Application of Ionic Liquids (ILs) for the preparation of nanostructured carbons as oxygen reduction reaction catalysts

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1. Introduction

Porous carbons, especially nanoporous and nanostructured carbons, including Activated Carbons (AC), Carbon NanoTubes (CNTs), etc., have been standardized in many technological applications and become a hot scientific topic, due to their unique properties such as their high thermal and mechanical stability, electric conductivity, microwave absorption capacity, catalytic activity, tunable surface chemistry, enhanced and tailorable pore structure and wide availability[1].

On the other hand, Ionic Liquids (ILs) are lately considered amongst the most effective precursors for the preparation of nanostructured carbons, because they do not decompose completely into volatiles under pyrolysis but leave behind significant amounts of recalcitrant char. Moreover, there is a great variety of different IL structures that contain nitrile functional groups (−C≡N), either in the form of anion or cation, thus yielding highly nitrogen-rich carbon samples[2].

This work is primarily focused on the investigation of the catalytic performance of carbon materials developed through the template method. To this end, various types of enhanced pore size Vycor® (eps-Vycor®) have been employed as hard templates/molds in the nanocasting/pyrolytic treatment of [BMIM][TCM] as IL precursor. Upon dissolution of the hard template, the recovered N-doped porous carbons have extensively been characterized by bi-modal micro-mesoporosity[3]. Afterwards, C,N-networks prepared by

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this method have succesfully been studied as ORR electrocatalysts showing a prevalent $4e^-$ reduction process under operation.

2. Materials and Methods

The IL used in this work was the 1-butyl-3-methylimidazolium tricyanomethanide ([BMIM][TCM]), which was provided by IoLiTech GmbH, with a purity over 98% and a moisture contamination of 150 ppm. Vycor® glass tube (Code 7913, Corning® USA), was selected as the hard template for the preparation of the nanostructured carbons.

Nanostructured carbon syntheses via templated precursor pathway include the casting of [BMIM][TCM] into raw and eps-Vycor® under vacuum, to facilitate the imbibition of the IL phase into the porous structure, followed by carbonization and template dissolution to recover the carbonaceous samples as Vycor® replica. The main target of etching process was to widen the pore necks and thicken carbon domains lying into Vycor®cavities.

Electrochemical measurements were carried out with a Rotating Ring Disk Electrode (RRDE working electrode, Pine Instrument Co) made of a disk of glassy carbon (GC, ∅ 5mm, A = 0.196 cm^2) and a platinum (Pt) ring with a surface of 0.11 cm^2. All carbonaceous samples produced were fabricated as RRDE electrodes and measurements were performed in a three-electrode cell operating in a 0.1M KOH solution, equipped with an [Ag][AgCl][KCl_{sat}] reference electrode and a Pt wire as counter electrode.

3. Results and Discussion

The porous structure of developed carbons was elaborated by interpreting the results of N_2 adsorption at 77 K. Adsorption isotherms were obtained on a Quantachrome porosimeter. BET (Brunauer-Emmett-Teller) method was applied to the calculation of the specific surface areas (SSA) of each sample while pore size distributions (PSDs) were obtained using the Quenched Solid Density Functional Theory (QSDFT) method. The PSDs were derived from both the adsorption and desorption (equilibrium) branches of the isotherm. QSDFT was selected as the most realistic theoretical analysis model for carbonaceous materials prepared via the templated precursor path and thus applied to samples featured by wrinkled and rough amorphous pore walls, the alternative NLDFT model being more appropriate in the case of porous carbons with flat and non-structured graphitic walls[4].

It can be argued that the carbons derived from the etched eps-Vycor® samples share common pore structural characteristics. However, there are distinct features related to the shape of the N_2 adsorption isotherms and the way the PSD curves decay at the region of large pore sizes (Figure 1a,b). The different shape of the N_2 adsorption isotherms and PSD curves is attributed to the different portion of the small and large fragments in the carbon samples.

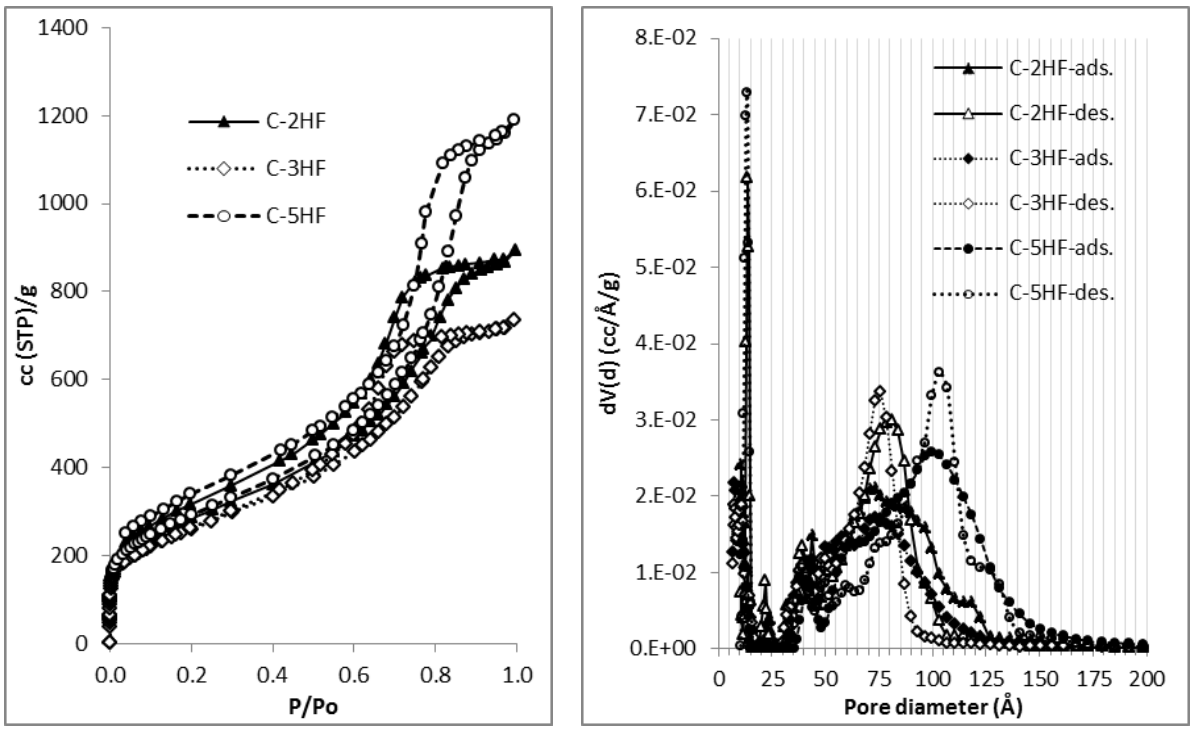

Figure 1: (a) N_2 adsorption isotherms at 77 K of the carbon samples derived from 2HF- Vycor®, 5HF- Vycor® and 7HF- Vycor®. (b) PSDs of the carbon samples derived from 2HF- Vycor®, 5HF- Vycor® and 7HF- Vycor®.

Table *1* summarizes the main properties of C-2HF, C-3HF and C-5HF samples related to their pore structural characteristics.

Table 1. Characteristics of the porous structure of C-4h and C-8h

Sample	S BET ($m^2\ g^{-1}$)	Total Pore Volume (TPV) ($cc\ g^{-1}$)	Mean pore diameter (d) (nm)
C-2HF	1012	1.38	1.4 and 7.5
C-3HF	930	1.14	1.3 and 7.5
C-5HF	1042	1.84	1.4 and 10

The prepared electrocatalysts were scrutinized with the Rotating Ring Disk Electrode (RRDE) and the corresponding voltametric curves are depicted in Figure 2. As it can be seen from the analysis of these electrochemical profiles, all electrocatalysts showed a well-defined ORR reduction peak with remarkable onset potential values (Eon).

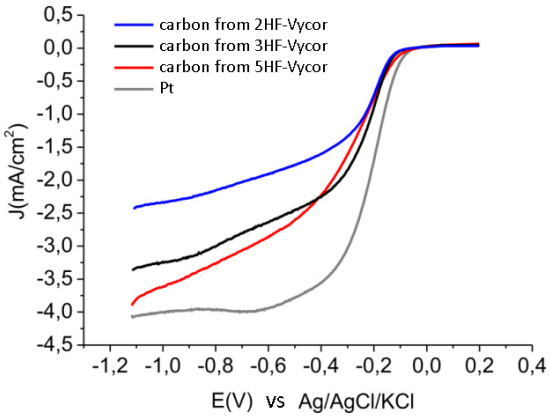

Figure 2: RRDE current-potential curves of carbon from 2, 3 and 5HF- Vycor® at 293 K in O_2 saturated 0.1 M KOH solution registered at GC disk (A = 0.196 cm^2). All samples were measured at a working electrode spin rate of 800 rpm.

4. Conclusions

In this work we showed that templated IL pyrolysis and unconfined IL pyrolysis followed by activation with CO_2, brings to N-doped C-materials with different pore structural characteristics and pore surface properties. It has also been concluded that the pore size of the template, which in this work consisted of pore etched Vycor® with different degrees of pore etching, also affects the properties of the derived carbons.

The N-doped carbons produced with the templated IL pyrolysis method were tested as catalytic materials for the challenging electrochemical ORR. All materials exhibited remarkable efficiency in oxygen reduction with the sample produced from the template with the smaller pores being the most effective one.

5. References

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