# Combining SOFC Technology for Electrolysis with $CO_2$ Recycling as an Approach to Hydrogen Storage

Session GHT44a H2 Production

Thursday, 19 November 2009

4:00-6:00 PM

CERAMATEC®

TOMORROW'S CERAMIC SYSTEMS

J. Hartvigsen, S. Elangovan, A. Nickens, L. Frost – Ceramatec, Inc.
C. Stoots, J. O'Brien, J.S. Herring – Idaho National Laboratory

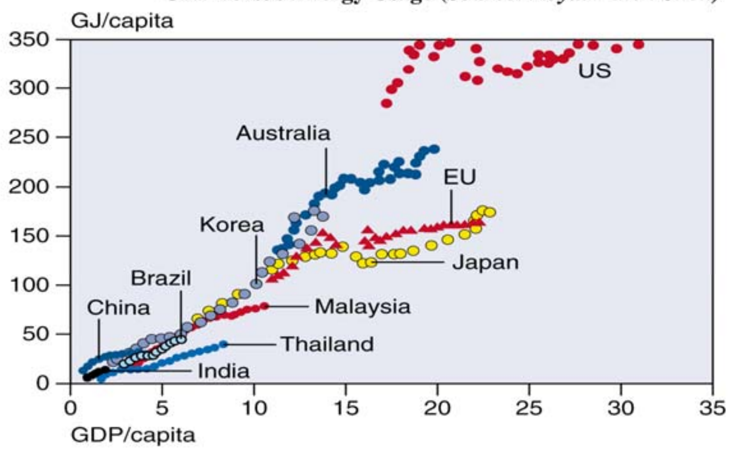
FUEL CELL SEMINAR & EXPOSITION

**November 16-19, 2009 Palm Springs Convention Center, Palm Springs, CA, USA**

# Energy, Environment & Economy

- Environment
  - Climate Change
    - GHG sources
      - 8 tons $CO_2$/kW-yr from coal or oil
      - Leaky natural gas pipelines
      - Ruminants
    - Ozone hole - no, that's a different topic
  - Habitat Impacts
    - Drilling in Arctic National Wildlife Refuge
    - Wind turbines in Chesapeake Bay
  - Air pollution
- Limited Resources
  - Oil
    - National security
  - Gas
    - Heating vs. power generation
    - Transportation issues
  - Renewables
- Energy as the key to prosperity

**GNP versus Energy Usage** (*Source: Royal Dutch Shell*)




CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

# Why Electrolytic Synfuels

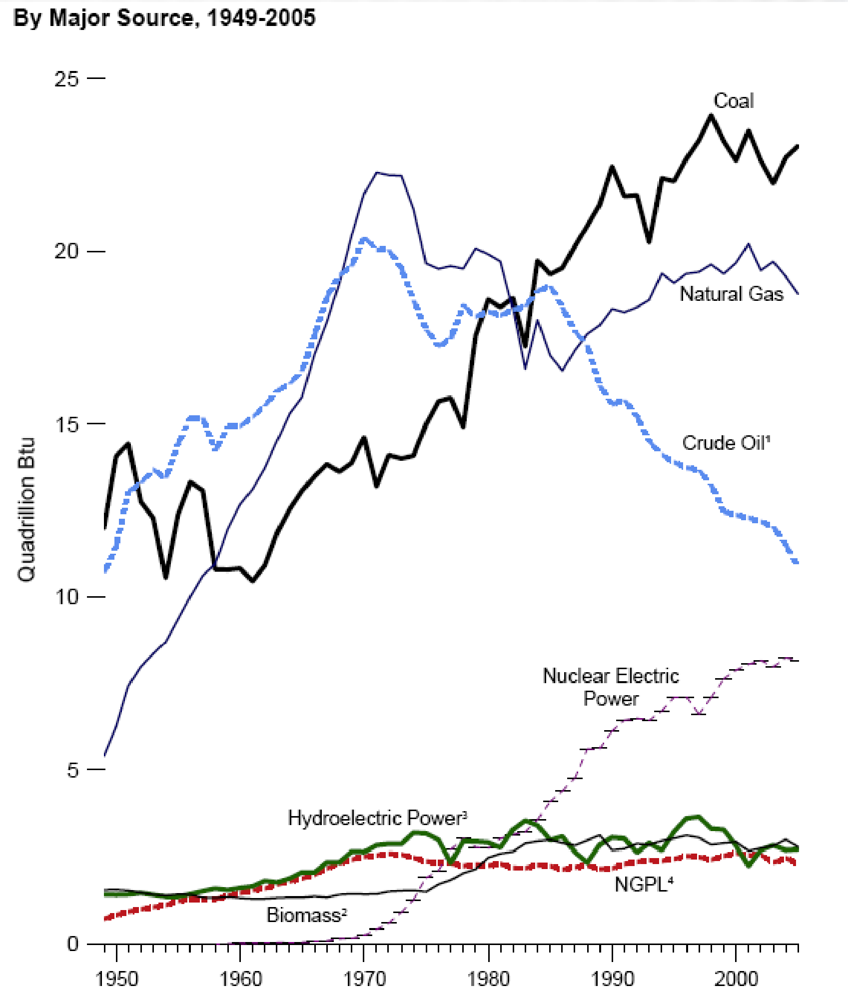
- Electrolysis efficiency
- Energy storage density
- Fits in existing distribution infrastructure
- Synergy with intermittent energy sources
- No added $CO_2$ emissions
- Reduced work of compression
- Compatible with existing vehicle fleet
  - 20 to 50 year crossover

# Storing Hydrogen With $CO_2$

- Energy Sources
  - Wind, Solar (PV & heat), Hydro, Nuclear
- Carbon Sources
  - Metallurgical Reduction, Cement Kilns
  - Fermentation, Digester gas
  - Biomass gasifiers
  - Fossil Power Systems
- Conversion Technology
  - SOFC electrolyzer, steam+$CO_2$=> syngas
- Products
  - SNG, Fischer Tropsch liquids

# Carbon Free Energy Source Options

- Hydrogen production from electrolysis
  - High temperature 29 tons/GW-hr
  - Conventional 21 tons/GW-hr
- Renewable energy resources
  - Large Scale Wind
    - 800 GW at class 4+ US wind sites
  - Small Hydro
    - 70GW new at existing dams (Chu 22 Sep09)
  - Concentrator Photovoltaic
    - Land area 12km$^2$ /GW
  - Biomass
    - Ag/Forestry byproduct
    - Carbon neutral cycle assuming production and processing are carbon free
- Nuclear
  - 25 new plants announced
  - Increased output of existing units
    - Note trend in figure since 1970




¹ Includes lease condensate.
² Wood, waste, and alcohol fuels (ethanol blended into motor gasoline).
³ Conventional hydroelectric power.
⁴ Natural gas plant liquids.

**http://www.eia.gov.doe.gov/emeu/aer/pdf/pages/sec1_6.pdf**

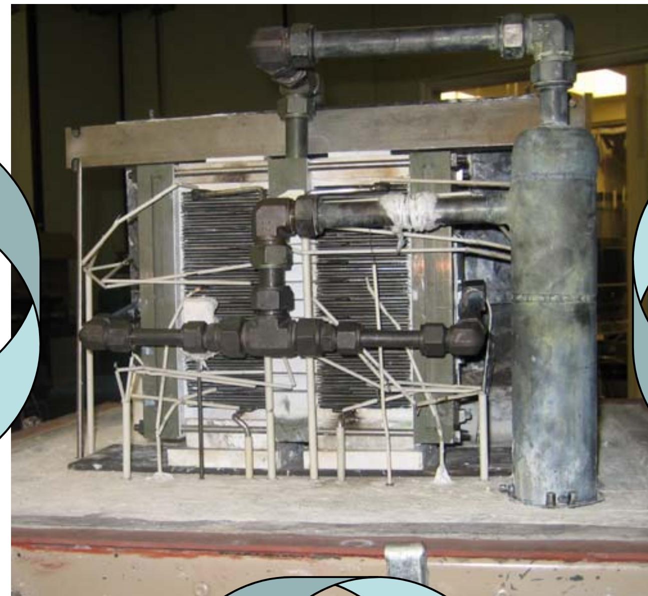
# One Technology - Multiple Modes Of Operation

