Photon Enhanced Thermionic Emission for Solar Energy Harvesting - Progress Report to the Global Climate and Energy Project

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Abstract

Photon Enhanced Thermionic Emission (PETE) is a newly proposed form of solar energy harvesting which relies upon a combination of quantum and thermal processes to generate electricity. Unlike standard solar cells which rapidly lose efficiency at elevated temperatures, PETE is designed to operate at temperatures commensurate with thermal solar devices. In concentrated solar power designs the PETE module will receive the direct incident light, convert a fraction to electricity and transfer its waste heat to a solar thermal cycle. Theoretical efficiencies of combined PETE/solar thermal cycles reach above 50% and may provide a route to affordable renewable energy on the utility scale. The key challenges to this technology are developing higher-efficiency cathodes that are stable at elevated temperatures, requiring both theoretical and experimental analysis of new materials. In the past months, theoretical work has established efficiency limits and determined several key materials properties and geometries to optimize PETE efficiency. We have constructed a new surface preparation and characterization chamber designed specially for PETE that can provide detailed measurements of material performance under anticipated operating conditions. Preliminary measurements have shown promising steps towards increasing efficiency.

Introduction

Solar harvesting technology usually takes one of two forms; the ‘quantum’ approach using the large per-photon energy as in photovoltaic (PV) cells, or the ‘thermal’ approach using solar radiation as the heat source for a classical heat engine. Quantum processes boast high theoretical efficiencies but suffer in practice from a limited spectral energy collection window, whereas thermal processes have inherently lower efficiency limits but take advantage of energy throughout the entire solar spectrum. Simple combinations of the two fail because PV cells rapidly lose efficiency at elevated temperatures, while heat engines rapidly lose efficiency at low temperatures. As a result, these two approaches remain disjointed.

Photon Enhanced Thermionic Emission (PETE) is a method of solar harvesting that uses the quantum nature of solar photons along with thermal energy to generate electricity at temperatures compatible with solar thermal engines. The method relies on a semiconductor cathode separated by vacuum gap from an anode (Figure 1). Incident photons excite electrons into the cathode's conduction band. If these carriers reach the surface before recombination, they can emit into vacuum and be collected by the anode, generating a voltage. Physical separation of the anode and cathode allows a large temperature differential, reducing the thermally generated reverse current which limits PV cells at high temperatures.[1] Thus, unlike other proposed "hot-electron" devices, [2-5] the PETE process is still efficient for fully thermalized electrons, providing a more realistic path to hot electron harvesting.

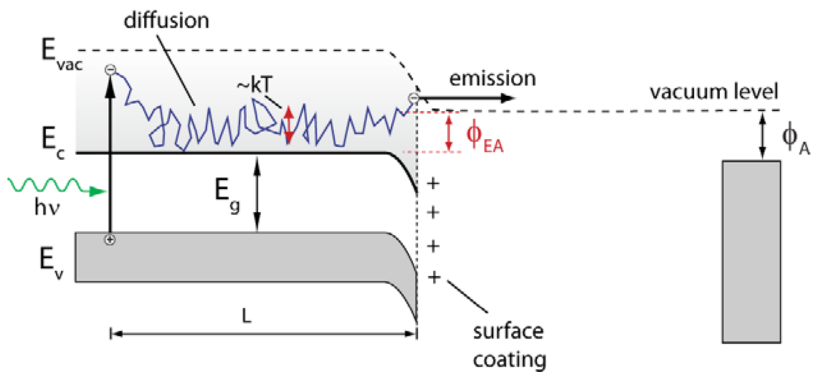

Figure 1: Schematic of the PETE process. Thermal energy assists photoelectron emission, harvesting both photon and thermal energy in the process

The possibility for efficient operation at elevated temperatures makes PETE an ideal candidate for high concentration solar applications, including use as a "topping cycle" for a solar thermal generator, wherein the PETE device would harvest a fraction of incident solar energy and deliver the rest as heat to a backing solar thermal engine (Figure 2). Even a PETE module with modest 20% efficiency in tandem with a 30% efficient Stirling solar thermal engine could boast a remarkable total system efficiency of 44%.

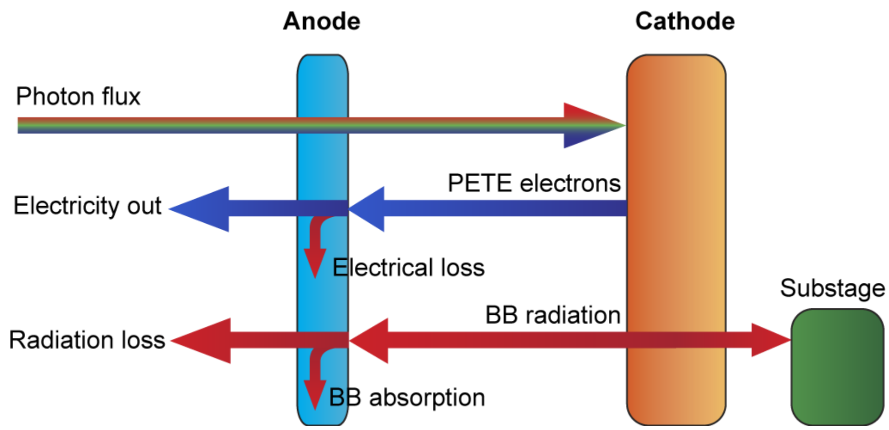

Figure 2: Energy flow for a tandem PETE/solar thermal cycle. Waste heat from the PETE device is used to power a conventional thermal engine, boosting the overall efficiency.

