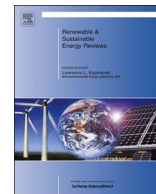




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Advances in hybrid solar photovoltaic and thermoelectric generators

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ABSTRACT

Development of renewable energies, particularly solar energy, is crucial for meeting future energy needs. Solar light and thermal energy can provide sufficient electricity needed in daily life. In this pursuit, photovoltaics and thermoelectrics have been developing for energy conversion. While photovoltaics mainly convert the UV and visible regions of the solar spectrum, thermoelectrics utilize the IR region. Combining the photovoltaic and thermoelectric effects can extend the effective spectrum range. In recent years, there have been studies on hybrid photovoltaic/thermoelectric systems toward improved conversion efficiency. This review intends to discuss the underlying concepts of photovoltaics and thermoelectrics and summarizes the current research accomplishments and the various approaches used to optimize hybrid photovoltaic/thermoelectric systems. As such, this review encourages further research into hybrid generators due to the promising results achieved. Future prospects and suggestions of potential approaches for further development of these generators are also discussed.

1. Introduction

There is an urgent need for the growth of energy supply from renewable energy resources. In the future, the rising energy demand cannot be fulfilled with the limited and depleting fossil fuels only. On the other hand, renewable energy resources are more ecofriendly and pose far less impact on climate change and air pollution. Therefore, there is a current trend toward switching from fossil fuels to renewable resources such as solar energy. Solar energy in the form of light and heat can be used directly or converted into electricity. This review focuses on photovoltaic/thermoelectric hybrid systems that can utilize both light and thermal energies of the solar radiation.

1.1. Development of photovoltaics

A solar cell, also known as photovoltaic cell, is a device that converts light energy into electricity based on the photovoltaic effect that was first discovered in 1839 by A.E. Becquerel. However, the first practical silicon solar cell with a p-n junction was developed in 1954 by Chapin et al. [1]. Since then, researchers have been investigating more efficient and cost-effective ways of converting sunlight to electricity.

Conventional solar cells are made of silicon wafers with conversion efficiency of about 6% when they were first manufactured. According to the National Renewable Energy Laboratory (NREL), modern silicon solar cell can reach up to 25% efficiency. The theoretical maximum efficiency of a single junction solar cell is about 31%, which is known as

the Shockley–Queisser limit.[2] A monocrystalline silicon solar cell has higher efficiency but also higher cost than a polycrystalline silicon cell. Other than bulk silicon cells, there are also thin film solar cells. A thin film refers to a layer of material whose thickness is within few micrometers. Cadmium telluride (CdTe), copper indium gallium selenide (CIGS) and amorphous silicon (a-Si) are common types of thin film solar cells which usually have a positive-intrinsic-negative (p-i-n) layer structure and are coated with a transparent conducting oxide (TCO). Thin film technology has several advantages; it can lower the fabrication cost by reducing the amount of material. It also uses lower deposition temperatures when compared to conventional silicon solar cells. Recently, it has also been used in tandem solar cells [3]. Organic solar cells is another class of thin film solar cell. Although there are various types of organic solar cells, they all involve large conjugated systems with localized pi-electrons. Organic materials are more flexible and less expensive than single crystal silicon. Organic solar cells require simpler manufacture processing and so lower cost. However, they have relatively lower efficiency than their inorganic counterparts. They are usually used in small devices such as watches and calculators. In 1991, Grätzel and O'Regan developed a cost-effective dye-sensitized solar cell (DSSC). The overall conversion efficiency of the DSSC was 12% under diffuse sunlight. DSSC is typically composed of an electron acceptor semiconductor oxide film coated with a layer of a charge-transfer dye and a liquid iodide/triiodide electrolyte [4]. Recent research of DSSC focuses on solid-state electrolyte and long term stability.[5–7].

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Traditional solar cells are single junction solar cells. These cells can only convert a specific region of solar radiation according to the active material used. In order to utilize the wider solar spectrum range and increase the efficiency, multijunction solar cells have been developed. A multijunction solar cell is a third-generation cell that can go beyond the Shockley–Queisser limit as it consists of various junctions. The absorption spectrum is divided into regions where each region is absorbed by a particular junction. The highest efficiency achieved to date is 46.0% [8]. Apart from multijunction solar cells, quantum dot solar cells represent another class of third-generation cells that is receiving growing attention. A quantum dot (QD) is typically a nanoparticle with strong optical absorption and light weight. The main advantage is that the band gap can be tuned by changing the size of the QD [9]. In addition; multiple electron-hole pairs can be generated by a single photon via impact ionization, which allows high conversion efficiency for QD solar cells [10].

