



# Significant impact on cathode performance of lithium-ion batteries by precisely controlled metal oxide nanocoatings via atomic layer deposition



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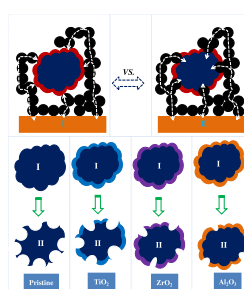
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## HIGHLIGHTS

- ALD derived metal oxide (TiO<sub>2</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>) coatings were successfully performed.
- Coatings could significantly increase battery performance of the commercial LiCoO<sub>2</sub>.
- Al<sub>2</sub>O<sub>3</sub> coating brings the best cycling stability.
- ZrO<sub>2</sub> coating contributes to the best rate capability.

## GRAPHICAL ABSTRACT



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## ABSTRACT

LiCoO<sub>2</sub> in the commercial lithium ion batteries has been suffering from its poor cycling performance at high cutoff voltages. In this study, we employ an atomic layer deposition (ALD) technique to surface-modify a LiCoO<sub>2</sub> material with various thickness-controlled metal oxide (TiO<sub>2</sub>, ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>) coatings to improve its battery performance. The effects of the metal oxide coatings on the electrochemical performance of LiCoO<sub>2</sub> electrode are studied in detail. It is demonstrated that a uniform and dense coating via the ALD route on LiCoO<sub>2</sub> powder can lower the battery performance due to an obvious decrease in lithium diffusion and electron transport with the coating layers. In contrast, it is revealed that a direct coating on prefabricated LiCoO<sub>2</sub> electrodes performs much better than a coating on LiCoO<sub>2</sub> powders. It is further disclosed that the improved electrochemical performance of coated LiCoO<sub>2</sub> electrode is highly dependent on the coating materials. Of the three coating materials, the Al<sub>2</sub>O<sub>3</sub> coating results in the best cycling stability while the ZrO<sub>2</sub> coating contributes to the best rate capability. It is thus suggested that the coating materials are functionally specific, and for the best improvement of a cathode, a particular coating material should be sought.

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## 1. Introduction

Various lithium transition metal oxides (such as LiCoO<sub>2</sub>, LiNiO<sub>2</sub>, LiCo<sub>x</sub>Ni<sub>1-x</sub>O<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, LiFe(Mn)PO<sub>4</sub>, LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>, etc) have

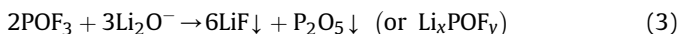
been successfully employed as cathodes in rechargeable lithium ion batteries (RLIBs) since the first commercialized RLIBs by SONY in 1991 [1–3]. LiCoO<sub>2</sub>, proposed by Goodenough et al. in 1980, [4] is the first commercialized cathode material in RLIBs [5,6], and has been considered as one of the most attractive cathodes due to its ease of production and superior battery performance including high energy density and high working potential (~3.9 V vs. Li/Li<sup>+</sup> couple) [7–9]. As an important cathode in RLIBs, the α-NaFeO<sub>2</sub>

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layer-structured LiCoO<sub>2</sub> (space group-R3m,  $a = 2.815\text{--}2.816 \text{ \AA}$ ,  $c = 14.05\text{--}14.08 \text{ \AA}$ ) with oxygen in a cubic close-packed arrangement is composed of consecutively arranged Li<sup>+</sup> and Co<sup>3+</sup> ions. Moreover, octahedral LiO<sub>6</sub> and CoO<sub>6</sub> share common edges between the layers in the unit cell of LiCoO<sub>2</sub> [7,10,11]. To reduce the cathode material size into the nanoscale is an important approach to increase cycling performance [9,12–17]. For example, nanostructured LiCoO<sub>2</sub> cathodes (representatively including nanoparticles [16], nanowires [17], and nanosheets [9], etc.) provide shortened diffusion pathway for lithium ion insertion/extraction and electron transport. In addition, the increased surface-to-volume ratio of nanostructured LiCoO<sub>2</sub> facilitates lithium ion accessibility from the electrolyte with higher efficiency over bulk LiCoO<sub>2</sub> [18]. However, the larger surface area of nanostructured LiCoO<sub>2</sub> often results in a heavier formation of solid electrolyte interphase (SEI) in comparison to its bulk counterparts. As a result, nanostructured LiCoO<sub>2</sub> is inevitably accompanied by the production of more heat [19]. In addition, a thicker SEI layer leads to deteriorated rate capabilities at high rates, due to its low electrical conductivity as a lithium-ion barrier [20]. Even worse, nanostructured LiCoO<sub>2</sub> suffers from its poor tap density, leading to the low RLIB energy density. In contrast, micron-sized LiCoO<sub>2</sub> cathode mitigates somewhat the above-discussed challenges, and shows more practical in commercial RLIBs. But, how to further increase battery performance of micron-sized LiCoO<sub>2</sub> cathode has been a crucial challenge in the RLIB development.

