



HydroGEN: High Temperature Electrolysis

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HydroGEN HTE Seedling Projects and Lab Collaboration

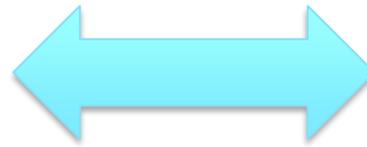
Project-driven tech transfer, resulting in

- Efficiency
- Yield
- Cost
- Durability
- Manufacturability

HTE Node Labs



Support through:



- Personnel
- Equipment
- Expertise
- Capability
- Materials
- Data

Interactive HTE Projects

Seedling FOA projects



p-SOEC

Lab call projects



o-SOEC

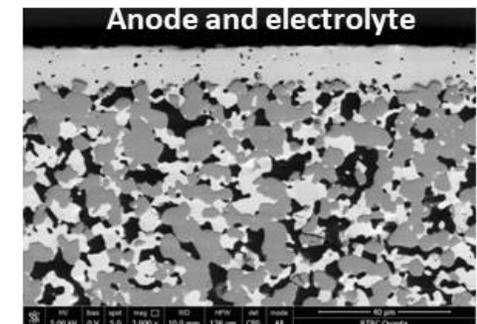
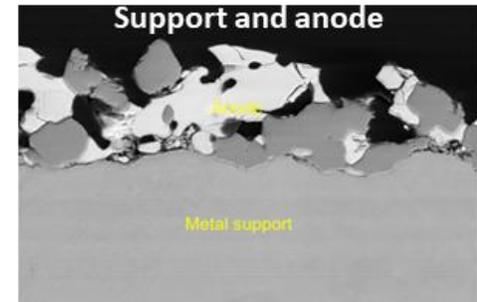
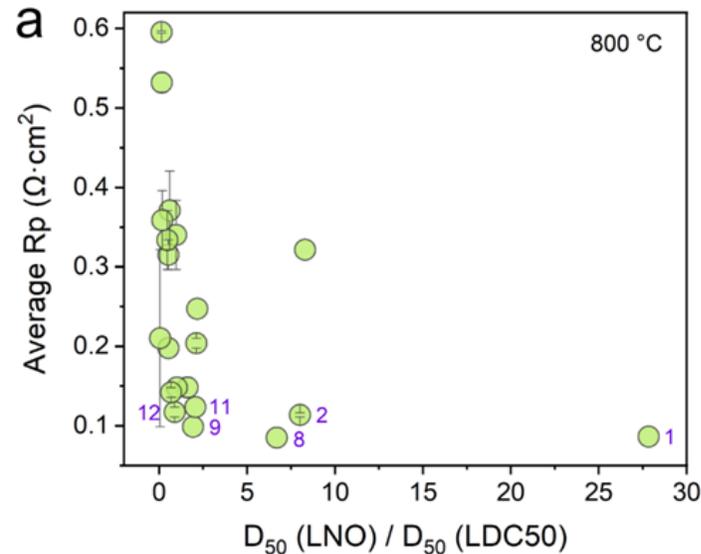
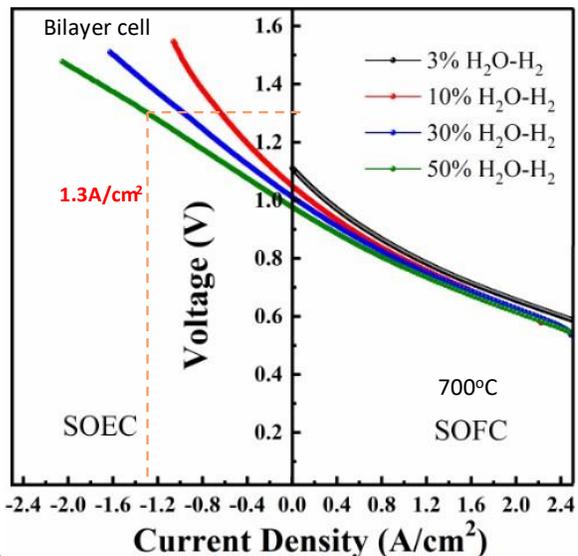




HydroGEN HTE Seedling Projects with Lab Capability Support

Technical Accomplishment Highlights

- **(USC, INL and NREL) A Multifunctional Isostructural Bilayer Oxygen Evolution Electrode for Durable Intermediate-Temperature Electrochemical Water Splitting:** Solid oxide electrolyzer featuring a bilayer air electrode was evaluated across various H₂O-H₂ ratios. The optimal performance was observed at 50% H₂O-50% H₂, achieving 1.3 A/cm²@1.3V at 700° C.
- **(Saint-Gobain and INL) Development of Durable Materials for Cost Effective Advanced Water Splitting Utilizing All Ceramic Solid Oxide Electrolyzer Stack Technology:** Symmetric cells were used to optimize the particle size ratio of Lanthanum Nickelate and Lanthanum doped Ceria, defining a working range to produce a composite air electrode with low polarization resistance and a tolerance to small batch to batch PSD variations. (p176)
- **(RTRC and INL) Thin Film, Metal-supported High Performance and Durable Proton-Solid Oxide Electrolysis Cells:** p-SOEC metal cells were produced with advanced manufacturing process, showed strong bonding of metal support and electrode with no Cr diffusion at the metal-electrode interface. (p154)



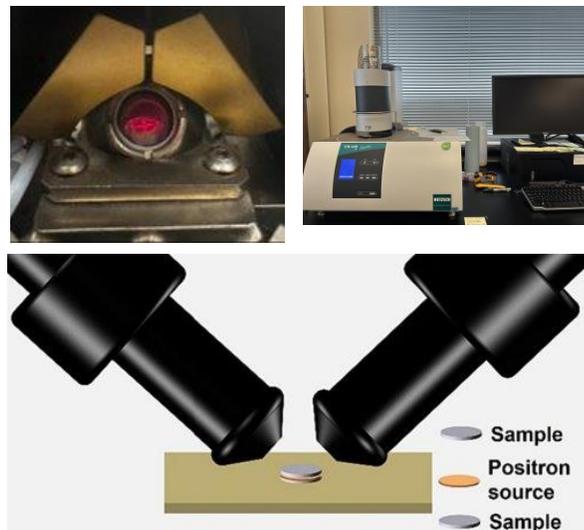
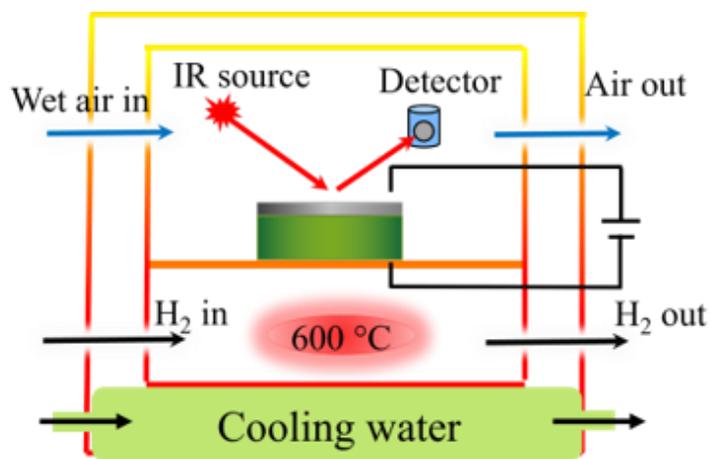
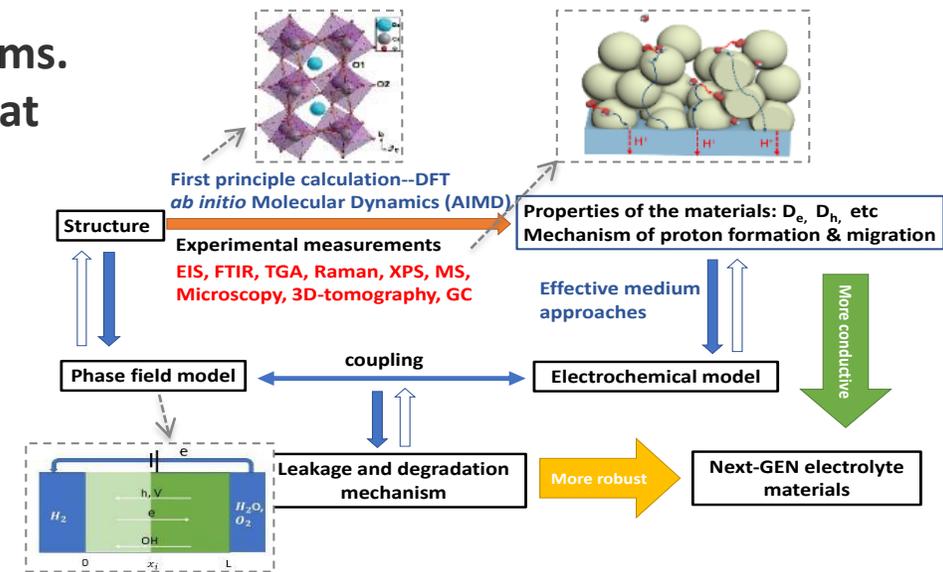


HydroGEN HTE Lab R&D p-SOEC Approach:

Combine Multi-Scale Computation and Experiment to Improve Faradaic Efficiency

- Develop effective approaches to suppress electronic leakage by understanding the proton conduction and electronic leakage mechanisms.
- Develop a robust, energy-efficient, and reliable electrolyte, for p-SOEC at 500-600°C, achieving high Faradaic efficiency (FE) and long durability.
- **Framework:** Established an efficient framework by integrating experiment and multi-scale simulation (DFT/AIMD, phase-field model) for mechanism study in broad time and size scales.
- **Experiments:** Developed advanced characterization techniques to assess electrolytes to disclose thermodynamic information for modeling.

