Probing the electrolyte infiltration behaviour of activated carbon supercapacitor electrodes by *in situ* neutron scattering using aqueous NaCl as electrolyte

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Abstract: I*n situ* contrast-matched neutron scattering was used to probe the electrolyte infiltration behavior of activated supercapacitor carbon electrodes using an aquoeus 1M NaCl solution. It was found that only about 20% of the pore volume was infiltrated at chemical equilibrium. The partial infiltration can be attributed to the co-existence of hydrophilic and hydrophilic pores. The study suggests that for the achievement of optimal capacitance, supercapacitor electrodes should be evacuated before electrolyte infiltration.

1. Introduction and Motivation

Supercapacitors have emerged as important energy storage devices, but are also employed in separation technologies, namely Capacitive Deionization of water and Supercapacitive Swing Adsorption of gases.[1-4] In aqueous supercapacitors for energy storage mostly KOH or sulfuric acids, electrolytes are used, however neutral electrolytes gain increasing importance because they allow for voltages higher than 1.2 V due to overpotentials at the electrodes which kinetically hinder Faradaic processes.[5-7] In supercapacitor applications the capacitance is one of the most important performance criteria. The capacitance is directly related to the surface area of the electric double layer (EDL) in the capacitor. The EDL is comprised of the surface charges on the pore surfaces and ions of opposite charge that adsorb on the pore surfaces due to electrostatic interactions. To form the EDL, these ions must migrate to the pore surfaces which can be an aqueous or non-aqueous solution of inorganic or organic salts, or an ionic liquid. This process is only possible if the pores are actually infiltrated by the electrolyte. Supercapacitor electrodes are typically made of high surface area activated carbons with micropores (< 2nm) and mesopores (2 nm to 50 nm). In principle, all pores could be filled with electrolyte as long as the pores sizes are large enough for the ions and the solvent molecules to enter. [8] However, pore infiltration can only occur when the adhesive forces between the electrolyte and the pore surfaces are stronger than the cohesive forces within the electrolyte, allowing "wetting". Activated carbons have irregular pore surfaces with surface functionalities that greatly vary by polarity.[9] For example, terminal C-H functionalities are very little polar while alcohol, carboxylic acid and keto-groups are very polar. Thus, a polar electrolyte should only infiltrate sufficiently hydrophilic pores, and this effect will have a substantial effect on the capacitance. Currently it is not clear which fraction of the pore volume is filled by the electrolyte due to this effect. There were previous efforts of using small angle neutron scattering (SANS) to probe the in-pore ion population, although they did not address the problem on efficiency of the wetting process.[10] Herein, we show by *in situ* contrast-matched neutron scattering that only about 20% of the pore volume in the tested activated carbon electrodes are infiltrated by an aqueous electrolyte (1M NaCl). Neutrons can fully penetrate the samples used while providing a strong contrast from the hydrogen in the electrolyte. Due to the high penetration of neutrons, the contrast measurements using the overall diffraction intensity allow for direct *in situ* quantification of the pore infiltration without knowledge about the internal structure of the carbon electrodes.

2. Experiments

To probe for the electrolyte infiltration behavior, supercapacitor electrodes with the dimensions of 16 mm x 8 mm x 1.7 mm were prepared from BPL 4x6 activated carbon (Calgon Carbon Corporation). BPL carbon is a commercially available activated carbon with a surface area of *ca* 1000 m^2 g^{-1} having both micropores and mesopores, which is typical for supercapacitor electrode materials. [11, 12] BPL Carbon has an oxygen content of 2-5 w% with mostly, alcohol, keto, and carboxylic acid functionalities. In a typical preparation, 1.4 g BPL4x6 carbon was ground with 112 mg phenol resin (Plenco, product number 14433) in about 5 mL ethanol. The mixture was ground until almost dry, after which the black mixture was compressed into a round pellet (Diameter = 50 mm) using a Buehler specimen mount press under a hydraulic pressure of 8000 psi. The pellet was 1.7 mm thick, and electrodes were obtained by cutting the pellet to a size of 8 mm x 16 mm having a mass of 0.134 g. The electrode was subsequently heated in a tube furnace under nitrogen atmosphere at 900ºC to carbonize the binder. The density of the electrodes was measured to be ρ_C = 0.615 g cm^{-3}.

