Journal of Functional Materials and Applied Engineering

Research Paper

Construction of Cellulose Polyvinyl Alcohol Ionic Gels and Application of Flexible Supercapacitors

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Abstract. Taking natural cellulose, polyvinyl alcohol (PVA), and the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF_4) as raw materials, a flexible energy storage material with both environmental friendliness and superior electrochemical performance was successfully prepared via a solvent replacement regeneration technique. This cellulose/polyvinyl alcohol composite ionic gel electrolyte, designated as Cel/PVA-BF_4 gel, exhibited a three-dimensional porous network structure as observed by scanning electron microscopy (SEM). Fourier transform infrared spectroscopy (FT-IR) confirmed the reconstruction of intermolecular hydrogen bonds, while X-ray diffraction (XRD) patterns indicated a significant decrease in crystallinity. Thermogravimetric (TG) analysis verified that the material remained stable over a wide temperature range from -18°C to 120°C. The introduction of [Emim]BF_4 enabled the Cel/PVA-BF_4 gel electrolyte to achieve an ionic conductivity of 18.2 mS/cm. An integrated flexible supercapacitor was successfully constructed using the Cel/PVA-BF_4 gel. This capacitor exhibited three breakthrough advantages: a high voltage window of 3.5 V, surpassing the limitations of traditional aqueous systems; an energy density of 24 Wh/kg, reaching the level of commercial lithium thin-film batteries; and demonstrating remarkable cycling stability, maintaining over 94% of its capacity after 5,000 charge-discharge cycles, which is superior to most reported values in the literature.

Keywords: *Cellulose; Polyvinyl alcohol;Ionic gel; High-voltage window; Integrated flexible supercapacitors*

Received on 15 Feb 2023, Accepted on 15 Apr 2023, Published on 28 Apr 2023

1 Introduction

Mounting exigencies for emission reduction and sovereign energy supplies have hastened the adoption of clean power ecosystems, fostering breakthroughs in storage mechanisms that integrate high throughput, extended durability, and minimal ecological impact. Supercapacitors—or electrochemical capacitors—navigate this technical continuum, bridging the high-power discharge rates of static capacitors with the sustained energy delivery of galvanic cells.Their defining attributes encompass superior power-to-mass ratios, near-instantaneous charge exchange dynamics (temporal magnitudes of seconds), and extraordinary operational longevity, regularly sustaining 10^5–10^6 charge-discharge sequences. These attributes render them indispensable for applications requiring quick bursts of energy and efficient energy recuperation, such as in regenerative braking for electric vehicles, frequency regulation in smart grids, and as power sources for a rapidly expanding universe of portable and wearable electronics [1-2]. However, the widespread adoption and performance ceiling of supercapacitors are fundamentally constrained by several intertwined challenges. A primary limitation is their relatively low energy density (typically ≤10 Wh/kg), which remains significantly inferior to that of lithium-ion batteries. This is intrinsically linked to the energy storage mechanism (primarily physical adsorption/desorption of ions) and, crucially, the narrow electrochemical stability window (ESW) of conventional electrolytes. Aqueous electrolytes are inherently limited to about 1.2 V due to water electrolysis, while organic electrolytes, though offering higher voltages (~2.5-2.7 V), introduce significant drawbacks including flammability, toxicity, packaging complexity to prevent leakage, and environmental concerns. Therefore, the rational design of electrolyte formulations that

harmonize extended voltage stability, superior ionic transport kinetics, and non-flammable characteristics stands as a pivotal determinant for unlocking advanced supercapacitor architectures with enhanced energy metrics [3-4].

In pursuit of safer and more integrable devices, research has vigorously shifted from liquid to quasi-solid or solid-state electrolytes, particularly gel-polymer electrolytes (GPEs) and ionogels. These materials combine the cohesive, leak-proof nature of a solid with the ion-transport properties akin to liquids. Within this domain, ionogels—comprising an ionic liquid (IL) immobilized within a three-dimensional polymer network—represent a particularly promising avenue. Ionic liquids, with their intrinsic properties such as negligible volatility, high thermal stability, wide electrochemical windows (>3.0 V for many), and good ionic conductivity, serve as an ideal conductive phase. The polymer matrix provides mechanical integrity, flexibility, and processability. However, a critical dissonance often exists between performance and sustainability. Established macromolecular scaffolds exemplified by PVDF-HFP and PMMA stem from non-renewable hydrocarbon sources and demonstrate negligible biodegradability, creating inherent tension with environmentally responsible engineering objectives and resource recovery strategies [5]. This highlights an urgent imperative to develop next-generation ionic conductors sourced from renewable, environmentally degradable precursors while maintaining uncompromised electrochemical functionality. Polymers originating from biological feedstocks—exemplified by cellulosic materials and PVA—present an attractive technological pathway. As nature's most plentiful biopolymer, cellulose exhibits remarkable tensile resilience, physiological inertness, inexhaustible replenishment, and extensive hydroxyl moiety coverage conducive to charge carrier migration. Yet, the dense hydrogen-bonded architecture pervading cellulose macromolecules fosters extensive crystallization and poor solvation behavior, impeding fabrication methodologies and commonly resulting in inflexible substances with restricted electrochemical utility. PVA, conversely—a laboratory-synthesized, water-compatible polymer—displays superior filmogenic attributes, considerable mechanical compliance, pronounced affinity for aqueous environments, capacity for biological assimilation, and satisfactory ionic charge accommodation, establishing it as a preferred foundational material for gel-mediated electrolyte configurations [6-7]. Its backbone, rich in hydroxyl groups, is conducive to forming hydrogen bonds and coordinating with ions. The strategic combination of cellulose and PVA holds the potential to create a synergistic composite: the robust cellulose fibrils can reinforce the mechanical scaffold, mitigating the potential excessive swelling or weakness of pure PVA gels, while the PVA matrix can improve flexibility, processability, and provide a continuous phase for efficient ion conduction, thereby overcoming the individual limitations of each component.

This study is therefore dedicated to the design, fabrication, and comprehensive evaluation of a novel, fully biobased, high-performance ionogel electrolyte that seamlessly marries sustainability with superior electrochemical functionality for flexible integrated supercapacitors [8-9]. We propose and demonstrate a facile yet effective solvent-replacement regeneration strategy to fabricate a cellulose/PVA composite ionogel, designated as Cel/PVA-BF_4 gel. Our innovative approach involves a two-step process: First, a homogeneous precursor gel (Cel/PVA-IL gel) is formed by co-dissolving microcrystalline cellulose and PVA in 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), a well-known cellulose-dissolving ionic liquid that effectively disrupts the native hydrogen-bond network. Subsequently, a solvent exchange process is employed, where the precursor gel is immersed in 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF_4). This operation instigates morphological reconfiguration of the polymeric scaffold, replacing [Bmim]Cl with [Emim]BF_4—a calculated choice grounded in its exceptional integration of attenuated flow resistance, expedited charge carrier dynamics, and widened electrochemical stability threshold indispensable for high-voltage utilization [10-12].We hypothesize that this methodology will yield an ionogel with an optimized interconnected porous architecture, enhanced intermolecular interactions (including hydrogen bonding between cellulose, PVA, and the IL anions), and effective immobilization of the highly conductive IL phase. The as-synthesized Cel/PVA-BF_4 gel is projected to demonstrate a distinctive combination of advantageous characteristics: extraordinary load-bearing capacity and conformability, thermodynamic persistence over wide temperature intervals, enhanced charge carrier transport properties, extended electrochemical inertness window, and native ecological mineralization potential of foundational components.In this work, we present a systematic investigation encompassing the morphological evolution, chemical structure, thermal stability, mechanical properties, electrochemical characteristics, and environmental degradability of the synthesized Cel/PVA-BF_4 ionogel. The formation of a dense, three-dimensional porous network is confirmed by scanning electron microscopy (SEM), while Fourier-transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD) provide insights into the hydrogen bond reconstruction

