# Prussian Blue: A Potential Material to Improve the Electrochemical Performance of Lithium-Sulfur Batteries

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Supporting Information



ABSTRACT: The Prussian blue, as a potential adsorbent of polysulfides to suppress the dissolution and shuttle of polysulfides for lithium-sulfur batteries, has been studied in this work. Our results show that Prussian blue improves the electrochemical reaction kinetics during discharge/charge processes. More importantly, the cathode with Prussian blue exhibits better cycling stability and higher discharge capacity retention (722 mAh  $g^{-1}$  at 0.2 A  $g^{-1}$  after 100 cycles) than the one without Prussian blue (151 mAh g<sup>-1</sup>). These improvements of electrochemical performances are ascribed to the fact that Prussian blue is very effective in suppressing the dissolution of polysulfides into liquid electrolyte by chemical adsorption.

KEYWORDS: prussian blue, lithium-sulfur batteries, polysulfides, electrochemical performances, chemical adsorption

# INTRODUCTION

Lithium-sulfur (Li-S) battery is a very attractive candidate for next generation high-energy storage device because of its high theoretical specific capacity (1675 mAh  $g^{-1}$ ) and specific energy density of 2600 Wh kg<sup>-1</sup>, which is five times greater than the present lithium-ion battery.<sup>1,2</sup> Furthermore, elemental sulfur is naturally abundant and nontoxic, thus Li-S battery is low cost and environmentally benign. However, it is still in infant stage for commercialization after many years of research. The development of Li-S battery is impeded by three major hurdles: (a) low electronic conductivity of sulfur ( $\sim 10^{-30}$  S  $cm^{-1}$ ) and its discharge products (i.e.,  $Li_2S/Li_2S_2$ ), which lead to low utilization of active sulfur and poor power density of the cell; (b) a large volumetric expansion, which results in structural and morphological instability during cycling; (c) high dissolution of polysulfides into electrolyte solution and shuttling of polysulfides between sulfur cathode and lithium metal anode.<sup>3,4</sup> Many efforts have been dedicated to address these issues, such as the designation of the cathode, the electrolyte, and the Li metal anode.<sup>5-11</sup> Among these, it is presumed that the dissolution and shuttle effect of polysulfides are the primary reasons for the rapid capacity fading, poor cycling stability, and low Coulombic efficiency of Li-S cells.<sup>12</sup>

The dissolved polysulfides can diffuse to the anode, where they can react with lithium and form insoluble Li<sub>2</sub>S/Li<sub>2</sub>S<sub>2</sub> on the lithium surface, causing massive loss of sulfur species and the increase of surface impedance. Therefore, much attention has been paid to confining the polysulfides in the cathode.<sup>13</sup>

One common strategy is using materials with pore structure to physically absorb polysulfides for confining sulfur species in the cathode. The most popular material is carbon-based hosts, such as meso-/microporous carbons, carbon nanospheres, carbon nanotubes, and graphenes.<sup>14–16</sup> These carbon materials not only provide physical barrier but also enhance electronic conductivity of the electrode. However, there are still continued polysulfides escaping from the carbon channels because of the weak chemical interaction between nonpolar carbons and the polar polysulfides, which leads to sustained capacity loss upon numerous cycles.<sup>17,18</sup> Therefore, a strategy of chemical

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adsorption is required to efficiently trap sulfur and reduce the loss of soluble polysulfides. Recent studies have discovered that surface-coordination unsaturated metal oxides/chalcogenides can form strong chemical interaction with polysulfides, which are favorable for suppressing polysulfides dissolution. For example, Cui et al. revealed that surface coordination environment could strongly influence the binding energy with S-species by comparing the TiO2-S and Ti4O7-S cathode.<sup>19</sup> Nazar et al. demonstrated the nature affinity between metal sulfide/oxide and polysulfides via first-principles calculations.<sup>20</sup> Besides, other oxyphilic metal compounds, such as NiFe2O4, SnO<sub>2</sub>, and MoS<sub>2</sub> are also reported to have the ability of maintaining cycling stability for Li–S system.<sup>21–23</sup> However, such chemical binding to polysulfides is only limited in metal oxides/chalcogenides, which inspires us to explore new materials with chemical adsorption in Li-S batteries for suppressing the polysulfides dissolution.

