Materials Challenges in Solid Oxide Fuel Cells

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A Lecture on Solid Oxide Fuel Cells
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Objectives of the Lecture

1) To serve as an introduction to SOFC; science and technology.
2) To identify key materials and microstructure- related parameters which determine performance of SOFC.
3) To identify and discuss thermo-mechanical issues concerning anode-supported cells.
4) To provide information on the fabrication of anode-supported SOFC and testing of button cells.
5) To provide a source of relevant literature.

Notes and Disclaimers

- The material given here is not complete, either in content, coverage of topics, and should be considered as reference material. There are numerous research articles, review articles, books, and symposia proceedings on this subject.
- Important source of literature is the series of proceedings volumes of ECS SOFC symposia, including the SOFC-IX being held at this meeting.
- The instructor's own knowledge of the field is by no means complete (it is a constant process of learning) and also the instructor cannot guarantee that it is without misconceptions.

Lecture Format

1) To provide a number of viewgraphs with several pictorials and illustrations.
2) To provide parametric equations that can assist in designing cells by allowing for parameter measurements - the objective is not to conduct detailed modeling.
3) To provide illustrative calculations.
4) To provide a list of selected references for one interested in further details.
5) The approach will be to give more material in these slides than can be covered in a two hour lecture.

Course Organization: Topics

Topic 1: A Brief Discussion of Solid Oxide Fuel Cell (SOFC) including relevant thermodynamics.

Topic 2: SOFC Materials: Electrolyte, Cathode, Anode; Cell Architecture on the Basis of Support

Topic 3: Sources of various voltage losses, and their dependence on cell parameters and test conditions.

Topic 4: Cell Design for Enhanced Performance

Topic 5: Cell Design – Thermo-mechanical Considerations

Topic 6: Cell Fabrication

Topic 7: Cell Testing

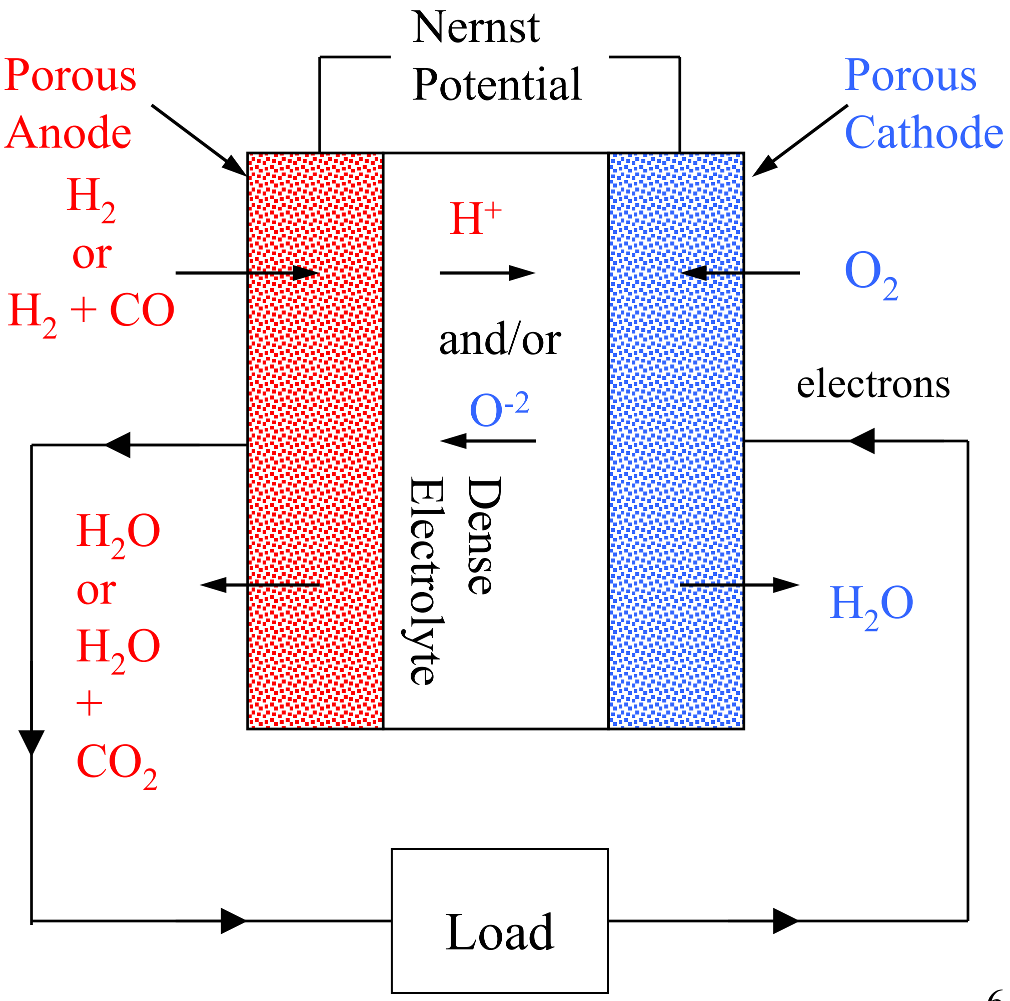
Topic 1: A Brief Description of Solid Oxide Fuel Cells (SOFC)

Three Components:

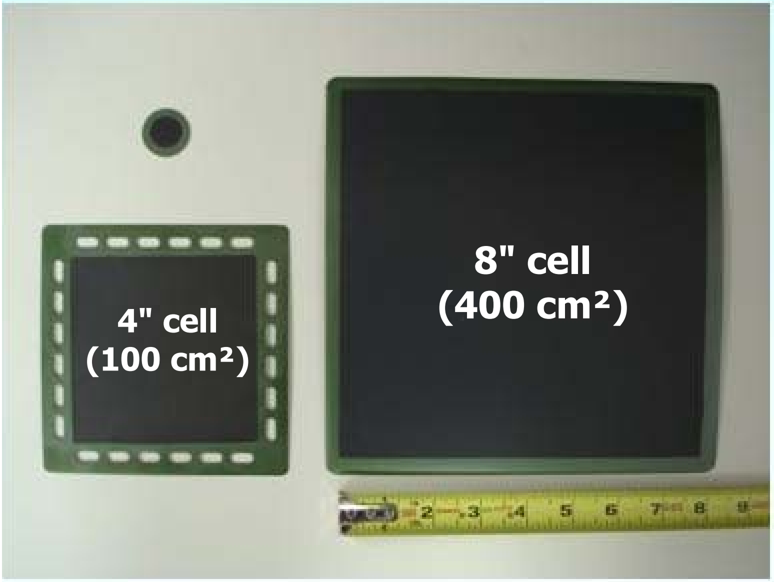
a) Cathode
b) Electrolyte
c) Anode

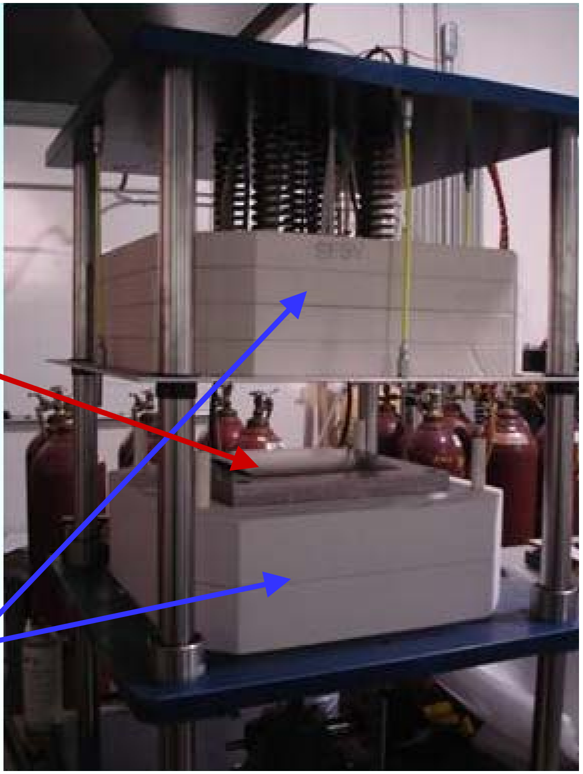
Most of the SOFC use oxygen ion (O^{-2}) conducting solid electrolyte. Limited work has been done on SOFC based on proton (H^+) conductors.

$$E = -\frac{\Delta G}{nF}$$



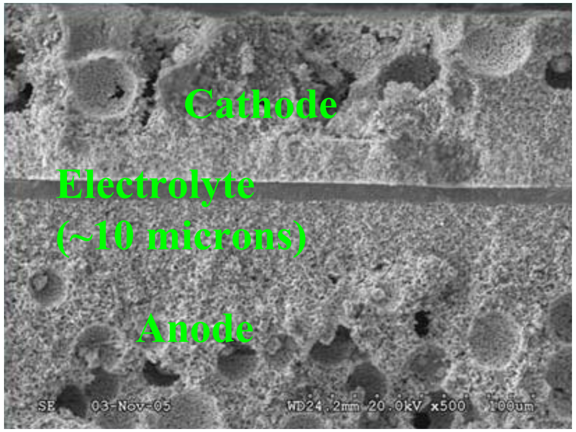
A Planar Cell and Test Fixture





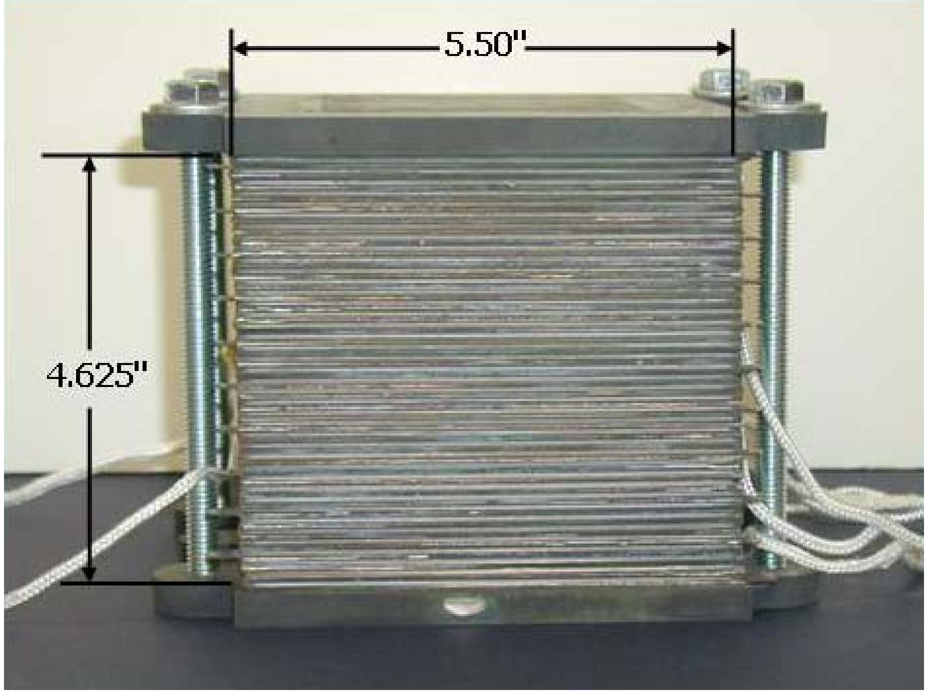
8" cell

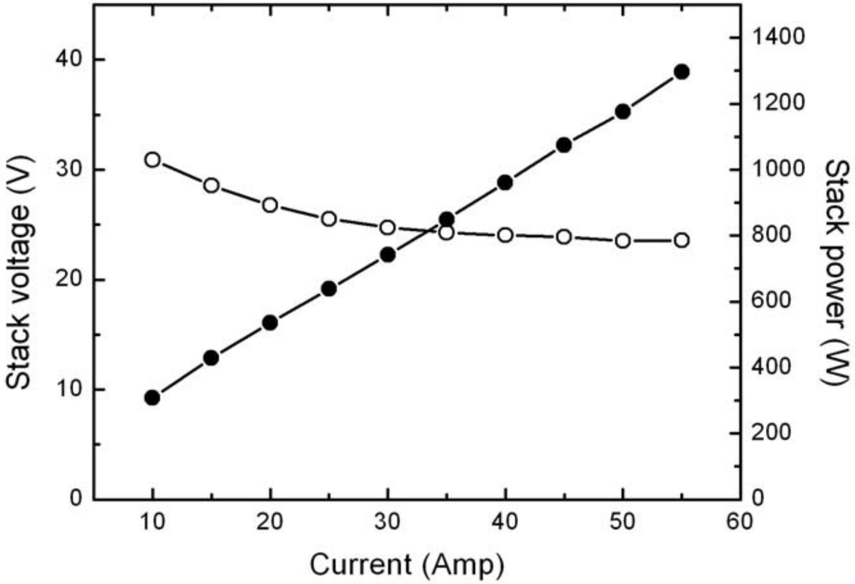
Cartridge heater + insulator



SEM Micrograph

SOFC 1 kW Stack





Stack dimensions: 5.5” × 5.5” × 4.625”
Volumetric power density = ~500 Watt/Liter
Internal manifolds; Cross-flow

Technology Objective: Higher specific power, greater efficiency, longer life, and lower cost

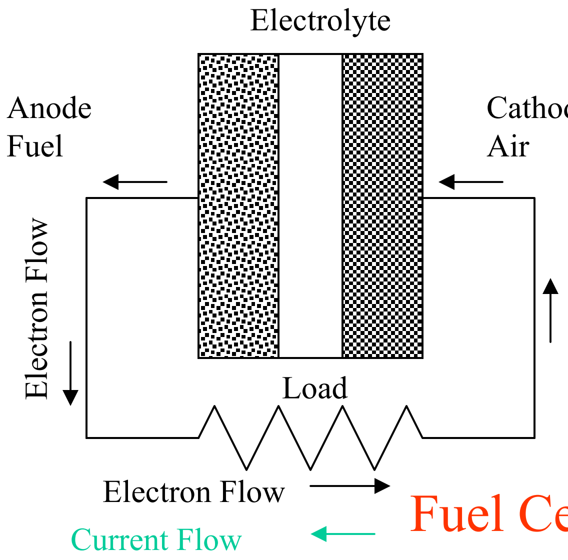
Functions of the Three Components

- Cathode: Transport of oxygen from the gaseous oxidant ($O_2 + N_2$) through the porous cathode to the cathode/electrolyte interface – diffusion/convection. Transport of electrons.
- Cathode: Conversion of O_2 into $2O^{-2}$ ions and transfer into the electrolyte – electrochemical reaction of reduction.
- Electrolyte: Transport of O^{-2} ions through the electrolyte towards the electrolyte/anode interface – ionic conduction.
- Anode: Transport of gaseous fuel (H_2 or H_2 + CO) through the porous anode towards the anode/electrolyte interface – diffusion/convection. Transport of electrons.
- Anode: Reaction of fuel (H_2 or H_2 + CO) with O^{-2} ions to form H_2O or $H_2O + CO_2$ and release of electrons for transport through the external circuit, through the load, to the cathode – electrochemical reaction of oxidation.

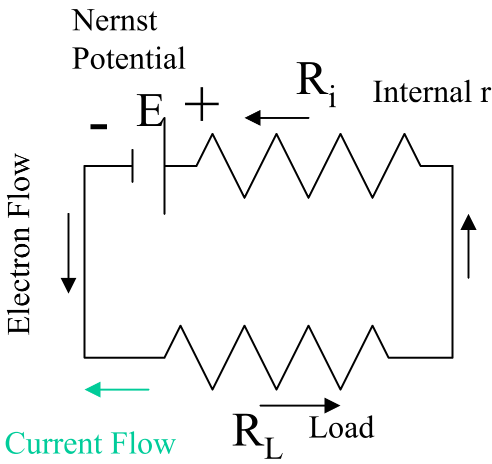
A Simplified Equivalent Circuit for SOFC

Ref. ‘Fuel Cells and Fuel Batteries’, H. A. Liebhafsky and E. J. Cairns

Fuel cell is essentially a primary battery where fuel is continually supplied to the anode, and oxidant is continually supplied to the cathode. The free energy of the oxidation of fuel is converted into electrical energy. The operation of the fuel cell is one way. Thus, it is not limited by the Carnot cycle, unlike a cyclic process, such as a heat engine. Being a battery, it can be represented by an equivalent circuit using a voltage source and, in the simplest case, using an internal resistance. When a load is connected in the external circuit, work is derived.

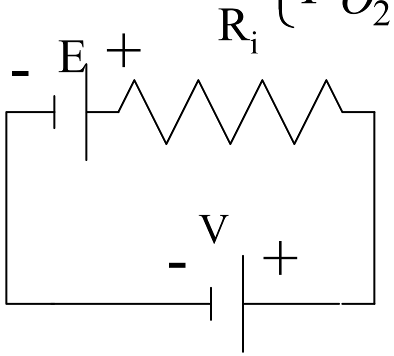


Fuel Cell



Equivalent Circuit

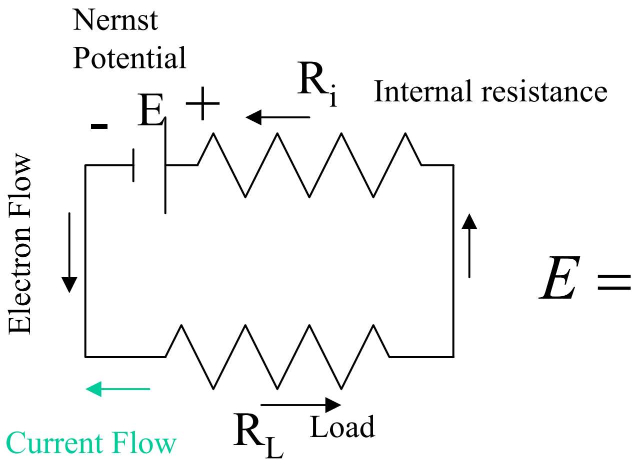
$$E = \frac{RT}{4F} \ln\left\{ \frac{p_{O_2}^{air}}{p_{O_2}^{fuel}} \right\}$$



Load Represented by a battery

V<E

Voltage vs. Current (or Current Density)



Equivalent Circuit

$$E = \frac{RT}{4F} \ln\left\{ \frac{p_{O_2}^{air}}{p_{O_2}^{fuel}} \right\}$$

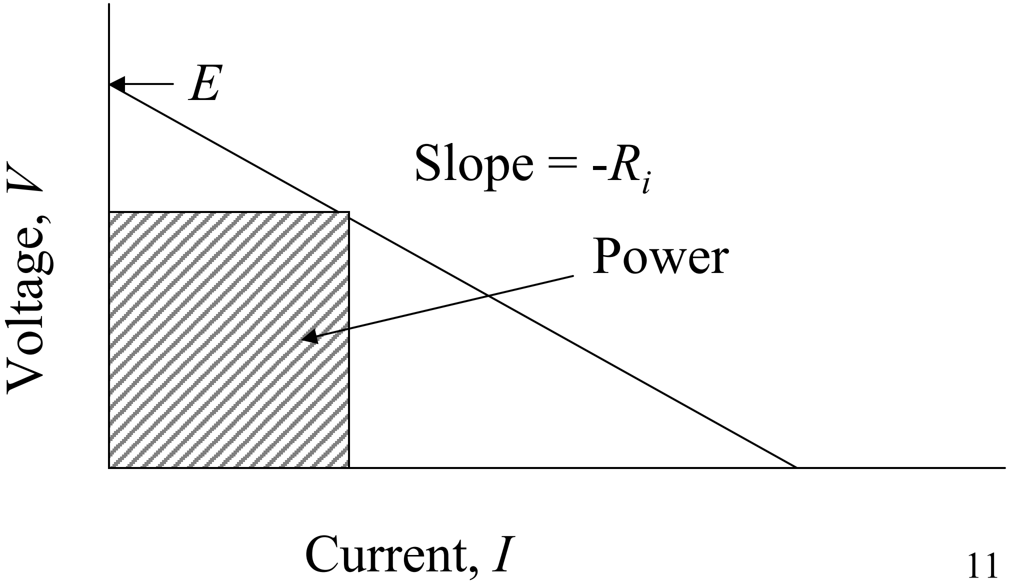
$$\text{Power} = I^2 R_L = \frac{V^2}{R_L} = \frac{E^2 R_L}{(R_i + R_L)^2} = VI$$

Current $I = \dfrac{E}{R_i + R_L}$

Voltage across Load or Cell $V = IR_L$

$$V = E - IR_i$$

Thus, by load we mean either R_L or I



Fuel Cell with Hydrogen as the Fuel

The chemical reaction with H_2 as the fuel is

$$H_2 + {}^1/_2O_2 \rightarrow H_2O$$

In a fuel cell, the reaction occurs electrochemically.
In what follows, we will assume the electrolyte to be an oxygen ion conductor. Then, the reactions at the two electrodes are:

Cathode: $\frac{1}{2}O_2 + 2e' \rightarrow O^{-2}$ Reduction of O atoms into O^{-2} ions

O^{-2} ions transport through the electrolyte towards the anode.

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

The electrons transport through the external circuit performing useful work. The overall reaction is the sum of the two.

The Overall Reaction: $H_2 + {}^1/_2O_2 \rightarrow H_2O$

ΔG^o :Standard free energy change

ΔG : Free energy change (partial pressures different from 1 atm).

Fuel Cell Efficiency (Standard State, Reversible)

Standard Gibbs Free Energy Change for the Reaction

Introduction to Thermodynamics of Materials D. R. Gaskell

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

All partial pressures are at 1 atm

ΔH^o = Standard enthalpy (H) change (H of one mole of H_2O at T and 1 atm. partial Pressure – H of one mole of H_2 at T and 1 atm. partial pressure – H of ½ mole of O_2 at T And 1 atm. partial rpessure)

ΔS^o = Standard entropy change.

F: Faraday constant (96,487 Coulombs/mol.)

Standard Gibbs Free Energy Change in terms of the Nernst Voltage

$$\Delta G^o = -2FE^o$$

'Introduction to Thermodynamics of Materials', D. R. Gaskell

Maximum Work (reversible process) in standard state is given by

$$w'^o_{\max} = -\Delta G^o = 2FE^o$$

Thermodynamic Efficiency when the cell is operated reversibly, and in standard state

$$\eta^o_{rev} = \frac{|\Delta G^o|}{|\Delta H^o|} = \frac{w'^o_{\max}}{|\Delta H^o|} = \frac{2FE^o}{|\Delta H^o|}$$

$E^o = 0.972$ at 800°C (1073 K)

When operated reversibly, the power is nearly zero.

Fuel Cell Efficiency (Non-Standard State, Reversible)

Gibbs Free Energy Change for the reaction when Reactants and products not in Standard States

Partial pressures different from 1 atm.

$$\Delta G = \Delta H - T\Delta S$$

Gibbs Free Energy Change in terms of the Nernst Voltage

$$\Delta G = -2FE$$

Maximum Work (reversible process) is given by

$$w'_{\max} = -\Delta G = 2FE$$

Thermodynamic Efficiency when the cell is operated reversibly

$$\eta_{rev} = \frac{|\Delta G|}{|\Delta H|} = \frac{w'_{\max}}{|\Delta H|} = \frac{2FE}{|\Delta H|} = \frac{2FE}{|\Delta H^o|}$$

For the assumption of an ideal gas, $\Delta H = \Delta H^o$

However, $\Delta S \neq \Delta S^o$

$S_{H_2} = S^o_{H_2} - R\ln p_{H_2}$ and similarly for other species.

$S^o{}_{H2}$ = Partial molar entropy of hydrogen in the standard state

Thermodynamic Efficiency

$$\Delta G^o = \Delta H^o - T\Delta S^o = \text{-247,500} + 55.85\,T \quad \text{j/mol.}$$

From Gaskell

$$\Delta G = \Delta H - T\Delta S = \Delta H^o - T\left(\Delta S^o - R\ln p_{H_2O}^{fuel} + R\ln p_{H_2}^{fuel} + \frac{1}{2}R\ln p_{O_2}^{air} \right)$$

	ΔH^o	ΔG^o	$\eta^o = \frac{\lvert\Delta G^o\rvert}{\lvert\Delta H^o\rvert}$	ΔG	$\eta = \frac{\lvert\Delta G\rvert}{\lvert\Delta H\rvert}$	$\eta_{0.8} = \frac{2F \times 0.8}{\lvert\Delta H\rvert}$
Temp. K	Standard Enthalpy (J/mol.)	Standard Free Energy (J/mol.)	Standard Therrmodynamic Efficiency (%)	$p_{O_2}^{air} = 0.21$ $\left(\frac{p_{H_2O}^{fuel}}{p_{H_2}^{fuel}}\right) = \frac{0.03}{0.97}$	Thermo -dynamic Efficiency (%)	Efficiency at 0.8 V (%)
1073	-247,500	-187,573	76%	-211,623	85.5%	78%
973	-247,500	-193,158	78%	-214,967	86.9%	78%
873	-247,500	-198,743	80%	-218,310	88.2%	78%
773	-247,500	-204,328	82.5%	-221,654	89.6%	78%
673	-247,500	-209,913	85%	-224,997	90.9%	78%
573	-247,500	-215,498	87%	-228,341	92.3%	78%

Free Energy and Reversible Work

Free Energy Change

$$\Delta G = G_{\text{products}} - G_{\text{reactants}}$$

$$\Delta G = \Delta G^o + RT\ln\left(\frac{p_{H_2O}^{fuel}}{p_{H_2}^{fuel}\sqrt{p_{O_2}^{air}}}\right) \quad \text{--(1)}$$

$$= \overline{G}_{H_2O}(\text{fuel}) - \overline{G}_{H_2}(\text{fuel}) - \frac{1}{2}\overline{G}_{O_2}(\text{air})$$

$\overline{G}_i$ = Chemical potential or partial molar free energy of i

Standard Free Energy and the Equilibrium Constant

$$\Delta G^o = -RT\ln K_{eq} = -RT\ln\left(\frac{p_{H_2O}^{fuel}}{p_{H_2}^{fuel}\sqrt{p_{O_2}^{fuel}}}\right) \quad \text{--(2)}$$

In the fuel itself, the reaction
$H_2(\text{fuel}) + 1/2O_2(\text{fuel}) \rightarrow H_2O(\text{fuel})$
Is in equilibrium. Thus,
$\Delta G = 0 = \Delta G^o + RT\ln K_{eq}$

Free Energy Change in terms of Oxygen Partial Pressures

Substitute for ΔG^o from (2) into (1)

$$\Delta G = -RT\ln\left(\frac{\sqrt{p_{O_2}^{air}}}{\sqrt{p_{O_2}^{fuel}}}\right) = -\frac{1}{2}RT\ln\left(\frac{p_{O_2}^{air}}{p_{O_2}^{fuel}}\right) \quad \text{--(3)}$$

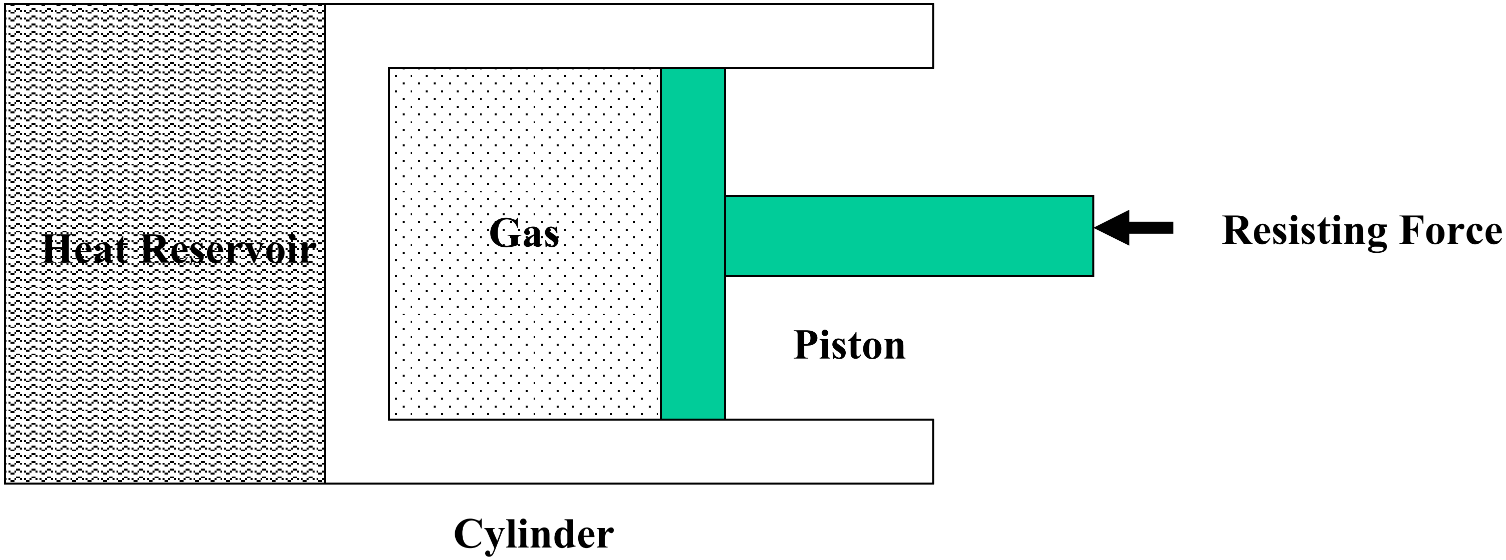
$$w = \int p\,dV = -RT\int\frac{dp}{p}$$

Maximum (Reversible) Work

$$w'^{\max}_{FC} = -\Delta G = \frac{1}{2}RT\ln\left(\frac{p_{O_2}^{air}}{p_{O_2}^{fuel}}\right)$$

Maximum work is the same as reversible, isothermal expansion of half a mole of oxygen gas.

Isothermal Reversible Expansion of an Ideal Gas



$$w'^{\max}_{FC} = -\Delta G = \frac{1}{2} RT \ln\left(\frac{p^{air}_{O_2}}{p^{fuel}_{O_2}}\right)$$

Free Energy and Reversible Work (contd.)

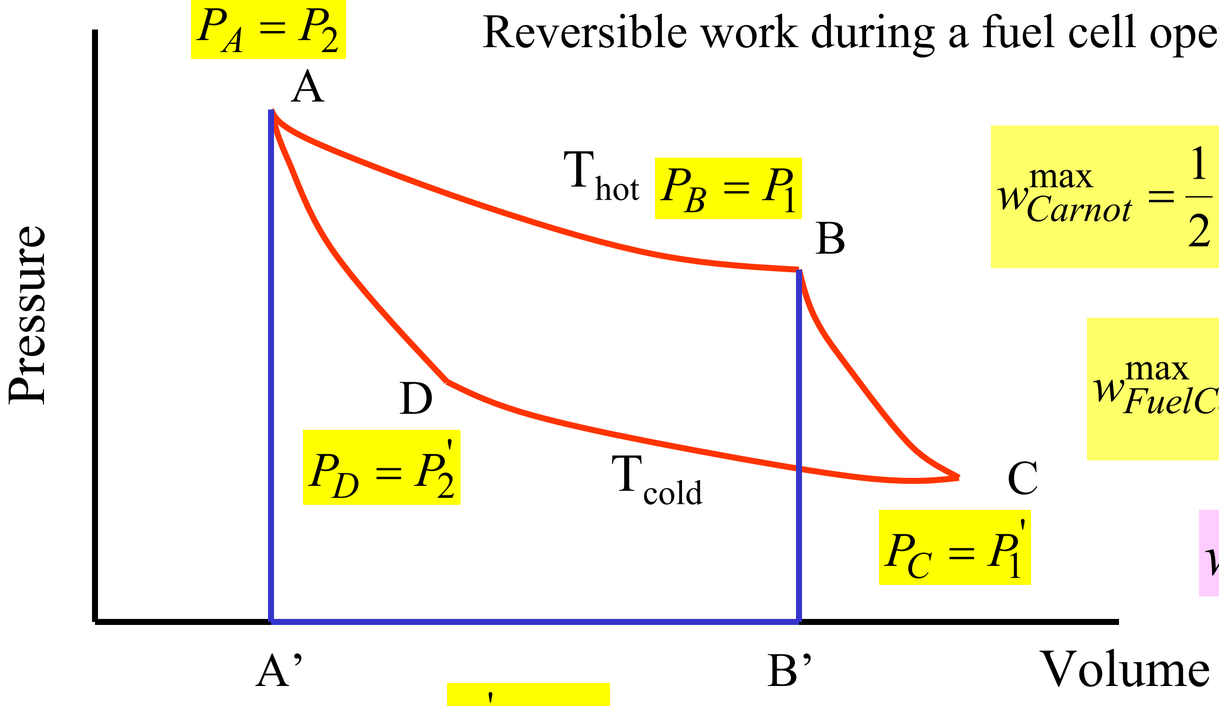
Maximum (Reversible) Work for a Carnot Cycle

$$w_{Carnot}^{\max} = \frac{1}{2} R\left(T_{hot} - T_{cold}\right) \ln\left(\frac{p_{O_2}^{air}}{p_{O_2}^{fuel}}\right)$$

Figure: A p-V diagram comparing a fuel cell and a Carnot engine.

