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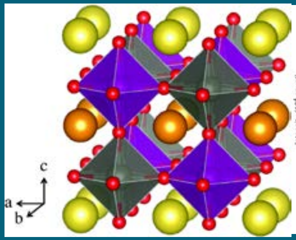
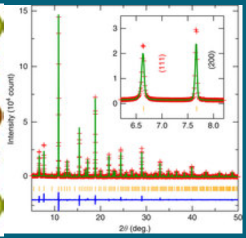
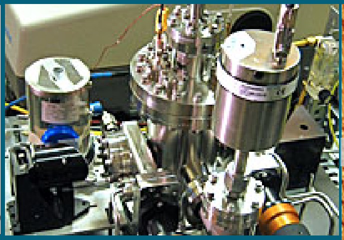
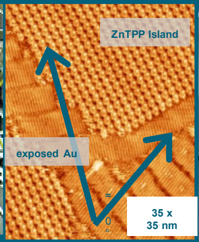
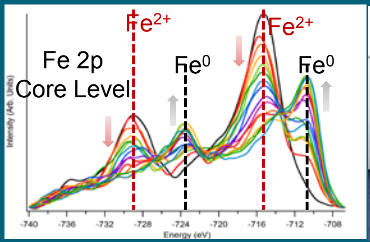
iAMDN Institute for Advanced Materials, Devices, and Nanotechnology

Department of Chemistry & Chemical Biology





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

G. Charles Dismukes (PI), Martha Greenblatt & Eric Garfunkel

Rutgers University

June 9, 2015

NSF-CBET/DOE-EERE joint

Project ID# PD121

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Project Start Date: Sept 1, 2014
- Project End Date: Aug 31, 2017
- Percent complete: 20%

Barriers addressed

- Replace costly low abundance noble metals used as catalysts in PECs & electrolyzers
- Shift from corrosive acid to alkaline electrolytes that extend materials durability w/o efficiency loss
- Photoanode materials for improved light to photochemical efficiency

Budget

- Total Project Budget: $749,996
  - Total Recipient Share:NSF disallows
  - Total Federal Share: $749,996
  - Total DOE Funds Spent*: $31,766

* As of 3/31/15

Unfunded Partners

✓Dr. Peter Khalifah (Stonybrook & BNL) perovskite received

✓ Dr. Andrew Rappe (Upenn) Ni_5P_4 HER theory

In planning:

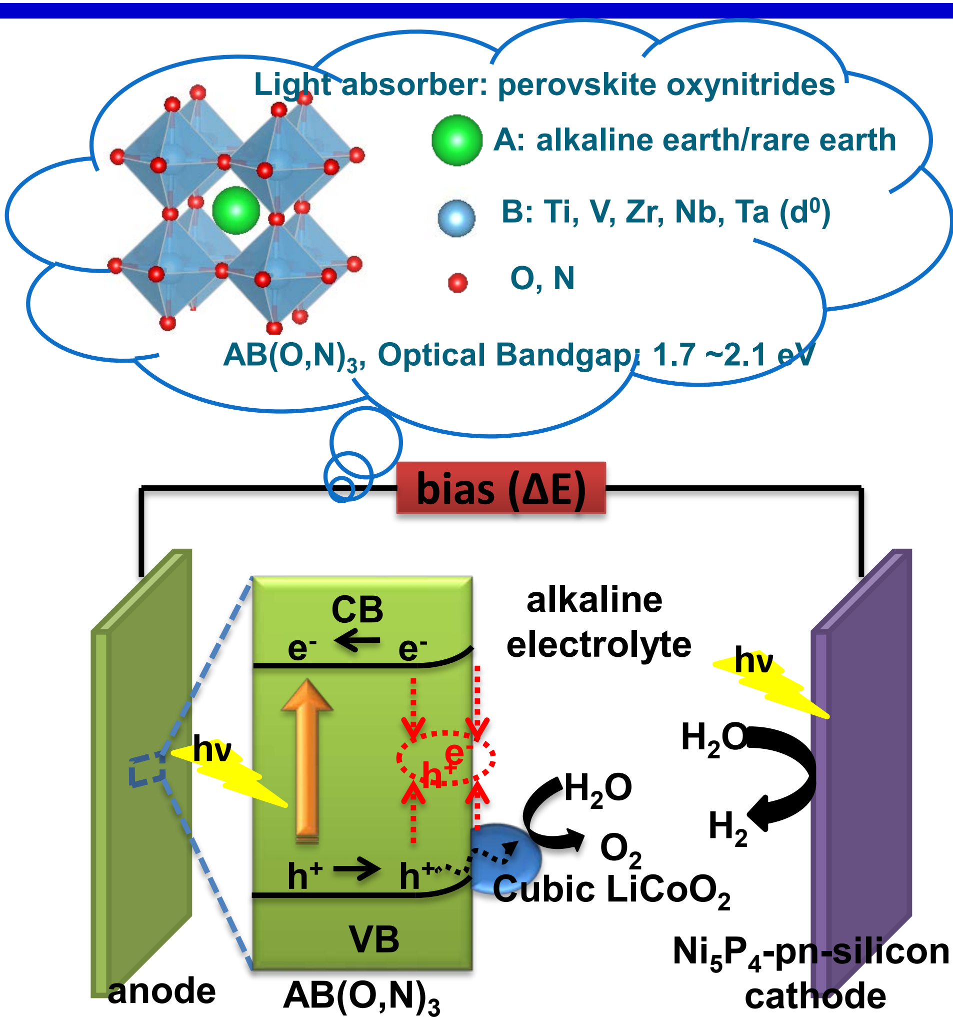
- Dr. Yu Seung Kim (LANL) AEM
- JCAP: testing

