IONIC THERMOELECTRIC MATERIALS FOR ENERGY HARVESTING

Dr Jay Prakash

Head Department of Physics, Kamla Nehru P.G College, Tej Gaon, Raebareli, Uttar Pradesh, 229215

singhjp1973@gmail.com

Abstract -A type of functional material known as a thermoelectric material has the capacity to transform both heat and electric energy. Low-grade heat energy (heat less than 130 °C) may be converted into electric energy. Ionic thermoelectric materials perform better than conventional electrical thermoelectric materials. The See beck coefficient has strong application prospects in compact thermoelectric generators and solar power generation because it can create ionic thermoelectric potential that is 2-3 orders of magnitude larger than that of electronic thermoelectric materials. Ionic thermoelectric materials may be classified into ionic thermoelectric materials based on the Soret effect and thermocouple effect, according to the thermoelectric conversion mechanism. In recent years, there has been significant advancement in the study of ionic thermoelectric polymers, a novel family of materials with considerable potential for use in low-grade waste heat harvesting. In this work, we provide a brief overview of the operation of such materials, the key scientific developments, and the key performance evaluation standards. Ionic conductive polymer and ionogels are two categories of polymer-based ionic thermoelectric materials that we investigate. We also look at the more typical ionic liquid electrolytes as a comparison.

INTRODUCTION

A type of functional material known as a thermoelectric material has the capacity to transform both heat and electric energy. It has high application possibilities in tiny thermoelectric generators and solar power generation because it can convert low-grade heat energy below 130°C into electric energy. Inorganic and organic thermoelectric materials are the two categories of conventional electrical thermoelectric materials: Due to their high thermal conductivity, mechanical strength, and thermoelectric conversion efficiency, inorganic thermoelectric materials like Bi2Te3 PbTe , SiGe , etc. and their alloys have been widely used in thermoelectric coolers, thermoelectric generators, and other devices. However, they have drawbacks like a high price, a difficult manufacturing process, and an easy way to produce heavy metal pollution. However, due to issues like low conductivity, a low power factor, low thermoelectric conversion efficiency, etc., organic thermoelectric materials typically require doping modification, composite materials with carbon , inorganic thermoelectric materials and other techniques to enhance their thermoelectric performance.

Ionic thermoelectric materials are a novel kind of thermoelectric material that have progressively come into people's awareness because to advancements in materials research. Ionic thermoelectric materials have a higher Seebeck coefficient than traditional electronic thermoelectric materials (typically several hundred times higher) and can generate 2-3 orders of magnitude more ion thermoelectric potential than electronic thermoelectric materials. These materials have a wide range of uses in pyrogen batteries and ion thermoelectric capacitors.

72% of the primary energy consumed globally in 2015, or 68.254 TWh, was lost as waste heat, according to study by Forman et al. With the escalating climate catastrophe and the limited availability of fossil fuels, recovering and reusing part of this lost energy can improve society's energy efficiency and aid in the development of a sustainable economy. The recovery of waste heat energy relies heavily on thermoelectric materials. They may produce a voltage gradient and hence an electrical current when a heat gradient is introduced. The Seebeck effect, also known as the thermo-diffusion of charge carriers, is what causes this. The Seebeck coefficient (Se, unit: V/K) gauges how strong this impact is. Several material qualities have a role when used in a thermoelectric generator (TEG), albeit this is not the sole factor impacting the effectiveness of energy harvesting.

To prevent heat from moving from one side of the device to the other and to maintain the temperature differential between the two sides of the thermoelectric device, for instance, the material's thermal conductivity (measured in W/m*K) should be low. The electrical conductivity, on the other hand, should be high to minimise energy loss due to Joule heating (measured in S/m). Researchers developed the following measure of merit with these factors in mind:

1.1 Introduction to Thermoelectric

Many renewable energy systems have been developed in recent decades. Thermoelectric (TE) energy conversion technology, as illustrated in Figure 1.1, is very promising since it can convert waste heat from power plants, factories, and computers into valuable electric power. The absence of harmful ingredients, maintenance-

free operation, long life reliability, and solid state operations are further benefits of this energy conversion technology. On the other hand, employing the Peltier effect, solid state thermoelectric devices may also transform electrical energy into thermal energy for cooling or heating. The poor efficiency of thermoelectric devices, however, restricts the practical applications of this technology. Novel thermoelectric materials with strong thermoelectric capabilities are desperately needed to compete with the current technologies.
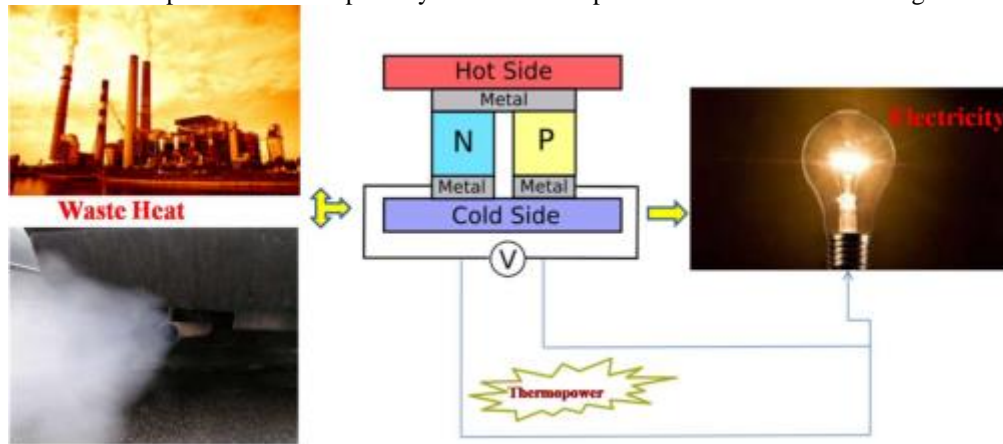

Figure 1: Thermoelectric cell-based waste heat to power conversion

1.2 The Theory behind Thermoelectric Phenomenon

1.2.1 Thermoelectric Effects

The carrier movement inside the material in response to the temperature differential causes the thermoelectric effect to occur A thermoelectric device is powered by three crucial processes, such as the Seebeck, Peltier, and Thomson effects, which are intricately linked to one another as seen in Figure 2. The thermo emf produced by a Seebeck effect results from temperature changes at the connections of two different materials.

