Thermogalvanic hydrogels for self-powered temperature monitoring in extreme environments†

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Thermogalvanic hydrogels have been highlighted in the design of flexible thermoelectric cells and sensors on account of their excellent physicochemical properties such as high thermal sensitivity, stretchability, and portability. However, the incident freezing and drying behaviors of hydrogels by using water solvent as the dispersion medium limit their scope of application greatly. Herein, a gel electrolyte-based thermogalvanic device with I⁻/I₃⁻ as a redox pair is fabricated, which shows a preferred temperature tolerance (−20 to 80 °C) and superior anti-drying capacity at reduced vapor pressure. These features stem from weakening the hydrogen bonds between water molecules by using a simple binary solvent strategy. Considering its decent thermogalvanic response, a gel-based temperature monitoring system was developed, which can be used as a comfortable electronic skin for human body monitoring. It could also be applied to build up a smart window system for self-powered monitoring of indoor or outdoor temperatures, even in extreme weather and climate events.

1 Introduction

Renewable energies are promising for mitigating the impact of fossil fuels and the urgency of the global energy crisis, as well as meeting the energy demand for generations to come.1−7 Low-grade heat, which can be obtained from industrial solar panels, geo-thermal reservoirs, and human bodies, is an attractive energy source due to its abundance and sustainability.8−10 Usually, the majority of this low-grade heat is wasted, which leads to a series of environmental problems.11−13 Fortunately, given the developments in the ambit of wearable electronics and e-skins, the growing need for self-powered energy supplies has attracted enhanced interest in energy harvesting from human beings or the environment.14−20

The most common method for utilizing low-grade heat is thermal–electric conversion.21 Traditional thermoelectric cells employing the Seebeck effect are mainly based on solid-state semiconductors or conducting polymers,22,23 with output voltages limited by the relatively low Seebeck coefficients. In addition, the vulnerability and high cost of thermoelectric materials and their complex production process are obstacles that restrict their applications.24,25 Therefore, thermogalvanic cells have received greater attention. In recent years, the performance of thermogalvanic cells has been continuously improved in low-cost waste heat utilization.26−31 However, device encapsulations are difficult due to the aqueous electrolytes used in thermocells. Inspired by the successful application of gel electrolytes in stretchable ionic

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conductors and solid-state electrochemical energy storage systems, we postulate that solid-state flexible gel electrolytes may allow for wearable applications of thermogalvanic energy devices. The traditional gel electrolyte thermal cells are subject to restriction in their application because the aqueous dispersion medium inevitably freezes at subzero temperatures due to strong hydrogen bonding. Polymer networks are restricted by decreased entropic elasticity, severely affecting the thermocell’s mechanical and thermoelectric properties. Therefore, there have only been rare occurrences where stretchable power sources can work in extreme environments, such as outdoors with extreme weather.

Herein, this work introduces a chaotropic agent to weaken the hydrogen bonds in the hydrogel, which not only enables entropic elasticity for polymer chains at subzero temperatures, but also improves the electrolyte solubility by employing H2O/GL (glycerol) as a binary solvent, thereby increasing the thermogalvanic potential. As a result, the fabricated gel thermocell is able to exhibit a wide operating temperature range of −20 to 80 °C as well as an excellent anti-drying capacity, which can potentially enable adaptation to harsh temperature environments. Based on its sensitive response to temperature variations, this self-powered temperature monitoring system has been demonstrated for actively monitoring abnormal ambient temperatures of both the human body and its surroundings.

2 Results and discussion

In general, common thermoelectric ions such as iron/ferricyanide [Fe(CN)64−/3−], cobalt(n/m) tris(bipyridyl), and iron(n/m) have been reported to have relatively high thermoelectric potentials. Here, we selected the redox couple of iodine/triiodide as the thermogalvanic ions due to their nontoxicity and environmental friendliness. For a solid-like polymer network, we chose PVA as the main monomer. Redox couples and other ions are also applicable for this purpose if they can facilitate stretchable networks and be well dispersed in the matrices. For a thermocell utilizing the redox couple of iodine, the reversible redox reaction is I− + I2 → I3− within a temperature gradient (Fig. 1a).

At the anode electrode, the oxidation reaction I3− → I− + e− is thermodynamically favorable due to the low temperature, where electrons are injected into the cold electrode, increasing its electrochemical potential and leading to a lower electrode potential. At the cathode electrode, the reduction reaction I− + e− → I3− is thermodynamically favorable due to the high temperature, with electrons being attracted to the hot electrode, decreasing its electrochemical potential and leading to a higher electrode potential. The oxidized iodine ions transfer to the low-temperature electrode via convection, diffusion, and migration, while the reduced iodine ions travel back to the high-temperature electrode, enabling a continuous cyclic reaction. Consequently, voltages are generated between the two electrodes under the temperature gradient in a quasi-continuous way.

