DEGRADATION AND RELIABILITY MODELLING OF POLYMER ELECTROLYTE MEMBRANE (PEM) FUEL CELLS

Michael Fowler

mfowler@uwaterloo.ca

OUTLINE

- **Introduction to Fuel Cell Technology**
- **Endurance Run of a Single Cell**
- **Reliability of Fuel Cells**
- **Voltage Degradation in PEM Fuel Cells**
- **Modelling of PEM Fuel Cell Degradation**
- **Conceptual Reliability Analysis a of PEM Fuel Cell Stack**

SURVEY OF FUEL CELL DEVELOPERS

- **“For continuous use products, one game changer may be accelerated testing of the fuel cell. There are currently no accurate models for forecasting failure modes, which is why our products are fairly short lived. We base their lifetime on actual data we have”**
- **Fuel Cell Industry Report, January 2002, Vol 3, No 1., Alexander Communications Group Inc.**

WHY FUEL CELLS FOR POWER GENERATION

- High Efficiency
- Low Environmental Burden and Emissions
- High Reliability
- Flexibility of Design
- Easily Refuelled

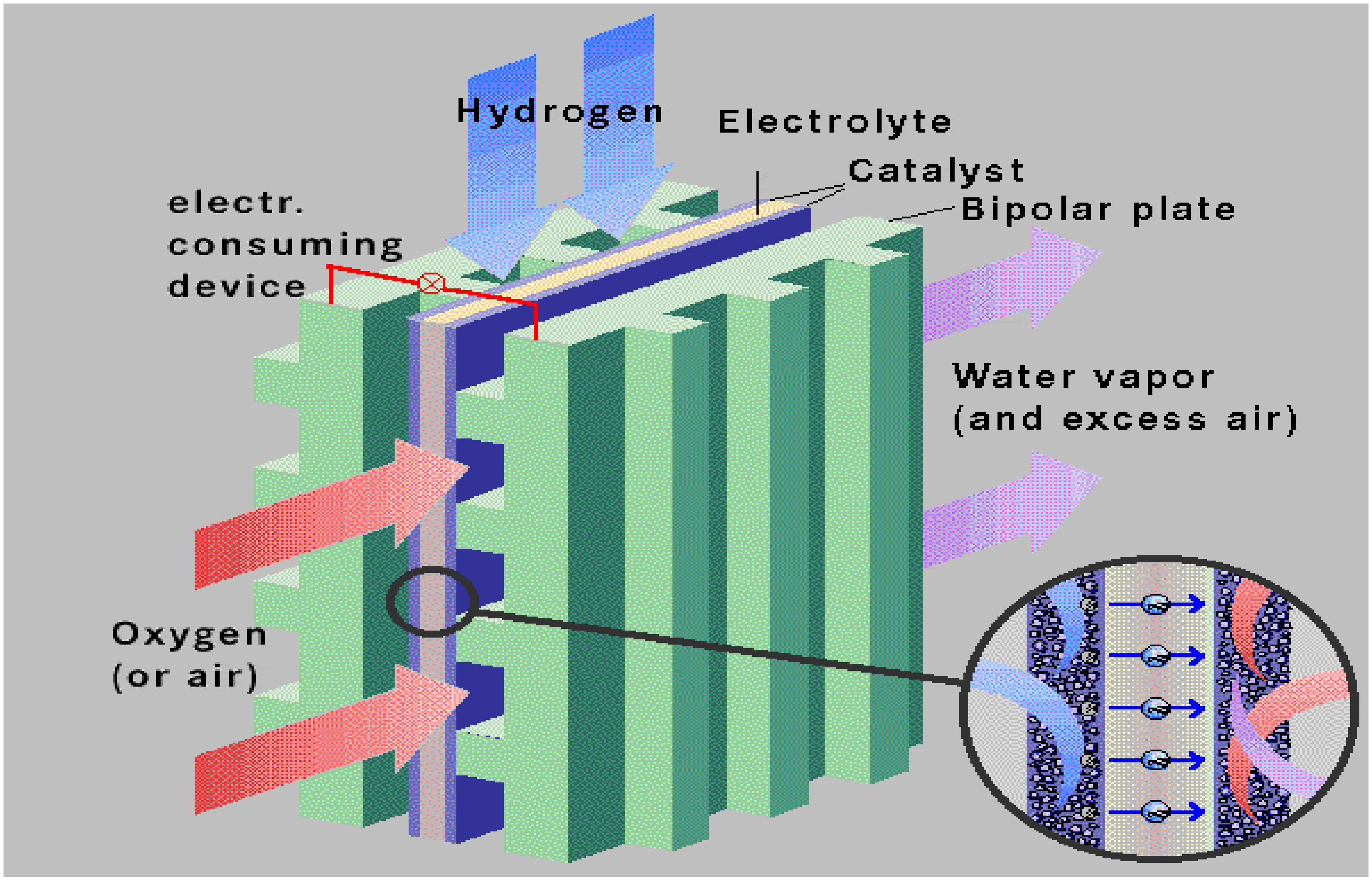
BARRIERS TO MARKET ACCEPTANCE OF FUEL CELLS

- Cost
- Endurance and reliability
- Refuelling infrastructure and 'supply chain' are not in place
- Public Perception of hydrogen

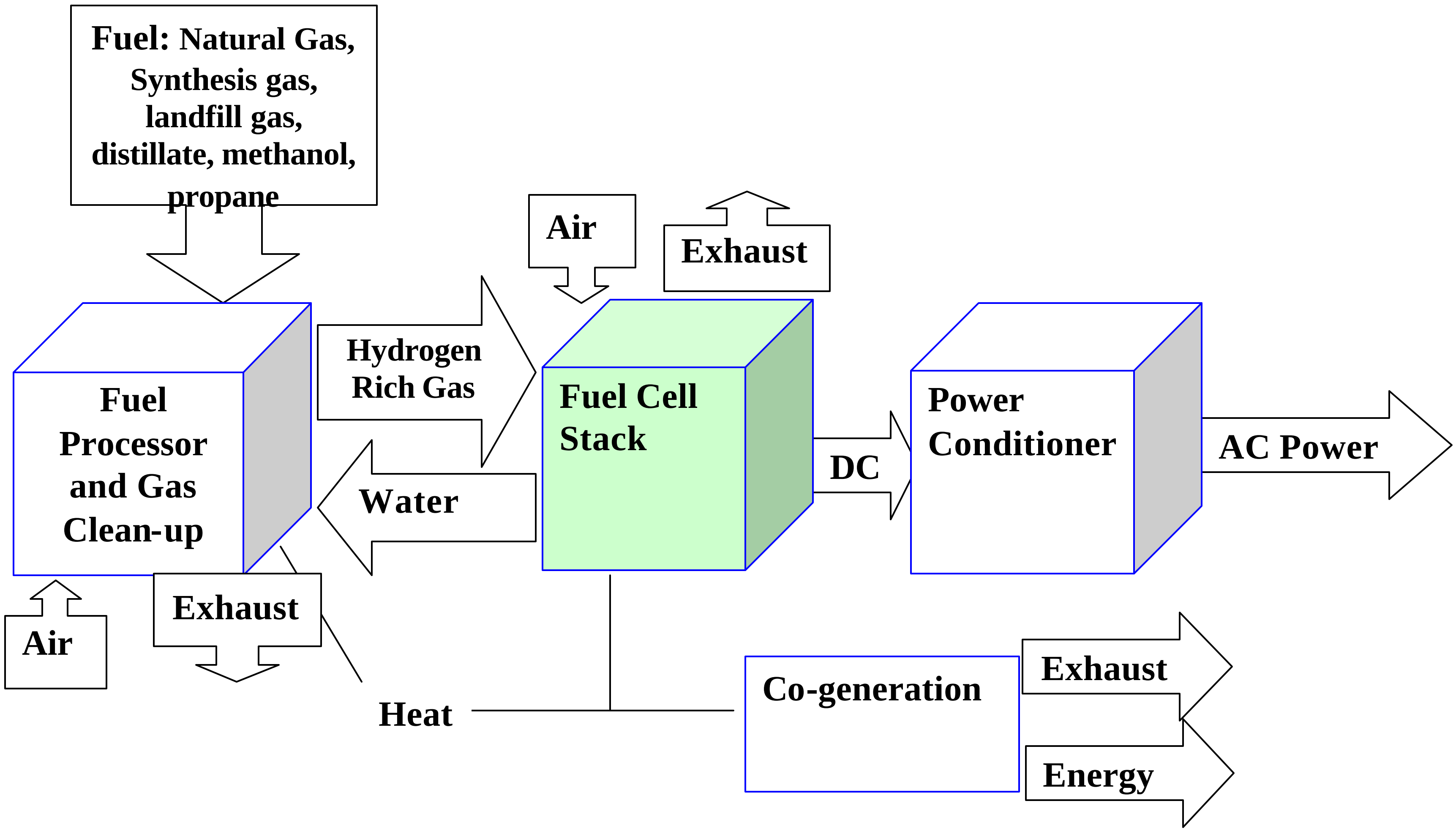
GOALS

- **Identify key failure modes associated with PEM fuel cells**
- **Develop a Generalized Steady State Electrochemical Degradation Model with ageing or voltage degradation terms**
- **Develop a conceptual model for fuel cell stack reliability**

