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Review on Thermionic Energy Converters

Kamarul Aizat Abdul Khalid, Thye Jien Leong, and Khairudin Mohamed

(Review Paper)

***Abstract*— Thermionic energy converter (TEC) is a heat engine that generates electricity directly using heat as its source of energy and electron as its working fluid. Despite having a huge potential as an efficient direct energy conversion device, the progress in vacuum-based thermionic energy converter development has always been hindered by the space charge problem and the unavailability of materials with low work function. It is only recently that researchers have started to look back into this technology as recent advances in manufacturing technology techniques have made it possible to solve these problems, making TECs a viable option in replacing current energy production systems. The focus of this paper is to review the challenges of producing efficient and practical TECs, along with recent findings and developments in mitigating these challenges. Furthermore, this paper looked into potential applications of TECs, based on recent works and technologies, and found that, with certain improvements, it can be applied in many sectors.**

***Index Terms*— Energy conversion efficiency, nanowires, space charge, thermionic energy conversion (TEC), work function.**

I. Introduction

HARVESTING renewable and clean energy is often associated with solar cells or photovoltaic cells, which are novel technology devices for collecting solar energy to produce useful electricity. These technologies have been evolving over the past several decades, to achieve the ultimate goal, i.e., higher conversion efficiency. In order to meet growing energy demands and to reduce our dependency on the conventional energy resources, alternative yet efficient methods of energy conversion from another easy-obtained source of energy (heat) are being considered and evaluated. Efficient, direct thermal energy to electricity conversions could be a suitable alternative to the conventional approaches, as they eliminate losses due to mechanical work during the conversion process, which reduces the overall efficiency. Although the technology has been discovered and promised good results back in the 1950s [1], the progress in the development of thermionic energy converters (TECs) has been limited due to the lack of advanced technology and fabrication techniques.

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The authors are with the School of Mechanical Engineering, Universiti Sains Malaysia Engineering Campus, Penang14300, Malaysia (e-mail: kamarulaizat@gmail.com; thyejien12189@yahoo.com; mekhairudin@usm.my).

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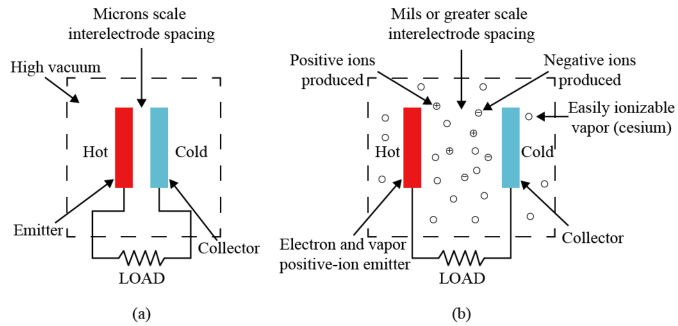

Fig. 1. (a) VTEC. (b) Vapor thermionic energy converter [1].

The idea of converting heat to electricity by means of thermionic emission (TE) was first suggested by Schlichter [2]. Further investigations continued in the 1950s, where Hatsopoulos from the Massachusetts Institute of Technology introduced two types of TECs, namely, vacuum TECs (VTECs) and vapor TECs, while doing work on thermoelectron engines [3], starting the evolution of TECs, which continues till today. In general, a VTEC has a small, highly evacuated interelectrode space to limit the number of electrons travelling within it, as presented in Fig. 1(a). Excessive numbers of electrons in transit will form an electron cloud, causing decreased efficiency due to the space charge effect, which will be discussed in detail later on in this paper. With a vapor TEC, on the other hand, there is not much concern about interelectrode spacing, because the space is filled with vapor, as shown in Fig. 1(b). The space charge effect in this converter type is neutralized by the positive ions, produced normally by caesium, as it is easily ionized. In terms of implementation capability, reports show that a VTEC is nearly impossible to implement in reality, due to unattainable stable low work function material and unachievable thermal isolation structure between electrodes, whereas vapor TECs had a significantly better performance. Nevertheless, vapor TECs suffer from intrinsic inability to achieve optimal performance due to implementation intricacies, such as inadequate positive ions required to neutralize the space charge effect, and unfavorable effects of elastic collisions in the interelectrode space [1].

This paper presents an overview of the fundamental principles of practical TECs, which includes the basic working principles of TECs, main challenges of designing an efficient VTEC, ways to solve the challenges, and possible applications of TECs. This is based on the research done in recent years, where several authors have proposed developments that could help create more practical TECs in the future,

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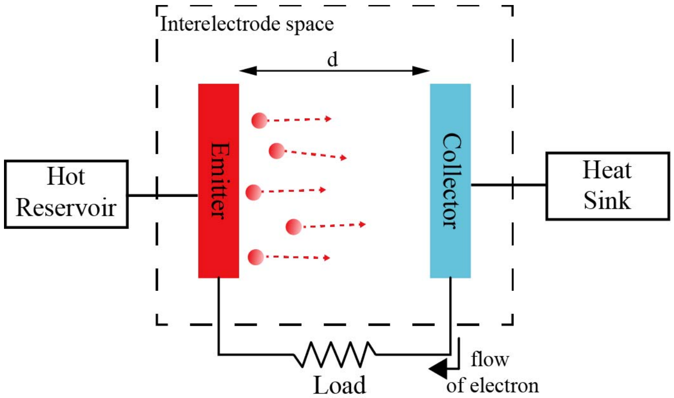

Fig. 2. Schematic of a TEC.

and discussed the influence of the various effects on the performance of TECs.

