Designing Internal Surfaces of Porous Electrodes in

Solid Oxide Electrolysis Cells for Highly Efficient and Durable Hydrogen Production

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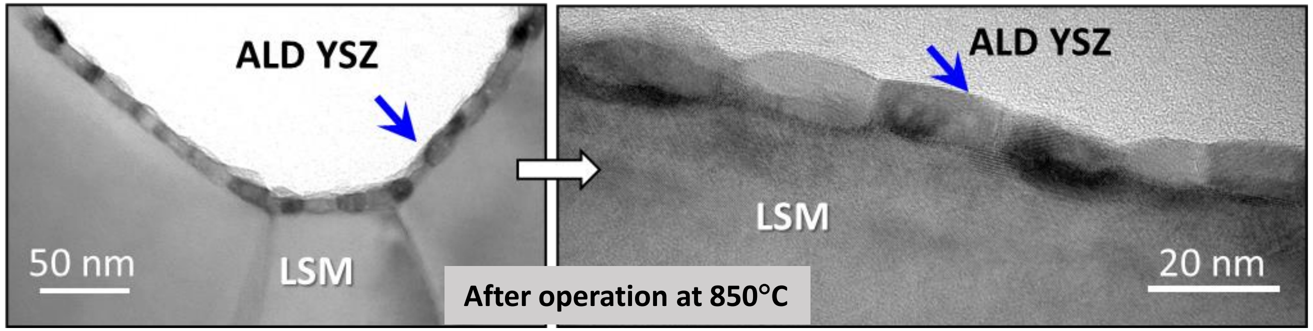
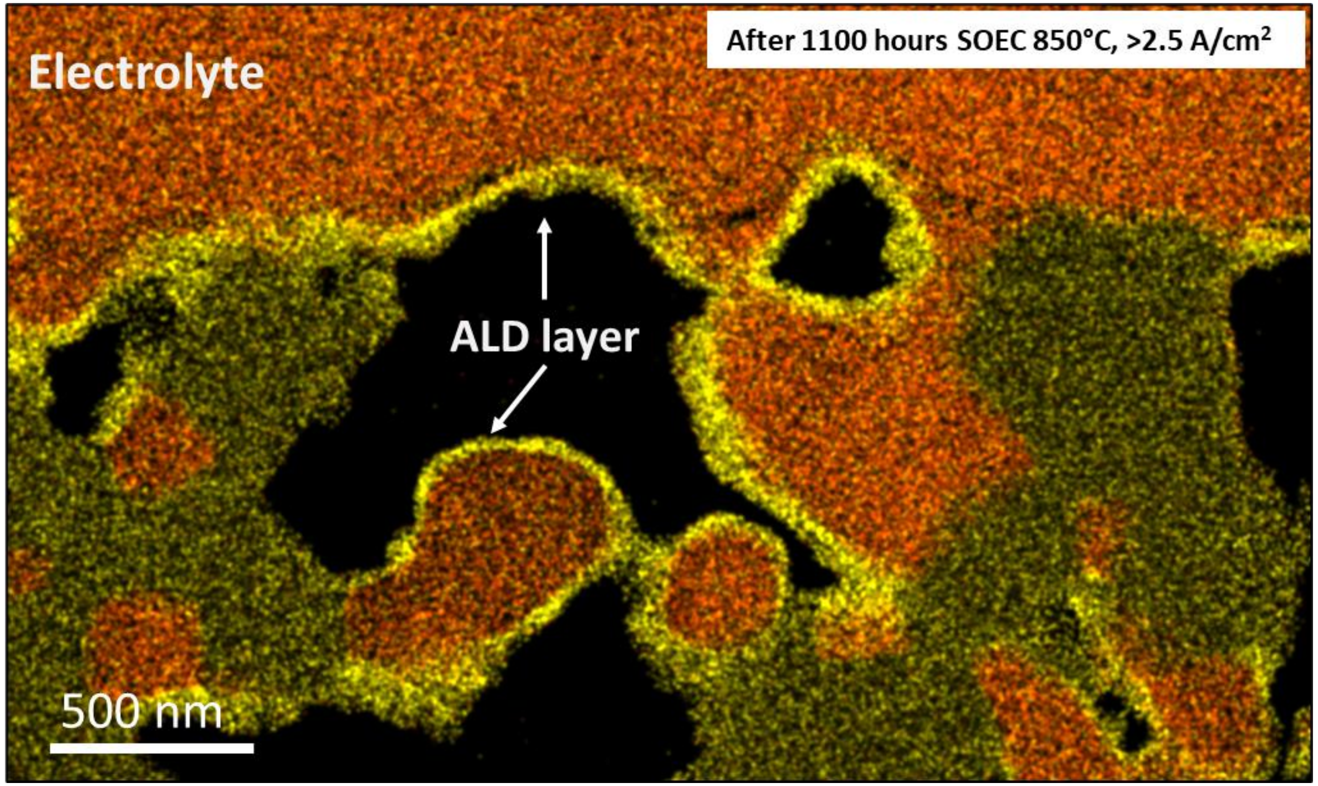
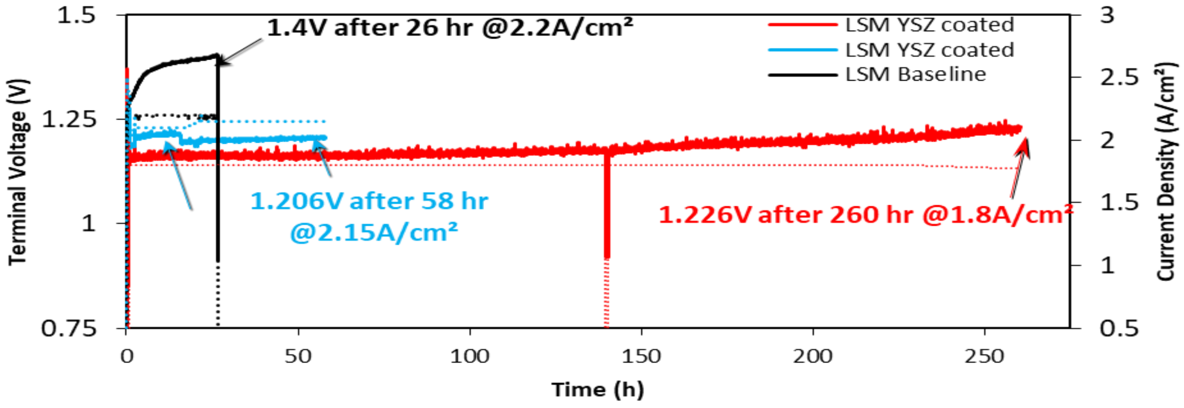
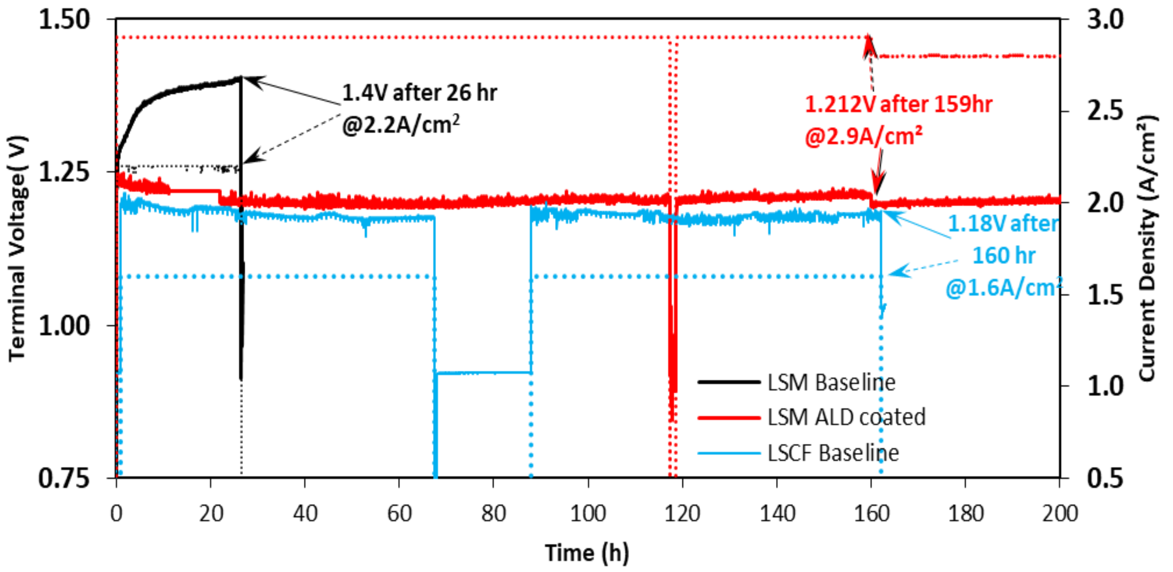
HIGHLIGHTS: ALD COATING POROUS ELECTRODE OF INHERENTLY FUNCTIONAL SOEC

INCREASED HYDROGEN PRODUCTION RATE; INCREASED DURABILITY; REDUCED CAPITAL COST







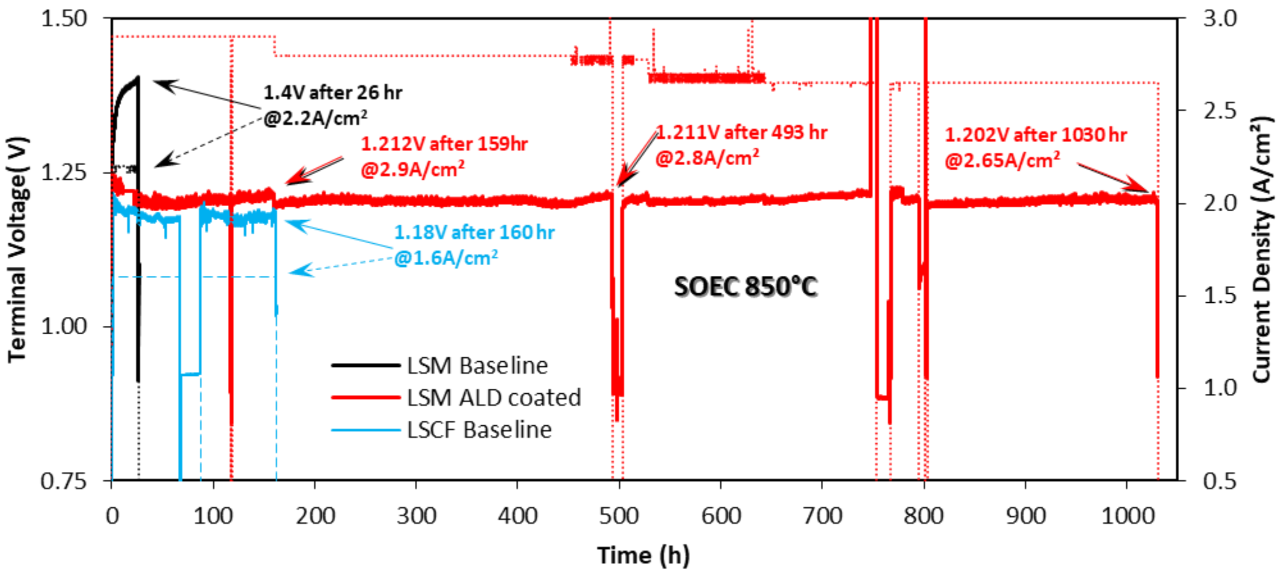


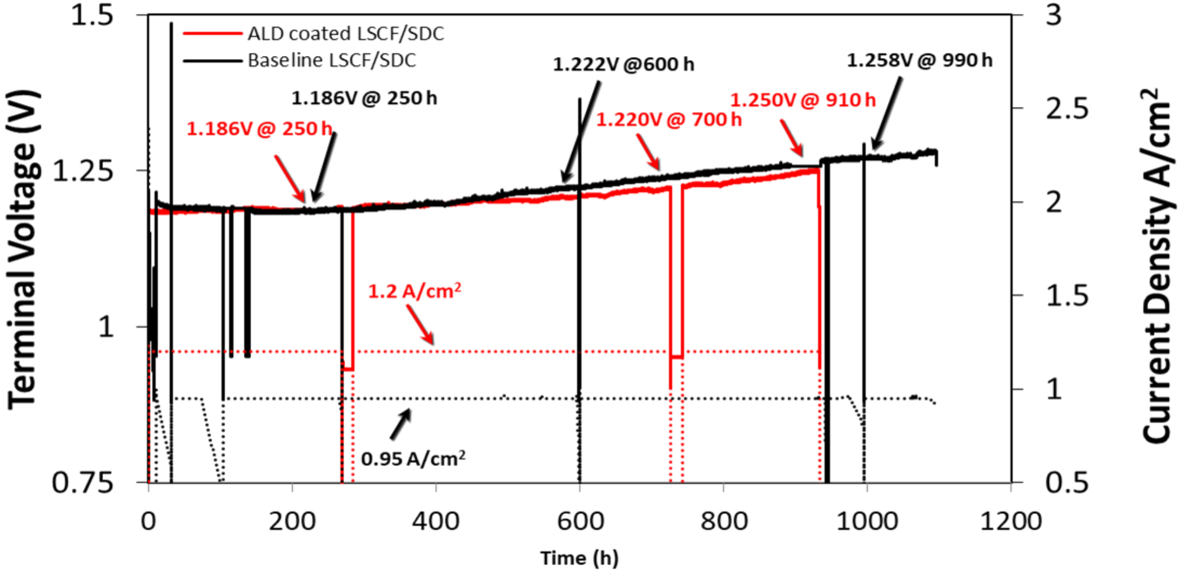
ALD Coating Mitigate Delamination, SOEC with ALD Coated LSM Based Electrode Outperformed SOEC with LSCF.