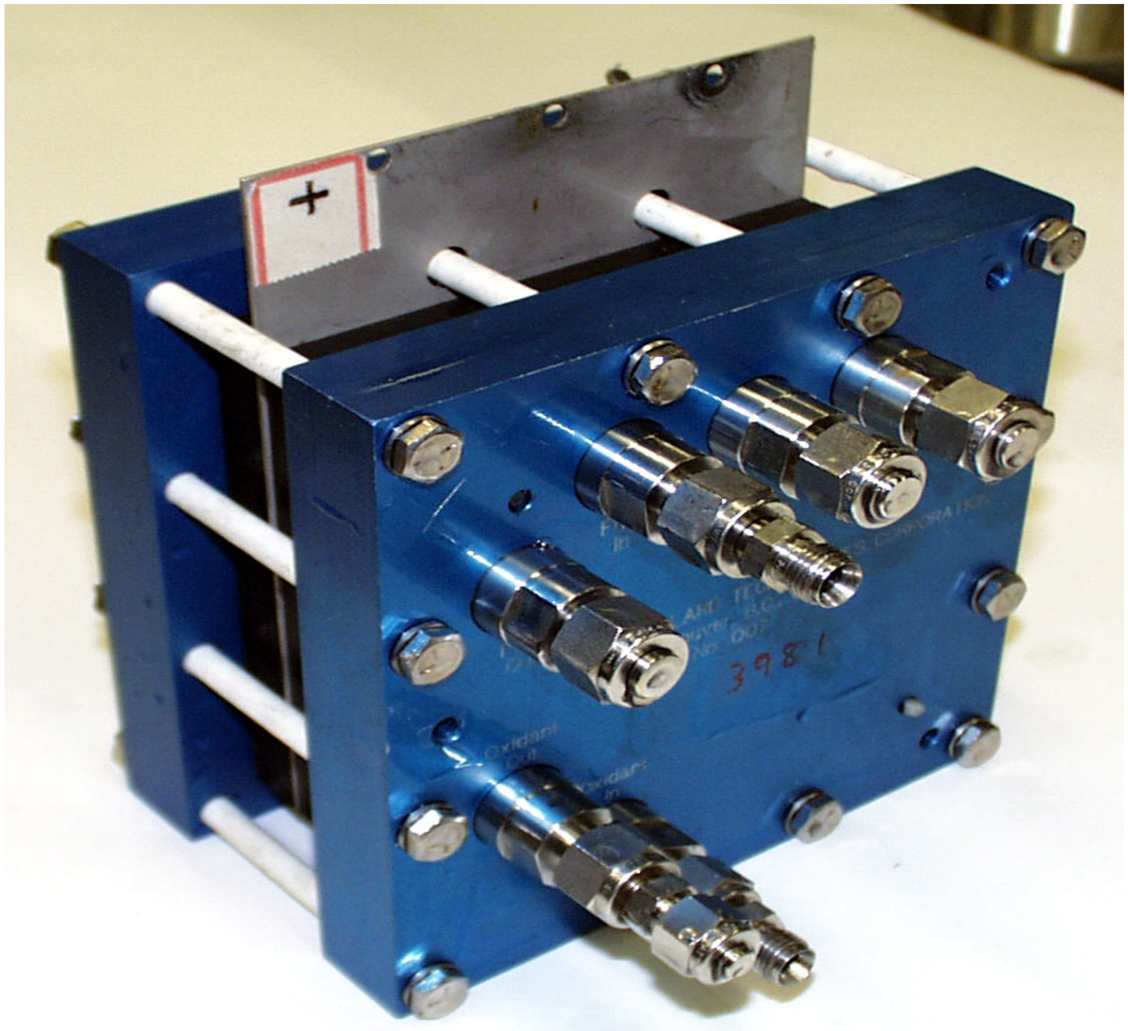
FUEL CELL OPERATION



PEM FUEL CELL SYSTEM

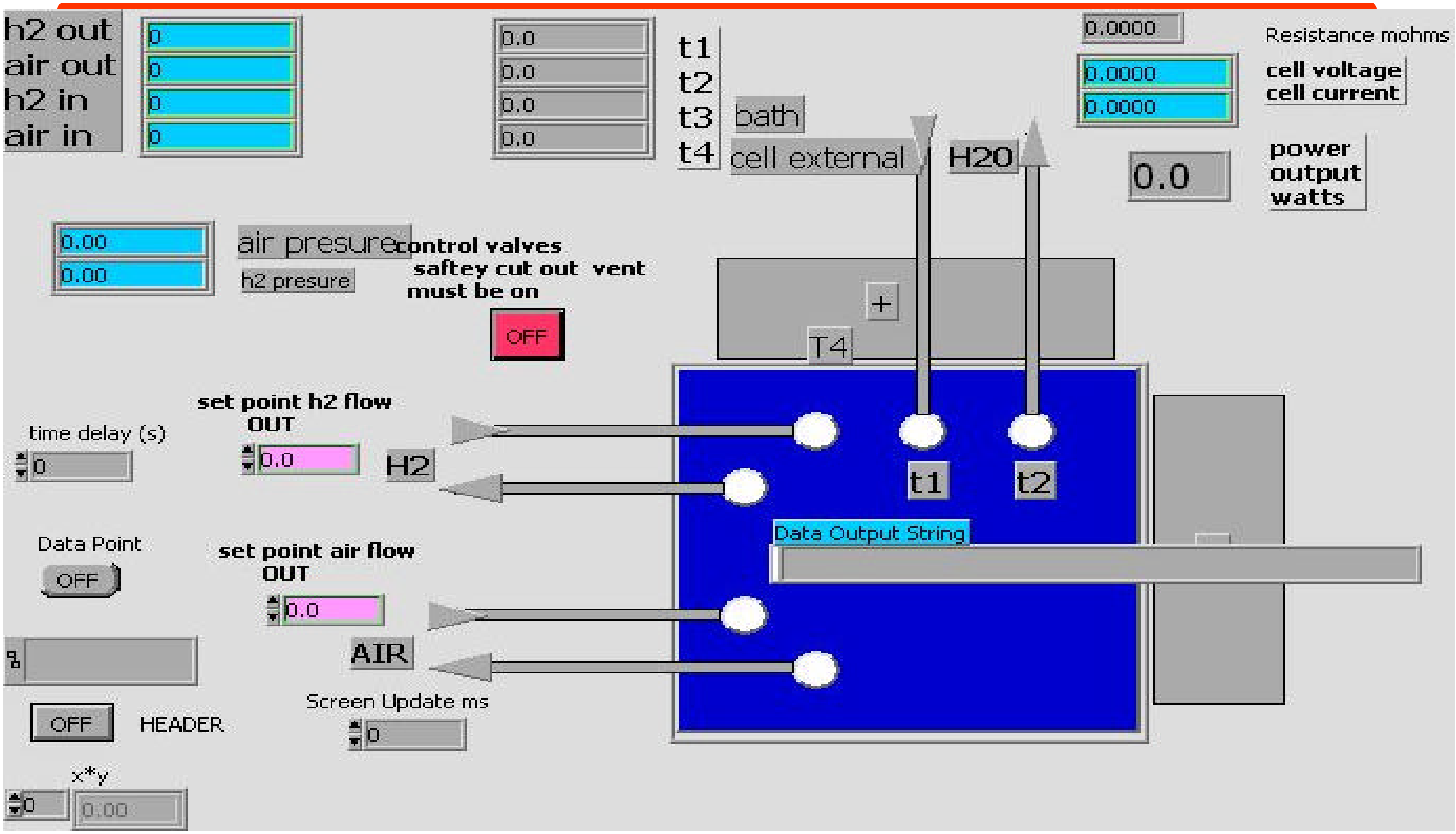


FUEL CELL HARDWARE

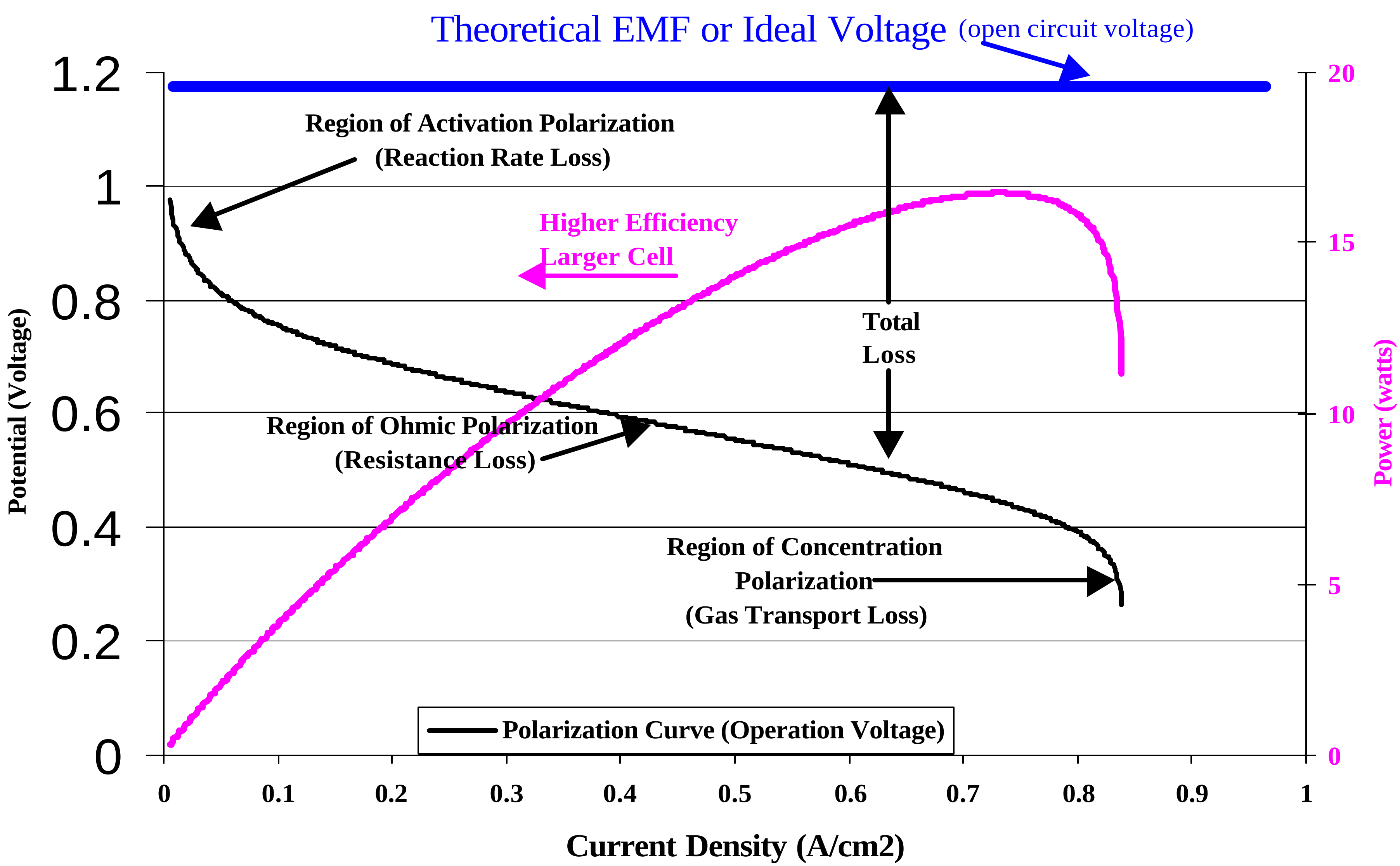


FUEL CELL TEST STATION

Labview VI – Monitoring System

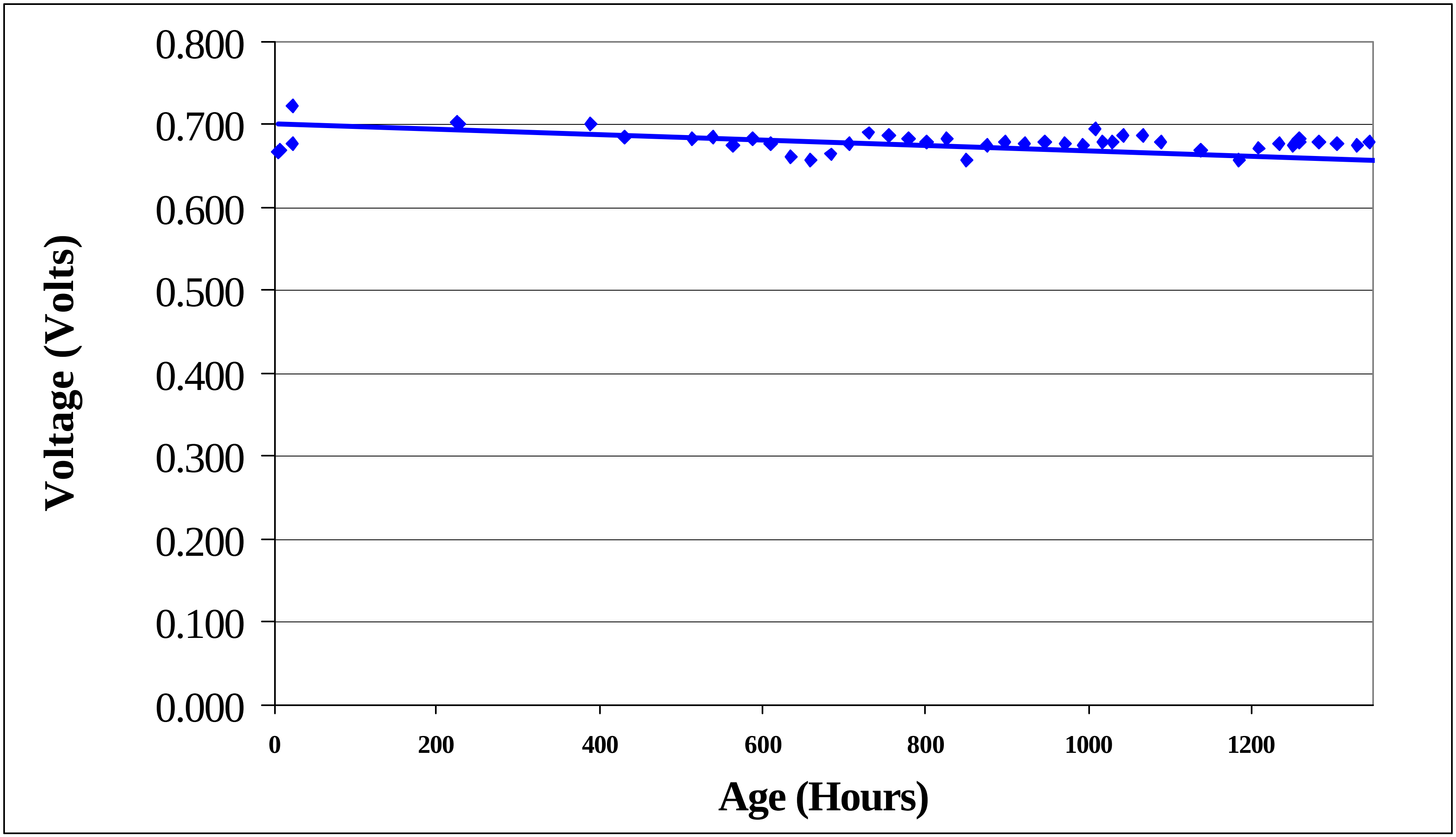


Ideal and Actual Fuel Cell Voltage/Current Characteristics

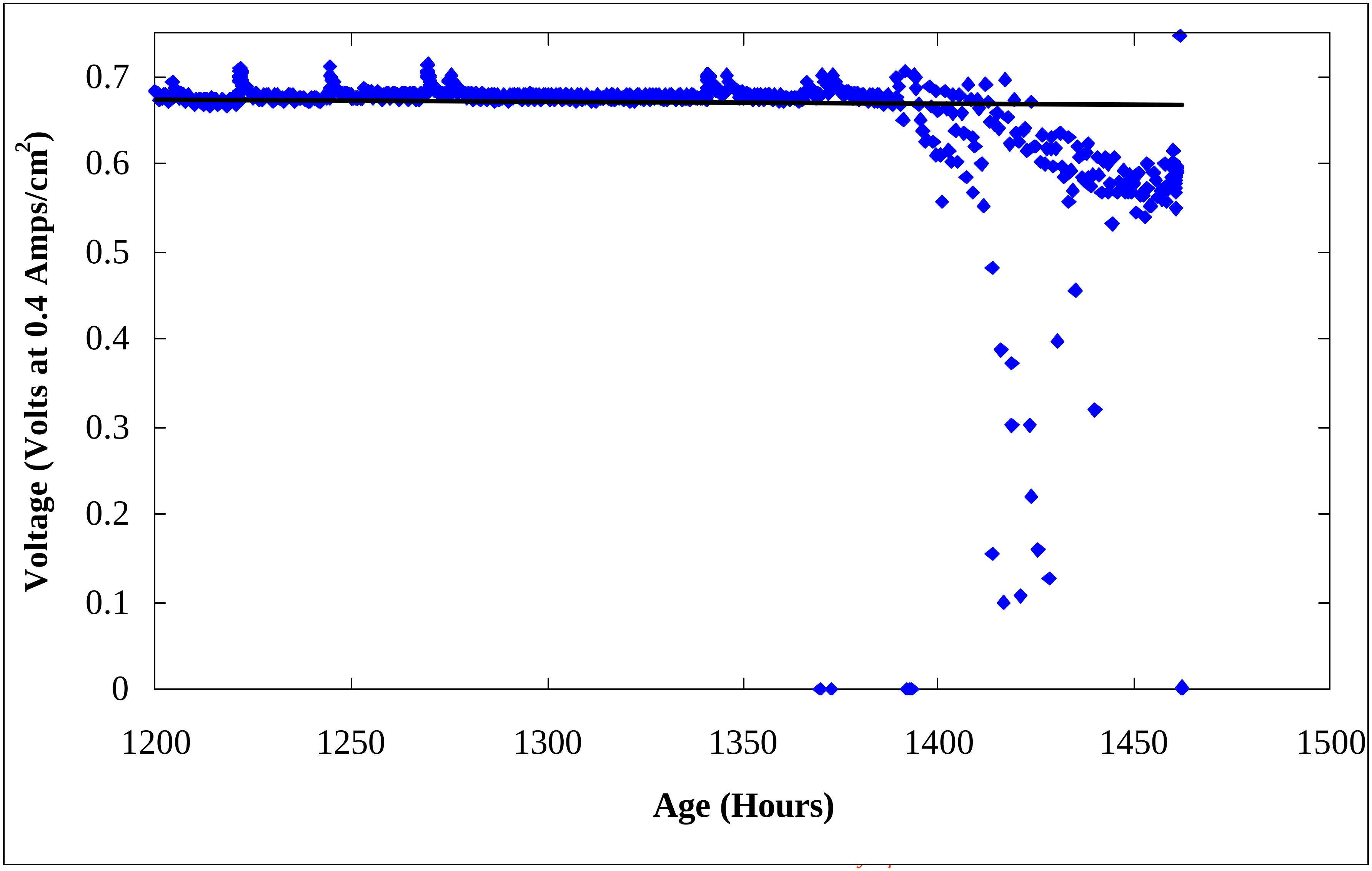


VOLTAGE DEGRADATION CURVE FOR A SINGLE PEM CELL

(Operated at 80°C, 0.4 amp cm^{-2}, 30 psig/30 psig, H2/Air – stoichiometric ratios 1.2/2)

