

Imparting Pulley Effect and Self-healability to Cathode Binder of Li-S Battery for Improvement of the Cycling Stability

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Electronic Supplementary Information

Abstract To construct structurally stable sulfur cathode of Li-S battery with improved cycling performance, poly(acrylic acid) (PAA) crosslinked by cationic hydroxypropyl polyrotaxane (HPRN⁺) via dynamically reversible boronic ester bonds is synthesized and serves as the cathode binder. The smart polymer networks offer multifunction including buffering the volume change of the cathode during charge/discharge through the pulley effect of polyrotaxanes (PR), suppressing the shuttle effect by adsorption of polysulfide using the plentiful carboxyl, hydroxyl and quaternary ammonium cationic groups, and self-healing the micro-damages to ensure stable conduction pathways of the electrode. As a result, the Li-S batteries based on this novel multifunctional binder and simple commercial sulfur/carbon composites cathode exhibit excellent specific capacity and cycling stability. In particular, the specific capacity decay per cycle of the cell is only 0.064% along with high Coulombic efficiency after 550 cycles at 1.0 C, which is superior to most of the reported binders. Even under high sulfur loading, moreover, the cathode can deliver superior areal capacity and cycling stability. This proposed binder provides a new way for the design of high-stability sulfur cathodes.

Keywords Pulley effect; Self-healing; Polyrotaxanes; Polymer binders; Lithium-sulfur battery

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INTRODUCTION

As one of the most promising candidates for the next-generation high-energy rechargeable electrochemical power sources, lithium-sulfur (Li-S) battery faces critical challenges like the large volume change (~80%) during charge/discharge processes due to the density difference between the active materials and discharge products, and the shuttle effect originating from the dissolution and migration of polysulfide intermediates that leads to drastic decay of the specific capacity.^[1–4] To address these issues, a few strategies have been proposed by employing novel carbon host materials,^[5,6] electrolytes^[7,8] and separators.^[9,10]

The polymeric binder is an important component of Li-S cathode, which affixes conductive agents and active materials to the current collector to ensure the good conduction pathways of the electrode.^[11–13] At present, the most widely

used binder in Li-S cells is poly(vinylidene fluoride) (PVDF), but it suffers from weak bonding strength. Besides, PVDF cannot adsorb polysulfide to inhibit the shuttle effect, resulting in severe irreversible loss of sulfur and drastic specific capacity fading. Moreover, toxic and high-boiling point organic solvent, such as *N*-methyl-2-pyrrolidone (NMP), is usually utilized to prepare PVDF based cathode slurry, which is harmful to the environment, and increases the volatilization loss of sulfur during the difficult desiccation.

Accordingly, exploration of novel multifunctional binders among commercial synthetic polymers, natural materials and water-soluble materials with polar groups (like —NH₂, —COOH and —OH^[11,14]) and cationic groups (like quaternary ammonium^[15–17]), which are able to effectively trap the soluble polysulfides and suppress the unwanted shuttle effect, has received various attentions. So far, however, the majority of the state-of-the-art binders in Li-S batteries are based on linear polymers,^[11,18] oligomers^[19–21] or polymers physically crosslinked by non-covalent bonds (including hydrogen bonds^[22,23] and ionic bonds^[24]). Their structural stability is limited, and the repeated expansion and contraction of the active materials in the course of continuous cycles, as well as the complicated deformations experienced during the cathode manufacturing, easily lead to the irreversible slippage

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and fracture of the binder's molecular chains, and hence damages at the interface between the active materials and conductive agents in sulfur cathode.

Recently, self-healable polymeric binders are employed to autonomously repair the above-mentioned ineluctable damages and defects on the sulfur cathodes, and improve the cycling performance of Li-S batteries.^[25–27] Up to now, however, the reported self-healing binders are still made of linear polymers, despite that secondary bonds (*i.e.*, hydrogen bonds) account for the damage rehabilitation. In this context, development of covalent bonds based self-healable and chemically crosslinked polymer binders would be more promising.

Here, we plan to develop a reversibly and chemically cross-linked binder for Li-S cells cathode from poly(acrylic acid) (PAA), which is capable of aim to simultaneously resist the remarkable volumetric expansion and suppress shuttle effect. PAA is commercially available and has stable chemical structure and excellent bonding properties. PAA and its derivatives have already been employed as binders for Li-S batteries,^[28,29] but the poor ductility greatly restricts its application. Keeping this in mind, we firstly crosslink PAA with both cationic hydroxypropyl polyrotaxane (HPRN⁺) through dynamically reversible boronic ester bonds to obtain polyacrylic acid-cationic hydroxypropyl polyrotaxane (PAA-B-HPRN⁺) networks (Scheme 1). Besides the excellent stickiness of PAA and the strengthening effect induced by crosslinking, the stress equalization offered by the pulley effect of PR proves to be able to toughen polymer network and buffer the above-mentioned volume variation of cathode during charging/discharging.^[30–32] Meanwhile, the dynamic reversible boronic ester bonds endow the network with self-healing capability, helping to autonomously repair the inevitably occurred microcracks formed by the volumetric change during repeated cycles.^[25,33] In addition, the quaternary ammonium cations attached to the HPRN⁺ and the polar carboxyl groups of PAA, as well as the hydroxyl groups in the HPRN⁺ would strongly absorb lithium polysulfides,^[15–17,34] inhibiting the unwanted shuttle effect, and conventional toxic and high boiling point organic solvents like NMP can be replaced by water to dissolve the binder *via* hydrolysis of the boronic ester bonds for making the cathode. It suggests that the PAA-B-

HPRN⁺ networks would be qualified for serving as environmentally friendly multifunctional binder for fabricating sulfur cathode of Li-S battery, which is an extra benefit. To the best of our knowledge, there has not yet been report concerning modified-PR based self-healing binders for lithium-sulfur batteries.

In the following, the feasibility of our design is carefully verified.

EXPERIMENTAL

Materials

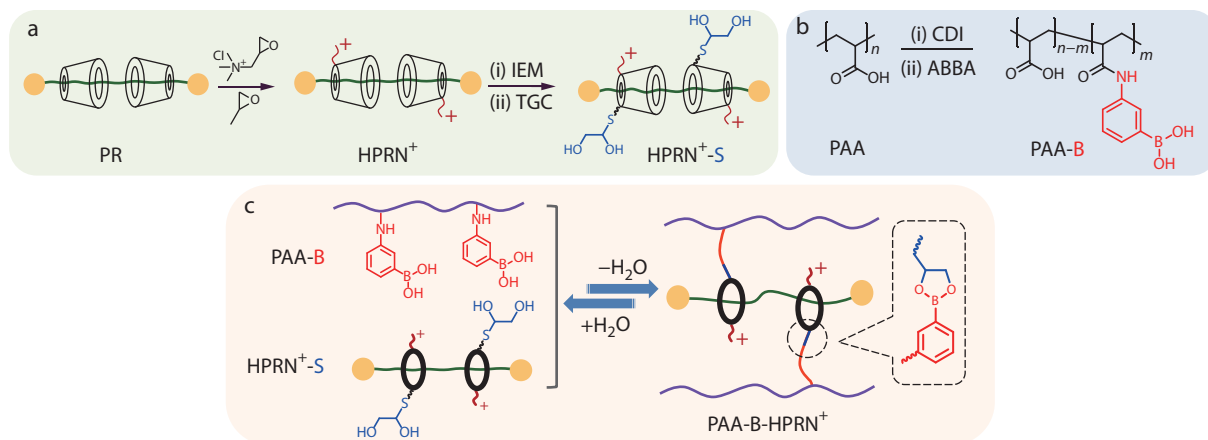
Poly(ethylene glycol) (PEG, $M_w=1\times10^4$ g/mol), α -cyclodextrin (α -CD, AR), 1,1'-carbonyldiimidazole (CDI, AR), 2,4-dinitrofluorobenzene (AR, 99%), propylene oxide, glycidyltrimethylammonium chloride (GTAC, AR), 2-isocyanatoethyl methacrylate (IEM, AR), *N,N*-dimethylformamide (DMF, AR), dimethyl sulfoxide (DMSO, AR), polyacrylic acid (PAA, $M_w=4.5\times10^5$ g/mol), 3-aminobenzeneboronic acid (ABBA, 98%), poly(vinylidene fluoride) (PVDF, $M_w=4\times10^5$ g/mol), *N*-methyl-2-pyrrolidone (NMP, AR) and dibutyltin dilaurate (DBTDL, AR) were purchased from Shanghai Aladdin Industrial Corporation, China. Tetrahydrofuran (THF, AR), ethanol (AR), methanol (AR), sodium hydroxide (NaOH, AR), ethylenediamine (AR, 99%) were purchased from Guangzhou Reagent Chemical Factory, China. Super P, acetylene black, aluminum foil and nickel foam were acquired from Ke Jing Co., Ltd., China. 1-Thioglycerol (TGC, AR, >98.5%), hexylamine (AR, 99%), 1,2-dimethoxyethane (DME, AR), 1,3-dioxolane (DOL, AR) and bis(trifluoromethyl sulfonyl)amine lithium salt (LiTFSI, AR) were collected from Sigma-Aldrich. The Celgard 2500 membrane was obtained from Celgard as the separator.

