Molecular-Scale Visualization of Solvation Structures of LiTFSI-PC Electrolyte on a Heterogeneously Charged Surface by Frequency Modulation Atomic Force Microscopy

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The solvation structures formed by ions and solvent molecules at solid/liquid interfaces critically influence the energy storage performance of lithium-ion batteries (LIBs). While prior work combining frequency modulation atomic force microscopy (FM-AFM) and molecular dynamics (MD) simulations elucidated molecular structures at mica/electrolyte interfaces [1], the variable number of residual potassium ions (K^+) after cleavage leads to uncertainty in surface charge density.

To resolve the relationship between solvation structures and surface charge density, we investigated solvation structures of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in propylene carbonate (PC) on a heterogeneously charged clinochlore surface using FM-AFM. Cleaving clinochlore yields a surface composed of alternating negatively charged talc-like and positively charged brucite-like layers [2]. Large-scale topographic imaging of clinochlore(001) in 100 mM LiTFSI-PC electrolyte (Figure 1a) revealed a height variation of 0.5 nm along the P–Q cross-section, consistent with the thickness of a brucite-like monolayer. Two-dimensional frequency shift map (Figure 1b) further distinguished solvation structures on each domain. On the talc-like layer we found a few dark stripes with about 0.4 nm spacing, indicating layered assemblies of PC molecules. In contrast, on brucite-like layer we found two bright stripes with a spacing of about 1 nm, suggesting $TFSI^-$ anions attracted to the surface formed solvated complexes such as $Li^+(PC)_3$, $Li^+(PC)_3TFSI^-$, $Li^+(PC)_4$, and $Li^+(PC)_4TFSI^-$. Complementary MD simulations of bulk electrolyte and the clinochlore/electrolyte interface provided mechanistic insights into these solvation structures at the interface.

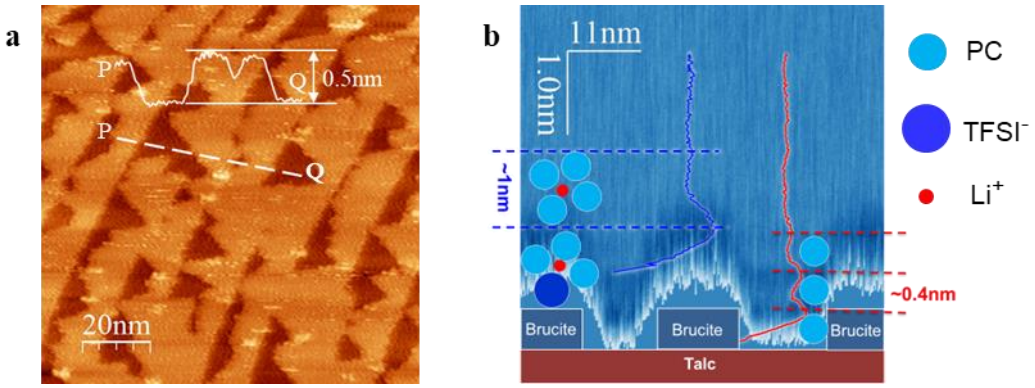

Figure 1. FM-AFM images of clinochlore in 100mM LiTFSI-PC electrolyte. **(a)** Topographic image of the clinochlore (001) surface with a cross sectional profile along the line P-Q. (**b)** 2D frequency shift map at the interface. Red and blue curves represent the averaged frequency shift profiles on the talc-like and brucite-like layers, respectively. Schematic representations of the proposed molecular arrangements at each interface region are superimposed.

Reference

[1] Y. Yamagishi, et al. Nano Lett. **22**, 9907 (2022). [2] K. Umeda, et al. Nat. Commun. **8**, 594 (2018).