

NOVEL EQCM-D-BASED METHODOLOGY FOR IN-SITU GRAVIMETRIC, VISCOELASTIC AND HYDRODYNAMIC PROBING OF BATTERY AND SUPERCAPACITOR ELECTRODES

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During about 3 years out of 6 we were focused on the use of electrochemical quartz-crystal microbalance (EQCM) for in-situ dynamic tracking of ions adsorption into nanoporous carbons during their charging. [1-5] Here EQCM served as a gravimetric probe of the compositional changes in the nanoporous carbon (resonance width was almost constant). A number of gravimetric problems related to charging mechanisms in nanoporous carbons (hardly assessed by other techniques) were solved: partial ions desolvation during adsorption, perm-selective behavior of carbons at high charge density, and its failure near the potential of zero charge, full gravimetric modeling of ions adsorption with incorporation of Gouy-Chapman-Stern model, the origin of selective ions adsorption, and many others.

However, we realized very soon that in case of a typical Li-ion battery electrode such as LiFePO_4 olivine, the change in the resonance peak width was comparable with the change of the resonance frequency, implying strong periodic, intercalation-induced deformation of the composite electrode [6,7]. The arising electrode deformation modifies solid-liquid interactions in the boundary hydrodynamic layer between the porous/rough electrode and the solution. When solid porous electrode is completely rigid, these interactions are fully tracked by the potential-dependent shifts of the resonance frequency and resonance peak width described in terms of the hydrodynamic admittance model which quantifies the electrode deformations. [7,8] Using this method a strong dependence of the deformation of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene electrode on the ion's charge-to-size ratio has been found, contributing to the understanding of the "capacitive paradox" of this unique one-dimensional electroactive material. [8] We also extended this methodology to identification of the effect of mechanical properties of the polymeric binders on the intercalation-induced expansion/contraction of the intercalation particles, and thereby, the entire deformation of the composite electrode (non-invasive in-situ dynamic monitoring of elastic properties of composite battery electrodes by EQCM-D). [9] This unique non-destructive technique has a potential to serve for early diagnostics of cycling life durability of batteries and supercapacitors.

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