1.1.1. Working principle of photovoltaics

Conventional p-n junction and excitonic solar cells have different working principles. A conventional photovoltaic consists of p-type and n-type semiconductors. When the energy absorbed is equal to or larger than the band gap energy of the semiconductor, electrons are promoted from the valance band to conduction band leaving holes behind. When the generated electron-hole pairs diffuse to the interface of the p-type and n-type materials, they get separated at the p-n junction because of the set-up electric field. Electrons move to the negative side and holes move to the positive side. Electrons then flow in the external circuit and current is thus generated (Fig. 1a). During the conversion process,

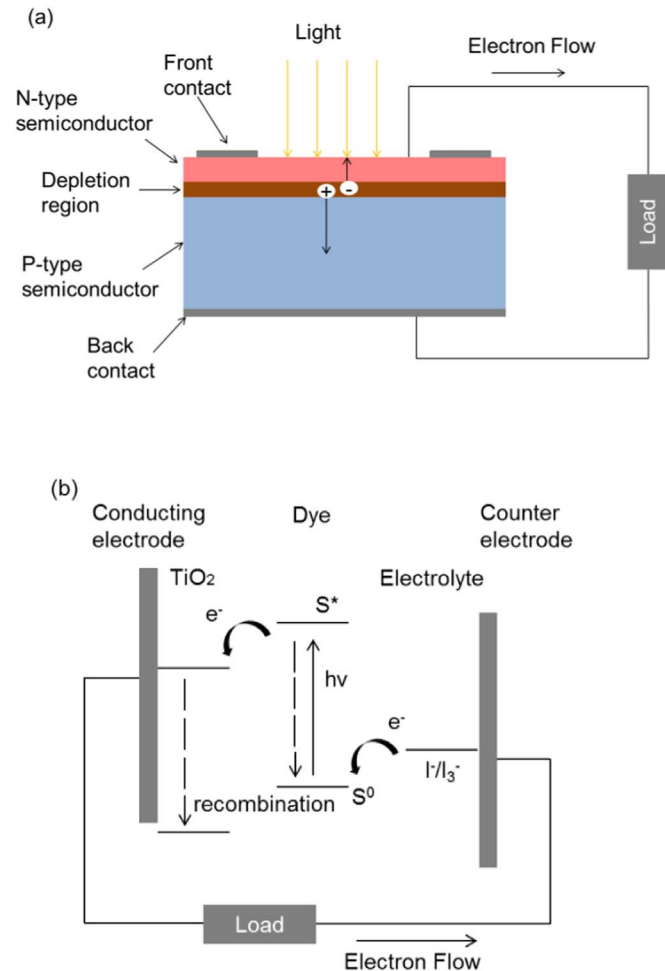


Fig. 1. Structure of p-n junction solar cell (a) and DSSC (b).

there are losses due to charge recombination or decay.

Excitonic solar cells are mostly organic solar cells such as DSSC. Instead of generating free electron-hole pairs, excitonic solar cells generate excitons upon light absorption. An exciton is a pair of electron and hole held by electrostatic force. Since many photovoltaic/thermo-electric hybrid devices are based on DSSC, the DSSC type is used as an example. In DSSC, the dye absorbs a specific region of the solar radiation and generates excitons. These excitons are then separated at the interface between the dye and an electron acceptor oxide semiconductor, such as titanium dioxide (TiO₂). The electron is then injected to the conduction band of the oxide and diffuses to the connecting electrode. The dye is then regenerated by receiving an electron from the electrolyte (Fig. 1b) [4].

1.2. Development of thermoelectrics

A thermoelectric element is a device that can convert heat into electricity and vice versa. The direct conversion of temperature difference to electricity is called the Seebeck effect that was discovered in 1821 by Thomas Seebeck. It states that when there is a temperature difference between two dissimilar materials, a potential difference that is proportional to the temperature difference is developed. In 1834, 13 years later, Jean-Charles Peltier discovered a related effect named Peltier effect. When there is an electric current passing through a junction of two dissimilar materials, heat is either absorbed or released at the junction depending on the direction of current flow.

