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Design and Evaluation of a Self-Healing, Highly Stretchable Double-Network Gel Polymer Electrolyte for Potential Use in Wearable Supercapacitors

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Cite This: *ACS Omega* 2025, 10, 32476−32485

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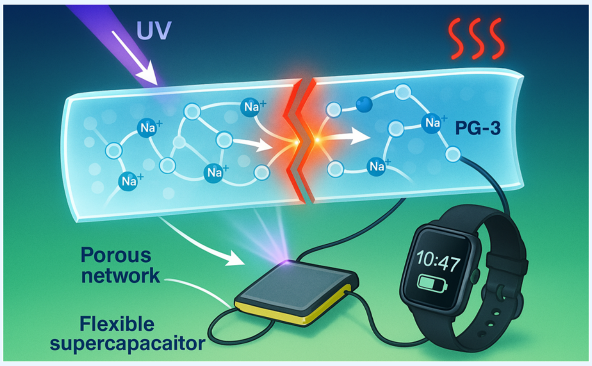

ABSTRACT: This work reports the design and synthesis of a novel self-healing and stretchable gel polymer electrolyte (GPE) based on a double-network (DN) architecture combining polyacrylamide (PAM) and gellan gum (GG). The GPE was fabricated via a UV-initiated one-pot photopolymerization process in the presence of Na^+ ions, which act both as ionic charge carriers and physical cross-linkers through electrostatic interactions. The optimized PG-3 DN GPE exhibited remarkable mechanical performance, achieving a tensile strength of 2.0 MPa and an elongation at break of 400%. Furthermore, the GPE demonstrated high ionic conductivity (0.29 S/cm) and excellent self-healing efficiency (>90%) at 60 °C under ambient pressure, without the need for additional healing agents. Spectroscopic and morphological characterizations (FTIR, XPS, ^{13}C NMR, SEM) confirmed the formation of a homogeneous and interconnected porous network that supports efficient ion mobility and structural integrity. The observed improvements in mechanical and electrochemical behavior were attributed to synergistic hydrogen bonding, Na^+-mediated ionic bridging, and optimized water retention. Compared to conventional GPEs, this PAM/GG-based DN system provides an environmentally friendly, biopolymer-integrated, and scalable platform suitable for next-generation flexible and wearable energy storage applications, particularly in supercapacitors.

1. INTRODUCTION

In the 21st century, the rapid advancement of energy storage technologies and the increasing demand for such systems have significantly heightened the need for efficient energy storage devices in the field of electrical engineering. Over the past decade, lithium-ion batteries and supercapacitors have become widely adopted as modern energy storage systems. Among these, supercapacitors stand out due to their high power density, rapid charge/discharge capability, long cycle life, and environmental safety.[1−3] A typical supercapacitor consists of electrodes and an electrolyte, where the nature and physicochemical properties of the electrolyte are crucial in determining the overall performance and capacity of the device.[4]

Although liquid electrolytes are widely used today due to their high ionic conductivity, they still suffer from several drawbacks such as volatility, flammability, corrosion, explosion risk, and environmental hazards.[5−7] These limitations pose serious safety concerns and hinder their integration into next-generation energy storage systems.[8]

In recent years, researchers have shown increasing interest in gel polymer electrolytes (GPEs), which offer advantages such as semisolid structure, improved thermal and chemical stability, reduced volatility, shape retention, and ease of processing.[9,10] More importantly, GPEs are nonleaking, structurally safe materials and are often considered environmentally friendly.[11]

However, one of the primary challenges of GPEs is their poor mechanical strength. Cracks caused by stretching, bending, or impact can disrupt the GPE structure, resulting in a significant drop in ionic conductivity and adversely affecting the reliability of the device.[12,13] While limited studies have focused on enhancing the mechanical properties of GPEs, several structural engineering strategies have been proposed, including slide-ring structures,[14] hydrophobic associations,[15] ionic cross-linking,[16] nanocomposites,[17] and particularly, double-network (DN) structures.[18]

DN hydrogels are complex structures composed of two interpenetrating networks—one brittle and rigid, and the other

Received: June 5, 2025
Revised: July 2, 2025
Accepted: July 9, 2025
Published: July 16, 2025

ACS Publications

https://doi.org/10.1021/acsomega.5c05335

soft and elastic (Figure 1). This architecture enables efficient energy dissipation during mechanical deformation and prevents crack propagation. Additionally, DN structures exhibit excellent thermal resistance and enhanced structural integrity due to strong physical and chemical cross-links.[18,19]

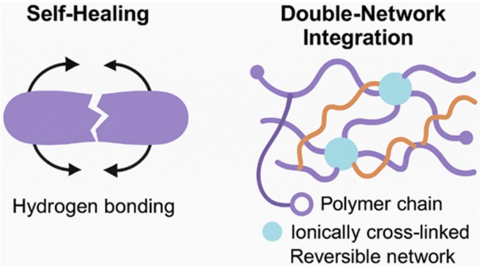

Figure 1. Theoretical basis of self-healing and double-network integration.

