Durable and High-Performance SOECs Based on Proton Conductors for Hydrogen Production

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DOE project award # FE0032115

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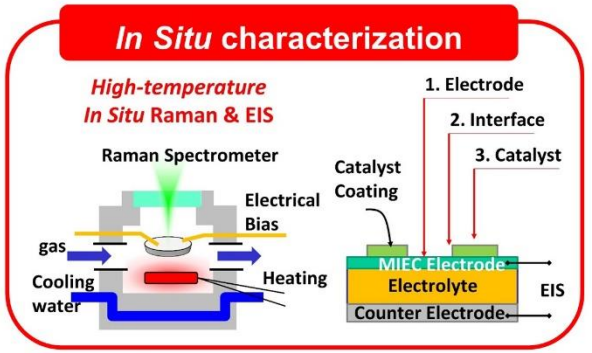
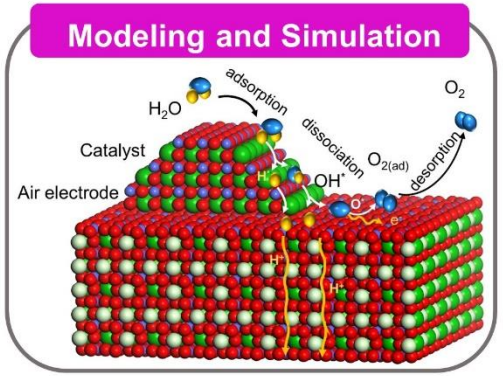
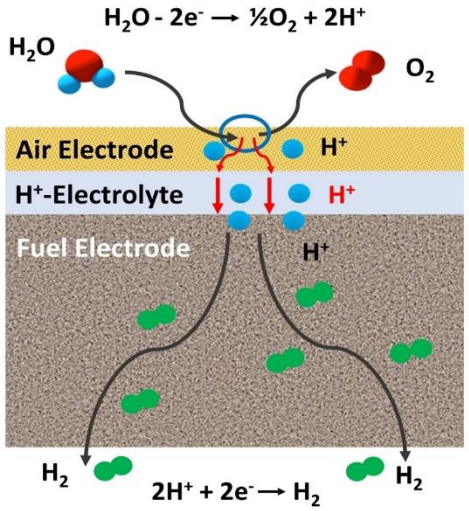
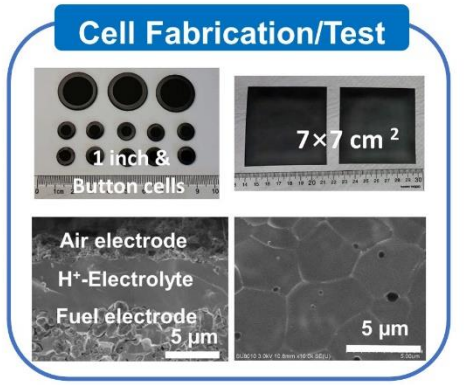
Georgia Institute of Technology

November 18, 2021









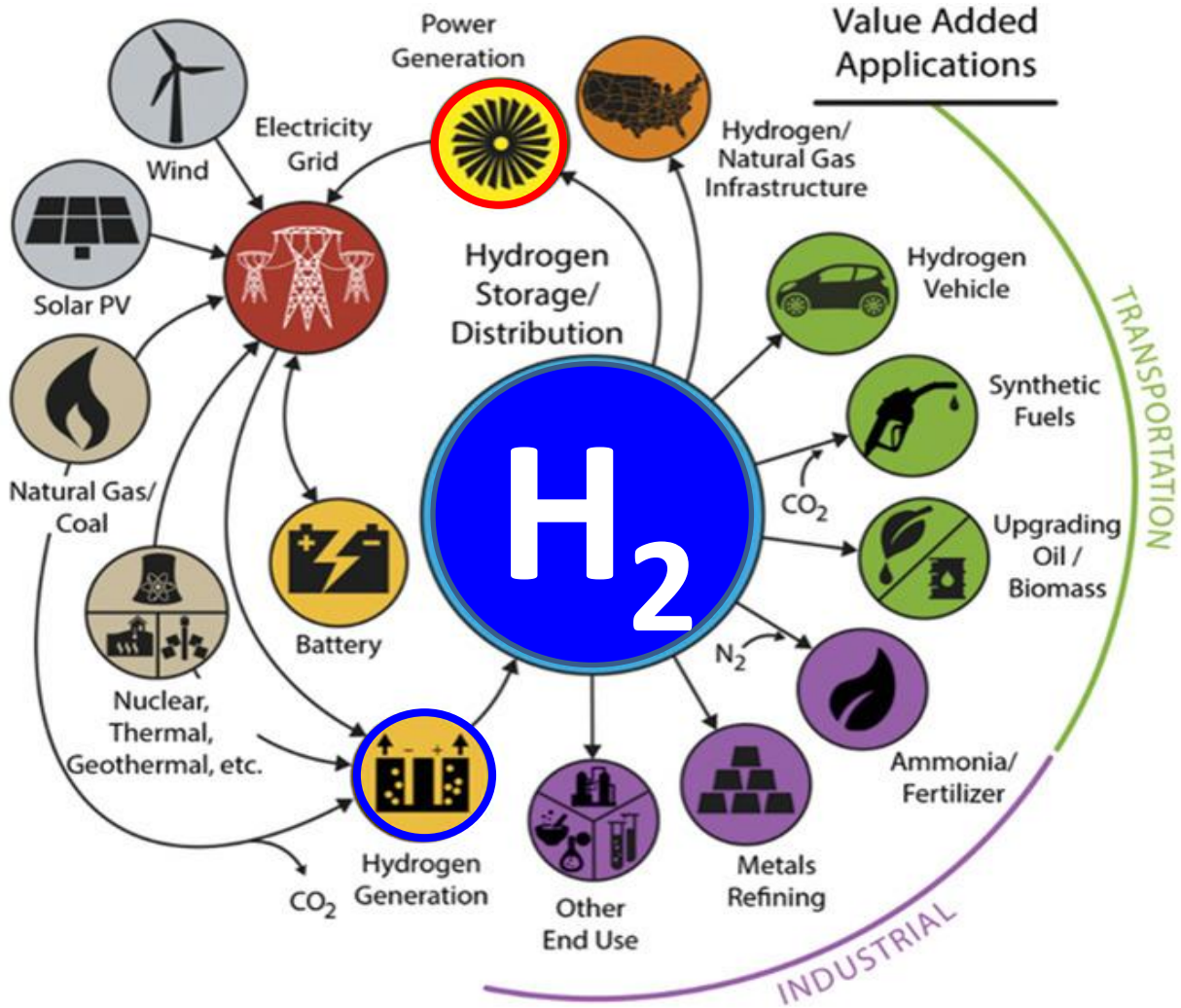
Proton-conducting SOEC

22nd Annual Solid Oxide Fuel Cell (SOFC) Project Review Meeting

Outline

- Motivation and Background
- Technical Approach
- Project Goal
- Project Schedule and Milestones
- Preliminary Results
- Acknowledgement

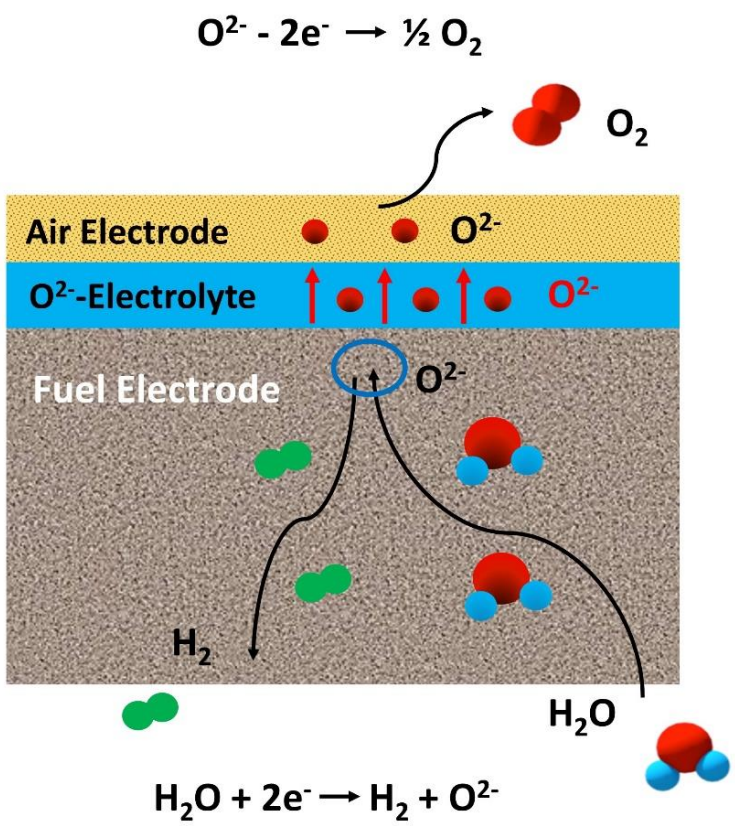
Motivation



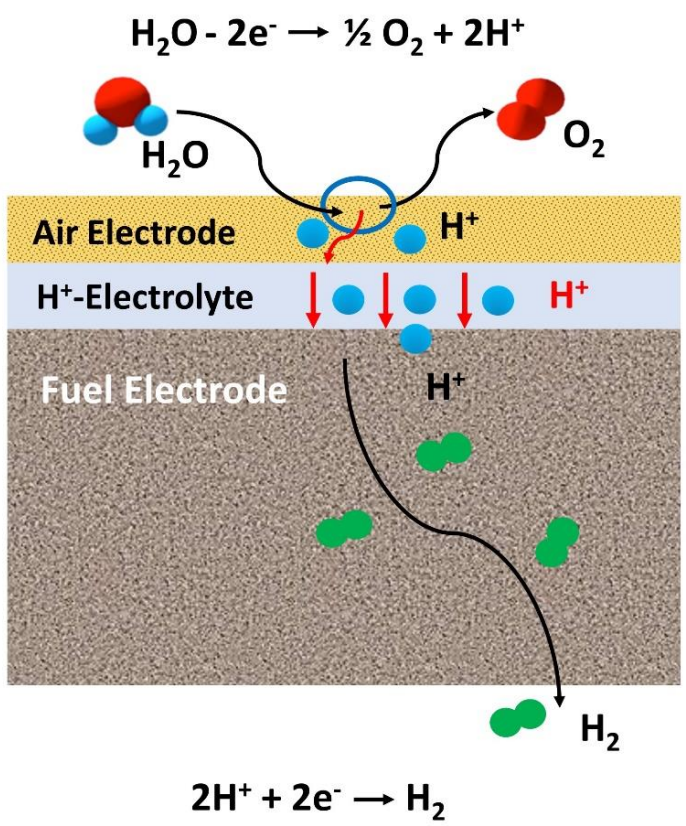
Electrochem. Soc. Interface 2018, **27**, 47

- H_2 is at the center for enhancing efficiency while reducing emission of many clean energy technologies.
- Solid oxide electrolysis cells (SOEC) has potential to offer highly efficient production of **green H_2.**
- Development of *new materials* and *fabrication processes* is vital to achieving high performance and durability at low cost.

