Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

P175

Intermediate Temperature Proton-Conducting Solid Oxide Electrolysis Cells with Improved Performance and Durability

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1, West Virginia University; 2, Colorado School of Mines; 3, National Renewable Energy Laboratory; 4, Idaho National Laboratory; 5, Sandia National Laboratory

May 2020

Project ID EE0008378

Project Overview

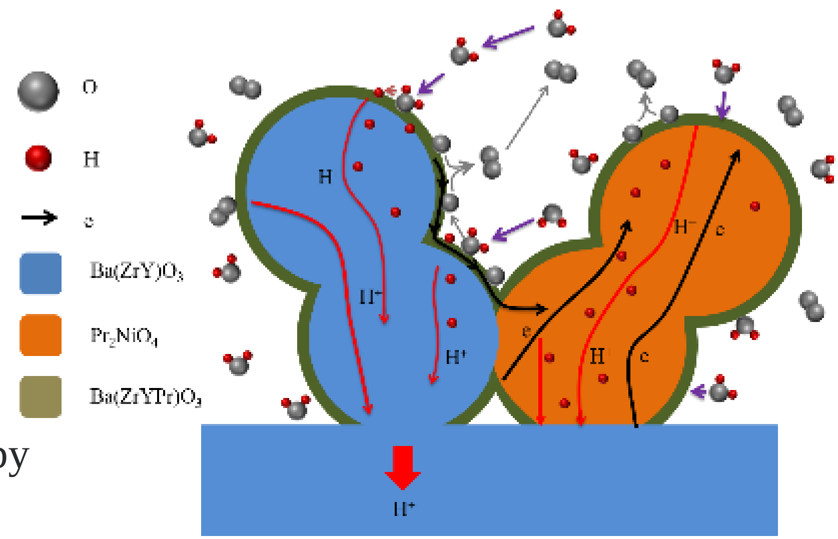
Project partners

- ❑ PI West Virginia University (WVU)
- ❑ Co-PI Colorado School of Mines (CSM)
- ❑ National Renewable Energy Laboratory (NREL)
- ❑ Idaho National Laboratory (INL)
- ❑ Sandia National Laboratory (SNL)

Award #	**EE0008378**
Start/End Date	**Nov. 2018 –Oct. 2021**
Total Project Value*	$1,129,523
Cost-share (%)	12%

Project Vision

We are solving the long-term degradation problem of SOECs at operating temperatures ≥ 800°C by developing IT H-SOEC at lower operating temperatures 600°C



Project Impact

Enabling significant performance enhancements in SOECs by developing IT H-SOEC

- High current densities > 1.0 A/cm^2 at 1.4 V/cell
- Long-term operating durability at ~600 °C for (<10 mV/1000 hr)

** this amount does not cover support for HydroGEN resources leveraged by the project (which is provided separately by DOE)*

Any proposed future work is subject to change based on funding levels

Approach: Summary

Project Motivation

WVU: expertise with all ceramic, nickelate-based electrodes in this study, significant cell fabrication and test facilities

CSM: combinatorial deposition and characterization of materials for reliable electrochemical performance

NREL: high-throughput screening with combinatorial thin-film deposition on electrolytes and electrode.

SNL: Operando measurements to screen the electrocatalyst formula via a lab-based E-XPS

INL: expertise in H-electrolyte development and electrode backbone 3D engineering

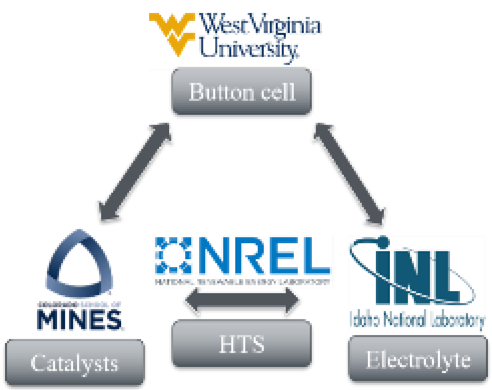
Current target	Units	State of 2018	1st year target	2st year target	3st year target
ASR in run	$\Omega \cdot cm^2$	0.57	< 0.35	< 0.35	< 0.35
Current density	A/cm^2	0.5A @ 1.3V	>1.0 @ 1.4V	>1.0 @ 1.4V	>1.0 @ 1.4V
Degradation	mV/1000 h	--	--	30	10
Temperature	°C	700	700	600	600

Barriers

- Inadequate activity of electrocatalyst at lower temperature
- Low long-term stability in humified environments
- Lack of scalable and cost-effective electrocatalyst conformal coatings fabrication
- Popped-off electrode layer

Approach-Summary

Partnerships



H-electrolyte at INL:

- Advanced powder synthesis techniques
  - — sol-gel and nitrate-combustion
- Post analysis
  - — SEM/EDX, TEM and XPS
- Conductivity improvements
- Electrode backbone3D engineering

Electrocatalyst at CSM,NREL,SNL

- Appropriate electrocatalyst compositions
  - — High-throughput screening
- Catalysis & local surface activity
  - — Operando ambient-pressure XPS

Button cell at WVU

- Electrochemical Modeling
  - — H_2O-splitting reaction kinetics
  - — Anode structural and composition
- Candidate anodes development
- Conformal catalyst layer coating
- Cell fabrication and performance characterizations

- ❑ An electrochemical model is developed to assess and validate microkinetic reaction mechanisms with thin-film electrode providing guidelines on electrode development
- ❑ Optimal electrocatalysts identified with high-throughput screening (HTS) of thin-film combinatorial coatings and E-XPS for probing local activity and overpotentials for H_2O splitting
- ❑ Conformal coating of catalyst on uniform BZCYYb scaffold providing good H_+-conductivity and kinetics of bulk H incorporation. Promising in Solving electrode layer Popped-off problem during long-term operation

HydroGEN Consortium resources:

SNL INL NREL

Approach: Innovation

Budget period 1&2 scope of work

Task or Subtask Title	Milestone Type	Milestone Number*	Milestone Description (Go/No-Go Decision Criteria)	Complete
2.1	Milestone	Q3	Identification of spectroscopic signals from E-XPS on PNO thin-film anodes and BZCYYb electrolyte to correlate with electrochemical activity for anode H_2O splitting.	70%
3.4	Milestone-Go/No-Go #1	Q4	Cathode-supported H-SOEC button-cell with novel anode developed in this project achieves ASR < 0.35 $\Omega \cdot cm^2$ and current density > 1.0 A/cm^2 at 1.4 V at 700 °C.	100%
1.2	Milestone	Q5	Development of PNO-based anode of model-guided composition with a 0.3 $\Omega.cm^2$ ASR at 600°C under operation condition	100%
3.1	Milestone	Q6	Prediction of the requirement of particle size, porosity, thickness and along with improved σ, k and D needed to reach a 0.35 $\Omega.\ cm^2$ ASR under operation at 600°C.	100%

Materials innovation

- ❑ PNO-BZCYYb composite anode with triple-conductivity was fabricated as the composite backbone.
- ❑ Electrochemical model development for assessing and validating microkinetic reaction mechanisms and performance enhancement guidance
- ❑ Optimal electrocatalysts identified by HTS thin-film combinatorial coatings and E-XPS
- ❑ Conformal coating of catalyst to enhance the H diffusion and kinetics of bulk H incorporation.

Relevance and Impact

By provide stable and highly-active electrocatalyst at lower temperature, there will be a significant leap in H-SOEC, providing fast and efficient strategy for hydrogen production.

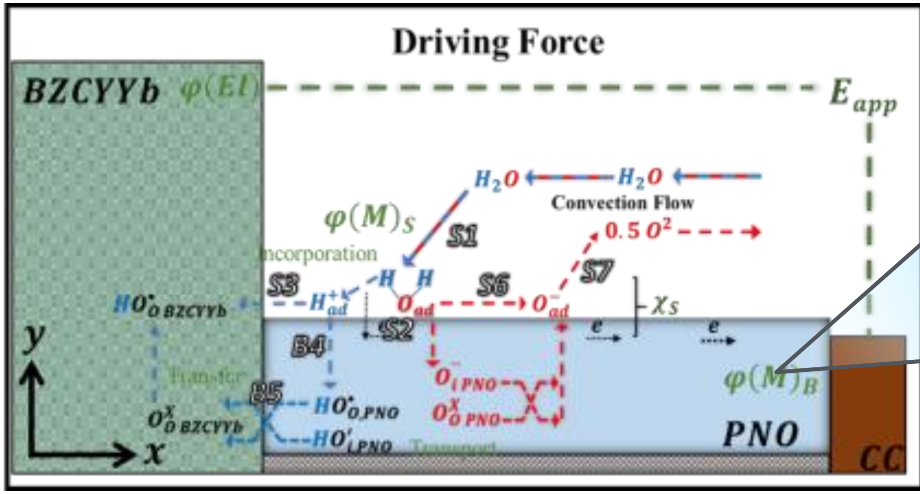
Assistance of E-XPS and high-throughput from CSM together with HydroGEN nodes (SNL NREL) will provide fast screen of electrocatalyst formula and support the microkinetic modeling development

- The spectroscopic signals from E-XPS will identify features in the O1s peak related to surface hydroxides and the cation oxidation states that correlate with high H2O-splitting activity. spatial resolution based on distance from the Au current collector will provide a measure of electrochemical activity for spreading the active electrocatalyst surface area.
- The E-XPS testing of the electrocatalysts will provide critical spectroscopic signals that will enable the team including WVU to develop improved microkinetic models that can assess what impact the enhanced electrocatalyst activity may have on full cells designation.

Fabricate 3D-structured mesh-like electrode structure from INL provides backbone structure with high porosity, the mechanical strength, particle size and porosity are balanced upon firing conditions.

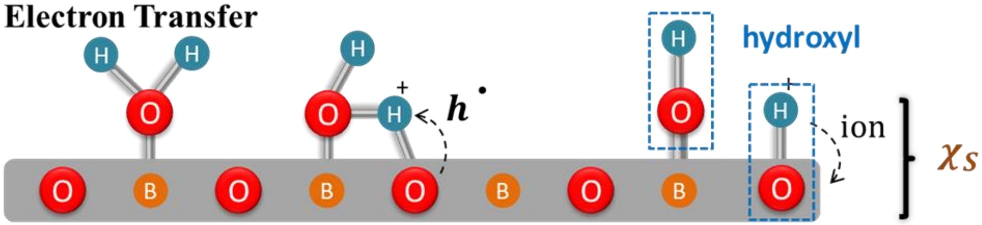
Accomplishments– Electrochemical modeling

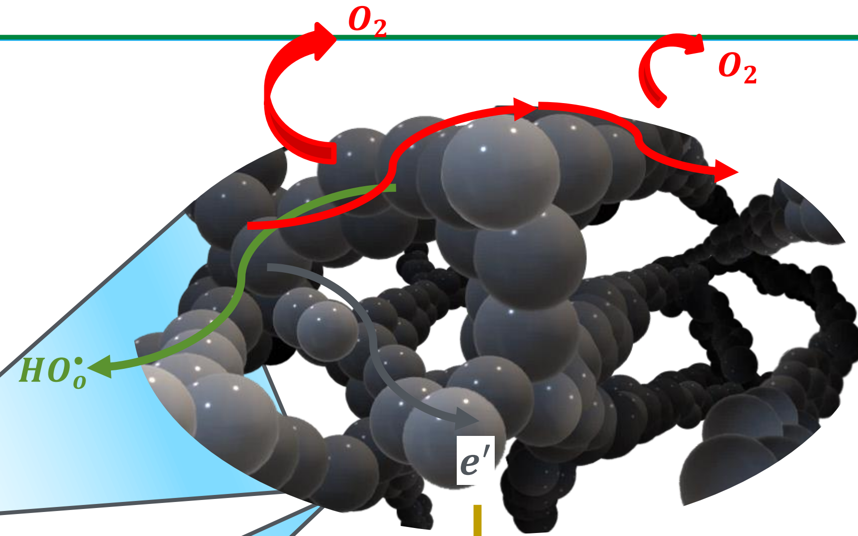
Modelling-Perspective



Multi-step charge-transfer

Electron Transfer





Bi-pathway kinetics

S1 → S2 → S3 → J_{diff} → S6 → S7

S2 → B4 → B5 → S6

Convection diffusion

$$\frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i + \vec{V}\nabla C_i$$

