

A biodegradable nano-composite membrane for high-safety and durable lithium ion batteries

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Abstract

As a key component of lithium-ion batteries (LIBs), separator plays a crucial role in the performance and safety of LIBs. In this paper, a cellulose based porous membrane modified by nano CaCO₃ is prepared conveniently by electrospinning. The membrane exhibits rich fibrous porous networks and uniform distribution of nanoparticles. Strengthened by CaCO₃, the tensile strength of the cellulose porous membrane elevates from 4.7 ± 0.4 MPa to 7.7 ± 0.7 MPa. Besides, the modified membranes possess improved thermal stability and can maintain their original size after treatment at 150 °C and 180 °C. Also, the electrolyte uptake of cellulose/CaCO₃ membrane is 73% higher than that of the pure cellulose membrane. Thus, the ionic conductivity of membrane achieves 1.08 mS cm⁻¹ and the electrochemical window is about 4.8V, which meets the practical requirements of LIBs. Significantly, LiFePO₄/Li battery this membrane can run for 230 cycles with a capacity retention of 97.4% and a discharge capacity of 149.0 mAh g⁻¹, demonstrating the huge potential for high safety and next-generation LIBs.

INTRODUCTION

Rechargeable batteries play a key role in liberating human production and life from dependence on fossil fuels and reducing greenhouse gas emissions.[1-3] Among them, lithium-ion batteries (LIBs) are generally composed of metal-containing active materials (Li, Co, Ni, etc.), flammable organic electrolytes and non-degradable polymer membranes (polyolefin).[4-6] However, the growing demand for LIBs is pushing up the price of raw materials and the existing battery materials cannot satisfy the energy demand. Accordingly, it is urgent to develop renewable, sustainable and green battery materials to realize sustainable development.[7-9] In this regard, natural biomaterials are increasingly attracting interest in green batteries due to the numerous advantages of biopolymers such as broad-resource, low-cost and environmental protection.[10, 11]

In the composition of LIBs, separator directly determines the electrochemical performance and the safety of the battery.[12-15] Although it does not directly participate in the electrochemical reaction of LIBs, its physical properties and structure play a key role in LIBs. Currently, widely used separators mainly include microporous polyolefin membranes formed by insulating polymer materials. However, due to its characteristics of large polarity difference with electrolyte and low thermal melting temperature, PP separators have some shortcomings such as poor infiltrative properties and poor thermal stability, which leads to a large safety hazard of LIBs.[16, 17] Therefore, it is urgent to develop next-generation separators to replace the existing polyolefin separator.

Cellulose and its derivatives are good alternatives to polyolefin-based materials because they are abundant in reserves, renewable, easy to access and low cost.[18-20] Till now, many researchers have reported novel cellulose-based membranes. For example, Du et al.[21] prepared a cellulose based gel membrane using epichlorohydrin (ECH) as a crosslinking agent. The ionic conductivity of the activated cellulose membrane with 5% ECH achieves 6.34 mS cm⁻¹. What's more, the assembled NCM523/Li battery can reach 145 mAh g⁻¹ at 0.2 C, and the capacity retention rate is as high as 90% after 50 cycles. Liu et al.[19] prepared

lignin-containing cellulose nanofibers (LCNFs) membranes from the unbleached pulp by a facile method. The LCNF porous membrane shows a high electrolyte uptake of 276% and high ionic conductivity of 1.86 mS cm⁻¹. With the higher requirements for battery safety, the composite membrane combining ceramic particles and polymer has attracted more attention from researchers. Thereby, nano-inorganic particles such as Al₂O₃, SiO₂ and TiO₂ can significantly improve electrolyte wettability, thermal stability and ionic conductivity of polymer.[22-25] Recently, Cui et al.[26] prepared a polyvinylidene fluoride (PVDF)/cellulose acetate (CA) based membrane by using non-solvent induced phase separation (NIPS) method. Meanwhile, Al(OH)₃ particles were used as added doping agents. The PVDF-CA/Al(OH)₃ separator has high porosity (68.6%), high electrolyte absorption rate (403.9%), excellent dimensional stability (4.6% thermal shrinkage at 160°C) and high ionic conductivity (2.85 mS cm⁻¹), endowing LIBs with good safety performance and cycling performance. However, batteries still suffer from a lack of cycle durability because LiPF₆ in liquid electrolytes can form hydrofluoric acid (HF) to damage the electrolyte/electrodes interfaces.[27, 28]

