Results of Recent High Temperature Coelectrolysis Studies at the Idaho National Laboratory

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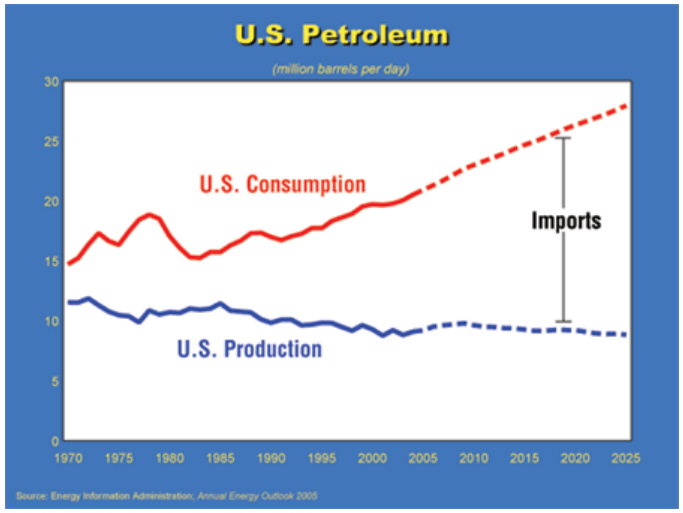
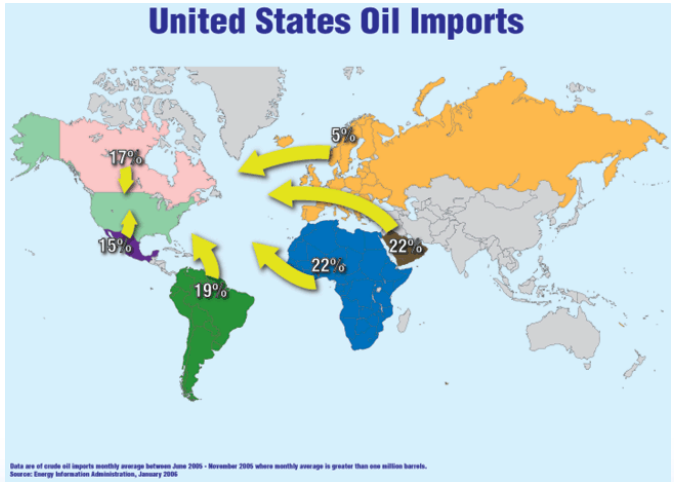
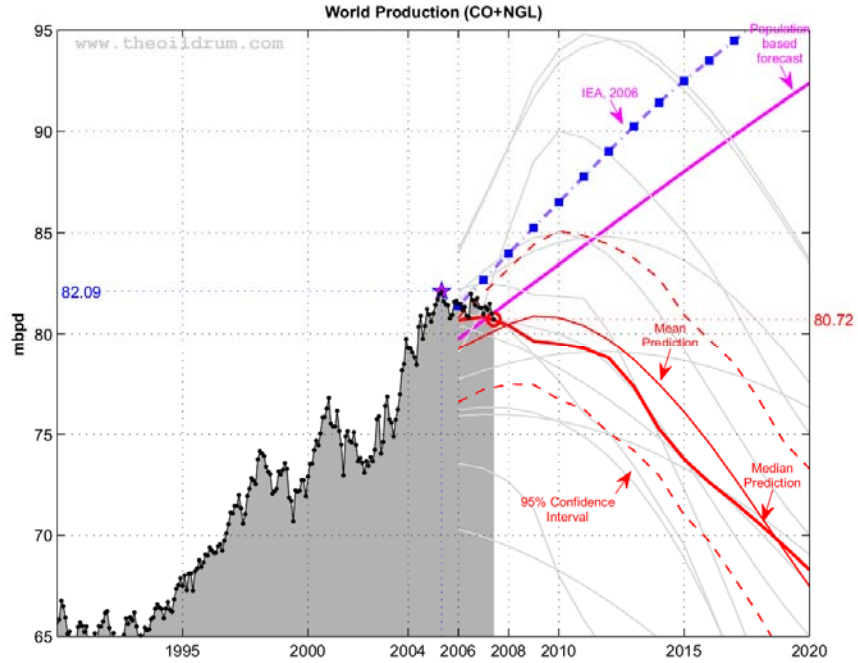
Worrisome Trends – Supply vs Demand





US Oil Consumption:

- holds ~3% of world's oil reserves
- consumes ~25% of the world's total oil output
- consumes ~3 gallons / per day per capita oil
- demand continues to increase
- 63% of oil from Middle East, North Africa, and Venezuela
- Most predictions show peak in world oil production ~2010



www.theoildrum.com, EIA

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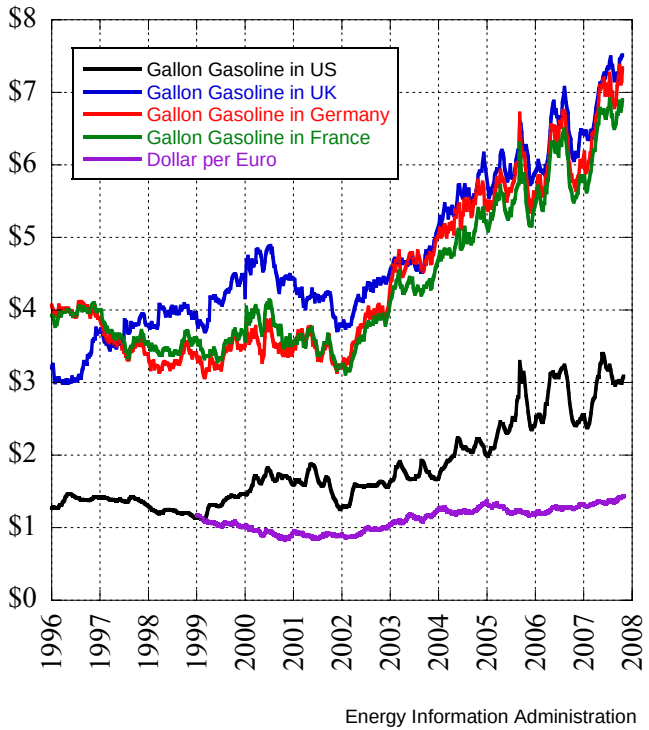
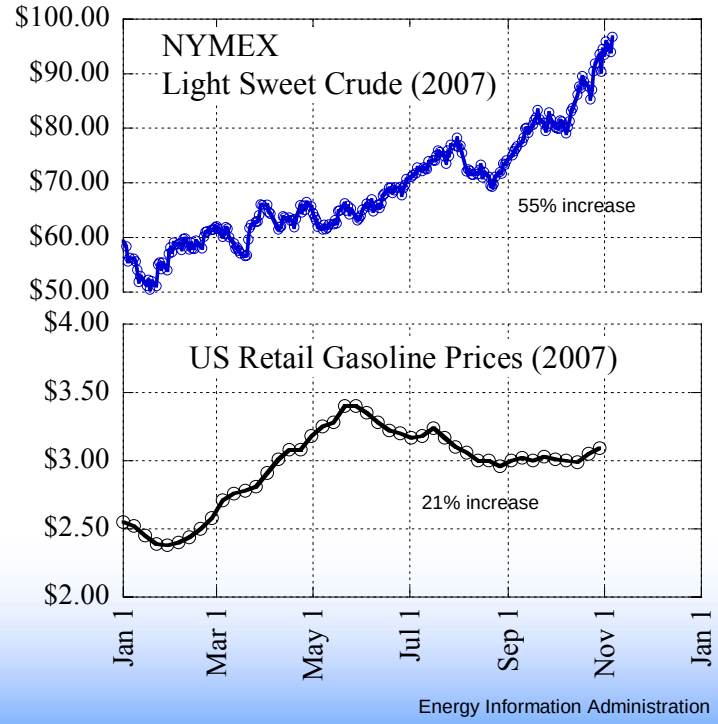
Worrisome Trends -- Price