II. Basic Working Principle

In this section, we outline the basic theory of thermionic energy power generation. In its basic form, a TEC consists of: 1) two electrodes—an emitter, which is heated to a sufficiently high temperature to emit high-energy electrons, and a collector, which receives the emitted electrons and is operated at a significantly lower temperature, separated from one another by an interelectrode gap, which can be comprised of vacuum, vapor, or plasma; 2) an electrical load; and 3) an electrical connection [1]. A heat source is connected to the emitter, to supply the thermal energy to the electron inside the emitter, and the collector is attached to the heat sink, to remove the heat from the collector. Initially, electrons in the outermost shell of the emitter atom are free to move around inside the surface, as they are prevented from escaping by a potential energy barrier called the work function. In order to escape, electrons must acquire a sufficient amount of energy to overcome this energy barrier. When the thermal energy from the heat source is supplied to the emitter, the kinetic energy of the electrons increases gradually, and as a sufficient amount of energy is gained, they are able to escape from the surface. These electrons then travel through the interelectrode space, and are collected into the colder collector. Eventually, a negative charge accumulates on the collector, inducing a voltage difference between these two electrodes and, by connecting them with an electrical load, the voltage difference will drive a current through the load resistance, where electric work is done. This flow of electrons, better known as electricity, will continue as these electrons flow back to the emitter and get emitted again after gaining energy from the heat source. In a way, a TEC may be viewed as a heat engine, which, in principle, receives heat produced by the emitter, ejected by the collector. Some parts of that heat are turned into work, done in the form of electricity in the load, and some parts of that heat are removed using the heat sink [4]. Fig. 2 shows the schematic of a TEC and its components.

The efficiency limit of every heat engine is given by the Carnot efficiency, which limits the fraction of heat that can be used, as the second law of thermodynamics entails that not all heat in a heat engine can be used to do work. The Carnot efficiency can be written as

$$\eta_{\text{carnot}} = 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}} \tag{1}$$

where η_{carnot} is the efficiency of the Carnot cycle, T_{hot} is the temperature at which the high temperature reservoir operates, and T_{cold} is the temperature at which the low temperature reservoir in TEC operates [5]. T_{hot} represents the temperature of the emitter, which is limited by the melting point of the material, and T_{cold} is the temperature of the collector. Theoretically, the overall TEC system can achieve a very high Carnot efficiency in the ideal case, as a very high temperature difference can be maintained between the emitter and the collector, considering that only a small amount of heat is transported through the vacuum. As compared with other conventional heat engines, a TEC offers remarkable advantages due to its compactness, high power density, silent operation, long operational lifespan, and clean energy generation [1].

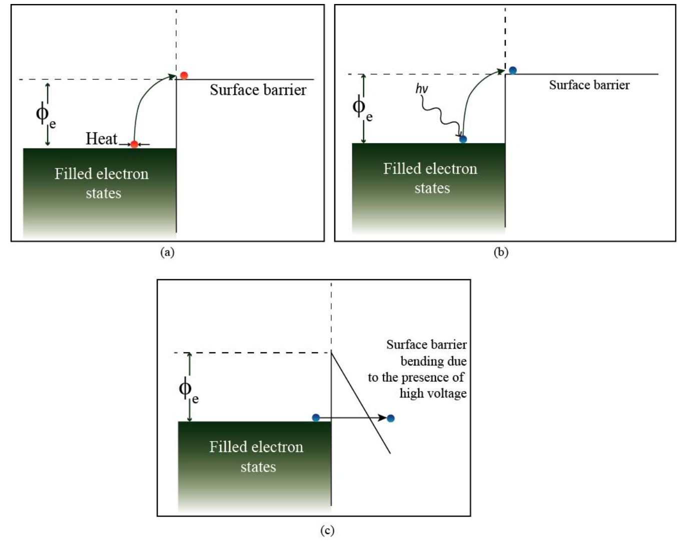

Fig. 3. Schematic of electron emission from a solid surface into vacuum. (a) TE. (b) PE. (c) Field emission. ϕ_e is the work function of emitter [6].

Electron emission from a solid can be achieved through three common mechanisms: TE, photoemission (PE), and field emission, as presented in Fig. 3 [6]. When electrons are emitted using the energy provided to the material in the form of thermal energy by heating the solid, it is known as TE. Thus, a TEC is a heat engine that converts thermal energy to electricity using TE. PE, or photoelectric emission, occurs when the energy is acquired in the form electromagnetic waves, and used to emit electrons. Field emission occurs when the potential energy barrier is lowered, due to the presence of a high electric field, and electron emission may occur due to the quantum tunneling phenomenon.

For TE, the current density J can be defined using the Richardson–Dushman equation

$$J_{\text{thermionic}} = AT^2 e^{\left(-\frac{\phi}{k_B T}\right)} \tag{2}$$

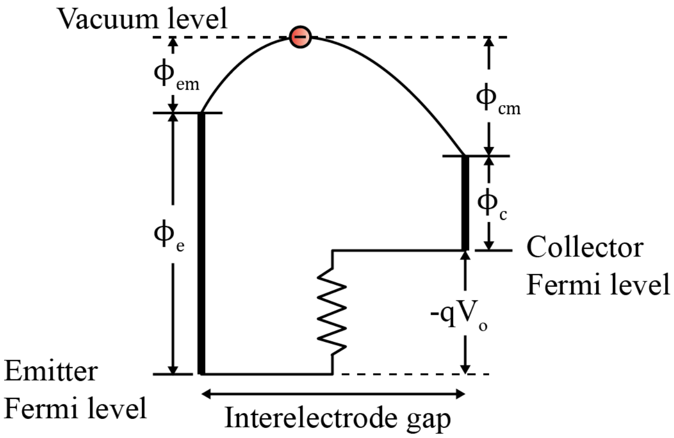

Fig. 4. Energy diagram of TEC. ϕ_e and ϕ_c are the work functions of emitter and collector, respectively. ϕ_{em} and ϕ_{cm} are the additional barriers of space charge effect of emitter and collector, respectively. V_O is the voltage difference between two electrodes. $-q$ is the electron charge [1].

where T is the absolute temperature, ϕ is the work function of the material, k_B is the Boltzmann constant, and A is the emission constant of the material [7]. Because (2) is dominated by the exponential function, small changes in the value of work function will results in a significant change in the current density. In order to obtain a high thermionic current density, the work function of the emitter must be low, and the temperature of the emitter must be high. However, the operating temperature is constrained by the material properties of the electrodes.

