

II.D.2 Tunable Photoanode-Photocathode-Catalyst Interface Systems for Efficient Solar Water Splitting

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Project End Date: August 31, 2017

Overall Objectives

- Design and construct a tandem configuration photoelectrochemical (PEC) cell by developing the knowledge base of a material's chemistry and semiconductor-catalyst interfaces (both photoanode and photocathode), which aim to attain or exceed the DOE benchmark of solar-to-hydrogen (STH) efficiency $\geq 10\%$
- Synthesize semiconductor light absorbers for the electrodes (photoanode and photocathode): investigate selected, phase-pure crystalline members of the perovskite oxynitride series $ABO_{3-x}N_x$ where A = alkaline earth or rare earth cations and B = Ti, V, Zr, Nb, or Ta
- Develop a robust and cost effective fabrication method for thin films of the above materials as light absorbers by pulsed laser deposition (PLD), atomic layer deposition (ALD), and/or spin-coated techniques in the second and third year
- Prepare Rutgers-patented oxygen evolution reaction (OER) catalyst (cubic-LiCoO₂) thin films on the light absorber using PLD or electrochemical deposition
- Produce stable interfaces between Ni₅P₄ (Rutgers-patented hydrogen evolution reaction [HER] catalyst) and various photocathodes (silicon and other low bandgap

semiconductors) to achieve efficient electron capture for HER

- Engineer stable interfaces between Ni₅P₄ and alkaline exchange ionomers to achieve efficient hydroxide transport, slow charge recombination, and provide long-term stability
- Investigate two electrolyte systems for connecting the photoelectrodes: (1) aqueous alkaline electrolyte solution (pH 14) and (2) alkaline exchange membrane (AEM)

Fiscal Year (FY) 2015 Objectives

- Synthesize semiconductor light absorbers with shorter wavelength absorption ($\lambda \leq 2.1$ eV): select phase-pure crystalline members of the perovskite oxynitride series $ABO_{3-x}N_x$, where A = alkaline earth or rare earth and B = Ti, V, Zr, Nb, or Ta
- Investigate the appropriate band-gap and band-edge of selected light absorbers while preventing sub-bandgap absorption
- Prepare thin films of the OER catalyst, cubic LiCoO₂, on the photoanode
- Develop alkaline electrolytes compatible with both the OER and HER half-reactions

Technical Barriers

This project addresses the following technical barriers from the Manufacturing R&D section (3.5.5) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

- (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 ratio 10% (and 20% by 2020). The project is conducting work to characterize La-doped SrNbO₂N and SrTaO₂N as light absorbers on the photoanodes, and is optimizing the conditions for high quality thin film fabrication of those same light absorbers by PLD and other techniques. Knowledge from these studies will be applied towards tandem PEC devices that aim to meet the following DOE targets:

- STH energy conversion ratio: 20% (2020)

- PEC electrode cost: \$300/m²
- Electrode replacement lifetime: 0.5 year

FY 2015 Accomplishments

Photoabsorbers

- Improved nitridation conditions and thus materials properties using a KCl flux treatment
- Established the possibility to dope elements (La) into the Nb-based oxynitride(s)
- Prepared phase pure SrTa(O,N)₃
- Determined accurate bandgaps of three synthesized oxynitride light absorbers, SrNbO₂N, La₂O₃:SrNbO₂N, and SrTaO₂N, using ultraviolet–visible (UV-VIS) spectrometry with integrating sphere
- Scaled up the synthesis of Sr₂Nb₂O₇ and Sr₂Ta₂O₇ precursors for the PLD target (10 g) using a solid-state reaction
- Completed PLD instrument training and initiated first experiments that produced an oxide precursor thin film by the PLD method

Catalyst interfaces

- Produced a thin film of lithium cobalt oxide OER catalyst on conducting substrate by electrosynthetic method and characterized its composition by X-ray photoelectron spectroscopy



INTRODUCTION

The ultimate goal of this project is to fabricate a PEC cell—in this case, a device that directly captures sunlight to aid in maximizing the electrolysis efficiency of decomposing water into fuel (hydrogen and oxygen). Current PEC devices suffer from low stability and efficiency; hence, this project aims to address both those needs by significantly increasing the solar-to-hydrogen conversion efficiency up to 10% while creating a stable device. To realize this goal, we will fabricate a tandem PEC—which is a system that uses two solar light absorbers (semiconductors)—in conjunction with OER and HER catalysts.

