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Theoretical studies of thermionic conversion of solar energy with graphene as emitter and collector

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Abstract. Thermionic energy conversion (TEC) using nanomaterials is an emerging field of research. It is known that graphene can withstand temperatures as high as 4600 K in vacuum, and it has been shown that its work function can be engineered from a high value (for monolayer/bilayer) of 4.6 eV to as low as 0.7 eV. Such attractive electronic properties (e.g., good electrical conductivity and high dielectric constant) make engineered graphene a good candidate as an emitter and collector in a thermionic energy converter for harnessing solar energy efficiently. We have used a modified Richardson–Dushman equation and have adopted a model where the collector temperature could be controlled through heat extraction in a calculated amount and a magnet can be attached on the back surface of the collector for future control of the space-charge effect. Our work shows that the efficiency of solar energy conversion also depends on power density falling on the emitter surface, and that a power conversion efficiency of graphene-based solar TEC as high as 55% can be easily achieved (in the absence of the space-charge effect) through proper choice of work functions, collector temperature, and emissivity of emitter surfaces. Such solar energy conversion would reduce our dependence on silicon solar panels and offers great potential for future renewable energy utilization. © The Authors. Published by SPIE under a Creative Commons Attribution 3.0 Unported License. Distribution or reproduction of this work in whole or in part requires full attribution of the original publication, including its DOI. [DOI: [10.1117/1.JPE.8.018001](https://doi.org/10.1117/1.JPE.8.018001)]

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1 Introduction

Thermionic energy converter(sion) (TEC) is an emerging technology for clean power generation. It uses the principle of thermionic emission of electrons from a heated solid surface (below the melting point). The thermionic current density J at temperature $T(K)$ is in general guided by Richardson–Dushman’s (RD) equation^{1–3}

$$J = 1.2 \times 10^6 T^2 \exp(-W/k_B T), \quad (1)$$

where W is the work function of the emitter and k_B is the Boltzmann constant. The emitted electrons when collected by a colder anode (collector) constitute electrical current that can drive a load [Fig. 1(a)]. Figure 1(a) shows a schematic diagram (on the left) of a TEC.^{5,6} If heat is continuously supplied to the emitter (cathode) then power can be extracted at the load subject to restrictions, such as the space-charge effect.^{4,7,8} Space charge is formed in between the emitter and collector space, which is to be maintained at vacuum and may be filled with positive cesium ions when all the emitted electrons from the emitter cannot be simultaneously collected by the anode. This is primarily due to intense electron repulsions among them. This causes scattering of the emitted electrons sideways and reduces (or limits) the electron current available at the anode from that given by RD [Eq. (1)] and hence the output (see Sec. 1.2) in a TEC. Space charges can be minimized by (i) keeping the separation constant

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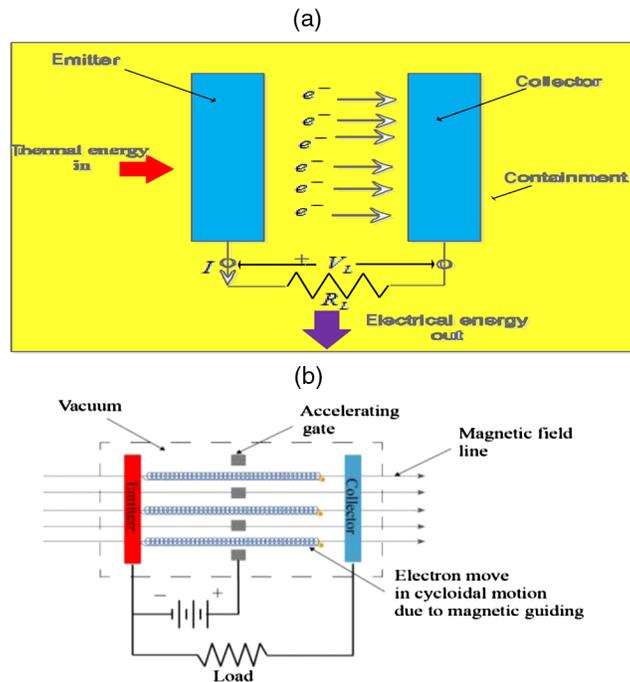


Fig. 1 (a) Schematic diagram of the TEC and (b) concepts based to minimize the effect of space-charge application via gate and magnetic.⁴

between emitter and collector on the order of microns, which is very difficult while maintaining a significant temperature difference and (ii) applications of magnetic field and gate voltage [Fig. 1(b)]. The latter is an innovative technique that is shown to be effective.⁴ Guided by an accelerating electric field and cycloidal path motion in the magnetic field, the electron scattering is reduced significantly. The diameter of the holes in the gate must be such that (i) it allows fairly uniform electric field directed normal to the emitter, (ii) while maximizing the hole space in the gate as much as possible (to minimize gate current), and (iii) it should be slightly higher than the cyclotron radius of most electrons. A high magnetic field can accomplish the latter.⁹⁻¹¹

The detailed principle of TEC is discussed in Sec. 1.2. This form of thermionic power generation is clean as it involves no toxic emissions, specifically, if the heat source is clean, such as solar energy. It forms a compact sustainable power source. Moreover, since TEC converts function best at high temperatures, these have been suggested to be used as a topping cycle in steam, gas turbine, and nuclear power generations, concentrated solar power (both steam and photovoltaic) systems, and even at home using gas burners.¹² Thus, TEC also has significant potential to augment conventional power generation and can have a long-working service life. Thermionic converters are tolerant of high acceleration and have no moving parts. They also exhibit a relatively large power-to-weight ratio. As a result of these excellent attributes, they are well suited for some applications in spacecraft.¹³

1.1 New Development in Thermionic Energy Conversion

Development work has so far focused on TEC systems to provide electric power from a nuclear reactor on board a spacecraft. Their efficiencies ranged from 12% to 15% at temperatures of 900 to 1500 K (about 600°C to 1200°C or 1200°F to 2200°F). These make them suitable power sources for terrestrial applications in certain remote or hostile environments. In the past years, TEC received considerable interest as part of the space program because of its good efficiency and power density. But the interest died down after 1973. Recently, there has been a renewed interest.¹⁴

Solar thermionic power generation is currently receiving attention.^{4,9,10,15-17} The SLAC/Stanford University research team is creating a new solid-state energy conversion technology based on microfabricated heterostructure semiconductor cathodes with appropriate band

engineering and photon-enhanced thermionic energy converters (PETECs). The microfabrication allows very small gaps (a few microns) between the emitter and the collector and thus reduces the space-charge effect drastically. When used as a topping cycle in concentrated solar thermal electricity generation, PETECs are expected to enable total system efficiencies in excess of 50%. However, a practical device has not yet been realized and the problem of PETEC is discussed below.

To generate a sizable amount of electrical power (several kW) from the sun using a thermionic converter, one needs large-sized parabolic concentrators.¹⁸ A parabolic concentrator of diameter ~ 2.6 ft. costs around \$200. One day with the advent of technology it is expected that a large-sized parabolic mirror (imaging type) of diameter 4 to 6 m can be purchased at a cost of around \$1500 to \$2000. Then cost-effective solar thermionic power conversion would be possible, as it can generate high temperatures onto a small surface to produce very high emission current density.

Solar TEC has possibility for future use as a topping cycle in concentrated solar thermal and in concentrated photovoltaic stations. However, to our knowledge, a practical solar TEC has not been realized yet. No theoretical study has been carried out either on how the efficiencies of solar TEC would depend on work functions of emitter, collector, and their temperatures and how the latter terms would be dictated by the incident solar power density, except for our earlier works,⁹⁻¹¹ where we have considered a different energy balance as explained later.

Many emitter materials have work functions in the range from 3 to 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.

