

# Temperature-resistant hydrogel wearable sensors and thermoelectric devices

by

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### **Author's Declaration**

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

## **Abstract**

With the rapid advancements in biosensing and healthcare technology, traditional polymer and semiconductor sensors and electronic devices are increasingly unable to meet people's needs. As researchers delve deeper into the study of quasi-solid and flexible materials, hydrogel materials have gradually gained prominence. Hydrogels, characterized by their high flexibility, elasticity, and biocompatibility, have become one of the preferred materials for wearable, flexible sensors, and electronic devices. Furthermore, their promising thermoelectric properties and environmental friendliness make them highly suitable materials for quasi-solid thermoelectric devices. However, hydrogels still face challenges in terms of poor temperature resistance in cold and hot region, limiting their application across a wide temperature range. In this thesis, hydrogels with enhanced mechanical performance and conductivity, specifically PVA/TA/Chitin hydrogels, were synthesized. The introduction of an ionic liquid was used to improve the low-temperature resistance of these hydrogels, enabling their application as wearable, flexible sensors in low-temperature environments. Additionally, gelatin-based hydrogel thermoelectric cells were synthesized. Through the introduction and selection of soluble ions, the thermoelectric performance and heat resistance of these hydrogel thermoelectric cells were enhanced, potentially facilitating their use in high-temperature applications.

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## Chapter 1. Introduction, literature review and outline of thesis

### 1.1 Hydrogel

#### 1.1.1 Overview

Hydrogel is a viscoelastic material with a 3D polymer network, as shown in **Figure 1.1**. Compared with traditional elastomer materials, it contains a large amount of water, similar to the water content of natural soft tissues. So, it can integrate tensile property <sup>[1-6]</sup>, electrical conductivity <sup>[7-12]</sup> and even self-healing <sup>[13-20]</sup>, and its performance can be improved through physical or chemical cross-linking <sup>[21-25]</sup>. However, it is still a great challenge to prepare hydrogels with good mechanical properties, electrical conductivity, strain sensitivity, and self-healing properties <sup>[26-30]</sup>.

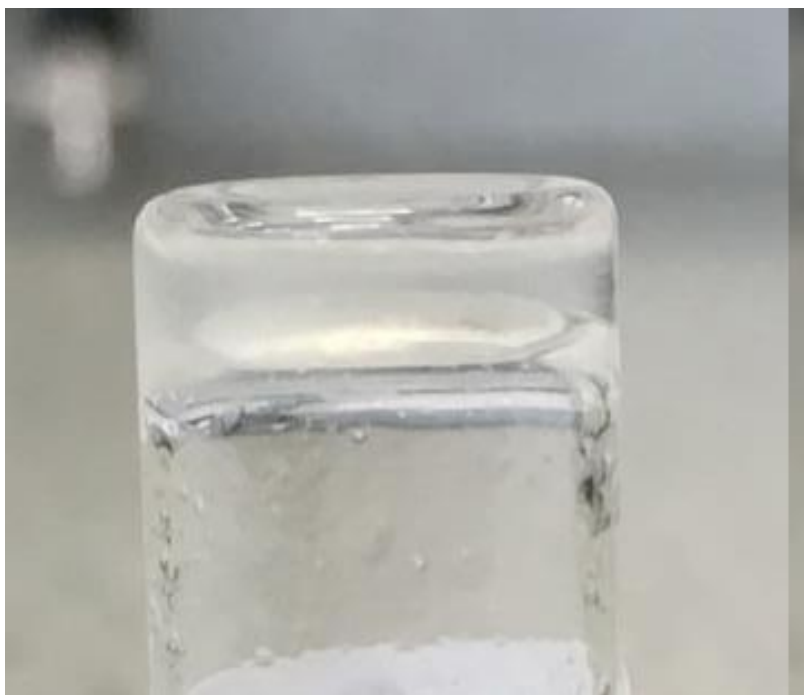


**Figure 1.1** Picture of hydrogel <sup>[31]</sup>.

Hydrogel polymers can be bound together by crosslinking, which is broadly categorized into two types: physical hydrogels and chemical hydrogels. Chemical hydrogels contain covalent crosslinks, while physical hydrogels have non-covalent bonds. Chemical hydrogels can form strong reversible or irreversible gels due to their covalent bonds. Some chemical hydrogels with reversible covalent crosslinks, like thiol-polymer hydrogels, are non-toxic and used in various pharmaceutical products. Physical hydrogels, on the other hand, are highly biocompatible, non-

toxic, and can be easily reversed by changing external stimuli such as pH, ion concentration, or temperature, and are also used in biomedical applications. Physical crosslinking involves hydrogen bonding, hydrophobic interactions, and entanglement of polymer chains, which generates "reversible" hydrogels. Chemical crosslinking, on the other hand, involves covalent bonds between polymer chains, which generates "permanent" hydrogels. Hydrogels are prepared by using a variety of polymer materials. According to their sources, they can be widely divided into two categories: natural polymers and synthetic polymers. Natural polymers used to prepare hydrogels include hyaluronic acid, chitosan, heparin, alginate, gelatin and silk protein. Some common synthetic polymers include polyvinyl alcohol, polyethylene glycol, sodium polyacrylate, acrylic polymers, and their copolymers. Although natural hydrogels are usually non-toxic and have many advantages in the medical field, such as biocompatibility, biodegradability, anti biological infection/antifungal performance, and improvement and regeneration of adjacent tissues, their stability and strength are generally significantly lower than those of synthetic hydrogels. Some synthetic hydrogels, such as polyethylene glycol (PEG), polyacrylates, and polyvinylpyrrolidone (PVP), are also used for medical applications.

### **1.1.2 PVA hydrogel**

Polyvinyl alcohol (PVA) is a non-toxic and widely used hydrophilic polymer that has gained significant attention in hydrogel research. PVA hydrogels are typically prepared through either chemical or physical methods.

Chemical crosslinking involves the use of multifunctional aldehyde molecules and radiation techniques; however, this method may lead to adverse reactions and interactions with other components.

On the other hand, physically crosslinked PVA hydrogels are preferred for biologically related applications due to their high purity and ease of gelation under mild conditions. In 1975, Peppas and his team successfully developed physically crosslinked PVA hydrogels through repeated freeze-thaw cycles, which resulted in phase separation and crystallization.<sup>[32]</sup> Since then, many other research groups have conducted studies on these hydrogels.

The key advantages of physically crosslinked hydrogels are their easy customization of properties, ultra-purity, biocompatibility, and high mechanical strength. Therefore, their popularity has grown exponentially since their discovery.

### 1.1.3 Gelatin hydrogel

Gelatin hydrogel is a material that has gained attention in the biomedical field due to its unique properties such as biocompatibility, solubility, low immunogenicity, low cytotoxicity, and ease of access <sup>[33]</sup>. Gelatin has a structure that closely resembles the natural extracellular matrix (ECM) <sup>[34]</sup>, making it an ideal material for *in vitro* cell culture. It contains arginine-glycine-aspartate (RGD) peptide sequences and matrix metalloproteinase (MMP)-degradable motifs, which promote cell growth and enzymatic degradation within cells. <sup>[35]</sup> In this thesis, gelatin is used in the manufacturing of hydrogel thermoelectric cells.

## 1.2 Wearable Sensor

### 1.2.1 Development of Wearable Sensor

A wearable sensor is a device that can continuously monitor an individual's biological characteristics, detecting small physiological changes over time. The first generation of wearable devices focused on biophysical monitoring, tracking physical activity, heart rate, or body temperature. For instance, in the 1960s, aerospace technology made it necessary to monitor the physical condition of astronauts in extreme environments. **Figure 1.2** depicts the Apollo Spaceflight Biomedical Sensors, which allowed for the continuous monitoring of astronauts' electrocardiogram, respiration, and body temperature.

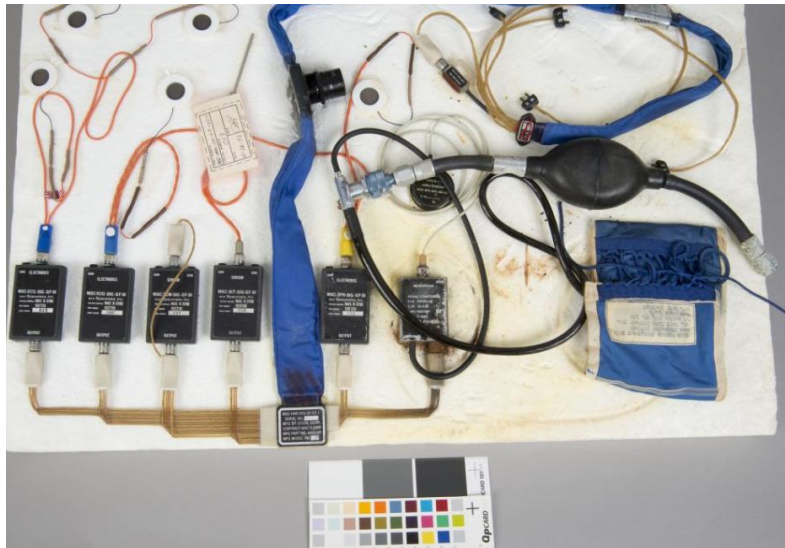


**Figure 1.2** Wearable sensors for the Apollo Space Program <sup>[36]</sup>.

The successful applications of the first-generation wearable devices as **Figure 1.2** have established a robust groundwork for the advancement of wearable sensor monitoring systems. The second-generation wearable devices utilize biometric components to convert specific actions and the presence of specific biochemical substances into signals, which are used to detect diseases and monitor human body health. In addition to the detection function, wearable devices also need excellent flexibility and resilience. Wearable sensor materials include natural materials, inorganic materials, polymers, and hydrogels <sup>[36]</sup>. Natural materials include cotton, wool, etc., which have good mechanical strength and flexibility. Inorganic materials include metal, semiconductor, and nanomaterials, which have good conductivity. Synthetic polymers have strong plasticity, while hydrogels have good biocompatibility.

### 1.2.2 Applications of Hydrogel-based Sensors

Biocompatible, flexible, and conductive hydrogels have always been a popular material for wearable flexible sensors. Recently, researchers have made efforts in different sensing system of hydrogel sensors. The hydrogel sensors can be used as wearable pressure sensors, temperature sensors, and biomolecular sensors. Zhang *et al* <sup>[35]</sup> added phytic acid (PA) into PVA (poly (vinyl alcohol)) hydrogel systems by freeze-thaw cycle, yielding conductive PVA-PA hydrogel wearable sensors that can monitor human motions and health conditions. The PVA-PA hydrogel has a strain of about 1100%, a good conductivity of 1.34k $\Omega$  cm, a high transparency of about 95%. Wu *et al* <sup>[37]</sup> designed a thin-film sandwich structure (TFSS) hydrogel-based wearable sensor to detect the surface temperature of human skin. The TFSS hydrogel-based wearable sensor has good thermal sensitivity of 24.54%/°C, a broad detection ranges from -28 to 95.3°C <sup>[37]</sup>, and high stability. Liang *et al* <sup>[38]</sup> reported a high performance, flexible and low-cost polyacrylamide-based double network hydrogels as wearable humidity sensors. The sensors have a maximum sensitivity of 13,462.1%/RH. <sup>[38]</sup> In conclusion, hydrogel-based wearable sensors have potential applications in different fields, and they have broad development prospects in the future.

Many polymers are used to fabricate hydrogel-based sensors. The chemically cross-linked 3D network structure of these sensors is formed molecular interactions such as covalent bonds or non-covalent interactions <sup>[39]</sup>. The polymers are used to improve mechanical properties and endow the hydrogel with various properties based on its own properties, such as stimulus responsiveness <sup>[40]</sup>, chemical detection <sup>[41][42]</sup>, conducting <sup>[43][44]</sup>, and self-healing <sup>[45-48]</sup> properties. Synthetic polymers such as polyacrylamide (PAM), polyvinyl imidazole (PVI), poly(vinyl

alcohol) (PVA), polyethylene glycol (PEG), and polyvinyl pyrrolidone (PVP) are also widely used in hydrogel sensors <sup>[49]</sup>.

