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Active sites-rich zeolitic imidazolate framework/MXene heterostructure modified separator with improved Li+ transport for high-performance Li-S batteries

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Active sites-rich zeolitic imidazolate framework/MXene heterostructure modified separator with improved Li$^+$ transport for high-performance Li-S batteries

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Abstract

The inevitable shuttle effect of lithium polysulfides (LiPSs) and sluggish redox kinetics restrict lithium-sulfur (Li-S) batteries real-world applications, although they have been paid plentiful attention. Herein, a thin and multifunctional heterostructure (ZIF-L/MXene), consisting of cobalt-containing zeolitic imidazolate framework in a leaf-like morphology (ZIF-L) and two-dimensional layered Ti$_3$C$_2$T$_x$ MXene nanosheets, is developed for modification of polyolefin-based separators. A good combination of the merits of the ZIF-L and MXene can hinder the restacking of MXene nanosheets and achieve a large specific surface area (SSA), thus exposing abundant active sites for adsorption and catalytic conversion of LiPSs. Taking these obviously synergistic effects, the ZIF-L/MXene heterostructure modified separators not only alleviate the shuttling of LiPSs but also promote their kinetics conversion. Furthermore, with an improved electrolyte affinity, the ZIF-L/MXene modified separators can accelerate the transport of Li$^+$. Thus, the modified separator endows a Li-S cell with a high initial discharge capacity of 1371.7 mAh g$^{-1}$ at 0.2 C and favorable cycling stability, with a slow capacity decay ratio of 0.075% per cycle over 500 cycles at 1.0 C. Even under a high sulfur loading of ~ 4.1 mg cm$^{-2}$, the Li-S battery can achieve a high initial capacity of 990.6 mAh g$^{-1}$ at 0.1 C and maintain an excellent cycling performance. The novel ZIF-L/MXene heterostructure modified separator in this work can provide an alternative strategy for designing thin and light separators towards high-performance Li-S cells, via the enhancement of kinetics conversion and reduction of shuttle effect of the LiPSs.

Keywords: Li-S batteries; zeolitic imidazolate framework; MXene; separators; synergistic effects
### 1. Introduction

With the increasing demand for high-energy-density energy storage devices, a great deal of attention was concentrated on developing promising energy storage systems. Lithium-sulfur (Li-S) batteries are considered one of the promising next-generation batteries with ultra-high theoretical energy density (~ 2600 Wh kg\(^{-1}\)), environmental-friendly, and low cost of raw materials\(^1\)-\(^3\). Nevertheless, the real-world application of Li-S batteries is limited by several challenging issues, mainly containing poor electronic conductivity of sulfur and Li\(_2\)S, the notorious shuttle effect resulting from the soluble lithium polysulfides (LiPSs), and sluggish reaction kinetics\(^4\)-\(^6\). Consequently, the electrochemical performances (such as rate performance, cycling lifetime, and Coulombic efficiency) of Li-S batteries suffer from a certain degree of damage\(^7,\,8\).

Various strategies have been developed to tackle the aforementioned issues, with attention toward innovative hybrid sulfur hosts\(^9\), optimizing electrolytes\(^10\), and modifying separators\(^11\) to boost the electrochemical performances of Li-S batteries. In the past few years, designing a functional separator has been considered a very effective way to alleviate the shuttle of LiPSs and facilitate the redox kinetics of sulfur\(^12\). Among them, polar materials are extensively employed for the modification of polyolefin separators due to their strong chemical adsorption capacity\(^13\). However, it is hard to relieve the shuttle effect continuously and efficiently via chemical adsorption. For reducing the dissolution of LiPSs to inhibit the shuttle effect from the root, materials with electrocatalytic effects on the conversion reaction of LiPSs are used for functional separators, such as transition metal sulfides\(^14\), transition metal nitrides\(^15\),\(^\,16\), MXenes\(^17\), and metal-organic frameworks (MOFs)\(^18\). MOFs possess catalytic metal centers and organic ligands with strong LiPSs adsorption capacity to immobilize LiPSs and facilitate their transformation\(^19\). Especially, as a new star of MOFs, leaf-like Co-containing zeolitic imidazolate frameworks (ZIF-L) with a thickness of a few hundred nanometers and a large specific surface area (SSA) are expected to show massive active sites for alleviating the shuttle effect and improving electrochemical performances of
Li-S batteries\textsuperscript{[20]}. Nevertheless, MOFs suffer from poor electrical conductivity, which can easily give rise to decreasing sulfur utilization and electrochemical performances of Li-S batteries when they are used as modified materials alone\textsuperscript{[21]}.