Yet, the Peltier effect demonstrated that at the interface between two different materials, heat is either absorbed or dissipated. When a temperature gradient promotes heat transfer in a single current-carrying medium, the Thomson effect occurs
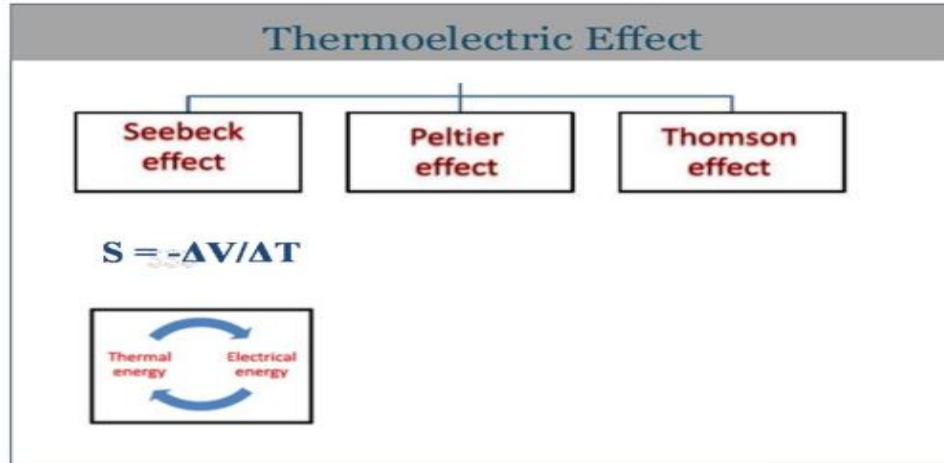
Figure 2: Different kinds of effects involved in thermoelectric
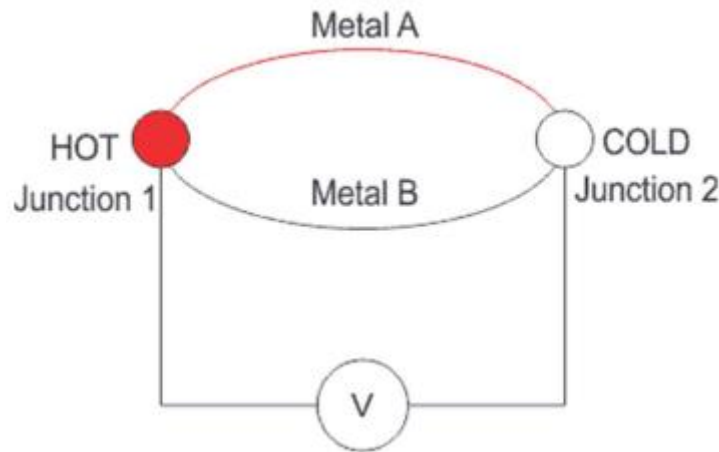
1.2.2 The Seebeck Effect

In the year 1821, Thomas Johann See beck made the key discovery that underlies the thermoelectric effect. He discovered that when two dissimilar metals were joined through junctions and heated differently, the compass needle would be deflected. See beck further deduced that the magnetic field, which was brought about by the passage of electric current, was the primary cause of the deflection. Temperature has an effect on this potential difference. Setback further suggested that the voltage's strength was inversely related to the temperature differential at the junctions. Hence, the thermo power designated as (S), which is typically measured in units of microvolt per Kelvin (V/K), is the proportionality difference between the thermo emf and the temperature gradient. The equation may be used to express the thermo power

$$S = -\frac{\Delta V}{\Delta T}$$

The Seebeck coefficient (S), the voltage difference (V), and the temperature differential (T) between the two junctions are all present. The temperature gradient that allows charge carriers to diffuse from the hot end to the cold end of the thermocouple is primarily responsible for the Seebeck coefficients.

The charge carriers in the materials migrate from the hot end to the cold end in accordance with the temperature gradient, as seen in Figure 1.3.

Thomas explains that one sort of heat engine that may be utilised to generate electricity is a thermocouple (Mark Ellse 2004). Similar to how particles travel towards the colder surface during the thermal expansion of a classical gas, the carrier diffusion in a thermocouple. A charge at one end of the device drifts due to the movement of the carriers, which ultimately results in a potential difference across the material. Charge carriers travel back towards the hot end of the thermocouple as a result of the potential difference opposing the diffusion current and inducing a current (Snyder & Toberer 2008; Morelli 2003).

Figure 3: An illustration of the Setback effect

1.2.3 Thomson Effect

William Thomson established the connection between the Seebeck and Peltier coefficients in the year 1851. The Thomson effect may be defined as the movement of an electron that transfers thermal energy. When a homogeneous material is exposed to a temperature differential while a current is flowing through it, the current flow will convey the heat within the material. Figure 1.5 illustrates how an electron moving against a positive thermal gradient would collect energy while moving against a negative thermal gradient will exhaust energy to its surroundings (Wang et al. 2011). The rate of heat generation per unit volume (q), which may be stated as follows, is often provided via the Thomson effect.

$$q = -\tau J \nabla T \qquad (1.3)$$

In this equation, J stands for current density, T for temperature gradient, and for the Thomson coefficient. Seebeck coefficient 8 typically fluctuates with temperature in a wide variety of materials, and temperature variations are mostly responsible for the gradient in the Seebeck coefficient. By using the Kelvin relationship, Seebeck, Peltier, and Thomson coefficients may be connected to one another. The first Thomson relationship is denoted by

$$\tau = \frac{d\pi}{dT} - S \qquad (1.4)$$

where T is the absolute temperature, is the Peltier coefficient, and S is the Seebeck coefficient. The writing for the second Thomson relationship is,

$$\Pi = ST \qquad (1.5)$$

Because to its specificity for various materials, the Thomson coefficient is used to calculate the absolute Seebeck and Peltier coefficient. This secondary consequence makes its real application value minimal.
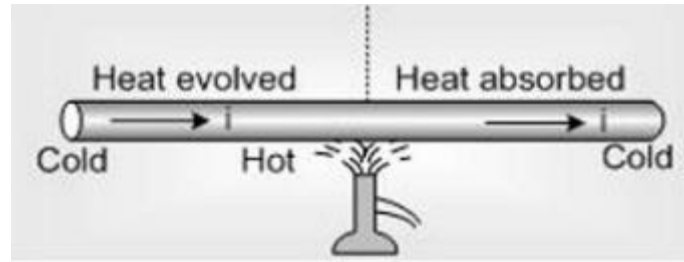
Figure 4: Schematic representation of Thomson effect

1.2.4 Figure of Merit

The performance of the materials used in thermoelectric devices is mostly related to the sort of conversion device that they are. The figure of merit (ZT) of a material has a direct relationship with the efficiency of a thermoelectric device. According to Altenkirch, the ZT is a dimensionless number that may be used to assess how well a material produces thermoelectric power at a particular temperature (Altenkirch 1911).

It may be written as follows and is often dependent on the Seebeck coefficient (S), thermal conductivity (κ), electrical conductivity (), and temperature (T), among other inherent qualities of the materials (Nag & Shuba 2014, Fergus 2012, Zhang et al. 2007),

$$ZT = \frac{S^2 \sigma T}{\kappa} \tag{1.6}$$

Both n-type and p-type materials are used in thermoelectric devices.

The marketed limit for ZT is around 1, yet there is no theoretical support for this constraint prior to the 1990s (Tritt & Subramanian 2006).

Altenkirch discovered that ZT may be enhanced by a material's electrical conductivity being increased while its thermal conductivity is decreased (Goldsmith 1960). He discovered that the electrical resistivity is proportional to thermodynamically irreversible Joule heating, which is expressed as

$$\frac{1}{\rho} = \sigma = ne\mu \tag{1.7}$$

When e denotes the charge on an electron, n denotes the carrier density, and denotes the mobility of the carriers (Grant & Phillips 1991).

1.2.5 Thermoelectric Efficiency

The Carnot efficiency and ZT intrinsic material properties are the major determinants of a thermoelectric device's performance. The material's ZT has a significant impact on thermoelectric efficiency. The goal of the generator's design is to increase the temperature gradient (Goldsmid 1960). The efficiency of a thermoelectric device () for power generation and cooling mode may be written as,

$$\eta = \left(\frac{T_{hot} - T_{cold}}{T_{hot}}\right) \left(\frac{\sqrt{1 + ZTavg} - 1}{\sqrt{1 + ZTavg} + \frac{T_{cold}}{T_{hot}}}\right) \tag{1.8}$$

$$\eta = \left(\frac{T_{hot} - T_{cold}}{T_{hot}}\right) \left(\frac{\sqrt{1 + ZTavg - \frac{T_{cold}}{T_{hot}}}}{\sqrt{1 + ZTavg} + 1}\right) \tag{1.9}$$

where Tavg is referred to as the average temperature and Carnot efficiency is the first term in both equations. High ZTavg and a large temperature gradient result in high conversion efficiency.