Mechanism study



- **Electrochemical modeling:** Built framework that leverages experimental measurements, electrochemical modeling and DFT simulation to predict Faraday efficiency of p-SOECs for various of electrolyte materials.
- **DFT/AIMD:** Unraveling factors affecting the mechanical properties of electrolyte at atomic scale.



Approach: Safety Planning and Culture

Top to Bottom Safety Focus

- **Design**
 - HAZOP
 - Subject Matter Expert review
 - Hydrogen and flame detection systems
- **Procurement**
 - Quality procurement program
 - Hydrogen material compatibility awareness
- **Installation**
 - Qualified and trained installation
- **Pre-operational Testing**
 - Inspections and monitoring for hydrogen and other leaks
- **Operation**
 - Alarms and operator aids
 - Routine checks and inspections of operating systems

Idaho National Lab Safety

- **Work Control**
 - What is and isn't authorized
 - Test plan reviews
- **Stop work**
 - If conditions are unsafe, anyone can call for a work stoppage.
- **Questioning mindset**
 - Briefings prior to the start of a new activity
 - Asking what could go wrong?
- **Training**
 - On-site training to facilitate broad institutional awareness of the safety considerations for hydrogen work.
 - NFPA 2 training
- **Flexible electrolysis system test platform**
 - Atmospheric testing with hydrogen recycle
 - Separate “Hot Box” module

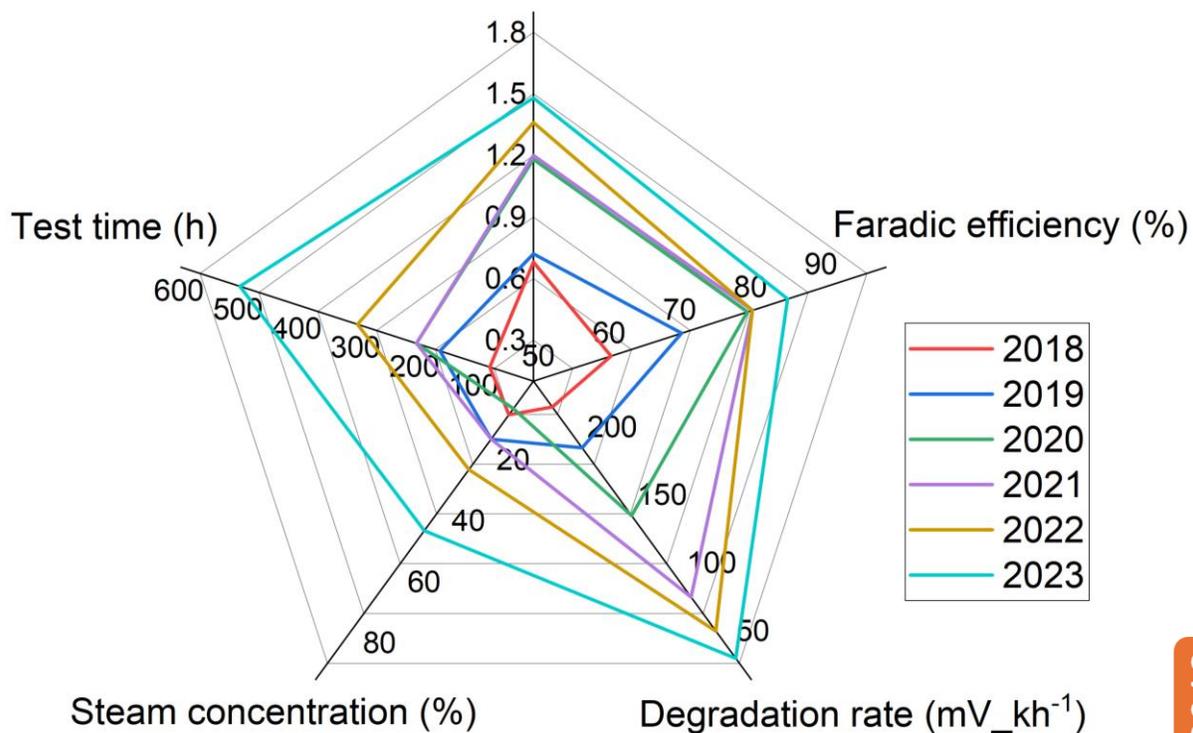


HydroGEN Lab R&D p-SOEC Technical Accomplishment:

Overall Progress and Figure of Merits

INL p-SOEC Technical Progress*

Current density @1.3V (Acm^{-2})



- Parameters in each year represent the upper limits we achieved where test time and steam concentration are facility-constrained and have been improved significantly
- INL is focusing primarily on FE and degradation rate for a given current density and steam concentration.

- A p-SOEC metrics target table has been developed, similar to the one H2NEW-HTE initiated, with the additional focus on FE, FE durability and specific metrics on cell scales (e.g. button cells, single unit cells and short stack).
- As an emerging technology, the recognition development and knowledge buildup are advancing, which is valuable to refine and reshape the technology roadmap.
- Increasing inquiries, discussions and licensing needs from industry are good signs for accelerating P-SOEC penetration to the market.
- Timely communication (technically and strategically) with DOE managers and stakeholders are the best practice we learned.

2018 Initiated P-SOEC work with focus on bolstering the current density

2020 FE is critical in P-SOEC where there is a controversy in literature. Document and report to DOE

2022 Electrolyte composition and operation condition influence FE simultaneously. Reached consensus with all seedling PIs

2023 Unrevealed the significance of interface engineering on performance and durability. Develop more specific metrics for P-SOEC

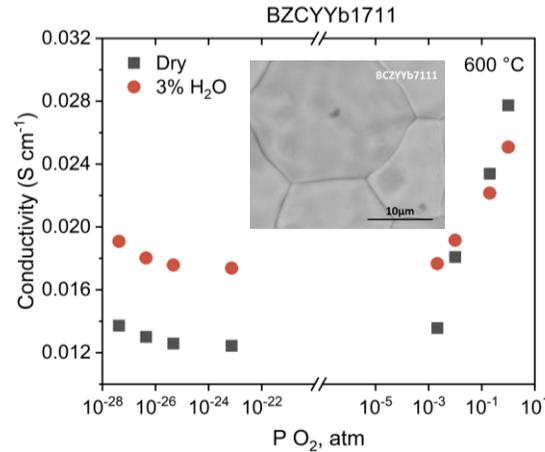


HydroGEN Lab R&D p-SOEC Technical Accomplishment:

Synergies between numerical simulations and experiments to derive Faradaic efficiency

✓ Conductivity of the electrolyte material determines the Faradaic efficiency for a given operation condition with some basic assumptions.

Total conductivity measurement

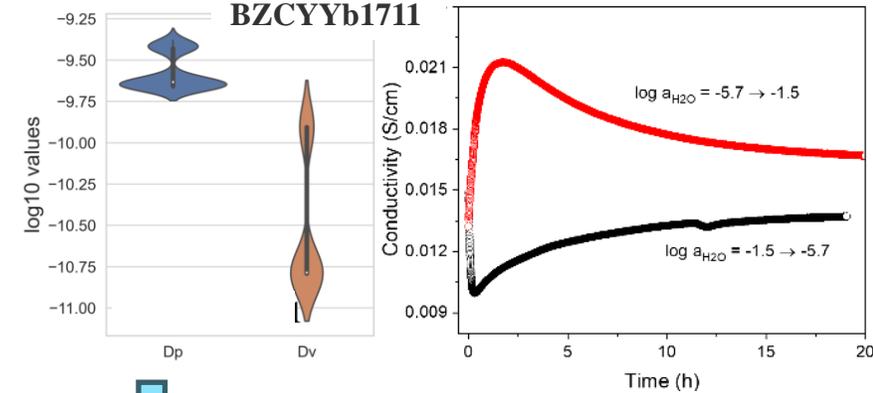


P Zhu, et al. under review

Parametric model: derive parameters

Verification: ECR experiments

Inform



Y Meng, et al. under review

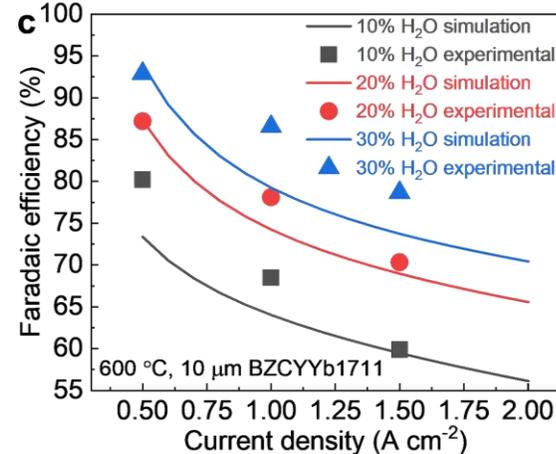
Feed-in

Validation

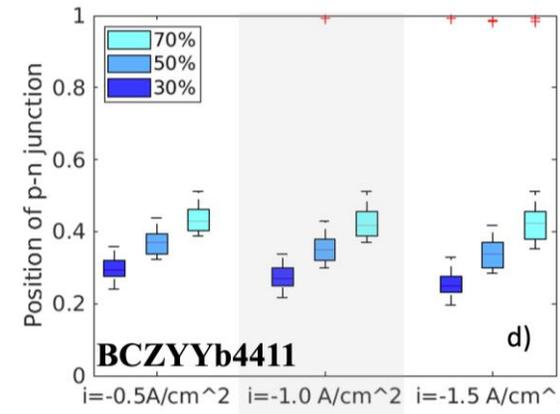
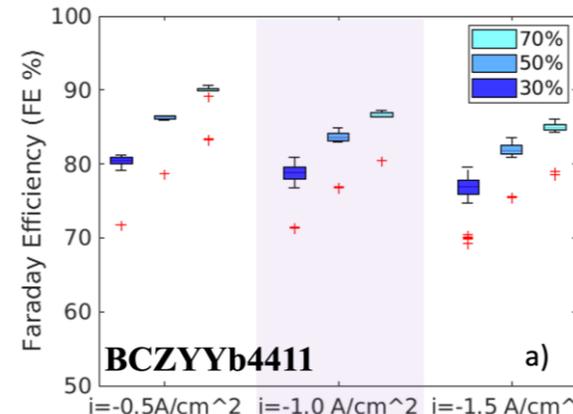
Experimental measurement