Relevance

- **Objectives:**
  - **Long-term:** develop the knowledge base of materials chemistry needed to predict and fabricate semiconductor/catalyst interfaces, both at the photoanode and photocathode, that attain or exceed the DOE benchmark STH efficiency (~10%)
  - **Specific to Current Year**:
    - Synthesize semiconductor light absorbers for longer wavelength absorption: selected 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
    - Prepare thin films of OER catalyst cubic $LiCoO_2$ both in direct contact with the photoanode and as a buried junction with intervening transparent conductor (TCO)
    - Develop alkaline electrolytes compatible with both the OER and HER half-reactions

- **Relevance to DOE H_2 & FC Program**
  - Materials Efficiency (Barrier AE) Photoanode materials for improved light to photochemical efficiency – perovskite oxynitrides
  - Auxiliary Materials (Barrier AI) Replace costly low abundance noble metals used as catalysts in PECs & electrolyzers - thin films of OER catalysts cubic $LiCoO_2$
  - Materials Durability- Shift from corrosive acid to alkaline electrolytes that extend materials durability w/o efficiency loss – developed alkaline compatible HER catalyst

Approach - Overview

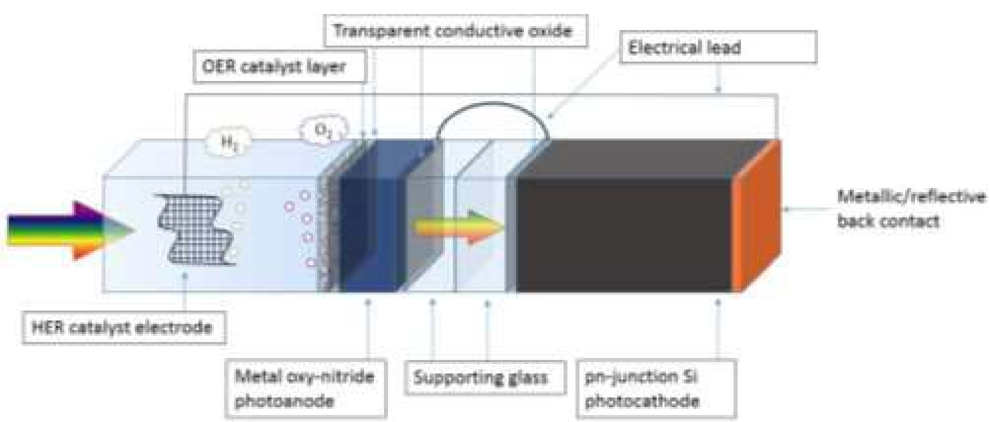


- Synthesize and investigate selected phase-pure members of perovskite oxynitride series AB(O,N)$_3$ as long wavelength absorbers
- Characterize the optical bandgaps and photoinduced carrier lifetime of these materials in preparation of attaching OER catalyst
- Using pulsed laser excitation deposit photoanode as thin film structure