- Dollar has weakened significantly
- Oil is priced in US dollars
  - weak dollar + supply risk + demand = higher oil prices
- This year:
  - oil prices up 55%
  - US gasoline prices up 21%
- Oil reached $97/barrel



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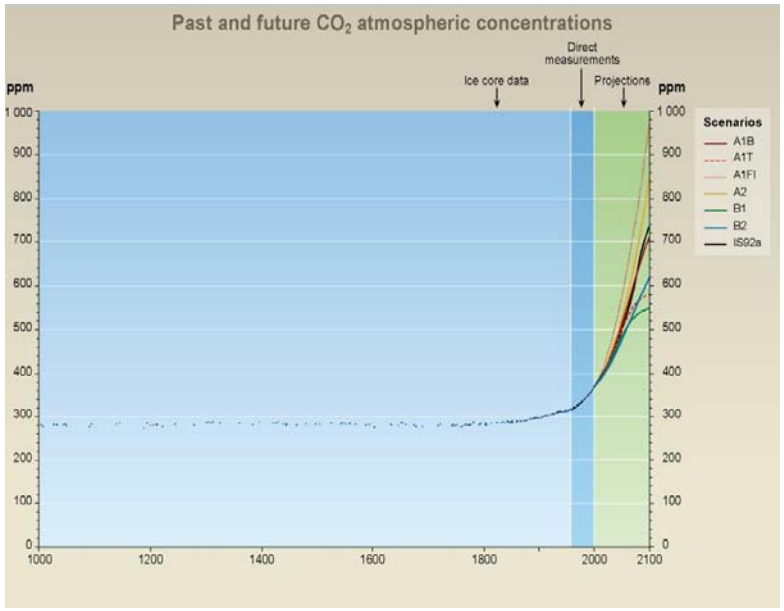
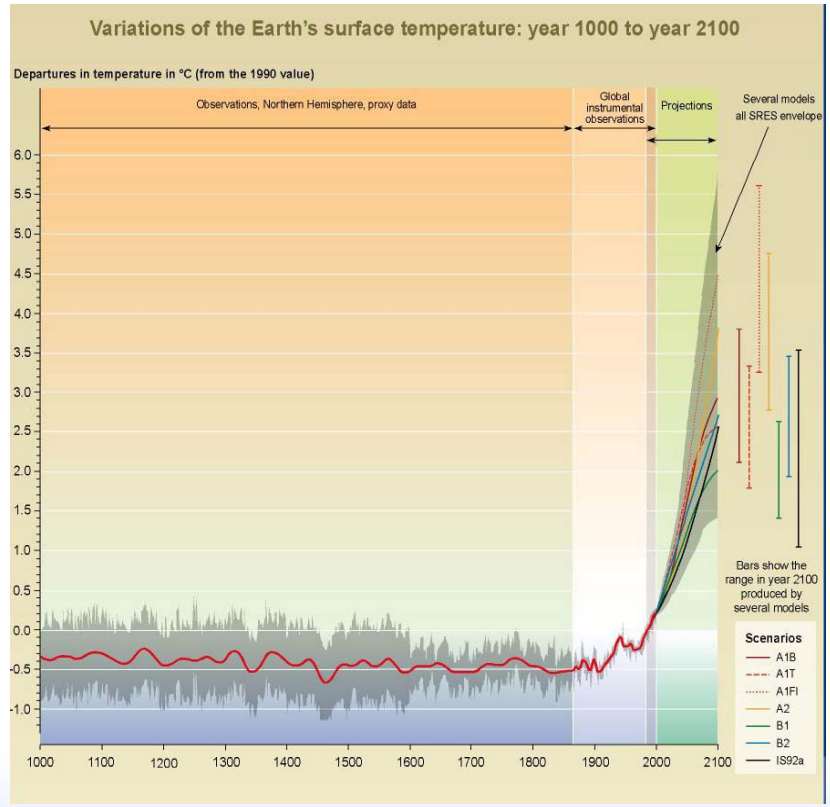
Worrisome Trends -- Greenhouse Gas Emissions & Global Warming





- Controversial issue
- CO_2 atmospheric concentrations going up
- Earth's surface temperature going up
- US produces ¼ of the world's carbon emissions

Source: Intergovernmental Panel on Climate Change

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Proposed Long Term Solution – H_2 Economy

- Hydrogen Economy - Goals
  - Reduce consumption of finite oil reserves
  - More independence from foreign oil
  - Reduce CO_2 emissions
    - Burning a gallon of gasoline produces ~20 lbs CO_2
  - Use water as the feedstock
  - Incorporate non-carbon emitting, renewable energy sources
    - Wind, solar, etc.
    - Nuclear
- Problems With Hydrogen As An Energy Carrier
  - Energy density per unit volume

	Energy Density per Unit Mass	**Energy Density per Unit Volume**
Gasoline	**13 kWh/kg**	**9.6 kWh/l**
H_2 (gas, atm. press.)	**37 kWh/kg**	**0.0034 kWh/l**

  - Filling your car at gas pump ~ 10MW
  - <u>Conversion to hydrogen economy will require decades</u>

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Interim – Retain Petroleum Infrastructure

1.) Utilize poorer quality oil sources
   - Athabasca Oil Sands (hydrogenation)
   - Requires substantial amounts of H_2

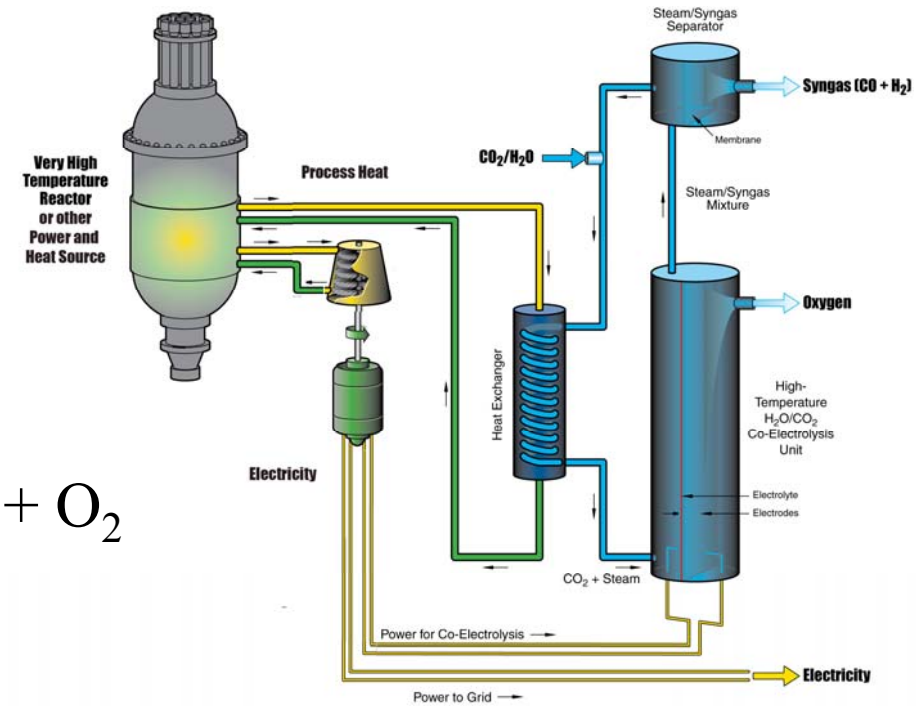
www.hydrocarbons-technology.com

2.) Synthetically produce petroleum fuels
   - i.e., Synfuels

North Dakota Gasification Great Plains Synfuels Plant
(www.netl.doe.gov)