In this study, the double-network (DN) strategy, previously utilized for hydrogels, was applied to gel polymer electrolyte (GPE) systems to improve their mechanical performance. Furthermore, the DN architecture introduced a critical feature to the GPE: self-healing ability. Self-healing refers to the capacity of a material to autonomously recover its mechanical and/or functional properties after external or internal damage (e.g., rupture, tearing, cutting, cracking, deformation) under specific environmental conditions and time (Figure 1). In nature, such behavior is observed in organisms like lizards, which can regenerate their tails after damage. This biological phenomenon has inspired material scientists to replicate similar mechanisms in synthetic polymer systems.[20]

When self-healing ability is successfully integrated into energy storage devices -especially supercapacitors—these systems can restore their original mechanical and electrochemical functionality even after mechanical stress or damage. As a result, the durability and operational reliability of these devices are significantly improved, especially under complex working conditions.[21,22]

Self-healing GPEs are typically engineered using reversible covalent bonds (e.g., disulfide bonds, Diels–Alder reactions) or supramolecular interactions (e.g., hydrogen bonding, metal–ligand complexes). These mechanisms enable structural recovery under external stimuli such as heat, pressure, or light. However, achieving an optimal balance between ionic conductivity, mechanical robustness, and healing efficiency remains a significant scientific challenge.[17,18,23]

Considering these scientific fundamentals and existing strategies, this study proposes a novel double-network GPE design. Polyacrylamide (PAM) was selected as the polymer matrix and primary network due to its water solubility, high molecular weight, amorphous structure, excellent ionic conductivity, mechanical flexibility, and water-absorbing ability. Compared to other hydrophilic polymers such as PEO, PVS, and PAA, PAM demonstrates superior structural stability and adaptability for GPE systems.[23,24]

For the secondary network, gellan gum (GG) a naturally occurring hydrophilic polysaccharide synthesized by Pseudomonas elodea was employed. GG is low-cost, biocompatible, nontoxic, and thermally stable. Notably, it can form robust physical cross-links through interactions with various ionic species without the need for chemical cross-linkers.[25,26] This capability facilitates the formation of a strong and efficient hydrogel framework. Thus, the PAM/GG-based DN-GPE system combines natural functionality, mechanical durability, and high ionic transport capacity.

Recent advancements in gel polymer electrolytes (GPEs) have highlighted the promise of double-network (DN) architectures integrated with self-healing functionalities to meet the mechanical and electrochemical demands of flexible energy storage systems. Studies from 2022 to 2024 report that DN-GPEs comprising polyacrylamide (PAM) and natural polysaccharides such as κ-carrageenan or gellan gum significantly improve stretchability, tensile strength, and ionic conductivity while maintaining structural resilience.[27,28] Incorporation of Na^+ ions not only facilitates physical cross-linking and ionic transport but also enhances self-healing efficiency under mild thermal conditions.[29] Although Na^+ is a monovalent ion, it can function as a physical cross-linking agent by electrostatically associating with carboxylate groups ($-COO^-$) present in gellan gum chains. This interaction facilitates ionic bridging between polymer chains, enhancing the structural integrity and mechanical strength of the gel network without requiring covalent bonding.[30,31] Moreover, DN-GPE-based supercapacitors have demonstrated excellent cycle stability, retaining over 90% capacitance after 10,000 cycles, confirming their practical applicability in deformable, wearable, and environmentally friendly devices.[32]

The novelty of this study lies in the use of natural gellan gum as an electrolyte material in a GPE system for the first time, with significantly enhanced mechanical and functional properties through the implementation of a double-network structure. Specifically, a self-healing GPE system based on PAM and GG was developed, in which two networks are physically cross-linked via hydrogen bonding. The structural, thermal, electrochemical, and mechanical properties of the material were comprehensively investigated. Additionally, the correlation between healing efficiency and ionic conductivity under varying temperature and time conditions was examined.

2. EXPERIMENTAL SECTION

2.1. Materials. Gellan gum (GG) powder was purchased from Shanghai Macklin Biochemical Co., Ltd. (China). Acrylamide (AM) and the photoinitiator 2-Hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959, MW = 224.25) were supplied by Aladdin Reagent Co., Ltd. (China). Anhydrous sodium sulfate (Na_2SO_4, M = 142.04) was obtained from Shangyangong Co., Ltd. (China). For electrode preparation, activated carbon (acetylene black, CB) and the binder poly(tetrafluoroethylene) (PTFE, 60% aqueous dispersion) were used. All reagents were used without further purification.

2.2. Preparation of Self-Healing GG/PAM Double Network GPE. The double-network GPE sample was synthesized via a one-pot photopolymerization method (Chen et al.). Initially, 0–0.5 g GG, 6 g AM, 0.2–1 mol Na_2SO_4, and 10 mL of deionized water were placed into a glass beaker. The mixture was stirred at 95 °C for 2 h. To eliminate bubbles, ultrasonic vibration and vacuum degassing were applied. Then, 0.085 g Irgacure 2959 was added, and the solution was stirred for an additional 10 min until homogeneous. The final solution was quickly poured into a glass mold with dimensions of 10 × 60 mm^2 and photopolymerized under a UV lamp (365 nm, 8 W) for 3 h. After UV exposure, the samples were kept at room temperature for 2

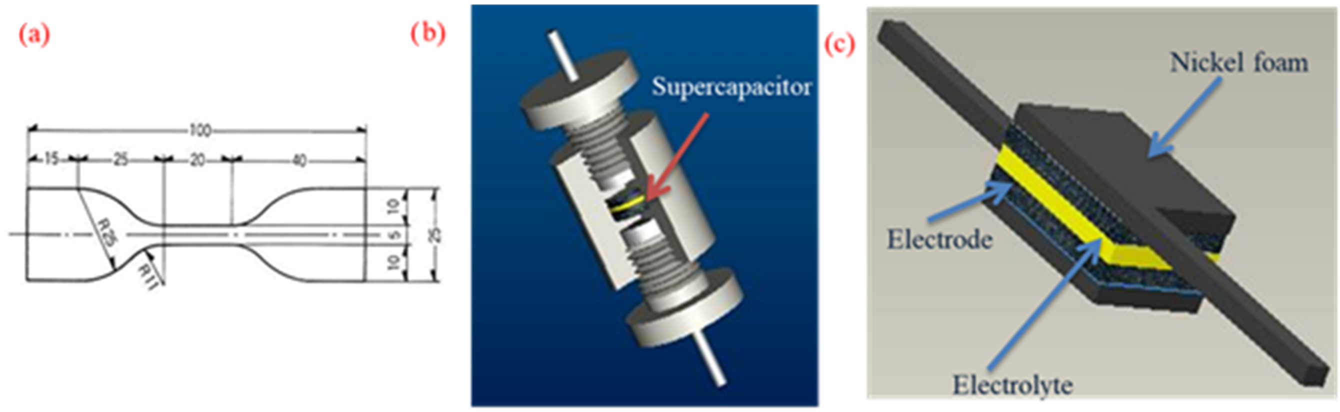

Figure 2. Schematic illustration of the supercapacitor: dumbbell-shaped sample (a), device 1 (b), and device 2 (c).

h to complete polymerization. As a control, PAM-based hydrogel without GG was synthesized using the same method.

