PVA-based high carboxyl group substituted modified cellulose nanofiber composite hydrogel for flexible new air battery

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Abstract. Zinc-air battery (ZAB) with high theoretical energy density and low-cost characteristics has become one of the future candidate energy storage devices for flexible and portable electronic devices. If the application of ZAB in this field is to be promoted, how to improve the performance of solid-state batteries (such as cycle stability, discharge capacity) is the main problem at present. Flexible solid electrolyte plays a vital role in it. In this work, Carboxyl modified cellulose nanofibers (C-CNFs) was prepared by controlling the degree of carboxyl modification, and polyvinyl alcohol (PVA)-based cellulose composite gel polymer electrolyte (GPE) was synthesized. The optimal PVA-based composite GPE was selected to exhibit high ionic conductivity (0.31 S cm⁻¹), excellent water retention and good tensile mechanical strength under environmental conditions. The assembled flexible zinc-air battery (ZAB) exhibits excellent cycle stability, discharge performance and power density. ZAB based on PVA-C-CNFs GPE can work continuously and stably for 50 hours, and at the same time has high cost-effectiveness and safety.

1. Introduction
In recent years, with the rapid development of flexible wearable electronic products, high efficiency, low cost, thinness and flexibility have become an urgent need for energy storage power supplies in the future. Zinc-air batteries (ZAB) have received widespread attention due to their high specific energy (up to 1086 Wh kg⁻¹), low cost and environmental friendliness [1, 2]. In order to meet this requirement, flexible and bendable semi-solid/solid electrolytes need to be used to replace liquid electrolytes with leakage risks and water evaporation problems [3]. At present, gel polymer electrolytes have been widely used in flexible ZAB due to their higher ionic conductivity than solid electrolytes and no need to consider the safety of liquid electrolytes [4].

Polyvinyl alcohol (PVA) has excellent chemical stability, electrochemical inertness, durability, and non-toxicity. It is one of the commonly used polymer matrixes [5]. However, ZAB using this traditional PVA GPE system has problems such as fast electrolyte volatilization, low liquid electrolyte content leading to low room temperature ion conductivity, poor mechanical tensile properties and poor stability. It has become a more feasible method by mixing fillers and other methods. For example, Fan et al. solved the problem of poor electrolyte absorption and water retention by adding SiO₂ filler, so that the assembled ZAB can work stably for 140 cycles [6].

Cellulose nanofibrils (CNFs), which are usually between 5 and 60 nm in diameter, have attracted great interest due to their abundance of hydrophilic hydroxyl groups, high aspect ratio, network structure and high mechanical properties [7]. In recent years, it has been proved that the use of carboxymethyl to replace the hydroxyl group to form crosslinks has high stability [8]. The modification
method of TEMPO chemical oxidation method has also been proved to be an effective and simple method, and it is an ideal gel electrolyte composite material[9].

Here, the optimized PVA-based nanocomposite GPE has higher ionic conductivity and higher electrolyte water retention rate, which is better than the traditional PVA-KOH GPE system. It also has good thermal and mechanical properties. Due to these advantages, the assembled ZAB has good cycle stability, discharge performance and rate characteristics.

2. Experimental Materials and Methods

2.1. Chemicals and materials
Polyvinyl alcohol (PVA, average molecular weight: 75000), 1,5-glutaraldehyde (GA, content 50%), and glycerol (Gl) are Sigma-Aldrich products. Isopropanol, monochloracetic acid, ethanol, potassium hydroxide, methanol, hydrochloric acid, potassium hydroxide (KOH, content 98%) were purchased from Aladdin (Shanghai, China). Zinc foil (0.2 mm thick) and 10 BN carbon paper (0.17 mm thick) were purchased from Alfa Aesar and SGL Carbon, respectively. Cellulose nanofibrils (CNFs) and sulfite softwood pulp were purchased from Jinan Sheng Quan Group Share Holding Co. Ltd (Jinan, China).

2.2. Preparation of carboxylated C-CNFs
The procedure was carried out according to the previously published TEMPO oxidation pretreatment. In brief, C-CNFs used 3, 6, 9, 12 mmol/g NaClO for TEMPO oxidation (C1, C2, C3, C4) and defibrillation at pH 10.0, respectively. Then, the pH was adjusted to 7.0 with 0.5 M NaOH and homogenized 5 times using a homogenizer (Microfluidizer LM20, USA) at 25,000 PSI to obtain C-CNFs[10].

2.3. Preparation of the composite GPE and assembly of ZAB
C-CNFs of a certain absolute dry mass (1% of PVA) after calculation was dissolved in deionized water under high-speed stirring for 15 minutes. PVA powders (3.6 g) were slowly added into the C-CNFs suspension and stirring continued for 12 hours. Then, added glutaraldehyde (GA, 3% of PVA) and glycerol (Gl, 2% of PVA) dropwise to the mixture. The HCl (0.1 M) was added dropwise to the mixed solution to adjust to pH = 2, and it was quickly introduced into a rectangular mold, and left to stand for 12 hours to achieve crosslinking. The nanocomposite GPE film were formed by immersing the polymer film in 6 M KOH for 24 hours.

