



Swansea University  
Prifysgol Abertawe



## Cronfa - Swansea University Open Access Repository

---

This is an author produced version of a paper published in:

*ChemSusChem*

Cronfa URL for this paper:

<http://cronfa.swan.ac.uk/Record/cronfa51618>

---

### Paper:

Mulla, R. & Dunnill, C. (2019). Powering the Hydrogen Economy from Waste Heat: A Review of Heat to Hydrogen Concepts. *ChemSusChem*

<http://dx.doi.org/10.1002/cssc.201901426>

---

This item is brought to you by Swansea University. Any person downloading material is agreeing to abide by the terms of the repository licence. Copies of full text items may be used or reproduced in any format or medium, without prior permission for personal research or study, educational or non-commercial purposes only. The copyright for any work remains with the original author unless otherwise specified. The full-text must not be sold in any format or medium without the formal permission of the copyright holder.

Permission for multiple reproductions should be obtained from the original author.

Authors are personally responsible for adhering to copyright and publisher restrictions when uploading content to the repository.

<http://www.swansea.ac.uk/library/researchsupport/ris-support/>

# **Powering the Hydrogen Economy from Waste Heat: A Review of Heat to Hydrogen Concepts**

Rafiq Mulla and Charles W. Dunnill\*

*Energy Safety Research Institute, Swansea University, Bay Campus, Fabian Way, SA1 8EN, UK.*

## **Abstract**

Ever increasing energy demand and environmental concerns requires new and clean energy supplies, many of which are intermittent and non-correlating with demand. In order to balance supply with demand a universal energy vector can be employed such that intermittent renewable energy can be stored and transported and then used when needed. Hydrogen is the perfect universal energy vector and one of the possible solutions that ensures environmental cleanness and maximum utilisation of renewable energy sources and high efficiency where the combustion of this fuel yields only water. One abundant and freely available energy source both anthropogenic and natural is heat. Heat can be obtained from industrial processes and is indeed often seen as a waste product with a premium to remove but is notoriously difficult to capture store and indeed transport. Capturing and storing low grade heat is therefore a significant opportunity and can be achieved via the coupling of thermoelectric generators and water electrolyzers. A thermoelectric generator is placed within a thermal energy gradient and produces a flow of current which is fed to the electrolysis unit with which it produces hydrogen and oxygen as the final products. The hydrogen can be stored for long periods and transported for “On demand” use in fuel cells for electricity of hydrogen burners for a return to thermal energy. This review summarizes the current state-of-the-art from researchers to implement thermoelectric generators and utilize heat as a primary energy source to produce hydrogen which could replace the need for extra electric power to run hydrogen production units. Further, discussion is made on suitable requirements, modifications and other related aspects associated with such a new and novel method of

hydrogen generation. Hydrogen produced from otherwise wasted energy sources can be considered to be green.

**Keywords:** Heat to hydrogen; H<sub>2</sub> production; thermoelectric; renewable energy; pollution; industrial waste.

\*Corresponding Author E-mail address: [c.dunnill@swansea.ac.uk](mailto:c.dunnill@swansea.ac.uk)  
Tel: +44 (0)1792 606244

## **1. Introduction**

The energy trilemma is one of the biggest concerns facing the future of mankind. How do we supply consistent, yet affordable and environmentally friendly energy to all? The rapidly increasing energy demand with rising cost of energy and global warming issues are well-known and a critical problems for the modern world. A rapidly increasing population, energy intensive modern lifestyle and industrialization of vast populations are all contributing to the problems associated with the energy crisis and development pathways of many nations. Fossil fuels (coal, oil, and natural gas) are the major source of energy for the entire world which leads to inevitable carbon dioxide pollution and anthropogenic global warming. Large-scale uptake of renewable energy is hampered by the correlation between supply and demand, and our ability to store and transport the clean energy over large distances and timescales.

The use of hydrogen as an energy vector allows us to store pretty much any form of renewable energy as well as decoupling supply from demand. In addition the ability to compile energy sources together such that large quantities of otherwise useless energy can be combined together into one useful mass. This review aims to highlight efforts in the conversion of industrial waste heat or solar thermal energy into hydrogen.

## **2. Heat**

### **2.1. Industrial heat**

Every year, about 474 EJ (1 EJ =  $10^{18}$  J) of energy is generated for various purposes, of which about 340 EJ is just rejected as waste heat, which reveals that about 70% of the global energy is lost to the environment without being utilized.<sup>[1]</sup> The loss of heat happens in many different ways in different sectors with a wide range of temperatures from 100 to 1000 °C.<sup>[2]</sup> There are several waste heat sources which emit low grade to medium to high temperature heat. For example, the industrial steam/water boilers, food, paper, textile industries generate low grade waste heat of temperature ~100-200 °C, chemical and other related industries

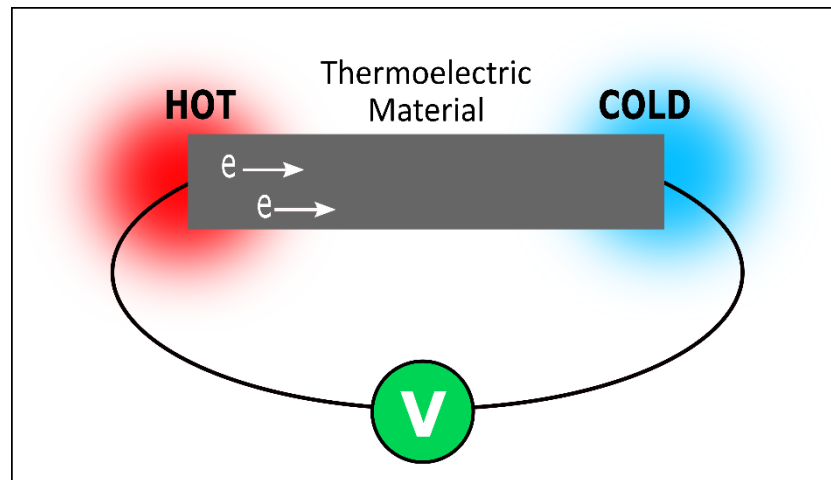
usually produce a waste heat up to  $\sim 500$  °C, while most of the metal and glass industries generate a waste heat in the high temperature range of  $\sim 500$ - $1000$  °C.<sup>[2]</sup>

## **2.2. Solar heat**

In the quest for green energy supplies to drive the hydrogen economy many researchers turn to the concept of photovoltaics in the desert. Indeed the Sahara desert receives enough solar radiation every day to power the entire globe for a year should it be possible to capture all of this energy. Photovoltaics currently operate at about 12 to 17% efficiency, but struggle to maintain efficiency when the panels themselves are hot, covered in sand or in need of complex maintenance. Solar heat however can be upwards of 80% efficient with very simplistic technology consisting of black painted pipes transporting a loop of water. Significant gains can be made in the overall energy efficiency of solar energy to an electrical output by utilising a solar heat array rather than a solar photovoltaic array.

## **3. Thermoelectric Generators**

Thermoelectric generators are solid state devices which are used to convert heat into electricity.<sup>[3]</sup> The basic components of a thermoelectric generator are thermoelectric materials which have an ability to convert thermal gradients into electric voltage. Thermoelectric materials work according to the principle of “Seebeck effect” which was discovered by T. J. Seebeck, a German Physicist. An applied temperature gradient ( $\Delta T$ ) to an electrical conductor generates an electric voltage ( $\Delta V$ ) due to the charge flow from hot side to cold side of the conductor. The ratio between the ‘generated voltage’ to the ‘applied temperature gradient’ is known as Seebeck coefficient ( $S$ ), a key parameter which shows the ability of material to produce electric voltage under given temperature gradient. **Figure 1** is an illustration of this mechanism.

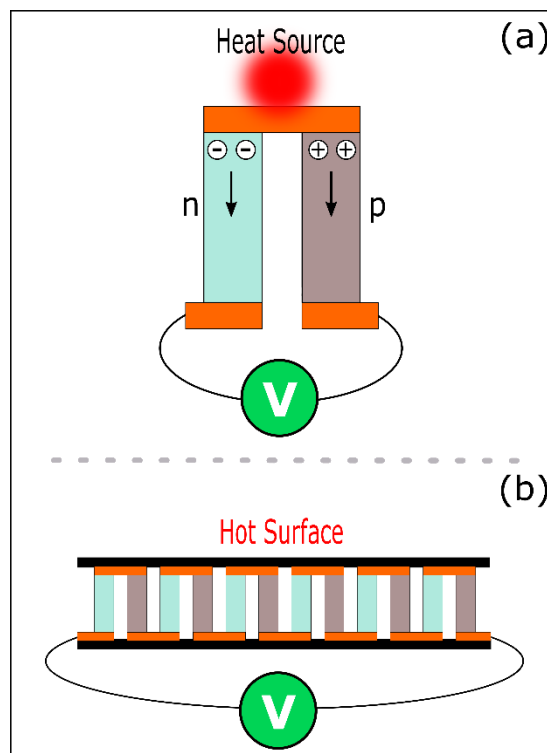


**Figure 1.** A schematic illustration of Seebeck effect.

In a thermoelectric generator, two dissimilar thermoelectric materials are joined at their ends to form junctions and multiples of such junctions are arranged in series. Usually n and p-type conductors are coupled together in this way to form a device.