2.3. Preparation of Activated Carbon Electrode and Supercapacitor Assembly. To prepare the active electrode, 80 wt % activated carbon (AC), 10 wt % acetylene black (CB), 10 wt % PTFE, and 10 wt % deionized water were mixed and homogenized using ultrasonic treatment. The resulting slurry was coated onto nickel foam and dried at 60 °C in a vacuum oven for 4 h. Each electrode had a mass loading of approximately 8−9 mg. The electrodes were soaked in Na_2SO_4 solution for 24 h. The supercapacitor (SC) device was assembled in a sandwich configuration using two electrodes and a GPE membrane. Electrochemical tests were performed using a two-electrode setup (Figure 2b,c).

2.4. Characterization and Measurements. *2.4.1. Mechanical Testing.* Hydrogel samples were cut into dumbbell shapes and tested using a universal testing machine (WSM-10kN, Changchun) at a speed of 100 mm/min under a 100 N tensile load.

2.4.2. Self-Healing Performance. Dumbbell-shaped samples, as shown in Figure 2a, were cut and stored at various temperatures (20, 40, 60, 80, and 100 °C) and time intervals (0.3, 2, 4, 8, 16, and 24 h). The healing tests were conducted by placing severed GPE samples in a **water bath maintained at 60 °C** for 0.3, 2, 4, 8, 16, and 24 h to prevent water loss from the gel matrix. The tensile strength of the healed samples was remeasured. Healing efficiency was determined by comparing the elongation at break values of healed and pristine samples. Healing efficiency (SH) was calculated using the formula

$$\mathrm{SH}\ (\%) = \frac{\sigma_{\text{self-healed}}}{\sigma_{\text{original}}} \times 100 \tag{1}$$

where, σ_{original}: Original tensile strength, $\sigma_{\text{self-healed}}$: Tensile strength after healing.

2.4.2.1. Morphology and Composition. Surface morphology and elemental distribution were examined using FESEM (FEI Quanta 250, 15 kV). Samples were fractured in liquid nitrogen and sputter-coated with gold. Chemical states of elements in GG were analyzed by XPS (Axis Ultra, Kratos, 225 W). FTIR spectra (Bruker IFS-25, 4000−400 cm^{-1}) were collected to confirm functional groups in PAM, GG, and their cross-linked networks. 13C NMR spectra were recorded using a Bruker Avance III 400 MHz spectrometer.

2.4.2.2. Water Content. Water content was calculated using

$$W_c\ (\%) = \frac{W_t - W_d}{W_t} \tag{2}$$

W_t: Wet mass, W_d: Dry mass after vacuum drying at 60 °C.

2.4.3. Ionic Conductivity and Electrochemical Testing. Ionic conductivity was measured using electrochemical impedance spectroscopy (EIS) over a frequency range of 0.1 Hz to 100 kHz. The conductivity was calculated using

$$\sigma = \frac{L}{A \times R_b} \tag{3}$$

where, L: Membrane thickness, A: Electrode area, R_b: Bulk resistance.

2.4.4. Capacitance Evaluation. Cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) measurements were performed over the potential range of 0.09−0.9 V at scan rates of 5−100 mV/s. Capacitance was calculated as

$$C = \frac{I \times \Delta t}{\Delta V \times m}, \quad C_s = 4 \times C \tag{4}$$

I: Discharge current, Δt: Discharge time, ΔV: Voltage range, m: Total mass of active material in both electrodes.

3. RESULTS AND DISCUSSION

Gellan gum (GG), a natural anionic polysaccharide produced by Pseudomonas elodea, has attracted growing attention in materials science due to its biocompatibility, biodegradability, nontoxicity, and cost-effectiveness. Traditionally, GG has been extensively applied in the food, pharmaceutical, and biomedical industries as a thickening, gelling, and stabilizing agent. Recently, however, its potential as a sustainable functional material for energy storage systems has been increasingly explored, particularly in the design of green and flexible gel polymer electrolytes (GPEs) for supercapacitors.

Despite its many advantages, GG-based hydrogels suffer from inherently poor mechanical properties, such as low tensile strength and poor elasticity, which significantly limit their application in practical, deformable energy devices. To address this limitation, polyacrylamide (PAM) -a synthetic hydrophilic polymer known for its high molecular weight, good flexibility, excellent film-forming ability, and water-absorption capacity -was incorporated to construct a double-network (DN) structure. The integration of PAM into the GG matrix aims to significantly reinforce the mechanical strength while preserving ionic transport properties.