MXenes, one of the fascinating family of two-dimensional (2D) laminar materials, have drawn massive interest in Li-S batteries because of their metallic conductivity, intensive polar sites, and catalytic activity\textsuperscript{[22, 23]}. Typically, MXenes derived from their parental MAX phases with a general formula of $M_{n+1}X_nT_x$ (n=1-4) are obtained by selectively removing the A layers, where “M” assigns to the early transition metal (e.g., Ti, V, Nb, etc.), “A” corresponds to the IIIA or IVA elements (e.g., Al, Si, etc.), “X” is carbon or/and nitrogen, and $T_x$ represents the terminations (e.g., –OH, –O, –F, etc.)\textsuperscript{[24, 25]}. The sulfophilic surface terminations and conductive Ti-C-Ti bonds can vigorously anchor LiPSs and accelerate the charge transfer kinetics, promoting sulfur utilization and optimizing the electrochemical performances of Li-S batteries\textsuperscript{[26]}. For example, Song et al. proposed a $\text{Ti}_3\text{C}_2T_x$ MXene modified separator with a thin modified layer of only 522 nm and a mass loading of only 0.1 mg cm$^{-2}$ for Li-S battery\textsuperscript{[27]}. The MXene-functionalized separator endowed the Li-S cell with an initial discharge capacity of 1046.9 mAh g$^{-1}$ at 0.2 C and maintained a capacity of 743.7 mAh g$^{-1}$ at 1.0 C due to its high conductivity and effective confinement of LiPSs. However, the van der Waals attraction and hydrogen bonding interaction lead to serious restacking of MXene nanosheets, thus reducing the number of exposed active sites and limiting catalytic activity\textsuperscript{[28]}. Jiao et al. thus rationally designed TiO$_2$-MXene heterostructures as the multifunctional catalyst of Li-S batteries\textsuperscript{[29]}. The uniformly distributed TiO$_2$ on MXene nanosheets not only acted as a barrier for inhibiting the restacking of MXene layers but also played a role in capturing LiPSs. With an improved adsorption ability and catalytic activity toward the LiPSs, the Li-S cell with the TiO$_2$-MXene heterostructure functionalized separator achieved high-rate performance and a long cycling lifetime. Ren et al. reported a heterostructure (CPNC) consisting of CoP and $\text{Ti}_3\text{C}_2$, in which the ingenious design alleviates the aggregation of CoP nanocages and restacking of $\text{Ti}_3\text{C}_2$ nanosheets, thus revealing plentiful active sites and facilitating the redox reaction of sulfur\textsuperscript{[30]}. As a result, the Li-S cell utilized the $\text{Ti}_3\text{C}_2$/CPNC modified separator obtained
excellent cycling stability. Tian et al. designed a modified separator consisting of carbon nanotubes (CNTs) and MXene@CoS$_2$ (MCCoS) for Li-S batteries$^{[31]}$. The CNTs were introduced to expose more active regions for LiPSs catalysis and provide channels for the transport of Li$^+$ because the size of CoS$_2$ was too small to prevent the stacking of MXene nanosheets.Benefiting from the bifunctional catalytic activity and adsorption ability toward LiPSs, the Li-S cell with a MCCoS/PP separator exhibited a high-rate performance of 368.6 mAh g$^{-1}$ at 20 C and superb cycling performance. Consequently, the rational structural design of MXene hybrids to reveal more active sites is considered a promising strategy for their efficient utilization in Li-S batteries.

Motivated by the above research, to expand the active sites for catalysis conversion sulfur-based species and to adsorb more LiPSs, in this work, we firstly prepared a novel ZIF-L/MXene heterostructure by $in situ$ growing the ZIF-L with abundant active metal sites on a conductive MXene. Then the commercial polypropylene (PP) separator was coated with the as-prepared ZIF-L/MXene heterostructure via a simple vacuum filtration process, to achieve a modified separator to boost the electrochemical performances of Li-S batteries. The MXene nanosheets in the ZIF-L/MXene heterostructure not only played the role of a conductive substrate to offer electrons for ZIF-L but also captured LiPSs through the formation of Ti-S bonds by Lewis acid-base interaction and accelerated the conversion of LiPSs. Moreover, the ZIF-L with a large SSA and sufficient active sites could relieve the restacking of MXene nanosheets to expose more active sites and provide a powerful catalytic effect for the redox reaction of sulfur species. Also, the improved electrolyte affinity of the ZIF-L/MXene@PP is beneficial to the permeation of electrolyte and the transport of Li$^+$. Profiting from the above many merits, the ZIF-L/MXene modified PP (ZIF-L/MXene@PP) separator indeed endows the Ketjen Black/sulfur (KB/S) cathode with a high initial discharge capacity of 1371.7 mAh g$^{-1}$ at 0.2 C and a capacity fading rate of 0.075% per cycle during 500 cycles at 1.0 C. Besides, the Li-S cell assembled by the KB/S cathode and ZIF-L/MXene@PP separator achieved a high discharge capacity of 990.6 mAh g$^{-1}$ at 0.1 C and good cycling performance under the mass loading of sulfur up to ~ 4.1 mg cm$^{-2}$ in a low ratio electrolyte to sulfur.
2. Results and Discussion

The preparation procedures of the ZIF-L/MXene heterostructure are shown in Figure 1A. Firstly, MXene with a lamellar morphology and plentiful terminations (–OH, –O, and –F) was obtained by removing the Al layer of Ti₃AlC₂ in a mixed aqueous solution containing LiF and HCl[32]. The mild synthesis route makes it easy to obtain MXene nanosheets with large lateral dimensions, which is conducive to the subsequently uniform loading of ZIFs[33]. The fluorine-containing etching method inevitably leads to a mass of surface terminations such as –OH, –O, and –F with negatively charged surface, which easily anchors metal cations. Subsequently, to uniformly obtain the ZIF-L/MXene heterostructure, Co(NO₃)₂·6H₂O and 2-methylimidazole (2-MI) dispersed in deionized water were introduced into the MXene nanosheets aqueous suspension with continuous stirring. Taking advantage of the negatively charged terminations of the MXene nanosheets, the leaf-like ZIFs can be in situ grown on the surface of MXene under room temperature (RT) through a coprecipitation reaction. After washing with deionized water and drying in a vacuum, the leaf-like ZIFs could be conveniently achieved. Herein, by cross-linking with the surface terminations of MXene nanosheets, the Co²⁺ could play a role of nucleation sites for the in situ growth of ZIF-L on MXene nanosheets and withstand the electrostatic repulsion between the nanosheets[34].