Characterization

Proton nuclear magnetic resonance (¹H-NMR) spectra were collected by an AVANCE III (400 MHz, Bruker, Germany) with DMSO-*d*₆ as the solvent.

Fourier transform infrared (FTIR) spectra were recorded on a Bruker EQUINOX55 FTIR spectrophotometer with a resolution of 4 cm^{−1} by the KBr sample holder method.

The sulfur content of the Super P@S composite was evaluated by the thermal gravimetric analysis (TGA) from 30 °C to



Scheme 1 Schematic illustrations of synthesis of the substances of interests. (a) Preparation of HPRN⁺-S from PR, (b) synthesis of PAA-B, and (c) crosslinking of PAA-B-HPRN⁺ through the reaction between PAA-B and HPRN⁺-S.

550 °C at a heating rate of 10 °C/min under N₂ atmosphere.

The microstructure and morphology of the cathodes were observed by scanning electron microscopy (SEM), (HITACH S4800).

Lap shear test was conducted at a crosshead speed of 5 mm/min to evaluate the adhesive property of the binders. The solutions of different binders were pasted onto iron plates, and then two plates were bonded by the same binder together within an adhered area of 25 mm × 12.5 mm, and dried at 60 °C for 48 h in vacuum. Three to five specimens were tested per sample, and the results were averaged.

Peeling off tests were conducted on a universal tensile machine (SANS). A 3M tape was attached to the electrodes containing different binders, and then the backside of the electrodes was pasted on a stainless-steel sheet. When the test started, the 3M tape was peeled off to the direction of 180° with a speed of 5 mm/min to measure the curve of force against displacement.

Tensile test was performed by the same machine with dumbbell-shaped specimens (15 mm × 2 mm × 1 mm) according to ISO527-2 at the crosshead speed of 2 mm/min.

Nanoindentation tests were carried out to evaluate the mechanical properties of different electrodes through loading-unloading mode by using Keysight UTM150 nanoindentation system equipped with Berkovich indenter (a three-sided pyramidal tip with a radius of 150 nm, 142.3° total included angles). The elastic modulus, E_r , was estimated from:

$$\frac{1}{E_r} = \frac{(1 - \nu^2)}{E} + \frac{(1 - \nu'^2)}{E'} \quad (1)$$

where E and ν are the Young's modulus and Poisson's ratio of the specimen, and E' and ν' are the corresponding parameters of the indenter, respectively.

Ultraviolet-visible (UV-Vis) spectra were measured by a Perkin Elmer Lambda 750 UV-Vis spectrophotometer.

The galvanostatic charge/discharge curves, cycling stability and C-rate performance of the Li-S cells were investigated via cycling the cells with a cut-off voltage of 1.6–2.8 V at room temperature by a battery analyzer (Land-CT2001A, Wuhan, China). Electrochemical impedance spectroscopy (EIS) was used to measure the impedance spectra of the Li-S cells with an electrochemical workstation (CHI 760E, Shanghai, China) over the frequency range of 0.01–1 MHz. Cyclic voltammetry (CV) tests were carried out on an electrochemical workstation (CHI 760E) between 1.6 and 2.8 V with a scanning rate of 0.1 mV/s.

Preparation of PR

PR was synthesized according to literature.^[30] First, the PEG that has been end capped by amino groups, PEG-(NH₂)₂, was prepared. Dried PEG (10.0 g, 1.0 mmol) and CDI (0.39 g, 2.4 mmol) were dissolved in 250 mL of THF and stirred for 18 h at 50 °C in N₂. Afterwards, ethylenediamine (1.2 mL, 18.0 mmol) was added and stirred for additional 2 h. The reaction mixture was poured into 600 mL of ethanol and placed in a 5 °C freezer for 2 h. Next, the white precipitate was collected by filtration, and the product PEG-(NH₂)₂ was dried under vacuum at 60 °C for 2 days.

Then, 1.0 g of PEG-(NH₂)₂ was dissolved in 30 mL of deionized H₂O and stirred at 80 °C for 30 min. When 4.0 g of α -CD was slowly added to the system and the homogeneous solution was placed in a 5 °C freezer, white paste appeared. Even-

tually, the poly(pseudo)rotaxane (PPR) was obtained by drying in a lyophilizer. Later on, 2.5 mL of 2,4-dinitrofluorobenzene in 10 mL of DMF was well mixed with the dried PPR. After 12 h, excessive DMSO was added to get homogeneous PR solution, and PR was precipitated from 1500 mL of 0.1% NaCl solution. Finally, the yellow product (PR, 1.25 g) was collected by centrifugation, sequentially washed by DMF, methanol and deionized water, and dried by a lyophilizer.

Preparation of Thioglycerol Grafted HPRN⁺ (HPRN⁺-S, Scheme 1a)

HPRN⁺ was prepared by modifying PR with propylene epoxide and GTAC according to the reference.^[35] Typically, 1.0 g of PR was dissolved in 100 mL of aqueous NaOH (1.0 mol/L) at 0 °C, and then 2.0 g of propylene oxide and 2.0 g of GTAC in 5 mL of water were slowly added within 1 h. The mixture was heated to 25 °C and stirred for additional 24 h. Moderately diluted HCl was added to neutralize the residual NaOH, and the HPRN⁺ was purified by dialysis against deionized H₂O. The yellow product (HPRN⁺, 0.75 g) was obtained after lyophilization.

After that, 1.0 g of HPRN⁺ was dissolved in 20 mL of DMSO, and then 0.5 g of IEM and one drop of DBTDL in 5 mL of DMSO were slowly added in N₂ at 40 °C and kept stirring for 48 h. Afterwards, 0.5 g of TGC and one drop of hexylamine in 5 mL of DMSO were incorporated to react for 48 h.^[36] Then, the mixture was poured into 300 mL of acetone, and the yellow precipitate HPRN⁺-S (0.72 g) was collected by suction filtration, dialyzed by DMSO, and then drying.

Preparation of Aminobenzeneboronic Acid Grafted PAA (PAA-B, Scheme 1b)

PAA (1.0 g) was dissolved in 20 mL of DMSO at 50 °C for 2 h, and then 0.02 g of CDI in 2 mL of DMSO was added and mixed under stirring for 12 h in N₂ atmosphere. After that, the PAA mixture was cooled down to room temperature and mixed with 0.017 g of ABBA in 2 mL of DMSO. Having been stirred for 30 min at room temperature, the reaction mixture was further stirred at 50 °C for additional 48 h. The resultant PAA-B was precipitated from excessive THF and filtered, and then lyophilized to yield a polymer film.

Preparation of PAA-B-HPRN⁺ Binder (Scheme 1c)

PAA-B (1.0 g) was dissolved in 10 mL of DMF, and then 0.1 g of HPRN⁺-S in 5 mL of DMF was added. The solution soon became a gel, which gradually dissolved into clear solution after adding a drop of water. Lastly, yellow polymer films were obtained after drying.

For comparison, PAA crosslinked with only HPRN⁺ (PAA-HPRN⁺) was prepared. Typically, 1.0 g of PAA was dissolved in 20 mL of DMSO at 50 °C for 2 h, and then 0.02 g of CDI in 2 mL of DMSO was added and mixed under stirring for 12 h in N₂ atmosphere. Afterwards, 0.1 g of HPRN⁺ was added and the system was stirred at 50 °C for additional 48 h. The resultant PAA-HPRN⁺ was precipitated from excessive THF and filtered, and then dried to yield a yellowish polymer.

