Introduction to Fuel Cells

Scott A Barnett, Northwestern University

Motivations, applications, history

Fuel cell types

Electrochemical Basics
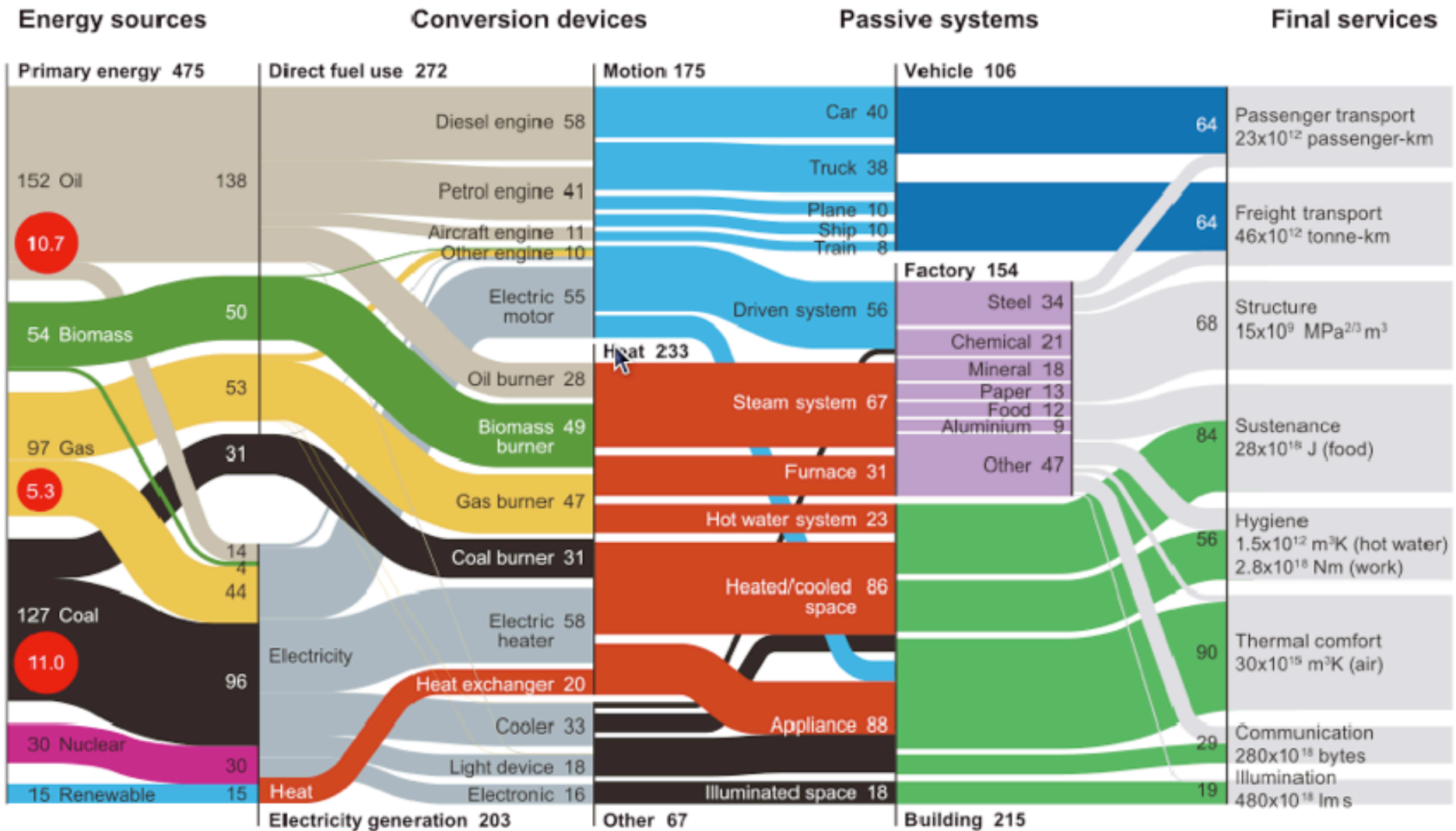
Electrochemical Kinetics

Charge Transport

Mass Transport

Stacks and Systems

Relevance of Electrochemical Devices: World Energy Flows Sankey Diagram

Energy sources | Conversion devices | Passive systems | Final services

Primary energy 475 — Direct fuel use 272 — Motion 175 — Vehicle 106

- 152 Oil — 138
- 10.7
- 54 Biomass — 50, 53
- 97 Gas — 31
- 5.3
- 127 Coal — 14, 4, 44, 96
- 11.0
- 30 Nuclear — 30
- 15 Renewable — 15

Diesel engine 58, Petrol engine 41, Aircraft engine 11, Other engine 10, Electric motor 55, Oil burner 28, Biomass burner 49, Gas burner 47, Coal burner 31, Electricity, Electric heater 58, Heat exchanger 20, Cooler 33, Light device 18, Heat, Electronic 16

Electricity generation 203

Car 40, Truck 38, Plane 10, Ship 10, Train 8, Driven system 56, Heat 233, Steam system 67, Furnace 31, Hot water system 23, Heated/cooled space 86, Appliance 88, Illuminated space 18

Other 67

Vehicle 106 — 64, 64

Factory 154 — Steel 34, Chemical 21, Mineral 18, Paper 13, Food 12, Aluminium 9, Other 47 — 68, 84

Building 215 — 56, 90, 29, 19

Passenger transport 23×10^{12} passenger-km

Freight transport 46×10^{12} tonne-km

Structure 15×10^9 $MPa^{2/3} m^3$

Sustenance 28×10^{18} J (food)

Hygiene 1.5×10^{12} m^3K (hot water) 2.8×10^{18} Nm (work)

Thermal comfort 30×10^{15} m^3K (air)

Communication 280×10^{18} bytes

Illumination 480×10^{18} lm s

Annual global flow of energy in 2005, EJ [10^{18} joules]

Annual global direct carbon emissions in 2005, Gt CO_2 [10^9 tonnes of CO_2]

2

Efficiency Comparisons
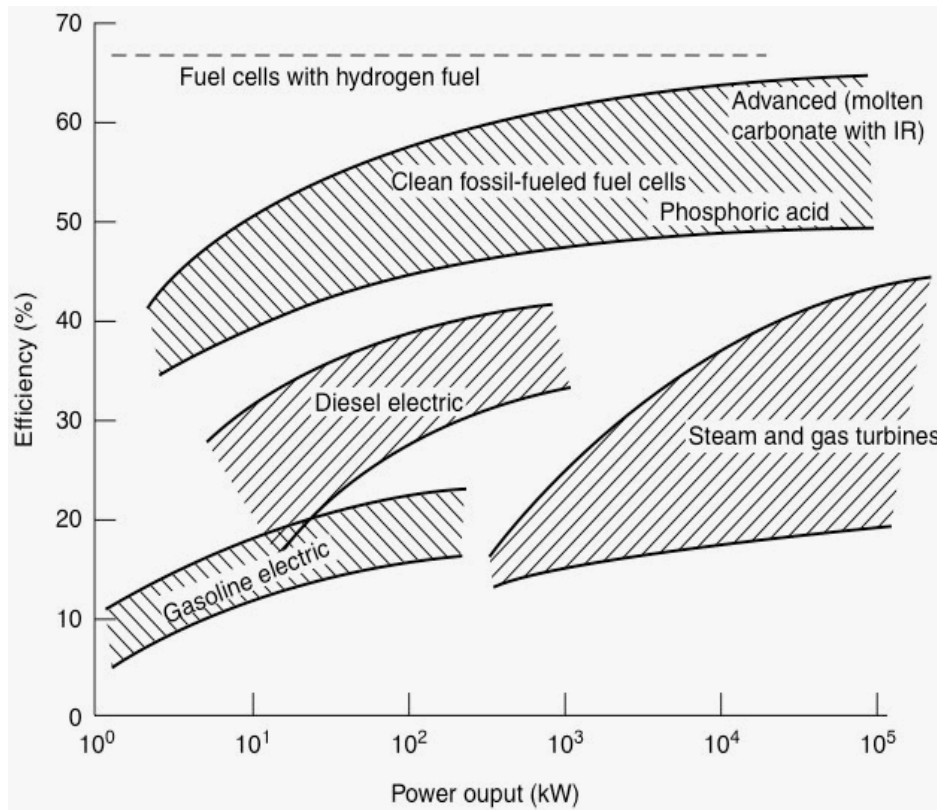
- High efficiency means low CO_2
- Low emissions of other pollutants
  - Sulfur removed
  - NOx not formed
  - No CO
  - No particulates
- Fuel cells can be sited near point of use
  - Allows direct use of waste heat - effective efficiency > 80%

Fuel Cell Introduction

- History
- Fuel cell issues
- Applications
- Overview of fuel cell types
    - Phosphoric acid
    - Proton exchange membrane
    - Alkaline
    - Molten carbonate
    - Solid oxide

Historical Origins of Fuel Cells

Sir Humphrey Davy, **1802**:
    Electrochemical cell with aqueous solution of nitric acid.
    A precursor of the fuel cell.

Christian Friedrich Schönbein, Basle, **1838**:
    The inventor of fuel cell. Electric current is
Generated from the chemical reaction of hydrogen
with oxygen or chlorine on platinum electrodes.

(1799-1868)

Sir William Grove, **1839**:
    Fuel cell of H_2-O_2 with solution of sulfuric
acid and platinum foil electrodes. Due to his
intensive research, he is considered the father
(and often, incorrectly so, the inventor) of fuel cell.

(1811-1896)

Water

Sulfuric Acid Solution

Ludwig Mond and Charles Langer, **1889**:
    They coin the name "fuel cell".
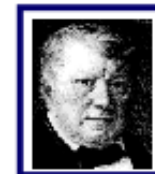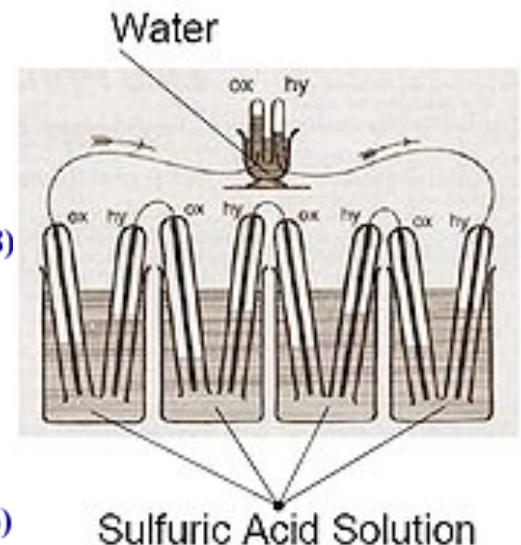
Fuel Cell Milestones

1902, **J. H. Reid**:
    The first description of an AFC (KOH).

Francis T. Bacon, UK:
1939:   Construction of an AFC (KOH) operating also on
                inverse mode (electrolytic unit). Pressure 220 bar,
                current density 13 mA/cm^2, maximum voltage 0,89 V.
1954:   Fuel cell of 150 W, 41 bar, 200°C.
1959:   Fuel cell of 6 kW, 38 bar, 200°C, 700 mA/cm^2.
1962-1966, **GEMINI Program**, USA:
    PEM fuel cells of 1 kW. **The first practical application.**

1967-1972, **APOLLO Program**, USA:
    Three AFC's of 1.4 kW each on each spaceship.

1977, **Space Shuttle**, USA:
    Three AFC's of 12 kW each on each space shuttle.
    Operating conditions: 4 atm, 60-70°C, 100 kW/kg.

2003, **Submarine by HDW**, Germany:
    Two modules of PEM fuel cells, 120 kW$_e$ each.

