



# Anode-originated SEI migration contributes to formation of cathode-electrolyte interphase layer



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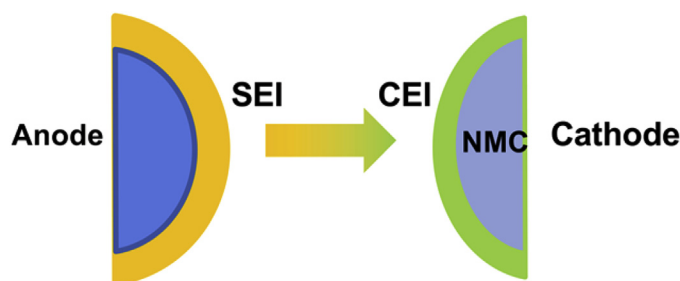
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## HIGHLIGHTS

- Electrolyte decomposition products migrate from Li, graphite anodes to NMC cathode.
- Cathode surface products are greatly reduced when using lithium titanate anode.
- XPS correlation analysis identifies three major products on cathode surface.
- Anode to cathode migration may be important in understanding cathode surfaces.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Cathode-electrolyte interphase (CEI) formation is a key process that impacts the performance of lithium-ion batteries. In this work, we characterized the composition and stoichiometry of CEI layer on  $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$  (NMC) cathodes via a novel combination of quantitative correlation analysis of X-ray photoelectron spectra and binder-free cathode formulation. By comparing the CEI formation in NMC-based cells with lithium, graphite and lithium titanate anodes, we demonstrate a CEI formation pathway via migration of surface species that originally formed on the anode side. A case study of cathodes coated by atomic layer deposition with a thin layer of  $\text{Al}_2\text{O}_3$  demonstrates that anode-to-cathode migration can be mitigated by ALD cathode coatings. This work highlights the importance of anode-mediated processes in order to correctly interpret surface phenomena on the cathode side and to guide further development of surface protection strategies.

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## 1. Introduction

The increasing demand for portable electronic devices, electric vehicles, and grid energy storage has continued to motivate the development of Li-ion batteries with reduced cost and improved

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performance. In recent years, there has been high interest in the layered  $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$  (NMC) cathode materials due to their higher capacity, lower cost, and enhanced safety compared to the conventional  $\text{LiCoO}_2$  cathode [1–13]. Representative materials such as  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  and  $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$  have been adopted in commercial Li-ion batteries [11]. However, the NMC material experiences a relatively large irreversible capacity loss during the first cycle and poor cycle performance, especially at high upper

cutoff voltages and at high temperature [3,5,14–16]. It is believed that electrolyte decomposition at the electrode-electrolyte interface accelerates capacity loss over extended cycling [17]. The term cathode-electrolyte interphase (CEI) is typically used to describe the cathode-side surface layer that is composed of solid-phase electrolyte decomposition products, while solid-electrolyte interphase (SEI) refers to what forms on the anode side. The formation of CEI and SEI depletes accessible lithium in the battery and impedes lithium transport at the electrode-electrolyte interface [18]. Among the efforts to improve NMC cycle life, one is to modify the cathode surface by coating with thin ceramic materials such as alumina to reduce irreversible capacity loss and prevent parasitic reactions on the surface [19–31]. In order to understand the working mechanism of coatings and guide future designs, it is highly desirable to systematically study the effect of coatings on interfacial phenomenon such as CEI formation and SEI-CEI crosstalk.

CEI formation is generally discussed as an isolated process in terms of cathode-specific electrolyte decomposition. However, a small number of studies have proposed that there is crosstalk between the reactions occurring at the cathode and anode in battery systems. Aurbach et al. [18] first described the possibility of reduction products on the anode saturating the electrolyte and reprecipitating on the cathode. More recently, Malmgren et al. [32] and Jung et al. [27] have included dissolution of SEI species as a potential pathway in their discussions of CEI formation. Jarry et al. [33] have reported transition metal ion dissolution from the cathode side and migration to the anode in the form of ligand-metal-complexes, which suggests the possibility of shuttling relatively large molecules between electrodes. However, to the best of our knowledge, no literature study has been designed to experimentally validate the migration pathway for anode-mediated CEI formation. For correct conceptualization of CEI formation and correct interpretation of CEI-related phenomenon such as the effect of cathode coatings, it is essential to understanding the potential role of anode-to-cathode SEI migration.

