Hydrocarbon fueled solid oxide fuel cells

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Energy Materials
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Overview

- SOFC operation
- SOFC fuels
  - Hydrogen
  - Methane/ natural gas
- Anode requirements
- Hydrocarbon operation
- Current strategies
- Conclusions

SOFC Operation

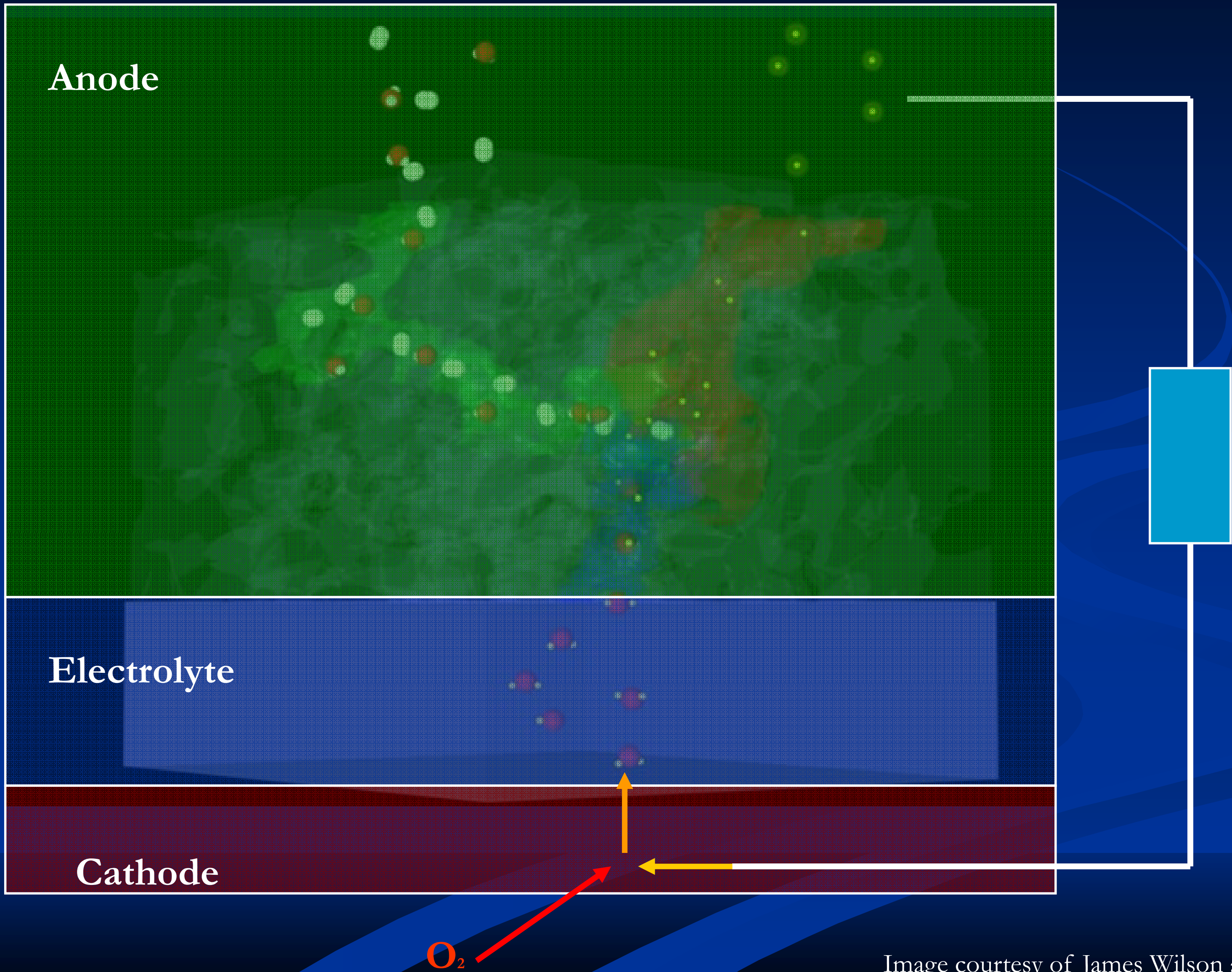
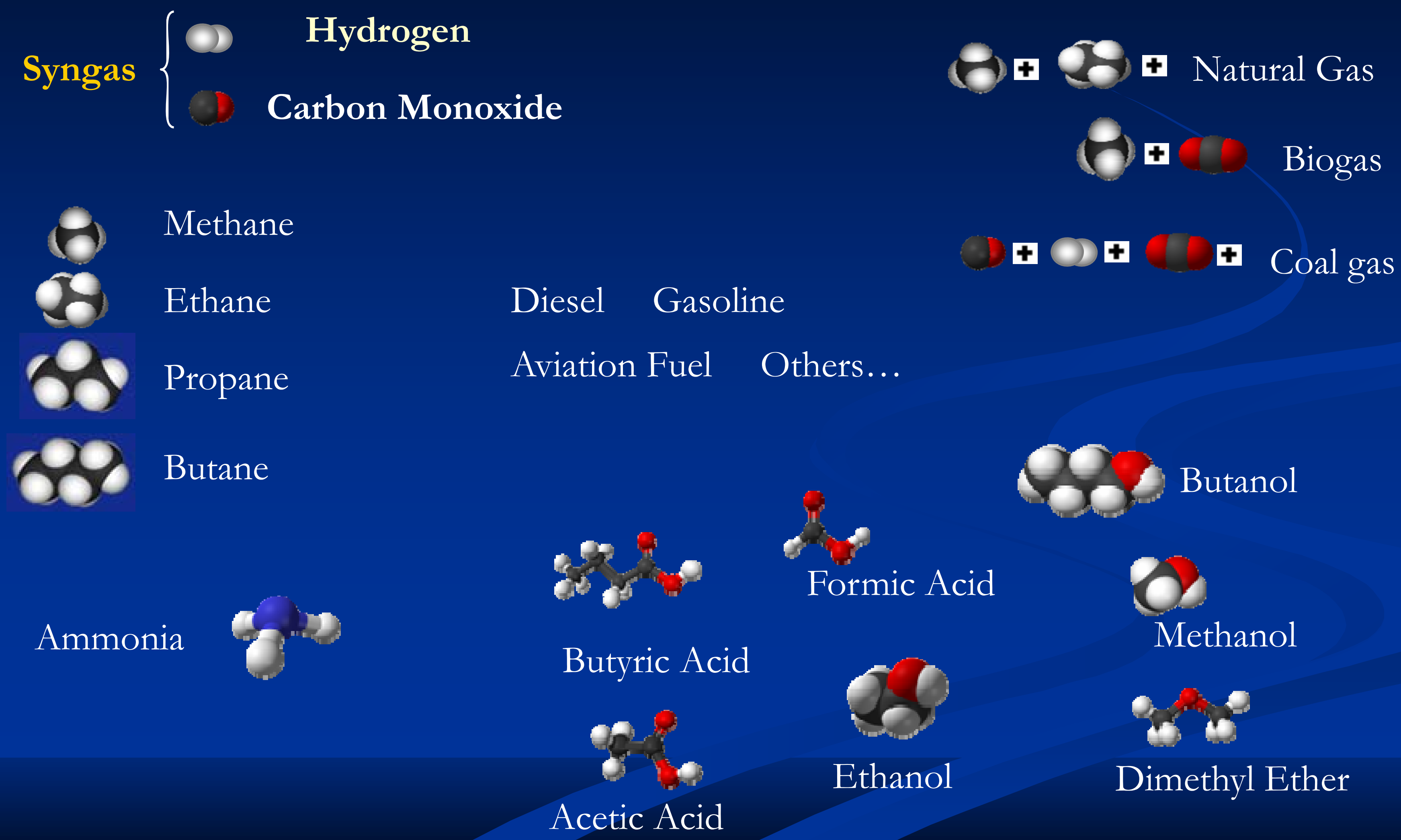


