Designing Internal Surfaces of Porous Electrodes in Solid Oxide Electrolysis Cells for Highly Efficient and Durable Hydrogen Production

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DOE Award – FE-0032112
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Contract Specialist: W. Ryan Simmons
Technology Manager: Dr. Shailesh Vora

Overview

➢ Project Background & Challenges

Solid Oxide Electrolysis Cells (SOEC) and Degradation

- ❖ Fuel electrode: Ni migration & loss of triple-phase boundaries for reactions
- ❖ Oxygen electrode: LSM/YSZ delamination, Cr contamination
- ❖ Oxygen electrode: LSCF/SDC decomposition, Sr surface segregation, Cr contamination

➢ Project Scope & Activities

- ❖ Project objective
- ❖ Technical approach
- ❖ Project structure, project schedule, project management plan, risk management

➢ Expected Outcome

Exciting and encouraging preliminary results from this project

- ❖ SOEC with Surface modified LSM/YSZ electrode with a record high current density (hydrogen production rate) of 1.65 A/cm^2 at 750°C
- ❖ Our established collaborations with ALD precursor providers, ALD machines manufactures, and Solid Oxide Cells manufacturers

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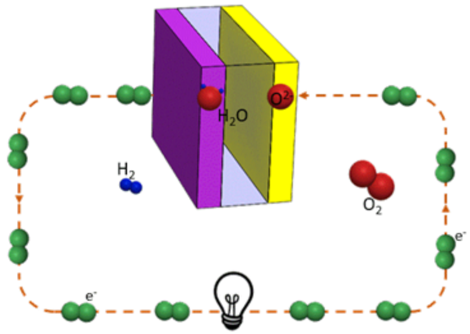
Solid Oxide Cells, SOEC Electrolyzing water to produce hydrogen

Solid Oxide Fuel Cells-SOFC:

- Oxidizing a fuel to produce electricity.
- High efficiency, fuel flexibility, low emissions.



Oxygen Electrode in SOFC

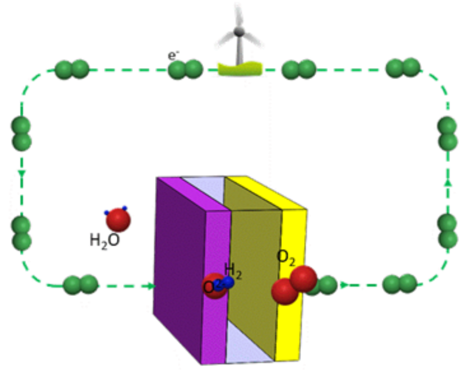
$$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$$

Fuel Electrode in SOEC

$$H_2 + O^{2-} \rightarrow H_2O + 2e^-$$

Solid Oxide Electrolysis Cells- SOEC:

- **Electrolyzing water to produce hydrogen and oxygen gases.**
- **Produce pure green hydrogen.**



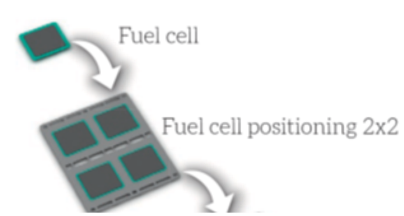
Oxygen Electrode in SOEC

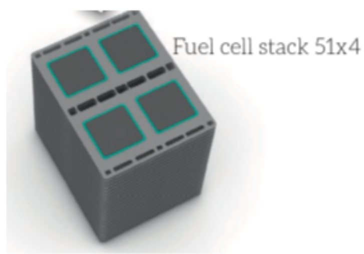
$$O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$$

Fuel Electrode in SOEC

$$H_2O + 2e^- \rightarrow H_2 + O^{2-}$$

SOEC systems are practically adapting the well-developed SOFC systems to shorten the development of SOEC devices.





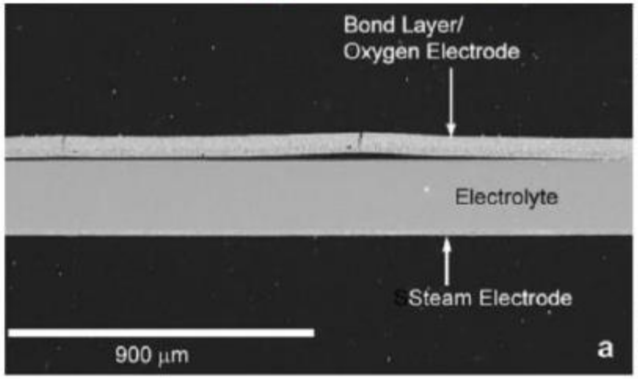
solidpower.com/en/bluegen/

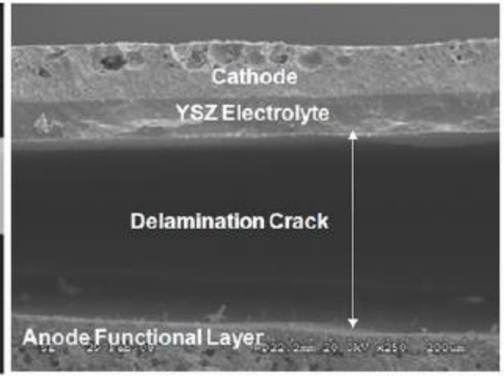
Operation of the SOEC stacks at higher current densities **over 0.75A/cm²** and a low degradation rate could enable cost-competitive production of synthetic hydrocarbon and hydrogen.

