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Enhanced Cyclability of Li/Polysulfide Batteries by a Polymer-Modified Carbon Paper Current Collector

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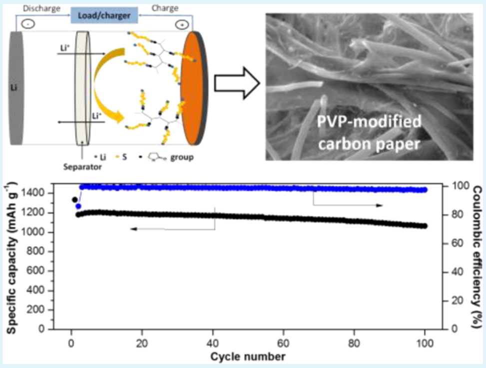
ABSTRACT: Lithium−sulfur (Li−S) batteries are considered to be the next-generation rechargeable systems due to their high energy densities and low cost. However, significant capacity decay over cycling is a major impediment for their practical applications. Polysulfides Li_2S_x ($3 < x \leq 8$) formed in the cycling are soluble in liquid electrolyte, which is the main reason for capacity loss and cycling instability. Functional polymers can tune the structure and property of sulfur electrodes, hold polysulfides, and improve cycle life. Herein, we examine a polyvinylpyrrolidone-modified carbon paper (CP-PVP) current collector in Li/polysulfide cells. PVP is soluble in the electrolyte solvent, but shows strong affinity with lithium polysulfides. The retention of polysulfides in the CP-PVP current collector is improved by ~50%, which is measured by a linear sweep voltammetry method. Without $LiNO_3$ additive in the electrolyte, the CP-PVP current collector with 50 μg of PVP can significantly improve cycling stability with a capacity retention of >90% over 50 cycles at C/10 rate. With $LiNO_3$ additive in the electrolyte, the cell shows a reversible capacity of >1000 mAh g^{-1} and a capacity retention of >80% over 100 cycles at C/5 rate.



KEYWORDS: *lithium−sulfur battery, polyvinylpyrrolidone, carbon paper, current collector, electrochemical performance*

1. INTRODUCTION

Rechargeable lithium−sulfur (Li−S) batteries, which were first developed in 1960s, have become an important focus of energy storage research over the past decades because of the high specific capacity of the sulfur cathode (i.e., 1672 mAh g^{-1}) and high theoretical specific energy (i.e., 2600 Wh kg^{-1}).[1−3] Comparing to Li-ion batteries with limited capacities (100−250 mAh g^{-1}) of transition metal oxide cathodes,[4] Li−S batteries have the potential to provide 2−3 times higher specific energies, e.g., 300−500 Wh kg^{-1}. In addition, sulfur has several appealing characteristics such as low cost, abundance, and environmental benignity. However, the commercial applications of Li−S batteries are not quite successful despite that many significant improvements have been made in the past decades. The major challenges include poor cycling performance, low active material utilization, shuttle phenomenon of dissolved polysulfides, and low Coulombic efficiency.[2] To overcome these challenges, many approaches, including the development of sulfur−carbon nanocomposites,[5−11] modification of cell component and configuration,[12−16] and introducing functional polymers in sulfur cathodes to hold polysulfides,[17−26] have been developed for improving the electrochemical performance of Li−S batteries.

As polysulfides are polar species, functional polymers instead of polytetrafluoroethylene (PTFE) or polyvinylidene fluoride (PVdF) binders can have tremendous benefits for improving the property and performance of sulfur electrodes.[27] For example, alternative binders such as poly(ethylene oxide) (PEO) or poly(acrylic acid) (PAA) have been used in sulfur electrodes and have shown improved cycling performance.[28−30] Polyvinylpyrrolidone (PVP) has been confirmed to have strong affinity with lithium polysulfides and lithium sulfide, which can improve cycling performance of lithium sulfide electrodes.[18] As lithium polysulfides can be synthesized *ex situ* and a binder-free carbon paper (CP) current collector can ensure high utilization of sulfur in Li/polysulfide cells,[31] this system can be used as a platform for studying polymer-modified current collectors to correlate the relationship between functional polymers and cell performance.

Herein, we report a study on PVP as a functional polymer in CP current collectors in Li/polysulfide cells. PVP can be dissolved in the electrolyte solvent and exhibits strong affinity with lithium polysulfides, which can reduce the diffusion of polysulfides. The retention of polysulfides in PVP-modified CP collector collectors was evaluated by a linear sweep voltammetry method, which can be used to quantify how much polysulfides are held in the current collectors and linked to the battery cycling performances. This study demonstrates

