

Contents lists available at ScienceDirect

### Journal of Alloys and Compounds



journal homepage: www.elsevier.com/locate/jalcom

# PVDF-based composite solid polymer electrolyte incorporated with $cubic-ZrO_{2-x}$ for long-cycle lithium metal batteries

Yulong Liu<sup>a</sup>, Huanyan Xu<sup>a,\*</sup>, Zhen Chen<sup>b,\*</sup>, Bo Li<sup>a</sup>, Qian Liu<sup>b</sup>, Serguei V. Savilov<sup>c</sup>, Minghua Chen<sup>b,\*</sup>

<sup>a</sup> School of Materials Science and Chemical Engineering, Harbin University of Science and Technology, Harbin 150040, China

<sup>b</sup> Key Laboratory of Engineering Dielectric and Applications (Ministry of Education), School of Electrical and Electronic Engineering, Harbin University of Science and

Technology, Harbin 150080, China

<sup>c</sup> Department of Chemistry, Lomonosov Moscow State University, Moscow 119992, Russia

#### ARTICLE INFO

Keywords: PVDF-(PVDF-HFP) Solid polymer electrolytes Oxygen vacancy Cubic-ZrO<sub>2-x</sub> Lithium metal batteries Solid electrolyte interphase

#### ABSTRACT

Solid-state lithium metal batteries (SSLMBs) have great potential as high-energy-density, high-power, and safe energy storage devices. Solid polymer electrolytes based on polyvinylidene fluoride-poly(vinylidene fluoride-cohexafluoropropylene) (PVDF-(PVDF-HFP)) have attracted significant attention due to their high ionic conductivity at room temperature, good flexibility, and unique ion transport properties, making them promising candidates for commercial applications. However, PVDF-based composite solid polymer electrolytes (CSPEs) exhibit poor lithium-ion transport properties and are prone to chemical reactions with the lithium metal surface, posing the risk of forming lithium dendrites. This degradation results in reduced battery performance and cycle life. This work investigates the effects of Co-doped cubic-ZrO<sub>2-x</sub> (C-ZrO<sub>2-x</sub>), a filler with abundant oxygen vacancies, on the electrochemical properties of PVDF-based CSPE. Zirconium in zirconia can provide Lewis acid sites, while oxygen vacancies can adsorb TFSI<sup>-</sup> and exhibit a pronounced ability to dissociate lithium salt and accumulate anchored anions. These effects are further amplified after phase transition, from unstable monoclinic phase with a small amount of oxygen vacancies to cubic phase with abundant oxygen vacancies, leading to a higher proportion of free Li<sup>+</sup> in PVDF-based CSPE. Additionally, the uniform distribution of solid electrolyte interphase with a single LiF component, indicates that C-ZrO<sub>2-x</sub> increases the interface stability between electrolyte and lithium metal. The corresponding Li|Li symmetrical cells show a stable cycle lifetime of 730 h at 0.1 mA cm<sup>-2</sup>. The specific discharge capacity of Li $|CSPE|LiFePO_4$  reaches 106.09 mAh  $g^{-1}$  at 1 C. Even after 550 cycles, the capacity retention rate is still 92.13 %. These findings ideally contribute to an effective way to achieve high performance and long cycle life of solid-state lithium metal batteries.

#### 1. Introduction

Fossil fuels are non-renewable, so promoting renewable energy and energy storage is crucial for energy security and structure. Rapid growth in electric vehicles and electronics is driving exponential growth in lithium metal battery (LMB) market share. LMBs have high energy density and negative electrode potential. Solid-state LMBs (SSLMBs) are projected to exceed 400 Wh/kg [1–3], making them a preferred, safe, and stable electrochemical energy storage solution [4].

Polyvinylidene fluoride (PVDF)-based composite solid polymer electrolytes (CSPEs) have shown immense potential in the development of SSLMBs due to their excellent flexibility, mechanical properties, and good processability [5–7]. PVDF-based CSPEs with a high dielectric constant ( $\epsilon_r \sim 8$  –10) accelerate lithium salt dissociation [8–10]. In these CSPEs, Li<sup>+</sup> transport occurs via C-F bond interactions with the Li (DMF)<sub>x</sub>TFSI complex (formed by lithium salts and residual N, N-dimethylformamide (DMF)) [11,12]. However, excess free DMF causes interfacial side reactions. Uneven DMF distribution leads to inhomogeneous SEI and polymer decomposition [13,14]. On the other hand, PVDF-based CSPEs still face challenges such as low ionic conductivity, high crystallinity, susceptibility to lithium dendrite puncture, and interface contact issues between CSPE and lithium.

Current work targets improving SPE ionic conductivity ( $\sigma$ ) and cycling stability at the polymer-Li metal anode interface. Modification

\* Corresponding authors. *E-mail addresses:* xuhuanyan@hrbust.edu.cn (H. Xu), chen.zhen@hrbust.edu.cn (Z. Chen), mhchen@hrbust.edu.cn (M. Chen).

https://doi.org/10.1016/j.jallcom.2025.179925

Received 8 January 2025; Received in revised form 10 March 2025; Accepted 19 March 2025 Available online 22 March 2025 0925-8388/© 2025 Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies. strategies include using organic molecules [15], inorganic fillers [16], and liquid additives [17]. Typically, the physical mixing of multiple polymers is employed to leverage the advantages of each component, thereby achieving enhanced overall performance. Introducing PVDF-HFP (with low crystallinity and 33  $\sim$  100 %  $\beta$  phase) [18] into a PVDF system (with high mechanical strength) through polymer blending can disrupt the microstructural order of the polymer, increase the proportion of the amorphous region, and facilitate ion conduction [19,20]. Simultaneously, the incorporation of adding inorganic fillers (such as TiO<sub>2</sub> [21,22], ZrO<sub>2</sub> [23], Li<sub>1.3</sub>Al<sub>0.3</sub>Ti<sub>1.7</sub>(PO<sub>4</sub>)<sub>3</sub> [24], Li<sub>6.25</sub>Al<sub>0.25</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> [25,26]) into the CSPEs reduces polymer crystallinity, boosting ionic conductivity. Chen et al. [27] showed ZrO<sub>2</sub> in CSPEs also offers Lewis acid sites, aiding Lithium salts dissociation. Besides typical inert/active fillers, functional organic fillers like metal-organic frameworks (MOFs) [28], succinonitrile (SN) [29], and C<sub>3</sub>H<sub>6</sub>N<sub>6</sub> (melamine) [30] have gained interest. Adding C<sub>3</sub>H<sub>6</sub>N<sub>6</sub> to PVDF creates a slightly alkaline environment, promoting PVDF defluorination [31,32], increasing PVDF's dielectric constant, enhancing Lithium salts dissociation, and interacting with the electrolyte's [DMF-Li<sup>+</sup>] complex.

For efficient Li<sup>+</sup> transport and cycling stability in PVDF-based CSPEs, alongside reduced crystallinity and enhanced Li salt dissociation, increasing free Li<sup>+</sup> and minimizing interfacial side reactions are vital. Oxygen vacancy (O<sub>V</sub>) defects improve Li<sup>+</sup> distribution and concentration [33-36], making O<sub>V</sub> enrichment strategies highly desirable. Therefore, through doping with low-cost Co, we successfully prepared oxygen vacancy-rich C-ZrO<sub>2-x</sub> which serves as an inorganic filler for the C-ZrO<sub>2-x</sub>/C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>/PVDF/PVDF-HFP/LiTFSI CSPE. C-ZrO<sub>2-x</sub> facilitates the dissociation of LiTFSI and immobilizes the anions. The increase in free lithium ions in the electrolyte leads to an increase in free TFSI-(from 12.4 % to 18.1 %) and increased lithium ion transference number  $(t_{Li^*})$  (from 0.27 to 0.43). The C-ZrO<sub>2-x</sub> with high adsorption capacity promotes the uniform distribution of DMF in the electrolyte, reducing side reactions caused by DMF aggregation and forming a highly stable (Solid electrolyte interface) SEI film. Consequently, these lead to significantly enhanced electrochemical performance in both symmetric Li||Li cells and Li||LiFePO4 full cells, accelerating the realization of practically long-cycle stable solid-state batteries.

