Constructing compatible interface between Li$_7$La$_3$Zr$_2$O$_{12}$ solid electrolyte and LiCoO$_2$ cathode for stable cycling performances at 4.5 V

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With high theoretical capacity and tap density, LiCoO$_2$ (LCO) cathode has been extensively utilized in lithium-ion batteries (LIBs) for energy storage devices. However, the bottleneck of structural and interfacial instabilities upon cycling severely restricts its practical application at high cut-off voltage. From another perspective, the compatibility between electrode and electrolyte is highly valued towards all-solid-state development. Herein, we construct a compatible interface between Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) and LCO through a facile surface modification strategy, which significantly improves the cycling stability of LCO at high cut-off voltage of 4.5 V. Characterization results demonstrate that the LCO@LLZO sample delivers a desirable capacity retention of 76.8 % even after 1000 cycles at 3.0 ~ 4.5 V with the current density of 1 C (1 C = 274 mA g$^{-1}$). Further investigation indicates that the LLZO modification layer could protect the LCO electrode through effectively alleviating the side reactions, which not only facilitates the Li$^+$ transportation at interface, but also mitigates the bulk structure degradation. Moreover, it is also established that a small amount of La and Zr ions could gradenly migrate into the surface lattice of LCO to generate a thin layer of surface solid solution Li-Co-La-Zr-O. Thus formed pinning region between the surface modified LLZO and LCO cathode could contribute both to their mechanical compatibility and Li$^+$ kinetics behavior upon repeated cycling. This work not only provides a strategy in broadening the operation potential and extracting higher capacity of LCO, but also sheds light on constructing compatible interfaces in LIBs, especially for all-solid-state energy storage and conversion devices.

Introduction

Rechargeable lithium-ion batteries (LIBs) with the advantages of high-energy density, long-cycle life and environmental friendliness, 1, 2 are widely applied as energy storage and conversion components in portable electronic devices and electric vehicles (EVs). 3, 4 Among various critical steps towards advanced LIBs, the development of cathode materials with high energy density and long cycling stability is so pivotal to be a hot research topic. 5-9 The candidates of LiNi$_{1-x}$Co$_x$Mn$_2$O$_4$ (0<x<1) and lithium-rich layered materials xLi$_2$MnO$_3$((1-x)Li(TM))O$_2$ (TM = Mn, Co, and Ni) have been widely explored and developed in order to achieve high-energy density. 10-17 However, their commercial application are still hindered by the rapid voltage/capacity deterioration, as well as the structural and thermodynamic instabilities upon cycling. 15-17 For example, layered LiCoO$_2$ (LCO), the first commercialized cathode material in 1991, 18, 19 the boom in its fundamental research and new applications continues and still presents competitive edge among high-capacity cathode materials, 12, 20-25 being one preferred cathode material for portable electronics due to its high redox potential (~ 3.9 V vs. Li/Li$^+$), large theoretical specific capacity (274 mAh g$^{-1}$), high electronic conductivity (~10$^{-4}$ S cm$^{-1}$), theoretical density (~ 5.06 g cm$^{-3}$) and compressed electrode density, as well as easy preparation. 26-29 Nevertheless, it can only steadily operate at a relative lower potential range of 3.0 ~ 4.2 V in order to maintain good structural and electrochemical stabilities, 20, 30 delivering a moderate discharge capacity of only ~140 mAh g$^{-1}$. To extract more capacity, it should be charged to a higher potential (over 4.2 V, with more Li$^+$ extraction/insertion), which will inevitably sacrifice its bulk structure stability. Simultaneously, the high voltage operations are always accompanied with a series of detrimental interfacial side-reactions. 22, 29, 31 Specifically, the interfacial side reactions between Li$_4$CoO$_2$ (0.5<x<1) cathode and electrolyte components lead to severe voltage/capacity decay, accompanied with oxygen loss, surface structure degeneration (from layered structure to the spinel structure), electrolyte decomposition, and the increase of interfacial impedance, etc. 20, 27, 31-33