III. Limitations of TECs and Its Recent Solutions

A. Work Function

One of the factors that significantly affect the efficiency of a TEC is the work function of the electrodes—the emitter and the collector. Work function is a material surface parameter, defined as the minimum amount of energy required to emit an electron from a solid to a point in the vacuum immediately outside the solid surface. In a TEC, work function plays the role of the emitter's energy barrier, to hinder the evaporation of electrons into the interelectrode space, as shown in Fig. 4. Electrons inside a material with a low work function require less energy to be emitted out of the surface. It is also ideal to apply low work function electrodes in a TEC, but within certain limits. Two important points should be carefully considered when choosing the material for the emitter and the collector, i.e., a large work function difference between the emitter and the collector should be attained and the work function for both the emitter and the collector should be low [1].

In order to maximize the efficiency of a TEC, a sufficiently large voltage difference between the emitter and the collector must be achieved. The emitter's work function must be at least 1 eV higher than the collector's work function [1]. Meanwhile, the work function of the collector must be kept as low as possible, to avoid operating the device at high temperatures, which would cause abundant heat loss to the surroundings. Fig. 5 presents a brief diagram that helps to understand the above-mentioned remarks. Unfortunately, not many low-cost materials have been found that also possessed high temperature stability with a sufficiently low work function characteristic. Hence, scientists and researchers have come up with alternative approaches to solve this problem.

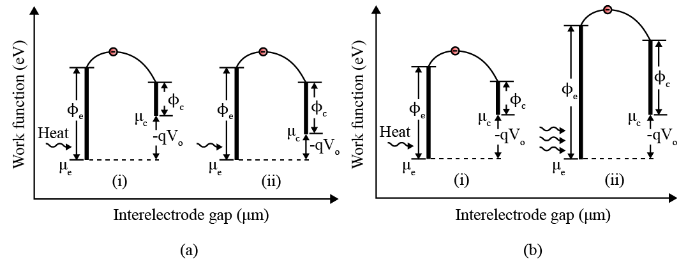

Fig. 5. (a.i) Larger work function difference between the emitter and the collector than (a.ii) resulting in larger voltage output. (b.i) and (b.ii) Similar voltage output but (b.i) required less heat than (b.ii) to emit electron. μ_e and μ_c are the Fermi levels of emitter and collector, respectively. ϕ_e and ϕ_c are the work functions of emitter and collector, respectively. V_O is the voltage difference between two electrodes. $-q$ is the electron charge.

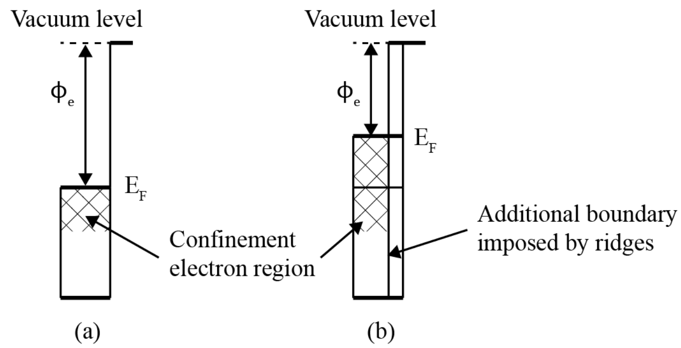

Fig. 6. (a) Substrate without ridged quantum well. (b) Substrate with ridged quantum well. ϕ_e is the emitter work function. E_F is the emitter Fermi energy level [11].

By using advanced coating approaches, a low work function material, barium oxide (BaO), was deposited onto a polycrystalline-silicon carbide substrate, with a thin tungsten layer in between for adhesion purposes [8]. A low work function of 1.7 eV was obtained, and the system was run stably for hours at the temperatures of 900–1400 K. Phosphorus-doped polycrystalline diamond films on metallic substrates exhibited a work function of 0.9 eV and the sustained temperatures of up to 765 °C [9]. Nitrogen-incorporated, ridged nanodiamond films on silicon substrates attained a work function of 1.39 eV, and were thermally stable at the temperatures of up to at least of 900 °C [10]. All of these studies demonstrate potential TEC electrode materials.

Surface nanostructuring of the thin metal ridged quantum-well layer coating on the emitter is one of the methods proven in work function reduction [11]. Additional boundary conditions imposed on the electron wave function at these periodic ridges prevent free electrons from filling into it. As a result, these electrons have to occupy high energy states, increasing the Fermi energy and reducing the work function of the emitter, as depicted in Fig. 6. A semiconductor substrate with a wide bandgap, e.g., silicon, is preferred as the emitter in this method, as it allows for greater electron confinement and a significant work function reduction.

Alkali metals are well known for their low work function characteristics, and hence, their unique behavior has been intensively studied. According to Langmuir [12], alkali atom adsorption on metal or semiconductor surfaces can reduce the work function. When alkali metal atoms with very low electronegativity values fall onto the substrate surface, their valence electrons tend to transfer to the substrate surface. A dipole moment is created in these atoms between the positive adatom ion cores and the surface negative image charges. The created dipole moment is antiparallel to the substrate surface dipole layer, resulting in work function reduction. A microscopic study on the work function reduction induced by caesium adsorption, was carried out on a metal substrate, namely platinum, and a semiconductor substrate, namely silicon [13]. Both samples demonstrated a remarkable work function reduction. Work function reduction from 5.6 to 1.4 eV in platinum using the caesium adsorption method has also been reported [14]. In the meantime, caesium adsorption had been adapted in the TE process for enhancing TEC efficiency [15]. Morini *et al.* [16] successfully reduced the work function of a hydrogen-passivated (100) p-type silicon substrate from 4.7 to 1.35 eV by coating it with potassium, in an oxidant atmosphere at room temperature.