Received: July 10, 2015
Accepted: August 25, 2015
Published: August 25, 2015

DOI: 10.1021/acsami.5b06214
ACS Appl. Mater. Interfaces 2015, 7, 20369−20376

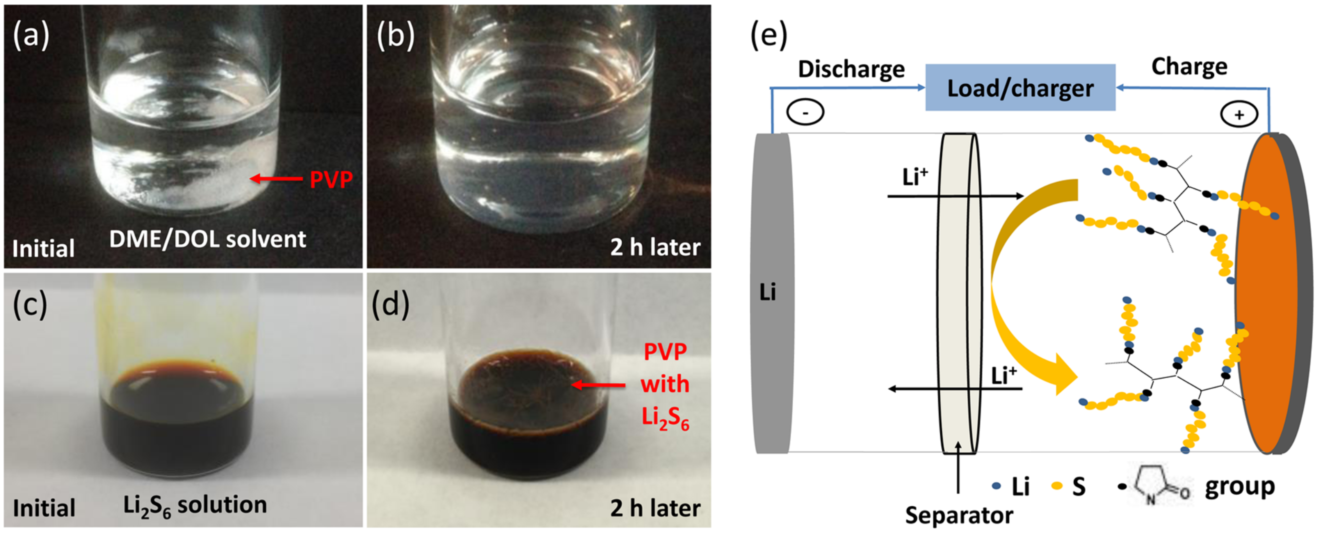


Figure 1. (a) Photograph showing PVP powder in the dimethoxy ethane (DME)/1,3-dioxolane (DOL) (1:1 v/v) mixture solvent. (b) Photograph showing PVP completely dissolved in the DME/DOL solvent after 2 h. (c) Photograph of a polysulfide solution of 0.25 M Li_2S_6 in the blank electrolyte. (d) Photograph showing PVP in the polysulfide solution forming separated viscous phases after 2 h. (e) Schematic showing that polysulfides are retained in the CP-PVP current collector in a Li/polysulfide cell.

that functional polymers like PVP are beneficial for Li/polysulfide cells to achieve improved cyclability.

2. EXPERIMENTAL SECTION

2.1. Preparation of Liquid Electrolytes. The blank electrolyte used in this study was prepared by dissolving lithium trifluoromethanesulfonate ($LiCF_3SO_3$, 98%, Acros Organics) in a mixture of dimethoxy ethane (DME, 99+%, Acros Organics) and 1,3-dioxolane (DOL, 99.5%, Acros Organics) (1:1, v/v) by magnetic stirring to render a 1.0 M $LiCF_3SO_3$ solution. Another electrolyte containing lithium nitrate ($LiNO_3$) additive was prepared by dissolving an appropriate amount of $LiNO_3$ (99+%, Acros Organics) in the blank electrolyte to render a 0.1 M $LiNO_3$ solution. To prepare the polysulfide catholyte, stoichiometric amounts of sulfur powder (S, Alfa Aesar) and lithium sulfide (Li_2S, Sigma-Aldrich) were mixed in a proper amount of the blank electrolyte or the electrolyte with $LiNO_3$ additive by magnetic stirring overnight at room temperature to render a 0.25 M Li_2S_6 solution. The electrolyte and polysulfide solution were prepared in an argon-filled glovebox.

2.2. Preparation of PVP Solutions. To prepare PVP solution, an appropriate amount of PVP (M_w = 1 300 000, Acros Organics) was dissolved in anhydrous ethanol (200 proof, 99.5%, Sigma-Aldrich) in the glovebox by magnetic stirring at room temperature. Three PVP solutions with different concentrations were prepared and used in this study; they are 0.065, 0.13, and 0.25 wt %.

2.3. Modification of Carbon Paper Current Collectors. Commercial binder-free carbon paper (CP) called buckypaper (Buckeye Composites) was used as the current collector in this study. The CP was cut into ~1 cm^2 discs (about 2.0 mg each) and dried at 100 °C for 24 h in a vacuum oven before use. To modify the CP current collector with PVP, a solution filtration method was used. A 50 μL aliquot of PVP solution was added into a CP disc slowly until all the solution was soaked in the paper; then, the disc was dried on a hot plate at 40 °C for 12 h in the glovebox to remove ethanol. The amounts of PVP in the CP are approximately 25, 50, and 100 μg, respectively, for the PVP solutions of 0.065, 0.13, and 0.25 wt %. These three PVP-modified CP current collectors are designated as CP-PVP-25, CP-PVP-50, and CP-PVP-100, respectively.

