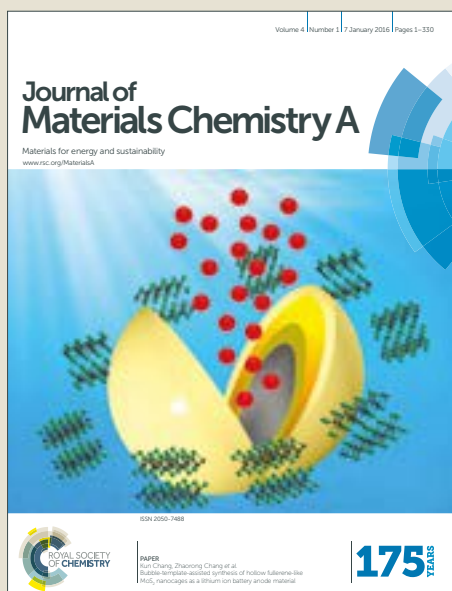


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A novel epoxy resin-based cathode binder for low cost, long cycling life, and high-energy lithium-sulfur battery

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An epoxy resin PEI-ER formed by *in-situ* cross-linking between an epoxide compound (ER) and polyethylenimine (PEI) is developed as a new cathode binder for lithium-sulfur (Li-S) batteries. Li-S batteries using this new binder showed high initial specific capacity along with remarkable cycling stability. A composite interlayer of PEI-ER and carbon black is also developed to further enhance the cycling stability. Li-S battery using a combination of the new binder and interlayer achieved a high initial specific capacity of 1174 mAh g⁻¹ and excellent capacity retention of 80% after 1000 cycles at a cycling rate of 0.5 C with 70 wt.% sulfur content in the cathode and areal sulfur loading of 1.9 mg cm⁻², which is among the best cycling stability reported for Li-S batteries up to date. A Li-S battery with a high areal sulfur loading of 5.4 mg cm⁻² demonstrated an initial capacity of 780 mAh g⁻¹, which corresponds to a high areal capacity of 4.2 mAh cm⁻², and excellent capacity retention of 72% after 500 cycles.

Introduction

With high theoretical specific energy of ~2600 Wh kg⁻¹ and abundant sulfur sources in nature, lithium-sulfur (Li-S) batteries have been considered to be one of the most promising high energy density and low-cost rechargeable battery technologies for electric vehicles (EVs), hybrid electric vehicles (HEVs) and portable devices.^{1–4} Despite decades of research and development, the performance of Li-S batteries still leaves much to be desired, particularly in terms of energy density (or specific capacity of the sulfur cathode) and cycling stability. The issues mainly originate from (i) the extremely low electrical conductivity of sulfur (5 × 10⁻³⁰ S cm⁻¹) that results in an ineffective use of sulfur, (ii) the large volume change (up to 76%) between elemental sulfur in the charged state and lithium sulfides in the discharged state during battery cycling, which causes a severe damage to the cathode structure, and (iii) migration of the soluble intermediate polysulfides (Li₂S_x, where x = 3 – 8) towards the Li anode during discharging and their shuttling back to the cathode during charging, which

reduce the sulfur utilization.^{5–11} To improve the specific capacity of the sulfur cathode, the use of a highly conductive material to blend with sulfur and a reduction of sulfur particle size into the nanometer regime, which can assist charge transport between sulfur and the electrode, have proven to be effective.¹² In comparison to the specific capacity, it appears to be more challenging to improve the cycling stability of the cathode material. Among many approaches to encapsulating sulfur, incorporation of host nanostructured materials such as porous carbon, carbon nanotubes, and graphene^{13–16} has been proven the best approach so far.¹⁷ These efforts have significantly improved the Li-S battery cycling time from tens of cycles in 2009¹³ to up to hundreds of cycles nowadays.¹⁷ To prevent the dissolution and diffusion of polysulfides, additives that can strongly interact or form chemical bonding with polysulfides such as metal oxide¹⁸ and N (nitrogen)-doped carbon materials^{19–21} were found to be effective.

Nonetheless, the majority of the approaches adopted so far have been focused on the improvement of either the specific capacity or cycling life of the Li-S batteries separately.¹⁷ Li-S batteries with both high capacity and long cycling life are rarely reported. Furthermore, many reported high performance Li-batteries used very expensive additives and elaborate processes to make the sulfur cathode, which will be barriers to commercialization.

In order to meet the high energy density requirement, a minimum sulfur content of 70 wt.% in the cathode is needed.²² The sulfur cathode in a typical Li-S battery is comprised of 70 wt.% sulfur, 20 wt.% conductive component, and 10 wt.% polymer binder. The polymer binder holds sulfur and the conductive component (e.g. carbon black) together and maintains strong adhesion of the active materials to the

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current collector. Polyvinylidene fluoride (PVDF) is the most widely used binder for Li-S batteries. However, at such a low loading amount (~10 wt.%), the polymer network formed by the entanglement of PVDF polymer chains through interchain van der Waals forces is expected to be weak and fails to maintain the structural integrity of the cathode material after repeated charge/discharge cycling. Some previous studies show that the cycling stability and capacity of Li-S batteries could be notably improved by using some alternative binders to PVDF.^{23–31} In this study, we developed a novel polymer binder based on a cross-linked epoxy resin, which can be readily prepared *in-situ* to form a robust network structure *via* strong covalent bonds to confine sulfur and the conductive component in the cathode. Very high specific capacity and excellent cycling stability have been achieved by using a cathode binder for Li-S batteries.

