Electrolytic Hydrogen Production Workshop

Manufacturing and Scale Up Challenges

Joseph Hartvigsen

Ceramatec, Inc.

National Renewable Energy Laboratory

Golden, CO

February 28, 2014

CERAMATEC®

TOMORROW'S CERAMIC SYSTEMS

Antipode Assertions

- Electric power generation is not the limitation
  - To misquote Jay Leno "Use all you want, we'll make more"
  - http://atomicinsights.com/2013/02/use-all-the-electricity-you-want-well-make-more.html
- High electric costs come from working the demand curve from below rather than above
- "Grid Storage" is a misleading notion
  - Constrains thinking to electricity in / electricity out viewpoint
  - Instead of asking what is the most beneficial instantaneous use of excess capacity
- A broader thought framework is "energy currency arbitrage"
  - Need efficient, economical, intensive conversion paths
- Electric utilities aren't fixed with the right mindset for the job
  - Business model optimized for their industry's historical constraints

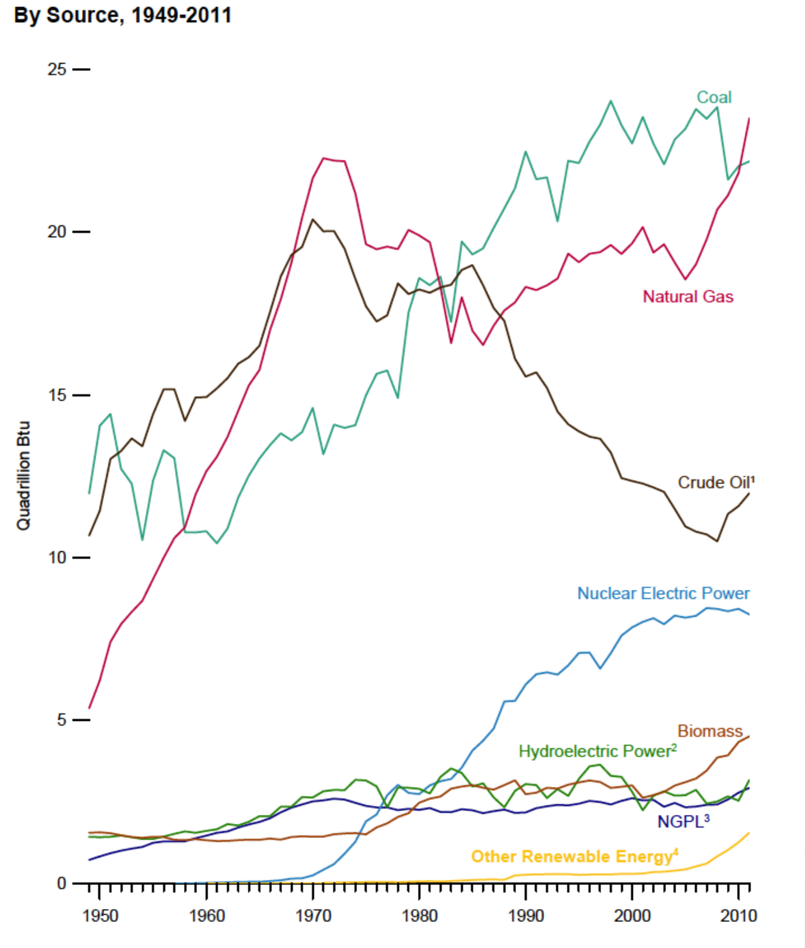
Renewable and Nuclear Power Grid Challenged

- Nuclear
  - PUC caps on profits
  - Risk averse utilities
  - Slow growth of grid demand
  - Rate payer opposition
    - Greater opposition in major urban centers with large loads
    - Bonding Whoops! (Specter of WPPSS ‘83 $2.25B bond default)
- Renewable
  - Dispatchability
    - Grid stability
    - Costly reserve requirements
    - Wind out of phase with diurnal load min-max
  - Transmission
    - Resource remote from load (population) centers
    - Transmission permitting difficult and construction costly

Energy Resources, Incl. RE, Are Abundant

- 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
    - Agricultural & Forestry residues
    - Carbon neutral cycle assuming production and processing are carbon free
- Nuclear
  - Increased output of existing units
    - Note trend in figure since 1970
- Hydrogen from electrolysis requires
    - 42-54 MW-hr/ton for water electrolysis
      - 18 to 24 tons/GW-hr
    - 34 MW-hr/ton for steam or co-electrolysis
      - 29 tons/GW-hr

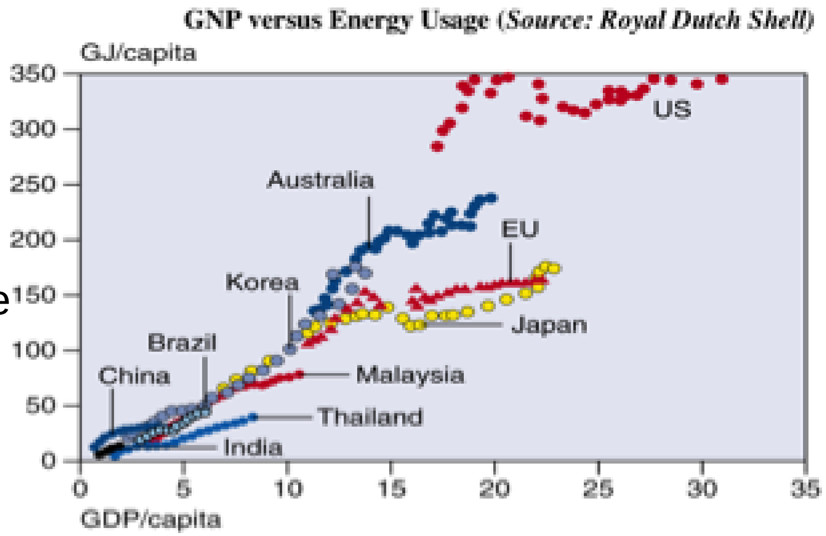
http://www.eia.gov/totalenergy/data/annual/archive/038411.pdf p6



CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

… but problematic, and the key to prosperity

- 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
- Regional resources may be limited
  - Oil
    - National security
  - Gas
    - Heating vs. power generation
    - Transportation issues
  - Renewables
- Energy as the key to prosperity
- Questions to consider



"Energy is not a necessary evil. Energy is good"
Sen. Lisa Murkowski (R-Alaska)
http://thehill.com/blogs/blog-briefing-room/news/282053-murkowski-energy-is-good#ixzz2PPJKOKVL

Which energy segment is most vulnerable?

- Electric generation
- Electric transmission
- Electric storage
- Carbon dioxide emissions
- Transportation fuels

CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

Which poses most severe economic penalties?

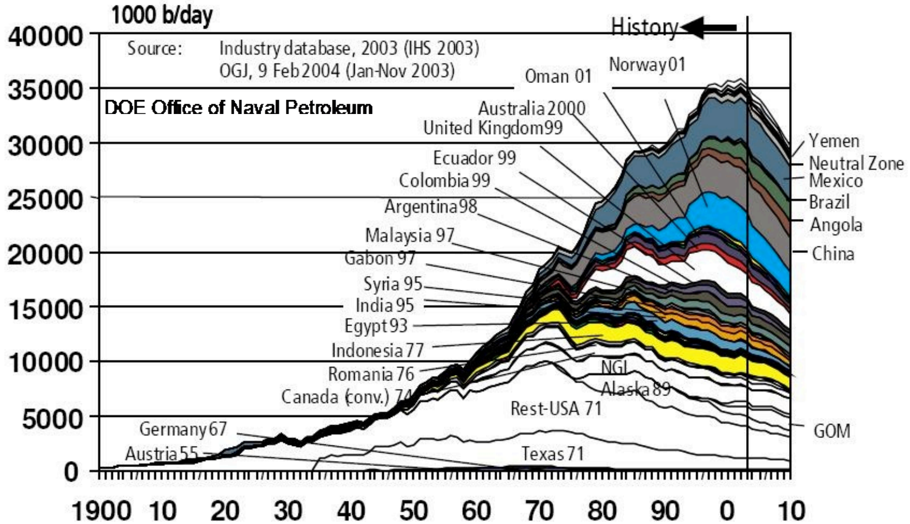
- Electric generation
- Electric transmission
- Electric storage
- Carbon dioxide emissions
- Transportation fuels

Where are energy's "golden" opportunities?

- Carbon dioxide sequestration
- Electric transmission
- Renewable energy
- Electric storage
- Hydrogen
- Transportation fuels

Petroleum Production

- The Most Successful Business Model in History
  - Climate Change
  - Global Destabilization Effects
  - Resource Limit
  - Demand Growth



- Why are hydrocarbons so valuable?
- What Next?

CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

Liquid Hydrocarbon Energy Storage Density

- Energy Density
  - JP-8 43 MJ/kg, 0.76 to 0.84 kg/liter
  - Diesel 42 MJ/kg, 0.86 kg/liter
  - Hydrogen at 690 bar (10,000 psi) Z=1.43
    - 4.4 MJ/liter (min. work of compression is 10-12% of LHV)

~1 MW-month on one tank truck

- Established markets for liquid fuels
  - US demand, 6.3 billion bbl/yr, >$600 billion/yr
  - Highly developed infrastructure
  - Existing vehicle fleet
- Liquid fuel's value commands a premium

23 MW, 2 minute "Recharge"

Liquid Hydrocarbons = High Value Density

- Carbon value strongest for light liquids
  - CO_2 -\$55/ton (Norway C tax)
  - Coal \$10 - \$65/ton (transportation cost dominate)
  - Natural Gas \$250/ton carbon (\$4/decatherm)
  - Bitumen ~ \$400/ton (50% Bitumen/WTI Crude)
  - Crude Oil \$800/ton carbon (\$95/bbl)
  - Refined fuel (pre-tax) ~\$1100/ton carbon

Hydrogen is not an energy dense storage medium,
but is used to synthesize energy and value dense hydrocarbons

Synfuels Historical Perspective

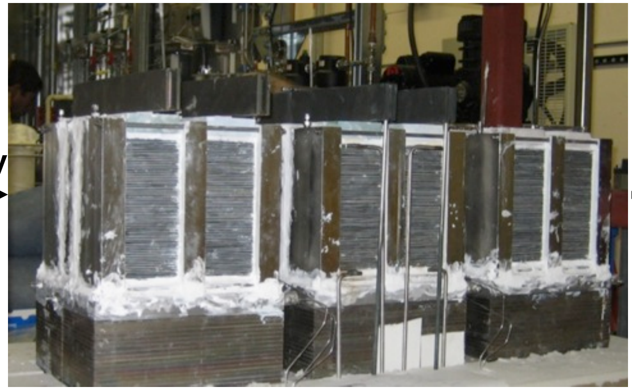
- Fischer-Tropsch Synthesis
  - First commercial plant in Germany, 1936
  - Continuous commercial operation in South Africa since 1955
    - Secunda plant is CTL
    - Also operate GTL
  - Shell GTL in Malaysia
  - Newer plant in Qatar (Oryx)
  - Primarily large scale CTL & GTL
- Syngas production cost ~5/6 of total
- Syngas conversion cost ~1/6 of total
- Challenge: *Produce a small scale plant at same cost per bpd capacity as large plant*