2.4. Morphological Characterizations. The morphological characterizations of the CP and CP-PVP current collectors and cycled electrodes were conducted with a JEOL JSM-7800F field emission scanning electron microscope (SEM). The elemental mappings were performed with energy-dispersive X-ray spectroscopy (EDX) attached to the SEM.

2.5. Cell Assembly. CR2032 coin cells were used to evaluate the blank CP and CP-PVP current collectors. These cells were assembled in the glovebox. To prepare the control cell, 20 μL of 0.25 M Li_2S_6 polysulfide catholyte (sulfur content: 0.96 mg) was added into a CP current collector, and then a Celgard 2400 separator was placed on the top of the carbon paper. Next, 20 μL of the blank electrolyte was added on the separator. Finally, the lithium metal anode was placed on the separator. The cell was crimped and taken out of the glovebox for testing. The same cell assembly procedures were used for the CP-PVP current collectors. Some cells were made with the blank electrolyte and polysulfide catholyte without $LiNO_3$ for studying the effect of PVP on cycling performance. The others were made with $LiNO_3$ additive in the electrolyte and polysulfide catholyte for evaluating long cycle life.

2.6. Electrochemical Measurements. Linear sweep voltammetry was performed to evaluate polysulfide retention in the blank CP and CP-PVP current collectors. The working principle and cell configuration were described in a previous publication from our group.[32] To prepare the cell, a piece of lithium metal was used as a counter and reference electrode in a homemade Swagelok cell. A piece of blank CP or CP-PVP current collector filled with 0.25 M Li_2S_6 polysulfide solution was placed on the top of a lithium metal reference electrode. A Celgard 2400 separator was placed on the top of the current collector to separate the carbon paper and working electrode, which is a stainless steel current collector. To minimize the polysulfide consumption due to the reaction with the lithium metal, all cells were tested within 10 min after assembling. The polysulfide in the current collector is in great excess, which can ensure the accuracy of this measurement. Voltage was swept from open-circuit voltage (OCV) to 4.5 V at a scan rate of 1 mV s^{-1} with a Bio-Logic potentiostat.

The cells without $LiNO_3$ additive were galvanostatically charged to 3.0 V and discharged to 1.5 V on an Arbin battery cycler with a 5 min rest time between cycles. For the cells with $LiNO_3$ additive, the discharge cutoff voltage was 1.8 V to avoid the reduction of $LiNO_3$.[33] All the cells were tested on the battery cycler without resting to minimize self-discharge. The C-rate used for cycling measurements was based on the mass of sulfur in the polysulfide catholyte in the current collectors (1C = 1672 mA g^{-1}). The specific capacity values shown in this paper are calculated by dividing the capacities obtained by the mass of sulfur. Cyclic voltammetry (CV) was performed on a Bio-Logic VSP potentiostat between 1.5 and 3.0 V at a scanning rate of 0.05 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) data were collected with a Bio-Logic VSP impedance analyzer in the frequency

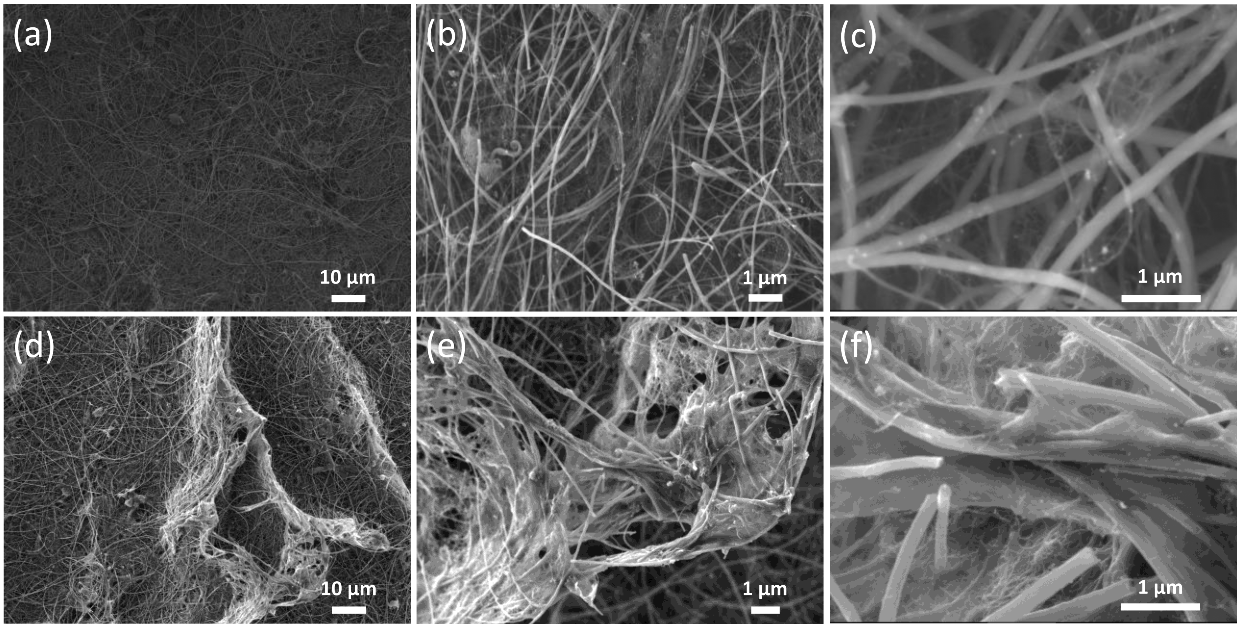


Figure 2. (a−c) SEM images of the blank CP current collector. (d−f) SEM images of the CP-PVP-50 current collector.

