

In situ Electrochemical Quartz Crystal Admittance (EQCA) Methodology for *in-situ* studies of unique transport phenomena in porous carbon electrodes and insertion electrodes

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The state-of-the-art in supercapacitors and capacitive deionization technology utilizes high-surface area carbons which store energy in electric double layers (EDL) at the carbon surface/electrolyte solution interface. In order to reach high energy density, fundamental understanding of the nature of ion and solvent adsorption into their porous volume is required. We will review in the presentation a novel approach to *in-situ* gravimetric monitoring of the compositional changes in porous carbon electrodes during their charging using the electrochemical quartz crystal admittance (EQCA) method. In addition to gravimetric sensing, mechanical changes in the electrode coating under different charge/discharge/storage regimes, can be monitored with high precision and sensitivity. Adsorption of ions in charged meso- and microporous carbons studied by EQCA are interpreted by linking them to the classical EDL models and capacitive deionization theory. Focus is provided for application of EQCA in characterizing adsorption of different series of ions, including determination of the number of solvent molecules accompanying ions in their adsorbed state, and monitoring the molecular interactions between the adsorbed ions and bulk water.

EQCA may be a highly interesting tool for the study intercalation reactions as well. As an example, we will demonstrate some work related to Li iron phosphate electrodes in aqueous media.

It is well known that LiFePO_4 is one of most promising cathode materials for lithium-ion batteries (LIBs) due to its superior rate handling ability, moderate cost, low environmental hazards, and safe long-term cyclability. In addition to the electrochemical information on the charge and discharge process, electrochemical quartz crystal admittance (EQCA) of LIB electrodes provides direct access to potential-driven frequency shifts (Δf_{exp}) and changes of the resonance peak width ($\Delta\Gamma$) due to Li-ions insertion/extraction. It is not only possible to monitor mass changes of the electrode, but the two parameters Δf_{exp} and $\Delta\Gamma$ also reflect mechano-structural changes caused by hydrodynamic solid-liquid interactions caused by the operation of a LIB. Applying a suitable model that takes into account such interactions, potential-induced changes of the effective thickness and permeability of the composite electrode have been determined. The latter shows that ion insertion/extraction results in a non-uniform deformation of the electrode. Using EQCA as a unique mechanical probe for insertion-type electrodes, the dynamic effect of the local host environment on Na^+ -ions insertion/extraction can be studied in mixed solution of Li- and Na-salts. As a highly reliable and quantitative tool, EQCA may enable a broader understanding of coupled electrochemical and mechanical events in LIB during their long-term

operation. This includes information about the distortion/deformation of the electrode intercalation particles and the entire composite electrode under polarization. Also, EQCA can help to clarify the role of polymeric binder in the composite electrodes as the factor stabilizing long-term cyclability of Li-ions batteries.

Finally, we intend to demonstrate how EQCA measurements are capable in tracking intercalation-induced phase transitions in Li-ion batteries materials by a simultaneous analysis of the state-of-charge and mechanical changes occurring in microarray of one/a few layers of intercalation particles in composite Li_xFePO_4 electrodes probed by the electrochemical quartz-crystal admittance (EQCA) method. A classical phase transition theory is used to describe nucleation and growth kinetics in Li_xFePO_4 particles, based on conventional intercalation charge-time dependences under constant applied potentials. The theory is extended to describe mechanical characteristics of microarray composite electrodes during Li-ions insertion/extraction, measured in parallel to the electrochemical response. Nucleation kinetic constants were derived from time dependence of intercalation charge and 2 mechanical characteristics of the electrode layer. The difference between them was rationalized in terms of different size of the particles and their non-uniform deformation upon Li-ion insertion/extraction.

In conclusion, we present herein an excellent novel *in-situ* technique for studying the dynamic behavior of various types of electrodes for energy storage & conversion devices.