Surface active site

$$\Gamma_M \quad \Gamma_O \quad \theta_i^0$$

specific 3PB length

$$S_{tpbl} = S_{tpbl,0}\left(1 - \frac{\varepsilon - \varepsilon_{fcc}}{1 - \varepsilon_{fcc}}\right)\frac{d_{g,0}^3}{d_g^3}$$

Specific gas kinetics

$$J = \frac{P_i}{\sqrt{2\pi M R_g T}}$$

Specific gas diffusivities

$$D_i = \frac{D_{i,Kn}^{eff} D_{ij}^{eff}}{D_{i,Kn}^{eff} + D_{ij}^{eff}}$$

Size-specific surface

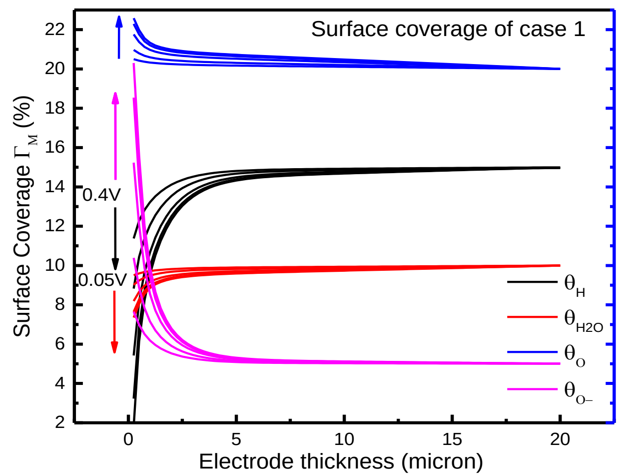
$$\left(\frac{\Delta S}{\Delta V}\right)_{ads} = \frac{6}{d_g}(1-\varepsilon)$$

Accomplishments– Electrochemical modeling

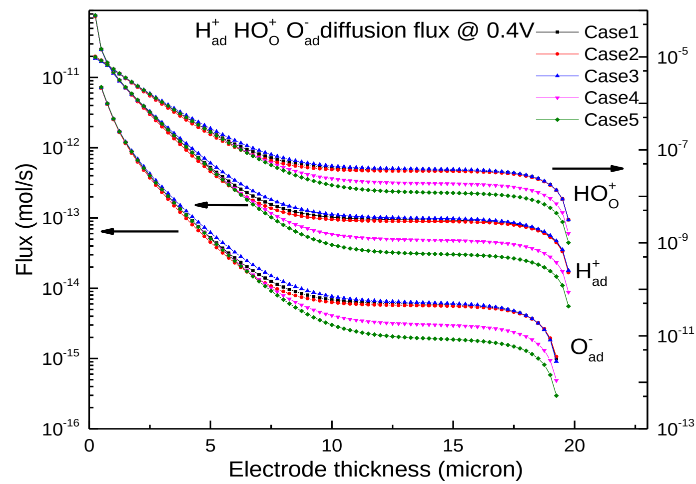
Model Capability

- WVU models are being adopted by Mines into Cantera thermochemical open framework for use by others in design.

