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Full Paper

Lignin@Nafion Membranes Forming Zn Solid--Electrolyte Interfaces Enhance the Cycle Life for Rechargeable Zinc-Ion Batteries

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Layer by layer: Planar $\text{ZnSO}_4 \cdot [\text{Zn}(\text{OH})_2]_3 \cdot x\text{H}_2\text{O}$ layers formed by Nafion membranes function as an effective solid electrolyte interphase (SEI) on Zn metal for aqueous rechargeable zinc-ion batteries (ZIBs), which prevents short circuits during stripping/plating.

Planar zinc sulfate zinc hydroxide layers formed by Nafion membranes function as an effective solid electrolyte interphase for rechargeable #ZincIonBatteries as reported by Madhavi Srinivasan and co-workers @NTUsg

batteries

membrane

Nafion

solid--electrolyte interface

zinc

Metallic zinc is an ideal anode material for rechargeable zinc-ion batteries (ZIBs), taking us beyond the lithium-ion era. In-depth understanding of the Zn metal surface is currently required owing to diverse but uncorrelated data about the Zn surface in mild environments. Herein, the surface chemistry of Zn is elucidated and the formation and growth of a zinc layer hydroxide is verified as an effective solid--electrolyte interface (SEI) during stripping/plating in mild electrolyte. The effects of battery separators/membranes on the growth of an effective SEI and deposited Zn are then investigated from the perspectives of structure, morphology, compositions, and interfacial impedance. Nafion-based membranes enable the formation of a planar SEI, which protects the metal surface and prevents short circuiting. Biomass@Nafion membranes are developed and assessed with a long cycle life of over 400^h compared with below 200^h for physical separators. The mechanism behind this is attributed to interaction between the membranes and Zn²⁺, which enables reshaping of the Zn²⁺ coordination in an aqueous medium. Together with the advantages of using the membranes in β -MnO₂/ZnSO₄/Zn, our work provides a feasible way to design an effective SEI for advancing the use of Zn anodes in rechargeable ZIBs.

Introduction

Metallic zinc is an ideal anode material for the development of rechargeable battery for the post-lithium-ion era.^[1] Zn possesses advantages of high theoretical capacity (820^{mAh}g⁻¹), low electrochemical potential (<0.762^V vs. the standard hydrogen electrode (SHE)), operability in aqueous electrolyte, high abundance, and environmental friendliness.^[1f] These advantages drive the recent booming development of rechargeable zinc-ion batteries (ZIBs).^[2] However, understanding of the complex chemistry of Zn anodes is essential to pursue the high cycling stability of rechargeable ZIBs. In alkaline zinc batteries, dendrite formation on the Zn surface is a century-old challenge, which is due to uneven Zn stripping/plating processes that cause internal shorting failure or detaching and further accelerated corrosion or passivation (ZnO). The advance of Zn metal anodes has been intensively investigated, for example, through the 3D architecture design and backside-plating configuration for alkaline zinc and zinc--air batteries.^[1f,2b,3] Although mild acidic/neutral electrolytes permit promising cycling, the chemistry on the Zn surface still remains

ambiguous. Current scattered reports on the polarization behavior,^[1f,^4] interfacial impedance,^[4a,^5] surface morphology,^[6] and non-comparable compositions of Zn anodes in different electrolytes,^[5,^7] imply that a comprehensive study is warranted on the surface/interface of Zn in mild media.

To facilitate reversible Zn insertion, the growth mechanism of electrodeposited Zn metal has been systematically investigated with inorganic, organic, and polymeric additives towards exposing the crystallographic (0⁰2) plane, which is unlikely to undergo dendrite growth.^[3e,^8] More than Zn metal, the electrolyte has attracted long-term attention and elaboration for rechargeable ZIBs.^[9] Water-in-salt electrolytes have been developed to reprogram the chemistry of the cation--solvent and solid electrolyte interface (SEI) in an aqueous environment.^[8b,^10] Recently, a high concentration hybrid salt has been developed, which rejuvenates ZIBs by manipulating the solvation sheath of Zn²⁺ to Zn²⁺(TFSI)_n from Zn²⁺(H₂O)₆.^[1f] This suppresses dendrite formation of Zn metal, leads to a highly reversible and stable Zn anode, and meanwhile expands the electrochemical stability window of the aqueous electrolyte. This concept can be extended towards gel electrolytes.^[5,^11] This points to manipulating Zn²⁺--anion species interaction/coordination as the potential key to achieve reversible Zn anodes. In the salt-in-water regime, using zinc electrolytes leads to different polarization behaviors during stripping/plating,^[4b] suggesting a potential influence from the solid electrolyte interface besides the interaction between Zn²⁺ and electrolyte. Further, two types of failure behavior were reported during Zn stripping/plating in mild acidic/neutral pH, that is, short circuit and open circuit,^[4,^12] where dendrite formation and growth alone is an insufficient explanation. To provide better understanding, the surface/interface chemistry for Zn metal warrants lucubration.

As a key component in batteries, functional coatings and membranes have been developed to suppress Zn dendrite formation,^[4a,^12] where polymeric membranes are employed in lithium and sodium metal batteries for solid electrolyte interfaces to inhibit dendrites, with their mechanical flexibility to accommodate strain, versatility for bespoke functional groups, and novel processing.^[13,^14] As the representative proton exchange membrane, Nafion finds wide application in energy storage devices.^[15] Pioneer reports on

zinc alkaline batteries reveal its effects of faster zinc distribution and dehydration of zinc.^[3a,b] Recently, Nafion has been applied in organic-based aqueous rechargeable ZIBs where dissolution of the discharged product from the organic cathode is effectively suppressed.^[16] However, the role of Nafion, as well as other types of battery separators, on Zn stripping/plating in mild electrolyte is still unclear. More than the cation conduction together with charge separation, the side group $\text{<C->SO}_3^{\text{M->}}$ in Nafion is able to provide binding sites for Zn^{2+} ions.^[17] Hence, Nafion may potentially benefit Zn stripping/plating by changing the Zn^{2+} coordination. Developing cost-effective and scalable methods to achieve highly reversible Zn metal insertion remains a challenge for rechargeable ZIBs.