Current density at a given temperature is exponentially higher for lower work function materials. Therefore, for TEC applications, research is recently focused on materials with low work functions. Such materials should also tolerate fairly high temperatures ~ 2000 K. Polycrystalline diamond films exhibited a work function of 0.9 eV when doped with phosphorus. Unfortunately, the film has been stable up to 765°C only.¹⁹ 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.²⁰

Nanomaterials (emitters) with high melting points are receiving attention for the conversion of the thermal energy to electrical power by TECs. By combining electrostatic gating with a Cs/O surface coating on a large area monolayer graphene grown by chemical vapor deposition (CVD) and then transferring it onto 20-nm HfO₂ on Si that enables high electric fields capacitive charge accumulation in the graphene, Yuan et al.²¹ were able to demonstrate that the work function of graphene can be reduced from 4.6 to 0.7 eV. Such ultralow work function graphene is an ideal candidate as the thermionic emitter in TEC, specifically, for low-temperature TEC. High bonding energy (~ 5.9 eV) between adjacent carbon atoms in graphene is among the highest in nature (slightly higher than the sp³ bonds in diamond)²² and graphene can tolerate high temperatures (up to 4600 K) in vacuum. With a single-atom-thick sheet of sp²-hybridized carbon atoms, graphene exhibits great promises for future applications in energy storage,²³ nanoelectronics,^{24,25} and composites.²⁶ Graphene has potential^{27,28} as a suitable candidate as an emitter in a thermoelectronic (with no ions involved) energy converter TEC. Liang et al.²⁹ proposed and theoretically studied a solid-state thermionic device comprising of van der Waals heterostructures of suitable multiple layers of transition metal dichalcogenides such as MoS₂, MoSe₂, WS₂, and WSe₂ sandwiched between two graphene electrodes to waste heat at 400 K and found efficiencies in the range from 7% to 8%.

Being a high-temperature material,³⁰ graphene can be a very suitable material for TEC, especially if the work function of graphene can be reduced from around 4.5 to 1.5 eV using some of the technologies as mentioned above. Technologies have been maturing for growth of mono to multilayers of graphene (Gr) on silicon carbide.^{31,32} The latter is a material that can also sustain high temperatures. Epitaxial Gr on silicon carbide (SiC) holds great promise for the development of new device concepts based on the vertical current transport at the Gr/SiC heterointerface.³³ Ease of vertical current transport in graphene-based TEC is needed to have high efficiency. Work function modulation of graphene on SiC has also been obtained recently through controlled use of nitric acid.³³

Recently, Kwon et al.³⁴ reported a chemical approach to the lower work function of graphene using K_2CO_3 , Li_2CO_3 , Rb_2CO_3 , and Cs_2CO_3 . The work functions are reported to be 3.7, 3.8, 3.5, and 3.4 eV, respectively. Such a remarkable property, along with good electrical conductivity and high dielectric constant, makes engineered graphene an ideal candidate to be used as both emitter and collector in a TEC.

Graphene has distinguished itself due to superior properties in linear band structure, ultrahigh electrical conductivity, high stiffness, light weight, and extreme mobility.³⁵ Graphene emitter, therefore, is a good candidate for thermionic engines. It has its place because of the presence of free electrons in linear band structure, which is in proximity to the Fermi level that is deficient in macromaterial.^{36–41} Alteration in the chemical potential across the graphene sheet provides room to tune the intrinsic Fermi level (chemical potential, μ) to a corresponding Dirac point by the choice of the investigator,⁴² and thus the work function, W ($W = E_v - \mu$). Thus, graphene can become the ideal candidate for thermionic power generation with the use of solar concentrators [Fig. 4(a)].

Thus, it is expected that with the advent of new science and technology, several layers of graphene on silicon carbide can be deposited such that the work function can be controlled at ease from around 4.6 to 0.7 eV as desired, while retaining its high-temperature tolerance. In Secs. 1.2 and 1.5, we would consider (i) the principle of TEC and the use of graphene as emitter and collector and (ii) PETEC for low-temperature applications, and finally we present our own works on solar TEC efficiency with graphene as emitter and collector.

In this paper, we assume that large-sized (2- to 6-m diameter) parabolic concentrators may eventually be possible, and that the graphene emitter (on silicon carbide) of the TEC is placed on the axis of the parabolic concentrator [Fig. 4(a)]. We assume that a magnet can be attached with its south pole on the collector and the magnet can be cooled at a rate Q_r . We then consider the energy exchange processes that take place in such a graphene TEC and compute the efficiency of the graphene TEC for various parameters such as solar insolation, anode temperature, diameter of parabolic mirror, emitter height, which determines the effective emitter cross section from the base of the mirror, mirror reflection coefficients, etc. To our knowledge, such a theoretical concept of computation of the efficiency of graphene TEC has not been applied by other workers and it is different from those discussed earlier in a different model by the authors in Refs. 13, 14, and 42. The calculation of efficiency in a TEC by other workers so far has excluded radiation heat losses and energy conservation processes.²⁷ In this paper, we have considered graphene surfaces on SiC and assumed that the graphene surfaces can be suitably engineered for work functions to be used as emitter and collector in a solar TEC. We shall not dwell on the space-charge effect that limits the power output from a TEC. It may be mentioned that a TEC once perfected can store the electrical energy by charging a battery with circuits just like that of a solar panel. It will reduce the dependence on silicon.

1.2 Principles of Thermionic Energy Converter

In Fig. 2, two metals are shown, A and B , with work functions $W_A < W_B$. For example, A can be aluminum ($W \sim 4.2$ eV) and B can be gold ($W \sim 5.3$ eV). The vacuum level, E_v , for them is the same. Work function is given by: $W = E_v - \mu$. Since $W_A < W_B$ and E_v is same for two bare metals, then $\mu_A > \mu_B$. When they are connected by a perfectly conducting wire (Fig. 3) then

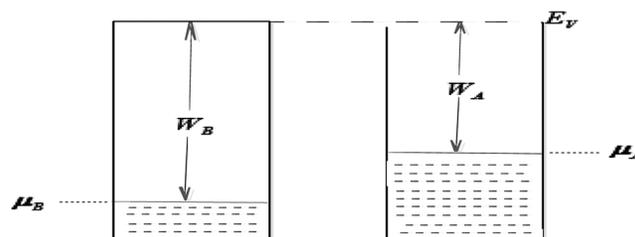


Fig. 2 Energy levels of two isolated metals work function $W_A < W_B$. $E = 0$ is the vacuum level.

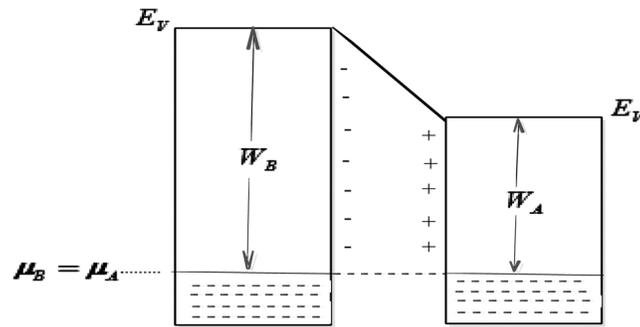


Fig. 3 When the two metals are connected electrically, electron flows from metal A (say, Al) to metal B (Au) and thus a potential barrier is formed $(W_B - W_A)/e$ that prevents further flow of electrons from metal A to metal B.

statistical physics demands that their chemical potentials (μ) be aligned (Fig. 3). 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 a different way, the chemical potential depends on electron concentration ($5.90 \times 10^{28}/\text{m}^3$ and $2.1 \times 10^{29}/\text{m}^3$ in Au and Al), therefore, some electrons must flow from metal A to metal B to make the chemical potentials the same when they are connected. This is also consistent with the picture that electrons in Al near the Fermi level have higher energies than those in Au. Thus, the flow of electrons is necessary for the chemical potentials to be aligned when they are connected electrically. This makes metal B have a negative potential and A have a positive potential. Thus, there will be a potential difference between metals A and B. Once that potential difference, $V_{AB} = (W_B - W_A)/e$, is fully set up, it will prevent further flow of electrons from metal A to B. Note that this 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 Fig. 2) is heated to a high temperature then a sufficient number of electrons will reach the vacuum level in metal B, overcoming the work function W_B and with kinetic energy. These electrons will find that an electric field exists that will sweep the electrons to metal A in the form of emission (from B to A) (similar to injection of electrons in a forward biased p_n junction). It will constitute an electric current, which can drive a load (Fig. 3) 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 metal B and will not deliver any output power. This is the principle of TEC (Fig. 3). If metal B is not connected to metal A, then the electrons from hot metal surface B will be emitted out of the metal-thermionic emission. Such thermionic emission will 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 potential remaining aligned. Thus, the energy of the electrons is delivered to the external load (Fig. 3). 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 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 very important in a TEC to have the temperature of A (collector) much lower than that of B (emitter). The output power in a TEC (Fig. 3), $P_{\text{out}} = (I_e - I_c)(W_B - W_A)/e$, 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 (discussed earlier), especially in the absence of a gate and magnetic field control (discussed earlier).