Year of First Successful Operation: Energy Conversion Devices

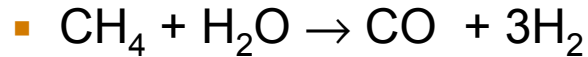|	
Steam engine	1769
Fuel cell	1839
Otto engine	1876
Steam turbine	1884
Diesel engine	1897
Gas turbine	1939

Fuel Cell Problems

- Cost
  - Cost of a new technology is always high initially
    - Until high-volume manufacturing brings cost down
  - Need initial applications without entrenched low-cost alternatives
- Fuels for fuel cells
  - Most fuel cells use only pure hydrogen fuel
    - Not available in large quantities
    - Difficult to store, transport, transfer, *etc.*
    - Usually linked with the "Hydrogen Economy"
  - Often chemically convert other fuels to hydrogen
- Cost
  - Technology is complex
  - Fuel cells themselves may be only 25% of total system cost

Example Fuel Cell Diagram: Ballard 250 kW System
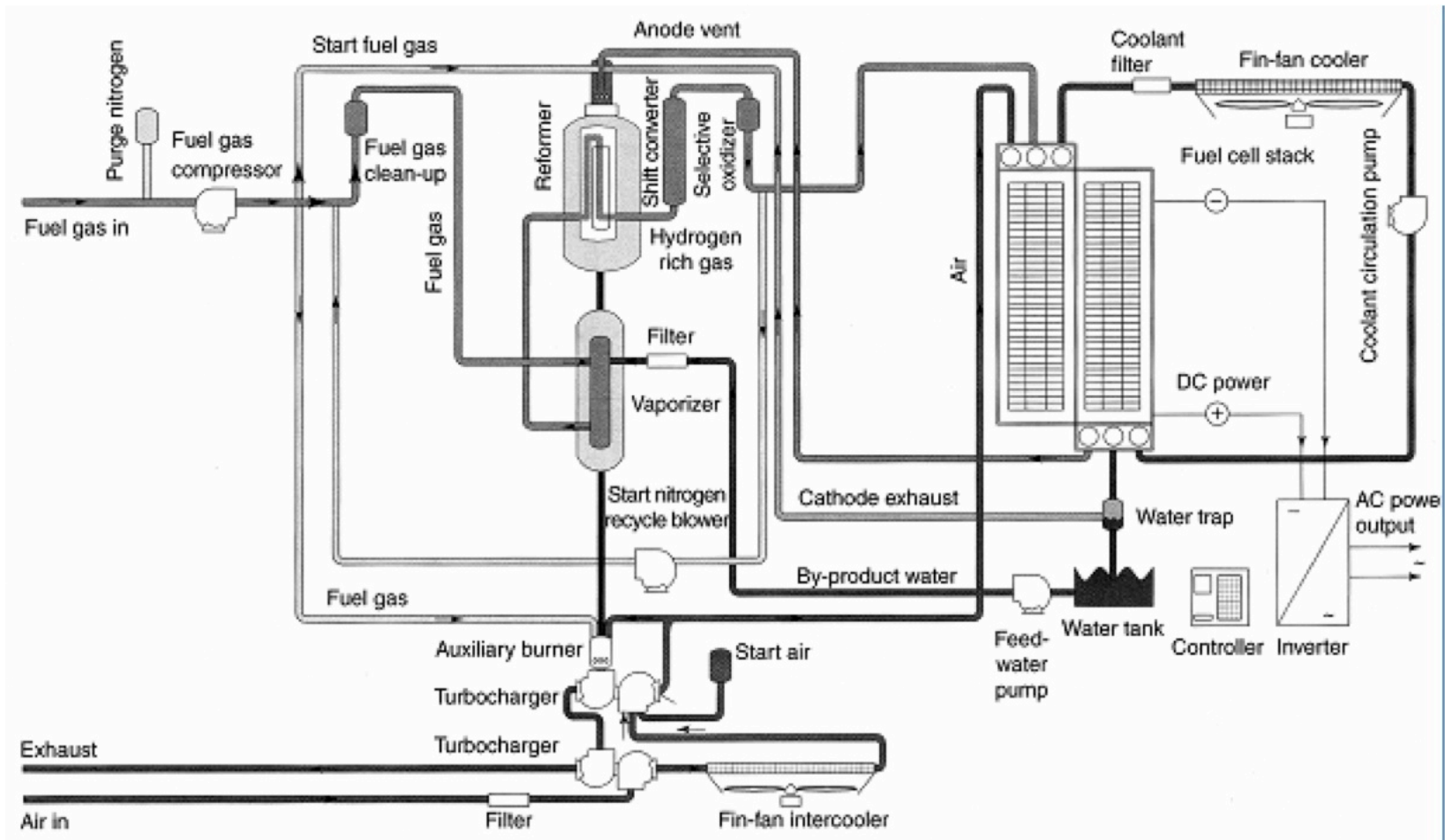
Supplying H_2 For Fuel Cells
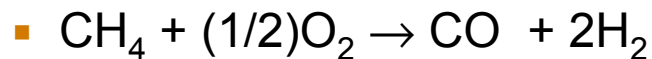
- **Steam or dry reforming (methane)**
    - $CH_4 + H_2O \rightarrow CO + 3H_2$ $\qquad \Delta H_{1000K} = 206$ kJ
    - $CH_4 + CO_2 \rightarrow 2CO + 2H_2$ $\qquad \Delta H_{1000K} = 247$ kJ
    - Four syngas molecules per CH_4
    - Endothermic - requires external heat
- **Partial oxidation reforming**
    - $CH_4 + (1/2)O_2 \rightarrow CO + 2H_2$ $\qquad \Delta H_{1000K} = -37$ kJ
    - Three syngas molecules per CH_4
    - Exothermic - no external heat needed
    - Nitrogen dilution when air is used
- **Autothermal - mixed reactions**
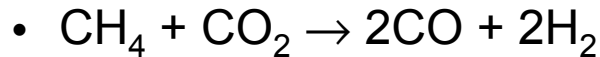
Applications

- Many successful demonstrations completed (according to www.fuelcells.org)
  - automobiles
  - bus demonstrations
  - specialty vehicles
  - stationary power plants

- Overall, very limited success in penetrating "commercial" markets
  - Difficult to replace entrenched technologies

- Specialty applications (initial market penetration candidates)
  - Stable power for telecommunications, banking, *etc*.
  - Use "waste" fuels (typically methane) from landfills / wastewater treatment / breweries
  - Forklifts without batteries or engine emissions
  - Portable power in < 1 kW range
    - Where electric grid is not available
    - Emergency backup, military (UAV), remote sensors

Electrochemical Basics

- Chemical reaction A + B = AB
  - Free energy of formation ΔG_R
  - Example reaction (combustion): $H_2 + (1/2)O_2 = H_2O$
- Electrochemical reaction
  - Electrolyte membrane separates reactants
    - Allows passage of ionic but not electronic current
  - Current associated with ion transport is balanced by external circuit
    - If A is transported as A^+ ions through electrolyte, equal numbers of electrons must go through the external circuit

Electrochemical Reactions

- Reaction is occurring at the A/electrolyte interface:

  $A = A^{+z} + ze^-$

  – Supplies A^+ into the electrolyte and e^- into external circuit

- Reaction occurring at other side of electrolyte:

  $A^{+z} + ze^- = A$

  – Ions arriving at electrolyte/AB interface combined with electrons from external circuit

- If B^{z+} ions rather than A^{z+} ions are present in the electrolyte, the electron flow direction and the sign of the voltage will be opposite

Distinction Between Fuel Cells & Batteries

- In a battery, A and B are usually solid or liquid
  - A and B can conduct electricity, and thereby can act as electrodes to supply/remove electrons
  - Reactants (A & B) contained within device*
    - When they are consumed the battery is fully discharged
- In a fuel cell, A, B, and AB are generally in the gas (or liquid) phase
  - They can be transported into and out of the cell continuously
  - Electrical connections are made to permanent electrodes instead of directly to A and B
   - These are porous to allow ingress of gases/liquids

* An exception is the "flow" battery, where liquid solutions flow continuously into the device

Fuel Cells:
Combustion Versus Electrochemistry

- Conventional method for using fuels - burn them!

$$2O_2 \longrightarrow \text{[flame]} \longrightarrow 2H_2O + CO_2, \text{heat}$$
$$CH_4 \longleftarrow$$
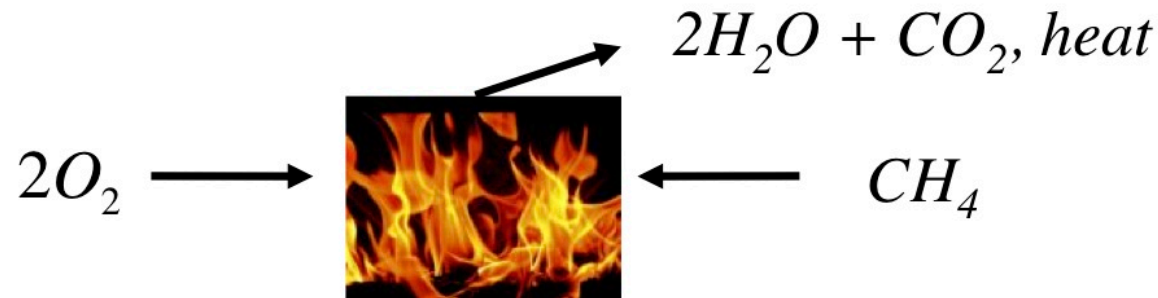
- Reactants (fuel and oxygen) are separated by an electrolyte, allowing one reactant, and no electrons, to pass

$$8e^- \longrightarrow \qquad \longrightarrow 8e^-$$
$$2O_2 \longrightarrow \quad 4O^{2-} \longrightarrow 2H_2O + CO_2$$
$$CH_4 \longleftarrow$$
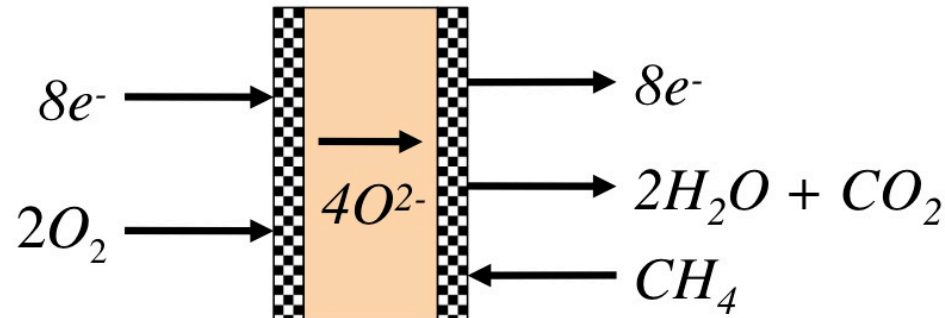
- Overall chemical reaction is the same
- Reactant is transported as an ion (O^{2-} in example above)
- Permanent electrodes on either side of electrolyte
  - Provide electrons, since reactants are gaseous or liquid

Fuel Cell Types

- Based on electrolyte material:
  - Polymer electrolyte, phosphoric acid: H^+ ions
  - Solid oxide: O^{2-} ions
  - Molten carbonate: CO_3^{2-} ions
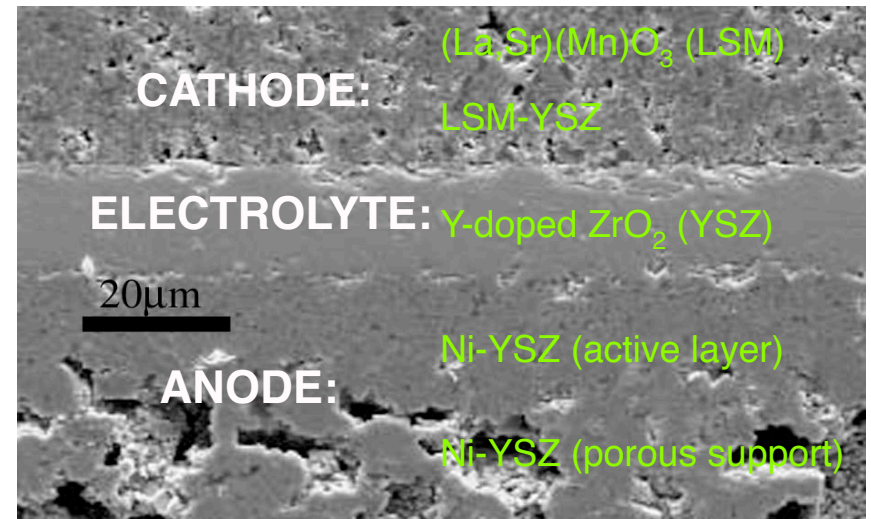 - Alkaline: OH^- ions

