

## IONIC LIQUID TAILORED CARBON AEROGELS

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### Introduction

Mesoporous carbon aerogels (CAs) of a wide range application potential are most frequently obtained from resorcinol-formaldehyde (RF) hydrogel precursors<sup>1</sup>. The sol-gel process used in the synthesis provides an efficient and versatile means of product control by systematic variation of process conditions such as pH, stoichiometry, additives, drying conditions, etc. The porosity of dried resorcinol-formaldehyde (RF) gel is conserved when to polymer is converted to carbon.

The use of room temperature ionic liquids (RTILs) as a novel medium is an expanding field of interest. Despite of their high prize they are one of the most promising solvents/reaction media of the future for their numerous beneficial properties (non-flammable, low vapour pressure, high temperature stability, etc.). When resorcinol-formaldehyde gels are synthesized in RTILs they are not a simple reaction medium but may concurrently act as catalyst and/or template.

The effect of various alkyl-substituted imidazolium based RTILs on the morphology of RF based carbon aerogels will be compared in the low water concentration range. The influence of water will be reported through the characterization of carbon gels synthesized in various water – 1-ethyl-3-methylimidazolium methyl sulfate mixtures.

### Materials and Methods

CAs were prepared by sol-gel technique. Resorcinol (R) and formaldehyde (F, 37% aq. solution) were mixed in the presence of Na<sub>2</sub>CO<sub>3</sub> catalyst (C) with different ionic liquids listed in Table 1. Polymer ionogels were also synthesized without any metal catalyst in [emim][EtSO<sub>4</sub>]/water mixed solvent with systematically set ratio (9 - 55 m/m% water). After exchanging water for acetone the latter was removed by supercritical carbon dioxide (scCO<sub>2</sub>) extraction<sup>2</sup>. Polymer aerogels were converted to carbon in a rotary quartz reactor in dry nitrogen flow at 800 °C.

**Table 1 The ionic liquids and their abbreviation used in this work**

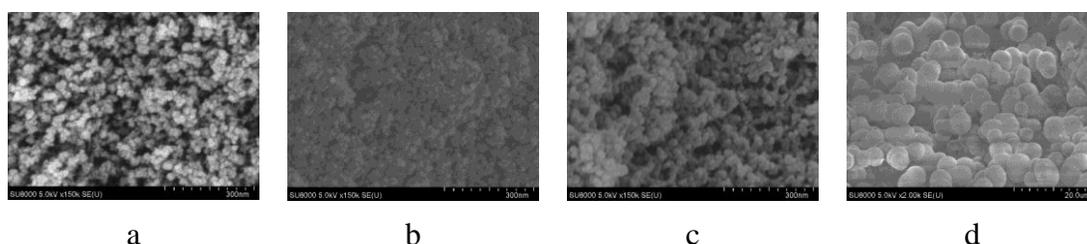
1-Ethyl-3-methylimidazolium methyl sulfate	[emim][MeSO <sub>4</sub> ]
1-Ethyl-3-methylimidazolium ethyl sulfate	[emim][EtSO <sub>4</sub> ]
1-Ethyl-3-methylimidazolium acetate	[emim][Ac]
1-Butyl-3-methylimidazolium acetate	[bmim][Ac]

The morphology of the CAs was investigated in a wide range of length scales using low temperature (-196 °C) nitrogen adsorption, scanning electron microscopic imaging (SEM) and small angle X-ray scattering (SAXS) techniques. The apparent surface area  $S_{BET}$  was calculated using the Brunauer–Emmett–Teller (BET) model. The micropore volume ( $W_0$ ) was derived from the Dubinin–Radushkevich (DR) plot. The pore size distribution was calculated by QSDFT model.

Transformation of all the primary adsorption data was performed by the Quantachrome software ASiQwin version 3.0. SEM micrographs were obtained by field emission SU8030 (Hitachi) equipment. The SAXS measurements were performed in the transfer momentum range  $0.01 \leq q \leq 2 \text{ \AA}^{-1}$  on the BM02 small angle scattering beam line at the European Synchrotron (ESRF), Grenoble, France.