Herein, nano-CaCO₃ is introduced into cellulose-based electrospinning membranes to reduce the crystallinity of polymer membrane, promote ion migration and neutralize acidic products. The morphology, thermal stability, mechanical properties and electrochemical properties of modified membranes are analyzed and explored in depth. Such inorganic particles with extremely high hydrophilicity and excellent surface properties can significantly improve the ionic conductivity of membrane. In addition, the rigidity and heat resistance of CaCO₃ guarantee the mechanical strength and thermal stability of membrane. Consequently, the composite membrane is superior to polypropylene (PP) separator in electrolyte wettability and thermal stability, leading to the outstanding performance of LiFePO₄/Li cells. We believe that cellulose/CaCO₃ composite membrane with the above advantages is a promising candidate for practical applications in advanced LIBs.

2. MATERIAL AND METHODS

2.1. Materials: Cellulose acetate (CA) was obtained from Aladdin Biochemical Technology Co., Ltd. CaCO₃ nanoparticle was purchased from Qianhai JYSA Technology Co., Ltd. Lithium hydroxide, N,N-Dimethylacetamide and acetone were provided via Kelong Chemical Reagents. N-Methylpyrrolidone (NMP), LiFePO₄, LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂, graphite, super P and poly(vinylidene fluoride) (PVDF) was supplied from Canrd New Energy Technology Co., Ltd. 1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (v:v:v=1:1:1) was purchased from Songjing New Energy Technology Co., Ltd. Polypropylene (PP) separator (Celgard 2500) was used as a control.

2.2. Nanofiber synthesis: Firstly, the cellulose acetate (15% w/w) and calcium carbonate (0, 0.5%, 1% w/w) were dissolved in DMAc/acetone (at a mass ratio of 3:7) to form a uniform mixture. After ultrasound and defoaming, the mixture was transferred into a syringe equipped with a Φ19mm needle. During electrospinning, the injection speed was 0.15mm/min and the voltage was 20 V. The nanofibers which accumulated on the collector were collected. The residual solvent of nanofibers was removed by drying at 80 °C to obtain white membranes, and subsequently immersed into 0.05M LiOH aqueous solution for hydrolysis for 12 h. Finally, the cellulose and cellulose/CaCO₃ membranes were obtained by vacuum drying.

2.3. Characterization: The morphologies characterizations were recorded via scanning electron microscope (SEM, JSM-7500F) at 15 kV. All samples were sprayed with gold before test. Energy dispersive X-ray (EDX) spectroscopy was used to test the element distribution mapping. X-ray diffraction (XRD) patterns were recorded by X'Pert Pro MPD diffractometer (Cu-Kα) in a scattering angle (2θ) range of 10°-60°. Thermogravimetric Analysis (TGA) was carried out by a NETZSCH TG 209 F1 in N₂ flowing at a heating rate of 10 °C min⁻¹.

$$\text{Electrolyte uptake} = \frac{W_t - W_0}{W_0} \times 100\%(1)$$

where W₀ and W_t represent the weight of the membrane before and after liquid electrolyte saturation, respectively.

Ionic conductivity of the membrane was measured with a coin cell by a CHI 760E electrochemical station from 1 Hz to 100 kHz. The membrane disk with a diameter of 19 mm was sandwiched between two stainless

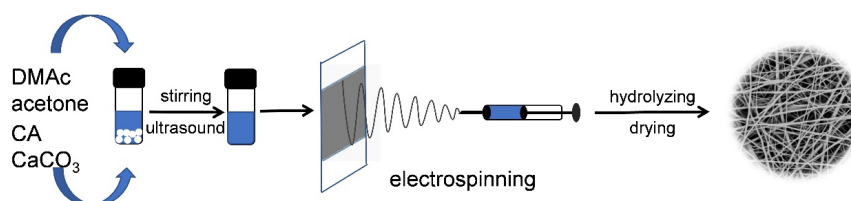
steels and then assembled in a CR2032 coin cell. The ionic conductivity was obtained by the equation (2):

$$\sigma = \frac{l}{SR} \quad (2)$$

where l , R and S refer to the thickness of the membrane, resistance, and the contact area between membrane and stainless steel, respectively.