Here, we first verify the formation of zinc hydroxide sulfate ($\text{ZnSO}_4 \cdot [\text{Zn}(\text{OH})_2]_3 \cdot x\text{H}_2\text{O}$, denoted as ZHS) on Zn metal during stripping/plating in ZnSO_4 . The significance of ZHS being an effective SEI on Zn is discussed for rechargeable ZIBs. The effects of separators/membranes on Zn stripping/plating on ZHS growth and deposited Zn are comprehensively investigated, from the perspectives of surface structure, microstructure, composition, and interfacial impedance. Nafion membranes outperform battery separators (filter paper, glassy fiber) in polarization and cycling stability. Most importantly, Nafion membranes are able to induce a planar ZHS layer as an efficient SEI on the metal surface. To provide further understanding, the interaction of $\text{<C->SO}_3^{\text{M->}} \cdots \text{Zn}^{2+}$ in the salt-in-water regime is studied, where DTF study supports the ability of $\text{<C->SO}_3^{\text{M->}}$ to reshape the coordination of Zn^{2+} in an aqueous medium. To achieve better performance and reduce the cost, composite Nafion membranes are synthesized by introducing biomass waste, lignin. In the constant capacity stripping/plating assessment, Nafion-based membranes exhibit impressively long stripping/plating cycle life compared with the others. Based on post-cycling analysis, different observed failure modes are discussed. The benefits of the membranes are further confirmed in $\beta\text{-MnO}_2/\text{Zn}$ rechargeable ZIBs.

Results and Discussion

Identification of Zn SEI

The surface of Zn foil was first investigated in a representative mild electrolyte for rechargeable ZIBs, that is, 2 M ZnSO₄. No membrane was applied in the electrolytic cells during stripping/plating (configuration in Figure S1^a in the Supporting Information). After the first cycle of stripping/plating, greyish layers can be observed for both positive and negative electrodes (Figure 1^a), compared with the bare Zn surface without electrolyte immersion. The layer became dense after 500 cycles (Figure S1 in the Supporting Information), where zinc dendrites with pits can be observed.^[18] FTIR--ATR (attenuated total reflection) was employed owing to its sensitivity to surface species (Figure 1^b). Pristine Zn foil presented a weak <C>OH vibration at approximately 3450 cm⁻¹. For the positive electrode after the first stripping, a similar broad <C>OH feature was observed; however, a pronounced <C>OH vibrational band at approximately 3360 cm⁻¹ emerged for the negative electrode (undergo plating simultaneously). After 500 cycles, sharp <C>OH features appeared at approximately 3549, 3424, 3362, and 3233 cm⁻¹, which can be assigned to hydroxide.^[19] In addition, evidence of splitting of the <C>SO₄²⁻ ν₃ mode from the first stripping for the negative electrode was confirmed by well-resolved peaks at approximately 1112 and 1155 cm⁻¹ for the foil after 500 cycles.^[19b] These FTIR characteristics suggest a possible formation of sulfate hydroxide.

The surface structure of the Zn foil was then analyzed by ex situ grazing-incidence X-ray diffraction (XRD). Figure 1^c (inset) zooms in on the low-angle range after one stripping/plating, where the diffraction peaks (2θ < 15°) at approximately 8.5° and 9.7° can be assigned to (0 0 2) for ZnSO₄·[Zn(OH)₂]₃·xH₂O with x=4 or 5 (PDF#44-0673, 39-0688) and x=3 (PDF#39-0689), respectively. A list of reference XRD patterns with different x values is provided in Figure S2 (in the Supporting Information). With incremental cycles, formation of ZHS is ascertained, where the broad (h⁰ 0) peaks indicate the coexisting hydrated states with different x values. After 500 cycles, the diffraction signal from ZHS became much stronger than that of metallic Zn, suggesting a surface layer of micrometer-scale thickness considering the attenuation depth for X-rays. Scanning electron microscopy (SEM) reveals that after the first cycle, plates with nanoscale thickness protruded out of the Zn foil surface (Figure 1^e, comparing with Figure S1 in the Supporting Information showing the relatively smooth surface of the pristine Zn foil). After 500 cycles,

micrometer-sized $\sim 100\text{ }\mu\text{m}$ plates with lateral dimensions above $100\text{ }\mu\text{m}$ and thicknesses of approximately $5\text{--}10\text{ }\mu\text{m}$ were observed, where phase contrast differentiated by low-angle back-scattered electrons (LABe) in Figure S1f confirms the presence of light elements from the "dark" micrometer-sized plates in the "bright" matrix dominated by heavier metallic elements. Information about the bonding states of the elements on surface were decoupled from the X-ray photoelectron spectroscopy (XPS) spectra in Figure S1d. The asymmetric S^{2p} peak can be attributed to C-SO with oxygen from octahedral layer of ZHS ($\approx 166.6\text{ eV}$ for 500th cycle) and oxygen from sulfate tetrahedra in the interlayer of ZHS ($\approx 167.5\text{ eV}$ for 500th cycle, where the relatively broad feature could be associated with the interlayer water).^[20] Note that after stripping/plating, both components showed reduced full width at half maximum values (FWHMs), indicating improved crystallinity, which is consistent with the XRD characteristics. Also, Zn^{2p} was deconvoluted into Zn-C-O, Zn-C-OH, and metallic Zn, where the oxidized states were confirmed by Zn Auger line L_{3M45M45} (Figure S1, see also discussion on XPS analysis in the Supporting Information). Together with analysis of O^{1s} (Figure S1 in the Supporting Information), the surface relative compositional ratio of Zn/S/O was then estimated to be about 4:1:12.5 for the foil after 500 cycles, which is consistent with the stereochemistry ratio in ZHS with x close to 3. Based on the above, it is clear that zinc hydroxide sulfate forms on the Zn surface during stripping/plating in ZnSO₄.

