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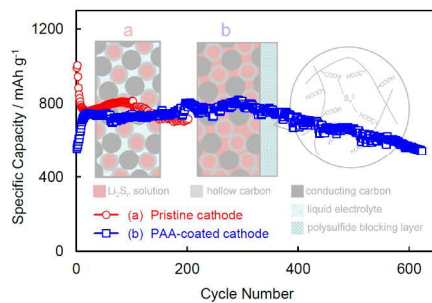
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A poly(acrylic acid) coated sulphur cathode significantly improves the cyclability of Li/S battery because resulting gel blocks the out-diffusion of lithium polysulphide via hydrogen-bonds.



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Paper

Poly(acrylic acid) gel as a polysulphide blocking layer for high performance lithium/sulphur battery

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Lithium/sulphur (Li/S) battery is the most promising electrochemical energy storage system beyond Li-ion, due to the high theoretical energy density and low cost of elemental sulphur. However, its development has been hindered by many problems in relation to the out-diffusion of dissolved lithium polysulphide (PS, Li_2S_n with $4 \leq n \leq 8$), the parts of sulphur reduction intermediates. In this paper we demonstrate a proof-of-concept for blocking the out-diffusion of the dissolved PS by employing a dual-layer structural sulphur cathode with a porous poly(acrylic acid) (PAA) membrane coated on the top surface. Upon activation of the liquid electrolyte, the porous PAA membrane becomes a gel and resulting gel chemically blocks the out-diffusion of PS anions by forming hydrogen-bonds between the $-\text{COOH}$ groups in the gelled PAA and the negatively charged PS anions. Verified visually by a potentiostatic polarization experiment at 1.7 V vs. Li/Li^+ , the out-diffusion of PS in an electrolyte-flooded Li/S cell is well blocked by the dual-layer structural sulphur cathode. As a result, the Li/S cell consisting of a dual-layer structural sulphur cathode exhibits much improved capacity retention while still providing the similar specific capacity, as compared with the cell using the conventional sulphur cathode.

1. Introduction

Considerable research interest has recently been in rechargeable lithium/sulphur (Li/S) battery because of the high theoretical energy density ($\sim 2600 \text{ Wh kg}^{-1}$), low cost and earth abundance of elemental sulphur.¹⁻⁴ These merits can be true only when the material process is cheap and the cathode is loaded with a high content of sulphur due to the low density of sulphur (2.07 g cm^{-3} at 0°C for the densest alpha-sulphur). By nature, sulphur and its reduction products are electrically insulating, which limits the utilization of sulphur active material and the rate capability of Li/S batteries. These drawbacks can be partially overcome by the high solubility of lithium polysulphides (PS, Li_2S_n with $4 \leq n \leq 8$), the parts of sulphur reduction intermediates, in organic liquid electrolyte, which transfers the cathode reaction from on a solid-solid (i.e., carbon-sulphur species) interface into on a solid-liquid (i.e., carbon-PS solution) interface.^{1,5} However, the dissolution of PS meanwhile raises many problems, including the loss of sulphur active material, low charging efficiency, high self-discharge rate, short cycle life as well as severe Li corrosion, because the dissolved PS diffuse out of the cathode and migrate across the electrolyte/separator into the anode where the PS chemically react with metallic Li or electrochemically reduce into shorter chain PS. As a solution to these problems, the sulphur-carbon composites based on various types of porous carbon materials have been intensely investigated to suppress the out-diffusion of the dissolved PS.^{2-4,6,7} In these composites, the dissolved PS are confined within the pores/hollows of carbon materials, and the interior walls of carbon pores/hollows serve as

the redox sites of the PS,^{6,7} as illustrated by Fig. 1a. Beside the extra cost of material and process, the improvement by this approach is achieved in exchange of the energy density because the composite introduces large amount of electrochemically inactive carbon and only these liquid electrolytes absorbed within the pores/hollows of carbon are accessible for the dissolution of PS. In fact, most of the liquid electrolytes in the cathode are present in the pores between the particles. For the maximized dissolution of the PS, the dissolved PS should be confined throughout the cathode, other than only within the pores of carbon particles, as illustrated by Fig. 1b. This concept has been successfully demonstrated by a PS-blocking layer in two types of designs: (1) applying a porous carbon layer to the top surface of sulphur cathode for absorbing the dissolved PS and serving as the additional redox sites of the PS,^{8,9} and (2) coating a cation-selective gel polymer electrolyte (GPE) onto the sulphur cathode¹⁰⁻¹³ or the conventional separator¹⁴⁻¹⁷ for blocking the out-diffusion of the dissolved PS. Of the cation-selective GPEs, commercially available Nafion polymer has been particularly selected as the polymeric host because of its easiness in gelation by the organic liquid electrolyte and high ionic dissociation in the resulting gel.¹⁴ However, the high cost of Nafion polymer limits its large scale application in the Li/S batteries. Moreover, the strong acidity of Nafion polymer could potentially initiate the ring-opening polymerization of 1,3-dioxolane, an essential solvent for the Li/S battery electrolytes, if the H^+ -formed Nafion polymer is used.

