Improved cycling stability of LiCoO$_2$ at 4.5 V via surface modification of cathode plates with conductive LLTO

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Abstract

The stability issue of LiCoO$_2$ cycled at high voltages is one of the burning questions for the development of lithium ion batteries with high energy density and long cycling life. Although it is effective to improve the cycling performance of LiCoO$_2$ via coating individual LiCoO$_2$ particles with another metal oxides or fluorides, the rate capacity is generally compromised because the typical coating materials are poor conductors. Herein, amorphous Li$_{0.33}$La$_{0.56}$TiO$_3$, one of the most successful solid electrolytes, was directly deposited on the surface of made-up LiCoO$_2$ cathode plates through magnetron sputtering. Not only the inherent conductive network in the made-up LiCoO$_2$ cathode plates was retained, but also the Li$^+$ transport in bulk and across the cathode-electrolyte interface was enhanced. In addition, the surface chemical analysis of the cycled LiCoO$_2$ cathode plates suggests that most of the stability issues can be addressed via the deposition of amorphous Li$_{0.33}$La$_{0.56}$TiO$_3$. With an optimized deposition time, the LiCoO$_2$ cathode plates modified by Li$_{0.33}$La$_{0.56}$TiO$_3$ performed a steady reversible capacity of 150 mAh/g at 0.2 C with the cut-off voltage from 2.75 to 4.5 V vs. Li$^+/Li$, and an 84.6% capacity gain at 5 C comparing with the pristine one.

Key words: Lithium ion batteries; LiCoO$_2$; High voltage; Cycling stability; Surface modification.
1. Introduction

Lithium ion batteries (LIBs) have been urged for high energy density, high rate capability, and long cycling life, with increasing energy storage demands in portable electronics, electrical vehicles, and stationary power sources [1-3]. The most direct way to increase LIBs’ energy density is to apply cathode materials with higher capacities and/or higher working voltages [4-8]. LIBs with LiCoO$_2$ (LCO) cathode has gained great commercial success in the past 3 decades, especially as the power source for portable electronics, benefiting from its high specific capacity, high redox potential, and long cycling life [9-12]. However, the generally utilized specific capacity of LCO can only reach 140 mAh/g, roughly half of its theoretical capacity of 272 mAh/g, with the upper cut-off voltage of 4.2 V vs. Li$^+$/Li [11-13]. Theoretically, the utilized specific capacity can be improved by increasing the cut-off voltage. However, the cycling stability of LCO is poor when the cut-off voltage exceeds 4.2 V vs. Li$^+$/Li [1]. In addition, it is demonstrated that the capacity decay of LCO below 4.5 V vs. Li$^+$/Li is mainly due to the cacoethic side reactions, Co dissolution, and HF corrosion at the liquid-solid interface between LiPF$_6$-based organic electrolyte and LCO cathode [14,15]. Therefore, great efforts have been made to realize a stable cathode-electrolyte interface at 4.5 V vs. Li$^+$/Li via surface modifications of LCO [16-18].

In terms of structural feature, the surface modifications can be divided into two types. In one type, the modification layer is coated on individual LCO particles before casting the cathode plates [16-18]. In the other type, the modification layer is deposited on the surface of made-up cathode plates [19,20]. Although the surface modification on individual LCO particles is effective to improve its cycling stability [16-18], and can be easily realized via low-cost wet chemical routes [21-24], there are some disadvantages limit its application. For example, the modification layer on particles may break due to the severe mechanical impacts during slurry mixing and electrode calendaring [13]. In addition, the modification layer on individual particles may tip the balance of ionic conductivity and electronic conductivity in the bulk of cathode plates [1]. Alternatively, the surface modification of made-up cathode plates, which is carried out after LCO granulating, slurry mixing, and electrode calendaring, and only
introduces a thin layer of modification materials on the surface of cathode plates, is potential to addressing the above issues [13,19,20,25].

In terms of material chemistry, the surface modifications can be realized by inert compounds including fluorides (AlF₃, CeF₃, LaF₃, etc.) [21,22] and oxides (Al₂O₃, MgO, ZrO₂, ZnO, etc.) [23-26], which are generally poor Li⁺ and e⁻ conductors, or ionic conductors for Li⁺ (LiAlO₂, Li₄Ti₅O₁₂, Li₃PO₄, Li₂CO₃, etc.) [13,19,20,27]. Although the surface modifications by inert compounds are helpful to stabilize the LCO-electrolyte interface at high voltages [27], they may cripple the rate capability of LCO cathode, since the charge transport and transfer would be limited by the low-conductive coating layer [19,27]. On the other hand, the surface modifications by Li⁺ conductors, would not attenuate the bulk conductive network in cathode significantly, while the interfacial stability can be improved [20,25]. Especially, a Li⁺-conductive interfacial layer would help the Li⁺ migration between LiPF₆-based electrolyte and LCO cathode, resulting in a desired small interfacial impedance [28].

