Current status of thermionic conversion of solar energy

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Recent advances in science and technology of materials fabrication, engineering of work functions, and micrometer gap machining between emitter and collector are making thermionic conversion/converter (TEC) of solar energy an emerging technology. As the converter is the lightest of all devices with highest direct power conversion density (per unit area of the converting surface), it has, potential for substituting photovoltaic technology to a large extent and for deployment in space as a power source. This article summarizes the current efforts/technologies in the field, and discusses their inherent merits and demerits towards realizing the goal of achieving high conversion efficiency and simulation of performance evaluation of a solar TEC. We also discuss the use of both metals and nanomaterials, critical roles of work functions of both emitter and collector, collector temperature, absorptivity and emissivity of the surfaces, radiation losses, and use of both metals and nanomaterials in the efficiency of conversion of solar energy. We further deal with the role of correcting thermionic emission current density equation in the simulation of solar TEC performance. We discuss briefly the possible methods of space-charge control in future in a solar TEC.

Keywords: Emission, solar energy, thermionic conversion, work function.

Also, TEC is easy to maintain and has higher efficiency potential close to the Carnot engine, even though there exist limiting factors such as work function of the materials, space charge build-up in the gap between emitter and collector of the TEC, heat loss, as well as physical and chemical factors. Specifically, the heat loss factor can be minimized to achieve optimum performance that is in tandem with the performance of the Carnot engine1,2. In recent time, TECs have been modelled as standalone systems with efficiencies >50% and also as combined-cycle systems with efficiencies >60% (ref. 3).

Evolution of thermionic energy conversion technology

The earlier idea of converting heat to electrical energy via thermionic energy was first conceived by Schlichter in 1915 (ref. 4), which later led to scientific collaboration between the then USSR, and USA in the 1950s to set up a thermionic energy converter that would power spacecraft4,5. Thereafter, a team of researchers in USA launched a thermionic nuclear fuel element (TFE) that worked at a high temperature for 12,500 h. The invention of Mark III reactor helped USA develop a TEC with an efficiency of 7–11%, and power output of 150 W at elevated temperature6. However, the technology faced harsh failure due to undying interest in the photovoltaic technology in the United States at that time. The heat source for a TEC is the major problem. So far, developmental work has focused on TEC systems using heat from a nuclear reactor aboard a spacecraft. The systems recorded efficiencies from 12% to 15% when operating at 600°C–1200°C. Interest in the use of TEC for space programmes died down after 1973, except for a vapour thermionic energy converter (VTEC) with a circulating liquid metal source7 that was built as topping engine for a fusion power plant with 47% efficiency and operating temperature of 1370 K (ref. 7). Consequently, TEC has existed as co-generator with steam turbine Rankine and Sterling engines for solar electricity8. In addition, high temperature at the emitter surface is needed to achieve high current density. Solar energy can be concentrated via suitable devices

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such as parabolic concentrator, parabolic trough mirror, heliostat, etc. and abundant sunshine is available in many parts of the world (Asian, African countries and in several parts of USA). Temperatures as high as 2000 K can be reached with a concentrator factor of 1500 and solar insolation of 650 W/m². This is kindling new interest in solar thermionic power generation.

USSR succeeded in building a TEC engine with 5–6 kW power source in order to launch a satellite into space. In the 1980s, the US researchers did not build any thermionic fuel element (TFE) but only proposed the average lifespan of TFE to be within 3–7 years.

Consequently, Naito et al. recorded the efficiency of their thermionic–thermoelectric engine as approximately 40%. In 1998, the research group of Japan Solar Upper Stage (JSUS) built a TEC that operated at power output 17.9 W and efficiency 23.2%. The effect of Smetsta was higher for power output and efficiency with carbonless emission in the environment led to the development of photoelectric–thermionic engine system. Subsequently, a high power advanced low-mass solar thermionic engine converter (HPALMSTEC) that was theoretically conceptualized to operate at a power output of 50 kW was experimentally achieved in 2006 with efficiency of 6.5% (ref. 18). Yaghoobi et al. used carbon nanotube as the emitter in TEC, which gave an efficiency of 10%.

