Fuel to Electricity via Solid Electrolyte Fuel Cells

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Contents

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  - *Growing consumption*
  - *Consequences*
  - *Sustainable energy resources*
- Fuel Cell Technology Overview
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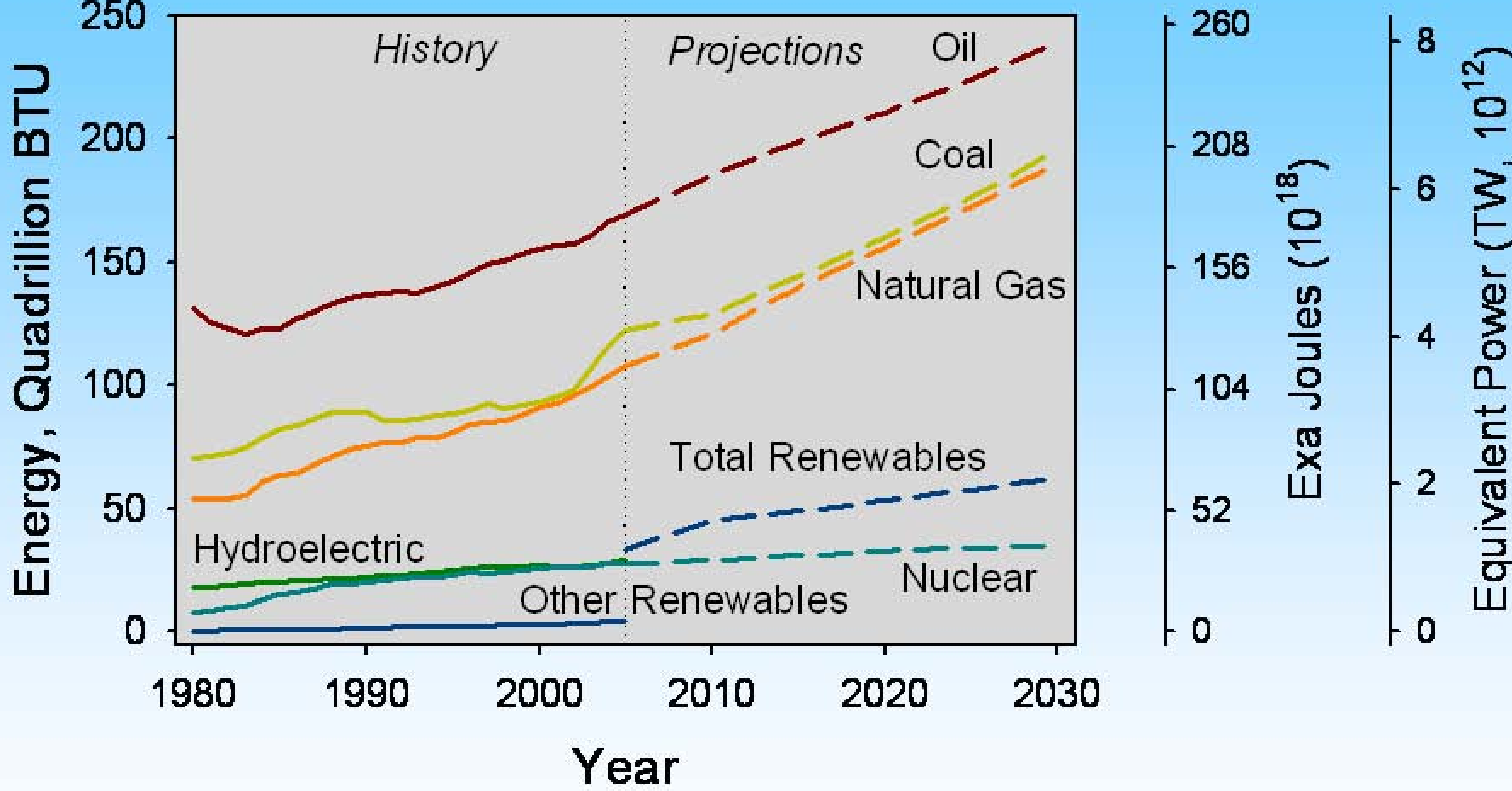
  - *Types of fuel cells and their characteristics*
- Selected (Caltech) Advances
  - *New category of fuel cells based on new proton conducting electrolytes*
  - *New component material (cathode) for high power output from solid oxide fuel cells*

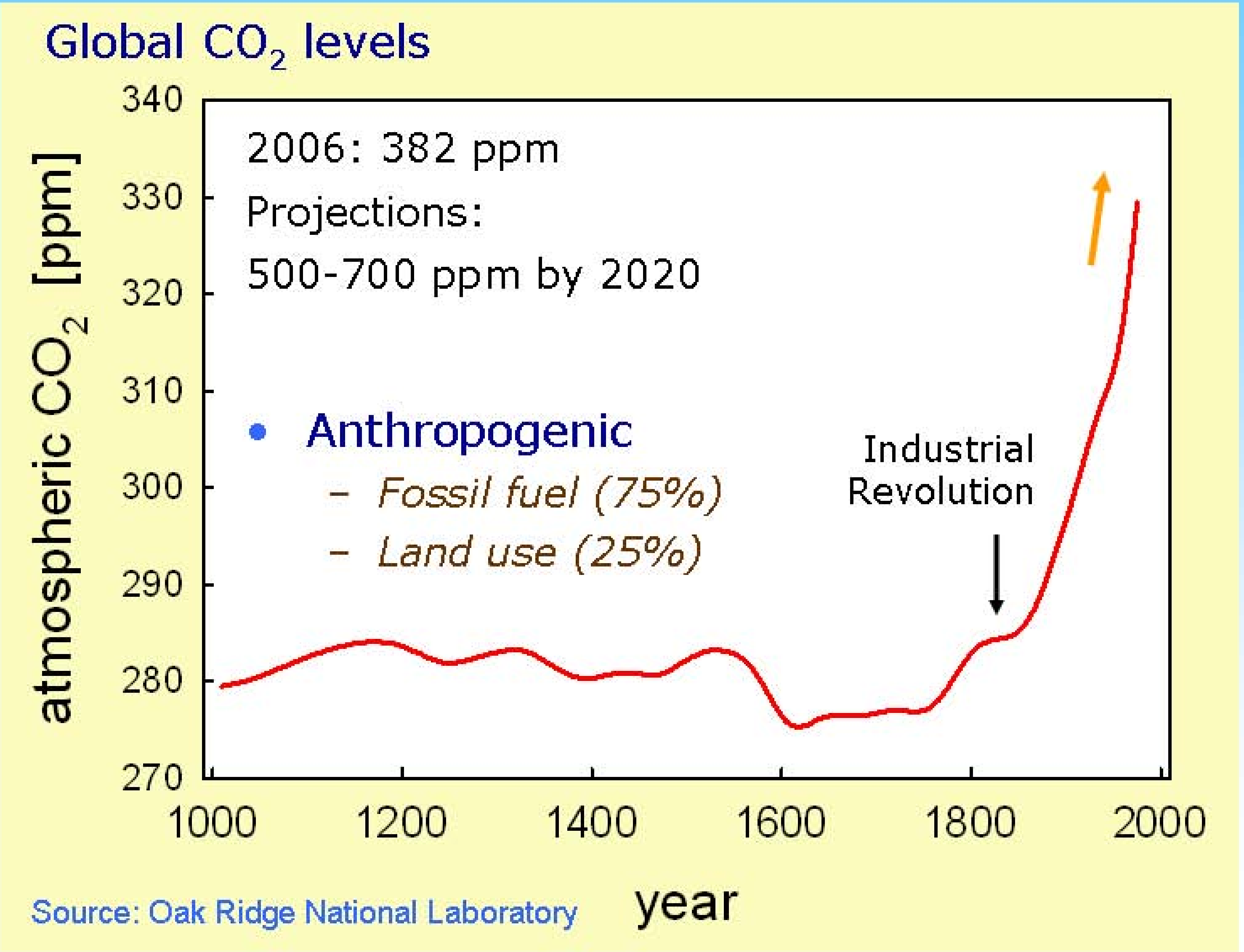
World Energy Consumption



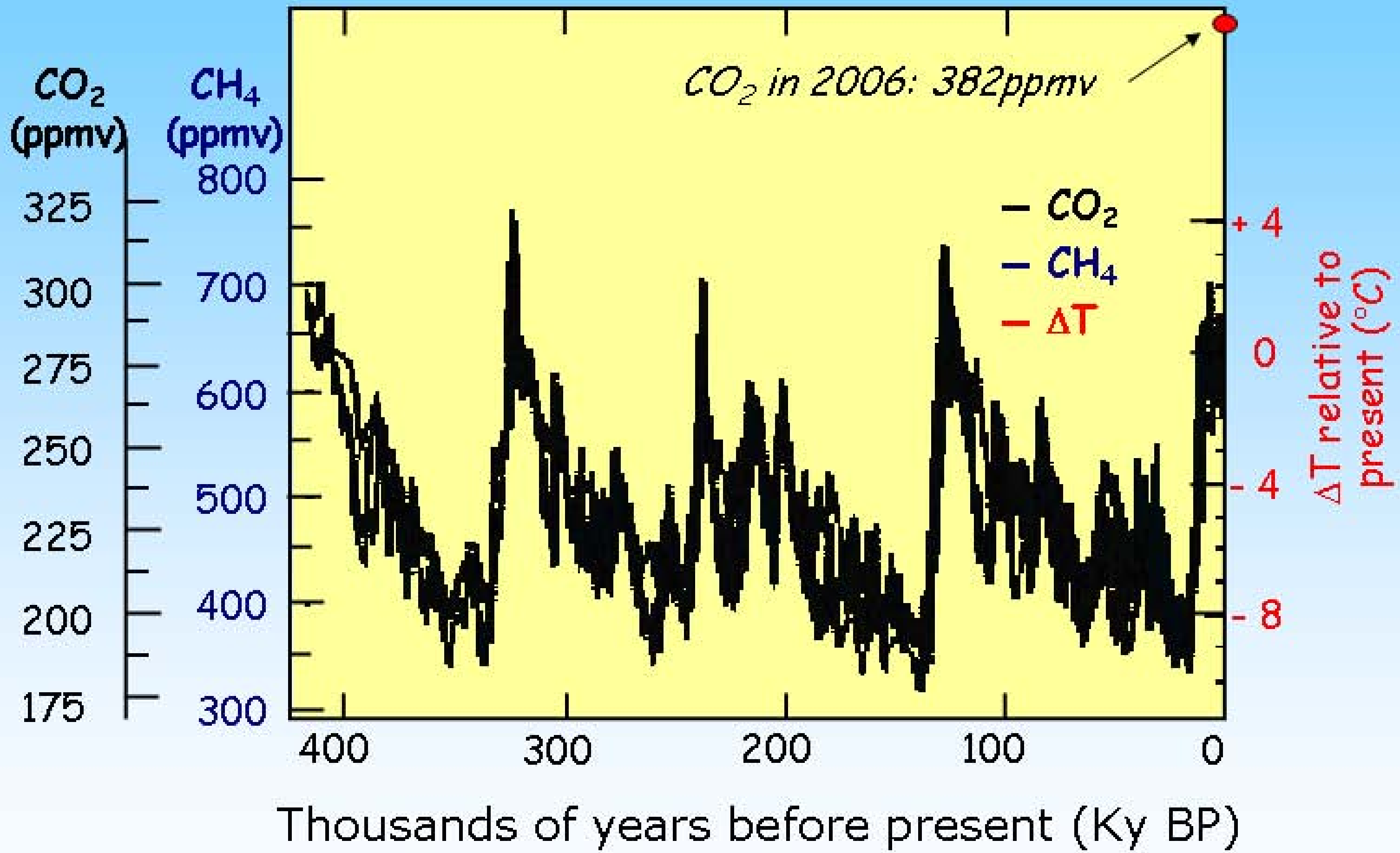
2005 totals:	490 Q-Btu,	515 EJ,	16TW	86% fossil
2030 projections:	720 Q-Btu,	760 EJ,	24TW	→ 81%

Source: US Energy Information Administration

Environmental Outlook



Environmental Outlook



Intergovernmental Panel on Climate Change, 2001; http://www.ipcc.ch
N. Oreskes, Science ***306****, 1686, 2004; D. A. Stainforth et al, Nature* ***433****, 403, 2005*

The Energy Solution

Solar
1.2 x 10^5 TW at Earth surface
600 TW practical

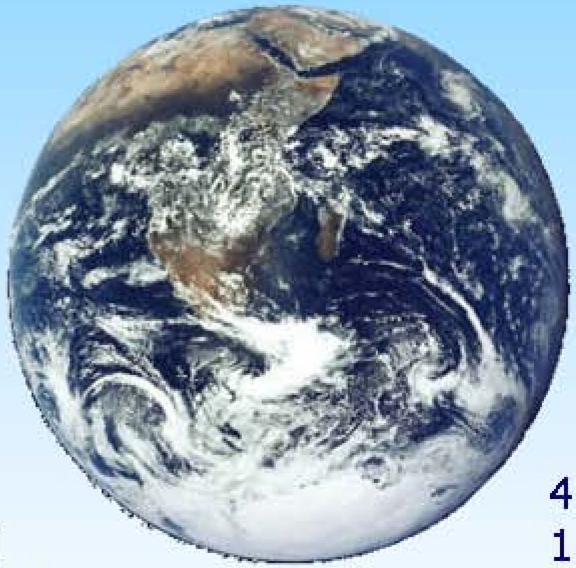
The need:
~ 20 TW by 2050

Wind
2-4 TW extractable

Tide/Ocean Currents
2 TW gross

Geothermal
12 TW gross over land
small fraction recoverable

Nuclear
Waste disposal
60 yr uranium supply

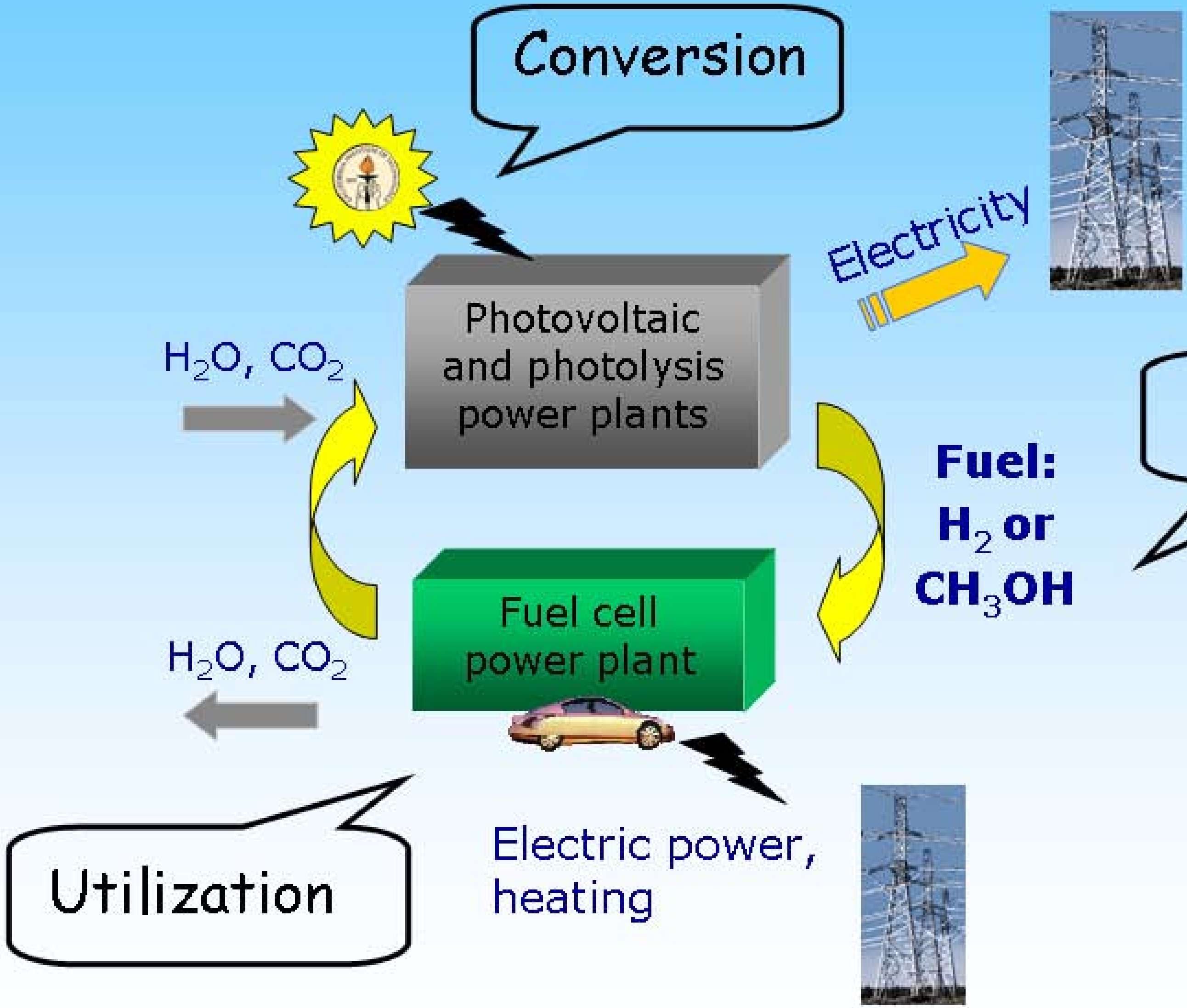


Biomass
5-7 TW gross
all cultivatable land not used for food

Hydroelectric
4.6 TW gross
1.6 TW technically feasible
0.9 TW economically feasible
0.6 TW installed capacity

