Preparation of microporous Cellulose/Poly(vinylidene fluoride-hexafluoropropylene) membrane for lithium ion batteries by phase inversion method

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HIGHLIGHTS

• A microporous Cellulose/PVDF-HFP membrane is developed for lithium ion batteries.
• Phase inversion method is used to create the porous and honeycomb structure.
• Improved ion conductivity, electrochemical and thermal stability are achieved.
• The membrane enables higher capacity, improved cycle and rate performances.
• The Cellulose/PVDF-HFP membrane has a high lithium transference number of 0.89.

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ABSTRACT

In this work, a porous and honeycomb-structured Cellulose/Poly (vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) membrane is prepared via a facile and ecofriendly phase inversion method by using glycerol as pore forming agent. Cellulose acetate, the source of cellulose, is easily converted into cellulose by hydrolysis in the presence of lithium hydroxide. Owing to the unique microstructure, the Cellulose/PVDF-HFP membrane offers several advantages, including high porosity, elevated electrolyte uptake, high ion conductivity, and wide electrochemical window (5.35 V). Compared with conventional polypropylene (PP) separator and PVDF-HFP membrane, the membrane developed in this work enables higher discharge capacity, higher lithium-ion transference number (0.89) and improved rate performance, which is able to maintain a high discharge capacity of 136 mAh g⁻¹ at 8 C, using LiCoO₂ as cathode and Li metal as anode. In addition, the Cellulose/PVDF-HFP membrane based batteries exhibit superior cycling performance that can maintain 91.7% capacity after 100 cycles at 0.2 C. The characterization and battery test results demonstrate that the membrane is highly compatible with lithium ion batteries.

1. Introduction

Lithium-ion batteries (LIBs) are widely used in portable electronics and electrical/hybrid vehicles, due to its high specific energy and long cycle lifetime [1–4]. Separator, sandwiched between anode and cathode, is a key component of LIBs, as it is designed to allow the rapid transport of Li ions but prevents electrodes from electronic contact, which significantly influences the battery performance. Currently, polyolefin, such as polyethylene (PE) and polypropylene (PP), is the most commonly used separator material in commercially available LIBs, since it owns acceptable electrochemical stability and considerable mechanical strength. However, due to the nonpolar nature, these materials show poor liquid electrolyte retention, and are unable to absorb electrolytes with high dielectric constants like cyclic carbonates, resulting in the disadvantages of low ionic conductivity and high electrolyte leakage rate.

Recently, polar polyvinylidene fluoride (PVDF) and its copolymer, poly vinylidene fluoride-hexafluoropropylene (PVDF-HFP), have received special attentions as promising host polymers for electrolyte in LIBs. Nevertheless, PVDF and PVDF-HFP membranes also have their own disadvantages, i.e. low thermal stability, poor electrochemical stability, low cyclic and rate performances, which limits the wide

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applications in lithium ion battery [5–7]. To overcome these issues, PVDF-HFP polymer has been modified by blending with other materials, such as another polymer [8–12], nano-fillers [13], lithium salts and ionic liquids [14–16]. Among these materials, cellulose, a commercially and naturally available material, shows great application potential due to its properties of excellent wettability, low processing cost, high porosity, and good mechanical properties [17], which enables the improved ion conductivity, electrolyte uptake, electrochemical and mechanical properties of the membrane [18,19].

Electrospinning was tried to prepare Cellulose/PVDF-HFP membrane [20,21], however, the strong evaporation of the solvent during this process creates difficulty to acquire the proper interconnected pores and desired pore volume, resulting in great leakage of electrolyte which cannot meet the requirements of LIBs [22]. Phase inversion has been proven as a simple and easily adaptable method to prepare porous membrane [23–26], as the solvent and non solvent exchange occurs when casting solution exposes into nonsolvent solution, thus resulting in a thermodynamically stable porous structure [27]. PVDF [28–31] and its copolymer PVDF-HFP [32–35] have been prepared by using phase inversion method. In this work, we further propose to develop the microporous Cellulose/PVDF-HFP membrane via the phase inversion method. The membrane preparation involves blending PVDF-HFP and cellulose acetate polymer in different weight ratios, followed by hydrolysis in LiOH solution to convert cellulose acetate into cellulose, and then phase inversion for film formation. The ion conductivity, electrolyte uptake, electrochemical and thermal stability were characterized and the experimental results prove that all these properties have been improved. Moreover, the LIBs performance tests clearly demonstrates that the microporous Cellulose/PVDF-HFP membrane enables higher discharge capacity and better capacity retention, owing to the improved membrane properties.