2. REVIEW OF LITREATURE

M Massetti 2021 Heat is a plentiful yet frequently wasted energy source. Hence, capturing even a little percentage of this enormous quantity of energy offers great potential for a society that is more sustainable. Carbon-based semiconductors have recently received a lot of attention as potential thermoelectric materials for low-temperature energy harvesting, mainly due to the high abundance of their atomic elements, ease of processing/manufacturing, and intrinsically low thermal conductivity. Traditional solid-state inorganic semiconductors have traditionally dominated the research stage on thermal-to-electrical energy conversion. The search for new materials has led to the development of a number of novel thermoelectric materials and ideas that can convert heat flow into an electrical current using one of three different types of charge-carrying particles: electrons, ions, or redox molecules. This has helped to broaden the potential uses for thermoelectric materials

beyond the straightforward transformation of heat into electricity. This review was inspired by this idea. There are three parts to this essay. In the first section, we lay out the fundamentals of the thermoelectric effects that result when electrons, ions, or redox molecules carry the electric charge, as well as the conceptual distinctions between the three thermodiffusion events. The development of devices that take advantage of these three phenomena is reviewed in the second section, where we also go into great detail about how their performance is constrained. In the third section, we cover the most recent thermoelectric materials that have been studied and give a thorough analysis of the factors that affect charge and energy transfer in each of these material classes.

W Liu, X Qian, 2021 Similar to the Seebeck effect of electrons and holes in solid-state materials, ionic thermoelectric (i-TE) materials use ions as the energy carrier and may produce a voltage when the temperature changes. Recent experiments have shown that quasi-solid-state i-TE materials have a high thermopower. These materials are appealing for capturing ambient heat because they can generate a large enough voltage under a small temperature difference to meet the voltage input requirements of sensors for internet-of-things applications. In this perspective piece, we discuss how i-TE materials compare and contrast with electronic-based thermoelectric materials as well as the various i-TE thermoelectric effects, such as the thermodiffusion (Soret) effect and the thermogalvanic effect, the latter of which includes the Soret effect and redox reaction entropy. Techniques for enhancing the performance of materials and gadgets are developed, along with the requirement for more study to comprehend the microscopic causes of various impacts.

B Russ, A Glaudel 2016 For organic electronic devices such as light photovoltaics and flexible displays, conjugated polymers and associated processing methods have been developed. These innovations have recently been exploited to produce organic thermoelectric materials, which have the potential to be used to generate energy at temperatures close to room temperature and for wearable heating and cooling systems. The greatest thermoelectric materials to date have been inorganic compounds with very low Earth abundances (such Bi2Te3) that are produced using extremely intricate vacuum processing methods. In addition to showing figures of merit that are on par with these inorganic materials, molecular materials and hybrid organic-inorganic materials also show unusual transport behaviours that point to previously unimaginable optimisation paths and device designs. In this Article, we address recent developments in high thermoelectric figures of merit organic materials and show how these materials may be combined into novel module designs that benefit from both their mechanical and thermoelectric capabilities.

D Zhao, A Würger, 2021 The invention of thermoelectric principles, which directly transform heat into electricity, was driven by the enormous quantity of lost heat from solar radiation and industrial dissipation. The high cost of materials and production is the fundamental obstacle to practical thermoelectric applications. Ionic thermoelectric have recently made significant advances that open up new opportunities for charging energy storage devices when exposed to a temperature differential. The electrolyte's ionic Seebeck effect between two electrodes generates the internal charging potential. As a result, ionic thermoelectric materials are defined as electrolytes having high thermoelectric figures of merit. The majority of ionic thermoelectric materials are made up of plentiful elements and have a thermal voltage that is hundreds of times greater than that of electronic materials. This newly developing thermoelectric category rekindles interest in ionic thermodiffusion and offers fresh promise for the fabrication of low cost, wide area heat-to-energy conversion devices. In this paper, we provide an overview of the current state of the art in the emerging subject of ionic thermoelectrics, including both material and application advancements as well as the ionic thermodiffusion's driving force. We outline a broad overview of ionic thermoelectric materials, talk about the distinctive qualities of each kind of reported electrolyte, and suggest potential improvements and new directions for ionic thermoelectric research.

YT Malik, ZA Akbar, 2022 Thermoelectric (TE) materials that can be stretched and self-heal provide up new possibilities for self-healing, flexible wearable technology. The issue lies in creating high-performance materials with such ideal TE and mechanical characteristics. This study reports on organic-inorganic ionic TE composites (OITCs) with strong self-healing and stretching capabilities as well as an unprecedentedly high ionic TE figure of merit (ZTi = 3.74 at 80% relative humidity). Inorganic SiO2 nanoparticles (SiO2-nps) are added to a polyaniline: poly(2-acrylamido-2-methyl-1-propanesulfonic acid): phytic acid (PANI:PAAMPSA:PA) ternary polymer to create the OITCs. By increasing the mobile proton concentration in OITCs and providing autonomous self-healing and stretchability, the SiO2-nps positively interact with the hybrid polymer, significantly enhancing the ionic TE characteristics of the OITCs (i.e., ionic Seebeck coefficient and ionic conductivity). Furthermore, despite extreme external pressures (50 cycles of 100% strain and 25 cycles of cutting/healing), the OITCs continue to be repeatedly stretchable and self-healing without losing their TE capabilities. An ionic TE supercapacitor (ITESC) with a maximum energy density of 19.4 mJ m2 is demonstrated using OITCs with multi-walled carbon nanotube electrodes at a temperature differential of 1.8 K.

G Fan, K Liu, 2022 A potential and essential method in sustainable development is the use of thermoelectric (TE) materials to harvest energy from common low-grade waste heat. There is a great demand for high-performance ionic thermoelectric (ITE) materials with flexible, affordable, mass-producible, and biodegradable properties. TEMPO-oxidized bacterial cellulose (TOBC) and an environmentally friendly solvent (ionic liquid, 1-ethyl-3-methylimidazolium dicyanamide, [EMIm][DCA]) are used to create a unique, flexible, and high-

performance ITE material called CBCIGs (carboxyl-functionalized bacterial cellulose-based ionogels). High tensile strength, skin-like stretchability, good adhesion, and biodegradability are all characteristics of the CBCIG in its as-fabricated state. In order to increase the electrical conductivity of the ionic TE materials, the ionogels were created to control the confinement of ILs within the functionalized natural biopolymer. The suggested CBCIG has a high ionic conductivity of 79 mS cm1 and contains 99.52 wt% [EMIm][DCA]. With CBCIGs-90 wt%, the greatest Seebeck coefficient of 11.55 mV K1 was recorded. It is also shown how the CBCIGs may be used as a flexible ionic thermoelectric capacitor (ITEC) for thermoelectric conversion. In order to use low-grade waste heat for flexible wearable self-powered devices, we anticipate that the development of flexible ITE materials will offer a practical option.

H Wang, D Zhao, 2017 Heat may be converted to electrical energy using thermoelectric materials. ZT = 2T/, where is the conductivity, is the so-called Seebeck coefficient, and is the thermal conductivity, is generally used to measure the performance of electronic thermoelectric materials. Yet, it has not been obvious how to assess ionic thermoelectric materials' performance, such as ionic solids and electrolytes. Because these systems rely on ions that cannot cross the boundary between the thermoelectric material and external metal electrodes, they cannot be employed directly in a conventional thermoelectric generator. Instead, by charging a supercapacitor, energy may be obtained through the ionic thermoelectric effect. The ionic thermoelectric characteristics of the polyelectrolyte sodium styrene sulfonate are examined in this paper, and the authors connect these qualities with the charging efficiency when utilised in an ionic thermoelectric supercapacitor (ITESC). The results demonstrate that the charging efficiency of the ITESC may be quantitatively connected to the figure of merit ZTi = iii2T/, which is analogous to electronic thermoelectric generators. As a result, it is possible to compare and forecast the performance of ionic thermoelectric materials using the ZT, which will be very helpful for designing high-performance ITESCs.

