DEGRADATION AND RELIABILITY ANALYSIS OF PEM FUEL CELL STACKS

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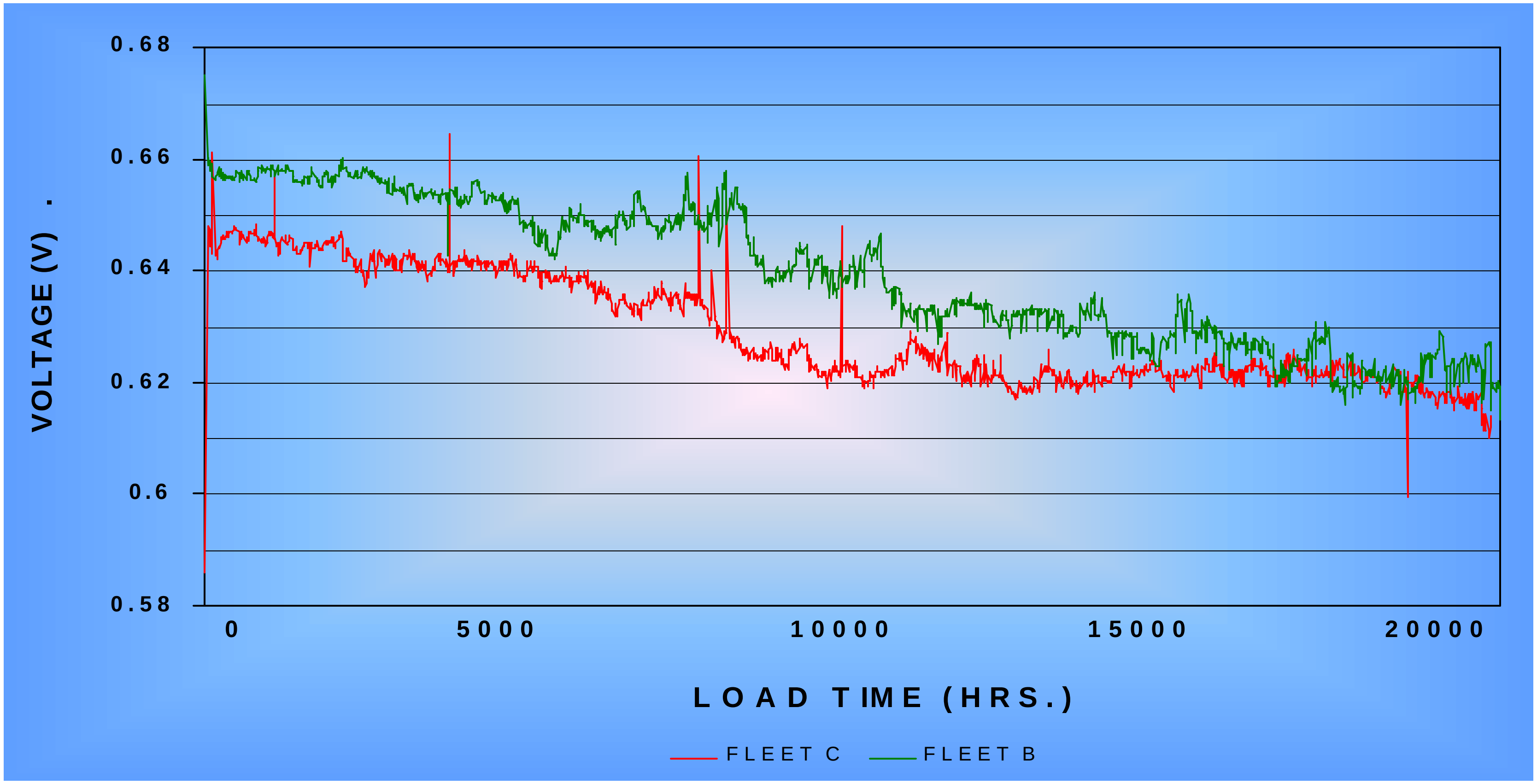
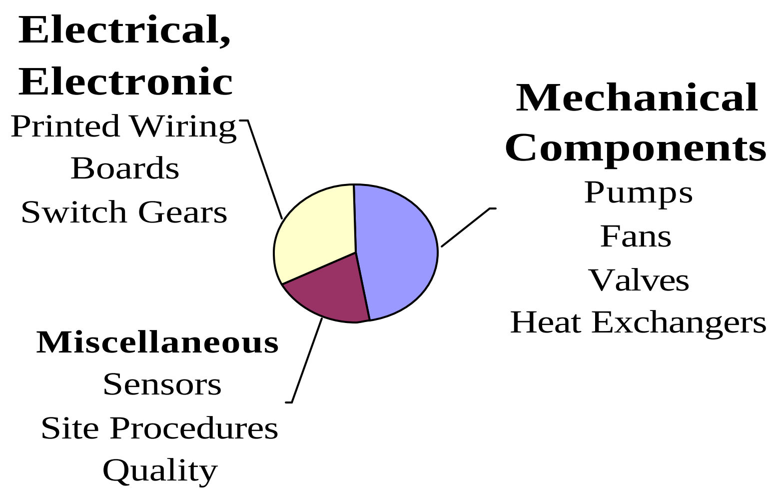
Average Cell Voltage



*U.S. DoD Fuel Cell program

BALANCE OF PLANT RELIABITLY (for the DoD program)

•Literature indicates that balance of plant is the most significant issue for fuel cell reliability at this time.



Data for a 'fleet' of 36 DoD PAFCs

BOP reliability simply an issue of:

engineering commitment, quality control and cost.

BALANCE OF PLANT

- **Pumps, Compressor/Expanders, Burners, Heat Exchangers, Condensers, Vaporisers, transformer/inverter, piping & connectors, switches, monitors, control systems (software), control strategy**
- **Power Conditioner (94-98% efficiency)**
- **Fuel Storage and Handling**

FUEL PROCESSING SYSTEM

- **Materials and Containment Issues**
- **Deactivation of Reformer Catalyst** ($Cu/ZnO/Al_2O_3$)

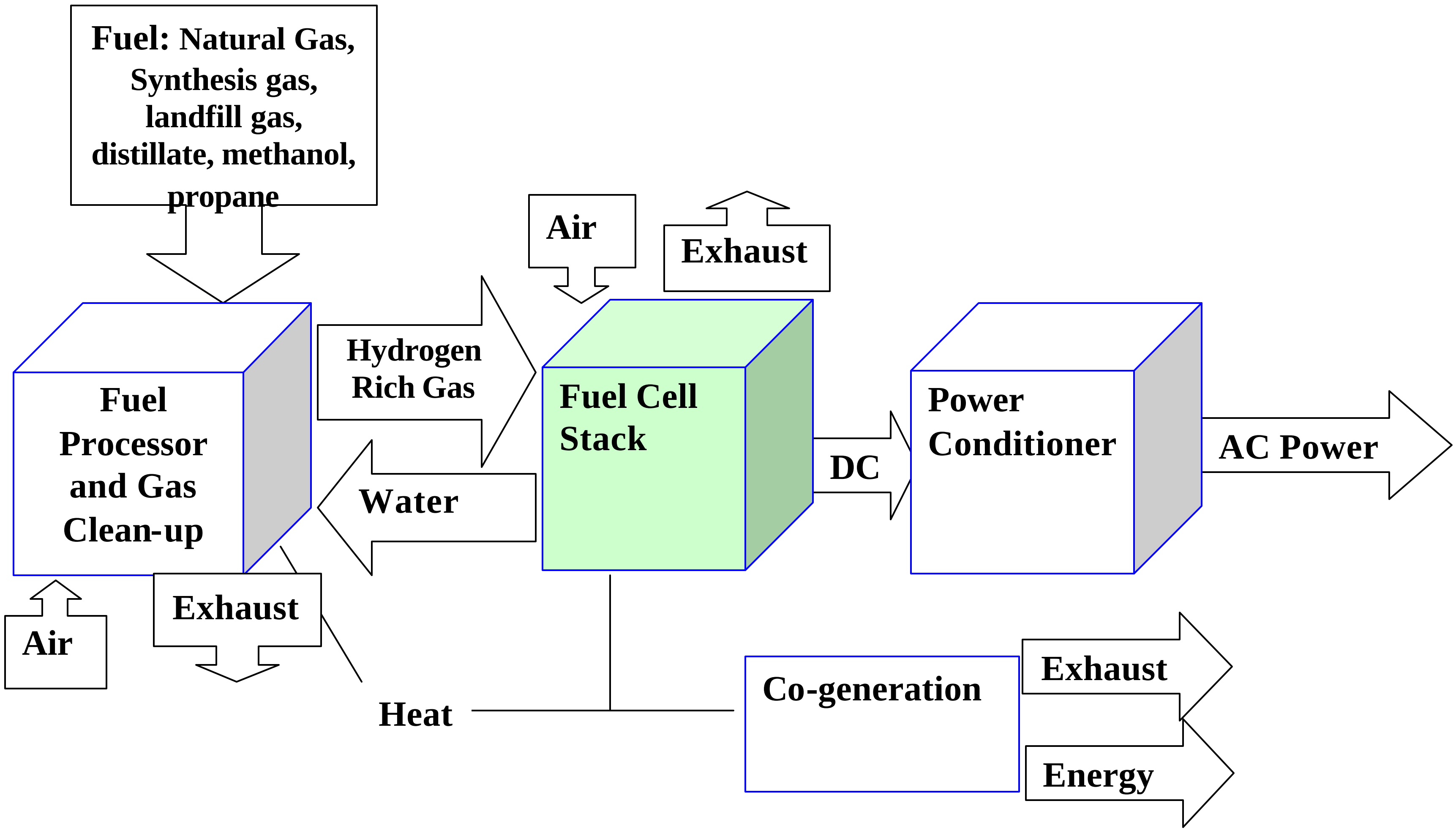
(physical causes, poisoning by impurities, poisoning by reactants or products)

- **Chlorides, Arsenic**
- **Sulphur (can be 'leached out of seals')**
- **Carbon** **('Coking')** **Deposition** **(function of Steam/Carbon ratio)**
- **Thermal Damage**
- **Sintering (Catalyst Deactivation)**
- **Dew Point Concern**

RELIABILITY JARGON

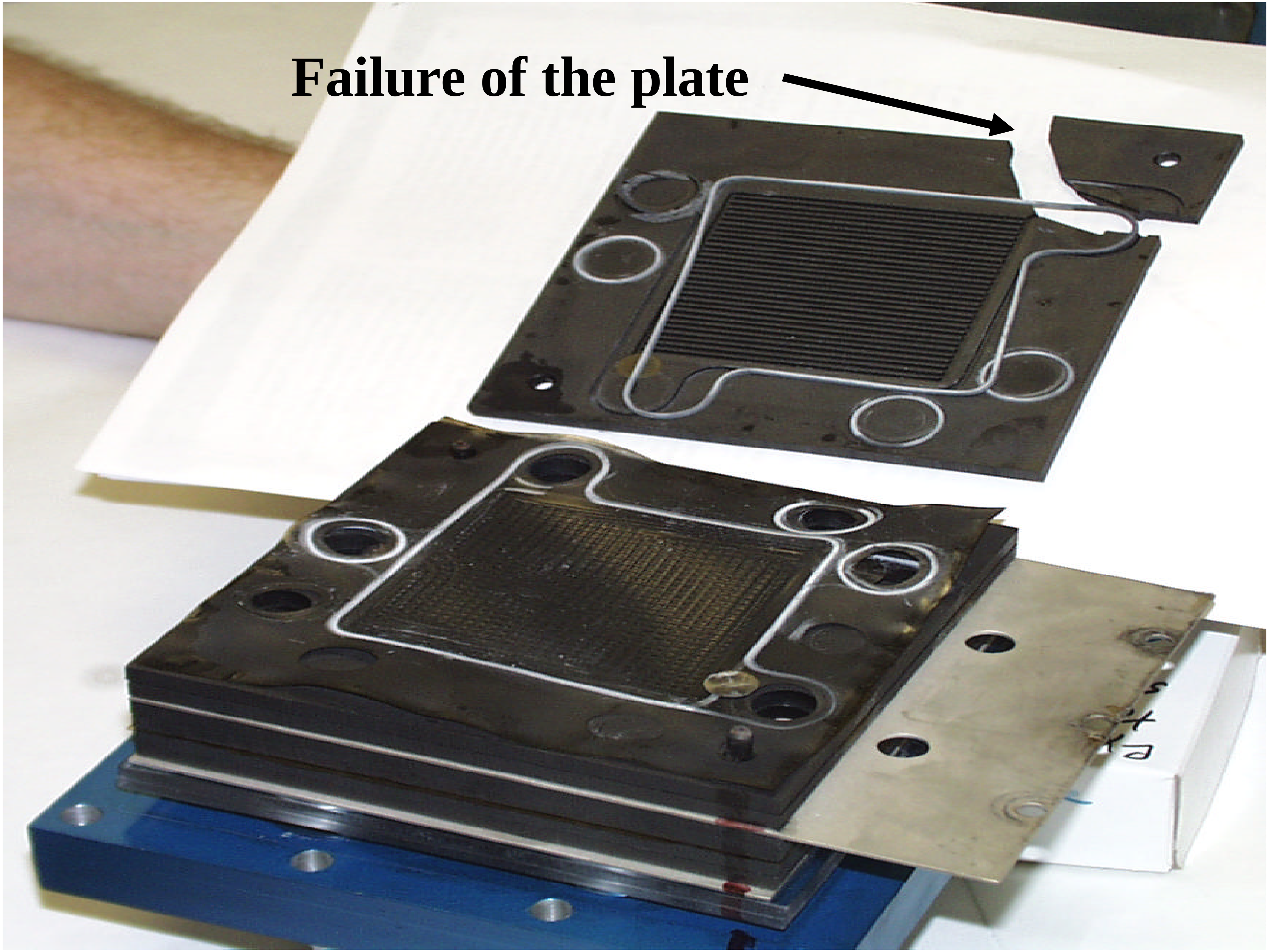
- ***Durability*** **- ability to resist permanent change in performance over time, i.e. degradation *or irreversible degradation*. This phenomena is related to *ageing*.**
- ***Reliability*** **- The ability of an item to perform the required function, under stated conditions, for a period of time. Combination of degradation, and failure modes that lead to catastrophic failure.**
- ***Stability*** **- recoverable function of efficiency, voltage or current density decay *or reversible degradation*.**

PEM FUEL CELL SYSTEM



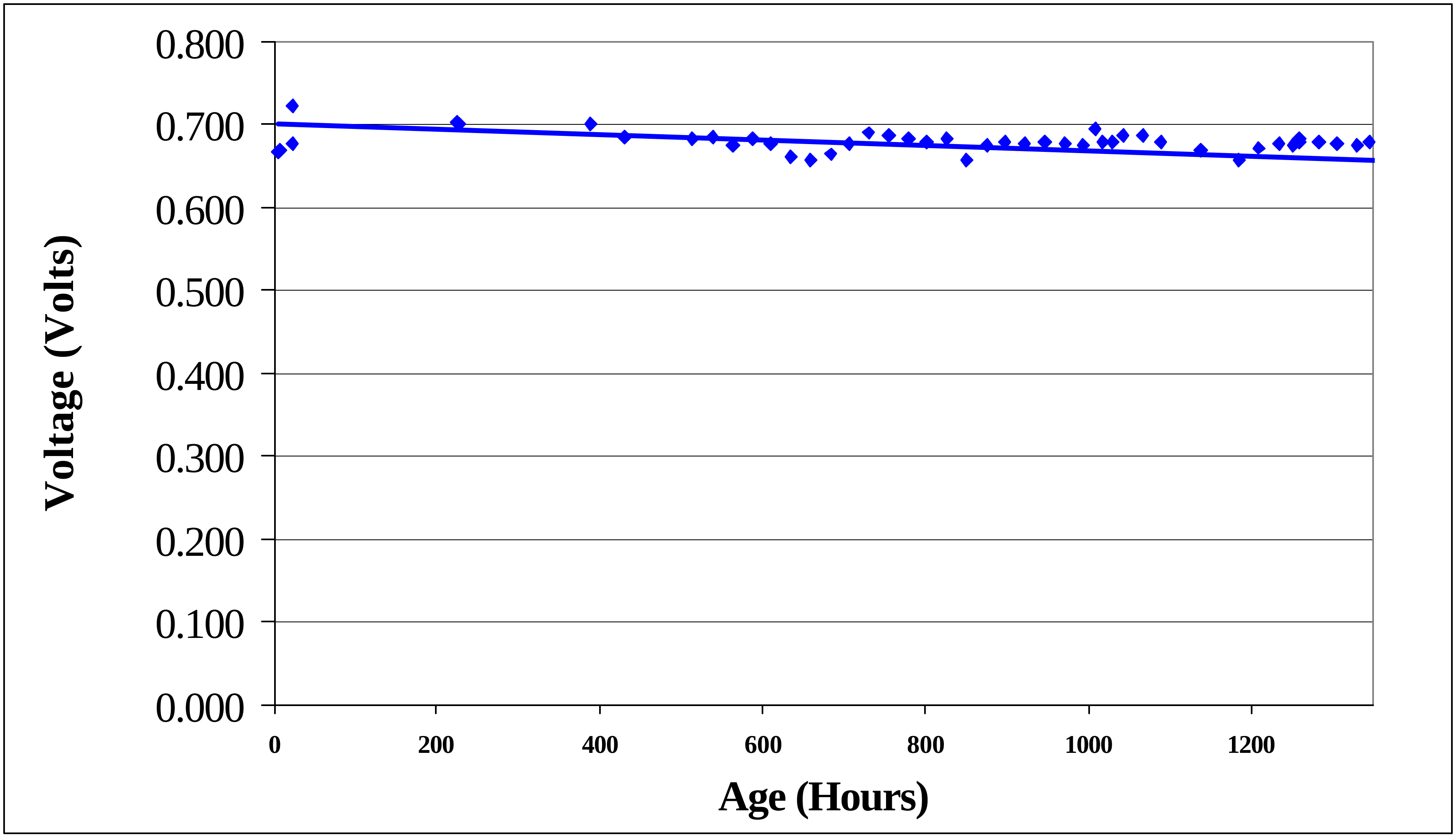
FMEA OF A FUEL CELL

- Plate
  - Cracking
  - Scorching
  - Corrosion / Pacification
  - Change in the Plate which will impact the MEA
    - Dimensional changes (warping, erosion, misalignment)
    - Contamination or debris released
- Seal Failure
- MEA
  - Pinhole Formation
  - Shorting
  - Degradation of Voltage


Failure of the plate

VOLTAGE DEGRADATION CURVE FOR A SINGLE PEM CELL

(Operated at 80°C, 0.4 amp/cm2, 30 psig/30 psig, H2/Air – stoichiometric ratios 1.2/2)



VOLTAGE DEGRADATION

- **Voltage Degradation will be the main factor governing the 'life' of the stack itself (*i.e.* time in service, performance and reliability at end of life)**
- **Degradation must be accommodated for in control systems**
- **Will be important in Life Cycle Analysis (especially the Life Cycle Costing)**

DEGRADATION FAILURE MODES

(leading to degradation of performance or *durability*)

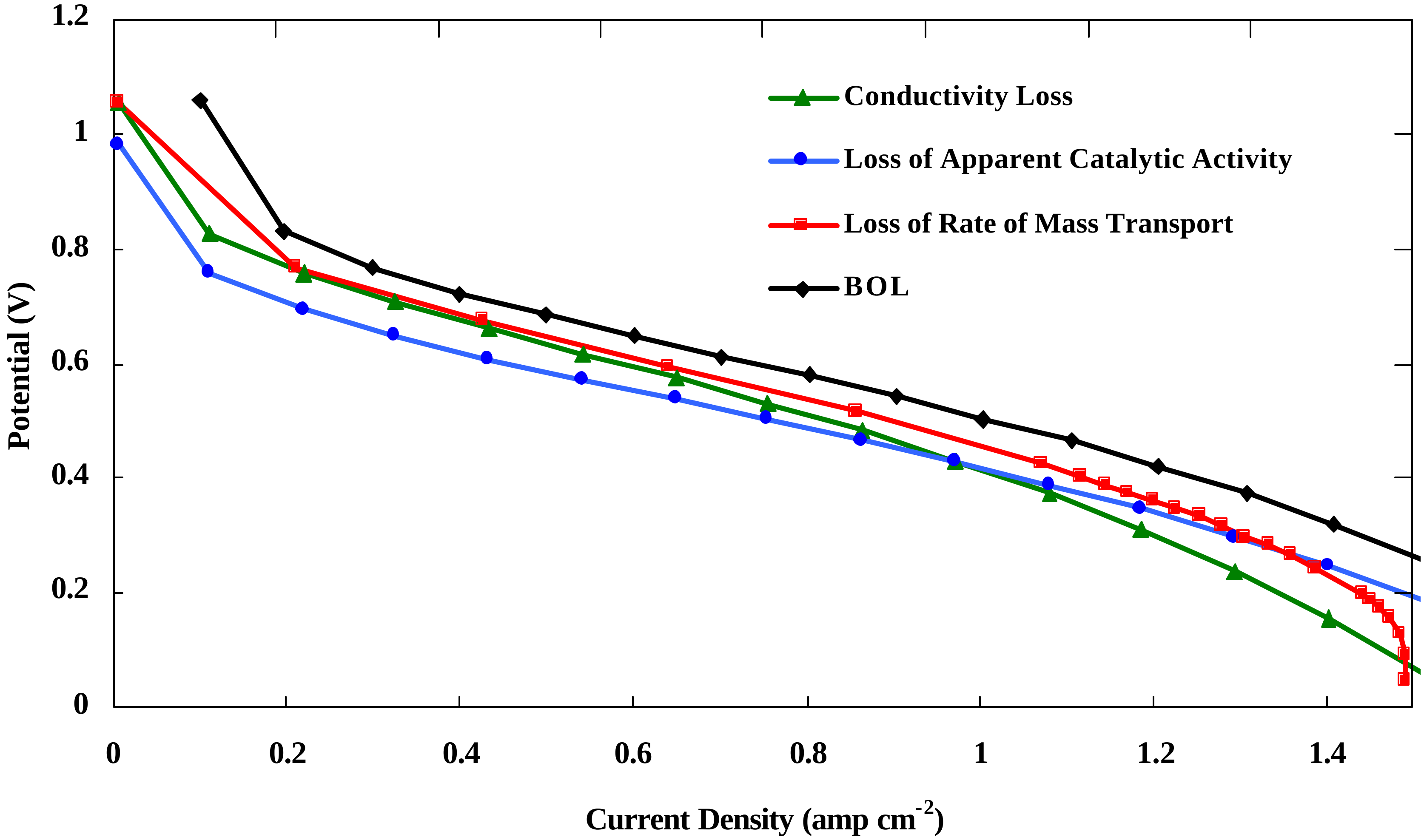
- **Kinetic or activation loss in the anode or cathode catalyst –**

  Loss of Apparent Catalytic Activity
- **Ohmic or resistive increases in the membrane or other components –**

  Loss of Conductivity
- **Decrease in the mass transfer rate of in the reactants flow channel or electrode –**

  Loss of Mass Transfer Rate of Reactants

VOLTAGE DEGRADATION MODES



LOSS OF APPARENT CATALYTIC ACTIVITY

- Catalyst sintering (catalyst migration or ripening)
- Loss of catalytic or electrolyte material
- Low levels of contaminants binding to active sites
    - Contaminants from reactants (including dust)
    - Contaminants leached from fuel cell components
- Poor water management may contribute to mechanisms (flooding and dehydration) or simply the presence of liquid water
- Degradation of Nafion in contact with active sites
- Carbon Corrosion

LOSS OF CONDUCTIVITY

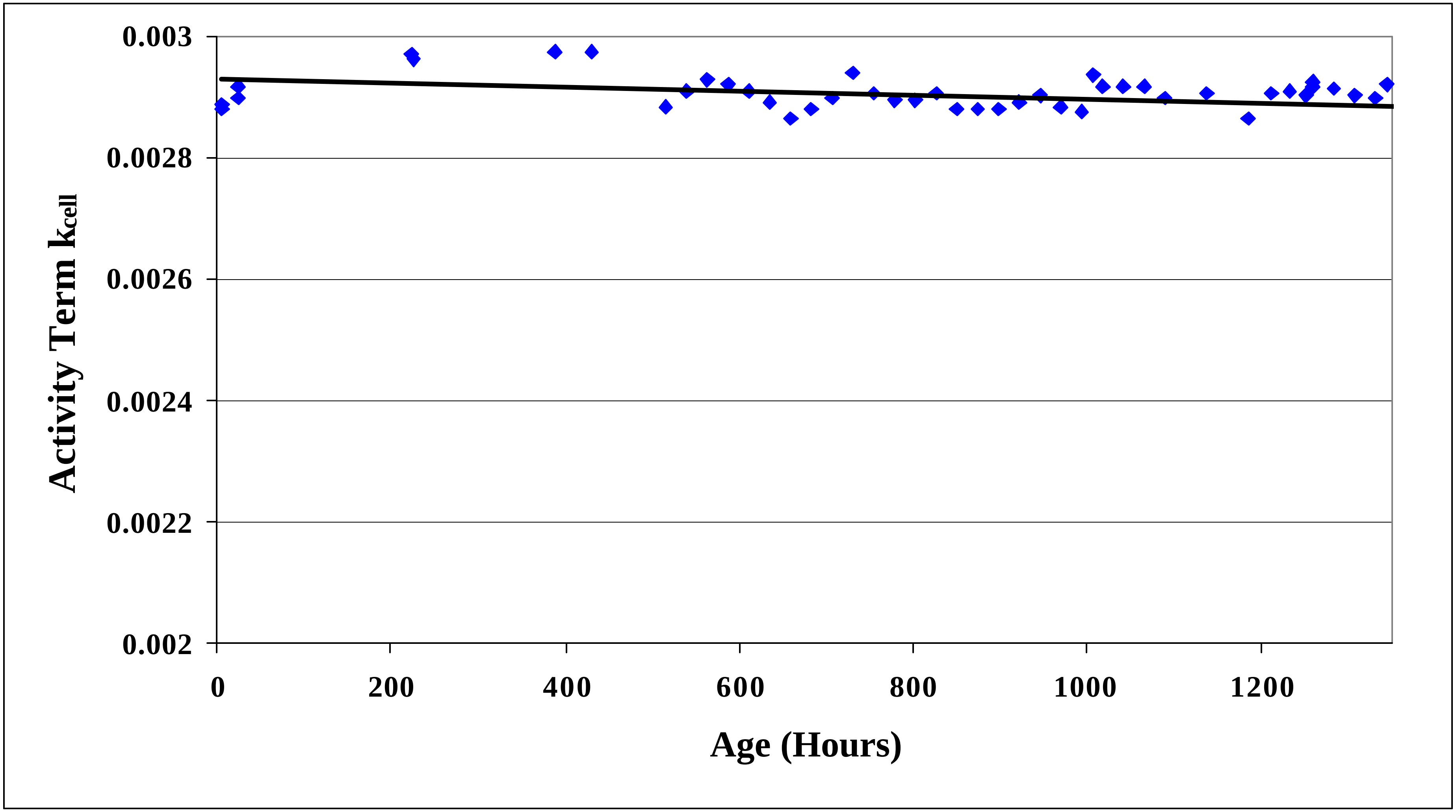
- **Low levels of cation contamination reducing the proton conductivity (this cause may be accelerated by high hydration levels as the water acts as a source and pathway for contaminates)**
- **Changes to eletro-osmotic drag properties**
- **Changes to the water diffusion characteristics of the membrane**
- **Corrosion of the plates leading to increased contact resistance**
- **Thermal or hydration cycling leading to mechanical stress cycling resulting in delamination of the polymer membrane and catalyst**

LOSS OF MASS TRANSFER RATE

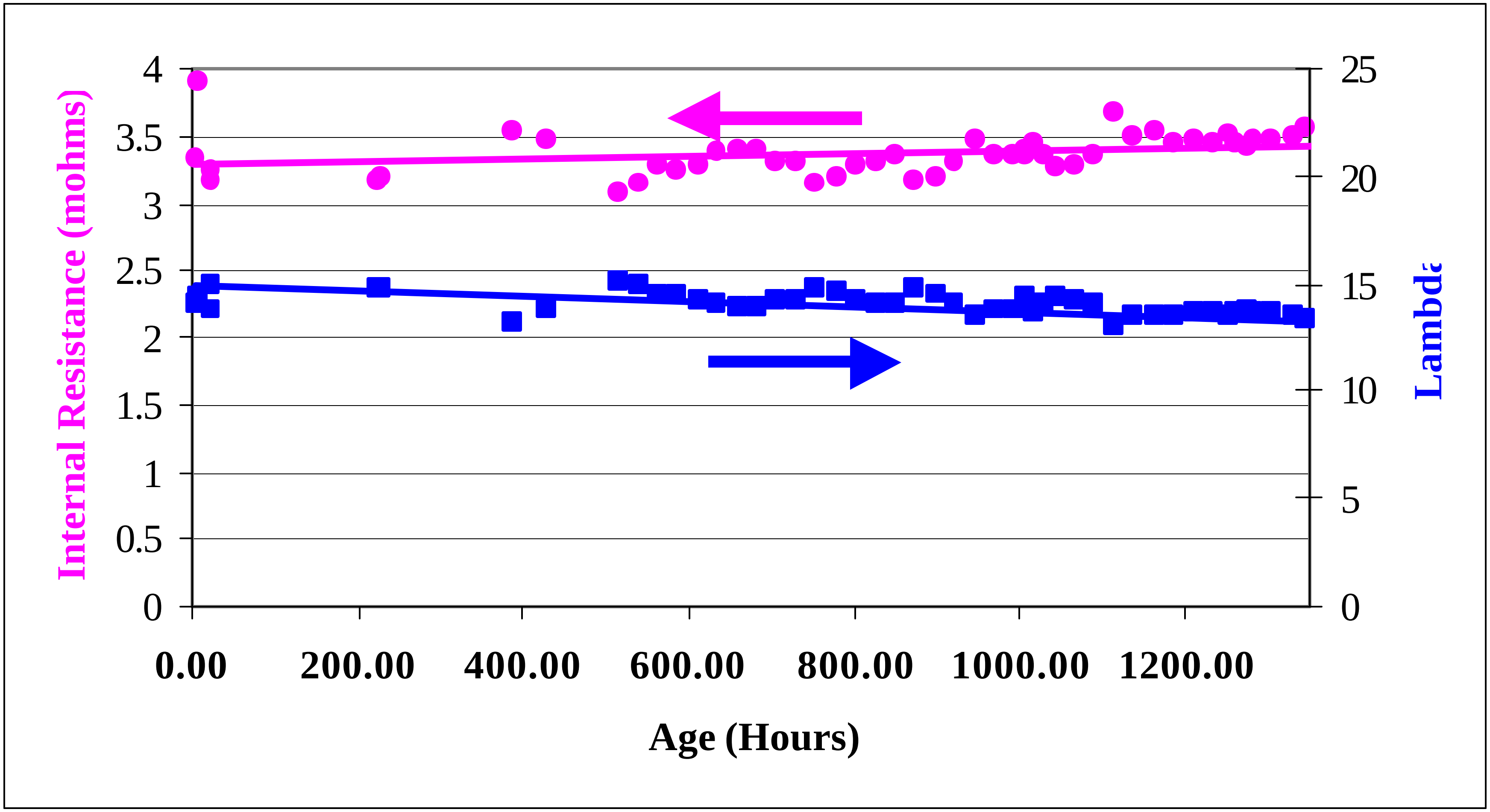
- Swelling of polymer materials in the active catalyst layer changing water removal characteristics
- Compaction of the gas diffusion layer due to mechanical stresses
- Surface chemistry changes in the gas diffusion layer making water removal more difficult
- Carbon Corrosion

ACTIVITY TERM k_{cell} (from the GSSEM) OF A SINGLE CELL

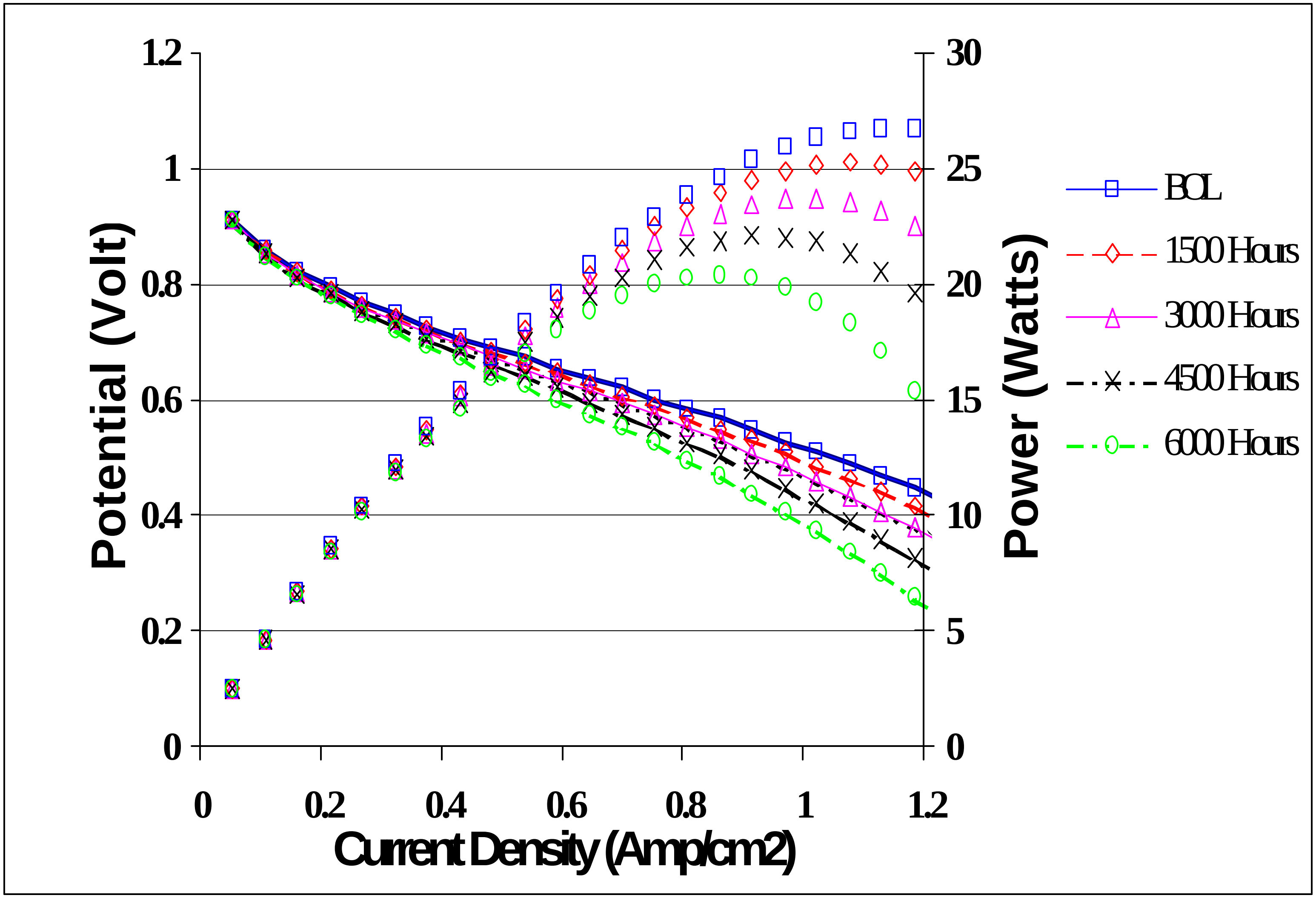
(Operated at 80°C, 0.4 amp/cm2, 30 psig/30 psig, H2/Air – stoichiometric ratios 1.2/2)



RESISTANCE INCREASE IN A SINGLE CELL



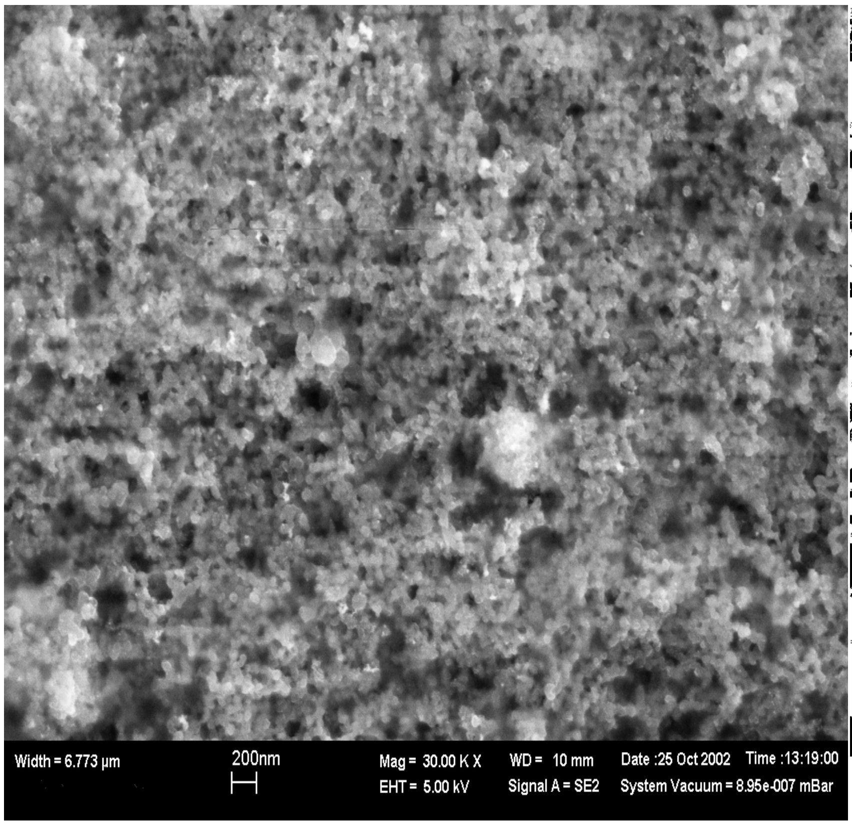
SIMULATION OF A SINGLE CELL USING THE GSSEM

