

EXPERIMENTAL DIAGNOSTICS OF PEM FUEL CELLS

By

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MASc PROJECT

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Outline

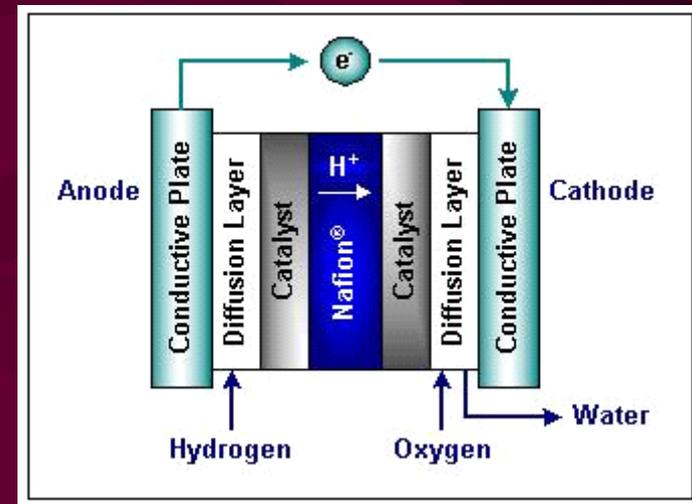
- Introduction
 - PEMFC
 - Effect of Operating Conditions
 - Scope of the project
- Literature Review
- Experimental Apparatus
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 - Assumptions
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- Results and Discussion
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Introduction

- POLYMER ELECTROLYTE MEMBRANE FUEL CELL
 - High power density, which offers low weight, cost and volume.
 - The immobilized electrolyte membrane simplifies sealing in the production process, reduces corrosion, and provides for longer cell and stack life.
 - PEMFC operate at low temperature, allowing for faster startups and immediate response to changes in the demand for power.
 - The PEMFC system is seen as the system of choice for vehicular power applications, but is also being developed for smaller scale stationary power.

Components

- Components of PEMFC:
 - A proton conducting membrane, such as a perfluorinated sulfonic acid polymer
 - Porous electrodes
 - The back of the electrodes is made hydrophobic by coating with a compound, such as Teflon . This wet proof coating provides a path for gas diffusion to the Catalyst layer.



PEMFC Components

- Components of MEA
 - Electrodes
 - Carbon cloth
 - Catalyst
 - Pt in Carbon base, inner sides of electrodes
 - Membrane
 - Nafion (DuPont)
- < 1mm thick



Operation

- Process:
 - Hydrogen at the anode provides a proton, freeing an electron in the process that must pass through an external circuit to reach the cathode. The proton, which remains solvated with a certain number of water molecules, diffuses through the membrane to the cathode to react with oxygen and the returning electron. Water is subsequently produced at the cathode.
- Features:
 - low-temperature operation of approximately 80°C is possible.
 - The cell also is able to sustain operation at very high current densities.
 - Compact and lightweight cell, particularly suited for vehicular power application.

Components Functionality

Components:

- Membrane (Nafion)
 - Proton transport resistance
 - Material
 - Humidification
- Interface Membrane-Electrode (Pt-C)
 - interfacial kinetics- humidification
- Electrodes (Pt-C)
 - Losses in cathode produced by limited
 - effective permeability of oxygen in the catalyst layer
 - proton conductivity through catalyst layer

Humidification

- Protons conduction require humidification
- Water transport
 - Increases with cell current density
 - Characteristics of the membrane
 - Electrodes
- Contributing factors to water transport:
 - The water drag through the cell, "electro-osmotic drag"
 - Back diffusion from the cathode
 - The diffusion of any water in the fuel stream through the anode
 - Excess air on cathode side also evaporates water

Water Management

Dehydration :

- Increases interfacial kinetics of membrane and the electrode(Pt-C)
- catalyst layer proton conductivity
- membrane conductivity for proton
- Caused by:
 - low current densities
 - larger reactant flow
 - higher temperature
 - Lower pressure

Humidification:

- High current densities enhances mass transport (proton) increases water drag
- causes problems with diffusing the gas to the electrode especially at Cathode
 - water formation and distribution limits cell output.
 - Dilution of reactant gases by water vapor
- Flooding caused by:
 - higher current,
 - smaller reactant flow,
 - higher humidity,
 - lower temperature, higher pressure

Temperature

- Operating temperature

- An increase in temperature lowers the internal resistance of the cell, mainly by decreasing the ohmic resistance of the electrolyte.
- Mass transport limitations are reduced at higher temperatures.
- Improving the cell performance limited by the high vapor pressure of water in the ion exchange membrane.

Pressure

- Pressure
 - A significant reduction in polarization at the cathode.
 - Performance improvements due to increased pressure must be balanced against the energy required to pressurize the reactant gases.

Stoichiometry ratio

- Stoichiometry ratio

- Higher the stoichiometry ratio, less percentage of the reactant consumed.
- The concentration of the reactant is higher
- Performance of the cell improves
 - » More catalyst can actively react
- lead to excessive wastage of the gas and hence the increased cost.

AC Impedance

- AC Impedance

- Ability to resolve in frequency domain the individual contributions of the various factors producing activation, ohmic and mass transport losses.
- Such a unique method of separation of losses producing components provides
- Optimization of the Polymer Electrolyte Membrane fuel cell design
- Selection of most appropriate operating conditions.

Report

- Measurement techniques of operating parameters and AC impedance developed for consistent results
 - Water flooding influences all the operating parameters and strong interdependence produces inconsistency
 - The correct measurement of parameters is key prerequisite for any kind of investigations and optimizations.

Literature Review

- Applications of AC impedance spectroscopy:
 - Cell performance with variations of operating conditions.
 - Catalyst layer: Platinum composition
 - Electrode: Supporting layers composition etc.
 - CO poisoning
 - Mariana Ciureanu, et. al [27]: H₂/air PEMFC in low-power conditions showed;
 - Increasing the air flow rate produces a rapid decrease of the impedance due to cathode backing with little influence of Catalyst.
 - humidification produces a decrease in impedance of the Nafion
 - Springer et al. [1] showed that insufficient hydration in PEM fuel cell causes three effects:
 - Interfacial kinetics reduced.
 - Catalyst layer proton conductivity decreases.
 - Membrane conductivity decreases
 - Wagner et. Al [17] classified diffusion with water transport effects.
 - At higher current densities at 25 Ampere an increasing contribution of water diffusion is observed as the impedance of PEMFC first decreases reaching minimum and then increasing.

Literature Review

- V. A. Paganin, T. E. Springer, et. al [18] studied limiting current density (JL) in terms of Oxygen reduction reaction and water transport
 - water drag from anode to cathode a back diffusion gradient of water was established in the membrane with the water vapor diffusion in the hydrogen gas, may limit the transport of protons
- Andreaus, A.J. McEvoy, G.G. Scherer [31] investigated performance loss at high current density is and found that anode mass transfer is also a significant factor
 - Impedance for membrane was found to be function of membrane thickness, ionic density and humidification of reactants.
- Tatiana J.P. Freire, Ernesto R. Gonzalez [24] measured impedance spectra for variation in humidification and temperatures for different membrane thickness using Nafion: 117, 115, 1135, 112 with operation history consideration.
 - thinner membranes present better characteristics of water management, being much less sensitive to temperature and current density changes
- Buchi, Gunther G. Scherer [15] measured Nafion 117 resistance insitu and outside
 - in situ less resistance indicating less hydration showing flow field design as an indicated parameter.