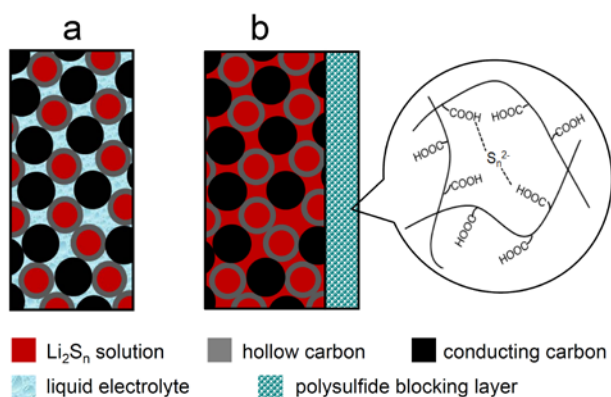


Fig. 1 Schematic concept for a polysulphide-blocking layer. (a) Pristine cathode, and (b) Dual-layer structural cathode with a PAA gel as the PS-blocking layer.

In order to retain the high energy density and low cost of Li/S batteries, in this work we developed a dual-layer structural sulphur cathode that has high sulphur loading ($>2 \text{ mg cm}^{-2}$ with 77 wt.% sulphur) and contains a porous poly(acrylic acid) (PAA) membrane on the top surface of the electrode. Such cathodes are suitable for the scale-up of fabrication, and are in low cost for both of the raw materials and process. Due to the highly porous structure, the liquid electrolyte can fast penetrate through the PAA membrane into the bulk of the sulphur cathode in the process of electrolyte activation, and the PAA membrane closes its pores upon the gelation by the liquid electrolyte. Unlike the Nafion polymer, PAA swells slightly and dissociates poorly in the organic liquid electrolyte. These features have made it suitable for a water-based binder of the sulphur cathode.^{18,19} However, the $-\text{COOH}$ groups in the gelled PAA are able to form hydrogen bonds with the PS anions, as schematically indicated by Fig. 1b, which chemically captures the PS anions and blocks the out-diffusion of the PS anions. In this paper, we present a proof-of-concept for the in-situ formed PAA gel as the PS-blocking layer in the liquid electrolyte Li/S battery.

2. Experimental

All chemicals were purchased from Sigma-Aldrich. Prior to use, dimethyl ether (DME) and 1,3-dioxolane (DOL) were dried over 4\AA molecular sieves for a week, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and LiNO_3 were dried at 110°C under vacuum for 10 h. A liquid electrolyte with a composition of 0.25 mol Kg^{-1} LiTFSI- 0.25 mol Kg^{-1} LiNO_3 dissolved in a 1:1 (wt.) DME/DOL mixed solvent was prepared in an argon-filled glove-box having a dew point of -90°C . A sulphur cathode consisting by weight of 77% sulphur, 10% Super-P carbon, 10% Ketjenblack EC-300JD carbon black and 3% binder was coated onto a carbon-coated aluminium foil by using poly(acrylonitrile-methyl methacrylate) (ANMMA, AN/MMA = 94:6, MW = 100,000, Polysciences, Inc.) as the binder and N-methyl pyrrolidinone as the solvent. On average, the cathode had a sulphur loading of 2 mg cm^{-2} . For making a dual-layer structural cathode, a 2 wt.% poly(acrylic acid) (PAA, MW = 3,000,000) solution was prepared by dissolving PAA powder into a 1:1 (wt.) water/isopropanol mixture. Resultant PAA solution was coated onto the top of a conventional sulphur cathode using a 10 milli-inch doctor blade, which resulted in a highly porous membrane with a PAA loading

of 0.35 mg cm^{-2} . Before use, the cathode was dried at 60°C under vacuum for 16 h.