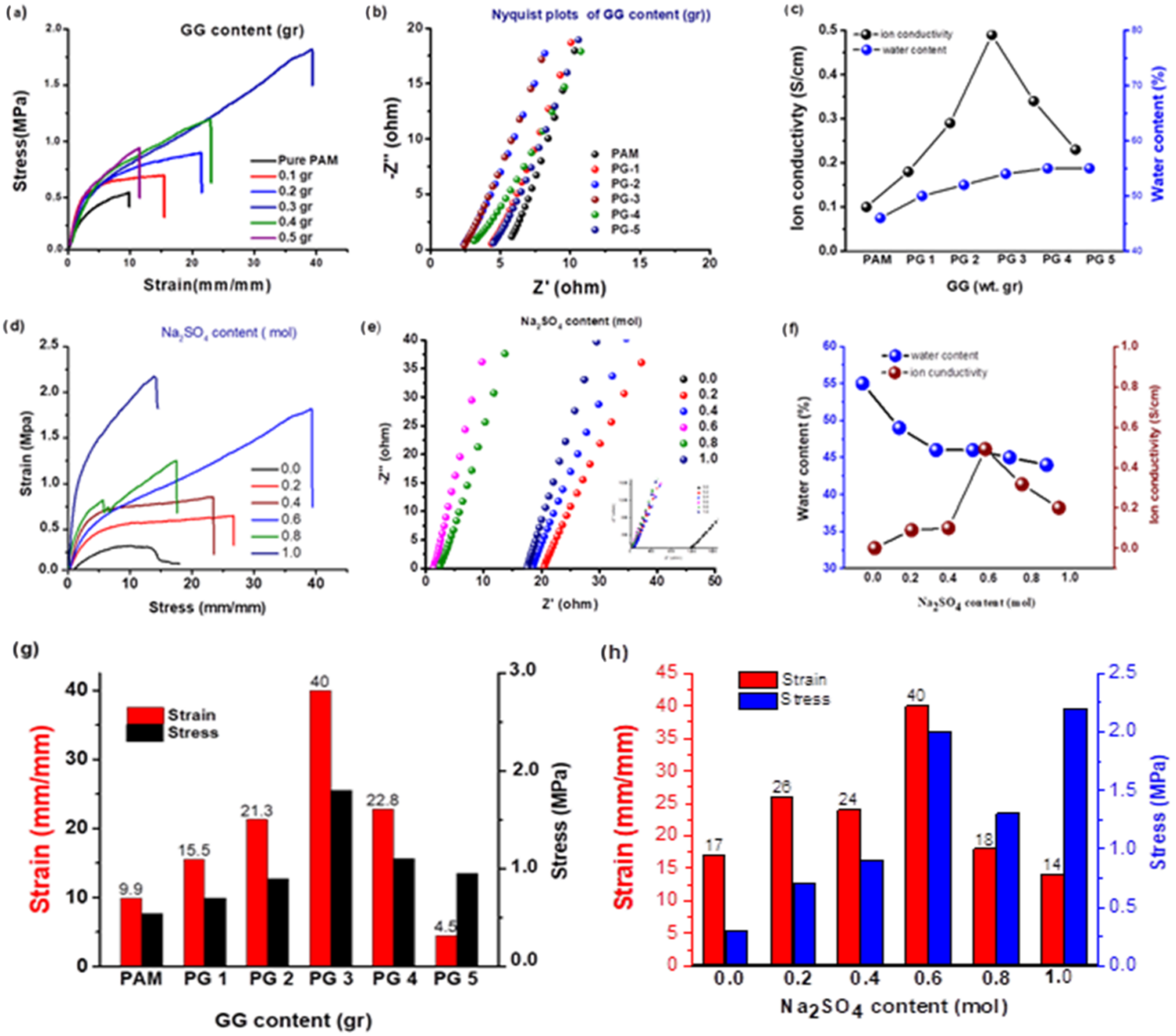

Figure 3. (a) Tensile stress−strain curves of PG DN GPEs with varying GG content; (b) Nyquist plots of PG DN GPEs with different GG concentrations; (c) effect of GG content on tensile strength and elongation at break of PG DN GPEs; (d) tensile stress−strain curves of PG DN GPEs with varying Na_2SO_4 content; (e) Nyquist plots of PG DN GPEs with different Na_2SO_4 concentrations; (f) effect of Na_2SO_4 content on tensile strength and elongation at break of PG DN GPEs; (g) effect of GG content on the tensile strength and elongation at break of PG DN GPEs; (h) effect of Na_2SO_4 content on the tensile strength and elongation at break of PG DN GPEs.

In this DN-GPE design, sodium sulfate (Na_2SO_4), a neutral, inexpensive, and stable inorganic salt, was selected as the ionic conducting medium. Na^+ ions play a dual role in this system. First, they facilitate ionic cross-linking among GG chains, thereby forming a physically cross-linked, stretchable first network. Second, they provide mobile charge carriers that enhance the ionic conductivity of the overall electrolyte matrix.

The second network is formed through free-radical polymerization of PAM, which provides a chemically cross-linked, robust framework that effectively bears mechanical load and enhances tensile properties. The combination of ionically cross-linked GG and chemically cross-linked PAM results in an intrinsically stretchable, tough, and self-healing GPE, capable of withstanding mechanical deformation and recovering from structural damage without external stimuli.

This synergistic DN configuration enables efficient energy dissipation and crack resistance, while maintaining high ionic conductivity -an essential characteristic for high-performance flexible supercapacitors. Moreover, the introduction of reversible physical interactions (e.g., hydrogen bonding and ionic coordination) contributes to the self-healing ability of the GPE, further extending its operational lifetime and structural reliability under repeated mechanical stress.

In this study, a "one-pot" synthesis approach commonly recognized in the literature as an efficient and convenient method was employed to prepare the double-network (DN) hydrogel electrolyte. This method involves a combination of thermal treatment and magnetic stirring, followed by UV-induced photopolymerization, enabling homogeneous dispersion of all components and efficient cross-linking within the gel matrix.

