

**Composite Based Polymer Gel Electrolyte for  
Thermoelectrochemical Cell Applications**



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(2024)

# **Composite Based Polymer Gel Electrolyte for Thermoelectrochemical Cell Applications**



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A thesis submitted to the National University of Sciences and Technology, Islamabad,

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Nanoscience and Engineering

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(2024)

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
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## DEDICATION

*"I would like to dedicate this thesis work to Allah **"The Creator"** (SubhanahuWaTa'ala) Almighty, my beloved **father, mother, grandmother** and **siblings** whose love, presence and unwavering support have been the cornerstones of my life. I am certain they would be filled with immense joy to witness my achievement of completing a Master in Nanoscience Engineering from SCME (NUST). I cherish every memory and lesson they bestowed upon me, and I carry their spirit in every challenge I overcome.*

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## LIST OF SYMBOLS, ABBREVIATIONS AND ACRONYMS

|      |  |
|------|--|
| TEC  | Thermoelectrochemical Cell             |
| TDC  | Thermodiffusion Cell                   |
| TE   | Thermoelectric Cell                    |
| PVA  | poly(vinyl alcohol)                    |
| PAM  | Polyacrylamide                         |
| PANI | Polyaniline                            |
| GE   | Gel Electrolyte                        |
| GPE  | Gel Polymer Electrolyte                |
| CMC  | Carboxymethyl Cellulose                |
| DMF  | Dimethylformamide                      |
| ECS  | Energy Conversion Systems              |
| XRD  | X-Ray Diffraction                      |
| SEM  | Scanning Electron Microscope           |
| FTIR | Fourier Transformation Infrared        |
| CV   | Cyclic Voltammetry                     |
| EIS  | Electrochemical Impedance Spectroscopy |

## ABSTRACT

The need for efficient and renewable ways to generate electricity is increasing as the world faces an ongoing energy crisis. Energy harvesting technologies like Thermo-electrochemical cells (TECs) are promising solution in this scenario which converts heat into electricity. This research explores the development and performance analysis of gel polymer electrolytes (GPEs) for TECs, focusing on a composite made from carboxymethyl cellulose (CMC), polyaniline (PANI), potassium ferricyanide ( $K_3[Fe(CN)_6]$ ) and potassium ferrocyanide ( $K_4[Fe(CN)_6]$ ), which is incorporated into copper (Cu) electrodes for use in wearable devices. The electrochemical testing of the Gel electrolyte was performed which involved four different compositions, specifically with 0.01g, 0.02g, 0.03g, and 0.04g of polyaniline (PANI) relative to carboxymethyl cellulose (CMC). Among these, the composition with 0.03g PANI exhibited the best performance and was subsequently selected for thermoelectric cell (TEC) testing. The p-type TECs demonstrated a significant increase in its seebeck coefficient 4.02mV/K at the temperature difference ( $\Delta T$ ) 30°C. The device showed a stable thermosensitive response over a wide temperature range of 5°C to 35°C, well-suited for typical operating conditions of wearable electronics and sensors. At  $\Delta T = 30^\circ C$ , the TEC produced a voltage output of 141mV. Furthermore, connecting two p-type TECs in series resulted in a cumulative boost in the overall voltage output.

**Keywords:** Thermo-electrochemical Cell, Polyaniline, Gel Electrolyte, Energy Storage, Seebeck Effect, Redox Active Polymer Gel Electrolyte.

# CHAPTER 1: INTRODUCTION

## 1.1 Motivation

The rising global demand for energy, coupled with concerns over climate change, has driven the need for sustainable and efficient energy solutions. Traditional energy generation methods, heavily reliant on fossil fuels, are not only limited but also contribute significantly to greenhouse gas emissions. These pressing environmental concerns underscore the importance of developing renewable and sustainable energy systems. Thermoelectric and thermoelectrochemical cells are emerging as promising technologies for harnessing waste heat, which is a byproduct of industrial processes, electronic devices, and even human activities. This vast source of low-grade waste heat remains largely untapped, and its effective utilization could significantly contribute to global energy efficiency[1].

The core motivation for this research lies in addressing the challenge of efficiently capturing and converting waste heat into electrical energy. TECs, which operate based on redox reactions driven by temperature gradients, offer a novel and sustainable solution. While the fundamental principles of TECs have been well-established, their widespread application has been limited by the performance of the electrolytes used within the cells[2].

Gel polymer electrolytes (GPEs) have gained considerable attention for their potential to overcome the limitations of conventional liquid electrolytes, which, although highly conductive, pose several practical challenges such as leakage, low thermal stability, and incompatibility with flexible devices. Solid electrolytes, though structurally stable, often suffer from low ionic conductivity, which hinders their effectiveness in TECs [3].

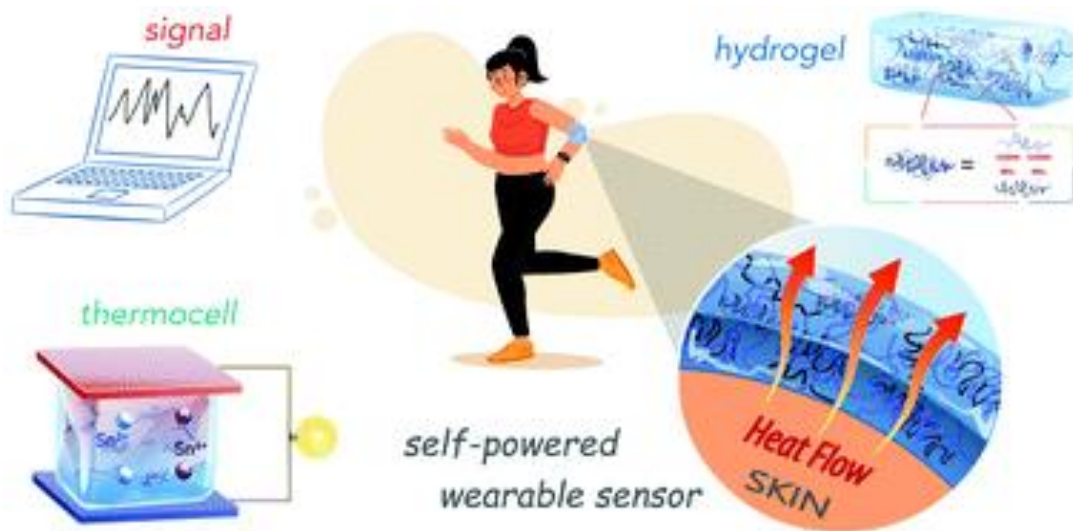
The societal and industrial implications of this research are profound. TECs integrated with GPEs could reduce global energy consumption by capturing waste heat and transform it into electricity for usage. This would not only enhance energy efficiency but also contribute to reducing the carbon footprint of various industries, aligning with global efforts to mitigate climate change [2].



Additionally, the ability to harvest and convert waste heat into electricity is highly attractive for industries such as manufacturing, transportation, and power generation, where significant amounts of energy are lost as heat. TECs with GPEs could be retrofitted to existing systems, capturing this lost energy without requiring additional fuel, thereby improving the overall efficiency of industrial processes.

In wearable technology, TECs that utilize body heat to power electronic devices, such as health monitors and sensors, offer a new level of autonomy. These devices could operate without the need for frequent battery replacements, significantly extending their operational life and convenience [4].

Thus, this research is motivated by the opportunity to address key energy challenges through the development of advanced materials that enhance the efficiency and applicability of TECs technologies. By focusing on the synthesis and optimization of GPEs, this work aims to contribute to the growing field of sustainable energy conversion and storage solutions, opening new possibilities for industrial applications and consumer devices.



**Figure 1.1:** Schematic showing TEC based self-powered wearable sensor [4].

## 1.2 Background

Tremendous efforts have been directed toward the development of energy conversion systems that can efficiently harvest waste heat and convert it into electricity. Among the most prominent technologies are thermoelectric devices (TEs), thermodiffusion cells (TDCs), and thermocells [5]. Each of these technologies operates on different principles, yet all share the common goal of converting thermal energy into electrical energy by exploiting temperature gradients. This approach is critical for enhancing the energy efficiency of industrial processes, electronic devices, and transportation systems, where significant amounts of energy are lost as waste heat.

### 1.2.1 Energy Conversion Systems (ECS) Overview

Waste heat, generated in a variety of industrial, transportation, and electronic processes, represents a significant energy source that is typically lost to the environment. Globally, an estimated two-thirds of the energy consumed in industrial processes is lost as heat. Harnessing even a fraction of this waste heat can lead towards the improvements in energy yield and reduced the hazardous gases in the environment. Various technologies have been developed to capture this thermal energy and convert it into electricity, with the most prominent being thermoelectric devices (TEs), thermodiffusion cells (TDCs), and thermo-electrochemical cells (TECs).

### 1. Thermoelectric Devices (TEs)

Thermoelectric devices (TEs) rely on the Seebeck effect, a phenomenon where a temperature gradient across a material induces the movement of charge carriers (electrons and holes), generating an electrical current. TEs are composed of multiple n-type and p-type thermoelectric materials connected in series to form thermoelectric couples. The charge carriers within these materials move from the hot side to the cold side, driving an electric current through an external circuit. The efficiency of TEs is determined by the figure of merit ( $ZT$ ), a parameter that depends on the material's Seebeck coefficient, electrical conductivity, and thermal conductivity. High  $ZT$  values indicate more efficient thermoelectric materials [6].

Although TEs are solid-state devices with no moving parts, making them durable and reliable for specific applications such as space exploration and remote power generation, their practical use is forbidden by low Seebeck coefficients, typically in microvolts per Kelvin ( $\mu\text{V/K}$ ). This results in relatively low power output, especially for low-grade waste heat applications where the temperature difference is minimal.

## **2. Thermodiffusion Cells (TDCs)**

Thermodiffusion cells (TDCs), also known as Soret cells, operate based on the Soret effect or thermophoresis. This effect describes the migration of ions within an electrolyte in response to a temperature gradient. In TDCs, the movement of these ions generates an electric potential across two electrodes, producing electricity. Unlike TEs, which depend on the movement of electrons, TDCs leverage the mobility of ions in an electrolyte, making them a type of electrochemical cell [7].

TDCs are often considered more environmentally friendly than other energy conversion technologies because they do not rely on external pressure or hazardous chemicals. This makes them suitable for applications where minimal environmental impact is critical. However, TDCs have limitations that affect their broader adoption. Specifically, they tend to have lower temperature ranges as well as lower power output compared to other technologies like TECs. Moreover, their design requires complex, leak-proof cell structures to handle gaseous components, further complicating their scalability for industrial use. These drawbacks make TDCs less favorable for large-scale applications, although they still hold potential for specific, low-power applications where environmental considerations are paramount.

## **3. Thermo-electrochemical Cells (TECs)**

Thermo-electrochemical cells (TECs) are a promising alternative to both TEs and TDCs, particularly for capturing low-grade waste heat. TECs utilize redox couples dissolved in an electrolyte, where the temperature gradient between two electrodes drives redox reactions. The temperature gradient induces an electrochemical potential difference,

resulting in the movement of electrons through an external circuit, thus generating electrical power [8].

TECs stand out for their higher Seebeck coefficients, typically on the order of millivolts per Kelvin (mV/K), which allows them to produce significantly more power compared to TEs, even at relatively small temperature differences. This makes TECs particularly well-suited for capturing low-grade waste heat, which is abundant in many industrial settings but typically operates at lower temperatures (below 200°C). TECs are also flexible in terms of materials, allowing the use of liquid electrolytes, solid electrolytes, or gel polymer electrolytes (GPEs), depending on the specific application [4].

### **1.3 Thermo-electrochemical Cell**

Thermoelectrochemical cells (TECs), often referred to as Thermocell, are specialized devices designed to convert thermal energy into electrical energy by leveraging redox reactions that occur across a temperature gradient. Unlike traditional thermoelectric devices (TEs), which operate based on the Seebeck effect that generates electricity by the movement of electrons within solid materials, TECs generate power through ion transport in a liquid or gel electrolyte. This ion movement, induced by temperature differences between two electrodes, creates an electrochemical potential, which drives electrons through an external circuit to generate electricity [8].

TECs have attracted significant attention due to their ability to capture and convert low-grade waste heat, a common byproduct of numerous industrial processes, electronic devices, and even human body heat. Waste heat under 200°C, often considered too low for effective capture by traditional energy recovery systems, is abundant in industries such as manufacturing, automotive, and even in daily-use electronics. TECs offer a promising way to utilize this previously untapped energy source, thereby improving overall energy efficiency and reducing energy waste.

The core operating principle of TECs is based on the thermogalvanic effect, where a redox couple (e.g.,  $\text{Fe}^{2+}/\text{Fe}^{3+}$  or  $\text{I}^-/\text{I}_3^-$ ) dissolved in the electrolyte undergoes oxidation and reduction reactions at different temperatures. When a temperature gradient is applied

between the two electrodes of the TEC, the redox reactions become thermodynamically favored on the hot side and less favored on the cold side, creating an electrochemical potential. This potential forces electrons to flow from the hot electrode (where oxidation occurs) to the cold electrode (where reduction occurs), through an external circuit, producing electrical power [9].

TECs are composed of three key components: **electrodes**, **electrolyte**, and the **external circuit**. The electrodes, typically made of conductive materials such as platinum, carbon, or metals, are the sites where oxidation and reduction reactions occur, driven by a temperature difference between them. The electrolyte acts as a medium that allows ions to move between the electrodes during these reactions, and it can be in liquid, gel, or solid form, with common redox couples like  $\text{Fe}^{2+}/\text{Fe}^{3+}$  or  $\text{I}^-/\text{I}_3^-$  facilitating ion transport. Lastly, the external circuit connects the electrodes, enabling the flow of electrons generated by the redox reactions, which produces electrical power. These components work together to convert thermal energy into electrical energy efficiently through a temperature gradient [8, 9].

