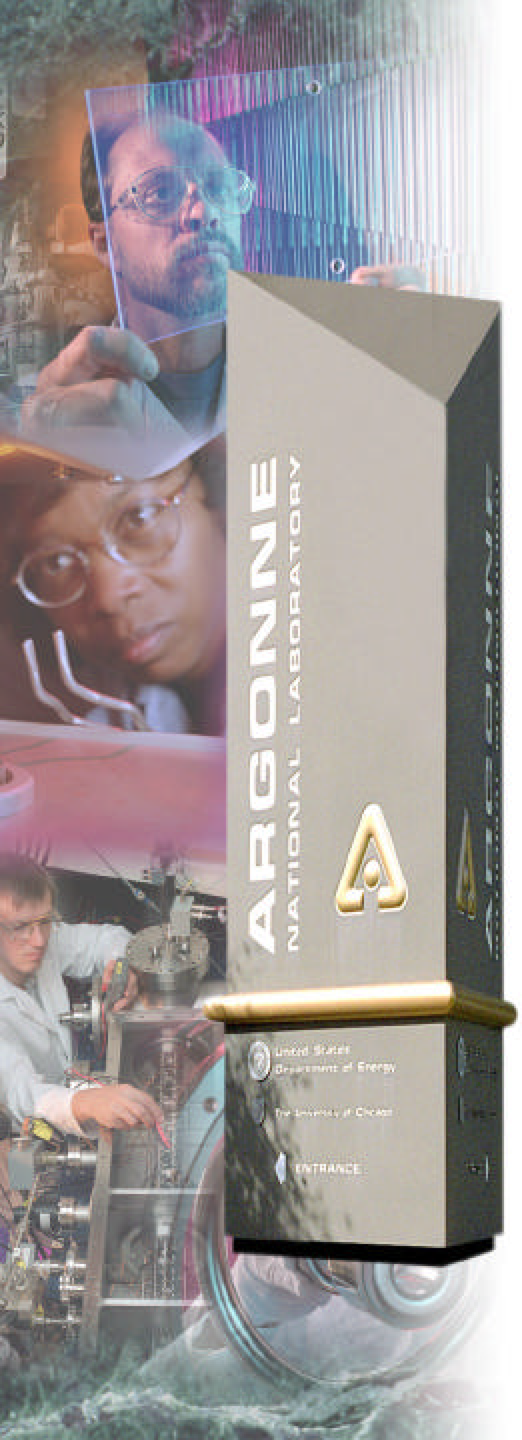

High-Temperature Electrolysis

Richard Doctor, Diana Matonis, Robert Lyczkowski
DOE Solar-Hydrogen Workshop
UMUC Conference Center – Adelphi, MD
9-10 November 2004

Argonne National Laboratory

Office of Science
U.S. Department of Energy

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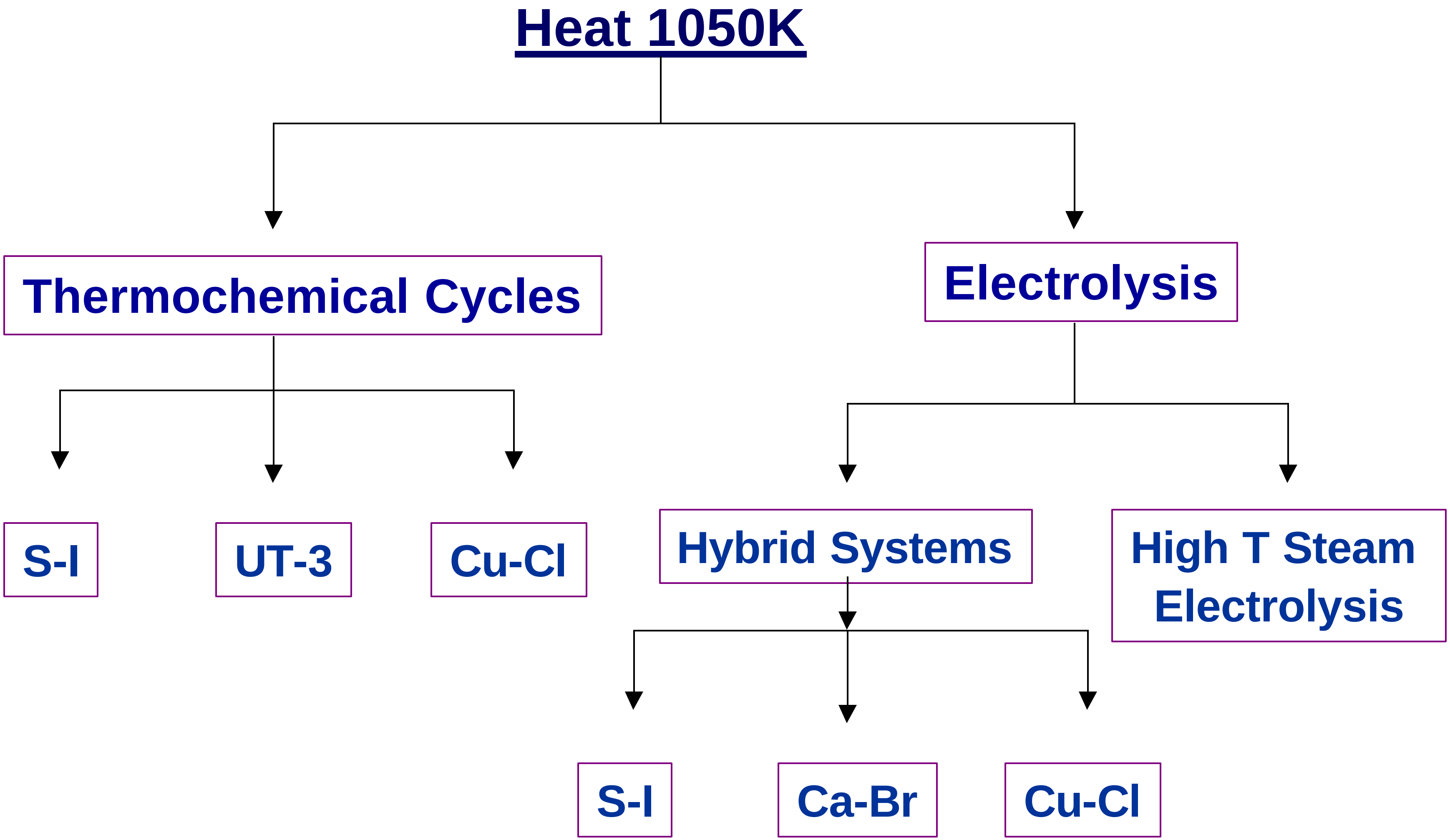
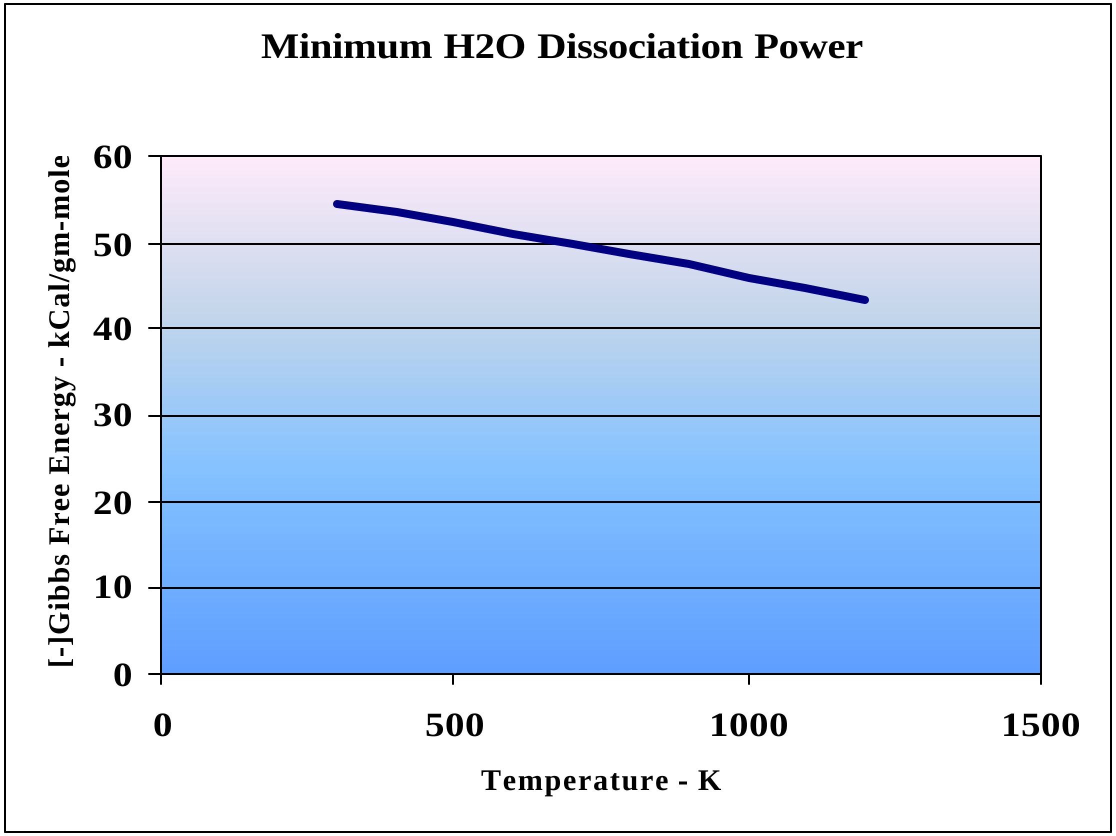
Evaluation of Cycles for Hydrogen Production