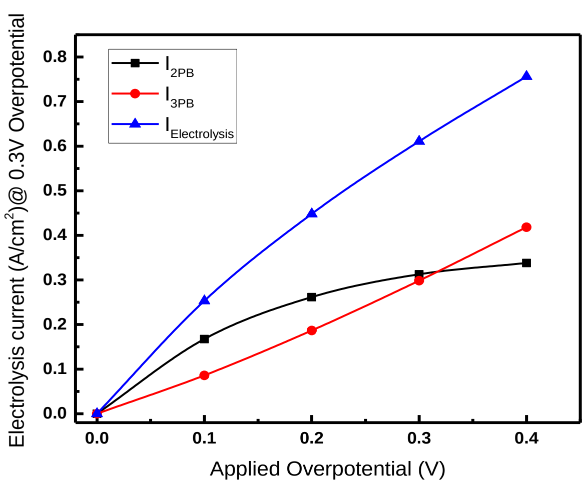
Surface Site



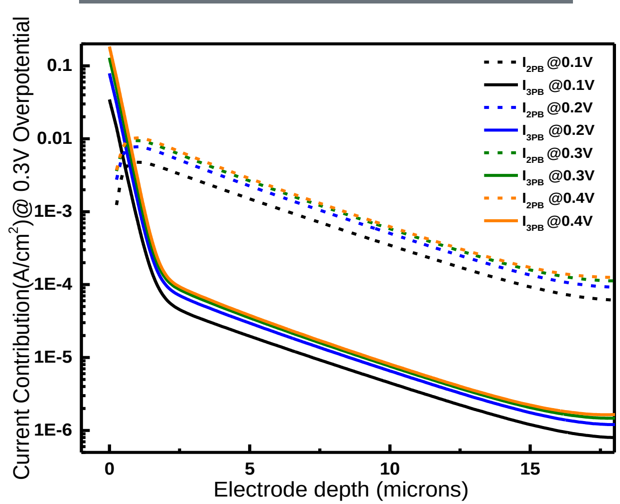
Mass Diffusion



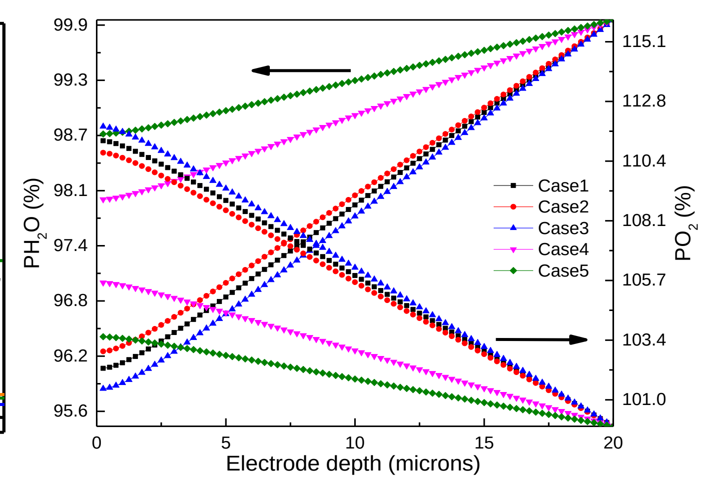
Bi-pathway kinetics



Local contributions

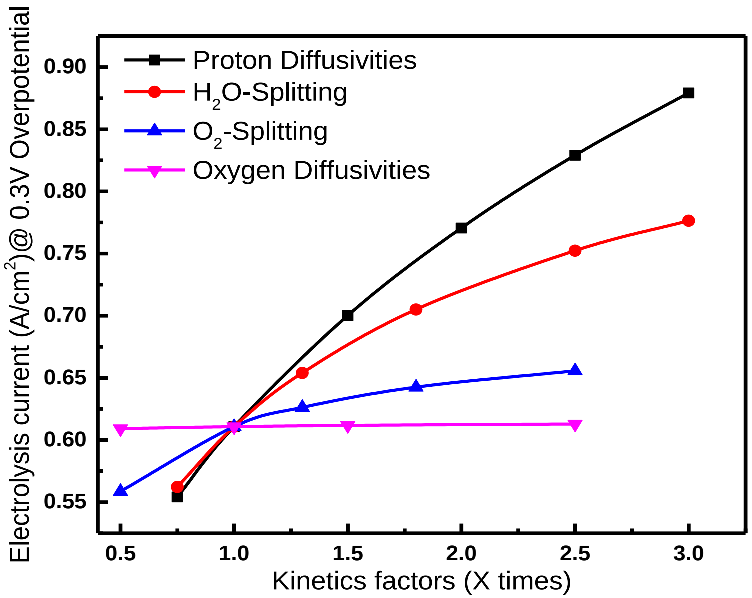


Gas Transportation



Accomplishments– Electrochemical modeling

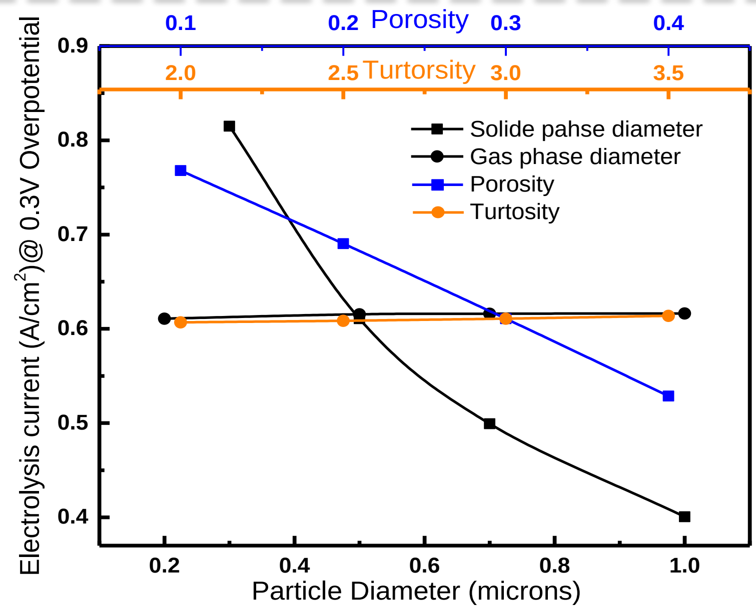
Model predication on performance



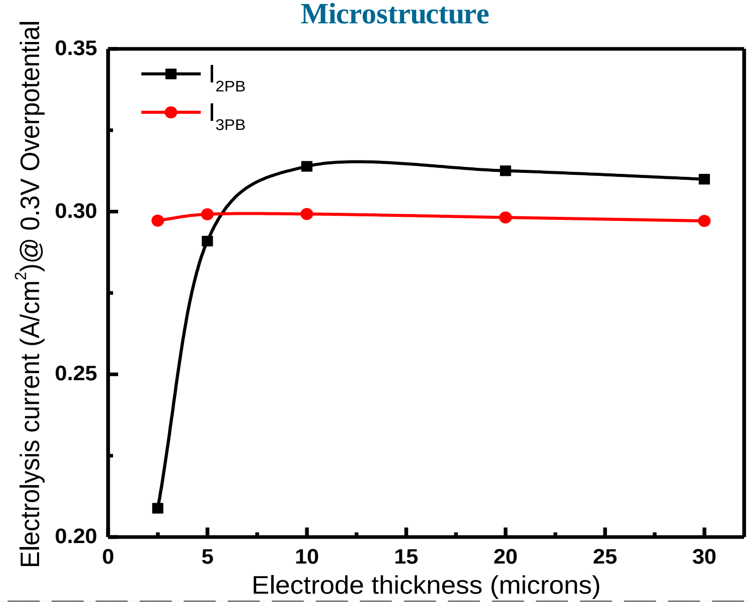
H_2O kinetics ∝ Electrolysis

O_2 kinetics are less related

Structure factors



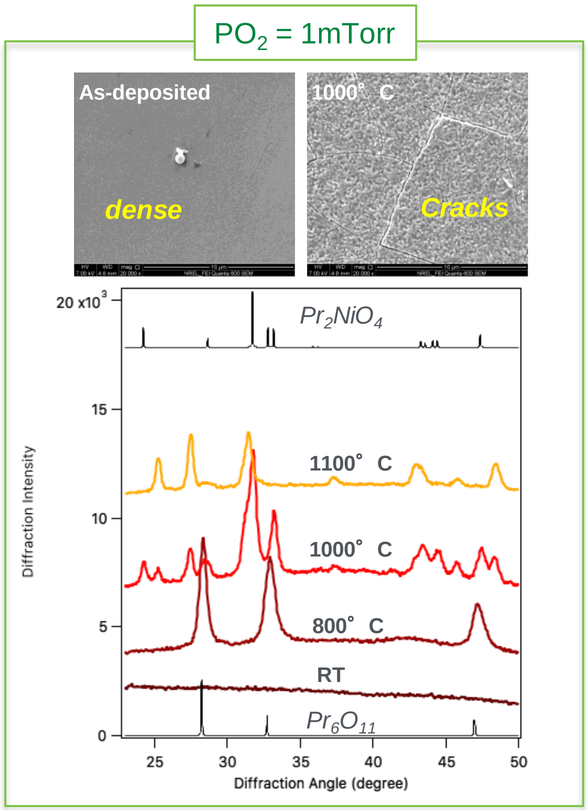
Microstructure

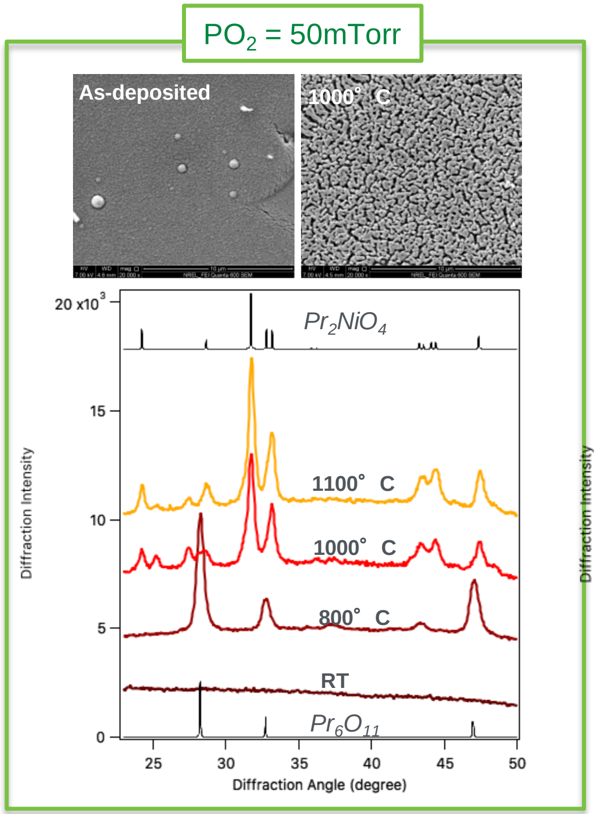


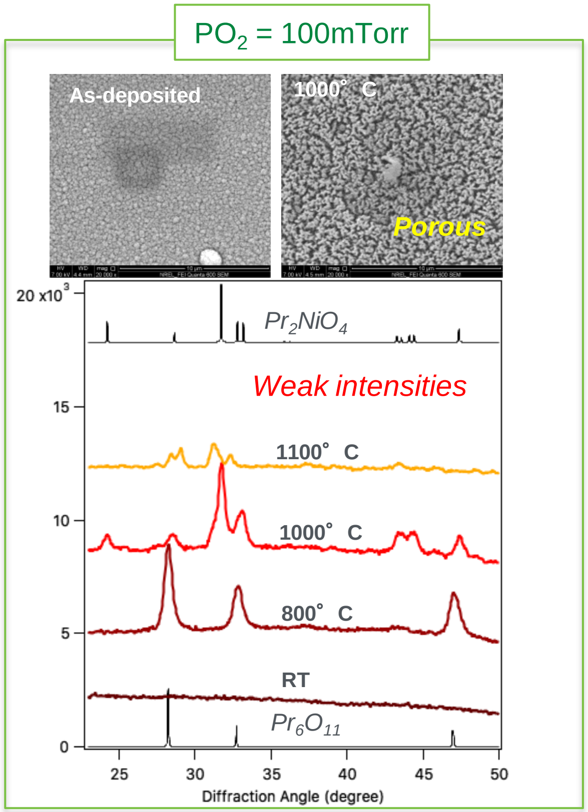
Accomplishments– E-XPS

PNO preliminary experiment

PNO / Silica substrates → Annealing





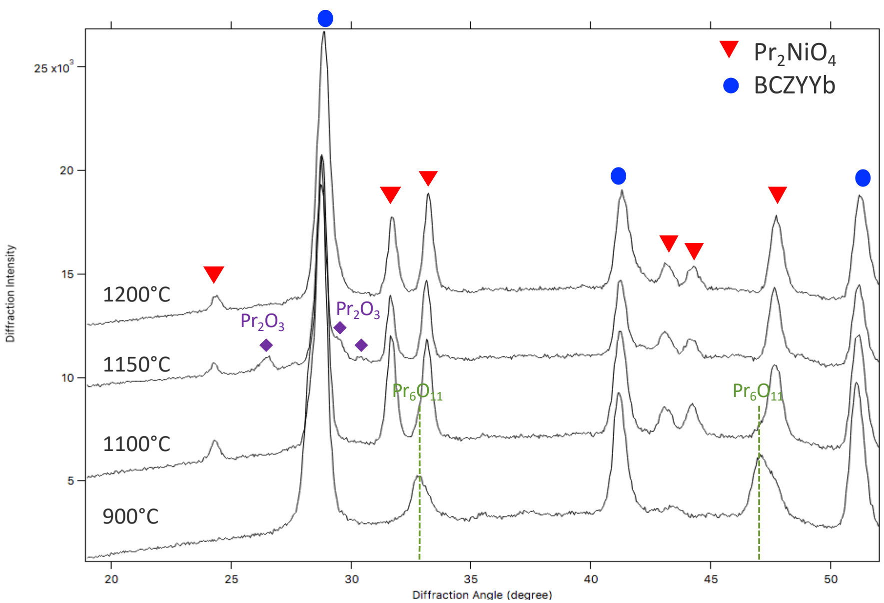


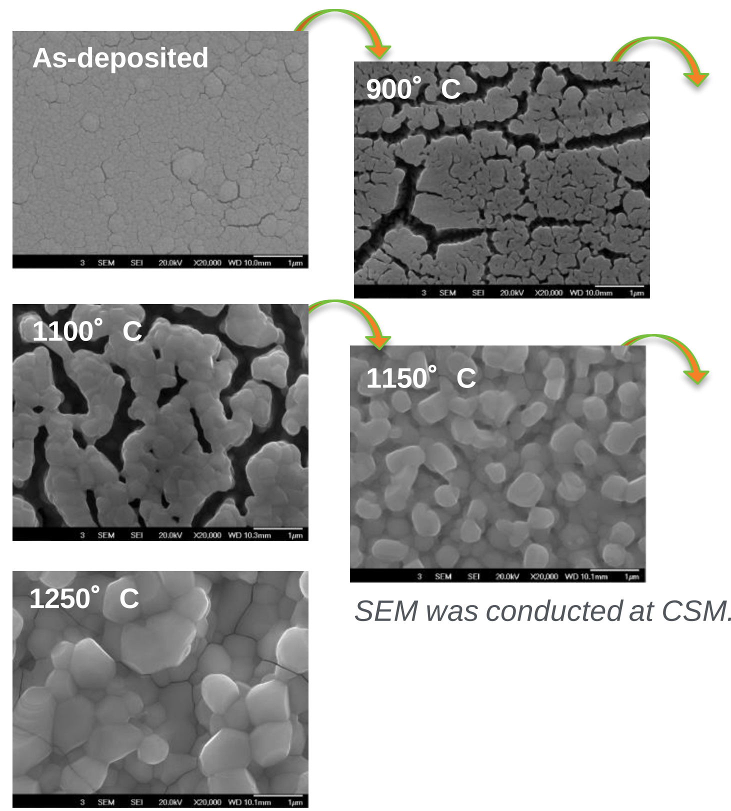
- PNO film synthesized at 50mTorr PO_2 has the most stable structure and morphology

Accomplishments– E-XPS

PNO deposition on BCZYYb pellet

PNO
BCZYYb
Annealing



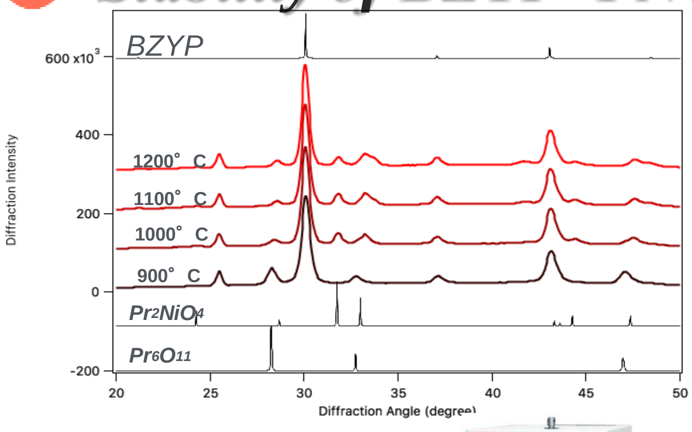


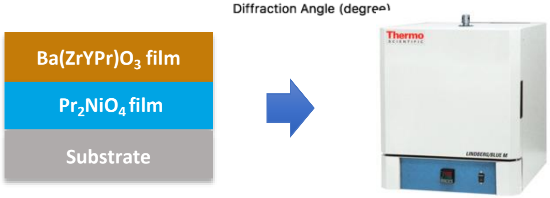
SEM was conducted at CSM.

- PNO film deposited on BCZYYb pellet showed stable structure and morphology after annealing 1250° C.

