
HydroGEN Seedling: Best-in-Class Platinum-Group-Metal-Free Catalyst Integrated Tandem Junction Photoelectrochemical Water Splitting Devices

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Overall Objectives

The project will engineer and compare two photoelectrochemical (PEC) cell configurations made with high-efficiency non-precious-metal catalysts for water splitting, together with two classes of photovoltaic materials chosen from proven high-performance semiconductors versus emerging low-cost semiconductors. The two configurations to be fabricated and compared are (1) high-efficiency (higher-cost) multijunction GaInP₂/GaAs photoabsorbers developed at the National Renewable Energy Laboratory (NREL) that are integrated with Rutgers-developed hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) catalysts (Ni₅P₄ and LiCo₂O₄, respectively); and (2) lower-cost devices created from emerging perovskite (oxy)nitride photoabsorbers also integrated with these Rutgers catalysts. The long-term goal (Year 3) is to compare the trade-off between performance and cost for these configurations while also achieving benchmark metrics in solar-to-hydrogen (STH) efficiency and durability.

Fiscal Year (FY) 2018 Objectives

- Fabricate stable non-platinum-group-metal (non-PGM) alkali LiCoO₂ electroanode (on par with published cubic-LiCoO₂ benchmark) with stable performance.
- Develop low-temperature thin film synthesis methods for catalyst (Ni₅P₄) and protection layers that are compatible with p-GaInP₂/p⁺GaAs.
- Evaluate photoelectrochemical performance of catalyst and protection layers on a p-GaInP₂/p⁺GaAs single-junction model device
- Synthesize and evaluate photovoltaic and photoelectrochemical properties of ZnSnN₂ photoanode.

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 Plan¹:

- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability.

Technical Targets

The goal of this project is to attain or exceed the DOE benchmark STH energy conversion efficiency of 10% (and 20% by 2020), working toward the DOE hydrogen cost goal of <\$2/kg H₂. This is being investigated in two thrusts by developing two competing monolithic PEC devices: one a high-performance device based on state-of-the-art GaAs/GaInP₂ tandem solar cells developed at NREL, and the second a high-value device based on earth-abundant photoabsorber materials. Both these devices will be paired with electrocatalysts developed for this purpose at

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

Rutgers by adapting them to thin films on the photoabsorbers. These catalysts are based on the HER catalysts (Ni_5P_4) and OER catalysts (LiCo_2O_4) previously developed at Rutgers for high-efficiency electrolyzers. Both monolithic devices will be based on a narrow and a wide bandgap material, a so-called tandem device. The aim is to meet the following DOE targets:

- STH energy conversion ratio: 20% (by 2020)
- Hydrogen cost: $< \$2/\text{kg H}_2$
- Electrode replacement lifetime: 0.5 years.

FY 2018 Accomplishments

- Synthesized and characterized activity and stability of electrochemical LiCo_2O_4 -based thin film anode. Performance achieved: >12 days sustained OER activity in 1 M NaOH.
- Successfully developed a thin film fabrication method for crystalline Ni_5P_4 at low temperature.
- Successfully fabricated TiN protection layer on p-GaInP₂/p⁺GaAs at low temperature and demonstrated it blocks atomic interdiffusion of catalyst and photoabsorber.
- Demonstrated that photoelectrochemical performance of HER catalyst and protection layers on p-GaInP₂/p⁺-GaAs exceeded the 10% goal and is on par with the PtRu benchmark catalyst. The performance was independently confirmed by the NREL Deutsch group.
- Synthesized ZnSnN_2 photoabsorber on glass and characterized by X-ray fluorescence, X-ray diffraction, Rutherford Backscattering, and conductivity measurements.
- Identified corrosion instability of ZnSnN_2 in 1 M NaOH.

INTRODUCTION

Current PEC devices suffer from low stability and efficiency; hence this project aims to address both those needs by significantly increasing the STH conversion efficiency above 10% while achieving long-term operation without corrosion.