Surface structure of the cathode was observed using a Quanta 200F scanning electron microscope (SEM), and electrochemical characterization of the cell was conducted on a Solartron SI 1287 Electrochemical Interface and a SI 1260 Impedance/Gain-Phase Analyzer. For potentiostatic polarization test, the same slurry as used in the cathode was coated onto a Ni strip by a simple dipping process, and the resulting cathode was potentiostatically polarized at $1.7 \text{ V vs. Li/Li}^+$ in an electrolyte-flooded cell. For cycling test, BR2335-type Li/S coin cell was assembled by using a Celgard 3401 membrane as the separator and activated with $20 \mu\text{L}$ liquid electrolyte. Before test, the cell was stored at 40°C for 2 h to allow the gelation of porous PAA membrane. Cyclic voltammetry was carried out by scanning at 0.2 mV s^{-1} from the cell's open-circuit potential (OCP), and ac impedance was measured at OCP in the frequency range from 0.01 to 100 kHz with an ac oscillation of 10 mV amplitude. The cell was galvanostatically cycled between 1.7 V and 2.8 V on a Maccor Series 4000 cyler.

3. Results and Discussion

Structure of sulphur cathode

Surface structure of the sulphur cathode is observed using SEM. Fig. 2 shows the SEM images of two types of sulphur cathodes. In the pristine cathode that contains 77 wt.% elemental sulphur (Fig. 2a), the large and irregular sulphur particles are partially surrounded by amorphous and highly porous carbon. In the PAA-coated cathode (Fig. 2b), however, most of sulphur particles and carbon are covered by a thin PAA membrane. Although this PAA membrane looks very dense in a detailed view (Fig. 2b, x2000), there are numerous cracks in view of the whole membrane (Fig. 2c, x50). A detailed view into the cracks indicates that the body of PAA membrane is highly porous (Fig. 2d, x2000). In the process of electrolyte activation, the cracks on the surface and the pores in the body of the membrane enable fast penetration of the liquid electrolyte throughout the cathode. A separate electrolyte penetration test shows no visible difference in the wettability between the pristine cathode and the PAA-coated cathode. Upon the activation of liquid electrolyte, the PAA membrane is gelled by storing the cell at 40°C for a certain time period, which makes the closure of the cracks and pores in the membrane, forming a dense and uniform PAA gel. In addition, it is shown that the crack and porosity of the PAA membrane are controllable by adjusting the ratio of solvents in PAA solution and the rate of solvent evaporation. Therefore, the PAA-coated cathode offers a facile and low cost approach for in-situ making the PAA gel in the Li/S batteries.

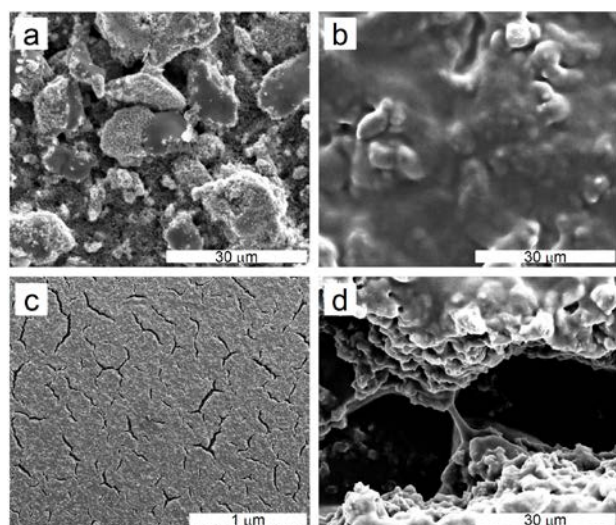


Fig. 2 SEM images of (a) Pristine cathode (x2,000), (b) PAA-coated cathode (x2,000), (c) PAA-coated cathode (x50), and (d) Detailed view into cracks on PAA-coated cathode (x2,000).

