The preparation of intrinsic DOPO-Cinnamic flame-retardant cellulose and its application for lithium-ion battery separator

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Abstract
A renewable and superior intrinsic thermal-resistant cellulose-based nonwoven was explored as lithium-ion battery separator via phase separation mechanism. Herein, we sparked a robust strategy for improving the flammability of cellulose, namely DOPO-Cinnamoyl Cellulose (DCC) with intrinsic flame retardant was obtained via the incorporation of 9,10-dihydro-9-oxa-10-phosphaphenantrene-10-oxide (DOPO) and Cinnamoyl Chloride attached on the backbone of cellulose. It demonstrates that the heat release rate and total heat release significantly reduced. Meanwhile the membrane displayed excellent self-extinction. Additionally, after the DCC membrane assembled into lithium battery, under the optimum formulation situation, the electrochemical properties established that the LIBs showed superior electrochemical performance compared with PP separator. The interface impedance of DCC separator was less than 300 Ω, which was much smaller than that of commercial separator of 410 Ω. After 50 cycles, the battery with DCC-0.11 separator retained 84.2% of its initial discharge capacity, which was higher than the commercial polypropylene separator with the numeric of 79.1%. In sum, this novel, environmental friendly and intrinsic DOPO-Cinnamic flame-retardant cellulose based separator can be considered as an expectant candidate for lithium ion battery separator with high performance.

1. Introduction

In the past decades, lithium-ion batteries has drawn wide-spread attention for grid-scale energy storage systems, the emerging fields such as low-emission vehicles and energy storage systems due to the high power, high energy density, excellent cycle performance and long cycle life. The separator in battery plays an important role in electrically isolating cathode and anode to prevent electrical short circuits and at the same time allow rapid transport of ionic charge carriers. Conventionally, microporous polyolefin separators, such as polypropylene (PP), polyethylene (PE) are widely used due to their relatively well-tailored physical property, good electrochemical stability and inherent shutdown function. Unfortunately, inferior thermal stability due to their low softening or melting temperature and infertile infiltration of the electrolyte restricts its further application. In addition, the polyolefins from the ever-decreasing fossil oil are not renewable, which may result in severe environmental pollution. An alternative way to solve this problem is to achieve the transition from fossil-based resources to biomass-based resources. Recently, The cellulose-based lithium ion membranes [1–5] have drawn considerable attention due to the excellent performance such as superior thermal stability (initial decomposition temperature > 250 °C) superior wettability with liquid electrolytes, high dielectric constant, good chemical stability, environmental benignancy and biocompatibility. It is worth mentioning that cellulose, as the substrate of lithium-ion battery separators, is the most abundant, biodegradable, renewable and biocompatible natural resources.

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polymer in nature [6–8], compared with the PP separator [3, 9–13], the commercial non-renewable petroleum material [14–17].

Unfortunately, the major drawback of cellulose lithium ion battery separator [18] is that the cellulose [6, 19–22] material is easy to burn, it is particularly flammable with a low limiting oxygen index [23, 24] (LOI about 19%), which challenges the safety performance of the separator [13, 25]. For example, the lithium ion battery separator may trigger fire when encountering the short circuit and overcharging. A lack of safety features may even result in some casualties. This makes it critical to examine thermal resistant and flame-retardant cellulose-based lithium-ion battery separators [4, 26, 27]. Considering the above reasons, modification of cellulose-based materials is imperative. Based on the literature, it showed that the facial method to improve the flame retardant property of cellulose is blending cellulose and fire retardant together [28–30]. However, the fatal flaw is that the fire retardant may fall off after a long time due to the fragile physical binding force. Thus, the reduced mechanical properties and flame retardant performance, even the environmental pollution may restrict its wider application [31]. If this mixture acts as lithium-ion battery separators, the shedding of the flame retardant may cause side reactions, and even cause the performance of lithium ion batteries to decline. In addition, the blending is difficult to achieve uniformly, owing to the incompatibility [32] of the hydrophilicity of cellulose and the hydrophobicity of flame retardant. Therefore, The fabrication of intrinsic flame retardancy based cellulose is particularly valuable, if it is used in lithium ion battery separator, it will have flame retardant performance with the premise of having excellent electrolyte wettability [33].