Preparation of Sulfur Cathodes and Li-S Cell Assemblies

The preparation of the Super P@S composite followed the reference.^[37] Na₂S₂O₃·5H₂O (2.90 g) was dissolved in 20 mL of water, and then 0.15 g of Super P was added. Next, 15 mL of HCl (4.20 mol/L) was added into the mixture and stirred for 24 h. The

solution was filtered, washed and dried at 60 °C for 24 h to obtain the Super P@S composites. The content of sulfur in the composite is about 65.2% by TGA shown in Fig. S1 (in the electronic supplementary information, ESI).

The cathode was made by mixing the slurry of Super P@S composite, acetylene black and PAA-B-HPRN⁺ binder (mass ratio=8/1/1). All the raw materials were suspensions in water. Then, the slurry was casted onto the surface of the aluminum foil current collector and dried under vacuum at 60 °C for 24 h. The cathode wafer with a diameter 12 mm was cut by a slicer and transferred to an argon-filled glove box. The contrastive electrodes containing PVDF, PAA and PAA-HPRN⁺ binders were also prepared by using NMP (for PVDF) or water (for PAA and PAA-HPRN⁺) as solvent. The areal sulfur loading of most electrodes is about 0.8 mg/cm².

CR 2032 coin-type cells were assembled in an argon-filled glove box (<0.1 ppm of oxygen and water) by using the Celgard 2500 (Ø18 mm) as the separator and commercial Li anode (Ø15.8 mm). The electrolyte composed of 1.0 mol/L LiTFSI in mixed solvents of DOL/DME (1/1, V/V) with 1.0 wt% LiNO₃. The electrolyte/sulfur ratio was kept constant at 30 µL/mg. For the high sulfur loading cathodes, the electrolyte/sulfur ratio was 20 µL/mg.^[21,38]

RESULTS AND DISCUSSION

Preparation of the Modified PAA Based Binders

As described in the Experimental section, the PR is prepared using α -CD and PEG through supramolecular self-assembly and molecular ends blocking method.^[39] Then, the resultant PR reacts with propylene oxide and GTAC to produce the HPRN⁺ (refer to Scheme 1a). The introduction of quaternary ammonium cations into PR not only improves solubility of the latter, but also facilitates the subsequent usage of quaternary ammonium cations for electrostatic adsorption of polysulfides and hence effectively suppress the shuttle effect.^[15–17,34] Furthermore, because the reactivity of the secondary hydroxyl groups at 2,3-position of α -CD is rather low due to the large steric hindrance, 2-isocyanatoethyl methacrylate (IEM) is allowed to react with HPRN⁺ converting part of —OH groups into methacrylic ones. The follow-up click reaction between the methacrylic and sulfydryl groups gives birth to thioglycerol grafted cationic polyrotaxane (HPRN⁺-S), which possesses 1,2-dihydroxyl groups with higher reactivity.

From the ¹H-NMR spectra (Fig. 1a), it is seen that the HPRN⁺ exhibits new peaks at chemical shifts of 1.03 and 3.15 ppm as compared to that of PR, which corresponds to the methyl protons in hydroxypropyl groups^[40] and the proton signal of methyl groups in the quaternary ammonium cation,^[15] respectively. In the case of HPRN⁺-S, the proton signal of —NH— in the carbamate group obtained by the reaction of —NCO with —OH is perceived at the chemical shift of 4.04 ppm. Besides, partial —OH signal and the proton signal of —CH₂— in thioglycerol appear at the chemical shifts of 2.65 and 1.15 ppm, respectively. No signal peak of the double bond in IEM is found near the chemical shift of 6.0 ppm, indicating a complete reaction between methacrylic and sulfydryl.^[31] Moreover, it is noted that the FTIR spectrum of HPRN⁺-S (Fig. S2 in ESI) exhibits a new C=O vibration band at 1720 cm^{−1}, and the N—H deformation vibration and the C—N

stretching vibration are observed at 1546 and 1036 cm^{−1}, respectively. After modification, in fact, HPRN⁺ and HPRN⁺-S are soluble in DMF and water, and their solubility is significantly improved in comparison to that of PR. It is thus known that the HPRN⁺-S has been successfully synthesized.

When PAA is modified by grafting ABBA to obtain PAA-B (Scheme 1b), new proton signals appear at 7.75 and 7.06 ppm of the ¹H-NMR spectrum of PAA-B (Fig. S3 in ESI), corresponding to the —OH in the phenylboronic acid groups and the

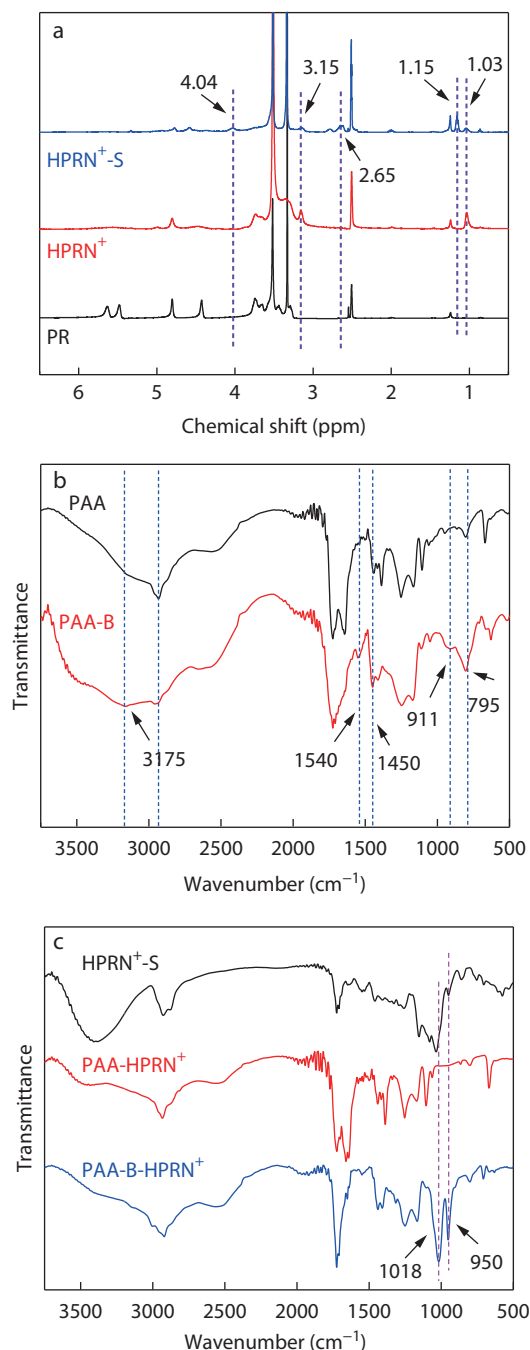


Fig. 1 (a) ¹H-NMR spectra of PR, HPRN⁺ and HPRN⁺-S; (b) FTIR spectra of PAA and PAA-B; (c) FTIR spectra of HPRN⁺-S, PAA-HPRN⁺ and PAA-B-HPRN⁺.

protons of the benzene rings, respectively.^[41] On the FTIR spectrum of PAA-B (Fig. 1b), the absorption at 3175 cm⁻¹ is assigned to the stretching vibration of the C—H bonds of benzene rings, while the C=C skeleton vibrations of the benzene rings at 1540 and 1450 cm⁻¹, and the C—H out-of-plane bending vibrations of the benzene rings at 911 and 795 cm⁻¹ are observed. Clearly, the results of ¹H-NMR and FTIR confirm the successful preparation of PAA-B.

With respect to the FTIR spectrum of the PAA-B-HPRN⁺ (Fig. 1c), new bands appear at 950 and 1018 cm⁻¹ in comparison with the spectra of HPRN⁺-S and PAA-HPRN⁺, which are attributed to the vibrations of B—O bonds and boronic ester rings,^[42] respectively. It implies that the boronic ester bonds have crosslinked PAA as expected. Consequently, the cross-linked PAA-B-HPRN⁺ has acquired higher thermal stability. The temperature at 5% weight loss is about 145 °C (Fig. S4 in ESI), which is suitable for application in Li-S battery.