Results and discussion

Epoxy resins have been widely used for many years in paints, coatings, adhesives, engineering plastics, etc. for a large variety of industrial and consumer applications because of their superb mechanical property, ease of processing, and low cost. In this study, an oligomeric bisphenol A diglycidyl ether (ER), and a polyamine hardener, a highly branched polyethylenimine (PEI), are chosen. The step-growth polymerization of ER and PEI to form the cross-linked network (PEI-ER) (Figure 1a), which involves the reactions of epoxide (or glycidyl) groups of ER with the primary (–NH₂) and secondary (–NH–) amine groups of PEI and the hydroxyl (–OH) groups of the intermediate products formed through ring-opening of the epoxide groups. The choice of this epoxy resin composition as a binder is based on several considerations. First, these two compounds are commercially readily available and inexpensive. Second, previous computational simulation studies have shown that nitrogen and oxygen atoms have strong binding energies to lithium polysulfides by forming coordination bond between nitrogen or oxygen and lithium atoms.³² The NH₂, –NH–, and –OH groups may also form hydrogen bond with lithium polysulfides.^{33,34} Third, the highly branched structure of PEI would form a highly cross-linked 3-D network structure for a stronger confinement of sulfur and the conductive component and to buffer the volume change between the elemental sulfur and sulfides during the discharge/charge process.

To verify the sulfide binding effects of nitrogen and oxygen atoms in PEI and ER, the adsorption binding energies (E_d) of the PEI-ER binder to lithium sulfides (Li₂S_x) with up to 8 sulfur atoms (x = 1–4, 6, and 8) were calculated by using the density functional theory (DFT). Representative polymer segments of PEI, ER, or the reference PVDF (Figure 1b and Figure S1–5) are used for the calculations, where two neighboring N atoms, O atoms, or F atoms are assumed to interact with one Li ion of a Li₂S_x. The results clearly revealed that the E_d 's with Li₂S_x are in the order of PEI > ER > PVDF for all the sulfide species calculated (Figure 1b). Especially, the E_d 's of PEI and ER towards longer sulfides (x > 2) are significantly greater than

the corresponding E_d 's of PVDF. It is interesting to note that when Li₂S₃ or Li₂S₄ was set to interact with one secondary N atom and one tertiary N atom in PEI-2, another neighboring secondary N atom was also found to bind with the same Li ion,

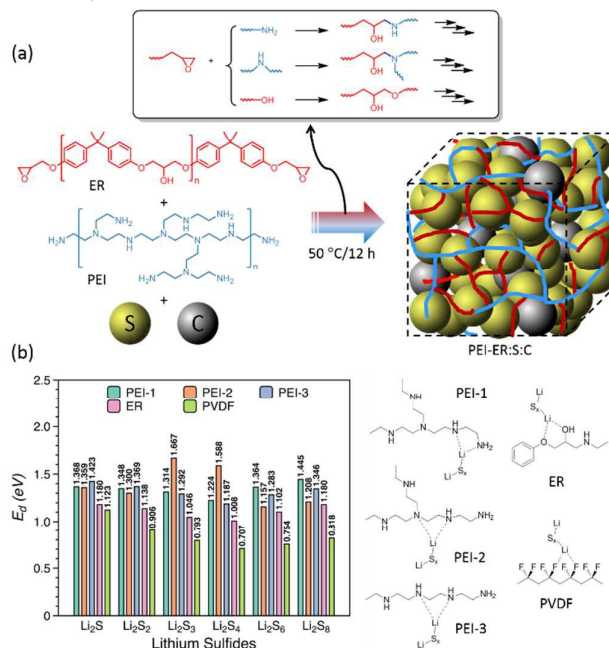


Figure 1. (a) *In-situ* step-growth polymerization of polyethylenimine (PEI) and epoxy resin (ER) in the presence of sulfur (S) and conductive carbon black (C) to form a PEI-ER:S:C cathode composite material, where S and C particles are tightly held by the highly cross-linked 3-D PEI-ER network. (b) The adsorption binding energies (E_d 's) of the representative nitrogen atoms in PEI, oxygen atoms in ER, and fluorine atoms in PVDF with some lithium sulfides. Note that the abnormally high E_d obtained between PEI-2 and Li₂S₃ or Li₂S₄ is due to the additional interaction of a third neighboring nitrogen atom (see Figure S2).

forming a tri-dent complex (Figure S2). Therefore, the E_d 's for PEI-2 with Li₂S₃ and Li₂S₄ are abnormally high.

To optimize the cross-linking conditions for the preparation of cathode material, the reaction between PEI and ER was first carried out without sulfur and conductive carbon. Specifically, PEI and ER at different weight ratios (from 2:1 to 1:5) were dissolved in NMP at a concentration of 20 wt.%. It was found that the PEI:ER binder solutions can be stored for 48 h at room temperature without obvious change in viscosity (Figure S6), which indicates that these solutions are reasonably stable under ambient conditions. The PEI:ER solutions were blade coated on Al foil substrates and the resulting films were dried briefly in air and then cured in a vacuum oven at 50 °C for 12 h, which are the common conditions for making sulfur cathodes. It was found that when the PEI:ER ratios are in the range between 1:1 and 1:4, the cross-linked films showed unnoticeable deformation after soaking in the electrolyte solution for 7 days (Figure S7), indicating the excellent stability of these films in the electrolyte solution. Next, the PEI-ER resin with a PEI:ER weight ratio of 1:1, 1:2, 1:3, or 1:4 was incorporated as a binder in the cathode material slurry by grinding a mixture of PEI, ER, sublimed sulfur (SS), and a conductive carbon Super P (SP) in NMP to determine the best PEI:ER ratio for optimal battery performance. Commercially

available carbon paper (CP) (Toray TGP-H-090), which has a porous 3D structure composed of inter-connected micrometer-sized conductive carbon fibers and sheets (Figure S8a), was used as the current collector in this work to avoid cracking of the thick cathode coating with areal sulfur loadings $\geq 2 \text{ mg cm}^{-2}$.^{35–37} The SS:SP:PEI-ER weight ratios were kept at 70:20:10. The slurries were blade coated on conductive carbon paper (CP) substrates, which were used as the cathode current

collectors, and dried and cured in a vacuum oven at 50 °C for 12 h before being assembled into CR2025 coin cells with a configuration that has been mostly adopted for the Li-S battery testing (Figure 2a). It was found that the cathode with a binder PEI-ER_{1:2}, which has a PEI:ER weight ratio of 1:2, exhibited the optimal overall performance with the highest capacity and the best cycling stability (Figure S9). Therefore, a PEI:ER ratio of 1:2 was used for further studies.