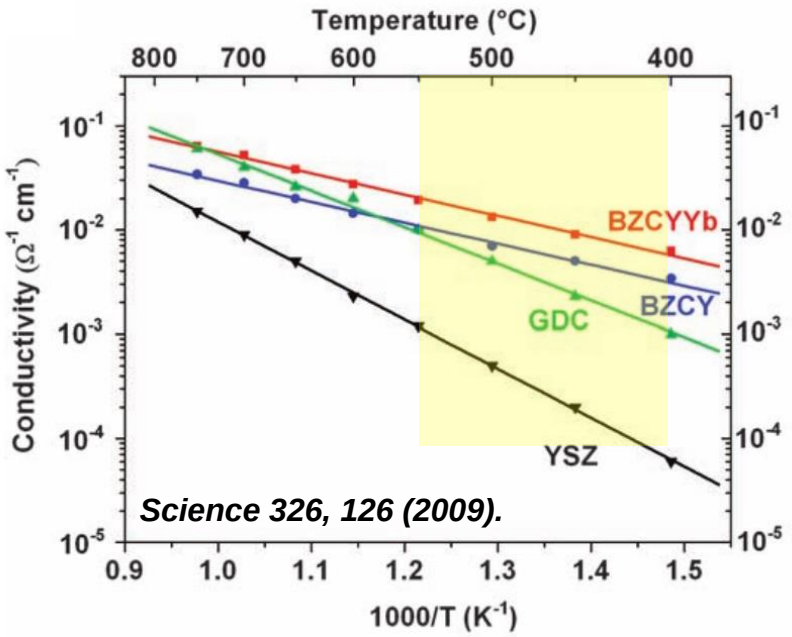
Background



SOEC – O^{2-}



SOEC – H^+

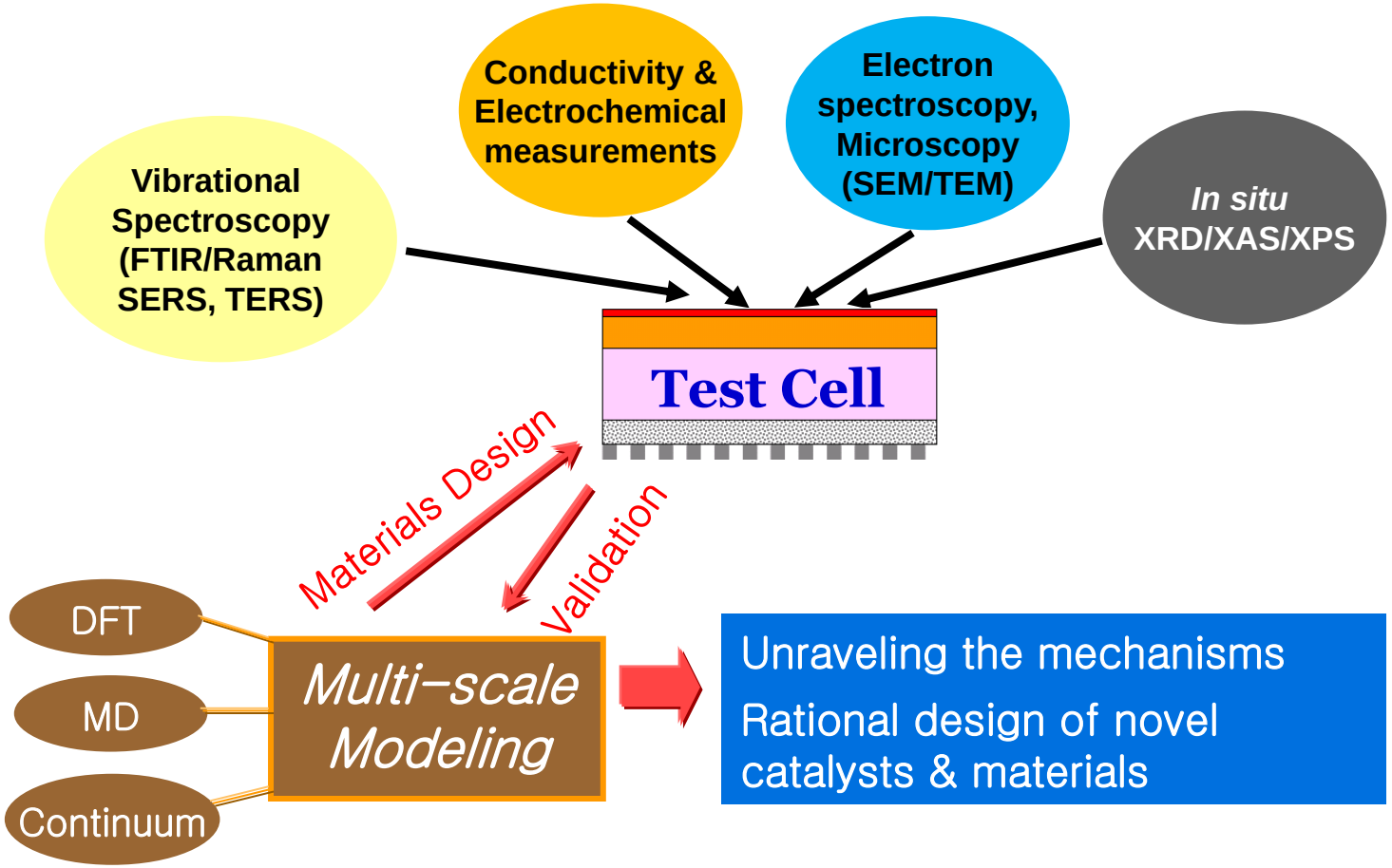


Science 326, 126 (2009).

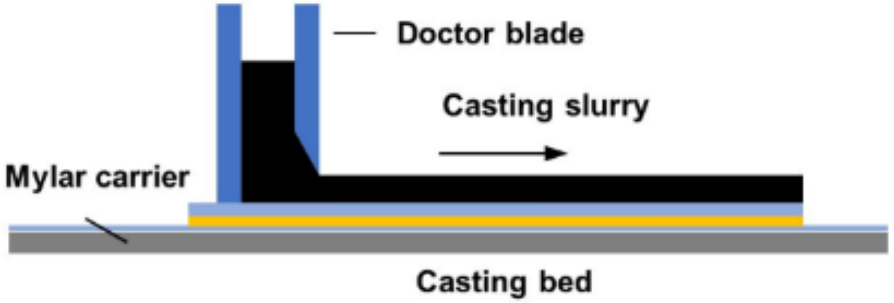
- High conductivity
- Low-temperature operation
- Dry H_2 (avoid Ni oxidation, H2 separation)
- Reduced cost
- Enhanced durability

Technical Approach

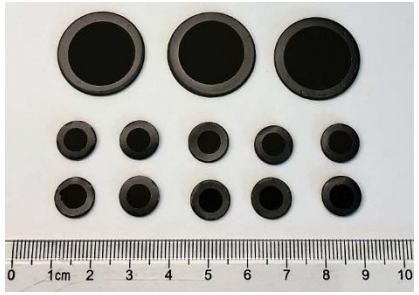
- ✓ Developing new composition and structure of proton conducting electrolytes;
- ✓ Tailoring the compositions, structure, and architecture of air electrodes;
- ✓ Optimizing compositions, thickness, morphology, and fabrication processes of catalysts;
- ✓ Understanding the degradation mechanisms using various *in situ*, *ex situ*, and *operando* measurements guided by theoretical analysis.