APPROACH

The industry-accepted benchmarking standard for photoelectrochemical performance is conducted with PGM catalysts (RuO₂ and PtRu). Our approach differs by developing methods to interface two classes of photoabsorbers with the Rutgers-developed non-PGM catalysts. Our approach to increasing the STH efficiencies up to 10% has two thrusts.

Thrust 1: using GaInP₂/GaAs devices with optimizing bandgap matching to the solar spectrum coverage that provide suitable voltages for splitting water (using an NREL photovoltaic cell with solar-to-electrical power efficiencies >16%).

Thrust 2: the development of novel photoabsorbers based on earth-abundant materials that have low fabrication costs.

Thrust 2 will increase the STH efficiency by three strategies:

1. Utilization of two light absorbers with different bandgaps in a tandem configuration each tuned to achieve optimal solar spectral coverage. Corrosion-resistant metal oxides with wide bandgap are good candidates for the photoanode but inefficiently absorb red light. Spectral shifting to lower the bandgap can be achieved by N doping or substitution, which increases the absorption and ideally preserves stability.
2. (band-bending) Each absorber will have a built-in electric field gradient achieved by gradient doping to allow matching of valence and conduction band energy levels to the electrochemical potential required for the OER and HER, respectively.
3. To improve charge separation efficiency and carrier lifetime we have developed methods for the creation of thin films of both OER and HER catalysts. The OER catalyst shows significant promise in independent laboratory testing (at Proton OnSite). The photoanode/OER interface will be coupled to a silicon absorber as photocathode and Rutgers' HER catalyst to achieve the tandem PEC design.

RESULTS

Synthesis and Testing of a High-Performance Back Contact Anode

To replace the state-of-the-art PGM catalysts in our high-performance PEC device, we need to develop a highly active and stable back contact anode using our previously published cubic-LiCoO₂ material [1, 2]. This will be integrated with the illuminated GaInP₂/GaAs cathode. To achieve this, we first needed to deposit the catalyst on a conductive and anodically stable substrate. Inspiration was drawn from the dimensionally stabilized anode (DSA) design using TiO₂/Ti microporous scaffolds to increase surface area and stability under applied anodic potential [3]. We note that the DSA utilizes Ru doping of the TiO₂ to achieve reasonable conductivity and circumvent the band bending of pristine TiO₂, which would hinder anode operation in the absence of ultraviolet illumination.

Figure 1A shows long-term stability of a DSA comprising Ti-foil with a native TiO_x oxide film and top layer of electrodeposited Li_xCoO₂ film. The most active film is grown by cycling the deposition potential repeatedly until the final activity is reached. In Figure 1A the effect of O₂ bubble formation is seen as spikes in the current, but overall the electrode shows great retention of activity. Figure 1B shows the rough and particulate surface morphology of the deposited Li_xCoO₂ before the 12.8 days of stability test.

