Fundamentals and implication of PZC determination for activated carbons in aqueous electrolytes

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The point of zero charge (PZC) is crucial for investigating molecular level charging mechanisms in energy storage systems, as demonstrated in electrochemical capacitors. In this work, three electrochemical techniques were studied for PZC determination in electrochemical quartz crystal microbalance (EQCM) applications: cyclic voltammetry (CV), staircase potentio electrochemical impedance spectroscopy (SPEIS) and step potential electrochemical spectroscopy (SPECS) for two activated carbons (ACs) with 0.1 mol L⁻¹ aqueous solutions of LiNO₃, Li₂SO₄, and KI. The porous AC charging process in aqueous electrolytes is a complex phenomenon; the ion mixing zone covered a wide potential region. Inadequate PZC determination could lead to obscure data evaluation, which could further provide a misguided mechanism description at the molecular level. In the aqueous solutions studied, the adsorption of specific ions and active participation of all ionic species in the electrical double-layer formation were considered. The SPECS technique was determined to be the most beneficial for the PZC determination in electrochemical quartz crystal microbalance (EQCM) applications. The advantage of this technique includes a short implementation step time (in this case, 1 mV s⁻ ¹). Moreover, the potential shift is quite gentle and enables detailed data to be recorded in the entire potential range, increasing the recorded data resolution and accuracy. These potential steps lead to a smooth behavior of probable redox reactions and balanced ion redistribution in the pores. Additionally, this method provides insights into the charging mechanism via a detailed specific capacitance division into a porous and a geometric one.



Figure 1: Specific capacitance vs. potential calculated from the three electrochemical techniques: CV (gray shade), SPECS (blue triangular scatter) and SPEIS (red square and green circular scatter) for YP-50F and 0.1 mol L-1 LiNO₃ in EQCM cell. The upper part of the plot represents the zoomed SPECS specific capacitance vs. potential in the E_{min} to E_{max} direction.

Acknowledgements

This work was financially supported by European Research Council within the Starting Grant project (GA 759603) under European Unions' Horizon 2020 research and innovation programme, Polish National Science Centre within the SONATA scheme (Project No.2019/35/D/ST4/02582).