**Figure 2 (a)** shows one such junction made up of one n-type and one p-type material.

In order to gain more electric power output, more couples are connected to each other that is illustrated in **Figure 2 (b)**.



**Figure 2.** Showing (a) a thermoelectric couple made up of one n-type and one p-type leg, and (b) multiple thermoelectric legs connecting in series to form a thermoelectric generator.

The conversion efficiency of heat into electricity is an important factor which decides how generators perform in practical applications. Basically, the efficiency of a thermoelectric generator mainly depends on the efficiency of thermoelectric materials to convert heat to electricity. The thermoelectric efficiency of a material is also known as “figure of merit” denoted as  $ZT$ , is a dimensionless number, and is defined as follows,<sup>[4]</sup>

$$ZT = \frac{S^2 \sigma T}{\kappa} \dots\dots\dots(1)$$

where  $S$  is the Seebeck coefficient,  $\sigma$  and  $\kappa$  are the electrical and thermal conductivities, and  $T$  is the temperature. Better value of  $ZT$  means better thermoelectric material.

The thermoelectric generator efficiency ( $\eta$ ) is mainly decided by this  $ZT$  value of the materials used in the fabrication of the generator. This is defined as<sup>[5]</sup>

$$\eta = \eta_c \left[ \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+\frac{T_c}{T_h}} \right] \dots\dots\dots(2)$$

The term  $\eta_c$  is the standard Carnot’s efficiency, which is given by

$$\eta_c = \frac{T_h - T_c}{T_h} \dots\dots\dots(3)$$

where  $T_h$  and  $T_c$  are the hot and cold temperatures under which the generator works. So, by looking at equation (2), it is clear that the  $ZT$  value has very important role. Further, the large operating temperature difference has also its own contribution but ultimately it is all about the material’s ability to drag heat and make it useful electric power.

Initially, thermoelectric generators were meant for niche applications.<sup>[6]</sup> They were preferred for such applications even though the conversion efficiency was very low due to their ability to generate power in remote areas with reliability and without any need of complex technology. It is during 21<sup>st</sup> century, the development of better thermoelectric materials able to expand its applications.<sup>[6]</sup> Earlier, there were only a few well known thermoelectric materials which were being used for the making of thermoelectric generators, which limited its use. Recently, many new class of materials such as metal sulphides,<sup>[7]</sup> selenides,<sup>[8]</sup> half-Heusler compounds,<sup>[9]</sup> filled skutterudites,<sup>[10]</sup> clathrates,<sup>[11]</sup> oxides,<sup>[12]</sup> organic/polymer materials,<sup>[13]</sup> Zintl compounds,<sup>[14]</sup> carbon based compounds,<sup>[15]</sup> etc. have been introduced with promising properties giving new hopes to the future of thermoelectric technology. Further, several strategies such as doping,<sup>[16]</sup> nanostructuring,<sup>[17]</sup> alloying,<sup>[18]</sup> resonant level filling,<sup>[19]</sup> band engineering,<sup>[20]</sup> etc. were also successful in improving the ZT value of the materials. For example, many studies have shown clear improvements in the ZT values of bulk materials by just bringing them to nanostructured dimensions.<sup>[21]</sup> This approach is able to decouple the electronic and thermal conductivity of the materials to a certain extent when they are brought into nano-dimensions which significantly improves ZT value. To best of our knowledge, Hicks and Dresselhaus were the first to show very fascinating results from a material when it undergoes into nano-regime with the help of their theoretical investigations.<sup>[22]</sup> Another interesting way that has been widely used to make better materials is creating complex crystal structures where the thermoelectric properties can be significantly improved.<sup>[23]</sup> This aspect of having complex crystal structures is usually referred as phonon glass - electron crystal (PGEC) concept, elucidated by Glen Slack.<sup>[24]</sup> This concept proposes that a good thermoelectric material should act like a glass for phonons where the thermal conductivity can be very low and it also be a perfect crystalline material for electrons where the electrical conductivity can be high. Such concepts and theories are very much useful for

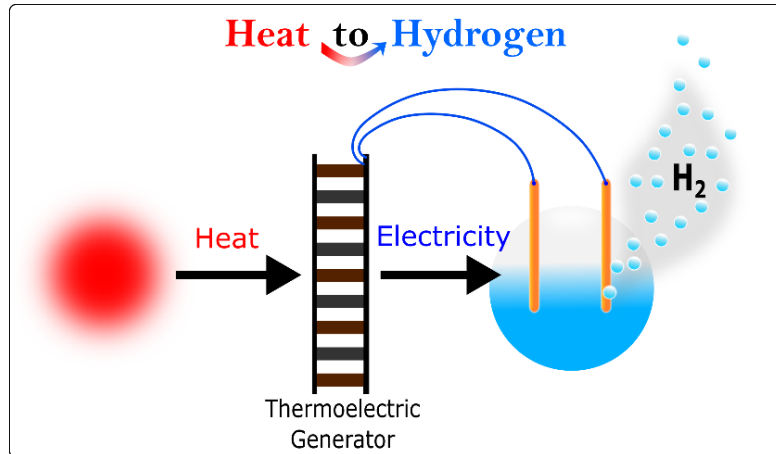


the researchers which guide in building new materials with more effective and better properties. Efforts are going on to make new cost effective thermoelectric materials to implement them into commercial thermoelectric generators for practical applications.

#### **4. Hydrogen Production**

Hydrogen can be produced in many different ways such as electrolysis, thermolysis, photocatalysis, steam methane reforming or indeed photocatalytic water splitting.<sup>[25]</sup> The simplest way of producing green hydrogen from renewable energy sources is to use water splitting by the application of electric current. For this, a DC electric supply is passed through a catalytic solution splitting water into its components of both hydrogen and oxygen and is usually referred as “electrolysis of water”.<sup>[26]</sup> High-purity hydrogen can be produced but, the supply of extra electric power demands up to two-thirds of total hydrogen production costs.<sup>[27]</sup> Thermal energy can be used in 2 ways to support hydrogen production via electrolysis. Some water splitting units can operate at higher temperature with heat supplied from the surroundings,<sup>[28]</sup> allowing for a higher efficiency process with some of the water splitting over potential being covered by the thermal energy. Alternatively electrolyser units can be coupled to thermoelectric technology or heat engines such that a heat gradient can generate the current which can be used to split the water.

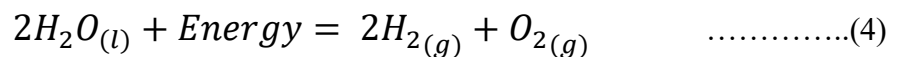
In this way otherwise wasted thermal energy can be captured as hydrogen, a storable, transportable and readily useable form. Thermoelectric generators convert heat into electricity and which can be directly supplied to the water electrolysis unit. A Schematic illustration of the “heat to hydrogen” concept is illustrated in **Figure 3**.

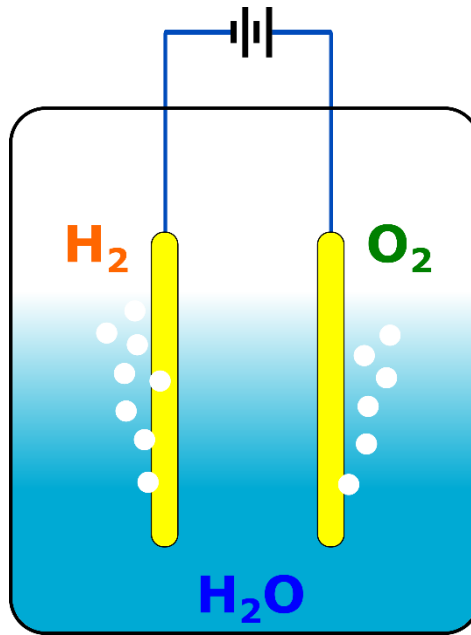


**Figure 3.** A Schematic illustration of the “heat to hydrogen” concept

#### 4.1. Electrolysers

The splitting of water is performed using “electrolysers”, which are the devices with two electrodes that use an electric current to splits a water molecule.<sup>[29]</sup> Typically, a DC power with a voltage in excess of 1.24 V is applied between the two electrodes which are immersed in water bath having aqueous electrolyte. As a result, hydrogen evolution occurs at the cathode and oxygen at the anode (**Figure 4**). The decomposition of water (H<sub>2</sub>O) into hydrogen (H<sub>2</sub>) and oxygen (O<sub>2</sub>) happens because the ions are forced to undergo either oxidation or reduction at the electrodes due to the application of electric voltage, which can be expressed as,

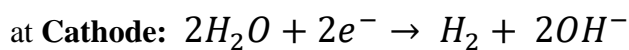
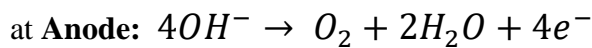




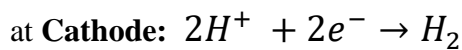
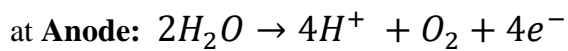
**Figure 4.** Showing a schematic electrolyser, a DC power is applied between the two electrodes which are immersed in water.

Depending on the nature of electrolyte used, electrolysis process can be carried out either in neutral, basic or acidic conditions. The reactions at the electrodes will be different for different pH conditions.