Buenecurpo et al. utilized light trapping to increase the efficiency of photo-enhanced thermionic emission (PETE) by 10%. Therefore, the essence of green energy technology is to provide a low cost alternative source of energy that is environmentally friendly and highly efficient. Moreover, photo-enhanced thermionic emission (PETE) as a topping cycle in concentrated solar thermal electricity generation, is expected to enable total system efficiencies in excess of 52.9% (refs 21, 22). In addition, a theoretical model calculated the efficiency of PETE at a concentration ratio of 1000 as 70.4%, which is yet to be experimentally validated.

In recent times, the Stanford Linear Accelerator Centre (SLAC)/Stanford University research team USA has focused on a new solid-state energy conversion technology using microfabricated heterostructure semiconductor cathodes with appropriate band engineering and photon-enhanced thermionic energy converters (PETECs). The microfabrication allows a small gap (a few microns) between the emitter and collector and thus reduces the space-charge effect drastically.

Wang et al. used NaCsSb as an emitter in the PETE engine to obtain 0.0197% efficiency. Liu et al. found the efficiency of GaAs nanowire cathode doped exponentially as 19.46% and GaAs nanowire cathode with aluminum composition matrix as 15.8%. Smerdov et al. concluded that the wafer production of GaAs is not technologically simple and that GaAs substrate is expensive. Therefore, their fabricated porous silicon (PS) and PS-based composition matrix yielded an efficiency of 20%. The flexibility of tuning the sensitivity of the bandgap, morphology and surface structure of PS and PS-based in TEC to a desirable point are of great interest to researchers. Table 1 elucidates the progress made so far in the development of TEC prototype, both experimentally and theoretically.

**Principles of thermionic energy converter**

In Figure 1, two metals A and B are shown with work function $W_A < W_B$. For example, $A$ can be aluminium ($W \sim 4.2$ eV) and $B$ can be gold ($W \sim 5.3$ eV). The vacuum level, $E_v$ for both is the same. The work function is by $W = E_v - \mu$. Since $W_A < W_B$ and $E_v$ is the same for the two bare metals, $\mu_A > \mu_B$. When they are connected by a perfectly conducting wire, the statistical physics demands that their chemical potentials ($\mu$) be aligned (Figure 2). Because of the lower work function, the free electrons in metal $A$ have higher chances to cross the vacuum level and go to metal $B$ than the electrons from $B$ coming to $A$. To see this in another way, the chemical potential difference cannot constitute a current through the wire as it would disrupt the Fermi energy (chemical potential) equilibrium.