The electrochemical stability window was determined by linear sweep voltammetry. The stainless steel and lithium metal were used as electrode and counter electrode, respectively. The voltage was swept at a scan rate of 1 mV s^{-1} over a potential range of 0 V to 6 V (vs. Li/Li^+).

Cycling performance of batteries was measured by battery test system (Shenzhen Neware Electronics Co., Ltd). The voltage ranges of cells are 2.5-4.2 V. The conventional slurry-coating method was used to prepare electrodes. The active material (LiFePO_4), acetylene black and PVDF were mixed with a weight ratio of 8:1:1. The active material weight is around 1.6 mg cm^{-2} . The weight of Li anode is 45.9 mg (15.6 mm in diameter and 0.45 mm in thickness).



Scheme 1. Preparation of cellulose/ CaCO_3 membrane.

3. RESULTS AND DISCUSSION

Scheme 1 displays the fabrication process of cellulose/ CaCO_3 membrane via a facile electrospinning method. CA is translated into cellulose by alkaline hydrolysis benefitting to improve the affinity with electrolytes.[29] The SEM images were used to record the micromorphology, and the corresponding results were shown in **Figure 1**. It can be found that nano CaCO_3 is spherical with a diameter of about 100 nm (**Figure 1a**). Nano CaCO_3 is commonly used as plastic filler with toughening and reinforcing effects, also improving the thermal deformation temperature and dimensional stability of polymers.[30, 31] The morphologies of cellulose membrane and cellulose/ CaCO_3 membranes are shown in **Figure 1b-d**, these membranes show randomly arranged nanofibers and porous networks, which helps for liquid electrolyte uptake and fast migration of ions.[32, 33] As shown in Figure 1b, for cellulose membrane, the diameter of assembled fibers is uniform and the surface of fibers is smooth (**Figure 1b**). After the introduction of nano CaCO_3 , the surface of cellulose/ CaCO_3 fibers becomes rougher and the diameter uniformity decreases accompanied by some humps after the addition of CaCO_3 . It is probably due to CaCO_3 particles being encapsulated inside the fibers. These rough protrusions become more numerous as the amount of CaCO_3 addition increases (**Figure 1c and 1d**). Furthermore, the uniform distribution of Ca elements indicates that CaCO_3 and polymer matrixes achieve compact and intact combination (**Figure 1e**). Notably, the high magnification image in **Figure 1f** exhibits that nanoparticles are also coated on the fiber surface.

