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# Na-S Batteries



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generation energy storage systems.<sup>[1]</sup> These batteries offer a high theoretical energy density of  $1274 \text{ Wh} \text{kg}^{-1}$  and are

more cost-effective than traditional lithium-ion batteries (LIBs). However, they encounter several challenges in

practical applications. The reduction reaction of sulfur with

# **Amorphous FeSnO<sub>x</sub> Nanosheets with Hierarchical Vacancies for Room-Temperature Sodium-Sulfur Batteries**

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**Abstract:** Room-temperature sodium-sulfur (RT Na–S) batteries, noted for their low material costs and high energy density, are emerging as a promising alternative to lithium-ion batteries (LIBs) in various applications including power grids and standalone renewable energy systems. These batteries are commonly assembled with glass fiber membranes, which face significant challenges like the dissolution of polysulfides, sluggish sulfur conversion kinetics, and the growth of Na dendrites. Here, we develop an amorphous two-dimensional (2D) iron tin oxide (A-FeSnO<sub>x</sub>) nanosheet with hierarchical vacancies, including abundant oxygen vacancies (O<sub>v</sub>s) and nano-sized perforations, that can be assembled into a multifunctional layer overlaying commercial separators for RT Na–S batteries. The O<sub>v</sub>s offer strong adsorption and abundant catalytic sites for polysulfides, while the defect concentration is finely tuned to elucidate the polysulfides conversion mechanisms. The nano-sized perforations aid in regulating Na ions transport, resulting in uniform Na deposition. Moreover, the strategic addition of trace amounts of Ti<sub>3</sub>C<sub>2</sub> (MXene) forms an amorphous/crystalline (A/C) interface that significantly improves the mechanical properties of the separator and suppresses dendrite growth. As a result, the task-specific layer achieves ultra-light (~0.1 mgcm<sup>-2</sup>), ultra-thin (~200 nm), and ultra-robust (modulus = 4.9 GPa) characteristics. Consequently, the RT Na–S battery maintained a high capacity of 610.3 mAh g<sup>-1</sup> and an average Coulombic efficiency of 99.9 % after 400 cycles at 0.5 C.

### Introduction

The increasing demand for high-energy-density, cost-effective rechargeable batteries have elevated room-temperature sodium-sulfur (RT Na–S) batteries to the forefront of next-

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Na ions cause huge volume expansion of 170 % (vs. 80 % in Li-S), resulting in disruption of the fine morphology of electrodes.<sup>[2]</sup> Additionally, the generation of undesirable intermediates, including long-chain polysulfides (Na<sub>2</sub>S<sub>n</sub>,  $3 \le$  $n \leq 8$ ), which are more susceptible to the "notorious shuttle" effect" (vs. lithium polysulfides), as well as the irreversible precipitation of short-chain Na sulfides, solid products with poor electronic/ionic conductivity, ultimately lead to slow sulfur reduction reaction (SRR) kinetics and irreversible active sulfur loss.<sup>[3]</sup> The high reactivity of Na anodes, compared to Li anodes, makes them prone to irreversible side reactions with the electrolyte, resulting in inhomogeneous deposition, and even the formation of Na dendrites, which can pose serious safety hazards.<sup>[4]</sup> These factors contribute to severe capacity degradation, poor Coulombic efficiency, and a shortened cycle life in RT Na-S batteries.

Previous studies have primarily focused on the development of sulfur-containing cathodes with various structures and compositions to improve sulfur electronic/ionic conductivity, buffer the significant volume change, and physically confine Na polysulfides.<sup>[5]</sup> Strategies have also included hybridizing sulfur with polar oxides,<sup>[6]</sup> sulfides,<sup>[7]</sup> or metalorganic frameworks (MOFs)<sup>[8]</sup> to chemically trap polysulfides and boost conversion kinetics. While these approaches have shown advancements, they often involve a large proportion of inactive materials, offsetting the high-energy advantage of sulfur cathodes. On the anode side, researchers have explored several strategies such as electrolyte additives,<sup>[9]</sup> or physicochemical pretreatment<sup>[10]</sup> to form a stable solid electrolyte interphase (SEI) on the Na anode. Despite these efforts, the application of Na metal anodes remains challenging due to their high reactivity and the limited mechanical and chemical stability of SEI.<sup>[11]</sup> Thus, a convenient and effective approach is needed to address both cathode and anode issues in Na-S batteries simultaneously.

The separator, in close contact with both the cathode and anode, emerges as a promising approach.<sup>[12]</sup> Polyolefin separators, commonly used in Li-S batteries, are not ideal for Na-S batteries due to poor surface wettability in electrolytes. Most Na-S cells use glass fiber (GF) membranes, and there have been some research efforts focused on modifying GF membrane (e.g. CoFe@FeOx nanoparticles) to boost SRR kinetics and further enhance the electrochemical performance of RT Na-S batteries.<sup>[13]</sup> However, GF membranes have considerable thickness (~300 µm) and micron-sized pore sizes, which are still the main culprits in reducing the weight/volumetric energy density of the battery, and increasing the risk of short circuits due to dendrites penetration. Additionally, their poor mechanical strength is a limiting fact for large-scale applications.<sup>[14]</sup> Meanwhile, several researchers have turned to the modification of polypropylene (PP) separators for Na-S cell and mainly focus on transition metal carbide (e.g. MXene). Although effective, these functional layers are currently both dense and thick (typically 3-10 µm), which can impede ion mobility and diminish sulfur utilization.<sup>[15]</sup> Consequently, developing efficient, thin polysulfides adsorption and conversion traps coated on separators remains a significant challenge for Na-S batteries applications.

In the pursuit of ideally thin modification layers for efficient adsorption and conversion of polysulfides, amorphous two-dimensional (2D) materials emerge as a suitable choice. Known for their high specific surface area and aspect ratio, these materials can effectively cover the separators.<sup>[16]</sup> Most of the past research has optimized the electrochemical performance of Li/Na-S batteries through defect engineering in crystals, exposing a large number of coordinatively unsaturated sites to promote polysulfides conversion.<sup>[17]</sup> Amorphization is also a potent method to introduce defects. The disordered nature of amorphous materials leads to numerous defects, offering strong adsorption and catalytic effects.<sup>[18]</sup> Anionic vacancies, such as oxygen,<sup>[19]</sup> sulfur,<sup>[20]</sup> and selenium,<sup>[21]</sup> expose more active sites, enhance electrical conductivity, and accelerate catalytic conversion processes.<sup>[22]</sup> However, research on the electrocatalytic mechanism of defects in amorphous materials for Na-S batteries is still nascent. Additionally, there is a gap in understanding how to achieve high-performance Na-S batteries by controlling defect concentration in amorphous materials.