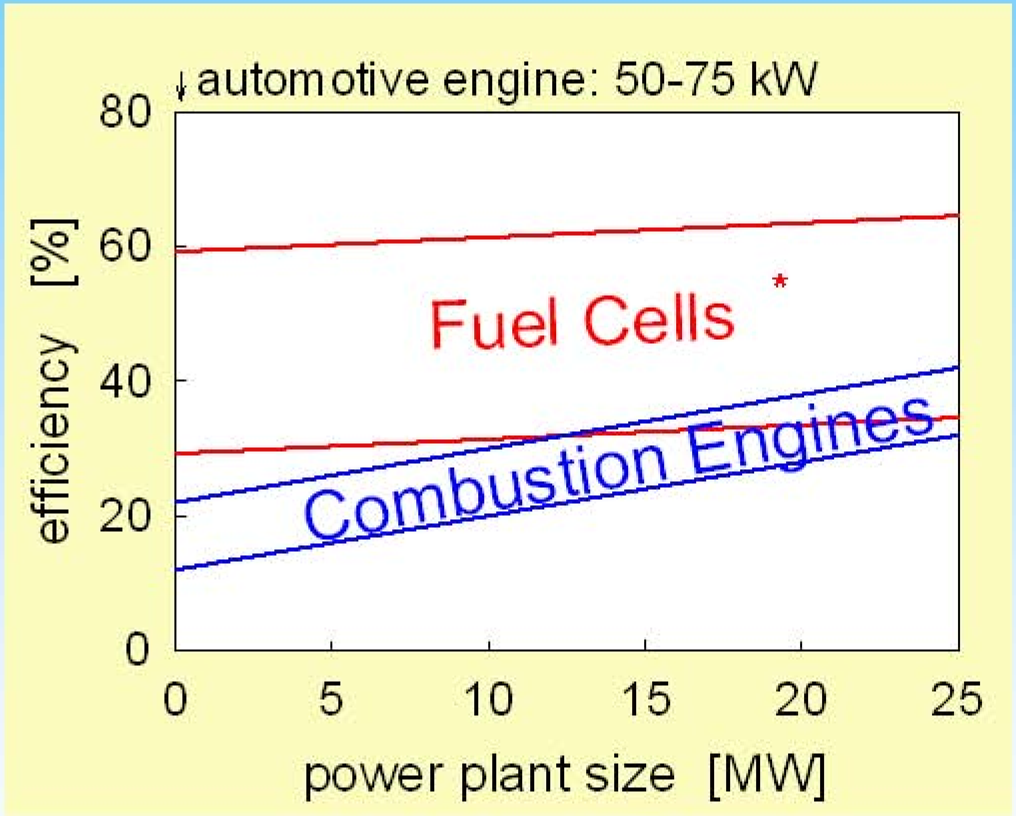
Fossil with sequestration
1% / yr leakage -> lost in 100 yrs

Caltech Center for Sustainable Energy Research



Harry Atwater
Harry Gray
Sossina Haile
Nathan Lewis

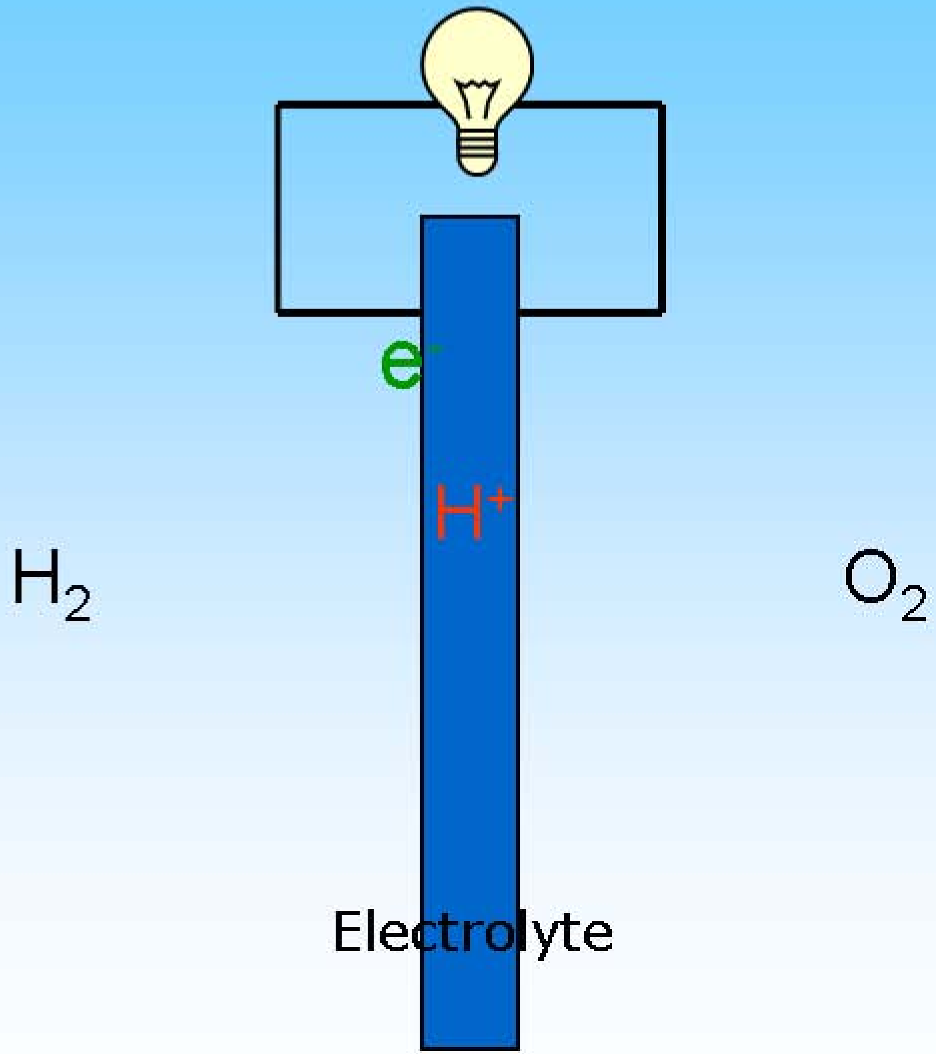
Fuel Cells: Part of the Solution?



- High efficiency
  - *low CO_2 emissions*
- Size independent
- Various applications
  - *stationary*
  - *automotive*
  - *portable electronics*
- Controlled reactions
  - *"Zero Emissions"*
- Operable on hydrogen
  - *(if suitably produced)*

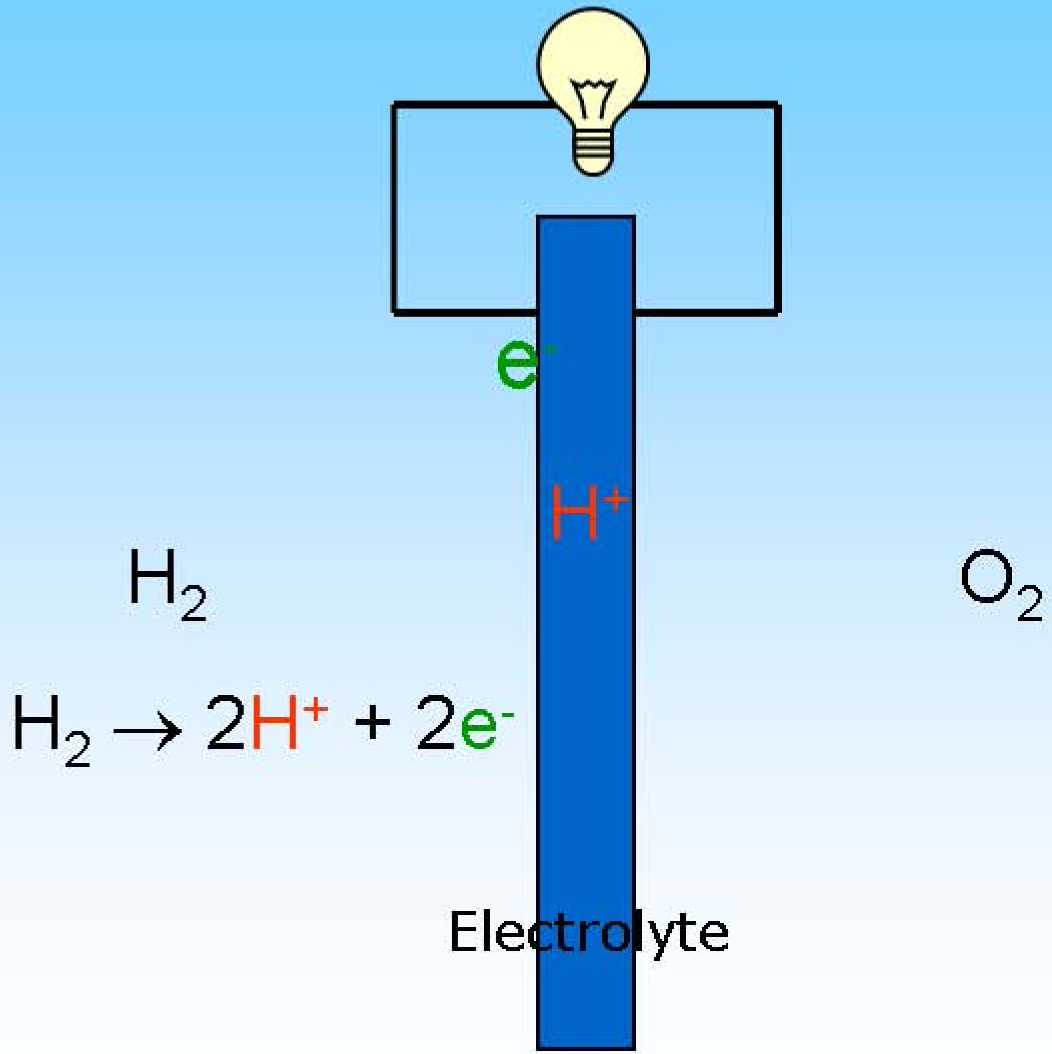
*Can be as high as 80-90% with co-generation

Fuel Cell: Principle of Operation



Overall: $H_2 + ½ O_2 \rightarrow H_2O$

Fuel Cell: Principle of Operation



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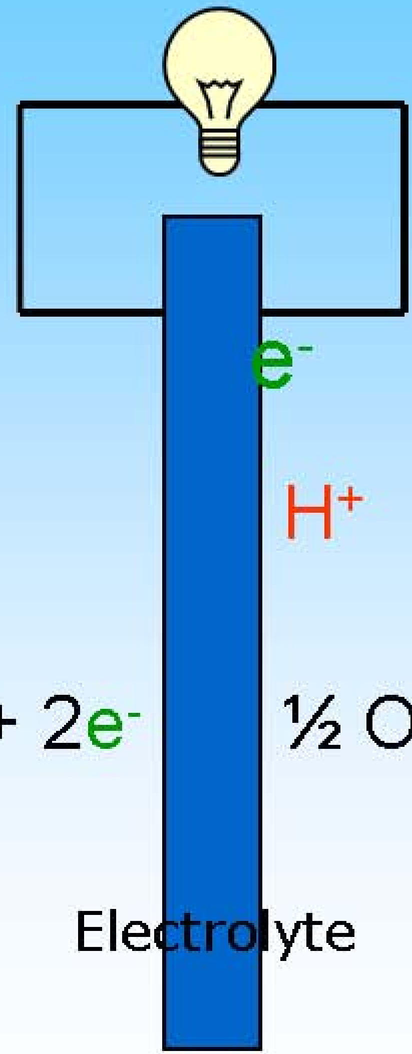
Fuel Cell: Principle of Operation

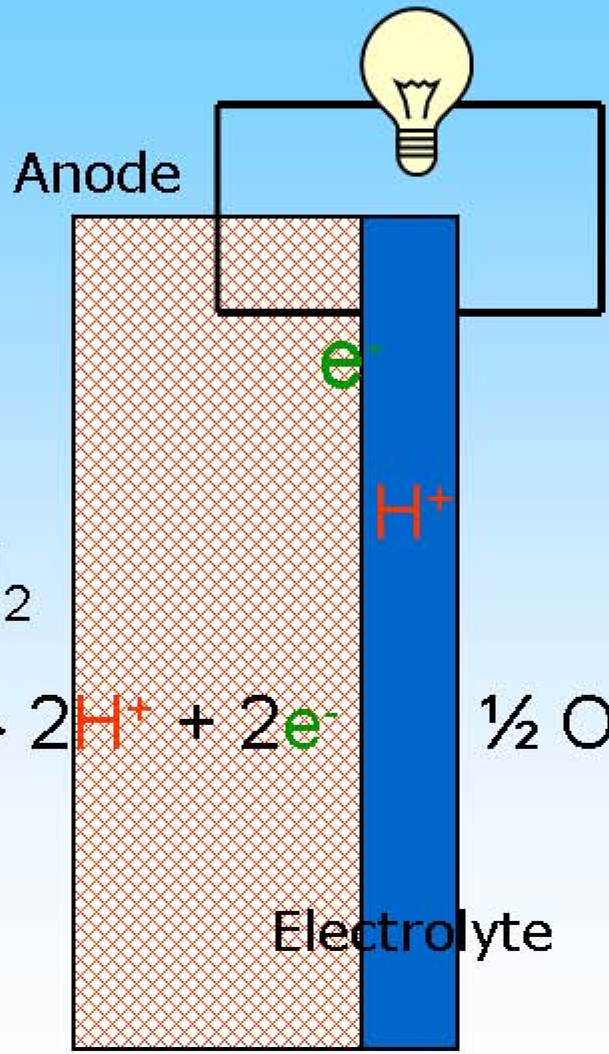


H_2 O_2

$H_2 \rightarrow 2H^+ + 2e^-$ $\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$

Overall: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

Fuel Cell: Principle of Operation



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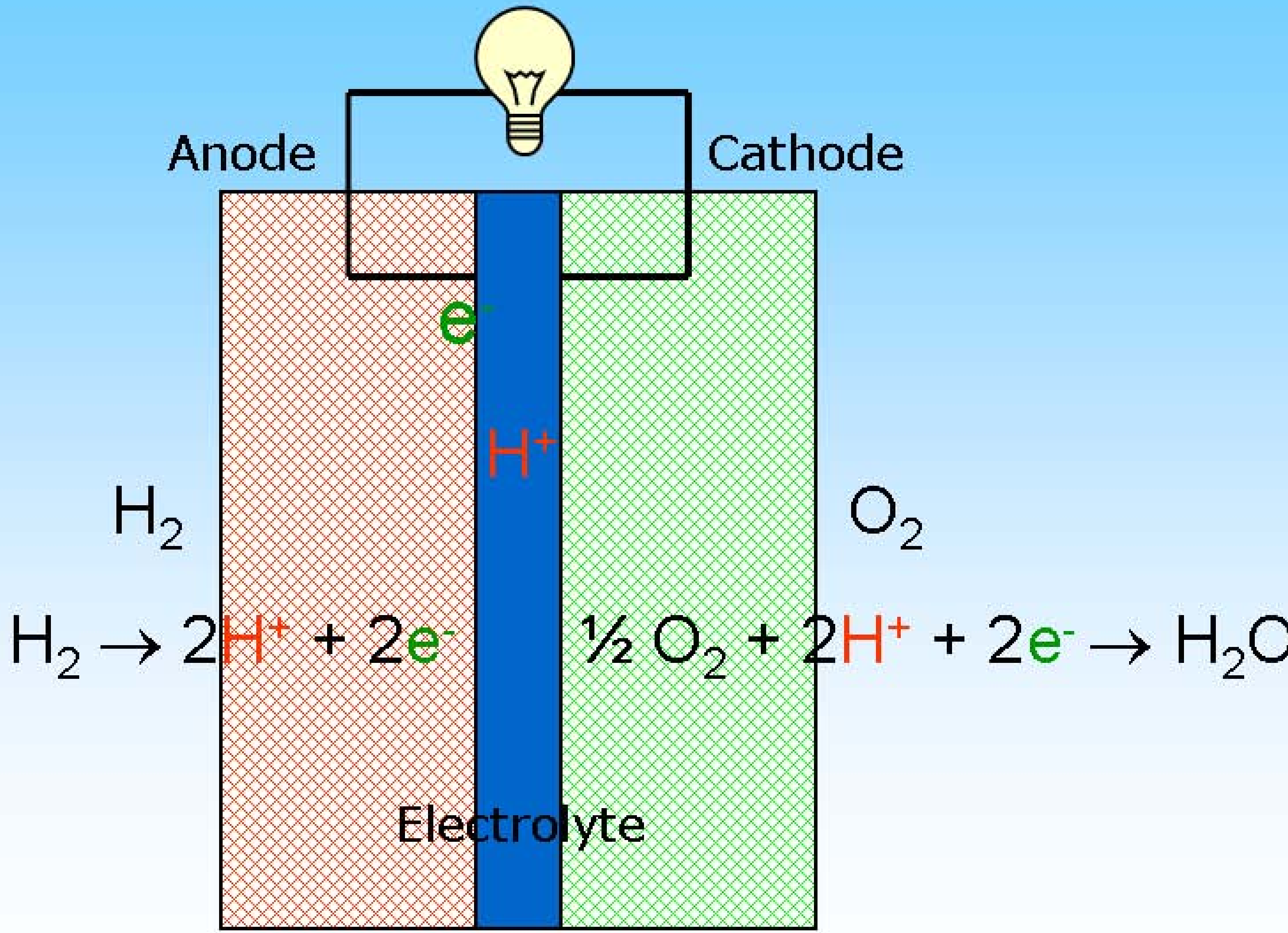
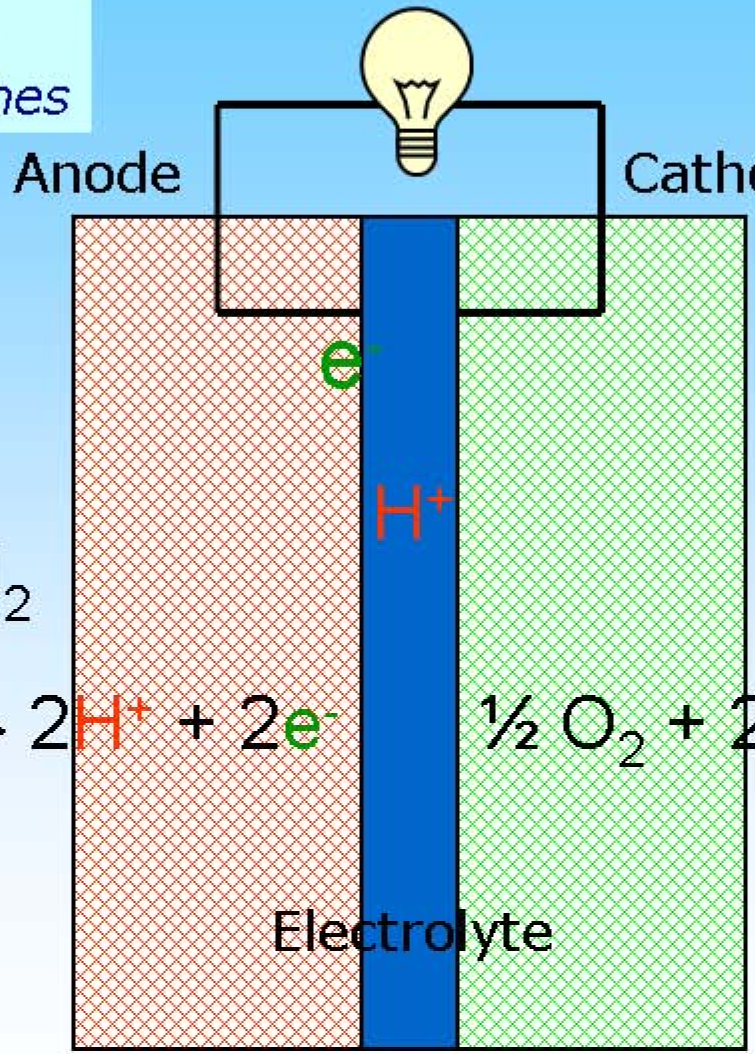