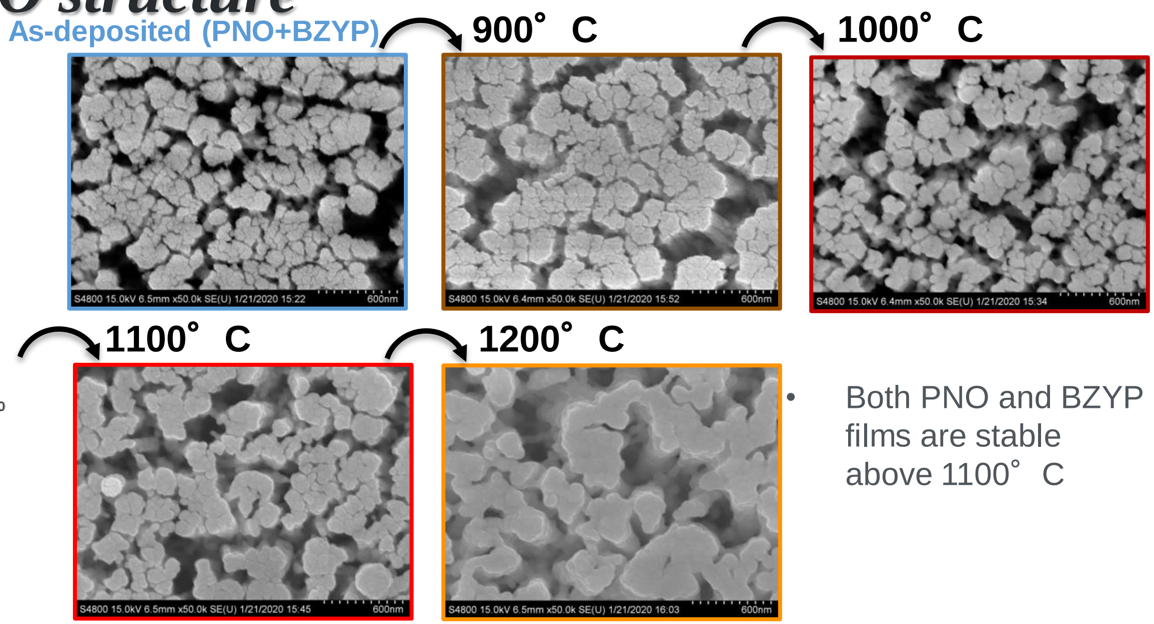
Accomplishments– E-XPS

Stability of BZYP+PNO structure



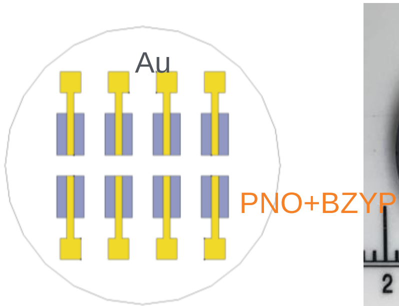


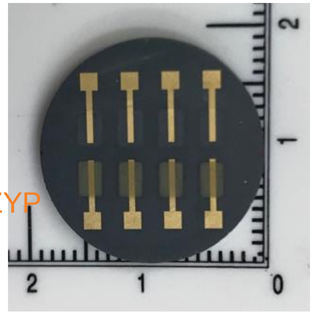
Annealing at 900-1200° C

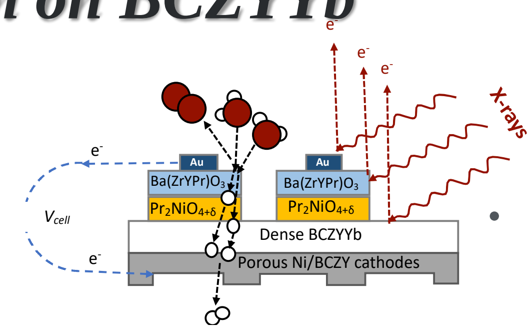


- Both PNO and BZYP films are stable above 1100° C

BZYP+PNO deposition on BCZYYb







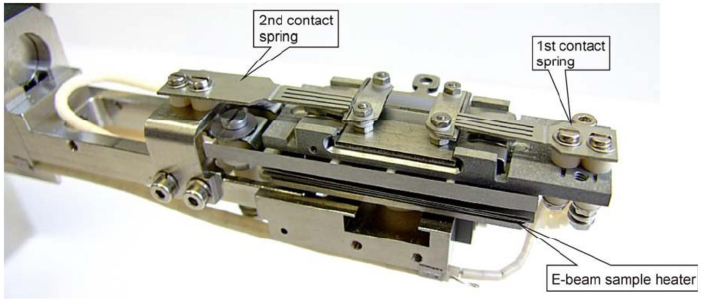
- E-XPS is currently in-progress in CSM.

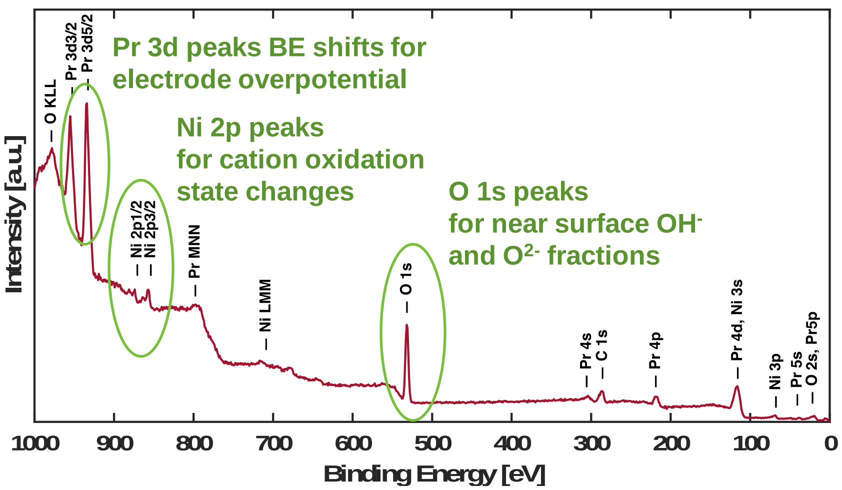
- Masking sheets of PNO + BZYP film and Au coat patterns have been fabricated for E-XPS.
- NREL has conducted the deposition of PNO+BZYP and gold coating with patterned masks.

Accomplishments– Thin Film Electrode E-XPS

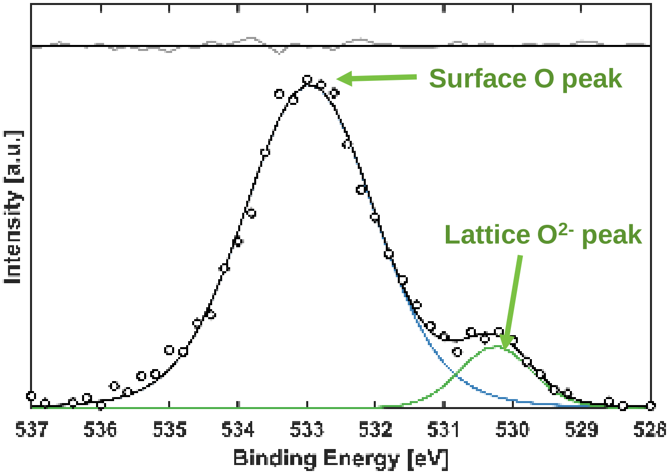
- Mines has re-established operation of the on-campus Scienta-Omicron E-XPS machine as of last month.
- Initial tests measured cation and O 1s peaks in dry environments.
- Wet environments at temperature are next step without electrochemical excitation.
- An E-XPS stage for electrochemical excitation has been purchased for testing in this coming quarter.

In operando electrochemistry heated stage for E-XPS



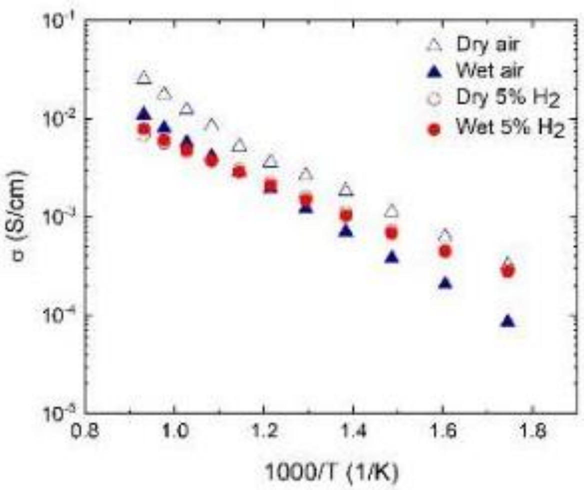


O 1s peaks In dry environment



Accomplishments– Electrolyte

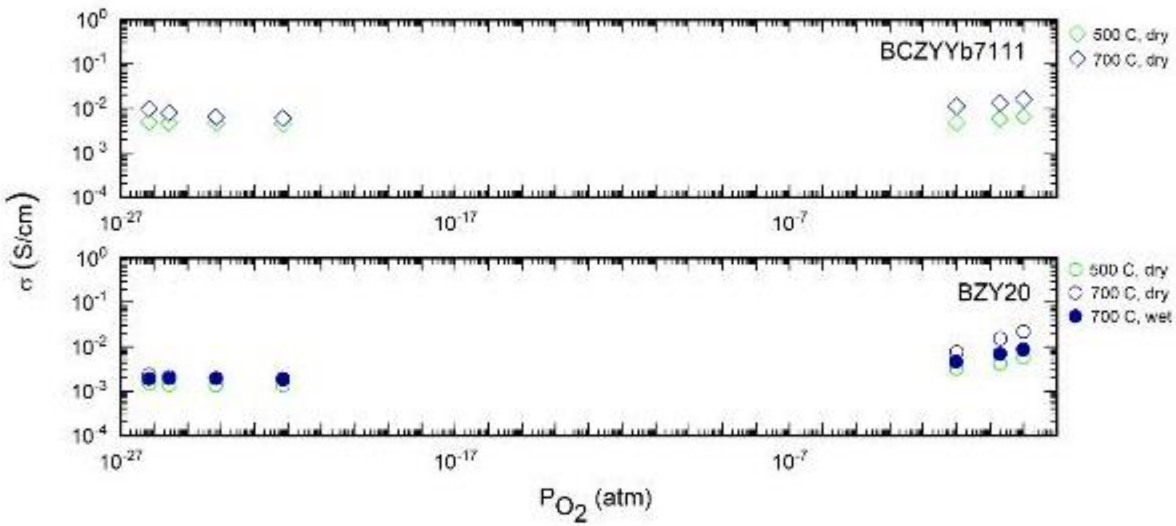
Composition effect on σ_i of BZCYYb-7111, 4411 and BZY20



Gas conditions	Activation energy
Dry air	0.45 eV
Wet air	0.51 eV
Dry 5% H_2	0.34 eV
Wet 5% H_2	0.36 eV

Conductivity of BCZYYb7111 as a function of temperature and gas conditions

Conductivity of BCZYYb7111 as a function of temperature and oxygen partial pressure

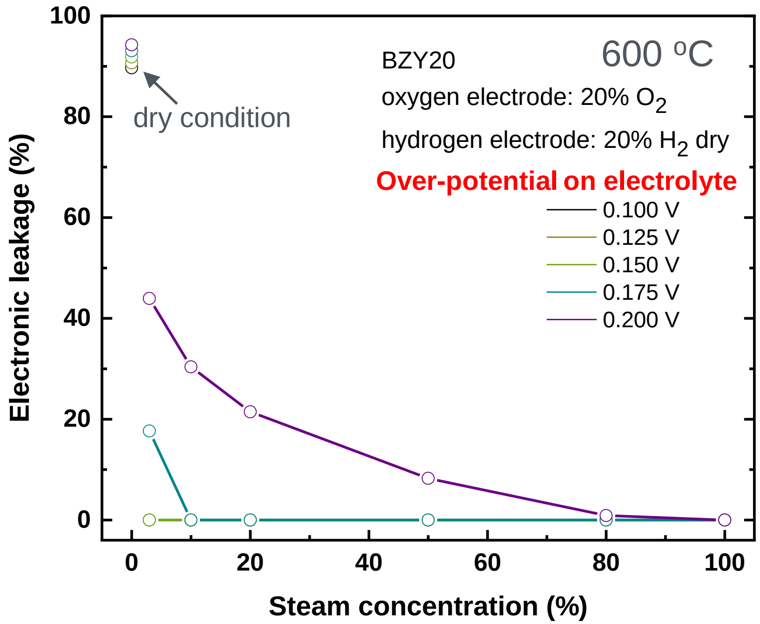


Accomplishments– Electrolyte

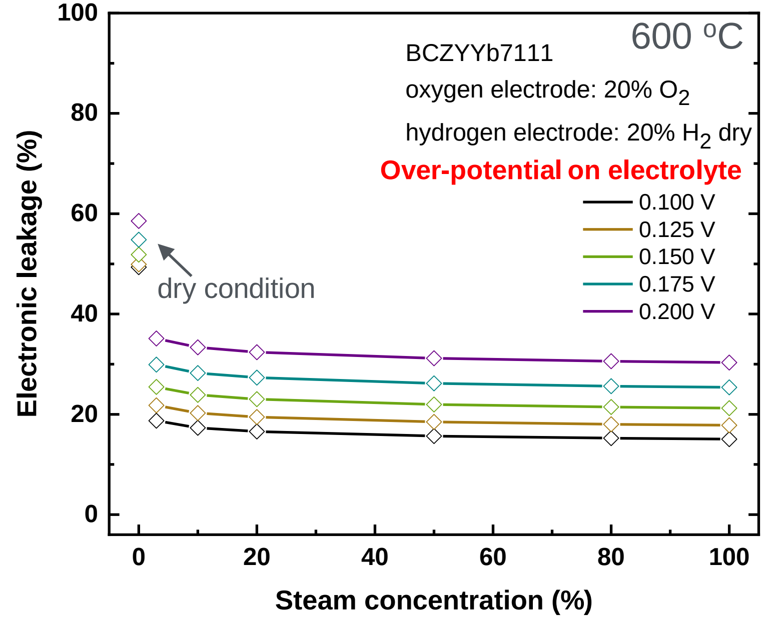
Electronic leakage of BCZYYb7111 and BZY20

West Virginia University

- The conductivity measurement as functional of oxygen partial pressure and steam concentration has shown the electron leakage for BCZYYb7111 under reducing condition and the higher over-potential leads to more leakage in the electrolytes.
- INL developed a model with defect chemistry and the experimental conductivities as input to predict the leakage behaviors under practical conditions within both electrolytes.
  - BZY20 shows much lower leakage when the over-potential is under 0.175 V;
  - Increased steam concentration decreases the leakage for both cases;
  - BCZYYb7111 shows the issue with electron conduction, increasing overall leakage.