Another way to reduce the work function using nanomaterials is through intercalation [17]. Intercalation is a process where guest molecules or ions are inserted or included into narrow spaces between host layers, normally carbon or graphite. Charge transferred between the host and the guest releases energy, weakening the van der Waals (vdW) forces and widening the gaps between host layers. A potential allotrope of carbon is a carbon nanotube (CNT), due to its excellent electrical conductivity, high aspect ratio, and thermal stability. Research by Westover *et al.* [17] showed that the intercalation of potassium into single-walled and multiwalled CNTs resulted in the work functions of 2 eV for both, but those results could only be sustained at the temperatures of up to 600 K. In addition, this temperature-dependant work function characteristic will slightly increase the work function readings of both single-walled and multiwalled CNTs as temperature rises, due to the deintercalation of potassium atoms. Many types of graphitic carbon nanofibers (GCNFs) have also been intercalated by molten potassium through stoichiometric reactions [18]. One of the types, stage-1 K with a herringbone GCNF, displayed a work function of 2.2 eV and remained thermally stable at the temperatures of up to 1000 °C.

Exploring suitable TEC emitter materials by not only lowering the work function of electrodes but also considering another mode of electron emission, namely field electron emission, has been extensively studied as well. Electrons are emitted when electrodes are induced by an electrostatic field, in the process normally referred to as cold emission, because it occurs at low temperatures. Pan *et al.* [19] used aligned CNTs to react with silicon oxide powder at certain conditions, yielding aligned SiC nanowires (SiCNWs) on

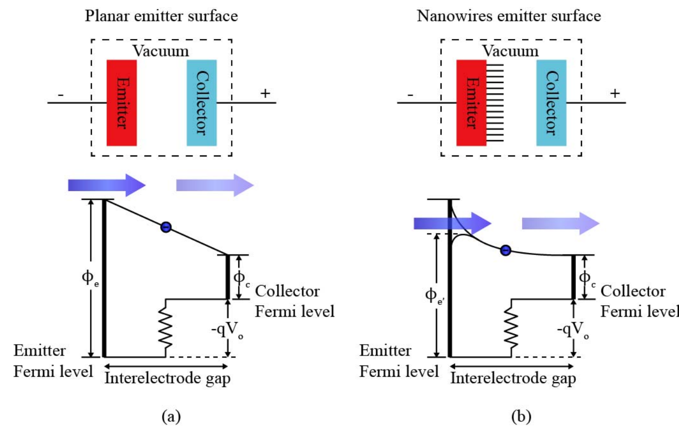

Fig. 7. Schematic energy diagram of two types of electron emission TEC from (a) planar emitter surface and (b) nanowires emitter surface [20].

stainless steel substrates. These oriented SiCNWs showed promising results in terms of field emission properties. The outcome experimentally proved that needle-like nanowires yielded a superior field enhancement factor, which can facilitate electron emission, given suitable materials and conditions. With the aid of nanotips as the emitter surface [20] and applied voltage across electrodes [21], electrons had an easier time overcoming the potential barrier of the emitter. This occurs because a lower effective work function results under these conditions, due to an effect called the Schottky barrier lowering [20]. Fig. 7 presents an energy diagram, comparing electron emission from different emitter surfaces. TECs with nanowire emitter surfaces exhibited lower effective work functions, due to larger field enhancement factors, compared with the TECs with planar emitter surfaces.

As observed from other publications, such as [22] and [23], SiCNWs exhibited excellent thermal and chemical stability. They were also compatible with the standard microfabrication techniques, making them suitable for high-temperature MEMS devices. In addition, numerous studies regarding SiCNWs' field emission properties have been done by interplaying the variables, such as morphology, density, dimension, and temperature, to yield better electron emission results [24]–[27]. These studies have actually revealed the possibility of a field-enhanced TEC that could overcome the limitations of a conventional TEC. Nonetheless, most of the research works [24], [25], [27] related to synthesizing SiCNWs involved high-temperature processes (at the temperatures of up to 1000 °C–1500 °C), and did not feature any tests in TEC. Hence, by considering the cost effectiveness of the device, our team has been seeking alternatives, in order to come up with low-temperature synthesis of SiCNWs [28]. In spite of its wide gap, which is not favorable in TEC electrodes, a promising method has been used to reduce the work function of nanotubes or nanowires by means of low work function material coating, using RF magnetron sputtering. A uniform, thin BaO or strontium oxide coating was successfully deposited on the surfaces of vertically aligned CNTs grown on tungsten ribbon. Although the field enhancement factor was reduced, due to the large diameters

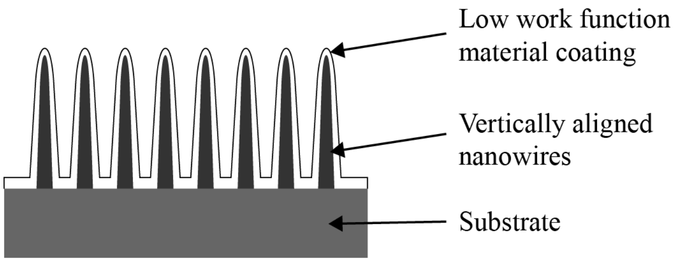

Fig. 8. Schematic of low work function material coated on the surface of vertically aligned nanowires grown on a substrate.

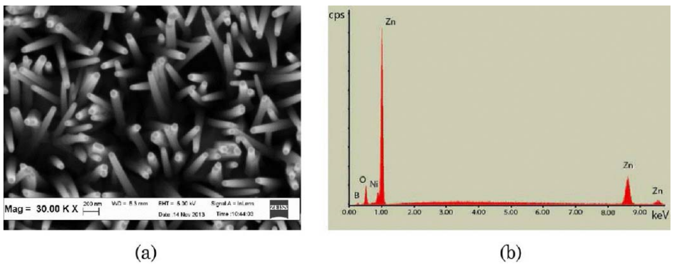

Fig. 9. (a) SEM image of ZnONWs grown using CVD method. (b) EDX spectrum of grown ZnONWs on Au/NiCr-coated borosilicate glass substrate [32].

of CNTs after the deposition of the oxide coating, the work function of coated CNTs was reduced to 1.9 eV from that of uncoated CNTs at 4.5 eV. The strong effect of work function reduction on electron emission overcame the effect of the decrease in the field enhancement factor. As a result, a combination of both field emission and TE experienced significant improvement [29]. Fig. 8 shows a schematic of low work function materials coated onto the surfaces of vertically aligned nanowires grown on a substrate.