3. THERMOELECTRIC DEVICE CONCEPT

3.1 Thermoelectric Generators (TEGs)

A thermocouple is the basic building block of a TEG. It is made of p- and n-type TE materials, connected electrically in series and thermally in parallel, and it has an internal electrical resistance (Rpn = Rp + Rn, without taking into account the metallic electrical interconnections). It is also subject to a temperature gradient, T = TH - TC. Because metal contacts have a high thermal conductivity, it is possible to ignore the losses caused by them while assuming that heat only moves from the hot to the cold side through the thermocouple. By combining the thermovoltage contributions from the two materials (S = Sp - Sn), this design is used to optimise the electrical output by generating a unidirectional charge flow inside the device. The three contributions to the thermal energy flow are I the rate of Peltier heat absorption from the hot side caused by the thermogenerated current I (QPeltier = STHI), (ii) the Joule heating emanating at the hot side caused by the thermogenerated current I (QJoule = 1/2I2R), and (iii) the heat flux crossing the leg (KT) in the absence of an electrical current (K is the thermal conductance of the thermocouple). The thermal input power at the hot junction is stated as follows:

$$Q_H = ST_H I - \frac{1}{2}RI^2 + K(T_H - T_C)$$

As the current flows through a load resistance (RL), the TEG produces the following amount of electrical power:

$$P = VI$$

when the voltage is open-circuit:

$$V = S\Delta T$$

and a current:

$$I = S\Delta T/(R + R_L)$$

The ratio of the thermal power input QH to the electrical power output P is the TEG's efficiency ():

$$\Phi = \frac{S\Delta TI}{(ST_H I - \frac{1}{2}RI^2 + K\Delta T)}$$

To match the internal resistance Rpn and the load resistance RL, the thermocouple components' size must be changed. Thus, the highest level of effectiveness max may be expressed as (46)

$$\Phi_{max} = \frac{\Delta T}{T_H} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_C/T_H}$$

$$Z = \frac{S^2}{K_{pn}R_{pn}}$$

where ZT represents the thermocouple's conversion efficiency and is a dimensionless figure of merit for the device. Another parameter (zT), depending on the thermoelectric characteristics of a single substance (S, k,), has been developed from this one:

$$zT = \frac{\sigma S^2}{k}T$$

Maximum power output and efficiency operating regimes are different. When the gadget is operating at full power, the internal resistance of the device equals the external load resistance (Figure 5). The output voltage, V = Voc/2, is half of the open-circuit voltage, and the resulting maximum power is as follows:

$$P_{max} = \frac{V_{oc}^2}{4R} = \frac{S^2(T_H - T_C)^2}{4R}$$
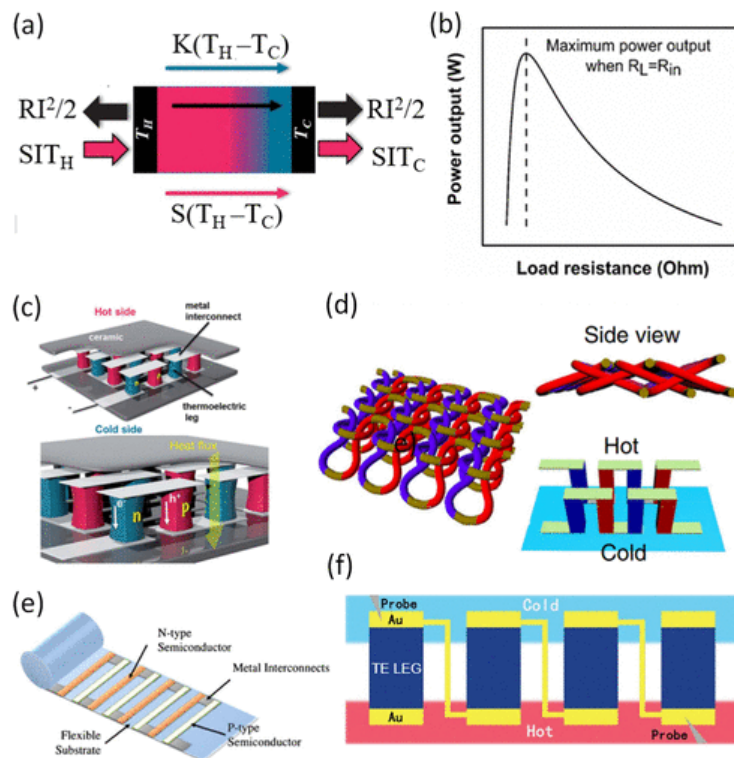
Figure 5: An illustration of the various thermal energy flows flowing through a thermoelectric leg under a temperature gradient

Taken from ref. with permission (49). Royal Society of Chemistry, 2012. ©. (b) A graph showing a typical power output vs load resistance for TEG. (c) Conventional thermoelectric modules built of ceramic plates, n- and p-legs, and interconnects. Reprinted from reference with permission (49). Royal Society of Chemistry, 2012. ©. (d) A woven-yarn structure that incorporates TEG for fibres into a textile. Reprinted from reference with permission (50). Nature 2020 Copyright. Planar thermoelectric module on a flexible substrate in sketch form (e). Reprinted from reference with permission (51). IOP 2011 Copyright. Planar, unipolar thermoelectric generator (optional). Reprinted from reference with permission (47). Royal Society of Chemistry. 2017-.

The aim is to link numerous thermocouples electrically in series and thermally in parallel in a high-density configuration to optimise the power extraction per unit area since the Seebeck voltage generated by a single

thermocouple (S 200 V K-1) is too low to power any application. In order to maintain proper heat conduction with the environment and prevent short circuits between the metal contacts, the thermoelectric module is finally sandwiched between ceramic plates. OTEGs come in a variety of sizes and shapes. OTEGs can be produced as flat plates for thin films or woven-yarn textiles for fibres in addition to the traditional vertical geometry, which incorporates bulky pellets of active ingredients (Figure 4d,e). Sometimes, unipolar OTEG may be produced using just one thermoelement (Figure 4f). (47,48) Furthermore, low-cost, low-temperature, and large-area manufacturing processes like printing and drop casting may be used to create OTEG.

3.2. Thermo galvanic Cells (TGCs)

A thermogalvanic cell is made up of two electrodes that are in contact with an electrolyte that contains a redox pair while being at different temperatures. The reductant (red) and the oxidant (ox) of one electrochemical half-reaction are both present in the redox electrolyte. It's crucial that this half reaction's electrode electron transfer be reversible. The thermogalvanic cell is an electrochemical thermoelectric generator that generates a difference in electric potential when a temperature gradient is applied between the two electrodes, as shown in Table 1. By connecting two electrodes to an external RL, a constant power may be obtained since the redox electrolyte will convey an electric current through molecular shuttles through convection, diffusion, and migration between the two electrodes.

Voltage \V	Current\ MA	Power Density\mWm2
11	0.2	11
16	0.4	18
21	0.6	12
28	0.8	22
33	0.6	26
39	0.8	29
42	0.9	31

Table 1: A typical thermogalvanic cell's schematic design and analogous circuit are shown in A thermogalvanic cell's I-V and P-V curves. Reprinted from reference with permission .