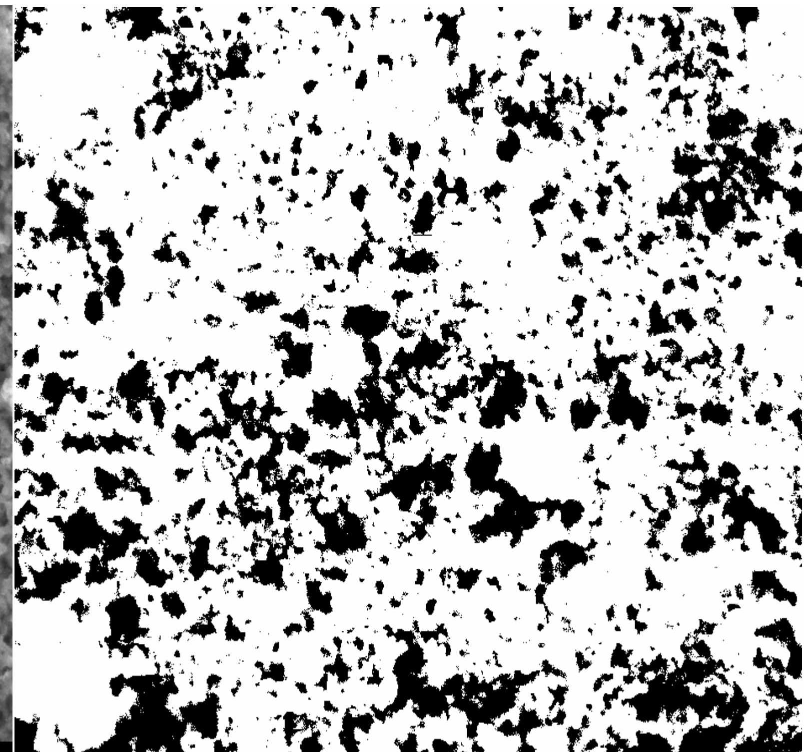


MEA ANALYSIS METHODS

- **DMTA**
  - **Mechanical behaviour, stress-strain curves**
  - **Hydrated studies are possible**
  - **Identification of thermal transitions**
- **DSC**
  - **Crystallinity changes**
  - **Melting point**
- **SEM**
  - **Porosity**
  - **Agglomerate Structure**
  - **Dimensions and cross sections**
  - **Delaminaiton**
  - **Composition and element migration**

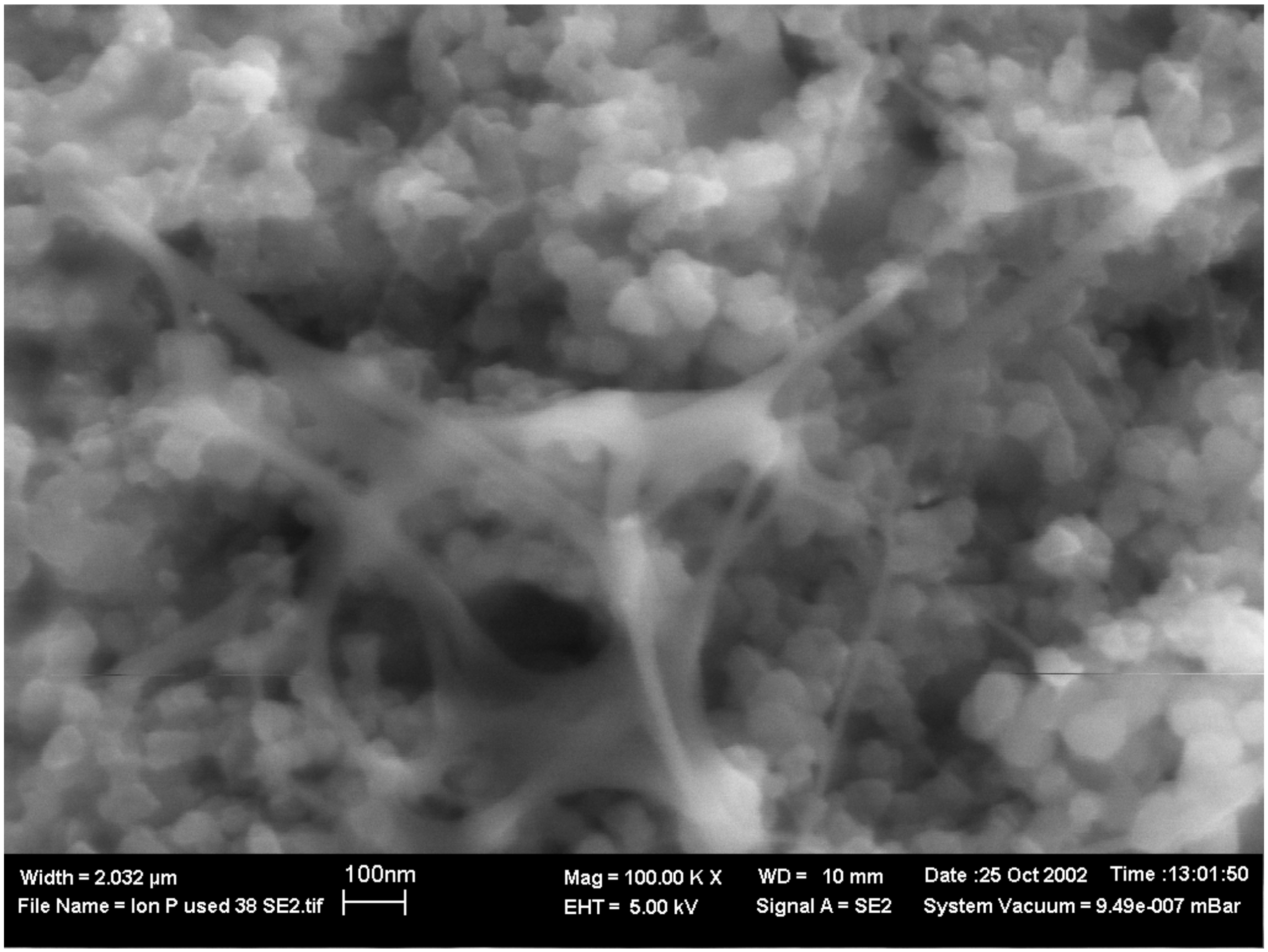
Porosity





Using SEM images and image analysis tools the surface porosity of this Ion Power MEA can be determined. We can also determine if porosity is changing over time and to what degree.

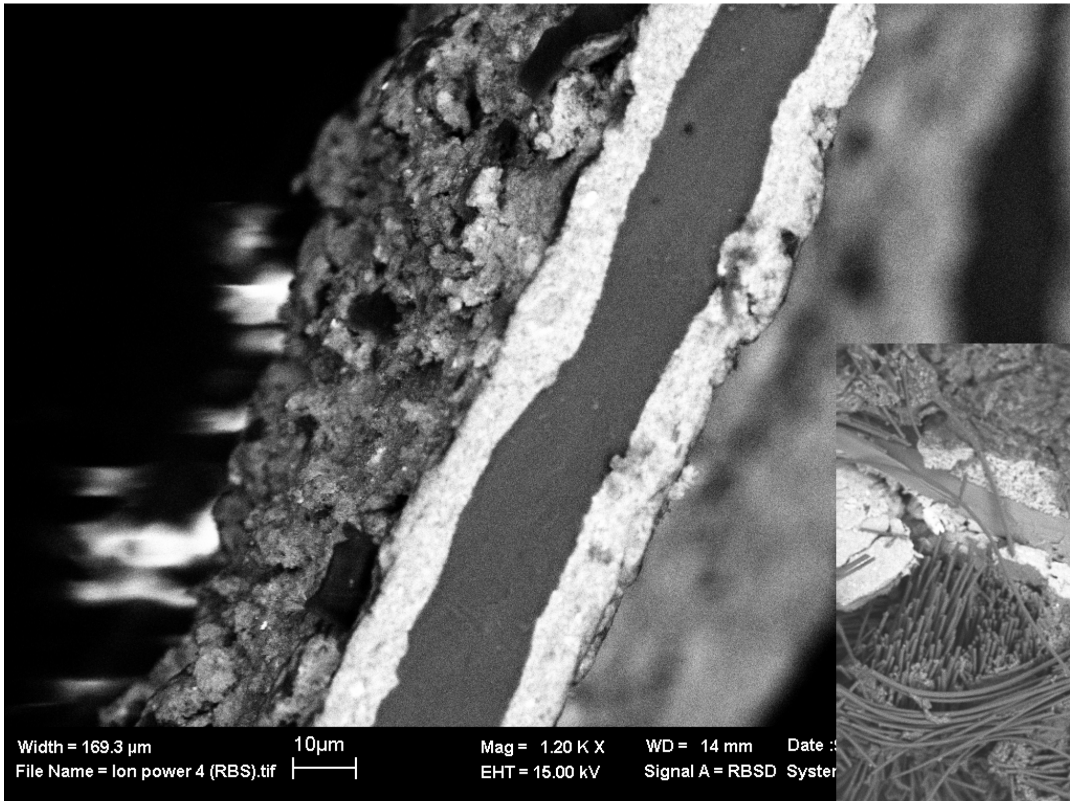
Agglomerate Structure



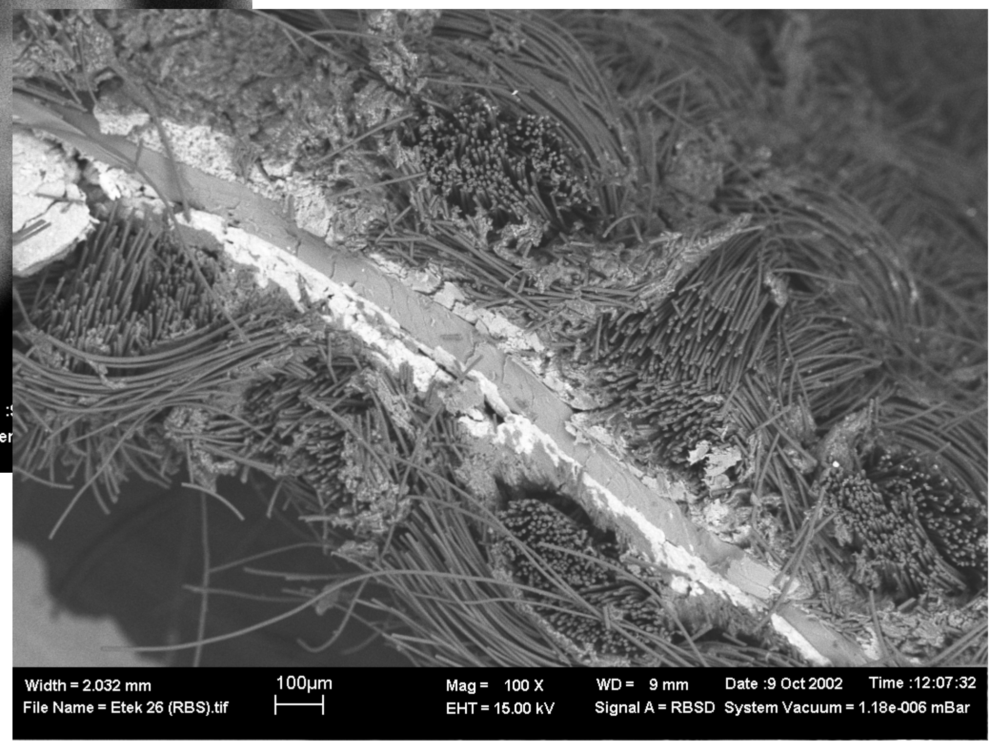
View of the three phase structure of the catalyst layer.

We can see the carbon particles (which are supporting the platinum catalyst) mixed with the Nafion.

Dimensions and Cross Sections

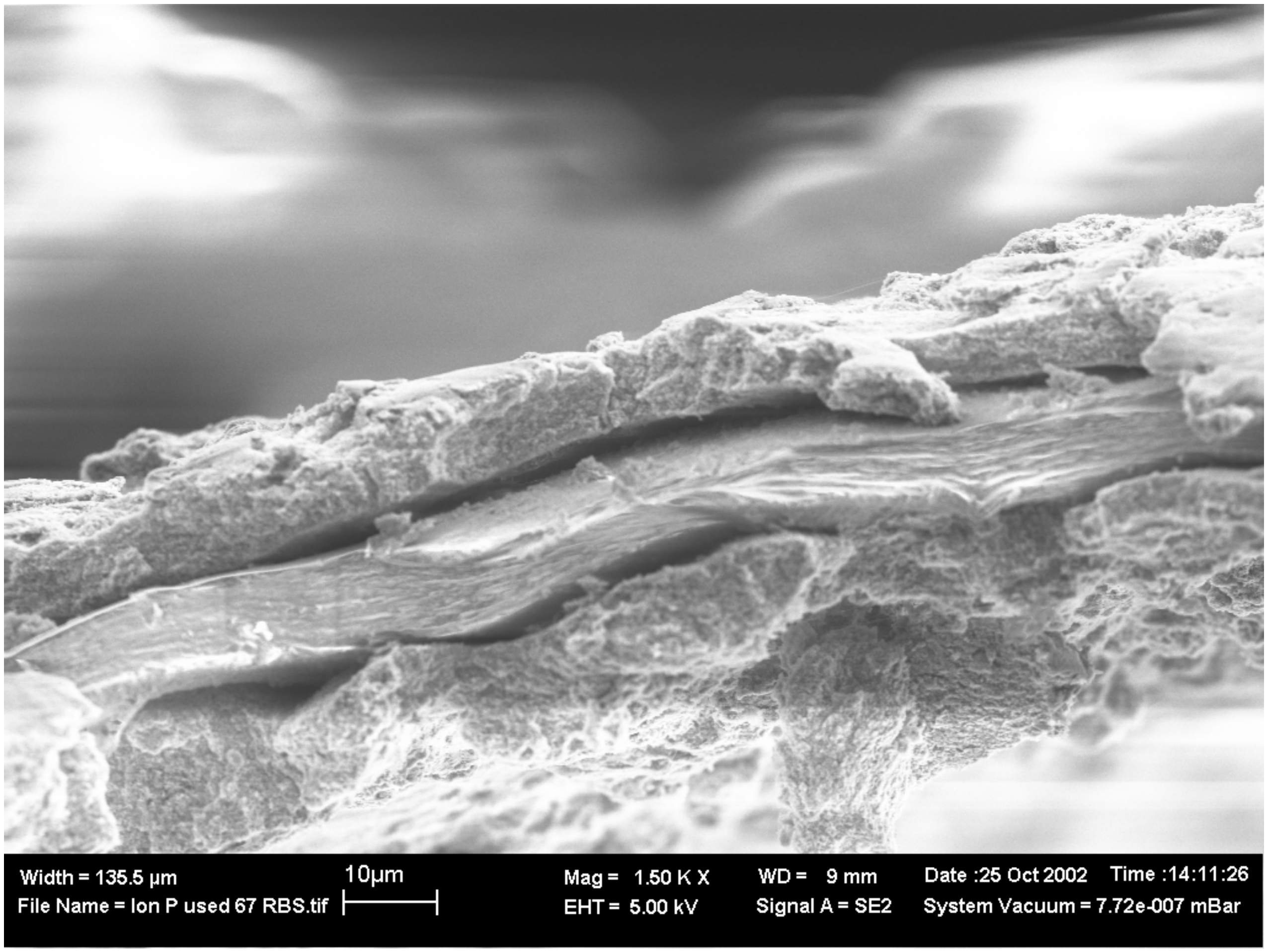


Cross section – freeze fractured



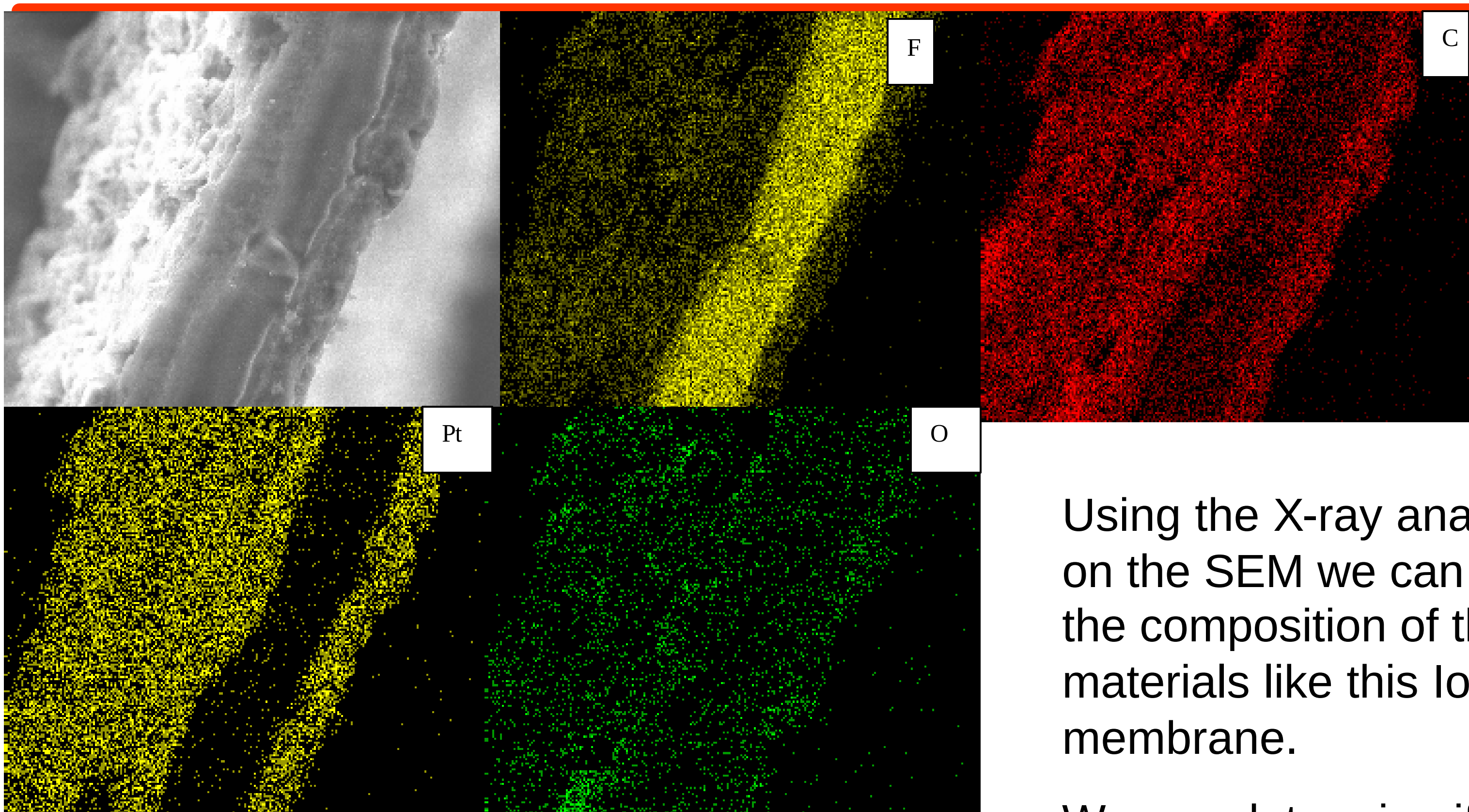
ETEK cross section – Cut

Delamination



Using the SEM we can determine the degree of delamination as seen in this Sample.

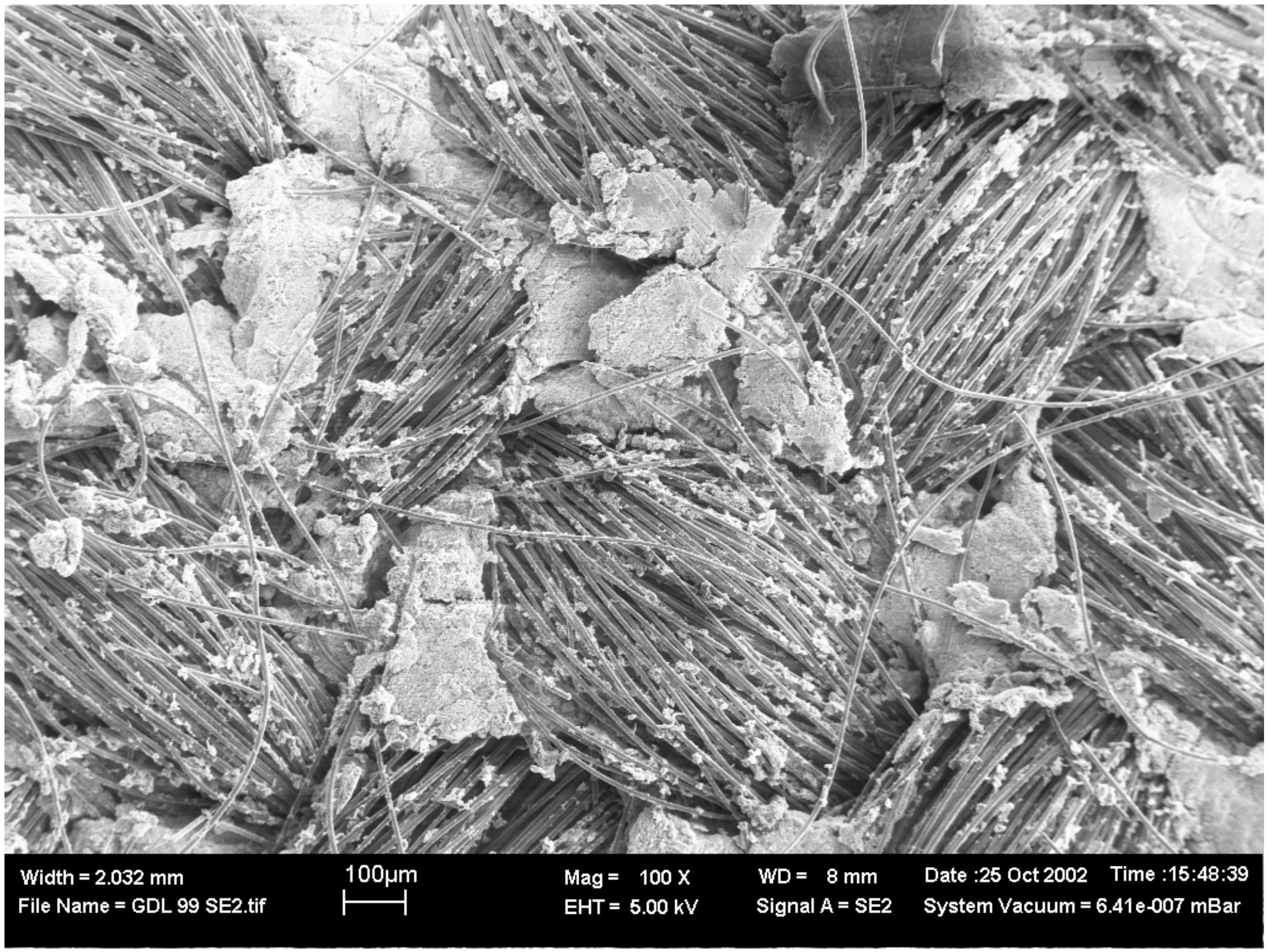
Compositional Analysis



Using the X-ray analysis tools on the SEM we can examine the composition of the materials like this Ion Power membrane.

We can determine if metallic bipolar plates are leaching ions onto the MEA.

GDL



As the GDL is used the Teflon coating may degrade and be washed away.

THE OBJECTIVE IS DESIGN IMPROVEMENT WITH RELIABILITY ANALYSIS

- **Must account for stochastic behaviour of cells**
- **Includes a Degradation Model', *(durability) where* 'Failure' is degradation to below threshold value for specific parameter (*e.g.* voltage, efficiency, power) Catastrophic failure of the MEA**
- **Goal of the analysis is to allow an understanding of the impact of design (*e.g.* redundancy - increase loading of catalyst) and operation changes (*e.g*. limitation of operating states) on EOL performance**

PERFORMANCE MEASURES OF A FUEL CELL STACK

Mean Time to Failure **(function of reliability and decay rate)**

- **Power Capacity** **- kW net electrical output**

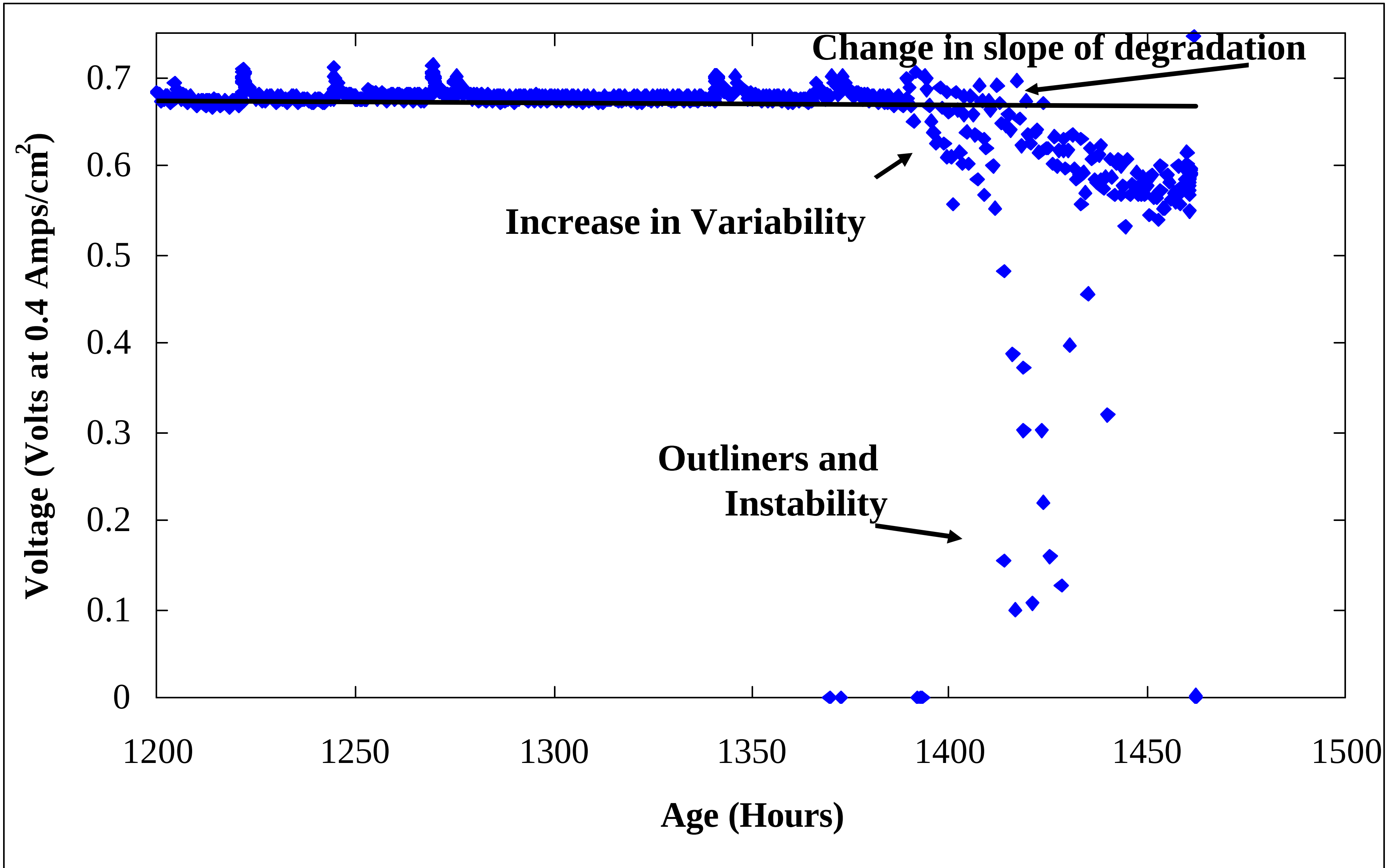
(Durability - <5% power degradation)

- **Fuel Efficiency** **- % based on LHV of fuel**

(60% at '25% peak power', and 48% at peak power)

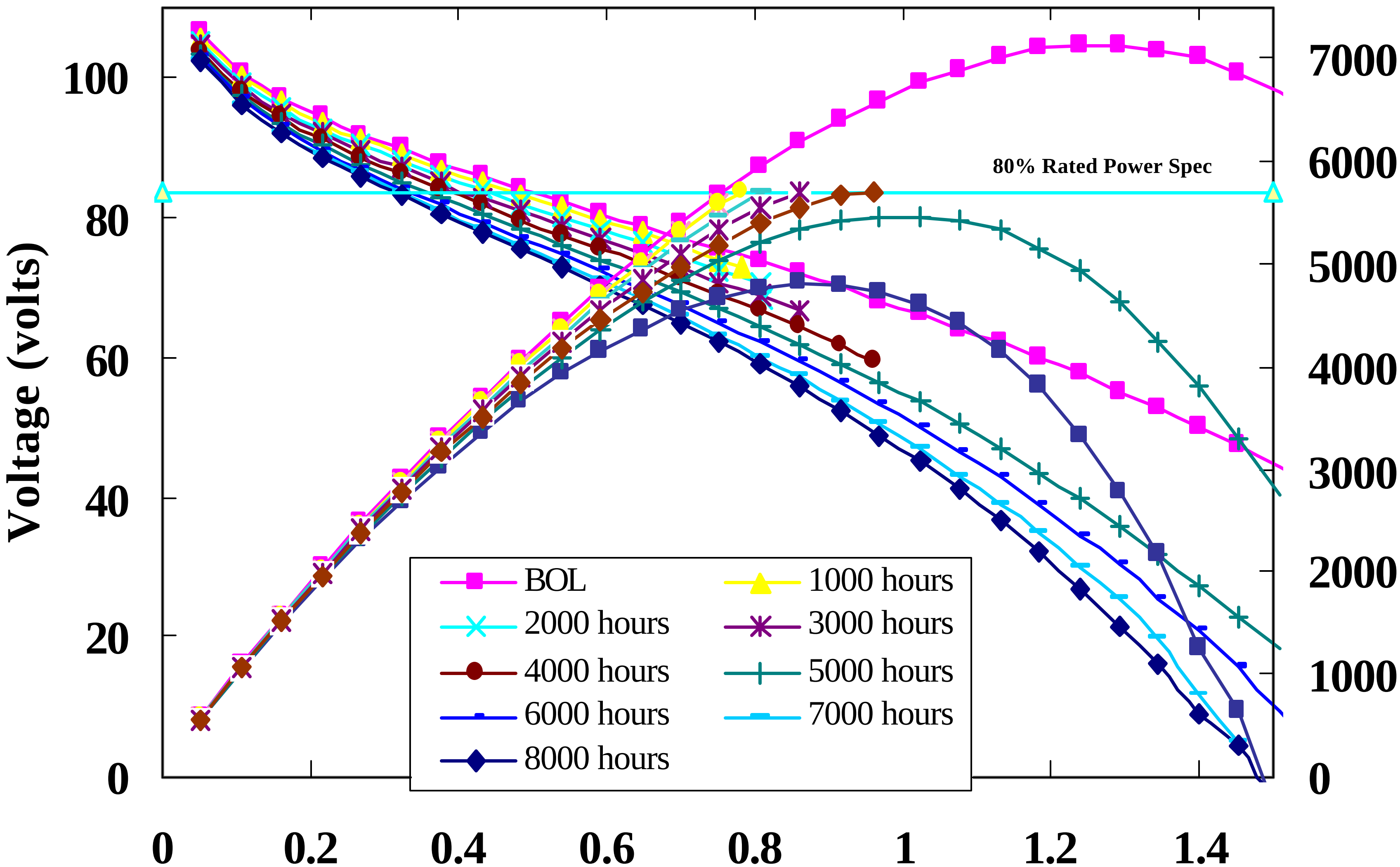
- **Minimum Voltage Output** **- volts**
- **'System' dominated parameters**
  - **Response Time** **- % power increase per minute from idle**
  - **(Emission Targets -)**
    - **(specific target values for particulate, VOC, SO_2, NO_x, CO_2)**
- **Voltage Deviation**
  - **Voltage Decay Rate** **- no higher than a number of Volts/hour of operation** (used as an indicator of life cycle)
  - **Increase in the Standard Deviation of the Voltage**
  - **Appearance of 'instability' or Outliners in performance**

Voltage Performance at End of Life

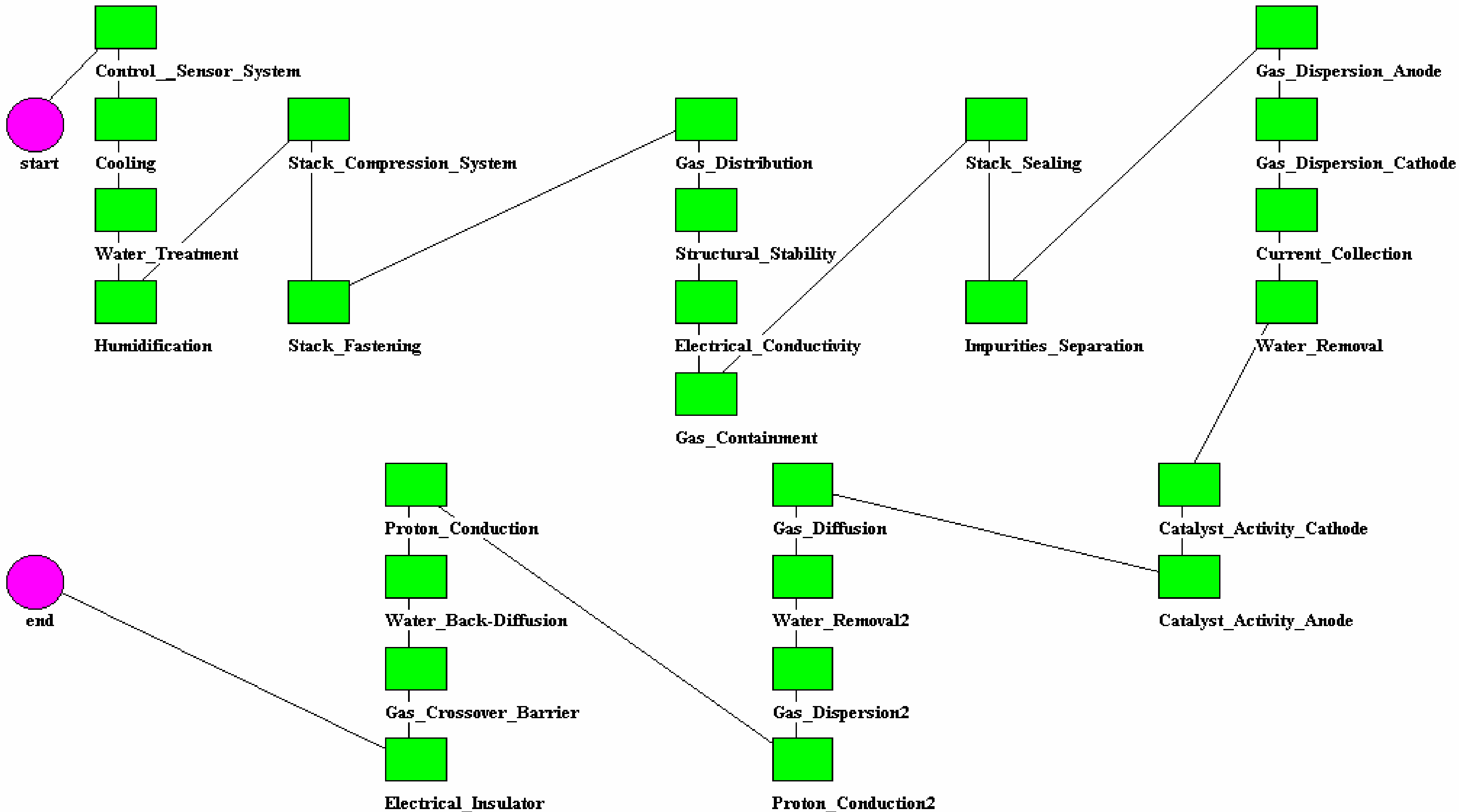


STACK AGEING MODEL

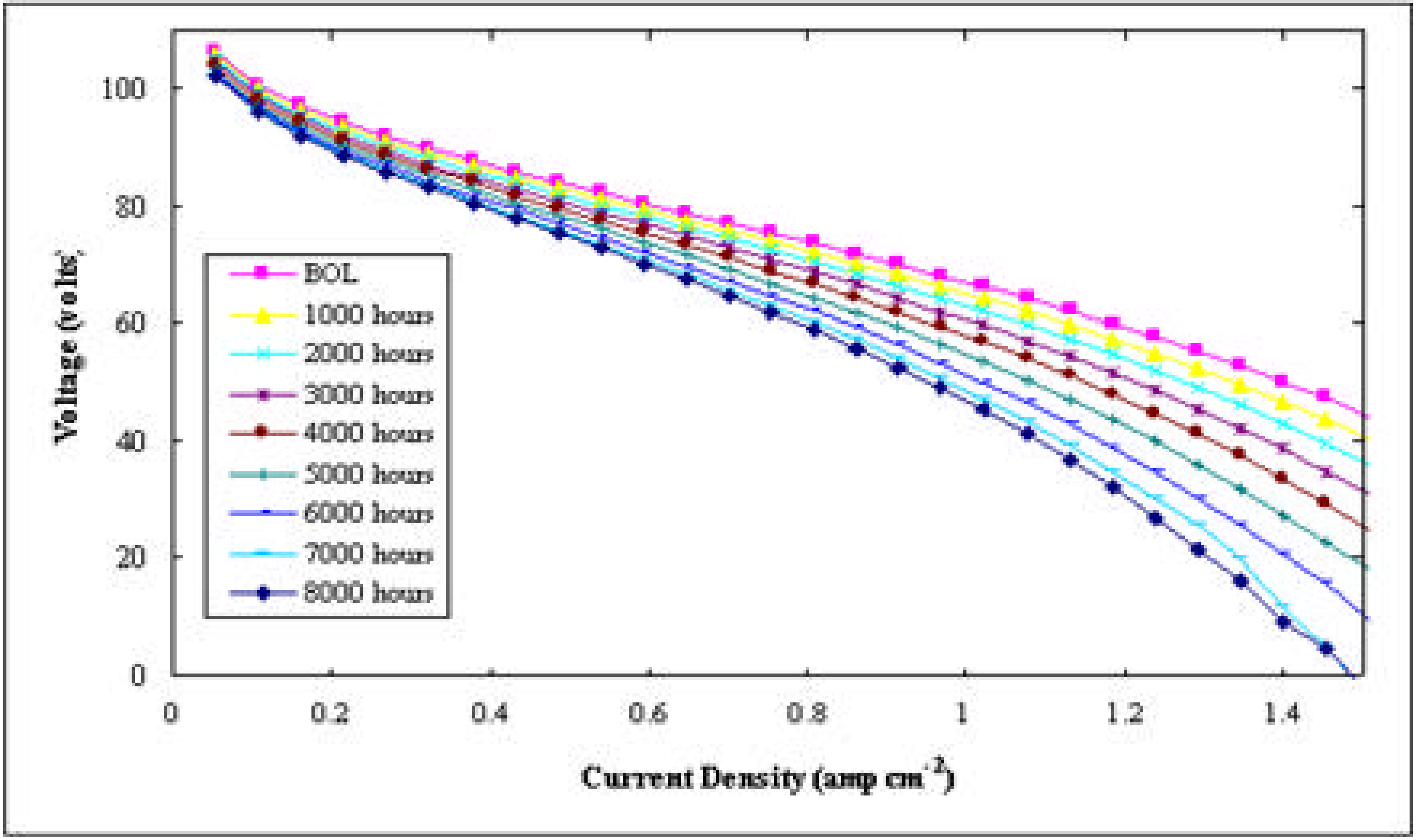
(100 CELLS – 100 cm²)