APPROACH

The Rutgers approach to increasing the STH efficiencies up to 10% has three strategies. The first strategy utilizes 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 sunlight. Spectral shifting to lower bandgap can be achieved by N doping, which increases the absorption and still preserves stability. Second, each absorber will have a built-in electric field (band-bending) achieved by doping to allow matching of valence (VB) and conduction (CB) band energy levels to the electrochemical required OER and HER potentials, respectively. Finally, to improve charge separation efficiency and lifetime, we will develop methods for creation of thin films of OER and HER catalysts recently developed at Rutgers which show significant promise in independent laboratory testing (Dr. Katherine Ayers, Proton OnSite). By coupling the photoanode to a low bandgap light absorber as photocathode and Rutgers' highly efficient catalysts, we expect to achieve a more cost effective PEC design.

RESULTS

Development of a semiconductor photoanode with durability, high carrier mobility, and appropriate optical bandgap and absorptivity is one of the keys for high STH efficiency PECs. The Rutgers team synthesized and characterized phase pure oxynitrides, LaNbON₂ and SrNbO₂N, which have relatively low bandgap (~1.8 eV) compared to other phase pure crystalline members in the perovskite oxynitride family. Solid-state synthesis using a KCl flux during the ammonia initiated nitridation step decreased the particle size while increasing particle uniformity. However, these light absorbers have sub-bandgap absorption in the near infrared (IR) range, which would limit performance of the longer wavelength active photocathode in the tandem device. This absorption is currently attributed to either Nb⁵⁺ reduction during high temperature ammonolysis or structure defects. The Rutgers team reassessed these photoanode light absorbers, and decided upon two different methods to overcome this limitation: (1) doping the *A* or *B* site on the Nb-based oxynitride, or (2) synthesizing different A/B members of crystalline oxynitrides, which have higher tolerance to unwanted reduction under the high temperature ammonolysis conditions.

1. For the Nb-based oxynitride, lanthanum was chosen to dope on to the *A*-site, because its higher oxidation state (3+ versus strontium's 2+) can suppress Nb⁴⁺/Nb⁵⁺ mixed valency. A La-doped Sr₂Nb₂O₇ precursor was synthesized post solid-state reaction after achieving a phase pure Sr₂Nb₂O₇ oxide precursor. After ammonolysis, lanthanum doping on the SrNbO₂N suppressed the near infrared (IR) absorption of the oxynitride (Figure 1). The expected stoichiometry of this product is La₂O₃:SrNbO₂N.
2. A Ta-based oxynitride, SrTaO₂N, was synthesized using a sol-gel method and its crystal structure was verified by powder X-ray diffraction (PXRD). The crystal

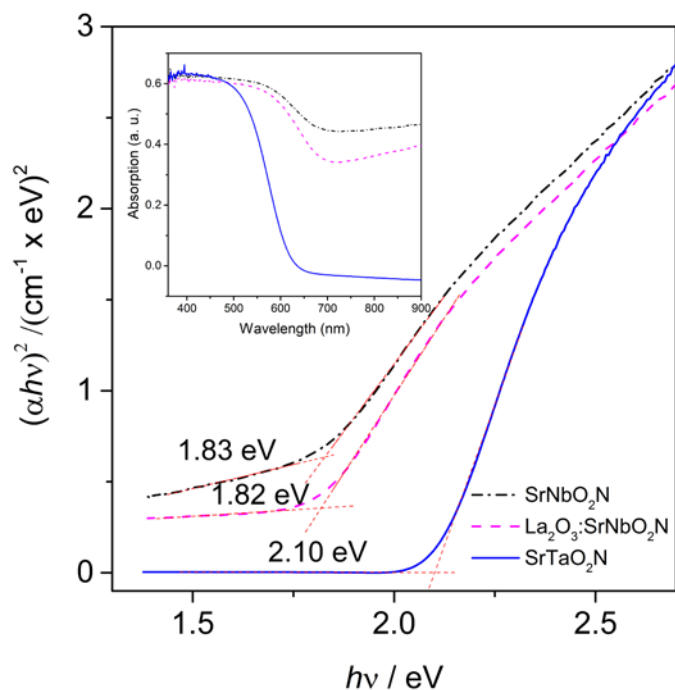


FIGURE 1. Tauc plot of SrNbO₂N, 5 mol% doped SrNbO₂N, and SrTaO₂N. Bandgap values of SrNbO₂N, 5 mol% doped SrNbO₂N, and SrTaO₂N were obtained as 1.83 eV, 1.82 eV, and 2.10 eV, respectively (UV-VIS diffuse reflectance spectra).