Ebbesen SD, Jensen SH, Hauch A, Mogensen MB. High temperature electrolysis in alkaline cells, solid proton conducting cells, and solid oxide cells. Chemical reviews. 2014; 114 (21): 10697-734.

SOECs usually present more severe degradation than SOFCs, Oxygen electrode

- LSM/YSZ Oxygen electrode, severe delamination taking place at the electrolyte and electrode interface

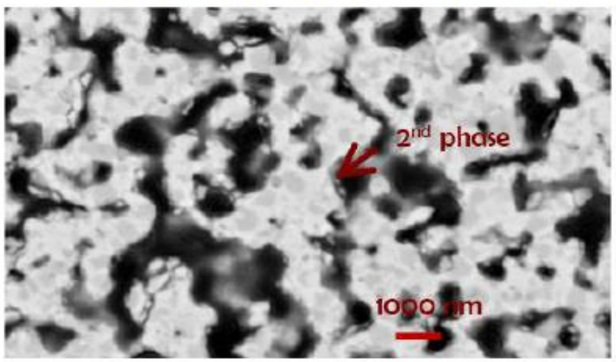


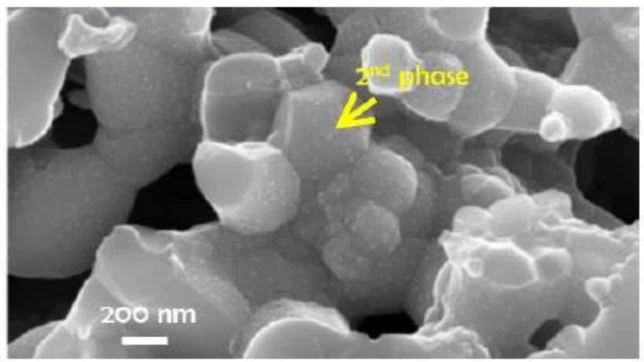


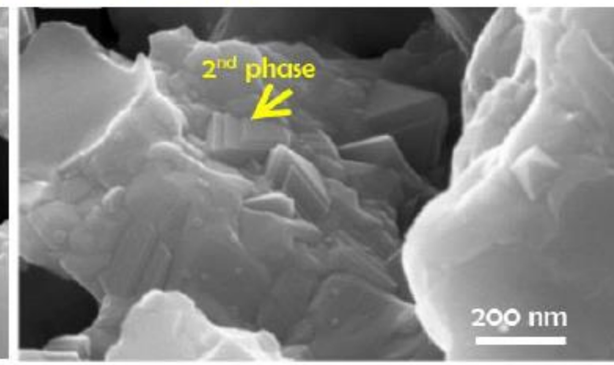
- Delamination, due to lack of ionic conductivity in LSM, could happen ~48 hours.
- For decades, such delamination is the biggest obstable for development of SOEC with LSM/YSZ electrode.
- Cr contamination also cause the degradation.

Mawdsley JR,. Post-test evaluation of oxygen electrodes from solid oxide electrolysis stacks. international journal of hydrogen energy. 2009;34(9):4198-207. Virkar AV, Lim H-T, Tao G. Failure of solid oxide fuel cells by electrochemically induced pressure. Procedia IUTAM. 2014;10:328-37.

- LSCF/SDC oxygen electrode, (1). LSCF decomposition, loss of the electrocatalytic activity, Sr surface segregation. (2). Cr vapor contamination from the interconnect, and their reaction with Sr.







Tietz F, Sebold D, Brisse A, Schefold J. Degradation phenomena in a solid oxide electrolysis cell after **9000 h** of operation. Journal of Power Sources. 2013;223(0):129-35.

SOEC degradation is taking place on both the fuel and oxygen electrodes.

- Ni/YSZ, LSM/YSZ, LSCF/SDC performance degradation is rooted in different nanostructure/chemistry reasons.
- All electrodes from state-of-the-art SOFC needed to be improved for SOEC application.

This project:

- ✓ Improving of SOEC performance of as-made SOCs through the surface modification of their porous electrodes.
- ✓ Improving of Ni/YSZ, LSM/YSZ, LSCF/SDC separately.

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- SOEC with Surface modified LSM/YSZ electrode with a record high current density (hydrogen production rate) of 1.65 A/cm^2 at 750°C
- Our established collaborations with ALD precursor providers, ALD machines manufactures, and Solid Oxide Cells manufacturers

Project Objective

The **objective** of this research is to achieve highly efficient and durable hydrogen production.

Approach: Decrease the electrode/cell resistance, increase the hydrogen production rate, and increase durability.