Electrochemical model: FE prediction

✓ The framework validated the experimental data from full cell testing well, and provided the FE predictions under extreme conditions



W Zhang, et al. under review



p-n junction verification: DFT simulation

Q Zhang, et al. under review

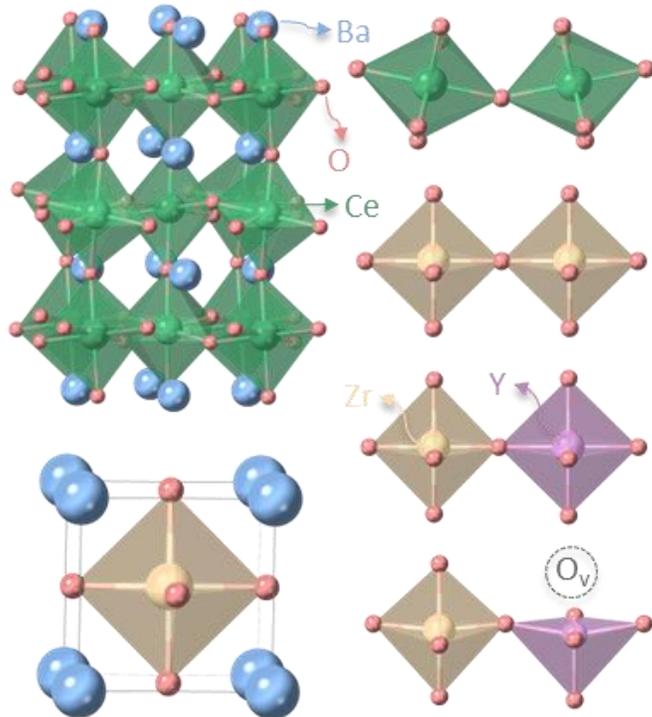


HydroGEN Lab R&D p-SOEC Technical Accomplishment:

Factors Affecting the Mechanical Properties of Proton-Conducting Perovskite Electrolytes

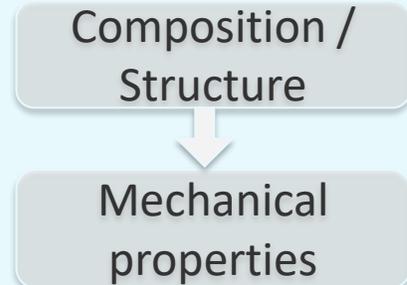
- **Key compositional and microstructural factors affecting mechanical properties**

- Composition (BaCeO_3 vs BaZrO_3)
- Lattice phase (Cubic vs. Orthorhombic)
- Defect (O_v)
- Octahedron (w/wo distortion)



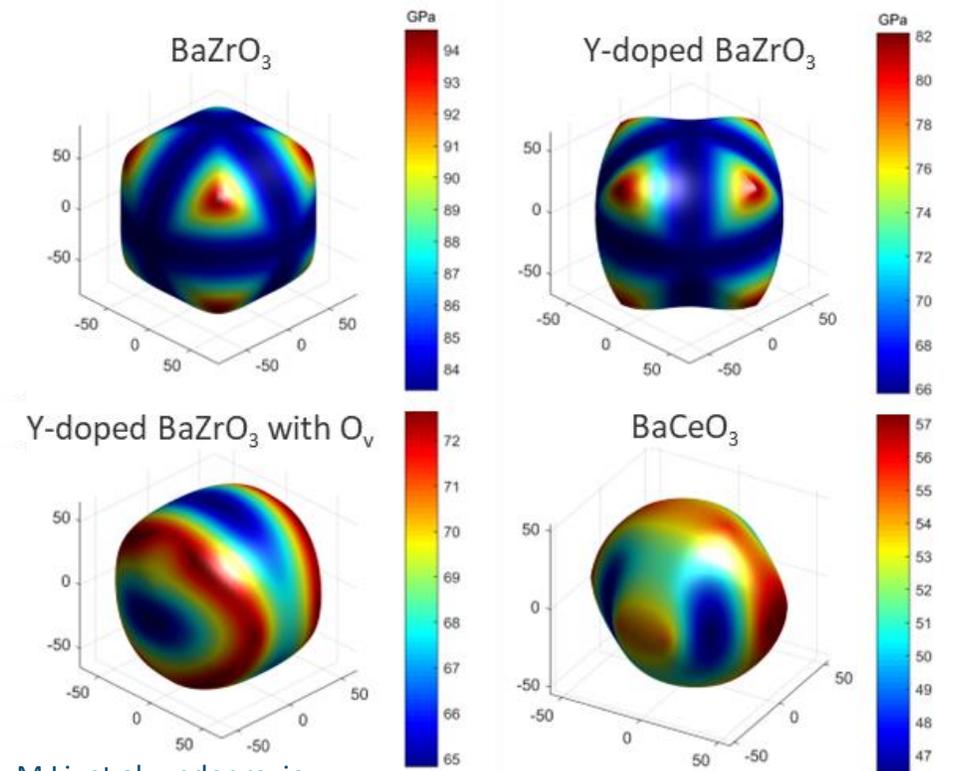
- **Mechanical properties from first-principles calculations at atomic scale**

- Doping and defects create elastic anisotropy and orientation-dependent elastic moduli, which may cause anisotropic fracture propagation and thermal expansion.
- Reducing lattice symmetry decreases elastic moduli, increasing susceptibility to failure under cycling.



Insights on mechanical properties at atomic scale:

- Deformation
- Fracture behavior
- Fatigue resistance
- Thermal expansion





HydroGEN Lab R&D p-SOEC Technical Accomplishment (LLNL):

Proton Incorporation and Defect Concentrations in Doped Ba{Zr,Ce}O₃ Electrolytes

Investigated alternative modes of proton incorporation

- Proton (H_i^+) incorporation in Y-Ba{Zr,Ce}O₃ more favorable with oxygen vacancies (V_O^{2+}) than without, particularly in BaZrO₃

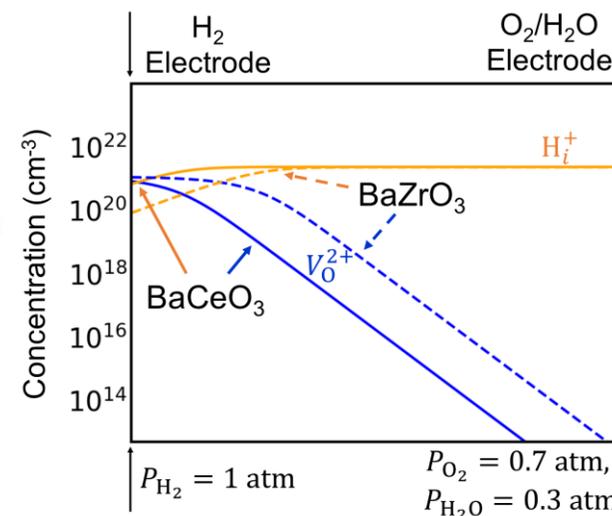
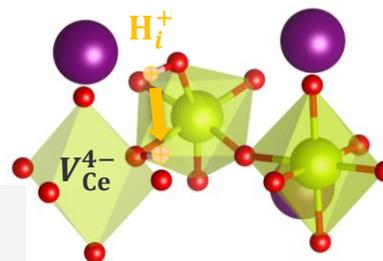
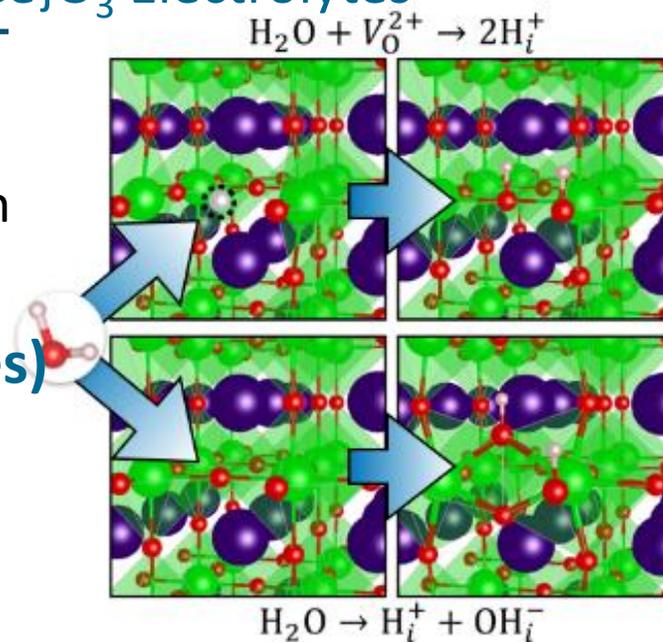
Studied ionic migration near defects (proxy for grain boundaries)

- H_i^+ , V_O^{2+} migration slower near (negatively charged) cation vacancies

Modeled defect concentrations for *operando* conditions

- H_i^+ usually the main charge carrier in electrolyte, but V_O^{2+} surpasses it near the H₂ electrode
- Particularly true in BaZrO₃ – **supports importance of Ce**
- Polarons/electrical carriers much less prevalent

High ionic conductivity can be achieved through optimizing synthesis conditions to maximize the concentrations of H_i^+ , as well as reducing defect-rich regions such as grain boundaries.