### *1.3.1 History of Thermoelectrochemical Cells (TECs)*

The history of **thermoelectrochemical cells (TECs)** is intertwined with advances in thermoelectricity and electrochemistry, particularly in harnessing temperature gradients to generate electrical energy. The roots of TECs can be traced back to the early 19th century when **Thomas Johann Seebeck** discovered the **Seebeck effect** in 1821, demonstrating how a temperature difference across two materials could generate an electric current [10]. While this discovery primarily influenced the development of solid-state thermoelectric devices (TEs), later research recognized the potential to apply similar principles using liquid electrolytes, leading to the development of TECs.

By the mid-20th century, scientists began exploring how redox reactions could harness thermal energy for electricity generation. Early TEC designs utilized various redox couples, such as **iron(II)/iron(III)** and **iodine/iodide**, which proved capable of converting low-grade waste heat into electrical power [11]. Despite their potential, these early TECs were constrained by challenges in maintaining electrolyte stability and

consistent temperature gradients. The global oil crises of the 1960s and 1970s revitalized interest in TECs, as they were explored as a solution for recovering industrial waste heat, providing an energy-efficient alternative in energy-hungry sectors.

The late 20th century brought significant advancements in TEC technology, particularly with the introduction of **gel polymer electrolytes (GPEs)**. GPEs overcame many of the limitations associated with liquid electrolytes, such as leakage and evaporation, while maintaining high ionic conductivity and flexibility[12]. This innovation enabled TECs to expand their applications into wearable technology and portable electronics, as the enhanced material properties supported more stable and efficient energy conversion system[5].

Further advancements in **nanotechnology** and the development of **Gel electrolytes** have improved TEC performance, allowing them to operate more effectively under smaller temperature gradients. These improvements have broadened the scope of TEC applications, including their integration into modern energy systems for industrial waste heat recovery and consumer electronics.

Today, TECs are recognized for their potential in sustainable energy harvesting, and research continues to focus on optimizing redox couples, electrode materials, and electrolyte formulations to improve efficiency and scalability[13]. By converting low-grade waste heat into electricity, TECs are increasingly being utilized in industries seeking to enhance energy efficiency while minimizing environmental impact.

### *1.3.2 Applications of Thermoelectrochemical Cell*

#### **Wearable Devices:**

- Ideal for powering devices such as smartwatches, fitness trackers, and health monitors.
- Converts body heat into electricity, providing continuous operation without the need for batteries

### **Medical Implants:**

Powers devices like pacemakers and other medical implants using body heat.

- Reduces the need for invasive battery replacements, enhancing patient comfort and safety

### **Automotive Applications:**

- Harvests waste heat from car engines to power auxiliary systems.
- Improves fuel efficiency and reduces overall emissions

### **Industrial Waste Heat Recovery:**

- Captures low-grade heat from manufacturing processes.
- Converts waste heat into usable energy, improving energy efficiency in industrial settings

### **Portable Electronics:**

- Powers smartphones, tablets, and portable chargers using ambient heat.
- Extends battery life and provides a sustainable energy source on the go

### **Space Exploration:**

- Converts heat from solar radiation and spacecraft equipment into electrical power.
- Ensures a reliable energy supply in extreme space conditions

### **Military Gear:**

- Powers communication devices and sensors embedded in military uniforms using body heat.

- Reduces reliance on external power sources

#### **Smart Fabrics:**

- Integrated into textiles to harvest body heat.
- Powers small electronics like wearable sensors, providing convenient energy solutions

#### **Energy Harvesting for IoT Devices:**

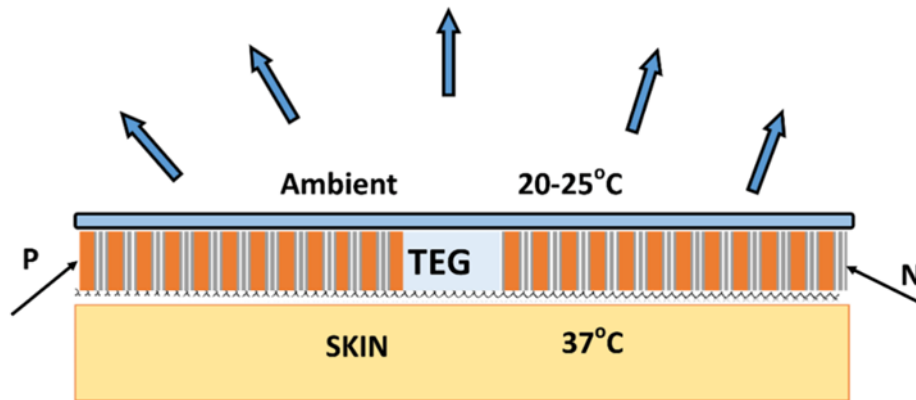
- Enables self-powered IoT sensors and systems.
- Improves device autonomy and operational lifetimes in remote locations where traditional power sources are unavailable[14]

#### *1.3.3 Working Principle of Thermochemical Cell*

A TEC functions by converting thermal energy into electrical energy through redox reactions that are driven by a temperature gradient between two electrodes. Unlike conventional thermoelectric devices, which rely on electron movement due to the Seebeck effect, TECs utilize ion transport within an electrolyte to generate an electrochemical potential difference. This potential difference facilitates electron flow through an external circuit, thereby generating electrical power[15].

The key components of a TEC include two electrodes, an electrolyte, and an external circuit. The electrodes, typically made of conductive materials like platinum or carbon, serve as the sites for oxidation and reduction reactions. The electrolyte, which can be in liquid, gel, or solid form, contains redox-active species, such as  $\text{Fe}^{2+}/\text{Fe}^{3+}$  or  $\text{I}^-/\text{I}_3^-$ , that participate in the redox reactions occurring at the electrodes [8].





. **Figure 1.2:** Schematics representation of a TEG wristband for harvesting body heat. [12]

**1. Establishment of a Temperature Gradient:** The operation of TECs begins with creating a temperature difference between the two electrodes. One electrode is maintained at a higher temperature (hot side), while the other is kept at a lower temperature (cold side). This temperature gradient is crucial for driving the redox reactions within the cell.

**2. Redox Reactions at the Electrodes:** At the hot electrode, oxidation occurs, while reduction takes place at the cold electrode. The temperature difference causes ions in the electrolyte to migrate toward the colder side. For instance, in a system utilizing  $\text{Fe}^{2+}/\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  ions are oxidized at the hot electrode, releasing electrons. These electrons then travel through the external circuit to the cold electrode, where they facilitate the reduction of  $\text{Fe}^{3+}$  ions back to  $\text{Fe}^{2+}$ .

**3. Ionic and Electron Transport:** As ions move between the hot and cold electrodes through the electrolyte, electrons generated by oxidation flow through the external circuit to the cold electrode, creating an electric current. This movement of electrons generates electrical power. As long as a temperature gradient is maintained between the electrodes, redox reactions continue, allowing the TEC to keep producing electricity[13]. The efficiency of this process depends on factors such as the redox couple used, the electrolyte's conductivity, and the magnitude of the temperature difference.

#### 1.3.4 Material Attributes

The performance and efficiency of TECs are highly dependent on the materials

used for the electrodes, electrolytes, redox couples, and substrates. Each component must be carefully selected to optimize electrical conductivity, ion transport, and mechanical stability, particularly for flexible and wearable applications.

#### *1.3.5 Electrode Material*

The choice of electrode materials plays a critical role in determining the overall efficiency of TECs. Electrodes are essential components where redox reactions occur, and the properties of these materials dictate the efficiency of electron transfer, which is fundamental to the cell's operation. High electrical conductivity is required to facilitate the smooth flow of electrons between the electrodes. While platinum is widely used due to its superior conductivity and excellent catalytic properties, carbon-based materials such as graphene and carbon nanotubes are gaining popularity as cost-effective alternatives. These materials offer high conductivity while reducing the overall cost of TECs[14].

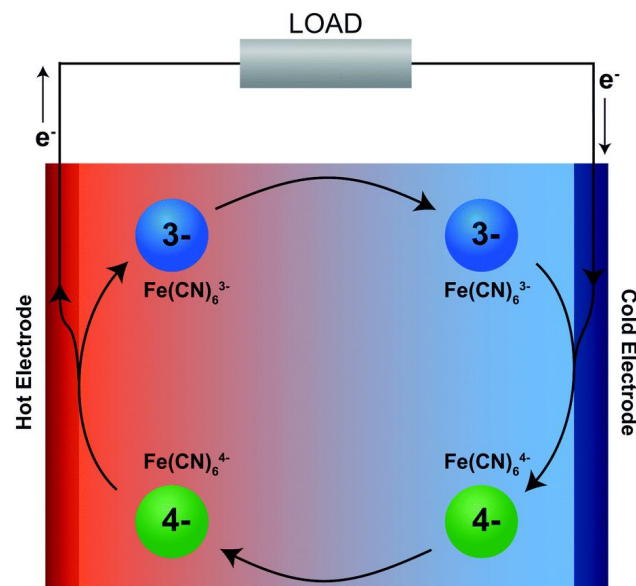
In addition to electrical conductivity, catalytic activity is another crucial factor that influences TEC efficiency. Materials with high catalytic activity accelerate the redox reactions, enhancing the kinetics and improving the overall performance of the cell. Platinum, again, is a preferred choice due to its outstanding catalytic properties, although carbon nanomaterials are becoming more popular due to their competitive catalytic efficiency and flexibility[15]. Flexibility is particularly important for applications in wearable and portable TECs, where electrodes must endure mechanical stress such as bending or stretching. Graphene and carbon nanotubes are well-suited for such applications because of their mechanical robustness and ability to maintain performance under deformation[14].

#### *1.3.6 Hot Side*

In TECs, the hot side refers to the electrode that is exposed to a higher temperature, typically sourced from industrial waste heat, electronic devices, or body heat in wearable applications. The elevated temperature induces oxidation reactions at the hot electrode, where ions in the electrolyte lose electrons. These electrons are transferred into the

external circuit, initiating the flow of electricity. Common redox-active species in the electrolyte, such as  $\text{Fe}^{2+}$  or  $\text{I}^-$ , undergo oxidation at the hot electrode[12].

As oxidation occurs, the ions in the electrolyte gain energy due to the temperature difference, which increases their mobility. This enhanced ion mobility is critical for TEC efficiency, as it ensures that ions migrate quickly toward the cold side of the cell. The performance of the hot side is influenced by the stability and conductivity of the electrode material under high temperatures.



**Figure 1.3:** Schematics representation of a TEG with hot, cold side and electrolyte [12].

Maintaining a consistent temperature gradient between the hot and cold sides is essential for sustaining efficient redox reactions and electron transfer. A larger temperature difference allows for more potential energy to be harnessed and converted into electrical power[16].

### 1.3.7 Cold Side

The **cold side** of the TEC is maintained at a lower temperature relative to the hot side. Here, reduction reactions occur as ions that migrated from the hot side are reduced at the cold electrode by gaining electrons that flow through the external circuit from the

hot electrode. This reduction process completes the electrochemical cycle, enabling continuous electricity generation[15].

On the cold side, materials must effectively catalyze reduction reactions while remaining stable under cooler thermal conditions. Stability under fluctuating temperatures is critical to ensure smooth progression of these reactions and to prevent material degradation over time.

In summary, while the hot side initiates oxidation reactions by supplying thermal energy, the cold side completes the cycle through reduction reactions. The interaction between these two sides, driven by the temperature gradient, forms the core operational mechanism of TECs. Proper material selection and maintenance of a stable temperature difference are vital for optimizing a TEC's efficiency in converting low-grade thermal energy into electrical power.

### *1.3.8 Electrolyte*

The **electrolyte** in TECs is a crucial component that facilitates ion transport between the hot and cold electrodes, enabling the redox reactions that generate electrical power. The electrolyte serves as the medium in which ions move, and its composition directly affects the efficiency, stability, and overall performance of the TECs[16]. The type of electrolyte used—whether liquid, gel, or solid—must meet specific requirements for ionic conductivity, thermal stability, and chemical compatibility to ensure optimal operation of the TEC.

For TECs, liquid electrolytes also need to maintain **high ionic conductivity** while withstanding significant temperature gradients between the hot and cold sides of the cell. To achieve this, the electrolyte must possess good conductance, at ambient temperature, ensuring that the ions can move efficiently between electrode[17]. However, the use of liquid electrolytes in TECs can be limited by risks like leakage, evaporation, and instability under extreme temperature conditions, which can affect long-term reliability and safety[18].

### *1.3.9 Evaluation of Thermochemical Cells (TECs)*

We need to analyze key parameters that determine TECs efficiency in converting thermal energy into electrical energy. These include the Seebeck coefficient, maximum power output (Pmax), thermal conductivity, and electrical conductivity. Below is a detailed explanation of each parameter, along with the relevant formulas and equations used to calculate them.

#### *1.3.10 Seebeck Coefficient*

The **Seebeck coefficient (S)** quantifies the voltage (or potential difference) generated per unit of temperature difference between the two electrodes as hot and cold. It is calculated as follows:

$$S = \frac{V_{oc}}{\Delta T} = \frac{\Delta S}{nF}$$

Where:

- S = Seebeck coefficient (V/K or mV/K)
- $V_{oc}$  = Open Circuit Voltage (V)
- $\Delta T$  = temperature difference between the hot and cold sides

The Seebeck coefficient is critical in determining how much electrical energy can be harvested from a given temperature gradient. For TECs, the Seebeck coefficient is generally higher than in traditional thermoelectric devices, often reaching values in the millivolt per Kelvin (mV/K) range. For instance, redox couples such as  $Fe^{2+}/Fe^{3+}$  and  $I^-/I_3^-$  are known to produce higher Seebeck coefficients, making TECs highly efficient at converting low-grade heat into electrical energy[19].

