Department of Chemistry & Chemical Biology

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Institute for Advanced Materials, Devices and Nanotechnology

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

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April 29, 2016

NSF-CBET/DOE-EERE joint
Project ID# PD121

Overview

Timeline

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

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

Barriers addressed

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

Unfunded Collaborators

Current:

- Dr. Andrew Rappe (Upenn)
  - Ni_5P_4 HER theory

EMN, pending:

- Dr. Andriy Zakutayev (NREL)
  - small E_g nitride films

Relevance

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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 (Eg ~ 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 H_2 & 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 overpotentital 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

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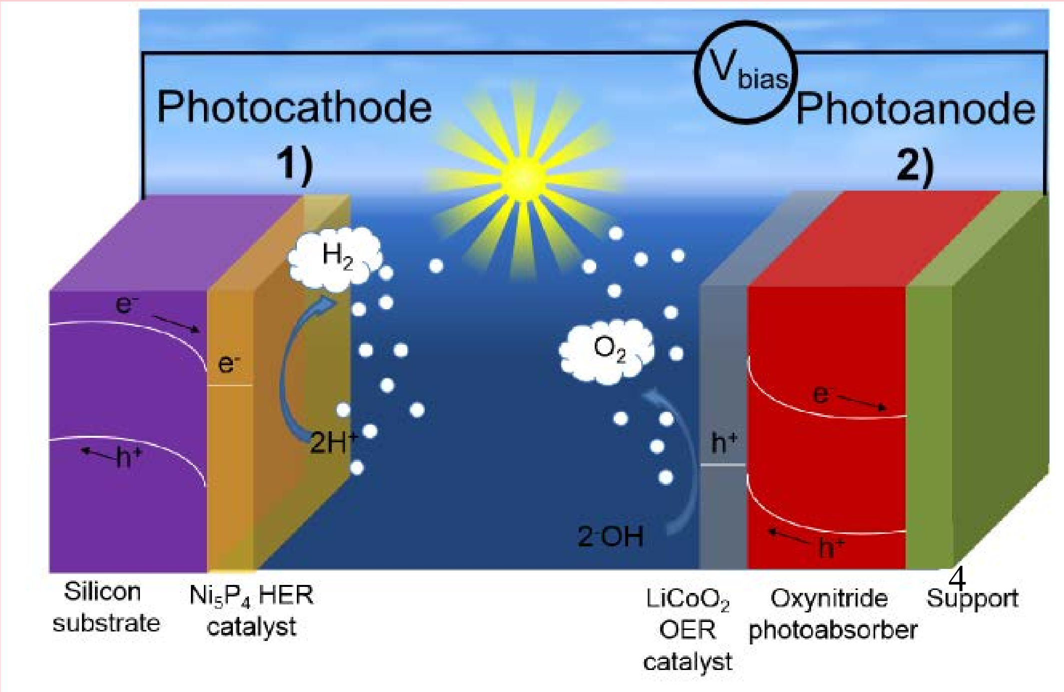
Approach

- Integrated Tandem PEC with STH up to 20%
  - Materials
    - Photoanode (1.7eV-2.1eV)
      - **A)** $SrNbO_2N$
    - Photocathode (above 0.8 eV)
      - **B)** n^+p-silicon junction
  - Interface
    - OER catalyst interface
      - **C)** Cubic $LiCoO_2$
    - HER catalyst interface
      - **D)** Ni_5P_4
  - Electrolytes
    - Aqueous alkaline solution
    - Alkaline exchange membrane

<u>Project Focuses for FY2016:</u>

A-D and combinations thereof

- Prepare and characterize thin films of **A**) $SrNbO_2N$
- 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



Approach – this year

Photocathode

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

- Achieve Ni_5P_4 conformal thin films of crystalline nickel phosphide (single phase Ni_5P_4) directly on glassy C electrodes, Ni_5P_4@gC, and on C fiber gas diffusion electrodes, Ni_5P_4@fC
- Achieve uniform crystalline nickel phosphides on photocathode (Si)

- Future effort (FY 2016)

- Half cell of thin Ni_5P_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 $SrNbO_2N$ on glassy carbon substrate and examine its electronic structure
- Achieve direct transfer of photoanode ($SrNbO_2N$) 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

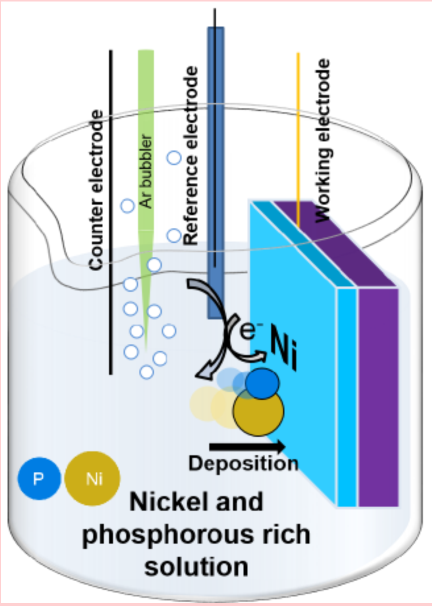
- Future effort (FY 2016)

- $LiCoO_2$/gradient doped perovskite oxynitrides photoanode
- Full device interfacial optimization and performance

Accomplishments:
Photocathode device

Thin films of Ni_2P and Ni_5P_4 on a p-type silicon photo absorber

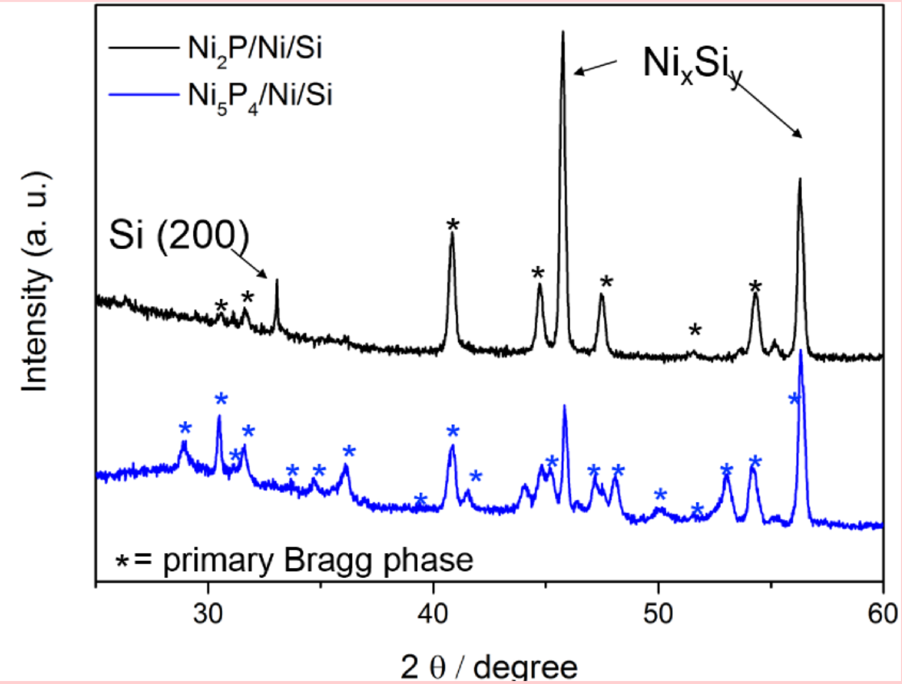
Electrochemical deposition nickel phosphide