1.3 Important Considerations of Thermionic Energy Conversion

Two important points should be carefully considered when choosing the material for the emitter and the collector, i.e., a large work function difference (~ 1 eV) between the emitter and the

collector should be attained and the work function for both the emitter and the collector should be low. The collector should be at a much lower temperature than the emitter so that current density from the emitter (metal *B*) [Fig. 1] is significantly higher than that from the collector (metal *A*). The emitter must tolerate high temperatures in vacuum. To obtain high power density ($>100 \text{ W/cm}^2$) with a potential difference $\sim 1 \text{ V}$, the current density J must be high ($>100 \text{ Amp/cm}^2$). At a given T , J is very sensitive to work function. For most metals, except for alkali and rare earth metals, work function is $>4 \text{ eV}$.

To achieve $J > 100 \text{ W/cm}^2$, this requires $T > 1900 \text{ K}$. Most of the metals except for iridium, molybdenum, niobium, osmium, platinum, ruthenium, tantalum, thorium, vanadium, and zirconium melt above 1900 K . So far, the work function of thermionic metal emitters has been reduced by introduction of cesium and rare Earth oxides. At high temperatures, this creates plasma in a TEC that reduces J . As discussed earlier, graphene can tolerate high temperatures (4600 K) in vacuum. Graphene work function can be controlled and can be made as low as 1 eV . Electronic conductivity of graphene is high due to the lack of defects in its crystallography. Defects perturb the electrons mean free paths of charges. These properties make graphene a good thermionic emitter for use in a TEC. Now since the work function of graphene can be tuned as discussed earlier, graphene can also be chosen as the collector with proper work function engineering.

Solar energy is abundant. In some places on Earth, long durations of sunshine with high solar insolation ($>600 \text{ W/m}^2$) is available. It can be concentrated onto an emitter with a parabolic mirror or Fresnel sheet. Thus, very high temperatures on a graphene surface can be obtained over a small area ($1 \text{ to } 4 \text{ cm}^2$). Current density rises fast with temperature. High density power output is possible at high temperatures. Now a days, a large parabolic trough is available. Thus, TEC with a graphene emitter and collector shows great promise for large-scale power generation. In a solar TEC for a given solar power input, there are two factors that need to be considered (apart from those discussed in Sec. 1.3); the heat radiation from both the emitter and the collector. In our earlier works,⁹⁻¹¹ we have investigated efficiency for high work function materials and with high solar power input concentrated on to a small area emitter with radiations from both emitter and collector. This gave high efficiency in the range 50% to 65% , depending on collector temperature and work function. However, in the models studied earlier, it would be difficult to employ a space-charge control using magnets to be placed on the collector. There was also another issue in the earlier investigation that was not fully investigated—the temperature stability of the collector for a given solar power input. In this paper, we have addressed the latter at least partially by setting the collector temperature fixed and considering the definite amount of heat that must be removed per unit time from the collector to achieve this. This scenario will allow magnets to be placed on the collector and the heat can be removed using a calculated amount of water flow. The energy balance equations are different from those studied earlier.

1.4 Power Output in a Thermionic Energy Conversion

In a TEC, thermionic currents I_e, I_c are emitted from both emitter and collector at temperatures T_e, T_c , respectively. In the absence of the space-charge effect, the net output current is $I = I_e - I_c = (J_e - J_c)s$. As discussed above, the output driving voltage is $\frac{(W_e - W_c)}{e}$. Thus, the maximum output power (in complete absence of space charge) in a TEC^{9,10}, $P_o = (I_e - I_c) \frac{(W_e - W_c)}{e} = (J_e - J_c)s \frac{(W_e - W_c)}{e}$. I_e, I_c are the emitter and collector emission currents. J_e, J_c are the corresponding current densities. These are primarily controlled by temperature and work functions of the emitter and collector, T_e, T_c, W_e, W_c the emitter collector configuration (i.e., the space between them), and arrangements that control space charge. To model a TEC specifically with graphene as an emitter, it is very important to obtain an accurate model of temperature dependence of W_e, W_c, I_e , and I_c . In our earlier papers, we have discussed the modified RD equation^{43,44} that fits J versus T data in graphene and carbon nanotubes far better than any existing models, including that of Liang and Ang.²⁸ The problems associated with the new theory²⁸ of thermionic emission for graphene has been discussed in Ref. 42.

1.5 Low-Temperature Photo-Enhanced Thermionic Energy Converter

Even though theoretical analyses predict PETEC conversion efficiency that can match or even exceed the efficiency of solar thermal and photovoltaic systems, there are complexities of the energy conversion, transport processes, and various loss mechanisms that require careful control of material properties and optimization of the device structure. As a result, no practical device has yet been built based on PETEC with high efficiency.¹⁷ Schwede et al.⁴⁵ have carried out interesting theoretical work on photo-enhanced thermionic emission from semiconducting surfaces in which incident photons photo excite the electrons in a semiconductor, which are then thermally emitted. The idea of the photo excitation of electrons and thermal ejection from the excited state seems to bear a resemblance to the idea proposed a long time ago on the creation of a high brightness-electron beam.^{46,47} They have seen evidence of enhanced emission in their measurements of temperature-dependent photoemission-yield from GaN. They conclude that a photo-enhanced solar thermionic converter could operate at temperatures 200°C and above. Now the work function of GaN is usually in the range from 3.64 to 3.7 eV. The thermionic emission current density is slightly above 200°C (say at 500 K) is 9.9×10^{-26} Amp/m². Thus, to measure photo-enhanced thermionic emission current, the effective work function of the photo excited electrons must be quite low. For a practical TEC to operate at such a low temperature, this should be around 1 eV or lower. It was not clear from their works how low these effective works functions are for the photo excited electrons. In the photo-enhanced mode, there is one inherent problem—it is difficult to arrange the exciting photons to strike the emitter surface facing the collector, because the gap between the two surfaces is usually less than a millimeter (and rather several microns).

In a practical device employing this technique, the exciting photons must be incident on the back surface of the emitter. Then the question is: what is the probability of these exciting photons or the excited electrons reaching the emitter surface facing the collector? Many of these electrons would be mean free path limited.

What fraction of the excited electrons could have effective work functions low enough (~1 eV) for a TEC to be practical at temperatures around 500 K? There is another important issue in such a low-temperature TEC. The collector work function W_c and temperature T_c must be lower than those of the emitter and yet $W_e - W_c$ should be between 0.5 and 1 eV to have high values of $I_e - I_c$ and for good power conversion efficiency. Even then there are issues for PE-TEC to be effective at such low temperatures. The radiation losses even at 500 K would overwhelm the TEC power output that might be possible with a suitable adjustment of W_e , W_c , and T_c and thus the efficiency would be quite low at such low temperatures, even if the work functions and temperature differences are sorted out correctly. Considering such problems with low TEC, we have considered in this work solar TEC without PE and operating at high temperatures obtained by concentrated solar energy on to a small emitter area. Such works can be realizable in practice with high efficiency if the space charge can be controlled. PE might enhance TEC efficiency at temperatures of 1000 K and above, provided the above-mentioned problems can be overcome and if the effective (dynamic) work function of photo excited electrons can be significantly lowered from the original one as in GaN (see above). More research is necessary on the latter aspect.

1.6 Back-Gated Graphene Thermionic Energy Conversion

Yuan et al.⁴⁸ studied TEC using a barium dispenser cathode as an emitter and a back-gated graphene as a collector (anode) with a 20-nm-thick HfO dielectric layer as the gate. They were able to observe TEC of 9.8% at a cathode temperature of 1000°C. Their works demonstrated the efficacy of using a positive gate, low gap between cathode and anode, and the work function reduction of both cathode and anode in enhancing efficiency.

In this work we have explored theoretically the possibility of obtaining high efficiency (~50%) with a solar TEC where both emitter and collector are made of graphene and high temperature can be created more easily and efficiently than conventional heat source.

We have explored the effect of work functions, the temperatures of emitter and collector, and their emissivity, solar insolation, diameter of parabolic mirror, etc., on the efficiency.

2 Modification of Richardson–Dushman Equation for Nanomaterials

2.1 New modified Richardson–Dushman Equation

Based on our earlier works^{43,44} considering the temperature dependence of work function, the modified Richardson–Dushman equation (MRDE) for thermoelectron current density (emitted along the z -direction) is given as

$$J = A_0 T^2 \exp \left(- \left\{ W_0 + 2\alpha T E_{F0} + \left[\begin{array}{l} (1 + 2\alpha T) \left(\frac{\pi^2}{12} \right) \left(\frac{k_B T}{E_{F0}} \right)^2 (E_{F0}) \\ + (1 + 2\alpha T) \left(\frac{7\pi^4}{960} \right) \left(\frac{k_B T}{E_{F0}} \right)^4 (E_{F0}) \end{array} \right] \right\} / k_B T \right). \quad (2)$$

Equation (2) gives us a new thermionic emission equation that should be applied for materials such as graphene and carbon nanotubes, which have low E_{F0} and at temperatures comparable with E_{F0}/k_B . In Eq. (2), the $2\alpha T$ takes care of the thermal expansion of two-dimensional graphene.

