Bacterial cellulose nanofiber membrane for use as lithium-ion battery separator

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Abstract. Separator plays a major role in lithium-ion batteries. For conventional polyolefin separators, low porosity is a serious problem, which will affect the electrochemical performance of lithium-ion batteries. In this work, we prepared membranes with different porosities by controlling the amount of oxidant in the Tempo oxidation process. 2, 2, 6, 6-tetramethylpiperidine-1-oxyl (TEMPO)-oxidation bacterial cellulose (TOBC8) separator exhibits suitable porosity (65%), excellent wettability, high lithium ion conductivity (0.388 mS cm⁻¹), and outstanding cycle stability.

1. Introduction
In recent years, with the development of emerging industries such as electronic equipment, new energy vehicles, and flexible sensors, renewable materials have received great attention[1]. Lithium-ion battery has the remarkable characteristics of high energy density, long life, and small self-discharge, which makes lithium-ion battery show great development potential. The separator is a key component of a lithium-ion battery and is located between the positive and negative electrodes. Its function is to prevent the positive and negative electrodes from contacting, while allowing lithium-ions to pass through[2].

At present, the microporous polyolefin separator is the most commonly used lithium-ion battery separator because of its advantages in performance, safety, and cost. However, its development has been limited due to the inherent shortcomings of polyolefin membranes[3]. For instance, polymer separators are made from non-renewable and non-biodegradable petroleum-based products, which will be harmful to the environment if widely used[4]. Besides, because of the low surface energy, the wettability of polyolefin separators to electrolyte is poor and consequently leads to the decrease of lithium-ion migration rate or even the inferior of electrochemical performance[5]. Furthermore, the thermal stability of polyolefin separators is poor due to intrinsic low melting point. In order to meet the needs of lithium-ion batteries, high-performance separators have become a research focus. Lee et al. coated the alumina nanoparticles on both sides of polyethylene separators, showing higher thermal stability and better electrochemical performance than pure polyethylene separators. Moon et al. used inorganic-organic hybrid coating technology to improve the dimensional stability and power capability by using atomic layer deposition and polydopamine treatment the surface of polyethylene separators. Zhang et al. developed a novel separator through coating a low molecular weight poly(p-phenylene terephthalamide) solution on polyethylene separators, which was found to have thermal shutdown function and excellent thermal stability when used as LIBs separators.
With the development of the times, the use of renewable environmentally friendly materials to replace environmentally harmful and non-degradable materials in lithium-ion batteries has attracted widespread attention[6]. Cellulose is an environmentally friendly material. Cellulose membrane can be prepared by some simple methods, such as papermaking and vacuum filtration. In recent years, cellulose membrane has been successfully applied to lithium-ion battery separators. However, the cellulose-based separator has a large porosity, which affects the electrochemical performance of lithium-ion batteries. Bacterial cellulose (BC) is a high molecular compound synthesized by microorganisms. Its chemical composition is similar to that of natural cellulose, but it has its particularity. BC has high purity, small diameter, and environmentally friendly. In our work, BC nanofiber membranes were successfully prepared by 2, 2, 6, 6-tetramethylpiperidine-1-oxyl (TEMPO)-oxidation method as separators for lithium-ion batteries. TEMPO-oxidation BC (TOBC) separators have suitable porosity and good electrolyte wettability. The porosity, wettability, ionic conductivity, and interface resistance of TOBC separator are characterized. Finally, the impact of TOBC separator on the performance of lithium-ion batteries is discussed.

2. Experimental

2.1. Materials
BC pellicles were obtained from Hainan Yide Food Co., Ltd. Tempo (98%), sodium bromide (NaBr, 99%), sodium hypochlorite (NaClO, 99%), anhydrous ethanol, n-butanol (99%) and N-methyl-2-pyrrolidinone (NMP, 99.9%) were provided by Aladdin Industrial Corporation. Lithium iron phosphate (LiFePO4), polyvinylidene fluoride (PVDF) and conductive carbon (Super P Li) and lithium metal anodes were purchased by Lizhiyuan Company. The liquid electrolyte, 1.0 M lithium hexafluorophosphate (LiPF6) in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1/1 by volume) were supplied by Calvin Ltd.