Natural polymers, including cellulose, starch, chitosan, proteins, and their derivatives, are also used in hydrogel sensors. Due to the different organic groups of the polymers, they have unique chemical or physical properties, thus they have better prospects for applications due to their biocompatibility, environmental responsiveness, and bioadhesive properties, making them suitable for sensing <sup>[50]</sup>.

Cellulose, one of the most abundant renewable materials, has been widely used in industries such as papermaking, packaging, food, textiles, and biomedicine. It is hydrophilic but insoluble in water and most common solvents due to strong hydrogen bonds between cellulose molecular chains. In recent years, cellulose has garnered attention in the form of nanocellulose, such as cellulose nanofibers (CNF) and cellulose nanocrystals (CNC), for mechanical properties enhancement in hydrogels. They exhibit a very high aspect ratio and high moisture absorption, wetting, and renewability. CNF and CNC consist of  $\beta$  (1-4) D-glucose units with a semi-crystalline structure and demonstrate impressive mechanical properties. They can be chemically modified to adjust surface chemistry and reactivity. The improvement in mechanical strength holds significant potential for cellulose-based strain sensors. It has been reported that the combination of CNF and PVA in hydrogel sensors is used to synthesize transparent, stretchable, and rapidly self-repairing hydrogel sensors <sup>[51]</sup>. A biodegradable resistive pressure sensor has been manufactured using cellulose fibers (non-conductive) and conductive multi-walled carbon nanotubes (MWCNT), where MWCNT provides conductivity. <sup>[52]</sup> Cellulose fibers impart flexibility and shape recovery due to their elastic properties, as shown in **Figure 1.3** <sup>[51]</sup>.

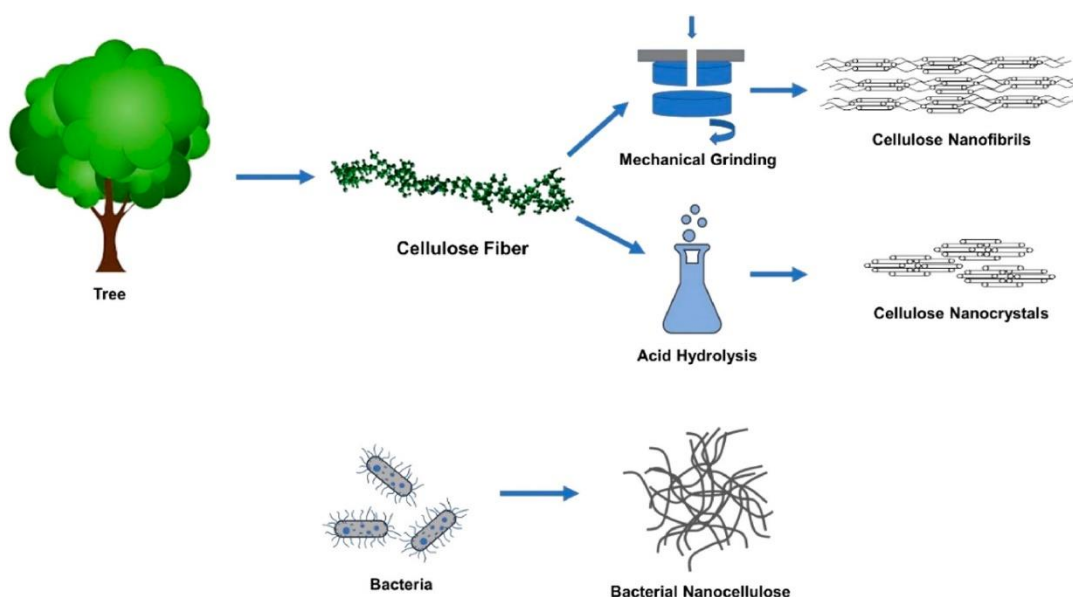


**Figure 1.3** Schematic simplified representations of different types of nanocelluloses <sup>[51]</sup>. Adaption from ACS applied biomaterials, Copyright of American chemical society.

Bacterial cellulose is one of the best natural celluloses. Because bacterial cellulose has high crystallinity, high mechanical properties and its high durability it is very suitable for reinforcing hydrogels <sup>[53]</sup>. The pure bacterial cellulose without lignin, hemicellulose, and pectin, makes it suitable for fabricating medical hydrogel sensors <sup>[54]</sup>.

Reinforcement agents can be functionalized and incorporated into sensor compositions. Zhou and Wang *et al* used cellulose hydrogels as a new material for fluorescence composite materials for nitrite detection <sup>[55]</sup>. In recent years, cellulose nanocrystals (CNC) have been widely used in hydrogel sensors due to their excellent mechanical performance and transparency. The CNC/alginate hydrogel of gold nanoparticle clusters with bovine serum albumin was used to detect heavy metal ions. <sup>[56]</sup> The hydrogel that is combined with CNC, PVA, and PVP has been reported as a wearable sensor with excellent conductivity, self-healing properties, and flexibility. <sup>[57]</sup> Celia *et al.* prepared a fluorescence hydrogel based on S, N co-doped graphene quantum dots (QDs) to enhance the detection sensitivity of triclosan <sup>[58]</sup>. Hiratani *et al.* reported that the shear orientation of CNC in hydrogels responds to ion concentration through significant color changes in a salt solution, which can be used as a pressure sensor <sup>[59]</sup>. A wearable sensor based on bacterial cellulose (BC), PVA, sodium alginate, modified carbon nanotubes, and carbon

black was prepared for strain sensing. <sup>[60]</sup>

Carboxymethyl cellulose (CMC) is a cellulose derivative widely used in industry for thickening, dispersing, or stabilizing formulations. Hydrogels made from CMC can be photo-tuned to provide regional swelling and shape-changing capabilities. <sup>[61]</sup> Regional tuning allows for innovative electronic circuit development, applicable in sensor development. The addition of CMC to hydrogels can stabilize insoluble compounds, resulting in a uniform and highly absorbent hydrogel suitable for humidity sensors and actuator applications <sup>[62]</sup>. For example, Barras *et al.* printed conductive flexible CMC-based hydrogel composite materials on paper for humidity sensing applications <sup>[63]</sup>. It has been reported that the mechanical strength of CMC-based hydrogels for strain sensors is significantly improved by introducing cations as cross-linking agents.

Starch is a major natural polysaccharide composed of several glucose molecules connected by  $\alpha$ -D-(1-4) or  $\alpha$ -D-(1-6) bonds, with numerous hydroxyl groups, making it suitable for hydrogel preparation or chemical modification <sup>[64]</sup>. It has excellent water-swelling capacity and has been used for dye adsorption, heavy metal capture, and water-fertilizer monitoring in agriculture <sup>[65]</sup>. Starch-based hydrogels have been reported as surface plasmon resonance (SPR) sensors for hydrogen peroxide detection, stabilizing silver nanoparticles. Starch-polydimethylsiloxane (PDMS) composite materials are hydrogel-based elastomers with good mechanical strength and conductivity <sup>[66]</sup>.

Chitosan is a positively charged polysaccharide containing N-acetyl-D-glucosamine and D-glucosamine residues connected by  $\beta$ -(1-4)-glycosidic bonds. It is obtained by 72% deacetylation of acetylated amines on the C<sub>2</sub>-carbon of chitin in shrimp shells <sup>[67]</sup>. Its biodegradability, biocompatibility, and antibacterial activity have attracted considerable attention in commercial and potential biomedical applications. Chitosan has been shown to be highly permeable to water and anions, adhering to negatively charged surfaces, aggregating with polyanionic compounds, chelating metal cations, and has been used as a biosensor. Chitosan hydrogels can be prepared by cross-linking or forming composite materials with other cross-linked polymers <sup>[68]</sup>. Typically, cross-linking of chitosan can be achieved covalently, through ionic hydrogels, or through physical cross-linking via freeze-thaw processes. The ionization degree of chitosan chains (chitosan-NH<sub>2</sub>/chitosan-NH<sub>3</sub><sup>+</sup>) increases under acidic conditions. The amino and hydroxyl groups of chitosan chains can be chemically modified to immobilize sensing compounds such as enzymes, conductive polymers, or stimulus-responsive polymers. Chitosan hydrogels have been reported in the detection of heavy metal ions due to their excellent absorbent properties. Another method for synthesizing sensors using chitosan hydrogels is by immobilizing chemicals in large molecules, such as phenols. Recently, Xiong

*et al.* prepared a highly selective fluorescence chitosan hydrogel for detecting nitrophenol and 2,4,6-trinitrophenol [69]. It is feasible to detect bacteria or enzymes by fixing them in chitosan hydrogels through chemical modification. Liu *et al.* reported an electrochemical sensor using silver nanoparticle-doped chitosan hydrogels for trichloroacetic acid detection [70]. The silver nanoparticle/chitosan hydrogel system has been developed into an SPR-based trichloroacetic acid sensor. Fu *et al.* studied the incorporation of Ag ions into chitosan-based hydrogels as an electrochemical sensing platform for antioxidant screening [71]. Chitosan hydrogels can be modified to obtain high-strength, flexible hydrogels for strain sensing. These double-network nanocomposite hydrogels exhibit flexibility, self-adhesion, and strain sensitivity, as demonstrated by Ismail *et al.*, who used a polyvinyl alcohol/chitosan hydrogel strain sensor to prepare artificial muscles [72].

PVA, PEG, and PAM have good mechanical properties, excellent flexibility, and controllable molecular structures, making them suitable for different types of sensors. PVA is a polymer utilized for its unique mechanical properties, biocompatibility, and biodegradability [73]. Its abundant hydroxyl groups allow for chemical modification of PVA polymer chains. Additionally, PVA cross-linking can be achieved through either chemical or physical means. Due to excellent solubility and ultra-high absorbance, PVA has been used in humidity sensors [74]. Besides humidity, PVA-based hydrogels have been reported for pH and metal cation sensing. In metal cation sensors, photonic crystal sensors composed of PVA-based hydrogels have been used for heavy metal detection [75]. It has been reported that PVA hydrogels can be used as glucose sensors. The mechanical strength and flexibility of PVA hydrogels have been enhanced for synthesizing pressure and strain sensors for motion detection [76].

PEG has various applications as sensors, especially biomedical applications, due to its good mechanical properties and biocompatibility. For decades, researchers have been exploring the potential of using PEG for hydrogels [77]. Like PVA, PEG hydrogels have been used for glucose detection and chemical sensing, with research focusing on PEG hydrogel biosensing conducted for several decades [78].

Similar to PVA and PEG, PAM hydrogels also have many applications as biosensors due to their excellent biocompatibility and well-defined protocols. Sun *et al.* developed PAM double-network hydrogels with good mechanical performance, flexibility, and sensitivity, which can be used as flexible strain sensors [79]. Sensors based on PAM hydrogels that are used as pressure sensors have been further developed and applied in wearable devices [80]. Hou *et al.* developed an injectable polysaccharide/PAM ion hydrogel system for high-performance strain sensors [81]. PAM hydrogels have also been used as glucose or pH sensors by tracking ion intensity based on photonic crystals [82]. Besides photonic crystal sensors, PAM hydrogels fixed with tyrosinase

can be combined with SPR devices for detecting phenolic compounds <sup>[83]</sup>. It has also been reported that PAM hydrogels are fixed with peptides, proteins, enzymes, or antibodies for molecular recognition <sup>[84]</sup>. In terms of humidity sensing, PAM hydrogels have been used in composite materials because of their good ability to absorb water <sup>[85]</sup>.