Overall: $H_2 + ½\ O_2 \rightarrow H_2O$

Fuel Cell: Principle of Operation

best of batteries, combustion engines

conversion device, not energy source



H_2

O_2

$H_2 \rightarrow 2H^+ + 2e^-$

$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$

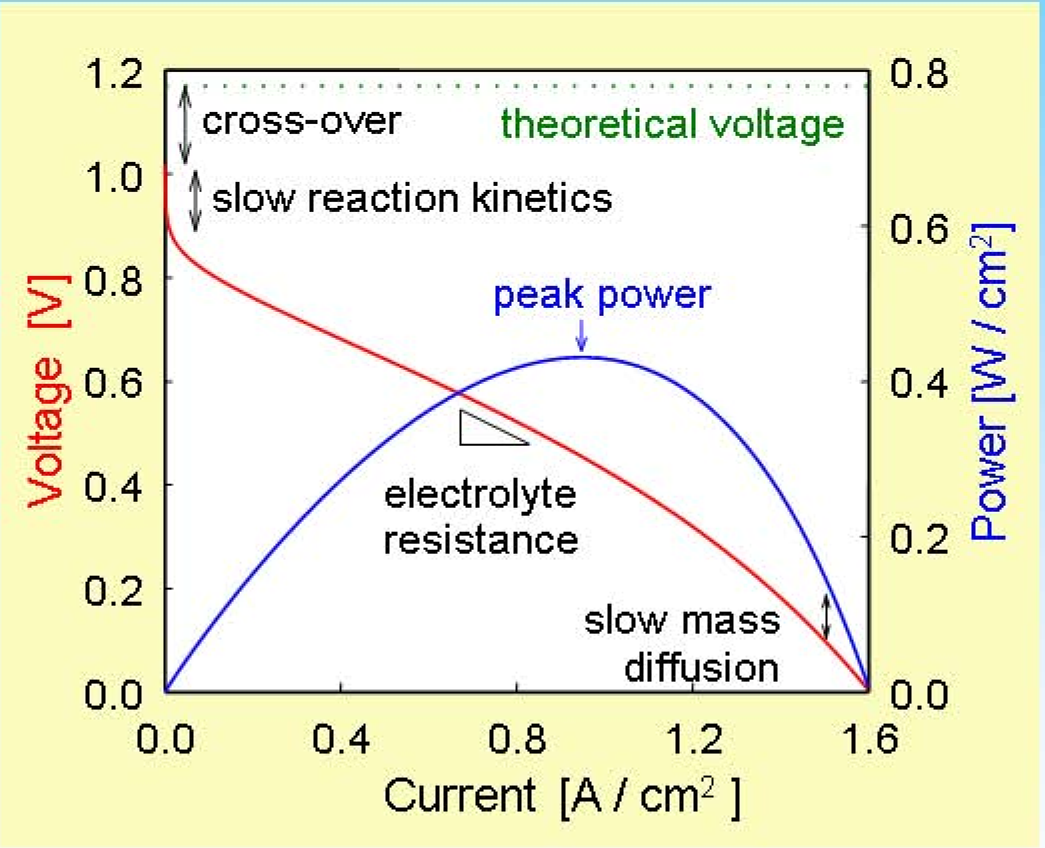
Overall: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

Fuel Cell Performance

$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

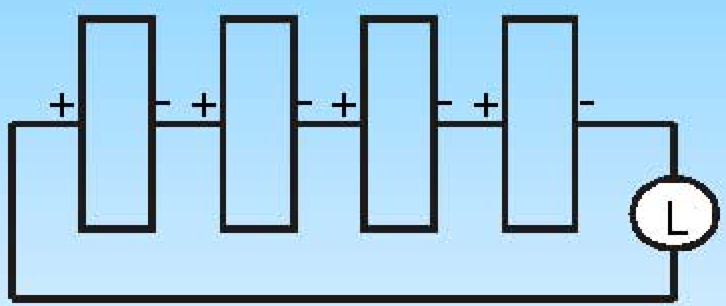
1.17 Volts (@ no current)

- voltage losses
  - *fuel cross-over*
  - *reaction kinetics*
  - *electrolyte resistance*
  - *slow mass diffusion*
- power = I*V
- peak efficiency at low I
- peak power at mid I



From a Single Cell to a Fuel Cell Stack

- Multiple cells
- Connect in series: $V = nV_o$



- Connect in parallel: $I = nI_o$
- Requires gas flows to each
- Thermal management
- Greater system complexity than batteries

Fuel Cell Types

Types differentiated by **electrolyte**, temperature of operation

Portable (PEM, AFC, PAFC) — Stationary (PAFC, MCFC, SOFC)

Type °C	**PEM** 90-110	**AFC** 100-250	**PAFC** 150-220	**MCFC** 500-700	**SOFC** 700-1000
Fuel	$H_2 + H_2O$	H_2	H_2	HC + CO	HC + CO
Electrolyte *Ion*	Nafion $H_3O^+ \downarrow$	KOH $OH^- \uparrow$	H_3PO_4 $H^+ \downarrow$	Na_2CO_3 $CO_3^{2-} \uparrow$	Y-ZrO_2 $O^{2-} \uparrow$
Oxidant	O_2	$O_2 + H_2O$	O_2	$O_2 + CO_2$	O_2

← Easy thermal cycling | Fuel flexibility, efficiency →

Most substantial recent investments and development activity

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← Easy thermal cycling

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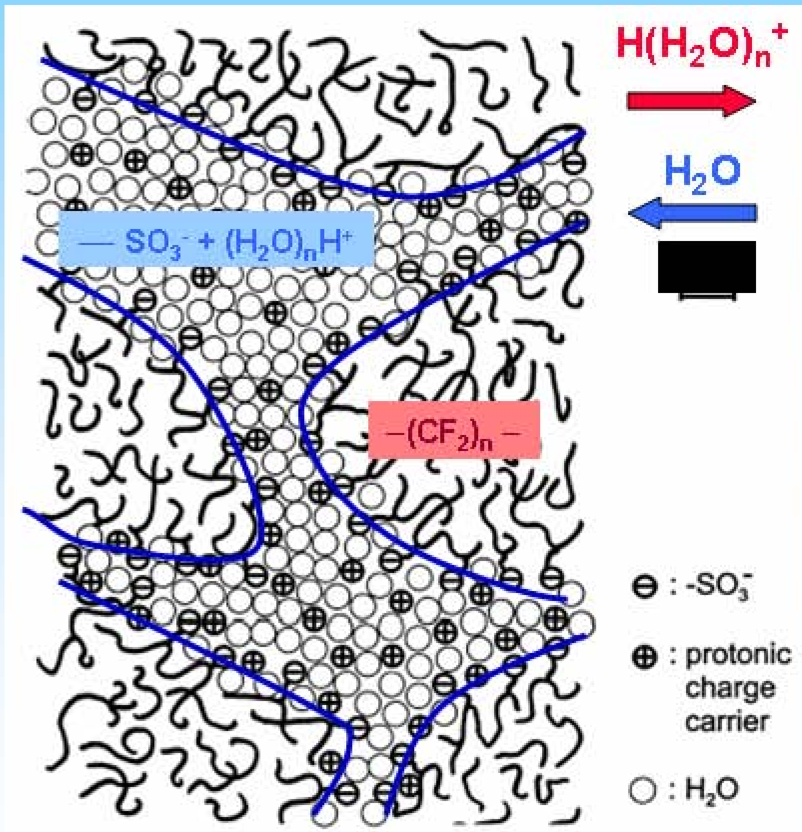
Ambient Temperature Fuel Cells

Proton Exchange Membrane or Polymer Electrolyte Membrane



Kreuer, *J. Membr. Sci.* **2** (2001) 185.

Nafion (Dupont)

- saturate with H_2O
  - *inverse micelle structure*
- $H(H_2O)_n^+$ ion transport ⇐

✓ High conductivity

✓ Flexible, high strength

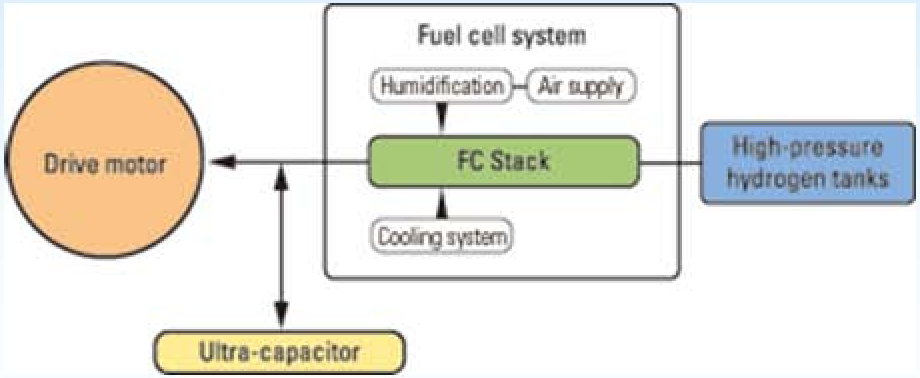
× Requires humidification & water management

× Operation below 90°C
  - Limits catalytic activity

× Permeable to methanol

× Permeable to O_2, H_2

Development Activities



- Honda FCX Clarity
  - *Leasing in summer 2008*
  - *H_2 available markets (LA)*
- 86 kW PEM fuel cell
- 68 mpg equivalent
  - *1.5 x gas-electric hybrid*
- 270 mile range
- 5,000 psi H_2 tank
  - *approx 4 kg H_2*
- Lithium-ion battery pack
  - *Replaces ultra-caps*

Some Fundamental Challenges

- Polymer conductivity scales with water content
- Methanol cross-over scales with water content
- Acidic water in polymer dissolves catalysts
  - *Coarsens fine particles*
  - *Causes Ru cross-over (used for methanol oxidation)*
- Ambient temperature operation requires Pt
  - *DOE target: 1 g/kW (0.75 g/hp)*
  - *125 hp engine $\Rightarrow$ 100g Pt $\Rightarrow$ $5,028*
  - *93% of US Pt is imported, 80% of world reserves in SA*
  - *Converting all registered US vehicles (~ 250 million)*
    - *Need: 25 million kg Pt*
    - *Reserves: proven ~ 7 million kg; inferred ~ 32 million kg*
  - *DOE longterm target: 0.2 g/kW*

Solid Oxide Fuel Cells

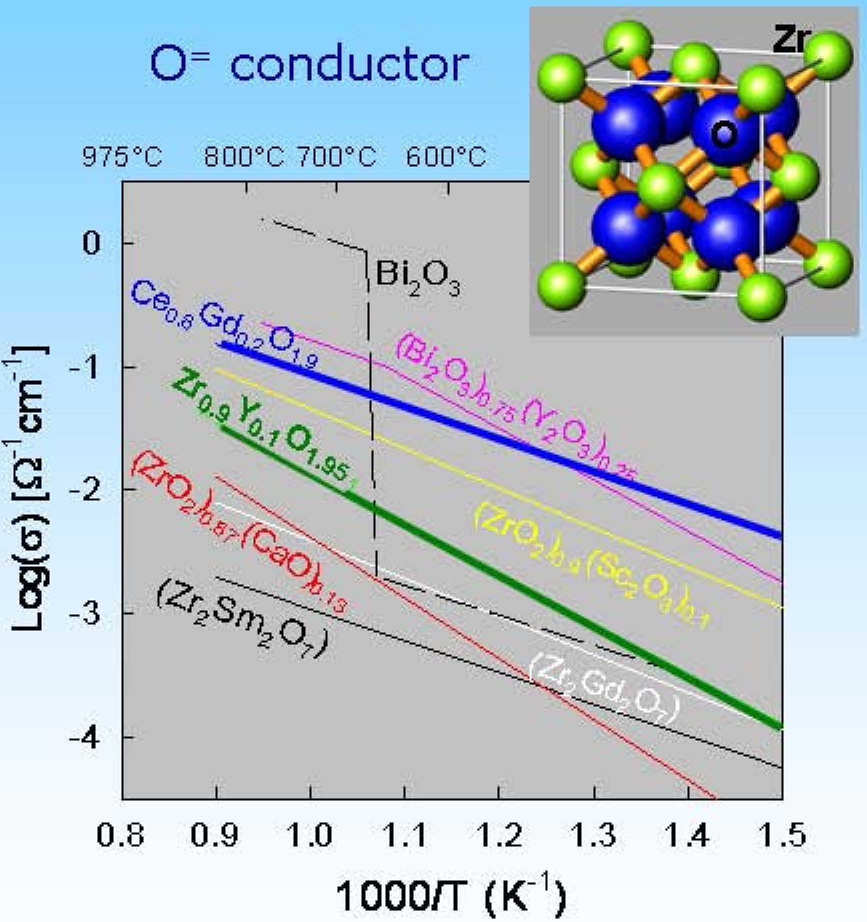
(La,Sr)MnO_3 | YSZ | Ni-YSZ

cathode | electrolyte | anode

- Anode or electrolyte supported
- 800 – 1000 °C operation
- Fuel flexible, efficient
- But…
  - *Costly (manufacture)*
  - *Poor thermal cyclability*

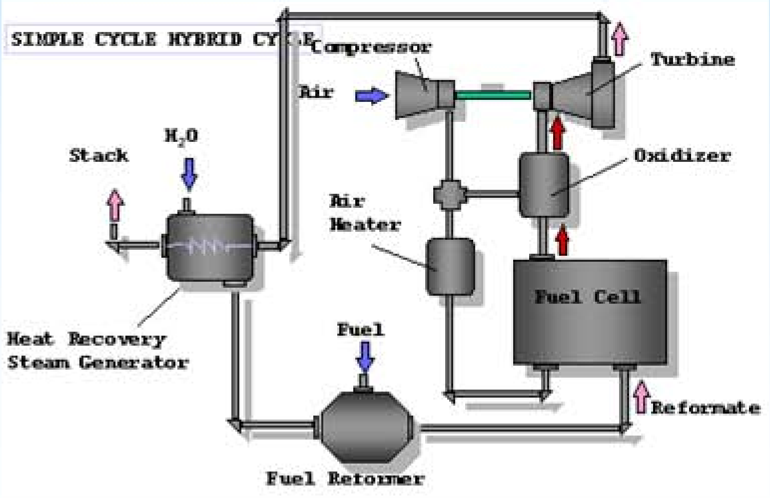
Goal: reduced temperature operation, 500 – 800 °C