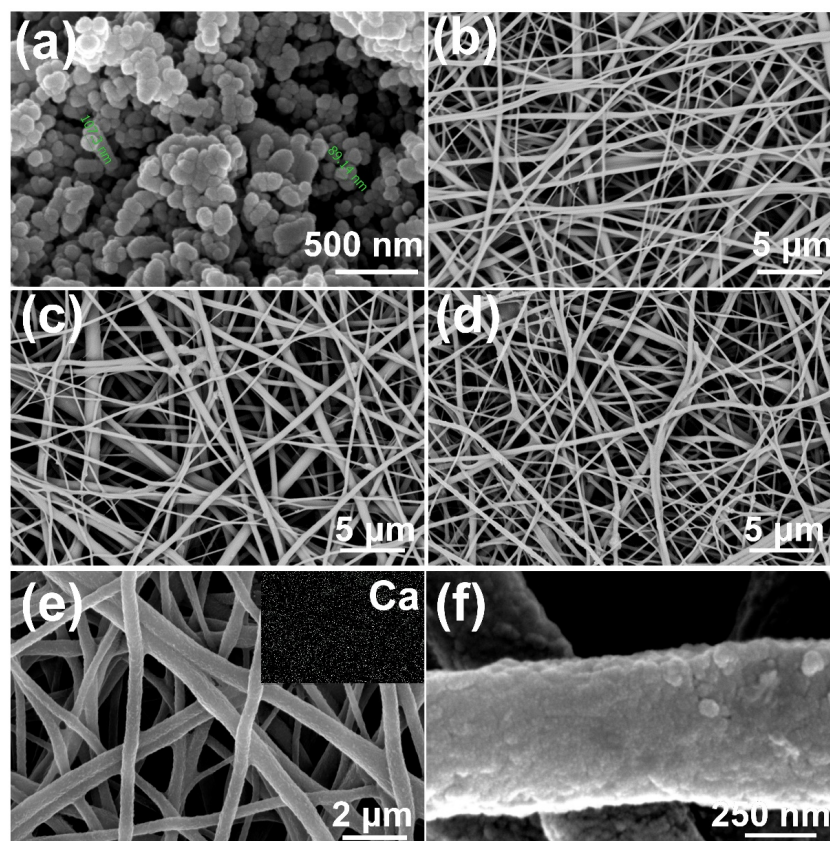


Figure 1. SEM images of (a) nano CaCO_3 , (b) cellulose, (c) cellulose/ CaCO_3 -0.5, (d) cellulose/ CaCO_3 -1 membranes and (e, f) corresponding high magnification images.

Hydrolysis treatment is beneficial to enhance the electrolyte wettability of porous membranes, leading to good electrochemical performance. The reason is that acetyl groups in the CA molecular chain are hydrolyzed under strongly alkaline conditions, and the hydrophobic acetyl groups disappear to form hydrophilic hydroxyl groups.[34] The FTIR was used to verify the complete hydrolysis of CA and the successful introduction of calcium carbonate. The spectra of CA and cellulose/ CaCO_3 membrane are presented in **Figure 2a**. It is obvious that the CA membrane exhibits a weak -OH peak at 3450 cm^{-1} and -CH₃ stretching vibrations peaks at 2962 cm^{-1} and 2872 cm^{-1} . [35] Besides, the C=O and C-O characteristic peaks can be seen at 1750 cm^{-1} and 1180 cm^{-1} , respectively. Compared to the CA membrane, all cellulose membranes show a strong and broad -OH peak at 3361 cm^{-1} and the C=O absorption peak at 1743 cm^{-1} disappeared, demonstrating the complete hydrolysis of CA. What's more, with the addition of CaCO_3 , the bending vibration peak of carbonate appears at around 874 cm^{-1} and the intensity of this peak increases as the content of CaCO_3 elevates.[36] From all above, the CaCO_3 was introduced to the CA membrane successfully.

Figure 2b shows the XRD patterns of porous membranes. The peaks at 20.4° and 21.8° correspond to the diffraction peaks of cellulose. The crystalline peak of CaCO_3 locates at 29.5° . With the increasing content of CaCO_3 , the crystalline peak at 29.5° became sharper, and the corresponding CaCO_3 peaks at 35.9° as well as 39.5° appeared.[37] However, the introduction of CaCO_3 had little effect on the crystallinity of cellulose.

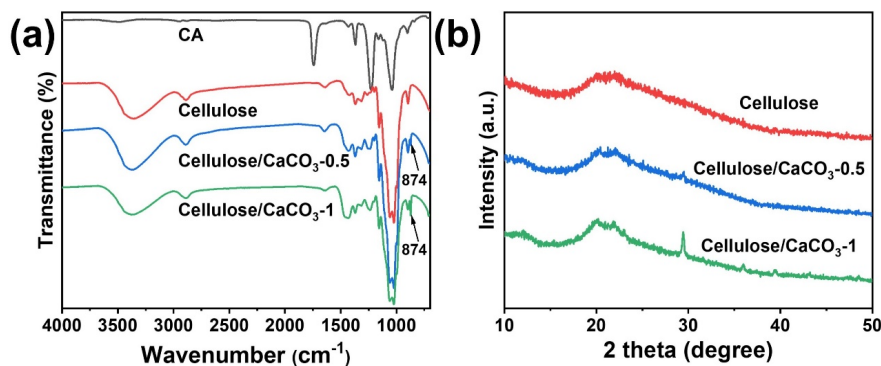


Figure 2. (a) ATR-FTIR spectroscopy and (b) XRD patterns of cellulose and cellulose/CaCO₃ membranes.