Herein, amorphous Li₀.₃₅La₀.₅₆TiO₃ (α-LLTO), which is one of the most successful solid electrolytes [29-31], was directly deposited on the surface of made-up LCO cathode plates through magnetron sputtering (Figure 1a). The sputter-deposited α-LLTO doesn’t require high temperature heat treatment, and performs a high ionic conductivity (1.54 × 10⁻₅ S/cm at room temperature). It is inspiring that the electrode level surface modification by α-LLTO not only doesn’t impair the bulk conduction in LCO cathode, but also enhances the charge transfer kinetics at LCO-electrolyte interface, which is favorable for rate capacity. In addition, the deposited α-LLTO effectively prevents Co dissolution, HF corrosion, and other side reactions at LCO-electrolyte interface. The LCO-LLTO-electrolyte configuration leads to a relatively stable interfacial polarization. As a result, the presented surface modification of cathode plates with α-LLTO, enables LCO steady operates for more than 100 cycles with an upper cut-off voltage of 4.5 V vs. Li⁺/Li, and a reversible capacity of 150 mAh/g at 0.2 C.

2. Material and methods

2.1. The preparation of LCO cathode and surface modification by α-LLTO
LCO cathode plates were prepared by spreading well-mixed commercial LCO powders (Aladdin, 80 wt%), acetylene black (MTI KJ Group, 10 wt%) and PVDF (Arkema, 10 wt%) on the surface of Al foil. N-methyl-pyrrolidone was used as solvent to form the slurry. The as-casted LCO cathode plates were dried in dynamic vacuum overnight at 110 °C to remove the solvent and trace water after calendering. The statistic thickness of the casted LCO cathode is ~ 40 μm, which is determined by a screw micrometer. α-LLTO was deposited on the surface of Si substrates or LCO cathode plates by magnetron sputtering. The cavity was evacuated to $5 \times 10^{-4}$ Pa or less. The LCO cathode plates were pre-heated at 120 °C for 30 min in vacuum to remove the trapped moisture and air. The Li$_{0.33}$La$_{0.56}$TiO$_3$ target was pre-sputtered for 5 min to remove dust and foreign particles on the surface. The distance between target and substrate was 15 cm. The sputtering power was 120 W. The working pressure was 1 Pa. The argon and oxygen ratio was 70 : 30 (sccm). The substrate temperature was kept at 120 °C. To obtain the modification layers with different thickness, the sputtering time was set to 10, 30, 60, and 100 min. Samples with different α-LLTO deposition time were denoted as LCO-LLTO-10, LCO-LLTO-30, LCO-LLTO-60, and LCO-LLTO-100, respectively. After the deposition of α-LLTO, the obtained samples were dried under vacuum for 24 h to remove trapped moisture prior to use. To determine the ionic conductivity of α-LLTO, it was deposited on a flat Si substrate. The deposition process parameters were similar to the surface modification of LCO cathode plates except for the deposition time was 240 min.

2.2. Materials characterizations

The thickness of LLTO films on Si substrate were determined using cross-section scanning electron microscopy (SEM). The phase analysis was performed by X-ray diffraction (XRD) using CuKα radiation. The surface morphology of LCO electrodes were observed by SEM. The elemental distributions of Co, C, La and Ti were analyzed by Energy Dispersive Spectrometer (EDS). X-ray photoelectron spectroscopy (XPS, Thermo Fisher Escalab Xi+) was used to analyze the surface chemical compositions of the electrodes.

2.3. Electrochemical measurements
The separators (polypropylene, Celgard 2400) were dried in vacuum overnight at 50 °C. The electrochemical properties of samples were tested in 2032 coin cells equipped with a lithium metal anode. The liquid electrolyte was 1 M LiPF₆ solution with the mixed EC : DMC : EMC (v/v/v = 1 : 1 : 1) solvent. All the cells were fabricated in an Ar filled glove box. Cycling tests were performed between 2.75 V and 4.5 V vs. Li⁻/Li with varied charge-discharge rates at room temperature by the battery test equipment (NEWARE CT-3008). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out by Princeton VersaSTAT 3F electrochemical analyzer. For EIS measurements, the amplitude voltage was 10 mV and the frequency range was 0.1 Hz to 100 kHz.