New Electric Energy Storage Paradigm
Electricity In, Storable & Transportable Fuel Out

Steam + CO_2

Renewable Electricity

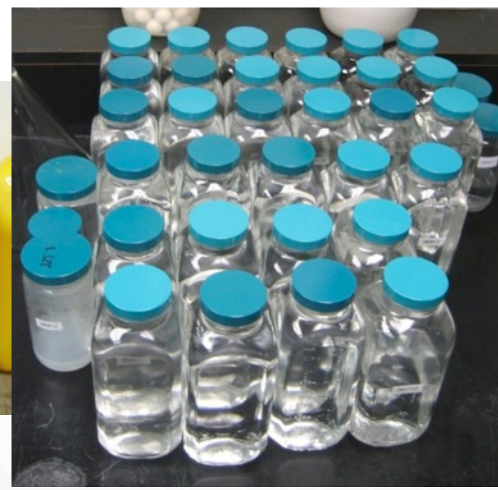
Solid Oxide Electrolysis Stacks



Syngas

Compression & Storage

Fischer Tropsch Reactor



FT Liquid & Wax Products

- Cetane 60.2 by ASTM D613
- FT 46.5 MJ/kg vs. diesel 46 MJ/kg & B100 FAME 40 MJ/kg

Various aspects of this work have been supported by the DOE (INL), ONR and State of Wyoming

Ceramatec Syngas Compression Skid

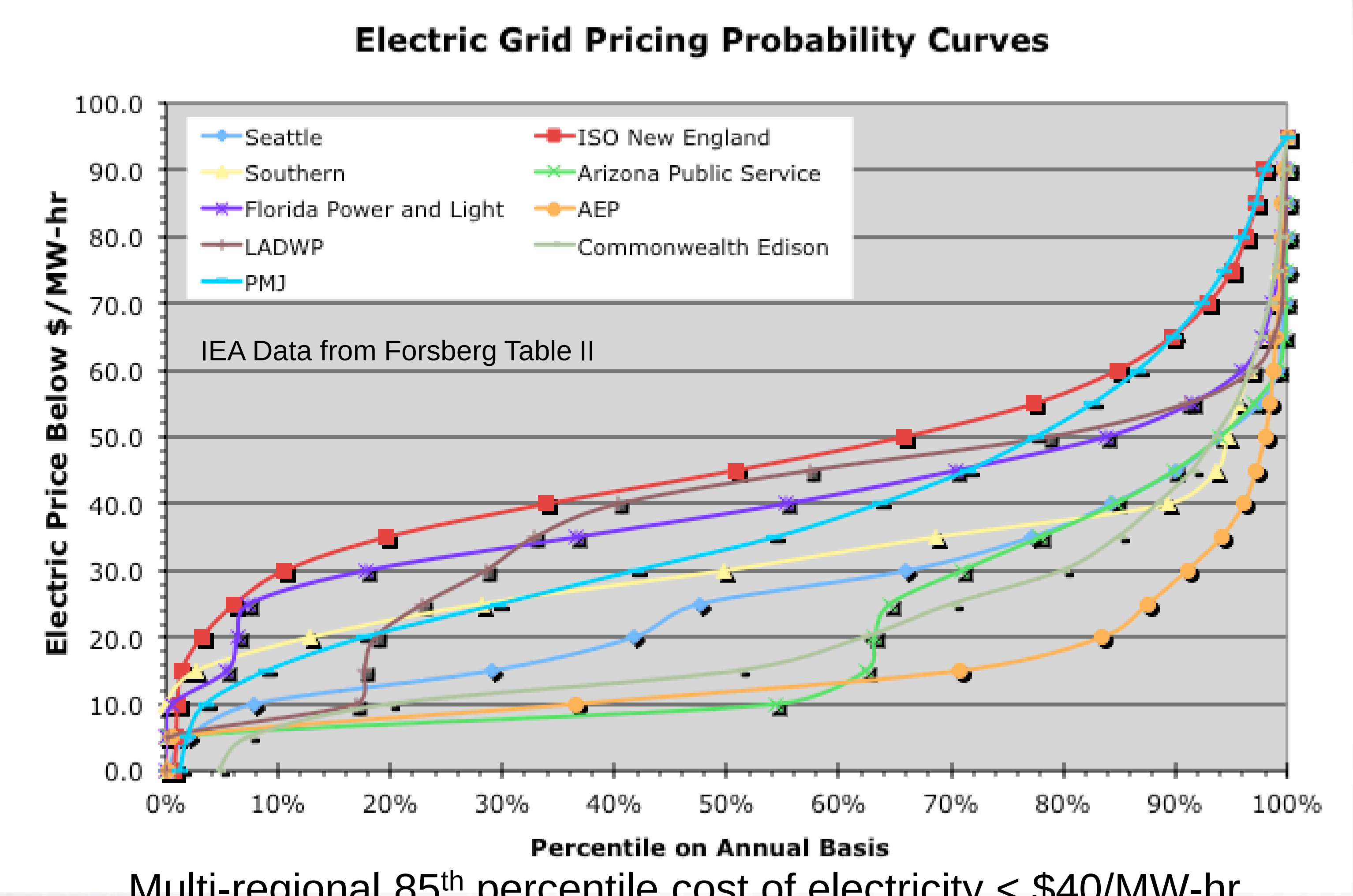
Syngas capacity: 100 SCFM (2 bbl/day)

Ceramatec 4 Inch FT Reactor Test Loop

- Scaled up approach from 1-1/2" reactor
- Single 4" Fixed Bed FT
- Thermal management structure
- Dual mode cooling loop
- Simplified flowsheet
- 5-10 gal/day
- Prove key technologies of 10 bbl/day pilot plant design
- Nearing commissioning

CE
TOMOR

Electric Power Costs Low Enough For H_2



Multi-regional 85th percentile cost of electricity < $40/MW-hr

Many H_2 cost models assume $70/MW-hr, 95th percentile of high cost regions

CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

H_2/Synfuel Market Size 3.5x > Grid Power

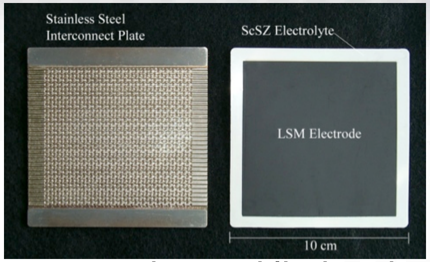
Electrolysis 1.285 V $40/MW-hr Syngas cost $90/bbl	**Annual Electrical Energy Demand GW-hr**	**Petroleum equivalent k-bbl**	**H_2/Synfuel electric energy as ratio to current demand**
Conventional Electric Load	4,119,388 47% of Capacity	1,801,874	1x 470 GW
US Crude Oil Imports		3,580,694	2x 940 GW
US Crude & Refined Imports		4,726,994 **$900k/min @ $97/bbl**	2.6x 1,220 GW
US Crude Oil Refinery Inputs		5,361,287	3.0x 1,410 GW
US Crude & Refined Refinery Inputs		6,277,893	3.5x 1,650 GW

http://tonto.eia.doe.gov/dnav/pet/pet_sum_snd_d_nus_mbbl_a_cur.htm
http://www.eia.doe.gov/cneaf/electricity/epa/epates.html

Grid stability restricts wind to ~ 1/6 of load, requires costly reserves, new transmission

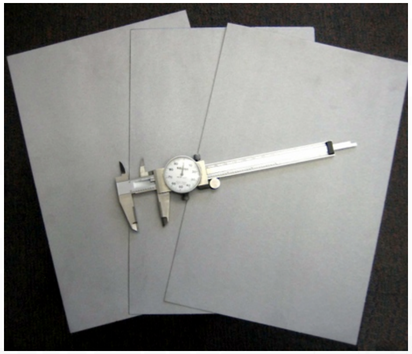
1000 GW Market with kW Stacks?

- Forecourt H_2 station of 1500 kg/day
  - 2.2 MW Electric power demand
  - 232cm^2 cell active area, 300 mA/cm^2
  - 23,800 cells (238, 9.1 kW 100 cell cell stacks)
  - Stack cost well under $200/kW
  - Plumbing and wiring costly … but possible?
- Central Hydrogen Plant of 50,000 kg/day
  - 72 MW Electric power demand
  - Approaching 8000 stacks or 800k, 232cm^2 cells
  - How to plumb and wire 8000 stacks?
  - Or … 184 stacks of 1m^2 (10,000cm^2) active area cells
- Need large format SOEC stacks for Central H_2



