Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

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

Xingbo Liu, West Virginia University

September 13, 2018

High Temperature Electrolysis Review Meeting

NREL
BERKELEY LAB
Sandia National Laboratories
INL Idaho National Laboratory
Lawrence Livermore National Laboratory
SRNL

HydroGEN Kick-Off Meeting

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

Xingbo Liu, West Virginia University
Greg Jackson, Colorado School of Mines
Dong Ding, Idaho National Laboratory
Andriy Zakutayev, National Renewable Energy Laboratory

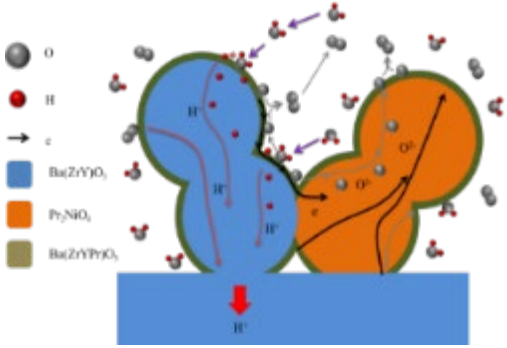
Award #	EE0008378
Year 1 Funding	$250K

Project Vision

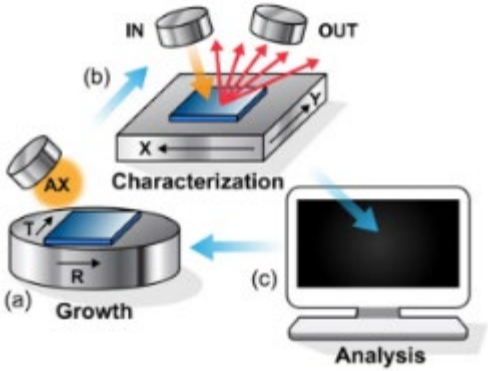
We are solving the low performance/high degradation of SOECs by developing intermediate-temperature H^+-conducting SOEC with robust electrode structure and intrinsically advantageous electrode kinetics.

Project Impact

- Expanding the frontier of SOEC development
- Strong support to low cost Hydrogen economy
- Networking complementary expertise of universities and EMN partners



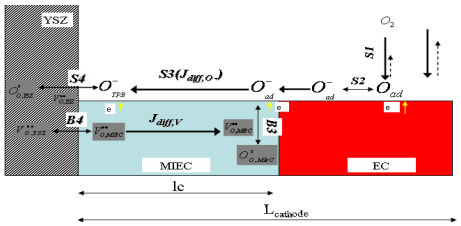
Triple-conducting anode with conformal coating



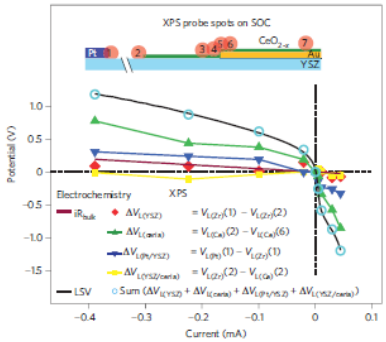
High-Throughput fast materials screening

Innovation and Objectives

Project history



H. Zhang, K. Gerdes, **X. Liu***: Surface Transport Mechanism and Bi-pathway ORR Kinetics for Solid Oxide Fuel Cell Cathode , *JES 161 F983-990*



C. Zhang, G. Jackson etc. "Measuring fundamental properties in operating SOEC by using in situ XPS, *Nature Mat. 9, 944*

Proposed targets

Metric	State of the Art	Proposed
Parameter 1	0.9A/cm^2 @850°C	>1A/cm^2 @600°C
Parameter 2	0.3~0.4 Ω·cm^2 ASR@800°C	0.35 Ω·cm^2 ASR@600°C
Parameter 3	3%/1000h	4 mV/1000 h or 0.3%/1000h