If the media is basic,



For the acidic media,



The electrochemical decomposition of water was first observed in the 18<sup>th</sup> century and later by Michael Faraday who described the relationship between the electric current and the amount of hydrogen and oxygen evolve at the electrodes which is as follows,

$$I = znF \dots\dots\dots(5)$$

where  $I$  is the current applied between the electrodes,  $z$  is the number of electrons involved in the reaction,  $n$  is the number of moles of hydrogen or oxygen produced, and  $F$  is the Faraday constant ( $F = 96485 \text{ C mol}^{-1}$ ). Expression (5) shows that there is direct relation between the applied current and the amount of hydrogen generated. The efficiency of an electrolyser can be defined as,<sup>[30]</sup>

$$\text{Efficiency} = \frac{\text{Useful Energy Output}}{\text{Total Energy Input}} \dots\dots\dots(6)$$

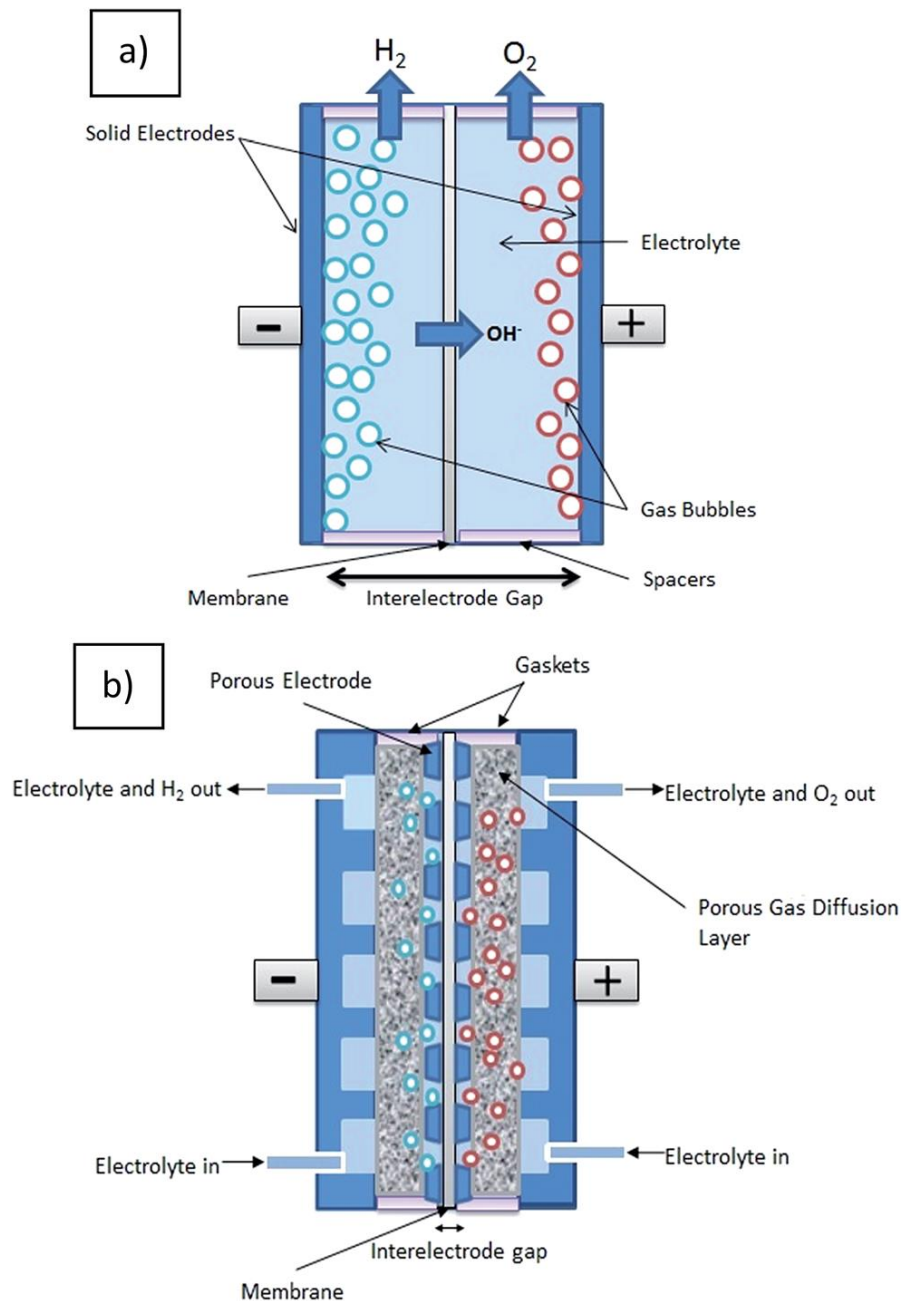
‘Useful energy output’ is referring to calorific value of the hydrogen produced and ‘total energy input’ is the energy consumed in the production of the hydrogen.

Several factors effect this aspect such as cell design, electrode material, electrode surface, electrolyte nature, etc.<sup>[26, 30-31]</sup> The efficiency of the system however also needs to consider the economic/value efficiency in that if the value of your hydrogen is higher than the value of the energy input then the process is profitable. Using otherwise wasted heat as a resource shows significant financial benefits irrespective of the energetic efficiency of the process, as the energy input is effectively free. Your capital costs are therefore split across the years of operation leading to an economic model whereby reduced capital costs are in many cases more important than small deficiencies in efficiency.

The major water electrolysis technologies are alkaline electrolysis cells (AEC), proton exchange membrane electrolysis cells (PEMEC) and solid oxide electrolysis cells (SOEC).<sup>[32]</sup> AECs are the one of the simple water electrolysis technologies widely used for applications. These AECs can be easily designed in a relatively low capital cost and are durable which have been in use in different industries.<sup>[33]</sup> AECs offering the advantage of simplicity and so the present research is mainly focussed on increasing current density and efficiency of the cells.<sup>[32]</sup> PEMECs are built with solid polymer electrolyte and are useful in small-scale applications as the cell design is complex and requires expensive catalyst and fluorinated membranes but, these cells provide high power density and efficiency.<sup>[34]</sup> Many novel

improvements have been achieved in the designs of PEM electrolyzers.<sup>[35]</sup> SOECs are designed using solid ion-conducting ceramics as the electrolyte. This makes them to use only at higher temperatures but these cells can provide high efficiency with low material cost.<sup>[32]</sup> Presently, the SOEC cells are only demonstrated on a laboratory scale and making them widely useful for commercial applications is under progress.<sup>[28, 36]</sup>

In general, the electrolyzers have three common components: electrodes, separators, and electrolyte. In the basic design, the two electrode plates are separated by a liquid electrolyte which usually faces difficulty in easy charge flow and always observes the low current densities. Recently, researchers are working on the improvements in electrolyser cell designs and a new concept is attracted the scientific community which is based on “zero gap cell”.<sup>[30]</sup> **Figure 5** shows the clear differences between these two cell designs. A “zero gap cell” is the direct compression of two porous electrodes having a hydroxide ion conducting membrane on them.<sup>[30-31]</sup> This design helps to significantly minimize the Ohmic resistance that occurs as a result of traditional design. This provides an alkali electrolyser with efficiencies close to that of the PEM system however significantly reduced capital costs due to the available material choice and the lack of platinum.

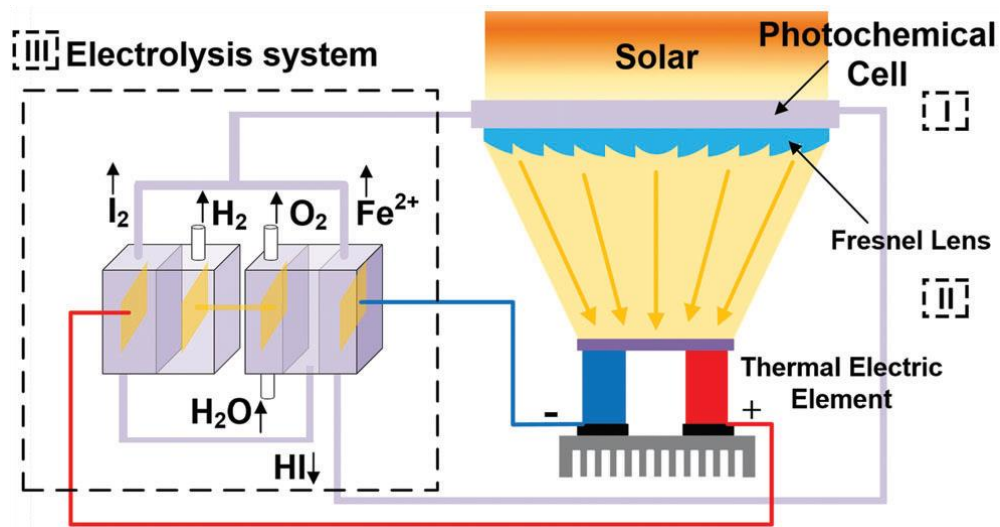


**Figure 5.** Showing the principal differences in (a) Standard setup, (b) zero gap setup designs. Reproduced from Ref. 30.