Hydrogen ion conducting electrolytes   Oxygen ion conducting electrolytes
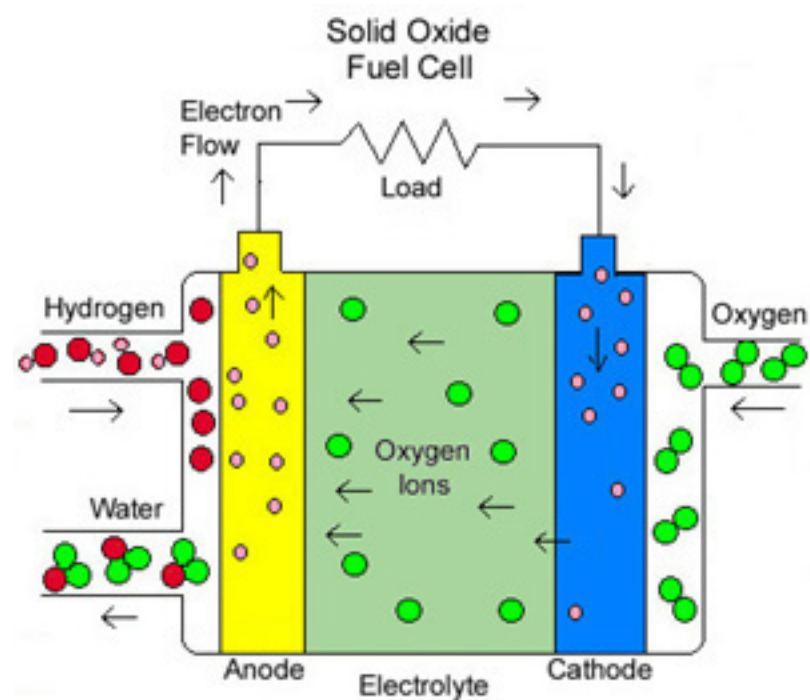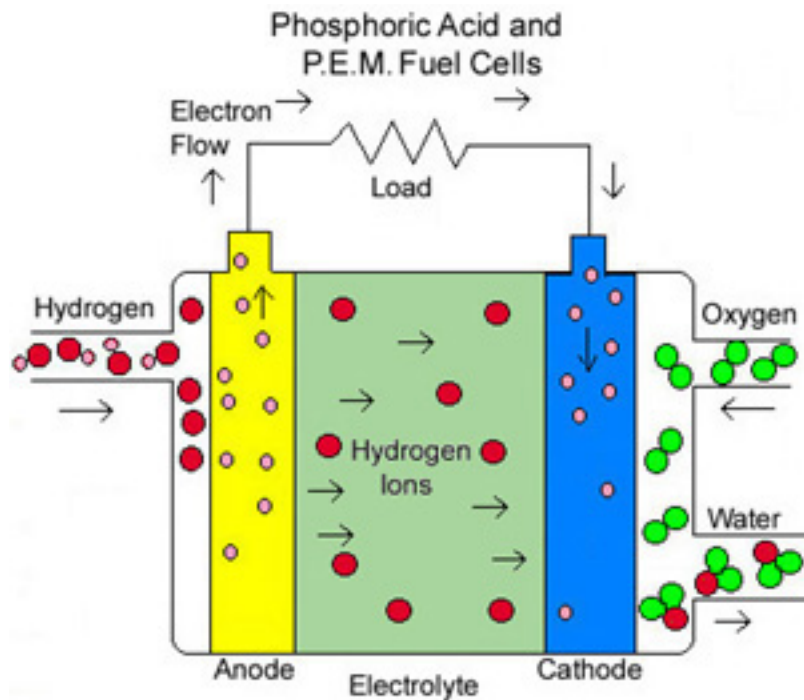
Solid Oxide Fuel Cell (SOFC)

- Electrolyte: solid oxide ceramic
  - Typically yttria-stabilized zirconia (YSZ)
  - Conducts O^{2-} ions
- Electrodes: anode usually Ni-YSZ
  - Typical cathode: $(La,Sr)MnO_3$
- Operating temperature 600 - 1000°C
  - High temperature has both advantages and disadvantages
- Fuel: H_2, methane, alcohols, *etc.*
  - No CO poisoning issue
- Reactions (assuming H_2 fuel)
  - Anode: $H_2 + O^{2-} \rightarrow H_2O + 2e^-$
  - Cathode: $(1/2)O_2 + 2e^- \rightarrow O^{2-}$
- Power density 300 - 1000 mW/cm^2
- Typical efficiency 50-60% (90% combined heat and power)

CATHODE: $(La,Sr)(Mn)O_3$ (LSM)
LSM-YSZ

ELECTROLYTE: Y-doped ZrO_2 (YSZ)

20μm

ANODE: Ni-YSZ (active layer)

Ni-YSZ (porous support)

SOFC 2

- Advantages:
    - Fuel flexibility
    - Non-precious metal catalyst
    - High-quality waste heat for co-generation
    - All solid state device
    - High power density
- Disadvantages:
    - Significant high-temperature materials issues
        - Seals, interconnects, balance of plant
    - Sealing and interconnecting issues

Phosphoric Acid Fuel Cell (PAFC)

- Electrolyte: H_3PO_4 (pure or highly concentrated)
  - Contained in a porous SiC matrix
    - Keeps electrodes separated, provides mechanical strength, and minimizes reactant gas crossover
  - Conducts hydrogen ions
  - Must be replenished against evaporation
- Electrodes: porous graphite coated with Pt
- Operating temperature from 180 - 210°C
  - Phosphoric acid solidifies below 42°C
  - Phosphoric acid phase transformation above 210°C
- Reactions (H_2 fuel)
  - Anode: $H_2 \rightarrow 2H^+ + 2e^-$
  - Cathode: $(1/2)O_2 + 2H^+ + 2e^- \rightarrow H_2O$
- Electrical efficiency: 40% (70% combined heat and power)
- Power density: 150 - 300 mW/cm^2
- Demonstrated as early as 1960's

PAFC 2

- Advantages:
  - Mature technology
  - Excellent reliability and long-term performance
  - Low cost electrolyte
- Disadvantages:
  - Cost of Pt catalyst
  - Pt catalyst susceptible to poisoning from reformate fuels
    - Can handle ~ 1 % CO
    - Maximum H_2S content of ~ 50 ppm
  - Electrolyte is corrosive and must be replenished continuously
  - Low power density: 150 - 300 mW/cm^2

Polymer electrolyte membrane (PEM) fuel cell

- Electrolyte: proton-conducting polymer membrane
  - Typically perfluorinated sulfonic acid polymer
    - Flexible, 20-200 µm thick
    - Must be maintained in hydrated state
- Electrodes: Pt catalyst on carbon electrode support
- Operating temperature <90°C
- Reactions (same as PAFC)
  - Anode: $H_2 \rightarrow 2H^+ + 2e^-$
  - Cathode: $(1/2)O_2 + 2H^+ + 2e^- \rightarrow H_2O$
- Fuels: typically H_2, but can also use methanol, formic acid
  - e.g. direct-methanol fuel cell (DMFC)
  - Pt catalyst readily poisoned by CO and S
    - Even worse than PAFC because of lower temperature
- Power density: 300 - 1000 mW/cm^2
- Electrical efficiency: 40 - 50%

PEMFC 2

- Advantages:
  - High power density
  - Good start-stop capability
  - Suitable for portable applications due to low temperature
- Disadvantages:
  - Cost of Pt catalyst
  - Expensive polymer membrane and ancillary components
  - Active water management often required
  - Very poor CO and S tolerance

Alkaline Fuel Cell (AFC)

- Electrolyte: aqueous KOH
  - Conducts OH^- ions
- Electrodes: porous graphite coated with Pt, or Ni
- Operating temperature from 60 - 250°C
- Fuel: pure H_2 (typically uses pure O_2 oxidant)
  - Cannot tolerate CO_2 in fuel/oxidant
    - Reaction $2OH^- + CO_2 \rightarrow CO_3^{2-} + H_2O$ depletes OH^-
    - Can form solid K_2CO_3
- Reactions
  - Anode: $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$
  - Cathode: $(1/2)O_2 + H_2O + 2e^- \rightarrow 2OH^-$
    - Water consumed at cathode, produced at anode
    - Oxygen reduction reaction (ORR) much faster in alkaline medium compared to acidic medium
- Power density: 150 - 400 mW/cm^2
- Electrical efficiency: 50%
- Successful use in spacecraft from 1960's

AFC 2

- Advantages:
  - Excellent cathode performance
  - Can use non-precious metal catalyst such as Ni
  - Low materials and electrolyte cost
- Disadvantages:
  - Must use pure H_2 and O_2 (no CO_2)
    - Difficult for terrestrial applications
  - KOH electrolyte may need periodic replacement
  - Must remove water from anode

Molten Carbonate Fuel Cell (MCFC)

- Electrolyte: molten mixture of alkali carbonates
  - Li_2CO_3 and K_2CO_3 immobilized in $LiOAlO_2$ porous matrix
  - Conducts CO_3^{2-} ions
- Electrodes: anode usually Ni-Cr alloy; Cathode: NiO:Li
- Operating temperature ~ 650°C
- Fuel: H_2, methane, simple alcohols
  - No CO poisoning issue
- Reactions (assuming H_2 fuel)
  - Anode: $H_2 + CO_3^{2-} \rightarrow CO_2 + H_2O + 2e^-$
  - Cathode: $(1/2)O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$
- CO_2 consumed at cathode, produced at anode
  - System must re-circulate CO_2 (mix exhaust with inlet air)
- Power density ~ 100 - 300 mW/cm^2
- Typical efficiency 45 - 55% (90% combined heat and power)
- Used continuously (stationary power) to avoid freeze/thaw

MCFC 2

- Advantages:
  - Fuel flexibility
  - Non-precious metal catalyst
  - High-quality waste heat for co-generation
- Disadvantages:
  - CO_2 recycling required
  - Corrosive, molten electrolyte
  - Degradation/lifetime issues
  - Relatively expensive materials

Electrochemical Thermodynamics

- Thermodynamics provides a foundation for understanding electrochemical devices
  - Relation between thermo and electrical quantities
- Topics
  - Nernst potential
  - Effects of T, P, and composition
  - Efficiency

Equilibrium Potential 1

- The cell (system) consists of three sub-systems, electrodes (1 and 2) separated by an electrolyte membrane (3)
- Equilibrium condition can be written in variational form in terms of Gibbs free energy:

  $\delta G \geq 0$
  - This states that all possible variations in the system yield constant or increasing G
    - Equivalent to the condition that G is at a minimum
- Total δG is sum of individual parts: $\delta G = \delta G^1 + \delta G^2 + \delta G^3$, where

  $\delta G^1 = -S^1 \delta T + V^1 \delta P + \sum_i \mu_i^1 \delta n_i^1 + \phi^1 \delta q^1$

  $\delta G^2 = -S^2 \delta T + V^2 \delta P + \sum_i \mu_i^2 \delta n_i^2 + \phi^2 \delta q^2$

  $\delta G^3 = -S^3 \delta T + V^3 \delta P + \sum_i \mu_i^3 \delta n_i^3 + \phi^3 \delta q^3$
- Free energy includes additional work terms:
  - Chemical work of adding (or removing) δn_i moles of species i at chemical potential μ_i: $\mu_i \delta n_i$
  - Electrical work of adding (or removing) δq moles of charge at electrical potential ϕ: $\phi \delta q$

Equilibrium Potential 2

- Consider cell at fixed T and P
- At steady state there is no net change in the composition or charge state in the electrolyte, so $\delta n_i^3 = 0$ and $\delta q^3 = 0$
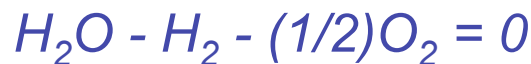- The equilibrium condition can now be written:

$$\delta G = 0 = \Sigma_i \mu_i^1 \delta n_i^1 + \Sigma_i \mu_i^2 \delta n_i^2 + \phi^1 \delta q^1 + \phi^2 \delta q^2$$

   – Using just the equality portion of the condition
- The δn_i and δq terms are not independent, but are related as given by the chemical reaction taking place in the cell
   – In general, a chemical reaction can be written as: $\sum_{i=1}^{r} v_i A_i = 0$
- For example, express $H_2 + (1/2)O_2 = H_2O$ in the form:

$$H_2O - H_2 - (1/2)O_2 = 0$$

   – In this example, $v_{H2} = -1$, $v_{O2} = -1/2$, $v_{H2O} = 1$

- If the system undergoes a transformation where n_1 varies by δn_1, n_2 varies by δn_2, etc., the increments are related by:

$$\delta n_1/v_1 = \delta n_2/v_2 = \ldots = \delta n_r/v_r = \delta n_{elec}/z = \delta \lambda$$

