

## II.C.7 Next-Generation Si Microwire Array Devices for Unassisted Photoelectrosynthesis

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### Overall Objectives

- Demonstrate a scalable and stable Si-microwire-array-based device for sunlight to clean H<sub>2</sub> fuel production, through hydrohalic acid splitting.
- Optimize the fabrication protocols for n-type crystalline Si microwire arrays and tandem Si-microwire-array-based devices containing an amorphous Si top layer.
- Quantify the solar-to-hydrogen (STH) efficiency of peeled, free-standing Si microwire arrays partially embedded in Nafion<sup>®</sup> proton exchange membrane.

### Fiscal Year (FY) 2013 Objectives

- Quantify the STH efficiency of free-standing Si-microwire-array devices for hydrohalic acid splitting.
- Demonstrate protection of Si from passivation and corrosion in hydrohalic acid solutions.
- Quantify the STH efficiency of tandem Si-microwire-array devices for hydrobromic acid splitting.
- Identify efficient and stable halide-oxidation catalysts.

### Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(AE) Materials Efficiency – Bulk and Interface

(AF) Materials Durability – Bulk and Interface

(AG) Integrated Device Configurations

### Technical Targets

This project investigates efficient and economically sustainable fuel-forming photoelectrosynthetic devices consisting of arrays of Si microwires. These devices are capable of storing 0.6–0.8 V of potential as H<sub>2</sub> fuel, which is a priority of the Hydrogen Production sub-program. Technical targets are listed in Table 1.

**TABLE 1.** Progress towards Meeting Technical Targets for Photoelectrochemical Hydrogen Production (Photoelectrode System)

Characteristics	Units	2011 Status	2015	Status Herein
STH Energy Conversion Ratio	%	Not Available	15	1
Electrode Replacement Lifetime	Years	Not Available	0.5	0.05

### FY 2013 Accomplishments

- Optimized radial emitter doping of n-type Si microwire arrays with boron and demonstrated >3% light-to-electrical energy conversion efficiency in aqueous hydroiodic acid solution, which is far below the 2015 DOE targets for STH energy conversion ratio.
- Demonstrated two successful tandem Si-microwire-array-based devices: one consisting of two crystalline Si microwire arrays of opposite doping configuration, partially embedded in Nafion<sup>®</sup>, and laminated back-to-back; and the other consisting of a crystalline Si microwire array with amorphous pin-doped Si deposited on top. Both generated open-circuit photovoltages in excess of 0.9 V, which is significant because a priority of the Hydrogen Production sub-program is to store 0.6–0.8 V of potential as H<sub>2</sub> fuel from sunlight.
- Fabricated a custom device sample holder and measurement system for the peeled, free-standing Si-microwire-array devices that was superior to previous designs.
- Discovered a method to fabricate a highly doped, axial n-type Si region at the base of microwires via in situ chemical vapor deposition. The method forms ohmic tunnel junctions with high-barrier-height contacts.
- Discovered stable catalysts for halide oxidation and materials to protect Si from corrosion and passivation: a nanoscale electrocatalyst requiring ~5 mV overpotential and that is stable for >4 hr in hydroiodic acid, at

$\sim 10$  mA/cm<sup>2</sup>; and poly(3,4-ethylenedioxythiophene): perchlorate (PEDOT:ClO<sub>4</sub>) requiring  $\sim 20$  mV overpotential and that is stable for  $\sim 20$  hr in HBr, at  $\sim 10$  mA/cm<sup>2</sup>.

- Optimized the composition and synthetic protocol for an electrically and ionically conductive membrane as well as the protocol to deposit/transfer it to the backsides of p-Si microwire arrays.



