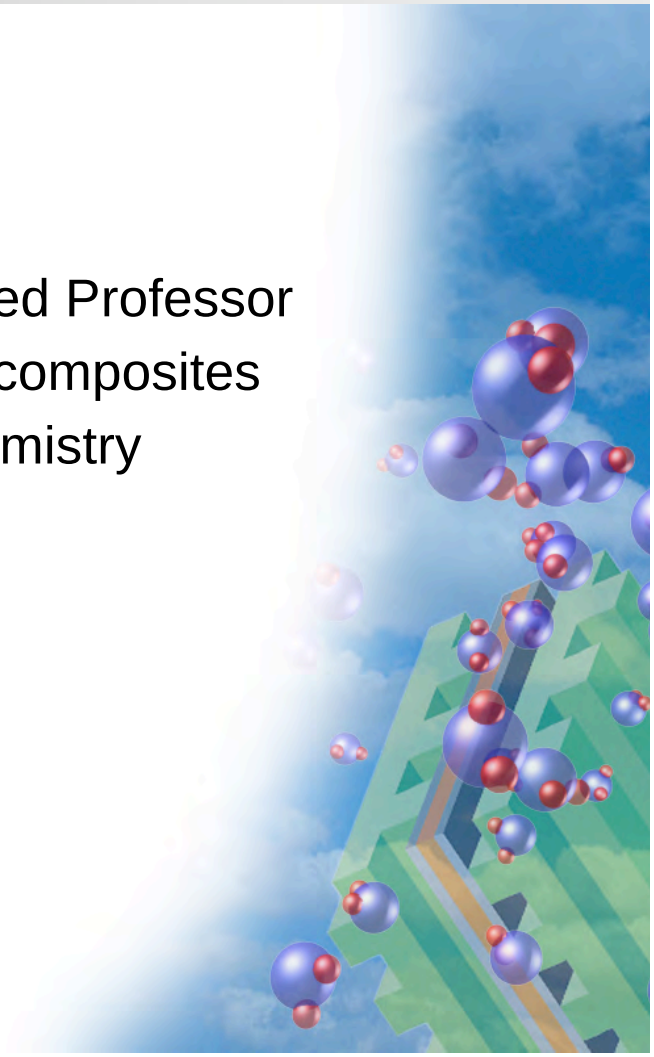
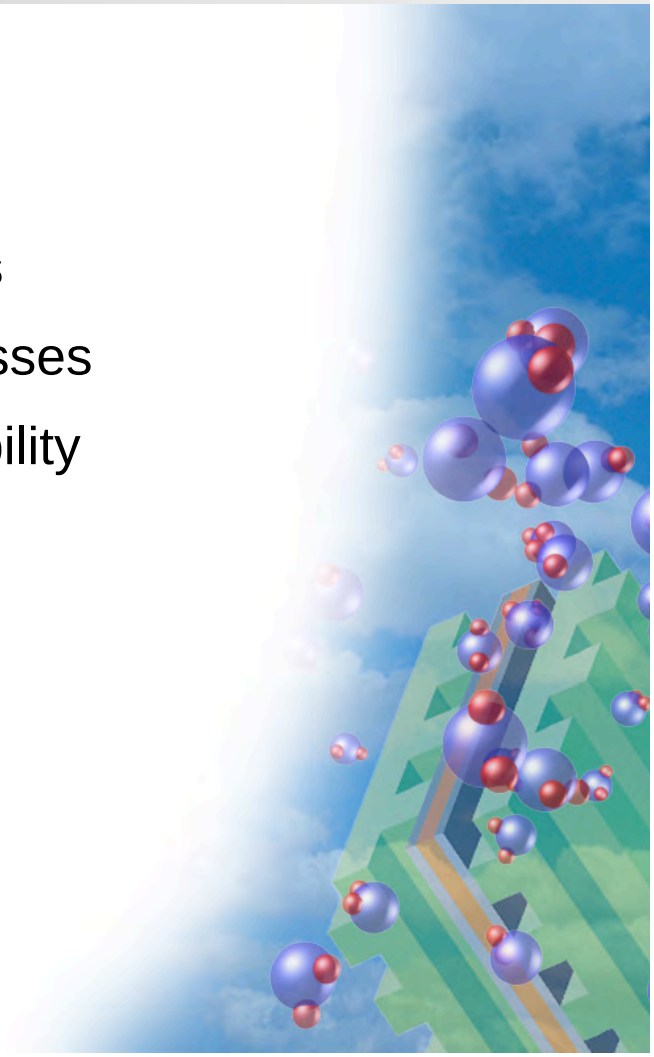
High Temperature PBI Membranes

Brian C. Benicewicz
USC Educational Foundation Distinguished Professor
CoEE Endowed Chair in Polymer Nanocomposites
Department of Chemistry & Biochemistry
USC NanoCenter
University of South Carolina
Columbia, SC 29208

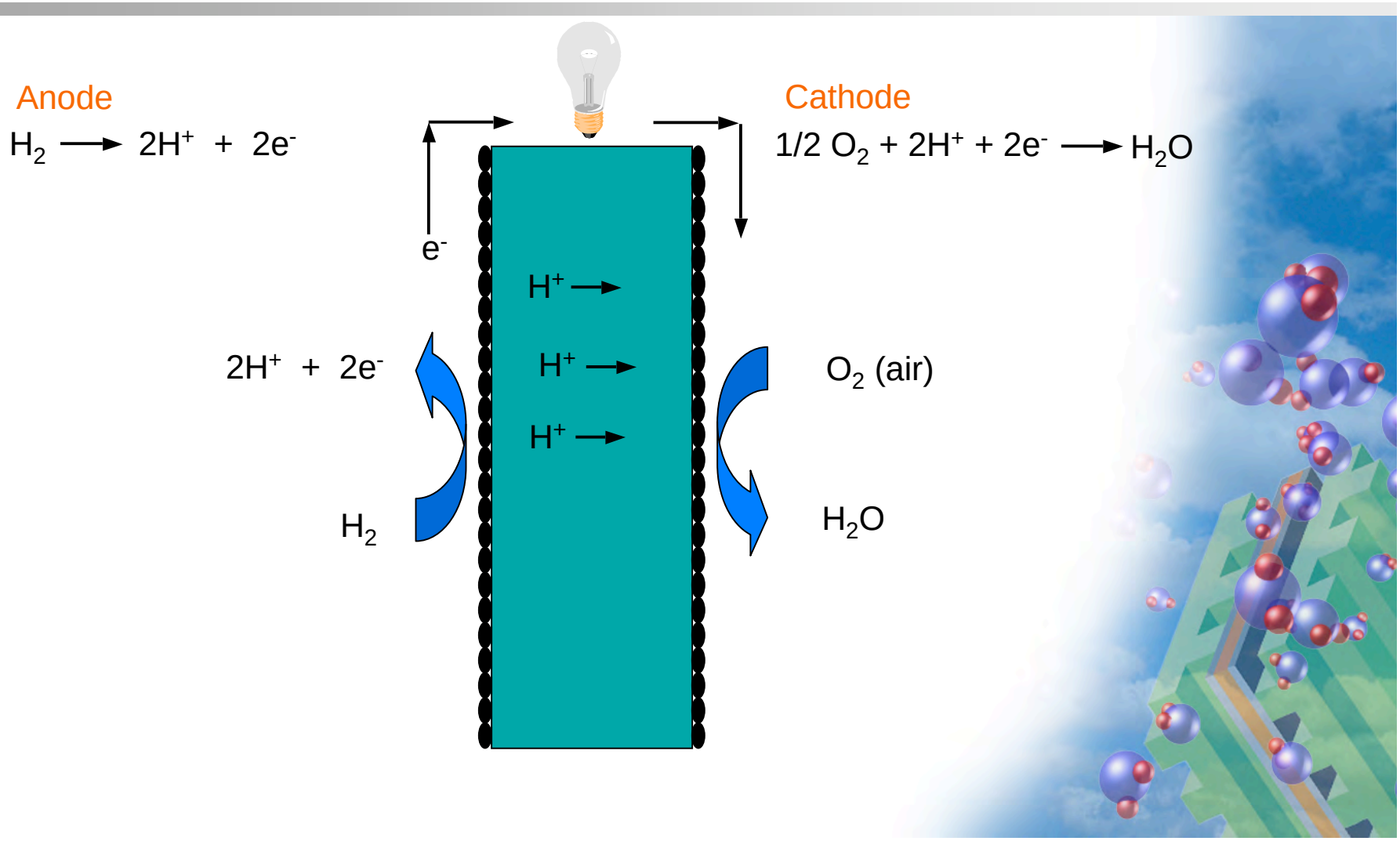


Outline - PBI Membranes

- Introduction and background - PBI
- PBI - Chemistry and sol-gel process
- Ionic conductivity & transport processes
- Fuel cell testing & operational durability
- Applications - Hydrogen pumping
- Summary & conclusions