After this initial adjustment, electrons in both metals still have the maximum energy at $E_F$, particularly at 0 K. There will be no electron flow between the two metals at 0 K. If metal $B$ (emitter; gold in Figure 1) is heated to a high temperature, then a sufficient number of electrons will reach the vacuum level in $B$, overcoming the work function $W_B$ and with kinetic energy. These electrons will experience an electric field that will sweep them to metal $A$ in the form of emission (from $B$ to $A$) (similar to the injection of electrons in a forward-biased $P-N$ junction). It will constitute an electric current, which can drive a load (Figure 2) under the voltage $(W_B - W_A)/e$, and one can get work output. Note that the reverse is not possible, i.e. electrons thermionically emitted from $A$ will have to work against the barrier to reach $B$, and will not deliver any output power.
<table>
<thead>
<tr>
<th>Author</th>
<th>Scientific focus</th>
<th>Experimental Findings</th>
<th>Author</th>
<th>Scientific focus</th>
<th>Theoretical Findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jurgens</td>
<td>Built sophisticated TEC to exploring weather parameters of planets.</td>
<td></td>
<td>Wu</td>
<td>Examined finite-time thermodynamic computation of TEC.</td>
<td>Power output of TEC was ( P_{\text{out}} = 988 \text{ W}. )</td>
</tr>
<tr>
<td>El-Gerk and Momozaki</td>
<td>Investigation of planar TEC that operated at low temperature with Mo electrodes and emitter–collector gap of 0.5 mm.</td>
<td>A graphite cylindrical cavity-type solar receiver built.</td>
<td>Lambda and Kaushik(^4)</td>
<td>Analysis of internal and external thermal losses of an irreversible thermionic generator (TIG)</td>
<td>Impact of space charge on TEC and its solutions.</td>
</tr>
<tr>
<td>Lee et al.</td>
<td>Optimization of cathode–collector interelectrode.</td>
<td>Molybdenum performed better than tungsten ( \eta_{\text{melt}} = 15.1% ).</td>
<td>Datas(^5)</td>
<td>Conceptualization of thermionic-photovoltaic generator (TIPV)</td>
<td>New theory has been formulated for TIG. Design and selection of emitter and collector work function of TIG made easy.</td>
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<tr>
<td></td>
<td></td>
<td>Higher efficiency for cesiated tungsten is within interelectrode 900 nm–3 ( \mu ) m. Variations of interelectrode for different electrodes.</td>
<td>Mishra et al.(^4)</td>
<td>Suitability of few-layer graphene as cathode (FLG) in TEC.</td>
<td>Powe density of TPV at 1650 K doubled thermionic (TI) and thermophotovoltaic (TPV).</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>Xiao et al.(^4)</td>
<td>Discussion of state-of-the-art of solar TEC.</td>
<td>Establish a model to predict the emission mechanism of FLG in TEC at low temperature.</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>Xiao et al.(^5)</td>
<td>Parametric examination of thermionic/thermoelectric hybrid generator.</td>
<td>FLG as a potential cathode for TEC.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Lim et al.(^4)</td>
<td>Effect of electron reflection on space charge in TEC via particle-(</td>
<td>\text{-})cell code Warp3D</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Hasen et al.(^6)</td>
<td>Investigation of hexaboride ((\text{La}<em>x\text{Ba}</em>{1-x})Ba), microstructure, the internal structure (morphology), work function and its emission constan</td>
<td>Obtained 35% efficiency.</td>
</tr>
</tbody>
</table>

(Contd)
Table 1. (Contd)

<table>
<thead>
<tr>
<th>Author</th>
<th>Experimental</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bellucci et al. 28</td>
<td>Built solar thermionic/thermoelectric generator (STG). STG attained 30% efficiency</td>
<td>Modelled graphene as a suitable candidate for cathode and anode of TEC.</td>
</tr>
<tr>
<td>Yuan et al. 2</td>
<td>Built a TEC that overcame space charge and an elevated anode work function.</td>
<td>Graphene is a suitable electrode for cathode and anode in TEC. Obtained 55% efficiency. Tuneability of graphene in TEC.</td>
</tr>
<tr>
<td>Bao et al. 30</td>
<td>Examination of structural, magnetic and thermionic emission features of hetaboride (La_{0.9}Ba_{0.1})B_6.</td>
<td>Nanomaterials as suitable electrodes for solar TEC.</td>
</tr>
<tr>
<td></td>
<td>La_{0.9}Ba_{0.1}B_6 at elevated 1873 K produced higher emission intensity of 20.02 Acm(^{-2}). Suitable cathode/emitter for TEC due to low-emission work function</td>
<td>APR generator converted the heat lost from VTIG to attain efficiency of 27.06% from 17.21%</td>
</tr>
<tr>
<td></td>
<td>Zhang et al. 52</td>
<td>Built solar-assisted co-generation system.</td>
</tr>
<tr>
<td></td>
<td>Built solar-assisted co-generation system that consists of a vacuum thermionic co-generator (VTIG) and an absorption refrigerator (APR)</td>
<td>Theoretically, thermionic-thermo-radiative solar cell (TIRSC) has the tendency to yield a high solar-to-electric conversion efficiency of 22.5% under 800 sun intensity, that is transcendent with multi-crystalline silicon wafer-based solar cells with 22.5% efficiency</td>
</tr>
</tbody>
</table>
continue if $B$ remains hot and electrically grounded to supply the electrons. In the case of TEC, i.e. when $B$ and $A$ are connected, the emitted electrons are collected by $A$ (anode or collector) and return to $B$, with the chemical potentials remaining aligned. Thus, the energy of the electrons is delivered to the external load (Figure 2). This continues if energy is supplied to $B$ to keep it hot. Thus, heat energy is converted to electrical energy. This is the principle of the TEC. Metal $A$ will also emit electrons in a TEC. The corresponding current density will tend to oppose the current density from $B$ for external work output. Thus, it is important in a TEC to have the temperature of $A$ (collector) much lower than that of $B$ (emitter). The output power in a TEC (Figure 2), $P_{\text{out}} = (I_e - I_c) (W_B - W_A)/e$, where $I_e$ is the emitter current and $I_c$ is the collector current. Again, the separation between emitter and collector has to be very small to reduce the space-charge effect, especially in the absence of a gate and magnetic field control.