## INTRODUCTION

A priority of the DOE Hydrogen Production sub-program is to demonstrate efficient and economically sustainable solar fuels devices that store 0.6–0.8 V of potential as hydrogen fuel. This was demonstrated in the 1980s by Texas Instruments Corporation through use of a  $\sim 9\%$  efficient device for converting the energy in sunlight into hydrogen from hydrobromic acid solutions [1]. This efficiency is  $\sim 10$  times that of photosynthesis from typical crops [2], and the reaction products can be combined in a flow battery to generate electricity when sunlight is sparse, e.g., at night. Texas Instruments Corporation used a scalable, serially connected Si–Si device; however, their device required high-purity materials and used expensive and sparse Pt–Ir alloy noble-metal electrocatalysts, which would far exceed the 2015 DOE cost target of \$2.0 M/yr-tonnes H<sub>2</sub> per day.

The project described herein utilizes new Si-microwire-array device architectures [3], decorated with electrocatalysts and embedded in a flexible proton exchange membrane, to drive hydrogen evolution from hydrohalic acid solutions using sunlight as the only energy input. From an economic standpoint, the microwire geometry uses  $\sim 5\%$  of the material required for conventional wafer-based solar cells, tolerates less pure Si, and the growth wafer substrate can be reused repeatedly. Such characteristics are advantageous for a technology with commercial potential and are of interest to the DOE Hydrogen Production sub-program. A  $>3.5\%$  light-to-electrical efficiency for sunlight-driven oxidation of hydroiodic acid to triiodide was demonstrated, which was stable for over 200 hr of continuous operation. In addition, a serially connected Si–Si device gave  $>0.7$  V of potential toward H<sub>2</sub> evolution. Lessons gleaned from these Si-microwire-array-based devices will be invaluable to future solar fuels devices.

## APPROACH

Si microwire arrays were grown by chemical vapor deposition using a vapor–liquid–solid growth catalyst and doped either in situ during growth or post growth via a thermal, diffusion process. Catalysts and protective layers

were deposited and Nafion® was coated into the microwire arrays via spin coating, followed by mechanical removal of the array using a razor blade. The samples were evaluated by traditional photoelectrochemical methods using a three-electrode arrangement. Peeled, free-standing devices were evaluated in a custom acrylic holder and glass cells fitted with inductive stirrers, fiber optic excitation and digital camera imaging, in situ electrochemical evaluation, and in situ and in operando product detection via mass spectrometry and optical transmission spectroscopy.

## RESULTS

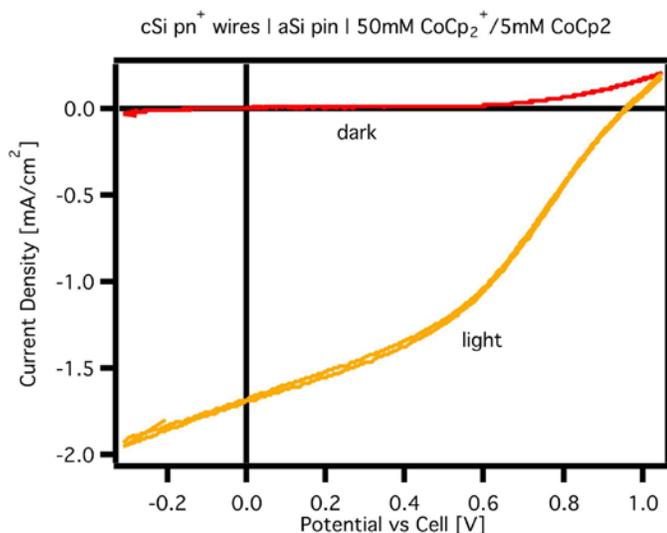
Three different functioning microwire arrangements were fabricated as free-standing, partially Nafion®-embedded Si microwire array devices for solar hydrogen formation from fuming hydroiodic acid: (a) radially doped pn<sup>+</sup>-Si employing Pt electrocatalysts; (b) axially doped n<sup>+</sup>n-Si, surface functionalized with methyl groups, and employing Pt electrocatalysts; and (c) a tandem Si–Si device consisting of a and b laminated together by an electrically and ionically conductive composite membrane. These were all milestones for the proposed project. Several apparatuses were designed and engineered to aid in the measurement of the reaction products. Each apparatus was incorporated into an ultraviolet-visual spectrophotometer and plumbed to a mass spectrometer to detect I<sub>3</sub><sup>-</sup> and H<sub>2</sub>, respectively, when formed at rates  $>100$   $\mu$ A/cm<sup>2</sup>. The final version of the apparatus affords better forced convection of each reaction vessel through inductive stirring and in situ and in operando monitoring of hydrogen bubble formation via a digital endoscope camera.