Prussian blue (PB), with the formula of  $Fe_4^{III}[Fe^{II}(CN)_6]_{37}^{24}$  contains polar  $Fe^{II}-C-N-Fe^{III}$  units.<sup>24–26</sup> PB is attractive because it is low cost, environmental friendly, and easy to synthesize. Furthermore, PB exhibits many interesting physicochemical functions, making it widely applied in catalysis, lithium-ion batteries, and sodium-ion batteries.<sup>27–29</sup> However, rare investigation has been reported on using PB in the field of lithium–sulfur batteries.

In this work, we synthesize sulfur/PB composites (SPB) and further investigate the influence of PB on the electrochemical performance of the sulfur cathode. The results reveal that PB has strong chemical adsorption for polysulfides demonstrated by X-ray photoelectron spectroscopy (XPS). The electrochemical measurements show that the SPB cathodes exhibit improved electrochemical reaction kinetics, better cycle-life and rate performance than that of the pure sulfur cathode. The use of PB may open new insights into better design of Li–S system with high cycling stability, high rate performances, and cost effectiveness.

## EXPERIMENTAL SECTION

**Sample Synthesis.** First, PB was prepared according to a typical procedure:<sup>24</sup> 50.0 mL of 0.1 M K<sub>4</sub>Fe(CN)<sub>6</sub> solution was added dropwise to 100.0 mL of 0.1 M FeCl<sub>3</sub> solution at 60 °C under continuous stirring for 3 h. Then, the as-synthesized PB nanoparticles were centrifuged and washed several times with deionized water and alcohol before finally dried in a vacuum oven at 60 °C for 12 h.

SPB composites were fabricated by mixing commercial sulfur powders (Beijing DK nano technology Co.LTD) with as-prepared PB nanoparticles in different weight ratios of 95:5, 92:8, and 90:10, respectively. For convenience, they were named as SSPB, 8SPB, and 10SPB, respectively. The mixtures were transferred into ball-type vessels with ethanol as blender at the weight ratio (4:1) of the  $ZrO_2$ balls to the mixtures. After ball-milling at 400 rmp for 6 h, the products were dried at 60 °C for 12 h. For comparison purpose, the pure commercial sulfur powders without PB were also treated with ballmilling as the above procedures.

Adsorption of Polysulfides by PB.  $Li_2S_4$  was synthesized by dissolving stoichiometric ratio of  $Li_2S$  and sulfur in 1,3-dioxolane (DOL) at 80 °C for 12 h. There are three vials, each with 5 mL  $Li_2S_4$  solution (20 mmol  $L^{-1}$  of  $Li_2S_4$  in DOL/1,2-dimethoxyethane (DME), 1:1, v/v), in which one is a blank control, one with 60.0 mg PB added, and the last one with 60.0 mg acetylene black (AB) added. The photos were taken after adding PB for 3 h. All procedures were completed in an argon-filled glovebox.

**Material Characterization.** X-ray diffraction data of the materials were collected on the Rigaku X-ray diffractometer (XRD, Miniflex600, Rigaku Corporation) using K $\alpha$  radiation operated at 40 kV and 15 mA.

The morphologies of the as-prepared materials were characterized with the field-emission scanning electron microscopy (SEM, S-4800, Hitachi Corporation). The proportion of sulfur in the SPB composites was analyzed by elemental analyzer (Vario-EL-III) and thermogravimetric analysis (TGA, SDT-Q600) in nitrogen from room temperature to 500 °C. The sulfur content in electrolyte was determined using the Genesys 10s ultraviolet–visible spectrophotometer (UV–vis, Thermo Scientific, USA). The Brunauer–Emmett–Teller (BET) surface area and porosity were obtained by Nitrogen adsorption–desorption isotherms with ASAP 2020. X-ray photoelectron spectroscopy (XPS) was carried out on the Quantum 2000 Scanning ESCA Microprobe spectrometer.