To address the aforementioned concerns of LCO, various modification strategies such as surface coating, bulk doping and the utilization of electrolyte additives have been extensively investigated. 34, 35 Metal oxides (MgO, 36-38 Al$_2$O$_3$, 39, 40 ZrO$_2$, 41, 42 MgAl$_2$O$_4$, 42), metal phosphates (AlPO$_4$, 43, 44 Mg$_3$(PO$_4$)$_2$) and fluorides (AlF$_3$, 45, 46 LaF$_3$, 47 MgF$_2$, 48, 49) have been extensively...
used as surface coating materials to improve the interface stability. Some metal ions (Al\textsuperscript{3+}, Mg\textsuperscript{2+}, Zr\textsuperscript{4+} etc.) especially transition metal elements have been selected as single-/multi-doping components to increase the electronic and/or ionic conductivity and structural stability of LCO.\textsuperscript{50-55} Liu et al. reported a La, Al co-doping technique for solving the long-standing issue of instability under high voltage to achieve higher capacity, wherein La acted as a pillar to expand c-axis distance and Al as a positively charged centre, to promote Li\textsuperscript{+} transport, restrain phase transition and stabilize the structure upon cycling.\textsuperscript{21} Li and Yu et al. employed a Ti-Mg-Al multi-doping strategy to achieve the stable cycling of LCO at a high cut-off voltage of 4.6 V.\textsuperscript{26} Similarly, previous literatures also confirmed the synergistic effect of surface coating and bulk doping, which not only contributed to the Li\textsuperscript{+} diffusivity but also stabilized the surface structure of LCO at high voltage.\textsuperscript{31, 55-57} Lu et al. prepared a class of ternary Li, Al, F-modified LCO using a facile hydrothermal-assisted hybrid surface treatment, and they attributed the excellent long-term cycling performance to the surface modification layer and Li-Al-Co-O-F solid solution, which effectively alleviated the loss of Co and bulk structure degradation.\textsuperscript{22} In this regard, we have explored Li\textsubscript{2}S\textsubscript{2}O\textsubscript{3} coating and F surface pinning on Li-rich cathode by two-step method and Li\textsubscript{3}V\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} coating on LNi\textsubscript{0.9}Mn\textsubscript{1.2}O\textsubscript{4} by one-step strategy, and verified their positive influence on the structural/interfacial stabilities as well as electrochemical performances of Li-rich and LiNi\textsubscript{0.9}Mn\textsubscript{1.2}O\textsubscript{4} cathode materials.\textsuperscript{8, 58} From another viewpoint, the rapid expansion of all-solid-state LIBs, with solid state electrolyte substituting traditional organic liquid electrolyte, both in fundamental research and in practical applications, has aroused great interest in the construction of compatible interfaces between solid electrolyte and electrode.

Except high ionic conductivity (~ 10\textsuperscript{-4} S cm\textsuperscript{-1}) and excellent mechanical property, garnet-type Li\textsubscript{2}La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{12} (LLZO) exhibits relative higher chemical stability from the thermodynamic point of view compared with the typical NASICON-type structured Li\textsubscript{4}Al\textsubscript{6}O\textsubscript{19}Ti\textsubscript{4}(PO\textsubscript{4})\textsubscript{3} (LATP) due to its deficiency in titanium (Ti).\textsuperscript{59-62} Herein, this promising solid-state electrolyte of LLZO has been successfully employed to modify the surface of LCO by a simple sol-gel method. It is found that a small amount of La and Zr ions could be gradiently doped into the surface lattice of LCO, besides the generation of an amorphous LLZO surface layer. In this case, the capacity retentions of LLZO modified samples could be significantly improved, which is attributed to the alleviated interface side reactions (HF attack etc.) and the enhanced surface mechanical compatibility as well as Li\textsuperscript{+} kinetics behaviour. The multi-functional surface modification of LLZO herein, paves the way for more promising prospects of LCO material in the era of all-solid-state LIBs.

**Experimental**

**Synthesis of LCO material**

The pristine LCO powder was synthesized by using a conventional molten salt method. Typically, CoO (AR, Aladdin), LiOH-H\textsubscript{2}O (98.0 %, Aladdin) and KCl (99.5 %, Aladdin) in a molar ratio of 1:0.1:1:4.0 were carefully mixed together, which were then loaded into an alumina crucible followed by calcination at 820 °C for 8 h in ambient atmosphere. After naturally cooling down to room temperature, the product was adequately washed with deionized water to remove any residue. Finally, the obtained LCO powder was thoroughly dried at 120 °C for subsequent treatments.