Reversible work during a Carnot cycle = Area ABCDA

Reversible work during a fuel cell operation = Area ABB’A’A



$$w_{Carnot}^{\max} = \frac{1}{2} R\left(T_{hot} - T_{cold}\right) \ln\left(\frac{P_2}{P_1}\right)$$

$$w_{FuelCell}^{\max} = \frac{1}{2} R T_{hot} \ln\left(\frac{P_2}{P_1}\right)$$

$$w_{FuelCell}^{\max} > w_{Carnot}^{\max}$$

$$\frac{P_2'}{P_1'} = \frac{P_2}{P_1}$$

An Illustration

Fuel: H_2=97%, H_2O=3%: 1 atm. p^o_{H2}=0.97 atm, p^o_{H2O} = 0.03 atm
Oxidant: Air (21% O_2): 1 atm. p^o_{O2} = 0.21 atm, T = 800°C = 1073 K

Standard Free Energy of $H_2(g) + {}^1/_2O_2(g) \rightarrow H_2O(g)$
$\Delta G^o = \Delta H^o - T\Delta S^o = -247{,}500 + 55.85T$

Data from book on thermodynamics, e.g. Gaskell

$$K_{eq} = \exp\left(-\frac{\Delta G^o}{RT}\right) = \frac{p^o_{H_2O}}{p^o_{H_2}\left(p^{fuel}_{O_2}\right)^{1/2}}$$

$$p^{air}_{O_2} = 0.21 \text{ atm}$$

$$p^{fuel}_{O_2} = \left(\frac{p^o_{H_2O}}{p^o_{H_2}}\right)^2 \exp\left(\frac{2\Delta G^o}{RT}\right)$$

$$p^{fuel}_{O_2} = 5.23\text{x}10^{-22} \text{ atm}$$

Nernst voltage: $E = \frac{RT}{4F}\ln\left(\frac{p^{air}_{O_2}}{p^{fuel}_{O_2}}\right) = \frac{8.3144\times1073}{4\times96487}\ln\left(\frac{0.21}{5.23\times10^{-22}}\right)$

$= 1.0966 \text{ V}$

Free Energy, Work and Efficiency

Fuel Cell Maximum (Reversible) Work and EMF

$$w_{FC}^{\max} = -\Delta H^o + T\left(\Delta S^o + R\ln\left(\frac{p_{H_2}^{fuel}\sqrt{p_{O_2}^{air}}}{p_{H_2O}^{fuel}}\right)\right)$$

Nernst Voltage

$$E = -\frac{\Delta G}{2F} = \frac{-\Delta H^o + T\left(\Delta S^o + R\ln\left(\frac{p_{H_2}^{fuel}\sqrt{p_{O_2}^{air}}}{p_{H_2O}^{fuel}}\right)\right)}{2F}$$

Work when the cell is operated irreversibly

$$w_{FC} = 2FV < w_{FC}^{\max}$$

Thermodynamic Efficiency

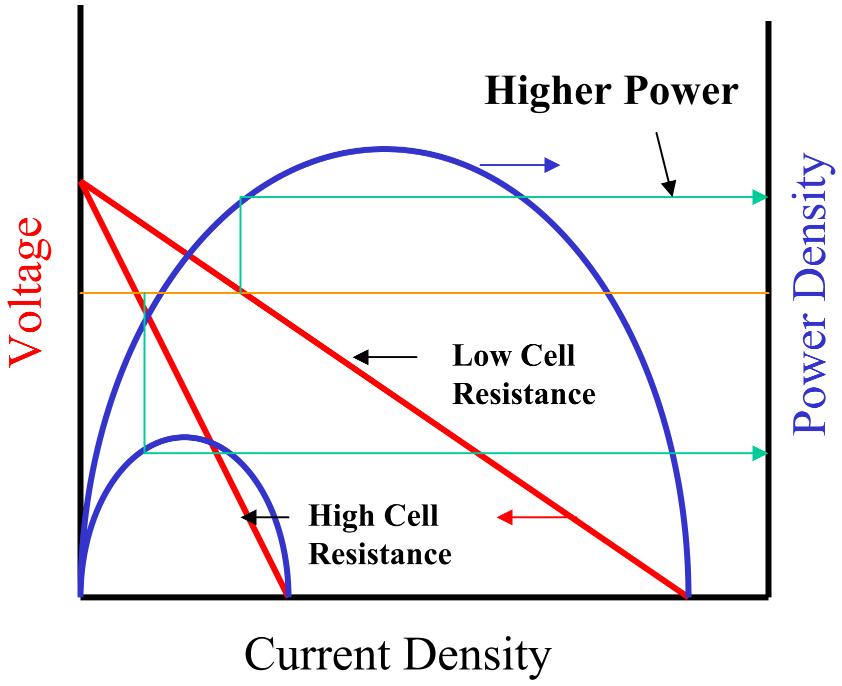
$$\eta = \frac{2FV}{-\Delta H} = \frac{\text{Work Derived}}{|\text{Enthalpy Change}|}$$

Voltage Efficiency

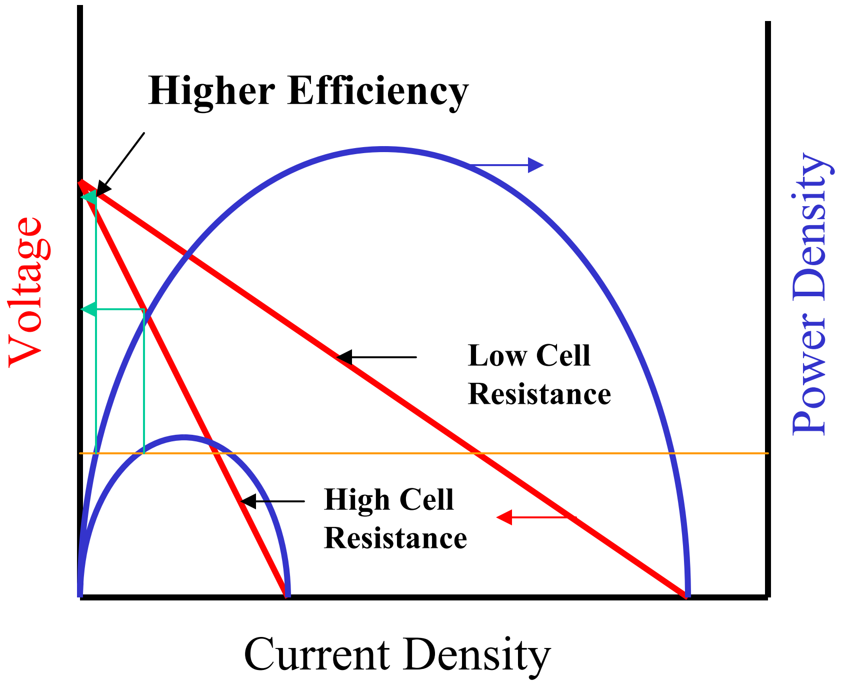
$$\eta_v = \frac{V}{E} = \frac{\text{Work Derived}}{|\text{Gibbs Free Energy Change}|}$$

The objective is to maximize η_v for a given power level, or maximize power at a given η_v.

Maximize Power at Given Efficiency or Efficiency at Given Power



Power Density at a Given Efficiency

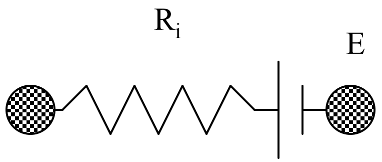


Efficiency at a Given Power Density

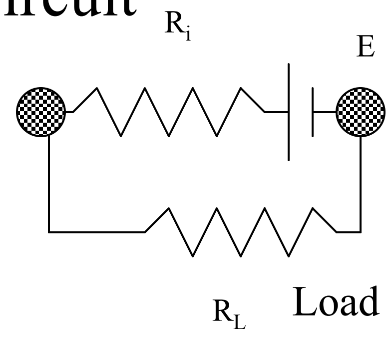
Either way, the lower the cell resistance, the better

Thermodynamics in Terms of Cell Parameters and Load

An Equivalent Circuit



Equivalent circuit for the cell

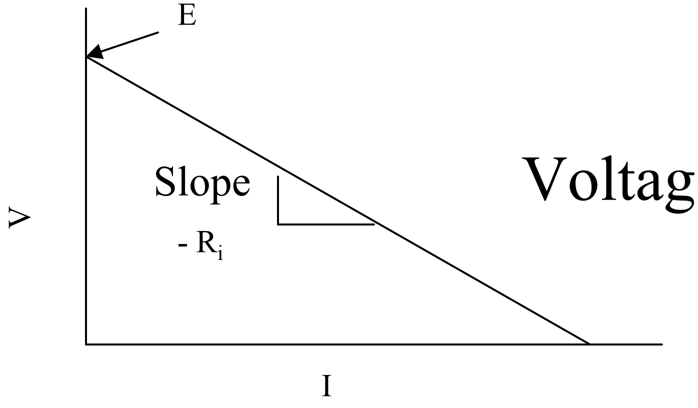


All sources of voltage losses in The cell are lumped into R_i.

(This is a simplification, made just for the sake of simplified discussion. The V-I curve is rarely linear).

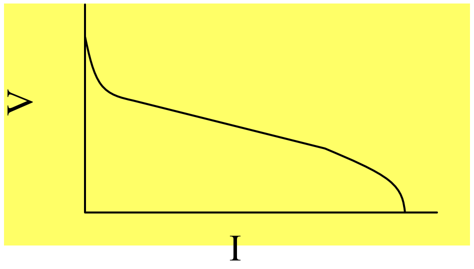
Voltage vs. Current Plot

Current, $$I = \frac{E}{R_i + R_L} = -\frac{\Delta G}{2F\left(R_i + R_L\right)}$$

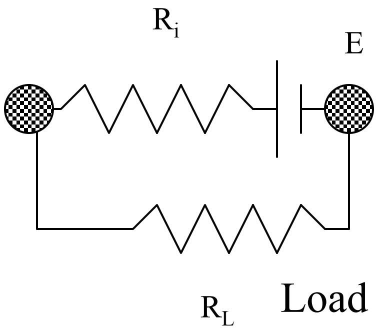


Voltage, $$V = IR_L = E - IR_i$$

The above is idealized. Usually, the V-I trace is nonlinear.



Thermodynamics in Terms of Cell Parameters and Load (contd.)



Equivalent Circuit

Power $P = VI$ Voltage $V = E - IR_i$ Current $I = \dfrac{E}{R_i + R_L}$

Internal Rate of Heat Dissipation into work or heat $\overset{\circ}{Q}' = I^2 R_i$ $\overset{\circ}{Q}' = I^2 R_i = \dfrac{E^2 R_i}{(R_i + R_L)^2}$

Rate of Free Energy Conversion $P + \overset{\circ}{Q}' = VI + I^2 R_i$ $P + Q' = EI = E\dfrac{dq}{dt}$

Time Required to Consume One Mole of Hydrogen $t = \dfrac{(R_i + R_L)2F}{E}$

Work Done $w' = Pt = VIt = 2FV = \dfrac{2FER_L}{(R_i + R_L)} = \boxed{-\Delta G \dfrac{R_L}{(R_i + R_L)}}$

Heat Dissipated $Q' = \overset{\circ}{Q}'t = \dfrac{2FER_i}{(R_i + R_L)} = \boxed{-\Delta G \dfrac{R_i}{(R_i + R_L)}}$

Recall

$\Delta G < 0$

The Sum $w' + Q' = 2FE = -\Delta G$

Thermodynamics in Terms of Cell Parameters and Load (contd.)

First Law $\Delta U = Q - w = U_2 - U_1$

Q = Heat absorbed by the system
w = Work done by the system

Isothermal Process $Q = T\left(S_2 - S_1\right) - T\Delta S_{irr}$

$$\Delta S = S_2 - S_1 = \frac{Q}{T} + \Delta S_{irr}$$

'Introduction to the Thermodynamics of Materials' D. R. Gaskell

Isobaric Process $w = w' + P\left(V_2 - V_1\right)$

For an Isothermal-Isobaric Process

$$\Delta G = G_2 - G_1 = U_2 + PV_2 - TS_2 - U_1 - PV_1 + TS_1$$

$$\Delta G = -2FE \qquad \Delta G = -T\Delta S_{irr} - w'$$

The above gives

Maximum possible work

Loss – degree of irreversibility.

$$w' = -\Delta G - T\Delta S_{irr} \qquad w' = \underset{\text{Maximum possible work}}{2FE} - \underset{\text{Loss – degree of irreversibility.}}{T\Delta S_{irr}}$$

We also have

$$w' = Pt = VIt = 2FV = \frac{2FER_L}{\left(R_i + R_L\right)} = 2FE - 2FE\frac{R_i}{\left(R_i + R_L\right)}$$

Thermodynamics in Terms of Cell Parameters and Load (contd.)

Degree of Irreversibility

$$\Delta S_{irr} = \frac{2FE}{T}\left(\frac{R_i}{R_i+R_L}\right) = \boxed{-\frac{\Delta G}{T}\left(\frac{R_i}{R_i+R_L}\right)}$$

Need to Lower R_i

Rate of Irreversible Entropy Production

$$\frac{dS_{irr}}{dt} = \frac{\Delta S_{irr}}{t} = \frac{2FE}{T}\left(\frac{R_i}{R_i+R_L}\right)\times\frac{E}{2F\left(R_i+R_L\right)} = \frac{E^2 R_i}{T\left(R_i+R_L\right)^2}$$

Thermodynamic Efficiency

$$\eta = \frac{2FV}{\left|\Delta H\right|} = \frac{2FE}{\left|\Delta H\right|}\left(\frac{R_L}{R_i+R_L}\right) = \eta_{rev}\left(\frac{R_L}{R_i+R_L}\right) = \boxed{\frac{\left|\Delta G\right|}{\left|\Delta H\right|}\left(\frac{R_L}{R_i+R_L}\right)}$$

Need to Lower R_i

Rate of Heat Exchange with the Surroundings

Heat produced per mole of hydrogen consumed

$$Q = T(S_2 - S_1) - T\Delta S_{irr} = T(S_2 - S_1) - 2FE\left(\frac{R_i}{R_i + R_L}\right)$$

Note that $\Delta S = S_2 - S_1 < 0$.

Rate of heat production (exothermic)

$$\overset{\circ}{Q} = \frac{Q}{t} = \frac{Q}{\frac{2F(R_i + R_L)}{E}} = \frac{T(S_2 - S_1)}{2F(R_i + R_L)} - \frac{E^2 R_i}{(R_i + R_L)^2}$$

Need to Lower R_i

What Does this all Mean For an SOFC?

1) Magnitude of free energy of the reaction (with free energy < 0) must be as high as possible to achieve the highest possible conversion of chemical energy into electrical energy. With H_2 (or CO) as the fuel, this implies, **the lower the temperature, the higher is the thermodynamic efficiency**.
2) The internal cell resistance must be as small as possible. Thus, every effort must be made to lower the overall cell resistance. Since the V-I relationship is usually nonlinear, it is necessary to address voltage losses (polarizations) at both electrodes as well. **The higher the temperature, the lower the resistance.**

Now we will devote next several slides on understanding what are the main contributions to the cell 'resistance', and how to lower the cell resistance, which is in fact the main part of this part of this lecture.

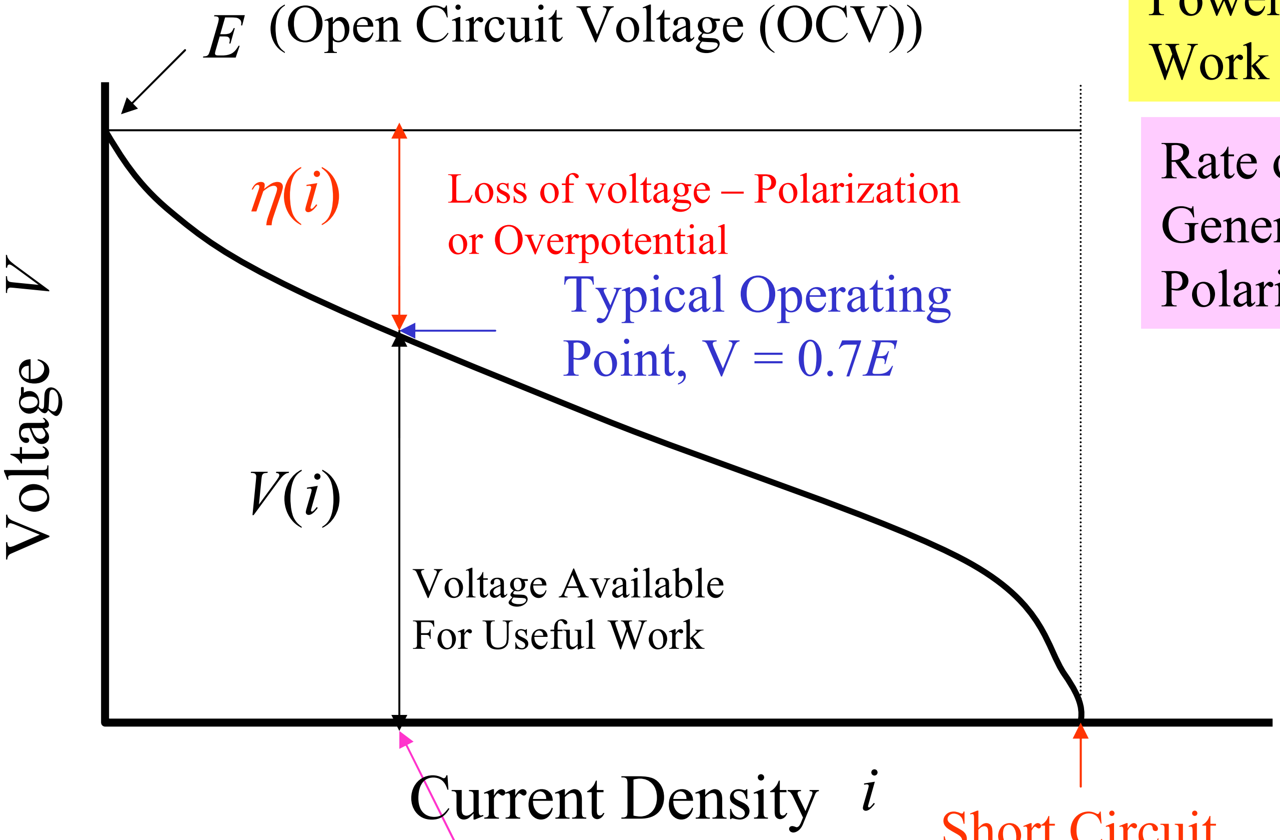
Solid Oxide Fuel Cells: General

$$E = -\frac{\Delta G}{nF}$$

Polarization or Overpotential $\eta(i)$

Power: Rate of Work Derived $= V(i)i \quad \mathrm{W/cm^2}$

Rate of Heat Generation by Polarization $= \eta(i)i \quad \mathrm{W/cm^2}$



E (Open Circuit Voltage (OCV))

Voltage V

$\eta(i)$

Loss of voltage – Polarization or Overpotential

Typical Operating Point, V = 0.7E

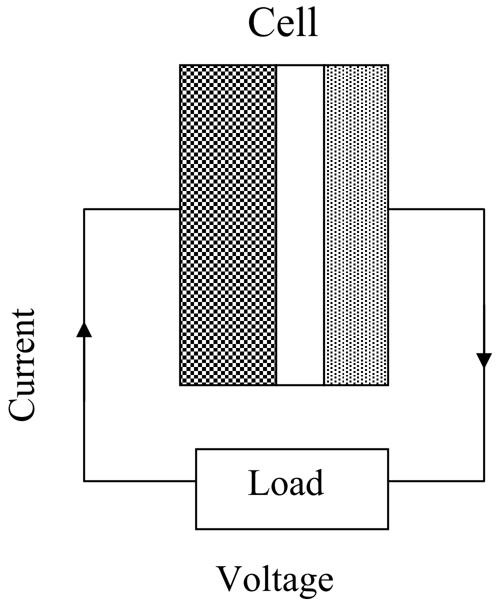
$V(i)$

Voltage Available For Useful Work

Current Density i

Operating Current Density

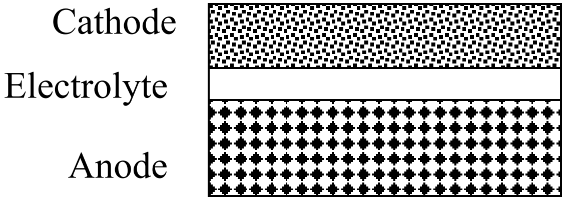
Short Circuit Current Density



Objective: Lower $\eta(i)$ to as low a value as possible.

Topic 2: SOFC Materials: Electrolyte, Cathode, Anode; Cell Architecture on the Basis of Support

- Electrolyte: A dense (no open, connected porosity) Yttria Stabilized Zirconia (YSZ) A solid solution between ZrO_2 and Y_2O_3 (~8 mol.% Y_2O_3, ~92 mol.% ZrO_2).
- Anode: A porous, two-phase composite of Ni + YSZ.
- Cathode: A porous, two-phase composite of LSM + YSZ. (LSM: Sr-doped $LaMnO_3$; typical composition – $La_{0.8}Sr_{0.2}MnO_{(3-\delta)}$).



YSZ Electrolyte: Defect Chemistry

$Y_xZr_{(1-x)}O_{(2-x/2)}$

Over the temperature and oxygen partial pressure ranges of interest, the predominant point defects are oxygen vacancies. The electroneutrality condition is given by

$$\left[Y_{Zr}^{'}\right] = 2\left[V_{O}^{\bullet\bullet}\right]$$

For this reason, YSZ is predominantly an oxygen ion conductor.

LSM Cathode: Defect Chemistry

LSM: $La_{(1-x)}Sr_xMnO_{(3-\delta)}$ is a perovskite

Mn is predominantly in +3 state. Sr substitution on the A-site (La-site) leads to the creation of oxygen vacancies. This further leads to the absorption of oxygen by oxidizing Mn from +3 to +4 states. Charge compensation is achieved by the formation of electron holes. Thus, LSM is predominantly a p-type material.

$$V_O^{\bullet\bullet} + \frac{1}{2} O_2(g) \rightarrow O_O^{\times} + 2h^{\bullet}$$

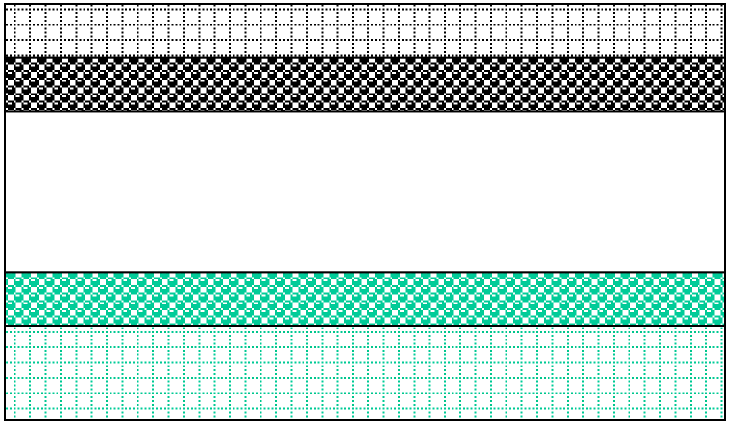
Electronic conductivity $\sigma_{el} \propto p_{O_2}^{1/4}$

Other SOFC Materials

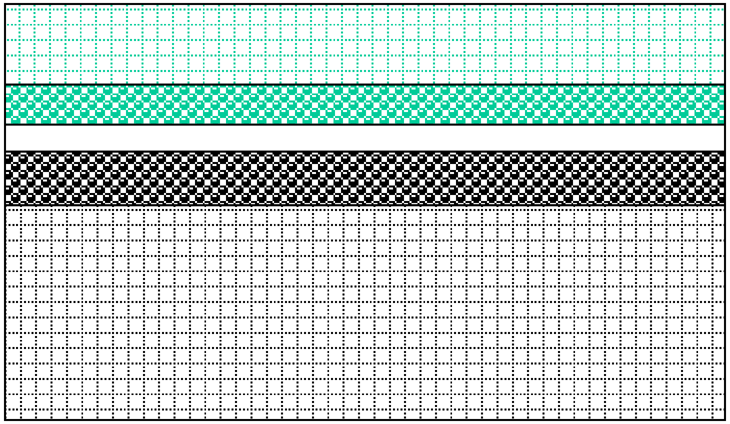
- Electrolyte: Rare earth oxide doped CeO_2 (e.g. Gd_2O_3-CeO_2 - GDC); Sr-doped and Mg-doped $LaGaO_3$ (LSGM).
- Cathode: Single Phase - Sr-doped $LaCoO_3$ (LSC), Sr-doped $LaFeO_3$ (LSF), LSCF, etc.; Composite – LSM + Rare earth oxide doped CeO_2 – e.g. GDC, LSM + LSGM; LSF + GDC, LSCF + GDC, etc.
- Anode: Ni + Rare earth oxide doped CeO_2 – GDC; Cu + CeO_2; La-doped $SrTiO_3$, etc.

Many of these materials are currently being explored as they offer certain advantages over the state of the art materials; e.g. LSGM has higher ionic conductivity than YSZ. However, there also are associated challenges. Thus, state of the art materials stated earlier (or small variations from them) continue to be widely used.

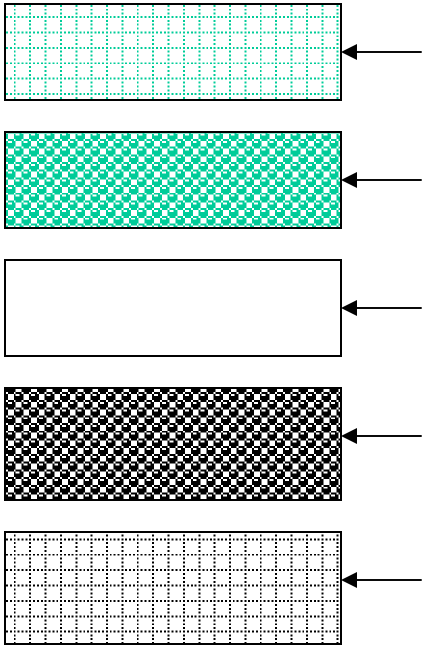
SOFC Designs Based on Relative Thicknesses



ELECTROLYTE-SUPPORTED



CATHODE-SUPPORTED



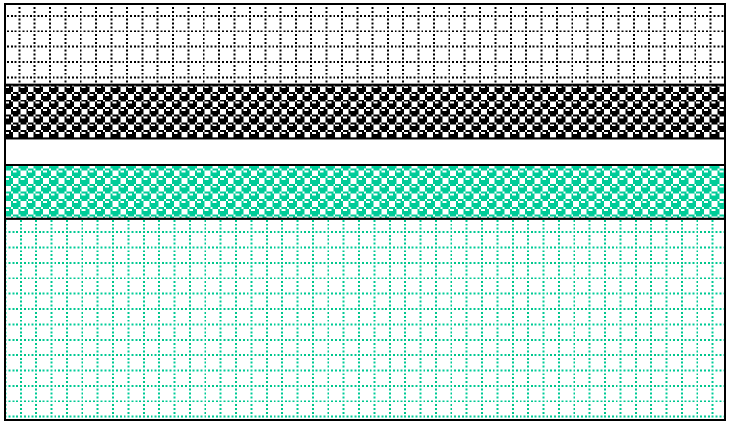
Anode Support or Anode Current Collector

Anode Functional Layer

Electrolyte

Cathode Functional Layer

Cathode Current Collector or Support



ANODE-SUPPORTED

Types and Approximate Magnitudes of Conductivities (Resistivities) of the Various Layers (800°C)

- Anode Support or Current Collector: Electronic ~1,000 S/cm (~0.001 Ωcm).
- Anode Functional Layer: Electronic ~500 S/cm (~0.002 Ωcm).
- Electrolyte: Ionic ~0.033 S/cm (~30 Ωcm).
- Cathode Functional Layer: Electronic ~50 S/cm (0.02 Ωcm).
- Cathode Current Collector or Support: Electronic ~100 S/cm (~0.01 Ωcm).