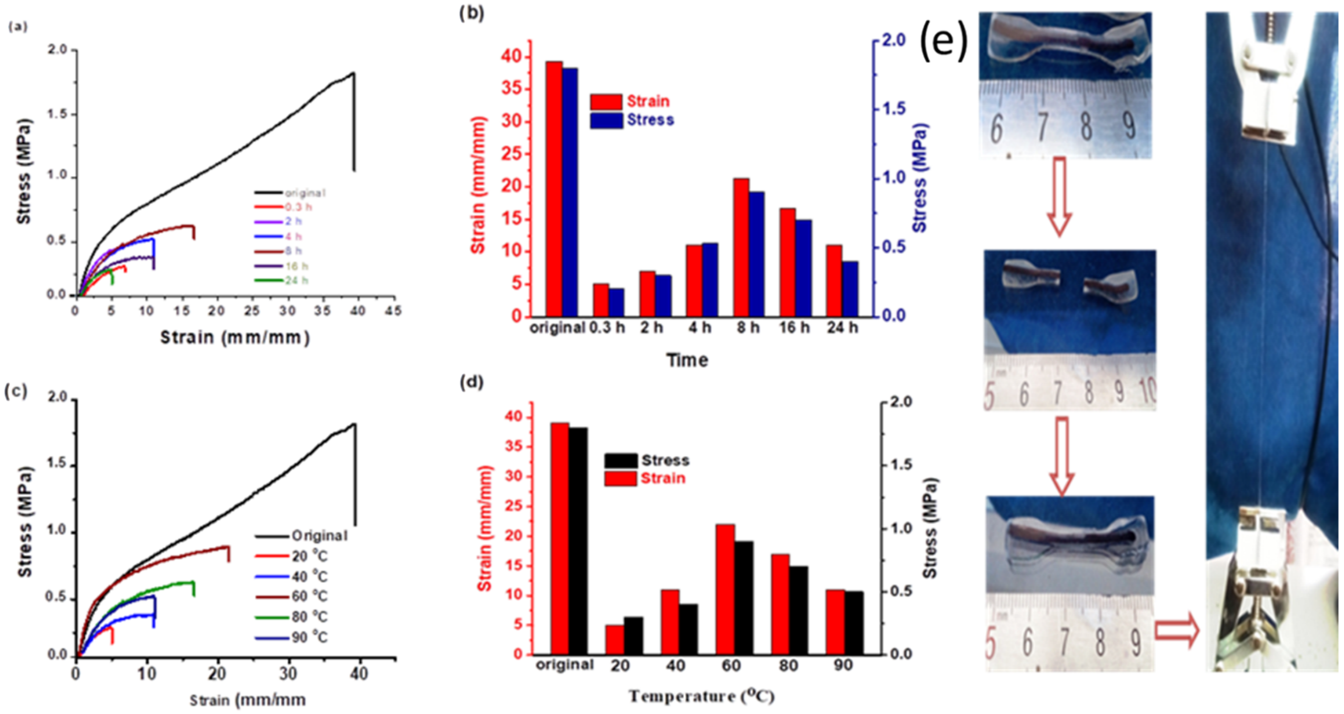

Figure 4. Self-healing test: Tensile strain−stress curves after healing different time (a) and temperature(c), tensile stress and elongation at break respectively (b,d), digital photo of self − healing test process(e).

Initially, the mechanical properties of the synthesized double-network (DN) gel polymer electrolytes (GPEs) were systematically investigated. To prepare DN-type self-healing GPEs with high ionic conductivity, various concentrations of gellan gum (GG) were incorporated into the formulation (denoted as PG DN GPE), while the contents of PAM and Na_2SO_4 were kept constant. As shown in Figure 3a,b, the tensile stress−strain behavior of pure PAM hydrogel and PG DN GPEs revealed a significant dependence on the GG concentration.

As the GG content was gradually increased from 0 to 5 g, the mechanical performance of the GPEs exhibited a nonlinear trend. The control sample composed solely of PAM (SN hydrogel) showed low mechanical strength, with an elongation at break of approximately 10 mm/mm and a tensile stress of 0.6 MPa. Meanwhile, the GG hydrogel cross-linked by Na^+ ions alone, without PAM, was structurally too weak to withstand the mechanical tester clamps.

Interestingly, the composite GPE with 3 g of GG (PG-3 DN GPE) demonstrated the highest mechanical strength, reaching up to 2 MPa approximately four times greater than that of the pure PAM hydrogel -and an elongation at break of nearly 400%, which slightly exceeded the extensibility of pure PAM. These findings confirm that the mechanical properties of the DN GPEs are strongly affected by the GG content.

However, further increasing the GG concentration beyond 3 g resulted in a noticeable decline in mechanical properties. This degradation is likely due to the increased viscosity of the GG/PAM mixture, which compromises homogeneity and entraps microbubbles within the hydrogel network during synthesis, thereby weakening its structural integrity.

In addition to mechanical performance, the ionic conductivity and water content of the GPEs also displayed a GG concentration-dependent trend. As the GG content increased from 0 to 5 g, the ionic conductivity improved from 0.1 to 0.29 S/cm, while the water content rose from 46% to 55% as calculated by eqs 2 and eq 3 (Figure 3c). This can be attributed to GG's highly hydrophilic nature and its ability to coordinate with ionic species, thereby enhancing both ion transport and water retention within the gel network.

Furthermore, the decreasing water content trend observed under increasing Na_2SO_4 concentrations (as illustrated in Figure 3c) provides additional evidence for the salting-out effect. This behavior leads to reduced swelling, promotes the formation of a denser polymer network, and contributes to enhanced mechanical rigidity as confirmed in Figure 3d. Together, these observations underline the interplay between ionic composition, hydration behavior, and mechanical properties in GPEs.

It is well-established that hydrogels without an ionic conducting medium exhibit negligible ionic conductivity. In this study, GG was doped into the PAM matrix and subsequently gelled via Na^+ cross-linking under neutral aqueous conditions. Hence, sodium sulfate (Na_2SO_4) plays a dual role: acting both as a physical cross-linker (via Na^+ ions) and as a mobile ion source, which is essential for maintaining high ionic conductivity.