Characterization of the Modified PAA Based Binders

In this work, three types of PAA-HPRN⁺ and four types of PAA-B-HPRN⁺ networks with different crosslinking densities were prepared by regulating the contents of CDI bridging agent and HPRN⁺ (Table 1 and Scheme S1 in ESI). To verify the reversibility of boronic ester bonds in the networks, 0.2 g of the obtained binder is added to 8 mL of DMF and heated at 50 °C for 5 h. Fig. S5 (in ESI) exhibits that PAA-HPRN⁺-1 produces a clear and transparent solution, indicating its good dispersion and solubility in DMF. However, with increasing the crosslinking density, a large portion of PAA-HPRN⁺-2 become insoluble, and PAA-HPRN⁺-3 only swells but not dissolves. In contrast, all PAA-B-HPRN⁺ samples crosslinked by boronic ester bonds undergo dissolution under the same conditions, which are attributed to rearrangement of the networks through the dynamically reversible exchange reaction of the boronic ester bonds.^[42,43]

In case sulfur cathode is prepared, the binder needs to be dissolved or dispersed in solvent and then mixed with the active materials and conductive additives to form homogeneous slurry. However, most chemically crosslinked polymers are hard to dissolve, which is a fatal problem for their application as binders of batteries. Some researchers tried to use the *in situ* crosslinking method to prepare the sulfur cathodes.^[44–46] The crosslinking of polymer monomers or oligomers had to be triggered at elevated temperatures, so that the electrode preparation becomes rather complex, and the volatile loss of sulfur-active substances would also take place.

Moreover, interfacial stress may be generated between the crosslinked polymers and the cathode materials as well as the current collector because of the uneven crosslink structures. Therefore, the development of structurally stable, soluble and mechanically excellent crosslinked polymer binders of batteries has been a great challenge. In this context, the use of dynamically reversible boronic ester-bonded crosslinked polymer (*i.e.*, PAA-B-HPRN⁺) is able to take advantages of both thermosetting and linear polymers.^[47] Meantime, the PAA-B-HPRN⁺ based binder can be dissolved in water through the hydrolysis of the boronic ester bonds (Fig. S6 in ESI). After removing water, the polymers can be cross-linked again along with the reformation of the boronic ester bonds. This habit is important for the application of PAA-B-HPRN⁺ as binder in Li-S cells.

On the other hand, since PAA-HPRN⁺-2 and PAA-HPRN⁺-3 have poor solubility in water, only PAA-HPRN⁺-1 is used as the reference of PAA-B-HPRN⁺ in the subsequent experiments and simply re-denoted as PAA-HPRN⁺.

Fig. 2(a) illustrates the typical tensile stress-strain curves of PAA-HPRN⁺ and PAA-B-HPRN⁺ networks. The strength of PAA-B-HPRN⁺-1 is 1.26 MPa, comparable to that of PAA-HPRN⁺-1 (1.47 MPa). Besides, the strength of PAA-B-HPRN⁺ increases with a rise in the crosslink density and the elongation at break decreases, which follows the general law of polymeric materials. Considering the fact that the elongation at break of PAA-B-HPRN⁺-4 (~270%) is much lower than the values of other three binders (425%–502%), it is not involved in the following electrodes manufacturing.

Fig. 2(b) depicts the bonding performance of the polymeric binders. The lap shear strengths of all the modified PAA binders are obviously higher than that of PVDF (0.16 MPa, Fig. S7 in ESI) and comparable to that of PAA (0.99 MPa, Fig. S7 in ESI). Besides, the strength of PAA-B-HPRN⁺ increases with a rise in the crosslink density and the elongation at break decreases, which follows the general law of polymeric materials. Considering the fact that the elongation at break of PAA-B-HPRN⁺-4 (~270%) is much lower than the values of other three binders (425%–502%), it is not involved in the following electrodes manufacturing. Fig. 2(b) depicts the bonding performance of the polymeric binders. The lap shear strengths of all the modified PAA binders are obviously higher than that of PVDF (0.16 MPa, Fig. S7 in ESI) and comparable to that of PAA (0.99 MPa, Fig. S7 in ESI).

To investigate the self-healing properties of PAA-B-HPRN⁺,

Table 1 Formulations of PAA-HPRN⁺ and PAA-B-HPRN⁺ binders. *

No.	Sample code	PAA		CDI	HPRN ⁺	Solubility in water
		m_{PAA} (g)		m_{CDI} (g)	m_{HPRN^+} (g)	
1	PAA-HPRN ⁺ -1	1.0		0.02	0.10	√
2	PAA-HPRN ⁺ -2	1.0		0.06	0.15	×
3	PAA-HPRN ⁺ -3	1.0		0.15	0.15	×
		PAA-B			HPRN ⁺ -S	
		m_{PAA} (g)	m_{CDI} (g)	m_{ABBA} (g)	$m_{\text{HPRN}^+-\text{S}}$ (g)	
4	PAA-B-HPRN ⁺ -1	1.0	0.02	0.017	0.10	√
5	PAA-B-HPRN ⁺ -2	1.0	0.06	0.051	0.15	√
6	PAA-B-HPRN ⁺ -3	1.0	0.15	0.13	0.15	√
7	PAA-B-HPRN ⁺ -4	1.0	0.25	0.22	0.15	√

* The symbol “m” in the table stands for the feeding amount of reagent.

a scratch is made on the surface of PAA-B-HPRN⁺-3 with a fresh blade. When the specimens are healed under different circumstances, visual inspection is conducted to examine the effect (Figs. 3a–3f). It is evident that the treatment at 60 °C for 6 h has completely recovered the damage (Figs. 3a and 3d),

indicating the boronic ester bonds have functioned. When the healing temperature decreases to 40 °C but one drop of DME/DOL is added on the scratched surface, crack healing also occurs (Figs. 3b and 3e). It means that PAA-B-HPRN⁺-3 can be self-healed with the aid of electrolyte solvent at lower

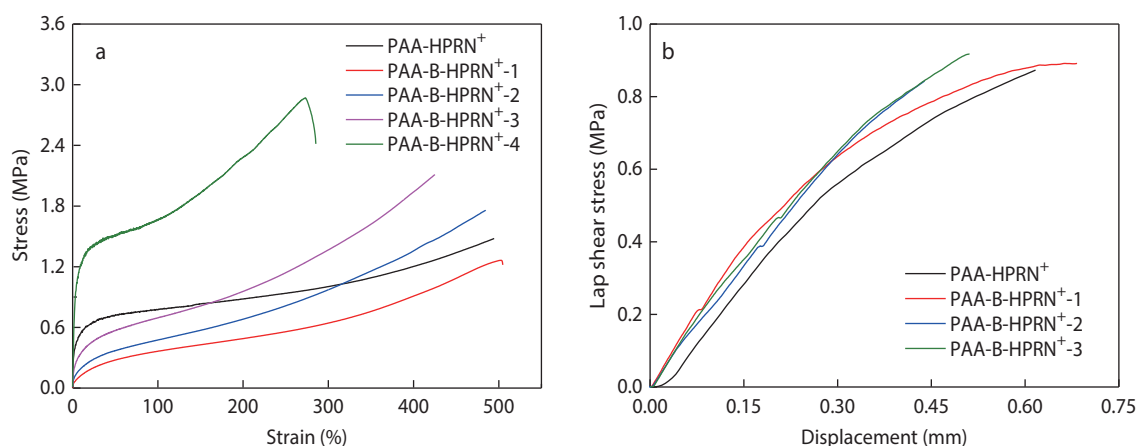


Fig. 2 (a) Typical stress-strain curves and (b) the lap shear strength of PAA-HPRN⁺ and PAA-B-HPRN⁺.