5 PAA gel as PS-blocking layer

The $-\text{COOH}$ groups in the gelled PAA are poorly dissociated due to the nature of weak acid. However, it is possible to form the hydrogen (H) bonds between the $-\text{COOH}$ groups and PS anions because the PS has higher PKa than the carboxylic acids. These H-bonds are able to chemically block the out-diffusion of the PS anions in the Li/S battery. To verify this concept, we conducted a potentiostatic polarization experiment on an electrolyte-flooded Li/S cell. Fig. 3 indicates the current-time (I-t) response of two cells using the pristine cathode and PAA-coated cathode, respectively. In the pristine cathode cell (Cell 1), the I-t response exhibits two distinct plateaus. That is, the upper current plateau reflects high reduction kinetics of sulphur and fast out-diffusion of resulting soluble Li_2S_n ($n \geq 4$), and the lower current plateau corresponds to the return (reduction) of the dissolved Li_2S_n from the solution, as verified by the visual observation. Since the electrode is flooded in extreme excess liquid electrolyte, in this case the concentration of PS in the electrolyte solution is low so that the currents of the lower plateau are almost close to the background. Before polarization, the electrolyte solution is clear and colorless (Photo a). As polarized to Point b, the brown Li_2S_n are diffused out of the cathode (Photo b). Whereas continuous polarization leads to slow decoloration of the PS solution (Photo c) because the out-diffused PS is reduced (returned) back from the solution. In contrast, in the PAA-coated cathode cell (Cell 2), the I-t response only shows a single region with the current monotonously declining against the polarization time. This is because the long-chain Li_2S_n formed in the first discharge stage is continuously reduced into short-chain PS without diffusing out of the cathode. This judgment is well supported by the visual observation (Photos a'-c'), which do not show any out-diffusion of the colorful PS. On the other hand, the blockage of the PS out-diffusion provides indirect evidence for the closure of the cracks and pores in the PAA membrane upon the formation of the PAA gel. It should be noted that direct evidence for the closure of cracks and pores is difficulty obtained from the cycled Li/S cell because after test the cathode and separator are tightly stuck together, which makes it impossible to separate them without

damaging of the cathode structure. The results above reveal that the PAA gel can act as an effective PS-blocking layer in the liquid electrolyte Li/S batteries.

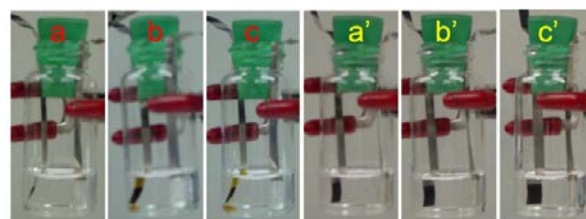
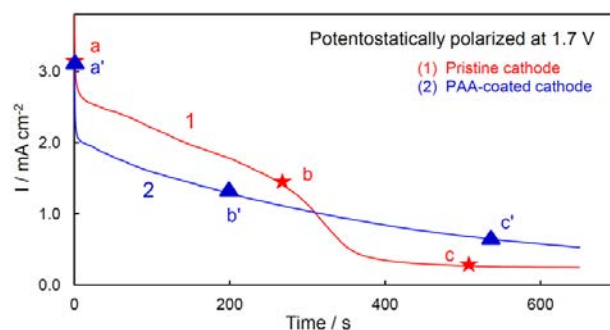


Fig. 3 Current-time response (top) and photographs (bottom) of an electrolyte-flooded Li/S cell during a potentiostatic polarization test at 1.7 V vs. Li/Li^+ , where the symbol with a letter indicates the position of photograph. (1) Pristine cathode, and (2) PAA-coated cathode.

Electrochemical characteristic of Li/S cell

Basic electrochemical characteristics of the Li/S cell employing the PAA-coated cathode are displayed in Fig. 4. It can be observed from Fig. 4a that when cycled at 0.2 mA cm^{-2} , the cell has a 1012 mAh g^{-1} of initial specific capacity, which falls to 819 mAh g^{-1} in the second cycle, followed by very stable capacity retention. When cycled at 0.5 mA cm^{-2} , however, the specific capacity of the first discharge declines to 557 mAh g^{-1} and the capacity exhibits an obvious activation period, during which the specific capacity progressively increases until reaching a maximum value at the 16th cycle. The activation phenomena have been frequently observed from the Li/S batteries,²⁰⁻²⁵ and their appearance can be attributed to the insufficient utilization of insulating sulphur in discharge Stage 1, which corresponds to a phase transition from the solid sulphur to liquid Li_2S_8 solution, due to the slow out-diffusion of the dissolved Li_2S_8 .^{23,24} In other words, the Li_2S_8 formed in Stage 1 is continuously reduced into less soluble or even insoluble Li_2S_n ($n < 4$) before the sulphur particles are completely reduced into the highly soluble Li_2S_8 . Affected by many factors such as the content and loading of sulphur in cathode, the electrolyte/sulphur ratio in cell, and discharge current rate, the activation period generally lasts longer with an increase in the discharge rate and the sulphur particle size. Since the resulting PAA gel blocks the out-diffusion of dissolved PS, the PAA-coated cathode shows more significant activation phenomenon, as compared with the pristine cathode.