In order to study the effect of CaCO₃ nanoparticles on the thermal stability of cellulose porous membranes, thermogravimetric tests were carried out on porous membranes, and the corresponding results are listed in **Figure 3** and **Table 1**. As shown in **Figure 3a**, the initial decomposition temperature did not change regularly after the addition of CaCO₃, probably due to the absorption of water by cellulose with a large number of hydroxyl groups. The maximum decomposition temperature increased with the addition of CaCO₃, from 351.3 °C to 355.7 °C and 356.7 °C respectively, indicating that CaCO₃ increases the thermal stability of the cellulose membrane. Moreover, the residual mass increased from 7.2% to 12.1% due to the decomposition temperature of CaCO₃ being greater than 700 °C.

As shown in **Figure 3b**, the commercial PP separator and the cellulose-based membranes prepared in this work were subjected to 150 °C and 180 °C for half an hour to evaluate the dimensional stability at high temperature. The commercial PP separator shrank significantly and can not maintain the initial round shape, and the shrinkage was severe at 180 °C. In contrast, the cellulose and cellulose/CaCO₃ membranes can remain the original shape even at high temperatures of 150 °C and 180 °C. Notably, excellent dimensional stability is important to effectively prevent short-circuiting when the battery is overheated. It can be predicted that LIBs with cellulose/CaCO₃ membranes would manifest improved safety performance than that with commercial PP separator.[38]

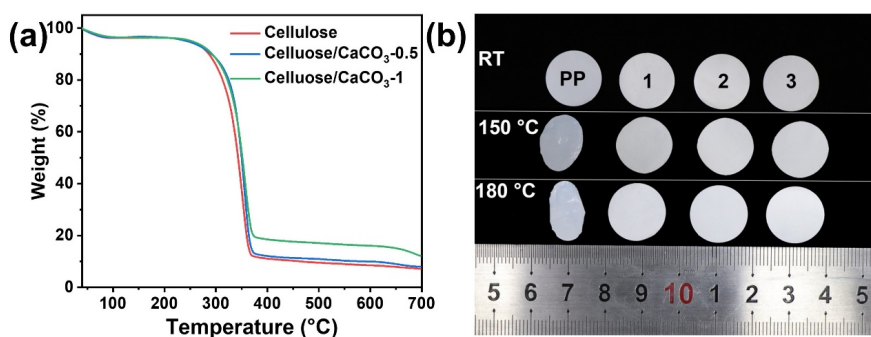


Figure 3. (a) TGA curves and (b) thermal shrinkages of cellulose and cellulose/CaCO₃ membranes at different temperatures.

Table 1. Thermal properties of cellulose and cellulose/CaCO₃ membrane

Sample	$T_{5\%}$ (°C)	$T_{\max}$ (°C)	Residual mass (%)
Cellulose	251.4	351.3	7.2
Cellulose/CaCO ₃ -0.5	243.3	355.7	8.0

Sample	$T_{5\%}$ (°C)	$T_{\max}$ (°C)	Residual mass (%)
Cellulose/CaCO ₃ -1	252.6	356.7	12.1

To characterize the nano CaCO₃ on the mechanical properties of the porous membranes, stress-strain curves of membranes were recorded and the results are shown in **Table 2** and **Figure 4a**. The neat membrane manifested a tensile strength of 4.7 MPa. The tensile strength increased with the increased adding mass of CaCO₃. Specifically, the tensile strength of cellulose/CaCO₃-0.5 membrane reaches 5.8 MPa. In particular, cellulose/CaCO₃-1 manifests a tensile strength of as high as 7.7 MPa, which is 63.8% increase compared to that of the initial membrane. Additionally, the introduction of nano CaCO₃ also slightly affects the elongation at break of the membrane. The elongations at break of neat CA, cellulose/CaCO₃-0.5 and cellulose/CaCO₃-1 membranes are 6.0%, 6.8% and 5.6%, respectively.

