



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

Y.X. Ren¹, H.R. Jiang¹, T.S. Zhao^{*}, L. Zeng, C. Xiong

HKUST Energy Institute, Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong SAR, China



HIGHLIGHTS

- The PBI membrane is employed to suppress polysulfide 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).

ARTICLE INFO

Keywords:

Na-S battery
Shuttle effect
Discharge product
Separator
Electrolyte additive

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 poly-benzimidazole-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

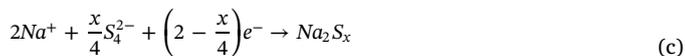
application. Lowering the operating temperature of the Na-S battery has been recognized as a meaningful topic that will affect this technology, developing the room-temperature (RT) Na-S battery into reliable, low-cost, scaled-up energy storage systems thus has attracted ever-increasing research interest [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. tetraglyme) as shown in the formulas below.

^{*} Corresponding author.

E-mail address: metzhao@ust.hk (T.S. Zhao).

¹ These authors contributed equally to this work.



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 NaI-P₂S₅ based electrolyte additive, partially dissolving Na₂S₂ by forming soluble Na₂S₂-P₂S₅ complex and realizing efficient Na₂S₂ decomposition by overcharging the battery into the voltage window representing I⁻/I₃⁻ 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 NaNO₃ was adopted as the electrolyte [31]. Additives including NaI-P₂S₅, Na₂S₈-P₂S₅ and NaI could be further added into the electrolyte, but the overall volume of the electrolyte was limited to 100 μ L. Moreover, owing to the excellent wettability (74 μ L 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 \sim 200 μ m 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 μ m 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 batterie 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 μ m) 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

Download English Version:

<https://daneshyari.com/en/article/7724823>

Download Persian Version:

<https://daneshyari.com/article/7724823>

[Daneshyari.com](https://daneshyari.com)