To produce the fully pre-infiltrated control samples, some electrodes with same dimensions were placed in a 50-mL side-armed flask, and high vacuum (~10 mTorr) was applied to the flask overnight to remove air from the pores. Then, 10 mL of a 1 M NaCl (BDH2986, 99%) solution in D_2O (Cambridge, 100 atom% D) was introduced to the flask through a septum using a syringe. The electrodes were let sit in the solution for two days to ensure all the pores were fully infiltrated with electrolyte and then stored in sealed aluminium pouches until the characterization by neutron scattering.

The neutron contrast measurements of the electrodes were performed on the VULCAN beamline at the Spallation Neutron Source at Oak Ridge National Laboratory. VULCAN is an engineering neutron diffractometer designed from the ground up for understanding functional materials under complex environments.[13] The electrode samples were loaded into quartz cells with inner dimensions of 20 mm x 8 mm x 2 mm and wall-thicknesses of 1 mm, and mounted on a positioning stage. The samples were aligned 45° to the incident neutron beam and the two detector banks are at 90° from the beam axis. The neutron beam was collimated down to a 5 x 12 mm^2 incident slit to allow an effective sampling volume of about 168 mm^3. The translation stage allowed measurements of different regions on the electrodes for comparison. A 30 Hz neutron beam centred at 2.0 Å with a bandwidth of 24.88 Å in a high intensity mode was used for the measurement. The total elastic and inelastic scattering intensity, *S(t)*, from the samples (normalized by beam flux) was measured to quantify the amount of materials in the beam and its change over time.

The *in situ* measurements were performed by filling the quartz cells containing dry electrodes with 1M NaCl solution in D_2O. Deuterated water is necessary to provide the optimal neutron scattering cross section for the current sample thickness.

3. Results and Discussion

Immediately after loading the electrolyte, the scattering intensity from the samples was measured continuously up to 7.5 hours. The arrival time and position of each neutron captured by the detectors are stored in the event-mode data. The continuous data was sliced and binned into constant time intervals and then reduced to d-space by time focusing for time-dependent results, as shown in **Fig. 1**. By doing so, the amount of electrolyte that infiltrated into the electrodes can be determined by measuring the increase of scattering intensity from the sampling volume illuminated by the neutron beam. The liquid solution lacks long-range order and as a result, the scattering from the solution is incoherent, appears as diffusive, and does not contribute additional Bragg peaks. As control samples, the fully pre-infiltrated electrodes were also measured with same instrument configuration.

The time-dependent neutron diffraction patterns (shown in Fig. 1) show that the increase in scattering intensity is dominantly incoherent, as expected from a liquid solution. The differential intensity does not have any structure in reciprocal space. There are two major peaks for the electrodes near 1.2 and 2.1 angstrom d-spacing. The one near 1.2 angstrom is likely from the hydrogen termination of the carbon surface.

The first observation from the time-dependent data of solution infiltration into dry electrodes is that the total scattering intensity, *S(t)*, increased rapidly during the first 90 minutes, then slowed down and plateaued after 120 minutes, as shown in **Fig. 2**. This behavior can be interpreted as a gradual infiltration of the electrodes until the chemical equilibrium is reached after 90 minutes. After that, the amount of scattering from electrolyte remains constant up to 4 hours. The result is reproduced in multiple samples with reasonable consistency. The estimated error bars for these experiments are small (less than 0.1%) compared to the observed effects.