High-Temperature Electrolysis for Hydrogen Production - Materials

- **Drivers for High-temperature electrolysis:**
  - Oxygen is the charge carrier, rather than hydrogen – this requires high temperatures, but no use of strategic metals
  - Low-footprint for this system, it is adaptable to many scales
  - Highest efficiency for electrolysis

Higher temperatures for steam electrolysis are one contributor to reduced power demands



High-Temperature Electrolysis for Hydrogen Production - Materials

- **(1) coordinate with the experimental work at INEEL that will demonstrate the improvements in performance for a high-temperature steam electrolysis system operating at up to 1,000 K and assure that the data required to conduct a detailed process design study are linked into an ASPEN-based process design**
- **(2) consider the issues affecting the long-term performance of electrolyzer cells in this service**
- **(3) consider the requirements for producing and handling reagent-grade water that will be employed for these cells, starting from a base of available non-potable water at the production facility site**

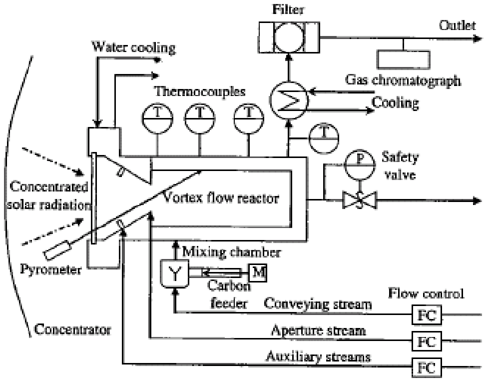
High-Temperature Electrolysis for Hydrogen Production - Materials

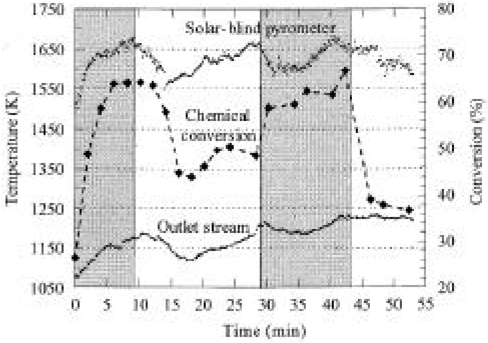
- **(4) examine the technological features as they link to process economics, surveying what would be needed to achieve commercial viability using these technologies, particularly the appropriate scale of operations**
- **(5) perform life-cycle emissions evaluations to quantify the reductions that can be achieved by using these technologies.**

OBJECTIVES – High Temperature Electrolysis

- **Optimize Hydrogen Production**
  - Choice of process
  - Optimize materials and operating conditions
- **Optimize Overall Plant System**
  - Integrate selected process into balance of plant
  - Heat Recuperation from product streams
    - *Perform a energy/pinch analysis*
  - Perform an overall efficiency analysis of plant.
- **Cooperative program with INEEL**

Linkage of steam-electrolysis to a solar energy system will improve scalability and economics





Hirsch and Steinfeld, Paul Scheer Institute in

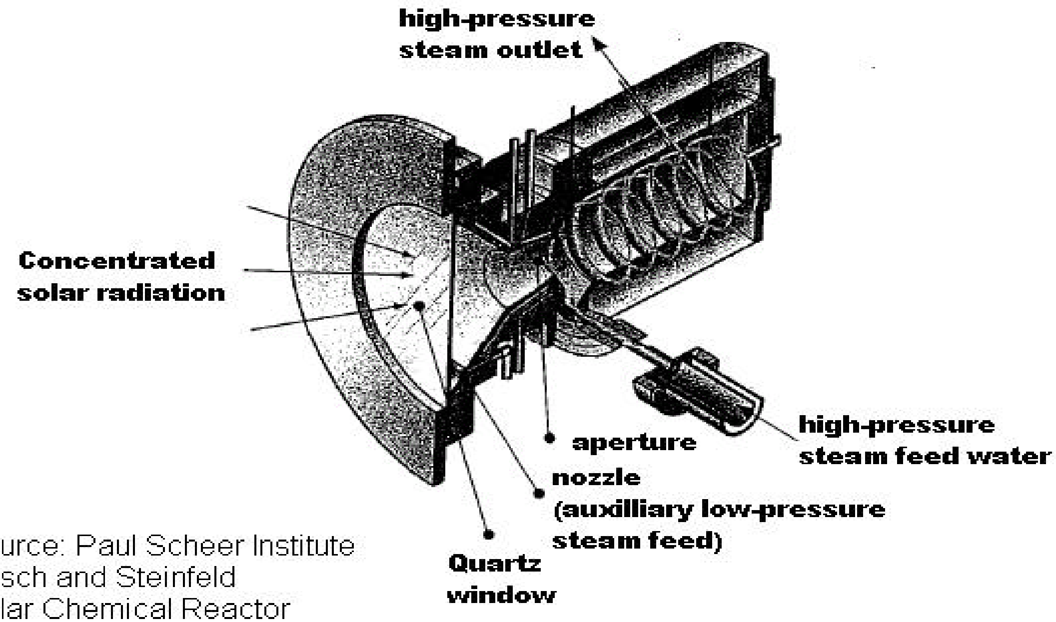
***Hydrogen Energy* 29, 2004 47-59**

Demonstrates very encouraging progress that could be directly applied to steam electrolysis