Although the role of ZHS on the cathode in ZIBs has been discussed,^[7,21] with its formation/dissolution behavior under pH evolution of electrolyte,^[22] there is no explicit report on its presence and role on Zn metal. Based on our analysis, the presence of the ZnSO₄·[Zn(OH)₂]₃· x H₂O family on the Zn surface is confirmed. Note that this type of SEI may result from a precipitation reaction rather than reduction of salt anion and solvent as in Li SEIs.^[1b] The proposed effective SEI is supported by recent findings in the reported aspects of polarization behavior,^[1f,4] interfacial impedance,^[4a,5] and surface morphology of Zn metal.^[6] Considering the prevailing existence of anion intercalated zinc hydroxide at neutral pH,^[19a,23] formation of a corresponding zinc layer hydroxide in mild electrolytes could be a general phenomenon for ZIBs. For example, formation of a zinc layer hydroxide was also observed during stripping/plating in 2^M Zn(CF₃SO₃)₂ as verified by XRD, LABe, and elemental

mapping (Figure^{S3} in the Supporting Information). Realizing that failure is reported for Zn symmetric cells in mild electrolytes, the role of the zinc layer hydroxide on Zn metal as an effective SEI layer needs to be explored in rechargeable ZIBs. Therefore, we address the controlled growth of ZHS with battery separators/membranes in the following sections.

Effects of membranes on Zn SEI

To study the effects of battery separators/membranes on Zn stripping/plating, filter paper, glassy fiber, and Nafion were selected. A mild wet chemistry route was employed to convert the cast Nafion membrane to Zn²⁺ type, by soaking the membrane in ZnSO₄ (electrolyte in this study) at an elevated temperature (see the Experimental Section). This method managed to improve the conductivity of the membrane from $4.6 \times 10^{-6} \text{ S cm}^{-1}$ before treatment to $1.4 \times 10^{-3} \text{ S cm}^{-1}$ after treatment (Figure^{2f}), together with enhanced H₂O channels (proton/cation conduction channels) indicated by the ionomer peak shifting from approximately 0.135 to $0.125 \text{ \AA}^{-1}$ (Figure^{S4} in the Supporting Information).^[24] To construct more conduction channels in Nafion, biomass waste lignin was introduced in view of its rich <C>OH groups and low cost. Through solution casting, which allows facile scaling, lignin@Nafion membranes can be obtained as in Figure^{2a,b}, denoted as NL10 and NL20 where the numbers refer to the corresponding weight percentages. Well-dispersed lignin was observed in the Nafion matrix (Figure^{2c}), where lignin tended to aggregate into elongated shapes (see also Figure^{S5} in the Supporting Information for Nafion and NL20). Small-angle X-ray scattering (SAXS) patterns in Figure^{2d} reveal the shift of the ionomer peak to $Q \approx 0.116 \text{ \AA}^{-1}$ and further to approximately $0.112 \text{ \AA}^{-1}$ when the input of lignin was increased from 10 to 20 wt%, which indicates the enrichment of proton/cation conduction channels as a result of the <C>OH groups of lignin. This is supported by continuous increase in water uptake with increasing lignin content (Figure^{S7} in the Supporting Information), the enhanced absorbance of <C>OH stretching with lignin addition (Figure^{2e}), and redshift of the symmetric vibration of <C>SO₃^{<M>} (from 1058.3 to 1055.9 cm^{-1}) owing to shielding effects of H₂O in the hydrated state (Figure^{S6} in the Supporting Information).^[25] As an important property for membranes in rechargeable batteries, the

conductivities of the membranes in 2^M ZnSO₄ electrolyte were extracted from electrochemical impedance spectroscopic (EIS) spectra. The conductivity of the membrane can increase up to $9.1 \times 10^{-3} \text{ S cm}^{-1}$ with 20^{wt%} lignin doping. This value is higher than the reported data for the divalent cation type of Nafion.^[17a] The observed correlation between the band intensity of the 1630^{cm}⁻¹ vibration peak (bending of H₂O molecule with hydrogen bonds between <C->SO₃^{M->} and other H₂O) and conductivity with increasing lignin content is consistent with their reported proportionality.^[25] To access the characteristics of water in the membranes, different states of <C->OH stretching were decoupled by deconvolution (Figure^{S6} and Table^{S1} in the Supporting Information). Compared with the spectra of pure solvents, that is, water and 2^M ZnSO₄, the water in the membranes displays characteristics more towards that in pure water with the treatment and added lignin, where both the ice-like liquid state and liquid-like amorphous state possess increasing percentages.^[26]

The galvanostatic cycling performance in symmetric Zn^{M/2} ZnSO₄^{M/Zn} coin cells with filter paper, Nafion, NL10, and NL20 at 0.2^{mA cm}^{M->2} are compared in Figure³^{figr3}^a. In the initial stages, the cells with Nafion and NL membranes showed lower polarizations of 102, 82, and 108^{mV}, respectively, than those with filter paper (127^{mV}) and glassy fiber (208^{mV}, Figure^{S8} in the Supporting Information). After increasing to a maximum of 123^{mV} at about 26^h, the cell with Nafion showed a stable polarization of 95^{mV} at 376^h (1000th cycle), compared with 152^{mV} for that with filter paper. Similar to the case for Nafion, the cells with NL10 and NL20 presented polarizations stabilized at 376^h of 80 and 91^{mV}, respectively. From the perspective of the energy barrier for metal nucleation, low polarization is desirable for inducing uniform metal plating.^[27] The advantage of applying Nafion-based membranes in Zn stripping/plating was further confirmed at a higher current density of 0.6^{mA cm}^{M->2} in both the initial and stabilized polarizations (Figure³^{xfigr3}^{b,d}).

