

## SYNTHESIS OF CARBON GELS BY SOL-GEL POLYMERIZATION OF COAL-DERIVED PHENOLIC OILS WITH FORMALDEHYDE

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### Introduction

Phenolic oils (PO) are low-value coal-derived liquids obtained from the distillation of coal tar. As they are rich in phenol, PO are *a priori* very interesting precursors for preparing low-cost carbon gels based on sol-gel phenol-formaldehyde polymerization routes. Synthesis of carbon gels from PO and their application as electrode materials for supercapacitors would constitute an important step towards the valorization of those liquids. However, the main difficulty to overcome is that PO has a multi-component nature, with many aromatic compounds and heterocycles of different reactivity. In this study, we synthesized porous carbon gels obtained by sol-gel polymerization of PO (~ 25 wt.% of phenol) with formaldehyde, using different solvents in either acidic or basic media. The porous texture of the carbons was further developed by KOH activation, and the resultant activated carbons were tested as supercapacitor electrodes. The physicochemical properties of the carbon materials were correlated to the electrochemical performances of the carbon electrodes.

### Materials and Methods

**Synthesis of activated carbons (ACs) from xerogels:** Two types of xerogels were prepared from: 1) 2.36 g PO, 2.36 g formaldehyde (F), 2.5 g n-propanol and 0.23 g NaOH; or 2) 15 g PO, 3.123 g para-formaldehyde (pF), 12.5 g i-propanol and 0.64 g p-toluenesulfonic acid (pTSA). Both reaction mixtures were put into sealed glass flasks and heated at 85°C for 5-7 days. The resultant alcogels were dried in an oven at 85°C to obtain xerogels, which were ground and chemically activated at 750°C during 1h in nitrogen atmosphere with different KOH/xerogel ratios, w= 2 to 5. The ACs were repeatedly washed with 1M HCl and subsequently with distilled water until free of chloride ions. Finally, they were dried at 105 °C for 12 h and labelled in each case: 1) CXw, where w is the KOH / xerogel mass ratio (CX0 carbon xerogel, where w = 0, was obtained by carbonization of the organic xerogel at 900°C for 1h); 2) Wi, where i = 0, 3, 4 and 5. Commercial ACs, MSC-20X and MSC-30X, were also used for comparison.

**Electrochemical characterisation:** carbon electrodes were prepared by spreading a paste (~ 3 mg) containing the AC, polytetrafluoroethylene (PTFE) and carbon black (85:10:5 wt.%) onto graphite foils, and were subsequently impregnated with 2 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> for 72 h. Cyclic voltammetry (CV) tests were performed in a three-electrode cell within the potential window of 0 - 0.74 V, using a platinum gauze as counter electrode and a saturated calomel electrode (SCE) as reference. Galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) tests were carried out in a two-electrode cell by placing two identical electrodes (~ 3 mg per electrode) separated by a glass fiber disc between two gold current collectors.

### Results and Discussion

Chemical activation greatly developed the porous texture of the xerogels by mainly creating micropores. Micropore volumes,  $V_{\mu\text{-NLDFT}}$ , were considerably higher than mesopore volumes,  $V_M$ , and the main pore size,  $L_0$ , of the ACs was < 2 nm, thus indicating that their porous textures were essentially microporous (**Table 1**). Given that the BET method overestimates the surface areas ( $A_{\text{BET}}$ ) of highly microporous ACs, the values obtained from the pore size distributions (PSDs),  $S_{\text{NLDFT}}$ , should be preferred [1].  $S_{\text{NLDFT}}$  of MSC30X was 2394 m<sup>2</sup> g<sup>-1</sup>, considerably lower than the

