Operando nanomapping of the 3D mechanical nanostructure of SEI in real Na-ion battery electrodes: A 3D nano-rheology microscopy

[1] M. Nagarathinam, [1]Y. Chen, [2]S. Menkin, [2]D. S. Wright, & [1]O. V. Kolosov
*Presenter, m.nagarathinam@lancaster.ac.uk
[1] Physics Department, Lancaster University, UK
[2] Yusuf Hamied Department of Chemistry, University of Cambridge, UK

The Solid Electrolyte Interphase (SEI) is a nanoscale thickness passivation layer formed as a product of electrolyte decomposition by a combination of chemical and electrochemical reactions in the cell. The creation of robust SEI that can withstand the repetitive insertion and extraction of alkali metal ions, volume change and prevent further consumption of alkali metal ions and electrolyte is crucial for improving the battery performance and safety. While the local mechanical properties of SEI provide a clue to this, their *operando* characterization is difficult as one must probe nanoscale surface features in a dynamically changing electrochemical environment. Here, we report novel 3D nano-rheology microscopy (3D-NRM) that uses a tiny (sub-nm to few nm) lateral dithering of the sharp SPM tip at kHz frequencies to probe the minute sample reaction forces. By mapping the increments of the real and imaginary components of these forces, as the tip penetrates the soft interfacial layers, we obtain the true 3D nanostructure of sub–nm thick layers [1]. 3D-NRM makes it possible to elucidate the key role of solvents, additives and the rate of SEI formation during charge/discharge and to predict the conditions for SEI formation for robust, safe and efficient Li-ion and Na-ion batteries.

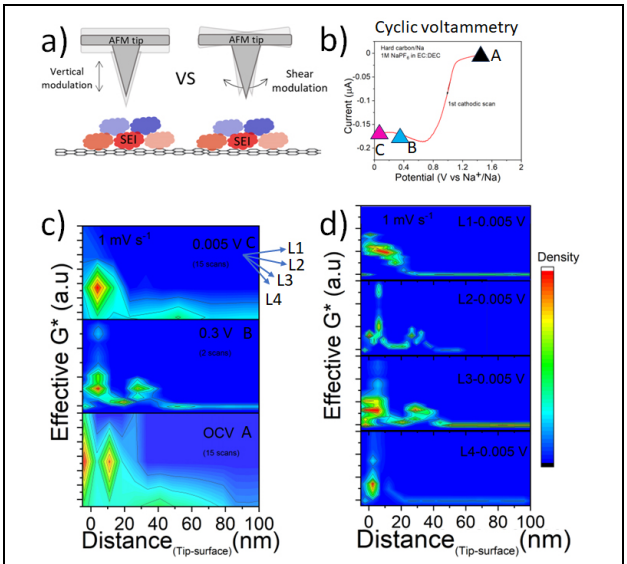

Fig.1 a) Principle of 3D-nanorheology, b) cyclic voltammetry (CV) of hard carbon / Na anode system, c) average mechanical moduli G* of SEI layer as a function of thickness *d*, at different stages of charge-discharge cycle d) Mechanical moduli G* of the SEI layer as a function of the thickness d at 0.005 V in different areas (L1-L4)

Here, we discuss the nanomechanical properties of the SEI on inhomogeneous, rough real composite (hard carbon, conductive carbon, binder) sodium ion battery electrodes. Essentially, the new approach enables the characterization of SEI at the nanoscale with a few nm precisions on electrodes with high surface roughness (~1000 nm), and the quantitative evaluation of the real and imaginary parts of the elastic moduli over the entire thickness of SEI layer. In addition, this helps to evaluate the growth of SEI and to identify the formation of different clusters of decomposition products with variation in shear modulus and thickness during sodiation as a function of the electrolyte, additives and charge-discharge rate. We believe that such evaluation of key interfacial nanomechanical properties of SEI will allow us to develop the electrochemically and mechanically robust SEI surface passivation layer and the development of efficient and safe rechargeable batteries.

References:

[1] Y. Chen, W. Wu, S. G.-Munoz, L. Forcieri, C. Wells, S. P. Jarvis, F. Wu, R. Young, A. Dey, M. Isaacs, M. Nagarathinam, R. G. Palgrave, N. Tapia-Ruiz, O. V. Kolosov, *Nature Comm.* 2023, **14**, 1321; S. J. O'Shea, M. E. Welland, J. B. Pethica, *Chem. Phys. Lett.* 1994, **223 (4)**, 336.