Unfortunately, when the temperature drops below 0 °C, the strong hydrogen bonds between water molecules inevitably freeze the medium, severely reducing the mechanical properties of the polymer chains and limiting the entropy difference.

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**Fig. 1** The PVA/GL hydrogel thermocell functioning at subzero temperatures. (a) Electrochemical potential of charge diagrams and the corresponding voltage distribution of the reversible redox reaction I− + e− → I3−, where ΔE represents the electric potential difference. (b) Schematic diagram of the hydrogel thermocell containing crosslinked networks (PVA), GL, water and redox couple within a temperature gradient. (c) The tensile curves of the PVA/GL hydrogel in 25, 0 and −20 °C environments. Insets: Photographs of the hydrogel when bent, twisted, and stretched. Scale bar (1 cm). (d) SEM images of a PVA/GL hydrogel (i) and PVA hydrogel (ii) after freezing and dehydration, and (iii and iv) energy-dispersive spectra. Scale bar (5 μm).
of redox ions.\(^{39}\) To address this issue, we introduced an organic co-solvent GL (Fig. 1b). In the H\(_2\)O/GL binary solvent, GL molecules form a variety of molecular clusters with H\(_2\)O, disrupting the strong hydrogen bonds between water molecules and lowering the freezing point below \(-20\) °C. Meanwhile, without ice crystallization, the increased entropic elasticity allows the thermocells to be mechanically adaptable in extremely cold environments. The lower freezing point eliminates the undesirable effects on the entropy difference of the redox ions at low temperatures as much as possible. As shown in Fig. 1c, the hydrogel thermocell can be elongated by approximately 430% before breaking at 25 °C. It still maintains 200% elongation before breaking when the temperature decreases to \(-20\) °C. Aside from its increased mechanical adaptability at low temperatures, the mechanical properties of the PVA/GL gel are comparable to that of the unmodified PVA gel (Fig. S1a and b, ESI\(^\dagger\)), and there is no excessive loss of elasticity after repeated stretching and compressing (Fig. S1c and d, ESI\(^\dagger\)). The surface morphology is confirmed by scanning electron microscopy (SEM). Fig. 1d-i reveals the smooth surface of the PVA/GL hydrogel, while the PVA hydrogel is evidently porous (Fig. 1d-ii). The smooth surface of the PVA/GL hydrogel is due to the combination of GL molecules with water molecules, which makes the hydrogel less likely to lose water molecules. The abundant hydrophilic hydroxyl groups and carbon–carbon double bonds that can be seen in the chemical structure shown in Fig. S2 (ESI\(^\dagger\)) prove that the gel contains GL and PVA molecules. An energy-dispersive X-ray spectrometry (EDS) mapping analysis of elements I and K (shown in Fig. 1d-iii and iv) from a selected area confirms that iodine is dispersed on the PVA/GL gel frame network uniformly.

The efficiency of thermoelectric materials has been determined by the dimensionless figure of merit \(ZT = (Se^2\sigma/k)T\), where Se is the Seebeck coefficient, \(Se = -(V_h-V_c)/(T_h-T_c)\) = \(-2\sigma_{II}, V_h\) and \(V_c\) are the voltages of the hot and cold terminals, respectively, while \(T_h\) and \(T_c\) are the temperatures of the hot and cold terminals, respectively. \(\sigma\) is the electric conductivity, \(k\) is the thermal conductivity, and \(T\) is an average temperature of the hot and cold terminals of the cell. Therefore, the magnitude of the thermopower of the hydrogel thermocell in a temperature gradient depends strongly on Se, similar to semiconductive thermoelectrics. Hence, we compared the difference between the PVA/GL and PVA hydrogels in three aspects—using the Seebeck coefficients (Se), electrical conductivities (\(\sigma\)), and thermal conductivities (\(k\)).