Calculations of the Approximate Ohmic Area Specific Resistance (ASR) at 800°C for the Three Types of Designs

Electrolyte Ionic Resistivity: $\rho_e = 30\ \Omega\text{cm}$

Cathode (Both Layers) Electronic Resistivity: $\rho_c = 0.01\ \Omega\text{cm}$

Anode (Both Layers) Electronic Resistivity: $\rho_a = 0.005\ \Omega\text{cm}$

Electrolyte Thickness: ℓ_e (cm) Anode (Total) Thickness: ℓ_a (cm)

Cathode (Total) Thickness: ℓ_c (cm)

Ohmic Area Specific Resistance (ASR): $R_i = \rho_e\ell_e + \rho_c\ell_c + \rho_a\ell_a$ Ωcm^2

Electrolyte Supported: $(30\text{x}0.015+0.01\text{x}0.01+0.005\text{x}0.01) = 0.4502\ \Omega\text{cm}^2$

Cathode Supported: $(30\text{x}0.001+0.01\text{x}0.2+0.005\text{x}0.01) = 0.0321\ \Omega\text{cm}^2$

Anode Supported: $(30\text{x}0.001+0.01\text{x}0.01+0.005\text{x}0.1) = 0.0306\ \Omega\text{cm}^2$

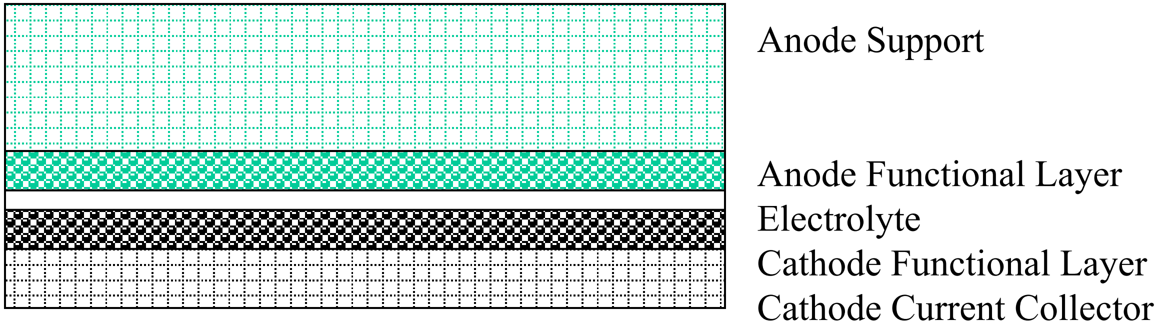
Electrolyte-Supported: High ASR

Electrode-supported: Low ASR

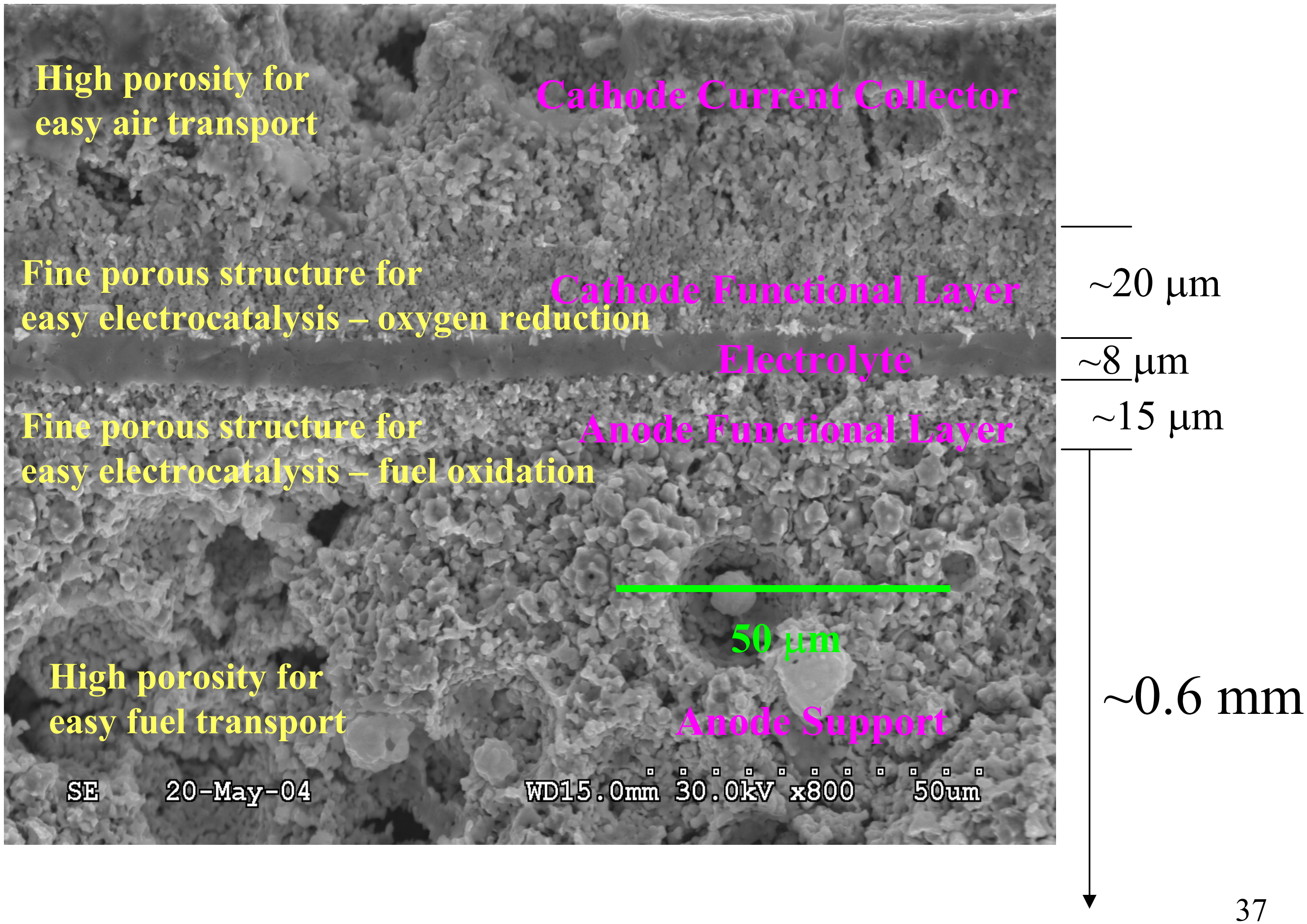
Cell Resistance = ASR (Ωcm^2)/Cell Area (cm^2) = Ω (ohms)

A Typical, Five Layer Anode-Supported Cell: Various Layers and their Functions

- **Anode support:** Ni + YSZ, ~0.3 to ~1 mm, ~40% porosity, Coarse microstructure: Electronic conduction, fuel gas transport.
- **Anode Functional Layer:** Ni + YSZ, ~10 to ~20 microns, ~25% porosity, fine microstructure: Mixed Ionic (YSZ) and Electronic (Ni) conduction, fuel gas transport - electrochemical reaction.
- **Electrolyte:** YSZ, ~5 to 10 microns, dense (no connected porosity), fine microstructure: Ionic conduction.
- **Cathode Functional Layer:** LSM + YSZ, ~10 to ~20 microns, ~25% porosity, fine microstructure: Mixed Ionic (YSZ) and Electronic (LSM) conduction, oxidant gas transport – electrochemical reaction.
- **Cathode Current Collector:** LSM, ~50 to ~150 microns, ~40% porosity, Coarse microstructure: Electronic conduction, oxidant gas transport.



An SEM Micrograph of an Anode-Supported Cell (Microstructure)



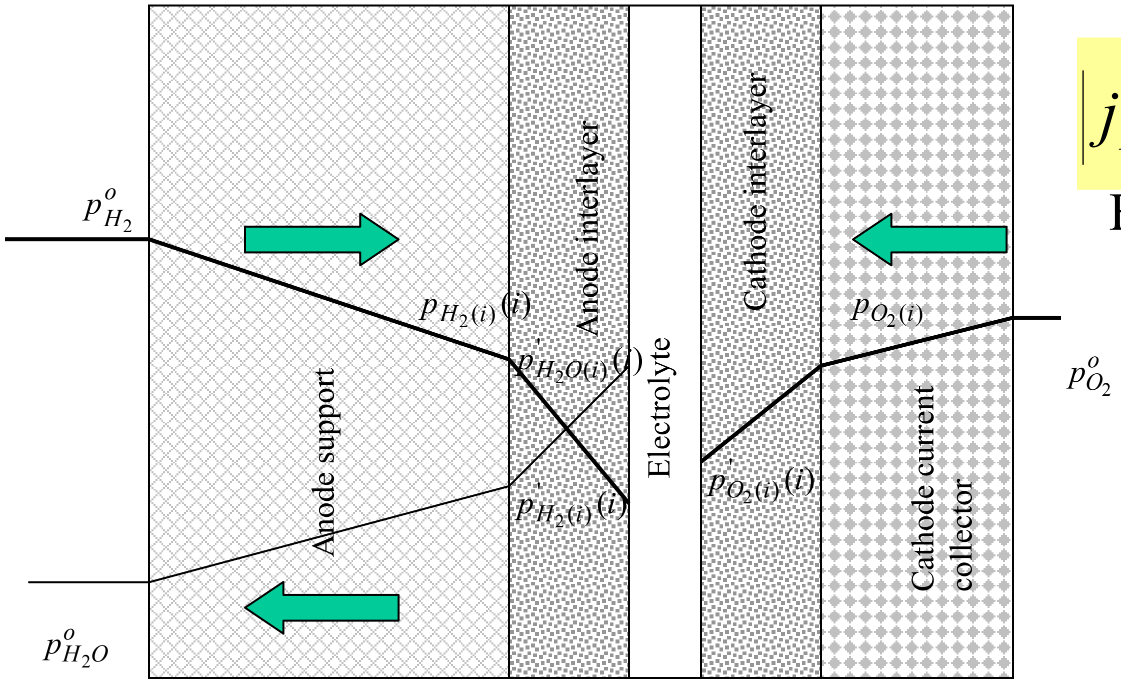
Attributes of Anode-Supported Design

- Easy fabrication with Ni + YSZ as starting materials.
- NiO and YSZ neither dissolve in each other nor react with each other.
- The presence of two phases helps maintain the microstructure fine.
- The electrolyte/anode bi-layer or cathode/electrolyte/anode tri-layer can be fabricated in a single firing step.
- The presence of a large amount of Ni improves heat transfer.
- Cell is quite robust.

Topic 3: Sources of various voltage losses, and their dependence on cell parameters and test conditions.

- Voltage loss associated with ‘resistance’ to gas transport through porous anode – Anode Concentration Polarization or Concentration Overpotential.
- Voltage loss associated with ‘resistance’ to gas transport through porous cathode – Cathode Concentration Polarization or Concentration Overpotential.
- Voltage loss associated with the ‘resistance’ to electrochemical oxidation of fuel at the anode – Anode Activation Polarization or Activation Overpotential.
- Voltage loss associated with the ‘resistance’ to electrochemical reduction of oxygen at the anode – Cathode Activation Polarization or Activation Overpotential.
- Voltage loss associated with resistance to ion transport through the electrolyte, electron transport through electrodes – Ohmic Loss.

Gas Transport through Electrodes



$$\left|j_{H_2}\right| = \left|j_{H_2O}\right| = 2\left|j_{O_2}\right| = \frac{iN_A}{2F}$$

Fluxes in #/cm^2.s

$$j_{H_2} \propto \left(p^o_{H_2} - p_{H_{2(\text{int})}}\right)$$

$$j_{O_2} \propto \left(p^o_{O_2} - p_{O_{2(\text{int})}}\right)$$

Fluxes of hydrogen and water vapor through anode depend upon: (1) Binary H_2-H_2O Diffusivity. (2) Porosity. (3) Pore size. (4) Tortuosity. (5) Thickness. (6) Partial pressure of hydrogen in the fuel, **p^oH_2**.

Flux of oxygen through cathode depends upon: (1) Binary O_2-N_2 diffusivity. (2) Porosity. (3) Pore size. (4) Tortuosity. (5) Thickness. (6) Partial pressure of oxygen in the oxidant, **p^oO_2**.

$H_2 + O^{-2} \rightarrow H_2O + 2e$ **Anode Interlayer** $^1/_2O_2 + 2e \rightarrow O^{-2}$ **Cathode Interlayer**

Fluxes and Current Density

$$i = \frac{I}{A}$$

$I =$ Current in Amps (A)

$A =$ Active Cell Area (cm^2)

$i =$ Current Density (A/cm^2)

$j_{H_2} =$ Flux of Hydrogen (moles/(sec.cm^2))

For every one mole of H_2 passed (consumed) per unit time per unit area 2 moles of electrons are passed in the external circuit; that is $2F$ where F = Faraday constant (96,487 Coulombs/mole). Thus,

$$i = 2Fj_{H_2}$$

Also, for every one mole of H_2 consumed per unit time per unit area half a mole of O_2 is consumed per unit time per unit area and one mole of H_2O is formed per unit time per unit area. Thus,

$$i = 2F\left|j_{H_2}\right| = 2F\left|j_{H_2O}\right| = 4F\left|j_{O_2}\right|$$

Gas Transport and Voltage Loss

Note

$$p_{O_2}^{'(c)} < p_{O_2}^{o(c)}$$

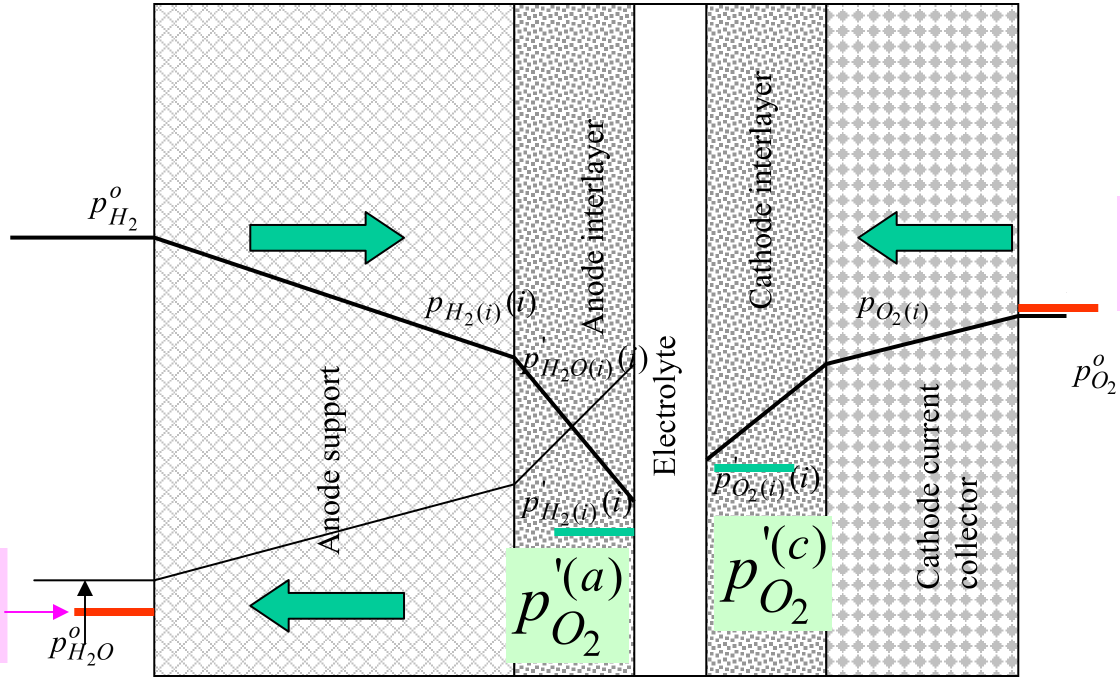
$$p_{O_2}^{'(a)} > p_{O_2}^{o(a)}$$

Nernst Voltages

$$E = \frac{RT}{4F} \ln\left(\frac{p_{O_2}^{o(c)}}{p_{O_2}^{o(a)}}\right)$$

$$E' = \frac{RT}{4F} \ln\left(\frac{p_{O_2}^{'(c)}}{p_{O_2}^{'(a)}}\right)$$

$p_{O_2}^{o(a)}$



$p_{O_2}^{o(c)}$

Thus, $E > E'$

Loss of voltage = $E - E'$

Concentration polarization or concentration overpotential at the anode + cathode

E' = Nernst voltage across the electrolyte when cell is under load (finite non zero current)

Electrode Design for Minimizing Concentration Polarization

- For a given current density, minimize partial pressure variations through the electrodes.
- Minimize the thicknesses of the electrodes – consistent with sufficient in-plane electrical conduction (low sheet resistance) and mechanical ruggedness.
- Increase porosity – again consistent with in-plane electrical conduction and mechanical ruggedness.
- Increase pore size.

Materials Processing procedures required to ensure that the desired microstructures at the desired places are realized

Gas Transport through Porous Bodies

Modes of Transport

- Binary diffusion: (Anode:H_2, H_2O; Cathode: O_2,N_2).
- Knudsen diffusion (if the pore size is comparable to the mean free path).
- Viscous flow.
- Surface diffusion.

Important Microstructural Parameters

(a)Volume Fraction Porosity, (b)Pore Size, (c) Tortuosity

From the standpoint of cell design, need parameters that can be readily measured. Assumptions:

1) Viscous flow neglected.
2) Surface diffusion neglected.
3) Transport by effective binary diffusion – treat tortuosity factor as a fitting parameter - not valid if the pore size is very small (less than about 0.25 microns).

For more details, see: 'Dusty Gas Model' Mason and Malinauskas

Effective Diffusivities

Effective Diffusivity through the Anode:

$$D_{eff(a)} = \frac{V_{v(a)}}{\tau_a} D_{H_2-H_2O}$$

$V_{v(a)}$ = Anode Volume Fraction Porosity

$D_{H_2-H_2O}$ = Binary Diffusivity

τ_a = Anode Tortuosity

Effective Diffusivity through the Cathode:

$$D_{eff(c)} = \frac{V_{v(c)}}{\tau_c} D_{O_2-N_2}$$

$V_{v(c)}$ = Cathode Volume Fraction Porosity

$D_{O_2-N_2}$ = Binary Diffusivity

τ_c = Cathode Tortuosity

$D_{H_2-H_2O}$, $D_{O_2-N_2}$: From handbooks or calculations

$V_{v(a)}, V_{v(c)}$: From measurements

τ_a , τ_c : No direct way to measure

$D_{eff(a)}, D_{eff(c)}$: Can be measured in principle.

Some Values of Binary Diffusivities

Chapman Enskogg Model for Binary Diffusivity

$$D_{AB} = \frac{1.86 \times 10^{-3} T^{3/2} (1/M_A + 1/M_B)^{1/2}}{p \sigma_{AB}^2 \Omega} \quad \text{cm}^2/\text{s}$$

'Mass Transfer in Fluids'
E. L. Cussler

M_A, M_B = Molecular weights

Ω = Collision Integral

σ_{AB} = Average Molecular Diameter (in Angstroms)

T = Temperature (K)

p = Pressure (in atmospheres)

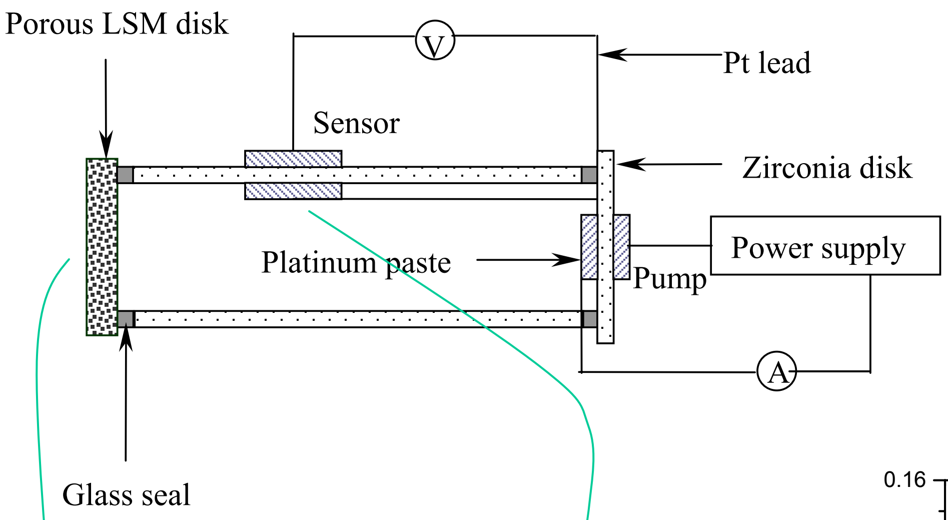
Values at 800°C

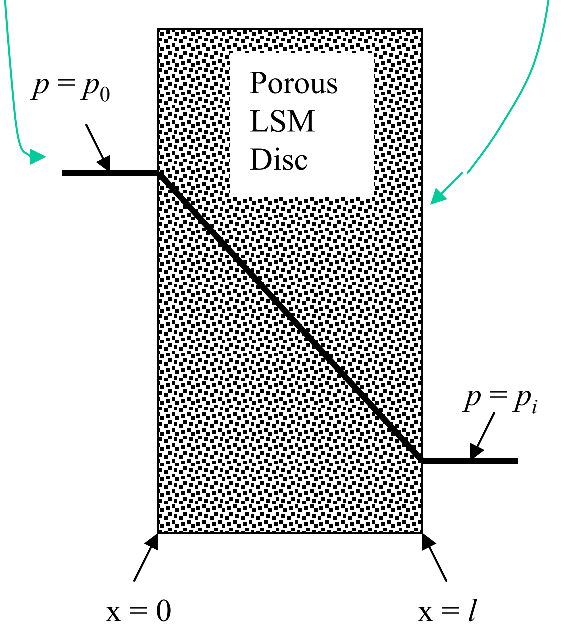
$D_{H_2-H_2O}$	~6.52 cm^2/s
$D_{O_2-N_2}$	~1.28 cm^2/s

Depending upon the porosity and tortuosity, these numbers can be lower by more than an order of magnitude. Design of electrode microstructure (porosity) is important.

Higher binary diffusivity of H_2-H_2O is another reason for choosing anode-supported.

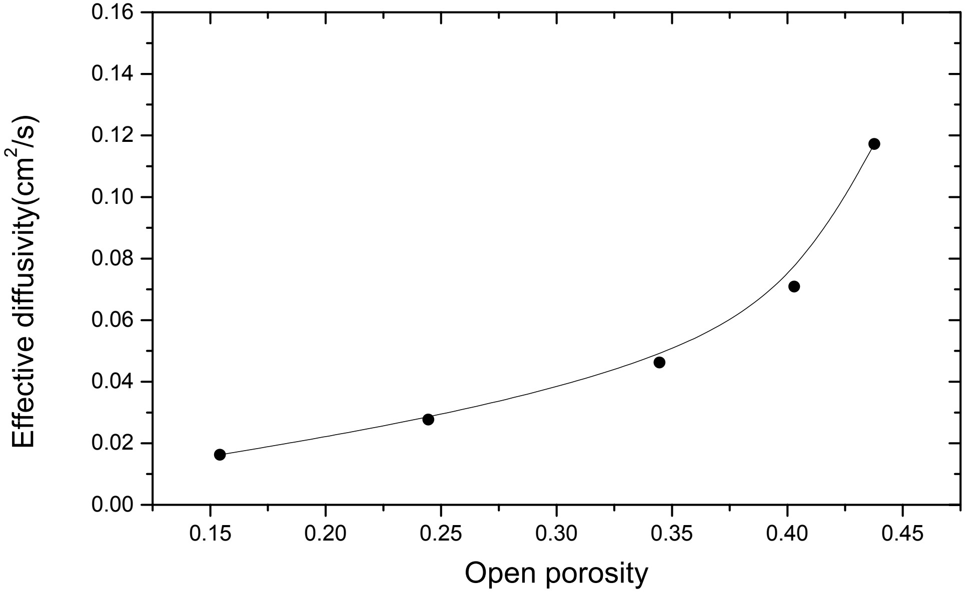
Measurement of Effective Diffusivities: An Electrochemical Method



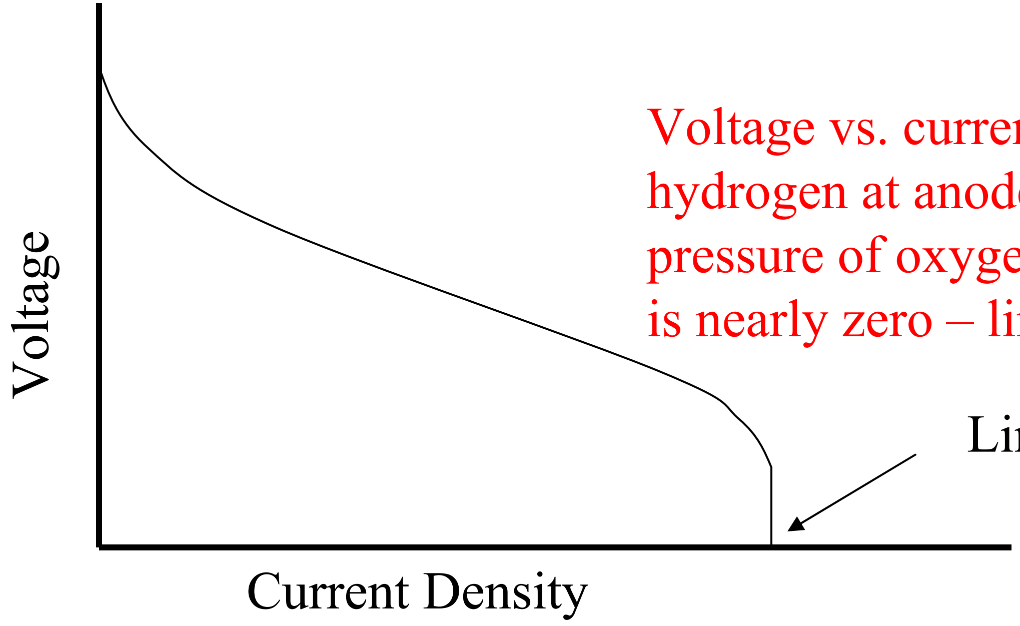


1) Measure current – relate gaseous flux to it.
2) Measure Nernst voltage – pO2 in the chamber
3) Estimate efefctive diffusivity

Experimentally measured effective O_2-N_2 diffusivity at 800°C as a function of porosity



How is the Voltage vs. Current Density Polarization Curve Influenced by Transport through Porous Electrodes?

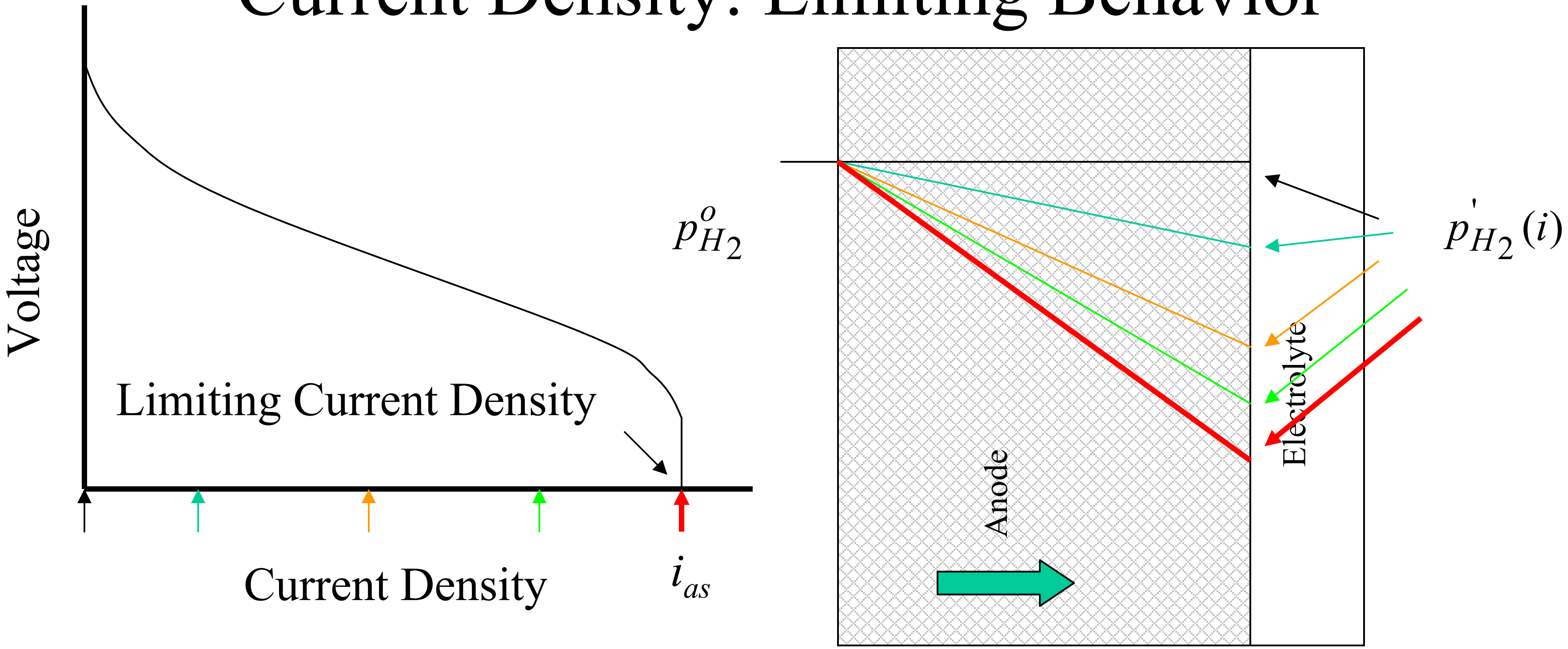


Voltage vs. current behavior when partial pressure of hydrogen at anode/electrolyte interface, or partial pressure of oxygen at cathode/electrolyte interface is nearly zero – limiting current density

i_{as} = Anode limiting current density (hydrogen partial pressure at the anode/electrolyte approaching zero)

i_{cs} = Cathode limiting current density (oxygen partial pressure at the cathode/electrolyte approaching zero)

Schematic of p_{H2} Variation as a Function of Current Density: Limiting Behavior



At the limiting condition, $p^o_{H_2} >> p'_{H_2}(i)$. This leads to a limiting flux.

That is, $j_{H_2} \propto (p^o_{H_2} - p'_{H_2}(i))$

or $j_{H_2} \propto p^o_{H_2}$ when $p^o_{H_2} >> p'_{H_2}(i)$

In the above schematic, the anode functional layer is ignored.

Anode Limiting Current Density Behavior

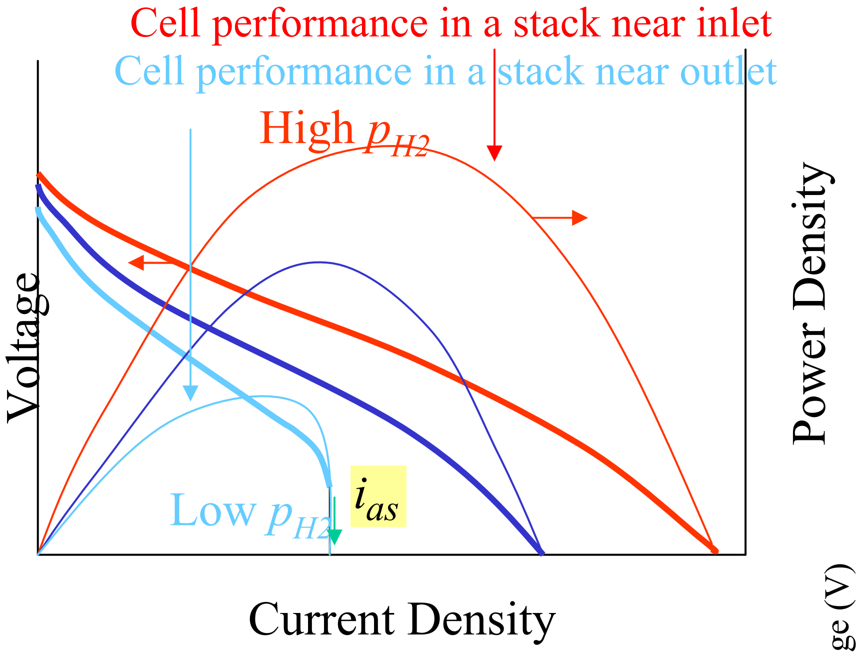
$$i_{as} \sim \left(\frac{2F}{RT}\right)\frac{p^o_{H_2}}{l_a}D_{eff(a)}$$

$p^o_{H_2}$: Partial pressure of hydrogen just outside the anode

l_a : Anode thickness

Under most operating conditions, this behavior is not observed. However, a cell can be operated using a diluted fuel (low partial pressure of hydrogen in the fuel) to induce this type of behavior. The purpose is to experimentally determine the effective diffusivity, which is usually not a strong function of the relative amounts of H_2 and H_2O.

