Experimental report

03/09/2022

Proposal:	**1-04-228**	**Council:**	4/2021
Title:	The specific role of water for ionelectrosorption at charged interfaces		
Research area:	Materials		

This proposal is a new proposal

Main proposer:	**Malina JOP**
Experimental team:	Max Valentin RAUSCHER Malina JOP Sebastian STOCK
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Samples: Aqueous electrolyte with RbBr salt
Nanoporous carbon electrode

Instrument	Requested days	Allocated days	From	To
D22	3	3	28/09/2021	01/10/2021

Abstract:

In this proposal, we plan to fundamentally improve the current understanding of the active role of water in the electric double layer (EDL) formation at charged carbon/aqueous electrolyte interfaces in electric double layer capacitors (EDLCs). This will be done by employing small-angle neutron scattering (SANS) at D22 in an in-situ EDLC cell set-up and contrast variation using H2O and D2O solvents in combination with RbBr salt. A very similar coherent scattering length of Rb and Br will allow to assume a three-phase system consisting of carbon, ions and solvent, to separate the Q-dependent contribution of the solvent upon charging and discharging. A third solvent with zero-scattering-length density (Z-SLD) water will further allow separating volume changes of the pore space due to adsorption induced deformation from changes of local solvent density. The obtained results from this proposed experiment are considered essential to improve the energy storage performance of EDLCs.

Experimental Report for Proposal 01-04-228:
“The specific role of water for ion electrosorption at charged interfaces”

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The aim of proposal 01-04-228 was to show the feasibility and applicability of small angle neutron scattering (SANS) for monitoring changes within the working electrode of electric double layer capacitors (EDLC) with aqueous electrolytes upon charging and discharging. Specifically, we wanted to get in-situ experimental access to 1) global ion concentration changes, 2) local ion rearrangement and 3) solvent and wetting effects at different electrical potentials.

1 M RbBr salt solvated in H_2O, D_2O and a zero-scattering-length density (Z-SLD) H_2O/D_2O mixture were used as electrolytes. Other than originally proposed, the 0.1 M RbBr electrolyte was replaced by 1 M CsCl due to too small anticipated changes in the scattering for a low concentrated 0.1 M electrolyte. Two commercially available bio-based activated carbon powders, YP80 and MSP20, together with 20 wt. % PTFE binder were used to produce sheet electrodes of 320 µm thickness. A custom-made sample cell for neutron scattering consisted of an electrode ring as a counter electrode (not in the beam) and circular working electrode (in the beam). A glass fiber separator was used as an electrolyte reservoir and to prevent short circuits due to direct contact between the electrodes and the titanium sample cell walls, that also acted as current collectors and as neutron windows. The set-up is schematically depicted in Figure 1a. Figure 1b shows the corresponding custom built in-situ SANS cell made from titanium (dark color) and PEEK (light color). Springs (red color) were used to ensure constant pressure on the electrode-separator-electrolyte set-up.

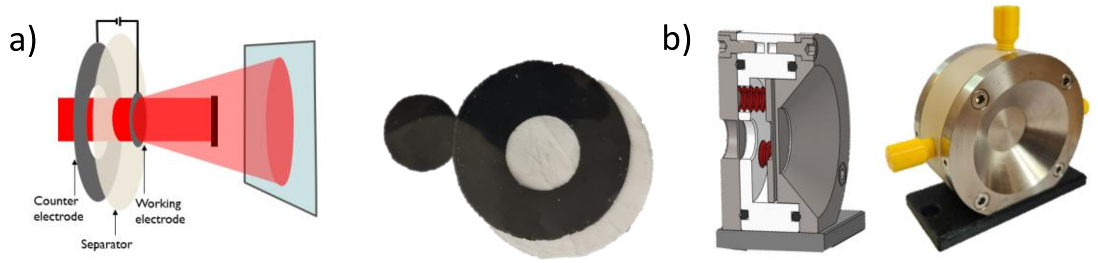

Figure 1: a) Schematic (left) and photographed (right) electrode set up, b) Drawing (left) and photograph (right) of the cell.

To make full use of the beam time, two in-situ EDLC cells were used simultaneously, with one being measured, while the other one was loaded and conditioned using standard cyclic voltammetry before the actual measurement cycle. A full SANS measurement cycle consisted of the following potential sequence: 0, 0.3, 0.6, 0.3, 0, -0.3, -0.6, -0.3, 0 V. The voltage was set using a Gamry Ref 600 and Interface 1010 B potentiostat. The holding time was 35 minutes for each voltage step, of which 5 minutes were used for equilibration and 30 minutes to actual neutron exposure time. In order to measure all planned electrolyte/carbon pairings during the limited beamtime, a reduced measurement cycle consisting of the potential sequence: 0, 0.6, 0, -0.6, 0 V and a time of 20 minutes (5 minutes equilibration, 15 minutes exposure time) had to be introduced for some of the samples. Table 1 shows the measured cycles for all electrolyte/carbon pairings.

Table 1: Applied measurement cycle for each electrolyte/carbon pairing.