### 1.3 Strategies for Biomimetic Anti-freezing Hydrogels

The hydrogel of pure water phase is affected by the freezing point of water and freezes at about 0°C, so it has challenges to work at a sub-zero temperature. The water captured by hydrogel is different from regular water, which experiences phase change for one time when freezing it. However, the water captured by hydrogel experiences phase changes for several times. There are three states of water in hydrogels: free water, intermediate water, and unfrozen water. The three states of water have different frozen point <sup>[86-88]</sup>. Free water has little interaction with hydrogel network. It is similar to regular water, and it freezes at about 0°C. Intermediate water has some interaction with hydrogel network, which makes it freeze below 0°C. Unfrozen water has strong interaction with hydrogel network. It keeps liquid state at -100°C. The principle of tuning the water states provides directions for changing the freezing points of hydrogels. Compared with intermediate water and unfrozen water, free water has high contents in hydrogels. To decrease the freezing point of hydrogels, strengthen the interaction between water molecules and hydrogel networks to reduce the content of free water. Moreover, the components of free water can be changed by adding ions or replacing with anti-freezing liquid to decrease the freezing point of hydrogels. As shown in **Figure 1.4**, the freezing point of hydrogels can be controlled by four different synthesis strategies: introduction of soluble ions, introduction of ionic liquid, addition of alcohols, and modification of hydrogel network <sup>[89]</sup>.

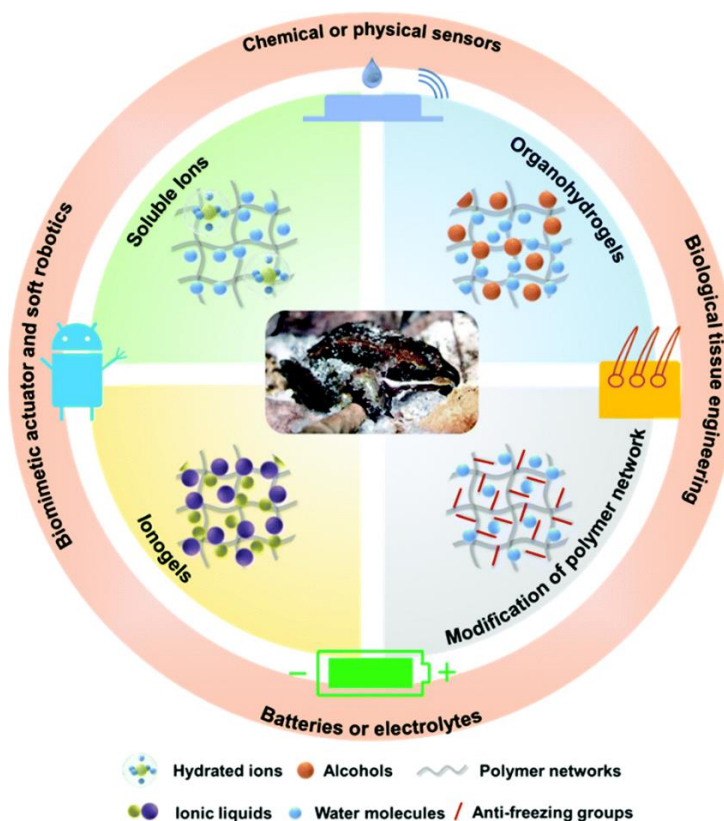


**Figure 1.4** Synthesis strategies of anti-freezing hydrogels <sup>[89]</sup>. Adapted from Advanced materials. Copyright of Wiley publishing group.

The introduction of soluble ions is a general method to control the freezing point of water and hydrogels. Salt is sprinkled on the road to melt ice and snow to avoid traffic accident in winter. Similarly, soluble ions are used to control the freezing point of solution by changing concentration of the ions. Researchers have shown that the freezing point of 23.3wt% NaCl solution is depressed to  $-21.1^{\circ}\text{C}$  <sup>[90]</sup>, and the freezing point changes with change of concentration of NaCl solution. Therefore, freezing point of hydrogels can be highly depressed if there are many soluble ions dissolved in hydrogels <sup>[91-94]</sup>. Inspired by soluble ions in anti-freezing solution, Morelle *et al.* <sup>[91]</sup> designed polyacrylamide-alginate double network hydrogels and soaked them into  $\text{CaCl}_2$  solutions with different concentrations to make the soluble  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  ions dispersed in the hydrogels, thus giving them anti-freezing properties. The concentration of  $\text{CaCl}_2$  effect the performance of hydrogel below  $0^{\circ}\text{C}$ . The hydrogel without  $\text{CaCl}_2$  freezes rapidly at  $-15^{\circ}\text{C}$ , becoming fragile and not transparent. In contrast, the hydrogel with 30wt%  $\text{CaCl}_2$  can keep its mechanical properties and transparency at the same temperature ( $-15^{\circ}\text{C}$ ). <sup>[91]</sup> Unlike the hydrogel without  $\text{CaCl}_2$  and with 30wt%  $\text{CaCl}_2$ , the hydrogel with 10wt%  $\text{CaCl}_2$  keeps its mechanical properties but lost its transparency. In addition,

Zhang *et al.* <sup>[92]</sup> synthesized hydrogels with ZnCl<sub>2</sub>, CaCl<sub>2</sub> and glycerol, giving them excellent anti-freezing properties. The hydrogel keeps unfrozen and its conductivity at -70°C, and the minimum freezing temperature reaches -100°C with the addition of glycerol. Moreover, Sui *et al.* <sup>[93]</sup> synthesized hydrogels with betaine or proline, which keep their mechanical properties at -40°C. Also, the hydrogels have good conductivity because of the addition of the zwitterions. Introduction of soluble ions has several advantages. Firstly, the synthesis process of hydrogel with the addition of soluble ions is simple. Secondly, hydrogels with movable ions have high conductivity. Thirdly, hydrogels with most soluble ions are biocompatible, which makes them suitable for wearable sensors for human skin. However, hydrogels with soluble ions have little water retention, and cannot effectively prevent evaporation of water, which influences the concentration of ions, the conductivity and mechanical properties of the hydrogels.

The introduction of ionic liquid is also useful for synthesis of anti-freezing hydrogels. Ionic liquid has similar properties to water, but it is hardly evaporated, and it has excellent conductivity <sup>[95][96]</sup>. The water in hydrogels is replaced by ionic liquid to obtain ion gels. Thanks to the unique properties of ionic liquid, ion gels have high transparency, good water retention, high conductivity, and good low temperature resistance <sup>[97][98]</sup>. Therefore, ionogels can be widely used as flexible wearable sensors <sup>[94-97]</sup>. Yin *et al.* <sup>[97]</sup> synthesized a new type of hydrogels with ionic liquid. They use *N,N*-methylenebisacrylamide (MBAA) as cross-linker, *N,N*-dimethylacrylamide (DMAA) as monomer, and 2,2-diethoxyacetophenone (DEAP) as photo initiator in ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF<sub>4</sub>) to obtain ionogels by radical polymerization. The ionogels have good mechanical properties, and they can keep their mechanical properties after tensile tests for 300 times. <sup>[97]</sup> Also, the ionogels have excellent conductivity and anti-freezing properties, and they can keep their electrical properties at about -40°C. Therefore, the ion gel can be used as anti-freezing flexible device. Cao *et al.* <sup>[98]</sup> designed poly (ethyl acrylate) based ionogels. In the ionogels, ethyl acrylate (EA) is used as monomer. Ethylene glycol methacrylate (EGDMA) is used as crosslinker, and [C2mim][NTf<sub>2</sub>] is used as ionic liquid. The ionogels have high transparency, high conductivity, and good mechanical properties. Because of the low vapor pressure of [C2mim][NTf<sub>2</sub>] ionic liquid, the ionogels can work at extreme temperatures, which can reach a maximum temperature of 100°C and a minimum temperature of -70°C. The type of ionic liquid and polymer network can be diversified. Thus, this synthesis method can be versatile to prepare different types of anti-freezing flexible hydrogels. Compared with water or ions solution based hydrogel, ionogel has excellent low and high temperature resistance. Besides, ionogel keeps a high conductivity at a wide range of temperatures. The excellent performance of ionogel makes it have a wide range of potential applications in the field of flexible wearable sensors and energy storage devices. However, ionogel still faces some challenges. Some ionic liquids have inherent biological

toxicity, preventing the applications in which contact with human body, such as detection of temperature of human skin and monitoring of human respiration. In addition, when ionogel contacts with water solvent, ionic liquid will diffuse out of the ionogel with concentration gradient of the solute between inside and outside of the ionogel. Moreover, the other solute additives may crosslink with ionic liquid to change mechanical properties of the ionogel.

The addition of organic solvent in water can change the freezing point of the solution. Organic solvent such as alcohol can decrease the freezing point of solution, which is like soluble ions. In organohydrogels, the interaction between hydrogel network and molecules in organic solution effect the freezing of solution and hydrogels. According to the related literature, researchers believe that the hydrogen bond between hydroxyl groups in organic molecules and water molecules depresses hydrogen bond between water molecules, which prevents organic solution from freezing at low temperature, thus decreasing the freezing point of the organic solution [99-110]. Chen *et al.* [99] introduced a simple method to obtain anti-freezing organic hydrogel. They soaked Ca-alginate-polyacrylamide hydrogel in the mixture of glycerol, glycol, and sorbitol. The water in the hydrogel is replaced by organic solvents in the process. The organohydrogels have good anti-freezing properties, which can be adjusted by changing immersed time or concentration of organic solvents. The organohydrogels keep flexible and soft at a minimum temperature of -45°C. Moreover, the organohydrogels have excellent water retention. They can be placed in dry air or vacuum with little mass loss because of their low vapor pressure. The organohydrogels also have better mechanical properties than water-based hydrogels because the interaction between organic molecules and hydrogel network is stronger than water molecules. Shi *et al.* [100] reported a type of PVA-glycerol/water hydrogel. They had added glycerol/water solvent into PVA solution before the hydrogel was formed. The type of hydrogel has good mechanical properties and anti-freezing properties. The PVA-glycerol/water hydrogel keeps unfrozen and some mechanical properties at -78.5°C. Ju *et al.* [102] synthesized hydrogels microfiber based on iron citrate redox reaction and glycerol. The hydrogel microfiber keeps unfrozen and good elasticity at a minimum temperature of -61°C. [102] In addition, due to the redox reaction, the hydrogel microfiber is sensitive to humidity. The resistance of the hydrogel microfiber varies with the change of humidity, which indicates that the hydrogel microfiber can be used as humidity sensors and has great application potential in the field. The introduction of organic solvents has advantage of simple synthesis. The organohydrogels have high freezing resistance, water retention, and evaporation resistance [108][111]. However, in general, the organic/water solution and organohydrogels have low conductivity, because organic solvents are usually electrically neutral with few free ions.

Introduction of soluble ions, ionic liquid and organic solvents can effectively improve the anti-freezing properties of hydrogels, but they face one same challenge: the additives may diffuse

out of the hydrogel with concentration gradient, reducing the anti-freezing properties of the hydrogel. To solve this problem, researchers stabilize the solutes in hydrogel networks by modifying the hydrogel network. If groups on the polymer chains have strong interaction with water molecules, the freezing point of hydrogel can be lower. Pei *et al.* <sup>[112]</sup> synthesized an alkalified polyacrylic acid (A-PAA) hydrogel. The polymer chains contain many carboxyl groups, which exhibit strong interactions with water molecules, enhancing the freeze resistance of the hydrogel. They show that the freezing point of the PVA hydrogel with a 10% KOH solution is -13°C, while the freezing point of the A-PAA hydrogel, also containing 10% KOH, is -25°C. <sup>[112]</sup> This demonstrates that the carboxyl groups in the A-PAA hydrogel lower the freezing point of the hydrogel. Due to its excellent conductivity and low-temperature resistance, the A-PAA hydrogel can be used for zinc-manganese dioxide batteries operating at low temperatures. Mo *et al.* <sup>[113]</sup> synthesized an ethylene glycol-based waterborne anionic polyurethane acrylates (EG-waPUA) hydrogel. The hydrogen bonding interactions between EG, water molecules, and PAAm in the hydrogel networks inhibit the freezing of the hydrogel, thereby reducing the freezing point of the hydrogel. The hydrogel exhibits excellent mechanical properties and good low-temperature performance, maintaining most of its elasticity and conductivity even at lower temperatures. This makes it suitable for use as a flexible wearable sensor in cold environments. The hydroxyl groups in EG chemically bind to the hydrogel networks, making it less prone to diffusion out of the hydrogel, thus solving the problem of additives diffusing from the hydrogel. Modifying the hydrogel network enhances the freeze resistance of the hydrogel but reduces its mechanical properties. Therefore, it is necessary to find a balance between them. Besides, the synthesis process of this method is more complex.