Previous literature has reported the use of X-ray photoelectron spectroscopy (XPS) to identify CEI composition and quantities [26,34–36]. XPS is a surface-sensitive technique with photoelectron escape depth on the order of a few nanometers, suitable for surface analysis. One challenge of XPS quantification of CEI is to differentiate CEI component in the presence of polyvinylidene difluoride (PVDF) binder, conductive carbon black and other CEI species. For example, in the C 1s region, C-O containing CEI gives rise to peaks between 286.5 and 287.0 eV, very close to PVDF binder signal at 286.45 eV [26]. The attempts taken to differentiate CEI signal from PVDF vary between studies. For instance, Niehoff et al. fit two peaks near 286 eV to represent CF<sub>2</sub> and CH<sub>2</sub> from PVDF and optimized their area to match PVDF stoichiometry [36]. Cherkashin et al. fit one peak in the 286 eV region and assigned it to PVDF/C=O/C-O mixture [34]. In previous studies, it has been common to assign one broad XPS peak to multiple species due to the lack of clear differentiation among possible carbon-containing species [26,34–36]. To bring more clarity into CEI assignment, we note the necessity of exploring alternative ways to assign the chemical formulation of CEI.

Here, we present a systematic XPS study of CEI formation pathway on NMC cathodes. The first section focuses on establishing a more definitive identification of CEI species via quantitative correlation analysis and use of a binder-free cathode formulation. The identity and approximate stoichiometry of CEI species was determined both by correlating the changes in elemental content of C, O, Li, F and P at the surface, and by investigating cathode surface species at the absence of PVDF binder. In the second section, we address the theory of anode-mediated CEI formation via SEI migration to the cathode. Two sets of experiments were designed:

the first one compared CEI formation in cells constructed with one and three separators, and the increased number of separators were used to increase the cathode-anode physical separation and thereby impede migration between the two electrodes; the second set of experiments compared CEI formation in NMC-Graphite and NMC-Lithium Titanate (LTO) full cells, and the different types of anodes were used to demonstrate dependence of CEI quantities on the SEI formation process. LTO is generally considered SEI-free because its lithiation potential is higher than most electrolyte materials [37–42]. Finally, we discuss the impact of the SEI migration theory on our interpretation of coating functions. A comparative CEI study was conducted on regular NMC cathodes and on cathodes with thin Al<sub>2</sub>O<sub>3</sub> coatings produced by atomic layer deposition (ALD), demonstrating that the extent to which anode-produced reaction products adhere to the cathode is also dependent on the properties of the cathode surface.

## 2. Experimental

### 2.1. Fabrication of NMC cathodes

The LiNi<sub>0.5</sub>Mn<sub>0.3</sub>Co<sub>0.2</sub>O<sub>2</sub> (NMC532) powder under investigation was supplied by TODA Inc. The composite NMC electrodes were prepared by mixing the active cathode powder (92% w/w), carbon black (3.5% w/w, Super P C65) and 4.5% of polyvinylidene fluoride (Solef) binder in N-methylpyrrolidone (NMP) solvent. The mixture was cast on Al foil with a 150 μm doctor blade. The film was dried under vacuum, pressed with a lab press at 3 ton/cm<sup>2</sup>, and dried again under vacuum at 150 °C overnight before use.

### 2.2. Fabrication of binder-free cathodes

The binder-free electrodes were prepared by mixing the NMC532 (95% w/w) and super P carbon black (5%) with NMP solvent. The slurry was cast on Al foil with 50 nm doctor blade. The film was dried at 150 °C under vacuum overnight.

### 2.3. Half-cell characterization

The half-cells were made from the fabricated NMC cathodes and lithium anodes (Chemetall Foote Corp). The electrolyte was 1M LiPF<sub>6</sub> in EC/DEC (1:1 vol%), obtained from Ube, Inc. The coin cells were cycled at constant current between 3 V and 4.3 V vs. Li on an Arbin battery testing unit. For samples cycled 1–4 times, the current was set to be C/10 (~0.23 mA). For long cycling, the first two formation cycles were at C/10, and the subsequent charge and discharge rates were C/3 (~0.8 mA) and 1C (~2.3 mA), respectively. The specific current value depends on the loading of each electrode. Cycle performance of the cells can be found in Fig. 6a, and rate performance in Fig. S1. For *post mortem* XPS analysis after cycling, the cell was disassembled and the cathode was soaked in fresh dimethyl carbonate (DMC) three times for 2 min each to remove excess salt and electrolyte.

### 2.4. Full-cell characterization

The full cells were made from matched NMC cathode and graphite or lithium titanate (LTO) anode films purchased from Electrodes and More. The electrolyte was 1M LiPF<sub>6</sub> in EC/DEC (1:1 vol%), obtained from BASF. The coin cells were cycled at constant current between 3 and 4.2 V vs. graphite, and 1.6–2.8 V vs. LTO. The C rates were the same as were used in coin half cells.

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