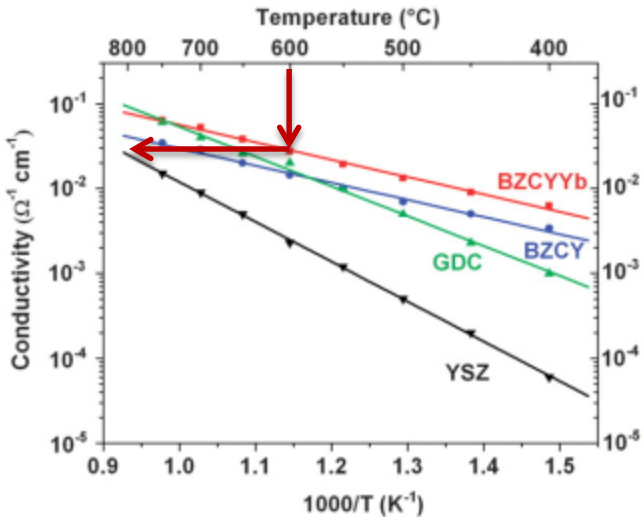
Barriers

- ❖ Long-term chemical stability of electrolyte materials in concentrated vapor ← Zr-riched phase or buffer layer.
- ❖ Morphology of conformal coating ← replace infiltration with ALD.
- ❖ Long-term real-time measurement ← INL physics-of-failure and accelerated testing.

Partnerships

- ✓ Greg Jackson (CSM): surface catalytic activity, **in operando environmental XPS**.
- ✓ Dong Ding (INL): advanced synthesis of proton conducting electrolyte, cell scale-up
- ✓ Andriy Zakutayev (NERL): novel materials for energy applications using **HTS** combinatorial research methods.

Technology Innovation

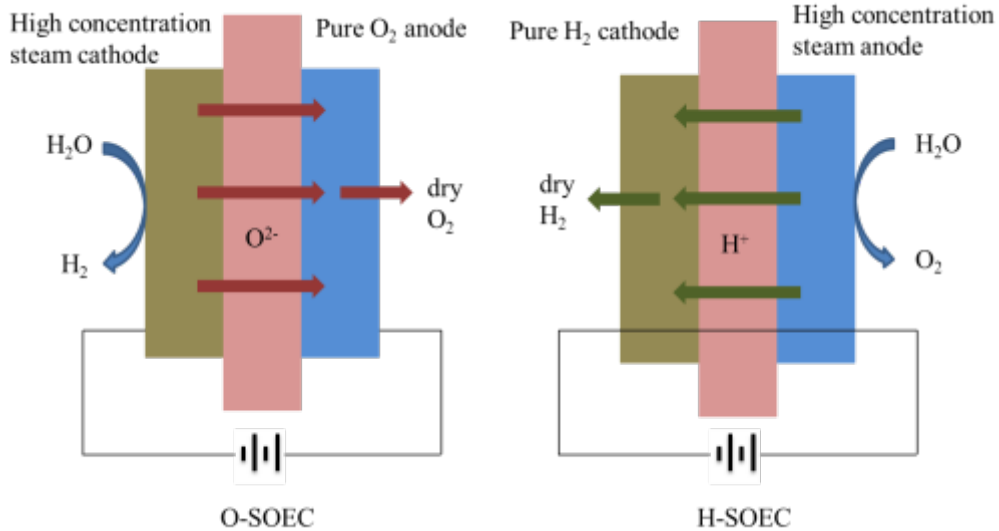


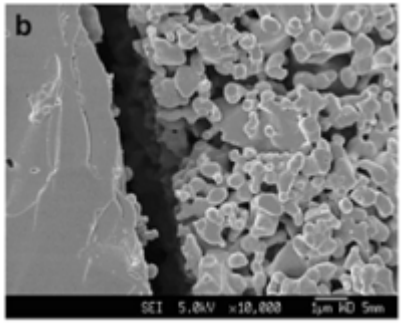
Liu et al. Science Vol. 326, Issue 5949, pp. 126-129

