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Coaxially MXene-confined solid-state electrolyte for flexible high-rate lithium metal battery

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ABSTRACT

Solid-state polymer electrolytes (SPEs) possess conspicuous merits of facile manufacturing, superior mechanical toughness, and favorable chemical stability with Li anodes, but the intrinsically low room temperature ionic conductivity ($\sim 10^{-8} - 10^{-6}$ S cm⁻¹) and negligible Lithium-ion transfer number (0.1–0.2) badly inhibited its commercial application in lithium metal batteries (LMBs). Herein, we design the three-dimensionally and coaxially MXene-confined solid-state polymer electrolyte (C-MX SPE) for the directional acceleration movement of Li⁺ ion by introducing MXene nanosheets into the polyacrylonitrile (PAN) fiber. Benefiting from the confinement effect, the homogeneously and coaxially MXene-confined SPE possess an impressive Li⁺ ion transference number of 0.72 and ionic conductivity of 3.07×10^{-3} S cm⁻¹ at room temperature, which are 3 and 20 times of magnitude higher than the randomly MXene-dispersed (R-MX) SPE (0.22 and 1.61 $\times 10^{-4}$ S cm⁻¹), respectively. Also, the Lithium/SPE/Lithium symmetric cell exhibits a flat galvanostatic charge/discharge under 1 mA cm^{-2} for 2000 h without dendrites, revealing its 3D skeleton structure could mechanically suppress Li dendrite growth. Based on it, the assembled flexible solid-state lithium metal batteries (SSLMBs) possess a ratecapability of 101 mAh g^{-1} @ 10 C, a capacity retention of 85.18% after 500 cycles @ 1 C at room temperature and a stability of bending-needling-cutting performance. Evidently, this three-dimensionally and coaxially MXene-confined SPE may represent a promising strategy to address the random distribution and agglomeration of inorganic fillers in SPE and guide a direction for the development of high-performance, secure, and flexible SSLMBs.

1. Introduction

Solid state batteries consisting of solid-state electrolytes (SSEs), high specific energy cathodes and lithium anodes, have been deemed to be a prospective next-generation energy storage device due to its intrinsically safe nature and desirable energy density compared with other energy conversion and storage such as supercapacitor and fuel cells [1–3]. Among several reported SSEs, solid-state polymer electrolytes (SPEs) show conspicuous merits, such as facile manufacturing, superior mechanical toughness, and favorable chemical stability with Li anodes [4–6]. Unfortunately, the low ionic conductivity ($\sim 10^{-8} - 10^{-6}$ S cm⁻¹) and subnormal Lithium-ion transfer number (0.1–0.2) of SPEs [7–9], which is induced by tardily molecular chain motion kinetics,

intrinsically inhibited its commercial applications in lithium metal batteries (LMBs) [10–12].

To facilitate the kinetics of Li^+ ions in SPEs, the as-developed inorganic or organic fillers addition strategy has been verified to be a simple way to inhibit polymer crystallization and to promote the segment motion [13–16]. Particularly, these inorganic or organic fillers consisting of rich functional groups (-F, -OH, -CN and so on) could be readily bonded to the ionic species via Lewis acid-base interactions [16,17], completely dissociating the lithium salts and thus promoting the kinetics of Li^+ ions between these fillers and polymer interfaces [18,19]. Consequently, fillers with high specific surface area and abundant functional groups, such as SiO₂ nanoparticles [20], MXene nanosheets [21], etc., are beneficial to form SPEs with highly ionic conductivity

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Full paper





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 $(>10^{-4} \text{ S cm}^{-1})$. Nevertheless, the randomly-dispersed fillers could not produce homogeneous fast Li⁺ transport channels between fillers and polymer, but only works in the specified reunion areas for fast Li⁺ transport [22,23].