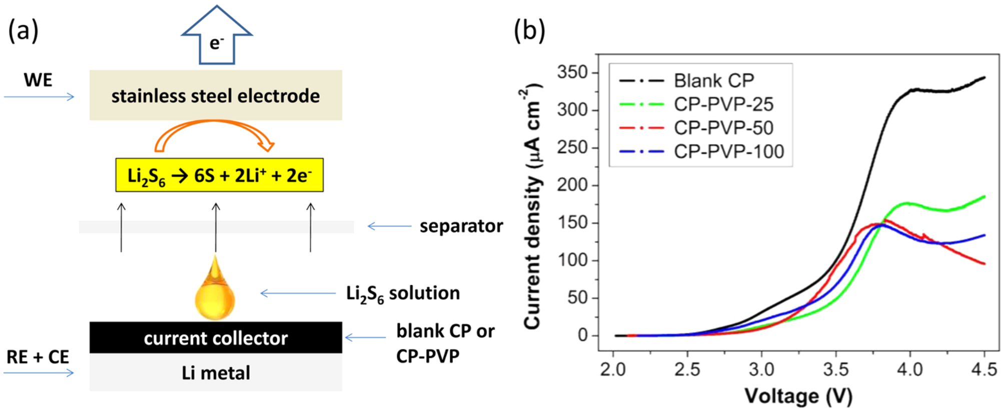


Figure 3. (a) Schematic of the experimental cell and working principle of the linear sweep voltammetry method for the evaluation of polysulfide retention in the blank CP or CP-PVP current collector, which is a reservoir for the polysulfide solution in the experiment. (b) Current density−voltage profile of cells with the blank CP, CP-PVP-25, CP-PVP-50, CP-PVP-100 current collectors.

range of 200 kHz−0.1 Hz on cells which were cycled on the Arbin battery cycler at *C*/5 in between these tests.

3. RESULTS AND DISCUSSION

Figure 1 shows the assessment of PVP's solubility in the electrolyte solvent and polysulfide solution. At initial, an appropriate amount of PVP powder was added in the DME/DOL (1:1 v/v) mixture solvent, as shown in Figure 1a. Two hours later, the PVP was completely dissolved in the solvent, forming a homogeneous solution, as shown in Figure 1b. This solution is transparent, and the viscosity is slightly increased. Figure 1c shows a polysulfide solution of 0.25 M Li_2S_6 in the blank electrolyte. After PVP was added in the polysulfide solution, floccules with separated viscous phases were formed, as shown in Figure 1d. This phenomenon indicates that PVP could form complexes with lithium polysulfides due to the affinity between them, which can increase viscosity and reduce flowability of the polysulfide solution. This result led to the study of PVP-modified CP current collectors in Li/polysulfide cells. The schematic in Figure 1e depicts the interaction between PVP and lithium polysulfides, which can enhance the retention of polysulfides in the current collector and reduce the shuttle of polysulfides to the lithium metal anode in a Li/polysulfide cell.

The morphology of the blank CP and CP-PVP current collectors was examined by SEM, as shown in Figure 2. It can be seen that the blank CP current collector has a flat surface, which is made of weaving carbon nanotubes (CNTs) and carbon nanofibers (CNFs), as shown in Figure 2a−c. The ultralong length and curved shape of CNFs enable the free-standing characteristic of the CP current collector. The large voids between CNTs and CNFs provide space for holding additional polymers and polysulfide catholyte. After a small amount (1.2−5.0 wt %) of PVP was added into the CP current collector by the solution filtration process, the surface becomes uneven, as shown in Figure 2d, which is due to the evaporation of ethanol. The magnified SEM images clearly show the presence of PVP within the CNT/CNF network, as shown in Figure 2e,f. This long chain polymer with an M_w of ∼1 300 000 acts as a glue bonding the CNTs and CNFs and fills some space among them. The PVP in the CP current collector changes the