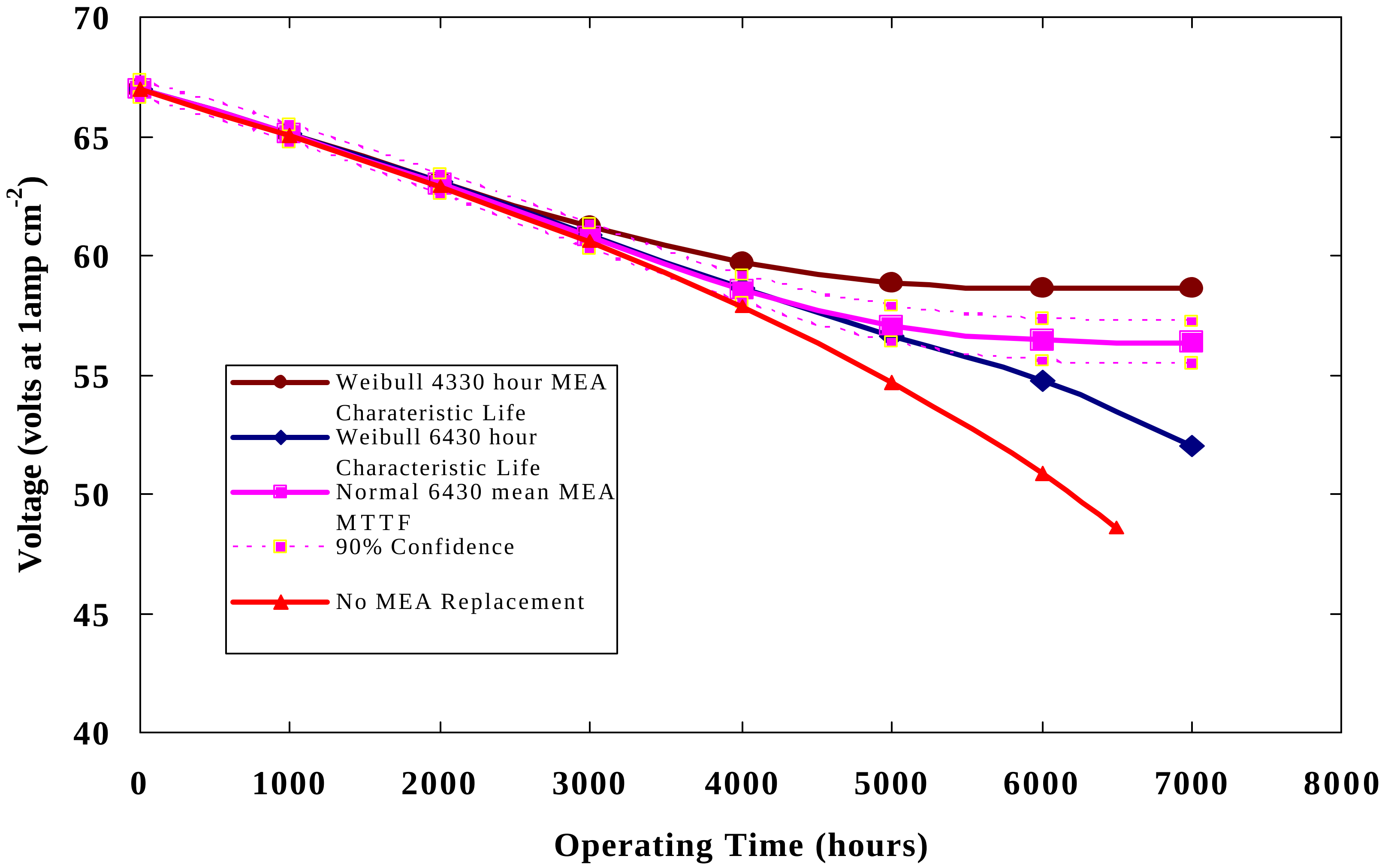
RELIABILITY BLOCK DIAGRAM



OPERATION WITH MEA FAILURE AND RENEWAL



RENEWAL RATE VARIATION



Michael Fowler –University of Waterloo - Presentation for ME 751

IMPROVING COMPONENT EFFECTIVENESS IN DESIGN

- Redundancy (e.g. increase weight of catalyst)
- Increase the robustness of key components
- Mechanical & Thermal integration
- Reduce Material flows
- Material Compatibility (especially replacement parts)
- Modularity / Commonality
- Strong QA/QC program
- Consistency in manufacturing

IMPROVING COMPONENT EFFECTIVENESS DURING OPERATION

- Limited by the ‘built-in’ Reliability / Performance
- Control System & Strategy improvements
  - Reduced cycling & operating states
  - Operation at less stressful conditions, *e.g.* operating voltage
  - Reduced variation of: temperature - pressure - fuel utilization
  - Pressure Balance across membrane
  - Improved water management
- Operator / Maintenance Training
- Maintenance Planing/Program (*e.g.* stocking of spares, strong PM program)
- Consideration of Reliability Centered Maintenance (RCM)
- Management System (records, corrective action system, procedures)

ACHIEVING RELIABILITY GROWTH

- **Operational Models**
- **Reliability Models / Projections**
- **Reliability Data Collection**
- **Review/Correlation of Reliability& Operational Data**
- **Performance Testing Program**
- **Continuous Operation vs. ‘Stress’ Testing Program (*i.e.* HALT, HASS testing)**
- **Life Cycle Analysis and Planning**
- **Constant communication with design and manufacturing teams**

Acknowledgement / References

- **Much of the work shown was performed while at Royal Military College**
- **Key References for Further Information:**

  - **M.W. Fowler, R.F. Mann, J.C. Amphlett, B.A. Peppley and P.R. Roberge, "Incorporation of Voltage Degradation into a Generalized Steady State Electrochemical Model for a PEM Fuel Cell", Journal of Power Sources, 106 (2002) 274-283.**

  - **M.W. Fowler, John C. Amphlett, Ronald F. Mann, Brant A. Peppley and Pierre R. Roberge, "Issues Associated With Voltage Degradation in a Polymer Electrolyte Fuel Cell Stacks", Journal for New Materials for Electrochemical Systems, 5 (2002) 255-262.**

  - **Michael Fowler, Ronald F. Mann, John C. Amphlett, Brant A. Peppley and Pierre R. Roberge, Chapter 56 Conceptual reliability analysis of PEM fuel cells, Handbook of Fuel Cells – Fundamentals, Technology and Applications - Volume 3: Fuel Cell Technology and Applications, Edited by Wolf Vielstich, Hubert Gasteiger, Arnold Lamm., John Wiley & Sons Ltd., 2003. (In Press)**

  - **Michael Fowler, "Demonstration of the Generalized Steady-State Electrochemical Model for a PEM Fuel Cell", Proceedings - Canadian Hydrogen Conference, Victoria, British Columbia, 19 – 22 July 2001.**

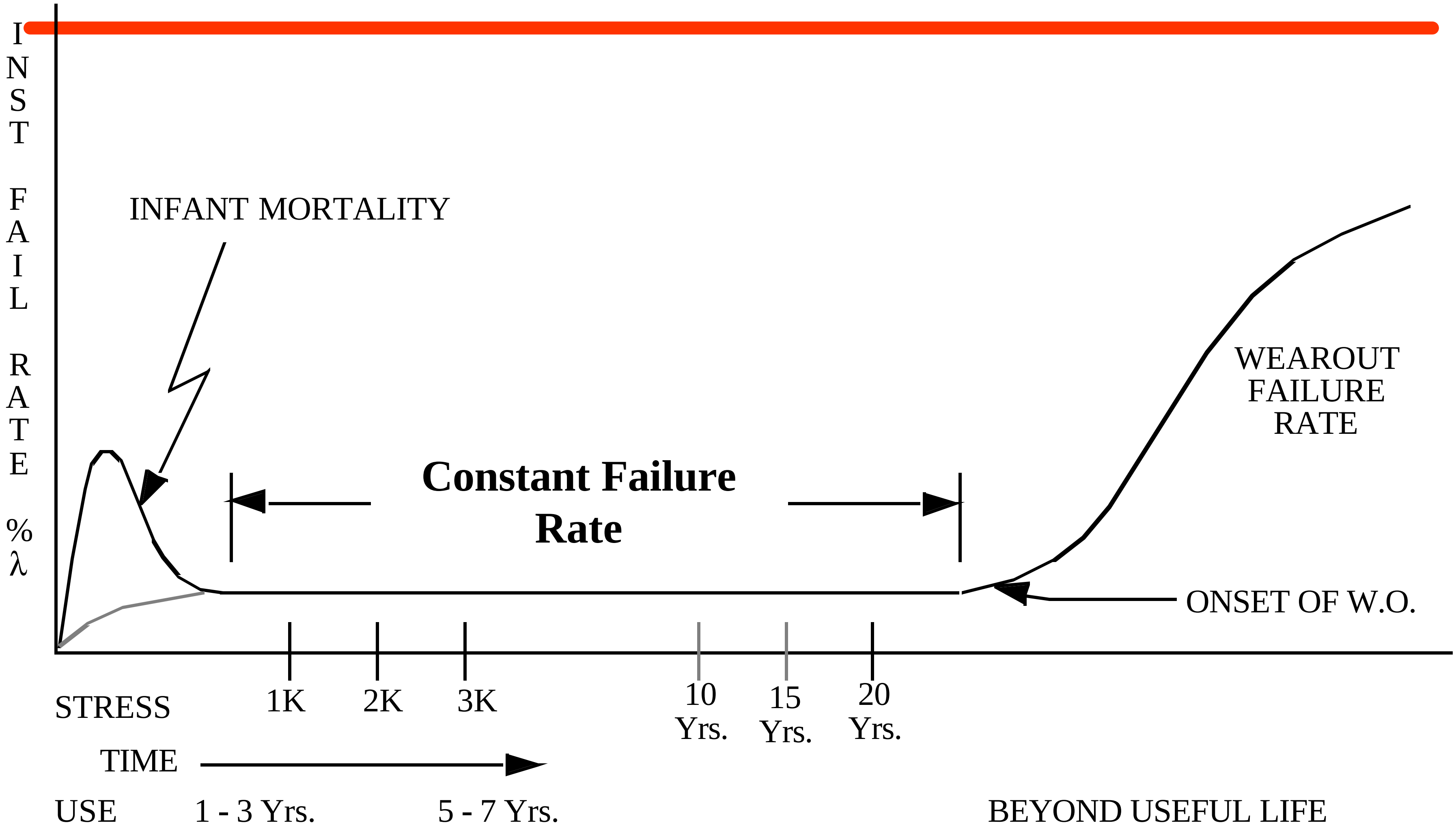
QUESTIONS

QUESTIONS

RESEARCH INTERESTS

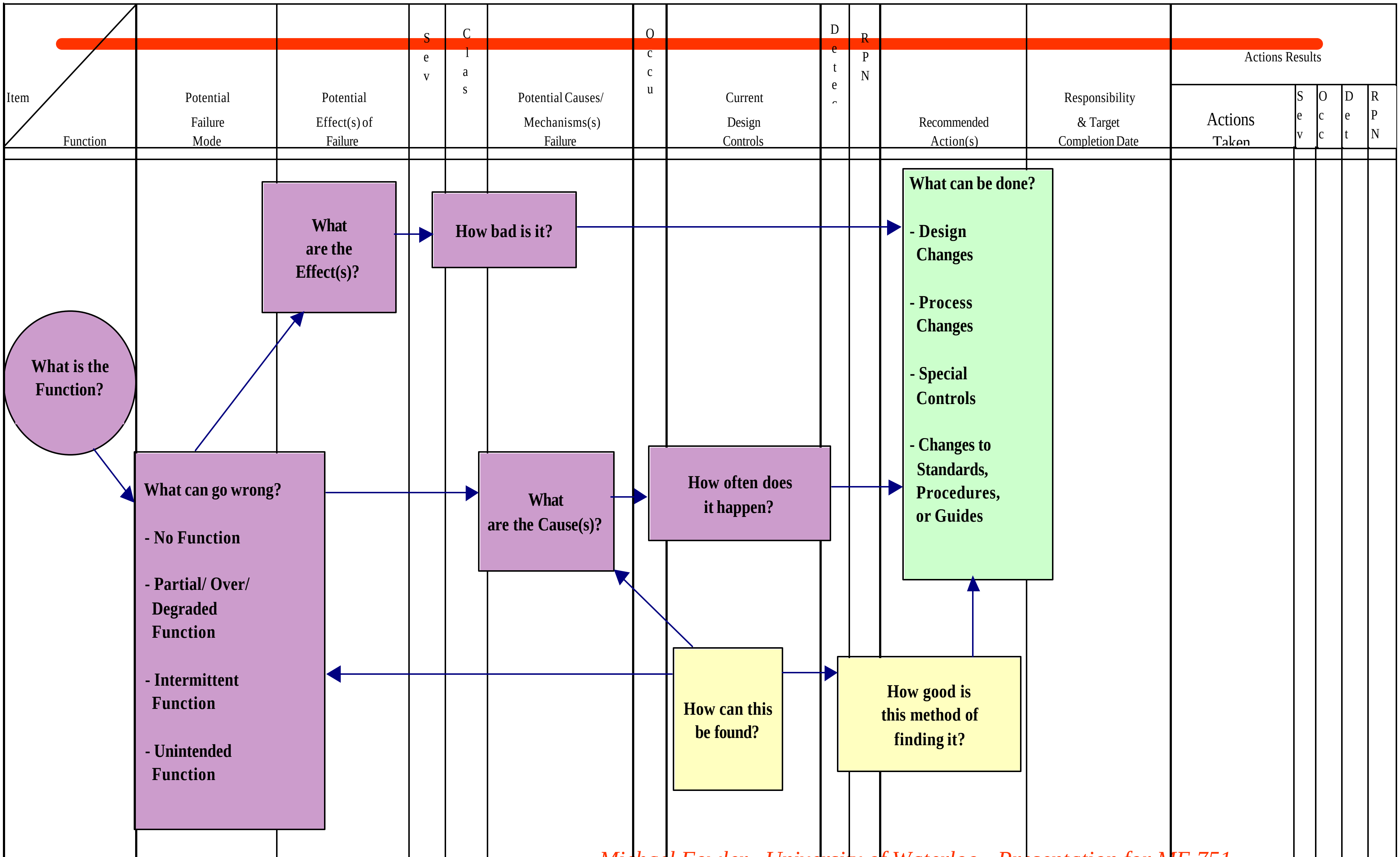
- **Operating a Fuel Cell Test Station now**
- **Reliability of PEM Fuel Cells/Stacks**
  - **Traditional FMEA**
  - **Cell/Stack degradation modelling**
  - **Systems reliability/availability models**
  - **Failure Diagnostics/Accelerated Testing**
- **Modelling of PEM Fuel Cells (and SOFC)**
- **Life Cycle Analysis of PEM Stacks and Systems**
- **Reliability of Polymeric Materials in PEM Fuel Cells**
- **Reliability and Modelling of PEM fuel cell systems linked to hydrogen generation systems**

RELIAIBLITY OF REPAIRABLE ITEMS
'Bathtub Curve'

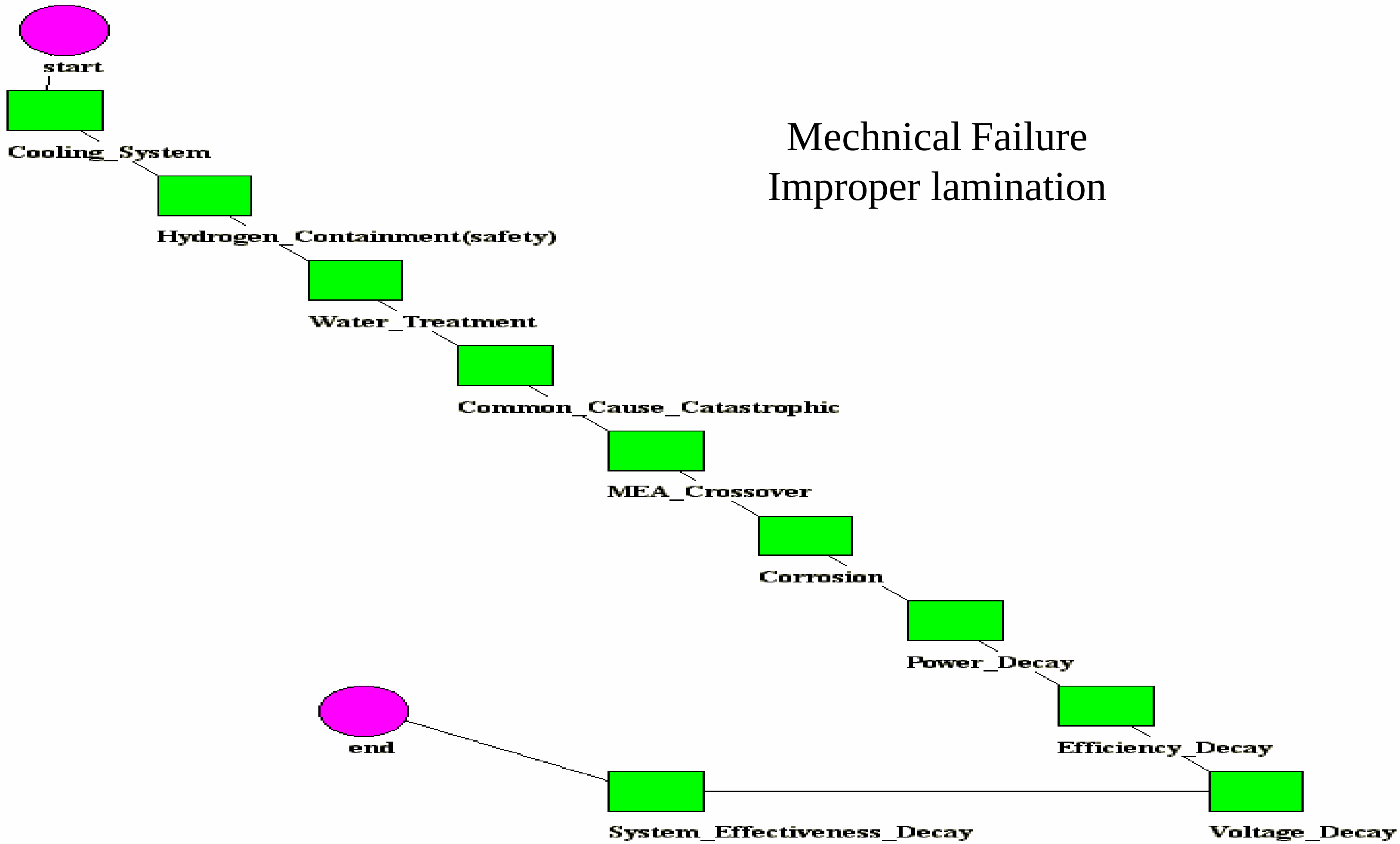


Potential

Failure Mode and Effects Analysis

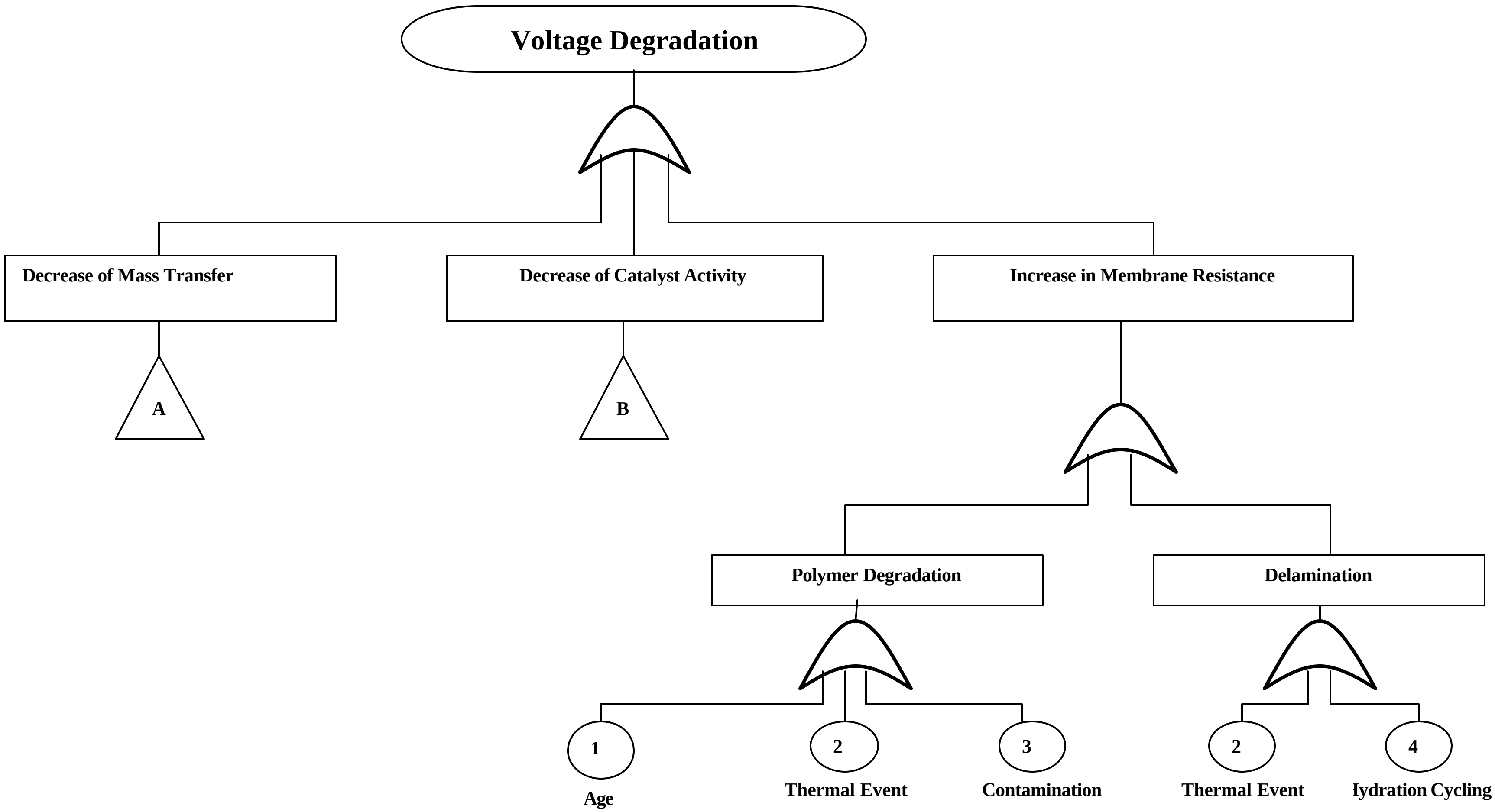


RELIABILITY BLOCK DIAGRAM (RBD)



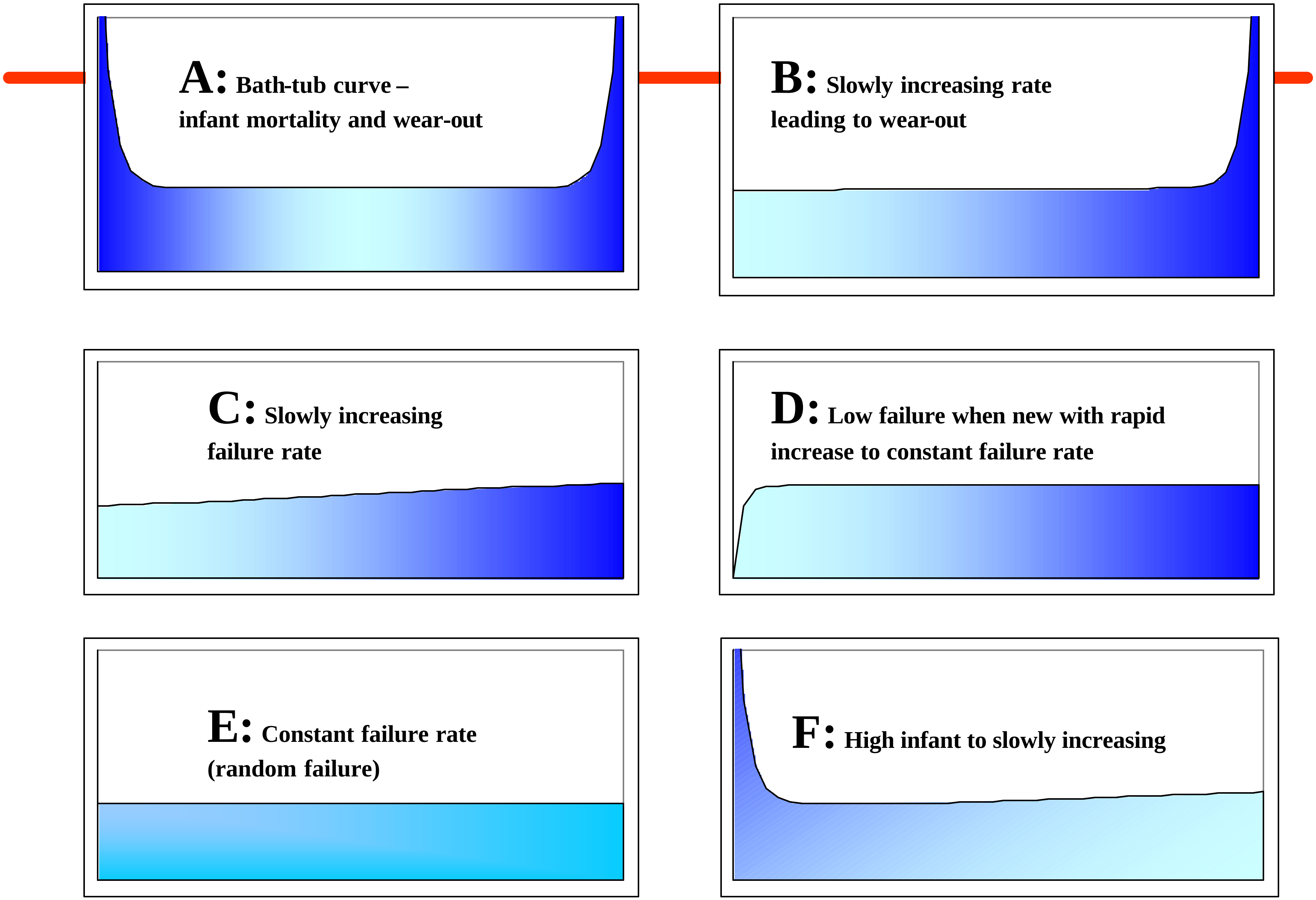
Mechnical Failure
Improper lamination

FAULT TREE ANALYSIS (FTA)

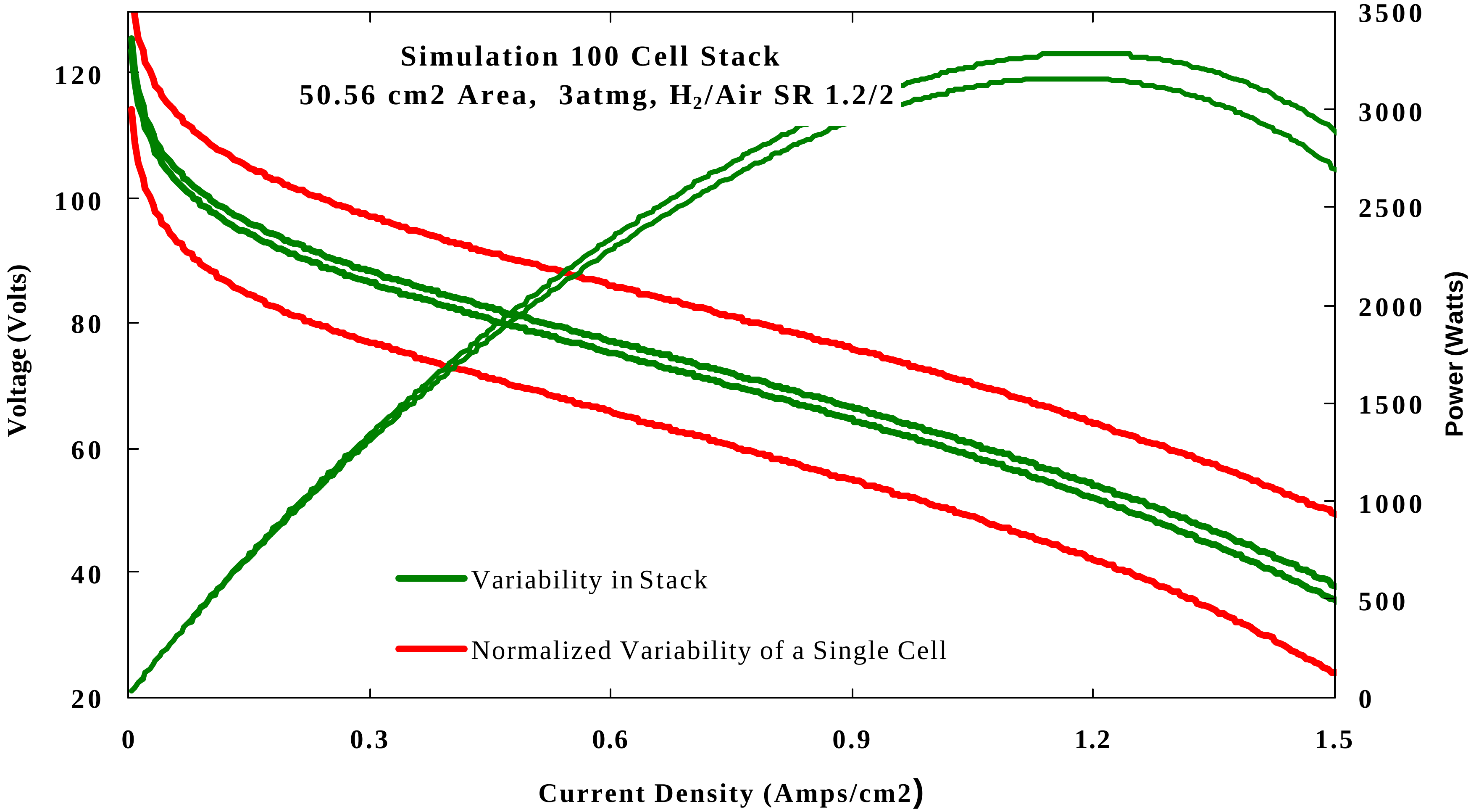


SIX PATTERNS OF FAILURE

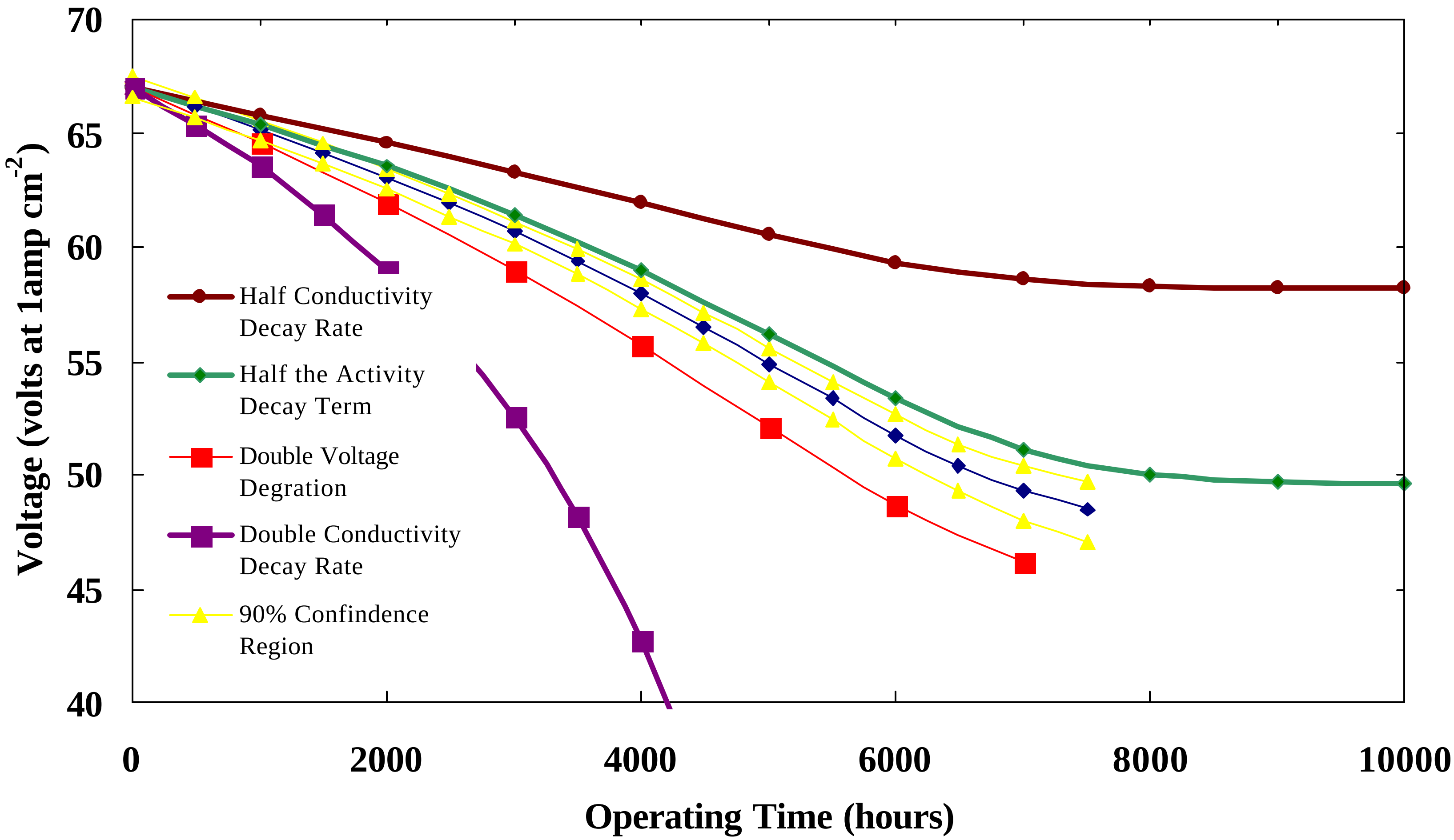
(Ref: Moubay, RCM)



MODELLING OF STOCHASTIC BEHAVIOUR



VARIATION IN DEGRADATION RATES



Major (ret) **Michael Fowler**

CD, rmc, BEng., MScEng., PEng., CEA

1986 B.Eng. Fuels & Materials Engineering, RMC (First Class Honours)

1988 M.Sc. Eng. Engineering Chemistry, Queen's (NSERC Scholarship)

1995 Certificate in Environmental Impact Assessment, Lakehead (5 course program - Honours)

2002 Ph.D. Chemical Engineering - Fuel Cell Reliability -RMC (in progress)

WORK HISTORY

- **Base Construction Engineering, Baden-Soellingen, Germany (1988 - 1992) (Base Garbage Officer)**
- **Acting Head of Environmental Impact Assessment, Director General Environment (1993 - 1996)**
- **Associate - Golder Associates Ltd., Environmental Consultant (1996 - 1998)**
- **Coordinator - RMC Institute for the Environment**
- **Principal, Retriever Environmental**
- **Ph.D. - Fuel Cell Reliability**
- **Lecturer – University of Waterloo – Chemical Engineering**

Short Courses

Both Taken and Taught

- Spill Control and Hazardous Material Management
- Environmental Impact Assessment
- Environmental Auditing and Environmental Law
- ISO 14,000 (EMS)
- Storage Tank Management
- Contaminated Site Assessment & Risk Assessment

Other Courses

- Process Hazard Analysis/Reliability
- Environmental Business Case Development
- Officer Professional Development Program (Honours)