#### *1.3.12 Why Flexible TECs?*

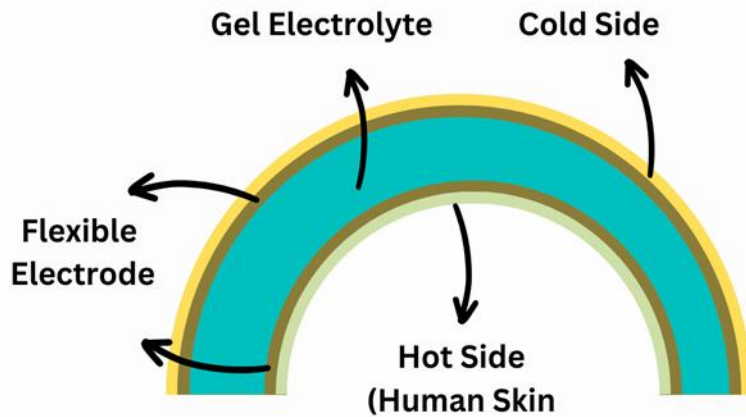
Flexible TECs are designed to harvest thermal energy and convert it into electrical power while offering the adaptability required in modern, dynamic applications. The flexibility of these devices allows them to be integrated into a variety of systems, including wearable technologies, portable energy sources, and industrial heat recovery systems. Unlike traditional rigid TECs, which are often bulky and less adaptable, flexible TECs

can conform to curve or moving surfaces, making them ideal for more versatile applications. These cells can effectively capture waste heat from various sources, including human body heat, electronic devices, and low-grade industrial heat[24].

Flexible TECs are particularly valuable in **wearable devices**, where the flexibility, bendability, and stretch-ability of power sources are critical. These devices can harvest body heat to power health monitoring systems, fitness trackers, or other wearable electronics without the need for frequent recharging. Human body heat is a consistent source of low-grade energy, and flexible TECs are optimized to capture and convert this into electrical energy. Such devices often require only small amounts of power, typically between 100 nW to 10 mW, to operate effectively [25].

Flexible TECs have emerged as a significant advancement in energy harvesting technologies, offering adaptable, lightweight, and portable power sources. Traditional TECs, while efficient at converting thermal energy into electrical energy, often suffer from rigidity and bulkiness, limiting their applicability in modern dynamic environments. The development of flexible TECs addresses these issues, creating new opportunities for their integration into wearable electronics, portable devices, and everyday textiles[26]. Research has shown that flexible TECs effectively power wearable devices, maintaining mechanical flexibility while enhancing user comfort. Beyond wearables, flexible TECs are ideal for portable energy applications. Devices that operate in remote or outdoor environments, such as camping gear or portable power banks, benefit from TECs embedded into lightweight structures.

The capacity of flexible TECs to conform to non-flat surfaces makes them suitable for integration into textiles and other everyday materials. Embedding TECs into fabrics or soft materials enables the creation of self-powered clothing that uses body heat to power small electronic devices. This capability is especially useful in military uniforms, outdoor gear, or medical devices that rely on constant heat generated by the human body or external sources[24].



**Figure 1.4:** Configuration of flexible wearable thermo-electrochemical cells

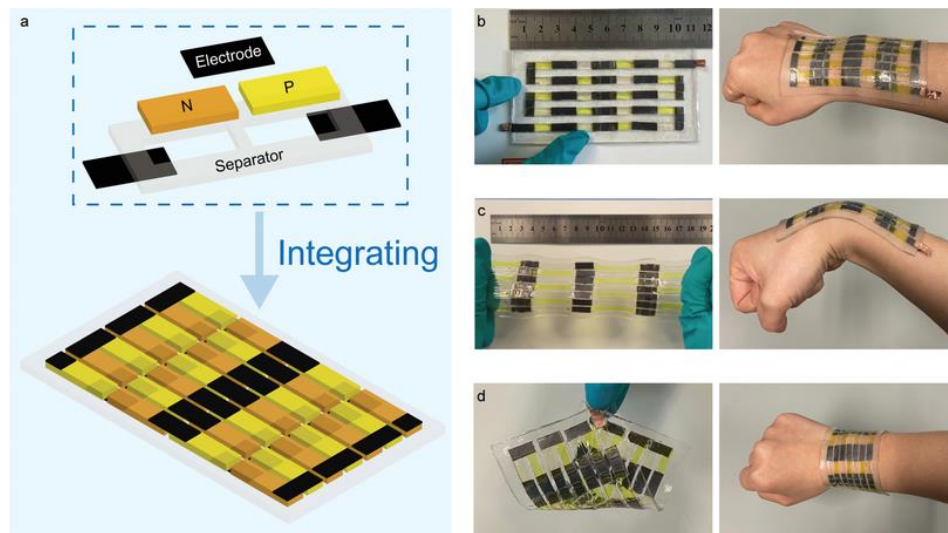
The green section represents the flexible gel polymer electrolyte, where the polymer matrix functions as a structural support, providing the necessary mechanical properties for the electrolyte. However, the polymer matrix itself does not usually participate in the redox reactions.

A key aspect of making TECs flexible and durable is using flexible electrodes and gel polymer electrolytes (GPEs). Traditional rigid electrodes are unsuitable for applications where flexibility and durability are essential. Flexible electrodes, made from materials like carbon nanomaterials, conductive polymers, or metallic nanowires, maintain electrical conductivity while allowing the device to bend or stretch. These electrodes ensure that the TEC continues performing well even when subjected to mechanical stress such as bending or twisting[5].

Moreover, flexible TECs are designed to endure mechanical stress, such as bending, stretching, or twisting, making them durable enough for various real-world applications. Their versatility ensures they can be used in challenging environments without compromising their energy-harvesting capabilities. Whether integrated into clothing, portable devices, or industrial equipment, flexible TECs maintain their performance even under constant movement or physical deformation[27].

### 1.3.13 Requirements for Flexible Thermo-electrochemical Devices

Flexible TECs are designed with similar principles as traditional TECs, but the materials used must accommodate stretching, compression, and twisting, particularly when used in wearable technologies. One of the essential components of flexible TECs is gel polymer electrolytes (GPEs), which provide the necessary flexibility while minimizing issues such as leakage, making them safe for wearable applications.



**Figure 1.5:** Wearable TEC integrated on the human body and undergoing various deformation [5]

GPEs also enhance temperature gradients by reducing thermal convection, improving the device's performance. However, challenges with GPEs include their higher viscosity and lower ionic conductivity compared to liquid electrolytes, which may reduce efficiency[28].

Flexible TECs typically consist of two flexible electrodes and a gel electrolyte, all encapsulated within materials such as polydimethylsiloxane (PDMS). PDMS is used for its thermal conductivity and mechanical flexibility, ensuring that the flexible TEC can maintain its functionality in various environmental conditions[29].

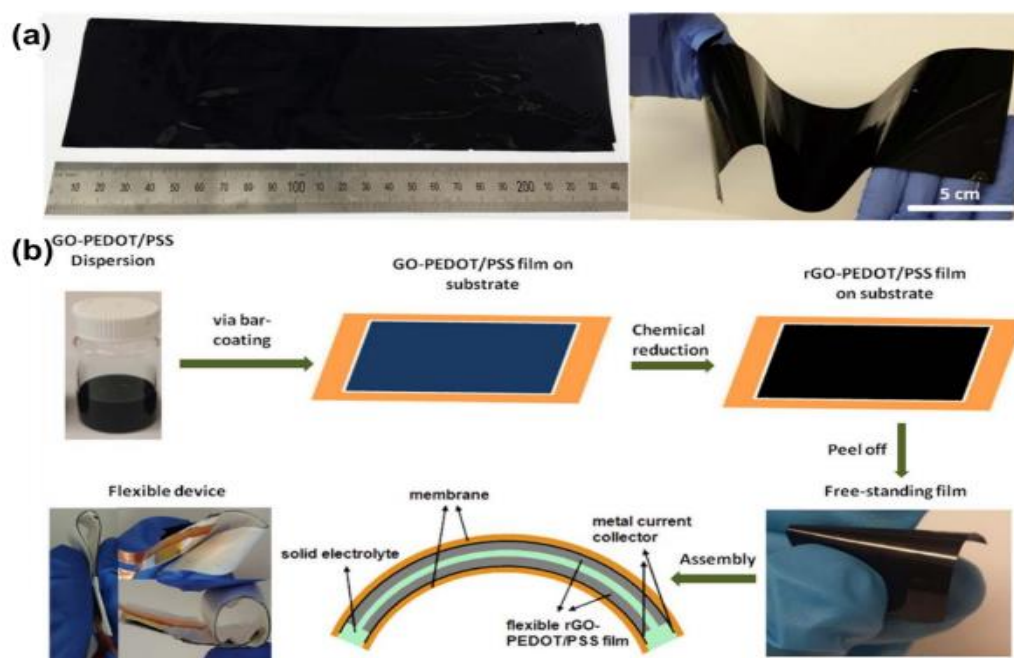


### 1.3.14 Flexible Electrodes

Flexible electrodes must balance high surface area, electrical conductivity, porosity, low tortuosity, and high thermal conductivity. These electrodes are often made from conducting polymers such as poly(3,4-ethylenedioxythiophene) (styrenesulfonate) (PEDOT), which offer flexibility and ease of preparation at a lower cost than traditional materials[30-33]

PEDOT has a conductivity of up to  $\sim 1000$  S/cm, making it a suitable choice for flexible electrode materials in TECs. It is also stable in air and water, making it versatile for various applications, including wearable electronics[34, 35].

However, one limitation of 2D polymer-based electrodes is their poor electrolyte penetration, which can impact electrochemical performance.



**Figure 1.6:** Photographs of the as-prepared, flexible PEDOT/PSS film and a schematic illustration of the rGO-PEDOT/PSS film preparation process, alongside the structure of the assembled supercapacitor devices [5].

Enhancing porosity through techniques like 3D printing or laser cutting could significantly improve the efficiency of redox reactions by allowing the GPE to better penetrate the electrode surfaces.

However, one limitation of 2D polymer-based electrodes is their poor electrolyte penetration, which can impact electrochemical performance. Enhancing porosity through techniques like 3D printing or laser cutting could significantly improve the efficiency of redox reactions by allowing the GPE to better penetrate the electrode surfaces.

### *1.3.15 Gel Electrolytes*

In flexible TECs, gel electrolytes (GEs) normally consist of a polymer framework, a crosslinker, a solvent, a redox couple, and a supporting electrolyte such as salt or acid. GEs need to strike a balance between high ionic conductivity, low thermal conductivity, and mechanical durability to maintain performance under stress[36]. A key challenge in developing GEs is optimizing the balance between mechanical flexibility and electrochemical efficiency. The ability to maintain the redox couple within the polymer matrix is essential for ensuring stable performance, making the concentration and molecular weight of the polymer crucial factors.

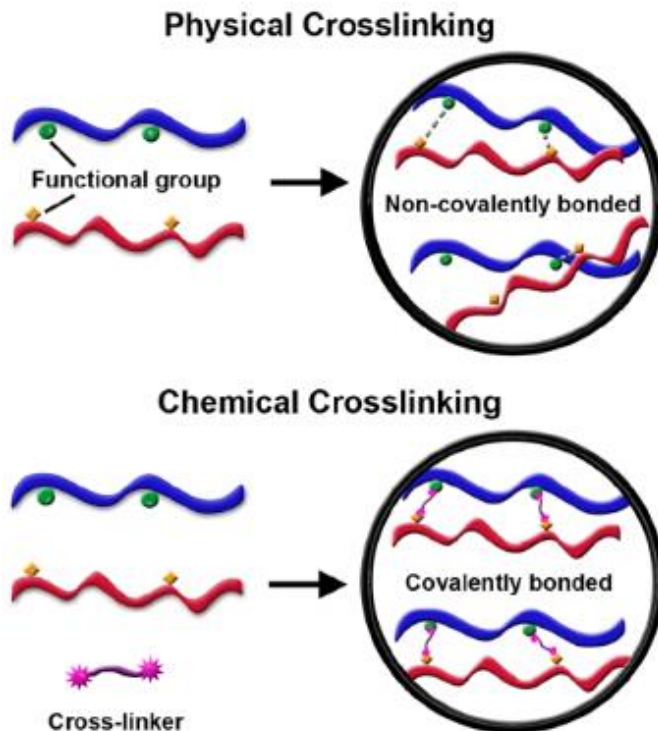
### **Crosslinking Strategies**

Crosslinking is a crucial process for stabilizing the polymer matrix in GEs, linking polymer chains together to form a cohesive network. There are two primary types of crosslinking: physical and chemical.

Physical crosslinking involves interactions such as hydrogen bonding or entanglement of polymer chains, producing reversible gels that can decompose at higher temperatures. This method is advantageous when incorporating highly reactive redox couples without requiring additional crosslinkers [37].

Chemical crosslinking forms permanent covalent bonds through chain-growth

polymerization or condensation reactions. Although this method provides greater stability, it may not always be compatible with certain redox couples such as  $\text{Fe}^{2+}/\text{Fe}^{3+}$  or  $[\text{Fe}(\text{CN})_6]^{3-}/^{4-}$  [38] .