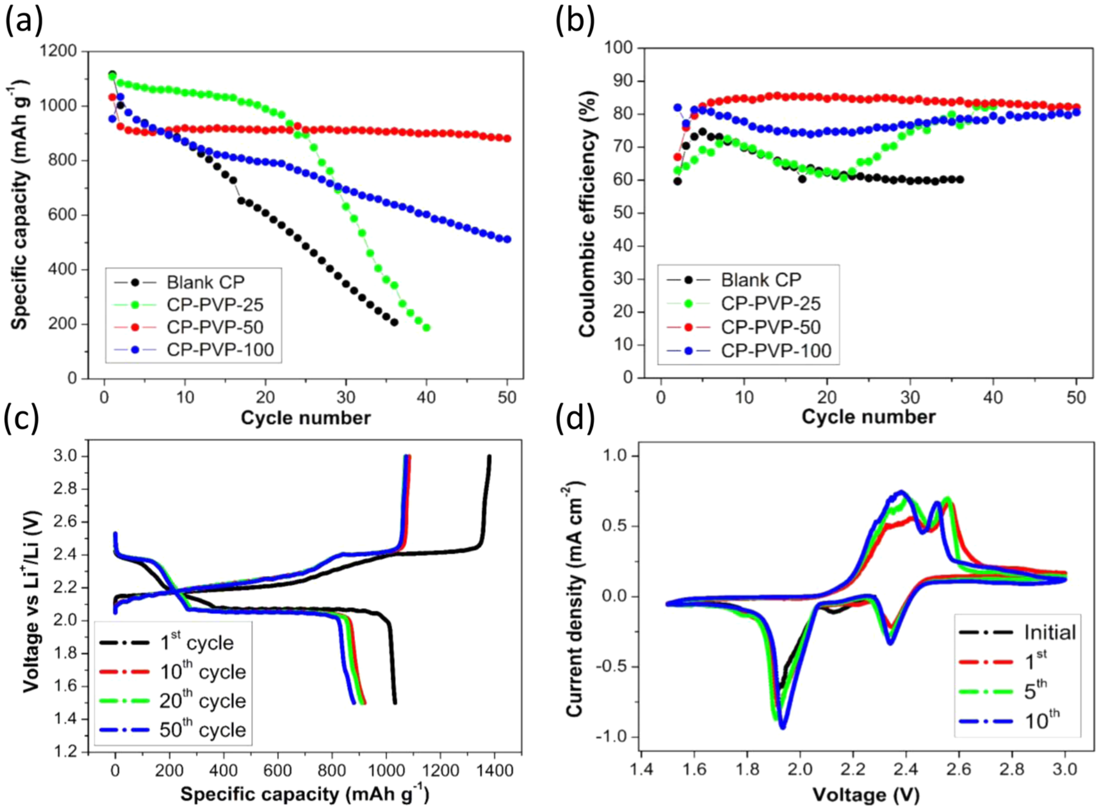


Figure 4. (a) Cyclability and (b) Coulombic efficiency of the cells with the blank CP and CP-PVP current collectors without $LiNO_3$ additive in the electrolyte at *C*/10 rate. (c) Voltage vs specific discharge capacity profiles of the 1st, 10th, 20th, and 50th cycles of the cell with the CP-PVP-50 current collector at *C*/10 rate. (d) Cyclic voltammograms of the cell with the CP-PVP-50 current collector at a potential sweep rate of 0.05 mV s^{-1} between 1.5 and 3.0 V.

inner porosity and morphology, therefore affecting its affinity with lithium polysulfides.

To evaluate the retention of polysulfides in the CP-PVP current collector, linear sweep voltammetry was performed on a designed cell, as shown in Figure 3a. This experiment can be used to evaluate the transport of polysulfides through separators, and it also can be used to evaluate the affinity property of CP current collectors to lithium polysulfides. Under an increasing sweeping potential, polysulfide anions can diffuse out of the CP current collector, migrate through the separator, and get oxidized on the working electrode to produce an anodic current, which can be measured by the potentiostat. The current measured is strongly related to the separator structure, polysulfide solution, and current collector.[32] Figure 3b shows the oxidation current density as a function of sweeping potential obtained with the blank CP and CP-PVP current collectors. The sweeping potential starts at OCV and ends at 4.5 V. Polysulfides are oxidized when the potential is above 2.5 V. The current density measured with the blank CP current collector increases significantly and reaches a peak at 325 μA cm^{-2} and then levels off, which indicates that the oxidation of polysuflides migrated through the separator is stabilized. In contrast, the current density peaks with the CP-PVP current collectors are only half of the former. The affinity between PVP and lithium polysulfides significantly enhances the retention of polysulfides in the CP-PVP current collector, reducing the oxidation current measured. With various amounts of PVP in the CP current collector, the current profile is similar. The charge in coulombs due to the oxidation of polysulfides is proportional to the area under the current curves. The areas of all CP-PVP current collectors under the curves are approximately 50% of that of the blank CP current collector, indicating that almost half the lithium polysulfides are retained in the paper due to the presence of PVP. This result demonstrates that PVP can help retain polysulfides in the CP-PVP current collectors. The CP-PVP-25 shows a slightly higher current and larger area under the curve than those of the CP-PVP-50 and CP-PVP-100. In contrast, the current obtained with the CP-PVP-50 is quite similar to that obtained with the CP-PVP-100. This means that only 50 μg of PVP is sufficient for holding most lithium polysulfides in this case.