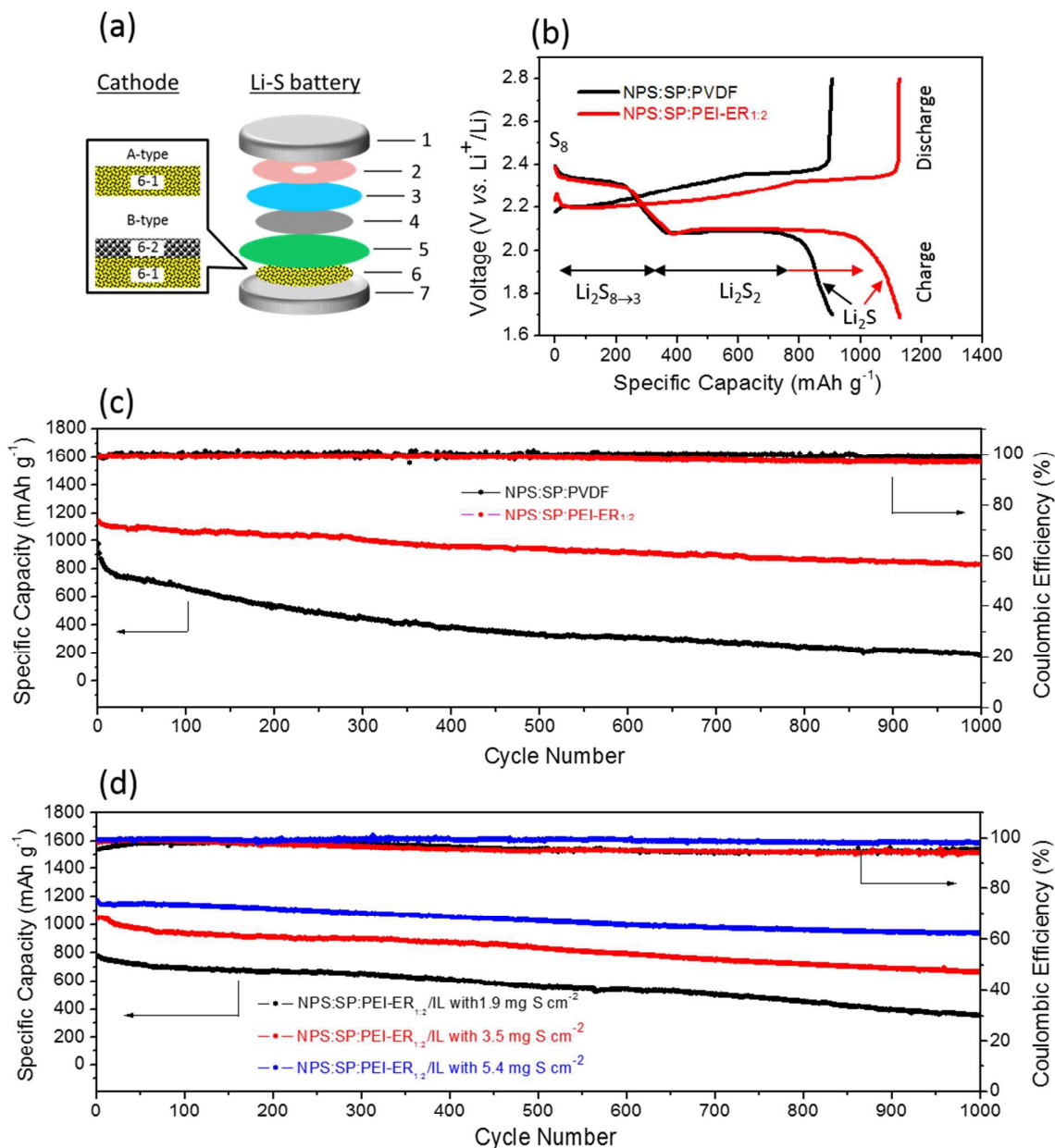


Figure 2. (a). The configuration of the CR2025 coin button Li-S battery used in this study: (1) anode cover; (2) shrapnel; (3) spacer; (4) Li anode; (5) separator; (6) cathode; (7) cathode cover. Two types of cathode structures were used: Type A is made of a composite layer (6-1), which is comprised of sulphur (sublimed sulphur (SS) or sulphur nanoparticles (NPS)) (70%), conductive carbon black Super P (SP) (20%), and the PEI-EP or PVDF binder (10%), coated on a carbon paper (CP) current collector; Type B is made of a composite layer (6-1) as above and an additional interlayer (IL) (6-2), which is comprised of the conductive component SP (67%) and the PEI-EP binder (33%). (b). Discharge-charge profiles of NPS:SP:PVDF and NPS:SP:PEI-ER_{1:2} cathodes (Type A in (a)) of Li-S batteries at 0.5 C. (c). Cycling performance of NPS:SP:PVDF and NPS:SP:PEI-ER_{1:2} cathodes (Type A in (a)) of Li-S batteries at 0.5 C. (d). Cycling performance of NPS:SP:PEI-ER_{1:2}/IL cathodes (Type B in (a)) with various S loading in Li-S batteries at 0.5 C.

