

Experimental report

10/10/2023

Proposal: 6-07-104

Council: 10/2022

Title: The specific role of water for ion electrosorption at charged interfaces

Research area: Physics

This proposal is a continuation of 1-04-228

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Experimental team: Sebastian STOCK
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Local contacts: Lionel PORCAR

Samples: Nanoporous carbon electrode
1 M RbBr, 1 M CsCl, 1 M SrBr₂ solvated in H₂O and D₂O

Instrument	Requested days	Allocated days	From	To
D22	4	3	31/03/2023	03/04/2023

Abstract:

The aim of the present proposal is the continuation of proposal 1-04-228 in order fundamentally improve the understanding of the active role of water in the EDL formation at charged carbon/aqueous electrolyte interfaces by gaining experimental in-situ access to 1) global ion concentration changes, 2) local ion rearrangement and 3) solvent and wetting effects. 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, CsCl and SrBr₂ salts. The obtained results from this proposed continuation are considered essential to improve the energy storage performance of EDLCs.

Experimental Report

“The specific role of water for ionelectrosorption at charged interfaces” (Experiment 6-07-104) performed at D22 from 31/03/2023 to 03/04/2023

Experimental Team: Sebastian Stock and Malina Seyffertitz

Local Contact: Lionel Porcar

Aim of the experiment

Proposal 6-07-104 was a continuation of proposal 01-04-228 and aimed at the in-situ investigation of the working electrode of electric double layer capacitors with aqueous electrolytes at various applied voltages using small angle neutron scattering (SANS) and H₂O and D₂O solvent contrast variation.

Experimental procedure

For a detailed descriptions of the experimental set-up and cell preparation procedure we refer to the associated experimental report linked to experiment 01-04-228. For this experiment, the same in-situ electrochemical cells were used, to investigate the processes at play in the working electrode of an electric double layer capacitor upon charging and discharging. Among the electrode materials probed in experiment 01-04-228, only the MSP-20X carbon electrodes exhibited noticeable, voltage-dependent, systematic changes in the scattering curves. Consequently, we chose to focus exclusively on MSP-20X carbon electrodes. Regarding the electrolyte, 1 M and 0.1 M RbBr and 1 M and 0.1 M SrBr₂ electrolyte with H₂O and D₂O solvent were used as proposed, which resulted in 8 electrochemical cells.

Each of these cells underwent a voltage sequence consisting of 0 V, 0.6 V, 0 V, -0.6 V, 0 V, 0.6 V, 0 V, -0.6 V, and 0 V, with each voltage step lasting an hour. The initial 30 minutes of each step were dedicated to achieving equilibrium, followed by the subsequent 30 minutes spent exposed to the neutron beam collecting data. This approach allowed us to efficiently utilize beamtime by concurrently employing two cells.

Results

By exploiting the high incoherent contribution of H₂O, we tracked global H₂O concentration changes at different applied potentials, as seen in Figure 1 (light blue, square symbols):

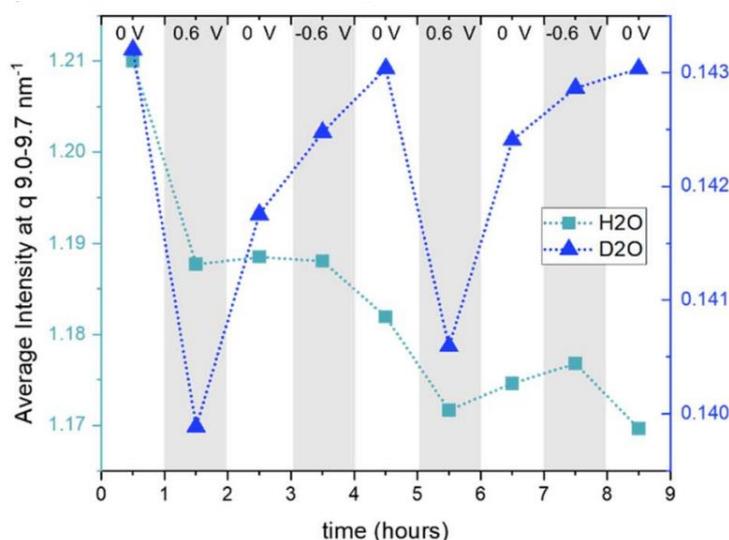


Figure 1: Average scattering intensity in the high q -regime for H₂O (light blue square symbols) and D₂O (dark blue triangular symbols), directly related to the incoherent scattering.