Cell Performance in Fuels with Different Hydrogen Partial Pressures

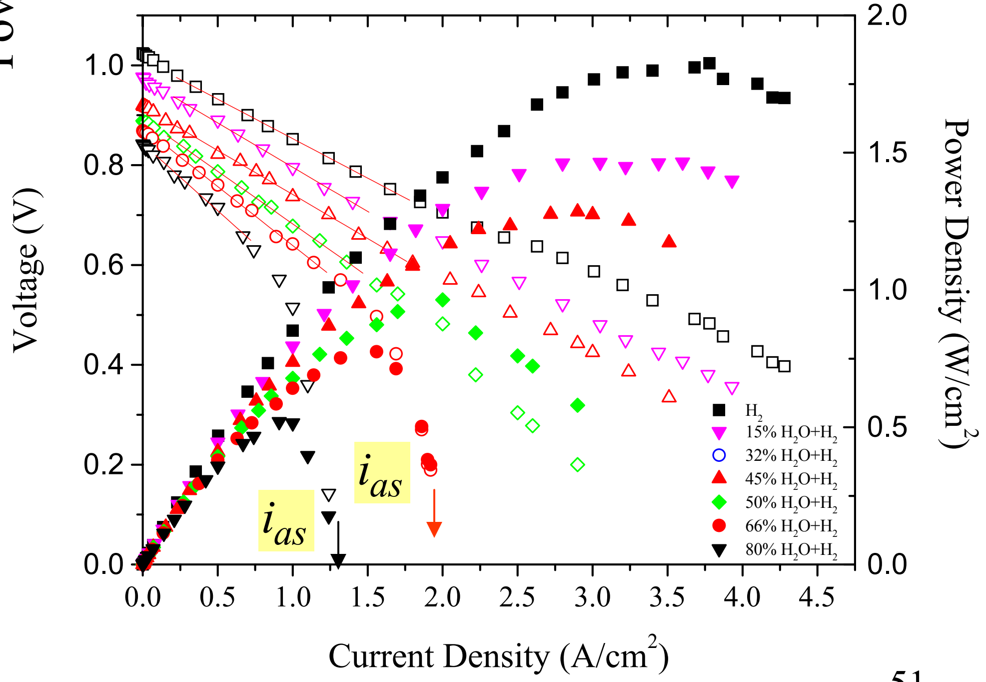


Schematic

In a stack of cells, portion of the cell at the inlet is exposed to a high p_{H2}, while that near the outlet is exposed to low p_{H2}, as the fuel gas becomes depleted in H_2.

Tests conducted under flooded conditions

Data on a button cell at 800°C

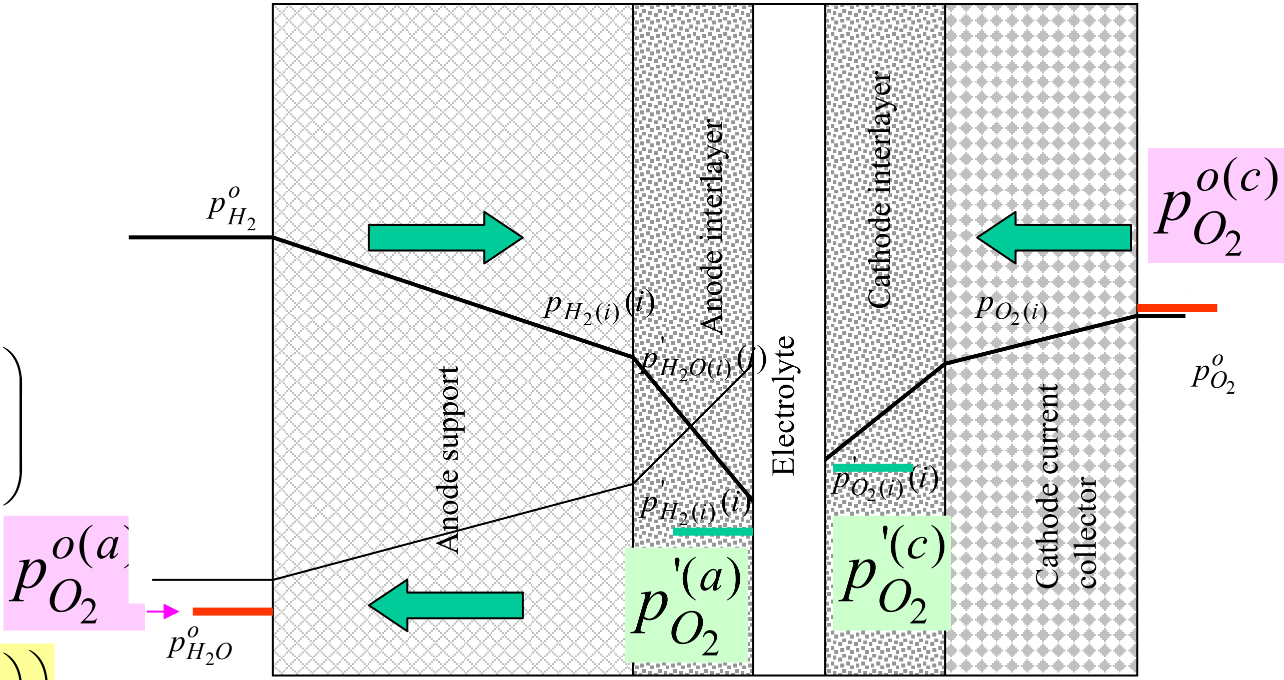


Anode Concentration Polarization or Overpotential

Voltage loss associated with fuel gas transport through the porous anode is known as anode concentration polarization or overpotential. It depends on the anode porosity, anode tortuosity, anode thickness; effective diffusivity, partial pressure of hydrogen in the fuel (how depleted is the fuel), and temperature.

$$\eta_{conc(a)} = -\frac{RT}{4F}\ln\left(\frac{p^{o}_{O2(a)}}{p^{'}_{O2(a)}}\right)$$

$$\eta_{conc(a)} = -\frac{RT}{2F}\ln\left(\frac{p^{o}_{H_2O}\,p^{'}_{H_2}}{p^{o}_{H_2}\,p^{'}_{H_2O}}\right)$$

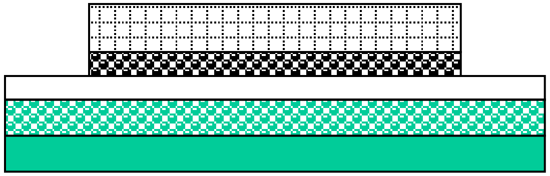


$$\eta_{conc(a)} = -\frac{RT}{2F}\ln\left(\frac{\left(1-\frac{i}{i_{as}}\right)}{\left(1+\frac{i}{i_{as}}\right)}\right)$$

$$i_{as} \sim \left(\frac{2F}{RT}\right)\frac{p^{o}_{H_2}}{l_a}D_{eff\,(a)}$$

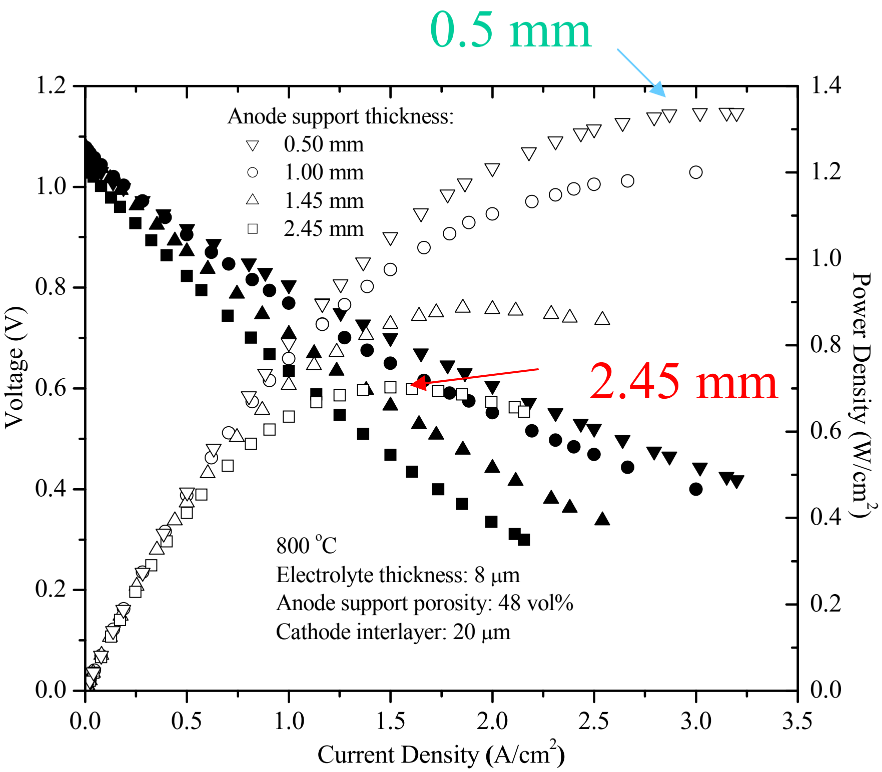
Experimental Evidence on the Effect of Anode Concentration Polarization on Cell Performance

$$i_{as} \sim \left(\frac{2F}{RT}\right)\frac{p^o_{H_2}}{l_a} D_{eff(a)}$$



$$\eta_{conc(a)} = -\frac{RT}{2F}\ln\left(\frac{\left(1-\frac{i}{i_{as}}\right)}{\left(1+\frac{i}{i_{as}}\right)}\right)$$

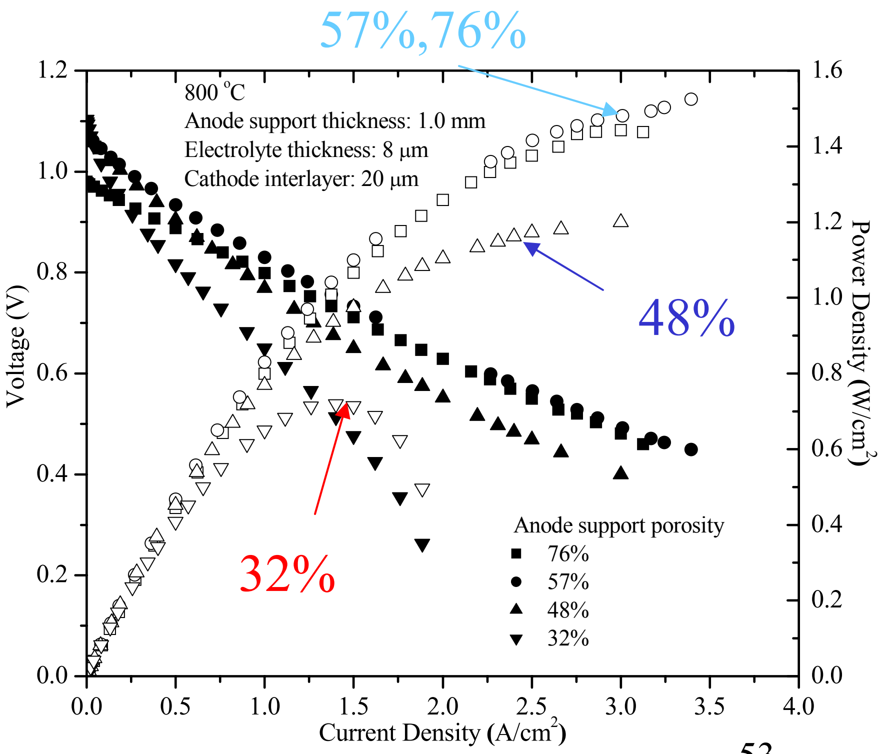
F. Zhao and A. Virkar, J. Power Sources, **141** 79-95 (2005)



0.5 mm

2.45 mm

Only Anode Support Thickness varied



57%,76%

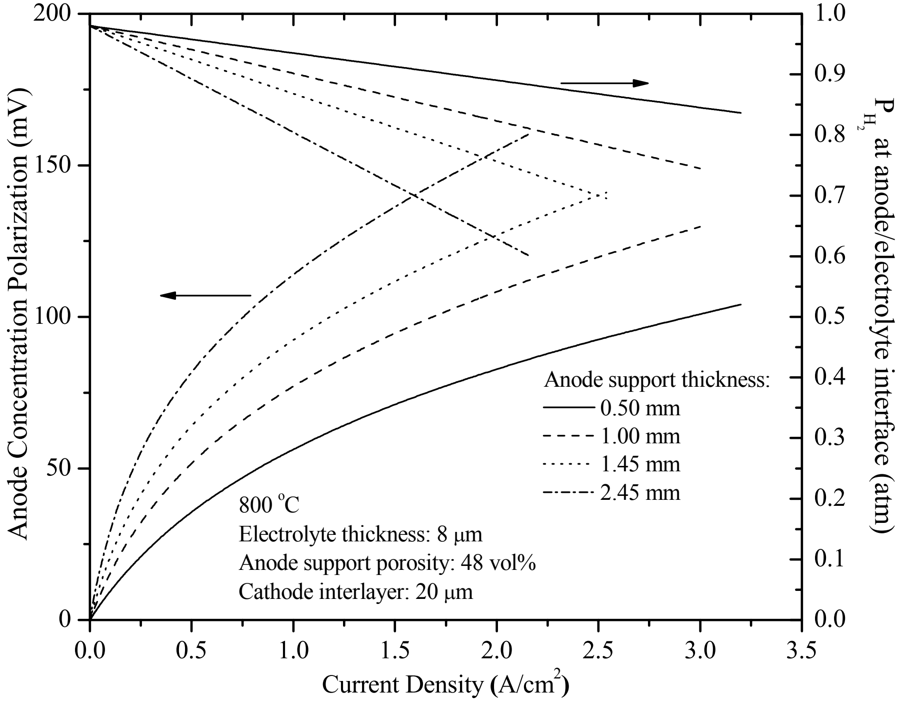
48%

32%

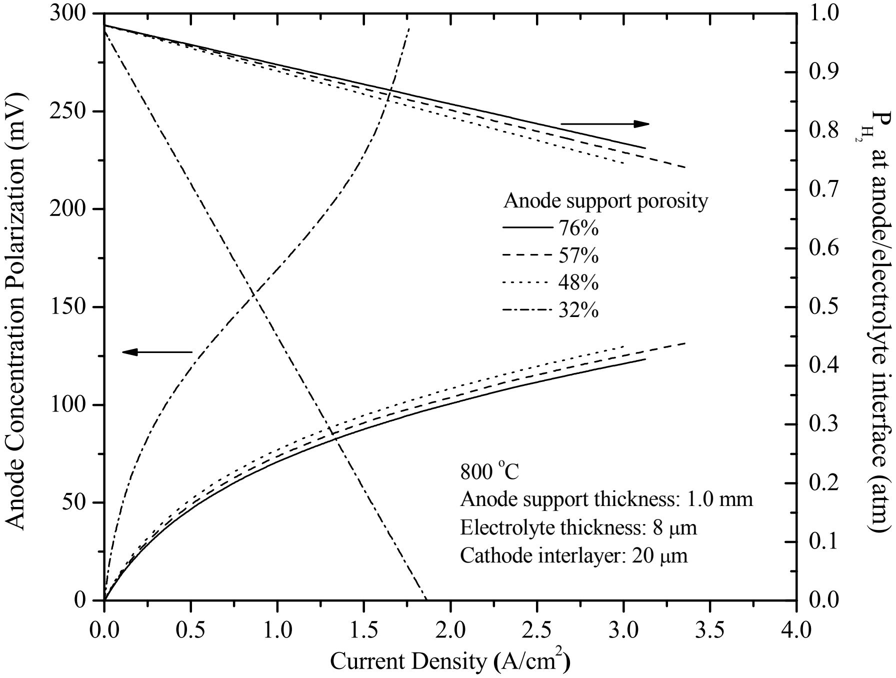
Only Anode Support Porosity varied

Anode Concentration Polarization - Calculations

These calculations assume p°H_2 = 0.97. Downstream in a stack, the p°H_2 << 0.97, due to depleted fuel. Thus, anode concentration polarization downstream is even greater.



Only Anode Support Thickness Varied

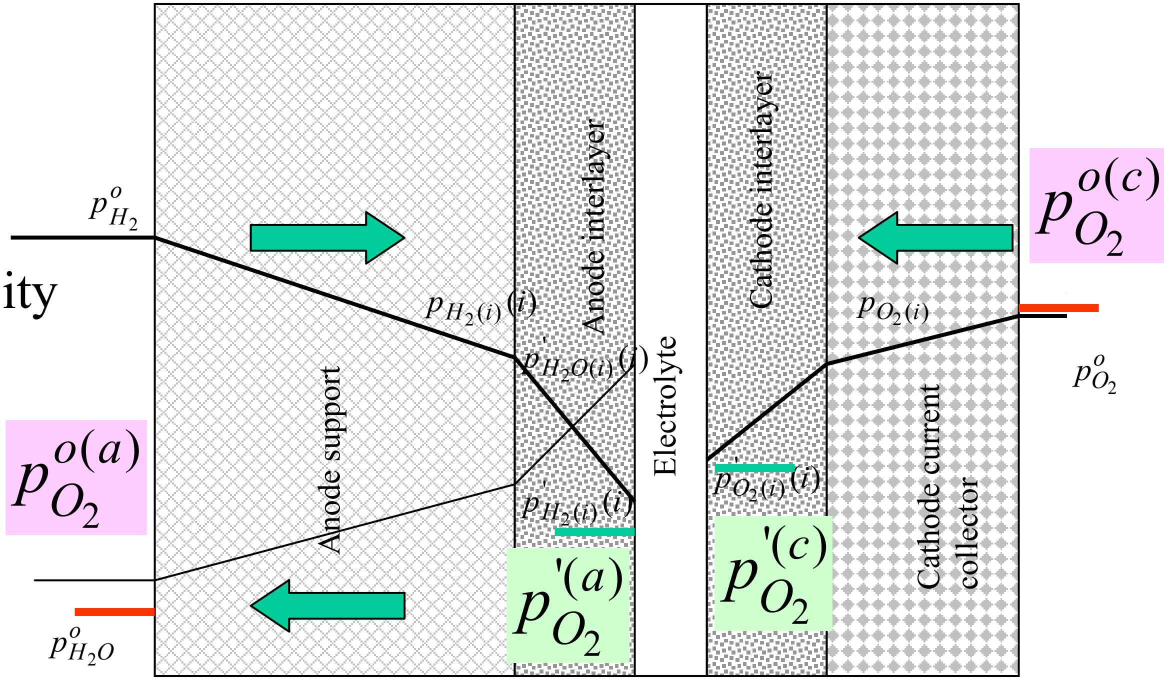


Only Anode Support Porosity Varied

Cathode Concentration Polarization or Overpotential

Cathode concentration polarization can be similarly estimated. In anode-supported cells this contribution is usually small, as long as the cathode is thin enough and porous enough. However, depending upon other design criteria, this may be significant.

$$\eta_{conc(c)} = -\frac{RT}{4F}\ln\left(\frac{p'^{(c)}_{O_2}}{p^{o(c)}_{O_2}}\right)$$



Cathode Limiting Current Density

$$i_{cs} \sim \frac{4F}{RT}\left(\frac{pp^{o(c)}_{O_2}}{p-p^{o(c)}_{O_2}}\right)\frac{D_{eff(c)}}{l_c}$$

Slightly different equation than i_{as} due to $j_{N_2} = 0$

$$D_{eff(c)} = \frac{V_{v(c)}}{\tau_c} D_{O_2-N_2}$$

In anode-supported cells, for typical cathode porosities and thicknesses, and over the range of operating conditions, the cathode concentration polarization loss is usually small – about 10 mV.

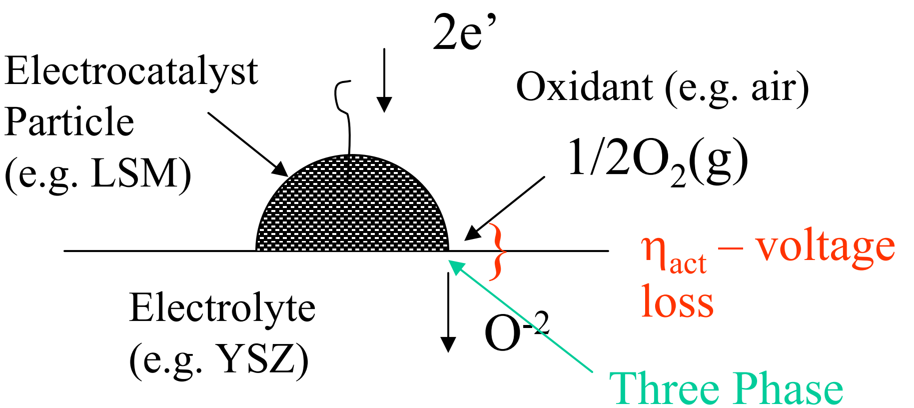
Voltage Loss Associated with Electrochemical Reactions at the Electrodes: Activation Polarization

- Cathode Reaction: $^1/_2O_2 + 2e' \rightarrow O^{-2}$
- Anode Reaction: $H_2 + O^{-2} \rightarrow H_2O + 2e'$
- Species in the Gas Phase: O_2(cathode), H_2(anode), H_2O(anode)
- Species in YSZ: O^{-2}
- Mobile Species in Electrode Materials: e'(LSM-cathode, Ni-anode)

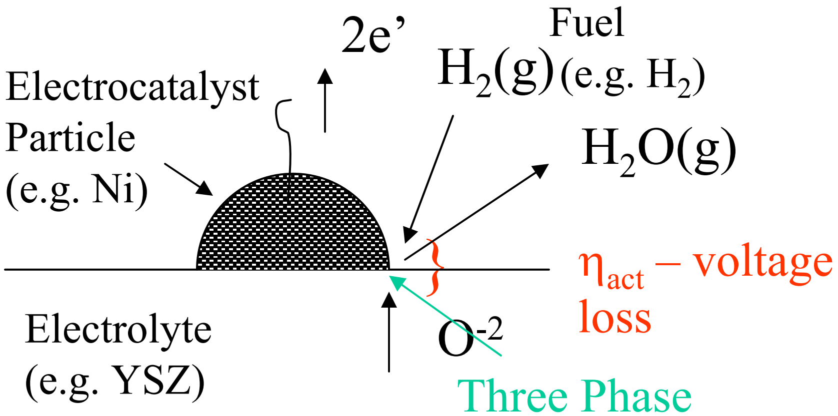
The above gives only the overall electrode reactions. These comprise of many series and parallel steps. These include: (a) Adsorption, (b) Dissociation, (c) Surface Diffusion, (d) Electron Transfer. If any one of the series steps is much slower than the other, one can describe the mechanism in terms of a rate-limiting step (RDS). Experimentally, this is very difficult to determine – and the literature is full of many different RDS. This underscores the difficulty in isolating such steps unequivocally. We will not much dwell on this topic. Our focus will be on identifying those material/microstructural parameters which influence electrode reactions, and can be experimentally measured and directly related to cell performance.

Activation Polarization

Activation Polarization or Overpotential: This is associated with the actual Charge transfer reaction, which in solid state electrochemistry generally occurs at a Three Phase Boundary (Electrolyte-Electrocatalyst-Gas Phase) (TPB).



Cathode



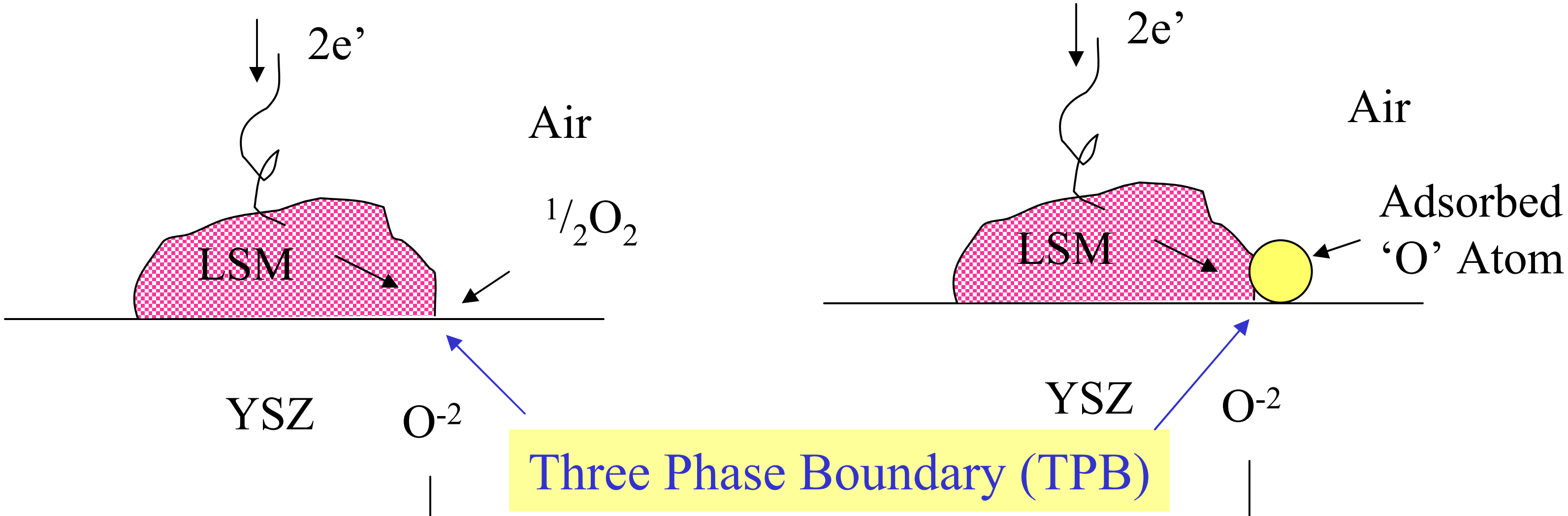
Anode

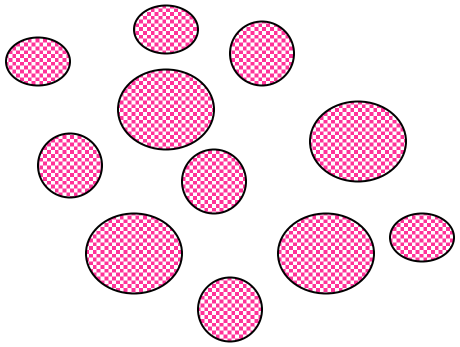
$$\frac{1}{2}O_2(g)+2e' \rightarrow O^{-2}$$

$$O^{-2}+H_2(g) \rightarrow H_2O(g)+2e'$$

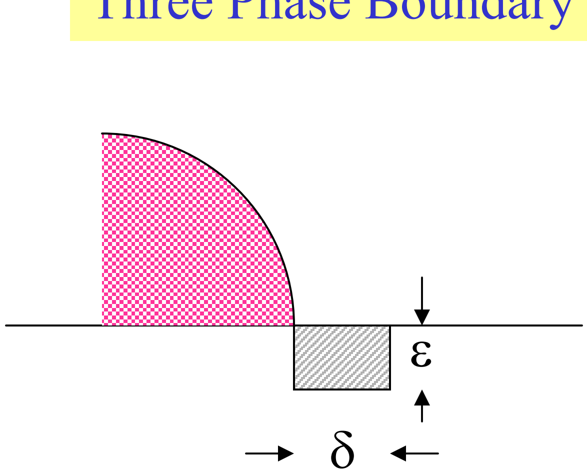
η_{act} : Voltage loss associated with the charge transfer reaction. This is usually a thermally activated process. A phenomenological equation, known as the Butler-Volmer equation, originally developed for aqueous electrochemistry, is often used to describe it.

The Cathode Reaction





View from top



$$R_p = \frac{\rho'_{ct}\varepsilon}{\delta\ell_{TPB}} = \frac{\rho_{ct}}{\ell_{TPB}}$$

$\rho'_{ct}, \varepsilon, \delta$ -cannot be measured independently

$R_p, \ell_{TPB}, \rho_{ct}$ -can be measured independently

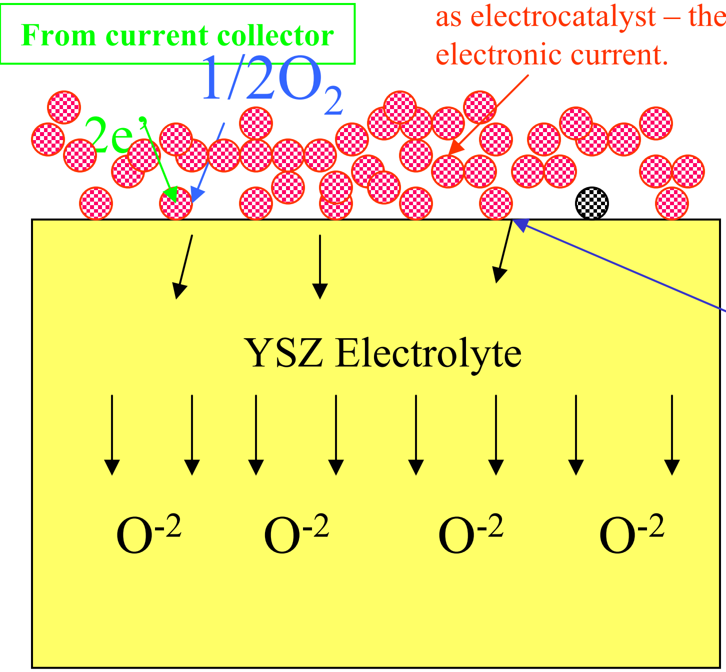
ℓ_{TPB} -Three Phase Boundary (TPB) Length/unit area (cm^{-1})

R_p - Ωcm^2

Monolithic (Screen-Printed) vs. Composite Cathode

LSM Cathode

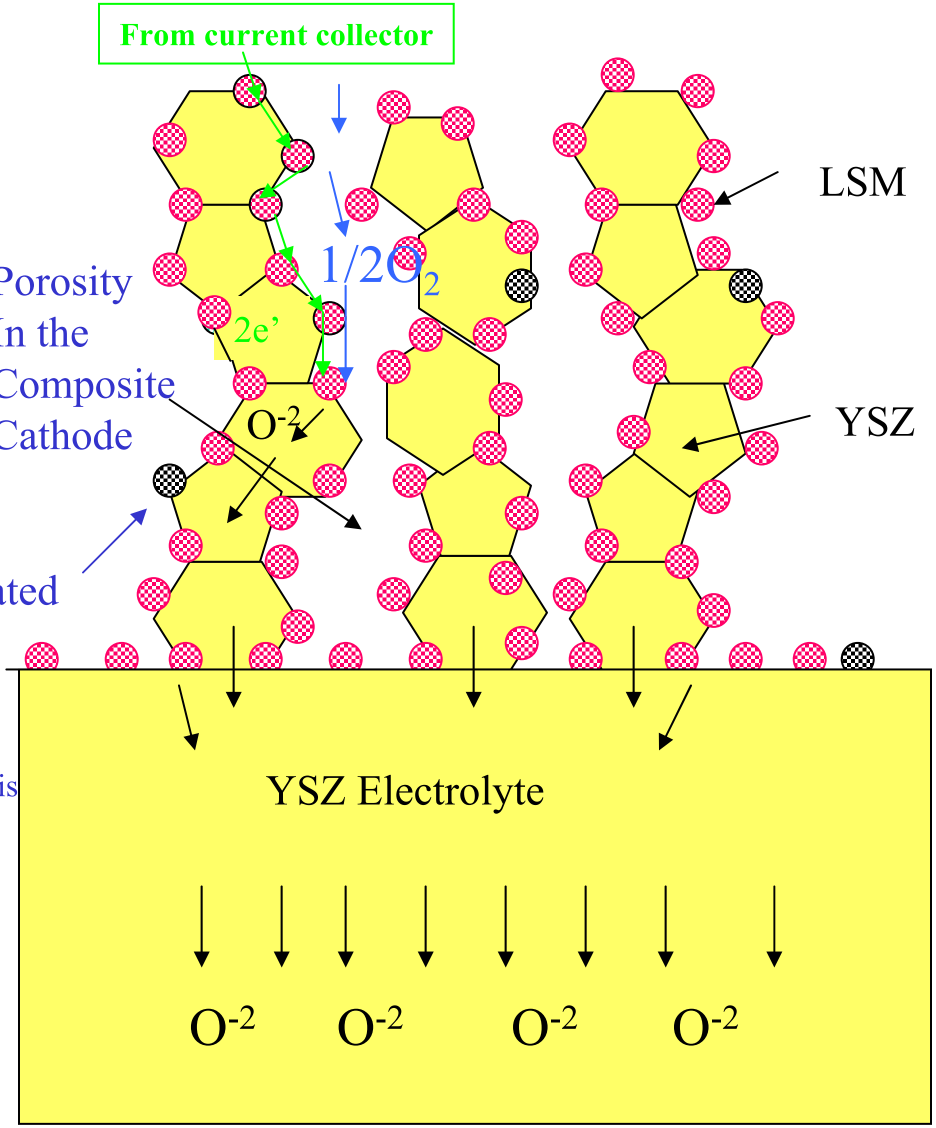
In a non-composite cathode, there are insufficient TPB’s. Thus, the resistance to charge transfer (electrochemical reaction) is large. Traditionally, LSM has been used until recently. The importance of using a composite cathode is now being recognized by the SOFC community.



