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A simple approach for superior performance of lithium/sulphur batteries modified with gel polymer electrolyte

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Gel polymer electrolyte (GPE) is superior to liquid electrolyte in reducing electrolyte leakage and flammability for the safety of rechargeable batteries. However, using GPE in lithium/sulphur (Li/S) battery reduces capacity because the highly viscous GPE traps lithium polysulfide (PS) within the electrolyte and make these PS electrochemically inactive. In order to compensate for the loss of capacity, a porous poly(ethylene oxide)-sulphur composite is selected to modify the commercial separator. It is shown that elemental sulphur in the composite layer not only serves as the pore-making agent to facilitate the filling of liquid electrolyte in the cell assembly, but also provides additional sulphur to increase the cell's capacity. As a result, the Li/S cell with GPE-modified separator has even higher capacity than the liquid electrolyte cell while still retaining the advantages of GPE. In this paper we discuss the effect of the composite's composition on the morphology, electrolyte wettability and cell's performance.

Introduction

Lithium/sulphur (Li/S) battery is fundamentally a liquid electrochemical cell, in which long-chain lithium polysulfide (PS, Li_2S_n , $n \geq 4$) inevitably dissolves into liquid electrolyte and serves as the liquid cathode, or called catholyte.^{1,2} Dissolution of PS on one hand transfers insulating sulphur species into the solution phase leading to high capacity and rate capability, but on the other hand causes many unwanted problems, such as the loss of active sulphur material, low charging efficiency, high self-discharge rate and short life span. All of these problems are related to the parasitic reactions between the dissolved PS and Li anode, and such reactions have been identified to be the source for thermal runaway at elevated temperature. Gel polymer electrolyte (GPE) is superior to liquid electrolyte in reducing electrolyte leakage and solvent flammability, and has been proposed to improve the safety of Li/S battery.^{3,4} From the viewpoint of battery manufacturing, the GPE is desired to be formed in situ by swelling a porous polymer membrane with a gel-forming liquid electrolyte,⁵⁻⁸ which requires the pre-preparation of porous polymer membrane. It is further required that for smooth electrolyte filling, the liquid electrolyte must fully penetrate into the porous polymer membrane before polymer is gelled. On the other hand, at elevated temperature the GPE naturally becomes a viscous fluid, losing dimensional integrity and mechanical strength. Therefore, modification of the conventional separator by GPE has been considered to be more practical for the performance improvement of rechargeable batteries.⁹⁻¹²

For poly(ethylene oxide) (PEO) polymer, we have shown that

the PEO composite containing high amount of inorganic filler offers a facile approach for making a porous membrane.^{12,13} In an effort to modify Celgard® separator,¹² we selected a 50PEO-50SiO₂ (by weight) composite and showed that the composite coating significantly enhanced the wettability of liquid electrolyte on the separator, and the GPE could be formed in situ upon the filling of liquid electrolyte. However, the Li/S cells with the GPE-modified separator suffered about 200 mAh g⁻¹ of capacity loss as compared with the control cell using pristine separator due to the strong adsorption of PS on the surface of SiO₂ and the high viscosity of GPE, both of which trap the dissolved PS within the separator and make these PS electrochemically inactive in the following discharge. Bearing this fact in mind, we predict that replacing SiO₂ filler with elemental sulphur can compensate for the loss of capacity while still retaining the benefits of GPE. According to this concept, elemental sulphur in the porous PEO-S composite is expected to first serve as the pore-making agent to facilitate the filling of liquid electrolyte in the cell assembly, and then provide the additional sulphur to increase the cell's overall capacity. In order to verify our concept, we modified the commercial Celgard® membrane using a series of PEO-S composites, and examined the impact of PEO-S composition on the wettability of liquid electrolyte and the performance of a Li/S cell. In this paper, we present the morphology of the PEO-S composite coating layer and discuss the superior performance of Li/S battery by the modification of PEO-S composite.