According to research that 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) [13, 14, 34–39], with non-toxic, halogen-free, low-smoke representative organophosphorus flame-retardants, can not only effectively reduce the heat release rate of materials, but it can also reduce the release of toxic gases. In addition, it has excellent stability and good hydrolysis resistance with a relatively durable flame-retardant effect, due to the presence of P–C bonds in its molecules. It can act in the vapor phase and in the condensed phase simultaneously [38]. Thus, DOPO and its derivatives can be used to modify the various polymeric materials such as electronics, synthetic fibers, plastics, and rubber for superior flammability performance [13]. Khalifah A [39] discovered that polyurethane (PU) modified by the novel DOPO based phosphonamidates exhibited superior thermal behavior and fire performance.

Different from coating inorganic nanoparticles or compositing retardant and other high performance polymers for enhance battery safety characteristics [3, 40, 41], we describe a clean, previously unexplored route for constructing an inherent flame-retardant cellulose film. It also permits us to use Cinnamoyl Chloride as a bridge linking the common phosphorus flame-retardant DOPO and the most abundant natural polymer cellulose, synthesizing a flame-retardant intrinsic cellulose film. Compared with the simple blending, grafting the flame retardant onto the hydroxyl group of cellulose can form a stable chemical structure, which can not only effectively increase the flame-retardant performance, but greatly increase the safety and stability of the battery separator. For this study, the formation of the inherent flame-retardant cellulose film was characterized by Scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (1HNMR) and Thermo Gravimetric Analyzer(TG), elemental analysis, mechanics performance testing, and snapshot photos during combustion, MCC and LOI. It aimed to explore the preparation of new cellulose-based materials with excellent film-forming properties, mechanical properties and flame-retardancy. In addition, the prepared membrane, with excellent infiltration of the electrolyte and flame-retardant performance, was assembled into a lithium ion battery. The corresponding battery characterization was then tested including its cycle stability and rate stability. The fascinating characteristics and enhanced battery performance would suggest this composite membrane is a very promising separator for high power applications, which broadens its application in the field of energy storage devices.

2. Materials and method

2.1. Materials

Cotton pulp (M30, DP = 500) was dried under vacuum at 80 °C for 48 h before using. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was purchased from Jiangyin Hanfeng Technology Co. Ltd, and dried under vacuum at 70 °C for 6 h before using. Azobisisobutyronitrile(ABIN), N,N-diethylethanamine (DMAC), LiCl, Cinnamoyl Chloride was of analytical grade and used without further purification. The lithium cobalt oxide (LiCoO2), lithium wafers and steel slices were purchased from Beijing Nonferrous Metals Research Institute. The electrolyte consisted of LiPF6 was provided by Dong Guan Battery Materials Co.Ltd.
2.2. Synthesis of DOPO-g-Cinnamic cellulose (DCC)

(1) The activation of cellulose
Firstly, the M30 cotton (DS = 860) was activated by soaking in sodium hydroxide (NaOH) solution (20 wt%) for 1 h aiming to make it swell. Subsequently, the suspension was diluted to neutral with diluted hydrochloric acid after suction filtration using a sand funnel, after that, the suspension was treated with H₂O, methanol and DMAC sequentially. Finally, the samples were dried in a vacuum oven. The activation of cellulose was to break the hydrogen bonds between cellulose molecular chains, thereby destroying the crystalline structure of cellulose. This process was favorable to its dissolution, and promoted a homogeneous reaction of cellulose.

(2) The preparation of cellulose solution
1.0 g cellulose was dispersed in DMAC under the protection of nitrogen. Cellulose was activated for 1 h at 160 °C. Afterwards LiCl (8 wt% of DMAC) was added to the solution before which was then cooled to 100 °C. The stirring process lasted two hours until it completely formed a homogeneous solution. Combining related literature and pre-test verification, 2 wt% cellulose solution was prepared for a subsequent series of reactions.

