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A high-wettability composite lithium anode for garnet-type solid-state electrolyte and copper current collector

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ABSTRACT

Garnet-type Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂ (LLZTO) solid-state electrolyte, due to its high ionic conductivity and excellent electrochemical stability with lithium, presents considerable potential for application prospects in solid-state lithium metal batteries (SSLMBs). Nevertheless, the poor wettability of the lithium anode with LLZTO solid-state electrolyte leads to contact defects and interface deterioration during cycling, resulting in pronounced lithium dendrite growth. A composite lithium anode (Li-KCO) has been developed by simply incorporating low-cost K₂CO₃ powder into molten lithium, demonstrating markedly improved wettability with LLZTO compared to pure lithium. Additionally, this composite anode exhibits excellent wettability with various other substrates, enabling a rapid formation of an ultra-thin lithium layer (~ 5 µm) on copper foil. Furthermore, Li-KCO |LLZTO interface composed of LiC₆ and Li₂O constructs *a* ion-electron conductive layer, achieving uniform lithium plating-stripping process and facilitating the diffusion of lithium ions (Li⁺), thus inhibiting the growth of lithium dendrites. Consequently, the symmetric cell has achieved a high critical current density of 1.0 mA cm⁻² a long with an extended cycle life of 4500 h at 0.2 mA cm⁻² at room temperature and 2500 h at 0.8 mA cm⁻² at 00 °C. Coupled with LiFePO₄ cathode demonstrates stable cycling performance for 120 cycles at 0.5 C with an initial discharge capacity of 154.5 mAh g⁻¹. This work provides pragmatic insights for the advancement of high-performance SSLMBs and ultra-thin lithium metal anodes.

1. Introduction

Lithium ion batteries, as critical energy storage devices, play a significant role in reducing carbon emissions yet accompaning by safety concerns and issues related to energy density [1]. Solid-state lithium metal batteries (SSLMBs), considered a promising development path for energy storage technology, are anticipated to address these challenges owing to their safety advantages and compatibility with lithium metal anode (3860 mAh g⁻¹, -3.04 V vs standard hydrogen electrode) which shows high energy density [2,3]. Hitherto, numerous solid-state electrolytes (SSEs) have been investigated and developed for constructing high-performance SSLMBs. In particular, garnet-type solid electrolyte (Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂, LLZTO) is preferred as the prospective electrolytes owing to its satisfactory ionic conductivity ($10^{-4} \sim 10^{-3}$ S cm⁻¹), broad kinetically stable electrochemical window (0–6 V, vs Li⁺/Li) that enables matching with high-potential cathodes, and stability towards lithium metal [4–6].

Unfortunately, despite the merits mentioned above, applications based on LLZTO in SSLMBs remain constrained by the excessive interfacial resistance that arises from the inadequate contact between the rigid garnet-type SSEs and lithium anode [7,8]. The poor interface with detrimental defects adversely affects the tightness of the solid-to-solid contact, while restricted contact area causes a non-uniform current distribution during cycling [9]. Li preferentially deposits in local areas with electron aggregation, which leads to an inhomogeneous distribution of Li⁺ throughout the cycling process [10]. Subsequently, as the number of voids escalates throughout the repeated lithium stripping process, the quality of interface contact progressively deteriorates. Additionally, the uneven distribution of lithium nucleation sites further exacerbates the formation of uncontrolled lithium dendrites and their infiltration into the electrolyte, eventually causing battery short-circuit failure (Fig. 1a). Therefore, enhancing the interfacial contact is generally recognized as crucial not only for minimizing the interfacial resistance, but for regulating lithium deposition along with mitigating the

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Received 19 February 2025; Received in revised form 9 April 2025; Accepted 12 April 2025 Available online 14 April 2025 0925-8388/© 2025 Published by Elsevier B.V. growth of lithium dendrites. [10,11].

Diverse initiatives have been undertaken to optimize the interfacial contact between LLZTO and lithium metal anode[12,13]. Reported methods include magnetron sputtering (MS) [14–16], atomic layer deposition (ALD) [17,18], tailoring wettability of lithium [19–21], and other methods [22–24]. While MS and ALD achieve precise and uniform deposition of interfacial layers, MS necessitates a high vacuum environment with substantial investment, and faces challenges in the large-scale fabrication of ultra-thin lithium metal on copper foil[25,26]. ALD encounters issues such as elevated equipment costs, low production efficiency, and precursor purity requirements[27]. Thus, methods with lower cost and higher efficiency still remain to be developed [20,21,28].