**Synthesis of LCO@LLZO materials**

The samples of LLZO-modified LCO (LCO@LLZO, with different weight percentages of 0.5, 1.0 and 2.0 wt. % of LLZO) were prepared by a conventional sol-gel method. The calculated amounts of LiNO\textsubscript{3} (99.0 %, Aladdin), La(NO\textsubscript{3})\textsubscript{3}-6H\textsubscript{2}O (99.0 %, Aladdin), Zr(NO\textsubscript{3})\textsubscript{4}-5H\textsubscript{2}O (AR, Kermel), and Ca\textsubscript{3}H\textsubscript{6}O\textsubscript{7}-H\textsubscript{2}O (AR, Sinopharm group chemical reagent Co., Ltd.) were respectively dissolved into anhydrous ethanol with vigorous stirring until transparent solutions were formed. Meanwhile, the as-prepared LCO powder was dispersed into anhydrous ethanol, and the above solutions were added dropwise into LCO dispersion solution with vigorous stirring. The mixed solution was then evaporated at 70 °C and dried at 120 °C to acquire a xerogel product, which was ground and calcined at 600 °C for 6 h to obtain LCO@LLZO samples with target content ratios. The scheme for the synthesis process of LCO and LCO@LLZO materials is illustrated in Fig. 1.

**Physical characterizations**

Crystalline structures of all the as-prepared materials were investigated by X-ray diffraction (XRD, Bruker D8 Advance, Germany) with Cu K\textalpha radiation (\lambda = 0.15418 nm) in 2\texttheta range of 10 °- 80°. The morphologies and microstructures were observed on scanning electron microscope (FESEM, JEOL 7001F, Japan) and high-resolution transmission electron microscope (HRTEM, FEI Tecnai G2 F20) respectively, meanwhile the structure and
element distribution were detected by electron diffraction spectroscopy (EDS) mapping and the fast Fourier transform of HRTEM image of the selected region by the software of Digital Microscopy. The chemical environments of all samples were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific, America) with Al Kα radiation (150 W, 1486.6 eV). And in-depth XPS profiles were collected on the spectrometer instrument (PHI 5000 Versa Probe-II, Japan) with Al Kα radiation (50 W, 15 kV) at a pressure of 10⁻⁶ Torr, in which argon-ion beam with a density of 25 μA mm⁻² was employed in etching process at an accelerating voltage of 2.0 kV. Fourier transformed infrared (FTIR) measurements were performed on the Nicolet AVATAR360 Fourier-transformed infrared spectrometer. The inductively coupled plasma (ICP) analysis, which was applied to determine the accurate chemical compositions and the relative proportions of elements in the samples, was conducted on Thermo Fisher ICAP 6300.

**Electrochemical Measurements**

To assemble the batteries, 80 wt. % active material (LCO or LCO@LLZO), 10 wt. % acetylene black (AB) and 10 wt. % polyvinylidene fluoride (PVDF) were firstly dissolved in N-methyl-2-pyrrolidone (NMP) solvent to obtain a slurry, which was uniformly spread onto an Al foil via a Four micro spreader and then dried in a vacuum oven at 110 °C for 12 h. Afterward, the cathode electrode foil was punched into round discs with 12 mm diameter and ~ 2.0 mg cm⁻² mass loading for cell assembly. Then, the as-prepared LCO or LCO@LLZO cathode electrodes were assembled in an Ar-filled glove box (with the contents of H₂O and O₂ are controlled below 1 ppm), using Li metal (CEL Tianjin Zhongneng Lithium industry Co., Ltd.) as counter electrode and 1 M LiPF₆ dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by volume) as electrolyte. The electrochemical performances of all LCO (LCO@LLZO)/Li half cells (CR2032-type) were evaluated via a LAND CT2001A (Wuhan, China) test instrument in the voltage range of 3.0 ~ 4.5 V. Cyclic voltammetry (CV) test at different scan rates and electrochemical impedance spectroscopy (EIS) measurement at the charged state of 4.5 V with an amplitude of 5 mV in a frequency range over 10⁻² ~ 10⁵ Hz (at room temperature) were accomplished on an electrochemical workstation (CHI660E, Shanghai Chenhua). Galvanostatic intermittent titration technique (GITT) was utilized at a galvanostatic pulse of 0.1 C for 10 min, followed by 2 h relaxation between each pulse (on LAND CT2001A). Different scanning calorimetry (DSC) analysis was measured on TA Q600 from 25 °C to 450 °C with a heating rate of 5 °C min⁻¹ in Ar atmosphere.