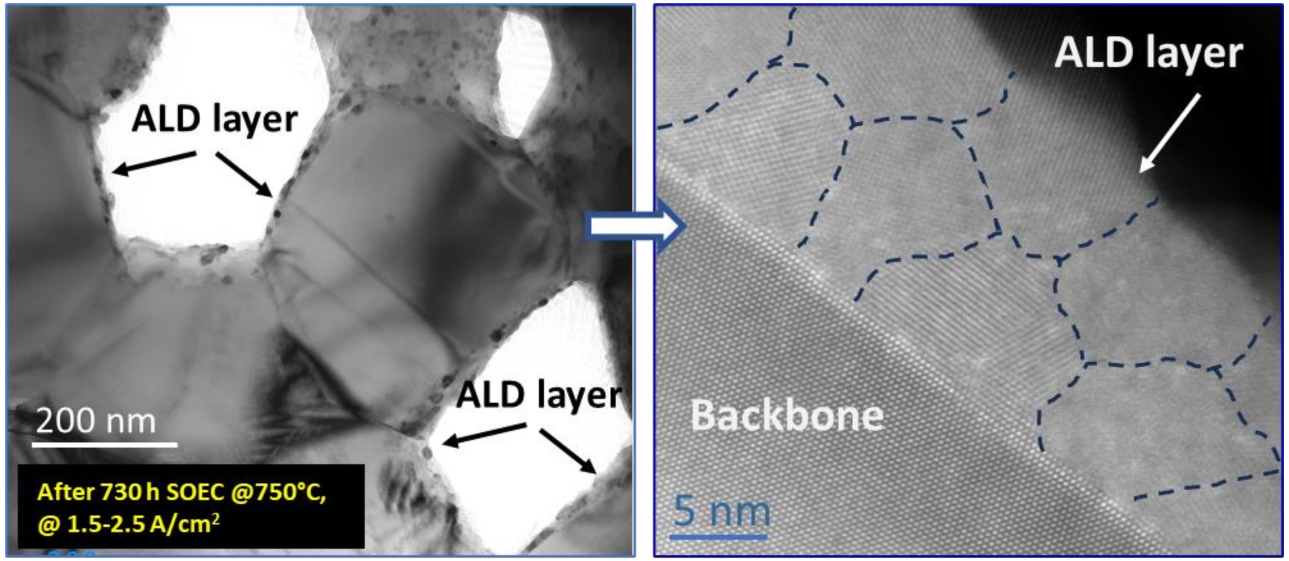
ALD coating porous electrode of commercial SOFC enabled SOEC with high H_2 production rate of >2.5A/cm^2.

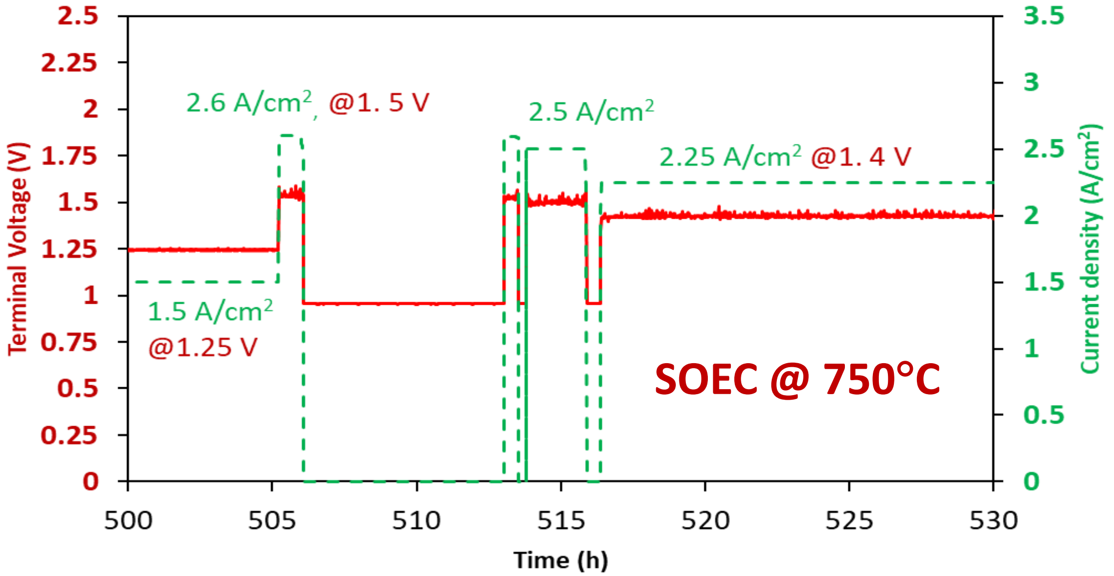
Highlights: ALD coating porous electrode of inherently functional SOEC

Increased hydrogen production rate; Increased durability; Reduced capital cost









ALD Enabled Extraordinary SOEC Stability; Dynamic Operation Under High Current Density With > 1.5 - 2.25 A/cm²

Overview

- Project Background & Challenges: SOEC Performance Requirements & Degradation
- Project Objective, Technical Approach, Success Criteria
- Current Results: ALD Coating Porous Electrode from Commercial Cells

Super Stable and Highly Effective ALD Layer for High-Rate Hydrogen Production

- ALD coating mitigating delamination; SOEC with ALD coated LSM electrode outperforms SOEC with LSCF
- ALD of LSM based electrode: High H_2 production rate @ >2.5A/cm^2 after 1000 h
- ALD of LSCF based electrode: Increase SOEC current density by 25%, superior stability for 1000 h
- ALD coating enabling dynamic operation with high H_2 production rate >2 A/cm^2
- Reduction of SOC system capital cost induced by ALD coating electrode

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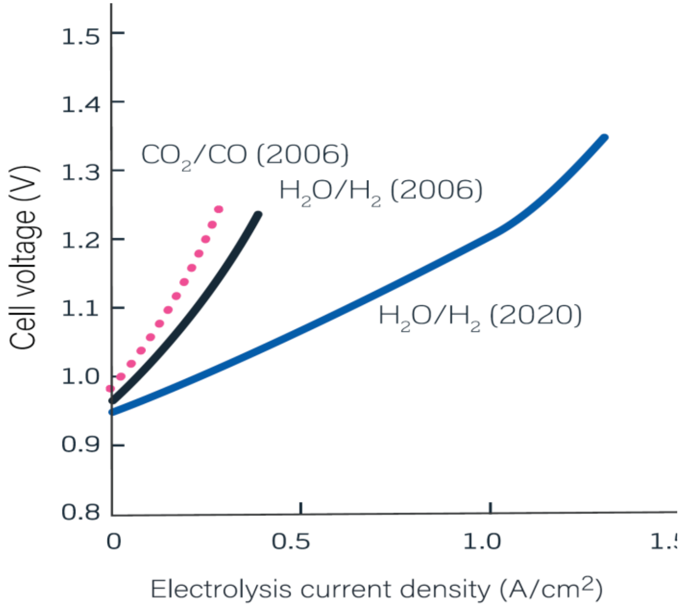
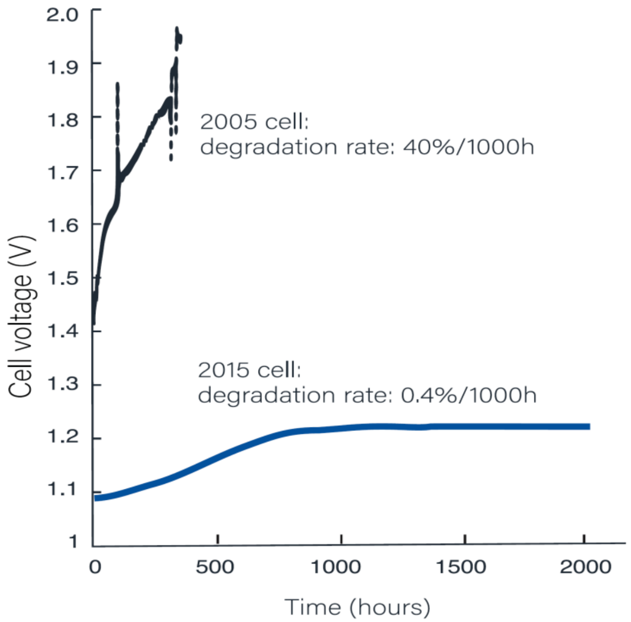
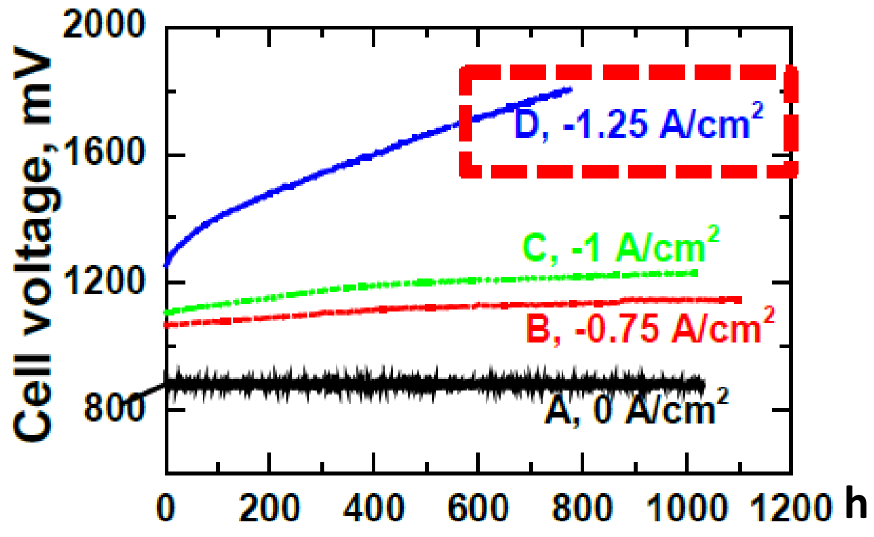
SOEC: Increasing hydrogen productivity >0.75A/cm² being pursued in Europe

Criteria of SOEC Hydrogen Production: Electricity consumption <40 kwh/kg; Production loss rate < 1.9%/1000 h; Current density 1.25 A/cm²; Steam conversation rate > 85%; Availability > 95% reversibility FC efficiency 54%.







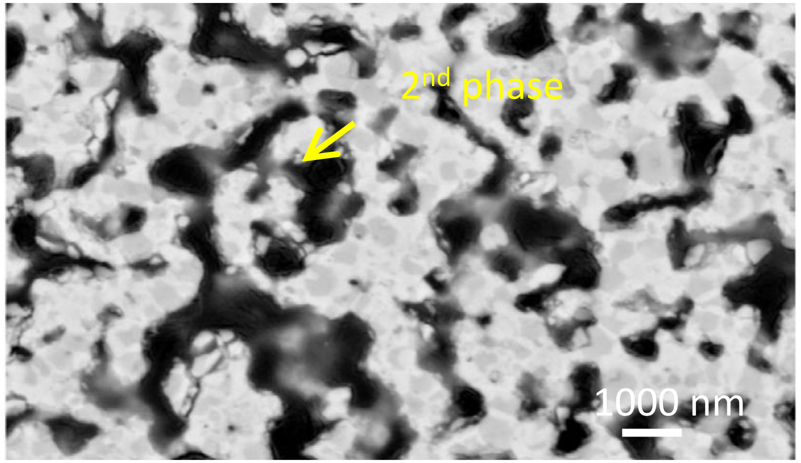
(left) Cell-level current-voltage curves for cells fabricated in 2006 and 2020 with data from at 750°C, (Middle) Durability test of H_2O electrolysis at 1 A/cm² on a cell fabricated in 2005 measured at 850°C and a cell fabricated in 2015 measured at 800°C.