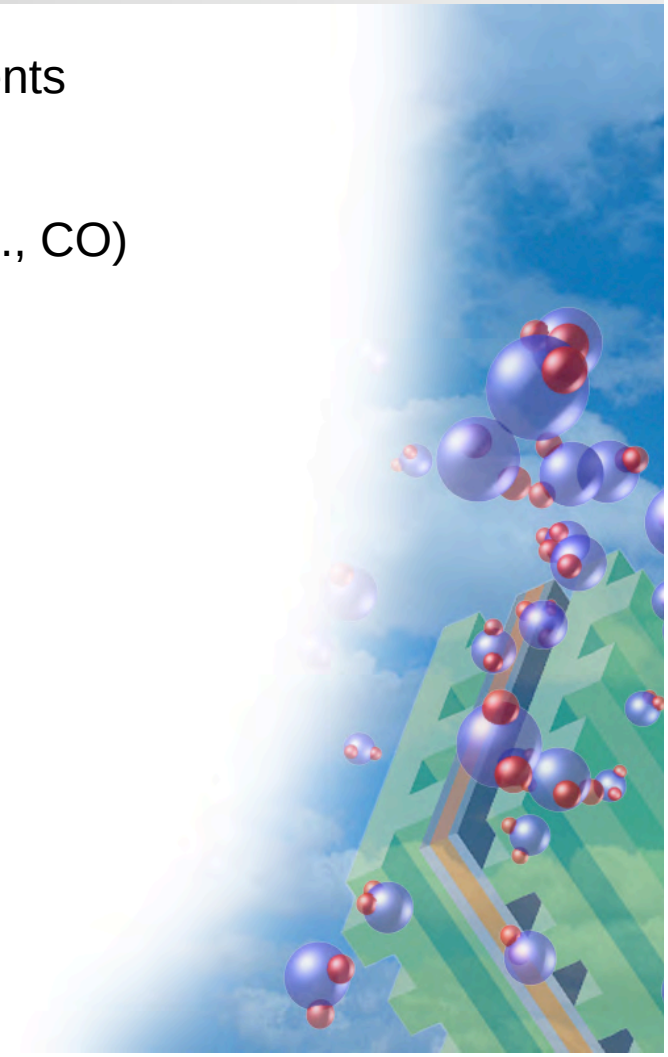


Proton Exchange Membrane



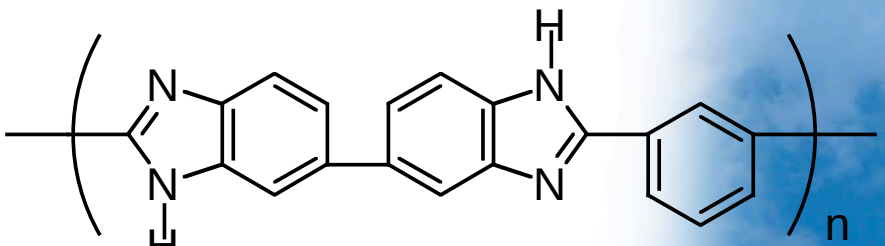
High Temperature Membranes

- Ease/eliminate humidification requirements
- Increase tolerance to fuel impurities (e.g., CO)
  - Wider fuel choices
  - Lower fuel reforming costs
- Improved electrode kinetics
- Higher conductivities
- Smaller heat exchangers/radiators



PBI for Fuel Cell Membranes

Poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole]

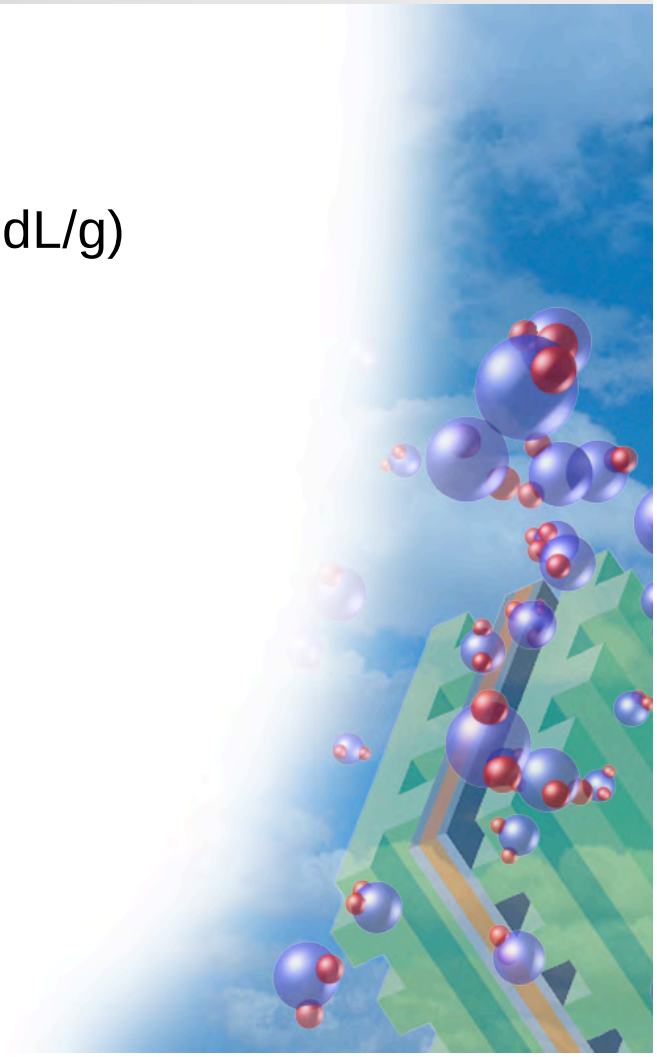


IV ~ 0.5 - 0.8 dL/g

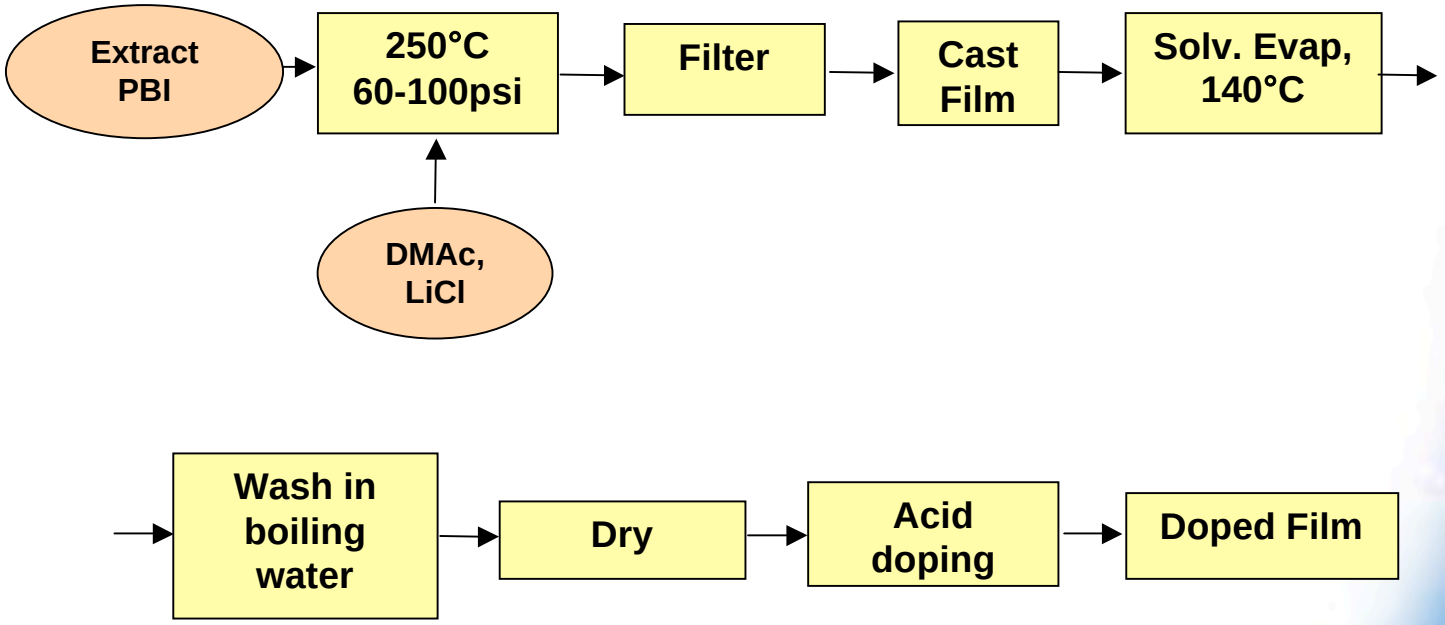
- Phosphoric acid electrolyte
- Operate up to 200˚C
- Water management problems alleviated
- PBI polymer is produced commercially
- Conventional membrane process - 6-10 moles PA/PBI

Perceived Problems with PBI

- Low mw's (IV's ≈ 0.5 - 0.8 dL/g)
- Phosphoric acid loading
- Phosphoric acid retention
- Membrane durability



The Conventional Imbibing Process



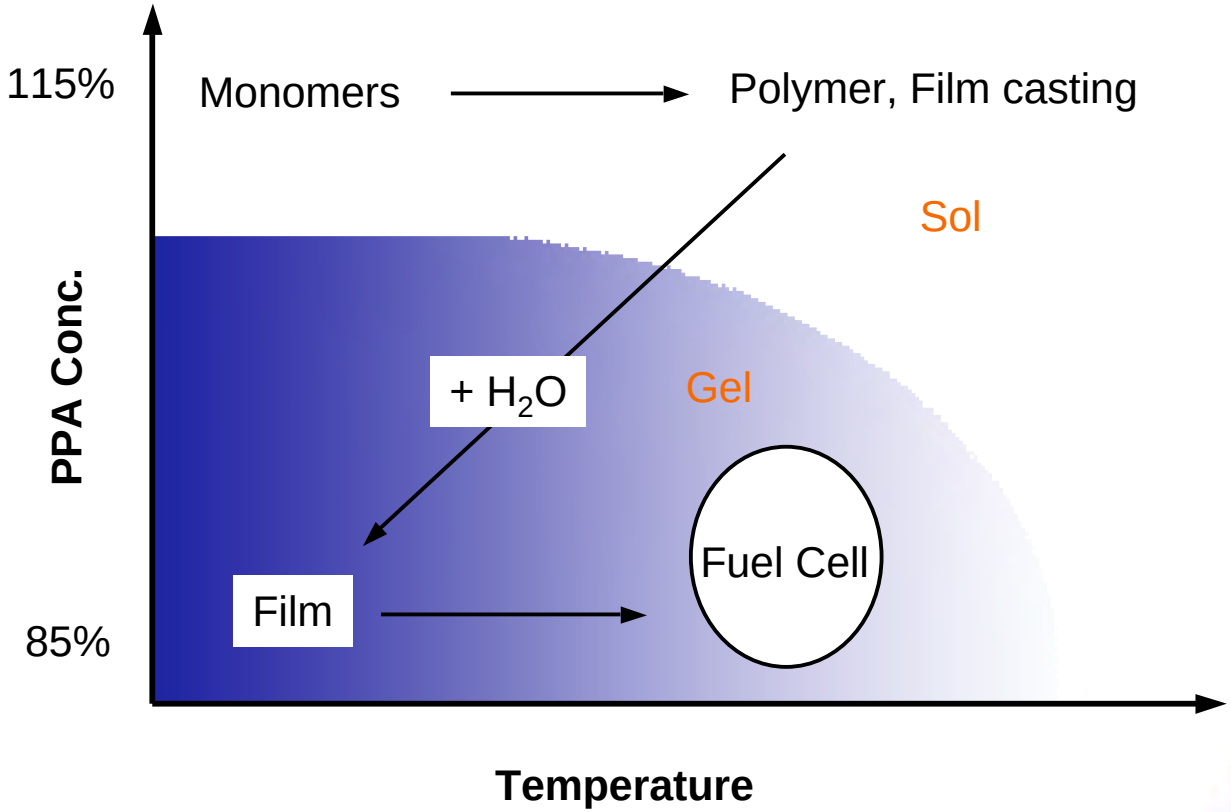
~ 6-10 PA/PBI molar ratio

Film Casting from PPA solutions
The PPA Process

- Films are cast directly from PPA solutions - no organic solvents
- Water is absorbed from the atm. - both PBI and PPA are hygroscopic
- PPA + H_2O react to form PA *insitu*
- *Sol-gel transition* produces gel films with high acid content
- Gel films exhibit much different properties than imbibed or "dip and soak" membranes

Chem. Mater. **2005**, *17*, 5328-5333.