**Cell Fabrication and Electrochemical Measurement.** The cathode was fabricated by mixing as-prepared SPB composite (5SPB, 8SPB, and 10SPB, respectively), AB, and polyvinylidene fluoride (PVDF) with weight ratios of 70:20:10. The slurry was stirred in *N*-methyl-2-pyrrolidinone for 1 h at room temperature and then coated onto aluminum foil with the doctor blade. Afterward, the electrodes were dried at 60 °C under vacuum for 12 h. The CR2016-type coin cells were assembled for electrochemical testing in an argon-filled glovebox (Mbraun, Gerany). A lithium metal foil was used as the counter/reference anode. The electrolyte was 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in DOL and DME (DOL: DME = 1:1, v/v). For comparison, the pure sulfur cathode was fabricated as the same as above, thus, the weight ratio of sulfur/AB/PVDF was 70:20:10. The typical mass loading of active material sulfur in the cathode is 1.2-1.4 mg cm<sup>-2</sup>.

The cells were galvanostatically discharged and charged at different current densities between 1.5 and 3.0 V (vs Li<sup>+</sup>/Li) using the battery test system (LAND CT2001A instrument, China). The discharge/charge profiles and cycling stability were studied at 0.2 A g<sup>-1</sup>. The initial cyclic voltammetry (CV) measurements were performed on the CHI660D workstation at a scan rate of 0.1 mV s<sup>-1</sup> in a voltage range of 1.5 to 3.0 V (vs Li<sup>+</sup>/Li). Electrochemical impedance spectra (EIS) of bare sulfur and 10SPB cathode discharged to 1.5 V were measured on electrochemical workstation (Autolab PGSTAT T302N) with the frequency range from 0.1 Hz to 100 kHz using two-electrode coin cells with lithium metal as the counter electrode and reference electrode. All the electrochemical data were obtained at the constant temperature of 25 °C.

## RESULTS AND DISCUSSION

Figure 1 reveals the XRD patterns of pure sulfur, as-prepared PB and SPB composites (5SPB, 8SPB, and 10SPB). All of the



Figure 1. XRD patterns of pure sulfur and as-prepared PB, SSPB, 8SPB, and 10SPB.

reflections of PB can be unambiguously indexed as a cubic phase of  $Fe_4[Fe(CN)_6]_3$  (JCPDS: 001-0239; space group Fm3m). The sharp reflection patters of pure sulfur are well matched with the crystalline data of orthorhombic sulfur (JCPDS: 089-2600, space group *Fddd*). The SPB composites show the reflections of both PB and sulfur, and the intensity corresponded to PB (at 17.7°) enhances with the increasing

ratio of PB, which indicates that PB nanoparticles are existing on the surface of sulfur.<sup>30</sup> There are not any new peaks in the SPB composites, which reflects no chemical reaction between PB and sulfur after ball-milling treatment.<sup>31</sup>

The SEM images in Figure 2 show the morphologies of asprepared PB and SPB composites (5SPB, 8SPB, and 10SPB). It



Figure 2. SEM images: (a) as-prepared PB, (b) 5SPB, (c) 8SPB, and (d) 10SPB.

can be seen from Figure 2a that as-prepared PB nanoparticles have the average size of 20 nm. Figure S1 shows that the size of pristine commercial sulfur powders range from 3 to 5  $\mu$ m and their surfaces are quite smooth. After mixing PB with sulfur powders by ball-milling (Figure 2b, c, and d), the surfaces of sulfur particles become rough as the PB nanoparticles randomly adhere to their surfaces. For 5SPB, most surfaces of sulfur particles expose to the outsides, owning to the small amount of PB (5%) in the 5SPB composites. While, as the amount of PB increases, less exposed surface of sulfur particles is observed. When the content of PB reaches 10% (10SPB), the sulfur particles are uniformly coated with PB nanoparticles. The elemental mapping (Figure S2) further confirms that the uniform distributions of iron, carbon, and nitrogen on the surface of sulfur particles in 10SPB. The results of SEM and elemental mapping analysis demonstrate the effective cover and uniform distribution of PB nanoparticles on the surface of sulfur, implying that the polysulfides may be effectively adsorbed in the case of 10SPB.