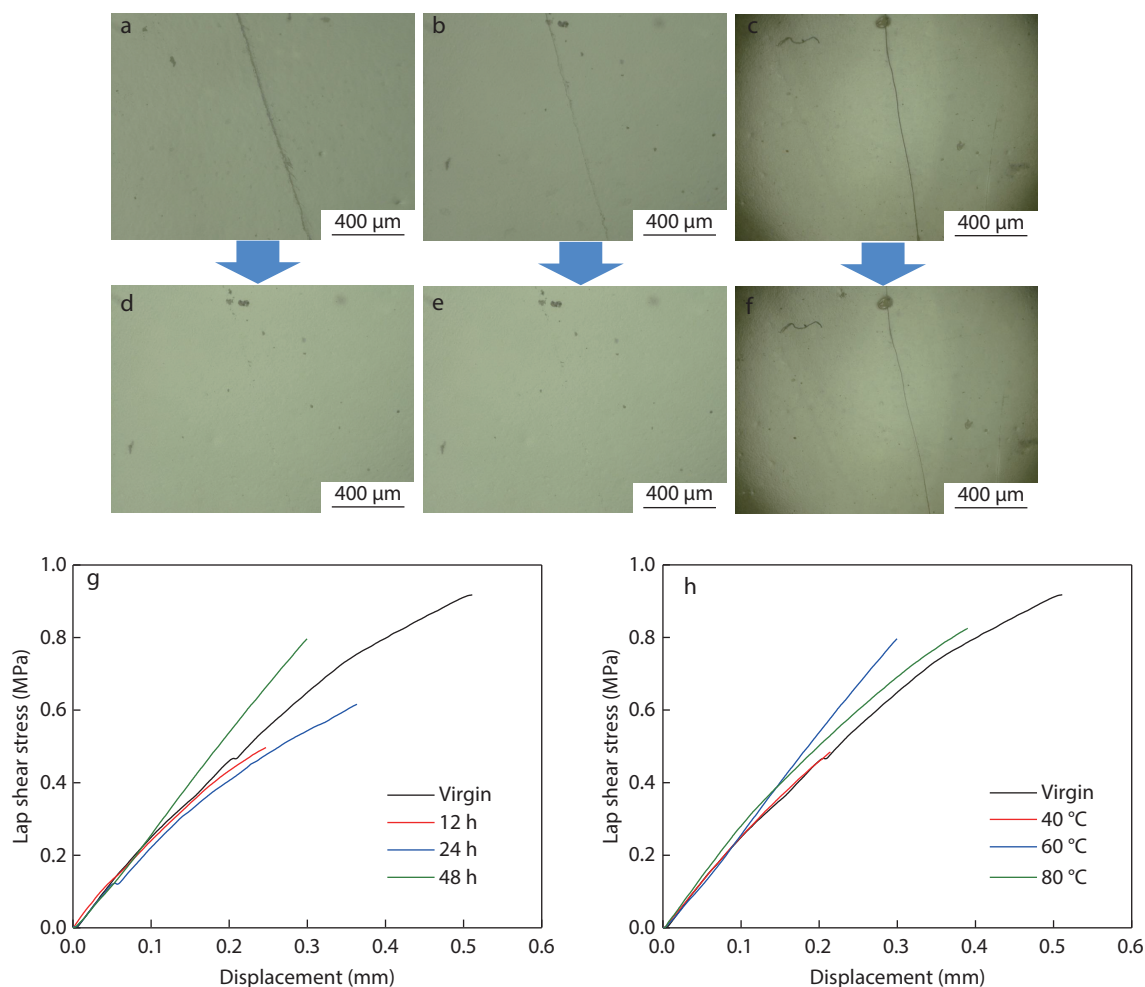


Fig. 3 Optical images of self-healing behaviors of (a, b, d, e) PAA-B-HPRN⁺-3 and (c, f) PAA-HPRN⁺. (a, b, c) Scratched and (d) healed at 60 °C for 6 h, (e) Healed at 40 °C for 6 h in the presence of DME/DOL. (f) Healed at 60 °C for 6 h in the absence of DME/DOL. Lap shear tests of PAA-B-HPRN⁺-3 showing the effects of (g) healing time and (h) healing temperature. Note: (g) Healing temperature = 60 °C, (h) healing time = 24 h.

temperatures. As for PAA-HPRN⁺ (Figs. 3c and 3f), PAA and PVDF (Fig. S8 in ESI), which do not contain any reversible bonds, however, the scratches on their surfaces still exist even after the treatment with DME/DOL at 60 °C for 6 h, because of lacking of self-healability.

The self-healing property of PAA-B-HPRN⁺-3 is further quantified by lap shear tests as follows. After separating the iron sheets bonded by PAA-B-HPRN⁺-3, an appropriate amount of DME/DOL (V/V=1/1) solution is dropped on the surface of the ruptured binder, and then the two iron sheets are jointed again and left in an oven for a period of time under the pressure of 0.15 MPa (Fig. S9 in ESI). The repaired specimen is tested to failure, and the healing efficiency is evaluated *via* the ratio of the lap shear strengths before and after healing (Figs. 3g and 3h). It is seen from Fig. 3(g) that the self-healing efficiency of the material gradually increases with the extension of healing time. Moreover, higher healing temperature benefits the restoration of adhesion (Fig. 3h). Comparatively, the self-healing ability of the controls (PVDF, PAA and PAA-HPRN⁺) is negligible (Fig. S10 in ESI).

Characterization of the Sulfur Cathodes Containing the Modified PAA Based Binders

For purposes of fabricating the sulfur cathode of Li-S battery, Super P@S, acetylene black and PAA-B-HPRN⁺-3 are mixed at a mass ratio of 8:1:1, and a homogeneously-dispersed slurry is obtained by adding appropriate amount of water. Then, the slurry is spread to the carbonized aluminum foil and dried to obtain the electrodes. The surface of the PAA-B-HPRN⁺-3@S electrode is rather flat with no obvious cracks (Fig. S11 in ESI). In the meantime, the EDS mapping tests show the uniform distribution of C, O, S and B elements (Fig. S11b in ESI), implying that the binder is evenly dispersed in the electrode. Hence, the dynamic reversible crosslinkages and the pulley effect of PR may be able to synchronously work.

The mechanical performance of different electrodes are assessed by nanoindentation test. The force curves (Fig. 4a and Fig. S12 in ESI) show that the indentation depths at the peak load of the PVDF@S and PAA@S electrodes are significantly higher than those of the cathodes made from the modified PAA binders as a result of PR pulley effect of the latter. Besides, the indentation depth of PAA-HPRN⁺@S electrode is also higher than that of PAA-B-HPRN⁺-1@S electrode. Overall, the indentation depth exhibits decline trend with increasing crosslinking density of PAA-B-HPRN⁺, which can be confirmed from Fig. 4(b) that the electrode based on PAA-B-HPRN⁺-3 provides the highest elastic modulus (258.9±25.7 MPa).

The 180° peeling tests of different electrodes (Fig. 4c and Fig. S12c in ESI) indicate that the averaged values of load/width of PVDF@S and PAA@S electrodes are about 0.51 and 1.57 N/cm, respectively, while that of the electrode containing PAA-HPRN⁺ is 2.05 N/cm, which is similar to the value of the electrode with PAA-B-HPRN⁺-1 (2.03 N/cm). As the crosslinking density increases, the peeling forces of the PAA-B-HPRN⁺-2@S and PAA-B-HPRN⁺-3@S cathodes increase to 2.10 and 2.22 N/cm, respectively.

In summary, the tests of mechanical properties show that the PAA-B-HPRN⁺ binders have acquired superior toughness and adhesion performance as expected.

Performance of Li-S Batteries with Sulfur Cathodes Containing the Modified PAA Based Binders

The electrochemical stability of PAA-B-HPRN⁺-3 in the analog electrode is evaluated by cyclic voltammetry (CV) measurement by using stainless steel sheets as the counter electrode. The absence of oxidation and reduction signals on the CV curves during multiple cyclic scans (Fig. S13 in ESI) demonstrates that