Although no failure mode during stripping/plating (e.g., short circuit) was observed with the well-retained integrity of separators/membranes (inset of Figure³^{xfigr3}^b), the evolving voltage profiles (Figure³^{xfigr3}^{c,d}) imply a complex interface.^[28] To shed

light on the reconstructed surface, the structure and morphology of the metal surface were monitored after a series of cycles. With filter paper, the surface showed a strong diffraction peak at **approximately** 12.3° , which can be assigned to ZHS (0^01) for $x=0$ (PDF#44-0675), (0^01) for $x=0.5$ (PDF#44-0674), (0^01) for $x=1$ (PDF#39-0690) (hereafter referred to as the water-deficient phase). Additionally, the broad peak at **approximately** 8.5° can be assigned to (0^02) ZHS for $x=4$ or (0^01) for $x=5$ (referred to as the water-rich phase). The water-rich phase started to grow as its signal emerged after the 10th cycle and became stronger after the 100th cycle (Figure⁴ a). The protruding plates were detected after the 10th cycle together with lateral ones (Figure^{S9} in the Supporting Information), whose phase contrast against the metallic matrix was differentiated by LAbE in Figure⁵ a. After the 1000th cycle, the water-rich phase grew with an intensity comparable to that of the water-deficient phase. Figure⁵ b shows that micrometer-sized plates with a lateral dimension of **around** $1\text{--}5\text{ }\mu\text{m}$ and submicrometer thickness were found perpendicular to the surface (large scale image in Figure^{S9} in the Supporting Information). Similarly, ZHS growing normal to the surface was observed when using glassy fiber (Figure^{S13} in the Supporting Information).

With Nafion, water-deficient ZHS showed a continuously increasing intensity with cycling, indicating its growth (Figure⁴ b). Weak diffraction from the water-rich phase was detected, which shifted during cycling to a higher angle, suggesting possible ZHS growth by losing water (e.g., from $x=5$ to $x=4$). The observed formation of the water-deficient phase is consistent with reported Nafion-induced dehydration of Zn electrodes.^[3a] Figure⁵ c shows the relatively smooth surface after the 10th cycle, where LAbE identified the ZHS characteristics of a planar submicrometer structure for the metal matrix (Figure^{S10} in the Supporting Information). Also, lateral nanoplates less than 50 nm were revealed growing from the metal matrix (inset of Figure⁵ c and see also elemental study in Figure^{S17} in the Supporting Information). After the 1000th cycle, the diffraction signal for the water-rich phase was barely observed. Additionally, the surface was covered with domains consisting of lateral micrometer-sized plates from $1\text{--}5\text{ }\mu\text{m}$ with well-defined facets as shown in Figure⁵ d. The boundaries between domains showed

nanoflakes emerging from the beneath surface in a perpendicular way, with submicrometer-sized lateral plates on top, which could play a protective role (Figure⁵ e).

With lignin added, the water-deficient phase showed a large increase in scattering intensity during cycling as exemplified by NL10 (Figure⁴ c). SEM uncovers lateral plates as large as $3\text{ }\mu\text{m}$ covering the surface after the 10th cycle (Figure⁵ f). Also, the dominant $(1\ 0\ 0)$ peak for ZHS with NL10 was stronger than that for Nafion through the cycles. This suggests favored ZHS growth with NL10. After the 1000th cycle, a wide range of $1\text{--}10\text{ }\mu\text{m}$ plates were found (Figure⁵ g), reflecting an Ostwald ripening process. Similarly, submicrometer-sized lateral plates on top of the potential protrusion area could be seen (Figure^{S11} in the Supporting Information). When the lignin content was further increased, the water-rich phase became detectable, and the nanoflakes started protruding between the lateral plates on the surface of NL20 (Figure^{S12} in the Supporting Information).

The cross-section view shows that except when using filter paper, no clear protrusion can be found on the Zn surface (Figure^{S14} in the Supporting Information). At 0.6 mA cm^{-2} , the plates grew accordingly with filter paper or Nafion membranes, as in Figure⁵ h,i. Note that under high current density, lateral plates also formed on top of the potential protrusion region as protection for the membranes (Figure^{S15} in the Supporting Information).

On the other hand, the separators/membranes lead to different preferred growth of deposited Zn. With filter paper, growth of Zn $(0\ 0\ 2)$ was favored whereas no significant change was found for Zn $(1\ 0\ 0)$. Suppression of Zn $(0\ 0\ 2)$ growth was observed for Nafion during cycling. With NL10, both suppression of $(0\ 0\ 2)$ growth and promotion of $(1\ 0\ 0)$ growth of Zn were observed. After 1000 cycles, the surface with filter paper showed an increase in the intensity ratio of $(0\ 0\ 2)/(1\ 0\ 0)$ (≈ 4.1) compared with pristine Zn foil (≈ 3.1). However, the ratio with Nafion decreased to 2.5, and further decreased to 0.6 with $10\text{ wt}\%$ lignin.