Current Engineering Options for Reliability Management

Modification can be done in either the stack design or control variables to improve reliability and prolong life.	
Using the Generalized Steady State Electrochemical Degradation Model for a the PEM, design features and control strategies can be developed that allow for the optimization of various performance factors within a fuel cell over its life cycle.	
Design Features	***Operating Strategies***
Cell Active area	Load cycling
Catalyst type	Hydrogen and Oxygen stoichiometric ratios
Catalyst loading	Stack temperature
Number of cells per stack	Stack pressures
Number and configuration (*e.g.* parallel or series) of cells or stacks	
Material Choice for polymer electrolyte and backlayer	

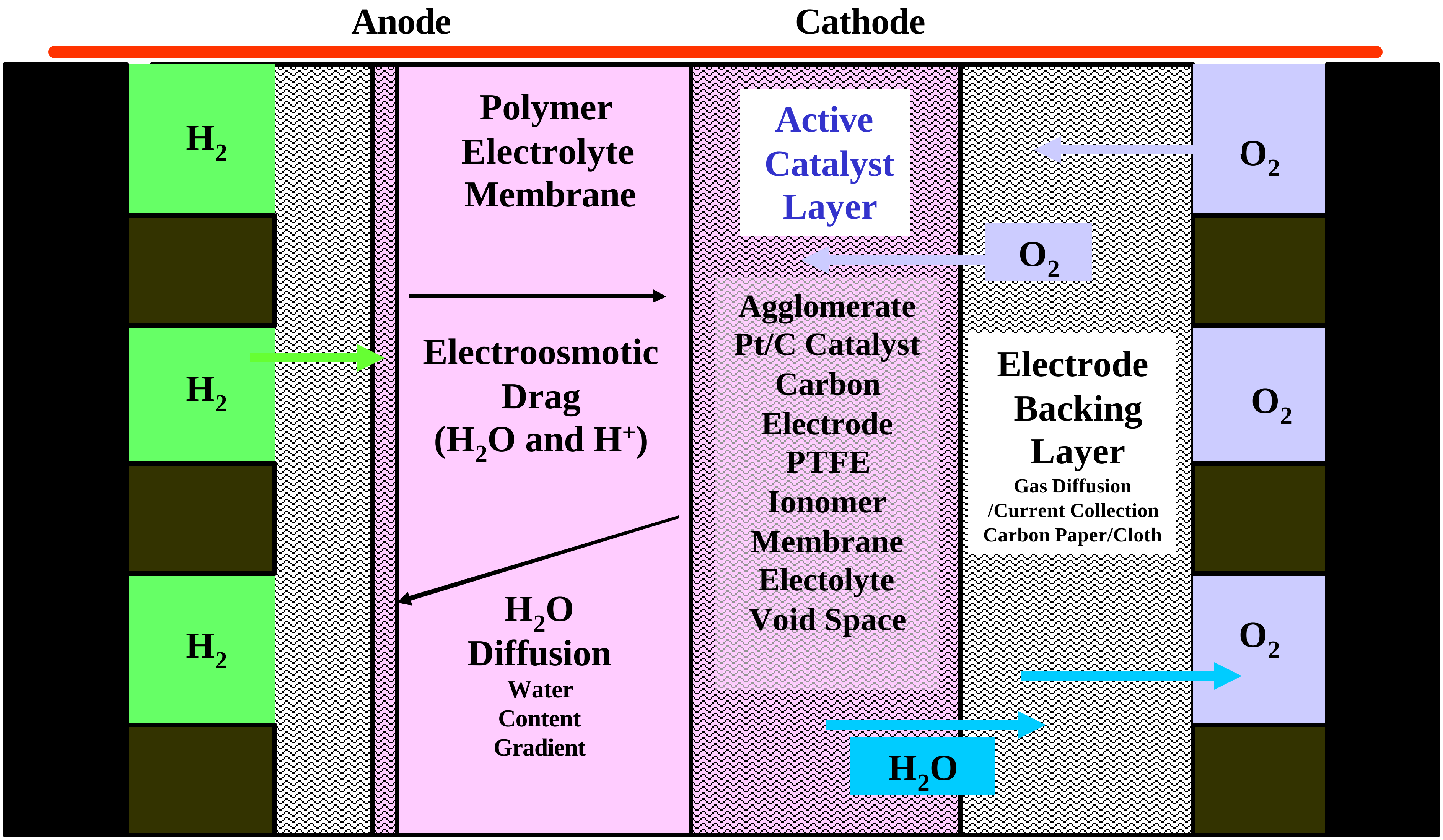
SELECTED CAUSES/ MECHANISMS OF THE FAILURE MODES

- Defect Propagation (leading to pinholes or shorting)
- Load stress and/or load cycling
- Thermal stress and/or thermal cycling
- Pressure stress and/or pressure cycling
- Hydration Cycling
- Start/stop cycling
- Reactant shortage
- Reactant flow configuration
- Uniformity of cell design and assembly
- Contaminants from reactants
- Contaminants leached from fuel cell components
- Degradation of electrode or electrolyte materials

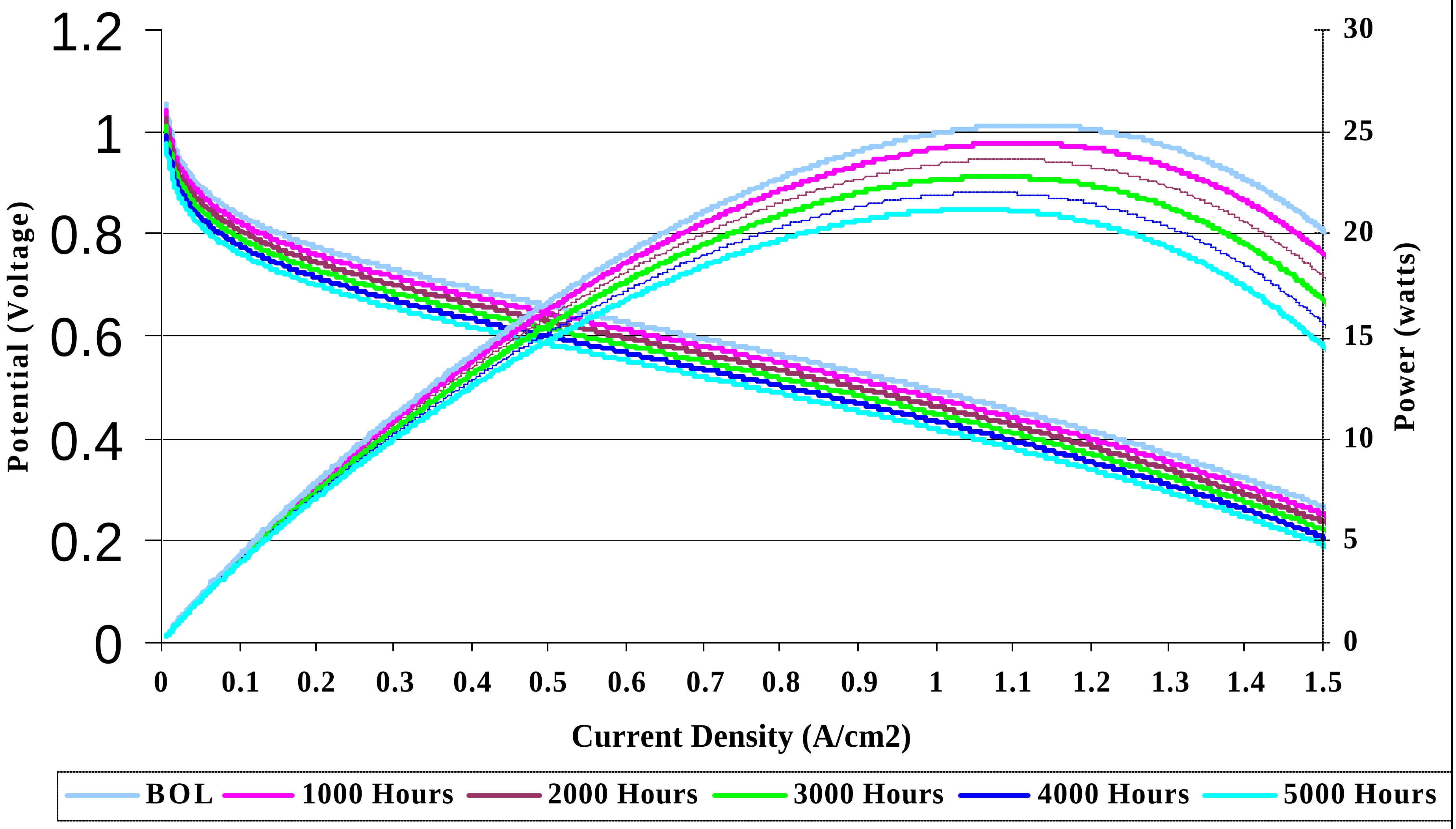
DETERIORATION CAN NOT BE AVOIDED

- **intrinsic reactivity (thermodynamic, chemical and physical instability), including material corrosion and degradation**
- **manufacturing irregularities and design flaws**
- **reactant contaminants (including those contaminants that may leach from the reactant storage and delivery systems)**
- **abusive handling**

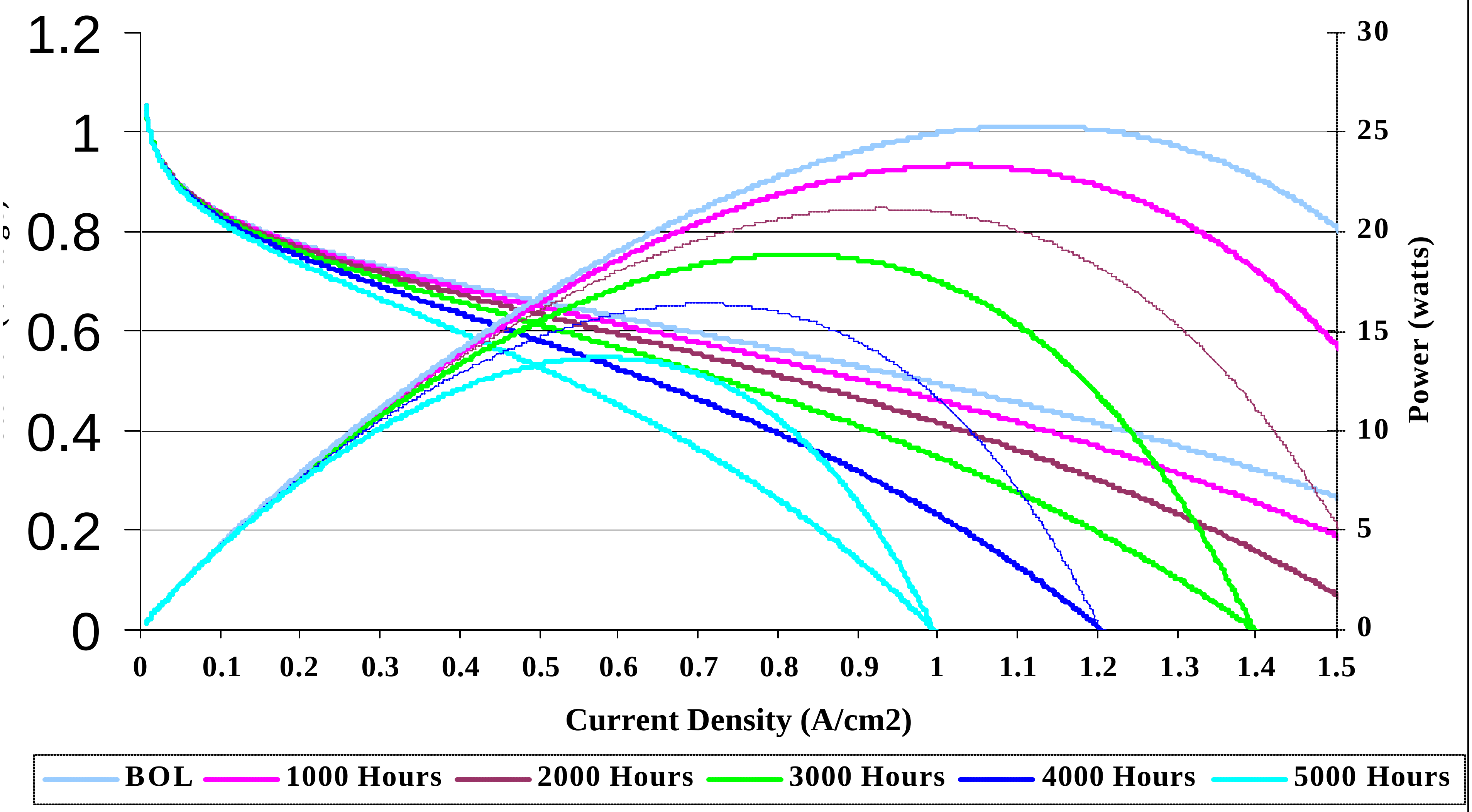
MEMBRANE ELECTRODE ASSEMBLY (MEA)



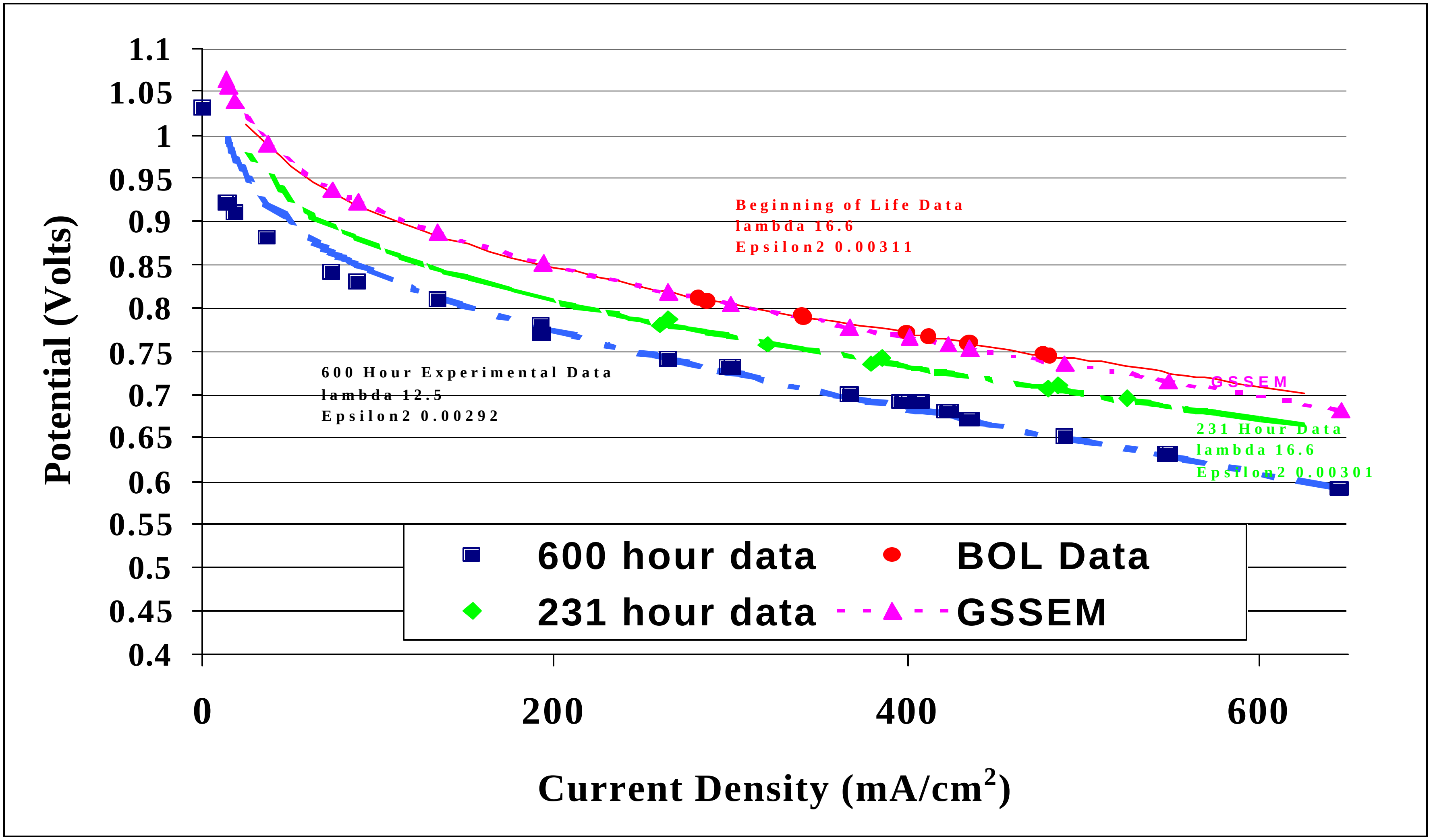
LOSS OF APPARENT CATALYTIC ACTIVITY



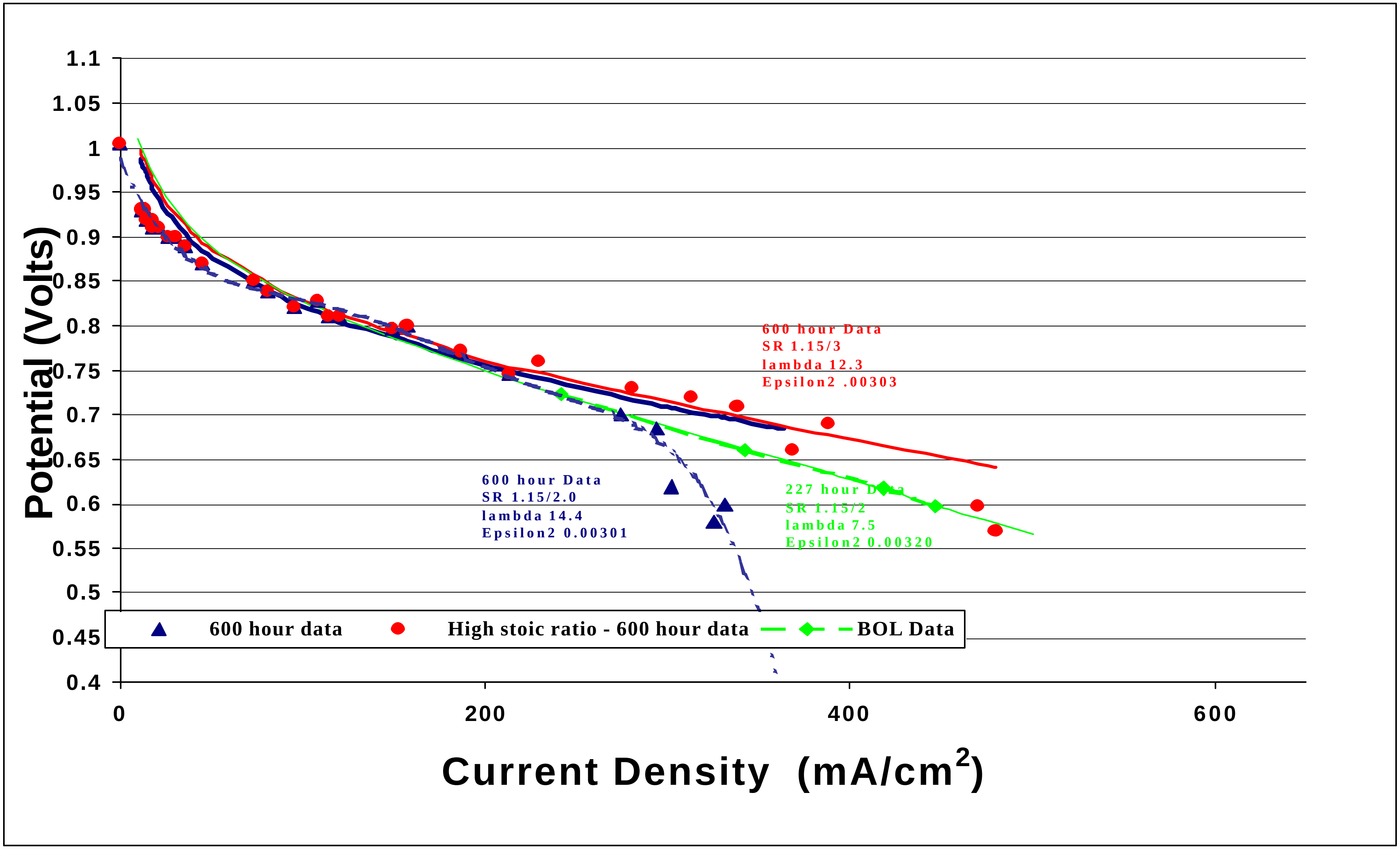
LOSS OF CONDUCTIVITY



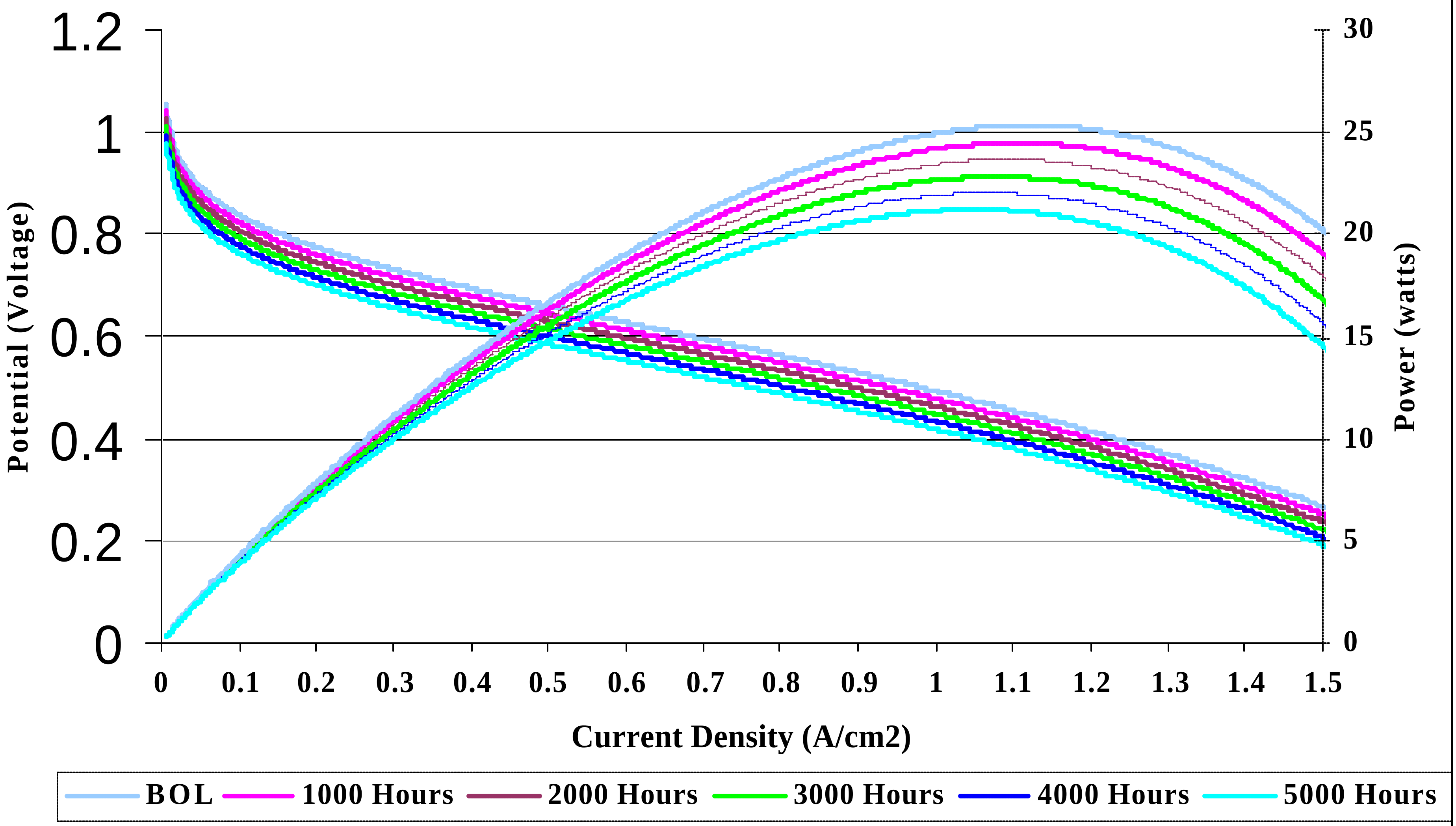
SINGLE CELL DEGRADATION
H_2/O_2 30 psig/30psig 80ºC



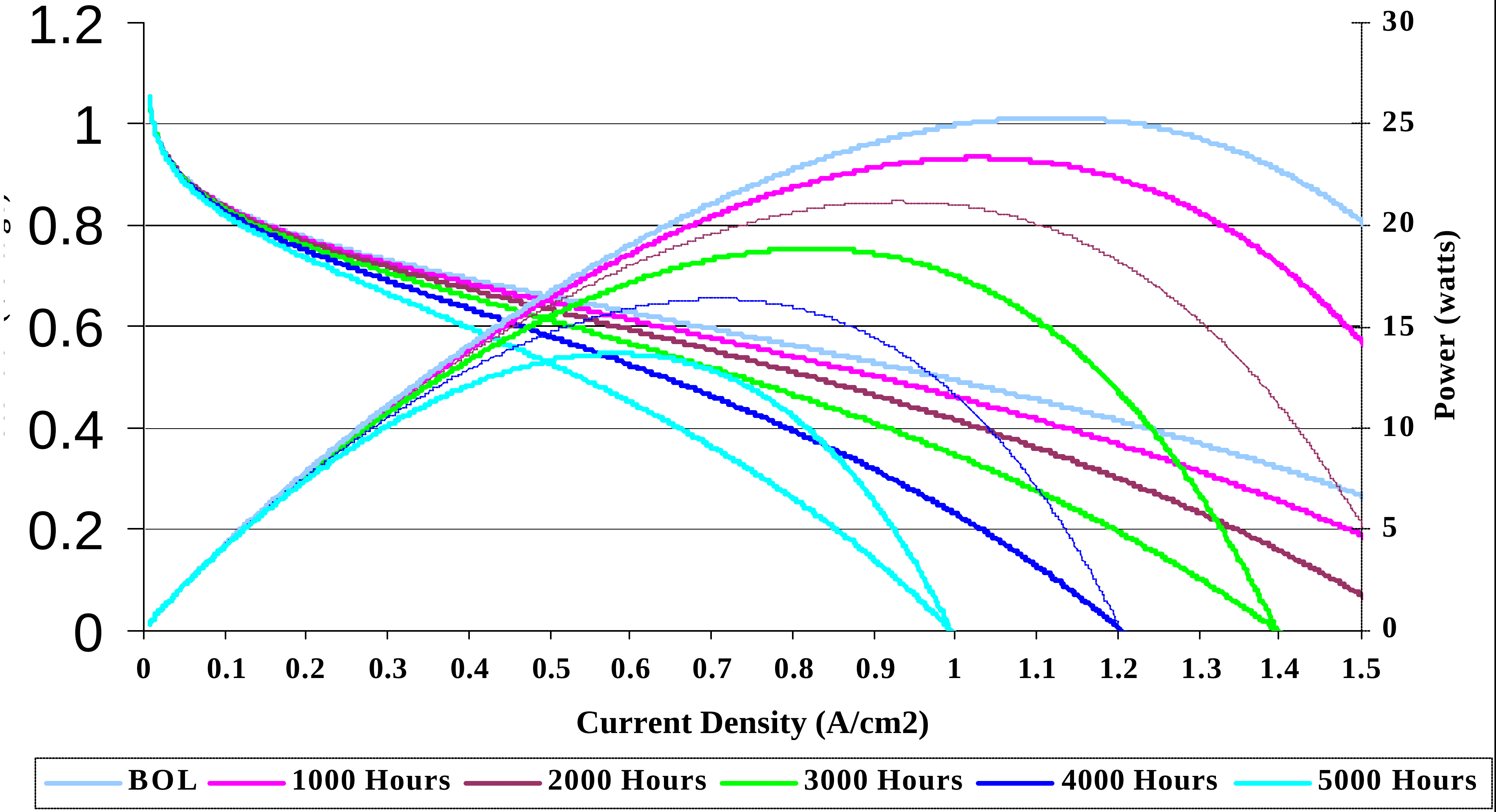
SINGLE CELL DEGRADATION
H_2/AIR 30 psig/30psig 80°C



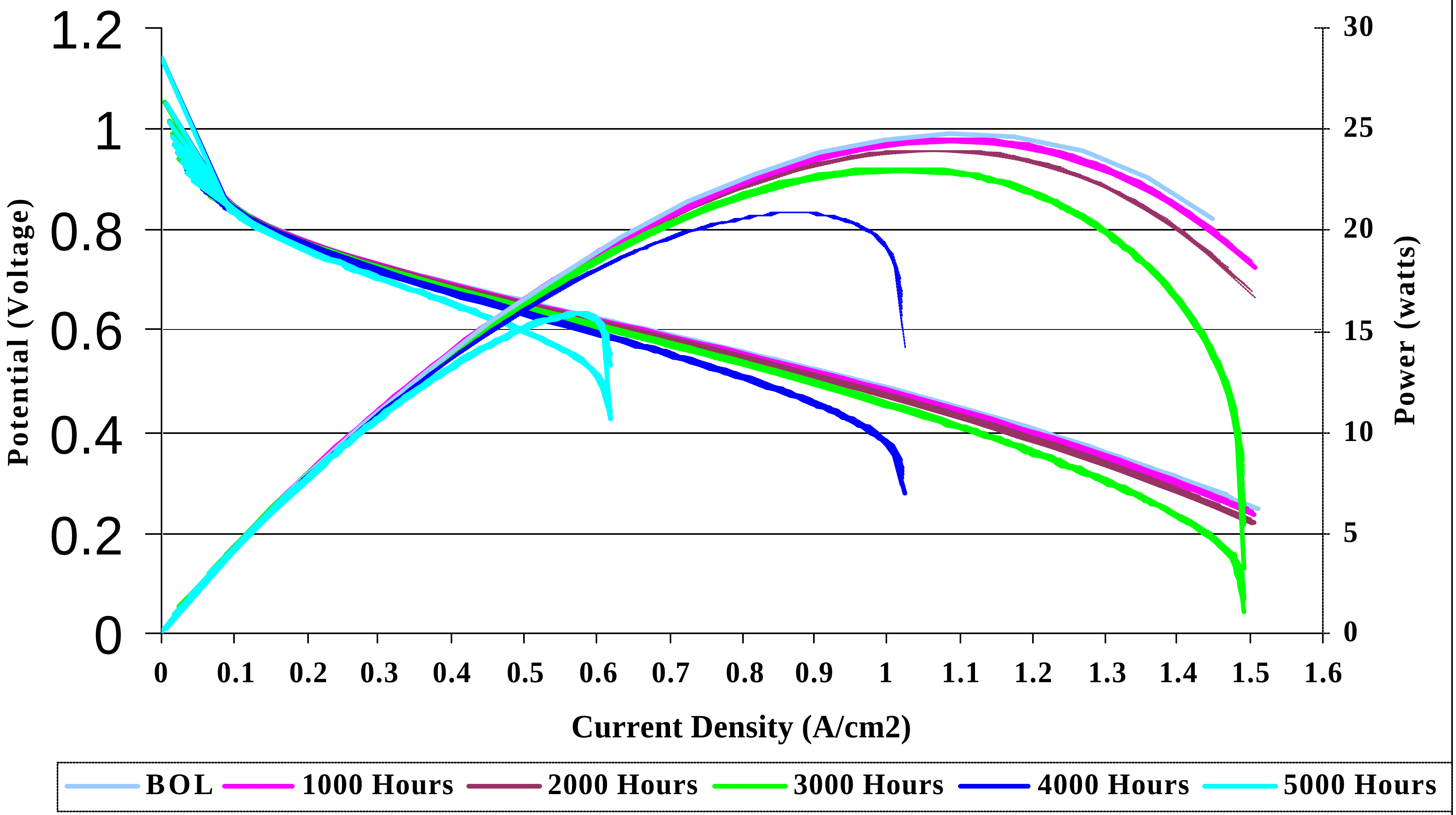
LOSS OF APPARENT CATALYTIC ACTIVITY



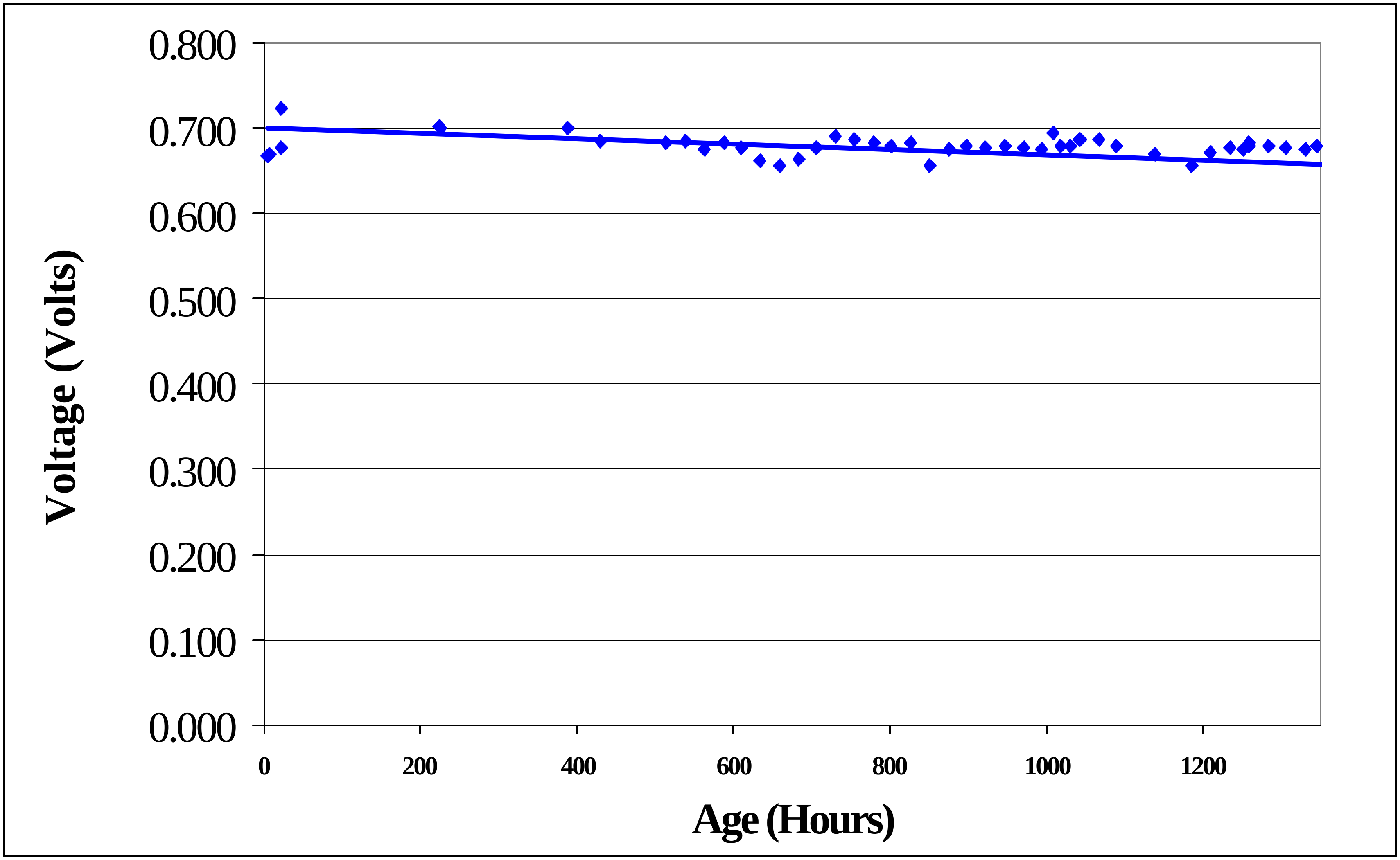
LOSS OF CONDUCTIVITY



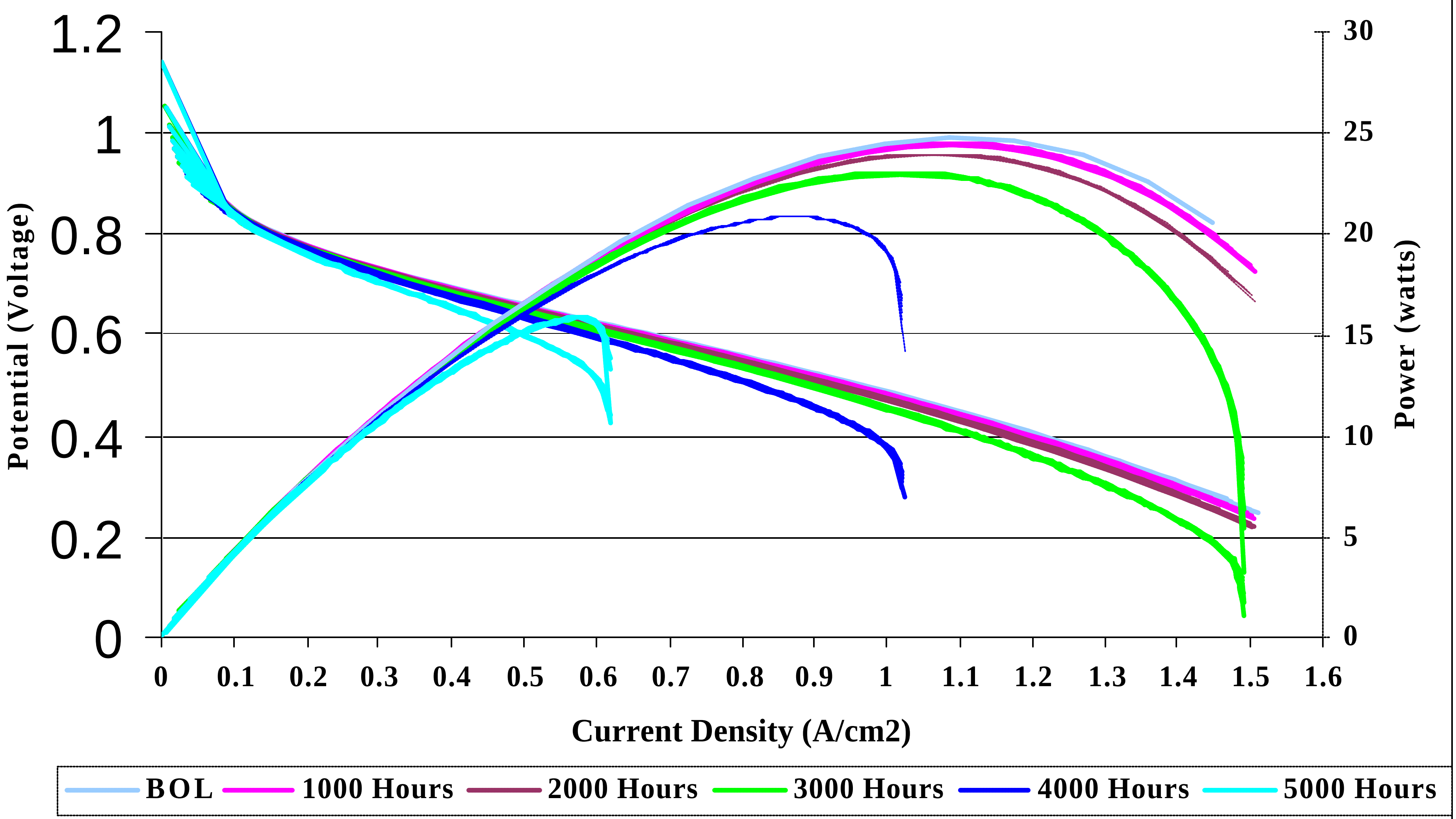
LOSS OF MASS TRANSFER RATE OF REACTANTS



VOLTAGE DEGRADATION CURVE FOR A SINGLE PEM CELL



LOSS OF MASS TRANSFER RATE OF REACTANTS



RELIABILITY OF FUEL CELL STACKS

- **High Reliability - no moving parts, modular design, no high mechanical stresses, few extreme operating conditions**
- **PEM stacks pass shock, vibration and angle tests**
- **Loss of integrity is a concern (physical damage, leaks, freezing of stack, or failure of compression system)**