Literature Review

- Solid-State Letters, 6 (4)A63-A66 [36] measured localized electrochemical impedance spectroscopy response since impedance was known to be a function of choice of internal circuitry, not known yet.
 - So bulk measurements are not the representative of local measurements since evidence of mass transport effects was found
- S. Rajendran et. al [33] optimized polymer composition for ionic conductivity
 - Poly (vinylidene fluoride) PVdF contents were increased, membrane conductivity increased.
- M. Eikerling, et. al [10] investigated the optimization of the structure and performance of porous composite Cathode to increase the oxygen kinetics
 - If the characteristic length scales of both transport processes (O₂ and H₂) are large compared to the catalyst layer thickness, then the impedance response is not a semicircle
 - Proton transport limitations is observed a straight line and more evident in high frequency domain
- Mark C. Lefebvre, et. al [14] determined the variation in resistivity of operating catalyst
 - capacitance decreased as distance into the catalyst layer increased because
 - Wetting decreases
 - Electrolyte penetration decreases

Literature Review

- J.M. Songa, et. al [28] applied AC impedance measurements (between carbon cloth and catalyst) to optimize the thickness and composition of the supporting layer
 - Optimum PTFE = 30 wt.%
- Mikhail A, et. al [26] analyzed grooming of film on the surface of the electrode with time
 - impedance of such electrodes increases in time due to the gradual growth of their thickness as well as to the change of their local characteristics
- Mariana Ciureanu, z and Hong Wang, [19] [20] CO poisoning of the Pt and Pt/Ru Gas-diffusion electrodes (GDE) is examined
 - poisoning of electrode is a function of cell voltage and CO content.
- Mariana Ciureanu, et. al. [22] determined CO tolerance for Pt and Pt50Ru50
 - CO tolerance is a function of CO concentration, Catalyst loading and temperature.

Literature Review

- Yong-Jun Leng, et. al [30] Analysed three catalysts at different temperatures and their tolerance of CO was analyzed with $H_2 + 2\% CO$
 - It was found that V critical (recoverable state) is a function of Catalyst and temperature. Higher temperature reduced V critical and also Pt Sn/C showed lowest critical voltage
- S.M. Song, et. al [34] analyzed polarization with ac impedance spectrography using mixture of O_2 with H_2 .
 - O_2 was used to introduce local anode reduction reaction at anode to take away CO poisoning while making it CO_2 .
 - Oxygen also consumed H^+ ions to produce water at catalyst and the mass transport polarizations increased.

Parameters

- The performance of PEMFC is influence by the following parameters:
 - Stoichiometric ratio
 - Humidity
 - Temperature
 - Pressure
 - Water flooding
 - Hardware issues:
 - Bipolar plate design
 - Manufacturing inconsistencies
 - Edge effect
 - Moisture content of Nafion
 - Orientation of fuel cell
 - Load requirements

Selection of Parameters

- **Pressure Variation:**

- Maximum pressure:

- The fuel cell under test, limits the maximum pressure to be 50 psig.
 - The default shutdown value of pressure in FCATS is 225 KPa
 - Since pressure surge is always expected in loading procedure when FCATS builds the corresponding flow rate to meet the input load value.
 - The maximum pressure was limited to: 200 KPa.

- Minimum Pressure:

- Since the flow field tends to drop pressure so ambient pressure at gas flow inlet is typically set to 15 KPa in order to generate a positive pressure at gas exit at all times.
 - Min : 15 KPa
 - Max: 200 KPa
 - Five pressure values selected (gauge):
 - 15 , 50 , 100, 150, 200 KPa

Selection of Parameters

- **Temperature:**

- Maximum Temperature:

- The maximum temperature of fuel cell under test limits the maximum value of 80 C.
 - The FCATS default alarm is at 80 C and shut down of 85 C.
 - The transient temperatures of reactants inlet reaching 90 ~ 100 C (beyond PEMFC manufactures maximum limit for membrane)
 - FCATS shutdown range of 85 C.

- Minimum Temperature:

- FCATS ability of minimum temperature is the ambient temperature.
 - The selected values of Anode and Cathode inlet gas temperature:
 - 30 C, 40 C, 60 C , 75 C, 80 C

Selection of Parameters

– Anode Relative humidity:

- FCATS variation observed up to 25 degree in dew point when loading is done. FCATS tends to adjust the new flow rates accordingly. In this variation is sustained for typical time of 10 minutes depending on other selected parameters.
- In order or analyze the relative humidity variation and to avoid the overlapping ranges of selected dew point temperatures, a typical difference of minimum of 25 C must be ensured when selecting valued for anode dew pt temperature.
- The selected values for dew pt and gas inlet anode:
 - Dew: 35, 50 75
 - Inlet: 50, 50, 50

Selection of Parameters

– Cathode relative Humidity:

- It is discovered that FCATS dew point temperature for cathode remains at ~ 70 C if dew point lower than this value is selected.
- FCATS 70 C dew pt limit contains about 20 C variation depending on the selection of other parameters like stoichiometric ratio.
- The Maximum gas inlet temperature already selected is 75 C limited by cell specifications and FCATS default shutdown range of 85 C.
- The selected relative humidity of Cathode as limited by FCATS ability is only 100 %.
- As dew pt $>$ Air inlet temperature

Selection of Parameters

- **Stoichiometric Ratio:**
 - The selected values for anode gas:
1.2, 2.0, 2.4, 2.5, 5.0
 - The selected values for cathode gas:
2.4, 3.0, 4.0, 5.0, 8.0

	Stoich	Set flow	Read back	Min flow	J mA/cm ²	I ampere
H2	1.2	20.9	0	50	40	2
Air	2	83.1	0.5			
H2	2.5	43.6	42.3	50	40	2
Air	4	166.2	164.6			

Test Requirements of PEMFC

- Reactants:
 - Hydrogen and Air
- Operating conditions set up:
 - Flow controller
 - Temperature controller
 - Dew point controller
 - Steam – bubbler humidifier
 - Back pressure controller
- Exhaust of H₂ and Air separately
- Condensed water drain
- Load Box
- AC impedance system
 - Sine wave generator
 - Read back and log

Assumptions

- **Assumptions:**

- Uniform effective ionic (H^+) conductivity in Catalyst Layer
- Uniform effective oxygen diffusion coefficient in Catalyst layer
- Negligible electronic resistance through out the electrode.
- Uniform porosity on the backing layer
- Uniform double layer capacitance with in the catalyst layer
- The catalyst layer is treated as an effective homogeneous medium, whose performance is characterized by specific proton conductivity.
- Ohmic losses in the well connected electronic conductor phase are neglected, so that the carbon phase will be considered equipotential.

