SOFC Materials and Processing Issues

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Presented at the SECA Core Technology Program Workshop
February 14, 2001

SOFC Stack Materials and Processing Issues

1) Cell design (Electrolyte-supported vs. Electrode-supported)
2) Anode-supported: Thermomechanical Issues
3) Cathode
4) Interconnect
5) Seals

New Cell Materials

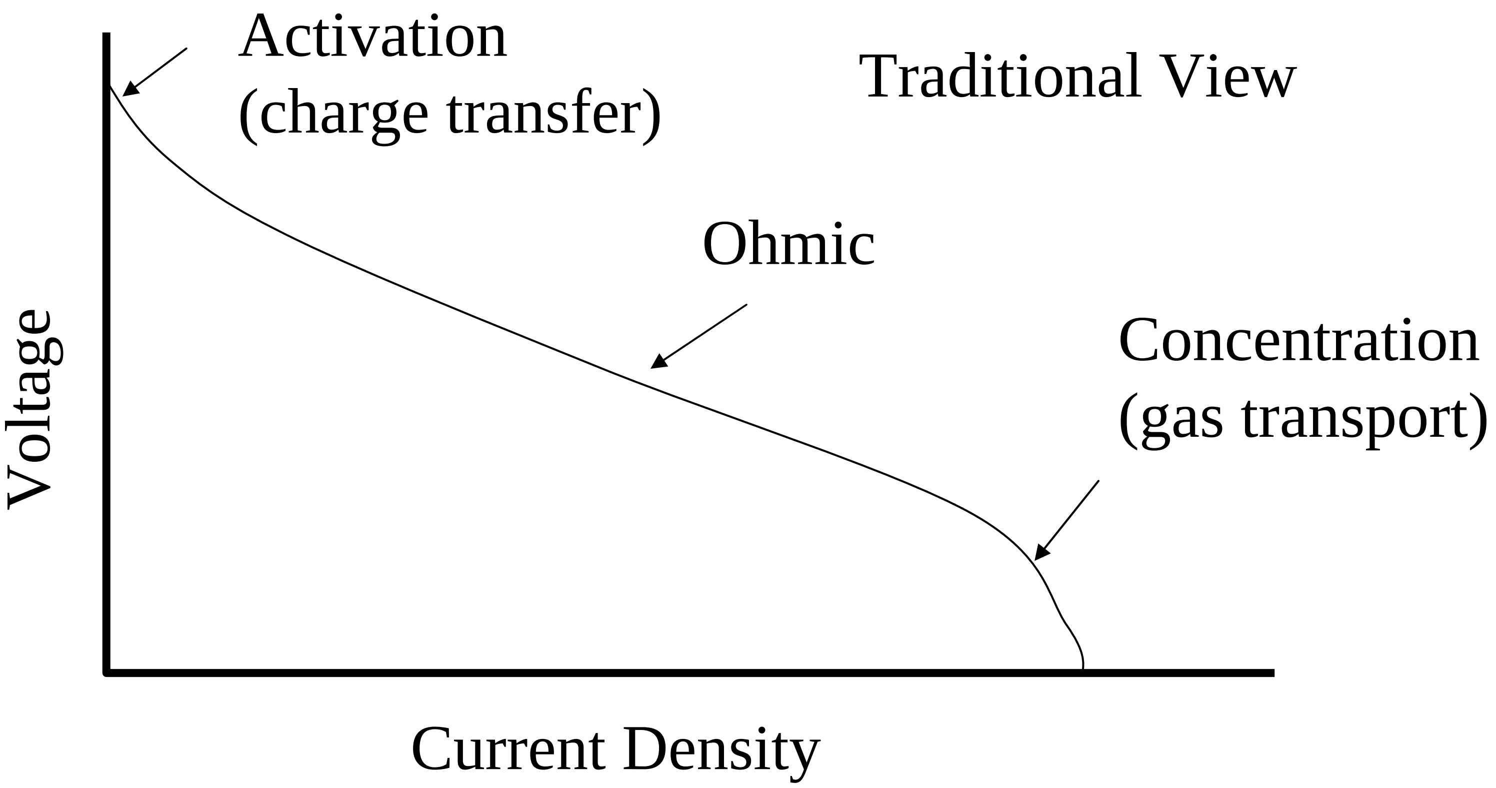
State-of-the-art SOFC Materials

Electrolyte: 8 mol.% Y_2O_3-Stabilized Zirconia (YSZ)
Ionic Resistivity (800°C): ~50 Ωcm
Thermal Expansion Coefficient: ~10.5 x 10^{-6} /°C

Anode: Ni + YSZ
Thermal Expansion Coefficient: ~12 to 15 x 10^{-6} /°C
YSZ addition improves anode stability, and enhances electrochemical performance.

Cathode: Sr-doped $LaMnO_3$ (LSM) + YSZ
Thermal Expansion Coefficient: ~10.5 x 10^{-6} /°C
YSZ addition improves electrochemical performance.

A Typical Voltage vs. Current Density Plot



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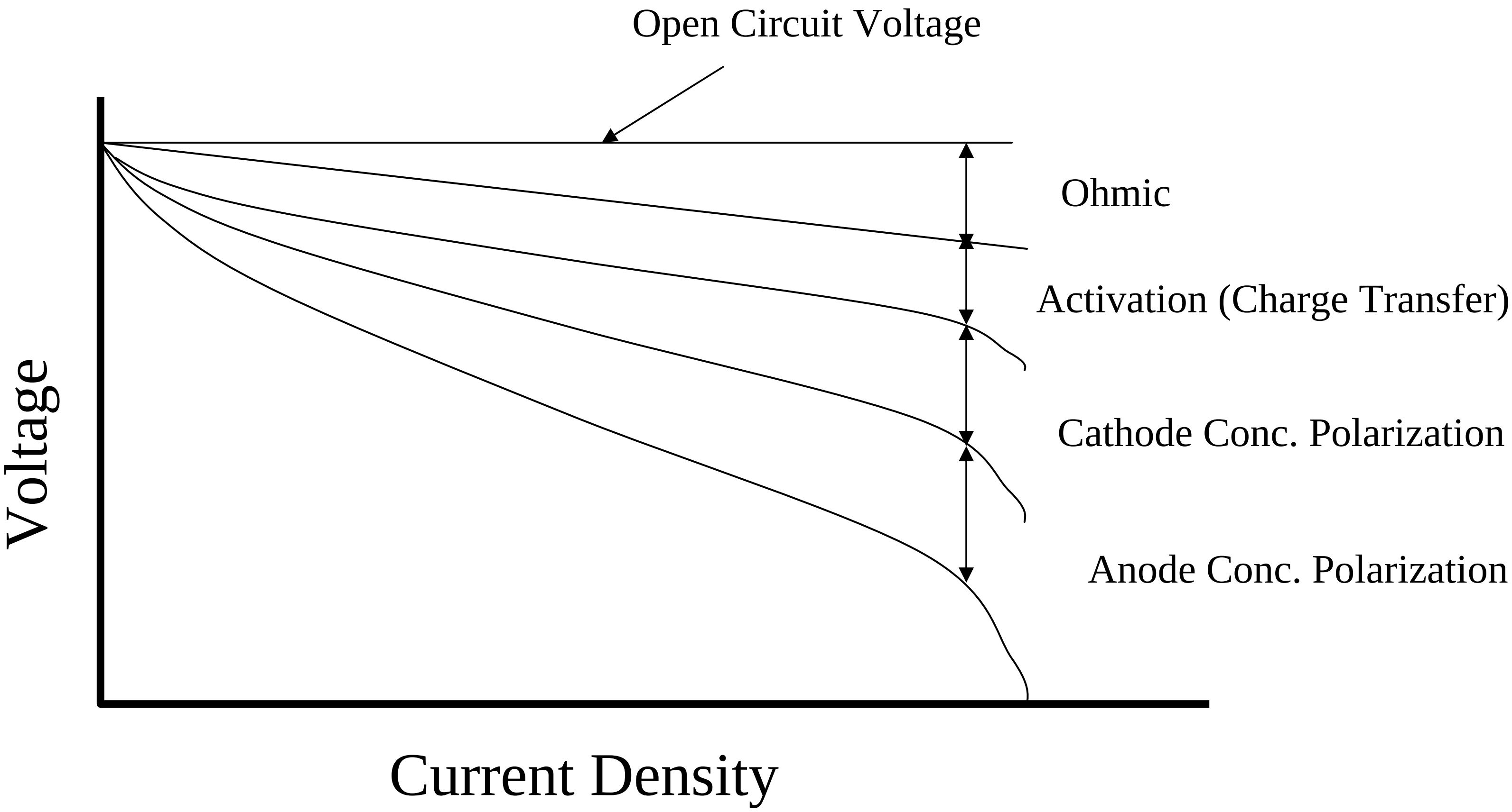
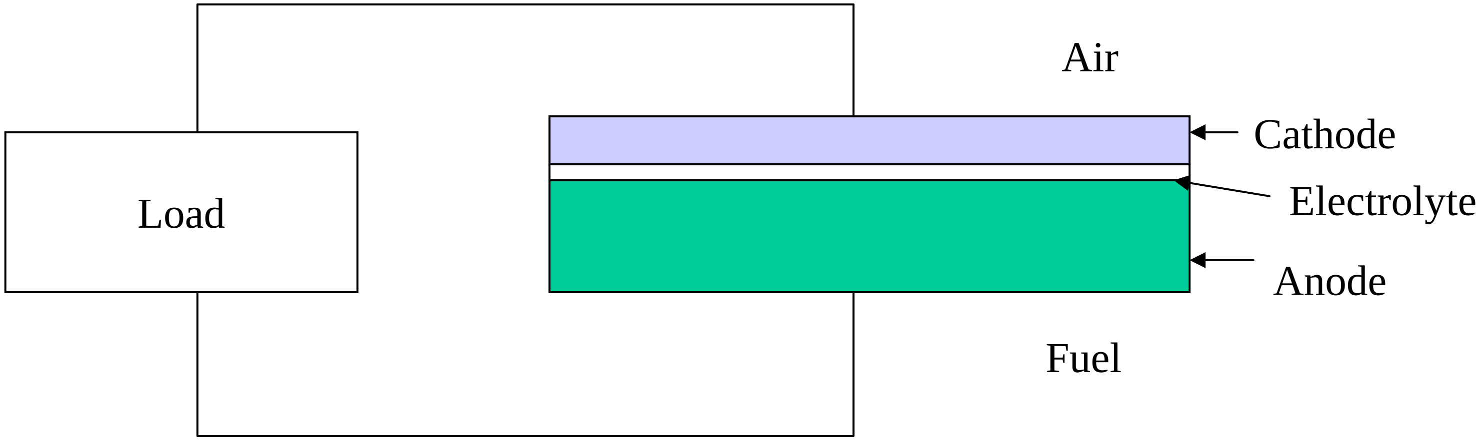