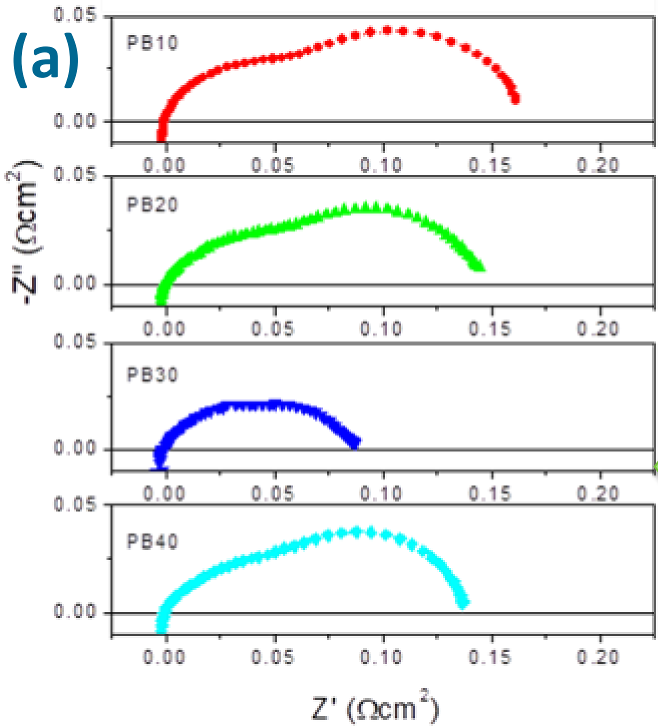
Predicted electronic leakage for BZY20



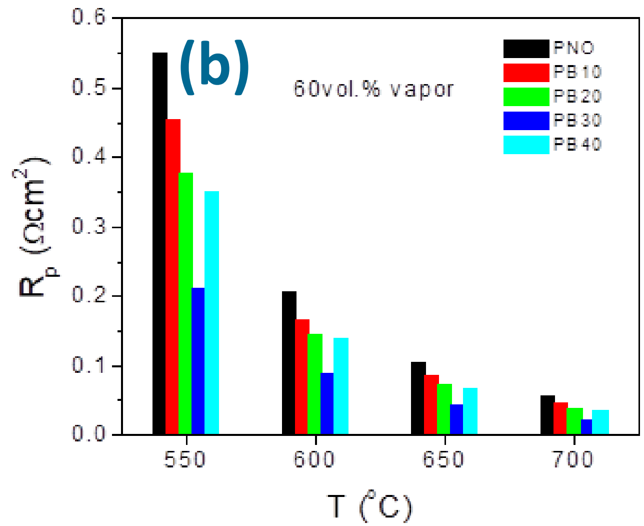
Predicted electronic leakage for BCZYYb7111

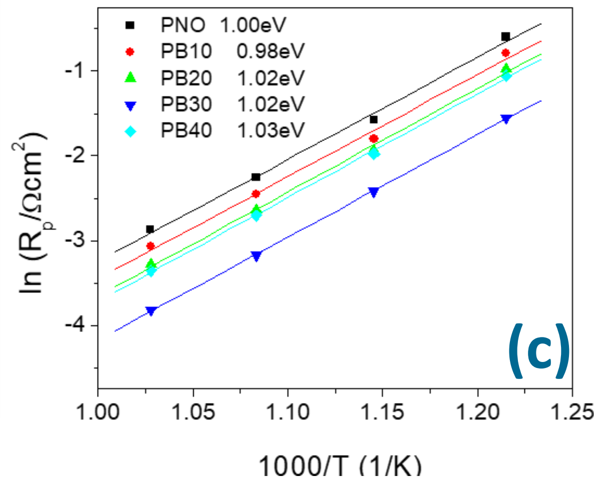
Accomplishments– Anode materials

Doped Pr_2NiO_4



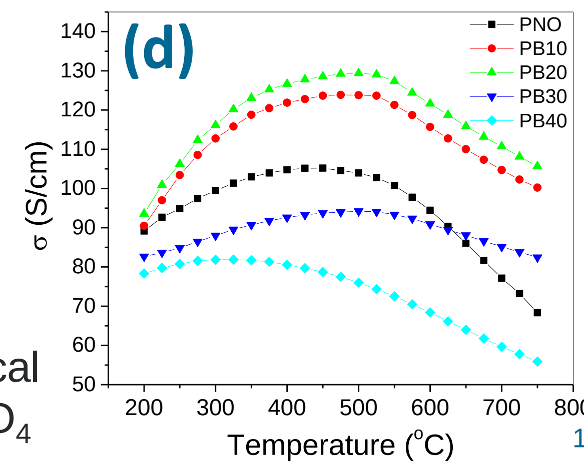
(a) $Pr_{2-x}Ba_xNiO_4$ at 600ºC in 60 vol.% steam Air





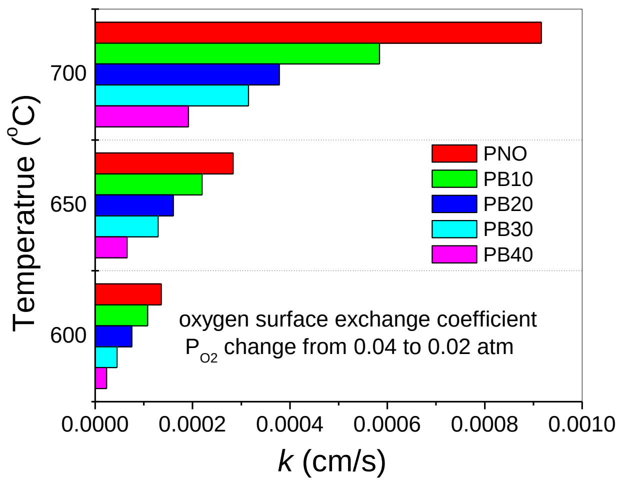
(b) ASRs in 60 vol.% steam Air 550-700ºC (c) apparent activation energy (*E*a) derived from the ASR results.

0.08 Ωcm^2 achieved @600ºC

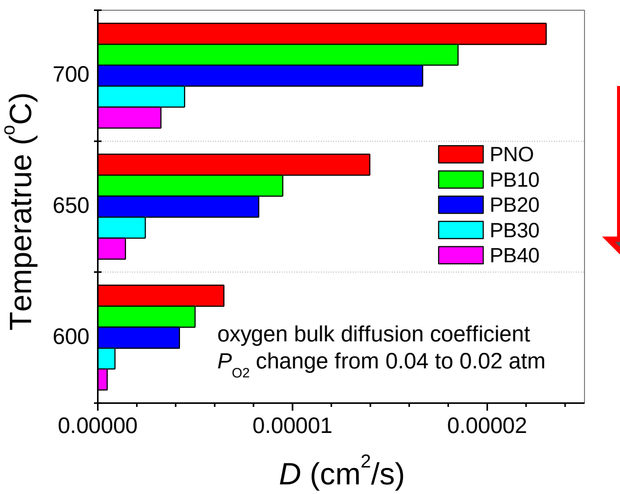


(d) Four-probe DC electrical conductivity of $Pr_{2-x}Ba_xNiO_4$

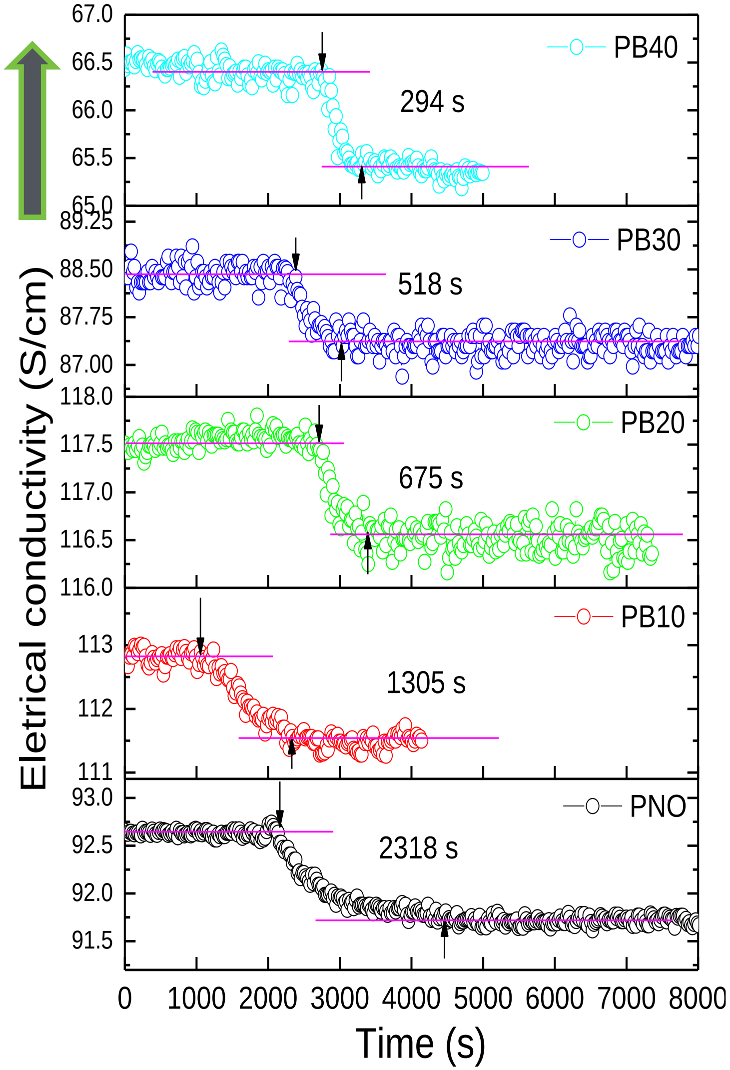
Accomplishments– Anode materials



H_2O kinetics



O_2 kinetics

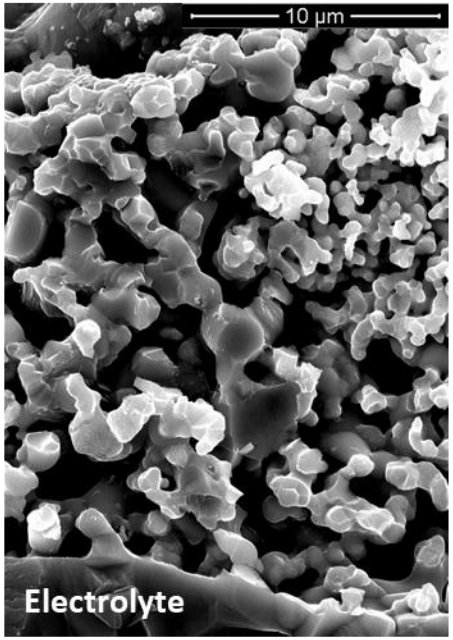


Oxygen surface exchange coefficient (*k*) and bulk diffusion coefficient (*D*).