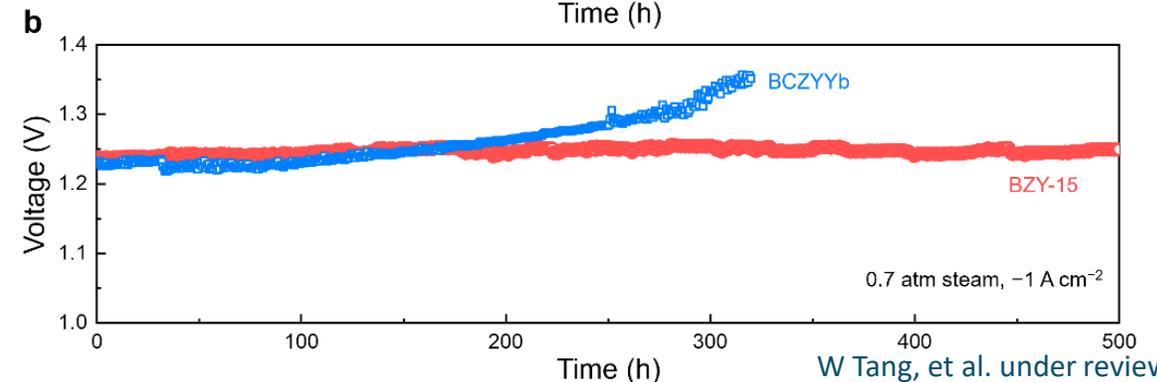
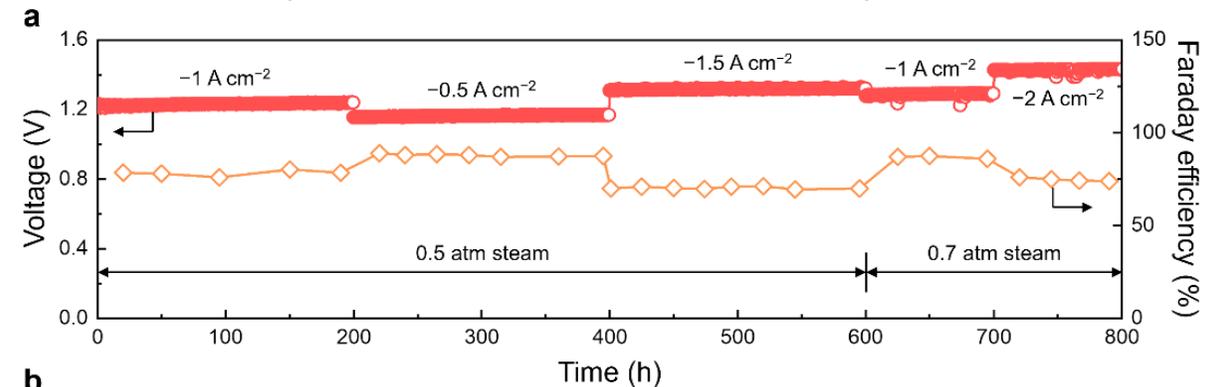
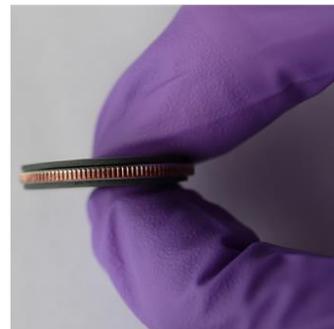
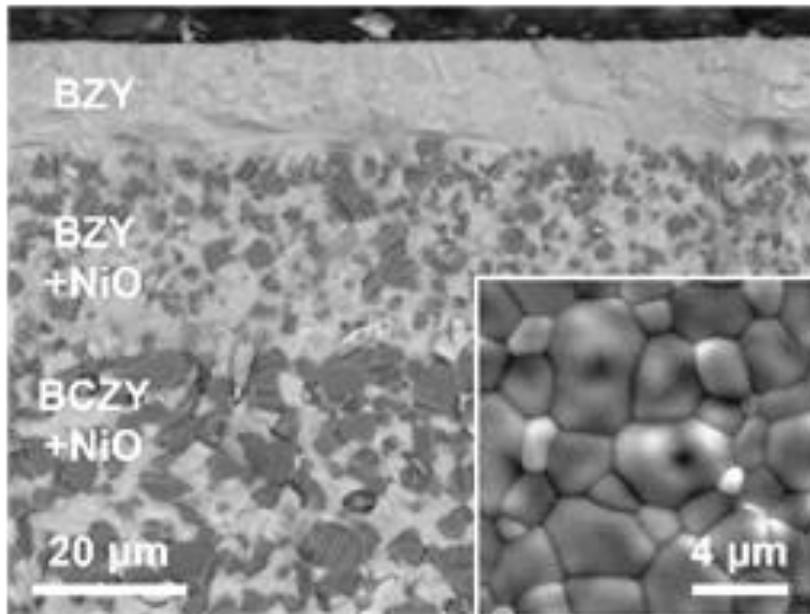


HydroGEN Lab R&D p-SOEC Technical Accomplishment:

Benchmarked BZY cells with enhanced electrolysis stability and Faradaic efficiency

Performance and durability of p-SOEC is equally important for its advancement and adoption by the market.

- Additional effort is placed on the full cell durability, especially under some extreme conditions.
 - Benchmarked electrolyte BZY is employed
 - Cells successfully underwent different current densities (up to 2 A cm^{-2}) and steam concentrations (up to 70%)
- New fabrication methods suppressed Ce effect on electrolyte and enabled the flat cells with clean grains.
- The Faradaic efficiency can be maintained at $\sim 90\%$ at -1 A cm^{-2} with 70% steam concentration at 600°C with a durable operation (single condition $>500 \text{ hrs}$ and multi-conditions $>800 \text{ hrs}$). Combined with the modeling prediction conducted under 99% steam concentration, it suggested the completion of the annual milestone (FE $>95\%$ and tested for 500 hrs)



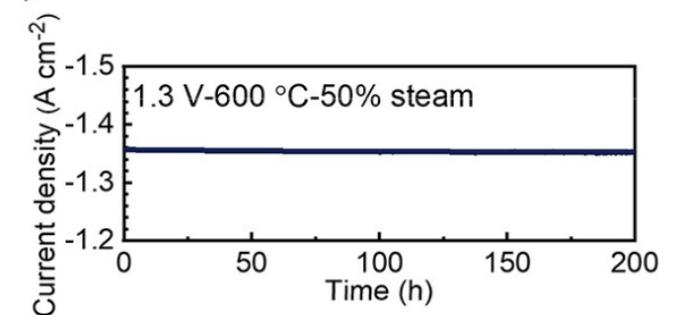
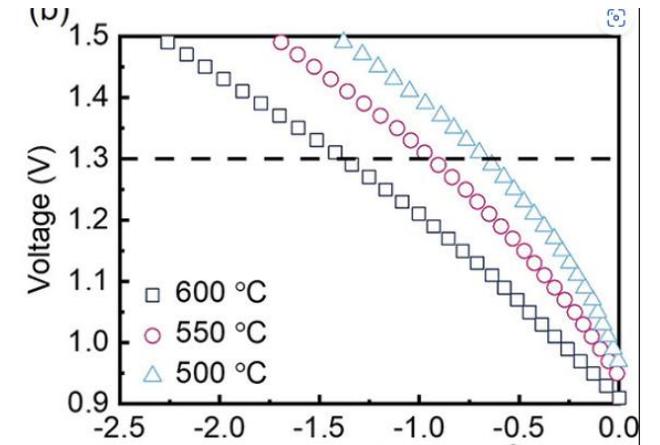
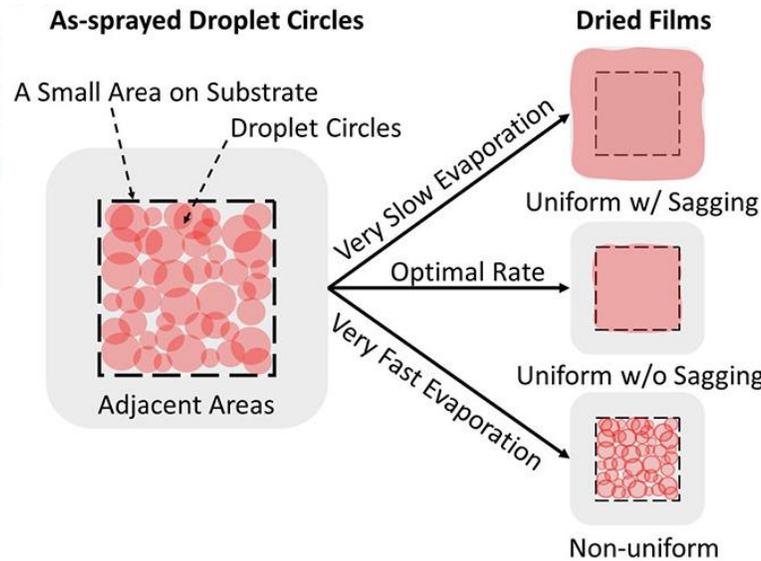
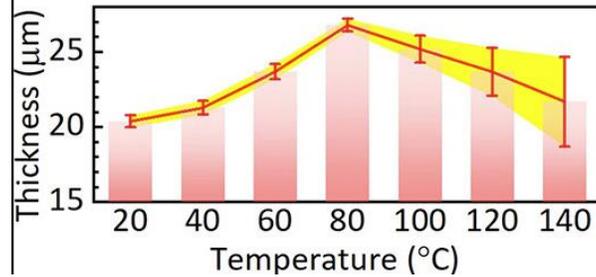
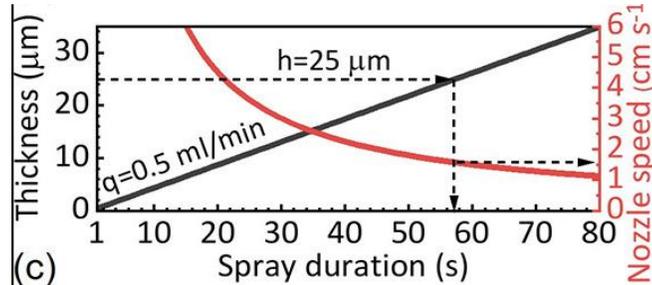


HydroGEN Lab R&D p-SOEC Technical Accomplishment:

Surface engineering enhances electrolyte layer uniformity

Electrolyte uniformity and quality affects cell performance substantially

- Proposed a facile and systematic parameter optimization for thin layer deposition, satisfying the requirements for throughput, thickness, and uniformity, simultaneously.
 - Thin electrolyte film with 30 μm thick PNC oxygen electrode by layer-by-layer deposition.
 - Full cell validation show current density of 1.36 A cm^{-2} at 1.3 V in the electrolysis mode, with minimal degradation over a period of 200 h.