- Deposit onto pn-silicon photocathode Ni_5P_4 HER catalyst
- Investigate two electrolytes system: aqueous alkaline electrolyte solution (pH=14) and alkaline exchange membrane
- Device expected: Photoelectrochemical cell with STH efficiency of ~10%

Approach - Overview

Rutgers team approach to high solar-to-H_2 efficiency

- **Integrated Tandem PEC with STH up to 10%**
  - materials
    - Photoanodes (1.7eV-2.1eV)
      - Perovskite oxynitrides
    - Photocathode (above 0.8 eV)
      - pn-silicon junction
  - interface
    - OER catalyst interface
      - Cubic $LiCoO_2$
    - HER catalyst interface
      - Ni_5P_4
  - electrolytes
    - 1) Aqueous alkaline solution
    - 2) Alkaline exchange membrane (AEM)

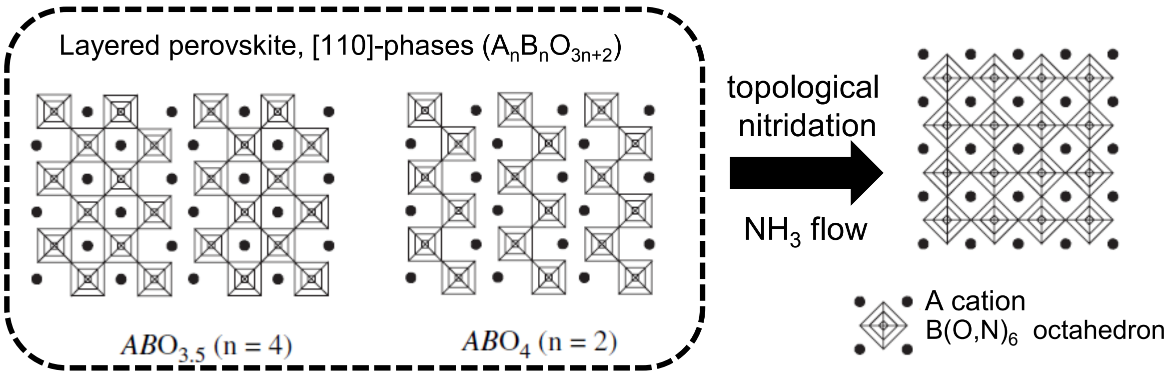


➢ Project Focus:

- longer wavelength absorber for photon capture & conversion
- Electrosynthesis methods to create photoelectrode-interfaces to OER/HER catalysts
- alkaline electrolyte for trouble-free op.

Approach – this year

- Photoanode materials with tunable optical absorbance – perovskite oxynitrides $ABO_{3-x}N_x$
- Method: convert layered perovskite oxides ABO_3 to perovskite oxynitrides by topological nitridization using NH_3 treatment



Merit:
easy to adapt to thin film preparation

- Future efforts (FY 2015):
- Optimize the stability & bandgap by tuning the N content (realized by doping the B site transition metal & controlling charge balance)

Approach – this year

How to selectively form a thin film of the cubic form of $LiCoO_2$ OER catalyst onto a conducting oxide?