## Results and Discussion

**Figure 1** compares the CAs prepared with  $\text{Na}_2\text{CO}_3$  catalysis in pure water, water – 1-ethyl-3-methylimidazolium methyl sulphate mixture (9 m/m% water) and the catalyst-free samples prepared in aq. 1-ethyl-3-methylimidazolium ethyl sulfate mixtures. Notice the outstanding size of the elementary beads in **Figure 1d**. **Table 2** summarizes the morphological data calculated from the  $n_2$  adsorption and SAXS measurements.



**Figure 1** Comparison of the CA aerogels synthesized in various conditions. All the magnifications are 150k.

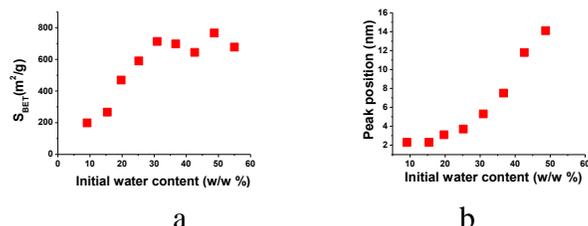
- (a) pure water,  $\text{Na}_2\text{CO}_3$  catalysis; (b) water – [emim][MeSO<sub>4</sub>] (9 m/m% water),  $\text{Na}_2\text{CO}_3$  catalysis;  
 (c) water – [emim][EtSO<sub>4</sub>] mixture (43 m/m% water), WITHOUT  $\text{Na}_2\text{CO}_3$  catalysis;  
 (d) water – water - [emim][EtSO<sub>4</sub>] mixture (55 m/m% water), WITHOUT  $\text{Na}_2\text{CO}_3$  catalysis.

**Table 2** Data deduced from gas adsorption, SAXS, and SEM

Carbon synthesized in aq.	$S_{\text{BET}}^a$	$W_{0,\text{DR}}^b$	$V_{\text{TOT}}^c$	$V_{\text{meso}}^d$	$S_{\text{SAXS}}^e$	$d_{\text{SAXS}}^f$	$d_{\text{SEM}}^g$
	m <sup>2</sup> /g	cm <sup>3</sup> /g	cm <sup>3</sup> /g	cm <sup>3</sup> /g	m <sup>2</sup> /g	nm	nm
[emim][MeSO <sub>4</sub> ]	580	0.23	0.54	0.32	1394	9.6	17 ± 3
[emim][EtSO <sub>4</sub> ]	210	0.08	0.13	0.05	992	8.8	13 ± 2
[emim][Ac]	845	0.33	0.97	0.64	1648	12.0	19 ± 3
[bmim][Ac]	639	0.25	0.76	0.51	1628	14.8	20 ± 4
water	865	0.34	1.66	1.32	1712	10.2	20 ± 4

<sup>a</sup> Specific surface area from BET model, <sup>b</sup> Micropore volume from DR method, <sup>c</sup> Pore volume at  $p/p_0 \rightarrow 1$ , <sup>d</sup>  $V_{\text{TOT}} - W_{0,\text{DR}}$ , <sup>e</sup> Specific surface area from BET model, <sup>f</sup> diameter of the spherical elementary beads from SAXS measurements, calculated from  $I(q)q^4$  vs  $q$  plot, <sup>g</sup> diameter of the beads from SEM (from 100 data)

In all the water - [emim][EtSO<sub>4</sub>] mixtures investigated we were able to perform the synthesis of the polymer precursor without any added catalyst and thus obtained really metal free CA<sup>3</sup>. **Figure 2** shows how the apparent surface area and the size of the most typical pores can be tuned by the water content.



**Figure 2** Effect of the water content of the solvent on the apparent surface area (a) and the maxima of the pore size distribution curve (b)

## Conclusions

It can be concluded that both the type of the investigated RTILs and the water content of the water – RTIL mixture have a strong influence on the morphology and the pore structure of the CAs. RTIL with substituted sulfate anions yields a more compact carbon structure than with acetate anions. Increasing the water content of the polymerization media makes the pore structure more open. Moreover the pore size in the mesopore range widens systematically with water content. That is, the size of the mesopores can be sensitively tailored not only by selecting the RTIL but also by changing the water content of the reaction media. The CAs in the water - [emim][EtSO<sub>4</sub>] systems were obtained with any additional catalyst.

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