ElectroChem: PEMFC FC50-01SP

Catalyst	Pt-supported on C	20% wt of Pt on Vulcan XC -72 R
	Loading	1mg Pt/cm ² , Hot pressed into Nafion 115
Electrode		Anode and Cathode are identical
		Catalyst is supported on Carbon Paper
	PTFE content	30%
	Active area	50 cm ² or 7.1 cm per side
	Thickness	8 mils
	Porosity	78%
Membrane	Nafion	115
	Size	50 cm ² or 7.1 cm per side
	Thickness	1 5 mils
MEA		Catalyst on GDL
		Hot pressed onto Membrane material
		Hydrophobic carbon paper to support 20% wt Pt based electrode on Nafion 115.
Monopolar plate	Materials	Graphite blocks
	Flow Field	Surpentine
Current collector		Gold plated with test jacks
End Plates		Aluminum with securing 12 bolts
Gaskets	Material	Silicon rubber
	Thickness	10 mils
Operation conditions	Temp + Humidification	61 -80 C
	Temp dry	61 - 75 C
	Maximum Pressure	50 psig

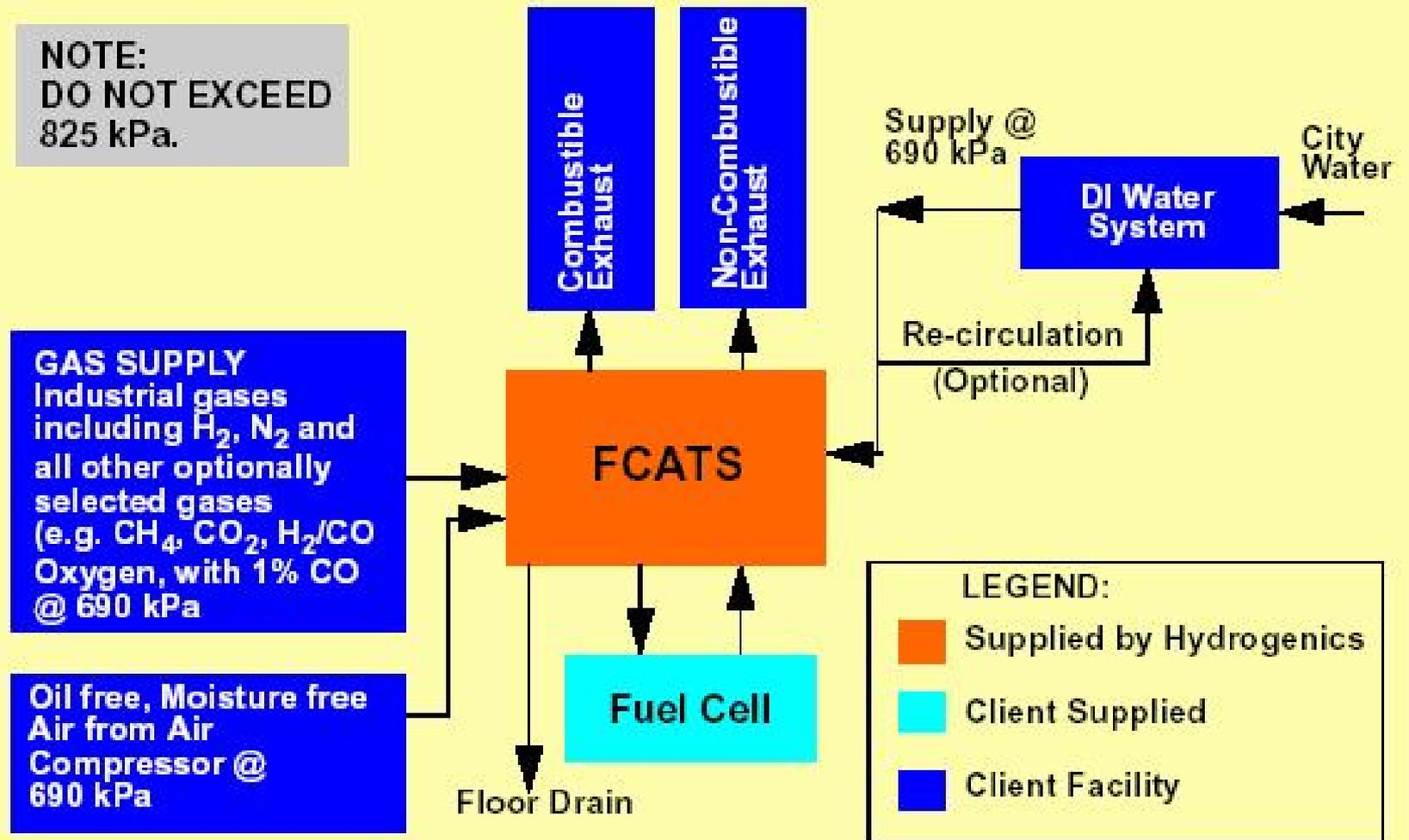
Fuel Cell Automated Test Station (FCATS)

- FCATS –S 800
 - Monitoring & Control of Fuel cell or Stack
 - Software:
 - Hyware:
 - Monitoring & Control
 - Acquire & log parameters
 - Safety verification
 - HyServer:
 - Hardware communication
 - HyAL
 - Automation language for script development



FCATS Installation

NOTE:
DO NOT EXCEED
825 kPa.