- Obstacles: avoid forming inactive layered $LiCoO_2$ polymorph and unstable Co_3O_4 spinel.
- Achieve uniform surface coverage with minimum defects and thickness
- Achieve low impedance (conducting) interface

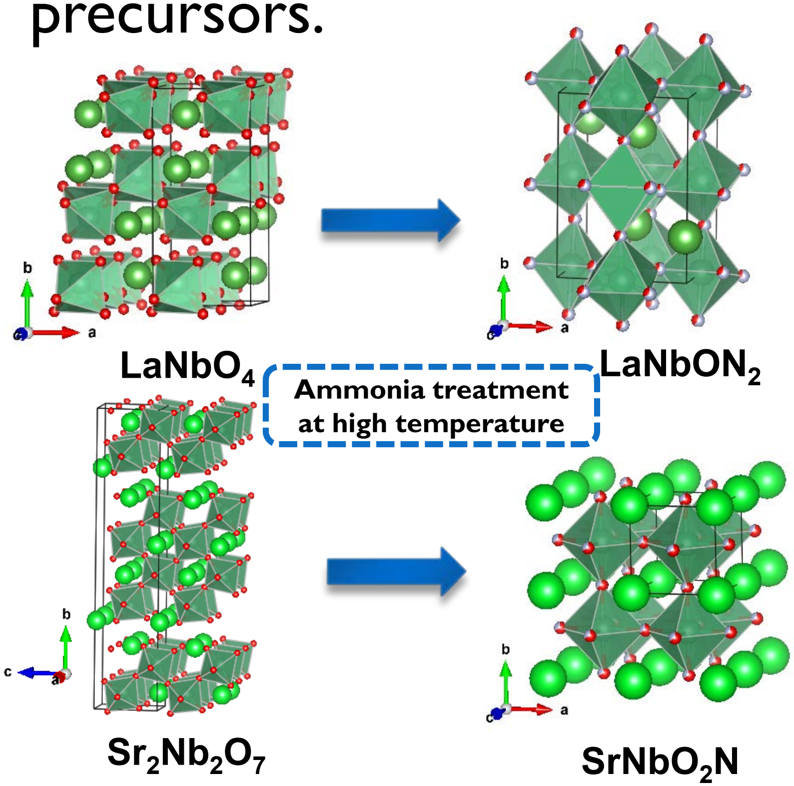
Future Effort (FY 2015): Apply above methods to fabricate these interfaces:

- OER/ photoanode perovskite absorber
- HER/photocathode pn-Silicon absorber
  - Achieve minimum optical defects & retain the above interfacial gains

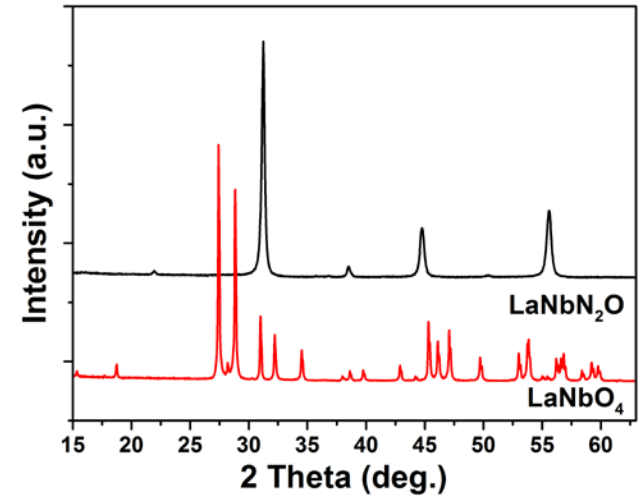
Accomplishments:

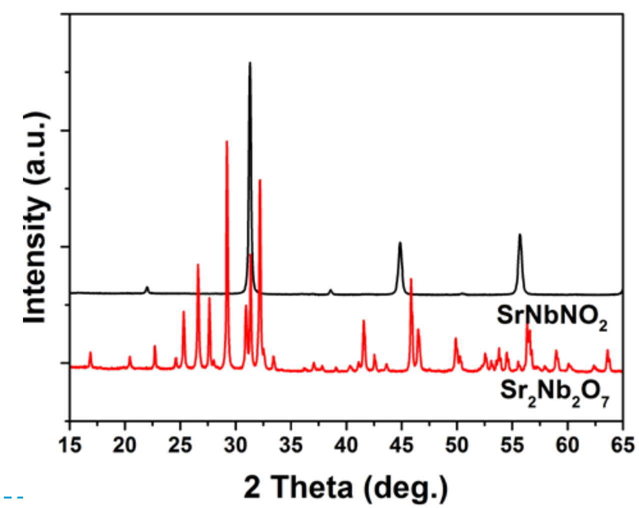
synthesis of $ANb(O,N)_3$ A = La & Sr

- Two phase-pure oxynitrides $LaNbON_2$ and $SrNbO_2N$ have been synthesized by using the topological nitridation of the oxide precursors.