## Solid Oxide Stack Module

**NG**
**Biogas**
**Diesel**
**JP-8**
**Coal**

**Fuel**

**Electricity**



**Syngas**

**$CO_2$ & Steam + Electricity**

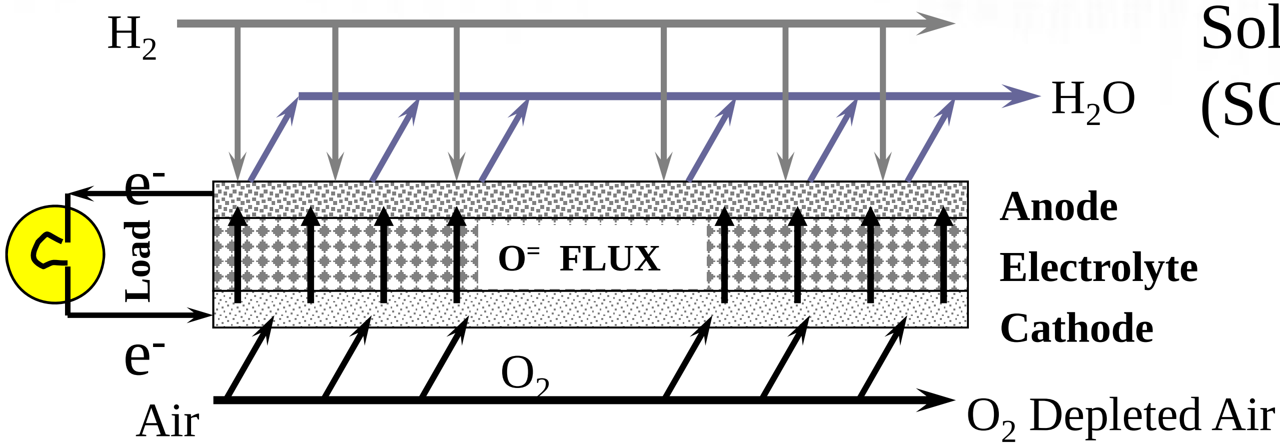
**Steam + Electricity**

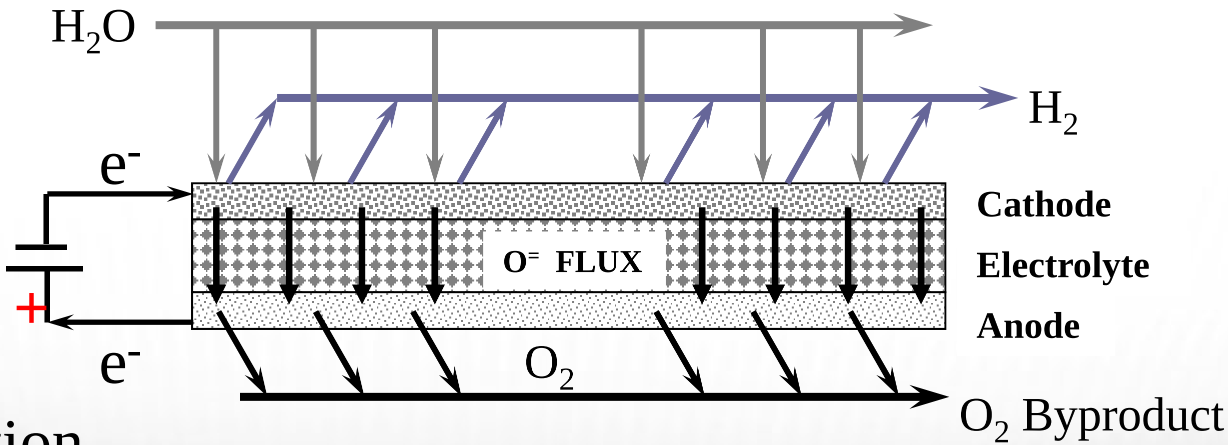
**Hydrogen**
**(High Purity)**

CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

# Steam Electrolysis Operating Principle

Solid Oxide Fuel Cell (SOFC) operation



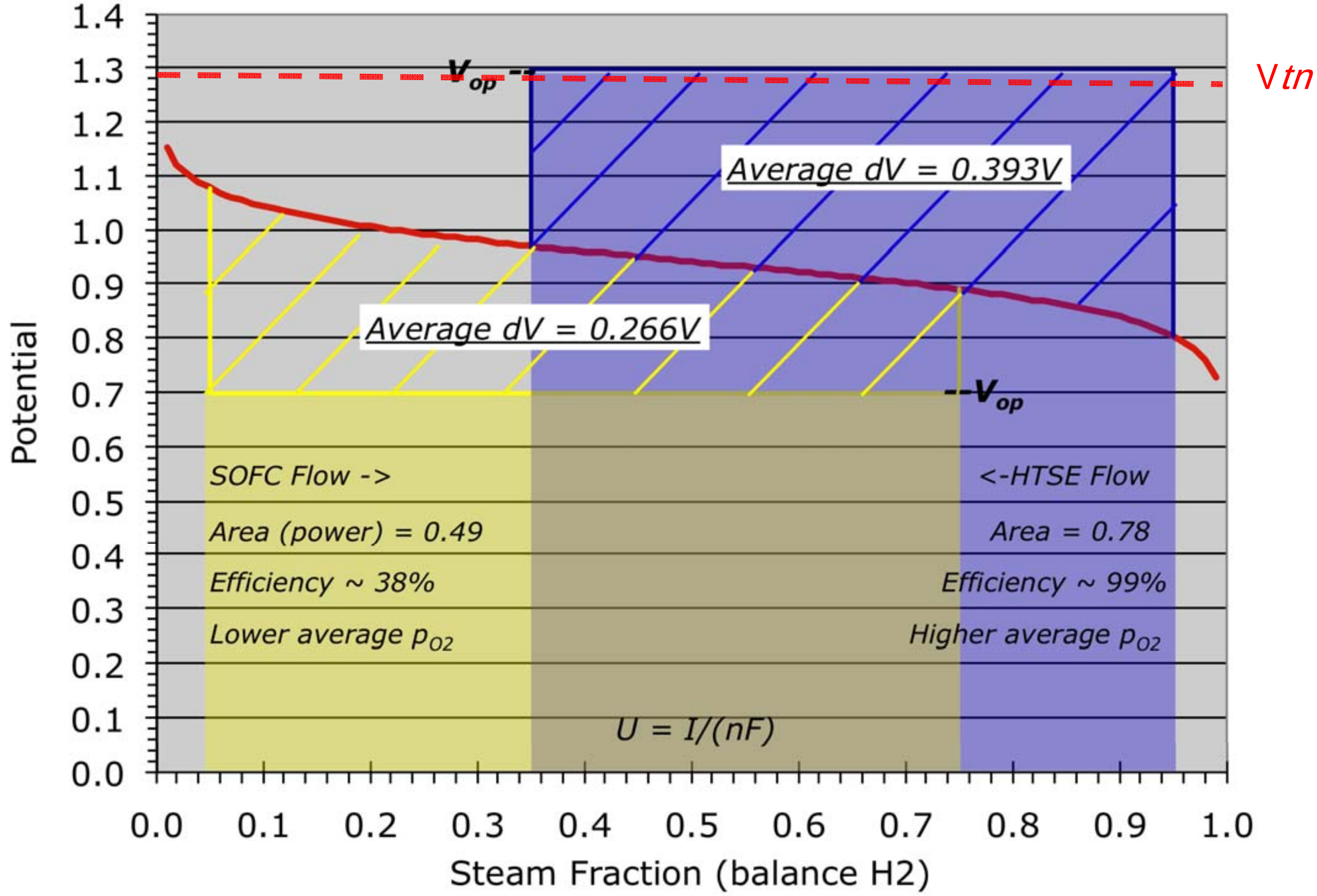

Same device in electrolysis operation

CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

# SOFC vs. SOEC Cell & Stack Designs

- Cells are virtually identical
  - Same electrolyte, electrodes, pattern, etc.
  - Oxygen evolution creates asymmetry in oxygen electrode supported SOEC
  - Opposite effect exhibited in hydrogen electrode supported SOFC
- SOEC seals more challenging
  - Higher back pressure on seals due to product collection vs. burner
  - Low molecular weight stream vs. reformate
    - Diffusion mechanism more active relative to hydrodynamic
    - Hydrogen permeation in metal icon destabilizes air side scale
- SOEC is more corrosive environment
  - High steam content
  - High oxygen concentration
  - Coating changes and seal compatibility study (glass fluxes scale)
- Potential icon design differences due to
  - Design air channels for heat rejection or injection (channel size)
  - SOEC has potential for very large cell areas

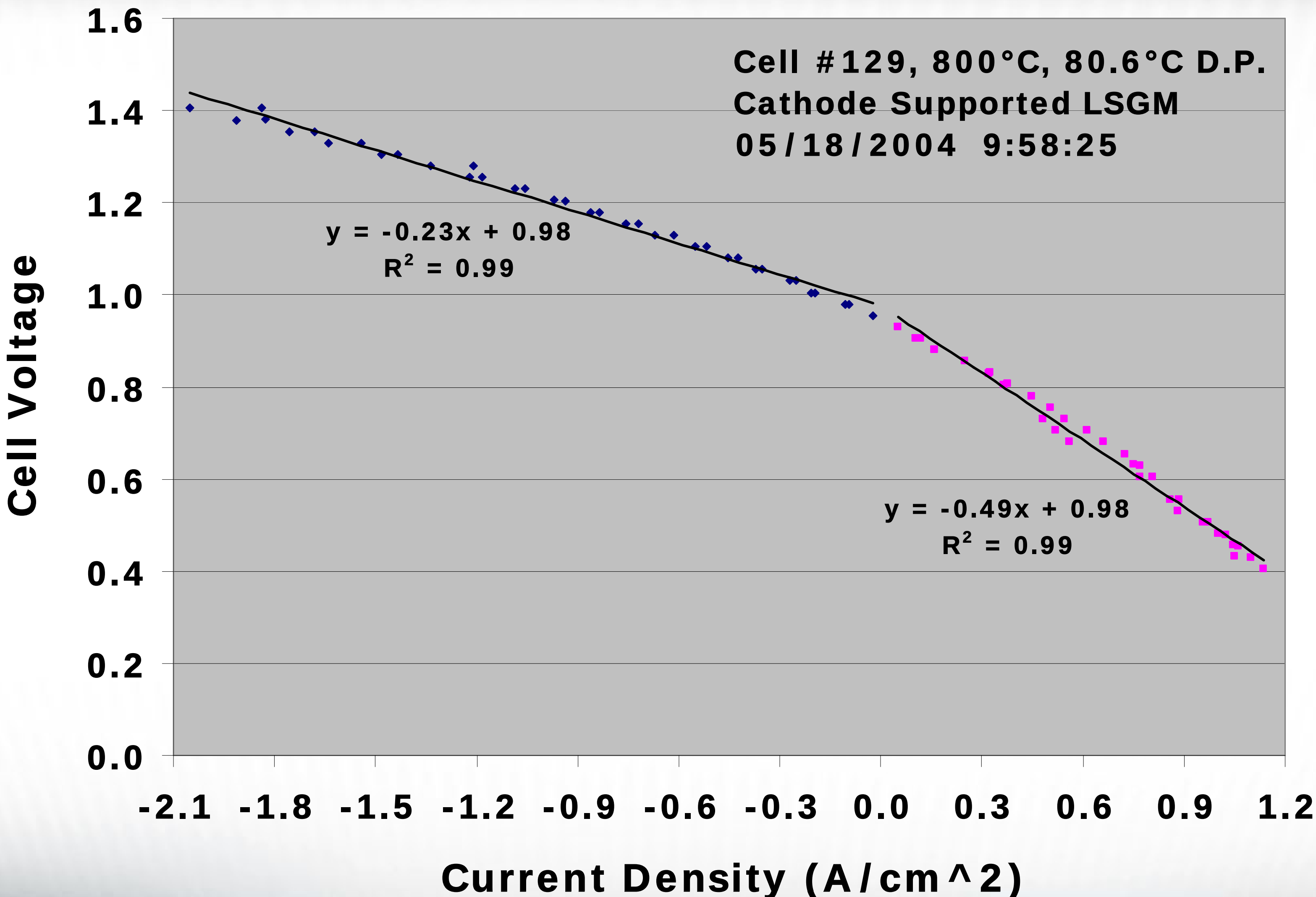
# SOFC-SOEC Contrasts in (V:$X_i$) Space




