Applied Energy 223 (2018) 134–145

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Thermodynamic assessment of solar photon-enhanced thermionic conversion

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HIGHLIGHTS

- Exergy and entropy analyses are conducted for solar photon-enhanced thermionics.
- Solar-to-electricity efficiencies of energy and exergy are 54% and 58% respectively.
- Photoexcited and thermalized exergy are discussed, as well as exergy losses.
- Thermionic emission exergy ratio is higher than that in conventional thermionics.
- Analysis of temperature-entropy diagram is proposed for thermionic energy conversion.

ARTICLE INFO

Keywords:
Photon-enhanced thermionic emission
Solar energy conversion
Thermodynamic assessment
Energy and exergy balance
Entropy analysis

ABSTRACT

Photon-enhanced thermionic conversion, an innovative solar power technology, combines photovoltaic and thermionic effects into a single process, and has the potential to surpass the Shockley–Queisser limit and conventional photo-thermal limit. However, there is little understanding about the energy conversion process from a thermodynamic point of view. A detailed thermodynamic model is proposed, encompassing energy and exergy balance, and entropy analysis to evaluate a process for solar photon-enhanced thermionic conversion. The correlation of photons, phonons and electrons is presented, as well as the energy transfer pathway in solar thermionic conversion. The total solar-to-electricity efficiency of energy and exergy are 54.32% and 58.42%, respectively, for a photon-enhanced thermionic converter combined with a Carnot engine, at a 1.20 eV bandgap with an electron affinity of 1.20 eV when the concentrated solar flux is 500 kW/m^2. The combination of photoexcitation and thermalization facilitates the overall thermionic emission exergy ratio up to 62.36%, higher than that of conventional thermionic conversion by 10.92%. Temperature-entropy diagrams with quantitative analysis are proposed for the thermodynamic processes of thermionic and photon-enhanced thermionic conversion. The electron fluid cycles from the Fermi level of the anode back to the valance band of the cathode with a reduced entropy, while being thermalized from the conduction band in photon-enhanced thermionic conversion, contributing to the entire conversion of photoexcited energy to electricity.

1. Introduction

Solar energy has attracted widespread attention due to its environmental friendliness and abundant reserves, which are particularly important in modern society given limited natural resources and pollution controls. Except for conventional photovoltaics [1,2] and solar thermal power [3], thermionics has the capacity to evolve solar power generation. The first solar thermionic converter fabricated by Jet Propulsion Laboratory achieved an electrical power output of 114 W_e and an experimental efficiency of ~7% in the early 1960s [4]. Another array-based thermionic system was proposed by U.S. Air Force to deliver an overall electrical power of 50 kW_e, where a single converter produced a maximum power of 30 W_e [5]. Recently, an innovative technology for solar thermionic power, i.e., photon-enhanced thermionic emission (PETE), has been developed and exhibits strong potential for solar power generation [6]. PETE conversion combines the photovoltaic effect and thermionic effect into a single process, which utilizes electrons as the working fluid. It can be described by a simple three-step process: (i) photoexitation of the valence electrons into a conduction band; (ii) thermalization and diffusion of the conduction

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https://doi.org/10.1016/j.apenergy.2018.04.044
Received 13 February 2018; Received in revised form 6 April 2018; Accepted 22 April 2018

Nomenclature

A	Richardson's constant
$E_{a,a}$	the anode's emitted electron energy flux
$E_{a,c}$	the anode's received electron energy flux
E_C	conduction band minimum of the cathode
$E_{c,a}$	the cathode's received electron energy flux
$E_{c,c}$	the cathode's emitted electron energy flux
$E_{F,n}$	electron quasi-fermi level
$E_{F,p}$	hole quasi-Fermi level
E_g	bandgap of the cathode
E_{in}	power input of the concentrated solar radiation
$E_{rad,c}$	thermal radiation of the cathode
$E_{rad,a}$	thermal radiation of the anode
E_V	valence band maximum of the cathode
Ex_{in}	exergy flux of the concentrated solar radiation
$Ex_{rad,c}$	exergy flux of the cathode's thermal radiation
$Ex_{rad,a}$	exergy flux of the anode's thermal radiation
K_{BB}	coefficient at which electrons recombine per volume
K_{PETE}	coefficient at which electrons emit per volume
N	net electron density for thermionic emission
N_a	emitted electron population from the anode
N_c	emitted electron population from the cathode
P_{Carnot}	power output of the Carnot engine
P_{ti}	power output of the PETE converter
P_{sun}	AM1.5 direct circumsolar spectrum
Q	rejected heat on the anode
S_{in}	entropy flux of concentrated solar radiation
$S_{rad,a}$	entropy flux of thermal radiation from the anode
$S_{rad,c}$	entropy flux of thermal radiation from the cathode
S_U	entropy flux of thermalized electrons
T_a	temperature of the anode
T_c	temperature of the cathode
T_s	temperature of the Sun
T_0	ambient temperature
U	net energy of working thermionic electrons in the cathode
V	output voltage
W_{PETE}	maximum power output of the PETE converter
X	concentration ratio
c	speed of light
dn	photon-enhanced conduction band electron density
e	electron charge
f	dilution coefficient of solar radiation
h	Planck's constant
k	Boltzmann's constant
m_n^*	effective electron mass
n	overall conduction band electron density
n_{eq}	equilibrium electron density
p_{eq}	equilibrium hole density