W_0 is the work function of graphene at 0 (K). The terms in the square bracket after W_0 are the temperature dependence parts of work function (W).

Eq. (2) can also be written as

$$J = A_{\text{eff}} T^2 \exp \left(- \left\{ W_0 + \left[\begin{array}{l} (1 + 2\alpha T) \left(\frac{\pi^2}{12} \right) \left(\frac{k_B T}{E_{F0}} \right)^2 (E_{F0}) \\ + (1 + 2\alpha T) \left(\frac{7\pi^4}{960} \right) \left(\frac{k_B T}{E_{F0}} \right)^4 (E_{F0}) \end{array} \right] \right\} / k_B T \right), \quad (3)$$

where

$$A_{\text{eff}} = A_o \exp(-\alpha E_{F0}/k_B). \quad (4)$$

The E_{F0} is related to the free electron concentration by the following equation:

$$E_{F0} = \left[\left(\frac{h^2}{2m} \right) \left(\frac{3n}{8\pi} \right)^{2/3} \right]. \quad (5)$$

3 Application of the New Thermionic Emission Equation for Solar Energy Conversion

In all the discussions that proceed from this point, the value of work function that is quoted in this work refers to W_o . With conventional heat sources, it is not energy efficient to produce high temperature only over the emitter area, moreover, it is difficult to estimate the various heat losses. In TEC efficiencies so far calculated in the literature, the heat losses have been neglected. It would then lead to estimation of efficiency higher than would be possible in reality. In this respect, concentrated solar energy offers many more advantages, if a large-sized parabolic concentrator can be designed and fabricated. A large-sized parabolic trough concentrator is now available. Moreover, as discussed earlier with the advancement of work function engineering techniques, graphene surface work function can be tuned as desired and efficient solar energy conversion would be possible with a large parabolic (trough) concentrator if several hurdles can be overcome

- i. The control of the space-charge problem as outlined in Sec. 1.
- ii. The proper combination of work functions of the emitter and collector and control of the collector temperature to achieve maximum efficiency possible under given solar insolation.

To achieve (ii), proper modeling of solar TEC is necessary with Eqs. (3) and (4). The item (i) could possibly be achieved through application of a magnetic field and positive gate [Fig. 1(b)]. However, strong permanent magnets with proper cooling arrangements are necessary.

3.1 Theoretical Analysis of Performance of Solar Thermionic Energy Conversion

In a solar TEC, let us assume that solar energy is focused on the emitter by a parabolic mirror [Fig. 4(a)]. The emitter surface area exactly matches the area of focus of the solar energy as shown in Fig. 4(a). An emitter of graphene of several layers thick is built on surface 2 of a silicon carbide⁴⁹ substrate [Fig. 4(b)] of about 100- to 250- μm thick. It can be deposited using selective chemical reactions between Co film and SiC.⁵⁰ High thermal conductivity of SiC would be essential for both emitter and collector containing graphene. The surface 1 [Fig. 4(b)] of the silicon carbide receiving the solar energy is coated with nickel oxide, which has high absorptivity (0.92) and low emissivity (0.08).⁵¹ This is expected to ensure a fast temperature rise and hold the temperature much longer (than would be possible with high emissivity coating) in the case of a momentary absence of sun light. Even though these values may be slightly temperature dependent, for the time being we have assumed temperature independence of these values. It helps low radiation losses and thus higher efficiency as can be seen below in this work. Finally, the silicon carbide surface facing the sun is encapsulated by a quartz glass cover to prevent exposure to air at high temperatures. This is necessary to protect the material from oxidation and other effects. The collector is placed at 500 μm to 1 mm from the emitter, separated by an insulating spacer, instead of a few microns separation as proposed recently in advanced TEC.¹⁶ The very low separation 1 μm is expected to minimize the effect of the space-charge problem but is very tedious to fabricate. However, when the space-charge problem is tackled with a magnetic field and gate, such a low separation will not be needed and a larger separation as high as 1 mm could do. This will ease the fabrication of the solar TEC. If magnets will be placed on the collector (with the S pole touching the collector), then no such coating is necessary on the collector back surface. The magnet will be cooled at a calculated rate, Q_r [see Eq. (9)] to keep the collector temperature fixed with a given solar power input

$$P_{\text{in}} = I_o(S - s). \tag{6}$$

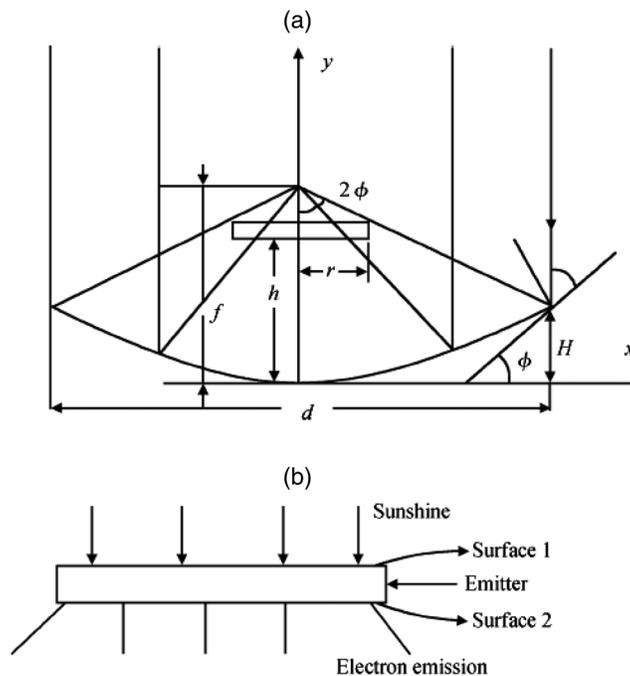


Fig. 4 (a). Schematic diagram with relevant parameters of the thermionic power converter with a parabolic concentrator. (b) Showing the graphene emitter on a silicon substrate. Surfaces 1 and 2 of a thermionic emitter considered in this work. Surface 1 (of SiC) is irradiated by concentrated solar energy. It is the surface 2 (graphene) that undergoes work function engineering to lower the work function.

3.2 Heat Exchange in Thermionic Section

We consider electron emission in the z -direction from a graphene surface. It has been shown by Meir et al.⁴ that each electron emitted in the z -direction takes an average energy $(W_e + 2k_B T_e)$ from the emitter. Looking at the emitter, which receives the concentrated solar energy, the electrons emitted from the emitter take a total energy $\frac{J_e s(W_e + 2k_B T_e)}{e}$ per sec., whereas the electrons collect a total of $\frac{J_c s(W_e + 2k_B T_e)}{e}$ from the collector surface per second. Initially, we assume blackbody radiation from the two surfaces of the emitter and 100% reflection coefficient of the parabolic mirror. The law of energy conservation (energy dynamics) says that, at constant emitter temperature, the solar power input at the emitter must be the same as the total power leaving the emitter surface due to (i) electron emission from emitter and collector, (ii) blackbody radiation from emitter and collector, and (iii) the heat conducted through the electrical terminals, structural components that could be joined to the emitter. Neglecting heat losses due to (iii), we get the energy balance assuming fixed T_c

$$I_0(S - s) = \left[\frac{J_e s(W_e + 2k_B T_e)}{e} - \frac{J_c s(W_c + 2k_B T_c)}{e} \right] + [\sigma s(T_e^4 - T_a^4) + \sigma s(T_e^4 - T_c^4)], \quad (7)$$

where I_0 is the solar insolation, S is the area of the parabolic concentrator, s is the area of the emitter, and σ is the Stefan Boltzmann's constant. The first term in the right-hand side of Eq. (7) is energy transport between the electrodes by the emitted electrons. It depends on J_e and J_c . It must be tuned to increase the electricity generation efficiency, while the second and the third terms lead to radiation losses. T_e and T_c in Eqs. (7) and (8) are the temperatures of the graphene emitter and the collector. The collector could be made of either graphene (with a work function lower than that of the emitter by about 0.5 to 1 eV). $J_e(2k_B T_e)/e$ is the thermal energy imparted on the anode (collector) by the electrons emitted from the unit area of the emitter (cathode) surface, whereas $J_c(2k_B T_c)/e$ refers to the thermal energy imparted on the emitter by the emitted electrons from the anode (collector). In Eq. (7), we assume that the latter is deposited back to the emitter in the absence of space-charge effect. The output electrical power P_{out} (assuming no space-charge effect)

$$P_{\text{out}} = (J_e - J_c)(W_e - W_c)s/e. \quad (8)$$

To maintain the temperature of the emitter at T_e and collector at T_c , the heat removal rate Q_r from the collector will be

$$Q_r = \left\{ J_e \left(\frac{2k_B T_e}{e} \right) - J_c \left[\frac{(2k_B T_c)}{e} \right] + \sigma \varepsilon_e (T_e^4 - T_c^4) + (J_e W_c + J_c W_e)/e \right\} s. \quad (9)$$