The cell performance of the control cell with the blank CP current collector and those with CP-PVP current collectors are compared in Figure 4a. It can be seen that the control cell shows a high initial discharge capacity of 1100 mAh g^{-1}, but a continuous decrease to 200 mAh g^{-1} after 36 cycles. The Coulombic efficiency shown in Figure 4b follows an increase-then-decrease trend and ends at 60% after 36 cycles. The large voids in the CP paper cannot hold polysulfides, resulting in continuous loss of active material in the cathode. The capacity fade also results from the degradation of the lithium metal anode due to polysulfide corrosion. Without $LiNO_3$ additive in the electrolyte, the Coulombic efficiency is low due to the severe shuttle effect and continuous reduction of polysulfide on the lithium metal anode.[34] With 25 μg PVP in the CP current collector, the cell shows a high initial capacity of over 1100 mAh g^{-1} and relatively stable capacities over 20 cycles, followed by a significant capacity fade. The initial high capacities are enabled by the presence of PVP in the CP current collector. Over cycles, PVP cannot hold polysulfides anymore due to

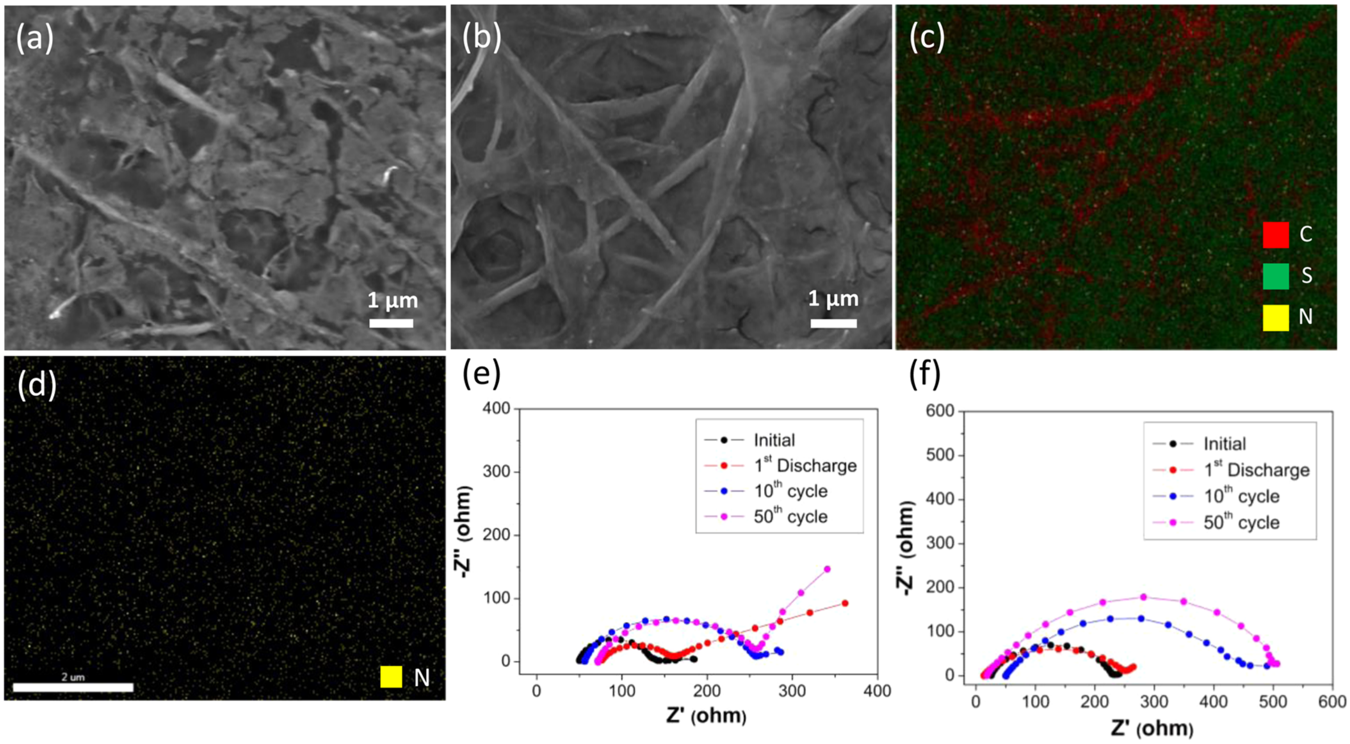


Figure 5. (a) SEM image of the blank CP current collector after 5 cycles. (b) SEM image of the CP-PVP-50 current collector after 5 cycles. (c) EDX elemental mapping of SEM image in (b). (d) Nitrogen elemental mapping of the SEM image in (b). (e) Nyquist plots of the control cell with the blank CP current collector after different cycles. (f) Nyquist plots of a cell with the CP-PVP-50 current collector after different cycles.

repeated deposition of insoluble sulfur and lithium sulfide, which could move PVP to dead spots in the current collector. When the PVP content increases to 50 μg, the cell shows an initial capacity of 1030 mAh g^{-1} and a stable capacity of over 900 mAh g^{-1} from the 2nd to the 50th cycle. When the PVP content further increases to 100 μg, the cell shows a continuous decrease in the cycling profile, but it is still much better than the control cell. With too much PVP in the CP current collector, the conductivity of the current collector would decrease and the viscosity of the polysulfide catholyte would increase, which can affect the electrochemical reversibility of sulfur. All the cells with CP-PVP current collectors show higher capacities than the control cell. In addition, the Coulombic efficiencies of these cells are higher than that of the control cell. These results demonstrate that the PVP in the CP current collector can improve the utilization of sulfur in Li/dissolved polysulfide cells, retention of polysulfide in the cathode, and Coulombic efficiency. The content of PVP can affect the complexes formed in the polysulfide catholyte, as shown in Figure 1d. More PVP would result in better retention of polysulfides in the electrode. However, dissolved PVP also changes the viscosity of electrolyte and conductivity in the current collector, which can affect the utilization of sulfur. An optimized content of 50 μg of PVP in this case leads to a good balance between the performance and affinity property of the CP current collector.