Herein, we develop a three-dimensionally and coaxially MXeneconfined solid-state polymer electrolyte (C-MX SPE) by introducing MXene nanosheets into the polyacrylonitrile (PAN) fiber. Benefiting from the confinement effect, the abundant F-H and -CN functional bonds between PAN fibers and MXene can dramatically facilitate the formation of Lewis acid-base interactions with PAN matrix, significantly enhancing the Li⁺ transportation in SPEs. Consequently, this homogeneously and coaxially MXene-confined SPEs delivered 20 and 3 times of larger ionic conductivity and Li⁺ ion transference number than the randomly MXene-dispersed (R-MX) SPE, reaching up to 3.07×10^{-3} S cm⁻¹ and 0.72 at 25 °C, respectively. Based on the C-MX SPEs, the enduring and extremely reversible Li plating/stripping could be accomplished (over 2000 cycles at room temperature under 1 mA cm^{-2}), revealing the excellent mechanical suppression effect of 3D skeleton structure on Li dendrite growth. In addition, the as-developed flexible solid-state lithium metal battery (SSLMB) exhibits an excellent rate (101 mAh g^{-1} @ 10 C), cycling performance (>85% after 500 cycles @1 C) at room temperature, a stability of bending-needling-cutting performance and broad temperatures adaptability ranging from 0 °C to 90 °C. Overall, this coaxially MXene confined strategy could achieve rapid Li⁺ kinetics and promote the high performance SSLMBs.

2. Results and discussion

Fig. 1a schematically presents the fabrication process of C-MX SPEs by coaxially introducing MXene nanosheets into the polyacrylonitrile (PAN) fiber. The free-standing MXene-Ti₃C₂ nanosheets are synthesisd through the classic chemical-etching method reported in our previous work [24] (Fig. S1). The size of the MXene nanosheets are \sim 500 \times 500 nm (Fig. S2). The two-stage orientation inducement from the fluid draft and electric field can effectively promote the coxial penetration of the MXene nanosheets into PAN fiber. This coaxial confinement of MXene into PAN matrix can orderly construct the continuous fast Li⁺ ion diffusion channels (Fig. 1b). Besides, abundant functional groups (such as -F, -O, -H -OH) on the surface of MXene nanosheets can fully adsorb the cationic surfactants of PAN, and these cationic surfactants could conversely self-assemble onto the surface of MXene nanosheets via their electrostatic and hydrogen interactions [25-27]. These abundant functional groups could provide the faster Li⁺ ion diffusion ability than the pure polymer matrix. As counterparts, coaxially PAN-dispersed (C-PAN) SPE and radomly MXene-dispersed (R-MX) SPE are prepared by the same method (Figs. S3-4).

In Fig. 1c and S5–6, the MXene nanosheets are coaxially confined in the 3D nanofiber with lateral size of 0.5 µm. This core/shell structure of confinement effect well inhibits the agglomeration issue of MXene nanosheets. TEM images (Fig. 1d-e) and energy dispersive spectrometer (EDS) images and the corresponding distribution spectrum of elements (Fig. 1g and S7) further domenstrate the successful confinement of MXene nanosheets into the PAN matrix. The Raman spectrum of MXene nanosheets have been tested in Fig. S38. The spectrum can be divided into three regions: the flake region, which corresponds to a group vibration of carbon, two titanium layers and surface groups, the T_x region, which represents vibrations of the surface groups, and the carbon region, where both in-plane and out-of-plane vibrations of carbon atoms are located. From Fig. 1f, the interface between PAN matrix and MXene nanosheets could be clearly observed. Fig. S8 shows the structural difference in interlayer spacing of with/without coaxially-confined MXene nanosheets arrangement. A minor left shift of (002) peak from 6.46° to 5.94° obviously indicates a slight increase of interlayer spacing after the coaxial confinement [28,29]. Besides, the molecular interaction between MXene nanosheets and PAN polymer matrix are verified via Fourier transform infrared reflection (FT-IR) and Raman spectroscopy

(Fig. S9-10). The typical absorption peaks of -C=O, -C=N – and -C-O– could confirm the successful fabrication of coaxially confined MXene SPE. After the coaxial confinement, the peaks around 200 cm⁻¹ (A_{1 g}) could be clearly observed [30]. Compared with R-MX, the peak of C-MX exhibits the distinct red shift, indicative of the higher interlayer spacing. Among the above three-dimensional structure fibers, originating from the numerous hydroxyl and cyano end groups on the coaxial and rigid nanosheets [31], C-MX shows the highest hydrophilic ability, indicating the better interface stability between electrolyte and electrode (Fig. S11) [32,33].

