Electronic Supplementary Information

Nitrogen-enriched Carbon Electrodes in Electrochemical Capacitors: Investigating Accessible Porosity Using CM-SANS

Anthony J. R. Rennie*, and Peter J. Hall

Department of Chemical & Biological Engineering, University of Sheffield, Sheffield, S1 3JD, UK

EXPERIMENTAL

Organic hydrogels were synthesised in a manner similar to those used in previous investigations where the polycondensation of an aqueous solution of resorcinol (R) with formaldehyde (F) was catalysed by the addition of sodium carbonate (C).[1,2] R/F molar ratio was kept at 0.5, R/C was 100 and R/W was 0.10 g cm⁻³. A typical synthesis procedure involved the dissolution of 0.10 moles of resorcinol (Aldrich, 1,3-dihydroxybenzene, 99%) in 110.0 cm³ of deionised water (W). 106.0 mg of sodium carbonate (Aldrich, Na_2CO_3, >99.5%) was added to the solution under stirring *i.e.* R/C molar ratio = 100. 0.20 moles of formaldehyde (Aldrich, CH_2O, 37 wt.%, stabilised with 10 - 15 wt.% methanol) were then added by volume under stirring. The R/F molar ratio was kept constant at 0.50 and R/W was maintained at 0.10 g cm⁻³. The solution was sealed in a bottle to prevent solvent evaporation and kept at 85ºC for 3 days. The resultant RF hydrogels were broken down into pieces roughly 10 mm in diameter and solvent exchange with acetone was carried out over a period of 3 days in an orbital shaker. The required mass fraction of *m*-phenylenediamine (Aldrich, 1,3-phenylenediamine, ≥99%) was solvated in roughly 100 cm³ acetone and added to the drained gel, which was then sonicated for 15 mins to encourage the thorough impregnation of *m*PDA solution into the pore network. Impregnated gels were then agitated for a further 3 days. Carbon precursors were then slowly dried to constant mass at 80°C under vacuum.

Carbonisation of the precursors was carried out in a tube furnace under flowing argon according to a schedule that was developed to retain the porous structure of RF gels[1] with a final carbonisation temperature of 850°C that was maintained for 120 mins. Activation under flowing CO_2 was carried out in a tube furnace at a temperature of 850°C for 60 mins. Activated carbon

materials were treated at 1000°C for 120 mins under different atmospheres to selectively remove surface nitrogen groups. The material treated under flowing hydrogen (BOC, N5.0) is denoted as C-H, and the materials treated under argon and a hydrogen/argon mix are denoted as C-Ar and C-HAr respectively. Materials underwent high-energy ball milling in a SpexSamplePrep 8000M Mixer/mill (using a silicon nitride vial and balls) for 60 mins prior to characterisation.

Nitrogen Adsorption/desorption isotherms at 77K were obtained using a Micromeritics ASAP 2420 instrument. Samples were degassed under vacuum at a temperature of 200°C for 10 h before analysis. Specific surface areas were estimated using the Brunauer-Emmett-Teller[3] (BET) method between relative pressures of 0.05 and 0.30. The total pore volume (V_{tot}) was determined at a relative pressure of 0.95-0.99. Average pore width was estimated using the relationship $4V_{tot}/SSA_{BET}$. Mesopore volumes and mesopore size distributions were evaluated using the Barrett-Joyner-Halenda[4] (BJH) method on the adsorption branch of the isotherms. Micropore volumes were determined using both the t-plot[5] method and Dubinin-Astakhov[6] method. The modal pore width was calculated from the obtained form of the Dubinin-Astakhov equation using the equation proposed by Medek.[7]

The carbon, hydrogen and nitrogen content of the carbon materials were determined using a Perkin Elmer 2400 Series II CHNS/O Elemental Analyser. Proximate analysis was performed using a Mettler Toledo TGA/DSC1 STARe instrument.

XPS was performed in an ion pumped VG Microtech CLAM 4 MCD analyser system using 200 W unmonochromated Mg X-ray excitation (1253.6 eV). The CLAM 4 has variable slits for small area analysis and the 5 mm slit was used in this case with no apertures selected.