Figure 4c shows the voltage profile of the 1st, 10th, 20th, and 50th cycles of the cell with the CP-PVP-50. The cell can be discharged to 1.5 V since no $LiNO_3$ reduction occurs at low potential ($\leq$1.65 V). With the presence of PVP in the current collector forming complexes with polysulfides, the retention of polysulfides in the electrode is significantly enhanced; therefore, the shuttle effect can be suppressed, which can be evidenced from the improved cycling stability. The charge and discharge plateaus are very close to each other except for the 1st cycle, which indicates that PVP can be an efficient binder for holding polysulfides from rapid diffusion and loss from the cathode. In addition, no increased overpotential is observed over 50 cycles. The significant capacity decrease after the 1st cycle could be because the PVP-modified current collector has to optimize itself when the cathode reactions occur. After self-optimization, the current collector reached stability, leading to stable cycle life. Figure 4d shows the cyclic voltammogram (CV) of the cell with the CP-PVP-50. There are two cathodic peaks at 2.35 and 1.95 V corresponding to the reduction reactions of sulfur to low-order polysulfides and low-order polysulfides to Li_2S, and two distinguishable anodic peaks at 2.35 and 2.45 V, which indicate the transition of Li_2S to high-order polysulfides/sulfur.[31] The cell exhibits a stable CV profile over 10 cycles without decay of peak intensity.

Figure 5a,b shows the morphology of two cycled electrodes: one is the electrode with the blank CP current collector (Figure 5a), and the other one is with the CP-PVP-50 (Figure 5b). After 5 cycles, the electrode with the blank CP current collector shows many cracks, which are due to the repeated formation of charged and discharge products resulting in significant volume change. The blank CP cannot hold the active material and electrolyte together upon cycling. In contrast, the electrode with the CP-PVP-50 shows a very uniform morphology without cracks after 5 cycles. The CP current collector is uniformly filled and covered with discharged products and electrolyte. The EDX analysis shows that the sulfur element in lithium sulfide and lithium salt is uniformly distributed in the pores of the CP paper, as shown in Figure 5c. A small amount of nitrogen element can also be detected, as shown in Figure 5d, which can be only from the PVP since no $LiNO_3$ additive was

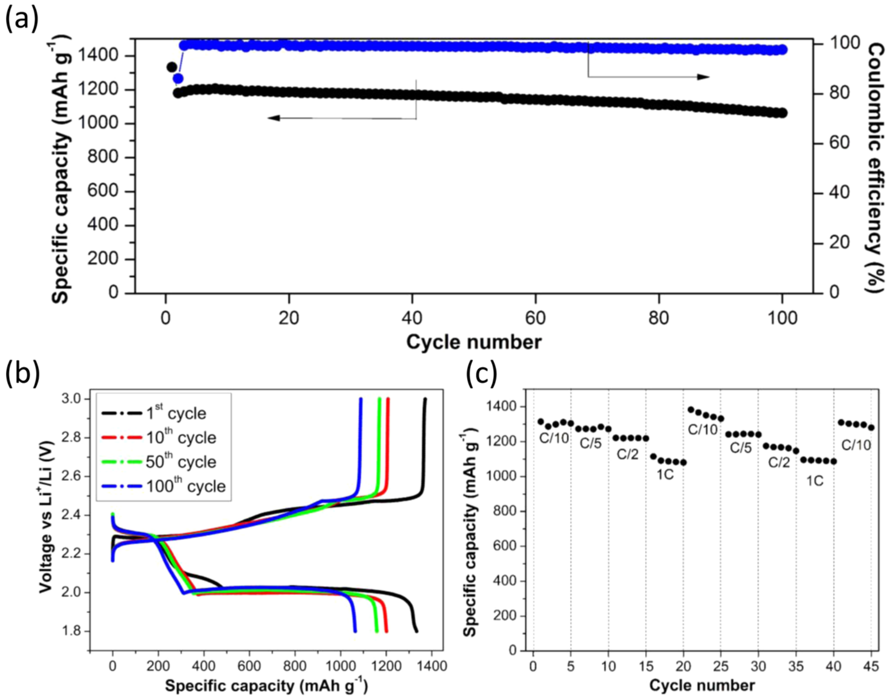


Figure 6. (a) Cyclability and Coulombic efficiency of the cell with the CP-PVP-50 current collector and 0.1 M $LiNO_3$ additive in the electrolyte at C/5 rate. (b) Voltage vs specific discharge capacity profiles of the 1st, 10th, 50th, and 100th cycles of the cell. (c) Cyclability of the cell at C/10, C/5, C/2, and 1C rates. The capacity values are in terms of the sulfur mass in the Li_2S_6 solution.

added in the polysulfide catholyte. It can be seen that PVP is also uniformly distributed across the electrode. The electrolyte-soluble PVP molecules can dynamically change their morphology to stabilize the electrode upon cycling, which is beneficial for maintaining a stable electrode in Li−S batteries.