A generator consisting of an ideal potential source (Seebeck voltage) in series with an internal resistance R makes up the electrical equivalent of a TGC (Figure 5b). The properties of the current-voltage flow after those of a Thevenin generator:

$$V = V_{oc} - RI$$

$$V_{oc} = -S_{redox}\Delta T$$

The slope of the I-V characteristic, the open-circuit voltage VOC, the intercept on the I-axis, and the short-circuit current ISC all contribute to internal resistance (Figure 5c). The power and thermogenerated current vary quadratically (Figure 6):

$$P = VI = V_{oc}I - RI^2$$

The greatest area within a rectangle, as indicated by the point (ISC/2, VOC/2) is where the criteria for maximum power are found on the I-V characteristics:

$$P_{max} = \frac{V_{oc}I_{sc}}{4}$$

If you choose a load resistance that is equivalent to the internal resistance, the maximum power will result (eq 24 and eq 16). The internal resistance is a result of three different forms of resistive phenomena: charge transfer resistance, ohmic resistance, and mass transfer resistance. (53−55) The bulk electrolyte resistance, the electrode resistance, and the resistance resulting from electrical connections to the external circuit are the sources of ohmic resistance. The ionic resistance of the electrolyte is frequently the main phenomena (RI):

$$R_I = \frac{L}{A\sigma}$$

where L is the distance between the two electrodes' separation and A is the cross-sectional area determined by the geometry of the two electrodes. The ionic conductivity is approximately represented by:

$$\sigma = \frac{F^2}{RT} \sum_i D_i c_i z_i^2$$

where c_i is the ionic concentration, z_i is the charge of the ion, and D_i is its diffusion coefficient.

As a result, lowering the internal resistance can be accomplished by raising the diffusion coefficient and redox electrolyte concentration. The ionic diffusion coefficient in the Stokes-Einstein model depends on the solvent's viscosity and the ions' hydrodynamic radius, rH:

$$D = \frac{k_B T}{6\pi\gamma r_H}$$

where T is the absolute temperature and k_B is the Boltzmann constant. Hence, low viscosity solvent and tiny, solvated ions are two variables that reduce the TGCs' internal resistance.

The exchange current, I0, which is represented by the charge transfer resistance RCT, influences the rate of the electron transfer process at the electrode/electrolyte interface:

$$R_{CT} = \frac{RT}{AnF|I_0|}$$

where R is the gas constant and A is the electrode's surface area. The Butler-Volmer formulation of the electrochemical current (Tafel equation) provides the exchange current:

$$\ln(I) = \ln(I_o) - \frac{anF\eta}{RT}$$

where the charge transfer coefficient is and the overpotential is. For instance, the electron transfer at the platinum electrode for a ferric/ferrocyanide redox pair in salty water can have an RCT as low as 1 in a good TGC. (56)

The three primary mechanisms (migration, diffusion, and convection) that control the mass transport resistance, or the movement of reactants from the solution to the electrode, restrict the current Ilim: (55)

$$R_{mt} = \frac{RT}{nF|I_{lim}|}$$

It may be expressed as follows if the diffusion of reactants limits the steady-state current |Ilim|:

$$I_{lim} = \frac{nFADc}{\delta}$$

where D is the electroactive species' diffusion coefficient, A is the active electrode area, c is the redox species' concentration, and is the thickness of the diffusion layer at the electrode, which is theoretically the largest interelectrode distance. Because of convection, in actuality is closer to the interelectrode distance. (55)

Due to the possibility of several resistive contributions limiting the thermogenerated current, the thermoelectric figure-of-merit ZT (eq. 19) cannot give a straightforward formulation for thermogalvanic cells. One resistive contribution may be prominent and a simpler expression may be recovered since those contributions can be observed in series, depending on the shape of the cell and the components (electrolyte, redox species, electrode). In many instances, the Rmt is bigger than the RCT utilising typical metal electrodes and the I RI with high salt and redox couple concentrations. Abraham et al. suggested the following phrase in the situation: (55)

3.3. Ionic Thermoelectric Super capacitors

Ions can move as electronic charge carriers along a temperature gradient, but they cannot move through a metal electrode to produce an external current (as illustrated in Figure 6). Instead, an electric double layer (EDL) will form where the metal electrodes and the electrolyte meet, accumulating ions that cause a transient current and may be used to represent the charge stored in EDL capacitors. (64,65) As a result, the ionic thermoelectric effect is not appropriate for conventional thermoelectric generators operating continuously. Alternately, the amount of accumulated charge can be significantly increased when using high capacitance electrode materials, such as carbon nanotubes and conductive polymers, and electrical energy can be harvested by charging supercapacitors (the so-called ionic thermoelectric supercapacitor ITESC) or batteries. Via the ionic thermoelectric effect, thermal energy is therefore transformed into stored electrical energy that may then be used up upon discharge.
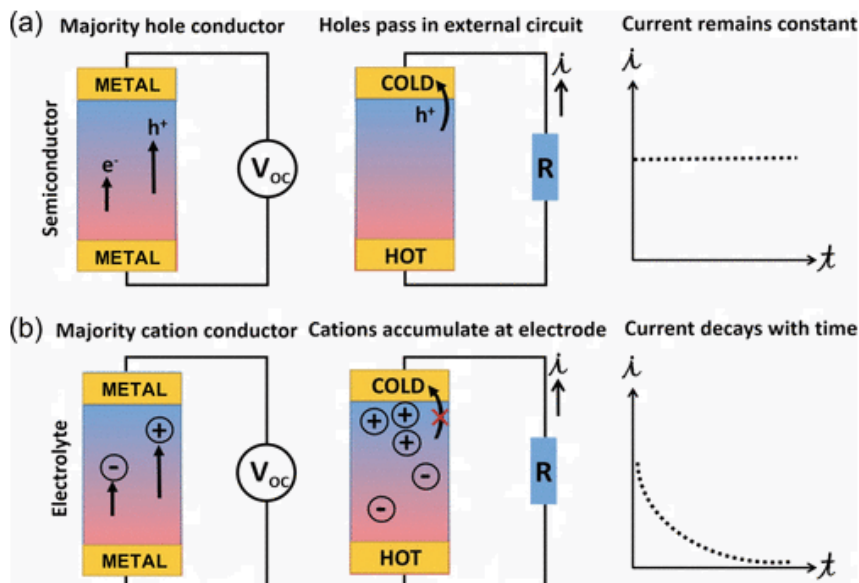
Figure 6: Thermoelectric effects involving ionic charge carriers in an electrolyte and electronic charge carriers (either electrons or holes) in a semiconductor, respectively. Reprinted from reference with permission (64). Wiley-VCH has the 2017 copyright.

Figure 6 shows the fundamental operational procedure for an ITESC. (24) I After a given amount of stabilisation time (tst), a thermovoltage achieves Vthermo = SiT between the two electrodes separated by an electrolyte. (ii) A load resistance connects the two electrodes, and Vthermo charges the supercapacitor. You may calculate the charge Qch stored at the electrodes of the ITESC by integrating the charging current. (iii) Once the battery has fully charged, the heat source is switched off and the external load resistance is removed (open circuit). Without T, the thermovoltage decays to zero, and the electrode/electrolyte interface's stored charge mostly determines the open-circuit potential. The gadget is finally discharged (iv) by coupling the two electrodes to an external circuit. The integration of the discharge current yields the charge quantity Qdis. The most electrical energy that may be stored is best represented as:

$$E_{ch} = \frac{1}{2}CV_{thermo}^2 = \frac{1}{2}C(\Delta TS_i)^2$$

which quadratically rises with the material's Seebeck coefficient. When a supercapacitor is charged electrically or thermoelectrically, the electrical energy stored inside is plotted against voltage in Figure 7b. An ITESC is appropriate for obtaining energy from sporadic heat sources, such as the sun. ITESCs can be heated by the sun during the day to charge them, and they may be discharged at night to use the stored electrical energy.