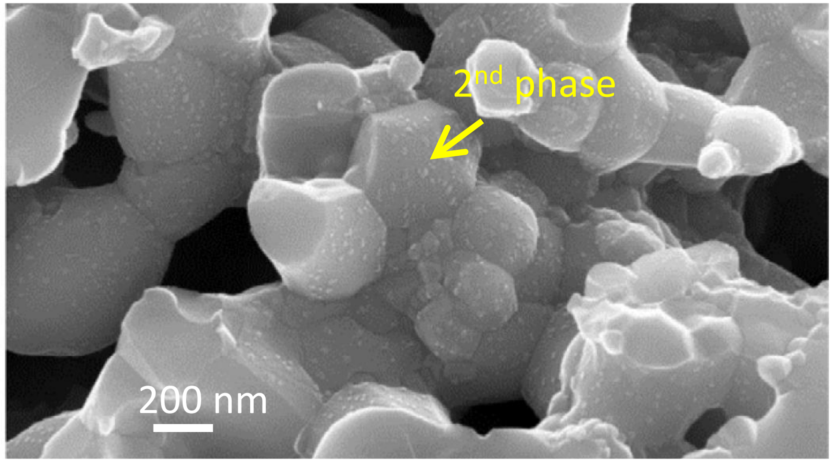
- **Hauch, A., R. Küngas, P. Blennow, A. B. Hansen, J. B. Hansen, B. V. Mathiesen and M. B. Mogensen (2020). "Recent advances in solid oxide cell technology for electrolysis." Science 370 (6513): eaba6118.**
- **Hagen A, Frandsen HL. Recent Highlights of Solid Oxide Fuel Cell and Electrolysis Research 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.**

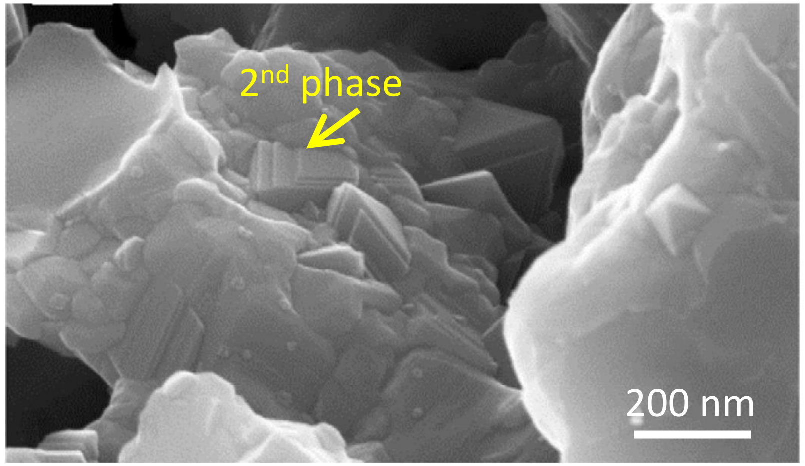
SOEC degradation is severe , during initial operation (first ~ 500 hours), especially at the higher production rate with the current density > 1A/cm² , regardless of SOEC operation temperature and cells.

SOEC presents more severe microstructure degradation than SOFC

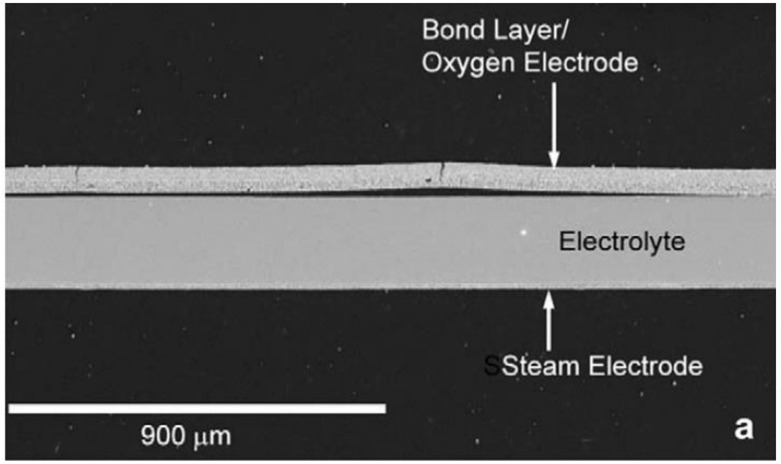
Degradation is dependent on electrolysis operating conditions, rooted in electrolyte, fuel and oxygen electrodes.

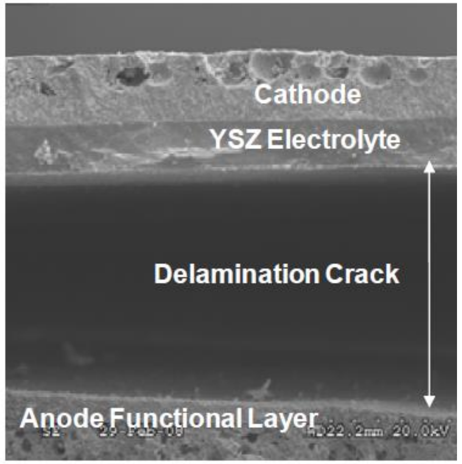






LSCF/SDC oxygen electrode: (1). LSCF decomposition, loss of electrocatalytic activity, Sr surface segregation. (2). Cr vapor contamination from the interconnect, and their reaction with Sr.





LSM/YSZ, severe delamination at the electrolyte and electrode interface; due to lack of ionic conductivity in LSM, could happen ~48 hours of SOEC operation.

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;

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.

Project Objective

Objective of this research is to achieve highly efficient and durable hydrogen production using commercial SOFCs.

Approach: Decrease electrode resistance, increase hydrogen production rate, increase durability, by ALD coating.

Scope of Work:

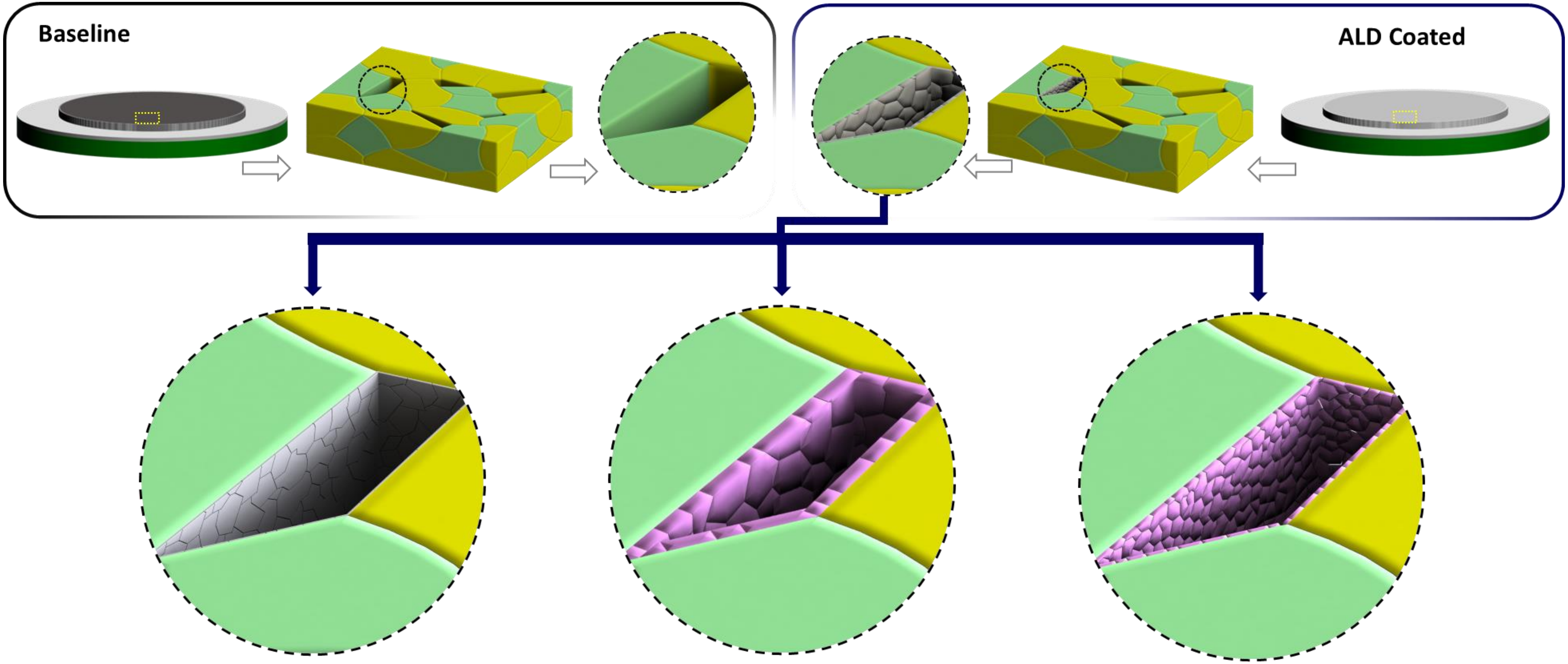
State-of-the-art commercial SOFCs, with excellent performance repeatability provided by different manufacturers.

- **ALD processing:** Commercial ALD system/machines: Computer-controlled automatic switching of the precursor with a one-step processing. The ALD processing will 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 are performed on baseline and ALD coated (internal surface-modified) cells.
- **Nanostructure evaluation:** ALD layer as-deposited nanostructure & evaluation through operation.

Success Criteria. All lab-scale cell SOEC testing will be performed at the industry-relevant operation conditions, (including steam level 50%), Long-term stability tests will be carried out **over 500 hours** of continuous operations. The desired operation current density is over **$0.75 A/cm^2$**.

Very challenging. For instance, baseline cells with LSM/YSZ experience delamination under high current even **after ~50 hours operation**.

ALD Coating & Designing Internal Surfaces of Porous Electrode of
Inherently Functional / Commercial SOC



ALD Coating (no precious metal) Layer Thickness & Chemistry Designed & Tuned Based on Different Electrode.