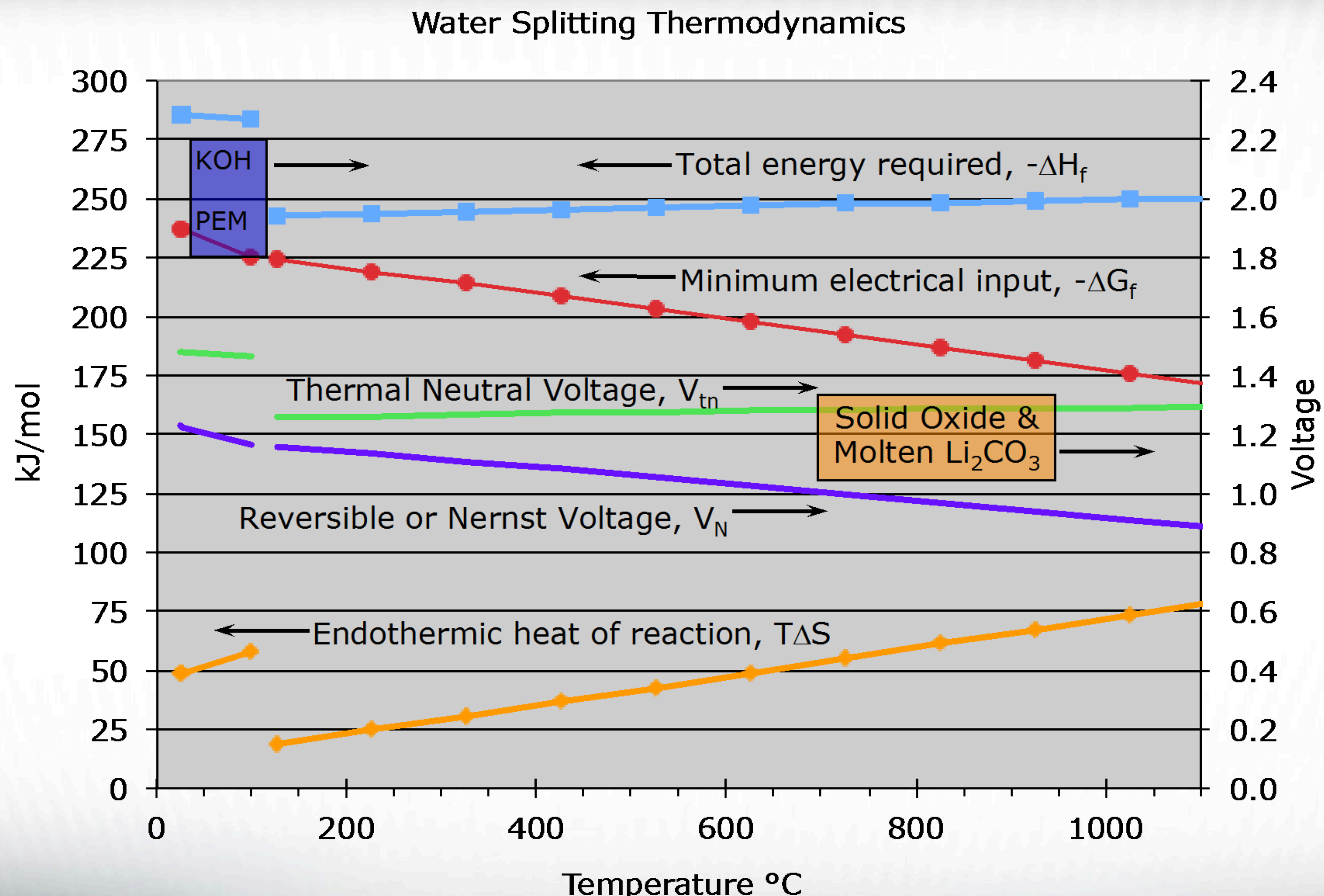
Tape cast sintered limits size

720 cell 12-stack module

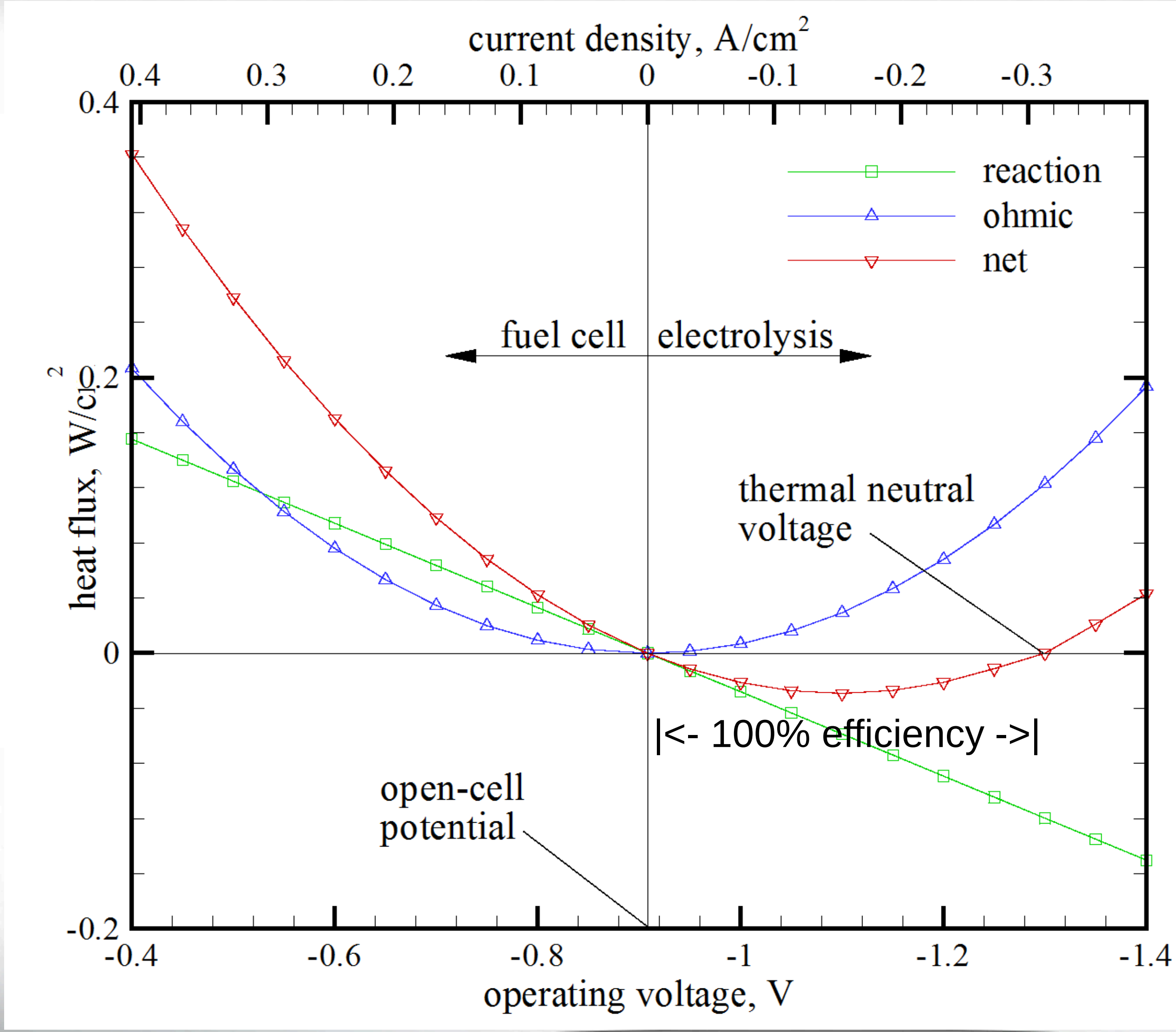


Sintered stainless supported 1 m^2 cells?

Thermodynamics Drives Efficiency at High Temperature



SOEC Endotherm Recuperates Resistive Losses



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

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

Steam Electrolysis
V_{tn} = 1.291 V at 1200 K

50:50 Co-Electrolysis
V_{tn} =1.376 V at 1200K

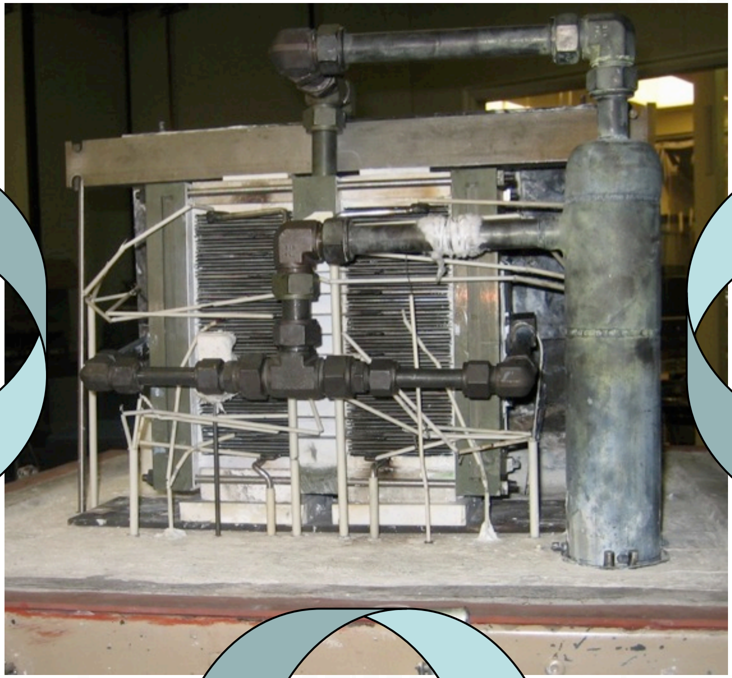
One Technology - Multiple Modes Of Operation

Solid Oxide Stack Module

NG
Biogas
Diesel
JP-8
Coal

Fuel

Electricity



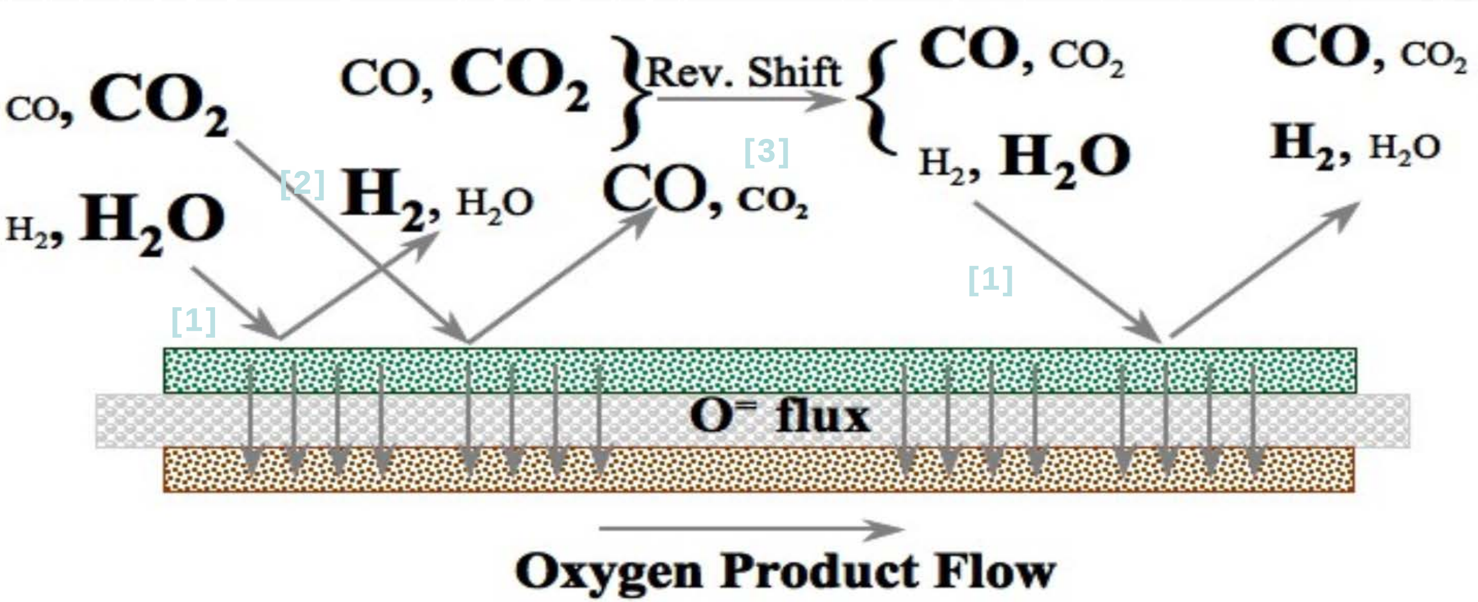
Syngas

CO_2 & Steam
+ Electricity

Steam + Electricity

Hydrogen
(High Purity)