Experimental

All chemicals were purchased from Sigma-Aldrich. Prior to use, dimethyl ether (DME) and 1,3-dioxolane (DOL) were dried over

4Å molecular sieves for a week, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and LiNO₃ 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 LiNO₃ 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 aluminum 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. Using the same procedure, a carbon electrode consisting of 90 wt.% Super-P carbon and 10 wt.% ANMMA was coated onto a carbon-coated aluminium foil. To modify the separator, homogenous PEO-S slurry with a specific amount of sulphur was prepared by weighing the calculated amounts of PEO powder (MW=5,000,000, Sigma-Aldrich) and sulphur powder (≥99.5%, Sigma-Aldrich) into a 7 mL polyethylene vial, to which added was deionized water until approximately 6% solid content, followed by shaking with a stainless steel ball having a diameter of 5 mm for 2 h on a 5100 Mixer Mill[®] machine (SPEX CertiPrep). Using a 10 mil gap doctor-blade, the resulting PEO-S slurry was coated onto a Celgard[®] 3401 membrane and dried in air. The composition of the composite layer was expressed in the form of (100-x)PEO-xS by weight. For convenient description, we refer to pristine Celgard[®] membrane as P-separator, and the PEO-S composite coated membrane as SC-separator. On average, the thickness of PEO-S composite layer in the SC-separator was 18 µm. Before use, the sulphur cathode and SC-separator were dried at 60 °C under vacuum for 16 h.

Morphology of the separator was observed and photographed using a Quanta 200F scanning electron microscope (SEM). Wettability of separator was visually observed by dropping a 2 µL droplet of triethylene glycol dimethyl ether (TEGDME) from about 1 cm height and photographed after different time intervals. For evaluation of the chemical stability of SC-separator against Li metal, a symmetric Li/Li cell having a 1.27 cm² effective area was assembled by sandwiching 2 pieces of separators between two Li foils with the composite layer orienting to metal Li. In order to obtain fresh Li surface, the Li/Li cell was first plated and stripped at 1 mA cm⁻² for 2 h three times, and then electrochemical impedance spectroscopy (EIS) was measured after various storage times at open-circuit potential in the frequency range from 0.01 to 100 kHz with an ac oscillation of 10 mV amplitude by using a Solartron SI 1287 Electrochemical Interface and a SI 1260 Impedance/Gain-Phase Analyzer. The resulting EIS was analyzed using ZView software. For testing of capacity release from SC-separator, a BR2335-type coin cell consisting of a Li anode, a (40PEO-60S) composite coated separator with the composite layer orienting to cathode, and a carbon cathode was assembled and cycled at 0.2 mA cm⁻² between 1.7 V and 2.8 V on a Maccor Series 4000 cycler. The same type of Li/S coin cells were assembled and cycled with the PEO-S composite layer orienting to sulphur cathode unless specified otherwise. All cells contained 20 µL liquid electrolyte and were cycled at room temperature (~22 °C) except for the EIS

that was measured at 20 °C. For rate capability test, the cell was charged at 0.5 mA cm⁻² and discharged at scheduled current densities to 1.5 V. Specific capacity was referred as to the mass of sulphur in cathode without counting for those in SC-separator.