The efficiency η of solar thermionic power conversion is then given by with W_e and W_c in eV

$$\eta = \frac{(J_e - J_c)(W_e - W_c)}{I_0(S - s)e}, \quad (10)$$

J_e, J_c are the emitter and collector current densities at respective temperatures T_e and T_c and are obtained from Eqs. (3) or (4).

The above equations give us a lot of information on the influence of solar insolation $I_0, S, s, T_e,$ and T_c, W_e, W_c on η . To model a TEC, it is thus very important to have the correct formulation of J versus T for nanomaterials. We have found such formulations [Eqs. (2) and (3)] that apply for graphene and CNT.^{43,44} CNT has also been found suitable for TEC.⁵²

3.3 Method of Computation

From the discussion above, for high efficiency of solar TEC, we need low W_e with large $W_e - W_c$ and large $T_e - T_c$. For a given TEC, T_e is primarily dictated by total solar power input $I_0(S - s)$ and the emitter area s . Control of T_c is a nontrivial task, especially when the emitter and collector separation is too small (say, a few microns). With separation of the order from

0.5 to 1.0 mm so that a positive gate can be placed in between and using a magnet in contact with the collector (for application of strong magnetic field to control the space charge), we expect to be able to control T_c at the desired level by cooling the magnet at an appropriate rate Q_r , given by Eq. (9). Solar energy is assumed to be incident parallel to the axis of the parabolic mirror [Fig. 4(a)] of cross-sectional area $S = \pi d^2/4$. The emitter is held perpendicular to the axis. J_e, J_c correspond to the temperatures T_e and T_c at which the energy conservation Eq. (7) is satisfied. To understand how η will be affected by W_e, W_c, I_o, s , and S , we first fix the temperature of the collector to a certain value, say 1000 K. To simulate the efficiency under concentrated solar irradiation, we proceed as follows: set $T_c = 1000$ K and $S = 3.14$ m² corresponding to a parabolic mirror of diameter 2 m. Now from our earlier investigation, we find that graphene⁴³ has $E_{F0} = 0.203$ eV. Using these values, for a given W_e and $W_c, I_o, s =$ say, 0.0001 m², we then evaluate the terms on the right-hand side of Eq. (7) separately and add them at each temperature, as T_e varies from say, 500 to 3900 K, at steps of 1 K. We find the temperature, T_e at which sum of the terms on the right-hand side of Eq. (7) matches very close (or the best) to the value of the term on the left-hand side. At this value, we then note the values of J_e and J_c and obtain P_{out} [Eq. (8)] and finally, the efficiency η [Eq. (10)]. From the same MATLAB simulation, we can obtain η for other values of s , when all other parameters remain the same. Then by changing W_e , we can obtain η for various values of s . In our computations below, the cross section of the emitter has been assumed to be the same as that of the collector. We also assume ideal blackbody radiation from the emitter and collector surface initially and for the time being that the space-charge effect is also assumed to be nil, that is, we study the ideal efficiency below. Effect of emissivity is considered at the end.

4 Results and Discussion

The results of calculations as presented below assume that an ideal parabolic concentrator with spherical aperture of radius 1 m and larger will be possible and available in the market in the future. An ideal parabolic concentrator would be able to focus all the solar energy incident parallel to its axis exactly on the emitter [Fig. 4(a)], the area of which varies in this calculation from 1 to 10 cm². For the emitter area of 10 cm², this amounts to a concentration factor of 3000. It may be mentioned that an average concentration factor of 2500 has been achieved with Euro-Dish Stirling parabolic dish solar collector. It is hoped that the factor can be increased in the future. For the smallest area, we have assumed an ideal parabolic concentrator mirror. The emitter area s of focus depends on the height h of the emitter from the base as shown below.

Figure 4(a) shows the emitter of radius r placed at the height h . $s = \pi r^2$ the relation of h with s (Fig. 3) can be calculated from the following equations. These refer to Fig. 4(a)

$$\tan \varnothing = \frac{H}{2R}, \quad (11)$$

$$r = (f - h) \tan 2\varnothing, \quad (12)$$

$$f = \frac{R^2}{4H}, \quad (13)$$

where \varnothing, R are the semiaperture angle and radius of the circular aperture of the parabolic mirror, respectively. H is the height of the edge of the aperture from the base point. f is the focal length of the paraboloid surface. r is the radius of the focus area (emitter) at height h from the base. The emitter should be exactly of area $s = \pi r^2$. $S = \pi R^2$.

4.1 Efficiency of Graphene Thermionic Energy Conversion at High Work Function Regime with Blackbody Emissivity of the Emitter's Solar Energy Receiving Surface

Figures 5–10 show the computed efficiencies for various emitter cross sections with the collector work function kept constant at 3.0 eV and emitter work function decreased from 4.0 to 3.4 eV at

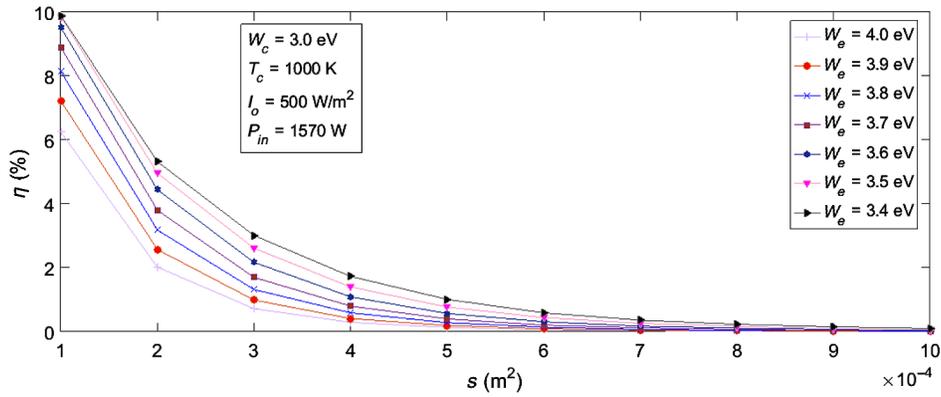


Fig. 5 Efficiency of solar TEC versus emitter cross section with solar insolation of 500 W/m² for different values of emitter cross section when the collector temperature and work function are fixed at 1000 K and 3.0 eV, respectively. The total solar power input on a parabolic mirror of radius 1 m is 1570 W. Efficiency calculated with modified RD equation.

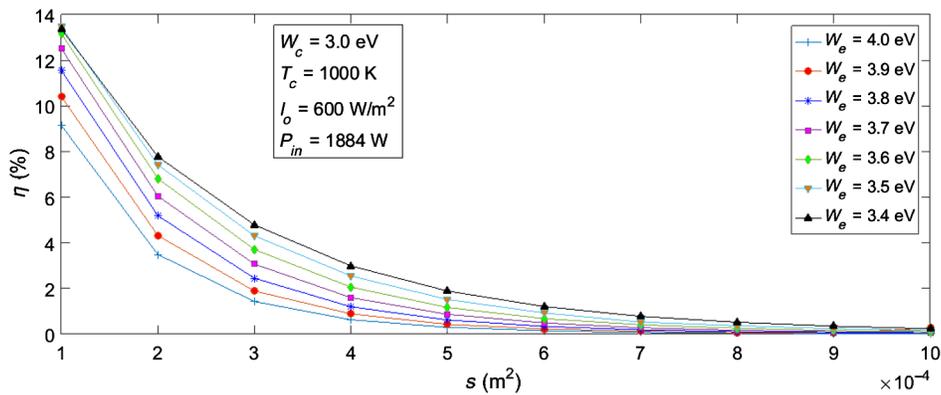


Fig. 6 Efficiency of solar TEC versus emitter cross section with solar insolation of 600 W/m² for different values of emitter cross section when the collector temperature and work function are fixed at 1000 K and 3.0 eV, respectively. The total solar power input on a parabolic mirror of radius 1 m is 1884 W.

