Functionalized Bacterial Cellulose as a Separator to Address Polysulfides Shuttling in Lithium-Sulfur Batteries

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Abstract

In lithium-sulfur batteries (LSBs), soluble long-chain polysulfide intermediates can easily shuttle between the cathode and the anode, causing rapid performance degradation. Although significant progress, through rational cathode structure and composition design, has been made to solve the polysulfide shuttling problem, this challenging issue still exists. Considering the function of a separator in a cell is to isolate the cathode and anode materials, the transport properties of species across the separator should be investigated. Using bacterial cellulose (BC) as an example of a functional separator, we hypothesize that grafting anionic function groups on the cellulose chains could create an energy barrier that will block the diffusion of polysulfides across the separator. In our study, BC is functionalized by oxidizing hydroxyl groups on cellulose chains into carboxylate groups. Physicochemical and electrochemical studies confirm polysulfide shuttling is effectively suppressed. As a result, functionalized BC separator equipped LSB cells with a sulfur load of 4 mg cm⁻² delivers \sim 1300 mAh g⁻¹ of specific capacity at 0.1C, which can be maintained after 100 cycles above 1000 mAh g⁻¹ at 0.3C, demonstrating its superior performance over commercial polyolefin-based separators.

Keywords: bacterial cellulose, functionalized separator, polysulfide shuttling, lithium-sulfur batteries

1. Introduction

With its potential to deliver a specific energy of more than 350 Wh kg⁻¹ at a low cost, the lithium-sulfur battery (LSB) has attracted considerable interest from the battery research and development community¹. In contrast to the one-electron chemistry in Li-ion batteries, LSBs feature a two-electron-based charge-discharge reaction per sulfur atom: $S_8 + 16Li^+ + 16e^- \leftrightarrow$ $8Li_2S$, where orthorhombic crystalline α -S₈ (*cyclo*-octasulfur) is the most thermodynamic stable of the roughly 30 solid allotropes of sulfur. The reduction of S₈ is a stepwise process with the formation of different long-chain polysulfide intermediates (Li₂S_x, $3 \le x \le 8$). Except for the short-chain Li₂S₂ and the final product Li₂S, the long-chain polysulfide intermediates are highly soluble in the currently available ether-based LSB electrolyte. And therefore, they can easily diffuse out of the cathode matrix to the anode side and then be reduced by the lithium metal. The resulted polysulfide shuttle effect leads to low Coulombic efficiency, rapid capacity decay, and fast battery failure, sabotaging the practical utilization of LS²⁻⁴. To minimize this efficiency-killing shuttle effect and address other challenges involving the optimization of the LSB performance, great efforts have been made in designing and optimizing the electrode, the electrolyte, and the separator of LSBs, using advanced structural engineering methods and rational compositional design.

To suppress the polysulfides shuttling between electrodes, previous studies have mainly focused on the use of physically trapping and chemically binding strategies to confine these soluble polysulfide species into a porous matrix of the cathode, employing porous carbon-based materials⁵⁻⁶, metal oxides, and sulfides⁷, conducting polymers⁸, or metal-organic frameworks⁹. These structures can catalytically accelerate the multi-step and liquid/solid phases redox conversions¹⁰⁻¹⁴. Electrolyte additives¹⁵ and solvents with a high Gutmann Donor Number (DN) are other methods to promote the redox reaction of sulfur species through stabilizing multiple states of polysulfide anions and altering the kinetic pathway¹⁶, and thus alleviating the polysulfide shuttling. Inserting a conductive interlayer between the cathode and the separator to form a polysulfide reservoir on the cathode side also reduces the leakage rate of polysulfides from the cathode¹⁷⁻¹⁹. Similarly, blocking the polysulfide pathway by downscaling the separator pore size or functionalizing the separator²⁰⁻²² can also slow down polysulfide diffusion.