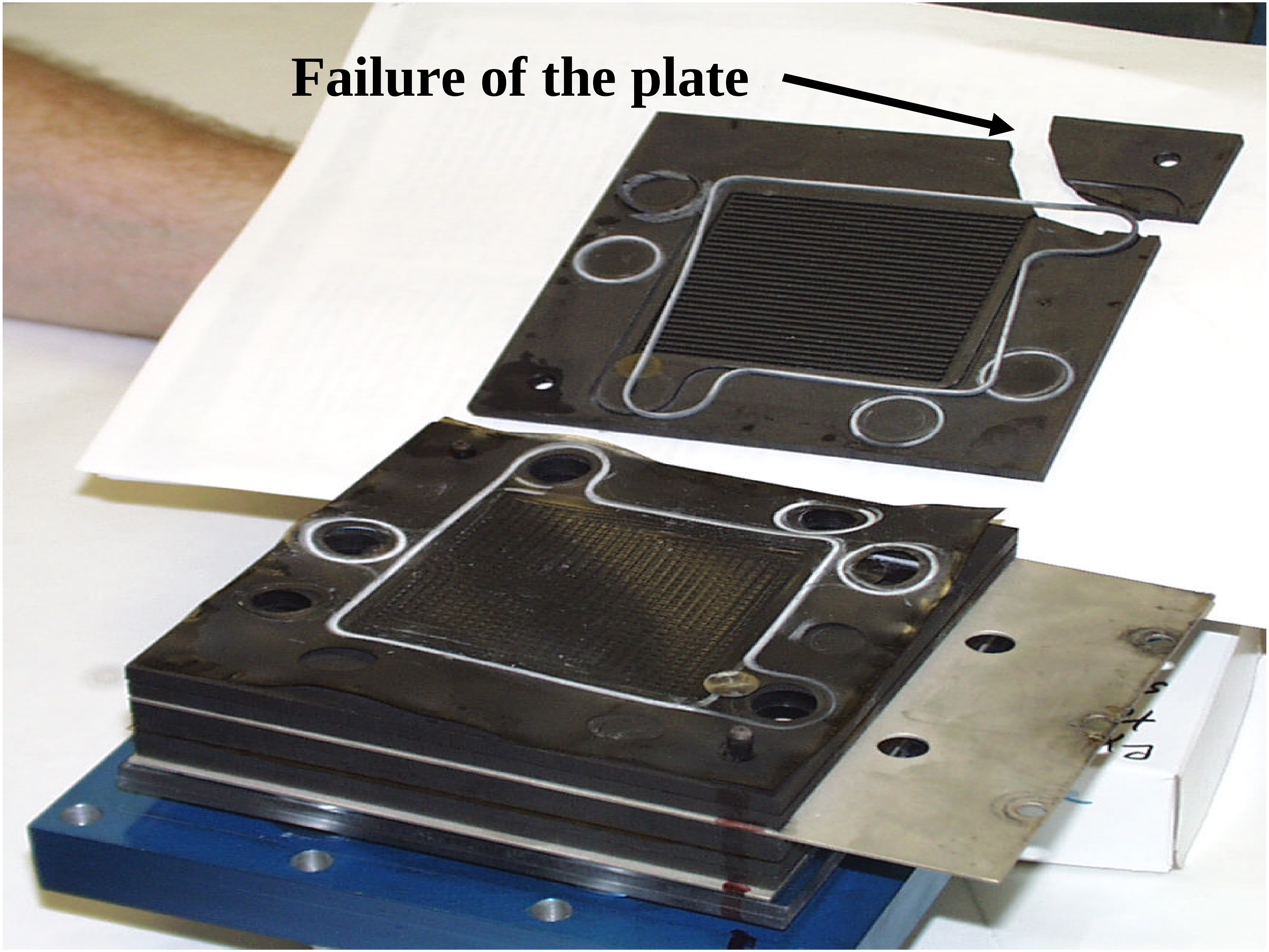


Voltage Performance at End of Life

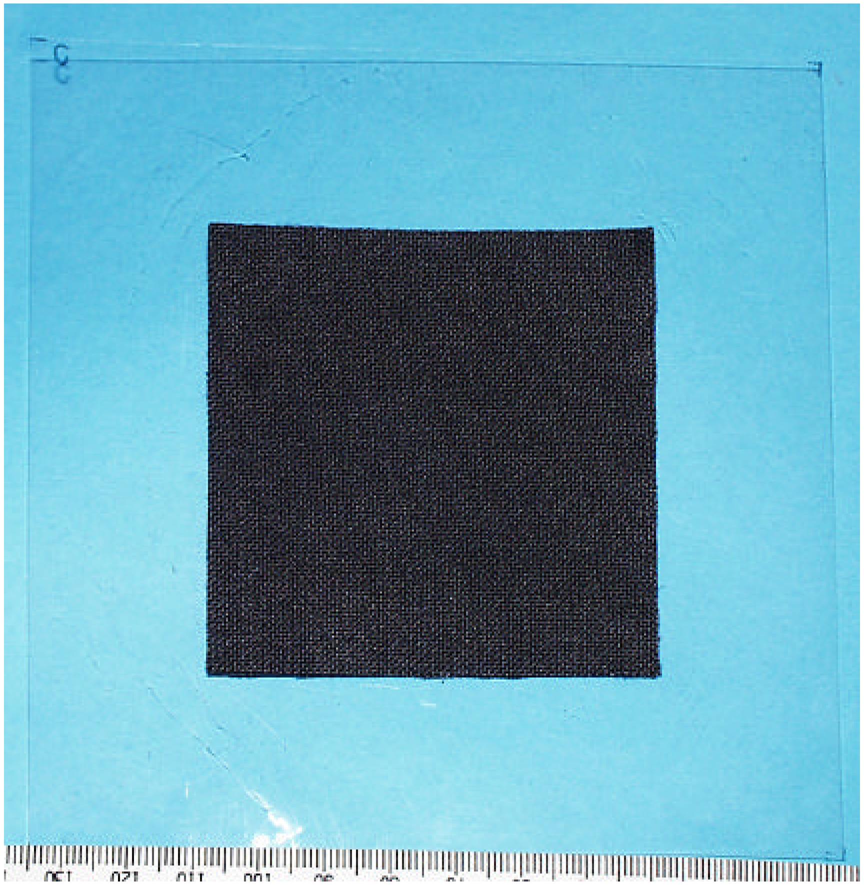


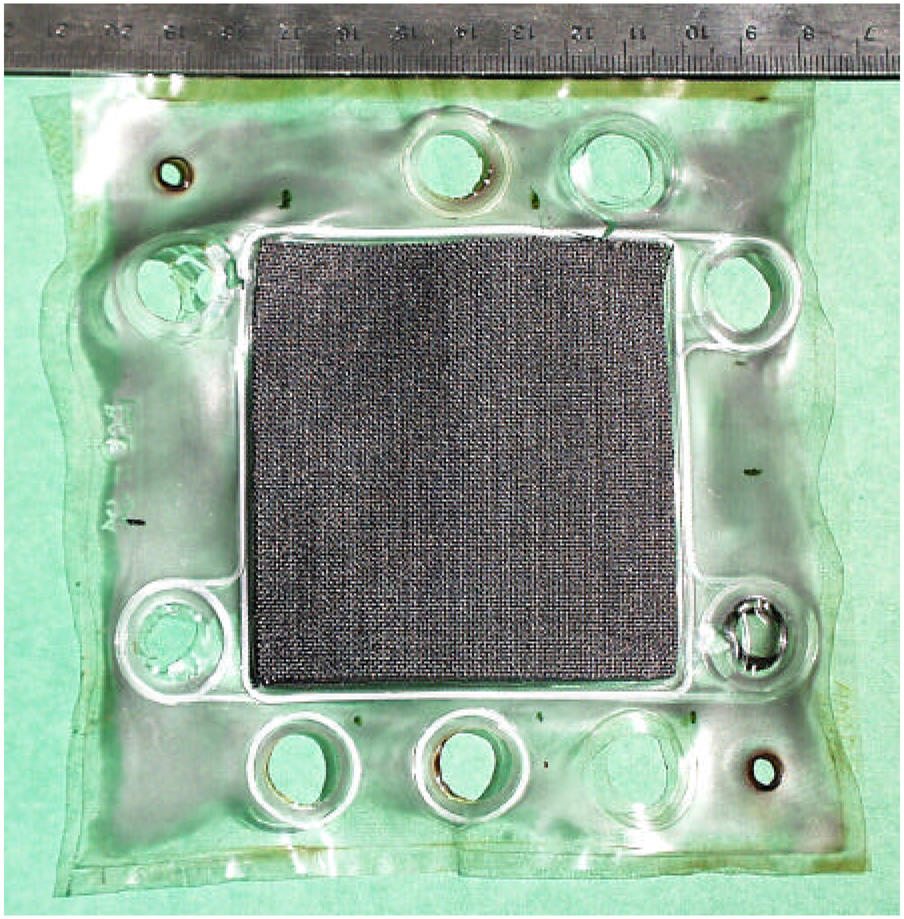
RELIABILITY JARGON

- ***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*.**

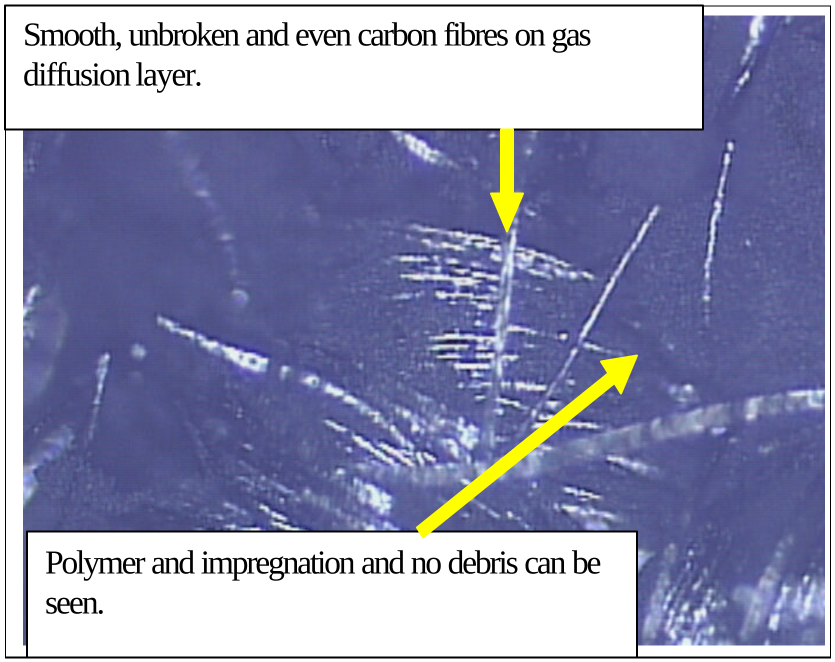

Failure of the plate

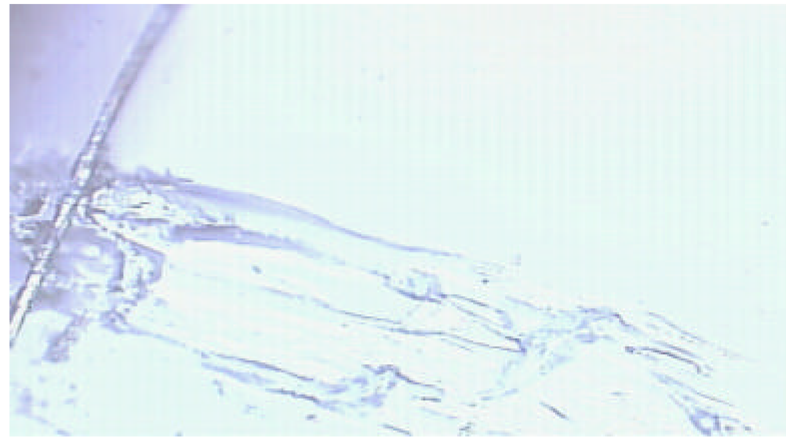
E-TEK MEA

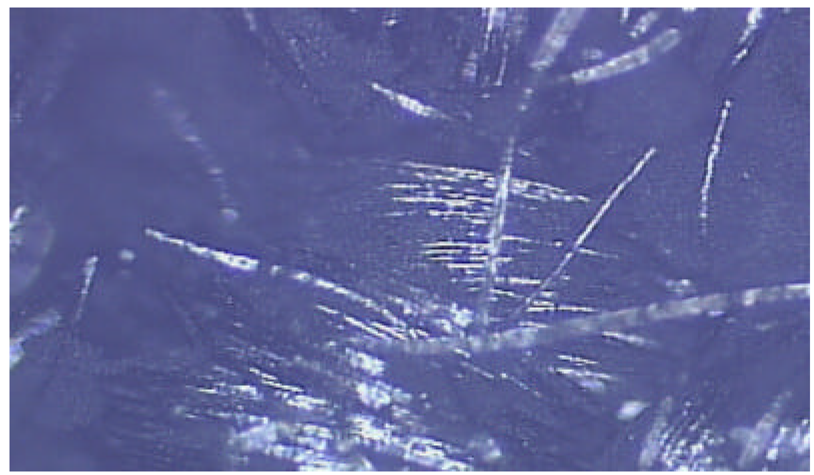




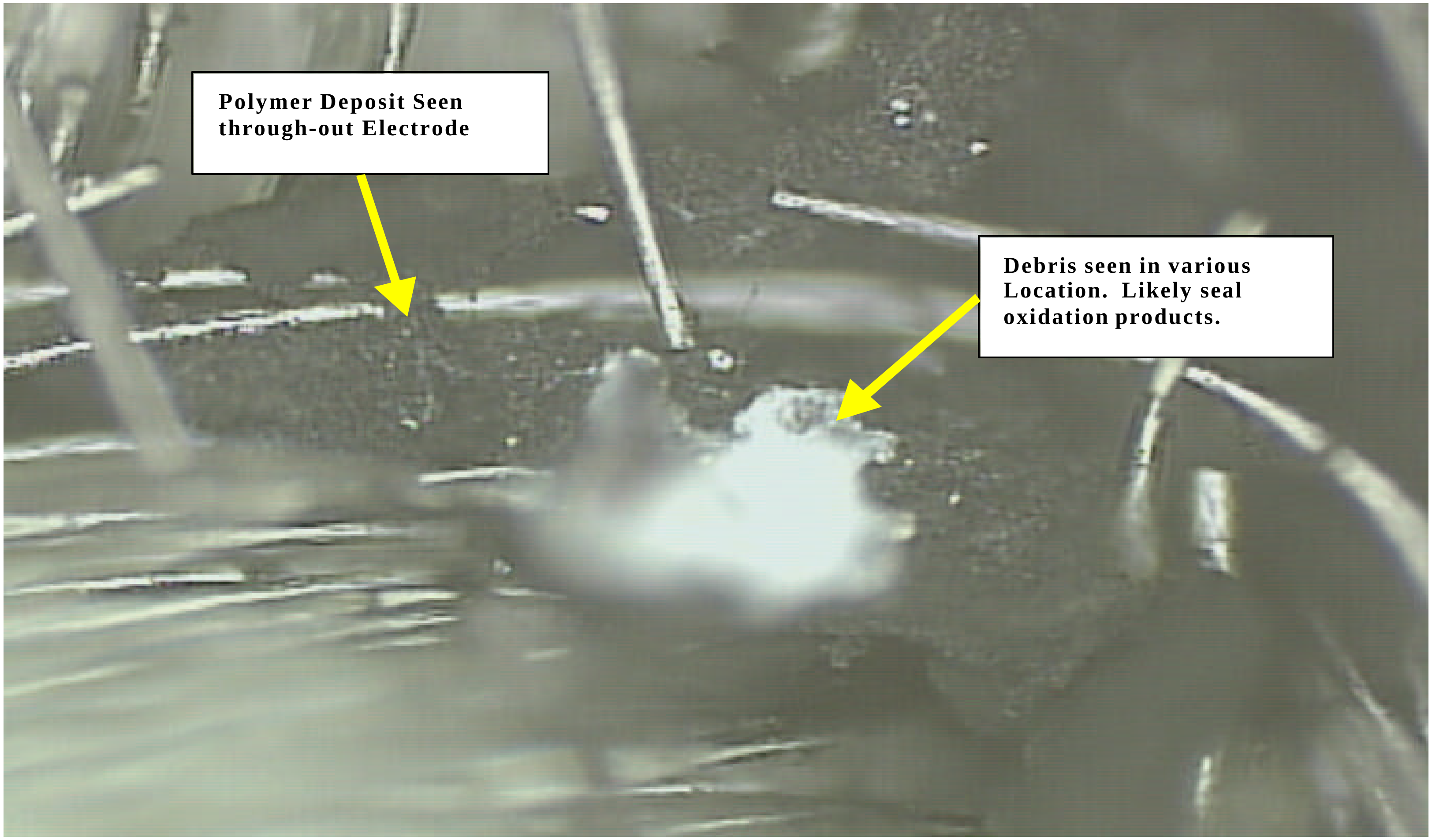
E-TEK MEA


Smooth, unbroken and even carbon fibres on gas diffusion layer.
Polymer and impregnation and no debris can be seen.