Post solvothermal anneal

- 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

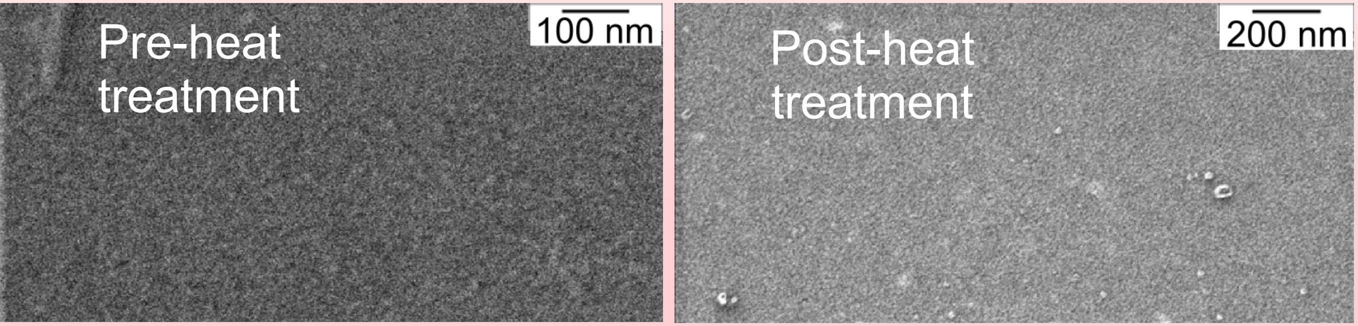
XRD



- Adjusting thin film processing conditions allows for Ni_5P_4 and Ni_2P to be preferentially prepared
- A nickel silicide secondary phase is observed and presumed to be localized interfacially

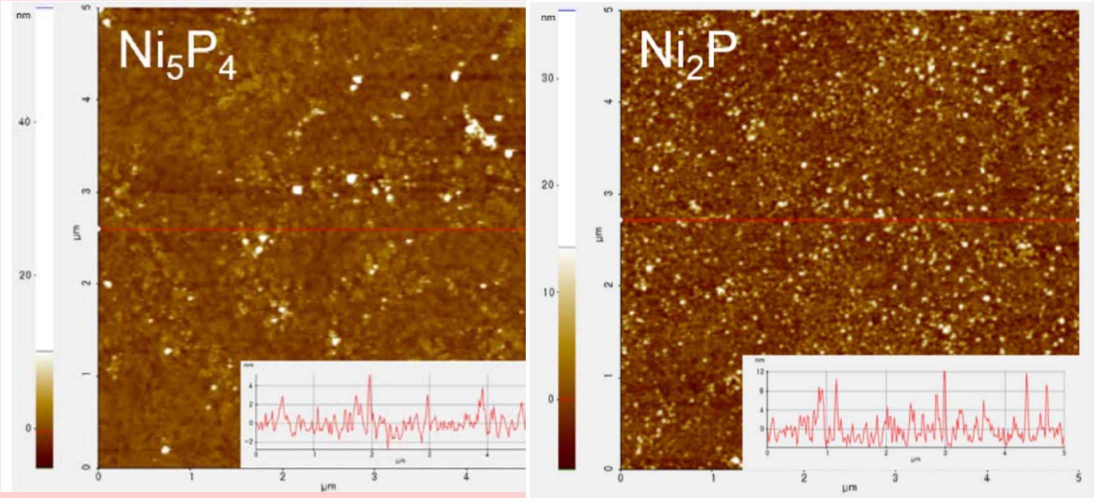
Accomplishments:
HER catalyst thin film characterization

Helium ion Microscopy



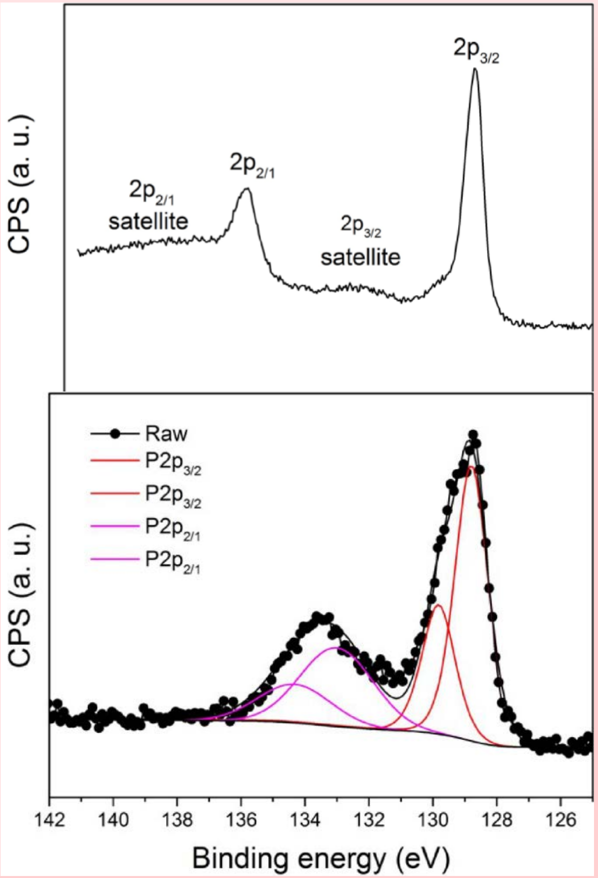
- Ni_5P_4 films maintain morphology and thickness through the solvothermal anneal step

AFM



Atomic smoothness of the films is obtained, with roughness, R_a, of 1nm (Ni_5P_4) and 2.4nm (Ni_2P) (bottom).

XPS



-Ni_5P_4 films are metallic in character without surface oxidation for both Ni 2p (up) and P 2p (down) core level spectra

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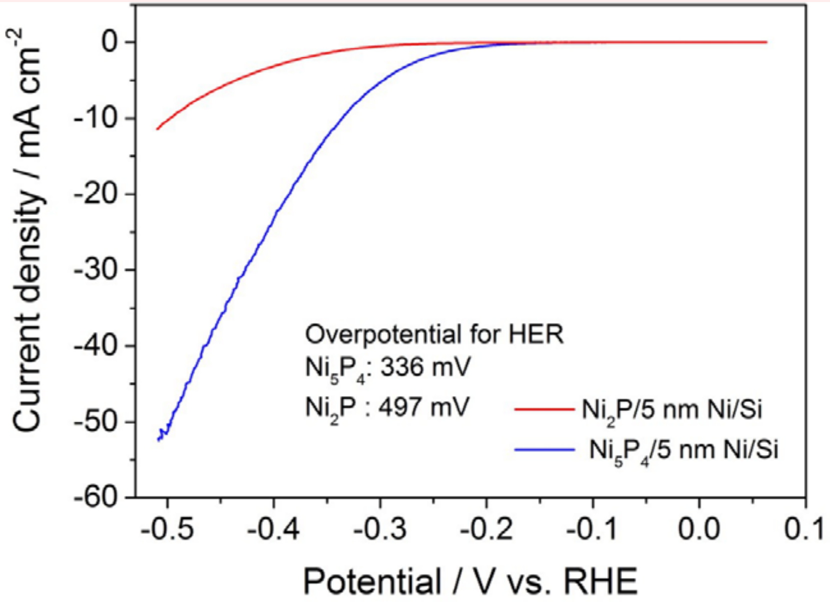
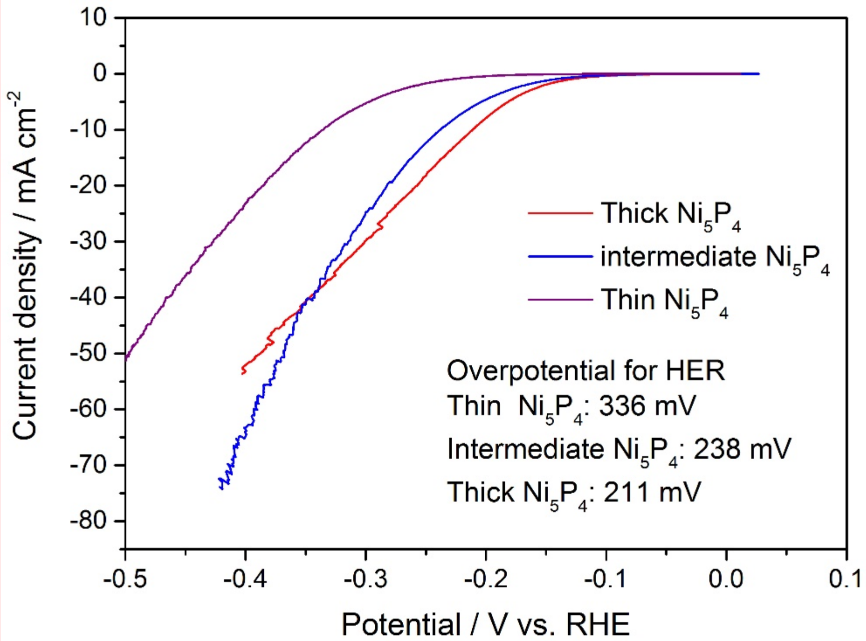
Accomplishments:
Photocathode electrocatalytic performance