Among these strategies, the approach of modifying the separator to shut off polysulfide shuttling is very straightforward and attractive²³⁻²⁷. After all, the intrinsic function of the separator is to isolate the active materials of the cathode and the anode. The separator

modification is also independent of the sulfur cathode structure design and therefore will not compromise its function. In the literature, polypropylene membrane modified by a secondary polymer embedment was developed by a fast dipping and drying process, and the micro-size pores in pure polypropylene membrane were successfully transformed into nano-size ones (< 2 nm) which could restrain the migration of polysulfide species effectively²⁸. Another attractive method to increase the capability of the separator in curbing the polysulfide shuttling is to graft polar functional groups on it^{25, 29}. Strong intermolecular forces can be established between these functional groups and polysulfide intermediates, confining the polysulfides in the cathode side. For instance, by using Nafion polymer to modify the commercial PP separator, sulfonic acid groups with high ionic selectivity capability can be introduced into the PP substrate, not only retarding the polysulfide diffusion process but also providing a fast lithium-ion transporting pathway³⁰.

Commercial separators are based on porous single- or multi-layer polyolefin films. Recently, natural polymers, particularly cellulose, have attracted attention for use as battery separators due to their good mechanical properties, outstanding thermal and chemical stability, excellent wettability, and low cost³¹. Cellulose-based separators have been demonstrated to be very promising in LIBs³². For battery separators, bacteria cellulose (BC) is superior to plant-derived celluloses since the higher purity and better crystallinity of BC vest it with much better mechanical, thermal and chemical properties³³.

In particular, the rich hydroxyl groups on cellulose chains render BC a highly polar polymer³⁴. We hypothesized that although the hydroxyl groups might initially absorb polysulfide intermediates *via* a hydrogen bond, they may subsequently prevent further

diffusion of polysulfides from the cathode to the anode because of electrostatic repulsion. More interestingly, the primary hydroxyl groups (C₆-OH) on cellulose chains can be oxidized into carboxylate groups *via* the TEMPO oxidation process³⁵⁻³⁶. These negatively charged carboxylate groups are assumed to prevent the polysulfides from migrating to the anode side by forming an energy barrier to diffusion. To verify our hypothesis, we demonstrate in this work that the oxidized BC membrane (o-BC) is superior to the pristine BC (p-BC) and the commercial Celgard 2400 (C-2400) separator in terms of alleviating the polysulfide shuttle effect and other physicochemical characteristics. Furthermore, by using the o-BC membrane as the separator and the carbonized BC film as a freestanding sulfur host, the assembled LSB cells delivered excellent electrochemical performances, as quantified by a specific capacity of 1300 mAh g⁻¹ at 0.1C and a sulfur loading of 4 mg cm⁻². The specific capacity could also be maintained at a level above 1000 mAh g⁻¹ at 0.3C for over 100 cycles. Results from cells with a sulfur loading of 6 and 8 mg cm⁻², corresponding to cathode sulfur content of 85% and 89%, respectively, are also reported with promising performance.

2. Experimental section

2.1 Preparation of oxidized bacteria cellulose

BC pellicles, produced in a fermentation process³⁷, were first washed in DI water several times and then purified by boiling in 0.5 M NaOH solution for 1 h. After washing thoroughly with DI water until a pH of 7 was attained, the BC pellicles were thoroughly minced. The TEMPO oxidation process³⁵ was then applied to modify the BC pulp. Briefly, 30 g of pulp was ultrasonically dispersed into 100 mL of DI water, and then 0.016 g of

2,2,6,6-tetramethylpyperidine-1-oxyl (TEMPO) and 0.1 g of NaBr were subsequently added into the solution while stirring vigorously. Small amounts of 13% NaClO solution were dropped slowly into the BC solution and a 0.5 M NaOH solution was added to maintain the pH of the mixture around 10. After 5 h of reaction, 5 mL of ethanol was used to quench the process.

2.2 Fabrication of p-BC and o-BC membranes

The o-BC was separated from the above solution and washed by using 0.1 M HCl and DI water in turns until pH~7.0. Then the obtained o-BC was ultrasonically dispersed into DI water. 30 mL of o-BC solution was filtrated through a 44 mm diameter membrane *via* vacuum filtration and then washed with ethanol. The obtained o-BC film was sandwiched between two glass slides and dried in a vacuum oven at 80 °C for 24 h. The obtained o-BC membrane was pressed again using an electric roller to reduce its porosity and to get desired thickness (~25 μ m, areal density ~3.76 mg cm⁻²). The unoxidized p-BC membrane was also prepared using the same procedure as described above. The fabricated o-BC and p-BC separators were stored in a glovebox to minimize moisture absorption.