SOFC Materials and Fuel



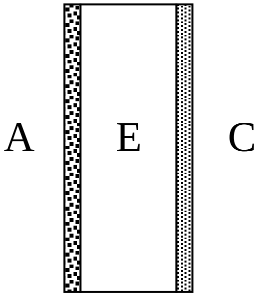
Materials for the State-of-the-art SOFCs

Electrolyte: YSZ (8% Y_2O_3- 92% ZrO_2) (~10 μm)
Anode: Ni + YSZ (~0.5 to 2 mm)
Cathode: LSM (Sr-doped $LaMnO_3$) + YSZ (~20 to 100 μm)

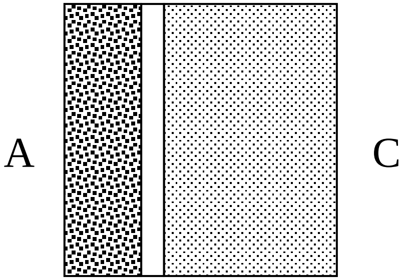
Temperature: >600°C (As high as 1000°C)

Fuel: Natural gas (methane), propane, gasifiable liquid hydrocarbons
Processed (reformed – internally or Externally)

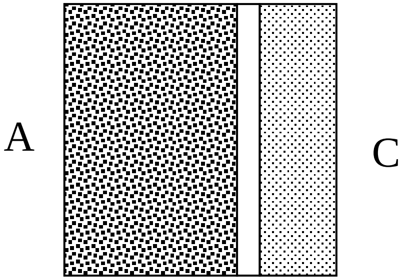
SOFC: Electrolyte-Supported vs. Electrode-Supported



Electrolyte-Supported: (1) **High Ohmic Contribution**
(2) **Low Cathode Concentration Polarization**
(3) **Low Anode Concentration Polarization**



Cathode-Supported: (1) **Low Ohmic Contribution**
(2) **High Cathode Concentration Polarization**
(3) **Low Anode Concentration Polarization**



Anode-Supported: (1) **Low Ohmic Contribution**
(2) **Moderate Anode Concentration Polarization**
(3) **Low Cathode Concentration Polarization**

Best Choice from Polarization Standpoint: Anode-Supported

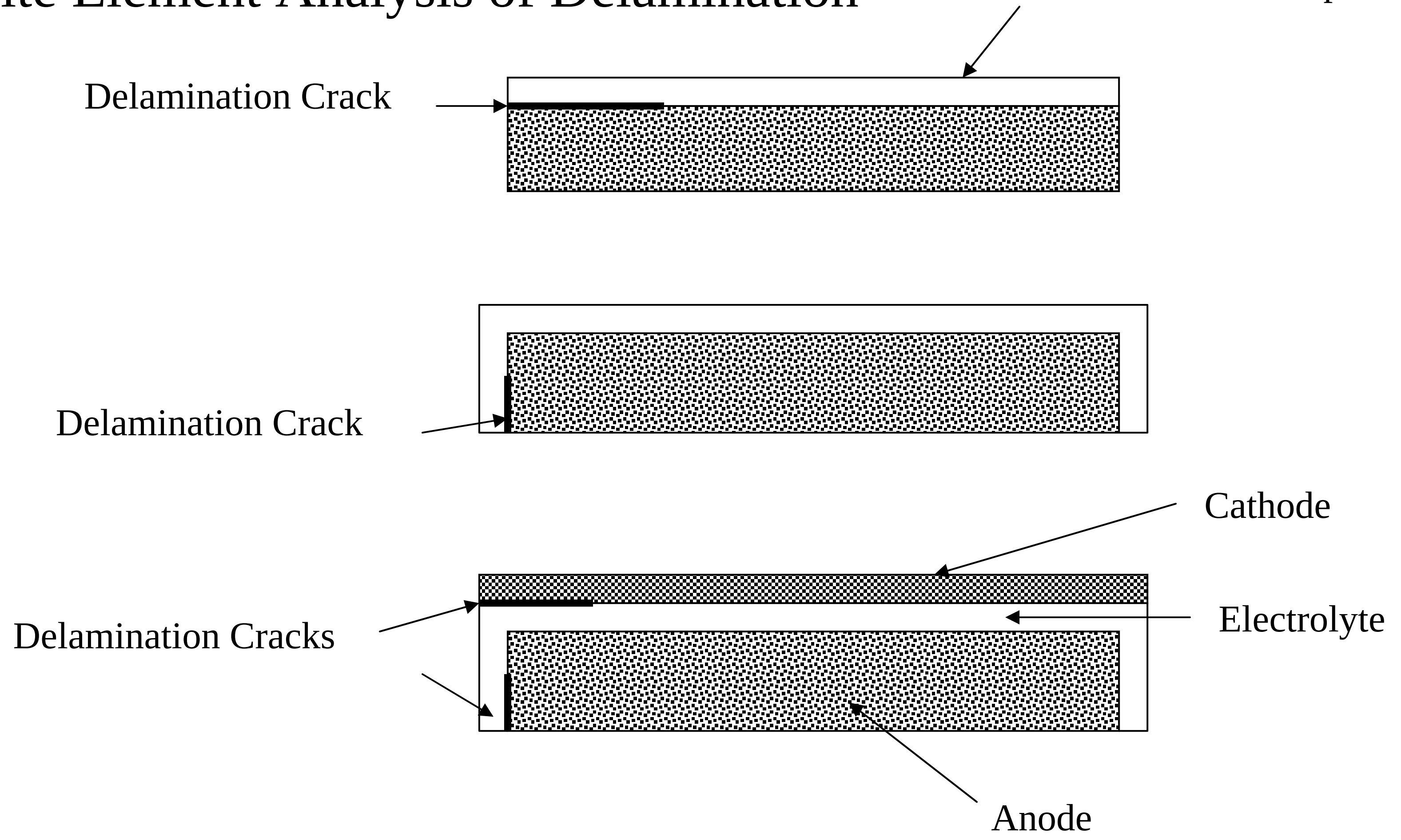
Thermomechanical Issues:

Thermal Expansion Mismatch Stresses and Propensity to Cracking or Delamination

1) Electrolyte-Supported: Minimal Tendency for Delamination due to Thermal Expansion Mismatch
2) Cathode-Supported: Minimal Tendency for Cracking or Delamination due to Thermal Expansion Mismatch.
3) Anode-Supported: Potential for Electrolyte Film Delamination exists as the YSZ Film is in Biaxial Compression

Thermomechanical Issues: Possible Delamination of the YSZ Electrolyte Layer, or the Cathode, from the Anode ($\alpha_{\mathrm{Anode}} > \alpha_{\mathrm{YSZ}}$)

Finite Element Analysis of Delamination



YSZ film in biaxial compression

Delamination Crack

Delamination Crack

Cathode

Electrolyte

Delamination Cracks

Anode

Finite Element Analysis of Delamination

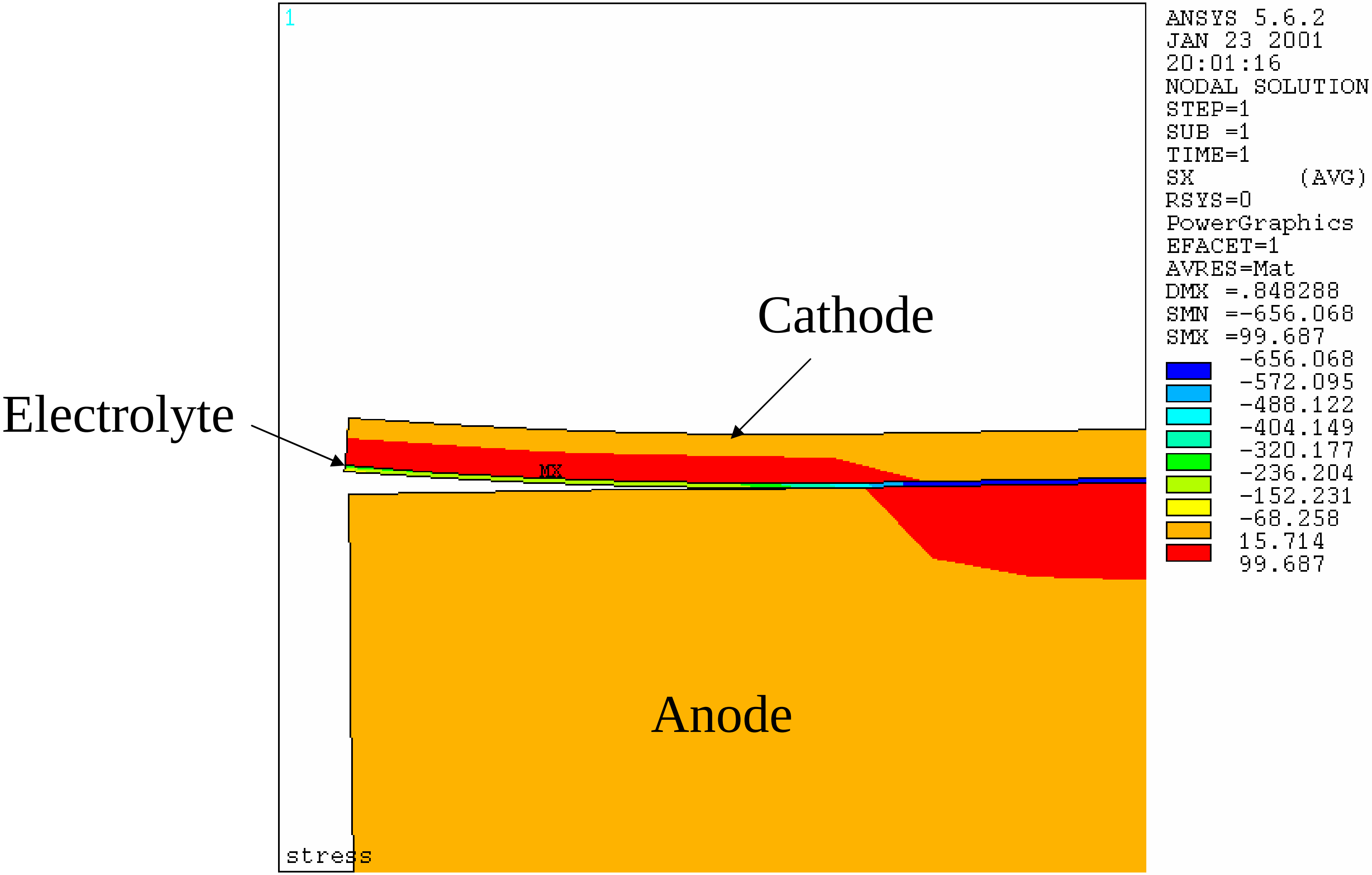
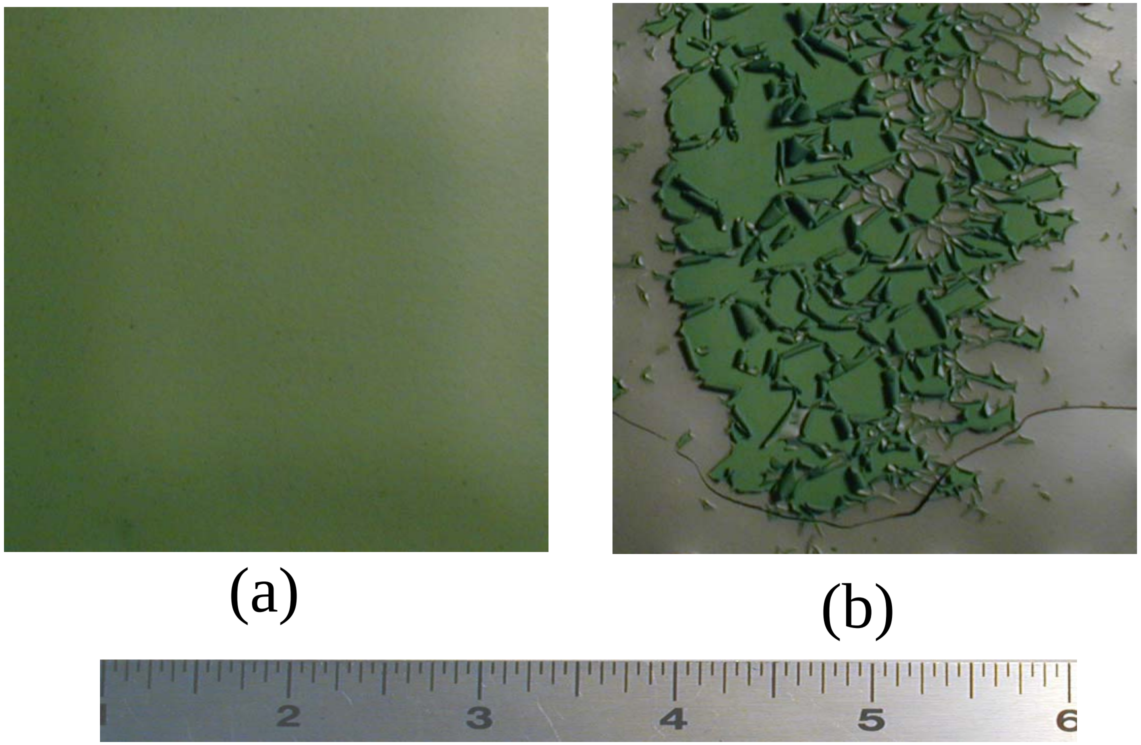


Figure showing a 1 mm crack between electrolyte and anode

Effect of Electrolyte Thickness on Propensity to Delamination



(a)

(b)

(a): Thickness ~6 microns

(b): Thickness ~60 microns

Results of Finite Element Analysis

Propensity for Delamination Increases
with Increasing Electrolyte Thickness: Thus,
Thinner Electrolyte is Preferred.