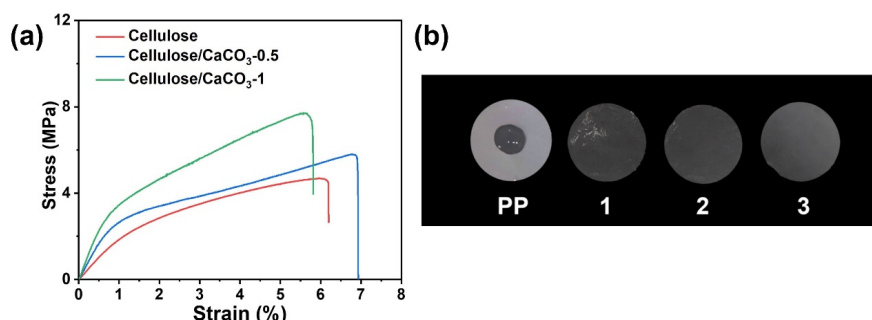


Figure 4. (a) Stress-strain curves of cellulose and cellulose/CaCO₃ membranes. (b) Photograph showing liquid electrolyte wettability of PP separator, cellulose and cellulose/CaCO₃ membranes.

Table 2. Mechanical properties of cellulose and cellulose/CaCO₃ membranes

Sample	Ultimate stress (MPa)	Elongation at break (%)
Cellulose	4.7 ± 0.4	6.0 ± 0.4
Cellulose/CaCO ₃ -0.5	5.8 ± 0.6	6.8 ± 0.6
Cellulose/CaCO ₃ -1	7.7 ± 0.7	5.6 ± 0.6

Electrolyte wettability determines the absorption rate and affinity of porous membrane. **Figure 4b** show visually the difference in wettability between PP separator and cellulose membranes, the liquid electrolyte droplet stands up on the PP separator due to the poor compatibility of non-polar polyolefin-based separators with traditional polar liquid electrolytes. By contrast, electrolyte can absolutely penetrate into cellulose/CaCO₃ membranes, which demonstrates the excellent performance of cellulose membranes in terms of electrolyte wettability. The good electrolyte wettability of membrane is conducive to the transport of lithium ions, which further affects the rate performance of battery. Besides, because the polar hydroxyl groups of cellulose have a good affinity for electrolytes, the membrane prepared by electrospinning has a loose porous structure to store a large amount of electrolyte. The cellulose/CaCO₃ membranes show a significant promotion in liquid uptake, reaching 220% at a mass fraction of 0.5 wt% of nano-CaCO₃, much higher than that of the PP separator (97%) (**Table 3**). Porosity as another important parameter for separators determines the electrolyte storage capacity and the permeability of the membrane. The cellulose membranes possess high porosity of 49% due to the fibrous-network structure. Furthermore, nano-CaCO₃ has no adverse effect on porosity.

Table 3. Physical properties of PP, cellulose and cellulose/CaCO₃ membranes

Sample	Electrolyte uptake (%)	Porosity (%)
PP	97	55
Cellulose	161	49
Cellulose/CaCO ₃ -0.5	220	49
Cellulose/CaCO ₃ -1	234	49

In order to measure the ionic conductivities of batteries assembled with cellulose membranes and investigate the effect of nano-CaCO₃ additions on electrochemical performances, the EIS of cellulose membranes before and after modification were tested at room temperature. The results are shown in **Figure 5a**. The PP separator has an ionic conductivity of 0.95 mS cm⁻¹, while the cellulose membrane decreases to 0.91 mS cm⁻¹. With the addition of CaCO₃, the ionic conductivities of membranes increases. Specifically, they can reach 1.05 mS cm⁻¹ and 1.08 mS cm⁻¹ at a value of 0.5 wt% and 1 wt% addition amount, respectively. This indicates that all three cellulose membranes have decent conductivities. Notably, nano-CaCO₃ can effectively increase the conductivities of the cellulose membrane, which may be due to the crystalline structure of CaCO₃. In addition, the effect of temperatures on conductivity is further investigated, and the impedances of membranes are tested at 25 °C, 35 °C, 45 °C, 55 °C and 65 °C. The results are shown in **Figure 5c-d**. It can be easily found that the resistance of membranes tends to decrease with increasing temperature. Specifically, the ionic conductivity of cellulose/CaCO₃-1 reaches 1.49 mS cm⁻¹.