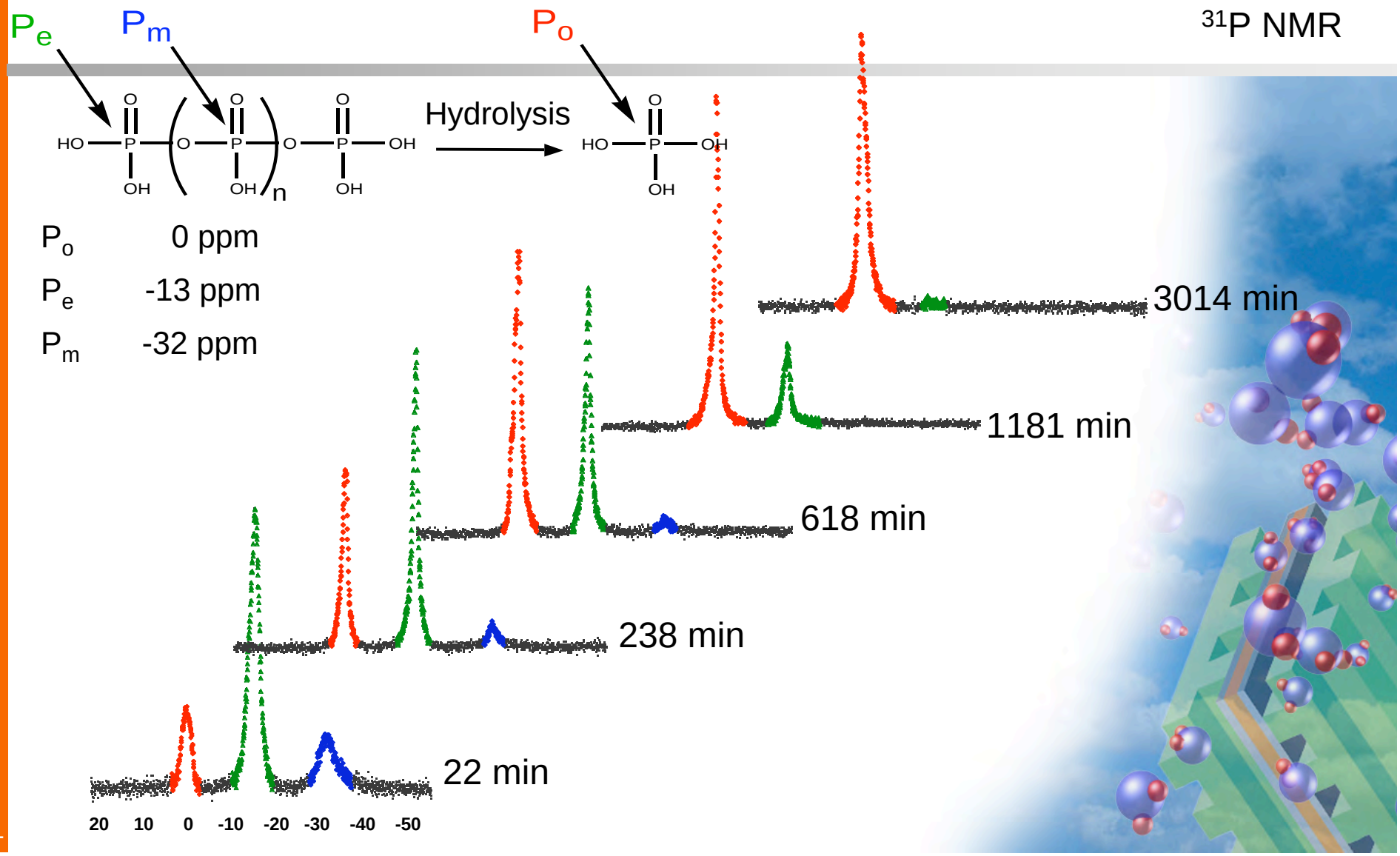
State Diagram



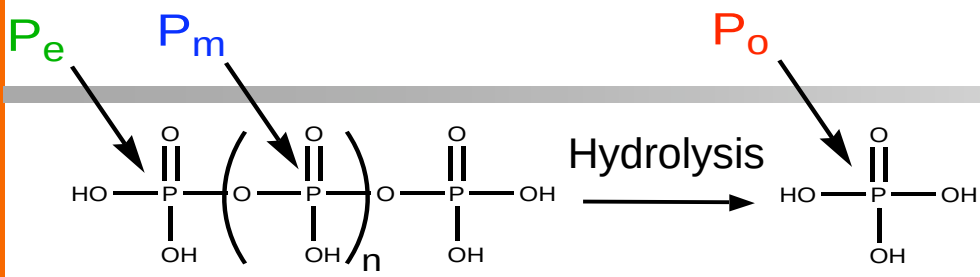
PPA Gel Film

[PA]/[PBI] 32/1

PPA Film Hydrolysis

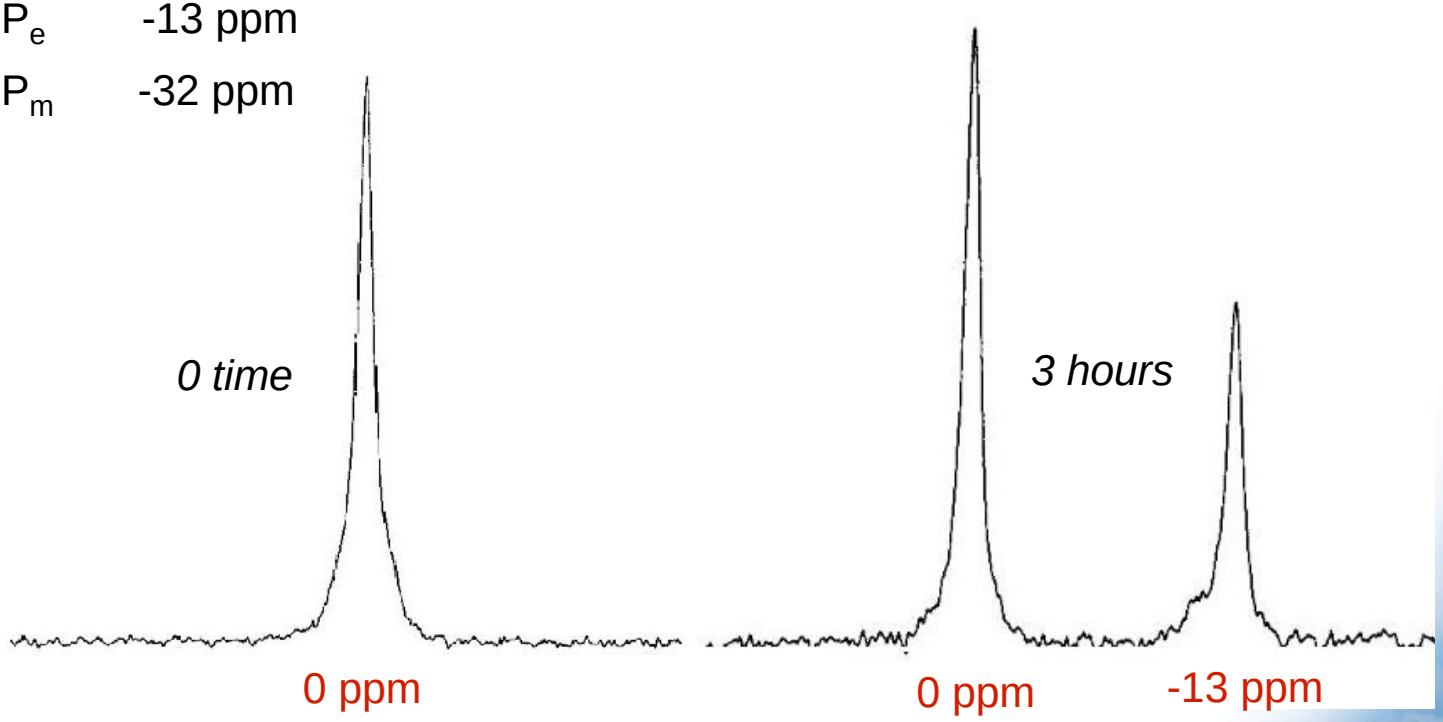