Milled carbon samples were supported on stubs using conductive carbon tape and were introduced to the instrument through a turbo molecular pumped entry lock. The entry lock was evacuated for about 15 mins before the sample was introduced into the analysis chamber. Wide-scan spectra between binding energies of 0 eV and 1100 eV were obtained with a pass energy of 100 eV at a step size of 1 eV. Higher resolution spectra of elemental signals were obtained with a pass energy of 20 eV and a step size of 0.1 eV. Sample charging was not observed as the binding energy of the C1s peak was centred at 284.7 eV for all samples. Data was obtained using the SPECTRA version 8 OS and processed using CASA XPS software. Peak areas were measured after satellite subtraction and Shirley-type background subtraction,[8] and were converted to atomic concentrations using empirically derived sensitivity factors.[9] Detailed N1s spectra were deconvoluted into four constituent curves using a 30% Lorentzian-Gaussian line shape.
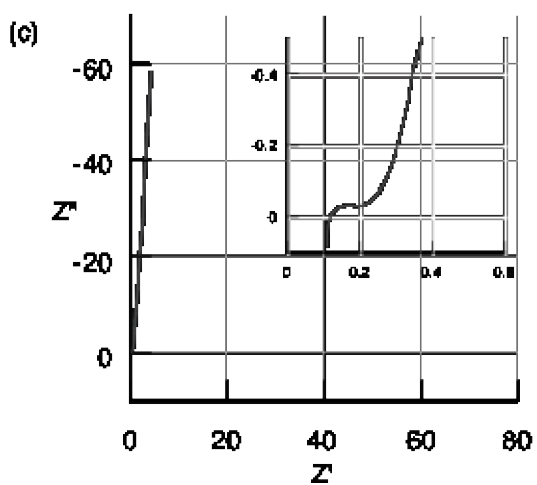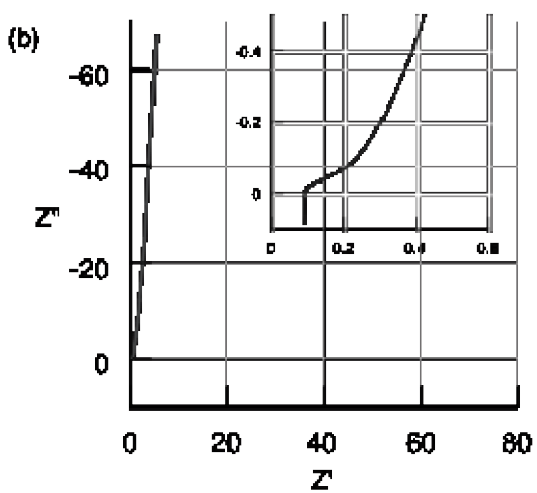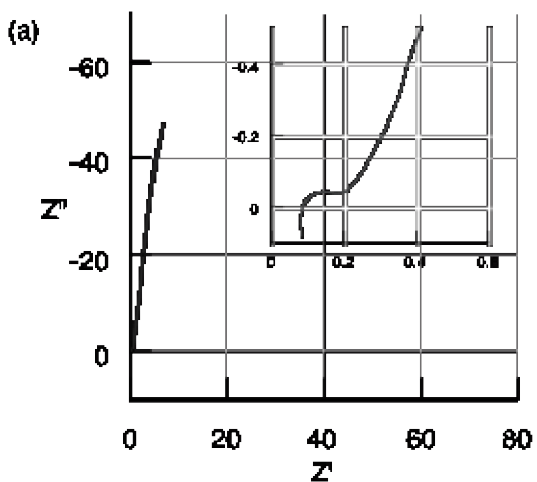
Small-angle neutron scattering (SANS) was performed using the LOQ small-angle diffractometer at the ISIS Pulsed Neutron Source (STFC Rutherford Appleton Laboratory, Didcot, U.K.).[10,11] LOQ is a fixed-geometry "white beam" time-of-flight instrument that utilises neutrons with wavelengths between 0.2 and 1 nm. Data was simultaneously recorded using an 8mm diameter beam on two, 2-dimensional position-sensitive neutron detectors, to provide a simultaneous Q range of 0.08 - 16 nm^{-1}. Each sample was placed in a 2 mm path length, rectangular quartz cuvette (Hellma Analytics). Pure deuterium oxide (D_2O, Aldrich, 99.9 atom % D) was used for contrast-matching experiments, and samples underwent brief sonication to encourage the penetration of contrast-matching fluid into all accessible pores. Transmission data was collected for 8 μAh, SANS for 60 μAh and CM-SANS for roughly 150 μAh in order to gather data of high statistical precision. SANS experiments were carried out for a shorter time