2. Experimental

2.1. Materials

PVDF-HFP and cellulose acetate (acetyl content 39.8%) purchased from Sigma Aldrich, were dried at 100 °C for 12 h under vacuum before use. Glycerol, analytical grade N-Methyl-2-pyrrolidone (NMP) were purchased from Sigma Aldrich. Commercial PP separator 2325 was purchased from Celgard company. Liquid electrolyte, 1.0 M LiPF₆ (ethylene carbonate + dimethyl carbonate with 1:1 vol ratio), was supplied by MTI Corporation.

2.2. Membrane preparation

A certain amount of PVDF-HFP and cellulose acetate was dissolved in NMP solvent to form homogenous and transparent solution. Then glycerol nonsolvent was added into the solution as a pore forming agent, followed by stirring the mixture at 80 °C for 4 h to make glycerol completely dissolved. The dispersion was casted on the glass plate by using knife blade, in turn conditioned at 35 °C and then delivered into a water bath. After that, the membrane is further dried at 80 °C for 24 h. It is worth pointing out that all the samples should be dipped into the electrolyte for 24 h to ensure the membrane becomes neutral. The thickness of all Cellulose/PVDF-HFP membrane samples are 115 μm and the thickness of comparative Celgard separator is 25–30 μm.

2.3. Regeneration of the cellulose

The prepared membranes were placed in closed containers with 0.05 M LiOH in ethanol solution under stirring for 12 h to convert cellulose acetate into cellulose via hydrolysis. Once hydrolysis was complete, the membrane was washed thoroughly with de-ionized water for 1 h, then oven-dried at 80 °C for 24 h and stored in a desiccator for further use. The complete mechanism can be seen in the Scheme 1.

2.4. Electrode preparation

Positive electrode was prepared as following: active material of LiCoO₂ (Sinopharm Chemical Reagent Co.,) acetylene black (Shenzhen Kejingstar Co.) and poly(vinylidene difluoride) (PVDF) with the weight proportion of 8:1:1 in NMP were mixed and then stirred for 8 h to prepare LiCoO₂ slurry. The obtained LiCoO₂ slurry was casted on an aluminum foil, which was further punched into round discs with a diameter of 14 mm and then dried in a vacuum oven at 120 °C for 12 h. Lithium negative electrode, purchased from Hefei Kejing Co., was also punched into round discs with a diameter of 14 mm. Commercial PP separator 2325 (Hefei Kejing Co.) was used as received for comparison. The Cellulose/PVDF-HFP and commercial PP separator 2325 were punched into round discs with a diameter of 16 mm relatively, which were larger than the electrodes. All the membranes and electrode discs were stored in an argon-filled glove box after drying treatment.

Coin cells (CR2025) were assembled in an argon-filled glove box with electrode laminates (LiCoO₂) as working electrodes, Li metal as the counter electrode, 1.0 mol L⁻¹ LiPF₆ in ethylene carbonate (EC): diethyl carbonate (DMC) (1:1, v/v) as the electrolyte, and Cellulose/PVDF-HFP membrane or Celgard® membrane as separator.

2.5. Physical and electrochemical characterizations

The structure of as-prepared membrane was observed by scanning electron microscopy (SEM, JEOL JSM-6700F). Fourier transform infrared (FTIR) spectra of Cellulose/PVDF-HFP membranes were performed on a IR/Nicolet 6700 Fourier transform infrared spectrometer. Thermogravimetric analysis (TGA-209F3, NETZSCH, Germany) was performed at a heating rate of 10 °C min⁻¹ under a flow of nitrogen. The porosity of different membranes was determined using n-butanol uptake method, in which the weight of the membrane was measured before and after soaking in n-butanol for 2 h at room temperature. The porosity was calculated by the following equation:

\[ P = \left( \frac{W_W - W_D}{W_D} \right) \times 100 \]  

where \( P \) stands for the membrane porosity, \( W_W \) and \( W_D \) represent the weights of wet membrane saturated with n-butanol and the dry membrane, respectively. \( \rho_d \) denotes the density of n-butanol, and \( V_M \) denotes the geometric volume of the membrane.