and the reduction in crystallinity, respectively. Its practical utility and performance are unequivocally demonstrated by constructing an integrated, flexible supercapacitor device, where the Cel/PVA-BF_4 gel functions simultaneously as the electrolyte, separator, and a flexible substrate. The device employs a asymmetric electrode configuration with activated carbon and a MoS_2/multi-walled carbon nanotube (MWCNT) composite as the active materials. The constructed supercapacitor device is subjected to exhaustive electrochemical evaluation encompassing voltage endurance limits, capacitive performance characteristics, gravimetric energy and power densities, and prolonged charge-discharge stability assessment.This research aims to establish a novel, green, and high-performance material platform, effectively bridging the gap between ecological design and the stringent performance demands of future flexible, wearable, and sustainable energy storage systems.

2 Materials and Methods

2.1 Synthesis of Cellulose/Polyvinyl Alcohol Ionic Gels

2.1.1 Synthesis of Cellulose/PVA-1-butyl-3-methylimidazolium chloride Ionic Gel (Cel/PVA-IL gel)

A mixture comprising 30 g [Bmim]Cl and 1.25 g cellulose was agitated at 85°C for a 2-hour duration. Subsequently, 0.156 g PVA was incorporated and agitated for 4 h, yielding a cellulose/PVA ionogel matrix comprising 4% cellulose and 0.5% PVA by mass. The resulting formulation was uniformly deposited via spin-coating onto a planar glass substrate and subsequently conditioned within a convection oven at 85°C for a minimum 12-hour period to eliminate entrapped gaseous inclusions. The glass substrate was then equilibrated under ambient conditions for approximately 12 h to yield the Cel/PVA-IL gel.

2.1.2 Synthesis of Cellulose/PVA-1-ethyl-3-methylimidazolium tetrafluoroborate Ionic Gel (Cel/PVA-BF_4 gel)

The Cel/PVA-IL gel was immersed in [Emim]BF_4 at room temperature for at least 48 h. After removing the surface liquid, the Cel/PVA-BF_4 gel was obtained.

2.2 Synthesis of the Integrated Flexible Supercapacitor

2.2.1 Preparation of Active Material

MoS_2 and multi-walled carbon nanotubes were combined in a 2:5 mass proportion and suspended within 15 mL anhydrous ethanol. The resulting suspension was subjected to acoustic cavitation at ambient temperature (20°C) for no less than 10 min, subsequently evaporated to dryness at 80°C over a 12-hour timeframe. The dried composite was subsequently pulverized for a minimum 30-min duration to afford the electrochemically active MoS_2&MWCNTs hybrid material.

2.2.2 Synthesis of the Cellulose/PVA Ionic Gel-based Integrated Flexible Supercapacitor

The Cel/PVA-IL gel was thermally conditioned at 80°C for 30 min. A layer of activated carbon was deposited onto one face of the preheated gel matrix. The assembly was returned to the 80°C oven for 10 min, then allowed to cool under ambient conditions for 2 h. The same method was used to coat MoS_2&MWCNTs on the other side. The coating density for the active material on both sides was 0.03 g/cm², with a mass ratio of 1:1. The single-sided nickel foam electrode was fabricated by homogenizing activated carbon, polymeric binder, and conductive carbon black in a 7:2:1 mass proportion; the opposing face was constructed by blending MoS_2&MWCNTs, PVDF, and carbon black at an identical 7:2:1 mass ratio [13].In a glove box, the Cel/PVA-IL gel coated with activated carbon and MoS_2&MWCNTs was immersed in [Emim]BF_4 for 48 h, and then assembled with the nickel foam coated with active material to form the integrated flexible supercapacitor.

2.3 Testing and Characterization

2.3.1 FT-IR Analysis

Sample spectra were measured using ATR mode, with data recorded in the range of 400 ~ 4000 cm^{-1}.

2.3.2 XRD Analysis

Samples were scanned in the range of 5° ~ 90° at 30 kV and 30 mA, with a scanning rate of 5°/min.

2.3.3 TG Analysis

Thermogravimetric analysis (TG) of the samples was performed using a thermogravimetric analyzer, heated from room temperature to 700°C at a heating rate of 10°C/min under a nitrogen atmosphere.

2.3.4 Thermal Stability Analysis

Sample temperature testing was conducted using an oven and a freezer, with data recorded in the range of -18 to 150°C.

2.3.5 SEM Analysis

The microstructure of the samples was characterized using a scanning electron microscope at a working voltage of 10 kV.

2.3.6 Degradation Performance Test

A 2 cm × 2 cm sample was placed 15 cm below the surface of natural soil. Photographs were taken to record the condition after 7, 14, and 21 days.

2.3.7 Electrochemical Stability Performance Test

An electrochemical workstation was used for AC impedance testing of the samples. After the samples underwent long-term treatment at high and low temperatures, their ionic conductivity (σ) was tested. The calculation formula is shown in Equation (1).

$$\sigma=L/(R\times A) \quad (1)$$

Where: L is the thickness of the sample, cm; R is the resistance of the sample, Ω; A is the effective contact area of the sample, cm^2.

2.3.8 Electrochemical Performance Testing of the Supercapacitor

Comprehensive electrochemical evaluation, incorporating electrochemical impedance spectroscopy, cyclic voltammetric analysis, and constant-current charge-discharge profiling, was performed on the fabricated capacitor configuration at room temperature utilizing a multifunctional electrochemical analyzer. The relevant calculation formulas are shown in Equations (2) to (4):

$$C=(I\times\Delta t)/(m\times\Delta V) \quad (2)$$

$$E=(C\times(\Delta V)2)/7.2 \quad (3)$$

$$P=(3600\times E)/\Delta t \quad (4)$$

Where: I is the discharge current, A; Δt is the discharge time, s; m is the total mass of the active material in the device, g; ΔV is the voltage window, V; C is the specific capacitance of the supercapacitor, F/g; E is the energy density, Wh/kg; P is the power density, W/kg.