## 5. Efforts on Heat to Hydrogen Concept

An effort to implement thermoelectric technology into hydrogen production was implemented during 1976 by Ohta *et al.* from Yokohama National University, Japan.<sup>[37]</sup> They proposed a hybrid thermochemical water splitting unit which primarily uses solar radiation. The proposed model consists of three subsystems, the schematic diagram of which is shown

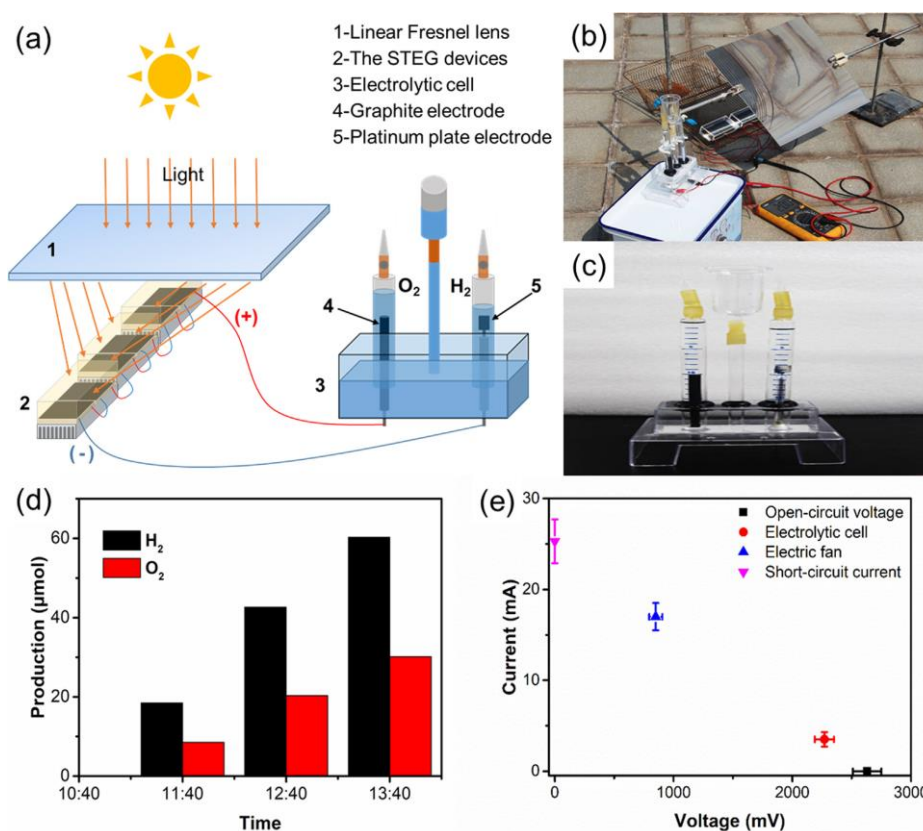
in **Figure 6**. The first subsystem is a flat transparent cell which work as a photochemical reactor. This cell is placed directly under sunlight to achieve photochemical reaction. Below this photochemical cell, a Fresnel lens is fixed which works for the second subsystem that consists of a thermoelectric generator, a solar radiation collector and a cooling plate. So, using such arrangements, a temperature gradient is achieved in the thermoelectric generator which then produces electric power. Finally, in the third subsystem, there are two electrolyzers that add the contributions from photochemical reactor and thermoelectric generator. The system is successfully demonstrated for the hydrogen production and a production rate of 1 litre hydrogen per hour was observed. The efficiency of this hybrid system was estimated as 15-25%. After this report, only recently we can see a few works on this aspect.



**Figure 6.** A proposed model of hybrid thermochemical water splitting unit, consists of three subsystems such as (i) photochemical reactor (ii) thermoelectric generator and (iii) electrolyzers. Reproduced from Ref. 37.

More recently, Zhang *et al.* have used commercial thermoelectric generators for the application of water splitting.<sup>[38]</sup> They have modified the thermoelectric generator surfaces by coating carbon nanoparticles via a simple candle flame. These are then used as solar thermoelectric generators in which solar light is used as source of heat.

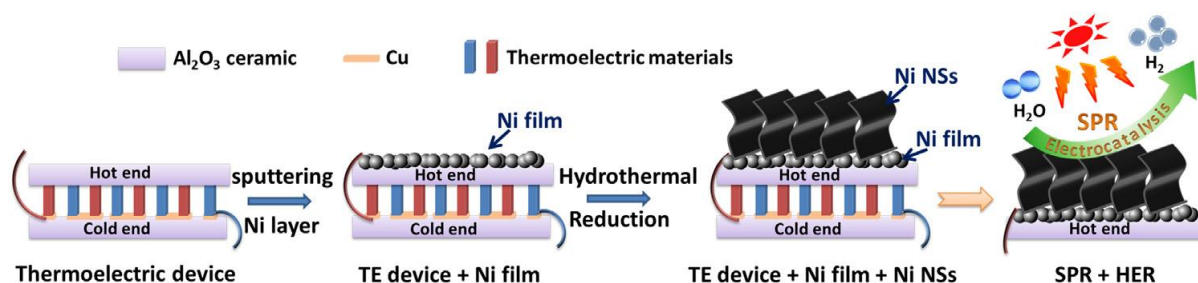
This coating helped in the efficient capturing of solar radiation and eventually in creating sufficient temperature gradient in the generators and hence more electric power output for the purpose. It is found that there was a 34 times better efficiency from the thermoelectric generators after coating. **Figure 7 (a-c)** shows the schematic water splitting system along with its real images, and **figure 7 (d)** gives the hydrogen and oxygen production data at different day time sunlight. **Figure 7 (e)** is the V-I characteristics of designed series of thermoelectric generators under different work states. Overall, a simple technique to lift the performance of the commercial thermoelectric generator is done by simply coating carbon using candle flame.



**Figure 7.** (a) An illustrative and (b) real picture of water splitting unit, (c) home-made electrolytic cell, (d) production quantity of H<sub>2</sub> and O<sub>2</sub> at different times, (e) I-V characteristics of thermoelectric generator in different work conditions. Reproduced from Ref. 38.



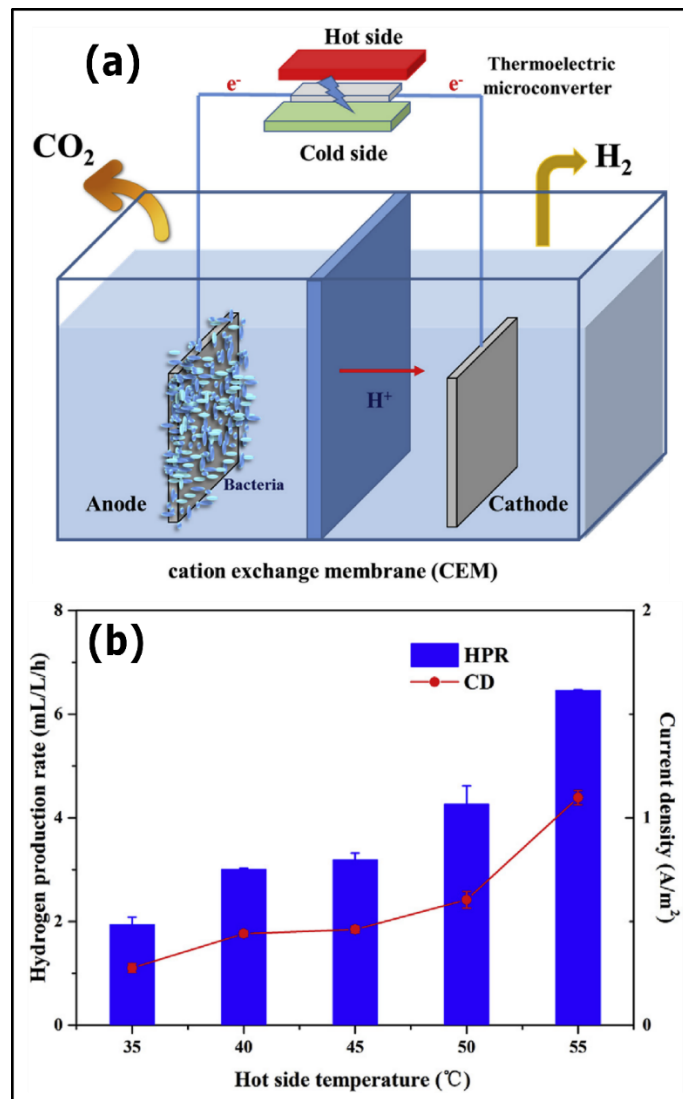
A similar effort of coating particles on thermoelectric generator has been reported by Zhao *et al.*<sup>[39]</sup> Here, an earth-abundant element, Ni has been deposited in the form of nanosheets layer grown on the hot side of the generator which act as a multifunctional agent. The schematic representation of Ni nanosheets array growth on thermoelectric device is shown in **Figure 8**. The as grown layer works as electrocatalysts as well as heat absorption layer for thermoelectric device and hence supports in the improvement of overall water splitting. The voltage generated from the thermoelectric device was given to water splitting unit. Ni nanosheets layer not only helps in achieving a good temperature difference in the thermoelectric device, but also works as an electrocatalysts for hydrogen evolution reaction. The hybrid system proposed has shown a good hydrogen production rate of 1.818 mmol/h. This method could be helpful in practical applications which can efficiently work by utilizing solar and waste heat.