In aqueous solutions, iodine monomers are only slightly soluble—however, the solubility is greatly increased in organic solvents. Therefore, in this work, the concentration of the redox couple was enhanced in the hydrogel containing binary solvents. In order to acquire the optimal Se, gels with different volume ratios of GL to water and different concentrations of iodine monomers were investigated. Fig. 2a shows the dependence of Se on the solvent ratio and iodine concentration, indicating that the optimal Se occurs at the GL volume ratio of 50% and I\(_2\) concentration of 0.08 M. In this work, unless otherwise stated, we chose the hydrogel thermocell with the largest Se for the following exploration. Fig. 2b shows the thermal voltage response of a single cell (with the electrode distance of 5 mm and radius of 5 mm) at various \(\Delta T\). The voltage of the PVA/GL thermocell is evidently much stronger than that of the PVA thermocell as \(\Delta T\) increases. The thermogalvanic Se of the PVA/GL and PVA thermocells are 0.63 and

![Fig. 2](image-url)  
**Fig. 2** Thermogalvanic performance of the independent PVA/GL and PVA gels. (a) Dependence of Se on the GL ratio and iodine concentration. (b and c) The open-circuit voltage and short-circuit current of a single cell at varying \(\Delta T\). Insets: Current response at \(\Delta T = 20^\circ\) C. (d) \(\sigma\) of the PVA/GL hydrogel at varying temperatures; the inset is \(\sigma\) of the PVA/GL and PVA gel near room temperature. (e) Frequency-dependent \(\sigma\) of the PVA/GL gel. (f) \(k\) of the gels at varying temperatures.
0.52 mV K⁻¹, respectively. Fig. 2c plots the current response of the PVA/GL and PVA thermocells as $\Delta T$ increases, demonstrating that the current increases linearly with the increasing $\Delta T$. At $\Delta T$ of 30 °C, both thermocells generate a steady current of nearly 15 μA, with the current curve of the PVA/GL gel thermocell at $\Delta T$ of 30 °C depicted in the inset of Fig. 2c. Due to the excellent quasi-solid feature of the gel, the gel components can be integrated both in parallel and in series to deliver a larger output. The output current and voltage of the integrated device, consisting of different numbers of cell units in parallel, is shown in Fig. S3a (ESI†). The current shows a linear increase with the increasing number of units, while the voltage remains relatively stable. The opposite is true for the output voltage and current of an integrated device with cells connected in series (Fig. S3c, ESI†). Fig. S3b and d (ESI†) show the output performance of 9 gel cells connected in parallel and series, with the output current and voltage reaching 130 μA and 160 mV, respectively, at $\Delta T$ of 30 °C.

The $\sigma$ of the optimized PVA/GL hydrogel was tested in a wide range of temperatures from −20 to 80 °C (Fig. 2d). The figure demonstrates that $\sigma$ is related to the hydrogel temperature, which increases as the temperature is elevated, with comparatively low values retained when the temperature falls below zero. For instance, $\sigma$ is just 0.06 mS cm⁻¹ at −20 °C, which is still considerable and much higher than that of solid-state LiPON electrolytes.43 Moreover, $\sigma$ increases more gradually above 0 °C and even more gradually above room temperature. The inset of Fig. 2d shows $\sigma$ of the PVA/GL and PVA gels at approximately room temperature. Evidently, $\sigma$ of the PVA/GL gel is slightly higher than that of PVA, and they both show a very small increase with the increasing temperature. Frequency-dependent $\sigma$ of the PVA/GL hydrogel is shown in Fig. 2e. The $\sigma$ was calculated by using the real portion of the impedance in the Nyquist plot of electrochemical impedance spectroscopy. The plot shows that at low frequencies, $\sigma$ is close to the values measured in Fig. 2d.

The $\kappa$ of the gels illustrated in Fig. 2f were measured by the transient steady-state method. At the same temperature, the $\kappa$ of the PVA/GL gel is slightly larger than that of the PVA gel. We infer that this discrepancy is due to the addition of organic solvents, which decreases the specific heat capacity of the solute and eventually leads to an increase in $\kappa$. An infrared image of the PVA/GL and PVA gels are shown in Fig. S4 (ESI†), demonstrating that the PVA/GL gel transfers heat slightly faster than the PVA gel. This negligible enhancement in $\kappa$ is acceptable due to the higher Se of the PVA/GL gel.

For most hydrogels, there are inevitable defects that seriously limit their application in daily life, such as icing up below 0 °C and dehydration at high temperatures. In this work, the prepared PVA/GL hydrogel exhibits an excellent anti-drying and anti-freezing property due to the presence of GL molecules.44 As shown in video 1, the PVA/GL hydrogel retains the desirable flexibility after being left at −20 °C for 24 h and can be easily bent, folded or even twisted. Conversely, the PVA hydrogel completely hardened under these conditions.