The flexible ZAB was assembled by a simple stacking method, showing a sandwich structure with 5 layers up and down. The zinc foil was first cut (10 mm×20 mm×0.3 mm), and deionized water and ethanol were used for multiple ultrasonic washing and drying. Then the cut composite GPE is placed between the zinc foil and the carbon paper air electrode for composite. In the same way, the conductive copper mesh is used as the current collector to compound with the electrode.

2.4. Characterization
Water retention value (WRV) measurements were used to detect the water holding capacity of CNFs and C-CNFs according to the modified standard SCANC 62:00. The surface morphology of C-CNFs and nanocomposite GPE were observed using Scanning Electron Microscopy (SEM). Fourier Transform infrared spectroscopy (FTIR) spectra was acquired using in the wavenumber ranging from 400 cm\(^{-1}\) to 4000 cm\(^{-1}\). Dynamic Light Scattering (DLS) (Malvern nano-ZS90, Malvern instrument, UK) was used to measured the Zeta potential of nanocellulose dispersions. The conductivity titrator (Raymag DDS-307 conductivity meter, Shanghai, China) was used to determine the carboxyl content of nanocellulose.

The KOH electrolyte retention properties of the mixed polymer gel were performed at room temperature (25°C). A texture analyzer (CTA-20H PRO, Tianjin, China) was used to test the tensile properties of gels prepared by doping C-CNFs with different carboxyl substitution degrees.
The electrochemical workstation (CHI660e, Shanghai, China) was used to record the electrochemical impedance spectra and ionic conductivity of GPE and ZAB, and record the polarization curve. A multi-channel battery test system (LAND CT2001A, Wuhan Lande Electronics Co., Ltd., China) was used to record the constant current charge and discharge (GCD) measurement values at a current density of 3 mA cm\(^{-2}\) for 20 minutes per cycle. The rate performance was tested at current densities of 1, 3, 5, and 10 mA cm\(^{-2}\).

3. Results and discussion

Figures 1a~d show the carboxyl substitution titration test results of C-CNFs after treatment with different NaClO concentrations. The carboxyl substitution results calculated according to the formula are shown in Table 1. With the increase of NaClO concentration, the carboxyl substitution degree of C\(_1\)-CNF, C\(_2\)-CNF, C\(_3\)-CNF, and C\(_4\)-CNF modified by carboxyl groups were 1.6, 2.02, 2.25, 2.63 mmol/g, respectively. Compared with CNFs prepared by direct homogenization, C-CNFs become more uniform and transparent (Figure 1e). Among them, the FTIR spectra of CNFs and C\(_3\)-CNFs are shown in Figure 1f. The C\(_3\)-CNF spectrum showed a new absorption peak at 1733 cm\(^{-1}\), which was attributed to the stretching vibration of C=O, which proved the successful introduction of carboxyl groups. In addition, it improves the dispersion and stability of the fiber itself, which is manifested by the continuous increase of its own Zeta potential, in which the Zeta potential of C\(_3\)-CNFs reaches -39.3 mV, an increase of 32.3% compared to CNFs.

![Figure 1](image)

Table 1: Physical and chemical properties of C-CNFs.

| Sample property                  | CNFs | C\(_1\)-CNFs | C\(_2\)-CNFs | C\(_3\)-CNFs | C\(_4\)-CNFs |
|----------------------------------|------|--------------|--------------|--------------|--------------|
| Degree of carboxyl substitution (mmol/G_{C-CNFs}) | -    | 1.6          | 2.02         | 2.25         | 2.63         |
| WRV (g/g)                        | 2.02 | 2.15         | 2.27         | 2.39         | 2.43         |
| Zeta potential (mV)              | -29.7| -31.2        | -35.6        | -39.3        | -39.7        |

The surface of CNFs and C-CNFs, as well as pure PVA and C\(_3\)-CNFs-based hybrid hydrogels were observed by SEM, and the surface morphology changes of the fibers and hybrid gels were analyzed.
(Figure 2). It can be seen from the SEM images that the morphology and size of CNFs and C-CNFs have not changed significantly (Figure 2a, b). The cross-sections of CNFs and C-CNFs are relatively constant and similar in length to diameter ratio of 100:1. The surface morphology of nanocomposite GPE is shown in Figure 2a and b. It can be seen that the surface of GPE based on pure PVA shows a relatively smooth and dense surface. However, due to the addition of C-CNFs, the surface of the nanocomposite GPE showed obvious flocculation. This can be attributed to the different interfacial compatibility of PVA and C-CNFs, which leads to uneven dispersion of the mixture.