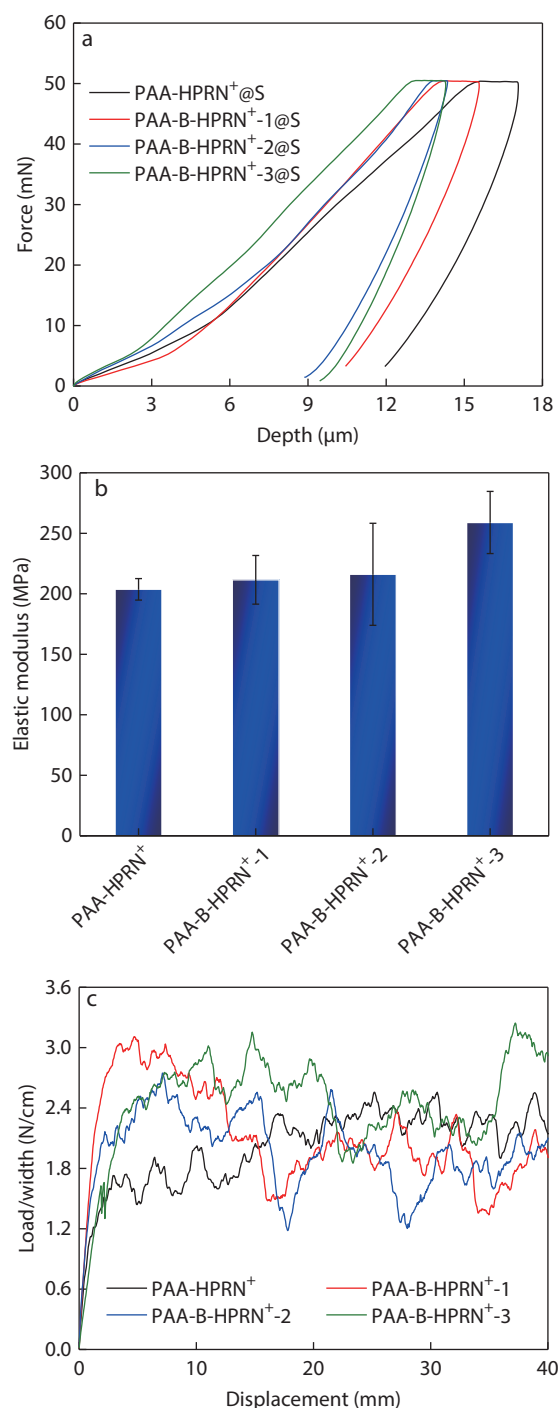


Fig. 4 (a) Typical loading-unloading curves and (b) elastic moduli of different electrodes containing different binders measured by nanoindentation; (c) Peeling force-displacement curves of different electrodes containing different binders.

PAA-B-HPRN⁺-3 is inactive within the voltage of 1.6–2.8 V so that it can act as a cathode binder for Li-S batteries. Accordingly, the sulfur cathode prepared by PAA-B-HPRN⁺-3 binder are assembled into CR 2032-coin cells, and the results of CV are shown in Fig. S14 (in ESI). It is found that two distinctive reduction peaks appear at 2.02 V and 2.33 V on the cathode scan curve, corresponding to the two stages in the course of discharging: (i) transformation of sulfur S₈ to high-order lithium polysulfide compound Li₂S_n (4 ≤ n ≤ 8), and (ii) the further reduction of the intermediate polysulfides component to low-order Li₂S_n (n < 4) and Li₂S. Meanwhile, on the succeeding anodic scan, a broad oxidation peak appears at 2.40 V, corresponding to the overall reverse reaction. Owing to the inevitable shuttle effect of polysulfides, the 1st CV curve shows higher current value in the region of 2.40 V than those measured during the 2nd–4th cycles, while the CV curves of the subsequent cycles present well-overlapped anodic/cathodic peaks to the second cycle, which reveals the excellent electrochemical stability of the electrode based on the PAA-B-HPRN⁺ binder.

To highlight the effectiveness of toughening and self-healing effects of PAA-B-HPRN⁺ in improving electrochemical performance of the sulfur electrodes, Li-S batteries with different binders are assembled and evaluated. First, the galvanostatic cycling measurements at 0.5 C are conducted after an activation process at 0.1 C for one cycle. Fig. 5(a) shows that the initial discharge specific capacities of PVDF@S, PAA@S and PAA-HPRN⁺@S cathodes are 535.8, 752.0, and 812.2 mAh/g, respectively. Because of the limited ductility to buffer the volume change and poor ability to capture the dissolved polysulfides, the PVDF@S cathode presents rather low discharge capacity. Along with the incorporation of HPRN⁺, however, the PAA-HPRN⁺ binder is provided with enhanced toughness and adsorption ability of polysulfides in comparison to PAA (Fig. S15 in ESI),^[34] so that the electrochemical performance of the relevant Li-S batteries is significantly improved. Interestingly, the initial discharge specific capacities of the batteries containing PAA-B-HPRN⁺-1@S, PAA-B-HPRN⁺-2@S and PAA-B-HPRN⁺-3@S cathodes can be further raised (*i.e.*, 836.3, 862.6 and 868.0 mAh/g, respectively). The dynamical reversible boronic ester bonds in the networks must account for the extra boost.

After 350 cycles, the discharge specific capacities of PVDF@S, PAA@S and PAA-HPRN⁺@S cathodes turn to be 194.3, 262.0 and 304.5 mAh/g, corresponding to the capacity retentions of 36.3%, 34.8% and 37.5%, respectively. Nevertheless, the electrodes based on PAA-B-HPRN⁺ binders exhibit significantly higher specific capacities even after 500 cycles, which are 356.4, 381.1 and 424.1 mAh/g in sequence, and the capacity retentions are 42.6%, 45.2% and 48.9%, respectively (Fig. 5a). The average Coulombic efficiencies (≥98.5%) and the charge/discharge profiles in different cycles of PAA-B-HPRN⁺-3@S electrode are presented in Fig. S16 (in ESI). The superior electrochemical performance of PAA-B-HPRN⁺-3@S cathode can be attributed to its good mechanical properties, stable conductive pathways and effective suppression of shuttle effect (Fig. S15 in ESI). The charge and discharge curves of the PAA-B-HPRN⁺-3@S electrode under different cycles show that the Li-S battery displays a typical "dual-platform" shape (Fig. S16b in ESI), as the sulfur in the cathode can undergo favor-

able oxidation-reduction reactions in 500 cycles.

Furthermore, the cycling capacities of the cathodes at various rates are investigated from 0.2 C to 3.0 C (Fig. 5b). The PAA-B-HPRN⁺-3@S electrode exhibits rather high discharge capacities. When the current density is switched back to 2.0 C and 1.0 C, the specific capacity increases to 583.5 and 611.1 mAh/g, respectively, implying the excellent rate reversibility and good structural stability after high current cycling. The corresponding charge-discharge profiles of PAA-B-HPRN⁺-3@S cathode (Fig. S17 in ESI) are also represented by the typical two-plateau discharge curves at various C-rates owing to the stable charge-discharge behavior.

To further understand the long-term cycling stability of PAA-B-HPRN⁺-3@S cathode, its prolonged charge-discharge performance is compared with PAA-HPRN⁺@S at 1.0 C (Fig. 5c). The initial discharge specific capacity of the former is 662.5 mAh/g after the first 2 cycles activation at 0.1 C and then slightly increases reaching the maximum of 746.3 mAh/g, which are higher than the corresponding values of PAA-HPRN⁺@S (*i.e.*, 619.6 and 658.1 mAh/g). The increase of capacity during the initial cycles may be ascribed to the activation and the improved utilization efficiency of sulfur.^[14,18,52] Subsequently, PAA-B-HPRN⁺-3@S cathode displays distinctly higher specific capacity and Coulombic efficiency. After 550 cycles, the PAA-B-HPRN⁺-3@S cathode still exhibits a high capacity of 429.3 mAh/g, and the specific capacity retention is 64.8%, corresponding to a capacity decay of 0.064% per cycle, which is superior to most reported binders of Li-S cells (Fig. 5d and Table S1 in ESI). In addition, the Coulombic efficiency of PAA-B-HPRN⁺-3@S cathode after 550 cycles is 98.5%, while that of the control cell is about 97.6%. Overall, the average Coulombic efficiency of PAA-B-HPRN⁺-3@S electrode during the long-term cycling is above ~99%, significantly higher than the reference. For the prolonged cycles (>550), the difference between electrochemical properties of aforesaid two samples remained almost unchanged because the sulfur electrodes have formed stable solid electrolyte interphases. Therefore, cycle tests after 550 cycles have not been shown. It is worth noting that the excellent cycling performance is based on the simple and commercial Super P host materials rather than the nanotubes and nanoporous materials with exquisitely designed structures and morphologies. The results confirm the efficient suppression of polysulfide shuttle effect^[64] and the excellent cycling stability of the electrode.