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- ALD of LSCF based electrode: Increase SOEC current density by 25%, superior stability for 1000 h
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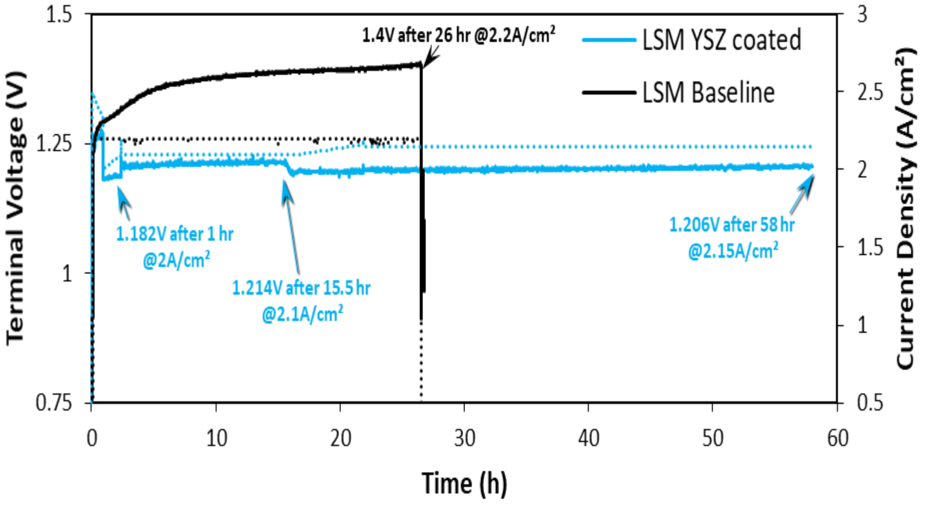
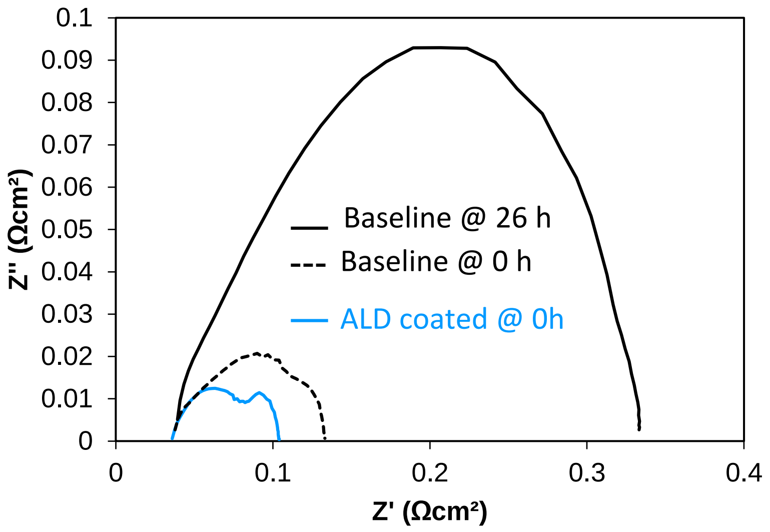
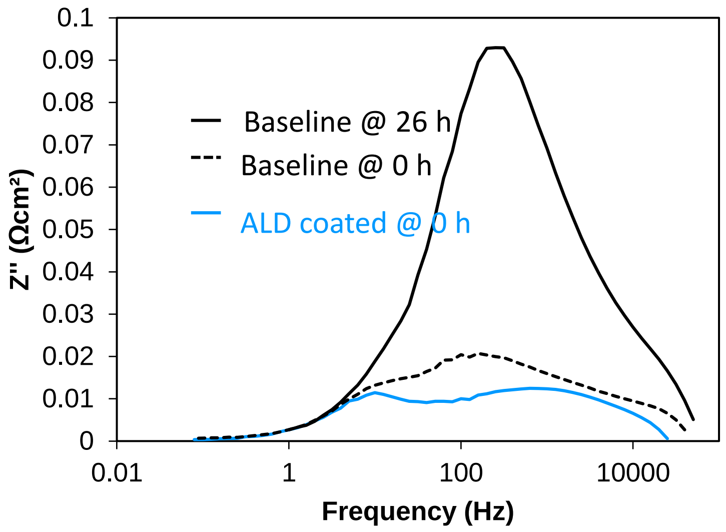
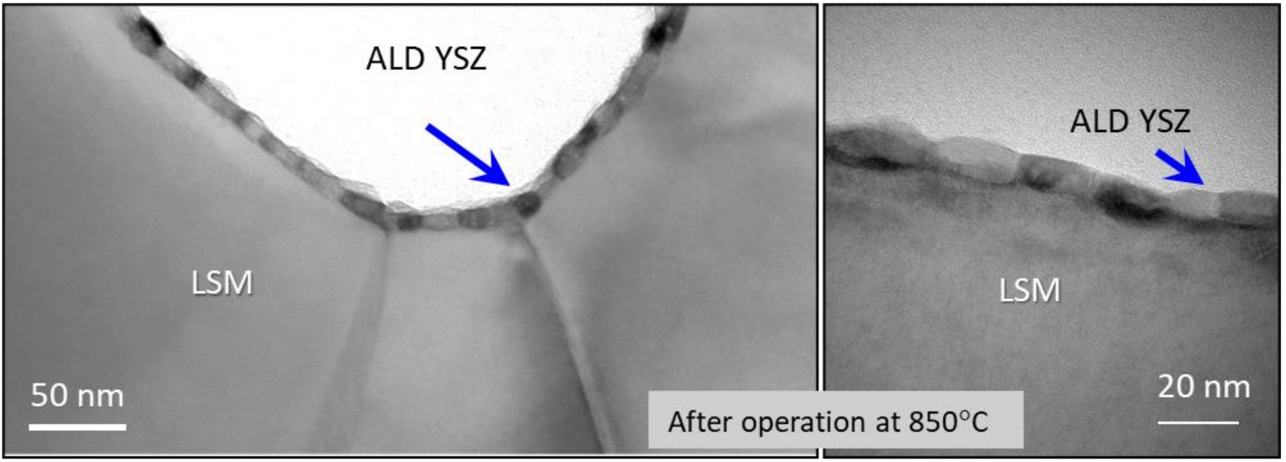
SOEC: ALD Coating YSZ Nanoionics (~ 10 nm thick) on LSM/YSZ









Baseline SOEC delamination after 26 hours @850°C

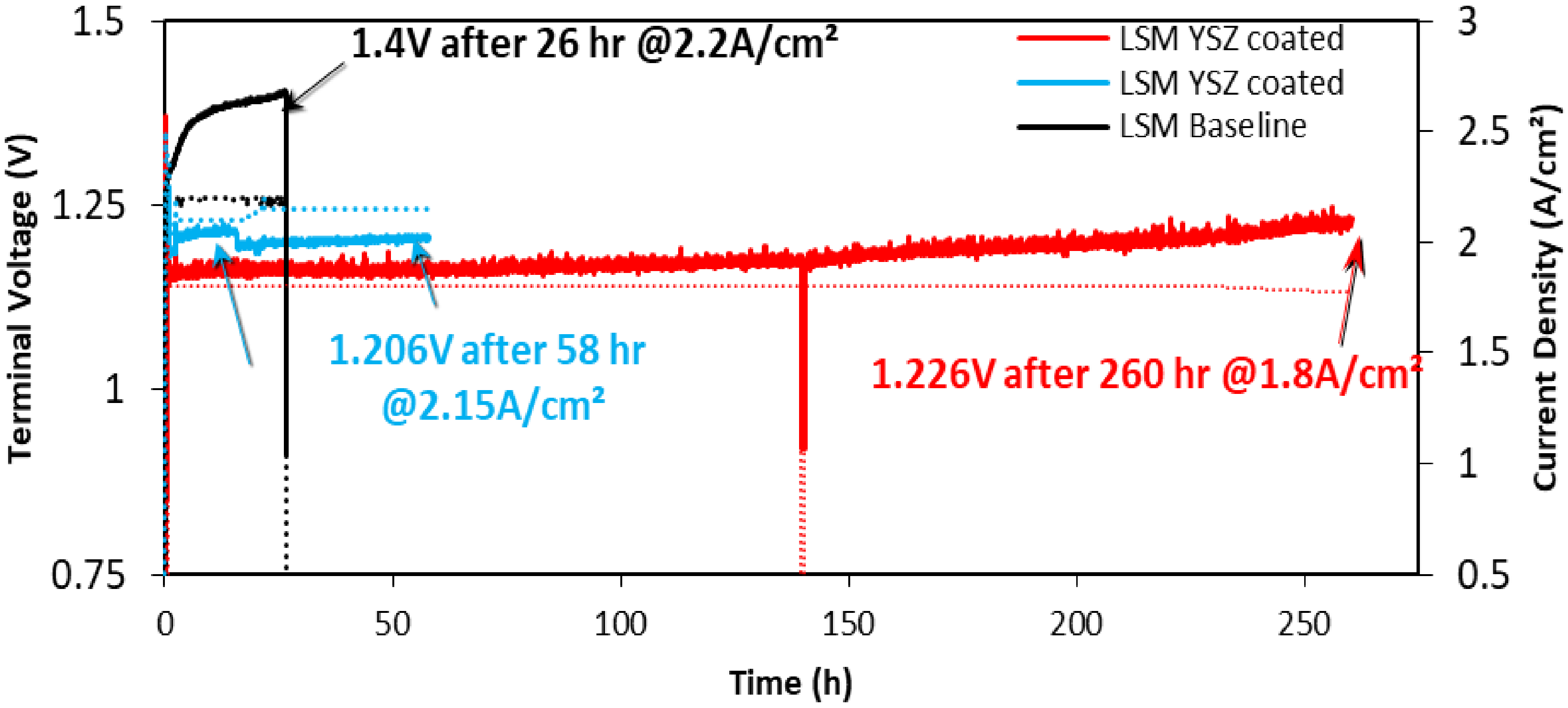
SOEC at 850°C, ALD coating of LSM/YSZ resulted in:

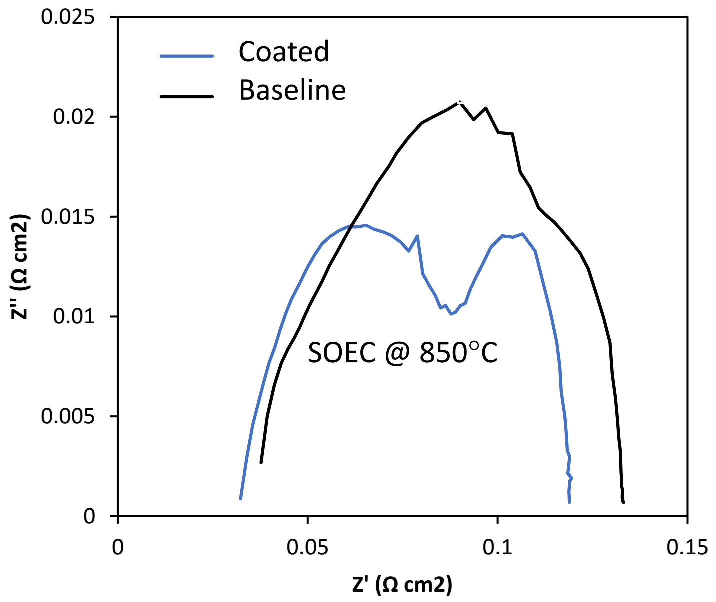
- **Reduced the cell polarization resistance.**
- **Low voltage < 1.2V @ high current of >2A/cm².**
- **ALD nano-YSZ, Exceptional stability. After 850 ° C for 150 hours, ALD nano-YSZ layer remains to be conformal ~ 10 nm in thickness without any agglomeration.**

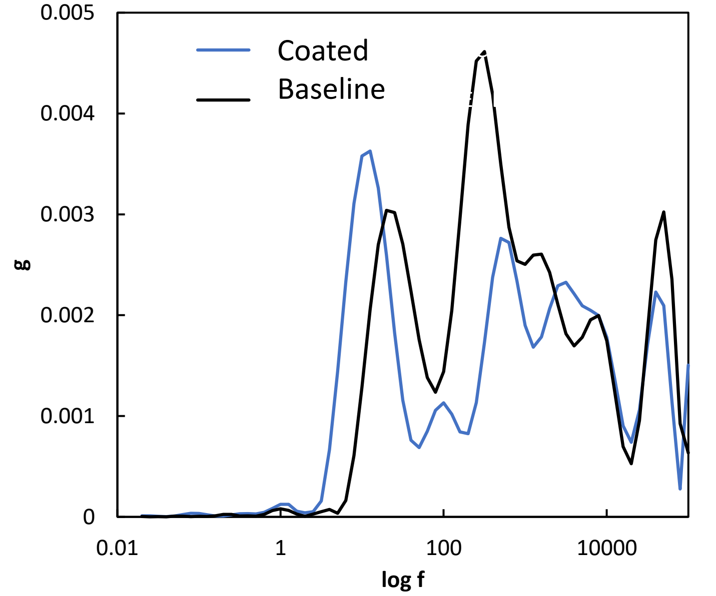
LSM-based SOC: No barrier layer needed, could be operated at higher temperature, lower SOEC voltage.

ALD coating YSZ nanoionics on LSM/YSZ, immediately mitigate the cell delamination, increased the cell durability.