Multiple paths for linking steam electrolysis to renewable energy are being pursued

Hirsch and Steinfeld, Paul Scheer Institute

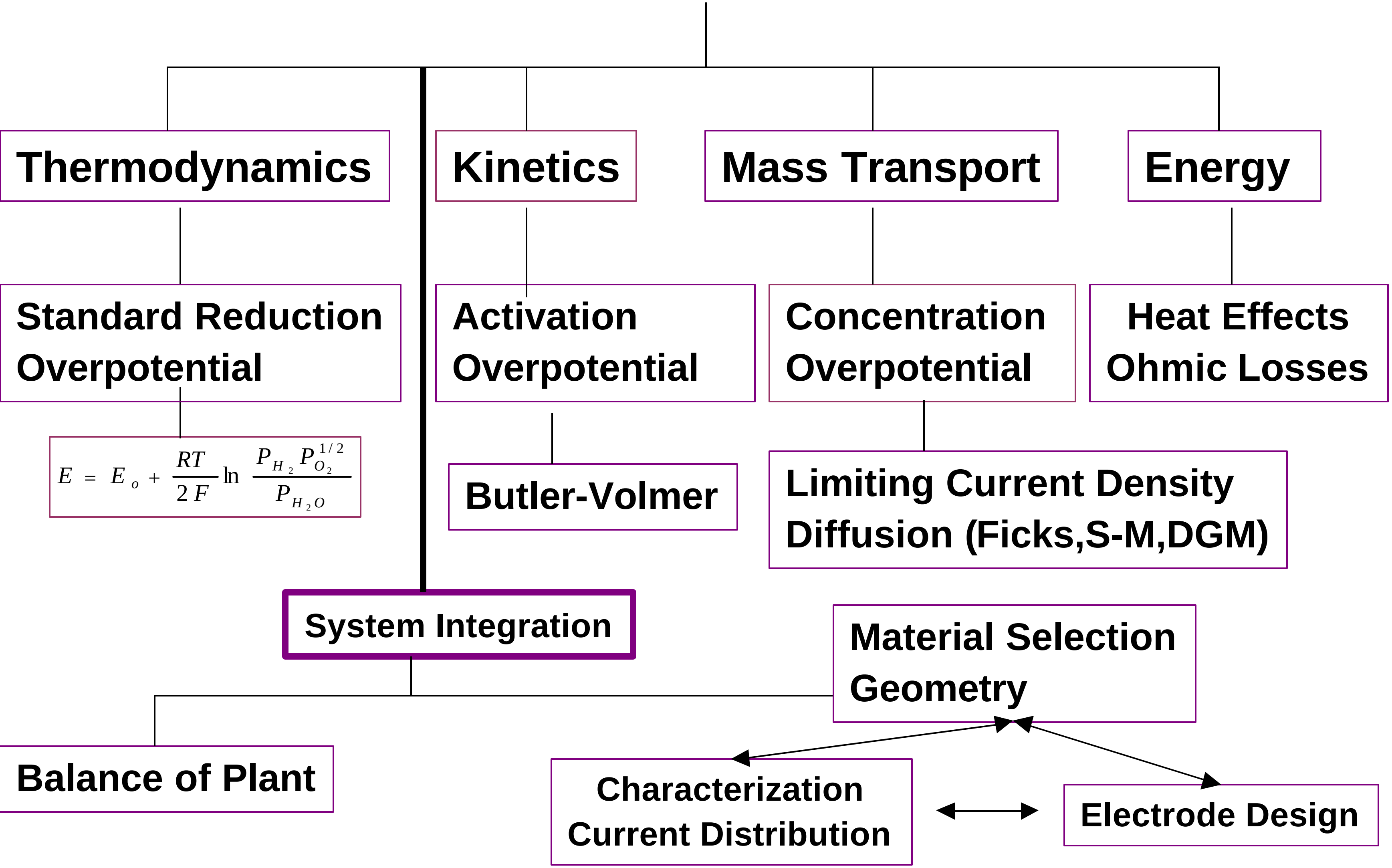
Hydrogen Energy 29, 2004 47-59



Source: Paul Scheer Institute
Hirsch and Steinfeld
Solar Chemical Reactor

Computational Fluid Dynamics

Electrochemistry Model



Thermodynamics

Kinetics

Mass Transport

Energy

Standard Reduction Overpotential

Activation Overpotential

Concentration Overpotential

Heat Effects
Ohmic Losses

$$E = E_o + \frac{RT}{2F}\ln\frac{P_{H_2}P_{O_2}^{1/2}}{P_{H_2O}}$$

Butler-Volmer

Limiting Current Density
Diffusion (Ficks,S-M,DGM)

System Integration

Material Selection
Geometry

Balance of Plant

Characterization
Current Distribution

Electrode Design

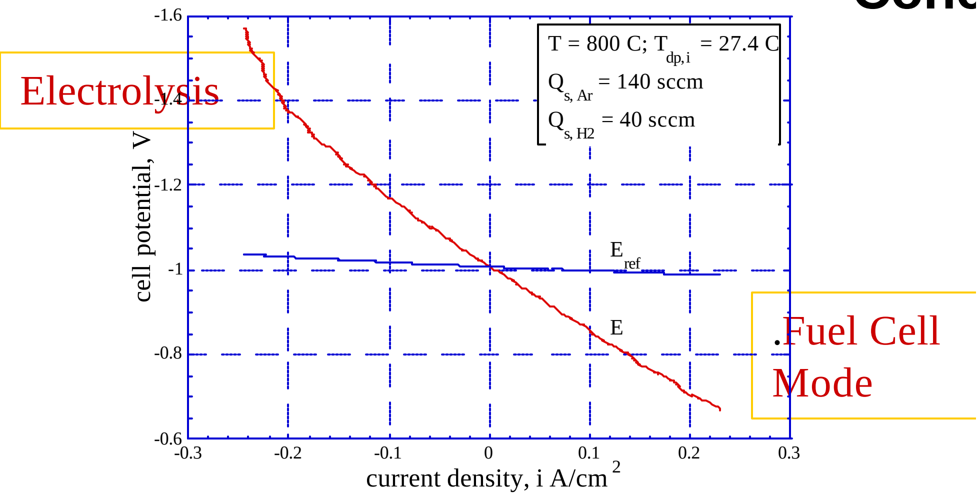
SOFC/SOEC Modeling Overpotential

$$E = \underbrace{E_o + \frac{RT}{2F}\ln\frac{P_{H_2}P_{O_2}^{1/2}}{P_{H_2O}}}_{\text{Reversible Cell Voltage}} + \underbrace{\eta_C + \eta_a + \eta_r}_{\text{Overpotential:}}$$