**Material aging analysis**

Before aging experiment, the as-prepared cathode materials (0.1 g pristine LCO and LCO@1.0 LLZO) were thoroughly dried to avoid any possible influence from the adsorbed water. Then, the powders were respectively dispersed into 50 ml electrolytes (the same as those used in electrochemical tests) in polytetrafluoroethylene (PTFE) containers, which were carefully sealed and aged at 50 °C with vigorous magnetic stirring. After specific time periods (1 and 4 weeks), 5 mL solution was carefully drawn out and followed by liquid-solid separation for subsequent ICP test to measure the concentration of dissolved Co in electrolyte.

**Results and discussion**

**Microstructural and morphological characterizations**

The collected XRD patterns and the corresponding Rietveld refinements of the LCO and LCO@LLZO powders are shown in Fig. 2a and Fig. S1a-d, from which no obvious difference could be observed after LLZO surface modification. The main diffraction peaks could be clearly indexed to the layered LCO with α-NaFeO₂ structure and R₃̅m space group (JCPDS No. 50-0653). Generally, the distinct separation of (006)/(012) and (100)/(110) peaks as well as appropriate c/a ratio (over 4.96) indicate the well-developed layered structure of LCO cathode material.54-66 The intensity ratio of I(003)/I(104) represents the degree of cation mixing in LCO bulk material, that is, the higher ratio indicates the lower disorder degree of cations in LCO structure.64-66 The detailed lattice parameters, I(003)/I(104) and c/a values, are calculated for all the as-prepared samples, as shown in Table S1. There is no significant change in the lattice parameters of all samples, suggesting LLZO surface modification influences little on the bulk structure of LCO. It is worth noting that the I(003)/I(104) values of LCO@LLZO samples are generally higher compared with that of LCO, implying the cationic mixing could be effectively mitigated after LLZO surface modification. No diffraction peak of LLZO appears in the XRD spectra of all LCO@LLZO samples even with high LLZO coating content of 5.0 wt. % (Fig. S1e), which indicates that the LLZO...
coating layer might be intrinsically amorphous under the lower calcination temperature since the LLZO was crystallized at a higher temperature of 870 °C in the control experiment (Fig. S1f).

SEM investigations in Fig. 2b display that all the as-prepared samples are composed of uniform particles, with average particle size of ~ 500 nm. Careful observation indicates that the surfaces of LCO@LLZO samples become more and more rough with increased coating content compared with that of pristine LCO, implying the success of LLZO deposition. Typically, the element distribution of LCO@1.0 LLZO material was characterized by EDS mapping analysis (Fig. 2c). It is found that La and Zr elements are evenly distributed on the surface of LCO particles, confirming the existence of LLZO modification. Additionally, HRTEM image in Fig. 2d provides more detailed microstructure information of LCO@1.0 LLZO. A distinct amorphous modification layer with a thickness ~ 5 nm (region I) could be found on the surface of the 1.0 wt. % LLZO treated LCO, while the pristine LCO particle presents sharp boundary (shown in the inset of this figure). The bulk lattice fringes with the interplanar distances of 0.47 and 0.24 nm (region III) are clearly observed before and after modification, which could be assigned to the (003) and (101) planes of the LCO hexagonal phase. With LLZO modification, a relatively increased lattice distance is found in the transition region II compared with bulk region III. This could be most possibly induced by the trace surface doping of La and Zr ions from the LLZO modification layer, with larger radii than that of the Co ion. It should be emphasized that the amorphous phase of LLZO layer is further proved by the fast Fourier transform image of the selected area (in the inset blue rectangular), consistent with the previous XRD results (Fig. 2a). The homogeneous LLZO surface modification layer herein might effectively prevent the direct contact of LCO cathode material with electrolyte, which could play an important role in improving the electrochemical stability of LCO cathode. In addition, ICP analysis indicates that the actual contents of LLZO are 0.35, 0.81, and 1.79 wt. % respectively, for the LCO@LLZO materials with nominal modification amounts of 0.5, 1.0 and 2.0 wt. %. For simplicity, the modified materials are still labelled as LCO@0.5, 1.0 and 2.0 LLZO hereafter.