As previously mentioned, 1-D nanostructures have been proved to augment the emission properties of field-enhanced TECs, due to their high field enhancement factors. For this reason, vertical zinc oxide (ZnO) nanowires were fabricated by our team as a part of our field-enhanced thermionic studies. ZnO nanowires (ZnONWs) were chosen to be synthesized on the surface of the emitter, due to their unique quantum confinement properties and convenient synthesizing processes [30], [31]. ZnONW emitters have demonstrated low threshold fields for electron field emission, and this is mainly attributed to the high aspect ratios, i.e., large height-to-radius of curvature ratios, of the nanoscaled emitting surfaces [30]. This property often makes them attractive for field emission device applications, but not for energy conversion purposes [31]. The ZnONWs were grown using a chemical vapor deposition process with a vapor trapping approach using a gold (Au) catalyst, as shown in Fig. 9 [32].

In addition, recent research confirms that the TE current acquired from CNTs is not following the Richardson–Dushman equation [33], [34]. This has been further validated using a tested model, where single-layer graphene plays the role of a TEC emitter without considering the effect of the substrate where it attaches. Notably, the deviation from the traditional Richardson–Dushman equation was shown by the derived analytical formula. Furthermore, it is predicted that a TEC with a graphene emitter with a work function of 4.514 eV, running at the temperature of 900 K, could achieve thermionic efficiency of ∼45% under certain circumstances [35]. In addition, a different modeling approach [36] has been explored, to study the field emission performance of graphene. A single-layer vertically aligned graphene sheet induced by an internal time-oscillating barrier is exposed to a biased dc field for field emission analysis. As a result, this model has the potential to increase the TEC current density at low applied fields [37]. However, integrating the field-enhancing model into a TEC still remains a challenge. There is another method of introducing multilayers or heterostructure into a TEC to overcome the limitations of VTECs, by lowering the work function of the emitter. This method will be discussed at the end of Section IV.

B. Space Charge

Another major problem that has been hindering the performance of a practical TEC is the formation of a space charge cloud in the interelectrode space. Unlike other types of heat engines, a TEC uses electrons, which, in nature, are negatively charged and repel each other, in its working fluid. As electrons are emitted into the interelectrode space, they tend to be pulled back into the emitter, which now has a positive charge after having lost some electrons, and to form a cloud of negative charges close to the emitter surface. This results in what is called the space charge effect, which later on repels the additional emitted electrons away from the collector, thus reducing the current transferred to the collector. The space charge effect also creates an additional potential barrier to electron emission. Only those electrons with sufficient kinetic energy are able to reach the collector.

Several approaches have been proposed to mitigate the space charge effect. One way is by inserting positively charged ions into the interelectrode space, to neutralize the negative charge. Caesium is commonly used for this purpose, due to its low ionization potential [38]. However, this approach has a drawback, in that the ionization of caesium takes up some energy during the conversion process, thus reducing the overall system efficiency. Furthermore, handling highly reactive material, like caesium, increases the complexity of the system. As an alternative to using positive ions, another way to suppress the space charge is by adjusting the material properties of the emission surface. Smith [39] suggested that using a hydrogen-terminated diamond material demonstrates the negative electron affinity (NEA) property, which lowers the vacuum level below the conduction band. Therefore, electrons that receive sufficient energy to be promoted to the conduction band can escape the surface as the vacuum level is already been lowered below the conduction band. The NEA property of the material can also be exploited to filter electrons with low energies that are responsible for the space charge emission.

Reducing the interelectrode space between the electrodes is another direct way to mitigate the space charge effect. As the distance between the emitter and the collector becomes small enough, there is not enough space and time for the travelling

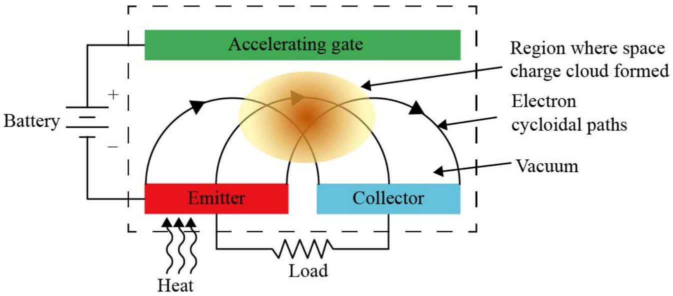

Fig. 10. Schematic of a magnetic triode TEC [1].

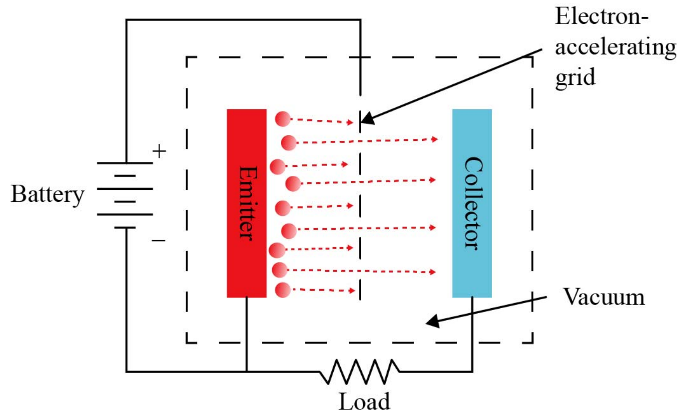

Fig. 11. Schematic of an electrostatic triode TEC [1].

