Remedies of capacity fading in room-temperature sodium-sulfur batteries

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HIGHLIGHTS

- The PBI membrane is employed to suppress polysulfi de crossover for Na-S batteries.
- Insoluble and insulating Na₂S₂ is determined as the final discharge product.
- P₂S₅ can complex with Na₂S₂ to improve the precipitation kinetics.
- The chemical mediation of I⁻/I₃⁻ promotes the dissolution of Na₂S₂.
- A much improved capacity retention is attained (92.9% for 50 cycles at 0.2C).

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ABSTRACT

Liquid-electrolyte sodium-sulfur battery operated at room temperature is encountering challenges brought by the complex sulfur redox reactions, including (i) the dissolved polysulfide intermediates trigger serious side reactions on Na anode surface; (ii) the short-chain sulfide precipitation exhibits sluggish kinetics and the sulfur utilization is generally below 50% with unclear reasons. In this work, employing an ion selective polybenzimidazole-based separator we successfully suppress the polysulfide corrosion on the Na anode, which allows the investigation of the precipitation reaction. Combining DFT calculation and characterization techniques, we determine Na₂S₂ particles as the final discharge product and reveal that Na₂S₂ passivation is the predominant attributes of large polarization and capacity fading. To address these issues, we present the use of a bifunctional NaI-P₂S₅ based electrolyte additive, which (i) improves the Na₂S₂ precipitation kinetics by forming soluble Na₂S₂-P₂S₅ complex and (ii) promotes the dissolution of Na₂S₂ by the chemical mediation of I⁻/I₃⁻. As a result, a much improved capacity retention (92.9% for 50 cycles at 0.2C) is attained, which sheds light on enabling the stable operation of sodium-sulfur batteries via combining advanced separator and electrolyte engineering strategies.

1. Introduction

For storing the fluctuating electricity generated by solar panels and wind turbines, alkaline metal based batteries have been proposed to meet the demand of high energy density. Electrochemical energy storage with the sodium (Na) and sulfur (S) chemistries is especially appealing as it well caters the low-cost and high-energy targets desired by the distributed grids. Success has been achieved by the high-temperature molten Na-S battery (> 300 °C) using the solid electrolyte [1–6]. Though promising in terms of power/energy densities and high efficiency with long cycle life, safety concern arising from high operating temperature as well as the complex system design to store the highly reactive molten Na and S species directly prohibits its extensive application. Lowering the operating temperature of the Na-S battery has been recognized as a meaningful topic that will affect this technology, developing the room-temperature (RT) Na-S battery into reliable, low-cost, scaled-up energy storage systems thus has attracted ever-increasing research interest [7–12].

Liquid electrolyte with a high ionic conductivity is employed in the RT Na-S battery. During the discharge process, Na stripping occurs at the anode, resulting in the production of Na⁺ and electrons. Meanwhile, multiple-step sulfur redox reactions happen under the existence Na⁺ ion, generally including the polysulfide dissolution reactions (a, b) and low-order sulfide precipitation (c) in the liquid electrolyte (e.g. tetruglyme) as shown in the formulas below.

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\[
\frac{1}{2}S_8 + e^- \rightarrow \frac{1}{2}S_8^{2-} \quad (a)
\]
\[
\frac{1}{2}S_8^{2-} + e^- \rightarrow S_i^2 \quad (b)
\]
\[
2Na^+ + \frac{x}{4}S_i^{2-} + \left(2 - \frac{x}{4}\right)e^- \rightarrow Na_2S_i \quad (c)
\]

Similar with the lithium polysulfide dissolution in the lithium-sulfur (Li-S) battery, sodium polysulfide intermediates formed from the reactions in (a, b) can be dissolved in the electrolyte and react with the Na metal, triggering a series of drawbacks, including lower discharge capacity, fast capacity fading and anode degradation [2,13-15]. In order to localize polysulfide species within the cathode, strategies have been proposed to fabricate sulfur/carbon composite that can encapsulate sulfur species in microporous as well as mesoporous carbon [16-23]. Considering the leakage of dissolved polysulfides from the host material, an ion selective interfacial material will be also desirable and Na+ conducting membrane such as β-alumina has been inherited from high temperature Na-S battery [24,25]. However, in consideration of the low ionic conductivity at a lower temperature and brittleness caused by the solid-state electrolytes, efforts of developing polymer and gel-polymer electrolytes are critically needed for room temperature Na-S battery [26-28].

Though it has been widely realized that discharge process of Na-S batteries involves both polysulfide dissolution and precipitation, few studies investigated the precipitation process and the corresponding effects on the battery’s performance [2,16,17,24]. The sulfur utilization for the reported RT Na-S battery was generally lower than 50% with unclear reasons [7,21,25,29-31]. Despite the low sulfur utilization ratio, the formed solid discharge product can enlarge polarization by covering the electrochemical reaction sites, which affects the rate capability. Moreover, compared with the excellent reversibility of dissolved polysulfide species, relatively poor reversibility of solid discharge product is supposed to be an essential factor affecting the battery’s cyclability. For example, for the previous work employing the solid-state electrolyte as the separator, although polysulfide crossover can be fully suppressed, a considerable fading can be still observed [24-26]. It thus occurs to us other attributes such as the formation of less reversible discharge product should be responsible for the capacity fading and there is an urgent need for us to shed light on the precipitation process occurring in RT Na-S batteries.