XPS spectra (Fig. S2) were recorded to explore the chemical environment of the all as-prepared materials. Careful observation indicates that the valence states of Co, La and Zr remain almost unshifted after LLZO surface modification. The signal intensities of Co 2p1/2 (794.74 eV) and Co 2p3/2 (779.80 eV) corresponding to the peaks of Co3+ are gradually weakened with increased LLZO modification content, which could be ascribed to the shielding effect of the LLZO modification layer. The lower binding energy (529.30 eV) of O 1s is generally representative for the lattice oxygen in the near-surface region of LCO with crystalline phase, and the higher peak (531.30 eV) could be identified as the surface oxygen.

The surface oxygen gradually strengthens in its relative intensity compared with that of the lattice oxygen with the increase of LLZO content, which confirms the success of LLZO surface deposition from another aspect. The signals of Zr 3d and La 3d appear in the spectra of all LCO@LLZO materials, which are absent in that of the pristine LCO sample, undoubtedly confirms the LLZO surface modification on the surface of LCO. Clearly, the peaks of La 3d3/2 (834.82 eV) and La 3d5/2 (838.80 eV), belonging to the trivalent La3+, as well as those of Zr 3d3/2 (181.95 eV) and Zr 3d5/2 (184.46 eV) from the quadrivalent Zr4+, gradually enhance in their intensities when increasing the LLZO coating contents.

To find more details of LLZO modification layer on LCO particle, in-depth XPS analysis was performed with an etching gap of 85 s per strip. The signals of Co 2p, O 1s, La 3d and Zr 3d were recorded along with successive etching treatment from surface to the near surface lattice of LCO@1.0 LLZO sample. Prominently, the intensities and their normalized results (Fig. 3a and b) of La 3d and Zr 3d decrease along with etching, accompanied with the gradual enhancement of the Co 2p signals. As for the signal of O element, the lattice O enhances in its intensity with the prominent intensity decay of surface O, in good accordance with the microstructure analysis in Fig. 2d. The above results clearly indicate that a small amount of La and Zr ions could be gradually migrated into the near surface of LCO lattice (corresponding to the slight lattice parameter change in region II, Fig. 2d), generating a Li-Co-La-Zr-O surface solid solution as a pinning/intermediate region, which could not only enhance the surface mechanical compatibility and strengthen the surface stability between the LLZO solid electrolyte and the active material LCO (as reported in previous literatures, surface solid solution will contribute to stabilizing the subsurface structure of active materials), but also will promote the surface Li+ kinetics upon cycling.
Electrochemical characterizations

Electrochemical performances of the as-prepared samples were systematically investigated by galvanostatic charge-discharge tests within the voltage range of 3.0 ~ 4.5 V at the current density of 0.1 C for the first five cycles and 1 C (1 C = 274 mA g⁻¹) for the subsequent cycles. As shown in Fig. 4a, the LLZO treated materials generally exhibit significantly enhanced capacity retentions compared with that of the pristine LCO. Besides the obvious improvement in capacity retention of LCO@1.0 LLZO electrode compared with the pristine material under 0.1 C (inset of Fig. 5a) and initial capacity (Fig. S3b), significant enhancement could also be observed under high current density test (Fig. S3a). Specifically, the LCO@1.0 LLZO treated material displays the distinctly improved capacity retention of 76.8 % after 1000 cycles (Fig. S3a) under 1 C, much higher than that of the pristine LCO (41.9 %) and relatively effective compared with the previously reported modification strategies (Table S2). Rate performances in Fig. S3c indicate that the rate capability of LCO electrode could be effectively promoted by LLZO modification, wherein the sample of LCO@1.0 LLZO again, displays the optimal rate performance. The discharge curves of the pristine and 1.0 wt. % LLZO modified samples are compared in Fig. 4b. Not surprisingly, the capacity degradation of LCO@1.0 LLZO is prominently alleviated relative to that of pristine LCO, and from another viewpoint, the attenuation of discharge median voltage is also greatly mitigated (Fig. 4b and c), which will synergistically contribute to the high energy density of LCO electrode. The inhibition of capacity and voltage fade could be preliminarily attributed to the enhanced structure stability and improved Li⁺ kinetics behaviour at the particle surface.