For liquid electrolyte uptake (EU) measurements, the dry membranes were weighed and then subsequently immersed in the liquid electrolyte of 1.0 M LiPF₆ in EC:DMC (1:1, v/v) for 2 h, followed by being weighed after removing the surface liquid with filter paper. The EU was calculated using the following equation:

\[ EU = \left( \frac{W_W' - W_D'}{W_D} \right) \times 100 \]  

where \( W_W' \) and \( W_D' \) are the weights of the membrane before and after wetting in the electrolyte.

Theionic conductivity of the liquid electrolyte soaked membrane was measured by electrochemical impedance spectroscopy (EIS) using CHI760e electrochemical workstation (Chenhua Instrument Co., Shanghai, China). Before impedance measurement, each membrane was dipped into electrolyte for 12 h and the electrolyte-soaked membranes were sandwiched between two stainless steels. The impedance measurement was conducted over a frequency range of 10⁵ Hz–0.1 Hz under AC amplitude of 5 mV at different temperatures. The ionic conductivity was calculated by following formula:

\[ I = L/(R \times A) \]  

where \( L \) and \( A \) are the thickness and the area of membrane sample, \( R \) is the tested resistance.

Lithium ion transference number was measured using formula described by Yu et al. [36], in which the sample membrane was sandwiched between two lithium electrodes and AC impedance was measured from 10⁵ to 0.1 Hz using CHI760e electrochemical workstation.
After the measurement of initial impedance, 10 mV voltage was applied to measure the final current and resistance when the current became steady. Lithium ion transference number was calculated by formula given below:

$$t^+_{Li} = \frac{I_s R_f (\Delta V - I_s R_f)}{L_s R_s (\Delta V - I_s R_f)}$$

where $\Delta V$ is the applied potential step, $I_s$ and $I_o$ are the stabilized current and initial current respectively during direct current (DC) induced polarization process. $R_{so}$, $R_{fo}$ are the charge transfer resistances of Li/membrane/Li cell before and after DC polarization, respectively. $R_i$, $R_f$ are the resistances of the membrane before and after DC polarization.

Charge/discharge measurements were performed between 2.5 V and 4.2 V at a constant current density at room temperature (25 °C) using a battery test system (LAND CT2001A). The cycling performance at different rates was investigated by (LAND CT2001A) battery cycler in a potential range of 2.5–4.2 V at various current densities (0.2 C, 0.5 C, 1 C, 2 C, 4 C, 5 C and 8 C) to evaluate C-rate performance. (C rate means that the applied current at which a fully charged cell would be completely discharged in 1/n h).

3. Results and discussion

As shown in the Scheme 1 the NMP solvent and glycerol nonsolvent are used during the blending of PVDF-HFP and cellulose. Conditioning at 35 °C creates a compact structure and it is effective for phase change of the membrane from liquid to solid [25]. After immersing the membrane into a water bath, the glycerol dissolves into the water, which further leads to porous structure. The mass ratio of cellulose to PVDF-HFP is given in Table 1.

FT-IR spectra of PVDF-HFP membranes, without and with cellulose contents were used to monitor the chemical changes through alkaline hydrolysis. In the blending membrane, as shown in Fig. 1, cellulose was confirmed by the peak at 1650.2 cm$^{-1}$ from the carbonyl (C-O-O) stretching, which is not prominent in membranes with the mass ratio of cellulose to PVDF-HFP from (0/10) to (3/7) because of low cellulose amount in membranes. The existence of cellulose can be further confirmed by the increased O-H stretching vibration at 3374.9 cm$^{-1}$ and 2894 cm$^{-1}$ [37,38]. As shown in Fig. 1, there is a prominent peak of cellulose acetate at 1749.74 cm$^{-1}$, corresponding to the C=O stretching vibration, which disappears after hydrolysis, thus indicating the cellulose acetate has completely converted into cellulose. The cellulose addition also strengthens the vibration at 1150 cm$^{-1}$.

As shown in Fig. 2, a porous honeycomb structure is formed within the membrane with uniformly distributed and interconnected pores after phase inversion. This kind of honeycomb structure can increase

![Scheme 1](image_url). Schematic diagram of the Cellulose/PVDF-HFP membrane preparation process.

![Fig. 1](image_url). FT-IR spectroscopy of Cellulose/PVDF-HFP membranes with different cellulose contents.

