

Surface Modification of Sulfur Electrodes by Chemically Anchored Cross-Linked Polymer Coating for Lithium–Sulfur Batteries

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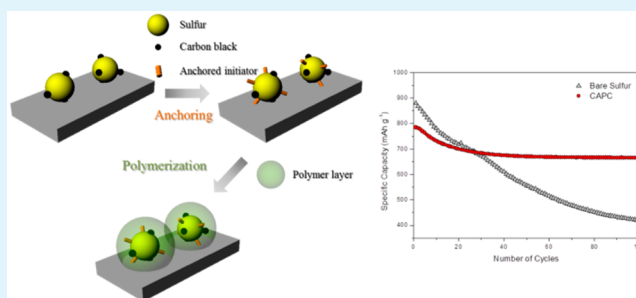
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Supporting Information

ABSTRACT: Lithium–sulfur batteries suffer from severe self-discharge due to polysulfide dissolution into electrolytes. In this work, a chemically anchored polymer-coated (CAPC) sulfur electrode was prepared, through chemical bonding by coordinated Cu ions and cross-linking, to improve cyclability for Li/S batteries. This electrode retained specific capacities greater than 665 mAh g⁻¹ at high current density of 3.35 A g⁻¹ (2C rate) after 100 cycles with an excellent Coulombic efficiency of 100%.

KEYWORDS: lithium–sulfur batteries, polymer coating, chemical bonding, Cu-anchoring, sulfur electrode, polysulfide dissolution



The need for energy storage is fast exceeding that can be achieved with lithium-ion batteries (LIBs), even at their maximum theoretical limits. As a result, alternative energy-storage systems with much higher theoretical energy capacities are needed.^{1,2} Among the advanced energy storage systems, Li/S batteries hold great promise because they have a high theoretical capacity (1675 mAh g⁻¹) and energy density (2600 Wh kg⁻¹). The high capacity of such batteries is afforded by the reaction of S₈ + 16 Li⁺ + 16 e⁻ ↔ 8Li₂S through long-chain lithium polysulfide intermediates Li₂S_x, 4 ≤ x ≤ 8. However, the practical energy density and cycling stability of the Li–S battery are limited by the poor electronic conductivity of sulfur, large volume changes, and the dissolution of intermediate polysulfides in the electrolytes.^{3–7} During the cycling of Li–S batteries, the high-order (or long-chain) lithium polysulfides are highly soluble in the electrolyte and can diffuse throughout the whole cell, leading to the shuttle effect and capacity loss of active materials, which are thought to be the main reasons for low Coulombic efficiency and rapid capacity fade in Li–S batteries.

Research investigating the composite structure of carbon and sulfur has been recently carried out to compensate for the poor electronic conductivity of sulfur by using diverse synthetic methods including the use of templates, pyrolysis and sulfur impregnation.^{8–12} Although the issue of poor conductivity of sulfur is greatly relieved by the sulfur–carbon composite structure, the impregnated sulfur active materials are still

accessible to the electrolyte, which leads to the problematic lack of sufficient cyclability and loss of active material.

One approach that has been investigated for reducing the polysulfide shuttle is coating the sulfur material with polymers so that polysulfides are restrained at the cathode through physical or chemical absorption.^{13–15} Various such polymer/sulfur composites with diverse chemical structures and morphologies have been generated to attempt to improve the stability of active sulfur material during electrochemical cycling,^{16–23} but these composites have not prevented capacity fading. However, it appears that most of these polymers easily disintegrate because they only weakly interact with the underlying sulfur; in fact, almost all the polymer coatings reported to date do not form any chemical interactions with the sulfur particles but only entrap them physically. These weak interactions are easily broken by the high-volume change of sulfur that occurs after cycling.

In the present work, we modified the surface of a sulfur carbon composite electrode by surface-induced cross-linking polymerization involving a strong chemical interaction between polymer and sulfur for the first time. The sulfur composite electrode was coated by a surface-induced cross-linking polymerization, initiated by a reactive species chemically anchored to the sulfur electrode via coordination through