To generate a sizable amount of electrical power (several kWs–MWs) from the sun using a thermionic converter, one needs a large-sized parabolic concentrator with good parabolicity\(^1\). The world’s largest parabolic antenna (diameter 305 m) used in world’s largest radio telescope is seen in Arecibo (Puerto Rico). If such an antenna could have a perfectly reflecting mirror and light enough to track the sun and its parabolicity good enough to focus the concentrated solar energy onto an area of 4 sq. m (where the main part of TEC would be placed). And with average solar insolation of 600 W/m\(^2\) for 8 h a day, a total of 140 MWh of energy can be generated per day, assuming a modest TEC efficiency of 40%. Even at reasonable efficiency of 20%, the total energy output is 70 MWh of energy per day (without good space-charge control). Obstacles to be overcome to achieve this possibility are the following: (i) covering the large parabolic surface with highly reflecting coating; (ii) making such a mirror light enough for solar tracking; (iii) using materials with low work function (in the range of 2.5–1 eV) which are capable of withstanding temperature in the range 3500–2000 K; (iv) using proper device to control temperature of the collector in relation to the emitter temperature to achieve the desired efficiency; (v) perfect space-charge control to achieve the desired efficiency (50% or higher) and (vi) light permanent magnets with a uniform field of 1000 G over large area of the emitter and collector (4 sq. m).

In concentrated solar thermal and concentrated photovoltaic stations, TEC could convert the heat loss into electrical power with considerably good efficiency. However, to the best of our knowledge, a practical solar TEC has not been realized yet. De and Olukunle\(^3\) first carried out conservation of energy principle, the dependence of efficiencies of solar TEC on work functions of the emitter and collector, and their temperatures, and how the latter terms would be dictated by the incident solar power density, except for their earlier published work\(^1,33\). Many emitter materials have work functions in the range 3–4.5 eV. These require very high temperatures (above 2000 K) to generate sizable current density. Except for a few (such as tungsten), most materials have melting points below 2000 K and therefore are not suitable for high-temperature TEC.

As current density at a given temperature increases exponentially with lowering of work function for TEC applications, research is now focused on fabrication of materials with low work functions. Such materials should also tolerate fairly high temperatures $\sim$2000 K. Polycrystalline diamond films exhibited a work function of 0.9 eV when doped with phosphorus. However, they were stable only up to 765°C (ref. 34). Nitrogen-incorporated, ridged nano-diamond films on silicon substrates attained a work function of 1.39 eV and were thermally stable at temperatures up to at least 900°C (ref. 35).

**Technological hurdles**

Basically, TEC is confronted with two scientific issues, namely electrode materials with low work functions that...
Table 2. Overview of electrodes in a TEC (ref. 44)