Image courtesy of James Wilson and Mark Seniw

SOFC Fuels



Syngas
Hydrogen
Carbon Monoxide
Natural Gas
Biogas
Coal gas
Methane
Ethane
Propane
Butane
Diesel
Gasoline
Aviation Fuel
Others…
Butanol
Formic Acid
Methanol
Ammonia
Butyric Acid
Ethanol
Dimethyl Ether
Acetic Acid

Hydrogen

from Bossel et al.- "The future of the hydrogen economy: bright or bleak?"

- Production
  - Electrolysis ~33% HHV
  - Steam reforming ~10% HHV
- Hydrogen compression (20MPa) >8%HHV
  - Thorough accounting ~40% HHV
- Hydrogen delivery
  - Pipeline (500km) ~7% HHV
  - Truck (100km) ~6% HHV

Hydrogen vs Liquid HC

Energy consumed for road transport of various fuels and hydrogen.

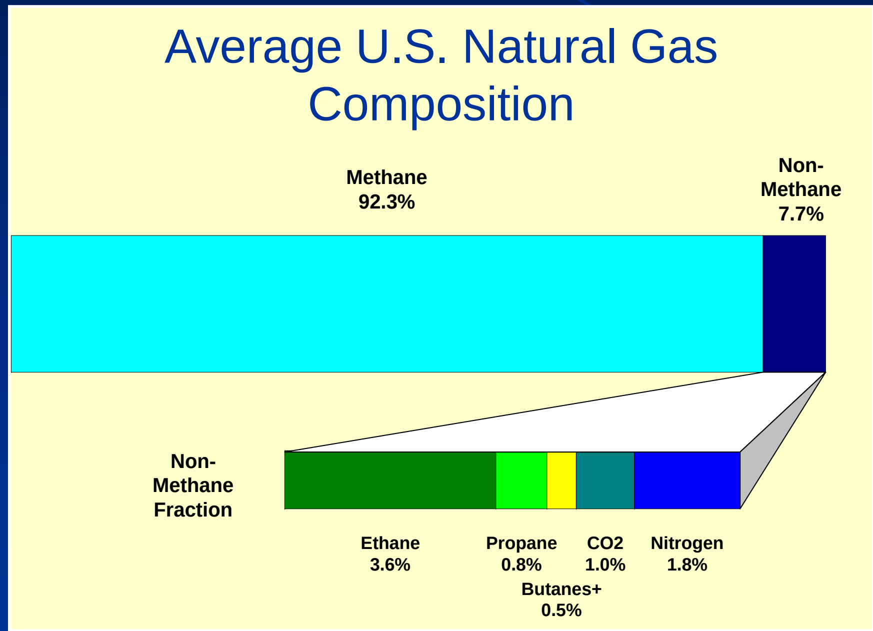
	Units	H_2 Gas	H_2 liquid	Methanol	Ethanol	Propane	Gasoline
Pressure	MPa	20	0.1	0.1	0.1	0.5	0.1
Weight to customer	kg	40,000	30,000	40,000	40,000	40,000	40,000
Weight from customer	kg	39,600	27,900	14,000	14,000	20,000	14,000
Delivered weight	kg	400	2,100	26,000	26,000	20,000	26,000
HHV of delivered fuel	MJ/kg	141.9	141.9	23.3	29.7	50.4	48.1
HHV energy per truck	GJ	57	298	580	771	1007	1252
Relative to gasoline	-	0.045	0.238	0.464	0.616	0.805	1
Diesel consumed	kg	79.6	57.9	54	54	60	54
Diesel HHV energy	GJ	3.56	2.59	2.41	2.41	2.68	2.41
IC engine vehicles:							
Energy consumed to HHV energy delivered	%	6.27	0.87	0.42	0.31	0.27	0.19
Relative to gasoline	-	32.5	4.5	2.2	1.6	1.4	1
No. of trucks for same no. of serviced cars	-	22.0	4.1	2.2	1.6	1.4	1
Fuel cell vehicles:							
H2-efficiency factor	-	0.7	0.7	1	1	1	1
HHV energy delivered	GJ/d	876	876	1252	1252	1252	1252
No. of trucks for same no. of serviced cars	-	15.4	2.9	2.2	1.62	1.24	1