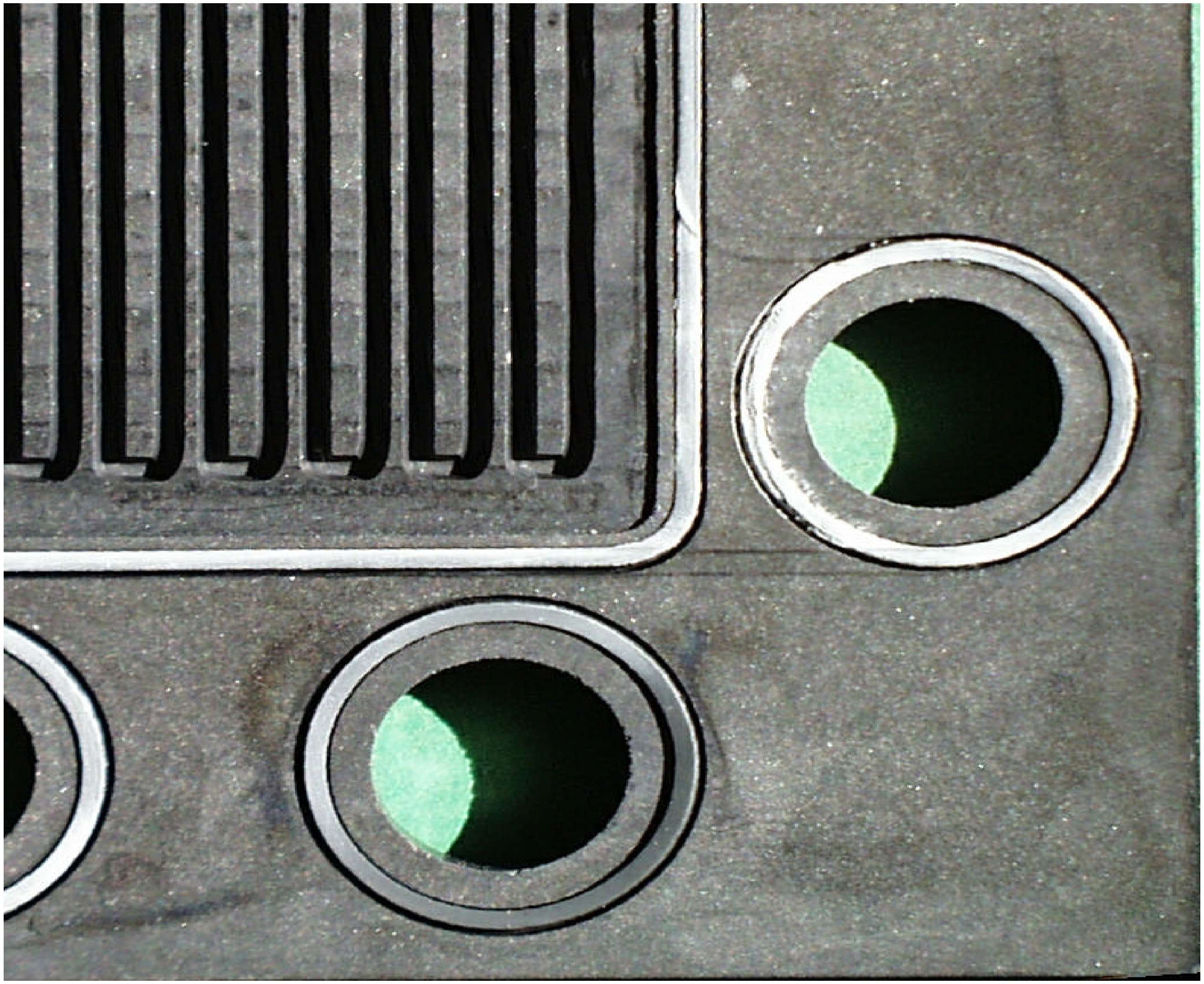




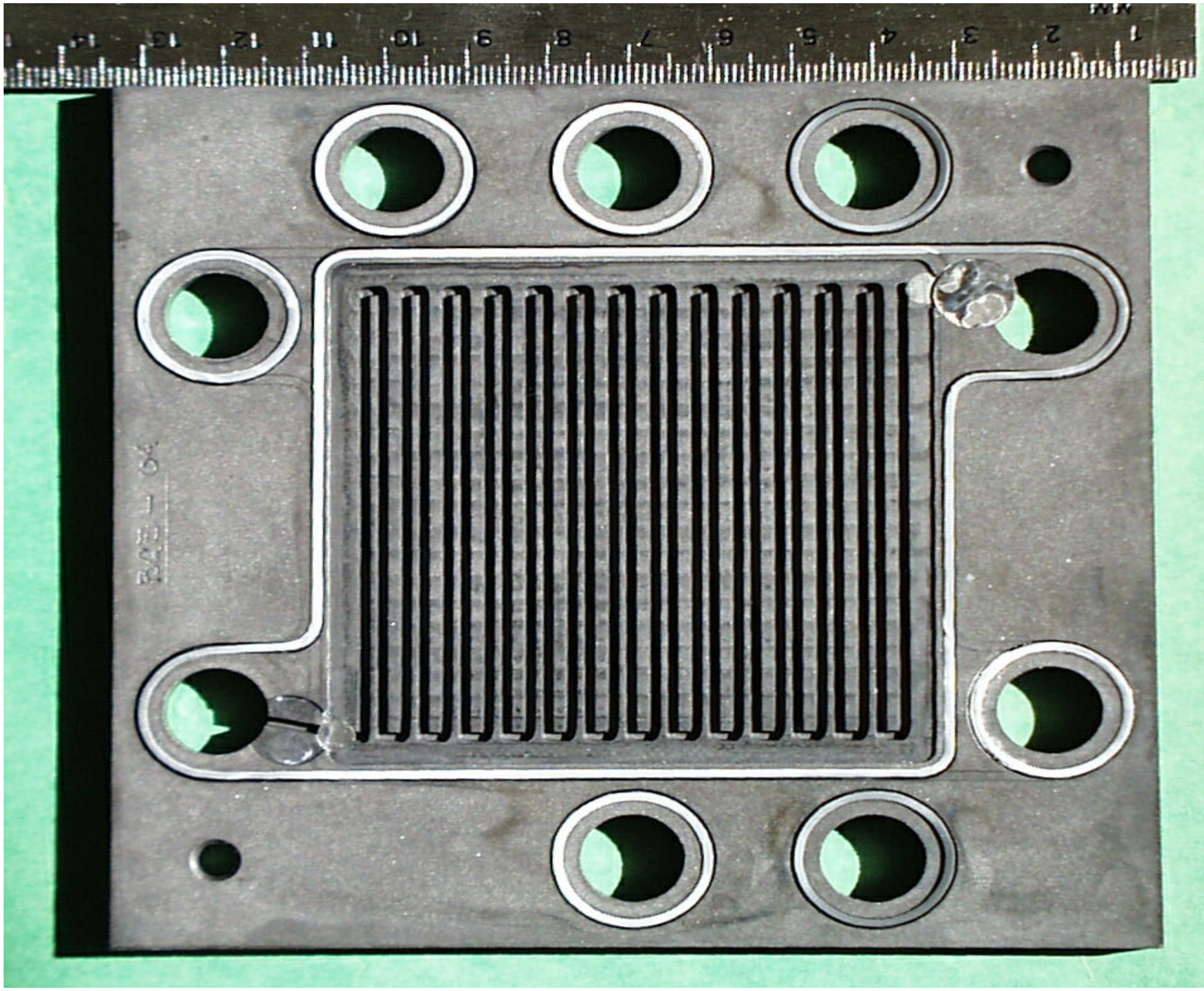
ENDURANCE TESTED MEA



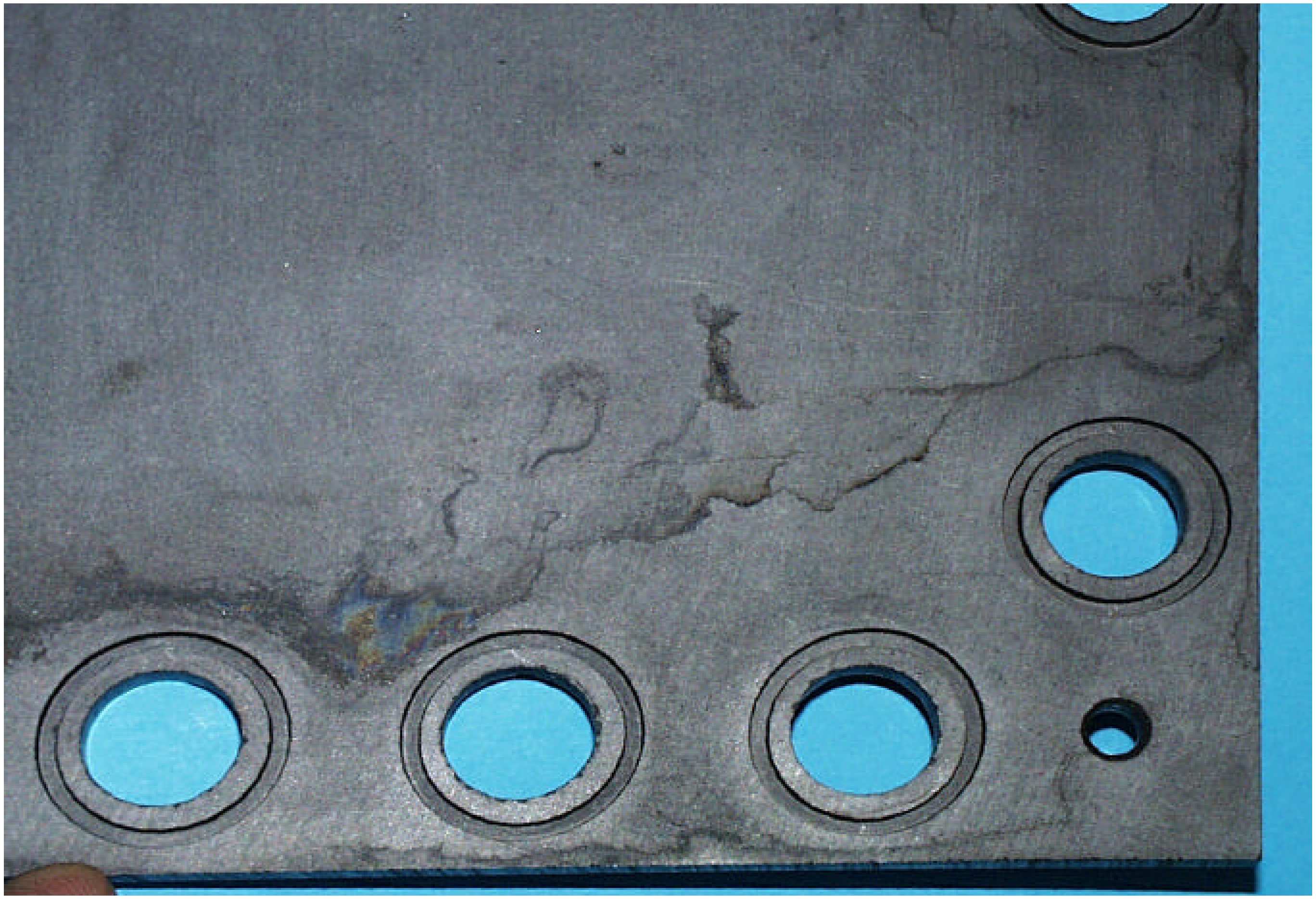
Seal Oxidation



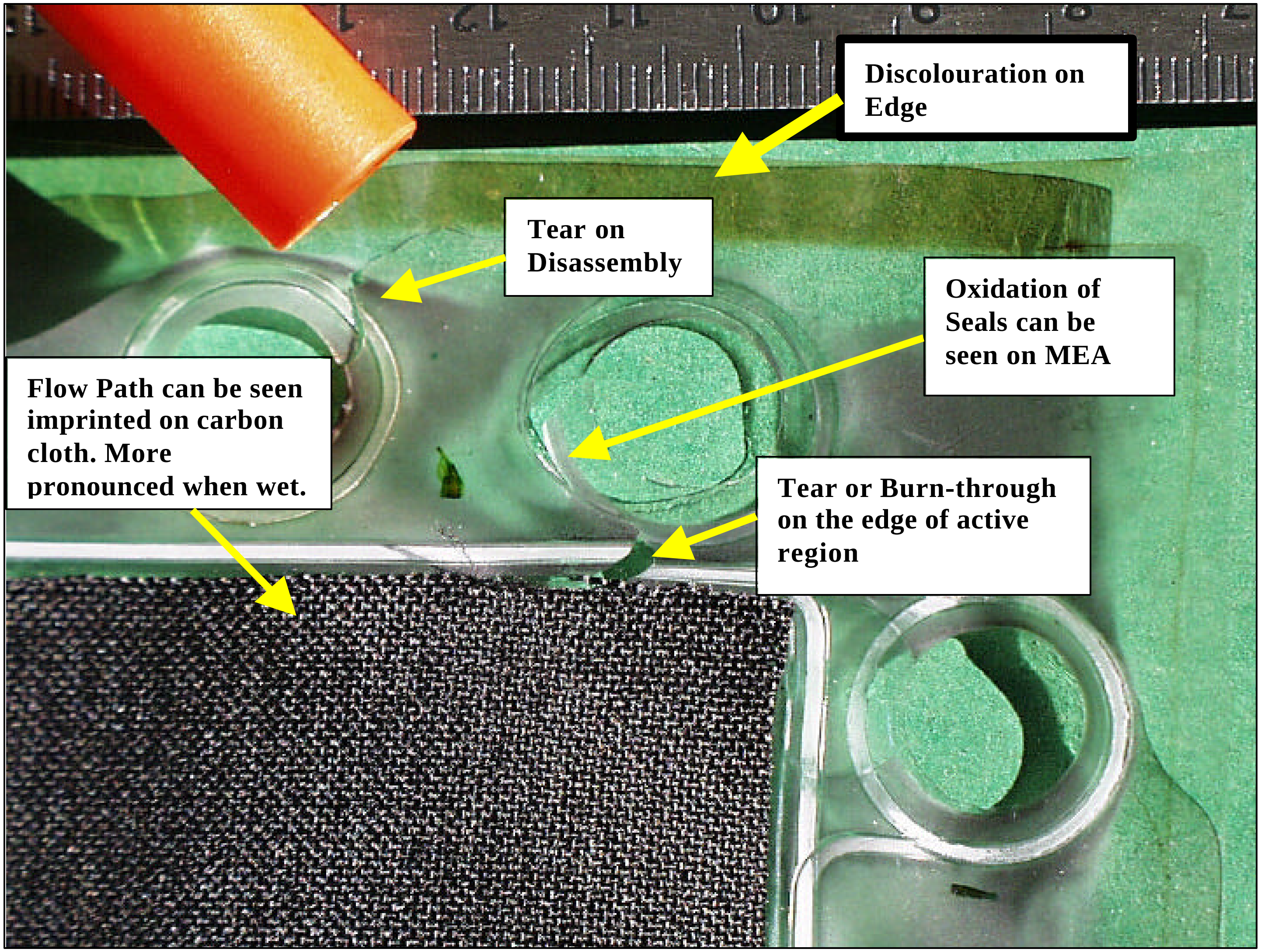
SCORCHING ALONG THE EDGE



SCORCHING



SUMMARY OF OBSERVED FAILURE



FMEA OF A FUEL CELL

- **Plate**
  - **Cracking**
  - **Scorching**
  - **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**

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*)

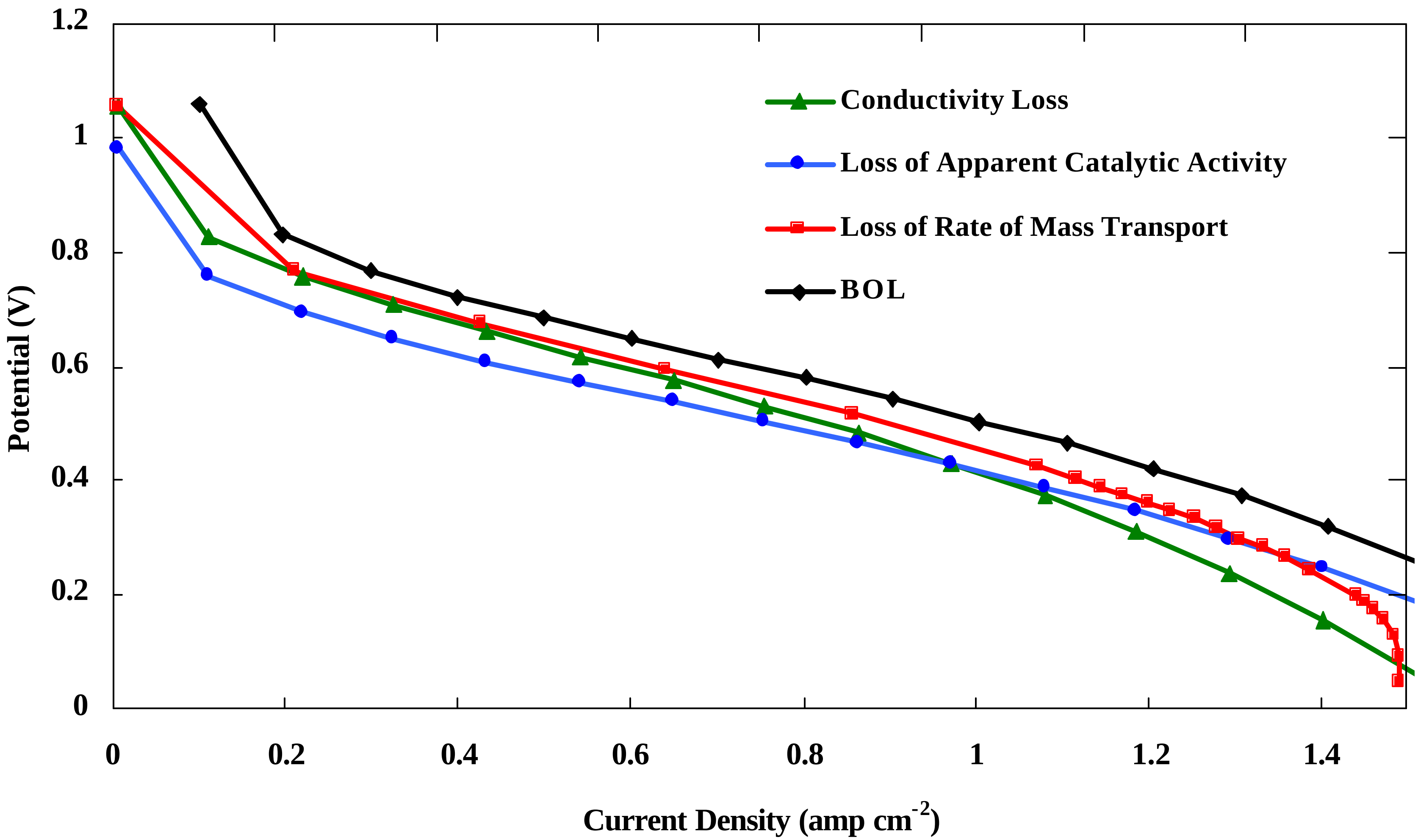
- **Kinetic or activation loss in the anode or cathode catalyst –**

  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 –**

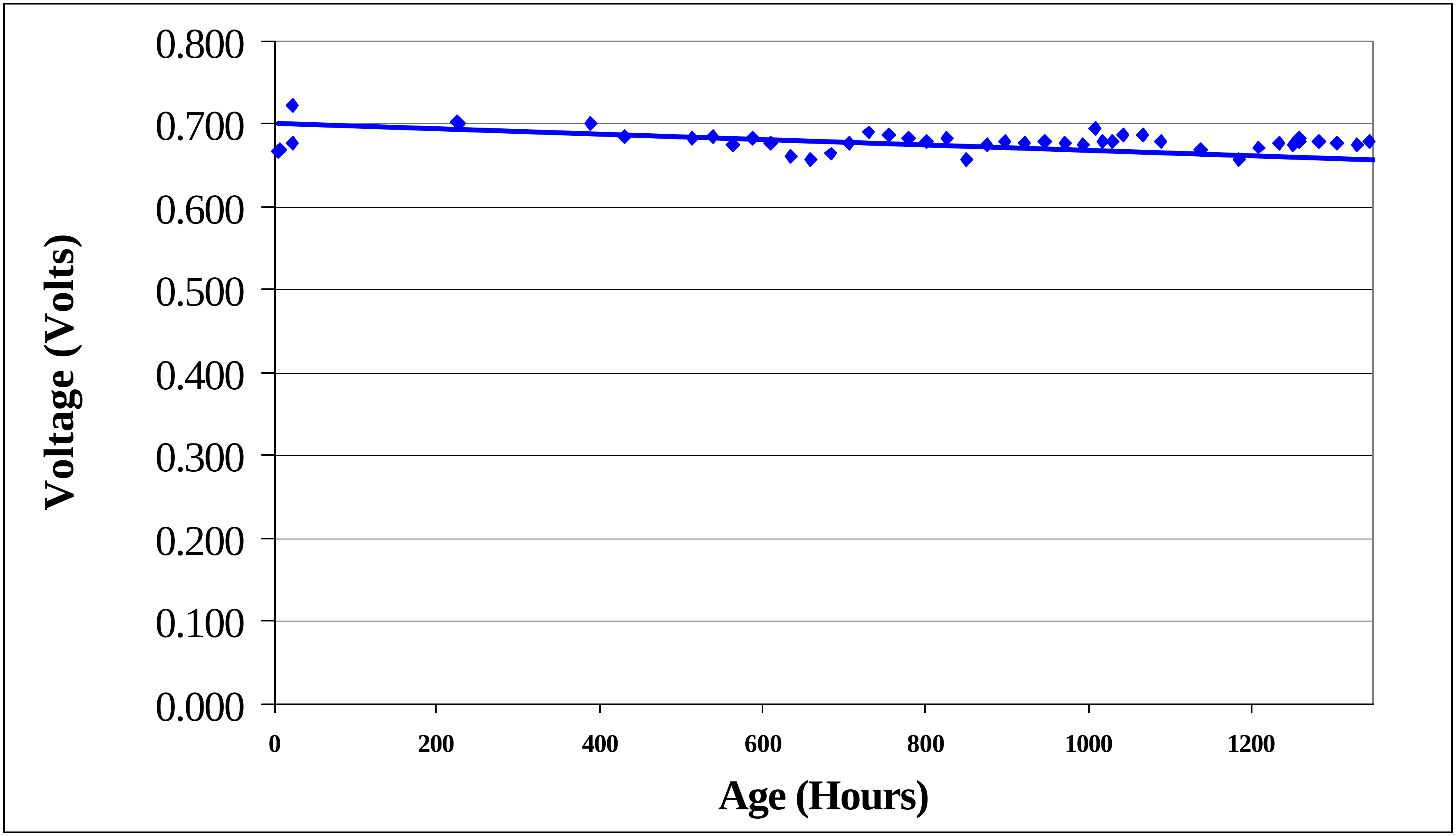
  Loss of Mass Transfer Rate of Reactants