The Seebeck effect and Peltier effect are the fundamental concepts for thermoelectric power generation and refrigeration systems, respectively. Radioisotope thermoelectric generators are currently used for space missions [11]. Application in next generation vehicles has been proposed to capture waste heat exhausted from the engine [11]. Thermoelectric refrigeration systems are usually used in localized and small-scale cooling such as air conditioners and refrigerators. The first solar thermoelectric generator (STEG) was developed in 1954 by Telkes [12]. The maximum efficiency of a flat-panel STEG was 0.63% [13]. In the past, there were only few applications of STEG due to their low conversion efficiency. Before 1990s, thermoelectric devices mainly consisted of bulk thermoelectric materials and showed little improvement. In 2011, Kraemer et al. developed a promising flat-panel STEG with efficiency several times higher [14]. Bismuth Telluride (Bi₂Te₃) is one of the most common thermoelectric materials because of its high figure of merit at room temperature. Recently, there have been investigations into new types of thermoelectric materials, such as nanostructured materials and phonon glass-electron crystal materials [15].

1.2.1. Working principle of thermoelectrics

A thermoelectric device is made of many thermoelectric couples which are connected electrically in series and thermally in parallel. Thermoelectric couples consist of p-type (hole carriers) and n-type (electron carriers) semiconductor materials [15]. When the thermoelectric device works as a power generator (TEG), it is connected to an external load. The temperature difference causes the electrons and holes to move from the hot to the cold side separately because of density difference (Fig. 2a). The electrons and holes finally recombine at the cold side of the device. This process creates a potential difference and drives a current through the device. The working principle of thermoelectric coolers is the opposite to that of thermoelectric generators, where a thermoelectric cooler is connected to a power supply rather than an external load (Fig. 2b). The thermoelectric efficiency (η_{TE}) of a TEG is given by

$$\eta_{TE} = \eta_C \left(\frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_C}{T_H}} \right)$$

where ZT is the figure of merit, η_C is the Carnot efficiency, T_C is the

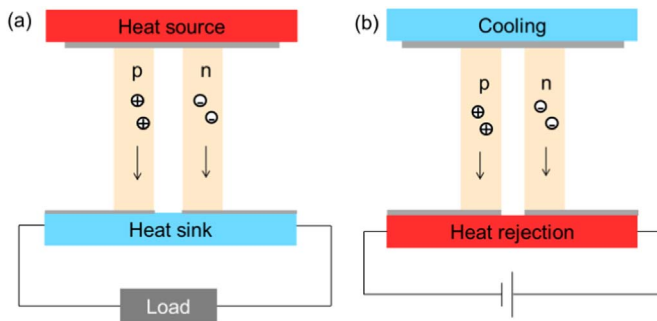


Fig. 2. Structure of thermoelectric generator (a) and thermoelectric cooler (b).

temperature of the cold side and T_H is the temperature of the hot side. A temperature gradient is essential for a TEG to maintain density difference; hence a cooling device is necessary. Otherwise, the two sides of the TEG will reach thermal equilibrium after a certain time.

1.3. Development of hybrid photovoltaic/thermoelectric systems

Recently, there have been several studies on combining different energy sources, such as light, heat, wave and sound, in order to improve the conversion performance [16]. For example, a hybrid system of DSSC and ZnO nanogenerator converts both light and mechanical energy to electricity [17]. This review article focuses on hybrid photovoltaic/thermoelectric (PV/TE) devices, which combine light and heat energy. When a photovoltaic device is exposed to sunlight, not all the solar radiation is absorbed by the optically active substance. Instead, the energy absorbed by the non-optically active substance is converted into heat. If heat energy can be converted to electricity, this greatly enhances the conversion performance. On the other hand, a photovoltaic is more likely to utilize the UV and visible light regions of the solar spectrum (200–800 nm), while a thermoelectric utilizes the IR region (800–3000 nm) [18]. To date, most researches focus on improving the efficiency of solar cells while paying less attention to their life span. A thermoelectric device does not only increase the energy conversion efficiency, but also minimizes the temperature increase and the heating up of the cell. In consequence, the life span of the solar cell can be extended when combining with a thermoelectric device. The working principle of the PV/TE hybrid device is the same as the PV and TEG modules working separately under the same condition.

2. PV/TE hybrid systems

All PV/TE hybrid devices consist of a PV module, a TEG and a cooling system, where different components are added or modified to optimize the device performance. The overall power output of the device is the sum of the power output of the PV module and TEG. In general, there are two designs for PV/TE hybrid devices; with and without reflective component.

2.1. With reflective component

These PV/TE hybrid devices have a reflective component, such as spectrum-splitter or prism [18–21], where the PV module and the TEG are placed perpendicularly. When sunlight irradiates the device from the top, part of the solar radiation is reflected by the splitter at a particular wavelength, so called cutoff wavelength. The radiation that is longer than the cutoff wavelength is reflected to the TEG; whereas those shorter than the cutoff wavelength transmit through the splitter and get absorbed by the PV module as shown in Fig. 3a. A cooling system is installed on the TEG to maintain the temperature difference. The PV module and the TEG work independently on converting solar energy into electricity.