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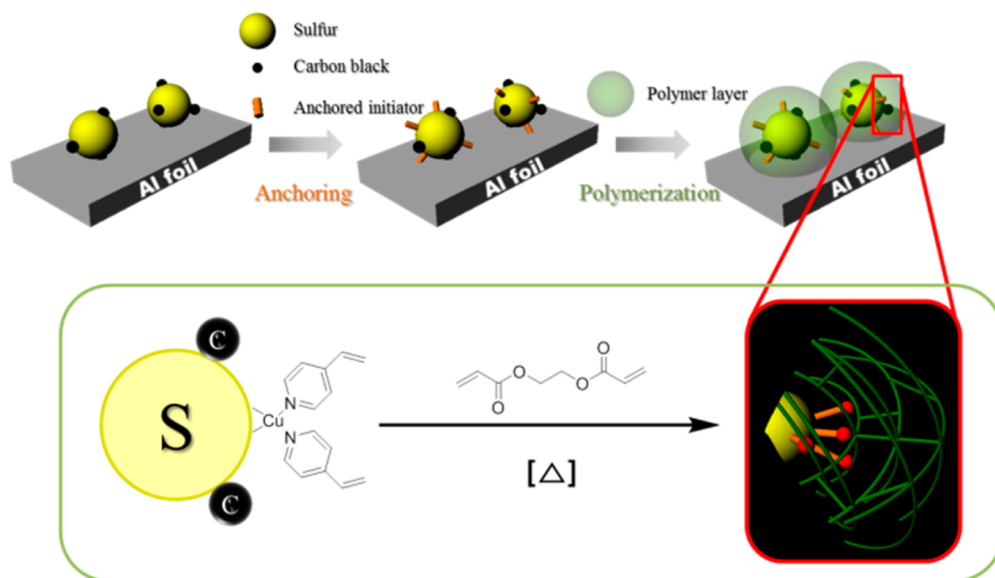


Figure 1. Schematic illustration for the preparation of the Cu-anchored cross-linked polymer-coated sulfur electrode.

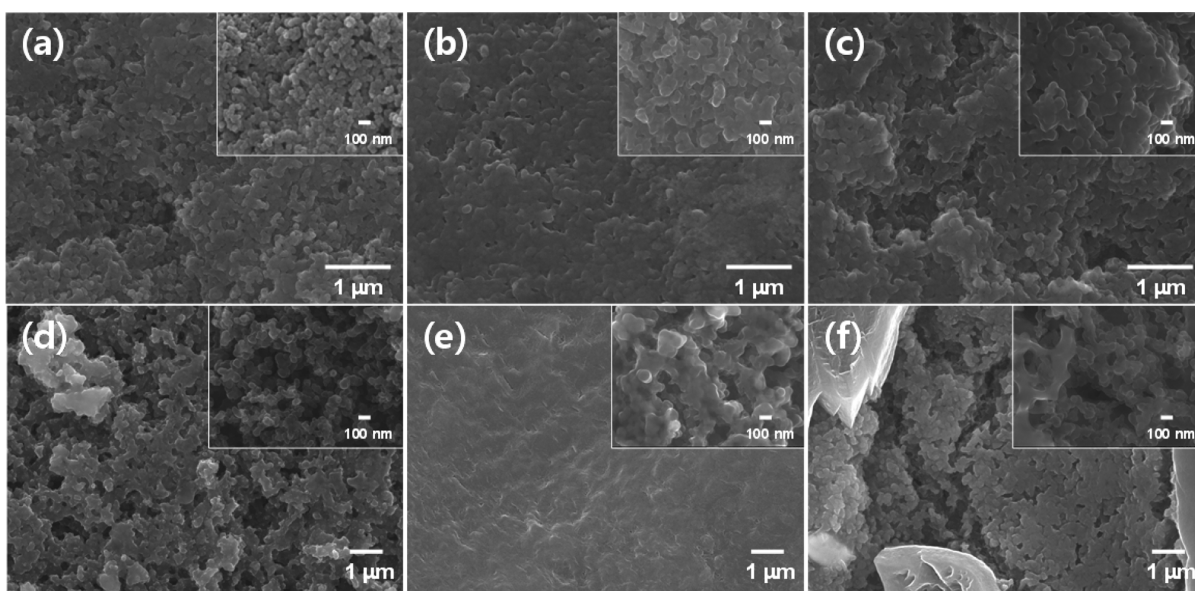


Figure 2. (a) SEM images of uncycled bare sulfur, (b) after Cu-anchored cross-linked polymer coating, (c) nonanchored cross-linked polymer coating, (d) cycled electrode of bare sulfur, (e) CAPC, and (f) NAPC sulfur electrodes, with the inset showing the high-resolution images.

copper. In other words, our approach is based on “chemical” modification of active sulfur species, which is originated from strong coordination chemistry between electrophilic Cu and nucleophilic S element. This means that loss of active sulfur species can be reduced and therefore it will be effective for long-term cycling of the Li–S cell. Another unique feature of our system is that we applied the polymer coating on the sulfur electrode rather than on the sulfur particles, suggesting that this method can be beneficial in terms of industrial processability. With these considerations in mind, the polymer-coated sulfur electrode was characterized and its electrochemical performances for LIBs were evaluated.