Elemental mapping in Figure⁵ i clearly shows the presence of Zn, S, and O, consistent with the ZHS constituents. Ideally, $\text{ZnSO}_4 \cdot [\text{Zn}(\text{OH})_2]_3 \cdot x\text{H}_2\text{O}$ has a

stoichiometry Zn/S/O ratio of 4:1:(10+x), where x refers to the number of crystal waters. As a semi-quantitative estimation, a normalized O/S atomic ratio <13 indicates a water-deficient phase, but a O/S ratio ≥ 14 indicates a water-rich phase. The micrometer-sized plates with filter paper in Figure⁵ show a compositional ratio of Zn/S/O $\approx 4:1:10$ indicating $x \approx 0$. Also, the nanoflakes emerging from the surface showed a ratio of approximately 31:1:17 (Figure^{S16} in the Supporting Information) suggesting $x > 4$. With Nafion, the plates parallel to the surface had a Zn/S/O ratio of about 10:1:11 indicating $x \approx 1$ (Figure^{S18}, see also Figure^{S19} in the Supporting Information for plates with Nafion under 0.6 mA cm^{-2} having a ratio of 5:1:10 ($x \approx 0$)). Based on the above, the micrometer-sized plates on the surface tend to have a water-deficient nature in both normal and parallel growth mode. However, the nanoflakes have a water-rich nature. The excess Zn (ratio > 4) can be explained by the Zn signal beneath the surface ZHS layer.

EIS spectra were conducted for the first 100 cycles to differentiate the interfaces formed during stripping/plating by the separator/membranes. All symmetric cells present increasing trends of interfacial resistance before stabilization as in Figure⁴ (also Figure^{S20} in the Supporting Information). For the initial open circuit, Nafion, NL10, and NL20 had resistances of approximately 51, 48, and 37Ω , which are slightly lower than that of 70Ω for filter paper. After the 100th cycle, the interfacial resistance for the cell with filter paper increased continuously to 673Ω , which is close to a ten-fold increase. However, for the cell with Nafion, the increase of interfacial resistance was much milder, that is, an increase to 190Ω at the 50th cycle (approximately one third of the value for filter paper), which was retained at the 100th cycle. The presence of lignin drove the resistance increase at the beginning. After the 10th cycle, cells with NL10 and NL20 presented higher resistances (213 and 206Ω , respectively) than that with Nafion (135Ω). However, NL10 showed a fast stabilization, where the interfacial resistance decreased to 175Ω at the 100th cycle. On the contrary, the cell with NL20 continued its increasing trend for resistance. Rapid increases in interfacial resistances during cycling for all the samples support the observed interfacial ZHS formation, more than metallic Zn. Diverse trends of interfacial resistance change are attributed to different growth modes of both ZHS (phase, morphology) and deposited Zn.

Interaction between membrane and electrolyte

To approach the effects of separators/membranes on the growth of both ZHS and deposited Zn, the interaction between Zn^{2+} and $\text{C}-\text{SO}_3^{\text{M-}}$ from the membranes was investigated. Hydrogen bonding was first examined to reflect the states of water with different anion or functional groups. $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ was selected, which provides $\text{C}-\text{SO}_3^{\text{M-}}$ groups in the electrolyte. Comparison of ZnSO_4 and $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ with the same molar concentrations is given in Figure [S7](#), which shows significant difference for the ice-like ($\approx 3230 \text{ cm}^{\text{M-}1}$) and ice-like liquid ($\approx 3410 \text{ cm}^{\text{M-}1}$) states. This suggests a disruption of water network through hydrogen bonding with $\text{C}-\text{SO}_3^{\text{M-}}$ groups.^[1f] On the other hand, the $\text{C}-\text{SO}_3^{\text{M-}}$ symmetric vibration is blueshifted in Nafion-- Zn^{2+} relative to Nafion-- H^+ , which is expected to redshift owing to the higher water content in Nafion-- Zn^{2+} (Figure [S6](#) in the Supporting Information).^[25] This suggests rearrangement of shielding H_2O between $\text{C}-\text{SO}_3^{\text{M-}}$ and Zn^{2+} . Consequently, the coordination of Zn^{2+} at the membrane/electrolyte interface is likely to be reconstructed from $\text{Zn}^{2+}(\text{H}_2\text{O})_6$ as an aqueous electrolyte.^[29] A density functional theory (DFT) study was performed by using Gaussian¹⁶ to visualize the interaction between Zn^{2+} and $\text{C}-\text{SO}_3^{\text{M-}}$ in water (Figure [S21](#) in the Supporting Information). The calculated interaction energy, defined as the energy required for one sulfonate group to be added to the Zn^{2+} cluster, is determined to be $\approx 1.35 \text{ eV}$. This value is within the range of successive energies for $\text{Zn}(\text{H}_2\text{O})_n^{2+}$, ≈ 0.95 to 4.42 eV (defined as the energy required to add one water molecule to $\text{Zn}(\text{H}_2\text{O})_{n-1}^{2+}$, where $n=1-6$), and specifically in between the value for $n=4$ and $n=5$.^[30] Above confirms the ability of $\text{C}-\text{SO}_3^{\text{M-}}$ to reshape the coordination of Zn^{2+} in the salt-in-water regime. The solvation-sheath model indicates reconstructing the Zn^{2+} coordination is able to benefit the Zn reversibility.^[1f] With changing the coordination species and number of Zn^{2+} , oxygen-containing anion groups (e.g., dodecyl sulfate) are able to induce the exposure/growth of Zn (002), which is less likely to undergo dendrite growth.^[3e, 10b, 31] Orientation of the deposited Zn can be crucial if its (002) plane is normal to the substrate surface and consequently the (100) plane is exposed to be a potential nucleation site for dendrite growth.^[8a] The $\text{C}-\text{SO}_3^{\text{M-}}$ groups from the conduction channels in the membrane could guide the planar growth of Zn (002)

on the polycrystalline commercial foil though with a lower intensity ratio of $(0^{002})/(1^{000})$. It is likely planar Zn (0^{002}) serves as a template for ZHS growth.