The electrochemical window is an important index for membrane used in LIBs, which determines the feasibility of applying it in high-voltage cathode materials. To verify the electrochemical stability of cellulose membranes, the linear sweep voltammetry (LSV) tests of PP and cellulose membranes with stainless steel and Li electrodes were performed. The corresponding curves were shown in **Figure 5b**. All membranes show stable currents below 4.5 V. Compared with a conventional commercial PP separator, cellulose based membranes display no obvious decomposition until 4.8 V. Besides, with the addition of CaCO₃, the oxidation peak currents drop. It is probably due to that CaCO₃ can absorb trace water and hydrofluoric acid (HF) in the LiPF₆ electrolyte, while these impurities affect oxidation reaction.

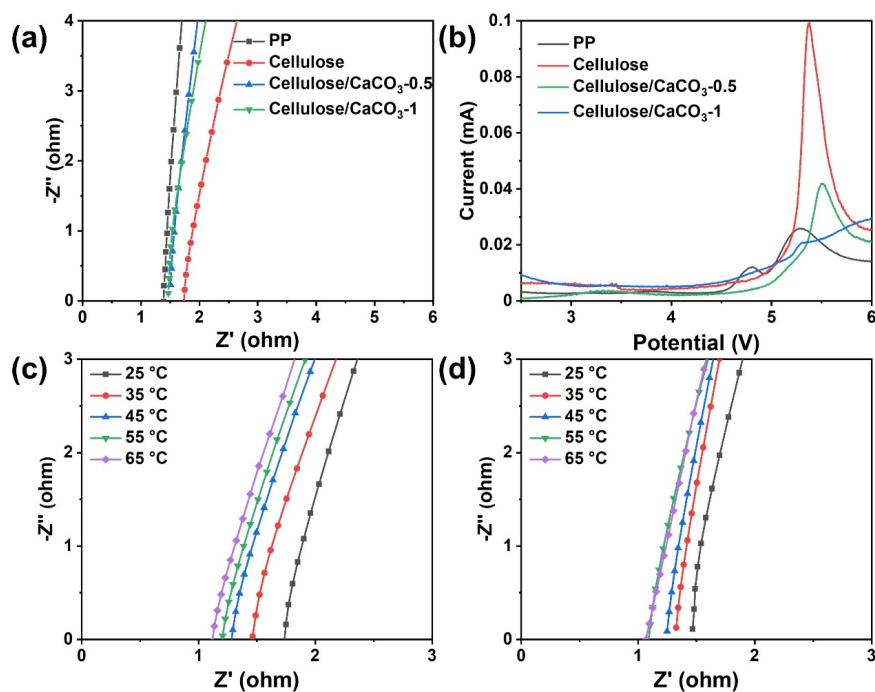


Figure 5. (a) Nyquist plots and (b) linear sweep voltammograms of PP, cellulose and cellulose/CaCO₃ membrane. Ionic conductivities of (c) cellulose and (d) cellulose/CaCO₃-1 membranes in variable temperatures.

The cycling performances of LiFePO₄/Li batteries assembled with cellulose and cellulose/CaCO₃-1 membranes were evaluated. As shown in **Figure 6a**, the initial discharge capacity of LiFePO₄/Li batteries assembled with cellulose/CaCO₃-1 membrane reaches 144.2 mAh g⁻¹, which is higher than that of cellulose membrane based battery (138.7 mAh g⁻¹). The reason may be attributed to the higher ionic conductivity of cellulose/CaCO₃-1 membrane. With the formation of solid electrolyte interface (SEI), the interfacial resistance reduces. Consequently, the discharge capacity of batteries increases steadily. For the battery with cellulose/CaCO₃-1 membrane, the stable capacity is 149.0 mAh g⁻¹. Moreover, capacity retention is as high as 97.4% after 230 cycles. In contrast, the battery with cellulose membrane has a severe decay and only remains 121.3 mAh g⁻¹ after 100 cycles. The excellent cycle performance is ascribed to the electrochemically interfacial stability.