With these considerations in minds, we investigated capacity fading phenomena in RT Na-S battery system and the strategies for performance enhancement. To mitigate polysulfide crossover, we employed a new-type polybenzimidazole-based separator, which critically enabled the stable battery operation at the voltage window of 1.8-2.8 V representing sulfur/polysulfides conversion. On the other hand, the formation process of solid discharge product in the RT Na-S batteries was studied. We determined insulating and insoluble Na2S2 as the main discharge product for Na-S batteries using ether-based electrolytes with evidence from XPS and Raman spectroscopy, testified by DFT calculation. To address the cathode passivation of Na2S2, we employed a Na-P2S5 based electrolyte additive, partially dissolving Na2S2 by forming soluble Na3S2P5 complex and realizing efficient Na2S2 decomposition by overcharging the battery into the voltage window representing 1- / 1+ redox reaction. The adequate modifications of separator and electrolyte additives allow the battery to achieve a much improved capacity retention (92.9% for 50 cycles at 0.2C).

2. Experimental

2.1. Material preparation

To prepare the polybenzimidazole (PBI) membrane, PBI solution 26 wt.% in N,N'-4 dimethylacetamide (DMAc) with intrinsic viscosity of 0.73 dl g-1 was purchased from PBI Performance Products Inc. The diluted PBI solution (1 wt.%) was sprayed on a hot electric plate to derive a dense PBI membrane. The solvents were completely evaporated at 160 °C in a vacuum oven.

2.2. Cell assembly and test

Battery assembly was conducted in the Ar-filled glove box with oxygen and water contents maintained below 0.1 ppm. Using the CR-2032 coin cell, one piece of polished Na foil (16 mm in diameter) was placed onto the bottom cell body. One piece of PBI membrane (18 mm in diameter) and one piece of Celgard 2500 separator were placed onto the Na foil with PBI on the Na anode side, following by the addition of electrolyte. Tetraglyme containing 1 M NaTFSI and 0.2 M NaN3O2 was adopted as the electrolyte [31]. Additives including Na3P2S5, Na2S8-P2S5, and Na could be further added into the electrolyte, but the overall volume of the electrolyte was limited to 100 μL. Moreover, owing to the excellent wettability (74 μL cm-2), mechanical strength and high surface area (310 m2 g-1), carbonized cellulose paper was used as the cathode current collector, which was prepared by carbonizing lab-supplied Kimwipes (CK) paper in the Ar atmosphere for 2 h at 800 °C [32,33]. Carbonized cellulose papers (8 pieces) with an uncompressed thickness of ~200 μm were then stacked together and punched into a circular disk (12 mm in diameter) for battery assembly. The sulfur powder (1.30 mg) was weighted and sprayed onto the carbon matrix surface and treated at 155 °C for 20 min to impregnated sulfur into the carbon matrix to derive an areal capacity of 1.90 mAh cm-2 based on the conversion from S8 to Na2S. To clearly observe the discharge product morphology, a piece of hydrophilic carbon cloth (12 mm in diameter) with a carbon fiber diameter of 9 μm was employed as the cathode. The assembly of Li-S battery follows similar procedures, but the electrolyte was replaced by 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME or glyme) solution (1:1 in volume) with the addition of 1 M LiTFSI and 1 wt% LiNO3 additive.

The galvanostatic discharge and charge tests were conducted on a battery testing system (Neware, CT-4008 W) at 25 °C. The electrochemical measurements were determined with a potentiostat (Princeton Applied Research, PARSTAT M2273). Electrochemical impedance spectroscopy (EIS) measurement using a frequency range from 100 kHz to 100 mHz with a wave amplitude of 5 mV was applied to the assembled batteries. Besides, the cyclic voltammetry (CV) was tested at a scanning rate of 0.05, 0.1 and 0.2 mV s-1 with the carbon electrode as the working electrode and sodium coil as reference electrode and counter electrode, respectively.

2.3. Material characterization

The electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) measurements were conducted on a potentiostat (Princeton Applied Research, PARSTAT M2273) via the two-electrode setup, where the sodium (Na) metal anode performs as both the reference and counter electrode and the cathode performs as the working and sensing electrodes. Here, the EIS measurement using a frequency range from 100 kHz to 100 mHz with a wave amplitude of 5 mV was applied to the charged battery at the open circuit voltage. The ionic conductivity of PBI membrane was measured by electrochemical impedance spectrum (EIS) from 100 kHz to 100 mHz with an alternating current amplitude of 5 mV. The test cells were assembled by a piece of PBI (8 μm) or Celgard 2500 membrane (18 mm in diameter for both) sandwiched between two stainless steel blocking electrodes. Prior to the EIS measurements, the cells were kept at each test temperature (from 25 °C to 55 °C) for 10 min in order to reach the thermal equilibrium [34].