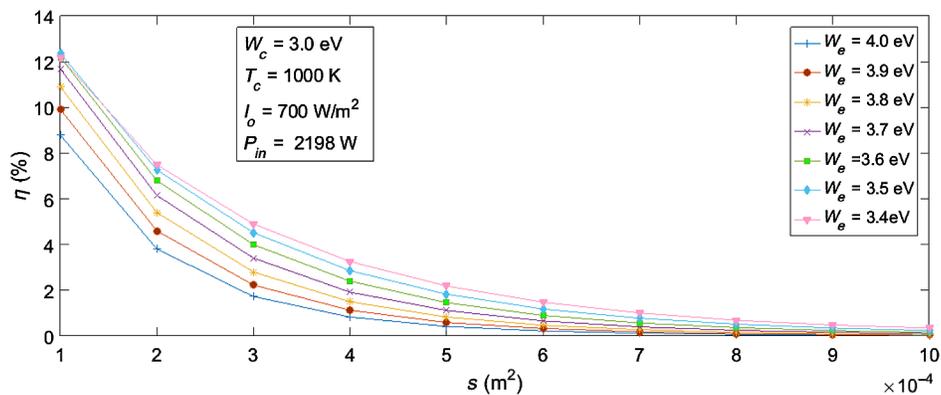


Fig. 7 Efficiency of solar TEC versus emitter cross section with solar insolation of 700 W/m² for different values of emitter cross section when the collector temperature and work function are fixed at 1000 K and 3.0 eV, respectively. The total solar power input on a parabolic mirror of radius 1 m is 2198 W.

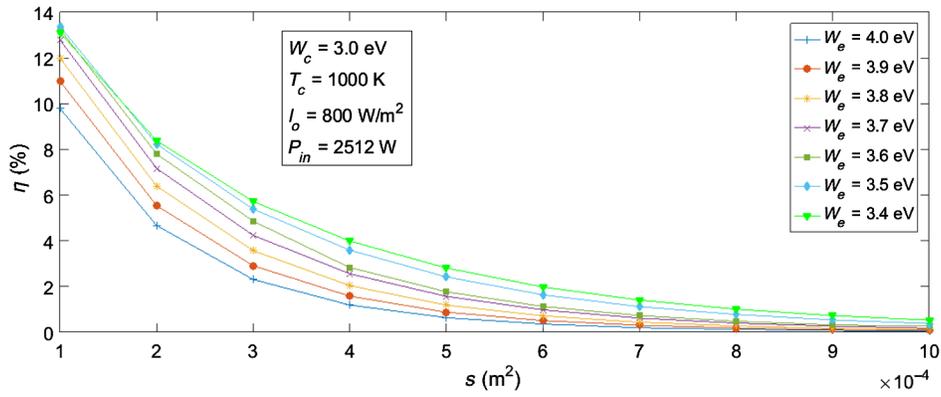


Fig. 8 Efficiency of solar TEC versus emitter cross section with solar insolation of 800 W/m^2 for different values of emitter cross section when the collector temperature and work function are fixed at 1000 K and 3.0 eV , respectively. The total solar power input on a parabolic mirror of radius 1 m is 2512 W .

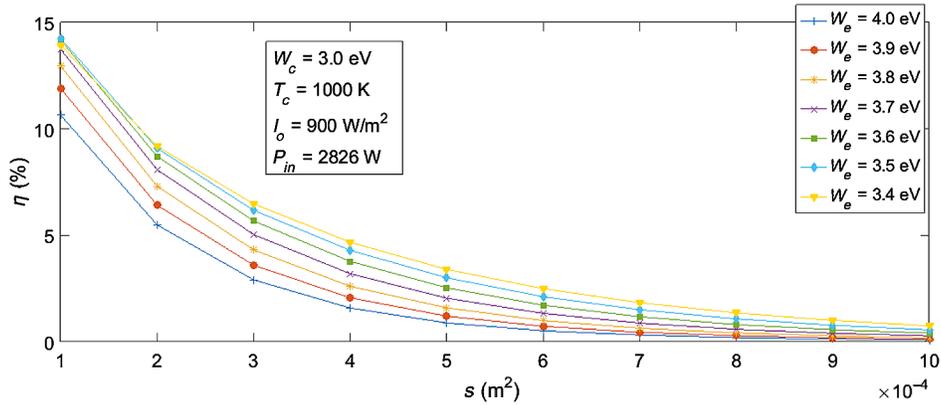


Fig. 9 Efficiency of solar TEC versus emitter cross section with solar insolation of 900 W/m^2 for different values of emitter cross section when the collector temperature and work function are fixed at 1000 K and 3.0 eV , respectively. The total solar power input on a parabolic mirror of radius 1 m is 2826 W .

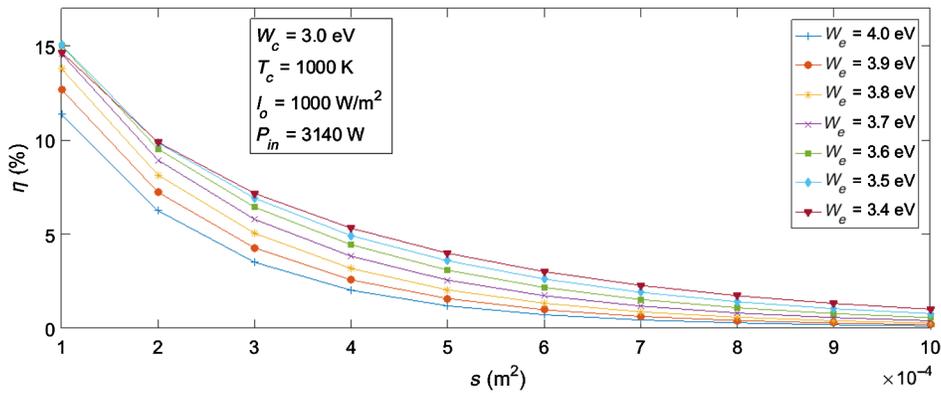


Fig. 10 Efficiency of solar TEC versus emitter cross section with solar insolation of 1000 W/m^2 for different values of emitter cross section when the collector temperature and work function are fixed at 1000 K and 3.0 eV , respectively. The total solar power input on a parabolic mirror of radius 1 m is 3140 W .

a step of 0.1 eV when the total incident solar power is 1570 W corresponding to solar insolation of 500 W/m² incident on a parabolic mirror of radius 1 m. In Fig. 5, which corresponds to $W_c = 4.0$ eV and $T_c = 1000$ K, we see that for $W_e = 4.0$ eV, efficiency decreases from nearly 6.3% for cross section of 1×10^{-4} m² (1 cm²) to negligible values when the emitter cross section is greater than 5×10^{-4} m². The main reason is that the emitter temperature decreases significantly when the solar energy is focused over a bigger area. This reduces J_e faster than the losses due to radiations. In the same Fig. 5, we see that the efficiency increases to 10% for $s = 10^{-4}$ m² when W_e is decreased to 3.4 eV. The corresponding T_e is 2925 K. However, it is to be noted that the efficiency starts decreasing as W_e is further reduced. This is because the output power is proportional to $(W_e - W_c)$ and when both are equal there would be no thermionic power output, P_{out} . Figure 6 shows total solar input power = 1884 W, corresponding to solar insolation 600 W/m². The efficiency increases for all W_e from 4.0 to 3.4 eV at a given s compared with those of Fig. 5. Efficiency η in thermionic solar energy conversion is dependent on total solar power incident on a given parabolic mirror, which focuses the energy onto the emitter of the same cross section as that of the area of focus. In Figs. 5–10, for $W_e = 3.4$ eV and $s = 10^{-4}$ m², η increases with solar power from 10% to 15% as the total solar input power P_{in} increases from 1570 to 3140 W.

In Fig. 10, we see that when W_e is reduced to 3.4 eV with collector work function at 3.0 eV, the efficiency increases to 15% for total solar input power, P_{in} of 3140 W. When the work function reduced to 3.3 eV, the efficiency becomes 14%. The efficiency continues to decrease with decrease of W_e .