LiCoO<sub>2</sub> cathode exhibits a theoretical capacity of 272 mAh g<sup>-1</sup>. However, when the battery is charged a cutoff voltage up to 4.2 V, only half lithium is extracted from LiCoO<sub>2</sub> to Li<sub>0.5</sub>CoO<sub>2</sub>, resulting in the limited capacity (only ~140 mAh g<sup>-1</sup>) in practical applications [21]. Thus, it is a well accepted strategy to charge LiCoO<sub>2</sub> cathode beyond 4.2 V, in order to utilize more lithium ions from the cathode and to increase the specific capacity and the energy density of LiCoO<sub>2</sub> [22,23]. However, previous studies also revealed that the inevitable moisture in the RLIB electrolyte could induce LiPF<sub>6</sub> decomposition and form HF acid, described as following [24]:



The formed HF acid aggravates the dissolution of LiCoO<sub>2</sub> cathode, moreover, the charge cutoff voltage over 4.2 V incurs the dissolution of LiCoO<sub>2</sub> into the electrolyte, thereby causing an increased capacity fade upon cycling [23,25,26]. In this context, it is critical to mitigate the capacity fading of LiCoO<sub>2</sub> in order to satisfy RLIB application.

The charge–discharge cycling of RLIB cathodes is highly related with their surface chemistry [27], thus surface modification via coating was demonstrated being an effective strategy to decrease the cathode dissolution. To date, many metal oxides (such as TiO<sub>2</sub>, ZrO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> et al.) were successfully reported as surface coatings [28–34]. Their functional roles may present in preventing the cathode materials from their direct contact with the electrolyte, simultaneously maintaining ionic conduction pathways, suppressing the release of oxygen and the phase transition, and decreasing the disorder of cations in crystal sites [35,36]. For example, a mechanothermal process was applied to coat TiO<sub>2</sub> on LiCoO<sub>2</sub> cathode to obtain higher cycling performance [28]. The ZrO<sub>2</sub> coated LiCoO<sub>2</sub> showed better battery performance than the pristine one at both room temperature and elevated temperature of 55 °C [30]. It was found that the ultra-thin Al<sub>2</sub>O<sub>3</sub> coating on LiCoO<sub>2</sub> resulted in 250% improvement in reversible capacity in comparison to the bare

one [32]. Of three reported different configurations of surface coating, i.e., rough coating, core–shell structure coating and ultra-thin film coating [34], the first one cannot fully coat a cathode material, and the intact area leaves the cathode vulnerable to the reactions with the electrolyte. In comparison, the second choice is successful in fully coating a cathode. Unfortunately, the resultant coatings are often very thick and thereby impede the transport of lithium and electron. Therefore, the ultra-thin film coating as the third choice is commonly regarded as the most promising approach, due to its pinhole-free films with complete protection from the electrolyte [34]. To fulfill last route, recently atomic layer deposition (ALD) is receiving an increasing attention ascribed to its unique capabilities in depositing controllable atomic-level thin films with high quality. A lot of efforts have been focused on ALD-coatings onto cathodes [33,37–42], anodes [43–45], and separator [46] to increase electrochemical performance of RLIBs. In case of deposition of metal oxides, ALD has numerous reports including Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub> etc. on various substrates [33,37–46]. To the best of our knowledge, however, a systematic study of various coating layers (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub>) on the electrodes, in particular from the point of view of electrochemical characterization, is scarce.

In this study, we conducted a systematic comparative investigation on the effects of three metal oxide coatings including TiO<sub>2</sub>, ZrO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> on the electrochemical performance of a commercial LiCoO<sub>2</sub> cathode material with micron-size. The controllable coatings were deposited via ALD. In addition, the effects due to coating thickness were also addressed in study. It was demonstrated that the controllable coatings are effective in improving both cycling stability and rate capability of LiCoO<sub>2</sub> cathode. More importantly, it was inspired from this study that ALD and its resultant materials may ultimately contribute more for robust and high-efficient RLIBs.

## 2. Experimental

### 2.1. Preparation of LiCoO<sub>2</sub> electrode

LiCoO<sub>2</sub> electrodes were prepared by slurry-casting on Al foils that served as current collectors. The slurry contained 80 wt% the cathode materials (commercial LiCoO<sub>2</sub> with the particle size of 3–10 μm, as shown in Fig. S1 in Supplementary data), 10 wt% carbon black and 10 wt% poly(vinylidene) fluoride binder in the *N*-methylpyrrolidinone (NMP) solvent. The obtained electrode was dried in a vacuum at 90 °C overnight.

### 2.2. Metal oxide coatings on LiCoO<sub>2</sub> electrode via ALD

Various metal oxides (TiO<sub>2</sub>, ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>) were directly coated on the LiCoO<sub>2</sub> electrode in an ALD reactor (Savannah 100, Cambridge Nanotechnology Inc., USA). Titanium tetraisopropoxide (TTIP), tetrakis dimethylamido zirconium (Zr(NMe<sub>2</sub>)<sub>4</sub>) and Trimethylaluminum (TMA) were chose as Ti, Zr and Al precursor respectively, while H<sub>2</sub>O was used as the oxidizer in three cases. The deposition temperature was set as 85, 100 and 150 °C for TiO<sub>2</sub>, ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, respectively. One ALD cycle was executed with the following six steps: (1) pulsing of the first precursor with  $t_1$  s; (2) a 3.0 s extended exposure of the first precursor to the cathode electrode; (3) purging of residual precursor and any byproducts with  $t_2$  s; (4) pulsing of the second precursor with  $t_3$  s; (5) a 3.0 s extended exposure of the second precursor to the cathode electrode; (6) purging of residual precursor and any byproducts with  $t_4$  s. The ALD sequence was expressed as  $t_1 - t_2 - t_3 - t_4$  in short. During an ALD process, the purging time is an important parameter, thus this parameter we used in this study was optimized. For example, as shown in Fig. S2, in a case of TiO<sub>2</sub> coated LiCoO<sub>2</sub>, when the purging time was set as 5 s,

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