HER activity in acid



- Film resistance using EIS is 18 and 20Ω for Ni_2P and Ni_5P_4, respectively
- Tafel slope for Ni_2P is 97 while Ni_5P_4 is 67 mv/decade
- HER at 10mA/cm^2 for Ni_5P_4 required 133 mV less than Ni_2P



- Thickness dependent study for Ni_5P_4 on p-Si Tafel slope for thick Ni_5P_4 is 50 and intermediate Ni_5P_4 is 70 mV/decade
- Overpotential to drive 10 mA/cm^2 is not significantly changed

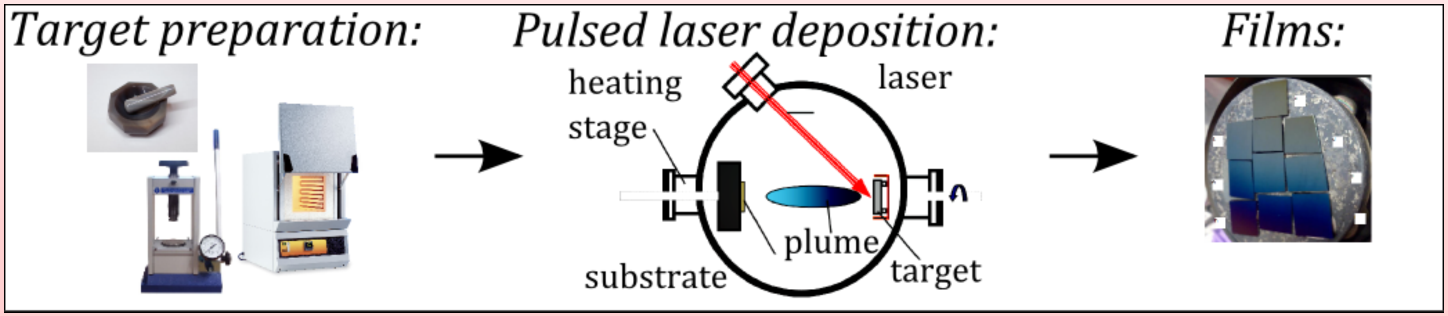
Overpotentials from lit.
MoP/n$^+$ Si: 237 mV
CoP/n$^+$ Si: 202 mV

Jaramillo *et al.*,
Adv. Energy Mater. **2015**, 1501758

Accomplishments:

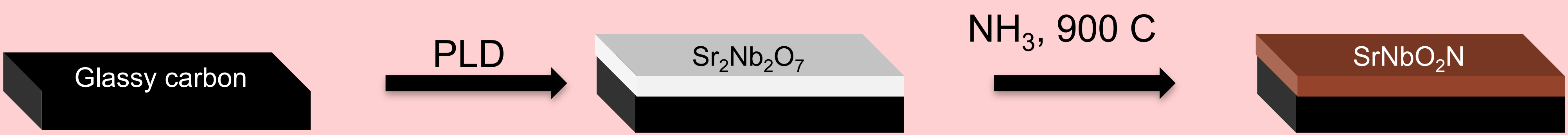
Electronic structure of absorber for photoanode

Pulsed laser deposition for thin film fabrication

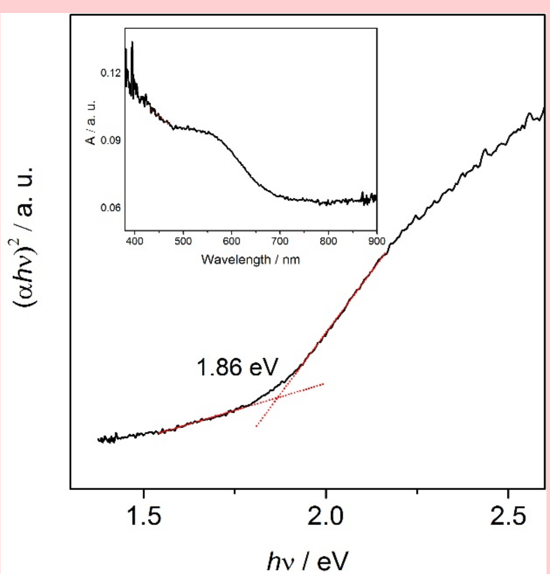


Wide bandgap photo absorber: perovskite oxynitride

Post annealing



UV-Vis DRS



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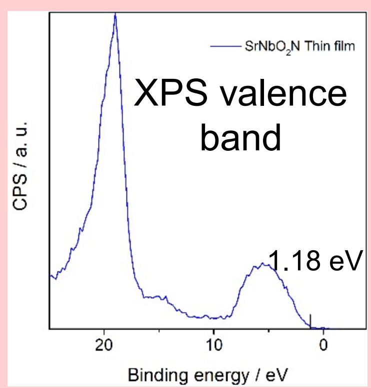
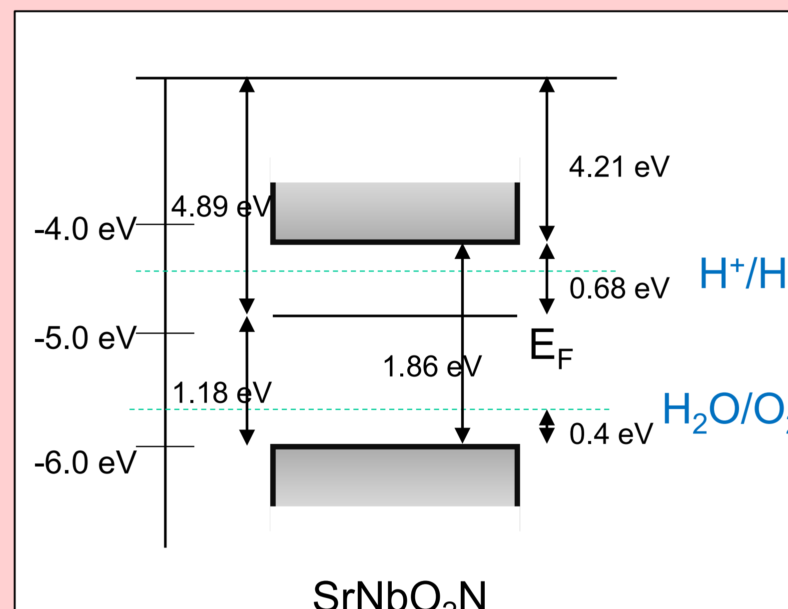