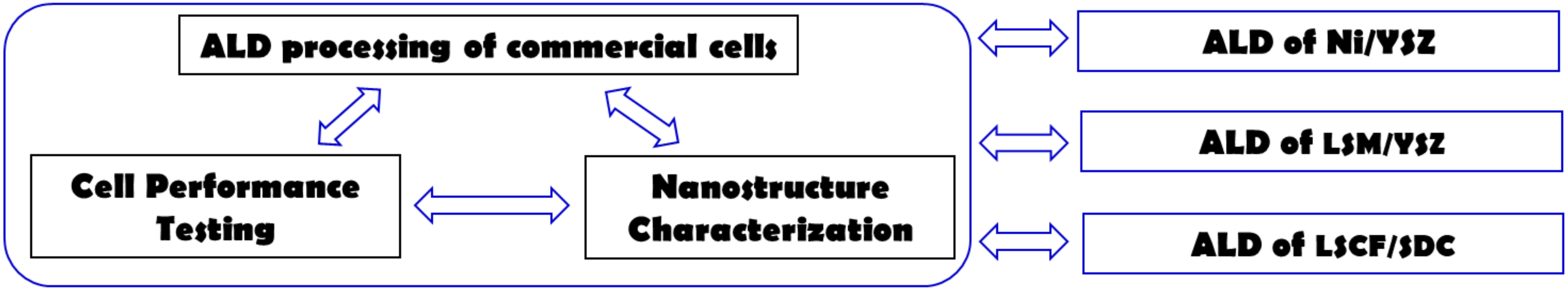
- The commercial cells adapted for this study consist of the Ni/yttria-stabilized zirconia (YSZ) fuel electrode and $La_xSr_{1-x}Mn_yO_3$-(LSM)/YSZ and $La_xSr_{1-x}Co_yFe_{1-y}O_3$ (LSCF)/Sm_2O_3 doped CeO_2 (SDC) oxygen electrodes.
- Highly active and robust nano-scale coating layers will be developed using the ALD and implanted to the internal surface of the porous electrode of as-fabricated commercial cells.
- For both the fuel and oxygen electrodes, innovative conformal surface nanoionics consisting of nanocrystalline ionic conducting materials will be incorporated into the ALD coating layer to provide structure protection for increased durability towards both the intrinsic and extrinsic degradation.

SCOPE OF WORK & common approaches for tasks.

Commercial Cells: We will work on **state-of-the-art commercial cells** provided by different manufacturers that are being developed and matured worldwide during the past two decades.

- **ALD processing:** ALD coating using a commercial ALD system: Computer-controlled automatic switching of the precursor with a one-step processing. The ALD processing procedure will be developed to control the chemistry and the thickness of the ALD layer.
- **SOEC hydrogen production evaluation:** Lab-scale cell testing of the commercial button and planar cells: The cell testing will be performed on baseline and surface-modified cells. The cells will be tested using the state-of-the-art test stations at the PI's lab. Testing conditions such as operation temperature, operation current density, operation voltage and durability, will be adjusted at the industrially relevant operating conditions.
- **Nanostructure evaluation:** ALD layer nanostructure evaluation of as-deposited cells and ALD layer nanostructure evaluation of cells after electrochemical testing.

Project Structure & Risk Management



Interface reaction between the ALD coating layer and the backbone, as well as the **electrochemical stability** of the ALD layer over long term electrochemical operation are **potential risks.**

Technical risks are managed to be minimum level through the following approach:

- **Potential interface reaction between the ALD layer and the cathode backbone that could be detrimental to the SOFC performance was identified.**

  The PI proposed to use a conductor oxide and electro-catalyst noble metal materials set. Such materials are fully compatible with the electrode commercial fuel cells, and the PI will develop a special nanostructure on the surface of the commercial composite cathode.

- **The effective ALD processing conditions are clearly identified.**
- **Proposed electrode surface architectures were largely validated through the preliminary data.**

  The effective ALD processing conditions and effective penetration of ALD chemical precursors into the cathode were clearly confirmed in the preliminary data. The three type architectures proposed for the activities are supported by the preliminary work including the cell performance testing and the nanostructure characterization.

Mitigation plan: If there is any ALD layer that has tested to be detrimental to the cell performance, based on the comprehensive electrochemistry test, such ALD coated cell will be subjected to nanostructure examination under microscopy (TEM) directly. Subsequent ALD layer coating will be adjusted accordingly based on TEM examination results.

Project Deliverables

Task / Subtask Number	Deliverable Title	Due Date
1.1	Project Management Plan (PMP)	Update due 30 days after award. Revisions to the PMP shall be submitted as requested by the NETL Project Manager.
1.2	Technology Maturation Plan (TMP)	The initial TMP is due 90 days after award. Updates to the TMP shall be submitted, as needed, throughout the project period of performance. A final TMP is due within 90 days of project completion.
2.1	ALD coating on Ni/YSZ	Inform completion of Task to NETL Project Manager via email.
3.2	ALD coating on LSM/YSZ	Inform completion of Task to NETL Project Manager via email.
4.2	ALD coating on LSCF/SDC	Inform completion of Task to NETL Project Manager via email.

ALD coating on the internal surface of the electrode developed by this project will integrate multiple functions.