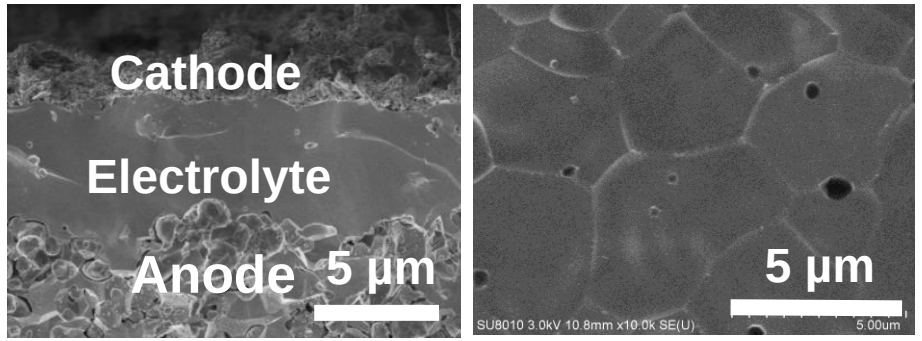
Single Cell Fabrication and Testing

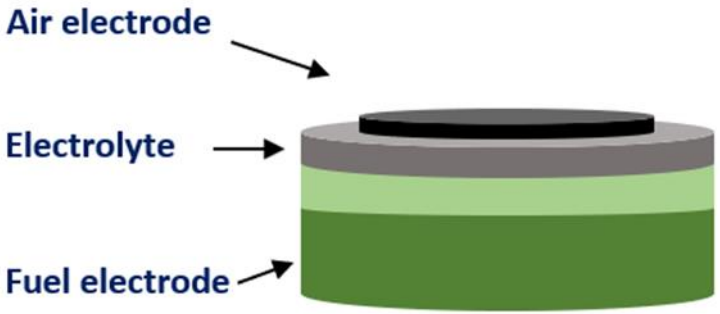


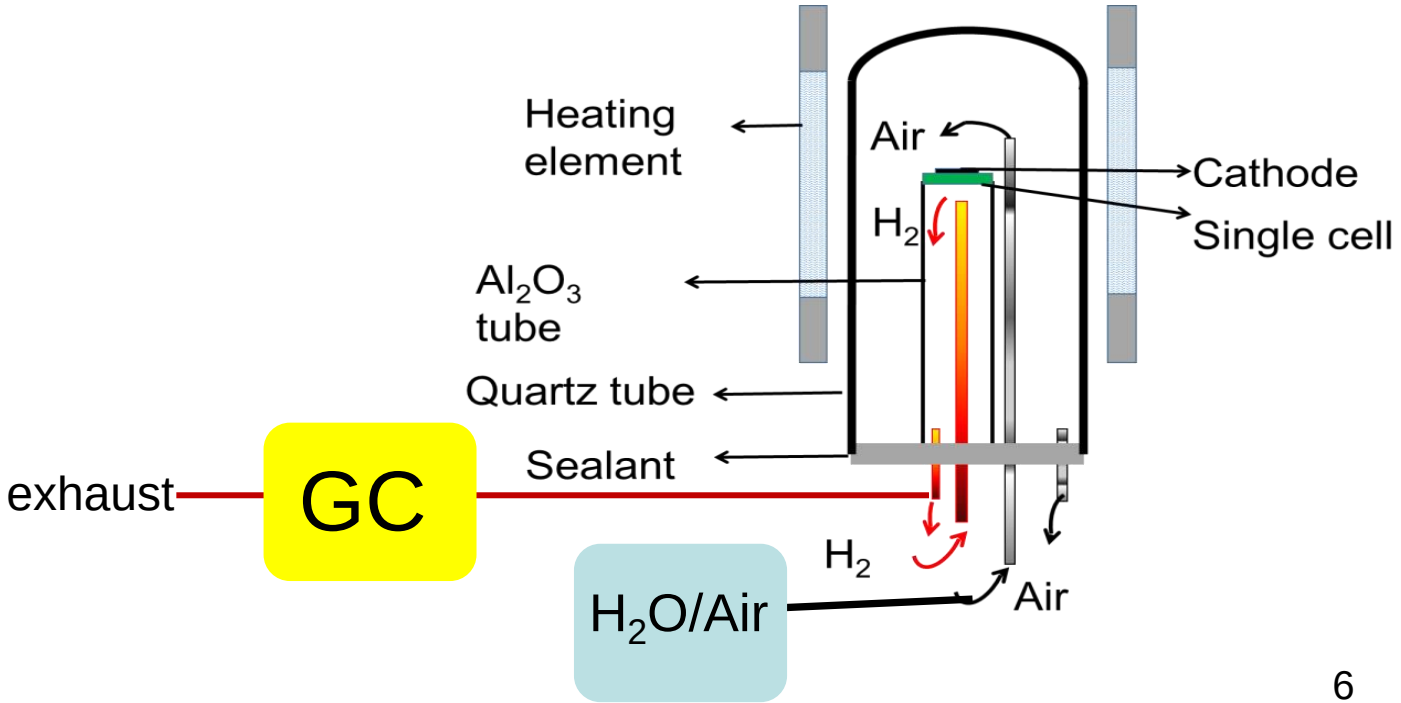
Co-tape casting



1 inch & button cells

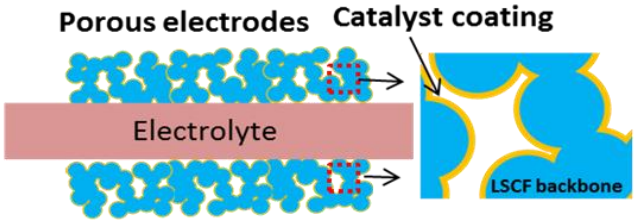




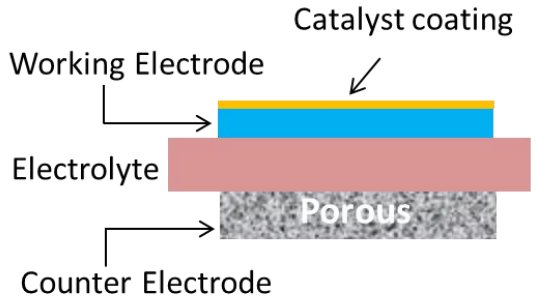


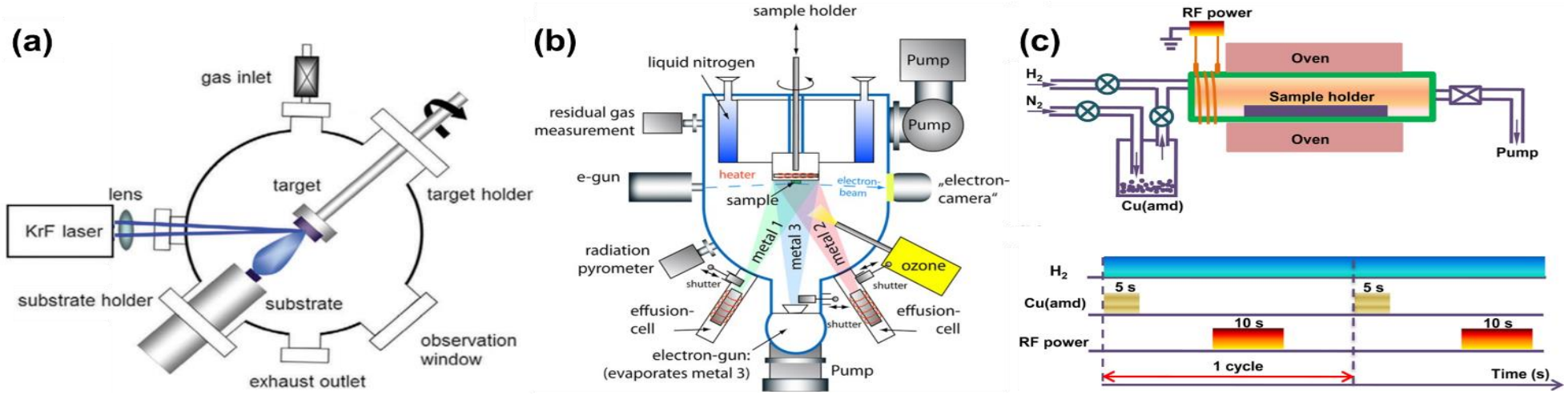
Model Cells for Mechanistic Study

Symmetrical Cell



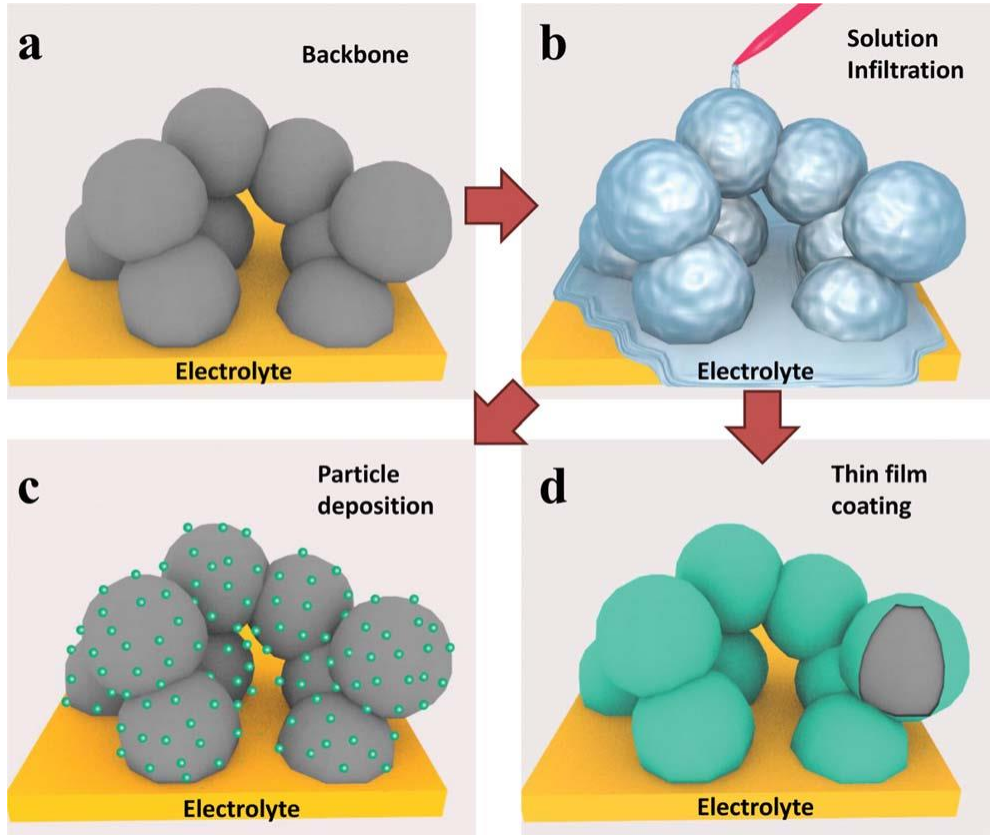
Model Cell

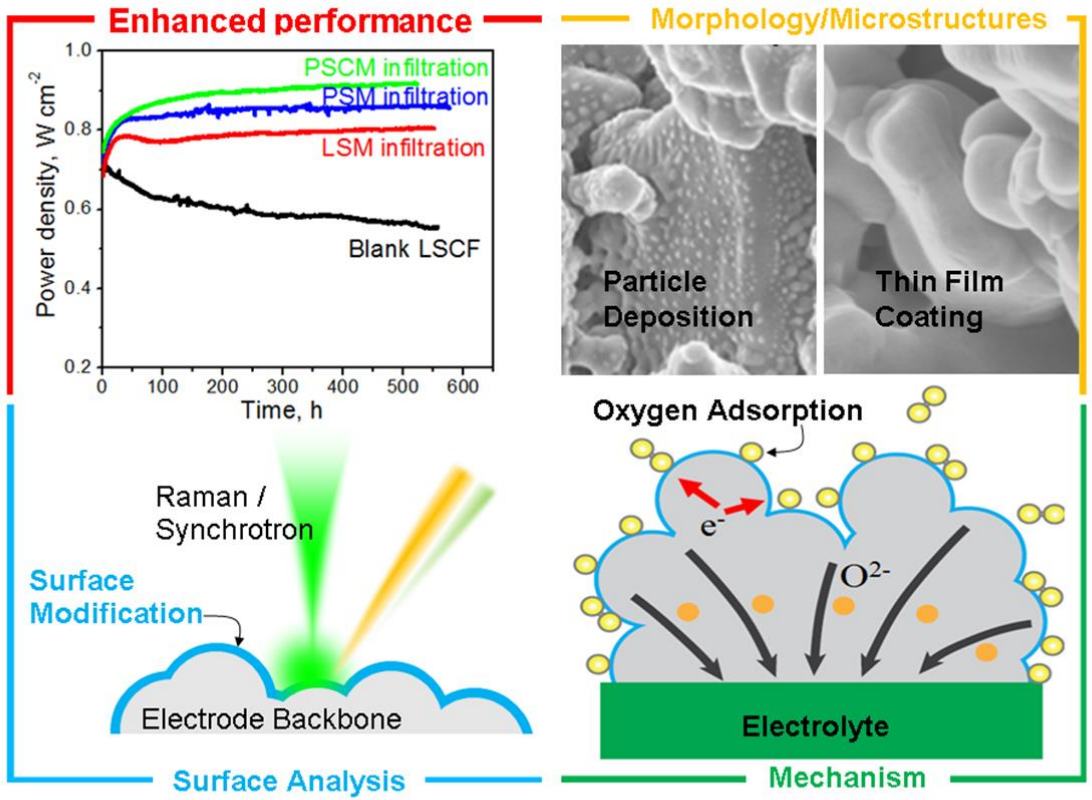




PLD MBE ALD

Surface Modification Through Infiltration





- **Significantly enhanced electro-catalytic activity and durability of electrodes**