CERAMATEC®

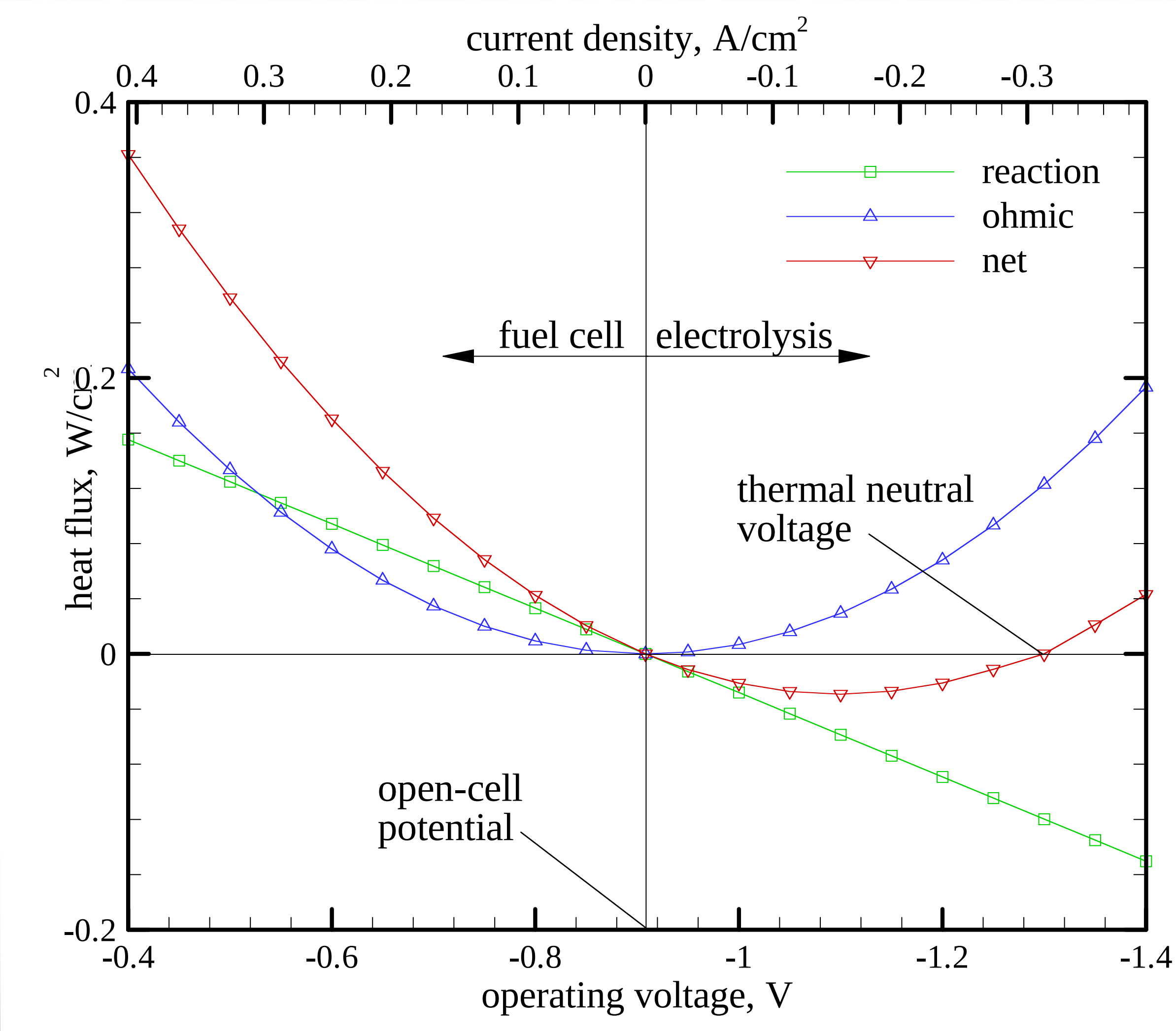
TOMORROW'S CERAMIC SYSTEMS

# Polarization of Oxygen Electrode Supported Cell




CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

# Energy of fuel-cell vs. electrolysis mode

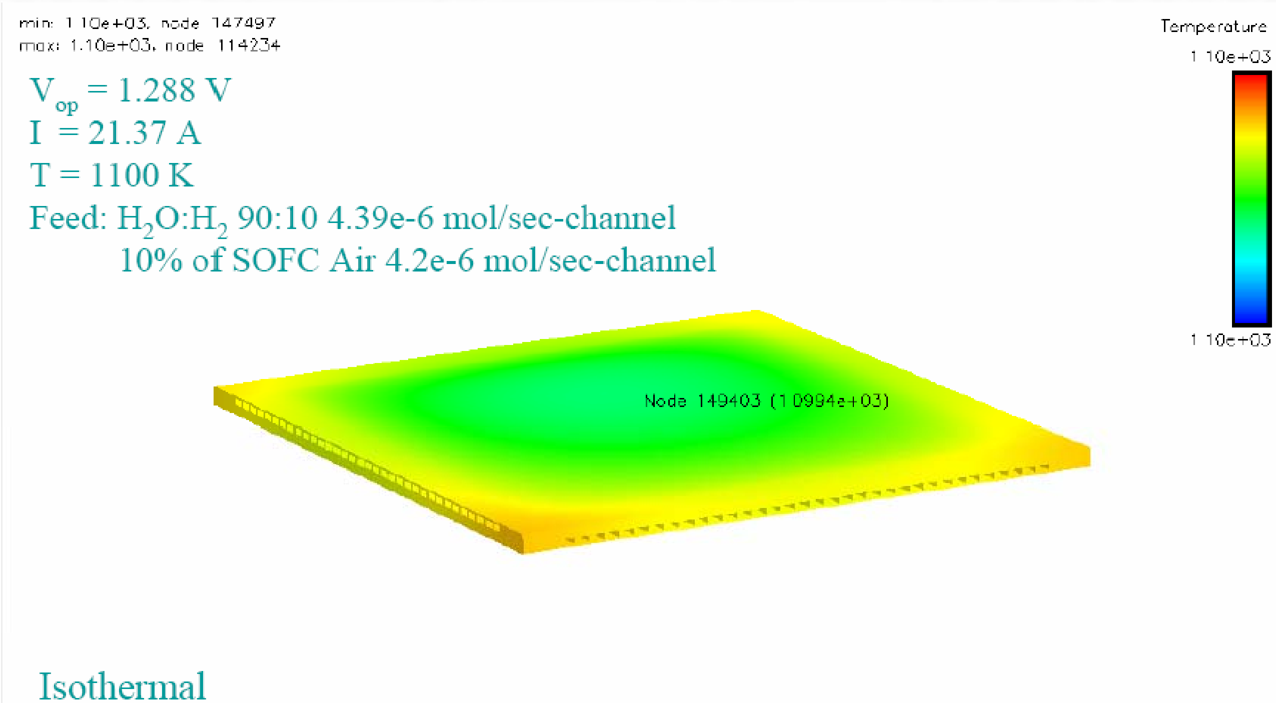


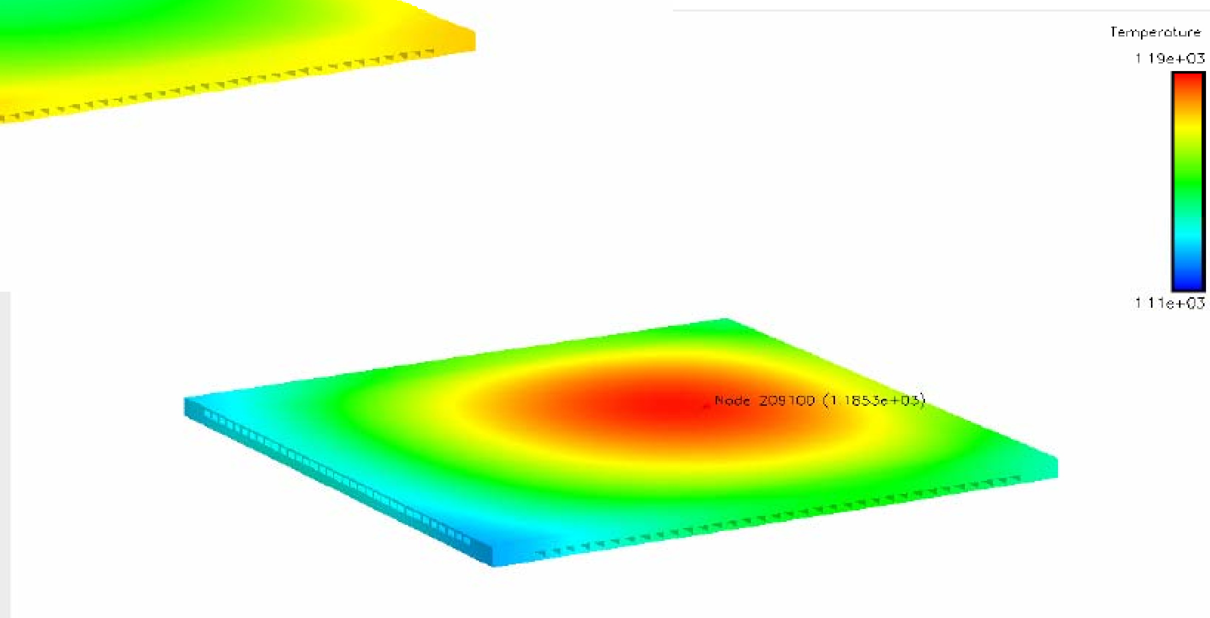

Stack ASR = 1.25,
T = 927 C,
$y_{H2,i}$ = 0.1,
$y_{H2,o}$ = 0.95

$$V_{tn} = \frac{-\Delta h_R}{2F}$$

(1.291 V at 1200 K)