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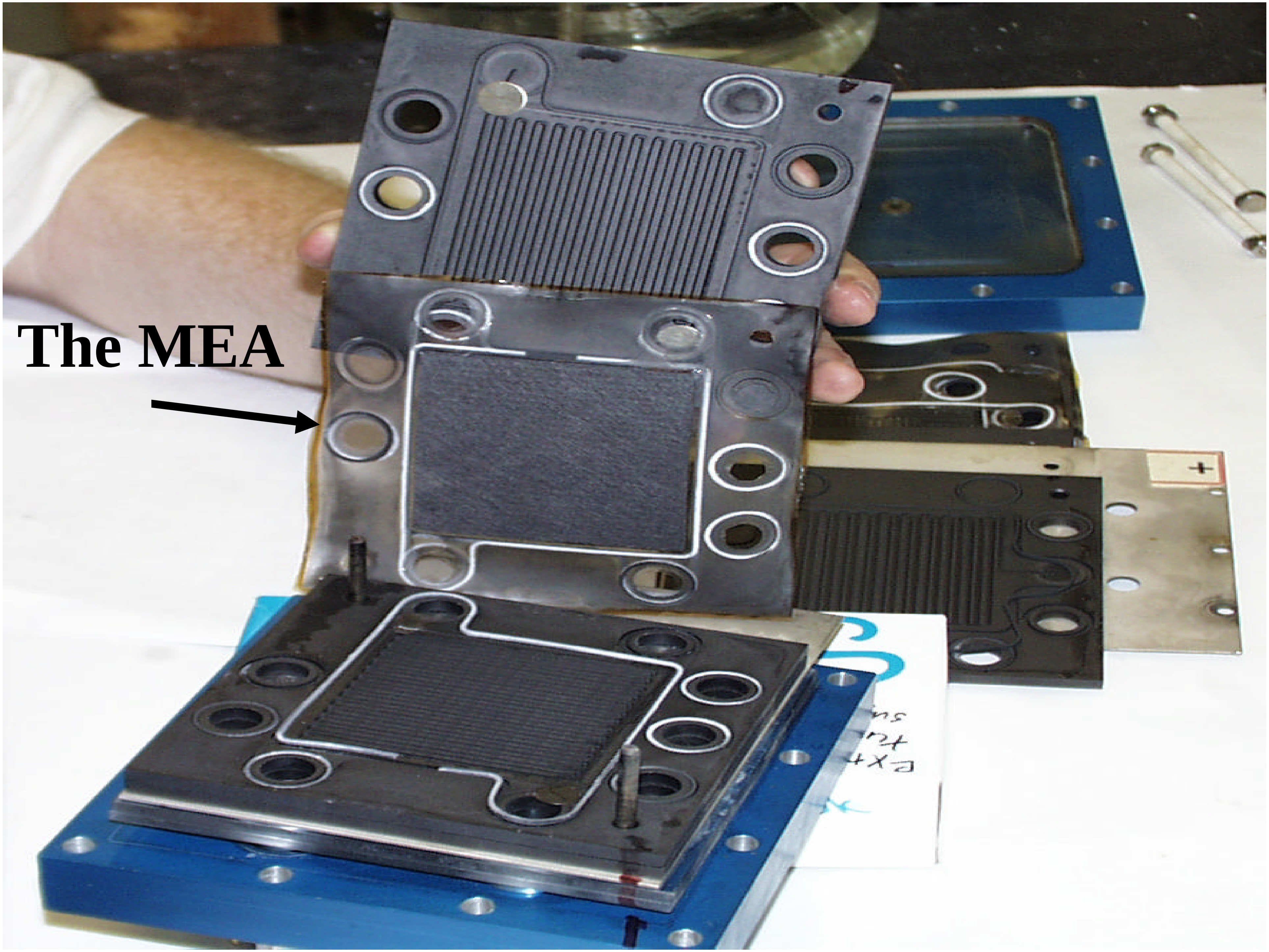
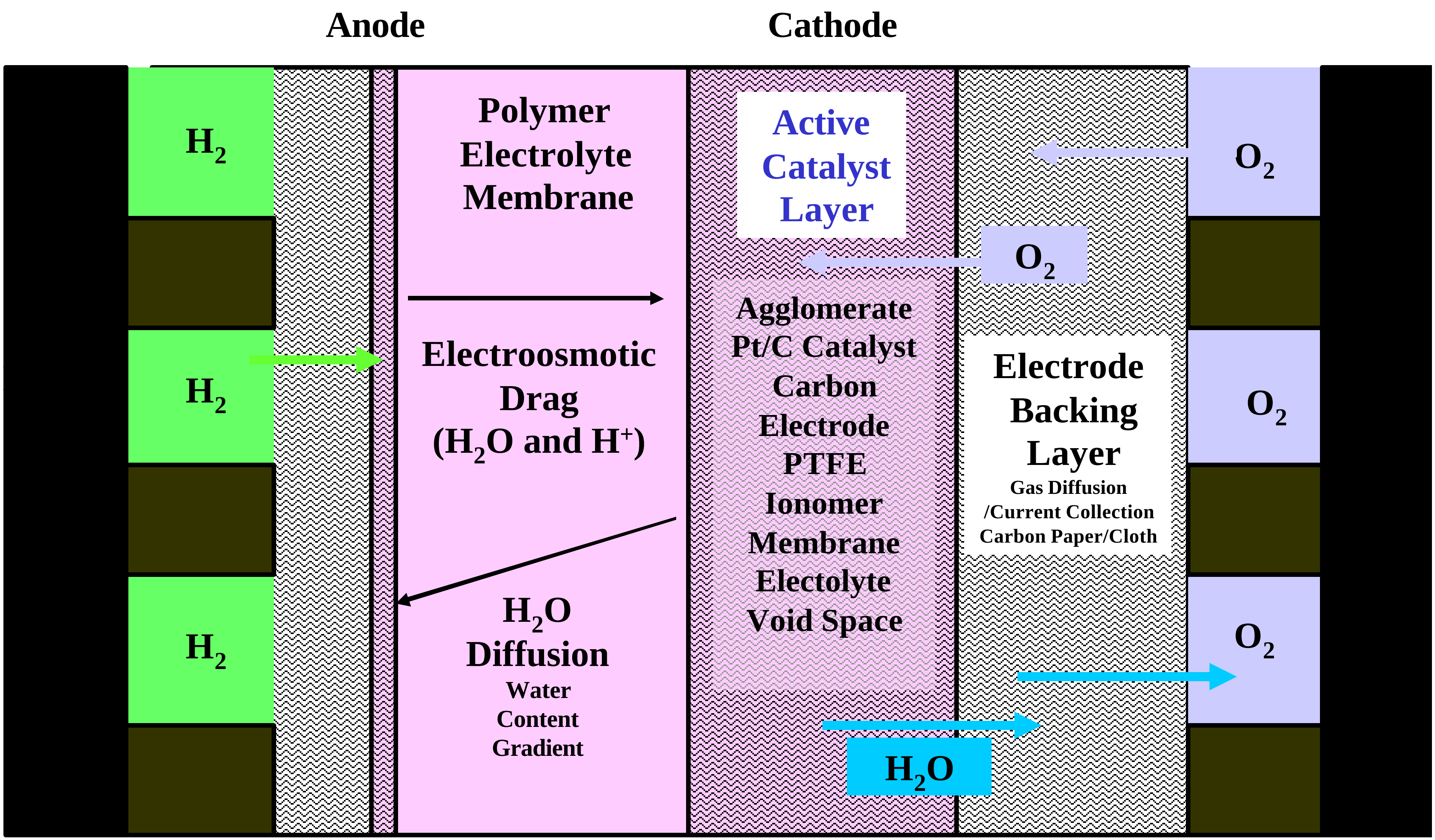
- **PEM stacks pass shock, vibration and angle tests**
- **Loss of integrity** **(physical damage, leaks, freezing of stack, or failure of compression system)**
- **Little attention to 'cycling' in the literature**
- **Stack Balance of Plant failures -** ***e.g.*** **cooling system failures, water treatment system failures, sensors, control system**
- **Maintenance Time, Stability Issues and Testing will effect** ***availability*****, but little data is available and this is not the focus of the research**


The MEA

MEMBRANE ELECTRODE ASSEMBLY (MEA)



MEMBRANE ELECTRODE ASSEMBLY (MEA)

- **Beyond burn-in period reliability is high (quality control issue)**
- **Membrane Integrity (cross-over concern)**
  - **differential pressure**
  - **'cycling' (thermal, pressure, hydration) will lead to mechanical stresses**
  - **thermal damage (heat or freezing)**
- **Electrode compaction/degradation**
- **Degradation of performance is principal failure 'effect'**

STABILITY ISSUES

- **Contamination/Poisoning (will result in voltage reversible degradation or long term irreversible degradation)**
- **Flooding or Dehydration**

OBJECTIVES OF THE RESEARCH

- **Further the application of a generalized PEM model (GSSEM)**
- **Incorporate 'degradation' into the PEM model**
- **Study the reliability and degradation in a context of PEMFC design and operation**
  - developing an understanding and framework for PEM component effectiveness

DEGRADATION FAILURE MODES

(leading to degradation of performance or *durability*)

- **Kinetic or activation loss in the anode or cathode catalyst**
- **Ohmic or resistive increases in the membrane or other components**
  - **Changes to eletro-osmotic drag properties**
  - **Changes to the water diffusion characteristics of the membrane**
- **Decrease in mass transfer rate in the reactant flow channel or electrode**
  - **Degradation of mass transfer rate of water in the cathode electrode**

DEGRADATION FAILURE MODES

(leading to degradation of performance or *durability*)

- **Loss of reformate tolerance of the catalyst**
- **Delamination of the membrane from the electrode**
- **Degradation of the electrode material that can either change the mass transport properties, or release material that can contaminate the membrane material**
- **Mechanical function loss or loss of integrity of the membrane or stack seals (efficiency loss)**

CAUSES/MECHANISMS OF THE DEGRADATION FAILURES MODES

(*i.e.* something that can be controlled)

- **Contaminants from reactants (including dust)**
- **Contaminants leached from fuel cell components**
- **Degradation of electrode or electrolyte materials**
- **Poor water management (flooding and dehydration) or simply the presence of liquid water**
- **Catalyst migration or ripening**
- **Loss of catalytic or electrolyte material**

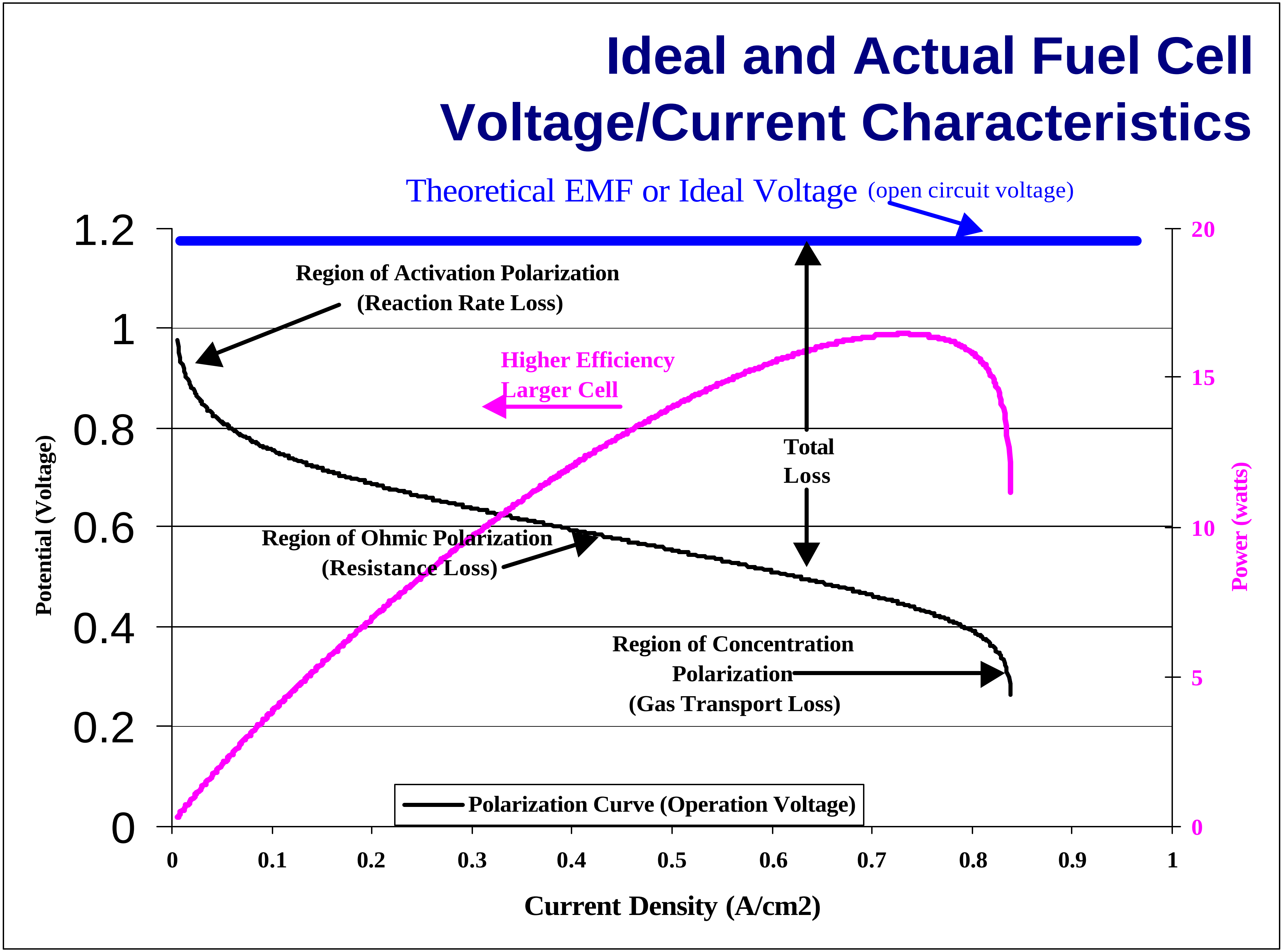
CAUSES/MECHANISMS OF THE FAILURES MODES (continued)

- **Load stress and/or load cycling**
- **Thermal stress and/or thermal cycling (including freezing)**
- **Pressure stress and/or pressure cycling**
- **Start/stop cycling**
- **Uniformity of cell design and assembly**
- **Reactant shortage**
- **Reactant flow configuration**

AGEING MODEL FOR THE FUEL CELL STACK

- **Based on the Generalized Steady State Electrochemical Model (thus - Generalized Steady State Electrochemical Degradation Model)**

  (Ageing Model and Degradation Model jargon still used interchangeably)
- **Largely mechanistic, but includes some empirical terms/expressions**
- **Currently limited to Nafion membranes, Pt catalyst**
- **Different life parameters that may be considered:**
  - **time-in-service, time-on-shelf, total energy output, start/stop cycles, load cycles, hydration events**



Ideal and Actual Fuel Cell Voltage/Current Characteristics
Theoretical EMF or Ideal Voltage (open circuit voltage)
Region of Activation Polarization
(Reaction Rate Loss)
Higher Efficiency
Larger Cell
Total
Loss
Region of Ohmic Polarization
(Resistance Loss)
Region of Concentration
Polarization
(Gas Transport Loss)
Polarization Curve (Operation Voltage)
Potential (Voltage)
1.2
1
0.8
0.6
0.4
0.2
0
Power (watts)
20
15
10
5
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Current Density (A/cm2)

PEM MODEL DEVELOPMENT

$$V_{\text{Cell}} = E_{Nernst} + \eta_{\text{act, a}} + \eta_{\text{act, c}} + \eta_{\text{ohmic}}$$

$$E_{Nernst} = 1.229 - 8.5\times10^{-4}(T - 298.15) + 4.308\times10^{-5}\cdot T\left(\boldsymbol{ln}\, p^{*}_{\text{H}_2} + ½\,\boldsymbol{ln}\, p^{*}_{\text{O}_2}\right)$$

$$h_{act,\,\text{c}} = \frac{1}{\boldsymbol{a}_{\text{c}}}\left[-1.036\cdot10^{-6}\cdot\Delta G_{e} + 8.62\cdot10^{-5}\cdot T\left(12.863 + \ln \text{A} + \ln k'_{\text{c}} + (1 - \boldsymbol{a}_{\text{c}})\ln c^{*}_{o_2} - \ln i\right)\right]$$

$$h_{\text{act, a}} = -\frac{\Delta G_{ec}}{2\text{F}} + \frac{\text{R}\,T}{2\text{F}}\ln\left(4\text{F}\cdot A\cdot k^{0}_{a}\cdot c^{*}_{\text{H}_2}\right) - \frac{\text{R}\,T}{2\text{F}}\ln i$$

TOTAL ACTIVATION OVERVOLTAGE

$$h_{\text{act}} = x_1 + x_2 \cdot T + x_3 \cdot T\,[\ln(c^*_{O_2})] + x_4 \cdot T[\ln(i)]$$

$$x_1 = -\frac{\Delta G_{ec}}{2F} - \frac{\Delta G_{e}}{a_c n F}$$

$$x_2 = \frac{R}{nFa_c}\ln\left[k_c^0\left(c^*_{H^+}\right)^{(1-a_C)}\left(c^*_{H_2O}\right)^{a_C}\left(k_a^0\right)^{\frac{na_c}{2}}\right] + \frac{R}{F}\ln\left(n2F^{3/2}\right) + \left(\frac{R}{2F} + \frac{R}{a_c nF}\right)\ln(A) + \frac{R}{2F}\ln\left(c^*_{H_2}\right)$$

$$x_2 = k_{cell} + 0.000197 \cdot \ln A + 4.3\times 10^{-5} \cdot \ln c^*_{H_2}$$

$$x_3 = \frac{R(1 - a_C)}{a_C nF}$$

$$x_4 = -\left(\frac{R}{2F} + \frac{R}{a_C nF}\right)$$

TOTAL OHMIC OVERVOLTAGE

$$\eta_{ohmic} = \eta_{ohmic}^{electronic} + \eta_{ohmic}^{proton}$$

$$= -i(R^{electronic} + R^{proton})$$

$$= -i \cdot R^{internal}$$

$$R^{proton} = \frac{r_M \, l}{A}$$

$$r_M = \frac{181.6 \cdot \left[1 - 0.03\left(\frac{i}{A}\right) + 0.062\left(\frac{T}{303}\right)^2\left(\frac{i}{A}\right)^{2.5}\right]}{\left[l - 0.634 - 3\left(\frac{i}{A}\right)\right]\exp\left(4.18\left[\frac{T-303}{T}\right]\right)}$$

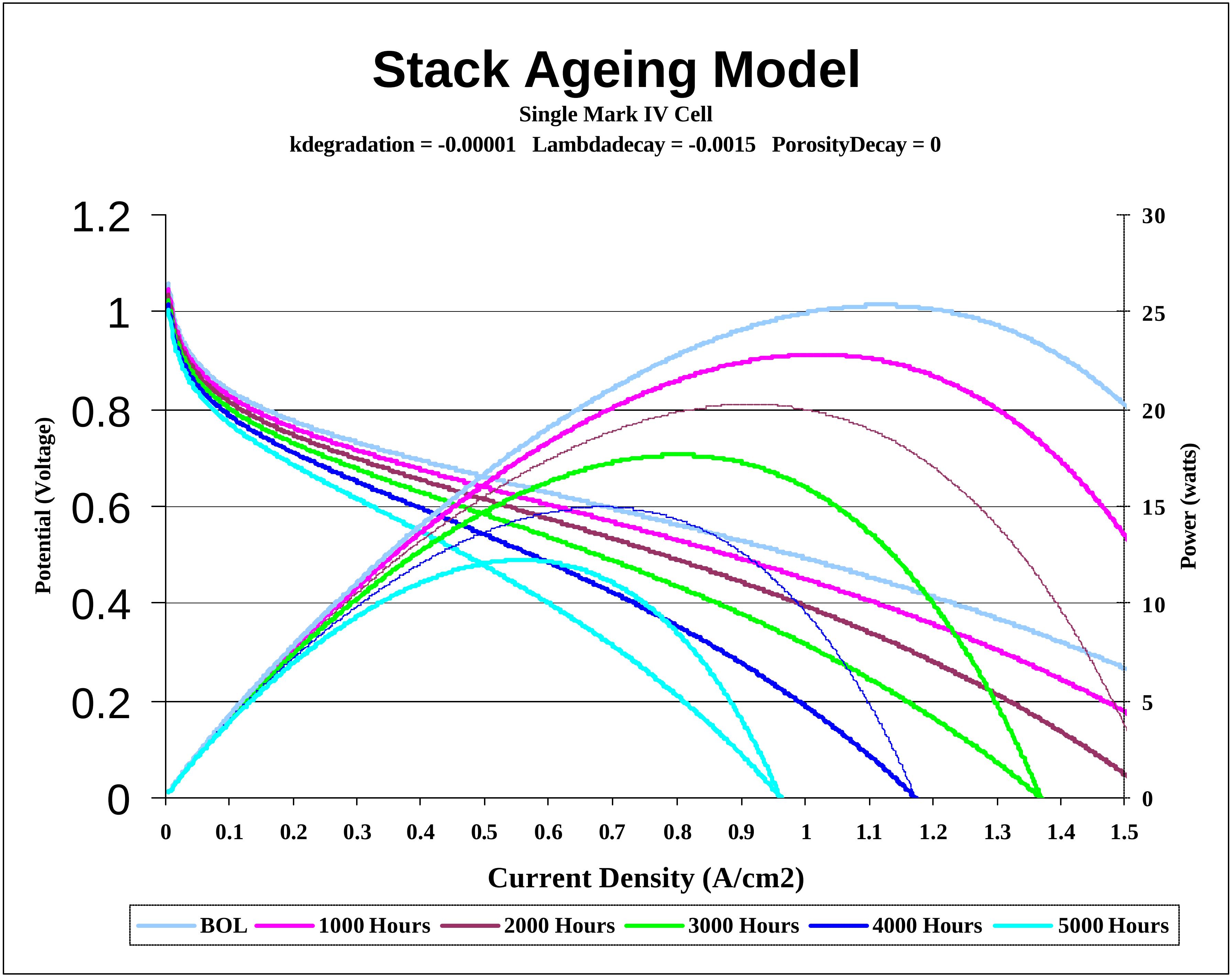
AGEING PARAMETERS

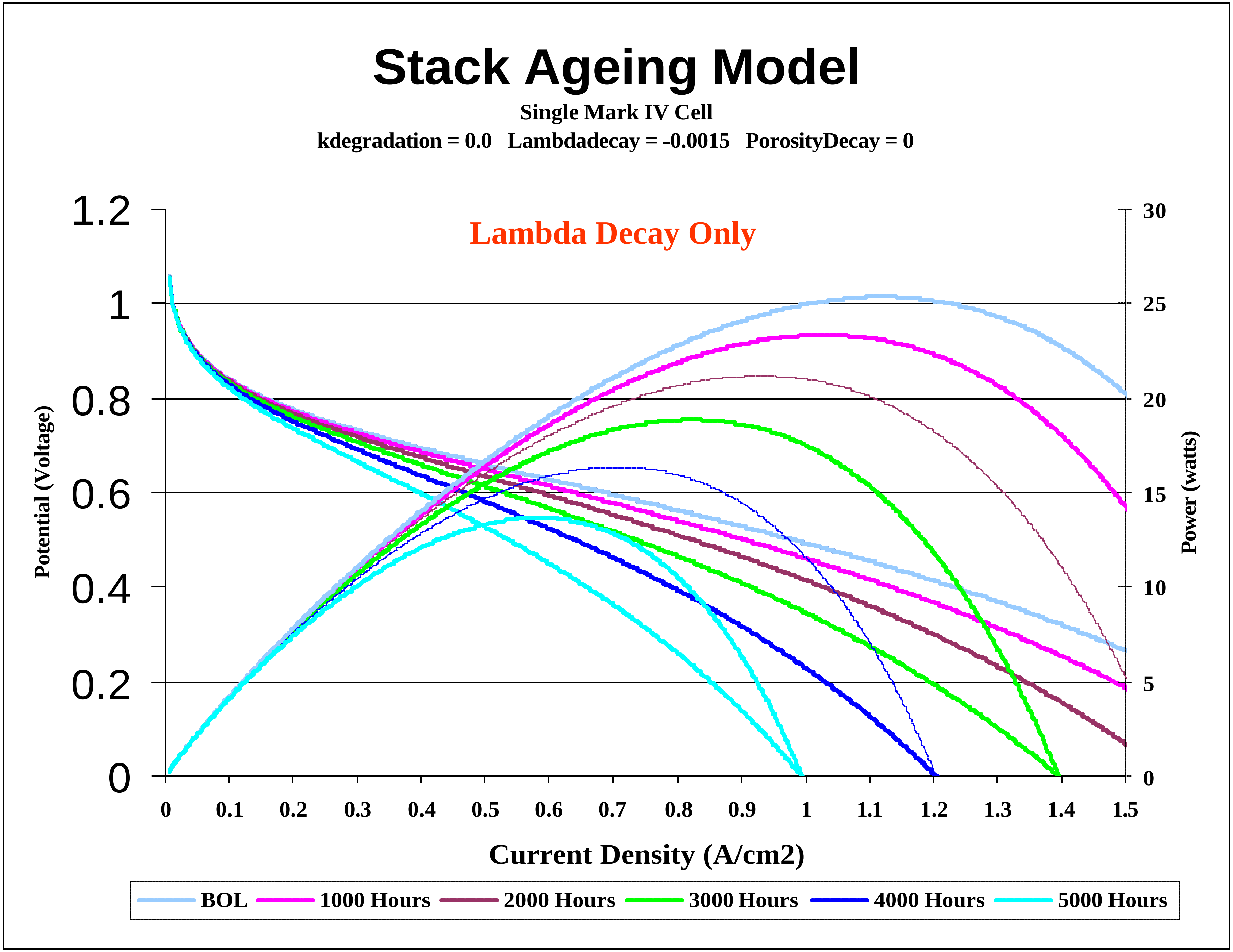
$$x_2 = \mathrm{k}_{DR} \times Age/T + \mathrm{k}_{\mathrm{cell}} + 0.000197 \cdot \ln A + 4.3 \times 10^{-5} \cdot \ln c^{*}_{\mathrm{H}_2}$$

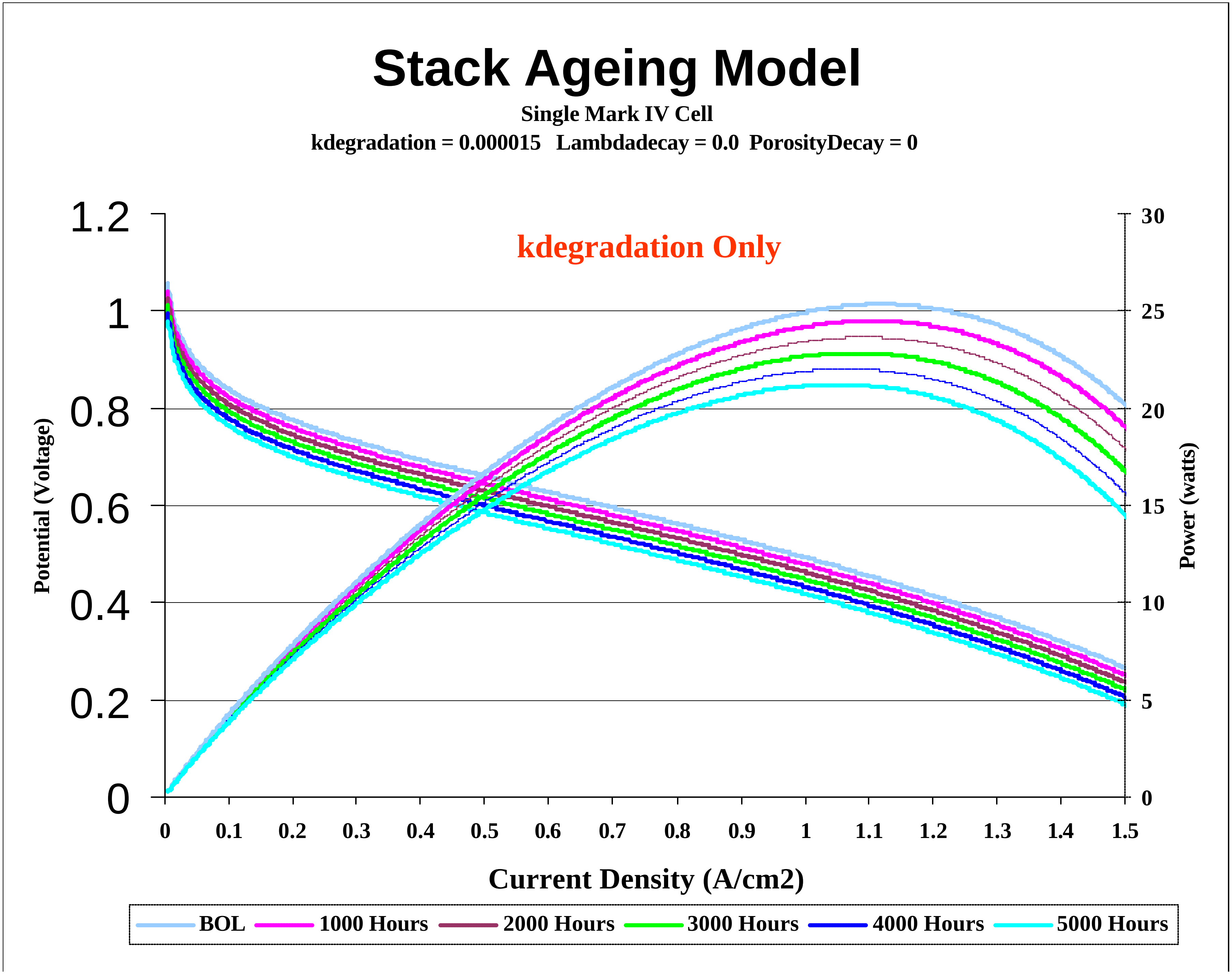
- **proposed ageing rate ($\mathbf{k}_{DR}$) of is -10 mV/hrK**

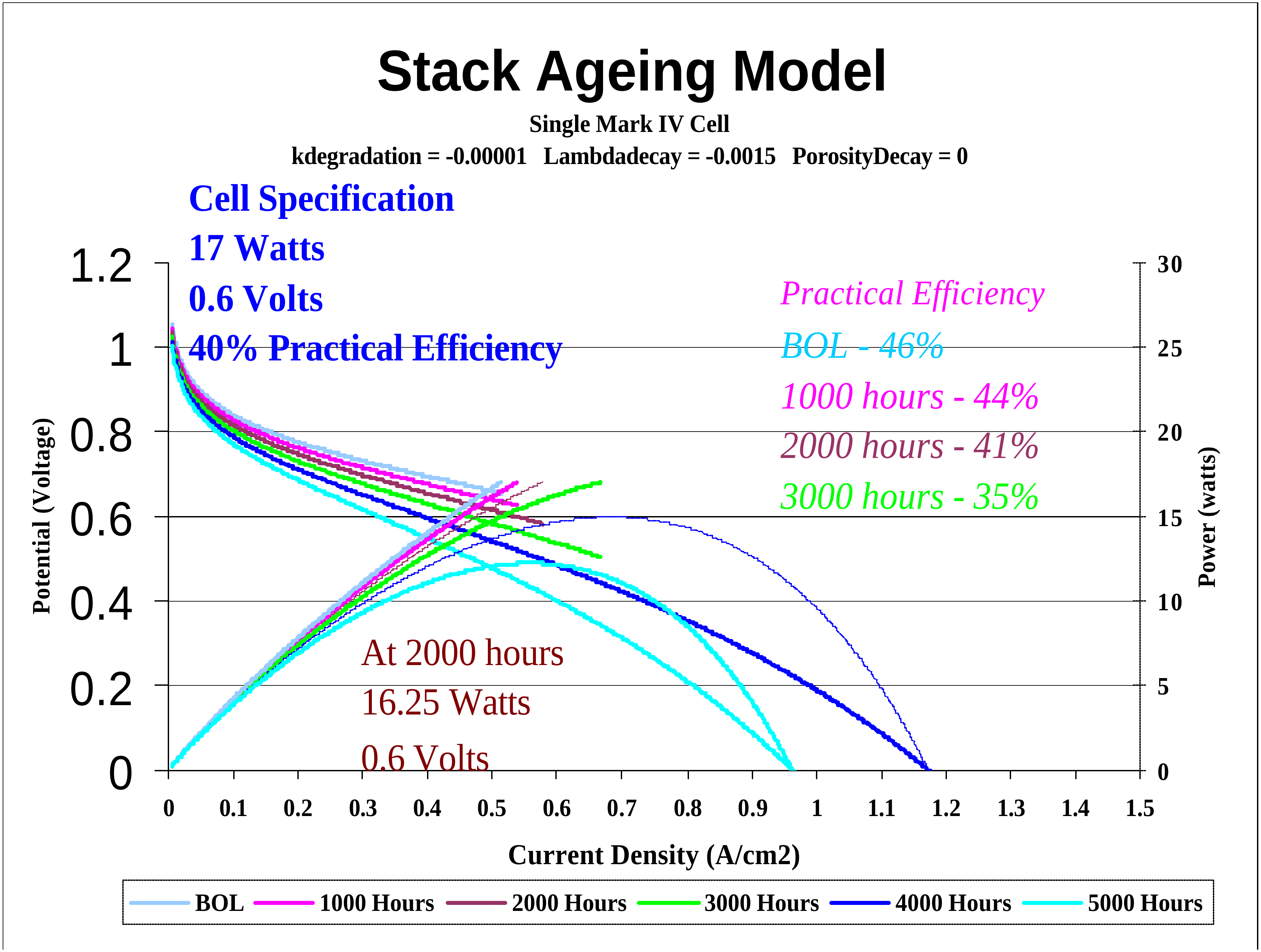
$$l_{age} = l + l_{DR} \times Age$$

- **–0.0015 $\mathbf{hr^{-1}}$ for l_{DR} represents approximately a 10 percent degradation is voltage (at a typical operating level) over 5,000 hours**
- **term related to the loss of mass transport of reactants (not yet included)**