Transmission electron microscopy (TEM) was utilized to investigate the morphologies and microstructures of the as-prepared samples. As shown in Figure 1B, the TEM image indicated that the achieved MXene nanosheets with ultrathin thickness and large lateral dimensions. As shown in Figure 1C, the leaf-like ZIFs were successfully grown on the MXene nanosheets. High-resolution TEM (HRTEM) image shown in Figure 1D exhibited a 0.244 nm lattice spacing associated with the (103) crystal plane of MXene. The diffraction rings in the selected area electron diffraction (SAED) pattern (Figure 1E) can be designated to the (101) and (110) crystal planes of MXene. All results demonstrated the successful synthesis of the ZIF-L/MXene heterostructure. The N₂ adsorption-desorption isotherms of the MXene nanosheets and
ZIF-L/MXene heterostructure are shown in **Supplementary Figure 1**, which indicates they are both II isotherms. The SSAs of the MXene and ZIF-L/MXene are respective of 2.9 and 49.9 m$^2$/g, the smaller SSA of the MXene can attributed to the restacking of MXene nanosheets resulted from their Vander Waals force between the different layers. In contrast, the larger SSA of the ZIF-L/MXene benefits from the addition of ZIF-L with a high SSA and its positive effect for hindering the stacking of MXene nanosheets. Furthermore, the good combination of the ZIF-L and MXene is beneficial to expose more active sites for enhancing the interaction with LiPSs when it was used to a modified interlay for Li-S batteries. As shown in **Supplementary Figure 1B-C**, the pore distribution curves exhibited that the pore sizes of the ZIF-L/MXene and MXene are mainly distributed in the mesoporous range and the corresponding total pore volumes are 0.075 and 0.017 cm$^3$/g, respectively. The abundant mesoporous pores are conducive to electrolyte penetration and Li$^+$ transport. Taking the above-discussed advantages of the ZIF-L/MXene heterostructure, it can act as an ideal material for separator modification in Li-S batteries.

**Figure 1.** (A) Schematic illustration for the synthesis procedures of the ZIF-L/MXene heterostructure. TEM images of the (B) MXene nanosheets and (C) ZIF-L/MXene heterostructure. (D) HRTEM image and (E) SAED pattern of the ZIF-L/MXene heterostructure.
The powder X-ray diffraction (XRD) patterns of MXene and ZIF-L/MXene are displayed in Figure 2A. The disappeared typical (104) peak of Ti₃AlC₂ and the downshift characteristic (002) peak demonstrated the successful removal of Al layers and the formation of MXene nanosheets. The XRD pattern of ZIF-L in the ZIF-L/MXene heterostructure is very similar to its reported simulated pattern, indicating it has the same framework type[35]. Additionally, compared with the MXene, the (002) peak attributed to the MXene in the of ZIF-L/MXene heterostructure further downshifts from 6.57° to 5.94°, indicating an expansion in interlayer spacing. The chemical compositions and the corresponding valence state of the corresponding elements of ZIF-L/MXene were characterized by X-ray photoelectron spectroscopy (XPS). As shown in Supplementary Figure 2, the Co 2p and N 1s peaks derived from ZIF-L are displayed in the XPS survey spectrum of ZIF-L/MXene. In the high-resolution Co 2p spectrum (Figure 2B), the peaks at 796.04 and 794.58 eV can be attributed to Co 2p₁/₂. And the two peaks at 780.30 and 778.67 eV correspond to Co 2p₃/₂. Co²⁺ is the main existing form in the ZIF-L/MXene because the energy gaps between Co 2p main peaks and satellites are around 6.0 eV, which are related to Co²⁺[34, 36]. The peaks at 800.98 and 784.37 eV are attributed to the shakeup satellites. The XPS spectrum of O 1s (Figure 2C) can divide into four peaks based on the fitting curve, including C-Ti-(OH)ₓ at 530.95 eV, C-Ti-Oₓ at 529.73 eV, C=O at 528.83 eV, and Ti=O at 527.95 eV, respectively[34, 37]. Figure 2D shows the XPS spectrum of Ti 2p, in which the two peaks at 462.27 and 459.47 eV belong to C-Ti-Tₓ and Ti-O of 2p₁/₂, respectively[23, 38]. The peaks of Ti 2p₃/₂ located at 456.58, 454.09, and 453.04 eV match to C-Ti-Tₓ, Ti-O, and Ti-C, respectively[38-40]. The deconvoluted N 1s spectrum (Figure 2E) reveals pyrrolic nitrogen, Co-N, and pyridinic nitrogen configurations with peaks at 398.98, 397.98, and 396.92 eV, respectively[41]. As shown in Figure 2F, the high-resolution spectrum of C 1s was deconvoluted into five components located at 286.79, 284.36, 283.00, 282.45, and 279.64 eV were ascribed to C=O, C-N, C-C, C-Ti-O, and C-Ti, respectively[37, 42, 43]. The XPS results demonstrate that the ZIF-L was successfully in situ grown on MXene nanosheets.
Figure 2. (A) XRD patterns of MXene and ZIF-L/MXene. The high-resolution XPS spectra of (B) Co 2p, (C) O 1s, (D) Ti 2p, (E) N 1s, and (F) C 1s of ZIF-L/MXene.