Syngas by Combined Steam and CO_2 Electrolysis

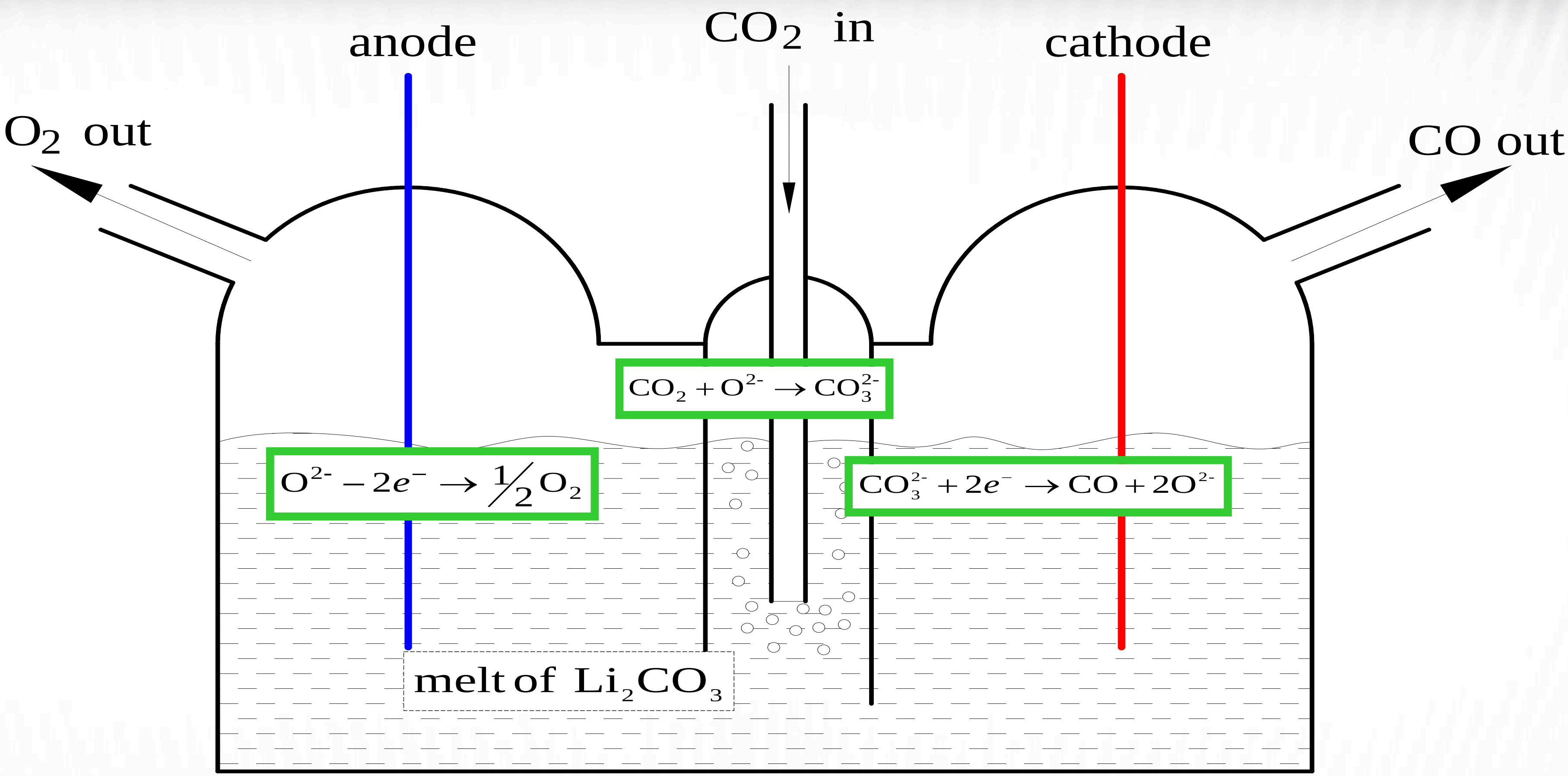


$H_2O + 2e^- \rightarrow H_2 + O^{2-}$	(electrolysis of steam)	kinetics favored	[1]
$CO_2 + 2e^- \rightarrow CO + O^{2-}$	(electrolysis of CO_2)	kinetics slower	[2]
$CO_2 + H_2 \leftrightarrow CO + H_2O$	(reverse water gas shift)	kinetics fast	[3]

Reverse shift reaction: $CO_2 + \Uparrow H_2$ <==> $CO + \Downarrow H_2O$
As steam is consumed and H_2 produced, the RWGSR converts CO_2 to CO

CO_2 electrolysis is as easy and efficient as steam electrolysis

Scalable Alternative High Temperature Electrolysis Route



Thermal neutral voltage: 1.46V/cell

Faradaic efficiency: 100 %

Thermodynamic efficiency: 100%

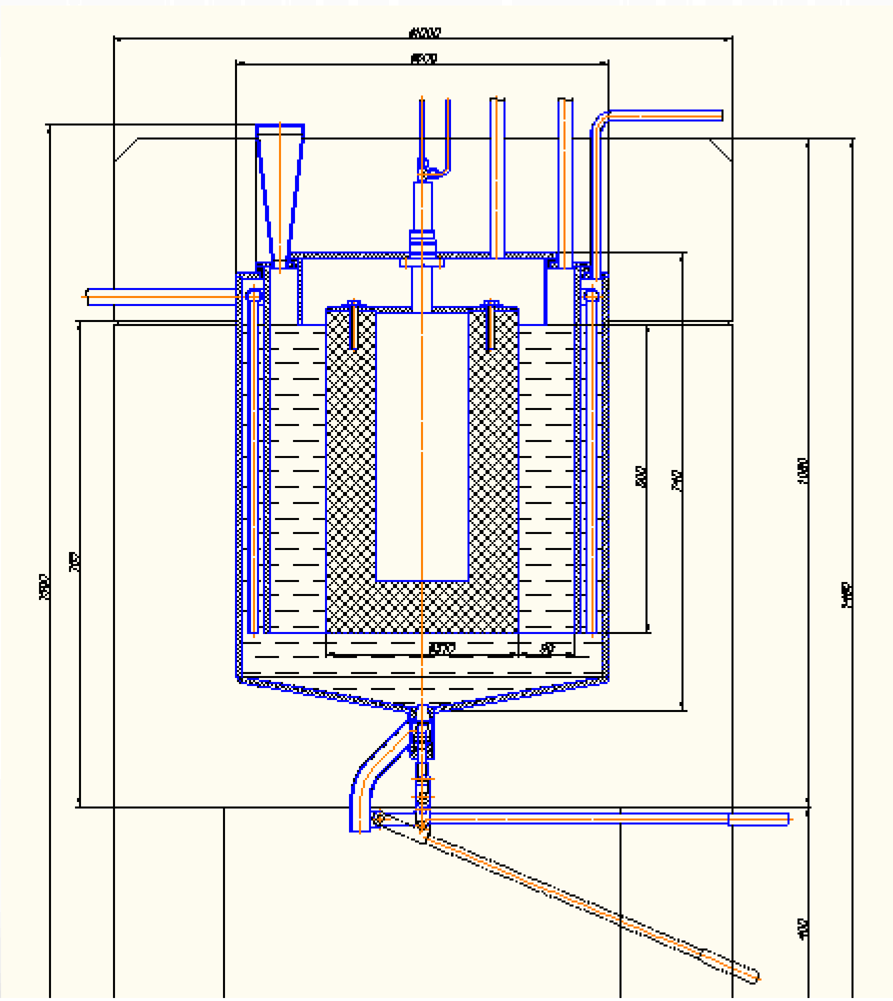
Cell voltage: 1.05±0.05V

Current density: 100 mA/cm^2

No Degradation in 700hr test

High Temperature Molten Salt Cells for Large Area

Ceramatec Initiated Collaboration With Weizmann Institute



(5 kA) prototype CO_2 electrolysis Li_2CO_3 cell constructed and tested by Campustech Ltd

Estimated Synfuel Cost Contribution

- Drop in synthetic fuel cost contribution
  - $100 - $120/bbl electrolysis cost ($40-$50/MW-hr)
  - $6.75/bbl FT reactor & catalyst
  - $12/bbl transportation of product & CO_2
  - ($10/bbl) avoided CO_2 tax at $25/ton CO_2 – or –
  - ($42/bbl) biodiesel tax credit at $1/gal
- $81-$123/bbl depending on
  - Electric rates (dominate cost factor)
  - CO_2 policy (carbon tax or biofuels tax credit)
  - SOEC & FT CAPEX secondary

Wind+Biofuels Production, 40x40 mile basis

- Biomass Feedstock
  - 22,700 TPD biomass (8.1 annualized dry 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
- Synfuel
  - Baseline 30,000 bbl/day biomass to liquids + 24 kTPD CO_2
  - Additional 58,000 bbl/day by wind electrolysis of CO_2
    - Wind: 4.7 GW with SOEC or 6.5GW with water electrolysis

The Electrolytic Synfuel Solution

- Electrolysis efficiency – 100% shown in practice
- Process negates RE shortcomings
  - Intermittency
  - Stranded due to limited transmission reach & capacity
- Efficient, concentrated, RE storage technology
  - 36 MJ/liter
  - 21-26 MW-days storage in a 10,000 gallon tank trailer
- Utilize all carbon content in BTL, CTL, & CC sys
- FT needs 20 bar comp. vs. 700 bar H_2 FCV
- Product compatible with existing dist. & vehicles
  - 20 to 50 years to retire existing fleet