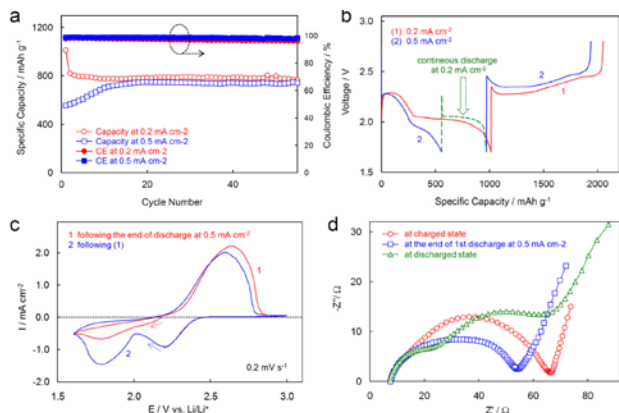


Fig. 4 Typical electrochemical characteristics of Li/S cells with a PAA-coated sulphur cathode. (a) Discharge capacity and coulombic efficiency, (b) Voltage profile of the first cycle, in which the green curve shows a continuous discharge at 0.2 mA cm⁻² following the end of discharge at 0.5 mA cm⁻², (c) Cyclic voltammogram following the end of discharge at 0.5 mA cm⁻², and (d) Impedance spectra at different states of discharge.

Our explanation to the activation phenomenon is well supported by the results of galvanostatic cycling, cyclic voltammetry, and ac impedance measurements, respectively, as exhibited in Fig. 4b-d. As indicated by Fig. 4b, the initial capacity is highly dependent on the discharge current density, i.e., 1012 mAh g⁻¹ at 0.2 mA cm⁻² and 557 mAh g⁻¹ at 0.5 mA cm⁻². However, the cell is able to release additional 413 mAh g⁻¹ of capacity in a continuous discharge at 0.2 mA cm⁻² following the end of discharge at 0.5 mA cm⁻², resulting in a total capacity of 970 mAh g⁻¹, which is very close to that (1012 mAh g⁻¹) obtained at 0.2 mA cm⁻². On the other hand, the cyclic voltammogram (Fig. 4c) shows significant reduction currents between the OCP and 1.7 V in the first cycle following the end of discharge at 0.5 mA cm⁻². Beside the above, the ac-impedance measurement gives indirect evidence that the initial discharge at 0.5 mA cm⁻² is incomplete. It has been repeatedly determined that charge-transfer resistances at the charged state and the discharged state are much higher than those in the midst of discharge.^{26,27} As shown in Fig. 4d, however, the cell's impedance at the end of discharge at 0.5 mA cm⁻² is smaller than those at the charged state and discharge state. The above results verify that the appearance of activation period in the Li/S batteries is due to the insufficient utilization of sulphur active material. In the present case, the dissolved Li₂S_n is confined within the cathode by the PAA gel layer, leading to an increase in the concentration and viscosity of PS around the carbon surface. As a result, the formed long-chain Li₂S_n does not diffuse away from the carbon surface, instead is continuously reduced into shorter chain PS. Resultant Li₂S₂ and Li₂S block the physical contact between the unreacted sulphur and carbon surface, leading to low utilization of the sulphur active material.

Advantage over pristine cathode

Performances of the Li/S cells employing the pristine cathode and PAA-coated cathode are compared in Fig. 5. Basically, two cells exhibit similar specific capacities in a range of 740-760 mAh g⁻¹ when the cells are cycled at 0.5 mA cm⁻² and the capacities become stable as indicated by Fig. 5a. During the initial few cycles, the pristine cathode cell shows a steep decrease in the

specific capacity whereas the PAA-coated cathode cell shows an activation period, in which the former is due to the loss of sulphur active material as a result of the out-diffusion of the formed long-chain Li₂S₈. After about 15 cycles, the specific capacities of two cells are changed in a similar pattern, namely starting with a slow increase followed by a linear decline. Fig. 5a shows that the pristine cathode cell remains a slow increase in the specific capacity until ~100 cycles whereas the PAA-coated cathode cell until ~300 cycles, which is three times longer than the pristine cathode cell. This observation is in a good agreement with our concept that the PAA gel blocks the out-diffusion of the dissolved PS. After 300 cycles for the PAA-coated cathode and ~100 cycles for the pristine cathode, the rate of capacity fading is accelerated. This is probably due to a decrease in the concentration of LiNO₃ as a result of the gradual consumption on the sulphur cathode and Li anode,^{5,26} a common phenomenon observed in the Li/S batteries using a LiNO₃-contained electrolyte.