(1) Dramatically **increasing the operating current density** for the high hydrogen production rate and **lowering operating voltage** for less electricity consumption, due to the decreased electrode resistance induced by the ALD coating;

(2) **Mitigating the electrode intrinsic degradation** and increasing the electrode structure durability by preventing the constituent elements' surface migration and surface segregation

(3) **Mitigating the electrode extrinsic degradation** and increasing the electrode structure durability by sealing off contamination such as Cr from penetrating into the electrode backbone.

As such, this project will provide a simple solution to various materials' challenges at the cell level and could further enable extensive and more efficient SOEC stacks and systems.

Success Criteria

Materials to be used for electrode surface architecture and cell testing temperature and testing conditions. The elements and materials to be used for engineering nano-architecture on the surface of the electrode will be commercial mature/available, low cost, environmentally friendly, and chemically and thermally fully compatible with materials for the-state-of-the-art commercial cells. The steps for tailoring the electrode surface architecture will be optimized and simplified through this project, and performance enhancement on the lab-scale button cells will be delivered for commercial operation throughout the entire SOEC operation range of 650-800° C.

The proposed work will accomplish the validation of concepts at a laboratory scale by direct comparison of the electrolysis performance of the as-received commercial baseline cells and the commercial cells subjected to subsequent to ALD coating developed through this project.

All lab-scale cell testing will be performed at the industry-relevant operation conditions as detailed below:

- Cells for testing will be **state-of-the-art commercial cells, with excellent performance repeatability**.
- Electrolysis performance evaluation will be carried out at **650-800°C,** and the SOECs will be operated under the customized thermal neutral current density. Long-term stability tests will be carried out over 500 hours of continuous operations. The desired operation current density is over **0.75A/cm^2**.

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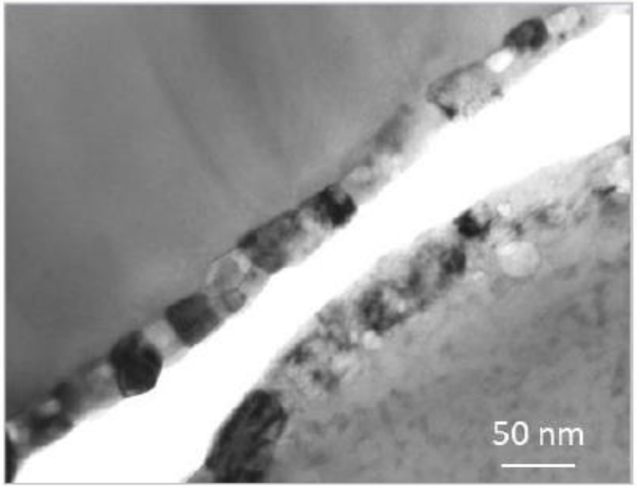
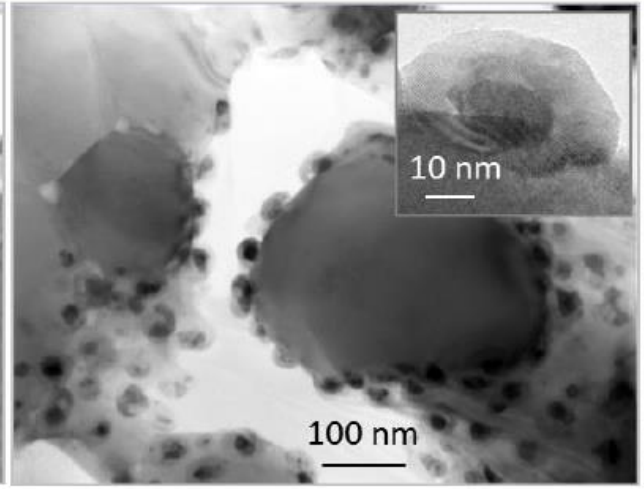
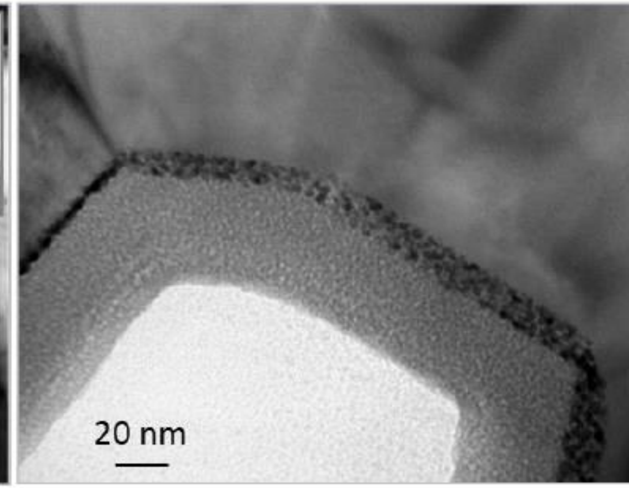
On-Demand Design of Nanostructure & Function of ALD Layer