Structural validation by powder XRD



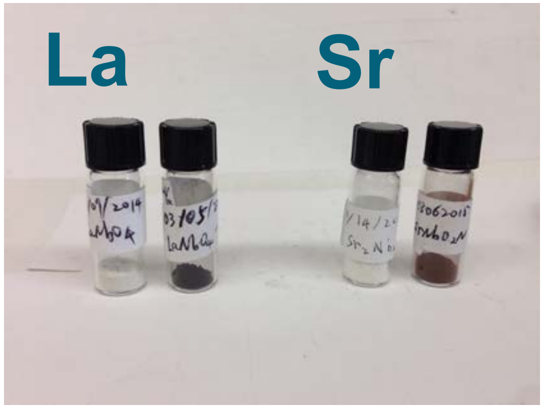


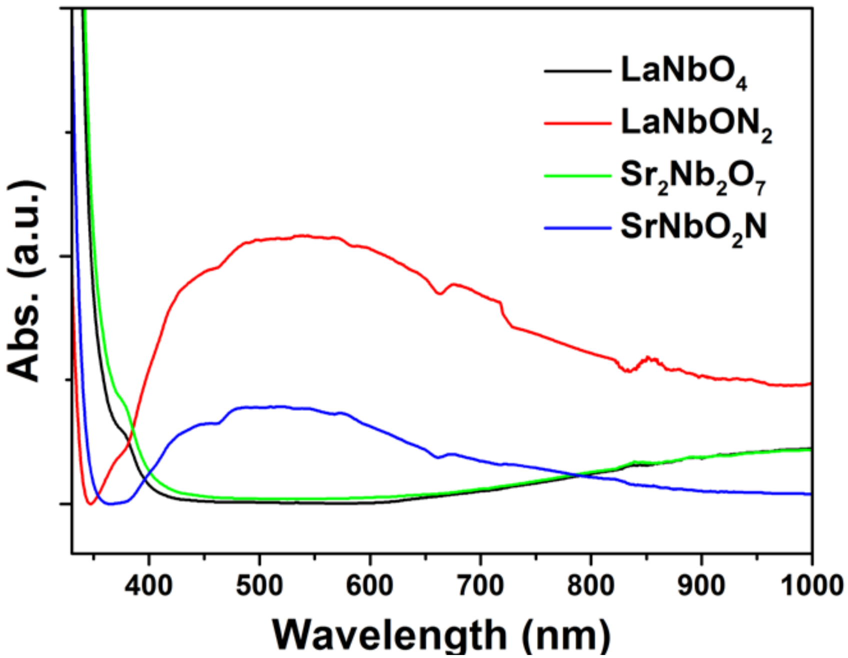
Accomplishments:

Optical properties of $ANb(O,N)_3$ A = La & Sr

- **Results:**
  - Both $LaNbON_2$ and $SrNbO_2N$ showed significant absorbance in the visible light region.
  - However, the optical bandgap is hard to determine from the UV-Vis spectra. The tail may be due to the partial reduction of Nb from 5+ to 4+. Further efforts will be made to modify the nitridization conditions.

- **Achievement to the goal:**
  - According to the design of our tandem PEC configuration, the photoanode requires a semi-conducting material with a bandgap in the range of 1.7eV ~ 2.1eV.
  - These oxynitrides are good candidates for this application, although further efforts are still necessary to optimize the optical properties.