Here, we prepared amorphous iron oxide  $(A-FeO_x)$  and iron tin oxide (A-FeSnO<sub>x</sub>) nanosheets, combined with trace amounts (5 wt. %) of monolayer MXene, and uniformly coated these mixtures on both sides of the PP separator (Figure 1). Both electrochemical performance and density functional theory (DFT) calculations confirm that the introduction of the Sn element into amorphous nanosheets increases oxygen vacancies (O<sub>v</sub>s) concentration, which effectively enhances the binding energy with polysulfides, lowers the energy barrier of polysulfides decomposition, and promotes the kinetics of polysulfides conversion. Unlike typical 2D material coatings that form a dense pack hindering Na ion migration, the nano-sized perforations on the A-FeSnO<sub>x</sub> nanosheets facilitate Na ions transport and regulate Na ions deposition mode. Moreover, a small amount of crystalline MXene with A-FeSnO<sub>x</sub> constructs the biomimetic amorphous/crystalline (A/C) interface, which significantly strengthens the overall mechanical properties of the separator (modulus = 4.9 GPa), effectively inhibiting dendrites growth. Leveraging these advantages, the Na-S battery assembled with the multifunctional layer on separator demonstrates excellent cycling performance with ultrastable capacity retention after 400 cycles, with a 0.013 % decay per cycle at 0.5 C. The loading of the A-FeSnO<sub>x</sub>@MXene modification layer, with its minimal areal density and thickness of only  $0.1 \text{ mg cm}^{-2}$  and  $\sim 200 \text{ nm}$ , represents the smallest modification material weight and thickness for functional separators in current Na-S batteries.

## **Results and Discussion**

# Fabrication and Characterization of the A-FeSnO $_{\rm x}$ @MXene/PP Separator

The A-FeSnO<sub>x</sub> nanosheets were synthesized using a confined ion exchange method<sup>[23]</sup> as shown in Figure S1



*Figure 1.* Schematic Illustration of Amorphous 2D Nanosheets for RT Na–S Batteries. Amorphous 2D nanosheets with abundant nano-sized perforations and  $O_v s$ , mixed with a small amount of monolayer MXene, are coated on PP separators. This simultaneously regulates uniform Na deposition, facilitates the kinetics of polysulfides conversion, and enhances the mechanical properties.

(Supporting Information). Initially, a layered micron-sized Cu<sub>2</sub>O-oleate composite precursor was synthesized under hydrothermal conditions and dispersed into an aqueous NaCl solution with vigorous stirring. Following this, a mixed solution of equimolar amounts of FeCl<sub>3</sub> and SnCl<sub>4</sub> underwent an ion exchange reaction with Cu<sub>2</sub>O. Concurrently, the CuCl generated in this reaction, along with excess Cl<sup>-</sup> ions, formed CuCl<sub>x</sub><sup>-</sup> complexes in the solution. This coordination reaction further facilitated the ion exchange between Fe<sup>3+</sup>/ Sn<sup>4+</sup> and Cu<sub>2</sub>O. After the reaction completion, an intermediate of FeSn-hydroxide-oleate complex was obtained. Scanning electron microscopy (SEM) characterization of both the Cu<sub>2</sub>O-oleate precursor and the FeSn-hydroxideoleate complex intermediate revealed a 2D lavered morphology (Figures S2 and S3, Supporting Information). Powder X-ray diffraction (XRD) analysis showed that both materials retained the oleic acid layered template; however, Cu<sub>2</sub>O crystal peaks were present in the precursor but absent in the intermediate. The FeSn-hydroxide-oleate intermediates were then subjected to rapid low-temperature calcination in a tube furnace to remove the oleic acid template, yielding A-FeSnO<sub>x</sub> powder as shown by the optical image in Figure S4 (Supporting Information). SEM and transmission electron microscopy (TEM) analyses confirmed the sheetlike morphology of the nanosheets (Figures 2a,b). Energy dispersive spectroscopy (EDS) elemental mapping verified the uniform distribution of Fe, Sn and O (Figure S5, Supporting Information). The Fe/Sn atomic ratio of 52:47 is close to the intended 50:50 (Figure S6, Supporting Information). XRD characterization indicated the amorphous nature of FeSnO<sub>x</sub> (Figure S7, Supporting Information). High-resolution TEM (HRTEM) revealed nanopores on the nanosheets with predominantly diameters of 8-10 nm (Figure 2c and Figure S8, Supporting Information). The formation of

Selected area electron diffraction (SAED) showed a halo ring which further confirmed the amorphous state (Figure 2c, inset). Increasing the annealing temperature of the EeSn-hydroxide-cleate complex to 800 °C resulted in full

during the heating process.<sup>[24]</sup>

these nanopore structures is mainly due to desorption of

moisture from the corresponding hydroxide-oleate complex

(Figure 2c, inset). Increasing the annealing temperature of the FeSn-hydroxide-oleate complex to 800 °C resulted in full crystallization (Figure S9, Supporting Information). The XRD of the resulting crystalline  $FeSnO_x$  (C-FeSnO<sub>x</sub>) displayed diffraction peaks for Fe<sub>3</sub>O<sub>4</sub> and SnO<sub>2</sub>, indicating a mixed product of these compounds. Although their 2D morphology had transformed into particles, the element distribution was still uniform (Figure S10, Supporting Information). The atomic structure and composition of the materials were characterized by high-angle annular darkfield scanning transmission electron microscopy (HAADF-STEM) and the corresponding electron energy loss spectroscopy (EELS). The area of the collected EELS signal is within the yellow border of the HAADF-STEM image of each sample (Figure 2d and Figure S11a, Supporting Information). Figure 2e and Figure S11a (Supporting Information) also presents the higher magnification HAADF-STEM images of A-FeSnO<sub>x</sub>, A-FeO<sub>x</sub>, and C-FeSnO<sub>x</sub>. Due to the amorphous nature, it is difficult to distinguish the arrangement of the atoms within the white-bordered region of both A-FeSnO<sub>x</sub> and A-FeO<sub>x</sub>. In the EELS spectra of Fe L-edge (Figure 2f and Figure S11b, Supporting Information), the energy-loss near-edge fine structure of the Fe L-edge exhibits two distinctive peaks, which are attributed to the energy loss associated with the  $L_3$  and  $L_2\ edges.^{[19,25]}$  The intensity ratio  $(L_3/L_2)$  between the L<sub>3</sub> and L<sub>2</sub> peaks of A- $FeSnO_x$  (2.64) is greater than that of A-FeO<sub>x</sub> (2.29) and C- $FeSnO_x$  (2.14), indicating that the Fe oxidation state of A-FeSnO<sub>x</sub> is the lowest. This may be due to the introduction of