To further explore the modification mechanism of LLZO on LCO cathode material, CV analysis of LCO and LCO@1.0 LLZO electrodes was performed in the range of 3.0 ~ 4.5 V with the scanning rate of 0.05 mV s⁻¹. As shown in Fig. 5a, both CV profiles of the pristine and 1.0 wt. % LLZO modified electrodes exhibit a reduction peak at ~ 3.9 V (corresponding to O3 phase transition), and two minor peaks at around 4.1 and 4.2 V (associated with order-disorder reversible transition near Li₂O₂CoO₂).²¹, ³⁹, ⁷⁴ It is clear that the redox peaks are generally sharper for LCO@1.0 LLZO (smaller full width at half maximum) compared with those of the pristine LCO, indicating facilitated Li⁺ kinetics behaviour in the modified electrode.²² Moreover, the potential differences of corresponding oxidation/reduction peaks are dramatically reduced after LLZO surface modification, confirming the effectiveness of LLZO coating layer in polarization restriction.²³ The above results of enhanced Li⁺ kinetics and alleviated polarization well explain the significantly improved rate capability of LCO@1.0 LLZO in Fig. S3c.

CV tests at different scanning rates were also performed on the pristine and LCO@1.0 LLZO electrodes (Fig. 5a, b) in order to accurately evaluate the apparent Li⁺ diffusion coefficients (D_li⁺) in the materials, which were calculated from the following equation:

\[ I_p = (2.69 \times 10^9)n^{3/2}D_{Li^+}^{1/2}C_{Li^+}^{1/2} \]  

in which \( I_p \) is the peak current, \( n \) is the number of charge transfer, \( A \) is the electrode area, \( C_{Li^+} \) is the Li⁺ concentration in cathode, and \( v \) is the scan rate. As demonstrated in Fig. 5c, the values of \( D_{Li^+} \) are calculated to be 2.13 \times 10⁻¹¹ (during delithiation state) and 4.65 \times 10⁻¹² cm² s⁻¹ (during lithiation state) for the pristine LCO, which could be prominently enhanced to 1.57 \times 10⁻¹⁰ (during delithiation state) and 2.87 \times 10⁻¹¹ cm² s⁻¹ (during lithiation state) for LCO@1.0 LLZO electrode. GITT test was also applied to investigate the Li⁺ diffusion behaviours during intercalation/deintercalation in the initial cycling. When \( E \) is linear with \( t^{1/2} \), the \( D_{Li^+} \) values could be calculated by the simplified equation:

\[ D_{Li^+} = \frac{4}{\pi t} \left( \frac{m_B V_m}{M_B S} \right)^2 \left( \frac{\Delta E}{\Delta t} \right)^2 \]  

wherein, \( t \) is relaxation time, \( m_B \) is mass, \( M_B \) is molecular, \( V_m \) is molar volume, \( S \) and \( L \) are the thickness and surface area of the electrode material, \( \Delta E \) is the difference between two steady-state voltages and \( \Delta E \) is the voltage change of constant current charge/discharge. The \( D_{Li^+} \) of single titration profiles (Figs. S5) around 3.91 and 3.93 V marked by the arrows are calculated to be 6.40 \times 10⁻¹¹ and 1.64 \times 10⁻¹¹ cm² s⁻¹ for the pristine and 1.0 wt. % LLZO modified LCO samples during the lithiated state. It is clear that both CV and GITT results unambiguously prove that a facilitated Li⁺ kinetics behaviour could be obtained by LLZO surface modification, which will be further discussed and explained in the following EIS analysis.