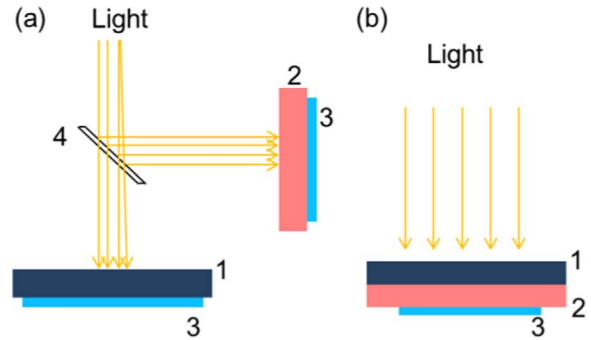


Fig. 3. PV/TE device: (a) with a reflective component; (b) without a reflective component. 1: PV module; 2: TEG; 3: heat sink; 4: reflective component.

2.2. Without reflective component

In these devices, the PV module and the TEG are placed in a parallel arrangement. Since the PV module mainly absorbs shorter wavelengths (visible and UV regions) and TEG absorbs longer wavelengths (IR region), the PV module is usually configured as the upper component and the TEG as the lower component, as shown in Fig. 3b [22–34]. A heat sink is placed at the back side of the TEG to keep the temperature low at the cold side. Under solar irradiation, the PV module absorbs UV and visible light, while the rest of the radiation transmits through the PV module to the underlying TEG. The IR radiation heats up the TEG top side creating a temperature difference with the cold side.

3. Current research on PV/TE

Researches have been working on optimizing PV/TE systems using different approaches. The performance of various systems is summarized in Table 1.

3.1. Optimization of the hybrid system

3.1.1. Absorption density

A concentrator can increase the light intensity in a reduced surface area. Consequently, it can lower the fabrication cost while maintaining cell efficiency. The concentrator can be installed either above the PV module or between the PV module and TEG [35]. The former design, termed concentrated photovoltaic, can concentrate the solar radiation being absorbed by the PV module and convert it to electricity. The latter design is only suitable in devices without a reflective component, where the concentrator collects and concentrates the remaining solar radiation on the hot side of the TEG after passing through the PV module.

Coating a layer of light absorber is another approach to increase light absorption. A solar sensitive absorber (SSA) with low reflectance in the IR region helps converting sunlight to heat, thus improving the conversion efficiency of the TEG. The efficiency of a DSSC/TEG hybrid system with and without SSA is 13.8% and 12.8%, respectively [22]. Lorenzi et al. suggested that it would be possible for a hybrid system with an absorbing layer to have an efficiency that exceeds the Shockley–Queisser limit of a single-junction cell [36]. Chemically converted graphene (CCG) is an ideal light absorber for TEG due to its strong light absorbing ability and low cost. Besides, it has high thermal conductivity facilitating heat transfer to the TEG [37].

An increase in the concentration ratio of the concentrator and SSA leads to a larger temperature difference, where the efficiency of PV/TE hybrid system increases with increasing concentration ratio to a certain level. However, when the concentration ratio gets beyond the optimal ratio, the device temperature and resistance increase, thus decreasing the conversion efficiency especially the PV module [19,29,38]. Therefore, the optimal range of concentration ratio should be taken

Table 1

The overall performance of various PV/TE systems.