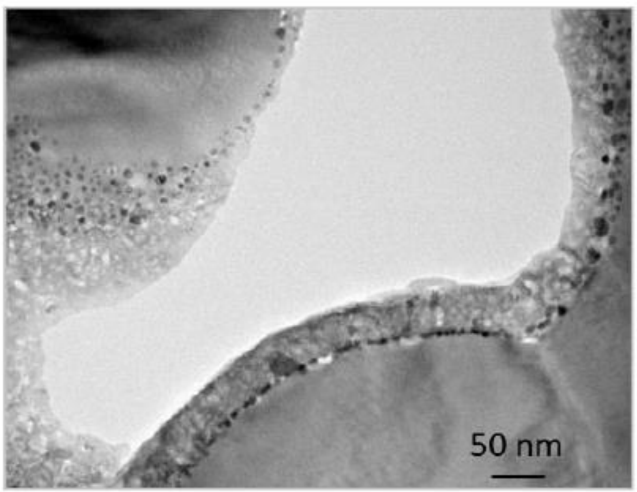
Single layered nanoionics



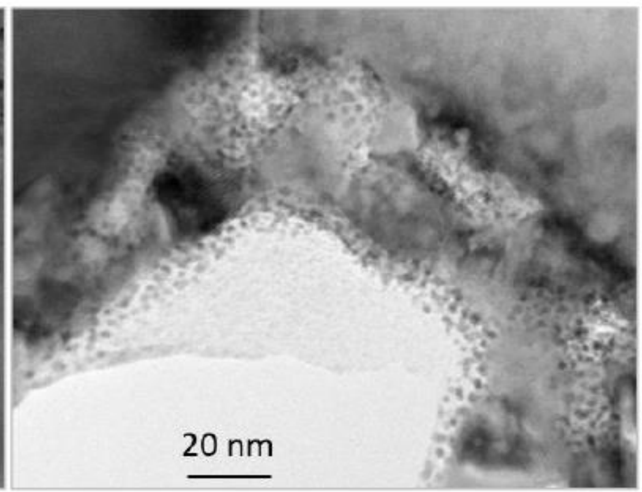
Discrete core-shelled catalysts

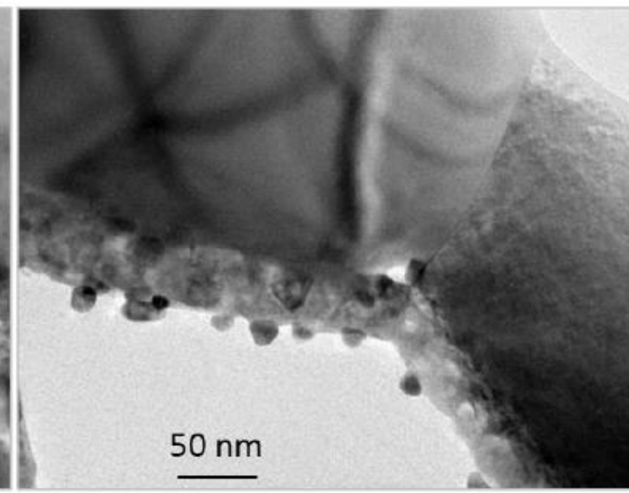


Multilayered nano-composite



Multilayered nano-composite



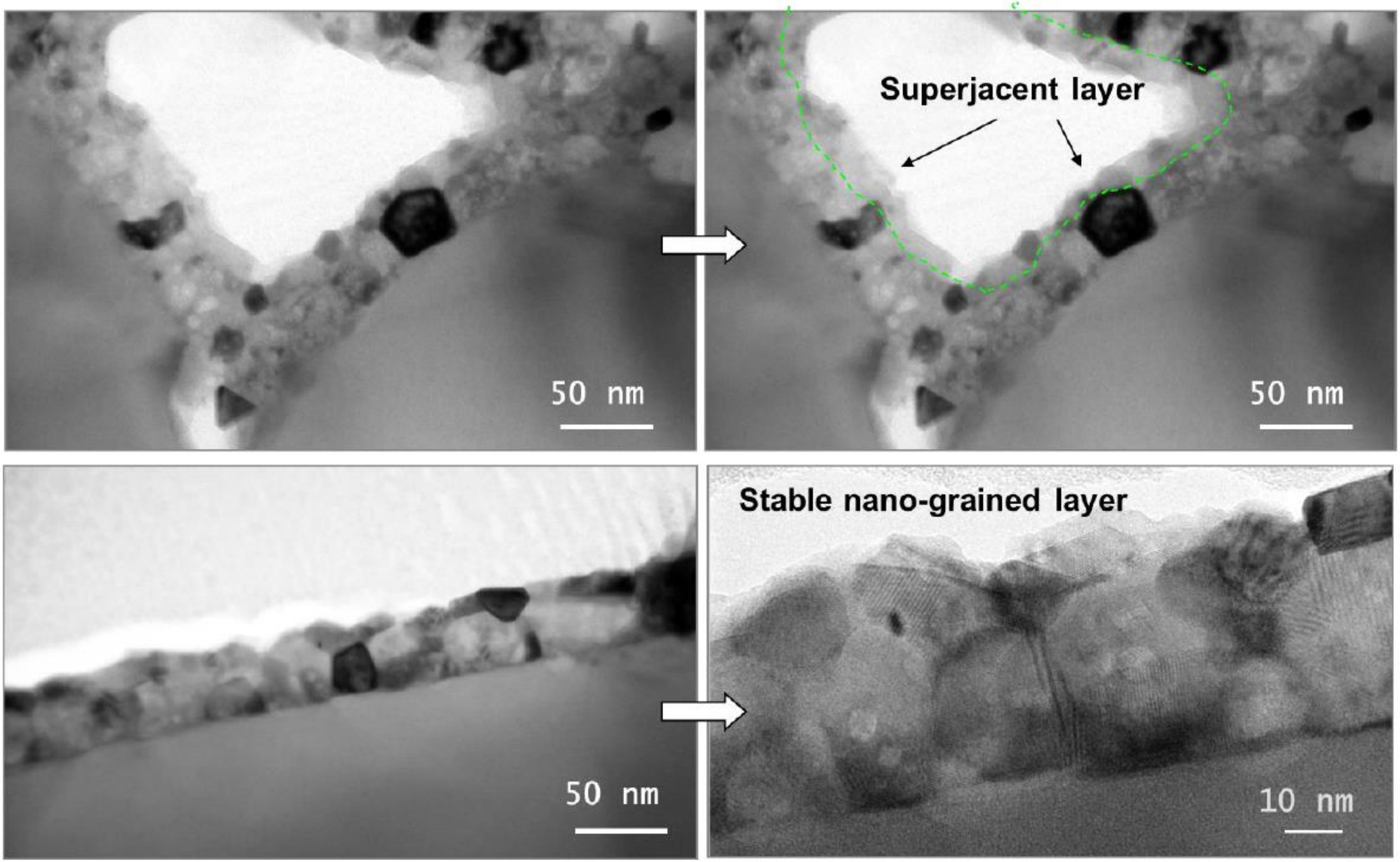


Porous composite having pores filled with nano catalyst

- ALD layer could be single layered, either conformal continuous layer or discrete particles.