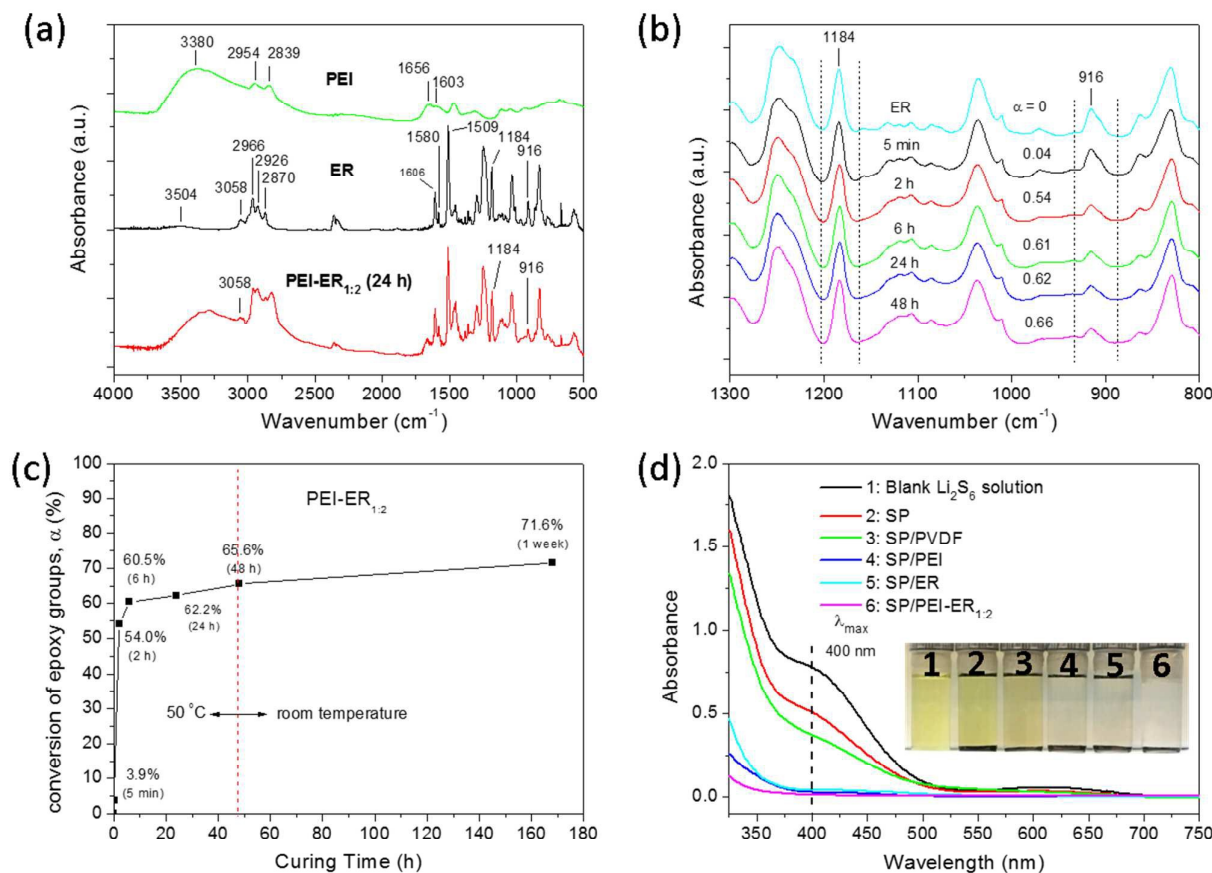


Figure 3. (a) FT-IR spectra of PEI, ER, and PEI-ER_{1:2} (cured for 24 h at 50 °C under vacuum). (b) FT-IR spectra and the conversion of epoxide groups (α) of pure ER and PEI-ER_{1:2} cured at 50 °C under vacuum for different times. (c) The conversion of epoxide groups (α) of the PEI-ER_{1:2} resin cured at 50 °C for up to 48 hours and kept at room temperature for up to one week. (d) UV-vis absorption spectra of the blank Li₂S₆ solution (0.5 mM) and Li₂S₆ solutions with addition of different absorbents for 24 h at room temperature.

To gain insight into the reaction between PEI and ER, Fourier-transform infrared spectroscopy (FTIR) was used to characterize the PEI-ER_{1:2} film at different curing times. Specifically, PEI and ER with a weight ratio of 1:2 were dissolved in chloroform, coated onto a sodium chloride disc to form a thin film and dried with a nitrogen gas flow. The sample was heated at 50 °C in a vacuum oven prior to the FTIR measurement. As a comparison, the FTIR spectra of pure PEI and ER were also collected. As shown in Figure 3a, PEI showed the N–H stretching of –NH₂ and –NH– groups at 3380 cm⁻¹, –CH₂ symmetric and asymmetric stretching at 2954 cm⁻¹ and 2839 cm⁻¹, and N–H bending of –NH₂ and –NH– groups at 1647 cm⁻¹ and 1571 cm⁻¹. ER showed characteristic O–H stretching at 3504 cm⁻¹, –CH₂– stretching of epoxide at 3058 cm⁻¹, C–H stretching of –CH₂–, –CH₃, aromatic and aliphatic C–H at 2966 cm⁻¹, 2926 cm⁻¹ and 2870 cm⁻¹, aromatic –C=C–H stretching at 1606, 1580 and 1509 cm⁻¹, C–O stretching of aromatic ring at 1184 cm⁻¹, and C–O stretching of epoxide at 916 cm⁻¹. As the reaction proceeds, the sample cured for 24 h showed a notable decrease in the intensity of the peak at 916 cm⁻¹ representing the C–O stretching of epoxide (Figure 3a

and 3b). The conversion of epoxide groups (α) was calculated using Equation (1):^{41,42}

$$\alpha = 1 - \frac{A_{916,t}}{A_{1184,t}} \frac{A_{916,0}}{A_{1184,0}} \quad (1)$$

where $A_{916,0}$ and $A_{916,t}$ represent the peak areas at 916 cm⁻¹ at reaction time zero and t , respectively, and $A_{1184,0}$ and $A_{1184,t}$ represent the peak areas at 1184 cm⁻¹ (the C–O stretching of aromatic ring of ER as an internal reference) at reaction time zero and t , respectively.

