

Computational Insights into Electrolyte-Dependent Li-ion Charge-Transfer Kinetics at the Li_xCoO_2 Interface

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Interface engineering remains a largely underexplored area and yet it holds the keys to high performance Li-ion (Li^+) batteries. The charge transfer across electrode-electrolyte interfaces is oftentimes a significant obstacle for achieving fast charging and high power performance without compromising battery lifespan. In this work we employ a Boltzmann-averaged first-principles workflow based on constant potential and constrained density functional theory for evaluation of atomic scale factors influencing coupled ion-electron charge transfer kinetics across battery electrode-electrolyte interfaces.¹ The approach estimates diabatic Li^+ interface energy landscapes as function of the interface character and operational conditions and use this information to simulate charging/discharging currents. Experimental trends for the Li_xCoO_2 ($0.5 \leq x \leq 1.0$) electrode are reproduced for varied organic electrolytes with LiPF_6 and LiClO_4 salts, identifying Li^+ transfer energy and Li^+ adsorption energy as decisive factors influencing the enhanced kinetics in LiClO_4 -based electrolytes over LiPF_6 . The talk will conclude by comparing the performance of the aforementioned high-fidelity methods with more approximative approaches. The latter methods result in a significant computational speed-up that allows for rapid screening of liquid- as well as solid-state electrolytes with fast interface kinetics.

¹ Stenlid et al., ACS Energy Lett. 2024, 9, 3608–3617