

Lessons Learned from SOFC/SOEC Development

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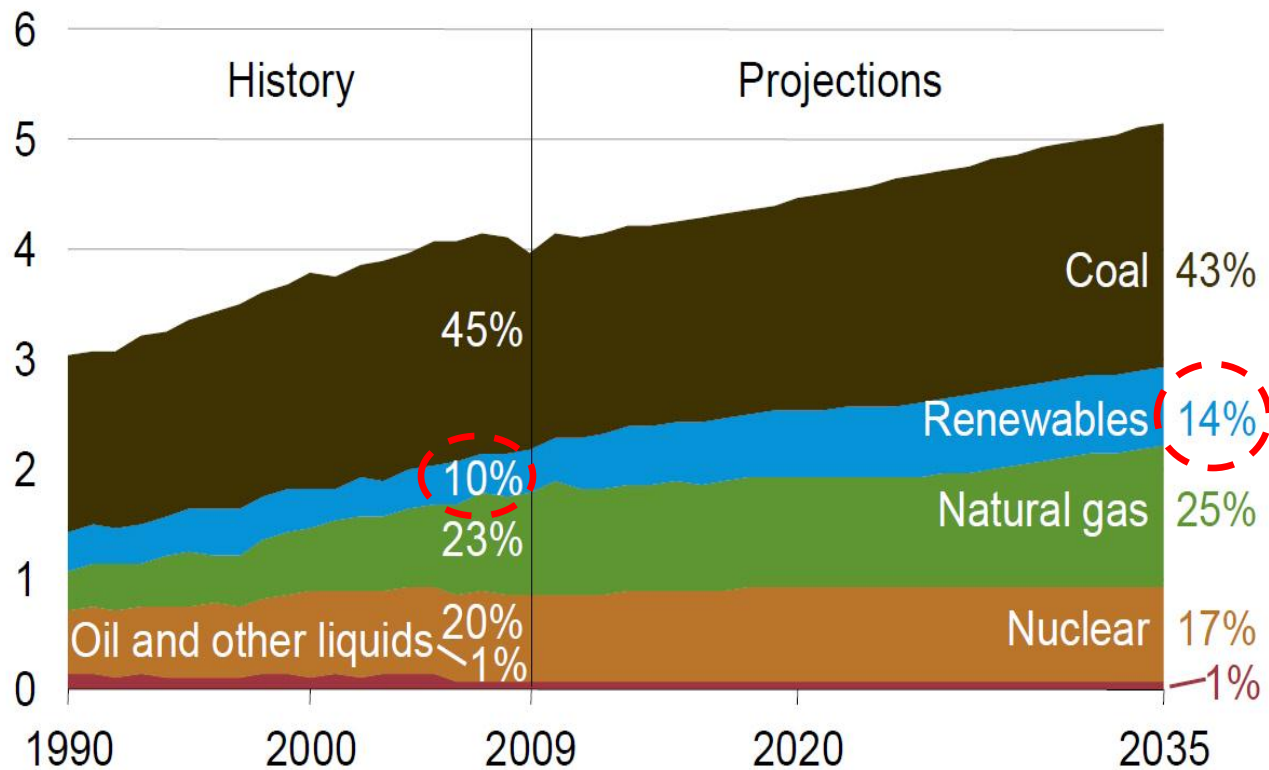
Crystal City, Virginia

April 19, 2011

U.S. Electricity Generation — present & future

Figure 12. Electricity generation by fuel, 1990-2035 *

Net electricity generation (trillion kilowatthours per year)



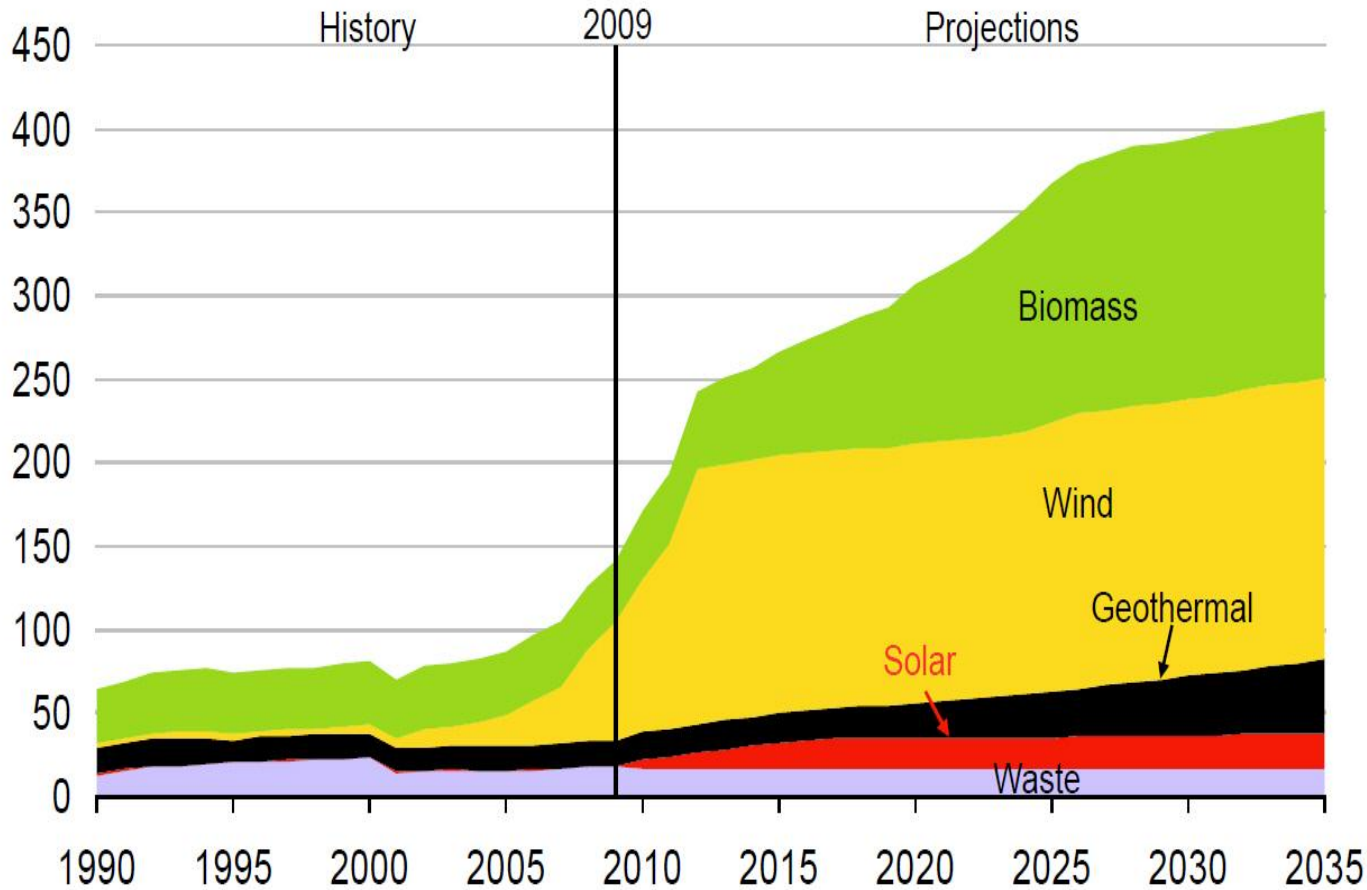
by year 2035:

- 80% of America's electricity from clean energy sources: wind, solar, clean coal, natural gas, nuclear, etc.
- Renewables represent the smallest share among the various sectors, but are significant
- Renewable generation increase from 10% to 14%: 415 billion kWh/yr to 725 billion kWh/yr (>75% increase)

* EIA Annual Energy Outlook AEO2011 Early Release, December 2010

Renewable Generation Breakdown

non-hydropower renewable generation *
billion kilowatthours per year



	2010	2011
	billion kWh	
<u>Solar</u>	4.82	20.81
<u>Geo</u>	16.91	44.47
<u>Wind</u>	91.75	168.91

* R. Newell, Annual Energy Outlook 2011 Reference Case, December 16, 2010

Renewable Energy Storage after Generation

Pros:

- Abundant
- Readily accessible

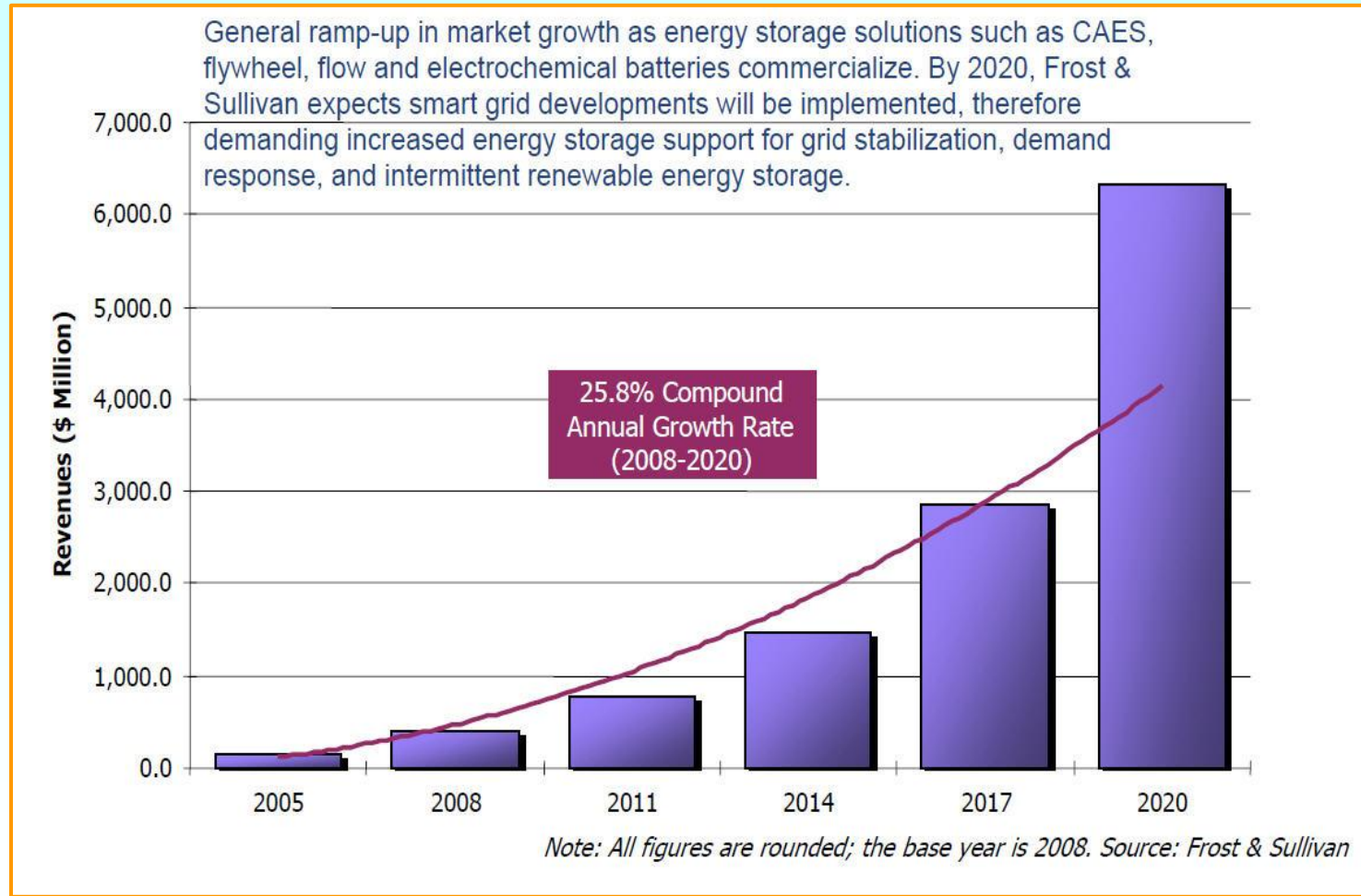
Cons:

- Resources are less controllable
- Intermittency
- Seasonal nature
- Lack of demand-based control (load following and regulation)
- Typically power plants are in remote areas

Solutions:

- Renewable energy storage and grid stabilization
 - electrical energy (e^-),
 - chemical energy (H_2 or synthetic fuels)
 - mechanical/potential energy (CAES, hydroelectric)

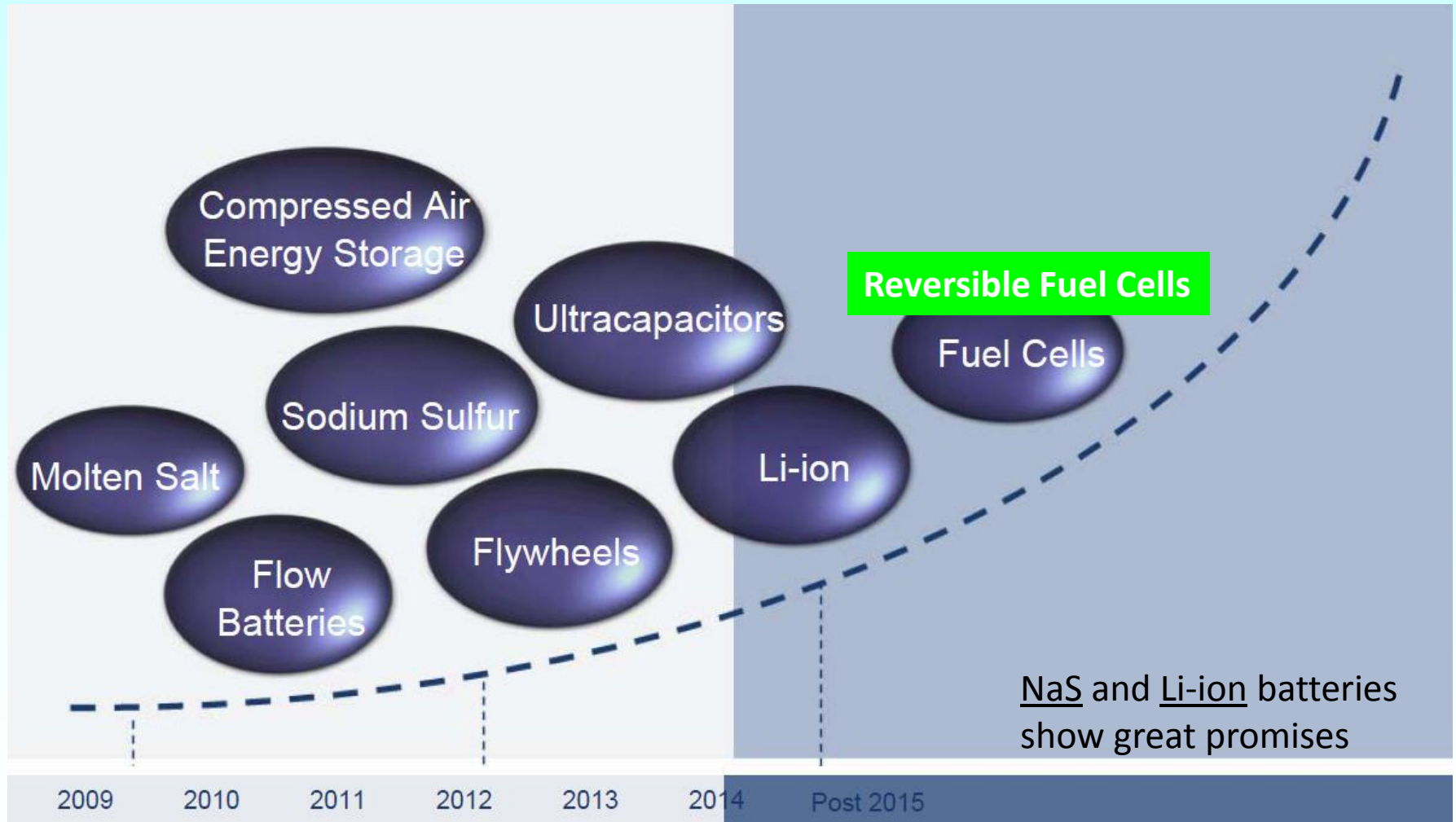
Grid Energy Storage Market in North America*



* "North American Grid Energy Storage Market", Frost & Sullivan Report, July 2009

Energy Storage Technologies

European Emerging Technology Roadmap 2009-2020*



* "Renewable Energy Storage – European Market Analysis", Frost & Sullivan Report, December 2009

What Can Reversible Fuel Cells Do?

To store excess electricity/energy and release it during times of heavy needs with its high quality power

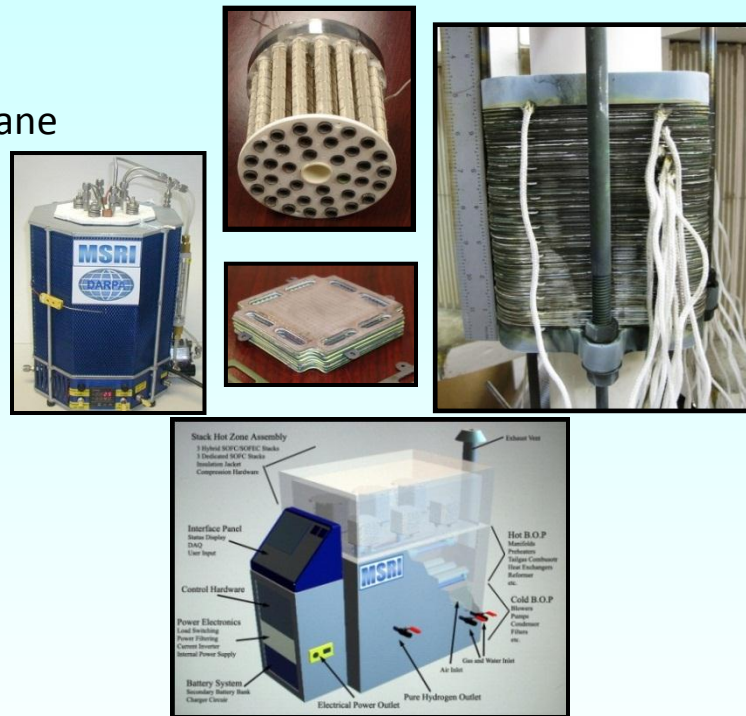
Pros compared to electrochemical batteries	Cons compared to electrochemical batteries
➤ Extensive R&D efforts on FC development, which can be leveraged to electrolyzers development	➤ Early commercialization technology
➤ Wider operating temperatures (80°C for PEM to 800°C for SOFC) than Li-ion batteries	➤ High cost per kWh
➤ Higher energy density than Li-ion (1000 Wh/kg vs. 160 Wh/kg)	➤ Low power density, ➤ Relatively low round-trip efficiency
➤ Modular-based technology, readily systems scale-up	➤ Lack of large scale (grid-scale) systems or field-test results, applicable to distributed/decentralized storage applications (near term)
➤ No moving parts, quiet operation, minimum maintenance	
➤ Good for power stabilization (improving power quality)	➤ Long response time
➤ Operation is independent of capacity (unlike batteries, capacities are limited by the amount of active electrode materials)	➤ Hydrogen fuel storage, or synthetic fuel production/storage
➤ No self-discharge issue, long shelf-life ➤ Charge (electrolyzer mode) /discharge (fuel cell mode) cycles degradation rate probably is less temperature dependent on operating temperatures than batteries	➤ Lack of supporting data on the charge/discharge cycle degradation rate ➤ High long-term degradation rate

MSRI's Fuel Cell / Electrolyzer R&D Activities

MSRI has expertise in materials and electrochemical technologies for power generation and energy storage applications, including fuel cells/electrolyzers, rechargeable batteries and thermoelectric converters.