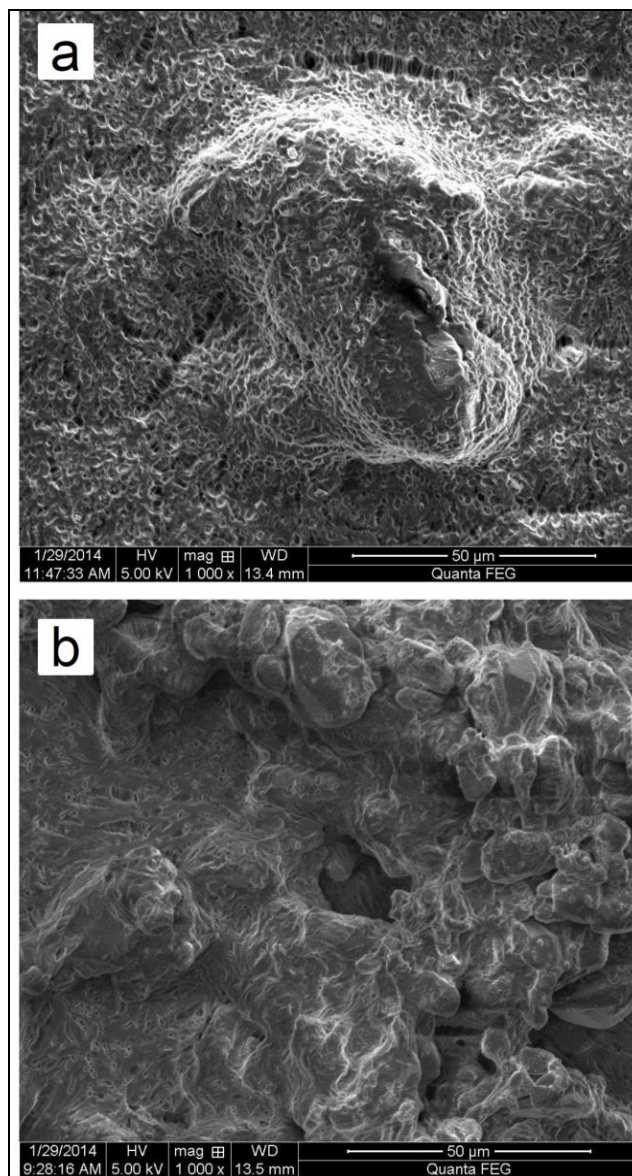


Fig. 1. SEM image of the surface of SC-separators with composition of (a) 80PEO-20S and (b) 40PEO-60S.

Results and Discussion

PEO-S slurry can be easily coated or sprayed onto the commercial Celgard[®] membrane, evaporation of the solvent leaves a thin PEO-S composite layer on the surface of the separator. Fig. S1 shows the SEM image of the SC-separators with different contents of sulphur. It is shown that the sulphur particles are evenly distributed on the surface and that the density of sulphur particles increases with the content of sulphur, i.e., x value in the formula of (100-x)PEO-xS. When x increases to 60%, sulphur particles start to agglomerate (see Fig.S1-f), and no uniform composite layer can be formed at x=70% due to severe

agglomeration of sulphur particles (not shown in Fig. S1). Fig. 1 compares the microstructure of the surface of the SC-separator with $x=20\%$ and 60% , respectively. In both cases, the sulphur particles or aggregates are well wrapped by a net-like, highly porous PEO membrane. In particular, sulphur particles in 80PEO-20S composite are fully embedded under the PEO membrane (Fig. 1a).

