An Electrochemical Gravimetric Perspective of Insertion and Extraction of Sodium-ions in Prussian Blue

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Prussian blue is commonly used as a type of cathode material in sodium-ion batteries due to its open framework and simple synthesis process. Many studies have been made on the charging and discharging process of Prussian blue and its analogues by using *in-situ* or *ex-situ* testing methods, such as IR, Raman spectroscopy and XRD. However, few results focus on the high sensitive operando mass change monitoring during the electrochemistry process.

Herein, a powerful analytical instrument, electrochemistry quartz crystal microbalance with dissipation (EQCM-D), has been used to study the mass change and mechanical properties of the Prussian blue film [1]. By combining the quartz crystal microbalance with cyclic voltammetry measurement, both electrochemical (voltage and current) and acoustical (resonance frequency and resonance bandwidths) information can be obtained simultaneously. The final analysis of the data requires a full combination of the structural parameter and viscoelastic properties of the thin film and the physical properties of the electrolyte solution.

During cycling, the insertion and extraction of Na^+-ion are reversible from the direct results of the change of frequency and via the calculation of the parameter, mass per electron (mpe), the intercalated ions are just sodium ions. However, a small amount of the solvent of the electrolyte, ethylene carbonate, is also incorporated in the structure of electrode thin film during ion exchange process. This can also be observed by comparing the experimental data with the faradic theoretical data and the Kanazawa theoretical line. Further, *in-situ* hydrodynamic spectroscopy, an *operando* directly tracking method, introduced by M. Levi for the first time [2], is applied to investigate changes of the porous electrode structure on the mesoscopic scale. By simulating the experimental data using hydrodynamic admittance models, the effective layer thickness, which is related to the effective penetration depth of the electrolyte into the electrode, shows that the sodium uptake occurs mainly at the outer surface of the composite electrode despite its porous structure.

[1] Levi M., Shpigel, N., Sigalov, S. et al., *Electrochimica Acta* **232**, 271-284(2017), DOI: 10.1016/j.electacta.2017.02.149; [2] Shpigel, N., Levi, M., Sigalov, S. et al. *Nature Mater*. **15**, 570–575 (2016), DOI: 10.1038/nmat4577