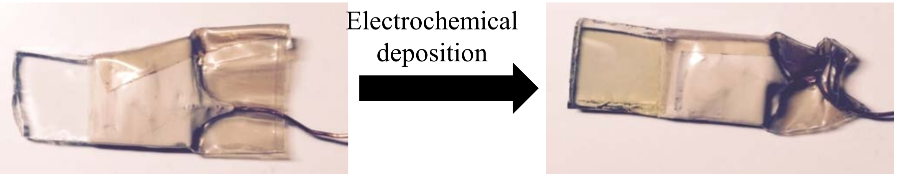


Accomplishments: Electrosynthesis of OER thin films

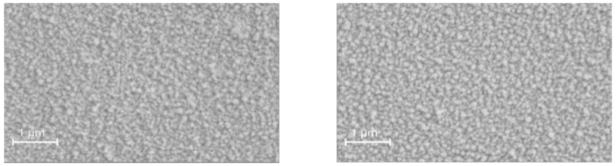
- Novel electrochemical synthesis of cubic spinel Li_xCoO_2 ($0 \leq x \leq 1$) film was achieved.
- Appropriate thickness confirmed by Scanning Electron Microscopy (SEM)
- Surface specific chemical composition of Co, O & Li determined by Rutherford Backscattering Spectrometry (RBS), & Nuclear Reaction Analysis (NRA)
- OER film performance confirmed by a) i-V polarization, b) O_2 production confirmed by GC, and (c) ohmic resistivity determined by electrochemical Impedance spectroscopy.

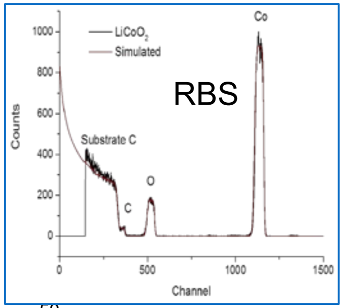
Bare TCO electrode

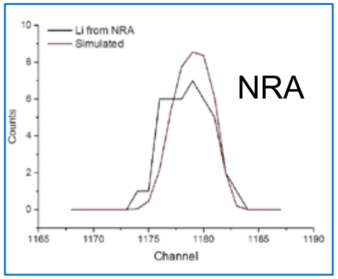
Li_xCoO_2/TCO electrode

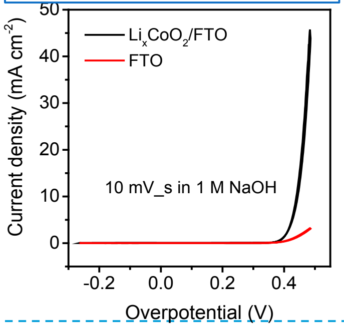


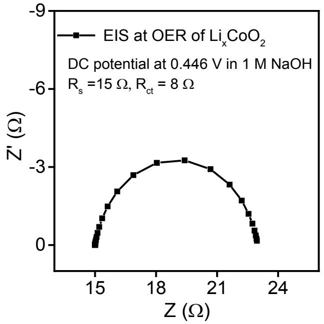
SEM of Li_xCoO_2/FTO film before (L) & after (R) 14 h electrolysis





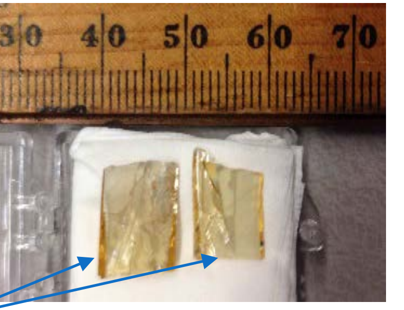




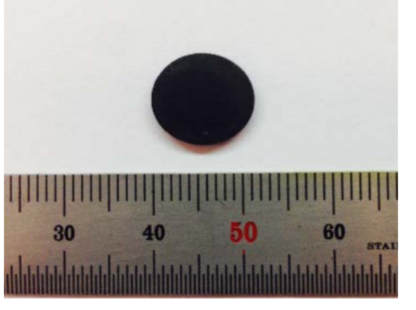


Accomplishments:
Towards Perovskite absorber-OER interface

- $La_2Ti_2O_7$ single crystal* perovskite to be used for developing pulsed laser desorption (pld) methods for OER film formation
- OER laser target for pld transfer was prepared from cubic $LiCoO_2$ material
- HER laser target for pld transfer was prepared from Ni_5P_4
- Access & training to Rutgers PLD system identified



$La_2Ti_2O_7$ single crystals



$LiCoO_2$ pellet for pld target

* provided by *Prof. Peter Khalifah*

Accomplishments:
Responses to previous year's reviewers' comments

- No reviews. This project began on Sept 1, 2014.