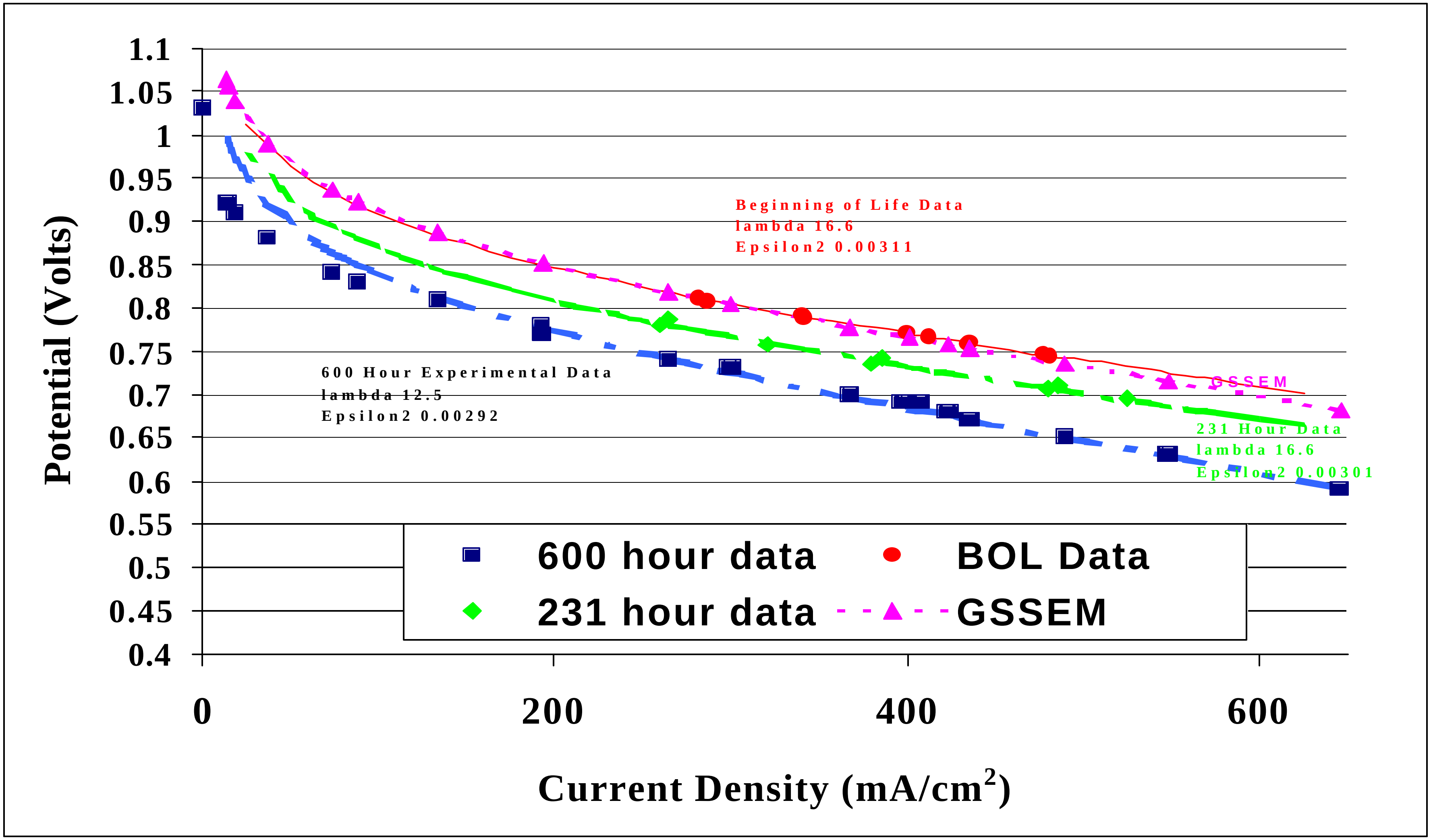

Stack Ageing Model
Single Mark IV Cell
kdegradation = -0.00001 Lambdadecay = -0.0015 PorosityDecay = 0
1.2
1
0.8
0.6
0.4
0.2
0
Potential (Voltage)
30
25
20
15
10
5
0
Power (watts)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
1.5
Current Density (A/cm2)
BOL
1000 Hours
2000 Hours
3000 Hours
4000 Hours
5000 Hours


Stack Ageing Model
Single Mark IV Cell
kdegradation = 0.0   Lambdadecay = -0.0015   PorosityDecay = 0
Lambda Decay Only
Potential (Voltage)
1.2
1
0.8
0.6
0.4
0.2
0
Power (watts)
30
25
20
15
10
5
0
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1 1.1 1.2 1.3 1.4 1.5
Current Density (A/cm2)
BOL
1000 Hours
2000 Hours
3000 Hours
4000 Hours
5000 Hours


Stack Ageing Model
Single Mark IV Cell
kdegradation = 0.000015 Lambdadecay = 0.0 PorosityDecay = 0
kdegradation Only
Potential (Voltage)
Power (watts)
Current Density (A/cm2)
1.2
1
0.8
0.6
0.4
0.2
0
30
25
20
15
10
5
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
1.5
BOL
1000 Hours
2000 Hours
3000 Hours
4000 Hours
5000 Hours


Stack Ageing Model
Single Mark IV Cell
kdegradation = -0.00001 Lambdadecay = -0.0015 PorosityDecay = 0
Cell Specification
17 Watts
0.6 Volts
40% Practical Efficiency
Practical Efficiency
BOL - 46%
1000 hours - 44%
2000 hours - 41%
3000 hours - 35%
At 2000 hours
16.25 Watts
0.6 Volts
Potential (Voltage)
Power (watts)
Current Density (A/cm2)
1.2
1
0.8
0.6
0.4
0.2
0
30
25
20
15
10
5
0
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1 1.1 1.2 1.3 1.4 1.5
BOL
1000 Hours
2000 Hours
3000 Hours
4000 Hours
5000 Hours

MARK IV DEGRADATION
H_2/O_2 30 psig/30psig 80°C



Michael Fowler –University of Waterloo - Presentation for ME 751

USES OF THE AGEING/ DEGRADATION MODEL

- **Tool to be used in Fuel Cell *Stack and System* Modelling**
- **Diagnosis of MEA and/or Stack design changes**
- **Projection of performance throughout desired life**
- **Tool to be used with testing programs (will allow for shorter testing periods)**
- **Tool for development and testing of Control Systems and Control Strategies**
- **Estimation of reliability throughout desired life period**
- **Tool to be used with a *reliability growth program***
- **Tool for comparison of the Component Effectiveness of different Stacks**

COMPONENT EFFECTIVENESS

- **The probability that the component can successfully meet operational demand within a given time when operated under specific conditions.**
  - **Technical performance (capability, operation parameters)**
  - **Efficiency (range, endurance)**
  - **Size/Weight**
  - **Reliability (i.e. durability, availability, stability, dependability)**
  - **Safety**
  - **Life**
  - **Life Cycle Costs (life cycle costs can be traded off with stack design & operational decisions)**

RELIABILITY ANALYSIS

- **Function of degradation evaluation, *i.e.* to below a certain level of Component effectiveness *(durability)***
- **Degradation to below threshold value for specific parameter *(durability)***
- **Catastrophic failure of the MEA or plate (cracking or smudging)**
- **Loss of Integrity leading to safety hazard**
- **Goal of the analysis is to allow an understanding of the impact of design (*e.g.* redundancy - increase weight of catalyst) and operation changes (*e.g*. limitation of operating states) on EOL performance**

UNIQUENESS OF THE RESEARCH

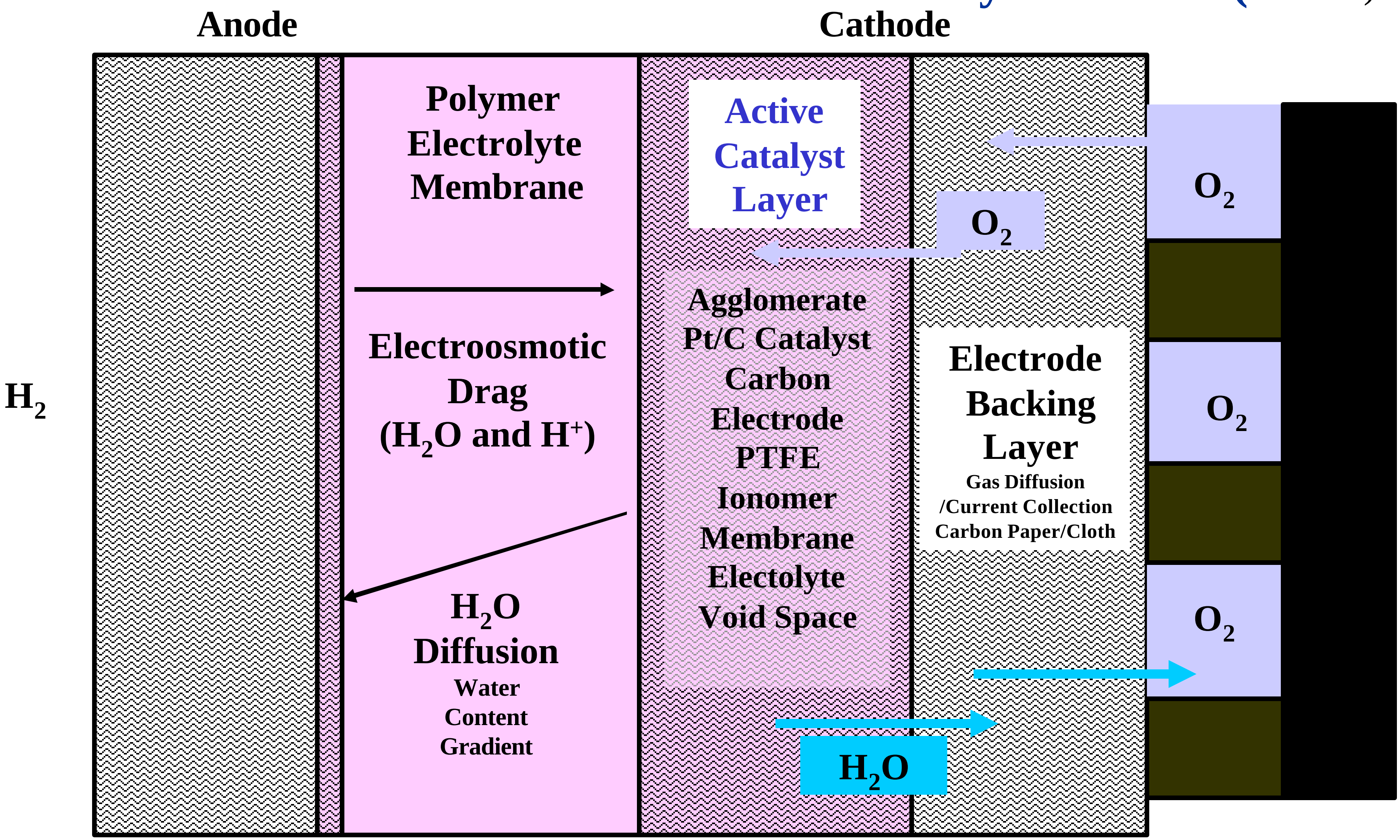
- **Incorporation of degradation factors in PEM modelling to predict EOL performance has not yet been done (GSSEDM is unique)**
- **PEM Stacks are relatively novel and not yet fully commercialized**
- **Discussion of 'Component Effectiveness' parameters for PEM fuel cells is limited (and will vary depending on the application)**
- **Reliability analysis for PEM Stacks is unique**
- **Use of mechanistic and degradation modelling in reliability analysis is novel**

Modelling Fuel Cell Performance as Stochastic Process

- **Variation in behaviour can be attributed to experimental error (the stochastic component):**
  - **environmental conditions;**
  - **reactant flow and pressure fluctuations;**
  - **varying rates of water accumulation;**
  - **difference in MEA quality from one MEA to the next;**
  - **differences in the contact resistance between the cells;**
  - **reactant conditions and quality (including contamination),;**
  - **instrumentation and measurement error; and,**
  - **control set point error.**

There will be some error associated with the inadequacy of model or lack of fit of the model. Note that a stack with a large number of cells will compensate for the variability in performance

PEM Membrane Assembly Electrode (MEA)



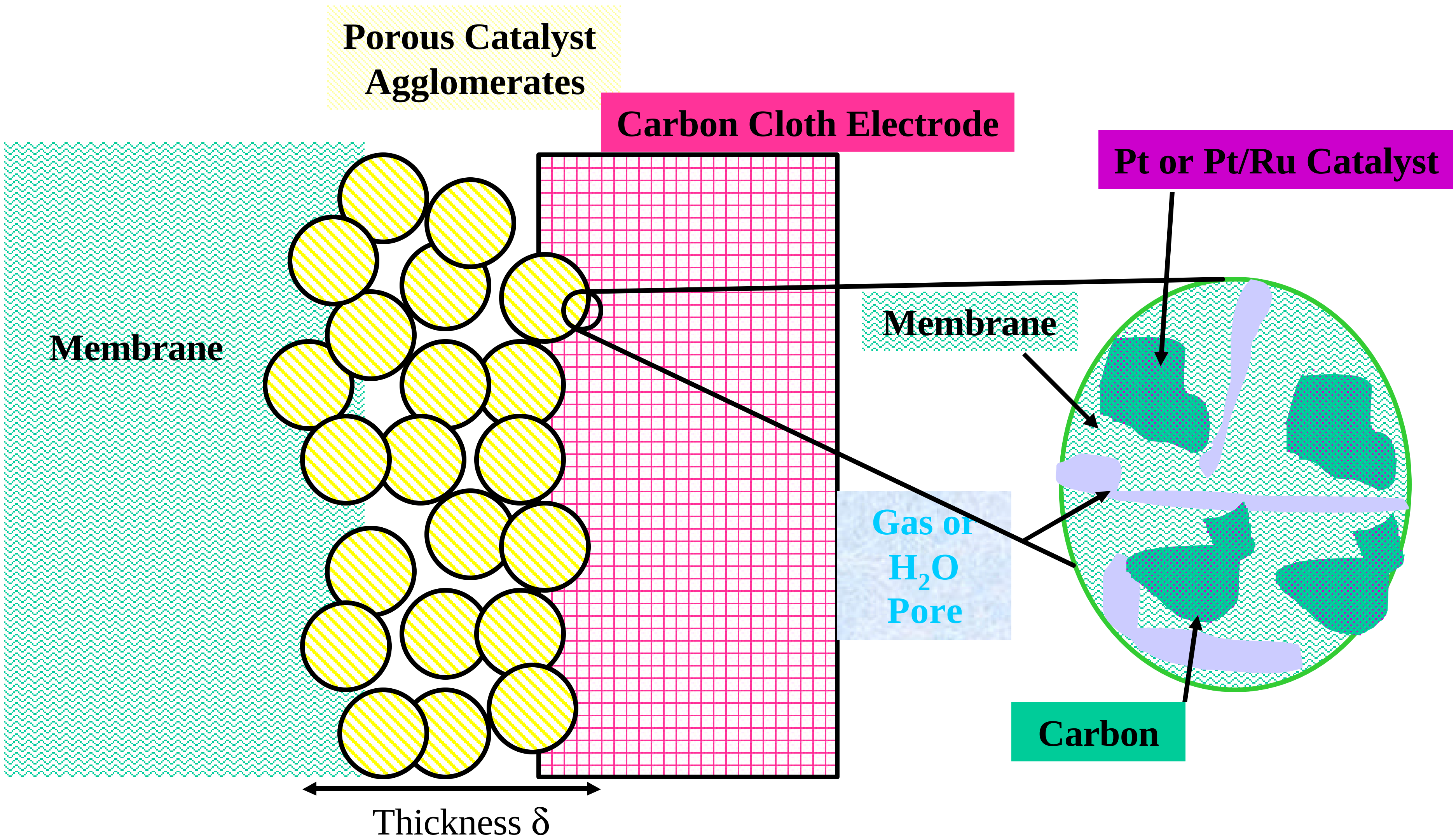
Anode : $H_2 \rightarrow 2H^+ + 2e^-$

Cathode : $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$

Cell : $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

$$E = E^\circ + (RT/2\Im)\ln[P_{H_2}]$$
$$+ (RT/2\Im)\ln[P_{O_2}^{1/2}]$$

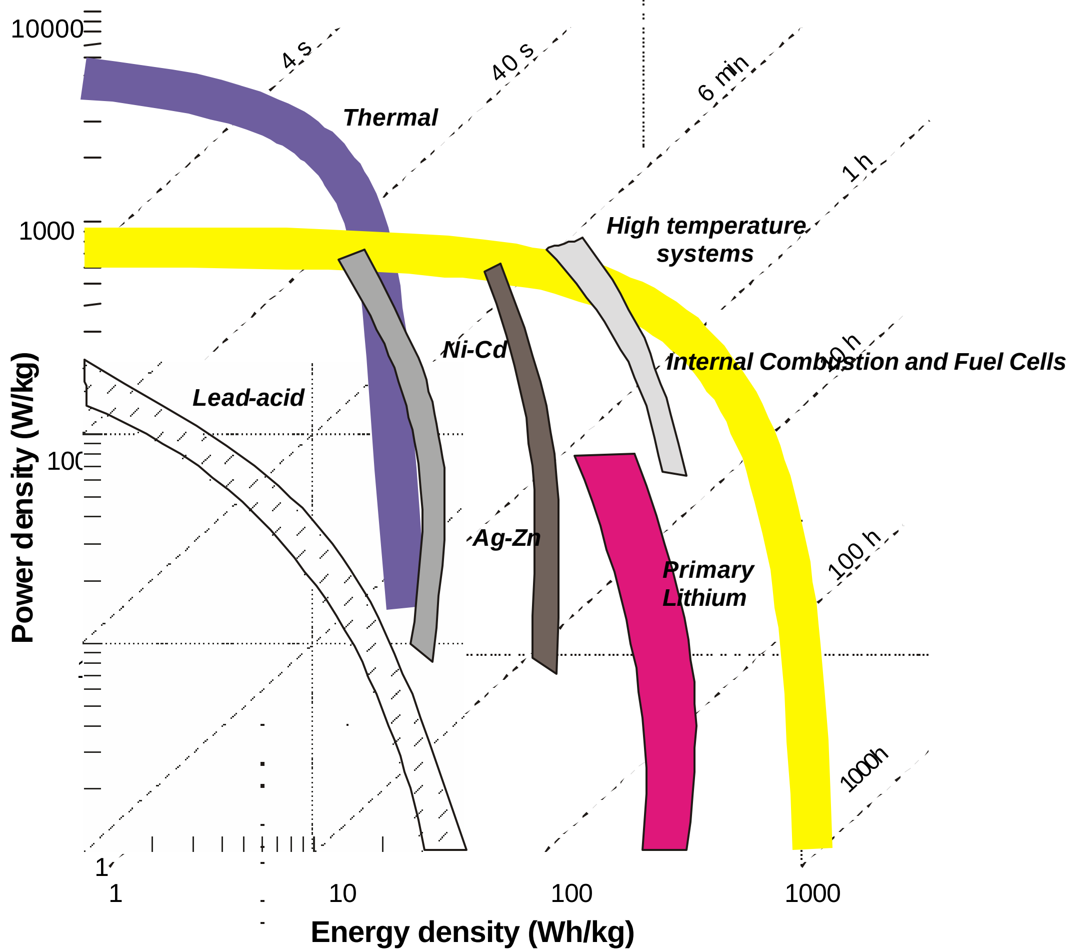
Active Layer Agglomerates



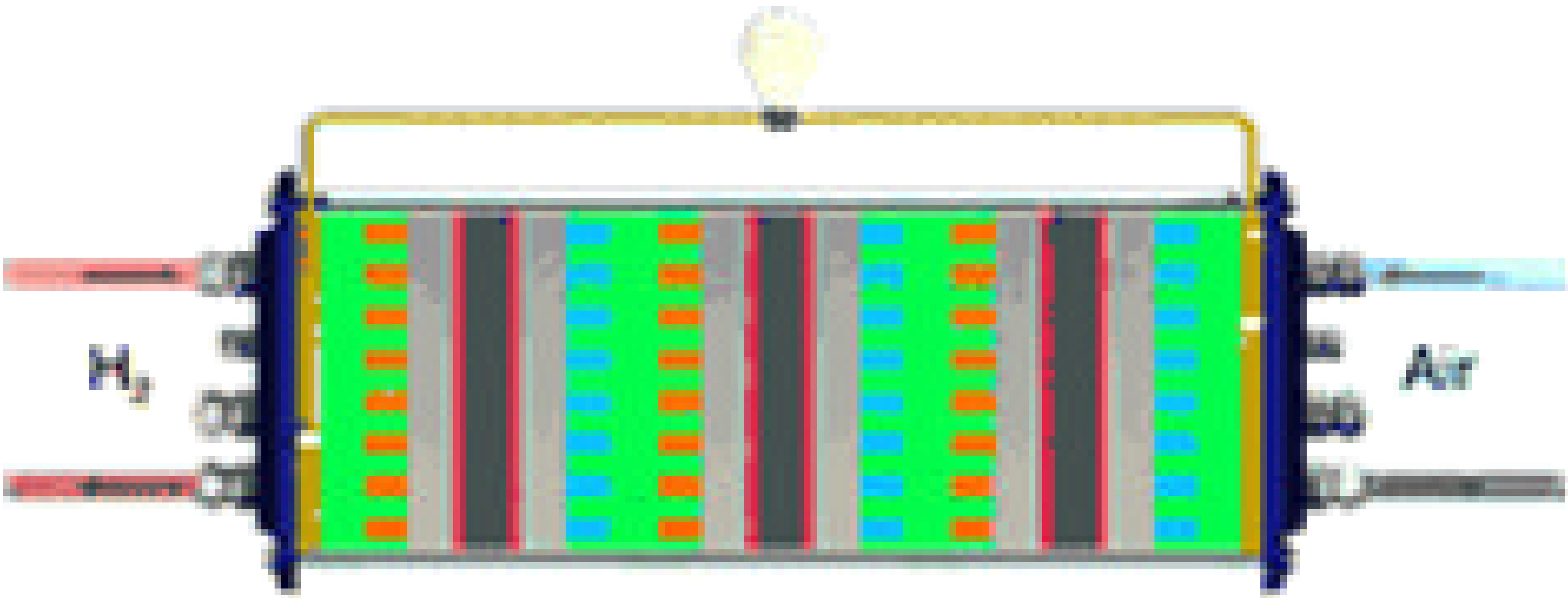
MEA MATERIALS

Layer	Bi-Polar Plate	Gas Diffusion Layer – Anode	Anode	Electrolyte Membrane	Cathode	Gas Diffusion Layer - Cathode
Material	Graphite in Vinyl Ester	PTFE Treated Carbon Paper	Pt/Ru on Carbon Support	Perfluoro-sulfonic Acid	Pt on Carbon Support	PTFE Treated Carbon Paper
Thickness (µm)	4750	100	20	40	20	100
Catalyst Loading (mg/cm^2)			Pt: 0.4 Ru: 0.2		Pt: 0.4	

Ragone Plot for Various Power Sources



PEM FUEL CELL STACK



STACK DESIGN PARAMETERS

- **MEA active area**
- **Aspect Ratio**
- **Number of Cells**
- **Plate Materials**
- **Flow configuration**
- **Gas Delivery System**
- **Cooling System (plate material, fluid choice)**
- **Stack construction and clamping pressure**

MEA DESIGN PARAMETERS

- **Membrane**
  - **type of material (PFSA/perfluorosulfonic acid or Nafion)**
  - **thickness**
  - **reinforcement material**
- **Catalyst**
  - **type**
  - **dispersion**
  - **amount**
- **Electrode**
  - **type of material**
  - **thickness & density**
  - **anti-wetting**
- **Impregnation material/method**

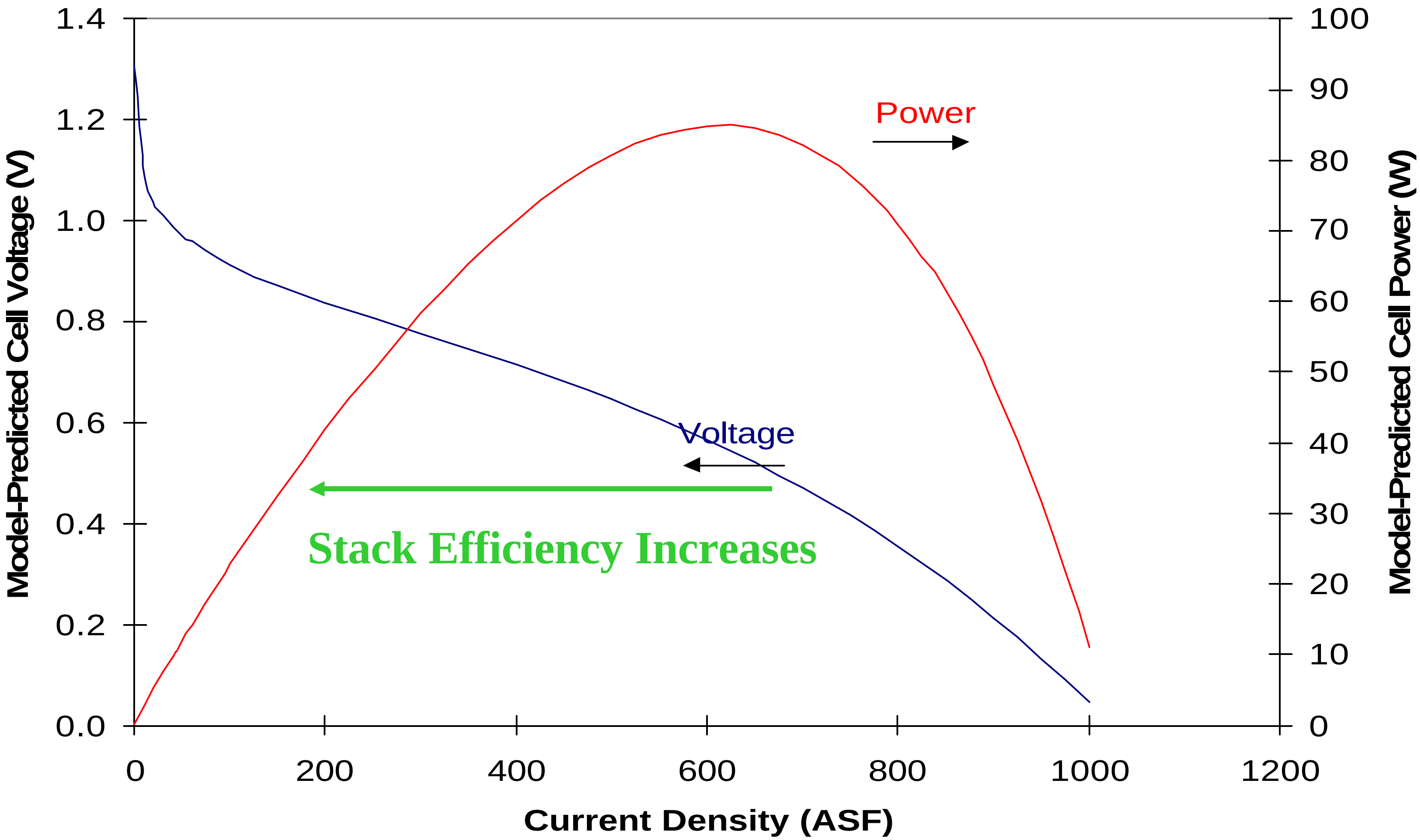
STACK OPERATING PARAMETERS

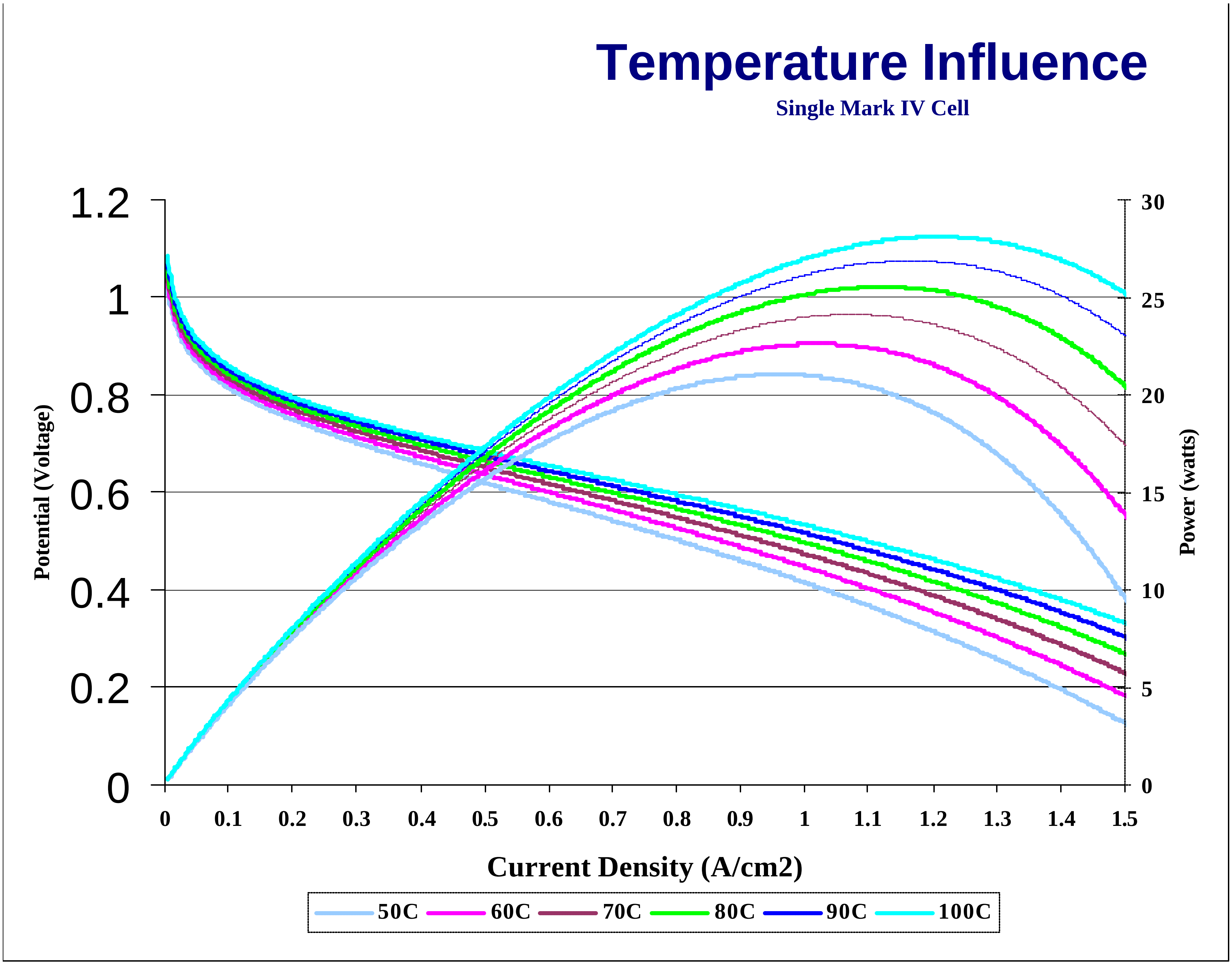
- Temperature (Increases will result in…)
  - increases stack efficiency
  - heat may be of a better quality, system may be more thermally matched
  - water management may become a problem
  - higher heat losses , sealing, thermal expansion and material corrosion issues
- Pressure (Increases will result in…)
  - increased stack efficiency, reduced heat lost, reduced piping
  - increased parasitic load & higher capital costs
  - more complexity, less reliability, different material considerations (corrosion)
- Humidification
- Stoichiometry (or Utilization)

POLARIZATION CURVE

PEM Ballard Mark V/35 Cell Stack

-increases in stack efficiency lead to decreasing power output

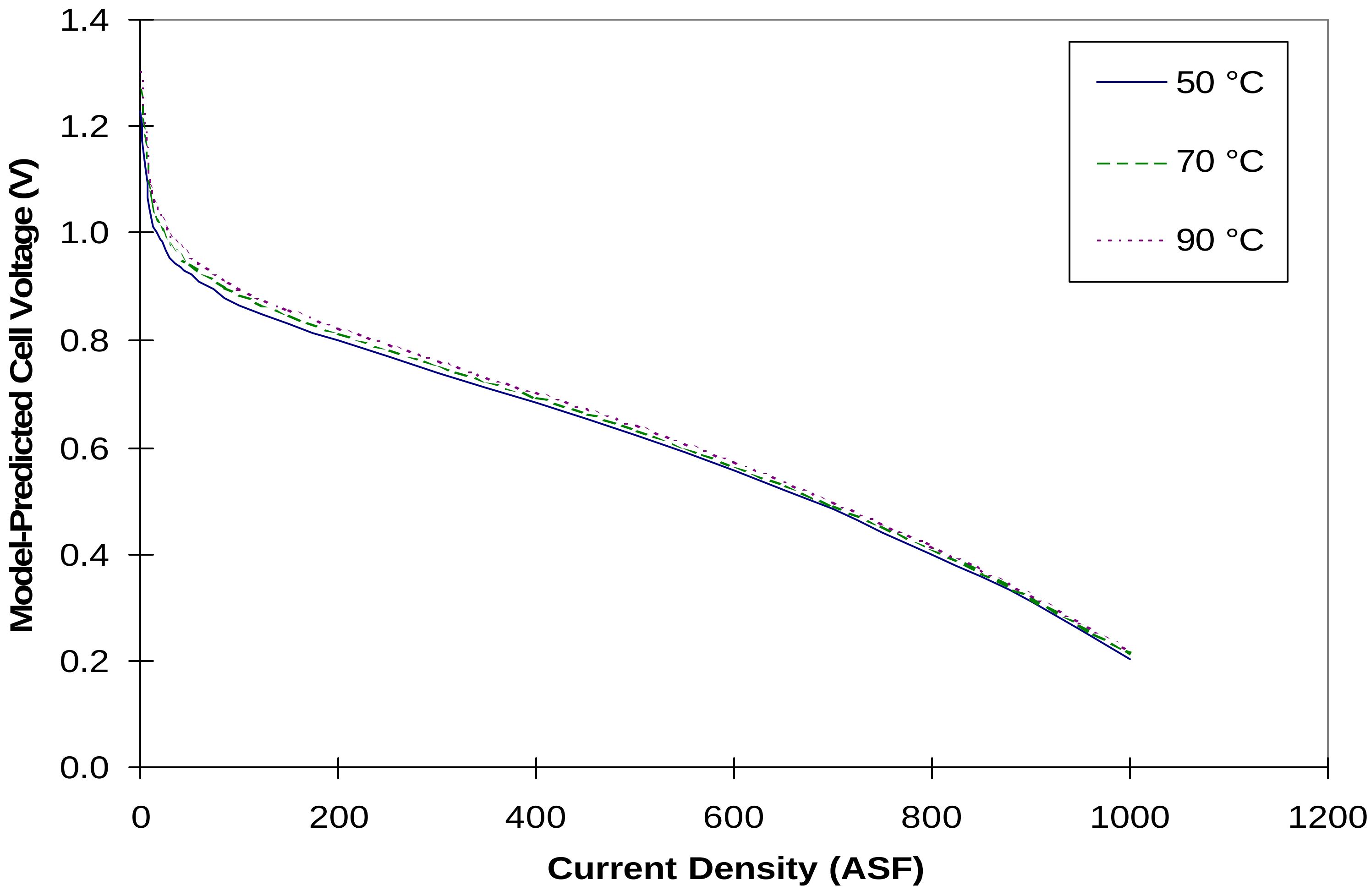




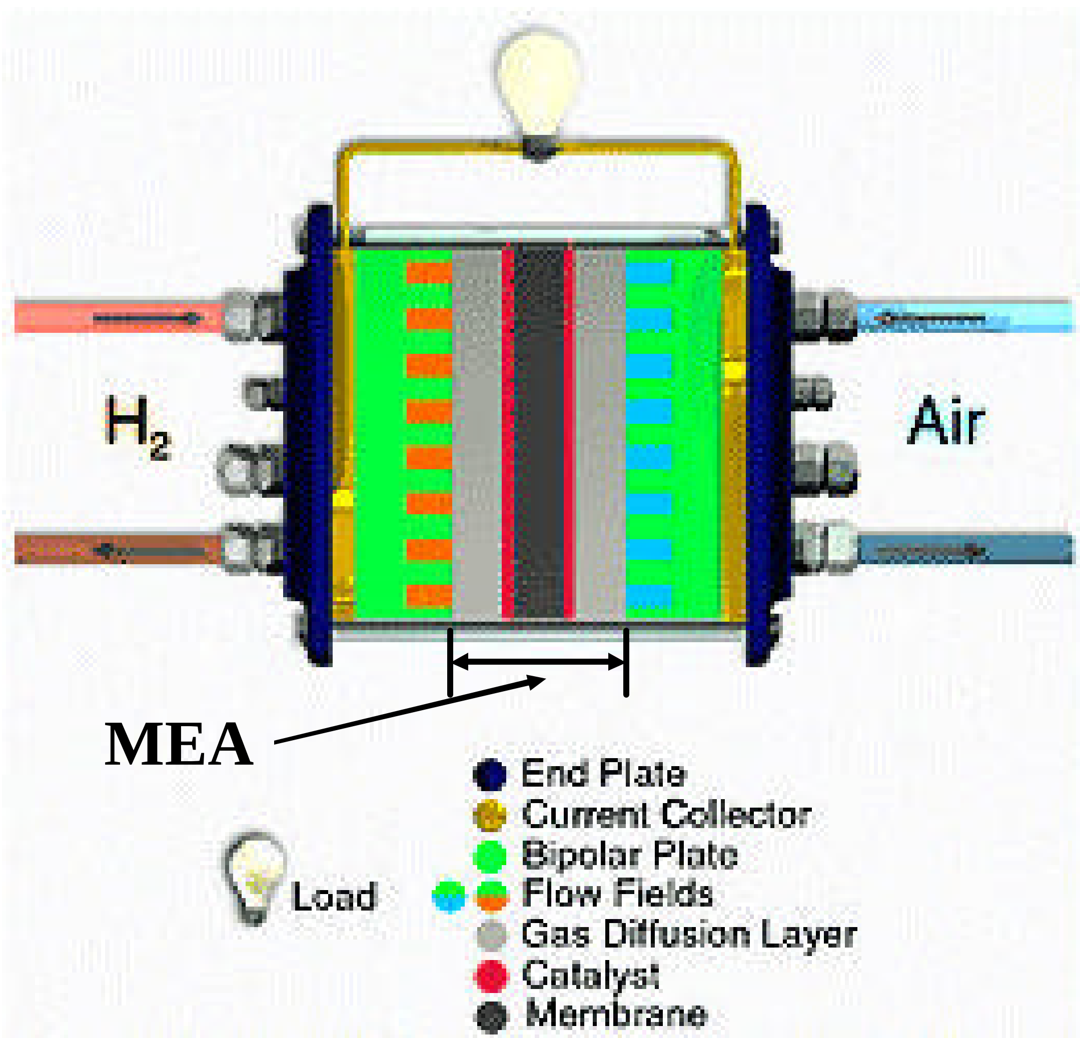
Temperature Influence
Single Mark IV Cell
Potential (Voltage)
Power (watts)
Current Density (A/cm2)
1.2
1
0.8
0.6
0.4
0.2
0
30
25
20
15
10
5
0
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1 1.1 1.2 1.3 1.4 1.5
50C
60C
70C
80C
90C
100C

TEMPERATURE INCREASES

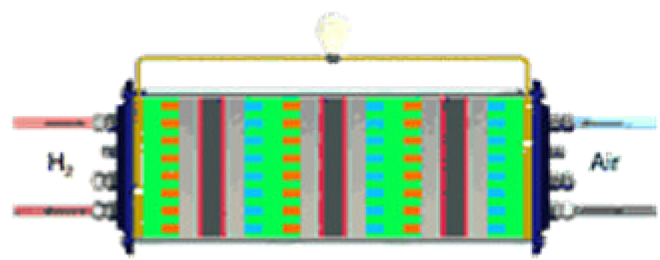
PEM Ballard Mark V Stack



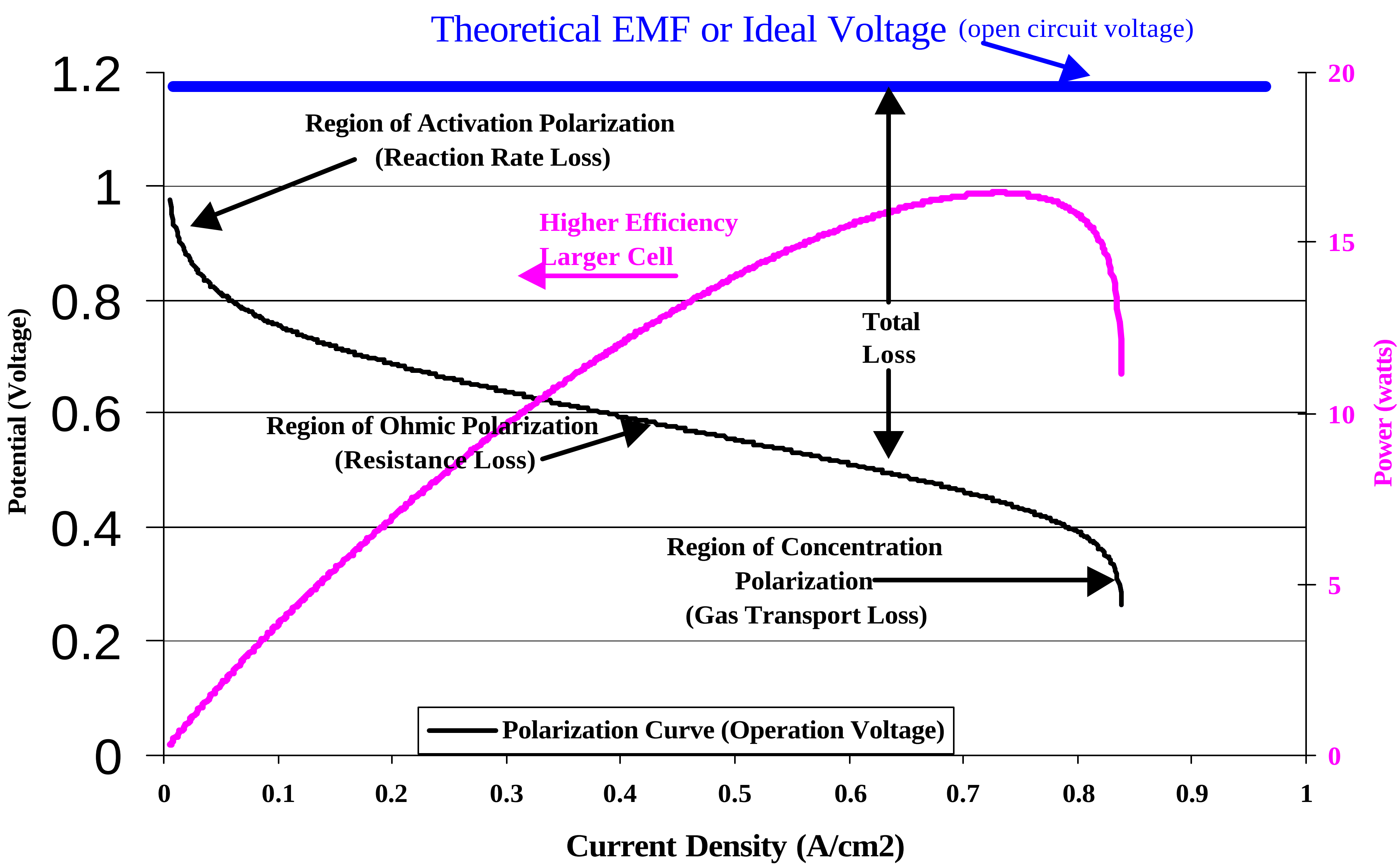
PEM FUEL CELL



Cells arranged to form a 'stack'.