Reversible Cell Voltage

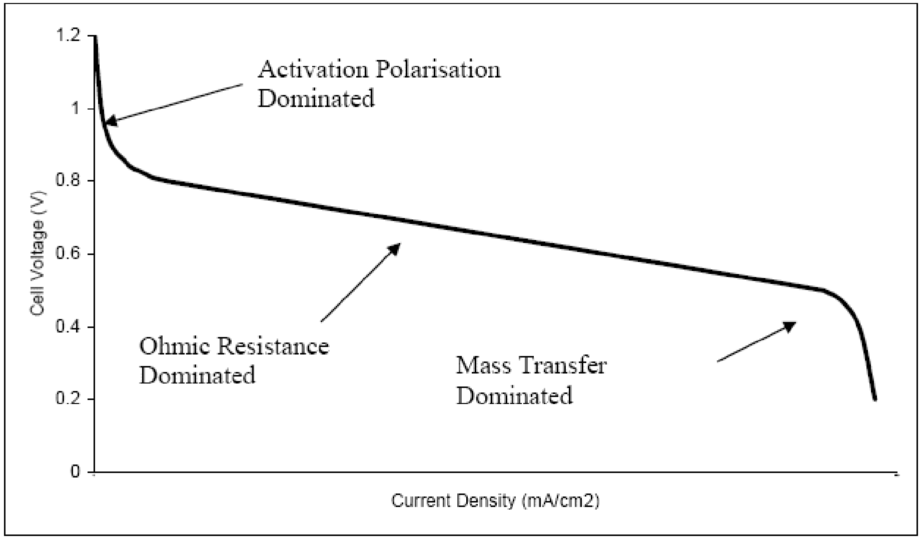
Overpotential:

Conc

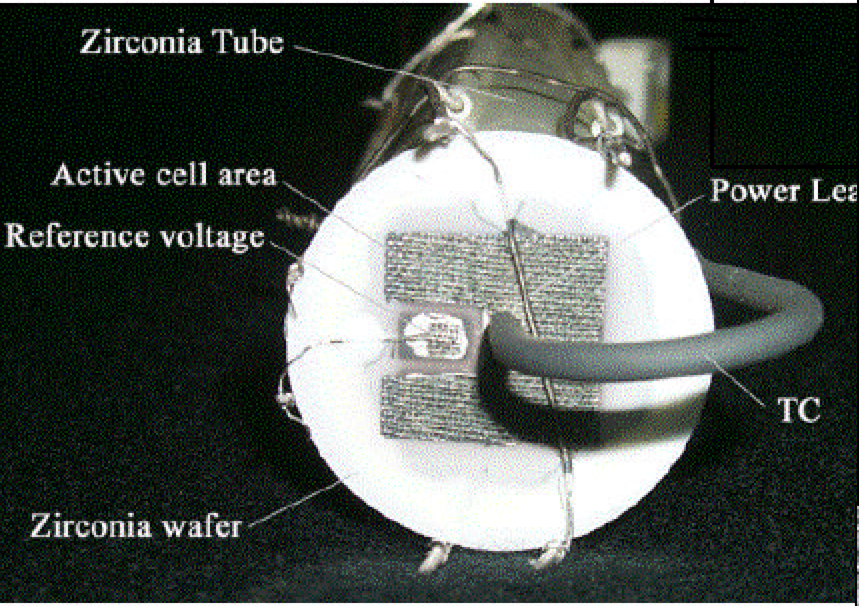


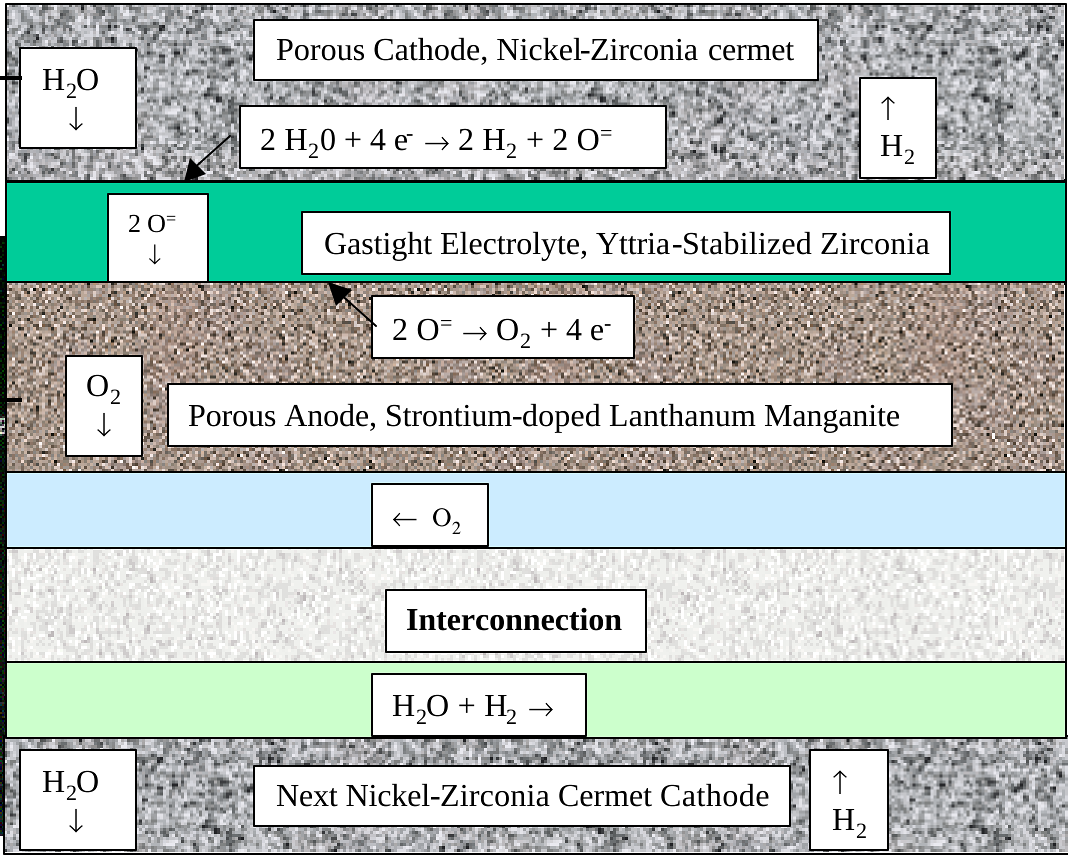
Electrolysis

.Fuel Cell Mode



Button and Stack SOFC/SOEC Experiment





4 e$^-$→

H_2O ↓

Porous Cathode, Nickel-Zirconia cermet

$2\ H_20 + 4\ e^- \rightarrow 2\ H_2 + 2\ O^=$

↑ H_2

$2\ O^=$ ↓

Gastight Electrolyte, Yttria-Stabilized Zirconia

$2\ O^= \rightarrow O_2 + 4\ e^-$

O_2 ↓

Porous Anode, Strontium-doped Lanthanum Manganite

← O_2

Interconnection

$H_2O + H_2$ →

H_2O ↓

Next Nickel-Zirconia Cermet Cathode

↑ H_2

Taken From INEEL report 2004, Steve Herring and Jim O’Brien, “High Temperature Solid Oxide Electrolyser System”