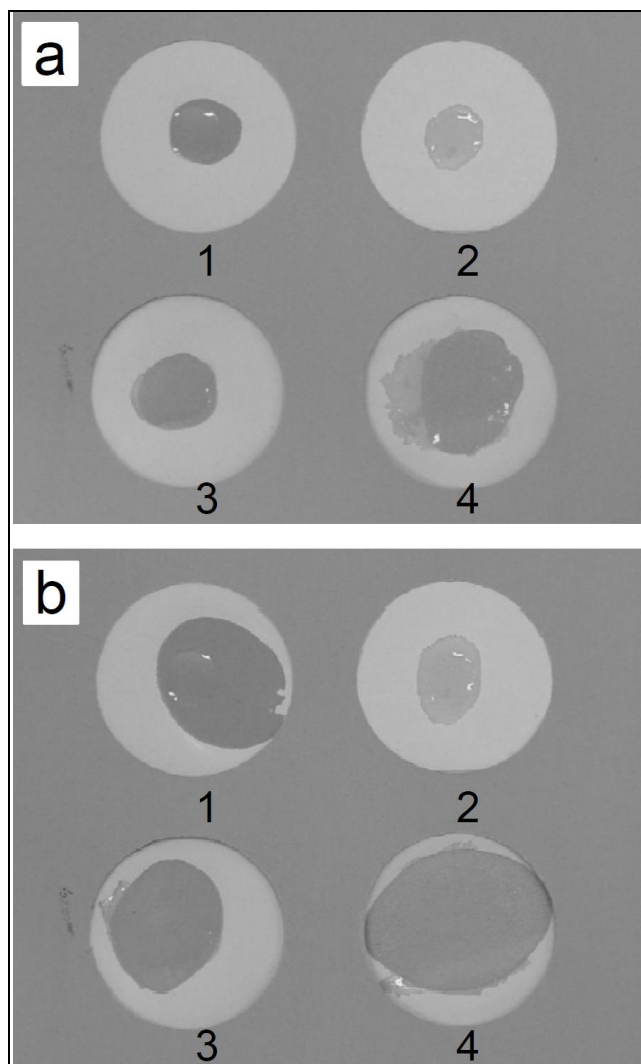


Fig. 2. Image for the wettability of separator after TEGDME droplet was applied for 2 minutes (a) and 20 minutes (b). (1) P-separator, (2) SC-separator with $x=0\%$, (3) SC-separator with $x=20\%$, and (4) SC-separator with $x=40\%$.

Fig. 2 compares the wettability of TEGDME solvent on P-separator and SC-separators, in which Fig. 2a was photographed after 2 minutes following the dropping of solvent droplet and Fig. 2b after 20 minutes. As indicated by sample #2 ($x=0\%$, i.e., coated by a thin pure PEO layer), the solvent is not able to wet due to the dense structure of the PEO layer as can be observed from Fig. S1-a. With incorporation of elemental sulphur into the composite, the wettability of solvent on SC-separator is enhanced gradually. When $x=20\%$ (sample #3), SC-separator reaches similar wettability as the P-separator as seen by comparing

samples #1 and #3. When x is further increased to 40% (sample #4), the wetting becomes nearly instant and no liquid droplet can stay on the surface after the dropping of solvent. The above results clearly indicate that sulphur is an excellent pore-making agent for increasing the wettability of PEO-modified separator. It should be noted that in addition to the content of sulphur, many other factors such as the thickness of the composite layer, particle size of sulphur, and the distribution/agglomeration of sulphur particles also essentially affect the wettability of SC-separator. Optimizing these factors can further improve the wettability of SC-separator. In our early work,¹² we have shown that upon the filling of a gel-forming liquid electrolyte, the PEO-based GPE can be formed in situ in the Li/S battery. Therefore, the GPE-modified Li/S batteries can be conveniently manufactured without changing the existing procedure of battery manufacture by simply replacing the conventional separator with a proper SC-separator.

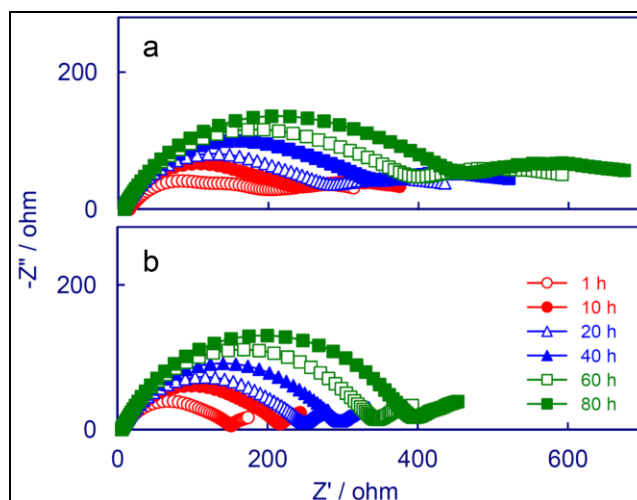


Fig. 3. EIS of Li/Li symmetric cell after storage at $20\text{ }^{\circ}\text{C}$ for different time. (a) Li/P-separator/Li cell, and (b) Li/SC-separator/Li cell having an x of 60% . Note that each cell used two pieces of separators and the composite layer faced metal Li for SC-separator.