Fuel Cells

- SOFC based-on oxygen ion conducting electrolyte membrane
- SOFC based-on high temperature proton conducting electrolyte membrane
- PEMFC
- SOFC cells from 1 to 400 cm² active area
- Planar SOFC stacks 75 W to 2 kW
- Tubular SOFC bundles up to 300 W



Hydrogen Production

- High temperature steam electrolysis
- Advanced fuel-assisted electrolysis
- H₂ production direct from coal and petcoke

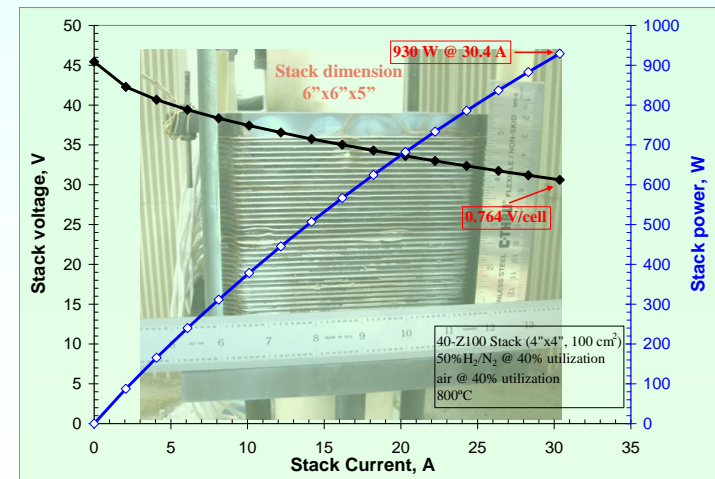
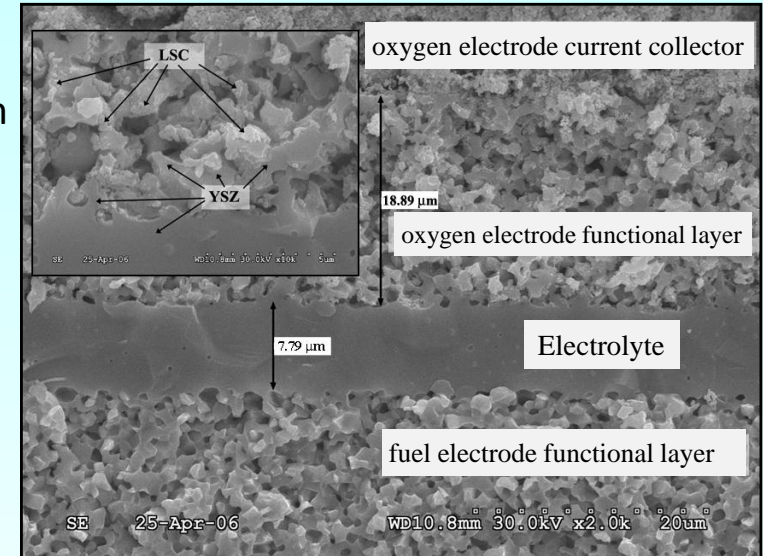


Solid Oxide Electrochemical Technologies

Fuel-electrode Supported Solid-Oxide Devices: SOFC & SOEC

specializing in cell/stack materials R&D

1. Nickel+zirconia-based fuel-electrode supports: $\sim 700\ \mu\text{m}$
 - mechanical strength; redox-tolerance; low concentration polarization losses; costs
2. Graded, fuel-electrode functional layer: $\sim 15\ \mu\text{m}$
 - sulfur-tolerance; redox-tolerance
3. Thin film electrolyte: $\sim 8\ \mu\text{m}$
 - enhanced conductivity
4. Graded, O_2 -electrode functional layers: $\sim 20\ \mu\text{m}$
 - Low sheet resistance; extended three phase boundary length; improved bonding
5. O_2 -electrode current collector layer: $\sim 50\ \mu\text{m}$
 - low ohmic/contact resistance
6. Metallic interconnect
 - low oxidation rate; low cost
7. Sealing gasket
 - Compliant/rigid seals; thermal expansion match; easy fabrication/assembly



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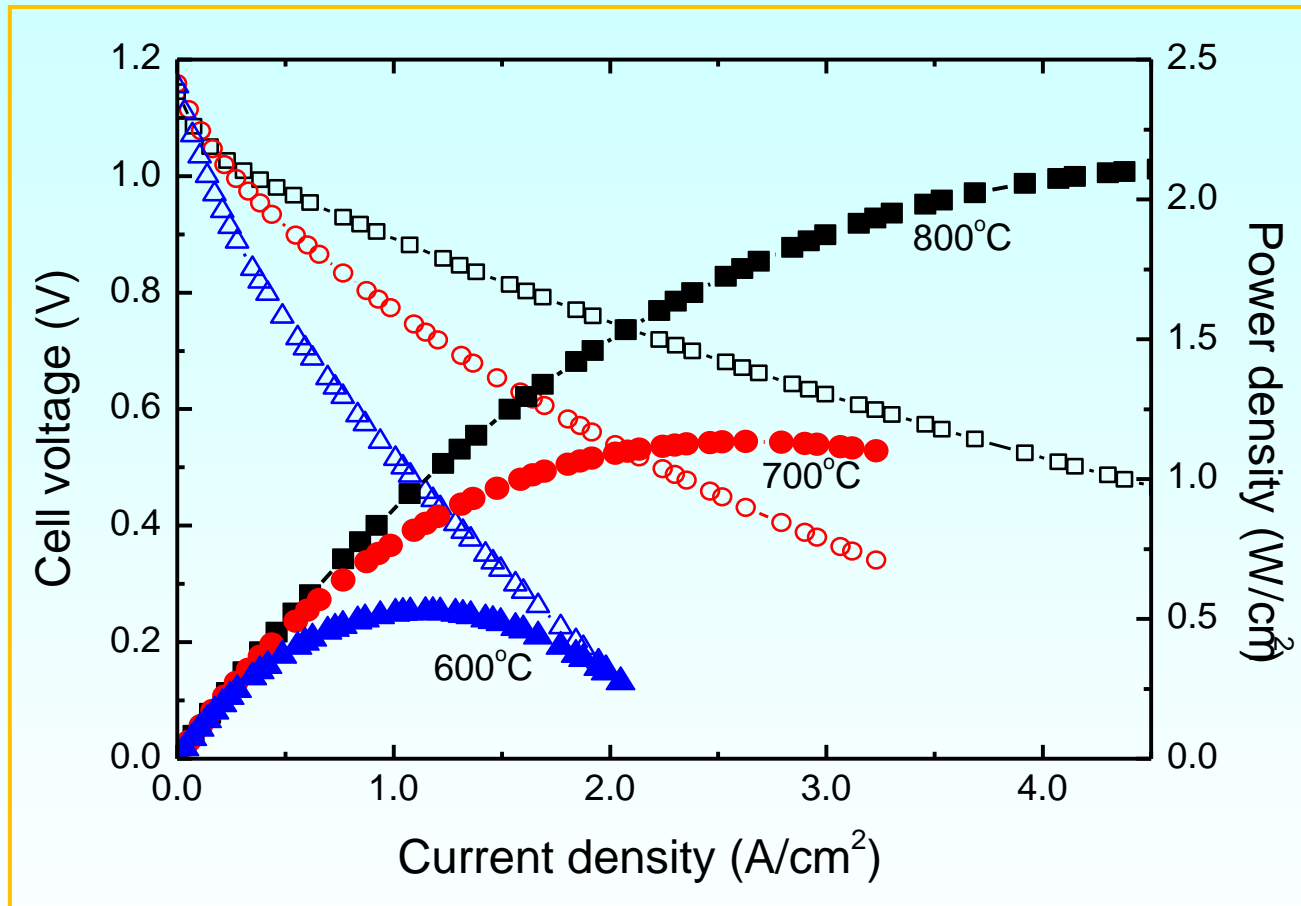
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SOFC Electrode Materials Development