Figure is from: Bossel, U., B. Eliasson, and G. Taylor, eds. *The future of the hydrogen economy: bright or bleak?* Vol. E08. 2003, European Fuel Cell Forum.

Natural Gas/Methane

- CHEAP and abundant
- Established delivery & storage infrastructure

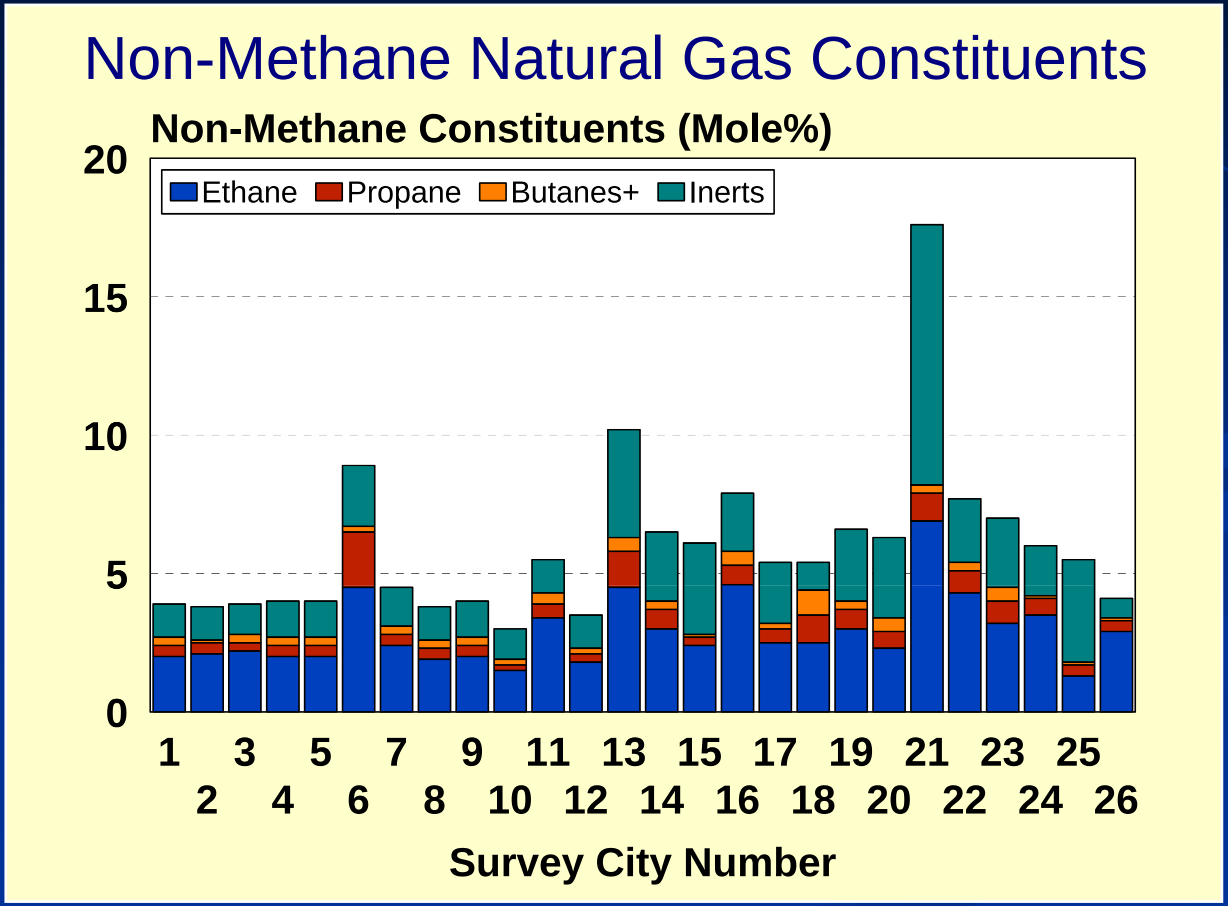
- Variable composition
- Added odorants
  - ~5ppm sulfur compounds