Chemical stability of SC-separator against metal Li is evaluated by monitoring the impedance of a Li/Li symmetric cell during storage at $20\text{ }^{\circ}\text{C}$. To do this, two pieces of SC-separators with $x=60\%$ were sandwiched between two Li foils with the PEO-S composite layer orienting to each of Li electrodes. Some of selected EISs are displayed in Fig. 3 and compared with those of the control cell using P-separator. Overall, the impedance of both cells is gradually increased with storage time, which is a typical characteristic of metal Li in liquid or gel electrolyte.^{14,15} However, there is a significant difference in the shape of EIS. That is, the EIS of the control cell consists of two flat semicircles, whereas that of a Li/SC-separator/Li shows only a broad semicircle followed by a somewhat sloping straight line. This observation reflects different electrochemical reactions occurring on the separator-lithium interface. On the interface between the SC-separator and Li, the reversible redox of sulphur also takes place in addition to the reaction of " $\text{Li} - e = \text{Li}^{+}$ ",¹⁶ which makes the EIS much more complicated. The broad semicircle in the EIS

of Li/SC-separator/Li cell can be considered to be the combined result of ionic conduction in the passivation layer, and lithium and sulphur charge-transfer processes on the separator-lithium interface.

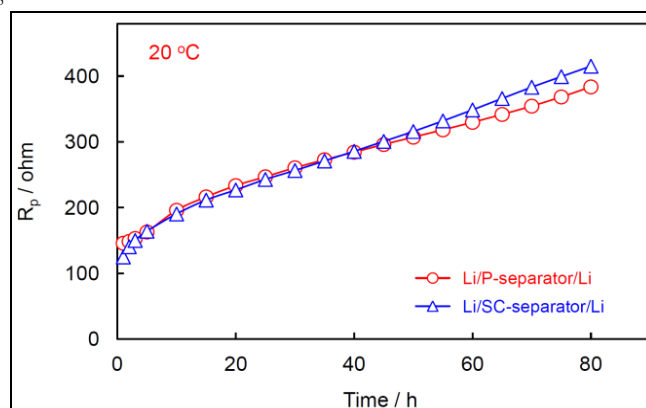


Fig. 4. Comparison of the R_p growth in Li/Li symmetric cell.

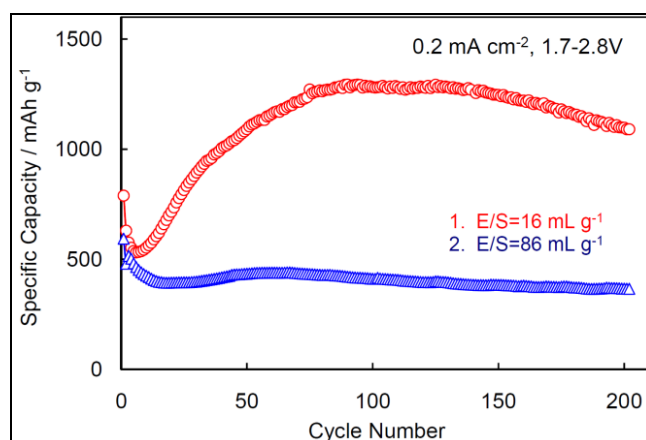


Fig. 5. Capacity release from SC-separator by a Li/SC-separator/carbon cell, where the SC-separator had an x of 60% and the composite layer faced carbon electrode.