# Typical SOEC and SOFC Temperature Maps

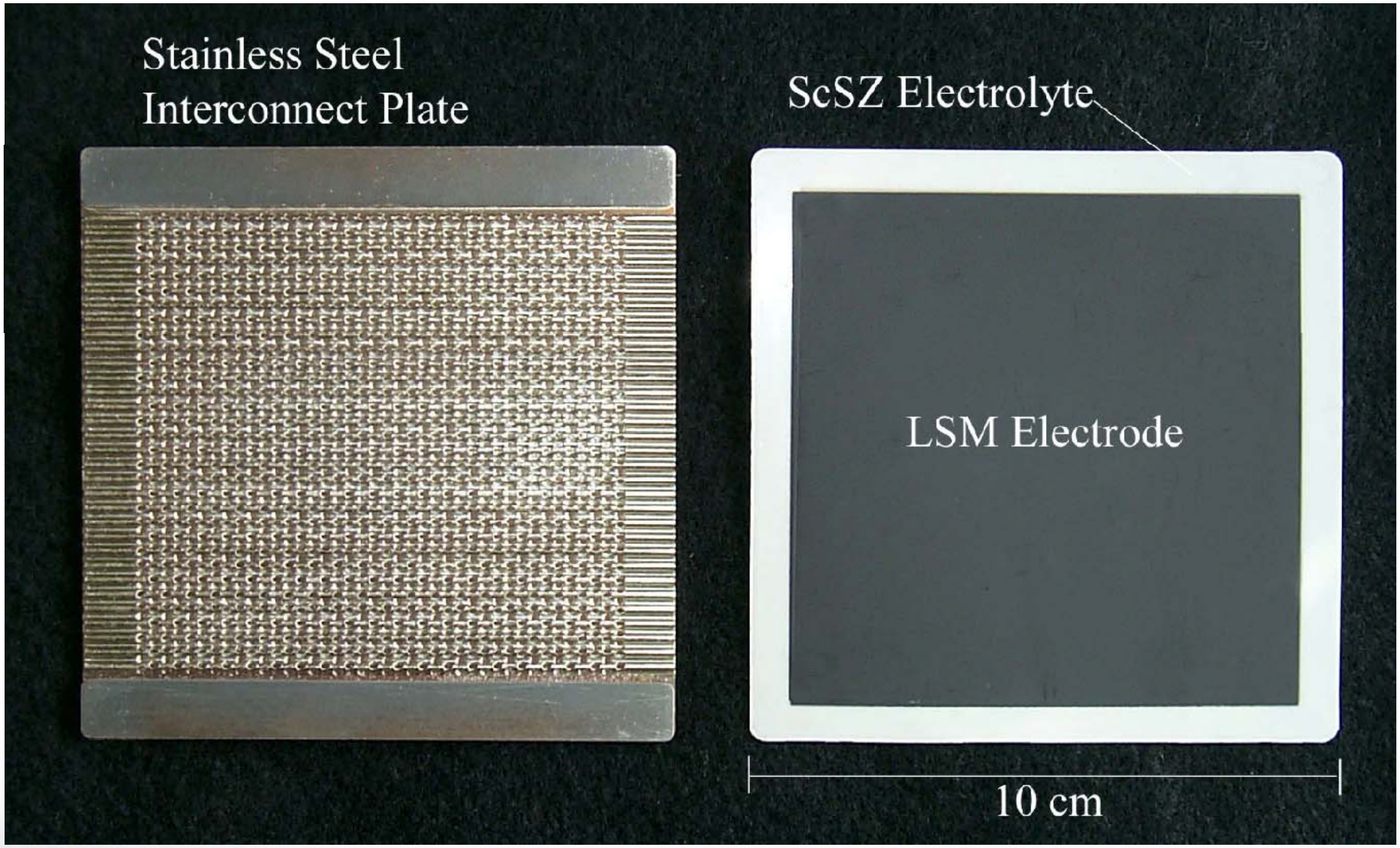



SOFC ΔT > 90°C
Resistance doubling ~ 67 °C
Thermal expansion issues

CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

# Stack Components




CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

# ILS System 5.7Nm$^3$/hr, 18kW $H_2$ Rate

CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

# Electrolysis Cells at 20cm Scale

# Electrolysis Module in Operation

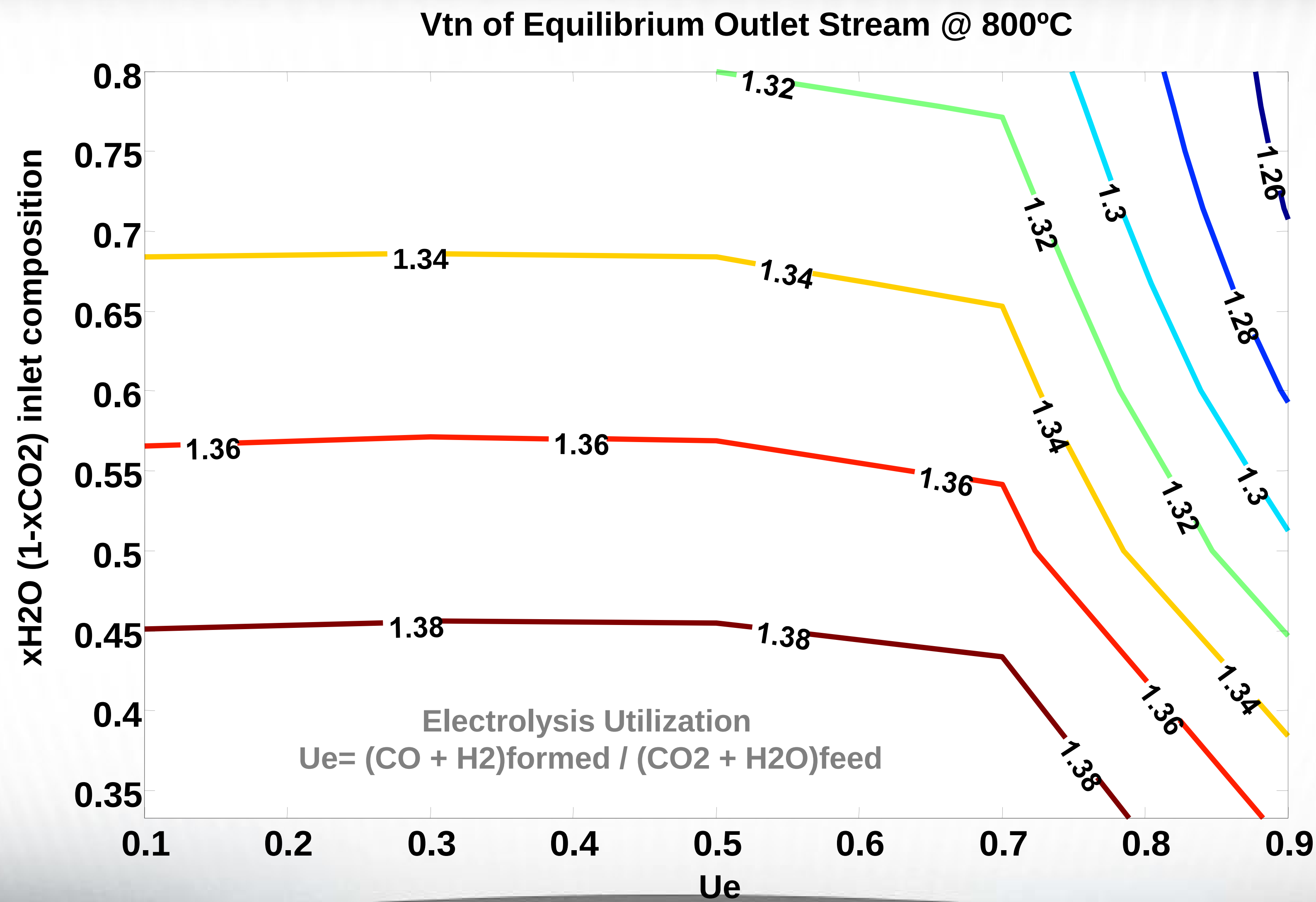
CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

# INL Internally Funded $CO_2$ Electrolysis Project

- Button cell testing
  - Gas analysis
    - INL – using $CO_2$ sensors
    - Ceramatec – micro-channel GC
- Analysis
  - Thermodynamic parameters
    - Thermal Neutral Voltage
    - CO & $CO_2$ reduction potentials
  - System process model
- Electro-kinetics of steam/hydrogen vs. $CO/CO_2$ reactions
  - Dry $CO/CO_2$
  - Wet ($CO_2/H_2$)
  - Wet to dry transient

CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

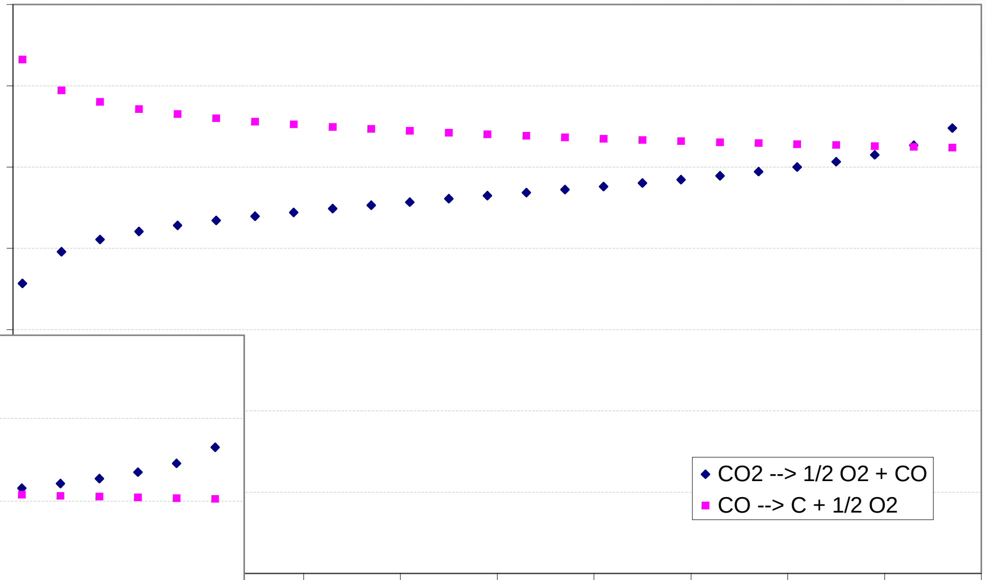
# Co-Electrolysis Thermal Neutral Voltage Map

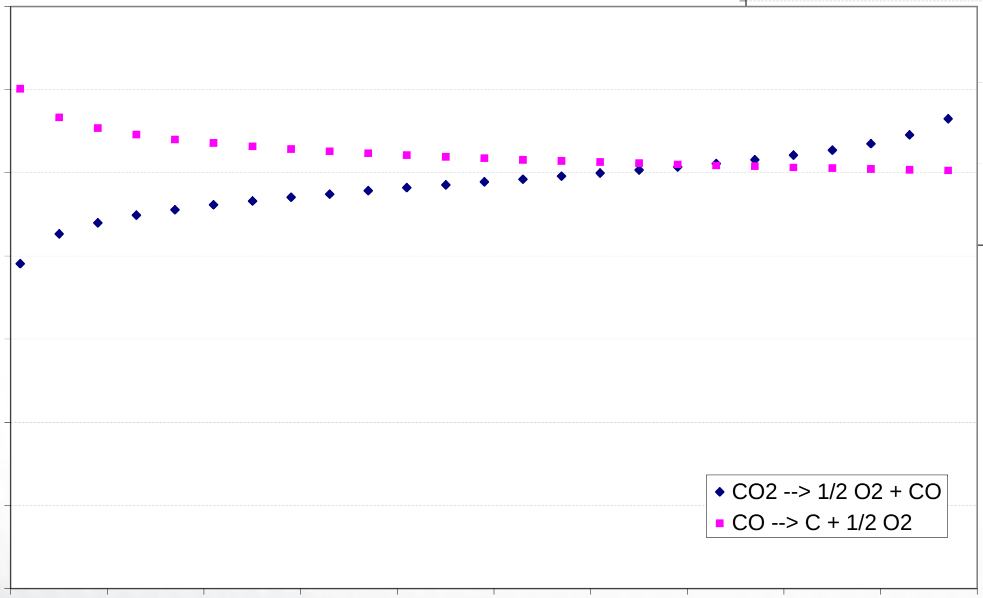



CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

# Reduction Potentials of $CO_2$ and CO

Restricts cell operating voltage
Cell to cell variation in a stack?
Favors high T, low $CO_2$ utilization
Solved with steam co-electrolysis