Energy (uj Cm2)	V charging (MV)
10	22
15	26
18	29
21	31
28	35
26	42
31	51

Table 2: The ionic thermoelectric supercapacitor has completed a full charge and discharge cycle (ITESC)

Kim et al. recently created an ITESC using a polystyrene sulfonic acid (PSSH) electrolyte, and they saw nearly no leakage current, demonstrating that the stored electric energy could be sustained for longer than 24 h. (66) The solid-liquid interface's equilibrium condition is disturbed as a result of temperature variations, and the interfacial potential is impacted by changes in ion density. The function of the electrode material's work function (68) was thoroughly investigated because, as the temperature changes, the charge motion alters the potential difference across the double layer at the electrode-electrolyte interface, allowing a direct correlation to be demonstrated between the two parameters. Moreover, additional research was done to examine the roles of ion concentration (69) and ion size (70). The findings indicated that the ion size is the primary factor affecting voltage generation (the bigger the ion, the lower the voltage generated for the same T), while the ion concentration appeared to play a secondary role.

The ratio of generated electrical energy to thermal energy going through the device might be used to determine the efficiency of the heating-cooling cycle in ITESCs. (64) The ITESC's maximum charging efficiency (Tch) is therefore denoted as:

$$\Phi_{\Delta Tch} = \frac{\Delta T}{2T_H + \frac{10\kappa}{\sigma S_i^2} - \frac{1}{2}\Delta T}$$

The three crucial material characteristics, I si, and k, which are combined to create the ionic thermoelectric figure-of-merit of an electrolyte zTi, are strongly connected to the maximum charging efficiency:

$$zT_i = \frac{\sigma_i S_i^2}{k} T$$

=

The efficiency will rise for electrolytes with high ionic conductivity, Seebeck coefficient, and low thermal conductivity, much like it does for conventional electronic materials. Moreover, they immediately deduced ch based on ZTi:

$$\Phi_{ch} = \frac{\Delta T}{T_H} \frac{ZT_i}{2ZT_i + \frac{10T}{T_H} - \frac{1}{2}ZT_i\frac{\Delta T}{T_H}}$$

Electrolytes have a lower thermal conductivity and a greater Seebeck coefficient when compared to electronic thermoelectric materials. However, their zTi values and efficiencies are lower than those of excellent electronic thermoelectric materials because of their comparatively poor ionic conductivity (Figure 8a). It should be noted that only the charging process is taken into account in this efficiency assessment, leaving out the heat required to warm the materials, which is inversely related to their mass and heat capacitance. Its contribution to thermal energy is initially considered to be equivalent for both an ITESC and a supercapacitor that is charged by a TEG. Remember that only when the electronic conductor is taken into account for a TEG linked in series with a supercapacitor can the comparison of zT between an electronic conductor and an ionic conductor have any significance. In fact, this circuit is an ITESC comparable circuit. Although having a very low efficiency, ITESC has one significant benefit over a TEG and supercapacitor when compared. Electronic thermoelectric materials with high performance, as Bi2Te3 alloys, have a lower Seebeck coefficient (200 V K-1) than ionic thermoelectrics (up to 10000 V K-1) at similar temperature differences. This means that the amount of energy held in the same supercapacitor (C = 1 mF) when it is charged with ionic thermoelectric materials is significantly higher than when it is charged with an electronic material, as shown in Table 3 .

Lonic materials	Electronic materials
2.2	1.3
2.9	1.9
3.1	2.0
3.5	3.5
4.2	3.9
4.6	4.5
5.2	6.2

Table 3: efficiency of common electrical and ionic thermoelectric materials vs zT (T = 10 K). (b) The amount of energy held in a 1 mF supercapacitor as a function of the Seebeck coefficient of various thermoelectric materials at 10 K. Taken from ref. with permission (64). Wiley-VCH has the 2017 copyright.
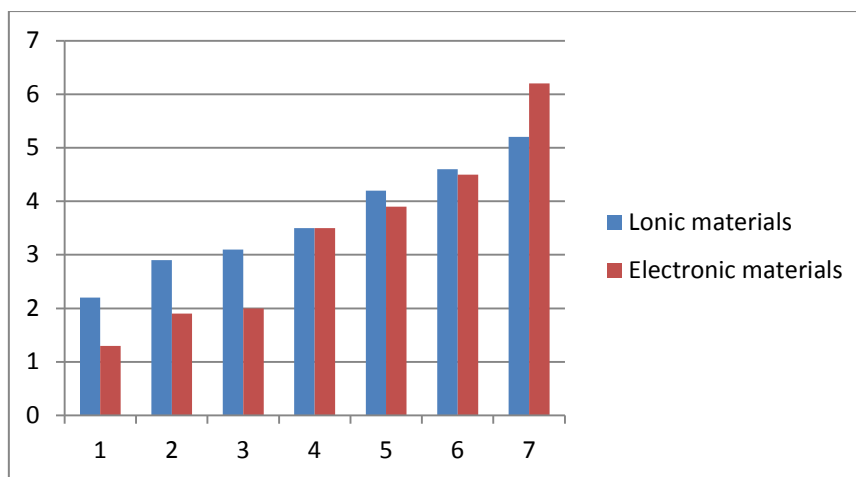
Figure 7: efficiency of common electrical and ionic thermoelectric materials vs zT (T = 10 K). (b) The amount of energy held in a 1 mF supercapacitor as a function of the Seebeck coefficient of various thermoelectric materials at 10 K. Taken from ref. with permission (64). Wiley-VCH has the 2017 copyright.

4. STATE-OF-THE-ART MATERIALS

4.1 Organic TE Materials

Organic conductors have a wide range of uses in thermoelectric applications due to their flexible chemical production, low-cost solution processability, and unique mechanical toughness. Nevertheless, when it comes to constructing vertical legs (thickness of 10-100 m) in the conventional design of a thermoelectric module, the low solubility of organic conductive materials is often a disadvantage. The anisotropy of charge transport in organic materials must also be taken into account, particularly in electrical conductivity where the difference between the in-plane/cross-plane can be extremely large (105 S cm–1 in PEDOT:PSS). (71) Of course, another option is to process powder into pellets, like is done commonly for inorganics.

Because solution-processable organic conductors may be designed into thin films, despite their poor solubility, this opens up new possibilities for the design of OTEGs, such as flat plates for thin films or woven-yarn fabrics for fibres. In the end, low-cost, low-temperature, and large-area manufacturing processes like printing and drop casting can be used to create OTEGs. OTEGs provide the potential for a wide range of innovative low-power applications despite the relatively low power density. (73) We discuss the material development and understanding stages since the primary focus of OTEGs is to maximise the thermoelectric characteristics of materials.
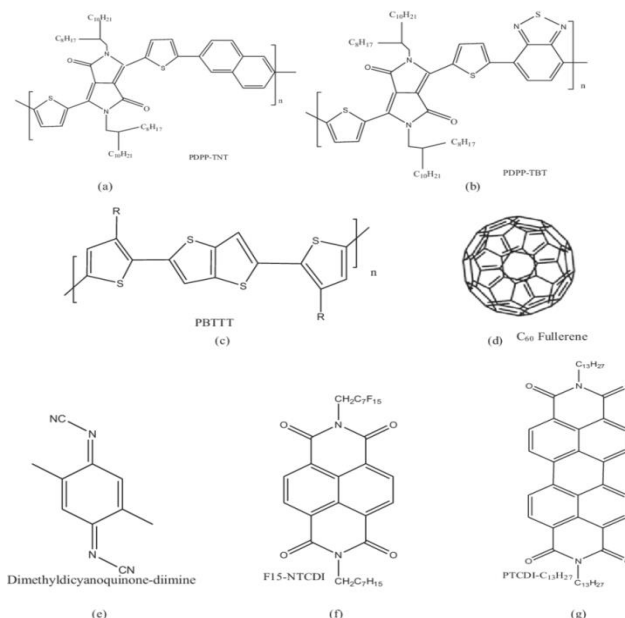
**Figure 8:** Chemical structures of the typical conductors and dopant molecules used in OTEGs.