$O^=$ conductor



Demonstration Activities

Siemens-Westinghouse Project at Natl Fuel Cell Res Ctr



"HYBRID" 220 kW Hybrid

- Solid Oxide Fuel Cell + Micro Turbine Generator
- 180 kW SOFC
- 40 kW Microturbine
- Installed 2000
- Operated > 1,500 hr
- Fuel-to-electricity
  - *53% demonstrated*
  - *60-70% future*
- Natural gas (100 psi)

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Oxidant	O_2	O_2 + H_2O	O_2	O_2 + CO_2	O_2

Fuel flexibility, efficiency →

← Easy thermal cycling

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Fuel	H_2 + H_2O	H		+ CO	HC + CO
Electrolyte *Ion*	Nafion H_3O^+ ↓	KO *OH*		$_2CO_3$ $_3^{2-}$ ↑	Y-ZrO_2 O^{2-} ↑
Oxidant	O_2	O_2 + H_2O	O_2	O_2 + CO_2	O_2

Corrosive liquids

Fuel flexibility, efficiency →

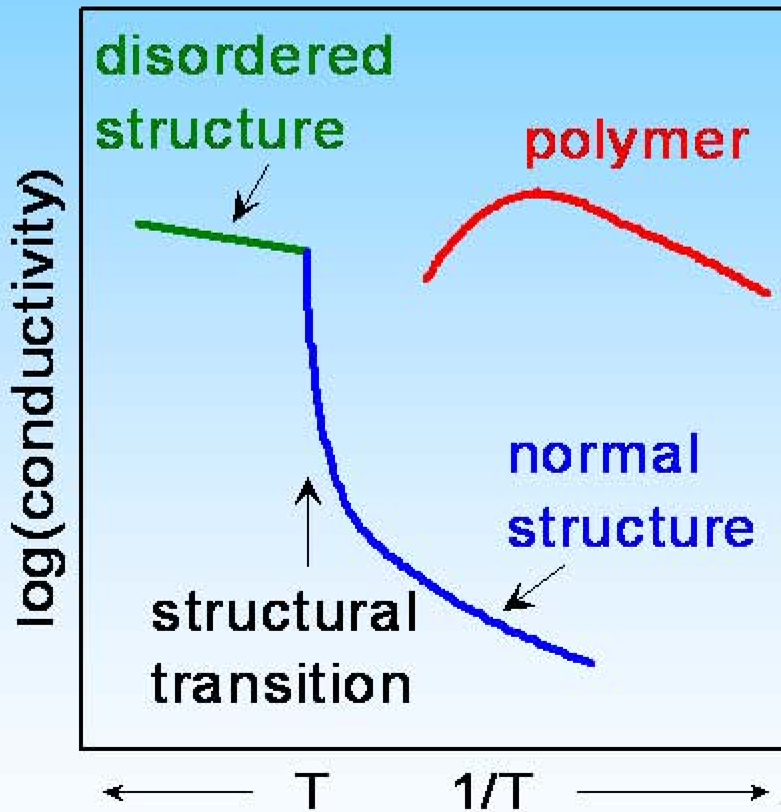
← Easy thermal cycling

Target regime

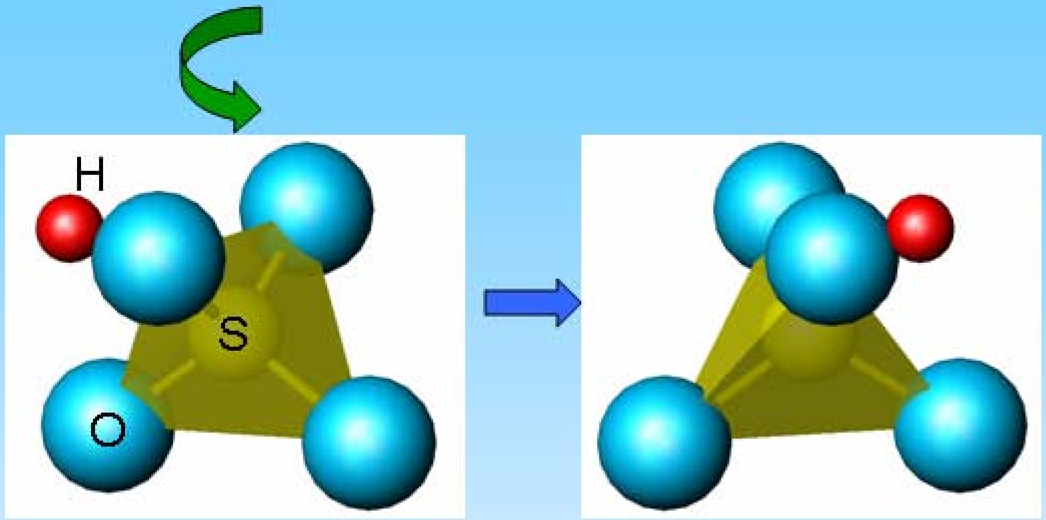
New Electrolytes: Solid Acids

- Chemical intermediates between normal salts and normal acids: "acid salts"

  ½(Cs_2SO_4) + ½(H_2SO_4) → $CsHSO_4$
- Physically similar to salts
- Structural disorder at 'warm' temperatures
- Properties
  - ✓ *Direct H^+ transport*
  - ✓ *Humidity insensitive*
  - ✓ *Impermeable*
  - × *Water soluble!! Brittle*



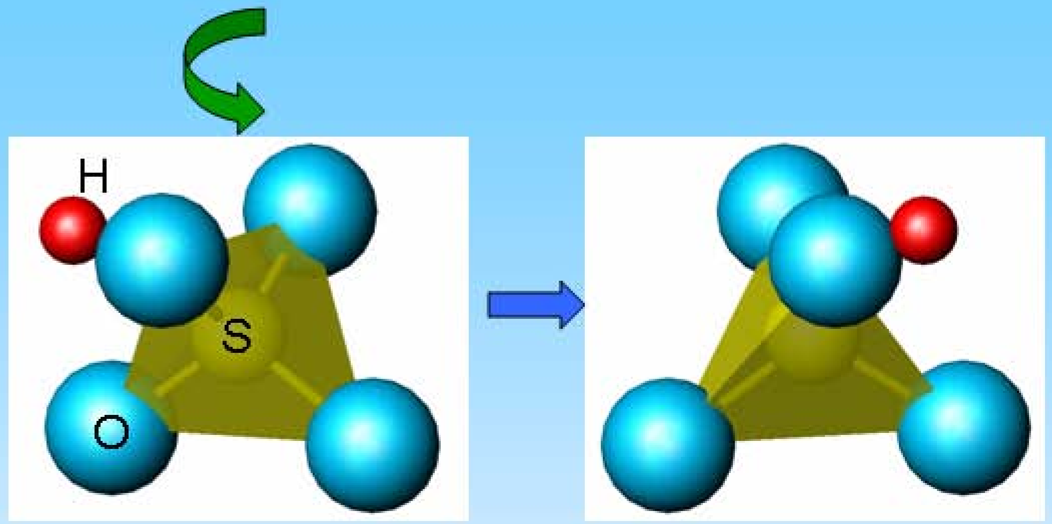
Proton Transport Mechanism



Sulfate group reorientation

10^{-11} seconds

Proton Transport Mechanism



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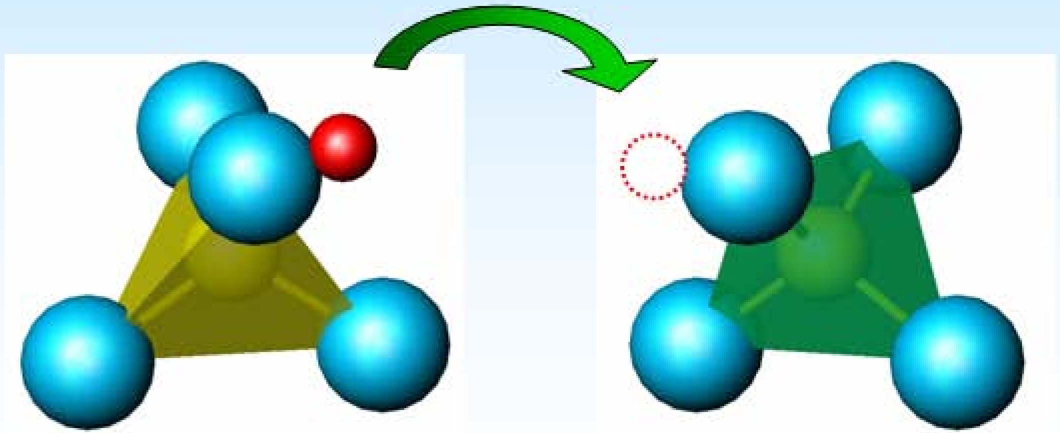
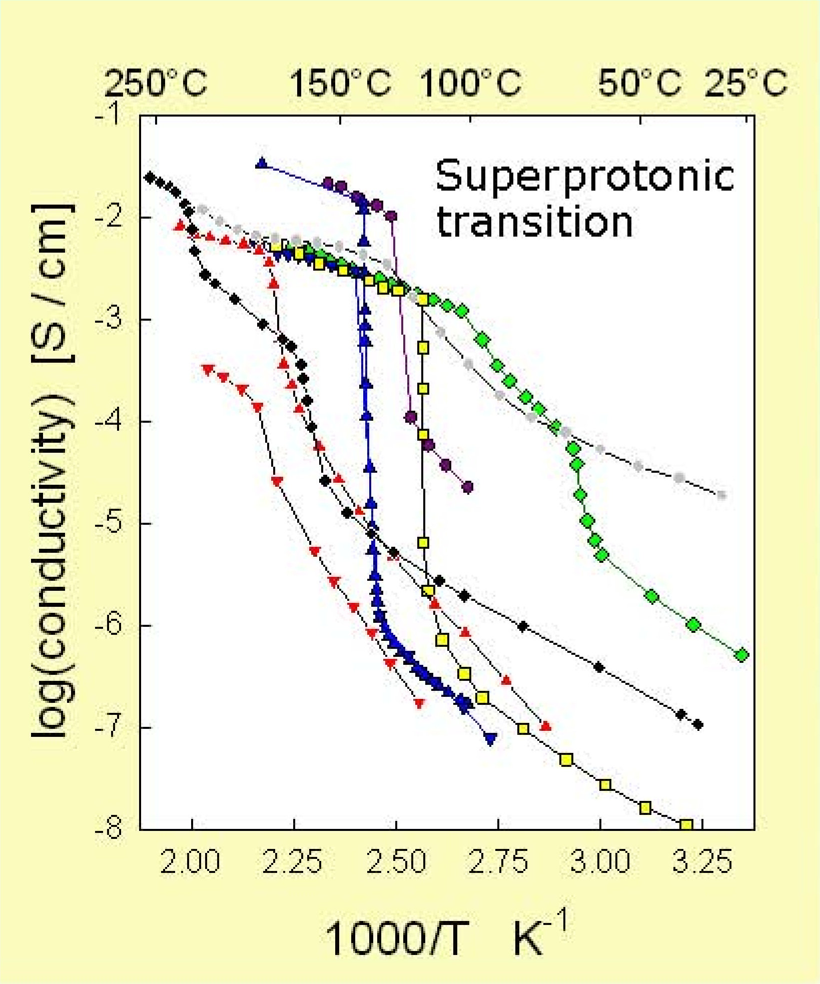


Proton transfer

10^{-9} seconds

Conductivity of Solid Acids

- $CsHSO_4$ [Baranov, 1982]
- $CsHSeO_4$ [Baranov, 1982]
- $(NH_4)_3H(SO_4)_2$ [Ramasastry, 1981]
- $Rb_3H(SeO_4)_2$ [Pawlowski, 1988]
- $Cs_2(HSO_4)(H_2PO_4)$ [Chisholm & **Haile**, 2000]
- β-$Cs_3(HSO_4)_2(H_2PO_4)$ [**Haile** et al., 1997]
- $K_3H(SO_4)_2$ [Chisholm & **Haile**, 2001]



But sulfates and selenates are unstable under reducing conditions…

CsH_2PO_4 as a Fuel Cell Electrolyte

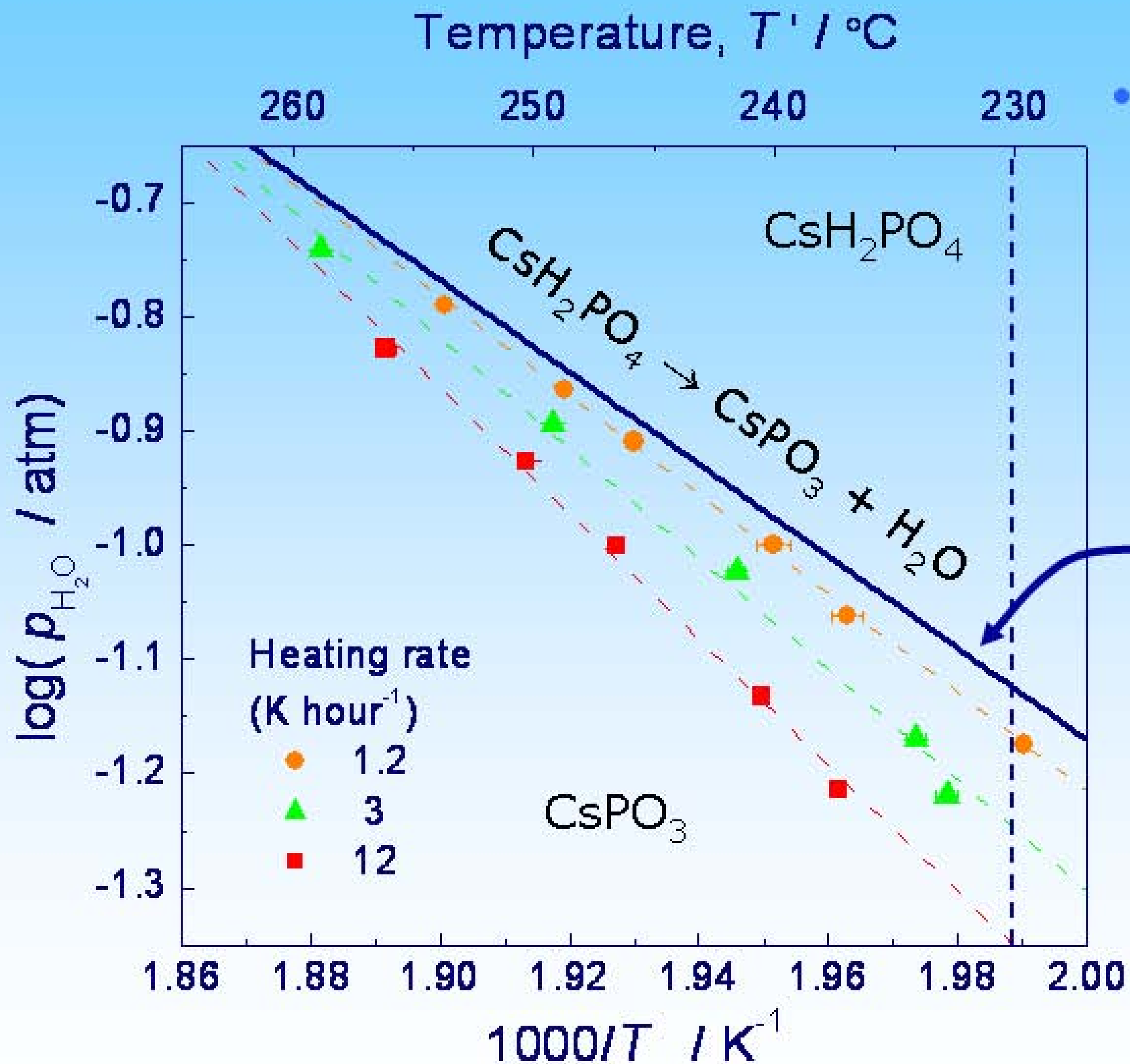
- Expected to have chemical stability
  - $3CsH_2PO_4 + 11H_2 \rightarrow Cs_3PO_4 + 3H_3P + 8H_2O$
  - $dG(rxn) >> 0$
- But does it have high conductivity?
- Does it have sufficient thermal stability?
- Literature dispute
  - *High conductivity on heating due to H_2O loss*
  - *High conductivity due to transition to a cubic phase*