## 1.4 Thermogalvanic cell

### 1.4.1 Current thermocell

Since the 1870s, to meet the annually increasing energy demands, countries around the world have increasingly used fossil fuels <sup>[114-119]</sup>. As a result, the consumption of non-renewable energy sources has increased, and the rate of consumption has accelerated, leading to a growing demand for the development of renewable energy sources <sup>[120-124]</sup>. Among these, thermal energy (such as solar energy, waste heat generated from daily activities like lighting and air conditioning, and industrial waste heat from factories) is a form of underutilized energy dissipated from human bodies or electronic devices, industries plants, which results in a wide distribution of low-grade heat, typically below 200°C, in the air <sup>[125-127]</sup>. Thermoelectric technology is a method for converting thermal energy into electrical energy through the Seebeck effect <sup>[128-131]</sup>. However, low-grade thermal energy typically has lower temperatures

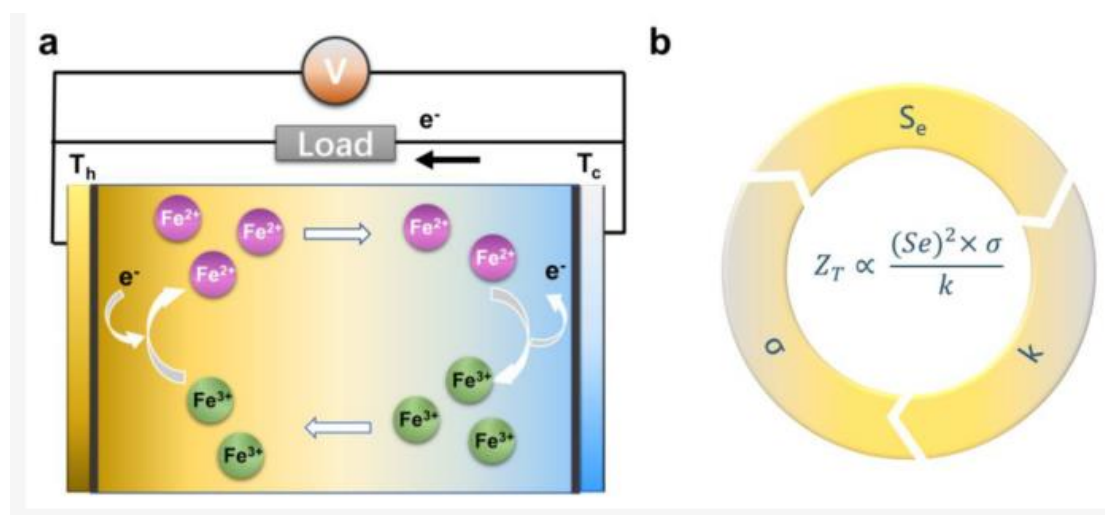
and efficiency, making it challenging for commercial applications <sup>[132]</sup>. Therefore, thermoelectric conversion devices need to be both efficient and cost-effective <sup>[133][134]</sup>. Traditional inorganic semiconductor thermoelectric generators suffer from high costs, poor mechanical performance, high synthesis complexity, low thermoelectric efficiency, as well as low thermal and electrical conductivity, making them almost impractical for commercial use <sup>[135-137]</sup>. In contrast, a notable advantage of thermoelectric cell technology is that its fabrication process is relatively straightforward, enabling the conversion of thermal energy into electricity. Furthermore, thermoelectric cells exhibit high thermal power, allowing them to generate high voltage even with small temperature differentials <sup>[138-142]</sup>. These qualities make thermoelectric cell (especially quasi-solid thermoelectric cell) technology promising for the repeated utilization of low-grade thermal energy, establishing it as a promising technology with broad application prospects.

#### 1.4.2 Seebeck effect

Thermoelectric batteries convert thermal energy into electricity through the Seebeck effect. The process of converting electrical energy into thermal energy in thermoelectric batteries consists of two parts: the oxidation-reduction reactions occurring at the electrodes and the transfer of ions within the electrolyte. When there is a temperature difference between the anode and cathode of a thermoelectric cell, temperature-sensitive oxidation-reduction reactions occur at both the anode and cathode. The anode undergoes an oxidation reaction, while the cathode undergoes a reduction reaction. Subsequently, the reduction products at the cathode diffuse and migrate through the electrolyte to the anode, where they are oxidized again. Similarly, the oxidation products generated at the anode are transferred to the cathode, where they undergo a reduction reaction. This results in a continuous series of oxidation-reduction reactions taking place within the thermoelectric cell, as shown in **Figure 1.5 a** <sup>[143]</sup>. Therefore, as long as the oxidation-reduction couples in the thermoelectric cell are not fully consumed, the oxidation-reduction reactions will occur continuously, generating a constant electric current in the

thermoelectric cell.

**Figure 1.5** (a) The principle of thermoelectric effect. (b) The effect factors of the conversion efficiency of thermoelectric cells. <sup>[143]</sup> Adaption from Micromachines journal. Copyright of MDPI publisher.



### 1.4.3 Thermoelectric Efficiency of Thermocell

As shown in **Figure 1.5 b**, the conversion efficiency  $ZT$  of thermoelectric cells is influenced by three parameters: the Seebeck coefficient ( $S_e$ ), electrical conductivity ( $\sigma$ ), and thermal conductivity ( $k$ ) <sup>[143]</sup>. The formula is as follows:

$$ZT = \frac{Se^2 \cdot \sigma}{k}$$

This formula describes the key factors affecting the performance of thermoelectric cells, where a higher  $ZT$  value represents higher conversion efficiency. Optimizing the Seebeck coefficient, electrical conductivity, and thermal conductivity can enhance the performance of thermoelectric cells. The Seebeck coefficient is influenced by the type of redox couples and the interaction between the solvent shell and the solvent. When the Seebeck coefficient increases, the voltage between the cathode and anode increases, leading to an increase in the current generated within the cell. Thermoelectric materials with low thermal conductivity can maintain a high temperature difference between the two electrodes, which preserves the potential difference between the two electrodes, thereby achieving higher thermoelectric conversion efficiency. Furthermore, the electrical conductivity of thermoelectric cells affects the reaction resistance at the electrodes and the transport resistance within the electrolyte, consequently

influencing the thermoelectric conversion efficiency. The higher the electrical conductivity of the thermoelectric cell, the lower the reaction resistance and transport resistance, resulting in a higher thermoelectric conversion efficiency. Most thermoelectric cells have a thermoelectric conversion efficiency of less than 1% [144-146]. However, a recent research suggests that thermoelectric conversion efficiency can be improved to a maximum of 11% with a liquid state thermoelectric cell [147]. Because the primary purpose of thermoelectric cells in commercial applications is to collect waste heat, the requirements for thermoelectric conversion efficiency are relatively low, typically ranging from 2% to 5% [148][149]. Furthermore, the feasibility of commercial applications is also influenced by the lifespan of thermoelectric cells.

There are two possible methods to improve the thermoelectric efficiency and lifespan of thermoelectric cells, especially quasi-solid (hydrogel) thermoelectric cells. The first method involves increasing the current density within the thermocell and the potential difference between the electrodes. The second method focuses on optimizing the polymer network to enhance the thermoelectric performance, mechanical properties, and long-term stability of the thermocell. Developing and using redox couples and electrolytes with higher Seebeck coefficients can increase the potential difference between the electrodes, thereby improving the thermoelectric efficiency of the thermocell. Additionally, high-surface-area, high-quality electrodes can enhance the current density within the thermocell. Developing and improving the encapsulation methods of thermoelectric cells can enhance their environmental stability, consequently extending their lifespan.

### **1.5 Quasi-solid thermogalvanic cell**

Recent advancements in the development and improvement of different types of electrodes, electrolytes, and oxidation-reduction couples have greatly benefited the research of liquid state thermoelectric cells [150-154]. In comparison to liquid thermoelectric batteries, quasi-solid thermoelectric cells exhibit similar performance and characteristics while avoiding issues related to liquid electrolyte leakage. Hydrogel thermoelectric cells represent quasi-solid thermoelectric cells, with a Seebeck coefficient significantly higher than inorganic semiconductor thermoelectric batteries. These hydrogel thermoelectric cells consist of simple device structure formed by the hydrogel and the electrolyte in the hydrogel additives, along with external electrodes. They have advantages such as low cost, environmental-friendly, flexible, and high thermoelectric performance. Researchers have developed various flexible sensors based on hydrogel thermoelectric cells, showing promising applications in temperature sensing, environmental temperature monitoring, body temperature monitoring and solar thermal energy harvesting [155][156]. Different hydrogel thermoelectric cells have similar

structures, but they differ in terms of their electrolytes, electrode materials, solvents, and redox couples <sup>[157][158]</sup>. Li *et al.* <sup>[159]</sup> synthesized a micro-sized PVA/Gelatin (PVA/GL) hydrogel. This PVA/GL hydrogel can generate voltage signals corresponding to temperature, as shown in **Figure 1.6**. Within 24 hours, the voltage curve generated matches the temperature differential curve. Using this method, indoor temperature has been monitored, enabling temperature sensing. Solar energy is an important renewable energy source and has been a hot topic in the field of energy research. Hydrogel thermoelectric cells have prospects for application in solar energy harvesting. Bai *et al.* <sup>[160]</sup> designed a PVA/Gelatin hydrogel. They further introduced DMSO/water as a solvent, which suppressed the formation of hydrogen bonds along the three-dimensional direction. The hydrogel exhibits high transparency, good mechanical properties, and high thermoelectric performance. After implanting the PDMS solar absorber, the PG hydrogel thermoelectric device was placed in sunlight for 12 hours. Under a temperature difference of up to 11.2 K, the open-circuit voltage of the hydrogel thermoelectric cell reached a maximum of 16.6 mV, demonstrating the potential for solar energy utilization. Zhang *et al.* <sup>[161]</sup> reported a  $K^{3/4}[Fe(CN)_6]$  hydrogel thermoelectric cell with Pt electrodes. They also introduced a GdmCl solution into the hydrogel as an electrolyte to enhance its thermoelectric performance. This hydrogel can serve as a wearable, flexible thermoelectric device, collecting heat from the human skin's surface and converting thermal energy into electrical energy. This demonstrates the potential application of hydrogel thermoelectric devices in harvesting body heat for power generation.

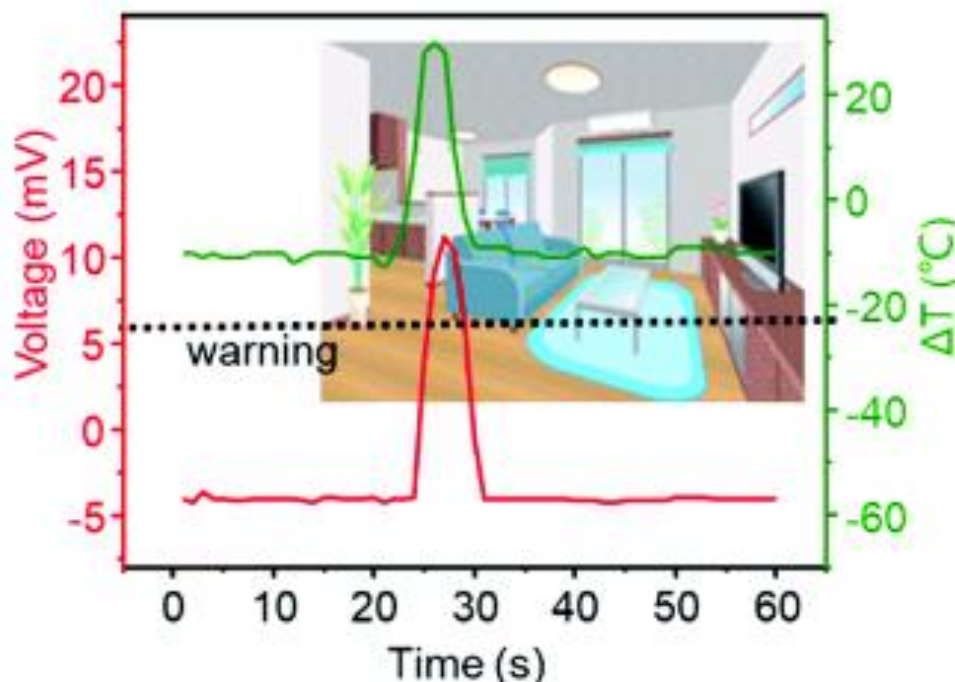


**Figure 1.6** Temperature difference and voltage signals at indoor temperature <sup>[159]</sup>. Adaption from Journal of Materials Chemistry C. Copyright of Royal Society of Chemistry.