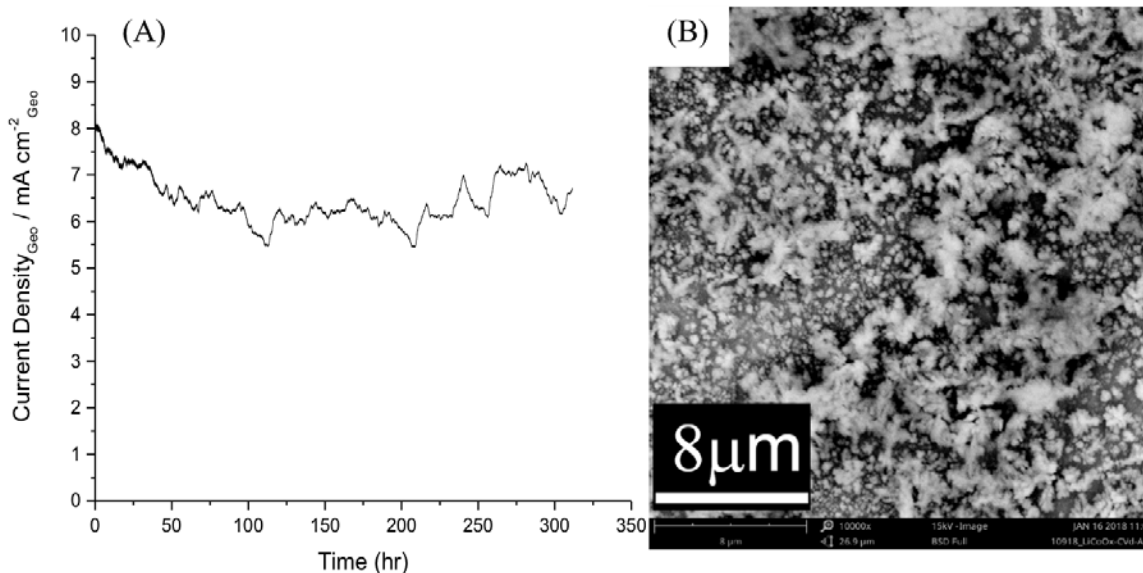


Figure 1. (A) Chronoamperometric analysis of and (B) scanning electron microscope image of the top surface of the as-synthesized electrodeposited Li_xCoO_2 thin film catalyst

Synthesis of a Protection Layer/Diffusion Barrier on High-Performance Photocathode ($\text{GaInP}_2/\text{GaAs}$ Buried-Junction Device)

For non-oxide photoelectrodes the air exposure during fabrication results in the formation of a surface oxide layer. In the case of GaInP_2 the surface oxide is a gallium indium oxide and phosphate of unknown exact composition. This oxide layer impedes the charge transfer to and capture by the catalyst layer and therefore must be removed immediately prior to deposition.

The first samples received from the NREL “III-V Semiconductor Epi-Structure and Device Design and Fabrication” node of $n\text{-GaInP}_2/p\text{-GaInP}_2/\text{GaAs}$ were therefore investigated for the best method for removal of any surface oxide from the GaInP_2 surface. X-ray photoelectron spectroscopy (XPS) studies of P, In, and Ga as a function of the etchant solution were conducted to find the optimal procedure for removing the surface oxide prior to the deposition of the protection layer. Based on three different etchants (aqueous hydrochloric acid, $\text{HF}:\text{NH}_4\text{F}$ (1:6), and aqueous ammonia solution) the indium oxide was removed most successfully by using the buffered HF etchant.

Finally, we deposited a TiN protection layer of approximately 4 nm thickness on top of a freshly cleaned GaInP_2 photocathode surface. The deposition was done using pulsed laser deposition from a TiN target at reduced temperature ($<120^\circ\text{C}$) to avoid loss of P from the GaInP_2 during deposition in high vacuum.

Development of Low-Temperature Ni_5P_4 HER Electrocatalyst Layer Synthesis and Transfer to $p\text{-GaInP}_2/p^+\text{-GaAs}$

Synthesizing phase-pure crystalline Ni_5P_4 on $\text{TiN}/\text{GaInP}_2$, without the decomposition of the photoabsorber due to interatomic diffusion into the catalyst layer and P loss, requires lowering the reaction temperature from the previous optimal conditions used for Si-photocathodes (i.e., 500°C and 3 hours). Lower temperatures can prevent atomic interdiffusion of GaInP_2 into the catalyst layer. We used a thicker Ni/TiN/Si geometry as a model system to systematically vary the temperature ($T < 400^\circ\text{C}$) and the reaction time to characterize multiple reaction conditions and probe the catalyst phase by regular X-ray diffraction, while preserving the $\text{GaInP}_2/\text{GaAs}$ samples provided by the NREL node for the final proof of concept at the optimized conditions.