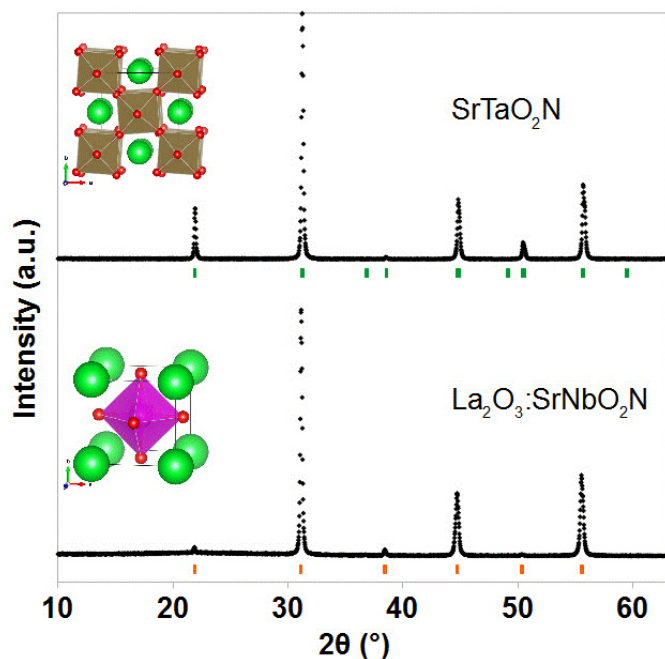


FIGURE 2. Laboratory X-ray powder diffraction for SrTaO₂N (black dots; top) and La₂O₃ doped SrNbO₂N (black dots; bottom) are matched to indexed peaks (green and orange ticks). Each structure (insets) contains Sr (green spheres), O/N (red), and a B-site cation (Nb = purple polyhedron, Ta = tan polyhedron).

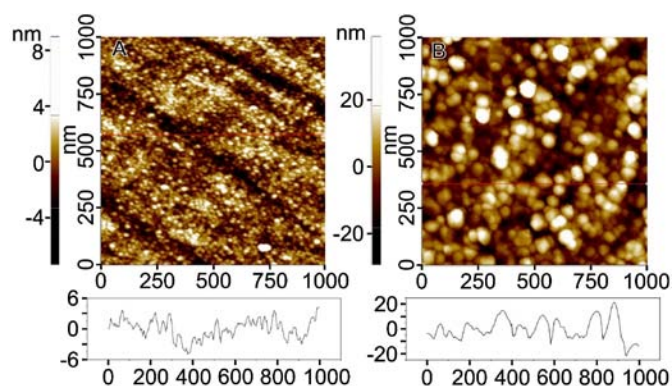


FIGURE 3. AFM image of (a) bare glassy carbon (GC) and (b) Sr₂Nb₂O₇ thin film deposited by PLD and line profile. Roughness of (a) and (b) are 1.3 nm and 7.8 nm, respectively.

structure and PXRD pattern are shown in Figure 2. Due to relativistic effects, tantalum (5+) is more redox stable than niobium (5+) and therefore SrTaO₂N is not expected to form the Ta (4+) oxidation state and thus should not show sub band gap absorption in the IR range. The measured absorption spectrum of SrTaO₂N confirmed this expectation of no IR absorption (Figure 1), while the bandgap was found to have a slightly higher threshold (2.1 eV).

Figure 1 compares the absorption spectra of all three synthesized materials: SrNbO₂N, La doped SrNbO₂N, and SrTaO₂N.

Homogeneous thin film light absorbers without defects are necessary to achieve high efficiency PEC devices. Thin film light absorbers can be deposited by the PLD method. In preparation for a high quality thin film, a robust and dense PLD target pellet is necessary for avoiding inhomogeneous and irreproducible films. High density, thick PLD targets of Sr₂Nb₂O₇ and Sr₂Ta₂O₇ were synthesized by solid-state reactions. Atomic force microscopy (AFM) confirmed the presence of a Sr₂Nb₂O₇ thin film and indicated the surface morphology (Figure 3).

Electrosynthesis of LiCoO₂ is a potentially rapid and cost effective technique to obtain conformal films on a conductive substrate of this OER catalyst. We have demonstrated synthesis of thin films of Li_xCoO₂ on glass carbon substrate and aim to extend this technique to a light absorbing film (photoanode) which has good electrical contact. Developing this technique was further investigated by X-ray photoelectron spectroscopy (XPS). Cobalt 2p XPS core level transitions reveal Co³⁺ and eliminates the presence of Co²⁺ on the electrodeposited film (Figure 4). Co²⁺ is not wanted here as it is more susceptible to dissolution during electrocatalysis and to corrosion in acid and base. This may explain why the electrodeposited film showed high stability during and following electrolysis.