![Table 1](image_url). The preparation routes for Cellulose/PVDF-HFP membranes with different cellulose contents.
the electrolyte uptake and offer the continuous ion transport paths, in turn helps to improve the ionic conductivity [26]. The pure PVDF-HFP membrane owns large pores only as shown in the cross-sectional images of Fig. 2(a–f). In contrast, as the cellulose amount in the membrane increases, the pore size continuously decreases. This is because the blending of cellulose and PVDF-HFP results in dense solution and enhances the trapping of the solvent, in turn shrinks the pores easily, which is preferred for large porosity and high electrolyte uptake. From the SEM images, it can be observed that when the cellulose amount is further increased (> 40 wt %), the membrane becomes dense and the interconnected porous structure diminishes.

As shown in Fig. 2g, the membrane porosity increases from 40.5% to 85.3% with the increase in cellulose content from 0 wt % to 30 wt %, but the further increase in cellulose leads to the reduction in porosity. Therefore, it can be concluded the addition of cellulose into PVDF-HFP membrane decreases the pore size and enlarges the porosity of the membrane within certain limits [39]. These phenomena reveal that the addition of glycerol produces large pores and the existence of cellulose creates small pores in the membrane during the phase inversion process.

The hydrophobic nature and the dense structure of pure PVDF-HFP lead to a low ion conductivity and limit its wide applications in LIBs. Aiming to the high membrane ion conductivity, PDVF-HFP is modified with cellulose to improve the wettability and create the microporous structure. Ion conductivity of the as-prepared membrane is measured via EIS by sandwiching the membrane between two stainless steel electrodes. As shown in Fig. 3a and Table 2, the membrane ion conductivity at room temperature increases when the mass ratio of Cellulose/PVDF-HFP increases from (0/10) to (3/7), and then decreases with further increase in cellulose amount. The increment of the membrane conductivity is attributed to cellulose which helps to absorb more electrolyte and contributes in enhancing the porosity. However, the

| Sample number | Electrolyte uptake (%) | Ion conductivity (mS cm⁻¹) | Porosity (%) |
|---------------|------------------------|-----------------------------|--------------|
| 0/10          | 170                    | 1.20                        | 40.5         |
| 1/9           | 180                    | 1.38                        | 60.5         |
| 2/8           | 290                    | 1.63                        | 80.03        |
| 3/7           | 310                    | 1.89                        | 85.3         |
| 4/6           | 210                    | 1.18                        | 54.9         |
| 5/5           | 161                    | 1.22                        | 32.5         |
| PP            | 120                    | 0.27                        | 40.0         |

Fig. 2. Surface morphology of Cellulose/PVDF-HFP membranes: (a) 0/10, (b) 1/9, (c) 2/8, (d) 3/7, (e) 4/6, (f) 5/5 with inserted cross-sectional image; (g) Porosity values of different samples.

Fig. 3. (a) EIS results of the commercial PP separator and Cellulose/PVDF-HFP membranes with different cellulose contents; (b) Arrhenius plots of PP separator, pure PVDF-HFP (0/10) membrane and the optimal Cellulose/PVDF-HFP membrane (3/7).

Table 2
Properties of various membranes.
excess amount of cellulose would clog the pores and in turn decreases the ion conductivity due to the smaller porosity. Based on the membrane thickness and EIS results, the ion conductivity of the optimal membrane (mass ratio - 3/7) is 1.89 mS cm$^{-1}$, much higher than those of the pure PVDF-HFP (0/10) membrane (1.20 mS cm$^{-1}$) and PP separator (0.27 mS cm$^{-1}$). It clearly demonstrates the existence of cellulose is able to enhance the ion conductivity by retaining the electrolyte and providing a continuous pathway for easy movement of the lithium ions through the membrane.

From the Arrhenius plot of conductivities, activation energy ($E_a$) can be calculated according to the Arrhenius equation:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{RT}\right)$$

where $E_a$, $R$, $T$, $\sigma_0$ represent the activation energy, gas constant,
temperature and pre-exponential factor, respectively. Fig. 3b shows the ion conductivities of various membranes at different temperatures from 30 to 70 °C. The temperature dependence is dominated by the electrolyte uptake of the membrane. At high temperatures, the conductivity of the commercial PP separator does not boost obviously, this is because PP separator and PVDF-HFP (0/10) loses the electrolyte quite fast at high temperatures due to its hydrophobic nature. In contrast, Cellulose/PVDF-HFP blending membrane exhibits superior electrolyte uptake and thus shows better performance at elevated temperatures.