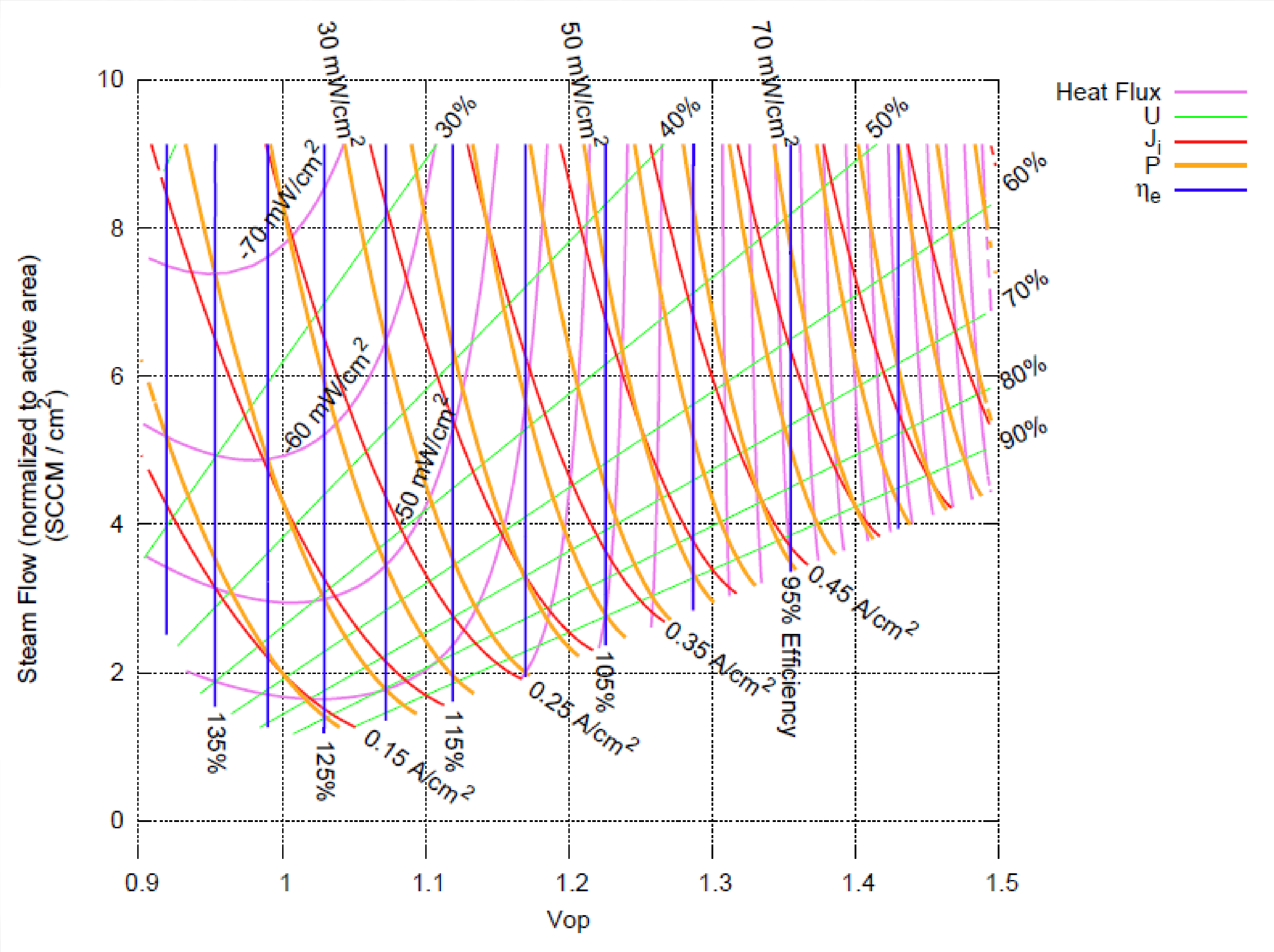
Parametric Techno-Economic Analysis

- Based on Ceramatec published SOFC TEA (SSI-12)
- Set steam flow and utilization at operating point
- Calculate parameters using performance model
  - V_{op}, $j_i(U, V_{op})$, $P(U, V_{op})$, and η_{stack}
- Size and price the stack based on operating conditions
- Determine steam flow to reach desired capacity
- Size and price insulation vs. heat requirement
  - Price insulation
  - Calculate heat loss through insulation
  - Update auxiliary heat requirement
  - Increment insulation until combined insulation and auxiliary heat cost minimum is determined

Techno-Economic Model

- Set steam flow and utilization at operating point
- Calculate parameters using performance model
  - V_{op}, $j_i(U, V_{op})$, $P(U, V_{op})$, and η_{stack}
- Size and price the stack based on operating conditions
- Determine steam flow to reach desired capacity
- Size and price insulation vs. heat requirement
  - Price insulation
  - Calculate heat loss through insulation
  - Update auxiliary heat requirement
  - Increment insulation until combined insulation and auxiliary heat cost minimum is determined

SOEC Performance and Cost Map Space



Variations in operating voltage and reactant flow space

Notaton

$\overline{E_N}(U)$	Average Nernst potential
η_{stack}	Stack efficiency
V_{tn}	Thermoneutral voltage
U	Steam utilization
j_f	Steam limiting current density
j_i	Stack current density
ΔV_f	Driving potential
V_{op}	Operating voltage
R''	Area specific resistance
$\dot{n}$	Steam molar flow rate

Electrolysis Equations

- Stack efficiency $$\eta_{stack} = \frac{V_{tn}}{V_{op}}$$
- Thermal neutral voltage $$V_{tn} = \frac{\Delta H}{nF}$$
- Steam utilization $$U = \frac{I}{\dot{n} n F}$$

Model Development

- Steam flow specific current density

$$j_f = \frac{\dot{n} n F}{A}$$

- Driving potential required to fully utilize steam
  - Difference between V_{op} and average Nernst potential $\overline{E_N}(U)$

$$\Delta V_f = j_f R''$$

- Nernst potential as a function of utilization

$$E_N(U) = E^\circ + \frac{RT}{nF} ln\left(\frac{U \cdot O_2^{1/2}}{1-U}\right)$$

CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

Model Development

- Average Nernst potential

$$\overline{E_N}(U) = \frac{\int_{U_\circ}^{U} E_N(U)dU}{U}$$

- $\overline{E_N}(U)$ is easily evaluated. However, we cannot obtain the inverse function to solve for U

Model Parameterization

- Steam utilization can be expressed in terms of the full utilization potential and the difference between the Nernst and operating potentials.

$$U = \frac{V_{op} - \overline{E_N}(U)}{\Delta V_f}$$

- U cannot be explicitly obtained

- Therefore, we parameterize in V_{op} and U

Operating point solution in (U, V_{op})

- Steam flow

$$\Delta V_f(U, V_{op}) = \frac{V_{op} - \overline{E_N}(U)}{U}$$

- Current density

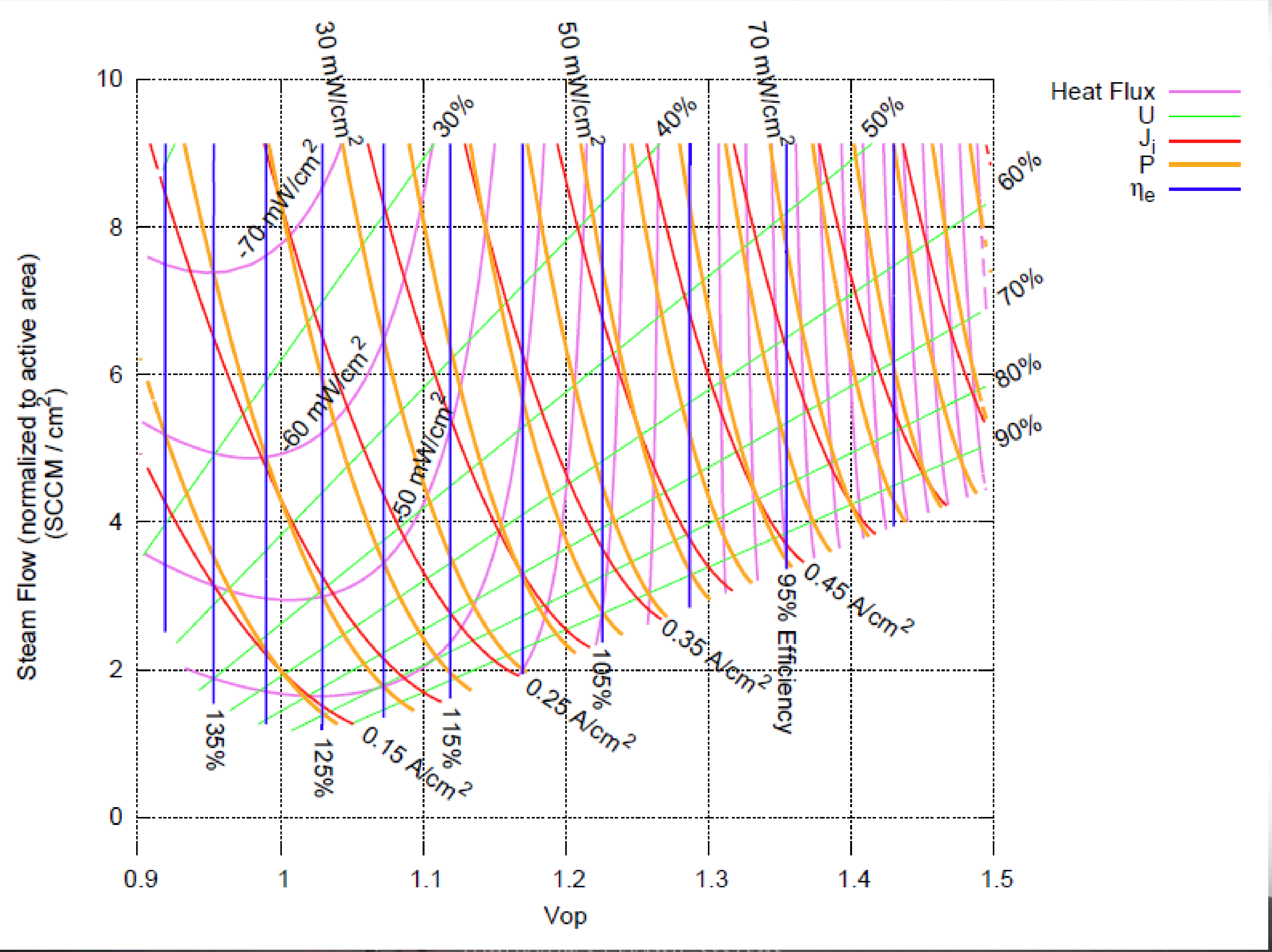
$$j_i(U, V_{op}) = \frac{V_{op} - \overline{E_N}(U)}{R''}$$