These LSM particles are not effective as electrocatalyst – they only carry electronic current.

Electrocatalysis occurs only at the TPBs. Very low TPB

LSM + YSZ Cathode



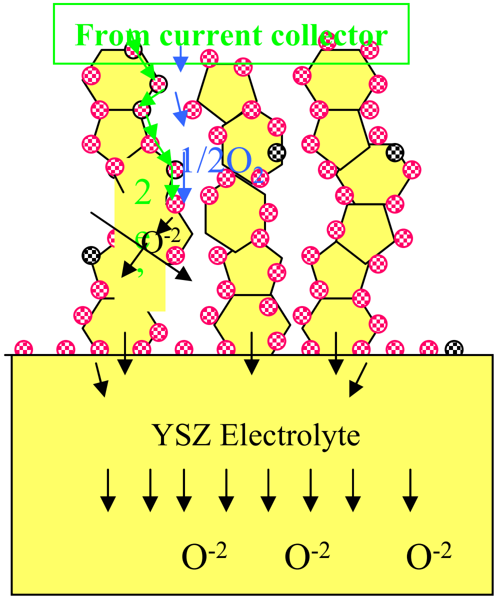
Porosity In the Composite Cathode

Isolated

Much larger TPB in composite cathodes

Composite Cathode Features

- The cathode functional layer is a mixture of an ionic (YSZ) and an electronic (LSM) conductor. This increases the total TPB and extends the reaction zone.
- YSZ must be contiguous – to carry ionic current.
- LSM must be contiguous – to carry electronic current.
- Porosity must be contiguous – for gaseous transport.
- There must be large TPB length – that is LSM should not completely cover YSZ particles.

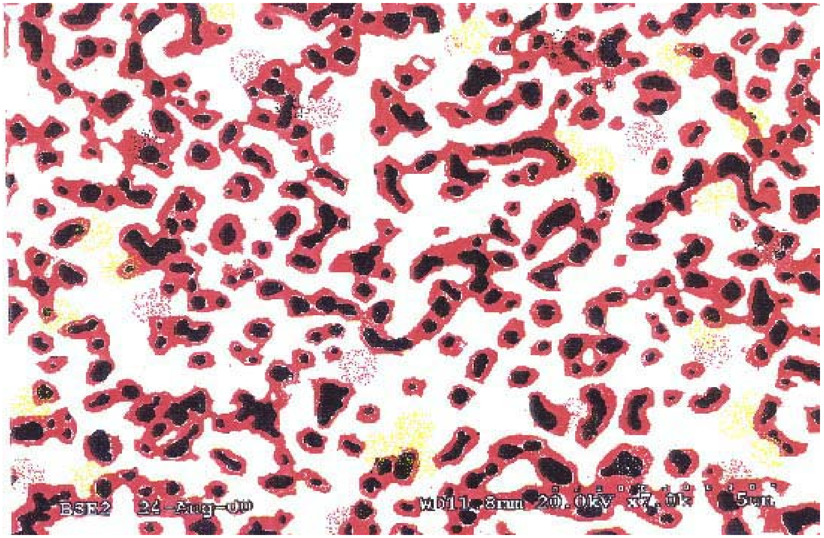


1) J. S. Newman and C. Tobias, J. Electrochem. Soc., **109** 1183 (1962).
2) T. Kenjo, S. Osawa, and K. Fujikawa, J. Electrochem. Soc., **138** 349 (1991).
3). C. W. Tanner, K-Z. Fung, and A. V. Virkar, J. Electrochem. Soc., **144** 21 (1997).

Role of Cathode TPB on Performance

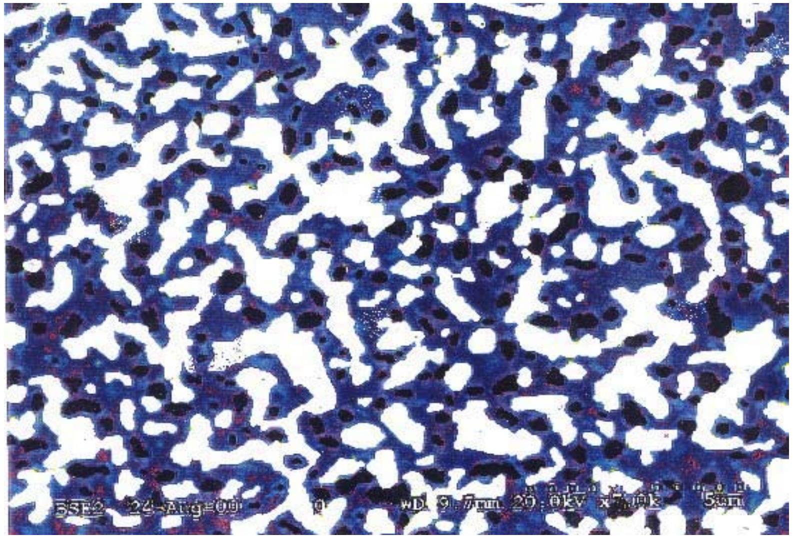
Black – Pores
White – YSZ
Red or Blue – LSM

Cell 1



Maximum Power density at 800°C was ~**0.33** W/cm^2.

Cell 2

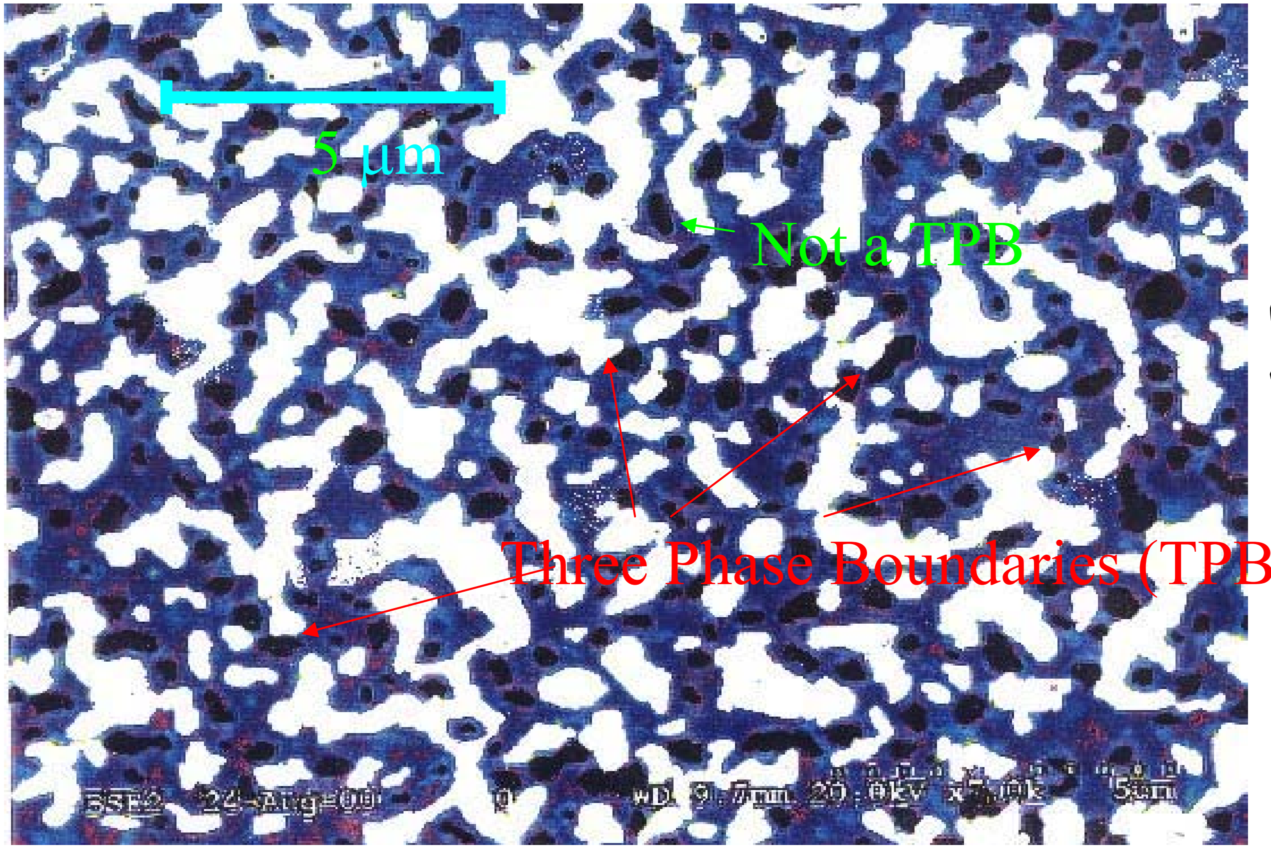


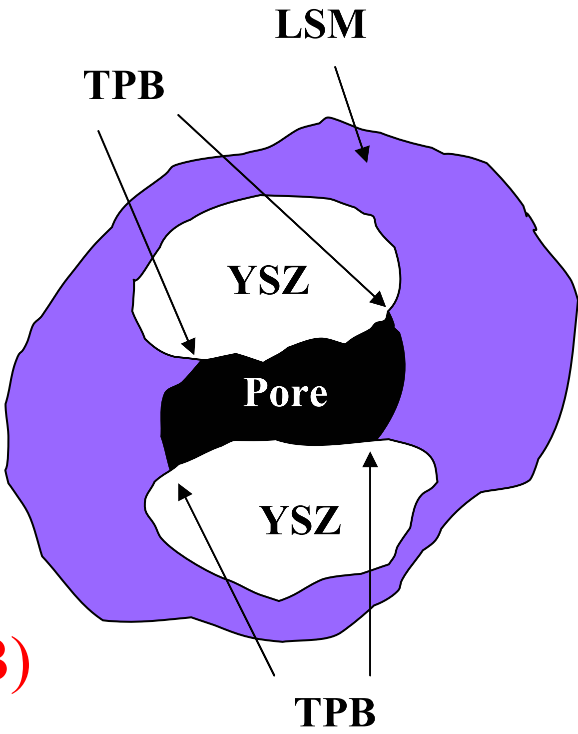
Maximum Power density was ~**1.1** W/cm^2 at 800°C.

Color-Coded Electron Micrographs (taken on an Electron Microprobe)

Good Cathode EPMA Micrograph

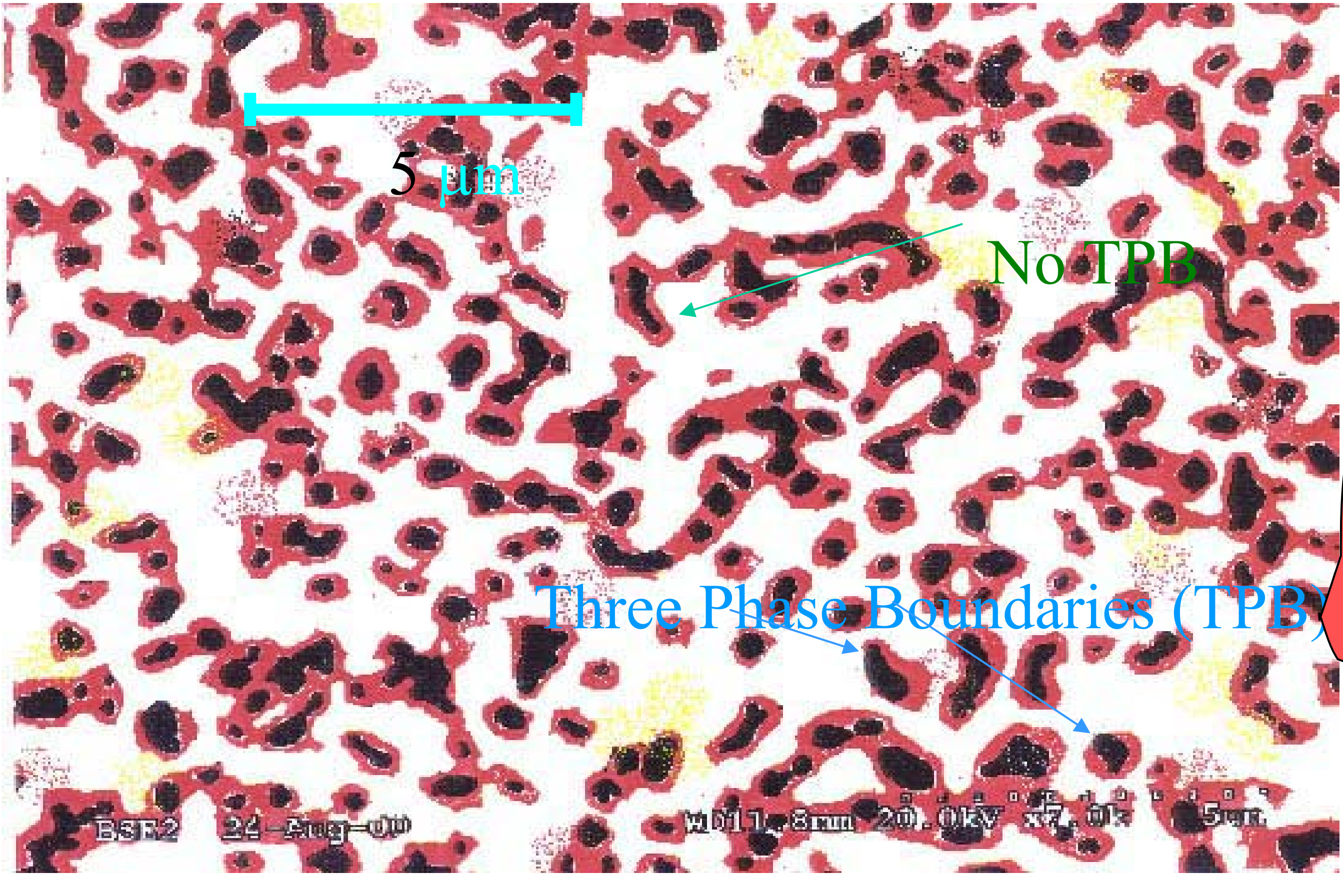
Maximum
Power density
Of this cell was
~1.1 W/cm^2 at
800^{o}C.

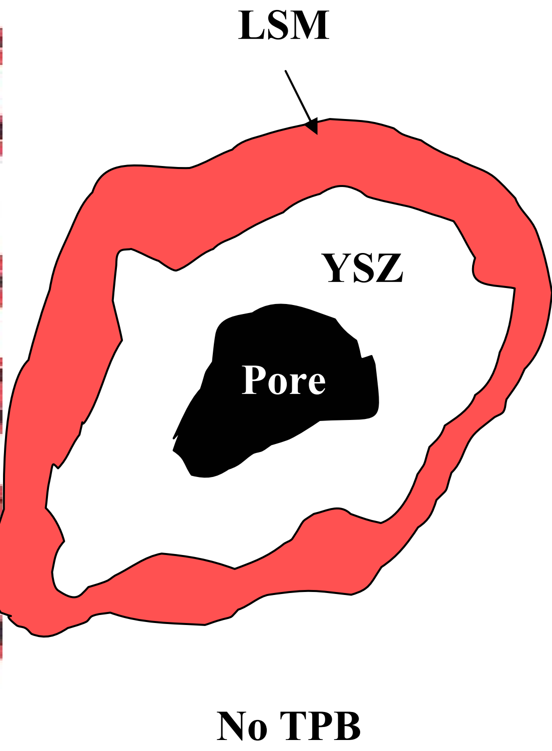




Poor Cathode
EPMA Micrograph

Maximum power density at 800°C was ~0.33 W/cm^2.



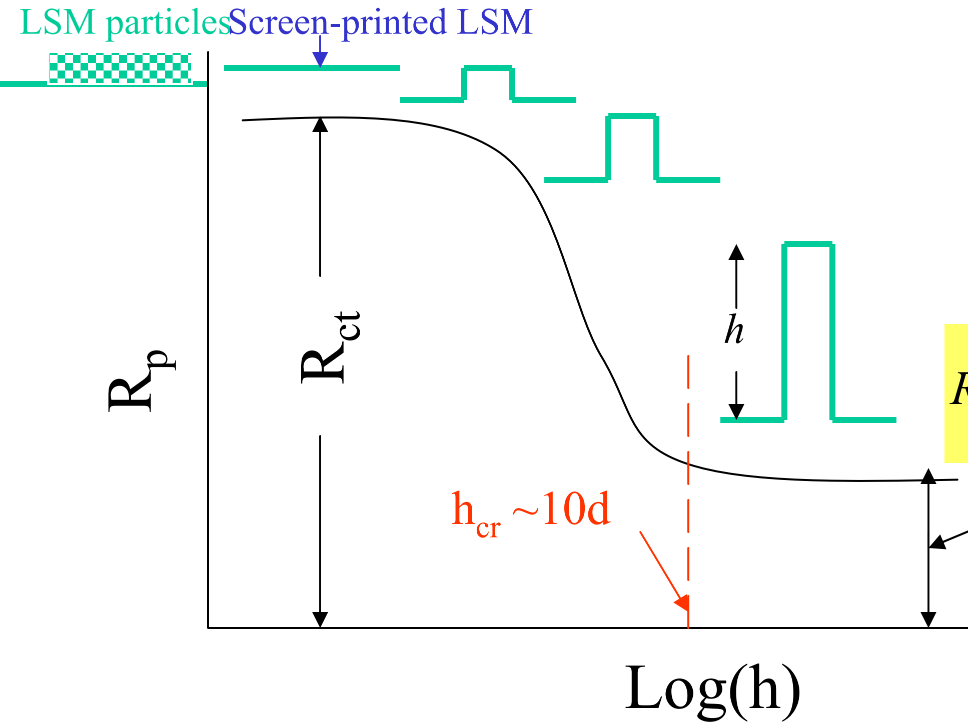


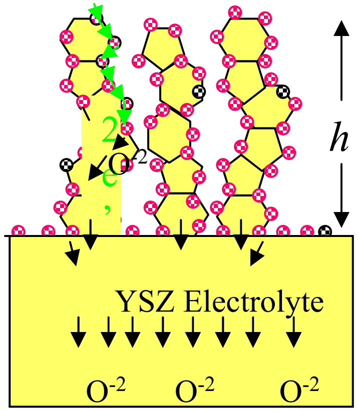
Quantitative Features of the Composite Cathode Parameters

- Ionic conductivity (σ_i) or resistivity ($\rho_i = 1/\sigma_i$) of the ionic conductor in the functional layer YSZ.(S/cm or Ω^{-1}cm^{-1})
- Particle size of the YSZ (d) in the functional layer (cm).
- Porosity of the functional layer (V_v).
- Charge transfer resistivity (ρ_{ct}). This is a function of temperature and oxygen partial pressure (local) (Ωcm).
- Three phase boundary length (l_{TPB}) (cm^{-1}).
- Thickness of the functional layer (h). Essentially no dependence for $h >> d$.

Assumptions: (a) Electronic conductivity of LSM is much greater than ionic Conductivity of YSZ. (b) Gas diffusion is fast (so porosity is not too low).

A Simple Model





$$R_p \approx \sqrt{\frac{\rho_i R_{ct} d}{(1-V_v)}} = \sqrt{\frac{R_{ct} d}{\sigma_i (1-V_v)}} = \sqrt{\frac{\rho_{ct} d}{\ell_{TPB} \sigma_i (1-V_v)}}$$

C. W. Tanner et al.
J. Electrochem Soc., **144** 21-30 (1997).

All parameters can be measured.

ρ_i = Ionic resistivity of the electrode

Illustrative calculation:

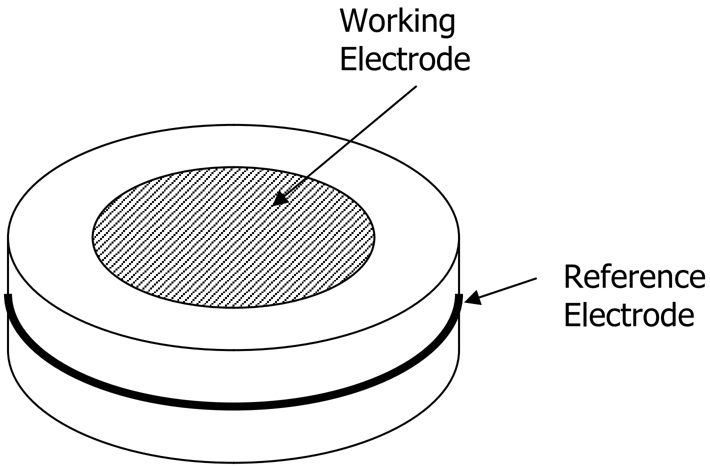
$R_{ct} = 1\ \Omega\text{cm}^2$

$\rho_i = 50\ \Omega\text{cm}$ $d = 1\ \mu\text{m}$ $V_v = 0.3$

Then, $R_p = 0.0845\ \Omega\text{cm}^2$ – a twelve-fold decrease in polarization resistance through microstructural design!

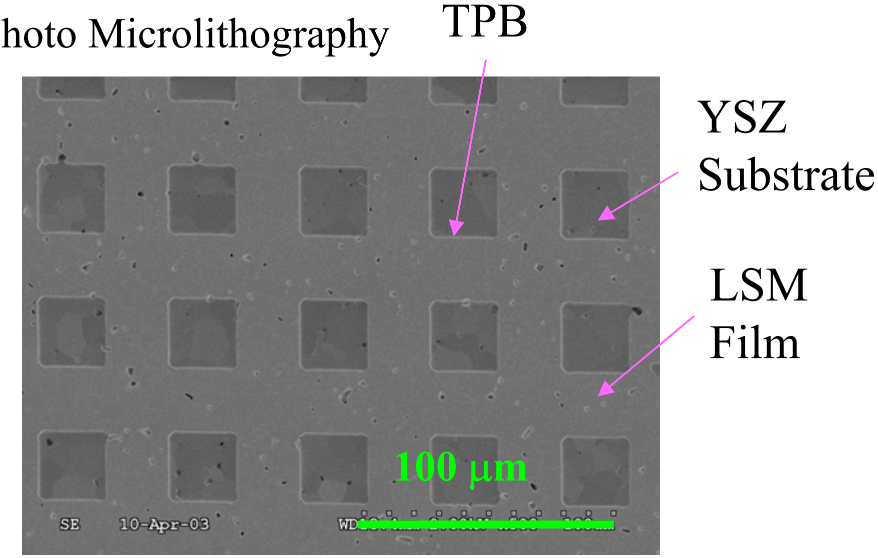
Fundamental parameter which governs electrochemical reaction is ρ_{ct}

How to Measure Charge Transfer Resistivity, ρ_{ct}?

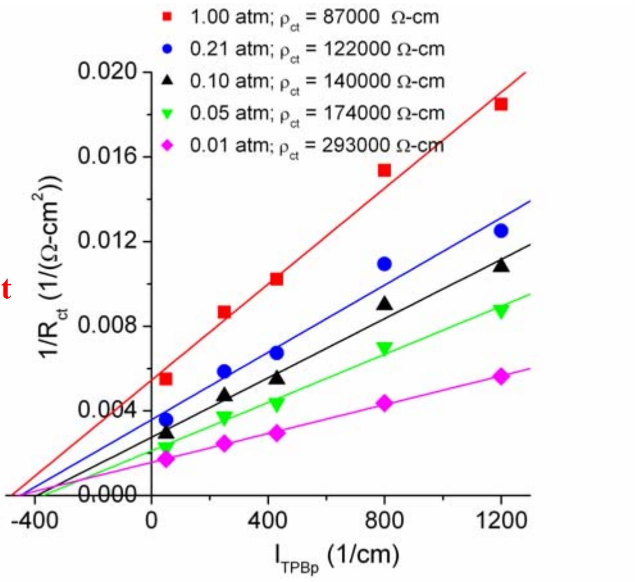


- Not very easily.
- Need to make electrodes with well-defined and varying three phase boundary length, l_{TPB}.
- This requires methods from microlithography.
- Measure area specific charge transfer resistance using methods such as impedance spectroscopy.

Photo Microlithography



Slope = $1/\rho_{ct}$



Activation Polarization at High Current Densities

- Polarization ‘resistance’ we described so far, including the effect of electrode microstructure, is applicable only at very low current densities – linear (not ohmic) relation between current and voltage (overpotential).
- At high current densities, relationship between current and voltage (overpotential) is not linear. The most commonly used phenomenological equation is known as the Butler-Volmer equation.
- In either low or high current density regime, the relationship is thermally activated – hence the term activation polarization.
- Experimentally, it is very difficult, if not impossible to determine the relationship between current and voltage. Hence, fitting to cell test data is the only practical approach – if the objective is to design a cell.
- The simplest approach is to use a limiting case of the Butler-Volmer equation, known as the Tafel equation, applicable at high current densities. The use of Tafel equation also allows one to lump activation polarizations at both the cathode and the anode into a single expression.

Butler Volmer Equation and the Low Current Density Regime

$$i = i_o\left\{\exp\left[-\frac{\alpha z F \eta_{act}}{RT}\right] - \exp\left[\frac{(1-\alpha) z F \eta_{act}}{RT}\right]\right\}$$

1)'Electrochemical Engineering Principles' G. Prentice
2) 'Electrochemistry, P. H. Rieger

z: Number of electrons participating in the reaction.

F: Faraday constant (96,487 Coulombs/mole).

R: Gas constant (8.3144 J/mol.).

T: temperature (K).

α: Transfer coefficient ($0 < \alpha < 1.0$).

i_o: Exchange current density (Amp/cm^2) (thermally activated).

We see that the Butler-Volmer equation gives the current density, i, as a function of the activation polarization, η_{act}, and not η_{act} as an explicit function of i. For very small values of the current density, the above simplifies to

$$\eta_{act} \approx \frac{RT}{zFi_o} i \approx R_p i$$

Linearized: Note; linear does not mean ohmic.

where $R_p = \frac{RT}{zFi_o}$ is the charge transfer resistance (Ωcm^2), a measure of the resistance to the electrochemical reaction.

Ωcm^2

Butler-Volmer Equation and the High Current Density Regime

The Butler-Volmer equation

$$i = i_o\left\{\exp\left[-\frac{\alpha zF\eta_{act}}{RT}\right] - \exp\left[\frac{(1-\alpha)zF\eta_{act}}{RT}\right]\right\}$$

At high η_{act}, that is $-\frac{zF\eta_{act}}{RT} >> 1$

$$\eta_{act} \approx \frac{RT}{\alpha zF}\ln i_o - \frac{RT}{\alpha zF}\ln i = a + b\ln i$$

Tafel Equation

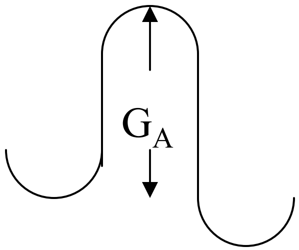
Or, for $\frac{zF\eta_{act}}{RT} >> 1$

$$\eta_{act} \approx -\frac{RT}{zF(1-\alpha)}\ln i_o + \frac{RT}{zF(1-\alpha)}\ln i = a + b\ln i$$

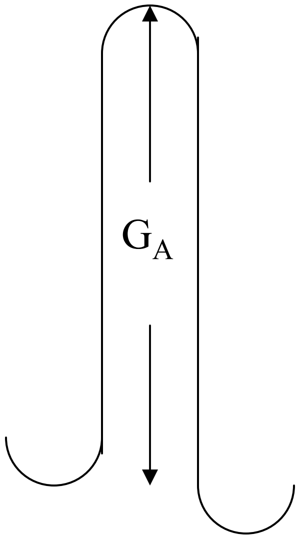
Tafel Equation

The Tafel equation is usually applicable for $i >> i_o$. In an SOFC, both of the electrode activation polarizations can be usually described by the Tafel equation at high overpotentials.

Exchange Current Density



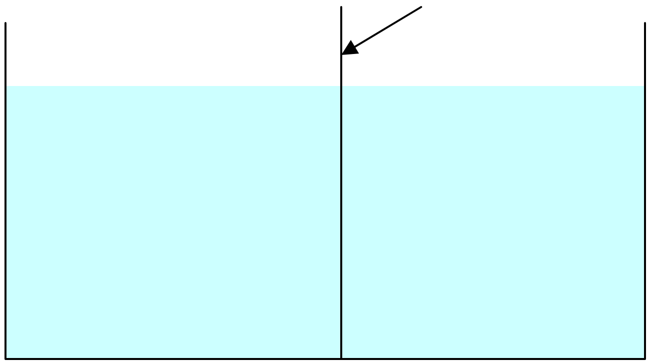
Fast Electrode Process
High Exchange Current Density



Slow Electrode Process
Low Exchange Current Density

G_A: Activation Energy

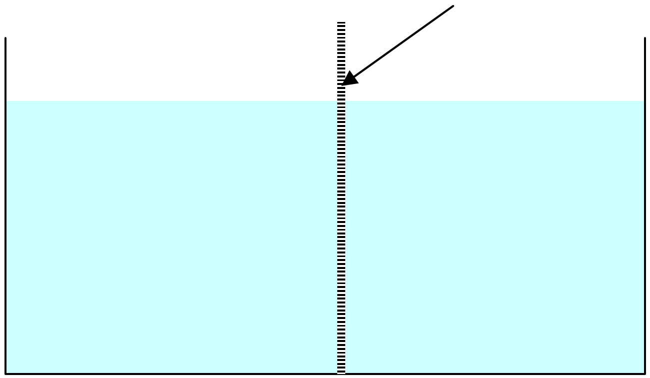
Understanding Exchange Current Density



Virtually no holes

Negligible exchange of water between compartments

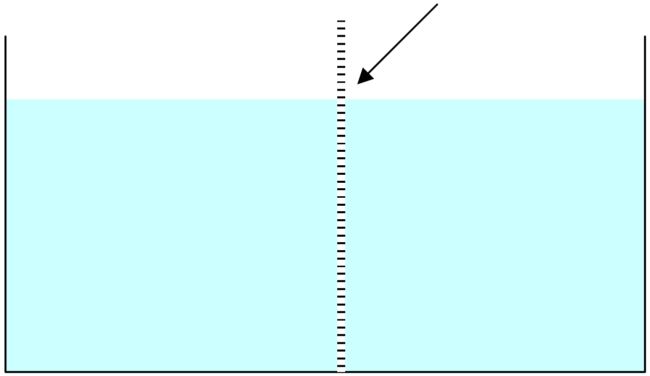
Equivalent to negligible exchange current density



Very fine holes

Some water exchange between compartments

Equivalent to low exchange current density



Larger holes

Greater water exchange between compartments

Equivalent to higher exchange current density

Activation Polarization: Summary Points

- Activation Polarization exists at both electrodes – cathode and anode.
- The general phenomenological equation used is the Butler-Volmer equation.
- In the general case, no simple relation can be given for the sum of activation polarization at the two electrodes as a function of current density.
- In the low current density regime, the relationship between overpotential, η_{act}, and current density, i, is linear. Thus, the activation polarization at the two electrodes can summed and expressed as a function of current density.
- In the high current density regime, the Tafel equation is assumed to be applicable. The η_{act} depends linearly on $\ln i$. Thus, in this case also, the activation polarization at the two electrodes can be summed and expressed as a function of the logarithm of current density.