According to Arrhenius plot, the activation energy of the PP separator, pure PVDF-HFP and Cellulose/PVDF-HFP membrane are 12.22 kJ mol$^{-1}$, 11.72 kJ mol$^{-1}$ and 12.14 kJ mol$^{-1}$, respectively. The cellulose/PVDF-HFP (3/7) activation energy is close to the electrolyte (1M LiPF$_6$ EC + DMC) activation energy which is 12.64 kJ mol$^{-1}$.

To investigate the thermal stability of membranes, the samples were placed in a vacuum oven for specific time. Shrinkage of PP membrane is very serious even with low membrane porosity because of the density difference between amorphous and crystalline regions, which cannot meet the LIBs' requirement of less than 5% shrinkage after 60 min at 90 °C. It can be observed from Fig. 4 that the thermal stability after cellulose modification of PVDF-HFP significantly improves, maintaining the structural integrity even at 200 °C.

The thermal stability of Cellulose/PVDF-HFP membranes was further characterized by thermogravimetric analyzer (TGA). For pure PVDF-HFP membrane, the weight loss at the stage of 500 °C might be the destruction of PVDF-HFP chain. The extraction of the HFP results in carbonization of the polymer and the polymer cross-linking at elevated temperatures carbonizes the remaining. Different from the pure PVDF-HFP, the blending membranes decompose through three stages: the first stage is the moisture extraction (before 200 °C, shown in Fig. 5a); the second stage is the cellulose decomposition which occurs above 350 °C; the third stage corresponds to the decomposition of PVDF-HFP above 464 °C, which contributes the major weight loss. As shown in Fig. 5b, the cellulose does not contribute in preventing from weight loss, but it enhances the degradation temperature. The samples with cellulose content of 10 wt%, 20 wt%, 30 wt%, 40 wt% and 50 wt% show weight losses of 2%, 1.5%, 5%, and 7% at the end of the first stage. This difference is the result of different amount of moisture trapped in the

Fig. 6. (a) AC impedance curve of (3/7) before and after polarization; (b) i-t curves of PVDF-HFP (0/10), Cellulose/PVDF-HFP (3/7) and PP separator 2325 cell at 23 °C, with total applied potential difference of 10 mV; (c) Attraction effect of PVDF-HFP and Cellulose towards LiPF$_6$ electrolyte.

Fig. 7. The stress-strain curves of Cellulose/PVDF-HFP (3/7) and pure PVDF-HFP (0/10) membranes.
blending membrane samples [20,40], as cellulose is hydrophilic in nature. Therefore, it clearly demonstrates the Cellulose/PVDF-HFP membrane owns good thermal stability within the battery operating temperature range.

The electrochemical stability window of the Cellulose/PVDF-HFP membrane was determined by linear sweep voltammetry (LSV), which was carried out on a Li/membrane/SS cell at a scan rate of 1.0 mV s \(^{-1}\) over the potential range of 2.5–6.0 V versus Li\(^+\)/Li to check the oxidative decomposition. Fig. 5c indicates the electrochemical stability window for pure PVDF-HFP membrane is 5.15 V. With the addition of cellulose, an enlarged window of 5.35 V is attained. This means that the membrane has better compatibility with carbonate electrolyte and highly compatible for commercial use without any chemical reaction in lithium ion battery.

The electrolyte uptake completely depends upon the membrane porosity and wettability. Due to hydrophobic nature, PVDF-HFP cannot hold much electrolyte, which can be modified by the blending of hydrophilic cellulose. After adding the cellulose into PVDF-HFP, the pore size decreases while the porosity increases as demonstrated above. To confirm the electrolyte uptake ability of this new membrane, uptake tests were conducted for Cellulose/PVDF-HFP membranes. It can be seen from Fig. 5d that the electrolyte uptake increases with the increase in cellulose content from 0 wt % to 30 wt %, but further increase leads to the decline the uptake. The optimal cellulose content in the blending membrane is 30 wt %, which is consistent with the porosity and conductivity results.