Available Commercial CFD Codes

- Code Selection
  - ✓ Femlab
  - ✓ Star-CD
  - ✓ Fluent

➢ **Calculations based on current**

➢ **Current density establishes rate of oxygen transport through electrolyte**

- STARCD
  - 350 Node Linux Parallel Cluster at ANL

V-I Characteristics

$$E = E_{rev} + \frac{(r_1 + r_2 T)}{A} I + (s_1 + s_2 T + s_3 T^2) \log_{10}\left(\frac{\left(t_1 + {t_2}/{T} + {t_3}/{T^2}\right)}{A} I + 1 \right)$$

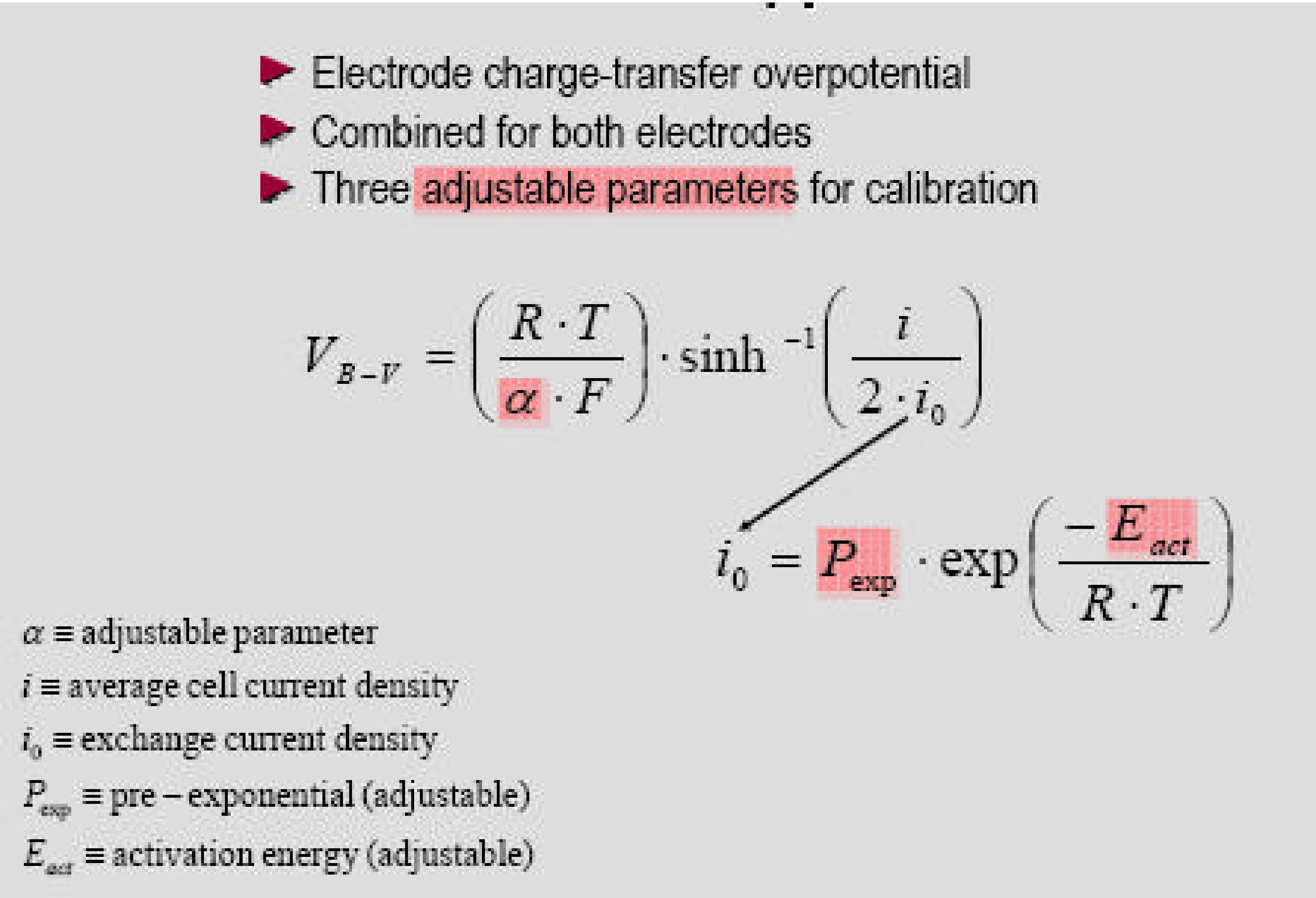
E operating cell voltage
E_{rev} reversible cell voltage
R ohmic resistance of electrolyte
s,t coeff for overvoltage on electrodes

Stand-Alone Power Systems For the Future: Optimal Design, Operating &Controle of Solar-Hydrogen Energy Systems, PhD thesis O. Ulleberg. 1998 Norwegian University of Science and Tch.

Ohmic Losses

- **Area Specific Resistance (ASR)**
  - **ASR = thickness/conductivity(ó)**
- **Voltage Loss due to Ohmic resistance**
  - **V=i*ASR**
- **Electrolyte offers considerable resistance**
  - **ó(YSZ)=0.3685 +0.002838exp(10300/T)**
- **Electrodes offer relatively small resistance and are given in literature.**
  - **Many treat as constants**
  - **Anode: 0.0014 Ù-cm**
  - **Cathode: 0.0186 Ù-cm**
- **Interfacial Resistances: ~0.1 Ù-cm**

Butler –Volmer Aproximation â=0.5 most assume for fuel cells



- Electrode charge-transfer overpotential
- Combined for both electrodes
- Three adjustable parameters for calibration

$$V_{B-V} = \left(\frac{R\cdot T}{\alpha\cdot F}\right)\cdot\sinh^{-1}\left(\frac{i}{2\cdot i_0}\right)$$