## 1.6 Summary

Hydrogels are a type of viscoelastic material that have high elasticity and flexibility, good self-healing capability, and are highly compatible with the human body. This has made hydrogel research an exciting area for scientists, as they have various potential applications in fields such as stress and temperature sensors, thermoelectric devices, and biosensors. However, hydrogels do have some limitations, such as poor resistance to low and high temperatures, as well as limited conductivity and mechanical properties.

## 1.7 Objectives and Scope of research project

In this thesis, we aim to solve the problem of poor resistance of hydrogel in low and high temperature. In Chapter 2, a hydrogel that is based on PVA/TA/Borax has been synthesized. This hydrogel has good mechanical properties and electrical conductivity. Additionally, the introduction of ionic liquid has improved the freeze resistance of the PVA/TA/Borax hydrogel, which demonstrates its potential as a low-temperature wearable strain sensor up to -

40°C. In chapter 3, by selecting soluble ions in the solvent, a gelatin-based heat-resistant hydrogel thermoelectric device has been synthesized, which has improved thermopower at high temperature up to 90 °C.

## Chapter 2. Anti-freezing hydrogel wearable strain sensor

### 2.1 Overview

Hydrogels made of pure water phase freeze at around 0°C, which limits their use in low temperature environments. To address this issue, researchers have come up with various solutions. For instance, Li *et al.* <sup>[162]</sup> developed a composite hydrogel by combining poly (vinyl alcohol) grafted with styrene pyridinium group (PVA SbQ) and TEMPO oxidized cell nanofibers (CNF). The composite gel can operate at about -20 °C, which is a significant improvement. This hydrogel shows broad prospects for applications in wound dressings and portable devices, especially in extreme environments such as low temperatures. Xu *et. al* <sup>[163]</sup> synthesized a graphene/PEDOT: PSS hydrogel fiber and introduced an anti-freezing polyvinyl alcohol (PVA) network. This improved the low-temperature performance of the hydrogel, allowing it to operate normally at -20°C. This hydrogel can be used as an anti-freezing supercapacitor.

Chitin is a natural material that is translucent and solid. It is commonly found in the cell walls of fungi, the exoskeletons of arthropods (such as shrimp, crab, insects), the tooth tongue or beak process of mollusks, and fish scales. Chitin is also biocompatible, non-toxic and has excellent mechanical performance, making it a possible additive to improve the properties of hydrogel.

Adding soluble ionic liquids into hydrogel can improve their low-temperature performance. In this chapter, ionic liquids are added to PVA hydrogel and chitin is introduced to improve the mechanical properties of the hydrogel. Adding tannic acid solution forms a cross-linked network with PVA, enhancing the mechanical and self-healing properties of the hydrogel. The addition of borax to PVA results in a chemically cross-linked coordination polymer. The inclusion of borax causes the PVA solution to lose its fluidity, facilitating the rapid formation of the hydrogel and enhancing its mechanical properties. The resulting PIC hydrogel is based on PVA, ionic liquid, chitin, tannic acid, and borax. This PIC hydrogel shows good mechanical and low-temperature properties and has potential applications as a wearable sensor.

Anti-freezing wearable sensors can operate in extremely cold environments, such as the polar regions, winter in Canada, where temperatures can drop to as low as -40°C. These environments offer potential applications for this anti-freezing hydrogel wearable sensor.

## **2.2 Experimental Methods**

### **2.2.1 Materials**

Polyvinyl alcohol (PVA, Mn = 89000-98000, sigma), Tannic acid (sigma), Borax (sigma), chitin (Sigma), dry ice (chemstore, uwaterloo), ultrapure water (chemstore, uwaterloo), EMImAc (sigma)

### **2.2.2 Preparation of chitin solution**

Dissolve sodium hydroxide and urea in ultrapure water with a mass fraction of 2:1 and put them into an ultrasonic processors for ultrasonic dissolution. Add 0.5% chitin and put it into the ultrasonic cell disruption instrument (ATPIO, China) for ultrasonic treatment. Freeze at -18°C for three hours, then thaw the solution. Repeat this process three times to obtain a clear and transparent chitin solution.

### **2.2.3 Preparation of PVA-TA-Ionic Liquid Hydrogel**

8g Polyvinyl alcohol powder was dissolved into 40ml solution at ~90°C, stirring for 2h, the solution becomes clear. After that, add 0.8g tannic acid into PVA solution and stir for 30 minutes. After adding 0.8g Borax into PVA-TA solution, stir for 30 minutes. Mix the solution with ionic liquids (EMIMAc) of specific concentrations to obtain solution with ionic liquid with different concentrations (20%, 30%, 40%, 50%, respectively). Place the solution at -20 °C refrigerator to obtain hydrogel for 24 hours.

### **2.2.4 Fabrication of anti-freezing PVA-TA-IL-Chitin Hydrogel**

8g Polyvinyl alcohol powder was dissolved into 40ml solution at ~90°C, stirring for 2h, the solution becomes clear. Add a specific proportion of chitin solution. After that, add 0.8g tannic acid into PVA solution and stir for 30 minutes. After adding 0.8g Borax into PVA-TA solution, stir for 30 minutes. Mix the solution with ionic liquids of specific concentrations to obtain solution with ionic liquid with different concentrations (20%, 30%, 40%, 50%, respectively). Store the solution in the fridge at -20°C for 24 hours.

### 2.2.5 Characterization

Surface and cross-sectional topographies of the as-prepared fibers were observed with a scanning electron microscope (SEM). Chemical compositions of samples were analyzed using a Fourier-transform infrared (FT-IR) spectrometer. The freezing point of PIC hydrogel is measured by differential scanning calorimeter (DSC). The measurement temperature range is set to -85°C to 25°C, and the cooling rate is 2 °C/min I-V curves of the hydrogel at room temperature (RT) were measured on an electrochemical workstation (Gamry Instruments Inc. USA). Conductivity ( $\sigma$ ) of the hydrogel was calculated with the equation:

$$\sigma = \frac{L}{R \times S}$$

where R is the resistance of the hydrogel, S is the cross-sectional area of the hydrogel device, and L is the length of the hydrogel device. Tensile test was conducted on an Instron (ADMET, USA) at the tensile speed of 5 mm/min in ambient temperature. The hydrogel was cut into a strip-shaped specimen with a 20 mm gauge length and 5 mm width for tensile test. Ionic conductivity at low temperature was also measured by electrochemical workstation (Gamry Instruments Inc. USA). Use copper foil and PET substrate to make hydrogel into wearable devices and use Parafilm as encapsulation materials. Mixing ultra-pure water with ethyl glycol in solutions of different concentrations, and these solutions have different freezing points. Continuously adding dry ice to the solution keeps its temperature close to the freezing point, thereby adjusting the temperature of the hydrogel wearable sensor. Use a thermometer to measure temperature of the solution. Combine the device with electrochemical workstation and use it to measure the ionic conductivity of devices, as shown in **Figure 2.1**.



**Figure 2.1** The experimental setup of ionic conductivity measurements.

## 2.3 Results and Discussion

### 2.3.1 Characterization of PIC Hydrogel

However, since the traditional hydrogel mainly consists of water, it freezes at low temperatures close to 0°C. This limits its performance, including mechanical and electrical properties. To overcome this limitation, ionic liquid (EMIMAc) was added to enhance the freezing resistance of the hydrogel. In **Figure 2.2 (a)**, the PIC hydrogel lifted weights of 10g, 20g, 50g, 100g, and 200g, indicating that it has impressive mechanical strength.

In **Figure 2.2 (b)**, the PIC hydrogel was tested for flexibility at temperatures of 25 °C and -40 °C, and it maintained its shape, flexibility and performance at -40 °C, indicating its high resilience. In **Figure 2.2 (c)(d)**, the surface morphology and cross-section of PIC hydrogel was examined using SEM. Finally, in **Figure 2.2 (e)**, the FTIR spectrum of the composite film at room temperature showed peaks representing chitin and PVA at 400-5000cm<sup>-1</sup>, which were physically mixed during the formation of the hydrogel. Both materials retained their unique chemical structures.

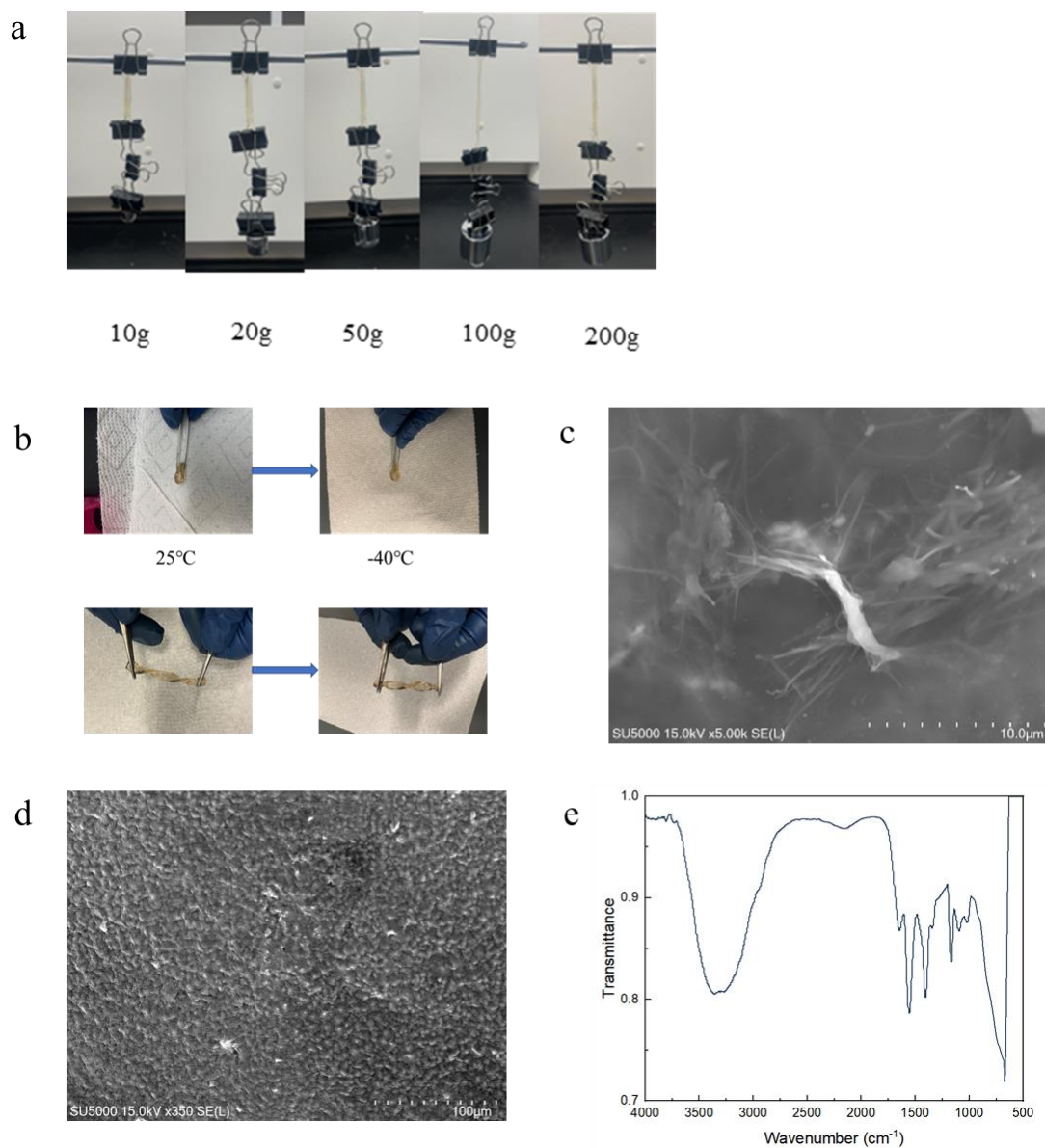


**Figure 2.2** (a) PIC hydrogel lifts 10g, 20g, 50g, 100g, 200g weight at room temperature; (b) PIC hydrogel retains most of its flexibility at -40°C; (c) SEM images of the surface of the PVA-IL-chitin hydrogel; (d) SEM images of the cross section of the PVA-IL-chitin hydrogel; (e) FTIR test of PIC hydrogel at room temperature.