As shown in Figure 3b, the reaction between PEI and ER was quite fast at first with the conversion of epoxide reaching 54% in 2 h, then slowed down likely due to the increased viscosity of the reaction mixture as well as the formation of a cross-linked structure that prevented the movement of the molecules. After curing for 48 h at 50 °C, the conversion of epoxide groups only slightly increased to 66%. Even after the sample was kept under ambient condition for one week, there

were still 28% of unreacted epoxide groups left ($\alpha = 0.72$) in the sample (Figure 3c).

To evaluate the lithium polysulfide adsorption ability, the PEI-ER_{1:2} binder was soaked in a lithium polysulfide solution and measured by UV-vis spectroscopy. Li₂S₆ was synthesized as an example of lithium polysulfides by reaction between elemental sulfur and Li₂S at a molar ratio of 5:1 in a mixed solvent of 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME) (v/v, 1/1).^{30,43} The SP/PEI-ER_{1:2} composite with a carbon/polymer weight ratio of 2:1 was added to the Li₂S₆ solution and kept for 24 h before the clear supernatant was taken out for UV-vis absorption measurement. SP, SP/PVDF composite, SP/PEI composite and SP/ER composite were also tested in a similar manner as comparisons. As shown in Figure 3d, the blank Li₂S₆ solution showed a yellowish color with a shoulder at ~400 nm in the UV-vis spectrum, which agrees well with literature.^{30,43,44} For the sample mixed with SP, a lighter color and a decrease in the intensity of the shoulder at 400 nm were observed suggesting that SP has some adsorption ability toward Li₂S₆. The sample mixed with SP/PVDF showed a further slight drop in the absorption intensity. In contrast, the samples mixed with SP/PEI, SP/ER and SP/PEI-ER_{1:2} all became colorless and their peak intensities at 400 nm were close to zero indicating that PEI, ER and PEI-ER_{1:2} have much stronger adsorption abilities towards Li₂S₆ than PVDF. The results are in excellent agreement with our theoretical calculations that PEI and ER have much higher binder energies towards lithium polysulfides than PVDF.

Due to the large volume change of sulfur cathode in Li-S batteries during cycling, the ability of a polymer binder to cushion the mechanical stress inside the battery is important. Next, we evaluated the mechanical properties of our newly developed PEI-ER binders. Cross-linked PEI-ER films were prepared by reaction of pure PEI with ER at different PEI/ER weight ratios from 1:1 to 1:4 and subjected to universal tensile test. As shown in Figure S12, the tensile strength of the PEI-ER_{1:1} film was only 1.5 MPa, much lower than those of other PEI-ER films, which can be attributed to the low cross-linking density of the PEI-ER_{1:1} film. As the PEI/ER weight ratio increased to 1:2, the tensile strength of the resultant film increased from 22.3 MPa. Further increasing the PEI/ER ratio to 1:3 and 1:4 led to a further increase of the tensile strength to 27.5 and 29.6 MPa, respectively, as a result of increasing cross-linking density. The elongations-at-break of PEI-ER films cross-linked at different PEI/ER weight ratios were similar (10.3–13.8%). The tensile strengths and elongations-at-break of the PEI-ER binders with PEI/ER weight ratios of 1:2 to 1:4 are similar to other polymer binders used for Li-S batteries, e.g. carboxymethyl cellulose (CMC) (25.5 MPa and 10.0%)⁴⁵ and gelatin (13.5 MPa and 26.5%).⁴⁶

The polymer binder, which takes up 10 wt.% of the total cathode in Li-S batteries, is not only responsible for binding sulfur particles, carbon black and current collector together, but also plays a role in Li⁺ ion conduction. A polymer binder with moderate electrolyte solvent uptake and good wettability to the electrolyte solvent is beneficial for Li⁺ ion conduction and electrochemical reaction kinetics although excessive

absorption of electrolyte solvent can reduce its binding strength and lead to loss of contact among electrode materials, carbon black and current collector.^{28,47–49} The electrolyte solvent uptake ability can be represented by the swelling ratio, which is defined as the ratio of the mass of the electrolyte solvent absorbed by the polymer film after soaking in the electrolyte solvent to the mass of polymer film before soaking. As shown in Figure S13, PEI-ER_{1:1} showed the highest percent swelling ratio of 26.5%, while PEI-ER_{1:3} and PEI-ER_{1:4} showed the lowest and similar value of 15.0%. The PEI-ER_{1:2} sample showed a moderate percent swelling ratio of 20.2%. This trend agrees with the increased cross-linking density accompanied with the increasing PEI/ER weight ratio, which led to their increased porosity for the higher amount of solvent uptake. The percent swelling ratio of 20.2% for PEI-ER_{1:2} is comparable to other binders in literature, e.g. 20.3% for poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS)²⁸, 28% for sodium carboxymethyl cellulose (CMC)⁴⁹, and 33% for N-guar gum (GG)-xanthan gum (XG).³⁷ The best stability observed for the battery using the PEI-ER_{1:2} binder (Figure S9) is likely due to the balanced mechanical properties and electrolyte uptake ability of this binder.