$$i_0 = P_{exp}\cdot\exp\left(\frac{-E_{act}}{R\cdot T}\right)$$

$\alpha \equiv$ adjustable parameter

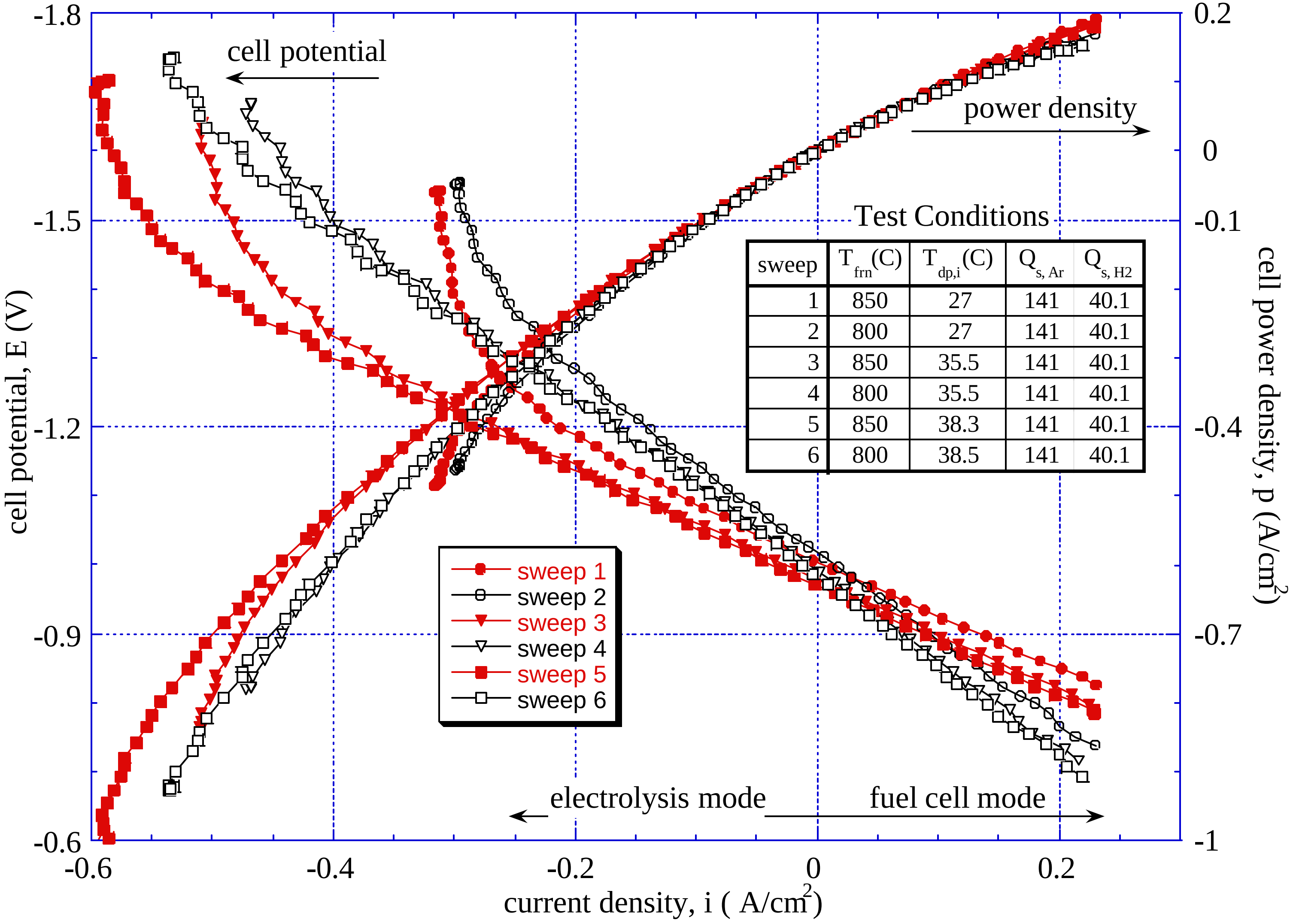
$i \equiv$ average cell current density

$i_0 \equiv$ exchange current density

$P_{exp} \equiv$ pre – exponential (adjustable)

$E_{act} \equiv$ activation energy (adjustable)

INEEL SUPPLIED V-I Curves



Test Conditions

sweep	T_{frn} (C)	$T_{dp,i}$ (C)	$Q_{s, Ar}$	$Q_{s, H2}$
1	850	27	141	40.1
2	800	27	141	40.1
3	850	35.5	141	40.1
4	800	35.5	141	40.1
5	850	38.3	141	40.1
6	800	38.5	141	40.1

Cathode Concentration Overpotential

Using Fick Law of Diffusion

$$J_A\left(\frac{gm-mol}{cm^2 s}\right) = -cD_{AB}\nabla x_A$$

$$V = \frac{RT}{2F}\left[\ln\left(1-\frac{i}{i_{H_2O}}\right) - \ln\left(1-\frac{i}{i_{H_2}}\right)\right]$$

$$i_{H_2} = \frac{2FP_{H_2}D^{eff}_{H_2}}{RTL_a}$$

$$i_{H_2O} = \frac{2FP_{H_2O}D^{eff}_{H_2O}}{RTL_a}$$

Ô=porosity

τ = tortuosity

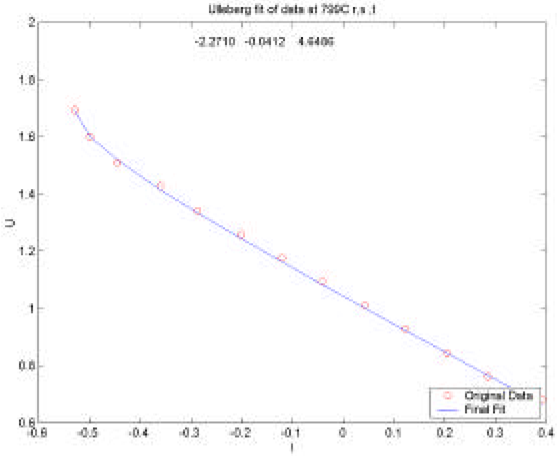
r = molecular radius

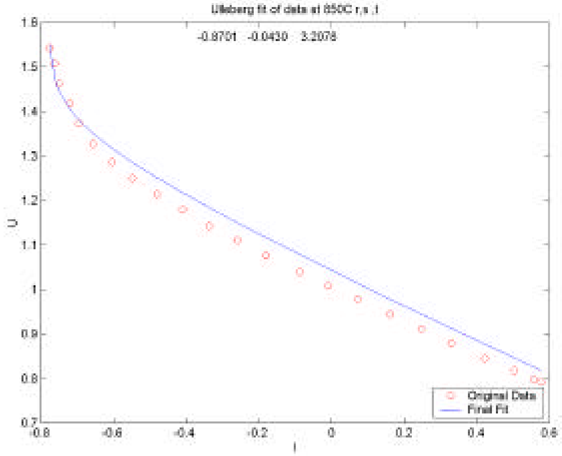
$$D^{eff}_{H_2O} = \frac{\phi D^{unary}_{H_2O}}{\tau}$$