(3) Preparation of the cellulose Cinnamoly Ester (CC)
A prescribed amount of Cinnamoyl Chloride (Molar ratio of AGU/Cinnamoyl Chloride = 1:5) was added to the 2 wt% cellulose solution synthesized above. After the addition of CC was completed, the temperature was subject to 80 °C and the reaction lasted for 24 h. Then the solution was cooled to room temperature with continuous stirring. Subsequently, methanol was added to the reactive mixture, and brown flocculent precipitate was obtained via filtration. The brown flocculent precipitate was then washed three times by methanol filtration and the product was dissolved in dimethylsulfoxide (DMSO). The cellulose CC was obtained after freeze drying.

(4) Synthesis of DOPO-g-cinnamic Cellulose (DCC)
9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was dissolved in DMAC, and then the catalyst Azobisisobutyronitrile (AIBN was 1% of n_DOPO) was added dropwise to form a mixture. Dry CC was dissolved in DMAC/LiCl to form 2 wt% homogeneous solution, then the dissolved mixture DOPO and AIBN was slowly dripped into CC solution through a constant pressure equalizing dropping funnel. After a period of reaction, similar to the processing steps above, methanol was added to the mixture, followed by multiple suction filtration. Ultimately, the yellow flocculent precipitate was obtained through freeze-drying before characterization and further reaction.

2.3. Preparation of membranes
Figure 1 shows the preparation route of the DCC membranes via phase inversion method. 4 wt% of DCC was added into DMAC (solvent) and dispersed by constant stirring for 4 h at 60 °C to obtain a homogeneous solution. After cooling to room temperature in air, the solution was degassed completely to ensure that there were no air bubbles before casting. The casting solution was cast onto a flat glass by MSK-AFA-III Automatic
Thick Film Coater with appropriate thickness. These membranes were evaporated for 30 s in air followed by gentle immersion in a coagulation bath (deionized water). Finally, the membranes were by freeze-dried for further characterization. The Schematic illustration for the experimental process and structures of composite membrane was showed as the figure 1.

2.4. Battery assembly
Before battery assembled, we measured the dried membranes’ thickness with the thickness gauge, and immersed membranes into n-butanol 2 h for testing their porosity. We also analyzed the membranes’ infiltration for the electrolyte in the electrolyte solution of LiPF₆. Considering electrochemical stability and operational safety of the cells, we assembled the button-type cells (LIR2025) in an Ar-filled glove box. The cell contained three parts: LiCoO₂ anode, Li metal cathode and the DCC membrane which was sandwiched between anode and cathode. After assembling, the cells were laid at room temperature for 24 h. Afterwards, the various electrochemical performance with the flame-retardant intrinsic type cellulose-based separator was tested.

2.5. Measurement and characterization
2.5.1. Physiochemical measurement of the samples
The Fourier transform infrared (FTIR) (Nicolet 6700) spectrometer was employed to record the characteristic peaks of samples from 650 to 4000 cm⁻¹ with 2 cm⁻¹ resolution. ¹H NMR spectra were acquired on Bruker AV-400 NMR spectrometer with 16 scans at room temperature in DMSO-d₆. A few drops of trifluoroaceticacid-d₁ were added to shift active hydrogen to a lower field area. The chemical compositions of DCC samples were analyzed by x-ray photoelectron spectroscopy (Thermo Escalab 250XI) using Al Kα x-ray source (hν = 1486.6 eV) at a pass energy of 93.9 eV. The chemical formula of the substituted monosaccharide group of DCC is: C₆₊₂1DSH₁₀+₁5DSO₃DSP. To better explain how the grafted cellulose had changed their chemical components, we calculated the contents of phosphorus in the DCC membranes, and the formula was:

$$P\% = \frac{31DS}{C₆₊₂1DSH₁₀+₁5DSO₃DSP} \times \frac{162 + 381.5DS}{31DS}$$

2.5.2. Flame-retardant performance of DCC membranes
The combustion experiments were carried out to investigate the flame-retardant performance of membranes with microscale combustion calorimeter (Govmark, USA). Each sample was heated from 25 °C to 650 °C at a rate of 50 °C min⁻¹. Thermogravimetric analysis was conducted on a TA-Q2000 differential scanning calorimeter (TA Instruments, USA) under air atmosphere. Each sample was heated from 25 °C to 700 °C at a rate of 20 °C min⁻¹.