Single Button-sized Cell Performance

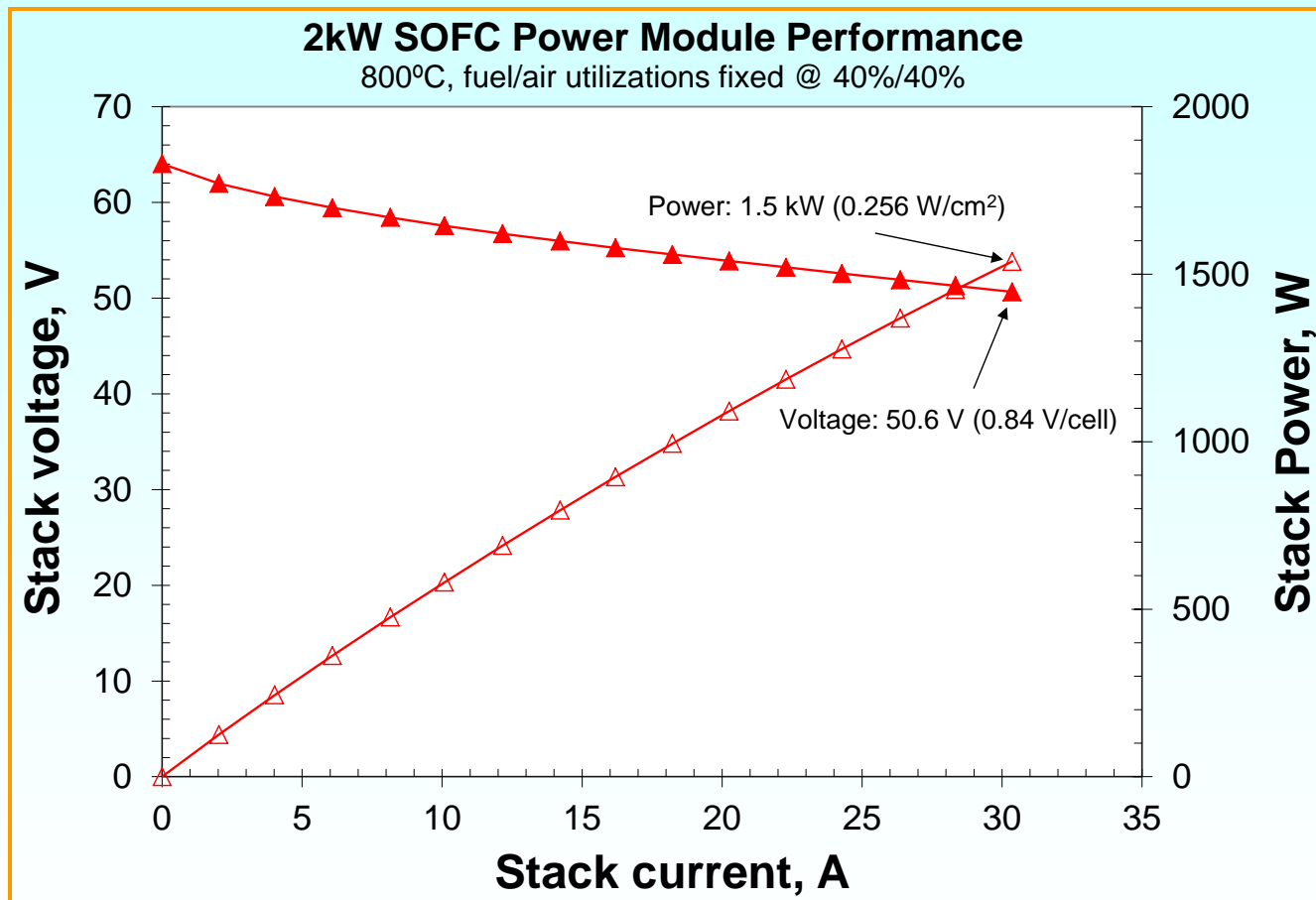
- Power density as high as 2.1 W/cm² on button-size cells
- > 5,000 hours with minimal degradation



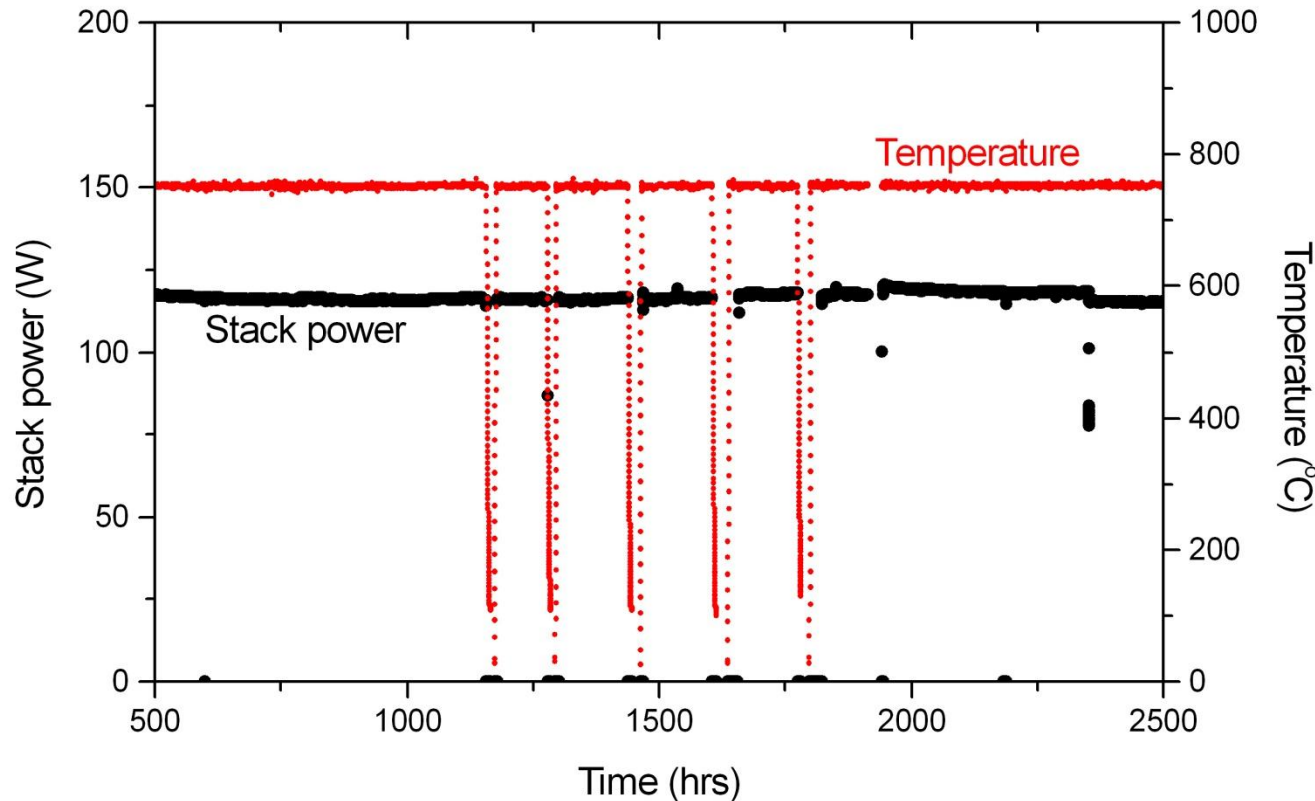
Fuel – humidified hydrogen, Oxidant - air

1 to 2 kW Capacity SOFC Stacks

kW-scale SOFC stack (100 cm² per-cell active area, 60 cells/stack)



SOFC Stack Long-Term Test with Thermal Cycles



Power degradation rate = 0.85% / 1000hrs over 2500 h testing

5 cell stack of 100 cm²/cell

50% H₂(bal. N₂) and air at 40% utilization @ 0.36A/cm²; 750°C

Metal interconnects

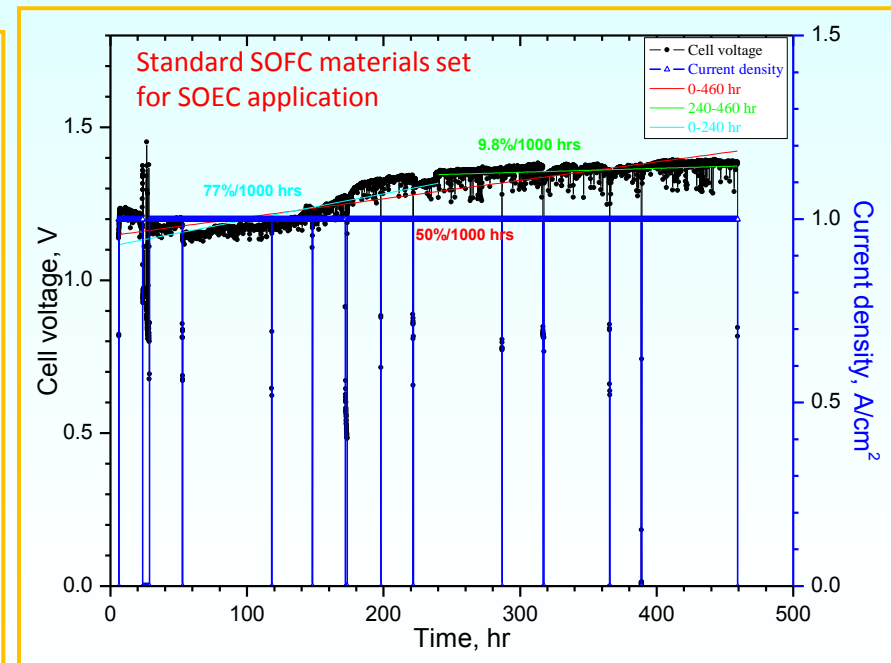
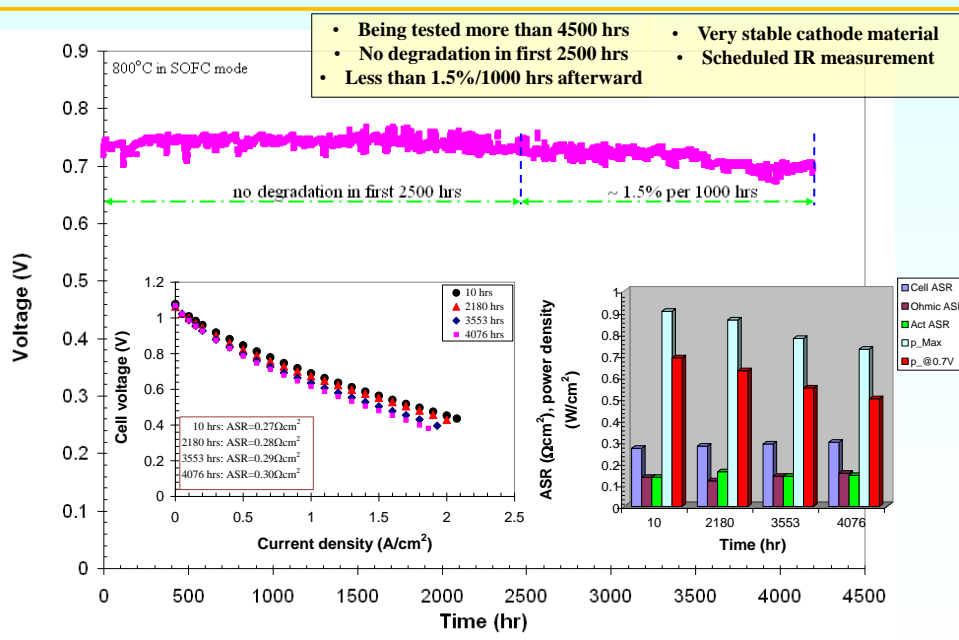
5 thermal cycles with no significant degradation