Source: Gas Technology Institute

Figure is from: "Natural Gas composition and Quality"
www.energy.ca.gov/.../documents/2005-02-17+18_workshop/presentations/GTI_rue_liss_pan_1_2005.ppt

Natural Gas/Methane- Composition



Source: Gas Technology Institute

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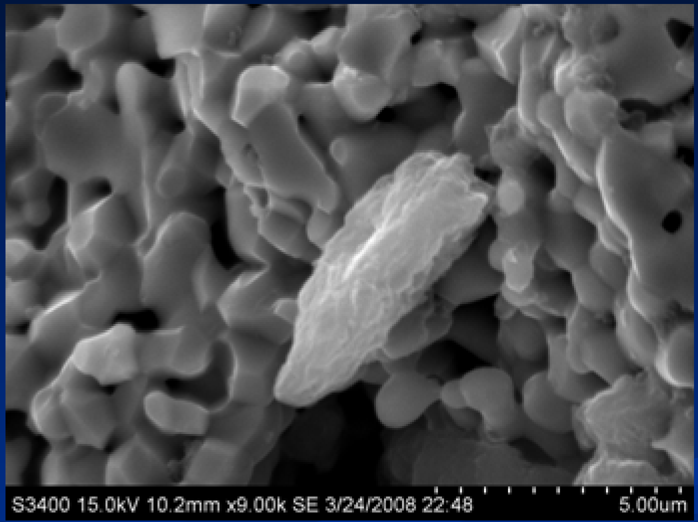
www.energy.ca.gov/.../documents/2005-02-17+18_workshop/presentations/GTI_rue_liss_pan_1_2005.ppt

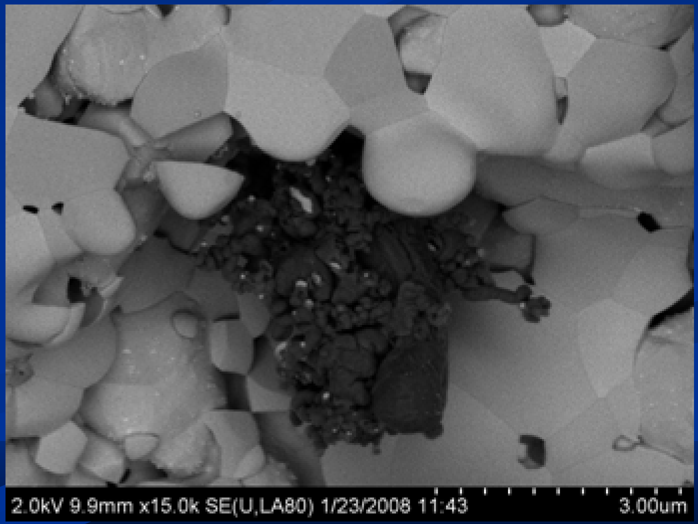
Anode Requirements

- Basic (hydrogen):
  - Electronic and ionic pathways
  - Porous
  - TEC compatibility
  - Chemical stability

  Ni-YSZ satisfies requirements
- Hydrocarbon req.:
  - Activity for HC oxidation
  - Low activity for HC pyrolysis
  - Stabile in impurities

  Ni-YSZ is not sulfur tolerant and has high activity for pyrolysis





Problem

- Hydrocarbons are excellent energy carriers
- Hydrogen is a poor energy carrier
- Hydrogen is best SOFC fuel
  - Anode requirements increase substantially for other fuels