Figure 1 shows a schematic illustration of the preparation of the sulfur–carbon black (with a 2:1 ratio by weight) composite electrode anchored with Cu(I)Br and 4-vinylpyridine initiator (4.6 and 1.9 mol %, respectively), followed by surface-induced thermal cross-linking polymerization using a solution contain-

ing 12 wt % ethylene glycol diacrylate (EGD) cross-linker in CH_3CN . More information on the experimental methods is described in the Supporting Information. For comparison, a cross-linked polymer-coated sulfur electrode was also prepared under the same conditions, but without the use of Cu(I)Br, which produced a polymer that only physically coated the sulfur electrode without forming chemical bonds.

The anchored copper-4-vinylpyridine complex on the sulfur–carbon composite electrode was analyzed by both FT-IR and Raman spectroscopic methods (see Figures S1 and S2 in the Supporting Information). (The sulfur–carbon composite electrode will hereinafter be referred to as the “sulfur electrode”.) The characteristic IR peak corresponding to the vinyl group was monitored at 1605 cm^{-1} . Peaks corresponding to the Cu–S bond at 360 cm^{-1} , Cu–N bond at 1404 cm^{-1} , and C=C bond at 1609 cm^{-1} were observed in the Raman spectra,

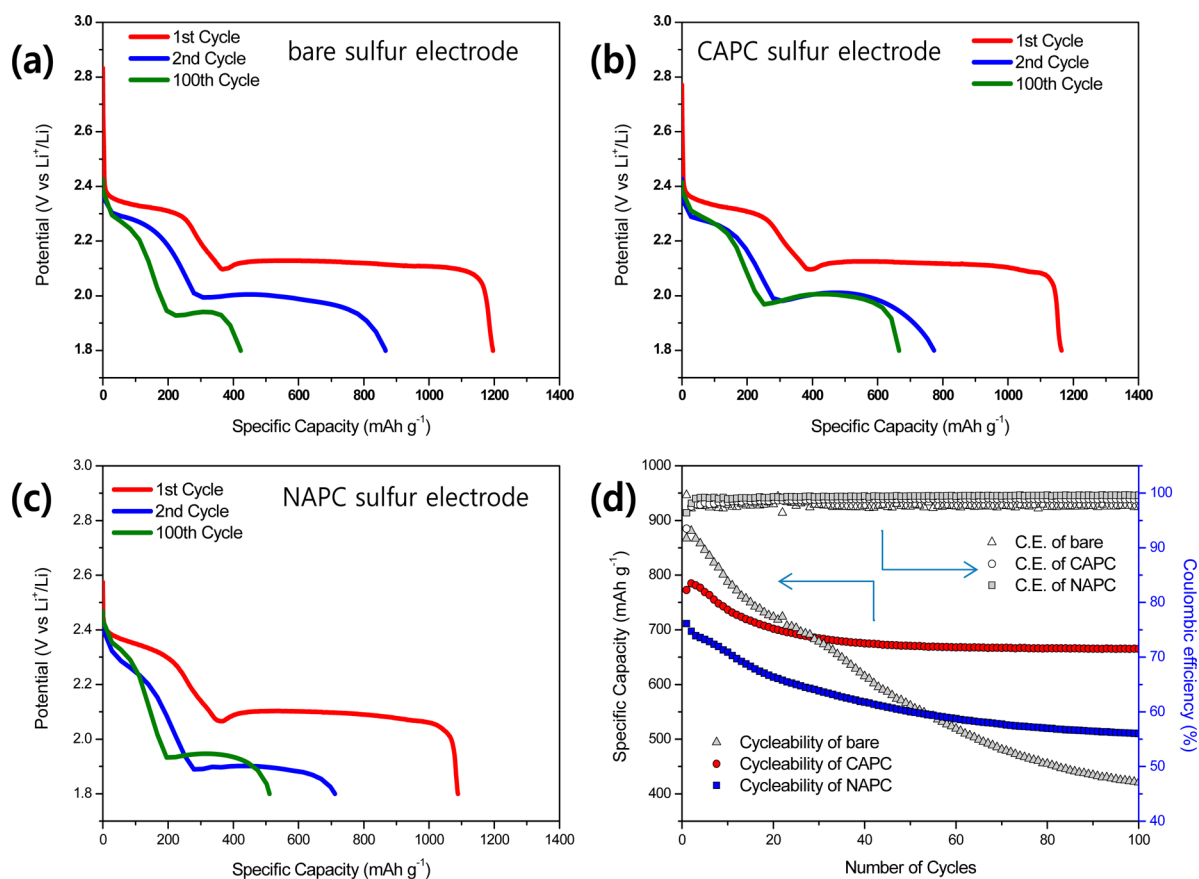


Figure 3. Electrochemical characterization of the sulfur electrodes between 1.8 and 2.6 V versus Li/Li^+ . Discharge voltage profiles at first, second, and 100th cycles of (a) the bare sulfur (BS) electrode, (b) Cu-anchored polymer-coated (CAPC) sulfur electrode, and (c) nonanchored polymer-coated (NAPC) sulfur electrode. (d) Cycling performance and Coulombic efficiency of the sulfur electrodes at high current density of 3.35 A g^{-1} after the initial slow charge and discharge.

clearly indicating that the desired S–Cu-vinylpyridine complex was successfully formed.

The subsequent cross-linked polymer film, produced by reaction between the 4-vinylpyridine initiator and the EGD cross-linker, was monitored by SEM and EDS (Figure 2 and Figure S3 and Table S1 in the Supporting Information). Anisometric growth of the polymer layer was observed, and decreased sulfur, together with increased carbon and oxygen wt %, was obtained for this chemically anchored polymer-coated (CAPC) sulfur electrode. Similar results were obtained for the nonanchored polymer-coated (NAPC) electrode, indicating that the cross-linked polymer effectively covered the sulfur electrodes without the use of Cu(I)Br anchoring medium. Without anchoring to copper, however, the NAPC is believed to only physically coat the sulfur electrode without chemical interaction with sulfur. Slightly less even coating was observed for the NAPC electrode in the SEM (Figure 2c), and the chemically anchored coating is expected to be more stable than nonchemically anchored counterpart after the cycling because of the physical breakdown from the large volume change of the sulfur and the harsh electrochemical condition. The morphology of the sulfur electrodes was further analyzed by SEM to support our assumption (Figure 2d–f). As expected, the surface-analysis revealed that the coating on the CAPC (Figure 2e) was highly preserved, but the surface morphology of the NAPC (Figure 2f) was close to that of the bare sulfur electrode (Figure 2d) because of the disintegration of the surface polymer coating.