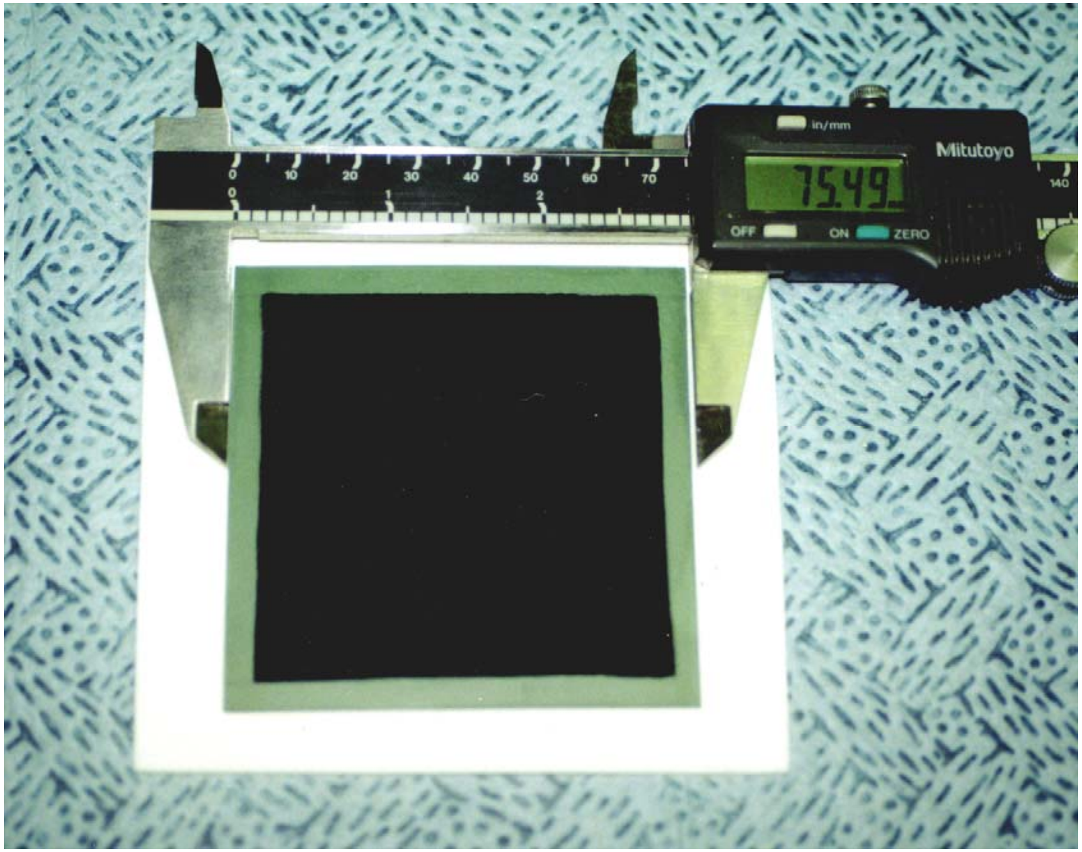
Effort Needed

1) To analyze selected cell configurations
2) To experimentally measure fracture mechanical parameters.

Issues Related to Fabrication

1) Type and Amount of Solvent, Binder: Cost, Combustion Products
2) Tape-Casting: Thickness Control and Uniformity
3) Bisque-Firing: Time, Dimension Control, Cracking
4) Deposition of YSZ Electrolyte: Thickness Control and Uniformity
5) Sintering (~1400^{o}C): Dimensional Control
6) Cathode Application: Uniformity

A Photograph of an Anode-Supported Cell



Issues Related to Accidental Re-oxidation of the Anode

Accidental Re-oxidation can occur provided at the operating temperature, fuel supply is cut off, and air leaks into the anodic chamber. This can lead to:

1) Cracking of the anode
2) Weakening of the anode.

A method to prevent accidental exposure of anode to air is required. Alternatively, an effort should be devoted to develop

1) Anode that can be reoxidized without cracking.
2) Anode which is resistant to reoxidation, once reduced.

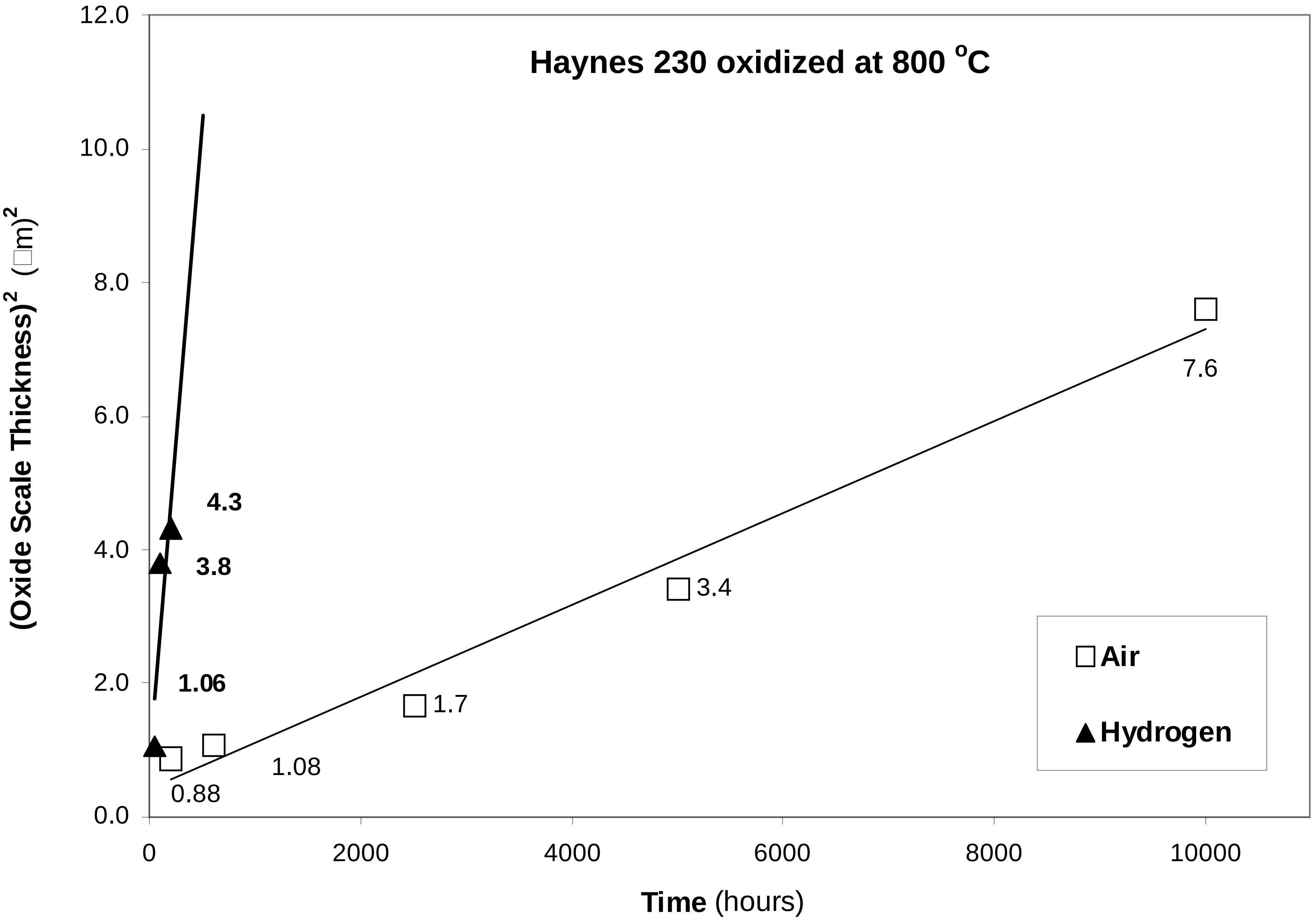
Issues Related to Deformation of the Anode under Stack Weight and/or Applied Sealing Forces

