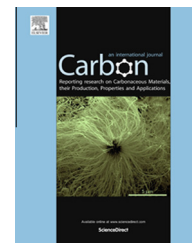


Available at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/carbon](http://www.elsevier.com/locate/carbon)

# Small and wide angle X-ray studies of impregnated activated carbons



J.W.H. Smith <sup>a</sup>, M. McDonald <sup>a</sup>, J.V. Romero <sup>a</sup>, L. MacDonald <sup>a</sup>, J.R. Lee <sup>a</sup>, J.R. Dahn <sup>a,b,\*</sup>

<sup>a</sup> Department of Physics and Atmospheric Science, Dalhousie University, Halifax, Nova Scotia B3H 3J5, Canada

<sup>b</sup> Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada

## ARTICLE INFO

### Article history:

Received 13 January 2014

Accepted 5 April 2014

Available online 13 April 2014

## ABSTRACT

Small angle X-ray scattering (SAXS) and powder X-ray diffraction (XRD) measurements were made on CuO-impregnated activated carbons, prepared with and without an HNO<sub>3</sub> co-impregnant, in order to determine the effect of impregnant loading and HNO<sub>3</sub> content on impregnant distribution. A comprehensive matrix of 30 CuO-impregnated samples with five HNO<sub>3</sub> concentrations and six impregnant loadings was prepared and studied. As a highlight, in Cu-based samples prepared with no HNO<sub>3</sub>, relatively small particle size CuO impregnant (approximately 3 nm) was observed at low impregnant loading and additional CuO appeared in large particles (>10 nm diameter) in meso and macropores as the impregnant loading increased. By contrast, when 4 M HNO<sub>3</sub> was present during the impregnation, the largest impregnant particles found were less than 4 nm. Results from SAXS data were shown to be in good agreement with XRD and data obtained from nitrogen gas adsorption isotherms. The combination of SAXS and XRD is shown to be a powerful combination in elucidating the nanostructure of impregnated activated carbons.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Activated carbons (AC) are commonly used in air filtration devices, such as gas mask canisters, to remove organic vapours from contaminated airstreams [1,2]. Impregnating the AC substrate with properly selected chemicals can increase adsorption of certain gases [3,4] or give the ability to adsorb toxins that un-impregnated AC cannot [5–16]. Impregnated activated carbons (IACs) capable of broad spectrum gas adsorption have been reported in the literature [7–11,14,17–19]. Copper oxide (CuO) is a common impregnant in broad spectrum IACs [5,6,8,10,14,17,18]. Our group has reported on the relationship between better impregnant distribution on the AC substrate and better gas adsorption capacity of the IAC [3,16,20–22]. It was observed that

co-impregnating with nitric acid (HNO<sub>3</sub>) improved the distribution of impregnant on the AC substrate [8,20–22]. In these works, wide angle powder X-ray diffraction (XRD) was found to be a useful tool to examine the distribution of impregnant on the AC substrate for relatively large grain size impregnant (>3–4 nm approximately). The XRD method could not provide information about relatively small nanocrystallites (<3 nm approximately).

Small angle X-ray scattering (SAXS) has been demonstrated to be a useful technique to study the structure of AC and other porous carbonaceous materials [23–30]. SAXS methods have also been employed to study two phase inorganic systems [31] and the particle size of supported catalysts [32,33]. In a recent report [34] a method for analyzing the SAXS data obtained from IACs was demonstrated. In the work

\* Corresponding author at: Department of Physics and Atmospheric Science, Dalhousie University, Halifax, Nova Scotia B3H 3J5, Canada. Fax: +1 902 494 5191.

E-mail address: [jeff.dahn@dal.ca](mailto:jeff.dahn@dal.ca) (J.R. Dahn).

<http://dx.doi.org/10.1016/j.carbon.2014.04.021>

0008-6223/© 2014 Elsevier Ltd. All rights reserved.

reported here a comparative study of some factors influencing impregnant distribution on IACs prepared from aqueous copper nitrate  $\text{Cu}(\text{NO}_3)_2$  ( $\text{Cu}(\text{NO}_3)_2$ ) solutions is reported. Some of the IACs were co-impregnated with nitric acid ( $\text{HNO}_3$ ). SAXS and XRD were used to study the changes in the IACs as a function of  $\text{Cu}(\text{NO}_3)_2$  and  $\text{HNO}_3$  concentration. Experimental results obtained using the SAXS and XRD methods were compared and found to be in good agreement. Experimental results from SAXS measurements were also compared to data obtained from nitrogen ( $\text{N}_2$ ) gas adsorption isotherms and good agreement was observed.

## 2. Experimental details

### 2.1. Chemicals used

The chemicals used to prepare the impregnating solutions were reagent grade copper nitrate hemi-pentahydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ ) and 70% concentrated  $\text{HNO}_3$  obtained from Sigma–Aldrich.