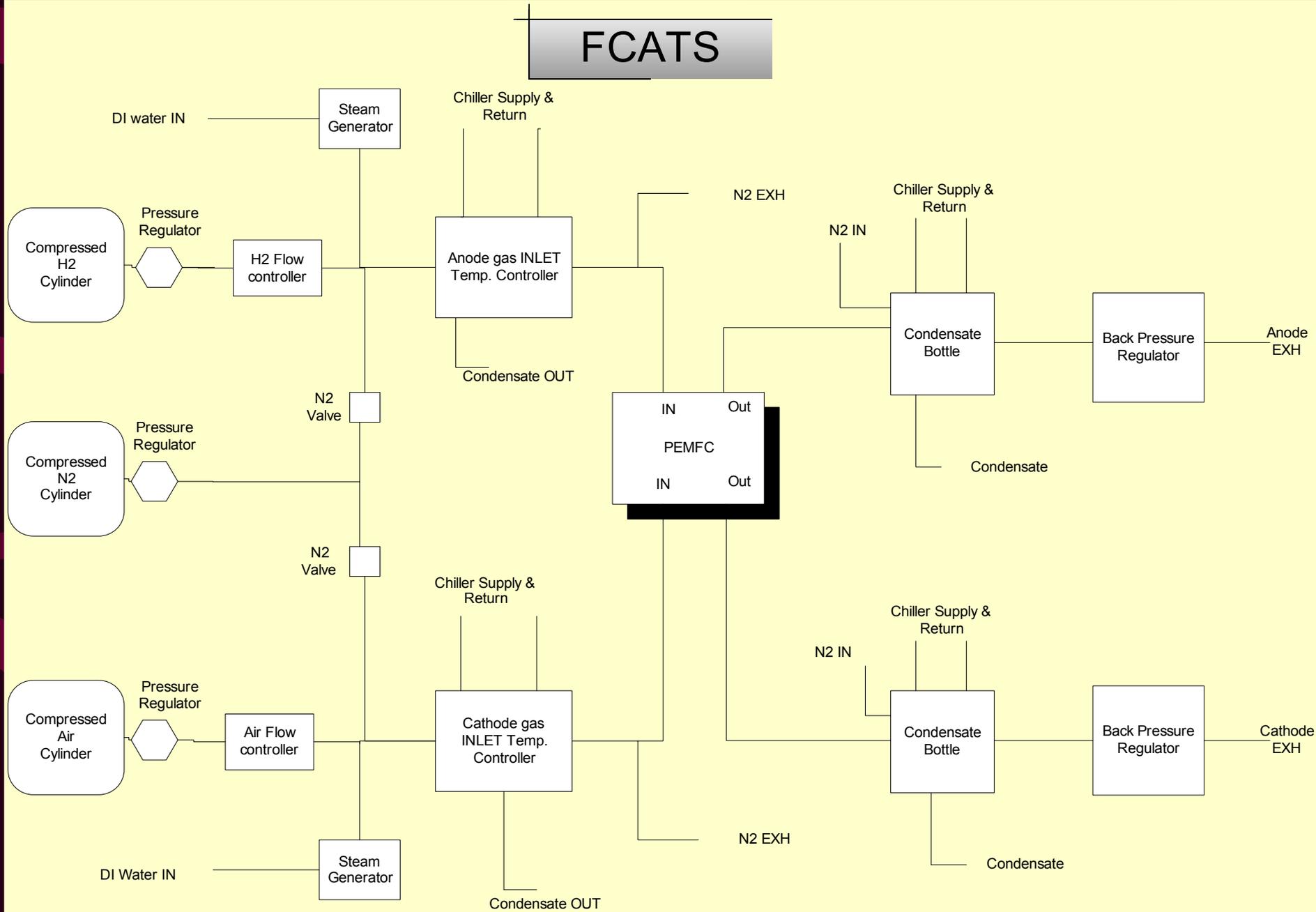


Facility / FCATS-S Connection Block Diagram

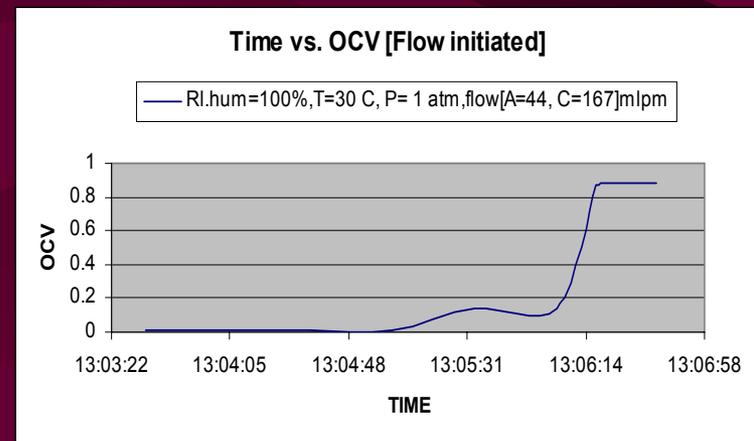
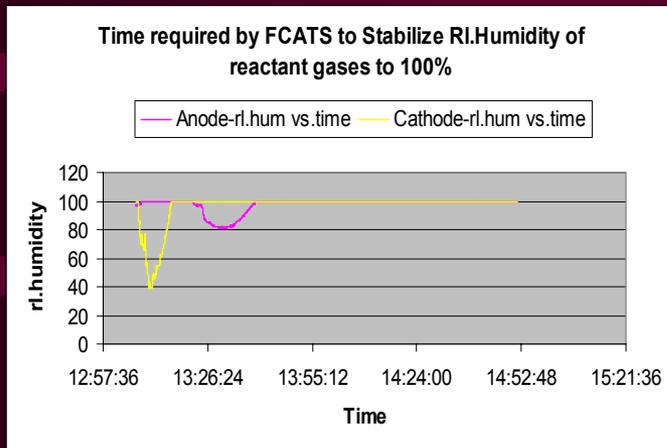
FCATS-Monitored Parameters

- All read back and set points for Anode and Cathode:
 - Load
 - Current
 - Voltage: min, max. and mean
 - Ac perturbation
 - Hz
 - Constant current shunt value
 - Relative Humidity
 - Dew point
 - Steam Temperature
 - Temperature
 - dew pt
 - H2 and Air gas inlets and outlets
 - Stack control
 - Pressure
 - FCATS facility: DI water, Chilled water, H2, Air & Nitrogen
 - Fuel cell inlet pressures
 - Differential Pressure
 - Pressure drop b/w anode and Cathode in.
 - H2 and Air Flow Rates
 - Stoichiometric ratio
 - Minimum flow (mA/cm²)
 - Stack flow both sides
 - Equivalent flow
 - Load Flow

FCATS SYSTEM BLOCK DIAGRAM



FCATS Response to set parameters



FCATS Accuracy-steady state

Flow:

+/- 1% of the full scale flow with a 1/20 turn down ratio

e.g 0-4000 mlpm: 1% = 40 mlpm

1/20 turn down = 5% of maximum. Any flow below 200 mlpm is not guranteed to be accurate.

Temperature:

+/- 2 degree Celsius

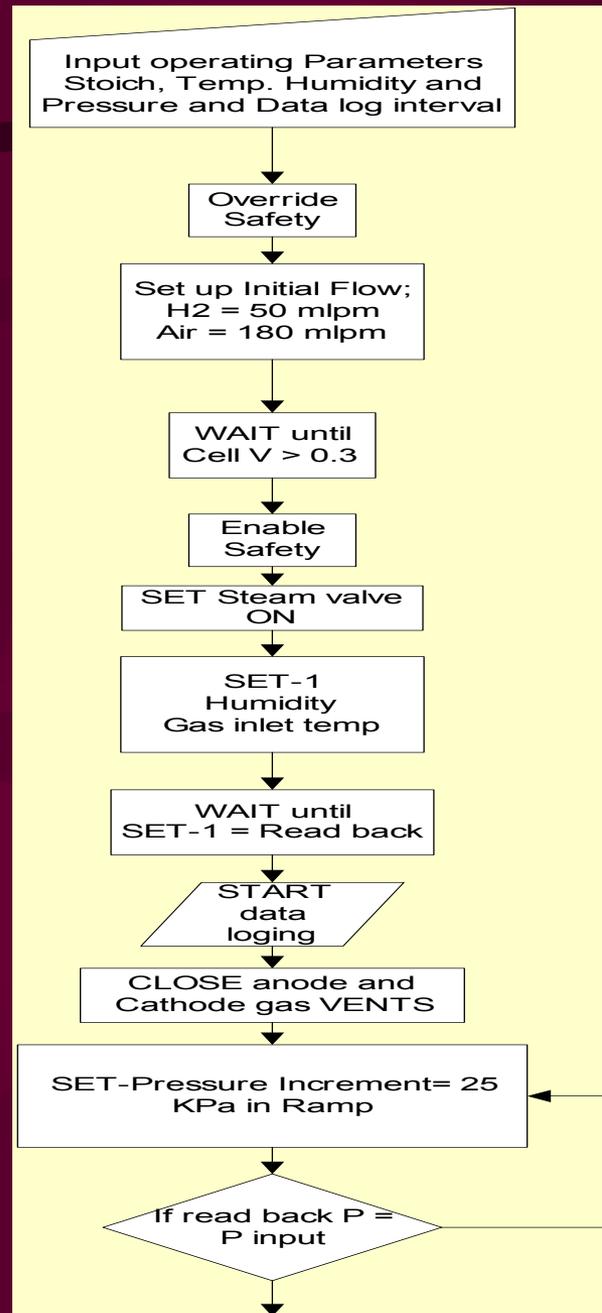
Pressure:

+/- 3 KPa

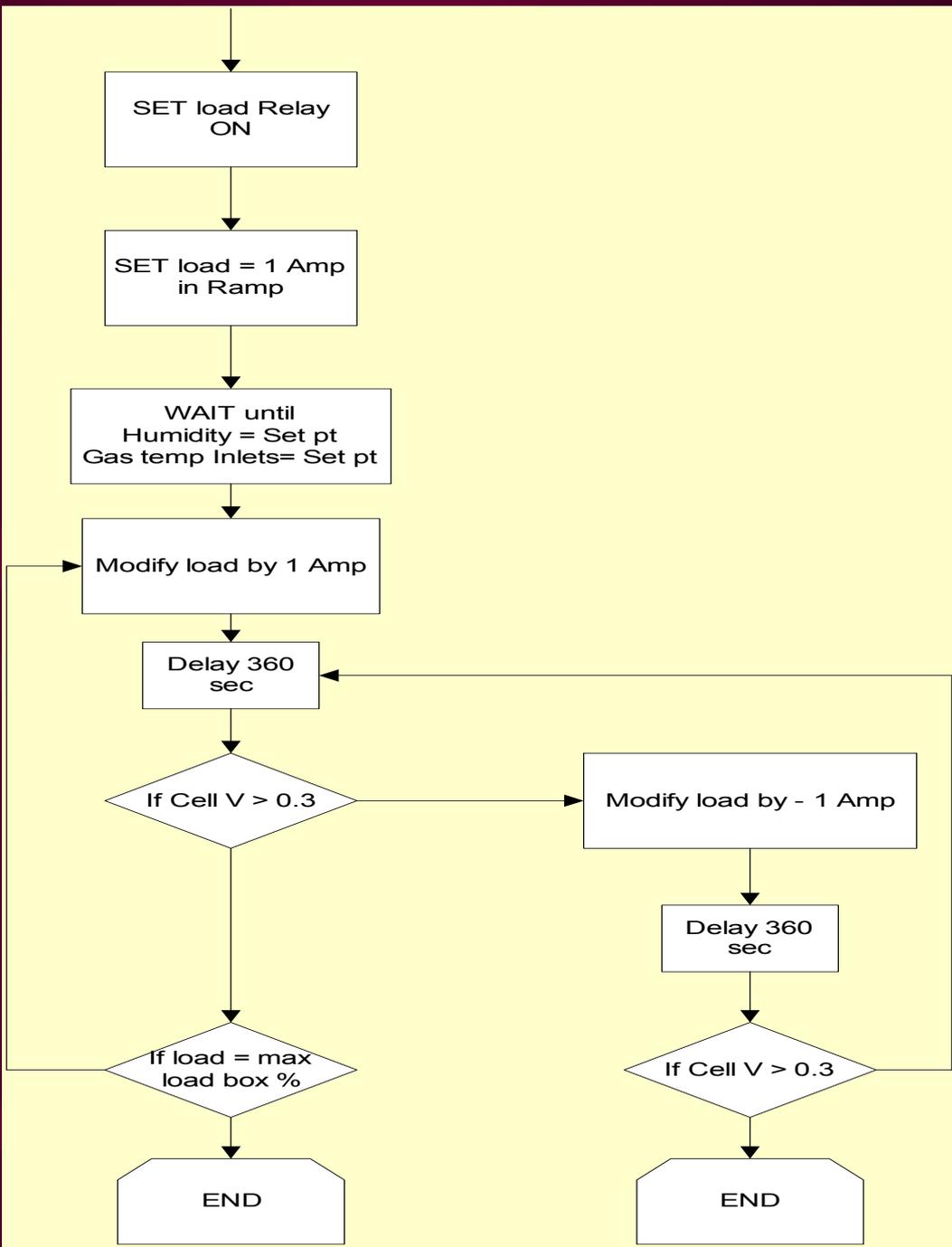
Script Flow Chart-1

Script:

- 1) Ensures all other operating conditions remains constant.
- 2) Constant time for steady state
- 3) Prevent unnecessary data log
- 4) Unattended operation