2.3 Preparation of sulfur-carbonized BC cathode (S/cBC)

The carbonization process that was used is more completely described in our priorpublication⁶. Briefly, the filtrated BC was first dried in a vacuum oven and then transferred into a tube furnace and pyrolyzed under 40 *sccm* nitrogen flow at 800 °C for 2 hours with a heating rate of 2 °C min⁻¹. The synthesized carbon film was cut into an 11 mm disk and used as a sulfur host to fabricate the freestanding sulfur cathode. 0.4 g of sulfur powder was dissolved into 4 mL of CS₂ and NMP solution³⁸, and specified amounts of sulfur

solution, depending on the targeted mass loading, were dropped onto the carbon disk and dried under room temperature for 6 h. They were then sealed in a glass vial and heated at 155 °C for 12 h before use. The sulfur loading was calculated based on the thermal gravimetric analysis method (TGA, METTLER).

2.4 Material characterization

The morphological and structural features of the samples were studied using field emission scanning electron microscopy (FE-SEM, Supra35, Gemini) and transmission electron microscopy (TEM, H-8100, Hitachi). X-ray diffraction (XRD) of the samples was performed using a Rigaku MiniFlex 6G diffractometer equipped with a Cu-K α radiation source. The chemical bonding information of different elements in the BC-based separators was characterized using an X-ray photoelectron spectroscope (XPS, 5000 Versa Probe, PHI) and HYPERION 2000 infrared microscope (Bruker Optics). The surface potential of BC chains was determined using a Zeta PALS analyzer (Brookhaven Corporation, NY).

2.5 Electrochemical test

For the full battery test, coin-type cells (CR2400) were assembled in a glovebox by using the S/cBC as the cathode, C-2400 or BC-based membrane as the separator, and lithium plate as the anode. The electrolyte used here was 1 M bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) and 0.1 M lithium nitrate (LiNO₃) dissolved in a 1:1 v/v% mixture of 1,3-dioxolane (DOL)/dimethylethane (DME) solution, with an E/S ratio of 10 (μ L mg⁻¹). The electrochemical performances of different separators were quantified using cyclic voltammetry (CV, scan rate: 0.1 mV s⁻¹, voltage range: 1.7-2.8 V) and electrochemical impedance spectroscopy (EIS, 0.1-100 kHz with an AC voltage amplitude of 10 mV) on a Bio-logic SP-150 electrochemical workstation. Then, the galvanostatic charge/discharge processes of the cells were evaluated over a 1.7-2.8 V voltage range at a number of select current densities using a battery tester (LANHE, CT2001A). The specific capacity was inferred based on the mass of sulfur in the electrode.

3. Results and discussion

The synthesis procedure is illustrated in **Figure 1**a. After the purification process, BC pellicles were minced into pulp and, with the assistance of ultrasonic waves, dispersed into DI water. In the TEMPO mediated oxidation process, with the hypochlorite/bromide as the regenerating oxidant in water, the primary hydroxyl groups (C₆-OH) of BC can be selectively converted into carboxylate groups, which is expected to strengthen the repulsive force toward polysulfide species and restrain their migration. In addition, the oxidation process is an effective way to weaken the hydrogen bonds in BC and separate BC into thinner nanofibers³⁹, thus resulting in improved dispersion performance. As shown in the digital photos of BC (p-BC) pulp and oxidized BC (o-BC) solutions in Figure S1, the o-BC solution becomes more transparent after the oxidation process. Thinner cellulose nanofiber can also create a more uniform membrane during the vacuum filtration process which is anticipated to have better pore distribution inside the film and improved mechanical strength.