![SEM images of (a) CNFs, (b) C-CNFs (C3), (c) pure PVA hydrogel and (d) PVA-C3-CNFs](image)

Figure.2  SEM images of (a) CNFs, (b) C-CNFs (C3), (c) pure PVA hydrogel and (d) PVA-C3-CNFs

The pure PVA and hybrid hydrogel were tested by AC impedance spectroscopy (EIS) (Figure 3a). The pure PVA-based GPE has a low ionic conductivity of 0.17 S cm\(^{-1}\). After mixing and adding C-CNF to the PVA matrix, the ionic conductivity increased significantly. This is related to the increase in liquid electrolyte absorption in the gel after adding C-CNFs. After increasing the carboxyl modification content of C-CNFs, the ionic conductivity continued to increase, and the highest ionic conductivity of PVA-C3-CNFs-based GPE was 0.32 S cm\(^{-1}\). It can be concluded that C-CNFs with higher carboxyl content are more conducive to the absorption, retention and conduction of electrolytes. After standing the mixed GPE at room temperature, it is found that the PVA-C3-CNFs-based GPE has the best ability to retain electrolyte. After standing for 48 hours, it loses about 13% of its mass, while the remaining C1, C2, and C4 modified C-CNFs mixed GPE also showed obvious electrolyte retention ability (Figure 3b). PVA-C-CNFs GPE shows excellent tensile properties. Figure 3c shows the tensile stress-strain curves of 1% PVA-based nanocomposite GPE with different carboxyl substitution degrees (C1, C2, C3, C4). The highest tensile stress of pure PVA can reach 40kPa, and the tensile strain is 130%. The best is the hybrid hydrogel prepared based on PVA-C3-CNFs. The tensile stress is increased to 69 kPa and the strain reaches 190%. In addition, the hydrogel can stretch up to 330% under normal conditions (Figure 3d).
Figure 3  (a) The EIS image, (b) quality change under normal temperature standing, (c) tensile strength, (d) schematic diagram of tensile performance of GPE

Figure 4a depicts the discharge polarization and power density curves of ZAB assembled based on composite GPE. Analysis shows that the maximum current density is based on the 124.3 mA cm\(^{-3}\) produced by ZAB assembled by PVA-C\(_3\)-CNFs GPE, and the maximum peak power density is 62.2 mW cm\(^{-3}\). Both are higher than pure PVA (72.3 mA cm\(^{-3}\), 36.2 mW cm\(^{-3}\)). As shown in Figure 4b, ZAB was treated with different rates of current discharge. The discharge potential of ZAB based on PVA-C\(_3\)-CNFs GPE decreased from 1.29 V for 1 mA cm\(^{-2}\) to 0.96 V for 10 mA cm\(^{-2}\). In addition, when the current was changed to 1 mA cm\(^{-2}\) again, the ZAB discharge potential based on PVA-0.8%-C-CNFs remained stable at 1.28V and not more than 10 mV, showing good rate performance. The ZAB constant current discharge curve is shown in Figure 4c. At room temperature, the discharge capacity of ZAB assembled based on pure PVA, PVA-C\(_3\)-CNFs, was measured with a current density of 3 mA cm\(^{-2}\). Among them, the highest initial discharge potential of ZAB using PVA-C\(_3\)-CNFs is 1.35 V, which is 120 mV higher than that of ZAB based on pure PVA. The longest discharge time using PVA-C\(_3\)-CNFs GPE is 33.5 hours, which is almost twice that of pure PVA. The specific capacity of solid ZAB is calculated. ZAB based on PVA–C\(_3\)-CNF can provide the highest specific capacity of 149.1 mAh cm\(^{-3}\), Higher than pure PVA (71.2 mAh cm\(^{-3}\)). At the same time, PVA-C\(_3\)-CNFs showed the best cycle stability, continuously and stably maintaining a charge-discharge cycle of more than 50h under a constant current, which was much higher than that of the ZAB battery using pure PVA (Figure 4d).
4. Conclusion

In summary, the research work in this paper innovatively proposes the use of natural modified cellulose nanofibers as fillers to improve the application performance of hydrogel electrolytes in solid ZAB. The PVA-based nanocomposite GPE was prepared by controlling the carboxyl content in C-CNFs to optimize the C-CNFs with the best degree of modification, showing excellent ionic conductivity (0.31 S cm⁻¹) and electrolyte retention. The solid ZAB prepared based on mixed GPE can continue to carry out stable charge and discharge reactions within 50 hours, and has good cycle stability. At the same time, it has high discharge capacity and stable discharge rate performance. The high flexibility of this PVA-based cellulose composite GPE greatly expands the application field of the assembled ZAB structure, and can become an important component of future wearable electronic devices.

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