3. Results and discussion

Energy density and rate capability are the two core requirements for cathode technologies. It raises the challenge for the surface modification of LCO cathode. The conductive network in cathode plate for Li⁺ and e⁻ should be maintained, while the LCO-electrolyte interface is stabilized via introducing inactive materials as little as possible. As shown in Figure 1a, we propose coating the made-up LCO cathode plate with α-LLTO through magnetron sputtering. The sputter-deposited α-LLTO would form a conformal, dense, and very thin overburden on the surface of LCO cathode plate. The following merits can be reasonably expected. First, the potential damages to the modification layer during the preparing process of cathode plates are avoided. Second, the mass fraction of α-LLTO in the modified cathode plate is very small. Third, the undesirable interactions between LCO and electrolyte can be suppressed effectively. Last and most importantly, the deposited α-LLTO will not undermine the transport pathways for Li⁻ and e⁻ in the cathode plate because it mainly exists near the top surface of the cathode plate.
Figure 1. (a) Schematic illustration of conventional LCO cathode plate and LCO cathode plate with an α-LLTO modification layer; (b) XRD patterns of LLTO target (blue line), Si substrate (dark-cyan line), α-LLTO thin-film on Si substrate (purple line), pristine LCO cathode (black line) and α-LLTO-modified LCO cathode plates with different deposition time of LLTO (red line for 10 min, pink line for 30 min, yellow line for 60 min, and green line for 100 min); (c) Top- and side-view SEM images of LLTO thin-film on Si substrate; (d) EIS cure of LLTO film on Si substrate; (e-g) Top-view SEM images of pristine LCO (e), LCO-LLTO-10 (f), and LCO-LLTO-100 (g); (h) EDS mapping of the surface of LCO-LLTO-10.

The X-ray diffraction peaks derived from the Li0.35La0.56TiO3 target used here are well identical with crystalline LLTO (PDF # 46-0465) (blue line in Figure 1b). However, no diffraction peaks belonging to crystalline LLTO can be observed in the XRD pattern of the LLTO thin-film on Si substrate (purple line in Figure 1b). The diffraction peak at 28.48° should ascribe to the Si substrate. It is reasonable to conclude the as-deposited LLTO thin-film is amorphous. As shown in Figure 1c, the as-deposited LLTO thin-film is homogeneous, dense, and without any crystalline grains, which further confirms it is amorphous. The ionic conductivity of α-LLTO thin-film is calculated based on its bulk resistance determined by the intercept on Zre axis of EIS.
curve (Figure 1d) and its thickness determined in the side-view SEM image (insert in Figure 1c). The as-deposited α-LLTO thin-film performs an ionic conductivity of $1.54 \times 10^{-5}$ S/cm at room temperature, which is comparable to the reported values for α-LLTO thin-film solid electrolytes [32-33]. Additionally, the previous literatures have demonstrated α-LLTO thin-film solid electrolytes are with excellent chemical and electrochemical stabilities [31]. Therefore, it is potential to construct a highly stable and conductive LCO-electrolyte interface via deposition of α-LLTO on the surface of LCO cathode plate.

A conformal coating of α-LLTO on LCO cathode plate can be realized by sputtering deposition. As seen in Figure 1e, pristine LCO cathode plate is with a porous microstructure. The surface modification by depositing α-LLTO for 10 min doesn’t change the surface morphology of cathode plate significantly (Figure 1f). When the deposition time is extended to 100 min, an overburden can be observed because of the accumulation and agglomeration of α-LLTO particles (Figure 1g). However, the distribution of La and Ti observed in EDS mapping images (Figure 1h) suggests that LCO cathode plate has been evenly and conformally covered by α-LLTO after 10 min deposition. Co and C are also detected by the surface composition analysis, which indicates the thickness of deposited α-LLTO is much thinner than the probing depth of EDS (~ 1 um). The XRD patterns of LCO cathode plates with and without α-LLTO modification are similar and in good agreement with the standard pattern of LCO (PDF#44-0145), even though the deposition time of LLTO is extended to 100 min (green, yellow, pink, red, and black lines in Figure 1b). This is consistent with the fact that the as-deposited LLTO is in an amorphous form.
Figure 2. (a) Cycle performances of cathode plates based on pristine LCO and that modified by α-LLTO with different deposition time; (b) Rate performances of pristine LCO and LCO-LLTO-10; (c, d) Voltage vs capacity plots of pristine LCO (c) and LCO-LLTO-10 (d) at the different cycling rates.

