

Maximizing Solar-to-Fuel Conversion Efficiency in Oxide Photoelectrochemical Cells Using Heat and Concentrated Sunlight

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Abstract

Our goal is to substantially increase the solar-to-fuel conversion efficiency in photoelectrochemical cells (PECs) by using heat and intense light from concentrated solar radiation. Ambient temperature PEC is one of the most intensely studied routes for storing intermittent solar energy in fuel molecules such as hydrogen and hydrocarbons. However, despite the high theoretical efficiency, demonstrated values are typically a few percent with stability measured in hours. The low efficiency arises from losses due to slow electro-catalysis, interfacial electron transfer, and minority carrier transport; stability issues arise mostly from photo-corrosion. We will address these shortcomings by designing earth-abundant, oxide-based heterojunction photoanodes that can operate at temperatures significantly above ambient. These oxide-based PEC aims to capture excess thermal energy resulting from the absorption of intense concentrated sunlight which is normally discarded. In the first six month of this work, we have made substantial progress in demonstrating the strong performance enhancement with temperature and optical concentration in iron oxide photoelectrode in liquid electrolytes. This result lays the foundation towards elevated temperature, high efficiency solid-state PECs.

Introduction

In one hour, more energy from sunlight strikes the Earth than the amount consumed by the entire planet in one year. Yet, despite the recent advent of relatively inexpensive silicon solar panels, the inherently intermittent nature of solar radiation is still the most critical bottleneck to replacing fossil fuels with renewable solar energy. Because of their high energy densities and transportability, solar fuels, such as hydrogen and hydrocarbons, are still the most promising mediums for storing and providing the energy when and where it is needed. Given this promise, the scientific community has devoted significant efforts towards hydrogen production using room-temperature PECs. The key challenge for PECs is identifying a combination of materials that absorb the visible solar spectrum, minimize overpotential losses, achieve proper energetic alignment between the light absorber and the electrochemical redox levels, and have excellent stability.

We are building a photo-electrochemical device for efficient and stable solar fuel production using earth-abundant materials that combines the beneficial traits of both room-temperature PEC and high-temperature electrolysis. By operating at elevated temperatures (400-600°C) using concentrated solar radiation, unused photons lost as heat can be used to accelerate kinetics of PEC reactions and to increase overall efficiency.

Background

The key challenge for PECs is identifying a combination of materials that absorb the visible solar spectrum, minimize overpotential losses, achieve proper energetic alignment between the light absorber and the electrochemical redox levels, and have excellent stability. Thus far, no one materials system has proven ideal for these stringent requirements, though progress is being made on light absorbers such as Si,¹⁻³ Fe₂O₃,^{4,8} Cu₂O⁹. Oxide light absorbers, in particular, are attractive due to their chemical stability, but many of them, such as α -Fe₂O₃, suffer from extremely low carrier mobility at room temperature due to strong electron-lattice interactions.¹⁰⁻¹¹ A logical improvement is to combine two materials together, known as a heterojunction PEC. It typically consists of a good light absorber (1.1-1.7 eV band gap) with high carrier mobility, coupled with a robust and thin overcoat layer (mostly oxides), often with a much larger band gap.^{2,6,12} Researchers have explored combinations such as Si-TiO₂,¹² Si-Fe₂O₃,⁶ WO₃-Fe₂O₃,¹³ WO₃-BiVO₄,¹⁴ and Cu₂O-TiO₂.¹⁵ However, these heterojunctions have had limited success at room temperature, due to low carrier mobility and uphill barrier at interfaces.

Carrier mobility in polaronic oxides like α -Fe₂O₃ exhibits a strong temperature dependence. Increasing the temperature from 25 to 600°C increases the carrier mobility by over seven orders of magnitude.¹⁰ High mobility directly translates into greatly improved minority carrier diffusion length and charge separation, even in the absence of nanostructuring. Hence, temperature is expected to significantly improve the photoelectrochemical properties of many oxides.

Results

During the first six months of the project, we examined the performance enhancement of hematite (Fe₂O₃)-based photoanode for water splitting to hydrogen and oxygen in NaOH electrolyte between 7 and 72°C and between 1 and 10 suns optical concentration. We observed a very strong improvement in the onset voltage, photocurrent, and the fill factor, consistent with the thermally-activated electron mobility discussed earlier. This result immediately highlights the advantage of combined heating and optical concentration for enhancing the solar-to-hydrogen efficiency, and is described below.