Phosphorus NMR

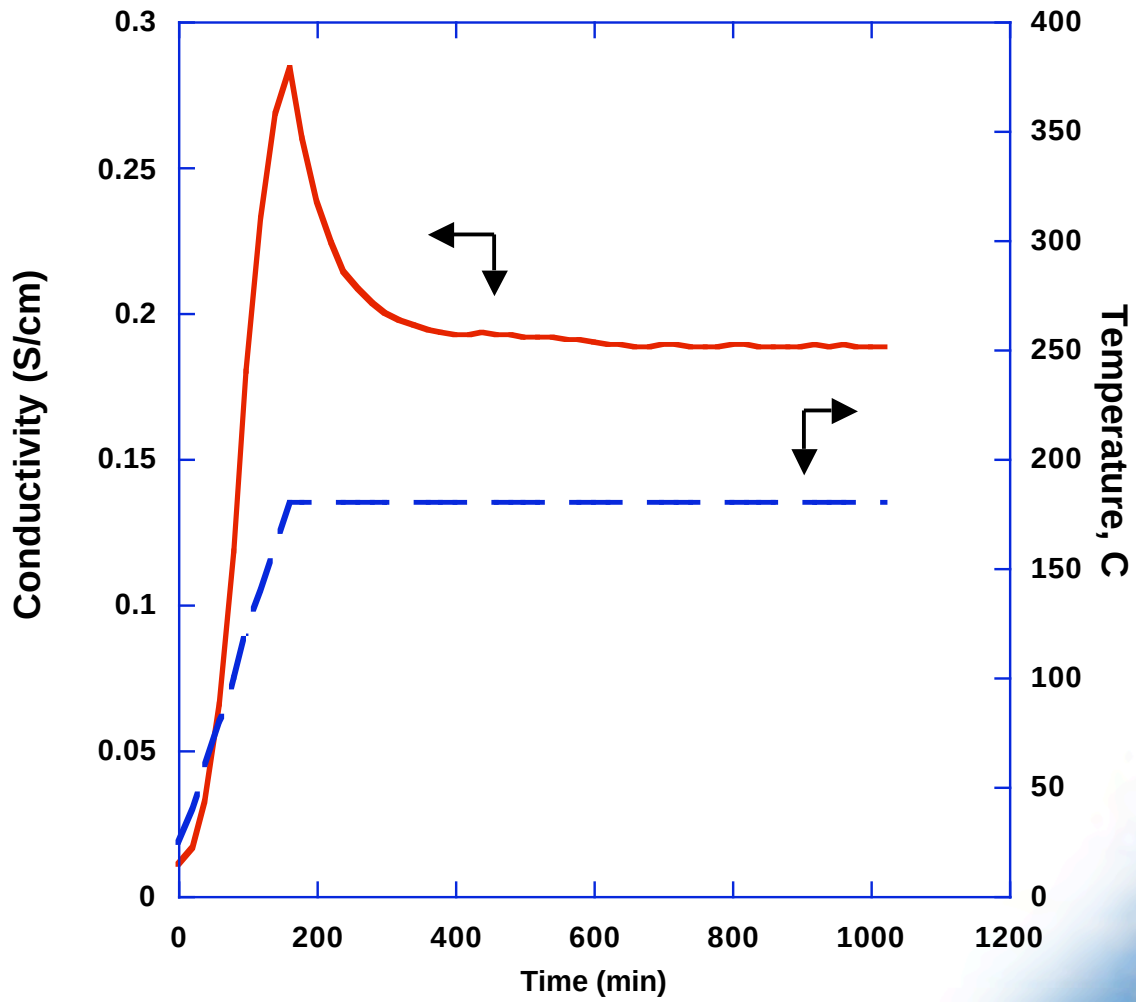


P_o	0 ppm
P_e	-13 ppm
P_m	-32 ppm

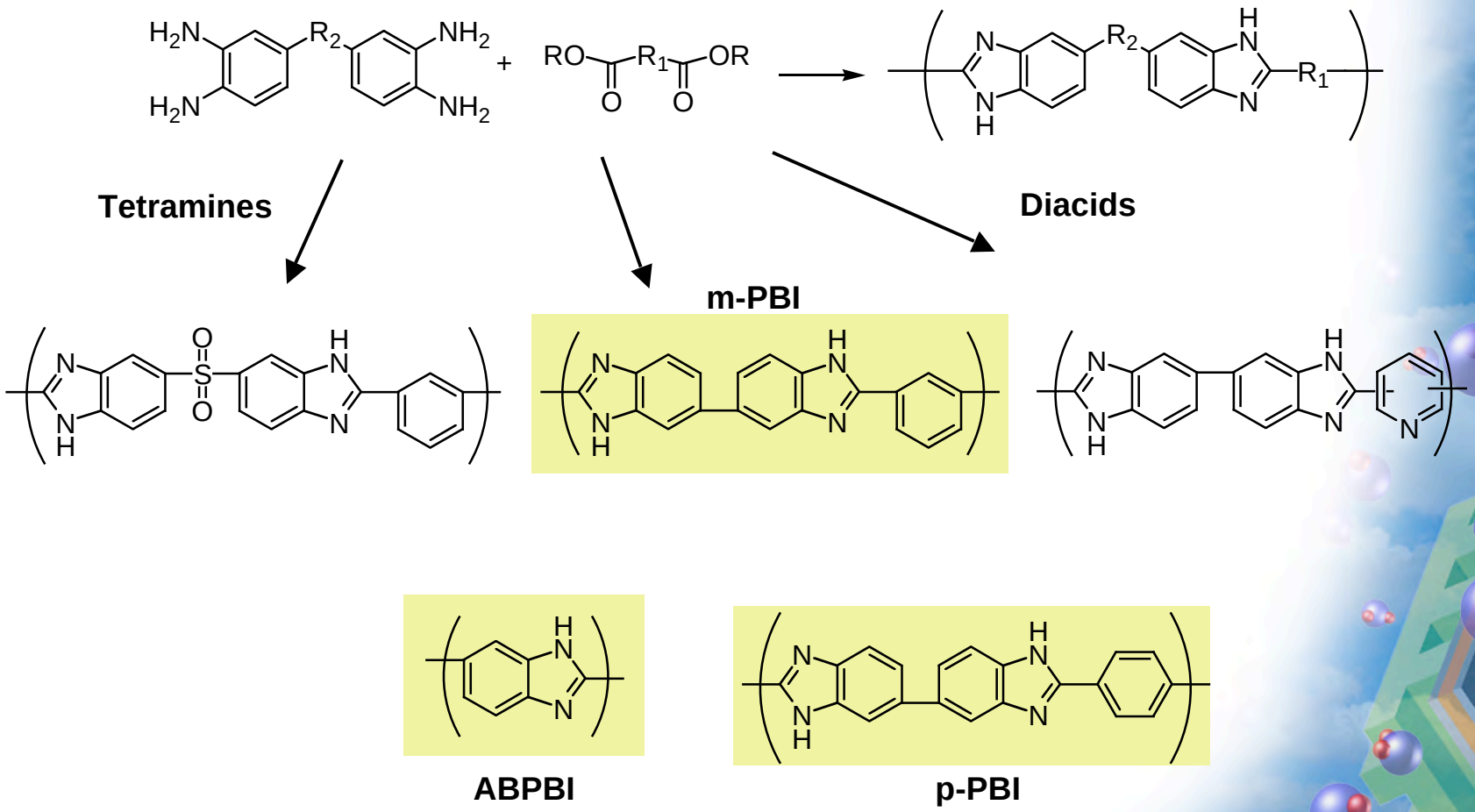
$$2\ H_3PO_4 \longrightarrow H_4P_2O_7 + H_2O$$