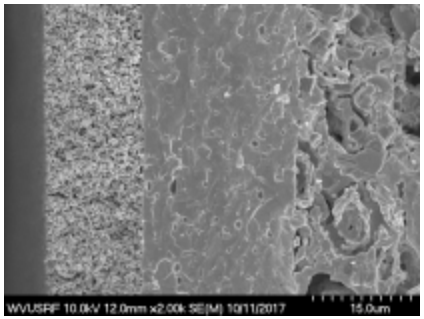
600C BZCYYb vs. 800 YSZ

High σ, low Ea → low operation T

- Less challenge in stack components
- Easier maintenance
- Slower materials deterioration
- Longer service life







Chen et al. Int j. hydrogen energy 36 (2011) 10541-10549

O-SOEC: O_2 exsolution leads to **popped-off** anode layer, **chemical reactions**: $La_2Zr_2O_7$, MnO_2 etc. **Mixture** of H_2 and H_2O product

H-SOEC: H_2 exsolution at cathode with **robust Ni/BZCY bond** after 1400°C co-sintering, **no chemical reactions**, **dry H_2**.

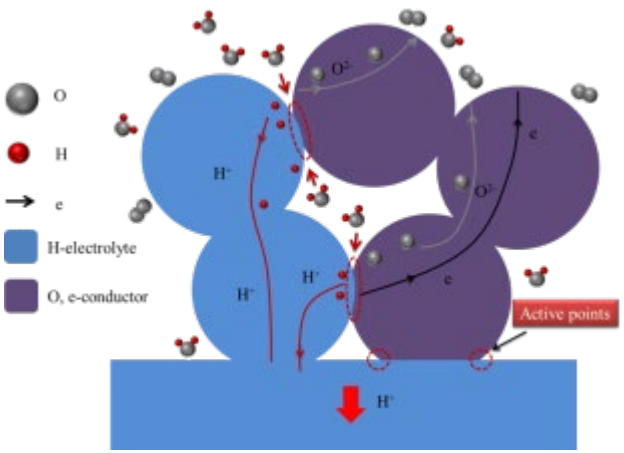
Technology Innovation – Triple Conducting Air Electrode

H - SOEC

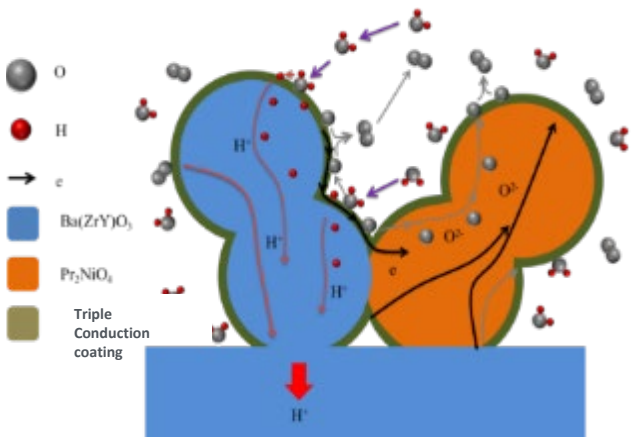
Air Electrode: $2H_2O \rightarrow O_2 + 4H^+ + 4e$

Electrolyte: $H^+\downarrow$

Hydrogen Electrode: $4H^+ + 4e \rightarrow 2H_2$



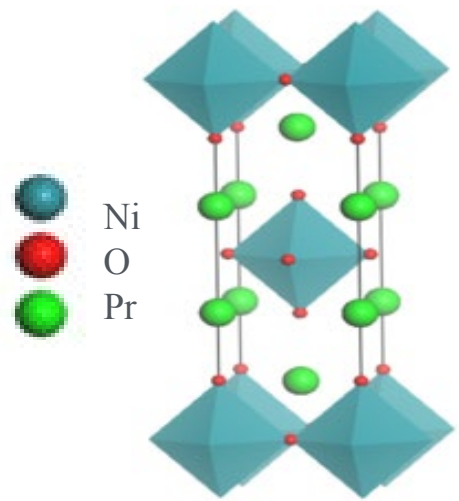
Traditional: O, e-conducting electrode, active sites at boundaries only