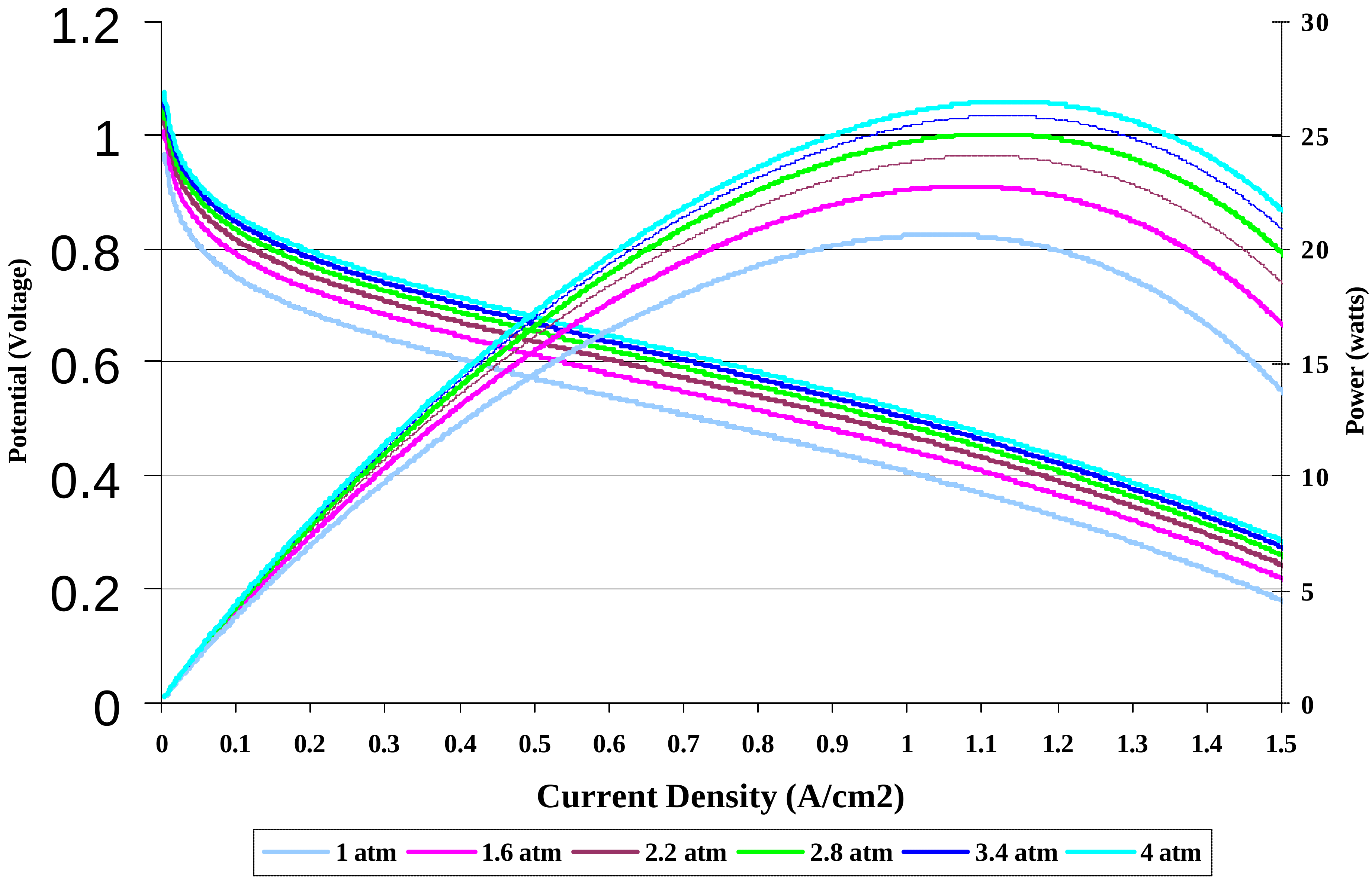


Ideal and Actual Fuel Cell Voltage/Current Characteristics



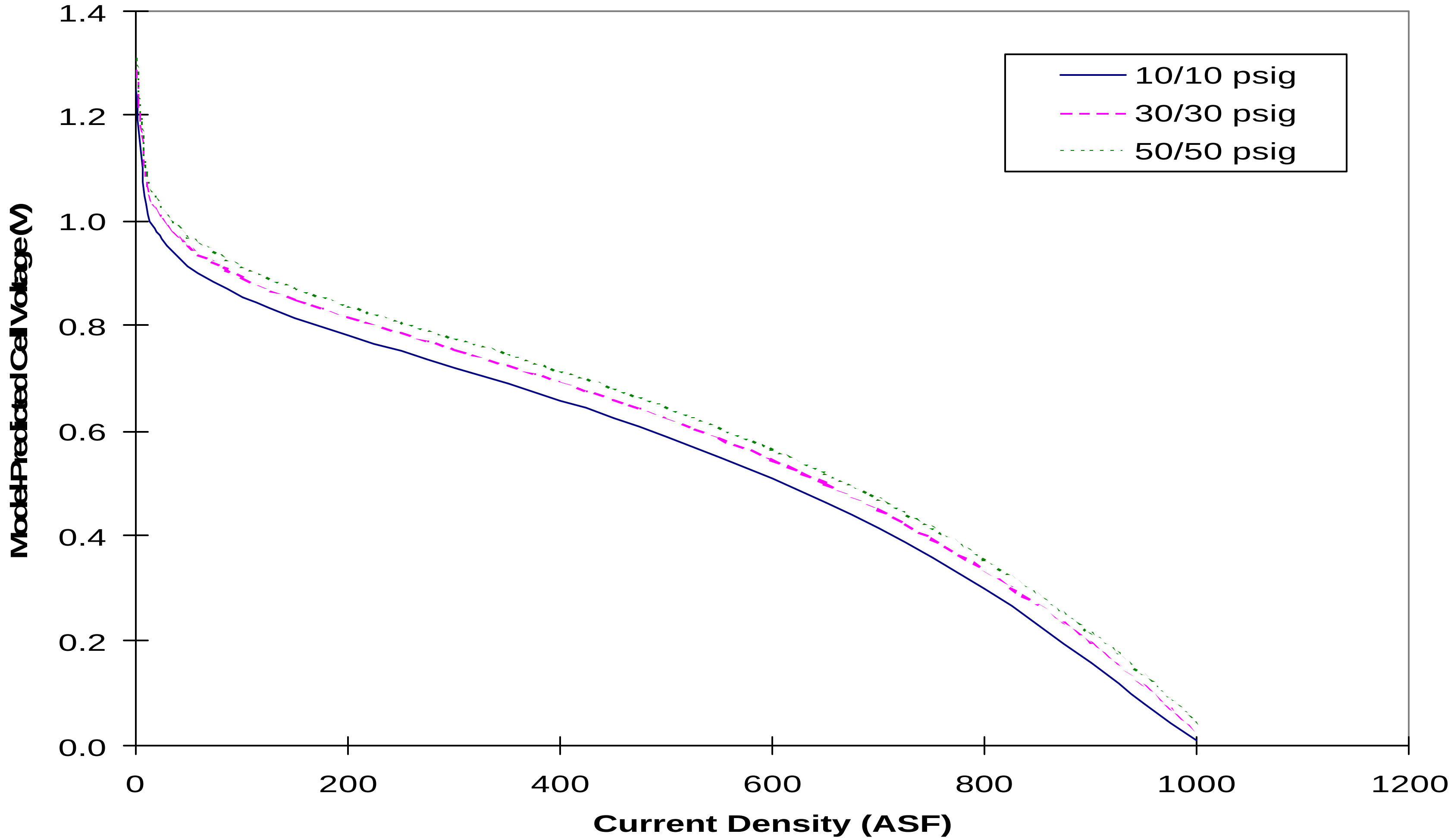
Pressure Influence

Single Mark IV Cell



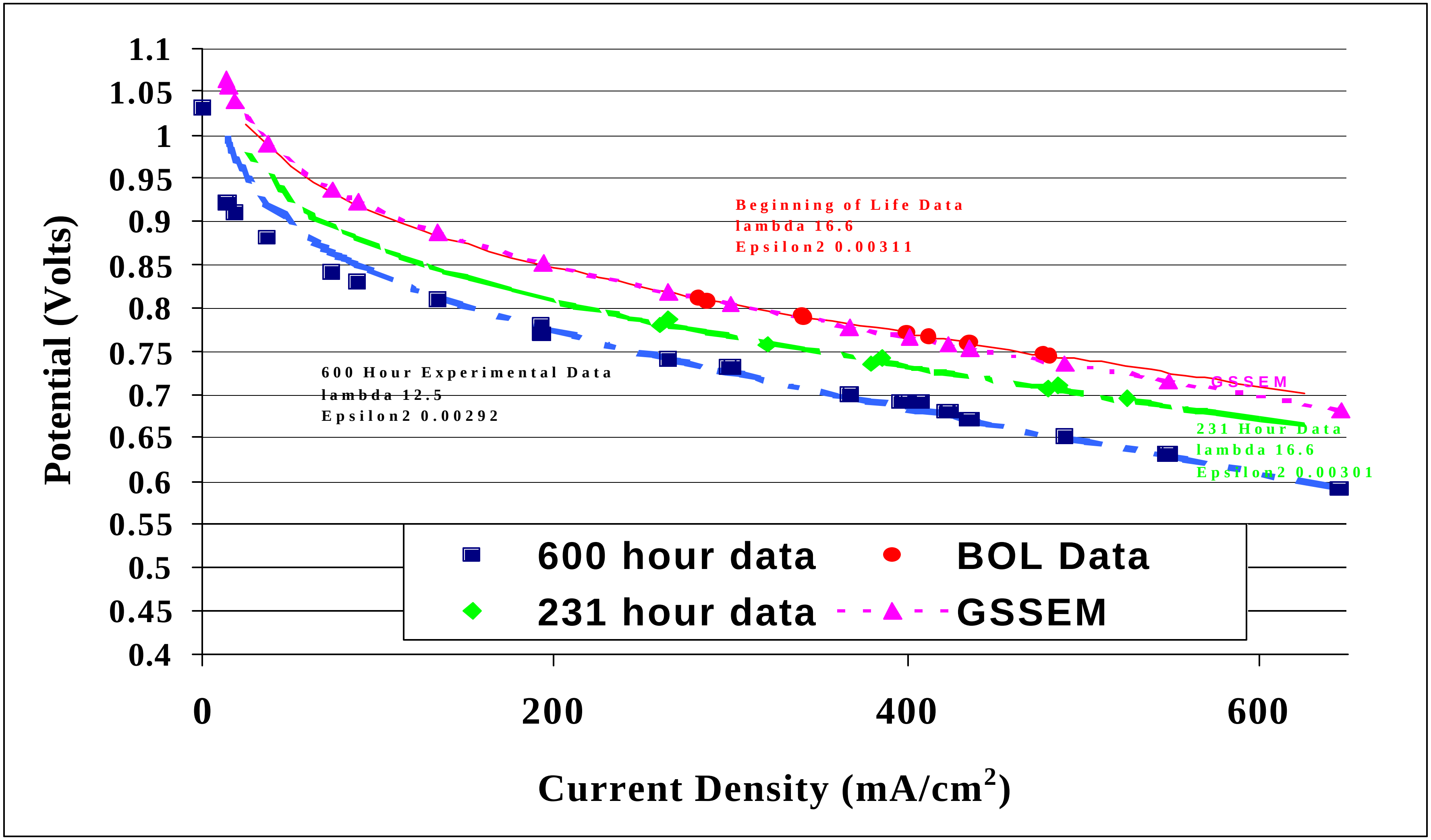
PRESSURE INCREASES

PEM Ballard Mark V/35 Cell Stack

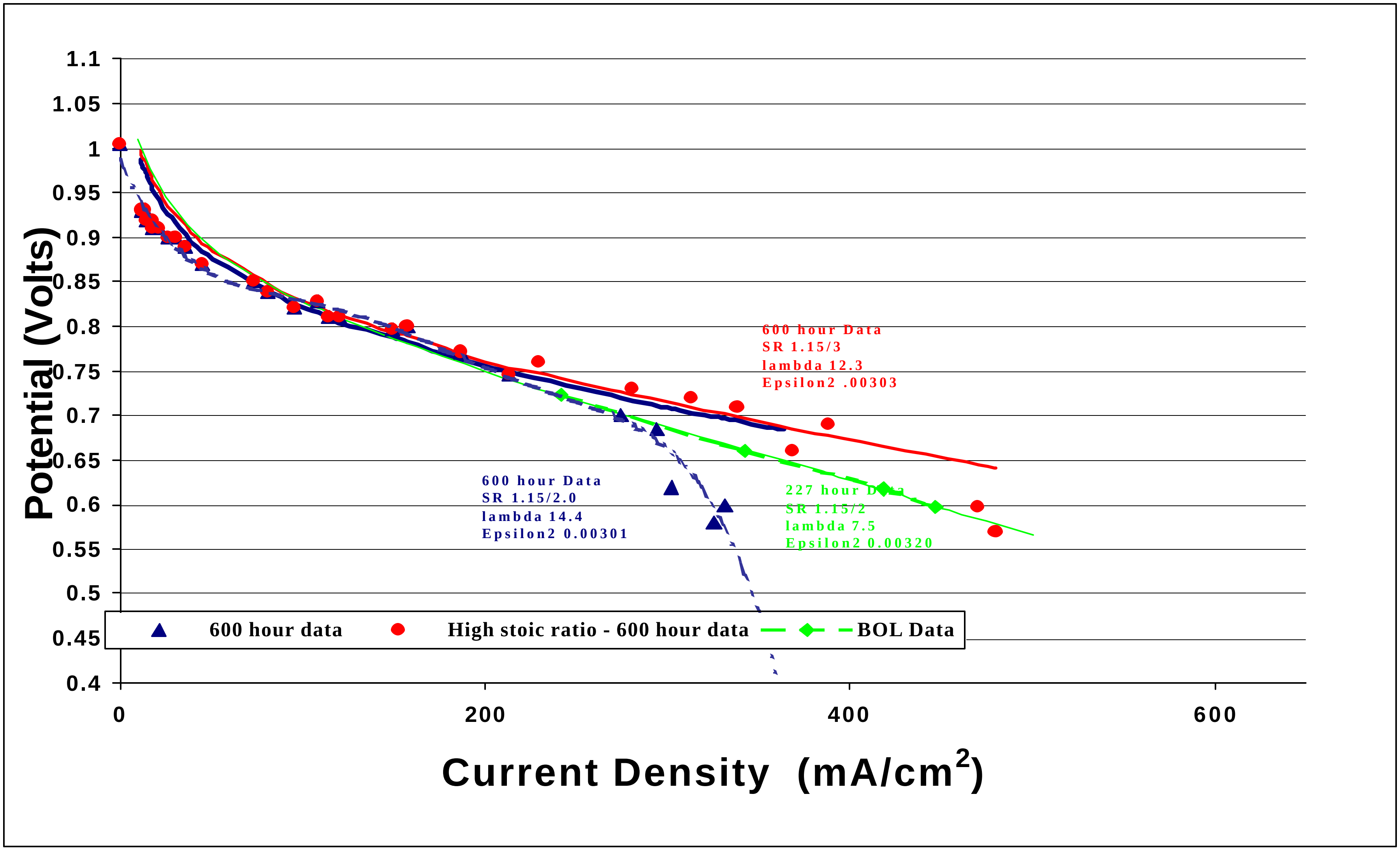


MARK IV DEGRADATION

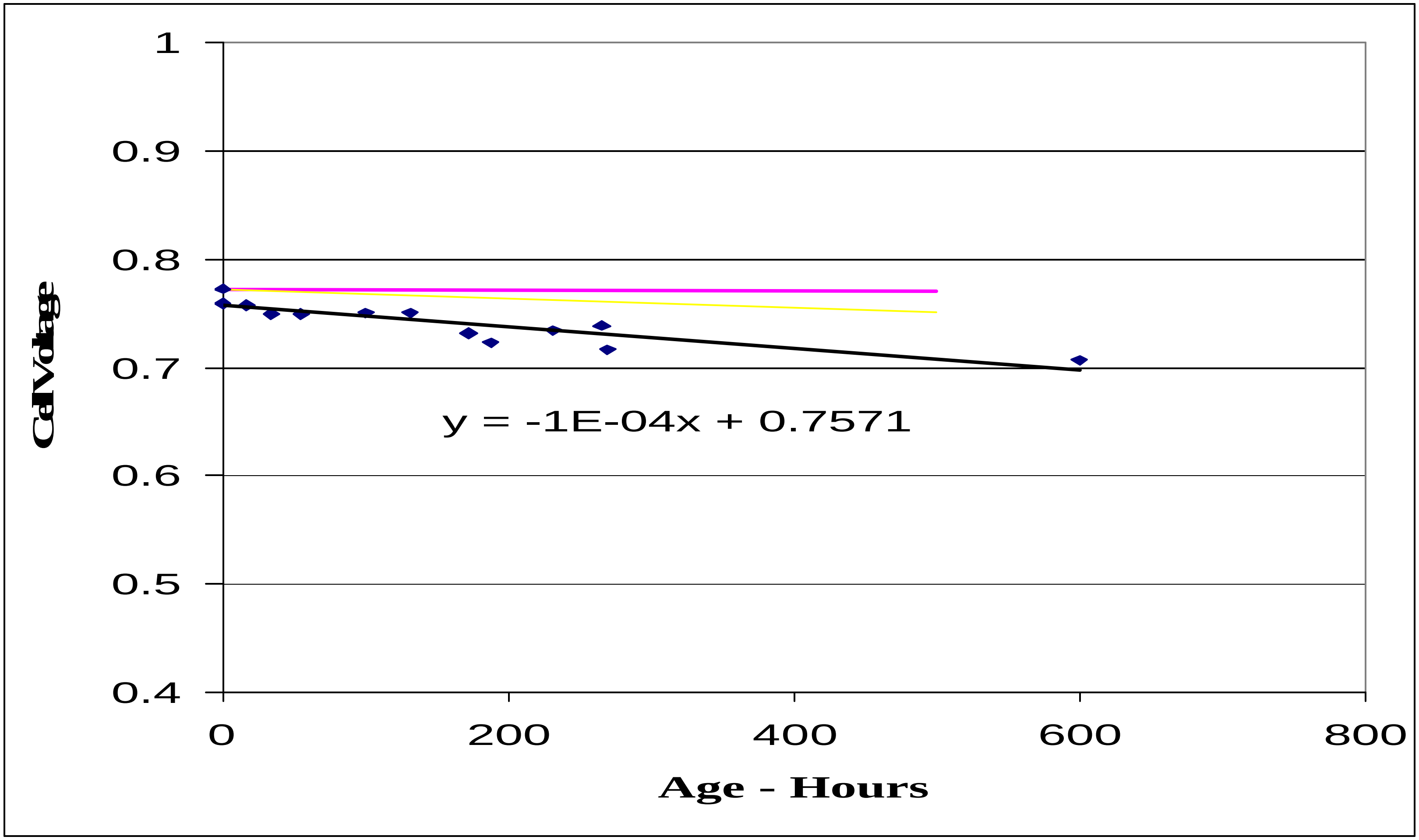
H_2/O_2 30 psig/30psig 80ºC



MARK IV DEGRADATION
H_2/AIR 30 psig/30psig 80°C



MARK IV - VOLTAGE DEGRADATION PLOT (0.431amp/cm2)



Catalyst Deactivation

- Ageing or Sintering (Physical Deactivation)
  - crystal agglomeration and growth
  - internal surface area of the catalyst and supports are reduced through the narrowing or closing of pores
- Poisoning (Chemical Deactivation)
- Coking (fouling - Chemical Deactivation)

CATHODE CONTAMINATES

- **SO_2 (can be 5ppm in cities)**
  - **dependent on operating conditions**
- **NH_3 and NO_2 (little or no impact, reversible)**
- **CO small reversible impact**
- **Salt Air not significant**
- **Battlefield Contaminants are an issue**

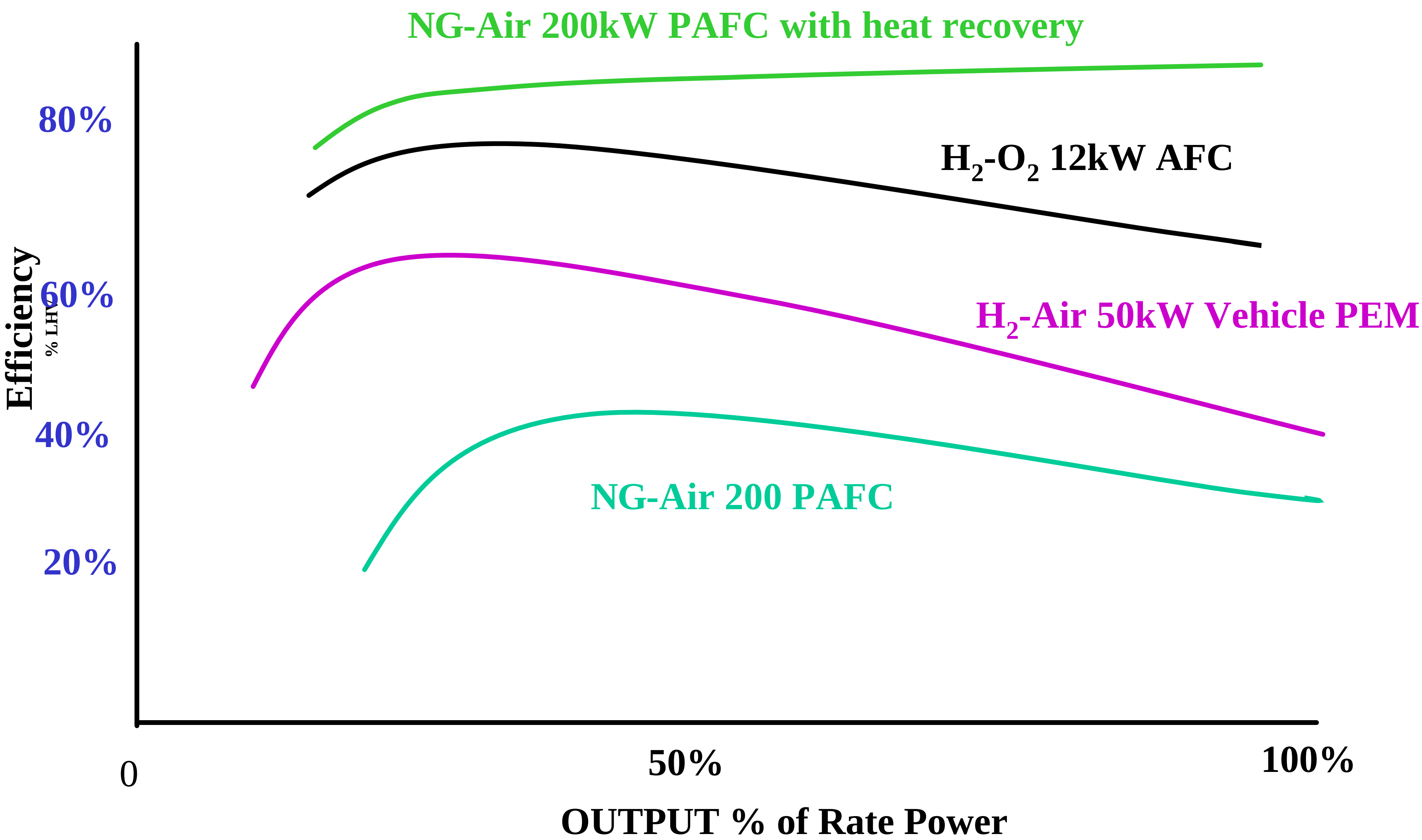
ANODE CONTAMINANTS

- **10ppm CO (reversible)**
- **Sulphur components**
- **N_2 and CO_2 inert**
- **CH_4 - relatively inert**
- **Methanol, Formaldehyde, Formic Acid, Methyl-format (reversible performance loss)**
- **Metals will damage the MEA**

OVERALL FUEL CELL SYSTEM EFFICIENCY

- **Thermal & Material Integration**
  - **matching sub-system temperatures**
  - **using the heat internally & efficient thermal transfer**
  - **using the product steam/water**
  - **Co-generation or Bottoming Cycle (turbine, space or water heater, chiller)**
- **Pressurization increase improves stack performance**
  - **but requires energy, increased cost & reduces reliability**
- **Temperature increase improves stack performance**
  - **but reduces reliability & increases corrosion**
- **Fuel Utilization and/or Flow Rate**
  - **Air/fuel flow needed for water and thermal management**
  - **fuel needed to heat the reformer**
- **Parasitic Power Losses & Complexity must be considered**

SYSTEM EFFICIENCY VS % RATED POWER



Ref:King, JPS 86

PERFORMANCE MEASURES OF A FUEL CELL STACK

*Performance targets over a 40,000 hour life-cycle, or 5,000 hours for automotive application

- **Mean Time to Failure (function of reliability and decay rate)**
- **Mean Time Between Forced Outages/Derating (dominated by stability issues)**
- **Overall Reliability/Availability (which includes stability issues):**
  - **Power Capacity - kW net electrical output**
  - **Fuel Efficiency - % based on LHV of fuel**
  - **Minimum Voltage Output - volts**
  - **'System' dominated parameters**
    - **Response Time - % power increase per minute from idle**
    - **(Emission Targets -)**
      - **(specific target values for particulate, VOC, SO_2, NO_x, CO_2)**
- **Voltage Decay Rate - no higher than a number of Volts/hour of operation** (used as an indicator of life cycle)

SYSTEM EFFECTIVENESS

- **The probability that the system can successfully meet operational demand within a given time when operated under specific conditions.**
  - **Technical performance (capability, operation parameters)**
  - **Efficiency (range, endurance)**
  - **Size/Weight**
  - **Reliability (i.e. durability, availability, stability, dependability)**
  - **Safety**
  - **Life**
  - **Life Cycle Costs (life cycle costs can be traded off with stack design & operational decisions)**

Managing System Effectiveness

Complex trade-off between stack efficiency, system effectiveness and operating parameters.
Reliability system will also depend on selection of operating parameters.

Reliability and System Effectiveness can therefore be managed (and monitored) through a control strategy.

PERFORMANCE MEASURES OF A FUEL CELL STACK

*Performance targets over a 40,000 hour life-cycle, or 5,000 hours for automotive application

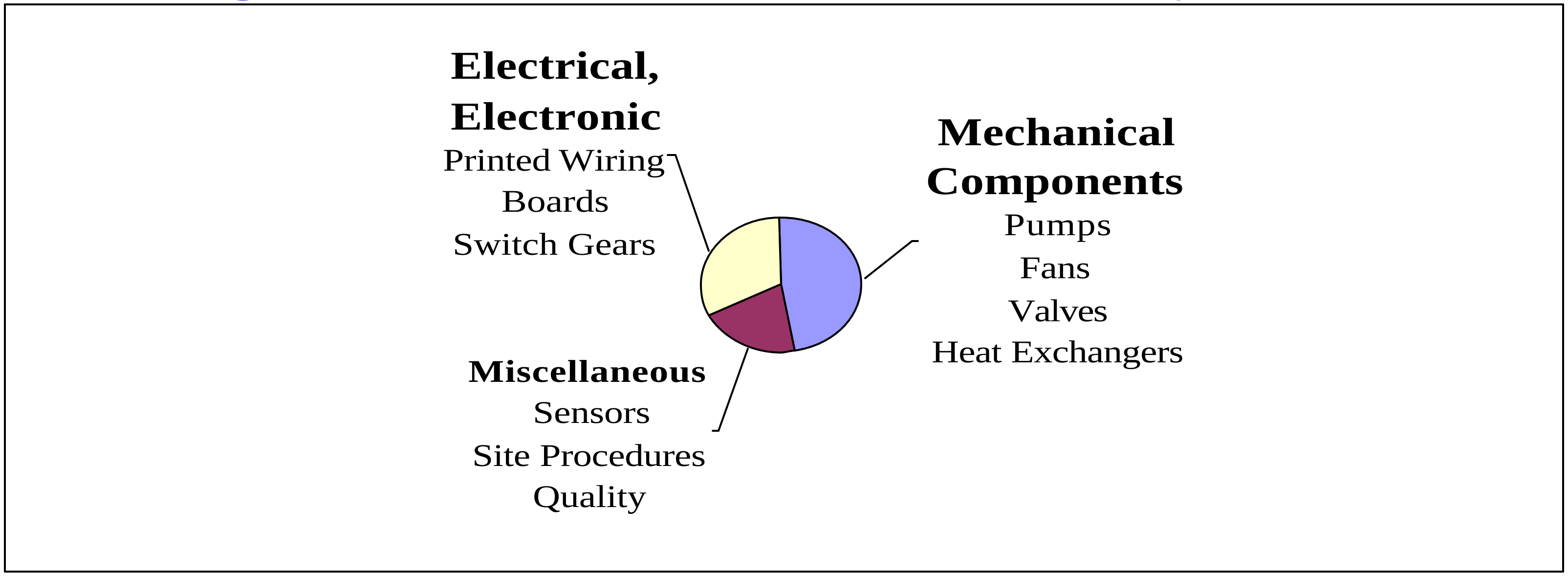
- **Mean Time to Failure (function of reliability and decay rate)**
- **Mean Time Between Forced Outages/Derating (dominated by stability issues)**
- **Overall Reliability/Availability (which includes stability issues):**
  - **Power Capacity - kW net electrical output**
  - **Fuel Efficiency - % based on LHV of fuel**
  - **Minimum Voltage Output - volts**
  - **'System' dominated parameters**
    - **Response Time - % power increase per minute from idle**
    - **(Emission Targets -)**
      - **(specific target values for particulate, VOC, SO_2, NO_x, CO_2)**
- **Voltage Decay Rate - no higher than a number of Volts/hour of operation** (used as an indicator of life cycle)

BALANCE OF PLANT

- **Pumps, Compressor/Expanders, Burners, Heat Exchangers, Condensers, Vaporisers, transformer/inverter, piping & connectors, switches, monitors, control systems (software), control strategy**
- **Power Conditioner (94-98% efficiency)**
- **Fuel Storage and Handling**

BALANCE OF PLANT RELIABITLY (for the DoD program)

- Literature indicates that balance of plant is the most significant issue for fuel cell reliability at this time.



Data for a 'fleet' of 36 DoD PAFCs

BOP reliability simply an issue of:

engineering commitment, quality control and cost.