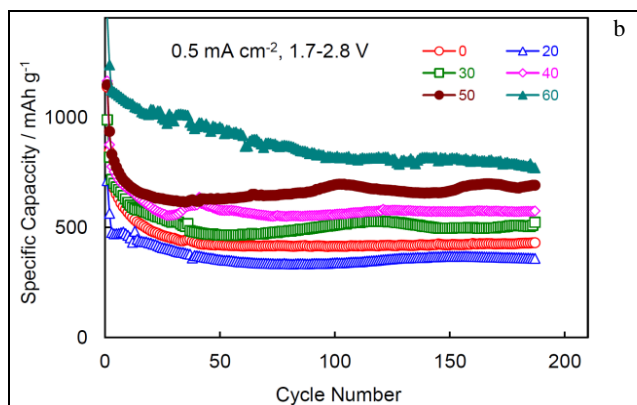
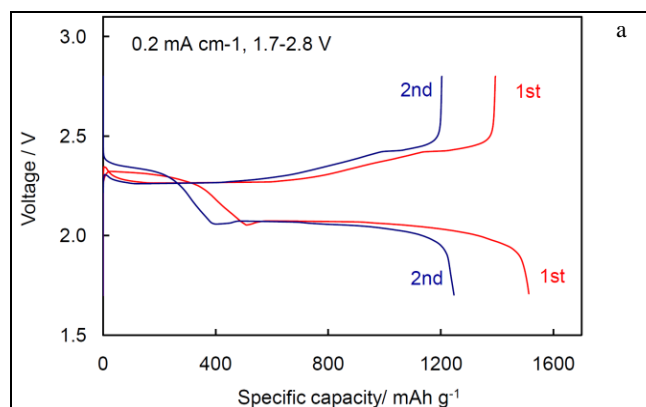


Fig. 6. Cycling performance of Li/SC-separator/S cell. (a) voltage profile of the first two cycles for SC-separator having an x of 60%, and (b) effect of sulfur content on the specific capacity and capacity retention where the numbers are the x value in (100- x)PEO- x S composite.

Based on the equivalent circuit described in Fig. S2 and the assumption that ionic conduction in the Li passivation layer has the same frequency range, the passivation resistances (R_p) for the P-separator and SC-separator cells are fitted and plotted as a function of storage time in Fig. 4. One clearly observes that the R_p by P-separator and SC-separator are very similar, and both increase with the storage time. This result reveals that the stable passivation layer still is formed and grown on the surface of metal Li despite the presence of sulphur in the SC-separator, and is in good agreement with the observation by Demir-Cakan et al¹⁷ who distributed sulphur powder on the surface of metal Li and showed the stable passivation layer being formed and grown on Li. In other words, the single-side coated SC-separator can be oriented to either of the sulphur cathode and Li anode in the Li/S battery without affecting the safety.

In addition to serving as the pore-making agent for the filling of liquid electrolyte in cell assembly, sulphur in the SC-separator also acts as the additional sulphur source to provide extra capacity. To demonstrate this, we assembled and cycled two Li/C cells by sandwiching a SC-separator ($x=60\%$) between a Li foil and a carbon electrode with the PEO-S composite layer orienting to the carbon electrode, followed by activating with different amounts of liquid electrolyte. Fig. 5 depicts that the capacity of sulphur can be released from the SC-separator although its value greatly varies with the amount of liquid electrolyte, or the electrolyte/sulphur (E/S) ratio as expressed elsewhere.¹⁸ As shown in Fig. 5, a high amount of electrolyte leads to faster capacity release but lower capacity (see the cell with E/S=86 mL g^{-1}). This is because a high amount of liquid electrolyte dilutes the concentration of PS, low viscosity of the diluted PS solution favours the dissolved PS diffusing out of the separator which results in larger loss of the sulphur active material. Similar phenomenon has also been observed from the conventional Li/S cells.^{18,19} In an opposite manner, a low amount of electrolyte results in slower capacity release but much higher capacity (see the cell with E/S=16 mL g^{-1}). In this case, the capacity of sulphur gradually increases and reaches a maximum (~1280 mAh g^{-1}) after about 80 cycles. Similar trends in the change of sulphur capacity with cycle number was also observed from the Li/C cell