**Figure 1.7:** Graphical representation of physical and chemical cross-linking [5]

The compatibility between the redox couple and the polymer matrix is a key challenge, and future research is needed to develop multifunctional hydrogels that can support both N-type and P-type redox couples in diverse environments.

#### 1.4 Limitations of Thermoelectrochemical Cell

TECs offer significant potential for energy harvesting, particularly from low-grade waste heat, but several limitations hinder their widespread application. Below are key challenges faced by TECs, which affect their efficiency, material properties, and operational viability.

#### *1.4.1 Low Power Density*

A major limitation of TECs is their relatively low power density when compared to traditional energy-harvesting technologies like thermoelectric devices (TEs) or batteries. TECs typically generate modest amounts of electrical power, which may be insufficient for applications with high power demands. The efficiency of TECs is largely dependent on the Seebeck coefficient and the temperature gradient between the electrodes. Although TECs are adept at converting low-grade heat into electrical energy, the power output remains limited, especially when minor temperature differences are involved. As a result, TECs are more suited for small-scale applications like wearable electronics or sensors, rather than large-scale industrial energy production [38].

#### *1.4.2 Slow Reaction Kinetics*

Another significant limitation of TECs is the slow reaction kinetics associated with the redox processes at the electrodes. Redox reactions in TECs rely on the movement of ions between the hot and cold electrodes, and the speed of these reactions has a direct impact on overall system efficiency. Common redox couples, such as  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and  $\text{I}^-/\text{I}_3^-$ , introduce kinetic barriers that slow the oxidation and reduction processes. While catalytic materials like platinum and carbon-based nanomaterials can help speed up these reactions, the overall reaction rates are still slower than in traditional thermoelectric devices. This slower reaction rate can reduce TEC efficiency, particularly in real-world operating conditions.

#### *1.4.3 Limited Operating Temperature Range*

TECs are primarily effective in low-temperature applications, which restricts their usefulness in broader energy-harvesting contexts. TECs operate most efficiently when converting waste heat in the range of 30°C to 200°C, but their performance deteriorates at higher temperatures, where solid-state thermoelectric devices tend to be more effective. This limited temperature range makes TECs suitable mainly for low-grade heat recovery, rather than for high-temperature industrial processes, where more substantial amounts of energy can be harnessed [29].

#### *1.4.4 Long-Term Stability and Degradation*

The long-term stability of TEC components, especially the electrodes and electrolytes, remains a challenge. Prolonged exposure to temperature variations, mechanical stress, and corrosive electrolytes can degrade the materials used in TECs over time. Liquid electrolytes are prone to evaporation or leakage, which can reduce the ion transport efficiency between the electrodes. Additionally, electrode materials may experience fouling or reduced catalytic activity over time, further diminishing the cell's performance[39].

#### *1.4.5 Complexity of Material Synthesis*

The advanced materials used in TECs, such as carbon nanomaterials for flexible electrodes or GPEs for electrolytes, often require complex and costly synthesis processes. For example, platinum, a common catalytic material used in TECs, is expensive and raises the overall cost of manufacturing these cells. Moreover, scalable production methods for flexible electrodes and GPEs have yet to be fully developed. The cost and complexity of material synthesis can hinder the commercial viability of TECs, making them less competitive with other energy-harvesting technologies[39]

#### *1.4.6 Sensitivity to Temperature Gradients*

TECs depend on maintaining a stable temperature gradient between the hot and cold electrodes. Any fluctuations in this gradient can dramatically affect the cell's efficiency. For instance, in outdoor environments where temperatures can fluctuate significantly, maintaining consistent energy output is challenging. Additionally, when the temperature gradient is minimal, TECs are less efficient at converting heat into electrical energy, further limiting their usefulness in environments with variable thermal conditions.

#### *1.4.7 Low Ionic Conductivity in Solid Electrolytes*

While solid electrolytes offer better thermal and mechanical stability than their liquid counterparts, they generally exhibit lower ionic conductivity. This slower ion mobility reduces the speed at which ions can travel between the hot and cold electrodes,

negatively impacting the overall efficiency of the TEC. Although GPEs offer a middle ground, combining the stability of solid electrolytes with the higher ionic conductivity of liquids, their performance still needs improvement to reach practical levels for widespread use[3].

### **1.5 Significance and Research Objectives**

The primary objective of this research is to evaluate the performance of **Gel Electrolyte (GE)** for TECs. As energy conversion devices have gained significant attention and become increasingly widespread, but emerging technologies like TECs still require further investigation to address their limitations. TECs offer a sustainable and efficient alternative for energy harvesting, especially from low-grade heat sources. However, the development of suitable materials, particularly in electrolytes and electrodes, remains a challenge. In this context, this study aims to explore the potential of GEs as innovative materials for TECs, focusing on their ability to enhance ion transport, thermal stability, and overall energy conversion efficiency.

### **1.8 Research Objectives**

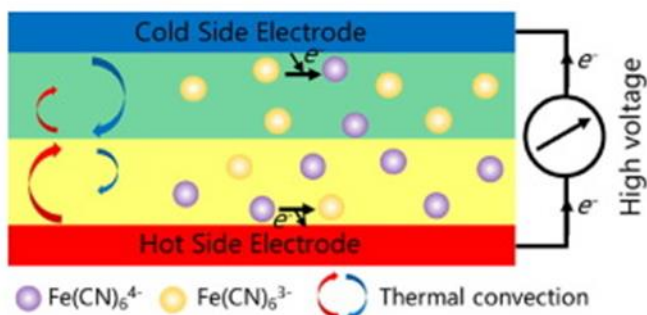
1. Synthesizing the Polyaniline and CMC based Gel electrolyte using wet chemistry route.
2. Synthesis of flexible TEC.
3. Electrochemical and Thermoelectrochemical Testing of the fabricated TEC Device.

## CHAPTER 2: LITERATURE REVIEW

### 2.1 Historical Background

Thermoelectrochemical cells (TECs) have a rich historical background, evolving from early work on thermoelectric devices (TEs) that harnessed temperature differences to generate electricity. Initially, TECs relied on liquid electrolytes, which offered high ionic conductivity but were limited by issues such as leakage, volatility, and poor mechanical stability. Researchers sought to overcome these challenges by developing gel polymer electrolytes (GPEs), which emerged as a critical advancement in the early 21st century. Early studies laid the groundwork for the use of GPEs in various energy conversion devices, with poly(ionic liquids) and high lithium salt concentration ionic liquids being explored for their excellent thermal and mechanical properties [40, 41].

In recent years, the development of TECs has accelerated, driven by the increasing demand for efficient energy harvesting systems, especially in flexible and portable applications. The use of in situ polymerization techniques for GPEs has gained traction, particularly for lithium-ion batteries and other high-energy-density applications, showing promising results in terms of enhanced electrochemical performance and stability [41]. Research has expanded to focus on improving the properties of GPEs for a wider range of temperatures, with a specific interest in materials that can maintain performance under extreme conditions [42, 43].



**Figure 2.1:** Working of thermoelectrochemical Cell [11]

TECs have emerged as an innovative technology for converting thermal energy into electrical power, particularly by utilizing waste heat. TECs leverage temperature gradients to drive redox reactions at their electrodes, generating electricity as a result. A significant milestone in the development of TECs has been the advancement of gel polymer electrolytes (GPEs), which have substantially improved their efficiency and performance. GPEs combine the benefits of both liquid and solid electrolytes, offering high ionic conductivity necessary for ion transport during charge and discharge cycles while maintaining enhanced mechanical stability [45].

One of the key advantages of GPEs over traditional liquid electrolytes is their improved thermal stability and broader operational temperature range, making them well-suited for fluctuating environmental conditions. Additionally, GPEs offer enhanced safety by reducing the risk of leakage and flammability, common issues with liquid electrolytes. Recent innovations in GPEs have resulted in ionic conductivities of over  $0.6 \times 10^{-2}$  S/cm at room temperature, comparable to those of conventional liquid electrolytes used in lithium-ion batteries. As the demand for efficient and sustainable energy solutions grows, researchers are focusing on novel materials such as transition metal chalcogenides (TMCs), which offer higher specific capacities compared to traditional materials. For example, SnS and ZnS demonstrate specific capacities of 755 mAh/g and 962 mAh/g, respectively, which significantly enhance the energy densities of next-generation TECs [46].

## **2.2 Role of Electrolytes in Thermochemical Cells**

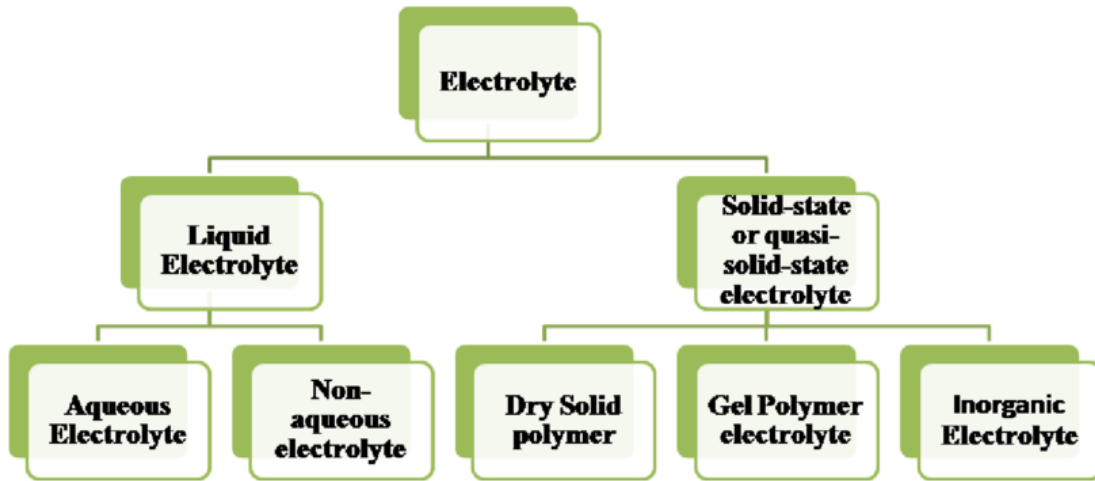
The role of electrolytes in TECs is critical to ensuring efficient conversion of thermal energy into electrical energy by facilitating ion transport between the anode and cathode.

In TECs, various types of electrolytes are employed to facilitate the conversion of thermal energy into electrical energy. The choice of electrolyte significantly influences the performance, efficiency, and operational stability of TECs. The primary categories of electrolytes used in TECs include aqueous electrolytes, non-aqueous electrolytes, molten salts, and solid electrolytes. Aqueous electrolytes are commonly used in TECs due to their fast ion diffusion and good compatibility with redox couples.



These electrolytes typically consist of water-based solutions containing salts or hydrophilic compounds that can undergo redox reactions. For instance,  $\text{KBr}/\text{Br}_2$  systems utilize bromine gas intercalation into graphite electrodes, enabling efficient charge transfer and energy conversion [12]. Other examples include solutions of potassium hydroxide ( $\text{KOH}$ ), lithium chloride ( $\text{LiCl}$ ), and sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), which have been shown to enhance electrochemical performance in activated carbon-based super-capacitors.

Solid electrolytes such as silver iodide ( $\text{AgI}$ ) and lead chloride ( $\text{PbCl}_2$ ) have also been explored for their potential to operate effectively at high temperatures while maintaining good ionic conductivity [8].



**Figure 2.2:** Classification of electrolytes [18]

The diverse range of electrolyte options enables researchers to tailor TEC designs for specific applications, ultimately enhancing their efficiency and practicality in real-world scenarios. Ongoing research continues to focus on optimizing electrolyte formulations and understanding the interactions between electrolytes and electrode materials to improve the overall performance of TECs. Recent studies have highlighted the importance of optimizing electrolyte composition and structure to enhance thermal conductivity and electrochemical performance, paving the way for more effective energy conversion technologies [5].

### 2.2.1 *Requirements of Electrolyte for TEC*

The ideal Gel Electrolyte for TECs must have several characteristics:

- ✓ High Ionic Conductivity
- ✓ Thermal Stability
- ✓ Mechanical Flexibility
- ✓ Chemical Compatibility
- ✓ Low Leakage Current
- ✓ Wide Electrochemical Stability Window
- ✓ Environmental Safety

### **2.3 Gel Electrolyte for Thermoelectrochemical Cell**

Gel electrolytes (GEs) have become an essential component in energy storage systems, particularly within TECs. They combine the benefits of both liquid and solid electrolytes by offering improved mechanical stability, flexibility, and reliable ionic conductivity. These properties are critical for modern applications like wearable devices, where the electrolyte must maintain performance despite frequent bending and deformation. The evolution of GEs focuses on enhancing electrochemical properties such as ionic conductivity and charge transfer efficiency, which are vital for efficient thermal-to-electric energy conversion. Recent research has led to optimized formulations that balance mechanical resilience and electrochemical performance, making GEs highly relevant in advanced TEC systems [47].

The importance of gel electrolytes extends beyond their flexibility and durability; they are crucial for improving the overall efficiency and safety of energy storage systems. GEs facilitate more efficient ion transport, which helps increase the overall performance of TECs while minimizing the risks associated with leakage, a common issue in liquid electrolytes. This makes GEs especially suitable for energy-harvesting applications in

portable and wearable devices, which often rely on body heat or other low-temperature sources. By providing both mechanical strength and improved ionic conductivity, GEs support the ongoing development of safer, more reliable energy storage technologies [5, 47].

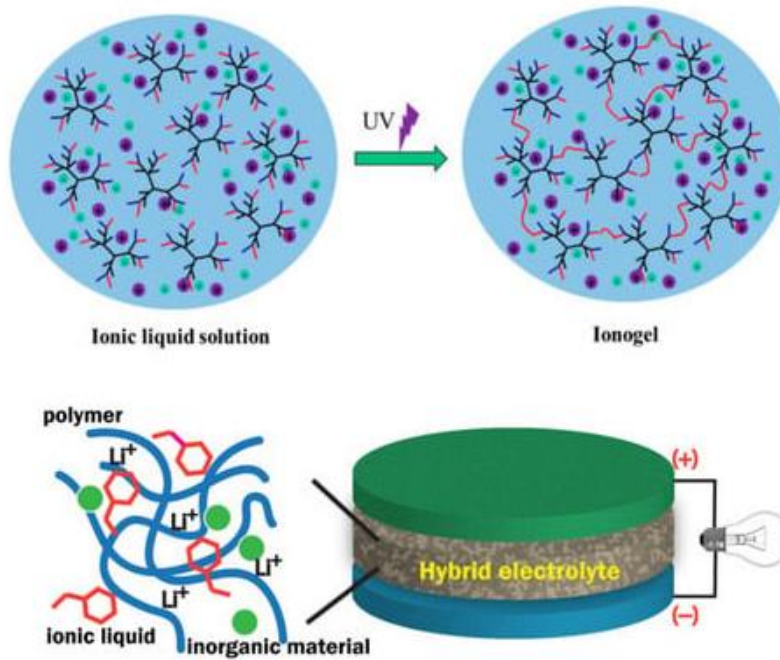
### *2.3.1 Polymer Matrix*

The polymer matrix is integral to the design and functionality of gel electrolytes, especially in TECs. It provides structural integrity, ensuring that the gel retains ionic liquids or salts while maintaining the mechanical flexibility necessary for dynamic applications. Polymers such as poly(vinyl alcohol) (PVA), polyacrylamide (PAM), and carboxymethyl cellulose (CMC) are commonly used due to their ability to form stable networks that enable ion retention without sacrificing flexibility. PVA, for instance, has been highlighted for its capacity to create stretchable gel electrolytes capable of withstanding significant mechanical deformation, making it ideal for use in wearable energy devices. The work by Zhou et al. showcases PVA's relevance in such applications. Additionally, PAM is known for its excellent mechanical properties, which contribute to the overall durability and robustness of gel electrolytes, as emphasized by [46, 47].

Incorporating biocompatible materials like CMC has drawn significant attention in the field due to its environmentally sustainable properties and compatibility with a range of chemical structures. Research by Zhang et al. shows that natural polysaccharides like CMC can enhance both mechanical strength and ionic conductivity, making them ideal for use in portable and wearable energy storage devices. These polymers not only offer improved electrochemical performance but also cater to the growing demand for environmentally friendly alternatives in energy storage systems. By integrating both synthetic and natural polymers, ongoing advancements aim to balance mechanical resilience, ion transport efficiency, and reduced environmental impact, marking gel electrolytes as a critical area of development for sustainable and high-efficiency energy devices [4].

### 2.3.2 Ionic Liquids

Ionic liquids (ILs) have gained significant attention as a critical component in the development of gel electrolytes (GEs) for TECs due to their advantageous properties, such as high ionic conductivity, thermal stability, and non-volatility. ILs, consisting entirely of ions, remain in a liquid state at low temperatures, making them ideal for applications in TECs, where efficient ion transport is critical for energy conversion.



**Figure 2.3:** Synthesis of IL-based gel by photo-polymerization [47]

Their ability to maintain conductivity over a wide temperature range and resist mechanical stress is particularly beneficial for flexible and wearable TECs.

Furthermore, ILs address the safety issues associated with traditional liquid electrolytes, such as evaporation and leakage, providing a safer and more stable solution for TECs operating under varying conditions [46].

Integrating ILs into polymer matrices to form GEs enhances the mechanical stability of TECs while maintaining high ionic conductivity. The flexible nature of polymer

matrices allows them to retain ILs while facilitating ion transport. Recent advancements have incorporated nanomaterials, like carbon nanotubes, into IL-based GEs to further improve electrochemical properties, enhancing overall device performance. However, the cost of ILs and optimizing their compatibility with various redox couples and electrode materials remain challenges. Despite these limitations, IL-based GEs show great potential in enhancing TECs, particularly in applications such as wearable electronics and portable energy systems that rely on low-grade thermal energy harvesting [17, 45, 47].

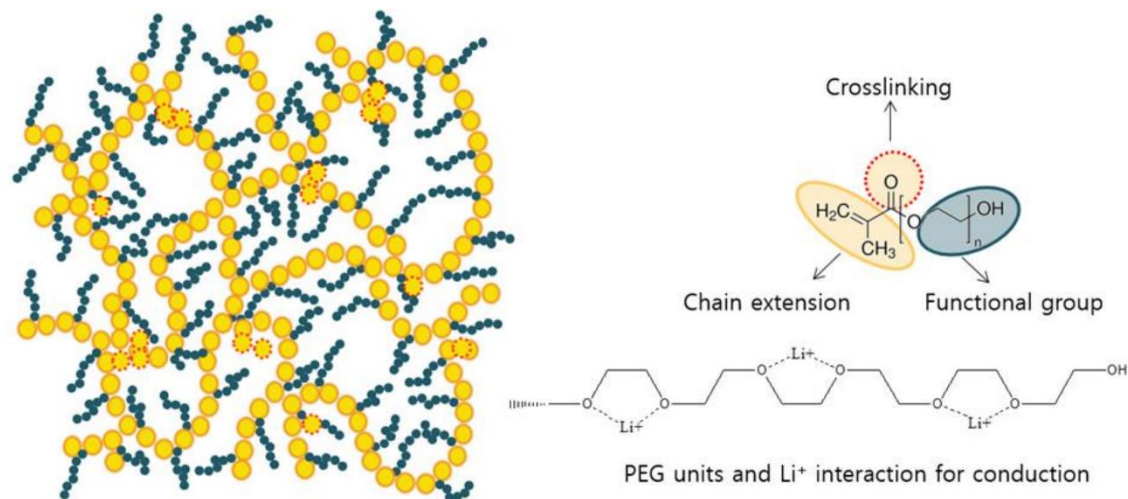
### 2.3.3 *Crosslinking strategies in Gel Electrolyte*

Crosslinking strategies are crucial in developing gel electrolytes (GEs) for TECs, significantly impacting their mechanical strength, ionic conductivity, and overall performance. These strategies primarily include physical and chemical crosslinking. Physical crosslinking relies on non-covalent interactions like hydrogen bonding and vander Waals forces to create flexible networks. While these gels can exhibit promising ionic conductivities, they may suffer from thermal instability at high temperatures, limiting their application [48].

In contrast, chemical crosslinking forms permanent covalent bonds through polymerization reactions, enhancing mechanical stability and durability—essential for wearable devices. Research shows that chemically crosslinked gels, such as those made from poly(vinyl alcohol) (PVA) with glutaraldehyde, offer superior ionic conductivity and mechanical properties, but the choice of crosslinking agents is critical to maintaining the stability of redox couples [39].

Moreover, dual crosslinking strategies that combine physical and chemical methods have emerged, offering enhanced mechanical flexibility and ionic transport. For instance, a dual-crosslinked PVA-based gel electrolyte has demonstrated superior stretchability and conductivity due to synergistic effects from both hydrogen bonding and covalent interactions [49].

Additionally, noncovalent interactions in ionogels and eutectogels utilize hydrogen bonding, solvophobicity, and columbic interactions to create robust networks.



**Figure 2.4:** Schematic diagram of the synthesis process of gel polymer electrolyte

[46]

Techniques like freeze-thaw cycles and template-assisted methods further improve the mechanical properties and ionic conductivity of hydrogels, making them suitable for lightweight, flexible TECs. Recent studies highlight the importance of optimizing gel electrolyte compositions to achieve higher energy conversion efficiencies in thermoelectrochemical applications [50, 51].

Hybrid crosslinking networks that integrate various strategies show great promise, particularly in enhancing mechanical strength and ionic conductivity. Redox-coupled crosslinking employs redox-active species to form reversible bonds within the gel matrix, facilitating energy dissipation during thermal cycling[52].

Overall, these crosslinking strategies are fundamental to designing gel electrolytes that meet the demanding requirements of flexibility, mechanical strength, and ionic conductivity necessary for efficient energy harvesting in thermoelectrochemical technologies. Continued exploration in this field is expected to lead to significant advancements in the practical applications of wearable devices and energy systems, as demonstrated by the novel thermogalvanic hydrogel electrolyte developed to harvest

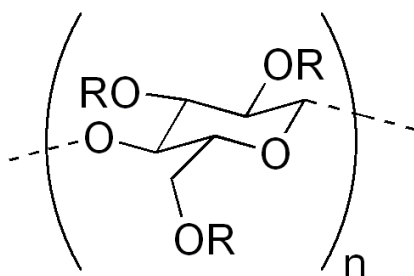
biothermal energy using a unique redox couple of sulfate ions, and the introduction of novel porous thermosensitive gel electrolytes for wearable TECs.

## 2.4 Why CMC and PANI as Gel Electrolyte Material

Carboxymethyl cellulose (CMC) and polyaniline (PANI) have emerged as promising materials for gel electrolytes in thermoelectrochemical applications due to their unique properties and synergistic effects. This section discusses the characteristics, advantages, and collaborative benefits of CMC and PANI, emphasizing their suitability for enhancing the performance of energy storage devices.

### 2.4.1 Properties of Carboxymethyl Cellulose (CMC)

CMC, a cellulose derivative, is characterized by its anionic nature and excellent film-forming ability. It is biodegradable, non-toxic, and environmentally friendly, making it an attractive choice for sustainable energy applications[53].



**Figure 2.5:** Chemical structure of carboxymethyl cellulose [53]

Key properties that contribute to CMC's effectiveness as a gel electrolyte include:

1. **High Hydrophilicity:** CMC's hydrophilic nature facilitates effective ion transport within the gel matrix, crucial for maintaining high ionic conductivity. Its water retention capability supports stable gel formation across various humidity conditions [54, 55].

2. **Biocompatibility:** Being a biopolymer, CMC is compatible with biological systems, reducing adverse reactions when in contact with skin or biological fluids. This is particularly beneficial for applications in wearable devices and bioelectronics [55].
3. **Versatile Modification:** CMC can be modified by blending with other polymers, salts, or conductive materials to enhance its electrochemical properties. This adaptability allows for optimization of ionic conductivity and mechanical strength, tailoring properties for specific applications [17].
4. **Thermal Stability:** CMC exhibits good thermal stability, ensuring reliable operation in thermoelectrochemical systems that may experience fluctuating temperatures during use.
5. **Self-Healing Properties:** Recent advancements suggest that CMC-based gels can exhibit self-healing capabilities due to dynamic interactions within the polymer matrix, significantly extending the lifespan of gel electrolytes by recovering from mechanical damage.

#### 2.4.2 *Properties of Polyaniline (PANI)*

PANI, a conductive polymer, is known for its excellent electrochemical properties and its incorporation into gel electrolytes offers several benefits:

1. **Redox Activity:** PANI's redox-active behavior enhances the electrochemical performance of TECs by facilitating charge transfer processes during operation.
2. **High Conductivity:** PANI's intrinsic conductivity improves ionic conductivity in gel electrolytes when blended with CMC. Its conductivity can be tuned through doping processes, optimizing performance based on application requirements.
3. **Structural Versatility:** PANI can be synthesized in various forms (e.g., nanofibers or nanoparticles), which enhances the surface area and interaction with electrolytic ions, boosting ion mobility and charge transport mechanisms.



4. **Environmental Stability:** PANI demonstrates good stability against oxidation and reduction processes, essential for maintaining long-term performance in TECs [56].

#### 2.4.3 *Synergistic Effects of CMC and PANI*

The combination of CMC and PANI in gel electrolytes creates synergistic effects that enhance both mechanical and electrochemical properties:

1. **Improved Mechanical Strength:** Adding PANI to CMC-based gels increases tensile strength and elasticity, making the electrolyte more suitable for flexible applications.
2. **Enhanced Ionic Conductivity:** PANI's presence not only contributes to conductivity but also helps maintain structural integrity during ion transport, reducing the likelihood of dendrite formation during charge-discharge cycles, which is critical in preventing short circuits.
3. **Thermal Stability:** The inclusion of PANI improves the thermal degradation characteristics of CMC, allowing for stable performance under varying temperature conditions.
4. **Self-Healing Properties:** The incorporation of PANI may impart self-healing capabilities, significantly extending the lifespan of gel electrolytes by allowing recovery from mechanical damage.

## 2.5 **N-type and P-Type Polymer for Thermoelectrochemical Cell**

Significant efforts have been made to developing gel electrolytes as alternatives to aqueous systems in thermocells (TECs). Therefore, the coexistence of redox couples and polymers poses considerable challenges due to compatibility. One of the primary concerns is the pH sensitivity of the polymer, as decomposition of the redox couple can occur in acidic or alkaline conditions. The  $\text{FeCl}_2/\text{FeCl}_3$  redox couple is widely recognized for its excellent performance in n-type TECs, largely attributed to its high Seebeck coefficient (Se).

This feature allows it to generate greater electrical energy from thermal gradients in contrast to n-type redox couples. However its high performance, FeCl<sub>2</sub> and FeCl<sub>3</sub> are affordable and easy to obtain, making them attractive for thermoelectrochemical applications. However, when designing a gel electrolyte for these redox couples, the compatibility of polymer and redox couples plays a pivot role in the final performance of TECs. The acidic nature of the FeCl<sub>2</sub>/FeCl<sub>3</sub> aqueous solution demands the use of neutral or acidic polymers to ensure stability and prevent degradation in the electrochemical system.