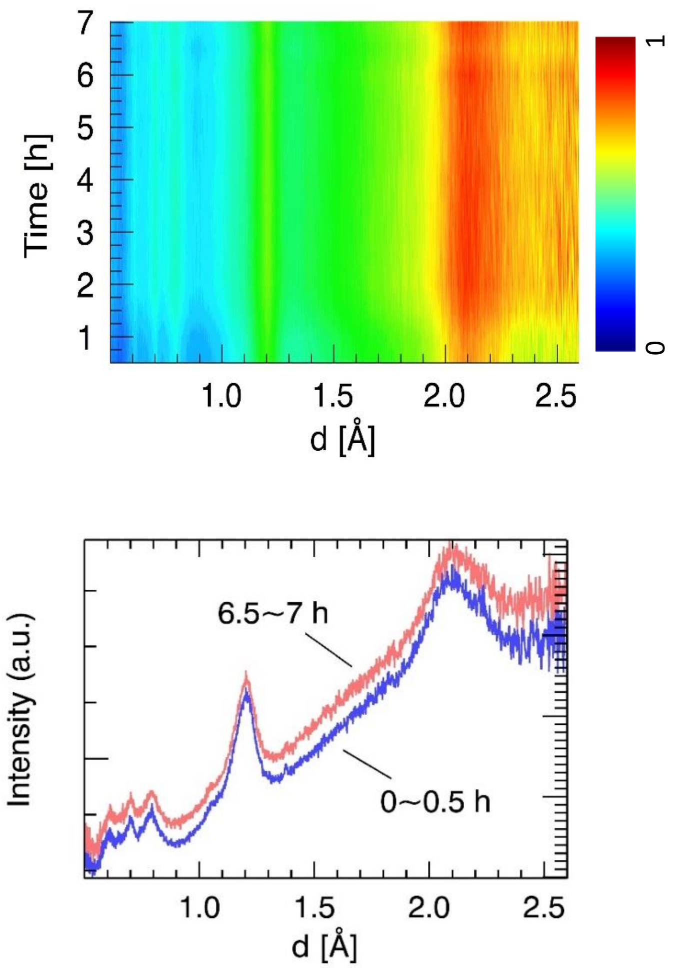

Figure 1. Diffraction patterns from the in-situ infiltration measurements. (Top): Intensity color map (Bottom): The integrated spectra at early and late stages of infiltration.

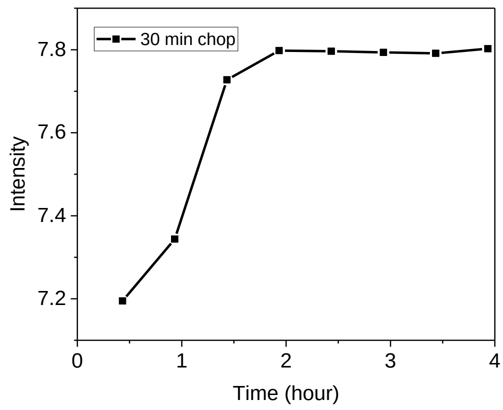

Figure 2. Time-dependent neutron-scattering total intensity of BPL carbon electrode.

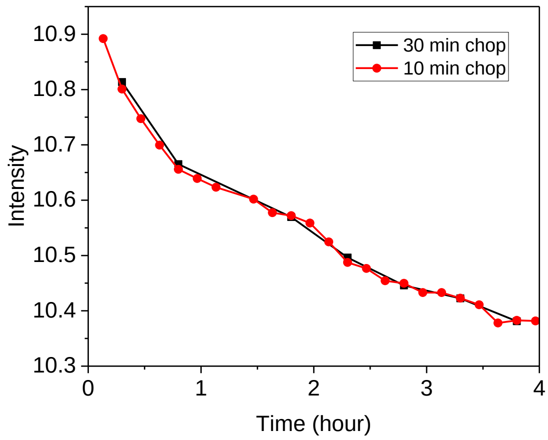

Figure 3. Time-resolved neutron-scattering intensity of vacuum-infiltrated BPL carbon reference electrode.

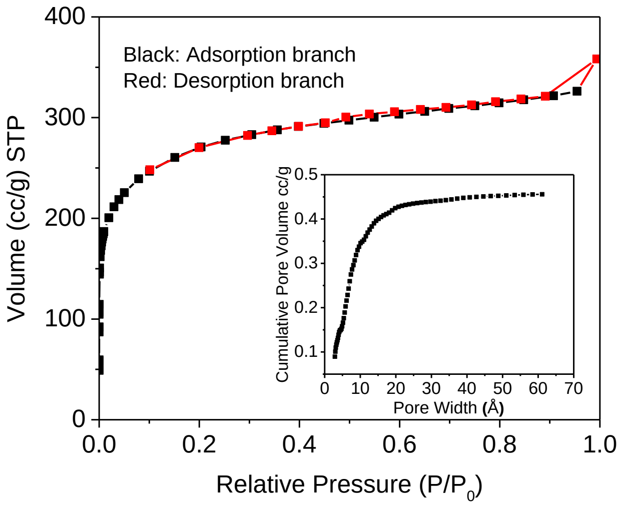

Figure 4. N_2 sorption isotherm of an electrode prepared from BPL Carbon 4x6. Inset is the cumulative pore volume calculated using NLDFT method based on carbon slit pores.