We successfully prepared dense hematite thin film photoanode by pulsed-laser deposition. We observed that the onset potential of the photocurrents shifts cathodically when heating and optical concentration are combined. To understand this synergistic effect, we examined the various potential shift contributions. As can be seen in Figure 1a, increased temperature enhances the reaction kinetics and decreases the equilibrium potential for water splitting. At the

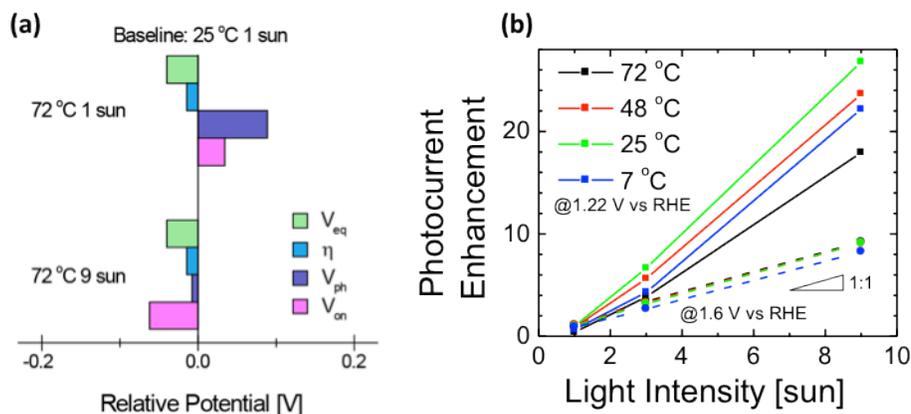


Figure 1: (a) Shifts in onset potential with temperature and optical concentration. (b) Photocurrent enhancement with light intensity. Ti-doped Fe₂O₃ photoanodes in NaOH.

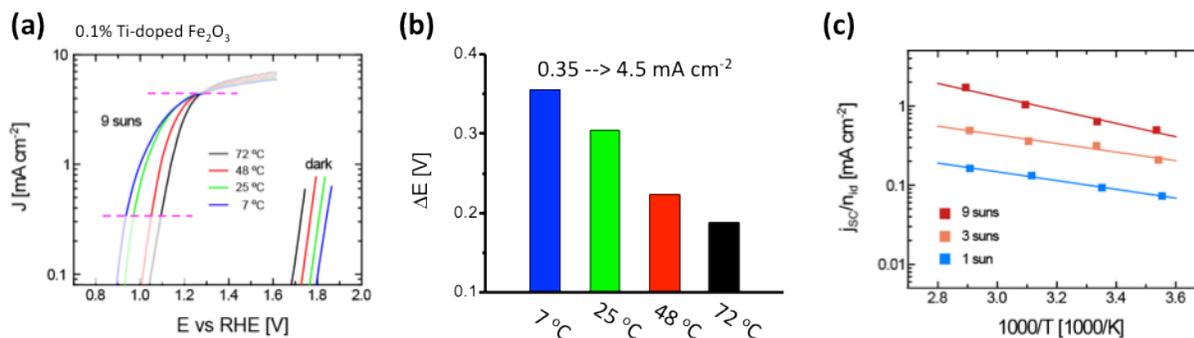


Figure 2: (a) Enhanced fill factor with temperature, which is quantified in terms of potential shift between 0.35 and 4.5 mA cm⁻² photocurrent in (b). (c) Temperature dependence of the ratio of short-circuit current density divided to the diode ideality factor.

same time, the photovoltage decreases with temperature, consistent with the rising reverse current. This negative effect is mitigated by the photovoltage enhancement with optical concentration, and highlights the origin of the overall enhancement.

Fig. 1b shows the photocurrent enhancement under 9 suns illumination as a function of temperature. Within the temperature range investigated, the photocurrent enhancement for all samples are significantly above the dashed line indicating a 9-fold enhancement. This promising observation suggests that beyond reducing the required illuminated area and the amount of materials required, increasing the light intensity does not adversely affect the PEC performance despite the increased temperature. Instead, there is an additional gain in photocurrent with combined concentrated sunlight and temperature. This observation contrasts with the typical solar cells, and points to temperature and optical concentration as key to improving performance of low-mobility yet stable oxide photoelectrodes such as hematite.

Beyond improvement in the onset potential and photocurrent, the fill factor of the photoanode also improves dramatically with temperature (Figure 2a,b). We analyzed the data to extract the ratio of the short-circuit current to the diode ideality factor, which exhibits an activation energy of 0.1 to 0.2 eV (Figure 2c). As the temperature increases, the photo-generated carriers are collected more efficiently at the interface, *i.e.* through the oxygen-evolution reaction. The combined effect of the reduced ideality factor and the enhanced short circuit current results in a smaller series resistance and thus a better fill factor.

Progress and Future Plans

The results so far shows that combining thermal enhancement and optical concentration is a promising way to improve the efficiency of iron oxide photoelectrodes. Our future plan is to explore this effect across multiple oxide material systems and implement an all solid-state PEC operating at elevated temperatures. The specific plan includes:

Heterojunction material development:

- 1) Identify optimal light absorber and mixed ionic and electronic conductor with suitable band gaps and band alignment. Current efforts are focused on Fe₂O₃ and BiVO₄ as the light absorbers and CeO₂ and BaZrO₃ as the mixed ionic and electronic conductors.
- 2) Develop interfacial modification strategies to minimize interfacial recombination velocity.

- 3) Understand the effect of temperature on the onset potential, photovoltage and photocurrent.
- 4) Increase long-term stability of the heterojunction at elevated temperature.

Solid-state PEC development:

- 5) Develop a solid-state PEC fabrication route using a solid-state electrolyte.
- 6) Construct a measurement platform to determine the solar-to-hydrogen efficiency.

Publications and Patents

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