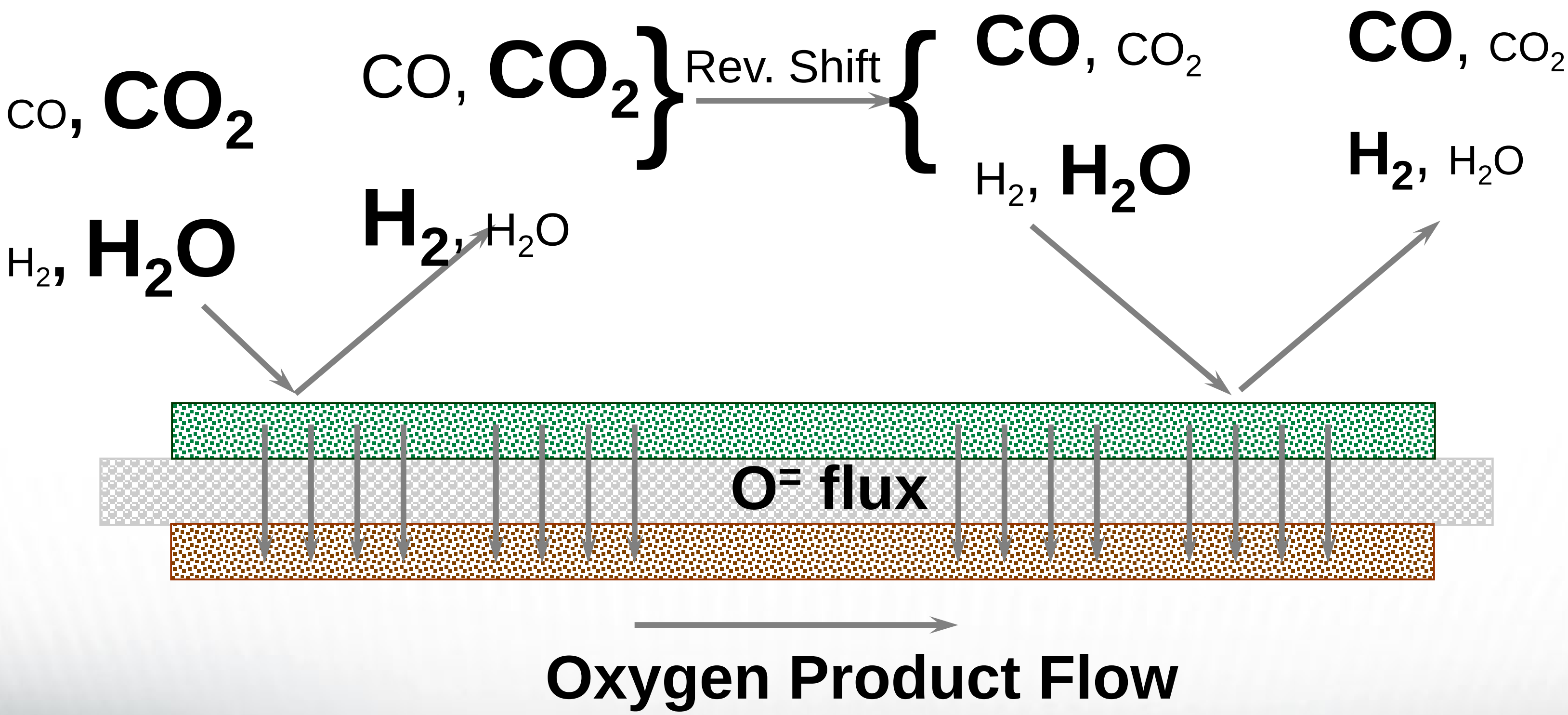

CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

# Reverse Shift & Electrolysis Of $CO_2$

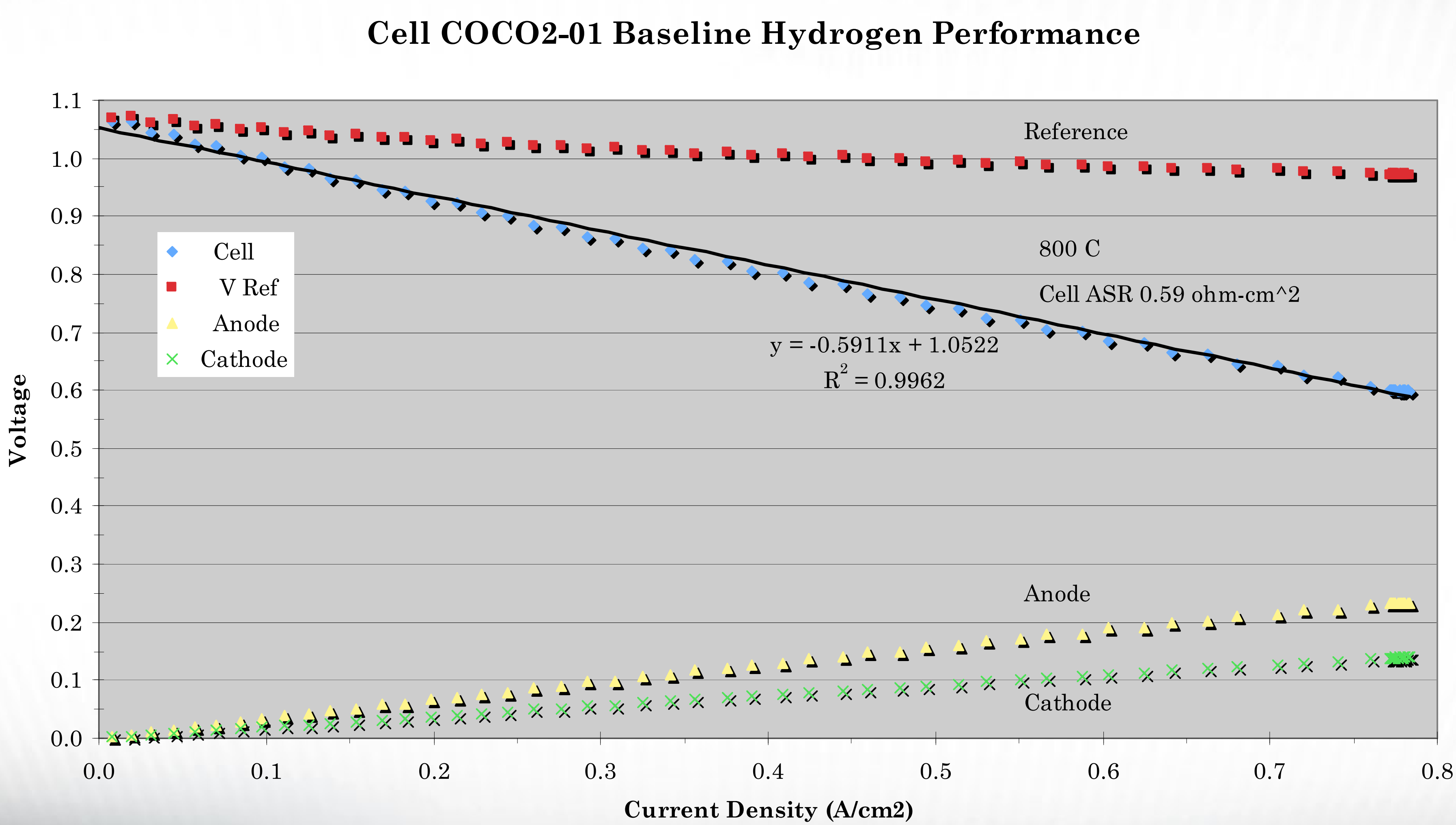
**Feed: $H_2O$, $CO_2$, (**minor $H_2$, CO)

**Reverse Shift Reaction: $CO_2$ + ⇑ $H_2$** <==> **CO + ⇓ $H_2O$**

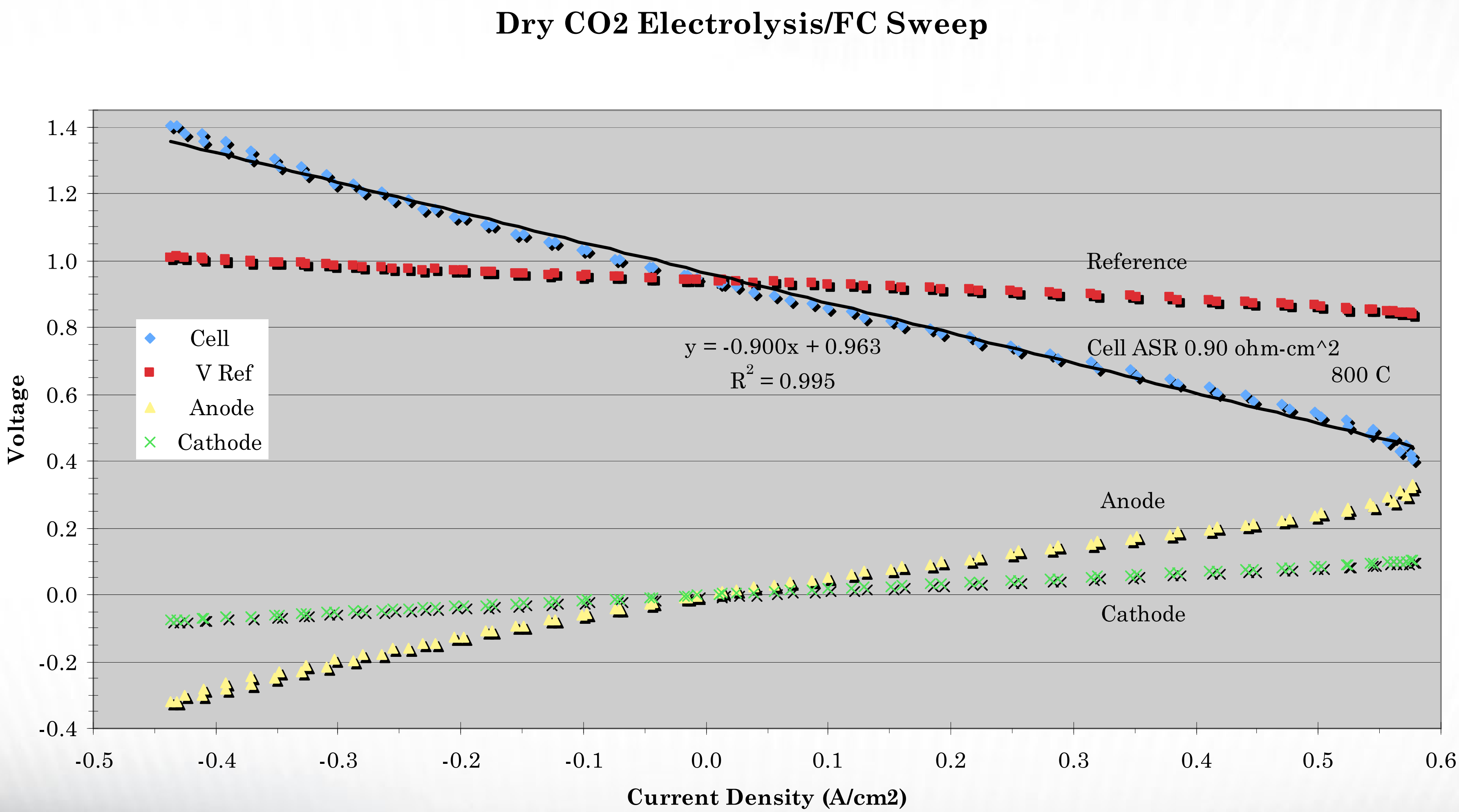
**As steam is consumed and H2 produced the RSR proceeds to the right**