1) Resistance to plastic deformation
2) Resistance to diffusional creep

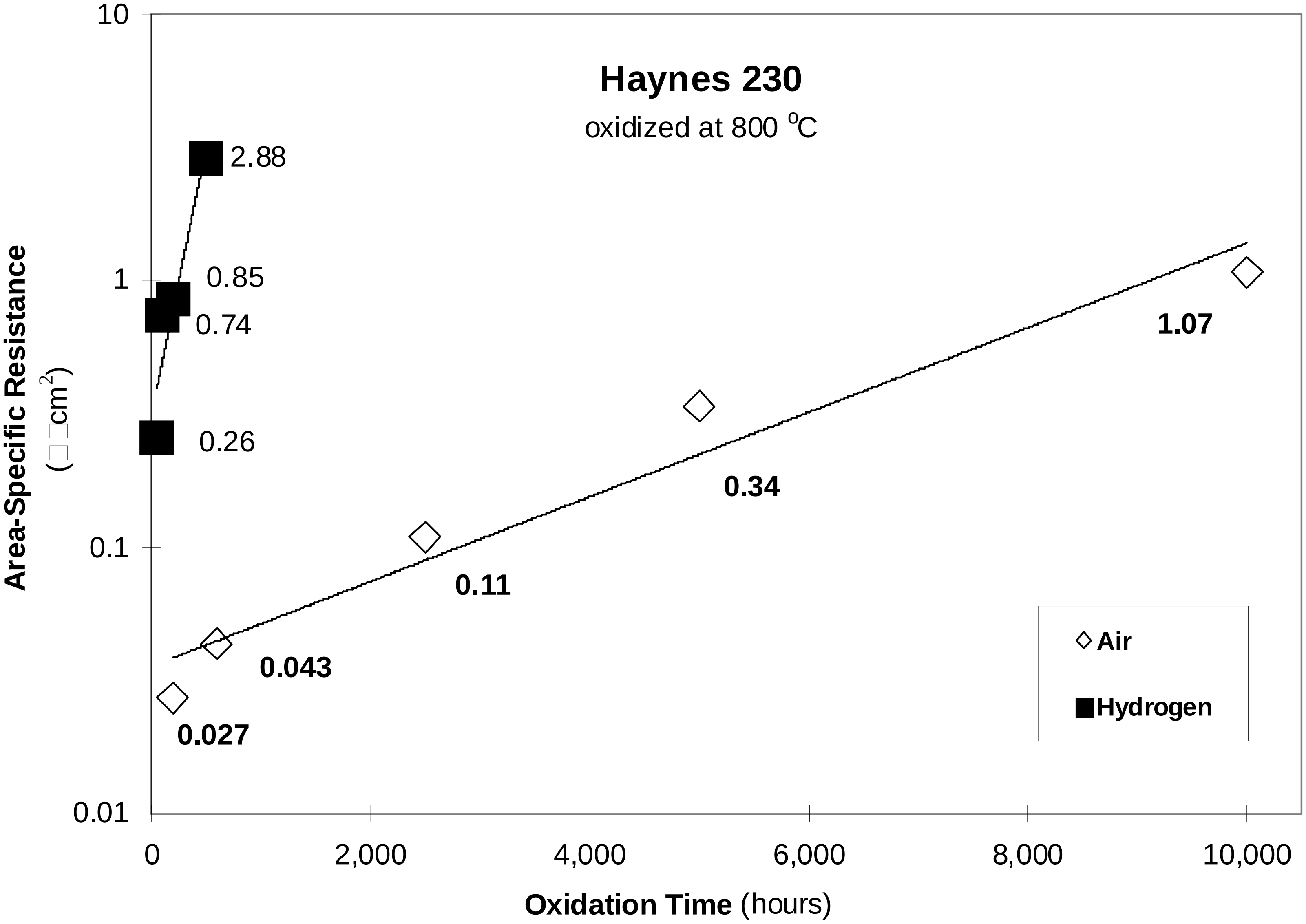
Metallic Interconnect - Requirements

1) Should be oxidation-resistant in both cathodic and anodic atmospheres.
2) Oxide film must be a good electronic conductor.
3) Oxide film must strongly adhere to the base alloy.
4) Must be inexpensive.

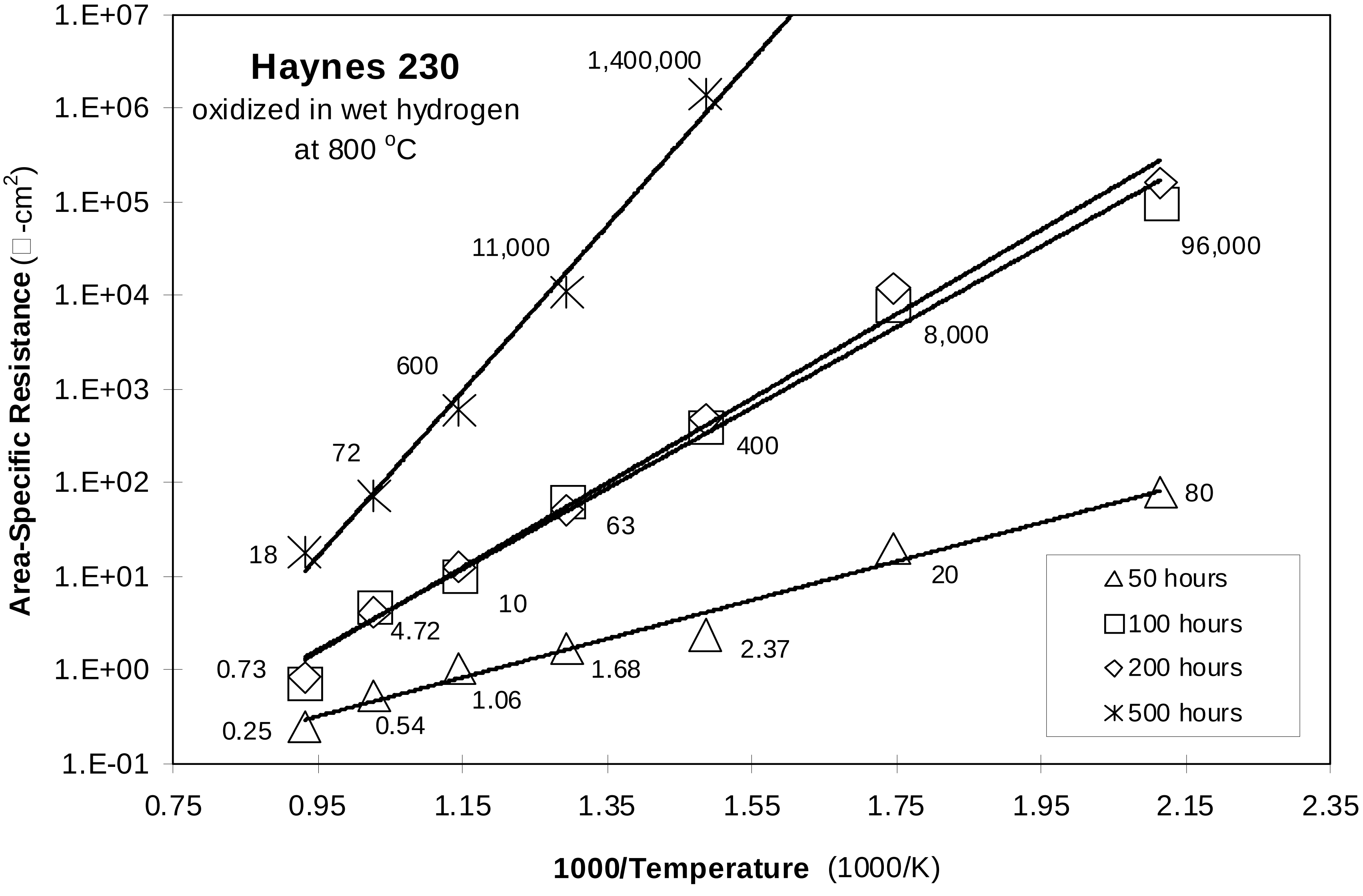
Kinetics of Oxidation of Haynes 230 in Air and Wet Hydrogen



Area Specific Resistance of Haynes 230 at 800°C as Function Of Oxidation Time (at 800°C) in Air and Wet Hydrogen