#### 2. Experimental procedures

#### 2.1. Synthesis of C-ZrO<sub>2-x</sub>

C-ZrO<sub>2-x</sub> was prepared using a typical co-precipitation method [37]. First, 1.5 g of ZrOCl<sub>2</sub>•8 H<sub>2</sub>O (Aladdin) and varying concentrations of CoCl<sub>2</sub>•6 H<sub>2</sub>O (i.e., 0 and 5 wt%; Aladdin) were completely dissolved in deionized water (DIW). Ammonia water was added dropwise to adjust the pH to 9 –10. The mixture was stirred for 1 h at 600 rpm, after centrifuged by DIW and ethanol, the obtained precipitates were dried in an oven (air, 70 °C, overnight). Furthermore, the dried product was ground with a mortar and pestle, following by a calcination step at 500 °C for 1 h in a furnace to obtain the C-ZrO<sub>2-x</sub> nanoparticles.

## 2.2. Synthesis of C-ZrO<sub>2-x</sub>/C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>/PVDF/PVDF-HFP/LiTFSI (C-Zr-E) & ZrO<sub>2</sub>/-C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>/PVDF/PVDF-HFP/LiTFSI (Zr-E)

The CSPEs were prepared using a solution casting method. 0.025 g of ZrO<sub>2</sub> (Aladdin)/C-ZrO<sub>2-x</sub>,  $C_3H_6N_6$  (Aladdin), 0.1 g of PVDF (Aladdin, Mw ~ 300 000), 0.4 g of PVDF-HFP (Macklin, Mw ~ 455 000, ~110 000), and 0.4 g of LiTFSI (Aladdin, 99 %) were pre-mixed in DMF (Alfa Aesar) and stirred at 40 °C for 12 h. The above mixture was poured onto a glass plate and dried at 80 °C for 2 h to form homogeneous C-Zr-E and Zr-E membranes with a thickness of 90–100  $\mu$ m. The prepared CSPEs were punched into disks with a diameter of 15.8 mm and stored in a glovebox with an argon atmosphere.

#### 2.3. Characterization techniques

The crystalline structure of the samples was measured by X-ray diffraction (XRD; Malvern Panalytical Empyrean) with Cu Ka radiation  $(\lambda = 1.5406 \text{ Å})$  in the 2 $\theta$  range of 5  $-90^{\circ}$ . Raman spectroscopy (WITec Alpha 300 R) with a 532 nm output wavelength was used to analyze the interactions between functional groups. The chemical bonds were detected using a FT-IR spectrometer (PerkinElmer) in transmission mode, covering the range of  $400 - 4000 \text{ cm}^{-1}$ . A universal mechanical testing machine (CMT6103) was employed for the tensile experiments. To confirm thermal stability of the electrolyte membranes, thermogravimetric analysis (TGA) was studied using a NETZSCH instrument under an air atmosphere, operated in the RT-800 °C temperature range at a heating rate of 5  $^\circ \mathrm{C}\,\mathrm{min}^{-1}$ . The phase transition behaviors of the samples was investigated by a differential scanning calorimeter (DSC; Mettler Toledo Instruments) at a scanning rate of 10 °C per minute from -50 °C to 200 °C. The samples' surface morphologies were examined using an SEM (Hitachi-SU8000). The surface micromorphology of cycled lithium metal pieces was observed using transmission electron microscopy (TEM, Talos F200S G2 S). The oxygen vacancy concentration of the samples was recorded by Electron paramagnetic resonance (EPR) spectra using a JES-FA SERIES instrument. The SEI of CSPEs after 100 charge--discharge cycles was investigated by X-ray photoemission spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi).

#### 3. Results and discussion

#### 3.1. Materials characterization

Fig. 1a depicts the preparation process of C-ZrO<sub>2-x</sub> powder and the corresponding C-Zr-E electrolyte film. Initially, the C-ZrO<sub>2-x</sub> is synthesized using ZrOCl<sub>2</sub>·8 H<sub>2</sub>O and CoCl<sub>2</sub>·6 H<sub>2</sub>O through a typical coprecipitation method. To prepare the C-Zr-E membranes, the above C-ZrO<sub>2-x</sub> was mixed with PVDF, PVDF-HFP, C<sub>3</sub>H<sub>6</sub>N<sub>6</sub> and LiTFSI in DMF and then cast on a glass plate. Photographs of the C-Zr-E precursor solutions before and after solvent evaporation are illustrated at Fig. S1. XRD patterns (Fig. 1b) reveal a complete transition of monoclinic ZrO<sub>2</sub> (JCPDS card No. 74-0815) to stable cubic phase (C-ZrO<sub>2-x</sub>) (JCPDS card No. 88 -1007) after doping low valence Co in the  $ZrO_2$  crystal. Based on the SEM images of synthesized C-ZrO $_{2-x}$  and ZrO $_2$  (Fig. S2), the former shows more uniform morphology with an average diameter of approximately 200 nm. According to the electron paramagnetic resonance (EPR) result (Fig. 1c), the sharp peak with a corresponding g factor of 2.05 indicates that both ZrO2 and C-ZrO2-x contain oxygen vacancies [38-40]. To keep the charge balanced, Co doping results in higher concentration of oxygen vacancies (Ov) in C-ZrO<sub>2-x</sub> than in ZrO<sub>2</sub>. This aligns well with the higher peak intensity of C-ZrO<sub>2-x</sub> observed in Fig. 1c. Further, XPS analysis was employed to evaluate variations in  $\mathrm{O}_{\mathrm{v}}$  concentration after co-doping (Fig. 1d) [41,42]. The O 1 s XP spectra show three peaks, i.e., lattice oxygen (O<sub>crvstal</sub>), oxygen vacancy (O<sub>v</sub>, O<sub>v1</sub>, O<sub>v2</sub>), and chemically adsorbed oxygen species (-OH), whose binding energies are 530.0, 531.4 and 532.4 eV, respectively. It is generally recognized that O<sub>v</sub> in metallic oxide consists of Vox (the neutral concerning the regular O<sub>2-</sub> site), VO• (containing one e<sup>-</sup>), and VO•• (containing no e<sup>-</sup>). If any of the  $e^-$  among them transfers from the  $V_{\rm O}$  site to a nearby  $Zr^{4+}$ ion, leading to the formation corresponding amount of  $\mathrm{Zr}^{3+}$  ion. This shift in oxidation state is confirmed through the Zr 3d spectrum, which can be deconvoluted into two primary peaks at 184.4 eV and 182.0 eV, corresponding to  $3d_{3/2}$  and  $3d_{5/2}$  of  $Zr^{(4-x)}$  +. These peaks are further divided into components representing  $ZrO_2$ ,  $ZrO_{x1}$  (2 > x1 > 1.5) and  $ZrO_{x2}$  (1.5 > x2 > 1), indicating varying oxidation states of Zr [43]. Therefore, after doping, the increase of  $O_v \mbox{ and } Zr^{3+}$  ion is consistent with the enlargement of the convolution peak of O<sub>v</sub> in O 1 s and ZrO<sub>x</sub> in Zr 3d separately. By the way, the XPS survey scan reveals the co-existence of the Zr and O elements in the final sample (Fig. S3).