<table>
<thead>
<tr>
<th>Material</th>
<th>Collector</th>
<th>$W_e$ (eV)</th>
<th>$T_e$ (K)</th>
<th>$P_{out}$ (W)</th>
<th>$\eta$ (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhenium</td>
<td>Molybdenum</td>
<td>1990</td>
<td>114</td>
<td>7.0</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Molybdenum</td>
<td>1850</td>
<td>17.9</td>
<td>23.2</td>
<td>69</td>
<td></td>
</tr>
<tr>
<td>Tungsten</td>
<td>Molybdenum (0.03) + niobium</td>
<td>1670</td>
<td>30</td>
<td>–</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>Tungsten oxide</td>
<td>Polycrystalline tungsten</td>
<td>1800</td>
<td>973</td>
<td>6</td>
<td>–</td>
<td>71</td>
</tr>
<tr>
<td>Tungsten</td>
<td>Nickel</td>
<td>1420</td>
<td>850</td>
<td>1</td>
<td>–</td>
<td>72</td>
</tr>
<tr>
<td>Grooved molybdenum</td>
<td>Molybdenum</td>
<td>1500</td>
<td>728</td>
<td>0.95</td>
<td>–</td>
<td>73</td>
</tr>
<tr>
<td>$ZrO_2$–$Mo$</td>
<td>$ZrO_2$–$Mo$</td>
<td>1523</td>
<td>2.5</td>
<td>–</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>SiC–C–W</td>
<td>Nickel</td>
<td>1630</td>
<td>900</td>
<td>2.1</td>
<td>–</td>
<td>75</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Stainless steel</td>
<td>1600</td>
<td>700</td>
<td>6</td>
<td>–</td>
<td>76</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Molybdenum</td>
<td>1650</td>
<td>750</td>
<td>4</td>
<td>–</td>
<td>77</td>
</tr>
<tr>
<td>SiC–C–W</td>
<td>Nickel</td>
<td>1375</td>
<td>900</td>
<td>0.2</td>
<td>0.5</td>
<td>78</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Nickel</td>
<td>1453</td>
<td>591</td>
<td>4.2</td>
<td>–</td>
<td>79</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Molybdenum</td>
<td>1573</td>
<td>1073</td>
<td>0.34</td>
<td>4.90</td>
<td>80</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Molybdenum</td>
<td>1673</td>
<td>973</td>
<td>2.27</td>
<td>15.10</td>
<td>81</td>
</tr>
<tr>
<td>Tungsten</td>
<td>Niobium</td>
<td>1600</td>
<td>1000</td>
<td>1.76</td>
<td>7.90</td>
<td>82</td>
</tr>
<tr>
<td>Grooved molybdenum</td>
<td>Smooth molybdenum</td>
<td>1673</td>
<td>873</td>
<td>2.18</td>
<td>12.90</td>
<td>82</td>
</tr>
<tr>
<td>Smooth molybdenum</td>
<td>Grooved molybdenum</td>
<td>1673</td>
<td>873</td>
<td>2.56</td>
<td>14.70</td>
<td>82</td>
</tr>
<tr>
<td>Smooth molybdenum</td>
<td>Smooth molybdenum</td>
<td>1673</td>
<td>873</td>
<td>3.74</td>
<td>17</td>
<td>82</td>
</tr>
<tr>
<td>Grooved molybdenum</td>
<td>Grooved molybdenum</td>
<td>1673</td>
<td>873</td>
<td>1.86</td>
<td>11.20</td>
<td>82</td>
</tr>
<tr>
<td>Graphene</td>
<td>Metallic</td>
<td>900</td>
<td>450</td>
<td>–</td>
<td>45</td>
<td>56, 83</td>
</tr>
<tr>
<td>Graphene</td>
<td>Metallic</td>
<td>1200</td>
<td>400</td>
<td>–</td>
<td>56</td>
<td>43</td>
</tr>
<tr>
<td>Graphene</td>
<td>Graphene</td>
<td>1500</td>
<td>1000</td>
<td>–</td>
<td>63.8</td>
<td>1</td>
</tr>
</tbody>
</table>

$W_e$ represents the work function of the emitter, $W_c$ is the work function of the collector, $T_e$ is the temperature of the emitter, $T_c$ is the temperature of the collector, $P_{out}$ is the power output and $\eta$ is the efficiency.

can withstand elevated temperatures and space-charge barrier that reduces the current density, power output and efficiency.

Next we discuss how nanotechnology seeks new emitters, collectors and solves the problem of space charge that exists within the emitter–collector of TEC.

Emitter work function

The physics of thermionic emission suggests that the emitter must be made of a material with low work function that can withstand elevated temperatures such as concentrated sunlight. In search of these materials, a tungsten emitter was doped with scandium oxide at elevated temperature, which reduced the work function of tungsten drastically and led to higher current density53,54. A polycrystalline diamond exhibited a work function of 1.4 eV, when it was doped with nitrogen9,10. More so, the addition of caesium to the platinum surface resulted in a low work function of 1.4 eV (ref. 55). Also, the work function of passivated hydrogen (100) p-type silicon substrate was tuned from 4.7 to 1.35 eV through the inclusion of potassium on silicon lattice12. In recent times, carbon nanotubes and graphene as emitters have been considered both experimentally and theoretically because of their excellent properties11,15,56–58. Their higher work functions have been reduced to desirable tolerance via barium-doped diamond12,59, emerging nanoscience and nanoengineering19,34,35. Consequently, the work function of mono-walled and poly-walled carbon nanotubes has been successfully intercalated at low temperature with potassium to 2 eV (ref. 60). Figure 3 shows vertical zinc-oxide tiny-wires deposited on the surface of the emitter because of their high field potential, high aspect ratio, exceptional quantum confinement attributes and easy deposition processes. Therefore, chemical vapour deposition together with catalytic gold was adopted to grow the tiny wires on the emitter81. Studies have proven that the electron negative affinity (NEA) from diamond, boron nitride and aluminium nitride can reduce higher work functions in emitters to lower values suitable for TEC applications, without compromising their higher electron emission property10,59,62,63. Alternatively, atomic layer deposition of thin oxide on emitter63 and the use of nanomaterials like graphene (emitter) as are suitable in a TEC (Table 2).

Collector work function

The fundamental role of using low collector work function in realizing higher power output in a TEC cannot be undermined. As such, obtaining substantial power output in the TEC configuration demands that the collector work function should be smaller than the emitter work function, and that the input voltage is approximately equivalent to the change in cathode and anode work functions33,63. Additionally, the physics of condensation of emitted electrons on the collector is such that its work function must be smaller than the vacuum level so as to reduce the thermal loss that exists between the emitter...
and the collector. Also, it has been observed that during heat radiation transfer, an anode with higher thermal reflectivity possesses the ability to drastically increase the efficiency of a TEC. Over the years, researchers have made limited efforts to probe the influence of higher collector work function and its surface resistivity on the power output of a TEC. However, the incorporation of scandium oxide together with porous metal might be a good candidate to reduce the work function and surface resistivity of a metal to a desirable amount. Therefore, scandium and phosphorus oxide have the highest doping power in diamond lattice with the collector work function lower to 0.9 eV (ref. 66). In recent times, a grid (graphene) mounted closer to the collector plate was found to lower the work function of the plate, reduce thermal losses and increase the efficiency of the TEC because the emitted electrons were under the vacuum level. NEA can also reduce the space-charge issue. The back-gated anode has shown promising application in the TEC because it reduces the space-charge effect and maintains low work function characteristics (Table 1). Therefore, a magnet can be attached to the anode to reduce heat losses and channel the back emission spontaneously to the emitter.

**Space charge**

Space charge is the spreading of charge over the entire space and not only a point. Therefore, researchers have developed different techniques of eliminating its effect in TEC. Thus, the addition of cesium at the middle of the electrodes helped reduce the space-charge problem. However, there was a 30–50% loss in the efficiency of TEC. The distance between emitter and collector was reduced to within 5–10 μm (ref. 15). With such a low distance, the emitted electrons are collected immediately as soon as they are emitted. An experiment was performed with small gap of 1.6 μm between the emitter and collector. Also, a separation distance of 10 μm generated a lot of heat loss, which negatively affected its efficiency. There was successful micromachining of 100 μm emitter–collector distance that withstood elevated temperature of 1400 K (refs 26, 90, 91). Furthermore, a negative electron affinity method has yielded positive results in reducing the ripple effect of space charge in a TEC. More so, the problem of space charge was overcome through insertion of the positive gate and magnetic field (Figure 4). This latter solution helped produce lightweight TEC with graphene (transparent to the emitted electrons) as the grid. Such micromachining is tedious. A novel method was originally suggested by Mier et al. and later modified by Olawole et al.