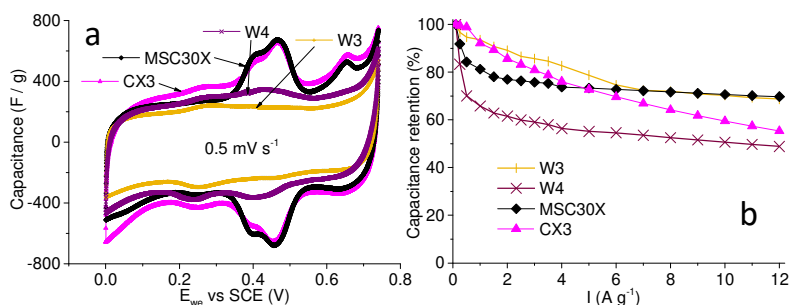
overestimated  $A_{\text{BET}}$  value of  $3305 \text{ m}^2 \text{ g}^{-1}$ . Among the ACs, W3 exhibited the most developed porous texture, having a  $S_{\text{NLDFT}}$  of  $2224 \text{ m}^2 \text{ g}^{-1}$ . CX3 exhibited the highest  $S_{\text{NLDFT}}$  of the CXw series,  $2041 \text{ m}^2 \text{ g}^{-1}$ , and possessed the highest  $V_{\mu\text{-NLDFT}}$  with diameters of  $0.7 - 2 \text{ nm}$ , which contributed in a greater extent to the  $S_{\text{NLDFT}}$ .

**Table 1. Textural properties of the ACs**

Sample	$A_{\text{BET}}$ $\text{m}^2 \text{ g}^{-1}$	$S_{\text{NLDFT}}^*$ $\text{m}^2 \text{ g}^{-1}$	$V_{\mu\text{-NLDFT}}^*$ $\text{cm}^3 \text{ g}^{-1}$	$V_{\text{M}}$ $\text{cm}^3 \text{ g}^{-1}$	$L_0^*$ nm
CX0	90	102	0.01	0.13	0.42
CX2	1848	1537	0.65	0.13	1.10
CX3	2729	2041	0.90	0.34	1.19
CX4	2673	1968	0.82	0.45	1.21
CX5	2383	1717	0.73	0.41	1.23
W0	620	891	0.24	0.10	0.62
W3	2694	2224	1.04	0.13	1.29
W4	2967	2278	1.08	0.28	1.51
W5	2494	2064	0.95	0.17	1.37
MSC20X	2363	2134	0.92	0.03	1.16
MSC30X	3305	2394	1.15	0.46	1.76

\*Applying 2D-NLDFT model with SAIEUS® software.

The ACs exhibited lower functionalization degree than the non-activated materials, due to the removal of functional groups by KOH. The bulk oxygen concentration was between 13.49 and 5.72 wt.% for CX0 and CX3, respectively. According to XPS re-sults, phenols, ethers, esters and anhydrides were the most abundant oxygen functionalities on the AC surface, followed by carbonyls, quinones and carboxylic acids. CX2 and CX3 presented intense redox peaks in the CV curves at the low scan rate of  $0.5 \text{ mV s}^{-1}$ , which may be related to specific oxygen functionalities (**Fig. 1a**).



**Figure 1. (a)** CV curves recorded at  $0.5 \text{ mV s}^{-1}$  scan rate in the voltage window of  $0-0.74 \text{ V}$ ; **(b)** Capacitance retention of the ACs vs the current density.

CX3 exhibited the highest capacitance of  $416 \text{ F g}^{-1}$  at  $0.5 \text{ mV s}^{-1}$ , which was higher than that of MSC30X at the same scan rate,  $380 \text{ F g}^{-1}$ , despite the highest  $S_{\text{NLDFT}}$  of the latter. This is explained by the higher  $V_{\mu\text{-NLDFT}}$  with sizes of  $0.7 - 2 \text{ nm}$  and the lower  $V_{\mu\text{-NLDFT}}$  with size  $< 0.7 \text{ nm}$  for CX3. W3 and MSC30X exhibited the highest capacitance retentions of 68 and 70%, respectively, up to  $12 \text{ A g}^{-1}$  (**Fig. 1b**).

ACs yielded energy densities between  $5.3 \pm 1.4$  and  $2.1 \pm 0.3 \text{ Wh kg}^{-1}$ , and power densities between  $46.4 \pm 3.2$  and  $4184 \pm 547 \text{ W kg}^{-1}$ , for current densities between  $0.1$  and  $12 \text{ A g}^{-1}$ . Power densities of the studied activated carbons are not that high due to their highly microporous textures, which hinder fast ion transport at high current densities.

## Conclusion

ACs were successfully prepared by chemical activation of xerogels obtained from phenolic oil in different solvents and using acidic or basic catalysts. Whereas the specific capacitances are quite high, still the electrochemical performances of the materials may be improved by increasing their mesoporosity further, since the highly microporous textures hinder ion transport at high scan rates or at high-current regimes.

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