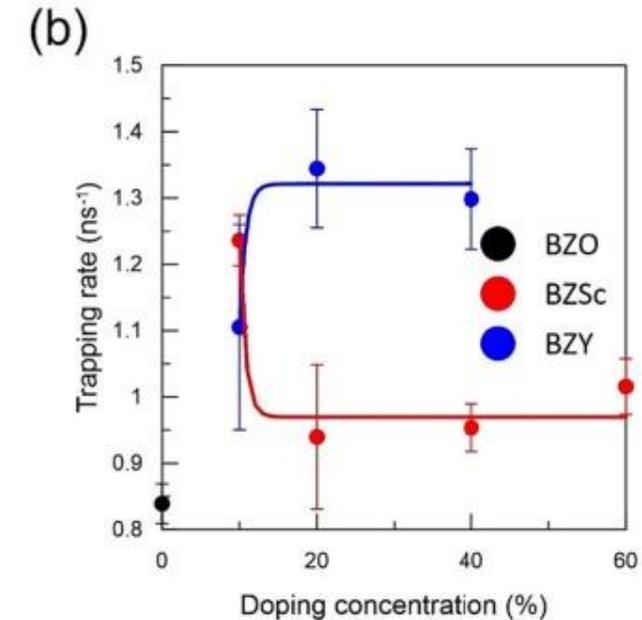
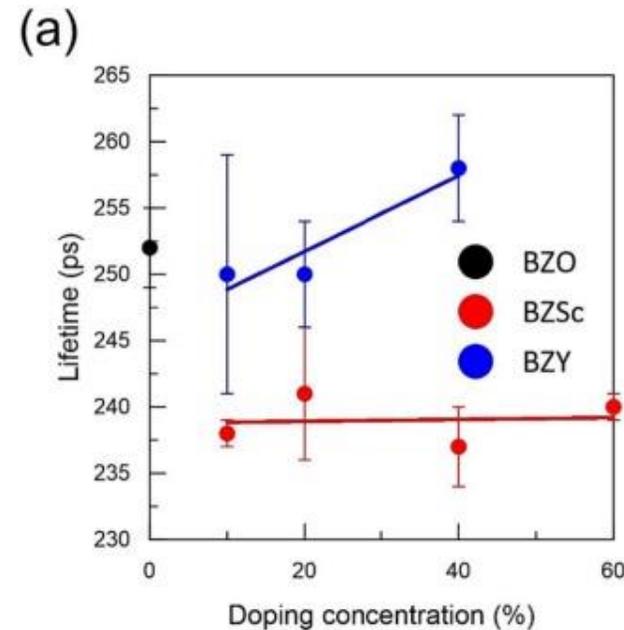
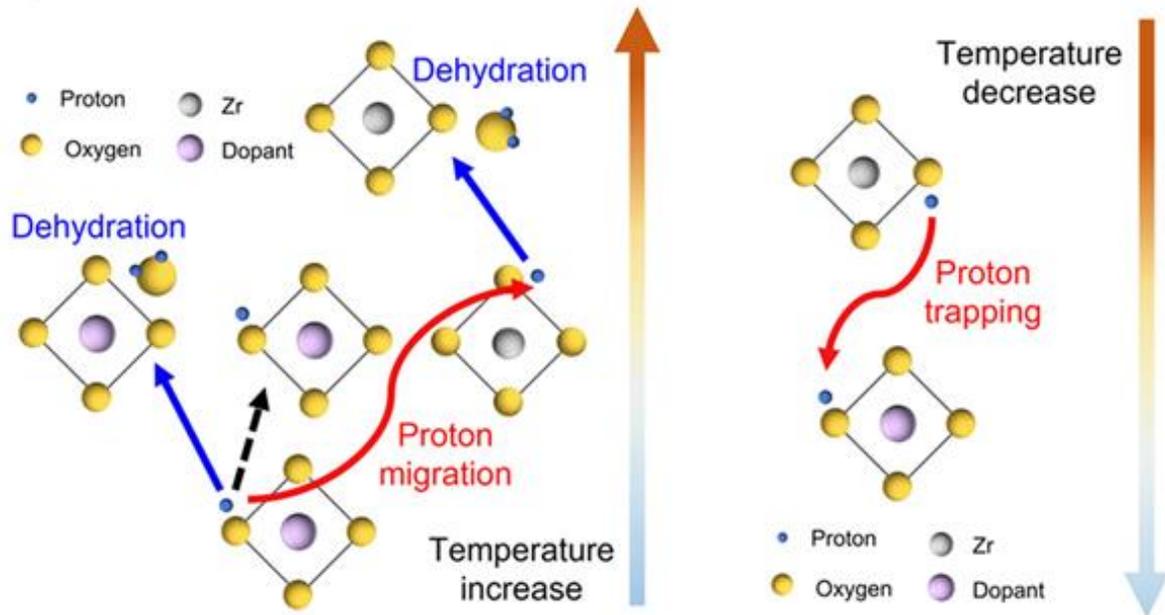


HydroGEN Lab R&D p-SOEC Technical Accomplishment:

Improving proton conductivity in perovskites and positron annihilation lifetime spectroscopy

Varying the dopant and concentration level in PCOs affects the hydration ability

- Scandium doping reduces the activation energy for proton migration and improves hydration of the material, both conditions may increase the proton conductivity in comparison to yttrium doped materials, suggesting it may be a good electrolyte candidate.
- Positron annihilation lifetime spectroscopy (PALS) is proven to be a powerful tool for studying the proton-trapping behavior and the defect chemistry of proton ceramics.



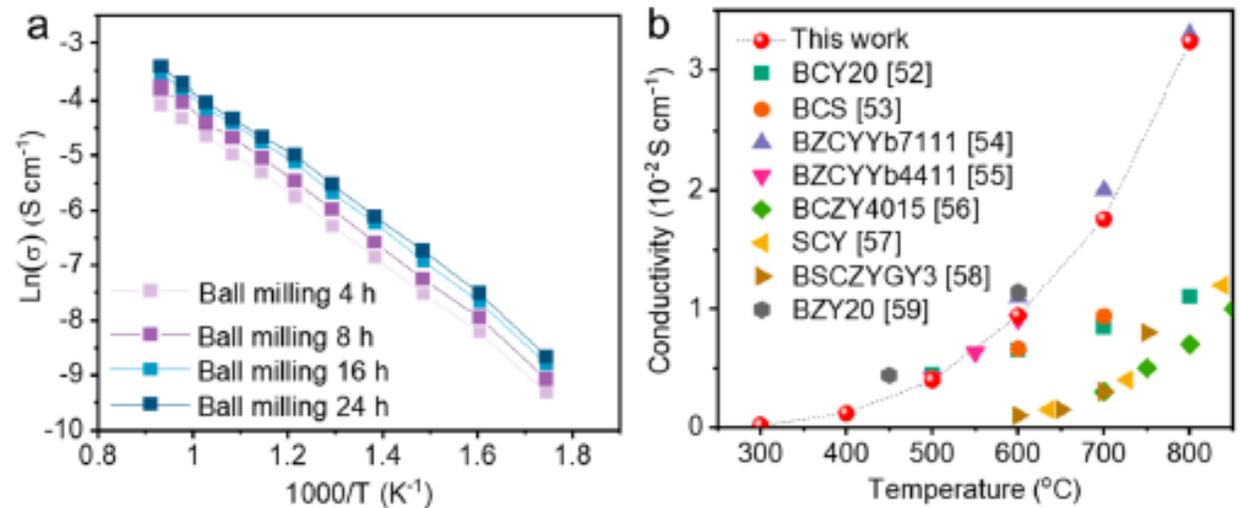
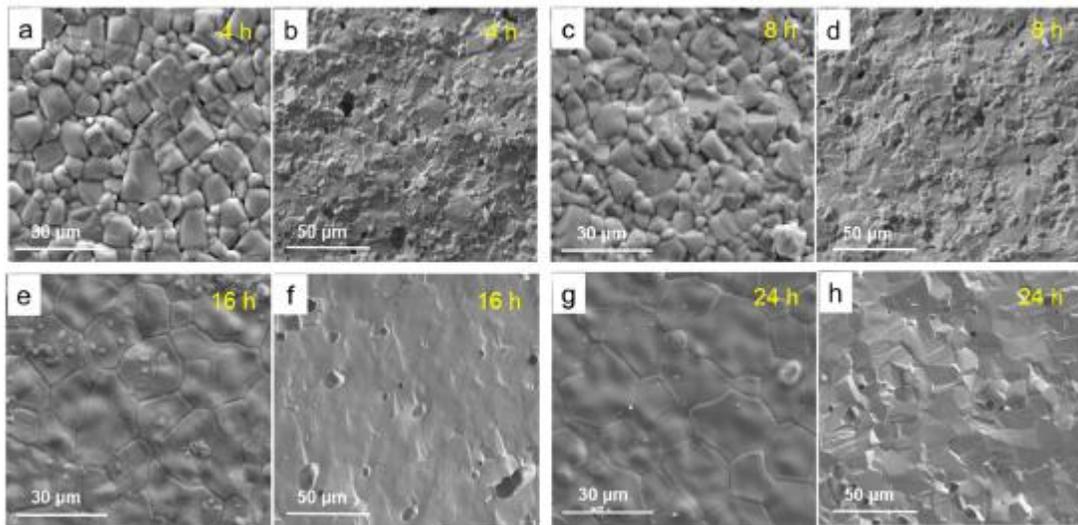


HydroGEN Lab R&D p-SOEC Technical Accomplishment:

Improved solid-state reaction method for synthesis of electrolyte materials

Synthesize high performance and cost-effective protonic electrolyte materials with reliable protocols

- The conventional solid-state reaction (SSR) method suffers from tedious synthesis procedures and low phase purity of the materials involved
- Improved SSR (i-SSR) method can produce high phase-purity electrolyte material $\text{BaZr}_{0.4}\text{Ce}_{0.4}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BZCYYb4411)
 - The ball-milled precursor powders are pelletized prior to calcination to reduce the length of the diffusion paths during perovskite phase formation.
 - The synthesis procedure and calcination temperature are carefully optimized based on the powder crystallization behavior.





