plotted together in Figure 3. It can be seen that, for both type of carbon fibres the potassium location for the samples obtained just after the heat treatment stage (without any washing) is different for the Hexcel ACFs (Sample 1) and for the Kureha ACFs (Sample 2). In the case of Kureha ACFs, potassium compounds seem to be stuck in the outer part of the fibre, although also reach the core of the fibre, while for the Hexcel ACFs, the maximum potassium concentration appears in the fibre core. After washing with water, the potassium compounds stuck in the external part of the Kureha ACFs are removed (Sample 2_H), but the concentration in the internal region remains quite high, and is similar to the signal obtained for the PAN ACFs (Sample 1_H). Finally, it can be observed that, a deep wash with hydrochloric acid followed by water washing is enough to almost completely remove the potassium compounds existing in Kureha ACFs (Sample 2_Cl). However, in the case of PAN ACFs, it seems to be more difficult to take out all the potassium compounds from inside the fibre, and this type of wash is not efficient enough (Sample 1_Cl). The different behaviour observed for these two types of fibres must be due to their different structure: Sample 2 has been prepared from isotropic pitch-based carbon fibres (Kureha) and, Sample 1 from anisotropic PAN-based carbon fibres (Hexcel), which consist of an oriented external ring and a more isotropic fibre core.

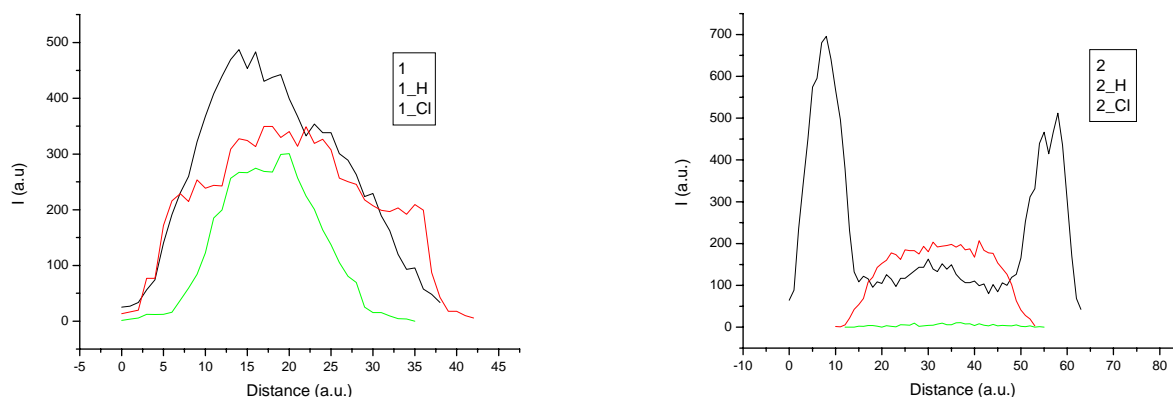


Figure 3. Profiles of potassium concentration (a.u.) versus the distance (a.u.) across the fibre diameter obtained from the cross-sections of: Left: Samples 1 (PAN-based ACFs) shown in Figure 1 and; Right: Samples 2 (pitch-based ACFs) shown in Figure 2.

In the case of the samples activated with NaOH, the microfluorescence analysis was much more difficult than for the samples activated with KOH, due to the low signal of sodium. Preliminary results indicate that NaOH penetration inside the carbon fibres is more difficulty than for KOH. These observations agree with the porosity characterisation results (not shown here), which show that KOH produces higher development of porosity than NaOH.

4. References

- [1] Lozano-Castello D, Lillo-Rodenas MA, Cazorla-Amorós D, Linares-Solano A. Preparation of activated carbons from Spanish anthracite: I. Activation by KOH. *Carbon* 2001; 39:741–749.
- [2] Linares-Solano A, Lozano-Castello D, Lillo-Rodenas MA, Cazorla-Amorós D. Carbon activation by hydroxides: Preparation and reactions, porosity and performances. *Physics and Chemistry of Carbon*. Elsevier. In press.
- [3] Lozano-Castelló D, Maciá-Agulló JA, Cazorla-Amorós D, Linares-Solano A, Müller M, Burghammer M, Riekell C. Isotropic and anisotropic microporosity development upon chemical activation of carbon fibers, revealed by microbeam small-angle X-ray scattering. *Carbon* 2006; 44: 1121–1129.