VOLTAGE DEGRADATION MODES



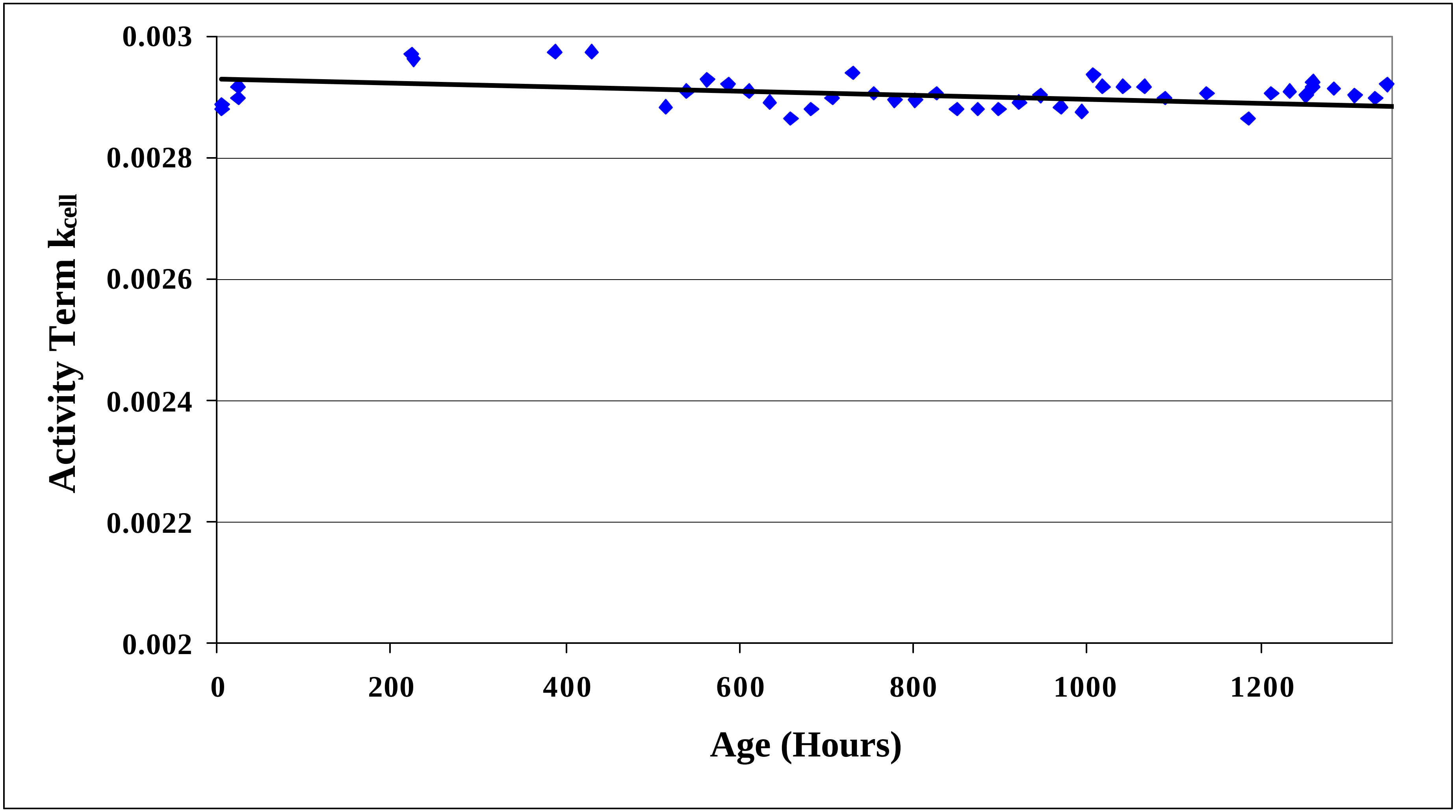
VOLTAGE DEGRADATION CURVE FOR A SINGLE PEM CELL

(Operated at 80°C, 0.4 amp cm^{-2}, 30 psig/30 psig, H2/Air – stoichiometric ratios 1.2/2)



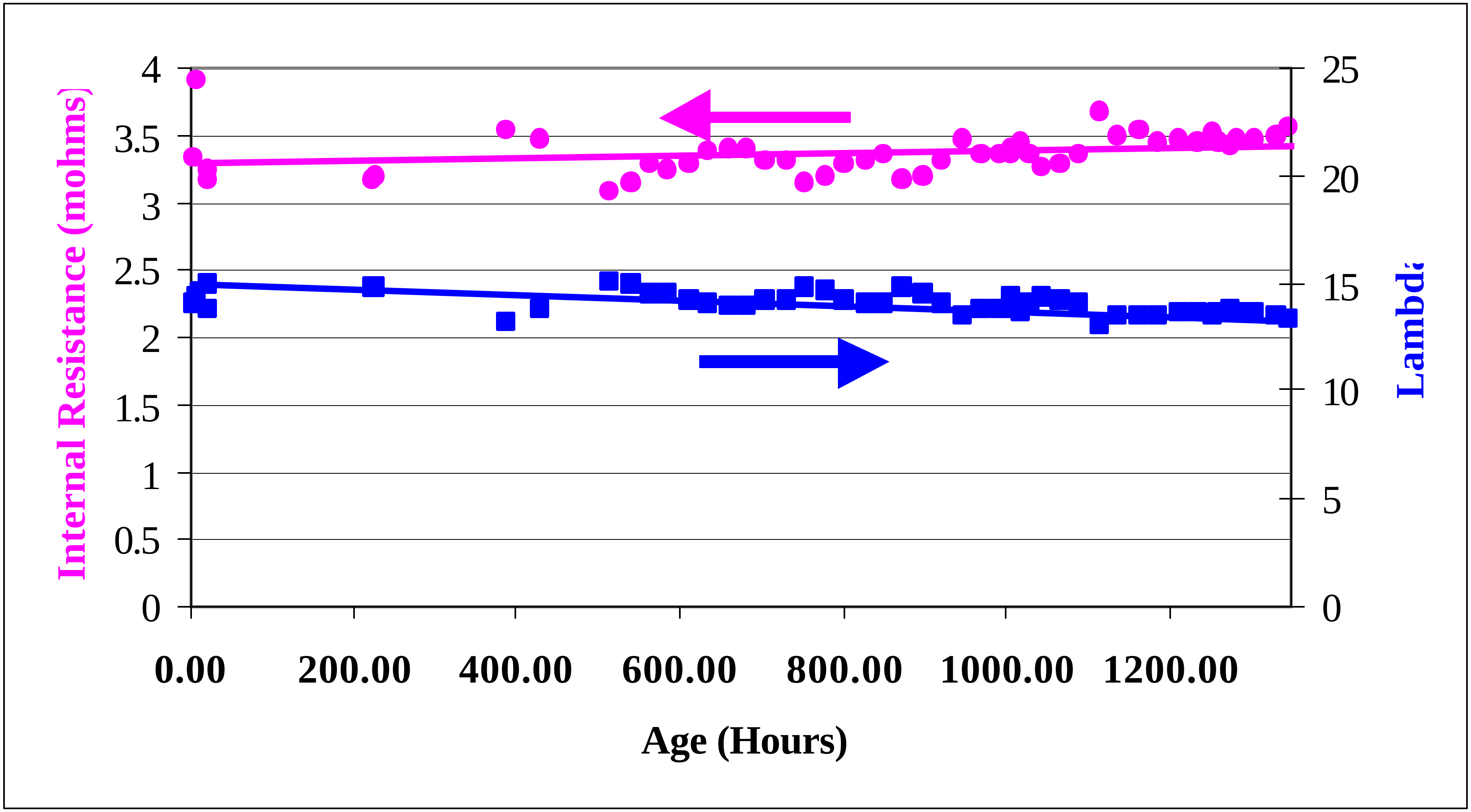
ACTIVITY TERM k_{cell} (from the GSSEM) OF A SINGLE CELL

(Operated at 80°C, 0.4 amp cm^{-2}, 30 psig/30 psig, H2/Air – stoichiometric ratios 1.2/2)

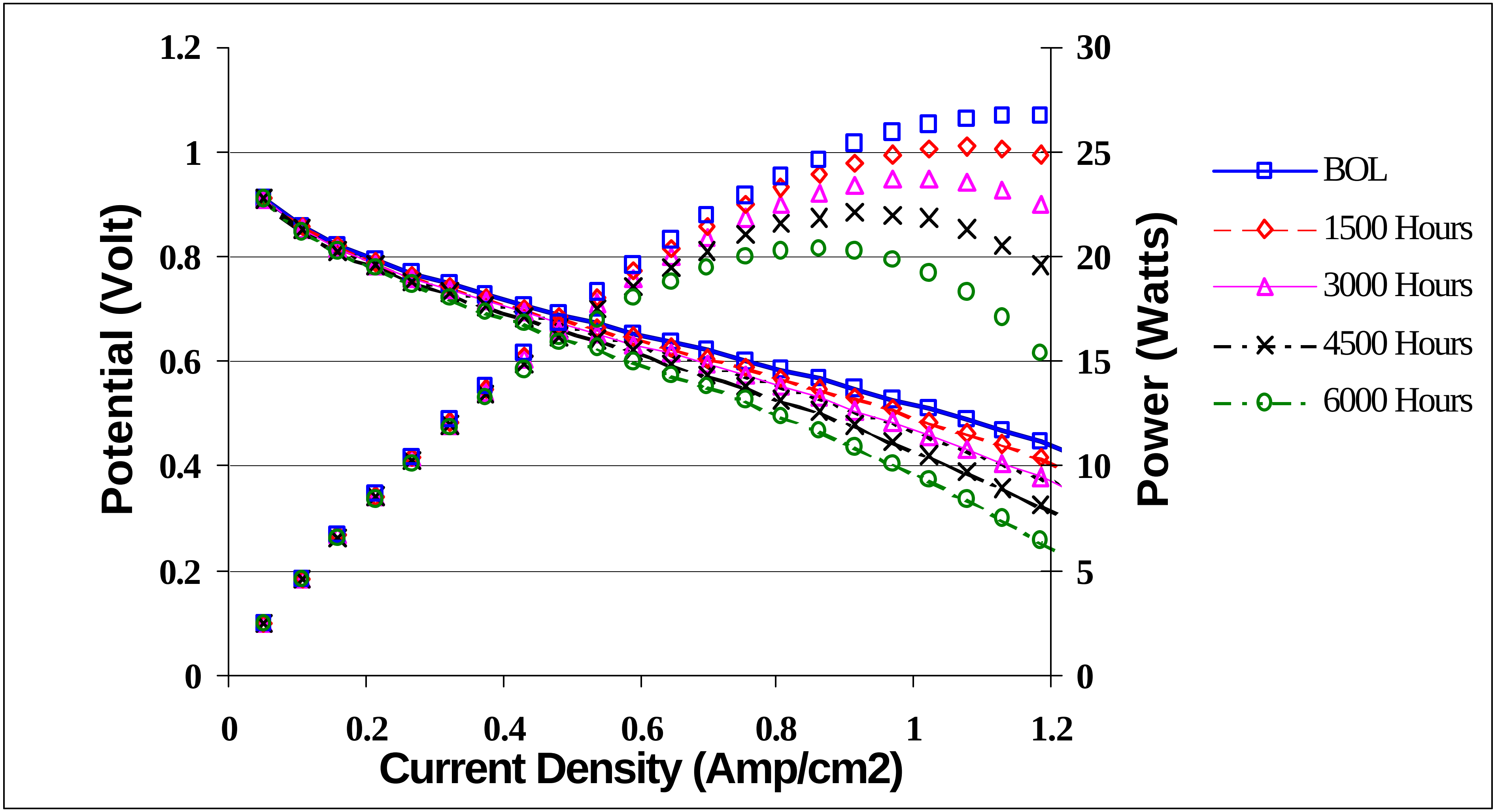


RESISTANCE INCREASE CURVE OF A SINGLE CELL

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



SIMULATION OF A SINGLE CELL USING THE GSSEDM



RELIABILITY ANALYSIS

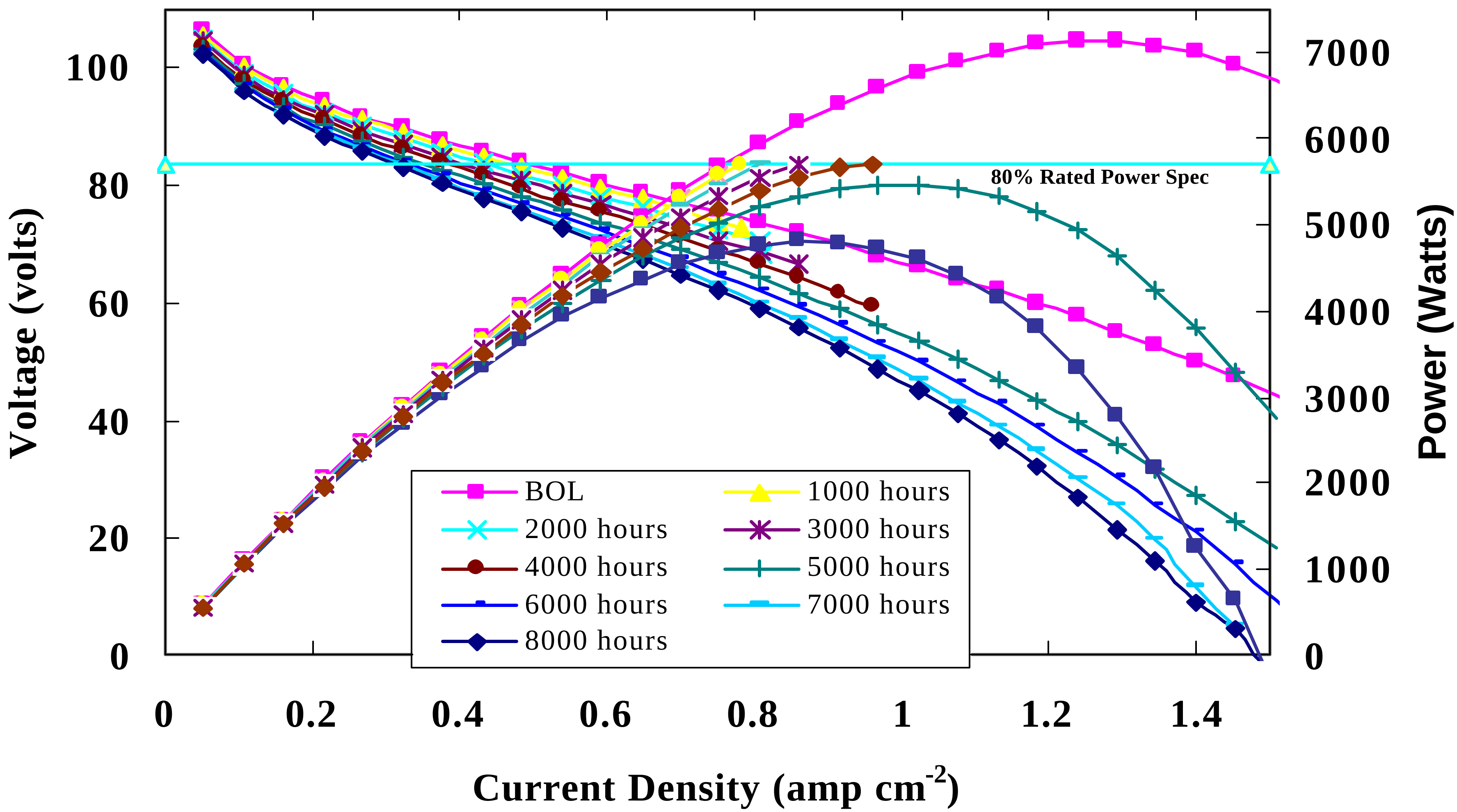
- **Must account for stochastic behaviour of cells**
- **Includes a Degradation Model', *(durability)* *where* 'Failure' is degradation to below threshold value for specific parameter (*e.g.* voltage, efficiency, power) Catastrophic failure of the MEA**
- **Goal of the analysis is to allow an understanding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