Energy Environ. Sci., 2014, 7, 552

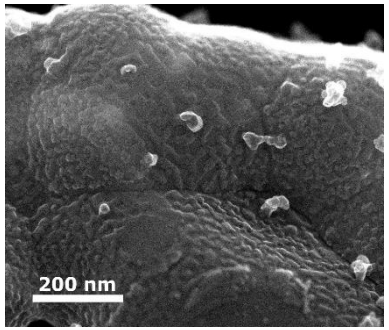
Surface Modification Through Surface Sol Gel

$$Ba(OC_3H_7)_2 + H_2O \rightarrow HOBa(OC_3H_7) + C_3H_7OH$$

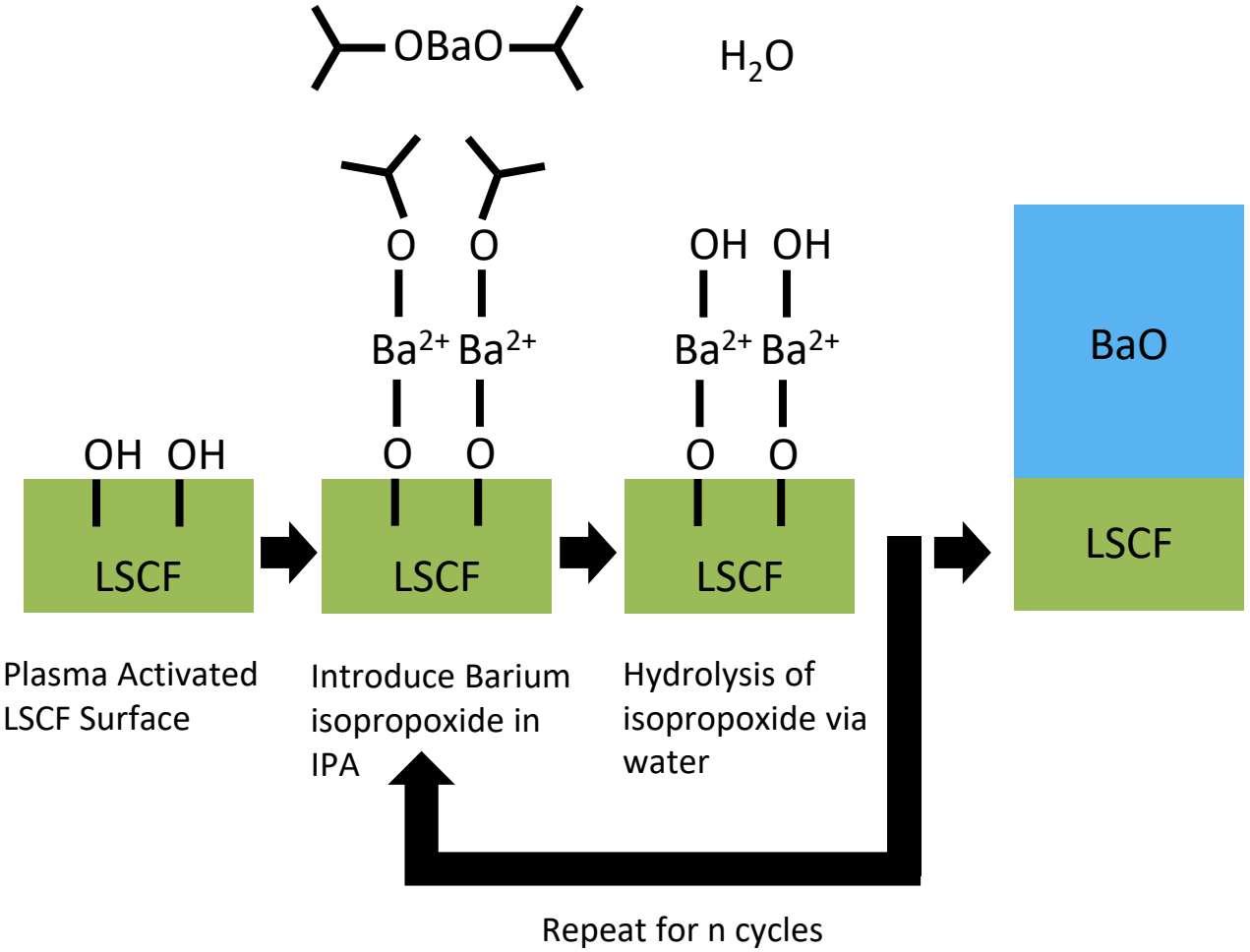
Layer by layer growth via two alternating self-limiting reactions:

1. **Chemisorption of metal alkoxide on surface**
2. **Hydrolysis via water to form oxide**
3. **Repeat for n cycles**

- **Achieves conformal coating**
- **Precise thickness control**
- **Low cost compared to ALD**



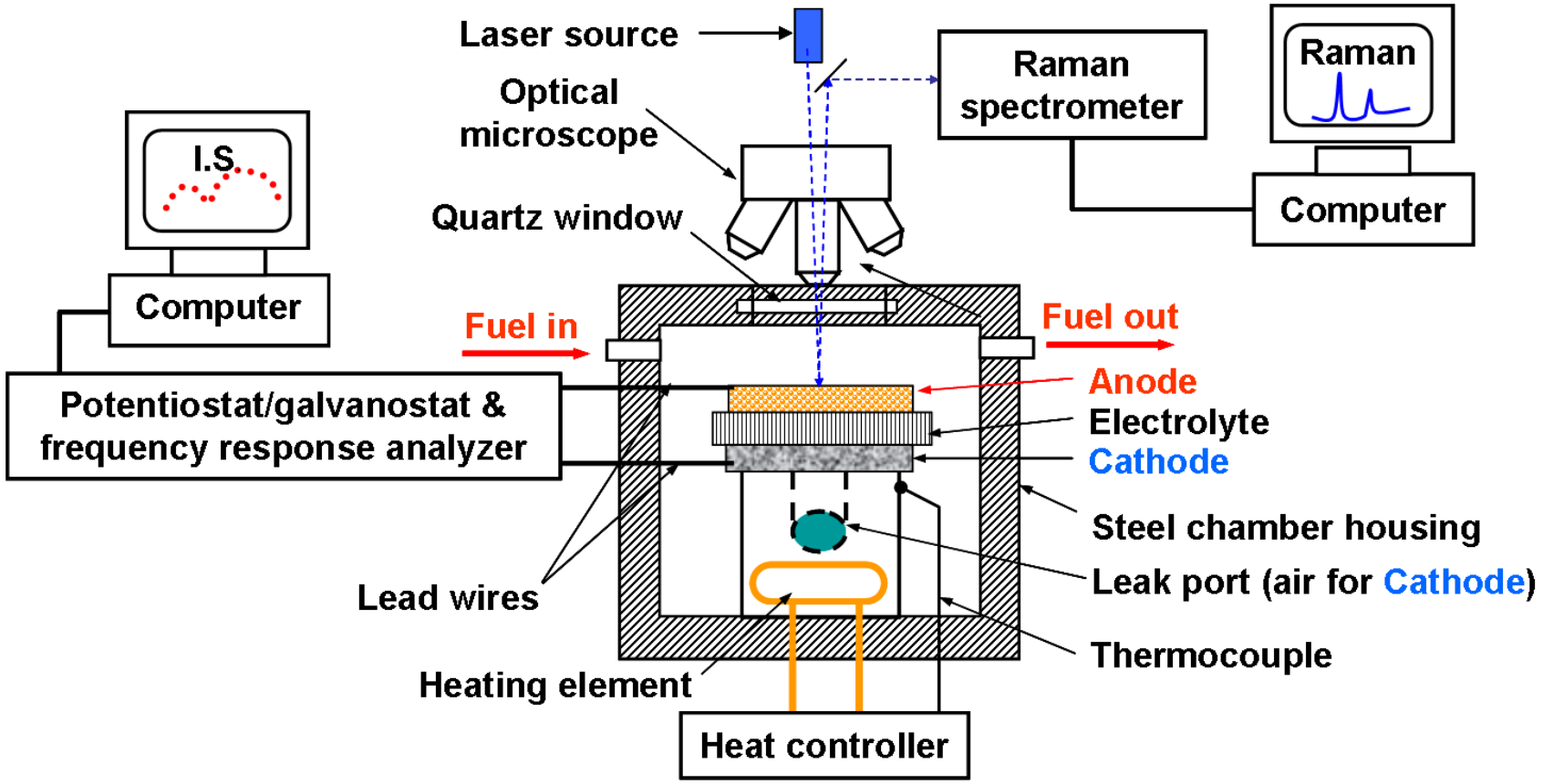
LSCF: $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$
SDC: $Sm_{0.2}Ce_{0.8}O_2$



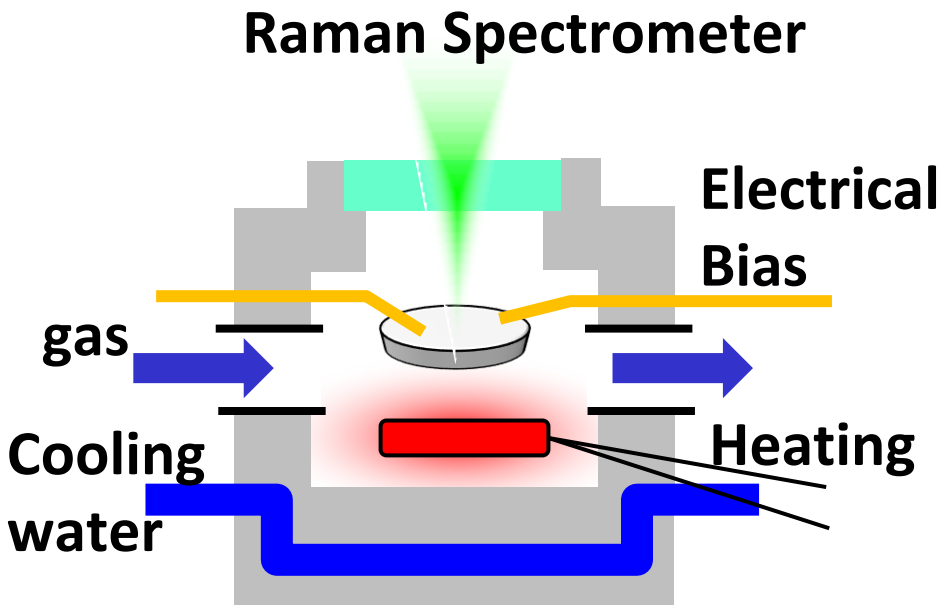
Surface Sol Gel (SSG) Process to Deposit BaO

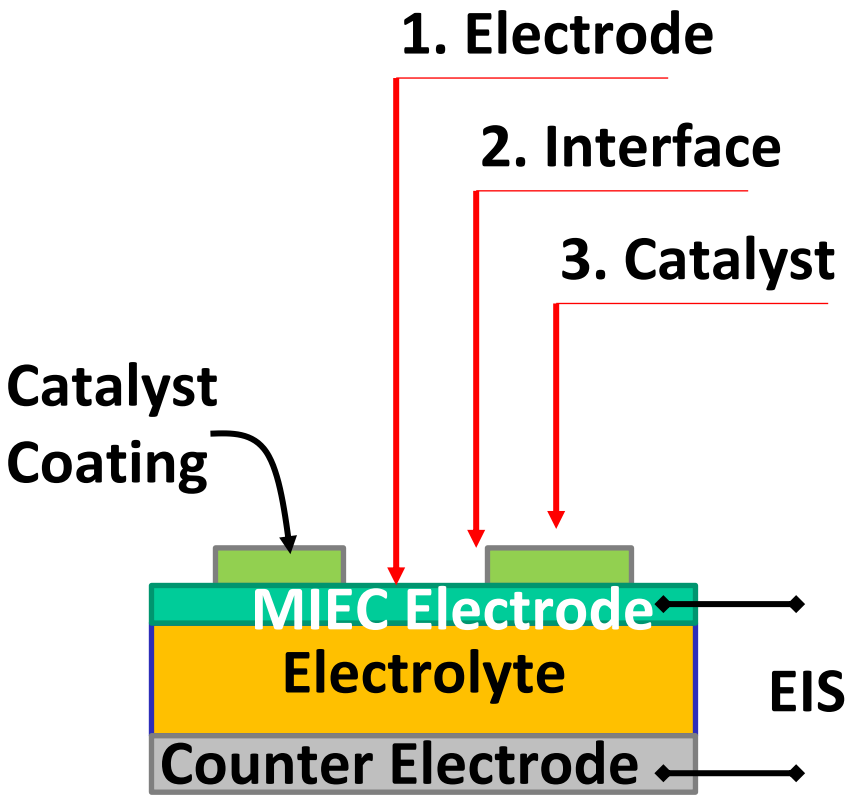
In Situ/Operando Raman & EIS

Changes in surface chemistry, structure, and morphology, with or without exposure to contaminants, will be directly correlated with the electrochemical properties as probed using EIS.