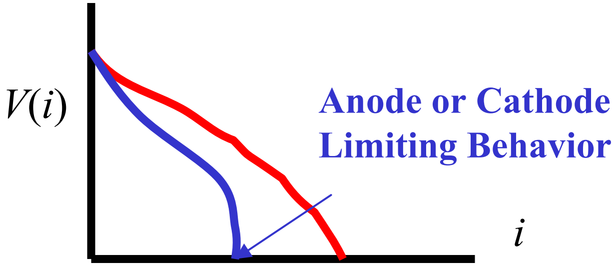
What to do for Designing a Good Cathode with a Functional Layer?

- YSZ Particle should be fine (~0.5 μm or finer). Commercially available YSZ with 8 mol.% Y_2O_3 is satisfactory.
- LSM particle size should be fine (~0.5 μm or finer).
- Mix YSZ and LSM in approximately 50:50 ratio.
- Apply on the YSZ electrolyte surface. Approximate thickness 10 to 20 microns. The porosity should be ~25%.
- Apply a layer of LSM over this layer. Thickness of this current collector layer should be ~50 to ~100 microns. Porosity should be about 45% or somewhat higher.
- Heat to ~1100 to 1200^{o}C for 1 hour.

A Simple Analytical Model for SOFC Performance

J. Electrochem. Soc., **146** [1] 69-78 (1999)

$$V(i) = E_o - \eta(i)$$



Cathode Concentration Polarization

Ohmic Loss

$$V(i) = E_o - iR_i - a - b\ln i + \frac{RT}{4F}\ln\left(\frac{p'_{O_2(i)}(i)}{p^o_{O_2}}\right) + \frac{RT}{2F}\ln\left(\frac{p'_{H_2(i)}(i)\,p^o_{H_2O}}{p^o_{H_2}\,p'_{H_2O(i)}(i)}\right)$$

OCV

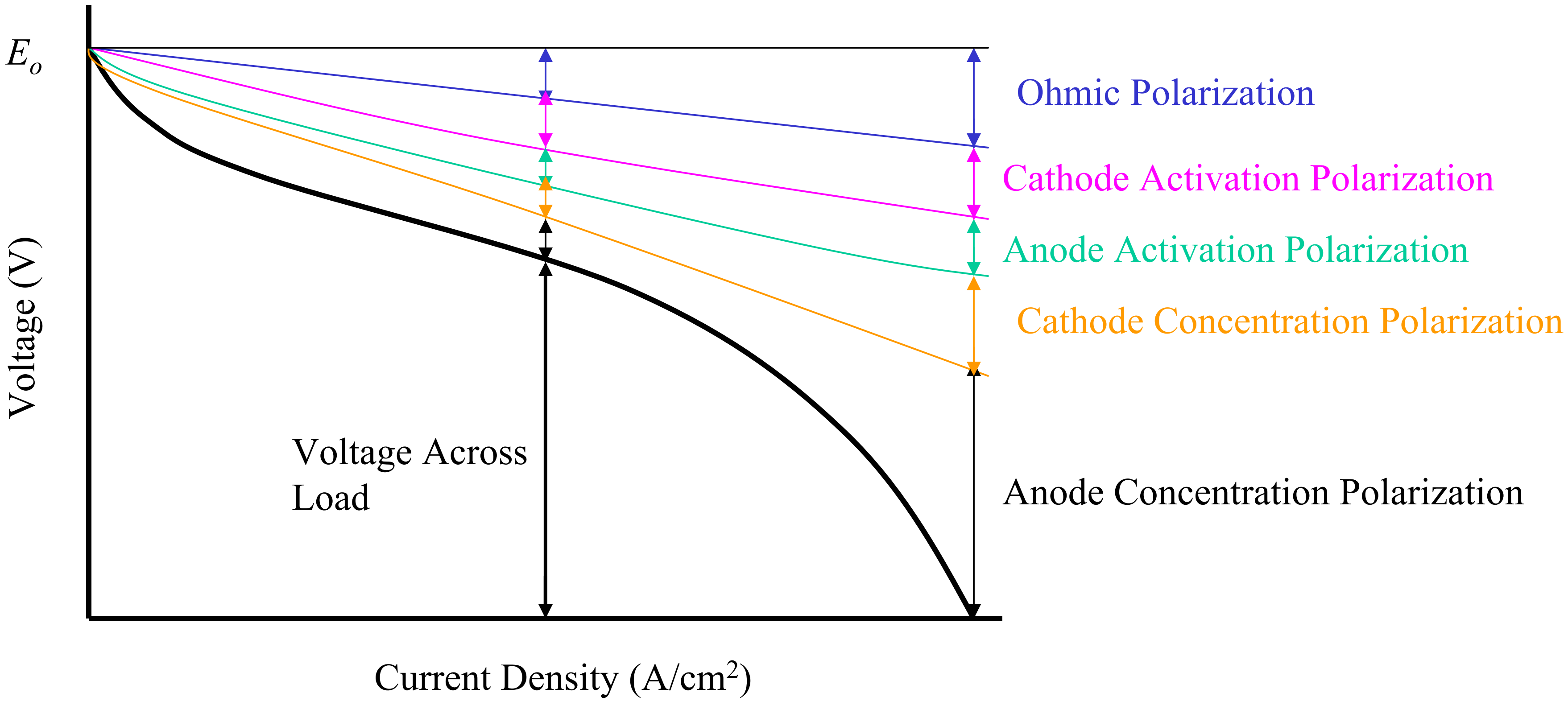
Activation Polarization (assumes the Tafel limit) -both electrodes

Anode Concentration Polarization

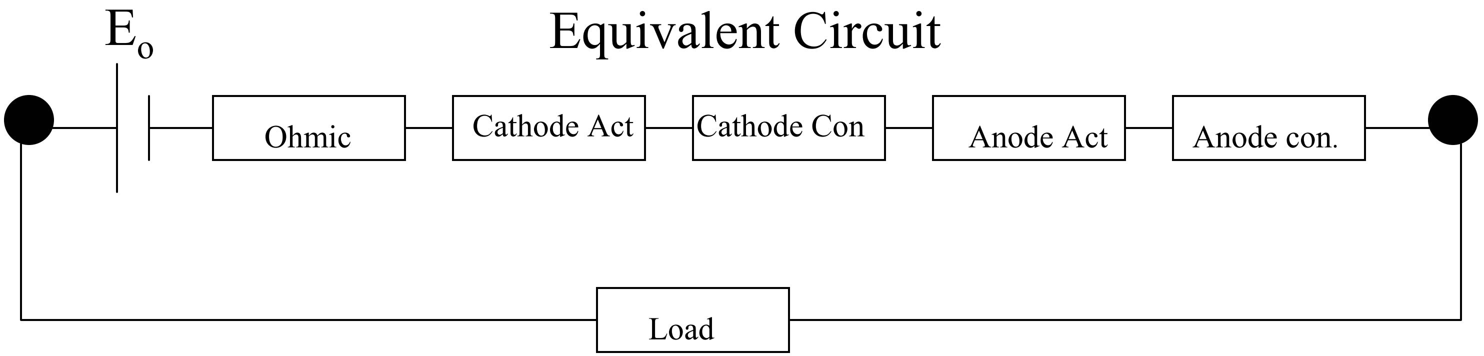
$$V(i) = E_o - iR_i - a - b\ln i + \frac{RT}{4F}\ln\left(1 - \frac{i}{i_{cs}}\right) + \frac{RT}{2F}\ln\left(\frac{\left(1 - \frac{i}{i_{as}}\right)}{\left(1 + \frac{i}{i_{as}}\right)}\right)$$

Minimum number of parameters required is 5 to describe performance. Unfortunately, voltage – current density plots are of very simple shapes, which can be fit with three arbitrary parameters. Thus, it is generally not possible to obtain a unique set of parameters by fitting to cell performance data.

Schematics of Various Polarizations

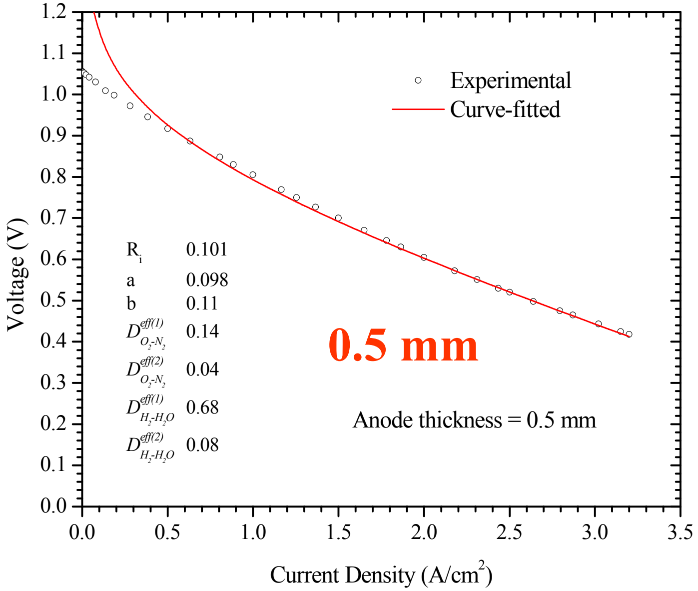


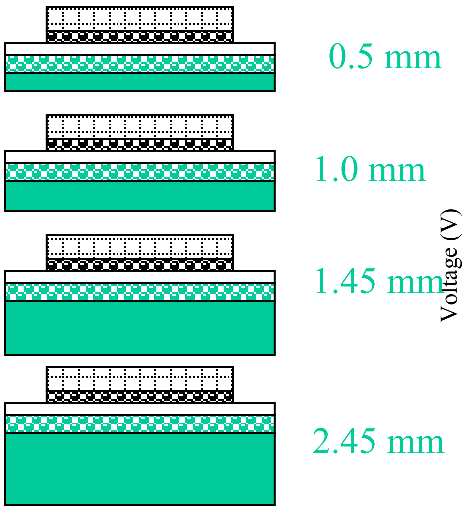
Equivalent Circuit

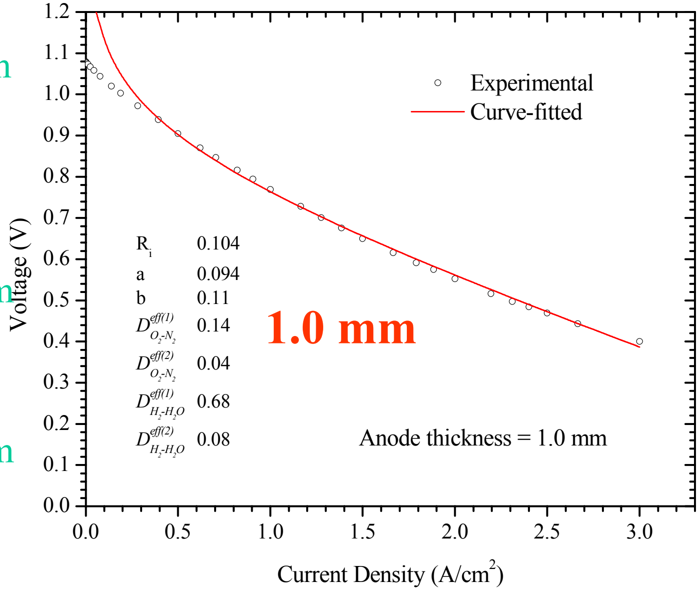


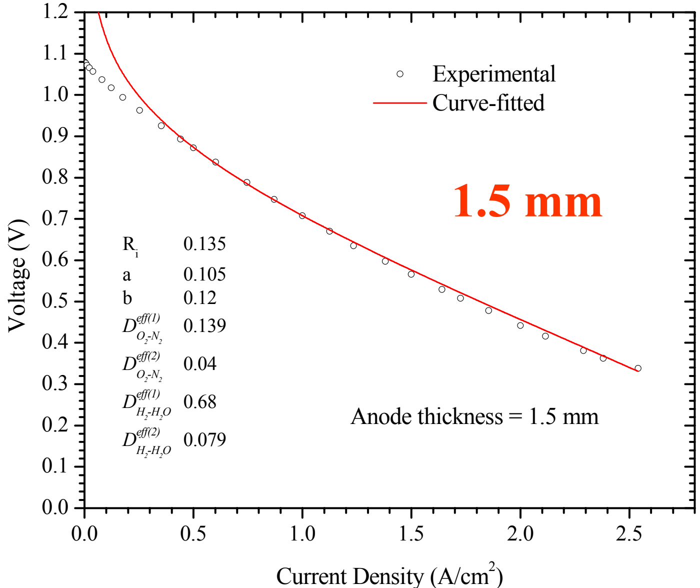
Curve Fitting: Anode Support Thickness Varied

Only anode support thickness varied. Note all polarization curves fitted with the same four effective diffusivities – experimental validation of the model









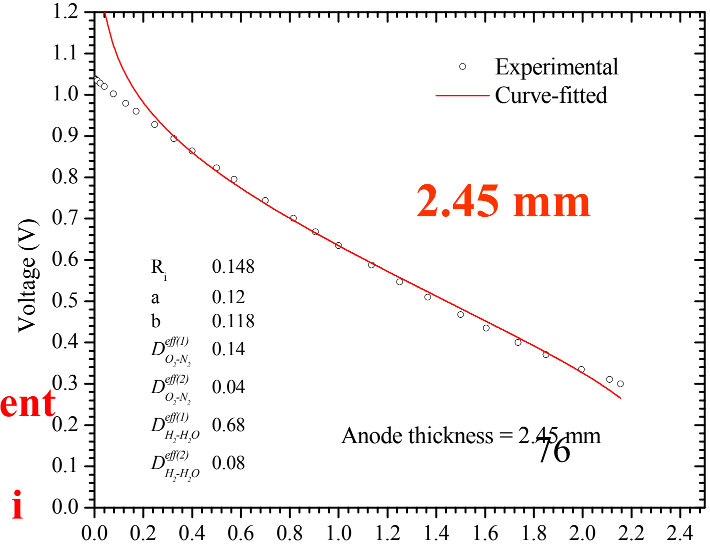
$$D^{eff\,(1)}_{H_2-H_2O} = 0.68\ \text{cm}^2/\text{s}$$

$$D^{eff\,(2)}_{H_2-H_2O} = 0.08\ \text{cm}^2/\text{s}$$

$$D^{eff\,(1)}_{O_2-N_2} = 0.14\ \text{cm}^2/\text{s}$$

$$D^{eff\,(2)}_{O_2-N_2} = 0.04\ \text{cm}^2/\text{s}$$

Divergence at low current densities since Tafel is not applicable at low i



Topic 4: Cell Design for Enhanced Performance

- A five layer anode-supported cell with standard materials (YSZ, LSM, Ni).
- Anode support of Ni + YSZ, approximately 50% of each by volume, porosity in excess of ~45% , coarse structure – pore size several microns; thickness as small as possible – practical 0.3 to 0.5 mm.
- Anode functional layer of Ni + YSZ, approximately ~60 vol.% YSZ, ~40 vol.% Ni, porosity ~25%, thickness ~5 to 20 microns; particle sizes on the order of 0.5 to 1 micron. If particle size is much smaller than 0.5 μm, reduce thickness to ~2-3 μm. Microstructure well-developed – good inter-particle contact.
- Electrolyte, approximately ~ 8 to 10 microns thick, dense.
- Cathode functional layer of LSM + YSZ, approximately ~60 vol.% YSZ, ~40 vol.% LSM, porosity ~25%, thickness ~5 to 20 microns; particle sizes on the order of 0.5 to 1 micron. If particle size is much smaller than 0.5 μm, reduce thickness to ~2-3 μm. Microstructure well-developed – good inter-particle contact.
- Cathode current collector, LSM, coarse structure, porosity ~45 or 50%; pore size several microns; thickness ~50 to 200 microns (0.05 to 0.2 mm).

Rationale for the Choices of Various Cell Microstructural/Geometric Parameters

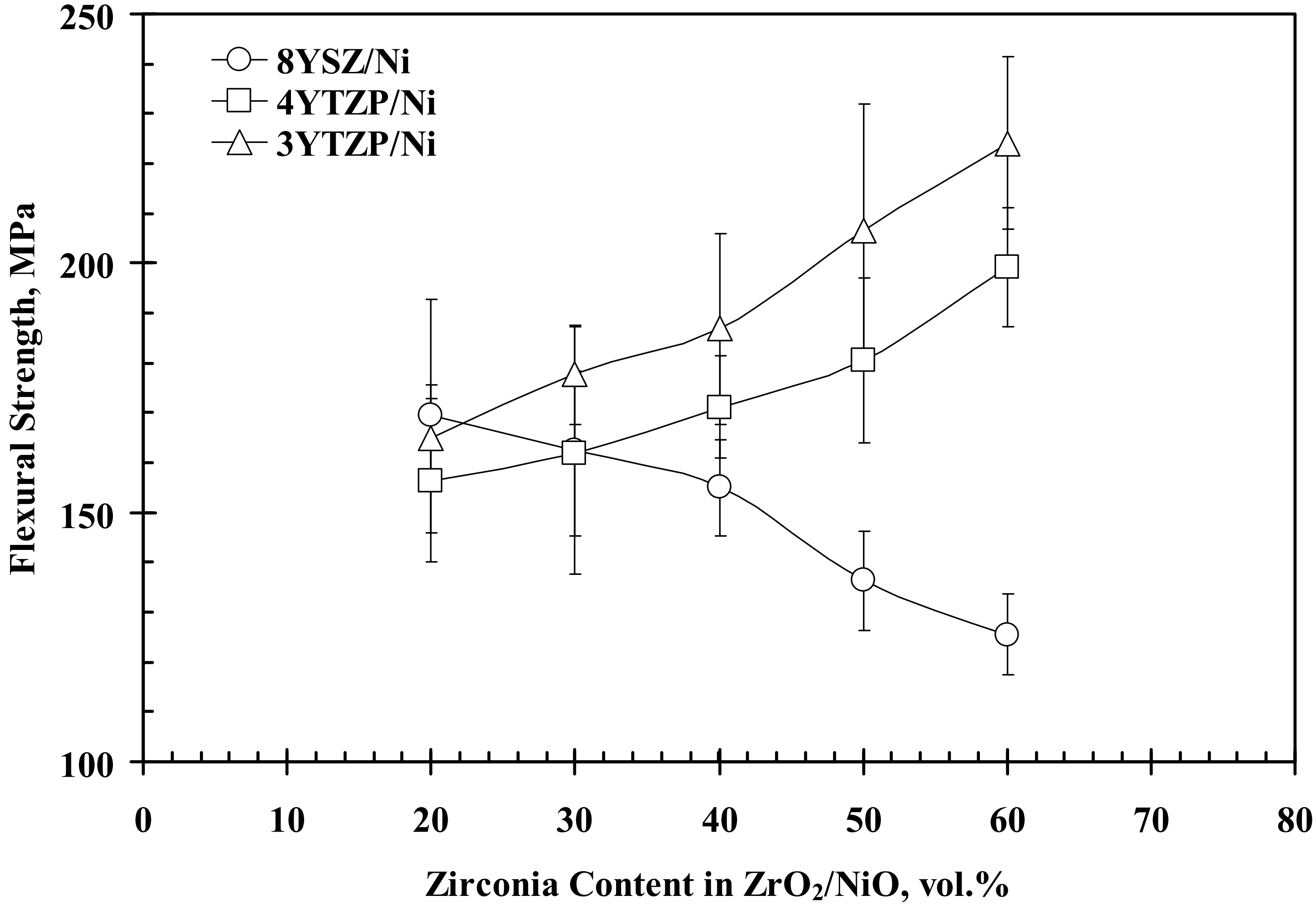
- Anode Support: Minimize concentration polarization, even at low pH_2 (high fuel utilization) – maximize i_{as}. Ensure sufficient strength (not too thin – not too porous), sufficient electrical conductivity.
- Anode Functional Layer: Minimize activation polarization, even at low pH_2 – large TPB length, small YSZ particle size, connected YSZ and connected Ni, modest porosity – thick enough to spread out electrochemical zone – thin enough to minimize concentration polarization.
- Electrolyte: Thickness not too critical, as long as below about 10 microns. Thick enough to be pinhole free.
- Cathode Functional Layer: Minimize activation polarization, even at low pO_2 – large TPB length, small YSZ particle size, connected YSZ and connected LSM, modest porosity – thick enough to spread out electrochemical zone – thin enough to minimize concentration polarization.
- Cathode Current Collector: Minimize concentration polarization, even at low pO_2 (high oxidant utilization) – maximize i_{cs}. Ensure sufficient electrical conductivity – minimize sheet resistance.

Topic 5: Cell Design – Thermo-mechanical Considerations

- All three components (anode, cathode, electrolyte) and the cell are brittle – can break, not bend.
- Strength is largely determined by the strength of the anode in anode-supported cells (thickest component). Typical strength is ~120 to ~150 MPa, sometimes even lower.
- Strength requirement is important from the standpoint of handling, thermal cycling, stresses due to non-uniform temperature distribution.
- Anode strength depends upon the relative amounts of Ni and YSZ, porosity, etc.
- Fracture toughness is another important fracture mechanical property.

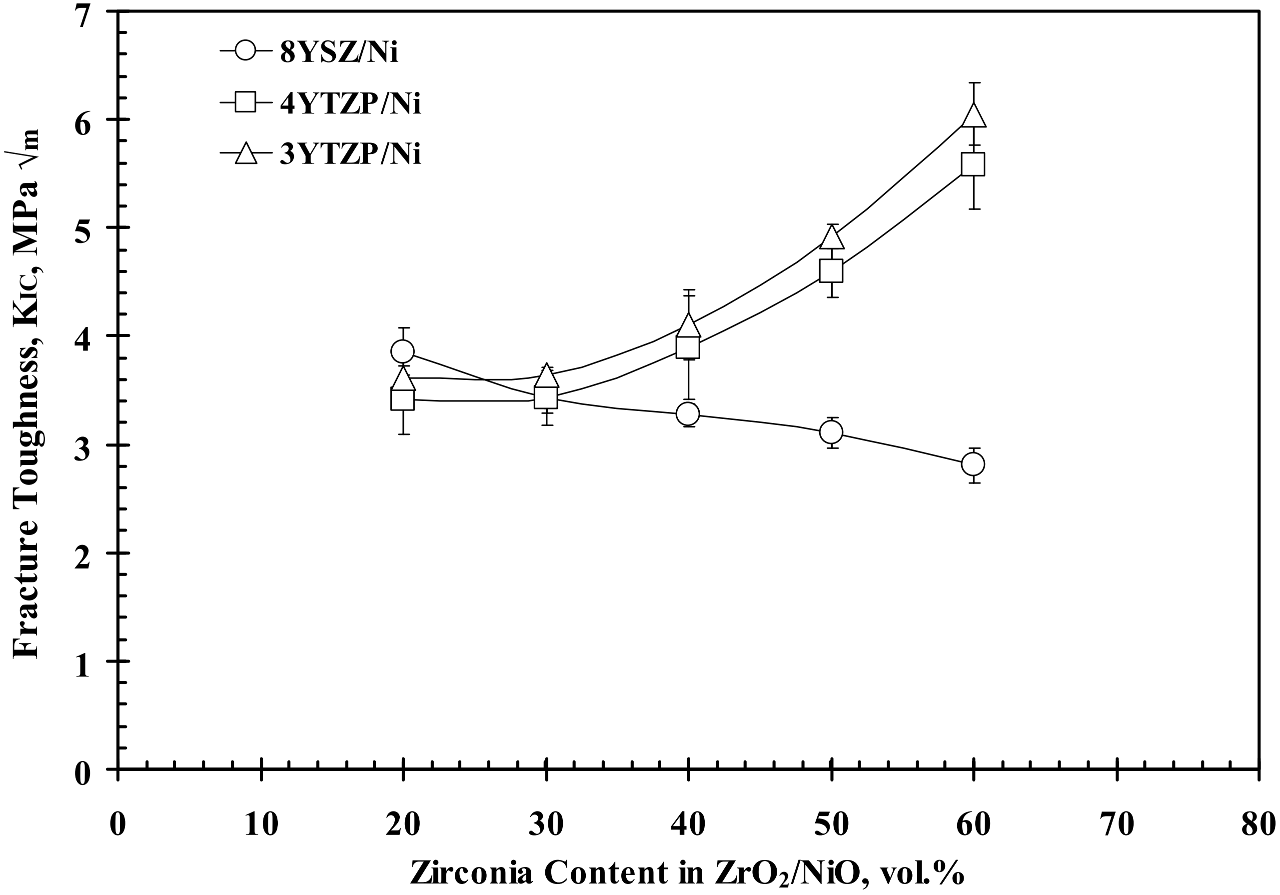
Four-Point Bend Strength of Zirconia/Ni Anode-Supports as a Function of Zirconia Content

(after reducing at 800°C for 24 hours under 5 liter/min of 10% H_2 + 90% N_2)



Fracture Toughness of Zirconia/Ni Anode-Supports as a Function of Zirconia Content

(Measured Using Single Edge Notch Bending (SENB) Technique, after reducing at 800°C for 24 hours under 5 liter/min of 10% H_2 + 90% N_2)



Thermo-mechanical Issues – Stresses in PEN

- PEN stands for the cell (Positive electrode – Electrolyte – Negative electrode).
- Thermal expansion coefficients of the three components are in general different.
- Elastic moduli (e.g. Young’s) of the three components are in general different.
- At the sintering or cathode firing temperature, there are negligible stresses in the PEN structure.
- When cooled to room temperature, different components tend to shrink to different sizes – dictated by their thermal expansion coefficients.
- However, they are bonded together. Thus, the unit as a whole needs to shrink as one body – without causing cracks or delaminations. This leads to the establishment of stresses.
- Stresses are the highest at room temperature – lower at the operating temperature.
- Objective is to design cells such that minimum possible damage occurs.

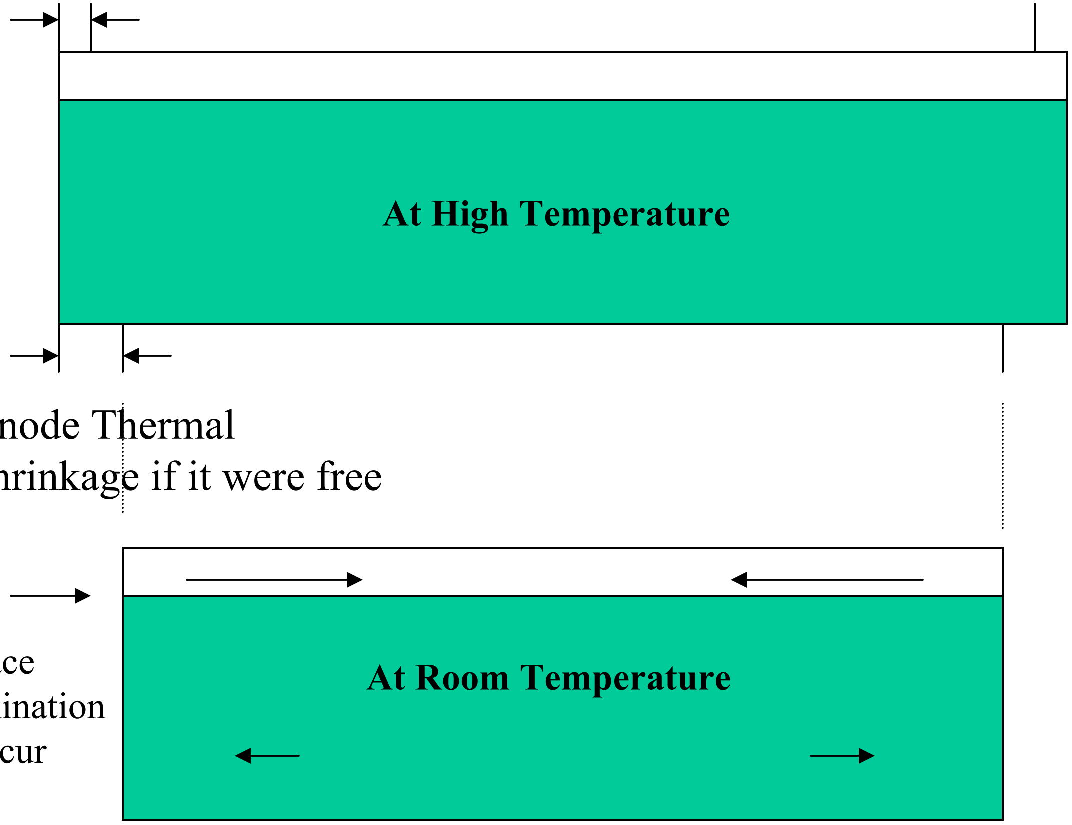
Thermo-Mechanical Considerations

- Differences in coefficients of thermal expansion.
- Differences in elastic properties, and component thicknesses.
- Cracking or delamination of layers.
- Flatness of the cell.
- Criteria for the selection of the best cell design.

What Happens when an Electrolyte-Anode Bi-layer is Cooled from the Fabrication Temperature?