SOEC: ALD Coating YSZ Nanoionics (~ 30 nm thick)





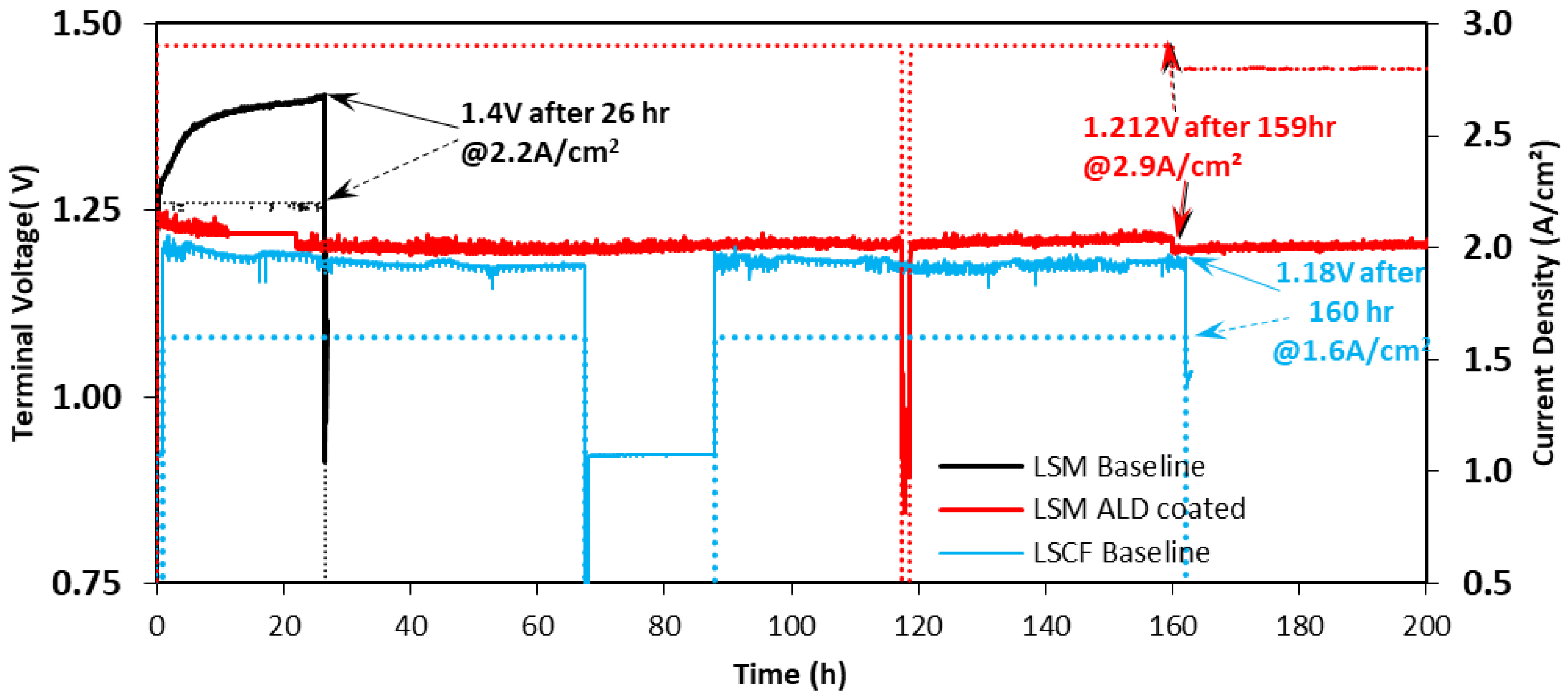


SOEC at 850°C, ALD coating of 30 nm thick YSZ on LSM/YSZ:

- **ALD nano-YSZ coating reduced both the ohmic resistance and polarization resistance, showing the additional ionic pathways induced by ALD coating.**
- **Further lower the SOEC operation voltage, than that of 10 nm YSZ.**
- **High SOEC current of 1.8A/cm², 1.23V, stable after 260 hours, no delamination.**

Conductivity of electrode/cell can be tuned through adjusting the thickness ALD layer applied on air electrode.

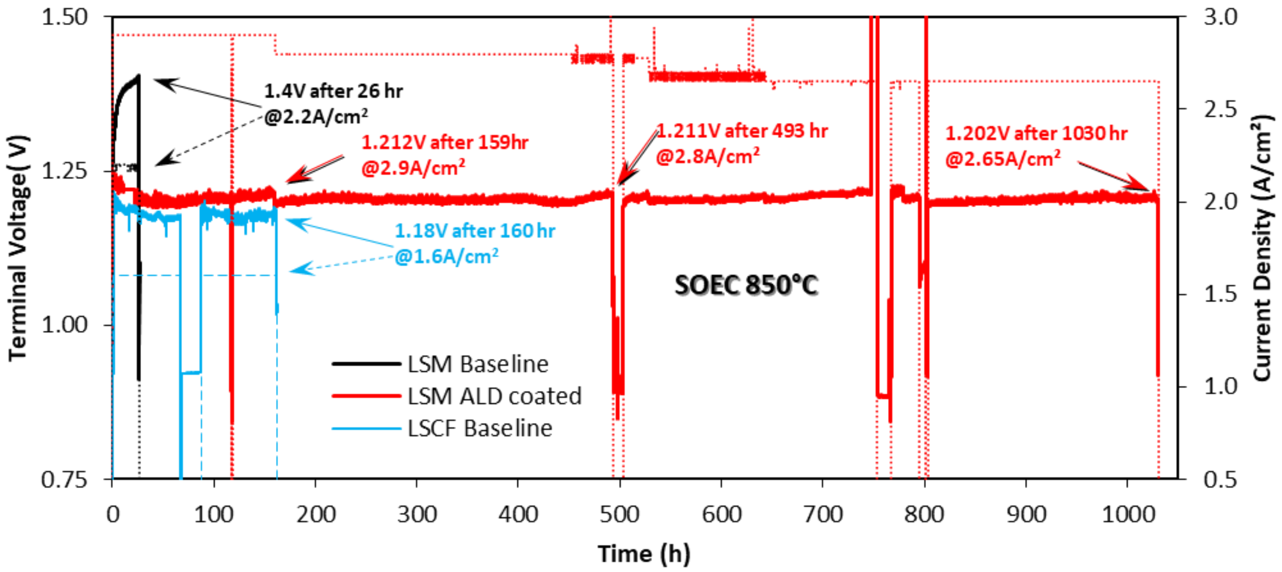
SOEC: ALD Coating mixed conducting electrocatalyst (~ 20 nm thick)



- LSM Baseline rapid deterioration SOEC operation at 2.2 A /cm² fails after 26 h.
- LSCF baseline SOEC: 1.6 A /cm², @1.18V; Stable for 200 hours.
- ALD Coating mixed conducting electrocatalyst (ALD layer of ~ 20 nm in thick) applied on LSM electrode:
  - ✓ ALD coating mitigating the delamination immediately.
  - ✓ ALD coated SOEC: 2.9 A /cm², @1.2V; Stable for 200 hours.
  - ✓ With the similar Voltage of 1.2V, H_2 production rate and current density of SOEC with ALD coated LSM is 2 times of that LSCF baseline.

SOEC with ALD coated LSM electrode outperforms SOEC with LSCF based electrode, at high current density.

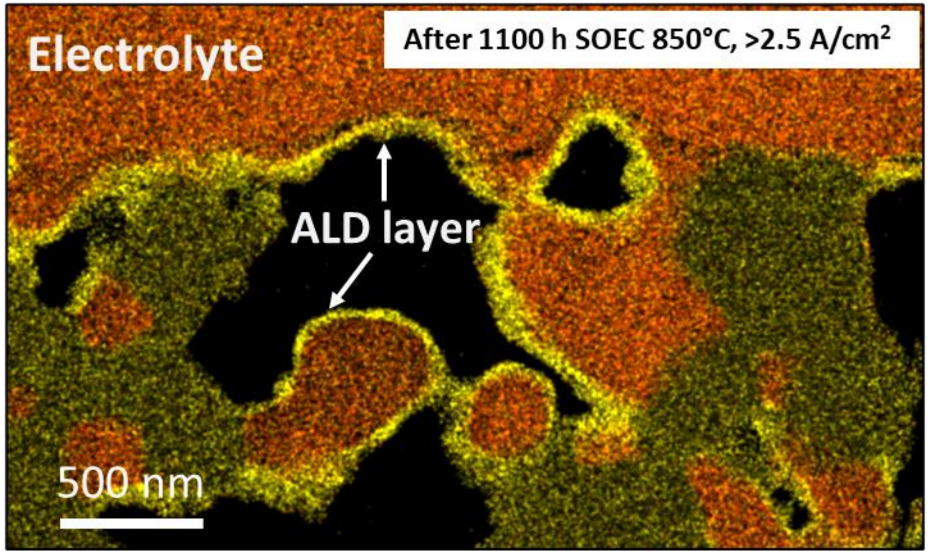
SOEC: ALD Coating mixed conducting electrocatalyst (~ 20 nm thick)

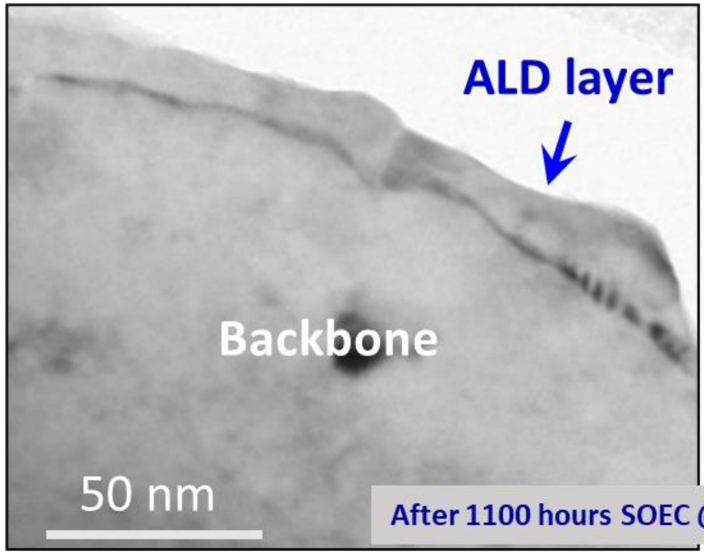


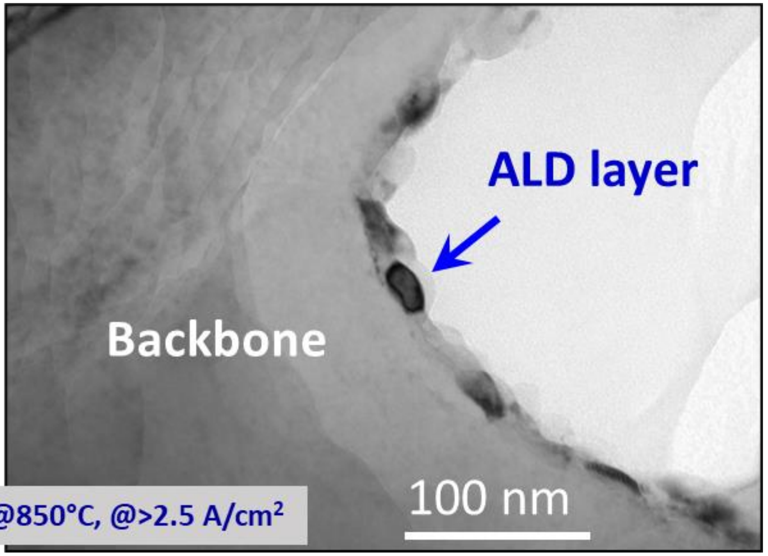
After 1000h, >2.5A/cm², @1.2V, at 850°C;
Highest SOEC performance for commercial cells.

ALD layer, after 850°C SOEC for 1000 h, is:

- **~ 20 nm thick consisting nano-grains.**
- **Having sharp interface with the backbone.**
- **With superior nanostructure stability with no sign of agglomeration.**



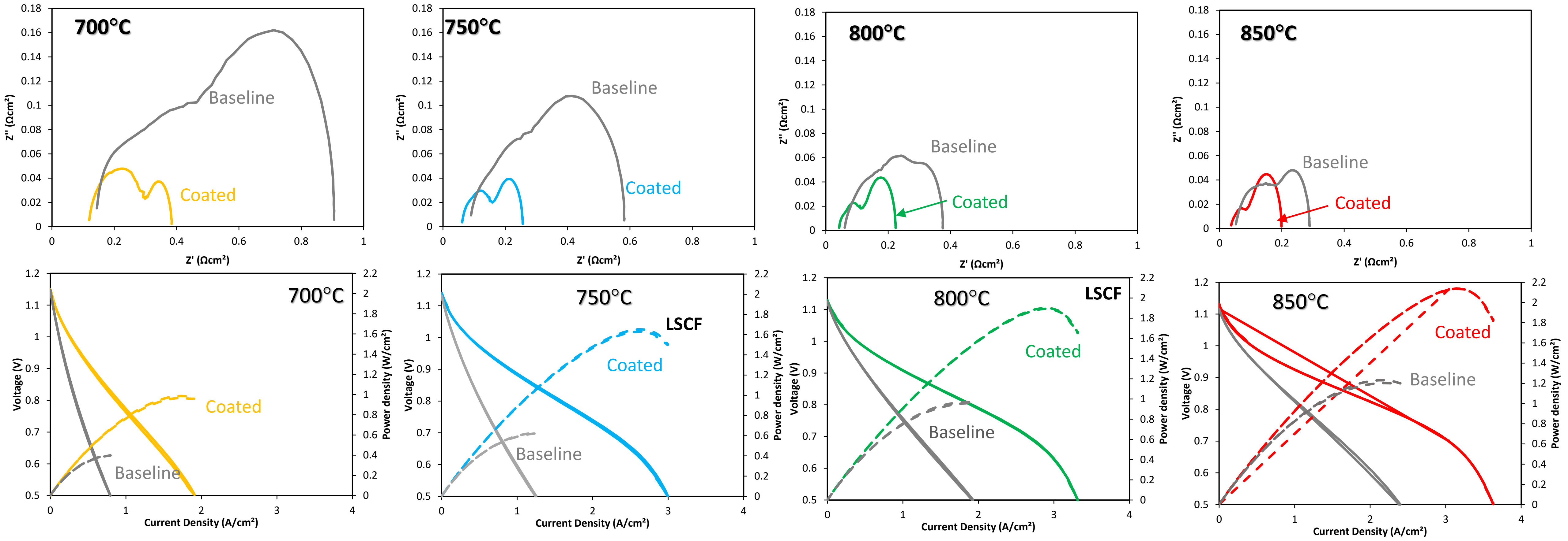




After 1100 hours SOEC @850°C, @>2.5 A/cm²

ALD layer, electrocatalyst oxide, exhibits extraordinary stability after 1000 hours SOEC operation at 850°C.