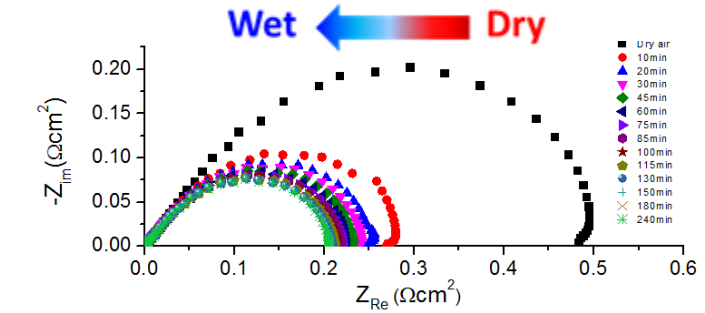
In Situ/Operando Study at High Temperatures

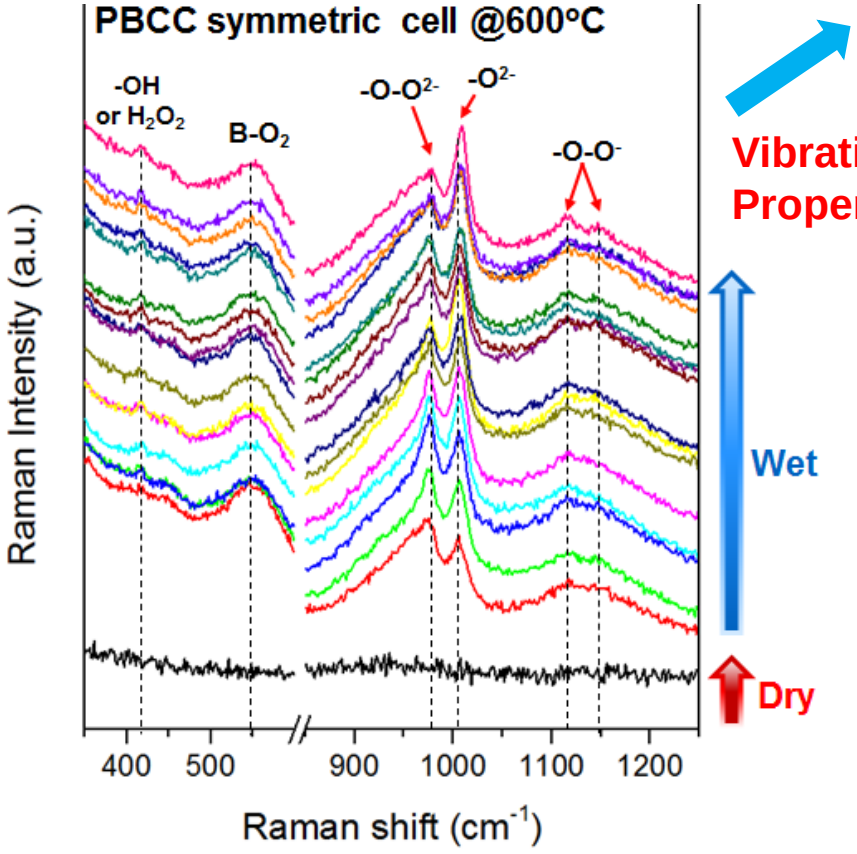




- Raman spectroscopy is sensitive to surface chemicals under *in operando* conditions.
- Environmental chamber allows the control of atmosphere, temperature, and electrical bias.

Correlation between Raman and EIS





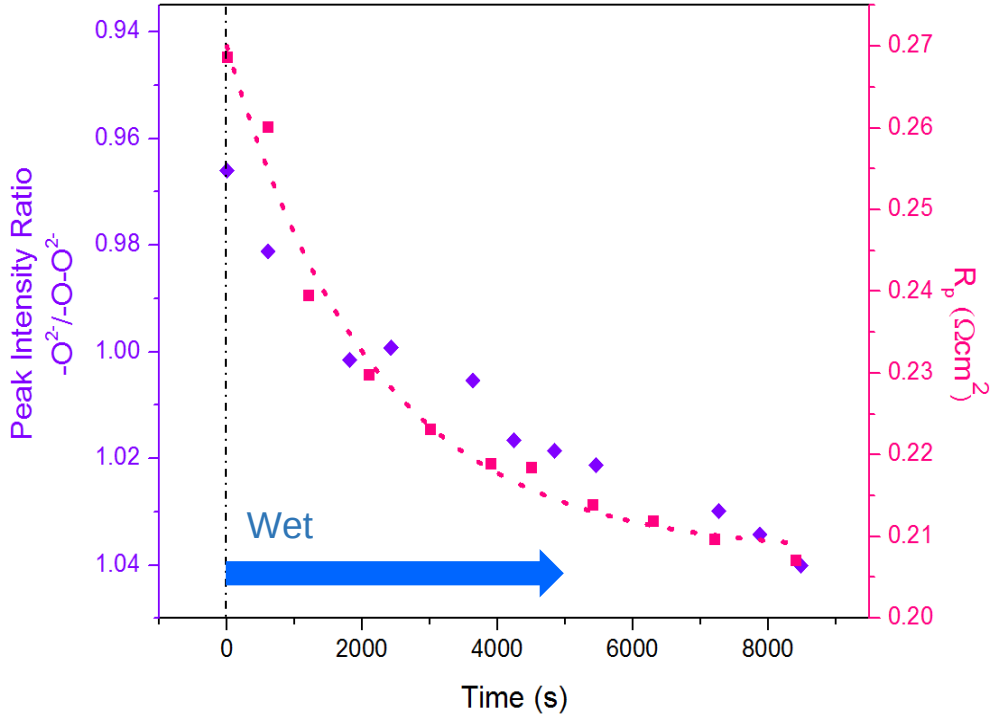
Electrochemical Property

Vibrational Property

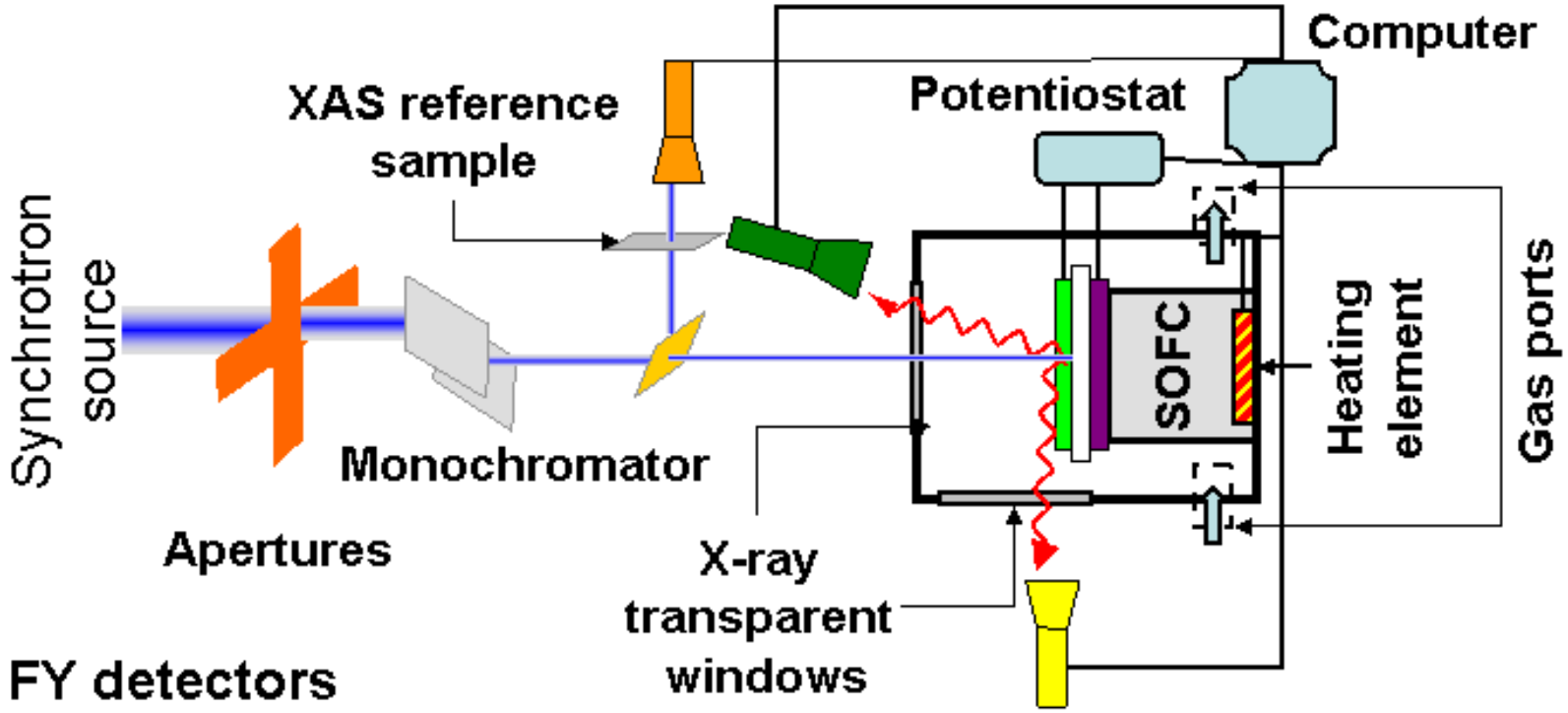
Quantitative Correlation

Energy Environ. Sci., 2021, 14, 1506.