Figure 1. (a) Schematic of the preparation process of the o-BC separator (upper left: TEMPO-mediated oxidation process; upper-middle: schematic of the enhanced repulsive force on polysulfides from carboxylate groups grafted on cellulose chains; upper right: a digital photo of the as-prepared o-BC film). b) ATR-FTIR spectra and (c) Zeta potential of the p-BC and o-BC samples. (d) Thermal stability and (e) wettability test of the C-2400 and o-BC films. (f) XRD pattern and (g) SEM image of the o-BC sample.

The chemical status of these samples was first investigated by the ATR-FTIR technique. As shown in Figure 1b, the two spectra derived from p-BC and o-BC have very similar absorption peaks representing OH stretching at ~3400 cm⁻¹, C-H stretching at ~2900 cm⁻¹, and C-O stretching at ~1110 cm^{-1[40]}. However, after the oxidation process, the peak intensities at around 1420 and 1640 cm⁻¹, which originate from the -COO stretching, are enhanced as a result of the emergence of carboxylate groups^{39, 41}. In comparison to the p-BC, the change of oxygen-containing functional groups on the surface of the o-BC can be further revealed by XPS analysis. In Figure S2, the full XPS spectra for both samples exhibit two distinct peaks, as a result of the difference in the binding energy of C1s (~284.5 eV) and O1s (~532.4 eV) electrons, confirming the purity of these BC-based films. The closely-spaced spectra of C1s and the corresponding fitting results presented in Figure S3a-S3c demonstrate the evolution of these functional groups in detail⁴². The o-BC sample shows a higher percentage of the O-C=O functional group (~288.2 eV) than the p-BC one, which is consistent with the peak fitting of the O1s XPS spectra (Figure S3d-S3f). The conversion of the hydroxyl group into the carboxylate group can also adjust the surface charge of cellulose. Figure 1c gives the zeta potential of these two samples. Due to the enhanced electronegativity of the carboxylate group, the zeta potential of the o-BC sample is lower (-48.5 mV) than p-BC (-40.0 mV). A high density of negatively charged functional (polar) group on the separator would provide a repulsive force against polysulfide species, retarding their diffusion and confining them within the cathode side⁴³.

As reported previously, the commercial C-2400 membrane will be molten at elevated operation temperatures (> \sim 100°C), causing immediate battery failure and potentially unsafe conditions^{44.45}. Replacing these separators with other polymer-based layers possessing good mechanical properties and high-temperature tolerance features will enhance battery safety. The thermal stability of the o-BC membrane was tested at different temperatures in an oven. As exhibited in Figure 1d, the BC membrane can fully maintain its initial shape even when

the temperature reaches 140 °C, indicating the oxidation process has an unnoticeable impact on its thermal stability property (Figure S4a). In contrast, the C-2400 membrane is completely molten at this temperature. The thermal stability of BC is related to its high crystalline quality, as confirmed by the XRD characteristics of o-BC in Figure 1f. There, the two distinctive peaks located at 14.5° and 22.5°, respectively correspond to the (101) and (002) lattice planes of cellulose⁴⁶.

Electrolyte wettability is another characteristic that establishes a separator's suitability and level of performance. For this demonstration, DOL/DME-based electrolyte was dropped onto the o-BC and p-BC film, and it quickly permeated into the films (Figures 1e and S4b). This is in dramatic contrast to the C-2400 separator where the electrolyte droplet maintains its original shape. The electrolyte uptake capability was tested next, and the results are presented in Figure S5. With approximately the same thickness (~25 µm), the o-BC membrane shows higher electrolyte uptake than C-2400, thanks to its higher porosity and electrolyte wettability. In addition, the crosslinked structure of cellulose nanofibers (Figure 1f) vests the BC-based films excellent flexibility. Even after repeatedly folding and unfolding, they can rapidly restore to their original form without any obvious visual changes (Figure S6).



Figure 2. (a) Nyquist plot of cells with stainless steel disks as electrodes and different samples as the separator for the ionic conductivity analysis (inset: enlarge part at the high-frequency range). (b) Polysulfide permeation tests for the C-2400 (top) and o-BC(bottom) separators. (c) CV curves of LSBs with C-2400 or o-BC separator at the scan rate of 0.1 mV s⁻¹. Nyquist plots of cells with different separators (d) before and (e) after the CV test. (f) CV curves recorded at different scan rates of LSB with an o-BC separator. (g) Linear fits of the peak currents derived from CV curves of LSB with C-2400 and o-BC separators. (h) Open circuit voltage profiles comparing the self-discharge behavior of LSB

cells using C-2400and o-BC separator, respectively.