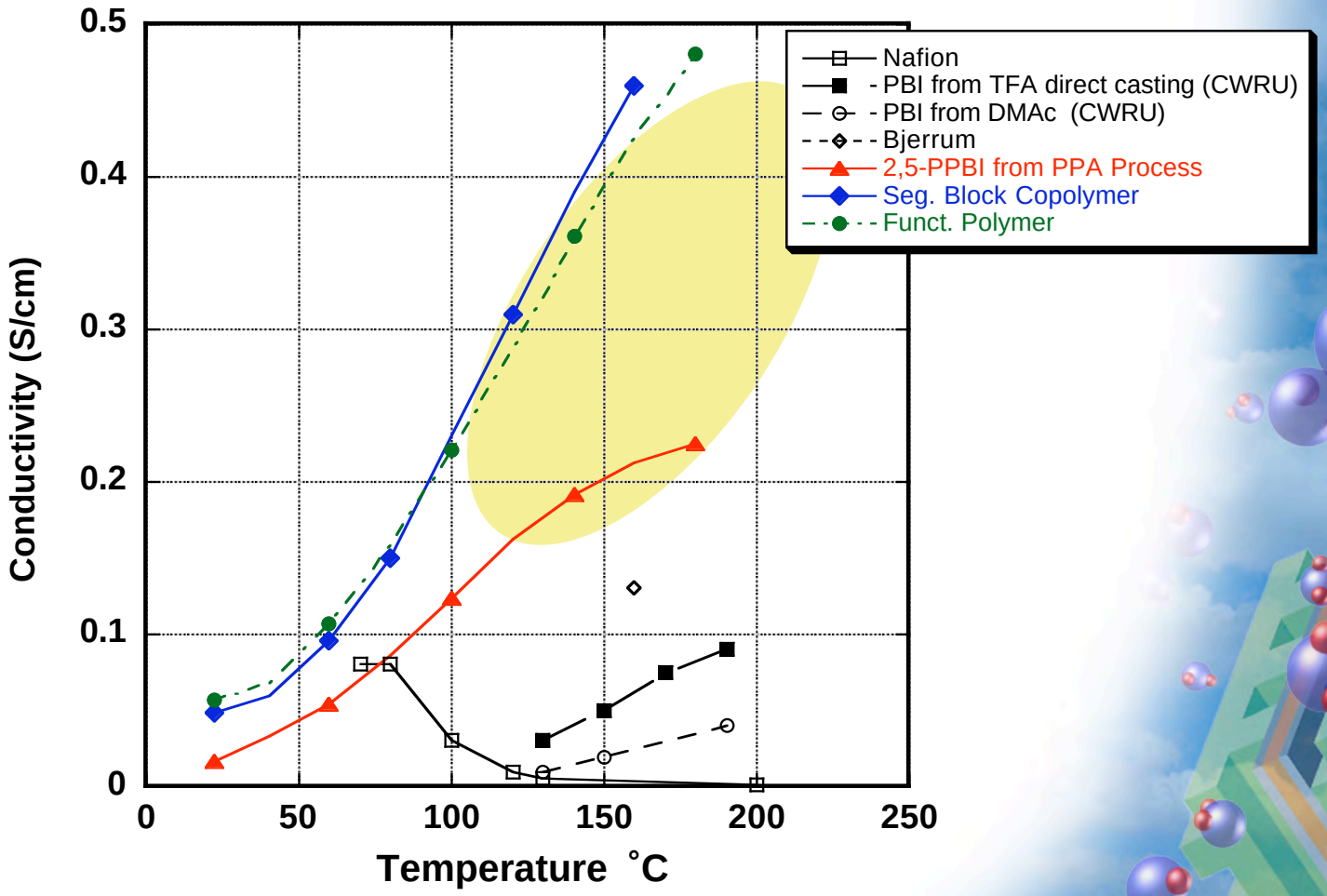
Ionic Conductivity



PBI Chemistry

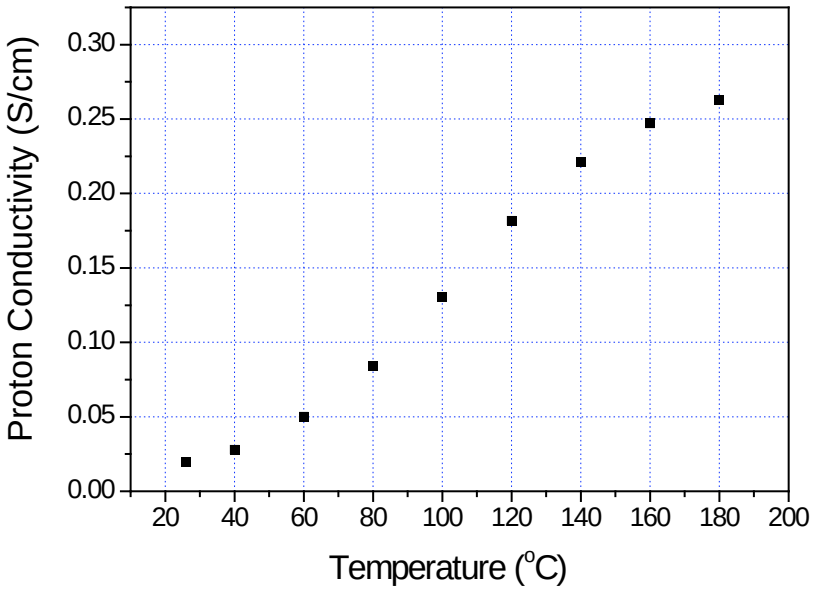


Ionic Conductivity

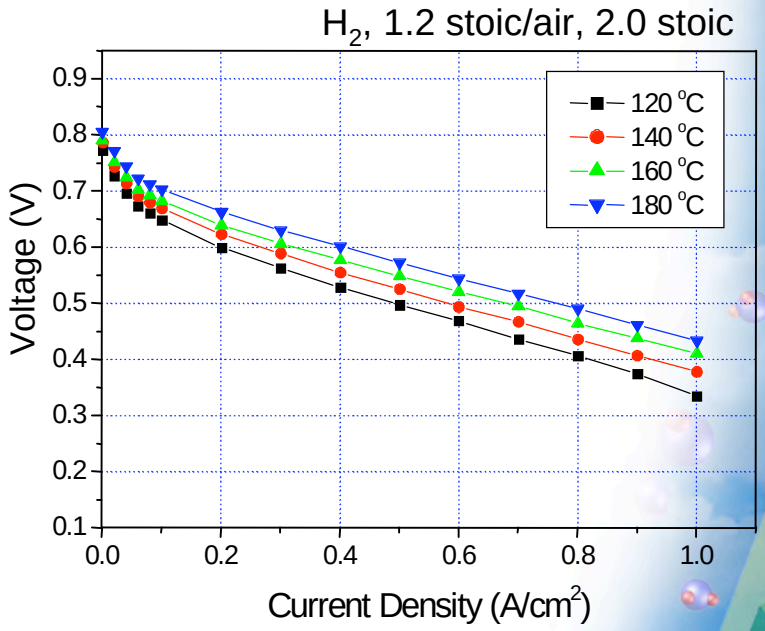


Baseline Data

Proton conductivity



Polarization curves at various temperatures



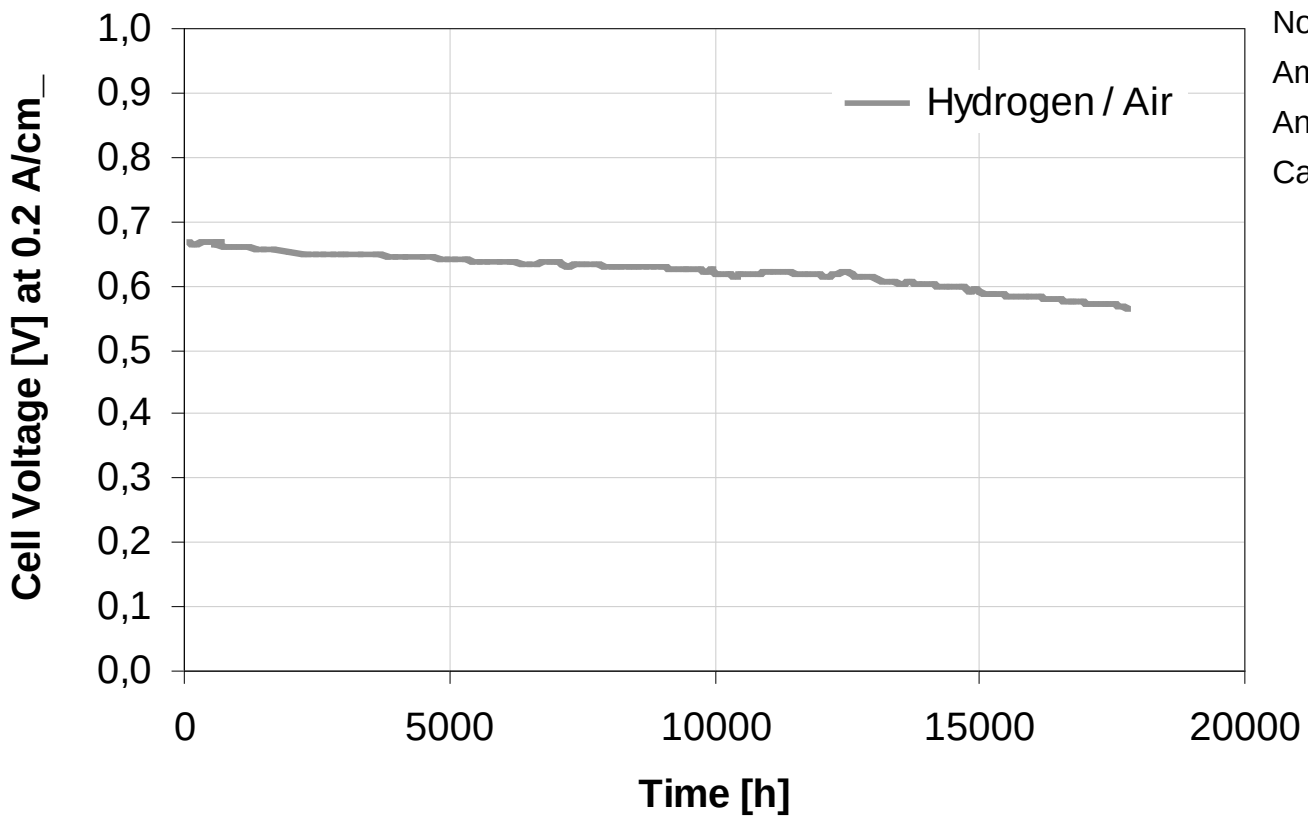
Proton conductivity = ~ 0.25 S/cm at 160 °C

~ 0.63 V @ 0.2 A/cm^2, 160 °C

Long-term Durability @ 160°C

No humidification

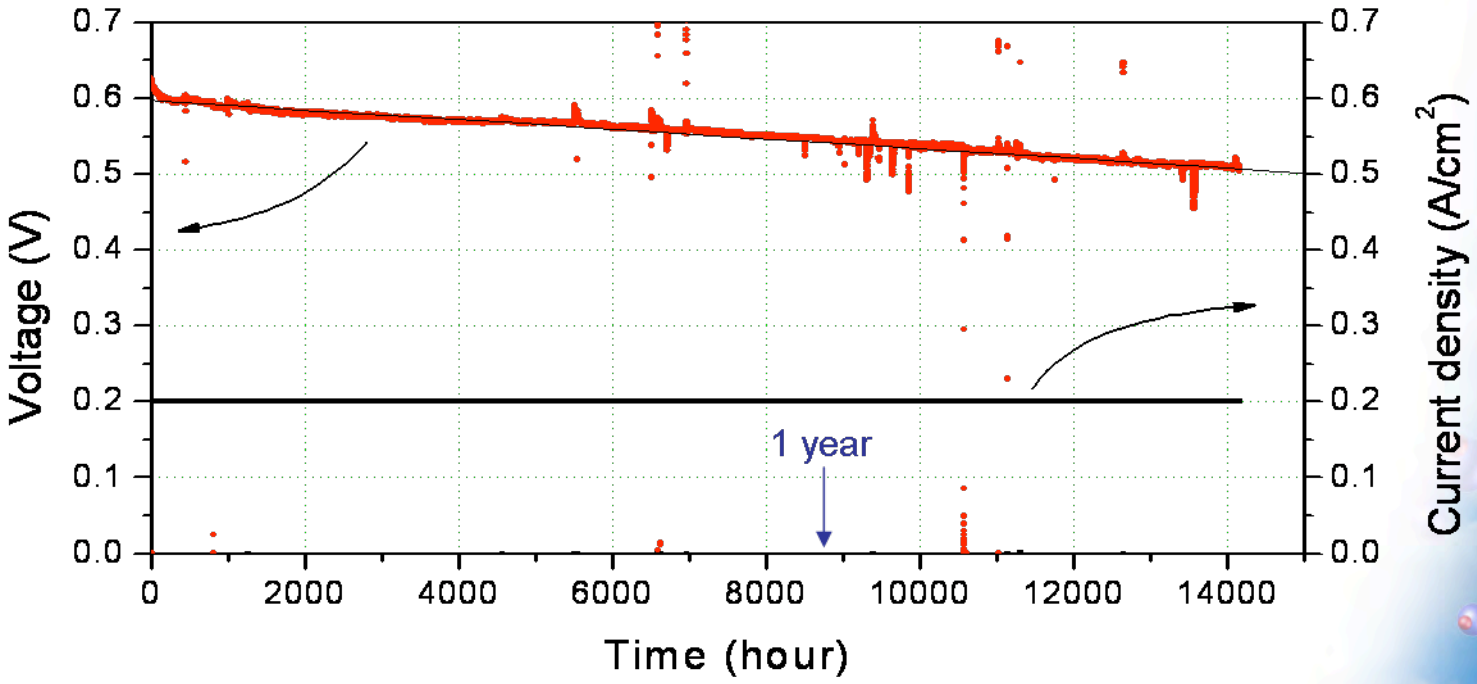
< 6 µV/hr



Active area: 45 cm²
Temperature: 160°C
No humidification
Ambient pressure
Anode: H2, lambda 1.2
Cathode: air, lambda 2.0