Figure 2 shows the X-ray diffraction patterns for samples at various phosphidation conditions (T=temperature and t=time): T1 >400°C and t1 >1 h; T2 <400°C and t2 <1 h for a 125 nm Ni/TiN/Si sample. We note that at high temperature, over-phosphidation occurs while some Ni is still unconverted; this indicates that the surface is converted far too fast compared to the diffusion of P into the Ni. Lowering the temperature and reducing the reaction time decreases the P vapor pressure and reduces the over-phosphidation (T2). These conditions generated a catalyst layer of Ni₅P₄ with significant amount of unreacted Ni (green trace) below the converted catalyst. Because the final electrode will utilize a much thinner Ni layer (3 nm), unreacted Ni may not be the problem in this case. To confirm that a thinner Ni layer would result in increased phase purity, a 80 nm Ni/TiN/Si sample was reacted under T2_t1 conditions (purple trace). The resulting powder X-ray diffraction pattern demonstrates the peak attributed to unreacted Ni was substantially decreased without the presence of NiP₂ and confirms the above conditions are suitable for a 3 nm–10 nm Ni film. We concluded that the reaction conditions were successfully optimized for generating a phase-pure Ni₅P₄ thin film.

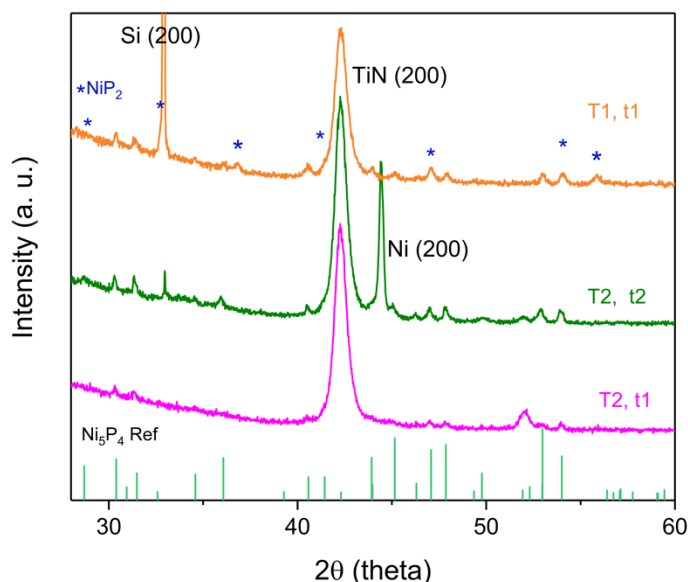


Figure 2. X-ray diffraction of different temperature and time of phosphidization on thick Ni layer with TiN protected single crystal Si model photocathode

Adapting Ni₅P₄ Synthesis on TiN/p-GaInP₂/GaAs

To transfer the above optimized reaction conditions for Ni₅P₄ synthesis on TiN/p-GaInP₂/GaAs, we evaporated a 3-nm thin layer of Ni onto the pre-cleaned GaInP₂/GaAs surface. XPS and helium ion microscope were used to confirm that only Ni and P are found at the top surface layer (~6 nm) and these uniformly cover the surface (Figure 3 and 4) seen by the absence of Ga and In. Figure 4A shows a uniform coverage of ~20 nm crystallite domains all apparently sintered together without pinholes.

To investigate the photoelectrocatalytic performance of these samples, we tested them in 0.5 M H₂SO₄ under simulated solar 1.5 AM G illumination. Figure 4B shows the current versus voltage curve (J-V curve) of Ni₅P₄/TiN on p-GaInP₂/GaAs compared to the benchmark PtRu/p-GaInP₂/GaAs tested at NREL under the same conditions. When comparing the J-V curve with the NREL benchmark, the performance of Ni₅P₄/TiN layers may be seen to be on par with the PGM-PtRu catalyst (base on V_{onset} and J_{sat}). To test the durability of Ni₅P₄/TiN/p-GaInP₂/GaAs photoelectrode, we ran chronoamperometry at 0 V vs. reversible hydrogen electrode under 1.5 AM G solar simulated illumination again in 0.5 M H₂SO₄. Figure 4C shows that less than 10% change in the photocurrent density is observed over 89 hours of testing (the duration of the test).

