Tunable Photoanode-Photocathode-Catalyst Interface Systems for Efficient Solar Water Splitting

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Project ID# PD121

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Timeline

- Project Start Date: Sept 1, 2014
- Project End Date: Aug 31, 2017
- Percent complete: 55%

Barrier addressed

- Identify methods for, and fabrication of, thin films of both HER and OER catalysts, enhancing amenability to any given photoabsorber system
- Characterize oxynitride perovskite and optimize oxynitride/substrate interfacial chemistry on route to full tandem device

Budget

- Total Project Budget: $749,996
  - Total Recipient Share: NSF disallows
  - Total Federal Share: $749,996
  - Total DOE Funds Spent: $285,942 as of 4/29/16

Unfunded Collaborators

Current:
- Dr. Andrew Rappe (Upenn)
  - Ni$_5$P$_4$ HER theory

Pending:
- Dr. Andriy Zakutayev (NREL)
  - small $E_g$ nitride films
Objectives:

**Long-term**: Effectively leverage the knowledge base of materials chemistry developed in the prior year to fabricate semiconductor/catalyst interfaces, both at the photoanode and photocathode, that attain or exceed the DOE benchmark STH efficiency (~20%). Combine these individual cells into a single device.

**Specific to Current Year (2015-2016):**

- The oxynitride that was determined to be most optimal as a wide gap photoabsorber (E_g ~ 1.8eV) in FY2015 studies, SrNbO_2N, has now been fabricated as a thin film by PLD. Interfacial chemistry with a variety of substrates (glassy carbon, Si (100), and TiN) and absolute electronic structure has been investigated.
- Thin films of OER catalyst cubic LiCoO_2 by a PLD method show stability as a electrocatalyst in base.
- Develop a electrodeposition route to variable thickness thin films of nickel phosphides. Study electrocatalytic properties of these prepared films on Au and n-Si in both acid and base.

Relevance to DOE H₂ & FC Program

**DOE section 3.5.5 of FCTO Multi-Year Research, Development, and Demonstration Plan**

- **System Cost (Barrier B)** – In lieu of pellets and to further decrease system costs versus noble metal catalysts, fabrication methods for films of both HER and OER catalyst materials have been developed.
- **Efficiency (Barrier C)** – Fabricated LiCoO_2 OER catalyst thin films that show long term stability (>12 hours) while retaining high performance (430mV overpotential at 12h; 10mV increase in overpotential versus initial).
- **Durability/Operability (Barrier D)** – Optimized growth conditions of nickel phosphide HER catalyst thin films with high, stable activity in both acidic and basic media.
Integrated Tandem PEC with STH up to 20%

Materials
- Photoanode (1.7eV-2.1eV)
  - SrNbO$_2$N

Photocathode (above 0.8 eV)
- n$^+$p-silicon junction
- Cubic LiCoO$_2$
- Ni$_5$P$_4$

Interface
- OER catalyst interface
- HER catalyst interface

Electrolytes
- Aqueous alkaline solution
- Alkaline exchange membrane

Approach

Project Focuses for FY2016:
A-D and combinations thereof
- Prepare and characterize thin films of A) SrNbO$_2$N
- Develop methods to OER and HER catalyst (C and D) thin films
- Fabricate functioning half cells, 1 and 2 (right) from the combination of A + C and B + D using above developed methodology
Photocathode

Thin film fabrication of hydrogen evolution reaction catalyst on conductive substrate and photocathode

- Achieve Ni$_5$P$_4$ conformal thin films of crystalline nickel phosphide (single phase Ni$_5$P$_4$) directly on glassy C electrodes, Ni$_5$P$_4$@gC, and on C fiber gas diffusion electrodes, Ni$_5$P$_4$@fC
- Achieve uniform crystalline nickel phosphides on photocathode (Si)

Future effort (FY 2016)

- Half cell of thin Ni$_5$P$_4$ – pn junction silicon and performance
Approach – this year

Photoanode

➢ Thin film fabrication of photoanode materials on desired substrates
   — Perovskite oxynitride $ABO_{3-x}N_x$

• Achieve thin film of SrNbO$_2$N on glassy carbon substrate and examine its electronic structure
• Achieve direct transfer of photoanode (SrNbO$_2$N) on photocathode (p-type Si) with TiN diffusion barrier, and characterization of its interfaces

