

Electronic Supporting Information

Hard carbon porosity revealed by adsorption of multiple gas probe molecules (N₂, Ar, CO₂, O₂ and H₂)

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1. Experimental part

1.1 Materials synthesis

HAB-1300 material was prepared by hydrothermal carbonization (HTC). An aqueous solution of 0.8 M was prepared by mixing glucose ($C_6H_{12}O_6$) and distilled water, which was placed in a stainless-steel autoclave and thermally treated at 180 °C for 20h. The obtained solid material (hydrochar) after cooling down the autoclave, was collected, dried overnight at 80 °C and heat-treated (5 °C min^{-1}) up to 1300 °C, under Ar flow (15 L h^{-1}) and kept to this temperature for one hour.

HPR-1300 material was obtained by implying a sol-gel approach. It consists in the dissolution of phloroglucinol (3.26 g) and glyoxylic acid (3.6 g) monomers in 40 mL of solvent (water – ethanol, 1:1 ratio) followed by aging for 48h at constant temperature (26 °C). Once the phenolic resin gel formed, it is dried at 150 °C (12h) and then thermally pyrolysed at 1300 °C, as described elsewhere [1].

TCA1400 hard carbon was synthesized as follows: phloroglucinol (1.64 g) and glyoxylic acid (1.44 g) were dissolved in water followed by the addition under stirring of 0.72 mL of TCA (thiophene carboxaldehyde). After few minutes, 0.72 g of L-Cysteine and 0.72 g of TEDA were introduced in the mixture, followed by aging for 24h. Next, the solid was recovered and dried overnight at 80 °C then thermally annealed at 1400 °C under Ar flow [2].

1.2 Materials characterization

To evaluate the materials structure, X-ray diffraction (XRD) analysis was performed using a Bruker D8 Advanced diffractometer with Bragg-Brentano θ - θ geometry equipped with a LynxEye XE-T high resolution energy dispersive 1-D detector (Cu $K\alpha_{1,2}$). Raman spectra were recorded at room temperature using a LabRAM BX40 (Horiba Jobin-Yvon) spectrometer equipped with a He-Ne excitation source (532 nm wavelength). For accurate analysis, several spectra were acquired (mapping) and the average spectrum was presented. High-resolution transmission electron microscopy (HRTEM) with a JEOL ARM-200F instrument operating at 200 kV was used to study the material structure. XPS was employed to determine the carbon surface chemical composition using a VG Scienta SES 2002 spectrometer equipped with a monochromatic X-ray source (Al $K\alpha$ $\frac{1}{4}$ 1486.6 eV) and a G Scienta XM780 monochromator.

Textural properties of the hard carbon materials were investigated by several gases. A Micromeritics ASAP 2420 instrument was used for N₂, O₂ and Ar gases as adsorbate (at 77K) and a Micromeritics ASAP 2020 instrument for H₂ (77K) and CO₂ (273 K) adsorbates. Prior to the analysis, the samples were outgassed for 12 h at 300 °C under vacuum, using the degassing port to remove moisture from the materials. Additionally, two hours of degassing were performed on the analysis port at the same temperature, to ensure removal of backfilling gas. For accurate isotherm measurement, the dead space (i.e., the effective void volume) was determined once the analysis finished [3]. The Brunauer-Emmett-Teller (BET) theory was used to determine the specific surface area (SSA) from the linear plot in the relative pressure range 0.01-0.3 P/P_0 for N₂, O₂, Ar and H₂ and 0.01-0.03 for CO₂. The Rouquerol criteria's were respected and therefore the adsorption data were considered up to the P/P_0 pressure where $V(1-P/P_0)$ exhibits a maximum [3]. Although less conventional, BET method was approached to determine the specific surface area in the case of H₂ adsorption as well, according to the literature [4, 5]. The pore size distribution (PSD) was obtained from N₂/CO₂/Ar/O₂/H₂ adsorption isotherms using the two-dimensional non-local density functional theory (2D-NLDFT) considering the heterogeneous surface pore model for carbon materials carried out by SAIEUS (Solution of Adsorption Integral Equation Using Splines) software (Micromeritics) [6].