In order to optically determine the retention of polysulfide species by the introduced PBI membrane, a static diffusion test setup was built following previous work [35]. Thereby, Na2S8 (0.5 M, 1 mL) in
tetraglyme solution was placed inside the glass tube, whereas the opposite side of the separator was filled with a conventional tetraglyme. During the experiment, the solutions rested without movement to exclude external influence on the diffusion test of polysulfides through the separator. The resulting color change was evaluated by visual examination.

The Na electrodes and discharged cathodes after cycling were washed by pure glyme and then dried in the Ar-filled glovebox before SEM observation. JSM-6700 F field emission SEM instruments were used for micrograph observation at an acceleration voltage of 5.0 kV. TEM images were taken on a high-resolution transmission electron microscopy (JEOL, 2010F TEM) using an accelerating voltage of 200 kV and the membrane samples were stained with periodic acid by placing the copper grids upon the evaporating aqueous solution containing the periodic acid to enlarge the contrast [36].

To study the surface compositions of the discharged cathode, X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Physical Electronics PHI5802 instrument using an X-rays magnesium anode (monochromatic Ka X-rays at 1253.6 eV) as the source. C 1s region was used as the reference and set at 284.8 eV.

Modification of a regular single cell was made for the Raman study, where the cathode end cap plate was cut with a hole and sealed with a quartz window. Raman spectra were collected using a spectrometer (Princeton Instruments, Spectrapro2500i) with a back illuminated charge-coupled detector attachment (Princeton Instruments, Spec 10) using an argon-ion laser with a wavelength of 514.5 nm and 50 mW laser power as the excitation source. To control the exposure time, the laser beam was chopped using a mechanical shutter. Raman spectra were obtained by accumulating 5 measurements, with an exposure time of 20 s.

Fourier transform infrared spectroscopy (FTIR) measurements were recorded using Vertex 70 Hyperion 1000 (Bruker) with the assistance of attenuated total reflectance (ATR) accessories. The absorption spectra were recorded from 3200 cm\(^{-1}\) to 400 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\).

The UV-Vis spectra were collected by SEC2000 UV-visible spectrophotometer (ALS Co., Ltd.). An SCE-C thin layer quartz glass cell with an optical path length of 4.5 mm was used as the holder.

2.4. DFT calculation

All density functional theory (DFT) based first-principles calculations were conducted adopting ABINIT code [37,38]. The exchange-correlation functional was coped with by generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) type and the electron-ion interactions were modeled by Projector-augmented-wave (PAW) potentials [39]. The DFT + D2 functional was used to include the physical van der Waals (vdW) interactions [40]. After the convergence tests, the energy cutoff of 24 Ha was used to ensure a satisfied convergence for wave-basis expansion. Ten Li/Na-S compounds were considered, including \(\alpha\)-S\(_8\) (128 atoms), \(\beta\)-S\(_8\) (48 atoms), Li\(_2\)S (12 atoms), \(\alpha\)-Li\(_2\)S\(_2\) (12 atoms), \(\beta\)-Li\(_2\)S\(_2\) (8 atoms), Li\(_2\)S\(_4\) (48 atoms), \(\alpha\)-Na\(_2\)S\(_2\) (12 atoms), \(\beta\)-Na\(_2\)S\(_2\) (8 atoms) and Na\(_2\)S\(_4\) (48 atoms), and the Brillouin zones were sampled on 4 × 4 × 4, 8 × 8 × 8, 8 × 8 × 10, 8 × 8 × 4, 4 × 4 × 4, 8 × 8 × 8, 8 × 8 × 10, 8 × 8 × 4 and 4 × 4 × 4 Monkhorst-Pack grids, respectively [41]. The convergence criterion of the electron self-consistent loop was \(4.0 \times 10^{-5}\) Ha Bohr\(^{-1}\) and that of structural optimization was \(4 \times 10^{-4}\) Ha Bohr\(^{-1}\).

The formation energy (\(E_f\)) of the compound Li\(_{x+y}\)S\(_{8-x}\)/Na\(_{4-x}\)S\(_{8-4x}\) was calculated by:
\[
E_f = E_{LiS/NaS_{li}} + E_{LiS/NaS_{Na}} - E_{LiS/NaS_{NaAD}}
\]

where \(E_{LiS/NaS_{li}}\), \(E_{LiS/NaS_{Na}}\) and \(E_{LiS/NaS_{NaAD}}\) are the DFT total energies of \(LiS/NaS\), \(LiS/NaS\) and \(LiS/NaS\) respectively. Due to the limited differences of calculated energies at 0 K and 300 K for solid-state products, it is reasonable to use the formation energies to represent for the Gibbs free energies in this question. Therefore, a negative formation energy indicates the formation of the compound is energetic favorable, and vice versa.