The galvanostatic electrochemical performances of both the chemically anchored, i.e., CAPC, and physically covered, i.e., NAPC, cross-linked polymer-coated sulfur electrodes were investigated at room temperature using a Li/S cell (2032-type coin cell), and were compared with those of the bare sulfur (BS) electrode. Figure 3a–c shows the discharge voltage curves of Li/S batteries for the BS (Figure 3a), CAPC (Figure 3b), and NAPC (Figure 3c) electrodes.

At the initial cycle (under the current of 0.168 A g^{-1} , which corresponds to 0.1C rate), all prepared electrodes displayed the high reversible capacities (up to 1221 mA h g^{-1}). With the pristine bare sulfur (BS) electrode, the two typical plateaus of the sulfur electrode were found at the first discharge (by decreasing the potential gap) at around 2.3 and 2.1 V with respect to Li/Li^+ because of the formation of the soluble long-chain lithium polysulfides and insoluble $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$, respectively (Figure 3a).¹⁷ The CAPC and NAPC sulfur electrodes showed similar patterns, indicating that they also accommodate large amount of lithium ions in the same way as does the pristine BS electrode (Figure 3b, c). Furthermore, other plateaus corresponding to unfavorable irreversible electrochemical side reactions were not observed for CAPC and NAPC electrodes. This result clearly suggests that the additional polymer-coated layers were electrochemically stable in the potential range of the Li/S system. Another important observation is that the first discharge specific capacities of the polymer-coated samples (CAPC and NAPC) were almost the same as that of the pristine sample (BS), which suggests that the coating layers did

not block lithium ions from passing through them to react with the buried active sulfur material.

Even at the high current density of 3.35 A g^{-1} (2C rate) for cycling, they showed excellent specific capacity at the subsequent cycles after the first cycle (up to 865 mAh g^{-1} , comparable to the result reported in the literature).^{24–26}

In addition, compared to the bare sulfur (BS) electrode, the Coulombic efficiencies of the coated electrodes (CAPC and NAPC) were higher, and reached almost 100% (Figure 3d). The irreversible capacity is thought to originate from loss of the active material after the large volume change of the sulfur electrode, and the polymer-coated layer effectively reduced those unfavorable phenomena with regards to energy efficiency. These passivation effects of the polymer coatings were also effective during consequent cycling, reflecting high Coulombic efficiency over many cycles.