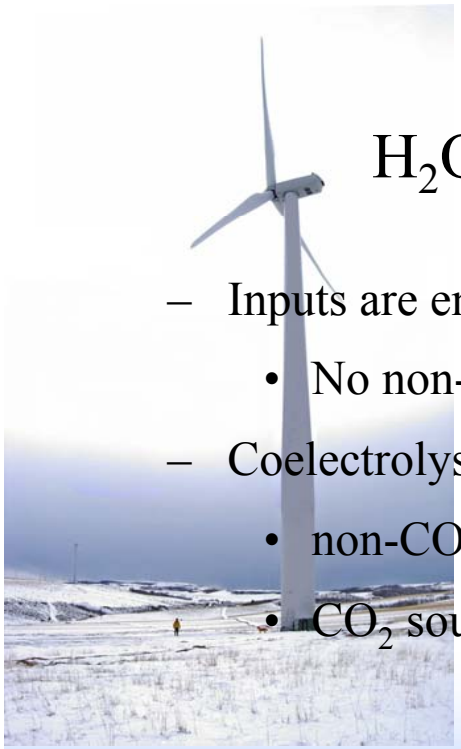
Coelectrolysis For Synfuel Production – The Answer?

- Synfuel requires Syngas (H_2 & CO)
  - Traditionally from coal
  - Increasingly produced from natural gas
- For coelectrolysis:



$$H_2O + CO_2 \xrightarrow{\text{electricity, heat}} H_2 + CO + O_2$$

Syngas



  - Inputs are energy, H_2O, and CO_2
    - No non-renewables such as natural gas
  - Coelectrolysis syngas production to synfuel utilization can be carbon-neutral if:
    - non-CO_2 emitting energy source is used (nuclear, wind, etc.)
    - CO_2 source is from biomass

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Coelectrolysis Is More Complex Than Steam Electrolysis

- Chemistry is more complicated due to multiple reactions
  - Steam electrolysis
  - CO_2 electrolysis
  - Reverse Shift Reaction (RSR)

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$

- CO electrolysis

$$CO \rightarrow C + \tfrac{1}{2} O_2$$

  - If cell potential is high enough
- Possible material compatibility issues
  - Corrosion
  - Seal leakage

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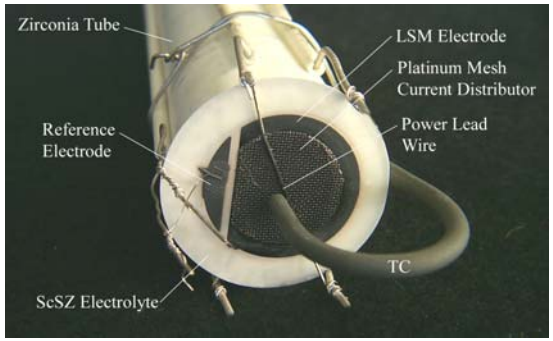
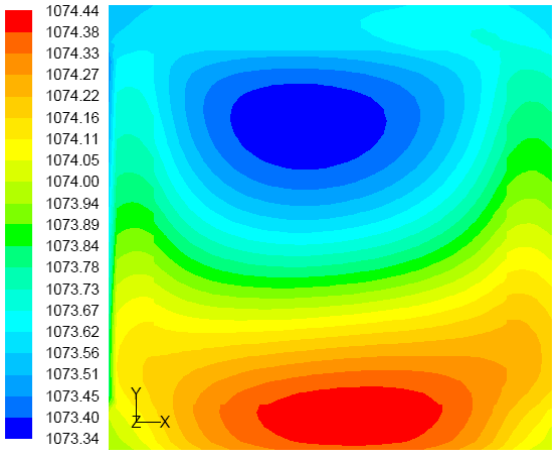
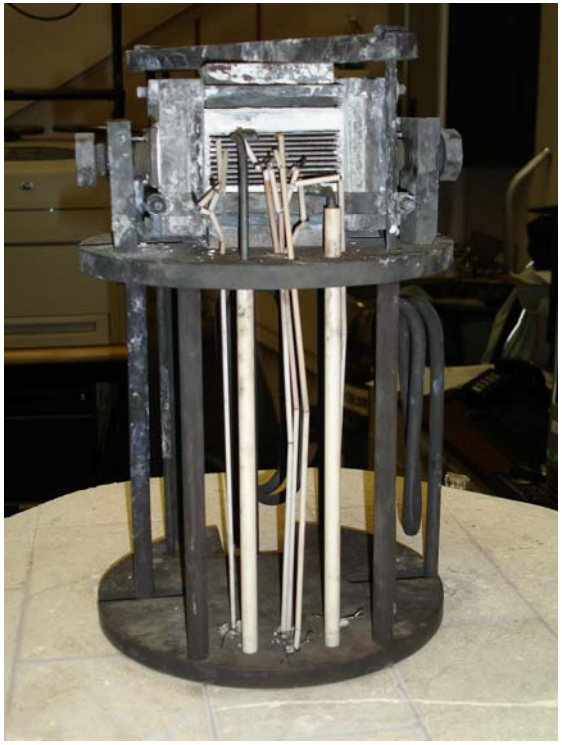
INL Coelectrolysis Activities