➢ Thin film fabrication of water oxidation catalyst and demonstration of its high catalytic activity

• Achieve thin film of LiCoO$_2$ and verify crystalline structure, morphologies
• Achieve demonstration of high catalytic activity and stability of LiCoO$_2$ thin film

➢ Future effort (FY 2016)

- LiCoO$_2$/gradient doped perovskite oxynitrides photoanode
- Full device interfacial optimization and performance
Accomplishments:
Photocathode device

Thin films of Ni$_2$P and Ni$_5$P$_4$ on a p-type silicon photo absorber

Electrochemical deposition nickel phosphide

- Use of a nickel and phosphorous rich solution under cathodic potentials allows for co-deposition of Ni-P films, which are solvothermally post-annealed, crystallizing nickel phosphides

- Adjusting thin film processing conditions allows for Ni$_5$P$_4$ and Ni$_2$P to be preferentially prepared

- A nickel silicide secondary phase is observed and presumed to be localized interfacially
Accomplishments: HER catalyst thin film characterization

Helium ion Microscopy

- Ni₅P₄ films maintain morphology and thickness through the solvothermal anneal step

AFM

Atomic smoothness of the films is obtained, with roughness, $R_a$, of 1nm (Ni₅P₄) and 2.4nm (Ni₂P) (bottom).

XPS

- Ni₅P₄ films are metallic in character without surface oxidation for both Ni 2p (up) and P 2p (down) core level spectra
- Film resistance using EIS is 18 and 20\(\Omega\) for \(\text{Ni}_2\text{P}\) and \(\text{Ni}_5\text{P}_4\), respectively
- Tafel slope for \(\text{Ni}_2\text{P}\) is 97 while \(\text{Ni}_5\text{P}_4\) is 67 mv/decade
- HER at 10mA/cm\(^2\) for \(\text{Ni}_5\text{P}_4\) required 133 mV less than \(\text{Ni}_2\text{P}\)

Accomplishments:

**HER activity in acid**

- Thickness dependent study for \(\text{Ni}_5\text{P}_4\) on p-Si
  - Tafel slope for thick \(\text{Ni}_5\text{P}_4\) is 50 and intermediate \(\text{Ni}_5\text{P}_4\) is 70 mV/decade
  - Overpotential to drive 10 mA/cm\(^2\) is not significantly changed

**Overpotentials from lit.**
- MoP/n\(^+\) Si: 237 mV
- CoP/n\(^+\) Si: 202 mV

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Accomplishments:
Electronic structure of absorber for photoanode

Pulsed laser deposition for thin film fabrication

**Target preparation:**

- Heating stage
- Laser
- Substrate
- Target

**Pulsed laser deposition:**

- Heating stage
- Laser
- Substrate
- Target

**Films:**

- Post annealing
  - NH$_3$, 900°C

Wide bandgap photo absorber: perovskite oxynitride

Glassy carbon → PLD → Sr$_2$Nb$_2$O$_7$ → NH$_3$, 900°C → SrNbO$_2$N

**UV-Vis DRS**

- 4.89 eV
- 0.68 eV
- 0.4 eV
- 1.86 eV

**XPS valence band**

- 4.21 eV
- 1.86 eV
- 1.18 eV
- 0.68 eV

Work function from KPFM

$W_{SrNbO_2N}$: 4.89 eV
Accomplishments: Photoanode/photocathode interface

Fabrication of thin film of photoanode on photocathode

- Cube-on-cube epitaxial growth
- SrNbO$_2$N layer poorly oriented

X-ray diffraction

HF etching for removing native SiO$_x$
- 3 distinct film layers
- Apparent thickness shows SrNbO$_2$N < TiN
- Oxygen content high in TiN layer
- TiN effectively blocks Si
- Sr is TiN permeable and migrates to SiO$_x$ layer to presumably form SrSiO$_3$

Accomplishments:
- Interface clean prior to post-anneal
- Apparent post-anneal SrSiO$_3$ intergrowth
- Ammonolysis introduces voids
PXRD shows epitaxial LiCoO$_2$ but phase determination is ambiguous from this peak: high temperature (HT) phase $<111>$ @ 19.2° and low temperature (LT) $<003>$ @ 18.9°.

- With 2 active modes expected (vs 4 for LT) at 487 and 597 cm$^{-1}$, Raman confirms HT-LiCoO$_2$.