The cycling stability and rate capacity of LCO can be effectively improved via depositing α-LLTO on the made-up cathode plates (Figure 2). The LCO cathode plates with and without α-LLTO coating were cycled in the cut-off voltage ranging from 2.75 to 4.5 V vs. Li+/Li at different cycling rates. LCO-LLTO-10 performs a superior cycle
performance (Figure 2a). At 0.2 C, all the samples show similar initial discharge capacities (~ 195 mAh/g). And their capacity degradations in the first 20 cycles are closed. In the sequential cycles, the positive effect of the deposited α-LLTO is gradually emerged. After 100 cycles, the discharge capacity of pristine LCO drops to 108 mAh/g. The capacity retention is only 55.4%, comparing with its initial discharge capacity. Meanwhile, LCO-LLTO-10 presents a stable discharge capacity as high as 150 mAh/g after 100 cycles, corresponding to a capacity retention rate of 76.9%. The discharge capacities of LCO-LLTO-30, LCO-LLTO-60, and LCO-LLTO-100 after 100 cycles fall in between the pristine LCO and LCO-LLTO-10, which are 122, 124, and 123 mAh/g, respectively. Since the mass of deposited α-LLTO is negligible to the whole cathode plates, the lower discharge capacities of LCO-LLTO-30, LCO-LLTO-60, and LCO-LLTO-100 shouldn’t ascribe to the increased weight of cathode plates. The results suggest that a thick layer of α-LLTO on the surface of LCO cathode plate possibly hinders the Li⁺ migration at LCO-electrolyte interface. For example, a thick overburden on the surface of porous cathode plate may hamper the infiltration of liquid electrolytes. Fortunately, LCO-LLTO-10 may achieve an optimized balance between the cycling stability and charge carrier transport at cathode-electrolyte interface in this study.

Table 1. The average discharge capacities (mAh/g) of pristine LCO and LCO-LLTO-10 at different cycling rates

| Cycling Rate | 0.1 C | 0.2 C | 0.5 C | 1 C  | 2 C  | 5 C  |
|--------------|-------|-------|-------|------|------|------|
| Pristine LCO | 200   | 195   | 184   | 163  | 107  | 39   |
| LCO-LLTO-10  | 200   | 194   | 187   | 175  | 142  | 72   |

As cycling rate increases, the positive effect of the α-LLTO modification becomes more and more notable (Figure 2b-2d). The average discharge capacities of pristine LCO and LCO-LLTO-10 at the different cycling rates are listed in Table 1. After two activating cycles at 0.1 C, the specific capacities of pristine LCO are slightly lower but very closed to that of LCO-LLTO-10 at 0.2 C and 0.5 C. However, LCO-LLTO-10 exhibits remarkably higher capacities than pristine LCO when the cycling rate surpassed 1 C. Especially, the discharge capacity of LCO-LLTO-10 reaches 72 mAh/g.
at 5 C, which is 84.6% higher than that of LCO (39 mAh/g). The superior rate capacity of LCO-LLTO-10 indicates that the surface modification with a proper α-LLTO deposition time, would not only retain the conductive network for Li⁺ and e⁻ in the cathode plates, but also somehow enhance its charge transport and/or transfer.

Figure 3. (a) Electrochemical Impedance spectra of pristine LCO and LCO-LLTO-10 and the equivalent circuit model; (b) The correlation between Zre and ω⁻¹/² of pristine LCO and LCO-LLTO-10; (c, d) CV profiles of pristine LCO (c) and LCO-LLTO-10 (d) at a sweeping rate of 0.05 mV/s between 2.75 and 4.5 V.

Table 2 The polarization voltage (ΔV) of pristine LCO and LCO-LLTO-10 in 5 cycles

|        | ΔV  | ΔV₁st (V) | ΔV₂nd (V) | ΔV₃rd (V) | ΔV₄th (V) | ΔV₅th (V) |
|--------|-----|-----------|-----------|-----------|-----------|-----------|
| Pristine LCO | 0.210 | 0.206     | 0.207     | 0.209     | 0.210     |           |
| LCO-LLTO-10 | 0.230 | 0.232     | 0.232     | 0.232     | 0.232     |           |

To investigate the effects of the deposited α-LLTO on the conduction in LCO cathode plates, EIS measurements of pristine LCO and LCO-LLTO-10 are conducted at room temperature with a cathode-liquid electrolyte-stainless steel configuration.
The different intercepts on $Z_{re}$ axis of their EIS curves indicate that tested cell with LCO-LLTO-10 possesses a much smaller total resistance than the counterpart with pristine LCO. The inclined line at low frequency is derived from Warburg impedance, which is related to Li$^+$ diffusion within LCO cathode plates [34]. The Li$^+$ diffusion coefficient $D_{Li^+}$ can be calculated by Equation 1 [35]:

$$D_{Li^+} = 0.5 \times \left( \frac{RT}{AeF^2n^2} \right)^2$$

(Equation 1)

where $R$ is the ideal gas constant (J/(mol*K)), $T$ is the Kelvin temperature (K), $A$ is the effective electrochemical interfacial area (cm$^2$), $n$ is the charge number of carrier ions, $F$ is the Faraday constant (C/mol), $C$ is the Li$^+$ concentration in the unit cell volume (mol/cm$^3$), and $\delta$ is Warburg coefficient ($\Omega^*(\text{rad/s})^{0.5}$). The Warburg coefficient $\delta$ can be determined by Equation 2 [35]:

$$Z_{re} = R_{total} + \delta \omega^{-1/2}$$

(Equation 2)

where $Z_{re}$ is the Warburg impedance, $R_{total}$ is the start resistance of the oblique line, and $\omega$ is the angular frequency corresponding to the impedance sweep frequency $f(\omega=2\pi f)$. According to the $Z_{re}$ vs $\omega^{1/2}$ plots shown in Figure 3b, the $D_{Li^+}$ of LCO-LLTO-10 is determined to be $7.52 \times 10^{-12}$ cm$^2$/s, which is much higher than that of pristine LCO ($2.32 \times 10^{-12}$ cm$^2$/s). This suggests the bulk ionic conduction in the LCO cathode plates is enhanced by the deposited $\alpha$-LLTO, which can be attributed to the following facts. First, the ionic conductivity of deposited $\alpha$-LLTO is much higher than that of LCO ($\sim 10^{-8}$ S/cm) [36]. Second, the sputtering process, which is a physical vapor deposition, enables the deposited $\alpha$-LLTO to form well-contacted interfaces with LCO particles [19, 20]. Third, the deposited $\alpha$-LLTO may provide additional Li$^+$ transport pathways in the cathode plates [19,35]. Comparing with the Li$^+$ conduction in bulk, the influence of the deposited $\alpha$-LLTO on the Li$^+$ transport across LCO-electrolyte interface should be more pronounced. Thus, the measured impedance spectra are further fitted with the equivalent circuit model shown in the inset of Figure 3a. Here, $R_s$, $R_i$, and $R_{ct}$ represent the bulk resistance of electrolyte, the resistance of the solid electrolyte interphase on the surface of cathode, and the charge-transfer resistance, respectively. Consequently, LCO-LLTO-10 exhibits a much lower $R_{ct}$ (40.9 $\Omega$) than LCO (101.8 $\Omega$), indicating the
deposited $\alpha$-LLTO drastically enhanced Li$^+$ transport across LCO-electrolyte interface. The above EIS analyses suggest the charge transport in bulk and transfer at interface are both improved via the deposition of $\alpha$-LLTO on the surface of LCO cathode plate. This well agrees with the observed excellent rate capacities of LCO-LLTO-10.

It is generally believed that a decreased $R_{ct}$ would lead to a smaller polarization voltage ($\Delta V$), which is the difference between redox peaks in CV profile. Figure 3c and 3d show the CV profiles of pristine LCO and LCO-LLTO-10 for 5 sweeping cycles. The values of $\Delta V$ are summarized in Table 2. Unexpectedly, LCO-LLTO-10 exhibits larger $\Delta V$ than pristine LCO for the 5 sweeping cycles. The contradiction between the smaller $R_{ct}$ and larger $\Delta V$ for LCO-LLTO-10 can be explained as follows. The experimentally determined $R_{ct}$ for LCO-LLTO-10 may be derived from the LCO-LLTO interface, while the $R_{ct}$ for pristine LCO is derived from the interface between LCO and liquid electrolyte. As above mentioned, the physical vapor deposition leads to a well-contacted LCO-LLTO interface, in turn bring about the decreased $R_{ct}$ for LCO-LLTO-10. Meanwhile, $\Delta V$ is derived from the total impedance from liquid electrolyte to LCO. The introduction of $\alpha$-LLTO may add two interfaces in the LCO-LLTO-electrolyte configuration, which are LCO-LLTO and LLTO-electrolyte interfaces. In addition, the ionic conductivity of $\alpha$-LLTO is much lower than that of liquid electrolyte, even though it is one of the most conductive solid electrolytes. Thus, larger $\Delta V$ are observed in the sample with LCO-LLTO-10. Since the charge transfer between cathode and electrolyte generally is the rate-limiting step, and the Li$^+$ transport between $\alpha$-LLTO solid electrolyte and LiPF$_6$-based liquid electrolyte should be relative fast [35], the better rate capacity and larger $\Delta V$ observed for LCO-LLTO-10 is reasonable. More importantly, LCO-LLTO-10 maintains a constant $\Delta V$ in the 5 sweeping cycles, while the $\Delta V$ for pristine LCO varies and shows an increasing trend (Table 2). This implies that the interface between pristine LCO and liquid electrolyte is continuously degrading, while the LCO-LLTO-electrolyte configuration leads to an excellent interfacial stability.
Figure 4. XPS spectra of pristine LCO and LCO-LLTO-10 after 100 cycles: (a) Full spectra, (b) Co 2p spectra, (c) C 1s spectra, and (d) F 1s spectra.