3 Results and Analysis

3.1 Morphology Study of the Gels

3.1.1 Macroscopic Morphology

The Cel/PVA-BF_4 gel was successfully prepared by introducing [Emim]BF_4 into the cellulose/PVA ionic gel system. As shown in Figure 1, the Cel/PVA-BF_4 gel maintained excellent flexibility similar to the Cel/PVA-IL gel, able to

withstand repeated bending without rupture, demonstrating good mechanical stability and structural integrity. Notably, after the introduction of [Emim]BF_4, the transparency of the gel changed, transforming from a transparent state to a slightly whitish translucent state. To quantitatively characterize this change in optical properties, the total transmittance and haze of the gels were measured. The results showed that the total transmittance of the Cel/PVA-IL gel and Cel/PVA-BF_4 gel was 89.95% and 89.21%, respectively, and the haze was 4.1% and 55.5%, respectively. The data indicates that the total transmittance of the Cel/PVA-BF_4 gel only slightly decreased, but the haze increased significantly by more than 12 times. This change in optical properties may be due to the introduction of [Emim]BF_4, which increased the entanglement degree of molecular chains within the gel, forming a denser network structure. This structural change may promote an increase in crystalline regions within the gel, thereby enhancing light scattering effects, ultimately manifested as a significant increase in haze.

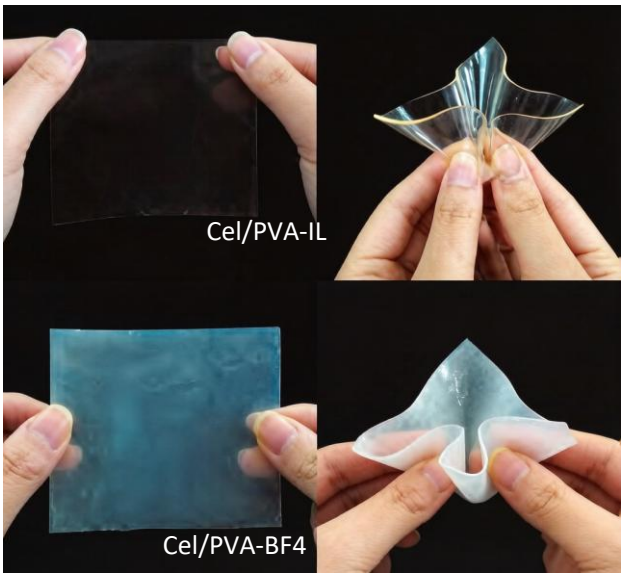

Figure 1 Optical photographs of gels

3.1.2 Microscopic Morphology

The two gel compositions were subjected to freeze-drying for thorough dehydration prior to surface morphology examination through SEM, with resulting images presented in Figure 2.The observation indicates that the introduction of [Emim]BF_4 caused significant changes in the microscopic morphology of the ionic gel. The Cel/PVA-IL gel exhibited a slightly wrinkled structure, while the structure of the Cel/PVA-BF_4 gel was denser. This is because the skeleton cellulose molecular chains and PVA molecular chains within the gel are more tightly entangled.

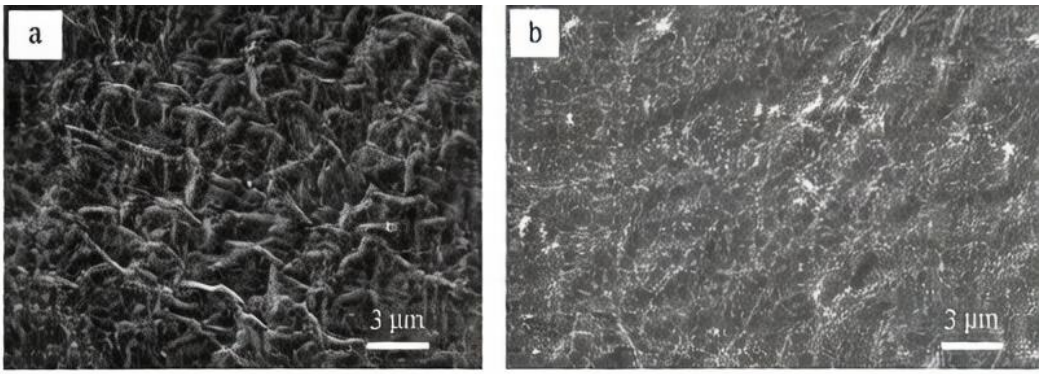

Figure 2 SEM images of cellulose/polyvinyl alcohol ionic gels

3.2 Molecular Structure of the Gels

3.2.1 FT-IR Analysis

To analyze the functional group structure, FT-IR characterization was performed on the Cel/PVA-IL gel and Cel/PVA-BF_4 gel, as shown in Figure 3(a).

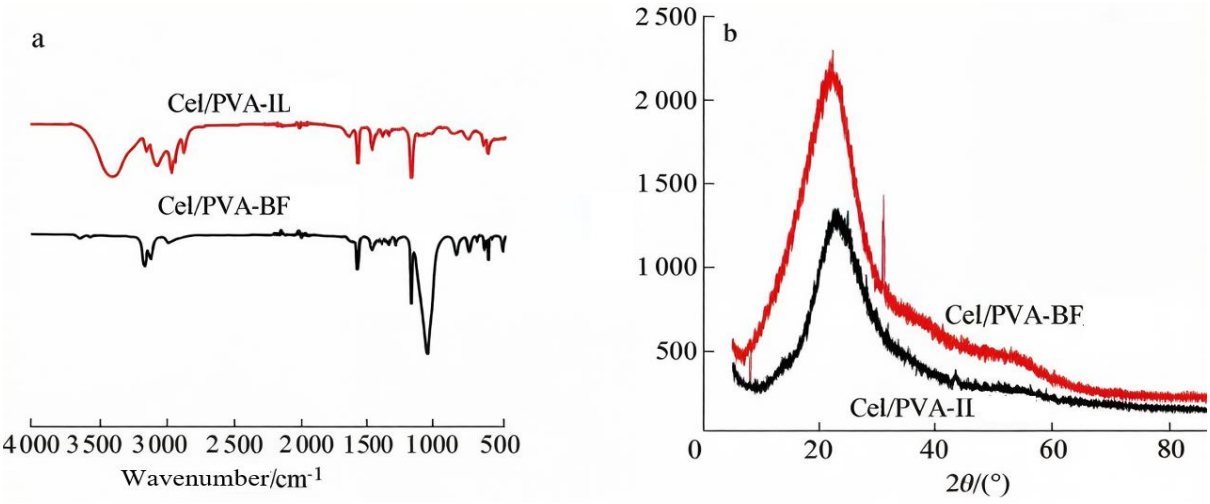

Figure 3 FT-IR spectra (a) and X-ray diffraction (XRD) patterns (b) of gels

FT-IR spectra of the Cel/PVA-IL gel display characteristic peaks: 3142–2876 cm^{-1} (C–H stretching of butyl and methyl on imidazolium); 1622 cm^{-1} (C=C stretching of imidazolium); 1572 cm^{-1} (C=N stretching of imidazolium); 875–625 cm^{-1} (C–H out-of-plane bending of imidazolium); 1173 cm^{-1} (C–O stretching of hydroxyl). The Cel/PVA-BF_4 gel shows: 3172–2986 cm^{-1} (C–H stretching of ethyl and methyl on imidazolium); 1634 cm^{-1} (C=C stretching); 1576 cm^{-1} (C=N stretching).The positions of these peaks are slightly shifted compared to those of the Cel/PVA-IL gel, showing a slight blue shift. This is because the change in the substituents on the cationic imidazolium ring of [Emim]BF_4 affects the position of the stretching vibration peaks. The 853–624 cm^{-1} interval similarly reflects C–H out-of-plane bending of the imidazolium moiety, while the 1171 cm^{-1} peak indicates C–O stretching adjacent to hydroxyl substituents.These two peaks are basically consistent with the Cel/PVA-IL gel. Notably, a new characteristic peak appears at 1062 cm^{-1}, belonging to the B-F bond stretching vibration in BF_4^-, which provides direct evidence for the successful introduction of [Emim]BF_4.