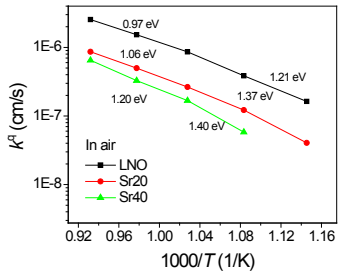
Proposed: H, e-conducting electrode, active at both boundaries and massive inner surface

- Real 3-D reactive anode lies in H-conductivity of electrode material
- Inherently good performance compared to O-MIEC
- Develop "conformal" coatings to further extend reaction areas to 2PB.

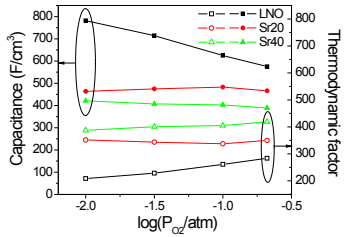
Ruddlesden-Popper Phase as SOC Electrode



- Ln_2MO_4 - Ruddlesden-Popper structure
- ABO_3 perovskite layers stacking alternatively with rock-salt Ln_2O_2 layers



B. Guan, W. Li, H. Zhang, **X. Liu**, *JECS 162 (2015) F707-F712*



. Li, B. Guan, X. Zhang, J. Yan, Y. Zhou, **X. Liu***, *PCCP 18 (2016) 8502-8511*

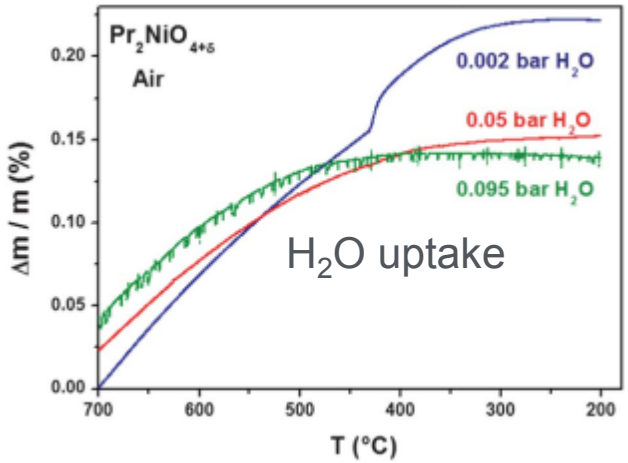
As Air Electrode in SOFC

- High chemical diffusion and surface exchange coefficients.
- Compatible TEC with GDC or LSGM.
- O-conduction via Oxygen interstitials
- Relative lower electrical conductivity than Co-based perovskite cathode