SOFC: ALD Coating electrode: Reduction of R_s & R_p, Increase Power Density



- **Reduction of R_s and R_p induced by ALD coating.**
- **SOFC peak power density increased to 174%-264%**

Cell	Rs (Ωcm²)	Rt (Ωcm²)	Rp (Ωcm²)	Cell	Rs (Ωcm²)	Rt (Ωcm²)	Rp (Ωcm²)
700°C ALD	0.1161	0.3848	0.2686	700°C Base	0.1356	0.9067	0.7711
750°C ALD	0.0591	0.2561	0.1970	750°C Base	0.0826	0.5832	0.5005
800°C ALD	0.0415	0.2240	0.1825	800°C Base	0.0587	0.3754	0.3167
850°C ALD	0.0351	0.1988	0.1636	850°C Base	0.0499	0.2890	0.2390

Baseline cell, commercial cell		ALD coated cell, commercial cell		
Operation time & temperature	Peak power density, W/cm^2	Operation time & temperature	Peak power density, W/cm^2	%compared with baseline
7 hr 700°C	**0.398**	**0 hr 700°C**	**0.986**	**248**
0 hr 750°C	0.627	0 hr 750°C	1.653	264
0 hr 800°C	0.969	0 hr 800°C	1.901	196
1 hr 850°C	**1.231**	**0 hr 850°C**	**2.139**	**174**

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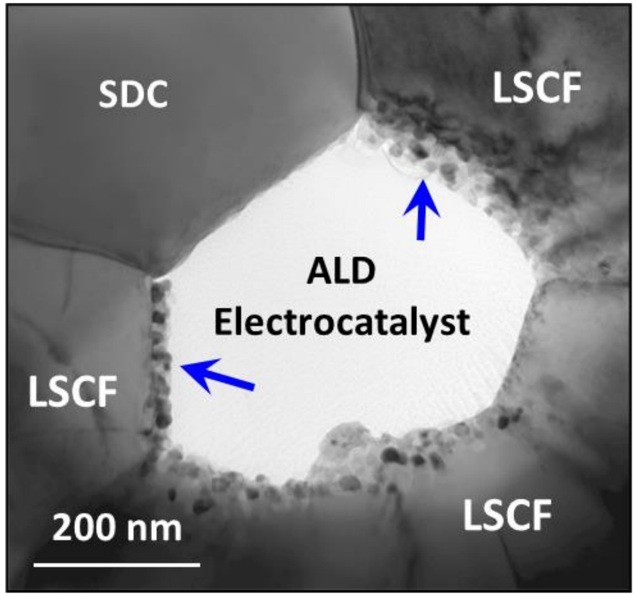
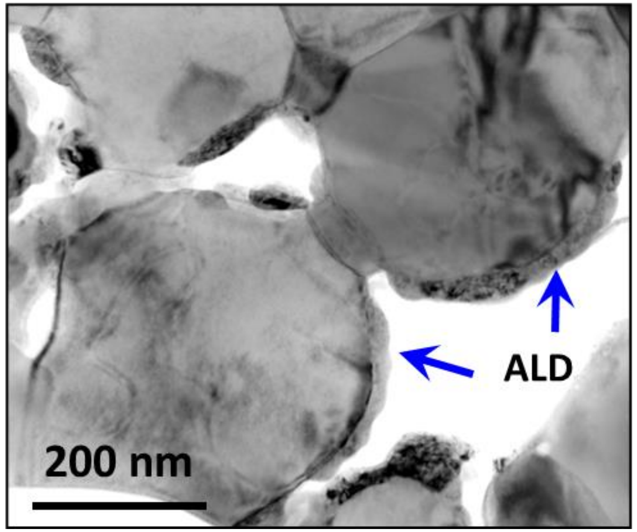
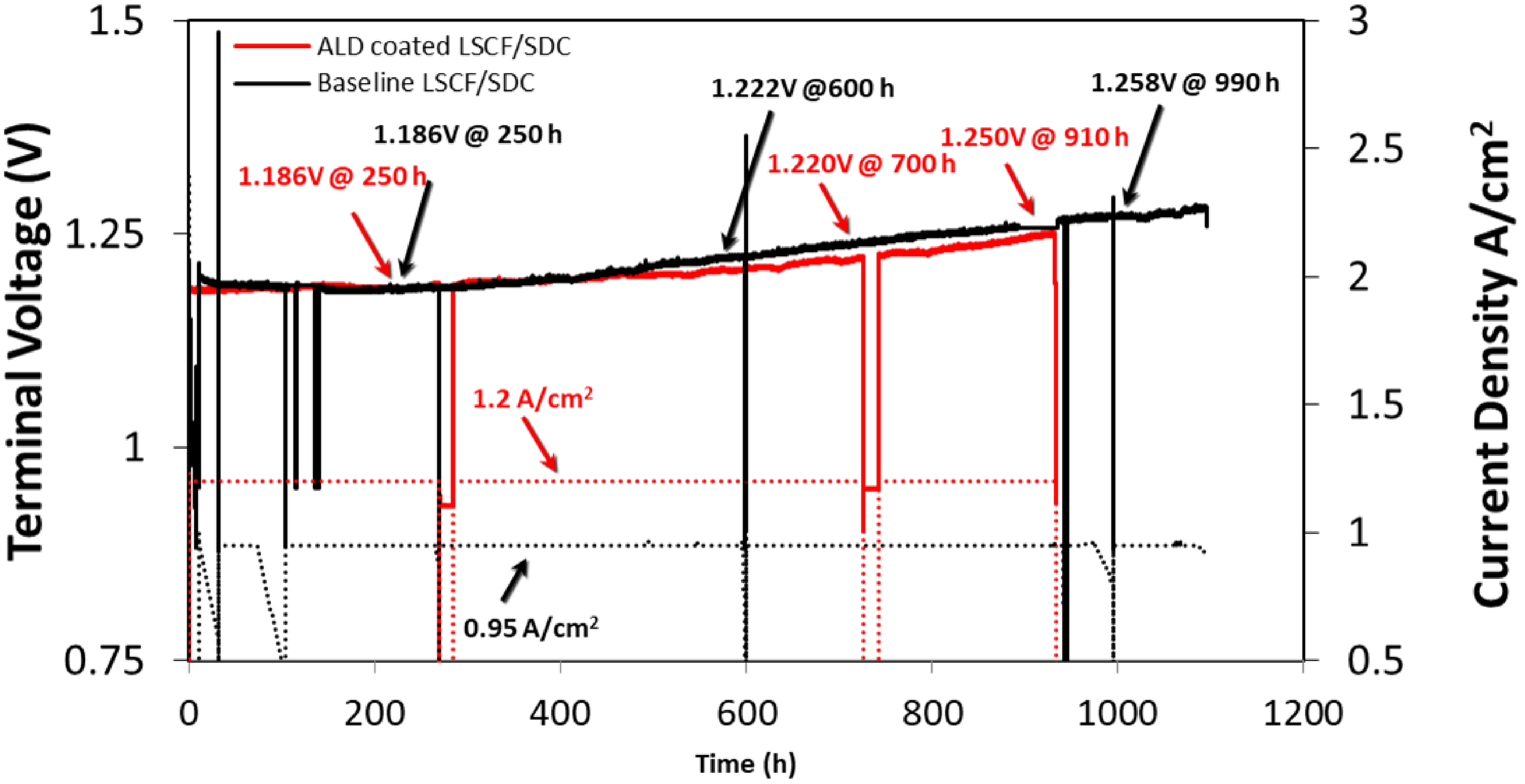
ALD coating LSCF/SDC of SOC: H_2 Production @ 1.2 A/cm^2, @<1.3 V, over 1000h



ALD coating Cr-resistant layer on LSCF to mitigate Sr segregation.

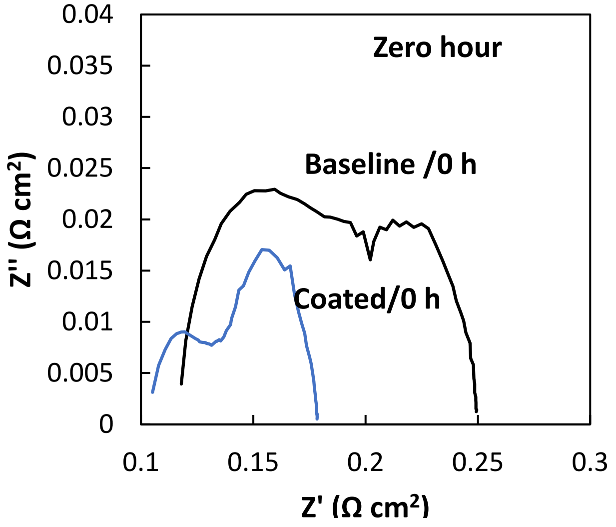


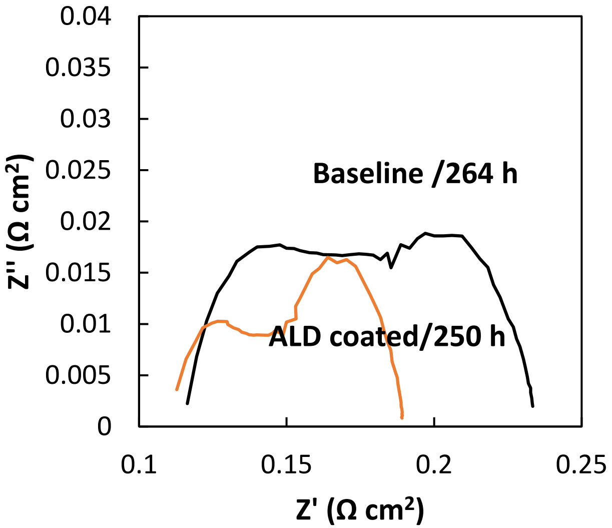


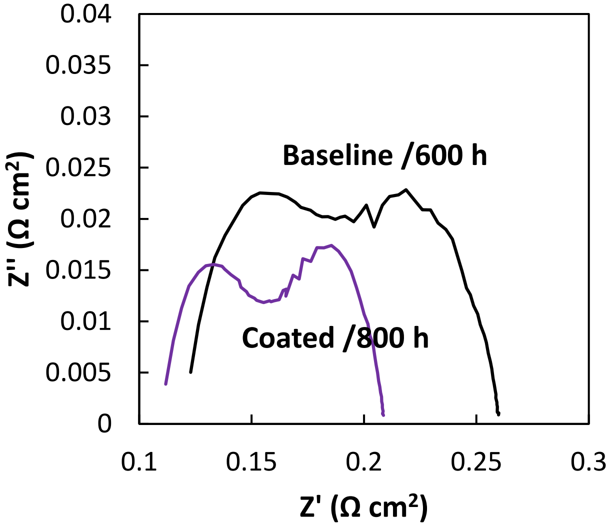
With the similar operation voltage (<1.25 V) during the 1000 hours SOEC @ 750°C;
Baseline cell operated at 0.95 A/cm^2. ALD coated cell operated at 1.2 A/cm^2.
ALD coated cell current density is 125% of the baseline cell.