   – Where λ is the progress variable

Equilibrium Potential 3

- The $\delta n_{elec}/z$ term is included for an electrochemical reaction
  - Relates the change in number of moles of electronic charge δn_{elec} to $\delta\lambda$
  - z = number of electrons in the reaction as written
- Thus, $\delta n_{elec} = z\delta\lambda$
- This can be converted to charge q in coulombs using:

$$\delta q = (eN_{Av})\,\delta n_{elec} = Fz\delta\lambda$$

  - Where e = coulombs/electron; N_{Av} = Avogadro's number
  - $F = eN_{Av}$ = Faraday's constant
- The charge flows between sub-systems 1 and 2, such that

$$\delta q^1 = -\delta q^2 = zF\delta\lambda$$

- Substituting into the equilibrium condition yields:

$$0 = \Sigma_i\mu_i^1\delta n_i^1 + \Sigma_i\mu_i^2\delta n_i^2 + zF\delta\lambda\,(\phi^1 - \phi^2)$$

Equilibrium Potential 4

- As the reaction proceeds, the δn_i values are given by the progress variable ($\delta n_i = \nu_i \, \delta\lambda$)

- Re-writing the chemical potential sum in terms of the progress variable:

$0 = \Sigma_\iota \mu_i^1 \, \nu_i \delta\lambda + \Sigma_\iota \mu_i^2 \, \nu_i \delta\lambda + zF\delta\lambda \, (\phi^1 - \phi^2)$

  – It's well known which side of the cell (electrode 1 or 2) each species is on: normally drop the superscripts on µ terms

- Combine sums: $0 = \Sigma_\iota \mu_i \nu_i \delta\lambda + zF\delta\lambda \, (\phi^1 - \phi^2)$

  – Be sure to evaluate each μ_i on the side where *i* appears

  – Or: $zF(\phi^1 - \phi^2) = -\Sigma_\iota \mu_i \nu_i$

- Note the general definition of reaction free energy: $\Delta G_R \equiv \left(\sum_{i=1}^{r} \nu_i \mu_i \right)$

$$E \equiv \Delta\phi = (\phi^1 - \phi^2) = -\frac{\Delta G_R}{zF}$$

  – *E* is the so-called Nernst potential

Cell Potential: Effect of Gas Composition

- In a case where the reactants and products are pure species in their standard states, $\Delta G_R = \Delta G^0_R$, such that $E^0 = -\Delta G^0_R / zF$

- In most cases, however, one needs to determine ΔG_R in terms of tabulated ΔG^0_R values for reactions
  - *E.g.* in a fuel cell with gas phase species at some selected partial pressures
- Relate chemical potentials to activities (& gas phase pressures):

  $$\mu_i = \mu_i^0 (T) + RT \ln a_i$$

  - *R* = gas constant
- Define standard reaction free energy:

  $$\Delta G_R^0 \equiv \left(\sum_{i=1}^{r} v_i \mu_i^0 \right)$$

- Thus:

  $$\Delta G_R - \Delta G_R^0 = \sum_{i=1}^{r} v_i (\mu_i - \mu_i^0) = RT \sum_{i=1}^{r} \ln a_i^{v_i} = RT \ln \prod_{i=1}^{r} a_i^{v_i}$$

- Dividing by -1/*zF* yields:

$$E = E^0 - \frac{RT}{zF} \ln \prod_{i=1}^{r} a_i^{v_i} = E^0 - \frac{RT}{zF} \ln K \qquad K = \prod_{i=1}^{r} a_i^{v_i}$$

Fuel Cells: Partial Pressure Dependence

- Generic fuel cell reaction (gas phase):
  - $aA + bB = cC + dD$
  - $\Delta G_R{}^o = cG_C{}^o + dG_D{}^o - aG_A{}^o - bG_B{}^o$
  - Thus, for the overall reaction:

$$E = E^o - \frac{RT}{zF} \ln \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

$$\Delta G_R = \Delta G_R^0 + RT \ln \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

  - where $E^o = -\Delta G_R{}^o/zF$

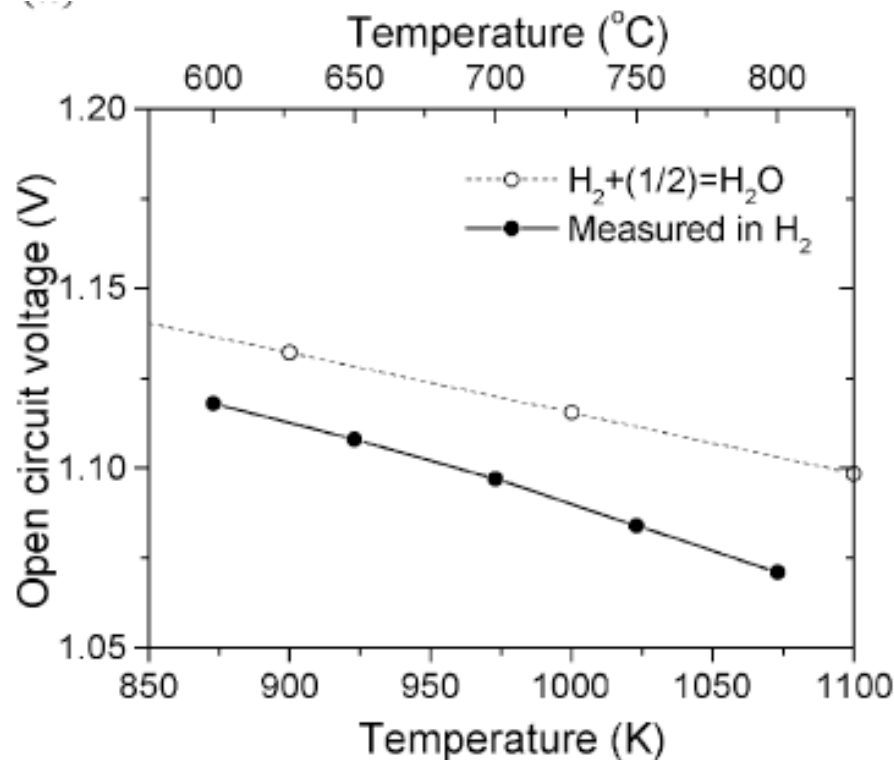- Specific reaction:
  - $H_2 + (1/2)O_2 = H_2O_{(gas)}$

$$E = E^0 + \frac{RT}{2F} \ln \frac{P_{H_2} P_{O_2}^{1/2}}{P_{H_2O}}$$

- Quantities going into $E^0 = -\Delta G_R{}^o/zF = -(\Delta H_R{}^o - T\Delta S_R{}^o)/zF$ from:
  - JANAF thermochemical tables
  - Also need heat capacities c_p

Comparison With Experiment

- Calculated cell potential decreases with increasing T
  - P_{H2} = 0.97atm; P_{H2O} = 0.03 atm
  - P_{O2} = 0.2 atm
- Experimental open circuit voltage slightly lower
  - Measured at above gas compositions

Fuel Cells: Energy Conversion Efficiency

- Efficiency usually defined:

$$\eta = \frac{\text{Useful energy obtained}}{\text{Energy available for conversion}}$$

- Useful energy: electrical work done: $\Delta W = \phi^1 \Delta q^1 + \phi^2 \Delta q^2$

  - Also from above: $\Delta q^1 = -\Delta q^2 = zF\Delta\lambda$

    - Work done moving charge from one potential to another

  - And

$$E \equiv (\phi^1 - \phi^2) = -\frac{\Delta G_R}{zF}$$

- Substituting, $\Delta W = -\Delta G_R \, \Delta\lambda$

- For reaction proceeding to completion, $\Delta\lambda = 1$: $\quad \Delta W = -\Delta G_R$

- Energy available for conversion: net heat input, $-\Delta H_R$

- Reversible "thermodynamic" efficiency:

$$\eta_{th} = \frac{\Delta G_R}{\Delta H_R} = \frac{\Delta H_R - T\Delta S_R}{\Delta H_R}$$

  - Efficiency lowered as T increases, if $\Delta S_R < 0$ (as usual)
  - Same expression for any energy generation system (*e.g.,* heat engines)

Fuel Cell Efficiency

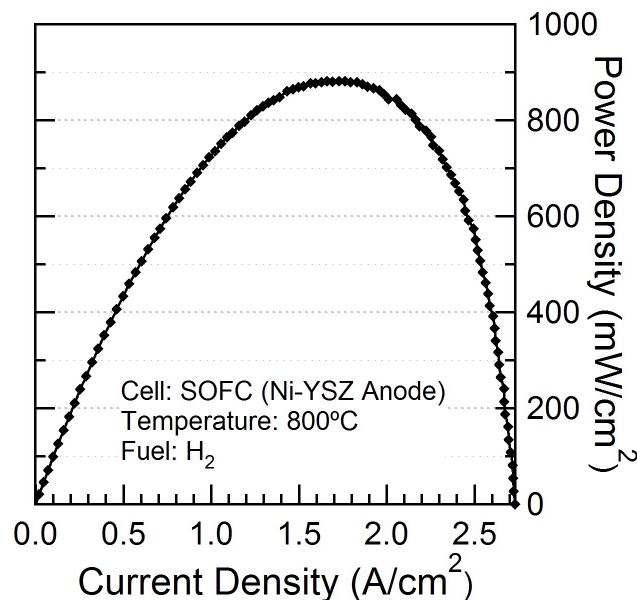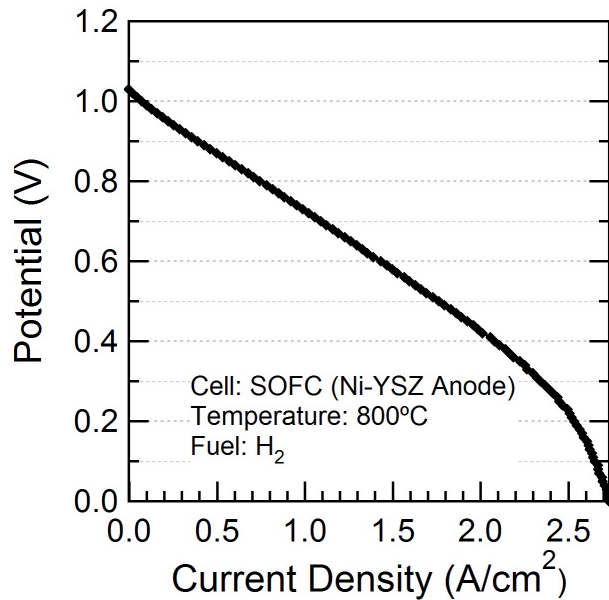$$\eta = \frac{\Delta G}{\Delta H} \frac{V_{cell}}{E} \chi$$

- Thermodynamic efficiency $\Delta G / \Delta H$
  - For H_2 oxidation, this equals 0.83 at RT
  - For a cell reaction where $\Delta S < 0$ (entropy decreases, e.g. H_2 oxidation), η decreases with increasing T
    - Note that $\Delta H < 0$
  - Follows decrease in E noted above
- Voltage efficiency
  - When a current flows in the cell, the operating voltage drops below the Nernst potential
  - Energy produced equals the charge transferred times voltage
  - Thus, the voltage efficiency equals V_{cell} / E
- Fuel utilization χ
  - There is a maximum fraction χ of the fuel that can be utilized, typically ~ 80%
    - Higher utilization decreases cell performance
      - Nernst potential drops when H_2O/H_2 ratio increases