The potential mechanisms causing the degradation of LCO cycled at high cut-off voltages include, but are not limited to, electrolyte oxidation by delithiated LCO [37], oxygen loss of LCO [38,39], Co dissolution [40], and HF corrosion at the cathode-electrolyte interface [41]. To reveal how the deposited $\alpha$-LLTO helps to stabilize the interface, the surface chemistry of the cathode plates based on pristine LCO and LCO-LLTO-10 are analyzed by XPS after 100 cycles. The signals of La, Ti and O are much stronger in the spectrum derived from the cycled LCO-LLTO-10, comparing with that derived from pristine LCO (Figure 4a). In other words, the deposited $\alpha$-LLTO still exists after 100 cycles. For LCO-LLTO-10, LCO particles would be protected from HF corrosion by the deposited $\alpha$-LLTO, if HF forms due to undesirable side reactions. In addition, the stronger O signal implies that the oxygen loss of LCO are potentially prevented by the deposited $\alpha$-LLTO. The peaks corresponding to Co 2p are almost
unobserved for LCO-LLTO-10, while that for pristine LCO is obvious (Figure 4b). The deposited $\alpha$-LLTO may prevent the diffusion of $\text{Co}^{3+/4+}$ to the surface of cathode plate and its dissolution into liquid electrolyte. The peaks around 283 eV, 285 eV, 286 eV, and 289 eV observed in C1s spectra (Figure 4c), are associated with carbon black, PVDF, polyether carbon (O-C-O), and carbonyl group (C=O), respectively [42,43]. Generally, the polyether carbon and carbonyl group are considered to result from electrolyte decomposition [42,43]. The absence of C=O peak in the curve derived from LCO-LLTO-10 demonstrates that at least part of the cacoethic side reactions are blocked by the deposited $\alpha$-LLTO. Additionally, LCO-LLTO-10 presents a much stronger peak ascribed to the absorbed liquid electrolyte solute, comparing with pristine LCO (Figure 4d). This indicates that the deposited $\alpha$-LLTO leads to a better wettability of liquid electrolyte on the surface of cathode plates, or restrains the decomposition of the liquid electrolyte. Based on the above analysis, most of the stability issues of LCO cathode at 4.5 V should be addressed by the deposited $\alpha$-LLTO.

4. Conclusions

In summary, the cycling stability and rate capacity of LCO at high cut-off voltage were improved via depositing $\alpha$-LLTO on the surface of made-up cathode plates. The effects of the deposited $\alpha$-LLTO on the LCO-electrolyte interface were studied in details. The results suggest that most of the stability issues of LCO at high cut-off voltage, such as HF corrosion, Co dissolution, and other undesirable side reactions, can be addressed by the deposited $\alpha$-LLTO. In addition, both of the Li$^+$ transport in bulk and the charge transfer across the LCO-electrolyte interface were enhanced through introducing the conductive $\alpha$-LLTO. With a proper deposition time, the surface modification by $\alpha$-LLTO enabled LCO steady cycled within 2.75 to 4.5 V vs. Li$^-$/Li, and performed a reversible capacity of 150 mAh/g at 0.2 C. At high cycling rates, the positive effects of the $\alpha$-LLTO modification would become more pronounced. The surface modification strategy for LCO presented here provides an encouraging avenue for improving the energy density and cycle life of LIBs.
Abbreviations
LIBs: Lithium ion batteries; LCO: LiCoO\(_2\); LLTO: Li\(_{3x}\)La\(_{2/3-x}\)TiO\(_3\); \(\alpha\): Amorphous; HF: Hydrofluoric Acid; SEM: Scanning electron microscopy; CV: Cyclic voltammetry; EIS: electrochemical impedance spectroscopy; XRD: X-ray diffraction; EDS: Energy Dispersive Spectrometer; XPS: X-ray photoelectron spectroscopy; PVDF: Poly(vinylidene fluoride); EC: Ethylene carbonate; DMC: Dimethyl carbonate; EMC: Ethyl Methyl Carbonate.

Availability of Data and Materials
The data supporting the conclusions of this article are included within the article and its additional files.

Competing Interests
The authors declare no competing financial interest.

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Authors’ Contributions
Shipai Song and Xiaokun Zhang conceived the experiment and carried out data analysis. Shipai Song carried out the samples fabrication with assistance from Kai Huang, Hao Zhang, and Fang Wu. Shipai Song and Xiang Peng performed the materials characterizations and electrochemical measurements. Shipai Song, Yong Xiang and Xiaokun Zhang wrote the paper. All the authors discussed the results and commented on the submitted manuscript.

References
[1] Wang L, Chen B, Ma J, et al. Reviving lithium cobalt oxide-based lithium secondary batteries-toward a higher energy density. Chem Soc Rev. 2018; 47(17): 6505-6602.
[2] Goodenough J B, Park K S. The Li-ion rechargeable battery: a perspective. J Am Chem Soc. 2013; 135(4): 1167-1176.
[3] Sun Y, Liu N, Cui Y. Promises and challenges of nanomaterials for lithium-based rechargeable batteries. Nat Energy. 2016; 1(7): 16071-16082.