3. Results and discussions

3.1. Performance of batteries at different voltage windows

A Na-S battery is consisting of a carbon matrix impregnated with sulfur or polysulfides as the cathode, a metallic Na anode, and a separator, all of which are immersed in the ether-based liquid electrolyte. First of all, to mitigate the capacity fading caused by polysulfide shuttle effect, we need to establish a protective shield for the Na anode in the corrosive electrolyte environment. As shown in Fig. 1a, we screen out the polybenzimidazole (PBI) membrane with heterocyclic groups for this purpose because of three folds of advantages, firstly, polysulfide species can be chemically adsorbed by the rich function groups containing nitrogen (pyridine-type nitrogen (-N = ) and pyrrole-type nitrogen (-NH-)) in the membrane; secondly, the pore size of PBI can be reduced to generally below several nanometer to enhance the size exclusion effect for polysulfides, while maintaining continuous porous structure to uptake liquid electrolyte; thirdly, PBI reaches a rather high tensile modulus (~82 MPa based on our previous report) so that it can attain a small thickness with sufficient mechanical strength [42-44].

As shown in Fig. S1, the as-prepared PBI membrane was characterized by FTIR, confirming its imidazole structure containing amine and imine functional groups [43, 45, 46]. Ionic conductivity of PBI membrane fully immersed in the electrolyte was measured at a temperature range from 25 to 55 °C (Fig. 1b) following the reported methods [34, 47]. The saturated PBI membrane (1 M NaClO4 in tetraglyme) gained an ionic conductivity around 4.27 × 10^{-4} S cm^{-1} at 25 °C, generally an order lower than the saturated Celgard 2500, but considerably higher than the non-porous sodiated Naion (2.7 × 10^{-5} S cm^{-1} at 25 °C) [29]. In addition to the excellent Na^+ conductivity, the diffusion test (Fig. 1c) provided a virtual evidence of the low polysulfide permeability of PBI membrane. For a static rest of 72 h, the transparent electrolyte side separated from NaS8 solution with a PBI membrane (8 μm) showed minor color change owing to the two-fold blocking effects contributed by the nanosized channels together with the polysulfide binding functional groups on the PBI. On the contrary, for the control group using the Celgard separator, the color changed to green, light yellow and dark yellow because of the polysulfide diffusion driven by the concentration gradient.

The polysulfide binding ability of PBI was also confirmed from the FTIR spectrum in Fig. S1. In a previous study, we have shown that the pyridine-type nitrogen (-N = ) and pyrrole-type nitrogen (-NH-) in the benzimidazole rings allow the absorption and interaction with the hard Lewis base such as KOH [36]. Sodium polysulfide species are soft Lewis bases, which, to some extent, allow them to interact with the pyridine-type and pyrrole-type nitrogen groups in the PBI membrane. In the region of 2000–1000 cm^{-1}, the narrow peaks representing the cycle vibrations and in plane N-H (also C-H) deformation modes were decreased significantly after soaking with polysulfides. Also, the alkyl C-N stretching at 1049 cm^{-1} together with C=O stretching at 1440 cm^{-1} were decreased. Moreover, the broad intense peak in the range of 2500–3500 cm^{-1}, related with the hydrogen bonding of N-H, almost disappeared after soaking with polysulfides. These changes to the nitrogen relevant peaks are attributed to the formation of the coordinated N-Na-S bond [44, 48].

Morphologies of the PBI membrane at different scales were further characterized with TEM and SEM. From the TEM image in Fig. 1d, for the stained PBI membrane, the spreading dark areas refer to the uniformly distributed nanochannels that are responsible for conducting Na^+ ions. In addition, from the SEM images (Fig. 1e and f), the membrane surface and cross-section showed a dense morphology without any observable macropores or cracks. Polysulfides that are anchored on the polymer matrix therefore can prevent the polysulfides from entering the nanochannels, facilitating the formation of an ion-selective cathode/separater interface.

Despite the investigation of ionic conductivity and selectivity, we examined the capability of PBI-based separator in suppressing dendrite. The Na/Na symmetric cell and cycled at 0.25 mA cm^{-2} with an areal capacity of 0.5 mAh cm^{-2} as shown in Fig. 1g. The PBI membranes (8 μm) were placed on the Na anode surfaces for each side with a Celgard 2500 separator inserted in between. Stable cycling without short circuit and voltage fluctuation was observed for 100 times. While for the counter part assembled with bare Na metals, cycling lasted for 77 times before dendrite occurred and the increase of overvoltage over cycling was considerable, which was attributed to the thickening of passivation layer on the Na anode and the increase of surface non-uniformity. We deduce that the achieved excellent symmetric cell performance is on one hand ascribed to the high modulus of PBI membrane, which can suppress Na anode surface deformation; on the other hand, the uniform structure of PBI allows for the even distribution of Na^+ ions, facilitating smooth Na deposition [13, 49–52]. The cross section and surface SEM images of the cycled Na electrodes can be found in Fig. S2, confirming the smooth Na deposition induced by the incorporation of the PBI membrane.