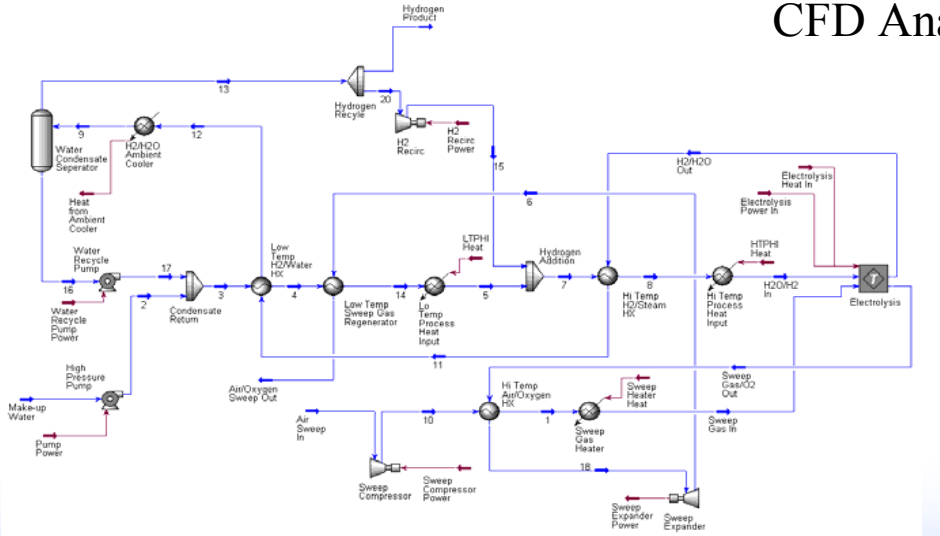
Button Cell



CFD Analysis



Stack Testing



Process Flowsheet Analysis

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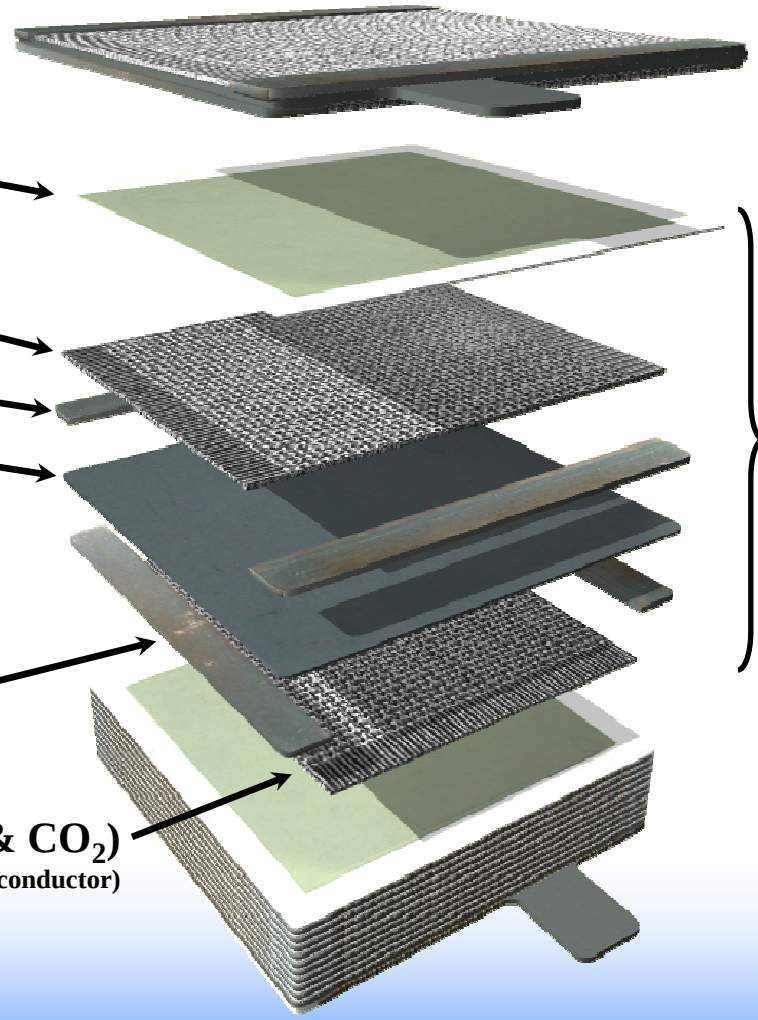
Ceramatec Electrolysis Stack



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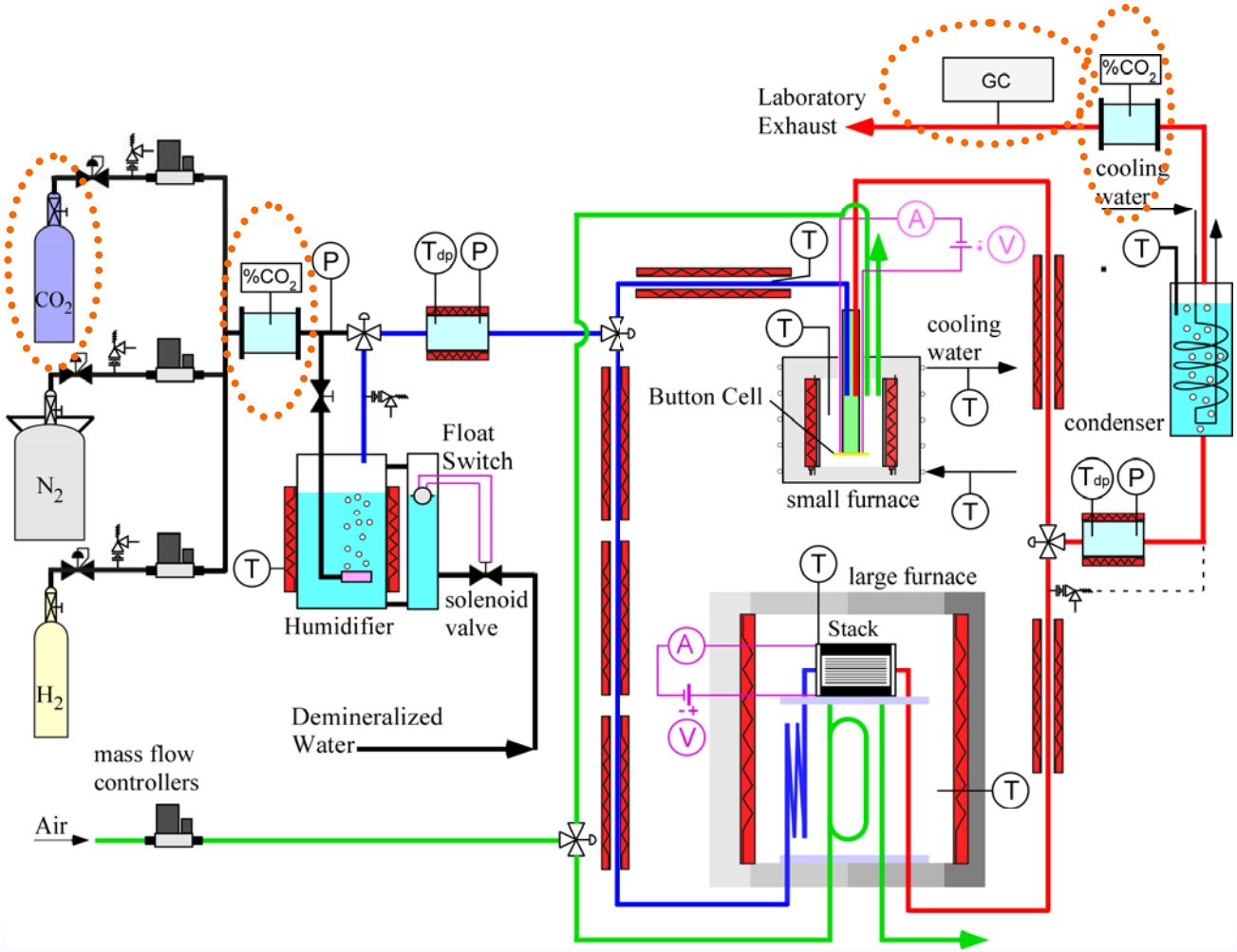
Coelectrolysis Experimental Apparatus



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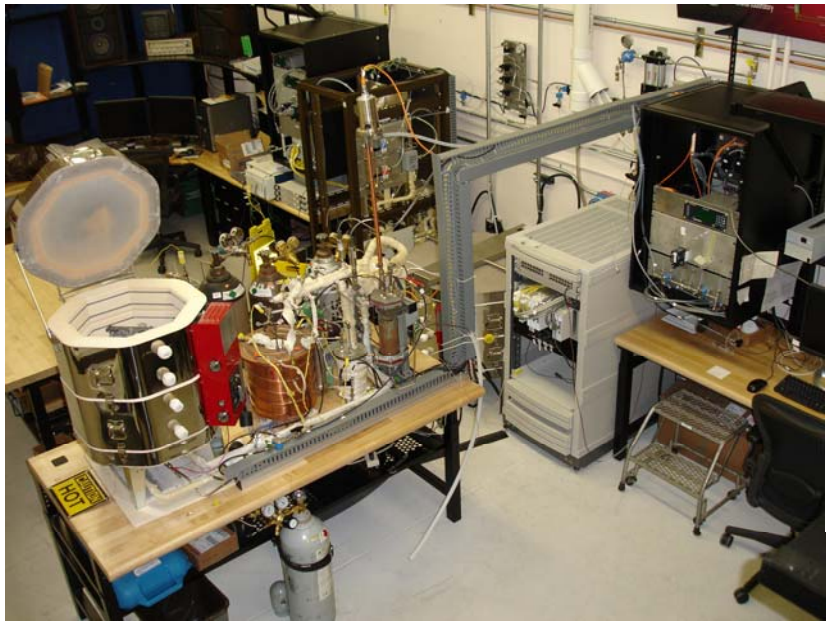
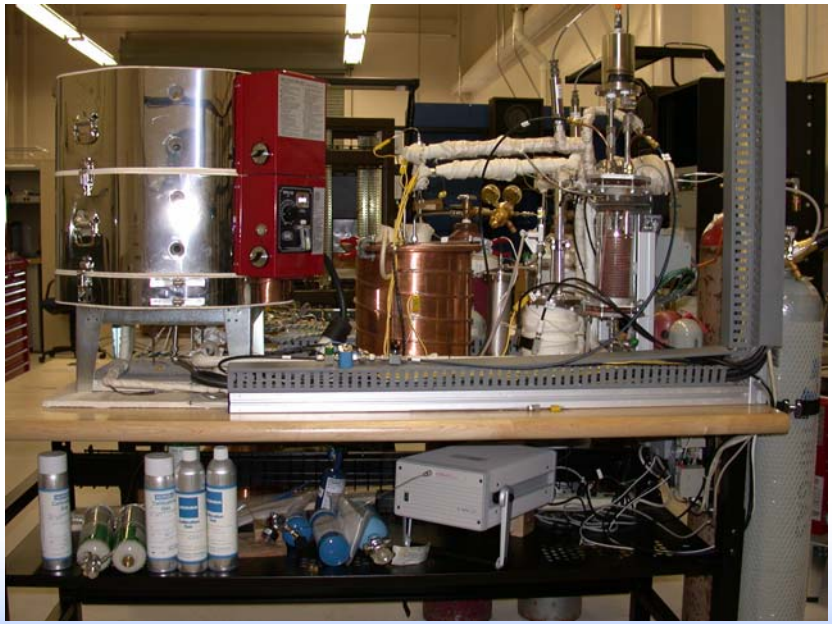
INL Coelectrolysis Experiment