[4] Ellis B L, Lee K T, Nazar L F. Positive electrode materials for Li-ion and Li-batteries. Chem mater. 2010; 22(3): 691-714.

[5] Kraytsberg A, Ein-Eli Y. Higher, Stronger, Better… A Review of 5 Volt Cathode Materials for Advanced Lithium-Ion Batteries, Adv Energy Mater. 2012; 2: 922-939.

[6] Zu C, Li H. Thermodynamic analysis on energy densities of batteries. Energ Environ Sci. 2011; 4(8): 2614-2624.

[7] Li J, Li S, Xu S, et al. Synthesis and Electrochemical Properties of LiNi0.5Mn1.5O4 Cathode Materials with Cr3+ and F- Composite Doping for Lithium-Ion Batteries. Nanoscale Res Lett. 2017; 12(1): 414.

[8] Lu L, Li S, Li J, et al. High-Performance Cathode Material of FeF3·0.33H2O Modified with Carbon Nanotubes and Graphene for Lithium-Ion Batteries. Nanoscale Res Lett. 2019, 14(1): 100.

[9] Goodenough J B, Kim Y. Challenges for rechargeable Li batteries. Chem Mater. 2010; 22: 587-603.

[10] Etacheri V, Marom R, Elazari R, et al. Challenges in the development of advanced Li-ion batteries: a review. Energy Environ Sci. 2011, 4(9): 3243-3262.

[11] Tarascon J M, Armand M. Issues and challenges facing rechargeable lithium batteries//Materials for Sustainable Energy: A Collection of Peer-Reviewed Research and Review Articles from Nature Publishing Group. 2011; 171-179.

[12] Whittingham M S. Lithium batteries and cathode materials. Chem rev. 2004; 104(10): 4271-4302.

[13] Xie J, Zhao J, Liu Y, et al. Engineering the surface of LiCoO2 electrodes using atomic layer deposition for stable high-voltage lithium ion batteries. Nano Res. 2017; 10(11): 3754-3764.

[14] Chen Z, Dahn J R. Methods to obtain excellent capacity retention in LiCoO2 cycled to 4.5 V. Electrochim Acta. 2004; 49(7): 1079-1090.
[15] Chen Z H, Dahn J R. Improving the capacity retention of LiCoO$_2$ cycled to 4.5 V by heat-treatment. Electrochem Solid-State Lett. 2004; 7: A11-A14.

[16] Zuo D, Tian G, Li X, Chen D, et al. Recent progress in surface coating of cathode materials for lithium ion secondary batteries. J Alloy Compd. 2017; 706: 24-40.

[17] Zhu Z, Chen X, Artificial interphase engineering of electrode materials to improve the overall performance of lithium-ion batteries. Nano Res. 2017; 10: 4115-4138.

[18] Kalluri S, Yoon M, Jo M, et al. Feasibility of Cathode Surface Coating Technology for High-Energy Lithium-ion and Beyond-Lithium-ion Batteries. Adv Mater. 2017; 29: 1605807.

[19] Zhou A, Dai X, Lu Y, et al. Enhanced interfacial kinetics and high-voltage/high-rate performance of LiCoO$_2$ cathode by controlled sputter-coating with a nanoscale Li$_4$Ti$_5$O$_{12}$ ionic conductor. ACS Appl Mater Inter. 2016; 8: 34123-34131.

[20] Zhou A, Xu J, Dai X, et al. Improved high-voltage and high-temperature electrochemical performances of LiCoO$_2$ cathode by electrode sputter-coating with Li$_3$PO$_4$. J Power Sources. 2016; 322: 10-16.

[21] Aboulaich A, Ouzaouit K, Faqir H, et al. Improving Thermal and Electrochemical Performances of LiCoO$_2$ Cathode at High Cut-Off Charge Potentials by MF$_3$ (M = Ce, Al) Coating. Mater Res Bull. 2016; 73: 362-368.

[22] Yang Z X, Qiao Q D, Yang W S. Improvement of Structural and Electrochemical Properties of Commercial LiCoO$_2$ by Coating with LaF$_3$. Electrochim Acta. 2011; 56: 4791-4796.

[23] Chen Y, Zhang Y, Wang F, et al. Improve the structure and electrochemical performance of LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ cathode material by nano-Al$_2$O$_3$ ultrasonic coating. J Alloys Compd. 2014; 611: 135-141.

[24] Wang Z, Wu C, Liu L, et al. Electrochemical Evaluation and Structural Characterization of Commercial LiCoO$_2$ Surfaces Modified with MgO for Lithium-Ion Batteries. J Electrochem Soc. 2002; 149: A466-A471.