**Figure 2.** Characterizations of the 2D Amorphous Nanosheets. a) SEM image of A-FeSnO<sub>x</sub>. b,c) TEM images of A-FeSnO<sub>x</sub>. d,e) HAADF-STEM images of A-FeSnO<sub>x</sub>. f) EELS curves of C-FeSnO<sub>x</sub> (purple line), A-FeO<sub>x</sub> (blue line), and A-FeSnO<sub>x</sub> (red line). XPS spectra of C-FeO<sub>x</sub>, A-FeO<sub>x</sub>, C-FeSnO<sub>x</sub>, and A-FeSnO<sub>x</sub>: g) Fe 2p, h) corresponding + 3/ + 2 valence ratio of Fe, i) Sn 3d, j) O 1s. k) Calculated defect formation energies of oxygen vacancies for A-FeO<sub>x</sub> and A-FeSnO<sub>x</sub>. I) EPR curves of C-FeO<sub>x</sub> (orange line), C-FeSnO<sub>x</sub> (purple line), A-FeO<sub>x</sub> (blue line), and A-FeSnO<sub>x</sub> (corresponding + 3/ + 2 valence ratio of Fe, i) Sn 3d, j) O 1s. k) Calculated defect formation energies of oxygen vacancies for A-FeO<sub>x</sub> and A-FeSnO<sub>x</sub>. I) EPR curves of C-FeO<sub>x</sub> (orange line), C-FeSnO<sub>x</sub> (purple line), A-FeO<sub>x</sub> (blue line), and A-FeSnO<sub>x</sub> (red line).

the highest number of O<sub>v</sub>s. Moreover, in the EELS O kedge spectra (Figure S11c, Supporting Information), the intensity ratio of the pre-peak a to b (a/b) was employed to assess the localized oxygen content at disparate samples.<sup>[26]</sup> Compared with the a/b of A-FeO<sub>x</sub> (1.24) and C-FeSnO<sub>x</sub> (1.30), the significant decrease of the a/b ratio at the A- $FeSnO_x$  (1.15), which indicates that the amount of  $O_vs$  is maximum for A-FeSnOx. Positron Annihilation Lifetime Spectroscopy (PALS) provides information including size, type, and relative concentration of various vacancies according to the lifetime of the positrons. Generally, smaller vacancies (such as monovacancies, etc.) or shallow positron traps (such as O<sub>v</sub>s) may reduce the surrounding electron density, which increases the lifetime of  $\tau_1$ .<sup>[27]</sup> As shown in Table S1 and Figure S12 (Supporting Information), the  $\tau_1$  of A-FeSnO<sub>x</sub> is significantly longer than that of A-FeSnO<sub>x</sub>. The prolongation of  $\tau_1$  for A-FeSnO<sub>x</sub> suggests that it is most likely due to the fact that A-FeSnO<sub>x</sub> has larger  $O_v$ s than that of A-FeO<sub>x</sub>.

X-ray photoelectron spectroscopy (XPS) was further used to investigate the chemical state and local atomic structure of both A-FeO<sub>x</sub> and crystalline iron oxide (C-FeO<sub>x</sub>), as well as A and C-FeSnO<sub>x</sub> samples. The XRD and TEM characterization for A-FeO<sub>x</sub> can be found in Figures S13 and S14 (Supporting Information), respectively. The

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XPS of Fe 2p in different samples displayed a mixture of +2 and +3 valences (Figure 2g). The concentration of  $O_v s$  was inferred from the Fe<sup>2+</sup>/Fe<sup>3+</sup> area ratio. A-FeSnO<sub>x</sub> exhibited a higher concentration of  $O_v s$  compared to A-FeO<sub>x</sub> (Figure 2h and Table S2, Supporting Information), due to Sn<sup>4+</sup> replacing some high-valent Fe atoms.<sup>[28]</sup> The XPS results are consistent with the EELS and PALS results.

In the Sn 3d spectra for Sn 3d<sub>3/2</sub> and Sn 3d<sub>5/2</sub> in A and C-FeSnO<sub>x</sub> (Figure 2i), the peak positions remained unchanged before and after crystallization, confirming no alteration in their valence states. Thus, the incorporation of the Sn element contributes to regulating the  $Fe^{2+}/Fe^{3+}$  ratio and increasing number of O<sub>v</sub>s. The O 1s peaks in A-FeSnO<sub>x</sub> can be deconvoluted into three peaks at 532.3, 531.2, and 529.8 eV (Figure 2j), representing adsorbed oxygen (O<sub>ads</sub>), O<sub>v</sub>s, and metal-oxygen (M–O) bonds.<sup>[28-29]</sup> Notably, the O<sub>v</sub>s defect areas in A-FeO<sub>x</sub> and C-FeSnO<sub>x</sub> were significantly smaller compared to A-FeSnOx. Interestingly, while hightemperature treatment in air typically eliminates Ovs in such samples, C-FeSnO<sub>x</sub> retains some O<sub>y</sub>s, likely because Sn<sup>4+</sup> stabilizes a certain amount of Fe<sup>2+</sup>, thereby preserving O<sub>v</sub>s.<sup>[30]</sup> Furthermore, to illustrate the impact of Sn element on enhancing O<sub>v</sub>s concentration, we calculated the O<sub>v</sub>s formation energy (Figure 2k), which is considerably lower for A-FeSnO<sub>x</sub> (2.56 eV) than for A-FeO<sub>x</sub> (2.93 eV). Addi-

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tionally, electron paramagnetic resonance (EPR) analysis further confirmed the presence of O<sub>v</sub>s in these samples (Figure 2l). The EPR signal at g=2.003, indicative of free electrons and oxygen defect sites, increased in intensity from C-FeO<sub>x</sub> to A-FeSnO<sub>x</sub>, aligning with EELS, XPS and PALS results. Additionally, the contact potential difference  $(V_{cpd})$ between the tip and the sample was identified by Kelvin Probe Force Microscopy (KPFM), providing an estimate of the work function (WF) (Figure S15, Supporting Information). Typically, the higher the measured surface potential of the sample, the lower the WF, and previous work has shown that an increase in the concentration of  $O_v s$  leads to a decrease in the WF.<sup>[31]</sup> Among the A-FeSnO<sub>x</sub>, A-FeO<sub>x</sub> and C-FeSnO<sub>x</sub> samples, the relative WF of C-FeSnO<sub>x</sub> is the largest, while the relative WF of A-FeO<sub>x</sub> is slightly larger than that of A-FeSnO<sub>x</sub>. Consequently, the highest concentration of O<sub>v</sub>s is observed in A-FeSnO<sub>x</sub>, which is also consistent with the characterization results above. In this study, we selected A-FeO<sub>x</sub>, C- and A-FeSnO<sub>x</sub> as comparative samples to investigate the effect of O<sub>v</sub>s concentration on polysulfides conversion.