### 2.3.2 Mechanism of physical crosslinked hydrogel network

The physical crosslinked hydrogel network is based on molecular interactions such as hydrogen bonds and van der Waals force. It has molecular networks that can be used as different types of sensors, such as temperature, pH, ionic strength sensors. Physical hydrogels can exhibit properties such as anti-freezing and good mechanical performance. Hydrogen bonding, metal coordination, cationic interactions, protein interactions, crystallization, host-guest interactions, and hydrophobic association are some of the methods used to make physical hydrogels <sup>[164]</sup>.

Hydrogen bonding is one of the most commonly used non-covalent interactions to construct hydrogels. It allows for a tunable microstructure and customized properties. Hydrogen bonding is a directional and reversible interaction based on the attraction between atoms with strong electronegativity and hydrogen atoms <sup>[165]</sup>. The bond energy of hydrogen bonds is typically around 10-40 kJ/mol, falling between covalent bonds and van der Waals forces <sup>[166]</sup>. Hydrogel precursors' functional groups such as carboxyl groups, amides, urease, phenolic hydroxyls, and many others can form stable hydrogen bonds. Additionally, the hydrophobic methyl groups can effectively promote this process. Molecules such as tannic acid (TA), lignin, and silicotungstic acid, which have both hydrophobic groups and groups capable of forming hydrogen bonds, are widely used in preparing hydrogels crosslinked via hydrogen bonding <sup>[167]</sup>. Hydrogen bonds in hydrogel networks can be single or multiple. Pure hydrogen bond interactions are typically weak and cannot maintain structural integrity over extended periods. Furthermore, the functional groups that create hydrogen bonds may weaken the hydrogel's ability to retain surrounding water molecules, leading to a reduction in hydrogel strength.

### 2.3.3 Mechanical Properties of PIC Hydrogel

The mechanical properties of PIC hydrogel were tested, and the results showed that the tensile strength and elongation of PI hydrogel, which only contains PVA, TA, Borax and Ionic liquid, were 0.17MPa and 750%, respectively (**Figure 2.3a**). In contrast, the tensile strength and elongation of PIC hydrogel are 0.33MPa and 460%, respectively (**Figure 2.3a**). With the addition of chitin, the elongation of the hydrogel decreases, and the tensile strength approximately increases by twice. The increase in mechanical strength and the decrease in ductility prove that the interaction between PVA-IL hydrogel and chitin exists. The fracture strength and strain of PIC hydrogel increase with the volume concentration of ionic liquid increasing (**Figure 2.3b**). The mechanical properties of PIC hydrogel were further studied in a wide temperature range (-40°C to 25°C), and the fracture strain of PIC hydrogel reached more than 700% at 25°C (**Figure 2.3c**). The fracture strength and strain of PIC hydrogel decrease

with decreasing temperature (**Figure 2.3c**). Before the temperature drops to 0°C, there is little change in mechanical properties. Moreover, PIC hydrogel can maintain nearly half of its fracture strength and strain at -40°C, which showed excellent low-temperature performance of PIC hydrogel (**Figure 2.3c**). This clearly shows that the ductility of the hydrogel is still very good even at temperatures as low as -40°C (**Figure 2.3c**). Finally, the PIC hydrogel can still retain 64% of its mass after being left at room temperature for 72 hours, which indicates excellent water retention property (**Figure 2.3d**).

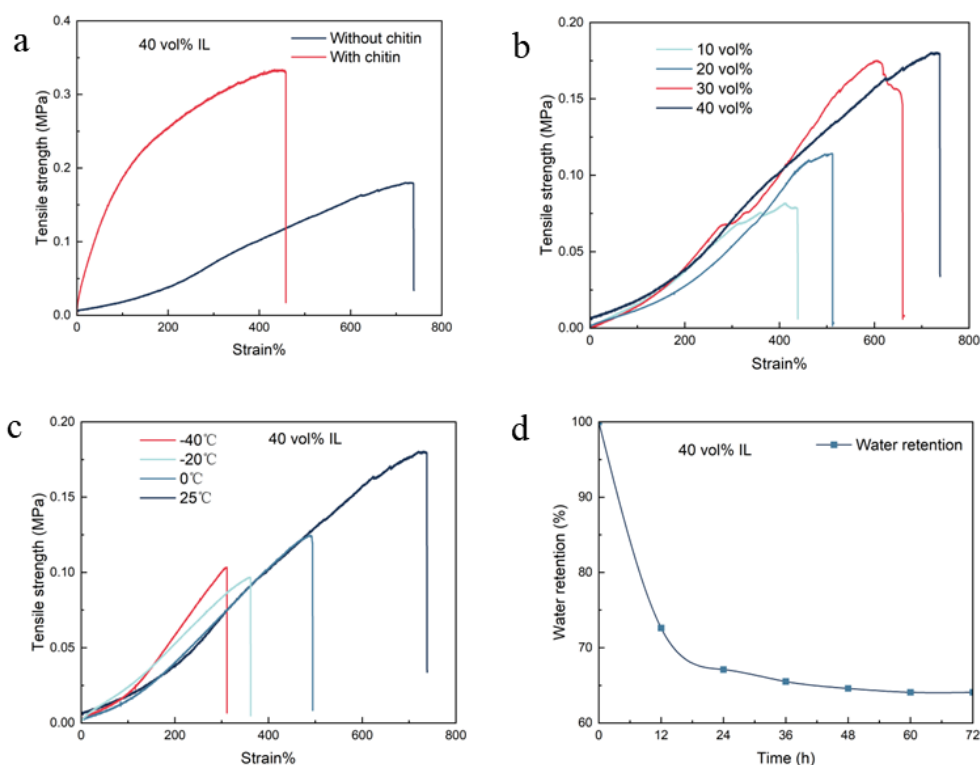


**Figure 2.3** (a) Tensile strength of PI and PIC hydrogel; (b) Tensile strength of PIC hydrogel with different volume concentration of ionic liquid; (c) Tensile strength of PIC hydrogel with 40% volume concentration ionic liquid at different temperature; (d) Water retention of PIC hydrogel with 40% volume concentration ionic liquid.

### 2.3.4 Anti-freezing Properties of PIC Hydrogel

Ionic liquid can be used to lower the freezing point of a solution, thus improving the low-temperature performance of gel. This enables it to function at lower temperatures. The result

of the differential scanning calorimetry (DSC) test indicates that the conventional PVA-TA-Borax hydrogel freezes at  $-18.69^{\circ}\text{C}$  in **Figure 2.4 (b)**. In contrast, the hydrogel containing ionic liquid has its freezing point significantly reduced. As shown in **Figure 2.4 (a)**, PIC hydrogels containing ionic liquids of different volume concentrations (20%, 30%, 40%) have distinct freezing points at  $-51.89^{\circ}\text{C}$ ,  $-63.96^{\circ}\text{C}$ , and  $-87.43^{\circ}\text{C}$ , respectively.

To evaluate the low-temperature performance of PIC hydrogel, including its ionic conductivity and mechanical properties, a customized measuring device was used. The measuring device comprises an external thermometer, PIC hydrogel device, and electrochemical workstation (Garmy instruments Inc., USA). **Figure 2.4 (c)** shows that PIC hydrogel maintained 83.5% ionic conductivity at  $-10^{\circ}\text{C}$  compared with room temperature. **Figure 2.4 (d)** shows the thermogravimetric analysis (TGA) test result of PIC hydrogel. During the TGA process, the mass change of the hydrogel can be divided into the loss of water content and the loss of PVA mass. Before reaching  $100^{\circ}\text{C}$ , the mass change is relatively small. Water content is primarily released in the temperature range of 100 to  $250^{\circ}\text{C}$ , while above  $250^{\circ}\text{C}$ , the main contributor to mass loss is the decomposition of PVA.<sup>[168]</sup> As the DTG test shown in **Figure 2.4 (d)**, the rate of mass loss in the hydrogel continues to increase until it peaks at  $175.46^{\circ}\text{C}$ , after which the rate starts to decline until reaching  $229.92^{\circ}\text{C}$ . This initial mass loss is primarily attributed to the evaporation of water from the hydrogel. Subsequently, the rate of mass loss sharply rises, reaching its peak at  $277.66^{\circ}\text{C}$ , and by  $500^{\circ}\text{C}$ , the rate of consumption slows down to almost zero. This latter portion of mass loss is mainly due to the consumption of PVA within the hydrogel.

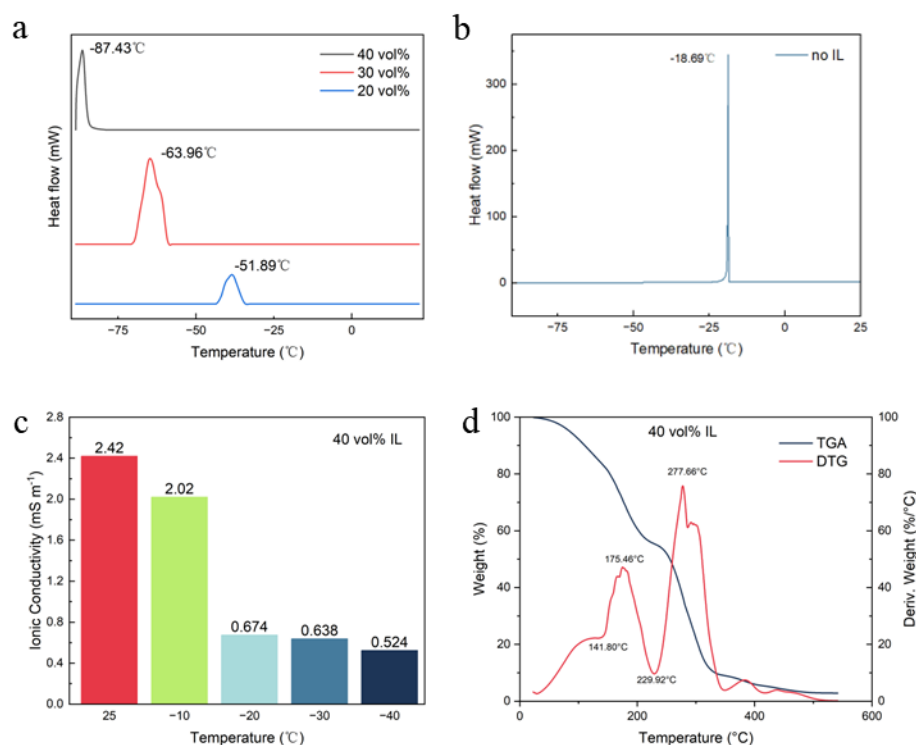


**Figure 2.4** (a) DSC test of PIC hydrogel with 40%, 30%, and 20% ionic liquid volume concentration; (b) DSC test of PVA-TA-Borax hydrogel; (c) Ionic conductivity of PIC hydrogel with 40 vol% ionic liquid at 25°C, -10°C, -20°C, -30°C, and -40°C; (d) TGA test and DTG analysis of PIC hydrogel with 40 vol% ionic liquid.