RELIABILITY ANALYSIS

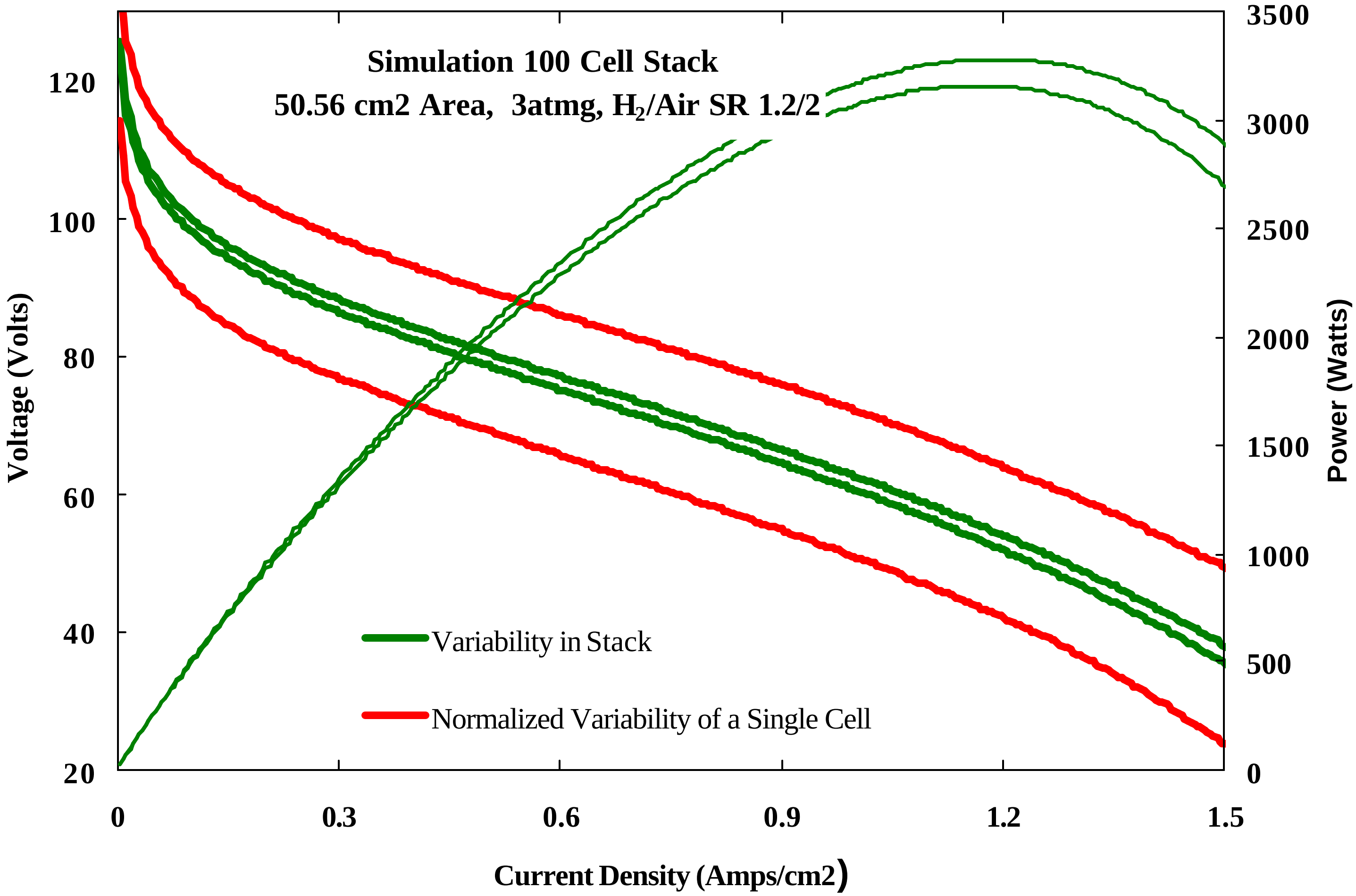
- **Will require some type of 'Degradation Model', which allows reliability to be function of degradation evaluation *(durability)***
- **'Failure' is degradation to below threshold value for specific parameter (*e.g.* voltage, efficiency, power)**
- **Should account for stochastic behaviour of cells**
- **Catastrophic failure of the MEA**
- **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**

STACK AGEING MODEL

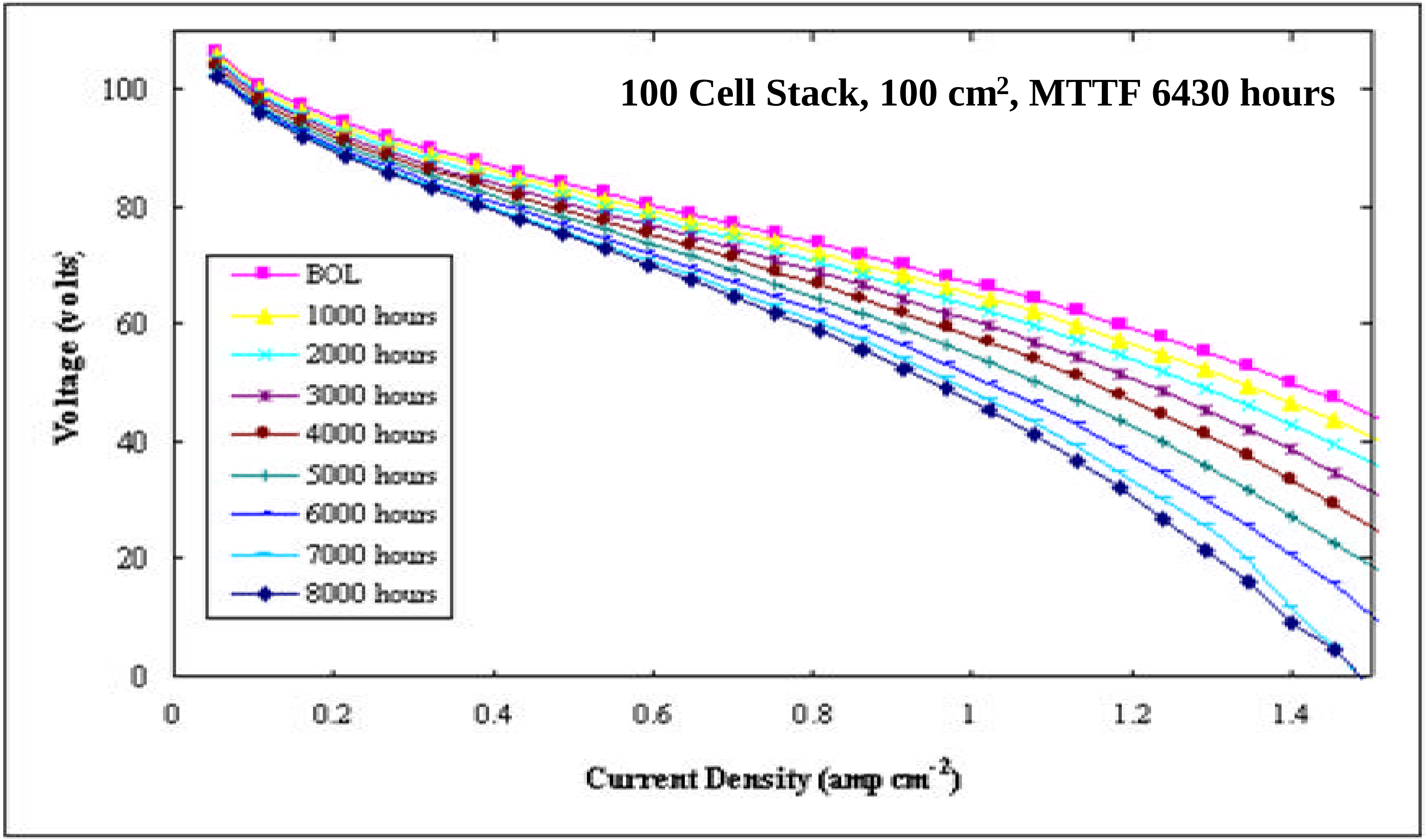
(100 CELLS – 100 cm²)