The Controversy

A. I. Baranov et al	Frequency Dielectric-Dispersion in the Ferroelectric and Superionic Phases of CsH_2PO_4.	1988
W. Bronowska	X-Ray Study of the High-Temperature Phase-Transition of CsH_2PO_4 Crystals.	1990
F. Romain et al	Raman-Study of the High-Temperature Phase-Transition in CsH_2PO_4	1991
R. A. Vargas et al.	Phase-Behavior of RbH_2PO_4 and CsH_2PO_4 in the Fast-Ion Regime	1993
A. Preisinger et al.	The Phase Transition of CsH_2PO_4 (CDP) at 505 K	1994
K. S. Lee	Hidden Nature of the High-Temperature Phase Transitions in Crystals of KH_2PO_4-Type: A Physical Change?	1996
Y. Luspin et al	Discontinuities in the Elastic Properties of CsH_2PO_4 at the Superionic Transition	1997
E. Ortiz et al	On the High-Temperature Phase Transitions of CsH_2PO_4: a Polymorphic Transition? A Transition to a Superprotonic Conducting Phase?	1999
E. Ortiz et al	On the High-Temperature Phase Transitions of Some KDP-Family Compounds: a Structural Phase Transition? A Transition to a Bulk-High Proton Conducting Phase?	1999
W. Bronowska	Does the Structural Superionic Phase Transition at 231 Degrees C in CsH_2PO_4 Really Not Exist	2001
K. S. Lee	Surface Transformation of Hydrogen-Bonded Crystals at High-Temperatures and Topochemical Nature	2002
J. Otomo et al	Protonic Conduction of CsH_2PO_4 and Its Composite With Silica in Dry and Humid Atmospheres.	2003
D. A. Boysen et al	High-Temperature Behavior of CsH_2PO_4 Under Both Ambient and High Pressure Conditions.	2003
J. H. Park et al	Physical Properties of CsH_2PO_4 Crystal at High Temperatures	2003
D. A. Boysen et al	High-Performance Solid Acid Fuel Cells Through Humidity Stabilization.	2004
J. H. Park	Possible Origin of the Proton Conduction Mechanism of CsH_2PO_4 Crystals at High Temperatures	2004
K. Yamada et al	Superprotonic Conductor CsH_2PO_4 Studied by H-1, P-31 NMR and X-Ray Diffraction	2004
J. Otomo et al	Effect of Water Vapor on Proton Conduction of Cesium Dihydrogen Phosphate and Application to Intermediate Temperature Fuel Cells	2005

Haile et al. *Faraday Disc* **134** (2007) 17-739

Equilibrium Dehydration



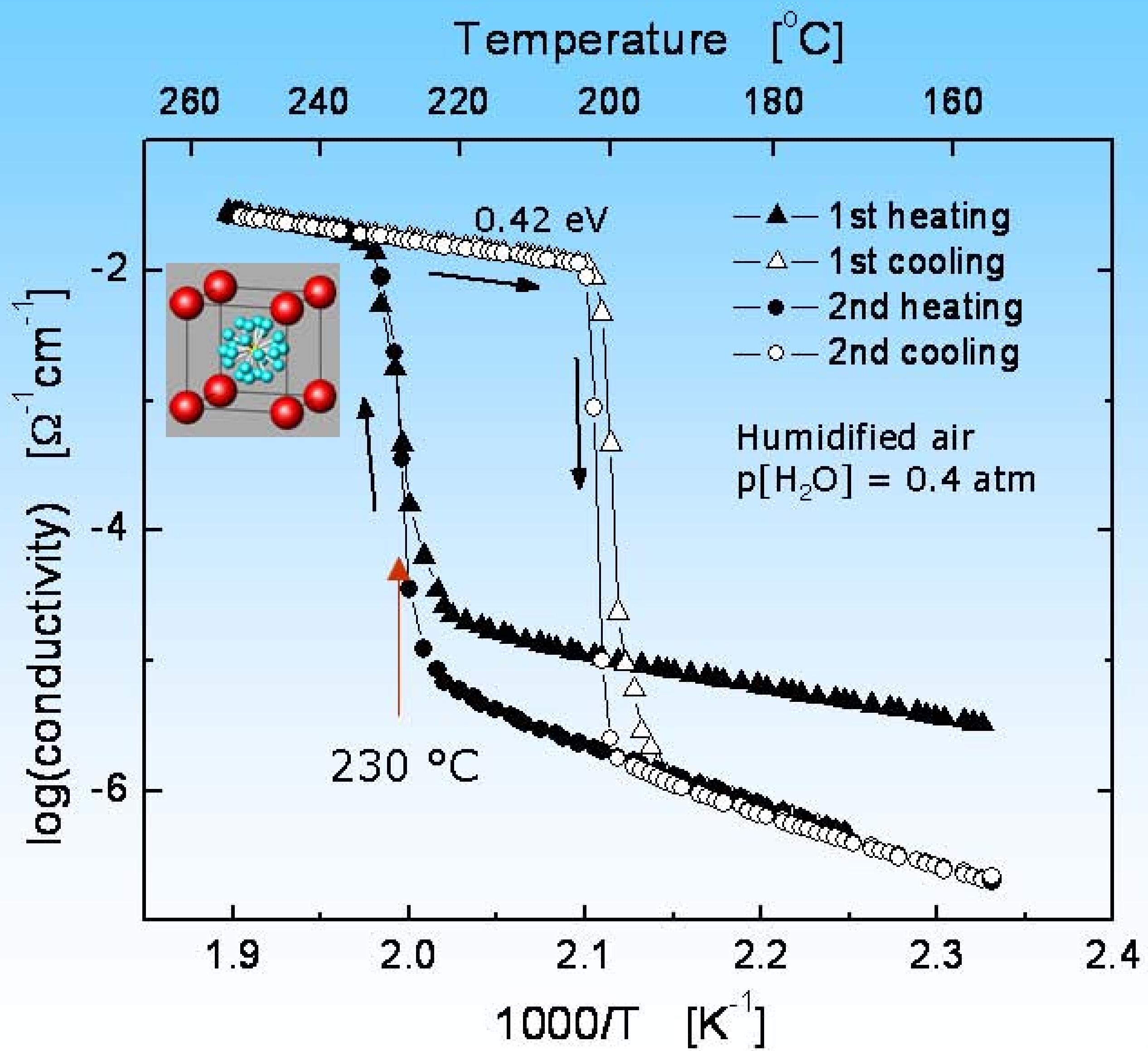
- Characterization methods
  - *Vary T, dT/dt, p(H_2O)*
  - *Track conductivity*
  - *Track weight*

Extrapolated to zero heating rate

$$T_{dehydr}^{finite} - T_{dehydr}^{equil} = k\left(\frac{dT}{dt}\right)^{1/2}$$

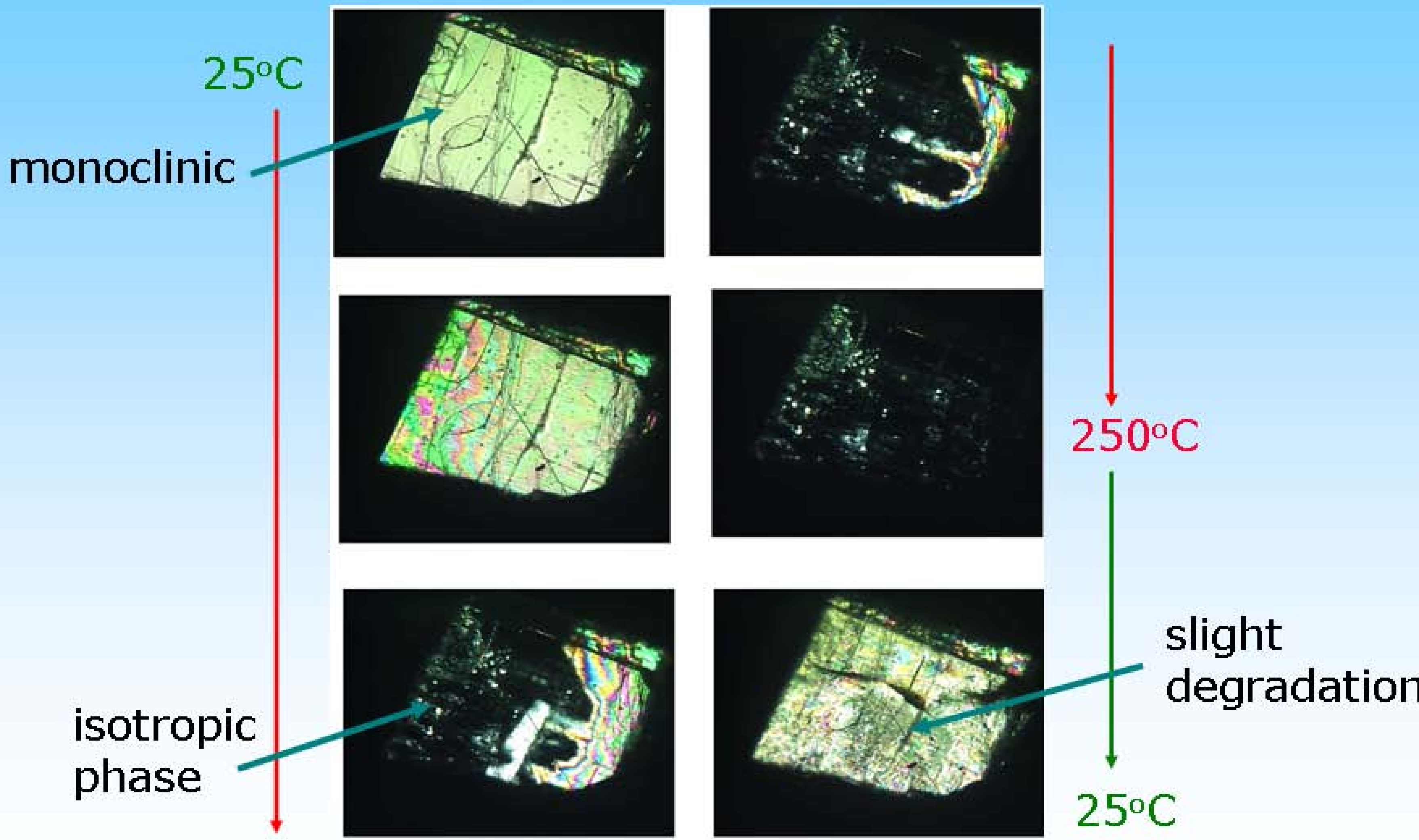
Taninouchi et al. *J. Mater. Chem Mat* **17** (2007) 3182-3189

Conductivity of CsH_2PO_4



Haile et al. *Faraday Disc* **134** (2007) 17-739

Optical Microscopy

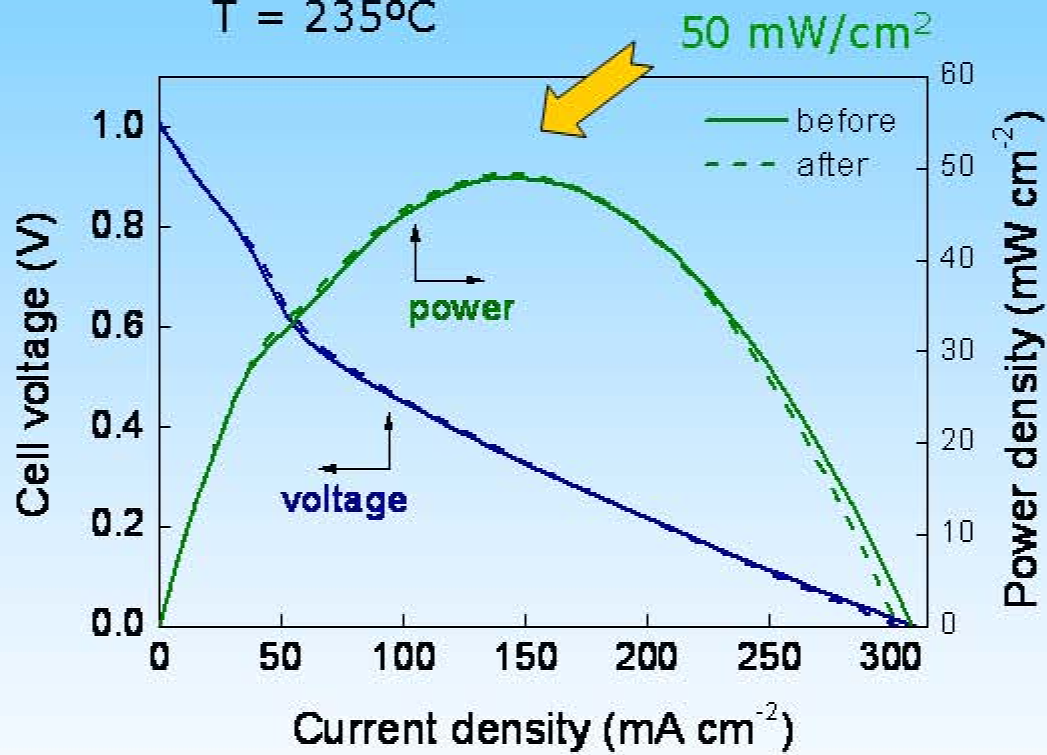


Boysen et al. *Chem Mat* **15** (2003) 727-736

Proof of Principle

H_2O, H_2 | Cell | O_2, H_2O

T = 235ºC



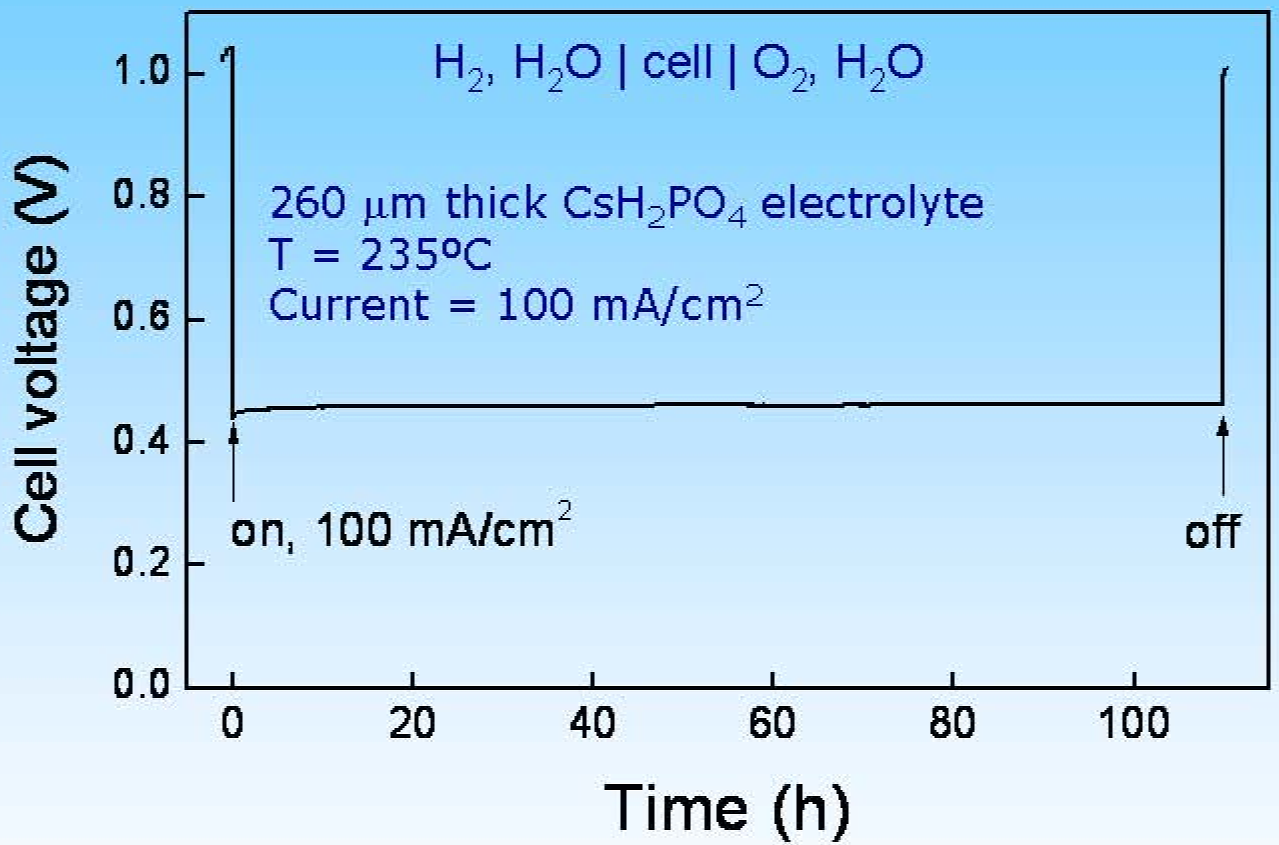
260µm membrane; 18 mg Pt/cm^2

Compared to polymers

- ✓ High open circuit voltage
  - *Theoretical: 1.15V*
  - *Measured: 1.00 V*
  - *Polymers: 0.8-0.9 V*
- × Power density
  - *Polymers: > 1 W/cm^2*
- • Platinum content
  - *Polymers: ~ 0.1 mg/cm^2*

D. A. Boysen, T. Uda, C. R.I. Chisholm and S. M. Haile, *Science* **303**, 68-70 (2004)

Fuel Cell Longevity: Stable Performance

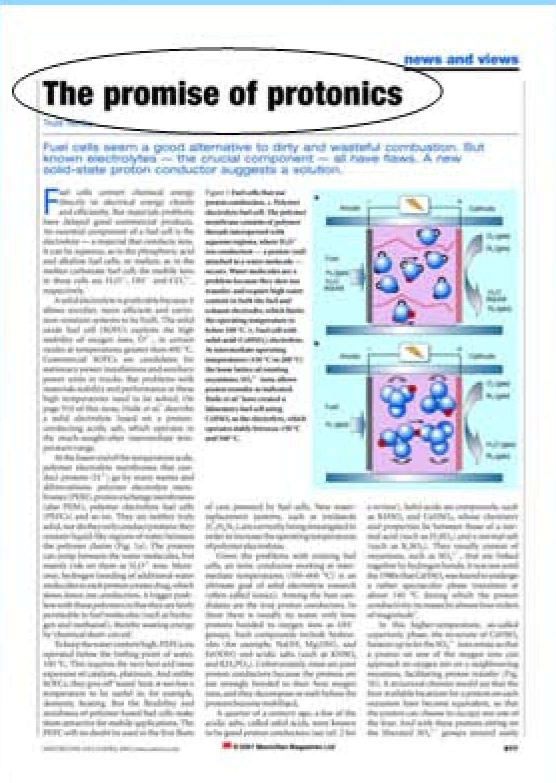


- CsH_2PO_4 – **no** degradation in 110 hr measurement
- $CsHSO_4$ – functions for only ~ 30 mins (recoverable degradation)

Impact

S. M. Haile, D. A. Boysen, C. R. I. Chisholm and R. B. Merle, "Solid Acids as Fuel Cell Electrolytes," *Nature* **410**, 910-913 (2001).