The obtained C-MX SPE could be prepared in large scale (Fig. 1h) and shows excellent mechanical flexibility (Fig. S12). The C-MX SPEs have a maximum 428% strain and a highest Young's modulus of 4.27 MPa, superior to the C-PAN (0.95 MPa) and R-MX (1.7 MPa). These mechanical flexibility discrepancies are mainly ascribed to the extra hydrogen interactions and 3D structure in C- MX SPEs [34,35]. Moverover, the C-MX exhibts a high specific surface area of $61.755 \text{ m}^2 \text{ g}^{-1}$, which is about 7 times higher than that of R-MX (8.286 m² g⁻¹, Figs. S13-14). Such high surface area could effectively promote the absorbtion and transportion of Li⁺ ion. The composition of coaxially-confined MXene and PAN matrix is also investigated by thermogravimetric analysis (TGA). The mass percentage of MXene in the acquired C-MX is determined to be around 8%. (Fig. S15). To evaluate the contents of LiTFSI and PC, we have conducted the TGA and FT-IR tests of C-MX SPEs in different states. The photographs of SPEs in three different states are shown in Fig. S16. From the TGA curves in Fig. S17, the content ratio of LiTFSI is approximately 18% in the C-MX SPEs, and the content ratio of PC in C-MX is less than 5%. Moreover, the FT-IR spectrum is shown in Fig. S18. The absorption peak near 3000 ${\rm cm^{-1}}$ and 1793 ${\rm cm^{-1}}$ could be assigned as the stretching vibration of C-H and C=O stretching vibration of PC, respectively. The peak at 1280 cm^{-1} is the stretching vibration of C–O–C in PC, and the characteristic peak exhibit a red-shift to 1290 cm⁻¹, due to the interaction between Li^+ and PC. The addition of Li^+ will weaken the interaction between Li⁺ and ether O atoms, destroy the crystalline structure of PAN, increase the amorphous region of PAN, and facilitate the migration of Li^+ .

In Fig. S19, the chronoamperometry (CA) measurements show a very low electronic conductivity of C-MX SPEs (1.18×10^{-10} S cm⁻¹), which is much lower than that of MXene-Ti₃C₂ (1.5×10^3 S cm⁻¹) [36,37]. This dramatical conductivity difference of shell/core would structually enhance the dielectric confinement effect and greatly improve the directional movement of electrons and ions [38]. Based on the above results, this coaxial confinement of MXene into PAN matrix should be a suitable strategy to strengthen the ion transportation for SPEs.

The ionic conductivity of SPEs are investigated via the EIS spectrum of symmetrical cells based on different SPEs at a broad temperatures ranging from -30 °C to 90 °C (Fig. S20). The thickness of C-MX SPEs is 150-160 µm (Fig. S21). The Arrhenius plot of SPE ionic conductivity shows a non-linear temperature dependency curve (Fig. 2a). And the well-fitting curve of ionic conductivity data upon Vogel-Tammann-Fulcher (VTF) equation demonstrates the Li⁺ ion transportation of SPEs follows the VTF mechanism [39-41]. Compared with C-PAN and R-MX SPEs, C-MX exhibits the highest ionic conductivity (3.07 \times $10^{-3}\,S$ cm^{-1}) and lowest activation energy (0.221 eV) at 25 °C. Even at -30 °C, the ionic conductivity of the C-MX can reach up to 2.52×10^{-4} S cm⁻¹, showing an excellent electrochemical performance at a wide range of temperature. Such high ionic conductivity of C-MX should be mainly ascribed to coaxially-dispersed fast ion transportation channels and numerous functional groups (-F and -OH from MXene and -CN from PAN) between MXene nanosheets and PAN matrix [35,41]. Meanwhile, these abundant polar functional groups on C-MX could provide high-voltage endurance ability [42,43]. The linear sweep voltammetry (LSV) curves disclose that C-MX SPEs could maintain electrochemical stability up to 5 V (vs. Li⁺/Li) (Fig. 2b), which is compatible to some high-voltage cathode materials for high density SSLMBs [44]. The Li⁺



Fig. 1. Design and physicochemical properties of coaxially MXene-confined SPE. a Schematic illustration of the coaxially MXene-confined solid polymer electrolyte and the internal interactions between MXene and PAN. b The comparison of Li^+ ion diffusion path between C-MX and R-MX SPEs. c SEM image of the C-MX SPE membrane and the corresponding EDX mapping results. d TEM image of the C-PAN SPE membrane and e C-MX SPE membrane. f HRTEM image of C-MX. g EDS line scan spectrum of C-MX and the corresponding element distribution results. h Optical photos of large scale size C-MX membranes.