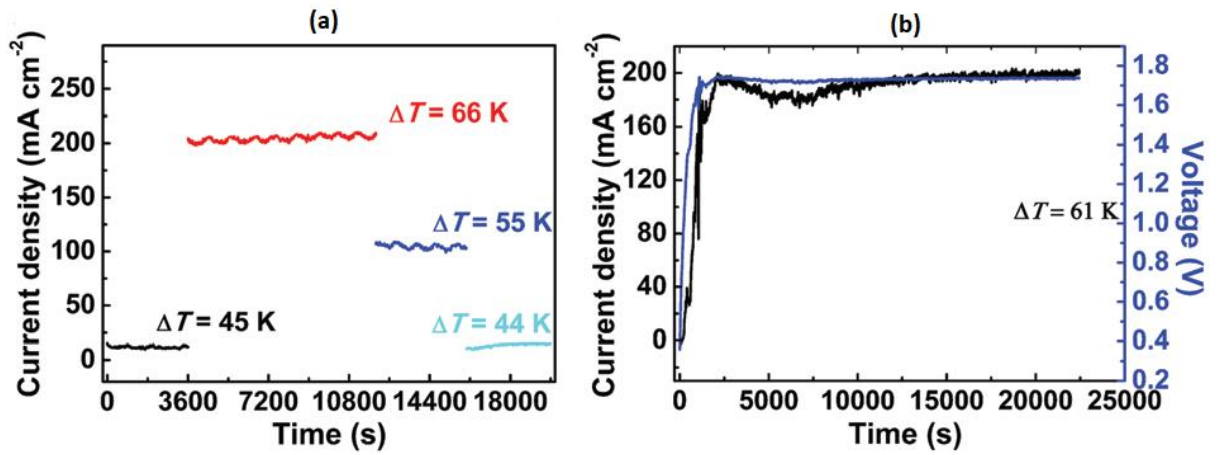
**Figure 8.** Schematic representation of Ni nanosheets array growth on thermoelectric device. Reproduced from Ref. 39.

Chen *et al.* have demonstrated hydrogen production in a microbial electrolysis cell coupled with thermoelectric generator.<sup>[40]</sup> The microbial electrolysis cells are one of the methods to produce hydrogen, and here also an extra voltage is required to achieve the release of hydrogen. **Figure 9 (a)** shows the illustrative scheme of the microbial cell with thermoelectric generator. It was observed that even at low temperature difference of just 5 K, there was generation of energy. **Figure 9 (b)** gives

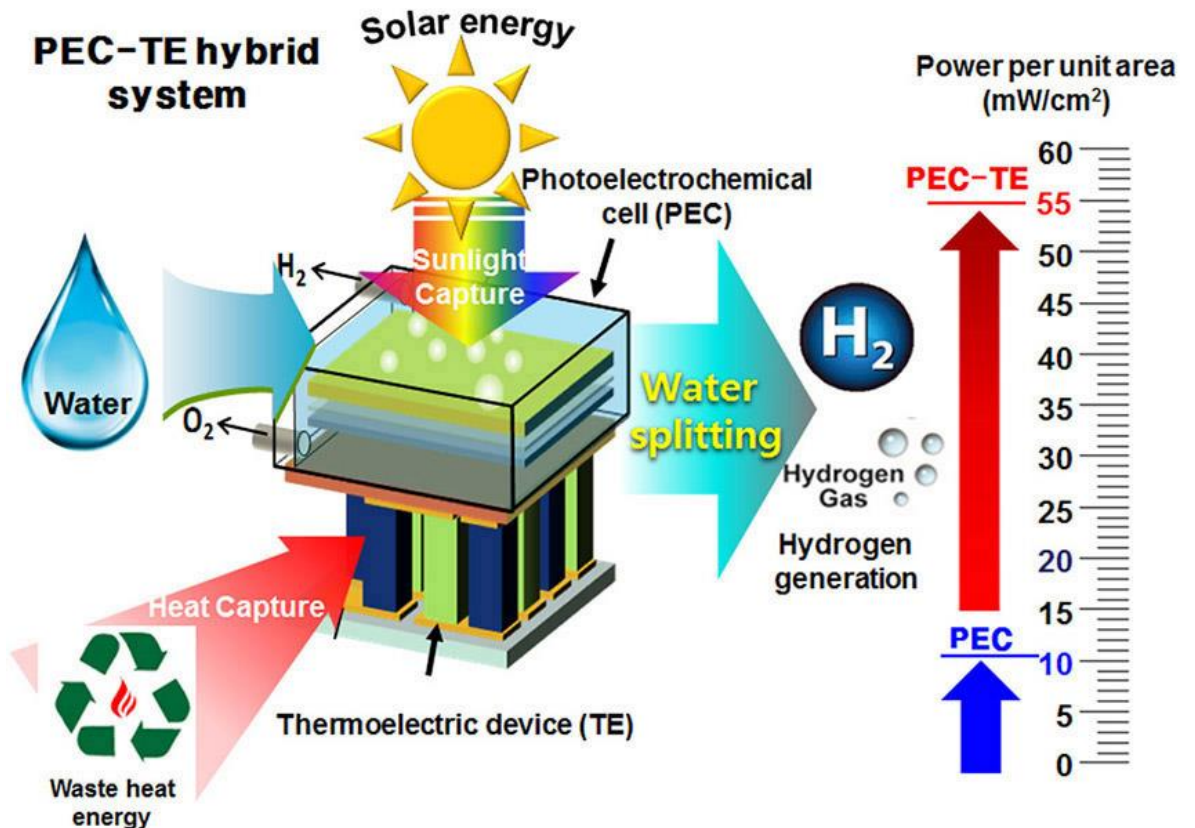
the details of current density and hydrogen production rate at different hot side temperature in the thermoelectric generator. They also showed that at high temperatures, the yield of hydrogen generation increased from 1.05 to 2.7 mol/mol acetate leading to a coulombic efficiency of about 83%, indicating a promising way to make hydrogen from microbial reactions. The implementation of thermoelectric generators for the water splitting was also trialled by Zhou *et al.*<sup>[41]</sup> **Figure 10 (a)** shows the real time values of current densities under different temperature gradients applied to the generator, and **figure 10 (b)** illustrates the real-time stability of the current and voltage generation for a fixed temperature gradient.



**Figure 9.** (a) An illustrative scheme of the microbial cell with thermoelectric generator, (b) hydrogen production rate and current density at different hot side temperature. Reproduced from Ref. 40.

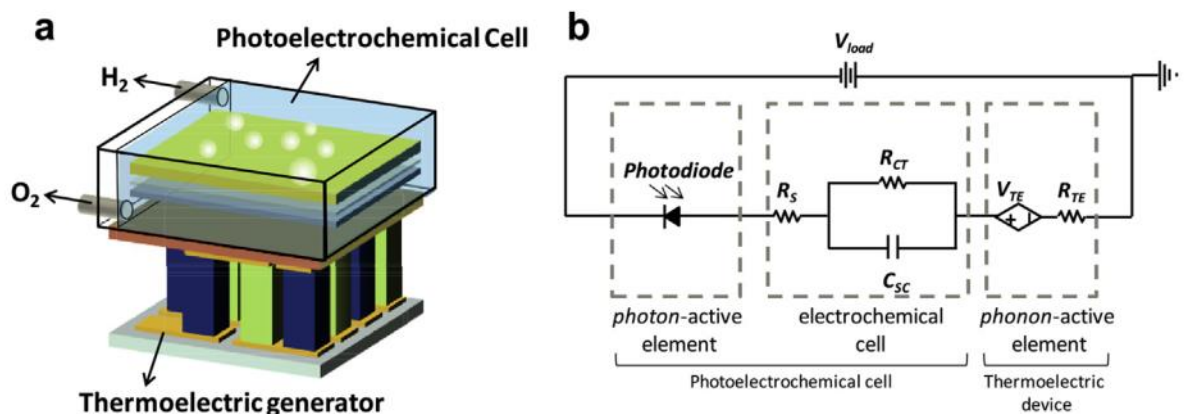


**Figure 10.** (a) Real time values of current densities under different temperature gradients applied to the generator, (b) real-time stability of the current and voltage generation for a fixed temperature gradient. Reproduced from Ref. 41.



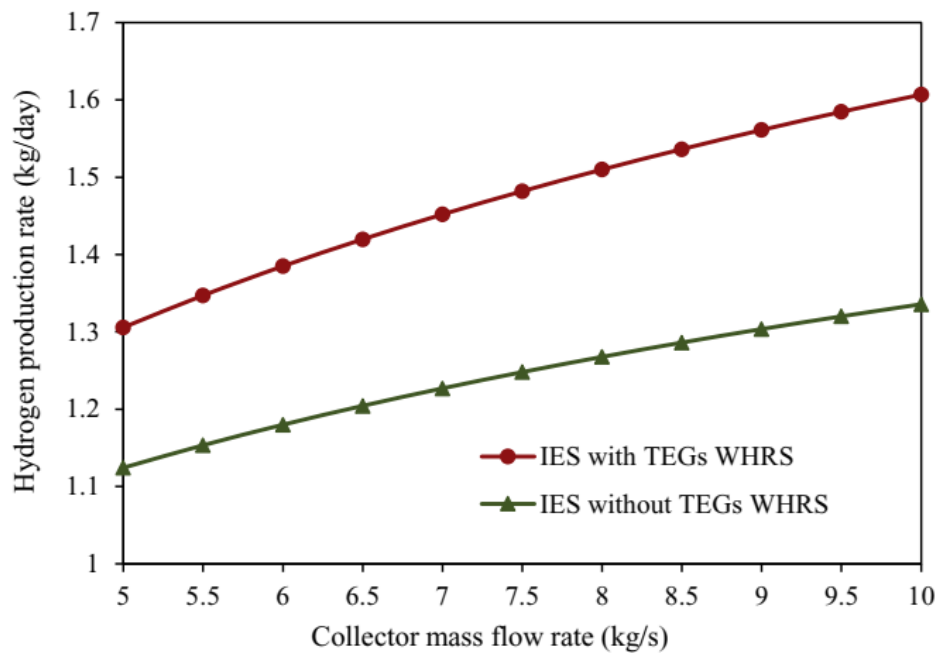
**Figure 11.** A schematic illustration of thermovoltage-driven solar water splitting hybrid system. Reproduced from Ref. 42.