[25] Ahn J, Jang E K, Yoon S, et al. Ultrathin ZrO$_2$ on LiNi$_{0.5}$Mn$_{0.3}$Co$_{0.2}$O$_2$ electrode surface via atomic layer deposition for high-voltage operation in lithium-ion batteries. Appl Surf Sci. 2019; 484: 701-709.
[26] Dai X Y, Wang L P, Xu J, et al. Improved Electrochemical Performance of LiCoO₂ Electrodes with ZnO Coating by Radio-Frequency Magnetron Sputtering. ACS Appl Mater Interfaces. 2014; 6: 15853-15859.

[27] Dai X Y, Zhou A, Xu J, et al. Extending the High-Voltage Capacity of LiCoO₂ Cathode by Direct Coating of the Composite Electrode with Li₂CO₃ via Magnetron Sputtering. J Phys Chem C. 2016; 120: 422-430.

[28] Chen J, Zhu L, Jia D, et al. LiNi₀.₈Co₀.₁₅Al₀.₀₅O₂ cathodes exhibiting improved capacity retention and thermal stability due to a lithium iron phosphate coating. Electrochim Acta. 2019; 312: 179-187.

[29] Chen R, Liang W, Zhang H, et al. Preparation and performance of novel LLTO thin film electrolytes for thin film lithium batteries. Chin Sci Bull. 2012; 57(32): 4199-4204.

[30] Zheng Z, Fang H Z, Liu Z K, et al. A Fundamental Stability Study for Amorphous LiLaTiO₃ Solid Electrolyte. J Electrochem Soc. 2015; 162: A244-A248.

[31] Zheng Z, Fang H, Liu Z, et al. A fundamental stability study for amorphous LiLaTiO₃ solid electrolyte. J Electrochem Soc. 2015; 162(1): A244-A248.

[32] Xiong Y, Tao H, Zhao J, et al. Effects of annealing temperature on structure and opt-electric properties of ion-conducting LLTO thin films prepared by RF magnetron sputtering. J Alloy Compd. 2011; 509(5): 1910-1914.

[33] Li C L, Zhang B, Fu Z.W. Physical and electrochemical characterization of amorphous lithium lanthanum titanate solid electrolyte thin-film fabricated by e-beam evaporation. Thin solid films. 2006; 515: 1886-1892.

[34] Levi M D, Salittra G, Markovsky B, et al. Solid-state electrochemical kinetics of Li-Ion intercalation into Li₁₋ₓCoO₂: simultaneous application of electroanalytical techniques SSCV, PITT, and EIS. J Electrochem Soc. 1999; 146(4): 1279-1289.

[35] Xu C L, Xiang W, Wu Z G, et al. A comparative study of crystalline and amorphous Li₀.₅La₀.₅TiO₃ as surface coating layers to enhance the electrochemical performance of LiNi₀.₈₁₅Co₀.₁₅Al₀.₀₃₅O₂ cathode. J Alloy Compd. 2018; 740: 428-435.
[36] Yu S, Wang M Y, Li Y, et al. Separating electronic and ionic conductivity in mix-conducting layered lithium transition-metal oxides. J Power Sources. 2018; 393: 75-82.

[37] Zhang J N, Li Q, Wang Y, et al. Dynamic evolution of cathode electrolyte interphase (CEI) on high voltage LiCoO2 cathode and its interaction with Li anode. Energy Storage Mater. 2018; 14: 1-7.

[38] Chebiam R V, Kannan A M, Prado F, et al. Comparison of the chemical stability of the high energy density cathodes of lithium-ion batteries. Electrochem commun. 2001; 3(11): 624-627.

[39] Ensling D, Cherkashinin G, Schmid S, et al. Nonrigid band behavior of the electronic structure of LiCoO2 thin film during electrochemical Li deintercalation. Chem Mater. 2014; 26(13): 3948-3956.

[40] Amatucci G G, Tarascon J M, Klein L C. Cobalt dissolution in LiCoO2-based non-aqueous rechargeable batteries. Solid State Ionics. 1996; 83(1-2): 167-173.

[41] Aykol M, Kim S, Hegde V I, et al. High-throughput computational design of cathode coatings for Li-ion batteries. Nat Commun. 2016; 7(1): 1-12.

[42] Zuo X, Fan C, Xiao X, et al. High-voltage performance of LiCoO2/graphite batteries with methylene methanedisulfonate as electrolyte additive. J Power Sources. 2012; 219: 94-99.

[43] Liu D, Qian K, He Y B, et al. Positive film-forming effect of fluoroethylene carbonate (FEC) on high-voltage cycling with three-electrode LiCoO2/Graphite pouch cell. Electrochim Acta. 2018; 269: 378-387.