SOFC vs. SOEC Operation – (button cells)

- Long-term test results comparison between two button cells tested in SOFC and SOEC modes
 - SOFC test (0.7 A/cm^2) was interrupted on schedule to measure the ohmic losses via current-interruption
 - SOEC test (1 A/cm^2) was frequently interrupted for refilling the water tank

SOFC mode (power generation):
no degradation in 2500 hrs, and $\sim 1.5\%/1000 \text{ hrs}$ afterward

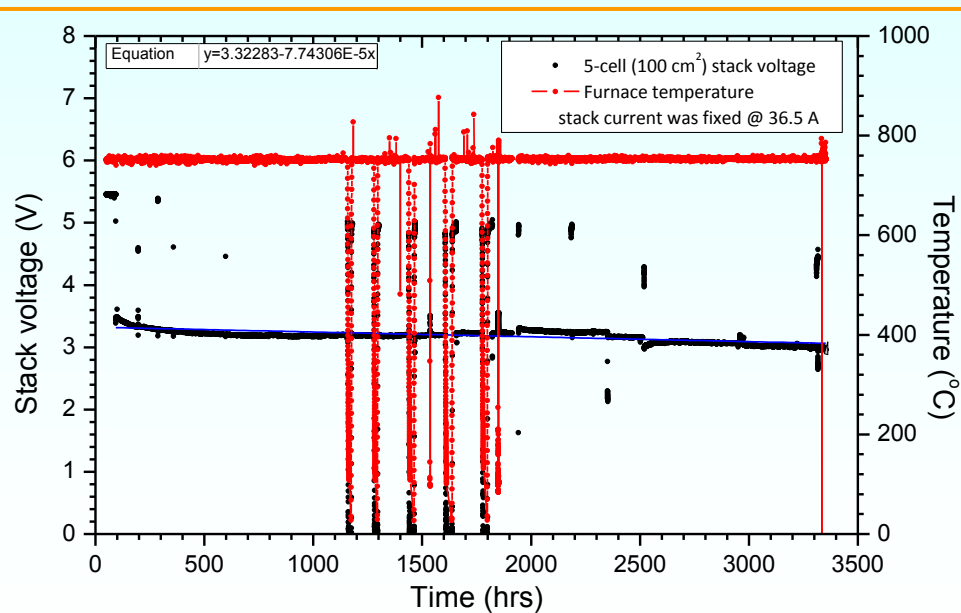
SOEC mode (hydrogen production):
Projected degradation rate $\sim 50\%/1000 \text{ hrs}$



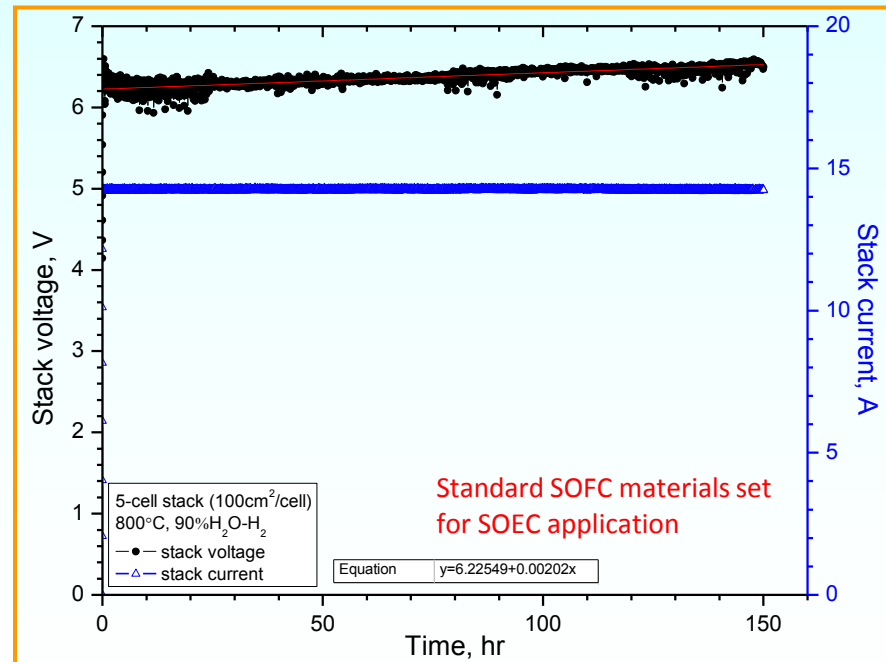
SOFC vs. SOEC Operation – (stacks)

- Long-term test results comparison between two 5-cell stacks tested in SOFC and SOEC modes
 - 100 cm² per cell active areas
 - Fixed reactant utilizations at 40%
 - Operating at fixed current mode (36.5 A and 14 A in SOFC and SOEC mode, respectively)

SOFC mode (power generation):
Voltage degradation rate < 2%/1000 hrs



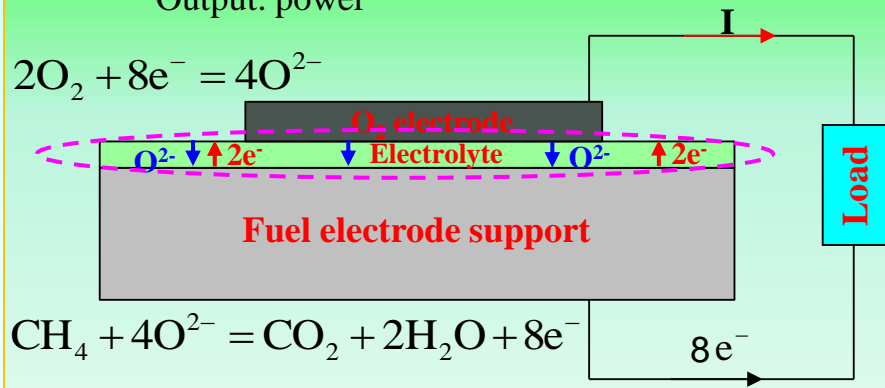
SOEC mode (hydrogen production):
Projected degradation rate ~ 30%/1000 hrs



SOFC Operation Vs. SOEC Operation

SOFC (power generation)

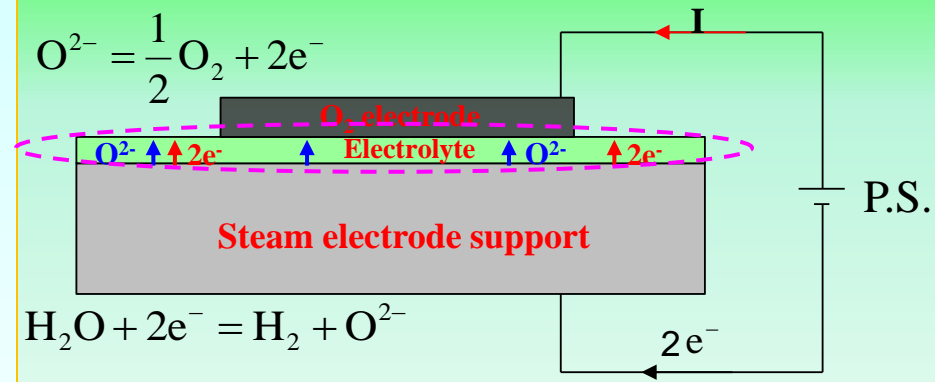
Input: CH_4 , syngas, biogas (fuel-electrode)
air (O_2 electrode)
Output: power



- SOFC operates typically at 700~850°C
- Per cell voltage is 0.7~0.85 V
- Flux of oxygen ions and electrons are on the opposite direction inside the electrolyte

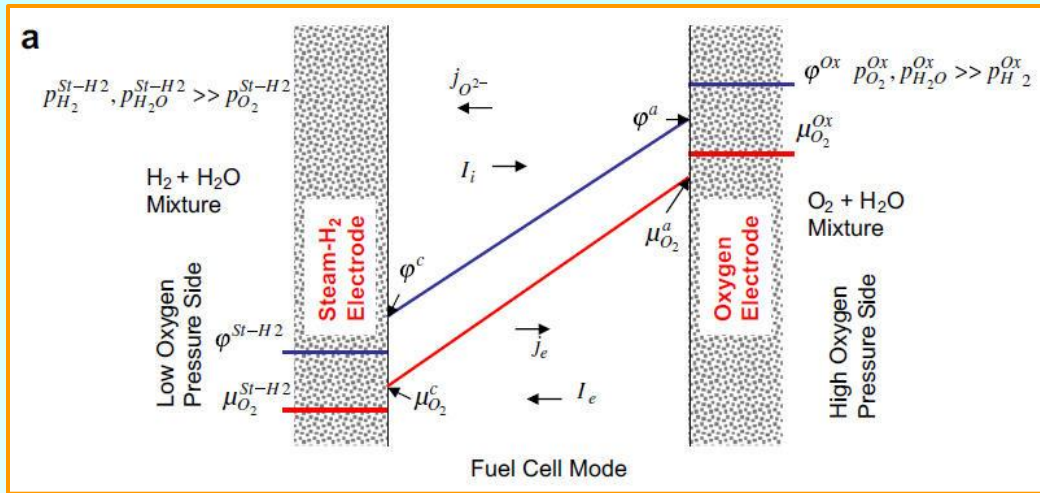
SOEC (H_2 production)