In this work, we report a low-cost and effective strategy to improve the wettability of the molten lithium with LLZTO by introducing K₂CO₃ powder to construct a composite lithium anode (Li-KCO). An interface featuring a stable ion-electron transport channel, composed of Li₂O and LiC₆, was generated in situ, improving the long-term cycling stability of the battery. The Li₂O functioned as an electron-blocking layer to suppress lithium dendrites formation and growth at interface [29]. While the LiC₆ ensured the homogeneous distribution of Li⁺ and strengthened the tightness of interface contact [30]. Besides, Li-KCO composite of high wettability exhibited rapid adhesion to various substrates, ultra-thin composite lithium anode can be obtained by simply coating onto copper foils. Consequently, low cost construction of high wettability lithium composite enables rapid wetting of LLZTO surface, intimate interface contact inhibiting local current hot spots, thus realizing superior electrochemical performance for the garnet-based lithium-metal batteries. The incorporation of K₂CO₃ improves the wettability of lithium metal in LLZTO and copper foils, eliminating the necessity for complex equipment or costly raw materials, thereby facilitating the large-scale production of high-performance SSLMBs and ultra-thin lithium metal.

2. Experimental section

2.1. Fabrication of Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂ (LLZTO) ceramic pellets

Stoichiometric ratios of Li₂CO₃, La₂O₃, ZrO₂ and Ta₂O₅ powders were mixed and grounded followed by heating at 900 °C in the alumina crucibles covered with alumina lids for 6 h. Subsequently, the mixed powders were ground in a ball mill for 12 h and then pressed using cold isostatic pressing at 220 MPa. Afterwards, the green pellets, covered with the identical mother powders in the alumina crucible to mitigate the lithium loss when heating in air, resulting in dense pellets with 10 mm in diameter approximately after annealed at 1140 °C for 16 h. At last, the prepared LLZTO pellets were polished using sandpaper with grits of 180, 500, 1000 and 5000 to achieve a clean and flat surface, while yielding an expected thickness of approximately 1 mm. The Archimedes ethanol displacement method was employed to ascertain the relative density of the LLZTO pellet.

2.2. Preparation of Li-KCO composite anode

Fresh lithium sheets were positioned in stainless steel container and heated to 350 °C on a heating platform. After molting, stainless-steel tweezers were utilized to cautiously eliminate the surface contaminants until the molten lithium displayed a metallic sheen. Immediately, K_2CO_3 powders were added into molten lithium in the designed mass ratio. Following the mixture was repeatedly stirred by stainless-steel tweezers until it was completely reacted and well mixed. The entire



Fig. 1. Schematic illustration depicts the preparation processes for (a) molten lithium and (b) Li-KCO, as well as the resulting interface contact behaviors with LLZTO. Poor interface contact with voids is rapidly converted into intimate contact through the incorporation of K_2CO_3 additive, which is conducive to uniform Li⁺ deposition and undesirable lithium dendrites suppression. (c,d) The digital photographs of contact angle for pure Li|LLZTO and Li-10KCO|LLZTO. (e,f) The cross-sectional SEM images of the pure Li|LLZTO and Li-10KCO|LLZTO interface. (g-i) Demonstration of contact angle for Li-10KCO composite anode on different sub-strates. (j) The cross-sectional SEM images of the Li-10KCO composite anode coated on copper foil.

procedure was conducted within an argon-filled glove box, maintaining oxygen and water content less than 0.1 ppm.

2.3. Cell assembly

To fabricate the Li-KCO|LLZTO|Li-KCO symmetrical cells, the LLZTO pellets were immersed in the molten Li-KCO composite at 350 °C, so that both sides are completely coated, followed by being sealed in CR2032 coin cells. For Li|LLZTO|Li cells, lithium sheets were also melted at 350 °C and removed impurities before the LLZTO pellets were immersed in, other steps are similar to those mentioned above. As for the LiFePO4 (LFP) cathode, which was synthesized by combining LFP powder, Super P, and polyvinylidene fluoride (PVDF) in a mass ratio of 8:1:1 with adding a suitable quantity of N-methyl-2-pyrrolidone (NMP). The mixture was stirred at a rotation velocity of 800 rpm s^{-1} for 24 h in a stirrer to create a homogeneous slurry. The slurry was evenly coated onto aluminum foil, later dried at 120 °C for 12 h in a vacuum oven. Afterwards, the foil was cropped to disks with a diameter of 8 mm. The mass loading of the active substance was approximately 2 mg cm^{-2} . To assemble the full cells, 10 µL of liquid electrolyte (1 M LiPF₆ in EC: DMC: DEC = 1: 1: 1 in volume) was introduced to improve the interfacial contact between the cathode and LLZTO by wetting the cathode surface. Finally, it is sealed in CR2032 coin cells under 5 MPa.