2.5.3. Mechanical properties of membranes
The tensile properties were tested on an INSTION 1185 electronic tensile testing machine under the following conditions: temperature, 20.0 °C; humidity, 50.0%; elongation, 5.0 mm min⁻¹.

2.5.4. Porosity of the Membranes and the uptake data of LiPF₆ electrolyte solution
The thickness of the membranes was measured by a thickness gauge, and the porosity of the membranes was adopted by immersing them in n-butanol for 2 h. The porosity (P) of membranes were calculated using the following equation:

$$P = \frac{\Delta m/\rho}{m/\rho m} \times 100\%$$

Where Δm was the weight difference before and after soaking in n-butanol; m was the initial weight of the separator; ρ was the n-butanol density (g·cm⁻³); ρm was the initial density of the separator (g·cm⁻³). The electrolyte uptake of the separators was analyzed by immersing the separator in the electrolyte solution of LiPF₆ in a glove box. The electrolyte update (Q) of membranes were calculated using the following equation:

$$Q = \frac{M_f - M_0}{M_0} \times 100\%$$

Where M₀ and Mᵻ was the weights of the membrane sample before and after sorption respectively.
2.5.5. Electrochemical measurements

The separators soaked with electrolyte were sandwiched between two stainless steel (SS) electrodes with 16 mm diameters and the cell was assembled for the ionic conductivity test. The ionic conductivity of separators was measured by AC impedance spectroscopy (EIS, CHI660E electrochemical work) at the frequency range of 1–10 KHz and the formula was calculated as following:

$$\sigma = \frac{L}{R_b \times S}$$

(4)

Where $\sigma$ was the ionic conductivity, $L$ was the thickness of separators, $S$ was the area of stainless steel electrodes and $R_b$ was the bulk resistance. We used LAND battery cycle system at 0.2 C (voltage range from 2.8 V to 4.2 V, 50 cycles) to evaluate the charge/discharge cycling performance of the LIB [42]. For C-rate performance, the cells were cycled at fixed charge/discharge current density of 0.2 C, 0.5 C, 1 C, 2 C and 4 C rates respectively to measure the discharge performance [43].

3. Results and discussion

3.1. Physiochemical performance

As observed from figure 2, the original cellulose material showed a rod-like structure with a relatively flat surface, and has no obvious defects. It can be seen that there were many needle-like nanoscale pores on the surface of the commercial PP membrane, which may have been caused by the dry drawing process. The DCC separator had a large number of elliptical holes prepared by the Nonsolvent Induce Phase Separation method. Moreover, the cellulose molecule contained a large number of hydroxyl groups absorbing a large amount of electrolytes, which was beneficial to improve the performance of the battery. In addition, from the DCC powder modified by cellulose and DOPO (figure S1 available online at stacks.iop.org/MRX/8/076404/mmedia), it can be intuitively seen that the cellulose fiber of DCC was much more rougher curled, which verified the generation of reaction above.

In the FTIR spectrum of CC (figure 3(a)), the existence of skeleton peak of benzene showed at 1450 cm$^{-1}$ and 1500 cm$^{-1}$. The appearance of the peak at 1719 cm$^{-1}$ and 1636 cm$^{-1}$ corresponded to C=O stretching vibration and C=C stretching vibration confirmed that Cinnamoyl Chloride was successfully grafted to the hydroxyl surface of cellulose. Compared with the infrared spectrum of cellulose, absorption bands at $\approx 3374$ cm$^{-1}$ ascribed to O–H stretching vibration appeared, which indicated that hydroxyl groups of cellulose had been modified. Similarly, in the spectra of DCC, the disappearance of the peak at 1636 cm$^{-1}$ and 2436 cm$^{-1}$ corresponded to P–H vibration and the appearance of P=O stretching vibration at 1270 cm$^{-1}$ and aromatic C–H out of plane bending vibration at 750 cm$^{-1}$ demonstrate that DOPO was successfully grafted to the glucose units of cellulose.