Fig. 3. In-situ characterization of fast kinetics in coaxially confined-MXene SPE. a Schematically illustrating the in-situ Electrochemical impedance characterization. b Nyquist plot of C-MX and C-PAN before in-situ EIS tests. c the corresponding DRT results of C-MX and C-PAN SPE. d sample residual plot of the real part and imaginary part of the Hilbert transformed impedance. e in-situ impedance spectra plot of C-MX. f DRT results as calculated from the measured in-situ impedance date during an entire cycling.

Ohm resistance (R_b, $10^{-6} \sim 10^{-5}$ s), solid-state electrolyte interface resistance (R_{SEI}, $10^{-4} \sim 10^{-1}$ s), and charge transfer resistance (R_{ct}, $10^{0} \sim 10^{1}$ s), respectively [54]. The C-MX shows the lower peak intensity than that of C-PAN, indicating the faster Li⁺ ion kinetics in the medium to high frequency region (Fig. 3d) [55,56]. During the discharging process, the peak intensity of R_{ct} and R_{SEI} increases with the decreasing voltage, which is corresponding to the formation of SEI layer between SPE and Li anode. Meanwhile, the peak intensity of Rct and RSEI increases with the increasing voltage during the charging process, indicating a highly invertible charge/discharge behavior in C-MX based SSLMBs [57,58] (Fig. 3e-f). After the full cycle, the peak intensity of R_{SEI} decrease to almost invisible, suggesting the formation of stable SEI layer between C-MX SPE and lithium anode. This could be consistent with the excellent Li/C-MX/Li symmetric battery performance. Moreover, the DFT calculation method (VASP) to obtain the adsorption energy of MXene and PAN for Li⁺ in Fig. S37 and Table S2. Obviously, MXene (-2.85 eV) exhibits lower adsorption energy than PAN (-0.91 eV) for the adsorption of Li⁺, indicating the Li⁺ would preferentially transport through MXene instead of PAN. Therefore, the high ionic conductivity of the C-MX SPE could be attributed to the coaxial MXene confined strategy. Thus, the rapid Li⁺ kenitics of C-MX SPE verified via in-situ EIS characterization and DFT calculation ensure its potentially promissing application in SSLMBs.

Attracted by the rapid Li⁺ kinetics of C-MX SPEs, we further explored the electrochemical performance of C-MX based SSLMBs. As shown in the CV curves of the SSLMBs (Fig. 4a and S24), two cathodic/anodic peak could be obvious observed (~3.65 V and ~3.25 V), which corresponds to the Li⁺ intercalation and deintercalation in LiFePO₄ (LFP), respectively [59]. With the steadily increasing scanning rates, a modest electrochemical polarization of peak shift could be observed from the CV curves. The ratio of peak current to square root of scan rate for C-MX and C-PAN SPEs are calculated to be 0.0145 and 0.011, respectively. This result ulteriorly verifies the faster reaction kinetics of C-MX SPEs [60–62] (Fig. 4b). Also, the interfacial resistance of C-MX (44 Ω cm²)