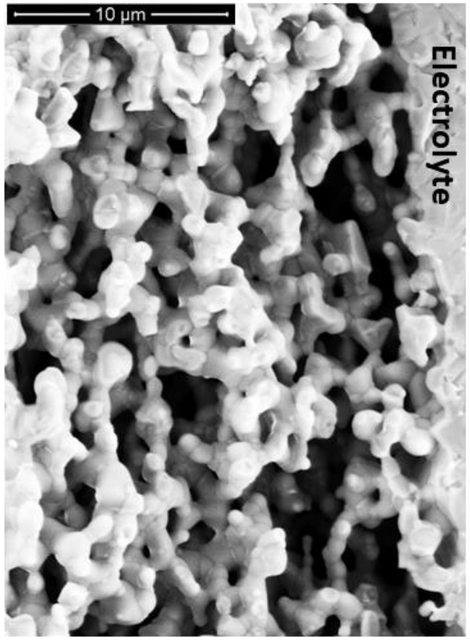
Transition of the electrical conductivity upon gas atmosphere shift from dry N_2 to 60 vol.% water vapor containing N_2.

Accomplishments-Anode conformal coating

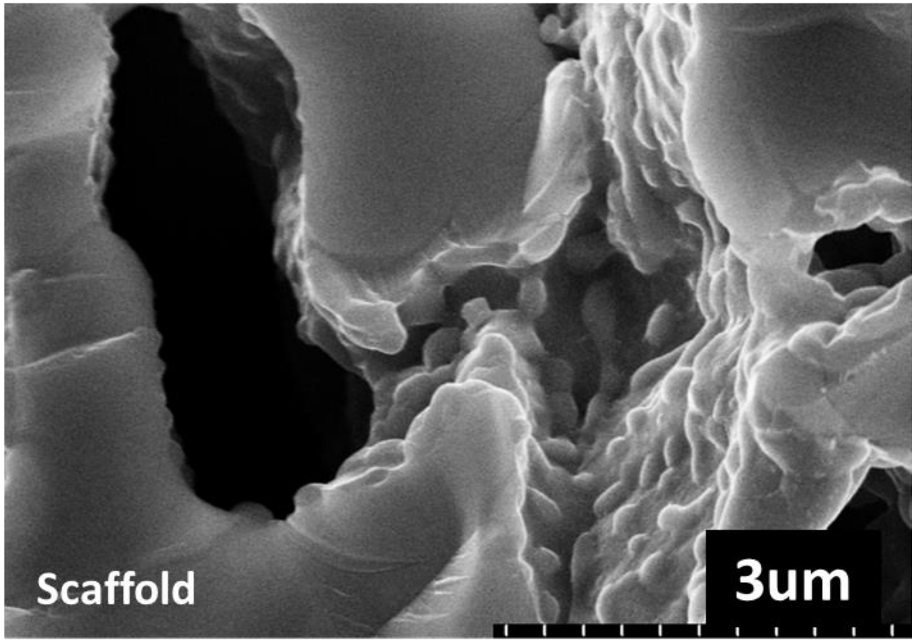
Composite PNO+BZCYYb 1150 °C



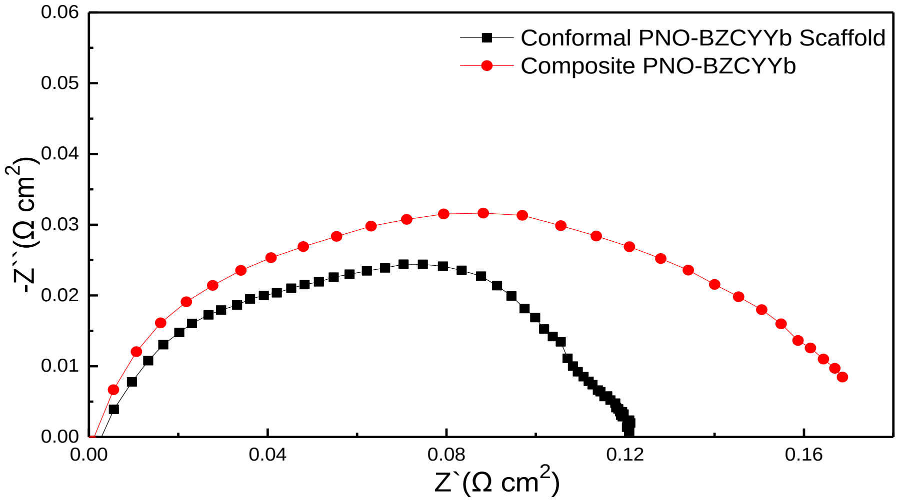
Co-fired scaffold 1300 °C



Conformal PNO coating 1000 °C

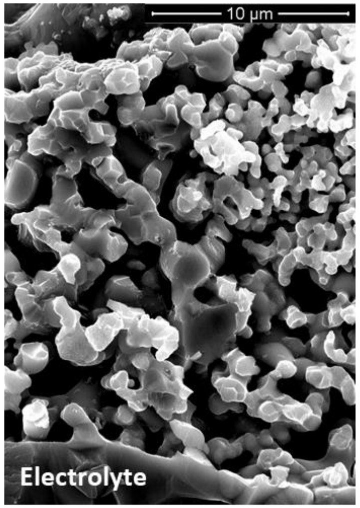


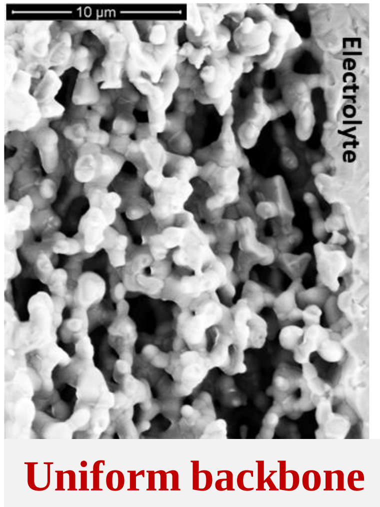
Uniform anode backbone

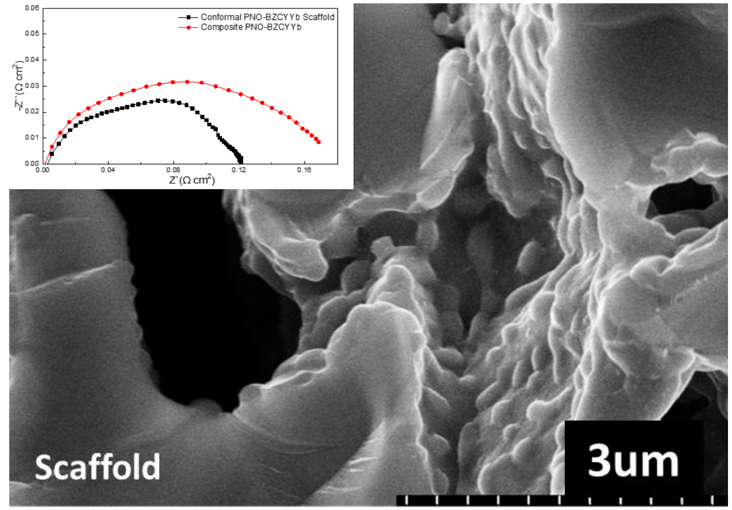


Accomplishments-Conformal coating & 3D Textile Electrode

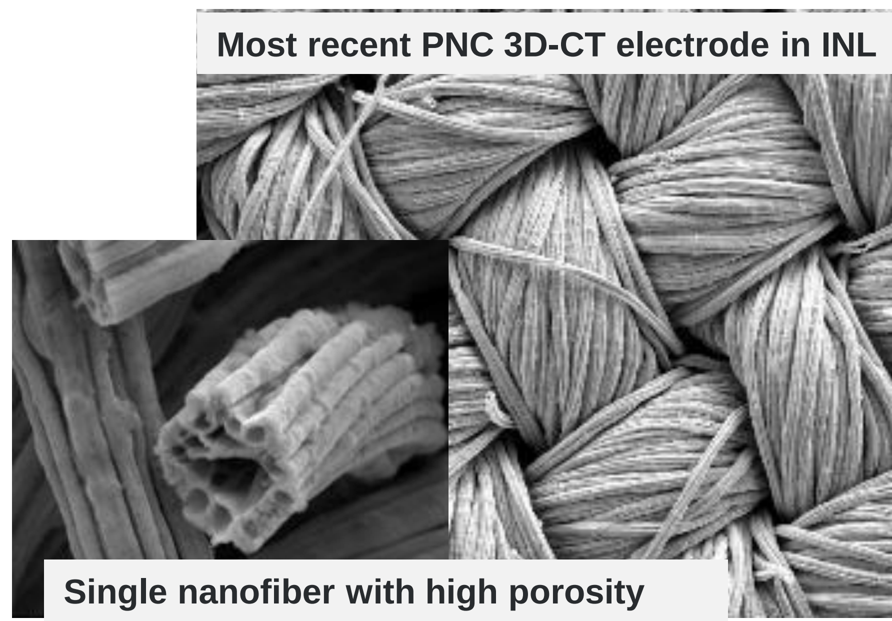
Composite PNO+BZCYYb 1150 °C | **Co-fired scaffold 1300 °C** → **Conformal PNO coating 1000 °C**



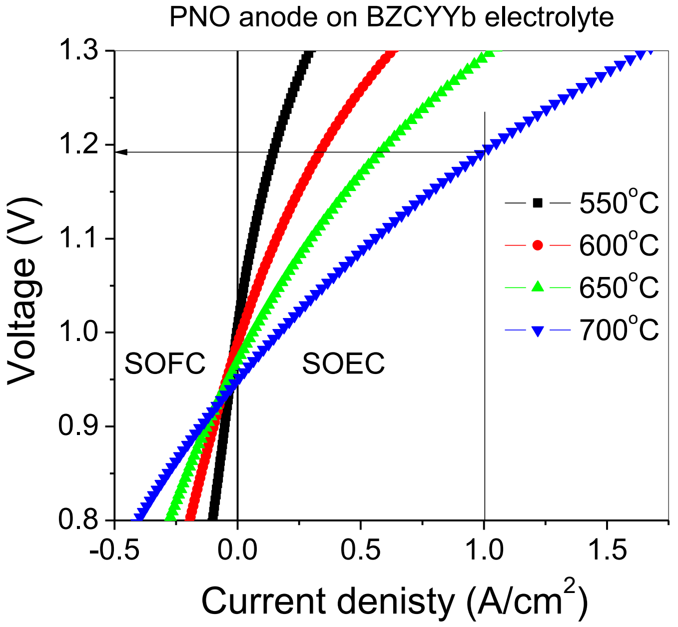




- ❑ INL initiated the work on optimization of the synthesis of 3D ceramic textile electrode backbone for incorporating VWU's electrode catalyst with infiltration method.
  - The synthesis temperature was attempted between 700~900 ºC and preliminary result shows high porosity of 64.4% and good mechanical strength can be achieved at 800 ºC;
  - The synthesis method can be easily for scaling up to make large electrode.