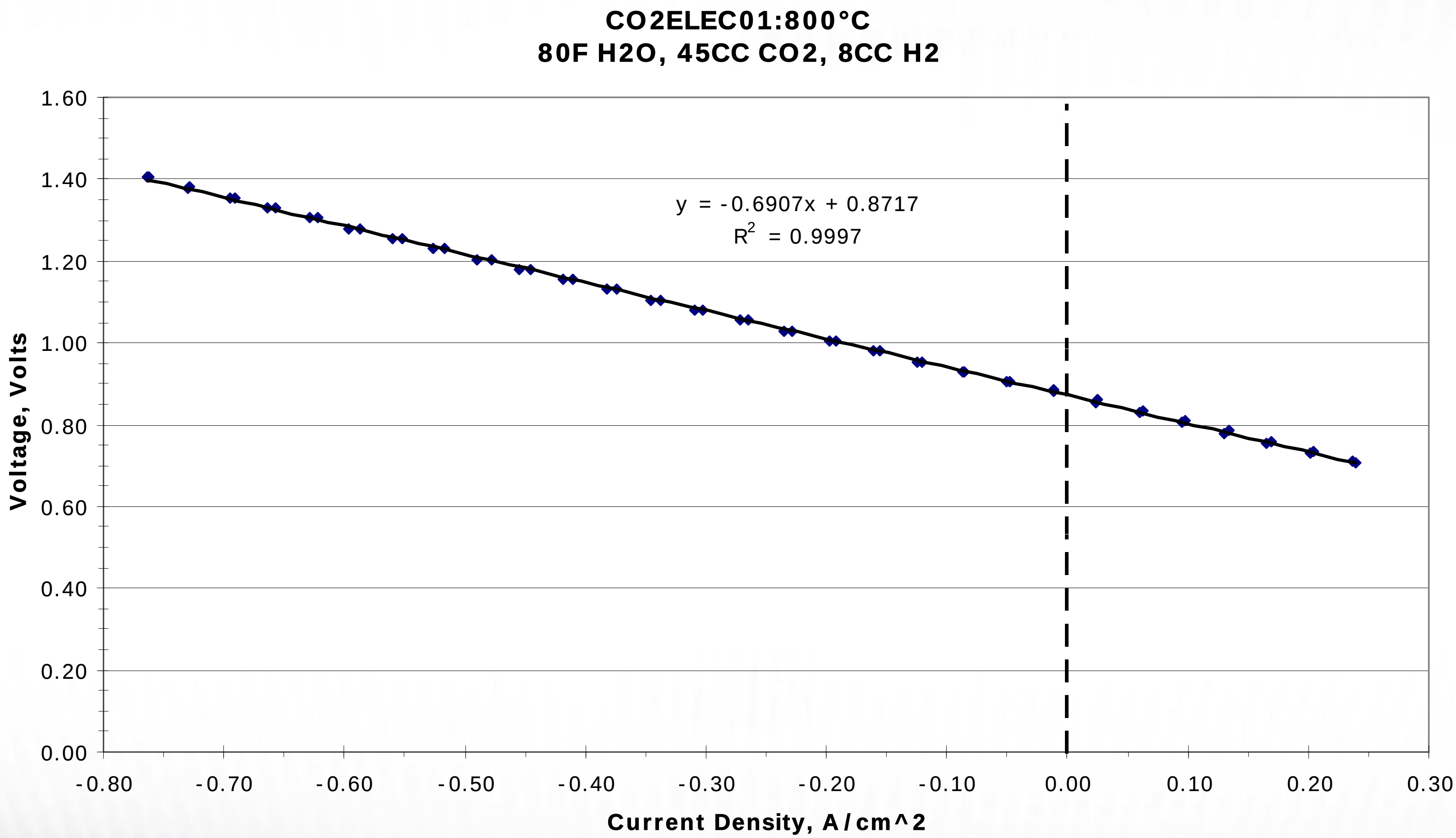
# Wet/Dry $CO_2$ Electrolysis Cell V-I Comparison