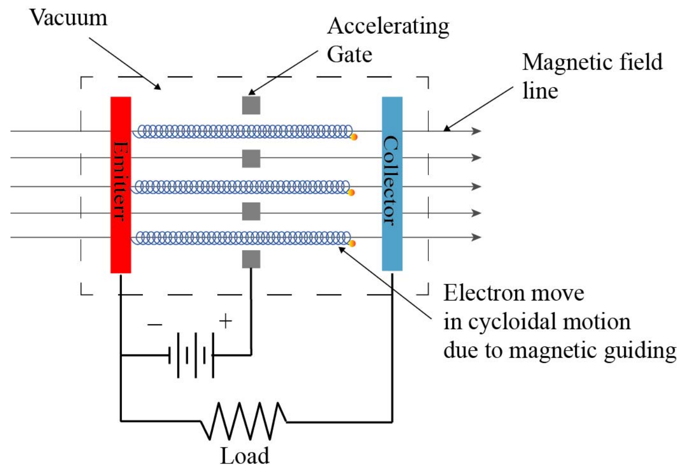

Fig. 12. Schematic of combined magnetic and electrostatic triode TEC concept [43].

electrons to collide with one another, reaching the collector in shorter time as the result. Historically, the closed-space approach has not been proved to be practical, because it is difficult to manufacture. Closed-spaced TECs have failed to show promising results, and have been abandoned as practical devices since the 1960s. However, it is until recently when Fitzpatrick *et al.* [40] showed the potential of a closed-spaced TEC in his experiment, in which the authors managed to actively control the spacing between the electrodes, with a gap spacing of <10 μm. However, another problem arose from the closed-spaced approach, as it is difficult to maintain large temperature differences within small vacuum gaps. Large gaps result in the space charge effect, which limits the current transport, whereas reducing the gap to less than a certain distance results in excessive heat transfer between the emitter and the collector, due to a phenomenon called the near field radiative heat transfer, which increases by many orders of magnitude if the interelectrode gap is too narrow [41], [42]. Lee *et al.* [42] reported that there is an optimal electrode gap range that maximizes the performance of VTECs (between 900 nm and 3 μm), found by interplaying the space charge effect and the near field radiative heat transfer.

Another approach to reduce the space charge effect while preventing radiative heat transfer between the emitter and the collector is to incorporate external electric and magnetic fields to mitigate the space charge effect. This allows one to control the movement of electrons in space to reduce the number of collisions between electrons. Two triode TEC configurations were introduced in [1], with the idea of minimizing the space charge as well as managing the heat transfer between the emitter and the collector. The first one is the magnetic triode TEC, which makes use of a crossed magnetic field and an electric field. In this configuration, electrons are thermally emitted from the emitter surface and find themselves in an accelerating electric field, produced by a gate, which has a high positive bias with respect to the emitter. Instead of going straight to the accelerating gate, these electrons are forced by the perpendicular magnetic field to follow a cycloidal path, and fall onto the collector surface. The acceleration of these electrons removes them from the interelectrode region near the surface of the emitter, which implies the suppression of the space charge cloud. As depicted in Fig. 10, the magnetic triode is unable to suppress the effect of space charge, as a region of space charge accumulation formed due to the intersection of electrons' paths. According to [1], there are also electrons that are collected by the accelerating gate. This is called the leakage current, and can drastically reduce the overall efficiency if it is too high.

Another configuration is an electrostatic triode TEC, in which a grid is placed between the electrodes to accelerate electrons away from the emitter, as shown in Fig. 11. This scheme also possesses the same problem as that of a magnetic triode TEC, as most of the accelerated electrons end up hitting the positively charged grid, which leads to efficiency loss due to the leakage current.

Both configurations were unsuccessful, as a high voltage had to be supplied to maintain the gate electric field, and some of the electrons ended up hitting the accelerating gate, which consequently reduced the overall conversion efficiency. Recently, the combination of the vacuum magnetic and the electrostatic triode concept has been proposed to eliminate the space charge effect, as demonstrated in Fig. 12 [43]. The concept is similar to that of an electrostatic triode, except that there is an applied external magnetic field to keep the electrons from hitting the gate. A large pair of neodymium magnets was used to force the electron radius of gyration to be smaller than the openings of the gate mesh, so that these electrons could pass through the gate and reach the collector.

Another work involving the use of the triode configuration, in combination with a longitudinal field to reduce the space

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charge effect using vapor TECs, was presented in [44]. Two different methods were suggested; a thermionic triode with auxiliary discharge in a longitudinal magnetic field and ion injection from the grid. For the first method, the hot electrons required for the generation of caesium ions are separated from other thermal electrons using the magnetic field and the grid, whereas for the second method, caesium ions are generated at the grid wires between the electrodes, before being injected into the space.

IV. Application of TECs

In the early 1960s, research into potential application of TECs in the production of useful electrical energy was conducted in the U.S. It focused primarily on solar- and nuclear-powered systems. Throughout the program, the corresponding teams failed to produce convincing results, and it was eventually terminated. The interest had, by then, been shifted to space applications in both the U.S. and the Soviet Union. In the U.S., most of the TEC research was related to the knowledge of thermoelectricity. In the Soviet Union, however, the TEC space applications were developed to a significant extent [45]. Two large nuclear reactors equipped with a 5-kW power TEC were successfully orbited and operated in space within the TOPAZ program in 1987. This program was then abandoned due to budget restrictions of political nature [46]. Another space application example, named alkali metal thermal-to-electric converter (AMTEC), was proposed and investigated by Van Hagan *et al.* [47]. A similar concept was demonstrated, where the temperature difference between hot and cold electrodes ran a vapor alkali metal in a closed loop, with the efficiency of 18%. Due to its feasibility, AMTEC has been still further studied and developed in both space and terrestrial applications [48], [49]. After that, in the 1990s, General Atomics proposed a space-based, solar thermionic power system, named high-power, advanced, low-mass (HPALM) program [45]. A conceptual design of an HPALM solar thermionic power system was developed by Begg *et al.* [50]. By preliminary estimation, this cylindrical, inverted, multicell thermionic converter should be converting heat to electricity, with the overall system efficiency of 6.5%. Several prototypes, based on a similar principle, were then been built and tested, revealing the feasibility of using solar heating to generate electricity by means of thermionic converters [51]–[53].

