



# Dynamic evolution of cathode electrolyte interphase (CEI) on high voltage LiCoO<sub>2</sub> cathode and its interaction with Li anode



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## ABSTRACT

Realizing the charging of LiCoO<sub>2</sub> to 4.6 V (vs. Li/Li<sup>+</sup>) reversibly has important value for achieving high volumetric and gravimetric energy density in rechargeable lithium batteries. However, the surface and interface instability of electrode at high voltage remains a primary problem. In this work, cathode electrolyte interphase (CEI) layer on LiCoO<sub>2</sub> has been studied by X-ray photoelectron spectroscopy (XPS). In LiCoO<sub>2</sub>/Li battery, the dynamic evolution of CEI layer upon charging and discharging has been observed. Based on quantitative XPS analysis, a strong correlation on interface products between cathode and Li anode has been established. Such correlation mainly originates from the reversible formation and dissolution of the SEI layer on Li anode. The CEI layer evolution can be attributed to the sequential reactions through electrolyte and possibly physical migration of SEI fragments from Li anode. While in LiCoO<sub>2</sub>/graphite battery, the changes of the CEI on LiCoO<sub>2</sub> becomes less significant due to the relative stable solid electrolyte interphase (SEI) layer forming on graphite anode, which further supports the strong correlation between CEI on cathode and solid electrolyte interphase (SEI) on Li anode. These results reveal the origin of the dynamical evolution of CEI on LiCoO<sub>2</sub>, and highlight that the impact of anode should be considered when interpreting the CEI on cathode, especially in rechargeable lithium batteries using lithium as anode.

## 1. Introduction

High energy density Li batteries are crucial to the daily increasing applications such as consumer electronics and electric vehicles [1–4]. With a high volumetric and gravimetric energy density of 3700 Wh L<sup>-1</sup> and 880 Wh kg<sup>-1</sup> (charged to 4.6 V vs. Li/Li<sup>+</sup>, about 220 mAh g<sup>-1</sup>), layered LiCoO<sub>2</sub> is competitive among various cathode candidates. As the first commercialized cathode material, layered LiCoO<sub>2</sub> has been researched for a long time [5–8]. However, it is still plagued with a series of detrimental problems for high voltage operation. A primary challenge of high voltage LiCoO<sub>2</sub> lies in the drastic structural change, which results from the repeated deep Li intercalation and deintercalation [9–11]. The resulted mechanical damage during high voltage cycling is directly related to battery fatigue. In addition, deep Li removal triggers oxygen instability and gas release at cathode surface. The problem of irreversible oxygen loss brings in security concern, which limits the high voltage application of layered LiCoO<sub>2</sub> [12,13]. It is worth noting that the released oxygen and highly oxidized cathode surface at high voltage may further arouse interfacial reaction between

electrode and electrolyte. The usually irreversible interfacial reaction and the so-called cathode-electrolyte interphase (CEI) layer formation have been detected by various research groups, which further contributes to capacity loss [14–18]. In order to overcome all these challenges, various strategies and schemes have been proposed and carried out in the past decades. Foreign atoms doping and protective layer coating are two major methods that are widely used [19–23]. These methods are proven effective in mitigating structural fatigue both in bulk and at surface, which can improve LiCoO<sub>2</sub> battery to higher voltage level. However, much remains unknown about the CEI layer which is directly related to battery performance. So far, there are still several important questions for CEI which need further study, including its chemical composition, physical properties, chemical and electrochemical stability as well as the influence on battery performance.

The presence of CEI layer on LiCoO<sub>2</sub> was first suggested by Goodenough et al. [24]. Later after that, numerous studies have been devoted to interpreting the compositions and formation mechanism of CEI layer. By utilizing diverse research methods and techniques, much

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progress has been achieved. Nowadays, it is widely accepted that the CEI layer contains both inorganic components such as LiF and organic species such as carbonates and oligomers/polymers [14,17,25]. Such combination results from the complicated chemical/electrochemical surface reaction between electrode and electrolyte, which is found to take place directly after LiCoO<sub>2</sub> contacting with non-aqueous electrolyte [26,27]. It was further evidenced by in-situ neutron scattering that CEI layer presents dynamic evolution during battery cycling within low cut-off voltage range (4.2 V vs. Li/Li<sup>+</sup>) while the CEI thickness gradually accumulates with cycle number [28]. Considering the increased interfacial reactivity at high voltage (out of the chemical window of electrolyte), CEI layer demonstrates even more complicated response during high voltage cycling. When LiCoO<sub>2</sub> is charged to 4.5 V, the CEI layer becomes less stable and decomposes during high voltage cycling, as reported by Cherkashinin et al. [29]. Delmas et al. further observed the continuous oxidation on the LiCoO<sub>2</sub> surface until almost all the lithium were extracted from the crystal lattice [30]. By virtue of in-situ AFM, the dynamic evolution of CEI during electrochemical cycling at high voltage has been verified by Lu et al. [31]. So far, the detailed constituent and electrochemical behavior of CEI layer is still under hot debate. However, it is generally accepted that this interphase layer is extremely sensitive to many factors such as cut-off voltage, cycle current and electrolyte composition.