- Efficiency

$$\eta_{stack}(V_{op}) = \frac{V_{tn}}{V_{op}}$$

CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

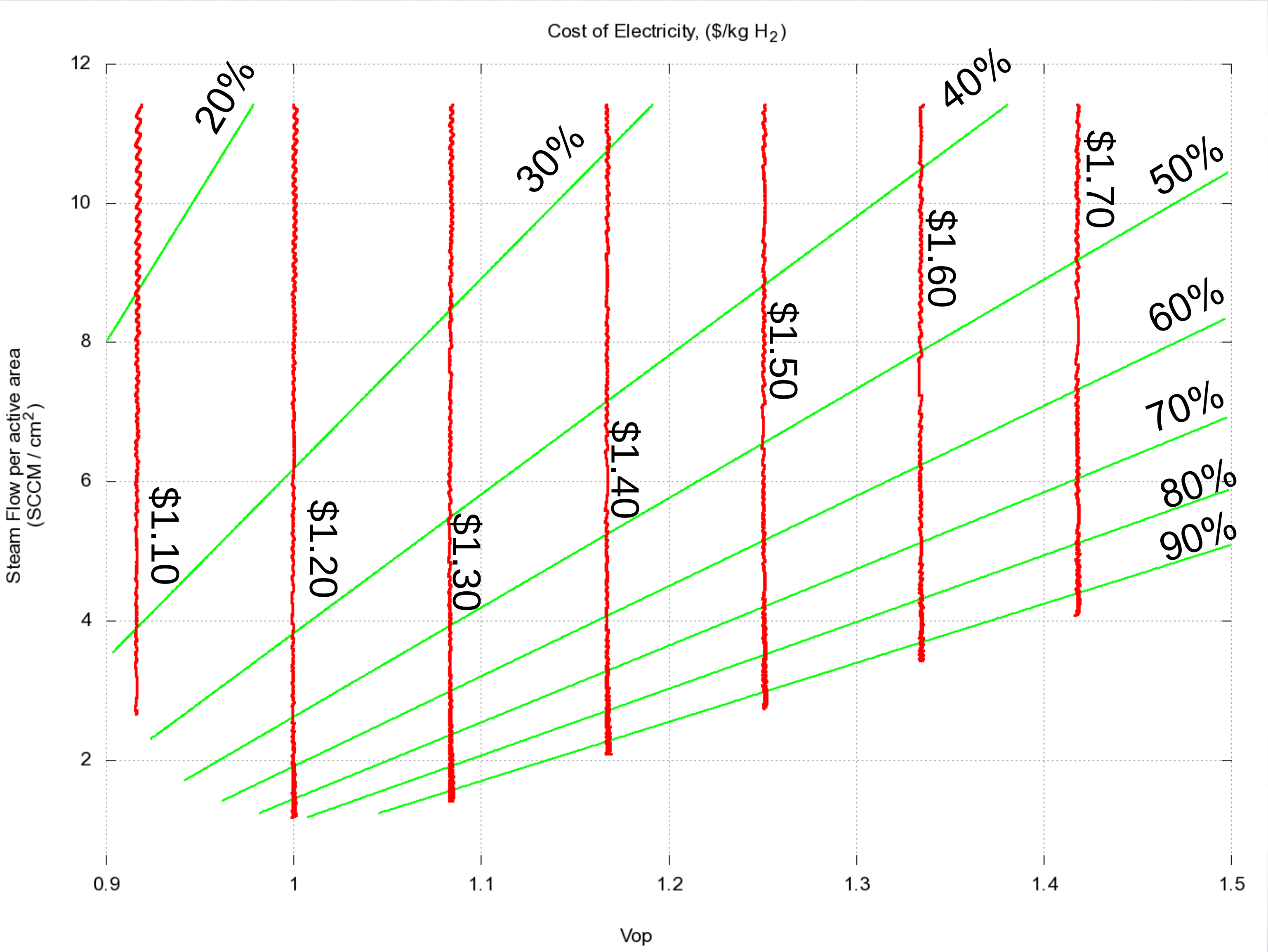
SOEC Performance Map



Economic Model (cont.)

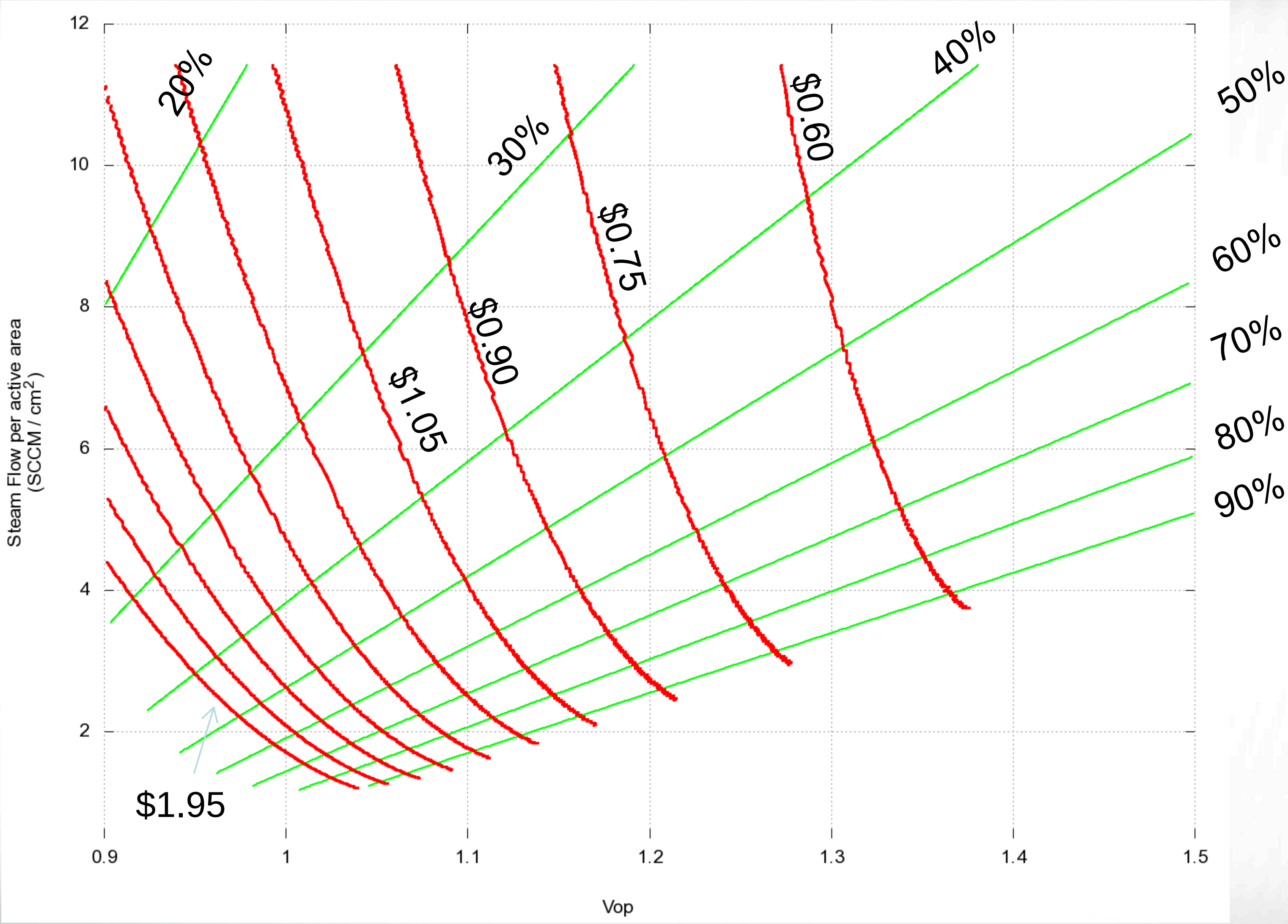
- Map total cost of $H_2, \left[\frac{\$}{kg}\right]$
- Map capital contribution to total cost
- Map auxiliary heat contribution to total cost
- Map electricity contribution to total cost

Electricity contribution [$/kg]



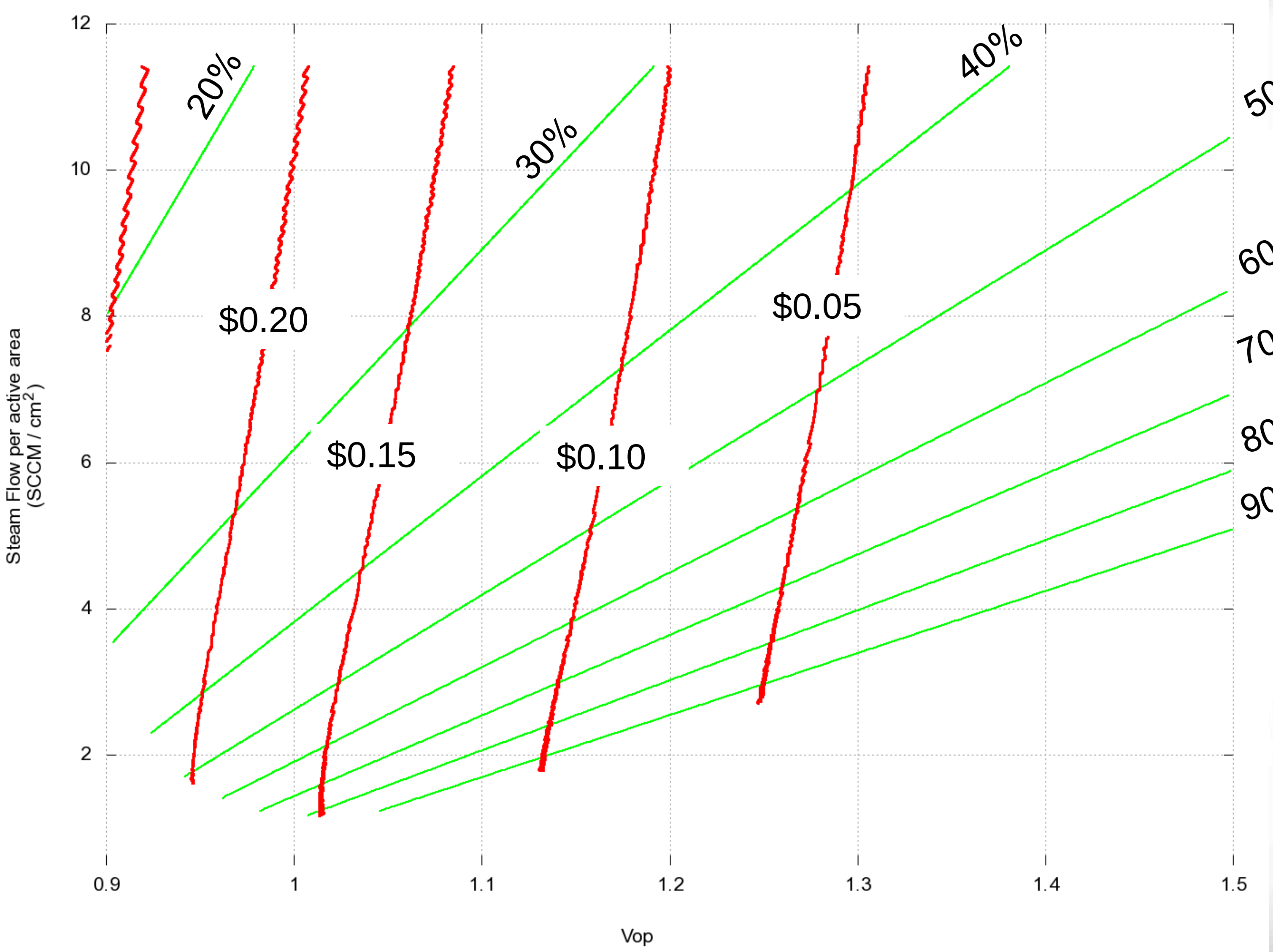
CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