Script Flow Chart-2

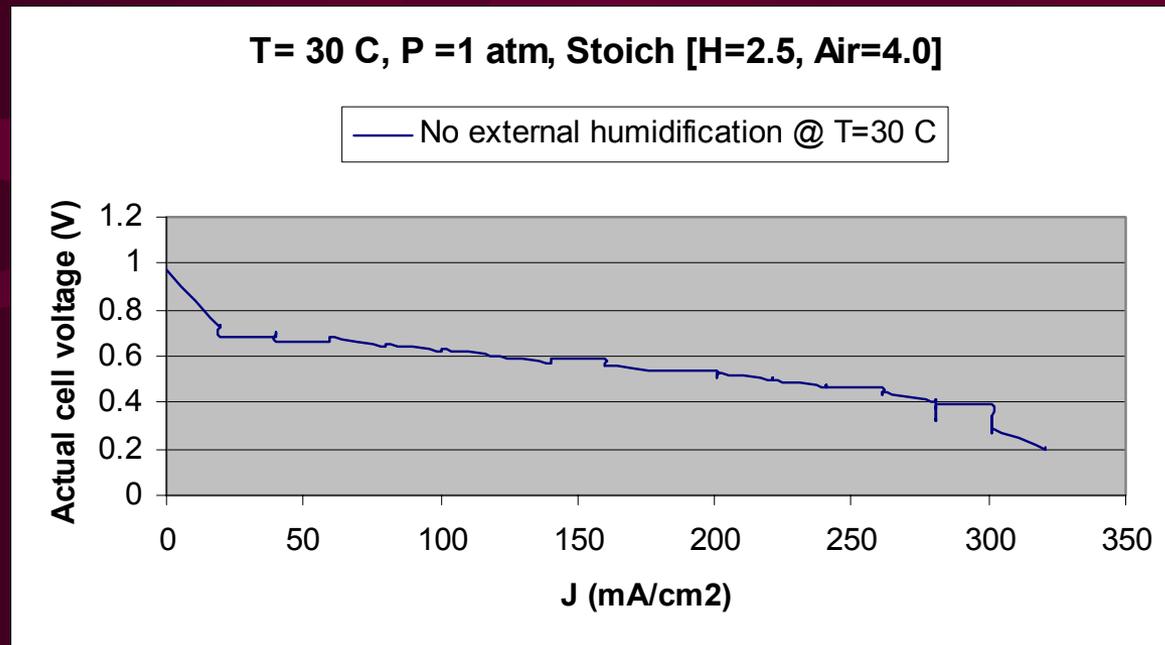


Results and Discussion

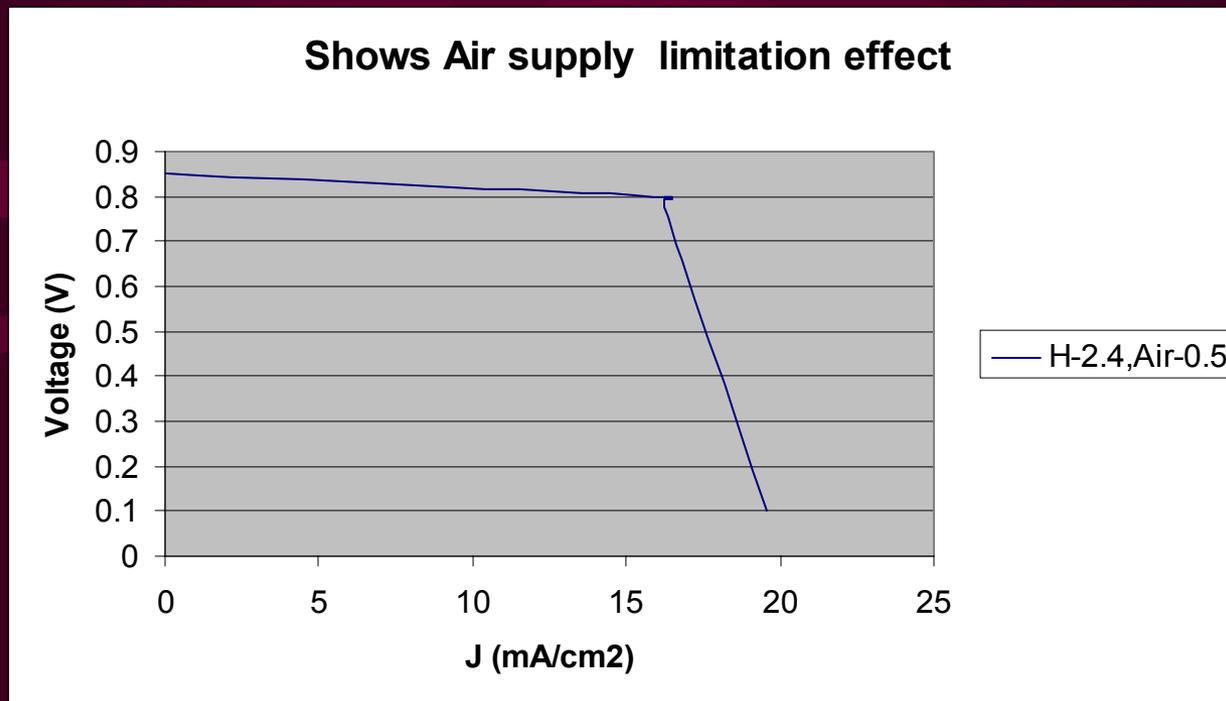
Water Removal Techniques

- **Cell Orientation**
 - 45 inclined towards gas outlet ports for complete drain
 - Flow field design
- **Cell Shaking**
 - Jerking manually
- **Anode Water Removal**
 - Back Diffusion
 - When water concentration Cathode $>$, Anode $<$
- **Hydraulic Permeation**
 - Pressure difference between cathode and anode gas inlets.
 - Anode pressure less than Cathode.