2.4. Electrochemical measurements

Electrochemical impedance spectroscopy (EIS) was measured utilizing an electrochemical workstation (Zahner Zennium) over a frequency range of 1 MHz to 0.01 Hz, with an AC amplitude of 10 mV. To assess ionic conductivity, gold electrodes were sputtered onto both surfaces of the LLZTO pellet for each side 10 min. The Au|LLZTO|Au cells were tested at various temperatures ranging from 30 °C to 80 °C. As for the electronic conductivity, conductive silver slurry pasted carefully on both surfaces of the polished LLZTO pellet, followed by curing at 120 °C for 40 min to fabricate Ag|LLZTO|Ag cells. The DC polarization for measuring electronic conductivity was performed at 1 V for 3600 s. The galvanostatic charge and discharge tests were carried out on the battery testing system (LAND CT2001A). The critical current density (CCD) tests are conducted in increments of 0.1 mA $\rm cm^{-2}$ for symmetric cells, with each charging and discharging cycle lasting half an hour. The full cells were evaluated within a cut-off voltage spanning from 2.5 to 4.0 V.

2.5. Materials characterization

The phase formation of the samples was recorded on an X-ray diffractometer (XRD, Rigaku Smart Lab SE) with Cu K α radiation (λ = 1.54 Å) at 40.0 kV in the 20 range of 10° to 80° with 5° min⁻¹. The feld-emission scanning electron microscopy (SEM, Hitachi SU8010) and energy dispersive spectroscopy (EDS, Oxford Instruments) were carried out on the microstructure and component analysis of samples respectively. The X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific K-Alpha) spectra were collected with Al K α radiation.

3. Results and discussion

3.1. Wettability of the composite lithium anode

The composition and the structure of the LLZTO electrolyte pellets used in this work are characterized by materials analysis techniques. The XRD patterns of LLZTO powders and pellets, as depicted in Figure S1a, can be matched to the garnet-type Li₅La₃Nb₂O₁₂ (PDF#45–0109) which aligns well with prior published studies [31,32]. The LLZTO pellet with stronger peak strength is attributed to the better crystallinity after sintering [33]. To reduce the presence of Li₂CO₃ impurities, the LLZTO pellet is carefully polished using sandpaper of different grit sizes to

achieve a flat and smooth surface. As observed in the cross-sectional images and element distribution of the LLZTO pellet (Figure S2) obtained through SEM and EDS, the sample exhibits clear and densely arranged grains, which is consistent with the high relative density results (91.3 %, Table S5) determined by the Archimedes drainage method. Hence, the prepared LLZTO pellet exhibits a high ionic conductivity (σ) of 5.2 × 10⁻⁴ S cm⁻¹ at room temperature (Figure S1b). As shown in Figure S3, according to the EIS spectra of Au/LLZTO/Au within the temperature range of 30 °C to 80 °C, the total impedance of LLZTO at different temperatures is measured. Stemed from EIS profiles obtained at different temperatures yielded an Arrhenius plot for the LLZTO pellet, indicating its activation energy (Ea) of around 0.37 eV (Figure S1c). The equivalent circuit of EIS spectrum fitting is depicted in Figure S4.The computed parameters of σ and Ea are in accordance with reports in the current literature [34]. In addition, the electronic conductivity of LLZTO, as measured by the i-t curve, is 5.16×10^{-10} S cm⁻¹ (Figure S1d). Hence, qualified LLZTO was synthesized.