Based on the principle of reduced vapor pressure of GL molecules, the PVA/GL hydrogel also exhibits a considerable anti-drying property. To analyze this anti-drying property of the
PVA/GL hydrogel, the hydrogels with different GL ratios were compared with those without GL at room temperature (the control hydrogel size was 3.5 × 1.5 × 0.5 cm). The water loss of the hydrogels within 12 h was qualitatively evaluated using \( W_t/W_{t=0} \) (anti-drying property), where \( W_{t=0} \) is the initial mass of the gel and \( W_t \) is the mass at different times. As shown in Fig. 3a, the weight of the hydrogel without GL was only 0.48 of the original weight after 12 h, while the weight of the hydrogel with 45–65% GL ratio was more than 0.75, which means the anti-drying properties of the hydrogels were significantly improved with the addition of GL. Fig. 3b shows the weight change of the PVA/GL and PVA hydrogels after 12 h, which illustrates that the PVA/GL hydrogel has an improved anti-drying property. Furthermore, Fig. 3c shows that the PVA/GL gel achieves an even better anti-drying property than the PVA gel in the temperature range of −20 to 65 °C (although the performance is similar at −20 °C). As shown in Fig. 3d, the higher the temperature is, the greater the difference in the anti-drying property between the PVA/GL hydrogels and PVA hydrogels. This feature can be visualized in Fig. S5 (ESI†). Fig. S6 (ESI†) shows that at 85 °C, the PVA polymer chains reached the melting point in the PVA hydrogel, resulting in the collapse of the gel structure. However, the PVA/GL hydrogel maintained its structural integrity due to the increased melting point of the binary solvent. Therefore, the PVA/GL hydrogel possesses a superior tolerance to extreme temperatures.

When one terminal of the gel thermocell was set to 30 °C, the output power/current–voltage curves were recorded at varying ΔT. Even in temperatures well above room temperature or below 0 °C (even to −20 °C), the gel thermocell shows a parabolic power–voltage relationship and linear current–voltage curve. Above room temperature, the thermocell has a short-circuit current of nearly 5 μA, an open-circuit voltage of about 6 mV, and a maximum power of about 6.6 mW at a ΔT of 10 °C (Fig. 4a). When the ΔT increases to 50 °C, the maximum power improves to about 166.5 mW with the corresponding voltage and current outputs shown in Fig. S7a and b (ESI†), respectively. While maintained in an environment below 0 °C, the current of the PVA/GL hydrogel decreases due to an extremely rapid decrease of σ in low temperature environments (Fig. 4b). However, even when the cold terminal temperature decreases to −20 °C, the maximum output of the PVA/GL hydrogel thermocouple is still more desirable, at about 29.3 mW, and the voltage and current outputs are presented in Fig. S7c and d (ESI†), respectively. The significant voltage and current outputs of the PVA/GL hydrogel under extreme conditions confirm that we have designed a PVA/GL hydrogel thermocouple with a significantly widened operating temperature range compared to ordinary hydrogel devices.

Due to its sensitive response to varying temperature, the thermogalvanic gel can not only collect low-grade heat, but is also capable of self-powered monitoring of ambient temperature by converting the temperature change into electronic signals. Given the widespread use of wearable sensors in healthcare monitoring, our gel patch can be used as a skin-like patch to monitor the ambient temperature. Compared to conventional clinical diagnosis that depends on expensive and bulky instruments, wearable sensors could realize real-time and continuous monitoring of health-related signals in a user-friendly way. In addition to monitoring health-related biomarkers, such as biochemical molecules, it is also possible to monitor external influences on an individual’s health.

![Fig. 4](https://example.com/fig4.png)

**Fig. 4** Thermogalvanic performance of the PVA/GL hydrogel thermocell. (a) Power/current–voltage curves for the PVA/GL gel thermocell at varying ΔT (the cold terminal is set to \( T = 30 \) °C). (b) Power/current–voltage curves for the PVA/GL gel thermocell at varying ΔT (the hot terminal is set to \( T = 30 \) °C).
As shown in Fig. 5a–c, a skin-like thermogalvanic patch was fabricated using the PVA/GL gel. This patch has clinical applications, such as functioning as a comfortable electronic skin for an individual with loss of temperature sensation. Since human body temperature is relatively constant and the patch’s output depends on the $\Delta T$ between the two ends of the PVA/GL gel, the device can detect and display the ambient temperature on a smartphone in real time to warn of possible scalding or frostbite. Fig. 5d illustrates the relationship between the output current and the temperature of the object in contact with the patch, showing that the current decreases from positive to negative when the temperature varies in the range of $-10$ to $75^\circ C$. As demonstrated in Movies 2 and 3 (ESI†), when a cold or hot object touches the gel patch worn on the back of the hand, the real-time ambient temperature is presented. Fig. 5e and f shows that the temperature can...
be accurately tracked when the device touches either a cold or hot object. Via an application interface, the real-time temperature and long-term temperature monitoring can be displayed on a smartphone.