Oxygen vacancies in ZrO2 and C-ZrO2-x are the main adsorption sites



**Fig. 1.** (a) Schematic diagram illustrating the preparation process of C-ZrO<sub>2-x</sub> filler and the C-Zr-E. (b, c) XRD patterns and EPR spectra of  $ZrO_2$  and C-ZrO<sub>2-x</sub>. (d) Zr 3d and O 1 s XP spectra of  $ZrO_2$  and C-ZrO<sub>2-x</sub> (e) Structural model diagram of  $ZrO_2$ -TFSI<sup>-</sup> (up), C-ZrO<sub>2-x</sub>-TFSI<sup>-</sup> (down), and adsorption of TFSI<sup>-</sup> on the  $ZrO_2$  and C-ZrO<sub>2-x</sub> (111) crystal plane. (f) The Raman peak fitting curves and quantified contributions of different coordination environment of TFSI<sup>-</sup> in CSPE, Zr-E, and C-Zr-E films.

of the  $-SO_2$  functional group of TFSI<sup>-</sup>[44]. To obtain more insights into the molecular interaction between oxygen vacancies and TFSI<sup>-</sup>, Density functional theory (DFT) calculations were conducted. Previous works [45–49] suggest that the oxygen vacancy concentration in monoclinic ZrO<sub>2</sub> is much lower than in C-ZrO<sub>2-x</sub>, prompting the selection of C-ZrO<sub>2-x</sub> for detailed analysis. The adsorption geometry of TFSI<sup>-</sup> coordination to Ov on the C-ZrO<sub>2-x</sub> (or ZrO<sub>2</sub>) surface through the  $-SO_2$  group is selected, as shown in Fig. 1e. The results show that the adsorption energies of TFSI<sup>-</sup> in ZrO<sub>2</sub> and C-ZrO<sub>2-x</sub> nanoparticles are calculated to be -1.38 eV and -7.00 eV, respectively, indicating that a strong electrostatic attraction between pristine C-ZrO<sub>2-x</sub> and TFSI<sup>-</sup>, and this strong adsorption enhances the conduction of free Li<sup>+</sup> in CSPE.

Positively charged oxygen vacancies readily immobilize negatively charged TFSI<sup>–</sup> anions through electrostatic interactions. This immobilization weakens the binding between lithium ions and anions within the lithium salt, enabling convenient movement of lithium ions. Raman spectroscopy provides evidence for this phenomenon, particularly by analyzing the Raman band within the frequency range of  $720 - 760 \text{ cm}^{-1}$  (Fig. 1f). The peak of TFSI<sup>–</sup> could be divided into three peaks at approximately 738 (free anions, Free TFSI<sup>–</sup>), 741 (TFSI<sup>–</sup> coordinating to a single lithium-ion, contact ion pairs (CIPs)), and 744 cm<sup>-1</sup> (TFSI<sup>–</sup> coordinating to two or more lithium ions, aggregates

(AGGs)), respectively [50,51]. The proportion of Free TFSI<sup>-</sup> could be calculated according to the following Eq. 1:

$$[\text{Free TFSI}^-] = \frac{A_{[\text{Free TFSI}^-]}}{A_{[\text{Free TFSI}^-]} + A_{[\text{CIP}]} + A_{[\text{AGG}]}} \times 100\%$$
(1)

where A presents the integrated intensity of the band. The percentages of Free TFSI<sup>-</sup>, CIP, and AGGs in pure CSPE are 12.4 %, 20.9 %, and 66.7 %, respectively. After adding C-ZrO<sub>2-x</sub>, the Free TFSI<sup>-</sup> percentage increases to 18.1 % (vs 16.3 % (ZrO<sub>2</sub>)). Those of CIP and AGGs respectively decrease to 37.8 % (vs 28.4 % (ZrO<sub>2</sub>)) and 44.1 % (vs 55.3 % (ZrO<sub>2</sub>)). It is suggested that oxygen vacancy materials aid in the dissociation of ion clusters, thus increasing the  $t_{\rm Li}^+$ , which will facilitate more [Li(DMF)<sub>x</sub>]<sup>+</sup> formation that is beneficial to the construction of fast lithium-ion transport channels in the electrolyte.

The FT-IR spectra of CSPEs are presented in Fig. 2(a) ~ (c). The peak at 1197 cm<sup>-1</sup> is attributed to the  $-CF_3$  functional group in PVDF/PVDF-HFP, while the peaks at 597 cm<sup>-1</sup> and 1350 cm<sup>-1</sup> represent the characteristic peaks of the SO<sub>2</sub> group. The peak at 1060 cm<sup>-1</sup> is assigned to an antisymmetric stretching of -SNS- group in LiTFSI (Fig. 2a) [52]. According to the magnified FT-IR spectra of CSPEs in a wavenumber range between 720 and 880 cm<sup>-1</sup> shown in Fig. 2b, peaks at 762 cm<sup>-1</sup> and 839 cm<sup>-1</sup> indicate the presence of both  $\alpha$  phase and  $\beta$  phase in the



Fig. 2. FT-IR spectra of (a) CSPE with and without DMF and LiTFSI. (b) CSPE, Zr-E and, C-Zr-E films. (c) FT-IT spectra of DMF + LiTFSI, Zr-E, and C-Zr-E. (d) TGA curves of the CSPE, Zr-E, and C-Zr-E films. (e) XRD patterns of ZrO<sub>2</sub> and C-ZrO<sub>2-x</sub> particles, CSPE, Zr-E, and C-Zr-E films. (f) Stress vs strain curves and (g-i) surface and cross-sectional SEM images of the CSPE, Zr-E, and C-Zr-E films.

PVDF-based electrolyte [53]. In the magnified FT-IR spectra (Fig. 2c) of CSPEs, the presence of a prominent peak locating at  $658 \text{ cm}^{-1}$  that corresponds to free DMF appears in the lithium salts and DMF solution, indicating that the anion predominantly exists as free TFSI-. On the contrary, there is no prominent peak of free DMF observed in Zr-E and C-Zr-E. However, the peak assigning to the bound DMF ( $658 \text{ cm}^{-1}$ ) indicates that the residual DMF is bound to form coordination compounds in the electrolytes, enhancing the stability of the electrolyte [54,55]. As investigated by TGA analysis, the residual DMF content in CSPE, Zr-E, and C-Zr-E are 24.79 %, 19.18 %, and 15.09 % respectively (Fig. 2d). It is noteworthy that the reduction of DMF in the electrolyte is beneficial to the interface stability of electrolyte and lithium, which is also confirmed in the subsequent characterization. Fig. S4 shows the FT-IR spectra of CSPEs' absorption peak in a wavenumber range between 1050 and 1650 cm<sup>-1</sup>. The peaks at  $1181 \text{ cm}^{-1}$  and  $1403 \text{ cm}^{-1}$  is attributed to the antisymmetric -CF2 stretching and -CH2 wagging functional groups in PVDF-HFP. Further characteristic bands in the fingerprint region for LiTFSI are located at  $617 \text{ cm}^{-1}$  and  $1354 \text{ cm}^{-1}$ (-SO<sub>2</sub> groups), and 1058 cm<sup>-1</sup> (-SNS- group). There are no significant changes in the absorption peaks within the mentioned range, indicating

that there is no evident chemical reaction between the filler and the PVDF-based polymer.