Input: power, H_2O (steam-electrode)
Output: H_2 (steam-electrode), O_2 (O_2 electrode)



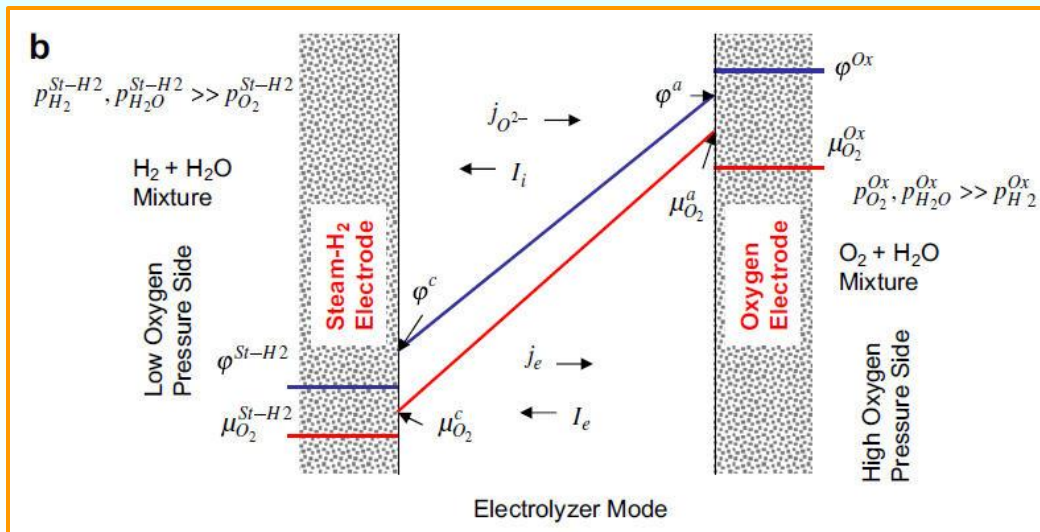
- SOEC operates typically at 700~850°C
- Per cell voltage is 0.9~1.3 V
- Flux of oxygen ions and electrons are on the same direction inside the electrolyte
- High steam concentration (or high P_{O_2}) on steam electrode

Analysis of SOFC Vs. SOEC Operation*



Schematic variation of measurable electric potential (ϕ) and oxygen chemical potential (μ_{O_2}) through the electrolyte in fuel cell mode (a) and electrolyzer mode (b).

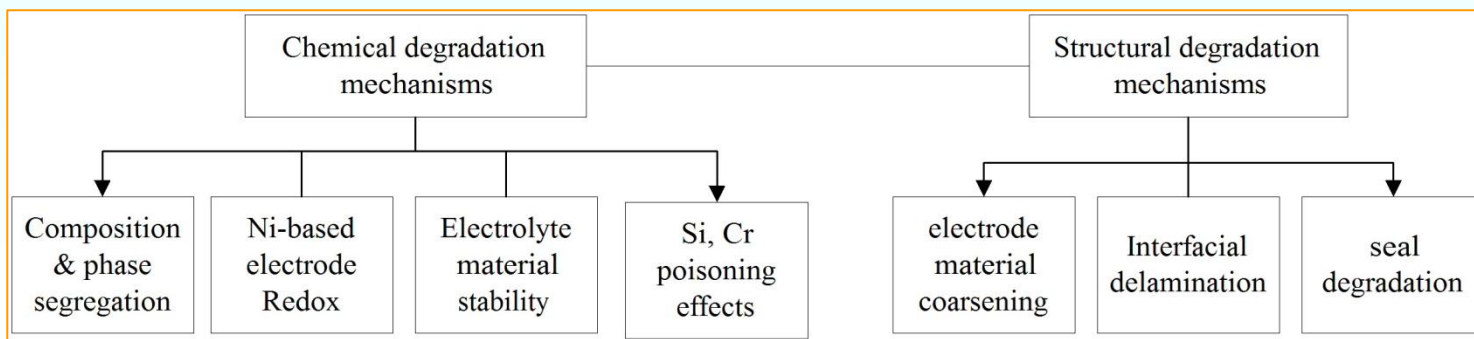
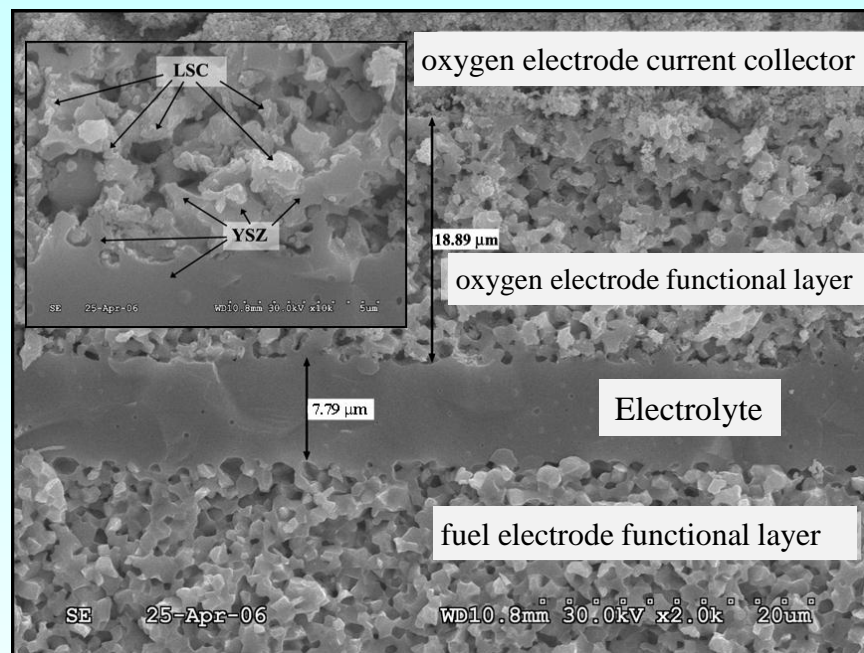
(a) In fuel cell normal operation mode, oxygen partial pressure inside the electrolyte is mathematically bounded by the oxygen partial pressures of two electrodes. High P_{O_2} is unlikely developed inside the electrolyte



(b) In the electrolyzer operation mode, the oxygen partial pressure inside the electrolyte is not mathematically bounded by the electrodes. Electrode delamination is possible under certain operation conditions

*: A.V. Virkar, "Mechanism of oxygen electrode delamination in solid oxide electrolyzer cells", Int. J. Hydrogen Energy 35 (2010) 9527-9543

Dissection of SOEC Performance Degradation



- **Focus on materials modification**
- **Improve oxygen electrode stability**

SOEC Development – at a Stack Level (5-cell stack)