Now if we keep the $W_c = 2$ eV, what happens to efficiency if we start decreasing W_e from 4.0 eV? At $W_c = 2$ eV, $W_e = 4.0$ eV, and $T_c = 1000$ K, the efficiency increases to 9.5% from 6.3% (Fig. 5) at $I_o(S - s) = 1570$ W. However, the corresponding emitter temperature is 3263 K. For $W_e = 3.4$ eV, $W_c = 2$ eV, the efficiency increases to 20.5% from ~10% of Fig. 5 with T_e still remaining 2925 K. For $W_e = 2$ eV, $W_c = 1.5$ eV, and $T_c = 1000$ K, the efficiency for $I_o(S - s) = 1570$ W, is 23.8%. The corresponding emitter temperature is 1844 K. When $W_e = 2$ eV, $W_c = 1.0$ eV, and $T_c = 1000$ K, the efficiency reduces to 12% (corresponding to $T_e = 1917$ K) and it increases rapidly with increase of $I_o(S - s)$. Why? Because at that low collector work function, the collector current overwhelms the emitter current for low solar energy input. Now let us see what happens if we fix $T_c = 500$ K for $s = 10^{-4}$ sq.m. For $W_e = 2$ eV, $W_c = 1.0$ eV, and $T_c = 500$ K, the efficiency increases to (i) 42.4% ($T_e = 1837$ K) for $I_o(S - s) = 1570$ W, (ii) 44% ($T_e = 1944$ K) for $I_o(S - s) = 3140$ W, and (iii) 45.6% ($T_e = 2055$ K) for $I_o(S - s) = 6000$ W. For $W_e = 2$ eV, $W_c = 1.5$ eV, and $T_c = 500$ K, the efficiency, η for $I_o(S - s) = 1570$ W is 23.7% ($T_e = 1837$ K). For $W_e = 2$ eV, $W_c = 1.5$ eV, and $T_c = 500$ K, the efficiency, $\eta = 25.02\%$ for $I_o(S - s) = 3140$ W ($T_e = 1944$ K). Thus, for a low emitter work function, W_e and at low T_c , η is very sensitive to value of W_c at a fixed value of W_e , while η increases slowly with P_{in} . It is because $P_{out} = (J_e - J_c)(W_e - W_c)s/e$. The efficiency, η values continue to decrease with an increase in the s . This is because for a given $I_o(S - s)$ value, emitter temperature will decrease with s with a consequent decrease in J_e . The above computation shows that for high efficiency, it is important to have low W_e and a proper combination of $W_e - W_c$ and T_c . We expect efficiency to increase slightly with P_{in} . Since graphene work function can be suitably engineered as discussed earlier, there is a possibility of getting high efficiency of solar energy conversion using graphene as both emitter and collector, if a very large-sized parabolic mirror or Fresnel sheet lens can be used to focus sunlight over a large area onto a small size emitter (say, 0.0001 or 0.0002 m²).

Assuming that this is possible, our calculations predict the efficiency for $I_o(S - s) = 6000$ W and 10,000 W to be 45.0% and 45.7%, respectively, for $s = 0.0001$ m² corresponding to $T_e = 2055$ and 2153 K, respectively [with $W_{eo} = 2$ eV; $W_{co} = 1.0$ eV]. This is assuming blackbody radiation from both emitter and collector. The emissivity effect is discussed below. $I_o(S - s) = 6000$ and 10,000 W, respectively, require a parabolic mirror or Fresnel sheet with an aperture of radii 1.784 and 2.304 m at a solar insolation of 600 W/m². With advancement in technologies, such concentrators would be possible in the future and solar TEC will become a reality.

4.2 Efficiency of Graphene Thermionic Energy Conversion With Low Emissivity of the Emitter's Solar Energy Receiving Surface of Graphene and Effect of Emissivity

In our model TEC, graphene is deposited/built on an SiC substrate (150- to 200- μ m-thick substrate). To study the effect of emissivity of the SiC surface absorbing the concentrated solar radiation, it is coated with a thin layer of a material with high solar absorbance (a) and low emissivity. One of such materials could be lead sulfide (PbS) film,⁵³ which has absorbance 0.92 and emissivity of 0.1. The material should have a high melting point. For PbS, it is 1391 K. Assuming that such material can be deposited on the silicon carbide surface facing, the sun we investigate the effect of emissivity, ϵ_s of this surface in this section through the energy balance equation, thus Eq. (8) changes to

$$I_0(S-s)ra = \left[\frac{J_e s(W_e + 2k_B T_e)}{e} - \frac{J_c s(W_c + 2k_B T_c)}{e} \right] + [\epsilon_s \sigma s(T_e^4 - T_a^4) + \epsilon_e \sigma s(T_e^4 - T_c^4)]. \quad (14)$$

The corresponding Q_r is given by

$$Q_r = \left\{ J_e \left(\frac{2k_B T_e}{e} \right) - J_c \left[\frac{(2k_B T_c)}{e} \right] + \sigma \epsilon_e (T_e^4 - T_c^4) + (J_e W_c + J_c W_e)/e \right\} s. \quad (15)$$

In both Eqs. (14) and (15), we assume no space-charge effect.

In Eq. (14), r is the reflection coefficient of the parabolic mirror; a and ϵ_s are the absorptivity and emissivity of the silicon carbide substrate surface on which the solar energy is focused. ϵ_e is the emissivity of the graphene emitter surface facing the collector. In Eq. (14) and (15), we assumed that the space-charge effect is nil. The effect of space charge on the simulation will be considered in our next article. Using Eq. (14), Table 1 shows some of the calculated values of efficiency and the corresponding emitter temperature for various values of emitter work function, W_e , collector work function W_c , collector temperature, T_c , and emissivity of emitter surface receiving solar energy, ϵ_s , for the given solar energy input $I_0(S-s)$ and with $\epsilon_e = 1$. In Tables 1 and 2, we assume $r = 1$ and $a = 1$.

Table 1 Efficiency, η for various values W_e , W_c , T_c , ϵ_s , and $I_0(S-s)$ at $s = 0.0001 \text{ m}^2$, with a η_c Carnot engine operating between T_e (heat source) and T_c (sink).

W_e (eV)	W_c (eV)	T_c (K)	ϵ_s	$I_0(S-s)$ (W)	T_e (K)	η (%)	Carnot efficiency $\eta_c = 1 - T_c/T_e$
2.5	1	500	1	1570	2233	45.6	77.6%
2.5	1	500	0.08	1570	2249	50	77.8
2.6	1	500	0.08	1570	2332	50.5	78.5
2.6	1	500	1	1570	2312	45.29	78.4
3.0	1	500	0.08	1570	2671	49.9	81.3
3.2	1	500	0.08	1570	2846	48	82.4%
2.6	1	500	0.08	4713	2579	54.36	80.6
2.6	1	500	1	3140	2467	49.71	79.7
2.6	1	500	0.08	3140	2481	53.2	79.8
3.0	1	500	0.08	3140	2870	54.4	82.6
3.2	1	500	0.08	3146	3082	53.6	83.8
2.4	1	500	1	1570	2154	45.6	76.8
2.4	1	500	0.08	1570	2167	49.3	76.9

Table 2 Efficiency, η for various values W_e , W_c , T_c , ϵ_s , and $I_o(S - s)$ for $s = 0.0001 \text{ m}^2$ with $\epsilon_e = 0.0016$.