The XRD patterns of Zr-E and C-Zr-E verify the existence of ZrO2 or C-ZrO<sub>2-x</sub> (Fig. 2e). The stress-strain curves exhibit a typical ductile fracture (Fig. 2f). The tensile properties follow the expected trend based on the addition of fillers in CSPE, with tensile strengths of 4.02, 4.29 and 4.93 MPa of CSPE, Zr-E, and C-Zr-E, respectively. The increased mechanical properties can better inhibit the lithium dendrites of LMBs. SEM images of CSPEs are displayed in Fig.  $2(g) \sim (i)$ . All the CSPEs exhibit microscopically phase-segregated structures resembling seaisland structures, primarily due to high fractions of LiTFSI. With the addition of fillers, the C-Zr-E demonstrates good compatibility, excellent homogeneity, and a rich three-dimensional morphology, and its fracture surface exhibits typical ductile fracture characteristics. As shown in the DSC curve (Fig. S5), neither C-Zr-E nor Zr-E exhibits a distinct glass transition temperature (Tg) peak. However, the crystallization temperatures of C-Zr-E (PVDF: 129 °C; PVDF-HFP: 101 °C) are lower than those of Zr-E (PVDF: 129 °C; PVDF-HFP: 107 °C). Furthermore, the melting temperatures of C-Zr-E (PVDF: 160 °C; PVDF-HFP: 126 °C) are significantly lower than those of Zr-E (PVDF β-phase: 165 °C; α-phase: 156 °C;

PVDF-HFP: 130 °C). These observations indicate that C-Zr-E exhibits a slower crystallization rate, allowing for a longer duration for crystal nucleation and growth compared to Zr-E. This extended crystallization process is believed to promote the formation of a more favorable three-dimensional morphology in the C-Zr-E electrolyte [6]. The electrolyte thickness is estimated to be around 80  $-120 \,\mu$ m. EDS mapping images of the cross-section of the CSPEs reveal an even distribution of all additives within C-Zr-E in Fig. S6.

#### 3.2. Electrochemical performance characterizations

The effect of modification on the electrochemical of the CSPE is illustrated in Fig. 3. As shown in Fig. 3a and Fig. S7, when the C-ZrO<sub>2-x</sub> content is at 5 %, the CSPE exhibits the highest ionic conductivity, with a value of  $4.7 \times 10^{-4}$  S cm<sup>-1</sup> at 25 °C, compared to  $2.4 \times 10^{-4}$  S cm<sup>-1</sup> for Zr-E. The temperature–dependent ionic conductivities of Zr-E and C-Zr-E samples are demonstrated in Fig. 3b, from which it is seen that the  $\sigma$  of C-Zr-E is higher than that of Zr-E over a wide temperature range. The interaction between rich oxygen vacancies and TFSI<sup>-</sup> anions promote the dissociation of lithium salt, resulting in more free lithium ions that combine with DMF to construct ordered ion channels through forming solvated molecules. These solvated molecules interact effectively with PVDF/PVDF-HFP chains to transfer lithium ions effectively. In addition, the increase in  $\sigma$  is related to the enlarged amorphous region of PVDF/PVDF-HFP after modification.

The electrochemical stability window (ESW) is a crucial factor of electrolyte stability, as illustrated in the LSV profiles of Zr-E and C-Zr-E. In Fig. 3c, the C-Zr-E exhibits higher oxidation stability than the Zr-E, as evidenced by the elevated upper voltage limit from 4.2 V to 4.5 V when setting the maximum current density at 5  $\mu$ A cm<sup>-2</sup>. The enhanced resistance to oxidation can be attributed to the relatively high bandgap value of approximately 6 eV for ZrO<sub>2</sub> fillers [56]. When incorporated into the electrolyte, the ZrO<sub>2</sub> fillers effectively reduce the overall highest occupied molecular orbital (HOMO) level of the polymer electrolytes, thereby suppressing oxidation caused by the positive electrode materials. During the negative scan (Fig. 3d), the reduction peak at 1.5 V represents the decomposition of TFSI<sup>-</sup> in residual DMF. After doping with C-Zr-E particles, the above peak disappears due to the decreased content of DMF and the immobilization of TFSI<sup>-</sup>.

The Li<sup>\*</sup> transference number is a key parameter that indicates the efficiency of cation transport and the effectiveness of lithium dendrite suppression. To determine the  $t_{Li}^{+}$  value, a symmetric Li|CSPEs|Li battery is assembled. Fig. 3e presents the Nyquist plots recorded before and after the chronoamperometry measurement. The calculated  $t_{Li}^{+}$  of C-Zr-E is 0.43, higher than that of the Zr-E (0.27, Fig. S8). This improvement is due to abundant oxygen vacancy adsorbed TFSI<sup>-</sup>, which promotes the transportation of lithium ions in the electrolytes. A larger  $t_{Li}^{+}$  makes it easier to inhibit the growth of space charge regions with the random nucleation of Li ions and severe lithium dendrites. At the same time, the exchange current density of the PVDF-based CSPE also increases from



Fig. 3. (a) Nyquist plots, (b) Temperature–dependent Arrhenius plot, and (c, d) LSV curves of Zr-E and C-Zr-E. (e) The determination of lithium-ion transference number of C-Zr-E. (f) Tafel curves of Zr-E and C-Zr-E. (g) CCD determination and (h) Li plating/stripping test of Li||Li symmetric cells using either Zr-E or C-Zr-E as the electrolytes.

0.18 to 0.22 mA cm<sup>-2</sup> (Fig. 3f), suggesting that the C-ZrO<sub>2-x</sub> could homogenize the Li<sup>+</sup> flux and enhance the lithium-ion transport rate.

Fig. 3g, the critical current density (CCD) of both cells is tested at an increasing density rate of 0.1 mA cm<sup>-2</sup> at 25 °C. After Co-doping, the cell's short-circuit current increases from 0.9 mA cm<sup>-2</sup> to 1.4 mA cm<sup>-2</sup>, implying that the C-Zr-E-based full cells could operate under a large current density. In Fig. 3h, the Li|Zr-E|Li cell lasts only 150 h, after which a sharp increase in overpotential occurs, primarily due to ongoing side reactions between DMF and lithium. For the Li|C-Zr-E|Li cell, the overpotential remains stable (less than 60 mV) for more than 730 h of cycling. The improved performance indicates that the addition of C-ZrO<sub>2-x</sub> could enable higher stability between Li metal and CSPE.

#### 3.3. Full cell performance

Fig. 4a presents the CV curves of the Li|C-Zr-E|LFP full cell. The pair of redox peaks in the voltage range of 3.00–3.80 V corresponds to a characteristic biphasic lithium-ion insertion/extraction mechanism in the LFP cathode. Additionally, due to the stable SEI components, the CV curves almost overlap after subsequent cycles, indicating highly reversible behavior and good compatibility at the electrolyte/electrode

interface. Fig. 4b compares the discharge capacities of both cells at different current densities. The Li|C-Zr-E|LFP full cell demonstrates significantly higher discharge capacities across all C-rates compared to the Li|Zr-E|LFP full cell. Specifically, the Li|C-Zr-E|LFP cell delivers discharge capacities of 169, 156, 131, 104, and 69 mAh g<sup>-1</sup> at 0.1 C, 0.2 C, 0.5 C, 1 C, and 2 C, respectively.

Fig. 4c illustrates the charge–discharge profiles of Li|C-Zr-E|LFP full cells under different rates ranging from 0.1 C to 2 C, exhibiting minimal overpotential. For instance, at 1 C, the activation energy (ΔE) is only 0.3 V, indicating a low internal resistance between C-Zr-E and electrodes. Fig. 4d demonstrates that the Li|Zr-E|LFP full cell is unstable and gets short-circuited rapidly after 115 cycles. However, the Li|C-Zr-E|LFP cell delivers an initial capacity of approximately 106.09 mAh g<sup>-1</sup> and retains a capacity of 97.74 mAh g<sup>-1</sup> after 550 cycles at 1 C, corresponding to a capacity retention rate of 92.13 %. In Fig. 4e, EIS was carried out to measure the resistance evolution of the Li|C-Zr-E|LFP full cells over cycling recorded at open circuit voltage (OCV). The initial impedance of the Li|C-Zr-E|LFP cell is 550 Ω, which gradually decreases with cycling and stabilizes at 150 Ω. These results affirm the successful development of high-performance CSPEs, which are also capable of high-current density operation with good cycle stability. Fig. 4f



**Fig. 4.** (a) CV curves of Li|C-Zr-E|LFP full cells at a scan rate of  $0.1 \text{ mV s}^{-1}$ . (b) Rate capability of Li|Zr-E|LFP and Li|C-Zr-E|LFP full cells. (c) Selective chargedischarge voltage profiles of Li|C-Zr-E|LFP full cells at different rates (0.1, 0.2, 0.5, 1 and 2 C). (d) Cycling stability of Li|Zr-E|LFP and Li|C-Zr-E|LFP full cells at 1 C. (e) Nyquist plots of C-Zr-E based full cells recorded upon cycling at open circuit voltage state. (f) Comparison of previously reported CSPEs- and the C-Zr-E-based full cell performance. (g) The scheme of a pouch cell and the digital photo demonstrating the powering of LED light by the pouch cell with C-Zr-E films.

compares the electrochemical performance of the Li||LFP batteries using C-Zr-E and other CSPEs [57–61] at 25 °C, demonstrating superior electrochemical performance. The excellent reversible capacity of C-Zr-E makes them highly suitable for flexible energy storage devices. A prototype pouch cell, assembled by sandwiching C-Zr-E between the LFP positive electrode and the lithium metal negative electrode (Fig. 4g), was able to power a "HUST" shaped logo containing 68 LEDs.