To investigate the effect of PB on the electrochemical performance of Li–S cells, the CV, galvanostatical discharge/ charge, rate performance, and EIS measurements were conducted. The capacity of each cathode was calculated based on the mass of sulfur in the electrode. According to the elemental analysis, the proportion of sulfur is 94.7%, 92.0%, and 90.3% in the SSPB, 8SPB, and 10SPB, respectively. TGA was further used to estimate the load of sulfur in the SPB composites. As shown in Figure S3, pure sulfur totally sublimes when heated to 306  $^{\circ}$ C in nitrogen. Pure PB also suffers weight loss, but remains a weight percentage of 80.0% at 306  $^{\circ}$ C. Therefore, we can calculate the proportion of sulfur in each composite (Table S1), which is in accordance with the results of elemental analysis.

The initial CV profiles of SPB cathodes were analyzed to understand the effect of PB on the oxidation/reduction reaction of sulfur cathode as shown in Figure 3a. During the first



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**Figure 3.** (a) The initial cyclic voltammetry profiles of Li–S cells, (b) corresponding peak voltages, and intensity, (c, d) initial discharge/ charge profiles for Li–S cells at 0.2 A  $g^{-1}$ .

cathodic scan, two remarkable reduction peaks at around 2.3 and 2.0 V are clearly observed in all electrodes. According to the previous reports,  $^{14,32}$  the first reduction peak at ~2.3 V is attributed to the formation of soluble polysulfides (Li<sub>2</sub>S<sub>n</sub>,  $4 \le n$  $\leq$  8). The second reduction peak at ~2.0 V is ascribed to the liquid-solid two phase reduction, referring to the formation of insoluble Li<sub>2</sub>S<sub>2</sub> and Li<sub>2</sub>S. In the subsequent anodic scan, only one oxidation peak at ~2.5 V is observed, which is related to the conversation of reduced products (Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S) back to elemental sulfur. It should be noted that the intensities and positions of cathodic and anodic peaks of the pure sulfur and SPB cathodes are quite different. We can clearly see from Figure 3b that two reduction peaks at 2.16 and 1.96 V and one oxidation peak at 2.54 V are observed in pure sulfur cathode. While, for the SPB cathodes, the two reduction peaks shift gradually to higher potential and the oxidation peak is negatively shifted with the increasing of PB loading, which is a proof of the improved reaction kinetics caused by the additive of PB. This result indicates that PB has a positive influence on lowering the activation energy of sulfur reduction and oxidation, accelerating the transformation between LiPSs and elemental sulfur. Such catalytic effect on Li-S redox reaction agrees well with the previous reports.<sup>33,34</sup>

Figure 3c and d compare the first galvanostatical discharge/ charge profiles of pure sulfur and 10SPB cathode at 0.2 A g Both discharge curves show two typical discharge plateaus. The first plateaus at ~2.3 V (region I) represents the formation of  $Li_2S_8$  from elemental sulfur, and the second plateaus at ~2.1 V (region III) corresponds to the conversion of dissolved Li<sub>2</sub>S<sub>4</sub> to insoluble  $Li_2S_2$  or  $Li_2S_3^{35,36}$  which is consistent with the result of CV in Figure 3a. The pure sulfur cathode shows the initial discharge and charge specific capacity of  $\sim$ 903 mAh g<sup>-1</sup> and ~1132 mAh  $g^{-1}$ , respectively. The higher charge specific capacity is an indication of the shuttle effect which is accompanied by side reactions at the Li metal anode.<sup>37</sup> In comparison, the 10SPB cathode exhibits the discharge capacity of 1112 mAh  $g^{-1}$  and the reversible charge capacity of 1065 mAh  $g^{-1}$  during the first discharge/charge cycle. No overcharge phenomenon is found in 10SPB cathode, which is an indication of the elimination of shuttle effect owning to the strong adsorption of PB to the polysulfides. The same situation is also