To further optimize the GPE, various concentrations of Na_2SO_4 were investigated. As shown in Figure 3e,f, the ionic conductivity of the PG DN GPE increased sharply from 0.0005 S/cm to 0.29 S/cm when the Na_2SO_4 concentration was raised from 0 to 1 mol. This enhancement is due to the increased availability of free ions, which improve the charge transport throughout the network. Meanwhile, the equilibrium water content showed a decreasing trend with higher Na_2SO_4 concentrations. This may be explained by the denser gel structure resulting from enhanced cross-linking, which reduces free volume and limits water uptake.

Moreover, Na_2SO_4 concentration also influenced the mechanical strength of the GPEs. As the salt concentration

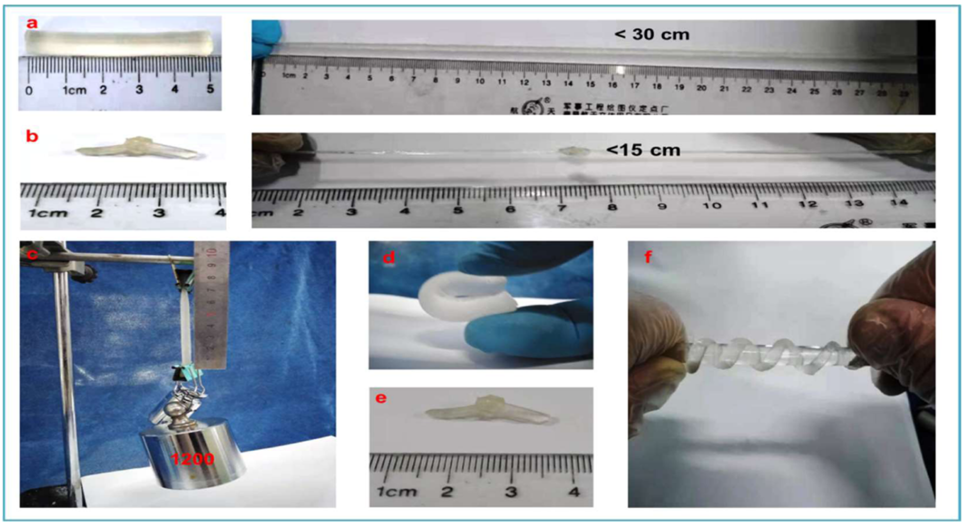

Figure 5. Digital photographs of the PG3 DN GPE stretchability, knot-stretchability, weight-loading (1200gr), bending, knotting and twisting respectively.

increased from 0 to 1 mol, the tensile stress improved significantly from 0.3 to 2.2 MPa while the elongation at break peaked at 40 mm/mm when Na_2SO_4 reached 0.6 mol (Figure 3d). The improved mechanical properties are likely due to stronger ionic bridging interactions between GG chains via Na^+ ions. In addition, the enhancement in tensile strength may also be attributed to the so-called "salt-out effect", particularly at higher Na_2SO_4 concentrations. As the ionic strength increases, water is expelled from the hydrogel matrix, which reduces its swelling capacity and promotes the formation of a denser and more compact polymer network. This structural densification enhances mechanical stiffness and limits excessive deformation. Similar salt-out-induced mechanical reinforcement effects have been reported in anionic polysaccharide-based hydrogels. However, at the highest salt concentration (1 mol), a decline in elongation at break (down to 15 mm/mm) was observed, potentially caused by excessive Na_2SO_4 aggregation, which may disrupt hydrogen bonding and introduce brittleness into the network.Considering both mechanical performance and ionic conductivity, the PG-3 DN GPE containing 0.6 mol of Na_2SO_4 was selected as the optimal composition for further investigation.

Considering the physical and chemical characteristics of gellan gum (GG) and polyacrylamide (PAM), both polymers possess the potential to exhibit intrinsic self-recovery capabilities under appropriate conditions. Interestingly, the PG-3 DN GPE demonstrated the ability to autonomously repair itself after experiencing mechanical damage, without the need for any external intervention. This property is particularly advantageous for prolonging the operational lifetime of the electrolyte in flexible and wearable supercapacitor applications.

To evaluate this behavior, a dumbbell-shaped PG-3 GPE sample was completely severed into two separate pieces and the cut surfaces were then rejoined by physical contact only, without the application of pressure, heat, or chemical stimulus, to assess its self-healing ability (Figure 4a−e). Upon cutting, hydrogen bonds at the fractured interfaces were disrupted. However, upon recontact, these hydrogen bonds tended to reform spontaneously, thereby facilitating structural reconstitution. This recombination of hydrogen bonds across the interface enabled the reconnected GPE to recover both its mechanical continuity and ionic conductivity, restoring its functional performance.

To quantitatively analyze the self-healing efficiency, the tensile properties of the PG-3 DN GPE before and after healing were measured at various healing times and temperatures. As illustrated in Figure 4, the tensile stress−strain curves of original and healed samples were compared for different healing durations (0.3, 2, 4, 8, 16, and 24 h) and temperatures (0, 20, 40, 60, 80, and 90 °C). The data clearly indicated that both tensile strength and elongation at break progressively increased with longer healing durations and higher healing temperatures.

The hydrogel sample healed at 60 °C for 8 h exhibited a tensile stress of 0.38 MPa and an elongation at break of approximately 420%, indicating a partial but not able recovery of mechanical performance. A maximum healing efficiency of 92.5% was achieved after 8 h of healing at 60 °C, conducted in a controlled water bath environment.

While the tensile strength remained lower than the pristine gel, the high elongation demonstrates efficient chain mobility and re-entanglement during the self-healing process.