Next, sublimed sulfur (SS) was replaced with sulfur nanoparticles (NPS) for making the cathode material since it was previously reported that a decrease in the sulfur particle size could lead to an enhancement of the cathode capacity.⁵⁰ Figure 2b presents the voltage-capacity profile of a battery using an NPS:SP:PEI-ER_{1:2} cathode during the second cycle. A reference battery using an NPS:SP:PVDF cathode was also fabricated and tested for comparison. The NPS:SP:PVDF cathode gives a specific capacity of 908 mAh g⁻¹. The discharge curve shows a typical two-step reduction process involving the formation of lithium polysulfide species (Li₂S_x, $x = 3 \sim 8$) at ~2.3 V, lithium disulfide (Li₂S₂) at ~2.1 V, and lithium sulfide (Li₂S) as the final discharge product.^{51–53,1,11} During charging, Li₂S was oxidized to form Li₂S₂ at ~2.2–2.3 V, Li₂S_{3–8} at ~2.3 V and then the final product sulfur at ~2.4 V. The battery with the NPS:SP:PEI-ER_{1:2} cathode showed a significantly increased specific capacity of 1127 mAh g⁻¹. It appears that the first discharge plateau at ~2.2–2.3 V of the NPS:SP:PEI-ER_{1:2} cathode is almost identical to that of the NPS:SP:PVDF cathode, which indicates that the reduction reactions to form the soluble polysulfides (Li₂S_{3–8}) were very similar in these two cathodes. However, the second discharge plateau at ~2.1 V to form Li₂S₂ is much longer for the NPS:SP:PEI-ER_{1:2} cathode, which suggests that a larger amount of the soluble polysulfides were involved in the reduction to form Li₂S₂. The fact that the NPS:SP:PVDF cathode showed an identical first discharge plateau as that of the NPS:SP:PEI-ER_{1:2} cathode might suggest that the diffusion of longer polysulfides (Li₂S_x, where $x > 4$) in the former seems similar to the NPS:SP:PEI-ER_{1:2} cathode probably due to their relatively fast conversion to the shorter polysulfides (Li₂S₄ and Li₂S₃). These shorter polysulfides, however, would stay longer (the second discharge plateau) before being fully reduced to Li₂S₂, which allows them to diffuse away from the conducting network and/or the cathode more readily in the NPS:SP:PVDF cathode. As shown in our DFT

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simulations, the higher binding energies of PEI-ER, especially the PEI-2 segment, towards Li_2S_3 and Li_2S_4 (Figure 1b) might be very beneficial for the confinement of these polysulfides, leading to the improved specific capacity of the NPS:SP:PEI-ER_{1:2} cathode.

The long-term cycling performance of NPS:SP:PVDF and NPS:SP:PEI-ER_{1:2} cathodes at a current rate of 0.5 C is shown in Figure 2c and Table 1. The initial discharge specific capacity of the NPS:SP:PVDF cathode is 973 mAh g⁻¹. After 500 charge/discharge cycles, the discharge capacity decreased to 332 mAh g⁻¹, corresponding to capacity retention of 34% or a decay rate of 0.132% per cycle. The NPS:SP:PEI-ER_{1:2} cathode, however, exhibited a much higher initial capacity of 1145 mAh g⁻¹. After 500 cycles, the cathode still had a capacity of 954 mAh g⁻¹ with capacity retention of 83%. Even after 1000 cycles,

the capacity remained at 72% of the initial value. The significant improvement of the cycling stability for the NPS:SP:PEI-ER_{1:2} battery was considered mainly due to the strong binding ability of the cross-linked PEI-ER binder to both sulfur and the soluble lithium sulfides.

To evaluate the binding ability of PEI-ER to elemental sulfur in comparison to PVDF, the NPS:SP:PEI-ER_{1:2} and NPS:SP:PVDF cathode materials were Soxhlet extracted with refluxing CS_2 , which is a good solvent for elemental sulfur. The NPS:SP:PEI-ER_{1:2} sample retained 31% of the initially loaded sulfur after extraction for 5 h and still had 26% of sulfur left even after 48 h, whereas the NPS:SP:PVDF sample lost all sulfur within 5 h. The significantly improved solvent resistance of the NPS:SP:PEI-ER_{1:2} sample indicates that the cross-linked PEI-ER binder has a strong

Table 1. Summary of cathode compositions and performance of the corresponding Li-S batteries.

Cathode	S loading (mg cm ⁻²)	Discharge capacity at 0.5 C (mAh g ⁻¹)		Retention after (n) cycles	Capacity decay rate per cycle	Areal capacity (mAh cm ⁻²)
		Initial	After (n) cycles			
NPS:SP:PVDF	1.9	973	332 (500)	34% (500)	0.132% (500)	1.8
			192 (1000)	20% (1000)	0.080% (1000)	
NPS:SP:PEI-ER _{1:2}	1.9	1145	940 (500)	83% (500)	0.034% (500)	2.1
			829 (1000)	72% (1000)	0.028% (1000)	
NPS:SP:PEI-ER _{1:2} /IL	1.9	1174	1025 (500)	87% (500)	0.026% (500)	2.2
			937 (1000)	80% (1000)	0.020% (1000)	
	3.5	1043	834 (500)	80% (500)	0.040% (500)	3.7
			665 (1000)	64% (1000)	0.036% (1000)	
	5.4	780	558 (500)	72% (500)	0.056% (500)	4.2
			355 (1000)	46% (1000)	0.054% (1000)	

ability to retain the elemental sulfur, which would partially contribute to the much improved cycling stability of the NPS:SP:PEI-ER_{1:2} cathode based Li-S battery.

Addition of an appropriate interlayer (IL) between the cathode and the separator has proven to be effective to prevent sulfur loss and migration of soluble polysulfides towards the anode to improve the Li-S battery cycling stability.^{54–57} Therefore, a PEI-ER:SP layer with an areal density of 0.17 mg cm⁻² was added as a protection interlayer on the top surface of the pre-cured NPS:SP:PEI-ER_{1:2} cathode by blade coating a slurry of PEI, ER (with a PEI:ER weight ratio of 1:2), and SP with a (PEI+ER):SP ratio of 1:2 and subsequently curing the sample at 50 °C in a vacuum oven for 12 h. The SEM images of the surface of the cathode with this protection layer showed a denser morphology with voids covered by the interlayer in comparison with the cathode without this protection layer (Figure S8b and c). The resulting cathode with this interlayer, NPS:SP:PEI-ER_{1:2}/IL, exhibited a slightly increased initial specific capacity of 1174 mAh g⁻¹ at 0.5 C compared with the cathode without the interlayer (Figure 2 and Table 1). The battery showed a significantly improved cycling stability with capacity retention of 80% after 1000 cycles, which corresponds to a very low capacity decay rate of 0.02% per cycle. A high Coulombic efficiency of > 99% was maintained after 1000 cycles. This is among the best cycling stability reported so far

for Li-S batteries.¹⁷ These results demonstrated that this additional interlayer could function as an effective barrier to further reduce the loss of sulfur species, leading to this remarkable long-term cycling stability.