A two-fold beneficial effect from Nafion is illustrated in Figure 6a: Zn (0^{002}) being deposited parallel to the metal surface and forming ZHS with a planar morphology parallel to the metal surface as an SEI. This interface is able to suppress dendrite formation and leads to a small and stable polarization even at high current density. With NL10, (0^{002}) growth can also be guided by $\text{Zn}^{2+}\text{--SO}_3^{\text{M-}}$, with promoted growth of Zn (1^{000}) and ZHS that could be attributed to $\text{Zn}^{2+}\text{--OH}$.^[32] As a comparison, there is negligible interaction between filter paper or glassy fiber and the electrolyte (Figure S22 in the Supporting Information), and the major role of the filter paper is to act as a physical barrier against the fast evolving Zn surface without separator even at 0.2 mA cm^{-2} (Figure S23 in the Supporting Information). In this case, deposited Zn (0^{002}) can align normal to the surface. ZHS can form on the exposed Zn (1^{000}) normal to the surface, but with a loose arrangement as in Figure 5b,j. The resulting loose layer is inefficient in suppressing dendrite growth under harsh conditions (Figure 6b).
It should be Figure 7a now. A dense planar SEI layer is promising to hinder the growth of dendrites or interfacial layers normal to the surface. We demonstrated further the effective SEI can be controlled through pre-deposition parameters, for example, a longer reaction time ($\approx 17\text{ h}$) can lead to an approximately $30\text{ }\mu\text{m}$ ZHS layer when using NL10 (Figure S24 in the Supporting Information).

Performance evaluation

In light of the above, galvanostatic stripping/plating until a constant capacity was applied to assess the performance of separators and the developed membranes (Figure 7a). Filter paper led to a short circuit at about 76 h and glassy fiber was somehow more durable until the cell short circuited at 175 h . On the contrary, Nafion was able to endure until approximately 345 h , giving a lifetime roughly five-times longer than that of filter paper and twice as long as that of glassy fiber. NL10 presented an even longer lifetime of approximately 410 h . Besides lifetime, different failure modes were observed. With filter paper or glassy fiber, short circuiting was found, similar to

the report using 3^M ZnSO₄ at 1^{mA}cm⁻² with filter paper.^[4b] This is ascribed to metal contact between the two opposite Zn electrodes, where the loosely packed ZHS plates are ineffective for preventing the dendrite growth. With Nafion and NLs, the polarization continuously increased after stabilized zones several times in a few cycles followed by unstable fluctuation. This behavior is rarely reported in the literature, which should be distinguished from the sudden increase of polarization by several volts in an open circuit failure.^[4a] Post-cycling analysis of NL10 (Figure^{S25} in the Supporting Information) revealed that the gray product penetrating through the membrane consisted of micrometer-sized plates. Elemental mapping identifies the presence of ZHS on the spotted region. XRD of the membrane showed a strong signal from water-deficient ZHS, dominating those of the water-rich phase and Zn metal. This finding suggests the failure could be due to planar contact of the effective SEI layers, the accelerated growth of which destroys the highly ionic conducting membrane. This demonstrates the prevention of direct shorting by the SEI formed in the Zn stripping/plating process. Moreover, dynamic mechanical analysis (DMA; Figure^{S26} in the Supporting Information) shows the increasing storage modulus as well as decreasing $\tan\delta$ as the lignin content increased. The enhanced elastic response may benefit the membrane performance. However, the deteriorated lifetime for NL20 might suggest fast growth of ZHS plays a more dominant role in offsetting the improved mechanical properties.

We further assembled β -MnO₂/Zn full cells with the separators/membranes. To exclude the effects from deposition of Mn²⁺, only ZnSO₄ was applied as the electrolyte.^[2d] In 2^M ZnSO₄, the cells with Nafion membranes showed better cycling performance compared with the cell with filter paper, with voltage profiles provided in Figure^{S27} (in the Supporting Information). The observed trends for capacity versus cycling can be ascribed to an activation process followed by loss of active mass,^[2b,d] and further associated with the deposition/dissolution balance of Zn-birnessite.^[21a] The maximum capacity at 0.1^C was 227^{mAh}g⁻¹ with Nafion and 236^{mAh}g⁻¹ with NL10, which are much higher than that with filter paper (186^{mAh}g⁻¹; Figure⁷). The cells with Nafion membranes showed better retention than that with filter paper (i.e., 137 vs. 115^{mAh}g⁻¹ after 40 cycles). Also, better rate capabilities of the cells with membranes at 1^C were

achieved in terms of maximum capacities and retained capacities after 120 cycles (Figure 7c).

Conclusions

We confirmed the formation of zinc hydroxide sulfate (ZHS) on metallic Zn surfaces during stripping/plating in ZnSO_4 . Based on the surface/interface analysis, we propose the presence of zinc layer hydroxides to be effective solid-electrolyte interfaces (SEIs) for Zn in mild electrolytes. The effects of separators/membranes on ZHS growth have been investigated. A two-fold advantage of Nafion was found in mild acidic/neutral systems: formation of a planar ZHS layer parallel to the metal surface as an effective SEI and deposited Zn (0°) parallel to the surface. The merits of membranes are attributed to $\text{C}-\text{SO}_3^{\text{M}-}$ Zn^{2+} interactions, which can reshape the Zn^{2+} coordination as supported by the DFT study. In comparison, using physical separators, for example, filter paper, leads to possible exposure of deposited Zn (1°) and subsequently a loose layer of ZHS protrudes, which deteriorates the performance. We further synthesized biomass waste lignin@Nafion composite membranes to enrich water channels, and consequently enhance the conductivity, and reduce the cost. With the presence of lignin, the growth of lateral ZHS parallel to the surface is promoted with favored growth of Zn (1°). In the constant capacity stripping/plating assessment, Nafion demonstrated a cycle life of about 345 h, several times higher than commercial physical separators. With 10 wt% lignin, the cycle life can be further increased to approximately 410 h. Post-cycling analysis points to the function of SEI being to prevent short circuiting. Meanwhile, our findings facilitate understanding of the different failure modes. We further demonstrated the advantage of using Nafion-based membranes in $\beta\text{-MnO}_2/\text{Zn}$ full cells with 2 M ZnSO_4 : higher maximum capacity and better capacity retention. The understanding of the surface/interface of Zn metal during stripping/plating and development of functional membranes able to reshape Zn^{2+} coordination highlights the significance of an effective SEI on Zn metal in mild electrolyte and open a feasible route to designing and fabricating effective SEIs for Zn metal towards high-performance rechargeable ZIBs.