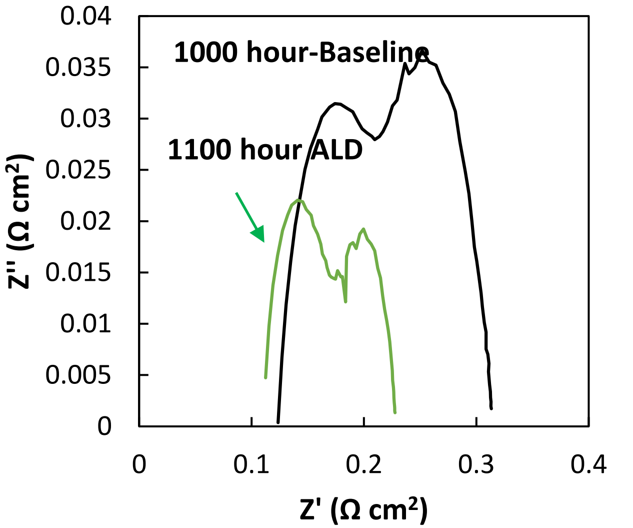
ALD coating LSCF/SDC leads to 25% increase of hydrogen production, commercial SOFC; SOEC @ 750°C.

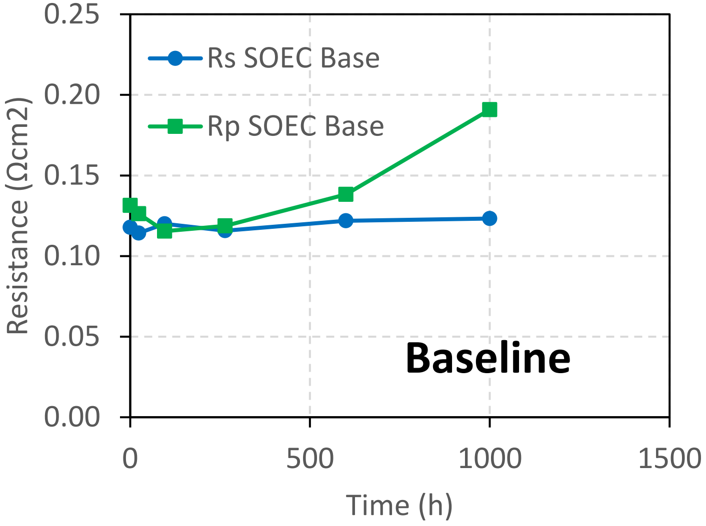
ALD coating LSCF/SDC of SOC: H_2 Production @ 1.2 A/cm², @<1.3 V, over 1000h



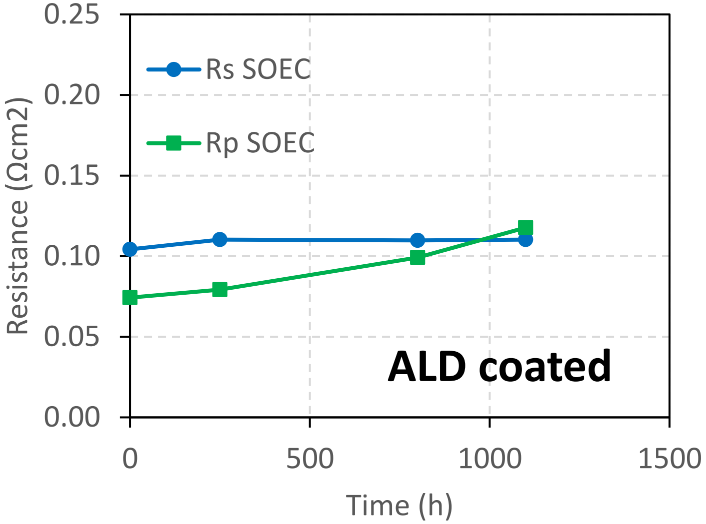








Operation time-baseline	Rs (Ω cm²)	Rp (Ω cm²)
0 h	0.1178	0.1314
264 h	0.1157	0.1187
600 h	0.1219	0.1382
1000 h	0.1233	0.1908

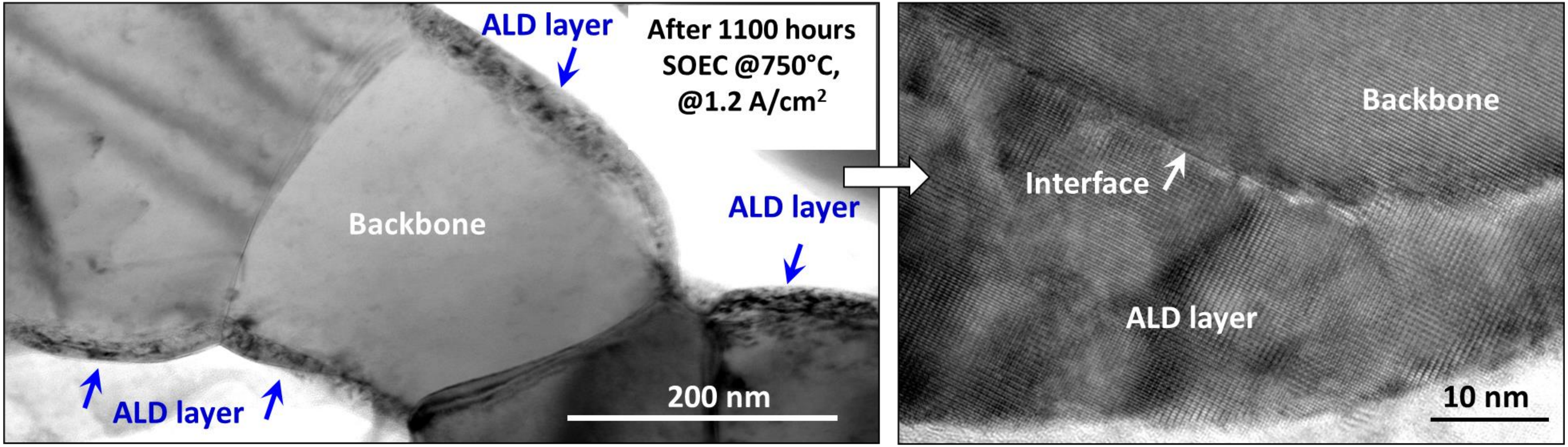


Operation time-ALD coated	Rs $(\Omega\ cm_2)$	Rp $(\Omega\ cm_2)$
0 h	0.1043	0.0742
250 h	0.1103	0.0792
800 h	0.1098	0.0992
1100 h	0.1103	0.1177

After 1100 h @750°C, ALD coated cell was with lower R_s and R_p than that of the baseline operated for 1000 hours.
After 1100 h @750°C, comparing with that of zero hour, ALD coated cell with negligible change in R_s & slight increase in R_p.

ALD coating LSCF/SDC resulted in significant reduction of both ohmic and polarization resistance of entire cell.

ALD coating LSCF/SDC of SOC: H_2 Production @ 1.2 A/cm^2, @<1.3 V, over 1000h



ALD layer is stable after 1000 hours, @750°C.

- **~ 20 nm ALD layer, strongly bonded to the backbone at the atomic scale.**
- **Sharpe interface between the backbone and ALD layer.**
- **Superior nanostructure stability for the first 1000 hours SOEC with no sign of agglomeration.**

Latest results: ALD coating of LSCF of commercial cells: SOEC H_2 production rate of 1.2A/cm^2, 1.16V, 750℃, with 50% steam.

Further improving the SOEC H2 production at @750℃ by designing the ALD layer chemistry & thickness.

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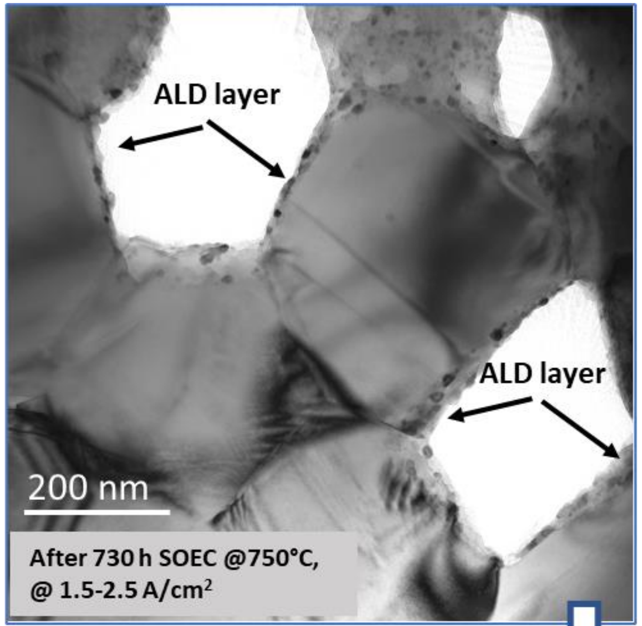
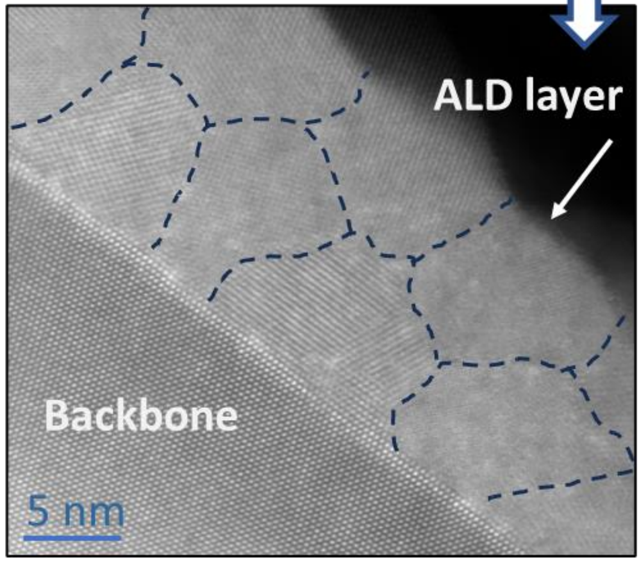
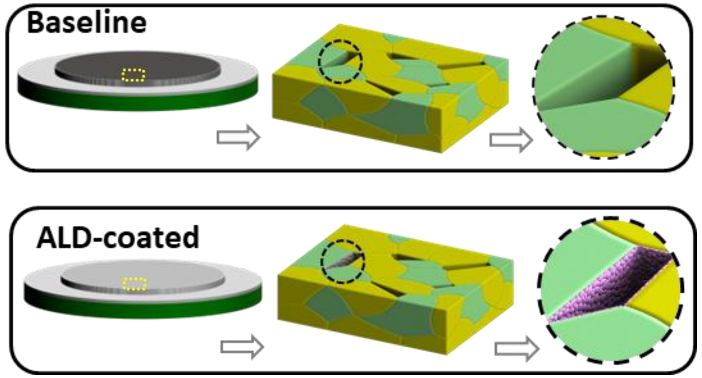
- ALD coating mitigating delamination; SOEC with ALD coated LSM electrode outperforms SOEC with LSCF
- ALD of LSM based electrode: High H_2 production rate @ >2.5A/cm^2 after 1000 h
- ALD of LSCF based electrode: Increase SOEC current density by 25%, superior stability for 1000 h
- **ALD coating enabling dynamic operation with high H_2 production rate >2 A/cm^2**
- Reduction of SOC system capital cost induced by ALD coating electrode

- Summary

ALD coating commercial SOFC enabled Dynamic SOEC Operation at 750° C





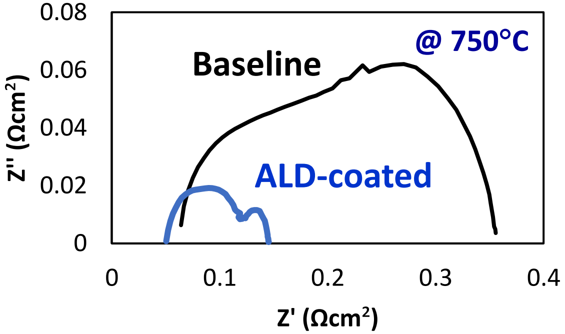


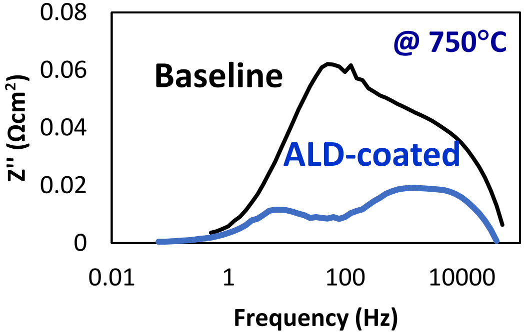
ALD layer: mixed conducting electrocatalysts.