with sulphur powder distributed on the surface of Li anode.¹⁷

Cycling performances of Li/SC-separator/S cell are presented in Fig. 6. Typically, the cell shows two discharge voltage plateaus at ~2.3 V and at 2.1 V, respectively, which correspond to two general phase transitions: (1) from solid to solution (i.e., from elemental sulphur to dissolved Li_2S_n) and (2) from solution to solid (i.e., from dissolved Li_2S_n to insoluble Li_2S_2 or Li_2S).^{1,2,18} As indicated by Fig. 6a, the Li/S cell with $x=60\%$ is able to deliver a 1513 mAh g^{-1} capacity in the first discharge and a 1247 mAh g^{-1} capacity in the second discharge. Fig. 6b shows that the content of sulphur in SC-separator greatly affects the specific capacity and capacity retention of Li/S cells. Except for $x=20\%$, the specific capacity is consistently increased with the content of sulphur, which agrees with our concept that the SC-separator serves as the additional sulphur source to provide extra capacity. The exception for $x=20\%$ is because in this case all sulphur particles are embedded under the net-like porous PEO membrane, as shown by Fig. 1a, so that these sulphur cannot diffuse out of the PEO membrane and on contrary the high viscous PEO matrix traps lithium polysulfide from the electrolyte solution.

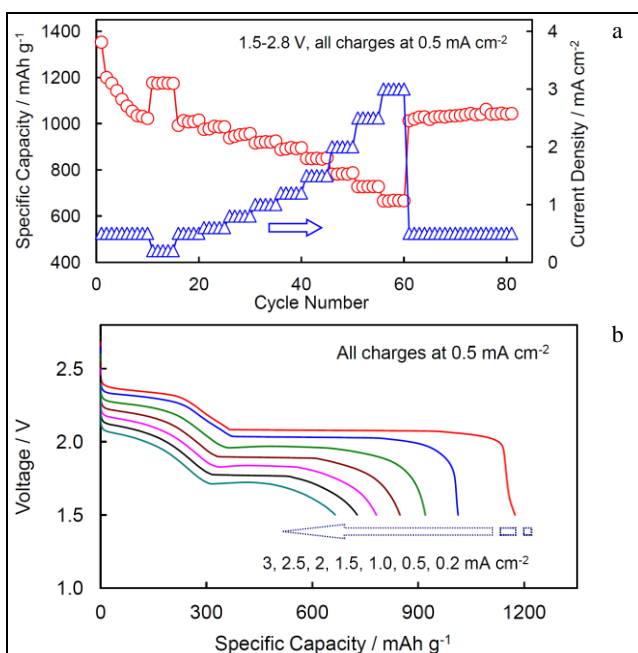


Fig. 7. Rate capability of Li/SC-separator/S cell having an x of 60%. (a) change of specific capacity with current density, and (b) voltage profile of discharge at different current density.

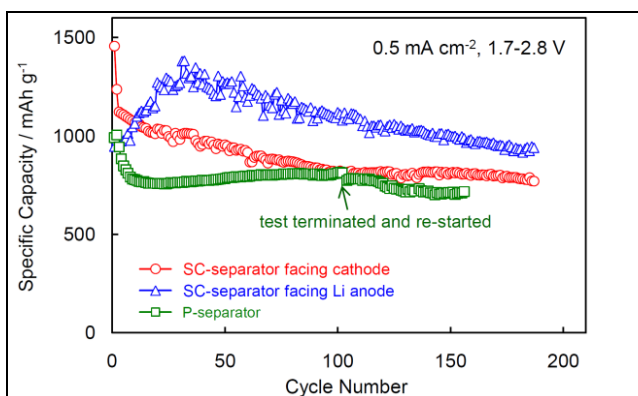
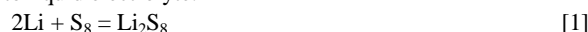


Fig. 8. Effect of the composite orientation on cycling performance of Li/S cell for a SC-separator having an x of 60%.