Experimental Section

Materials

Commercial Zn foil (without coating, Goodfellow) was used in this study. The commercial separators used were filter paper (Advantec) and glassy fiber (Whatman). β -MnO₂ was synthesized based on a literature method.^[2d]

Preparation of Nafion-based membranes

The Nafion membranes were re-casted from Nafion D520 dispersion (Alfa Aesar). The solution was dried at 60°C to remove the solvent and re-dispersed in *N,N*-dimethylformamide (Sigma) with a concentration of 40 mg mL⁻¹. The resulting solution was cast in a customized glass template. The casting was conducted at 60°C for 8 h to allow the formation of a solid membrane, followed by curing at 120°C for 12 h in a vacuum oven. The obtained membrane underwent electrolyte soaking (e.g., 2 M ZnSO₄) at 90°C for 12 h followed by H₂O soaking at 90°C for 2 h. For comparison, the membranes went through a similar procedure but soaking with 2 M H₂SO₄ at 90°C for 12 h as a standard reference.

Kraft lignin (Aldrich) underwent an acid washing process,^[33] followed by drying in a vacuum oven at 60°C before use. A certain amount of lignin with designed weight percentage was mixed with Nafion solution at room temperature. The mixture then underwent the casting and electrolyte treatment procedures described above. Note that 20 wt% Kraft lignin doping is the maximum percentage we were able to achieve in this study, where a further increase of lignin led to brittleness.

Materials characterization

Fourier-transform infrared spectroscopy measurements were conducted with a Frontier MIR spectrometer (PerkinElmer) with an attenuated total reflectance compartment. Small-angle X-ray diffraction was performed with a Naoinxider (Xenocs) with CuK α radiation. The membranes saturated with electrolyte were encapsulated in a customized cell for measurement under vacuum and data reduction was executed by using FOXTROT. Grazing-incidence XRD measurements were performed with a Shimadzu XRD-6000 thin film X-ray diffractometer with CuK α radiation, and an incident angle of 3°. The SEM study was performed with a FESEM 7600F (JEOL) equipped with an electron back-scattering detector and energy-dispersive X-ray spectroscopy (EDS) detector (Oxford). XPS spectra

were collected with a Kratos AXIS Supra XPS with dual anode (Al/AgK_α) X-ray monochromatic source.

Water uptake

The water uptake percentage of the membrane was calculated using Equation⁽¹⁾:

$$\text{water}^{\text{uptake}} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (1)$$

yes, it is ok to express it in percentage form.

where W_{wet} and W_{dry} refer to the weights of the fully hydrated and dry states in gram, respectively. The activated membrane was immersed in deionized (DI) H₂O at 80°C for 12 h. The excess water was carefully wiped off and the W_{wet} was measured. The membrane was then dried in a vacuum oven at 120°C for 12 h, and weighted to obtain W_{dry} .

Ion exchange capacity

Ion exchange capacity (IEC) in mol g⁻¹ was obtained by a titration method.^[34] All membranes first underwent activation by addition of 2 M H₂SO₄ at 80°C for 12 h. They were then dried in a vacuum oven at 120°C for 12 h and weighed. Typically, approximately 0.1 g membrane was soaked in 1 M NaCl solution (10 mL) at 80°C for 24 h to allow thorough exchange of Na⁺. The membranes were removed carefully, and the solution was titrated with 0.01 M NaOH solution until the pH reached 7 (pH meter M3000 process, Mettler Toledo). The IEC value was then calculated using Equation⁽²⁾:

$$\text{IEC} = \frac{VC}{W} \quad (2)$$

where V is the volume used for titration (mL), C is the concentration of NaOH (M), and W is the membrane weight (g).

Impedance measurements

The EIS spectra of the membranes were acquired by using a Solartron 1256 B electrochemical workstation. The measurements were conducted at room temperature. The membranes were cut into disc shapes with an appropriate diameter and 2 M ZnSO₄ was used as the electrolyte.

The conductivity σ [S cm^{-1}] was calculated as following [Eq.(3)] by:

$$\sigma = \frac{d}{AR}, \quad (3)$$

where d is the thickness of the membrane in μm , A is the cross-section area of the membrane (cm^2), and R is the resistivity obtained by impedance fitting (Ω). The thicknesses of the membranes were measured by using calipers after the test, which were determined as 59 ± 2 , 62 ± 4 , and $63 \pm 2 \mu\text{m}$, respectively.

Stripping/plating

Zn/M/Zn symmetric cells were assembled by using 16 mm Zn foil in disc shape separated by separator/membranes (19 mm) in CR2016 coin cell configuration. The electrolyte used was 2 M ZnSO_4 . The stripping/plating cycling was performed by using a Neware battery testing system. Galvanostatic mode was applied at current densities of 0.2 mA cm^{-2} and 0.6 mA cm^{-2} for 1000 cycles. EIS was applied to monitor the impedance at the 0th, 10th, 50th, and 100th cycles, with a frequency from 1 to $9 \times 10^5 \text{ Hz}$. Further, the symmetric cells underwent galvanostatic mode at 0.2 mA cm^{-2} until a constant capacity of 0.6 mAh cm^{-2} was achieved. The test lasted approximately 500 h. As a reference, stripping/plating of Zn/M/Zn symmetric cells was measured in an electrolytic cell without separator/membrane.