A-FeSnO<sub>x</sub>, when dispersed in ethanol, exhibits a transparent brown color and high dispersibility. Figure S16 (Supporting Information) shows a greenish-black MXene solution. A pronounced Tyndall scattering effect is observed when these solutions are exposed to a side-incident beam. Surface potentials of A-FeSnO<sub>x</sub>, and MXene solutions, were measured using a zeta ( $\zeta$ ) potentiometer. The  $\zeta$ -potentials for A-FeSnO<sub>x</sub> and MXene were 18 mV and -27 mV, respectively (Figure S17, Supporting Information). The positive charge on A-FeSnO<sub>x</sub> primarily arises from O<sub>y</sub>s, while the charge on MXene sheets is due to -F and -OH groups terminating the surface Ti atomic layer. For this study, MXene was mixed with A-FeSnO<sub>x</sub> in weight ratios of 1:19, 1:9, and 1:4, with additional acoustic waves to ensure homogeneous dispersion. Electrochemical tests revealed that the 1:19 composition exhibited the best performance (Figure S18, Supporting Information), hence this paper focuses on the morphological and structural characterization of this optimal ratio. Typically, directly modifying hydrophobic PP separators results in poor adhesion<sup>[15]</sup> (Figure S19, Supporting Information), but incorporating few-layer MXene (Figure S20, Supporting Information) into the A-FeSnO<sub>x</sub> suspension synergistically improves the adhesion of this functional layer to PP. As shown in Figures S21 and S22 (Supporting Information), the modified layer adheres well to the PP, demonstrating high flexibility without cracking and enhanced thermal stability.

Representative SEM images of a conventional PP separator reveal a network of long-slit channels approximately 60–100 nm wide and 200–500 nm in length (Figure S23, Supporting Information). During filtration, A-FeSnO<sub>x</sub>@MXene forms a continuous modification layer on the separator, as shown in the Figure S24 (Supporting Information). Compared to the slit holes on the separator, the 2D nanosheets, measuring 2–3  $\mu$ m laterally, provide effective physical shielding against polysulfides. Elemental mapping studies confirm the homogeneous distribution of Fe, Sn, and Ti in the A-FeSnO<sub>x</sub>@MXene layers on the

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separator (Figure S25, Supporting Information). The crosssection of the modified layer also observed under SEM, shows a 3D stacked structure with uniformly distributed elements (Figure 3a), while the top of the layer appears warped. In contrast, C-FeSnO<sub>x</sub>@MXene on the separator, as seen from the top view, shows incomplete coverage with particle agglomerates, adversely affecting the polysulfides barrier (Figure S26, Supporting Information). Raman spectroscopy was used to investigate the interaction between MXene and A-FeSnO<sub>x</sub>, with results displayed in Figure 3b. The pristine A-FeSnO<sub>x</sub> film shows peaks at 289 and 406 cm<sup>-1</sup>, corresponding to Fe–O vibrations in the hematite structure.<sup>[32]</sup> The MXene sheets exhibit peaks at ~598 and 394 cm<sup>-1</sup>, attributed to Ti–C and Ti–O vibrations, respectively.<sup>[33]</sup> The modified layer shows combined characteristics of both components, with Ti-O bonding energy at about 370 cm<sup>-1</sup>, and overlapping Fe–O and Ti–C bonding energies between 500–675 cm<sup>-1</sup>. The shift of Ti–O energy from 394 to 378 cm<sup>-1</sup> and the characteristic Ti-C halo from approximately 630 to 609 cm<sup>-1</sup> suggest a strong interaction between MXene and A-FeSnO<sub>x</sub> nanosheets.

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images (Figure 3c) clearly show the modification layer to be ~200 nm thick. This ultra-thin thickness of 200 nm and ultra-light density of 0.1 mg cm<sup>-2</sup> is in stark contrast to the several-micron thickness typical of separator modification layers in existing literature (Figure 3h). Notably, the MXene layer within this modified layer forms a closely connected interface with A-FeSnO<sub>x</sub>, termed the A/C-interface, corroborating with the Raman spectroscopy findings. Significant improvements in overall mechanical properties have been demonstrated at similar interfaces in biomaterials such as nacre and enamel.<sup>[34]</sup> Therefore, we believe that this finding may have an inhibitory function for the growth of dendrites when applied to separator modification. The stiffness of A-FeSnO<sub>x</sub>@MXene and A-FeSnO<sub>x</sub> was assessed through quasi-static nanoindentation. As illustrated in Figures 3d,e, the modulus of A-FeSnO<sub>x</sub>@MXene is significantly higher than that of pure A-FeSnO<sub>x</sub>, approximately double. For context, commercial PP separator has a modulus of 1.53 GPa, substantially lower than that of A-FeSnO<sub>x</sub>@MXene (modulus=4.9 GPa). Additionally, 3D contour maps within a 0.3 by 0.3 mm area confirm the homogeneity of Young's modulus  $(E_{Y})$  across the modified layer (Figure 3e). This suggests that A-FeSnO<sub>x</sub>@MXene layer possesses both mechanical homogeneity and enhanced resistance to external stresses, largely due to the A/C interface. Given that PP separator is vulnerable to dendrites penetration, which poses safety risks, the mechanically robust modified layer presents a promising solution.