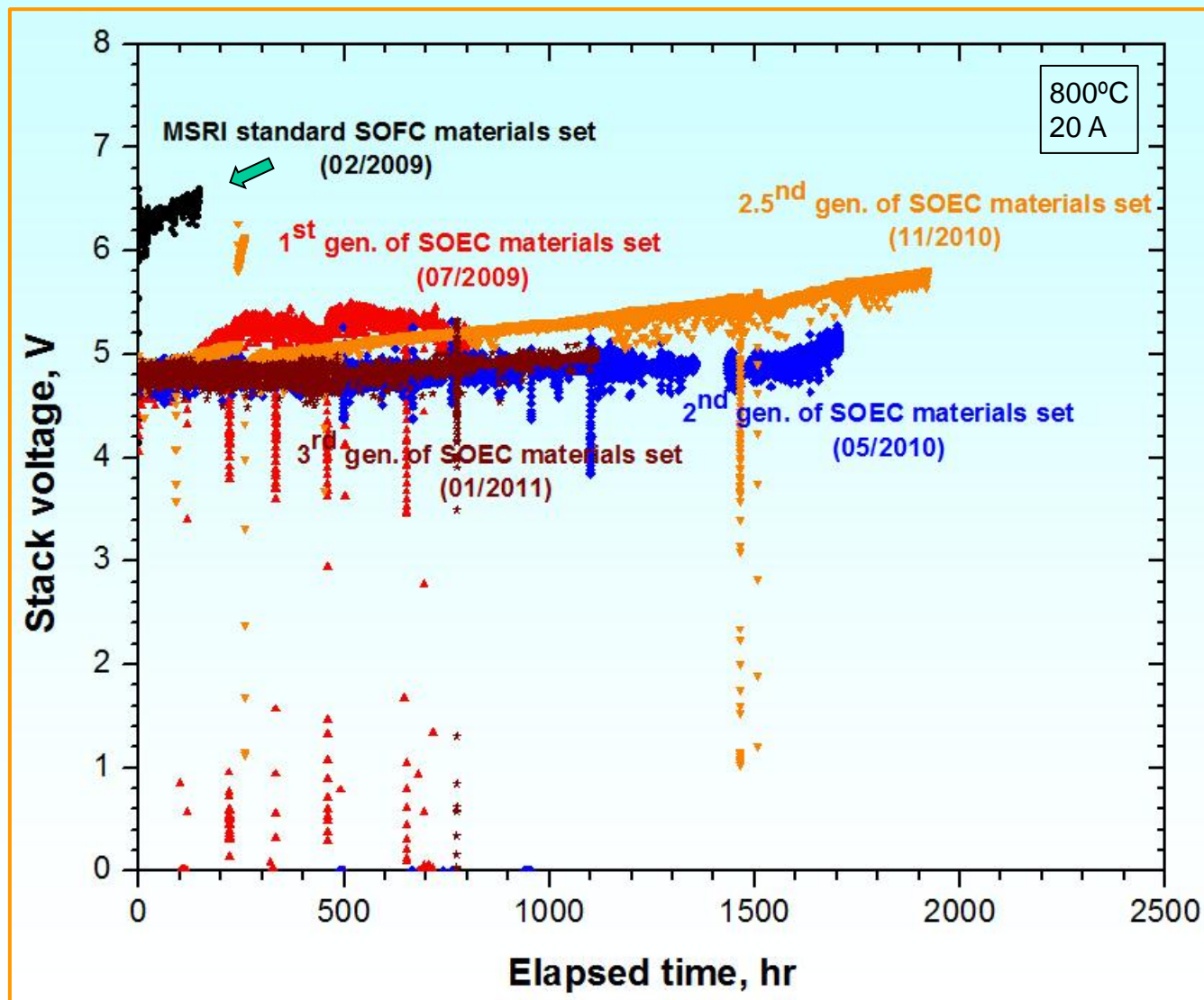


Five-cell stack assembly (post-test)

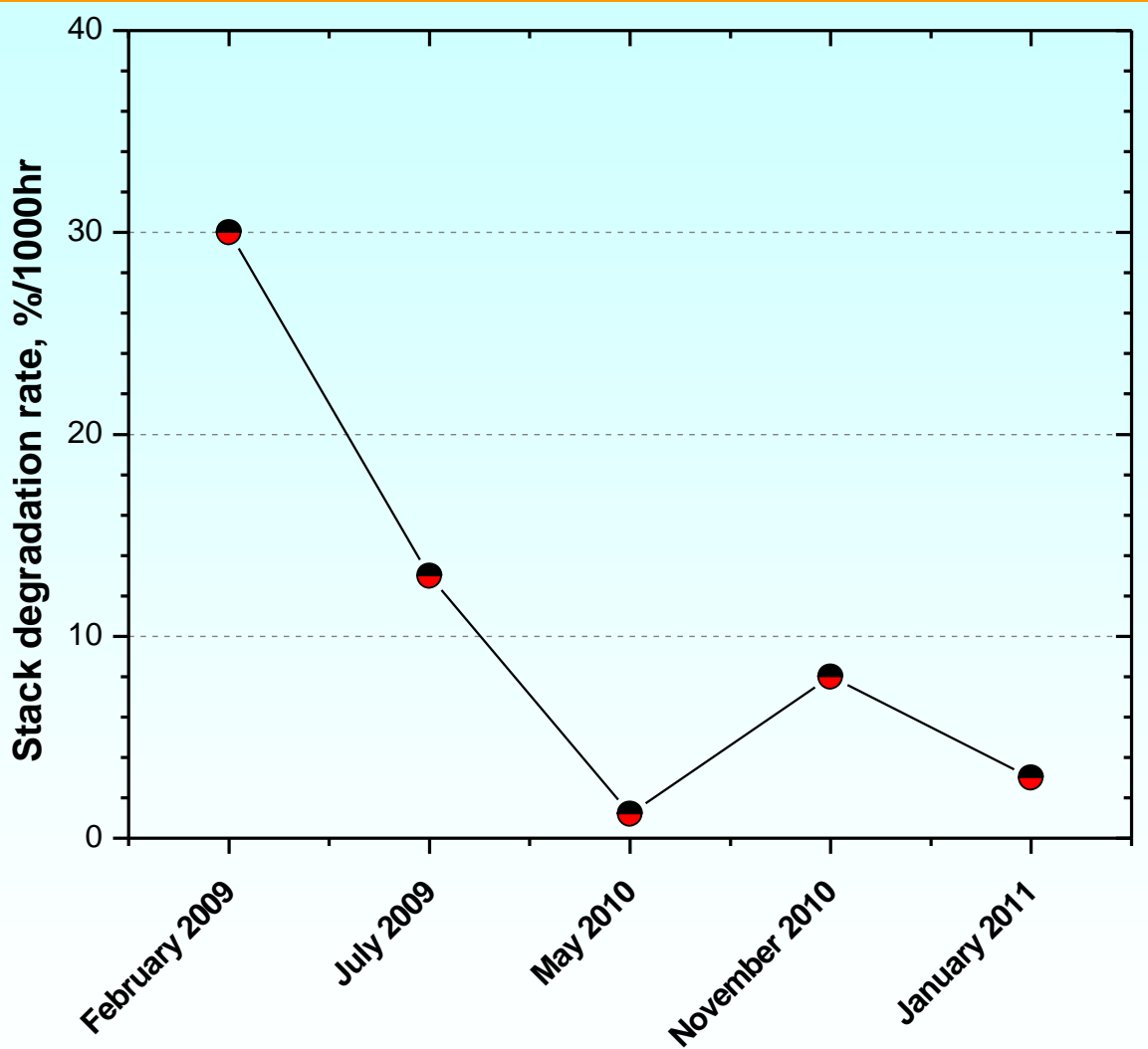
Stack testing protocol:

- 5-cell/stack, 100 cm²/cell active area
- 800°C
- Initial test was performed in the SOFC mode as a baseline, followed by SOEC tests
- The fuel-electrode gas compositions varied from pure H₂ to 10%H₂, bal. H₂O
- Long-term tests were performed for hydrogen production using 70%H₂O bal. H₂ as the reactant (SOEC mode)
- SOEC long-term tests were performed at a constant current (fixed current)
- In addition, the long-term SOEC tests were interrupted for scheduled SOFC tests