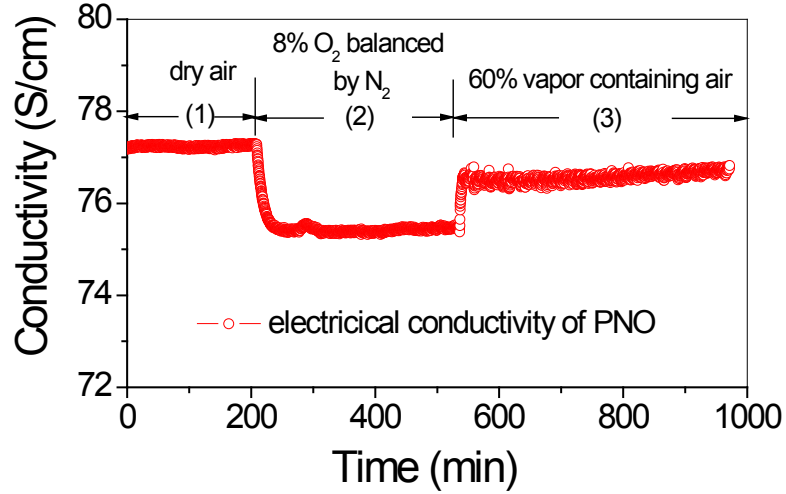
As Air Electrode in H-SOEC

- Wide channel for ion (specially H) conduction
- Readily alterable composition

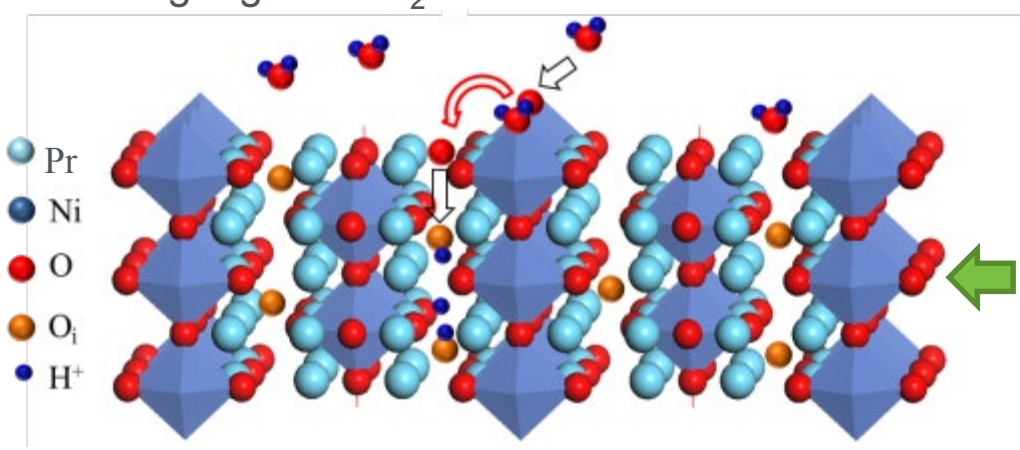
Technology Innovation



Grimaud et al. J. Mater. Chem 2012 (22) 16017



4.4 at.% H into PNO for every 0.1% weight gain of H_2O.



ALL REACTIONS from (1) to (2),

$$2h + O_i^{2-} \leftrightarrow 0.5O_2 + V_i$$
$$2h + O_0^x \leftrightarrow 0.5O_2 + V_0^{\bullet\bullet}$$

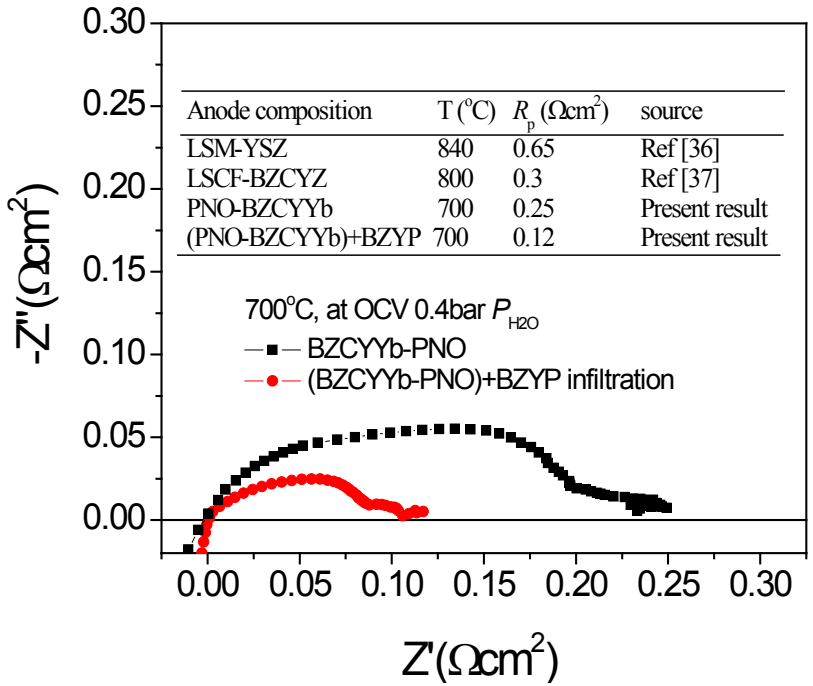
loss of charge carriers, decrease σ_e

From (2) to (3)