# Wet/Dry $CO_2$ Electrolysis Cell V-I Comparison



# Humidified $CO_2$ Cell V-I Characteristic

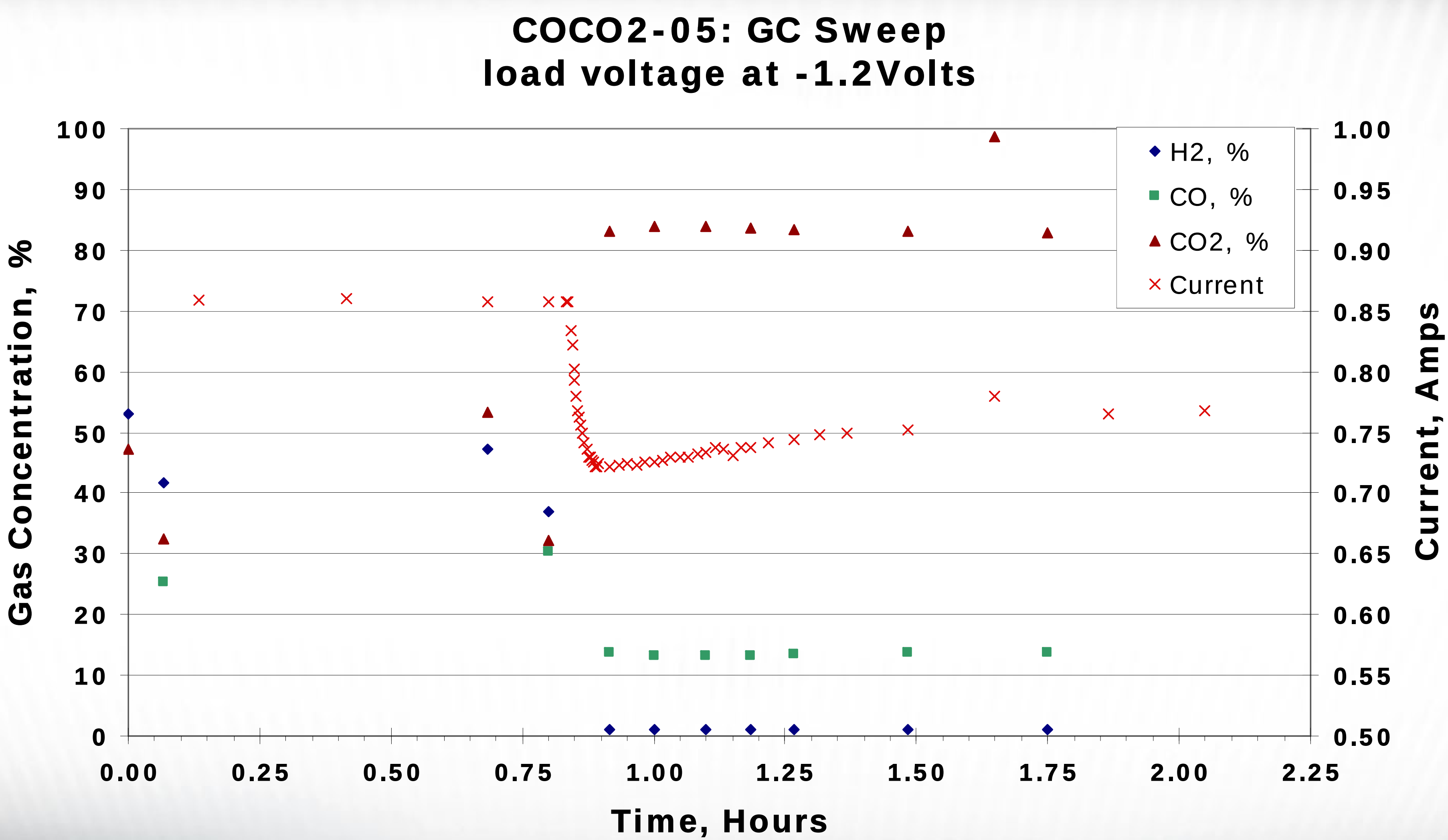



No reduction in performance compared to cells with steam electrolysis

CERAMATEC

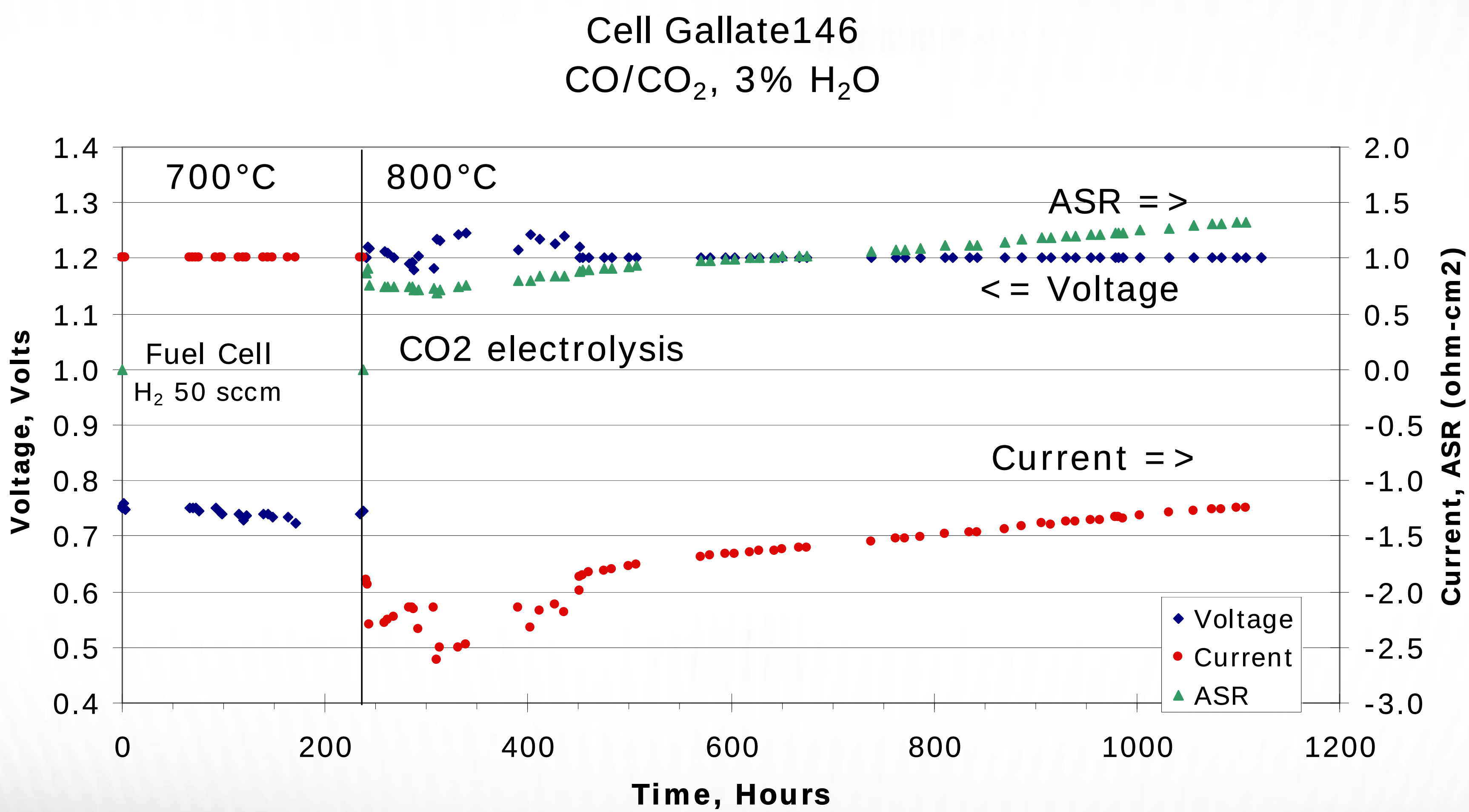
TOMORROW'S CERAMIC SYSTEMS

# Wet to Dry Transient




CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

# 1100 Hour $CO_2$ Electrolysis Operation

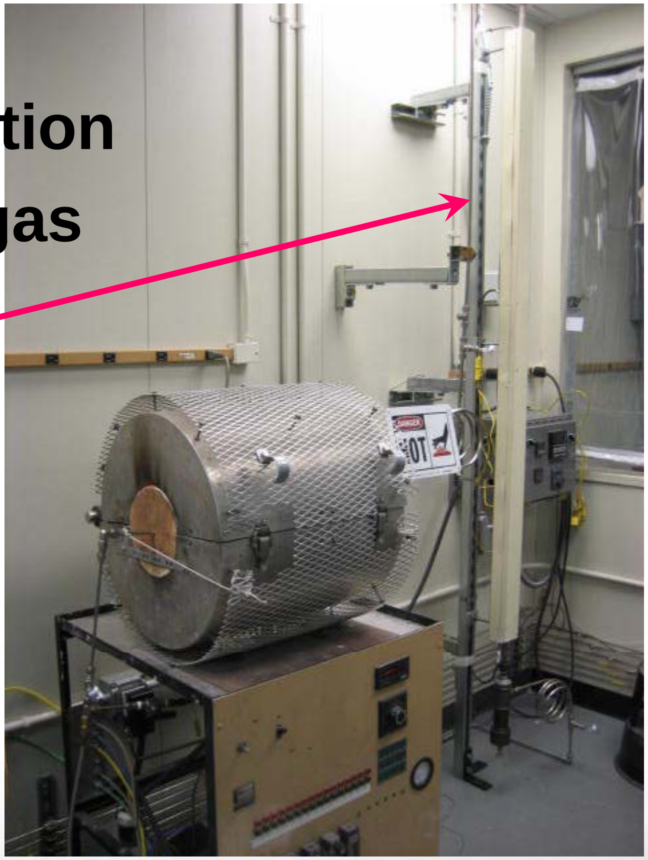



CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

# Ceramatec laboratory scale FT unit

- **Syngas production and storage**
  - **co-electrolysis of steam and carbon dioxide**
- **Reforming/Methanation catalyst**
- **Synthesis gas compressors installation**
- **FT liquids test run on compressed gas**

**Fixed bed FT column**



- **Caution: Maintain Ni catalyst T > ~300° C to avoid highly toxic $Ni(CO)_4$ formation**

CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

# Syngas Compression and Storage Facility

CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

# Synthetic methane from electrolysis of $CO_2$

Gas analysis in volume %

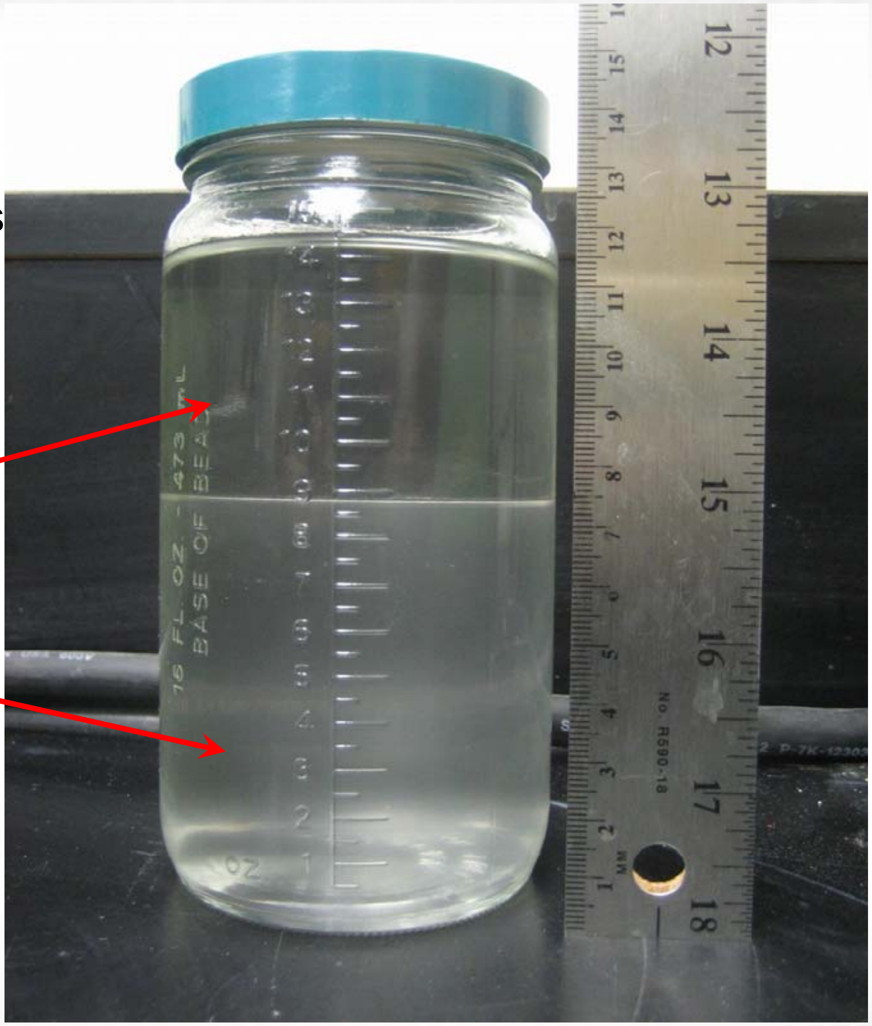
| | From Electrolysis | | | From FT Unit | | |
|---|---|---|---|---|---|---|
| | $CH_4$ | $CO$ | $H_2$ | $CH_4$ | $CO$ | $H_2$ |
| Test 1 | .0 | 14.3 | 60.7 | 42.5 | 0 | 13.8 |
| Test 2 | .7 | 18.5 | 58.0 | 47.7 | 0 | 9.2 |
| Test 3 | .3 | 20.1 | 63.5 | 50.0 | 0 | 9.4 |
| Test 4 | .1 | 15.8 | 58.9 | 42.0 | 0 | 4.6 |
| Test 5 | .1 | 15.2 | 59.5 | 40.4 | 0 | 8.2 |

***FEED TO ELECTROLYSIS IS $CO_2$ + $H_2O$ + ELECTRIC ENERGY***

CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

# FT- Liquid Products

- Ceramatec produced catalyst
  - FeCuK composition
  - 8mm La promoted alumina rings
  - Automated in-situ reduction profile using dewpoint controlled temperature ramp
  - Oil fraction
  - Water fraction

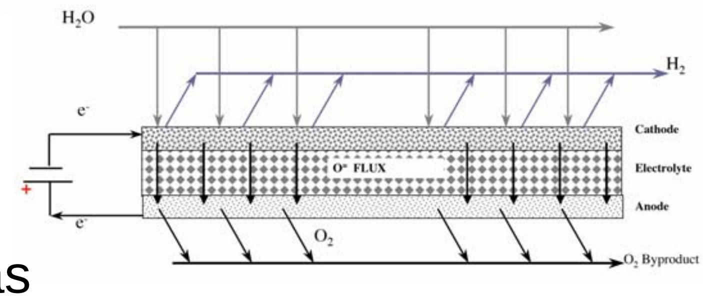


235° C Reactor Operation

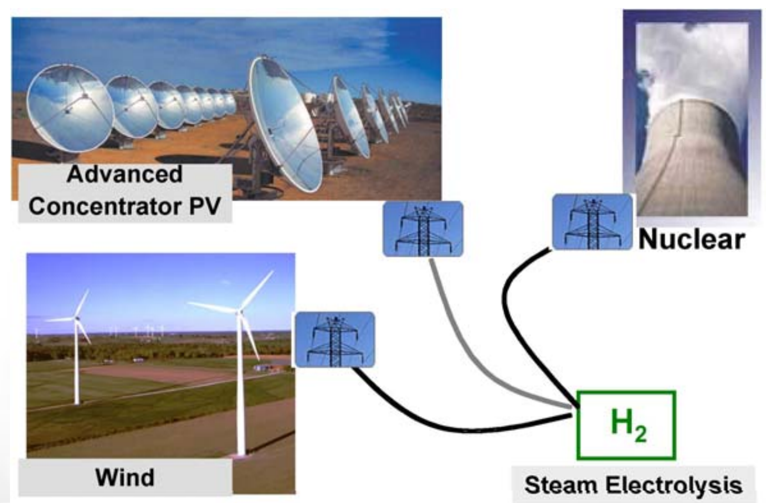
CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