Long-term Durability @ 120°C

No humidification

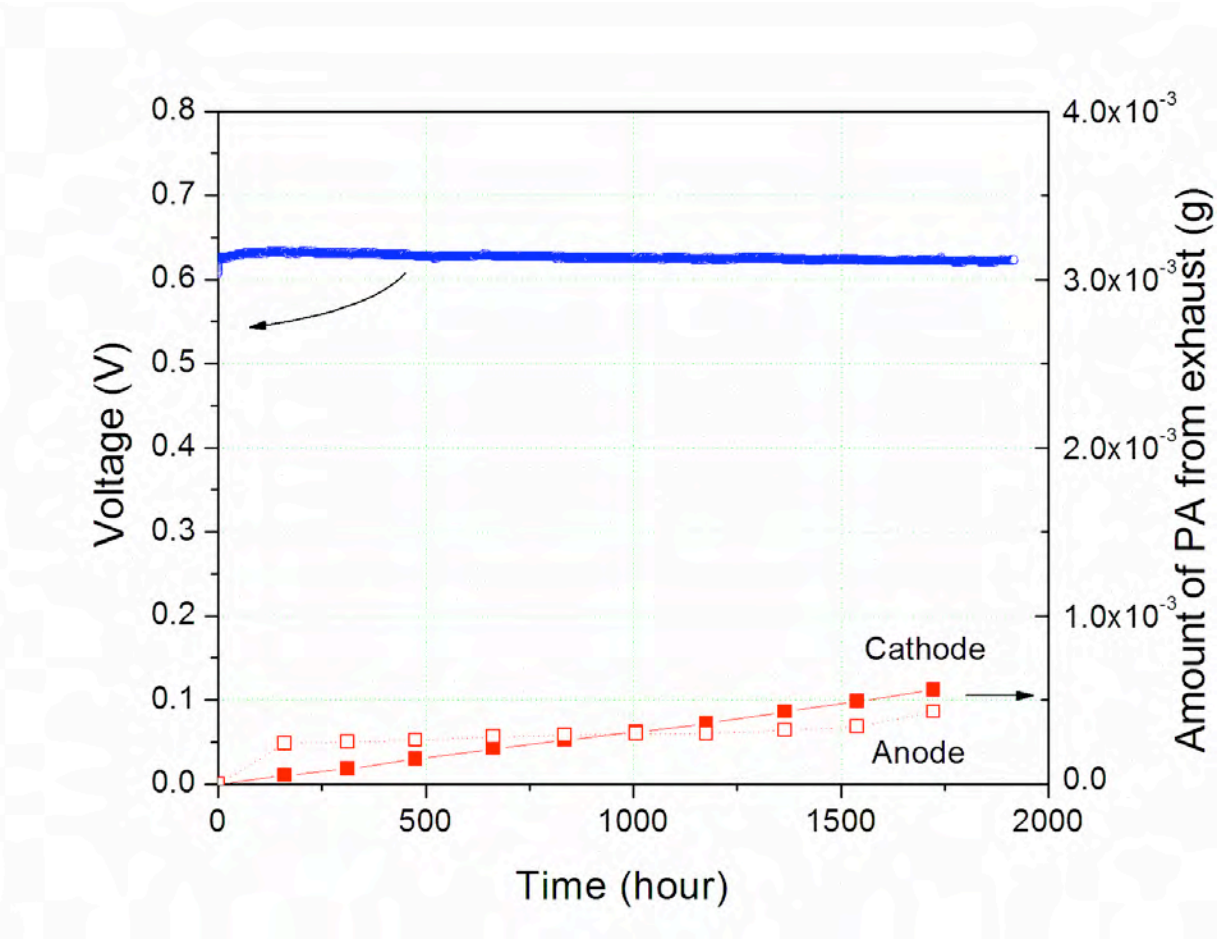


Degradation rate ~ 5 μV/hr

PA Retention

160 ˚C, Non-humidified

50 cm^2, steady-state operation @ 0.2 A/cm^2



5.8 µV/hour

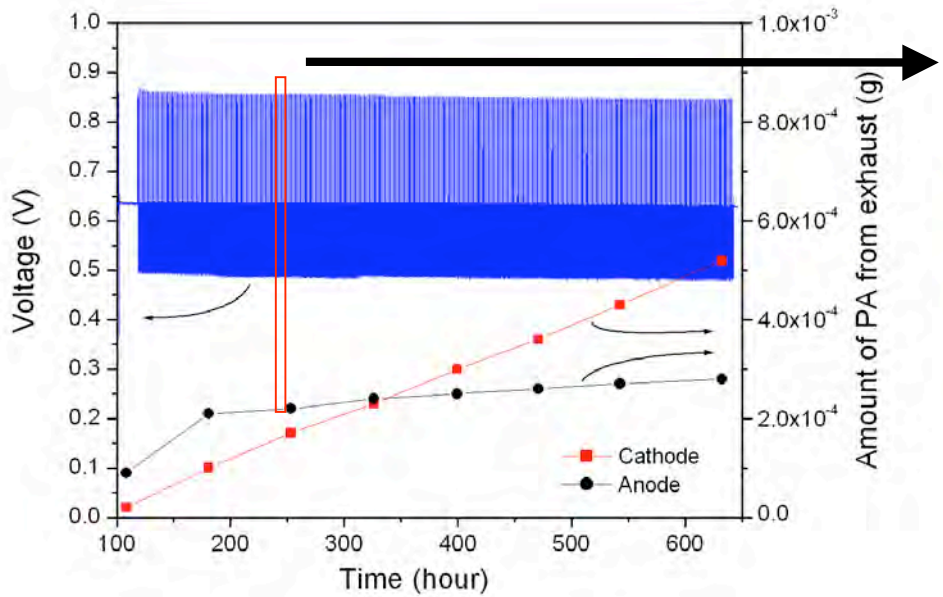
C: 7.1 ng/cm^2hr

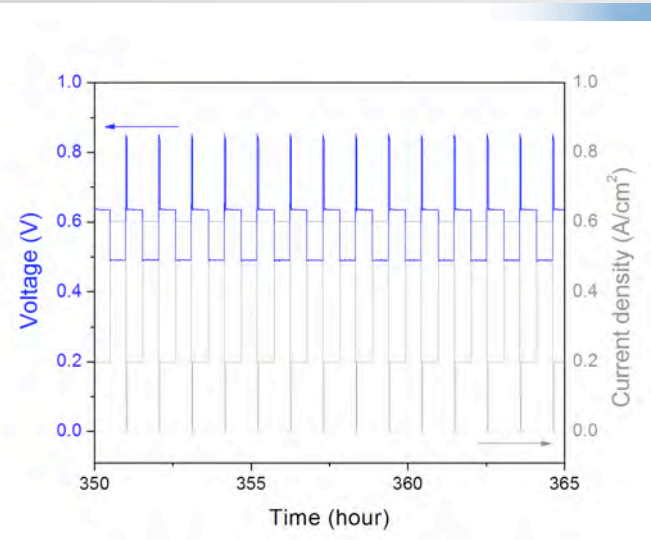
A: 1.5ng/cm^2hr

Load Cycling Test

500 cycles

Constant stoic, 160 C





Voltage drop

6.2 µV/hour @ OCV, 4.5 µV/hour @ 0.2 A/cm²

28 µV/hour @ 0.6 A/cm²

Voltage drop is comparable to static operation

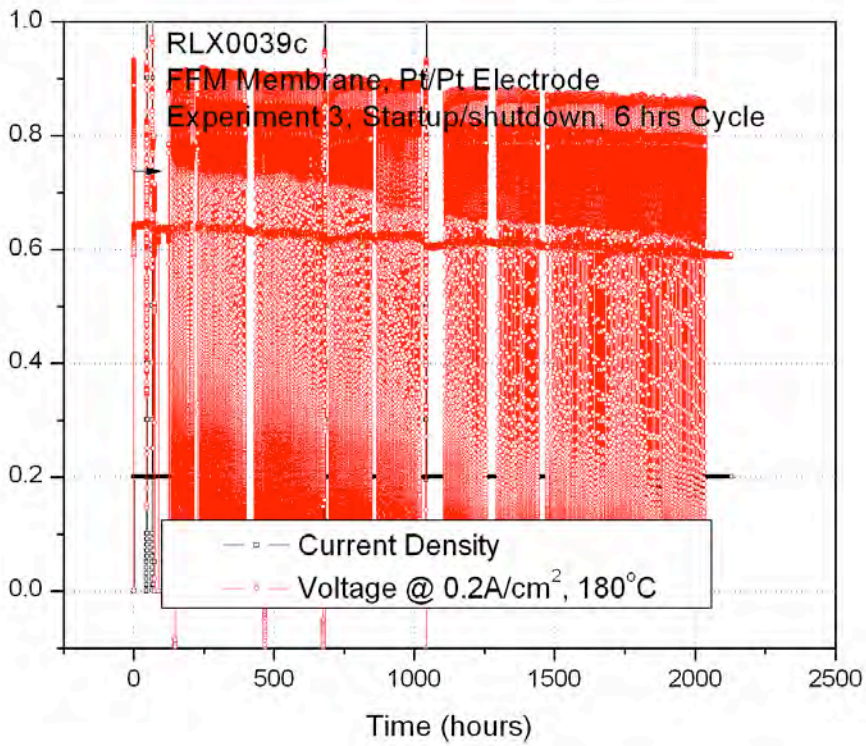
Acid loss

18.2 ng/cm²hr @ cathode

9.8 ng/cm²hr @ anode

28 ng/cm²hr @ both electrode sides

Shut down-Start up Testing



262 cycles completed

Degradation rate @0.2 A/cm2

~0.13mV per cycle

~ 2000 hours total time

Prototype 5 kW Residential Unit - Plug Power

Eliminate:

- Large radiator
- Humidifier
- Water pump
- Low temp shift
- PROX

Micro Portable Applications

UltraCell
TM

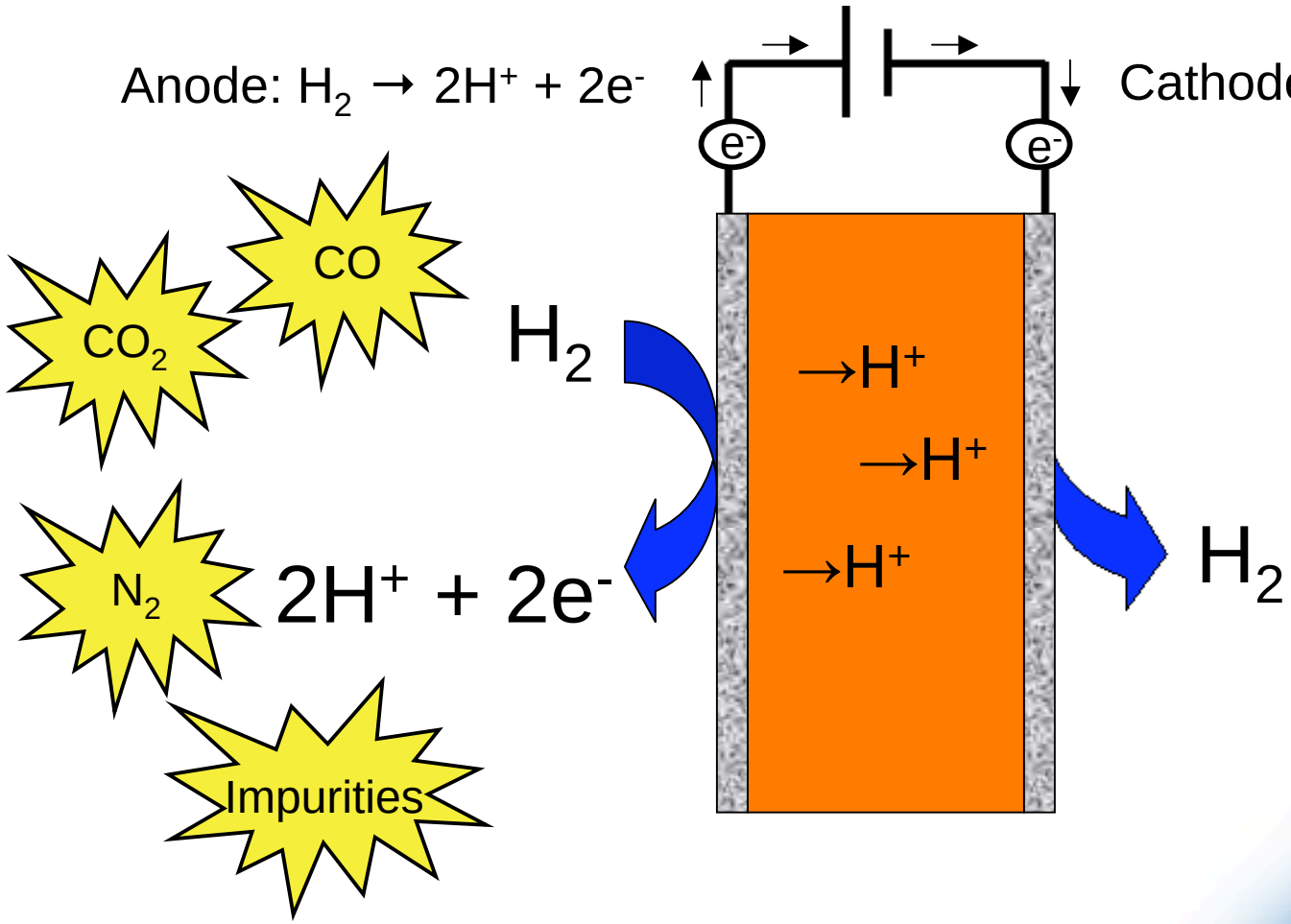
- Fuel Cells generate power for laptops, GSP and communication systems
- Power range: 5 W – 50 W
- Advantages: Independent from power grid, less weight and waste than batteries, cost effective
- Based on liquid fuels, e. g. Methanol
- BASF Fuel Cell provides the core products for this technology

Back-up Power Systems

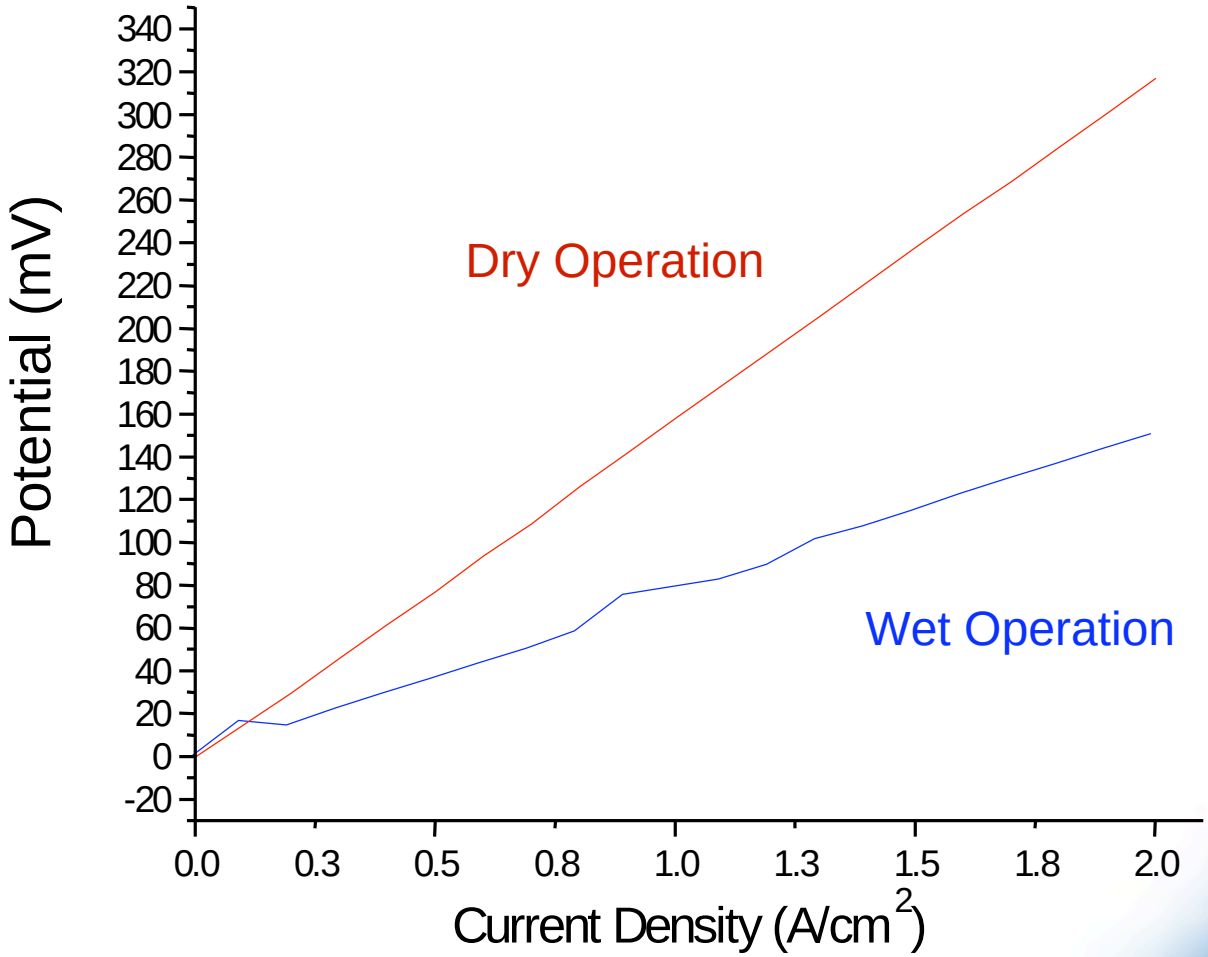
- Fuel Cells provide backup power for telecommunication, emergency centers, hospitals etc. when the power grid fails
- Power range: 1 kW to 10 kW
- Advantages: Silent, low emissions, high reliability
- BASF Fuel Cell provides core products for this technology