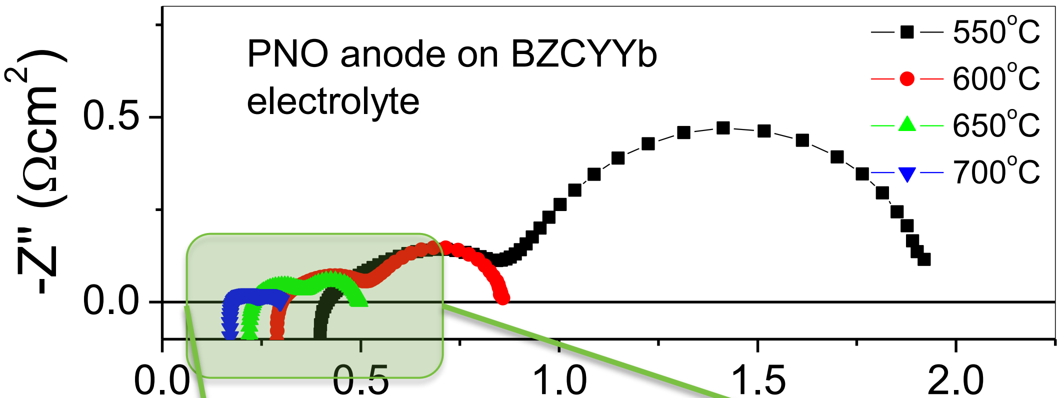


Accomplishments– Button Cell performance

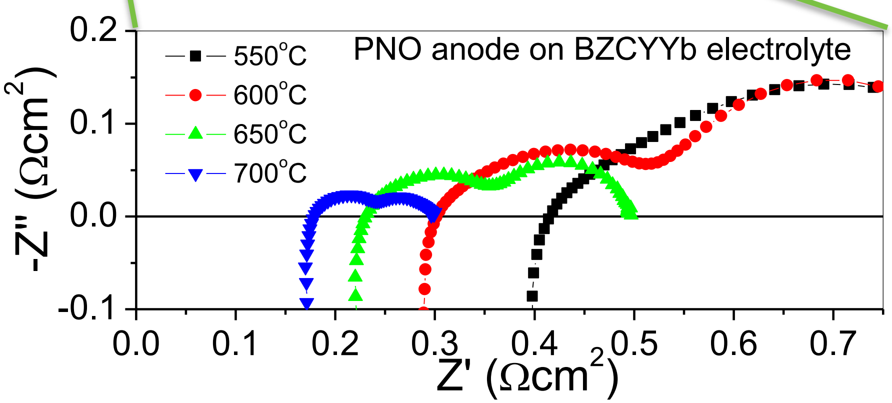


Go-No/Go Criterion 1st year

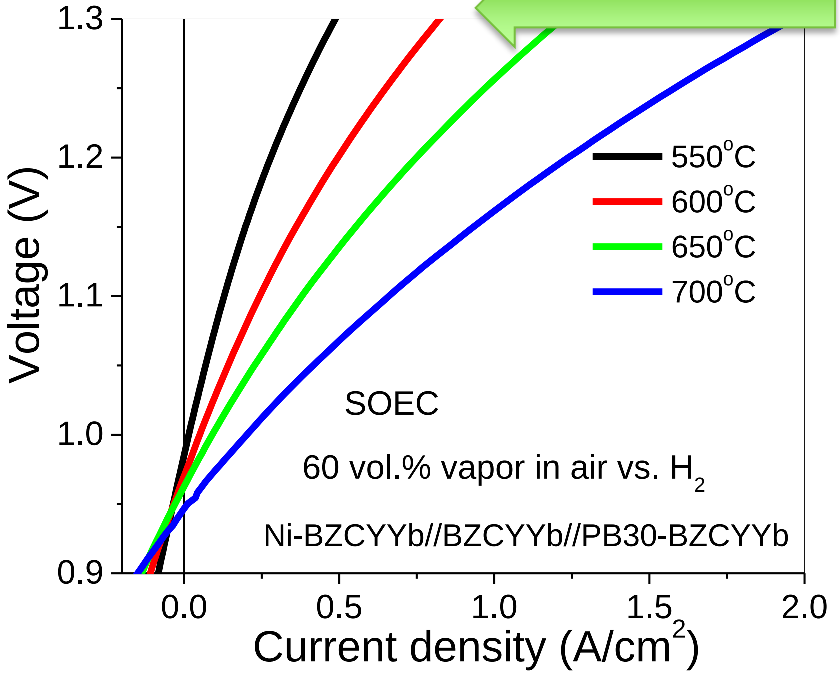
Hit 1A/cm^2 at 1.2 V@ 700°C vs. the goal 1.4V

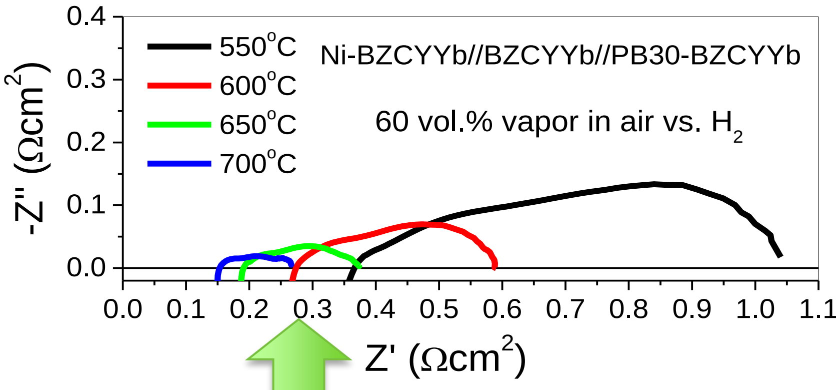


0.30 Ωcm^2 @ 700°C vs. the goal 0.35 Ωcm^2



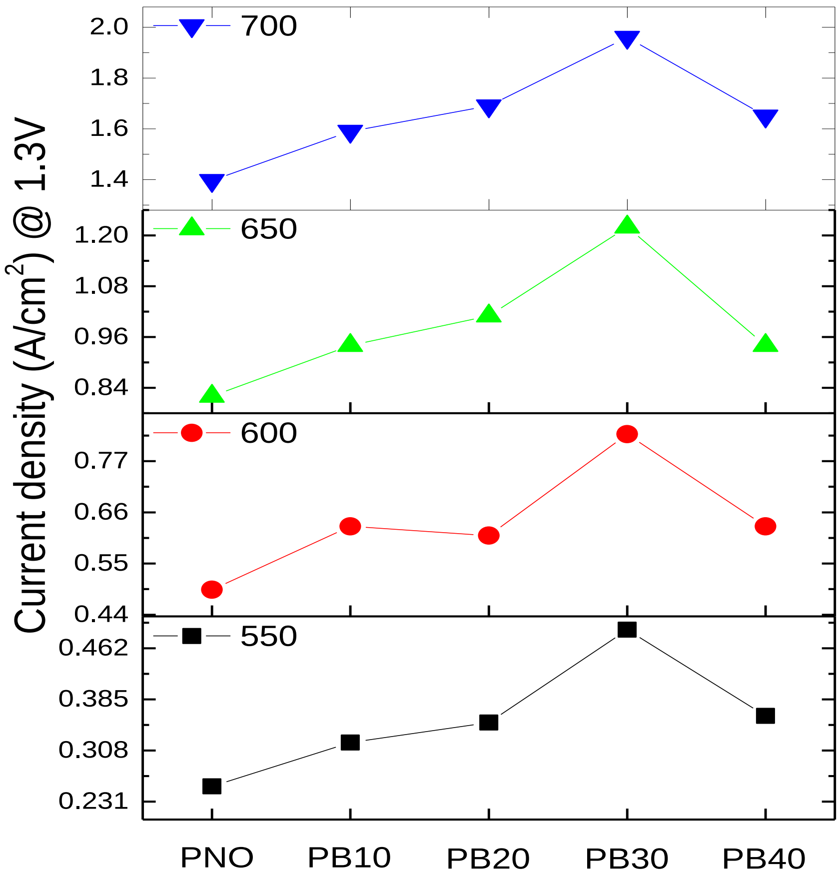
Accomplishments– Button Cell performance





0.58 Ωcm^2 @ 600°C

Hit 0.82A/cm^2 at 1.3 V@ 600°C



H_2O kinetics ∝ Electrolysis

O_2 kinetics are less related

in consistence with the model predication

Responses to Previous Year Reviewers' Comments

- Combinatorial studies are difficult to set up to ensure no false positives or negatives are produced. Unless the testing is being done in a relevant environment, misleading results may occur.

Response: the team aims to understand and promote the materials from a more comprehensive evaluation setting. It is indeed challenging to keep high fidelity standard across very different experimental sets. We screened routes ever possible to our ability to minimize the discrepancy in this combinatorial studies. Composition, phase and condition are made the same or very similar between E-XPS, electrochemical and modeling studies.

- There is a reasonable outline of the next steps. It would be good to see some modeling added to guide materials composition selection.

Response: our electrochemical continuum modeling is capable of guiding/predicting electrode reaction limits vs. materials physiochemical properties, electrode/electrolyte mixture composition and electrode microstructure. D, k values, gas diffusion, charge transfer under detailed structural and potential parameters are all considered and optimized. But this model is not capable of deriving optimal chemical stoichiometric composition of steam electrode from the aimed physiochemical properties.

- It is suggested that the team do the durability testing in a lower steam concentration (below 60%).

Response: experimental results shows steam concentration higher than 30 vol.% won't introduce a perceptible influence to the performance. We use up to 60 vol% steam to unveil possible chemical stability issue in long-term operation of electrolyte and electrode.

Collaboration: Effectiveness

Interactions with NREL:

To develop the High-throughput screening with combinatorial studies of $Ba(Zr_{1-x-y}Y_xPr_y)O_3$-based phases, NREL is now working together with CMS on the synthesis and sintering of Ba, Zr, Pr pellet precursors for HTS. The sample will be characterized by CSM E-XPS facility. The outcome date will give useful guidance on the **Task 1** modeling, **subtask 3.2** anode development and **subtask 3.3** catalyst layer development.

Interactions with INL:

Recently studied BZCYYb series electrolyte properties on conductivities and electronic leakage will provide guidance on button cell designation. The 3D Ceramic Textile electrode is expected to significantly improve the button cell performance. I-V, EIS, and polarization curves will be examined, and the button cell will be used in **subtask 3.3**

Expected benefits

The characterization of BZCYYb-PNO materials and button cell with BZCYYb-LCO bi-layer will benefit HydroGEN Consortium by enrichment of related materials system database and guidance for the future functional designation. The modeling of the water-splitting kinetic will serve as basis of understanding the mechanism of electrolysis and improvement of the performance

Remaining Challenges and Barriers

- Updating modeling programming to connect the physical properties and electrochemical impedance response
- Improving electrode faradic efficiency >80% and durability in high steam concentration
- Balance between durability and catalytic activity within a full cell

Any proposed future work is subject to change based on funding levels

Proposed Future Work

Remainder of FY 2020

- Model prediction of the requirement needed to reach a 0.35 $\Omega.cm^2$ ASR @ 600^oC.
- Continue working on high temperature screen of anode and catalyst
- Characterization PNO & BCZYYb with E-XPS without electrochemical bias
- Exploring the effect of Zr/Ce ratio on electrolyte's properties
- Combinatorial catalyst layer coating on button cell with enhanced activity
- Full cell durability characterization with degradation<30 mV/1000 hr .