Background

Thermionic emission has been explored previously as a possible method of solar energy harvesting. In this scheme, concentrated solar radiation heats a refractory metal cathode to excite electrons above the vacuum level. Because thermionic current density depends exponentially on cathode temperature and work function, temperatures exceeding 1600ºC are often necessary to generate usable current densities. While possible efficiencies of 20-30% or more are predicted, measured efficiencies are typically less than 10%. [6-7] In contrast, photoexcited electrons in the PETE cathode must only overcome the electron affinity which can be much smaller than a material's work function. By relaxing this requirement a wide range of materials and operating temperatures become feasible.

While progress towards a practical thermionic device has been limited, research into thermionic emitter materials may hold promise for PETE. F.A.M. Koeck, et al. recently reported that phosphorous doped diamond has an exceptionally low work function of 0.9 eV and is stable to at least 765ºC.[8] PETE efficiency depends strongly on the work function of the anode (Figure 3), thus this advancement make PETE more realizable. Using phosphorous doped diamond as an anode material, efficiencies of over 40% may be possible, providing significant encouragement for the prospect of creating high-efficiency devices.

The pressure to incorporate renewable means of energy generation has accelerated growth in utility scale solar thermal harvesting. In the last year, Southern California Edison has announced contracts with BrightSource and eSolar for 1,300MW and 245MW solar thermal plants, respectively.[9-10] Stirling Energy Systems, who recently announced a record 31.25% solar-to-grid conversion efficiency, has signed power purchase agreements for two plants which could provide up to 1,750MW.[11] These developments make investigations into topping cycles to boost conversion efficiency of these installation an important component for a solar economy.

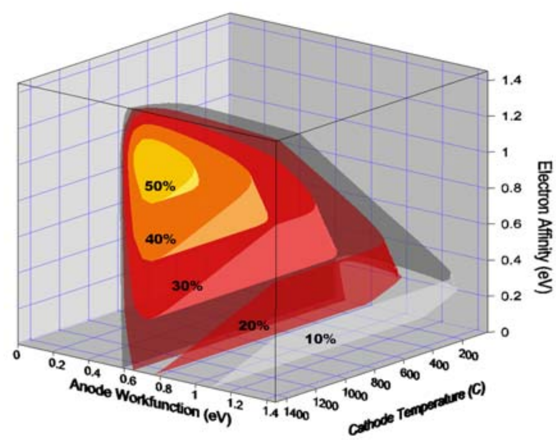

Figure 3: Theoretical PETE efficiency as a function of cathode temperature, anode work function, and cathode electron affinity. E_g is fixed at 1.4 eV, the number of collisions with the surface is 10^4, and the anode temperature is 327ºC.

Progress

Essential steps in laying theoretical groundwork and building experimental infrastructure have been achieved over the last several months. Theoretical analysis has been developed for the PETE process, which extends conventional theoretical treatments to include high-temperature conditions. The maximum PETE efficiency calculated for the AM 1.5 solar spectrum is shown in Figure 3 as a function of electron affinity, anode work-function and temperature. In this model, we focus on the emission probabilities of electrons which have thermalized within the conduction band, discounting the contributions of hot electrons. Even using existing anode materials and operation at moderate temperatures, PETE efficiency can be higher than the Shockley-Queisser limit for Si (~34%). Operation at 1000ºC with an anode workfunction of 0.9 (the best reported) can produce up to 50% conversion efficiency for PETE alone. When combined with a thermal cycle to harvest the waste heat, this increases to 65%.

Establishing instrumentation to create and measure PETE devices is well underway. Because most material work functions are too high for visible light to emit electrons, a low work function coating must be deposited onto a cathode's surface. A surface preparation and characterization chamber has been constructed in which photoyield can be measured during the surface preparation process and at high temperatures. This chamber is being integrated with existing analysis tools such as low energy electron diffraction and angle resolved photoemission spectroscopy to gather detailed information about a cathode's surface geometry and underlying electronic structure. With this foundation in place, progress is being made towards determining a cathode material and geometry that could be used in a realistic PETE device.

Through integration with existing solar thermal infrastructure, a modular PETE module could boost utility scale power generation efficiency while minimizing additional expense. This would substantially lower the cost of utility scale power generation, potentially lowering the cost below that of non-renewable resources. This research could thus have an obvious and dramatic impact on global greenhouse gas emissions. The progress, both theoretical and experimental, is encouraging for this new approach to solar energy harvesting.

Future Plans

Several parameters that will be vital to this project's success have been identified through recent work. Future efforts will focus on 1) continuing to optimize cathode geometries to enhance photon absorption and electron emission, 2) experimentally demonstrating increase in photoyield with temperature for a material with suitable electron affinity, and 3) finding highly thermally stable cathode materials and surface treatments. The ultimate goal will be to combine a high temperature, visible spectrum photocathode with low work function anode to create a highly efficient solar harvesting device.

Publications

1. J.W. Schwede, N.A. Melosh, and Z.-X. Shen,"Thermally Enhanced Photoemission for Solar Energy Harvesting," patent pending.
2. J.W. Schwede, I. Bargatin, D.C. Riley, R.T. Howe, Z.-X. Shen, and N.A. Melosh, "Photon Enhanced Thermionic Emission (PETE) for Solar Concentrator Systems," in preparation.

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