Efficiency Illustration
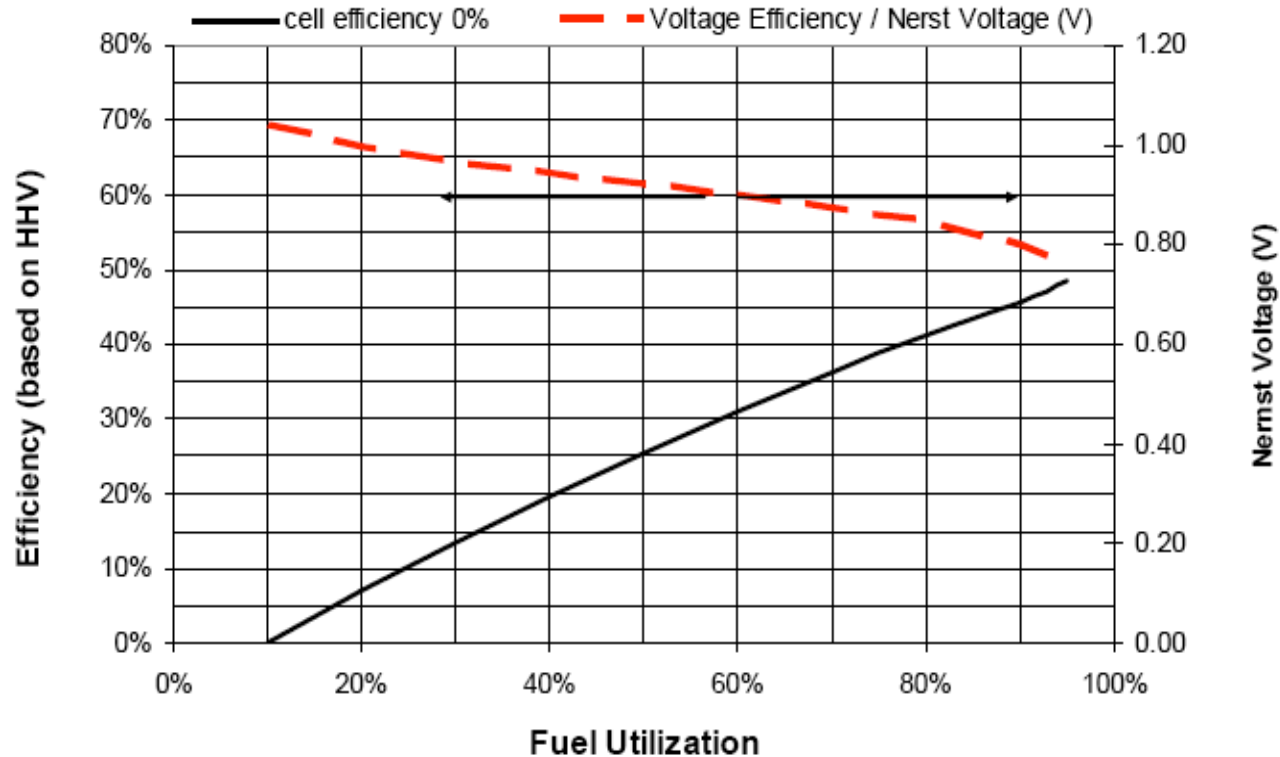
- Example: SOFC
- Red curve: Nernst potential versus fuel utilization
  - Nernst voltage as low as 0.8V for depleted fuel
- Black curve: overall efficiency
  - Includes both fuel utilization and voltage efficiency

Performance Measures:
Power and Efficiency

Potential (V) vs Current Density (A/cm^2)

Cell: SOFC (Ni-YSZ Anode)
Temperature: 800ºC
Fuel: H$_2$

Power Density (mW/cm^2) vs Current Density (A/cm^2)

Cell: SOFC (Ni-YSZ Anode)
Temperature: 800ºC
Fuel: H$_2$

- Voltage versus current density example

- Power density = Voltage x Current density
- Maximum power density
  - Typically at ~ 0.5 V per cell
  - Good value is ~ 1 W per square cm of cell area
    - 0.5V x 2 A/cm^2

- Efficiency
  - Proportional to output voltage
- Trade-off between power output and efficiency
  - Often operate closer to 0.7 V to increase efficiency

Example: Solid Oxide Fuel Cell
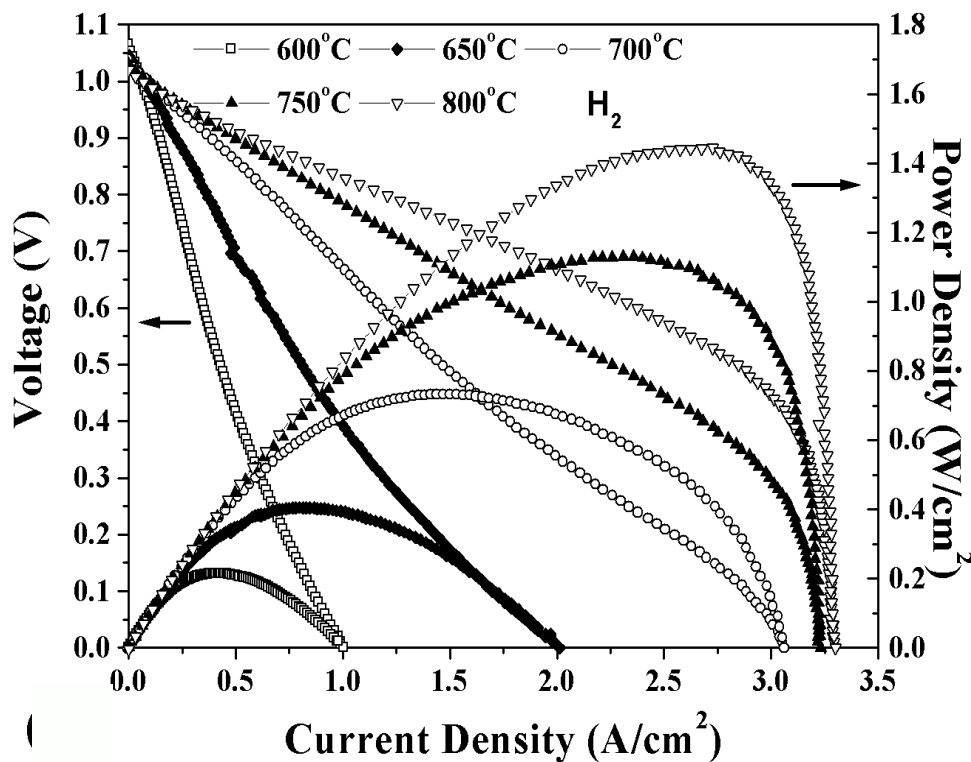
- Air;LSM-YSZ | YSZ | Ni-YSZ;H_2

- Typical plot shows:
  - Voltage versus current density
  - Power density (*VJ product*) versus current density

- Losses generally increase with decreasing temperature!
  - Power density drops

- Considerable variation in form of curves

Loss Mechanism Discussion

- Kinetic considerations provide a basis for understanding current-voltage response
  - Goal: predict electrochemical device performance under a range of loading conditions
- The section below gives detailed descriptions of:
  - Activation polarization associated with charge transfer
    - Butler-Volmer and Tafel equations
  - Activation polarization limited by adsorption
- The following sections discuss:
  - Ohmic polarization
  - Mass transport (concentration) polarization

Introduction: Electrochemical Cell Losses

Region of Activation Polarization (Reaction Rate Loss)

Theoretical EMF or Ideal Voltage

Total Loss

Region of Concentration Polarization (Gas Transport Loss)

Region of Ohmic Polarization (Resistance Loss)

Operation Voltage, V, Curve

Cell Voltage — 1.0, 0.5, 0

Current Density (mA/cm2)

Various losses related to matter/charge transport reduce the cell voltage V:

$$V = E - \eta_{Ohm} - \eta_{act}^{C} - \eta_{act}^{A} - \eta_{mass}^{C} - \eta_{mass}^{A} - \eta_{x}$$
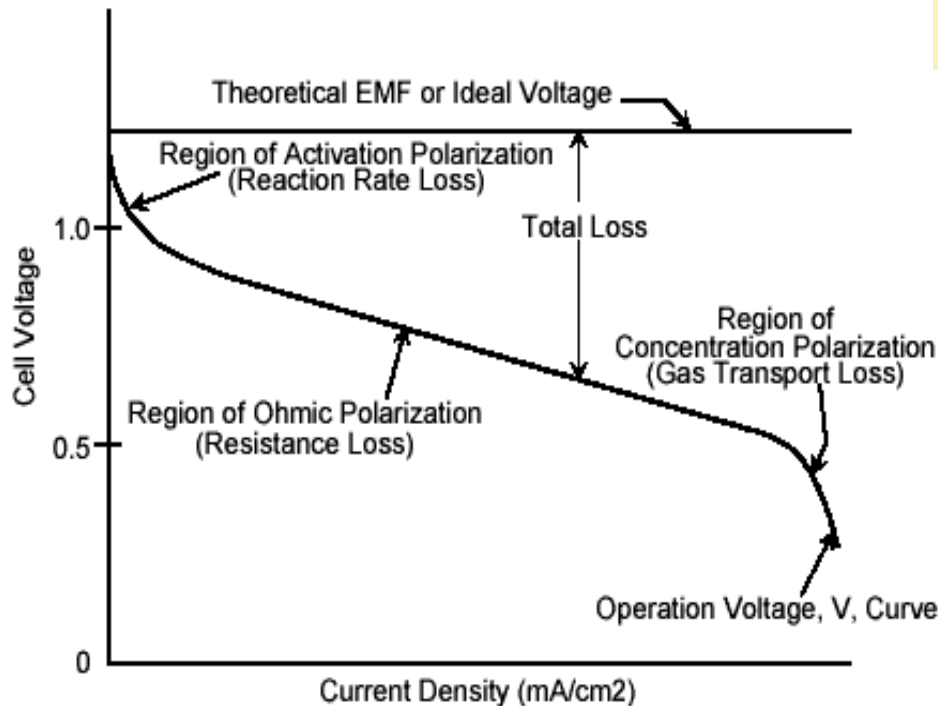
- E = Nernst potential
- η_{Ohm} = Ohmic resistance
  - Often dominated by electrolyte
- η^{A} = anode polarization
- η^{C} = cathode polarization
- Each of the electrodes can have two main categories of polarization:
  - Activation (low current)
  - Mass transport (high current)
- η_{x} = decrease in cell potential due to crossover currents

Charge Transfer 1

- For a generic reaction (R → P), transition state theory gives molar flux of product formation $J = dC_P^*/dt = kC_R^*$; k depends on:

  - Probability of "activated complexes" at energy maximum
  - Rate at which they cross the barrier towards products

$$k = \frac{k_B T}{h} \exp\left(\frac{-\Delta G^{0\pm}}{RT}\right) = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{0\pm}}{R}\right) \exp\left(\frac{-\Delta H^{0\pm}}{RT}\right)$$

  - $\Delta G^{0\ddagger}$ = energy difference between reactant and activated states ($\Delta H^{0\ddagger}$ & $\Delta S^{0\ddagger}$, associated enthalpy and entropy)
  - R = gas constant; T = temperature (K); h = Planck const

  - C_R^*, C_P^* = concentration of reactant/product species at surface

  - Reaction rate J_1 ("1" denotes forward direction) given by:

    $J_1 = C_R^* f_1 \exp(-\Delta G_1^{\ddagger}/RT)$

  - $k_B T/h$ = decay rate from activated to product state - often replaced by a frequency factor f
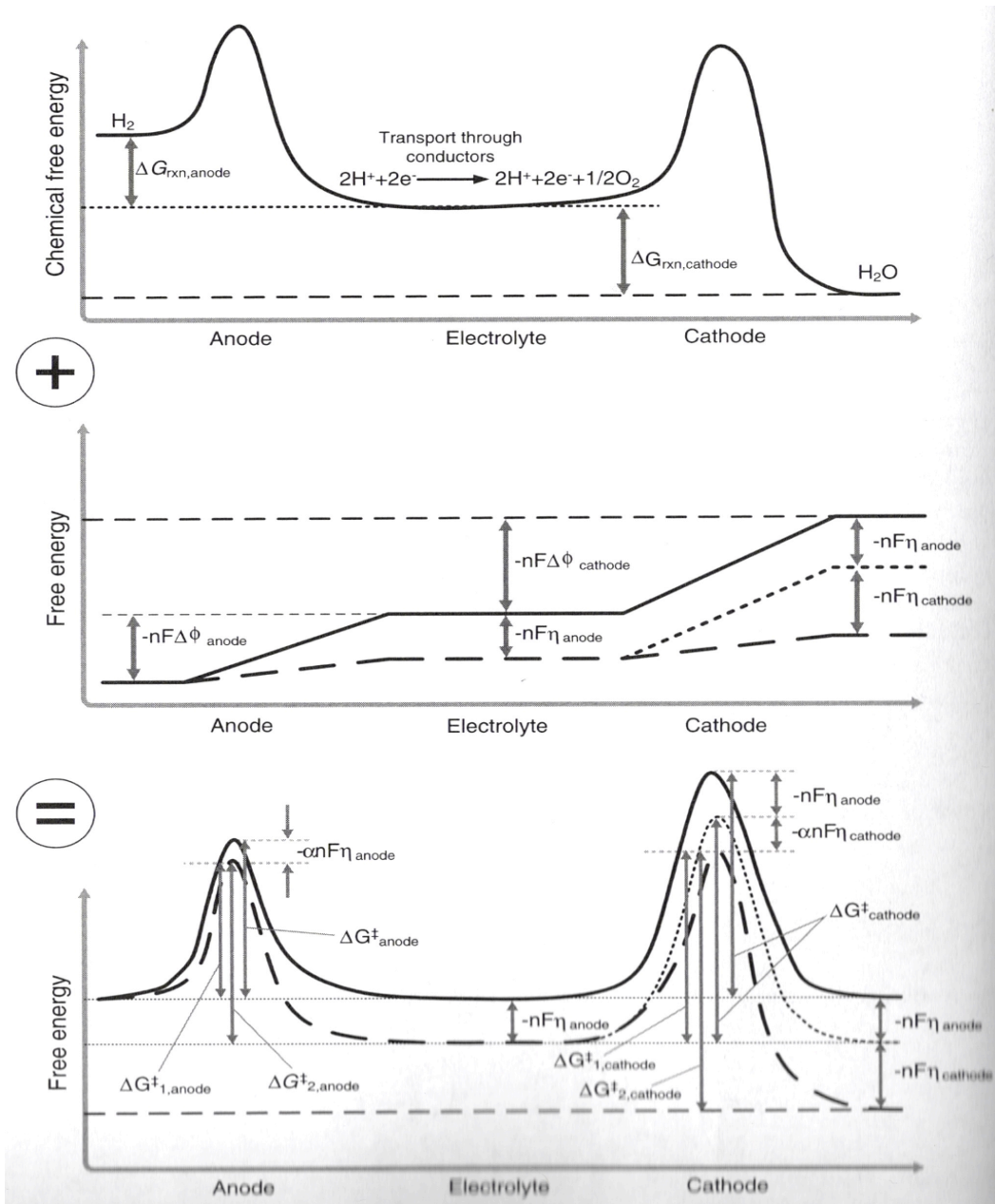
Charge Transfer 2