The pore average diameter (L_0) was determined using the following formula:

$$L_0 = \frac{1}{n} \sum_{i=1}^n \frac{w \frac{dV}{dw}}{\frac{dV}{dw}}$$

where:

L_0 – average pore diameter [nm],

w – pore width [nm],

$\frac{dV}{dw}$ – differential pore volume per pore width [cm³ nm⁻¹].

1.3 Materials electrochemical tests

The electrode preparation and the electrochemical test conditions were described in detail in our previous work [1, 2]. Briefly, the electrode was prepared by mixing the hard carbon powder with polyvinylidene fluoride (PVdF) binder and carbon black (SUPER C45, from TIMCAL) conductive additive in a mass ratio of 94:3:3, using N-methyl-2-pyrrolidone (NMP) as solvent. The obtained slurry was coated on Al current collector. The electrochemical tests were performed in coin-type cells and half-cells were assembled in an argon-filled glove box using sodium metal as counter/reference electrode and a glass fiber separator. An electrolyte made of 1 M NaPF₆ dissolved in ethylene carbonate (EC)/ dimethyl carbonate (DMC) mixture with a 1:1 volume ratio was used. Galvanostatic charge-discharge tests were conducted at a constant current in a voltage window between 0.01 and 2 V (versus Na⁺/Na) at C/50 rate.

2. Results

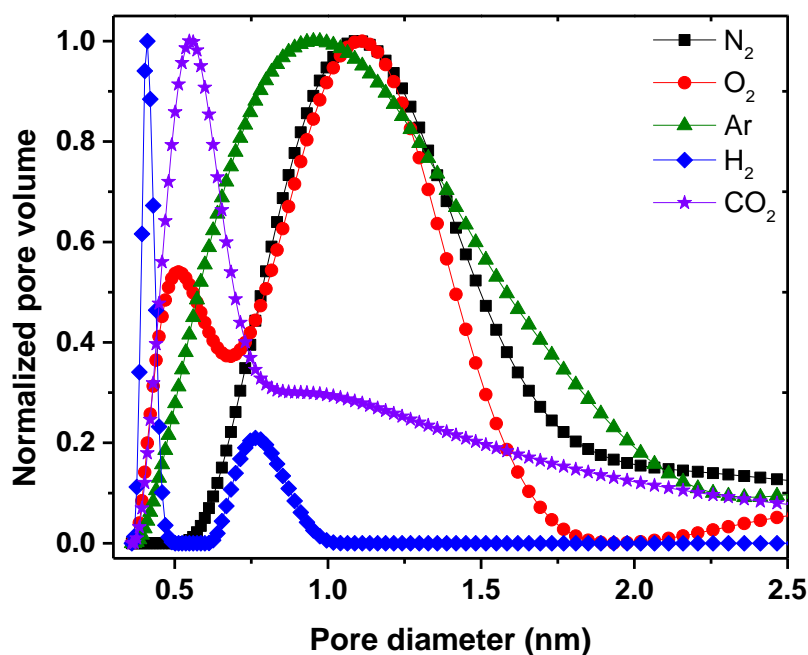


Figure S1: Normalized 2D-NLDFT pore size distribution of HAB-1300 obtained using different adsorbates.

Table S1: Physico-chemical and electrochemical properties of three hard carbons including specific surface area (SSA) determined by different gas adsorbents, the interlayer space (d_{002}) and the oxygen content obtained by XPS (O_{XPS}), the initial irreversible capacity (1st cycle) expressed in both percentage (%) and mAh g⁻¹ and the reversible capacity of the HC materials.