Jung and Lee have successfully designed a thermovoltage-driven solar water splitting device.<sup>[42]</sup> It is a hybrid water-splitting setup, having photoelectrochemical and thermoelectric devices. The proposed setup can efficiently runs water-splitting reaction to produce storable hydrogen. The system harnesses solar radiation from photoelectrochemical device and waste heat from thermoelectric device. A schematic illustration of this hybrid system is shown in **Figure 11**. The power scale in the figure indicates the significantly higher energy generation in case of this hybrid structure than in photoelectrochemical alone. Such a hybrid design concept was previously reported by Lee and co-workers,<sup>[43]</sup> the clear schematic structure and its equivalent block diagram can be seen in **Figure 12**. Recently, Yang *et al.* have fabricated a hybrid energy cell for water splitting that is composed with a triboelectric, a thermoelectric, and a solar cell.<sup>[44]</sup> These three individual energy production cells can be used to simultaneously or individually by harvesting mechanical, thermal, and/or solar energies. The hydrogen production speed from this hybrid device is found to be  $4 \times 10^{-4}$  mL/s.



**Figure 12.** (a) Schematic structure and (b) its equivalent block diagram of thermovoltage-driven solar water splitting hybrid system. Reproduced from Ref. 43.

Habibollahzade *et al.* have done optimization of an integrated energy system which is composed of a thermoelectric generator, a parabolic solar collector and an electrolyser.<sup>[45]</sup> Similarly, Khanmohammadi *et al.* have shown a clear enhancement in the performance of an integrated system for hydrogen production using waste heat recovery with the help of thermoelectric generators.<sup>[46]</sup> To make it realize they have studied the hydrogen generation rate from the proposed system with and without thermoelectric generator and found a clear change between them, and it can be clearly observed in **Figure 13** which gives hydrogen generation rate in these two systems.

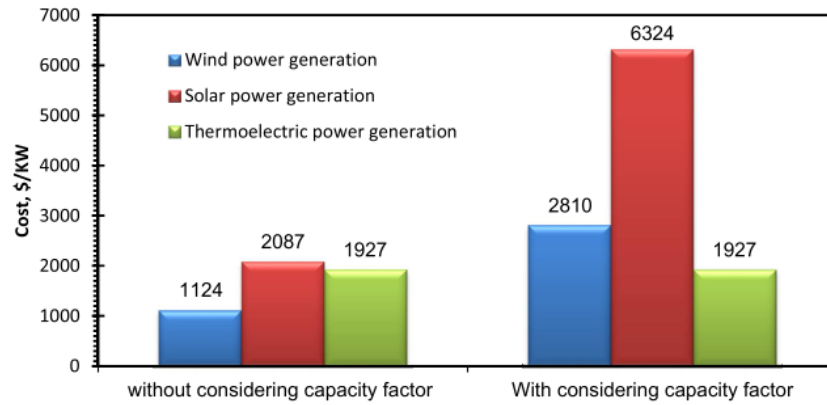


**Figure 13.** Hydrogen generation rate in the systems with and without thermoelectric generator. Reproduced from Ref. 46.

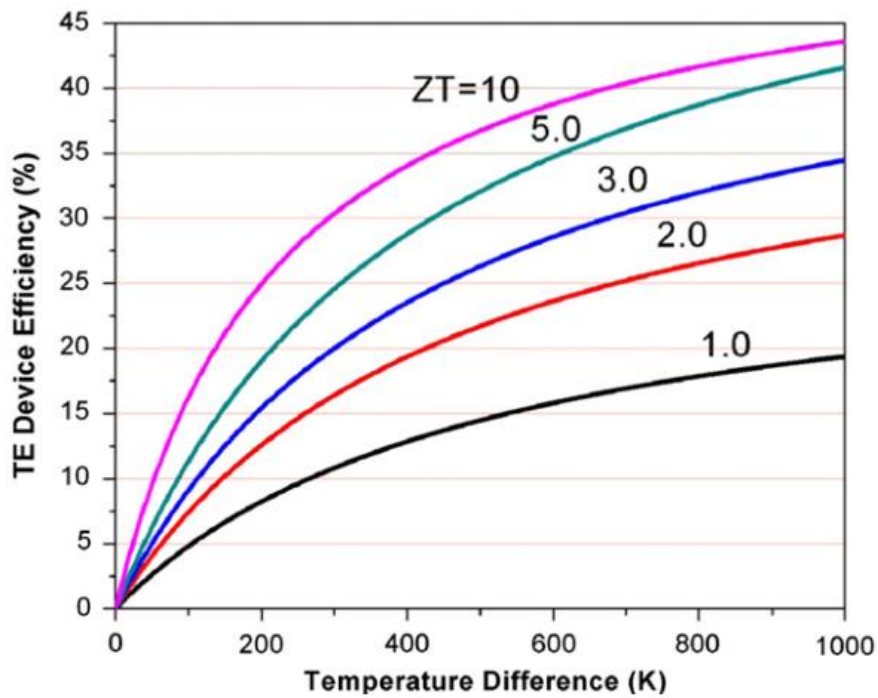
A slightly different approach of coupling thermoelectrics and electrocatalysis to produce hydrogen has been reported by Liu and co-workers.<sup>[47]</sup> Here, there is no actual use of thermoelectric generator but the thermoelectric phenomenon play its role in the process. PbTe-PbS/TiO<sub>2</sub> electrodes are prepared for the splitting of water into

hydrogen. PbTe nanolayer was deposited on TiO<sub>2</sub> nanotubes and then conversion of PbTe to PbSe was done by linear sweep voltammetry, finally forming PbTe-PbS/TiO<sub>2</sub> structure. This kind of electrodes possess gradient p-n-n band configuration. In the system, PbTe-PbS/TiO<sub>2</sub> was used as anode, Pt as cathode. The electrolyte act as hot side and the electrochemical reaction being endothermic act as cold side with the hydrogen production. Inside the electrode, there is heat-excitation of electrons from n-type PbTe and holes from p-type PbS. This type of heat-excited charge carriers in the PbTe-PbS/TiO<sub>2</sub> electrodes stimulate the hydrogen evolution from the surface of the cathode electrode. The proposed system produced hydrogen at a rate of 6.1 mL cm<sup>-2</sup> h<sup>-1</sup>. This is also a useful idea to make use of low quality waste heat of the system by the help of thermoelectric phenomenon to produce clean energy in the form of hydrogen.

When it comes to the conversion of heat to hydrogen or other useful form of energy, in general, electricity, there are many options. But among all, thermoelectric heat conversion is the one which converts without any need of mechanical work during the conversion. It is just a direct conversion. Therefore it can work better when it is with solar heat or waste heat. To show this aspect practically, Liu *et al.* have designed a thermoelectric generator of output power 500 W, which they call it as “direct heat to electricity (DHE) technology”.<sup>[48]</sup> For this, 96 thermoelectric modules were assembled to get an output power of 500 W at a temperature difference of 200 K. By detailed study, they found that, in terms of equivalent energy generation, the cost of DHE power generator is lower than that of photovoltaics. The cost comparison has also been made with other generation technologies which is shown in **Figure 14**, clearly showing that it is not costlier than others.



**Figure 14.** The cost comparison between different power generation technologies. Reproduced from Ref. 48.



**Figure 15.** The efficiency of the thermoelectric generators with respect to the ZT values. Reproduced from Ref. 21.

Further, the efficiency of the thermoelectric generators with respect to their ZT values is shown in **Figure 15**. Under different temperature gradients the generators work with efficiency as shown in the figure.<sup>[21]</sup> At present, the highest achieved ZT value is around 2-3 and the available waste heat particularly from high temperature