- ALD layer could be heterogenous composite, layered or porous filled with nano catalysts.

Scientific Reports 6, 32997, 2016   *J Power Sources, 405, 45-50, 2018.*   *ACS Catalysis, 9(8), 6664-6671, 2019*   *Nano Letters, 19(12), 8767-8773, 2019*

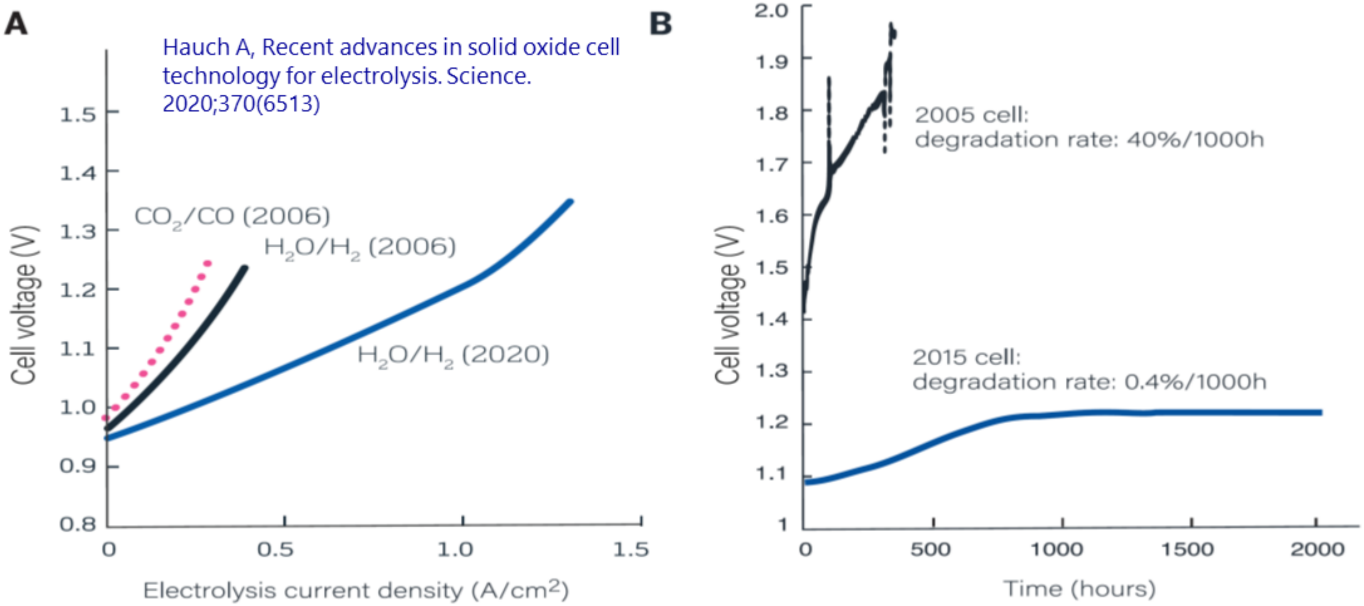
Factor of 2.7 performance enhancement, stable composite



Total layer thickness of ~ 25 nm, Strongly bonded interfaces.