EIS tests were conducted at the deep delithiated state of 4.5 V after different cycles. As could be observed in the Nyquist plots (Figs. 5d and e), two semicircles locate in high/middle-
frequency regions followed by an oblique line in the low-frequency region. The equivalent circuit is drawn in the inset of Fig. 5d, wherein the $R_s$, $R_{Li}$, $R_d$ and $W_1$ represent the ohmic resistance related with the intercept in the high-frequency region, the resistance of the cathode-electrolyte interface film (CEI) (high-frequency), the charge transfer resistance of the Li$^+$ diffusion in the space charge layer (middle-frequency) and the Warburg impedance of the solid-state diffusion of Li$^+$ in the bulk (low-frequency), respectively.\textsuperscript{8, 40, 77} In Figs. 5d and e, it is clear that the radii of two semicircles for both electrodes grow gradually upon cycling. The fitted values of $R_d$ and $R_s$ are listed in Table S3 and visually compared in Fig. 5f with the normalized resistances based on the first cycle. More sluggish growth of $R_d$ and $R_s$ values for LCO@1.0 LLZO could be observed, indicating that the LLZO modification could effectively inhibit undesirable side reactions and accelerate the Li$^+$ kinetics behaviour at the cathode/electrolyte interface, which could contribute to the enhanced interface stability and cell longevity. The Li$^+$ diffusion coefficient $D_{Li^+}$ could also be calculated by the following equations:

$$D_{Li^+} = \frac{q^2T^2}{4k_nF^2C_L^2}$$  

$$Z_{real} = K - \sigma \omega^{-1/2}$$

herein, $R$ is the gas constant, $T$ is the absolute temperature, $A$ is the surface area of the electrode, $n$ is the number of the electrons associated in the oxidation–reduction reaction, $F$ is the Faraday’s constant, $C$ is the concentration of Li$^+$, $\sigma$ is the Warburg factor which equals to the plot slope of $Z_{real} - \omega^{-1/2}$ line, and $\omega$ is the angular frequency. Thus the $D_{Li^+}$ value of LCO electrode is calculated to be $2.19 \times 10^{-12}$ cm$^2$ s$^{-1}$, lower than that of LCO@1.0 LLZO ($2.45 \times 10^{-11}$ cm$^2$ s$^{-1}$), which is also consistent with the previous CV and GITT test (Fig. S5) results. From different aspects herein, the kinetics behaviour after LLZO modification has been established to be significantly enhanced, undoubtedly confirming the advantages of side-reaction inhabitation and surface solid solution contribution in accelerating Li$^+$ diffusion at the interface of LLZO solid electrolyte and LCO.

The depression of surface HF corrosion and detrimental side reactions by LLZO could also be verified by FTIR spectra analysis. Fig. S6 compares the FTIR vibrations of LCO and LCO@1.0 LLZO electrodes before and after 20 cycles. The characteristic vibrations in the range of 500 ~ 700 cm$^{-1}$ are ascribed to the asymmetric stretching of Li-O and Co-O bonds.\textsuperscript{63, 66} Although the curves between LCO and LCO@LLZO are similar, more absorption peaks appear with stronger intensities in the spectrum of LCO electrode with respect to that of the LCO@1.0 LLZO, as revealed in the figure. These new bands could be assigned to the typical ingredients of CEI film composed of Li$_2$CoO$_3$, RCOOLi and ROCO$_2$Li (Table S4), generated from the inevitable surface side reactions during electrochemical cycling.\textsuperscript{77, 81} The suppression of side-reactions by LLZO surface modification are consistent with the previous EIS results (Fig. 5d and e), which contribute both to the interface stability and the surface kinetics as discussed in the former context, finally leading to prominently enhanced electrochemical performances.

Generally, the HF attack and detrimental side reactions at high voltage could lead to the dissolution of transition metal ions from the surface lattice upon cycling, which will inevitably inducing bulk structural degradation.\textsuperscript{75, 82, 83} Fig. S7a displays the XRD patterns of the pristine and 1.0 wt. % LLZO modified LCO samples after 100 cycles at a high cut-off voltage of 4.5 V and an elevated temperature of 55 °C, in which the characteristic peak of (006) disappears for both samples and new minor peaks (assigned to CoO, marked with asterisks) appear in the cycled pristine LCO, suggesting more significant structural degradation for the bare sample.\textsuperscript{58, 84} From another perspective, the broadened main diffraction peak (003) for the pristine LCO electrode is more remarkable compared with that of the LCO@1.0 LLZO electrode, which also confirms the more robust structural stability after LLZO surface modification upon cycling. The morphology degradation for the pristine and cycled LCO@1.0 LLZO electrodes are intuitively compared in Fig. S7b. Obviously, the surface topography of the pristine LCO decays significantly compared with that of LCO@1.0 LLZO after the same electrochemical treatment. More impurities enwrapped outside the particle of pristine LCO, verifying the results of more sever side-reactions in the above FTIR analysis and XRD pattern. All these results unexceptionally indicate that the LLZO modification could effectively suppress the growth of CEI and promote the structure stabilization of LCO cathode material.