and C-PAN (162 Ω cm²) SPEs based SSLMBs could confirm the successful construction of rapid Li⁺ transportation channel via the coaxially confined-MXene strategy (Fig. 4c) [54]. In addition, we further carry out the galvanostatic intermittent titration technique (GITT) to qualify the ion transfer capability of SPEs (Fig. 4d and S25). The diffusion coefficient increases from 3.52×10^{-9} cm² s⁻¹ to 2.06×10^{-8} cm² s⁻¹ after the coaxially confined-MXene strategy. We believe that C-MX based SSLMBs would exhibit outstanding rate performance since the diffusion overpotential and diffusion coefficient are highly correlated to the transport kinetics of Li⁺ between electrode and electrolyte [63]. In Fig. 4e and S26, the C-MX based SSLMBs exhibit high rate performance of 167 mAh g⁻¹, 163 mAh g⁻¹, 158 mAh g⁻¹, 148 mAh g⁻¹, 132 mAh g⁻¹, 130 mAh g⁻¹, 124 mAh g⁻¹, 117 mAh g⁻¹ at 0.1, 0.2, 0.5, 1, 2, 3,4 and 5 C, respectively. Even at the 10 C, the specific capacity of C-MX based SSLMBs could still maintain 100 mAh g⁻¹. The corresponding charging/discharging voltage curves of SSLMBs are shown in Fig. 4f and S27-28. The C-MX has smaller polarziation voltages than other SPEs, indicating the higher polarization suffertibility. The two characteristic peaks (~3.4 V and 3.5 V) of the dQ/dV profiles of C-MX SPE based LMBs (Fig. 4g) correspond well to the platform voltage of the charge and discharge curve. Moreover, After a few days of standing, the self-discharge performances of the batteries have been tested in Fig. S39. the capacity of the C-MX based SSLMBs changed from 170.64 to 170.06 mAh g^{-1} , the calculated self-discharge rate is about 99.66%, indicating its extremely low self-discharge behavior of C-MX SPEs. At the same time, in order to make full use of the high electrochemical stability window of C-MX SPE, we matched it with the high voltage cathode material (LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂, NCM), and tested a series of electrochemical properties (Fig. S29-S33). The C-MX based SSLMBs achieved the rate performance of 201 mAh g^{-1} , 178 mAh g^{-1} , 154 mAh g^{-1} , 136 mAh g^{-1} , 118 mAh g^{-1} at 0.2, 0.3, 0.5, 1, and 2 C, respectively. These results show that even if the charging voltage reaches 4.6 V, C-MX SPE can still maintain good electrochemical stability and provide excellent electrochemical performance of the battery. This further confirms the

potential of C-MX SPE to increase the energy density of SSLMBs.

To demonstrate the practical performance of the C-MX based SSLMBs, we further investigate the rate performance over a wide temperature range of 0 °C to 90 °C (Fig. 4h). C-MX based SSLMBs could work properly at 0 °C (112 mAh g^{-1} @0.1 C and 93 mAh g^{-1} @1 C). When compared to 25 °C (165 mAh g^{-1} @0.1 C and 148 mAh g^{-1} @1 C), this battery still maintian a high capacity retention of 68%. Even the temperature rises from 25 to 90 °C, this C-MX based SSLMB still posses a capacity up to 165 mAh g^{-1} @ 0.1 C and 149 mAh g^{-1} @ 1 C. These results could be attributed to rapid Li⁺ kinetics via the coaxially confined-MXene strategy. After alternating high and low temperature tests, the capacity of SSLMBs can still be recovered well when the temperature returns to 25 °C, suggesting the excellent environmental adapability of the C-MX based SSLMBs. As for the long-term cycle performance, the C-MX based SSLMBs are able to cycle effective for 500 cycles and the reversible capacity retains 124 mAh g^{-1} @ 1 C at 25 °C with ~99.9% Coulombic efficiency (Fig. 5a-b). After the long-term cycling, the interfacial resistance of C-MX based SSLMBs only increases from 67.6 Ω cm⁻² to 88.1 Ω cm⁻² (Fig. 5c), suggesting the formation of a stable SEI laver between C-MX and Lithum anode. Except the long-term cycling at the low current density, the C-MX based SSLMBs also exhibt a considerable capability at the high current density. The reversible capacity of SSLMBs could still retain 75 mAh g⁻¹ @ 5 C at 25 °C (Fig. 5d). Overall, the above-mentioned considerable electrochemical performance could be ascribled to the coaxially confined-MXene strategy and excellent stablity toward lithium metal anodes of SPEs [13,64].