**Theory of electricity generation thermionic energy converter**

In recent times, theorists have shown that the Richardson equation lacks merit to predict the current density of a TEC built using nanomaterials. Liang and Ang showed a theoretical efficiency of about 45% using eqs (1) and (2). Khatoon et al. considered current density as a function of the cube power of temperature.

\[
J = \frac{eT^3k_B^3}{\pi v_F^2 h^3} \exp \left(\frac{-W - E_F}{k_B T}\right),
\]

\[
\eta = \frac{(J_c - J_a)(\Phi_c - \Phi_a)}{(J_c(\Phi_c + 2k_BT_c) - J_a(\Phi_a + 2k_BT_a))},
\]

where \(A_0 = ek_B^3 / \pi v_F^2 h\) is the Richardson–Dushman constant for graphene (115.8 Am² K⁻¹), \(\Phi\) the work function of the material, \(E_F\) the Fermi energy, \(v_F\) the Fermi velocity, \(T\) the temperature, \(e\) the electronic charge, \(\Phi_c\) the work function of the cathode, \(\Phi_a\) the work function of the anode, \(J_c\) the cathode (emitter) current density, \(J_a\) the collector (anode) temperature, \(T_c\) the emitter temperature, \(T_s\) the collector temperature, \(h\) the reduced Planck’s constant and \(k_B\) is the Boltzmann constant.

Olawole and De have shown the highest theoretical efficiency of 63.8% with their well-modelled energy

![Figure 3](image-url)  
**Figure 3.** Surface engineering of emitter work function.

![Figure 4](image-url)  
**Figure 4.** Effect of the gate in the emitter–collector interelectrode.
dynamic equations and modified Richardson–Dushman equation for nanomaterials\textsuperscript{1,33}
\begin{equation}
I_0(S-s)_{eq} = \left[ \frac{J_e s(W_c + 2k_BT_e)}{e} - \frac{J_c s(W_c + 2k_BT_e)}{e} \right] + [e_e \sigma_s(T_e^4 - T_s^4) + e_e \sigma_s(T_e^4 - T_s^4)], \tag{3}
\end{equation}
where $P_{out}$ is the power output, $J_e$ the emitter current density, $T_e$ the emitter temperature and $\eta$ the efficiency of solar thermionic power conversion, $r$ the reflection coefficient of the parabolic mirror, $\sigma$ and $e_e$ are the absorptivity and emissivity of the silicon carbide substrate surface on which the solar energy is focused, $e_e$ the emissivity of the graphene emitter surface facing the collector, $P_{out}$ the power output, $J_e$ the emitter current density, $J_c$ the collector current density, $T_e$ the emitter temperature and $T_c$ is the collector temperature. Kahtoon et al.\textsuperscript{91} modified the Richardson–Dushman equation to show that both work function and Fermi energy are a function of temperature in a TEC.

\begin{equation}
J = A_0 T^2 \exp \left( - \frac{W_0 + \left( \frac{\pi k_BT}{12} \right) \left( \frac{7\pi^4}{960} \right)}{k_BT} \right), \tag{4}
\end{equation}

where $A_0$ is the assumed Richardson–Dushman constant for graphene (120 Am\textsuperscript{2} K\textsuperscript{-2}), $W_0$ the work function of the material, $T$ the temperature, $W_c$ the work function of the emitter, $W_e$ the work function of the collector, $\alpha$ the coefficient of thermal expansion, $E_{F0}$ the Fermi energy, $k_B$ the Boltzmann constant, $\eta$ the efficiency of solar thermionic power conversion, $r$ the reflection coefficient of the parabolic mirror, $\sigma$ and $e_e$ are the absorptivity and emissivity of the silicon carbide substrate surface on which the solar energy is focused, $e_e$ the emissivity of the graphene emitter surface facing the collector, $P_{out}$ the power output, $J_e$ the emitter current density, $J_c$ the collector temperature, $T_e$ the emitter temperature and $T_c$ is the collector temperature.

Conclusion

There is an omission of emissivity in eq. (2), which will adversely affect the efficiency of the TEC. Thus the efficiency recorded by eq. (2) (ref. 93) was far less (18%) than that by eq. (5) (ref. 1). Also, Kahtoon et al.\textsuperscript{91} did not evaluate the efficiency of the TEC, which may be due to the weakness of the theory in predicting the efficiency of the TEC accurately. This study has shown the progress made in achieving a highly efficient thermionic energy converter in a real world. Specifically, the pace of advancement of surface engineering and nanoengineering towards commercialization of TEC is a signature to the fact that flexible TEC with higher performance is realizable.


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