Other than space-based utilization, the thermionic principle has also been considered in concentrated solar power (CSP) applications. One big lead in the discovery of the high-efficiency solar energy conversion is the introduction of photon-enhanced thermionic emission (PETE) [54]. Essentially, PETE is an improvement on a typical TEC, similarly consisting of two different electrodes in parallel plate formation inside the vacuum, and connected by electrical load resistance, but having a p-type semiconductor as the emitter instead of a metal. The electron emission process takes place in three major steps. First, solar radiation acts as a thermal boost, to excite electrons from the valence band into the conduction band. Second, these excited electrons are immediately heated up in the conduction band by the heat source provided to the emitter. Finally, electrons with energies greater than the emitter's electron affinity will be emitted into the vacuum gap and collected by the collector. PETE is intensively studied in solar cell utilization for its combination of PE and TE processes that allow emitted electrons to carry both the photon energy and the energy from thermalization, as well as photon absorption losses. Several theoretical studies, thermodynamically modeling entropy production and parameter improvement, have been analyzed by different groups of researchers, to actualize the application of PETE in solar cell energy conversion systems [55]–[58]. An analytical and numerical study was carried out by Segev *et al.* [56], to validate the efficiency limit of a PETE converter given the concentration of 1000 suns. The efficiency of 70.4% was achieved by a secondary thermal cycle, with the aid of a thermally coupled dual bandgap system, but has yet to be validated experimentally.

Increasing the cost effectiveness and making solar energy conversion more competitive are the motivations for developing higher conversion efficiency devices. A conversion module brought forth by the E^2PHEST^{2}US project was fabricated for serving CSP applications and patented in 2012 [59]. This module was named ST^{2}G (solar thermionic–thermoelectric generator), involving both thermionic and thermoelectric conversion stages connected in thermal series. The calculated overall conversion efficiency was claimed to be up to 30% or greater. Bellucci *et al.* [60] conducted experiments in the laboratory and obtained preliminary results. Suffering from poor vacuum encapsulation, inappropriate electrode work functions, and a large interelectrode gap, only low output powers in the range of tenths of microwatt and of tens of milliwatt were gained by thermionic and thermoelectric stages, respectively. To address the impediment of low intensity for thermionic solar conversion, Yaghoobi *et al.* [61] came up with the first compact thermionic solar cell, in conjunction with the heat-trap' effect in CNTs on an emitter substrate, which allowed the device to be heated by a low-power light. As reported in the related paper reports [61], CNTs are excellent light absorbers for wavelengths ranging from ultraviolet to infrared. They can be effectively heated with the aid of the heat-trap' effect, and, thus, are potentially implemented jointly with the PETE concept. Nonetheless, the preliminary results of low current density, gained in the experiments due to the negligence of the space charge effect and other crucial factors, such as work function, interelectrode gap, and temperate, are not up to optimization. Therefore, follow-up efforts have been made to resolve this problem. Khoshaman *et al.* [62] proposed a high precision method to calculate the output characteristics of TECs. By doing so, one can solve the reverse problem to obtain the above-mentioned important parameters, i.e., work function, interelectrode gap, temperature, and effective surface area of a TEC, which can be easily optimized to achieve better results. A group of researchers have worked on prototyping a thermionic device specifically for its high theoretical efficiency and the capacity for using the solar spectrum [63]. By synthesizing

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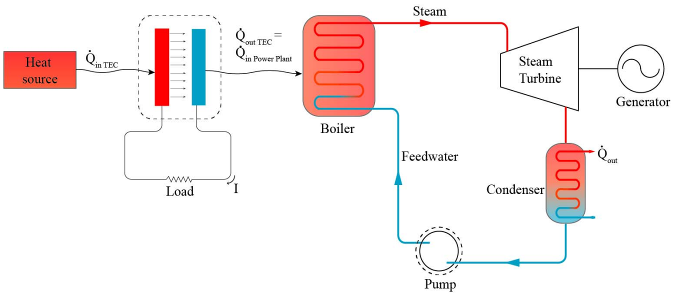

Fig. 13. Schematic of TECs as topping cycle for steam power plant.

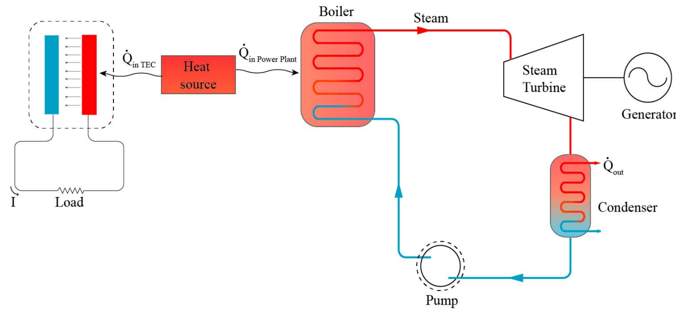

Fig. 14. Schematic of TECs as cogeneration for steam power plant.

several types of emissive materials, determining gap materials, designing proper devices, and experimental testing, some preliminary results were obtained. These results have shown, to some extent, that this device can be the best candidate to replace the conventional, low-efficiency, high-complexity, and high-running-cost steam generators, converting heat to electricity by further optimizing the essential parameters.

