

Probing interfacial reaction pathways between cathodes and PF₆-based carbonate electrolyte in Li-ion batteries through *in-situ* spectroscopic technique

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Transforming into Ni-rich regime for conventional Li-ion battery cathodes LiNi_xMn_yCo_{1-x-y} (NMC) significantly improves its initial discharge capacity, but Ni-rich cathodes also degrade much more drastically upon cycling due to higher surface reactivity¹. However, up to now, fundamental understanding of the interfacial (electro-)chemical reactions between cathode and electrolyte is lacking. The quest for high energy density and stable cathode materials hinges on the ability to unequivocally identify the reaction mechanism under realistic operating conditions. In the past few decades, researchers have developed a wide range of spectroscopic and imaging tools to enable a detailed study of the chemical and structural changes at the solid/liquid interface, whereas the interpretation of results obtained from isolated techniques can be challenging.

In this work, we combine various spectroscopic and theoretical techniques to unravel the (electro-)chemical reaction pathways of Li-ion cathodes and electrolyte interface upon charge/discharge. Here, we are specifically focused on the interaction between LP57 electrolyte (1 M LiPF₆ in EMC:EC 7:3) and a variety of cathode materials including Ni-rich NMC during the charge/discharge process. The molecular-level understanding of the interfacial electrochemical processes on various cathode materials using *in-situ* Raman spectroscopy and *in-situ* attenuated total reflection infrared (ATR-IR) spectroscopy is particularly discussed. *In-situ* Raman spectroscopy captures the change in metal-oxygen chemical bonding and the deprotonation process of ethylene carbonate (EC) molecules on the cathode surfaces. *In-situ* ATR-IR spectroscopy provides further information on the detailed (electro-)chemical decomposition pathway of solvent and salt during the electrochemical process. Moreover, we also lend support from density functional theory (DFT) calculations to identify the chemical footprints of key reaction intermediates observed in the spectroscopy results and investigate the interfacial reaction energetics and landscape. Through this study, we have provided a more holistic picture of the interplay between cathode and electrolytes during cycling and a detailed PF₆-based electrolyte decomposition pathway. We expect to shine a new light for future DFT reaction pathway studies for electrode-electrolyte interface and high-throughput screening for more stable electrolyte and high energy cathodes.

References:

1. H.-J. Noh, S. Youn, C. S. Yoon and Y.-K. Sun, *J. Power Sources*, **233**, 121 (2013).