found in the cases of SSPB and 8SPB (Figure S4). In addition, we can see that the SSPB, 8SPB, and 10SPB cathodes exhibit higher discharge capacity than that of the pure sulfur cell during the process of discharge. This is attributed to the strong PB-polysulfides interaction which reduces the diffusion of soluble polysulfides out of the cathode, leading to the enhanced utilization of active material. Thus, these data further prove that the PB additive has a positive effect on reducing polysulfides dissolution into the electrolyte, and increasing the active material utilization.

The cycling behavior of the pure sulfur, 5SPB, 8SPB, and 10SPB cathodes are compared at 0.2 A  $g^{-1}$ , as shown in Figure 4a. The pure sulfur cathode suffers from rapid capacity decay,



**Figure 4.** (a) The cycling performance of the Li–S cells at 0.2 A  $g^{-1}$ ; (b) the discharge profiles of the Li–S cells at different rates (0.1, 0.2, 0.5, 1, 2 A  $g^{-1}$ ); (c, d) EIS of Li–S cells of the first, fifth, and tenth cycling at 0.2 A  $g^{-1}$ .

fading from 903 mAh  $g^{-1}$  to only 151 mAh  $g^{-1}$  after 100 cycles. After adding a certain amount of PB, a higher initial specific discharge capacity and better cycling stability are achieved. Among them, the 5SPB shows the least improvement in the cycling stability. It is supposed that the insufficient amount of PB results in ineffective attachment to the surfaces of sulfur particles (Figure 2b), thus large amounts of sulfur species easily diffuse into the electrolyte and poor cycling performance is obtained. While, the 10SPB cathode exhibits the best cycling performance due to the uniform distribution of PB nanoparticles on the surfaces of sulfur particles according to the result of SEM (Figure 2d). Its initial discharge capacity is up to 1112 mAh  $g^{-1}$  with the reversible capacity of 722 mAh  $g^{-1}$  after 100 cycles. The retention rate of discharge capacity is about 65%, much higher than 17% of the pure sulfur cathode. The improved discharge capacity indicates the more efficient utilization of active material because of the improved adsorption of the polysulfides to cathode which otherwise are soluble in electrolyte and diffuse away from cathode to anode. Furthermore, the Coulombic efficiency of cathodes (Figure S5) shows that the pure sulfur cathode suffers from serious overcharge phenomenon in the first five cycles, leading large loss of sulfur species in the electrolyte and anode. In comparison, the SPB cathodes exhibit nearly 100% Coulombic efficiency over the 100 cycles. In addition, Table S2 listed the cycling performance of various cathode materials using the similar method. Though the performance of 10SPB is not

outstanding, it is still attractive when considering the sulfur loading and initial discharge capacity.

The rate performance of bare sulfur and 10SPB cathodes were evaluated at different current densities (from 0.1 A g<sup>-1</sup> to 2 A g<sup>-1</sup>) as shown in Figure 4b. The bare sulfur cathode shows the significant discharge capacity decline from 1105 mAh g<sup>-1</sup> (at 0.1 A g<sup>-1</sup>) to 519 mAh g<sup>-1</sup> (at 2 A g<sup>-1</sup>). The continuous capacity loss with increasing rates is caused by the increasing polarization at high rates, suggesting the formation of ion-insulator solid Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S on lithium anode.<sup>21</sup> By contrast, the cell with 10SPB composite shows that its discharge capacities at different current densities of 0.1 A g<sup>-1</sup>,  $\sim$  1112 mAh g<sup>-1</sup>,  $\sim$  916 mAh g<sup>-1</sup>, and 2 A g<sup>-1</sup> are  $\sim$ 1275 mAh g<sup>-1</sup>, respectively. The obvious improvement in the rate performance is consistent with the analysis result of CV (Figure 3a). It further demonstrates that adding PB to cathode can enhance the reaction kinetics and reduce the electrode polarization through suppressing the polysulfides dissolution and shuttle process.