It should be noted that the healing process was conducted in a water bath at 60 °C, effectively preventing significant water loss from the gel matrix. The decrease in healing efficiency observed after 8 h is therefore not related to water evaporation, but rather to the dynamic polymer network reaching a quasi-equilibrium state. Beyond this point, the formation of reversible hydrogen bonds and ionic interactions stabilizes, limiting further mechanical recovery. Additionally, extended exposure may cause localized structural rearrangement constraints and gradual saturation of ion diffusion-driven reorganization, reducing further chain mobility. These findings confirm that the DN GPE not only possesses inherent self-healing capability, but also maintains excellent mechanical integrity after damage, making it a promising electrolyte for flexible and self-healing energy storage systems.

At the molecular level, the self-healing mechanism of the DN-GPE operates via dynamic supramolecular interactions. Abundant hydroxyl (−OH) and carboxylate ($-COO^-$) groups in PAM and gellan gum establish reversible hydrogen bonds, which spontaneously reform upon contact after mechanical

Figure 6. Digital photographs of the PG3 DN GPE excellent self-healingability.

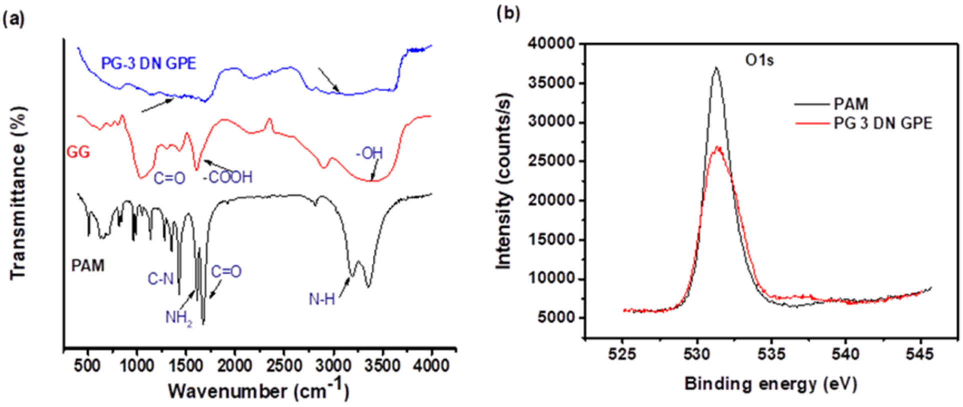

Figure 7. (a) FTIR and (b) XPS characterize of PG 3 DN GPE.

damage. Additionally, Na^+ ions facilitate ionic bridging between negatively charged sites, promoting chain alignment and hydrogen bond reformation. The hydrated environment and elevated temperatures further enhance polymer chain mobility, allowing chain segments to diffuse and re-entangle across the interface, restoring the network's integrity. This multimodal mechanism enables the DN-GPE to achieve efficient mechanical recovery and durability after damage, making it a promising electrolyte for flexible and self-healing energy storage systems.

As depicted in Figure 5, the as-prepared PG DN GPE displayed a uniform white appearance with a nontacky, self-supporting structure. The material was highly flexible, easily handled, and capable of maintaining its integrity under mechanical deformation without cracking or fracture.

Specifically, the PG-3 DN GPE was fabricated as a transparent, elastomeric thin film, exhibiting outstanding stretchability and mechanical resilience. The sample could undergo uniaxial and biaxial stretching, as well as bending, twisting, knotting, and even weight loading, without any sign of structural failure (Figure 5a–f).

In particular:

- The intact gel could be stretched up to 6 times its original length without breaking (Figure 5a).
- A knotted sample withstood strains as high as 600% while maintaining integrity (Figure 5b).
- The GPE could support a 1.2 kg weight (approximately 1200 g) without disconnection (Figure 5c).
- Furthermore, the material could be bent and rolled repeatedly without cracking or delamination (Figure 5d–f).

These results highlight the exceptional mechanical robustness and flexibility of the PG DN GPE, confirming its suitability for integration into next-generation flexible and deformable energy storage systems.

As a practical demonstration of its functional advantages, the outstanding self-healing property of the PG-3 DN GPE electrolyte was fully exploited. The hydrogel electrolyte was intentionally cut into multiple segments and then reassembled by placing the pieces in close contact, whereupon they autonomously reconnected into a continuous structure without the need for external force or adhesive.

To highlight the tailorability and design flexibility of the material, the reconnected segments were arranged to form the acronym "HPU" (representing Henan Polytechnic University), as illustrated in Figure 6. This example showcases the potential of PG-3 DN GPEs for developing custom-shaped, flexible, and self-healable energy storage devices. Such materials pave the way for next-generation wearable electronics and smart energy systems, where personalized layouts and modular assembly are essential.

To confirm the successful formation of the PG-3 DN GPE and to investigate its structural properties, multiple analytical techniques including X-ray diffraction (XRD), solid-state ^{13}C nuclear magnetic resonance (NMR), Fourier-transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) were employed. Among them, FTIR analysis was particularly useful in verifying the cross-linking interactions between polyacrylamide (PAM) and gellan gum (GG) in the DN network.

In the FTIR measurements, potassium bromide (KBr) was used as a matrix to ensure spectrum accuracy. This is because KBr does not absorb infrared radiation in the studied range and does not chemically interact with the sample, thereby eliminating background interference in the IR spectra.