To quantify the fraction of the infiltrated pores, pre-infiltrated control electrodes were measured under the same conditions. In this case, the electrodes were evacuated before the same electrolyte was added to ensure that the pores were freed from air so that they would be completely infiltrated regardless of their chemical surface properties. As expected, it was found that the scattering intensity, S_{full}, was nearly time-independent for the vacuum-infiltrated samples because the electrodes were already fully infiltrated (**Fig. 3**). For calculation, an average total scattering intensity, S_{full}, is used.

In order to obtain the total pore volume, separate measurements were carried out with dry and fully filled electrodes in quartz cells. The background from the quartz cell are subtracted from total scattering. The result shows that the ratio of total scattering intensities between D_2O and carbon in the fully filled samples is $S_{full,D2O}$: $S_{full,C}$ =0.497:0.503. If we assume the total scattering intensity is mostly incoherent, then

$$S_{full,D2O}\colon S_{full,C} \; = \; \frac{\rho_c \sigma_c}{M_C}\colon\frac{k\rho_{D2O}\sigma_{D2O}}{M_{D2O}}$$

where σ is the total neutron scattering cross section and M is the molar mass. From the equation, the volumetric percentage of the pores, *k*, is calculated to be 26.6%, which is the volume percentage accessible by the electrolyte. This result is consistent with the porosity predicted by the density of the material. As shown in **Fig. 4**, the NLDFT pore volume calculated from the N_2 sorption isotherm is 0.456 cc g^{-1}. The density of the dry electrode is 0.615 g cc^{-1}. Therefore, the volumetric percentage of the pores calculated from gas adsorption is 28.0%. The results show that practically all pore volume accessible for N_2 is also accessible to H_2O.

Assuming the pre-infiltrated sample is fully filled, the percentage infiltration defined as fraction of the infiltrated pore volume over the pore volume (available for electrolyte), *p(t)*, may be calculated from the scattering intensities measured in the experiments (**Fig. 5**):

$$\mathrm{p(t)} = \frac{\mathrm{S(t)} - \mathrm{S_0}}{\mathrm{S}_{full} - \mathrm{S_0}}$$

where S_0 is the total scattering intensity at t = 0 and may be estimated from the linear extrapolation of the data from first 90 minutes using least square regression.

The electrolyte remains homogenous through the process for neutron scattering because deuterium accounts for majority of the total scattering section. The results show that the infiltration percentage quickly reaches 21% within the first 90 min. After that the infiltration percentage remains almost constant. The results suggest that in chemical equilibrium only about 1/5 of the available pore volume of the electrode is infiltrated by the electrolyte. Taking into account the available pore volume, the results also show that in equilibrium the electrolyte takes up about 5.6% of the total volume of the carbon electrode.

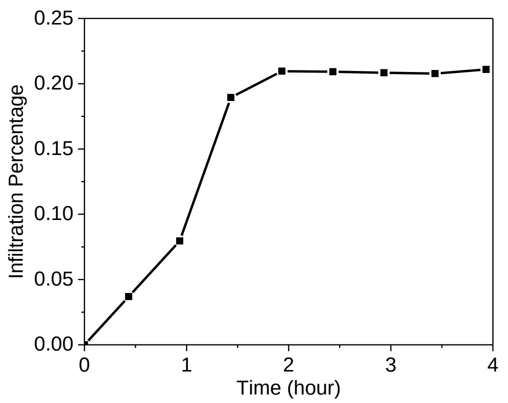

Figure 5. Time-resolved infiltration percentage of BPL carbon electrode.

4. Conclusions

In conclusion, we have shown that the as-prepared activated carbon supercapacitor electrodes are only about 20% infiltrated by a 1 M NaCl solution in chemical equilibrium, and that a large fraction of the available pore volume remains unoccupied. The electrolyte can only infiltrate pores that are hydrophilic enough so that adhesive forces are larger than cohesive forces. Other electrolyte systems but aqueous 1M NaCl will probably lead to different degrees of electrolyte infiltration as those measured in this study due to the uniqueness of the interactions between a specific electrolyte with a specific carbon. To ensure optimal performance of supercapacitors, the electrolyte should be added to outgassed, evacuated electrodes.

Conflicts of interest

There are no conflicts to declare.

Acknowledgement

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