The aging experiment of the pristine and LCO@1.0 LLZO samples has also been conducted and the measured Co contents in electrolytes have been qualitatively illustrated in histogram of Fig. S8 and quantitatively compared in Table S5. As could be observed in Fig. S8, the Co dissolution deduced by HF
attack in the electrolyte become more prominent with aging time, reflecting structure degradation both in the pristine and LCO@1.0 LLZO materials. And it should be noted that the dissolution of Co ions in the LCO@LLZO sample is generally more mildly than that in the pristine material. This finding from another perspective implies that the LLZO modification layer is beneficial to the HF resistance and structure stabilization of LCO in chemical aging process, again confirms the previous XRD results in Fig. S7a.

Besides the electrochemical exploration, the influence of LLZO surface modification on the thermal stability of bulk LCO was further detected by DSC analysis. As displayed in Fig. S9a, the exothermic peak of LCO@1.0 LLZO electrode is delayed to a higher temperature (12 °C difference) with a reduced peak area compared with that of pristine LCO, indicating that the thermal stability of LCO could be effectively ameliorated by LLZO modification, which is also confirmed by the electrochemical tests under high temperature (55 °C). Fig. S9b compares the capacity retentions of LCO and LCO@1.0 LLZO electrodes, which clearly shows that the modified electrode not only delivers a higher capacity in the initial cycle (187.1 vs. 180.6 mAh g⁻¹), but also remains significantly improved capacity retention rate even after 200 cycles (56.8 % vs. 25.5 %). This could be attributed to the enhanced interface stabilities derived from the inhibition of side-reactions and the ameliorated interface compatibility.

Conclusions

In this work, a facile approach of synergetic LLZO surface modification and accompanied La, Zr surface doping is applied to improve the interface and cycling stabilities of LCO cathode material at high voltage. With the optimal content of LLZO modification, the LCO@1.0 LLZO electrode exhibits significantly improved electrochemical performances, including rate capability, cycling and thermal stabilities. Specifically, its capacity retention could be significantly increased (by 35.9 %) compared with that of pristine LCO even after 1000 cycles at the high voltage of 4.5 V under 1 C. Intensive investigations indicate that the enhanced performances of LCO@1.0 LLZO could be attributed to the synergistic effect of LLZO surface coating and the generated Li-Co-La-Zr-O surface solid solution originated from gradient element doping. As illustrated by Fig. 6, the amorphous LLZO modification layer could effectively protect LCO cathode from electrolyte erosion (HF attack) upon cycling, thereby suppressing the progressive accumulation of undesirable surface side reactions associated with insulating CEI formation to improve both the interfacial stability and Li⁺ diffusion behaviour. On the other hand, the gradiently doped La and Zr elements could contribute to the formation of Li-Co-La-Zr-O surface solid solution as a pinning region, which is not only beneficial in enhancing the interface compatibility and mechanical/structure stability under repeated Li⁺ delithiation/lithiation, but also could promote the Li⁺ diffusion kinetics at the interface. The multifunction of solid electrolyte LLZO surface modification, taking the full advantage of electrode-electrolyte separation and surface pinning effect, effectively enhances the interface stability and kinetics behaviour of LCO cathode material under high cut-off voltage. This work is believed to accelerate the broader application of high energy density LCO material. Moreover, the construction and optimization between the interface of solid electrolyte and active material provides a valuable strategy to address the bottleneck of interfacial concerns in the development of all-solid-state LIBs as well as the other secondary energy storage and conversion devices.

Conflicts of interest

There are no conflicts to declare.

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Notes and references