Capital cost contribution [$/kg]



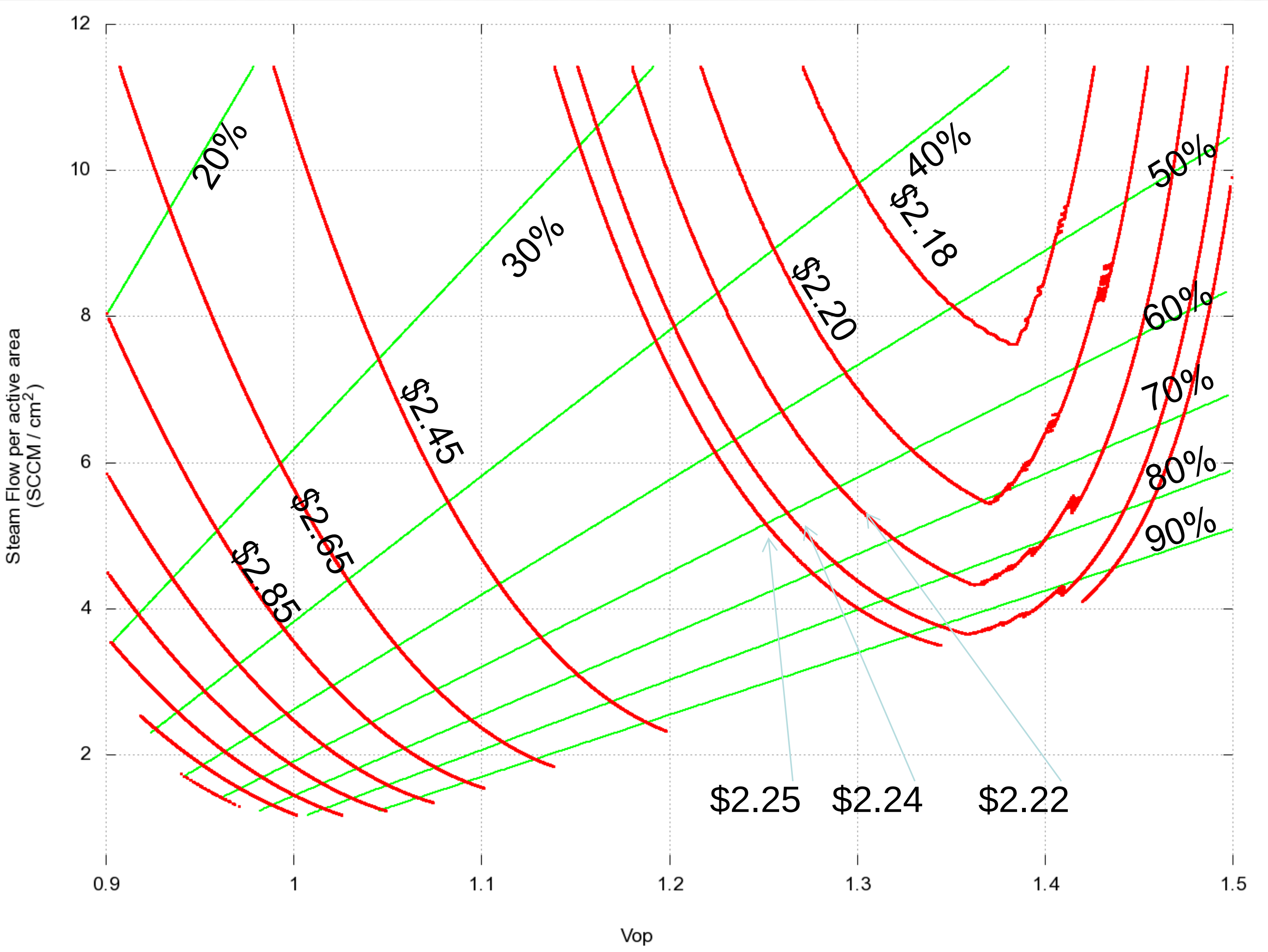
CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

Cost of Auxiliary Heat [$/kg]

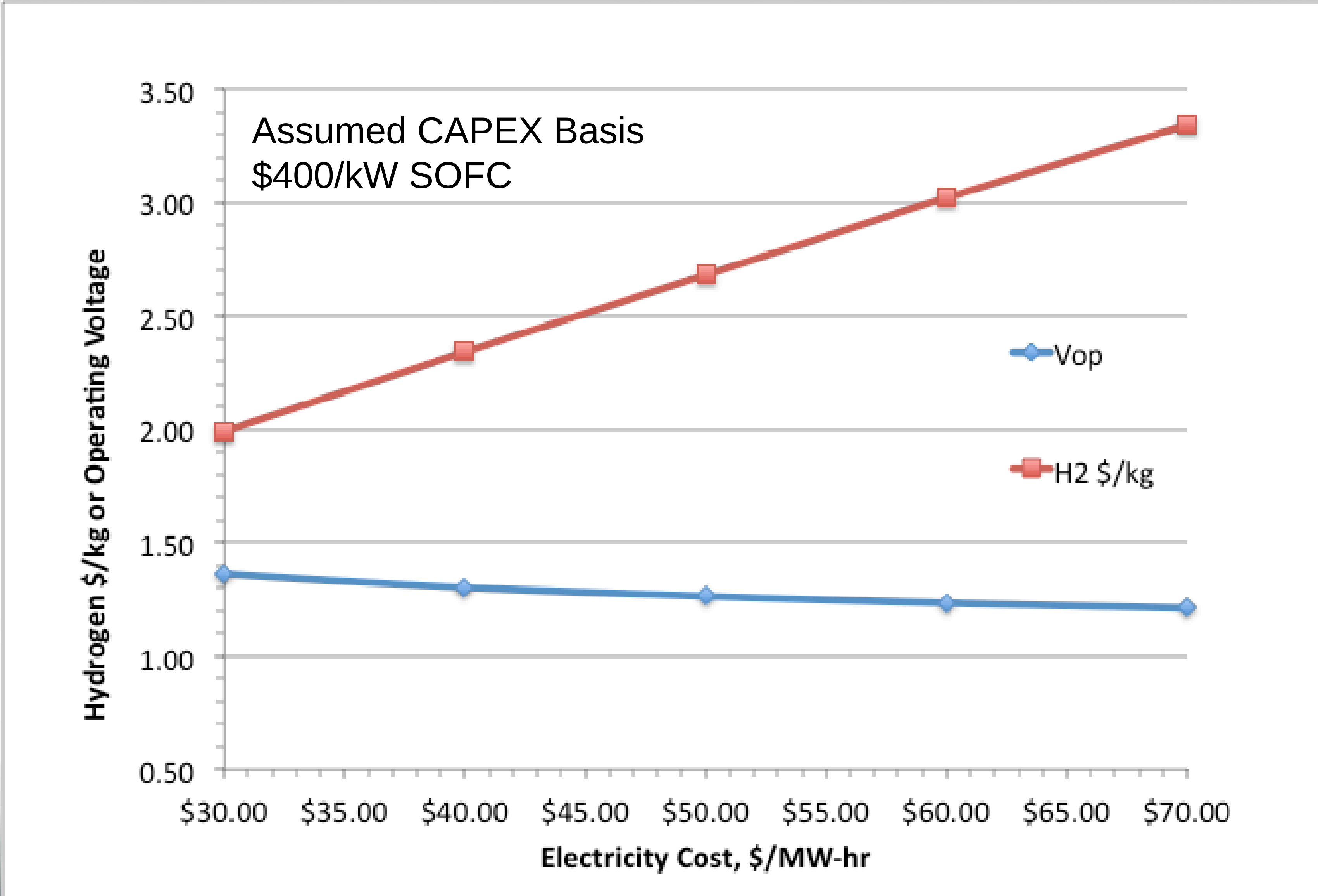


CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

Total cost of H_2 [$/kg]