Polyvinyl alcohol (PVA) is often chosen as the host polymer because of its impressive mechanical properties, non-toxic nature, low cost, good optical characteristics, resistance to high temperatures, and hydrophilicity. Polyvinyl alcohol can be crosslinked chemically or physically, and glutaraldehyde (GA) is frequently used as a chemical crosslinker. GA reacts with PVA's hydroxyl groups in acidic conditions, creating a three-dimensional polymer network. The acidic environment provided by the Fe<sup>2+</sup>/Fe<sup>3+</sup> redox couple further enhances this crosslinking without introducing unwanted ions that could interfere with the TEC's performance.

Studies have demonstrated that PVA can form quasi-solid-state gel electrolytes with strong mechanical properties. For example, Yang et al. employed a PVA-based gels that shown stretch two to four times their original length and can endure mechanical stresses of up to 0.1 MPa, making them ideal for wearable electronics. A Thermocell based on Polyvinyl alcohol gel electrolyte mounted on skin generated an open-circuit voltage (Voc) of approximately 0.7 V and a short-circuit current (Jsc) of about 2 μA at a low ambient temperature of 5°C [57].

A freeze-thaw method is another effective approach to improving the properties of PVA gels, where freezing and thawing cycles help form hydrogen-bonded networks among PVA chains. This method avoids the need for residual crosslinkers, enhancing mechanical properties. For example, Bai et al. developed a flexible, self-generated body temperature monitoring device using a freeze-thaw processed PVA-FeCl<sub>2</sub>/FeCl<sub>3</sub> gel electrolyte. The device not only measured body temperature in real-time through current changes but also help cool patients experiencing fever.

When 25 thermoelectric cells are connected in parallel, their combined Voc and Jsc can reach up to 0.5 V and 100  $\mu\text{A}$ , respectively, at a temperature difference of 30°C. Additionally, the device exhibits rapid thermal sensitivity, with a fast response and recovery time and a temperature detection limit as low as 0.1 K [58].

Besides PVA, polyacrylamide (PAM) hydrogels have also shown potential as gel electrolytes for n-type TECs. PAM hydrogels provide high ionic conductivity and chemical stability when paired with various redox couples, and a porous structure that supports better ion transport. These properties, along with their cost-effectiveness and ease of preparation, make them viable candidates for TECs.

Natural polymers such as carboxymethyl cellulose (CMC) have shown promise as gel electrolytes for TECs. CMC is both biocompatible and stable when interacting with various redox couples, including  $\text{FeCl}_2/\text{FeCl}_3$  and  $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ . Its ability to facilitate smooth redox reactions minimizes side effects that could hinder performance. Russo et al. utilize a freeze-thaw method for physical cross-linking, a CMC gel was synthesized using freeze thaw method with 0.4M  $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ , achieving a Seebeck coefficient of  $-1.25 \text{ mV K}^{-1}$ .

The  $\text{FeCl}_2/\text{FeCl}_3$  redox couple offers excellent properties for such systems, while polymers like PVA and PAM provide strong mechanical and electrochemical stability, contributing to the overall effectiveness of the TEC. A brief comparison between different gel electrolytes is illustrated in Table 2.1

**Table 2.1:** Literature survey of Polymer based Gel Electrolytes for TECs.

| Polymer | Cross-Linking Methods                      | Redox Couple Concentration [M]        | Seebeck [mV/K] | Ref. |
|---------|--|---------------------------------------|----------------|------|
| CMC     | Physical Crosslinking (freeze–thaw method) | 0.4M $\text{Fe}(\text{CN})_6^{3-/4-}$ | - 1.25         | [59] |

|  |   |  |                |         |
|--|---|--|----------------|---------|
| CMC                                    | -   | 0.4M Fe(CN) <sub>6</sub> <sup>3-/4-</sup>  | 1.17           | [4, 58] |
| PVA                                    | Physical crosslinking (freeze-thawing)          | 0.05M Fe(CN) <sub>6</sub> <sup>3-/4-</sup> | -1.47          | [60]    |
| PAM                                    | Chemical crosslinking (MBA)                     | 0.1M Fe(CN) <sub>6</sub> <sup>3-/4-</sup>  | -1.24          | [61]    |
| Gelatin                                | -   | 0.25M Fe(CN) <sub>6</sub> <sup>3-/4-</sup> | -12.7 to -17.0 | [62]    |
| PVA                                    | -   | 0.1M Fe(CN) <sub>6</sub> <sup>3-/4-</sup>  | -1.2           | [63]    |
| AMPS:AM                                | Chemical crosslinking<br>UV curing (MBA, PEGDA) | 0.4 M Fe(CN) <sub>6</sub> <sup>3-/4-</sup> | -1.4           | [65]    |
| PAA (50% potassium neutralized by KOH) | Chemical crosslinking (MBA)                     | 0.4M Fe(CN) <sub>6</sub> <sup>3-/4-</sup>  | - 1.26         | [42]    |
| METAC                                  | Chemical crosslinking (MBA)                     | 0.4 M FeCl <sub>2/3</sub>                  | 1.12           | [17]    |

|     |                            |  |      |          |
|-----|----------------------------|--|------|----------|
| PAM | Chemical crosslinking      | 0.1 M FeCl <sub>2/3</sub>                    | 1.05 | [29]     |
| PVA | Quasi-solid state          | 0.1 M Fe(CN) <sub>6</sub> <sup>3-/4-</sup>   | 1.02 | [57]     |
| PVA | Chemical crosslinking (GA) | 1 M FeCl <sub>2</sub> /1 M FeCl <sub>3</sub> | 0.8  | [29, 58] |

## CHAPTER 3: MATERIALS AND METHODS

This chapter provides a comprehensive description of the synthesis protocols of gel Electrolyte and device fabrication for TEC application. The gel with various concentration of polymers are synthesized for used as electrolyte in thermoelectrochemical cell and each section details the respective procedures.

### 3.1 Reagents and Chemicals

The following reagents and chemicals were employed in the synthesis processes:

- Carboxymethyl Cellulose (CMC)
- Polyaniline (PANI)
- Dimethylformamide (DMF)
- Potassium Ferricyanide ( $K_3Fe(CN)_6$ )
- Potassium Ferrocyanide ( $K_4Fe(CN)_6$ )
- Deionized Water (DI)

### 3.2 Synthesis of Composite Polymer Gel Electrolyte

The methodology described below outlines the preparation of a gel polymer electrolyte by varying the concentrations of polyaniline (PANI). This process is divided into several steps, beginning with the preparation of PANI solutions, followed by the formation of a carboxymethyl cellulose (CMC) solution, and culminating in the creation of a homogeneous polymer gel electrolyte with the incorporation of a redox couple solution

#### *3.2.1 Preparation of PANI Solutions*

To vary the concentration of PANI within the gel polymer electrolytes, different amounts of polyaniline were dissolved in dimethylformamide (DMF) as the solvent. Specifically, 0.01 g, 0.02 g, 0.03 g, and 0.04 g of PANI were weighed out separately. Each portion of PANI was then dissolved in 5mL of DMF, ensuring the solvent volume remained constant across all concentrations. The PANI and DMF solutions were stirred using a

magnetic stirrer for a prolonged period (overnight) to guarantee complete dissolution of the polymer. This step is critical as incomplete dissolution of PANI could lead to inconsistencies in the electrolyte formation process and, ultimately, affect the performance of the final TEC.

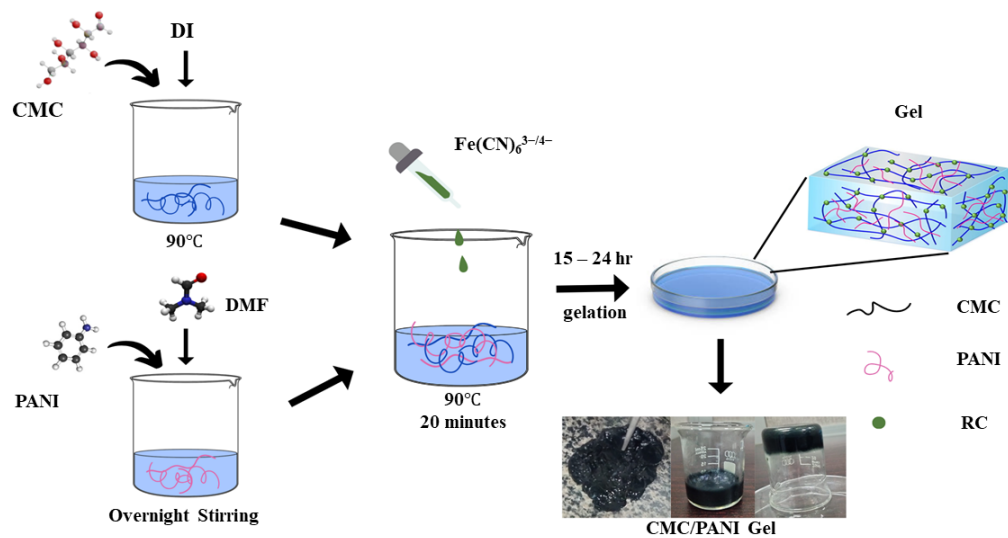
### *3.2.2 Preparation of Carboxymethyl Cellulose (CMC) Solution*

In a separate step, a solution of carboxymethyl cellulose (CMC) was prepared. First, 0.5 g of CMC was accurately weighed and gradually added to 10 mL of deionized (DI) water that had been preheated to a temperature range of 80–90°C. The heating of the DI water prior to the addition of the CMC is crucial, as the elevated temperature facilitates the dissolution of the CMC powder. The mixture was stirred vigorously using a mechanical stirrer. This stirring process continued for approximately 10 minutes, during which the CMC completely dissolved, resulting in a transparent, viscous solution. It is essential that the temperature of the water is controlled carefully during this stage to ensure uniform dissolution and to prevent the formation of any agglomerates or undissolved particles in the solution.

### *3.2.3 Formation of Polymer Gel Electrolyte*

Once the CMC solution had been prepared and the PANI solutions had fully dissolved, the next step involved combining the two components to form a polymer gel electrolyte. For each PANI concentration, 5 mL of the respective PANI solution was measured and added slowly to the 10mL CMC solution. Despite the varying amounts of PANI used, the amount of CMC in each sample was kept constant to ensure that the primary variable affecting the properties of the gel electrolyte was the concentration of PANI.

The mixing process was carried out using a mechanical stirrer, as this type of stirring ensures a more thorough blending of the solutions than manual stirring or magnetic stirrers alone. The mechanical stirrer was set to a consistent speed to achieve a homogeneous mixture.



**Figure 3.1:** Schematic Illustration of Gel Electrolyte Synthesis

Stirring continued until no visible phase separation or uneven homogeneity is crucial for ensuring the consistency of the final gel product.

**Table 3.1:** Sample Compositions for CMC, PANI, and Redox Couple for each sample.

| SAMPLES         | COMPOSITIONS |          |                    |
|-----------------|--------------|----------|--------------------|
|                 | CMC (g)      | PANI (g) | Redox Couple (1 M) |
| CMC             | 0.5g         | 0        | 2ml                |
| CP <sub>1</sub> | 0.5g         | 0.01     | 2 ml               |
| CP <sub>2</sub> | 0.5g         | 0.02     | 2 ml               |
| CP <sub>3</sub> | 0.5g         | 0.03     | 2 ml               |
| CP <sub>4</sub> | 0.5g         | 0.04     | 2 ml               |



### 3.2.4 *Incorporation of Redox Couple Solution*

Once the CMC-PANI mixture reached a state of complete homogeneity, 2 mL of a 1M redox couple solution, consisting of potassium ferricyanide ( $K_3[Fe(CN)_6]$ ) and potassium ferrocyanide ( $K_4[Fe(CN)_6]$ ), was carefully introduced into the solution. This step is vital as the redox couple plays a significant role in the electron transfer processes that occur within TECs, which the electrolyte will ultimately be used in. Stirring was continued until the mixture was fully homogeneous, and no phase separation between the different components was observed.

### 3.2.5 *Gelation Process*

After the complete mixing of the PANI-CMC-redox couple solution, the gelation process was initiated by allowing the solution to cool gradually to room temperature. This cooling phase was conducted without any disturbance to ensure a smooth polymerization process. Over the course of approximately 15 - 24 hours, polymerization occurred, leading to the formation of a stable gel.

The cooling and polymerization process is critical as it determines the final mechanical properties and structural integrity of the gel. To avoid any unwanted air bubbles or inconsistencies in the gel structure, the solution was left undisturbed during this entire period. These gels, with varying PANI concentrations, were stored under controlled conditions to maintain their properties before further testing or use in TEC devices. The gels were subjected to further characterization to assess their ionic conductivity, electrochemical stability, and suitability for TEC applications.

## 3.3 **Device Fabrication**

### 3.3.1 *Fabrication of Electrodes*

The thermoelectrochemical cell electrodes were fabricated using pristine copper foil due to its high electrical conductivity and compatibility with thermoelectric applications. Copper has long been utilized in various electrochemical and thermoelectric devices for its excellent thermal and electrical properties. In this work, copper foil served

as the base electrode, offering efficient electron transfer within the thermoelectrochemical cell.

To ensure mechanical stability and electrical insulation, a Kapton sheet was employed as the backing material for the copper foil support. Kapton, a polyimide film known for its high heat resistance, electrical insulation properties, and mechanical flexibility, was chosen because it can withstand the wide temperature ranges typically encountered in thermoelectrochemical devices.