The promise of protonics


news and views

The promise of protonics

Fuel cells seem a good alternative to dirty and wasteful combustion. But known electrolytes — the crucial component — all have flaws. A new solid-state proton conductor suggests a solution.

Nature: News & Views

Some Like It Medium Hot


Some Like It Medium Hot

Just right. Fuel cells might someday power automobiles cleanly and efficiently, but only if they can run within a reasonable temperature range.

Science Now Magazine

Solid Acids Show Promise...


Physics Today July 2001 Page 1 of 4

Search & Discovery

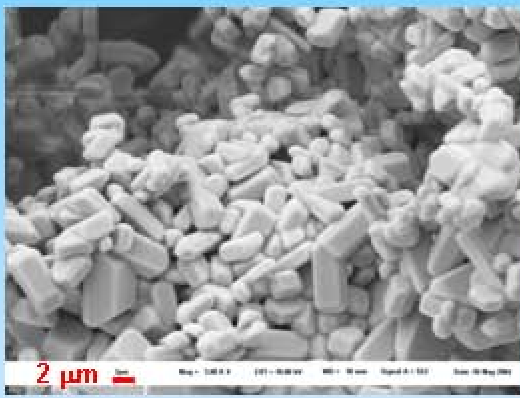
Solid Acids Show Potential for Fuel Cell Electrolytes

Solid acids can have high proton conductivities. Recent experiments demonstrate that they may be sufficiently stable to form the core of new, higher efficiency fuel cells.

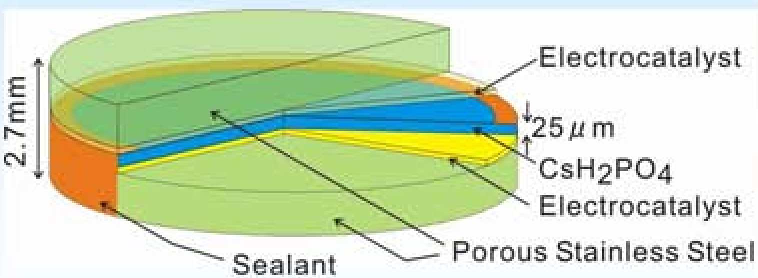
Physics Today Online

Fuel Cell Operation

Fine CsH_2PO_4

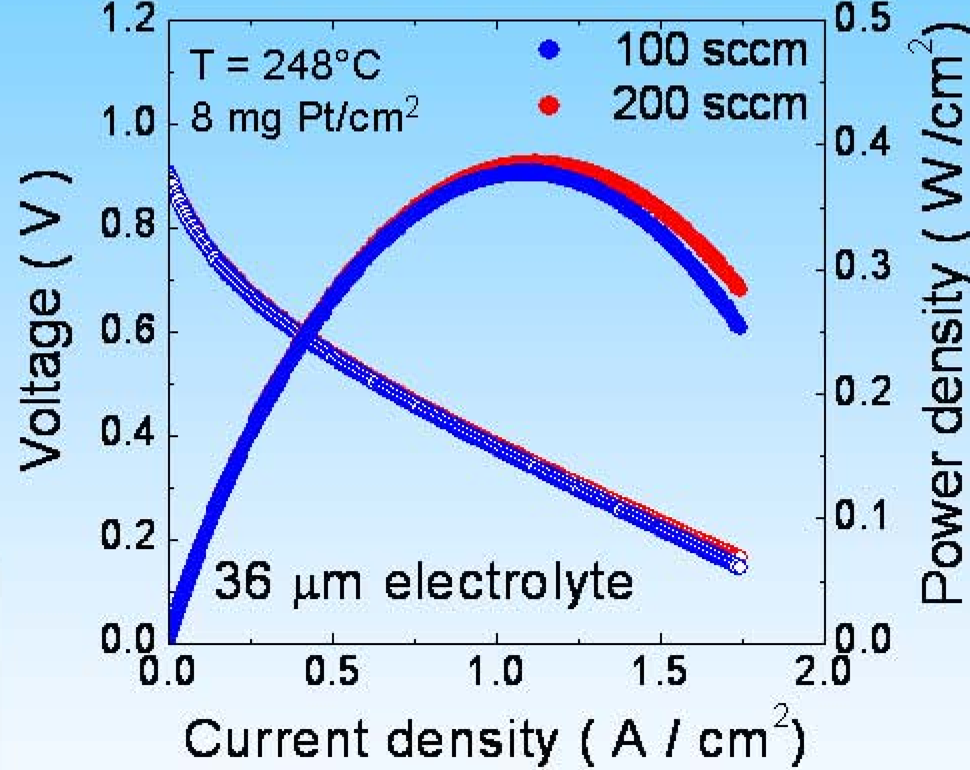


Slurry deposit



10-40 µm pores, ~40% porosity

H_2, H_2O | cell | O_2, H_2O



T. Uda & S.M. Haile, *Electrochem & Solid State Lett.* **8** (2005) A245-A246

Open circuit voltage: 0.9-1.0 V *Peak power density: 285-415 mW/cm²*

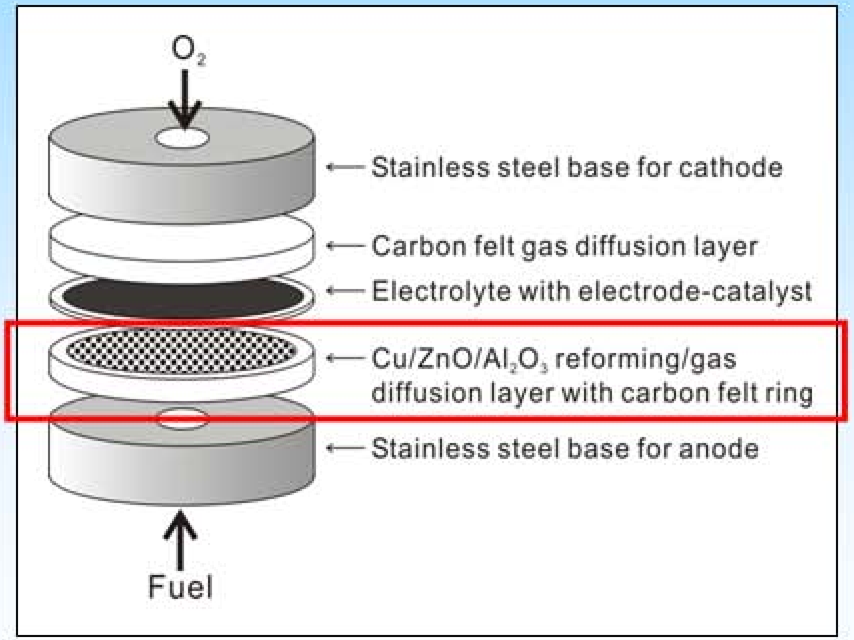
'Direct' Alcohol Fuel Cells

Methanol in proton exchange membrane fuel cells

$$CH_3OH + H_2O \rightarrow 6H^+ + CO_2 + 6e^-$$

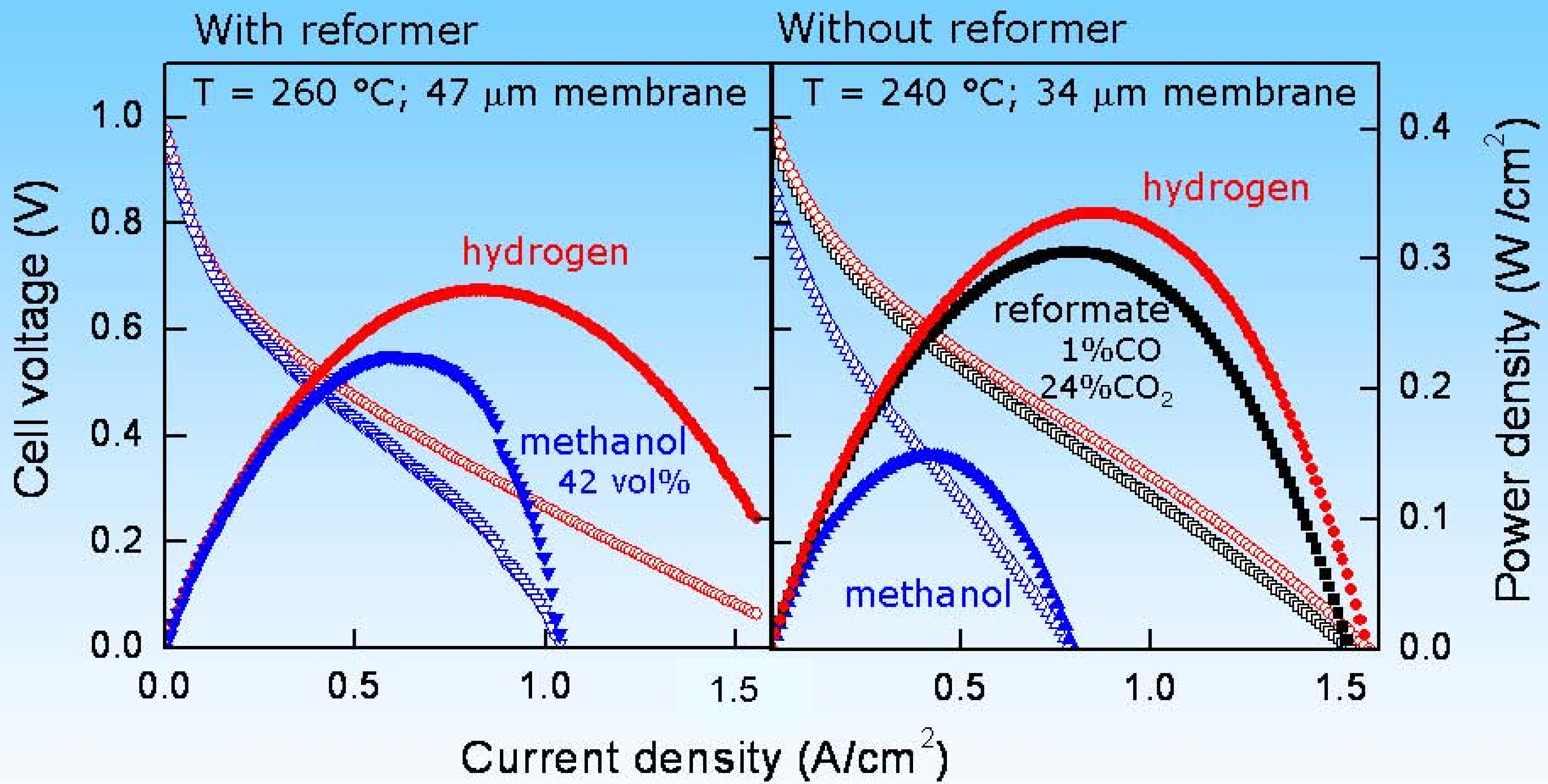
$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2$$

- SAFCS ideal thermal match
  - *Reforming rxn: 200 – 300°C*
  - *Electrolyte: 240 – 280°C*
  - *Steam reforming: endothermic*
  - *Fuel cell rxns: exothermic*
- Integrated design
  - *Incorporate alcohol reforming catalyst in anode chamber*



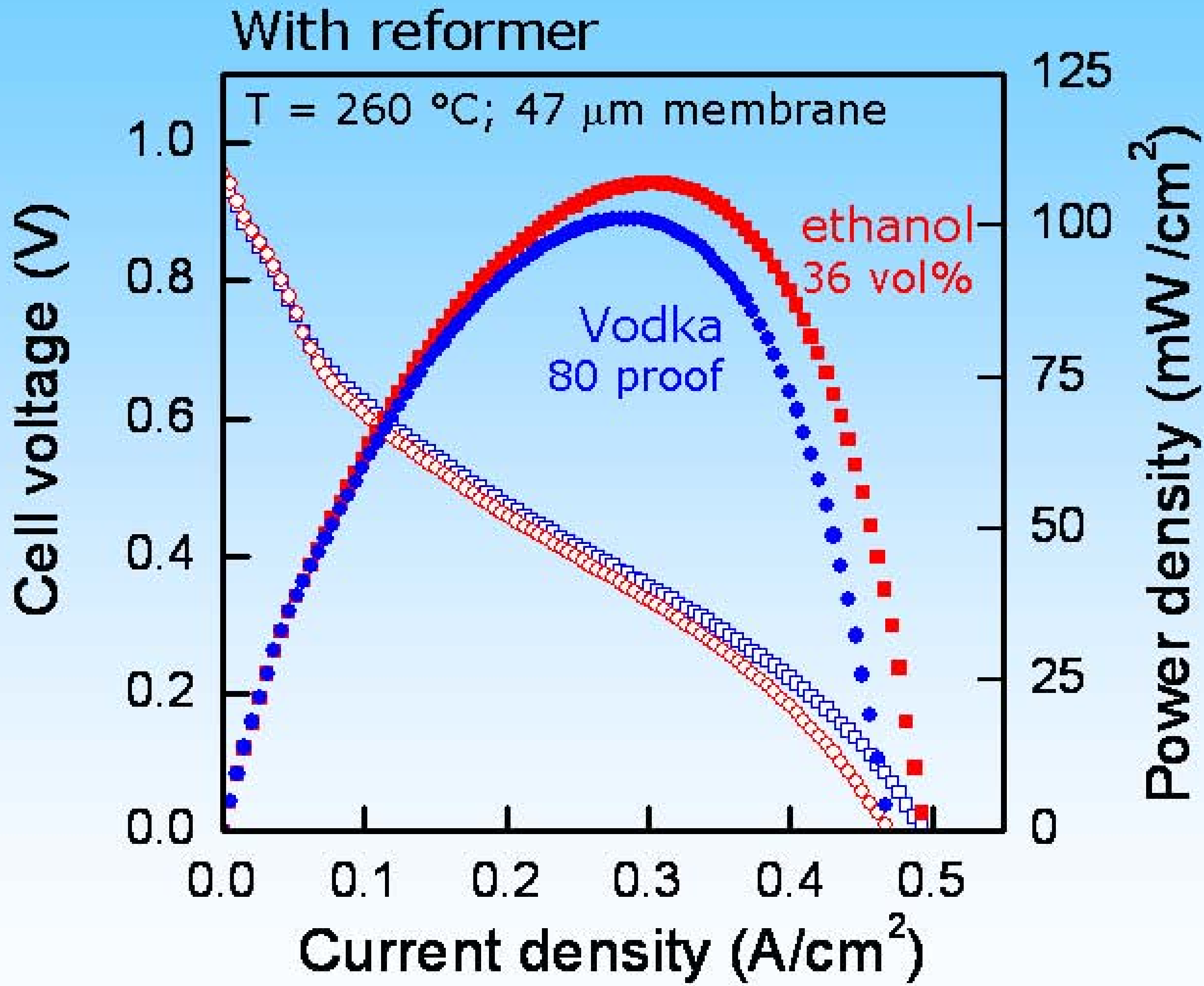
T. Uda et al., *Electrochem & Solid State Lett.* **9** (2006) A261-A264

‘Direct’ Methanol Fuel Cells



- Methanol power ~ 85% H_2 power
- For polymer fuel cells ~ 10%
- Reformate power ~ 90% H_2 power
- Methanol power ~ 45% H_2 power

'Direct' Alcohol Fuel Cells



- Ethanol power ~ 40% H_2 power

From Breakthrough to Product

2001

1 cm^2 of fuel cell area

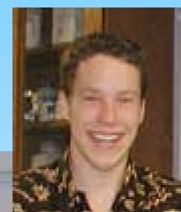
36 mg Pt for 10 mW

43 g Pt for 60 W bulb

~ $2,163 in Pt

Dane

Calum



2007

1 mg Pt for 200 mW

2.5 g Pt for 60 W bulb

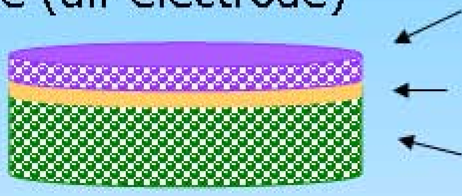
~ $126 in Pt

SUPERPROTONIC

Tom Friedman talking to his wife on an SAFC powered cell phone

State-of-the-Art SOFCs

Component Materials

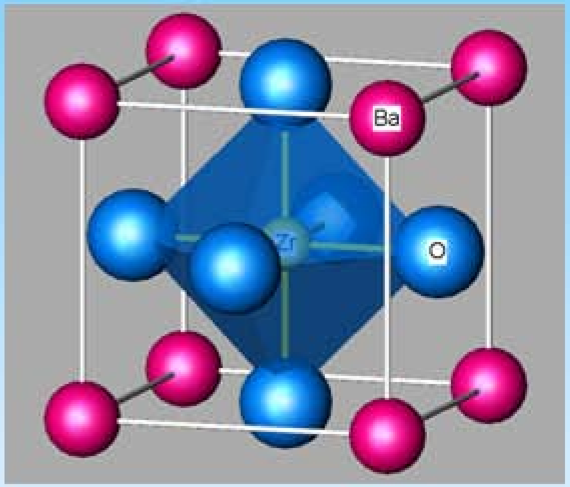


- Cathode typically exhibits highest losses
  - *Prepared as thinnest component*
  - *Murky literature on impact of cathode composition on O_2 electroreduction rates*
  - *General but not detailed mechanistic understanding*
  - *DOE has an SOFC 'cathode working group'*