3.2.2 XRD Analysis

This investigation performed crystallographic analysis of Cel/PVA-IL and Cel/PVA-BF_4 gels utilizing X-ray diffraction methodology with the objective of elucidating the structural modifications induced by [Emim]BF_4 incorporation on the crystalline architecture of the ionogel matrix. As shown in Figure 3(b), both the Cel/PVA-IL gel and Cel/PVA-BF_4 gel exhibit broad diffraction peaks near $2\theta = 25°$, and the shapes of their diffraction peaks are similar, indicating they have similar crystal structure characteristics. However, the diffraction peak intensity of the Cel/PVA-BF_4 gel is significantly higher than that of the Cel/PVA-IL gel. This result indicates that the introduction of [Emim]BF_4 significantly regulates the crystallization behavior between cellulose and PVA molecules, leading to enhanced partial crystallinity while promoting the rearrangement of molecular chains. This rearrangement forms smaller microcrystals or locally ordered regions, which is manifested as increased diffraction peak intensity in XRD. The ionic liquid can induce polymer chain segment motion, forming a structure that is locally ordered but overall amorphous.

3.3 Study on High-Temperature and Low-Temperature Stability of Cellulose/Polyvinyl Alcohol Ionic Gels

3.3.1 TG Analysis

To investigate the effect of introducing [Emim]BF_4 on the thermal stability of the gel, thermogravimetric (TG) testing was performed (Figure 4). The slight weight loss of both gels within 100°C is due to the volatilization of

free water inside the gel. The temperature at which the Cel/PVA-IL gel begins to lose weight is 225°C, at which point bonds within the cellulose and [Bmim]Cl molecules begin to break. In contrast, the temperature at which the Cel/PVA-BF_4 gel begins to lose weight is 285°C. Compared to the Cel/PVA-IL gel, the decomposition temperature of the Cel/PVA-BF_4 gel is significantly increased. This is because the cellulose and PVA molecular chains inside the Cel/PVA-BF_4 gel have stronger interactions, and the [Emim]BF_4 itself within the gel has a higher decomposition temperature.

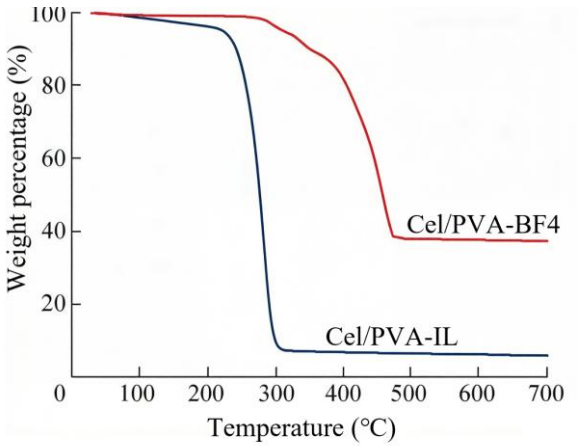

Figure 4 TG curves of gels

3.3.2 High-Temperature and Low-Temperature Stability Analysis

The thermal behavior of Cel/PVA-BF_4 gel was systematically investigated by monitoring morphological transformations across varied temperature regimes and exposure intervals.As illustrated in Figure 5, the Cel/PVA-BF_4 gel retains remarkable dimensional integrity and pliability following thermal conditioning at 120°C for 6 h and cryogenic exposure at -18°C for 72 h. This significant high- and low-temperature stability is primarily attributed to the ionic liquid contained within the ionic gel. Unlike traditional water-based gels, ionic liquids are non-volatile and possess excellent frost resistance. Their unique chemical structure prevents them from volatilizing or freezing like water solvents at high or low temperatures, thereby avoiding structural damage caused by temperature extremes.

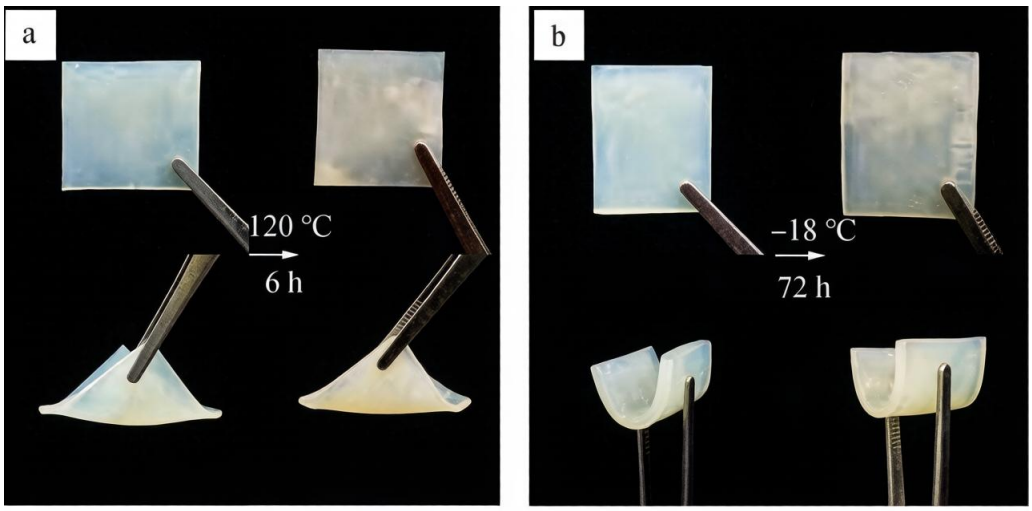

Figure 5 Optical images of Cel/PVA-BF_4 gel after treatment at 120℃ (a) and -18℃ (b)

To more scientifically and rigorously evaluate the high- and low-temperature stability of the Cel/PVA-BF_4 gel, this

study measured the volume and volume retention rate of the ionic gel after being placed under different temperature conditions for varying durations (Table 1). The measurement results indicate that the Cel/PVA-BF_4 gel exhibits excellent stability in both high- and low-temperature environments. Specifically, after being placed in a 120°C high-temperature environment for 6 h, the volume retention rate of the Cel/PVA-BF_4 gel remains above 96%. This phenomenon can be attributed to the slight seepage of a small amount of ionic liquid from the gel in the high-temperature environment. Although there is a slight volume change, the overall flexibility of the gel is not significantly affected. Furthermore, experimental results show that after being placed in a -18°C low-temperature environment for 72 h, the volume change of the Cel/PVA-BF_4 gel is minimal, fully demonstrating its excellent frost resistance. This gel material exhibits superior frost resistance and high-temperature stability, with performance significantly better than traditional water-based gel systems. This provides an important scientific basis and technical support for its practical engineering applications under wide temperature range conditions.