#### 3.4. Analysis of pristine and cycled Li electrodes

To assess the enhanced performance of Li|C-Zr-E|LFP, cycled Li| CSPEs|Li full cells were disassembled for ex-situ analyses [62–64]. The cycled lithium metal surface was characterized by SEM (Fig. 5a and Fig. 5b), XPS (Fig. 5c and Fig. 5d), and TEM (Fig. 5e and Fig. 5f) of recovered from Li|Zr-E|LFP and LFP|C-Zr-E|Li cells after 100 cycles. The pristine lithium metal shows a smooth surface morphology (Fig. S9). Ex-situ SEM images reveal a more smooth and dense lithium surface over a large area in Fig. 5b, contrasting with the uneven and mossy morphology observed in Fig. 5a.

The composition of the SEI layer was further analyzed by XPS [65, 66]. The results show that the SEI on the Zr-E cell contains LiF and Li<sub>3</sub>N contribution simultaneously, LiF, with its wide bandgap, effectively prevents electron tunneling, has low lithium-ion diffusion energy, and

Li<sub>3</sub>N has faster ionic conductivity than lithium fluoride LiF. Although LiF-Li<sub>3</sub>N can reap those above benefits at the same time, Li<sub>3</sub>N is not stable and most likely comes from DMF decomposition, morever, with the charging and discharging process, the thicker the SEI, the more DMF is consumed, making the electrolyte in an unstable state. In contrast, only a LiF peak is present in the C-Zr-E sample, without excessive consumption of electrolyte components to produce relatively stable SEI, so the passivation layer ensures the cycling stability of the electrolyte, which is confirmed by the improved cycling performance. Furthermore, TEM images after cycling (Fig. 5e and Fig. 5f) show that the SEI on C-Zr-E consists of both an amorphous phase and LiF crystalline phases, with a uniform thickness of approximately 15 µm. This homogeneous SEI promotes even Li deposition and stripping, ultimately benefiting the system's overall performance. On the other hand, the SEI on Zr-E contains uneven crystalline phases of LiF and Li<sub>3</sub>N, contributing to the instability observed in the symmetric batteries, which fail to cycle stably.

In summary, when Zr-E is used as the electrolyte, the inorganic components of SEI formed at the lithium metal interface consist of both LiF and  $Li_3N$  components, with an irregular morphology. In contrast, the SEI in the C-Zr-E electrolyte is composed solely of LiF, resulting in a more uniform and stable structure (Fig. 5g).



Fig. 5. Comparative SEM analysis of cycled lithium metal electrodes recovered from (a) Li|Zr-E|LFP and (b) Li|C-Zr-E|LFP full cell. Ex-situ Li 1 s and N 1 s XP spectra of cycled (c) Zr-E or (d) C-Zr-E membrane (the side which contacts with Li metal) recovered from the Li|C-Zr-E|LFP and the Li|Zr-E|LFP full cells, respectively. TEM image of SEI films with (e) Li|Zr-E|LFP and (f) Li|C-Zr-E|LFP full cells after cycling. (g) The mechanism diagram of Li deposition in (a) Li|Zr-E|LFP or (b) Li|C-Zr-E|LFP.

#### 4. Conclusions

In this work, we reveal the impact of different zirconia crystal phases on LiTFSI dissociation by comparing composite solid electrolytes using monoclinic-phase zirconia and cubic-phase zirconia as fillers. The main conclusions were as follows:

- 1. The cubic-phase zirconia is obtained by doping monoclinic zirconia with  $Co^{2+}$  at the  $Zr^{4+}$  sites, leading to the introduction of oxygen vacancies to balance the charge. The formation of oxygen vacancies typically causes lattice distortion in zirconia, resulting in a phase transformation to cubic zirconia.
- 2. Through experiments and theoretical simulations, we found that cubic-phase zirconia with abundant oxygen vacancies facilitates LiTFSI dissociation in PVDF-based CSPE, improving the  $\sigma$  and  $t_{\rm Li}^{\perp}$  of C-Zr-E, reaching values of  $4.72\times10^{-4}~S~cm^{-1}$  and 0.43 at 25 °C, respectively.
- 3. The formation of a single-component inorganic SEI layer in the C-Zr-E electrolyte reduces side reactions between the electrolyte and electrodes, improving the cycling performance of Li|C-Zr-E|LFP batteries (92.13 % capacity retention after 600 cycles at 1 C), offering a valuable reference for developing high-performance solidstate electrolytes.

#### CRediT authorship contribution statement

Chen Minghua: Writing – review & editing, Supervision, Resources, Methodology, Formal analysis. Liu Yulong: Writing – original draft. Xu HuanYan: Writing – review & editing, Supervision, Data curation. Liu Qian: Writing – review & editing, Software, Formal analysis. Savilov Serguei V: Methodology, Conceptualization. Chen Zhen: Writing – review & editing, Supervision, Funding acquisition. Li Bo: 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.

#### Acknowledgment

This work is supported by the Nation Natural Science Foundation of China (Grants 52277215 and 52122702) and the Postdoctoral Science Foundation of Heilongjiang Province of China (LBH. Z23024).

#### Supporting information

Experimental section, Detailed calculation information on ionic conductivity (eq S1), lithium ion transference number (eq S2); Electrode Preparation and Cell Assembly; Electrochemical Characterization Techniques; Theoretical calculation method, the adsorption energy (eq S3); Photographs of the C-Zr-E precursor solutions before and after solvent evaporation (Fig. S1); The SEM images of (a)ZrO<sub>2</sub>, and (b) C-ZrO<sub>2-x</sub> powders (Fig. S2); The XPS survey scans of (a) ZrO<sub>2</sub> and (b) C-ZrO<sub>2-x</sub> (Fig. S3); The FT-IR spectra of SPE, Zr-E and C-Zr-E (Fig. S4); DSC profiles of the Zr-E and C-Zr-E (Fig. S5); SEM images and corresponding EDS mappings of sulfur, fluorine, zirconium and cobalt of (a) SPE, (b) Zr-E, and (c) C-Zr-E (Fig. S6); Ionic conductivities of various C-Zr-E films with different filler content (X = 0, 1, 3, 5 and 7) (Fig. S7); The determination of Li<sup>+</sup> transference number of Zr-E (Fig. S8); The SEM image of pristine lithium metal surface (Fig. S9); The main electrochemical performance of this work with ZrO2 based solid polymer electrolyte membrane (Tab. S1).

#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2025.179925.