The morphology of the sulfur cathode surface before and after cycling (for 1000 cycles) was also studied by SEM. As shown in Figure S8d, the NPS:SP:PEI-ER_{1:2} cathode showed micrometer-sized aggregates after cycling, which is likely due to the diffusion (relocation) of the soluble lithium polysulfides and recrystallization of sulfur after charging. The fact that there were no large isolated sulfur crystals formed indicates that the sulfur particles were still well dispersed within the cathode composite together with SP and the PEI-ER_{1:2} binder. On the other hand, the NPS:SP:PEI-ER_{1:2}/IL cathode showed no obvious difference in morphology before and after cycling, indicating that sulfur was mostly confined behind the interlayer.

The above Li-S battery with the NPS:SP:PEI-ER_{1:2}/IL cathode has sulfur loading of 1.9 mg cm⁻². The areal capacity is calculated to be 2.2 mAh cm⁻² (Table 1). To further increase the areal capacity, batteries with higher sulfur loading were fabricated by increasing the amount of the NPS:SP:PEI-ER_{1:2} composite through coating/curing the cathode material slurry two or three times. As shown in Figure 2d, the cathodes with sulfur loading of 3.5 mg cm⁻² and 5.4 mg cm⁻² exhibit initial

discharge capacities of 1043 mAh g⁻¹ and 780 mAh g⁻¹ at 0.5 C, which correspond to areal capacities of 3.7 mAh cm⁻² and 4.2 mAh cm⁻², respectively. Most Li-S batteries reported in the literature had sulfur loading lower than 2 mg cm⁻² and showed specific capacities of less than 1000 mAh g⁻¹ or less at 0.5 C, which corresponds to areal capacities of less than 2 mAh cm⁻².^{2,17} The areal capacity of commercial Li-ion batteries is about 3 mAh cm⁻². Therefore, the areal capacity of 4.2 mAh cm⁻² achieved by our NPS:SP:PEI-ER_{1,2}/IL cathode with 5.4 mg cm⁻² sulfur loading is higher than those of most Li-S batteries reported and the commercial Li-ion batteries. After 500 discharge/charge cycles, the capacities of batteries with sulfur loading of 3.5 mg cm⁻² and 5.4 mg cm⁻² remained at 833 mAh g⁻¹ and 558 mAh g⁻¹, corresponding to capacity retention of 80% and 72%, respectively. While the cycling stability of these two batteries are still very high, the batteries become less stable with increasing sulfur loading. A similar phenomenon was observed in a previous study of a different type of sulfur cathode for Li-S batteries.⁵⁸ One possible reason might be the relatively low electrical conductivity (~5-30 S cm⁻¹) of SP,⁵⁹ which resulted in the poor charge transport from the sites that are remote from the current collector, resulting in lower sulfur utilization. The use of an alternative conductive component with a higher conductivity may lead to Li-S batteries with a higher areal capacity together with a better cycling stability.

Experimental section

Materials and instrumentation

Polyethylenimine (PEI) (M_w = ~25,000, branched), epoxy resin compound (ER) (Araldite® 506), polyvinylpyrrolidone (PVP) (M_w = ~40,000), carbon paper (CP) (Toray TGP-H-090), Super P (SP) (Timcal) and other materials were obtained from commercial sources and used as received. FTIR spectra were collected with a Shimadzu 8400S spectrometer. Universal tensile test was carried out on an Instron Series 4400 Universal Testing Instrument with a gauge length of 14.0 mm at a cross-head speed of 0.2 mm min⁻¹. The SEM images of the samples were obtained using a Zeiss LEO 1550 high-resolution field emission scanning electron microscope.

Preparation of PEI, ER and PEI-ER_{1,2} samples for FTIR characterization.

PEI in chloroform solution and ER in chloroform solution were prepared. Then a few drops of the solutions were added onto clean NaCl pellets and blow-dried with N₂ gas. Pure PEI and ER with a mass ratio of 1:2 were weighed first and immediately diluted with chloroform. A few drops of the PEI-ER_{1,2} solution were added onto a clean NaCl pellet and blow-dried with N₂ gas. After that the pellets were inserted into the FTIR spectrometer for collecting the spectra. For monitoring the cross-linking reaction with FTIR, the same pellet onto which the PEI-ER_{1,2} film was attached was repeatedly put into the 50 °C vacuum oven for reaction and taken out of the vacuum oven for collecting the FTIR spectra at different reaction times (2 h, 6 h, 24 h, and 48 h).

Preparation of PEI-ER_{1,2} films for tensile test.

PEI and ER with weight ratios from 1:2 to 1:4 were mixed thoroughly in a flask with a glass rod at 0 °C, degassed under vacuum for 5 min, poured into a plastic mold, and transferred into the vacuum oven for cross-linking reaction at 50 °C for 48 h. The resultant films were cut into stripes with dimensions of length 40.0 mm × width 5.0 mm × thickness 0.5 mm for universal tensile test.

UV-vis absorption measurement.

Li₂S₆ was synthesized by reaction of elemental sulfur with Li₂S at a stoichiometric ratio of 5:1 in DOL/DME (v/v, 1:1) solvent in a sealed vessel at 80 °C overnight. SP/PVDF, SP/PEI, SP/ER and SP/PEI-ER_{1,2} composites were prepared by mixing SP with polymer at a mass ratio of 2:1 in NMP. The slurries were coated onto glass petri dishes, dried in a convection oven at 50 °C, and then transferred to a vacuum oven at 50 °C. After drying, the resultant solids were ground into fine powders in an agate mortar to eliminate the influence of particle size. In a typical Li₂S₆ adsorption experiment, 15 mg of Super P/polymer composite which contains 10 mg of Super P and 5 mg of polymer was added into 3.5 ml of 0.5 mM Li₂S₆ solution. The mixture was well mixed by shaking the vial 4 times at an interval of 0.5 h. After being kept at room temperature for 24 h, the clear supernatant was taken out for UV-Vis absorption measurement. As a comparison, the Li₂S₆ adsorption of the same amount of Super P (10 mg) was also tested.

