bat409 Molecular-Level Understanding of Cathode/Electrolyte Interface

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Introduction

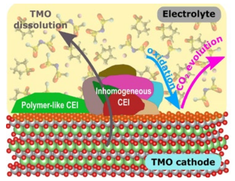
Cathode/Electrolyte Interface (CEI) in Batteries

High-energy next-generation lithium ion batteries (LiBs) require the utilization of high-voltage cathodes. Carbonate-based electrolytes (electro)chemically degrade at the highly reactive cathode surfaces and at higher potentials, resulting in unstable cathode electrolyte interphase (CEI). A lack of mechanistic understanding of cathode-electrolyte interactions and electrolyte degradation mechanisms hinders development of cathode surface stabilization strategy

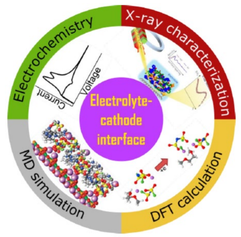
Challenges with CEI Studies

Buried Interfaces hinder direct experimental access

Heterogeneous nature of transition metal oxide (TMO) cathodes interphase create challenges for probing (electro)-chemical processes regarding the evolution and stabilization of CEI



Approach



Electrolytes:
From baseline carbonate-based electrolytes to fluorinated electrolytes

TMO Cathodes:
From particles to model thin-films (grown by pulsed laser deposition, PLD) with controlled surface structure

Interfaces:
From chemical reaction to electrochemical interphase

Combining molecular-scale modeling with advanced X-ray surface scattering and spectroscopy, and electrochemical characterization using model, PLD thin-film electrodes and high-purity electrolytes

Relevance/Publications

1. Understanding underlying chemistry process that control interfacial cathode-electrolyte reactions in high-voltage LIBs
2. Elucidating the cathode degradation mechanism in carbonate – based electrolytes
3. Developing informed strategies that enable the stabilization of cathode surface under the electrochemical conditions

Publications:

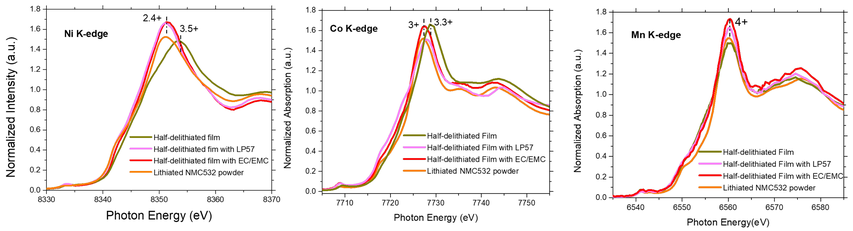
1) *iScience* 2020, 23, 100844-1008854 (citation: 15);
2) *Small 2019, 15, 1804670-1804680 (citation: 20);*
3) *J. Pow. Sour. 2020, 461, 228159-228169 (citation: 3);*
4) *Chem. Mater. 2020, 32, 3028-3035 (citation: 9).*

Approaches

1. Chemical and electrochemical studies of PLD-derived $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC532) thin-film
2. Density functional theory (DFT) study of interfacial reaction between the electrolyte components and the charged cathode surface
3. Synchrotron scattering and spectroscopy studies of cathode interphase evolution from the interfacial reactions
4. Comparison of X-ray and molecular dynamics (MD) analysis of interphase formation mechanism

Combined Experimental and Theoretical Studies

Chemical transformation PLD-derived half-delithiated NMC532 in carbonate-based solvent and electrolyte



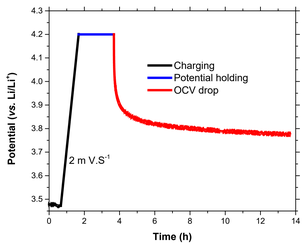
Total reflection X-ray absorption near edge structure (XANES) spectra of the half-delithiated NMC532 films before and after an exposure to LP57 electrolyte and EC/EMC solvent and the lithiated NMC532 particles at Ni, Co, and Mn K-edges, respectively

- ✓ X-ray spectroscopy revealed the **transition metal-dependent reduction of cathodes in carbonate electrolytes :**
  - Ni (reduced by 1.1 e) > Co (reduced by 0.3 e) > Mn (small changes)
- ✓ **EC/EMC solvents** appear to be the major contributor to the reduction
- ✓ Half-delithiated NMC532 is reduced during this chemical transformation process
- ✓ OCV drops confirming the self-discharge degradation in charged NMC532

Crystal structure largely unchanged | **Chemical reduction of Ni and Co**

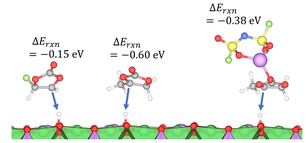
Due to small size of proton

Self-discharge degradation of NMC532 in carbonate-based electrolyte

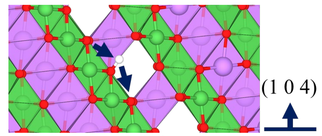


The potential profiles of NMC thin-film as function of time in LP57 electrolyte during the charging, potential hold, and open-circuit voltage (OCV) monitoring

Theoretical modeling of solvent deprotonation and the proton transfer in layered cathode



Solvent (EC) and salt decomposition on $Li_{0.5}NiO_2$ surface

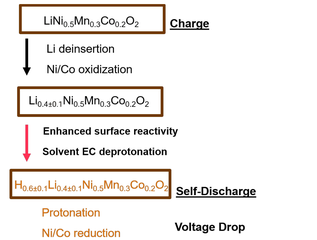


Proton transport in the layered cathode

rationalization of cathode protonation combining the experimental results from X-ray scattering and spectroscopic studies respectively

modeling elucidated the interfacial cathode - electrolyte reactions

- ✓ compared with salt, **solvent EC** tend to be more reactive due to the interfacial deprotonation reaction at charged layered cathode surface
- ✓ Possible cathode **protonation pathway** in layered cathode



Upon charging, Ni and Co in NMC are oxidized due to delithiation. EC deprotonation solvent donates proton to NMC lattice, and reduces Ni and Co sites, leading to the voltage drop in the self-discharge

The combined X-ray and theoretical studies

- ✓ **Revealed the underlying interfacial protonation reactions between charged cathode and solvent**
- ✓ **Uncovered the protonation-induced self-discharge degradation in cathode**
- ✓ **Offered fundamental insights into the reactivity of charged cathode, which rationalizes stabilization strategies of high-voltage cathodes in LiBs**

Conclusions & Plans

- Combined synchrotron scattering and spectroscopy studies elucidated the reduction transformation of Ni and Co sites in the charged cathode thin films in carbonate-based solvents and electrolytes
- Uncovered the interfacial protonation-induced self-discharge degradation of cathode in LiBs
- DFT calculations revealed the mechanisms of the solvent (EC) deprotonation on the charged layered cathode surfaces and the directed cathode protonation
- Quantitative confirmation of protonation in charged and cycled films using deuterated solvent and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)
- Electrochemical study of NMC532 thin films and particles with the fluorinated electrolytes
- *Operando* X-ray scattering and spectroscopy studies of the epitaxial thin films with different conditions
- Further computational studies of cathode-electrolyte protonation interactions and interphase evolution

Acknowledgements

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