# High Temperature Electrolysis

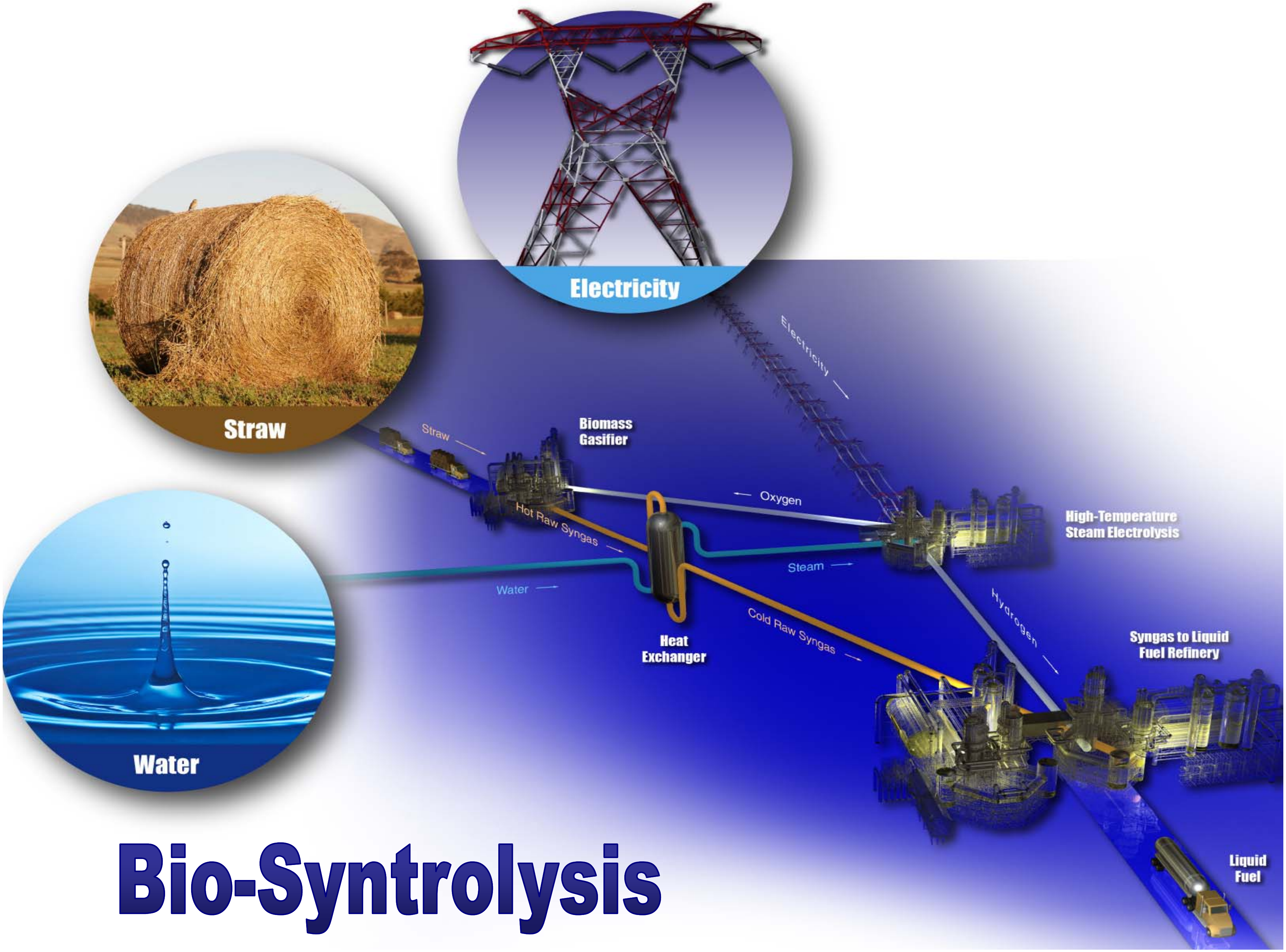
- Leverage decades of SOFC R&D
- Inputs
  - $e^-$ (green electrons)
  - steam => hydrogen
  - co-electrolysis of $H_2O + CO_2$ => syngas
  - heat input optional, depends on operating point




- Most efficiency means of hydrogen production
  - $e^-$ to hydrogen
    - $\eta$=100% at 1.285V
    - $\eta$= 95% at 1.35V
    - $\eta$=107% at 1.20V, (heat required)
- Hot $O_2$ and steam byproduct
  - Valuable for biomass gasification

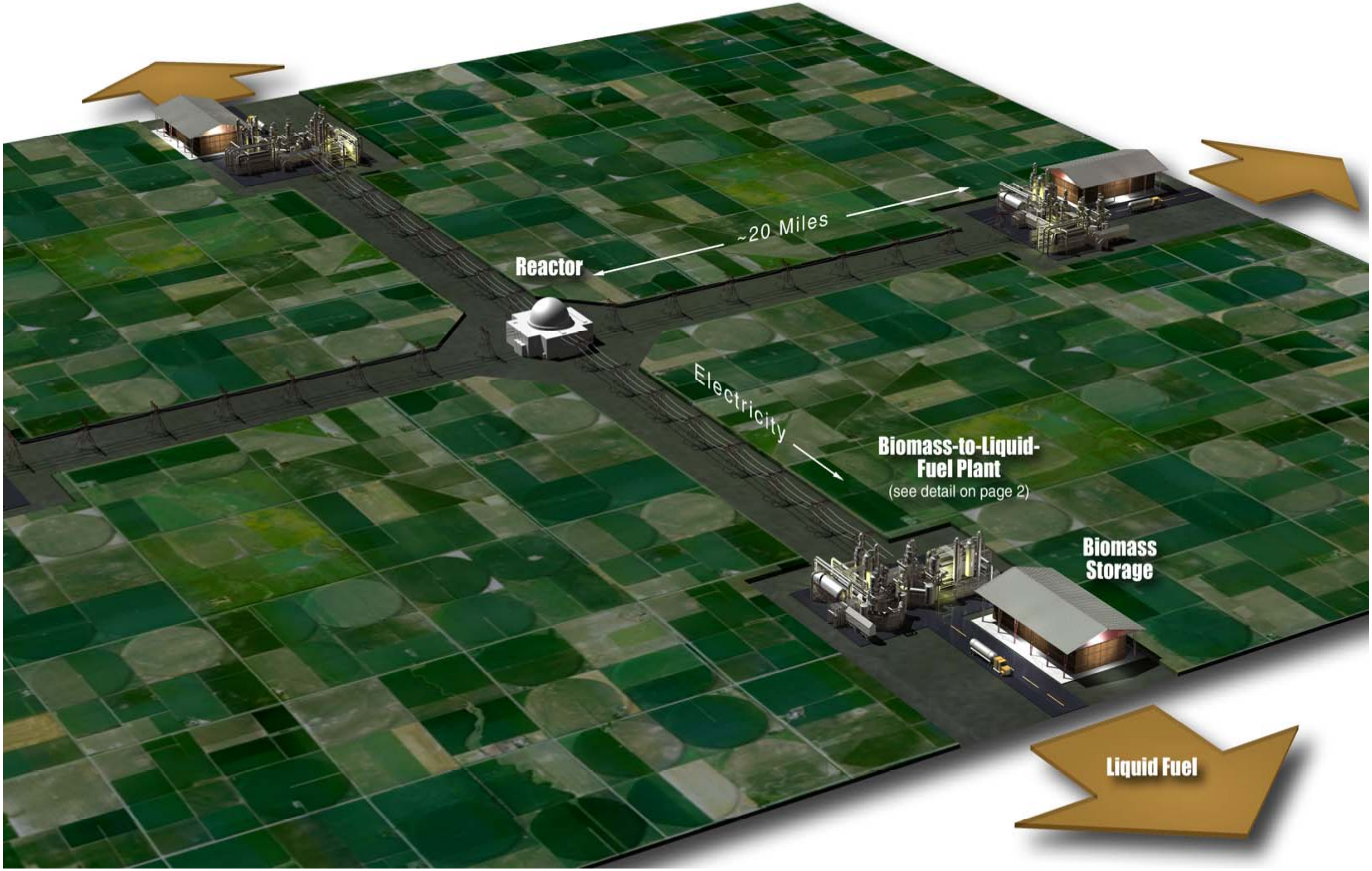



CERAMATEC
TOMORROW'S CERAMIC SYSTEMS




# Bio-Syntrolysis

# Bio-Syntrolysis: Regional Concept



# What Can Be Produced on 40x40 Miles?

- Biomass Feedstock
  - 22,700 annualized TPD dry biomass (8.1 Tons/acre)
    - 10,000 TPD C, 1,400 TPD H from cellulose
- Wind Energy
  - 5 $MW/km^2$ wind turbine density over 1600 square miles
  - 20 GW wind power potential (only need 5 to 7 GW for fuel)
- Electrolytic Hydrogen or Syngas
  - 3,300 TPD $H_2$ required for all biomass C to fuel
  - 1800 gpm net water consumption after rev-shift & FT
- Synfuel
  - 30,000 bbl/day biomass to liquids + 24 kTPD $CO_2$
  - Additional 58,000 bbl/day combining $CO_2$ and electrolysis
    - 4.7 GW with HTE or 6.5GW with water electrolysis

CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

# Synergies

- Grid Stabilization
  - Non-dispatch nature of wind/solar
    - Limits wind to small % of total generation mix
    - More nuclear for $H_2$ enables more wind for $H_2$
  - Dispatch controlled electrolysis loads
    - More power => more hydrogen => lower cell efficiency
    - Less power => less hydrogen => higher cell efficiency
    - Increase fraction of wind in total generation mix
- Transmission Backloading
  - Wind often at end of line, rural site
  - Co-locate load and production
  - Co-locate electrolysis and biomass gasifier

# Conclusions

- Hydrogen may be fined tuned via HTE to obtain desired $CO/H_2$ syngas ratio for fuel processing
- Source of pure, high temperature, oxygen greatly reducing nitrogen containing pollutants
- All process heat for HTE is supplied by gasifier
- If electricity is powered by non-fossil sources, the process is carbon neutral
- HTE technology may be scaled to small distributed biomass processing units to reduce transportation cost of biomass gathering
- Syngas production efficiencies between 70% to 80% may be achieved

CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

# Conclusions

- Over 90% of the carbon in the biomass is converted to syngas resulting in low carbon dioxide emissions during fuel processing
- Higher carbon-to-hydrogen ratios in the biomass provide for better carbon conversion
- Low mass heating value promotes a high syngas production efficiency