Because TECs work best at high temperatures, they have the potential to increase the overall power plant efficiency when employed as part of a conventional fossil fuel power plant's topping cycle. The combustion of fossil fuels such as coal, oil, natural gas, or nuclear fission, in general, produces high-quality heat with the temperatures of over 2000 K, but only low-temperature heat is needed to power up a steam turbine in a conventional power plant, typically 800–1300 K [64]. This is due to the fact that materials making up turbomachinery components cannot withstand extreme temperatures. The overall system efficiency can be improved if a wider temperature range could be used. Therefore, one of the ways to overcome the temperature constraint is to add TECs that take advantage of the higher temperatures without using any moving parts. Because fossil fuel combustion temperatures are much higher than the turbine operating temperature, they are used to heat the emitter of the TECs, and the waste heat from the collector could then be used to power the steam turbine connected to a separate generator, as illustrated in Fig. 13 [65]. Electricity is then produced by TE from TECs and from the turbine's generator. Early research on TECs to be used as topping cycles for electric generating stations in the U.S. was done by Rasor Associates after the reduction of the space program in 1973 [66]. They evaluated the performances of working vapor TECs at a range of temperatures for both the emitter and the collector. Moreover, Rasor Associates proposed using TECs as a topping cycle for fusion power rather than fission or fossil-fuel-generating power plant, because TECs could fully exploit the higher-temperature regime [66]. They estimated that, using a circulating liquid metal to heat the thermionic emitter to the operating temperature of 1370 K, the topping cycle net plant efficiency increased from 41.3% to 47%, and the generating capacity increased by 27.6%. A TEC is also a good match for automotive applications. After working on direct conversion of heat into electricity using TEC devices, Gabor suggested that a particular application be implemented in the drive for a motor vehicle, with dc motors directly driving the wheels [64]–[67]. With the elimination of moving gear trains, a motor driven by a TEC offered advantages over internal combustion engines, including the generation of maximum torque during starting and the production of electricity during braking. Due to the high level of heat generation from diesel and gasoline combustion, incorporating a TEC into a Stirling engine implied additional benefits over an internal combustion engine working alone [4]. Moyzhes and Geballe [44] proposed a method featuring the topping cycle using triode-type vapor TECs in combination with a longitudinal magnetic field in reducing the heat loss.

As TECs can operate at high temperatures, they also have great potential in industrial and domestic cogeneration applications. With respect to industrial cogeneration, a study was done by Margulies *et al.* [68], where they presented a conceptual design for a thermionic cogeneration system, in which multiple TECs were used on the external surfaces of industrial boilers in a chlorine soda production plant. For domestic cogeneration applications, central heating in homes is one of the suitable TEC applications, because the TECs make best use of high-temperature heating. In this case, the high-temperature heat (2000 °C) is used to heat domestic hot water to a temperature of 60 °C [69]. A group of researchers from the Netherlands and Russia was formed during the 1990s for the development of a thermionic domestic boiler system running on natural gas, called TECTEMSs [70]. It is a small cogeneration unit, consisting of a combustion-heated TEC equipped with a radiative burner-recuperator, which typically produces ~1.5 kW of electricity [70]. It is unclear whether, in the present, the system is still commercially available to consumers. Fig. 14 depicts the conceptual schematic of TECs as cogeneration units for a steam power plant, which can be implemented into industrial and domestic cogeneration applications.

In other cases, a TEC could potentially be used as an alternative refrigeration technology. By reversing the work principle, a heat-harvesting TEC can be used as refrigerator. One could consider the simplest form of a TEC, which consists of two parallel plates, separated by a gap and being kept at same temperatures. A net electron flow from one plate to another will result when an applied bias is induced across the device. Electrons with kinetic (thermal) energy flowing from the cathode (emitter) to the anode (collector) results in a net heat current flow, making the cathode side the cooler and anode side the heater. Mahan [71] proposed a thermionic refrigerator, theoretically achieving 80% Carnot efficiency at the temperature of 500 K. Nevertheless, a major challenge has impeded the progress of thermionic refrigerator development. In order to make it feasible at room temperature, the work function of the cathode must be as low as 0.34 eV [71]. Years later, multilayer or heterostructure integrated thermionic cooling devices have been proposed [72]–[74], to overcome the limitation of vacuum thermionic devices at room temperature. The proposed high electron mobility, low thermal conductivity materials [72] could actually produce different barrier heights (0–0.4 eV) in the cathode and the anode. Recently, Liang and Kee Ang [75] introduced a vdW heterostructure thermionic device with graphene electrodes. It is claimed that the cooling efficiency of a room temperature refrigerator can achieve >50% Carnot value and a 10%–20% efficiency in harvesting low-grade wasted heat at the temperature of 400 K.

V. Conclusion

This review presented the fundamental principles of practical TECs, including the limitations that constrained these devices and the corresponding solutions found by researchers, as well as applications that are being developed in the field. Since their introduction decades ago, TECs have generally been categorized into two types, which are the VTEC and the vapor TEC. The former has been reported to be outweighed by the latter, due to practical limitations and technology deficiency. However, as great strides have been made in technology development, particularly in the MEMS process technique and the discovery of advanced nanoscale functional materials, the VTEC application is no longer an unachievable objective. As noticed in other published works, investigations into work function reduction, space charge effect mitigation, geometric structuring, thermal isolation, and other novel approaches have been intensively carried out, to assist VTECs in achieving better efficiency.

Despite of several challenges and limitations in implementing a high efficiency TEC, it is an excellent nominee clean energy harvesting due to its noiselessness, scalability, reliability, and long lifetime characteristics. Further exploration and refinement of this device type could potentially commercialize it, making it widely applied in industry and other favorable sectors in the near future.

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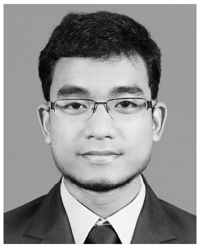
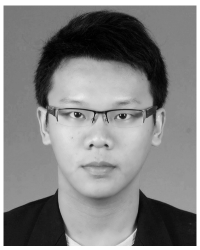


Kamarul Aizat Abdul Khalid received the B.S. degree in mechanical engineering from Vanderbilt University, Nashville, TN, USA, in 2012. He is currently pursuing the Ph.D. degree in advanced manufacturing with the School of Mechanical Engineering, Universiti Sains Malaysia Engineering Campus, Perak, Malaysia.



Thye Jien Leong received the B.S. degree in mechanical engineering from the Universiti Teknologi Malaysia, Johor Bahru, Malaysia, in 2013. He is currently pursuing the Ph.D. degree in advanced manufacturing with the School of Mechanical Engineering, Universiti Sains Malaysia Engineering Campus, Perak, Malaysia.

Khairudin Mohamed received the M.E. and Ph.D. degree in engineering (nanotechnology) from the University of Canterbury, Christchurch, NZ, USA, in 2005 and 2009, respectively.

He has been a Senior Lecturer with the School of Mechanical Engineering, Universiti Sains Malaysia Engineering Campus, Perak, Malaysia, since 2010. His current research interests include nanofabrication of top down and bottom up techniques and fabrication of 3-D nanostructures.