CLEAREDGE POWER

Electrochemical Hydrogen Pump

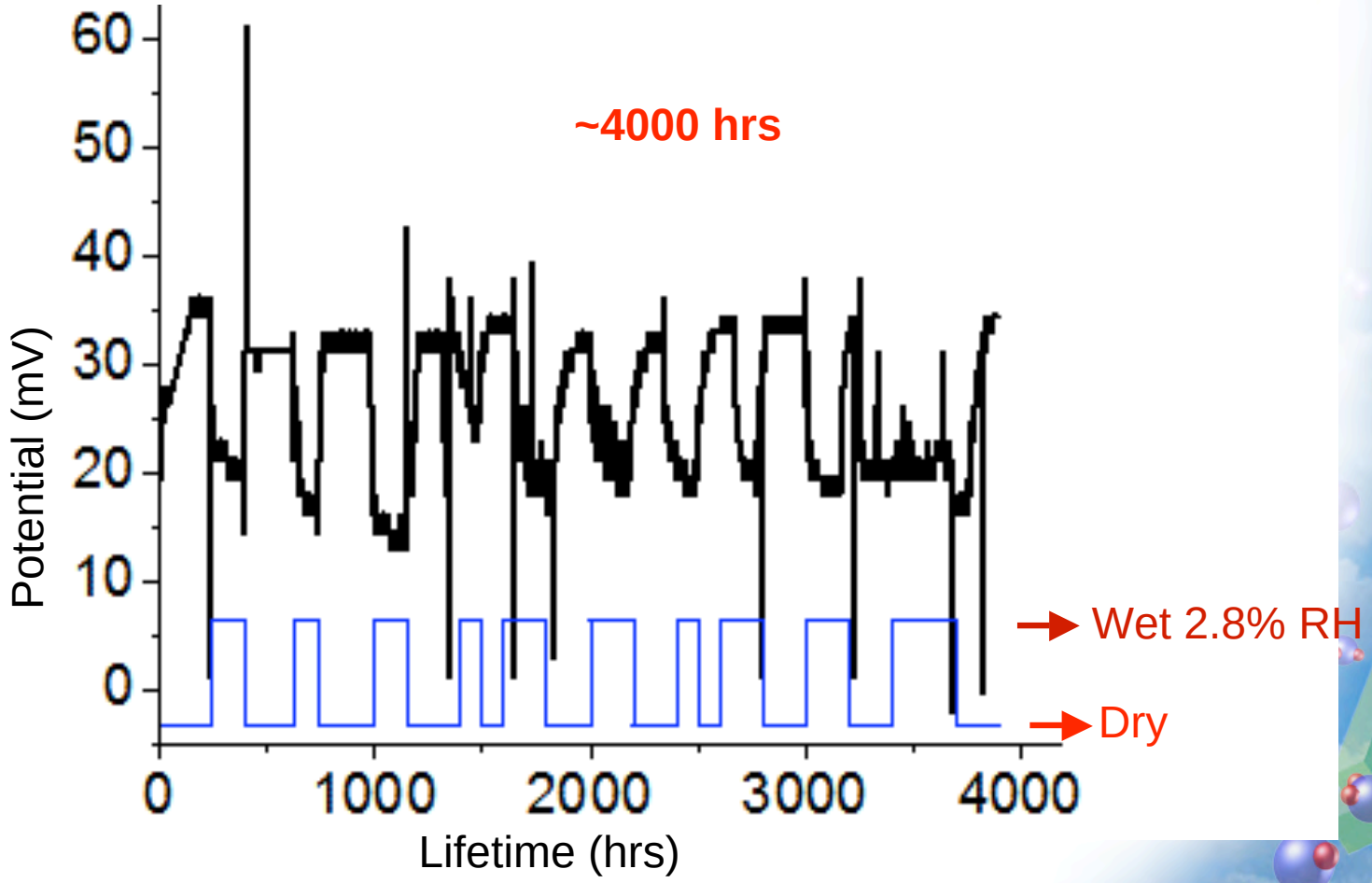


Demonstrated Cycled Wet/Dry Operation

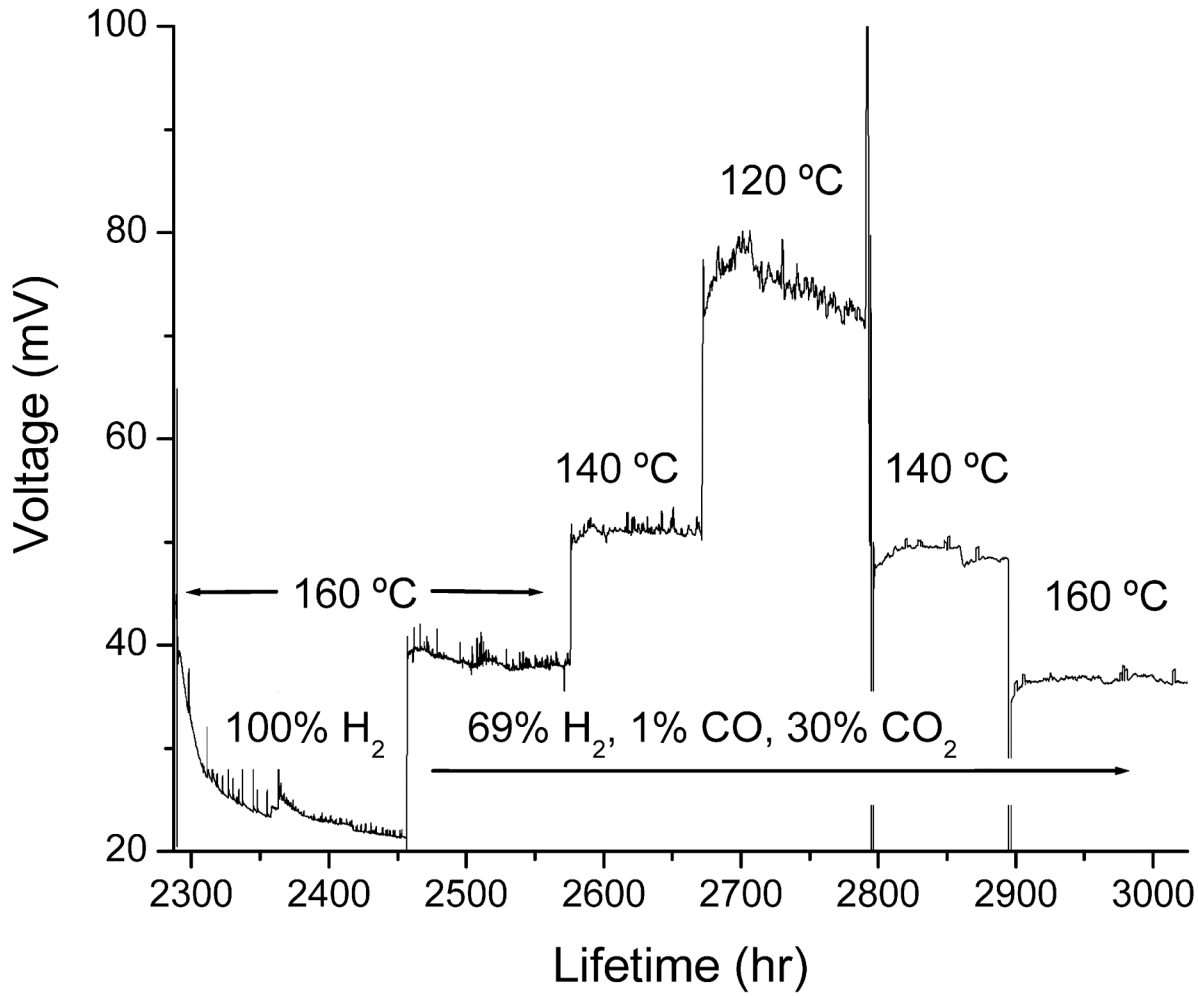


Durability

160 ˚C



Hydrogen Pumping on Reformate



Stack Design and Build

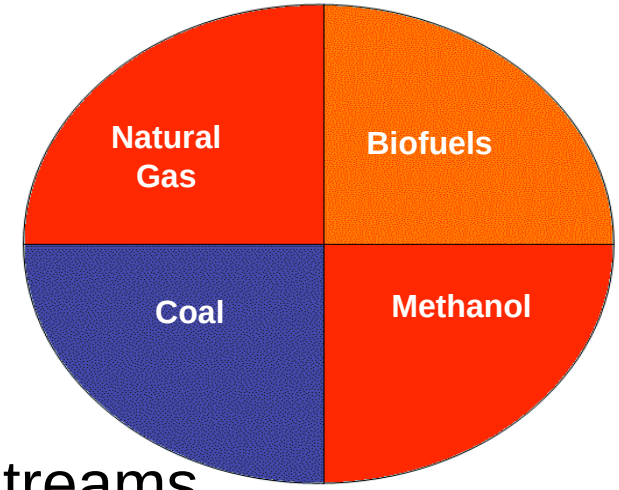
H2 Pump™

- ***H2 Pump*** stack
- 120 cells
- Capability ~ 20 kg H_2/day

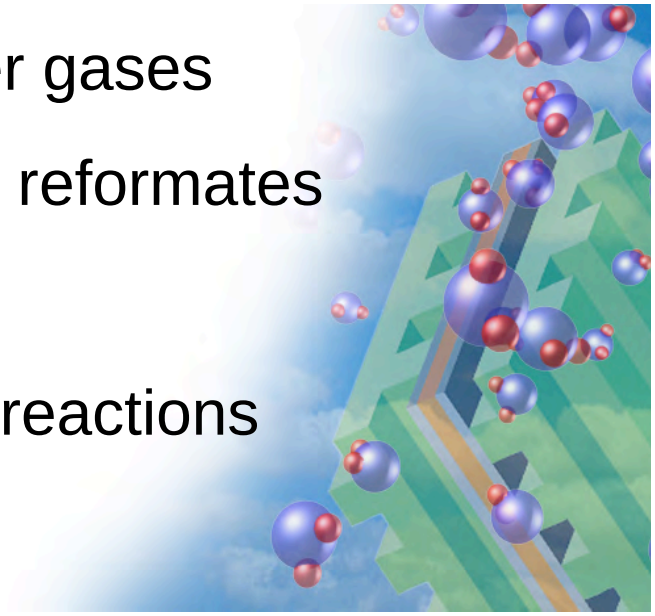
System Plan - 2009

Engineering Model
- Flow Rate: 500 cubic feet per hour
- Dimensions: 128 x 80 x 55 (cm)

Potential Benefits of a Hi-Temp Hydrogen Pump



- Very high efficiencies
- Purification of gas streams
  - Removal of CO, CO_2 from fuel streams
  - Separation of hydrogen from carrier gases
- Applicable to natural gas, coal, methanol reformates
- Pressurization of hydrogen gas streams
- Removes complicated oxygen reduction reactions



Summary & Conclusions

- Chemistry, process, structure and morphology important for determining properties - bulk and NMR measurements
- PA level also effects conductivity
- Excellent long-term stability at 120-180˚C, maybe even greater range
- Early cyclic load testing and thermal testing show low degradation rates
- Phosphoric acid loss rates measured under different static and cyclic operating conditions indicate 10,000's hours lifetime
- Early applications in residential, portable, back-up *and others* are being tested

Acknowledgments

PEMEAS Fuel Cell Technologies

BASF The Chemical Company

plug power

U.S. Department of Energy
Energy Efficiency and Renewable Energy

NSF Integrative Graduate Education and Research Traineeship *in Fuel Cells*

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