The copper foil electrodes were prepared by affixing them onto Kapton tape. This method provided a secure and stable platform for the subsequent electrical measurements. The Kapton-backed copper electrodes were essential for determining the thermoelectrochemical performance of the cell, as well as for enabling the integration of multiple cells into series-connected arrays. Such arrays are critical for enhancing the overall output voltage and efficiency of the thermoelectrochemical system.

For the purpose of external connections and output measurements, wires were soldered directly to the copper foil. These wire-electrode connections were crucial for harvesting the electrical output generated by the temperature gradient across the TECs.

### *3.3.2 TEC Device Assembly*

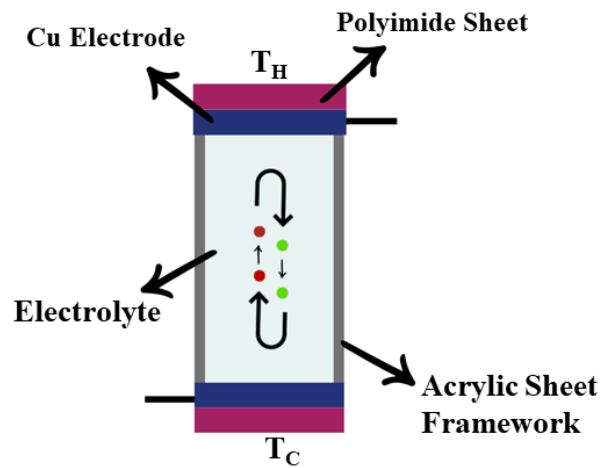
The assembly of the thermoelectrochemical (TEC) device involved the construction of P-type cells, each of which was connected in series to increase the overall output voltage of the system.

This configuration was chosen because series connections allow the voltages generated by individual cells to add up, resulting in a higher net output, which is beneficial for practical applications. The structural framework of the device was constructed using an acrylic sheet with dimensions of  $30 \times 30 \times 2$  mm. Acrylic was selected for its strength, transparency, and ease of fabrication, which allowed for precise control over the device dimensions. The framework served as a support structure, ensuring the proper alignment and spacing of the electrodes and gel electrolyte, thereby maintaining.



**Figure 3.2:** Device Fabrication (a) Device Parts including wires, acrylic framework, copper foil and Kapton Sheet (b) & (c) Assembled TEC (c) Gel Polymer Electrolyte in framework.

Copper electrodes were assembled onto the acrylic framework using silicon sealant and UHU adhesive. UHU, a widely used adhesive, provided additional bonding strength and stability to the assembly. Once the framework and electrode were securely in place, the gel electrolyte was carefully injected into the framework.



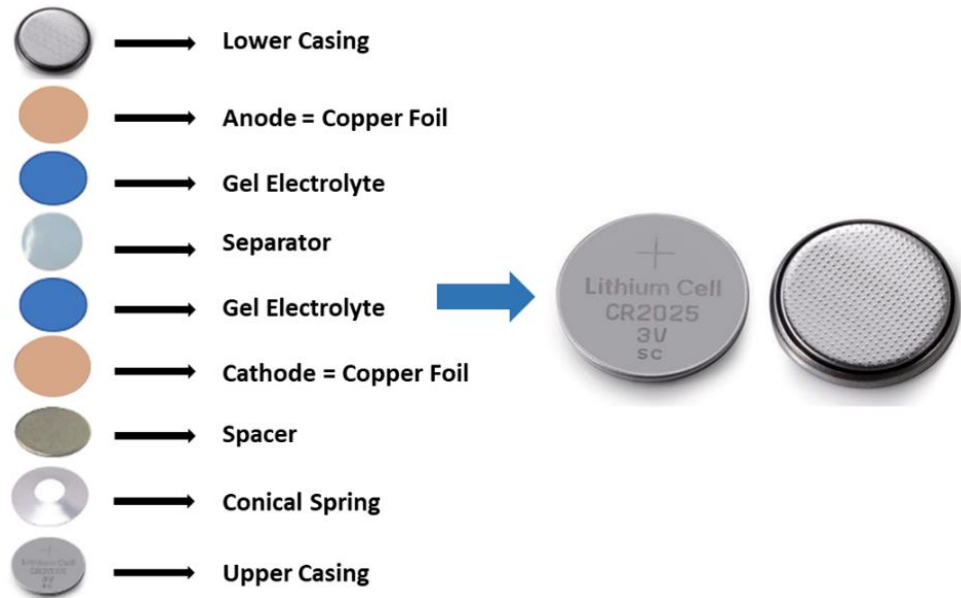
**Figure 3.3:** Schematics illustration of TEC device.

Proper injection of the gel ensured a uniform distribution of the electrolyte, allowing for efficient thermoelectric conversion. Following the injection of the electrolyte, the opposing electrode was carefully affixed and sealed using additional adhesive to complete the device assembly.

To initiate the thermoelectrochemical process, the TEC device was positioned between two thermal reservoirs—one hot and one cold—to create the necessary temperature gradient. The temperature difference between the hot and cold sides of the device drove the thermoelectric effect, which in turn generated electrical power.

### 3.3.3 Coin Cell assembly and electrochemical measurements

The electrochemical behavior of the Gel electrolyte was evaluated using Cyclic Voltammetry and EIS by fabricating CR-2025-coin cells. The pure copper foil is used as an electrode and were cut with a diameter of 12mm. The 2025-coin cell was fabricated in glove box, using a copper foil as both working and counter electrode and Celgard-2400 film employed as a separator with the synthesized material used as an electrolyte.



**Figure 3.4:** Schematic of coin cell assembly for testing the electrochemical properties of

samples.

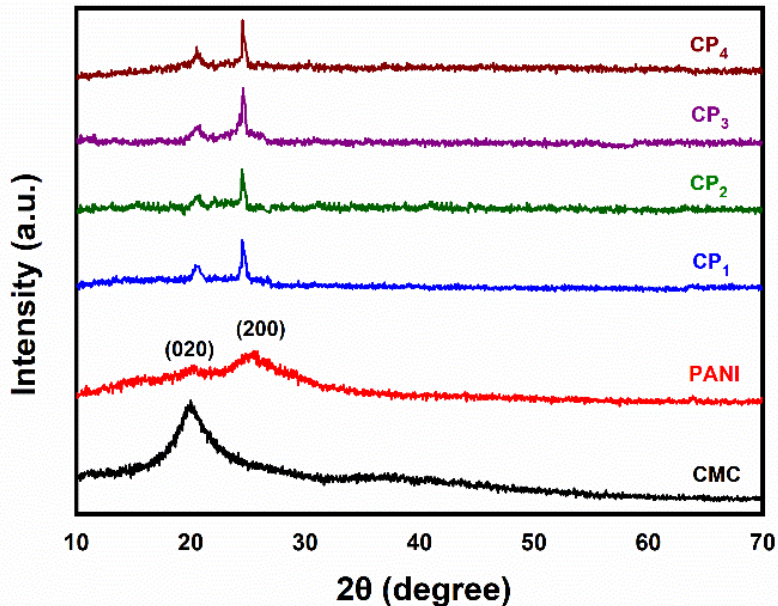
The Gel electrolyte is placed on the both side of the separator and with the thickness of 0.5mm. The fabricated half-cell was tested by cyclic voltammetry (0.1 to 1.0 with scan rate of  $50\text{mVs}^{-1}$ ) by using electrochemical workstation, electrochemical impedance spectroscopy and (0.1 Hz to 100 kHz with an amplitude of 10mV at the Gamry workstation).

## CHAPTER 4: CHARACTERIZATION

### 4.1 Structural, Morphological and Compositional Analysis

#### 4.1.1 X-Ray Diffraction Analysis (XRD)

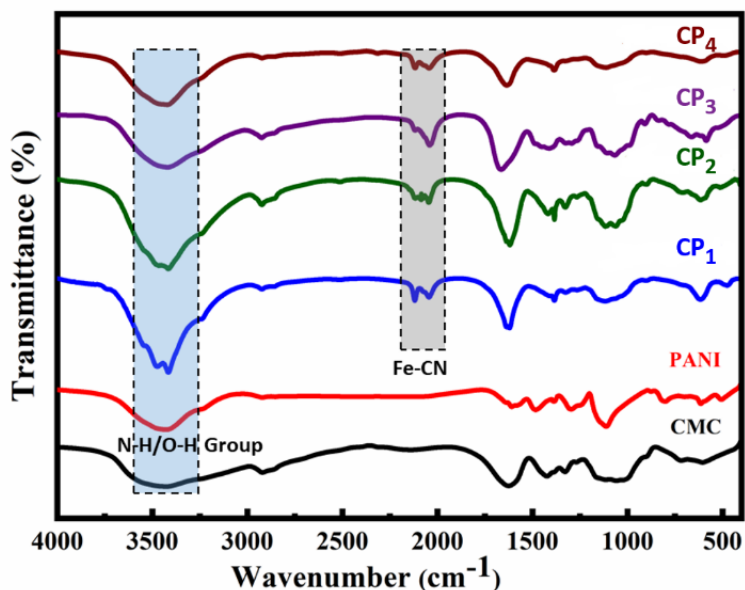
The phase and crystal structure of prepared gel electrolyte was confirmed by XRD analysis, which are provided in **Figure 4.1**. The typical XRD patterns for CMC shows two peaks at  $19.5^\circ$  and  $35.5^\circ$  corresponding typical cellulose II partially crystalline nature. For polyaniline (PANI), the notable peak at a  $2\theta$  angle of  $25.2^\circ$  corresponds to scattering from the alignment of PANI chains in the (200) direction. Additionally, a smaller peak at  $2\theta = 20.4^\circ$  is associated with the alternating distance between layers of polymer chains (020). The XRD results of all gels samples exhibited two diffraction peaks at  $2\theta = 19.5^\circ$  and  $2\theta = 25.2^\circ$  were from the PANI present in the composite membranes. There is no more impurity peak in results, exposing the purity of synthesized materials.



**Figure 4.1:** XRD spectra of CMC, PANI, CP<sub>1</sub>, CP<sub>2</sub>, CP<sub>3</sub>, and CP<sub>4</sub>.

#### 4.1.2 FTIR Analysis

The chemical structure and availability of various functional groups were analyzed using FT-IR spectra illustrated **Figure 4.2**.



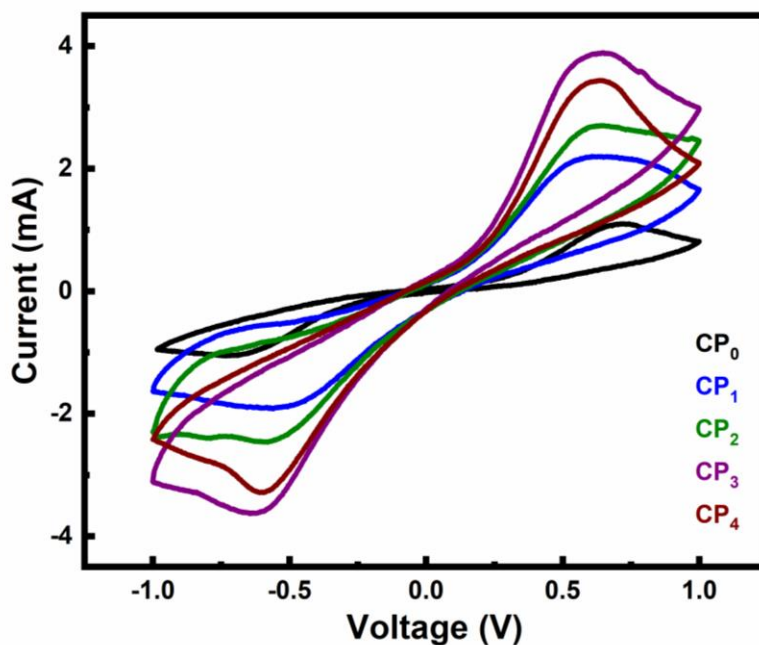
**Figure 4.2:** FTIR spectra of FTIR spectra of CMC, PANI, CP<sub>1</sub>, CP<sub>2</sub>, CP<sub>3</sub>, and CP<sub>4</sub>.

The broad peak appeared at around 3419  $\text{cm}^{-1}$  corresponds to overlapping stretching vibrations of O-H band (CMC) and N-H band (PANI), while the peak at 2924  $\text{cm}^{-1}$  corresponds to C-H stretching vibrations from aliphatic chains. The peaks at 2116  $\text{cm}^{-1}$  and 2041  $\text{cm}^{-1}$  corresponds to the stretching vibrations  $\text{Fe}(\text{CN})_6^{3-/4-}$  redox couple which interacts with the hydrogel matrix. The appearance of the peak at 1665  $\text{cm}^{-1}$  is attributed to C=O stretching in CMC. Additional Peaks at 1410  $\text{cm}^{-1}$  and 1293  $\text{cm}^{-1}$  are attributed to the C=O symmetric stretching from -COOH group (CMC) and C-N stretching (PANI) respectively. The peak at 1066  $\text{cm}^{-1}$  corresponds to C-O (CMC) stretching, whereas peaks at 662  $\text{cm}^{-1}$  and 585  $\text{cm}^{-1}$  indicate Fe-CN bending vibrations respectively indicating the hydrogel's molecular structure. A prominent peak 908  $\text{cm}^{-1}$  is associated with the C-H out-of-plane bending (PANI) [66-68].