SOEC Stacks Long-term Degradation Study

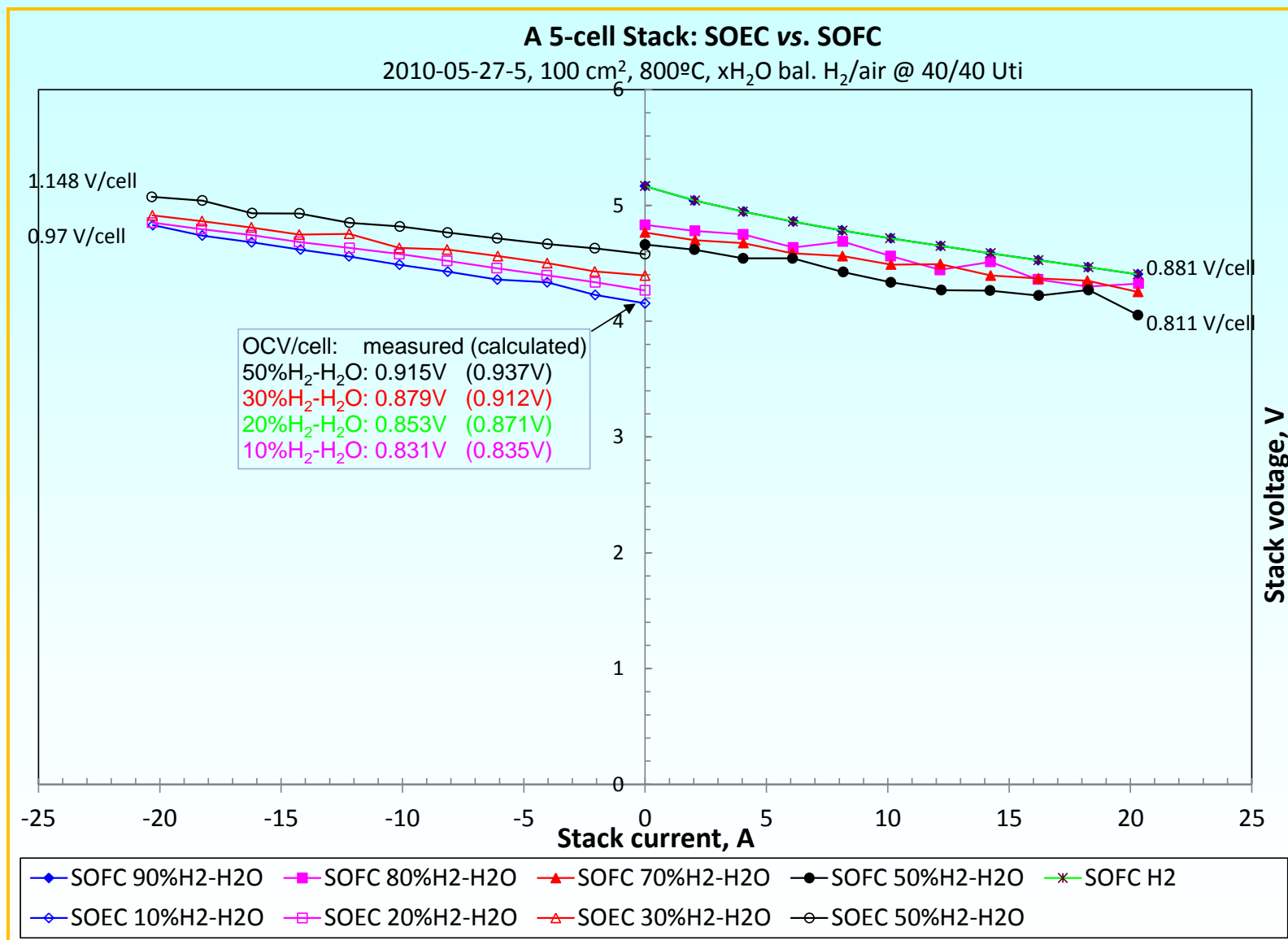


SOEC Degradation Study Progress



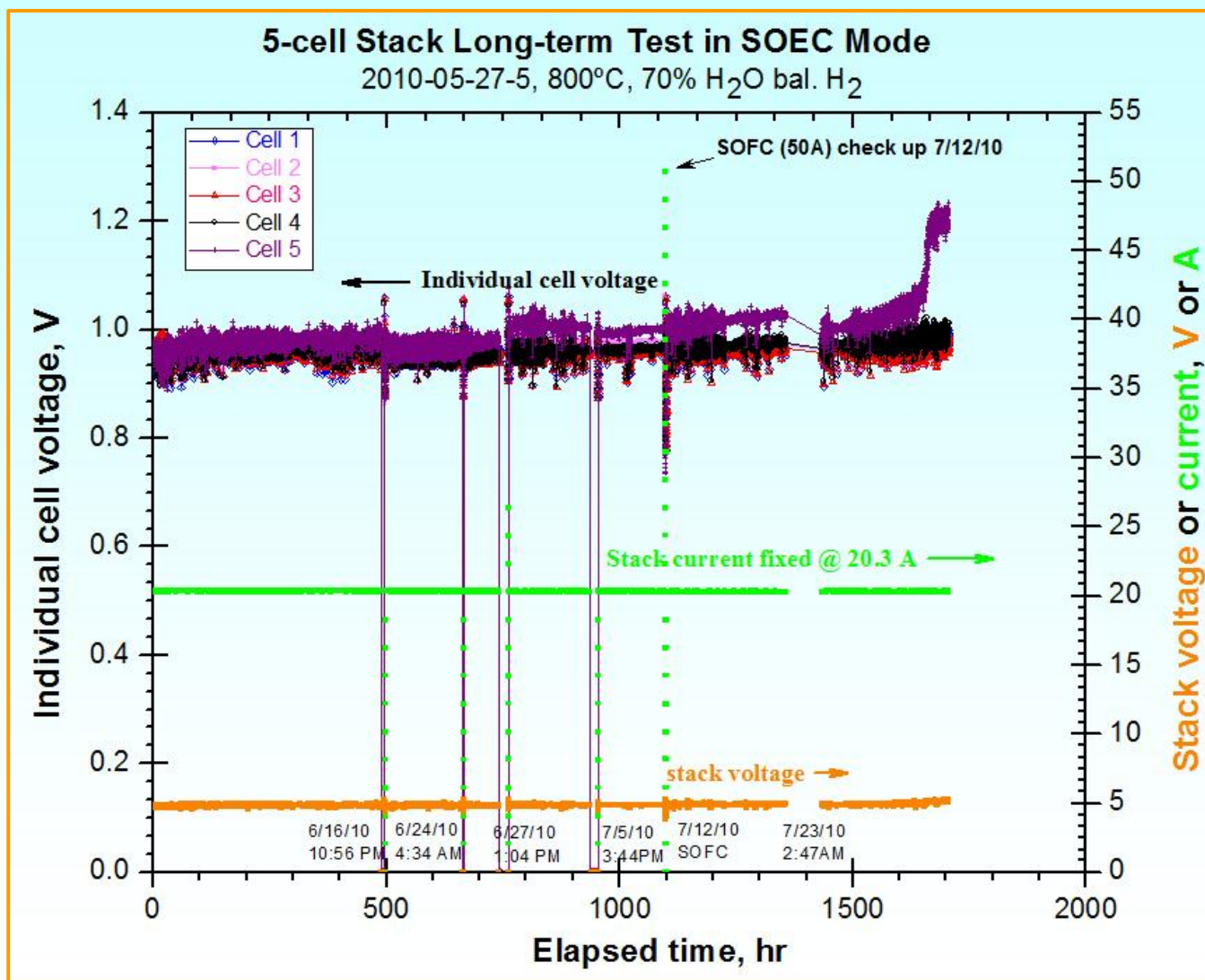
- MSRI has developed materials sets suitable for reversible SOFC/SOEC application
- In last 2 years, MSRI has tested 5-cell stacks in SOEC mode, with accumulated 10,000 stack-hours
- Degradation rate reduced from initial 30%/1000hrs to < 2%/1000hrs
- Independent tests on our 5-cell stacks by a third party achieved similar results

5-cell Stack Tests in SOFC & SOEC Modes

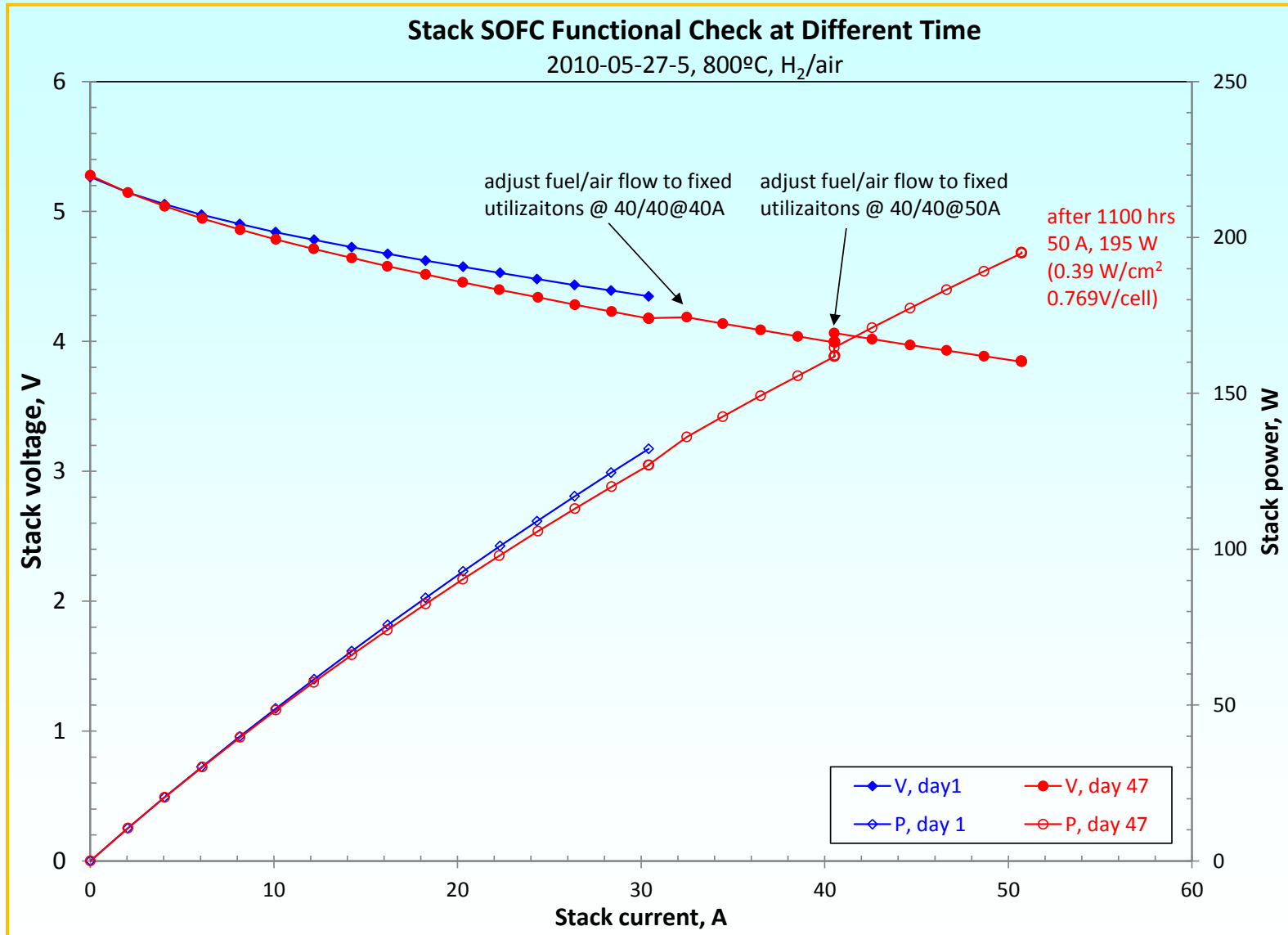


5-cell Stack Long-term Test in SOEC Mode

Fixed the stack current @ 20.3 A, degradation rate ~ 1.2%/1000 hrs



Scheduled SOFC Tests During SOEC Long-term Test @ Different Time



Summary

- Reversible SOFC/SOEC shows logical promise for storing renewable electricity/energy
- But for a near-term target, it is more applicable to distributed/decentralized storage applications
- Due to the different operation mechanisms between SOFC and SOEC, cell materials developed for SOFC may not be suitable for SOEC applications
- SOECs typically show a higher degradation rate than SOFCs
- MSRI has investigated and developed high-performing material sets for reversible SOFC/SOEC applications
- With knowledge gained from the accumulated 10,000 stack-hours tests, MSRI has successfully reduced the SOEC stack degradation rate from initial 30%/1000hrs to <2%/1000hrs
- Fundamental studies of cell materials are needed to further improve reversible SOFC/SOEC performance

Acknowledgements

- ❑ The SOEC degradation study is funded by the Idaho National Laboratory
- ❑ Support from Drs. Manohar Sohal, James O'Brien, Carl Stoots and Stephen Herring at the Idaho National Laboratory is much appreciated