Firstly, the wetting performance of the Li-KCO composite and pure lithium on LLZTO are investigated. When the polished LLZTO pellet was immersed into the pure molten lithium, its poor wettability towards garnet electrolyte hindered the formation of a tight interface with LLZTO (Fig. 1a). Molten lithium is hemispherical on LLZTO, exhibiting a contact angle of 62° (Fig. 1c), which signifies its high surface tension [35]. The morphology of the crosssection of Li|LLZTO interface was characterized by SEM. Fig. 1e reveals the interface with defects like huge voids where inhomogenous lithium ion transport through, and are going to be the hotspots for lithium dendrites formation since concentration of local current density [36]. To develop a composite lithium anode achieving superior Li|LLZTO interface intimate contact with uniform Li⁺ deposition and fast diffusion ability, defined as Li-10KCO composite hereafter, is synthesized via adding 10 wt% K₂CO₃ powders into molten lithium with continuous stirring at 350 °C (Fig. 1b). The composition and morphology of commercial K₂CO₃ powders are examined for quality qualified (Figure S5). Conversely, the Li-10KCO composite anode demonstrates remarkable wettability, reflected in a low contact angle of around 18° (Fig. 1d). The substantial reduction in contact angle from 62° to 18° indicates a rapid decrease in surface tension, which is advantageous for the efficient wetting on LLZTO pellet. From the distinction between Video S1 and Video S2, the surface tension was largely decreased via the introduction of K₂CO₃. The Li-10KCO composite exhibited excellent fluidity and spreaded out flat on LLZTO pellet within 2 s, while pure molten lithium faild to contact on electrolyte surface. Furthermore, Fig. 1f demonstrates seamless interface contact, devoid of gaps and voids, validating the tight and robust contact in microscale. These analysis confirm that Li-10KCO composite promote wettability against LLZTO pellet, thereby facilitating intimate contact.

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With the purpose of demonstrating the wettability and versatility of this material, we also studied this lithium composite on the basis of welding method using several familiar substrates, including copper (Cu) foils, stainless steel (SUS) foils and titanium (Ti) foils. The wetting experiment verification of these three types of substrates is completed at a temperature of 210 $^\circ\text{C}.$ Pure molten lithium assumes hemispherical droplet on Cu foil with a contact angle of 88°, showing a poor contact between pure Li and the Cu foil (Figure S6a). In contrast, the molten Li-10KCO composite spontaneously spreads on the Cu foil with a small contact angle of 22° (Fig. 1g). From the comparision of video S3 and S4, it is apparently that the molten Li-10KCO composite is able to rapidly extend throughout the whole Cu foil within 2 s. Using doctor-blade casting approach to spread and to control the thickness of the Li-10KCO composite on the Cu foil, obtained lithium composite can be as thin as 5 µm (Fig. 1j). The Li-10KCO composite demonstrates excellent wettability with the Cu foil, making it possible to construct ultra-thin

lithium metal film for anode or pre-lithiation applications [37,38]. Similar improvements to wettability can be achieved on stainless steel and titanium substrates. As shown in Figure S6b, obviously, the molten lithium depicts its lithiophobic towards SUS foil with a pristine droplet shape of huge contact angle. Video S5, in addition, verifies this poor wettability of pure lithium. In contrast, the Li-10KCO composite coats better on the SUS foil with a inferior contact angle of 62° (Fig. 1h). Video S6 demonstrates that Li-10KCO composite have faster spreading speed at the same time. Figure S6c and Fig. 1i depicts that Ti foil wetted by the molten lithium and the Li-10KCO composite with significant differences of contact angle, the latter can be uniformly coated on it simply. According to the video S7 and video S8, although molten lithium can partially wet Ti foil, the Li-10KCO composite covered almost the entire area. These results demonstrate the impressive wettability for battery application of this lithium composite coating various substrates.

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It is noteworthy that this composite anode method and its cost has comparitive advancement in recent reports (Figure S7a and Table S1). In addition, as illustrated in Figure S7b, the addition of 10 wt% K₂CO₃ has little impact on both quality cost and capacity cost. K₂CO₃, an industrialgrade bulk commodity, is characterized by its low cost, stable supply chain, and the absence of critical raw material restrictions in its production process. Compared to other existing methods, particularly sophisticated processes such as MS and ALD, this approach reduces both equipment costs and spatial requirements while demonstrating superior coating efficiency relative to the deposition efficiency of these processes. Moreover, the production of high-purity ultra-thin lithium foil over large areas is both challenging and expensive, and the mechanical rolling method to achieve lithium foil thicknesses below 5 µm presents significant difficulties [39]. The fabrication of 5 µm ultra-thin lithium metal requires only molten lithium combined with K₂CO₃ and applied it onto copper foil, thereby eliminating the requirement for intricate mechanical rolling or vacuum deposition equipment. It is compatible with current roll-to-roll production processes and is feasible for large-scale manufacturing.