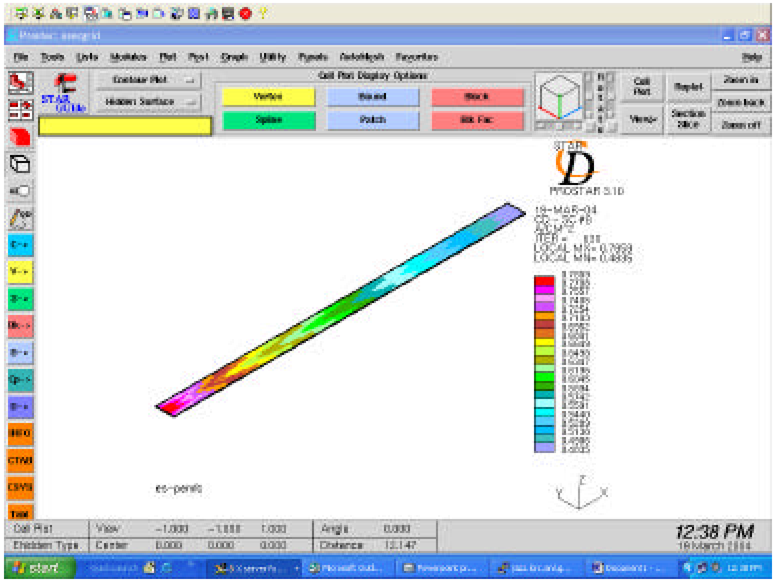
$$D^{binary}_{ij} = \frac{0.001T^{1.75}\sqrt{\frac{1}{M_i}+\frac{1}{Mj}}}{P(r_i+r_j)^2}$$

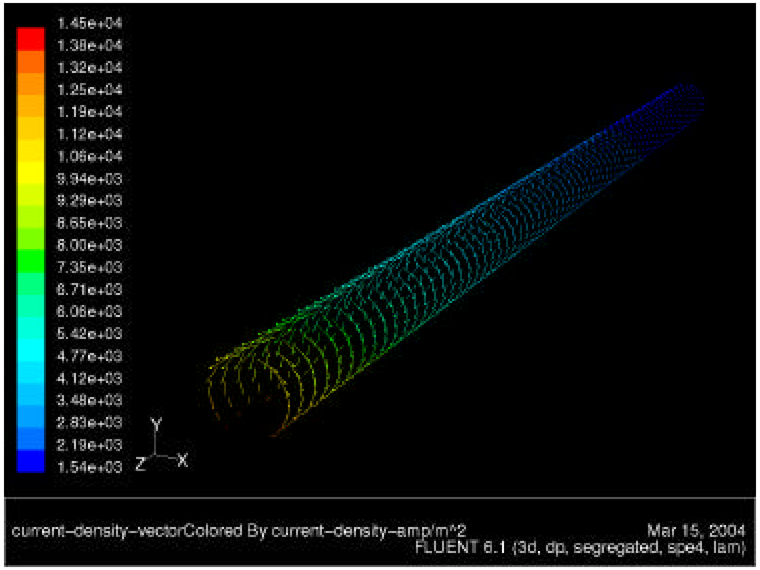
***Pulsed Gradient Spin Echo NMR measurements of the time-dependent diffusion coefficient,* D(t).**

CFD Simulations will be a very necessary elements of SOEC development









System Integration

Extra components needed to

-Gases need to be circulated through the stack

-Compressors, pumps or blowers

-Electric motors to drive pumps, blowers and compressor

-Fuel cell needs to connected to load like DC/DC converter for simple voltage regulator as used by INEEL expt.

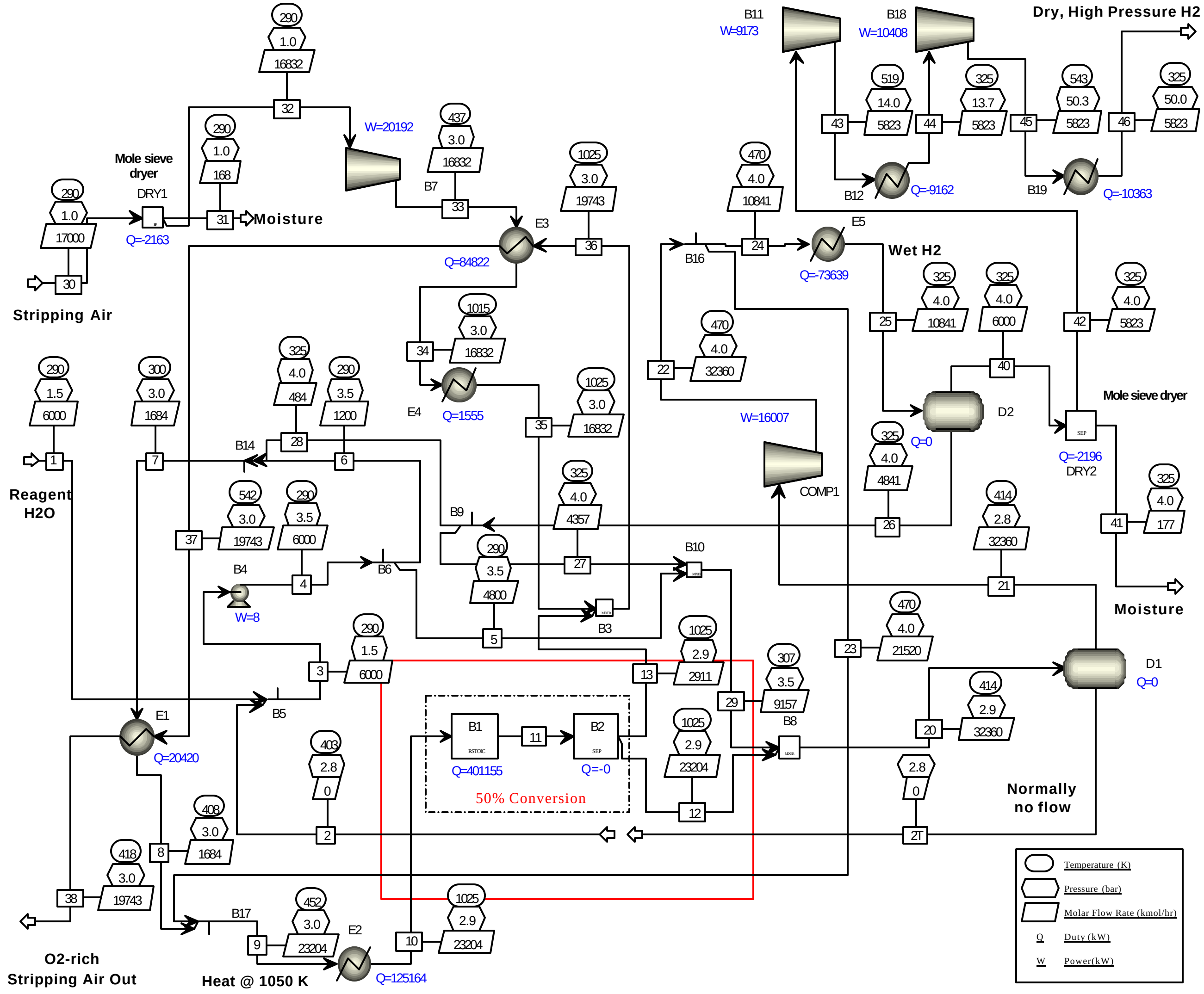
-Cooling system, air-preheater

Low-temperature Electrolysis – 1 kg/h H_2

H2 (kW-HHV/kg) = 39.447

	cost	cost basis			power (kW)
Housing/Forecourt dispenser (NEPA Compliant)	$12,000				
Electric Power Transformer	$14,000	0.20	$/W	-5%	3.50
Water System-manifolding	$1,250				0.10
Electric Power Invertor/Conditioning	$45,932	0.85	$/W	-5%	2.70
Electrolytic Cells ($/kW)	$143,199	$2,650	$/kW	73%	54.04
Hydrogen Compression (ambient - 100 psi)	$20,000				1.05
Hydrogen Compression (100 - 5,000 psi)	$78,678			15%	3.60
Hydrogen dispensing (5,000 psi)	$17,984				0.50
800kW-Natural Gas Compression/Hythane (50 - 3,600 psi)	$29,974				2.09
800kW-Hythane dispensing (3,600 psi)	$11,990				0.50
Oxygen system manifolding	$2,500				0.15
Controls/Auxiallry	$25,585	7.0%			0.80
Cooling fan	$1,250			1.4%	0.98
Profit	$60,657	15.0%			
TOTAL	$465,000			Power ($kW_{electric}$)	70.00