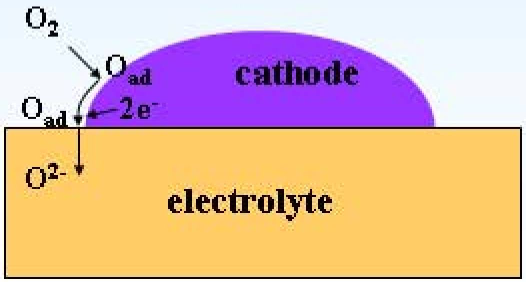
Solid Oxide Fuel Cell Cathodes

- Traditional cathodes
  - *$A^{3+}B^{3+}O_3$ perovskites*
  - *Poor O^{2-} transport*
  - *Limited reaction sites*
- Our approach
  - *High O^{2-} flux materials*
  - *Extended reaction sites*
  - *$A^{2+}B^{4+}O_3$ perovskites*

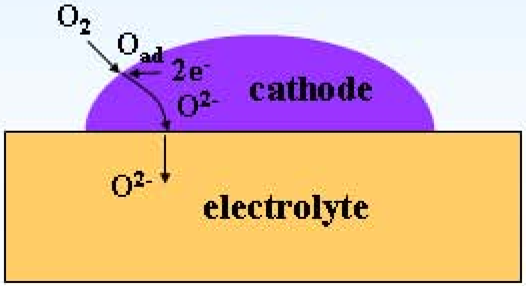
$(Ba_{0.5}Sr_{0.5})(Co_{0.8}Fe_{0.2})O_{2.3}$



'triple-point' path

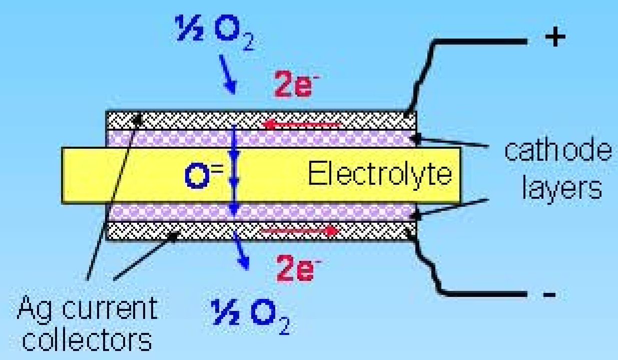


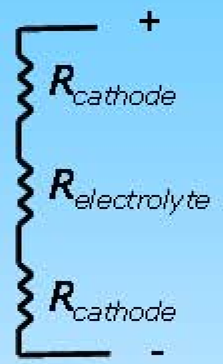
electrode bulk path



Cathode Electrocatalysis

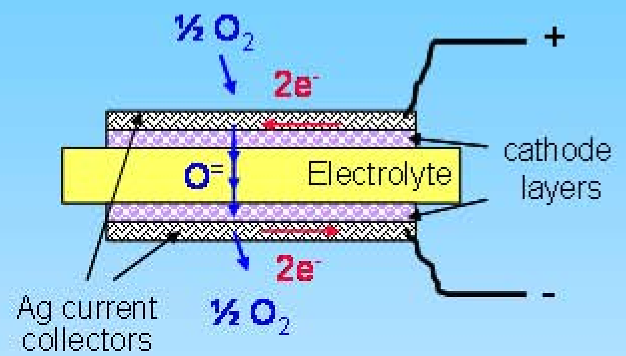
- Symmetric cell resistance measurements

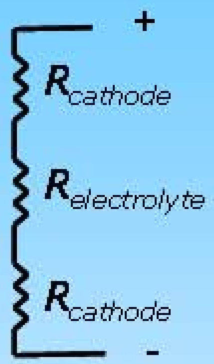




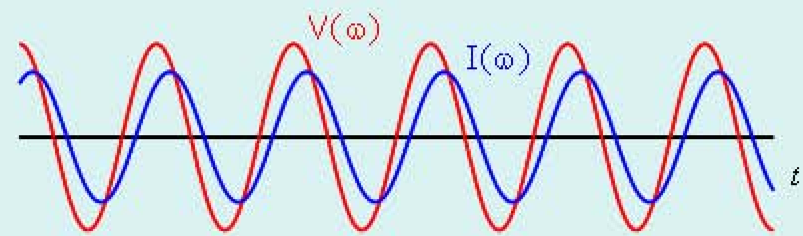
Cathode Electrocatalysis

- Symmetric cell resistance measurements





- A.C. Impedance Spectroscopy

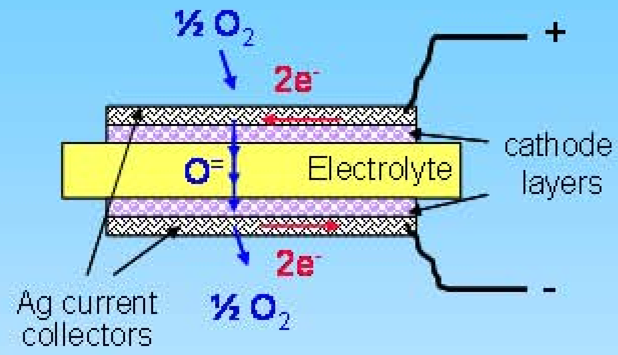


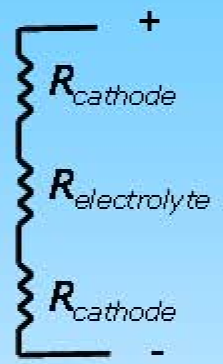
$$Z(\omega) = \frac{V(\omega)}{I(\omega)} = |Z|e^{-i\phi(\omega)t} = Z_r(\omega) + iZ_i(\omega)$$

Towards a Sustainable Energy Future

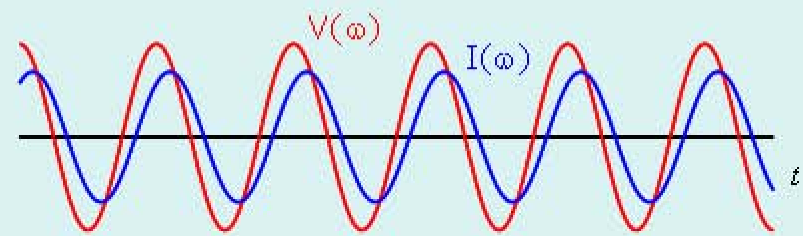
Cathode Electrocatalysis

- Symmetric cell resistance measurements





- A.C. Impedance Spectroscopy



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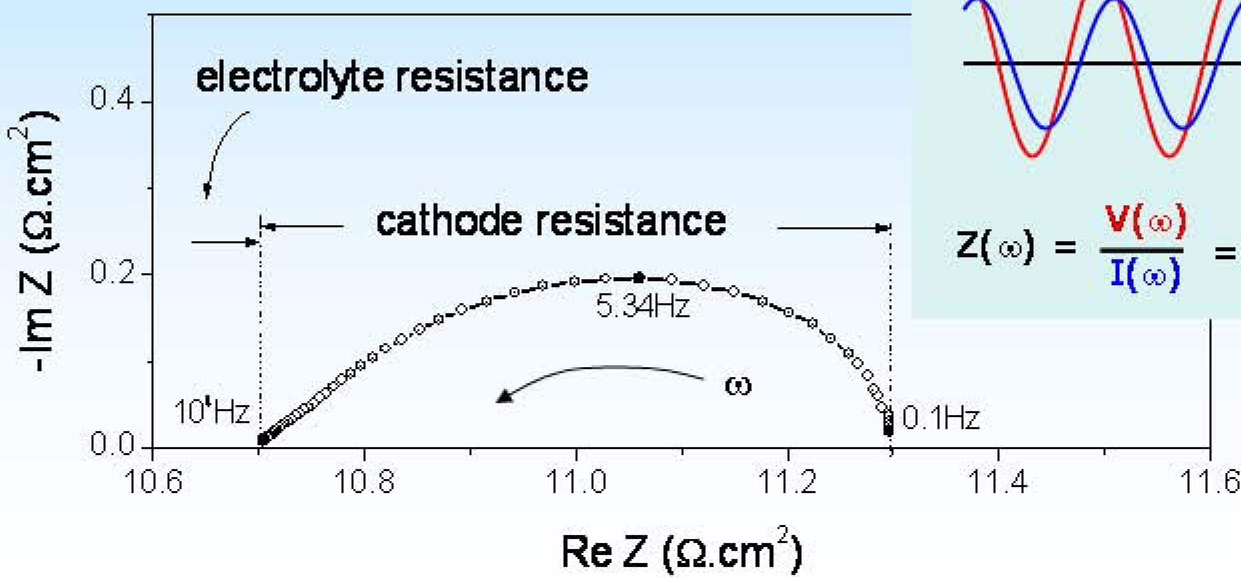
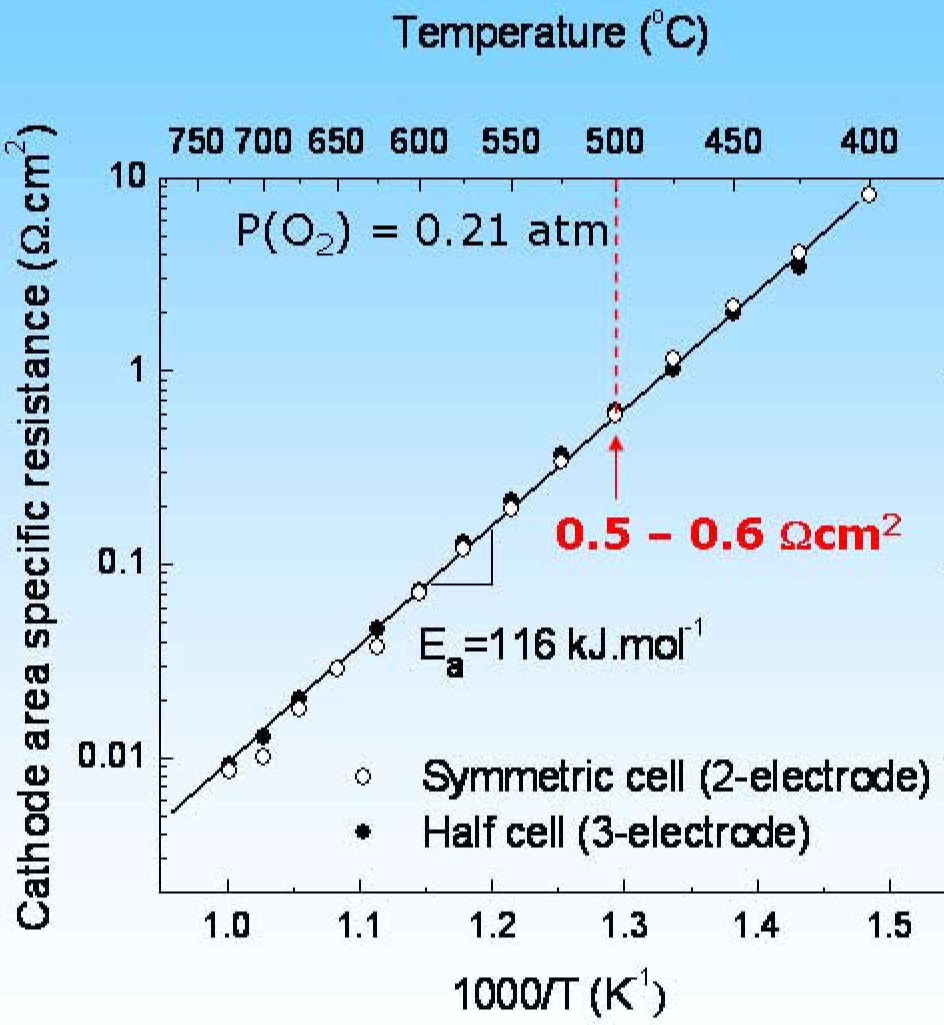
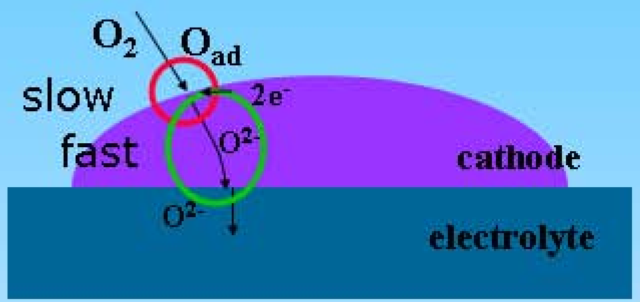


Cathode Electrocatalysis





E_a same as oxygen surface exchange (113 kJ.mol^{-1})

Bulk diffusion is fast (46 kJ.mol^{-1})

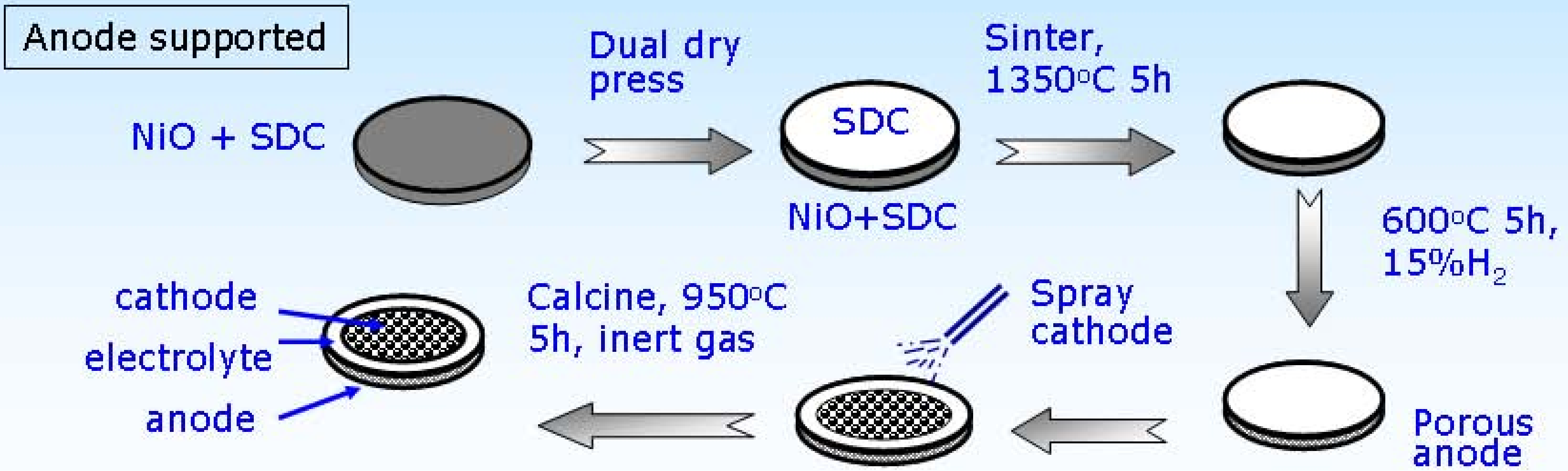
Other 'advanced' cathodes
$(PrSm)CoO_3$: 5.5 Ωcm^2
$(LaSr)(CoFe)O_3$: 48 Ωcm^2

This slide was not available

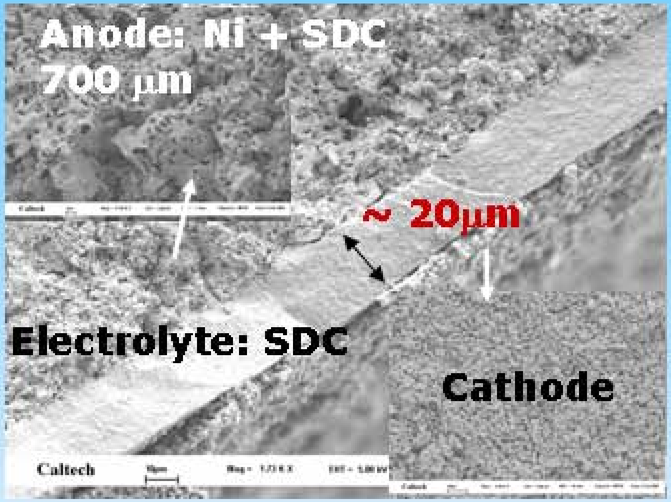
Fuel Cell Realization

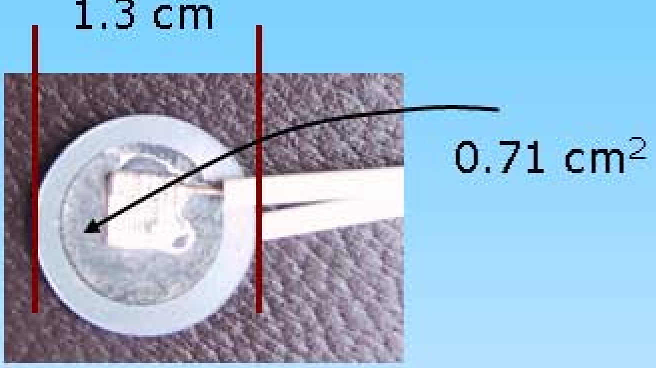
Component	Material
Electrolyte	Sm-CeO_2 [SDC]
Anode	SDC-NiO [SDC-Ni]
Cathode	Many types