4.2 Ionic Thermoelectric Materials

Results related to voltage production via the thermal diffusion of electronic charge carriers have been discussed so far in this study. The so-called Sorest effect, on the other hand, can cause ionic charge carriers to wander in the presence of an external heat gradient. Due to quicker ion movement in liquid/electrolyte medium, this impact is particularly noticeable at high humidity levels. These materials are more suited for capacitor-like

applications than for continuous power production because, unlike the electronic Setback effect, the thermo diffused ions do not escape from the film and instead are retrieved by the electrodes. We point the reader to a just-released review by Sohn et al. for a more thorough description of the function of humidity. (449)

The combined ion-electron conducting polymer PEDOT:PSS showed an ionic Setback effect in 2015, according to Wang et al. (450) It was discovered that the ionic conductivity significantly increased along with an increase in ambient humidity from 10% to 80% RH, raising the Setback coefficient of PEDOT:PSS from 10 V K-1 to 215 V K-1. When the thermo generated current decreased with time, it was clear that the ionic contribution was not constant even though the resulting instantaneous power factor could be enhanced by 4 orders of magnitude. Subsequently, Ail et al. investigated the underlying mechanism of this phenomena and found that, under high humidity, thermo diffusion of protons in PEDOT:PSS encouraged an internal electrochemical process within the mixed ion-electron conductor film. (451) With the application of a temperature gradient, the time dependence of the open-circuit voltage Voc(t) displayed a peak that matched the ionic Setback contribution, which subsequently fell until reaching a constant value at equilibrium; this behaviour was attributed to the electronic Setback effect. As the ionic Setback effect in mixed polymer conductors loses its influence over time, it cannot be utilised to generate much more power in a TE module. Instead, a three-parameter sensor (pressure, humidity, and temperature) made of the polymer aerogel was used to independently sense the humidity and temperature gradient using the ionic Seebeck effect, (452) which takes advantage of the ion thermo diffusion in high humidity environments to increase the sensing capability of previously published results. (453,454) Zhao et al. provided other instances of thermo diffusion-based temperature sensors by modulating the current of an electrolyte-gated organic transistor (with P3HT as the active material) using a PEO-NaOH electrolyte, increasing the sensor's sensitivity to tiny temperature changes. (455) A fresh route to the creation of a new generation of thermal harvesters was provided by the high Seebeck values related to ion transport in polymers.

With the addition of polystyrene sulphuric acid (PSSH), the first instance of a persistent thermionic effect in PEDOT:PSS films was reported in 2016. It displayed an ionic conductivity of 9 S m-1 and an ionic Seebeck value of 7.9 mV K-1 at 70% humidity. Later, Wang et al. investigated how humidity affected the ionic mobility and Seebeck coefficient of polystyrene suffocate sodium (PSS-Na+). PSSNa served as a polyanionic membrane because the cations were the only species that could move, while the negative charges (suffocate) were covalently attached to the polymer chain and therefore effectively immobile. The ionic Seebeck coefficient increased from 0.26 mV K-1 to 4 mV K-1 when the humidity was raised from 50% to 100%. (64) By presenting a mixed polymer film of PEDOT:PSS doped with PSSH in 2018, Kim et al. extended on these findings. They did this by employing a formulation of PEDOT:PSS with a greater PSS content (1:6) and PSSH that had a comparable molecular weight (Mw) to the PSS. In this example, the conductivity was found to be 29 S m-1 at 90% relative humidity, while the Seebeck coefficient reached 16 mV K-1 and remained constant throughout time. (456) PSSH served as a proton dopant by forming PSS-rich domains that allowed H+ ions to travel easily in humid environments (Figure 53a,b). Lastly, they used a hydrogen bilayer design for the thermoelectric generator to maintain high humidity levels, allowing the utilisation of the maximal harvesting capacity of such material. This showed that the high thermionic characteristics were stable under ambient settings.
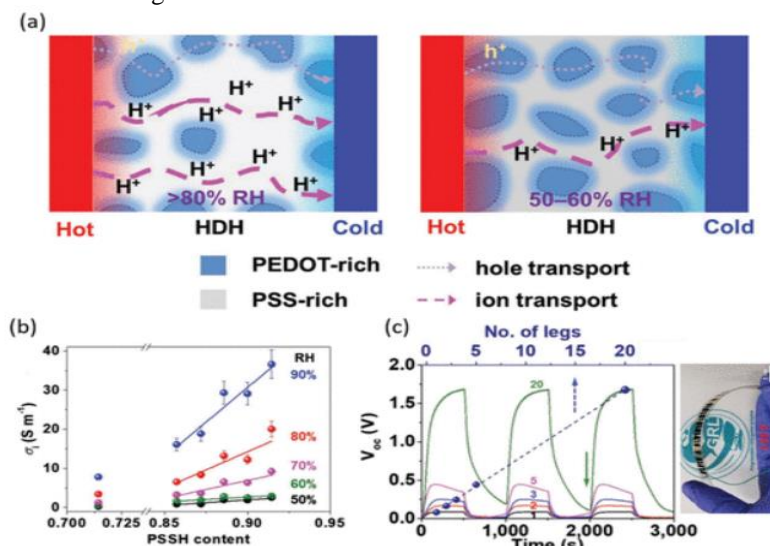
Figure 9: An illustration showing the movement of ions and electrons inside PEDOT:PSS films at high (left) and low (right) relative humidity levels. (b) Ionic conductivity at various RH levels (from 50% to 90%) and as a function of PSSH content.

The same group reported in 2019 that the addition of copper chloride (CuCl2) salts caused the thermionic characteristics of PEDOT:PSS to switch from p- to n-type. (457) A Cl- channel inside the film was visible due

to metal interaction with the PSS domains, producing a S of 18 mV K-1 and a PF of 1.7 mW m-1 K-2 at 80% RH (Figure 9). Moreover, they combined their p- and n-type thermionic materials into a generator made of ten thermocouples, attaining 1.55 V with a difference in external temperature of 4.5 K and with a RH of 80%. (Figure 9).
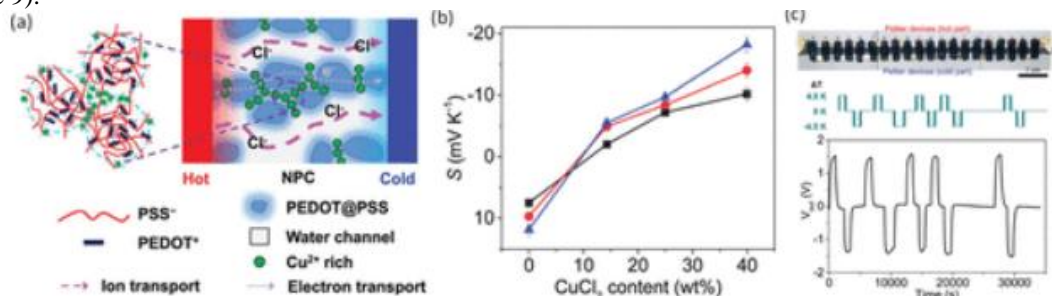
Figure: 10 Ion transport and film morphology of PEDOT:PSS CuCl2 are shown schematically in (a). (b) Seebeck coefficient vs CuCl2 concentration (wt%) for relative humidity levels of 60% (black), 70% (red), and 80% (blue). (c) A picture of the thermionic generator together with data on temperature change and voltage output over time. Reprinted from reference with permission (457). Royal Society of Chemistry 2019 Copyright.