Solution

- Reform natural gas, then operate on H_2 generated

Strategies: External Reforming

External Reformer (Autothermal)

$$C_nH_{2n+2} + nH_2O \rightarrow nCO + (2n+1)H_2$$

$$C_nH_{2n+2} + n/2\,O_2 \rightarrow nCO + (n+1)H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

Hydrocarbon, H_2O, O_2 or CO_2 → External Reformer → Syngas → SOFC → H_2O and CO_2

- Utilize advantages of hydrocarbons and hydrogen
- Increased balance of plant costs

$C_nH_{2n+2} + nH_2O \rightarrow nCO + (2n+1)H_2$

Strategies: Internal Reforming

Hydrocarbon

H_2O, O_2 or CO_2

SOFC

$$C_nH_{2n+2} + nH_2O \rightarrow nCO + (2n+1)H_2$$

$$C_nH_{2n+2} + n/2\,O_2 \rightarrow nCO + (n+1)H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

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

H_2O and CO_2

- Large thermal gradients
- System cost and complexity are greatly reduced
- Energy loss from heat transport avoided

$C_nH_{2n+2} + (3n+1)O^{2-} \rightarrow nCO_2 + (n+1)H_2O + 2(3n+1)e^-$

Strategies: Direct Oxidation

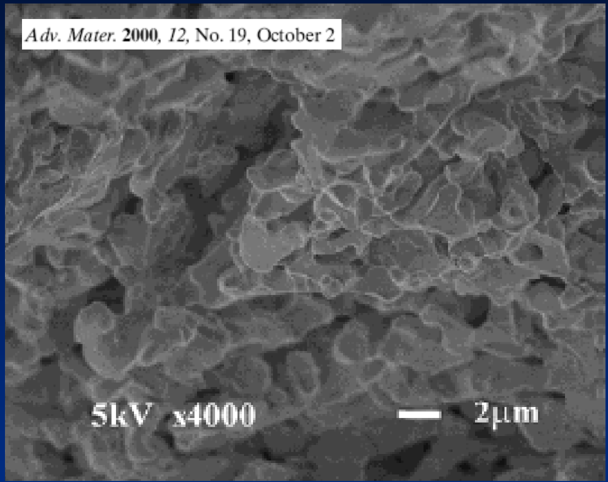
Hydrocarbon → **SOFC** → **H_2O and CO_2**

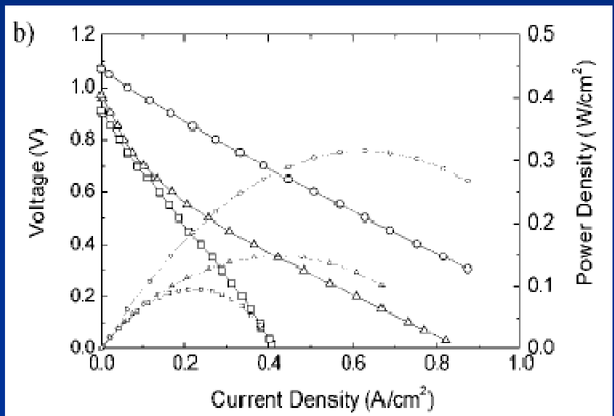
$$C_nH_{2n+2} + (3n+1)O^{2-} \rightarrow nCO_2 + (n+1)H_2O + 2(3n+1)e^-$$

- No added reformate- the fuel stream is not diluted and the cell voltage is not reduced
- Large thermal gradients avoided
- System cost and complexity are greatly reduced
- Energy loss from heat transport avoided
- Better materials needed