Accomplishments:
Structure analysis of OER catalyst

XRD

Raman

<table>
<thead>
<tr>
<th>Intensity / a. u.</th>
<th>Raman shift / cm$^{-1}$</th>
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<tr>
<td>10</td>
<td>200</td>
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<td>60</td>
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<td>70</td>
<td>800</td>
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<tr>
<td>LiCoO$_2$ film on Au $T_d = 450$ C</td>
<td>592 cm$^{-1}$</td>
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<tr>
<td>LiCoO$_2$ film on Au $T_d = 400$ C</td>
<td>483 cm$^{-1}$</td>
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<tr>
<td>Au (111)</td>
<td>Au substrate</td>
</tr>
<tr>
<td>Au (100)</td>
<td>592 cm$^{-1}$</td>
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</table>
XPS confirms presence of Li and Co^{3+} oxidation state. Top is phase pure cubic LiCoO_2 and bottom is thin film fabricated by PLD.
Accomplishments:
Thin film OER catalyst electrochemistry

- Water oxidation active requiring 0.42V overpotential initially increasing to 0.43V at 12hrs (vs 0.41V for pressed pellets)

- Tafel slope decreases from 57mV/decade to 55mV/dec. at 12 hrs

Overpotential $\theta_h = 0.42\,\text{V at 10 mA/cm}^2$
Overpotential $\theta_{12h} = 0.43\,\text{V at 10 mA/cm}^2$

1 M NaOH, 5 mV_s
Accomplishments: OER catalyst thin film stability

- Stable in 1M NaOH for >12 h

- Samples undergo an initial induction period, possibly indicative of surface reorganization

Electrolysis at current density = 10 mA cm$^{-2}$
Accomplishments: OER catalyst morphology

Atomic force microscope:

Pristine LiCoO₂  12 h cycled LiCoO₂

Surface roughness ($R_a$) unchanged over course of reaction:
11.8 initially, to 12.2 nm at 12 h
Conformal thin films of crystalline nickel phosphide (single phase Ni$_5$P$_4$) have been synthesized directly on glassy C electrodes, Ni$_5$P$_4$@gC, and on C fiber gas diffusion electrodes, Ni$_5$P$_4$@fC.

Cathodic overpotentials for HER on thin films of Ni$_5$P$_4$@fC are significantly lower than prior spray coated Ni$_5$P$_4$ gas diffusion electrodes, enabling significantly improved cathode performance: 10-fold higher current densities with greatly diminished current spiking from H$_2$ bubbling.

Conformal thin films of HT-LiCoO$_2$ (layered polymorph) have been transferred to gold via PLD and have been converted in situ to spinel-LiCoO$_2$ (the active OER catalyst) electrochemically.

Electrocatalytic activity of the LiCoO$_2$ thin films is comparable to those reported for pressed pellets, efficient and long-term stable.

Thin films of the photoanode oxide material have been transferred to clean silicon surface by PLD and have been converted to the corresponding oxynitrides by ammonolysis to form light absorbers in the 1.8-2.1 eV bandgap region.

TiN has been employed as a thermal diffusion blocking layer for the photoanode/photocathode interface and is effective for Si and Nb, but not for Sr.

Conclusions
Relating to Energy Materials Network

- **Needs:**
  - Wide and/or narrow band gap semiconductors
  - Potential sources:
    - NREL? III-Vs? or JCAP?

- **Unique services Rutgers (we) can provide:**
  - Thin film HER and/or OER catalyst integration with your device
  - Characterization
    - “ultra”-Scanning Tunneling Electron Microscope (STEM)
      - Sub-nm scale
      - Vibration, plasmon, interband-transition and core-shell transition spectra capable
    - Medium Energy Ion Scattering (MEIS)
      - High-resolution-surface- “Rutherford backscatter technique”
    - Helium Ion Microscopy (HeIM)
      - High resolution even for an untreated semiconductor

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http://www.physics.rutgers.edu/meis/MEIS.html
Objective: Investigate and develop tunable photoanode-photocathode-catalyst interface systems for efficient solar water splitting

Key FY2016 technical results:

- Identify methods for, and fabrication of, thin films of both HER and OER catalysts, enhancing amenability to any given photoabsorber system
- Characterize oxynitride perovskite wide bandgap absorber and optimize oxynitride/substrate interfacial chemistry on route to full tandem device