2.2. Preparation of TOBC membranes
BC wet films were boiled in 1M sodium hydroxide solution for 1 hour, and then washed with deionized water to neutrality. For the typical Tempo-oxidation reaction, First, BC wet film (1 g) is soaked in a mixed solution containing Tempo (0.015 g) and NaBr (0.1 g) for 30 minutes. Then, after adding the NaClO solution (4 mmol, 8 mmol and 12 mmol, respectively), use a pH meter to closely observe the pH of the solution to keep it around 10. Finally, when the pH value is stable at 10, add 5 ml of absolute ethanol to stop the oxidation reaction and wash the BC nanofiber suspension to neutral. The BC suspension was formed into a film by vacuum filtration and dried at 100°C for 30min. when the amount of NaClO was 4 mmol, 8 mmol and 12 mmol, the names of the corresponding samples were TOBC4, TOBC8, and TOBC12, respectively.

2.3. Characterization
Observe the surface morphology of TOBC separator with scanning electron microscope (SEM, Hitachi). Fourier transform infrared spectrometer to determine what kind of functional groups exist in the sample (FTIR, Bruker TENSOR 27). X-ray diffraction (XRD) can measure the lattice type and unit cell constant of the sample. Thermogravimetric analysis (TGA) is a thermal analysis technique that characterizes the thermal stability and composition of materials by measuring the changes in sample mass and temperature under program-controlled temperature. The contact angle meter was used to analyze the wettability of the separator. The porosity of the sample was calculated by the following formula: Porosity = (Wm − Wb) / ρbVp × 100%, where Wm and Wb are the weight of separator before and after immersed in n-butanol for 1 h, ρb and Vp are respectively the density of n-butanol and the volume of dry separator. The electrolyte uptake can be calculated by the following equation: Electrolyte uptake (%) = (M2 − M1 )/M1 × 100%, where M1 and M2 are the mass of the separator before and after immersion in the electrolyte for 2 h, respectively[7]. The electrochemical impedance spectroscopy and linear sweep voltammetry (LSV) curve of the separator were measured by the electrochemical workstation. The cycle performance...
of the lithium-ion battery was measured by LAND battery testing system.

3. Results and discussion
The surface micromorphology of TOBC separators were observed with a scanning electron microscope (SEM). Fig. 1 shows the surface morphology of TOBC4, TOBC8, and TOBC12 separators. It can be clearly seen that the surface of the TOBC separator is very flat and the three-dimensional network fiber structure is clearly visible. After BC was oxidized by Tempo oxidation method, the nanofibers were easily dispersed in water due to the presence of aldehyde groups and acetal groups[8]. Fig. 2 shows the diameter of BC nanofibers with different oxidation degrees after forming. The fiber diameters of TOBC4, TOBC8, TOBC12 diaphragms are 43, 40.99 and 32.63 nm, respectively. The size of the fiber diameter will affect the porosity of the separator.

![Figure 1 SEM images of (a) TOBC4, (b) TOBC8, and (c) TOBC12.](image)

![Figure 2 Diameter distributions of nanofibers on a separator of (a) TOBC4, (b) TOBC8, and (c) TOBC12.](image)

Analysis of functional groups of TOBC separator by FTIR spectra. As shown in Fig. 3a, the broad strong absorption peak of TOBC separator at 3335 cm\(^{-1}\) indicates that its structure contains O-H. The characteristic peak near 2895 cm\(^{-1}\) is the C-H stretching vibration peak. The characteristic peak between 1000 cm\(^{-1}\) and 1050 cm\(^{-1}\) (near 1029 cm\(^{-1}\)) refers to the stretching vibration of C-O-H, indicating the existence of C-O-H structure. No absorption peak of C=O tensile vibration at about 1740 cm\(^{-1}\) was detected in the spectrum of TOBC sample, indicating that the aldehyde group changed to other groups.
after oxidation[9]. In Fig. 3b, there are two peaks at 2870 and 2850 cm$^{-1}$ attributable to the C-H stretching vibration in the acetal, which indicates that the generated aldehyde group is converted into an acetal group with adjacent hydroxyl groups.