EIS measurements were carried out to comprehensively understand the reason for better electrochemical performances of the SPB cathode. Figure 4c and 4d illustrate the Nyquist plots of pure sulfur and 10SPB cathodes at the fully charged state (3 V vs Li<sup>+</sup>/Li) in the first, fifth, and tenth cycles. The depressed semicircle in the high-to-medium frequency region represents the charge-transfer resistance  $(R_{ct})$ , which is mainly from the interface between the electrode and electrolyte. The low frequency region displayed an inclined line is the Warburg impedance  $(W_0)$  related to the Li-ion diffusion in the bulk of electrode. It is found that the value of  $R_{ct}$  of the 10SPB cell is much lower than that of bare sulfur cell in all cases, which indicates a better Li-ion transport and electric conductivity, better electrochemical reaction kinetics, and thus better electrochemical performance in the case of the 10SPB cathode. In addition, it is noticeable that the changes in the impedance have different tendencies for the pure sulfur and 10SPB cathodes during the subsequent cycles (fifth, tenth). The charge-transfer impedance of cell with pure sulfur as cathode shows an increasing impedance as cycling continues. In comparison, the 10SPB cathode exhibits a decreasing trend in impedance, which indicates an increasing rate of charge transfer between the interface of electrode and electrolyte. Since all other factors are the same, we believe that PB somehow facilitates lithium ion transfer in the electrode.

Furthermore, an ex-situ SEM analysis was performed on the pure sulfur and 10SPB electrodes (charged to 3 V at 0.2 A g<sup>-1</sup> after 50 cycles) to study the change of surface morphology. As shown in Figure 5a and c, the pristine films of the pure sulfur and 10SPB electrodes are quite similar before cycling. After 50 cycles, an excessive agglomeration in the pure sulfur cathode is markedly observed (Figure 5b), which can be attributed to the repetitive dissolution/deposition of sulfur on the cathode surface.<sup>38,39</sup> The agglomeration would elongate the tortuous pathway for Li-ions transportation and diffusion as well as cause the loss of electric contact, either of which would increase the cell impedance and deteriorate cell performance. Impressively, there is no significant change of surface morphology for 10SPB cathode film even after 50 cycles (Figure 5d). The wellpreserved morphology of the 10SPB cathode allows us to suggest that the PB is very effective to suppress the dissolution of polysulfides into electrolyte solution and the agglomeration of active material. Our results agree well with other reports that the morphology change on the electrode surface during cycling



Figure 5. SEM images of electrodes: (a) pure sulfur before cycling, (b) pure sulfur after 50 cycles, (c) 10SPB before cycling, and (d) 10SPB after 50 cycles.

is responsible for poor cycling stability and low sulfur utilization.<sup>40</sup> This provides evidence for good cycling stability and rate performance in 10SPB cathode.

To further confirm that PB has a strong interaction with polysulfides to suppress their dissolution into the electrolyte, the UV-vis spectra were used to detect the loss of sulfur from 10SPB cathode (charged to 3.0 V after 50 cycles) to electrolyte. For pure sulfur cathode, 80.4% of sulfur mass is lost into the electrolyte, while only 32.8% of the sulfur mass is found in the electrolyte for 10SPB cathode, showing PB is a very efficient additive to "lock up" sulfur in the cathode, which is further confirmed through visual observations (Figure 6a).