3.2. Composition and structure of high-wettability composite lithium anode

XRD was applied to investigate the phase composition of the Li-10KCO composite and pristine lithium, with the results presented in Fig. 2a and Figure S8. The broad peak at 18.5° is ascribed to the Kapton membrane aimed to avoid sample oxidization and pollution [40]. For the Li-10KCO composite, additional diffraction peaks were observed beyond those displayed by lithium metal, which belong to Li₂O, LiC₆ and K. It was inferred that the K₂CO₃ powder reacted with molten lithium, in consideration of the XRD peak signal of K₂CO₃ has not been detected. XPS was employed to obtain more comprehensive details regarding the chemical states of C, Li, O and K elements present in the Li-10KCO composite. It can be seen that the chemical valence state information of XPS matches the phase composition determined by XRD. As illustrated in Figs. 2e and 2f, the peaks corresponding to the LiC₆ is observed at 285.95 eV of C1 s spectrogram and at 56.5 eV of Li1 s spectrogram, respectively. In O 1 s spectra (Fig. 2g), the peak appeared at 531.3 eV belong to Li₂O further confirmed its presence in the Li-10KCO composite

[41]. CO_3^{2-} is also detected, which may be originated from inevitable surface impurities that arise during the preparation and testing of samples [42]. The K 2p spectra (Fig. 2h) exhibit two peaks centered at 293.3 eV and 296.2 eV, corresponding to the K⁰ and its spin orbit splitting peaks respectively. Trace amounts of potassium, which possess large atomic radium, may decrease surface tension and diminish the bond energy between lithium atoms, thereby improving the wettability of molten lithium composite [28,43]. Furthermore, the elemental linear scan reveals the composition distribution at the interface between composite lithium anode and LLZTO (Fig. 2b), which indicates that LiC₆, Li₂O, and K are mainly distributed at the interface. Not only does the formed LiC₆ compound improve the interfacial contact [44], allowing Li⁺ to diffuse across the interface with lower transfer barrier, but also plays an crucial role in regulating interface current distribution to guide uniform deposition and stripping of lithium [30]. The Li₂O with a high band gap enable to inhibit the electron tunneling effect so as to prevent lithium dendrite growth and enhance cycling stability [29,45]. The energy barriers for Li⁺ migration in Li₂O is lower than that in pure Li, facilitating efficient transport of Li⁺ which enhance the uniformity of Li deposition [46]. The Ea for both the Li-10KCO LLZTO interface and the LilLLZTO interface is calculated according to the Arrhenius formula [47], yealding values of 0.58 eV and 0.61 eV, respectively (Fig. 2c). The reduction of interfacial Ea is correlated with the lifted ionic conductivity along with the decreased energy barrier for Li migration inside LiC₆ and Li₂O in Li-10KCO composite [48]. Tafel curve showed that the exchange current density of the Li-10KCO compiste is 0.589 mA cm $^{-2}$, which was 4.06 times greater than that of the pure Li (0.145 mA cm $^{-2}$) (Fig. 2d). Through further data processing of the Tafel curve, according to the equation below [49]:

$$R_{CT} = \frac{R \times T}{F \times i}$$

R is the gas constant, T is the temperature, F is the Faraday constant, and i is the exchange current density. It is calculated that the interface charge transfer resistance (R_{CT}) of Li-10KCO|LLZTO is 0.055 Ω , which is smaller than that of the Li|LLZTO (0.224 Ω). Higher exchange current density and smaller charge transfer resistance mean faster charge transfer rate and electrochemical reaction at the interface, resulting in more uniform lithium deposition and smaller voltage lag [50].

3.3. Electrochemical performance of lithium symmetric batteries

Aim to conduct a deeper investigation into the stability of the interface between the Li-KCO composite anode and LLZTO, Li-KCO [LLZTO]Li-KCO cells were fabricated for electrochemical test. The Li-KCO composites, prepared with varing mass ratios of K_2CO_3 powder, were designated as Li-1KCO (1 wt% K_2CO_3), Li-5KCO (5 wt% K_2CO_3), Li-10KCO (10 wt% K_2CO_3), Li-15KCO (15 wt% K_2CO_3), and Li-20KCO (20 wt% K_2CO_3) to analyze the impact of K_2CO_3 content on the performance of the Li-KCO composite anode.

The area specific resistance (ASR) is a critical evaluative indicator for assessing the stability of interface, as it reflects the difficulty of Li⁺ transport at the interface and tightness of electrode to electrolyte[51]. The initial semicircle corresponding to the high-frequency region denotes the impedance of the electrode-electrolyte interface, half of resistance could calculate as the ASR considering the two interfaces in the symmetric cells. Fig. 3a exhibits the EIS of the Li|LLZTO|Li symmetric cells and Li-10KCO|LLZTO|Li-10KCO symmetric cells, in which the Li-10KCO composite anode with ASR of merely 32.5 Ω cm², instead of the Li|LLZTO interface has a higher ASR of 181.6 Ω cm². The substantial reduction in interface resistance of the Li-10KCO|LLZTO| Li-10KCO cell mainly comes from the excellent wetting behavior which reduces the voids at the interface. Furthermore, Figure S9 proves that different proportions of Li-KCO can reduce interfacial impedance, ASR are 89.7 Ω cm² (Li-1KCO), 66.9 Ω cm² (Li-5KCO), 59.2 Ω cm² (Li-15KCO), and 59.9 Ω cm² (Li-20KCO), separately. It proves that the