#### Data availability

The processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

#### References

- R. Sahore, Z. Du, X.C. Chen, W.B. Hawley, A.S. Westover, N.J. Dudney, Practical considerations for testing polymer electrolytes for high-energy solid-state batteries, ACS Energy Lett. 6 (6) (2021) 2240–2247.
- [2] C.S. Bao, C.J. Zheng, M.F. Wu, Y. Zhang, J. Jin, H. Chen, Z.Y. Wen, 12 μm-thick sintered garnet ceramic skeleton enabling high-energy-density solid-state lithium metal batteries, Adv. Energy Mater. 13 (13) (2023) 2204028.
- [3] M. Yang, K.Q. Yang, Y.J. Wu, Z.X. Wang, T.H. Ma, D.X. Wu, L. Yang, J.R. Xu, P. S. Lu, J. Peng, Z.W. Jiang, X. Zhu, Q.F. Gao, F.Q. Xu, L.Q. Chen, L. Hong, W. Fan, Dendrite-free all-solid-state lithium metal batteries by in situ phase transformation of the soft carbon-Li<sub>3</sub>N interface layer, ACS Nano 18 (26) (2024) 16842–16852.
- [4] P.P. Ding, Z.Y. Lin, X.W. Guo, L.G. Wu, Y.T. Wang, H.X. Guo, L.L. Li, H.J. Yu, Polymer electrolytes and interfaces in solid-state lithium metal batteries, Mater. Today 51 (2021) 449–474.
- [5] Q. Wu, M. Fang, S. Jiao, S. Li, S. Zhang, Z. Shen, S. Mao, J. Mao, J. Zhang, Y. Tan, K. Shen, J. Lv, W. Hu, Y. He, Y. Lu, Phase regulation enabling dense polymer-based composite electrolytes for solid-state lithium metal batteries, Nat. Commun. 14 (1) (2023) 6296.
- [6] Y.F. Huang, T. Gu, G.C. Rui, P.R. Shi, W.B. Fu, L. Chen, X.T. Liu, J.P. Zeng, B. H. Kang, Z.C. Yan, F.J. Stadler, L. Zhu, F.Y. Kang, Y.B. He, A relaxor ferroelectric polymer with an ultrahigh dielectric constant largely promotes the dissociation of lithium salts to achieve high ionic conductivity, Energy Environ. Sci. 14 (11) (2021) 6021–6029.
- [7] K. Yang, L.K. Chen, J.B. Ma, C. Lai, Y.F. Huang, J.S. Mi, J. Biao, D.F. Zhang, P. R. Shi, H.Y. Xia, G.M. Zhong, F.Y. Kang, Y.B. He, Stable interface chemistry and multiple ion transport of composite electrolyte contribute to ultra-long cycling solid-state LiNi<sub>0.8</sub> Co<sub>0.1</sub> Mn<sub>0.1</sub> O<sub>2</sub> /lithium metal batteries, Angew. Chem. Int. Ed. 60 (46) (2021) 24668–24675.
- [8] Q. Kang, Y. Li, Z.C. Zhuang, D.S. Wang, C.Y. Zhi, P.K. Jiang, X.Y. Huang, Dielectric polymer based electrolytes for high-performance all-solid-state lithium metal batteries, J. Energy Chem. 69 (2022) 194–204.
- [9] Y.F. Huang, J.P. Zeng, S.F. Li, C. Dai, J.F. Liu, C. Liu, Y.B. He, Conformational regulation of dielectric poly(vinylidene fluoride)-based solid-state electrolytes for efficient lithium salt dissociation and lithium-ion transportation, Adv. Energy Mater. 13 (15) (2023) 2203888.
- [10] J.M. Zhang, Y.P. Zeng, Q.P. Li, Z. Tang, D. Sun, D. Huang, L. Zhao, Y.G. Tang, H. Y. Wang, Polymer-in-salt electrolyte enables ultrahigh ionic conductivity for advanced solid-state lithium metal batteries, Energy Storage Mater. 54 (2023) 440–449.
- [11] Y.F. Zhu, Z.J. Lao, M.T. Zhang, T.Z. Hou, X. Xiao, Z.H. Piao, G.X. Lu, Z.Y. Han, R. H. Gao, L. Nie, X.R. Wu, Y.Z. Song, et al., A locally solvent-tethered polymer electrolyte for long-life lithium metal batteries, Nat. Commun. 15 (1) (2024) 3914.
- [12] W.J. Yang, Y.W. Liu, X.Y. Sun, Z. He, P. He, H.S. Zhou, Solvation-tailored PVDFbased solid-state electrolyte for high-voltage lithium metal batteries, Angew. Chem. Int. Ed. 63 (18) (2024) e202401428.
- [13] Y.P. Zeng, L. Zhao, J.M. Zhang, Q.P. Li, D. Sun, Y. Ren, Y.G. Tang, G.H. Jin, H. Y. Wang, La<sub>2</sub>O<sub>3</sub> filler's stabilization of residual solvent in polymer electrolyte for advanced solid-state lithium-metal batteries, Small Sci. 3 (6) (2023) 2300017.
- [14] Q.J. Sun, Z. Cao, Z. Ma, J.L. Zhang, W. Wahyudi, T. Cai, H.R. Cheng, Q. Li, H. Kim, E.Q. Xie, L. Cavallo, Y.K. Sun, J. Ming, Discerning roles of interfacial model and solid electrolyte interphase layer for stabilizing antimony anode in lithium-ion batteries, ACS Mat. Lett. 4 (11) (2022) 2233–2243.
- [15] X. Yang, L. Fang, J. Li, C. Liu, L.F. Zhong, F. Yang, X.T. Wang, Z.S. Zhang, D.S. Yu, Multipolar conjugated polymer framework derived ionic sieves via electronic modulation for long-life all-solid-state Li batteries, Angew. Chem. Int. Ed. 63 (23) (2024) e202401957.
- [16] S.S. Lv, X.W. He, Z.F. Ji, S.F. Yang, L.X. Feng, X.W. Fu, W. Yang, Y. Wang, A supertough and highly-conductive nano-dipole doped composite polymer electrolyte with hybrid Li<sup>+</sup>-solvation microenvironment for lithium metal batteries, Adv. Energy Mater. 13 (44) (2023) 2302711.
- [17] X.Y. Yang, J.X. Liu, N.B. Pei, Z.Q. Chen, R.Y. Li, L.J. Fu, P. Zhang, J.B. Zhao, The critical role of fillers in composite polymer electrolytes for lithium battery, Nano-Micro Lett. 15 (1) (2023) 74.
- [18] M. Kundu, C.M. Costa, J. Dias, A. Maceiras, J.L. Vilas, S. Lanceros-Méndez, On the relevance of the polar β-phase of poly(vinylidene fluoride) for high performance lithium-ion battery separators, J. Phys. Chem. C. 121 (47) (2017) 26216–26225.
- [19] X.Y. Chen, X.J. Gao, H.Y. Wu, Y.L. Liu, X.F. Yang, R.C. Sun, Lignin-reinforced PVDF electrolyte for dendrite-free quasi-solid-state Li metal battery, Rare Met. 43 (3) (2024) 1006–1016.