The electrolyte wettability of separators is crucial for the electrochemical performance of batteries.<sup>[35]</sup> To visualize this, the static contact angle was measured (Figure 3f). Equal amounts of electrolyte were placed on PP, A-FeO<sub>x</sub>@MXene/PP, C-FeSnO<sub>x</sub>@MXene/PP, and A-FeSnO<sub>x</sub>@MXene/PP, and A-FeSnO<sub>x</sub>@MXene/PP, and A-FeO<sub>x</sub>@MXene/PP, and A-FeO<sub>x</sub>@MXene/PP, and A-FeO<sub>x</sub>@MXene/PP, and A-FeO<sub>x</sub>@MXene/PP, separators were 47.10°, 29.76° and 17.06°, respectively. However, the angle dropped to just

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*Figure 3.* Characterizations of the Functional Separators. a) Cross-sectional SEM image of A-FeSnO<sub>x</sub>@MXene/PP separator, along with corresponding elemental mappings of Fe, Sn, and Ti. b) Raman spectra of MXene, A-FeSnO<sub>x</sub>, and A-FeSnO<sub>x</sub>@MXene. c) Cross-sectional TEM image of the A-FeSnO<sub>x</sub>@MXene/PP separator. d,e) The static nanoindentation tests of PP, A-FeSnO<sub>x</sub>/PP, and A-FeSnO<sub>x</sub>@MXene/PP separators to measure Young's modulus and corresponding 3D contour maps. Error bars show the standard deviation, with n=3. f) The static contact angles for a 1 M NaTFSI solution in EC:EMC:DMC (1:1:1 by volume) with 5 wt.% FEC are shown on various separators. g) Na ion conductivity measurements are presented for different separators. Error bars are included to represent the standard deviation from data obtained from five samples. h) Comparison of the total thickness of different separators. This includes data from several Na–S cells reported in previously published literature<sup>[13,15,36]</sup> and this work.

4.48° for the A-FeSnOx@MXene/PP separator, indicating super electrolyte-wetting due to higher surface energy and more O<sub>v</sub>s defects from A-FeSnO<sub>x</sub>.<sup>[37]</sup> Consequently, as shown in Figure 3g and Figure S27 (Supporting Information), the Na ion conductivity of A-FeSnO<sub>x</sub>@MXene/PP separators  $(1.224 \text{ mS cm}^{-1})$  exceeds that of the pristine PP  $(1.040 \text{ mS cm}^{-1}),$ A-FeO<sub>x</sub>@MXene/PP separators  $(0.965 \text{ mS cm}^{-1})$ , and C-FeSnO<sub>x</sub>@MXene/PP separators  $(0.898 \text{ mS cm}^{-1})$ . This high ionic conductivity is not solely due to excellent wettability endowed by A-FeSnO<sub>x</sub> but also to the abundance of nano-sized perforations on the A-FeSnO<sub>x</sub> nanosheets, facilitating rapid and unobstructed cation movement. In contrast, although the C-FeSnOx@MXene/PP separator surface coating improves wettability, the C-FeSnO<sub>x</sub> particles impede ionic migration, leading to significantly lower conductivity compared to PP. Additionally, the ultra-light density of A-FeSnO<sub>x</sub>@MXene contributes to this high ionic conductivity. Together with its ultra-thinness, this would facilitate its close contact with the cathode, thus allowing the captured polysulfides to be reused with the cathode material, thus reducing the possible charge transfer resistance  $(R_{ct})$ .<sup>[38]</sup> Using A-FeSnO<sub>x</sub>@MXene as the separator modification component, we achieved the objectives of conformal, ultra-light, and ultra-thin characteristics. Most importantly, with the remarkably increasing concentration of O<sub>v</sub>s, the thin layer can greatly retard polysulfides shuttling by fast polysulfides conversion and

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effective physical inhibition, enhanced kinetic reactions, and improved sulfur utilization and cycle life.

#### **Electrochemical Performance**

The effectiveness of various separators was evaluated through the RT Na | 1 M NaTFSI in EC:EMC:DMC (1:1:1 by volume) with 5 wt. % FEC@separators | S@biomass porous activated carbon (AC) cells. The cathode material preparation process is detailed in the Supporting Information. Figures S28 and S29 (Supporting Information) show that the AC has a porous structure with a large abundance of micropores. The nitrogen adsorption-desorption measurement of AC displays a typical type I isotherm with a hysteresis loop at high relative pressure.<sup>[39]</sup> Based on the Brunauer-Emmett-Teller (BET) method, the specific surface area of the AC is calculated to be 1587  $m^2g^{-1}$ , suitable for sulfur accommodation. Figures S30 and S31 (Supporting Information) confirm successful sulfur impregnation into the AC porous structure, and thermogravimetric analysis (TGA) indicates that the AC@S composite contains about 50 wt. % sulfur.

The rate performance of RT Na–S batteries using different separators was assessed. Discharge-charge curves are shown in Figure 4a and Figure S32 (Supporting Information). The Na–S cell with the A-FeSnO<sub>x</sub>@MXene/PP separa-

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Figure 4. Electrochemical Performance of Na–S Batteries. a) Rate performance and b) cycling performance of batteries using various separators. c) Typical discharge/charge profiles of batteries with different separators. d) EIS spectra of batteries using GF membrane and A-FeSnO<sub>x</sub>@MXene/PP separator at 0.1 C. e) Cycling performance of batteries with different separators at 0.5 C over 400 cycles. f) Symmetric Na||Na cells voltage profiles using various separators at a current density of 0.1 mA cm<sup>-2</sup>.

tor exhibits excellent performance, delivering specific capacities of 1289.2, 892.7, 730.6, 577.4, and 415.7 mAh g<sup>-1</sup> at 0.1, 0.2, 0.5, 1, and 2 C (1 C =  $1675 \text{ mAh g}^{-1}$  based on sulfur loading), respectively, which also represents the better rate performance than previous reports (Table S3, Supporting Information). In contrast, cells with A-FeO<sub>x</sub>@MXene/PP and C-FeSnO<sub>x</sub>@MXene/PP separators show significantly lower capacities. The cell with the C-FeSnO<sub>x</sub>@MXene/PP separator could not operate at 0.5 C (Figure S33, Supporting Information), likely due to reduced O<sub>v</sub>s, uneven coating layers, and resultant polysulfides shuttling. The cell using GF membrane demonstrates extremely low discharge capacity at 2 C, with the sulfur reduction plateau nearly vanishing a substantial discharge-charge potential gap. Furthermore, the battery with the bare Celgard 2500 PP separator fails in the first cycle due to poor electrolyte wettability and polysulfides shuttle (Figure S34, Supporting Information). Cycling performance and specific discharge/ charge profiles of the different separators at 0.1 C are displayed in Figure 4b and Figure S35 (Supporting Information). The Na-S cell using the A-FeSnO<sub>x</sub>@MXene/PP separator initially achieves a reversible charge capacity of 1409.6 mAhg<sup>-1</sup> with a high average Coulombic efficiency, maintaining a capacity of 759.7 mAh g<sup>-1</sup> after 200 cycles. By comparison, the GF membrane, C-FeSnO<sub>x</sub>@MXene/PP, and A-FeO<sub>x</sub>@MXene/PP separators show less stability over long-term cycling. For instance, only a capacity of 454.1 and 590.7 mAhg<sup>-1</sup> remains for the GF membrane and A-