To facilitate the electrode reactions and minimize the cells' internal resistance, maintaining a small Li-ion resistivity across the separator is important. Electrochemical impedance spectroscopy (EIS) was used here to estimate Li⁺ conductivity in different separators. For this measurement, testing cells were assembled that use stainless steel disks for both the positive and negative electrodes and C-2400 or BC-based membrane soaked with the blank electrolyte as a separator. The Nyquist plots of their EIS spectra are presented in **Figure 2**a, where the tilted line indicates the ion diffusion process within the separator, while the resistance *R* defined at the intersection of this line with the Zre-axis is used to calculate Li⁺ conductivity based on $\sigma = L/RA$, where *L* and *A* are the thickness and the area of the separator, respectively. The o-BC separator shows the Li⁺ conductivity of 0.35 mS cm⁻¹ (Figure S7), which is larger than that of the p-BC (0.29 mS cm⁻¹) and C-2400 (0.24 mS cm⁻¹) separators. The higher ion conductivity of the o-BC separator is attributed to its substantial electrolyte uptake capability, well-defined ion diffusion pathways, and improved lithiophilic property after the oxidation process.

Besides the conductivity, the lithium-ion transference number (t^+) is another important factor that determines battery performances⁴⁷. This number is affected by the morphology and the surface chemistry of the separator⁴⁸⁻⁴⁹. To analyze the transference number, the C-2400, the p-BC, or the o-BC separator was sandwiched between two lithium plates, and a DC potential of 10 mV was applied for a specified time duration. The Chronoamperometry curves are presented in Figure S8. Similar to the reported value of the C-2400 separator that has a measured transference number of ~0.59, the p-BC and o-BC separator show a t^+ value of ~0.61 and ~0.64, respectively, suggesting favorable Li-ion transport performance.

Another merit of o-BC, when used as a separator in LSB, is its superior ability to curb the migration of polysulfide from the sulfur cathode to the Li anode, which is visually revealed by the polysulfide permeation test shown in Figures 2b and S9a. Small vials filled by 20 mM Li₂S₆ solution and blank electrolyte were kept apart by an o-BC, p-BC or C-2400 separator. The color change of the blank electrolyte was recorded as a function of time. When the C-2400 separator is used, the blank electrolyte turns yellowish after 6 h. For the o-BC case, the blank electrode remains transparent and does not turn yellow until after 48 h. This experiment conclusively demonstrates that the o-BC membrane is much better than the C-2400 in retarding the diffusion of polysulfides through the separator.

We have presented evidence that the o-BC membrane has significant advantages over C-2400 as a separator in improving Li⁺ conductivity and suppressing polysulfide species from crossing-over diffusion. To confirm that these merits of o-BC can be leveraged to improve LSB performance, full cell studies are called for to obtain direct evidence. In this study, the LSB cathode is sulfur loaded carbonized BC membrane as a freestanding electrode (S/cBC). Its preparation process is schematically illustrated in Figure S10. The morphology of cBC is revealed by the SEM and TEM images in Figure S11. As the scaffold of the electrode, the highly crosslinked carbon nanofiber structure converted from BC was reported to have desirable properties for use as an LSB cathode scaffold^{6, 50-51}. The crosslinked nanofiber structure provides not only an excellent electronic conductivity for the cathode but also a large surface area for anchoring sulfur species and blocking the diffusion of polysulfides.