Collaborations- Unfunded Partners – this year:

- Stony Brook University

  Prof. Peter Khalifah – $La_2Ti_2O_7$ single crystal sample received. For use in developing PLD methods for transfer of OER material to perovskite absorber

- UPenn Materials Science and Pennergy Center

  Prof. Andrew Rappe – computational studies initiated of nickel phosphides and their interfaces for applications to interfacial charge transfer and HER catalysis

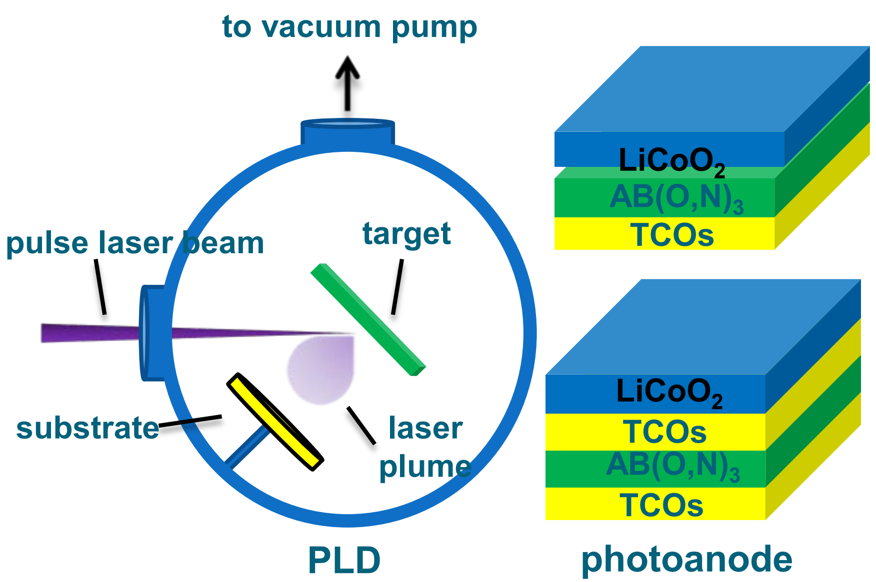
- Proton OnSite

  Dr. Katherine Ayers – will test OER activity of $LiCoO_2$ in alkaline membrane electrolyzer stack

Remaining Challenges and Barriers

- Evaluation of the stability of perovskite oxynitrides-electrolyte junctions under illumination will be key challenges to evaluate in the coming year (no effort thus far)

- Formation of charge transfer interfaces between photocathode and existing HER Ni_5P_4 catalyst, and between photoanode and existing OER $LiCoO_2$ will be key challenges to evaluate in the coming year (no effort thus far)