To investigate the lithium transference number, the membrane is sandwiched between lithium metal and undergoes DC polarization. AC impedance results of (3/7) is shown in Fig. 6a and the DC polarization and corresponding i-t curves for (0/10), (3/7) and PP separator can be seen in Fig. 6b. For PP separator 2325, pure PVDF-HFP membrane (0/10) and Cellulose/PVDF-HFP (3/7), the values are 0.27, 0.35, and 0.89 respectively which are calculated by Eq. (4). The lithium transference number of PVDF-HFP (0/10) is lightly larger than that of PP separator due to its high polarity. The PVDF-HFP with cellulose content boosts the lithium ion transference number based on the following mechanism: on one hand, the polarity of the PVDF-HFP matrix contributes to the improvement of the lithium ion transference number since H atoms in the PVDF-HFP main chain will interact with F atoms in the PF\(_6^-\) anions to form H-F hydrogen bonds, and thus hinder the movement of the anions. On the other hand, there is also strong H-F hydrogen bonding interaction between F atoms in PF\(_6^-\) anions and H atoms in the -OH groups of the cellulose [41], which hinders the movement of PF\(_6^-\) anions from passing through. As a result, a higher lithium ion transference number is achieved. Overall phenomenon is depicted in the Fig. 6c.

Mechanical strength is also one important factor for the separator to prevent the shutdown of the battery and ensures the membrane integrity within the battery without structural changes. As shown in the Fig. 7, ultimate strength for (0/10) and (3/7) are 3.87 MPa and 1.44 MPa respectively. With the addition of cellulose, the mechanical stability decreases due to the rigid nature of cellulose, while it can still meet the requirement of LIB membrane for use. The Cellulose/PVDF-HFP (3/7) can stand for larger elongation value before break (20%), indicating a better flexibility. The reason behind increment in elongation is that cellulose has a lot of polar groups which can bond with PVDF-HFP and it is considered beneficial for the better stability.

Fig. 8a–c shows the specific capacity of LIBs with PVDF-HFP (0/10) membrane, Cellulose/PVDF-HFP membrane (3/7) and PP separator for 100 cycles. The cell assemble with Li/Cellulose/PVDF-HFP/LiCoO\(_2\).
The LiCoO₂ material has high energy density, high cycling life, stable performance and high reversible capacity. Therefore, it is a suitable active material to evaluate the membrane performance which can avoid the uncertainties from the active materials. The battery with Cellulose/PVDF-HFP (3/7) membrane presents the initial discharge capacity of 171.08 mAh g⁻¹, realizing 62% of the theoretical specific capacity of LiCoO₂ (274 mAh g⁻¹). After 100 cycles, its specific capacity is still as high as 156.9 mAh g⁻¹, which is maintained 91.7% of the initial value.

In contrast, the initial capacity with pure PVDF-HFP and PP separator is 141 mAh g⁻¹ and 132 mAh g⁻¹, and the capacity retention after 100 cycles is 84% and 79%, respectively. Fig. 8d shows the discharge capacity at different C rates. Discharging performance declines significantly with increasing C rate with the PP separator and (0/10) pure PVDF-HFP membrane, in contrast, the rate performance is improved with the use of Cellulose/PVDF-HFP membranes. For instance, the Cellulose/PVDF-HFP membrane (the one with optimal cellulose content) based LIB maintains a capacity of 136 mAh g⁻¹ at 8 C (Fig. 8d), much larger than that with pure PVDF-HFP (93 mAh g⁻¹) and PP membrane (70 mAh g⁻¹). These experimental results clearly demonstrate the Cellulose/PVDF-HFP membrane enables high initial discharge capacity, improved overall columbic efficiency which is 99% in this case, excellent capacity retention, as well as superior rate performance.

In the battery performance with the Cellulose/PVDF-HFP membrane can be attributed to two factors: (i) the membrane enables higher lithium transference number (0.89); (ii) cellulose is able to retain the electrolyte efficiently, keeping the interfacial stability between electrolyte and electrode and preventing possible reaction between them.

4. Conclusion

The porous Cellulose/PVDF-HFP blending membrane is successfully prepared via phase inversion method in this work. With the addition of cellulose, the membrane porosity is improved from 40% (pure PVDF-HFP) to 85% (with the optimal cellulose content, 30 wt %), meanwhile, the electrolyte uptake is enhanced from 170% to 310%, thus leading to a high ion conductivity of 1.89 mS cm⁻¹. Lithium transference number for Cellulose/PVDF-HFP (3/7) is 0.89. In addition, the superior electrochemical and thermal stability of the membrane have been confirmed by the wide electrochemical window (5.35 V) and low shrinkage at high temperatures. The battery assembled with the composition-optimized membrane can offer a high capacity of 171.1 mAh g⁻¹ and 91.6% of the initial capacity can be maintained even after 100 cycles. Experimental results clearly prove this type of membrane is able to improve the discharge capacity, cycling and rate performances of LIBs.

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