Figs. 5(e) and 5(f) show the EIS and the equivalent circuits of different cells before and after repeated cycles. The fitting results of the Nyquist plots are listed in Table S2 (in ESI). The Nyquist plots of the fresh batteries consist of a depressed semicircle in the high frequency region and an oblique line in the medium frequency region, which represent the charge transfer resistance, R_2 , and the Warburg impedance controlled by Li⁺ diffusion, W_1 , respectively. Before cycling, the electrodes based on PAA-B-HPRN⁺ binders exhibit lower interfacial resistances than PAA-HPRN⁺@S electrode (Table S2 in ESI). Specifically, the R_2 of PAA-B-HPRN⁺-3@S cathode is about 30.0 Ω, while that of PAA-HPRN⁺@S is 56.6 Ω. The lower impedance should be attributed to the dynamical reversible boronic ester bonds, which can recover damages as well as defects on the electrode surface during the preparation of the electrode and the usage of the battery, and therefore facilit-

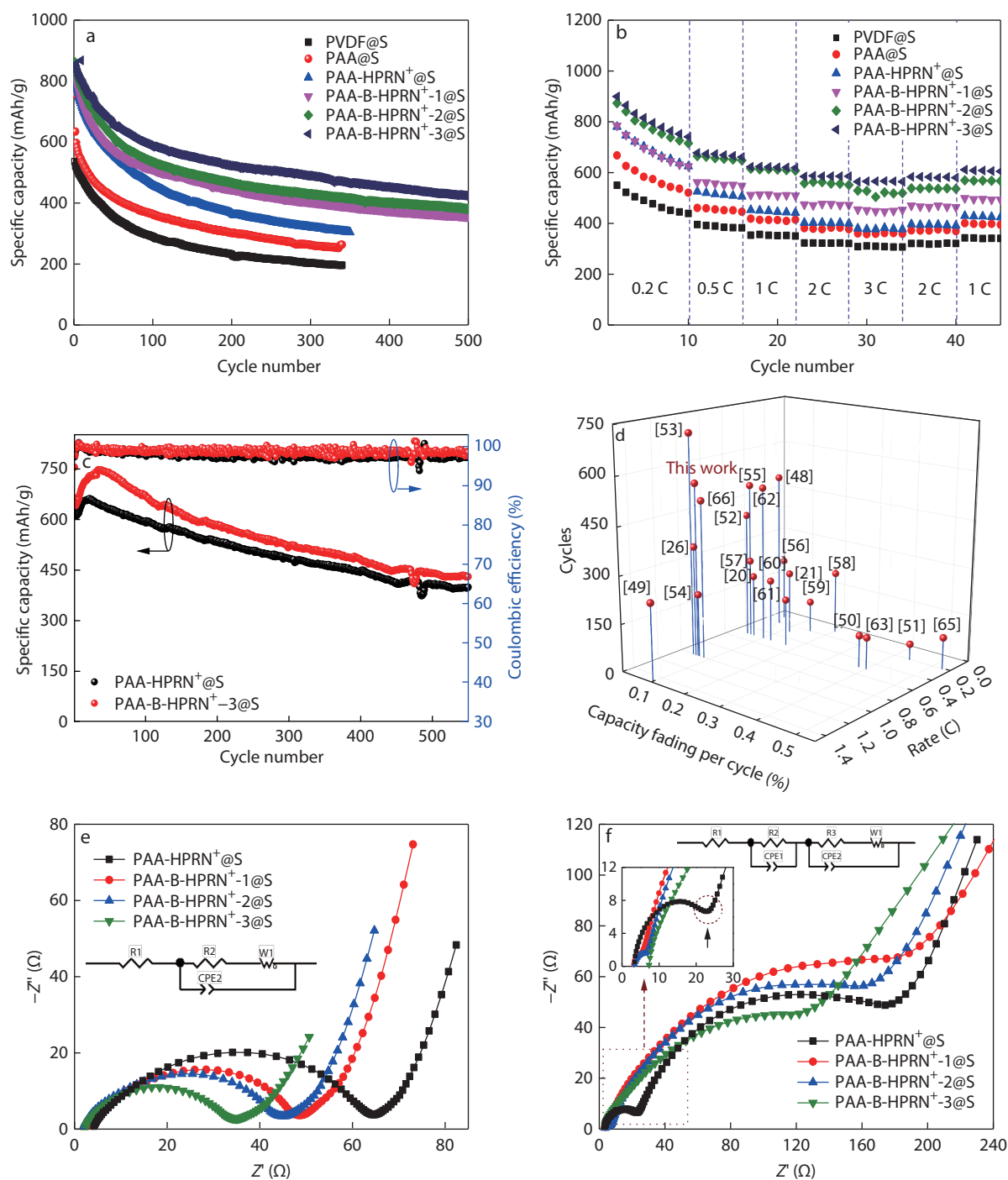


Fig. 5 (a) Cycling performance of different electrodes at 0.5 C; (b) Discharge specific capacities of different cathodes at various C-rates. (c) Prolonged cycling performance of the sulfur cathodes measured at 1.0 C. (Note: partial data of PAA-HPRN⁺@S are cited from Ref. [34]). (d) Performance comparison of the Li-S cells with different binders.^[20,21,48–66] Nyquist plots and equivalent circuits of different cells (e) before and (f) after 200 cycles at 0.5 C.

ate the interfacial contact of electrolyte. After 200 cycles at 0.5 C (Fig. 5f), the PAA-B-HPRN⁺-3@S cathode still has the lowest charge-transfer resistance of 177 Ω , comparing to that of PAA-HPRN⁺@S of 227 Ω (Table S2 in ESI). With increasing concentration of the dynamic reversible boronic ester bonds^[67] in the binder, the corresponding sulfur cathodes exhibit lower interfacial resistance before and after cycling, indicating the

improved conductivity and superior charge transfer ability with the help of the self-healing binder. In contrast, the PAA-HPRN⁺@S displays a distinct large semicircle in the high frequency region as marked by the arrow, ascribing to the increased interfacial resistance.

SEM images of the sulfur cathodes before and after 200 cycles at 0.5 C are given in Fig. 6 and Fig. S18 (in ESI). Some

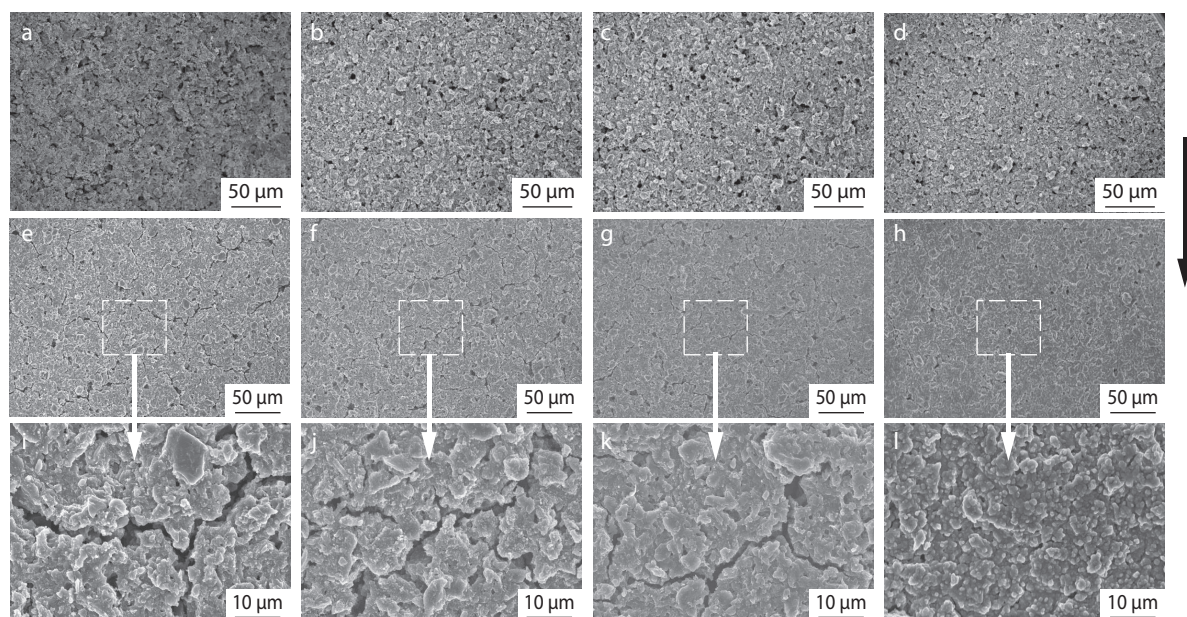


Fig. 6 SEM images of (a, e, i) PAA-HPRN⁺@S, (b, f, j) PAA-B-HPRN⁺-1@S, (c, g, k) PAA-B-HPRN⁺-2@S and (d, h, l) PAA-B-HPRN⁺-3@S electrodes (a–d) before and (e–l) after 200 cycles of charge/discharge.

distinct cracks and holes can be observed on the surfaces of fresh PVDF@S and PAA@S, and much wider and more cracks appear after cycling (Figs. S18a–S18d). These structural damages result from the insufficient mechanical and binding properties of PVDF and PAA binders to effectively maintain the electrical pathway of cathodes, and the finite suppression of shuttle effect to protect structural stability of sulfur cathodes during cycling. For the fresh electrodes derived from PAA-HPRN⁺ and PAA-B-HPRN⁺ binders, the sulfur and conductive agent are homogeneously distributed, and the electrodes exhibit smooth surface without obvious flaws (Figs. 6a–6d). Therefore, it can be concluded that the HPRN⁺ component possessing pulley effect in the crosslinked networks is conducive to the preparation of intact sulfur cathode. After cycling, although the sample surfaces look rather smooth (Figs. 6e–6h) under the same magnification as Fig. S18 (in ESI), a few small cracks are detected on the amplified images (Figs. 6i–6k). Compared to the case of PAA-HPRN⁺@S (Fig. 6i), the amount and width of the cracks on the PAA-B-HPRN⁺-1@S and PAA-B-HPRN⁺-2@S cathodes are reduced with increasing the content of boronic ester bonds (Figs. 6j–6k). In particular, the PAA-B-HPRN⁺-3@S electrode excellent structural stability and promote the electrochemical performance.