	YP80	**MSP20**
1 M RbBr H2O	full cycle	full cycle
1 M RbBr D2O	full cycle	full cycle (measured twice)
1 M CsCl H2O	full cycle	reduced cycle
1 M CsCl D2O	full cycle	reduced cycle
1 M RbBr Z-SLD	full cycle	reduced cycle

After standard SANS data reduction and first evaluation, it unfortunately became evident that the measurements with the YP80 carbon electrodes or measurements with reduced cycle show extremely small voltage dependent changes in the SANS signal and could therefore not be evaluated quantitatively due to insufficient counting statistics. For the second carbon electrode type (MSP20) voltage dependent changes in the SANS data were detected (see below). As both materials had already been investigated with X-rays in earlier experiments [1], such differences were not to be expected. At present, we do not know the reason for this discrepancy.

The recorded full cycle scattering signal for 1 M RbBr in H_2O and D_2O and an MSP20 electrode is depicted in Figure 2 a) and shows – even if small –voltage dependent changes in the scattering curve and therefore enables to study details about global ion concentration changes, local ion rearrangement as well as wetting and solvent effects. These changes will be presented and preliminary discussed in the following:

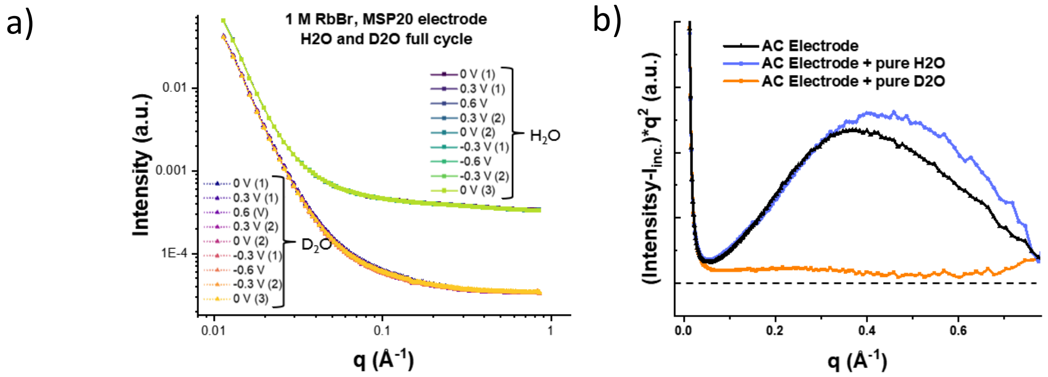

Figure 2: a) Full cycle scattering signals for 1 M RbBr and MSP20 electrode with H_2O and in D_2O solvents, b) Kratky Plot of the unfilled electrode and with H_2O/D_2O solvent showing contrast matching (D_2O) and enhanced contrast (H_2O).

D_2O as a solvent: The coherent scattering length densities of the D_2O solvent ($SLD_{coh..,D2O}$ = 6,40*10^{-6} A^{-2}) and the carbon electrode ($SLD_{coh., carbon}$ = 6,83*10^{-6} A^{-2}) are almost identical, as also seen in the Kratky plot in Figure 2 b), where the peak related to nanopores disappears upon D_2O filling due to contrast matching. Therefore, ions of similar coherent scattering lengths in the electrolyte ($b_{coh., Rb}$=7.09 fm, $b_{coh., Rb}$= 6.80 fm) create a quasi-two-phase system, where the overall coherent scattering is now governed by the global ion concentration in a uniform activated carbon and D_2O matrix. The results of the integrated intensity over the whole measured q-range of $0.01 < q < 0.84$ A^{-1} after subtraction of incoherent contributions is a measure of the coherent scattering and hence a measure for the global ion concentration, as depicted in Figure 3 on the left. Together with electrochemical data, the integrated intensity also allows to draw conclusions about ion exchange mechanisms in electric double layer formation. These results agree well with earlier findings from our group, where the two ion species Rb^+ and Br^- were tracked individually using anomalous small angle scattering (ASAXS) [2]. In that ASAXS study as well as with the present SANS approach, the mechanisms for electric double layer formation were found to be co-ion expulsion (expulsion of Rb^+) at positive potential and ion exchange at negative potential, even though the used carbon was different. 1 M RbBr with MSP20 as an electrode was measured twice in a full cycle (not consecutively after each other but in two independent measurement runs). Both measurement runs show very similar results, and therefore, underline the reproducibility of the measurement.

H_2O as a solvent: With H_2O as a solvent, the coherent scattering signal cannot be approximated by a simple quasi-two-phase system due to the large difference in coherent SLDs of H_2O ($SLD_{inc.,H2O}$ = -0.56*10^{-6} A^{-2}) and the carbon electrode ($SLD_{inc.,carbon}$ 6,83*10^{-6} A), as illustrated in Figure 2 b), where enhanced contrast between the nanoporous carbon and the H_2O filled pores can be seen in the Kratky plot. A power law (Eq. 1) was fitted to the scattering curve at large q in the range $0.55 < q < 0.75$ A^{-1}.

$$I = A*q^{-2.36} + C \qquad (1)$$

The exponent of -2.36 was obtained by fitting the this power law to the carbon electrode without electrolyte. Therefore, the pre-factor A is proportional to the coherent scattering intensity in the Porod limit, whereas C is proportional to the incoherent scattering contribution. As for H_2O the incoherent SLD (16.91*10^{-6} A^{-2}) is dominant compared to the carbon electrode (-0.01*10^{-6} A^{-2}) and the ions, the fitted values of the constant C of Eq. (1) are a measure of the incoherent scattering and therefore a direct measure of the H_2O concentration or density at different potentials. The fitted values for C and the corresponding qualitative changes in the water concentration are shown in Figure 3 right.