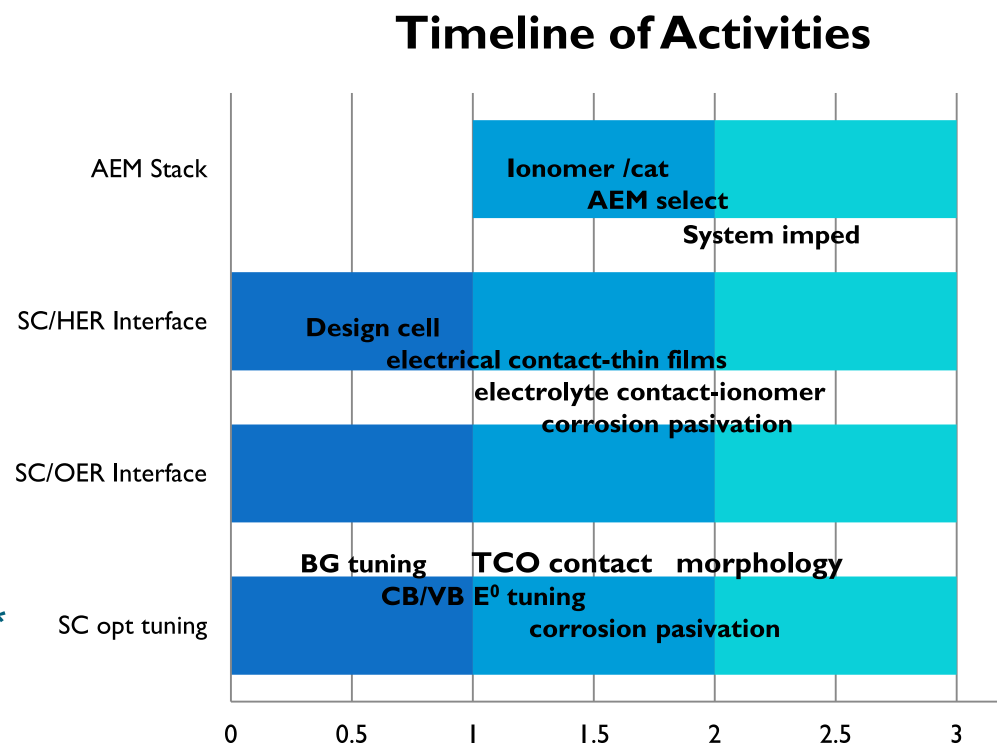
Proposed Future Work

A timeline of expected activities during the 3 year grant period broken down in five activities:

1) Photoanode optical tuning
2) Photoanode/OER catalyst interface
3) Photocathode/HER catalyst interface
4) Alkaline exchange membrane/PEC stack integration
5) System testing

In 2015-16 we shall:

- Optically characterize photoanode absorbers: $LaNbON_2$ and $SrNbO_2N$
- HER Ni_5P_4 stability/activity with AEM*
- OER $LiCoO_2$ stability/activity with AEM*
- Create these interfaces by PLD
  - HER Ni_5P_4 /pn-Silicon
  - OER $LiCoO_2$ /perovskite



Technology Transfer Activities

- Evaluation of $LiCoO_2$ as potential replacement for IrO_2 anode in alkaline electrolyzer configuration will be conducted by Proton OnSite (Dr. Katherine Ayers)

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Summary

- Successful synthesis of phase pure forms of two perovskite oxynitrides: $LaNbON_2$ and $SrNbO_2N$, has been achieved
- Optical characterization of these materials as long wavelength absorbers is in progress
- Novel electro-synthesis method developed for formation of thin films of cubic $LiCoO_2$ OER catalyst
- Successful testing of OER $LiCoO_2$ and HER Ni_5P_4 catalysts in alkaline electrolyte, pH 14 NaOH
- PLD targets made for OER and HER materials and PLD in progress
- Archtypical perovskite single crystal acquired for thin film deposition

Publications & Presentations (this year)

- G.C. Dismukes, E. Garfunkel, M. Greenblatt. Poster presented at the AMR Hydrogen program annual review (June 9 2015). Tunable Photoanode-Photocathode-Catalyst Interface Systems for Efficient Solar Water Splitting
- G. C. Dismukes (Rutgers University), 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"
- G. Gardner, P. Smith, C. Kaplan, J. F. Al-Sharab, Y. B. Go, M. Greenblatt, and G. C. Dismukes (Rutgers University). 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"
- Bin Liu, E. Garfunkel, M Greenblatt, and G. C. Dismukes. Poster presented to the Metropolitan New York Catalysis Society annual meeting March 18 (award poster) "Perovskite-related oxynitrides as photoanodes in photoelectrochemical cells"
- Bin Liu, E. Garfunkel, M Greenblatt, and G. C. Dismukes. Poster presented to the 29th Annual Symposium of the Laboratory for Surface Modification April 2. "Perovskite-related oxynitrides as photoanodes in photoelectrochemical cells"