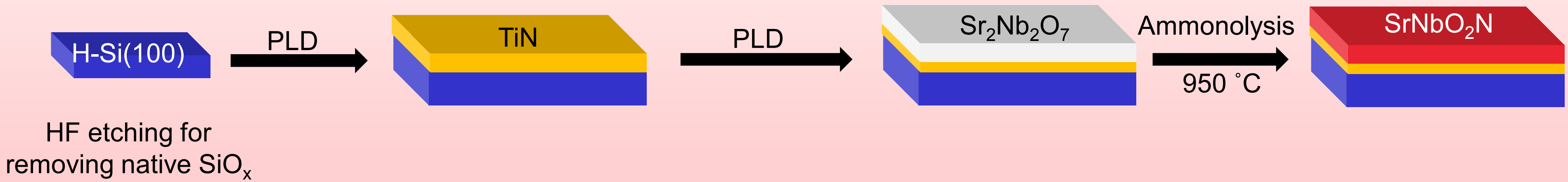
Work function from KPFM

$W_{SrNbO2N}$: 4.89 eV



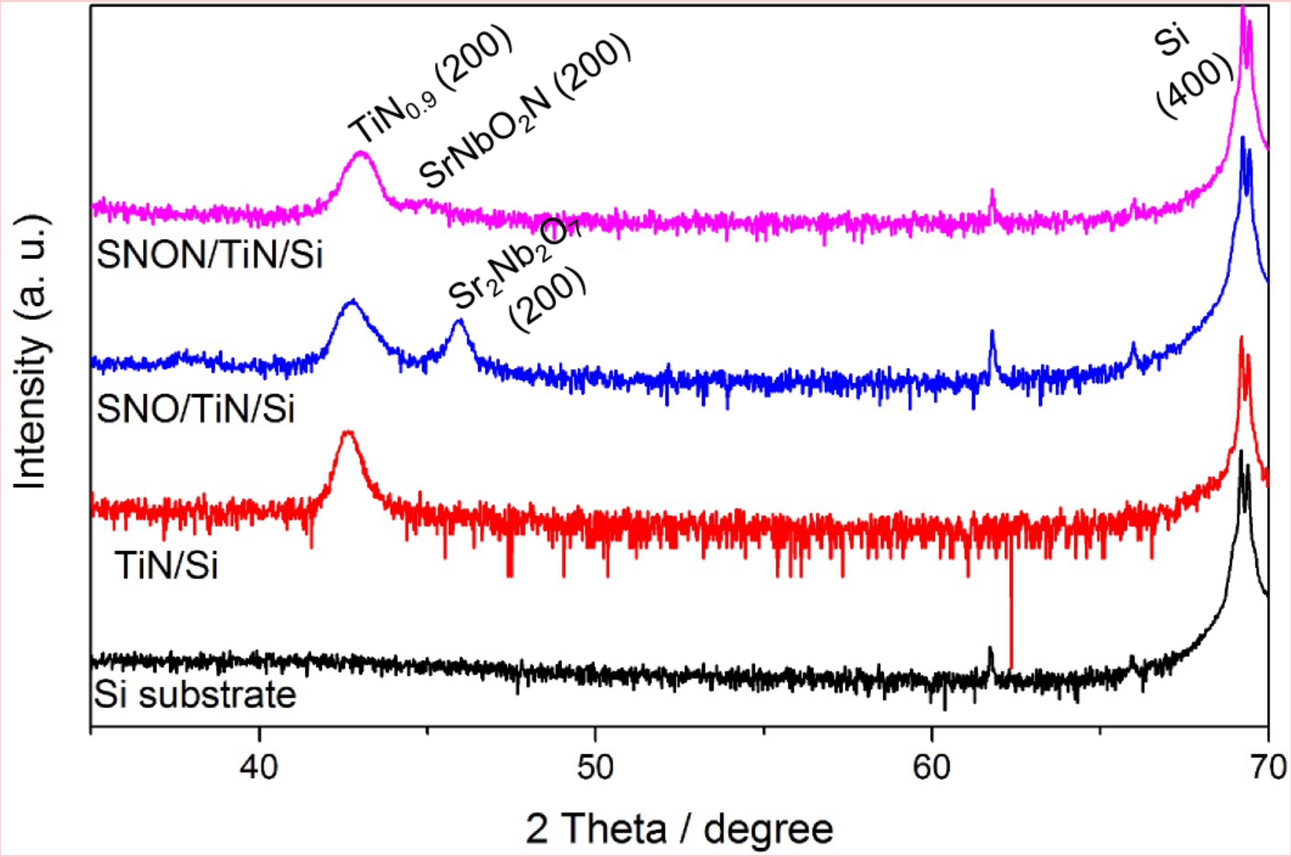
Accomplishments:
Photoanode/photocathode interface

Fabrication of thin film of photoanode on photocathode



X-ray diffraction

- Cube-on-cube epitaxial growth
- $SrNbO_2N$ layer poorly oriented



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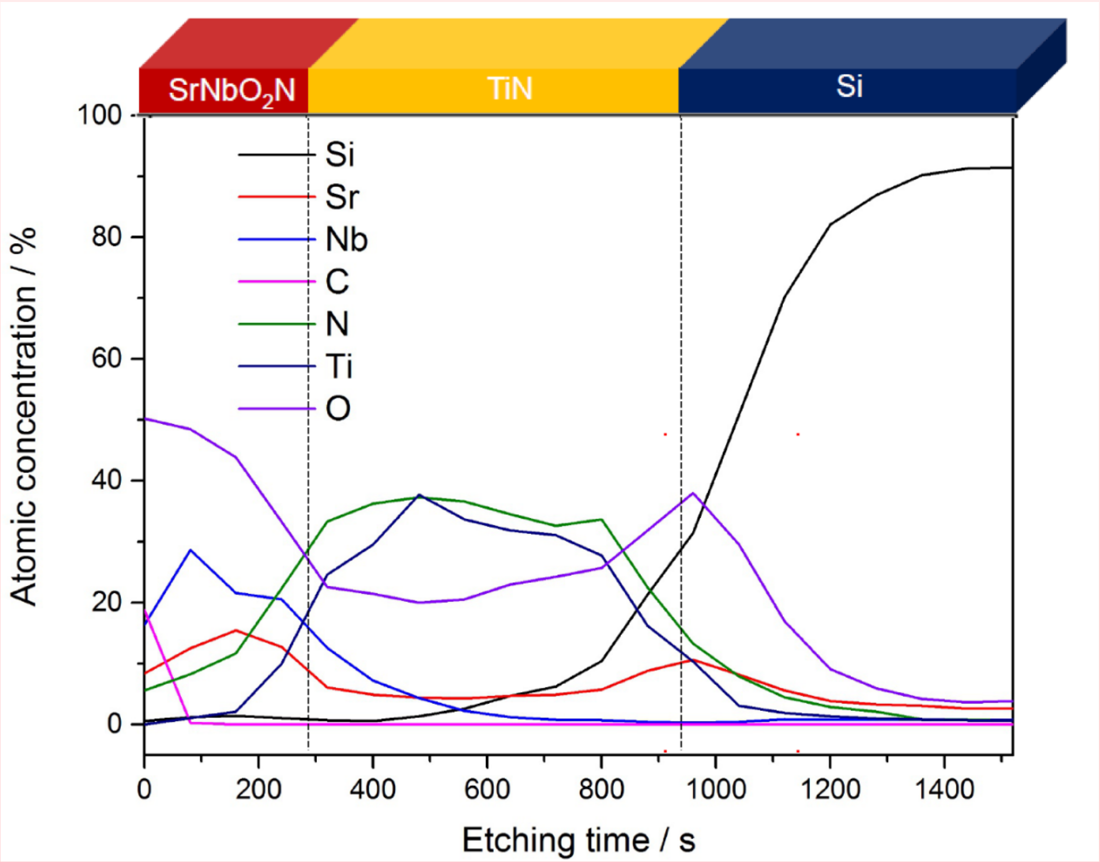
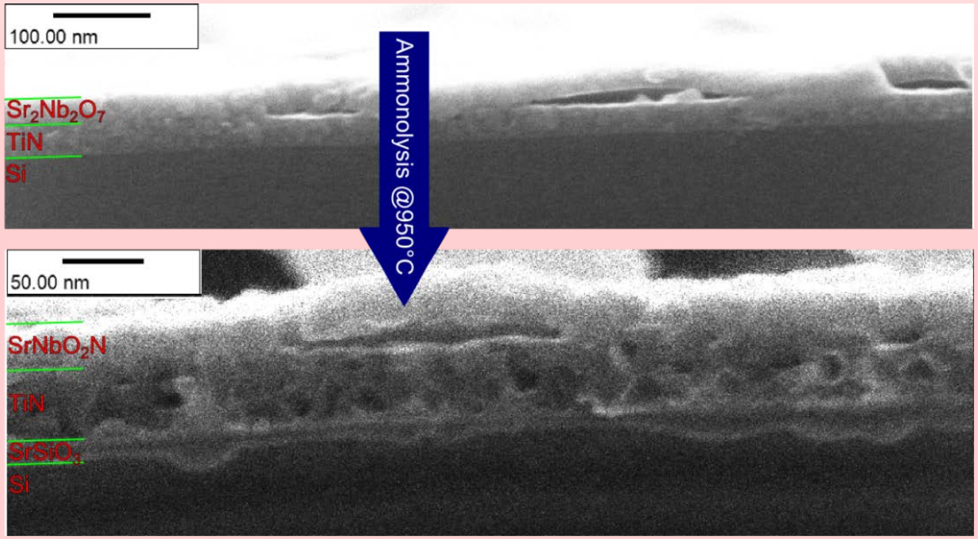
Accomplishments:
Photoanode/photocathode interface