Electrochemical impedance spectroscopy (EIS) and corresponding equivalent circuits were conducted on cells using different separators (Figure 4d and Figure S38, Supporting Information). Compared to the cell with the GF

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FeO<sub>x</sub>@MXene/PP separator after 200 cycles, and cycling of the Na-S cell with the C-FeSnO<sub>x</sub>@MXene/PP separator fails after about 100 cycles. Additionally, the GF membrane exhibits a noticeable IR drop in the second cycle discharge/ charge profile, indicative of the polysulfides shuttle and corresponding corrosion of the Na anode. In sharp contrast, the cell with the A-FeSnO<sub>x</sub>@MXene/PP separator shows a flatter voltage plateau, suggesting that abundant O<sub>v</sub>s defects effectively intercept polysulfides and enhance SRR kinetics. Given the excellent chemisorption for polysulfides, the cell using A-FeSnO<sub>x</sub>/PP separator without MXene could also deliver a high initial reversible capacity of 963.75 mAh g<sup>-1</sup> and stably operated over 50 cycles at 0.1 C (Figures S36 and S37, Supporting Information). However, for extended cycling performance, MXene is required to enhance adhesion and mechanical properties of the modification layer. Specific charge/discharge profiles were analyzed to further investigate the catalytic properties of A-FeSnO<sub>x</sub> (Figure 4c). The overpotential for cells using the A-FeSnO<sub>x</sub>@MXene/PP  $(\Delta V = 0.604 \text{ V})$  separator is notably smaller than the GF membrane  $(\Delta V = 0.672 V),$ A-FeO<sub>x</sub>@MXene  $(\Delta V =$ 0.615 V), and C-FeSnO<sub>x</sub>@MXene ( $\Delta V = 0.648$  V), attributing to the higher number of accessible O<sub>v</sub>s on the surface of A-FeSnO<sub>x</sub>.

membrane, the cell with the A-FeSnO<sub>x</sub>@MXene/PP separator exhibits much lower  $R_{\rm ct}$  and fewer interfacial side reactions (R<sub>SEI</sub>) (Table S4, Supporting Information), a result of enhanced electrolyte wettability and the presence of abundant O<sub>v</sub>s and perforations on the A-FeSnO<sub>x</sub>.<sup>[38]</sup>

Leveraging the advantages of the A-FeSnO<sub>x</sub>@MXene/PP separator, we explored its cycling performance at a high current density of 0.5 C (Figure 4e). Impressively, the separator maintained a high capacity of 610.3 mAh g<sup>-1</sup> after 400 cycles, with a minimal capacity decay of only 0.092 % per cycle. Particularly noteworthy is its performance with a high sulfur loading of 2.08 mg cm<sup>-2</sup>; the Na-S cell achieved an initial reversible capacity of 872.12 mAh g<sup>-1</sup> and retained 66 % of this capacity after 200 cycles at 0.2 C (Figure S39, Supporting Information). Benefiting from the improved electrolyte-wetting ability of the A-FeSnOx@MXene/PP separator, the cells were assembled with different E/S ratios (electrolyte to sulfur ratio) to evaluate the practical electrochemical performance under lean electrolyte. The cells using A-FeSnO<sub>x</sub>@MXene/PP separators with E/S ratios of 25 and  $20 \text{ mLg}^{-1}$  maintained a capacity of 694.9 and 501.1 mAhg<sup>-1</sup>, respectively, after 150 cycles at 0.1 C (Figure S40, Supporting Information), demonstrating fast ion transport and improved electrocatalytic effects on polysulfides. In addition, a pouch cell was assembled to evaluate the A-FeSnO<sub>x</sub>@MXene/PP separator under practical application. As illustrated in Figure S41 (Supporting Information), a light-emitting diode (LED) is illuminated by the Na-S pouch cell, and a high reversible capacity of  $927.38 \text{ mAh g}^{-1}$ can be achieved. The pouch cell can stably operate over 20 cycles, suggesting the superiority of our multifunctional coating. Moreover, the excellent chemisorption and catalytic performance of the A-FeSnO<sub>x</sub> nanosheet for polysulfides was also verified in Li-S batteries, further demonstrating its universality and application prospect (Figures S42-45, Supporting Information).

Symmetric Na||Na cells were fabricated to further validate the superiority of perforated A-FeSnO<sub>x</sub> nanosheets for the modification of PP separators. The Na||Na symmetric cell with the A-FeSnO<sub>x</sub>@MXene/PP separator exhibited a stable voltage hysteresis for over 800 h and an area capacity of 0.2 mAh cm<sup>-2</sup> at a current density of 0.1 mA cm<sup>-2</sup> (Figure 4f and Figure S46, Supporting Information). In contrast, the cell with the GF membrane showed a gradual increase in voltage hysteresis, suggesting interphase instability due to continuous SEI destruction and formation. Additionally, the Na||Na symmetric cells with C-FeSnO<sub>x</sub>@MXene/PP and A-FeO<sub>x</sub>@MXene/PP separators display significant fluctuations and abrupt drop at around 34 h and 320 h, respectively. This behavior indicates internal short circuits caused by uncontrollable dendrites growth piercing the separator, while the synergistic effect of mesopore regulation for ions and the robust mechanical properties from the A/C-interface endowed by A-FeSnO<sub>x</sub>@MXene layer effectively eliminate dendrites growth. Consequently, the corresponding symmetric cell exhibits low polarization voltage and stable cycling performance. The role of porous A-FeSnO<sub>x</sub> in regulating Na ions was corroborated using COMSOL simulations (Figure S47 and Table S5, Supporting Information). These simulations show that Na ions concentrations along routine PP separators fluctuate significantly, leading to non-uniform ion distribution and sharp Na dendrites formation. However, the abundance of perforations on the A-FeSnO<sub>x</sub> surface uniformly regulates and redistributes Na ions, resulting in dense Na deposition.<sup>[40]</sup>

#### Adsorption and Catalytic Performance of A-FeSnO<sub>x</sub>.

To further investigate the adsorption and catalytic performance of A-FeSnO<sub>x</sub>, a series of cyclic voltammograms (CVs) were conducted at various scanning rates. As depicted in Figures 5a,b, the contour plot of the CVs pattern for the A-FeSnO<sub>x</sub>@MXene/PP separator displays a higher response current at corresponding scanning rates. Notably, there is a smaller deviation of 0.11 V from 0.1 to 0.5 mVs<sup>-1</sup> compared to the GF membrane (0.16 V) as seen in Figures S48 and S49 (Supporting Information), indicating the enhanced ion diffusion. To substantiate this observation, Na ion diffusion  $(D_{Na^{+}})$  coefficients were calculated using the Randles-Sevick equation (Table S6, Supporting Information).<sup>[41]</sup> The diffusion coefficients for peaks  $\alpha$  and  $\beta$  in the A-FeS $nO_x@MXene/PP$  separator are 2.62×10<sup>-8</sup> and 3.74×10<sup>-8</sup>, respectively, surpassing those of the GF membrane  $(9.38 \times 10^{-9} \text{ for peak } \alpha \text{ and } 1.43 \times 10^{-8} \text{ for peak } \beta)$ . This result suggests that the introduction of A-FeSnO<sub>x</sub>@MXene significantly promotes ion diffusion, thereby enhancing the electrocatalytic performance of polysulfides.