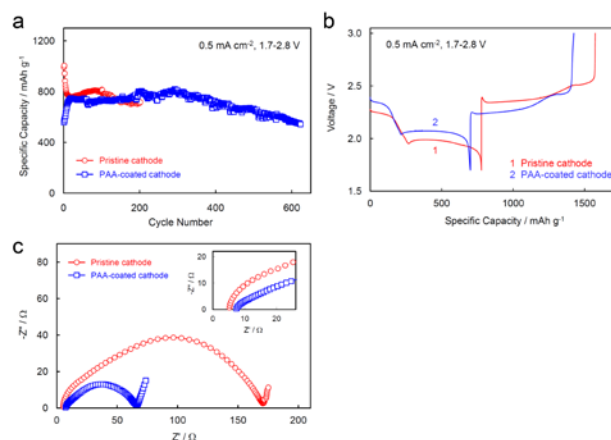


Fig. 5 Comparison for Li/S cells with pristine cathode and PAA-coated cathode, respectively. (a) Cycling performance at 0.5 mA cm⁻², (b) Voltage profile recorded in the 10th cycle, and (c) Impedance spectrum at charged state.

Beside the cycling stability, the PAA-coated cathode is also superior in the cycling energy efficiency as suggested by Fig. 5b. In comparison with the pristine cathode cell, the PAA-coated cathode cell suffers smaller polarization, namely, it discharges at higher voltages while is charged at lower voltages. This result is surprising because extra PAA gel must add ohmic resistance into the cell, which normally increases the cell's polarization. In order to understand this unusual behaviour, we measured and compared the impedance spectra of these two cells at the charged state, as indicated in Fig. 5c. It can be seen from the inset of Fig. 5c that the PAA-coated cathode cell does have slightly higher bulk resistance as compared with the pristine cathode cell, being in consistency with the fact that the extra PAA gel layer increases ohmic resistance of the cell. However, the PAA-coated cathode cell has significantly smaller cell reaction resistance (R_{cr}), here the R_{cr} is defined as the overall resistance of the electrode surface layer and charge-transfer process on the electrode-electrolyte interface.²⁸ The similar results also have been reported on the Li/S cell with a Nafion-coated sulphur cathode, in which the out-diffusion of the dissolved PS is hindered by the electrical repulsion of the negatively charged Nafion gel.¹¹ Therefore, the smaller polarization observed from the PAA-coated cathode cell

can be reasonably attributed to the reduced R_{ct} as a result of the PAA gel blocking the out-diffusion of the dissolved PS.

4. Conclusions

In summary, we demonstrated a proof-of-concept for a poly(acrylic acid) (PAA) gel as the polysulphide-blocking layer for high performance Li/S batteries. In the PAA gel, the $-\text{COOH}$ groups are poorly dissociated due to the nature of weak acid, however, they are able to form H-bonds with the polysulfide anions, which chemically blocks the diffusion of the polysulfide anions out of the cathode. The blocking effect of the PAA gel on the out-diffusion of polysulphide anions has been experimentally verified by a potentiostatic polarization test at 1.7 V vs. Li/Li^+ and a galvanostatic cycling test at 0.5 mA cm^{-2} , respectively. It is shown that the PAA gel increases the cycle life of a Li/S cell from 100 cycles to 300 cycles. The PAA gel can be in situ formed upon the activation of liquid electrolyte by employing a dual-layer structural sulphur cathode that consists of a porous PAA membrane on the top surface. The porous PAA membrane can be easily applied to a conventional sulphur cathode by a simple solution coating process. The cracks and pores of the membrane can be conveniently controlled by the solvent composition and solvent evaporating rate. Due to the easiness for fabrication and the low cost for raw materials, the dual-layer structural sulphur cathode based on a porous PAA membrane offers a facile and low cost approach for improved performances of the liquid electrolyte Li/S batteries.

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Notes and references

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