Table 1 The volume and volume retention of Cel/PVA-BF_4 gel

	Treatment for 6 h at Different Temperatures					**Treatment at -18°C for Different Durations**			
Gel	Room Temp.	50℃	80℃	100℃	120℃	0 h	24 h	48 h	72 h
Volume/ cm^3	1.464	1.456	1.452	1.451	1.420	1.853	1.818	1.773	1.773
Volume Retention/ %	100	99.43	99.18	99.09	96.95	100	98.11	98.11	98.11

3.4 Mechanical Properties of Cellulose/Polyvinyl Alcohol Ionic Gel

As shown in Figure 6, the Cel/PVA-BF_4 gel exhibits outstanding mechanical properties, with its strength-to-mass ratio performance being particularly notable. Experimental data shows that a gel sample weighing only 0.47 g can easily withstand the pulling force of a 500 g weight (equivalent to 1064 times its own mass). This performance indicator is significantly better than most reported flexible electrolyte materials [15-17]. This extraordinary mechanical characteristic originates from the unique microscopic structural design of the material: Firstly, the strong interaction between cellulose molecular chains and PVA molecular chains provides robust skeletal support. Secondly, [Emim]BF_4 not only acts as a conductive medium but also serves as an intermolecular lubricant, effectively dispersing stress and preventing crack propagation. Leveraging its superior mechanical characteristics, the Cel/PVA-BF_4 gel demonstrates substantial promise for deployment in deformable energy storage systems, body-integrated electronic apparatus, and additional sectors demanding elevated structural robustness and operational consistency,furnishing robust underpinning for the advancement of forthcoming generations of compliant electronic systems.

Figure 6 Tensile property of Cel/PVA-BF_4 gel

3.5 Electrochemical Performance of Cellulose/Polyvinyl Alcohol Ionic Gel

3.5.1 AC Impedance Analysis

The electrochemical impedance spectroscopy (EIS) test results (Figure 7) clearly reveal the enhancing effect of introducing [Emim]BF_4 on the gel's conductivity. Through fitting calculations, it was found that the introduction of the ionic liquid significantly increased the ionic conductivity of the gel from 13.43 mS/cm to 18.16 mS/cm (an improvement of 35.2%). This significant enhancement in conductive performance is mainly attributed to: the low viscosity characteristic of [Emim]BF_4, which greatly reduces the flow resistance for ion migration; the compact structure of $[Emim]^+$ with shorter side chains, which is conducive to the rapid directional movement of cations. Moreover, the abundant hydroxyl groups on the cellulose and PVA molecular chains provide rich sites for ion diffusion. The synergistic effect of these factors constructs efficient ion transport channels, thereby significantly improving the ionic conductivity of the gel system.

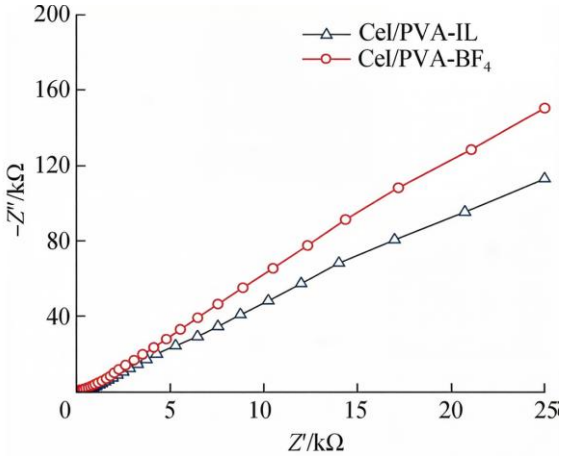

Figure 7 AC impedance

3.5.2 Electrochemical Stability Analysis

To comprehensively evaluate the applicability of the Cel/PVA-BF_4 gel in extreme environments, the variation pattern of its ionic conductivity under different temperature conditions was studied. Experimental results show that the gel exhibits excellent high-temperature stability. After continuous operation for 12 h in a 120°C high-temperature environment, its ionic conductivity significantly increases to 214% of the initial value (Table 2). This phenomenon can be attributed to the following synergistic mechanisms: First, the high-temperature conditions effectively reduce the viscosity of [Emim]BF_4, significantly enhancing the migration rate of ions and charge carriers. Second, the increased temperature promotes the movement of cellulose and PVA molecular chain segments, optimizing the ion transport channels within the polymer network.

Table 2 Ionic conductivity and retention of Cel/PVA-BF_4 gel treated at different temperatures and times

	Treatment at 120°C for Different Durations							**Treatment at -18°C for Different Durations**						
Gel	0 h	2 h	4 h	6 h	8 h	10 h	12 h	0 h	12 h	24 h	36 h	48 h	60 h	72 h
Ionic Conductivity / (mS·cm^{-1})	18.16	42.62	40.39	36.63	39.31	39.06	38.86	13.67	14.28	13.10	11.72	13.09	10.93	12.61
Conductivity Retention / %	100	234.7	222.4	201.7	216.5	215.1	214.1	100	104.5	95.83	85.81	95.76	79.96	92.25

More importantly, the strong interactions formed between cellulose and PVA molecules further enhance the thermal stability of the gel, thereby ensuring material stability while improving conductive performance. These characteristics enable the Cel/PVA-BF_4 gel to demonstrate excellent long-term operational stability in high-temperature application scenarios. In low-temperature tests, after 72 h in a -18°C low-temperature environment, the ionic conductivity retention rate of the Cel/PVA-BF_4 gel still exceeds 92% (Table 2). Due to the uneven

distribution of ions within the gel, over time, ions undergo redistribution, moving to positions more favorable for conduction, causing a temporary increase in conductivity. This result indicates that even under low-temperature conditions, the Cel/PVA-BF_4 gel can maintain good ion transport capability.

3.6 Study on the Degradability of Cellulose/Polyvinyl Alcohol Ionic Gel

To evaluate the environmental friendliness of the Cel/PVA-BF_4 gel, its biodegradability was studied. As shown in Figure 8, by comparing the degradation of Cel/PVA-BF_4 gel samples of the same size with polypropylene (PP), polyvinyl chloride (PVC), and the commercially available degradable material poly(butylene adipate-co-terephthalate)-polylactic acid (PBAT+PLA) in natural soil, it was found that this gel exhibits significant degradation advantages. In the initial stage of the experiment (0~7 days), all materials showed no obvious signs of degradation. Starting from the fourteenth day, the Cel/PVA-BF_4 gel was the first to show physical fragmentation, indicating that microorganisms had begun to decompose the polymer molecular chains in the gel. By the twenty-first day, this gel had completely degraded. This rapid degradation characteristic mainly stems from the fact that the glycosidic bonds and ester bonds in the cellulose and PVA molecular chains are easily broken under the action of microbial enzymes, and the presence of the [Emim]BF_4 ionic liquid does not affect the degradation performance of the gel [24]. While possessing excellent ionic conductivity (18.16 mS/cm) and high/low temperature (120°C/-18°C) stability, the Cel/PVA-BF_4 gel's rapid and complete degradability will promote the development of green electronic devices.