With the achieved results, we have confirmed the excellent ionic conductivity, ion selectivity and strong mechanical properties of the as-prepared PBI membrane. The Na-S batteries were assembled for performance evaluation at different rates and voltage windows. As shown in Fig. 2a, at the voltage window of 1.8–2.8 V, where the transformation between S8 and Na2S8 occurs, the battery using a routine Celgard separator decayed dramatically showing a rather low coulombic efficiency due to the polysulfide dissolution and Na anode degradation. In sharp contrast, minor capacity fading was observed for the battery with a PBI-based separator in 160 cycles, which evidences the excellent shielding effect of PBI for the Na anode. Despite excellent stability, the EIS measurement results in Fig. S3 also show the batteries assembled with the 8 μm-PBI membrane exhibited an acceptable bulk resistance around 22Ω. From the voltage profiles in Fig. S3, the small thickness achieved by the PBI membrane is essential for achieving low polarization. As shown in Fig. 2b and c, the battery exhibited excellent rate performance (0.1C, 0.15C, 0.2C). The discharge capacity and profile of the higher voltage plateau are generally similar with what have been observed for the Li-S battery [53]. This implies that sulfur dissolution reactions follow similar reaction pathways in both Li-S and Na-S batteries [2, 54]. However, if we discharged the batteries into the voltage window representing both polysulfide dissolution and precipitation (1.2–2.8 V), the battery exhibited a rapid capacity fading (Fig. 2d).

With these results, we proceed to evaluate the battery’s rate capability within the voltage window of 1.2–2.8 V (Fig. 3a and b). Despite improvement of capacity retention compared to the battery with a routine separator, rather fast capacity decay was generally observed. In Fig. 3c, the Na-S battery discharge curve at 0.05C depicted a sloping higher voltage plateau and a flat lower voltage plateau, which are of almost identical capacities. Despite being discharged at a rather small current density (0.05C), the battery’s capacity is generally below 837 mAh g^{-1} (the theoretical specific capacity based on S8/Na2S conversion is 1675 mAh g^{-1}), indicating that Na2S might not be formed as the final discharge product. This is in sharp contrast with the Li-S battery, where the lower voltage plateau that represents the Li2S precipitation is usually 2–3 times of the higher voltage plateau as shown in Fig. S4. From the rate capability test (0.05, 0.1, 0.2, 0.3C) as shown in Fig. 3c, the lower voltage plateau that represents the formation of solid-

phase discharge product declined significantly due to the enlarged overpotential at a higher discharge rate. From the cyclic voltammetry curves in Fig. 3d, there existed two separated anodic peaks at 1.87 V and 2.42 V respectively, and reversible cathodic peaks at 1.62 V and 2.26 V, corresponding to the observed two-plateau voltage profiles. It is found that the peak current densities for the two-step reactions are very close, in adequate agreement with the charge-discharge voltage profile.

From the above results, we realize that when operating the Na-S batteries at the voltage window of 1.2–2.8 V, the specific capacity and Coulombic efficiency at 0.1C with and without the protection of PBI membrane, the specific capacity and Coulombic efficiency at different rates, the corresponding voltage profiles for the battery with protection of PBI membrane, the voltage profiles for the battery at different rates with the PBI membrane, and the cyclic voltammetry curves (1.2–2.8 V) at different scan rates with the PBI membrane.
battery at a voltage window of 1.2–2.8 V, three major issues will arise, one is the relatively low sulfur utilization (< 50%), which might be ascribed to the intrinsic reaction mechanisms; the others are the fast capacity fading and sluggish kinetics. In order to conduct rational engineering approaches to enhance the battery performance, we firstly need to probe the intrinsic mechanism of solid discharge product formation.

3.2. Analysis of the discharge product formation process and compositions

Few studies attempt to address the formation mechanism as well as chemical composition of the discharge product at the lower voltage plateau. To study what is indeed happening at the lower voltage plateau, the carbon cloth with well-defined interwoven carbon fiber was chosen, as a model system for use in the experiment and the corresponding discharge curves can be found in Fig. S5a. Due to the smaller surface area of carbon cloth, the rate capability was inferior to the batteries with carbonized cellulose paper electrode [32,33]. But the typical two-plateau voltage profiles were still well maintained, which will allow us to study the discharge product formation processes.

Fig. 4a–d show the morphologies of the discharged and charged state carbon cloths at a moderate discharge rate (0.1C). Fig. 4a shows the initial charged electrode surface covered with the amorphous precipitated sulfur [55]. After the dissolution of sulfur into polysulfides occurring at the higher voltage plateau, small burst of particles emerged at the onset of the lower voltage plateau as shown in Fig. 4b. This is shown in Fig. 4c by the presence of more uniformly distributed precipitates observed in the middle of the lower voltage plateau at around 1.6 V, smaller particles developed as progressive nucleation commences. The sizes of particles continued to grow and nearly dominated the electrode surface toward the end of discharge (1.2 V) in Fig. 4d. With these results, the surface passivation of solid discharge product occurring at the lower voltage plateau is seemingly dominated by the nucleation and growth process [56–58].