Some Current Strategies

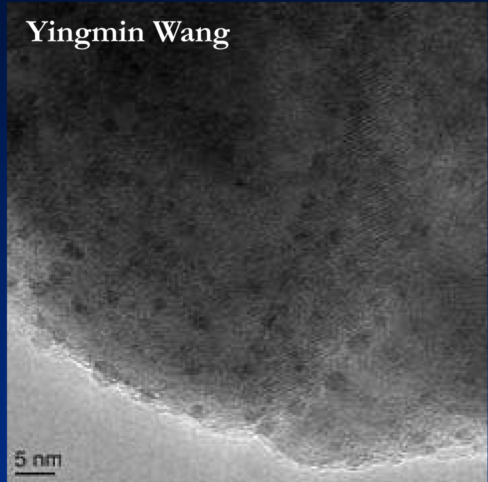
Cu -Cermet

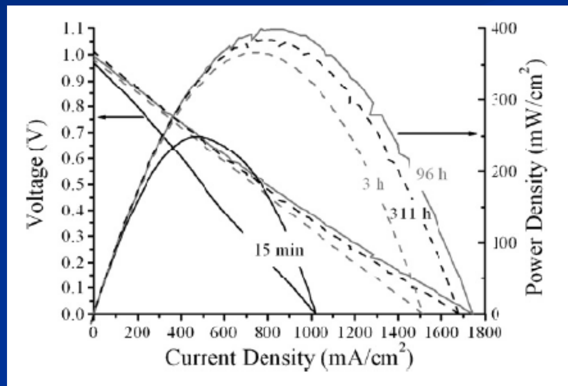




Adv. Mater. 2000, 12, No. 19, October 2

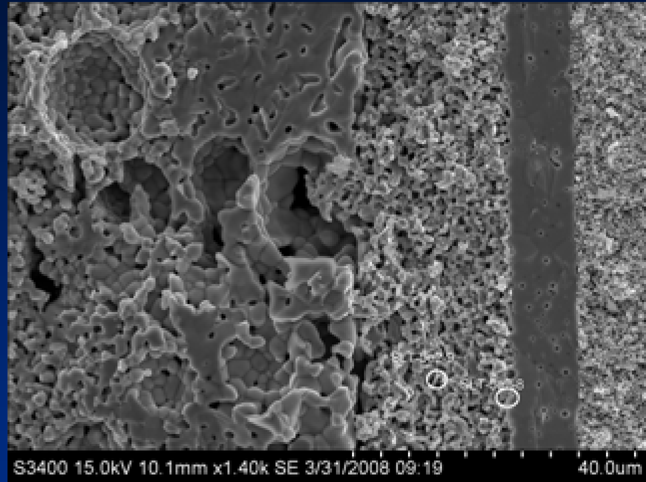
Oxide anodes

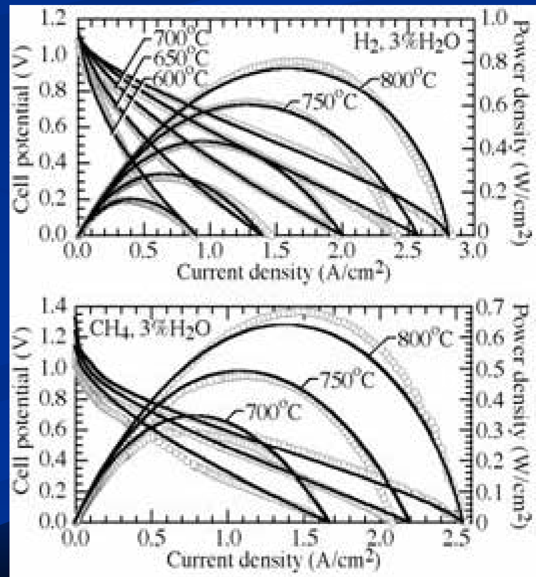




B.D. Madsen et al. / Journal of Power Sources 166 (2007) 64–67

Diffusion barrier layer





Pillai, M.R., et al., Electrochemical and Solid-State Letters (In Press), 2008.

Conclusions

- Hydrogen currently a poor energy carrier
- Natural gas a good SOFC fuel
- Most current SOFCs reform methane, operate on syngas generated
- Direct oxidation is ideal operating mode