To verify this conclusion, we assembled symmetrical cells using different separators with  $Na_2S_6$ -containing electrolytes, including the MXene/PP separator (0.01 mg cm<sup>-1</sup>, twice the amount used in the A-FeSnO<sub>x</sub>@MXene/PP separator). As shown in Figure 5c, despite previous reports on polysulfides adsorption and catalysis by MXene, the CVs curve of the symmetric cell with the MXene/PP separator exhibits limited response current. In contrast, the CVs curve for the  $Na_2S_6$ -containing symmetric cell with the A-FeSnO<sub>x</sub>@MXene/PP separator shows a high current response and distinct peaks, further evidencing enhanced electrochemical conversion kinetics and efficiency facilitated by O<sub>v</sub>s.

To visualize polysulfides adsorption by A-FeSnO<sub>x</sub>, A- $FeSnO_x$  powder was directly added to a  $Na_2S_6$  solution. After 24 h of resting, the polysulfides suspension became almost clear, and the adsorption peaks around 412 nm, associated with  $S_6^{2-}$ , were nearly invisible (Figure 5d). This outcome demonstrates the effective adsorption of polysulfides through the chemical anchoring of O<sub>v</sub>s and the intrinsic electrostatic force of A-FeSnO<sub>x</sub>. In addition to the adsorption of A-FeSnO<sub>x</sub> on polysulfides, A-FeSnO<sub>x</sub>@MXene can also act as a protective barrier to inhibit the shuttle effect of polysulfides anions. To assess the permeation resistance of A-FeSnO<sub>x</sub>@MXene/PP separators to soluble polysulfides, permeation measurements were conducted using an H-type glass cell. In this setup, one-half of the cell contained, polysulfides solution (5 mM  $Na_2S_6$  in PC), while the other half was filled with blank PC solvent. The cells, separated by GF membrane, C-FeSnO<sub>x</sub>@MXene/PP, and A-FeS-

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*Figure 5.* Polysulfides Adsorption and Catalytic Capability of the A-FeSnO<sub>x</sub>@MXene/PP Separator. Contour plots of CVs patterns for a) A-FeSnO<sub>x</sub>@MXene/PP separator and b) GF membrane. c) CVs curves of symmetric cells with  $Na_2S_6$  solutions at a scan rate of 5 mV s<sup>-1</sup>. d) UV-vis adsorption spectra of  $Na_2S_6$  solutions with and without the addition of A-FeO<sub>x</sub>/A-FeSnO<sub>x</sub> after 24 h. Corresponding optical images are provided in the inset of Figure 5d. XPS spectra of A-FeSnO<sub>x</sub> after adsorption of  $Na_2S_6$ : e) Fe 2p, f) Sn 3d, and g) O 1s. h) Raman spectra of the suspension solution of A-FeSnO<sub>x</sub> after  $Na_2S_6$  adsorption and a pure  $Na_2S_6$  solution. i,j) Top view SEM images of Na metal anodes after 200 cycles are shown for cells with GF membrane and A-FeSnO<sub>x</sub>@MXene/PP separator, respectively.

nO<sub>x</sub>@MXene/PP separators, respectively (Figure S50, Supporting Information), demonstrated significant findings. After 12 h, the transparent PC solvent in the cells with PP and C-FeSnO<sub>x</sub>@MXene/PP separators showed noticeable color changes, indicative of polysulfides migration. However, no such change was observed in the cell with the A-FeSnO<sub>x</sub>@MXene/PP separator even after 24 h, suggesting effective interception of polysulfides. Therefore, the A-FeSnO<sub>x</sub>@MXene layer proves to be an effective barrier in the RT Na-S batteries. After adsorption, the Fe 2p peak of A-FeSnO<sub>x</sub> shifts to lower energy level and develops an additional shoulder peak, suggesting the formation of Fe-S species at 723.69 eV and 710.28 eV (Figure 5e).<sup>[42]</sup> However, in the Sn 3d spectra, two characteristic peaks at 494.67 eV and 486.25 eV shifts to 494.49 eV and 486.17 eV, respectively, with a minor energy separation of ~0.1 eV, indicating negligible chemical anchoring between Sn species and polysulfides. Meanwhile, the high-resolution O 1s spectrum shows a shift towards higher binding energies, which occurs as the unsaturated electronegative oxygen atoms, due to the presence of  $O_v s$ , coordinate with the Na in Na<sub>2</sub>S<sub>6</sub>. Therefore, the presence of O<sub>v</sub>s defects displays a significant role in the chemical adsorption and fast conversion of polysulfides, which is essential for ultra-stable RT Na-S batteries. The nitrogen adsorption-desorption measurement and conductive Atomic Force Microscopy (c-AFM) were performed to rule out the observed differences in polysulfides adsorption and catalysis that may be due to the differences in specific surface area and conductivity. The specific surface areas of A-FeSnO<sub>x</sub> and A-FeO<sub>x</sub> are 64.19 and 62.52 m<sup>2</sup>g<sup>-1</sup>, respectively, and the difference is extremely small (Figure S51, Supporting Information). Moreover, as displayed in Figure S52 (Supporting Information), the conductivity of A-FeSnO<sub>x</sub> and A-FeO<sub>x</sub> do not much differ from each other, and both are slightly higher than that of C-FeSnO<sub>x</sub>, which are not responsible for the large difference in electrochemical properties as well as adsorption and catalytic performance toward polysulfides.

Figure 5h displays Raman spectra of  $Na_2S_6$  solution and A-FeSnO<sub>x</sub>-Na<sub>2</sub>S<sub>6</sub> suspension, further confirming the interaction between A-FeSnO<sub>x</sub> and  $Na_2S_6$ . The  $Na_2S_6$  solution comprises both long and short-chain polysulfides due to complex disproportionation reactions.<sup>[43]</sup> Compared to the S–S bonds in the  $Na_2S_6$  solution, the peaks in the A-FeSnO<sub>x</sub>- $Na_2S_6$  suspension become significantly broadened and less visible, shifting to lower wavenumbers. This suggests the disruption of S–S bonds due to the strong interaction with A-FeSnO<sub>x</sub>, facilitated by the abundant O<sub>y</sub>s defects.