To further explore the possibilities of the as-prepared ZIF-L/MXene heterostructure in separator modification for high-performance Li-S batteries, the ZIF-L/MXene heterostructure was thus coated onto the PP separators by a vacuum filtration, to achieve the ZIF-L/MXene@PP separators. The cross-sectional SEM image of the ZIF-L/MXene@PP separator is shown in Supplementary Figure 4, in which the thickness of the modification layer onto the PP separator is only 3.3 μm. The ultra-thin modification layer is conducive to reducing unnecessary mass/volume gain and achieving high-energy-density Li-S batteries. Additionally, the SEM and the corresponding element mapping images of the ZIF-L/MXene@PP separator displayed in Supplementary Figure 5 indicating that the C, N, O, Co, and Ti elements uniformly distribute onto the ZIF-L/MXene heterostructure. The top-view SEM images displaying the morphologies of the PP, MXene nanosheets modified PP (MXene@PP), and ZIF-L/MXene@PP separators were shown in Figure 3A-C, respectively. Compared with a mass of macropores distributed on the surface of the PP separator, the macropores of the MXene@PP and ZIF-L/MXene@PP separators were fully covered by the uniform MXene nanosheets and ZIF-L/MXene heterostructure, respectively. The PP separator with plentiful macropores was hard to efficiently inhibit the shuttling effect of LiPSs,
thus resulting in poor electrochemical performances of Li-S batteries. In contrast, the MXene@PP and ZIF-L/MXene@PP separators with abundant active sites distributed in the functional layers could immobilize LiPSs and facilitate their conversion. Moreover, the ZIF-L/MXene@PP separator possesses a relatively loose and porous structure than the MXene@PP separator, which naturally leads to a faster diffusion and transfer of Li\(^+\). The wettability of the PP, MXene@PP, and ZIF-L/MXene@PP separators toward the electrolyte was revealed by their corresponding contact angle, respectively. As shown in Figure 3D, the contact angle of the original PP separator is 37.6°, indicating that the PP separator can be moderately wetted by the electrolyte. The contact angle of the MXene@PP (7.6°) separator is much lower than that of the pristine PP separator, showing a higher infiltration capability toward the electrolyte (Figure 3E). Compared with the partly wettability of the PP and MXene@PP separators, the contact angle of the ZIF-L/MXene@PP separator shown in Figure 3F is as low as 0°, demonstrating complete wettability. The admirable wettability of the ZIF-L/MXene@PP separator can be ascribed to the strong polarity of the ZIF-L/MXene heterostructure, which is conducive to the permeation of electrolyte and transport of Li\(^+\), thus optimizing the electrochemical performances of Li-S batteries. To evaluate the physicochemical barrier and adsorption ability of the PP and ZIF-L/MXene@PP separators toward Li\(_2\)S\(_6\), a series of permeation measurements were carried out with the H-type electrolytic cells. The Li\(_2\)S\(_6\) infiltrate from Li\(_2\)S\(_6\) solution to blank solution with the PP and ZIF-L/MXene@PP separators during 8 h is displayed in Figure 3G. After 8 h, the color of the right bottle changes from colorless to yellow, suggesting the PP separator is hard to resist the permeation of Li\(_2\)S\(_6\). For the device with the ZIF-L/MXene@PP separator, there is nearly no color change on the right bottle, demonstrating an excellent adsorption effect towards Li\(_2\)S\(_6\), which is mainly attributed to the high SSA and exposed sulfurophilic active sites.
Figure 3. (A-C) Top-view SEM images of the PP, MXene@PP, and ZIF-L/MXene@PP separators. (D-F) The contact angle tests between electrolyte and PP, MXene@PP, or ZIF-L/MXene@PP separators. (G) Li$_2$S$_6$ permeation measurements of the PP and ZIF-L/MXene@PP separators.

To further investigate the LiPSs adsorption capacity of these modified materials, MXene and ZIF-L/MXene of the same mass were added into 2 mM Li$_2$S$_6$ solution for standing for 6 h. Also, the blank Li$_2$S$_6$ solution was standing at the same time for comparison. As shown in Figure 4A, there was no change in the color for the blank Li$_2$S$_6$ solution, but the color of the yellow Li$_2$S$_6$ solution containing MXene became lighter, indicating that MXene can effectively adsorb Li$_2$S$_6$. In contrast, the Li$_2$S$_6$
solution containing ZIF-L/MXene turned almost colorless, demonstrating a better adsorption effect on Li$_2$S$_6$. The ultraviolet-visible (UV–vis) spectrum of the blank Li$_2$S$_6$ solution displays a characteristic peak at around 275 nm, which contributes to the S$_6^{2-}$ species$^{[44]}$. After adsorption by the MXene and ZIF-L/MXene heterostructure, the intensity of the S$_6^{2-}$ peak both decreased. Furthermore, the peak intensity from the supernatant in the bottle containing the ZIF-L/MXene heterostructure is the weakest, indicating the lowest concentration of Li$_2$S$_6$ and the best adsorption capacity toward LiPSs.