### 2.3.5 Wearable Strain Sensor Based on PIC Hydrogel.

Wearable strain sensors made of PIC hydrogel can receive signals from various human activities. PIC hydrogel has excellent strain sensitivity, which makes it suitable for monitoring human motion activities (**Figure 2.5**). The flexible device made of PIC hydrogel can detect specific frequencies when pressed with a finger, as shown in **Figure 2.5 (a)**. Similarly, attach the hydrogel wearable sensor closely to the throat to obtain test data by simulating actions such as coughing, swallowing, and breathing. When coughing, swallowing, or breathing at a specific frequency, the corresponding signals can also be detected by the device, as shown in **Figure 2.5 (b)-(d)**. The PIC hydrogel wearable strain sensor is also capable of receiving clear signals even when pressed at a low temperature of -40 °C, as demonstrated in **Figure 2.5 (e)(f)**. This proves its potential for use in low temperature environments. The hydrogel can act as a flexible sensor to detect strain changes at low temperatures.

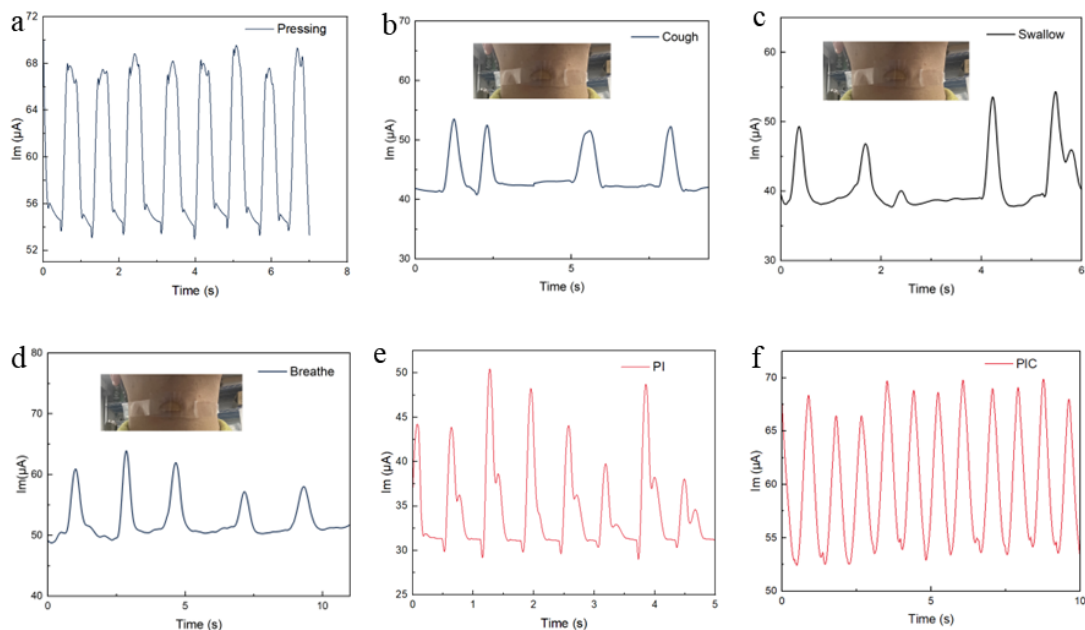


**Figure 2.5** PIC hydrogel is used as a wearable strain sensor to receive (a) pressing, (b) cough, (c) swallowing; (d) breathing motions from the human body and release signals, Sensing signal for (e) PI hydrogel at (-40 °C); and (f) PIC hydrogel at low temperature (-40 °C).

## 2.4 Summary

A hydrogel called PVA-Ionic Liquid-Chitin (PIC) has been created with excellent conductivity, mechanical properties, and low-temperature performance. The PIC hydrogels can maintain their conductivity even at subzero temperatures (-40 °C) as the ionic liquid in the hydrogel provides the conductive path and prevents ice crystals from forming. The chitin molecules provide better mechanical properties. Therefore, the hydrogel is suitable for flexible wearable strain sensors for human body monitoring. A PIC conductive hydrogel based wearable strain sensor has been demonstrated to monitor the human body's motion signal with high sensitivity. Due to all the properties mentioned above, it is believed that this conductive PIC hydrogel will be a promising material for applications at subzero temperatures in various applications such as flexible electrodes, sensors, and wearable devices.

## Chapter 3. Thermoelectric performance of gelatin-based hydrogels at High Temperature

### 3.1 Overview

The growing demand to power Internet-of-Things (IoT) sensors that harvest renewable energy such as waste heat has ignited extensive interests in the field of energy collecting from environment. One prominent approach is thermoelectric energy conversion technology, which harnesses the Seebeck effect and taps into readily available waste heat sources to satisfy the power the needs of IoT sensors, ranging from microwatts to megawatts<sup>[169][170]</sup>. Traditional electronic-thermoelectric (e-TE) materials typically consist of narrow-bandgap inorganic semiconductors that employ electrons or holes as energy carriers. In the case of a typical thermoelectric material, the thermopower (or Seebeck coefficient) hovers around 100 to 200  $\mu\text{V K}^{-1}$ . Consequently, generating a useful voltage of 1 to 5 V in a room temperature environment either requires the intricate integration of thousands or even tens of thousands of diminutives  $\sim 50\text{-}\mu\text{m}$  thermoelectric elements<sup>[171]</sup> or the adoption of a DC-DC voltage booster to amplify the voltage of a standard-sized device with millimeter-sized legs by up to 100 times<sup>[172]</sup>. This makes it impractical for the applications.

Another method for harvesting energy from heat is utilizing ions instead of electrons in semiconductors, employing two distinct principles. One mechanism hinge on redox reactions occurring at two electrodes maintained at different temperatures, resulting in the creation of devices known as thermogalvanic cells<sup>[173][174]</sup>. The other mechanism involves ionic thermodiffusion under a temperature gradient, devoid of redox reactions, a phenomenon referred to as the Soret effect<sup>[175][176]</sup>. Continuous electricity generation is achieved through the thermogalvanic mechanism as redox reactants are rebalanced by ionic diffusion<sup>[177]</sup>. Thermodiffusion cells operate in a capacitive mode<sup>[178]</sup>. After a temperature difference establishes a voltage disparity, the accumulated charges on the electrodes can be discharged to an external load. Subsequently, the temperature gradient is removed to enable system recovery and then reapplied for the next cycle. Attentions has been attracted on either the thermogalvanic or thermodiffusion cell configurations. In the case of thermogalvanic cells, liquid electrolytes featuring redox couples such as cobalt (II/III) tris(bipyridyl)<sup>[179][180]</sup>, iron (II/III)<sup>[181]</sup>, iodide/triiodide<sup>[182][183]</sup>, and ferro/ferricyanide  $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ <sup>[184-192]</sup> have demonstrated an absolute temperature coefficient of a few millivolts per degree Kelvin, which is much higher than inorganic semiconductors. Notably, an aqueous system utilizing the  $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$  redox couple and chaotropic guanidium salts achieved one of the most significant negative temperature coefficients, amounting to  $-4.2 \text{ mV K}^{-1}$ <sup>[191]</sup>. In the thermodiffusion cell configuration, a thermopower of  $+11 \text{ mV K}^{-1}$  was attained using NaOH in a polyethylene oxide (PEO) solution<sup>[178]</sup>. Nevertheless, liquid electrolyte thermocells

encounter challenges in terms of encapsulation, rendering them less suitable for wearable devices <sup>[193-195]</sup>. As an alternative, quasi-solid-state electrolytes have garnered attention <sup>[196-198]</sup>. When utilizing the  $\text{Fe(CN)}_6^{4-}/\text{Fe(CN)}_6^{3-}$  redox couple in the poly(sodium acrylate) and polyvinyl alcohol matrix, temperature coefficients of  $-1.09$  and  $-1.21 \text{ mV K}^{-1}$  were observed, values lower than those of the redox couple in liquid solutions <sup>[196][197]</sup>. High thermodiffusive thermopower has been noted in the quasi-solid-state polymer gel composite of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and polyethylene glycol (PEG) with ionic liquid as charge carriers, and the thermopower can be adjusted from  $-4$  to  $14 \text{ mV K}^{-1}$  by modifying the composition <sup>[197]</sup>. Additionally, a remarkable thermopower of up to  $+24 \text{ mV K}^{-1}$  has been reported by leveraging the high ionic selectivity of the NaOH-PEO aqueous solution within confined nanocellulosic channels, where Na serves as the predominant mobile ion <sup>[199]</sup>. Hydrogel was used for thermoelectric harvesting <sup>[200-202]</sup> with thermal power up to  $17 \text{ mV K}^{-1}$  <sup>[200]</sup> at near room temperature. Nevertheless, the question of whether the thermodiffusion effect and thermogalvanic effect can synergistically collaborate to enhance the ultimate thermopower in a single ionic thermoelectric (i-TE) system remains an open issue, primarily due to their fundamentally distinct physical principles. In this work, different types of soluble ions are introduced in the thermocell and selected according to their thermopower and heat resistance, and  $\text{Fe(CN)}_6^{4-}/\text{Fe(CN)}_6^{3-}$  is added as the redox couple. We achieved  $7.33 \text{ mV K}^{-1}$  from the temperature range of  $25^\circ\text{C}$  to  $90^\circ\text{C}$ . This type of gelatin-based thermoelectric device can operate in extremely high-temperature environments, such as tropical regions and areas with desert climates.

## 3.2 Experiments and Methods

### 3.2.1 Fabrication of gelatin-based hydrogels with different ion providers

Firstly, dissolving gelatin powder in ultrapure water in a 2:8 ratio. This solution is heated and stirred under magnetic agitation in a  $55^\circ\text{C}$  oil bath for 4 hours, resulting in a clear and transparent 20% gelatin solution. The prepared gelatin solution is poured into a rectangular mold and rapidly frozen using liquid nitrogen to shape the gelatin. The formed gelatin is removed from the mold and immersed in various soluble ion solutions, then frozen at  $0^\circ\text{C}$  for 24 hours. Afterward, the gelatin is rinsed with ultrapure water to remove ions from the surface and then sealed for storage, obtaining gelatin samples containing different ion providers.

### 3.2.2 Fabrication of gelatin-based hydrogels with selected ions

After selecting the appropriate ions, a clear and transparent 20% gelatin solution is prepared using the same method. The solution is then mixed with the  $\text{FeCN}^{3-/4-}$  redox couple and stirred magnetically at the same temperature for 2 hours. The resulting solution is poured into a mold and rapidly cooled and shaped using liquid nitrogen. Subsequently, the gelatin is immersed in the selected soluble ion solution, placed at 0°C for 24 hours, and then cleaned with ultrapure water, resulting in Gelatin- $\text{FeCN}^{3-/4-}$ -selected ions hydrogels.

### 3.2.3 Thermopower Measurement and Calculation

The measurement and calculation of  $S_e$  are carried out using the customized equipment setup shown in **Figure 3.1 (a) and (b)**. Two commercial Peltier chips are employed as the hot side and cold side to generate the temperature difference. A glass substrate is used for electrical insulation. Copper tape electrodes, with a width of approximately 5 millimeters, are placed at the ends of the sample, with one end connected to the hot side and the other to the cold side. To prevent moisture loss during long-term electrochemical measurements, the sample is wrapped in Parafilm. The open-circuit voltage is recorded at the electrochemical workstation (CHI Instruments Inc. USA, Model 660E), and the temperature is measured using an infrared thermometer. The thermopower is calculated using the following formula:

$$S_e = -\frac{V_h - V_c}{T_h - T_c} \frac{d_1}{d_2}$$

Where  $V_h$  and  $V_c$  are the voltage at hot and cold sides, respectively.  $T_h$  and  $T_c$  is the temperature at hot and cold sides, which is measured by an infrared thermometer.  $d_1$  is the distance between two electrodes, while  $d_2$  is the distance between two temperature detecting points.