C-MX SPEs can be manufactured on a large scale for high capacity soft-pack batteries (Fig. S34). Soft-package SSLMBs based on C-MX SPEs have been assembled in Fig. 5e. The internal resistance of soft-package SSLMBs is as low as 70.43 Ω cm⁻² (Fig. 5f). After 100 cycles @ 1 C at room temperature, the capacity retention of the C-MX based soft-package battery is still over 96%, indicating an excellent cycle stability of C-MX SPEs for soft-package SSLMBs. Besides, this pounch cell could success light on 400 green ligh-emitting diode (LED) lights and LED board (Figs. S35-36, Movie S1–3). To further demonstrate the safety of the C-MX SPEs based soft-package SSLMBs, this battery is subjected to cutting, bending and penetration tests. Fig. 5h shows that the soft-package SSLMB could still power up a blue LED even suffering 180° bending, half cutting and penetration. Evidently, the robust mechanical properties of C-MX SPE can ensure the high safety for the practical application of SSLMBs.

Supplementary material related to this article can be found online at doi:10.1016/j.nanoen.2024.109312.

3. Conclusion

In conclusion, a coaxially MXene-confined polymer electrolyte has been proposed for the enhanced aligned-fast of Li⁺ kinetics and stably rechargeable SSLMBs. This confinement effect could dramatically facilitate the formation of Lewis acid-base interactions from the abundant F-H and -CN functional bond between PAN fibers and MXene, significantly enhancing the Li⁺ transportation in SPEs. The C-MX SPE exhibits an impressive Li^+ ion transference number of 0.72 and ionic conductivity of 3.07 \times 10⁻³ S cm⁻¹ at 25 °C. Based on the C-MX SPEs, the Lithium/SPE/Lithium symmetric cell delivers a flat galvanostatic charge/discharge curves (over 2000 cycles at room temperature under 1 mA cm⁻²). The as-developed SSLMBs deliver outstanding room temperature rate (101 mAh g^{-1} @ 10 C), cycling performance (>85% after 500 cycles @1 C), stability of bending-needling-cutting performance and the ability of withstanding broad temperatures ranging from 0 °C to 90 °C. This coaxially-confined strategy is expected to address the random distribution and agglomeration of inorganic fillers in SPE and achieve high energy density and long cycle life SSLMBs for nextgeneration energy storage devices.

4. Experimental section/methods

4.1. Materials

Polyacrylonitrile (PAN, average Mn ~150,000) is purchased from Aladdin. Ti₃AlC₂ ceramics powder is directly purchased from 11 Technology Co., Ltd. N, N-dimethylformamide (DMF) and propylene carbonate (PC) are purchased from Chengdu Kelon Co., Ltd. Lithium iron phosphate (LiFePO₄, LFP, battery grade), N-methylpyrrolidone (NMP), polyvinylidene fluoride (PVDF, battery grade), lithium foil (~50 µm) and Conductive carbon black are produced by Hefei Kejing Material Technology Co., Ltd. LFP active material, PVDF binder and conductive carbon black were mixed and coated on the aluminum current collector according to the ratio of 8.5:0.5:1, and the mass loading amount of the active material is controlled to be 5–6 mg cm⁻². The as-prepared LFP cathodes are cut into disc with a diameter of 12 mm and dried under vacuum for 12 h at 120 °C before use.

4.2. Preparation of MXene nanosheets

To selectively etch Al from Ti₃AlC₂, 2 g of Ti₃AlC₂ ceramics powder with mesh size under 45 µm and 2 g LiF are carefully added into 40 mL etchant (12 M HCl: DI water is 3:1). The solution is stirred in water bath under 40 °C for 24 h. The single layered Ti₃C₂T_x nanosheets (MXene) are centrifuged at 3500 rpm for 10 min several times while being reiterated rinsed with deionized water until the pH of the supernatant surpassed 6. Then the bottom sediment that resembles clay is further cleansed using vacuum filtering. The filter cake is collected and vacuum-dried over 24 h at 40 °C for further use.