Tandem Si–Si devices were fabricated as described above. In addition, a tandem device using amorphous Si on crystalline Si microwire arrays was demonstrated. These devices generated  $>1$  V open-circuit photovoltage by photoelectrochemistry (Figure 1). This is extremely relevant to the DOE Hydrogen Production sub-program's desire to store 0.6–0.8 V of potential in H<sub>2</sub> fuel.

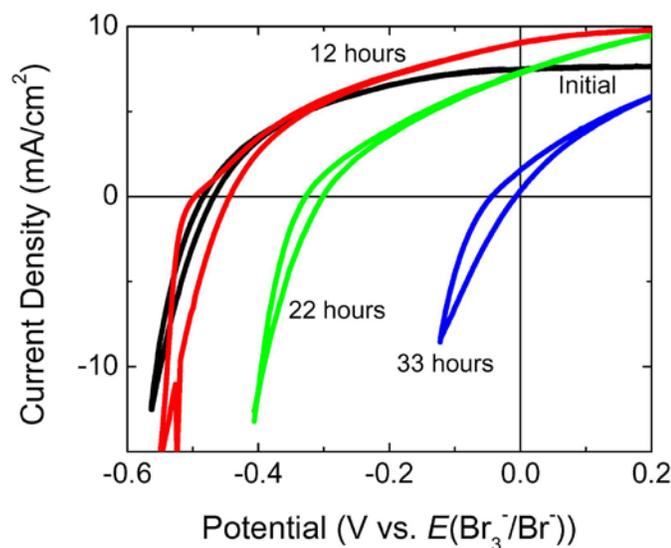
Original reports on hydrogen evolution from Si microwire arrays in acidic electrolytes used Pt electrocatalysts [4]. Previous reports from this DOE-funded research also utilized Pt for both hydrogen evolution and halide oxidation from hydrohalic acid solutions. FY 2013 progress included hydrogen evolution from pn<sup>+</sup>-Si microwire arrays functionalized with electrochemically deposited amorphous MoS<sub>x</sub>, and efficient and stable halide photo-oxidation using electropolymerized PEDOT:ClO<sub>4</sub> on planar n-Si–CH<sub>3</sub> wafers (Figure 2).

## CONCLUSIONS AND FUTURE DIRECTIONS

This project demonstrated sunlight-driven, unassisted hydrogen evolution in hydroiodic acid solutions using



**FIGURE 1.** Dark and illuminated current density vs. potential relationship for a tandem Si-Si device consisting of  $\text{pn}^+$ -Si microwire arrays coated in a  $\sim 200$ -nm thick layer of amorphous pin-Si immersed in Ar-purged acetonitrile electrolyte containing cobaltocene/cobaltocenium.



**FIGURE 2.** Illuminated current density vs. potential relationships at the indicated times for a planar n-Si-CH<sub>3</sub> wafer with electropolymerized PEDOT:ClO<sub>4</sub> on top immersed in Ar-purged HBr solution.

peeled, free-standing silicon microwire arrays. For FY 2013, a tandem functioning device was also demonstrated. In addition, major results this year included protection of Si from corrosion during iodide and bromide oxidation using surface chemistry and earth-abundant PEDOT:ClO<sub>4</sub> polymers, respectively; stable sunlight-driven hydrogen evolution using sulfide and phosphide electrocatalysts; and a transparent electrically and ionically conductive membrane.