MnO_2 /M/Zn full cell

The working electrode was fabricated by mixing the synthesized β - MnO_2 , Super P (TIMCAL), and polyvinylidene fluoride in a weight ratio of 7:2:1 and by using N,N -dimethylformamide as solvent. The obtained slurry was coated on carbon paper and dried in a vacuum oven at 80°C for 48 h. The loaded mass of the active material was $1.5\text{--}2 \text{ mg cm}^{-2}$. The coin cell was then assembled by using the dried working electrode (12 mm), 2 M ZnSO_4 , separator or the cast membrane (19 mm), and Zn foil (14 mm) in CR2016 configuration. The assembled cells were tested under galvanostatic charging/discharging with a voltage window of 0.9–1.9 V by using a Neware tester.

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Conflict of interest

The authors declare no conflict of interest.

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Figure¹ a) Optical image of Zn foils in Zn²⁺/ZnSO₄/Zn after the first cycle of stripping/plating at 1 mA cm⁻². The notations of positive and negative signs follow the connection configuration, and cycles start with stripping of the positive electrode (with simultaneously plating on the negative electrode). Blue arrows indicate the clamping position and electrolyte soaking position in a top-down manner. b) FTIR--ATR spectra for the surfaces of Zn foils with stripping/plating. Vibrational peaks of -OH and -SO₄²⁻ are highlighted by blue dashed lines. c) Grazing angle XRD spectra for Zn foils after the 1st and 500th cycles. The inset enlarges the low-angle diffraction range for the 1st cycle and 10th cycles. The diffraction peaks at 2θ = 36.4, 39.1, and 43.3° were indexed to Zn (002), (100), and (101), respectively (PDF#04-0831). d) XPS of S_{2p} for the positive electrode after the 1st and 500th cycles. e) SEM image of the positive electrode after the first cycle. The inset shows the nanoplates protruding on surface. f) LAbE image of the positive electrode after the 100th cycle.

Figure² a) Scheme illustrating the design of composite biomass waste lignin@Nafion membranes. b) Optical image of lignin@Nafion with a size of $7 \times 7 \text{ cm}^2$. c) SEM image showing well-dispersed lignin in the Nafion matrix for NL10. d) SAXS patterns of the membranes in a double-log plot showing a continuous shift of ionomer peaks towards lower diffraction angles. The diffraction feature at about $0.06 \text{ \AA}^{-1}$ for Nafion was attributed to its matrix knee.^[24] panels c and d were swapped to match caption and description in text, ok?) FTIR spectra of the C-OH stretch ($4000\text{--}2500 \text{ cm}^{-1}$) of the membranes with references of pure H_2O and 2 M ZnSO_4 . (f) Conductivities of the membranes as a function of lignin content, together with the deconvoluted contributions from C-OH bending. A nearly linear relation between the intensity of the 1630 cm^{-1} peak and lignin content is observed, where the open symbols represent conductivity ($\circ$) and relative vibrational intensity at 1630 cm^{-1} ($\square$) for the untreated membrane.

Figure³ Galvanostatic Zn stripping/plating in Zn/Zn symmetric cells at a) 0.2 mA cm^{-2} and b) 0.6 mA cm^{-2} with filter paper, Nafion, NL10, and NL20. The inset of (b) displays optical images of the separators/membranes after cycling. c, d) Voltage profiles of the first and last ten cycles at 0.2 mA cm^{-2} (c) and 0.6 mA cm^{-2} (d).

Figure⁴ Ex situ grazing-incidence XRD patterns for Zn metal at different stripping/plating cycles with a) filter paper, b) Nafion, and c) NL10 at 0.2 mA cm^{-2} . Spectra were normalized with respect to the most dominant Zn (1^01) diffraction. d) Change of the interfacial resistance in the first 100 cycles for the symmetric cells with the separators/membranes, where bands associated with the curves individually provide a guide to the measured data ranges.

Figure⁵ a) LAbE of the Zn metal surface for the cell with filter paper after the 10th cycle at 0.2 mA cm^{-2} , where typical protruding micrometer-sized plates are circled with red dots. b) SEM image of micrometer-sized plates grown normal to the surface after the 1000th cycle. c) LAbE of the surface of the cell with Nafion after the 10th cycle showing the growth of lateral plates, where the inset refers to the area circled in blue dots, revealing the

growth of nanoplates below 50 nm from the metal matrix. d) Faceted lateral plates formed after the 1000th cycle; with e) plates formed on top of the potential protrusion region as a protection barrier. f) LAF of the surface with NL10 after the 10th cycle, showing enhanced coverage of lateral plates on the surface, where the inset enlarges area circled with blue dots. g) Surface covered by micrometer-sized plates of broad sizes after the 1000th cycle. h) Lateral plates with Nafion after the 1000th cycle at 0.6 mA cm⁻². i) Protruding plates with filter paper after the 1000th cycle at 0.6 mA cm⁻², with the corresponding EDS elemental mappings for j) Zn, k) O, and l) S.

Figure 6 a) Proposed scheme to summarize the effects of membranes on the surface of Zn metal. The interaction between SO_3^- from Nafion and Zn^{2+} may alter the Zn^{2+} coordination from its state in the electrolyte ($\text{Zn}^{2+}(\text{H}_2\text{O})_6$). As a result, distinct growth modes of ZHS and deposited Zn are obtained. b) FTIR spectra comparing 2 M ZnSO_4 and $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ with the distinct characteristics of hydrogen-bonded water states.
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Figure 7 a) Stripping/plating until a constant capacity of 0.6 mAh cm⁻² for the separator/membranes to assess their cycle lives. The cycling performance of $\beta\text{-MnO}_2/\text{Zn}$ full cells in 2 M ZnSO_4 compares filter paper, Nafion, and NL10 at b) 0.1 °C and c) 1 °C.