$$H_2O + 0.5O_2 + 2V_i \leftrightarrow 2OH_i' + 2h$$

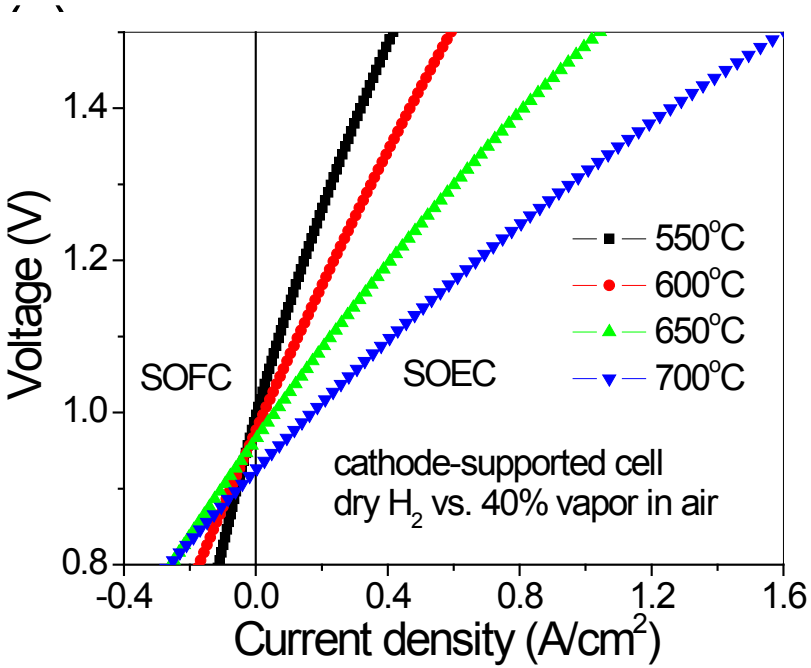
introduce H^+-conducting and increase σ_e

Technology Innovation



Anode composition	T (°C)	R_p (Ωcm²)	source
LSM-YSZ	840	0.65	Ref [36]
LSCF-BZCYZ	800	0.3	Ref [37]
PNO-BZCYYb	700	0.25	Present result
(PNO-BZCYYb)+BZYP	700	0.12	Present result

Preliminary performance of PNO-based anodes, as compared with LSM & LSCF.



Performance of primary cathode supported Ni/BZCY//BZCY//PNO-BZCY full cell

* Wenyuan Li, Bo Guan, Liang Ma, Shanshan Hu, Nan Zhang, **Xingbo Liu***: Highly Performing Triple-Conductive Pr2NiO4+δ Anode for Proton-Conducting Steam Solid Oxide Electrolysis Cell, *Journal of Materials Chemistry A (2018) DOI: 10.1039/C8TA04018D*