As shown in figure 3(b), the peak of 7.0–8.0 ppm is attributed to the aromatic protons of CC, and the peak of 2.5–3.0 ppm is assigned to the protons of C=C bonds. The emergence of these chemical shifts confirmed the reaction between Cinnamoyl Chloride and Hydroxyl groups on cellulose surface. Chemical shifts located at 3.4 ppm and 2.5 ppm corresponded to chemical shifts of protons of H$_2$O and DMSO, respectively. However, the peak of the protons of C=C and the protons of P–H belonging to DOPO (8.7 ppm) for DCC both disappeared,
and the peak of aromatic protons for DCC became much sharper, which confirmed that DOPO was introduced to CC through the reaction between P–H and C=–C bonds. As for the substitution of DOPO during the reaction, it can be analyzed from the above table S.1. The result demonstrated that the ratio is the most critical factor for the substitution of DOPO in the target product DCC, compared with time and temperature.

The x-ray diffraction (XRD) pattern (figure 3(c)) of cellulose shows characteristic diffraction peaks at 14.76°, 16.62° and 22.81°, corresponding to I/β allomorph of cellulose [44]. However, the crystallization properties of cellulose activated by sodium hydroxide did not change except that the crystallization strength decreased compared to the raw materials, indicating that the part of its crystal structure were destroyed after activation by alkali solution. It showed that the crystallization properties of cellulose esterified by Cinnamoyl Chloride and further reactions with DOPO changed greatly. The characteristic peak of diffraction at 4.76°, 16.62° and 22.81° all disappeared, which was similar with the amorphous scattering characteristics of solid state. The observed changes between the raw materials and modified cellulose suggested that cellulose was successfully modified, not only the hydroxyl group the cellulose distributed in the amorphous region reacted with Cinnamoyl Chloride and DOPO, but also the portion of the crystallization zone reacted with Cinnamoyl Chloride and DOPO. The

Figure 3. Characterization of various samples. FT-IR spectra (a), HNMR spectra (b), XRD patterns (c), TGA curves (d), MCC curves (e) and stretching curves (f).
reaction destroyed the crystalline region of cellulose, and it results in the XRD spectrogram of modified cellulose showing a wide diffraction peak, which agreed with the effect observed in the IR and NMR.

From the thermogravimetric graph (figure 3(d)), it can be seen that the initial decomposition temperature of pure cellulose was 285 °C. However, when Cinnamoyl Chloride reacted with the hydroxyl group of cellulose, its thermal decomposition temperature decreased. This may be attributed to the fact that hydrogen bonding between cellulose molecules was weakened by large steric hindrance induced by Cinnamoyl Chloride. However, when DOPO was incorporated to CC, the thermal decomposition temperature of DCC increased due to the formation of relatively more carbon caused by DOPO. Meanwhile, in constructed with pure cellulose, the char residual of DCC had been increased a lot and the char yield at 600 °C went up from 0 to 20%. The excess amounts of residual char may block the spread of heat and isolate the combustion of flammable gases, thereby achieving a flame-retardant effect.

During the pyrolysis process of pure cellulose, the hydrogen bonds network structure are broken at the beginning, following the segmentation of the cellulose glucosidic bonds. As the temperature gradually rises to 285 °C, the transfer reaction of glucose groups within and between molecules of cellulose begins to occur. Then the disproportionation and cracking reactions of combustible volatiles occur and the condensed phase further polymerizes. Gases, combustible volatiles and fixed coke form during the process. We can observe more residual carbons of the DCC flame retardant cellulose appear than that of neat cellulose, it is because that the flame retardant absorbs heat during the combustion process, which promotes formation of carbon. Meanwhile, phosphoxy radicals also release to capture hydrogen radicals in the degradation process. In addition, the released non-combustible gas can dilute the oxygen and flammable gas around the samples and the residual carbon of samples increases because of the effect of flame retardants.