![Figure 3 (a-b) FTIR spectra of TOBC4, TOBC8, and TOBC12.](image)

It can be seen from Fig. 4, the thermal weight loss temperature of TOBC separator is around 300°C, and the slight weight loss before heating to 300°C is mainly due to the volatilization of moisture absorbed by the surface. In contrast, the thermal weight loss temperature of PP diaphragm is around 403°C, and there is almost no obvious thermal weight loss below 400°C. The degree of oxidation does not change the thermal performance of the TOBC separator. In addition, PP separators tend to shrink at high temperatures, which has a negative impact on the safety of lithium-ion batteries.

![Figure 4 TGA curves of the PP separator and TOBC separator.](image)

The smaller the contact angle, the better the wettability of the separator. Fig. 5 shows the contact angle of the sample. The contact angles of TOBC4, TOBC8, and TOBC12 are 30.2°, 20.3°, and 25.6°, respectively. The wettability affects the ionic conductivity of the separator, which in turn affects the electrochemical performance of the battery. Table 1 shows the relevant parameters of TOBC separator. The porosity of TOBC4, TOBC8, and TOBC12 separators are 55%, 65%, and 60%, respectively. Appropriate porosity is very important for the separator. A separator with sufficient porosity can store enough electrolyte to ensure the normal transmission of ions between the positive and negative electrodes[10].

![Figure 5 (a-c) Contact angle images of the TOBC separators.](image)
Table 1. Related indicators of TOBC separator.

| Sample | Thickness (μm) | Porosity (%) | Volume resistance (Ω) | Electrolyte uptake (%) | Ionic conductivity (mS cm⁻¹) |
|--------|----------------|--------------|------------------------|------------------------|-----------------------------|
| TOBC4  | 25             | 55           | 19.86                  | 297                    | 0.063                       |
| TOBC8  | 25             | 65           | 3.22                   | 322                    | 0.388                       |
| TOBC12 | 25             | 60           | 13.89                  | 309                    | 0.090                       |

Calculate the ionic conductivity of the separator by electrochemical impedance spectroscopy, and sandwich the separator immersed in the electrolyte between two stainless steel (SS) plates. Ion conductivity affects the transfer rate of lithium-ion, which in turn affects the electrochemical performance of lithium-ion batteries. It can be seen from Fig. 6 that the volume resistance of TOBC4, TOBC6, and TOBC12 separators are 19.86, 3.22, and 13.89 Ω, respectively. The ionic conductivity of TOBC4, TOBC8, and TOBC12 separators are 0.063, 0.388, 0.090 mS cm⁻¹, respectively. The ionic conductivity of TOBC8 separator is the highest. This is mainly because the wettability of TOBC8 separator is better than other samples. It can be seen from Fig. 6c that the interface resistances of TOBC4, TOBC8, and TOBC12 separators are 348, 246, and 314 Ω, respectively. Fig. 6d shows the electrochemical stability window of the separator. It can be seen that the TOBC separator has a substantial increase in current around 4.5 V.

Figure 6(a-b) are electrochemical impedance spectra of SS/separator/SS battery; c electrochemical impedance spectrum of lithium/separator/lithium battery; d LSV of SS/separator/Li battery.

Fig. 7 shows the cycle stability of the battery when the current density is 1 C. The initial discharge specific capacity of batteries with TOBC4, TOBC8, and TOBC12 separators are 112, 140, and 120 mA g⁻¹, respectively. The battery with TOBC8 separator has a capacity retention rate of 89% after 100 cycles.
4. Conclusions
This work successfully prepared TOBC separators for lithium-ion batteries. In particular, the TOBC8 separator has suitable porosity and good wettability, and the ion conductivity can reach 0.388 mS cm\(^{-1}\). In addition, the lithium-ion battery with TOBC8 separator still has a high specific capacity after 100 cycles.

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