Electrolyte Thermal
Shrinkage if it were free

Anode Thickness >> Electrolyte Thickness



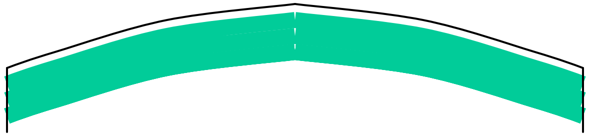
Cell assumed flat at high temperature

Anode Thermal
Shrinkage if it were free

Interface
Delamination
can occur

Net Result

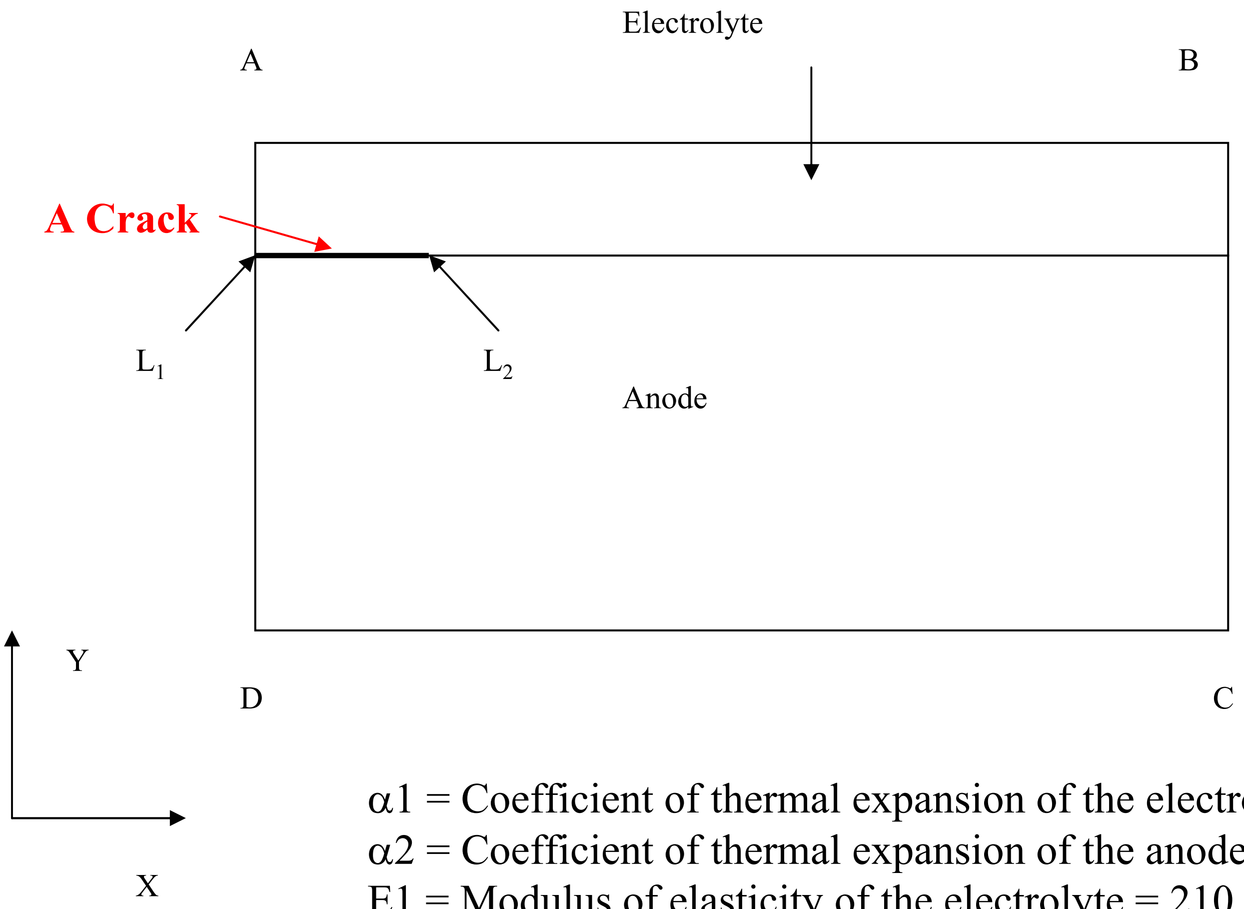
a) Electrolyte under bi-axial compression
b) Anode under bi-axial mild tension
c) The bi-layer exhibits a convex up bow



But anode and electrolyte are bonded across the interface

Shrinkages and bow are shown exaggerated

Electrolyte/Anode Bi-Layer Structure



$\alpha 1$ = Coefficient of thermal expansion of the electrolyte = 10.5 E-06/ °C

$\alpha 2$ = Coefficient of thermal expansion of the anode = 13 E-06/°C

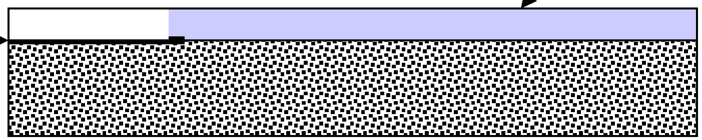
E1 = Modulus of elasticity of the electrolyte = 210 GPa

E2 = Modulus of elasticity of the anode = 170 GPa

Objective: To identify conditions under which a crack may develop – then in practice avoid such situations

Finite Element Analysis of Anode-Supported Cells

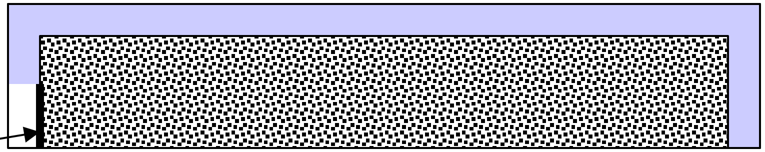
Finite Element Analysis of Delamination



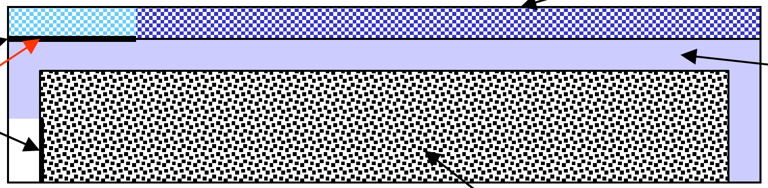
YSZ film in biaxial compression

Delamination Crack

Light violet color indicates the presence of a compressive stress in the electrolyte. If a crack forms, stress in the cracked part of the electrolyte is relieved. This is shown in white.



Delamination Crack



Cathode

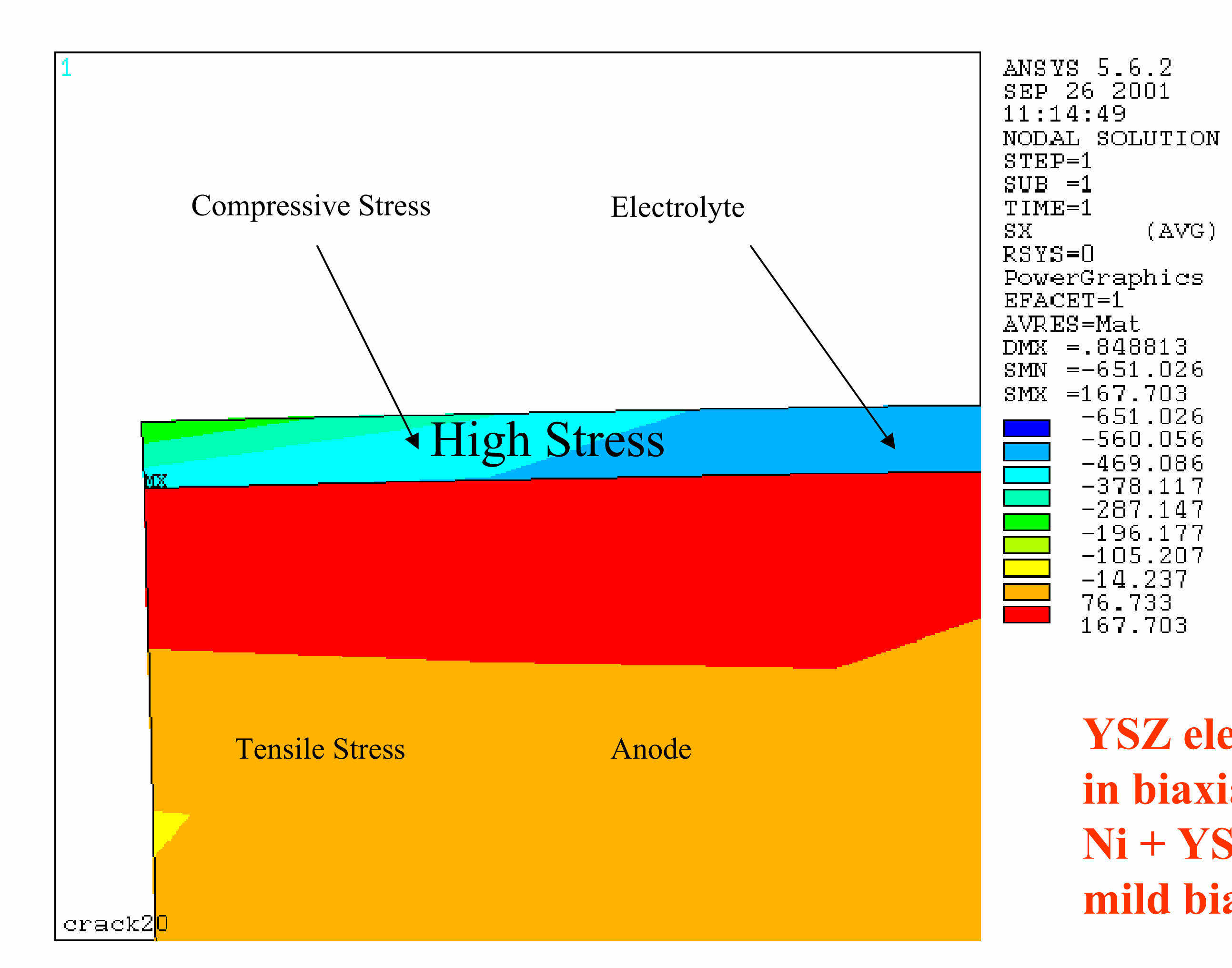
Electrolyte

Delamination Cracks

Anode

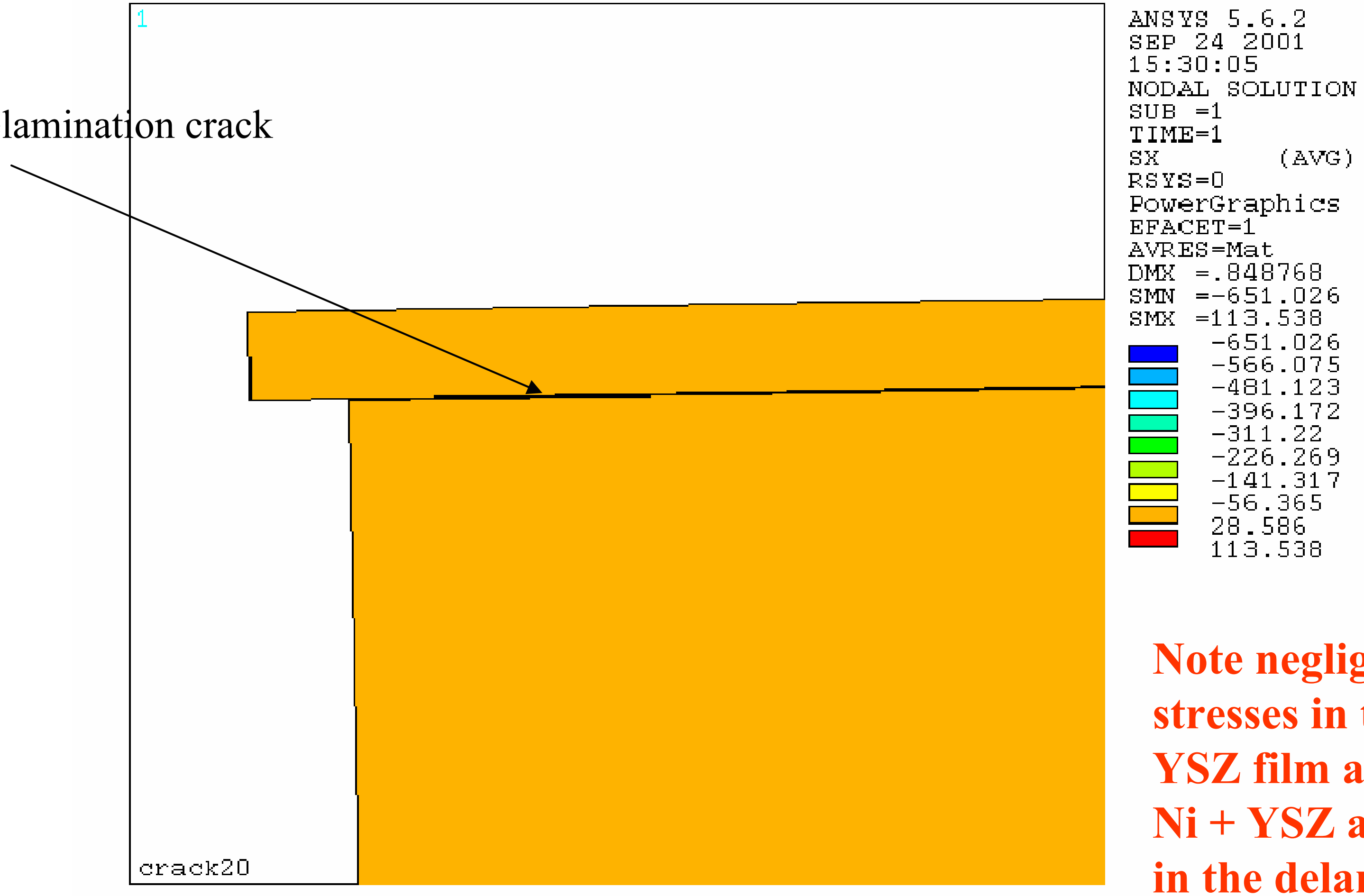
In this case, delamination crack is assumed to occur along the cathode-electrolyte interface. Thus, stress from the cracked part of the cathode is relieved – shown in light blue.

Bi-Layer without a Delamination Crack



YSZ electrolyte film in biaxial compression Ni + YSZ anode in mild biaxial tension

What Happens if Crack Develops along the Interface?



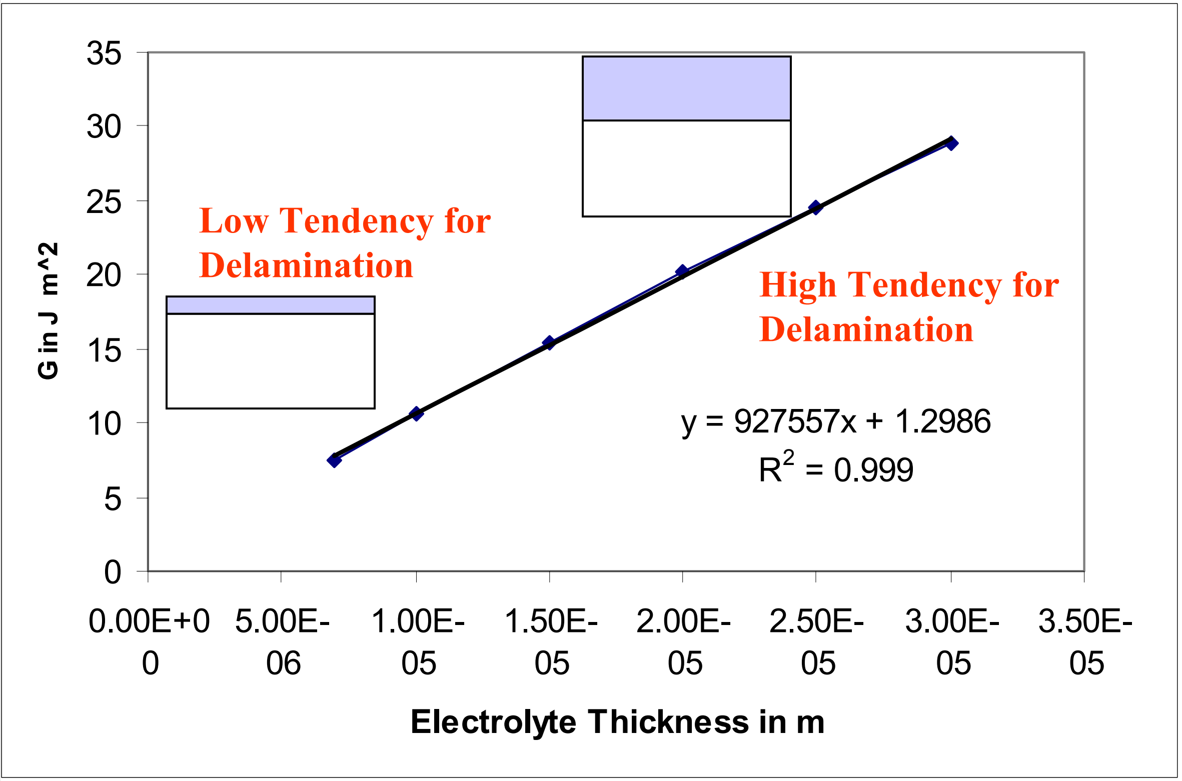
A delamination crack

Note negligible stresses in the YSZ film and the Ni + YSZ anode in the delaminated region.

Release of Strain Energy by Cracking along Interface

G: Strain Energy Released when a Delamination Crack forms

Electrolyte Thickness (μm)	G (J m^2)
7	7.5
10	10.6
15	15.5
20	20.1
25	24.6
30	28.8



Conclusion: For an anode-supported cell design, the thicker The YSZ film, the greater is the tendency for cracking

Message: Make the electrolyte as thin as possible from the standpoint of mechanical integrity – fortunately, this good for resistance as well

An Illustration: An Estimation of the Maximum Electrolyte Thickness in Anode-Supported Cells

Typical Values

$E_{el} \approx$ 200 GPa

Bending Neglected

$\alpha_{el} \approx$ 10 x 10^{-6} /°C

$\alpha_{an} \approx$ 13 x 10^{-6} /°C

$T_h \approx$ 1200°C = 1473 K

$T_l \approx$ 25°C = 298 K

30 J/m^2 (rather approximate – could be off 20%)

Maximum allowable electrolyte thickness

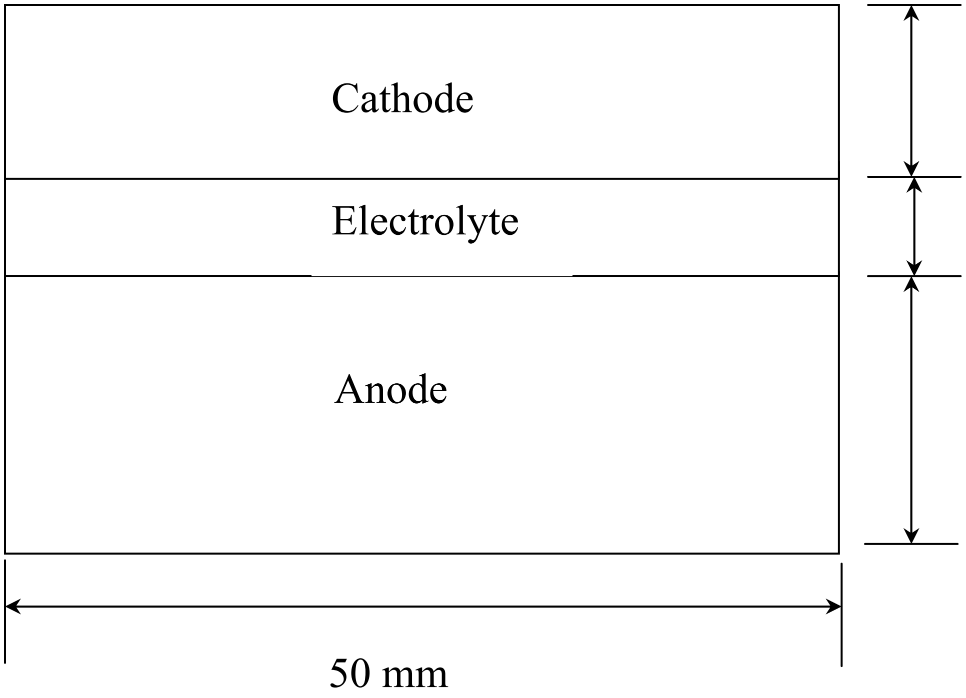
$$t_{el} < \frac{2\gamma_{\text{int}}}{E_{el}(\Delta\alpha\Delta T)^2} \sim 24\ \mu\text{m}$$

Typical electrolyte thickness ~5 to 10 μm

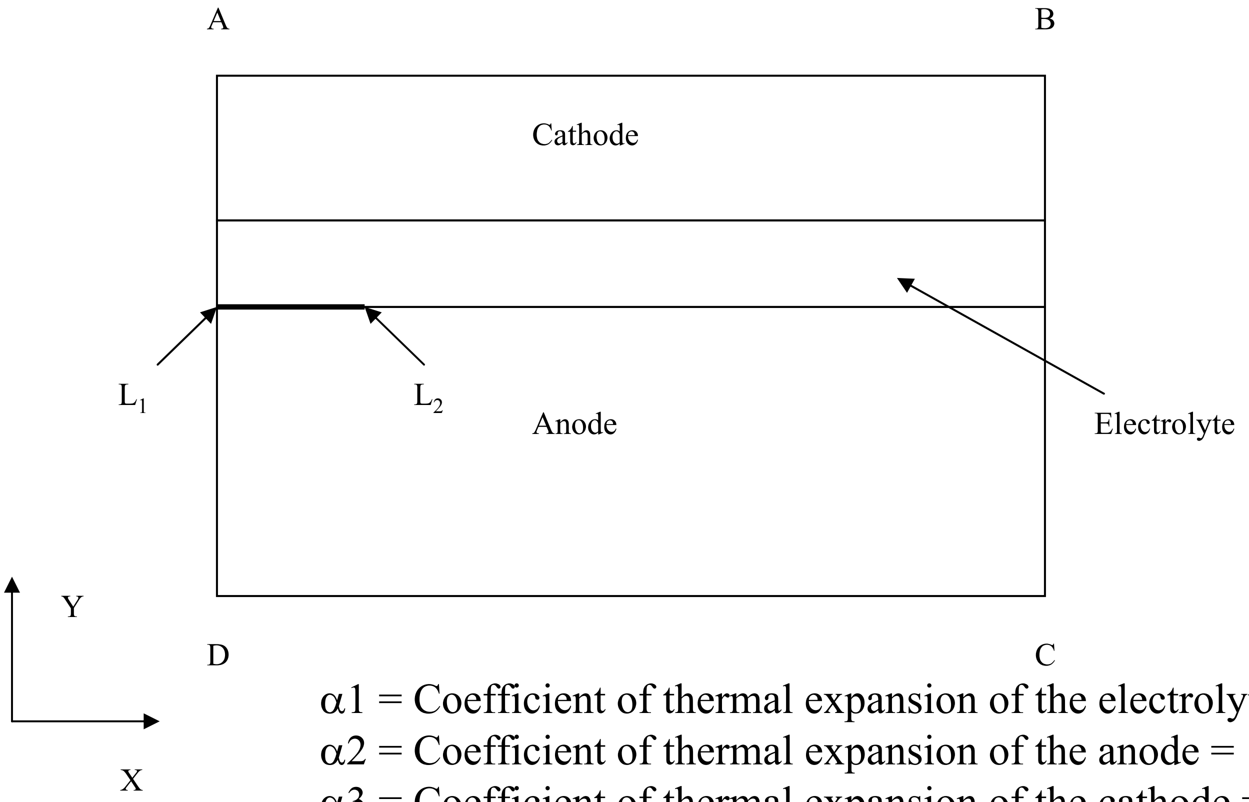
Complete Cathode-Electrolyte-Anode (PEN) Structure

Stress Analysis of the complete tri-layer structure can be similarly done using Finite Element Analysis (FEA) using commercial software (e.g. ANSYS). Data Required are: (a) Elastic properties of the three layers (or as many layers are there), (b) Thermal expansion properties of the three (or as many) layers, and (c) Thicknesses of the three (or as many) layers.

Results of some calculations

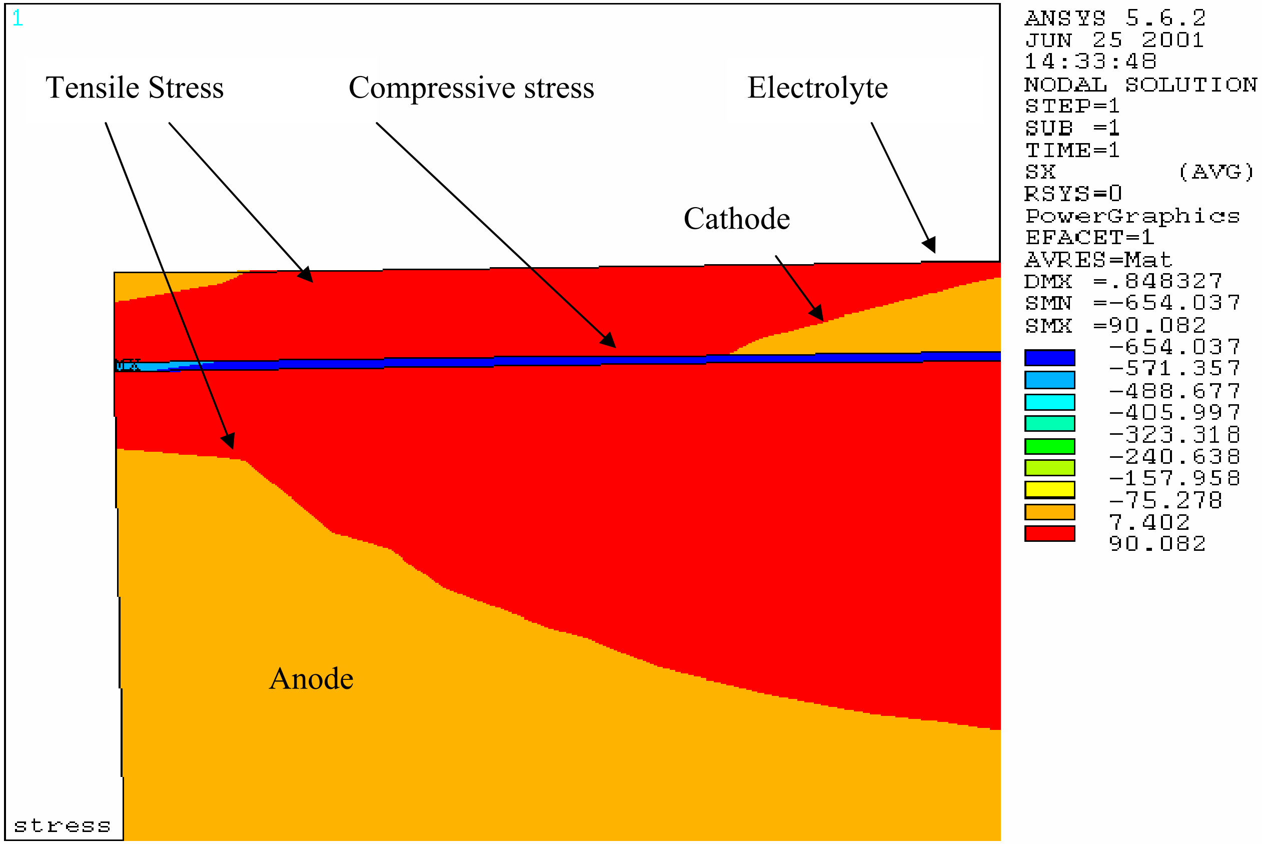


Cathode-Electrolyte-Anode Tri-layer: Crack Along Electrolyte-Anode Interface: Cathode matched with Anode



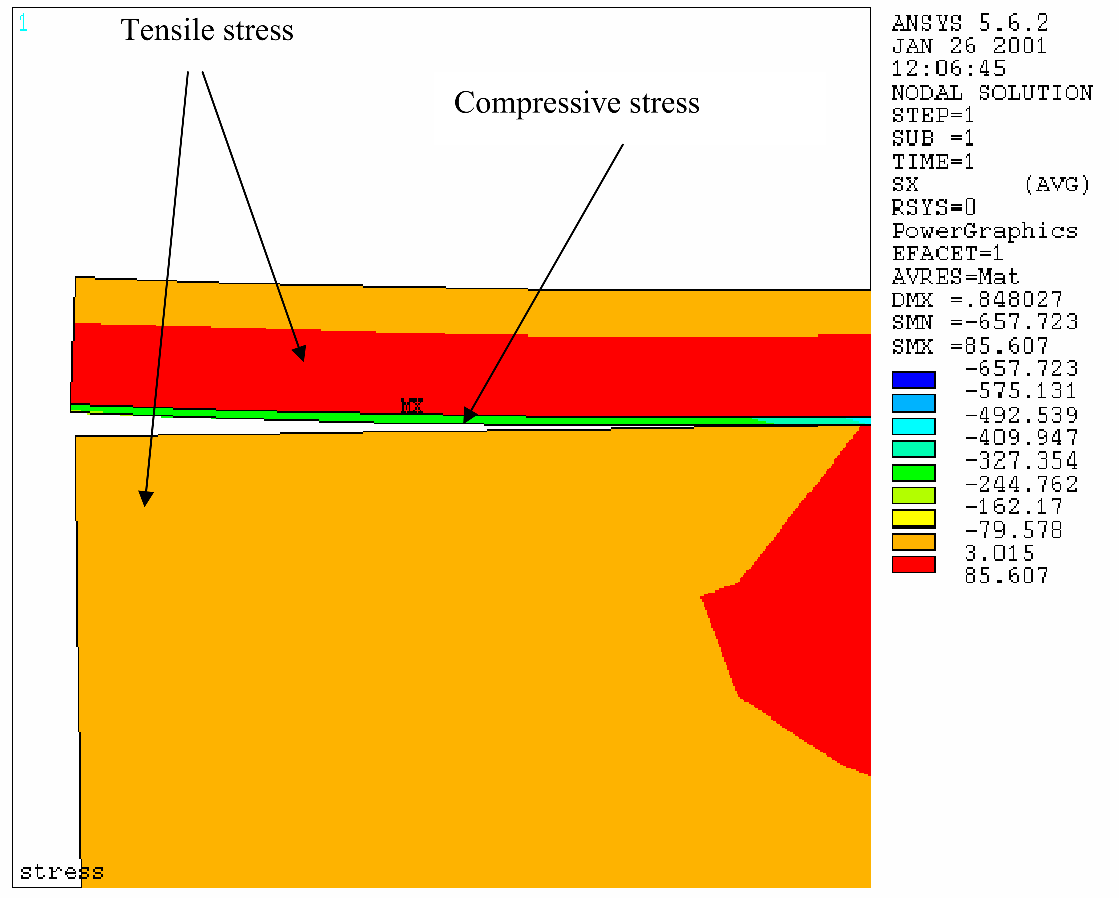
α1 = Coefficient of thermal expansion of the electrolyte = 10.5 E-06/ °C
α2 = Coefficient of thermal expansion of the anode = 13 E-06/°C
α3 = Coefficient of thermal expansion of the cathode = 13 E-06/°C
E1 = Modulus of elasticity of the electrolyte = 210 GPa
E2 = Modulus of elasticity of the anode = 170 GPa
E3 = Modulus of elasticity of the cathode = 50 GPa

Stress State in the Absence of a Crack: Cathode Matched with Anode



Note mild tensile stresses in both the anode and the cathode

Stresses when Delamination Crack forms between Anode and Electrolyte: Cathode Matched with Anode

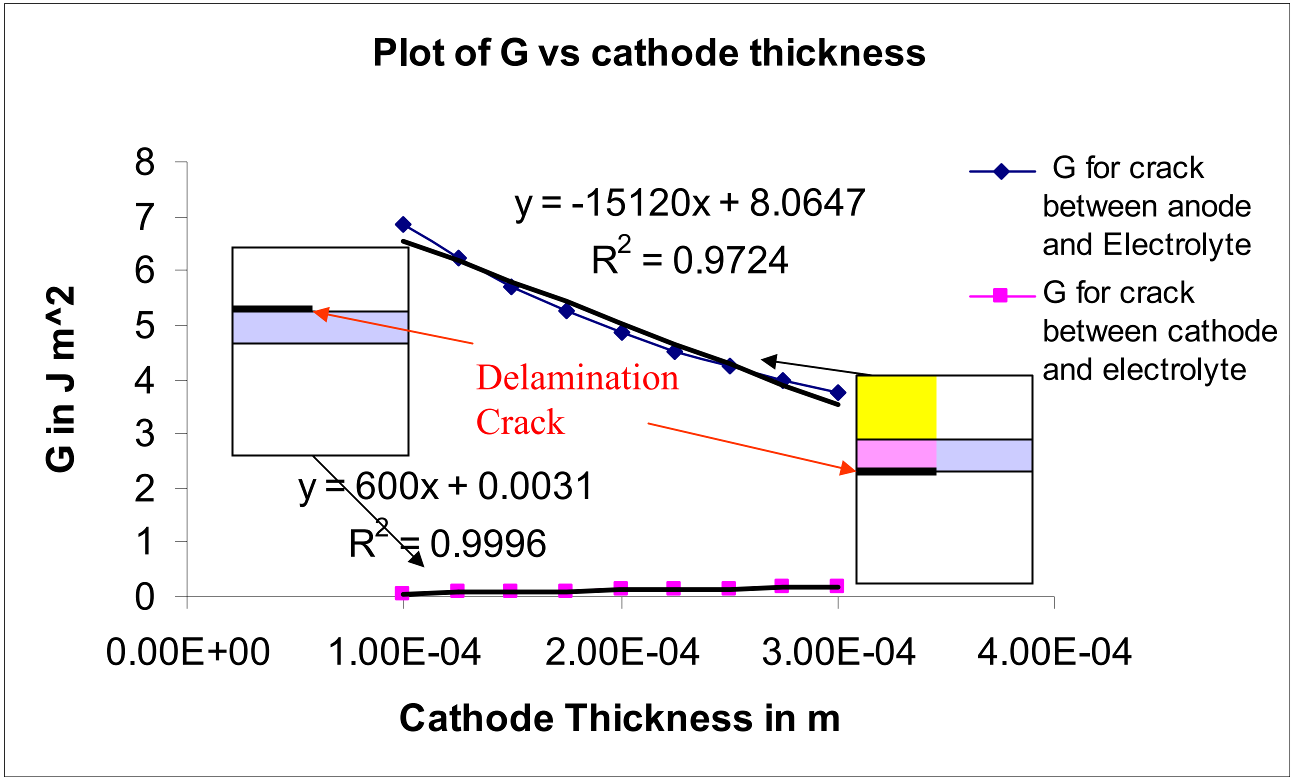


```
ANSYS 5.6.2
JAN 26 2001
12:06:45
NODAL SOLUTION
STEP=1
SUB =1
TIME=1
SX        (AVG)
RSYS=0
PowerGraphics
EFACET=1
AVRES=Mat
DMX =.848027
SMN =-657.723
SMX =85.607
     -657.723
     -575.131
     -492.539
     -409.947
     -327.354
     -244.762
     -162.17
     -79.578
     3.015
     85.607
```

Note relaxed stresses in the delaminated regions. Also note bending of the cathode-electrolyte bi-layer in the delaminated region.