ASR of Haynes 230 vs. Temperature: Oxidized in Wet H_2



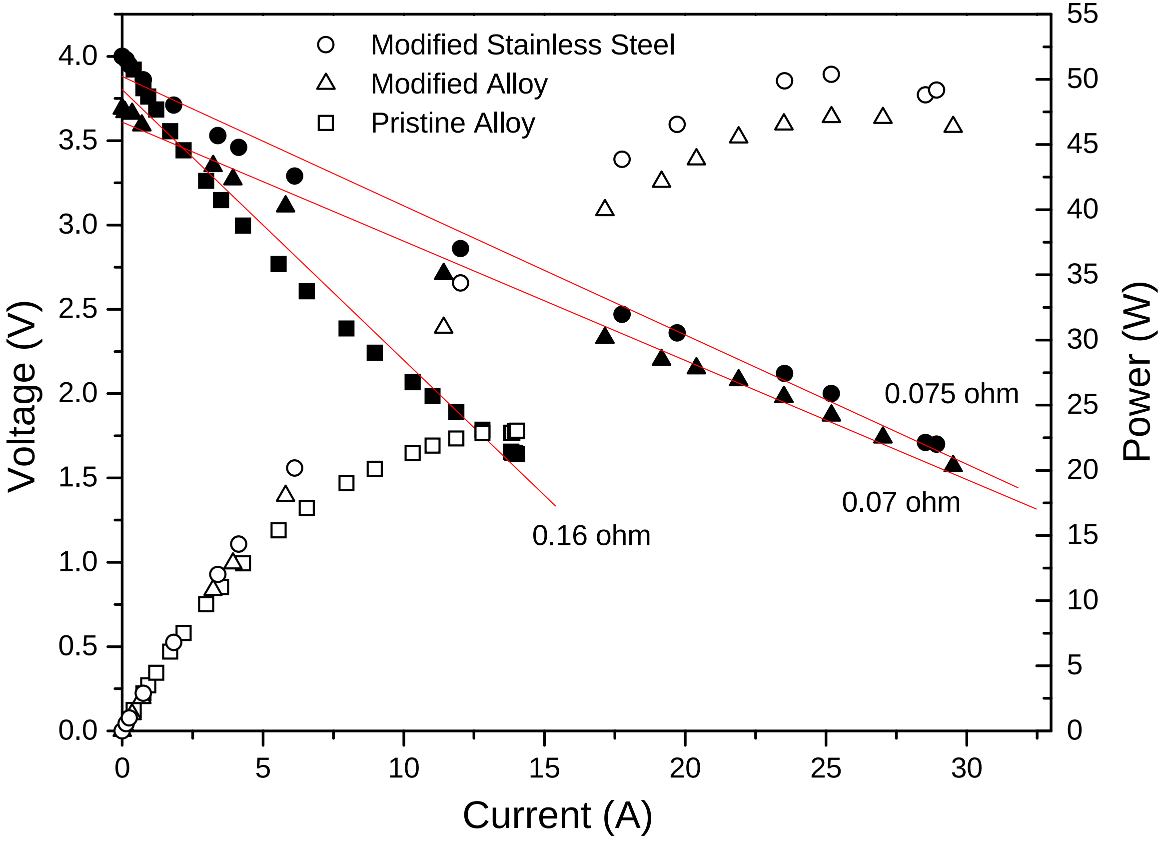
Sample Calculation

Single cell performance that can be achieved routinely is equivalent to maximum power density ~1.2 W/cm^2 at 800^{o}C (OCV ~1.04 V). The corresponding ASR is ~0.225 Ωcm^2. After about 50 hrs., the interconnect ASR alone is ~0.3 Ωcm^2. The corresponding maximum power density is ~0.52 W/cm^2.

Possible Solutions

1) Modification of the surfaces of currently available alloys to suppress oxidation kinetics and/or reduce electronic resistance of the oxide scale.
2) Development of new alloys exhibiting desired characteristics.

Incorporation of Surface-Modified Metallic Interconnects in Small Four-Cell Stacks



Electrode Microstructure Effects

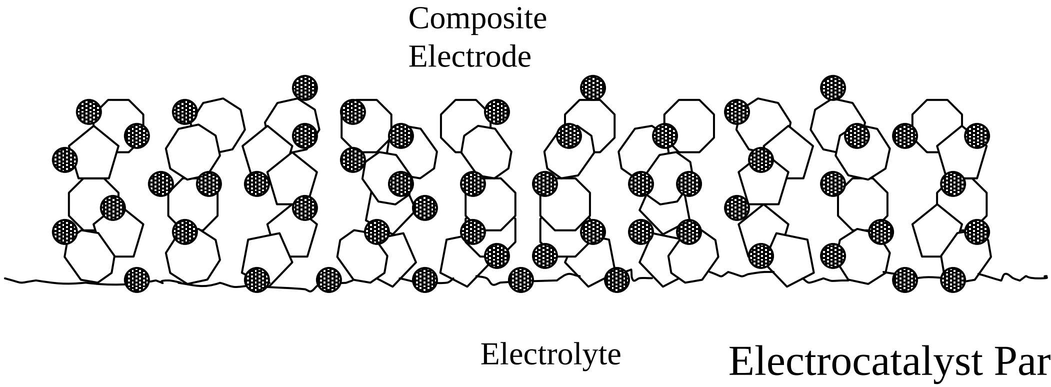
Experimental Observations

Two electrodes of identical composition can lead to vastly different cell performance. It can be shown, both theoretically and experimentally, that electrode microstructure has a profound effect on cell performance, i.e., the overall ASR.

Effort is needed to: (1) Understand the role of electrode microstructure using standard materials (LSM, YSZ).
(2) Develop optimum electrode microstructures.
(3) Develop methods to quantify microstructures.
(4) Develop better electrodes using other materials.

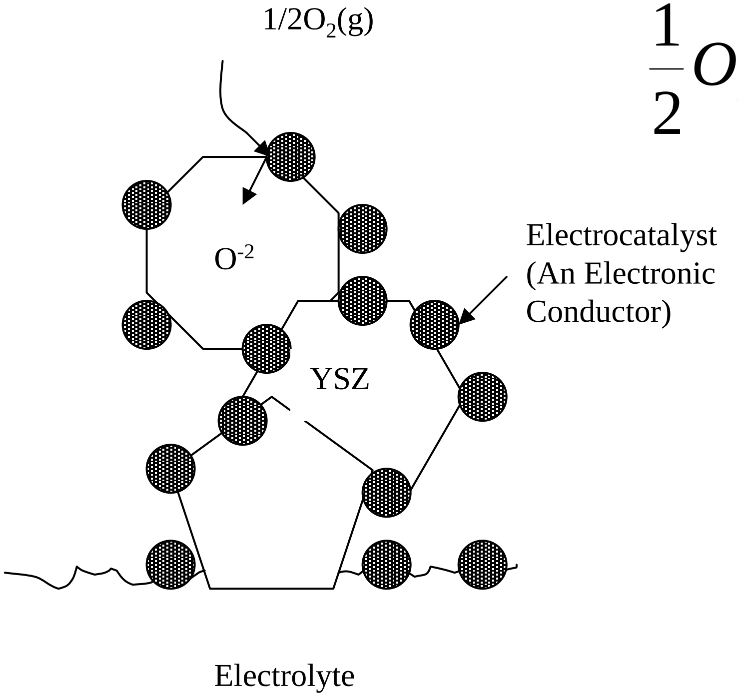
Major contributor – cathode polarization.