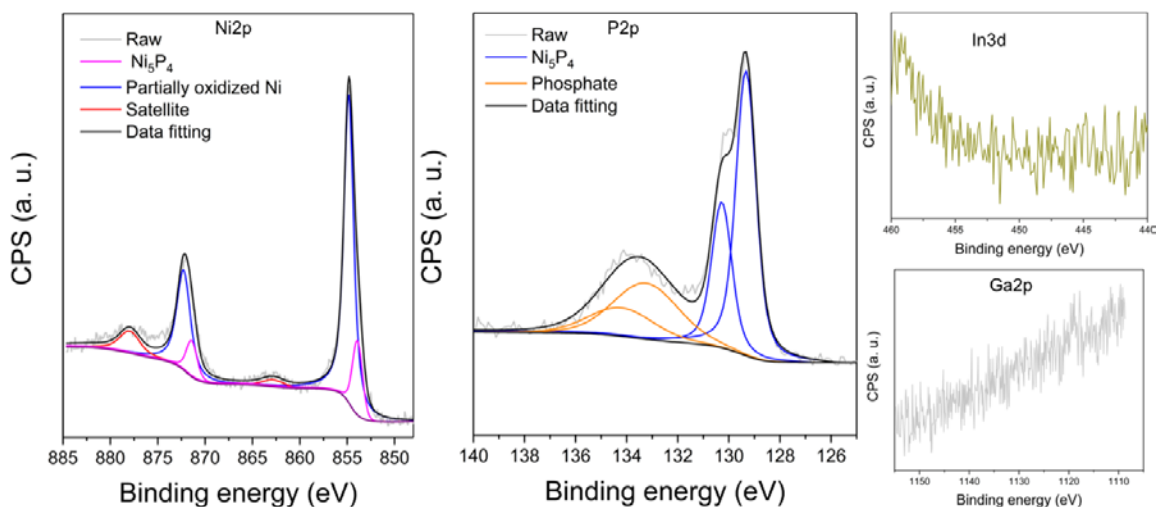


Figure 3. XPS of Ni2p, P2p, In3d, and Ga2p core levels of top layer Ni₅P₄/TiN/p-GaInP₂/GaAs

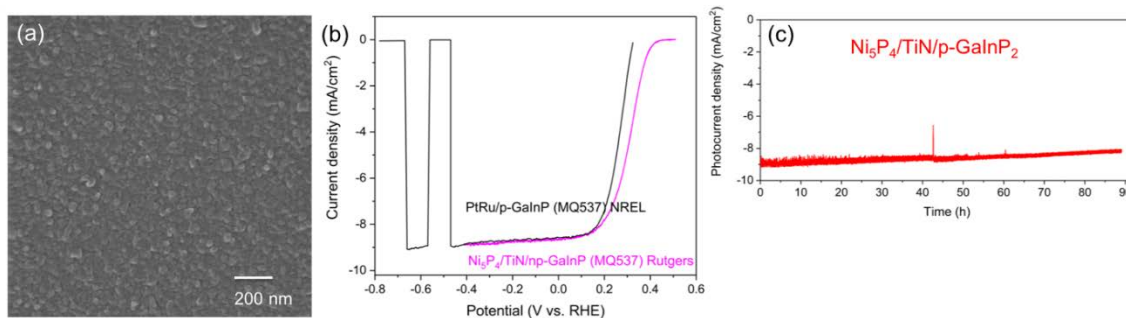


Figure 4. Helium ion microscope image of Ni₅P₄/TiN/p-GaInP₂/GaAs

CONCLUSIONS AND UPCOMING ACTIVITIES

The following conclusions are derived from the work in FY 2018:

- TiN protection layers on GaInP₂/p⁺-GaAs have demonstrated good interdiffusion protection from photoabsorber into the catalyst layer.
- Ni₅P₄ thin film synthesis was successfully adapted to lower reaction temperature on the TiN-protected p⁺-GaAs/p-GaInP₂.
- Insights gained from studying the tandem photoabsorber interface have significantly advanced progress toward a wireless, tandem PEC utilizing GaInP₂/GaAs dual junction.
- ZnSnN₂ photoabsorbers show low stability in alkali and rapid dissolution.