To further explore the active temperature monitoring, a smart window was constructed by embedding a tiny PVA/GL hydrogel that maintains its function at ~20 °C. The fabrication process of the hydrogel-based window (H-window) is illustrated in Fig. S8 (ESI†). Due to the negligible size of the implanted hydrogel, the window can operate normally, as illustrated in Fig. 6a. The illustration shows that the hydrogel can generate a voltage signal that responds according to the outdoor temperature, assuming that the indoor temperature is relatively constant. Fig. 6b reveals that the output voltage rises linearly with a sensitivity of 0.41 mV K⁻¹ as the outdoor temperature continuously decreases. The inset of Fig. 6b shows a photograph of a constructed H-window prototype. In this practical application, the output voltage signal and ΔT of the H-window over the course of 24 h are plotted in Fig. 6c. The voltage curve shows almost the exact same waveform as the ΔT, indicating that the output voltage can accurately track the outdoor temperature. We evaluated the time required for the H-window to achieve the steady state and found that it needed less than 35 s at ΔT of 10, 15, and 20 °C (Fig. 6d). Based on this, two other simulated scenarios are demonstrated below. The temperature inside conventional refrigeration storage is generally maintained at around ~18 °C. We can utilize this H-window to track the ΔT between the inside temperature and the outside temperature, which determines whether the refrigeration storage is operating normally according to the generated voltage signal. If the voltage exceeds ~8 mV, it indicates that the inside temperature of the refrigeration storage has risen above 0 °C (supposing that the outdoor temperature is keep stable at about 20 °C), leading to a warning being issued (Fig. 6e). The indoor–outdoor temperature difference changes as shown in the infrared schematic of Fig. S9a (ESI†). Furthermore, the H-window can also track the indoor temperature in daily life. If the induced voltage is more than 8 mV, it implies that the indoor temperature is abnormally high, and a fire alarm can be activated (Fig. 6f). Overall, the H-window can be widely used for self-powered temperature monitoring in various scenarios. The indoor–outdoor temperature difference changes as shown in the infrared schematic of Fig. S9b (ESI†).

3 Conclusions

To summarize, we designed an adaptable and stretchable PVA/GL hydrogel thermocell utilizing the $\Gamma^-/I_3^-$ redox pair for self-powered temperature monitoring in extreme environments. It holds a collection of compelling features, including satisfactory thermogalvanic, antifreezing and antidrying properties. It could not only resist freezing even at ~20 °C, but also shows an enhanced water-retaining capability. With a wide operating temperature range, the hydrogel thermocell represents a solid step towards practical self-powered temperature monitoring.

4 Experimental section

Materials

PVA (molecular weight 126 000 to 146 000, 98 to 99% hydrolyzed) was purchased from Shanghai Macklin Biochemical Technology Co. Ltd. Deionized water was purified using Milli-Q Direct 8 ultrapure water system (Millipore, Billerica, MA), with a minimum resistivity of 18.2 MΩ cm. GL (glycerol) was purchased from General Reagent. All chemicals were used without further purification.

Preparation of PVA/GL hydrogels

First, PVA (2 g) powder was dissolved into a mixture of 10 ml distilled water and 10 ml GL at 105 °C with stirring for 1 h to create solution 1. Then, $I_2$ (0.25 g) and KI (1 g) were added to 5 ml of the mixture of water and GL stirred at 60 °C for 30 minutes to create solution 2. Solution 2 was mixed with solution 1 and stirred for 20 minutes. After mixing and defoaming, the PVA/GL solution was poured into a mold, frozen at ~20 °C for 24 h, then thawed at room temperature for 12 h to fabricate the hydrogels.

Fabrication of the electronic skin gel patch and H-window

The PVA/GL hydrogel was prepared according to the above method and formed into a rectangular block of 3.5 × 1.5 × 0.5 cm. The top and bottom sides were covered with electrodes and wires, and the hydrogel was fixed to the polyimide film substrate with PU tape (a kind of insulating tape). Using a laser cutter, a 3 × 3 cm pit was carved out of the middle of a square piece of glass. After the prepared PVA/GL gel was embedded in the glass, electrodes and wires were implanted on both sides of the gel. Finally, a piece of 1 mm thick glass was placed on each side of the hydrogel and secured with PET glue.

Conflicts of interest

There are no conflicts to declare.

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References