Superjacent ~ 5 nm; subjacent ~20 nm.

Increased productivity >0.75A/cm² has been pursued in Europe



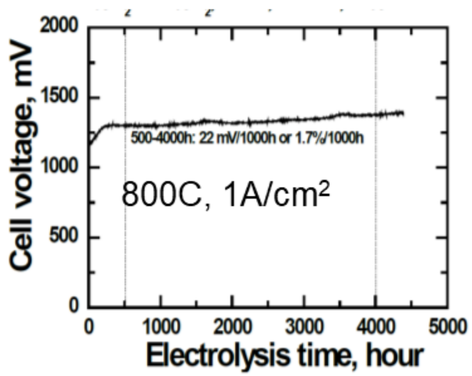
Electricity consumption < 40 kWh/kg

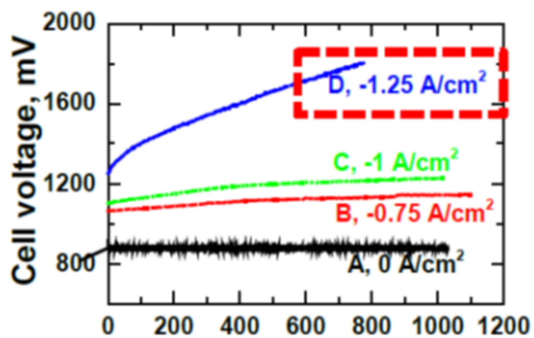
Production loss rate < 1.9%/1000h

Availability >95%
Reversible FC efficiency 54%

Current density 1.25A/cm2
Steam conversion rate > 85%

Cell-level improvements. (A) Current-voltage curves for cells fabricated in 2006 and 2020 with data from at 750° C, measured in H2O/H2 = 1 or CO2/CO = 1. (B) Durability test of H2O electrolysis at 1 A/cm2 on a cell fabricated in 2005 measured at 850° C and a cell fabricated in 2015 measured at 800°C. All cells were supported by a Ni-YSZ electrode and had an active area of 16 cm2.



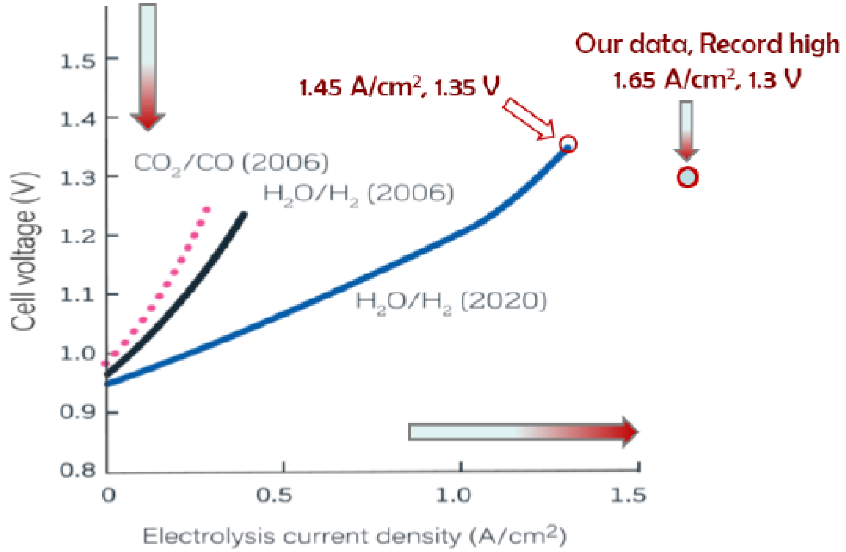


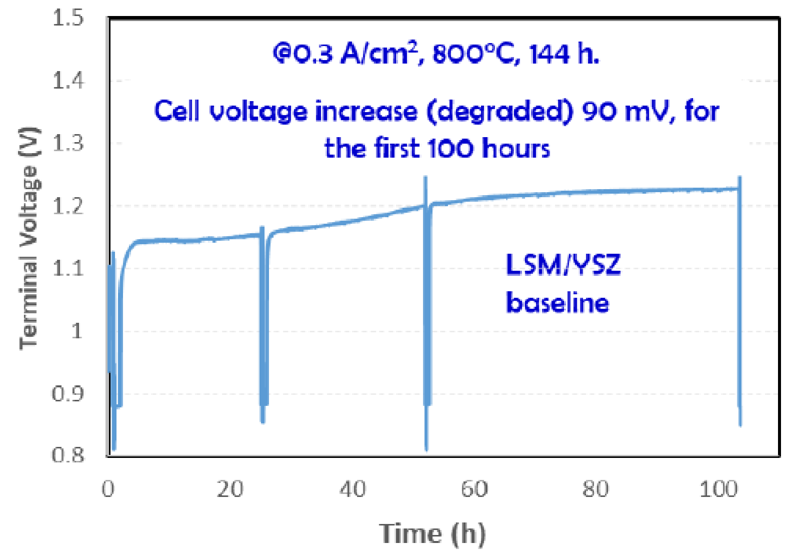
- Hagen A, Frandsen HL. Recent Highlights of Solid Oxide Fuel Cell and Electrolysis Research at DTU Energy. Ecs Transactions. 2021;103(1):327.
- Atanasiu M, Tsimis D, Aguilo-Rullan A, Lymperopoulos N, Dirmiki D, editors. (Plenary), The Status of SOFC and SOEC R&D in the European Fuel Cell and Hydrogen Joint Undertaking Programme. ECS Meeting Abstracts; 2021: IOP Publishing.
- Chen M, Tong X, Ovtar S. Lessons Learned from Operating a Solid Oxide Electrolysis Cell at 1.25 a/cm2 for One Year. Ecs Transactions. 2021;103(1):475.

