3D nanoscale morphology and local physical properties of Li/Na-ion-battery solid-electrolyte-interphase via scanning probe 3D *operando* nanorheology

Yue Chen [1,2], Samuel Jarvis [1], Sara, Rodrigues Costa. Nuria[2,3], Tapia Ruiz [2,3], Oleg V. Kolosov [1,2],

[1]*Department of Physics, Lancaster University, LA1 4YB, UK*, [2] *The Faraday Institution, Quad One, Harwell Science and Innovation Campus, OX11 0RA, UK*, [3]*Department of Chemistry, Lancaster University, Lancaster LA1 4YB, UK*

The physico-chemical properties of solid–electrolyte interphase (SEI) dominate the interfacial reactions and charge-carrier-transportation, both being crucial to the lithium/sodium battery performance. The detailed understanding of SEI chemistry and structure, especially for the new generation batteries such as sodium-ion-batteries (SIBs) [1-3] is still under debate, to great extent due to the lack of adequate in-situ nanoscale characterisation tools [4, 5]. The progress is further complicated by the diversity of surface reactions taking place in interlinked sequences varying for different battery formation protocols, the state of charge/discharge and the type of anode active materials and electrolytes [6].

To understand the nanoscale details of the formation mechanism behind different SEI structures, here we introduce a novel approach of scanning probe microscopy based "3D *operando* nanorheology" [7]. It allows direct nanoscale characterisation of SEI formation by revealing 3D structure (organic/inorganic moieties within the SEI layer), quantifying the nanomechanical properties of SEI organic and inorganic components, and providing a common denominator for evaluating the SEI properties (mechanical, thermal, electrical) formed on lithium/sodium battery anodes.

By using new methodology, we were able to directly observe that the SEI formation on the non-intercalation graphitic carbon basal plane follows the impurity adsorption nucleation and precipitation mechanism resulting in a 3D nano-mosaic and multilayer hybrid structure with randomly mixed organic and inorganic SEI layer. This was very different to the intercalation-active graphitic carbon edge planes where the ion intercalation assisted electrolyte salt decompositions resulted in a single inorganic layer. On the other hand, the SEI formation on the electrochemical deposition based new-generation Li/Na anodes showed more complicated and dynamic structures. In this case, the interface structure varies during the Li/Na plating and stripping, and highly depends on the electrolyte solvent structures within the inner Helmholtz layer. By further comparing the nanomechanical/rheology properties of SEI formed on various carbon, lithium and sodium metal anodes, we deduce the intrinsic material properties of SEI layers such as elastic moduli, plasticity and relaxation time, predicting the SEI quality in commercial batteries after their formation by correlating quantitatively measured nanoscale SEI properties with the battery performance. This novel "3D *operando* nanorheology" characterization methodology provides a novel

paradigm for battery community, that can be effectively used for SEI measurements in different type of battery electrode-electrolyte systems. Predicting the SEI quality based on this new methodology will be extremely beneficial for selecting a new electrolyte, optimising formation process and reducing the time and cost of battery formation process.

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Reference

1. Bommier, C. and X. Ji, *Electrolytes, SEI Formation, and Binders: A Review of Nonelectrode Factors for Sodium-Ion Battery Anodes.* Small, 2018. **14**(16): p. 1703576.
2. Goktas, M., et al., *Graphite as Cointercalation Electrode for Sodium-Ion Batteries: Electrode Dynamics and the Missing Solid Electrolyte Interphase (SEI).* Advanced Energy Materials, 2018. **8**(16): p. 1702724.
3. Mogensen, R., D. Brandell, and R. Younesi, *Solubility of the Solid Electrolyte Interphase (SEI) in Sodium Ion Batteries.* ACS Energy Letters, 2016. **1**(6): p. 1173-1178.
4. Liu, D., et al., *Review of Recent Development of In Situ/Operando Characterization Techniques for Lithium Battery Research.* Advanced Materials, 2019. **31**(28): p. 1806620.
5. Li, H., S. Guo, and H. Zhou, *In-situ/operando characterization techniques in lithium-ion batteries and beyond.* Journal of Energy Chemistry, 2021. **59**: p. 191-211.
6. Peled, E. and S. Menkin, *SEI: past, present and future.* Journal of The Electrochemical Society, 2017. **164**(7): p. A1703.
7. Chen, Y., et al., *Controlling Interfacial Reduction Kinetics and Suppressing Electrochemical Oscillations in Li4Ti5O12 Thin-Film Anodes.* Advanced Functional Materials, 2021. **31**(43): p. 2105354.