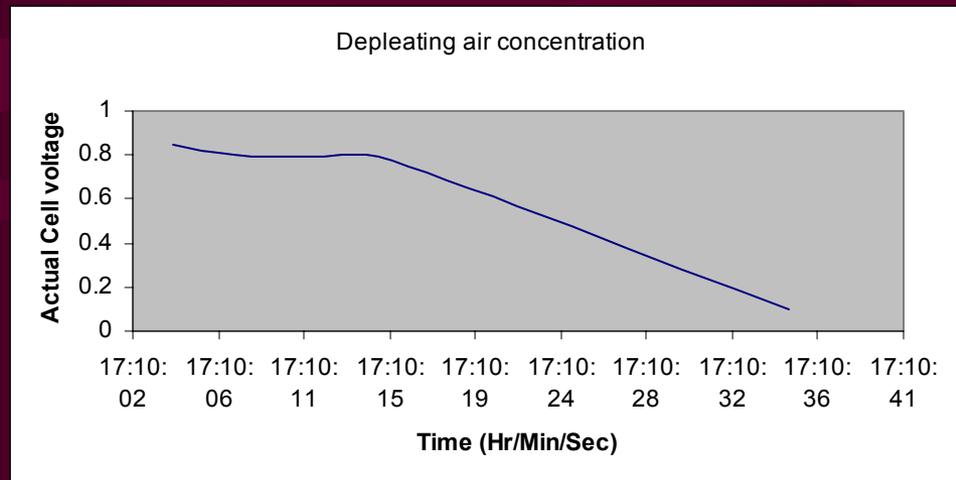
Ohmic Polarization



Reactant Limitation effect



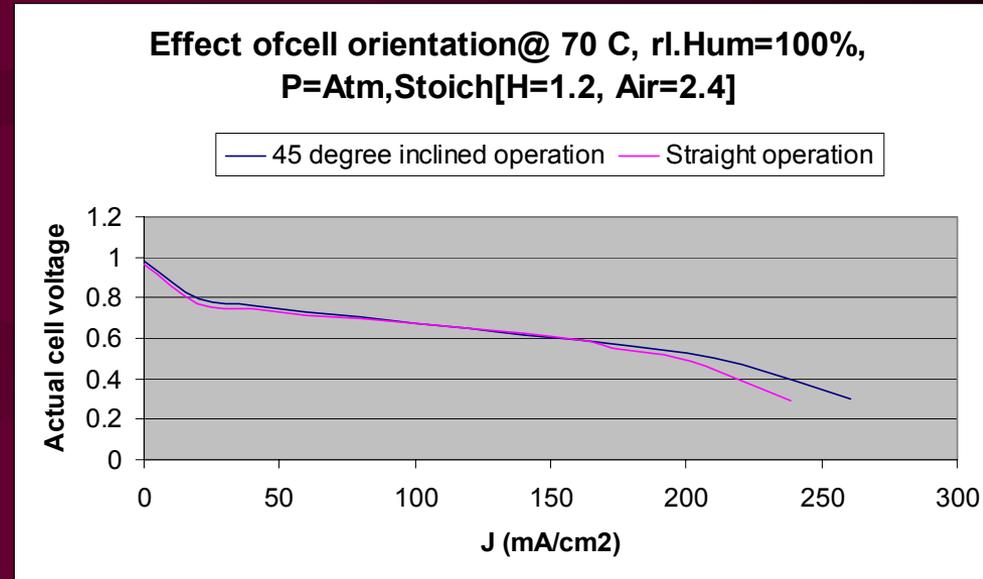
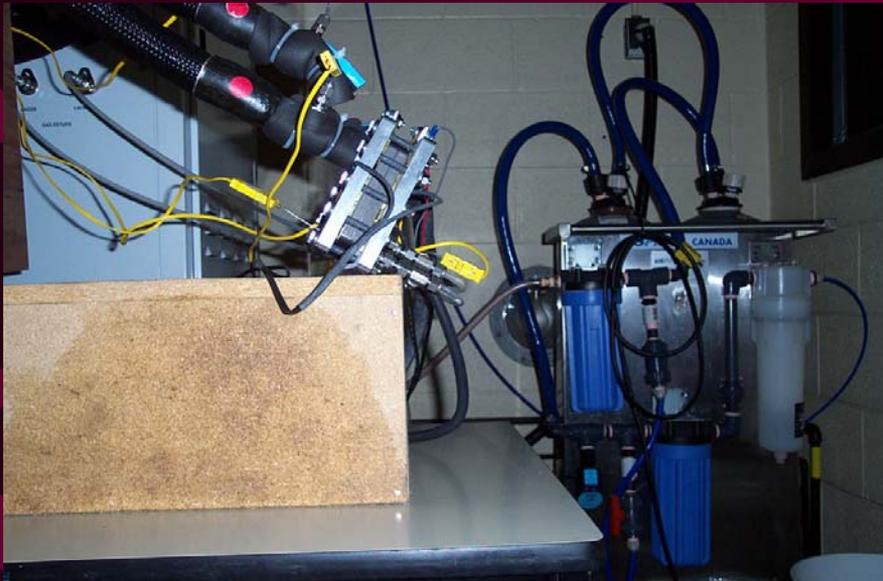
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[..\RESULTS\Stoichiometry ratio\No use\Air-Stoich\(0.5\)\\(H-2.4,Air-0.5\)\\(H-2.4,Air-0.5\).xls](#)

Cell Orientation

Cell Orientation Effect- inclined to 45 towards gas outlet ports



[_RESULTS\Temp-variation\no water removed\comparison steady 60 vs 70.xls](#)

Open Circuit Volts

- OCV

= f (time)

- J_0

- recovery method

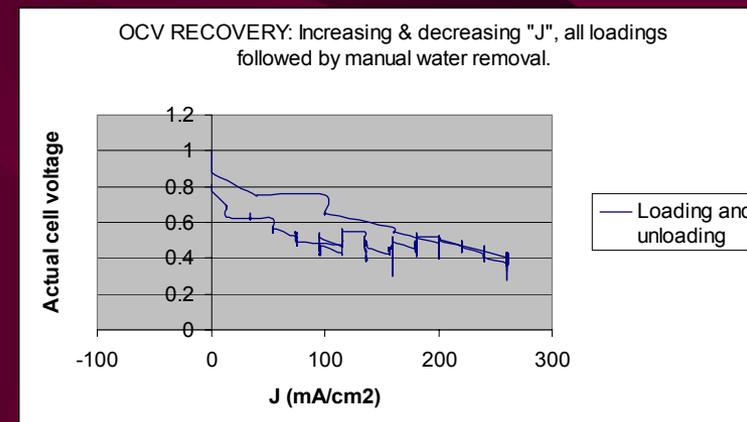
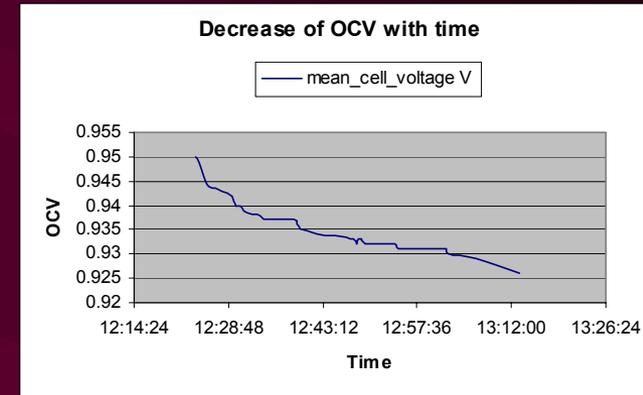
= f (outlet pressure)

- Impurities

- Positive Pressure 15 KPa

ADDED

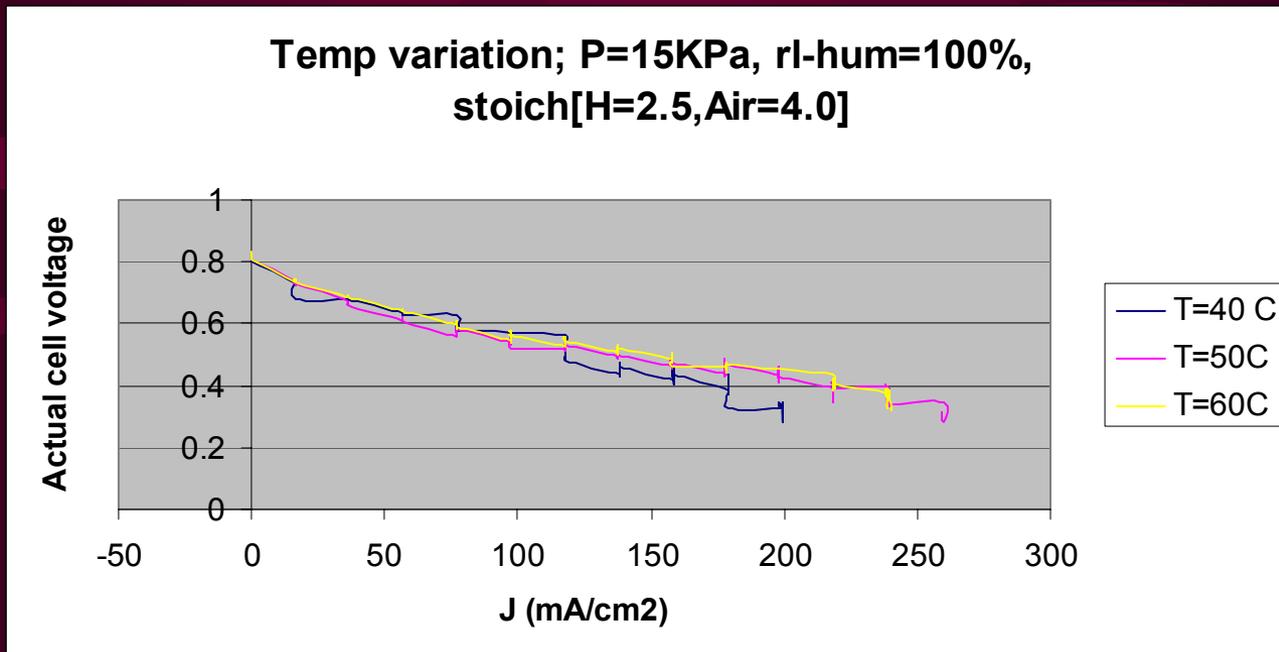
	Dew	Dew - SET	In	In-SET	P	Stoich
Anode:	42	30	32	30	15	2.5
Cathode:	89	30	76	30	15	4