0.2

53

Fig. 2. (a) XRD pattern of Li-10KCO composite. (b) Elemental line scan along the cross-section of Li-10KCO with LLZTO. (c) Interfacial activation energies of Li-10KCO|LLZTO and Li|LLZTO interface. (d) Tafel curves of Li-10KCO|LLZTO|Li-10KCO symmetric cells and Li|LLZTO|Li symmetric cells. (e-h) XPS spectrum of Li-10KCO composite.



Fig. 3. (a) Comparison of EIS spectra for the Li|LLZTO|Li and Li-10KCO|LLZTO|Li-10KCO cell at room temperature. (b,c) Time-constant mode of CCD for Li-10KCO| LLZTO|Li-10KCO cell at room temperature and at 60 °C. (d,e) Continuous charge-discharge cycling performance of Li-10KCO |LLZTO|Li-10KCO cell operating at 0.2 and at 0.8 mA cm⁻².

incorporation of K_2CO_3 powders to molten lithium is an efficacious strategy for improving interfacial wettability and enhancing the rapid transport of Li⁺ at the interface.

CCD test is typically used to evaluate the ability to oppose dendrite penetration during cycle and the maintenance of stability, as well as to assess the ion migration capability at anode-electrolyte interface [52]. With a fixed duration of 30 min for Li stripping/plating, and with stepwise increasing galvanostatic currents of 0.1 mA cm^{-2} , the upmost current density that the battery can endure is determined by the potential plunge resulting from the lithium filament penetration. By virtue of unsatisfying interface contact characterized by holes and gaps, the Li LLZTO/Li cells easily occurred short circuit at 0.5 mA cm⁻² in short time, accompanied by huge polarization voltage at room temperature (Figure S10a). By comparison, the CCDs for Li-KCO/LLZTO/Li-KCO cells (Fig. 3b, Figure S11) are prior than origin group, showing a trend of first rising and then decreasing through the substantially increased ratio of K₂CO₃ powders addition. In specific, the Li-10KCO|LLZTO|Li-10KCO cell presents the CCD of 1.0 mA cm^{-2} , whereas the other symmetrical cells constructed with Li-1KCO, Li-5KCO, Li-15KCO and Li-20KCO, the CCDs sequentially are 0.5, 0.6, 0.9, and 0.8 mA cm^{-2} . Therefore, 10 wt % K₂CO₃ supplement is the propriate balance to improve the suppression of lithium dendrite under the condition of ensuring high wettability. This is also consistent with the impedance variation trend mentioned above. Exactly as Fig. 3c indicated, Li-10KCO|LLZTO| Li-10KCO symmetric cells exhibit the impressive capability to sustain

a current density of up to 2.2 mA cm⁻², triple amplitude than that of Li| LLZTO|Li cells at 60 °C (Figure S10b). In addition, through the construction of Li|LLZTO|Li-10KCO asymmetric cell, we have shown that the incorporation of K₂CO₃ into the molten lithium does not result in a significant change in the electrode potential (Figure S12).

Given to the outstanding capability for lithium dendrites suppression, correspondingly, cycling performance for the symmetrical cells are additionally evaluated. Under testing conditions of 0.2 mA cm^{-2} with a plating-stripping capacity of 0.1 mA h cm⁻², the Li|LLZTO|Li symmetric cell occurred short circuit issue after 925 h of cycling (Figure S13a). Figure S13b demonstrates that the overpotential of the Li|LLZTO|Li cell at 60 °C exhibits a rapid decline after 1 h at 0.8 mA cm⁻², ultimately decreasing to 17 mV after 9 h, which indicates a short circuit. It implies that the LilLLZTO interface deteriorated with the rapid propagation of lithium dendrites. However, as illustrated in Fig. 3d, Li-10KCO|LLZTO| Li-10KCO cell can function steadily for 4500 h at 0.2 mA cm⁻², exhibiting longer cycling performance. Furthermore, the inserted images in Fig. 3d indicate that the overpotential exhibited slight fluctuation without apparent polarization, which demonstrates its outstanding cycling stability. As shown in Figure S14a, the Li|LLZTO interface experienced degradation during long-term cycling. The huge gap at the interface restricts contact between the lithium anode and LLZTO, resulting in high local current density that promotes lithium dendrite growth. Inversely, the Li-10KCO|LLZTO interface exhibited good contact after 4500 h of cycling (Figure S14b), implying that the Li-10KCO