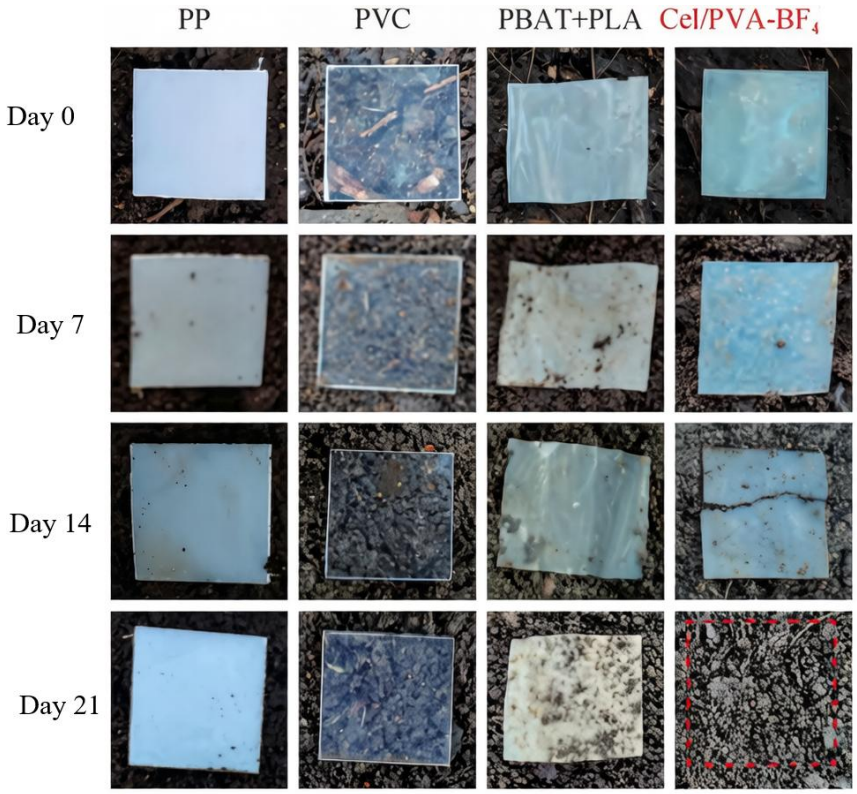

Figure 8 The biodegradability of Cel/PVA-BF_4 gel

3.7 Application of Cellulose/Polyvinyl Alcohol Ionic Gel in Integrated Flexible Supercapacitors

3.7.1 Electrochemical Performance Analysis

To further study the practical application value of the Cel/PVA-BF_4 gel in integrated flexible supercapacitors, a flexible supercapacitor was assembled using the Cel/PVA-BF_4 gel as the electrolyte and MoS_2&MWCNTs and activated carbon as the active materials for electrochemical testing. According to Figure 9(a), the slope trend of the device is almost stable, indicating that the device has ideal capacitive behavior and ion diffusion capability. Figure 9(b) shows the cyclic voltammetry (CV) curves of the device at different scan rates. With escalating

potential sweep velocities, the integrated area within the cyclic voltammetric profiles progressively expands.During the charging and discharging process, the curves show no redox peaks, indicating that the device has good capacitive behavior and stability. Moreover, the CV curve shape remains intact at a voltage window of 0~3.5 V, indicating that the supercapacitor's voltage window is stable. As depicted in Figure 9(c), the galvanostatic charge-discharge profile measured within a 3.5 V potential window exhibits pronounced symmetry, signifying favorable electrochemical reversibility of the charge storage device.The calculated specific capacitance of the flexible device at current densities of 0.1~1 A/g is shown in Table 3. The table shows that as the current density increases from 0.1 A/g to 1 A/g, the specific capacitance gradually decreases from 14.15 F/g to 4.02 F/g. At high current densities, the ion migration rate accelerates, which may lead to incomplete ion transport inside the electrode material, thereby reducing the specific capacitance. The energy density decreases from 24.07 Wh/kg (0.1 A/g) to 6.83 Wh/kg (1 A/g). Energy density is related to specific capacitance and voltage window; as specific capacitance decreases, energy density also decreases. The power density significantly increases from 87.5 W/kg (0.1 A/g) to 875 W/kg (1 A/g). The Cel/PVA-BF_4 gel exhibits excellent electrochemical performance at different current densities. At low current densities, its high specific capacitance and high energy density make it suitable for high-energy storage scenarios; at high current densities, its high power density makes it suitable for high-power output scenarios. This versatile functionality furnishes critical underpinning for the evolution of deformable energy storage systems and body-conformable electronic apparatus.

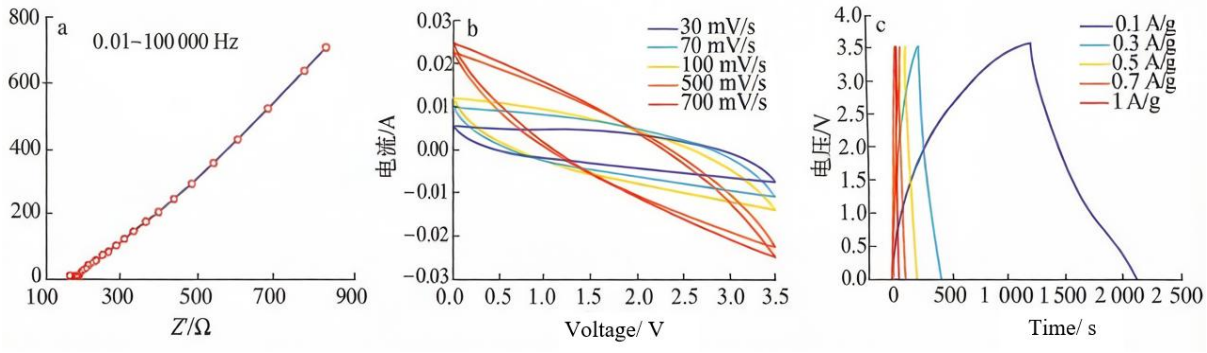

Figure 9 Electrochemical performance of the integrated flexible supercapacitor with Cel/PVA-BF_4 gel as electrolytes

Table 3 Performance of Cel/PVA-BF_4 gel-based integrated flexible supercapacitors at different current densities

Current Density / ($A \cdot g^{-1}$)	Mass Specific Capacitance / ($F \cdot g^{-1}$)	Energy Density / ($Wh \cdot kg^{-1}$)	Power Density / ($W \cdot kg^{-1}$)
0.1	14.15	24.07	87.5
0.3	8.57	14.58	262.5
0.5	7.17	12.19	437.5
0.7	5.47	9.31	612
0.9	4.34	7.38	787.8
1	4.02	6.83	875

3.7.2 Stability Analysis

Prolonged cycling stability was evaluated by subjecting the integrated flexible capacitor to repetitive charge-discharge protocols at a constant specific current of 1 A/g.Electrochemical measurements demonstrate that the supercapacitor sustains 94% of its initial specific capacitance after 5,000 repetitive galvanostatic cycles, indicating exceptional long-term stability.Notably, multiple brief capacitance drop phenomena were observed during the cycling process. The main reasons are as follows: During continuous charge-discharge cycles, ions ($[Emim]^+$ and BF_4^-) in the ionic gel undergo periodic intercalation/deintercalation processes, occasionally experiencing localized ion transport blockages. However, thanks to the excellent stability of the ion channels in the cellulose/PVA network structure, these blocked ions can quickly rediffuse to the active sites of the electrodes, allowing the capacitive performance to recover rapidly. This self-healing characteristic, combined with the stable interfacial contact between the ionic gel and the active materials, jointly ensures stable electrochemical

performance of the device during long-term cycling.