High-T Electrolysis Balance of Plant



Aspen Plus 12.1 Run:Electrolysis 2004-10-29a 50%H2O-50% Conversion 10/29/2004 11:29:04 AM

High-temperature Electrolysis – 1 kg/h H_2

		H2 (kW-HHV/kg) =			33.721
	Cost	Cost basis			Power (kW)
Housing/Forecourt dispenser (NEPA Compliant)	$18,000				
Electric Power Transformer	$10,000	0.20	$/W	-5%	2.50
Water System-manifolding	$500				0.10
Steam system	$8,000				0.00
Electric Power Invertor/Conditioning	$30,820	0.85	$/W	-5%	1.81
Electrolytic Cells ($/kW)	$123,282	$3,400	$/kW	93%	36.26
Hydrogen Compression (ambient - 100 psi)	$27,000				1.05
Hydrogen Compression (100 - 5,000 psi)	$78,678			15%	3.60
Hydrogen dispensing (5,000 psi)	$17,984				0.50
800kW-Natural Gas Compression/Hythane (50 - 3,600 psi)	$29,974				2.09
800kW-Hythane dispensing (3,600 psi)	$11,990				0.50
Oxygen system manifolding	$20,000				0.70
Controls/Auxiallry	$25,076	7.0%			1.20
Moisture dryers	$2,150				0.00
Cooling fan	$875			1.4%	0.71
Profit	$60,671	15.0%			
TOTAL	$465,000		Power ($kW_{electric}$)		51.02
			Power ($kW_{Q@1050K}$)		10.66

Capital Cost Comparison

	High-T	Low-T
Housing/Forecourt dispenser (NEPA Compliant)	$18,000	$12,000
Electric Power Transformer	$10,000	$14,000
Water System-manifolding	$500	$1,250
Steam system	$8,000	
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Oxygen system manifolding	$20,000	$2,500
Controls/Auxiallry	$25,076	$25,585
Moisture dryers	$2,150	
Cooling fan	$875	$1,250
Profit	$60,671	$60,657
TOTAL	$465,000	$465,000

Power use comparison

	High-T	Low-T
Housing/Forecourt dispenser (NEPA Compliant)		
Electric Power Transformer	2.50	3.50
Water System-manifolding	0.10	0.10
Steam system	0.00	0.00
Electric Power Invertor/Conditioning	1.81	2.70
Electrolytic Cells ($/kW)	36.26	54.04
Hydrogen Compression (ambient - 100 psi)	1.05	1.05
Hydrogen Compression (100 - 5,000 psi)	3.60	3.60
Hydrogen dispensing (5,000 psi)	0.50	0.50
800kW-Natural Gas Compression/Hythane (50 - 3,600 psi)	2.09	2.09
800kW-Hythane dispensing (3,600 psi)	0.50	0.50
Oxygen system manifolding	0.70	0.15
Controls/Auxiallry	1.20	0.80
Moisture dryers	0.00	0.00
Cooling fan	0.71	0.98
Profit		
Power ($kW_{electric}$)	51.02	70.00
Power ($kW_{Q@1050K}$)	10.66	0.00

Cross-Cutting Research Directions

Membranes and Separation

- Ceramic membranes used for the separation of oxygen from air must simultaneously achieve high-flux oxygen transport and equally large electronic transport, and, at the same time, must survive the extreme conditions of the membrane reactor
  - high temperatures
  - reactive environments
  - highly reducing conditions on one surface of the membrane

Characterization and measurement techniques

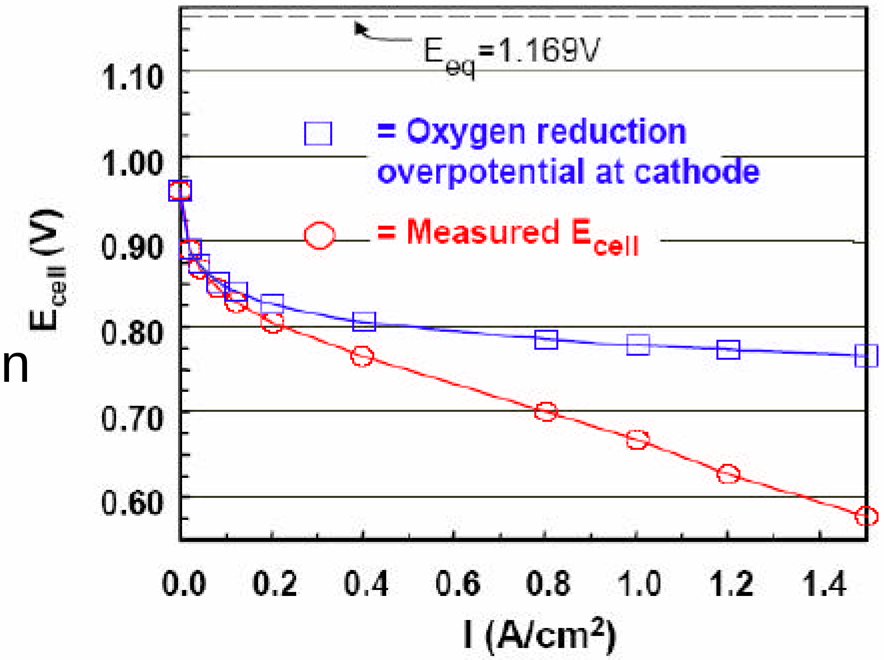
- Advanced Photon Source
- Electron Microscopy

Theory,modeling and simulation

- Diffusion Models
- Continued Interdisciplinary Effort

Issues with High-Temperature Electrolysis

- **Desirable for product hydrogen to be produced at high pressures**
  - Robust cell design necessary
- **Electrical energy intensive**
  - High ohmic losses due to thick electrolyte
    - *High strength design needed*
  - High overpotential on oxygen electrode
  - High overpotential and degradation of steam/hydrogen electrode
  - High thermodynamic potential to overcome



Conclusions – High Temperature Electrolysis

- **Capital Costs appear competitive**
- **Physical plant footprint will be lager**
- **Premium *(Electric)* Power demands are much lower**
- **Premium heat demands now needed**