The redox kinetics of soluble LiPSs plays an important role in inhibiting the shuttle effect and improving electrochemical performance$^{[45]}$. To investigate the catalytic effect of the modified materials on LiPSs, symmetric cells were assembled by the identical MXene electrode or ZIF-L/MXene electrode with 0.2 M Li$_2$S$_6$ electrolyte, and the CV tests were conducted using the assembled symmetric cells between the potential window -1.5 to 1.5 V. Also, the CV curve of the ZIF-L/MXene electrode in electrolyte without Li$_2$S$_6$ was utilized for comparison to eliminate the capacitive contribution. As shown in Figure 4B, it is found that the lowest current density in the battery assembled by the ZIF-L/MXene electrode without addition of Li$_2$S$_6$, which demonstrated that the lithiation/delithiation reactions were the major contribution to current response$^{[46]}$. Specifically, the ZIF-L/MXene-based symmetric cell with Li$_2$S$_6$ electrolyte exhibited a higher current density and lower polarization potential than that of the MXene-based symmetric cell at 10 mV s$^{-1}$, respectively, indicating a better catalytic effect on conversion of Li$_2$S$_6$ and less barrier for ions migration. Generally, this catalytic behavior is conducive to efficiently utilizing active sulfur-based species at high rate for Li-S cells. In addition, the redox current of the ZIF-L/MXene-based symmetric cell was greatly improved, and there was no obvious change after 5 cycles at 1000 mV s$^{-1}$ (Supplementary Figure 6), which indicated that the good catalytic effect can be well maintained during the battery cycle. The catalytic activity of the modified materials was further studied by CV curves of Li-S cells with different modified separators. As shown in Figure 4C, the cathodic peaks of peak I and II correspond to the reduction of solid
sulfur into soluble LiPSs and the conversion of soluble LiPSs to insoluble short-chain Li$_2$S/Li$_2$S$_2$, respectively[46]. The anodic peak III and peak IV are associated with the oxidation of insoluble Li$_2$S/Li$_2$S$_2$ into soluble long-chain LiPSs and the conversion of soluble LiPSs to solid sulfur, respectively[46]. It can be observed that the peak current densities of reduction and oxidation peaks of the ZIF-L/MXene@PP-based Li-S cell are obviously higher than those of the MXene@PP and PP-based Li-S cells, respectively, which is beneficial from the improved utilization of sulfur by the ZIF-L/MXene@PP. Furthermore, it is observed that the reduction and oxidation peaks of the ZIF-L/MXene@PP-based Li-S cell shifted to the higher and lower potential, respectively. These results demonstrated that the ZIF-L/MXene can indeed promote the conversion of sulfur-based species in both reduction and oxidation reactions. The Tafel slopes of the reduction and oxidation process in Figure 4D-E show that the fitted slopes follow the order of ZIF-L/MXene@PP<MXene@PP<PP, indicating that the ZIF-L/MXene improved the redox reaction kinetics of sulfur species[46]. The CV curves (Figure 4F and Supplementary Figure 7) were measured at different scan rates to further investigate the Li$^+$ diffusion kinetics, which was critical to understand the redox kinetics of sulfur species. In general, the Li$^+$ diffusion efficiency can be evaluated according to the Randles–Sevcik formula[46]:

$$I_p = (2.69 \times 10^5) n^{1.5} A D_{Li^+}^{0.5} C_{Li^+}^{1/2} v^{0.5}$$

(1)

where $I_p$ represents the peak current density, $n$ is the number of charges transferred, $A$ is the area of the electrode, $D_{Li^+}$ is the diffusion coefficient of Li$^+$, $C_{Li^+}$ is the concentration of Li$^+$, and $v$ is the scan rate. The $D_{Li^+}$ is positively correlated to the absolute value of the slope for the fitted lines shown in Figure 4G-I, among which the ZIF-L/MXene@PP displays the largest absolute value, implying that the ZIF-L/MXene@PP possesses a higher Li$^+$ diffusion in both oxidation and reduction process in the Li-S cells, respectively, thus boosting the redox reaction of LiPSs[47].
Figure 4 (A) UV-vis spectra of the supernatants (inset: digital images of blank Li$_2$S$_6$, Li$_2$S$_6$-MXene, and Li$_2$S$_6$-ZIF-L/MXene solutions, respectively). (B) CV curves of symmetric cells at 10 mV s$^{-1}$. (C) The first CV curves of the PP, MXene@PP, and ZIF-L/MXene@PP-based Li-S cells at 0.1 mV s$^{-1}$. Tafel plots of the (D) cathodic peak and (E) anodic peak derived from the CV curves. (F) CV curves of ZIF-L/MXene@PP-based Li-S cell at the scan rates of 0.1, 0.2, 0.3, 0.4, and 0.5 mV s$^{-1}$, respectively. Plots of peak current densities for (G) peak I, (H) peak II, and (I) peak III versus the square root of the scan rate.