3.2. Microscale combustion calorimeter (MCC) of cellulose and DCC
From the figure 3(e) and table 1, in contrast to pure cellulose, with the introduction of DOPO into the cellulose chains, the peak heat release rate (PHRR) and total heat rate (THR) observably decreased. The PHRR value decreased from 159.7 W g⁻¹ to 39.83 W g⁻¹, and the THR decreases from 14.1 KJ g⁻¹ to 3.6 KJ g⁻¹. The addition of a flame retardant endows cellulose with a rapid dehydration and carbonization function when subjected to high heat. The release of water reduces the surrounding temperature. The carbonized cellulose forms a carbon layer on its surface, which blocks diffusion of oxygen and prevents oxidation free radicals release. The heat releases decreases during combustion.

The successful grafting of DOPO for DCC membrane delays the combustion of samples, it can be attributed the following reasons. On the one hand, the DCC membrane decomposes into phosphoric acid and it polymerizes to form polyphosphate, which can be explained by the flame retardant mechanism of the condensed phase. A layer of covering is formed on the surface to isolate oxygen and heat transfer to achieve flame retardant effect. On the other hand, from the perspective for the flame retardant mechanism of the gas phase, at high temperatures the sample releases incombustible gases to dilute the oxygen and combustible gases around the sample, reducing and delaying the release of heat. In addition, phosphoxy radicals also release to capture hydrogen radicals in the degradation process, which are also helpful for the flame retardant performance.

3.3. Comparison of mechanical properties of cellulose, CC and DCC
From the figure 3(f), it showed that compared with the original cellulose in the DMAC/LiCl system, the mechanical strength of the obtained DCC film via the method of phase transfer film was reduced. Although breaking strength of the obtained DCC films increased, but they still maintain a high value with relative mechanical properties. The breaking strength reached 45 MPa and the breaking elongation reached 8.5%. It is speculated that two benzene rings with the addition of DOPO group increased steric hindrance, which caused hydrogen bonding interaction, making links between the cellulose chains weaker. As a result, it reduced the strength of the DCC.

3.4. LOI and snapshot photos of cellulose and DCC
As can be seen from the table 2, the limiting oxygen index (LOI) of pure cellulose is 18, which indicates it is a flammable product. When cellulose was modified by Cinnamoyl Chloride and DOPO, the resultant DCC demonstrated that the limiting oxygen index can reach 31. National flame-retardant standards stipulate that...
oxygen index $\geq 28$ is a flame-retardant material, thus DCC is a product displaying good flame-retardant properties. The result corresponded with the flammability experiment and MCC above. This was because that during the combustion process, DOPO exerts both the gas phase and the solidified phase flame-retardant mechanisms. As an intumescent flame-retardant, it can promote the formation of char. In addition, as the gas phase retardant, PO radicals released by DOPO can quench H and HO radicals generated during the combustion of cellulose, which could improve thermal stability of DCC.

It showed from figure 4 that the cellulose film burned vigorously and quickly once ignited, and all of the samples were completely burned within a very short time, leaving few ashes. In other words, pure cellulose was highly flammable. DCC modified by Cinnamoyl Chloride and DOPO displayed positive self-extinguishing properties after being removed from the flame, and the residual char increased significantly with a dense, continuous and homogeneous topography. The DCC film self-extinguished within seconds after being ignited, exhibiting good flame retardancy. It also proved that DOPO as a flame-retardant was successfully incorporated into CC. The result may be due to cellulose modified with DOPO having a certain flame-retardant effect. During the combustion process, the phosphorus Phenanthrene fragments of DOPO contributed to the formation of carbon char, which can play a role of condensed phase flame-retardant effect for polymer. From the perspective of gas-phase flame-retardant mechanism, the P–C bonding of the Phenanthrene group may break at high temperatures to form phosphorus-oxygen radicals, etc. The phosphorus-oxygen radicals can quench the alkane radicals and hydroxide radicals generated during the combustion process, terminating the chain reaction, and thus achieving a flame-retardant effect.