PV	TE	Overall efficiency (%)	Overall power (mW)	ΔT (K)	Solar concentrating ratio	Reference	Remark
c-Si	Bi_2Te_3	16.3	65.2	15	–	Park[30]	–
c-Si	Not mentioned	23	24,500 (9 solar cells)	52	–	Zhu[50]	–
c-Si	$\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$	~18.6	–	–	~11	Zhang[48]	Optical conc. system
Si thin film	$\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$	~13.9	–	–	~10	Zhang[48]	Optical conc. System
Poly-Si	Bi_2Te_3	12.4	2290	36	–	Kossyvakis[51]	–
CIGS (copper indium gallium selenide)	$\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$	~23.6	–	–	~18	Zhang[48]	Optical conc. system
Cd- free CIGS	Bi_2Te_3	22.02	–	11.6	–	Hsueh[59]	Use of ZnO nanowire
GaAs	$ZT = 1$	25.40	–	45	50	Cui[43]	–
Multi-junction	Bi_2Te_3	32.09	190	4.5	20	Beeri[29]	High conc. system
Multi-junction	Bi_2Te_3	22.35	1948	67.5	288	Beeri[29]	High conc. system
DSSC	Bi_2Te_3	13.8	13.8 per cm^2	6.2	–	Wang[22]	Use of SSA
DSSC	0.89% Bi_2Te_3 in TiO_2 anode	7.33	–	15	–	Chen[23]	–
DSSC	p-type: $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ n-type: $\text{Bi}_{2.85}\text{Se}_{0.15}\text{Te}_3$	9.08	–	–	–	Zhou[49]	–
DSSC	Bi_2Te_3	9.7	2280	36	–	Kossyvakis[51]	–
Perovskite	ceramic	18.6	–	–	1	Zhang[34]	Use of SSA
Polymer solar cell	Bi_2Te_3	–	11.29 per cm^2	9.5	–	Zhang[33]	–
Polymer solar cell	$\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$	~13.4	–	–	~2	Zhang[48]	Optical conc. System

into consideration when designing a hybrid system.

3.1.2. Spectrum splitting

Spectrum splitting is especially beneficial for highly concentrated solar system, where different solar irradiation regions are directed to the PV and the TEG. This allows for low operating temperature and thus maximizing the conversion efficiency [39]. The cutoff wavelength of the splitter is associated with the band gap of the light harvesting material of the PV module. Therefore, a spectrum splitter, such as dichroic splitter, should be selected according to the material of the hybrid system. The cutoff wavelength can be determined from the intersection of the spectral conversion efficiency of the PV and the TEG [40], which show different energy contributions at different cutoff wavelengths. The maximum power output of GaAs-CoSb₃ hybrid system is obtained when the cutoff wavelength is between 850–950 nm.[19].

3.1.3. Material design

The figure of merit (ZT) of a thermoelectric material is given by $ZT = \frac{S^2 \sigma}{\kappa} T$ where S is the Seebeck coefficient, σ the electrical conductivity, κ the thermal conductivity and T the absolute temperature. Semiconductors have different values of ZT at different temperatures. Hence, the selection of thermoelectric materials depends on the operating temperature regimes. For examples, bismuth telluride (Bi_2Te_3) under 500 K, lead telluride (PbTe) between 500–900 K, and germanium-silicon based solid solution (Ge-Si) above 900 K.[41].

The efficiency is also affected by the concentration of the thermoelectric material present. There is an optimum level, where higher percentage of the thermoelectric material does not necessarily mean higher efficiency. Chen et al. investigated the performance of a DSSC incorporating Bi_2Te_3 nanoplates at four different concentrations (0%, 0.34%, 0.89% and 1.78%).[23] The device with the second highest Bi_2Te_3 concentration (0.89%) showed the highest power conversion efficiency. Apart from the conversion efficiency, a higher percentage of the thermoelectric material lowers the device temperature and thus extends the life span of the device. However, this device did not include a cooling system, hence after a period of time of operation, the device would reach a thermal equilibrium and the temperature gradient would no longer exist. However, the device performance was only assessed for

150 min. Although the conversion efficiency of the device with 0.89% Bi_2Te_3 remained stable within this period, it is not clear how the device stability is affected at longer exposure. Moreover, the ability of the device to maintain its output over this period suggests the improvement in efficiency may have been associated with increased light absorption by Bi_2Te_3 rather than a thermoelectric effect.

3.1.4. Structural modification

Guo et al. investigated the impacts of different connection configurations of DSSC and TEG on device performance [24]. The DSSC and the TEG modules were either stacked (HTC1) or connected in series (HTC2). There were three additional configurations of DSSC for further improvement; all parallel, two series and three series. The maximum power output of HTC1 was higher than that of HTC2 because the two components did not match. When connected in series, the current is limited by the smaller current. The two series pattern resulted in the highest power output compared to the other configurations. This may suggest the output current of DSSC under two series is close to that of TEG under maximum power point (MPP), where the two components can work at their respective MPP.

The length of the thermoelectric element affects the overall efficiency. While the heat transferred is inversely proportional to the length, the resistance is proportional to the length, however there is an optimal length for achieving maximum efficiency. Mizoshiri et al. designed a thin film TEG module and analyzed the surface temperature distribution using a finite element method [20]. Copper heat sinks were placed at the cold side of the TEG module. Three types of heat sink with the same heat capacity but different aspect ratios were used. They showed maximum power per pair of p-n elements at different element lengths. If the width of the heat sink is shorter, the maximum power per pair of p-n elements occurs at longer element length. The effect of the cross-sectional area of the TEG module and the operation environment (vacuum and non-vacuum) on power output has also been investigated [42].