4.3. Preparation of coaxial MXene solid polymer electrolyte

First, 12 wt% PAN and 10% wt% MXene nanosheets are subsequently dissolved in DMF solution, respectively. A dark and homogenous solution (MXene) and yellow solution (PAN) are prepared by vigorously stirring the mix solution for 12 h at 50 °C. A stainless steel needle is then used to put these two kinds of solution into a 10 mL syringe. The direct current voltage is controlled by $1 \ \rm kV \ \rm cm^{-1}$ during electrospinning. After 4-5 h of spinning, the coaxial-MXene solid polymer electrolyte (C-MX SPE) membrane is acquired by annealing at 50 °C for completely removing residual solvent. Then, this membrane is cut into disks with a diameter of 12 mm, and immersed into the solution of bis(trifluoromethane)sulfonimide lithium (LiTFSI, Aladdin) in ethyl acetate for 24 h. The C-MX SPE fully absorbs the lithium salts through immersion. The films are transported into the solution of propylene carbonate (PC) and swollen with PC for 12 h to reduce the crystallinity of PAN. After that, the films are vacuum-dried at 60 °C for 12 h and transferred into the glove box to completely remove the remaining PC solvent. The coaxial-PAN (C-PAN) SPE is also prepare via the same procedure of C-MX except the introducing of MXene. Random MXene (R-MX) SPE is prepared via the solution casting methods instead of electrospinning process.

4.4. Material characterizations

The morphology and microstructure of as-prepared C-MX SPEs are characterized by field emission scanning electron microscope (SEM, JEOL 7800 F, 5 kV) as well as EDS mapping. The TEM, high-resolution TEM experiments were carried out using a JEOL JEM-2100 F microscope that was operated at 200 kV in a scanning mode with a nominal analytical beam size of 0.5 nm. Pore size and specific surface area are measured with automated surface area and pore size analyzer (BET, Quadrasorb evo). The X-ray diffraction (XRD, PANalytical) are applied to investigate the crystal structures of SPEs and MXene nanosheets. The X-ray diffraction specimens were prepared by means of grinding and flattening the powders or membranes on small slides. Fourier transform



Fig. 5. Cycling performance and stability of C-MX based SSLMBs. a 500 Cycles performance and Coulombic efficiency of C-MX and C-PAN SPEs based LMBs at the current density of 1 C. b Charge/discharge profiles of C-MX SPEs based LMBs after 1, 100, 200, 300, 400 and 500 cycles, respectively. c Interfacial resistance of C-MX SPE based LMBs after 1, 100, 200, 300, 400 and 500 cycles, respectively. c Interfacial resistance of C-MX SPE based LMBs after 1, 100, 200, 300, 400 and 500 cycles, respectively. c Interfacial resistance of C-MX SPE based LMBs after 1, 100, 200, 300, 400 and 500 cycles, respectively. c Interfacial resistance of C-MX SPE based LMBs after 1, 100, 200, 300, 400 and 500 cycles, respectively. c Interfacial resistance of C-MX SPE based LMBs at the current density of 5 C up to 100 cycles. e Schematic diagram of the internal structure of soft-package all-solid-sate LMBs. f Interfacial resistance of C-MX SPE based soft-package all-solid-sate LMBs. g Cycling performance and Coulombic efficiency of C-MX SPEs based soft-package all-solid-sate LMBs at the current density of 1 C up to 100 cycles. h The working states of soft-package LMBs in difficult circumstances, including bending, cutting, folding and penetration.

infrared spectroscopy (FT-IR) spectra are collected using a Bruker Invenio. A HORIBA Jobin-Yvon with a 532 nm laser and an air-cooled CCD detector was used for the Raman spectroscopic study. Tensile strength is carried out on a LDW1 Tensile Tester (100 N Load Cell). Thermogravimetric analyses (TGA) are carried out on a Mettler Toledo analyzer at a ramp rate of 10 $^{\circ}$ C min⁻¹ under N₂ atmosphere.

CRediT authorship contribution statement

Weiqing Yang: Writing - review & editing, Project administration, Funding acquisition, Conceptualization. Haitao Zhang: Writing - review & editing, Funding acquisition. Hanyu He: Resources, Methodology. Junfeng Huang: Writing - review & editing, Formal analysis. Hongzhi Peng: Visualization, Methodology, Investigation. Qi Tang: Visualization, Validation, Methodology, Data curation. Haichao Huang: Methodology, Formal analysis, Data curation. Zhong Xu: Writing - review & editing, Writing - original draft, Data curation, Conceptualization.

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.

Data availability

No data was used for the research described in the article.

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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.nanoen.2024.109312.

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