Figure 2c and Figure S9b show the cyclic voltammetry (CV) curves recorded at 0.1 mV s⁻¹ within the voltage window of 1.6 to 2.8 V for cells with C-2400, p-BC or o-BC separator. Three redox peaks at 2.25, 1.95, and 2.45 V originate from the $S_8 \rightarrow Li_2S_x$, $Li_2S_x \rightarrow Li_2S/Li_2S_2$, and $Li_2S \rightarrow Li_2S_x$ reactions (x \geq 4), respectively. For the o-BC separator-based cell, these redox peaks show a higher current density and a smaller redox peak potential difference than the C-2400 or p-BC separator-based cell, suggesting faster reaction kinetics. The EIS Nyquist plots in Figures 2d and S9c were measured in fresh cells, and all the curves are comprised of a semi-circle at higher frequencies and a tilted line at low frequencies, corresponding to the charge transfer and lithium-ion diffusion processes⁵². By employing the equivalent circuit described in Figure 2d, the values of Re and Rct can be estimated from data fitting which are summarized in Table S1. The o-BC and p-BC separator-based cells have relatively lower Re and R_{ct} values than the C-2400-based one, indicating that the o-BC separator with abundant oxygen functional groups facilitates the Li⁺ diffusion⁵³⁻⁵⁴. After CV cycling, the cells were subjected to the EIS test to study the change in their electrochemical processes. As shown in Figures 2e and S9d, the Nyquist plot in the high-frequency region splits into two semicircles. The appearance of a 2nd semicircle corresponds to the Li⁺ migration through the solid-electrolyte interface (SEI) film formed during the cell activation process $(R_s)^{55}$. The reduced Re and Ret values (Table S1) of all these three cells after CV cycling, which were derived from data fitting based on the equivalent circuit in Figure 2e, are presumably a result of the redistribution of S in the carbon nanofiber matrix and the penetration of the electrolyte into the electrode⁵⁶⁻⁵⁷. In addition, the Li⁺ diffusion coefficients (D_{Li}^+) for C-2400, p-BC, and o-BC separators-based cells were quantitatively calculated by linear fitting the peak currents

and the square root of scan rates extracted from a series of CV curves at different scan rates (Figures 3f, S12, and 3g)^{49, 58}. As summarized in Table S2, the D_{Li}^+ values calculated from Peak C1, C2, and A1 for both samples are in the same order of magnitude, and again, suggesting the good Li⁺ diffusion capability in the o-BC-based cell (the oxygen functional groups have been considered to generate smooth Li⁺ flux⁵⁹).

The self-discharge behavior of the LSB cell is another factor that defines the difference in performance among the o-BC, the p-BC, and the C-2400 separators. The self-discharge rate of the corresponding cells was measured by monitoring their open-circuit voltage (OCV) after conducting the first full discharge-charge processes. The results are represented in Figures 2h and S9d. Within a few hours, the C-2400 separator-based cell exhibits a fast voltage drop from ~2.40 to ~2.35 V and the p-BC-based one shows a moderate OCV drop from ~2.42 to 2.39 V, while the o-BC-based cell has a relatively stable OCV except the initial trivial decay. Such a behavior contrast further confirms that the o-BC separator efficiently slows down the cell's self-discharge rate by preventing crossover diffusion of polysulfides.



Figure 3. (a) voltage profiles of LSB cells with C-2400, p-BC, and o-BC separator at 0.3C. (b) Cycling performance of LSB cells by using o-BC, p-BC, and C-2400 as separators with ~4 mg cm⁻² of sulfur loading. (c) Voltage profiles at different current densities. (d) The rate capability of the cell with the o-BC separator. (e) The cycling performance of cell with o-BC separator at 0.5C for 300 cycles. (f) Voltage profiles of cells using o-BC separator with high

sulfur loadings at 30th cycle. (g) The cycling performance of cells with 6 and 8 mg cm⁻² sulfur loadings.