The electrode morphology after the battery cycle can reveal the actual electrochemical reaction condition of the battery. In order to further analyze the difference in battery performance, the surface of Li anodes after cycling was observed (**Figure 6b**). As for cellulose based battery, Li anode became black according to the digital photo, which is caused by the diffusion of active cathodes.[27] As regards the CaCO₃-modified battery, Li anode can retain the original appearance even after 230 cycles. Besides, the morphologies were observed by SEM, and corresponding results are supplied in **Figure 6b**. Notably, the Li structure of cellulose based battery is broken, while the CaCO₃ modified battery is complete. Furthermore, the electrolyte/electrode interface is damaged by HF generated by electrolyte decomposition. Conversely, the negative impact of HF on cellulose/CaCO₃-1 based battery can be eliminated through the neutralization of nano-CaCO₃. With higher thermal and dimensional stability, the battery equipped with cellulose/CaCO₃-1 membrane exhibits high-performance and great potential application in new energy fields.

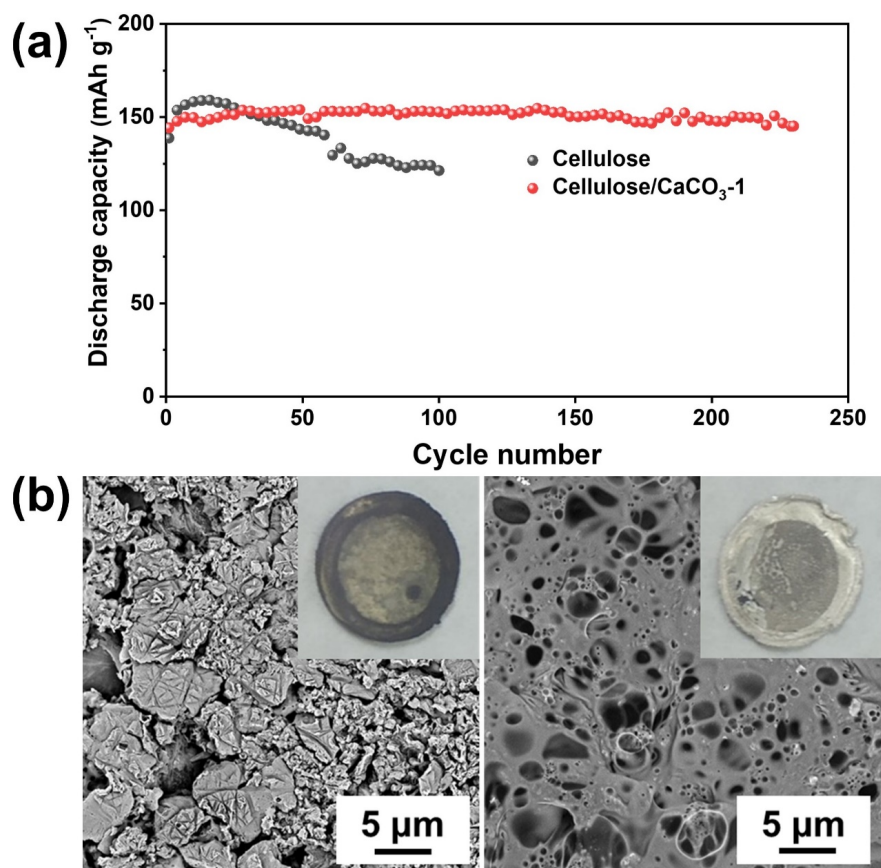


Figure 6. (a) Cycling performance of LiFePO₄/Li batteries with cellulose and cellulose/CaCO₃-1 membranes. (b) SEM images and photographs of Li anodes after cycling. (left: cellulose, right: cellulose/CaCO₃-1)

4. CONCLUSION

In summary, a novel cellulose/CaCO₃ porous membrane was fabricated by electrospinning method. The as-prepared membrane used as separator possesses excellent thermal and dimensional stability at harsh temperatures, thus significantly enhancing the thermal safety of batteries. In addition, the electrolyte uptake (234%) and ionic conductivity (1.08 mS cm⁻¹) of membrane are superior to that of PP separator. Furthermore, the LiFePO₄/Li battery assembled with cellulose/CaCO₃ membrane can run for 230 cycles with 97.4% capacity retention. Taking the above advantages into consideration, cellulose/CaCO₃ membrane manifests great potential application in sustainable and high-performance LIBs.

AUTHOR CONTRIBUTIONS

Ting Wang: sample preparation, data analysis, manuscript writing. Na Liu: sample preparation. Hui Zhou: investigation, data analysis. Mingjun Chen: review and editing.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The datasets used in this study are available from the corresponding author.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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