![Figure 4. Snapshot photos of membranes: cellulose membranes (a) and DCC membrane (b).](image)

| Table 2. LOI of cellulose and DCC membranes. |
|---------------------------------------------|
| Sample | LOI/\% |
| Cellulose | 18 |
| DCC-1.02 | 31 |

| Table 3. DCC membranes resistance and conductivity. |
|---------------------------------------------------|
| Membrane | Thickness (\(\mu\)m) | Porosity (%) | Electrolyte uptake (%) | Resistance (\(\Omega\)) | Conductivity (mS/cm) |
|----------|------------------|--------------|------------------------|------------------|------------------|
| PP separator | 25.00 | 40.3 | 96 | 2.83 | 0.45 |
| DCC-0.11 | 31.00 | 67.8 | 235 | 1.37 | 1.12 |
| DCC-0.53 | 35.00 | 68.1 | 245 | 1.84 | 0.95 |
| DCC-1.02 | 32.00 | 65.4 | 268 | 2.25 | 0.76 |
3.5. Electrochemical performance

As shown in the table below, the thickness, porosity and electrolyte absorption rate of different separators were listed in detail. These results demonstrated that DCC membranes have excellent porosity compared to commercial PP membranes due to the method of phase transfer separation, which allow the DCC diaphragm to

Figure 5. AC impedance plots (a), Arrhenius curves of various membranes (b), interface impedance plot of Li/separator/Li cells (c), Linear sweep voltammogram of SS/separator/Li cells (d), electrochemical performance of LiCoO₂ cells, initial charge and discharge properties (e), cycling behavior (f), and rate behavior (g).

3.5. Electrochemical performance

As shown in the table 3 below, the thickness, porosity and electrolyte absorption rate of different separators were listed in detail. These results demonstrated that DCC membranes have excellent porosity compared to commercial PP membranes due to the method of phase transfer separation, which allow the DCC diaphragm to
exhibit multi-level holes. Similarly, DCC membranes exhibited superior electrolyte wettability than to commercial PP separator, owing to the strong polarity of DCC membranes caused by the hydroxyl of the skeleton structure of cellulose and introduction of the DOPO group. These factors resulted in superior electrolyte absorption, causing the polymer electrolyte to have more carriers, which is conducive to improve lithium ion conductivity and battery performance.

The figure 5 shows the AC impedance spectrum of a commercial PP separator and DCC separator at 25 °C. The intersection point between each straight line and the X axis in the Fig is the bulk resistance of the separator. The ionic conductivity of each separator is calculated according to the formula (4). The data is shown in the table 3. It can be seen that the bulk resistance of DCC separator was lower than that of a commercial PP separator. The rapid change for ionic conductivity is due to the ultra-high electrolyte liquid absorption of cellulose-based flame-retardant separator. It meant that more electrolytes were absorbed and the number of carriers increased, which can improve the lithium ion transmission rate. The decrease of hydroxyl groups in DCC weakens electrolyte absorption by the separator. Figure 5(b) showed that the log $\sigma$ of the composite separator at different temperature (25 °C–75 °C) was linear with $T^{-1}$, and belonged to the typical Arrhenius model. It demonstrated that the composite diaphragm and commercial PP membrane has the same lithium ion transport mechanism, and follows the Arrhenius law.

The figure 5(c) shows the interface impedance of commercial separators and various DCC flame-retardant separators at room temperature. It can be seen that the interface impedance of DCC separator was less than 300 $\Omega$, which was much smaller than that of commercial separator of 410 $\Omega$. This may be attributed to the exposed hydroxyl groups on the cellulose, which promotes the electrolyte’s absorption of DCC separator. Meanwhile, with the increment of the degree of substitution, the interface impedance of DCC increases gradually. It is because that with the increase of the content of substituents, fewer hydroxyl groups of DCC result in inferior wettability of the DCC separator.