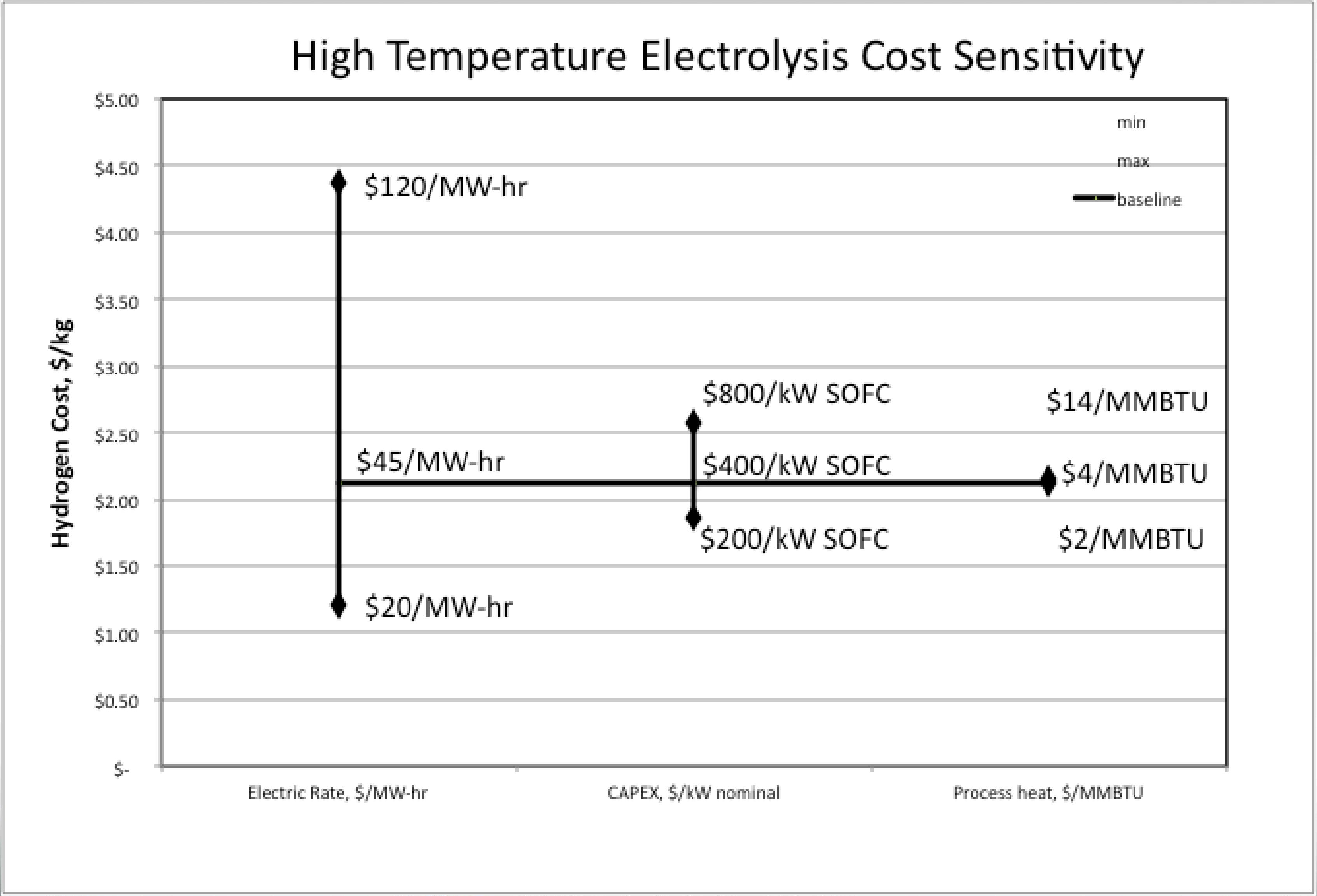


Optimal Vop vs. Electric Price



CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

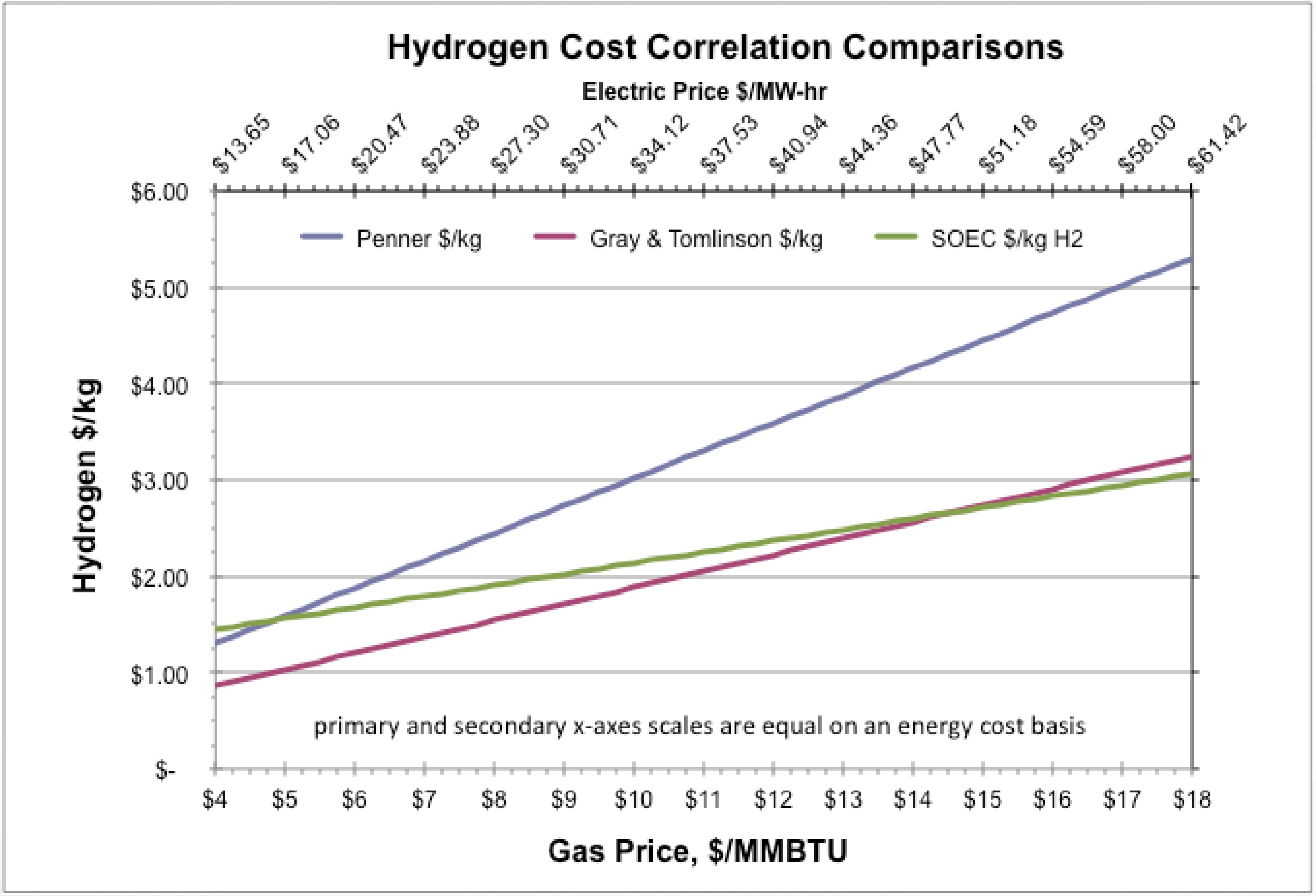
Electrolysis H_2 Cost Model Sensitivity



CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

Electrolysis Cost Comparison

With SMR Cost Correlations



With comparable energy costs, SOEC H_2 cheaper than SMR H_2

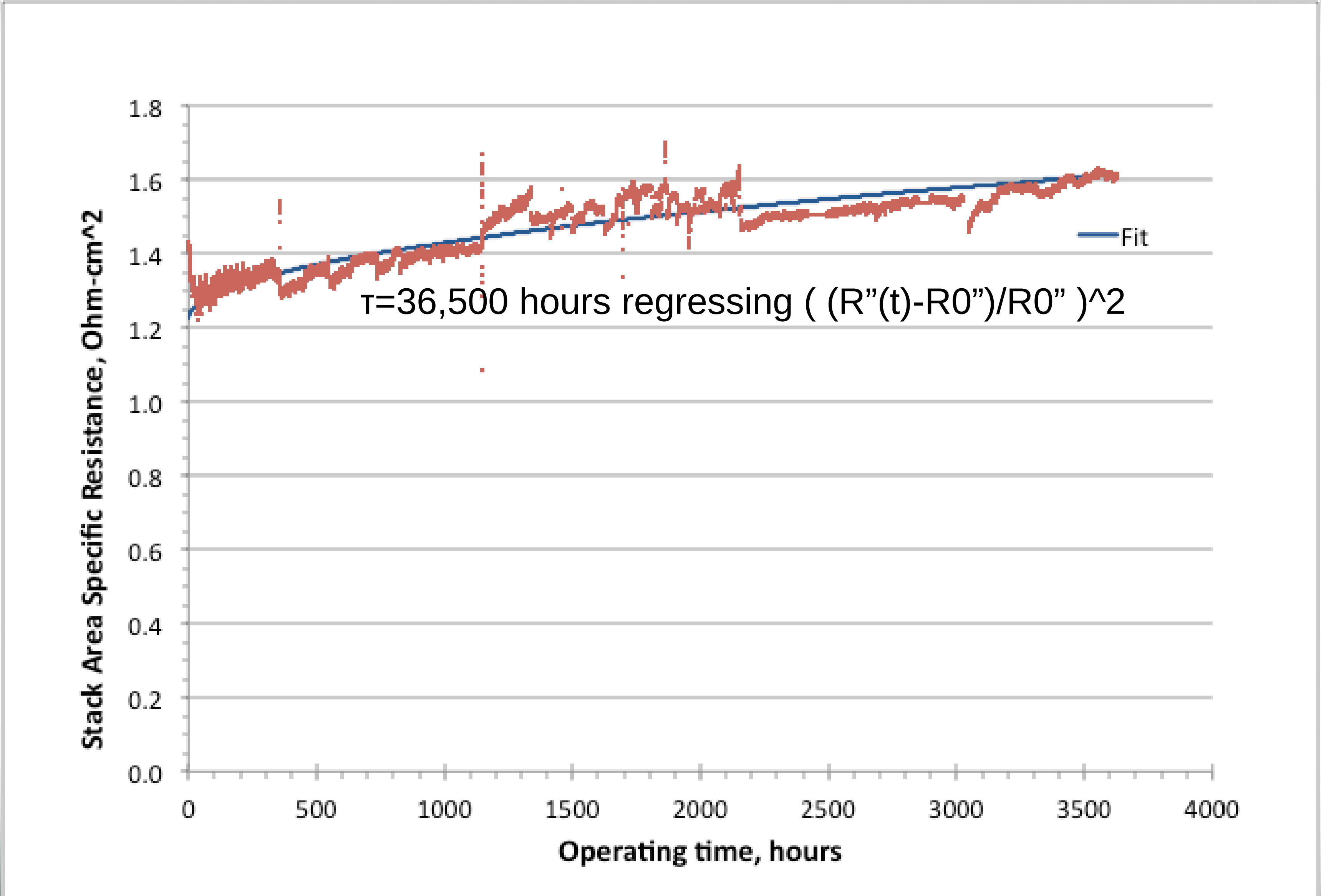
Degradation & Lifetime Model

- Diffusion limited degradation processes
  - Oxide scale growth
  - Cation interdiffusion & reaction layers
- Leads to a parabolic rate law
  - $R''(t)=R0''*(1+\mathrm{sqrt}(t/\tau))$ where tau is time to double area specific resistance
- Integrate $1/R''(t)$ for ave lifetime production
  - Integration substitution variable $U=1+\mathrm{sqrt}(t/\tau)$
  - Lifetime fraction of initial production rate

$$2*(U-\ln(U)-1)/(t/\tau)$$

CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

Fit to Stack With Low Degradation



CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

Economic model assumptions

- BOP: based on SECA target of $400/kW SOFC operated at 0.7 V, scaled to 1.3 V SOEC
- Ground up mfg cost model substantially lower $/kW
- Insulation: $2180/m^3
- Heat Exchanger: $400 /m^2
- Electricity: $45/MW-hr
- Auxiliary heat: $4.50 per 10^6 BTU
- Depreciation: Stack 24k hours, BOP 10 years, 10% continuous ROI
- Duty factor: full load 8600 hours/year

CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS