



## Porous carbons from ionic liquid precursors confined within nanoporous silicas



O. Tzialla<sup>a</sup>, G. Kakosimos<sup>a</sup>, C. Athanasekou<sup>b</sup>, E. Galata<sup>a</sup>, G.E. Romanos<sup>b,\*</sup>, G. Pilatos<sup>b</sup>, L.F. Zubeir<sup>c</sup>, M.C. Kroon<sup>c</sup>, B. Iliev<sup>d</sup>, T.J.S. Schubert<sup>d</sup>, K.G. Beltsios<sup>a,\*\*</sup>

<sup>a</sup> Department of Materials Science and Engineering, University of Ioannina, 45110 Ioannina, Greece

<sup>b</sup> Institute of Nanoscience and Nanotechnology, National Center for Scientific Research Demokritos, Agia Paraskevi, Athens 153 10, Greece

<sup>c</sup> Separation Technology Group, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Den Dolech 2, 5600 MB Eindhoven, Netherlands

<sup>d</sup> IOLITEC, Ionic Liquids Technologies GmbH, Salzstraße 184, D-74076 Heilbronn, Germany

### ARTICLE INFO

#### Article history:

Received 2 August 2015

Received in revised form

27 October 2015

Accepted 2 November 2015

Available online 14 November 2015

#### Keywords:

Ionic liquids

Carbon precursor

Nanopore confinement

Microporous carbon

Mesoporosity

### ABSTRACT

We propose Vycor<sup>®</sup> porous glass and various types of enhanced pore size Vycor<sup>®</sup> (hereafter referred to as eps-Vycor<sup>®</sup>) as hard templates for the development of micro-mesoporous N-doped carbons via nanocasting/thermolytic treatment of 1-alkyl-3-methylimidazolium tricyanomethanide Ionic Liquids (ILs). Vycor<sup>®</sup> is less costly than mesoporous ordered silicas of the type SBA-15 and MCM-41 which are sometimes employed for the development of micro-mesoporous carbons (CMK-3) as inverse replicas from the solid matrix; in addition Vycor<sup>®</sup> and eps-Vycor<sup>®</sup> can also be used in the form of sheets or tubes, thus opening the road for the development of composite carbon/silica substrate membranes with molecular sieving characteristics. We find that the nitrile functional groups in the anion of the IL lead to enhanced carbon yield while nanocasting and nanoconfinement are decisive for producing functional carbons with high levels of microporosity. In addition, the developed functional carbons exhibited extended mesoporosity with characteristic H2 or H1 types of hysteresis in their N<sub>2</sub> adsorption isotherms (77 K), solely in the cases when eps-Vycor<sup>®</sup> was applied as the hard template. The widening of the Vycor<sup>®</sup> pores, especially of the pore constrictions by treatment in HF for varying periods led to the formation of thicker carbon nanodomains that exhibited the required mechanical stability to retain the inverse structure (replica) upon dissolution of the hard template.

© 2015 Elsevier Inc. All rights reserved.

### 1. Introduction

Using Ionic Liquids (ILs) as carbon precursors is a hot topic in current fundamental and applied materials research [1,2]. Notwithstanding the fact of their high cost, ILs bring many benefits and simplify the carbonization procedure leading to the avoidance of common complications and difficulties during the pyrolytic synthesis of carbon such as distillation, sublimation and volatile intermediates formation [3]. This is the major advantage over other carbon precursor materials and is attributed to the charged nature and the concomitant negligible vapor pressure of ILs, which are

moderately volatile up to their decomposition temperature [4]. Therefore, the use of ILs for the fabrication of functional carbon materials has the potential to offset their high cost by simplifying the thermolytic treatment procedure. Furthermore, carbonization is a process that does not impose the application of highly pure ILs, since many of the impurities can be distilled (more volatile or less thermally stable compounds than ILs) and are not finally incorporated into the structure of the derived functional carbons. ILs are perceived as expensive solvents, mostly owing to the complex post- or pre-production processes necessary for the removal of traces of unwanted substances such as halides, moisture, impurities in the reactants and unreacted raw materials. However, depending on the application, trace quantities of impurities may have no effect on the property of interest. Recently the authors showed that impurities in 1-alkyl-3-methylimidazolium tricyanomethanide ILs had no effect on the CO<sub>2</sub> absorption capacity and kinetics and that even the leaching of MnS from the surface of mild steel to the bulk of the IL

\* Corresponding author. Tel.: +30 2106503972; fax: +30 2106511766.

\*\* Corresponding author. Tel.: +30 2651007206; fax: +30 2651007034.

E-mail addresses: [g.romanos@inn.demokritos.gr](mailto:g.romanos@inn.demokritos.gr) (G.E. Romanos), [kgbelt@cc.uoi.gr](mailto:kgbelt@cc.uoi.gr) (K.G. Beltsios).

or the on purpose addition of anti-corrosive agents (sodium molybdate) in corrosive ILs such as the pyrrolidium-2-one bis[(trifluoromethyl)sulfonyl]imide had not any effect on the defined Henry constants of CO<sub>2</sub> absorption and on the binary CO<sub>2</sub>/IL diffusivities [5].

Besides the simplification they bring to the carbonization process and the possibility to use them in their less expensive/not refined state, ILs are “designed solvents” offering the additional advantage to choose among a huge number of possible anion/cation combinations. Thus, via appropriate choice of the anion and cation and the overall hydrophilicity/hydrophobicity of the system, ILs could wet any surface and fill the cavities of any porous material without the need to use additional solvents or pressure. What is more important, ILs with nitrile-functionalised imidazolium cation and tricyanomethanide or dicyanoamide anions, contain tightly conjugated nitrogen atoms that stay incorporated within the carbonaceous nanostructure, thus creating nitrogen doped (N-doped) functional carbons. It has already been shown that many properties of carbon such as the electrical conductivity, basicity, oxidation stability and catalytic activity, can be enhanced by adjusting the respective nitrogen content [6]. Except from their role as a nitrogen source, nitrile groups condense at lower temperatures during carbonization, undergoing a trimerization reaction towards triazines which are the thermally stable crosslinks responsible for the high carbon yield up to the elevated temperatures required for carbonization [7,8]. It should be therefore stressed that despite the negligible vapor pressure, the intermediates formed after the first thermal decomposition may be volatile and therefore the carbon precursor potential of ILs exhibits substantial variability. Confinement of the ILs into the nanocavities of several porous materials arises as the most appropriate way to circumvent the evaporation of decomposition products and is already proven to increase the carbonization yield of any IL [9]. Porous inorganic oxides such as silica and alumina have already being used as hard templates, not only for the enhancement of the carbon yield but also for the generation carbons with varying nanostructure from high carbon yield ILs such as methyl-butylpyridinium dicyanamide or ethyl-methylimidazolium dicyanamide [10,11].

In this work, we have initially studied the carbonization effectiveness of five ILs (pyrrolidium-2-one bis(trifluoromethylsulfonyl) imide ([BHC][BTA]), 1-Ethyl-3-methylimidazolium acetate ([EMIM][Ac]) and 1-Alkyl-3-methylimidazolium tricyanomethanides ([RMIM][TCM], with R = butyl, hexyl and octyl)) in their free (unconfined) state and we have further investigated their relative hydrophilicity in conjunction with their capacity to fill the pores of Vycor<sup>®</sup> glass, a highly hydrophilic nanoporous solid matrix. Following the determination of the best carbon precursor (1 butyl-3-methylimidazolium tricyanomethanide [BMIM][TCM]), we establish that the optimum thermolysis temperature (as regards porosity, pore size, surface area and nitrogen content of the derived functional carbons) is 800 °C. Furthermore we present a detailed study of the effect of the pore size of the hard template (Vycor<sup>®</sup>) on the nanostructural characteristics of the derived functional carbons and we show that just one immersion in IL does not suffice for the inversion of the Vycor<sup>®</sup> structure in the derived functional carbons. Despite this, the as produced carbons exhibit inherent micro- and mesoporosity with BET surface areas reaching the value of 1000 m<sup>2</sup> g<sup>-1</sup> upon thermolytic treatment at 800 °C. We further conclude that when the pore necks, (a widely abundant feature in the pore framework of Vycor<sup>®</sup>), are significantly widened via controlled HF etching, the inherent pore structure characteristics of the derived carbons are complemented by quite extended mesoporosity. The N<sub>2</sub> adsorption isotherms (77 K) of the as derived carbons presented type H2 and type H1 hysteresis in the case of the short and long treatment of the Vycor<sup>®</sup> samples with “short” and

“long” referring to the period of the HF exposure. Type H2 hysteresis is characteristic for the connectivity of mesopores with different size and shapes while type H1 hysteresis characterizes mesopores with uniform size. In this context we suggest that widening the pores of the hard template (especially the pore constrictions) results to the formation of thicker carbonaceous domains with enhanced connectivity forming a carbon framework that exhibits the mechanical strength to retain the replica structure and conclude to functional N-doped carbons with enhanced micro and mesoporosity.

## 2. Experimental

### 2.1. Ionic Liquids

Details on the synthesis of the ILs can be found elsewhere [12]. In brief, the 1-alkyl-3-methylimidazolium tricyanomethanides ([RMIM][TCM], with R = butyl, hexyl, octyl) were produced by metathesis reaction of the corresponding imidazolium-based IL chloride with sodium tricyanomethanide in dry dichloromethane. The pyrrolidium-2-one bis(trifluoromethylsulfonyl)imide ([BHC][BTA]) was produced through reaction of one equivalent of pyrrolidin-2-one and one equivalent of the corresponding acid (trifluoromethanesulfonimide) in toluene. 1-Ethyl-3-methylimidazolium acetate ([EMIM][Ac]) was produced through reaction between one equivalent of 1-ethyl-3-methylimidazolium methylcarbonate [EMIM][MeCO<sub>3</sub>] and one equivalent of acetic acid under constant stirring at RT until ceasing of the CO<sub>2</sub> evolution.

### 2.2. Preparation of the carbon/Vycor<sup>®</sup> composites and nanostructured carbons

Tubes of Vycor<sup>®</sup> glass (OD = 7 mm, ID = 6 mm) were cut into samples of 2–3 cm length and immersed into H<sub>2</sub>O<sub>2</sub> solution (30% w/w) at 95 °C for 0.5 h. The samples were thoroughly rinsed with deionized water and kept in a desiccator until their use. The casting with the IL was performed in glass containers under high vacuum (10<sup>-3</sup> mbar). Each Vycor<sup>®</sup> sample was evacuated inside the glass container at 160 °C and 10<sup>-3</sup> mbar for 24 h. Then a certain amount of the IL, which was enough for flooding the entire Vycor<sup>®</sup> sample, was suctioned under vacuum at room temperature. A special manifold connected to the each glass container allowed suctioning of the IL avoiding any contact of the solid sample with the atmospheric air. The samples were left immersed in the IL under vacuum for varying periods ranging from 30 min to several days. Weighing of the Vycor<sup>®</sup> samples before and after IL imbibition allowed us to calculate the amount of IL infiltrated into the pores. Further, the IL/Vycor<sup>®</sup> samples underwent thermolytic treatment in a tubular oven for 2 h at 4 different temperatures (500, 600, 700 and 800 °C) under Ar flow (150 ml/min) and a ramp rate of 10 °C/min. The produced carbon/Vycor<sup>®</sup> composites have been reweighed in order to calculate the carbon yield of the IL.

In order to extract the functional carbons nesting inside the pores of Vycor<sup>®</sup>, the silica part of the composite was dissolved in HF and after centrifugation, neutralization and several washings with D.I. water the retained carbon was dried overnight and kept in a desiccator.

The various eps-Vycor<sup>®</sup> samples were produced via controlled HF etching according to a procedure that is due to Chapman and Elmer [13] and relies on the immersion of the sample into ammonium bifluoride (NH<sub>4</sub>HF<sub>2</sub>) solution (10% in water) for 1 h followed by immersion into HNO<sub>3</sub> (1 N) at 95 °C for varying periods. We choose 2, 3 and 5 h for the in situ production of HF inside the pores upon immersion into the HNO<sub>3</sub> solution and we refer to these as short, medium and long treatments. The procedure for

Download English Version:

<https://daneshyari.com/en/article/72290>

Download Persian Version:

<https://daneshyari.com/article/72290>

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