FY 2021

- Optimization of electrolyte properties for higher faradic efficiencies
- Further development on cell stability with degradation <10 mV/1000 hr .
- Cathode-supported H-SOEC button-cell with 3D hierarchical structure anode

Any proposed future work is subject to change based on funding levels

Project Summary

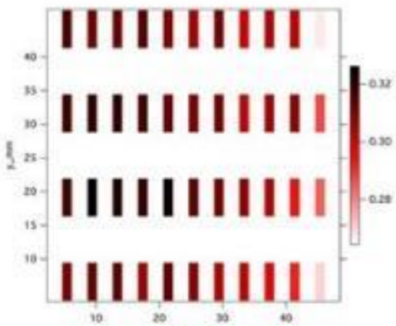
- Electrochemical model on anode reaction, structural and composition effects of H-SOEC has been established
- PNO + BZYP film and Au coat patterns have been fabricated by NREL
- E-XPS is currently in-progress in CSM
- Composition effects on BZCYYb electrolyte characterized experimentally
- Defect chemistry model developed to predict the leakage behaviors of electrolyte under practical conditions
- 3D Ceramic Textile (3D-CT) Oxygen Electrode initiated
- Conformal catalyst coating technology established
- Year 1 target of Button cell performance of PNO-base H-SOEC achieved
- Model guided anode materials with ASR<0.3 developed

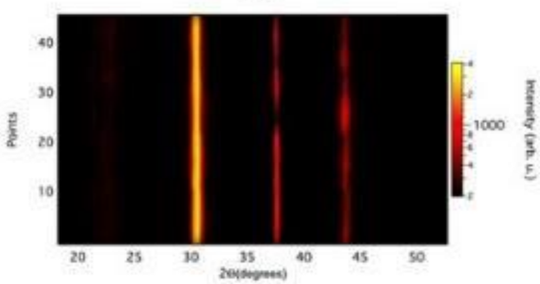
Any proposed future work is subject to change based on funding levels

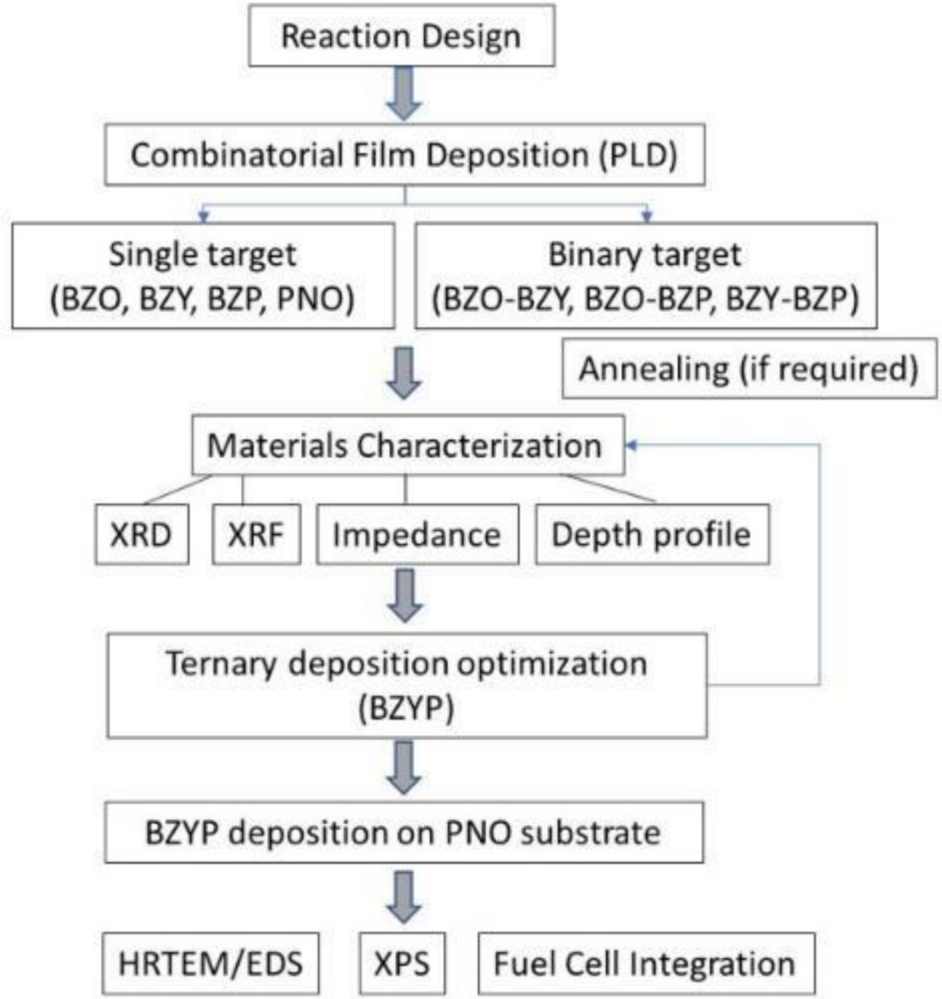
Technology Back-Up

The thin films will be characterized by:

- Crystallinity (XRD)
- Structure (XRD)
- Composition (XRF)
- Surface chemistry (XPS)
- Ionic/electronic conductivity (Impedance Spectroscopy)
- Activation Energy (Impedance Spectroscopy)





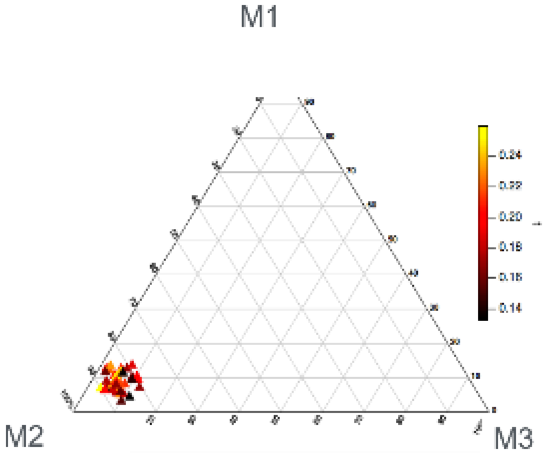


Any proposed future work is subject to change based on funding levels

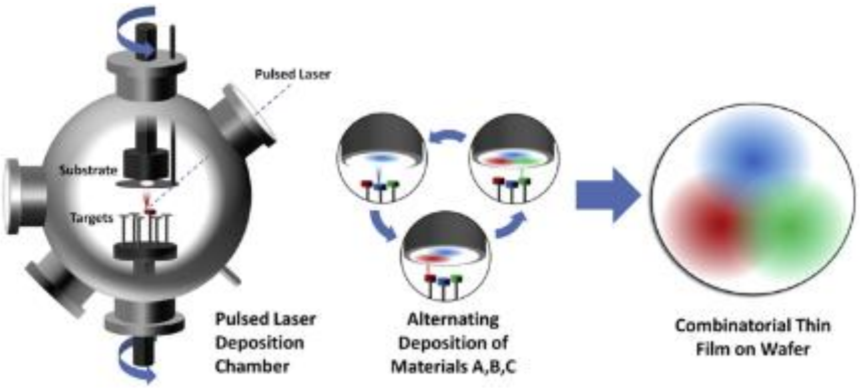
Technology Back-Up

NREL will perform deposition of Ba(ZrYPr)$O_{3-\delta}$ thin film sample libraries with Zr/Y/Pr composition gradients as well as gradient-free baseline samples to establish the BZYP combinatorial synthesis process.

Single	binary	ternary
$BaZrO_3$	$BaZrO_3$ + $BaZr_{0.7}Y_{0.3}O_3$	$BaZrO_3$ + $BaZr_{0.7}Y_{0.3}O_3$ + $BaZr_{0.7}Pr_{0.3}O_3$
$BaZr_{0.7}Y_{0.3}O_3$	$BaZrO_3$ + $BaZr_{0.7}Pr_{0.3}O_3$	
$BzZr_{0.7}Pr_{0.3}O_3$	$BaZr_{0.7}Y_{0.3}O_3$ + $BaZr_{0.7}Pr_{0.3}O_3$	
Pr_2NiO_4		



- Pulsed laser deposition system will be used for the combinatorial thin films.
- Preliminary tests will be conducted with single and binary targets with different temperature, pressure, pulse, etc.
- The thin films will be deposited on glass and ITO substrates and characterized for composition, structure, morphology, thickness, Impedance and so on.



Any proposed future work is subject to change based on funding levels

Technology Back-Up

Effective Leveraging of the EMN Resource Nodes

INL-Advanced Electrode and Solid Electrolyte Materials for Elevated Temperature Water Electrolysis

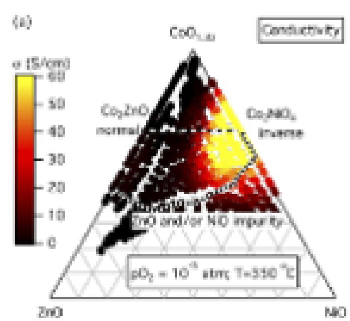
- Synthesis and optimization of $BaZr_{1-x-y-z}Ce_xY_yYb_z$ H-electrolyte.
- Planar, 5cm x5cm full cells, short-stack.

✓ **More focused studies**
✓ **Complementary expertise**

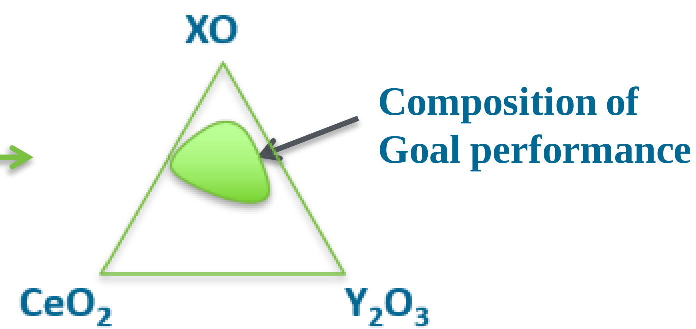
NERL-High-Throughput Experimental Thin Film Combinatorial Capabilities

- HTS composition for electrocatalytic conformal coating on $Pr_2NiO_{4+\delta}$ anode backbone

✓ **Fast blanket screening**
✓ **Optimal materials**



NERL CoO-CuO example



Any proposed future work is subject to change based on funding levels

Technology Back-Up

Optimization of electrolyte properties of $BaCe_{0.8-x}Zr_xY_{0.1}Yb_{0.1}O_3$ (x=0.1, 0.2, 0.4) system

Electrolyte synthesis and evaluation

Measure electrical conductivity in different gas conditions and temperatures;

Examine structure stability in high vapor conditions at 700°C

Electrolyte Integration

Fabricate dense electrolyte membrane on electrode support sintered under 1450°C and send powder/cells to WVU;

Support WVU with INL's high temperature R2R manufacturing capability

Electrolyte Determination

Examine electrolyte and electrode polarization resistances in SOEC;

Measure Faradaic efficiency under different electrolysis current densities to determine the optimal composition

Any proposed future work is subject to change based on funding levels

Publications and presentations

- Yi Wang, Wenyuan Li, **Xingbo Liu***: Degradation of Solid Oxide Electrolysis Cell: Phenomena, Mechanisms, and Emerging Mitigation Strategies – a Review, J*ournal of Materials Science & Technology (2010)* https://doi.org/10.1016/j.jmst.2019.07.026

- Wenyuan Li, Bo Guan, Liang Ma, Zhongqiu Li, Hanchen Tian**, Xingbo Liu***: Synergistic Coupling of Proton-Conductors $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ and $La_2Ce_2O_7$ to Create Chemical Stable, Interface Active Electrolyte for Steam Electrolysis Cells, *ACS Applied Materials & Interfaces 11 (2019) 18323-18330*

- Wenyuan Li, Bo Guan, Liang Ma, Shanshan Hu, Nan Zhang, **Xingbo Liu***: Highly Performing Triple-Conductive $Pr_2NiO_{4+\delta}$ Anode for Proton-Conducting Steam Solid Oxide Electrolysis Cell, *Journal of Materials Chemistry A 6 (2018) 18057-18066*