Depth profiled XPS



HeIM



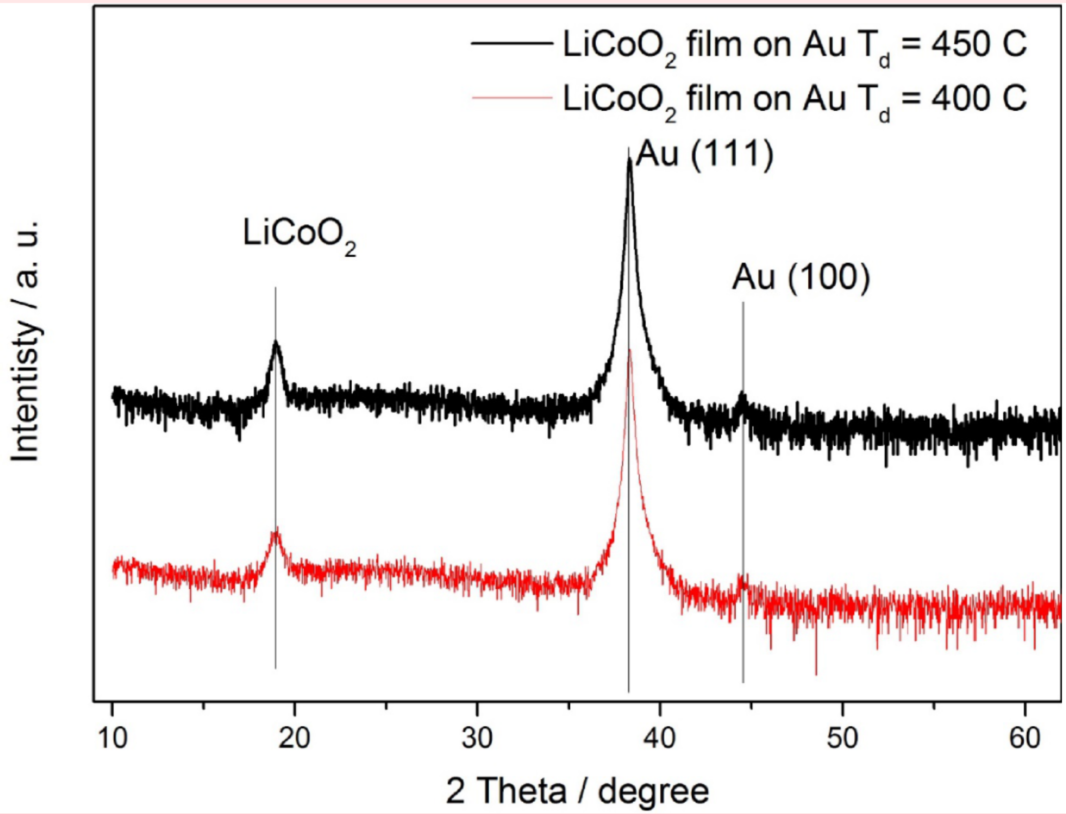
- 3 distinct film layers
- Apparent thickness shows $SrNbO_2N$ < TiN
- Oxygen content high in TiN layer
- TiN effectively blocks Si
- Sr is TiN permeable and migrates to SiO_x layer to presumably form $SrSiO_3$

- Interface clean prior to post-anneal
- Apparent post-anneal $SrSiO_3$ intergrowth
- Ammonolysis introduces voids

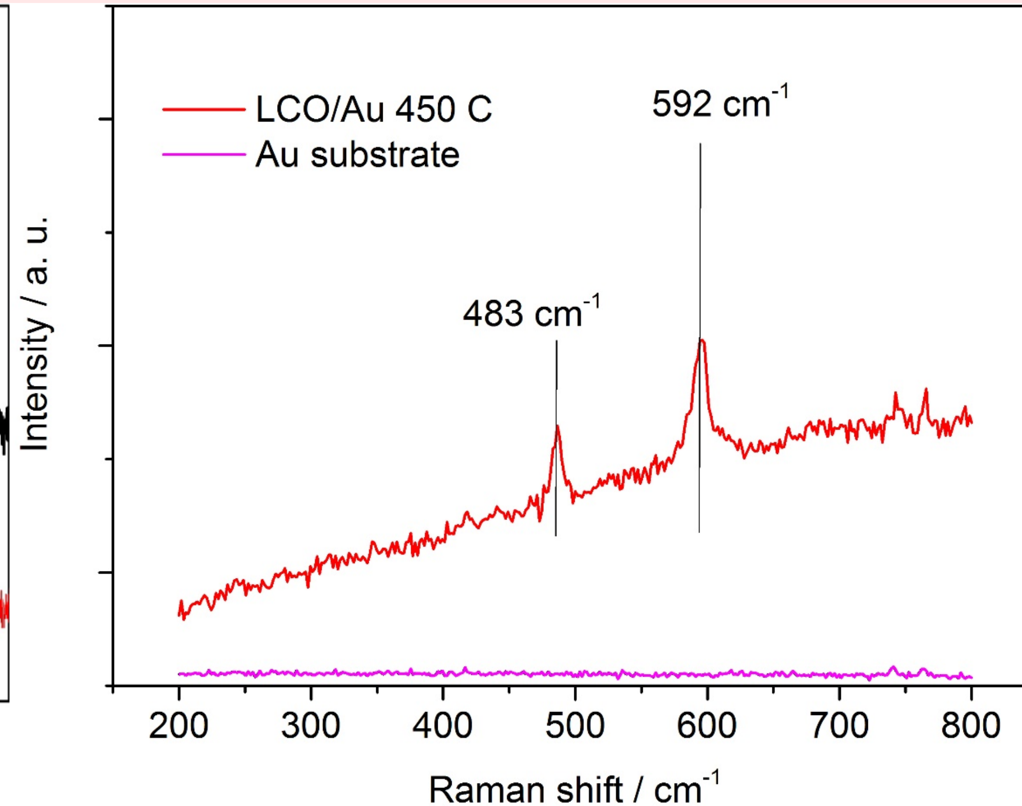
Accomplishments:

Structure analysis of OER catalyst

XRD



Raman

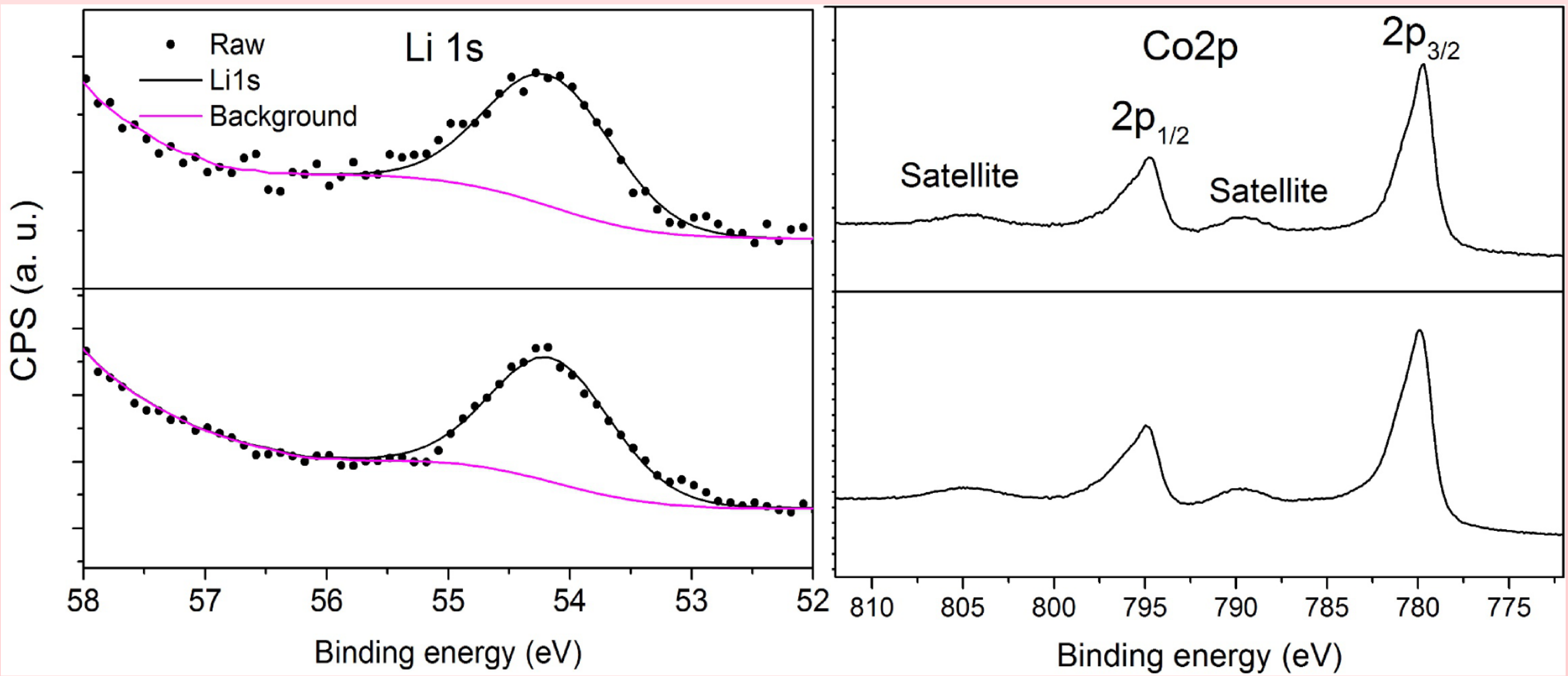


- PXRD shows epitaxial $LiCoO_2$ but phase determination is ambiguous from this peak: high temperature (HT) phase <111> @ 19.2° and low temperature (LT) <003> @ 18.9°

- With 2 active modes expected (vs 4 for LT) at 487 and 597 cm^{-1}, Raman confirms HT-$LiCoO_2$

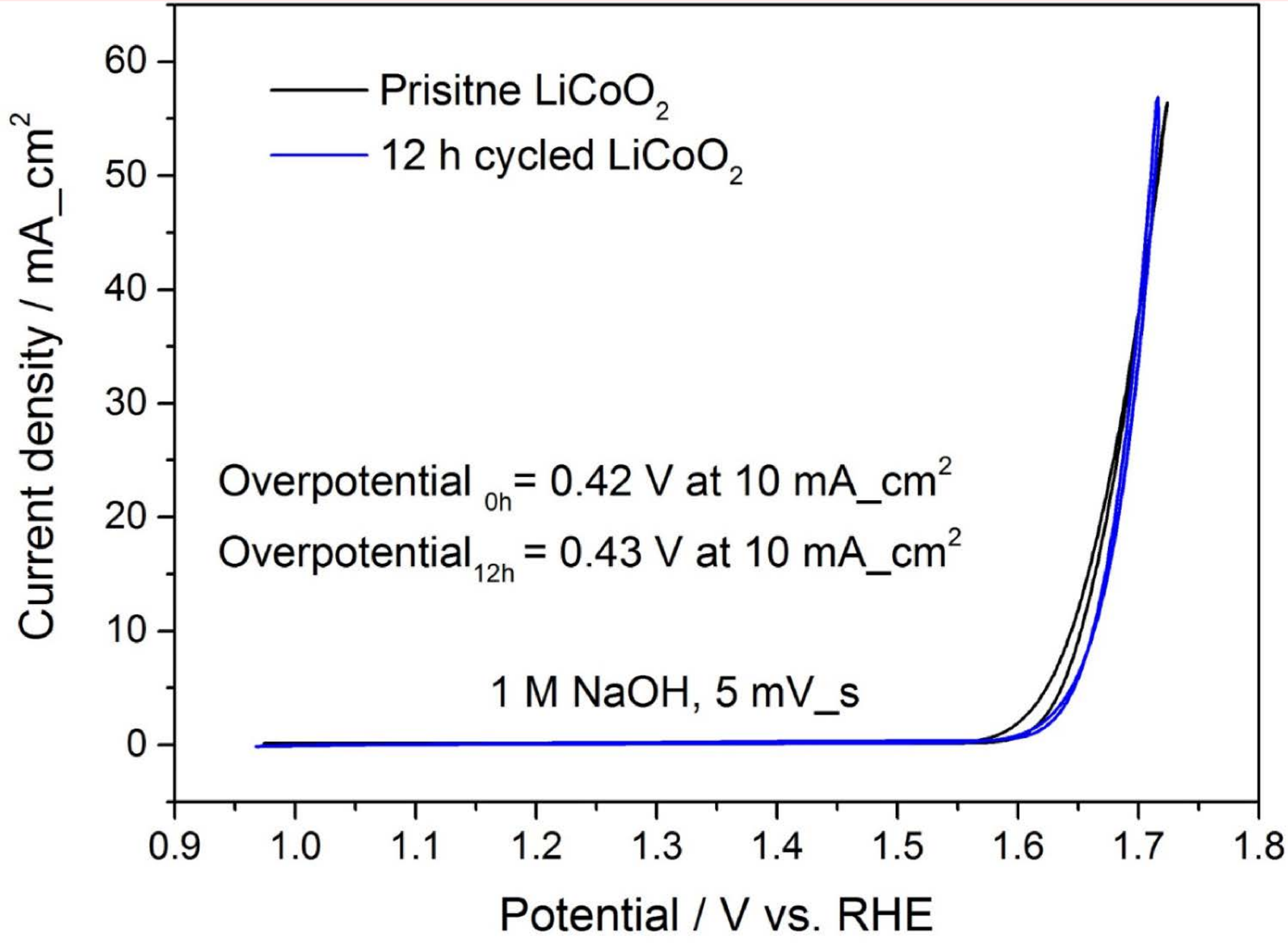
Accomplishments:
OER catalyst characterization

XPS: Composition and oxidation state analysis



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.