### 2.2. Sample preparation

All of the IAC samples were prepared using Kuraray GC granular activated carbon (Kuraray Chemical Co. (Osaka, Japan)). Kuraray GC (referred to as “GC” from this point forward) is derived from coconut shells and has a particle mesh size of  $12 \times 35$  (particle size of  $\sim 1.70 \text{ mm} \times 0.5 \text{ mm}$ ) and an ash content of 0.4% (wt/wt). Nitrogen adsorption experiments were performed using a Micromeritics ASAP 2010 gas adsorption porosimeter (described below). The data was analyzed using the Brunauer–Emmet–Teller (BET) model (for specific surface area) and non-local density functional theory (for pore size distribution (PSD)) on software supplied by Micromeritics. Details of these measurements have been reported previously [35]. Table 1 summarizes the results of the gas adsorption measurements performed on GC carbon. Boehm titrations [36] have been performed on GC in previous work [37,38] and show that this carbon has a total of  $\leq 0.18 \text{ mmol/g}$  acidic surface groups.

IAC samples were impregnated with  $\text{Cu}(\text{NO}_3)_2$  and in some cases  $\text{HNO}_3$ . The concentrations of  $\text{Cu}(\text{NO}_3)_2$  used were 0.31 M, 0.79 M, 1.60 M, 2.40 M and 3.10 M and the concentrations of  $\text{HNO}_3$  used were 0 M, 0.5 M, 2.0 M, 4.0 M and 8.0 M. Due to solubility issues, the IAC prepared from the most concentrated acid solution was 2.0 M  $\text{Cu}(\text{NO}_3)_2/6.6 \text{ M HNO}_3$ . All of the IACs were impregnated using the imbibing or incipient wetness method [37,38]. Typically 11–12 mL of solution was added to approximately 15 g of GC.

The IAC samples were heated under flowing argon in a sealed, cylindrical aluminum container that was located inside an oven. Prior to heating, the container was purged

with argon flowing at approximately 200 mL/min. The argon flow rate was approximately 60 mL/min during heating. The IACs were heated at  $T_F = 180^\circ\text{C}$  for approximately 3 h. After heating all of the IACs were cooled under flowing argon until they reached room temperature.

The impregnant loading after heating was determined using the equation:

$$\% \text{ Loading} = \{(\text{mass}_{\text{final}} - \text{mass}_{\text{initial}})/\text{mass}_{\text{initial}}\} \times 100\%, \quad (1)$$

where  $\text{mass}_{\text{final}}$  is the mass of the IAC after heating, and  $\text{mass}_{\text{initial}}$  is the mass of the unimpregnated GC (determined after drying at  $120^\circ\text{C}$  in air). The  $\approx 15 \text{ g}$  IAC samples were weighed using a Sartorius balance with an accuracy of  $\pm 1 \text{ mg}$ . The uncertainty associated with the % loading is 2–3% primarily due to inability to avoid some exposure to moist air while weighing and storing the samples. The predicted impregnant loading (expressed in mmol impregnant/g GC) was estimated from the volume and concentration of impregnating solution added to the GC. The relative uncertainty is 0.1 mmol impregnant/g GC.

### 2.3. Sample characterization

Contact angle measurements were performed using a First Ten Angstroms (FTA) 135 drop shape analyzer. A drop of solution was formed on the tip of a syringe. The drop was deposited onto a highly oriented pyrolytic graphite (HOPG) substrate by slowly lowering the syringe until the drop contacted the substrate. Then the syringe was lifted up. The base of the deposited drop was approximately 3 mm in diameter. A snapshot of the drop was then taken and the data was imported into a computer where the drop shape was analyzed using software supplied by the manufacturer. The HOPG substrates were obtained from SPI Supplies. Grades of SPI-1 and SPI-3 were used and there were no discernible differences in the results obtained from the two different grades. The HOPG was cleaved after each contact angle measurement using adhesive tape. The reported contact angle measurements are an average of 6–12 measurements per solution.

X-ray diffraction experiments were performed using a Phillips PW 1720 X-ray generator operated at a voltage of 40 kV and a current of 30 mA. The system is equipped with a Cu target X-ray tube and an incident beam monochromator which selects Cu  $K\alpha$  radiation. The system is coupled to an Inel CPS 120 curved position sensitive detector. A typical dwell time used was 1200 s/sample. Samples were ground to a fine powder prior to measurement using a mortar and pestle.

SAXS experiments were performed using a Bruker NanoStar system. The X-ray generator operates at 40 kV and 650  $\mu\text{A}$ . The system is equipped with a Cu target X-ray tube and has Göbel mirrors and a series of pinhole collimators to select a 400  $\mu\text{m}$  diameter beam of Cu  $K\alpha$  radiation

**Table 1 – Characteristics calculated from  $\text{N}_2$  adsorption experiments performed on GC.**

BET surface area ( $\text{m}^2/\text{g}$ )	Micropore volume ( $\text{cm}^3/\text{g}$ )	Meso and micropore volume ( $\text{cm}^3/\text{g}$ )
1550	0.53	0.55

Download English Version:

<https://daneshyari.com/en/article/1413828>

Download Persian Version:

<https://daneshyari.com/article/1413828>

[Daneshyari.com](https://daneshyari.com)