Composite Electrode

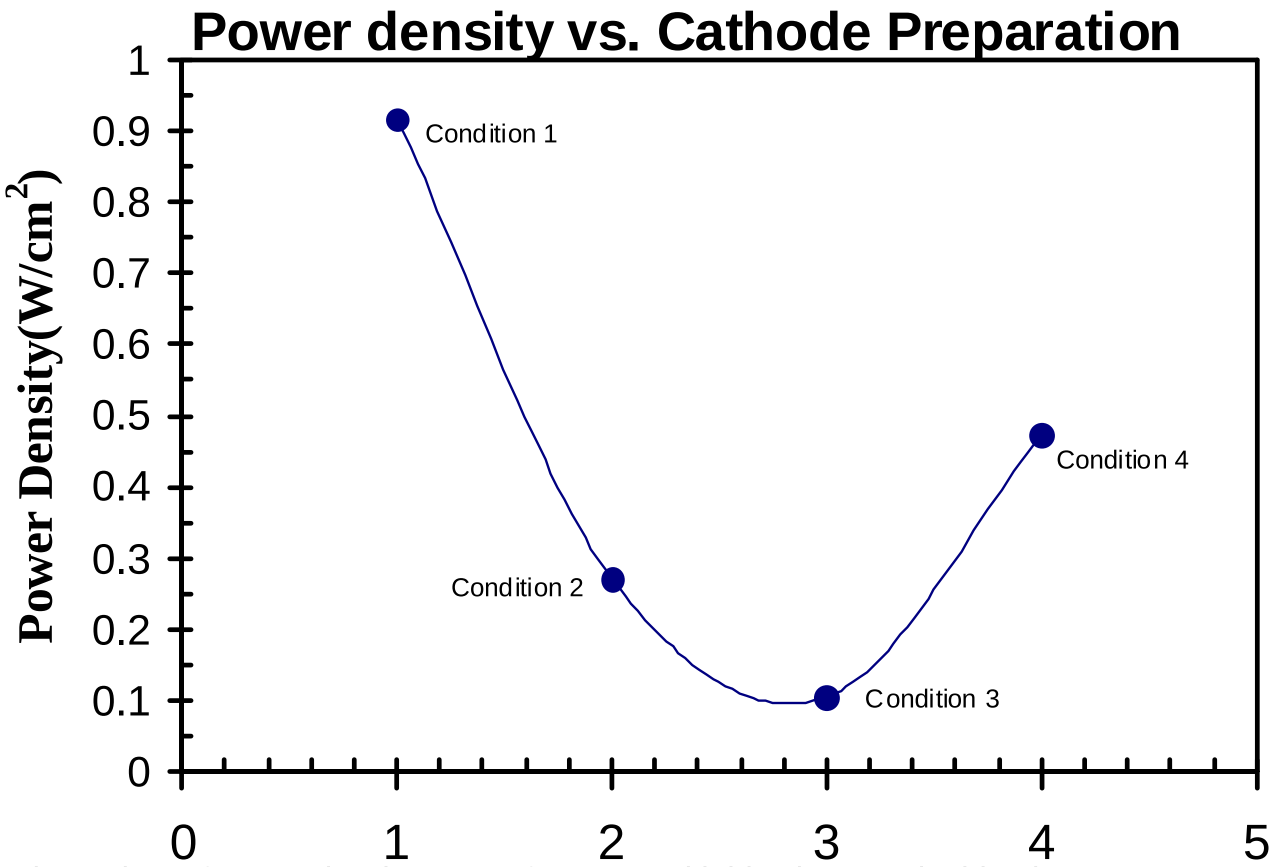


Electrocatalyst Particles are Contiguous

$$\frac{1}{2}O_2(g) + 2e'(Electrocatalyst) \rightarrow O^{-2}(YSZ)$$

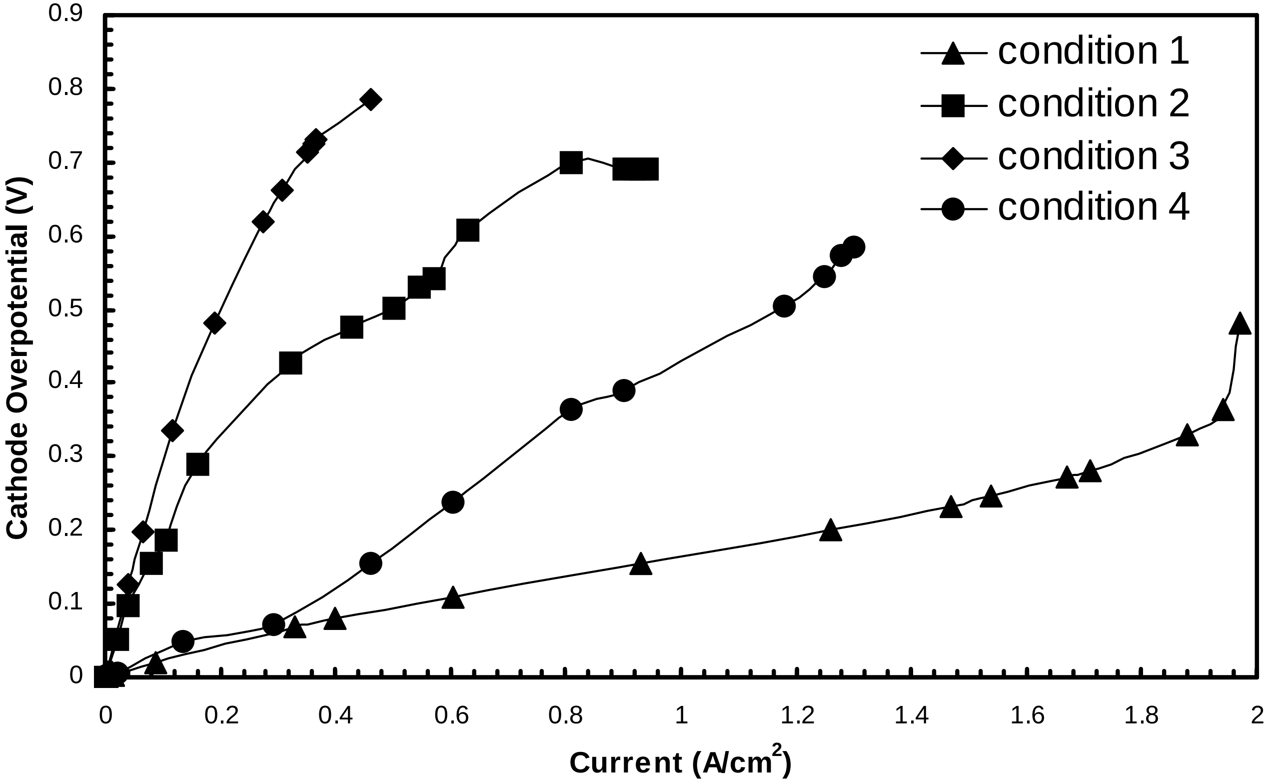


Effect of Electrode Microstructure



The above data of power density are on four cells with identical anode, identical electrolyte, and identical cathode material. The only difference from cell to cell was the method of cathode application (liquid used); which led to differences in cathode microstructures. The cathode firing conditions were also identical. These results show that cathode preparation conditions can significantly affect cell performance, even when using identical cathode materials.

Effect of Electrode Preparation Condition



Cathode: Composition and morphology

Effort needed to quantitatively characterize cathode morphology (microstructure). A simple, qualitative examination of electrode microstructure is not sufficient.

Sealing: With or Without Glass

Seals with glass: (1) Potentially easier to form a hermetic seal. (2) Resultant stack is a rigid body – greater tendency for thermal stress fracture; must be heated or cooled slowly. (3) When one cell cracks, the entire stack must be discarded.

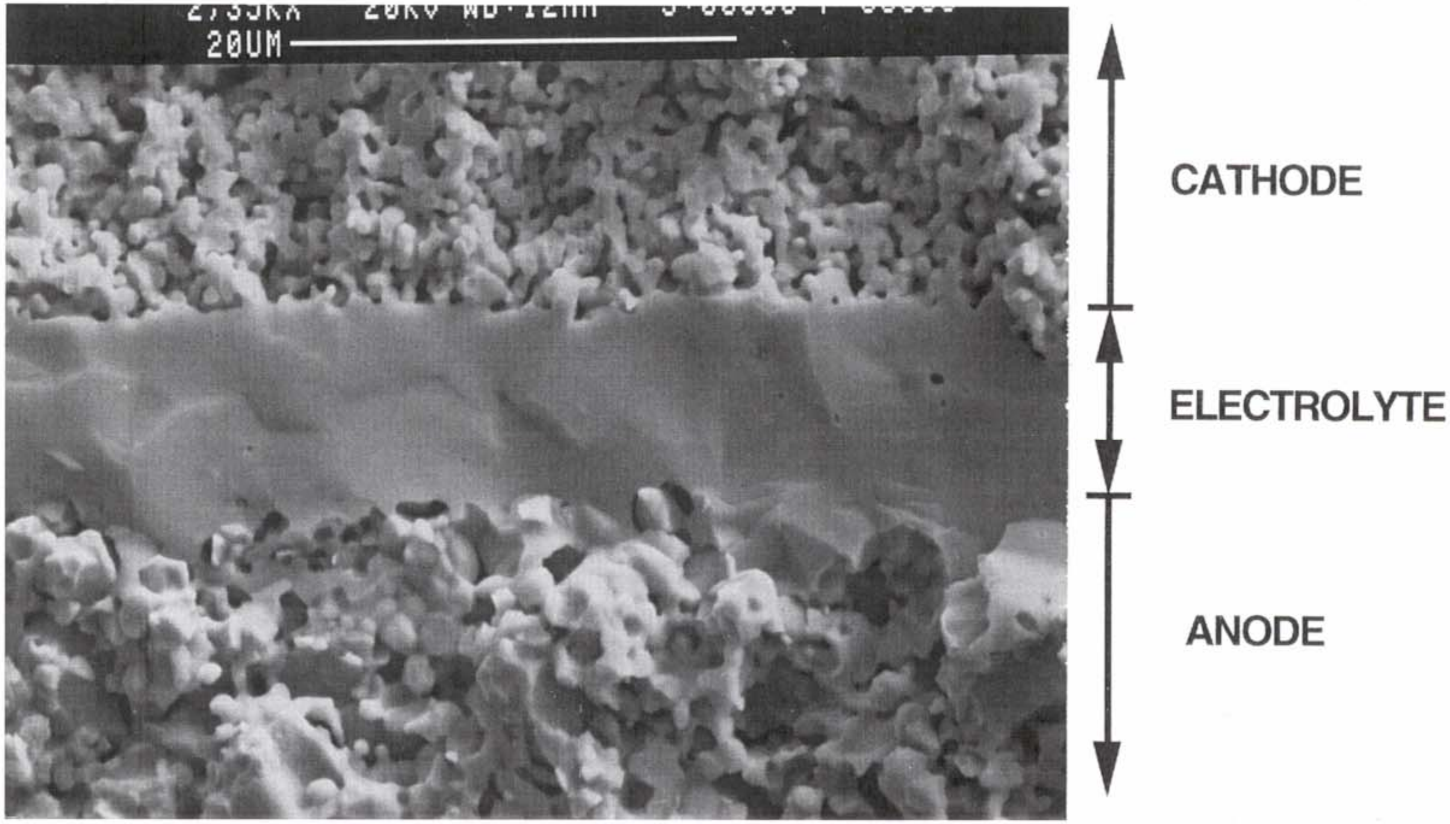
Glass-free compression seals: (1) Good control over component dimensions is needed to ensure good seal. (2) Resultant stack is not a rigid body – reduced tendency towards thermal stress fracture. (3) Cracked cell can be removed and replaced.