R_p & Peak Ratio (-O^{2-}/ -O-O^{2-}) shows good agreement



Synchrotron-Enabled XRD, XAS, & XPS

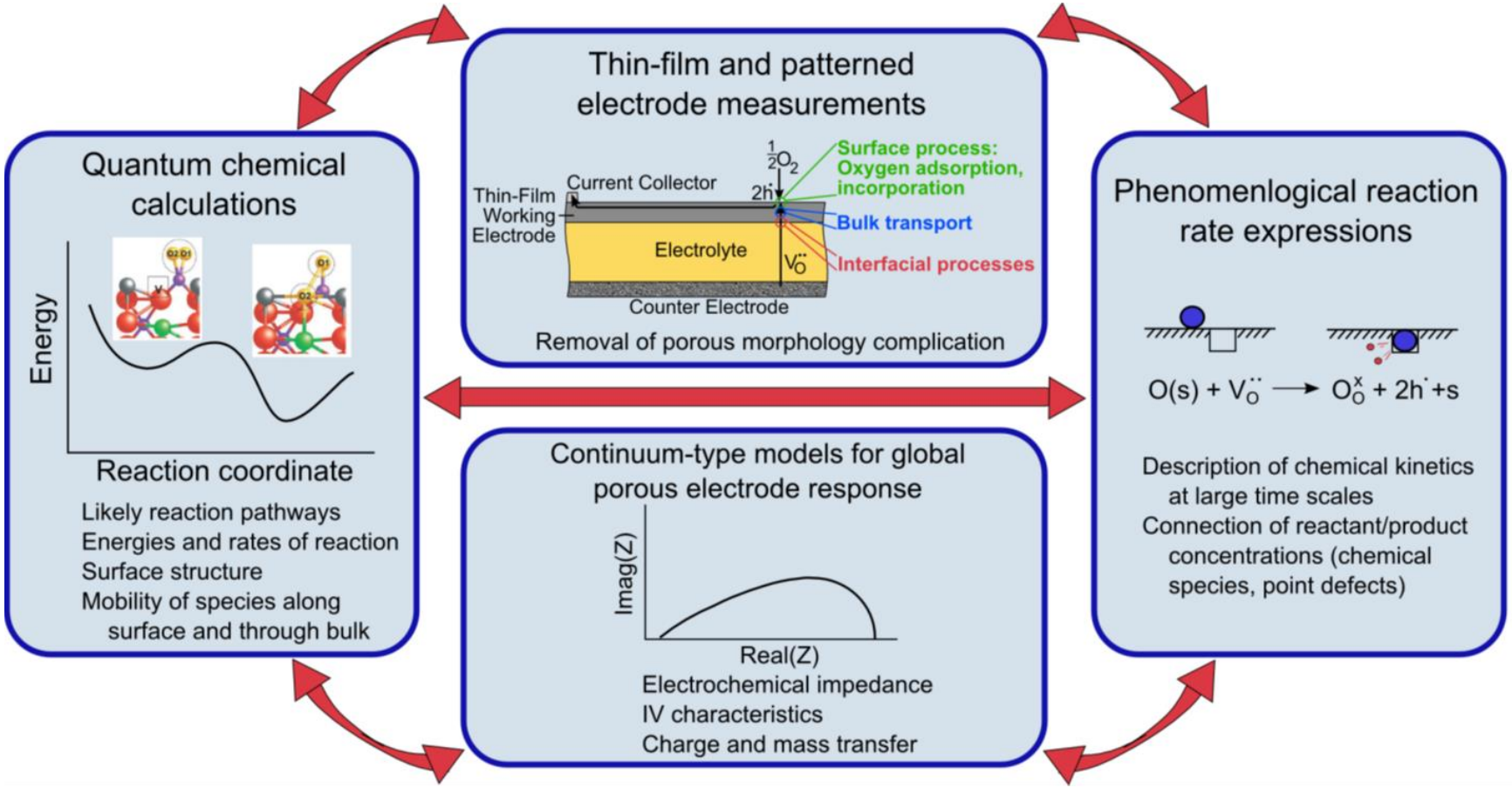


- Provides unique ability to study ***bulk and surface structures*** simultaneously via fluorescent X-ray absorption spectroscopy (XAS), Auger electron yield, and X-ray diffraction (XRD)
- Probe ***near-surface*** of electrode and identify surface composition, structure and chemical environment of specified element under *in situ* conditions: temperature, atmosphere, and bias
- Examine ***interface reactions*** between electrode and electrolyte under *in situ* conditions: temperature, atmosphere and bias

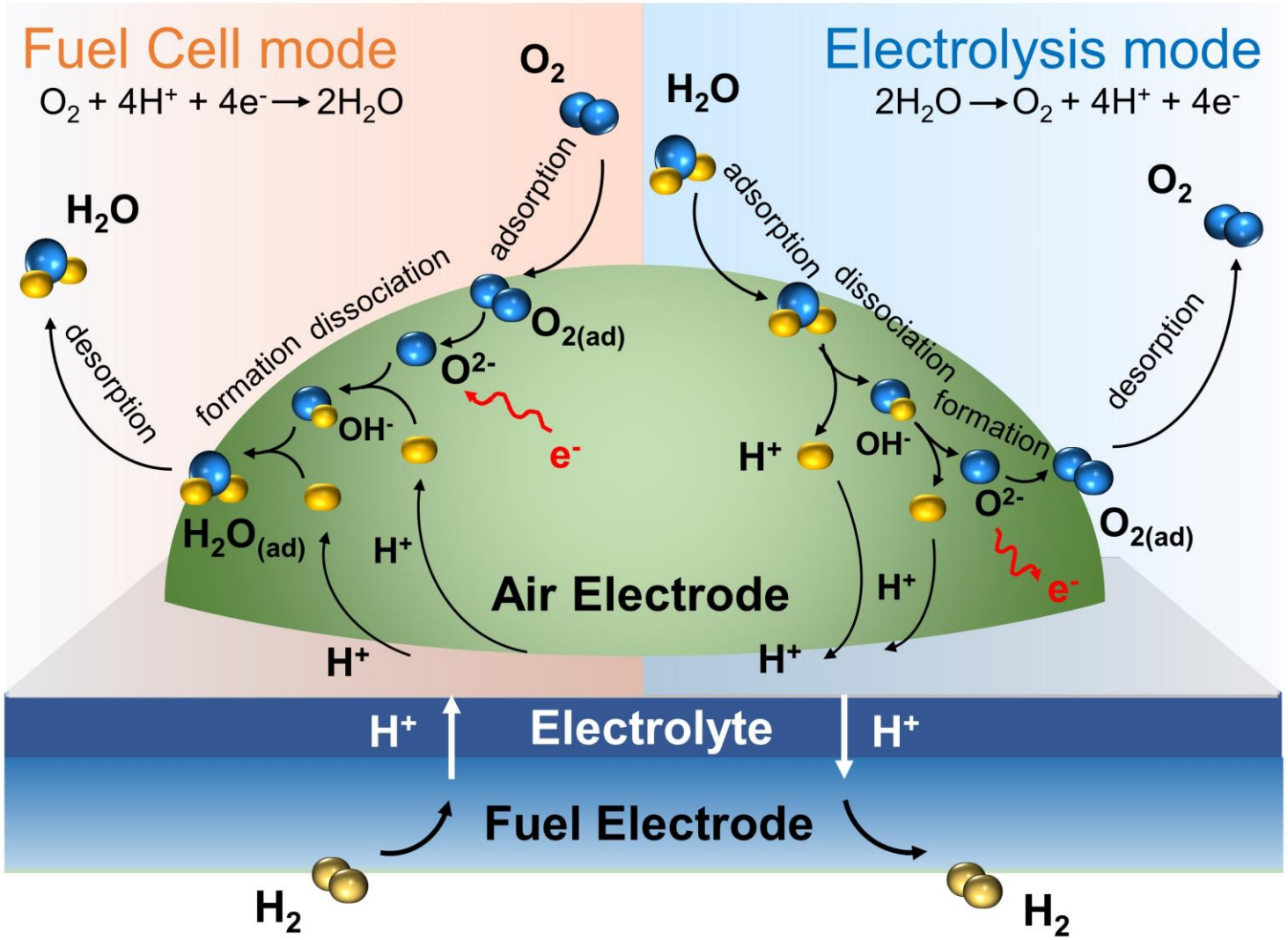
Materials today (2011) 14, 534.

Modeling and Simulation

Modeling, simulation as well as prediction tools will be used to help in formulating an effective strategy to mitigate the stability issues and predict new catalyst materials that can enhance the stability of electrode.