Future efforts toward FY 2018–2019 include the following.

Thrust 1:

- Assemble a full dual junction device of GaInP₂/GaAs with TiN and Ni₅P₄, with a RuO_x based non-illuminated anode, then characterize the photoactivity and stability.
- Test full device under on-sun conditions.

Thrust 2:

- Assemble a photoanodic device comprising OER/perovskite photoabsorber and test photoabsorbers based on either oxynitrides (with NREL Zakutayev node) or hybrid-organic/inorganic perovskite (NREL Kai node).
- Develop oxynitride photoabsorber synthesis using sputtering deposition facilities available at NREL.
- Develop hybrid-organic/inorganic perovskite photoabsorber interface with protection layers.

FY 2018 PUBLICATIONS/PRESENTATIONS

Publications

1. S. Hwang, S.H. Porter, A.B. Laursen, H. Yang, M. Li, V. Manichev, K.U.D. Calvinho, V. Amarasinghe, M. Greenblatt, E. Garfunkel, and G.C. Dismukes, “Creating stable interfaces between reactive materials: Titanium nitride protects photoabsorber-catalyst interface in water-splitting photocathodes,” (Submitted 2018).

Presentations

1. E. Garfunkel, “Photoelectrochemical Water Splitting to Form Hydrogen,” Semiconductor Surface Chemistry Meeting, Telluride, CO, 2018.
2. S. Hwang, S.H. Porter, A.B. Laursen, H. Yang, M. Li, V. Manichev, K.U.D. Calvinho, V. Amarasinghe, M. Greenblatt, E. Garfunkel, and G.C. Dismukes, “Titanium Nitride as a Conducting Interfacial Layer Between Hydrogen Evolution Catalyst and Si Photocathode for Stable Solar-to-Hydrogen Water Splitting Devices,” 233th ECS meeting in Seattle, 2018.
3. E. Garfunkel, M. Greenblatt, G.C. Dismukes, A.B. Laursen, and S. Hwang, “RU-EMN—Best-in-Class Platinum Group Metal-Free Catalyst Integrated Tandem Junction PEC Water Splitting Devices,” U.S. DRIVE Hydrogen Production Tech Team, teleconference, Feb. 6, 2018.
4. S. Hwang, S.H. Porter, A.B. Laursen, H. Yang, M. Li, V. Manichev, K.U.D. Calvinho, V. Amarasinghe, M. Greenblatt, E. Garfunkel, and G.C. Dismukes, “Nickel Phosphide Catalyst and Titanium Nitride Protection Layer for High Efficient and Stable Silicon-based Photocathode,” Annual Meeting at Catalysis Society of Metropolitan New York at Lehigh University, 2018.
5. A. Kashi, S. Hwang, A.B. Laursen, and G.C. Dismukes, “Characterization of Highly Active Electrodeposited Li_xCoO_2 Thin Film Anodes in PGM-free Photoelectrochemical Cells,” Annual Meeting at Catalysis Society of Metropolitan New York at Lehigh University, 2018.

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1. G.P. Gardner, Y.B. Go, D.M. Robinson, P.F. Smith, J. Hadermann, A. Abakumov, M. Greenblatt, G.C. Dismukes, *Angew. Chem. Int. Ed.* 51 (2012): 1616.
2. G. Gardner, J. Al-Sharab, N. Danilovic, Y. B. Go, K. Ayers, M. Greenblatt, G.C. Dismukes, *Energy Environ. Sci.* 9 (2016): 184.
3. S.M. Hoseinie, F. Ashrafzadeh, M.H. Maddahi, *J. Electrochem. Soc.* 157 (2010): E50.