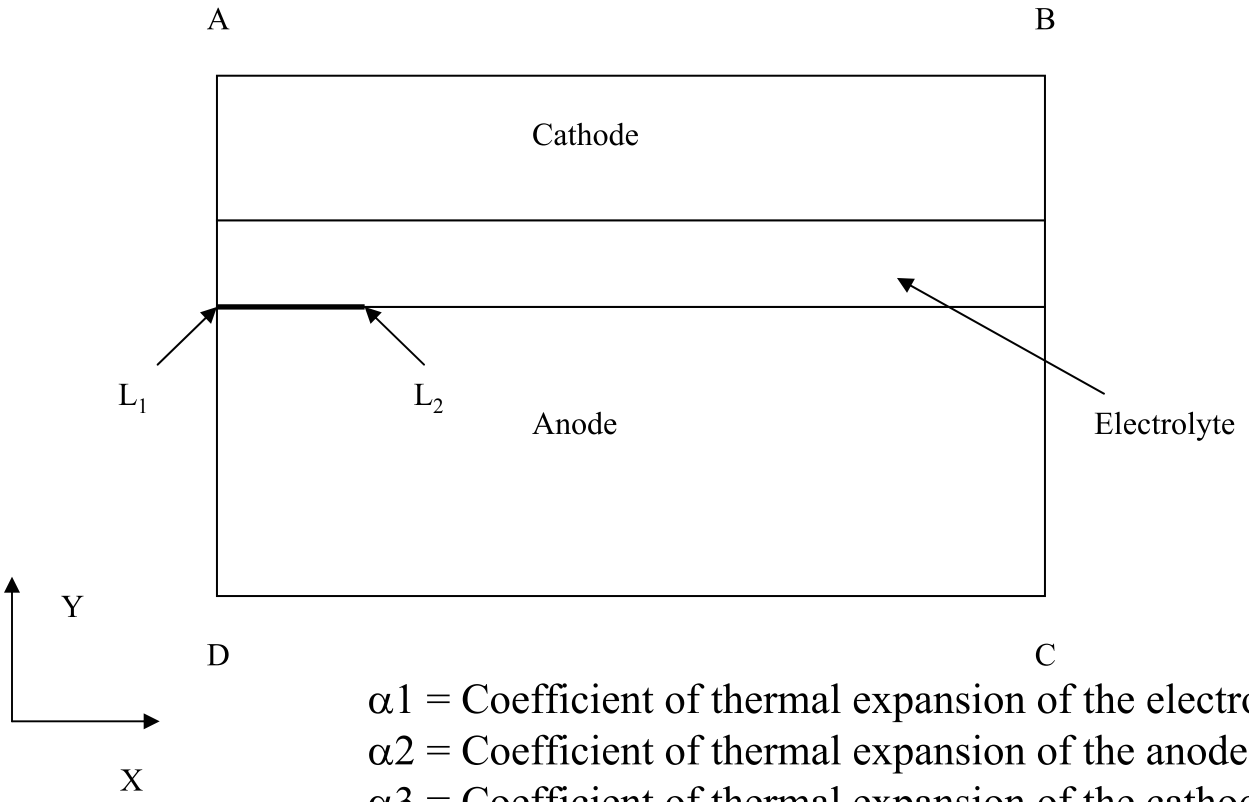
Elastic Energy Release Rate Cathode Matched with Anode

Elastic energy release rate, G, is the energy released per unit area of the interface IF a crack forms. For a crack to form, this must exceed a certain material And structure (PEN) parameter – here $2\gamma_{int}$. That is, if $G > 2\gamma_{int}$, crack will form. Thus, the lower the G, the lower the tendency for crack formation.



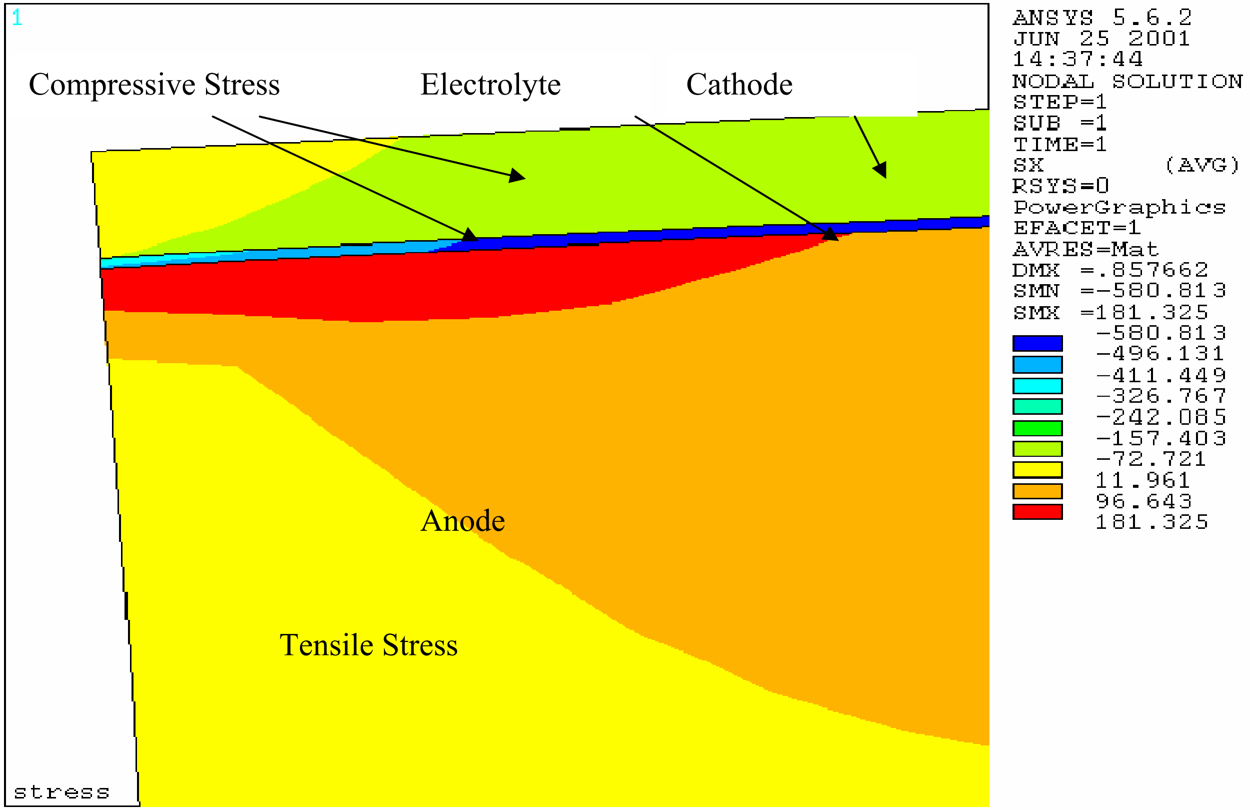
The above implies that crack will most likely occur along electrolyte/anode interface, And not along cathode/electrolyte interface, assuming the γ_{int} is the nearly the same for both interfaces. But note the rather low values of G.

Cathode-Electrolyte-Anode Tri-layer Crack Along Electrolyte-Anode Interface Cathode matched with Electrolyte



α1 = Coefficient of thermal expansion of the electrolyte = 10.5 E-06/°C
α2 = Coefficient of thermal expansion of the anode = 13 E-06/°C
α3 = Coefficient of thermal expansion of the cathode = 10.5 E-06/°C
E1 = Modulus of elasticity of the electrolyte = 210 GPa
E2 = Modulus of elasticity of the anode = 170 GPa
E3 = Modulus of elasticity of the cathode = 50 GPa

Stress State in the Absence of a Crack
Cathode Matched with Electrolyte



Compressive Stress

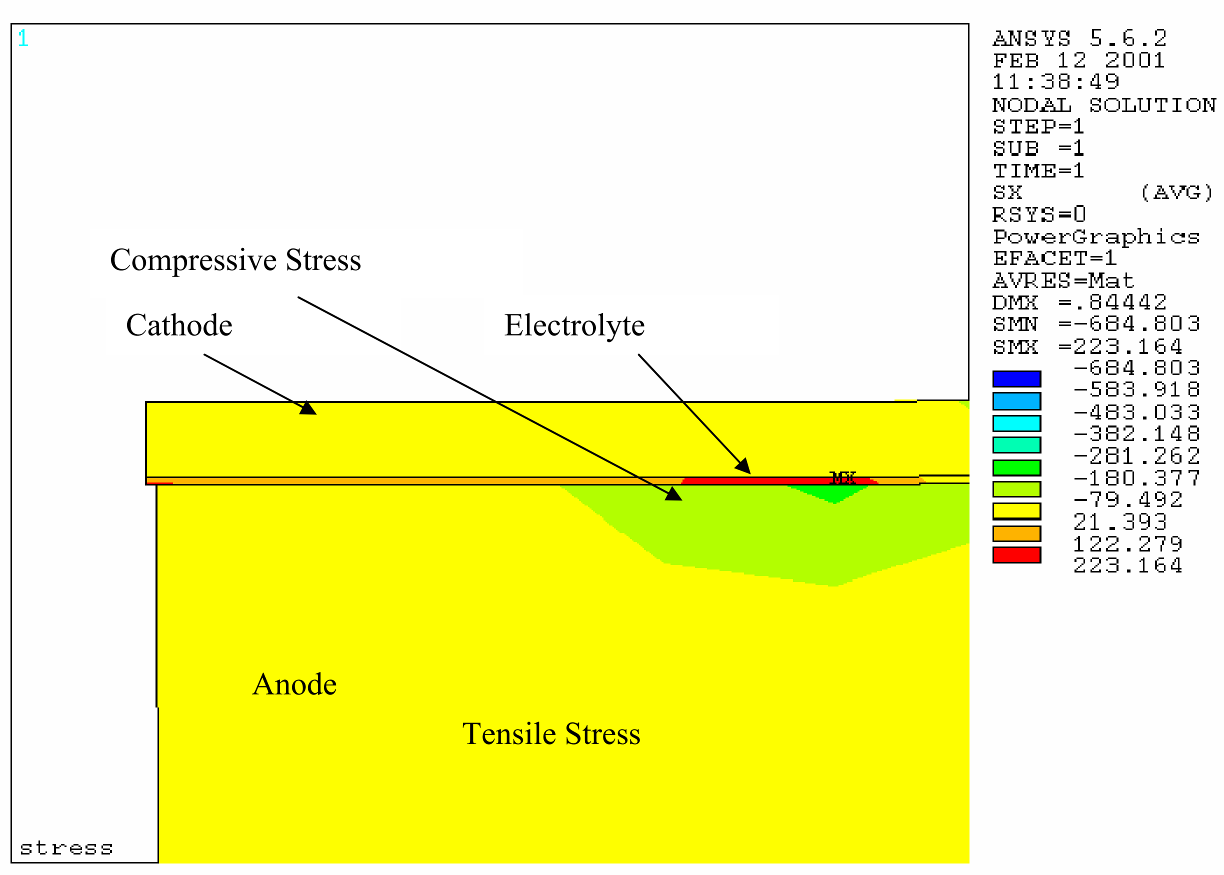
Electrolyte

Cathode

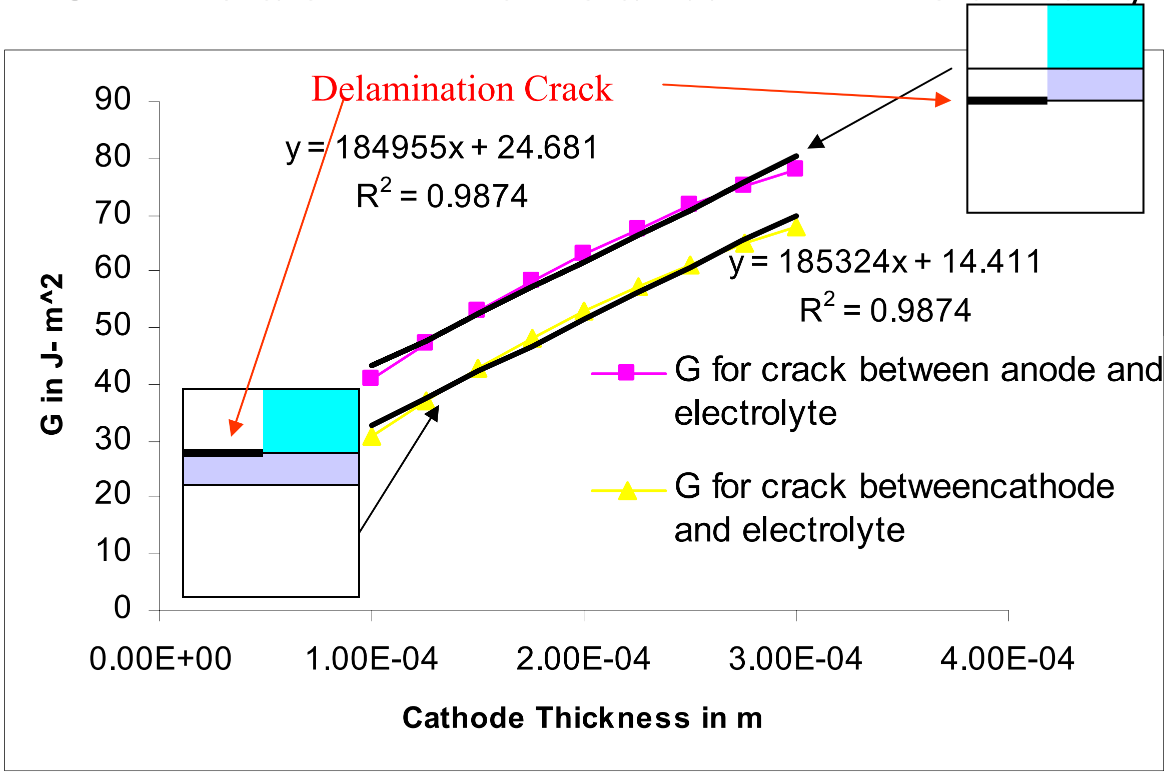
Anode

Tensile Stress

Stresses when Delamination Crack forms between Anode and Electrolyte Cathode Matched with Electrolyte



Elastic Energy Release Rate Cathode Matched with Electrolyte



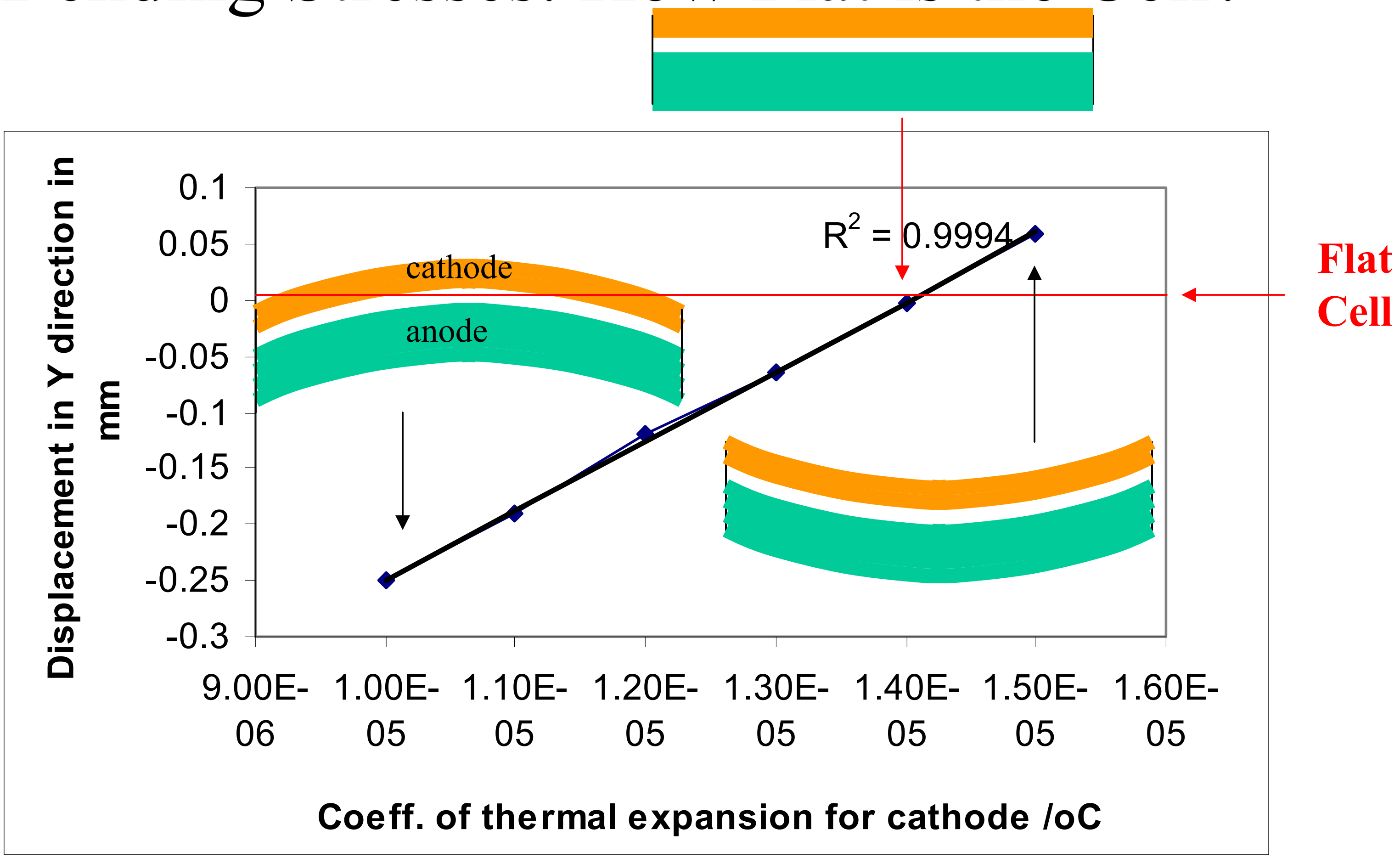
Note: The G is high for cracks along both interfaces. Thus, cracking may occur along either interface. Also, the G is higher in this case (cathode matched with electrolyte) than in the previous case (cathode matched with anode).

Message: For anode-supported cells, better to match Cathode with anode – not with the electrolyte

Effect of Properties on Cell Flatness

- So far, we have neglected the role of bending stresses – which is actually significant.
- Bending occurs due to differences in stresses in the various layers. Bending can be calculated using equilibrium conditions; Sum of forces = 0, Sum of moments = 0.
- Since thermal expansion coefficients are of the various layers are different, the level of bending (bow) will vary with temperature.
- Whether or not cells are flat is important in both stack assembly procedure used, and stresses that are generated.
- By choosing appropriate values of thermal expansion coefficients, elastic properties, and thicknesses, bow can be minimized.

Bending Stresses: How Flat is the Cell?



Thus, for α_{cathode} ~14 x 10^{-6} /°C, for the chosen values, the cell will be flat at room temperature.

E_1 = Electrolyte Modulus = 210 GPa
E_2 = Anode Modulus = 170 GPa
E_3 = Cathode Modulus = 50 GPa

α_1 = Electrolyte Th. Ex. Coeff. = 10.5 x 10^{-6}/°C
α_2 = Anode Th. Ex. Coeff. = 13 x 10^{-6} /°C
α_3 = Cathode Th. Ex. Coeff. = 10 to 15 x 10^{-6} /°C

Topic 6: Cell Fabrication

Cell fabrication by tape-casting followed by sintering is described in this section. This is probably the most common method of cell fabrication, although there likely are significant differences among developers insofar as the details are concerned. What is described is one of the approaches, and by no means the only approach. Also, it is to be emphasized that many details and variations from the process described here that are actually implemented in our process, are not given due to the proprietary nature of the work.

Cell Fabrication Steps

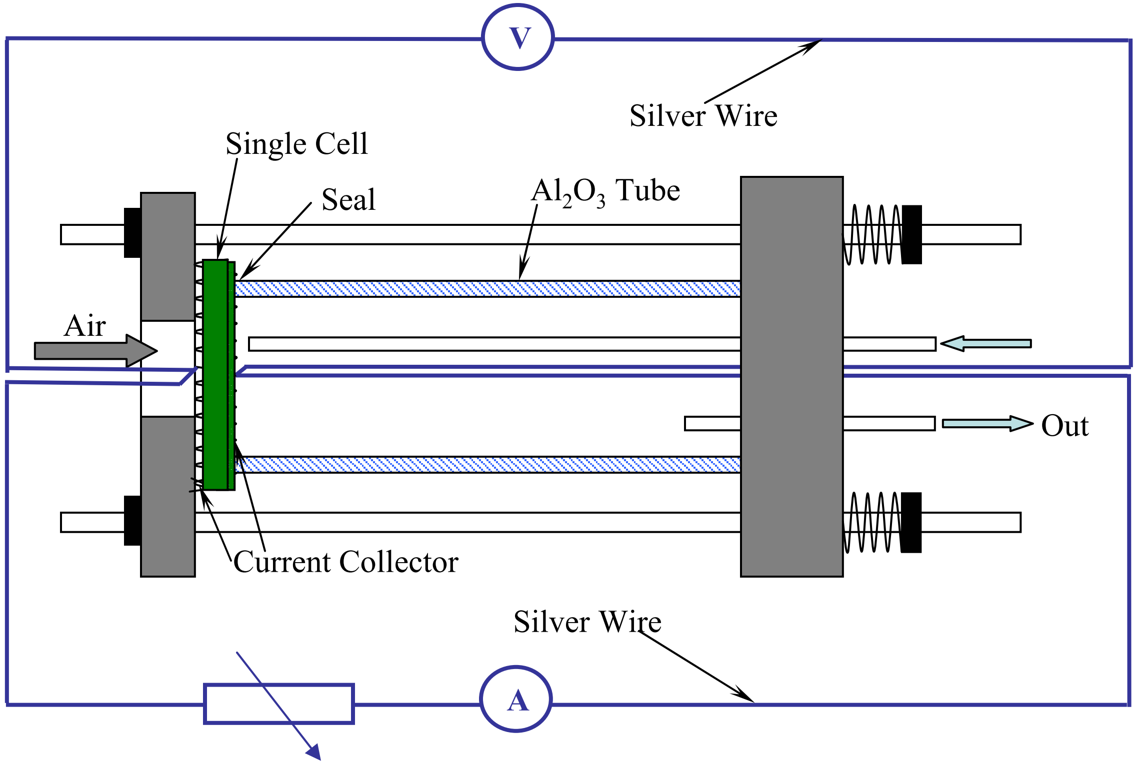
1) Raw materials and formulation
2) Tape casting the anode support, cutting to desired size
3) Applying the anode functional layer
4) Applying the electrolyte
5) Bisquing to ~1000°C for binder burnout
6) Application of the electrolyte layer
7) Sintering (1300 to 1500°C)
8) Applying the cathode functional layer
9) Applying the cathode current collector layer
10) Firing at ~1200°C

Processes have been developed for co-sintering the complete cell in a single high temperature step

Topic 7: Cell Testing

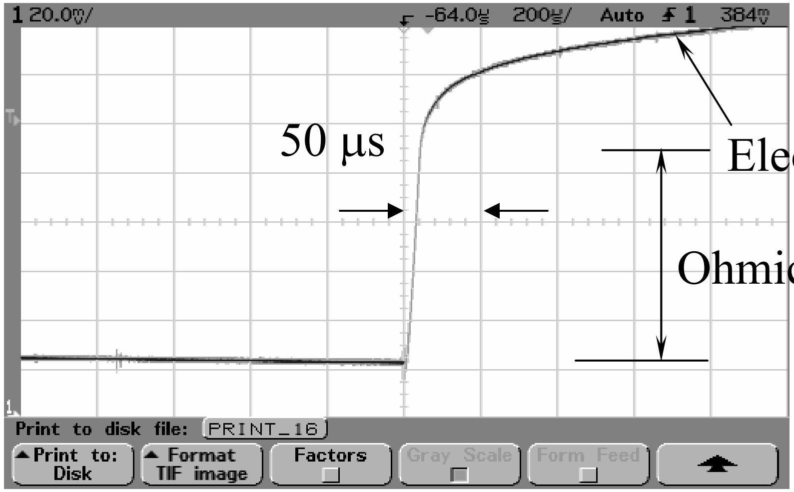
1) Button size cells (typical cathode area of 1 to 2 cm^2) are typically tested for general cell characterization.
2) Cells are tested under flooded conditions (high flow rates for both fuel and oxidant) – thus during such tests, fuel and oxidant utilizations are very small. In such cases, the measured parameters correspond to a given set of fuel and oxidant utilization (depending upon gas compositions).
3) Cell is secured (using either glass or compression seals) in a test fixture, placed inside a furnace.
4) Cell is heated to ~700°C, and a mixture of $H_2 + N_2$ is passed over anode to reduce NiO to Ni – leads to the creation of porosity. Then the fuel is passed over the anode ($H_2 + H_2O$ mixtures), and air (or $O_2 + N_2$ mixtures).
5) An electronic load box and/or a resistor box is used for testing.
6) Voltage vs. current data are collected. Usually, voltage (y-axis) is plotted vs. current density (x-axis).
7) Using a fast response electrochemical measuring instrument, sudden change in voltage that occurs immediately after interrupting the current is measured. This gives a measure of the ohmic contribution from the cell.

A Test Fixture for Testing Button Cells



Current Interruption

An oscilloscope trace



Print to disk file: PRINT_16

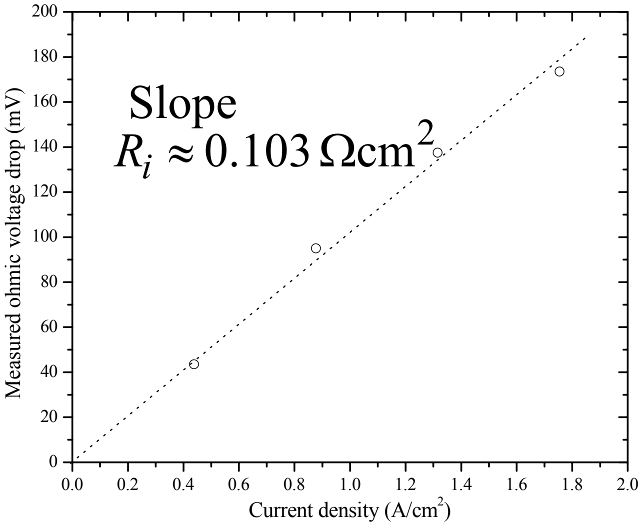
Print to: Disk

Format TIF image

50 µs

Electrode Processes (slow)

Ohmic Contribution = ΔV

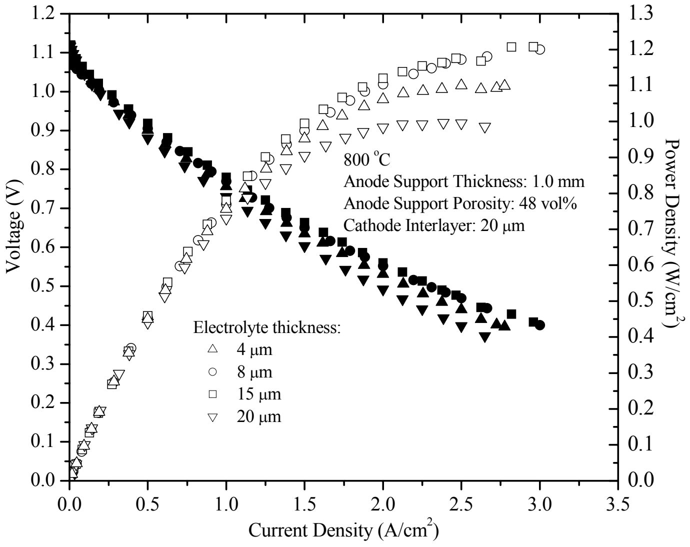


Slope

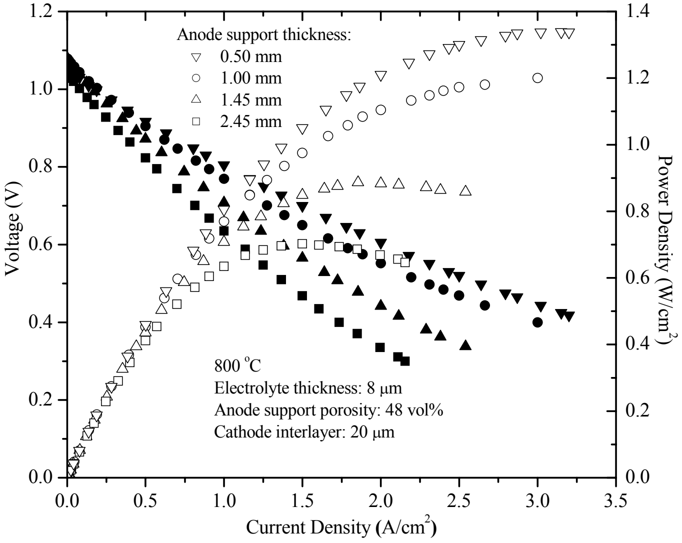
$R_i \approx 0.103\ \Omega\text{cm}^2$

Ohmic Area Specific Resistance $R_i = \dfrac{\Delta V}{i}$ Ωcm^2

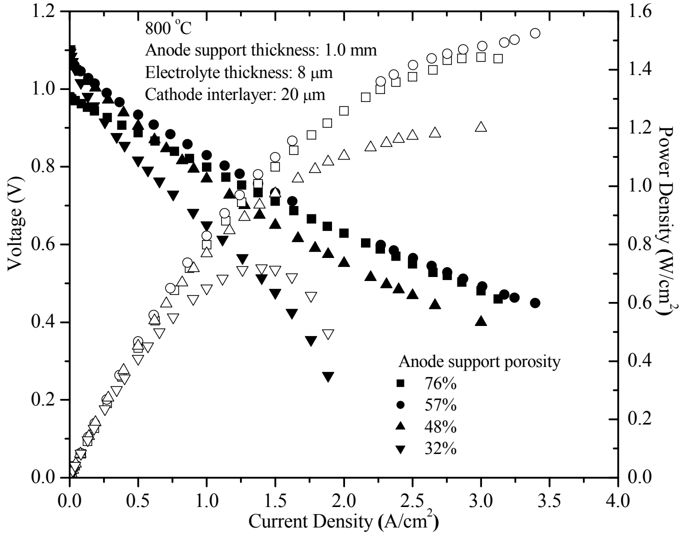
Effect of Various Cell Parameters on Performance



Electrolyte Thickness Varied



Anode Support Thickness Varied



Anode Support Porosity Varied

The phenomenological equation stated earlier can be used to fit to the data. Some of the parameters can be obtained through separate, out of cell, measurements.

Summary Statements

- I have tried to give some material on fundamental concepts for designing high performance, robust cells.The material given here is by no means complete. It is hoped that this might be useful as a starting point for someone interested in the subject. There are numerous articles in the literature one should read for further learning.