- Net rate J includes forward and reverse reactions: $J = J_1 - J_2$
  - Using an expression for J_2 similar to that for J_1

    $J = C_R^* f_1 \exp(-\Delta G_1^{\ddagger}/RT) - C_P^* f_2 \exp(-\Delta G_2^{\ddagger}/RT)$

    - C_P^* = product surface concentration
    - $\Delta G_2^{\ddagger}$ = energy barrier between product and activated states

- The above can be written in terms of the forward activation barrier and the Gibbs potential change for the reaction ΔG_R
  - Use $\Delta G_R = \Delta G_1^{\ddagger} - \Delta G_2^{\ddagger}$

  $J = C_R^* f_1 \exp(-\Delta G_1^{\ddagger}/RT) - C_P^* f_2 \exp[(-\Delta G_1^{\ddagger} + \Delta G_R)/RT]$

- Relate above flux terms (J's) to current densities j using $j=zFJ$
  - For example, the forward current $j_1 = zFC_R^* f_1 \exp(-\Delta G_1^{\ddagger}/RT)$
  - Reverse current: $j_2 = zFC_P^* f_2 \exp[(-\Delta G_1^{\ddagger} + \Delta G_R)/RT]$

- At equilibrium, forward and reverse currents are equal: $j_0 = j_1 = j_2$
  - Termed the "exchange" current density
  - No net current - dynamic equilibrium

Charge Transfer 3

- A way of viewing the electrochemical process at equilibrium:
  - Offsetting effects of chemical reaction energy and electric potential energy ($\Delta G_R = -zF\Delta\phi$)
    - ΔG_R = Gibbs potential of specific electrode reaction
    - $\Delta\phi_{int}$ = electric potential energy across interface
      - Only part of overall potential across cell
        - "Galvani potential"
    - Reaction wants to proceed forward
    - Electrical potential retards and exactly balances this
- Externally applied voltage or a reduction of the cell potential E (e.g. by loading) cause deviations from this equilibrium
  - Portion of this "overpotential" at electrolyte/electrode interfaces called "activation overpotential" η_{act}
  - Electric potential directly impacts e⁻ energy vs rxn coordinate
  - Changes reaction rates: changes the size of the activation barriers differently in the forward and reverse directions
  - Occurs at both electrodes - must provide equal currents

Schematic Fuel Cell Energy Barriers

- At equilibrium (solid):
  - Electrical potential exactly offsets chemical potential
  - Equal barrier heights in both directions - no net current
- With activation polarization (dashed):
  - Different barrier heights
  - Net current flows

Charge Transfer 4

- Change in activation barriers due to applied potential
  - Forward barrier: $\alpha z F \eta_{act}$
  - Reverse barrier: $(1-\alpha) z F \eta_{act}$
    - α = transfer coefficient - depends on symmetry of barrier
      - Symmetric barrier, α = 0.5, often assumed
- Effect of η_{act} on current density
  - Recall that at equilibrium (no added potential η_{act} = 0)

  $j = 0 = zFC_R^* f_1 \, exp(-\Delta G_1^{\ddagger}/RT) - zFC_P^* f_2 \, exp[(-\Delta G_1^{\ddagger} - \Delta G_R)/RT]$

    - Where each of the two terms, j_1 and j_2, respectively, are equal: $j_0 = j_1 = j_2$
  - With non-zero η_{act}, the first term becomes

  $zFC_R^* f_1 \, exp[(-\Delta G_1^{\ddagger} + \alpha z F \eta_{act})/RT] = j_0 \, exp(\alpha z F \eta_{act}/RT)$

  - And similarly for the second term, such that

  $j = j_0 \, [exp(\alpha z F \eta_{act}/RT) - exp-(\{1-\alpha\} z F \eta_{act}/RT)]$

Charge Transfer 5

- Assumes that C_R^* and C_P^* are unaffected by η_{act}
- A better expression that accounts for this:

$$j = j_0^0 \left(\frac{C_R^*}{C_R^0} e^{\alpha z F \eta_{act}/RT} - \frac{C_P^*}{C_P^0} e^{-(1-\alpha)z F \eta_{act}/RT} \right)$$

  - j_0^0 = exchange current density measured for concentrations present at zero current
  - Butler-Volmer equation
    - Exponential dependence of j on η_{act}
    - Drawing current from a cell requires that the voltage be reduced from the equilibrium value E
    - Can be approximated as linear for small j
    - Generally applicable to single-electron transfer events
    - Very good approximation for single-step electrochemical reactions
      - Or for multi-step reactions where electron transfer step is rate limiting

Exchange Current Density

- A good fuel cell or battery should achieve large j at a low η_{act} in order to produce power with relatively little voltage loss
- In the Butler-Volmer equation, the pre-factor j_0 is a key term determining j
  - Recall the equation for j_0: $j_0 = zFC_R^* f_1 \exp(-\Delta G_1^{\ddagger}/RT)$
    - (Written for the forward reaction)
- A higher j_0 value can be achieved by:
  - Increasing the reactant concentration C_R^*
    - e.g., by pressurizing the device
  - Decreasing the activation barrier $\Delta G_1^{\ddagger}$
    - Introduce electrode surfaces with "catalytic" properties, i.e. that have a lower barrier height
  - Increasing the temperature T
  - Increasing number of possible reaction sites per unit area
    - By increasing the interface roughness
    - Electrode microstructure is important

Butler-Volmer: Simplified Forms

- η_{act} is very small ($j << j_0$), typically < 15 mV at ambient T
  - Use the simplified form of B-V equation where the concentrations don't vary with current

    $j = j_0 \, [exp(\alpha zF\eta_{act}/RT) - exp\text{-}(\{1\text{-}\alpha\}zF\eta_{act}/RT)]$

    yields

    $j = j_0 \, zF\eta_{act}/RT$

  - Linear relation between overvoltage and current
  - Polarization resistance: $R_{P,act} = \eta_{act}/j = RT/j_0 \, zF$

- η_{act} is large ($j > j_0$), typically > 50-100 mV at ambient T
  - Forward reaction term dominates:

    $j = j_0 \, exp(\alpha zF\eta_{act}/RT)$ or, solving for η_{act}

    $\eta_{act} = \text{-}(RT/\alpha zF) \, ln \, j_0 + (RT/\alpha zF) \, ln \, j$

  - "Tafel equation" form:

  $\eta_{act} = a + b \, ln \, j$

    - $b = RT/\alpha nF$ = Tafel slope
    - $a = \text{-}(RT/\alpha nF)ln j_0$ -- measurement yields j_0 value
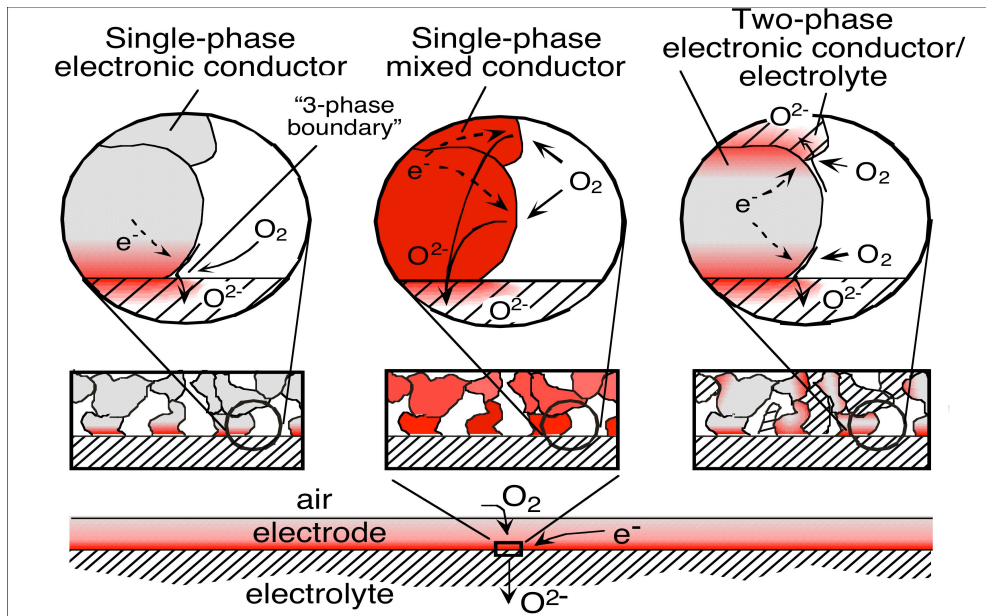
Example: Tafel Behavior
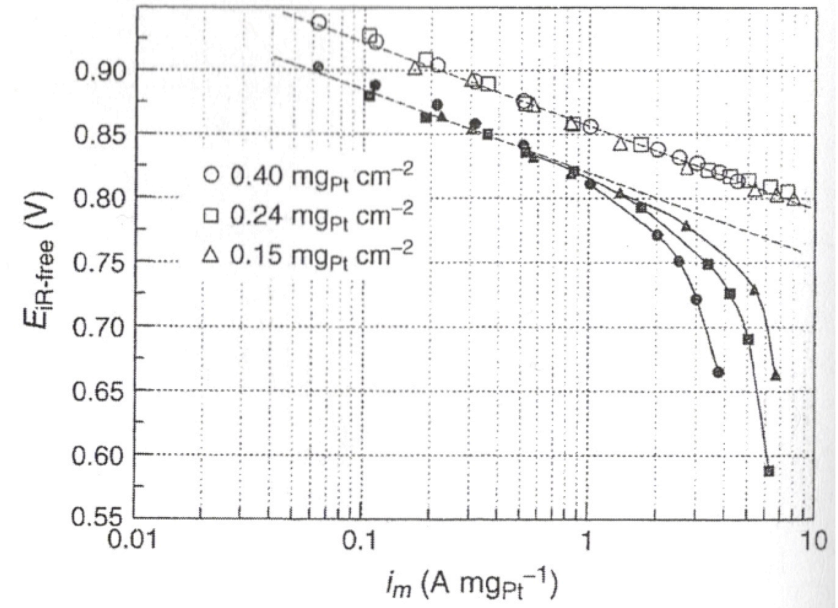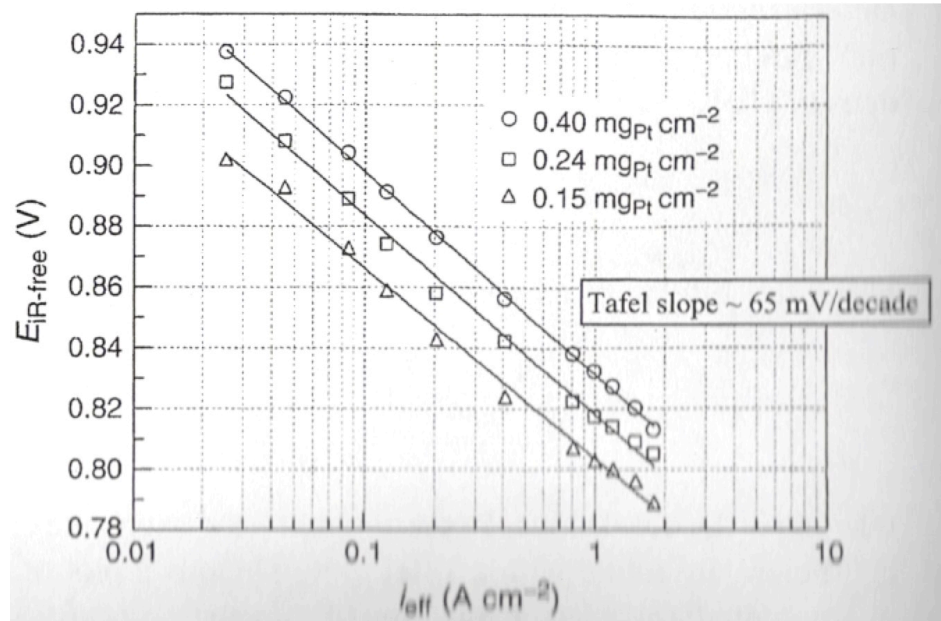
- For PEM cathodes, 80°C, H_2/O_2 with different Pt loadings
- Accurate measurement of potential across cathode requires that ohmic losses and anode losses be removed
- LEFT: Increasing Pt increases density of reaction sites, increases *a*, exchange current density
- RIGHT: replot as current normalized to Pt loading
  - Exchange current density per unit area of Pt is constant

