

Elucidating Lithium-ion Surface Adsorption on Electrode Materials using ⁷Li Dark-State Exchange Saturation Transfer NMR Spectroscopy

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Interfacial chemistry plays a central role in the development of next-generation high energy Li-ion electrode materials, and ideally should provide efficient and stable cationic transport. Yet, rational design of new surface treatments that would act as beneficial electrode electrolyte interphases (EEI's) is hindered by the challenges involved in probing their ion transport properties and deconvoluting the different transport processes¹. Here we demonstrate how Dark-State Exchange Saturation Transfer (DEST)² by ⁷Li NMR can be used to directly measure the Li-ion desolvation and surface adsorption processes at the solid-liquid interface, the first, and presumed rate-limiting step of the cationic journey from electrolyte to electrode. DEST is a method primarily utilized to probe ligand binding in biological systems, which we adapted to probe electrochemical interfaces. In this case, the observable is the electrolyte Li-ion resonance which is imprinted with the properties of the hidden environment of the adsorbed cations to extract the liquid-solid exchange rate. Development of an optimized model system composed of monodisperse sub-micron particles allowed for accurate comparison between different surface chemistries, silica, titania, alumina with and without organic functionalization, in terms of their Li-ion affinity. Coupling DEST with surface sensitive solid-state NMR approaches enabled detection of the surface species participating in the adsorption process and correlation with their Li-ion binding properties. Simulations and modelling³ of the surface adsorption process yielded a quantitative analysis of the exchange rates and binding properties of the measured surfaces. We found that silica irreversibly adsorbs Li ions and that the addition of polar organic groups to aluminum-based electrode coatings improves Li-ion surface binding, as well as affects the binding site density. With the presented ⁷Li DEST approach we are finally able to disentangle the elusive Li-ion interfacial processes, previously measured only in convolution, and characterize them in terms of their kinetics. Thus, DEST is cemented as a valuable tool for elucidation of the structure-function relationship in electrode materials and enabling rational design of robust EEI's.

1 Xu, K. *J Power Sources* 559, 232652 (2023)

2 Anthis, N. J. *et al. Q Rev Biophys* 48, 35–116 (2015)

3 Zaiss, M. *et al. NMR Biomed* 26, 507–518 (2013)