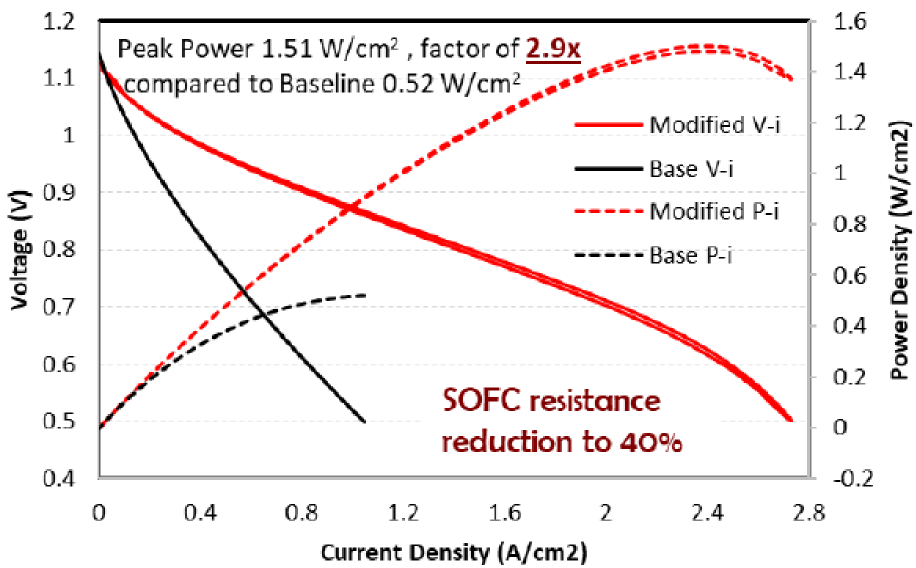
- Extensive (> 9000 hours) long term SOEC testing has been performed in Europe.
- Significant degradation during initial operation (first ~ 500 hours), regardless of temperature and cells.
- Degradation is severe especially at the higher production rate with the current density > 1A/cm²

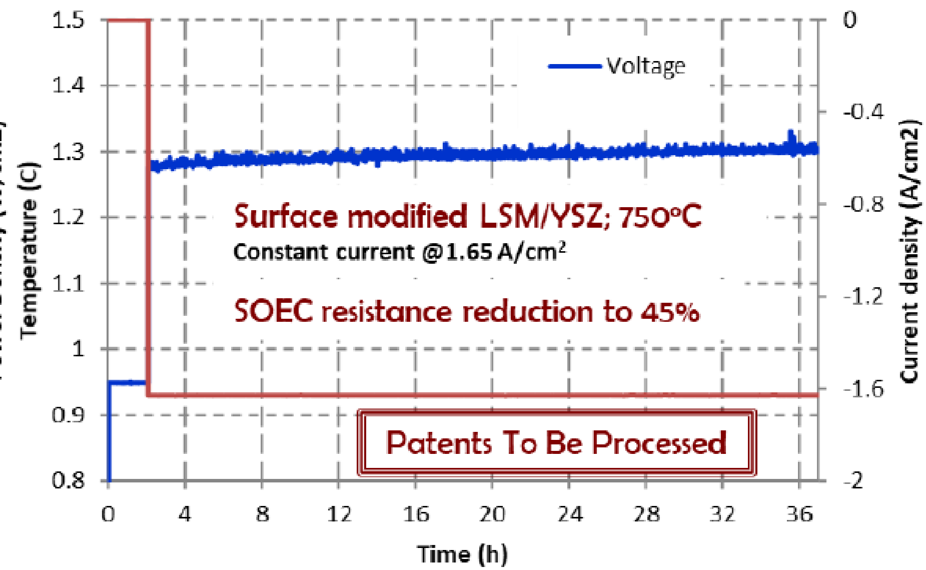
Preliminary Results: SOEC, Surface modified LSM/YSZ, LSM/YSZ-Ni/YSZ

Hauch A, Recent advances in solid oxide cell technology for electrolysis. **Science**. 2020









Surface modified LSM/YSZ provide record high hydrogen production rate of 1.65 A/cm² at low voltage of <1.3 V. At 750C- High performance for LSM.

ACKNOWLEDGEMENTS

DOE-SOFC Program

National Energy Technology Laboratory

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Contract Specialist: W. Ryan Simmons

Technology Manager: Dr. Shailesh Vora