Figure 5e,f compares the Nyquist plots of two cells with the blank CP and CP-PVP-50 current collectors. The impedances were measured after different cycles. The intercepts of Nyquist plots in the high-frequency regions are attributed to the bulk resistance of the liquid electrolyte, and the semicircles in the high-medium frequency regions are charge transfer resistances of the electrode/electrolyte interfaces.[17] The linear segment in the low-frequency region corresponds to the diffusion limitation within the electrodes. It can be seen that the cell with the CP-PVP-50 has a lower bulk resistance (26 ohms) but higher charge transfer resistance (206 ohms) than the cell with the blank CP current collector before cycling. PVP can hold polysulfides in the cathode side and reduce diffusion of polysulfides into the bulk electrolyte between the cathode and lithium metal anode, which helps maintain a low bulk resistance. However, its insulating property makes the charge transfer difficult at the electrode/electrolyte interface. After the 1st and 50th cycles, the bulk resistance slightly decreases when the CP-PVP-50 was used in the cell, whereas the bulk resistance significantly increases when the blank CP current collector was in the cell. After the 50th cycle, the charge transfer resistance increases from 94 to 186 ohms in the cell with the blank CP current collector and from 206 to 483 ohms in the cell with the CP-PVP-50.

To further improve the cycling performance, the CP-PVP-50 was tested with the electrolyte containing $LiNO_3$ additive, which can show a synergistic benefit. Figure 6a shows the cycling performance of the cell. A high initial discharge capacity of over 1300 mAh g^{-1} and a reversible capacity of 1200 mAh g^{-1} in the first 20 cycles were obtained. Afterward, the cell maintains an average capacity of about 1000 mAh g^{-1} for 80 cycles. The Coulombic efficiency is 95−99%. With $LiNO_3$ additive in the electrolyte, the lithium metal anode is passivated, which stops aggressive reduction of polysulfides, therefore improving capacity retention and Coulombic efficiency.[33] Figure 6b indicates the voltage profile of the 1st, 10th, 50th, and 100th cycles. After 100 cycles, the capacity is over 1000 mAh g^{-1} on the voltage profile. During the first 100 cycles, the capacity fade is only 0.25% per cycle and the voltage plateaus are relatively stable. The rate capability of the cell is shown in Figure 6c. A specific capacity of about 1300 mAh g^{-1} is achieved at C/10, and a specific capacity of 1250 mAh g^{-1} is achieved at C/5 rate. The specific capacity is around 1200 mAh g^{-1} at C/2 and 1100 mAh g^{-1} at 1C rate, respectively. When the rate was switched back to C/10 rate after 1C rate, the capacity is a little higher than that before. The slight capacity decay observed during the cycling is not permanent. After multiple C rate tests, the capacity at C/10 rate in the 3rd cycle is back to the high capacity level of more than 1200 mAh g^{-1}. These results show the good rate capability and reversibility of cells enabled by the PVP-modified CP current collectors with $LiNO_3$ additive in the electrolyte.

4. CONCLUSIONS

In summary, we have studied PVP-modified CP current collectors in Li/polysulfide cells. PVP is soluble in the electrolyte solvent, but it can form complexes with lithium polysulfides because of the affinity between them, which can improve the retention of polysulfides in the current collector. About 50% of lithium polysulfide Li_2S_6 can be retained in the CP-PVP current collectors when only 50 μg of PVP was used, which is measured by the linear sweep voltammetry method. The PVP-modified CP current collectors can increase utilization of sulfur and Coulombic efficiency, enhance cycling stability, and maintain integrity of the electrode. Although PVP can increase charge transfer resistance in the cell due to its insulating property, it can help maintain a low bulk resistance by preventing polysulfides in the cathode from diffusing into the blank electrolyte. When the CP-PVP current collector worked with electrolyte containing $LiNO_3$ additive, a high reversible capacity of over 1000 mAh g^{-1} with a high Coulombic efficiency of close to 100% was achieved at C/5 rate for 100 cycles. This study demonstrates that functional polymers like PVP can optimize the property of CP current collectors, which can lead to improved cycling stability in Li/polysulfide cells.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the startup grant from the Purdue School of Engineering and Technology and Department of Mechanical Engineering at Indiana University-Purdue University Indianapolis (IUPUI). This work was also partially supported by the Enhanced Mentoring Program with Opportunities for Ways to Excel in Research (EMPOWER) grant from the Office of the Vice Chancellor for Research at IUPUI. We would like to acknowledge the Integrated Nanosystems Development Institute (INDI) at IUPUI for use of their JEOL7800F Field Emission Scanning Electron Microscope, which was awarded through NSF grant MRI-1229514.

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