than the CM-SANS runs to prevent saturation of the detector. Transmission data showed that no multiple scattering effects occurred. Each raw scattering data set was then corrected for the detector efficiencies, sample transmission and background scattering, and was converted to scattering cross-section data ($d\Sigma/d\Omega$ *vs* Q) using the instrument-specific COLETTE software. Results were placed on an absolute scale using the scattering data from a standard sample in accordance with established procedures.[12]
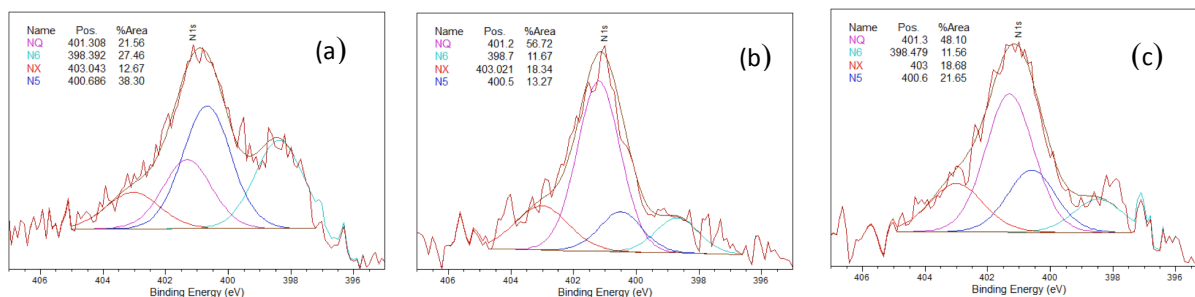
Electrodes were manufactured by mixing the material under study with polymer binder (KynarFlex® 2801) and milled carbon black (Cabot, Vulcan XC72), in an 80/10/10 ratio by mass. Acetone was added under stirring to create an homogenous slurry which was then spread to a wet film thickness of 500 µm on a glass plate using a micrometer adjustable gap paint applicator (RK Print Coat Instruments Ltd., UK). Electrode sheets were removed from the glass and discs were pressed from the sheet using a 13 mm diameter punch. The average electrode mass was roughly 10 mg, and paired electrodes differed in mass by 0.1 mg at most. Pairs of electrodes were soaked in potassium hydroxide solution (Aldrich, 28.5±0.5wt.%) and sonicated for 15 mins, then soaked in electrolyte for at least 3 days prior to cell manufacture to encourage electrolyte diffusion into the smallest pores. Symmetric two-electrode EC cells were constructed using a version of a test cell used in previous investigations.[2] 50 µm thick nickel foil discs (Goodfellow, >99.99%) were used as current collectors and a disc of glass fibre filter paper was used as the separator.

Electrochemical tests were carried out using a Solartron Analytical 1470E Multichannel Potentiostat/Galvanostat with 1455A Frequency Response Analyser and MultiStat v1.1b software, (Scribner Associates, Inc.). The cell temperature was maintained at 25°C (±0.1°C) in a

Friocell temperature control cabinet. Cells were cycled between 0.0 and 1.0 V (*vs* OCP) Galvanostatically at various rates between 0.1 and 10 Ag^{-1}. Electrochemical impedance spectra were obtained at a potential bias of 0.1 V (*vs* OCP) using a 10 mV perturbation over the frequency range 100 kHz to 10 mHz. Cyclic Voltammetry was performed between 0.0 and 1.0 V (*vs* OCP) at sweep rates of 10 mV s^{-1} and 100 mV s^{-1}. Specific capacitance values are based on the mass of active material and are expressed on a three-electrode basis.[13]

Figure S1. Nyquist plots of EIS data with magnified region (inset) for (a) C-Ar, (b) C-HAr, and

(c) C-H

Name	Pos.	%Area
NQ	401.308	21.56
N6	398.392	27.46
NX	403.043	12.67
N5	400.686	38.30

(a)

Name	Pos.	%Area
NQ	401.2	56.72
N6	398.7	11.67
NX	403.021	18.34
N5	400.5	13.27

(b)

Name	Pos.	%Area
NQ	401.3	48.10
N6	398.479	11.56
NX	403	18.68
N5	400.6	21.65

(c)

Figure S2. Detailed X-ray photoelectron spectra with deconvolution curves for (a) C-Ar, (b) C-HAr, and (c) C-H

SMALL ANGLE NEUTRON SCATTERING (SANS)

The *Porod Invariant* (Q in Equation 1) is a quantity determined over the analysed q-range that can be used as an indicator of the volumetric surface area of the sample[14], and can be used to compare surface areas when the samples are of similar composition.[15–18]

$$Q = \int_0^\infty q^2 \frac{d\Sigma}{d\Omega}(q)dq$$

1

Porod Invariants were calculated using the relationship seen in Equation 1 for each of the samples over the range $0.009 < q < 0.275$ Å^{-1} and values of 2.201, 2.089 and 1.552 (arbitrary units) were found for C-H, C-HAr and C-Ar respectively. The trend seen in the values of Porod Invariant confirms the trend seen in specific surface areas determined using the BET method *i.e.* the specific surface area and Porod Invariant of C-H > C-HAr > C-H. Further experimental runs

using a different instrument geometry would be required to ascertain accurate values of volumetric surface area for these samples.

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