50

Electrode Microstructure: PEMFC

20 nm
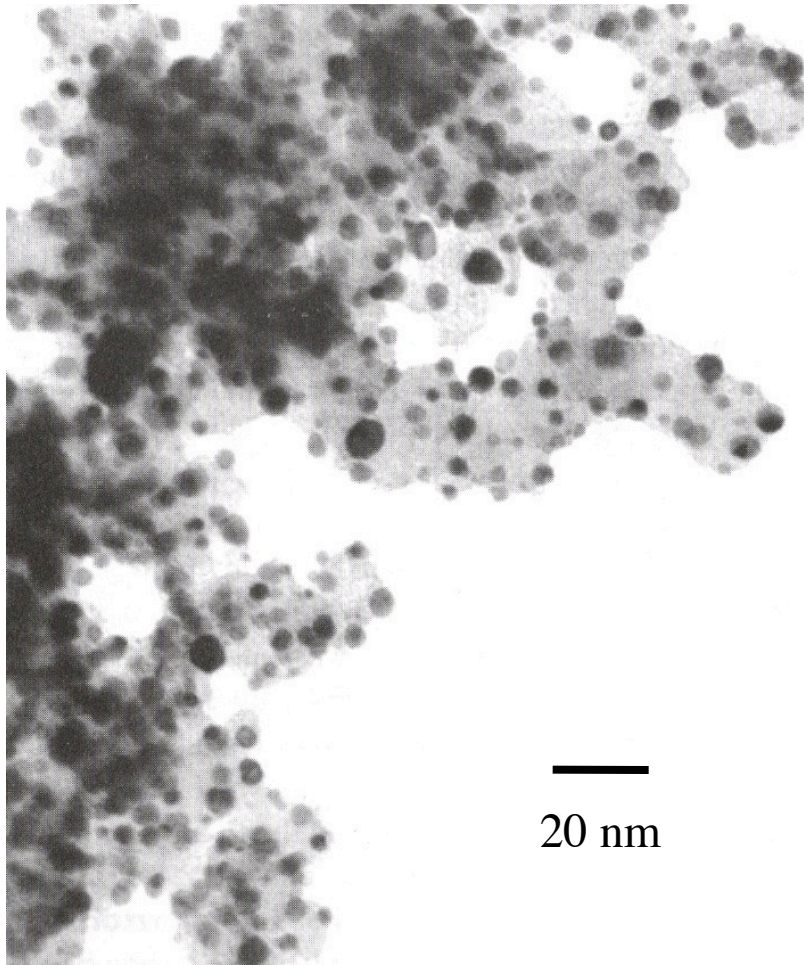
- Use high surface area carbon powder decorated with nano-scale (2-3 nm) Pt particles
  - Achieves high three-phase boundary density with minimum amount of Pt
  - Also introduces stability issues due to Pt coarsening
  - Image: TEM micrograph of Pt/C
- Percolating electronic pathway from gas diffusion layer to C to Pt
- Percolating ionic pathway through Nafion phases
- Percolating pore pathways to allow reactant/product access

SOFC Electrode Types: Microstructure

Single-phase electronic conductor   Single-phase mixed conductor   Two-phase electronic conductor/electrolyte

"3-phase boundary"

e^- O_2 O^{2-} O_2 O^{2-} O_2 e^- O_2 O^{2-}

air

O_2

electrode

e^-

electrolyte

O^{2-}

- Schematic views of three basic electrode types
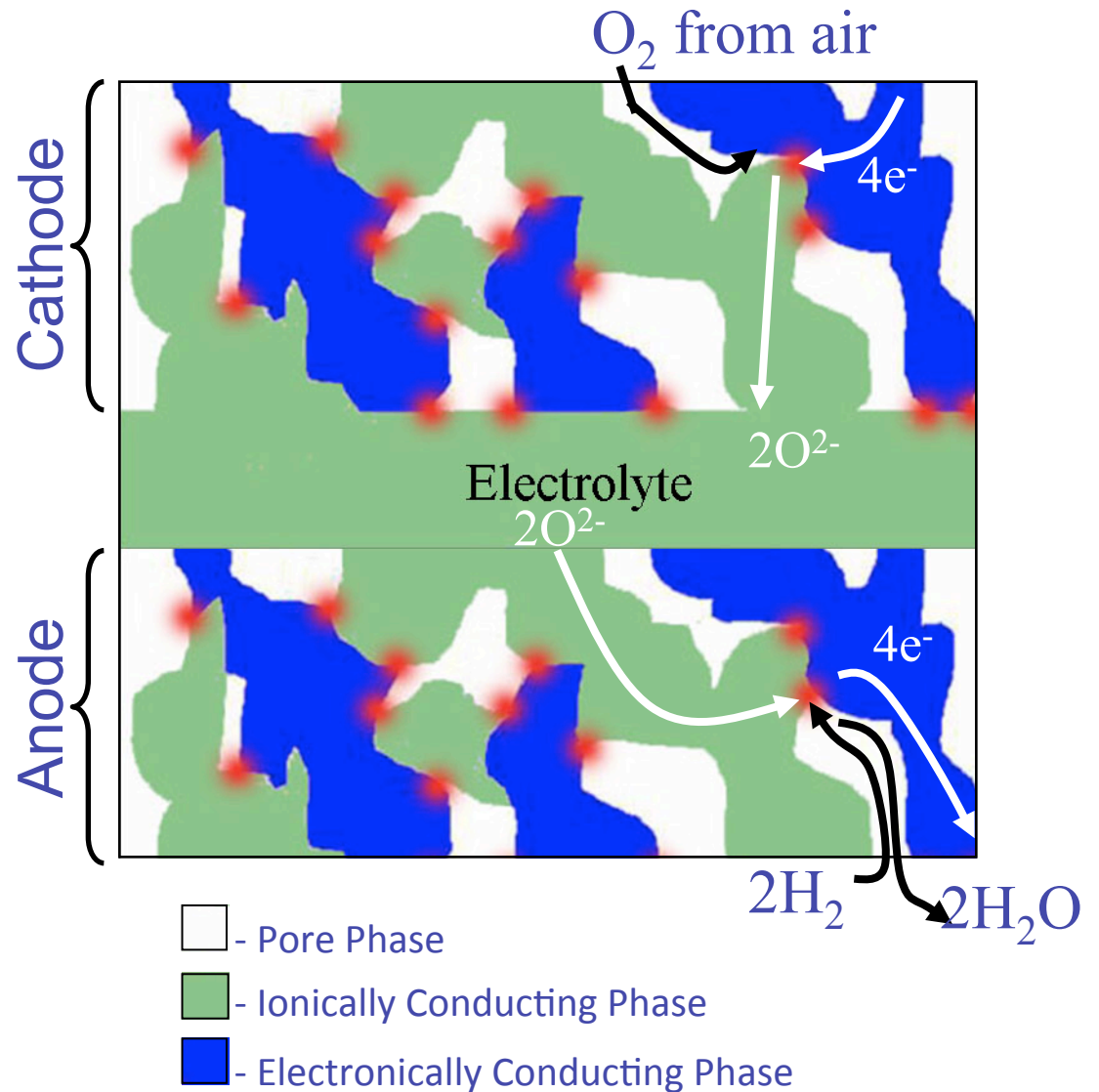- Red indicates interfaces where electrochemical reactions occur

S.B. Adler, Chem. Rev., **104** (2004) 4791–4843

- Electrode types
  - Electronic conductor
    - $(La,Sr)MnO_3$ (LSM)
  - Mixed conductor
    - $(La,Sr)CoO_3$ (LSC)
  - Two-phase
    - LSM-YSZ, Ni-YSZ
- Key quantities
  - Three-phase boundary length
  - Phase connectivity
  - Phase tortuosity
  - Surface areas

SOFC Composite Electrodes

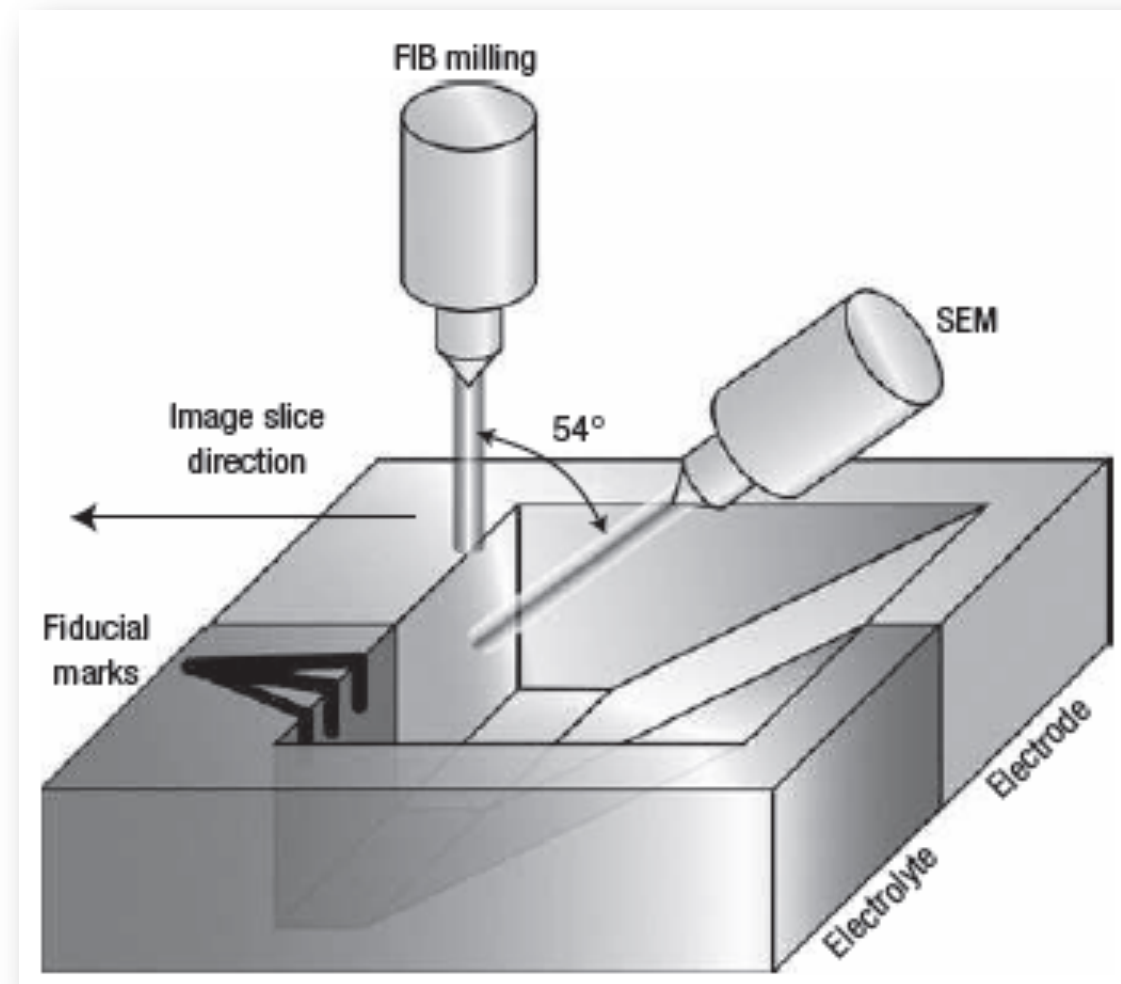## Important Features:

- Three Phase Boundaries (TPBs)

- Phase Connectivity*

- Phase Tortuosity*

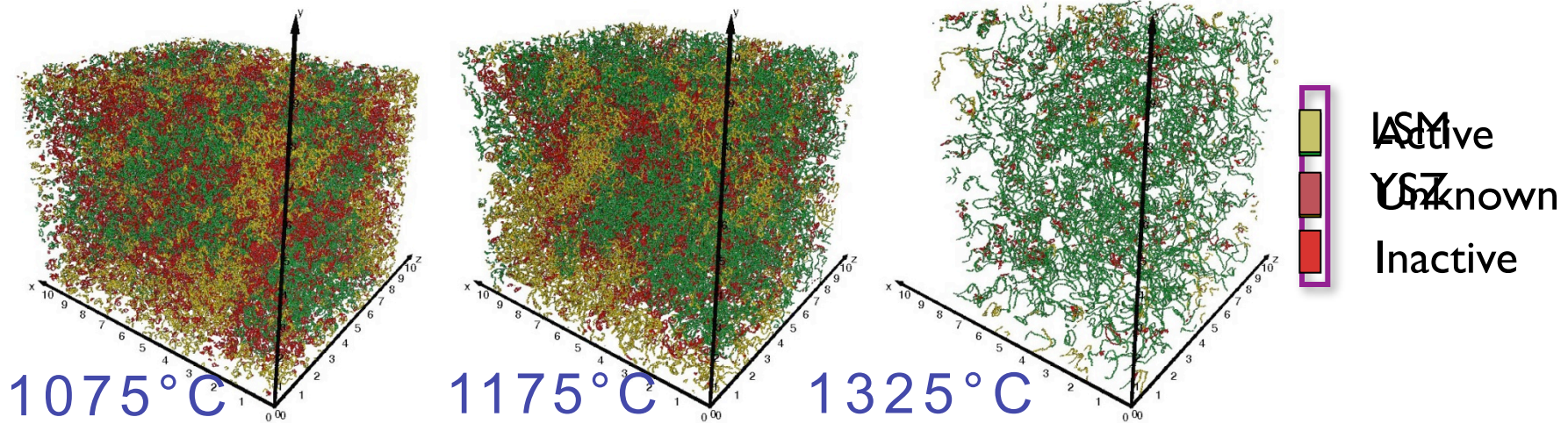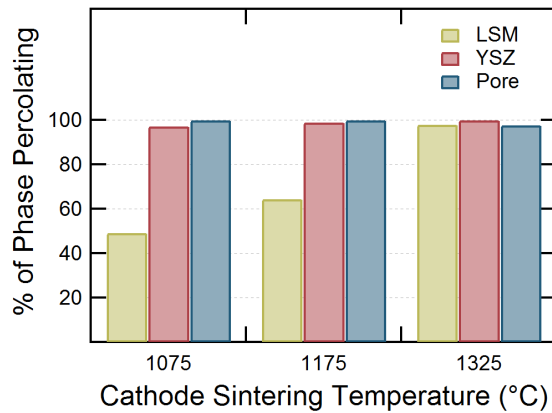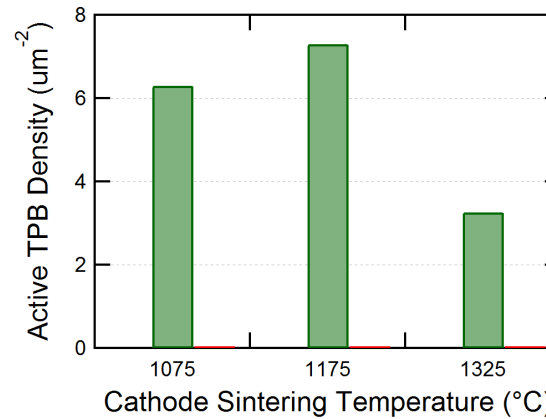*Not available from 2D imaging and stereology*

O_2 from air

Cathode

$4e^-$

$2O^{2-}$

Electrolyte

$2O^{2-}$

Anode

$2O^{2-}$

$4e^-$

$2H_2$ $2H_2O$

☐ - Pore Phase

🟩 - Ionically Conducting Phase

🟦 - Electronically Conducting Phase

FIB-SEM Tomography

3D Structural Analysis

1075°C   1175°C   1325°C

LSM / Active
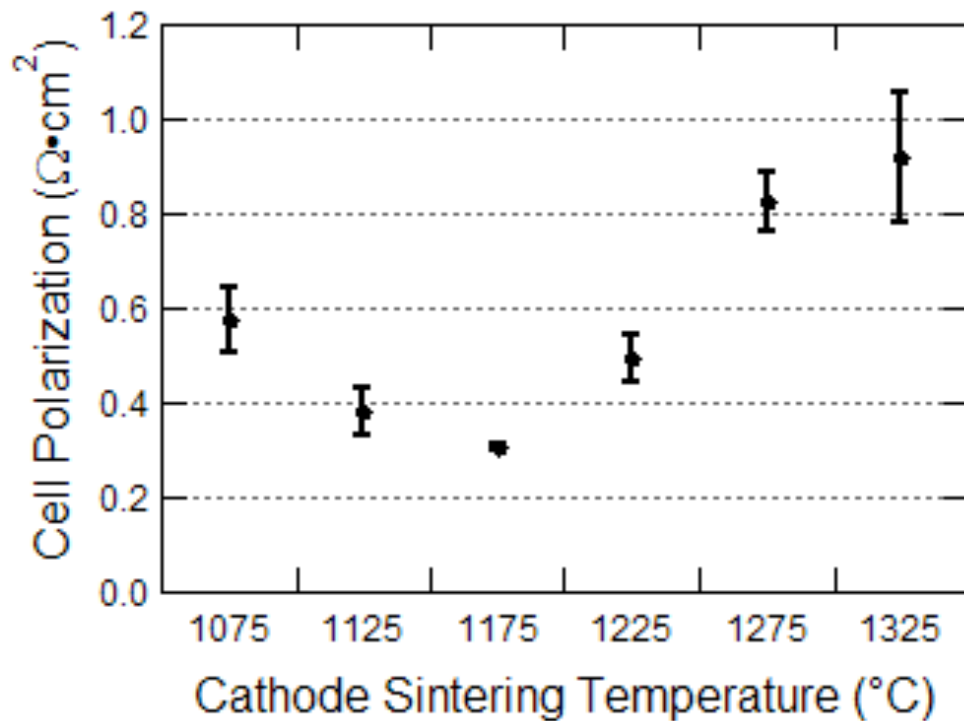YSZ / Unknown
Inactive

Phase Percolation (%)

Active TPB Density

Cronin et. al, *J. Electrochem. Soc.*, **159**, B385 (2012).

LSM-YSZ Firing Temperature: Polarization Resistance

- 50:50 wt % LSM:YSZ
- Symmetrical cell EIS measurements
- Minimum polarization at 1175°C

Cronin et. al, *J. Electrochem. Soc.*, **159**, B385 (2012).

Sources Of Fuel Cell Ohmic Resistances

$$\eta_{Ohm} = i \sum_{k=1}^{n} r_k = i \left(\frac{\rho_{el} l_{el}}{A_{el}} + \frac{\rho_{an} l_{an}}{A_{an}} + \frac{\rho_{ca} l_{ca}}{A_{ca}} + \frac{R_{con}^{AS}}{A_{con}} + \frac{\rho_{int} l_{int}}{A_{int}} \right)$$

- Ionic resistance of electrolyte
  - In a well-designed fuel cell, this term dominates
- Electrodes *("an" and "ca")* may be important in some designs
- Resistance of bipolar plates, interconnects *("int")*
  - Usually small for metallic parts
  - Can be large for conducting ceramic parts (SOFC)
- Contact resistances between parts *("con")*
  - Dependent on surface finish and applied pressure
    - Machining, tolerances, flatness important
  - Surface oxidation a factor, especially for SOFC
  - Define area-specific ("*AS*") contact resistance $R_{con}{}^{AS}$ (Ω cm^2)
    - Effectively contact thickness times resistivity
  - A_{con} much less than cell area - interconnect includes gas-flow channels and lands
- Trade-off between electrical contact, gas flow, electrode resistance

Anode-Supported SOFC

- Ni-YSZ support
- Ni-YSZ electrochemically active layer with fine microstructure
- Thin YSZ electrolyte
- LSM-YSZ active layer
- Image: 33 cm x 33 cm cell
  - Ni-YSZ support by tape casting
  - Screen print YSZ and co-fire
  - Print and fire LSM layers
- LSM current
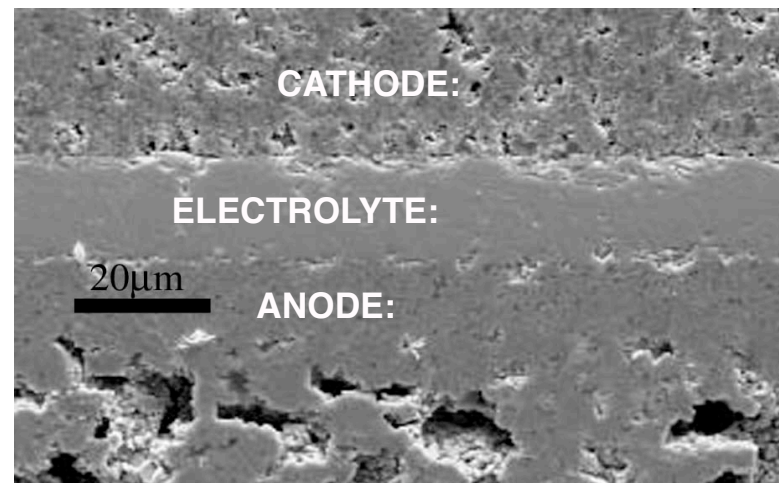
Typical SOFC Microstructure

CATHODE:	(La,Sr)(Mn)O$_3$ (LSM)
	LSM-YSZ
ELECTROLYTE:	Y-doped ZrO$_2$ (YSZ)
20μm	Ni-YSZ (active layer)
ANODE:	Ni-YSZ (porous support)
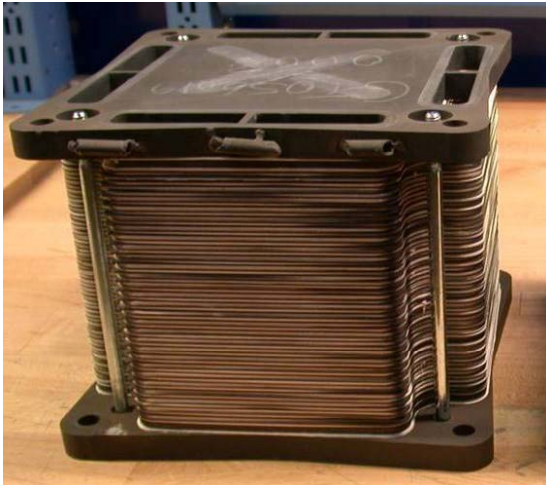
- **Ferritic stainless steel sheet metal interconnect**
- **Cross-flow gas delivery with manifolds integrated into the interconnect**
- **Compressible ceramic gasket seals**
- **Cell Active Area = 121 cm^2**
- **Number of Cells = 28**
- **Successfully implemented in a 4 x 1 kW configuration, with multiple long term tests**

- Note mechanical compression used in gas sealing

Conclusions

- Fuel cells carry out chemical to electricity conversion with high efficiency and low pollutant emission
- Wide range of applications
- Five major classes based on type of electrolyte
- Theoretical cell potential and efficiency depend on thermodynamics of reaction and operating conditions
  - Predicted Nernst potential
- Various kinetic terms limit cell current (and power) density
  - Electrochemical charge transfer rate
    - Butler-Volmer and Tafel equation
  - Surface adsorption
  - Electrical resistance
  - Mass transport: gas flow and diffusion
- Numerous challenges in manufacturing, sealing, interconnecting, stacking, and system design