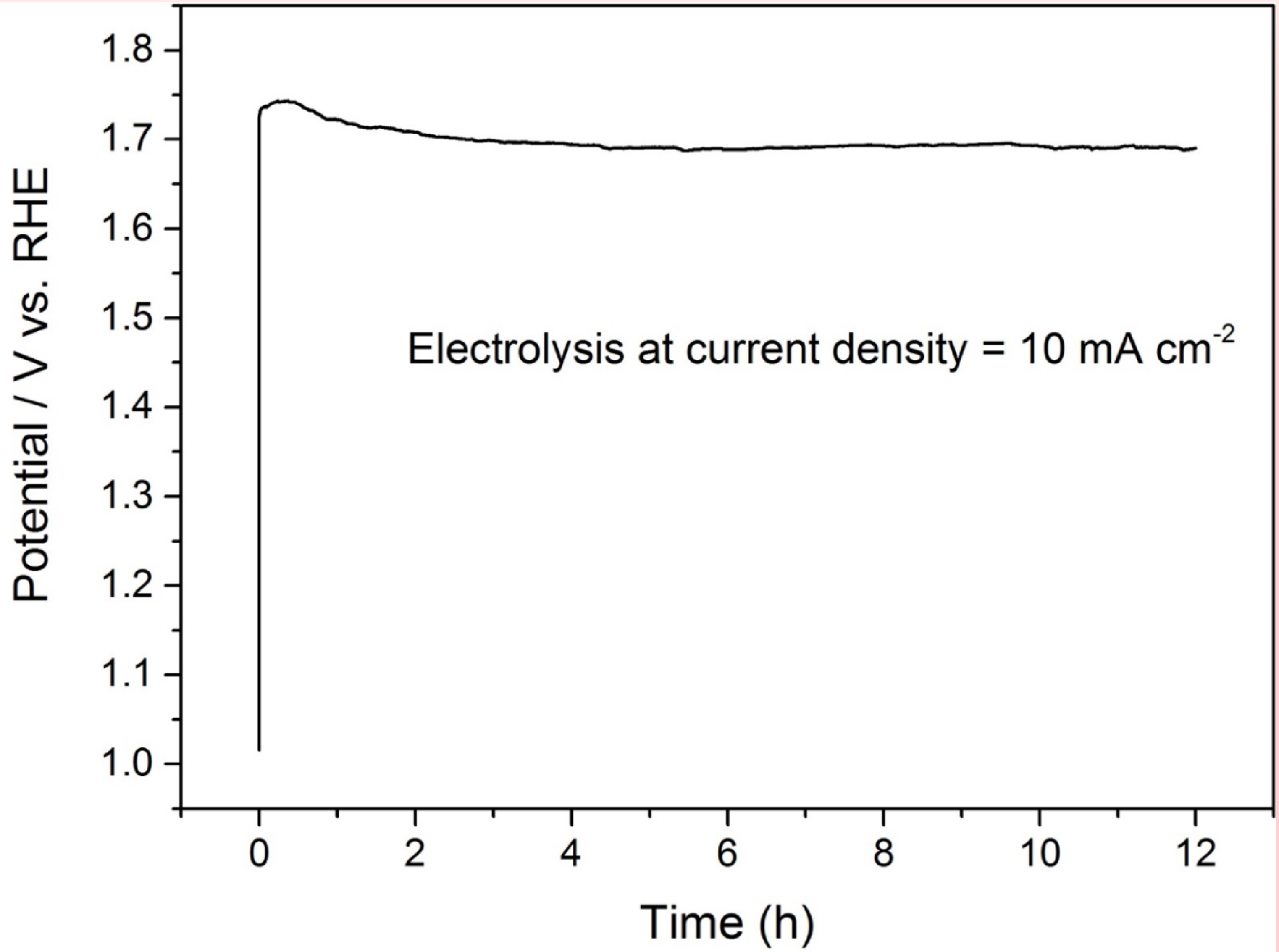
Accomplishments:
Thin film OER catalyst electrochemistry