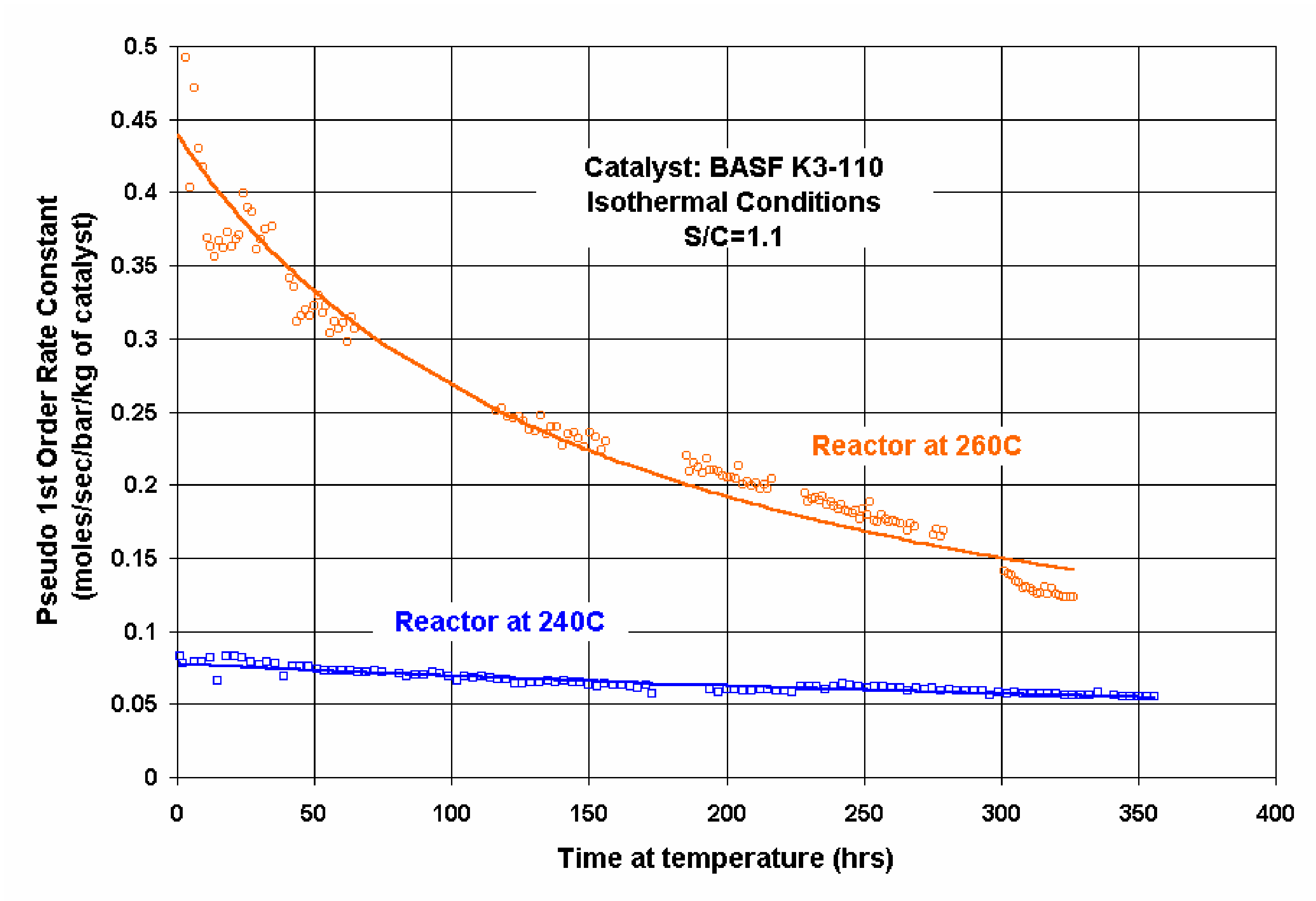
FUEL PROCESSING SYSTEM

- **Materials and Containment Issues**
- **Deactivation of Reformer Catalyst** ($Cu/ZnO/Al_2O_3$)

(physical causes, poisoning by impurities, poisoning by reactants or products)

- **Chlorides, Arsenic**
- **Sulphur (can be 'leached out of seals')**
- **Carbon ('Coking') Deposition (function of Steam/Carbon ratio)**
- **Thermal Damage**
- **Sintering (Catalyst Deactivation)**
- **Dew Point Concern**

Reformer Catalyst Deactivation Curves

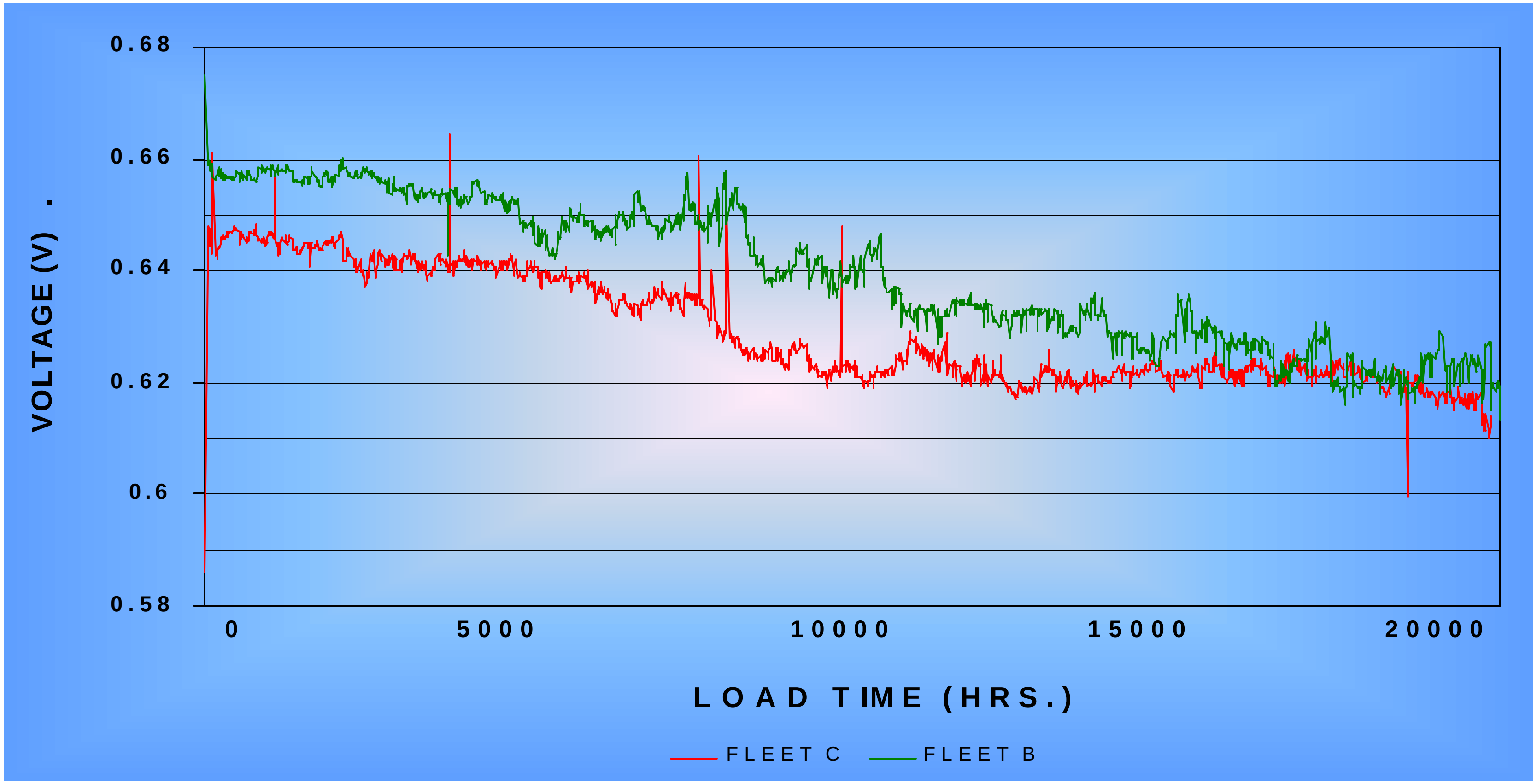


U.S. DoD FUEL CELL DEMONSTRATION PROGRAM

- **30 PAFC - natural gas fuel cells**
- **Unadjusted Availability**
  - **Model B Fleet 64%**
  - **Model C Fleet 80%**
- **Reported as above 95% availability on the manufacture's web site**

* from DoD presentation at Grove 1999

Average Cell Voltage

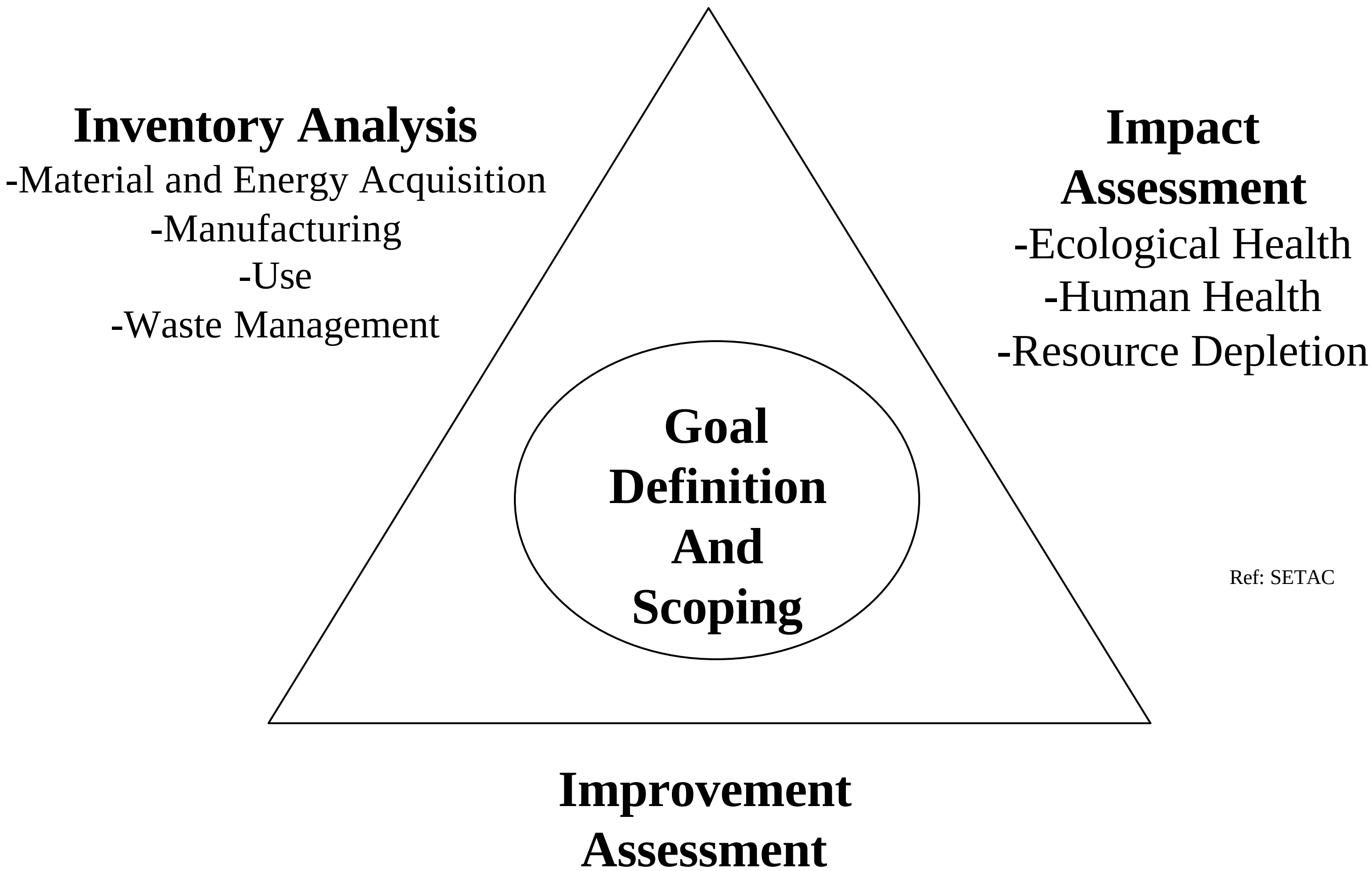


*U.S. DoD Fuel Cell program

LIFE CYCLE COSTING (LCC)

- **The economic evaluation of the design concepts as an element of each product development / selection process.**
- **'Total Cost of Ownership': acquisition, fuel, maintenance, disposal, waste disposal, environmental costs**
- **Four most common methods for such a life-cycle economic assessment are:**
  - **Total Cost Accounting**
  - **Life-Cycle Costing**
  - **Full Cost Accounting**
  - **Environmental Life-Cycle Cost**
- **'Design for the Environment' considers the Environmental / Economic impacts occur over an entire product life-cycle**

Technical Framework for Life Cycle Assessment



LIFE CYCLE ANALYSIS STEPS

1) **Goal definition:** **the basis and scope of the evaluation are defined.**
2) **Inventory Analysis:** **create a process tree in which all processes from raw material extraction through waste water treatment are mapped out and connected, mass and energy balances are closed, and emissions and raw material and energy consumption are accounted.**
3) **Impact Assessment:** **Environmental loading identified in the inventory are translated into environmental effects. The environmental effects are grouped and weighted.**
4) **Improvement Assessment: Areas for improvement are identified.**

LIFE CYCLE ANALYSIS / ASSESSMENT (LCA)

- **LCA is an assessment technique based on the cradle-to-grave concept.**
  - **evaluating the potential environmental and economic impacts (LCC or Life Cycle Costing) of a product or service,**
  - **considering such aspects as extracting and processing raw materials, manufacturing, distribution, recycling, resource consumption and waste management.**
- **Valuable decision-support tool**
- **Three well-documented and used methods for environmental analysis are:**
  - **Eco-Points method**
  - **Environmental Priority System**
  - **Eco-Indicator**

RELIAIBILITY JARGON

- ***Availability*** **-**
  - **% of a power sources fully operational hours divided by the planned/expected hours**
  - **‘Available’ if all performance specifications are achievable**
  - **Conditionally Available (Derated) if 30%-100% of performance factor is achievable**
  - **Not available - down time, maintenance periods**
  - **Not in service, or cold stand-by time not included**
  - **Mean Time Between Forced Outages (MTBFO)**

IMPROVING COMPONENT EFFECTIVENESS IN DESIGN

- Redundancy (e.g. increase weight of catalyst)
- Increase the robustness of key components
- Mechanical & Thermal integration
- Reduce Material flows
- Material Compatibility (especially replacement parts)
- Modularity / Commonality

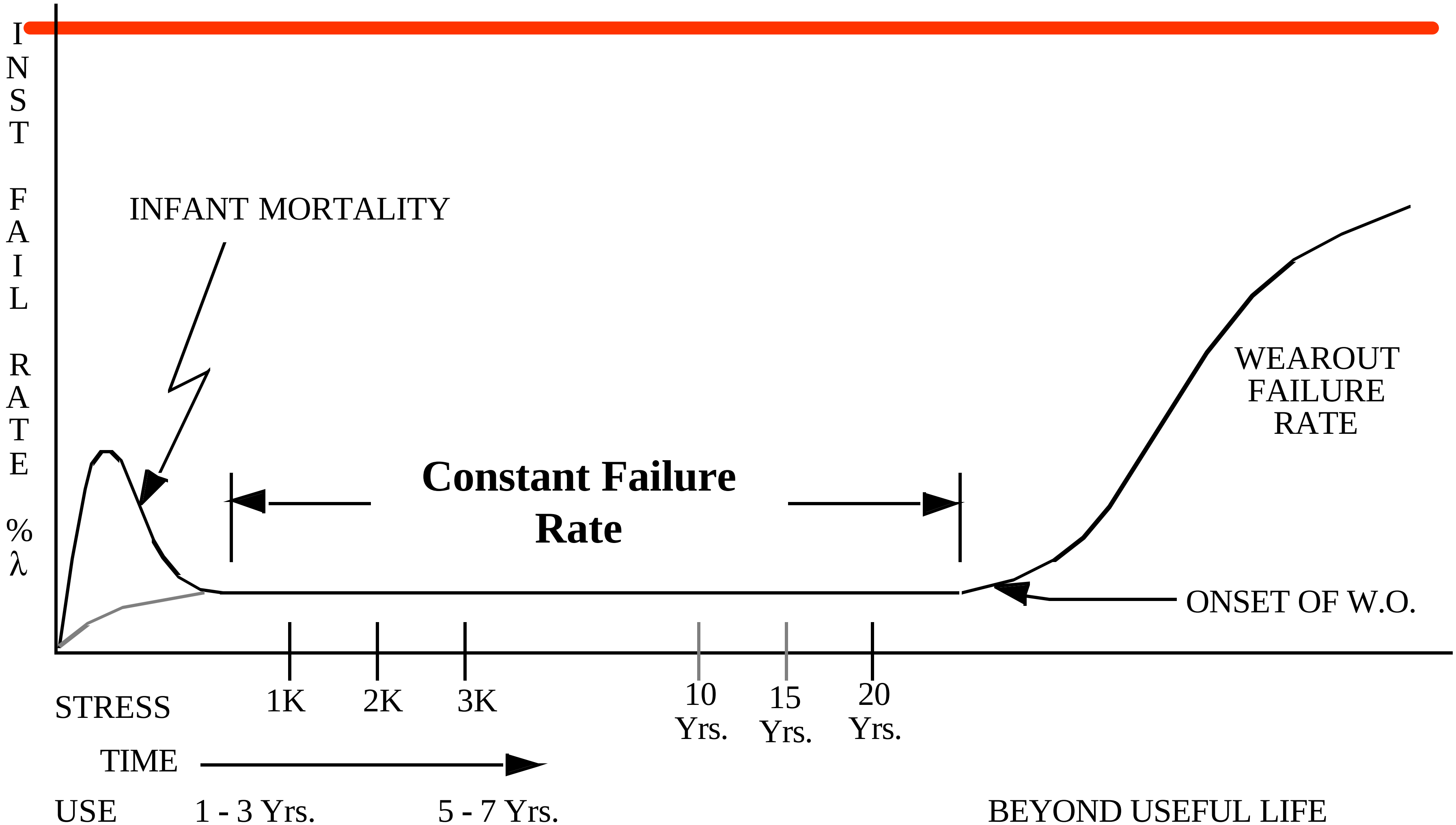
IMPROVING COMPONENT EFFECTIVENESS DURING OPERATION

- **Limited by the 'built-in' Reliability / Performance**
- **Control System & Strategy improvements**
  - **Reduced cycling & operating states**
  - **Operation at less stressful conditions, *e.g.* operating voltage**
  - **Reduced variation of: temperature - pressure - fuel utilization**
  - **Pressure Balance across membrane**
  - **Improved water management**
- **Operator / Maintenance Training**
- **Maintenance Planing (stocking of spares)**
- **Consideration of Reliability Centred Maintenance (RCM)**
- **Management System (records, corrective action system, procedures)**

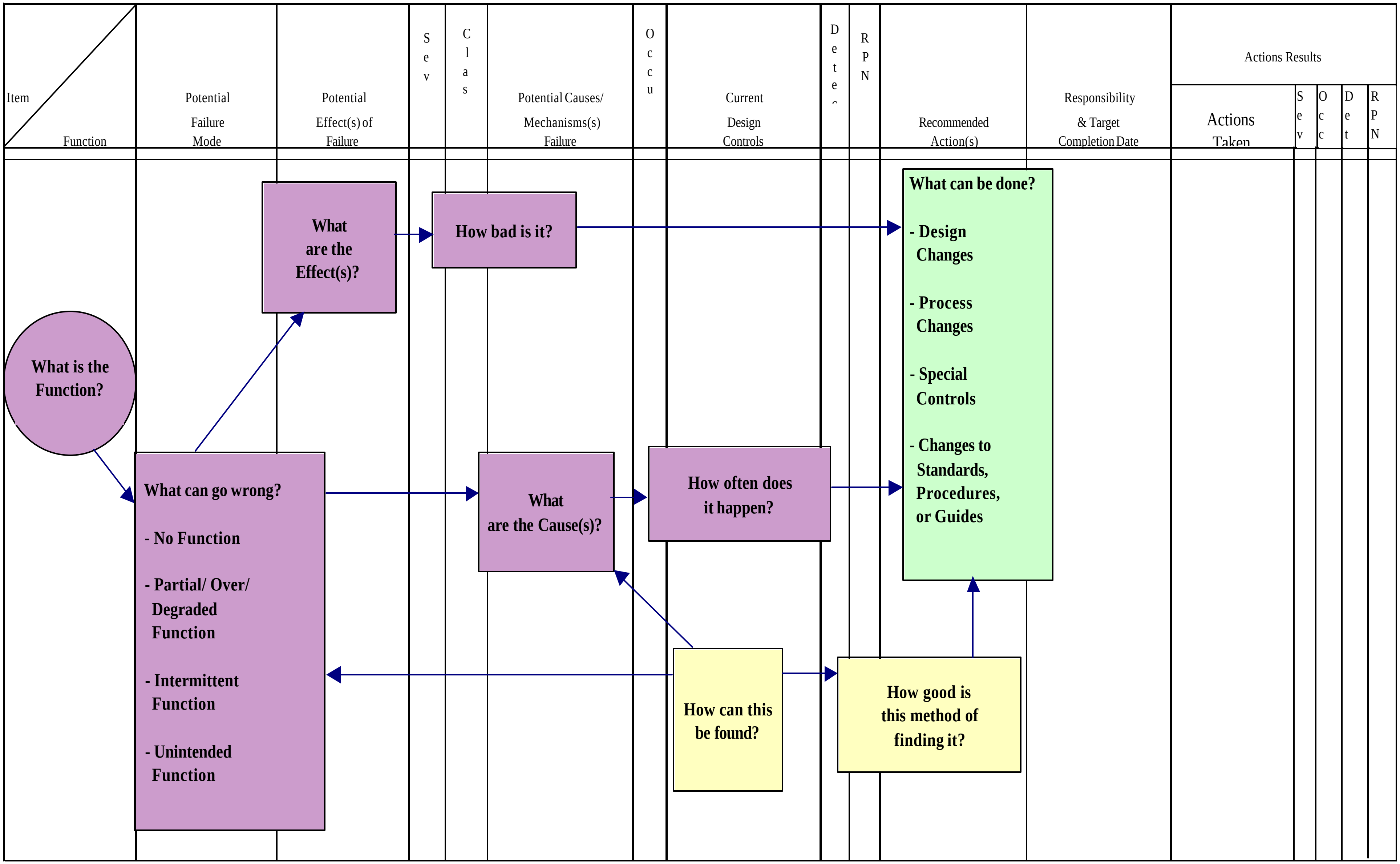
ACHIEVING RELIABITIY GROWTH

- Operation Models
- Reliability Models / Projections
- Reliability Data Collection
- Review/Correlation of Reliability& Operational Data
- Performance Testing Program
- Continuous Operation vs. ‘Stress’ Testing Program
- Life Cycle Analysis and Planning
- Constant communication with design and manufacturing teams

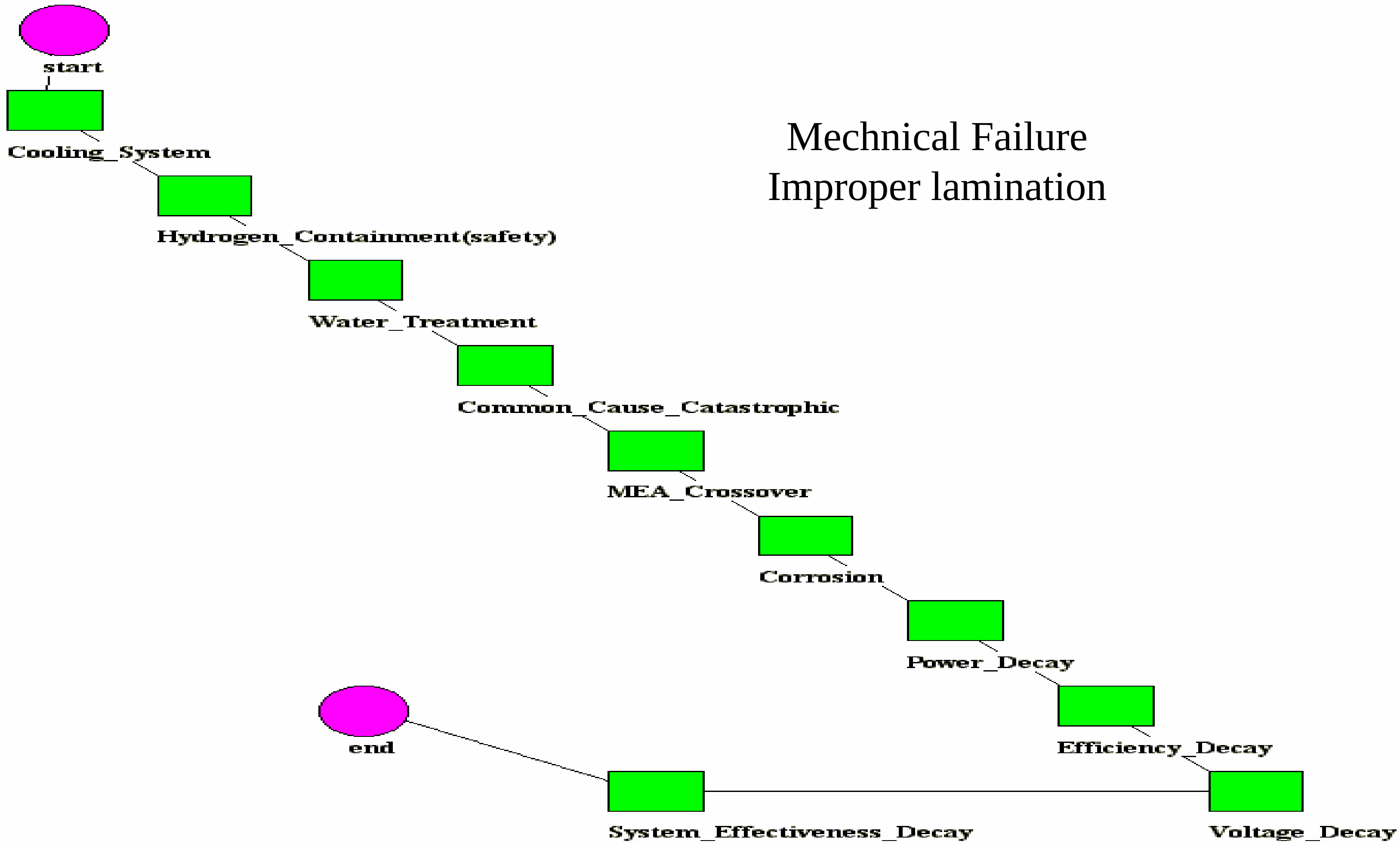
RELIAIBLITY OF REPAIRABLE ITEMS
‘Bathtub Curve’



Potential
Failure Mode and Effects Analysis

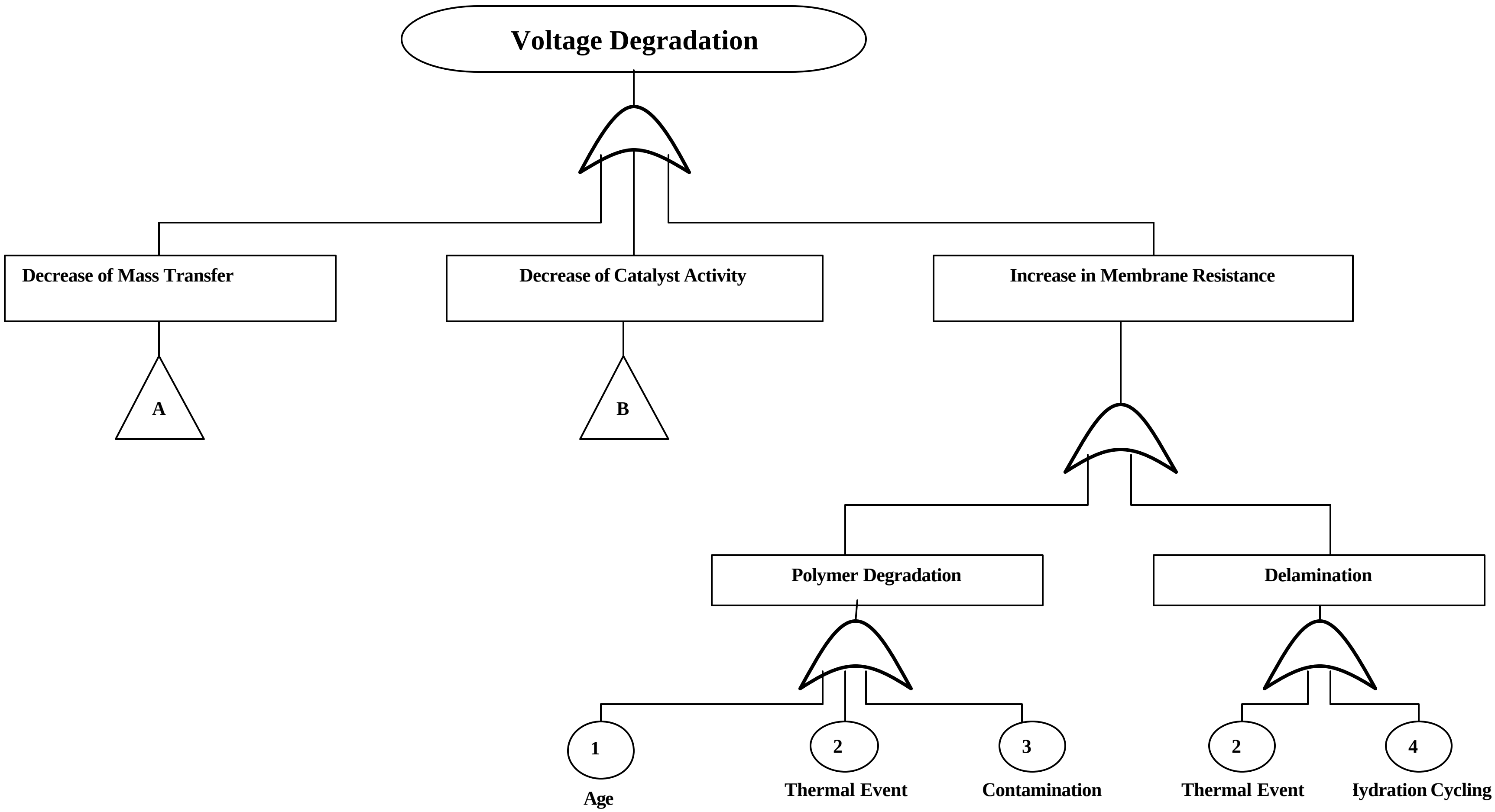


RELIABILITY BLOCK DIAGRAM (RBD)



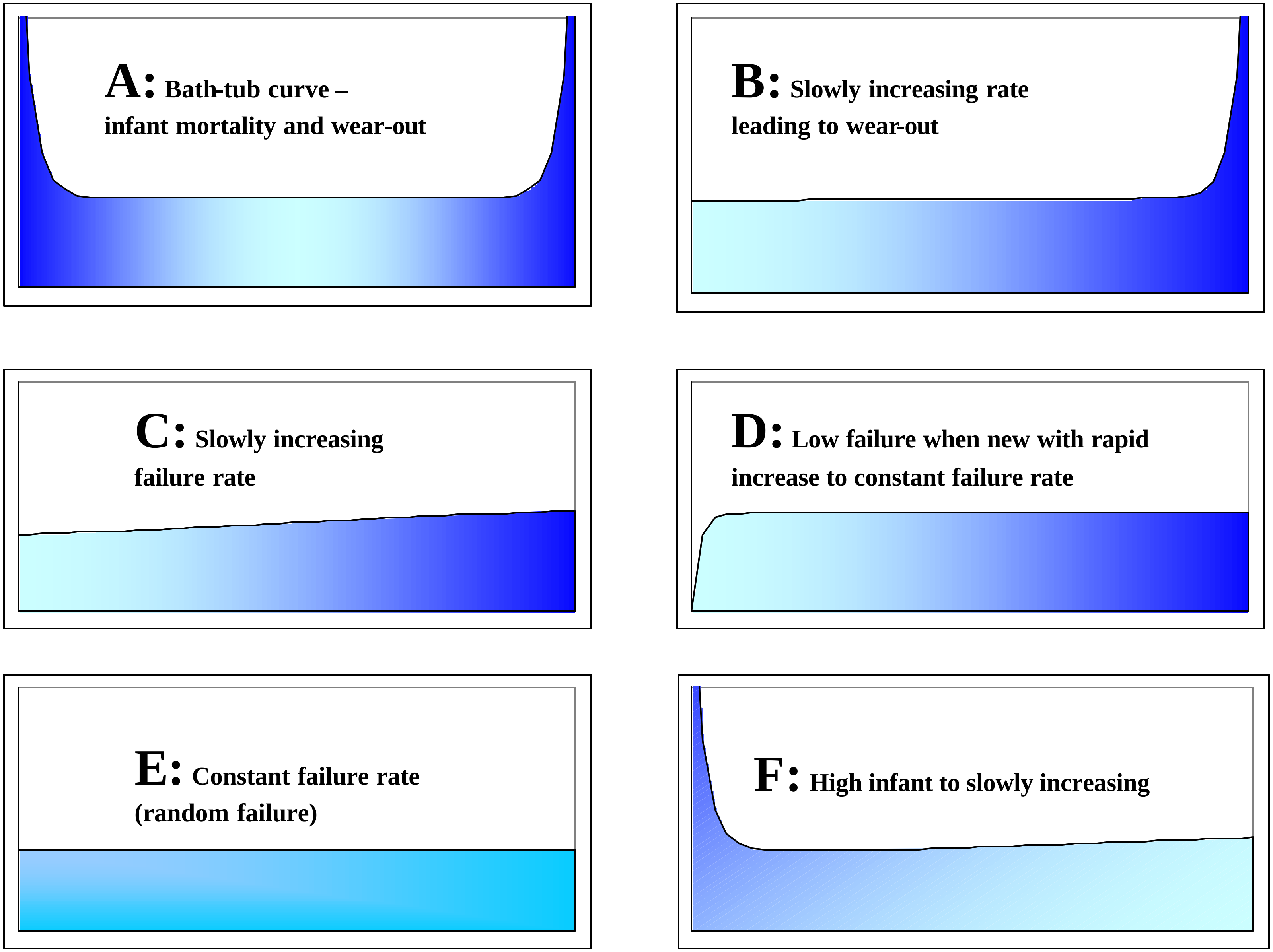
Mechnical Failure
Improper lamination

FAULT TREE ANALYSIS (FTA)



SIX PATTERNS OF FAILURE

(Ref: Moubay, RCM)



PROCESS & CONTROL TEST

- **Performance**
  - **Maximum Capacity**
  - **Minimum Power**
  - **Load Change Rate (5% per minute)**
  - **Emissions (noise, water, vibration - as per regulations)**
- **Reliability/Safety**
  - **Operation Time**
  - **Load Operation 30-100%**
  - **Load Trip 30-100% to 0% (safety stop)**
  - **Differential Pressure**
- **Operating Procedure**
  - **Procedure Established Hot/Cold Start**
  - **Cold Start**
  - **Hot Start**

MY ACADEMIC INTERESTS

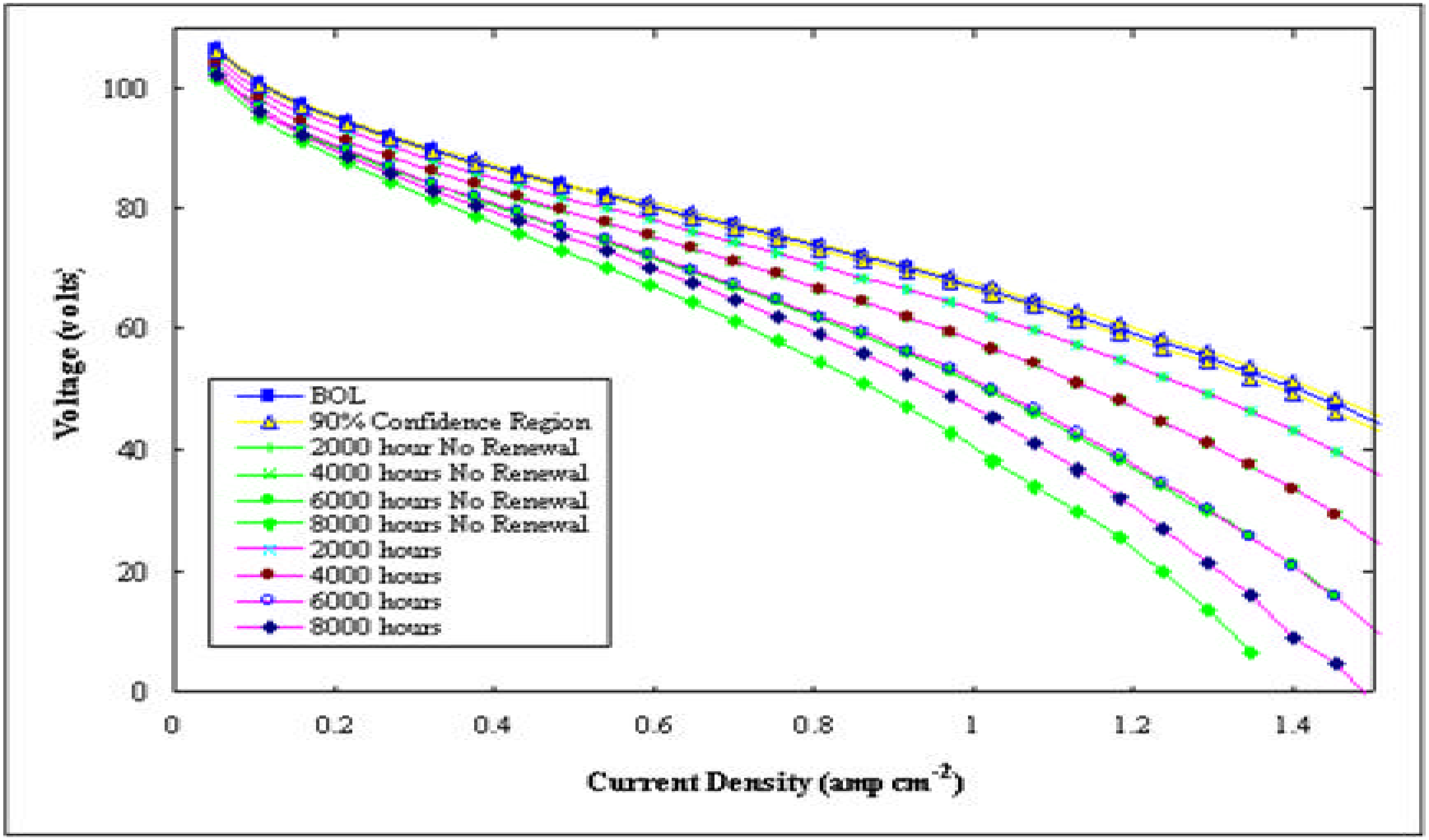
- **Developing the concept of**
  Component Effectiveness of Fuel Cell Systems
- **Development and Demonstration of a Concurrent Engineering Technique - Reliability / System Effectiveness Modelling**
- **Integrating Systems Models with System Effectiveness Models**
- **Life Cycle Analysis / Costing**
  - **Environmental Life Cycle Analysis**
  - **Life Cycle Engineering / RCM**

MY INTERESTS

(part of an academic program at RMC)

- **Fuel Cell System Technology**
- **Developing the concept of**
  Component Effectiveness of Fuel Cell Stacks
- **Reliability / Component Effectiveness Modelling**
- **Integrating Systems Models with Component Effectiveness Models**
- **Life Cycle Analysis / Costing**
  - **Environmental Life Cycle Analysis**
  - **Life Cycle Engineering / RCM**
- **Working with real systems (Stationary PEM, Marine PEM, SOFC)**
- **Concurrent Engineering**

MEA RENEWAL VS NO RENEWAL



Current Engineering Options for Reliability Management

Modification can be done in either the stack design or control variables to improve reliability and prolong life.	
Using the Generalized Steady State Electrochemical Degradation Model for a the PEM, design features and control strategies can be developed that allow for the optimization of various performance factors within a fuel cell over its life cycle.	
Design Features	***Operating Strategies***
Cell Active area	Load cycling
Catalyst type	Hydrogen and Oxygen stoichiometric ratios
Catalyst loading	Stack temperature
Number of cells per stack	Stack pressures
Number and configuration (*e.g.* parallel or series) of cells or stacks	
Material Choice for polymer electrolyte and backlayer	