Rate capability of the Li/SC-separator/S cell with $x=60\%$ is further evaluated and illustrated in Fig. 7. Before testing, the cell was cycled at 0.5 mA cm^{-2} for 10 times to reach a relatively stable capacity (Fig. 7a). One can see from Fig. 7a and Fig. 7b that the specific capacity and discharge voltage declined with an increase in the current density. This is a common nature of the batteries, and can be attributed to the IR polarization. In particular, the SC-separator cell retained a 666 mAh g^{-1} capacity at 3 mA cm^{-2} and recovered to 1040 mAh g^{-1} as the current density decreased to 0.5 mA cm^{-2} , which are twice of the analogous cell employing a 50PEO-50SiO₂ (wt.) composite coated separator (324 mAh g^{-1} at 3 mA cm^{-2} and $550\text{--}560 \text{ mAh g}^{-1}$ at 0.5 mA cm^{-2}).¹²

Since the PEO-S composite is coated on a single side, the orientation of composite layer affects the performance of the Li/S cell. The effect of composite orientation on the specific capacity and capacity retention of Li/S cells is depicted in Fig. 8, in which the performance of the control cell is also plotted for the purpose of comparison. When the composite layer is oriented to the cathode, the capacity of sulphur in the SC-separator can be released directly through electrochemical reduction on the surface of cathode (exactly on the surface of carbon in the cathode), as occurred in the dual-layer structural sulphur cathode that is composed of a carbon layer and a pure sulphur layer.^{20,21} In this case, the capacity of sulphur can be rapidly released from the SC-separator, after which the cell experienced a normal decline in the specific capacity. When the composite layer is oriented to the Li anode, the capacity of sulphur in the SC-separator is released through the following three routes: (1) reaction with metal Li as described by eq. 1, (2) combination with PS to form longer chain PS as described by eq. 2, and (3) dissolution of elemental sulphur into liquid electrolyte.



All three routes are highly resistive because route-1 is suppressed by the stable passivation layer on Li, route-2 by the slow reaction kinetics, and route-3 by the low solubility of elemental sulphur in liquid electrolyte. As a result, the capacity release of sulphur from the SC-separator was much slower. In this case, the capacity release became a sustained process so that the specific capacity of Li/S cell kept increasing until reaching the maximum (1320 mAh g^{-1}) at the 25th cycle. In particular, the specific capacity at the 185th cycle was 925 mAh g^{-1} for the cell with the composite orienting to Li anode and 788 mAh g^{-1} for the one with the composite orienting to sulphur cathode, respectively. With either of these orientations, the SC-separator cells had higher specific capacity than the P-separator cell.

Conclusions

The commercial polyolefin separator can be conveniently modified by a PEO-S composite. Sulphur in the composite on one hand serves as the pore-making agent for enhancing penetration of the liquid electrolyte, and on the other hand provides the additional sulphur for increasing the capacity of Li/S battery. Once the content of sulphur reaches 40 wt.% or higher, the PEO-

S composite coated separator is able to offer superior performance in the wettability of liquid electrolyte and the overall capacity of Li/S battery as compared with the conventional liquid electrolyte cell. Upon the filling of a gel-forming liquid electrolyte, the GPE can be formed in situ. Therefore, the GPE-modified Li/S battery can be manufactured by simply modifying the separator without the need to change the existing procedure of battery manufacture. Modification on the commercial separator by the PEO-S composite offers an excellent opportunity for the Li/S battery taking the benefits of GPE without sacrifice in overall capacity.

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Notes and references

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