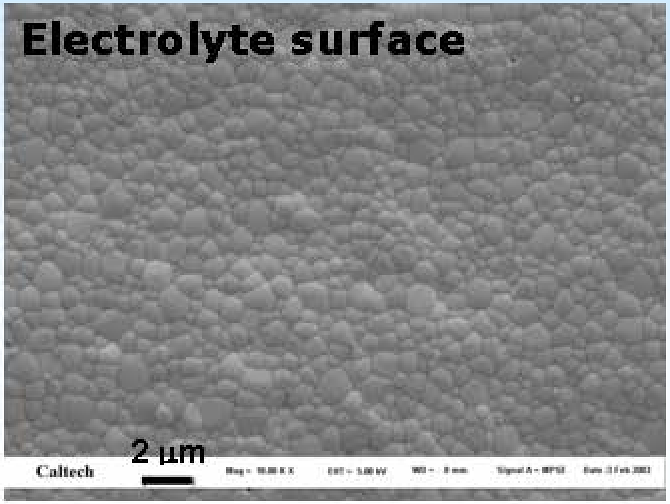
- Characteristics
  - *Anode supported, thin electrolyte*
  - *Careful matching of sintering rates*
  - *Bilayer suited to cathode screening*

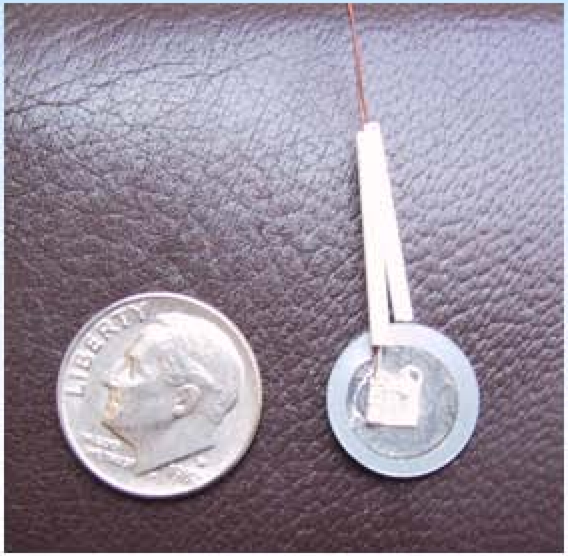


Typical Fuel Cell Structures

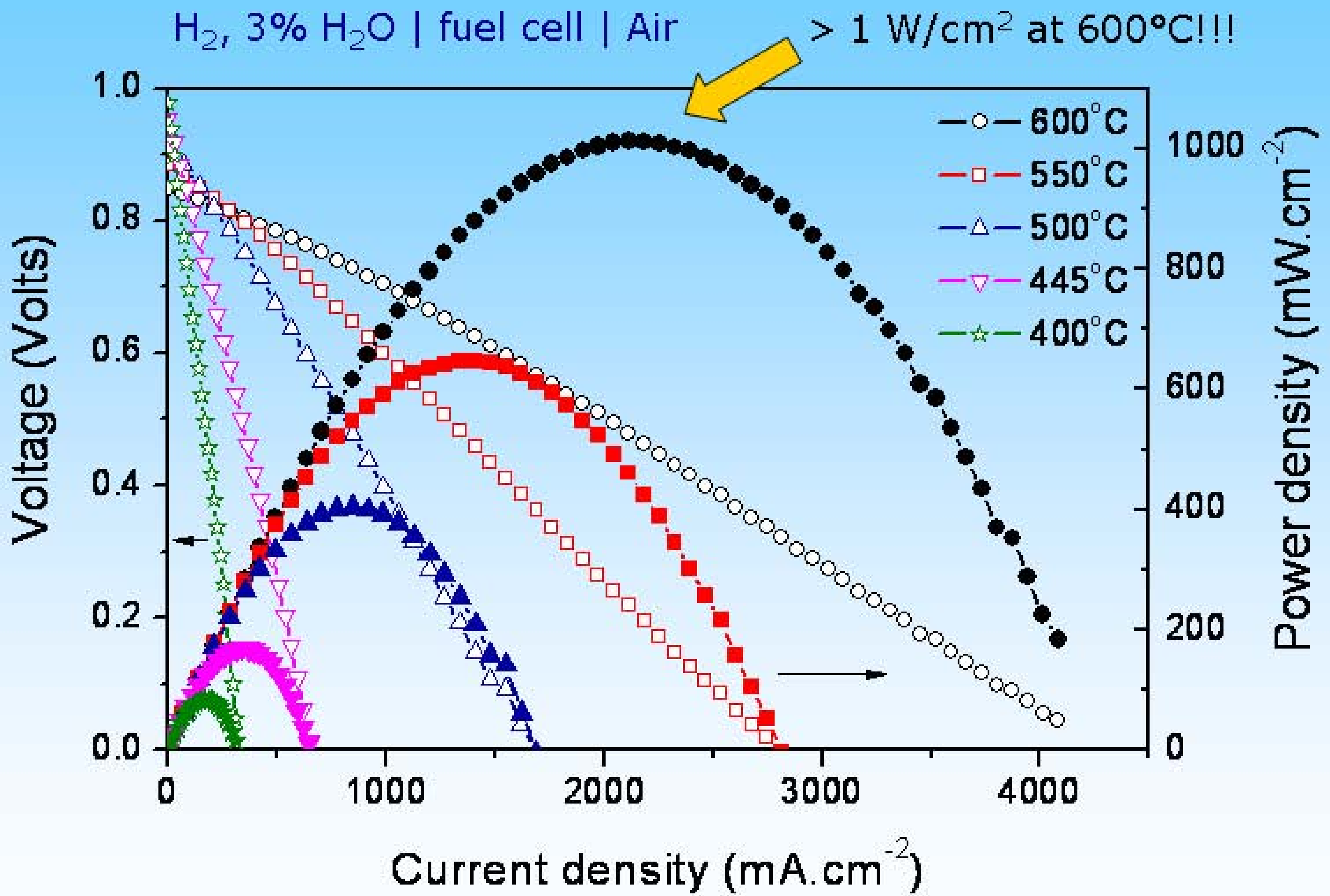








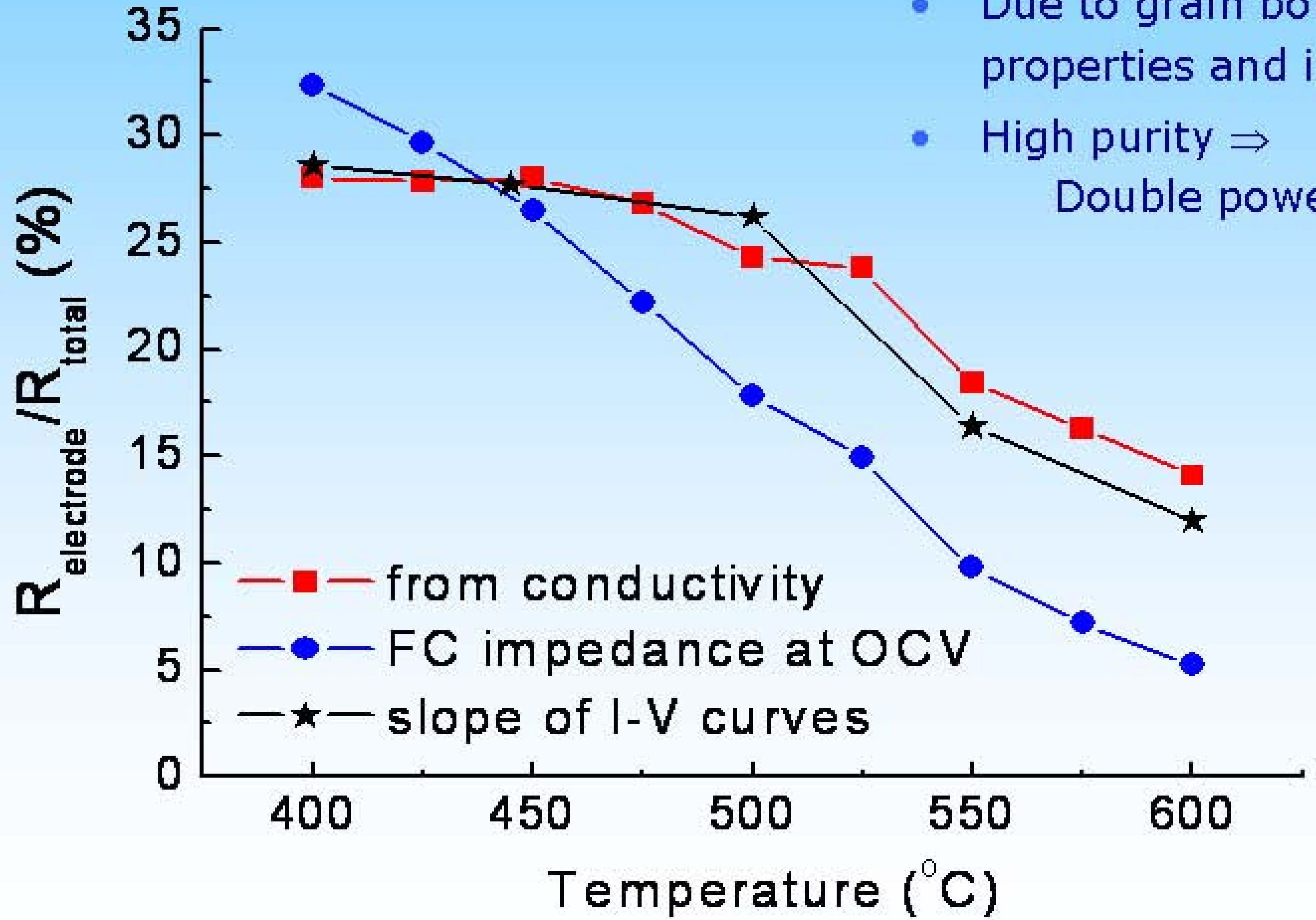
Fuel Cell Power Output



Comparison: literature cathode material ⇒ 350 mW/cm^2 at 600°C

Sources of Polarization Losses

Electrolyte contributes 85-95% of polarization losses at 600°C!



- Due to grain boundary properties and impurities
- High purity ⇒ Double power densities

Impact

Z. Shao and S. M. Haile, "A High Performance Cathode for the Next Generation Solid-Oxide Fuel Cells," *Nature* **431**, 170-173 (2004).

Cooler Material Boosts Fuel Cells

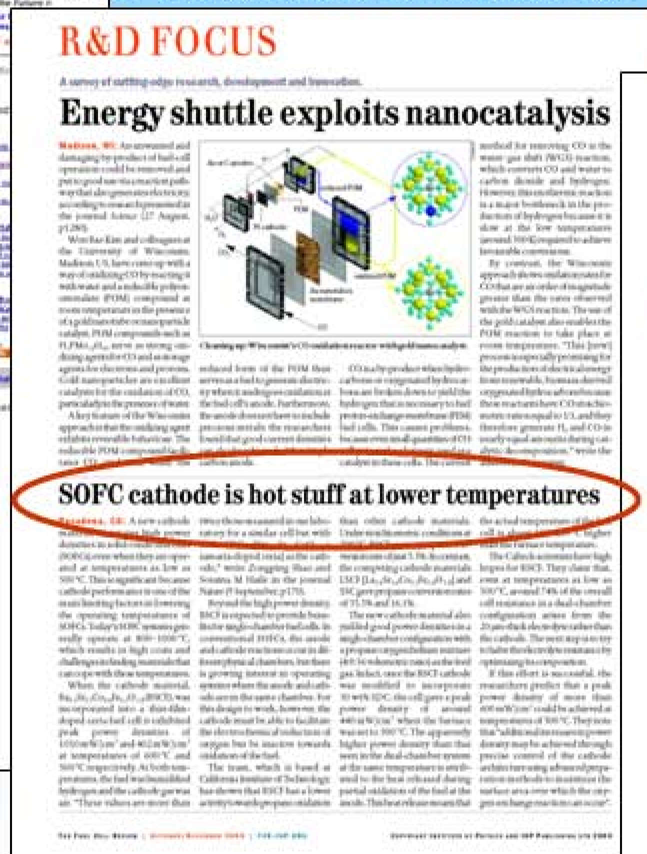

TRN

The Latest Technology Research News

Cooler material boosts fuel cells

Tech Research News

SOFC cathode is hot stuff…

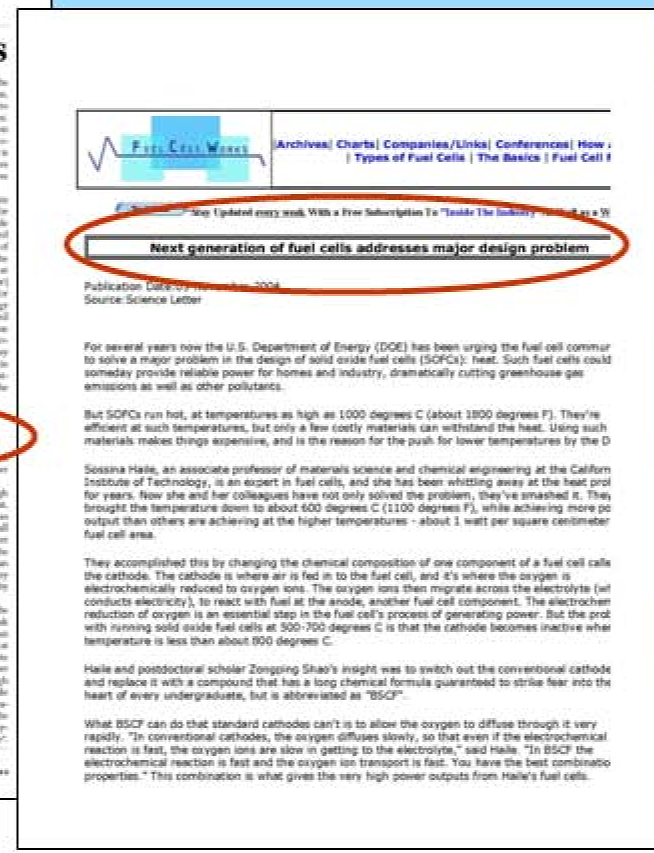

R&D FOCUS

Energy shuttle exploits nanocatalysis

SOFC cathode is hot stuff at lower temperatures

R & D Focus

Next generation of fuel cells…


Next generation of fuel cells addresses major design problem

Fuel Cell Works

Summary & Conclusions

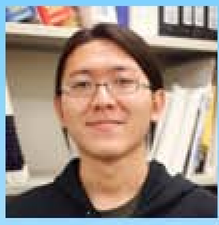
- Sustainable energy is the 'grand challenge' of the 21st century
  - *Solutions must meet the need, not the hype*
  - *Fuel cells can play an important role*
- Solid acid fuel cells
  - *Radical alternatives to state-of-the-art*
  - *Viability demonstrated; spin-off company established*
- Solid oxide fuel cells
  - *Promising alternative cathode discovered*
- Still plenty of need for fundamental research

"The stone age didn't end because we ran out of stones."

-*Anonymous*

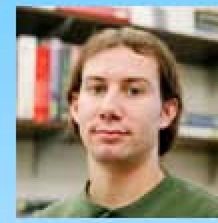
The People

- Current Students

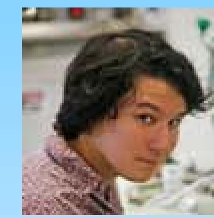

Chatr


Ayako


Mary

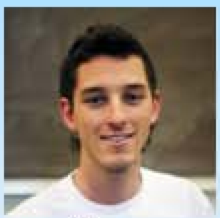

Drew


Mikhail

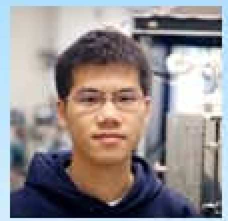

Kenji


Justin


Áron

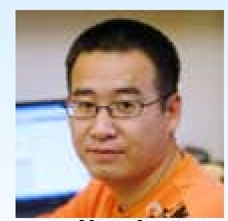

Evan

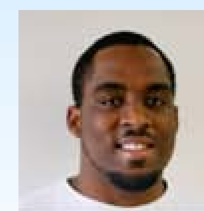

Tae-Sik

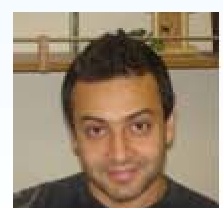

William

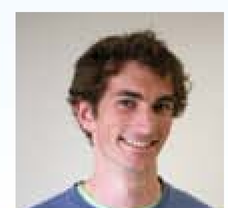
- Current Post-docs


Yoshi


Jianhua

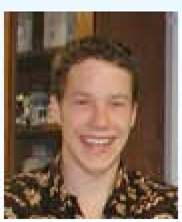

Marion


Ali


Eric


Teruyuki

- Former, who contributed to results


Calum


Tetsuya


Dane


Zongping


Wei