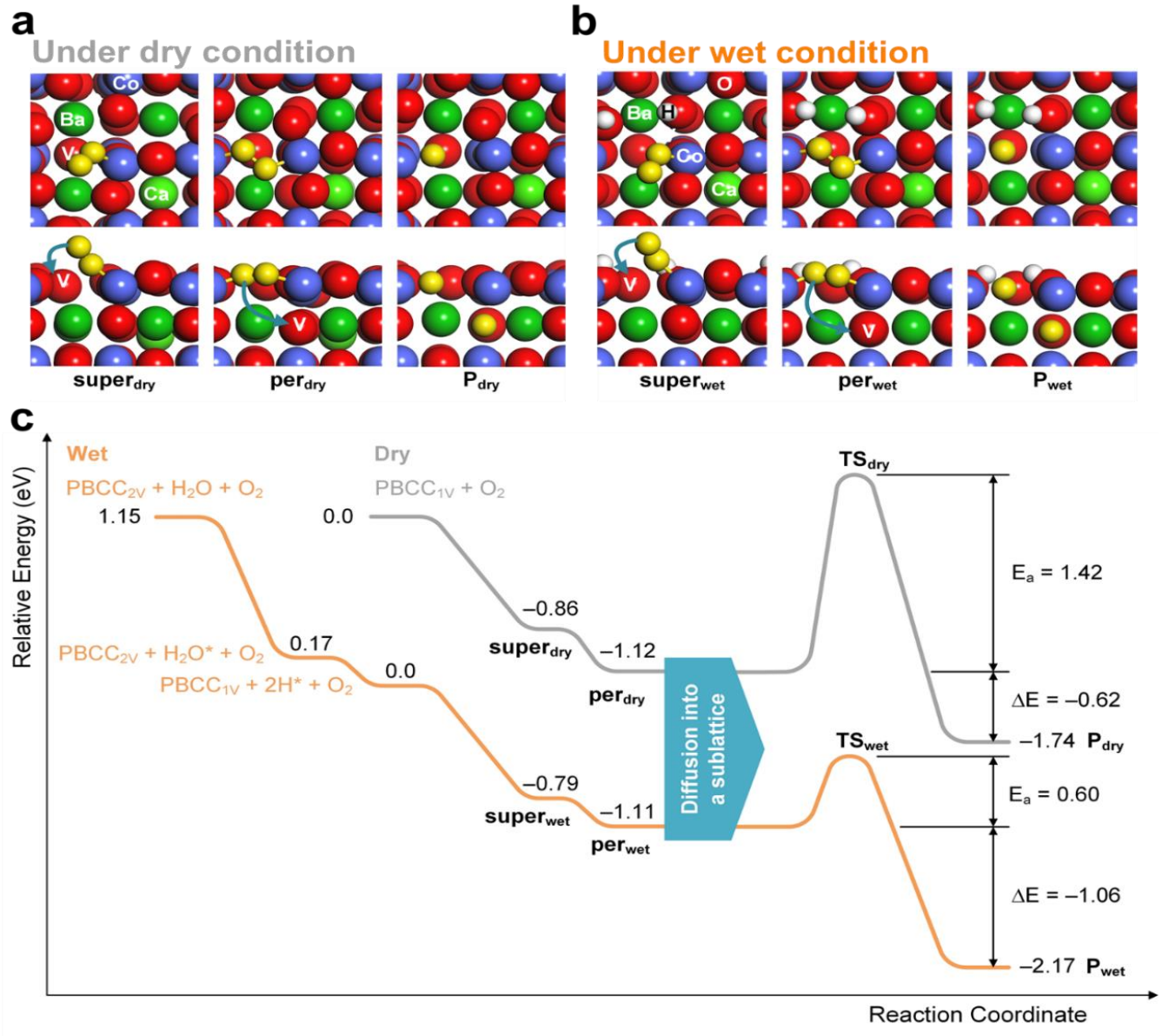


Understanding the Mechanisms of Electrode Reactions



- **Cell performance is limited by the sluggish ORR/OER in the air electrode**

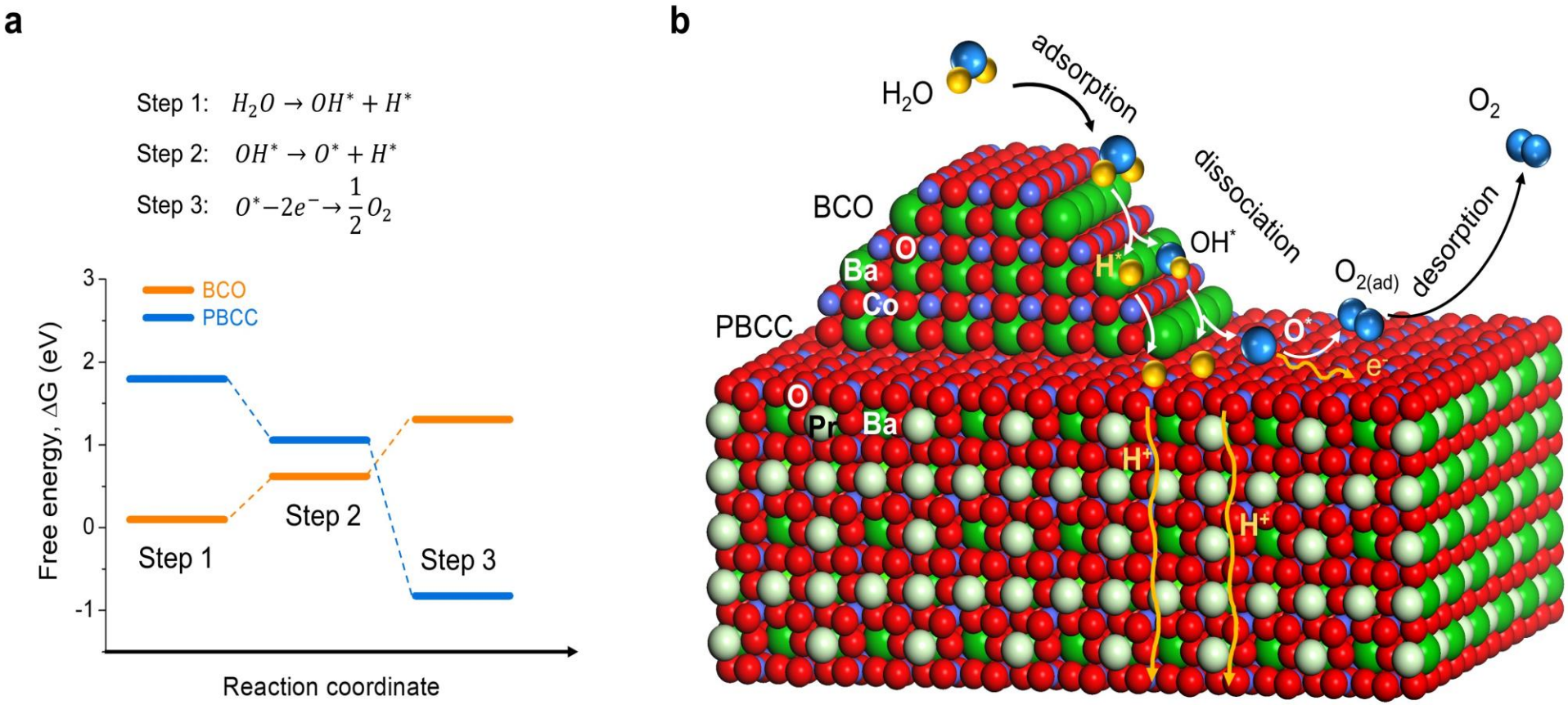
Oxygen Reduction Reactions (ORR)



- **Water-promoted dissociation and diffusion processes**

Energy Environ. Sci., 2021, 14, 1506.

Oxygen Evolution Reactions (OER)



- **The high OER activity is attributed to the rapid water dissociation on BCO nanoparticles and fast oxygen desorption on PBCC.**

ACS Energy Lett., 6 (2021) 1511-1520.

Project Goal

To establish the scientific knowledge for rational design, fabrication, and demonstration of a robust, highly efficient, and low-cost Solid Oxide Electrolysis Cell (SOEC) based on a proton conducting electrolyte for H_2 production.

- To optimize proton conductivity while enhancing Faradaic efficiency and durability of proton conducting membranes under electrolysis conditions;
- To optimize the air-electrode materials for fast ionic and electronic transport, high electro-catalytic activity, and durability;
- To optimize the air-electrode catalysts for enhanced bi-functional electro-catalytic activity and durability against various contaminations;
- To gain understanding of the degradation mechanisms of cell materials and interfaces.

Project Schedule

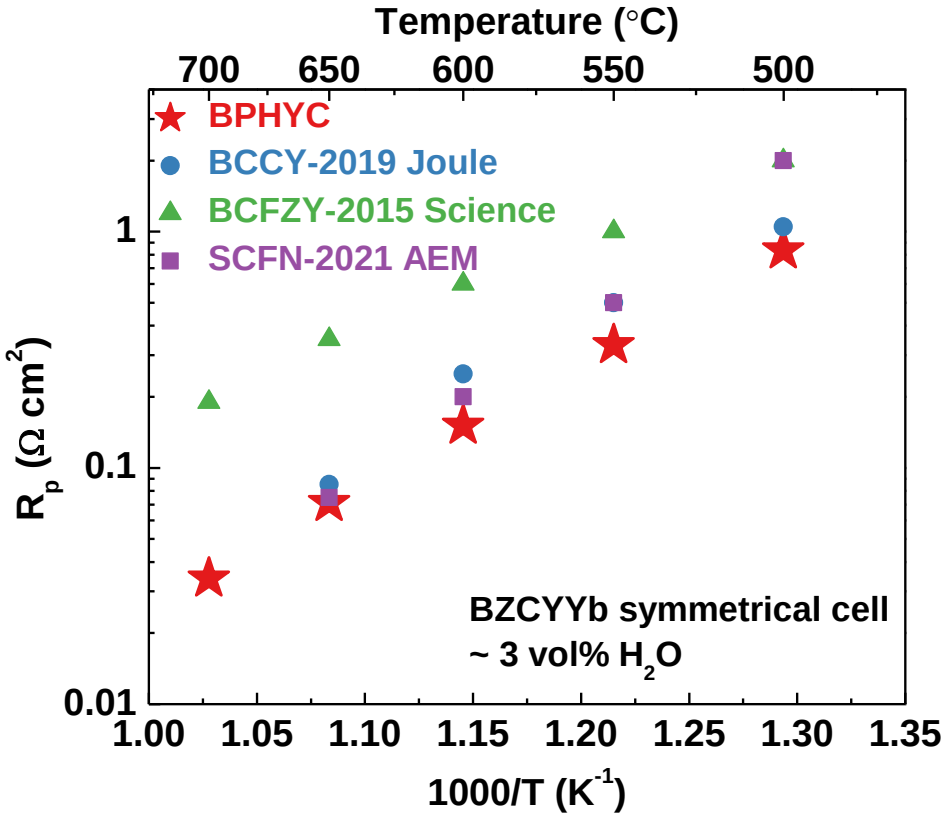
Task 1: Project Management and Planning
Task 2: Design and Optimization of Proton-conducting Electrolytes
Task 3: Development and Optimization of Air Electrodes
Task 4: Development and Investigation of Catalysts for Air Electrode
Task 5: Investigation of Degradation Mechanism

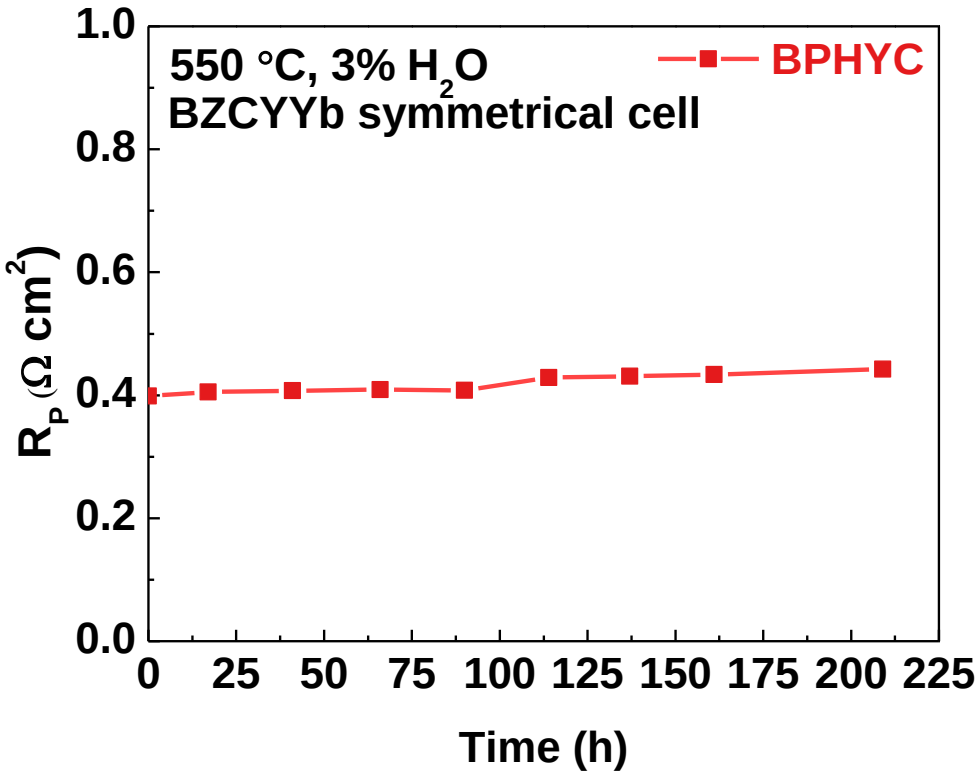
Task	Milestones	FY2021	FY2022				FY2023		
		Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8
1	1.1	→							
	1.2	→							
2	2.1	→							
	2.2	→	→						
3	3.1		→	→					
	3.2		→	→	→				
4	4.1			→	→	→			
	4.2				→	→	→		
5	5.1				→	→	→	→	
	5.2					→	→	→	→

Milestones

Date	Description	% Complete
12/21	Complete electrolyte development with conductivity >0.01 S cm^{-1} in Ar (3%H_2O) and ionic transference numbers >0.95 at 600 ºC.	15%
03/22	Complete bi-layer electrolyte development with the durability of at least 500 h with a degradation rate of <0.5% per 1,000 h.	10%
06/22	Complete air electrode development with a R_p of <0.3 Ω cm^2 at 600 ºC in Air (3%H_2O).	10%
09/22	Complete air electrode optimization with a R_p of <0.2 Ω cm^2 at 600 ºC in Air (3%H_2O).	Not started
12/22	Complete the catalyst modification of the air electrode with a R_p of <0.15 Ω cm^2 at 600 ºC in Air (3%H_2O), and the durability evaluation for at least 500 h with a degradation rate of <0.5% per 1,000 h under the presence of contaminations (e.g., H_2O and Cr).	Not started
03/23	Complete *in situ* and *ex situ* characterization of surface morphology and surface species using experimental and modeling work to determine the activity and stability of the cells as a function of contaminant presence, relevant operating conditions, and catalyst content.	Not started
06/23	Complete the fabrication of button cells with a current density of >1.8 A cm^{-2} at 1.3 V in electrolysis mode at 600 °C and ≥75% roundtrip efficiency in both SOFC and SOEC modes at ≤ 650 °C.	Not started
09/23	Complete the long-term durability evaluation of button cells for at least 500 h with a degradation rate of <0.5% per 1,000 h.	Not started