Greek symbols

μ	chemical potential of the cathode
χ	electron affinity of the cathode
σ	Stephan–Boltzmann constant
φ_a	motive barrier of the anode
φ_c	motive barrier of the cathode
ϕ_a	work function of the anode
ϕ_c	work function of the cathode
Γ_{PETE}	rate of photon-enhanced thermionic emission
Γ_{recom}	rate of electron recombination
Γ_{sun}	rate of photoexcitation
$\delta E_x'$	exergy loss in solar-electron conversion
$\delta E_x''$	exergy loss in vacuum electron transport
ΔS_{ab}	entropy production in solar-electron conversion
ΔS_{ti}	total entropy production in vacuum electron transport
$\Delta S_{ti,a}$	entropy production of the anode-emitted electron stream
$\Delta S_{ti,c}$	entropy production of the cathode-emitted electron stream
η	overall energy efficiency
ψ	overall exergy efficiency
ψ_{PETE}	PETE exergy efficiency

Abbreviations

PETE	photon-enhanced thermionic emission
TE	thermionic emission

electrons throughout the cathode; and (iii) emission of the thermalized electrons into a vacuum and collection by the anode [7,8].

1.1. Thermodynamics of solar power generation

The first law of thermodynamics is widely used for the performance evaluation of solar power systems, including photovoltaics and solar thermal power. As a complementary tool for energy analysis, exergy analysis (i.e., second law of thermodynamics) can evaluate quantitatively and qualitatively a process of energy transformation and conversion, thus indicating the possibilities of thermodynamic improvement [9]. With exergy analysis, Padilla et al. [10] considered solar receiver has a higher exergy destruction than heat-power conversion process for solar tower system, and Zhai et al. [11] claimed that the main energy and exergy losses take place at the parabolic trough collector for a hybrid solar heating, cooling and power system. These studies provide good references for analyzing and comparing solar thermionic processes, e.g. thermionic emission (TE) and PETE.

1.2. Advances on photon-enhanced thermionic conversion

According to the principle of detailed balance, Schwede et al. predicted that an optimal solar PETE converter achieves an ultrahigh efficiency of ~43% at a concentration ratio of 1000 [6]. However, the intricate interaction of working electrons with other particles (i.e., photons, phonons and electrons) undermines ideal performance in the PETE converter. Thus, several improved models were established to predict a more realistic efficiency [12]. Varpula et al. developed Schwede's model, considering electron diffusion, inhomogeneous photogeneration, and bulk and surface recombination into PETE conversion [13]. It is known that a GaAs or Si cathode achieves high efficiency with an electron-blocking junction at the back contact [14]. However, an InP cathode exhibits better performance on account of the stronger photon absorption and higher electronic efficiency [15]. The space charge effect creates an extra barrier for electron transportation in a vacuum, especially with a gap width of a few microns or more [16]. Fortunately, the reduction in efficiency of the PETE converter is relatively unnoticeable compared to that of conventional thermionic converters, which is attributed to the electron recycling to the conduction band [17]. When the gap narrows to nanoscale, the quantum tunneling effect and image force correction dominates the electron transport in the vacuum [18]. The calculated results showed that the nanoscale vacuum gap enhanced the efficiency of the PETE converter due to the reduced potential barrier. On the other hand, the PETE efficiency is further enhanced when combined with a secondary power system (e.g., thermoelectrics [19,20], photovoltaics [21] and conventional thermal cycles [22]). According to the first law of thermodynamics, an overall theoretical efficiency of ~70% is obtained when a dual bandgap PETE converter is cascaded with a Carnot engine [23]. Reck et al. tried to introduce entropy analysis to better understand the mechanism of PETE