composite lithium anode improved the interface contact and regulated the uniform deposition and stripping of Li during cycling, thereby inhibiting the formation of lithium dendrites. Additionally, the slight variation in impedance of the Li-10KCO|LLZTO|Li-10KCO symmetric cell after cycling also confirms the stability of the Li-10KCO/LLZTO interface (Figure S15). In addition, at higher current densities (0.4 mA cm^{-2}) and higher surface capacities $(0.2 \text{ mAh cm}^{-2})$, the Li LLZTO Li cell experienced failure after 4 h of cycling (Figure S16a). Conversely, the Li-10KCO|LLZTO|Li-10KCO cell maintained a stable potential and endured 200 h of cycling (Figure S16b). The rapid shortcircuit failure of the Li|LLZTO|Li cell at increased current density is in sharp contrast to the steady cycling performance of the Li-10KCO| LLZTO Li-10KCO cell, further indicating that Li can quickly and uniformly deposit/strip at the Li-10KCO|LLZTO interface. Surprisingly, under the circumstance of 0.8 mA cm^{-2} in 60 °C, it can still realize smooth and stable curve up to 2500 h with a durable overpotential of 74 mV (Fig. 3e). Moreover, the enlarged voltage profiles of the Li-10KCO|LLZTO|Li-10KCO cell cycling at 795-800, 1595-1600, 2395-2400 h (inserted images in Fig. 3e) manifest the firm voltage shape. This observation implies the steady lithium stripping and plating processes at interface.

To further investigate the performance of the Li-10KCO composite anode, symmetrical cells were tested under low-temperature conditions. The Li|LLZTO|Li cell can only cycle for 8 h at -10 °C before experiencing a short circuit failure (Figure S16c), while the Li-10KCO|LLZTO| Li-10KCO cell demonstrates stable cycling for 200 h at the same current density of 0.1 mA cm⁻² (Figure S16d). The reduction in temperature results in a decreased rate of Li⁺ transport at the interface; thus, the stable operation of the Li-10KCO|LLZTO|Li-10KCO cell is attributed to the stability of the Li-10KCO|LLZTO interface and the lowered energy barrier for Li⁺ migration, further demonstrating the effectiveness of the Li-10KCO composite anode. All the aforementioned discussions indicate that the Li-10KCO composite anode enable to maintain intimate interface contact with uniform Li deposition during cycle. Without using complicated methods, we can achieve gratifying electrochemical performance comparable to the recent literatures (Table S2, Table S3).

3.4. Electrochemical performance of full cells

Full cells were constructed using the LiFePO₄ cathode to ulteriorly verify the practicality of Li-10KCO composite anode in SSLMBs. A small quantity of liquid electrolyte was applied to wet the cathode, so as to alleviate the influence of the cathode-LLZTO interface resistance [40]. Under long-cycle situation at 0.5 C rate, the difference of interface stability is significant. The Li-10KCO|LLZTO|LFP cell, featuring a high initial specific capacity of 154.5 mAh g⁻¹, presents an impressive cyclic stability (Fig. 4a). Meanwhile, there is virtually no loss of discharge capacity after 120 cycles. While the Li|LLZTO|LFP cell reveals lower initial coulombic efficiency (85.5%) and poor cycle stability at 0.5 C, with an initial discharge specific capacity of 134.9 mAh g^{-1} , which decays to basically 1.7 mAh g^{-1} after cycling 38 times. What's more, as illustrated in Fig. 4b, nearly overlapping voltage plateaus displayed by the Li-10KCO|LLZTO|LFP cell across multiple cycles signifies the intimate interface contact [42]. This sharply contrasts with the swift reduction in Li|LLZTO|LFP cell specific capacity illustrates in Fig. 4c, which the voltage gap between charge and discharge profiles increased from 222 mV to 576 mV, attributing to the increased polarization caused by interface instability. Therefore, the good electrochemical capability of Li-10KCO|LLZTO|LFP cell is related to stable Li-10KCO| LLZTO interface contact, as evidenced by the impedance comparison before cycling in Fig. 4d. Li-10KCO/LLZTO/LFP cell exhibits the lower total resistance of 231 Ω cm², yet Li|LLZTO|LFP cell delivers 333 Ω cm².