Properties	HPR-1300	HAB-1300	TCA-1400
N ₂ SSA (m ² g ⁻¹)	20	19	23
CO ₂ SSA (m ² g ⁻¹)	71	91	343
O ₂ SSA (m ² g ⁻¹)	90	181	431
d_{002} (Å)	4.0	4.1	3.8
O _{XPS} (at%)	6.6	2.9	4.2
Irreversibility (%)	21	23	32
Irrev. Capacity (mAh g ⁻¹)	60	68	110
Rev. Capacity (mAh g ⁻¹)	256	243	238

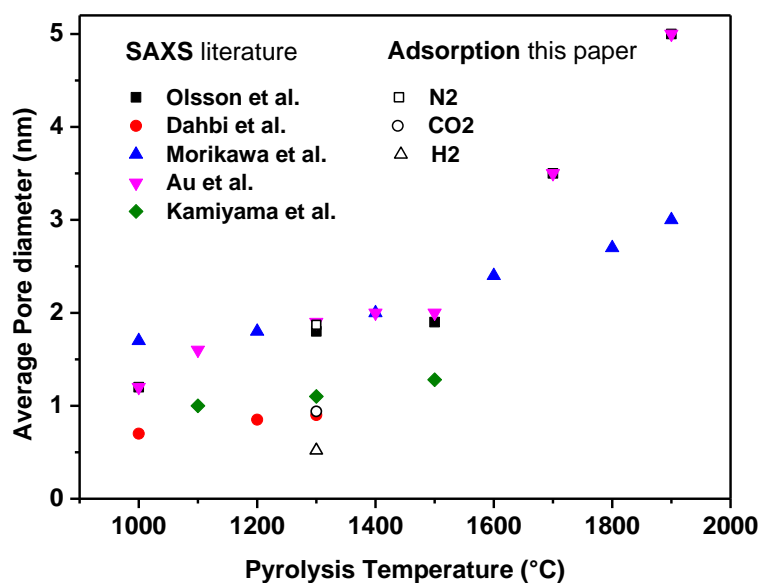


Figure S2: Average pore size determined from SAXS measurements (full symbols) on different hard carbons published in the literature vs. their pyrolysis temperature [7-11]. Comparison with average pore size (L_0) derived from gas adsorption in this work (empty symbols).

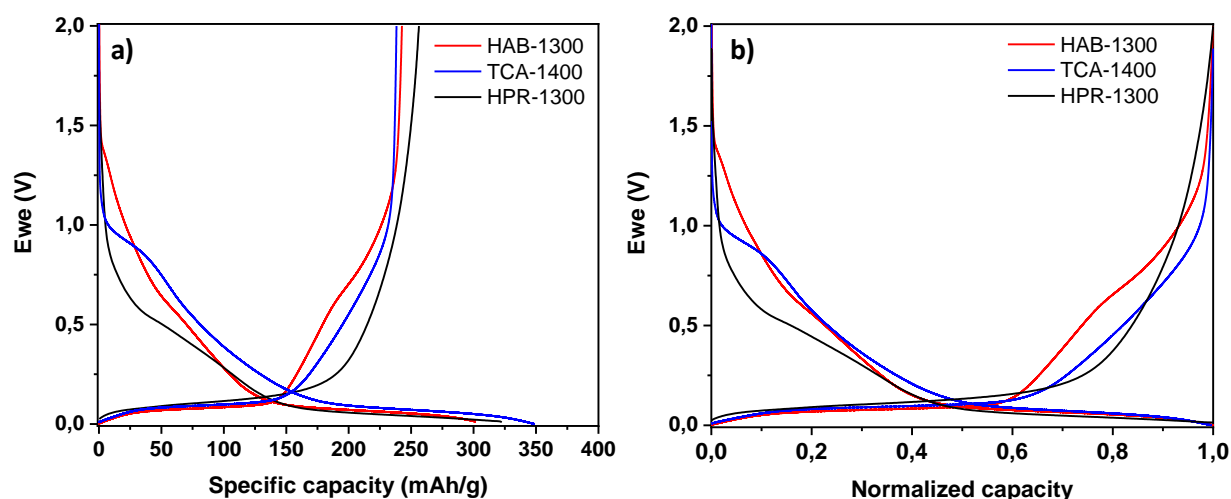


Figure S3. Electrochemical performance of three hard carbon materials, characterized by different textural properties, in sodium ion batteries: a) specific capacity and b) normalized capacity during the first sodiation-desodiation process.

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