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INL Computer Modeling Efforts

- 3-Dimensional CFD (FLUENT)
- In-house Coelectrolysis Chemical Equilibrium Model
- Systems Modeling Using UniSim

- These models are discussed by next speaker

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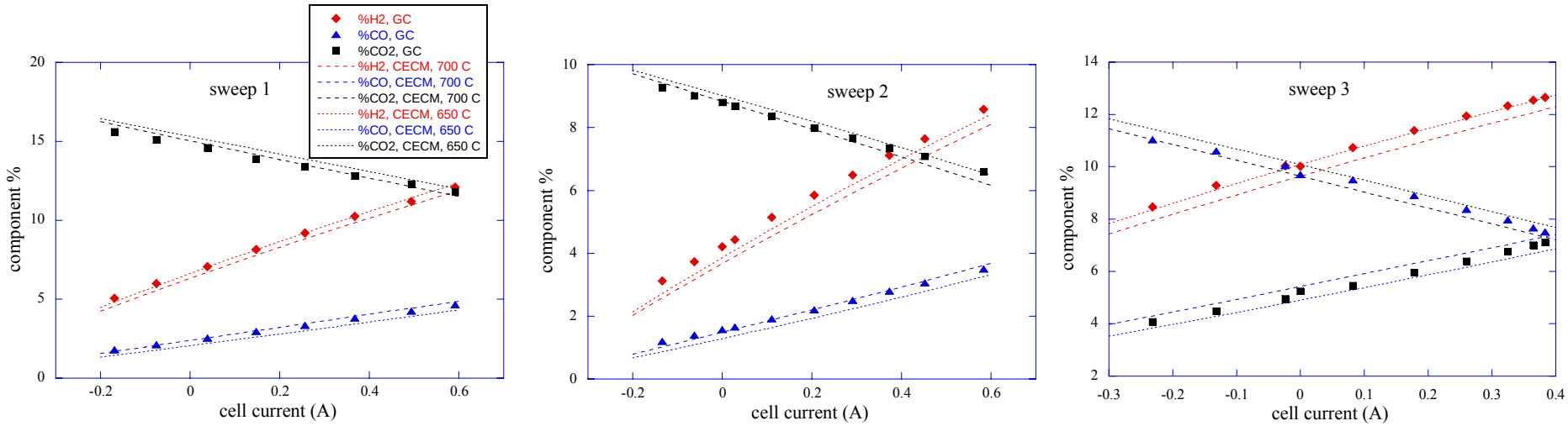
Chemical Equilibrium Model / Button Cell GC Data Comparison



- For coelectrolysis:
  - CO_2 and H_2O (not shown) decrease
  - H_2 and CO increase
- good agreement between model and data

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10-Cell Stack Experimental Matrix

Test #	Stack #	Sweep Type	Stack Age	$T_{furnace}$ (C)	Flow Rates			Inlet Dew Point (C)	Molar Composition			
					H_2 (sccm)	CO_2 (sccm)	N_2 (sccm)		H_2 (mol %)	CO_2 (mol %)	N_2 (mol %)	H_2O (mol %)
0	1	Fast	Fresh	800	497	0	3010	51.5	12	0	72.6	15.4
1	1	Fast	Fresh	800	497	605	3010	51.5	10.2	12.4	61.9	15.5
2	1	Slow	Fresh	800	497	605	3010	51.5	10.2	12.4	61.9	15.5
3	1	Slow	Fresh	800	497	505	2510	45.5	12.6	12.7	63.3	11.4
4	1	Slow	Fresh	800	497	705	1010	66	15.6	22.2	31.8	30.4
5	1	Slow	Fresh	800	497	756	3010	74	6.7	10.1	40.2	43
6	1	Slow	Fresh	828	497	605	3011	51.5	10.2	12.4	61.9	15.5
7	1	Slow	Fresh	828	497	756	3513	65.3	7.3	11.2	52	29.5
8	2	Fast	Fresh	800	450	0	1413	75.3	13.2	0	41.4	45.4
9	2	Fast	Fresh	800	449	753	1414	59.8	13.2	22.2	41.6	23
10	2	Fast	Fresh	800	334	564	1064	59.7	13.1	22.2	41.8	22.9
11	2	Fast	Fresh	800	213	378	710	60.7	12.4	22.1	41.5	24
12	2	Slow	1 Week	800	449	753	1414	59.8	13.2	22.2	41.6	23
13	2	Slow	1 Week	800	334	564	1064	59.7	13.1	22.2	41.8	22.9
14	2	Slow	1 Week	800	213	378	710	60.7	12.4	22.1	41.5	24
15	2	Slow	1 Week	830	497	756	3513	65.3	7.4	11.2	52	29.4
16	2	Slow	2 Weeks	800	450	752	1410	60.3	13.2	22	41.3	23.5
17	2	Slow	2 Weeks	800	334	564	1064	60.2	13	22	41.5	23.5
18	2	Slow	2 Weeks	800	213	378	710	60.7	12.4	22.1	41.5	24
19	2	Slow	2 Weeks	830	497	756	3513	65.3	7.4	11.2	52	29.4
20	3	Fast	Fresh	800	996	0	1009	80	22.5	0	22.7	54.8
21	3	Fast	Fresh	800	996	1003	0	80	22.5	22.6	0	54.9
22	3	Fast	Fresh	800	0	1500	0	0	0	100	0	0