The aforementioned approach, however, was not the only one taken to improve the ionic contribution's temporal responsiveness and provide consistent power. In order to permit a thermogalvanic effect, Chang et al. introduced Ag cations (using Ag-based salts) to Nafion (Ag-Nafion) and polystyrene-sulfonate (Ag-PSS), (458) which over time produced a constant thermogenerated current in addition to the nonconstant ionic Seebeck effect. The Seebeck coefficient values for two distinct blends are shown in Figure 55b: a positive Seebeck coefficient of about 5 mV K-1 for the 100% Ag+/SO3- molar ratio in PSS and a maximum negative S of 1.5 mV K-1 for silver nitrate (AgNO3) in Nafion. Instead, a maximum was found for the ion conductivity (Figure 55b) at low Ag+ concentrations (33%), which corresponds to 2.7 mS cm-1 for Ag-PSS and 4.3 mS cm-1 for Ag-Nafion. Chang et al. looked at how humidity affected the conductivity and Seebeck coefficient of these materials since the ionic conductivity of Nafion is very ionic because of water-assisted ion transport (Figure 10)

5. CONCLUSION

This paper categorises ionic thermoelectric materials into two groups based on the various thermoelectric conversion mechanisms: thermoelectric materials for thermo electrochemical cells (thermocouple effect) and thermoelectric materials for ionic thermoelectric capacitors (Soret effect). Their most recent advancements in thermoelectric conversion devices are also discussed. Small thermoelectric conversion devices have been evolving towards wearable technology over the past several years. Its thermoelectric performance and conversion efficiency have substantially increased, and the flexibility and stretch ability of thermoelectric conversion materials have received greater attention. Ionic thermoelectric materials' conversion efficiency has increased in comparison to conventional electronic thermoelectric materials, however there is still opportunity for improvement. Because to their excellent performances and efficiencies, solid-state inorganic semiconductors now dominate research on the conversion of thermal to electrical energy. The idea of electron-crystal/phonon-glass behaviour has been the inspiration for the creation of novel materials in this situation. Nevertheless, because to the high prices of materials and manufacturing, this technology has only found use in specialised fields like space (for example, powering satellites) and scientific apparatus (for example, cooling detectors). Due to the significant availability of its atomic components, carbon-based semiconductors have received attention in the last 20 years as promising thermoelectric materials for low-temperature energy harvesting. Its cheap prices and large-area (low T) processing utilising printing techniques are associated with further benefits. Also, the fact that they naturally have lower thermal conductivities gives them a huge edge when it comes to capturing energy from slight temperature variations.

REFERENCES

1. Kim SI, Lee KH, Mun HA, et al. Thermoelectrics. Dense dislocation arrays embedded in grain boundaries for high-performance bulk thermoelectrics. Science. 2015;348(6230):109-114
2. Pei Y, Shi X, Lalonde A, et al. Convergence of electronic bands for high performance bulk thermoelectrics. Nature. 2011;473(7345):66-69
3. Joshi G, Lee H, Lan Y, et al. Enhanced thermoelectric figure-of-merit in nanostructured p-type silicon germanium bulk alloys. Nano Letters. 2008;8(12):4670-4674
4. Bin W, Helong Z, Yu L, et al. Research progress in organic thermoelectric materials. Journal of Nanchang Hangkong University (Social Sciences) 2020, 34(01): 31-42.
5. Guangbao W. Preparation of N-type Organic Thermoelectric Materials Baesd on Single-Walled Carbon Nanotubes and Organic Small Molecules. Vol. Master. Shandong: Qingdao University of Science and Technology; 2017. p. 83

6. Shi W, Qu S, Chen H, et al. One-step synthesis and enhanced thermoelectric properties of polymer–quantum dot composite films. Angewandte Chemie. 2018;130(27):8169-8174

7. Quickenden TI, Mua Y. A review of power genera-tion in aqueous thermogalvanic cells. Journal of the Electrochemical Society. 1995;142:3985-3994

8. Jiao N, Abraham TJ, Macfarlane DR, et al. Ionic liquid electrolytes for thermal energy harvesting using a cobalt redox couple. Journal of the Electrochemical Society. 2014;161(7):D3061-D3065

9. Taheri A, Macfarlane DR, Pozo-Gonzalo C, et al. Quasi-solid-state electrolytes for low-grade thermal energy harvesting using a cobalt redox couple. ChemSusChem. 2018;11(16):2788-2796

10. Taheri A, Macfarlane DR, Pozo-Gonzalo C, et al. Application of a water-soluble cobalt redox couple in free-standing cellulose films for thermal energy harvest-ing. Electrochimica Acta. 2019;297:669-67

11. Laux E, Jeandupeux L, Uhl S, et al. Novel ionic liq-uids for thermoelectric generator devices. Materials Today: Proceedings. 2019;8:672-679

12. Yang P, Liu K, Chen Q, et al. Wearable thermocells based on gel electrolytes for the utilization of body heat. Angewandte Chemie International Edition. 2016;55(39):12050-12053

13. Zhou Y, Liu Y, Buckingham MA, et al. The signifi-cance of supporting electrolyte on poly (vinyl alcohol)–iron(II)/iron(III) solid-state electrolytes for wearable thermo-electrochemical cells. Electrochemistry Communications. 2021;124:106938

14. Wu J, Black JJ, Aldous L. Thermoelectrochemistry using conventional and novel gelled electrolytes in heat-to-current thermocells. Electrochimica Acta. 2017;225:482-492

15. Han C, Qian X, Li Q, et al. Giant thermopower of ionic gelatin near room temperature. Science (American Association for the Advancement of Science). 2020;368(6495):1091-1098

16. Duan J, Yu B, Liu K, et al. P-N conversion in ther-mogalvanic cells induced by thermo-sensitive nanogels for body heat harvesting. Nano Energy. 2019;57:473-479

17. Im H, Moon HG, Lee JS, et al. Flexible thermocells for utilization of body heat. Nano Research. 2014;7(4):443-452

18. Romano MS, Gambhir S, Razal JM, et al. Novel carbon materials for thermal energy harvesting. Journal of Thermal Analysis and Calorimetry. 2012;109(3):1229-123

19. .Romano MS, Li N, Antiohos D, et al. Carbon nano-tube - reduced graphene oxide composites for thermal energy harvesting applications. Advanced Materials. 2013;25(45):6602-6606

20. .Kang TJ, Fang S, Kozlov ME, et al. Electrical power from nanotube and graphene electrochemical thermal energy harvesters. Advanced Functional Materials. 2012;22(3):477-489

21. .Cheng H, He X, Fan Z, et al. Flexible quasi-solid state ionogels with remarkable seebeck coefficient and high thermoelectric properties. Advanced Energy Materials. 2019;9(32):1901085

22. Chang WB, Fang H, Liu J, et al. Electrochemical effects in thermoelectric polymers. ACS Macro Letters. 2016;5(4):455-459

23. Wang H, Ail U, Gabrielsson R, et al. Ionic seebeck effect in conducting polymers. Advanced Energy Materials. 2015;5(11):1500044

24. Kim SL, Lin HT, Yu C. Thermally chargeable solid-state supercapacitor. Advanced Energy Materials. 2016;6(18):1600546

25. .Chang WB, Evans CM, Popere BC, et al. Harvesting waste heat in unipolar ion conducting polymers. ACS Macro Letters. 2016;5(1):94-98