Figure 3d also shows how the layers of polymer coating on the sulfur electrode can greatly affect the capacity retention. At the first cycle, after the formation cycle at 0.1C, the BS exhibited 869 mAh g^{-1} , and this was followed by the CAPC with 775 mAh g^{-1} , and the NAPC with 711 mAh g^{-1} . The specific capacities of the polymer coated samples were not as high as that of the BS due to the resistivity of the extra surface layer. The higher capacity of CAPC than that of NAPC was ascribed to the fact that the CAPC formed more homogeneous and uniform surface coating compared to NAPC caused by the presence of the chemical bonding and the prevention of the polymer aggregation on the surface of electrodes for CAPC. However, the obtained specific capacity of BS sample rapidly fell as the number of cycles increased due to an increased polarization caused by the loss of conducting path and active materials, together with an increased resistance of the surface to migration of lithium ions by formation of inactive film generated by the dissolved lithium polysulfides.^{4,25} Overall, the specific capacity of the bare sulfur sample was exceeded by those of the polymer-coated samples (CAPC and NAPC) after several tens of cycles, indicating that the polymer coatings on the sulfur, by stabilizing the surface, were effective in maintaining cyclability.

Furthermore, the strong chemical bonds formed between the polymer and the sulfur electrode in the Cu-anchored polymer-coated sample and the much better cyclability of this sample (CAPC) than that of the nonanchored polymer-coated sample (NAPC) are indicative of the importance of the surface mechanical strength of the coating layer. The volume of lithiated sulfur indeed shrinks when the sulfur is recovered by delithiation. In the case of the NAPC sample, the polymer coating, which in this sample merely physically entraps the sulfur particles of the electrode, could be disintegrated during cycling, causing lower stability and hence lower cyclability.

The AC impedance spectra represented as a Nyquist plot were monitored for the Cu-anchored polymer-coated (CAPC) sample to further address the enhanced electrochemical performance of the coated sample after cycling, and were compared with those of the bare sulfur (BS) sample (Figure S4 in the Supporting Information). It was previously reported that the diameters of the semicircles at the high-frequency and low-frequency regions are attributable to the charge-transfer resistance and the interfacial resistance, respectively, and the perpendicular line reflects ion diffusion into the electrode.²⁴ Both polymer-coated (CAPC) and bare sulfur (BS) electrodes revealed two distinct semicircles, but the CAPC electrode maintained a lower interfacial resistance even after 100 cycles,

whereas a considerable increase of interfacial resistance was observed for the pristine BS sample. This observation may be ascribed to the improved surface stability for the CAPC electrode, and the data from the AC impedance correspond to the result of above-mentioned electrochemical performances of the Li/S cell.

One of the most significant requirements of an Li/S system is that the electrode holds on to the active material so that this active material does not dissolve into the electrolyte. The effect of polymer coating on inhibition of lithium polysulfide dissolution was therefore investigated as follows: the Cu-anchored polymer-coated (CAPC) sulfur electrode was disassembled when it was half-discharged, and stored in the electrolyte for 6 h (see the Supporting Information for more information on the experimental methods); the electrolyte was then filtered using a membrane filter to eliminate undissolved active materials, which could prevent an accurate determination of the concentration of dissolved sulfur; and the amount of sulfur in the clear filtered solution was finally determined using inductively coupled plasma (ICP) spectroscopy. The same experiment was carried out with the BS electrode for comparison, and it was found that the sulfur concentration in the electrolyte was much lower for the CAPC sample than for the BS counterpart (Table S2 in the Supporting Information), indicating that the chemically anchored polymer coating successfully prevented direct contact between the sulfur and the electrolyte or adsorbed the soluble lithium polysulfides. These results show that the dense polymer film on the sulfur electrode prevented migration of the soluble lithium polysulfide, thus resulting in a decrease in the loss of active materials.

In summary, a polymer-coated sulfur electrode has been successfully prepared by using simple surface-induced cross-linking polymerization, initiated by a reactive species anchored to a sulfur electrode via coordination through copper. This novel modified Li–S cell revealed excellent electrochemical performances for LIBs. Even after 100 cycles, more than 85% of the specific capacity was retained for this chemically anchored polymer-coated sulfur electrode, and much lower capacities were obtained for both the bare sulfur electrode and for the electrode in which the polymer coating merely physically covered the sulfur rather than chemically bonded with it. In addition, the ICP experiment demonstrated that the chemically anchored surface-coated polymer film effectively blocked the dissolution of active material into the electrolyte. We believe that our inexpensive and efficient method paves the way for the realization of an effective Li/S battery.

■ ASSOCIATED CONTENT

📄 Supporting Information

Detailed experimental procedures, characterizations, and further electrochemical properties are included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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