The capacity, rate capability, and cycling performance of LSB cells with C-2400, p-BC, and o-BC separators were examined further. The voltage profiles of the three different cells at 0.3C are compared in Figure 3a. The discharge plateau at higher voltage (~ 2.3 V), which contributes a capacity $Q_{\rm H}$, represents the reduction of S_8 into high-order soluble polysulfides, and the dominant one at a lower voltage (~ 2.1 V) with a capacity of Q_L is originated from further reduction of polysulfides into insoluble Li₂S/Li₂S₂⁶⁰. The o-BC-based cell delivers both higher Q_H and Q_L than the p-BC-based and the C-2400-based cells which is a direct consequence of the improved polysulfide confinement effect provided by the o-BC separator. The aforementioned cells with ~4 mg cm⁻² sulfur loading were subjected to charge-discharge processes for 100 cycles (Figure 3b). The o-BC separator-based cell delivers a higher specific capacity of ~1170 mAh g⁻¹ at the first cycle and is maintained at ~1033mAh g⁻¹ even after 100 cycles. They are much better than the specific capacity of ~1135 and ~895 mAh g⁻¹ for the p-BC-based cell, and ~1060 and ~640 mAh g⁻¹ for the C-2400-based cell at the 1st and 100th cycle, respectively. In addition, the o-BC cell also shows higher overall Coulombic efficiency than both p-BC and C-2400 cells, which proves the higher effectiveness of the o-BC separator in suppressing polysulfide shuttle during battery cycling.

The rate capability of the different LSB cells was further quantified. As shown in Figures 3c, 3d and S13, the o-BC-derived cell delivers a reversible specific capacity of 1175, 1119, 984, 867, 626 and 510 mAh g⁻¹ at 0.1, 0.2, 0.3, 0.5, 1 and 2C, respectively. When the

charge-discharge rate cycles back to 0.3C from high rates, the cell recovers a specific capacity of 896 mAh g⁻¹. The other two cells based on p-BC and Celgard separators delivered much lower specific capacity and have difficulties to recover more specific capacity when the rate decreases from 2C to 0.3C. To examine its long-time cycling stability, the o-BC cell was initially cycled at 0.1C for 10 cycles, 0.3C for 40 cycles, and 0.5C for another 250 cycles (Figure 3e). After the capacity dropped in the first few activation cycles, due to SEI formation, the cell regained its stability at 0.3C and delivers a specific capacity of 735 mAh g⁻¹ by the 300^{th} cycle. This corresponds to an average capacity loss of as small as 0.07% per cycle at 0.3C. The cycling test suggests that the o-BC separator is an excellent candidate for use in the development of long-term stable LSBs.

Toward a practical LSB design that requires high sulfur loading, another two cells with \sim 6 and 8 mg cm⁻² of sulfur loading in the cathode were assembled using the o-BC separator. The sulfur mass content in the cathode of these two cells is around 83.9% and 86.9% (Figure S14, the weight percentage of different sulfur cathodes based on TGA results), respectively. Their voltage profiles at 0.2C are plotted in Figure 3f. The cells with a high sulfur loading can still maintain a well-defined discharge and charge plateaus, giving a respectable specific capacity of ~788 and ~677 mAh g⁻¹, the areal capacity of 4.18 and 4.80 mAh cm⁻², and Coulombic efficiency of ~98.4% and ~97.6% (Figure S15) for 6 and 8 mg cm⁻² sulfur loading, respectively. And impressively, after 100 cycles, the two cells have a specific capacity of ~754 and ~613 mAh g⁻¹, respectively, with their Coulombic efficiency around ~98%. These preliminary results suggest that our o-BC membrane can be considered as an excellent candidate as a separator for the development of LSBs that can operate at high sulfur loadings

to deliver practical levels of power and energy.

4. Conclusion

We have developed a functionalized BC-based separator for LSBs by oxidizing the cellulose chain *via* a TEMPO mediated process to convert part of the hydroxyl groups into carboxylate groups. The introduced carboxylate groups barrier to the negatively charged polysulfides, restraining the diffusion of polysulfides to the anode side. This hypothesis has been verified through various physicochemical characterizations and LSB cell electrochemical studies. Furthermore, cells with high sulfur mass loading (6 and 8 mg cm⁻²) and high sulfur content (85% and 89%) have exhibited large areal capacities. Further considering the excellent mechanical, thermal and chemical stability of the BC polymer, this proposed separator has great potential in developing practical LSB technology.

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Supporting Information

Digital photos of BC pellicle, p-BC, and o-OB in water, XPS analysis for p-BC and o-BC, the electrolyte-uptake capability of Celgrad, p-BC, and o-BC separator, flexible demonstration for BC separator, Li⁺ transference comparison for C-2400, p-BC and o-BC separator, SEM and TEM of cBC, EIS and CV analysis for o-BC separator.

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