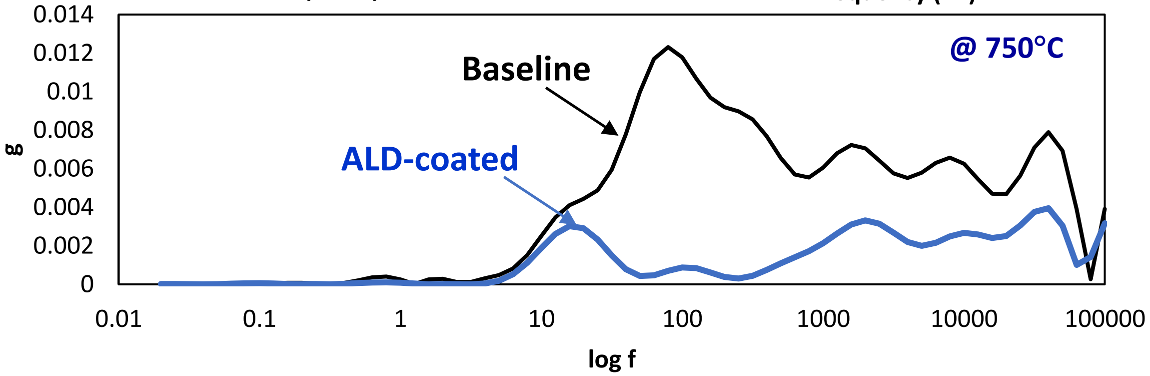
After 730 h SOEC @750°C, @ 1.5-2.5 A/cm²

ALD layer is conformal & uniform:

~10 nm in thickness, ~5 nm in grain size.





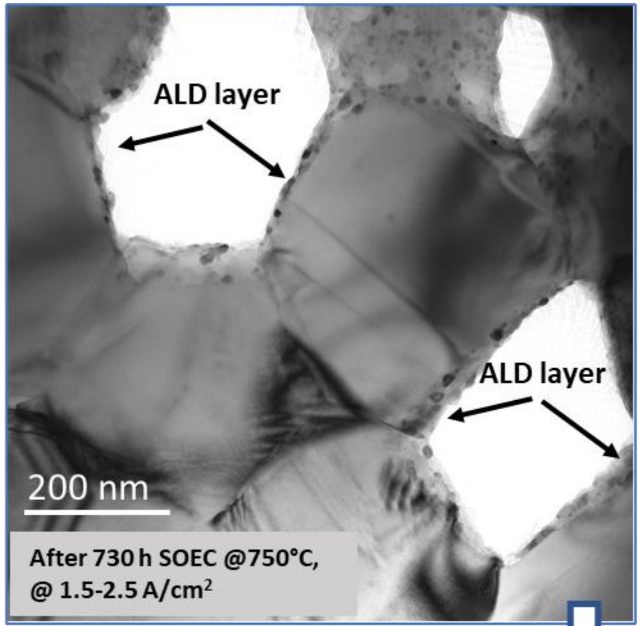


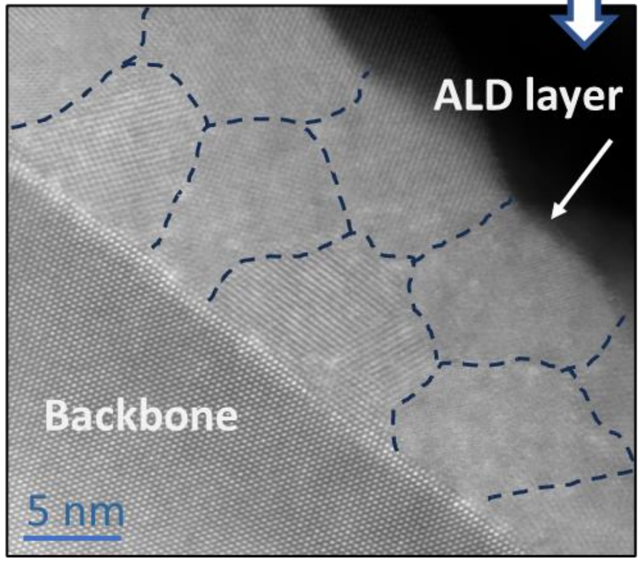
Operation time (SOEC 750 °C)	R_s (Ω cm²)	R_s % reduced vs Baseline	R_t (Ω cm²)	R_t % reduced vs Baseline	R_p (Ω cm²)	R_p % reduced vs Baseline
ALD coated 0 h	0.0508	16 %	0.1454	59 %	0.0946	68 %
Baseline 0 h	0.0606	---	0.3567	---	0.2961	---

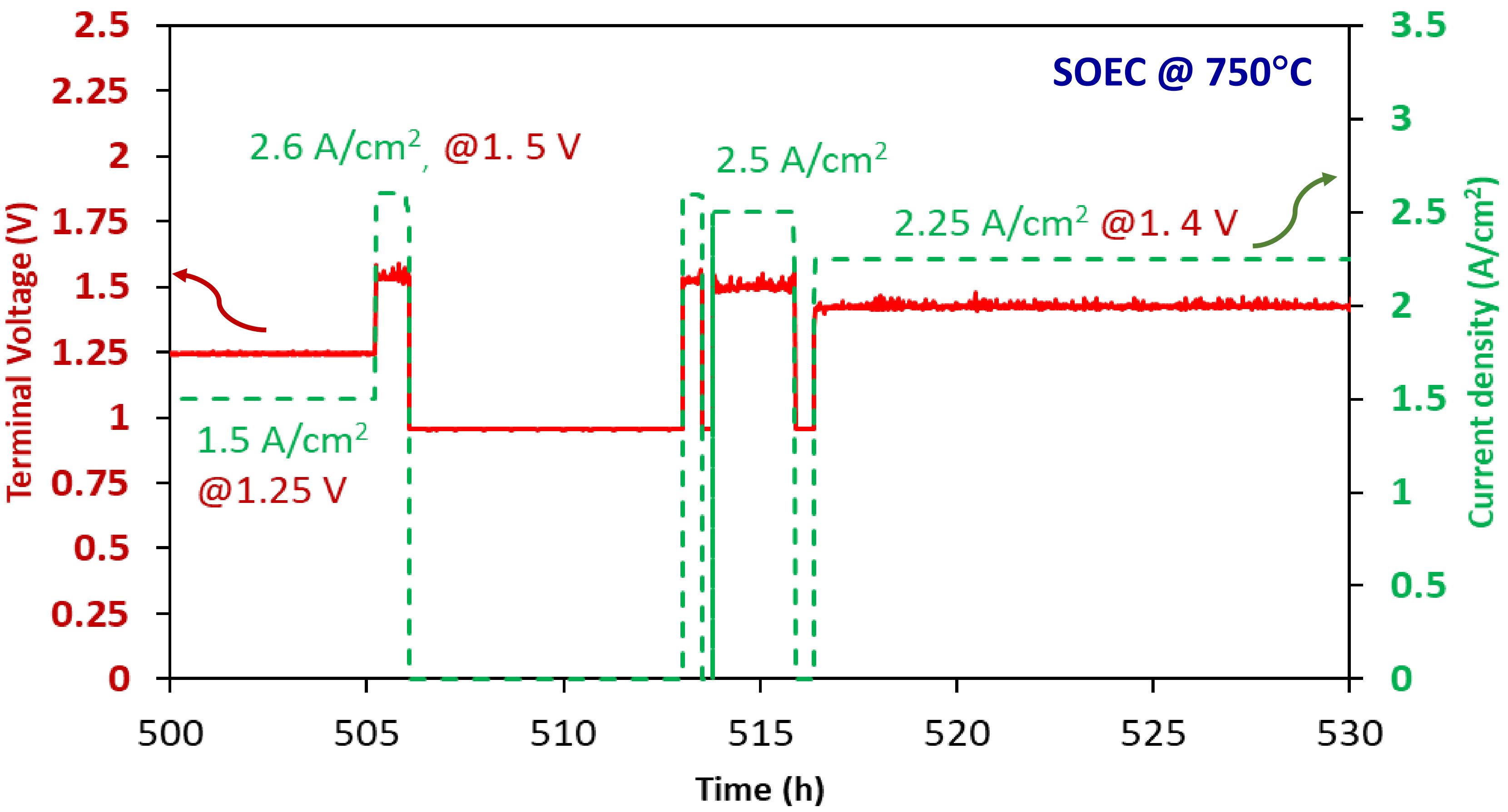
- ALD of electrocatalysts on oxygen electrode reduce ASR of the entire cell by 40%.
- Simultaneously reduction of both ohmic resistance R_s and polarization resistance R_p.
- R_p of ALD coated cell is reduced to that of 30% of the baseline cell.

ALD layer is conformal of the entire internal surface of backbone; Extraordinarily stable after 730 h @750°C.

ALD coating commercial SOFC enabled Dynamic SOEC Operation at 750° C







Conformal ALD coating (10 nm, nano grained) enabled stable dynamic operation at 750° C:

- ✓ high current density of ~1.5 - 2.5 A/cm².
- ✓ 1.5 A /cm² @ 1.25 V
- ✓ 2.25 A/cm² @ 1.4 V

Best performance at 750° C reported for SOEC.

ALD layer is conformal of the entire internal surface of backbone; Extraordinarily stable after 730 h @750°C.

OVERVIEW

- Project Background & Challenges: SOEC Performance Requirements & Degradation
- Project Objective, Technical Approach, Success Criteria
- **Current Results: ALD Coating Porous Electrode from Commercial Cells**

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- **Reduction of SOC system capital cost induced by ALD coating electrode**

- **Summary**

ALD coating porous electrode of inherently functional SOEC: Increased hydrogen Production rate; Increased durability; Reduced capital cost

Commercial and state-of-the-art cells from different manufactures is with **~1 A/cm² at ~1.3 V.**

ALD coating oxygen electrode, commercial cells achieved:

- **~2.5A/cm² & ~ 1.2V** is **2 times** the hydrogen production rate of current state of the art.
- **~2.5A/cm² & ~ 1.2V** could achieve an ~ **two-fold reduction** in stack and Balance of Plant cost & footprint.

If electrolysis current density is **2.5A/cm²**, one 1.5 kW SOFC stack is estimated to generate ~15 kg of hydrogen per day (~5,200 kg per year). If **green hydrogen** market price is ~$5/kg, revenue is on the order of **~$25,000/yr.**

<u>ALD is scale-up ready:</u> Beneq ALD systems for large scale industry processing

- Can accommodate parts up to 1300 × 2400 mm (1.3 m x 2.4 m) in size.
- **Ready for processing multiple SOEC cells & stacks simultaneously.**

Summary

ALD coating of commercial SOFC lead to SOEC with high H_2 production current density of 1.2-3 A/cm^2; @ 1.2V. Exceeding the proposed success criteria of this project; Exceeding the DOE 2026 program goals at cell level.

- **ALD coating increased durability and increased hydrogen production rate.**
  - **<u>ALD coating mitigating electrode delamination</u>**
    - ✓ **ALD layer of nano-YSZ presents extraordinary structural stability after SOEC @850°C.**
    - ✓ **Increased conductivity induced by ALD coating is tunable upon adjusting ALD layer thickness.**
  - **<u>ALD coating mixed conducting metal oxide, discrete nano-grains of 20 nm</u>**
    - ✓ **ALD layer reduce both the polarization resistance R_p & ohmic resistance R_s.**
    - ✓ **ALD coated SOEC showed superior stability for the first 1000 hours.**
    - ✓ **ALD coated SOEC showed a very high current density of >2.5A/cm^2 @ a low voltage of only 1.2V.**

- **ALD coating of LSCF/SDC electrode of commercial cell, with the similar operating voltage during the 1000 hours, achieved current density 125% of the baseline cell. ALD coating LSCF/SDC resulted in >1.2A/cm^2, <1.3V.**

- **Ultra-think ALD coating, with 10 nm in layer thickness enabled dynamic operation with high current density 1.5-2.5A/cm^2 @ 750°C.**

ALD coating porous electrode of functional SOEC: Increased hydrogen production rate; Increased durability; Reduced capital cost

Atomic Layer Deposition Coating Porous Electrode of Commercial SOFC for Their Direct SOEC Application

5 Granted and Pending Patents.

ACKNOWLEDGEMENTS

DOE-SOFC Program

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