Steam Electrolysis

Coelectrolysis

- 3 stacks
- varied composition, temperature, total flow rates

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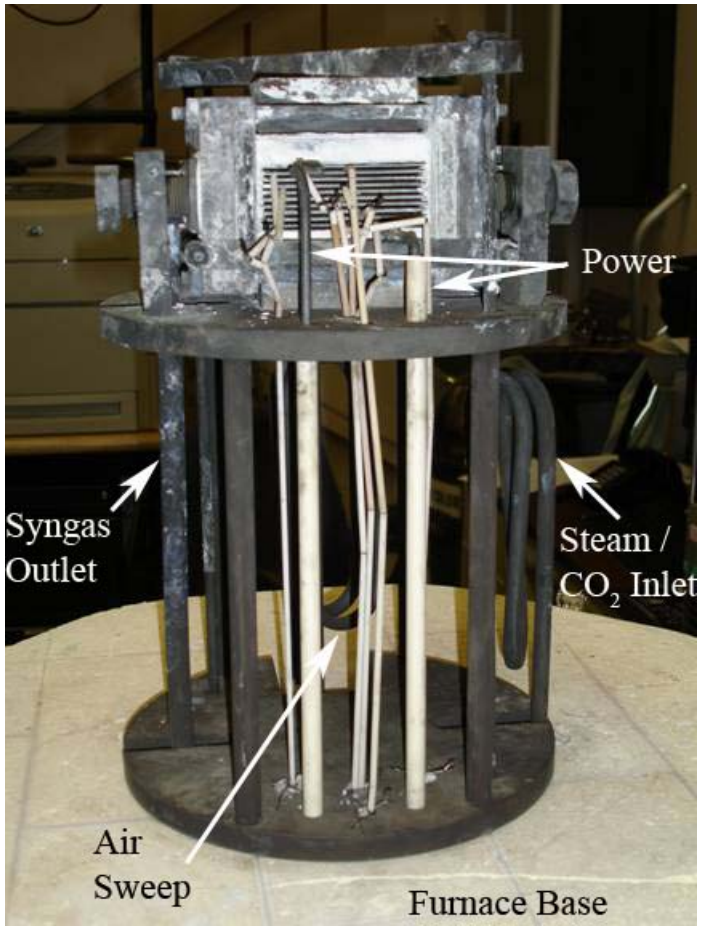
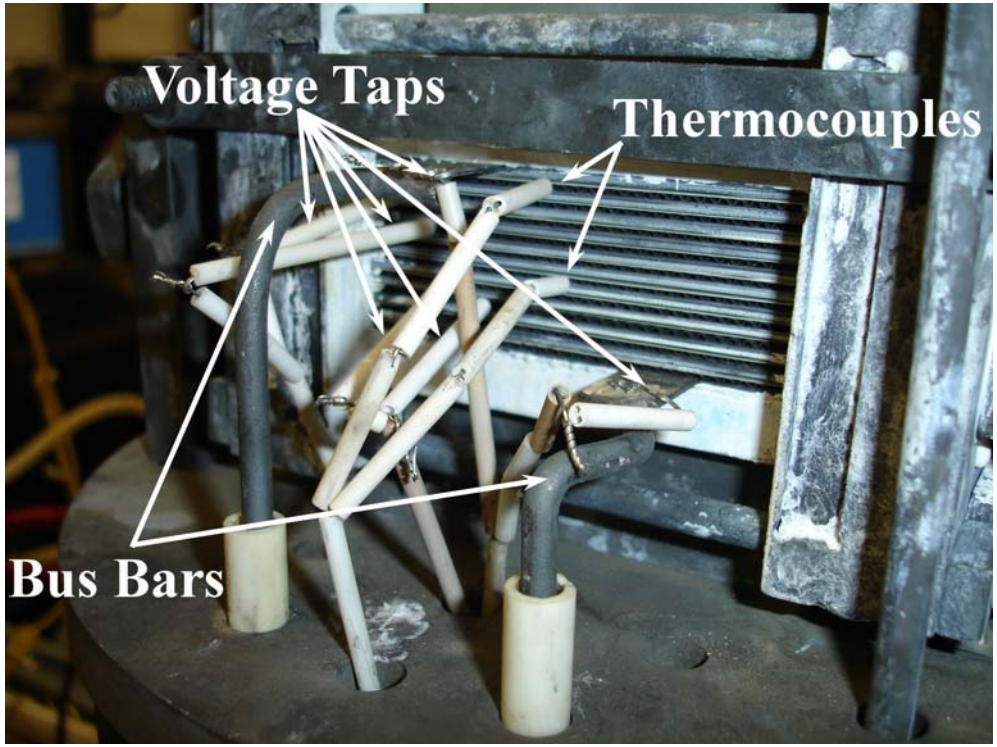
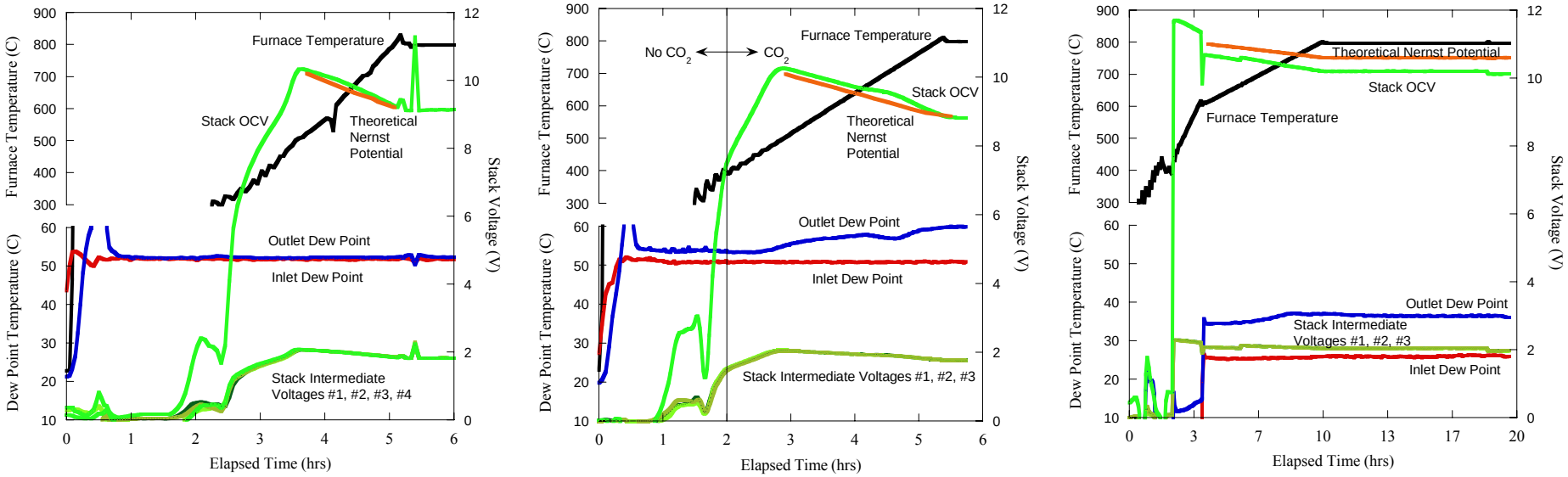
10-Cell Coelectrolysis Stack





Stack Heatup



- 2 C / min heatup rate
- Stacks 1 & 3 -- Heatup with humidified N_2/H_2
- Stack 2 -- CO_2 above 350 C
  - Reverse Shift Reaction
- Stack 3 – outlet dew point > inlet dew point
  - possibly some leakage
- No open cell potential until above 350 C
- Theoretical Nernst potential agrees well with OCV

$$\overline{V}_{Nernst} = \frac{-\Delta G_{H2O}(T_{furnace})}{2F_{Faraday}} - \frac{RT_{Furnace}}{2F_{Faraday}} \ln\left(\frac{y_{H2O}}{y_{H2}\, y_{O2}^{1/2}}\right) + \frac{RT_{Furnace}}{4F_{Faraday}} \ln\left(\frac{P_{Test}}{P_{std}}\right)$$