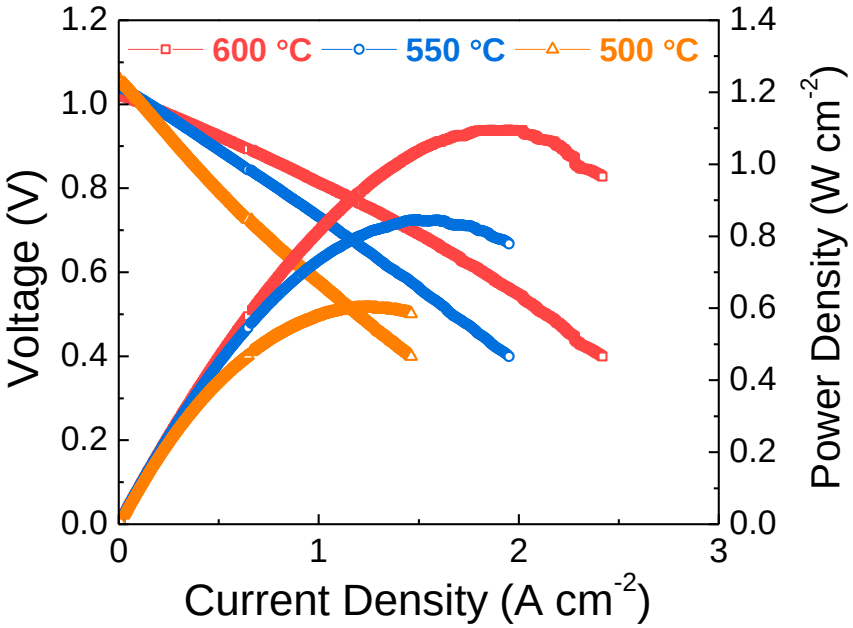
Preliminary Results: New Air Electrode Materials

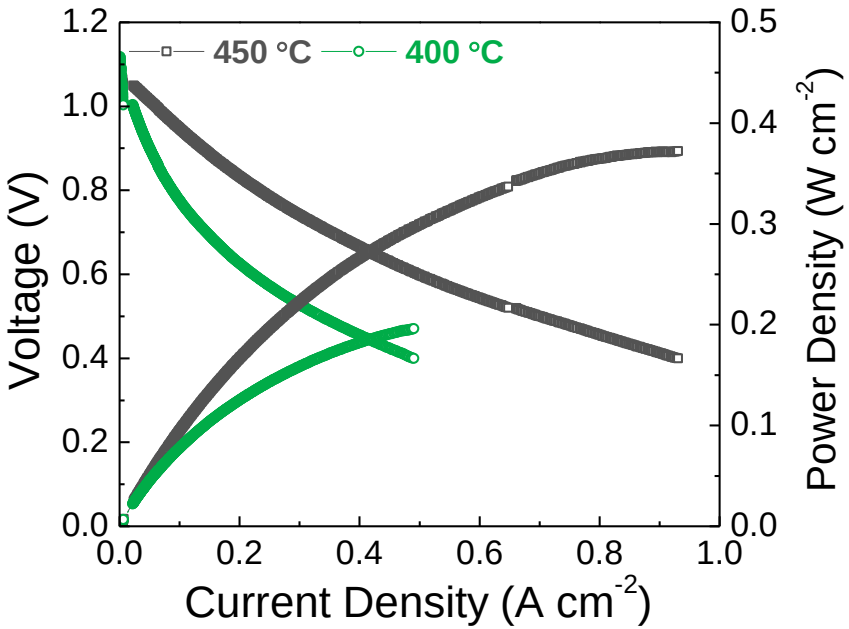


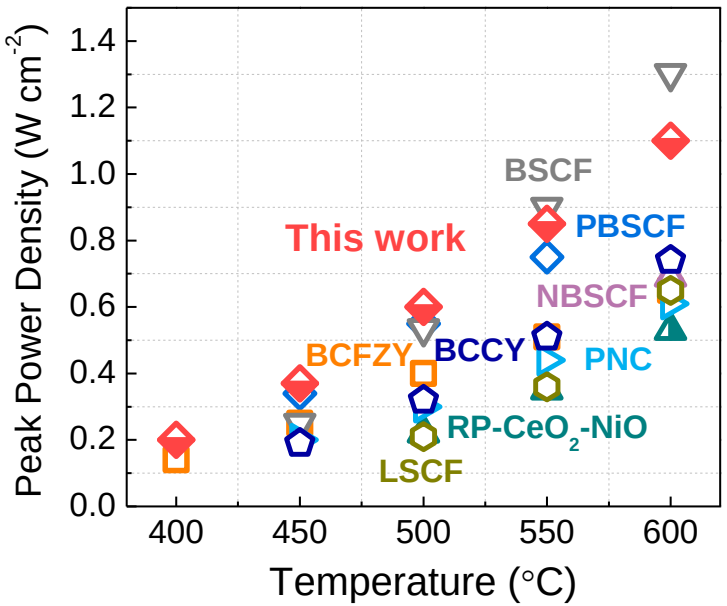


- ❑ Developed a new triple-conducting BPHYC air electrode;
- ❑ Achieved electrode polarization resistance of < 0.2 Ω cm^2 at 600 ºC;
- ❑ Demonstrated high activity and stability under operating conditions.

Preliminary Fuel Cell Performance

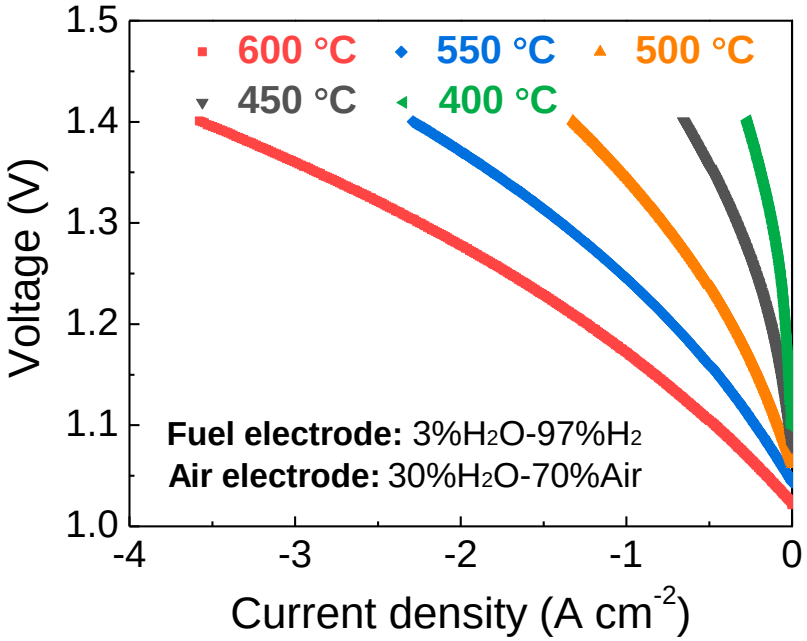


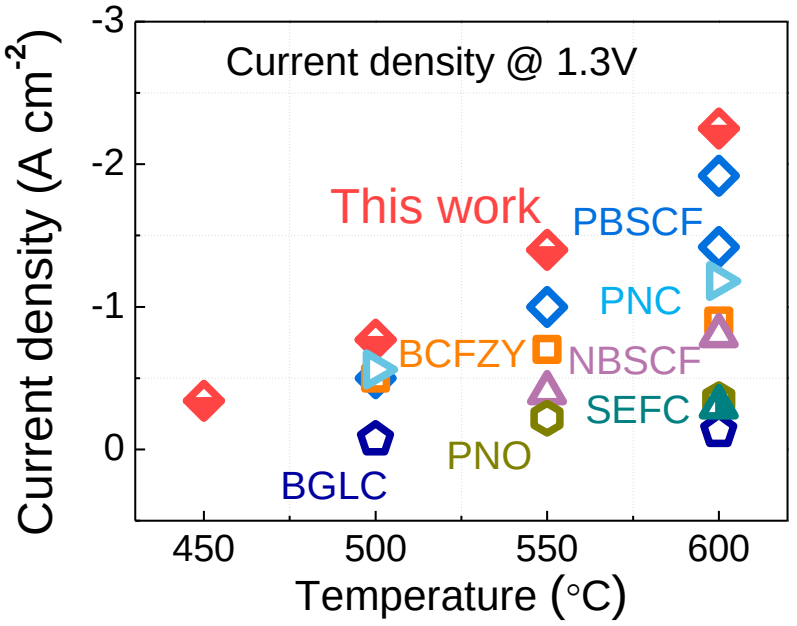


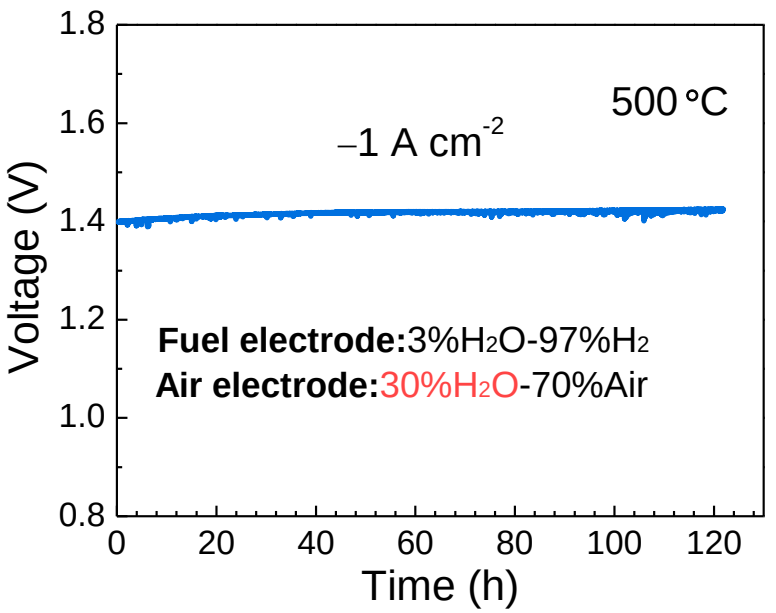


- Ni-BHCYb/BHCYb/BPHYC cell demonstrated high performance
- Cell operation temperature is reduced to 400 ºC

Preliminary Electrolysis Cell Performance







- ❑ Demonstrated high performance: 2.3 A cm^{-2} at 1.3 V and 600 ºC
- ❑ Showed good stability for water electrolysis

Future Work

Date	Brief Description	Complete
12/21	Complete electrolyte development with conductivity >0.01 S cm^{-1} in Ar (3%H_2O) and ionic transference numbers >0.95 at 600 ºC.	15%
03/22	Complete bi-layer electrolyte development with the durability of at least 500 h with a degradation rate of <0.5% per 1,000 h.	10%
06/22	Complete air electrode development with a R_p of <0.3 Ω cm^2 at 600 ºC in Air (3%H_2O).	10%

End of Project Goal:	Demonstrate a current density of >1.8 A cm-2 at 1.3 V in electrolysis mode at 600 °C and ≥75% roundtrip efficiency in both SOFC and SOEC modes at ≤ 650 °C. Complete >500-h operation with a degradation rate of <0.5% per 1,000 h.	FY23

Acknowledgement

Discussions with Evelyn Lopez, Seth Lawson, and other DOE management team members

U.S. Department of Energy
Award No. FE0032115

Thank you for your support