3D nanoarchitecture of battery interfaces: from molecular arrangements to the nanostructures via multimodal NC-SPM

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Molecular structure of liquids neighboring solid surfaces defines key phenomena in biology, chemistry and material science. In rechargeable batteries, the molecular arrangement of the electrolyte near the solid electrode provides vital clues for surface chemical reactions, transport of ionic species and, ultimately, battery peak power, storage capacity and operational safety.

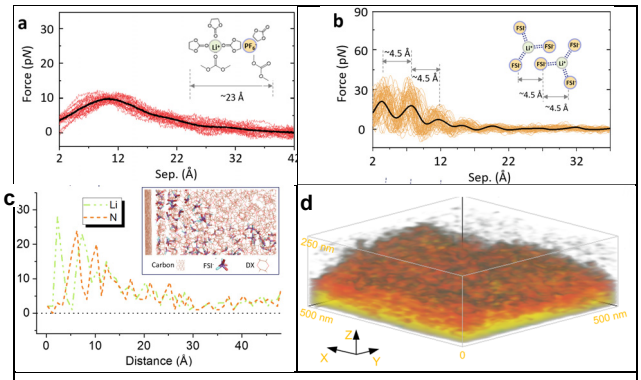

Figure 1 Surface force-distance spectrocopy (SFS) for a) "good" EC-MEC and b) "weak" DX electrolytes on the HOPG surface. c) MD modelling of the density distribution of anions for the "weak electrolyte. d) 3D-NRM of the formed SEI in the Li-ion battery.

The key challenge in such studies is to establish a role of these molecular-scale electric double layers (EDL) in the formation of thicker, but nevertheless nanoscale dimensions key battery interface namely, the "surface electrolyte interphase" (SEI), a crucial element defining performance and operation of rechargeable batteries.

To address this, we combined for a first time a traditional non-contact surface force-distance spectroscopy (SFS) [1] mapping the molecular arrangements of the electrolyte ions and solvent molecules near the electrode surface and the formation of the SEI nanolayer using complementary non-contact three dimensional nanorheology microscopy (3D-NRM) AFM technique [2] directly in the *operando* electrochemical environment. The SFS was realized in the AC mode over 5 nm distance using high frequency (0.6 MHz in air) 30 Nm^{-1} cantilever with standard Garcia-Perez force recovery algorithm providing molecular forces near solid surface with 0.1 nm resolution (Fig 1a,b). In 3D-NRM the sample is laterally dithered by sub-nm amplitude at a few kHz frequency while the shear forces acting on the AFM cantilever provided measure of local rheology of generally viscoelastic SEI layers at the nanoscale distances away from the solid surface. By taking the differential of Re/Im components of the shear force vs tip-surface z distance, and rastering the approach points in x-y direction, 3D NRM provided the 3D map of the layers away from the solid electrode surface (Fig 1d). By comparing two solvent-electrolyte systems, of "good" high dielectric constant polar carbonate solvent and non-polar dioxane, "weak" solvent, the *operando* SFS observed that in the weak solvent the cations are located much closer to the solid surface, that was supported by the MD modelling [2], whereas 3D NRM maps showed that this resulted in the inorganic solid SEI, improving the SEI stability and battery operation.

The novel combination of atomic scale two non-contact techniques of SFS and 3D-NRM can provide unique opportunity for real-space non-destructive investigation of chemical, catalytic and biological interfaces with the nanoscale resolution.

References

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