Technology Innovation

Cell configuration	Steam in anode (atm)	T (°C)	Polarization resistance (Ωcm²)	Current density (mA/cm²)	Applied potential /overpotential (V)	Year and Ref
$Pr_2NiO_{4+\delta}$-BZCY// $BaZr_{0.2}Ce_{0.6}Y_{0.2}O_{3-\delta}$ (20 μm)//Ni-BZCY	0.4	700	0.31	977	1.3/0.37	This study
$Pr_2NiO_{4+\delta}$-BZCY//$BaZr_{0.2}Ce_{0.6}Y_{0.2}O_{3-\delta}$ (20 μm)//Ni-BZCY	0.4	600	0.4	600	1.3/0.33	This study
$Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ -BCZY//$BaCe_{0.5}Zr_{0.3}Y_{0.2}O_{3-\delta}$ (20 μm)//Ni-BCZY	0.5	700	0.57	500	1.3/0.35	2010[23]
(LaSr)$CoO_{3-\delta}$-BZCYbCo//$BaCe_{0.48}Zr_{0.4}Yb_{0.1}Co_{0.02}O_{3-\delta}$ (45 μm)//Ni-BCZYbCo	0.3	700	-	60	1.3/0.30	2011[22]
$(La_{0.75}Sr_{0.25})_{0.95}Mn_{0.5}Cr_{0.5}O_{3-\delta}$-BZCYZ//$BaCe_{0.5}Zr_{0.3}Y_{0.16}Zn_{0.04}O_{3-\delta}$ (75 μm)//Ni-BCZYZ	0.03	700	~21.4	1000	1.3/1.17	2012[28]
$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$-BZCYZ//$BaCe_{0.5}Zr_{0.3}Y_{0.16}Zn_{0.04}O_{3-\delta}$ (2mm)//Ni-BCZYZ	0.03	800	7	25	1.3/0.67	2013[29]
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$-BZCYZ//$BaCe_{0.5}Zr_{0.3}Y_{0.16}Zn_{0.04}O_{3-\delta}$ (2mm)//Ni-BCZYZ	0.03	800	14.4	23	1.3/0.6	2013[29]
$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$-BZY20// $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ (15 μm)//Ni-BZY20	0.03	700	-	208	1.3/0.57	2015[24]
$LaNi_{0.6}Fe_{0.4}O_{3-\delta}/La_2NiO_{4+\delta}$-BCZD//$BaCe_{0.5}Zr_{0.3}Dy_{0.2}O_{3-\delta}$ (30 μm)//Ni–BCZD	0.9	700	-	300	1.3/0.37	2016[52]
$Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$-$BaZr_{0.8}Y_{0.2}O_{3-\delta}$//BZY(16 μm)//Ni–BZY	0.03	650	-	310	1.3/0.45	2017[53]

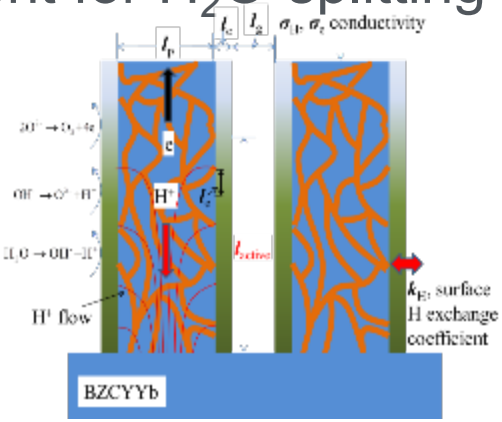
* Wenyuan Li, Bo Guan, Liang Ma, Shanshan Hu, Nan Zhang, **Xingbo Liu***: Highly Performing Triple-Conductive Pr2NiO4+δ Anode for Proton-Conducting Steam Solid Oxide Electrolysis Cell, *Journal of Materials Chemistry A (2018) DOI: 10.1039/C8TA04018D*