#### Y. Liu et al.

- [20] L.M. Song, S.H. Sun, S.J. Zhang, J.F. Wei, Hydrogen production and mechanism from water splitting by metal-free organic polymers PVDF/PVDF-HFP under drive by vibrational energy, Fuel 324 (2022) 124572.
- [21] J.T. Li, G.W. Hu, R.H. Yu, X.B. Liao, K.N. Zhao, T.Y. Li, J.X. Zhu, Q. Chen, D. Su, Y. Ren, K. Amine, L.Q. Mai, L. Zhou, J. Lu, Revolutionizing lithium storage capabilities in TiO<sub>2</sub> by expanding the redox range, ACS Nano 17 (21) (2023) 21604–21613.
- [22] B. Luo, W.G. Wang, Q. Wang, W.J. Ji, G.H. Yu, Z.H. Liu, Z.W. Zhao, X.W. Wang, S. B. Wang, J.F. Zhang, Facilitating ionic conductivity and interfacial stability via oxygen vacancies-enriched TiO<sub>2</sub> microrods for composite polymer electrolytes, Chem. Eng. J. 460 (2023) 141329.
- [23] S.H. Wang, Y.Q. Liao, S.Y. Li, C. Cui, J.N. Liang, G.F. Du, Z.M. Tong, L.X. Yuan, T. Y. Zhai, H.Q. Li, Ultrathin all-inorganic halide solid-state electrolyte membranes for all-solid-state Li-ion batteries, Adv. Energy Mater. 14 (6) (2024) 2303641.
- [24] X.Y. Li, Y.J. Zhou, J.W. Tang, S.L. Zhao, J.Y. Zhang, X. Huang, B.B. Tian, Optimizing Li1. 3Al0. 3Ti1. 7 (PO4) 3 Particle Sizes toward High Ionic Conductivity, ACS Appl. Mater. Interfaces 15 (30) (2024) 36289–36300.
- [25] Y. Wang, Z. Chen, Y.X. Wu, Y. Li, Z.Y. Yue, M.H. Chen, PVDF-HFP/PAN/PDA@ LLZTO composite solid electrolyte enabling reinforced safety and outstanding lowtemperature performance for quasi-solid-state lithium metal batteries, ACS Appl. Mater. Interfaces 15 (17) (2023) 21526–21536.
- [26] W.J. Ji, B. Luo, Q. Wang, G.H. Yu, Z.X. Zhang, Y. Tian, Z.W. Zhao, R.R. Zhao, S. B. Wang, X.W. Wang, B. Zhang, J.F. Zhang, Z.Y. Sang, J. Liang, Interface engineering enabling thin lithium metal electrodes down to 0.78 µm for garnet-type solid-state batteries, Nat. Commun. 15 (1) (2024) 9920.
- [27] R.J. Chen, W.J. Qu, J. Qian, N. Chen, Y.J. Dai, C. Guo, Y.X. Huang, L. Li, F. Wu, Zirconia-supported solid-state electrolytes for high-safety lithium secondary batteries in a wide temperature range, J. Mater. Chem. A 5 (47) (2017) 24677–24685.
- [28] S.L. Liu, W.Y. Liu, D.L. Ba, Y.Z. Zhao, Y.H. Ye, Y.Y. Li, J.P. Liu, Filler-integrated composite polymer electrolyte for solid-state lithium batteries, Adv. Mater. 35 (2) (2023) 2110423.
- [29] J.X. Sun, Y. Wang, Y. Li, F. Wei, Fluorinated polycarbonate-based solid electrolyte plasticized using succinonitrile for 4.5 V lithium metal batteries, Sci. China Mater. 67 (2024) 1393–1402.
- [30] Y.H. Shan, L. Li, X.C. Chen, S.B. Fan, H. Yang, Y.X. Jiang, Gentle haulers of lithiumion-nanomolybdenum carbide fillers in solid polymer electrolyte, ACS Energy Lett. 7 (7) (2022) 2289–2296.
- [31] T. Nshizirungu, M. Rana, M.I.H. Khan, Y.T. Jo, S.J. Park, J.H. Park, Rare metals recycling from spent NCM cathode materials and simultaneous dehydrofluorination of polyvinylidene fluoride (PVDF) in subcritical water, J. Environ. Chem. Eng. 11 (1) (2023) 109160.
- [32] X.R. Yi, Y. Guo, S.J. Chi, S.Y. Pan, C.N. Geng, M.Y. Li, Z.S. Li, W. Lv, S.C. Wu, Q. H. Yang, Surface Li<sub>2</sub>CO<sub>3</sub> mediated phosphorization enables compatible interfaces of composite polymer electrolyte for solid-state lithium batteries, Adv. Funct. Mater. 33 (35) (2023) 2303574.
- [33] Q.H. Liu, X.Y. Han, G.Y. Wei, H. Zhang, Y. Li, L. Wang, J.G. Li, X.M. He, Abundant oxygen vacancy nanotube-incorporated composite solid electrolyte boosting longlife all-solid-state batteries, J. Power Sources 575 (2023) 233213.
- [34] D.Y. Xiong, L. Yang, Z.W. Cao, F.R. Li, W.T. Deng, J.G. Hu, H.S. Hou, G.Q. Zou, X. B. Ji, In situ construction of high-density solid electrolyte interphase from MOFs for advanced Zn metal anodes, Adv. Funct. Mater. 33 (29) (2023) 2301530.
- [35] B. Luo, W.G. Wang, Q. Wang, W.J. Ji, G.H. Yu, Z.H. Liu, Z.W. Zhao, X.W. Wang, S. B. Wang, J.F. Zhang, Facilitating ionic conductivity and interfacial stability via oxygen vacancies-enriched TiO<sub>2</sub> microrods for composite polymer electrolytes, Chem. Eng. J. 460 (2023) 141329.
- [36] J.X. Zhu, S. He, H.Y. Tian, Y.M. Hu, C. Xin, X.X. Xie, L.P. Zhang, J. Gao, S.M. Hao, W.D. Zhou, L.Q. Zhang, The influences of DMF content in composite polymer electrolytes on Li<sup>+</sup> conductivity and interfacial stability with Li-metal, Adv. Funct. Mater. 33 (25) (2023) 2301165.
- [37] Z.Z. Wang, L. Yang, C.L. Xu, J.C. Cheng, J.M. Zhao, Q.S. Huang, C. Yang, Advances in reactive co-precipitation technology for preparing high-performance cathodes, Green. Carbon 1 (2) (2023) 193–209.
- [38] Y. He, J.P. Sheng, Q. Ren, Y.J. Sun, W.C. Hao, F. Dong, Operando identification of dynamic photoexcited oxygen vacancies as true catalytic active sites, ACS Catal. 13 (1) (2022) 191–203.
- [39] Q.J. Xu, J.W. Jiang, X.F. Wang, L.Y. Duan, H. Guo, Understanding oxygen vacant hollow structure CeO<sub>2</sub>@In<sub>2</sub>O<sub>3</sub> heterojunction to promote CO<sub>2</sub> reduction, Rare Met. 42 (6) (2023) 1888–1898.
- [40] W.P. Yang, F.Y. Qi, W.J. An, H.C. Yu, S.T. Liu, P.P. Ma, R. Chen, S.X. Liu, L.L. Lou, K. Yu, Local electronic structure modulation of interfacial oxygen vacancies promotes the oxygen activation capacity of Pt/Ce<sub>1-x</sub>M<sub>x</sub>O<sub>2-δ</sub>, ACS Catal. 14 (8) (2024) 5936–5948.
- [41] X. Wu, X.B. He, Z.C. Li, F.X. Yin, Cerium zirconium solid solution with high faradaic efficiency for electrochemical nitrogen reduction reaction under ambient condition, ChemElectroChem 8 (20) (2021) 3875–3881.
- [42] Y.L. Wang, X.X. Liu, S.K. Pan, Q.S. Zhou, J. Shu, Local structure regulation and spectroscopy study of blue cubic zirconia, CrystEngComm 25 (11) (2023) 1582–1588.
- [43] N.H.M.D. Dostagir, R. Rattanawan, M. Gao, J. Ota, J.Y. Hasegawa, K. Asakura, A. Fukouka, A. Shrotri, Co single atoms in ZrO<sub>2</sub> with inherent oxygen vacancies for selective hydrogenation of CO<sub>2</sub> to CO, ACS Catal. 11 (15) (2021) 9450–9461.