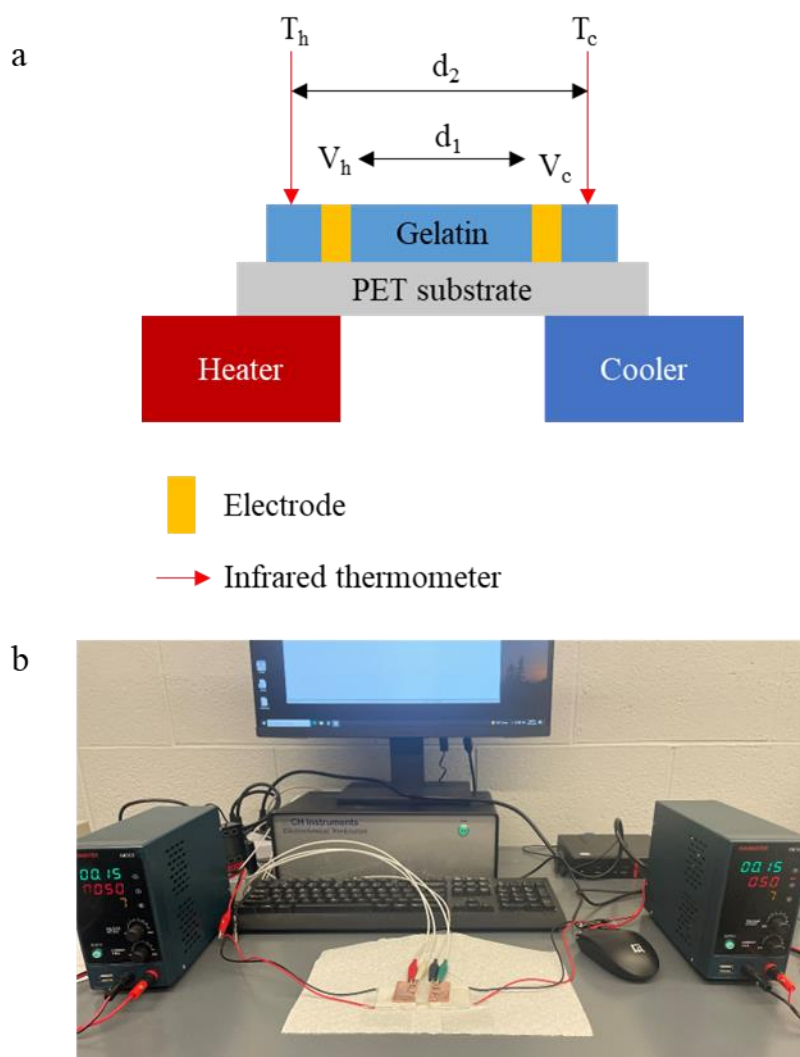


**Figure 3.1** (a) Schematic of experimental setup and (b) image of the platform for thermopower measurements.

### 3.3 Results and Discussion

#### 3.3.1 Ions selection for thermopower and heat resistance

In order select the best ions for thermopower. The introduction of different ions changes the interaction between water and gelatin, modifying their molecular structure, thereby affecting the maximum working temperature of gelatin-based thermoelectric devices.

We measured ion modulated thermopower for gelatin hydrogel without  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$  redox pair. The results of ions modulated thermopower and heat

resistance in gelatin hydrogel is shown in **Table 1**. Open-circuit voltage with temperature increasing is measured versus time, which is shown in **Figure 3.2**. Over time, the output power of the power source is changed at a certain rate to change the temperature on the hot side. With an increase in temperature, the open circuit voltage of gelatin-based thermoelectric devices increases. Compared to KCl, Gelatin- $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$  has a higher working temperature, allowing it to function over a broader temperature range, even under extreme conditions, as shown in **Figure 3.2 (a) and (b)**.

Compared to pure gelatin hydrogel and samples containing other soluble ions, KCl gelatin hydrogel exhibits a higher Seebeck coefficient, reaching up to 3.17 mV/K (**Table 1**). However, the maximum operating temperature of KCl gelatin is close to that of pure gelatin, approximately 35°C. Thus, KCl gelatin's limited heat resistance falls short of meeting the requirements for a high-temperature thermoelectric cell.

In contrast,  $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$  gelatin hydrogel has a relatively lower Seebeck coefficient, at 2.30 mV/K, but it still surpasses pure gelatin. Moreover,  $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$  gelatin boasts the highest maximum operating temperature, reaching as high as 90.2°C, indicating strong heat resistance. Therefore,  $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$  has been chosen as the soluble ion additive for the scaffold for adding  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$  redox pair.

**Table 1.** Measured Seebeck coefficient and maximum working temperature of the gelatine hydrogel thermoelectric cell with different soluble ions.

| Sample | The ions (1.5M) in 20% gelatin              | Seebeck Coefficient(mV/K) | Maximum working temperature (°C) |
|--------|---------------------------------------------|---------------------------|----------------------------------|
| 1      | $\text{Li}_2\text{CO}_3$                    | 0.803                     | 37.4                             |
| 2      | $\text{Li}_2\text{SO}_4$                    | 0.70                      | 40.1                             |
| 3      | $\text{CH}_3\text{CO}_2\text{Li}$           | 2.14                      | 43.5                             |
| 4      | $\text{NaCl}$                               | 2.66                      | 40.8                             |
| 5      | $\text{CH}_3\text{CO}_2\text{Na}$           | 1.7                       | 47.7                             |
| 6      | $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ | 2.30                      | 90.2                             |
| 7      | $\text{Na}_2\text{SO}_4$                    | 2.52                      | 37.6                             |
| 8      | $(\text{CH}_3\text{CO}_2)_2\text{Mg}$       | 1.69                      | 48.4                             |

|    |                                            |       |      |
|----|--------------------------------------------|-------|------|
| 9  | $\text{CH}_3\text{CO}_2\text{K}$           | 1.892 | 41.4 |
| 10 | $\text{C}_6\text{H}_5\text{K}_3\text{O}_7$ | 2.01  | 84.0 |
| 11 | $\text{K}_2\text{SO}_4$                    | 1.96  | 43.5 |
| 12 | $\text{KCl}$                               | 3.17  | 35.4 |
| 13 | $\text{FeSO}_4$                            | 0.84  | 40.1 |
| 14 | $\text{C}_6\text{H}_5\text{FeO}_7$         | 0.82  | 44.0 |
| 15 | $\text{CaCO}_3$                            | 1.389 | 36.4 |
| 16 | Pure gelatin                               | 1.77  | 35   |

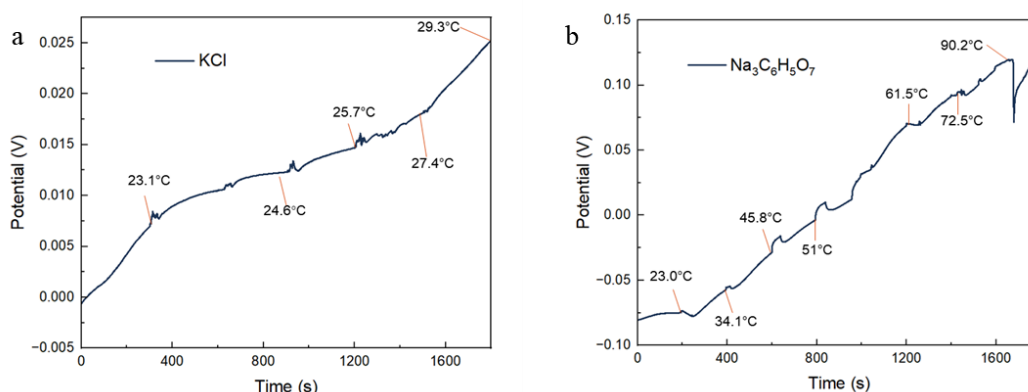


**Figure 3.2** Open circuit potential measurements of (a) Gelatin-KCl and (b) Gelatin- $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ .

### 3.3.2 Thermopower and heat resistance of gelatin-based hydrogels with selected ions

**Figure 3.3 (a)** shows the thermopower of the Gelatin hydrogel thermoelectric cells of Gelatin- $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ , Gelatin-KCl, and Gelatin- $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7\text{-FeCN}^{3-/4-}$ . As shown in **Table 1**, Gelatin-KCl thermoelectric cell exhibits the highest thermopower, reaching up to 3.17 mV/K, whereas Gelatin- $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$  thermoelectric cell has a thermopower of only 2.30 mV/K. However, with the addition of  $\text{FeCN}^{3-/4-}$  to the Gelatin- $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$  gelatin system, the thermopower of the thermoelectric cell significantly increases (**Figure 3.3a**). This results in the Gelatin- $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7\text{-FeCN}^{3-/4-}$  thermoelectric cell with a high thermopower of up to 7.33

mV/K and strong high-temperature resistance, capable of operating at temperature as high as 90°C. As shown in **Figure 3.3 (b)**, compared to previously reported hydrogel thermoelectric devices based on individual thermoelectric effects, the Gelatin- $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7\text{-FeCN}^{3-/4-}$  thermoelectric cell exhibits a high Seebeck coefficient and an exceptionally high maximum working temperature, surpassing all the previously reported thermoelectric cells.

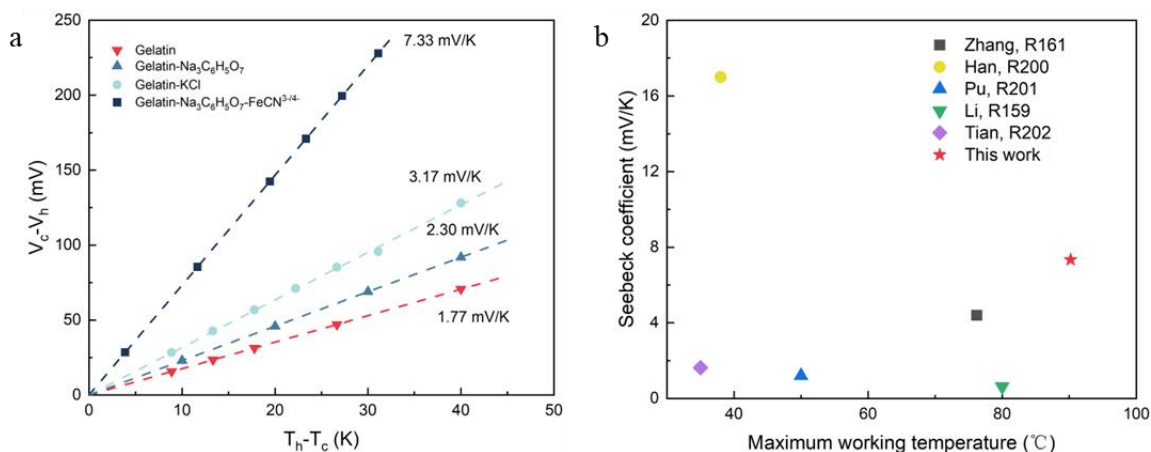


**Figure 3.3** (a) Thermopower measurement for the hydrogel thermoelectric cells of Gelatin, Gelatin- $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ , Gelatin-KCl, and Gelatin- $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7\text{-FeCN}^{3-/4-}$ . (b) The comparison of the Seebeck coefficient and maximum working temperature of the hydrogel thermoelectric cell in this work with previously reported results.

### 3.4 Summary

In this work, a gelatin-based hydrogel thermoelectric cell, containing soluble ions and exhibiting high thermoelectric performance, was prepared, and its maximum Seebeck coefficient can reach 7.33 mV/K. Most importantly, the hydrogel thermoelectric cell exhibits excellent high-temperature resistance and can work effectively at around 90°C. This work lays the foundation for the application of quasi-solid thermoelectric cells in high-temperature environments and provides a promising route for further research.

## **Conclusion**

This thesis is dedicated to temperature resistance wearable sensors and thermoelectric batteries based on hydrogels, with a particular emphasis on investigating methods to enhance their temperature resistance at low and high temperature.

In the first study, an anti-freezing hydrogel based on Polyvinyl alcohol is synthesized. The mechanical properties of the hydrogel are improved by introducing substances such as borax and chitin. The incorporation of an ionic liquid enhances the low-temperature resistance of the hydrogel. Through a series of experiments, it is demonstrated that this hydrogel has the potential for use as a wearable strain sensor in low-temperature environments.

In the second study, a hydrogel-based thermoelectric cell is designed using gelatin hydrogel. By introducing and selecting different soluble ions, the thermoelectric cell based on the hydrogel is endowed with higher thermal power. Simultaneously, this hydrogel-based thermoelectric cell also exhibits excellent high-temperature resistance, showcasing its significant potential as a high-temperature thermoelectric device.

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