Monolithic design: (1) Can potentially circumvent sealing issue; if a stack can be sintered. (2) Resultant stack is a rigid body – greater tendency for thermal stress fracture; must be heated or cooled slowly. (3) When one cell cracks, the entire stack must be Discarded.

New Cell Materials

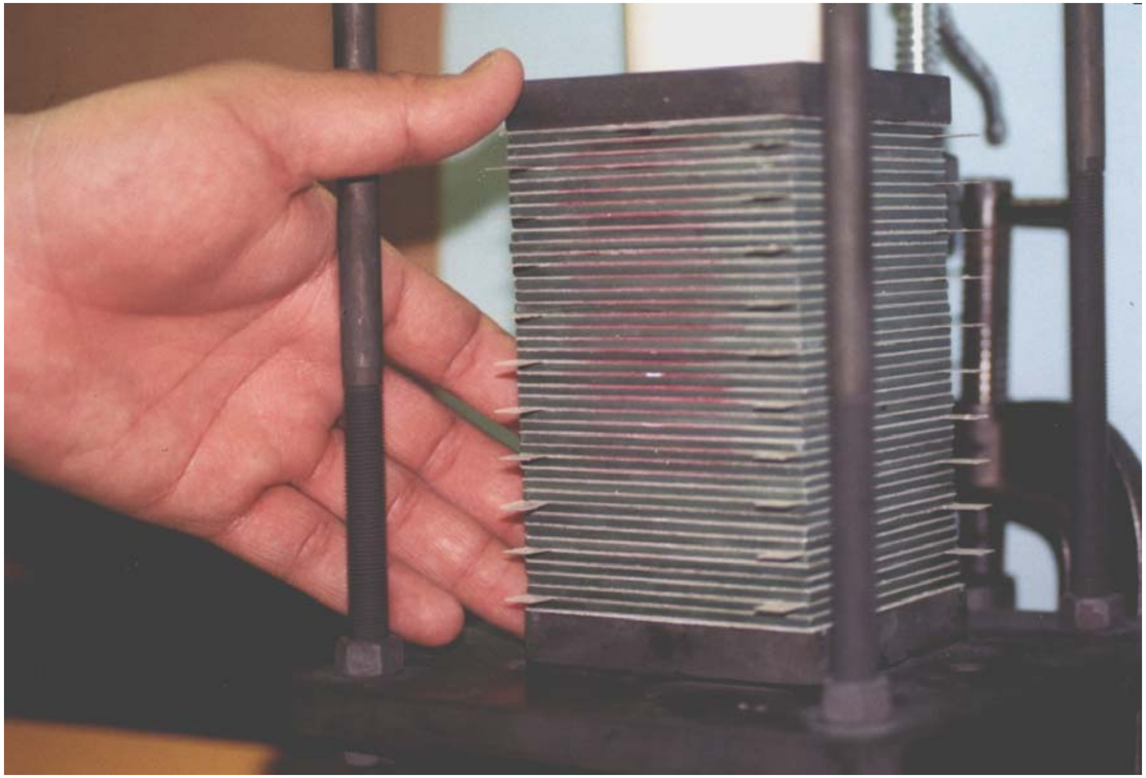
1) Electrolyte: LSGM or rare earth oxide-doped CeO_2, or some other
2) Cathode: Perovskites containing other rare earths; cobalt instead of Mn.

Typical Cell Microstructure



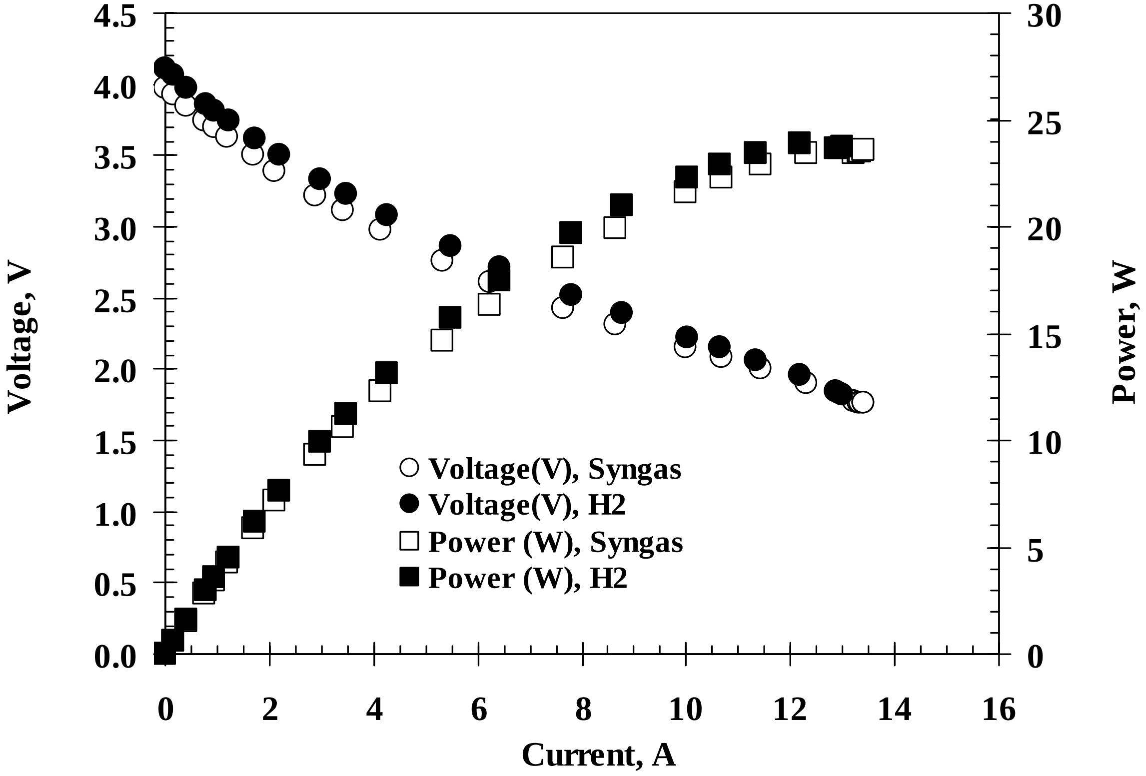
A Photograph of a 40 Cell Internally Manifolded Stack

A Photograph of a 250 W Stack



Projected power level ~400 W

Testing of a 4-Cell Stack with Reformed Methane



08-18-2000 Testing--4-Cell Stack: DWP 8020 regular cells
Fuel: Pure H_2 (138 hours) and Syngas :CH_4, H_2O, CO, CO_2
and H_2 (switched to syngas for 8 hours) (CH_4 : H_2O = 1 : 3)

Key Technical Issues

1. Low-cost, durable metallic separator
2. Development of a stable, reoxidizable anode
3. Improved electrodes for high performance at low (≤600°C) temperatures