3.1.5. Other improvements

Ju et al. studied the influence of the heat transfer coefficient of the heat sink [19] According to the results of this study, the temperature difference and efficiency of TEG is independent of the heat transfer

coefficient. However, the heat transfer coefficient influences the performance of the PV module. For a hybrid system with higher heat transfer coefficient, the heat sink had higher overall efficiency where the efficiency increased sharply from 500 to 3000 W/m² K but changed only slightly above 3000 W/m² K. For practical application, the heat transfer coefficient of a cooling system should be 1–2 times higher than the optimal range.

Very recently, Cui et al. introduced the use of phase change material (PCM) to reduce the fluctuant solar irradiance and thus the daily total efficiency was improved from 25.55 to 26.57% [43]. Unlike conventional PV/TE systems, the stored thermal energy in the PV/PCM/TE system can be used for generating electricity when there is no sunlight.

Different integrations of PV/TE system installation result in different performance. The impact of installation conditions can be represented by the coefficient c according to $T_M = T_A + cG$, where T_M is the module temperature, T_A the ambient temperature and G the irradiance [44]. Different values of coefficient c affect the module temperature and consequently the system efficiency. A roof-integrated system has a higher coefficient c than a free-standing counterpart. The value of coefficient c ranges between 0.02 and 0.058 [45]. The higher the coefficient c , the lower is the PV efficiency but the higher is the TE efficiency [46].

3.2. Effectiveness of coupling PV module with TE

Many studies on hybrid PV/TEG systems show that the hybrid system has better performance than single PV and TEG [35,46–50]. However, it is always challenging to optimize the performance of both PV and TE. Kossyvakis et al. showed that the use of TEG with shorter thermoelements allowed lower operating temperature for PV, and resulted in better overall efficiency [51]. It should also be noted that optimization of the combined circuits of PV and TE cells is necessary [30]. Otherwise, the overall performance may deteriorate due to increased total series resistance.

At the same time, more and more studies focus on other hybrid devices such as PV/thermal device. Instead of TEG, a PV/thermal hybrid system incorporates a water heat collector. The device performance is improved by a cooling effect rather than a thermoelectric effect. To date, there are few studies comparing the performance of these hybrid devices. Yang et al. compared the overall efficiency of three types of solar panels: single PV system, PV system with hot water tube (PV/HW), and PV system with hot water tube and TEG (PV/TE/HW). Both hot water tube and TEG elements can improve the device performance compared with a single PV system. The PV cell efficiency of the three types of solar panels under 1200 W/m² irradiation was 7.1%, 10.6% and 8.5%, respectively [25]. PV/HW system increases the efficiency through a cooling effect and has the highest efficiency among the three systems. Although PV/TE/HW absorbs waste heat and provides additional electricity, it lowers the cooling effect. As the figure of merit of bulk Bi₂Te₃ material is about 1, the thermoelectric efficiency of the TEG may not be high enough to compensate the loss in cooling. Hence, PV/TE/HW has a lower efficiency than PV/HW. Therefore, it is crucial to consider the efficiency of TEG. A thermoelectric material with higher figure of merit should be pursued and its performance should be compared with PV/HW. In some cases, it would be more efficient to simply couple a PV module with hot water collector only.

4. Future outlook

Although, there have been many studies of single photovoltaics and thermoelectric generators since 1880s, hybrid PV/TE devices are receiving increasing attention toward a breakthrough of solar energy utilization. In the future, there is room for potential developments of the PV/TE hybrid device. Here, suggestions of potential approaches for future development of these generators are discussed.

4.1. TPV/TE hybrid system

Apart from thermal energy, infrared radiation can also be converted to electricity by thermophotovoltaic (TPV) cells. Since the source for TPV is a thermal emitter instead of the sun, the operation time of TPV cells is not limited to day time. In addition, it allows the use of materials with lower band gap, such as GaSb and InGaAsSb [52,53]. However, the thermal emitter must be stable at high temperature (1400–1600 °C), and this limited the range of material selection. Today, tungsten is a commonly used emitter. Due to the advantages of TPV, it has been studied in a number of applications, such as residential heating systems and electric vehicles [54–57]. For example, the TPV system presented by Colangelo et al. could produce up to 6 kW with an efficiency of 24.5% [56]. Although there are advantages of TPV over PV, very few studies have been carried out on TPV/TE integrated systems. Qiu et al. demonstrated that installed GaSb TPV cells and TE converter could generate 123.5 W and 306.2 W, respectively [58]. The efficiency of the integrated system is higher than that of individual TPV and TE. TPV/TE is an interesting alternative system of PV/TE and requires more studies in the future.