The research challenges that remain include:

- Determining protocols for the deposition of materials on microwires to serve as protective layers from highly oxidizing electrolytes.
- Altering Si-microwire-array fabrication protocols so that dopants at the bases of the microwires are not gettered through oxidation processes, and so that emitters are conformal along the length of the microwire.
- Reinvestigating methods to cast Nafion® proton-exchange membrane and mechanically remove partially Nafion®-embedded Si microwire arrays from their growth substrate.

## SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Postdoctoral Research Award, American Chemical Society, Physical (PHYS) Division (2013).
2. Ardo, S.; Lewis, N.S. (*pending*) Patent, California Institute of Technology (2013) (Provisional patent (2012) 61/697,422). Light-Driven Hydroiodic Acid Splitting from a Free-Standing Microwire Array Partially Embedded in an Ionomer Membrane.
3. Ardo, S.; Shaner, M.; Coridan, R.; Strandwitz, N.; McKone, J.; Fountaine, Katherine; Atwater, H.A.; Lewis, N.S. (*pending*) Patent, California Institute of Technology (2013) 13/856,353 (Provisional patents (2012) 61/619,661 and (2012) 61/621,819). Semiconductor Structures for Fuel Generation.
4. Ardo, S.; Lewis, N.S. (*pending*) Patent, California Institute of Technology (2012) 13/539,335 (Provisional patent (2011) 61/503,083). A Tandem Solar Cell using a Silicon Microwire Array and Amorphous Silicon Photovoltaic Layer.

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3. Pinaud, B.A.; Benck, J.D.; Seitz, L.C.; Forman, A.J.; Chen, Z.; Deutsch, T.G.; James, B.D.; Baum, K.N.; Baum, G.N.; Ardo, S.; Wang, H.; Miller, E.; Jaramillo, T.F. *Energy Environ. Sci.* (2013) 6(7): 1983–2000. Technical and economic feasibility of centralized facilities for solar hydrogen production via photocatalysis and photoelectrochemistry.
4. Shaner, M.R.; Fountaine, K.T.; Ardo, S.; Coridan, R.H.; Atwater, H.A.; Lewis, N.S. (*submitted*) Photoelectrochemistry of Core-Shell Tandem Junction n-p<sup>+</sup>-Si/n-WO<sub>3</sub> Microwire Array Photoelectrodes.

5. Nielander, A.C.; Bierman, M.J.; Petrone, N.; Strandwitz, N.C.; Ardo, S.; Yang, F.; Hone, J.; Lewis, N.S. (*submitted*) Photoelectrochemical Behavior of n-type Si(111) Electrodes Coated by a Single Layer of Graphene.
6. McDonald, M.B.; Ardo, S.; Lewis, N.S.; Freund, M.S. (*submitted*) Use of bipolar membranes for maintaining steady-state pH gradients in membrane-supported solar-driven water splitting.
7. Ardo, S.; Warren, E.L.; Roske, C.; Brunschwig, B.S.; Atwater, H.A.; Lewis, N.S. *Materials Research Society, Spring National Meeting (2013)* San Francisco, CA. Demonstration of Artificial Photosynthesis with Peeled Silicon Microrod Arrays.
8. Ardo, S.; Roske, C.; Warren, E.L.; Brunschwig, B.S.; Atwater, H.A.; Lewis, N.S. *American Chemical Society, Fall National Meeting (abstract accepted)*, Indianapolis, IN.

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1. Johnson, E.L. *IEEE* **1981**, 2 - 6.
2. Blankenship, R.E.; Tiede, D.M.; Barber, J.; Brudvig, G.W.; Fleming, G.; Ghirardi, M.; Gunner, M.R.; Junge, W.; Kramer, D.M.; Melis, A.; Moore, T.A.; Moser, C.C.; Nocera, D.G.; Nozik, A.J.; Ort, D.R.; Parson, W.W.; Prince, R.C.; Sayre, R.T. *Science* **2011**, 332, 805 - 809.
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