Fig. 4. Electrochemical performances of full cell with LFP cathode at 25 °C. (a) Comparison of cycle performance at 0.5 C of Li-10KCO|LLZTO|LFP full cell and Li| LLZTO|LFP full cell respectively. Charge/discharge performance at different cycles of (b) the Li-10KCO|LLZTO|LFP full cell and of (c) the Li|LLZTO|LFP full cell at 0.5 C. (d) Comparison of EIS plots for the Li-10 KCO|LLZTO|LFP full cell and the Li|LLZTO|LFP full cell.

Table S4 gives the comparative analysis of the long-term cycle performance of our study against recent literature findings, sustainable cycle stability and high-capacity retention rate of this work illustrating the effectiveness of Li-10KCO|LLZTO interface.

In practical applications, overcharging and over-discharging are critical issues that pose safety risks and shorten battery life. Consequently, safety testing is a crucial component in facilitating the transition of batteries from laboratory research to large-scale applications. As illustrated in Figure S17a, the safety of the Li-10KCO composite anode was verified based on the Li-10KCO|LLZTO|LFP full cell. When the Li-10KCO|LLZTO|LFP full cell was overcharged to 4.2 V, it discharged steadily down to 2.5 V. Subsequent to the second charge to 4.0 V, the Li-10KCO|LLZTO|LFP full cell was over-discharged to 2.0 V, yet it continued to operate normally during the third cycle within the standard cycle voltage range (2.5 V-4.0 V) without any short circuit failures. The Li-10KCO|LLZTO|Li-10KCO symmetric cell further confirms the safety of the Li-10KCO composite anode at a current density of 0.1 mA cm⁻ (Figure S17b). The cell achieved stable cycling after being overcharged to 2.0 V, and the overpotential remained consistent with the initial charging potential. Furthermore, after discharging to -2.0 V, the cell continues to cycle smoothly. The inset in Figure S17b indicates that the potential remains stable throughout the constant current cycle before and after overcharging and over-discharging. This suggests that the Li-10KCO|LLZTO interface can maintain stability during substantial lithium deposition and stripping processes. It is the Li-10KCO composite anode design that enhance the wettability and interface contact, eventually suppressing lithium dendrite growth during cycling with uniform Li⁺ deposition and guaranteeing superior electrochemical performance in SSLMBs.

4. Conclusions

In summary, the Li-KCO composite electrode, characterized by superior wettability, offers a viable solution without the need for specialized equipment or expensive raw materials, allowing for rapid application onto diverse substrates such as ceramic electrolytes, copper foils, stainless steel, and titanium foils. An ultra-thin lithium metal layer can be efficiently formed on copper foil, potentially functioning as a prospective material to boost energy density of batteries while addressing the cost issues associated with excessive lithium. Additionally, applying ultra-thin lithium metal to copper current collector can serve as an anode-side pre-lithiation agent, improving the initial coulombic efficiency and extending the battery's cycle life. By diminishing the surface tension of molten lithium, the improvement of the wettability on LLZTO electrolyte enhances interface contact, resulting in lower interface impedance during the cycle. The formation of an ionconducting yet electron-insulating layer, consisting of K, Li₆C, and Li₂O phases, ensures the uniform distribution of Li⁺ flux and enhances the kinetics of electrode reaction, thus enabling dendrite-free lithium deposition at a high CCD of 1.0 mA cm^{-2} . Benefiting from these advantages, it demonstrates steady cycling performance for 4500 h at 0.2 mA cm^{-2} and 2500 h at 0.8 mA cm^{-2} at $60 \degree$ C. Additionally, following 120 cycles at 0.5 C, Li-10KCO|LLZTO|LFP full cell sustained high reversible specific capacities of 155.3 mAh g⁻¹, exhibiting satisfactory cycling performance. This work proposes a viable strategy for high-wettability composite lithium to realize SSLMBs characterized by excellent stability, and applicable to the field of ultra-thin lithium metal anodes.

CRediT authorship contribution statement

Zhang Zhihao: Formal analysis. Zhang Wendi: Visualization. Fan Qianxiao: Methodology, Formal analysis. Peng Guanxiong: Writing – original draft, Methodology, Investigation, Data curation. Li Meicheng: Writing – review & editing, Supervision, Resources, Funding acquisition. Liu Kai: Writing – review & editing, Supervision, Resources, Conceptualization. Wang Wenzhuo: Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2025.180411.

Data Availability

Data will be made available on request.

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