Figures 5i,j examine the surface morphology of cycled Na metal anodes from Na–S cells with GF membrane and A-FeSnO<sub>x</sub>@MXene/PP separator, respectively. Given the excellent adsorption and catalytic performance of A-FeS- $nO_x$ , there is less Na<sub>2</sub>S<sub>2</sub>/Na<sub>2</sub>S deposition from polysulfides corrosion. The Na metal anode using the A-FeS- $nO_x$ @MXene/PP separator exhibits a smooth, crack-free structure compared to that of the GF membrane. This difference is ascribed to the high mechanical toughness, superior electrolyte-wetting ability, and ion-corrected depo-

sition of multifunctional A-FeSnO<sub>x</sub>@MXene layer.<sup>[44]</sup> Additionally, A-FeSnO<sub>x</sub> remains amorphous even after hundreds of cycles, confirming its long-term stability (Figure S53, Supporting Information).

DFT calculations were conducted to explain the differences in electrochemical performance among A-FeO<sub>x</sub>, A-FeSnO<sub>x</sub>, and C-FeSnO<sub>x</sub>. As illustrated in Figure 6a and Figure S54 (Supporting Information), the orbital projected density of states (PDOS) of different elements in these materials was analyzed. A-FeSnO<sub>x</sub> exhibits a higher density of states near the Fermi level, indicating improved ionic and electric conductivity due to more Ovs, thus facilitating charge transfer and enhancing the SRR kinetics. Furthermore, A-FeSnO<sub>x</sub> shows stronger adsorption for polysulfides, especially for low-order polysulfides like Na2S2 and Na2S (Figure 6b), acting as an effective barrier against polysulfides shuttling. Meanwhile, the Na ion migration barrier in A-FeSnO<sub>x</sub> significantly decreases with the increasing O<sub>y</sub>s defects, and the lower surface diffusion barrier, which can lead to a faster diffusion, is beneficial to the uniform deposition of Na<sub>2</sub>S (Figure S55, Supporting Information). Gibbs free energies of the discharging process in Na-S reactions (conversion from  $S_8$  to  $Na_2S$ ) were calculated on A-FeO<sub>x</sub>, C-FeSnO<sub>x</sub>, and A-FeSnO<sub>x</sub> substrates to explore catalytic ability. The optimized structure of A-FeO<sub>x</sub>, C-FeSnO<sub>x</sub>, and A-FeSnO<sub>x</sub> and the corresponding configuration of the adsorbed intermediates are shown in Figure 6c and Figure S56 (Supporting Information). Compared to A-FeO<sub>x</sub> and C-FeSnO<sub>x</sub>, A-FeSnO<sub>x</sub> energy differences per step are small and almost constant, with energy barriers as low as about 0.11 eV at each step, verifying A-FeSnO<sub>x</sub> robust catalytic ability. The specific value change of charge transfer and bond length in Na<sub>2</sub>S after adsorption on the substrate was calculated according to the optimized structure configurations (Figure S57, Supporting Information). A significant change in the charge of S in Na<sub>2</sub>S from -1.48 eV to -0.8 eV suggests a huge electron transfer between S and A-FeSnO<sub>x</sub>, which is essential for the polysulfides conversion. Such a strong interaction is mainly attributed to the higher concentration of O<sub>v</sub>s defects resulting in a higher proportion of  $Fe^{2+}$ , which is prone to interact with S in Na<sub>2</sub>S. In contrast, interaction between A-FeO<sub>x</sub>/C-FeSnO<sub>x</sub> and Na<sub>2</sub>S experience less internal charge transfer and thus little change in the bond length of Na<sub>2</sub>S, suggesting poor adsorption and catalytic performance of A-FeO<sub>x</sub> and C-FeSnO<sub>x</sub>. The calculated charge differential distributions of the Na<sub>2</sub>S molecule-oxides substrate are consistent with the above result of Bader charge analysis, indicating that from C-FeSnO<sub>x</sub> to A-FeSnO<sub>x</sub>, more electrons are transferred due to the strong adsorption for polysulfides endowed by higher O<sub>v</sub>s concentration (Figure S58, Supporting Information). This combination of strong adsorption and excellent catalytic performance, resulting from substantial O<sub>v</sub>s, is key to the superior electrochemical performance of Na-S batteries.



**Figure 6.** Theoretical Calculations of Adsorption and Catalytic Capabilities for C-FeSnO<sub>x</sub>, A-FeO<sub>x</sub>, and A-FeSnO<sub>x</sub>. a) PDOS analyses for A-FeO<sub>x</sub>, C-FeSnO<sub>x</sub>, and A-FeSnO<sub>x</sub>. b) Adsorption energies of polysulfides on A-FeO<sub>x</sub>, C-FeSnO<sub>x</sub>, and A-FeSnO<sub>x</sub>. c) Gibbs free energy profiles for reducing Na polysulfides on A-FeO<sub>x</sub>, C-FeSnO<sub>x</sub>, and A-FeSnO<sub>x</sub>, are shown in the inset.

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### Conclusions

In conclusion, A-FeSnO<sub>x</sub> nanosheets, abundant in O<sub>y</sub>s and perforations (size of 8-10 nm), have been developed for modifying commercially available PP separators. The O<sub>v</sub>s defects on A-FeSnO<sub>x</sub> not only provide numerous catalytic sites for fast SRR but also significantly enhance electron and ion conductivity as well as electrolyte wettability. Moreover, nano-sized perforations on the A-FeSnO<sub>x</sub> surface regulate Na ion transport, ensuring uniform ion deposition. The A/Cinterface formed with MXene boosts the mechanical properties of the modified layer, effectively inhibiting dendrites growth. As a result, the multifunctional A-FeSnO<sub>x</sub>@MXene layer on PP separator achieves ultra-light (~0.1 mg cm<sup>-2</sup>), ultra-thin (~200 nm), and ultra-robust (modulus=4.9 GPa) characteristics. This work thus achieves long cycle life, and high-capacity RT Na-S batteries by leveraging the hierarchical vacancies engineering of amorphous nanosheets and the robust A/C-interface construction.

### **Date Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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### **Conflict of Interest**

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** Room Temperature Sodium-Sulfur Batteries • Amorphous Two-Dimensional Nanosheets • Oxygen Vacancy • Amorphous/Crystalline Interface

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