The separator must be chemically stable against the electrolyte. The figure 5(d) shows the electrochemical stability window curves of commercial PP separators and DCC separators. It showed that decomposition voltage of commercial PP is 4.5 V. The decomposition voltage of DCC diaphragms with different degrees of substitution is slightly better than commercial diaphragm, which meets the practical application standards of lithium-ion batteries. The stable electrochemical stability of DCC separator is attributed to the superior electrolyte wettability [8] caused by the exposed hydroxyl groups on the surface, which is conducive to the transmission of lithium ions. Owing to the introduction of DOPO, it destroy the original crystalline structure of cellulose, thus the composite separator has more amorphous areas to store the electrolyte, it help the lithium ion transfer more smoothly. In addition, the growth rate of lithium dendrites slowed down to a certain extent. This result indicates that DCC separator exhibits good compatibility with the electrolyte when compared to commercial separator [17].

As can be seen from the first charge and discharge curve (figure 5(e)), the charging and discharge platforms of commercial PP and DCC diaphragms are all concentrated around 3.9 V. The first discharge specific capacity of DCC diaphragms with different degrees of substitution presented better than that of commercial PP diaphragm. Figure 5(f) below shows the cycling capabilities of the separators during 50 cycles, and it performed at a current density of 0.2 C and room temperature. During the process of the charging and discharging cycle, the discharge specific capacity of all the batteries shows a downward trend. After completion, compared to the initial test, the commercial PP separator has a capacitor retention rate of 79.1%, while the DCC separator with lower degree of substitution exhibited lower-cyclic capability, with the capacity retention rate of around 84.2% due to its excellent ionic conductivity, interface stability, and electrochemical stability. The DCC separator with the largest degree of substitution, however, demonstrated poor cycling performance with a slightly decrease, possibly ascribed to less hydroxyl on the surface and large space steric hindrance. Thus, it makes lithium ion transport relatively difficult.

As the figure 5(g) shows, after the introduction of DOPO, the composite membrane showed better rate performance. The discharge capacities of the battery decreased with increasing discharge rates, but it still kept a relatively high capacity as a whole. Specifically, the DCC-0.11 separator kept the discharge capacity of 120 mAh·g$^{-1}$ under 1 C, but the PP commercial separator was 112 mAh·g$^{-1}$. The discharge capacities of DCC-0.11 separator and PP commercial separator at 4 C were 107 mAh·g$^{-1}$ and 87 mAh·g$^{-1}$, respectively. Then, the capacities of the cells at 0.2 C after a large current discharge with the DCC-0.11 separator and PP separator were 129 mAh·g$^{-1}$ and 123 m Ah·g$^{-1}$. It showed that the DCC separator with a lower degree of substitution exhibited a much better capability rate when compared to that of PP separators. It is reasonable to deduce that the separator with a lower degree of substitution possessed more hydroxyl groups exposed on the surface promoting the infiltration of electrolytes. The improvement is mainly due to the combination of the lithium ions and hydroxyl groups of DCC separator. Therefore, based on the interaction, the efficiency of the battery increased and it can meet the high power conditions of Lithium ion batteries. In brief, the improvement of superior rate performance was owing to the lower interfacial resistance and the higher ionic conductivity of the DCC.
4. Conclusion

This paper studied the synthesis of intrinsic flame retardant cellulose material via chemical grafting. Furthermore, some preliminary exploration of the cellulose-based flame retardant material in lithium ion battery separator was carried out. The results showed that DCC had film-forming properties with significantly improved toughness. The strength and the elongation at the break of the film was 45 Mpa and 8.3%, respectively. Meanwhile the open flame combustion proved that after the modification of DOPO, it can self-extinguish quickly after ignition. The analysis of microcalorimetric (MCC) demonstrated that PHRR value decreased from 159.7 W g⁻¹ to 39.83 W g⁻¹, and the THR decreased from 14.1 KJ g⁻¹ to 3.6 KJ g⁻¹. The LOI decreased from 18 to 31 during the combustion process. Additionally, after the DCC membrane assembled into lithium battery, the electrochemical properties established that the LIBs showed excellent electrochemical performance. The result showed that the ionic conductivity was 1.12 mS cm⁻¹. The electrochemical properties further established that the LIBs showed superior general performances including the cycle and rate capability. In sum, this novel and environmentally friendly composite separator can be considered as an excellent candidate for high performance of lithium ion battery.

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