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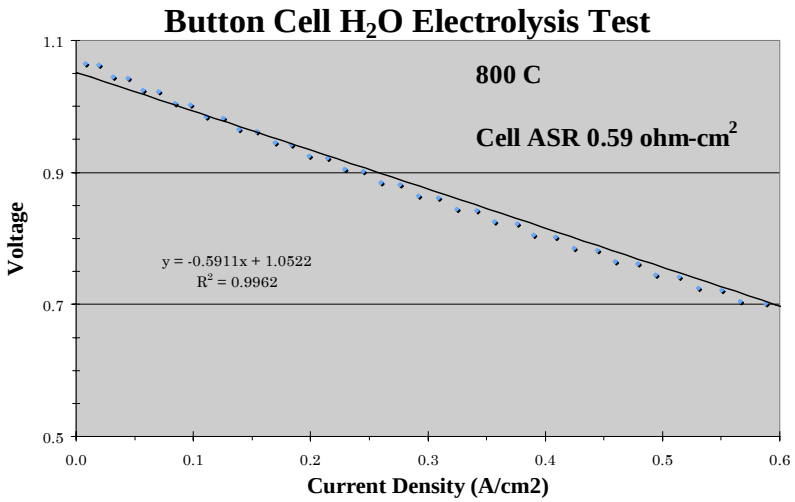
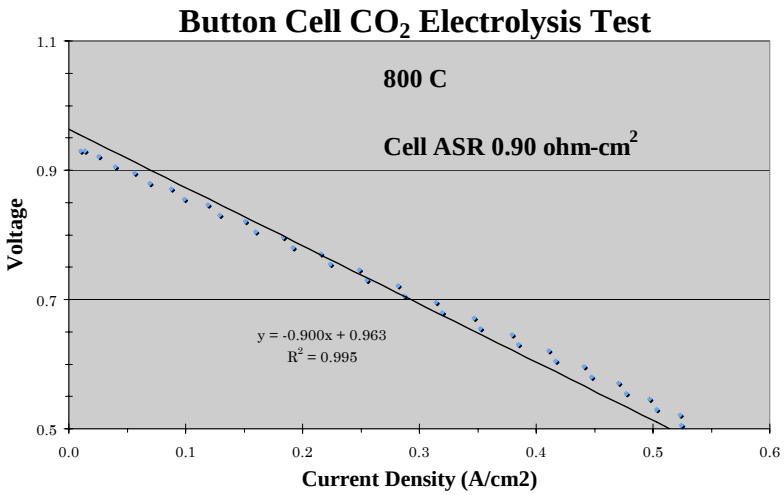
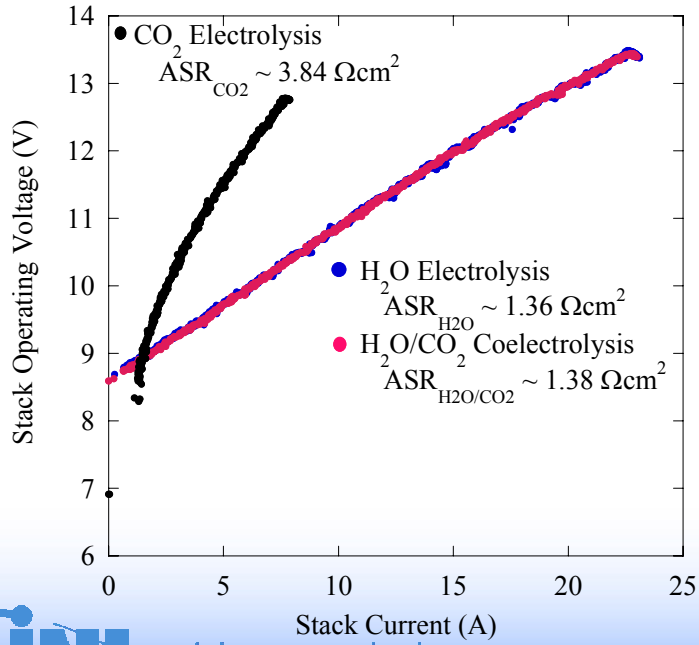
Steam vs. Coelectrolysis ASRs







CO_2 ASR higher than steam ASR

- CO_2 electrolysis slower kinetics
- Higher voltage required for given currrent or production rate
- Efficiency inversely proportional to voltage
- Indicative of relative efficiencies

Stack performance same for steam electrolysis or coelectrolysis

- In coelectrolysis, RSR relied upon for CO
- Electrical requirement is less

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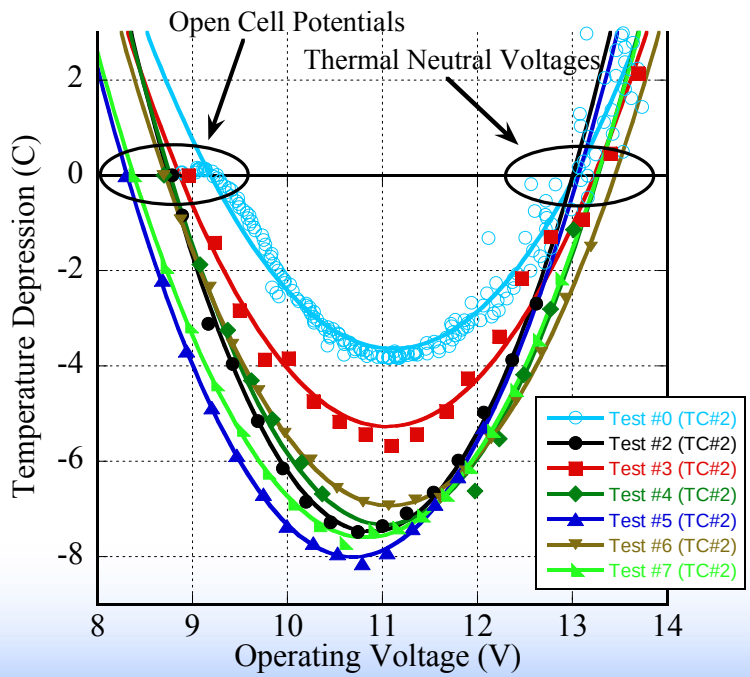
Open Cell Potentials, Thermal Neutral Voltages

- Coelectrolysis is endothermic
- Temperature is depressed until ohmic heating dominates
  - Thermal Neutral Voltage
  - In H_2O electrolysis, $V_{TN} = f(T)$
  - In coelectrolysis, $V_{TN} = f(T, y)$