In accordance to the increasing requirements for high-energy density rechargeable batteries, high sulfur loading electrodes with PAA-B-HPRN⁺-3 binder are prepared *via* a blade coating method on a Ni foam current collector. Fig. 7(a) shows that the initial discharge areal capacities of the cathodes with 4.92 and 5.20 mg/cm² sulfur loadings are 5.52 mAh/cm² at 0.25 C and 5.74 mAh/cm² at 0.2 C, respectively, and the corresponding discharge areal capacities after 60 cycles become 4.50 and 4.78 mAh/cm². Besides, the average Coulombic efficiencies of the two cathodes exceed 95%, indicating the effective suppression of shuttle effect. In addition, the high sulfur loading cathodes are cycled at higher current density, 0.5 C, for example. As displayed in Fig. 7(b),

the initial discharge areal capacities of the electrodes with 4.47 and 5.20 mg/cm² sulfur loadings are 3.78 and 4.48 mAh/cm², respectively. After 105 cycles, the areal capacities are 3.08 and 3.42 mAh/cm², respectively, corresponding to the capacity retentions of 81.5% and 76.3%, and the average Coulombic efficiencies are still higher than 98%.

When the sulfur loading approaches to 11.5 mg/cm² and the assembled cell is cycled at 0.1 C, the cathode exhibits an initial discharge specific areal capacity of 13.02 mAh/cm² (Fig. 7c), indicating a high sulfur utilization efficiency. After 20 cycles, the specific areal capacity becomes 12.03 mAh/cm², and the average Coulombic efficiency is higher than 96%. Further, the cathode with the sulfur loading at 17.40 mg/cm² delivers an ultrahigh initial areal discharge capacity of 21.27 mAh/cm² at 0.8 mA/cm² and the typical two-plateau discharge curves (Fig. 7d). The superior electrochemical performance benefited from the high-loading sulfur cathode indicates the practical application potential of this tough and self-healable PAA-B-HPRN⁺ binder in high energy density Li-S batteries.^[68]

CONCLUSIONS

The PAA crosslinked by HPRN⁺ *via* dynamically reversible boronic ester bonds (PAA-B-HPRN⁺) demonstrates to be a potential binder of the sulfur cathode in Li-S battery. The toughened and self-healable polymer networks can effectively preserve the structural integrity and stability of sulfur cathode, suppress the polysulfides shuttle effect, and hence improve the cycling performance of the sulfur cathode. As a result, the Li-S batteries containing the PAA-B-HPRN⁺ binder possess superior electrochemical performance (including discharge capacity, cycling stability and C-rate capacity). Especially, the PAA-B-HPRN⁺-3@S cathode exhibits capacity retention of 64.8% after 550 cycles at 1.0 C with 0.064% capacity fading per cycle and ~99% average Coulombic efficiency. Furthermore, the high

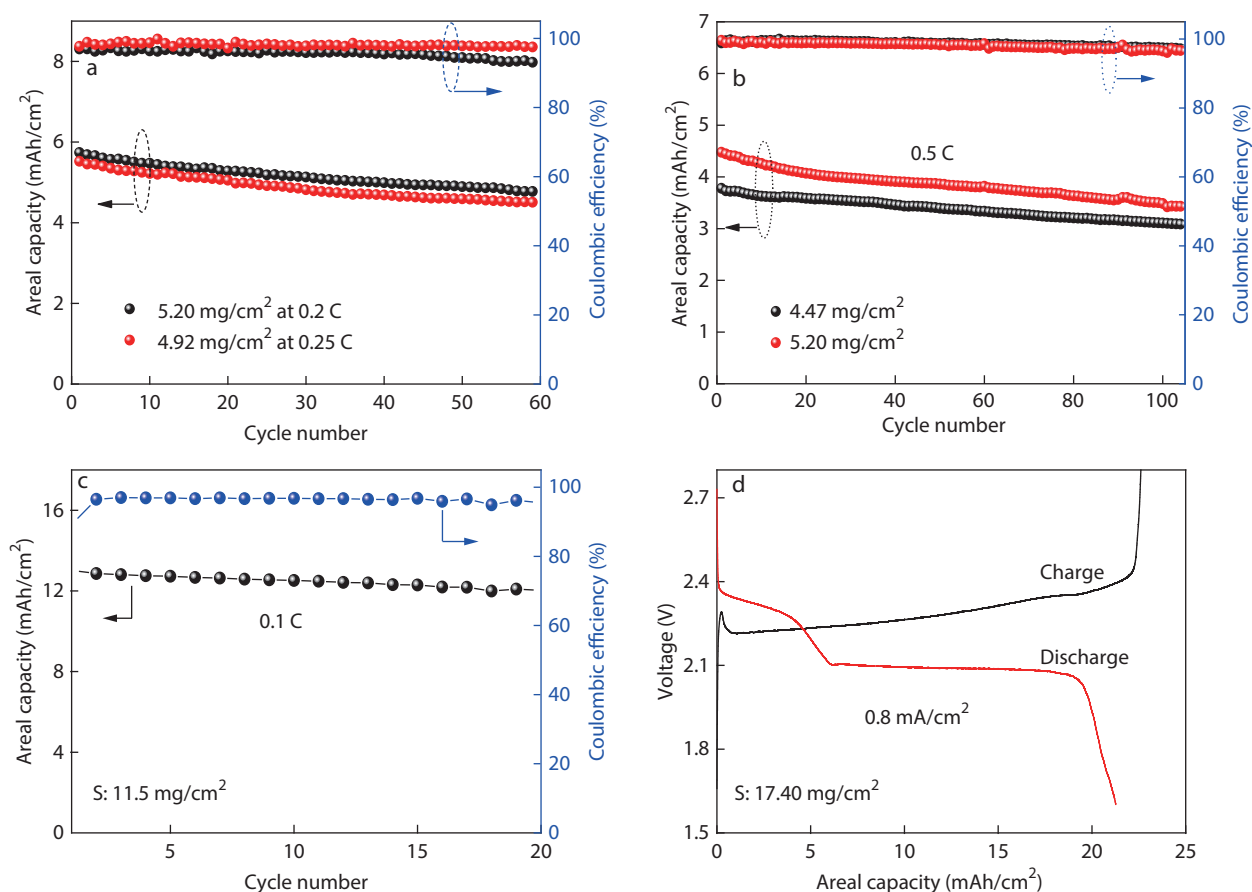


Fig. 7 Cycle performance of the PAA-B-HPRN⁺-3@S electrodes with high S loadings under different current densities: (a) 4.92 mg/cm² under 0.25 C and 5.20 mg/cm² under 0.2 C, (b) 4.47 and 5.20 mg/cm² under 0.5 C, (c) 11.5 mg/cm² under 0.1 C and (d) 17.40 mg/cm² under 0.8 mA/cm².

sulfur loading cathodes (4.47–5.20 mg/cm²) stably work at 0.2–0.5 C with high Coulombic efficiencies, and the cathodes containing ultrahigh sulfur loading (≥ 11.5 mg/cm²) also show high areal capacity. After repeated cycles, the PAA-B-HPRN⁺-3@S electrode has the lowest interfacial impedance, remains compact and high stable surface. This novel multifunctional binder embedding superior toughness, effective suppressing of shuttle effect and self-healing capabilities provides a promising application for stable and high energy density Li-S batteries.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2820-3>.

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