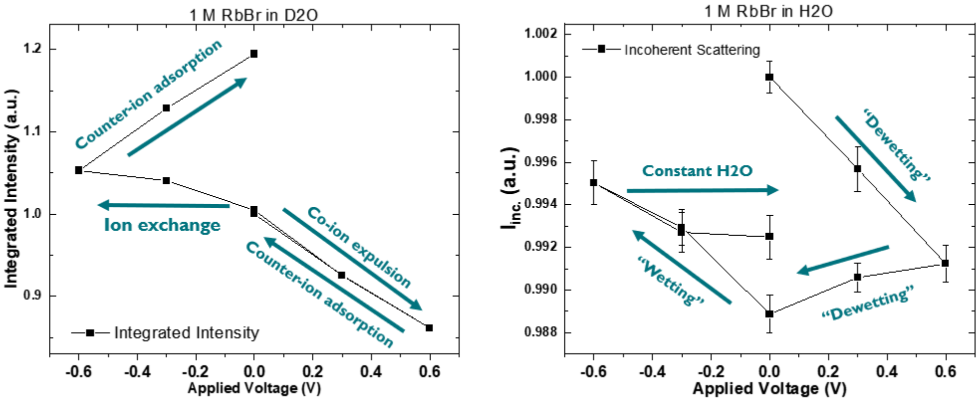

Figure 3: D_2O solvent integrated intensity showing global ion concentration changes (left) and H_2O solvent dominant incoherent scattering intensity (right) for different applied potentials.

Relative intensity changes as a function of applied potential and scattering vector length are illustrated in Figure 4, after subtraction of incoherent contributions. It is clearly seen that the intensity changes are q-dependent, thus the effects being dependent on the confinement (or pore size). This indicates underlying information on local ion rearrangement in different pore size regimes, but also renders data interpretation challenging. It will therefore require further detailed simulation and modelling.

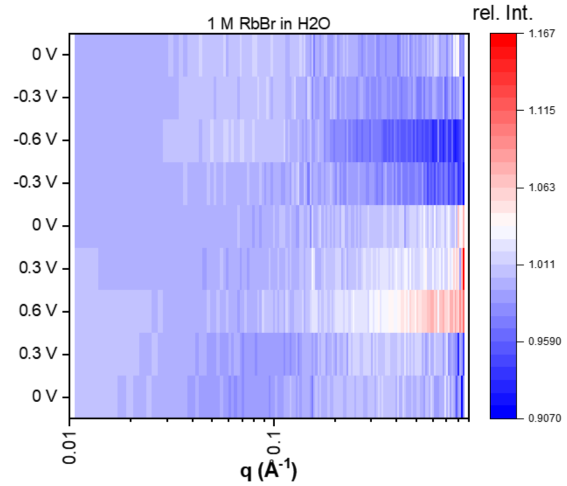

Figure 4: Relative Intensities for 1 M RbBr in H_2O after subtraction of incoherent contributions.

In summary, the main goal of this proposal has been reached. As one of the first in-situ SANS measurements on the working electrode in EDLC with aqueous electrolytes, we have successfully demonstrated the feasibility of such experiments. With D_2O as a solvent, global ion concentration changes and EDL formation mechanisms could be explained, while with H_2O as a solvent, additional wetting/density changes were found. More detailed data modelling and simulation will help to further elucidate local ion and solvent rearrangement. The findings from this beamtime have been presented as an oral contribution at the International Conference of Neutron Scattering (21.-25.08.2022 in Buenos Aires, Argentina) and gained quite some interest in the neutron community.

In order to further explain the effects and mechanisms upon EDL formation as a function of confinement, we propose the continuation and completion of the proposed experiment with all originally planned electrolytes with the now determined required exposure time and suitable carbon electrode material. In addition, it will be crucial to measure more than one consecutive cycle, to understand long term changes in ion and solvent behavior and to exclude artifacts. We believe that in-situ SANS has considerable potential to contribute to a better understanding of EDLCs and further improve their energy storage performance.

[1] C. Prehal, C. Koczwara, N. Jäckel, A. Schreiber, M. Burian, H. Amenitsch, M.A. Hartmann, V. Presser, O. Paris, , Nat. Energy. 2 (2017). https://doi.org/10.1038/nenergy.2016.215.

[2] C. Koczwara, C. Prehal, S. Haas, P. Boesecke, N. Huesing, O. Paris, ACS Appl. Mater. Interfaces. (2019). https://doi.org/10.1021/acsami.9b14242.