Project Timeline

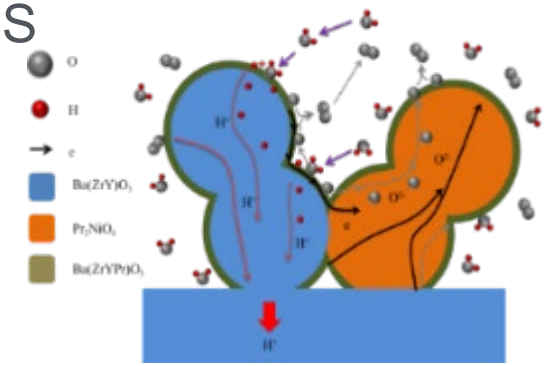
TASK DESCRIPTION	Q 1	Q 2	Q 3	Q 4	Q 5	Q 6	Q 7	Q 8	Q 9	Q 10	Q 11	Q 12
Task 1: ***Electrochemical modeling on reaction kinetics, compositional and structural effects***												
1.1: H_2O-splitting reaction kinetics modeling												
1.2: Anode structural & composition effects												
Task 2: ***High throughput screening on anode and catalyst compositions***												
2.1: in operando E-XPS of anode												
2.2: HTS of electrocatalyst												
Task 3: ***Development of button cells***												
3.1: H-electrolyte development												
3.2: Anode development												
3.3: Development of the catalyst layer through conformal coating technology												
3.4: Cathode supported button cell development												
3.5: Post-mortem examination												
Task 4: ***Short stack demonstration to meet the performance and durability target***												
4.1: Short stack fabrication & assembly												
4.2: Performance & durability measurements												
4.3: Post-mortem examination												
♦ :Milestone ● :Go/No-Go												

Research Tasks – Phase I (Year 1)

- **Task 1.0:** Electrochemical model development for H_2O-splitting anode design (M1-M12)
  - **Subtask 1.1:** Modeling of the intrinsic water splitting reaction kinetics (M1-M12)
  - **<u>Milestone Q1</u>:** Construction of the 1-D model, consistent with experimental results.



- **Task 2.0:** HTS to develop anode and catalyst material formulas
  - **Subtask 2.1**: Development of in operando E-XPS for anode characterization
  - **<u>Milestone Q3</u>:** 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.
  - **Subtask 2.2**: HTS for conformal coating of electro-catalyst for H_2O splitting



Research Tasks – Phase I (Cont'd)

- **Task 3.0:** Development and characterization of button cells (M1-M12)
  - **Subtask 3.1**: H-electrolyte development and optimization (M1-M12)
  - **Milestone Q2:** Development of H-electrolyte with a conductivity ≥ 0.1 S/cm at 700 ° C.
  - **Subtask 3.2**: Development and characterization of anode material (M4-M12)
  - **Subtask 3.3**: Development of catalyst layer through conformal coating technology (M7- M12)
  - **Subtask 3.4**: Fabrication and characterization of cathode supported H-SOEC (M7- M12)
  - **BUDGET PERIOD 1 GO/NO-GO DECISION POINT:** Cathode-supported H-SOEC button-cell ASR < 0.35 $\Omega \cdot cm^2$, current density >1.0 A/cm^2 at 1.4 V/cell electrolyzing potential at 700 ^oC.
  - **Subtask 3.5**: Post-mortem examination of button cells (M10-M12)

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**

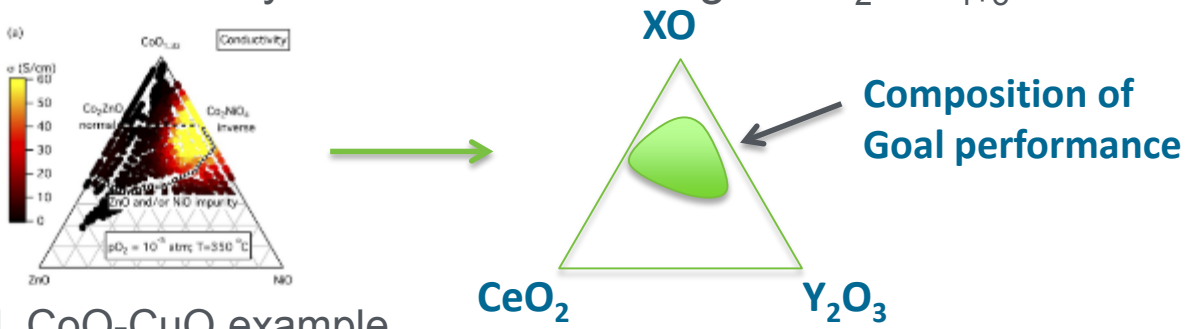
✓ **Complementary expertise**

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