3.7.3 Comparison with Similar Capacitors

Compared with similar electrolyte-based capacitors such as liquid electrolyte supercapacitors and solid polymer electrolyte capacitors, gel-based capacitors offer superior safety. Solid or semi-solid gel-like electrolytes pose no risk of liquid leakage and can avoid problems such as corrosion and short circuits that may be caused by liquid electrolytes. Flexible electronic devices prepared using the Cel/PVA-BF_4 gel exhibit stronger stability and broader applicability in scenarios involving high temperature and mechanical deformation (such as bending, squeezing). The gel has stronger stability, is not prone to volatilization or decomposition, and experiences slower performance degradation (such as capacitance characteristics, internal resistance) during long-term use or under extreme environmental conditions (such as a wide temperature range), with a longer cycle life, superior to some liquid electrolyte systems that are prone to drying out or aging [26-29]. Additionally, the gel exhibits superior adaptability, establishing effective surface contact with various electrode compositions such as graphitic carbon derivatives and metallic oxide compounds.Thereby minimizing charge transfer resistance and enhancing the comprehensive electrochemical characteristics of the assembled system.Its adaptability is better than some electrolytes that have stringent requirements for electrodes.

Based on the comprehensive data presented in the document, the exceptional performance enhancement of the Cel/PVA-BF_4 ionogel electrolyte stems from a synergistic molecular design and a uniquely engineered multi-phase structure. The core mechanism is the strategic integration of three components: microcrystalline cellulose provides a robust, renewable scaffold; polyvinyl alcohol (PVA) offers a flexible, hydrophilic, and film-forming matrix rich in hydroxyl groups; and the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF_4) serves as a high-performance ionic conductor. The two-step solvent-replacement regeneration process is pivotal. First, dissolving cellulose and PVA in [Bmim]Cl disrupts the strong native hydrogen bonds in cellulose, enabling molecular-level mixing. Subsequently, exchanging with [Emim]BF_4 reconstructs the network, where the BF_4^- anions form new hydrogen bonds with the -OH groups of cellulose and PVA, as confirmed by FT-IR peak shifts. This reconstruction leads to a denser, more entangled three-dimensional porous network (observed via SEM), which enhances mechanical integrity. The [Emim]BF_4, with its low viscosity and compact cation structure, is effectively immobilized within this polymer mesh, creating efficient, continuous ion transport pathways. This explains the high ionic conductivity of 18.2 mS/cm—a 35% increase over the precursor gel—and the remarkable mechanical strength-to-weight ratio, where a 0.47g sample sustains a 500g load.

The performance enhancements are multifaceted and interrelated.The widened potential stability (3.5 V) is inherently attributable to the moisture-free constitution and superior electrochemical durability of [Emim]BF_4, thereby bypassing the oxidative and reductive limits that confine water-containing electrolytes. The outstanding thermal stability (-18°C to 120°C) and high ionic conductivity retention under extreme temperatures are due to the non-volatile nature of the IL and the stabilizing effect of the strong cellulose-PVA-IL interactions, which prevent structural collapse or freezing. The high energy density (24 Wh/kg) of the resulting flexible supercapacitor is a direct consequence of this high voltage window combined with efficient ion transport. Furthermore, the excellent cycling stability (94% capacitance retention after 5,000 cycles) can be attributed to the stable interfacial contact between the gel electrolyte and the electrodes, as well as the elastic network's ability to accommodate volume changes during ion intercalation/deintercalation. Ultimately, the mechanism is one of complementary synergy: cellulose provides strength and sustainability, PVA offers flexibility and processability, and [Emim]BF_4 delivers superior ionic transport and electrochemical stability, all integrated into a single, environmentally benign material platform.

4 Conclusion

A high-performance cellulose/polyvinyl alcohol ionic gel (Cel/PVA-BF_4 gel) was successfully prepared using cellulose, polyvinyl alcohol (PVA), and 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF_4) as raw materials. Tests and analyses were conducted on the microscopic morphology, chemical structure, environmental stability, mechanical properties, electrochemical stability, and degradability of the Cel/PVA-BF_4 gel. The results indicate that: This gel possesses excellent environmental stability, maintaining its original physical form and flexibility over a wide temperature range (-18~120°C); it has outstanding mechanical properties, with

a sample weighing only 0.47 g capable of withstanding a pulling force equivalent to 1064 times its own mass; it exhibits excellent electrochemical stability, maintaining high ionic conductivity under both high-temperature (120°C) and low-temperature (-18°C) conditions; it can completely degrade within 21 days, demonstrating good degradability. Using the Cel/PVA-BF_4 gel as the electrolyte for an integrated flexible supercapacitor, the device achieves a relatively high specific capacitance (14.15 F/g) and energy density (24.07 Wh/kg), placing it in the mid-to-upper level among similar studies. It outperforms traditional organic electrolyte supercapacitors but is slightly lower than some high-performance composite electrode or new electrolyte systems. It further demonstrates outstanding cycling durability, maintaining 94% of initial capacitance following 5,000 repetitive charge-discharge sequences.

References

[1] ZHAO D W, ZHANG Q, CHEN W S, et al. Highly flexible and conductive cellulose-mediated PEDOT: PSS/MWCNT composite films for supercapacitor electrodes[J]. ACS Applied Materials & Interfaces, 2017, 9(15): 13213-13222.

[2] ZHAO D W, CHEN C J, ZHANG Q, et al. High performance, flexible, solid-State supercapacitors based on a renewable and biodegradable mesoporous cellulose membrane[J/OL]. Advanced Energy Materials, 2017, 7(18): 1700739[2025-03-01]. https://doi.org/10.1002/aenm.201700739.

[3] WANG S F, GUO X, ZHANG Y X, et al. Construction of MXene/aramid nanofiber flexible self-supporting electrodes and their application in supercapacitors[J]. Materials Engineering, 2024, 52(6): 51-58. (in Chinese)

[4] ZHU X Z, JIANG G Y, WANG G, et al. Cellulose-based functional gels and applications in flexible supercapacitors[J]. Resources Chemicals and Materials, 2023, 2(2): 177-188.