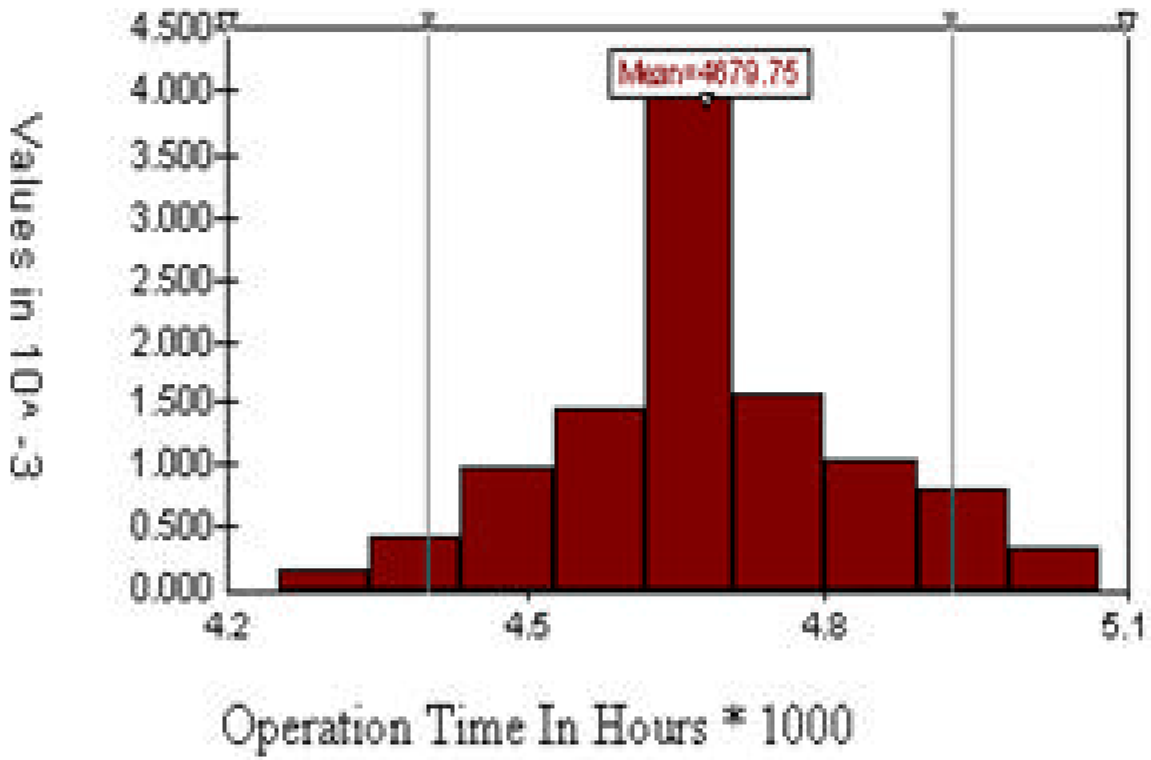
MODELLING OF STOCHASTIC BEHAVIOUR



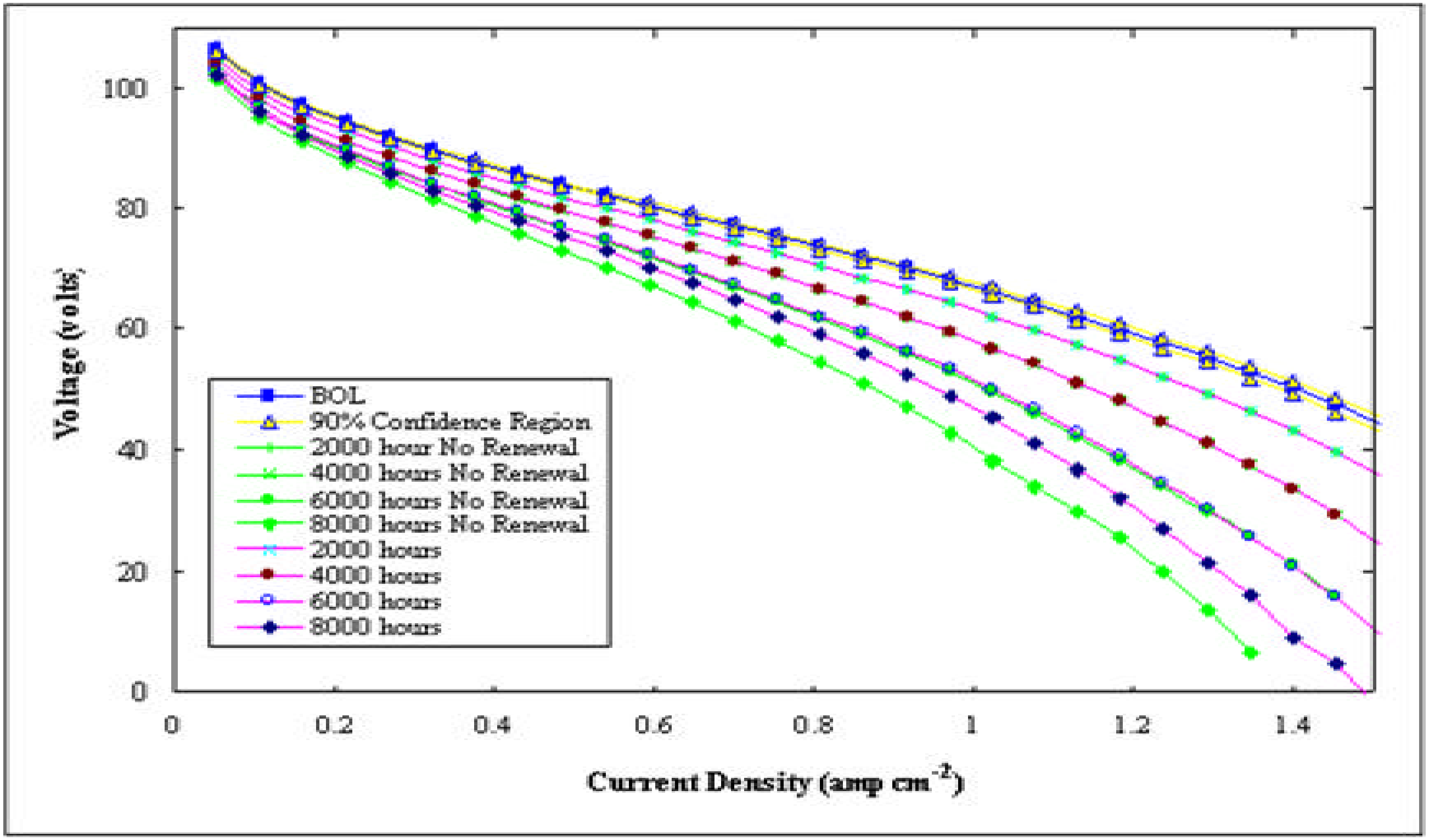
OPERATION WITH MEA FAILURE AND RENEWAL



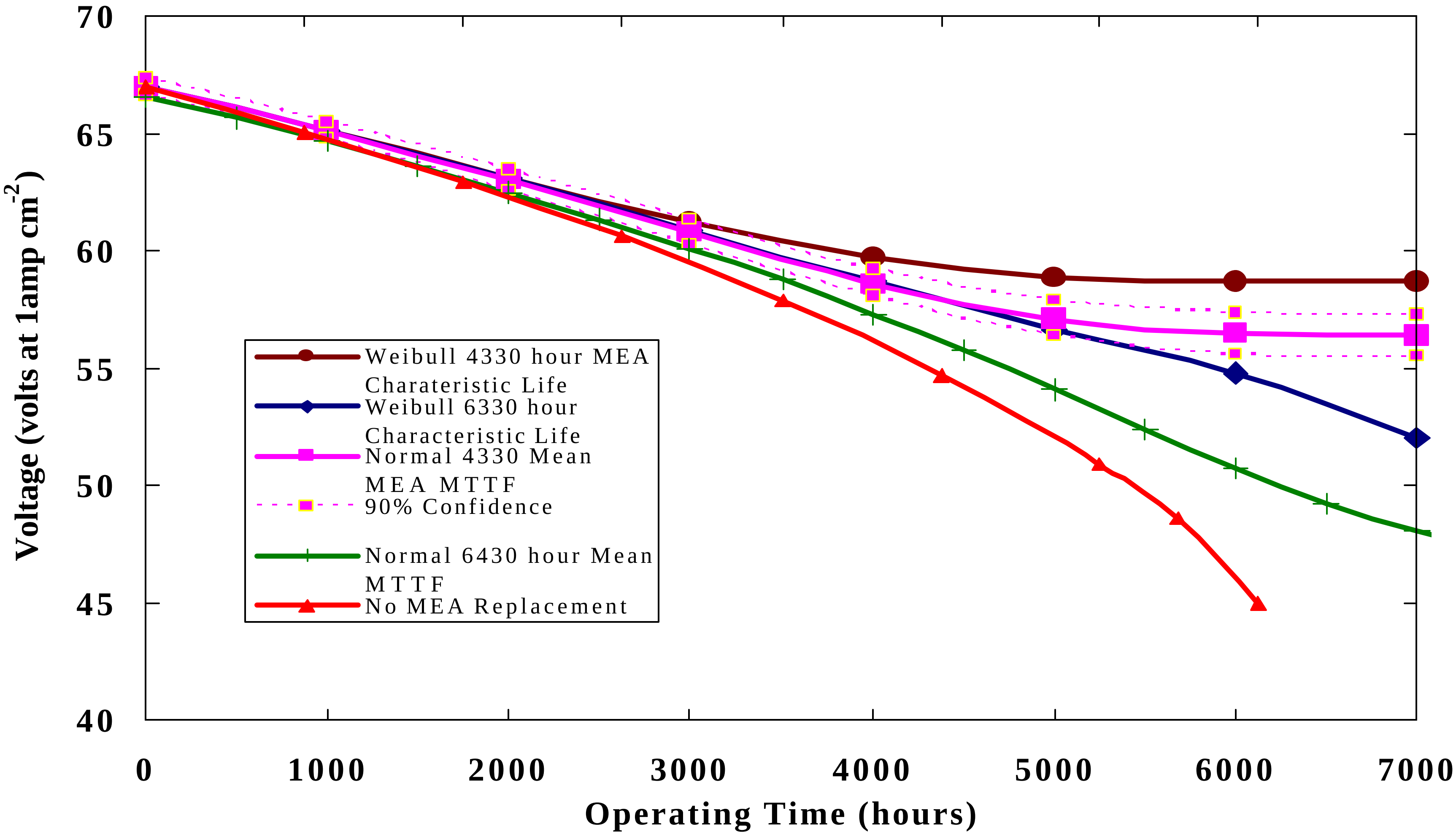
MTTF –
MEAN TIME TO FAILURE



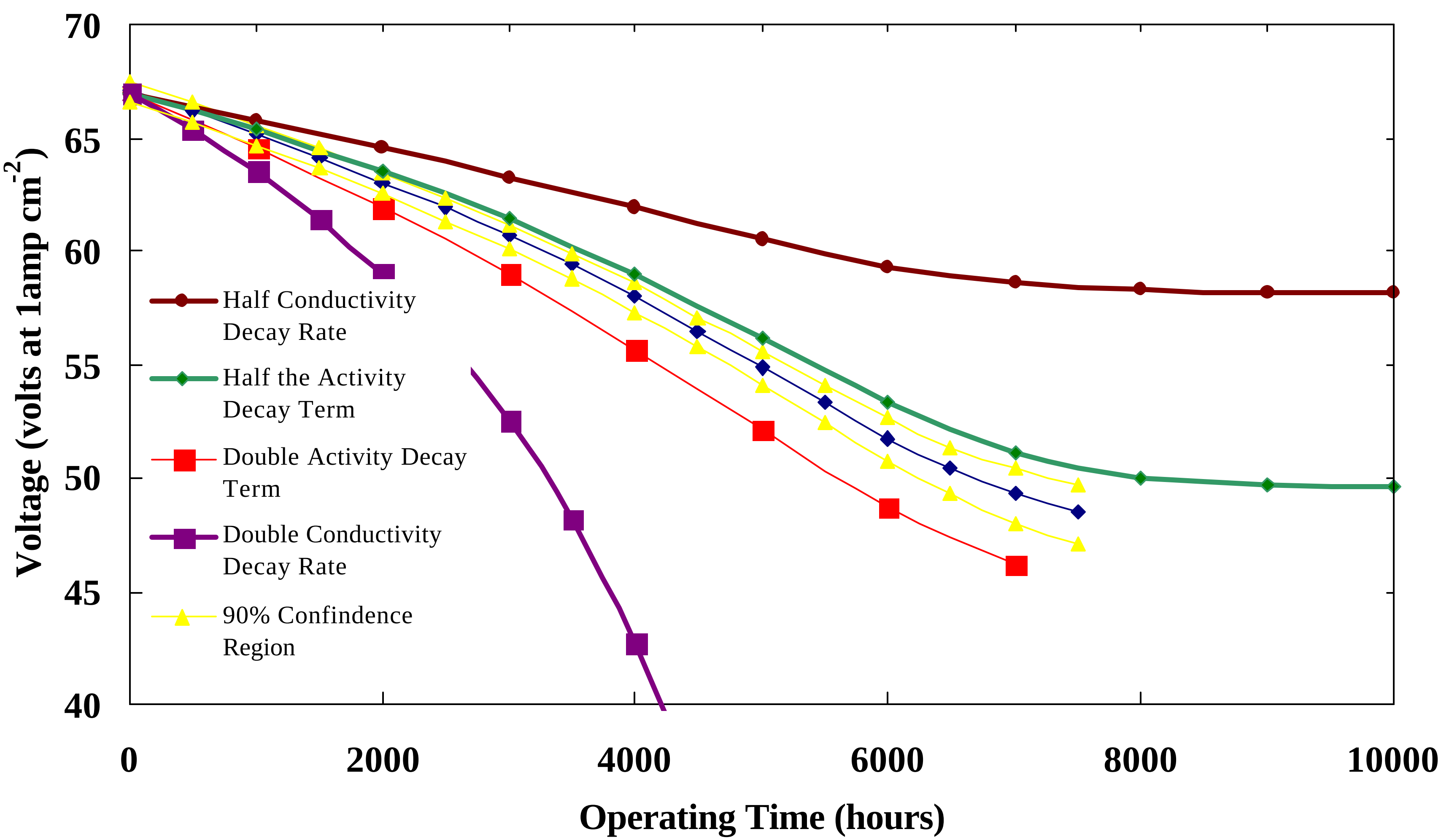
MEA RENEWAL VS NO RENEWAL



RENEWAL RATE VARIATION



VARIATION IN DEGRADATION RATES



MAJOR CONTRIBUTIONS OF THIS WORK

- **Identification of key failure modes associated with PEM fuel cells**
- **Development of GSSEDM, modelling the performance of a cell with operating age**
- **Develop a conceptual model for fuel cell stack reliability.**

Acknowledgement / References

- NSERC, National Defence, Support of the Electrochemical Power Sources Group at RMC.

- 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, <u>Handbook of Fuel Cells – Fundamentals, Technology and Applications - Volume 3: Fuel Cell Technology and Applications,</u> 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

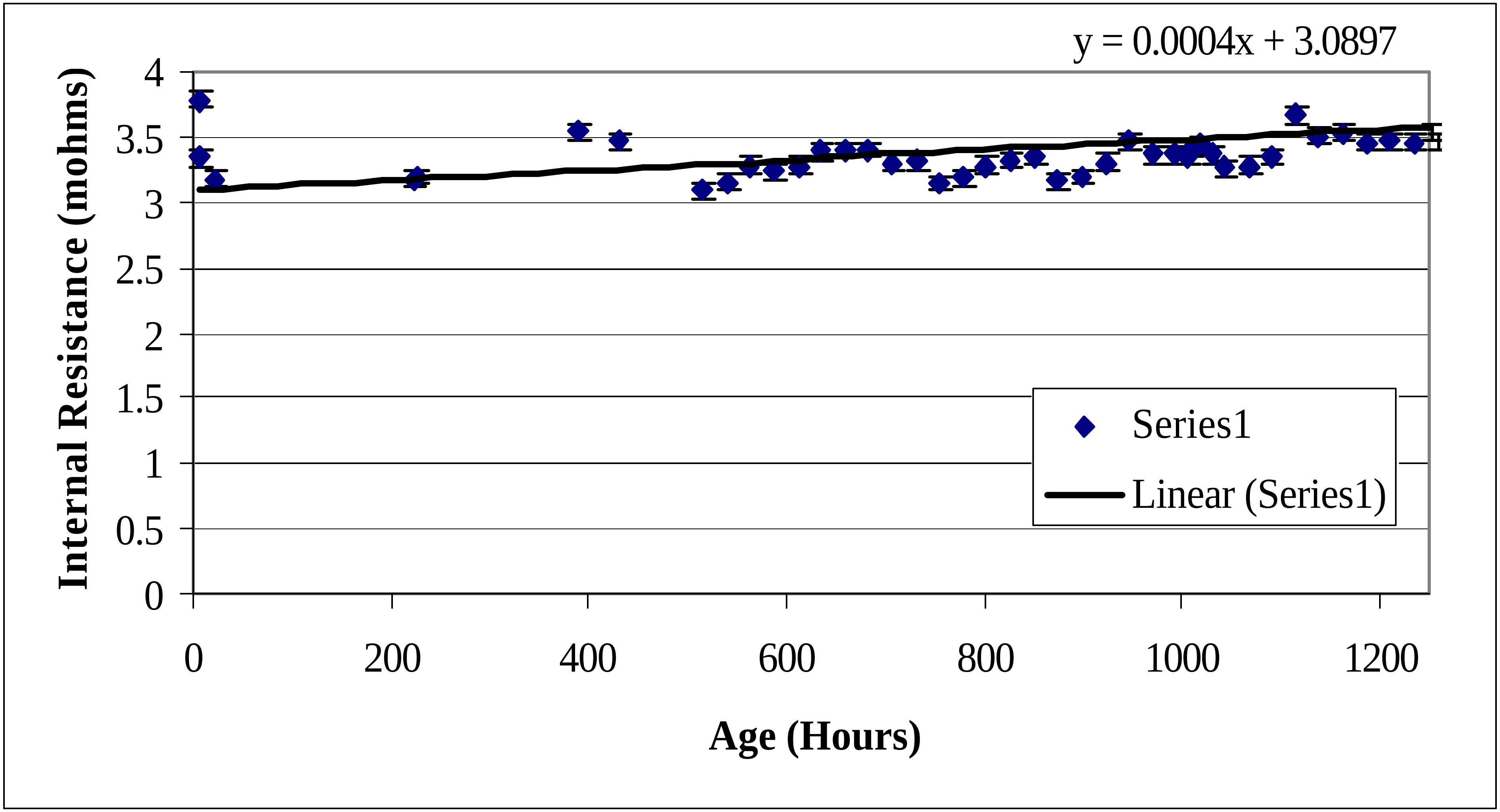
Measurement Error

Function	Device	Stated Error	Measurement Error
Resistance	HP 4328A	2% of full scale 3 mohm	0.06 mohms
Flow Controllers	Cole Palmer	1.5% of full scale	1.5 cc min^{-1} anode 5 cc min^{-1} cathode
Flow Meters	Aalborg GFM 171	1.5% of full scale	1.5 cc min^{-1} anode 5 cc min^{-1} cathode
Signal Processing	National Instruments 5B30	0.05% of span	
Current	Shunt		.025 Amps or .0005 Amps cm^{-2}
Voltage			0.05mV
Temperature	Thermal Couple	0.1°C (calibrated)	0.1°C
Pressure	Transducer	0.5% of full scale*	0.15 psig

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**
- **defect propagation**

Instrument Error



PEM MODEL DEVELOPMENT

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

$$E_{Nernst} = 1.229 - 8.5\times 10^{-4}(T - 298.15) + 4.308\times 10^{-5}\cdot T\left(\boldsymbol{ln}\, p^{*}_{\mathrm{H_2}} + ½\,\boldsymbol{ln}\, p^{*}_{\mathrm{O_2}}\right)$$

$$h_{act,\,\mathrm{c}} = \frac{1}{\boldsymbol{a}_{\mathrm{c}}}\left[-1.036\cdot 10^{-6}\cdot \Delta G_{e} + 8.62\cdot 10^{-5}\cdot T\left(12.863 + \ln \mathrm{A} + \ln k'_{\mathrm{c}} + (1 - \boldsymbol{a}_{\mathrm{c}})\ln c^{*}_{o_2} - \ln i\right)\right]$$

$$h_{\mathrm{act,\,a}} = -\frac{\Delta G_{ec}}{2\mathrm{F}} + \frac{\mathrm{R}\,T}{2\mathrm{F}}\ln\left(4\mathrm{F}\cdot A\cdot k_{a}^{0}\cdot c^{*}_{\mathrm{H_2}}\right) - \frac{\mathrm{R}\,T}{2\mathrm{F}}\ln i$$

TOTAL ACTIVATION OVERVOLTAGE

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

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

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

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

$$x_3 = \frac{R(1 - a_C)}{a_C n F} \qquad x_4 = -\left(\frac{R}{2F} + \frac{R}{a_C nF}\right)$$

TOTAL OHMIC OVERVOLTAGE

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

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

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

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

$$r_M = \frac{181.6 \cdot \left[1 - 0.03\left(\frac{i}{A}\right) + 0.062\left(\frac{T}{303}\right)^2 \left(\frac{i}{A}\right)^{2.5}\right]}{\left[l - 0.634 - 3\left(\frac{i}{A}\right)\right] \exp\left(3.25\left[\frac{T-303}{T}\right]\right)}$$

AGEING PARAMETERS

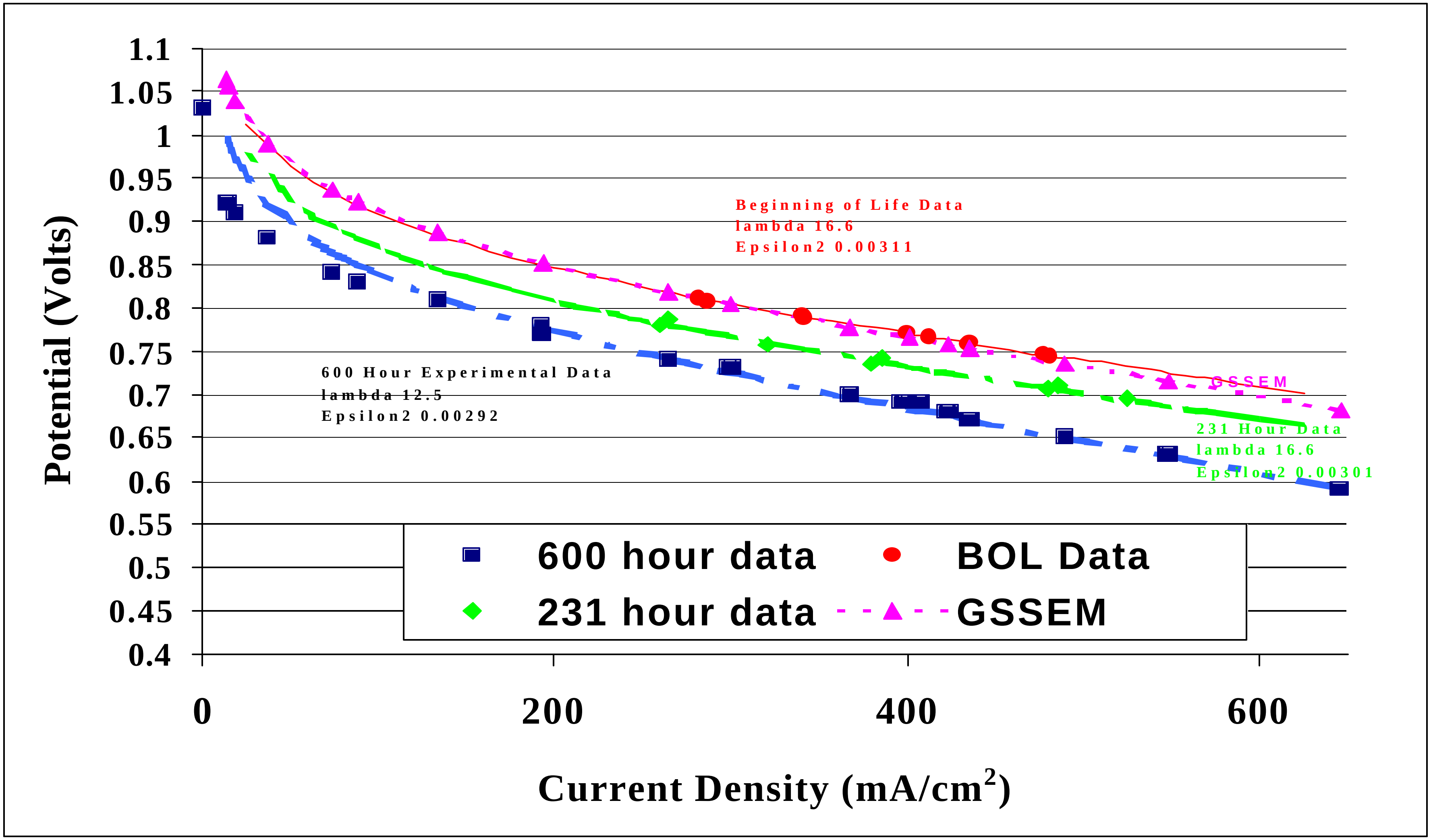
$$x_2 = \mathbf{k}_{DR} \times Age/T + \mathbf{k}^{\circ}_{\mathbf{cell}} + \mathbf{0.000197} \cdot \mathbf{ln}\ A + \mathbf{4.3} \times \mathbf{10^{-5}} \cdot \mathbf{ln}\ c^{*}_{H_2}$$