Technology Transfer: p-SOEC

- **Exclusive license option agreement executed with a U.S. based start-up for multiple technologies supported by HFTO in 2023.**
 - Market focus for this company is green hydrogen production.
 - Negotiations to convert the option into an exclusive license are expected to conclude mid 2024.
- **Expanded patent portfolio for p-SOEC (details see “Intellectual Property” slide).**
 - 1 Granted Patent
 - 1 PCT Application
 - 1 Provisional Application
 - 1 Invention Disclosure Record (IDR) submitted and elected for patent filing.



HydroGEN HTE Lab R&D Technical Accomplishment:

LBL Metal-Supported Solid Oxide Electrolysis Cell (MS-SOEC)

Project targets at 700°C, 50:50 H₂O:H₂

Cell size (complete)

Target: >40 cm²

FY23 status: 5 cm²

FY24 Status: 50 cm²

Performance (complete)

Target: > 1.0 A/cm² at 1.4V

FY23 Status: 1.2 A/cm² at 1.4V

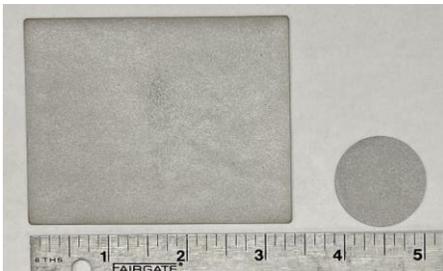
FY24 Status: 1.3 A/cm² at 1.4V

Durability (ongoing)

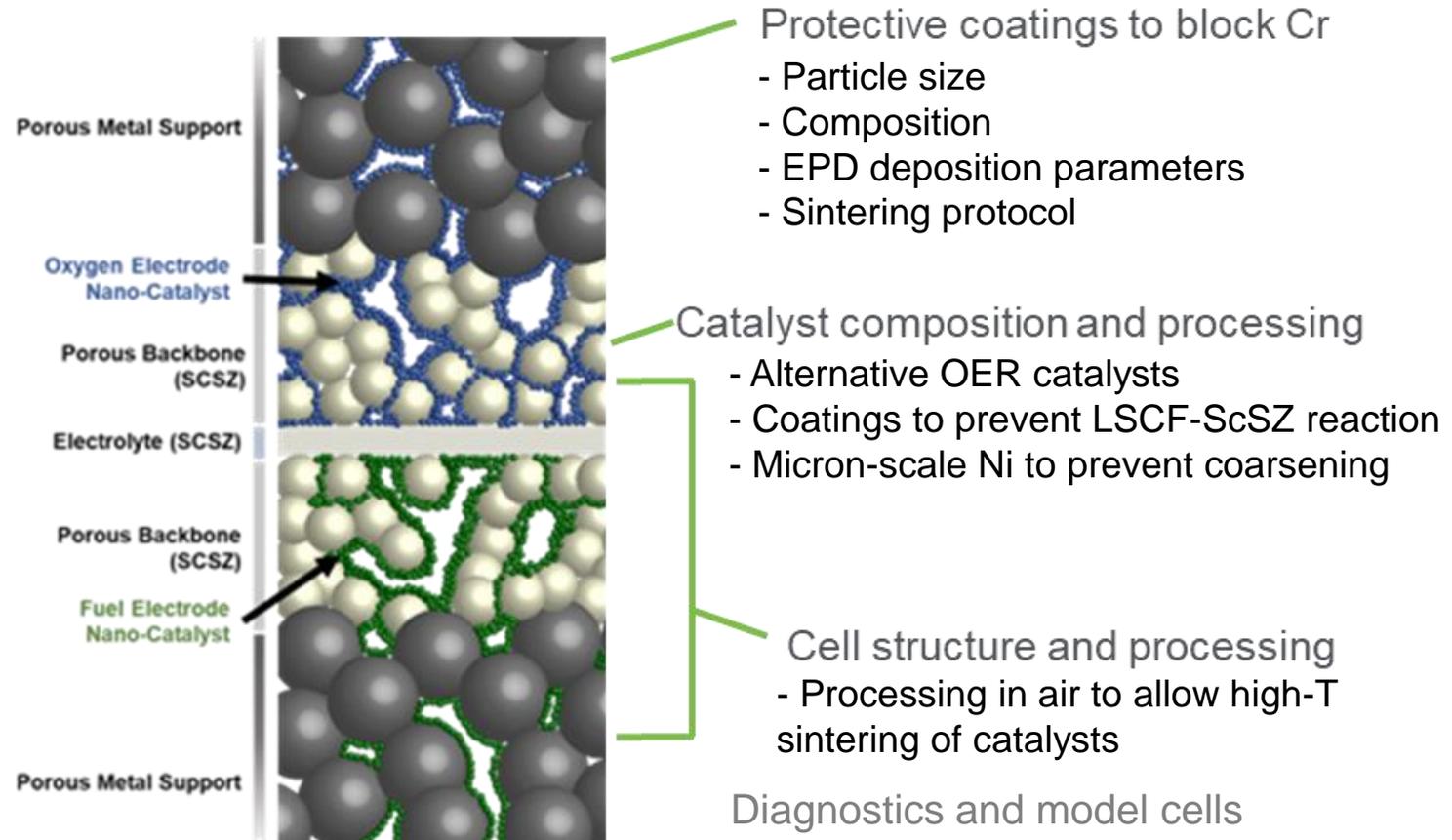
Target: <5%/kh

FY23 Status: 13%/kh at 0.5 A/cm²

FY24 Status: 11%/kh at 0.5 A/cm²



Approaches to improve performance and durability

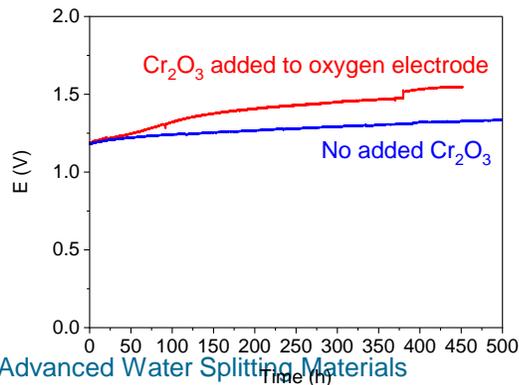
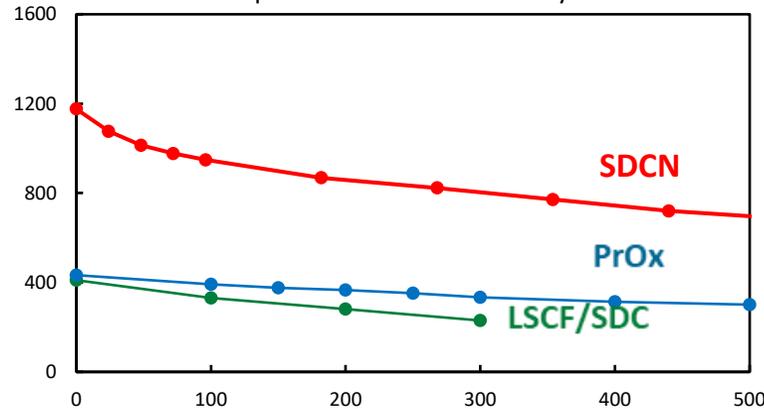




MS-SOEC Model cells to assess degradation modes

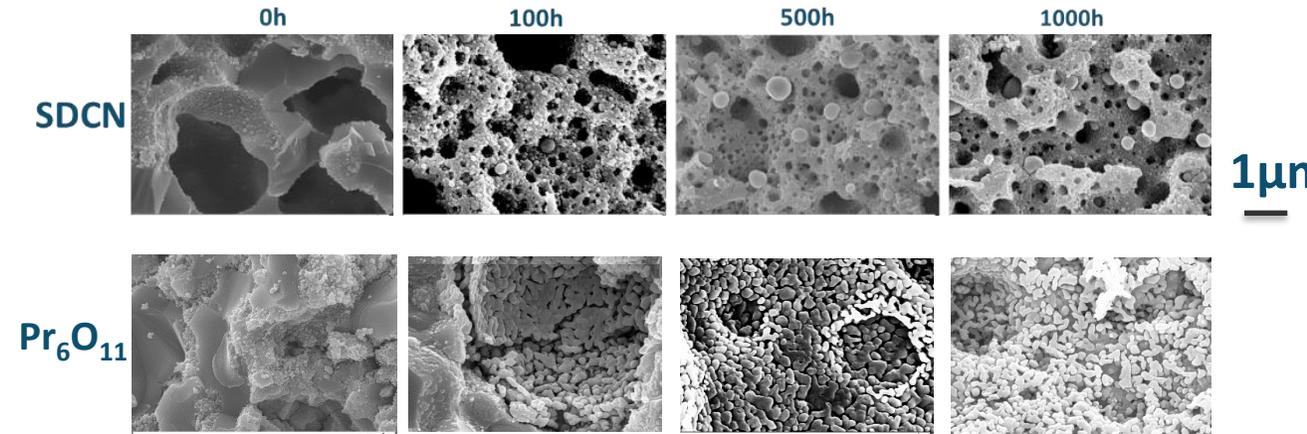
Symmetric cells

Oxygen catalysts dominate
- lower performance and durability than SDCN



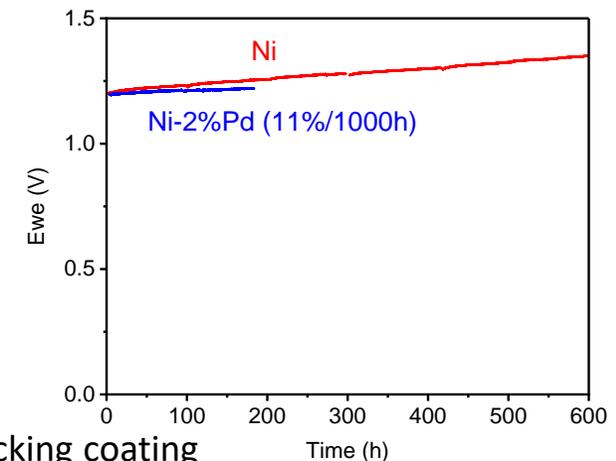
Detailed post-mortem analysis

Separating break-in and long-term degradation phenomena



Ni alloy

2% Pd doping increases stability
- suggests less expensive alloys may be fruitful