To further reveal the enhanced redox kinetics, electrochemical impedance spectroscopies (EIS) of the Li-S cells with different separators were performed at the open-circuit potentials, respectively. As shown in Figure 5A, the Nyquist plots of the fresh Li-S cells all displayed three parts, which are the intercept between the semicircle and the coordinate axis ($R_1$, the solution resistance of the electrolyte), the semicircle at high frequency ($R_2$, the charge transfer resistance), and the sloped line at low frequency ($W_1$, the Warburg impedance)\textsuperscript{15}. The $R_2$ of the PP, MXene@PP, and ZIF-L/MXene@PP-based Li-S cells are 99.56, 72.18, and 70.17 $\Omega$, respectively. The lowest
of the ZIF-L/MXene@PP-based cell is attributed to the unique structure of ZIF-L/MXene, which conduces to fast charge transfer and Li$^+$ diffusion. The rate performances of PP, MXene@PP, and ZIF-L/MXene@PP-based Li-S cells were measured at the current densities ranging from 0.2 to 2.0 C. As shown in Figure 5B, the ZIF-L/MXene@PP-based cell achieved specific capacities of 1371.7, 878.5, 797.1, and 710.2 mAh g$^{-1}$ at 0.2, 0.5, 1.0, and 2.0 C, respectively. In contrast, the Li-S cells with the MXene@PP and PP separators only obtained 1197.6 and 1157.2 mAh g$^{-1}$ at 0.2 C, and 543.0 and 517.0 mAh g$^{-1}$ at 2.0 C, respectively. The improved specific capacity of the ZIF-L/MXene@PP-based cell benefits from the large exposed active surface of the ZIF-L/MXene heterostructure with good adsorption and catalytic effect toward LiPSs. The galvanostatic charge/discharge (GCD) curves of the Li-S cells with different separators were tested at 0.2 C, as shown in Figure 5C. The lowest polarization potential ($\Delta E$) reveals the fastest LiPSs conversion kinetics of the ZIF-L/MXene@PP-based cell. Also, the ratio of the $Q_L$ to $Q_H$ is utilized to evaluate the catalytic ability for boosting the conversion of soluble LiPSs to insoluble discharge products, among which the $Q_L$ and $Q_H$ represent the low and high discharge plateau, respectively. The results shown in Supplementary Figure 8 demonstrate the highest value of the $Q_L/Q_H$ for the ZIF-L/MXene@PP-based cell corresponds to the excellent catalytic activity of the ZIF-L/MXene heterostructure. For further investigating the long-term cycling stability, the Li-S cells with different separators were measured at 1.0 C for 500 cycles (Figure 5D). The average capacity decay rates per cycle are 0.075%, 0.093%, and 0.106% for ZIF-L/MXene@PP, MXene@PP, and PP-based Li-S cells, respectively. Additionally, the ZIF-L/MXene@PP, MXene@PP, and PP-based Li-S cells exhibited Coulombic efficiencies of 96.7%, 95.7%, and 93.2% after 500 cycles, respectively. The superior cycling performance is originated from the strong suppression of the shuttling of LiPSs through the synergistic effect of the ZIF-L and MXene. When the ratio of E/S decreased to 10 $\mu$L·mg$^{-1}$ with a high sulfur loading up to ~ 4.1 mg cm$^{-2}$, the Li-S cell with the ZIF-L/MXene@PP also achieved a good initial capacity of 990.6 mAh g$^{-1}$, Coulombic efficiency of 97.3% and maintained a high capacity retention of 77.2% after 100 cycles (Figure 5E). The self-discharge behavior
also is one of the crucial evidence to evaluate the inhibition of the LiPSs shuttle effect, which is caused by the reduction of sulfur species and shuttle effect in the Li-S cells\[^{49}\]. As shown in Figure 5F, the open circuit voltages of the Li-S cells are tested with ZIF-L/MXene@PP, MXene@PP, and PP separators. The open circuit voltages of the Li-S cells decreased within a few hours and gradually stabilized over the following time. It is found that the open circuit voltages of the ZIF-L/MXene@PP, MXene@PP, and PP-based Li-S cells were 2.69, 2.49, and 2.41 V for 25 h rest, demonstrating that the modified separators could effectively relieve the shuttle effect of the soluble LiPSs and the ZIF-L/MXene@PP separator exhibited a better effect. The self-discharge behavior of the ZIF-L/MXene@PP-based cell was further investigated at 0.1 C under a high sulfur loading and lean electrolyte. As shown in Figure 5E, the ZIF-L/MXene@PP-based cell was cycled for 100 cycles, followed by 124 h rest, and then was cycled for 50 cycles. The ZIF-L/MXene@PP-based cell exhibited a capacity decay of 204.9 mAh g\(^{-1}\) after 124 h rest, but the capacity recovered its condition before rest during the second discharge process after rest, indicating an excellent ability for suppressing the self-discharge using the modified ZIF-L/MXene@PP separator. The schematic illustrations of the adsorption and conversion of LiPSs on ZIF-L/MXene@PP are shown in Figure 5G. Based on the synergistic effect of the ZIF-L and MXene, the LiPSs were anchored on ZIF-L/MXene@PP, followed by rapid conversion to improve the electrochemical performances of Li-S cells.
Figure 5. (A) EIS curves of the fresh PP, MXene@PP, and ZIF-L/MXene@PP-based Li-S cells, respectively. (B) Rate performance, (C) the GCD curves measured at 0.2 C, and (D) cycling performances at 1.0 C of the Li-S batteries with different separators, respectively. (E) Cycling performance of high-sulfur-loading (~ 4.1 mg cm⁻²) Li-S cell with the ZIF-L/MXene@PP separator at 0.1 C and then rest for 124 h. (F) The open circuit voltages of the PP, MXene@PP, and ZIF-L/MXene@PP-based Li-S cells, respectively. (G) Schematic illustrations of the adsorption and conversion of LiPSs on ZIF-L/MXene@PP.

To further reveal the effect of modified separators on relieving the shuttling of LiPSs, Li-S cells with PP, MXene@PP, and ZIF-L/MXene@PP separators were cycled at 1 C for 300 cycles and then disassembled to characterize the erosion degree of the Li anode after the cycles. As shown in Figure 6A, the Li-S cell with a PP separator exhibits a severely corrosive microstructure on the surface of the Li anode. In contrast, the MXene@PP-based cell displays a flatter and smoother surface for the Li anode (Figure
6B), indicating an effective effect on inhibiting the shuttling of LiPSs. As shown in Figure 6C, the flattest and smoothest surface of Li foil was achieved by the Li-S cell which employed the ZIF-L/MXene@PP separator, demonstrating the most ability of relieving the shuttle effect of LiPSs. The element content and element mapping images of the surface of Li foils are shown in Figure 6D-F and Supplementary Figure 9-11.