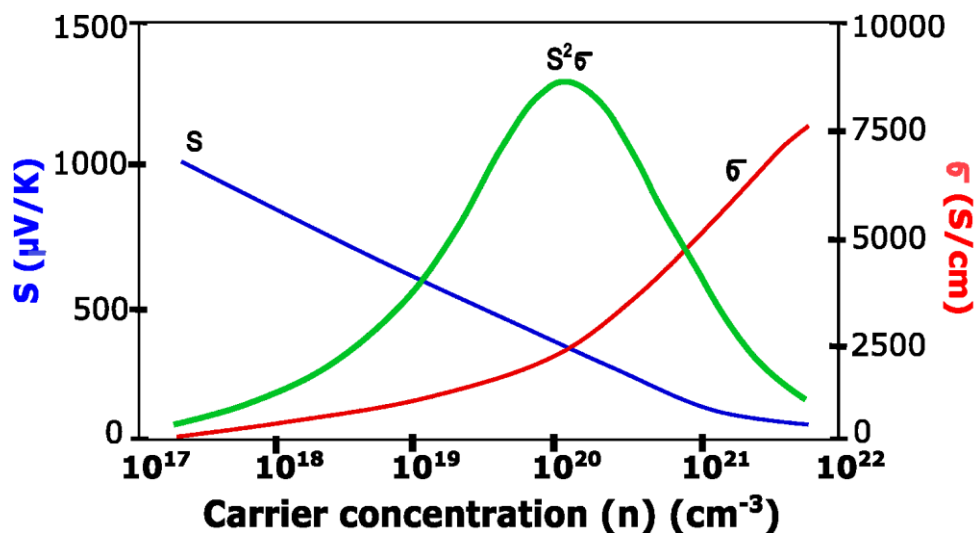
industries could easily provide temperature gradients of 100 to 300 K. For example, a thermoelectric generator designed with materials of  $ZT = 3$  can work with an efficiency of 15% under a temperature gradient of 200 K and it can further reach 20% for 300 K. There are various proposed designs on how effectively the waste heat can be utilized by thermoelectric generators. One of the designs could be having a hollow cylindrical shaped or closed rectangular shaped generator that can be fixed to the high temperature exhaust pipes of the industries. Further, the use of thermoelectric generators not only limited to the conversion of waste heat but also used in the utilization of solar radiation.<sup>[49]</sup> Concentrating solar thermoelectric generators (STEG) where the sunlight is focused on thermoelectric elements by using concentrating lenses, are successfully demonstrated with a conversion efficiency of 7.4%.<sup>[49]</sup> So, looking at these aspects, it is proposed that the concept of 'heat to hydrogen' can be successfully implemented in the water splitting units which can make the technology as a clean way of hydrogen production.

## **6. Summary and Outlook**

The hydrogen production by water electrolysis is very simple and straightforward method. Further, the use of waste heat or industrial heat by means of thermoelectric materials would have made it popular but, it is not. In reality, the technology has some difficulties and therefore there is a less progress and not much increase in the utilization of this very interesting method of producing a clean energy. The main reason could be the need of continuous external power supply for the water splitting which makes it economically inefficient. Further, alkaline based electrolysis technology is the most common and simple method for generating hydrogen but also least efficient than recent technologies such as proton exchange membrane electrolysis and solid oxide electrolysis cells. However, cost wise this is far better than these recent methods. If the water splitting model is hybrid in nature,



like having thermoelectric generator coupled with it, then the difficulty in extra power supply can be resolved. The next question is whether the heat into electricity generation happens efficiently in thermoelectric generators? We find that there are some associated problems. As, it is mentioned earlier, the generator efficiency mainly rely on the efficiency of thermoelectric materials that is the ZT value. The equation (1) which defines ZT, the parameters in the numerator are Seebeck coefficient and electrical conductivity and at the bottom, we have thermal conductivity. So, clearly, a material with high Seebeck coefficient and good electrical conductivity is needed whilst low thermal conductivity. However, all these three electronic parameters are so strongly coupled to each other that the enhancement in the ZT value cannot easily be achieved. For instance, a good electrical conductor, such as a metal, will have very high electrical conductivity but the Seebeck coefficient will be negligible, so the  $S^2\sigma$  will not be high. The thermal conductivity is also very high which leads to a very low ZT value, which means less efficient conversion of heat into electricity. **Figure 16** shows how the Seebeck coefficient and electrical conductivity are coupled in materials.<sup>[5]</sup>



**Figure 16.** Variation in the Seebeck coefficient and electrical conductivity with respect to charge carrier concentration in thermoelectric materials. Reproduced from Ref. 5.

This figure shows the variation of Seebeck coefficient and electrical conductivity with carrier concentration. If the material is less conducting then Seebeck coefficient is very high and as

number of carriers increase, there is a fall in the value. Ultimately a high power factor occurs for moderately conducting materials, such as some semiconductors or doped semiconductors. There therefore must be a trade-off for the application and material choice. The continuous scientific efforts have been successful in improving the ZT value by different approaches like alloying, doping, nanostructuring, etc. These efforts have helped in reaching a decent value that is  $ZT = 2$  to  $3$ , which has been observed in some materials. But, in order to make it commercially successful, there is a need of further enhancement of the ZT value. Another issue which has received concern is that many of the best thermoelectric materials are not cost effective and are toxic in nature.<sup>[50]</sup> The present commercial thermoelectric generators are mainly based on  $\text{Bi}_2\text{Te}_3$  and  $\text{PbTe}$  like materials. This is potentially the main drawback to implement technology on a large scale. For example, the element which is a key ingredient in successful thermoelectric materials is tellurium (Te). This element is very scarce, toxic and even its abundance is less than gold (Au). Nevertheless, new designs to capture heat efficiently is also an important need to make the technology more efficient. So, more research on finding better materials is a must to make the technology useful.

In conclusion, Hydrogen is a green fuel as it only produces water as a by-product when combusted. Thermoelectric materials are very essential to make this “heat to hydrogen” concept useful, recycling low grade waste heat. However, finding better and less-toxic and cost effective thermoelectric materials is very important. There are some difficulties and concerns regarding the efficiency and toxicity but, it cannot be just ignored.

**Acknowledgements:** Authors are thankful to Welsh Government (EU’s European Regional Development Fund) for funding the RICE (Reducing Industrial Carbon Emission) project.

- [1] C. Forman, I. K. Muritala, R. Pardemann, B. Meyer, *Renewable and Sustainable Energy Reviews* **2016**, *57*, 1568-1579.
- [2] M. Papapetrou, G. Kosmadakis, A. Cipollina, U. La Commare, G. Micale, *Applied Thermal Engineering* **2018**, *138*, 207-216.
- [3] H. Yao, Z. Fan, H. Cheng, X. Guan, C. Wang, K. Sun, J. Ouyang, *Macromolecular Rapid Communications* **2018**, *39*(6), 1700727.
- [4] G. J. Snyder, A. H. Snyder, *Energy & Environmental Science* **2017**, *10*(11), 2280-2283.
- [5] R. Mulla, M. H. K. Rabinal, *Energy Technology* **2018**, *0*(0), 1800850.
- [6] J. He, T. M. Tritt, *Science* **2017**, *357*(6358), eaak9997.
- [7] aH. Tang, F.-H. Sun, J.-F. Dong, Asfandiyar, H.-L. Zhuang, Y. Pan, J.-F. Li, *Nano Energy* **2018**, *49*, 267-273; bR. Mulla, M. K. Rabinal, *Applied Surface Science* **2017**, *397*, 70-76; cY. He, T. Day, T. Zhang, H. Liu, X. Shi, L. Chen, G. J. Snyder, *Advanced Materials* **2014**, *26*(23), 3974-3978.
- [8] aM. R. Burton, T. Liu, J. McGettrick, S. Mehraban, J. Baker, A. Pockett, T. Watson, O. Fenwick, M. J. Carnie, *Advanced Materials* **2018**, *30*(31), 1801357; bL.-D. Zhao, S.-H. Lo, Y. Zhang, H. Sun, G. Tan, C. Uher, C. Wolverton, V. P. Dravid, M. G. Kanatzidis, *Nature* **2014**, *508*, 373; cS. Chandra, K. Biswas, *Journal of the American Chemical Society* **2019**, *141*(15), 6141-6145.
- [9] aQ. Y. Xue, H. J. Liu, D. D. Fan, L. Cheng, B. Y. Zhao, J. Shi, *Physical Chemistry Chemical Physics* **2016**, *18*(27), 17912-17916; bH. Zhu, R. He, J. Mao, Q. Zhu, C. Li, J. Sun, W. Ren, Y. Wang, Z. Liu, Z. Tang, A. Sotnikov, Z. Wang, D. Broido, D. J. Singh, G. Chen, K. Nielsch, Z. Ren, *Nature Communications* **2018**, *9*(1), 2497; cL. Huang, Q. Zhang, B. Yuan, X. Lai, X. Yan, Z. Ren, *Materials Research Bulletin* **2016**, *76*, 107-112.
- [10] aW. Li, J. Wang, Y. Xie, J. L. Gray, J. J. Heremans, H. B. Kang, B. Poudel, S. T. Huxtable, S. Priya, *Chemistry of Materials* **2019**, *31*(3), 862-872; bS. Wang, J. R. Salvador, J. Yang, P. Wei, B. Duan, J. Yang, *Npg Asia Materials* **2016**, *8*, e285; cD. Qin, B. Cui, X. Meng, P. Qin, L. Xie, Q. Zhang, W. Liu, J. Cao, W. Cai, J. Sui, *Materials Today Physics* **2019**, *8*, 128-137.
- [11] aE. Alleno, N. Lamquembe, R. Cardoso-Gil, M. Ikeda, F. Widder, O. Rouleau, C. Godart, Y. Grin, S. Paschen, *physica status solidi (a)* **2014**, *211*(6), 1293-1300; bB. B. Iversen, A. E. C. Palmqvist, D. E. Cox, G. S. Nolas, G. D. Stucky, N. P. Blake, H. Metiu, *Journal of Solid State Chemistry* **2000**, *149*(2), 455-458; cJ.-A. Dolyniuk, B. Owens-Baird, J. Wang, J. V. Zaikina, K. Kovnir, *Materials Science and Engineering: R: Reports* **2016**, *108*, 1-46.
- [12] aY. Yin, B. Tudu, A. Tiwari, *Vacuum* **2017**, *146*, 356-374; bL. Ji, in *Metal Oxides in Energy Technologies* (Ed.: Y. Wu), Elsevier, **2018**, pp. 49-72; cC. Ou, J. Hou, T.-R. Wei, B. Jiang, S. Jiao, J.-F. Li, H. Zhu, *Npg Asia Materials* **2015**, *7*, e182.
- [13] aB. Russ, A. Glauzell, J. J. Urban, M. L. Chabiny, R. A. Segalman, *Nature Reviews Materials* **2016**, *1*, 16050; bS. Kee, H. Kim, S. H. K. Paleti, A. El Labban, M. Neophytou, A.-H. Emwas, H. N. Alshareef, D. Baran, *Chemistry of Materials* **2019**, *31*(9), 3519-3526; cJ. F. Ponder Jr, A. K. Menon, R. R. Dasari, S. L. Pittelli, K. J. Thorley, S. K. Yee, S. R. Marder, J. R. Reynolds, *Advanced Energy Materials* **2019**, *0*(0), 1900395; dM. Bharti, A. Singh, S. Samanta, D. K. Aswal, *Progress in Materials Science* **2018**, *93*, 270-310.
- [14] aK. Kihou, H. Nishiate, A. Yamamoto, C.-H. Lee, *Inorganic Chemistry* **2017**, *56*(6), 3709-3712; bK. Pal, J. He, C. Wolverton, *Chemistry of Materials* **2018**, *30*(21), 7760-7768; cB. R. Ortiz, P. Gorai, L. Krishna, R. Mow, A. Lopez, R. McKinney, V. Stevanović, E. S. Toberer, *Journal of Materials Chemistry A* **2017**, *5*(8), 4036-4046.
- [15] aD. Abol-Fotouh, B. Döring, O. Zapata-Arteaga, X. Rodríguez-Martínez, A. Gómez, J. S. Reparaz, A. Laromaine, A. Roig, M. Campoy-Quiles, *Energy & Environmental Science* **2019**, *12*(2), 716-726; bY. Zhou, Y. Liu, X. Zhou, Y. Gao, C. Gao, L. Wang, *Journal of Power Sources* **2019**, *423*, 152-158; cO. Hwan Kwon, J. Kim, W.-G. Koh, Y. H. Kang, K.-S. Jang, S. Y. Cho, Y. Yoo, *Materials Science and Engineering: B* **2019**, *243*, 199-205.
- [16] P. Jood, R. J. Mehta, Y. Zhang, T. Borca-Tasciuc, S. X. Dou, D. J. Singh, G. Ramanath, *RSC Advances* **2014**, *4*(13), 6363-6368.