Conclusions

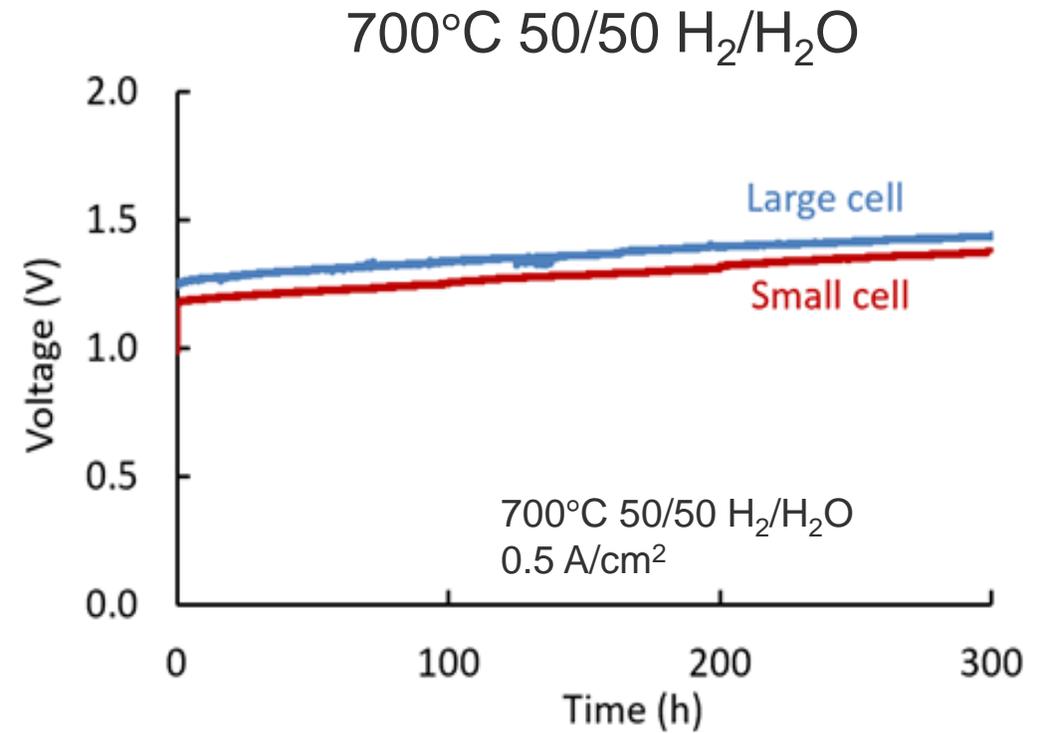
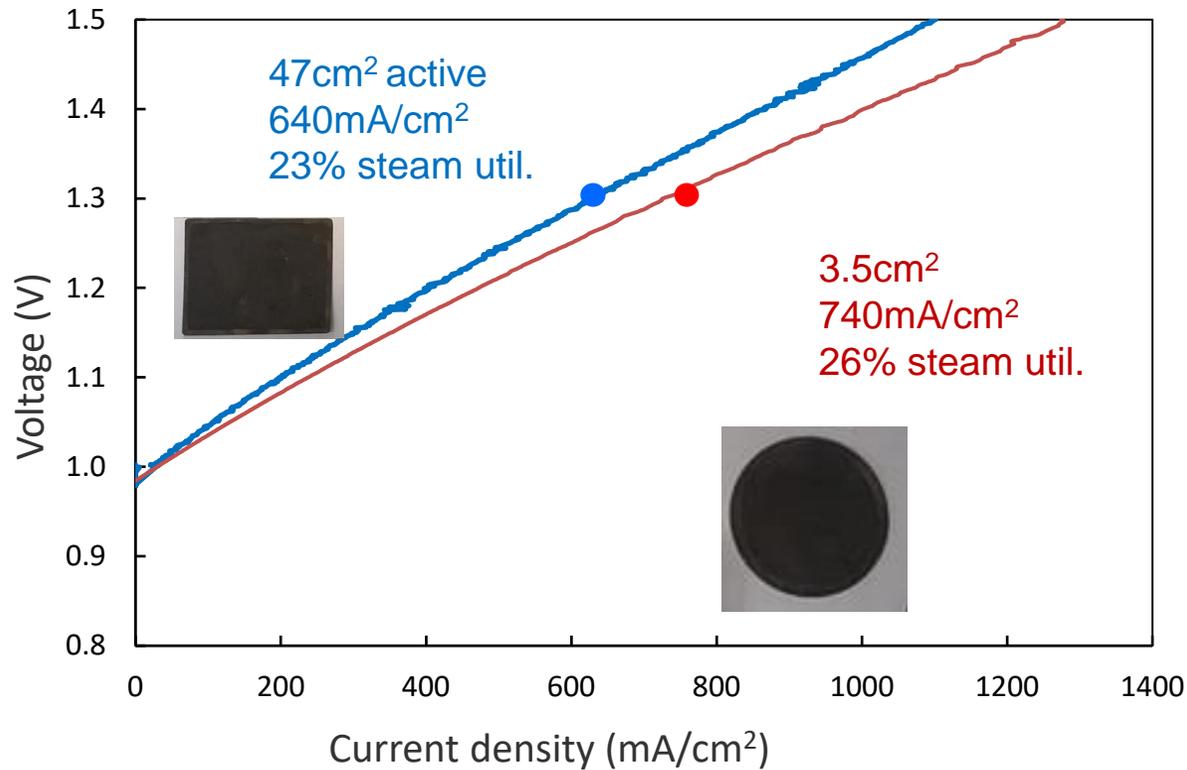
- Oxygen electrode limits performance and durability
 - Cr poisoning is significant in SOEC mode
- Ni coarsening is complete at <500h
- PrOx coarsening is complete at 100h
- SDC coarsening is minor

Priorities

- Cr-blocking coating
- Increase Ni and LSCF/Pr particle size
- Alternative to infiltrated catalysts
 - Ni alloy or exsolution
 - conventional OER catalyst



MS-SOEC Scale-up to 50 cm² cell size

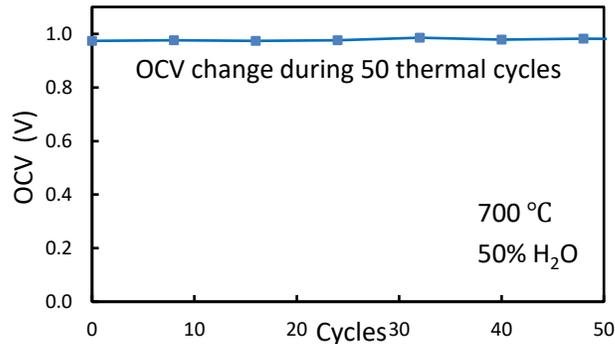
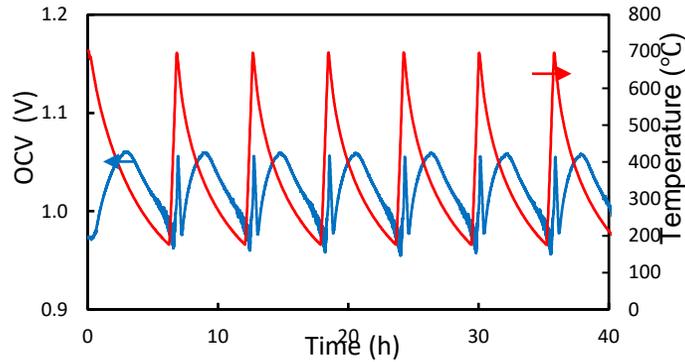


- Good performance for large planar cell
- Performance and durability is similar to button cell
- 86% of button cell current density at 1.3V (exceeds target of 75%)



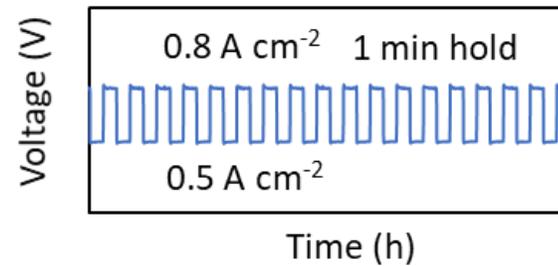
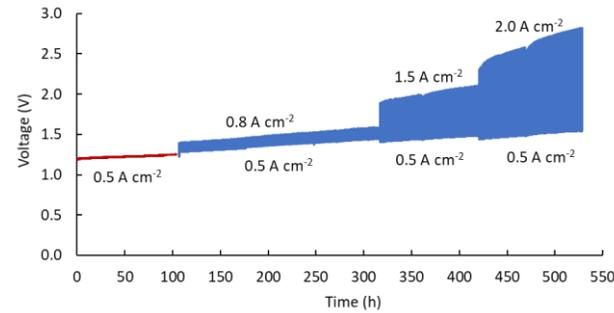
MS-SOEC Dynamic Operation at 700°C