4.2. Light and heat harvesting

Light absorption can be increased using one-dimensional nanowires or nanorods [59]. The high surface-to-volume ratio of 1-D nanowire allows more light absorption per unit. Apart from nanomaterials, light trapping can be enhanced using diffraction gratings, where multiple gratings have been developed [60,61]. In order to further improve the light trapping, installations of both antireflection layer and back diffraction grating have been trialed [62]. The antireflection layer is important for solar cells, particularly multi-junction type. As reflection occurs at every junction resulting in significant absorption loss in multi-junction cells, it is crucial to prevent reflection at the top of the solar cell. A combination of anti-reflection and light-trapping concepts opens the opportunity of utilizing the full spectrum. Xu et al. proposed a simulation model consists of moth-eye and inverted-parabolic arrays on the top surface with plasmonic back reflector and metallic gratings on the back side [63]. The model shows high absorption in 300–1100 nm and high transmission in 1100–2500 nm. Zhang et al. described a similar model composed of biomimetic parabolic-shaped Si surface and SiO₂ anti-reflection coating [64]. Apart from diffraction gratings, plasmonics is another possible solution for light absorption [65]. Plasmonics can maintain the optical absorption while reducing the thickness of the PV. Optimization of these new approaches requires further study in the future. For thermal absorption, a planar fishnet structure can be employed at the back of PV module to create a larger temperature gradient [66,67]. However, the absorbed solar intensity strongly depends on the geometry, material and parameters of the fishnet [66]. Even when the same component is used, the structure design and geometry have to be carefully considered in order to optimize the overall absorption of the solar radiation for both PV and TE. However, most of the above studies are solely based on simulation models and the working conditions in reality could be significantly different. Moreover, few results on the efficiency of the hybrid system and generated electricity have been reported thus far.

PV modules produce waste heat which can be transferred from PV to TE. Heat can be lost through conduction, convection and radiation. Up to date, there are few studies on the utilization of waste heat. Dallan and co-workers have investigated the conversion of photoelectric waste heat to electricity [68]. The experimental results reveal that the generated electricity by TE from waste heat is negligible. Instead, TE works rather as a heat pump thus enhancing the conversion efficiency of the PV module. Future studies may not only focus on harvesting heat from solar radiation, but also how to capture waste heat produced by the PV module. Besides, new heat absorbing coatings with high thermal

conductivity for the TE module should be promising.

4.3. Thermoelectric material

A good thermoelectric material should have high mobility carriers but low lattice thermal conductivity in order to achieve high figure of merit [15]. As seen in Table 1, researchers are mainly using Bi_2Te_3 . It will be interesting to investigate other types of thermoelectric materials. Nanostructured thermoelectric materials, such as QD-based materials are drawing increasing attention, as they have higher figure of merit than their bulk counterparts. Rai et al. successfully synthesized nanoporous Bi_2Te_3 and Sb_2Te_3 , and further improved the TE performance using polyaniline-coated carbon nanotubes as conductive fillers [67]. The TE module generated around 150 mV when the temperature difference between the hot and cold sides was 35 °C. Scheele et al. synthesized Bi_2Te_3 nanoparticle sintered to a macroscopic pellet [69]. Since the size of the nanoparticle affects the thermal conductivity, further study of the optimal particle size is needed. In addition to nanostructured thermoelectric materials, higher figure of merit can be achieved through the following approaches.

4.3.1. Heterogeneous approach

Many existing thermoelectric materials have heterogeneous compositions. Zhang et al. synthesized micro-nano heterostructured bismuth telluride, where phonon scattering is enhanced at the heterogeneous particle boundaries [70]. Increasing phonon scattering reduces the phonon mean free path and so the thermal conductivity leading to improved figure of merit.

Using mesoporous materials is one of the methods used to reduce the thermal conductivity while maintaining the electrical conductivity [71]. In the 1990s, Slack proposed phonon-glass electron-crystal (PGEC) materials with high figure of merit [72]. PGEC is a material with glass-like thermal conductivity and crystal-like electrical conductivity. Filled skutterudites is a class of PGEC. There are studies showing that filled skutterudites have lower thermal conductivity than unfilled one [73–75]. When filling the voids with atoms, rattling of the atoms generates low frequency vibration. Scattering of low frequency and heat-carrying phonons reduces the thermal conductivity [73]. Alkaline metals especially lithium cannot be filled because of their light weight and small ionic radius [76]. Recently, lithium has been successfully filled into CoSb_3 -based skutterudites by high pressure synthesis (HPS) [77]. Skutterudites are usually filled with rare earth elements. The technique of filling alkaline metals requires further investigation, so that abundant and less expensive metals can be used.