- [17] A. J. Minnich, M. S. Dresselhaus, Z. F. Ren, G. Chen, *Energy & Environmental Science* **2009**, 2(5), 466-479.
- [18] S. Wongprakarn, S. Pinitsoontorn, S.-a. Tanusilp, K. Kurosaki, *Materials Science in Semiconductor Processing* **2018**, 88, 239-249.
- [19] J. P. Heremans, V. Jovic, E. S. Toberer, A. Saramat, K. Kurosaki, A. Charoenphakdee, S. Yamanaka, G. J. Snyder, *Science* **2008**, 321(5888), 554.
- [20] Y. Pei, H. Wang, G. J. Snyder, *Advanced Materials* **2012**, 24(46), 6125-6135.
- [21] Z.-G. Chen, G. Han, L. Yang, L. Cheng, J. Zou, *Progress in Natural Science: Materials International* **2012**, 22(6), 535-549.
- [22] L. D. Hicks, M. S. Dresselhaus, *Physical Review B* **1993**, 47(19), 12727-12731.
- [23] aG. J. Snyder, E. S. Toberer, *Nature Materials* **2008**, 7, 105; bK. Koumoto, I. Terasaki, R. Funahashi, *MRS Bulletin* **2006**, 31(3), 206-210.
- [24] M. Beekman, D. T. Morelli, G. S. Nolas, *Nature Materials* **2015**, 14, 1182.
- [25] K. Christopher, R. Dimitrios, *Energy & Environmental Science* **2012**, 5(5), 6640-6651.
- [26] G. Passas, C. W. Dunnill, *Journal of Fundamentals of Renewable Energy and Applications* **2015**, 5, 188.
- [27] S. A. Grigoriev, V. I. Porembsky, V. N. Fateev, *International Journal of Hydrogen Energy* **2006**, 31(2), 171-175.
- [28] M. A. Laguna-Bercero, *Journal of Power Sources* **2012**, 203, 4-16.
- [29] T. Ogawa, M. Takeuchi, Y. Kajikawa, *Sustainability* **2018**, 10(2).
- [30] R. Phillips, C. W. Dunnill, *RSC Advances* **2016**, 6, 100643.
- [31] R. Phillips, A. Edwards, B. Rome, D. R. Jones, C. W. Dunnill, *International Journal of Hydrogen Energy* **2017**, 42(38), 23986-23994.
- [32] O. Schmidt, A. Gambhir, I. Staffell, A. Hawkes, J. Nelson, S. Few, *International Journal of Hydrogen Energy* **2017**, 42(52), 30470-30492.
- [33] X. Zhang, S. H. Chan, H. K. Ho, S.-C. Tan, M. Li, G. Li, J. Li, Z. Feng, *International Journal of Hydrogen Energy* **2015**, 40(21), 6866-6919.
- [34] M. Carmo, D. L. Fritz, J. Mergel, D. Stolten, *International Journal of Hydrogen Energy* **2013**, 38(12), 4901-4934.
- [35] K. Zeng, D. Zhang, *Progress in Energy and Combustion Science* **2010**, 36(3), 307-326.
- [36] Y. Leng, G. Chen, A. J. Mendoza, T. B. Tighe, M. A. Hickner, C. Y. Wang, *Journal of the American Chemical Society* **2012**, 134(22), 9054-9057.
- [37] aT. Ohta, S. Asakura, M. Yamaguchi, N. Kamiya, N. Gotgh, T. Otagawa, *International Journal of Hydrogen Energy* **1976**, 1(2), 113-116; bY. Zhang, M. Xie, V. Adamaki, H. Khanbareh, C. R. Bowen, *Chemical Society Reviews* **2017**, 46(24), 7757-7786.
- [38] X. Zhang, W. Gao, X. Su, F. Wang, B. Liu, J.-J. Wang, H. Liu, Y. Sang, *Nano Energy* **2018**, 48, 481-488.
- [39] L. Zhao, Z. Yang, Q. Cao, L. Yang, X. Zhang, J. Jia, Y. Sang, H.-J. Wu, W. Zhou, H. Liu, *Nano Energy* **2019**, 56, 563-570.
- [40] Y. Chen, M. Chen, N. Shen, R. J. Zeng, *International Journal of Hydrogen Energy* **2016**, 41(48), 22760-22768.
- [41] H. Zhou, F. Yu, Q. Zhu, J. Sun, F. Qin, L. Yu, J. Bao, Y. Yu, S. Chen, Z. Ren, *Energy & Environmental Science* **2018**, 11(10), 2858-2864.
- [42] J.-Y. Jung, J.-H. Lee, *Thermovoltage-driven solar hydrogen for commercialized water splitting*, **2016**.
- [43] S.-M. Shin, J.-Y. Jung, M.-J. Park, J.-W. Song, J.-H. Lee, *Journal of Power Sources* **2015**, 279, 151-156.
- [44] Y. Yang, H. Zhang, Z.-H. Lin, Y. Liu, J. Chen, Z. Lin, Y. S. Zhou, C. P. Wong, Z. L. Wang, *Energy & Environmental Science* **2013**, 6(8), 2429-2434.
- [45] A. Habibollahzade, E. Gholamian, P. Ahmadi, A. Behzadi, *International Journal of Hydrogen Energy* **2018**, 43(31), 14140-14157.

- [46] S. Khanmohammadi, M. Saadat-Targhi, *Energy* **2019**, *171*, 1066-1076.
- [47] S. Gao, B. Wang, Z. Liu, *Journal of Colloid and Interface Science* **2017**, *504*, 652-659.
- [48] C. Liu, P. Chen, K. Li, *International Journal of Hydrogen Energy* **2014**, *39*(28), 15497-15505.
- [49] D. Kraemer, Q. Jie, K. McEnaney, F. Cao, W. Liu, L. A. Weinstein, J. Loomis, Z. Ren, G. Chen, *Nature Energy* **2016**, *1*, 16153.
- [50] A. Zevalkink, E. S. Toberer, W. G. Zeier, E. Flage-Larsen, G. J. Snyder, *Energy & Environmental Science* **2011**, *4*(2), 510-518.

## Author's Biographies



### **Dr. Charles W. Dunnill**

Dr Charles W. Dunnill is a senior lecturer at Swansea University specialising in Sustainable Hydrogen Innovation and Technology. He was awarded his PhD from Glasgow University in Nanomaterials before taking up a post-doctoral researcher post at UCL. He was a Ramsay Fellow at UCL. Charlie advocates and researches the use of hydrogen as the perfect universal energy carrier to store, transport and correlate renewable energy supplies and demand for energy, as well as photocatalytic water splitting as a method of solar energy harvesting.



### **Dr. Rafiq Mulla**

Rafiq Mulla was born in India. He completed his Masters in Physics in 2012 and Ph.D. in thermoelectrics in 2018 from the Karnatak University, Dharwad, India. He is currently working with Prof. Charles W. Dunnill at Energy Safety Research Institute, Swansea University to develop cost-effective thermoelectric materials.