At different rates, SEM images of the discharged cathodes were presented. The cathodes discharged at a lower rate (0.05C) were found to have larger hemispherical particles (~200 nm) as shown in Fig. 4e, while those discharged at a higher rate (0.2C) demonstrated conformal, film-like precipitates composing of uniform nanoparticles as shown in Fig. 4f. When comparing Fig. 4e and f, a higher nuclei density can be observed in the cathode discharged at a higher rate, resulting in smaller amounts of precipitates, which are in well consistence with the classical heterogeneous nucleation theory [56,58,59].

As either Na2S2 or Na2S is insulating, when the precipitates crowd together to cover the electrode surface, the overpotential will be increased significantly because of the insufficient reaction sites, especially when the areal current density is higher. While at a low areal current density (e.g. 0.05C, Fig. 4e), there is still available electrode surface indicating that active species (polysulfides) might be depleted, leading to the voltage drop [60–62]. In all cases, the sulfur utilization is generally below 50% if we assume the Na2S as the final discharge product. Therefore, we suggest Na2S2 other than Na2S is formed as the final stage of discharge, which will be testified in the following section.

To determine the chemical compositions of the precipitate, X-ray photoelectron spectroscopy (XPS) was applied on the cathode sides, which were discharged to different cut-off voltages as shown in Fig. 5a. The cathode discharged to 1.7 V, which is the onset of lower voltage plateau, showed the peaks of central and terminal polysulfides, representing sulfur atoms in the center of the chain (central) and sulfur atoms at the end of the chain (terminal) [18,58]. The decrease of central polysulfide peak during discharge thus leads to the fact that polysulfide species with longer chains such as Na2S4 and Na2S5 were consumed on the lower voltage plateau. When the battery was continuously discharged, S2p peaks at 162.5 eV representing Na2S2 showed

Fig. 4. (A–d) SEM images of the electrodes taken from different stages of discharge (0.1C): (a) 2.8 V; (b) 1.7 V; (c) 1.6 V; (d) 1.2 V. The corresponding voltage profiles can be found in Fig. S5b. (e, f) discharged electrode (1.2 V) at 0.05C (e); at 0.2C (f). The sizes of discharge precipitates decrease with the increase of the discharge currents.

Fig. 5. (A, b) The corresponding XPS (a) and Raman (b) spectra of the electrodes taken from different stages of discharge (1.7 V; 1.6 V; 1.2 V).
a visible rise besides the peak for terminal polysulfides, indicating that long-chain polysulfides were reduced to form solid Na$_2$S$_2$ at the lower voltage plateau. There was however no peak representing Na$_2$S, which should be located at 161.8 eV [63].

To further clarify the chemical compositions of the discharge intermediates and discharge product, Raman spectroscopy measurement was conducted as shown in Fig. 5b, which is capable of clearly separating the peaks for different species. Based on the previous Raman study conducted on the high temperature Na-S system, we found that at 1.7 V, peaks at 205 and 443 cm$^{-1}$ can be observed, related with the crystalline phase $\alpha$-Na$_2$S$_4$, and the wide shoulder peak at around 475 cm$^{-1}$ can be assigned to multiple polysulfide species such as Na$_2$S$_3$ and Na$_2$S$_5$ [64]. Over discharging, sharp peaks were observed to emerge at 449 cm$^{-1}$, which indicates the formation of $\beta$-Na$_2$S$_2$, together with the peaks at 468 and 479 cm$^{-1}$ representing $\alpha$-Na$_2$S$_4$. To more clearly observe the insoluble discharge product, the discharged electrode was rinsed with glyme and dried in the Ar-filled glove box. We found that the final discharge product was indeed a mixture of Na$_2$S$_2$ with peaks at 205 and 443 cm$^{-1}$ can be observed, related with the crystalline phase $\alpha$-Na$_2$S$_4$, and the wide shoulder peak at around 475 cm$^{-1}$ can be assigned to multiple polysulfide species such as Na$_2$S$_3$ and Na$_2$S$_5$.