- [44] S.K. Guo, S.D. Tan, J.B. Ma, L.K. Chen, K. Yang, Q.N. Zhu, Y.T. Ma, P.R. Shi, Y. P. Wei, X.F. An, Q.K. Ren, Y.F. Huang, Y.F. Zhu, Y. Cheng, W. Lv, T.Z. Hou, M. Liu, Y.B. He, Q.H. Yang, F.Y. Kang, Dissociation mechanism of lithium salt by BaTiO3 with spontaneous polarization, Energy Environ. Sci. 17 (11) (2024) 3797–3806.
- [45] Q.Y. Liu, T. Yu, H.C. Yang, S.J. Xu, H.C. Li, K. Chen, R.G. Xu, T.Y. Zhou, Z.H. Sun, F. Li, Ion coordination to improve ionic conductivity in polymer electrolytes for high performance solid-state batteries, Nano Energy 103 (2022) 107763.
- [46] L. Fang, W. Sun, W.S. Hou, Y.Q. Mao, Z.H. Wang, K.N. Sun, Quasi-solid-state polymer electrolyte based on highly concentrated LiTFSI complexing DMF for ambient-temperature rechargeable lithium batteries, Ind. Eng. Chem. Res. 61 (23) (2022) 7971–7981.
- [47] N. Wu, P.H. Chien, Y.M. Qian, Y.T. Li, H.H. Xu, N.S. Grundish, B.Y. Xu, H.B. Jin, Y. Y. Hu, G.H. Yu, J.B. Goodenough, Enhanced surface interactions enable fast Li<sup>+</sup> conduction in oxide/polymer composite electrolyte, Angew. Chem. Int. Ed. 59 (10) (2020) 4131–4137.
- [48] R. Paste, C. Hanmandlu, P.Y. Su, C.H. Hou, H.A. Chen, C.W. Pao, J.J. Shyue, K. H. Chen, H.L. Wu, H.C. Lin, C.W. Chu, Intimate interaction of TFSI<sup>−</sup> anions with MoO<sub>3-x</sub> oxygen vacancies boost ionic conductivity of cathode-supported solid polymer electrolyte, Chem. Eng. J. 452 (2023) 139088.
- [49] T. Pinheiro Araujo, C. Mondelli, M. Agrachev, T. Zou, P.O. Willi, K.M. Engel, R. N. Grass, W.J. Stark, O.V. Safonova, G. Jeschke, S. Mitchell, J. Perez-Ramirez, Flame-made ternary Pd-In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst with enhanced oxygen vacancy generation for CO<sub>2</sub> hydrogenation to methanol, Nat. Commun. 13 (1) (2022) 5610.
- [50] T. Li, X.Q. Zhang, N. Yao, Y.X. Yao, L.P. Hou, X. Chen, M.Y. Zhou, J.Q. Huang, Q. Zhang, Stable anion-derived solid electrolyte interphase in lithium metal batteries, Angew. Chem. Int. Ed. 60 (42) (2021) 22683–22687.
- [51] X.D. Peng, B. Liu, J.J. Chen, Q.P. Jian, Y.J. Li, T.S. Zhao, A steric-hindranceinduced weakly solvating electrolyte boosting the cycling performance of a micrometer-sized silicon anode, ACS Energy Lett. 8 (8) (2023) 3586–3594.
- [52] S.Y. Zhou, S.J. Zhong, Y.F. Dong, Z.Z. Liu, L.W. Dong, B.T. Yuan, H.D. Xie, Y.P. Liu, L. Qiao, J.C. Han, W.D. He, Composition and structure design of poly(vinylidene fluoride)-based solid polymer electrolytes for lithium batteries, Adv. Funct. Mater. 33 (20) (2023) 2214432.
- [53] M.L. Li, H.W. An, Y.J. Song, Q.S. Liu, J. Wang, H. Huo, S.F. Lou, J.J. Wang, Iondipole-interaction-induced encapsulation of free residual solvent for long-cycle solid-state lithium metal batteries, J. Am. Chem. Soc. 145 (47) (2023) 25632–25642.
- [54] X. Zhang, S. Wang, C.J. Xue, C.Z. Xin, Y.H. Lin, Y. Shen, L.L. Li, C.W. Nan, Response to comment on "self-suppression of lithium dendrite in all-solid-state lithium metal batteries with poly(vinylidene difluoride)-based solid electrolytes", Adv. Mater. 32 (14) (2020) e2000026.
- [55] X. Zhang, J. Han, X.F. Niu, C.Z. Xin, C.J. Xue, S. Wang, Y. Shen, L. Zhang, L.L. Li, C. W. Nan, High cycling stability for solid-state li metal batteries via regulating solvation effect in poly(vinylidene fluoride)-based electrolytes, Batter. Supercaps 3 (9) (2020) 876–883.
- [56] E.H. Penilla, L.F. Devia-Cruz, A.T. Wieg, P. Martinez-Torres, N. Cuando-Espitia, P. Sellappan, Y. Kodera, G. Aguilar, J.E. Garay, Ultrafast laser welding of ceramics, Science 365 (6455) (2019) 803–808.
- [57] Y.N. Ye, X.G. Zhu, N. Meng, F. Lian, Largely promoted mechano-electrochemical coupling properties of solid polymer electrolytes by introducing hydrogen bondsrich network, Adv. Energy Mater. 33 (45) (2023) 2307045.
- [58] X. Wu, X.H. Jie, X.H. Liang, Q.C. Hu, L.Y. Zhang, J. Wang, S.F. Wu, Dual polymer (PVDF-HFP and PES) matrix/Li<sub>6</sub>,4La<sub>3</sub>Z1<sub>1</sub>,4Ta<sub>0</sub>,0<sub>12</sub> composite solid electrolyte with good stability for solid state lithium ion batteries operating at different temperatures, Ceram. Int. 50 (23) (2024) 52110–52117.
- [59] Z.Y. Ding, Q. Tang, Q. Zhang, P.H. Yao, X.J. Liu, J.W. Wu, A flexible solid polymer electrolyte enabled with lithiated zeolite for high performance lithium battery, Nano. Res 16 (7) (2023) 9443–9452.
- [60] B.Y. Li, H. Wang, W.T. Zhou, F. Liu, J.X. He, G.H. Du, Q.M. Su, In Situ construction of PVDF/LLTO, Electrolyte stable Electrolyte/Electrode Inter. Integr. Solid-State Lithium Batter., J. Alloy. Compd. 969 (2023) 172352.
- [61] Y.T. Ma, C.R. Wang, K. Yang, B.Y. Li, Y.H. Li, S.K. Guo, J.S. Lv, X.F. An, M. Liu, Y. B. He, F.Y. Kang, Ultrathin and robust composite electrolyte for stable solid-state lithium metal batteries, ACS Appl. Mater. Interfaces 15 (14) (2023) 17978–17985.
- [62] Y.X. Wu, Y. Li, Y. Wang, Q. Liu, Q.G. Chen, M.H. Chen, Advances and prospects of PVDF based polymer electrolytes, J. Energy Chem. 64 (2022) 62–84.
- [63] X. Wang, Z. Chen, K. Jiang, M.H. Chen, S. Passerini, 3D host design strategies guiding "bottom-up" lithium deposition: a review, Adv. Energy Mater. 14 (19) (2024) 2304229.
- [64] M.H. Chen, S.A. Xie, X.Y. Zhao, W.H. Zhou, Y. Li, J.W. Zhang, Z. Chen, D.L. Chao, Aqueous zinc-ion batteries at extreme temperature: mechanisms, challenges, and strategies, Energy Storage Mater. 51 (2022) 683–718.
- [65] H.T. Zhang, C. Shen, Y.B. Huang, Z.P. Liu, Spontaneously formation of SEI layers on lithium metal from LiFSI/DME and LiTFSI/DME electrolytes, Appl. Surf. Sci. 537 (2021) 147983.
- [66] B. Luo, Q. Wang, W.J. Ji, G.H. Yu, Z.W. Zhao, R.R. Zhao, B. Zhang, X.W. Wang, J. F. Zhang, Suppressing lithium dendrite via hybrid interface layers for high performance quasi-solid-state lithium metal batteries, Chem. Eng. J. 492 (2024) 152152.