After adding PB, the color of  $\text{Li}_2\text{S}_4$  solution changes from tawny color to completely colorless, while the color of solution added AB has no obvious change. The sharp contrast confirms a strong absorption of  $\text{Li}_2\text{S}_6$  by PB.<sup>21</sup> The nitrogen adsorption desorption test (Figure 6b) reveals that the PB nanoparticles possess specific surface area of 343.1 m<sup>2</sup> g<sup>-1</sup> and the average



Figure 6. (a) Photos of lithium polysulfides solution ( $\text{Li}_2\text{S}_4$  dissolved in DOL/DME solvent), added PB and AB, (b) N<sub>2</sub> adsorption– desorption isotherms, and corresponding pore size distribution (insert), (c, d) XPS spectra of 10SPB cathode before and discharged to 1.5 V.

pore size of 3.5 nm. Therefore, to clarify whether the adsorption of PB to polysufides was via physical or chemical interaction, XPS was used to reveal the chemical status of PB and polysufides during discharge. Figure 6c and d depict the S 2p and Fe 2p XPS spectra of 10SPB electrode before and discharge to 1.5 V. As shown in Figure 6c, two obvious peaks at 165.3 and 164.2 eV are observed in the fresh electrode, which are the characteristic peaks of S 2p.<sup>41</sup> After discharged to 1.5 V, the strong peak of Li<sub>2</sub>S at 159.5 eV associated with the weak peak of  $Li_2S_2$  at 161.5 eV suggests that majority of sulfur is reduced.<sup>42–44</sup> While, the peaks at about 161.0 eV can be ascribed to the S-Fe (III) binding.<sup>45,46</sup> In the Fe 2p3 XPS spectra, the peaks of Fe  $2p_{3/2}$  and Fe  $2p_{1/2}$  are located at 712.5 and 721.4 eV, respectively, which come from high-resolution Fe (III). The peak at 708.6 eV indicates the presence of Fe (II) in PB.<sup>47,48</sup> When discharged to 1.5 V, the additional peak at 709.5 eV is obtained, which can be attributed to the Fe (III)-S.49 The XPS result further confirms that PB can adsorb polysufides through strong chemical interaction.

Based on these results, we can deduce that the better rate performances and better capacity retention of the SPB cathodes can be attributed to the strong adsorption of PB for polysulfides. As illustrated in Figure 7, for pure sulfur cathode,



Figure 7. Schematic illustration of the adsorption and catalysis effect of PB on polysulfides: (a) pure sulfur cathode, (b) SPB cathode.

the polysulfides generated during the reduction are easy to dissolve and diffuse to the electrolyte, leading to low utilization of sulfur. While, in the case of SPB cathode, due to its naturally hydrophilic property, PB exhibits a strong adsorption to polysulfide, resulting in more active material remaining in the sulfur cathode and thus polysulfide diffusion is weaken.

#### CONCLUSION

In summary, we have applied a new class of material, the PB, to trap polysulfides in Li-S batteries by fabricating SPB composites. Our studies show that the addition of PB to the cathode has a pronounced effect on improving its electrochemical reaction kinetics, rate performance, and stabilizing its cycling performance. These improvements of SPB cathodes are mainly attributed to the strong interaction of PB with polysulfides, efficiently reducing the polysulfides dissolution in electrolyte solution and eliminating their diffusion toward and deposition on lithium anode. As a result, the 10SPB cathode exhibited the enhanced initial discharge capacity of 1112 mAh  $g^{-1}$  at 0.2 A  $g^{-1}$  and maintained 722 mAh  $g^{-1}$  after 100 cycles. To our best knowledge, this is the first time that the PB is reported as the adsorbent of polysulfuldes for Li-S batteries. Considering PB nanoparticles utilized in this work are environmentally friendly, low-cost, and easily synthesized, we believe that PB is a promising material to suppress polysulfides dissolution for design of Li-S batteries with long cycle life.

# ASSOCIATED CONTENT

## **Supporting Information**

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SEM images of commercial sulfur powders; SEM image of 10SPB and corresponding elemental mapping of S, Fe, C, and N; TGA curves of sulfur, PB, and SPB composites in  $N_2$ ; weight percentages; initial discharge/charge profiles; efficiency of sulfur, 5SPB, 8SPB, and 10SPB cathodes; and cycling performance of various sulfur cathode materials (PDF)

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## Notes

The authors declare no competing financial interest.

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