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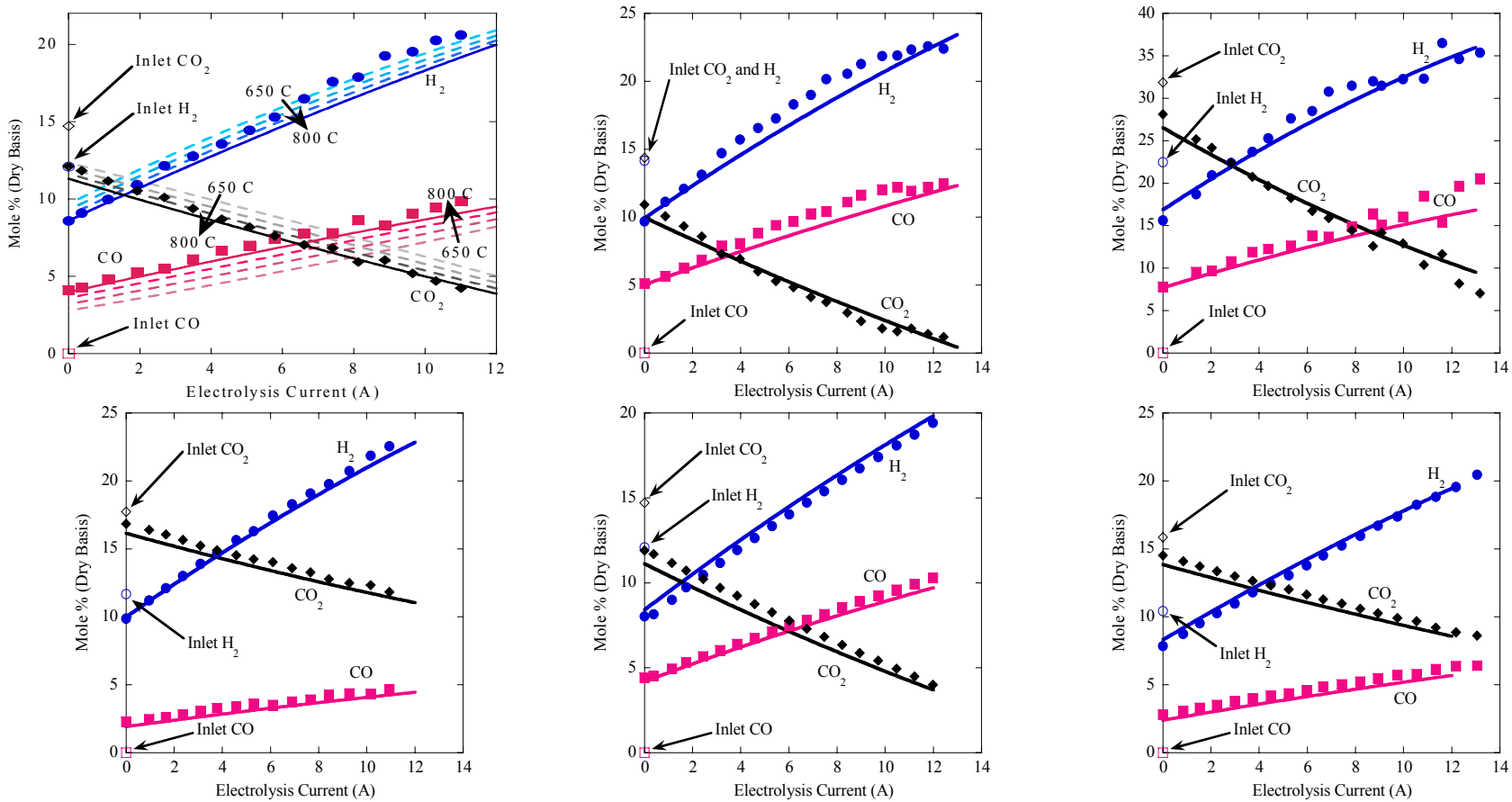

"Inlet" compositions → cold inlet stream

Zero-current values → "hot" RSR equilibrium composition, no electrolysis

$$k_{RSR}(800\,C) = \frac{[CO_2][H_2]}{[CO][H_2O]} \approx 1.0$$

As current is increased, H_2 and CO are produced

Coelectrolysis effectively increases (can double) syngas yield

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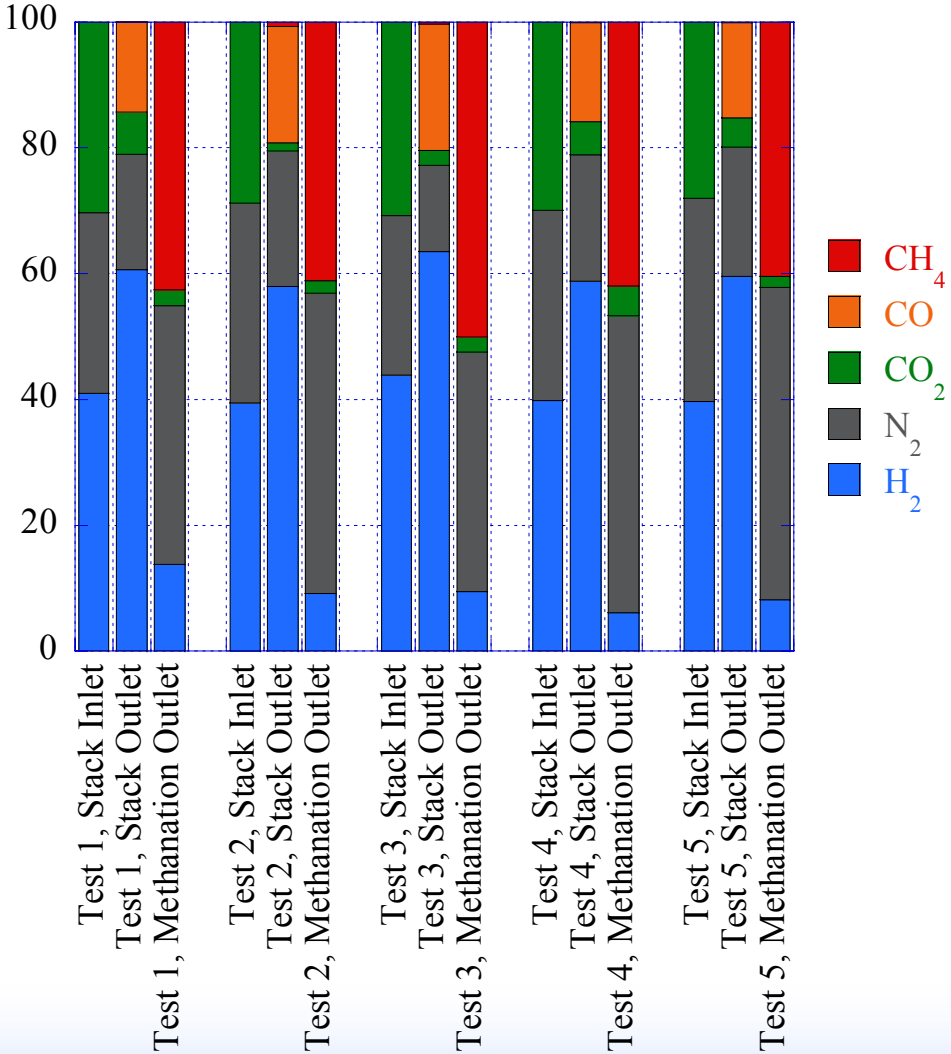
Coelectrolysis With Subsequent Methanation



Ceramatec extended coelectrolysis with downstream methanation reactor

- 18mm x 1.5m tube
- Commercial steam reforming catalyst (R-67R, Haldor Topsoe)
- Outer sleeve to reduce axial temperature gradient
- Reactor T = 300 C
- 40% - 50% CH_4 (by volume) produced

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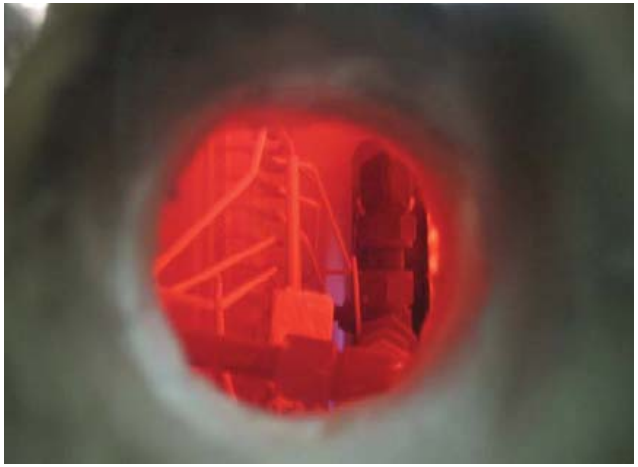
Summary

- Coelectrolysis inputs are energy, H_2O, and CO_2
- Stack performance (ASR) in coelectrolysis ~same as steam electrolysis
- INL coelectrolysis model compares well with experimental data
- Coelectrolysis increases yield of syngas over RSR equilibrium concentration
- Coelectrolysis appears promising for large-scale syngas production



High temperature coelectrolysis stack at 800 C

Syngas

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