W_e (eV)	W_c (eV)	T_c (K)	ϵ_s	ϵ_e	$I_o(S - s)$ (W)	T_e (K)	η (%)	Carnot efficiency $\eta_c = 1 - T_c/T_e$
2.4	1	500	1	0.016	1570	2163	49.6	76.9
2.4	1	500	0.08	0.016	1570	2176	53.5	77.0
2.4	1	500	1	0.016	3140	2292	51.4	78.2
2.4	1	500	0.08	0.016	3140	2302	53.9	78.3
2.5	1	500	1	0.016	1570	2245	50.4	77.5
2.5	1	500	0.08	0.016	1570	2261	55.0	77.9
2.5	1	500	1	0.016	3140	2382	52.5	79.0
2.5	1	500	0.08	0.016	3140	2393	55.5	79.1
2.6	1	500	1	0.016	1570	2327	50.9	78.5
2.6	1	500	0.08	0.016	1570	2346	56.5	78.7
2.6	1	500	1	0.016	3140	2472	53.3	79.8
2.6	1	500	0.08	0.016	3140	2486	56.9	79.8
3.0	1	500	1	0.016	1570	2661	50.7	81.2
3.0	1	500	0.08	0.016	1570	2703	61.0	81.5
3.0	1	500	1	0.016	3140	2850	54.9	82.5
3.0	1	500	0.08	0.016	3140	2883	61.8	82.7
3.2	1	500	1	0.016	1570	2832	49.1	82.3
3.2	1	500	0.08	0.016	1570	3104	63.8	83.9
3.2	1	500	1	0.016	3140	3053	54.4	83.6
3.2	1	500	0.08	0.016	3140	3104	63.8	83.9
3.2	2	500	0.08	0.016	3140	2919	40.1	82.9

At this point, we need to consider the emissivity ϵ_e . Matsumoto et al.⁵⁴ reported the successful fabrication of a type of blackbody material based on a graphene nanostructure and found that the nanostructure exhibited blackbody radiation with emissivity of 0.99 over a wide range of wavelengths. Brar et al.⁵³ studied electronic control of blackbody emission from graphene plasmonic resonators on a silicon nitride substrate and they have shown that graphene resonators produce antenna-coupled blackbody radiation, and manifest as narrow spectral emission peaks in the mid-IR. Freitag et al.⁵⁵ investigated the thermal radiation from graphene that is self-heated by an electrical current. They found a wavelength-independent emissivity of $(1.6 \pm 0.8) \%$ in the near infrared, in agreement with measurements of optical absorption. Lawton et al.⁵⁶ have investigated the spatial and spectral characteristics of midinfrared thermal emission from large area graphene deposited by CVD, transferred onto SiO₂/Si, and found that the emission is broadly that of a gray-body emitter, with emissivity values of $\sim 2\%$ and 6% for mono- and multilayer graphene. From Eq. (14), the efficiency η [Eq. (13)] would be lowest for $\epsilon_e = 1$ (perfect blackbody) and would be maximum for the lowest value of ϵ_e . In this paper, to study the effect of emissivity on efficiency η of solar TEC, we consider $\epsilon_e = 1$ (perfect blackbody)^{54,53} for the values of η in Table 1 and $\epsilon_e = 0.016$ (gray-body emitter)^{55,56} for the values of η in Table 2.

Comparing the first two rows (Table 1), we see that the efficiency increased from 45.6% to 50% when the emissivity ϵ_s decreased from 1 to 0.08. The reason for this is less heat radiation for

the second case and thus more solar heat energy available for TEC. This trend is seen for all emitter work functions and total solar energy input. To our knowledge, the finding that the efficiency depends to some extent on the total solar energy input has not been predicted by others earlier. Interestingly, with an increase in the total solar energy input, the emitter temperature, T_e [for a given emitter cross section at which energy balance of Eqs. (6) or (7) occurs] also increases. Although not shown in Table 1, when the emitter cross section increases, the efficiency and T_e somewhat decrease. It is to be remembered that solar TEC is different from other forms of TEC where the heat sources are, say coal, nuclear, etc. There the temperature of the emitter is somehow maintained constant by controlling the heat flux. However, in the latter case it is very difficult to estimate the total heat losses and thus the calculation of efficiency, unlike that in the present case (ignoring the space-charge effect), would be in error.

As said earlier in Table 1, we have assumed perfect blackbody radiation ($\epsilon_e = 1$) from the graphene emitter. In Table 2, we see the effect of changing emissivity from $\epsilon_e = 1$ to $\epsilon_e = 0.0016$ corresponding to the gray-body emission. We see that for all values of Table 1, there is an increase in the efficiency by 4% to 10% in Table 2 with the highest efficiency being 63%. This shows that emissivities of both the solar energy receiving surface and the emitter surface, which emits thermal radiation have significant roles in deciding the efficiency of the graphene-based solar TEC. For higher efficiency, we would need both the emissivities to be as low as possible. In both the tables, we have assumed no space-charge effect. One important observation in Table 2 is that when we change W_c from 1.0 to 2.0 eV with $W_e = 3.2$ eV, the efficiency drops from 63% to 40%. This shows how critical it is to have a proper combination of W_e and W_c even when the emissivities of emitter energy receiving and electron emitting surfaces are low.

It may be mentioned that the above-calculated efficiencies are significantly less than the models of Meir et al.,⁴ which give the expression for efficiency as

$$\eta = \frac{(J_e - J_c)(W_e - W_c)/e}{\left[\frac{J_e s(W_e + 2k_B T_e)}{e} - \frac{J_c s(W_c + 2k_B T_c)}{e} \right]}$$

Liang and Ang²⁸ also used such an expression. The emitter and collector are assumed to be at temperatures T_e and T_c , regardless of the actual energy input. Such an expression ignores radiation losses, which are important at high temperatures of emission and even at low temperatures' (500 to 1000 K) operation as discussed earlier (see Sec. 1.4). In a realistic TEC radiation, losses cannot be avoided. Even in an enclosed environment, where radiation could be contained, and energy is made input, it is bound to change the temperatures despite the energy conversion. Otherwise, one could get 100% efficiency of conversion, which is never possible thermodynamically. Our model is the most realistic approach to a realizable solar TEC. To apply our model to TEC with other energy sources, one must know the total energy input over the actual surface of the emitter and energy input over other areas must be negligible for good efficiency. In the calculation of energy efficiency, the input and output powers are the two most important parameters that can be estimated with certainty in the case of solar TEC with a parabolic concentrator. If we compute the ideal Carnot efficiency $\eta_c = 1 - T_c/T_e$, then we see that the efficiencies of Table 1 are quite below the values of η_c . A TEC with radiation losses cannot be an ideal Carnot engine since radiation losses are irreversible. This is consistent with the fact that no engine/device can have efficiency equal to η_c (because of irreversible energy losses, such as radiation losses).

Efficiency at high work function regime: Our investigations show that it is possible to have good conversion efficiency with emitter and collector work functions in the regime from 2 to 3.4 eV, provided the difference is maintained around 0.6 to 1 eV. This, however, would require the emitter to operate at higher temperatures than materials with low work functions. To obtain high efficiency even with materials of low work functions, it is necessary to have a large-sized mirror that can focus solar power above 3000 W onto an emitter of cross section 1×10^{-4} to 4×10^{-4} m². At lower total energy input, the energy balance of Eqs. (6) or (7) occurs at a lower temperature and the energy output is less.

5 Conclusion

Since graphene work functions can be engineered suitably, in this work we have considered properly engineered different graphene surfaces on two separate SiC substrates to be used as emitter and collector in a solar TEC. We considered energy exchange in a model that allows placing a magnet on the collector for control of space charge (in combination with a positive gate in between the emitter and collector). Neglecting space charge, we then have considered various possibilities of the work functions and collector temperatures to estimate the efficiencies of TEC for various solar power inputs. We have seen that (i) for high work functions, efficiencies are low, (ii) efficiency depends on solar input power, (iii) for a given solar input power, efficiency depends on emitter cross section, collector temperature, and emissivities of the emitter's energy receiving surface and the electron emitting surface, (iv) for a given solar TEC and with given solar input power, to maintain T_c fixed, one has to remove heat from a collector at a fixed rate Q_r , (v) efficiency increases if both the surfaces of the emitter can have suitable coatings of low emissivity without affecting the desired work functions, (vi) efficiency as high as 60% of energy conversion is possible with suitable combinations of W_e , W_c , T_c , $I_o(S - s)$, low emissivity of the emitter surfaces, and high absorbance of the energy receiving surface, (vii) a higher emitter temperature yields higher efficiency, and (viii) at emitter temperature 3108 K, efficiency as high as 63% can be obtained (Table 2). Since graphene tolerates very high temperatures (4600 K) and graphene work function can be suitably engineered, there is a possibility of getting much higher efficiency (assuming no space-charge effect), if a very large-sized parabolic mirror or Fresnel sheet lens can be used to focus sunlight over a large area of a small-sized emitter (say, 0.0001 to 0.0004 m²). The Carnot efficiencies corresponding to various W_e , W_c , and T_c emissivities are also given in Tables 1 and 2. Efficiencies close to Carnot efficiencies can only be reached if the radiation losses and heat conduction losses can be minimized. Some researchers have reported low emissivity of graphene in the infrared region. Our works show that this property would be an added plus along with high-temperature tolerance for graphene for its use in solar TEC, for high efficiency TEC. We have discussed ideas qualitatively (based on ideas published by Mier et al.⁴) of how to control the space charge. However, the influence of the space-charge effect on the efficiency calculations has not been studied in this paper. This will be done in our next work.

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