It is worth noting that while previous studies are informative and important, the CEI layer is usually treated as a standalone scientific issue, which is independent of reactions on anode side. With the ongoing research efforts, increasing evidences have indicated the interaction between cathode and anode [32–34]. A well known example is the transition metal ion dissolution from cathode surface, which will affect the interface reactions on both electrodes [16,35]. Recently, by investigating into the gas generation during long time storage, Xiong et al. verified the interaction between cathode and graphite anode in batteries operating at high temperature and high voltage [36]. Jung et al. further demonstrated the enhanced performance of high voltage LiCoO<sub>2</sub>/graphite battery by mitigating the coupled side reactions through alumina coating [37]. Note that plenty of researches on CEI layer are carried out with Li metal as the chosen anode, where solid electrolyte interphase (SEI) layer formation occurs due to thermodynamic instability. When cathode is cycled in high voltage range, the repeated formation and decomposition of SEI layer on Li anode and its influence on cathode interface reaction become prominent. However, corresponding investigation has been missing. A deep investigation into the correlation between reactions on cathode and Li anode is then necessary to collect credible properties of CEI layer on cathode as well as to achieve comprehensive understandings of the formation mechanism.

In this work, we investigate the dynamic evolution of CEI formation and decomposition on LiCoO<sub>2</sub> cathode cycled in the voltage range of 3.0–4.6 V. By virtue of XPS measurement and quantitative analysis, the detailed chemical constituent of both CEI on LiCoO<sub>2</sub> cathode and SEI on Li anode can be figured out and its evolution along with battery cycling can be fingerprinted. By comparing the CEI evolution of normal battery and the battery with renewed Li foil at charged state, we are able to establish the synergistic interaction between surface reactions on LiCoO<sub>2</sub> cathode and Li anode. The strong correlation is further evidenced by the less significant change of CEI layer within LiCoO<sub>2</sub>/graphite battery, where stable SEI forms on graphite anode. The findings in this work are directly related to batteries with high voltage cathode and Li anode. Note that the chosen LiCoO<sub>2</sub> can be viewed as the prototypical material for layered Li-intercalation oxides, and the relative simple chemical constituent avoids the interaction among substituent transition metal elements in typical cathodes. Considering the surface layer involvement feature of this effect, the dynamic interaction between cathode and anode can be viewed as a general phenomenon, which is not limited to LiCoO<sub>2</sub> itself but has exemplary significance for investigations on other high voltage cathode

candidates. The introduction of metallic Li anode into battery systems, which is attracting much attention in solid state battery research, further adds to the significance of the investigation on surface layer change on Li anode. Moreover, high voltage LiCoO<sub>2</sub> exhibits practical significance due to its high volumetric mass density (at material level) and compact density (at the electrode level). As a result, the investigation on layered LiCoO<sub>2</sub> is of vital importance to both fundamental research and practical applications.

## 2. Experimental methods

### 2.1. Sample preparation

The LiCoO<sub>2</sub> electrodes were obtained from CITIC GUOAN Mengguli Inc. The loading density of LiCoO<sub>2</sub> active material is 22.5 mg cm<sup>-2</sup> (4.5 mA h cm<sup>-2</sup>, charged to 4.6 V vs. Li/Li<sup>+</sup>). The working electrode was prepared by rolling out the mixture active material 97.5 wt%, carbon black 1.25 wt% and polytetrafluoroethylene 1.25 wt% onto thin Al foil with a compact density about 4.0 g cm<sup>-3</sup>. The electrodes were punched into circles with 14 mm diameter and then dried at 110 °C in vacuum for 6 hours.

### 2.2. Electrochemical measurements

All the electrochemical tests were conducted using CR 2032 coin cell, assembled in an argon-filled glove box. 1 M LiPF<sub>6</sub> in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume) was used as electrolyte. Li foil or graphite were used as the counter electrode and Al<sub>2</sub>O<sub>3</sub> coated polyethylene was used as the separator. The charge and discharge tests were carried out using a Land CT2001A battery test system (Land, Wuhan, China) in voltage range of 3.0–4.6 V at room temperature.

### 2.3. XPS measurements

The XPS spectra were recorded by ESCALAB 250 Xi, Thermo Fisher with monochromatic 150 W Al K $\alpha$  radiation. The data was analyzed with program Advantage and the binding energies were referenced to the C1s line at 284.4 eV from adventitious carbon. For all ex situ characterizations, the batteries were disassembled or re-assembled at different states of charge and discharge, and the samples were washed in DMC before drying, in an argon-filled glove box. Extreme cautions were paid when dealing with the charged sample to prevent any contact with air/moisture, as it is very easy to convert back to the discharged states. All samples were protected from air and moved to the detector cavity by the transfer equipment provided by Thermo Fisher.

### 2.4. X-Ray diffraction (XRD) and scanning electron microscopy (SEM)

The structure of LiCoO<sub>2</sub> electrode was characterized using a Bruker D8 Advance X-ray Diffractometer equipped with a Cu K $\alpha$  radiation source ( $\lambda_1 = 1.5406 \text{ \AA}$ ,  $\lambda_2 = 1.5444 \text{ \AA}$ ) and a LynxEye\_XE detector. The XRD patterns were collected in the scan range (2 $\theta$ ) of 10–130° with an increase of 0.02°. The morphologies of the samples were characterized by field emission scanning electron microscopy (S4800, Hitachi).

## 3. Results and discussion

Fig. 1 shows the cycle performance of LiCoO<sub>2</sub>/Li battery cycled in voltage range of 3.0–4.6 V at the current rate of 0.1 C (1 C = 274 mA h g<sup>-1</sup>). The cycle stability comparison between high voltage 3.0–4.6 V range and typical voltage 3.0–4.3 V range are shown in Fig. S1. The charge-discharge profiles display conventional lithium storage behavior of LiCoO<sub>2</sub> in layered O3 structure. The LiCoO<sub>2</sub>/Li

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