- 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

Accomplishments:
OER catalyst thin film stability



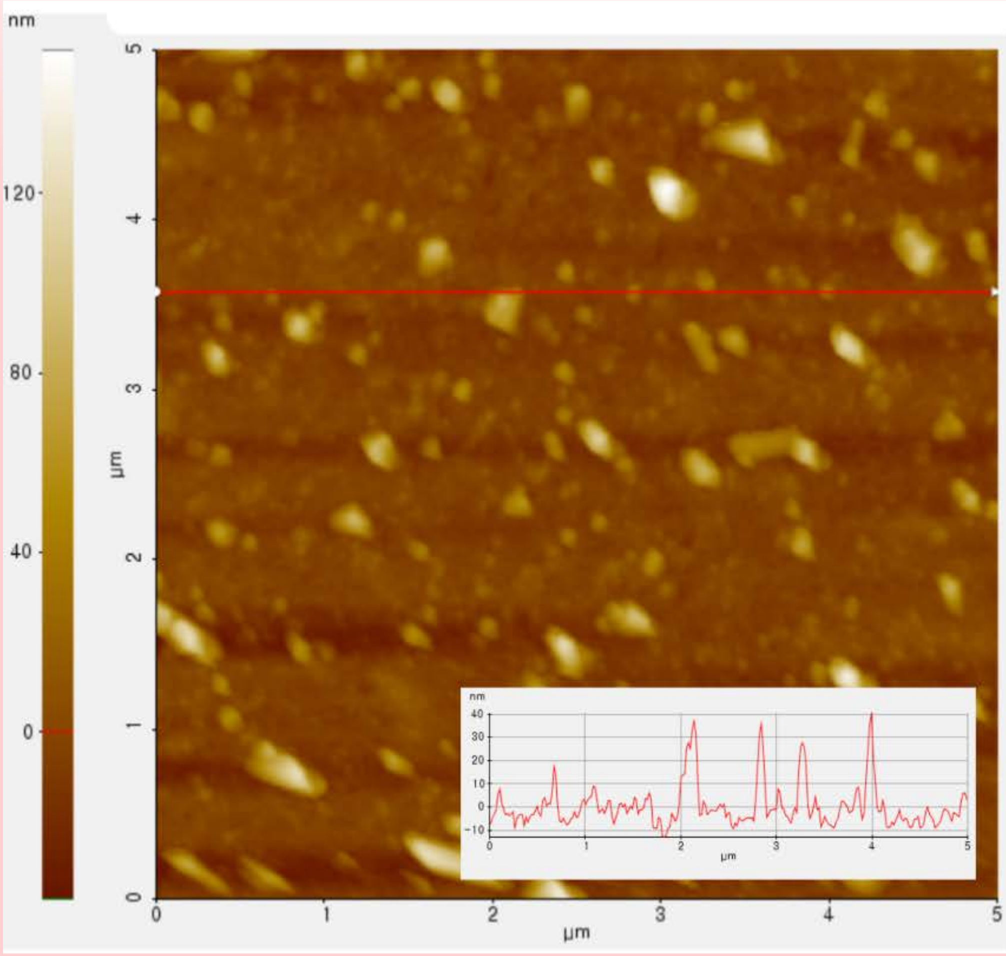
- Stable in 1M NaOH for >12 h

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

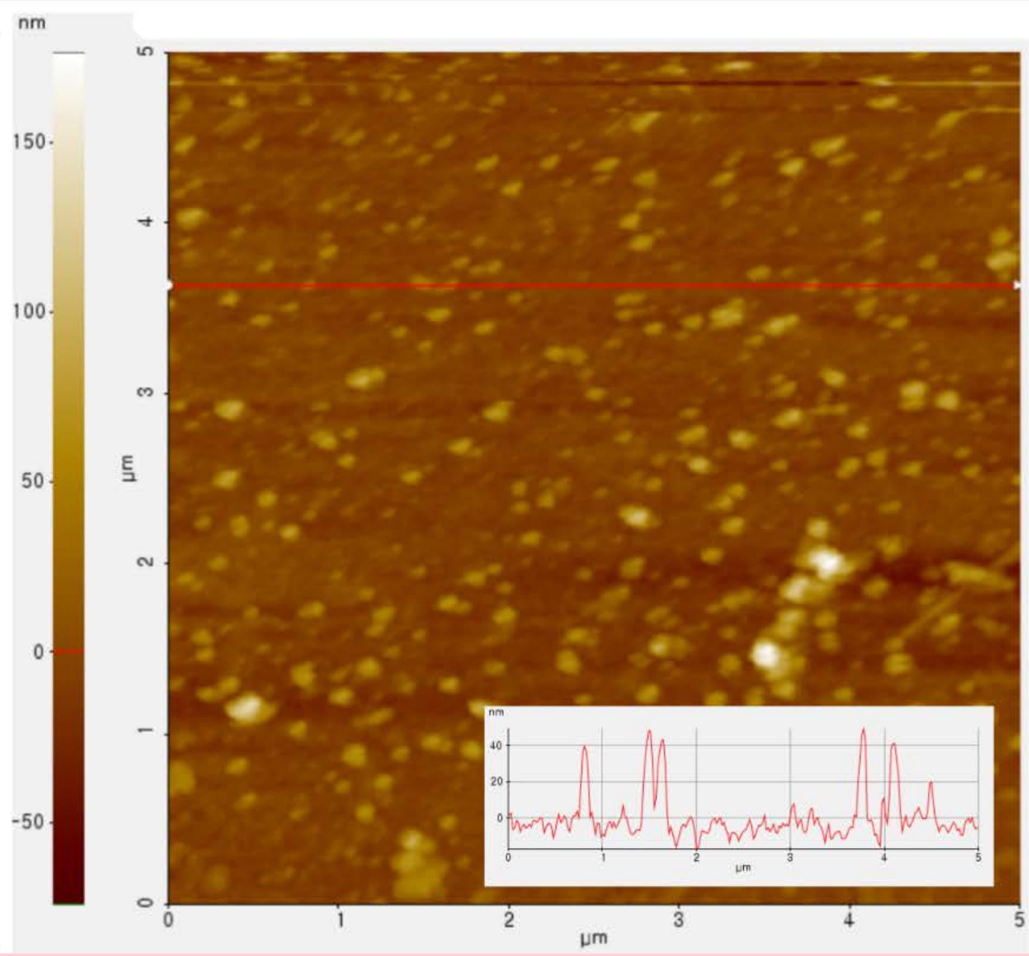
Accomplishments:
OER catalyst morphology

Atomic force microscope:

Pristine $LiCoO_2$



12 h cycled $LiCoO_2$



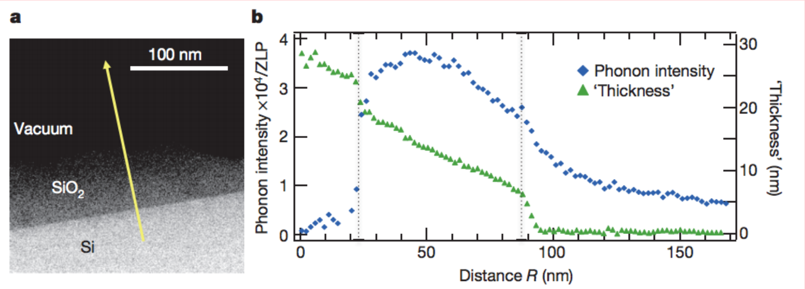
Surface roughness (R_a) unchanged over course of reaction:
11.8 initially, to 12.2 nm at 12 h

Conclusions

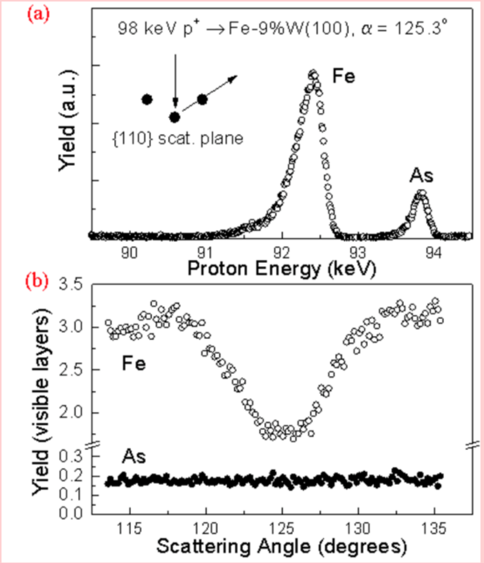
- Conformal thin films of crystalline nickel phosphide (single phase Ni_5P_4) have been synthesized directly on glassy C electrodes, Ni_5P_4@gC, and on C fiber gas diffusion electrodes, Ni_5P_4@fC.
- Cathodic overpotentials for HER on thin films of Ni_5P_4@fC are significantly lower than prior spray coated Ni_5P_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

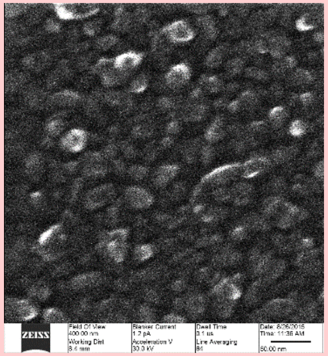
Relating to Energy Materials Network

- <u>Needs:</u>
  - Wide and/or narrow band gap semiconductors
    - Potential sources:
      - **NREL?** III-Vs? or **JCAP?**
- <u>Unique services Rutgers (we) can provide:</u>
  - 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



Krivanek, O. L., Lovejoy, T. C., Dellby, N., Aoki, T., Carpenter, R. W., Rez, P., Egerton, R. F. *Nature*, **2014**, *514*(7521), 209-212.





http://www.physics.rutgers.edu/meis/MEIS.html

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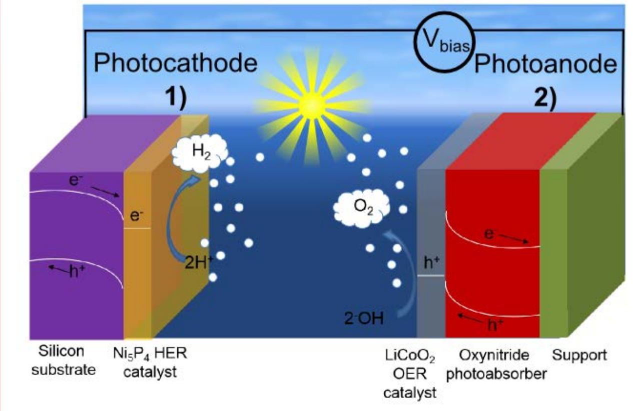
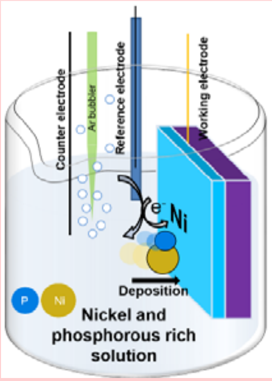
Project summary

- **<u>Objective</u>: Investigate and develop tunable photoanode-photocathode-catalyst interface systems for efficient solar water splitting**





- <u>Key FY2016 technical results</u>:
  - Identify methods for, and fabrication of, thin films of both HER and OER catalysts, enhancing amenability to a(ny) given photoabsorber system
  - Characterize oxynitride perovskite wide bandgap absorber and optimize oxynitride/substrate interfacial chemistry on route to full tandem device