As shown in Figure 7a, the FTIR spectrum of pure PAM exhibited characteristic bands at 3420 and 3194 cm^{-1}, corresponding to N–H stretching vibrations in the primary amide group. Additionally, bands at 1653 and 1616 cm^{-1} were attributed to C = O stretching and NH_2 bending vibrations, while the peak at 1420 cm^{-1}was associated with C–N stretching vibrations.[22]

In the spectrum of gellan gum (GG), a broad absorption band in the range of 3500–3200 cm^{-1} was observed, which corresponds to O–H stretching. Peaks at 1715 cm^{-1} and 1614

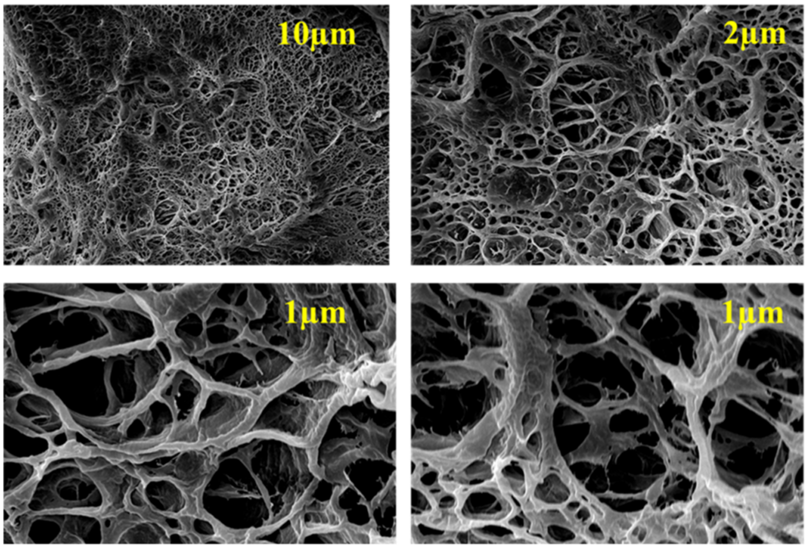

Figure 8. Surface morphology and internal microstructure of the PG-3 DN.

cm^{-1} were assigned to the C=O stretching of carboxylic acid and the asymmetric stretching of COO^{-}groups, respectively.[22,25,26] GG gel also showed a distinct broad peak at 3414 cm^{-1} for hydroxyl groups (−OH), and peaks at 2923 cm^{-1} and 2853 cm^{-1}, corresponding to asymmetric and symmetric C−H stretching of methylene groups. The C=O stretching vibration of the − COOH group was identified at 1708 cm^{-1}.[25]

In the case of the PG-3 DN GPE, noticeable spectral changes were observed. Specifically, the intensity of the C−O stretching band (originating from C−OH groups) was reduced compared to those of individual PAM and GG spectra. Conversely, an increase in the symmetric C−O stretching peak associated with the C−O−C structure was detected in the DN GPE, indicating intermolecular hydrogen bonding between the hydroxyl groups of GG and the methylene groups (−CH) of acrylamide monomers. These interactions likely promoted the grafting of PAM chains onto the GG backbone, leading to the formation of a well-integrated double network structure.

Furthermore, after the incorporation of Na_2SO_4, a sharp decrease in the characteristic absorption peaks of both PAM and GG was observed. This suggests that Na^+ ions not only contribute to ionic conductivity, but also act as ionic cross-linking bridges between the GG and PAM networks. These findings confirm the successful construction of a chemically and physically interconnected DN GPE framework, stabilized through both hydrogen bonding and Na^+-mediated ionic coordination.

The surface morphology and internal microstructure of the PG-3 DN gel polymer electrolyte samples were thoroughly examined using **scanning electron microscopy (SEM)** (Figure 8). SEM images revealed that the GPE exhibited a **porous and tunnel-like microstructure**, which facilitates fast and efficient ion transport throughout the material. Such architecture plays a crucial role in enhancing the **ionic conductivity** and, consequently, the **electrochemical performance** of the material.

In contrast to the structure of **pure gellan**, which presents a relatively dense wall morphology with fewer pores and a smoother surface—offering less favorable conditions for ion migration—the PG-3 DN sample demonstrated a **highly fibrous network** composed of **thin-walled pores** and **spider web-like interconnected structures**. This results in a more irregular and textured surface, which is beneficial for ion transport pathways.

Moreover, the SEM images confirmed that PAM and gellan polymers were uniformly distributed throughout the volume of the hydrogel, forming a tightly interconnected network—an essential feature of double-network (DN) polymer hydrogel architectures. This intricate, multibranched structure contributes not only to the improvement of mechanical properties and water absorption capacity, but also to the efficient immobilization and retention of Na^+ ions within the GPE matrix.

Thus, the unique microstructure of PG-3 DN GPE ensures not only high ionic conductivity and electrochemical activity, but also enhances the long-term operational stability, mechanical durability, and elasticity of the material. As a result, PG-3 DN GPE emerges as a high-performance and innovative material with great potential for application in advanced electrochemical devices, such as batteries and supercapacitors, and has drawn considerable scientific and technological interest.

4. CONCLUSIONS

In summary, we successfully developed a novel, self-healing, and highly stretchable gel polymer electrolyte (GPE) using a double-network (DN) strategy integrating gellan gum (GG) and polyacrylamide (PAM). The one-pot photopolymerization process yielded a PG-3 DN GPE that demonstrated superior mechanical robustness (tensile strength of 2.0 MPa and elongation of 400%), high ionic conductivity (0.29 S/cm), and autonomous healing efficiency exceeding 90% under mild conditions.

Structural analysis using FTIR, XPS, and SEM revealed the formation of an interconnected polymer matrix with porous morphology, which facilitated efficient ion transport and mechanical integrity. These properties, combined with environmental friendliness, processability, and biocompatibility, position the developed GPE as a viable candidate for next-generation wearable and flexible electrochemical energy storage devices.

Moreover, the integration of physically cross-linked GG and chemically cross-linked PAM, along with Na^+ ion coordination, introduces a new design paradigm in solid-state electrolyte engineering. Future research may focus on incorporating multifunctional additives or nanomaterials to further enhance thermal and electrochemical stability. The approach outlined in this work can be extended to a broad range of energy storage systems, including lithium-ion batteries, hybrid capacitors, and bioelectronic devices.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support from **Henan Polytechnic University** and **Namangan State Technical University** for providing laboratory resources. Special thanks are extended to **Professor Gang Qin** for his valuable guidance and support. We also thank our colleagues for their insightful suggestions and continuous encouragement throughout this research.

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