Coherent scattering data using H₂O (Figure 2 a) and c)) and D₂O (Figure 2 b) and d)) revealed local solvent behavior, including rearrangements and partial structure factors, while also highlighting the need to move beyond simple qualitative models. A more quantitative descriptions of water-water and ion-water interactions could be extracted from detailed atomistic modelling or the evaluation of partial structure factors through complementary in-situ diffraction experiments.

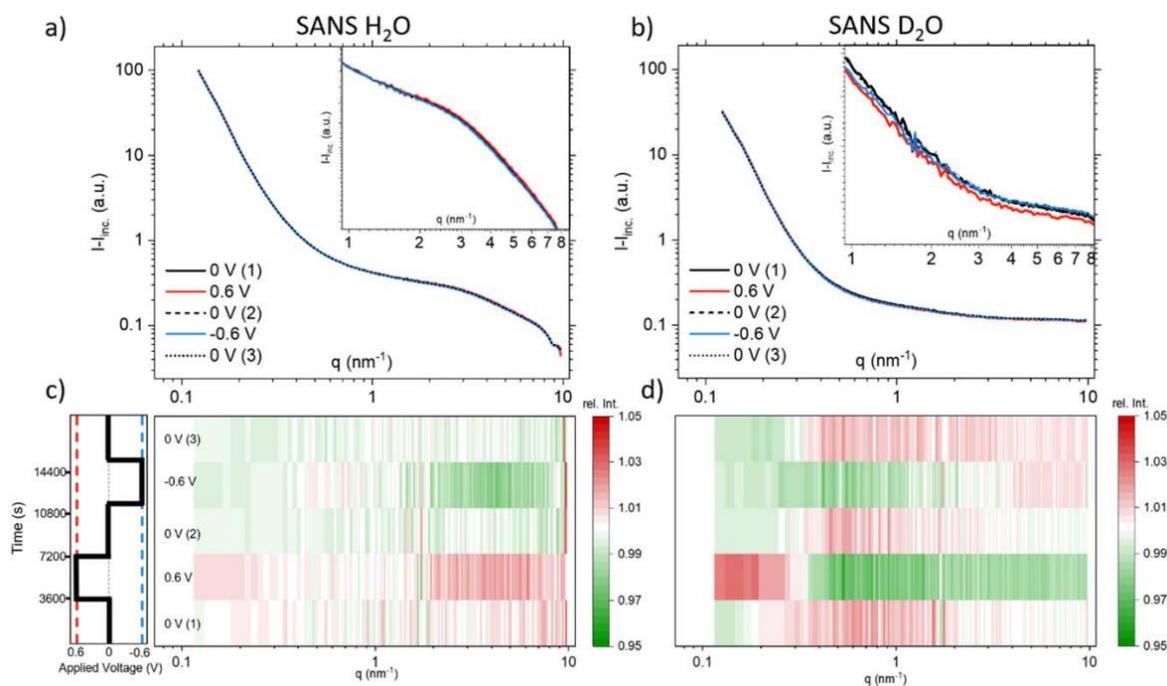


Figure 2: Coherent SANS scattering curves and corresponding heat-plots displaying relative intensity changes for H₂O (a) and (c), and D₂O (b) and (d).

Detailed analysis of the data their implications can be found in the associated publication [1].

Associated publication

- [1] M. Seyffertitz, S. Stock, M.V. Rauscher, C. Prehal, S. Haas, L. Porcar, O. Paris, Are SAXS and SANS suitable to extract information on the role of water for electric double-layer formation at the carbon - aqueous electrolyte interface?, Faraday Discuss. (2023). <https://doi.org/10.1039/D3FD00124E>.