Compared with the PP and MXene@PP separators, the ZIF-L/MXene@PP separator exhibited a more obvious effect on adsorbing and confining LiPSs, because the Li foil from the ZIF-L/MXene@PP-based cell exhibits less sulfur species on the surface. All results indicated that the ZIF-L/MXene@PP separator with a high LiPSs adsorption and obvious catalytic effect can effectively boost the electrochemical performances of Li-S batteries.

Figure 6. SEM images and corresponding element contents of Li metal anodes from (A, D) PP, (B, E) MXene@PP, and (C, F) ZIF-L/MXene@PP-based Li-S cells after 300 cycles at 1 C.

3. Conclusion

In summary, we successfully prepared a thin and multifunctional heterostructure with the leaf-like ZIF-L distributed on 2D MXene nanosheets that possess enhanced LiPSs adsorption and catalytic activity as the functional modified layer of separator for Li-S battery. Profiting from the large exposed active sites and improved electrolyte
affinity of the ZIF-L/MXene heterostructure, the ZIF-L/MXene@PP separator with a thickness of ~ 3.3 μm for coating layer exhibits an excellent initial discharge capacity of 1371.7 mAh g⁻¹ at 0.2 C, high Coulombic efficiency, and good cycling stability for a Li-S battery. Furthermore, even under a high sulfur loading of ~ 4.1 mg cm⁻² and lean electrolyte, the assembled Li-S cell with this modified separator also achieved a high initial discharge capacity and long cycling life. Therefore, the ZIF-L/MXene heterostructure can provide an idea of thin and light design toward a modified layer of separator for high-performance Li-S batteries.

4. Experimental section

4.1. Synthesis of the MXene nanosheets

2.0 g of LiF was put into 40 mL of HCl (9.0 M) aqueous solution, and the mixture was stirred for 30 min at 35 ℃. Ti₃AlC₂ powder (2.0 g) was then slowly added to the mixture. After 36 h, the product was washed with deionized water until the pH became neutral. Subsequently, the MXene nanosheets were obtained by repeated shaking and centrifugal treatments.

4.2 Fabrication of the ZIF-L/MXene heterostructures

The ZIF-L/MXene heterostructure was prepared by an in situ growth method at RT. Firstly, 0.1 g of MXene, 0.4 g of Co(NO₃)₂·6H₂O, and 0.9 g of 2-methylimidazole were dispersed in 20 mL deionized water, respectively. Subsequently, the above solution was mixed and stirred at RT for 4 h. The ZIF-L/MXene heterostructure was collected after washing with deionized water and vacuum drying process.

4.3 Preparation of the ZIF-L/MXene@PP and MXene@PP separators

The modified PP separators were prepared through a vacuum filtration method. Typically, 20 mg ZIF-L/MXene was dispersed in methanol with sonication under an ice bath. Then, the obtained suspension was vacuum filtered on the PP separator, and the as-prepared ZIF-L/MXene@PP separator was dried at RT over 12 h. Similarly, the MXene@PP separator was fabricated by the same process except the ZIF-L/MXene
was replaced by MXene. Finally, the ZIF-L/MXene@PP and MXene@PP separators were cut into circular disks with a mass loading of ~ 0.13 mg cm⁻².

**Declarations**

**Authors’ contributions**

**Leiping Liao:** Methodology, Characterization, Data analysis, Writing-original draft.  
**Huanhuan Duan:** Data analysis, Writing-review.  
**Guohua Chen:** Writing-review & editing.  
**Yuanfu Deng:** Conceptualization, Supervision, Writing-review & editing, Funding resources. All authors have given approval to the final version of the manuscript.

**Availability of data and materials**

All data are available in the manuscript and the Supplementary Material.

**Financial support and sponsorship**

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**Conflicts of interest**

All authors declared that there are no conflicts of interest.

**Ethical approval and consent to participate**

Not applicable.

**Consent for publication**

Not applicable.
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Active sites-rich zeolitic imidazolate framework/MXene heterostructure modified separator with improved Li$^+$ transport for high-performance Li-S batteries

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1. Experimental section

1.1. Materials

MAX (Ti$_3$AlC$_2$) was bought from Jilin 11 Technology Co., Ltd. Hydrochloric acid (HCl) was purchased from Guangzhou Chemical Reagent Factory. Lithium fluoride (LiF) and 1-methyl-2-pyrrolidone (NMP) solvent were obtained from Shanghai Macklin Biochemical Co., Ltd. Cobalt nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O), 2-Methylimidazole, 1, 2-dimethoxyethane (DME), and 1, 3-dioxolane (DOL) were supplied by Aladdin Reagent Co., ltd. Polyvinylidene difluoride (PVDF) and lithium foils were received from Guangdong Canrd New Energy Technology Co., Ltd. Sublimed sulfur (S) was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. All chemicals were used directly without further purification.