Thermal Cycling



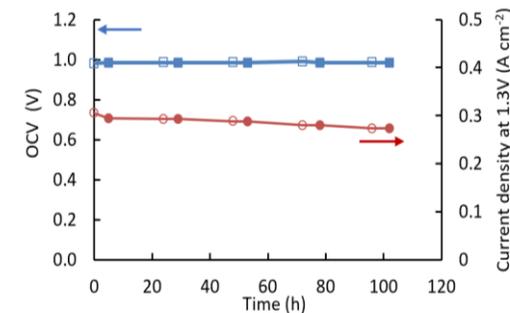
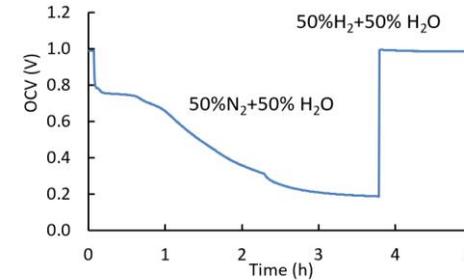
50 cycles from
160°C to 700 °C

Current Cycling



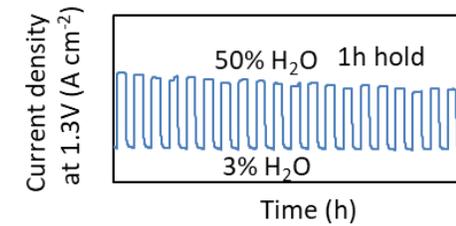
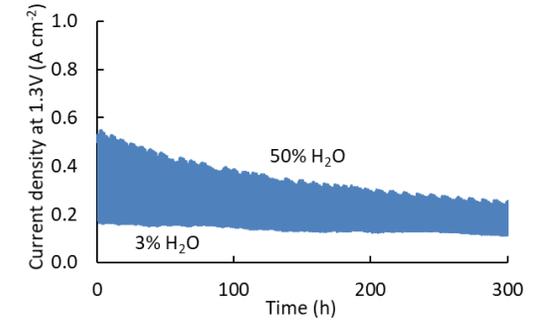
13,500 cycles between
0.5 A/cm² and 0.8-2 A/cm²

Redox Cycling



5 cycles from
Ni to NiO

Steam Content Cycling



150 cycles from
3% to 50% H₂O:H₂ ratio

MS-SOEC tolerates aggressive dynamic operation conditions

First report of MS-SOEC dynamic operation



Collaboration and Coordination

- Interfacing between HydroGEN and existing seedling projects.
- Interfacing between HydroGEN and H2NEW for exchanging information.
- Interfacing between HydroGEN and industry for benchmarking, technology transfer, and potential collaborations



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Michael C. Tucker
Zhikuan Zhu
Boxun Hu



Andrew Rowberg
Shenli Zhang
Joel Varley
Tadashi Ogitsu



Future Work

- Continue leveraging the lab node support for the existing and upcoming FOA projects.
- Benchmark and develop the p-SOEC electrolyte materials that have higher proton conductivity, better stability, less electronic leakage, and better chemo-mechanical properties.
- Develop MS-SOEC with further improved durability; Develop alternative cell architecture and fabrication approaches

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



Summary of Accomplishments

- **Lab capability support:** Effective collaborations between the seedling projects and the lab nodes, significantly accelerating both o- and p-SOEC technology advancement.
- **p-SOEC Lab R&D:** Investigated the fundamentals of protonic ceramic electrolytes and emphasized equal importance in performance and stability of p-SOEC with improved Faradaic efficiency, based upon the benchmarked electrolyte materials.
- **MS-SOEC Lab R&D :** Demonstrated robustness of MS-SOEC to dynamic operation; scale-up to cell size 50 cm²; systematic analysis of degradation phenomena; screening of concepts to improve durability.



Responses to Reviewers

Comments: Some work, such as the Chemours project and HTWE, overlaps with the Hydrogen from Next-generation Electrolyzers of Water (H2NEW) scope of work.

Response: Lab work has a clear distinction where p-SOEC is within HydroGEN while H2NEW covers o-SOEC work. It makes sense that some o-SOEC seedling projects were funded through HydroGEN prior to H2NEW.

Comments: Proton-conducting solid oxide electrolysis cell (P-SOEC) Faraday efficiency should increase with current density (slide29).

Response: Our discoveries revealed that the overpotential has more significant impact on Faradaic efficiency (FE) which caused the FE decrease with current density. It is consistent with the observations from the WVU and RTRC seedling projects as well as those reported by other groups and companies in US and Europe.

Comments: Metal-supported SOEC should address Cr poisoning under high steam conditions, and the operating temperature of 700C seems too high for metal support.

Response: i) Under normal operating conditions, Cr evaporation is prevalent on the oxygen side but is not expected on the steam side. At very high steam concentrations, volatile chromium oxyhydroxide may form. We plan to address this mechanism in the future via post-mortem study and direct measurement of Cr transpiration. ii) Oxidation of the metal support is temperature-dependent. Recently, we have studied oxidation of porous stainless steel in SOEC conditions in the temperature range 600-800C. In the case that the metal support is preoxidized and coated with catalysts (standard procedure), the oxidation rate at 700C is acceptable for long-term integrity of the metal support.



Intellectual Property

- Dong Ding, Hanping Ding, Wei Wu and Chao Jiang. Electrochemical cells for hydrogen gas production and electricity generation, and related structures, apparatuses, systems, and methods. US Patent (No. 11,557,781), 2023
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Publications

1. Puvikkarasan Jayapragasam, Yeting Wen, Korey Cook, Jacob A. Wrubel, Zhiwen Ma, Kevin Huang, and Xinfang Jin, “Crack Growth Rate at Oxygen Electrode/ Electrolyte Interface in Solid Oxide Electrolysis Cells Predicted by Experiment Coupled Multiphysics Modeling”, **Journal of the Electrochemical Society**, 2023, **170**, 054509. DOI 10.1149/1945-7111/acd4f1.
2. Clarita Y. Regalado Vera, Hanping Ding, Jagoda Urban-Klaehn, Meng Li, Frederick Stewart, Hanchen Tian, Xingbo Liu, Yanhao Dong, Ju Li, Meng Zhou, Hongmei Luo, Dong Ding. Improving Proton Conductivity by Navigating Proton Trapping in High Scandium Doped Barium Zirconate Electrolytes. **Chemistry of Materials**. 35 (2023) 5341-5352
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6. Yeting Wen and Kevin Huang, “Predicting the Rate of Degradation Related to Oxygen Electrode Delamination in Solid Oxide-Ion Electrolyzers”, **Journal of the Electrochemical Society**, in revision.



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1. J. Pietras, B. Oistad, X. Qian, S. Gopalan, Y. Zhong, W. Li, “Development of Durable Materials for Cost Effective Water Splitting”, 244th ECS Meeting (October 8-12, 2023)
2. Yeting Wen and Kevin Huang, “exploring the safe operational current density for high temperature solid oxide electrolyzers”, ICACC2023, January 22-26, 2023, Daytona Beach, FL.
3. X. Jin , P. Jayapragasam, and Y. Shoukry, Multiphysics Modeling for Solid Oxide Electrolyzer Cell with Heterogenous Synthetic Microstructure, 243rd ECS Meeting, Boston, MA, 05/28/2023-06/02/2023.
4. X. Jin, and Y. Shoukry, Current Leakage and Faradaic Efficiency Simulation of Proton-Conducting Solid Oxide Electrolysis Cells, 243rd ECS Meeting, Boston, MA, 05/28/2023-06/02/2023.
5. P. Jayapragasam , Y. Wen, X. Jin, and K. Huang, A 3D Simulation of DC-Biased Electrochemical Impedance of Solid Oxide Electrolysis Cell: Effects of Delamination, 243rd ECS Meeting, Boston, MA, 05/28/2023-06/02/2023.
6. Y. Wen and K. Huang, Predicting Lifetime of Solid Oxide Electrolytic Cells through Oxygen Electrode Performance, 243rd ECS Meeting, Boston, MA, 05/28/2023-06/02/2023.
7. K. Huang, annual project AMR meeting, June 5-7, 2023, Washington DC.
8. Dong Ding. Intermediate Temperature Solid State Energy Conversions by Protonic Ceramics: A Key for Cost-Effective Decarbonized Economy Invited Presentation. 48th International Conference and Expo on Advanced Ceramics and Composites (ICACC2024). Daytona Beach, January 28-Feb 2, 2024.
9. Dong Ding. Advancement of Proton Conducting Solid Oxide Electrolysis Cells (p-SOEC) for Hydrogen Production at Idaho National Laboratory. Invited Presentation. The 243th ECS conference. Boston, May 28-June 2, 2023.
10. Qian Zhang, Clarita Y. Regalado Vera, Hanping Ding, Wei Tang, Wei Wu, Scott Barnett, and Peter Voorhees, Dong Ding. Dependence of Faraday Efficiency on Operation Conditions and Cell Properties for Proton Ceramic Electrolysis Cells. Oral Presentation. The 243th ECS conference. Boston, May 28-June 2, 2023.



Presentations Cont'd

- Yuqing Meng, Qian Zhang, Haiyan Zhao, Dong Ding. Operando Characterizations of Proton Exchange in Proton Conducting Solid Oxide Electrolysis Cells (p-SOECs). Oral presentation. The 243th ECS conference. Boston, May 28-June 2, 2023.
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