Electrolyte solvent uptake test.

Pre-weighed cross-linked PEI-ER thin films at PEI/ER weight ratios from 1:1 to 1:4 with dimensions of length 10.0 mm × width 5.0 mm × thickness 0.5 mm were soaked in mixed DOL/DME solvent (v/v, 1/1) in sealed vials, and taken out for measuring the weight change after certain soaking times. For the PEI-ER_{1,1} and PEI-ER_{1,2} films, the weight change reached the maximum after about 4 days, while it took about one week for PEI-ER_{1,3} and PEI-ER_{1,4} films. After the films were taken out of the electrolyte solvent, they were dried with clean paper towels before weighing. The swelling ratio is defined as the weight of electrolyte solvent absorbed by the PEI-ER film divided by the weight of the PEI-ER film before soaking.

Synthesis of sulfur nanoparticles (NPS).

Sulfur nanoparticles (NPS) were synthesized following a previously reported method.⁶⁰ Aqueous solutions of 80 mM Na₂S₂O₃ (50 mL) and 0.4 M PVP (the concentration was based on the repeat unit of PVP) (50 mL) were mixed at room temperature. Then, concentrated hydrochloric acid (0.4 mL; 37%) was added under stirring. After 2 h, the reaction mixture was centrifuged at 4000 rpm for 15 min to isolate the precipitates, which were washed with deionized water 5 times and dried in air and then under vacuum at room temperature. The sulfur content is ~99% as determined by thermogravimetric analysis (TGA) (Figure S10). The average diameter of the NPS is ~120 nm estimated by the SEM image (Figure S11).

ARTICLE

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Preparation and solvent resistance testing of cross-linked PEI-ER samples.

PEI-ER binders at different PEI:ER weight ratios (2:1, 1:1, 1:2, 1:3, 1:4, and 1:5) were prepared by mixing PEI and ER at a total concentration of 20 wt.% in *N*-methyl-2-pyrrolidone (NMP). The solutions were coated on Al foils with a blade. The obtained films were dried briefly in air and then in a vacuum oven at 50 °C for 12 h. To test the solvent resistivity, the PEI-ER films were peeled off from the Al foil and soaked in an electrolyte solution for 7 days. The electrolyte solution used was 1M lithium bis-trifluoromethanesulfonylimide (LiTFSI) in 1,3-dioxolane (DOL)/dimethoxyethane (DME) (1:1, v/v) containing 2 wt.% LiNO₃. The weight losses of the sample were measured to assess the solvent resistance of sulfur inside the sample (Table S1).

Preparation of NPS:SP:PEI-ER cathodes.

NPS (70 wt.%), SP (20 wt.%), a freshly prepared solution of PEI and ER (10 wt.%) at different PEI:ER ratios were mixed in NMP with a solid concentration of 20 wt.% and the mixture was ground for 40 min in a mortar. The obtained slurry was blade coated on a CP substrate and dried briefly in air and then in a vacuum oven at 50°C for 12 h. A protective layer comprised of PEI-ER and SP was optionally blade coated on top of the cured NPS:SP:PEI-ER cathode layer and was subject to cross-linking at 50 °C in a vacuum oven for 12 h. The slurry for coating the protective layer was prepared by mixing PEI and ER (1:2) and SP with a total solid content of 20 wt.% in NMP, where the (PEI+ER):SP weight ratio was 1:2. The cathode using PVDF as the binder was prepared similarly by blade coating a slurry comprising NPS, SP, and PVDF at weight ratios of 70:20:10.

Battery assembly and electrochemical measurements.

CR2025 coin cells were assembled in an argon-filled glove box. The battery structure is shown in Figure 2a. A shrapnel, a spacer, a Li anode film, and a Celgard 2500 separator were placed sequentially in an anode cover. Then the electrolyte (50 μL), 1M LiTFSI in DOL/DME (1:1, v/v) containing 2 wt.% LiNO₃, was added on top of the separator with a syringe. The CP coated with the cathode material as described above, which was cut into a circular disk with a diameter of 12 mm, was loaded as the cathode. Finally, the stacked layers were pressed to complete the battery assembly. Discharge-charge measurements were carried out within a voltage window of 1.7–2.8 V at different current densities at room temperature on a LAND battery tester.

Conclusions

In summary, we developed an epoxy resin PEI-ER based on a branched polyethylenimine and an epoxy compound for the cathode in Li-S batteries. This epoxy resin formulation can react *in-situ* under mild conditions to form a robust cross-linked 3-D network to hold sulfur and the conductive carbon. The abundant nitrogen and oxygen atoms in the PEI-ER binder provide strong chemical affinity to lithium sulfides, especially

the soluble intermediate polysulfides. Moreover, the PEI-ER binder is combined with conductive carbon to form an interlayer between the cathode and the separator to further prevent the shuttling of soluble polysulfides. As a result, the Li-S batteries using the cathode and interlayer made with this binder achieved a high capacity of 1174 mAh g⁻¹ and a remarkable cycling performance with high capacity retention of 80% after 1000 cycles at 0.5 C at a sulfur loading of 1.9 mg cm⁻². With a high sulfur loading of 5.4 mg cm⁻², the battery reached a high areal capacity of 4.2 mAh cm⁻² and still showed high capacity retention of up to 72% after 500 cycles at 0.5 C. Our study demonstrates that this new polymer binder is very promising for the realization of low cost Li-S batteries with outstanding cycling lifetime and high energy density.

Conflicts of interest

There are no conflicts to declare.

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Graphical abstract

An epoxy resin PEI-ER formed by *in-situ* reaction between an epoxide compound and polyethylenimine (PEI) is used as a new cathode binder for lithium-sulfur (Li-S) batteries.