1.2. Characterizations

The morphology and structure of the samples were characterized by a scanning electron microscope (SEM, Merlin) and transmission electron microscope (TEM, JEM 2100F). The specific surface area and pore size distribution of the samples were investigated by a Micrometitics surface analyser (ASAP 2460) at 77 K. X-ray diffraction (XRD) was performed on a D8 Advance Powder Diffractometer. X-ray photoelectron spectroscopy (XPS, Kratos Axis Supra+) was employed to analyze the surface chemical compositions of the samples. The electrolyte contact angle of the modified separators was obtained with a Dataphysics OCA40 Micro. Ultraviolet–visible spectroscopy measurement was tested on a SHIMADZU UV-2600 spectrometer. The content of sulfur in KB/S was collected from a thermal gravimetric analyzer (TGA, TGA 550).

1.3. Visualized Adsorption of Polysulfides

2 mM Li$_2$S$_6$ solution was obtained by dissolving S and Li$_2$S (molar ratio of 5:1) into the solution of DME/DOL with a volume ratio of 1:1, and then stirring at 60 ℃ for 12 hours in an argon-filled glovebox. 20 mg of MXene and ZIF-L/MXene were added into 2 mL Li$_2$S$_6$ solution for comparison, respectively.

1.4. Assembly of Li$_2$S$_6$ symmetric batteries

Symmetric batteries were assembled with two identical ZIF-L/MXene or MXene electrodes,
a Celgard 2500 separator, and 40 μL of Li$_2$S$_6$ electrolyte. The electrodes with a mass loading of 0.3 mg cm$^{-2}$ were prepared by loading the homogeneous slurry of ZIF-L/MXene and PVDF in a weight ratio of 9:1 onto carbon-coated Al foils (circular disks with a diameter of 14 mm), followed by vacuum drying. For comparisons, the MXene electrodes were prepared by the same method. 0.2 M Li$_2$S$_6$ electrolyte was obtained by dissolving S and Li$_2$S (molar ratio of 5:1) into electrolyte which containing 1.0 M lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) with 2 wt% LiNO$_3$ in DME/DOL (volume ratio of 1:1). The CV curves of the symmetric batteries were collected from a CHI660D electrochemical workstation at scan rates of 10 and 1000 mV s$^{-1}$ between a voltage range of -1.5 to 1.5 V.

1.5. Cathode preparation and electrochemical tests

S and KB powder were mixed in ethanol with stirring for 40 min and dried at 60 °C. Then, the KB/S composite was obtained through a melt-diffusion process with heat treatment at 210 °C for 12 h in an argon (Ar) atmosphere. The TGA curve shown in Supplementary Figure 3 suggested that the sulfur content in the KB/S composite is 75.5%. The as-prepared KB/S composite and PVDF were stirred in NMP with a mass ratio of 9:1 to obtain a homogeneous slurry. Subsequently, the aforesaid slurry was coated on carbon-coated Al foils (circular disks with a diameter of 14 mm) and dried under vacuum at 60 °C for later use. The S mass loadings of regular cathodes were between 1.2-1.5 mg·cm$^{-2}$ and the high loading was up to ~ 4.1 mg·cm$^{-2}$.

The electrochemical performances were carried out by using CR2016-type coin cells, and the cells were assembled in an Ar-filled glove box. Pure lithium metal and ZIF-L/MXene@PP MXene@PP were used as the anodes and separators, respectively. 1.0 M LiTFSI dissolved in DME/DOL (volume ratio of 1:1) with 2 wt% LiNO$_3$ additive as electrolyte. The ratio of electrolyte/S was 20 μL·mg$^{-1}$ for the ordinary electrodes and 10 μL·mg$^{-1}$ for the high sulfur loading electrodes. The GCD tests were measured on a multichannel battery test system (Neware CT-3008W) with a voltage range from 1.7 to 2.8 V. CV measurements were performed on an electrochemical workstation (CHI660D), and the EIS was tested from 0.01 Hz to 100 kHz.
2. Supplementary figures and tables

Supplementary Figure 1. (A) N\textsubscript{2} adsorption-desorption isotherms of the MXene and ZIF-L/MXene. The pore distribution curves of the (B) ZIF-L/MXene and (C) MXene.
Supplementary Figure 2. XPS survey spectrum of the ZIF-L/MXene.
Supplementary Figure 3. TGA curve of the KB/S at N2 atmosphere.
Supplementary Figure 4. (A) SEM and (B) Cross-sectional SEM images of the ZIF-L/MXene@PP separator.
Supplementary Figure 5. (A) SEM and (B-F) the corresponding element mapping images of the ZIF-L/MXene@PP separator.
Supplementary Figure 6. CV curves of the ZIF-L/MXene-based symmetric cell at 1000 mV s\(^{-1}\).
Supplementary Figure 7. CV curves of the (A) PP-based and (B) MXene@PP-based symmetric cells at different scan rates.
Supplementary Figure 8. (A) $Q_L/Q_H$ and specific capacities of the PP, MXene@PP, and ZIF-L/MXene@PP-based Li-S cells, respectively. The charge–discharge curves of the (B) PP, (C) MXene@PP, and (D) ZIF-L/MXene@PP-based Li-S cells at different rates, respectively.
Supplementary Figure 9. (A) SEM image and (B-F) corresponding element analysis of Li metal anode from the PP-based Li-S cell.
Supplementary Figure 10. (A) SEM image and (B-F) corresponding element analysis of Li metal anode from the MXene@PP-based Li-S cell.
**Supplementary Figure 11.** (A) SEM image and (B-F) corresponding element analysis of Li metal anode from the ZIF-L/MXene@PP-based Li-S cell.
**Supplementary Table 1.** Electrochemical performance comparisons of the ZIF-L/MXene-PP separator with other functional separators in recent literature.

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