Fig. 6. Crystal structures and respective space groups for Na$_2$S, $\alpha$-Na$_2$S$_2$, $\beta$-Na$_2$S$_2$, $\alpha$-Na$_2$S$_4$, and $\beta$-S$_8$. Purple and yellow spheres represent sodium and sulfur atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 7. (A-c) SEM images of the electrodes taken at the cell voltage of 1.8 V at different cycles. (d) Schematic of the discharge process with the addition of P$_2$S$_5$ as a complexation agent; (e) schematic of the charge process for Na-S battery with the addition of NaI as the redox mediator.
different phases. The main peak at 183 cm$^{-1}$ should be ascribed to the formation of crystalline $\alpha$-$\text{Na}_2\text{S}_2$, corresponding to a lattice mode of [S-S]$^2-$, while the shoulder at 458 cm$^{-1}$ indicates the stretching mode of [S-S]$^2-$ [64]. Moreover, bands that appear at 451 cm$^{-1}$ and 131 cm$^{-1}$ indicate the formation of $\beta$-$\text{Na}_2\text{S}_2$. However, there are almost no peaks that can be assigned to Na$_2$S (186, 246, 437 cm$^{-1}$). In that case, it is reasoned that Na$_2$S$_2$ is the dominant final discharge product for Na-S batteries.

With the achieved experimental results, Na$_2$S$_2$ other than Na$_2$S has been identified as the final discharge product for RT Na-S battery. An interesting question thus arises: why disulfide cannot be further reduced to form sulfoxide in the Na-based system? To shed light on the final discharge product formation mechanism, we compare the calculated formation energy of discharge products at different discharge stages of Li-S and Na-S batteries respectively. Li$_2$S$_2$ has been rarely observed to exist in Li-S batteries experimentally [56,65–67]. Our calculation shows that Li$_2$S$_2$ is electrochemically more active than Li$_2$S, and that the formation energy of Li$_2$S$_2$ is less negative than that of Li$_2$S plus S$_8$ by calculating the Gibbs free energy of the following reactions:

\[
\begin{align*}
3\text{Li}_2\text{S}_2 &\rightarrow 2\text{Li}_2\text{S} + \text{Li}_2\text{S}_4, \; \Delta G = -0.0069 \text{ eV} \\
\text{Li}_2\text{S}_2 &\rightarrow \text{Li}_2\text{S} + \frac{1}{8} \text{S}_8, \; \Delta G = -0.0862 \text{ eV}
\end{align*}
\]

The corresponding crystal structures and respective space groups for Li$_2$S$_2$, $\alpha$-Li$_2$S$_2$, $\beta$-Li$_2$S$_2$, $\alpha$-Li$_2$S$_4$ and $\beta$-S$_8$ are shown in Fig. S6. Physically, these results suggest that solid Li$_2$S$_2$ is not thermodynamically stable in Li-S batteries. In real battery operation, Li$_2$S$_2$ when emerges as an intermediate can quickly disproportionate into Li$_2$S and long-chain polysulfides. On the contrary, we show that solid Na$_2$S$_2$ is thermodynamically stable in Na-S batteries. The stability of sodium disulfide, Na$_2$S$_2$, a compound whose presence may limit capacity, was assessed. The corresponding crystal structures and respective space groups for Na$_2$S, $\beta$-Na$_2$S$_2$, $\beta$-Na$_2$S$_4$, $\alpha$-Na$_2$S$_4$ and $\beta$-S$_8$ are shown in Fig. 6 and the calculated lattice parameters are shown in Table 1. Either $\alpha$-Na$_2$S$_2$ or $\beta$-Na$_2$S$_2$ is predicted to be stable with respect to a two-phase mixture of Na$_2$S and Na$_2$S$_4$ or Na$_2$S and $\beta$-S$_8$ by calculating the Gibbs free energy of the following reactions:

\[
\begin{align*}
3\text{Na}_2\text{S}_2 &\rightarrow 2\text{Na}_2\text{S} + \text{Na}_2\text{S}_4, \; \Delta G = 0.19 \text{ eV}
\end{align*}
\]

<table>
<thead>
<tr>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>$\alpha$ (%)</th>
<th>$\beta$ (%)</th>
<th>$\gamma$ (%)</th>
</tr>
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<tbody>
<tr>
<td>$\beta$-S$_8$</td>
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<td>10.95</td>
<td>11.13</td>
<td>96.42</td>
<td>90</td>
</tr>
<tr>
<td>Li$_2$S</td>
<td>5.71</td>
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<td>5.71</td>
<td>90</td>
<td>90</td>
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<tr>
<td>$\alpha$-Li$_2$S$_2$</td>
<td>6.83</td>
<td>6.83</td>
<td>5.02</td>
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<tr>
<td>$\beta$-Li$_2$S$_2$</td>
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<td>3.99</td>
<td>9.60</td>
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<td>90</td>
</tr>
<tr>
<td>Li$_2$S$_4$</td>
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<td>9.21</td>
<td>10.82</td>
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<tr>
<td>Na$_2$S</td>
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<td>6.57</td>
<td>6.57</td>
<td>90</td>
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<td>7.68</td>
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<tr>
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<td>4.51</td>
<td>10.29</td>
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<td>90</td>
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<td>11.98</td>
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</table>
we can observe two absorption peaks at around 295 and 366 nm, representing $I_{3}^-$ anion. For the sample with a lower fraction of Na$_{2}$S$_{2}$, the peaks of $I_{3}^-$ anion were replaced by polysulfides including S$_{2}^{2-}$ (325, 420 nm) and S$_{2}^{2-}$ (350, 475 nm), while for the sample with a higher fraction of Na$_{2}$S$_{2}$, the polysulfides peaks were negated without the appearance of $I_{3}^-$ peaks, indicating $I_{3}^-$ anion is sufficiently oxidative to dissolve solid Na$_{2}$S$_{2}$ into long-chain polysulfides [77]. The cyclic voltammetry (CV) investigation was conducted for the Na metal battery with the addition of NaI as the electrolyte additive as shown in Fig. S7. The anodic and cathodic peaks of $I_{3}^- / I_{3}^-$ redox reaction were at 3.01 and 2.77 V respectively, showing excellent reversibility of $I_{3}^- / I_{3}^-$ redox pair. Also, from the charge-discharge test in Fig. S7, at the voltage window that triiodide/iodide redox reaction takes place, the battery can be stably cycled with minor capacity decay. The polyiodide crossover is supposed to be blocked by the PBI membrane as the size of polyiodide anion (0.63 nm) is similar with the size of polysulfide anions [78].