[5] PANDEY D, KUMAR K S, THOMAS J. Supercapacitor electrode energetics and mechanism of operation: Uncovering the voltage window[J/OL]. Progress in Materials Science, 2024, 141: 101219[2025-03-01]. https://doi.org/10.1016/j.pmatsci.2023.101219.

[6] WANG X, ZHOU J H, ZHU Y, et al. Assembly of silver nanowires and PEDOT: PSS with hydrocellulose toward highly flexible, transparent and conductivity-stable conductors[J/OL]. Chemical Engineering Journal, 2020, 392: 123644[2025-03-01]. https://doi.org/10.1016/j.cej.2019.123644.

[7] CHENG W K, ZHU Y, JIANG G Y, et al. Sustainable cellulose and its derivatives for promising biomedical applications[J/OL]. Progress in Materials Science, 2023, 138: 101152[2025-03-01]. https://doi.org/10.1016/j.pmatsci.2023.101152.

[8] TEODORESCU M, BERCEA M, MORARIU S. Biomaterials of PVA and PVP in medical and pharmaceutical applications: Perspectives and challenges[J]. Biotechnology Advances, 2019, 37(1): 109-131.

[9] SERAIRI L, SANTILLO C, BASSET P, et al. Boosting contact electrification by amorphous polyvinyl alcohol endowing improved contact adhesion and electrochemical capacitance[J/OL]. Advanced Materials, 2024, 36(27): 2403366[2025-03-01]. https://doi.org/10.1002/adma.202403366.

[10] HU Y X, DU H L, LU J, et al. Interface synergistic stabilization of zinc anodes via polyacrylic acid doped polyvinyl alcohol ultra-thin coating[J/OL]. Journal of Energy Storage, 2024, 87: 111444[2025-03-01]. https://doi.org/10.1016/j.est.2024.111444.

[11] LI X, JIANG G Y, WANG G, et al. Promising cellulose-based functional gels for advanced biomedical applications: A review[J/OL]. International Journal of Biological Macromolecules, 2024, 260: 129600[2025-03-01]. https://doi.org/10.1016/j.ijbiomac.2024.129600.

[12] WANG X, ZHOU J H, PANG B, et al. Rapid microwave-assisted ionothermal dissolution of cellulose and its regeneration properties[J]. Journal of Renewable Materials, 2019, 7(12): 1363-1380.

[13] MIAO X, ZHUO R L, WEI Z, et al. Intercalated hydrates stabilize bulky MoS_2 anode for Lithium-ion battery[J/OL]. Chemical Engineering Journal, 2023, 470: 144282[2025-03-01]. https://doi.org/10.1016/j.cej.2023.144282.

[14] CHEN S, JIANG G, ZHOU J, et al. Robust Solvatochromic gels for self-defensive smart windows[J/OL]. Advanced Functional Materials, 2023, 33(20): 2214382[2025-03-01]. https://doi.org/10.1002/adfm.202214382.

[15] SI Y B, HONG Y W, BAO C L, et al. Hydrogels with extreme stretchability, ultralow hysteresis, self-adhesion, and antifreezing performance as flexible self-powered electronic devices[J]. Transactions of Tianjin University, 2025, 31(1): 15-28.

[16] ZHU J S, WANG M Z. A hydrogel sliding ring gel with high mechanical strength[J]. Chemical Education, 2012, 33(2): 1-3.
[17] WANG Z J, LIN J, NAKAJIMA T, et al. Hydrogel morphogenesis induced by force-controlled growth[J]. Proceedings of the National Academy of Sciences, 2024, 121(27): 2402587121[2025-03-01]. https://doi.org/10.1073/pnas.2402587121.
[18] LI X, JIANG H B, ZHANG Y, et al. Stimulation-reinforced cellulose-protein ionogels with superior mechanical strength and temperature resistance[J/OL]. Advanced Functional Materials, 2024, 34(48): 2408160[2025-03-01]. https://doi.org/10.1002/adfm.202408160.
[19] JIANG G Y, WANG G, ZHU Y, et al. A scalable bacterial cellulose ionogel for multisensory electronic skin[J/OL]. Research, 2022, 2022: 9814767[2025-03-01]. https://spj.science.org/doi/10.34133/2022/9814767.
[20] LV H Y, WANG Z E, GAO Z Y, et al. Highly stretchable, self-healable, and environment-adaptable ionogel-based high-output triboelectric nanogenerator for self-powered wearable ionotronics[J/OL]. Chemical Engineering Journal, 2025, 509: 161247[2025-03-01]. https://doi.org/10.1016/j.cej.2025.161247.
[21] WANG Z, WANG L, JIANG W, et al. Development of flame-retardant ion-gel electrolytes for safe and flexible supercapacitors[J]. Science China Materials, 2023, 66(8): 3129-3138.
[22] WANG Y, ZHANG X, JI P, et al. High toughness antifreeze conductive double network zwitterionic gel electrolyte for flexible supercapacitors[J/OL]. Journal of Applied Polymer Science, 2024, 141(31): 55727[2025-03-01]. https://doi.org/10.1002/app.55727.
[23] LI Q, LIU G, CHENG H, et al. Low-temperature electrolyte design for lithium-ion batteries: Prospect and challenges[J]. Chemistry-A European Journal, 2021, 27(64): 15842-15865.
[24] ZHANG S Y, LONG Q, JIANG G Y, et al. A robust, high-temperature-resistant, Protective cellulose gel enabled by multiscale structural engineering[J/OL]. International Journal of Biological Macromolecules, 2024, 277(4): 134520[2025-03-01]. https://doi.org/10.1016/j.ijbiomac.2024.134520.
[25] WANG L F, WANG H Y, WU C X, et al. Moisture-enabled self-charging and voltage stabilizing supercapacitor[J/OL]. Nature Communications, 2024, 15(1): 4929[2025-03-01]. https://doi.org/10.1038/s41467-024-49393-9.
[26] JING X Z, JING Y L, JI S, et al. Highly stretchable, anti-freezing, self-adhesion and self-healing zwitterionic hydrogel electrolytes for flexible electronic devices[J/OL]. Chemical Engineering Journal, 2025, 508: 161021[2025-03-01]. https://doi.org/10.1016/j.cej.2025.161021.
[27] RAPHAEL D C B, GUILHERME K M, MATEUS G M, et al. An easy to assemble PDMS/CNTs/PANI flexible supercapacitor with high energy-to-power density[J]. Nanoscale, 2022, 14(6): 2266-2276.
[28] LO H J, HUANG M C, LAI Y H, et al. Towards bi-functional all-solid-state supercapacitor based on nickel hydroxide-reduced graphene oxide composite electrodes[J/OL]. Materials Chemistry and Physics, 2021, 262: 124306[2025-03-01]. https://doi.org/10.1016/j.matchemphys.2021.124306.
[29] HONG S, YUAN Y, LIU C, et al. A stretchable and compressible ion gel based on a deep eutectic solvent applied as a strain sensor and electrolyte for supercapacitors[J]. Journal of Materials Chemistry C, 2020, 8(2): 550-560.