- **proposed ageing rate (k_{DR}) of is -0.055 mV/hr**

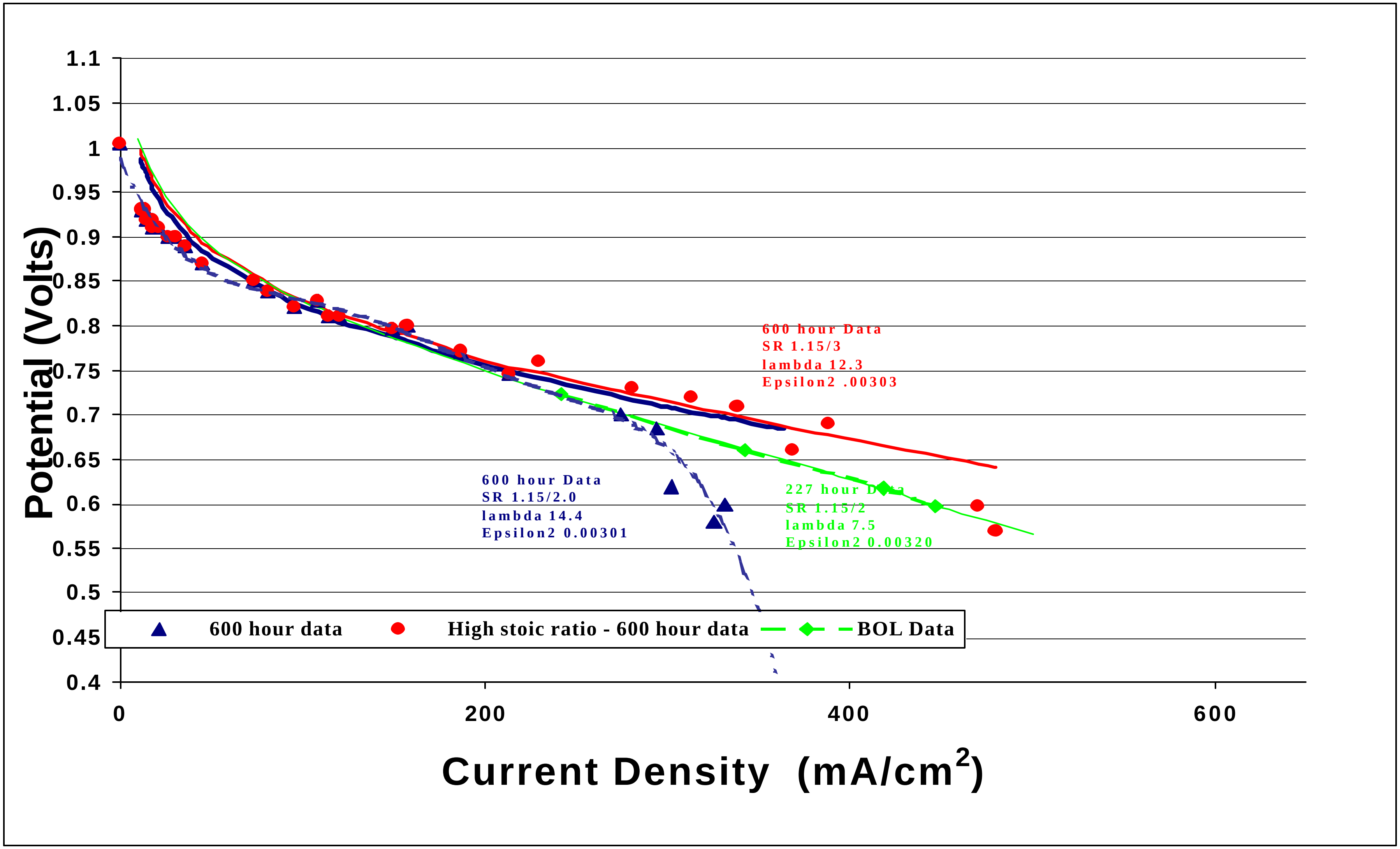
$$?_{age} = ?^{\circ} + ?_{DR} \times Age$$

- **–0.0007 hr^{-1} for l $_{DR}$**
- **term related to the loss of mass transport of reactants (not developed in this work)**

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



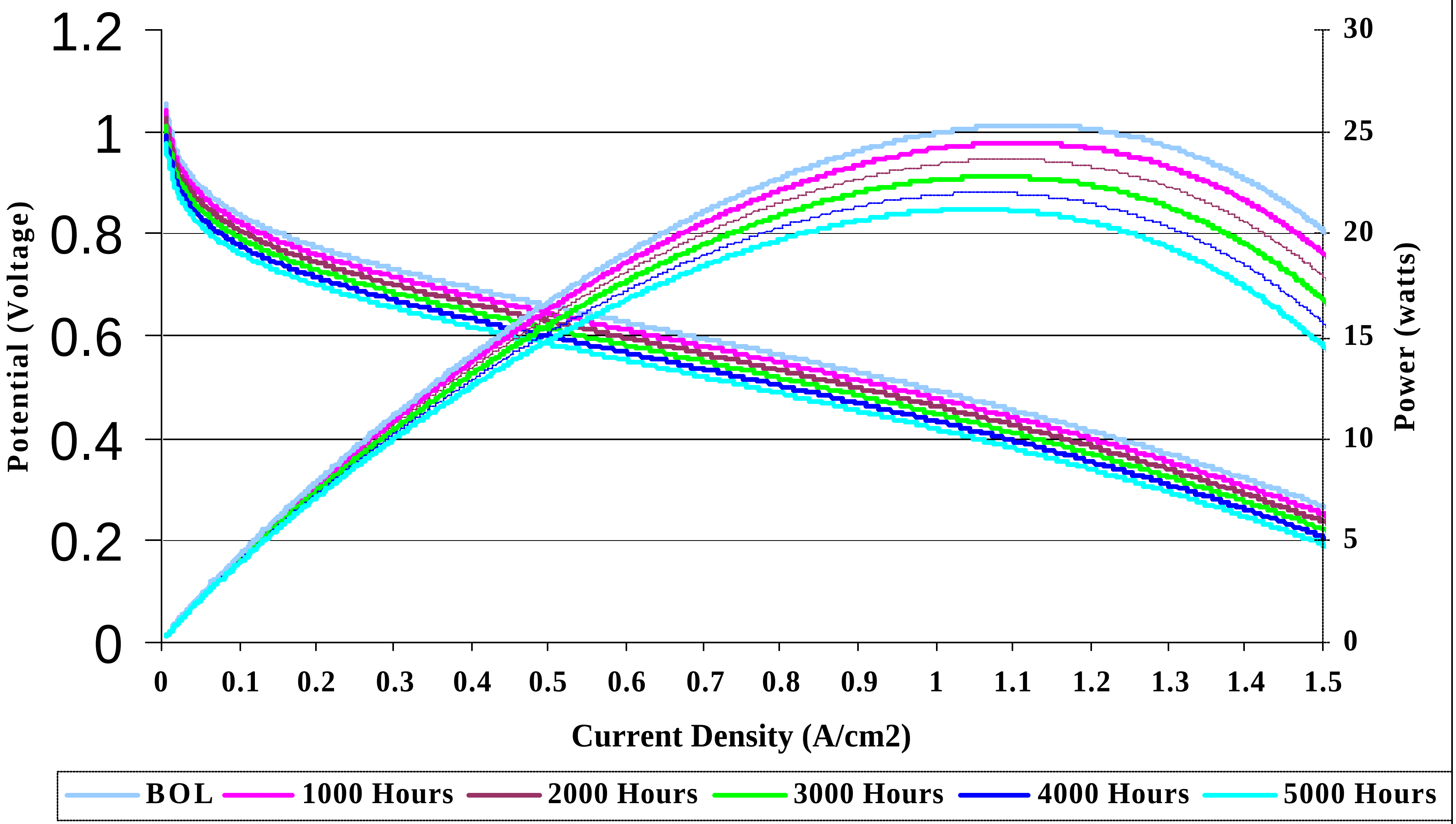
SINGLE CELL DEGRADATION
H_2/AIR 30 psig/30psig 80ºC



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 effectiveness of catalytic sites (flooding and dehydration) or simply the presence of liquid water
- Degradation of Nafion in contact with active sites
- Carbon Corrosion

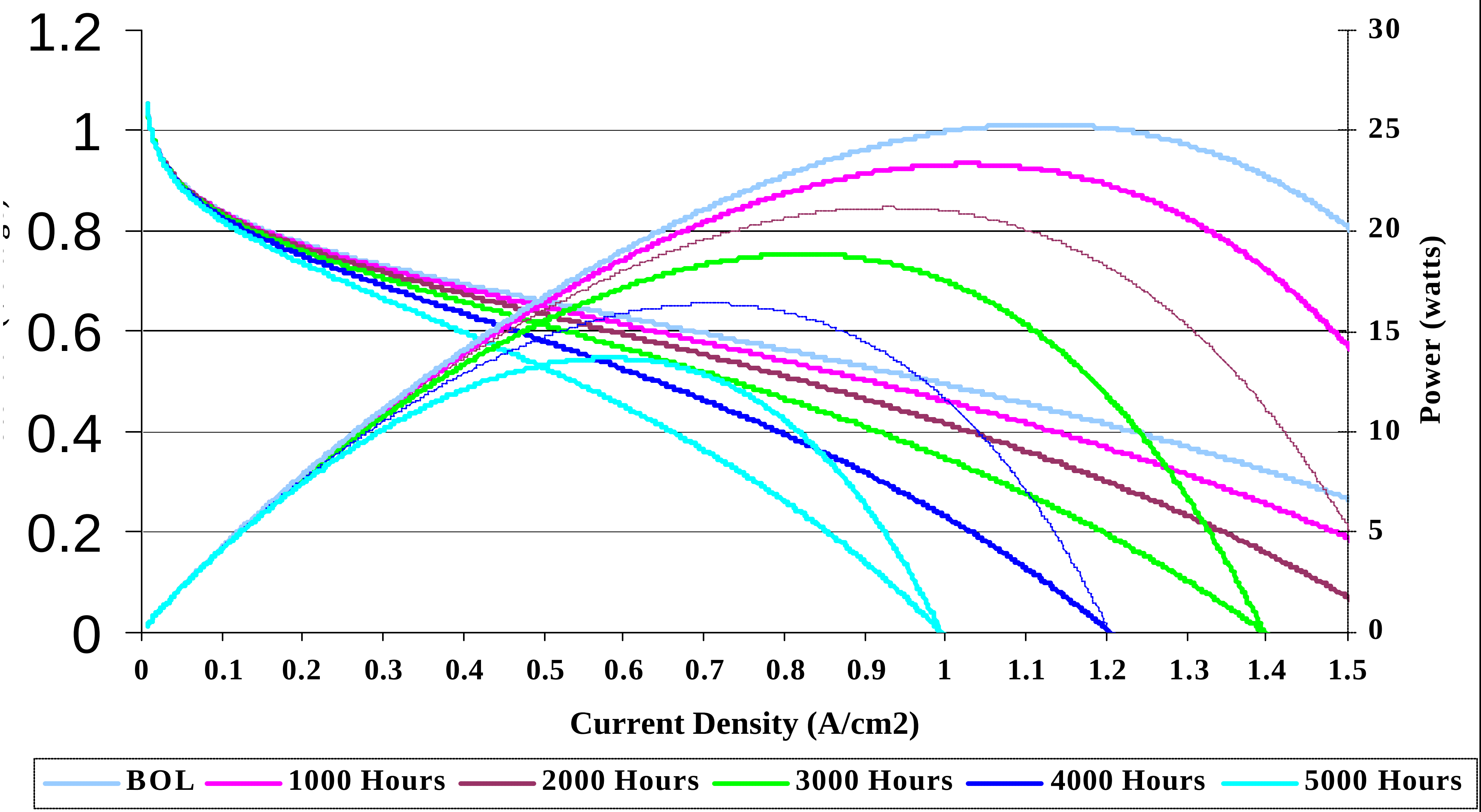
LOSS OF APPARENT CATALYTIC ACTIVITY



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**

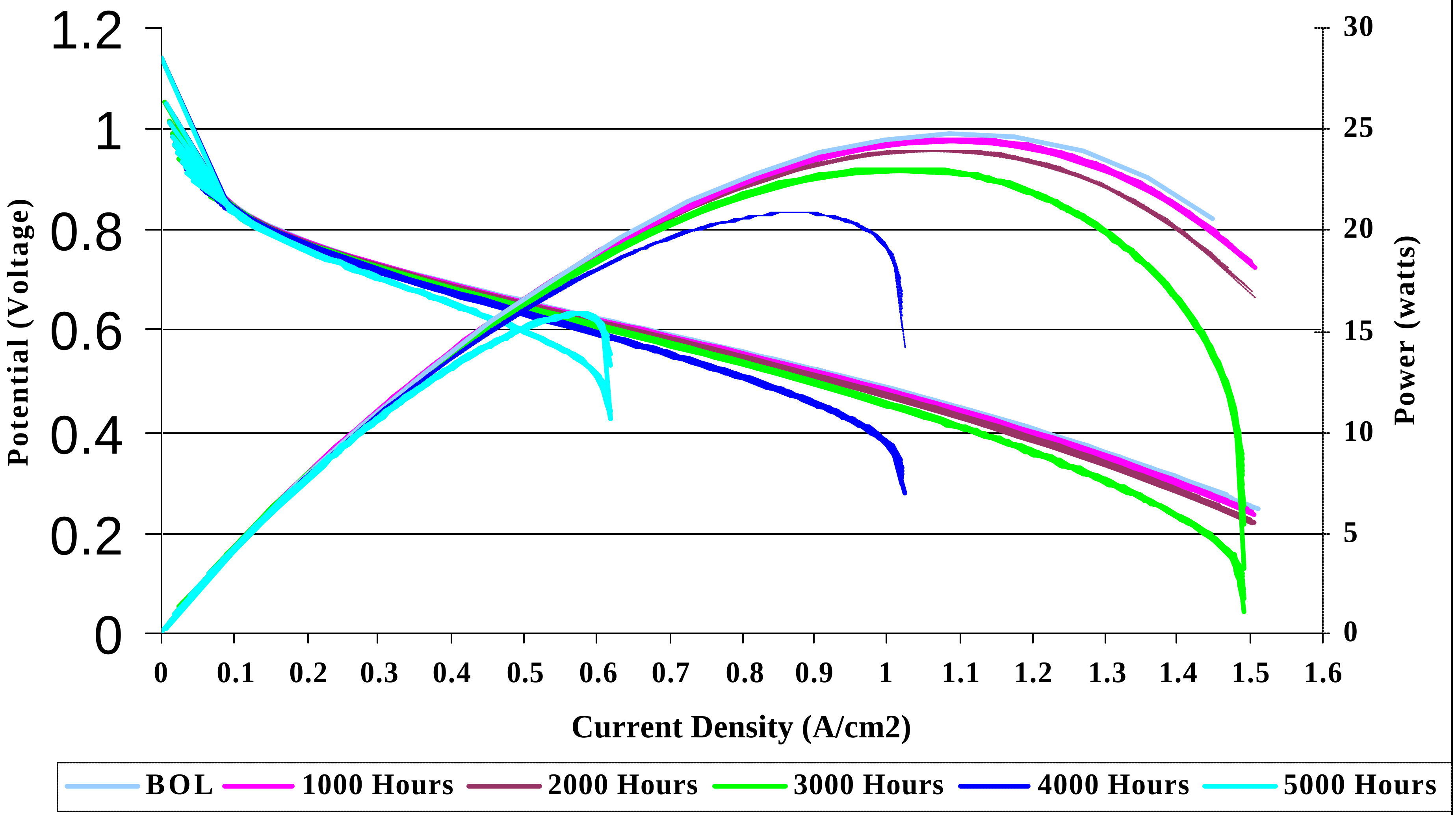
LOSS OF CONDUCTIVITY



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

LOSS OF MASS TRANSFER RATE OF REACTANTS



RELIABILITY BLOCK DIAGRAM