Performance comparison was conducted for the batteries added with 25 μL 0.20 M NaI-P$_{2}$S$_{5}$, NaI and Na$_{2}$S$_{2}$-P$_{2}$S$_{5}$ electrolyte additives respectively as shown in Fig. 8e. For the battery using 0.2 M Na$_{2}$S$_{2}$-P$_{2}$S$_{5}$ additive, Na$_{2}$S$_{2}$ will function as the active material, which also derives an areal capacity of 1.90 mAh cm$^{-2}$. As in Fig. 8e, the highest capacity retention and coulombic efficiency was achieved for the battery with Na-P$_{2}$S$_{5}$ based additive. Corresponding voltage profiles at 0.2C can be found in Fig. 8f, where discharge voltage plateaus representing triiodide reduction (2.75–2.5 V), sulfur dissolution (2.3–1.7 V) and Na$_{2}$S$_{2}$ precipitation (1.7–1.2 V) can be clearly observed. Over charging, $I_{3}^-$ was generated above 3.0 V, where part of the electrochemical oxidation (charge capacity) was offset by the chemical reduction of $I_{3}^-$/I$_{3}^-$. When scanned within the voltage window of 1.2–3.4 V in the CV test in Fig. 8g, separated peaks representing the $I_{3}^-$/I$_{3}^-$ reduction, sulfur dissolution and Na$_{2}$S$_{2}$ precipitation can be clearly observed, in well consistence with the charge/discharge curves. Compared with the batteries without NaI additive, substantial enhancement in terms of the batteries’ cyclability can be observed, testifying our hypothesis that overcharging the battery into the voltage window representing $I_{3}^-$/I$_{3}^-$ redox reaction can effectively decompose the residual Na$_{2}$S$_{2}$ and improve the cyclability.

Moreover, the lower discharge voltage plateau can be found to be elevated for the battery with P$_{2}$S$_{5}$ additive, owing to the improved precipitation kinetics contributed by the complexation effect of P$_{2}$S$_{5}$. As shown in Fig. 8 (h, i), SEM images of the discharged electrodes with Na$_{2}$S$_{2}$-P$_{2}$S$_{5}$ and NaI-P$_{2}$S$_{5}$ show that the sizes of discharge product can be satisfactorily decomposed into solid Na$_{2}$S$_{2}$ and deposited as sulfur. The electrodeposition of Na$_{2}$S$_{2}$ thus accounts for poor cycling stability and reversibility of the cathode.

4. Conclusion

In this paper, we have proposed effective methods to mitigate capacity fading of RT Na-S batteries. Polybenzimidazole (PBI)-based separator was applied, effectively shielding the Na anode surface in the corrosive electrolyte environment containing polysulfides. Combining DFT calculation and characterization techniques, we for the first time reveal that Na$_{2}$S$_{2}$ particles will precipitate on the electrode surface as the final discharge product. Na$_{2}$S$_{2}$ passivation is recognized as the predominant attributes of large polarization and capacity fading. To address the aforementioned issues, we present the use of a bifunctional Na-P$_{2}$S$_{5}$ based electrolyte additive, which (i) partially solubilize Na$_{2}$S$_{2}$ by forming Na$_{2}$S$_{2}$-P$_{2}$S$_{5}$ complex and (ii) promotes the dissolution of Na$_{2}$S$_{2}$ by the chemical mediation of $I_{3}^- / I_{3}^-$, demonstrating that the battery's cyclability can be considerably improved with the cooperative effects of Na$_{2}$S$_{2}$-P$_{2}$S$_{5}$ based electrolyte additive. The efficient strategies to facilitate the reversible formation and decomposition of solid

$$\text{Na}_2\text{S}_{2} \rightarrow \text{Na}_2\text{S} + \frac{1}{8} \text{S}_8, \ \Delta G = 0.25 \text{eV}$$