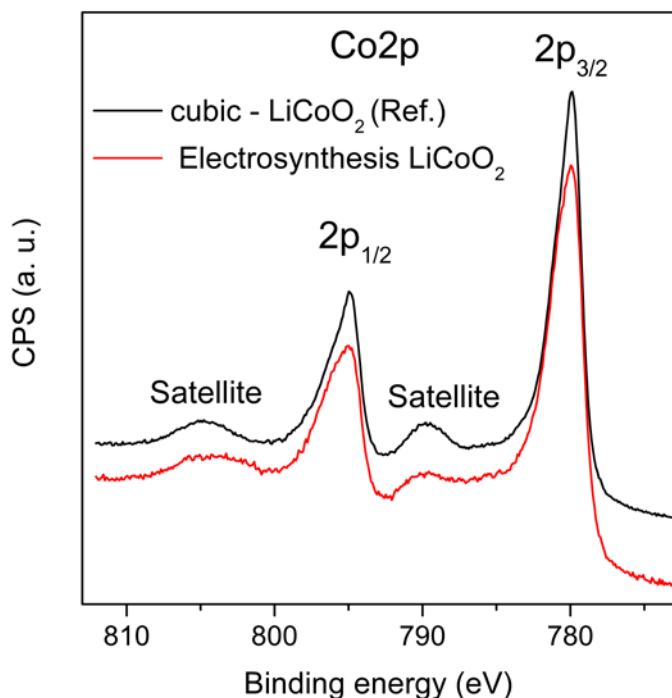


FIGURE 4. X-ray photoemission Co_{2p} spectra of cubic - LiCoO_2 and electrosynthesis LiCoO_2 . $2p_{3/2}$ (780 eV) and satellite peaks (790 eV) are attributed to Co^{3+} .

CONCLUSIONS AND FUTURE DIRECTIONS

Conclusions derived from the work in FY 2015 include the following:

- Lanthanum (3+) doping of SrNbO_2N suppresses near IR absorption, which benefits the optical performance of this material as photoanode.
- Synthesis of a light absorbing oxynitride, SrTaO_2N , was achieved with relatively low bandgap and no absorption in the near IR range.
- Thin film deposition of $\text{Sr}_2\text{Nb}_2\text{O}_7$ by the PLD method was achieved.
- An electrodeposited LiCoO_2 film was produced, and its Co^{3+} oxidation state and OER electrocatalytic activity were confirmed.

Future efforts toward FY 2015–2016 will include the following:

- Enhance carrier mobility in the photoanode perovskite absorber by choice doping
- Fabricate the OER-photoanode perovskite absorber interface
- Fabricate the interface of HER-photocathode pn-silicon absorber

FY 2015 PRESENTATIONS

1. Bin Liu, E. Garfunkel, M. Greenblatt, and G.C. Dismukes. Poster presented to the Metropolitan New York Catalysis Society annual meeting March 18 (1st place, graduate student award poster). “Perovskite-Related Oxynitrides as Photoanodes in Photoelectrochemical Cells.”
2. S. Hwang, G. Gardner, E. Garfunkel, and G.C. Dismukes. Poster presented to the Metropolitan New York Catalysis Society annual meeting, March 18 “Selective Electrochemical Deposition of LiCoO_2 and Its Properties as an Electrocatalyst for Water Oxidation/Oxygen Evolution.”
3. Bin Liu, E. Garfunkel, M. Greenblatt, and G.C. Dismukes. Poster presented to the 29th Annual Symposium of the Laboratory for Surface Modification (Rutgers), April 2. “Perovskite-Related Oxynitrides as Photoanodes in Photoelectrochemical Cells.”
4. S. Hwang, G. Gardner, E. Garfunkel, and G.C. Dismukes. Poster presented to 29th Annual Symposium of the Laboratory for Surface Modification (Rutgers), April 2. “Selective Electrochemical Deposition of LiCoO_2 and Its Properties as an Electrocatalyst for Water Oxidation/Oxygen Evolution.”
5. G.C. Dismukes, A. Laursen, B. Liu, K. Patraju, and M. Greenblatt (Rutgers). Oral presentation to the Electrochemical Society, Chicago, May 28 (Invited). Renewable Hydrogen Evolution on Nickel Phosphide Electrocatalysts: A Comparative Study of Efficiency and Tolerance to Corrosion.”
6. G. Gardner, P. Smith, C. Kaplan, J.F. Al-Sharab, Y.B. Go, M. Greenblatt, and G.C. Dismukes. Oral presentation to the Electrochemical Society, Chicago, May 28. “Understanding the Influence of Structure on Activity and Stability in the Catalysis of the Oxygen Evolution Reaction (OER) Using Crystalline Oxides as a Platform.”
7. G.C. Dismukes, E. Garfunkel, and M. Greenblatt. Poster presented at the DOE Hydrogen and Fuel Cell Program Annual Merit Review (June 9 2015). “Tunable Photoanode-Photocathode-Catalyst Interface Systems for Efficient Solar Water Splitting.”
8. Graeme Gardner, Jafar Al-Sharab, Yong Bok Go, Martha Greenblatt, and G. Charles Dismukes, “Structural Basis for Differing Electrocatalytic Water Oxidation by the Cubic, Layered and Spinel Forms of Lithium Cobalt Oxides,” manuscript in review.