## 4.2 Electrochemical Measurements

### 4.2.1 Cyclic Voltammetry

Cyclic Voltammetry was performed and analyzed for the synthesized gel-type electrolyte CMC, CP<sub>1</sub>, CP<sub>2</sub>, CP<sub>3</sub>, and CP<sub>4</sub> gel electrolytes were recorded at a scan rate of 50 mVs<sup>-1</sup> as shown in **Figure 4.3**. As can be seen in the graph, CMC has shown the lowest current density in response to redox potential. The gradual increase in redox peaks appears by the addition of PANI. The CP<sub>3</sub> PANI had shown the most prominent and highest current density redox peaks. The peak-to-peak separation ( $\Delta E_p$ ) tells about the kinetics of the redox process whereas the CV graph indicates the reversible process. As the concentration of PANI increased up to 0.04g in CMC compromises the redox potential and significant decrease in the potential peak is observed in the graph. We can see that the peaks are overlapping that tells us about the stability of the prepared material and at the same time, both redox peaks can be seen in the CV curves. The area under the curve increases as the PANI concentration increase until 0.03g.

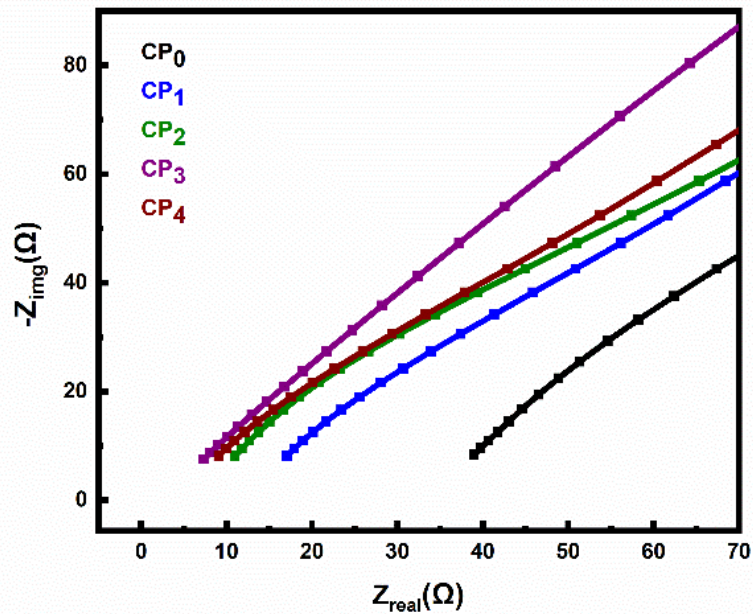


**Figure 4.3:** CV curves of CMC, CP<sub>1</sub>, CP<sub>2</sub>, CP<sub>3</sub>, and CP<sub>4</sub> Gel Electrolytes at a scan rate of 50 mVs<sup>-1</sup>.



#### 4.2.2 EIS Testing

EIS was also analyzed and it showed the same trend in correspondence to CV where CMC has the highest resistance relevant to ionic and charge transfer representing the ideal behavior. To probe the effect of PANI on the  $\text{Cu}^+$  ion transport kinetics of CMC gel electrolyte, EIS was conducted in the frequency range of 0.1 Hz to 100 KHz. **Figure 4.4** displays the Nyquist plots of CMC, CP<sub>1</sub>, CP<sub>2</sub>, CP<sub>3</sub>, and CP<sub>4</sub> concentrations samples of with pristine copper foil as an electrodes. The intercept of the impedance curve with the real axis ( $Z'$ ) represents the Solution resistance ( $R_s$ ). CP<sub>3</sub> sample gives the lowest  $R_s$  value of 7.314  $\Omega$ . Clearly, four electrode material electrodes exhibit low  $R_s$  showing that with the addition of PANI, the ionic conductivity of the Gel Electrolyte improved.



**Figure 4.4:** EIS Nyquist plot of pure CMC, CP<sub>1</sub>, CP<sub>2</sub>, CP<sub>3</sub>, and CP<sub>4</sub> samples tested with pristine Cu-Foil as electrodes calculated over the AC frequency range from 0.1 Hz to 100 kHz

As the PANI concentration increases further from 0.03g, the area under the curve of CP<sub>4</sub> sample decreases and the  $R_s$  value also increases to 9.08 $\Omega$ . This suggests that the

system reaches a saturation point and further increasing the PANI concentration will initiate the internal channeling of electrons.

**Table 4.1:** EIS fitting parameters of all the synthesized samples

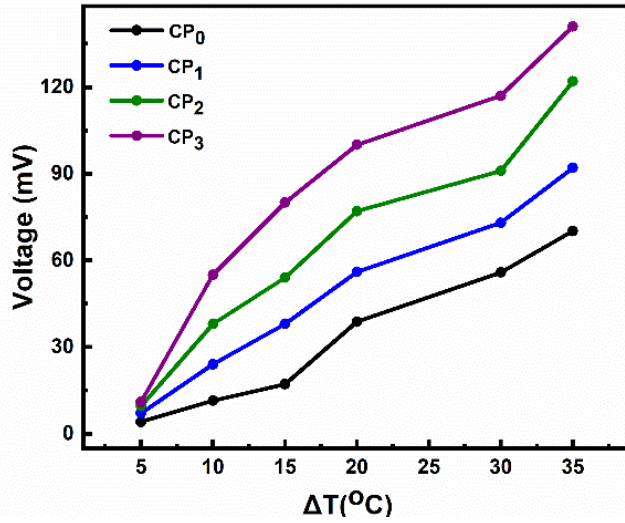
| Samples         | $R_s$ ( $\Omega$ ) |
|-----------------|--------------------|
| CP <sub>0</sub> | 38.97              |
| CP <sub>1</sub> | 17.08              |
| CP <sub>2</sub> | 11.97              |
| CP <sub>3</sub> | 7.3                |
| CP <sub>4</sub> | 9.08               |

### 4.3 Thermoelectrochemical Measurement

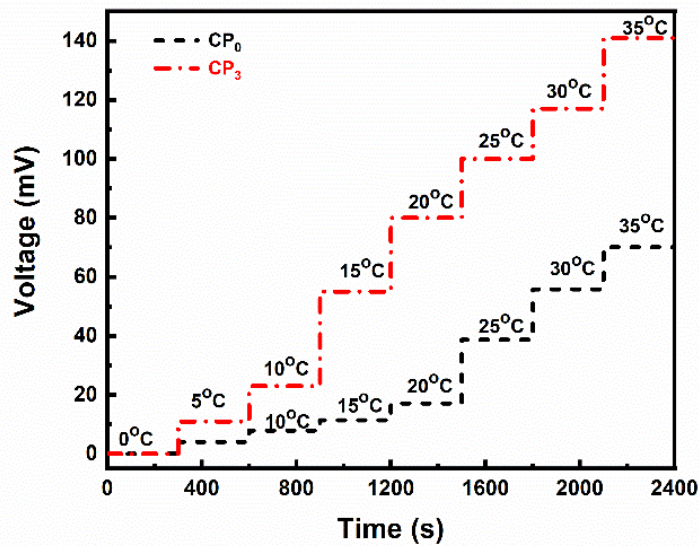
The thermoelectrochemical properties of the samples were tested under varying temperature difference ( $\Delta T$ ), as illustrated in **Figure 4.5**. Initially, the open-circuit voltage ( $V_{oc}$ ) of the TEC containing CMC-based hydrogel electrolyte, consisting of potassium ferricyanide and ferrocyanide ( $[K_3/4[FeCN_6])$  as the redox couple, was measured. At a  $\Delta T = 0$  °C, the  $V_{oc}$  was recorded for 300 s. Then, the temperature of the hot electrode was increased by 5 °C, held for 300 s at each temperature, reaching up to  $\Delta T = 35$  °C. The  $V_{oc}$  increased linearly from 4mV at 5 °C to 70.15mV at 35°C, with the Seebeck coefficient 2 mV/K as shown in **Figure 4.6**.

Subsequently, other synthesized samples were tested under the same temperature gradient. CP<sub>1</sub> gives the maximum  $V_{oc}$  90mV at  $\Delta T$  35 °C started from 9.1mV/K at 5 °C. CP<sub>2</sub> gives the maximum  $V_{oc}$  122mV at  $\Delta T$  35 °C started from 11mV/K at 5 °C. CP<sub>3</sub> sample gives the maximum  $V_{oc}$  141mV at  $\Delta T$  35 °C. The seebeck coefficient is calculated as the

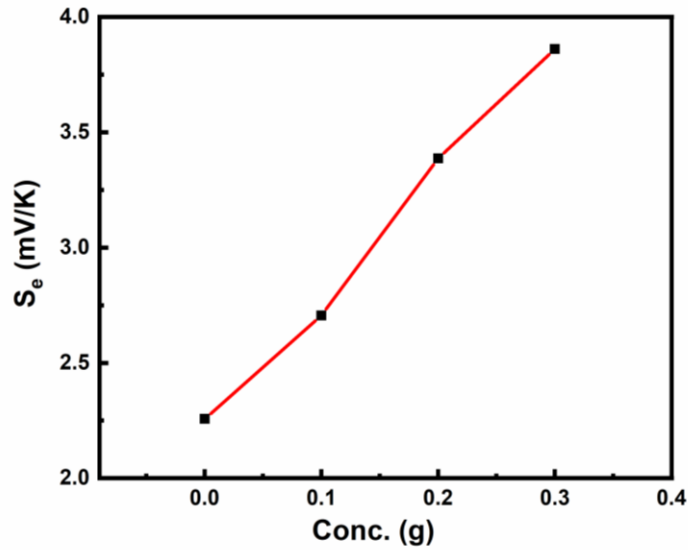
slop of  $V_{oc}$  vs  $\Delta T$  also showed improvement, reaching a maximum of 4.02 mV/K. The overall efficiency of the TEC increases as the concentration of PANI increased from 0.01g to 0.03g as shown in **Figure 4.7**. This is basically due to increase in concentration of PANI as it boost up the redox activity of the gel electrolyte.



**Figure 4.5:**  $V_{oc}$  of the CMC, CP<sub>1</sub>, CP<sub>2</sub>, and CP<sub>3</sub> under varied  $\Delta T$

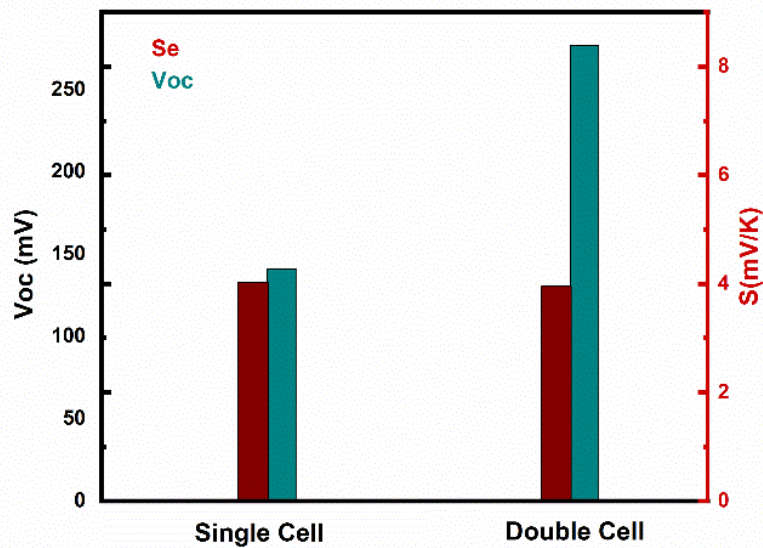


**Figure 4.6:** The  $V_{oc}$  of CMC and CP<sub>0</sub> under varied  $\Delta T$  and time



**Figure 4.7:** The Seebeck Coefficient of gel electrolyte with respect to concentration.

The observed improvements in  $V_{oc}$  and Seebeck coefficient with the addition of PANI suggest that the composite material offers superior thermoelectric performance compared to the undoped CMC-based electrolyte.



**Figure 4.8:**  $V_{oc}$  and Seebeck Coefficient of Both Single TEC and Double TECs connected in series

To efficiently harvest waste heat, individual TECs can be connected in series to enhance potential output or in parallel to boost current output as shown in **Figure 4.8**. Here, we used only identical TECs, in order to avoid a thermal short circuit, alternating TECs with identical S are arranged both thermally and electrically in series. As expected, when two cells are connected in series the voltages increased from 141mV to 277mV relative to individual cells, while the current remained the same.

## CHAPTER 5: CONCLUSIONS AND FUTURE RECOMMENDATION

### 5.1 Conclusion

In conclusion, we have developed stretchable and biocompatible CMC-PANI gel electrolytes with varying compositions (0.01g, 0.02g, 0.03g, and 0.04g PANI concentration relative to CMC), identifying the CP<sub>3</sub> composition as the optimal choice for thermoelectric applications. This composition resulted in a significant improvement in the Seebeck coefficient 4.02mV/K at  $\Delta T$  30°C. The electrochemical impedance spectroscopy (EIS) revealed that the CP<sub>3</sub> composition had the lowest interfacial resistance ( $R_s$ ) among all samples, with a value of 7.314 $\Omega$  that indicates superior ionic conductivity and enhanced the overall reaction kinetics. The optimized gel electrolyte also exhibited excellent mechanical flexibility making it well-suited for use in wearable TEC devices. Furthermore, when two p-type TECs were connected in series, a significant voltage increase of approximately 277mV was observed, further boosting the device's energy output. This research provides a pathway for the development of high-performance thermoelectrochemical cell, addressing key challenges related to mass transport, mechanical durability, and energy efficiency in wearable technologies.

### 5.2 Future Recommendations

For the future prospective, more focus should be on the synthesis of ultra-stretchable, biocompatible, temperature tolerance, and self-healing gel electrolytes to improve their durability in wearable devices.

Additionally, testing copper foil coated with other high redox potential materials already reported in the literature could further improve the electrochemical performance of the system. This gel electrolyte can be tested for batteries and other energy storage or conversion devices.

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