Polymer-inorganic thermoelectric materials are potential due to their low cost and high electrical conductivity [78]. Polyaniline and poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) are commonly used in emerging polymer-inorganic thermoelectric materials. Currently, the interfacial bonding between the polymer and inorganic material is poor. New and promising methods are required to ensure stable interfacial bonding in the composite material.

4.3.2. Homogeneous approach

A number of researchers attempted to reduce the thermal conductivity by introducing heterogeneous compositions. However, scattering of electrons at the hetero-interface also reduces the electrical conductivity. Therefore, investigation of homogeneous materials, which do not suffer from scattering, is suggested. However, in order to reduce the thermal conductivity, homogeneous structures should be constructed in a way that allows many interfaces similar to heterojunction. Xiao et al. synthesized homo-junction of $\text{AgBi}_{1-x}\text{Sb}_x\text{Se}_2$ nanoplates and this can be a promising approach for future thermoelectric materials [79].

4.4. Cooling system

Since a temperature gradient is essential for TEG, a cooling system is necessary to keep one side cool. Besides, keeping the device temperature low avoids damaging of the device especially the PV module. Water cooling is the most common cooling system as water has high specific heat capacity. However, it is not practical in arid areas where there is deficiency of water. In such a case, an air cooling system would be an alternative option to dissipate heat. On one hand, it has been proven that nanofluid removes waste heat more efficiently than water.[27,80] However, the cost and stability of nanofluid remain an open question. There have been limited studies on the optimization of the system geometry. In order to save energy, a passive cooling system, such as IR reflective coating would also be a promising approach. IR reflective materials can be coated at the cold side of the TEG, where IR radiation is reflected keeping the cold side cool.

4.5. Heat storage

Sunlight is not always available; therefore it is beneficial to include a heat storage system with high storage capacity. Heat storage includes sensible and latent heat [81]. These systems store heat by raising the temperature or through phase change of the storage material. When connecting a heat storage system to a hybrid PV/TE under solar irradiation, cooling of the hybrid device is facilitated as heat transfers to the storage system. During night time, heat is then supplied from the storage system to the device creating a temperature difference. TEG can then operate and supply electricity when sunlight is not available. Up to date, only limited studies have been carried out in this direction, and therefore investigation on coupling of phase change materials and design optimization is thus recommended.

4.6. Flexible hybrid system

Current inorganic solar cells and thermoelectric devices are mostly rigid. Research on flexible hybrid device is needed in order to broaden the application. Recently, PbTe nanocrystals have been coated on the surface of a glass fiber using solution-phase deposition [82]. PbTe is a thermoelectric material commonly used between 500–900 K. The PbTe coating has a curvature of 84.5° and a thickness of 300 nm. It is possible to coat PbTe nanocrystals on a flexible substrate and couple it with flexible organic solar cells. Moreover, coating PbTe by thin film technology can reduce the raw material needed and so the manufacture cost. Further investigation may focus on other thermoelectric materials and coating technologies. Recently, Zhang et al. presented a PV/TE hybrid system consisted of a flexible polymer solar cell [33]. With the development of flexible photovoltaics and thermoelectric materials as well as coating technologies, flexible systems might be the next generation of PV/TE hybrid generators.

5. Conclusions

Solar energy is one of the renewable energy resources with significant potential. PV and TE generators have been witnessing continuous improvements and as such they are becoming more practical and reliable. Combining PV and TE generators efficiently constitutes a breakthrough of solar energy utilization. In particular, a PV/TE hybrid system with high concentration ratio multi-junction PV and Bi_2Te_3 TE has shown a high conversion efficiency of 32.09%. Another potential design for a number of potential applications, such as residential heating systems and electric vehicles, is the integration of TPV cells with up to 6 kW of output power and 24.5% efficiency. Furthermore, the rapid development of flexible photovoltaics and thermoelectric materials as well as coating technologies, could make flexible systems the next generation of PV/TE hybrid generators. With the promising results achieved and the potential of the suggested

approaches for further development, it is believed that hybrid PV/TE systems will play an important role in future energy supply.

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