Temperature Variation

Cell Orientation- 45 inclined

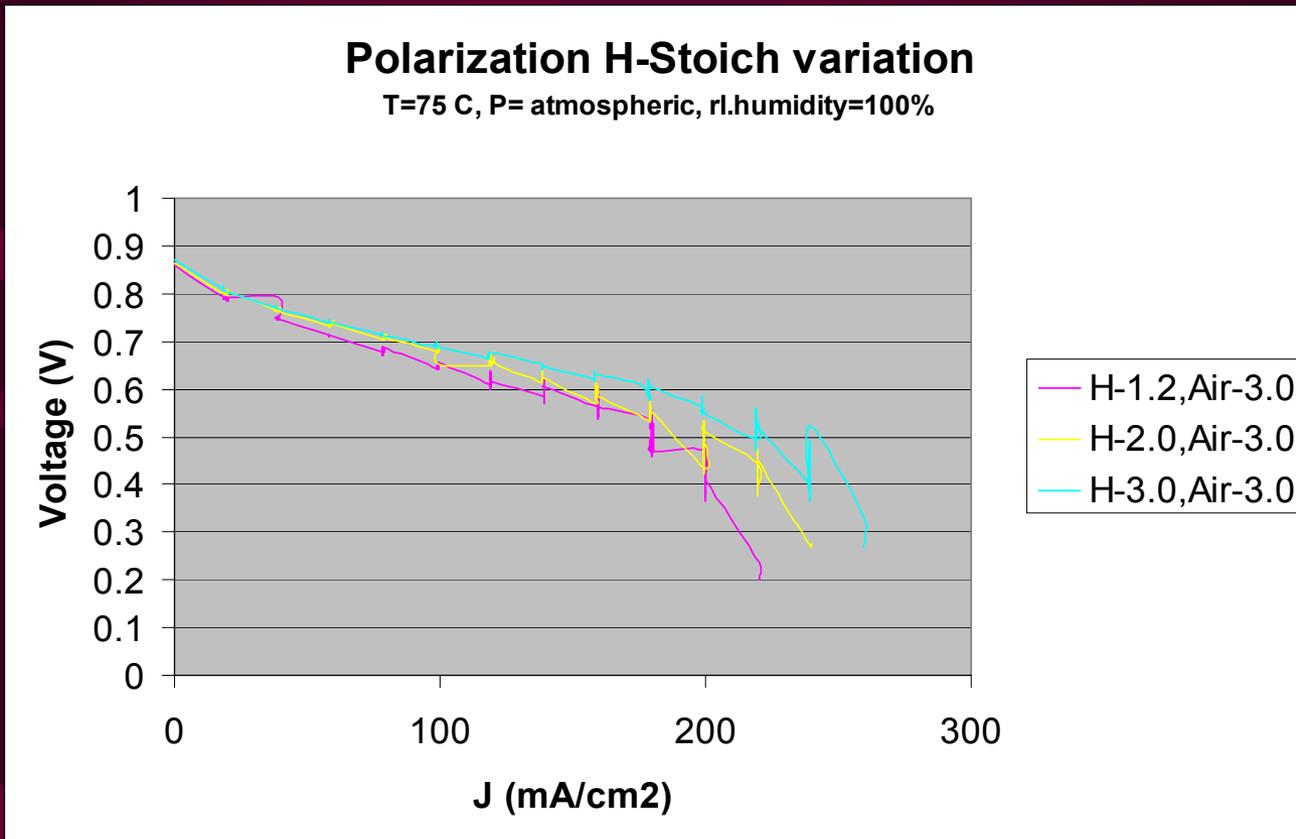
Cell Shaking- each current increment



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H₂ Stoichometric variation

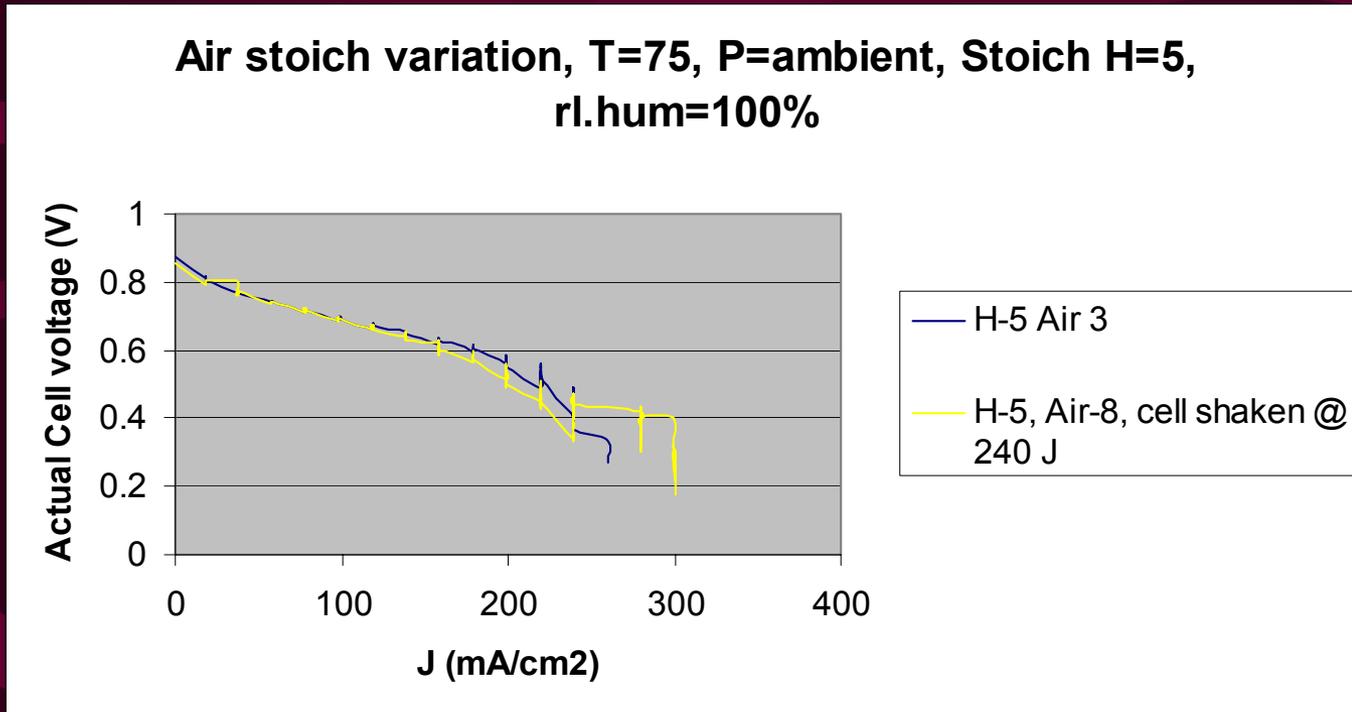
Cell Orientation- 45 inclined



Air Stoichometric variation

Cell Orientation- 45 inclined

Cell Shaking- **ONLY** for stoich: H-5, Air-8 @ 240 mA/cm²

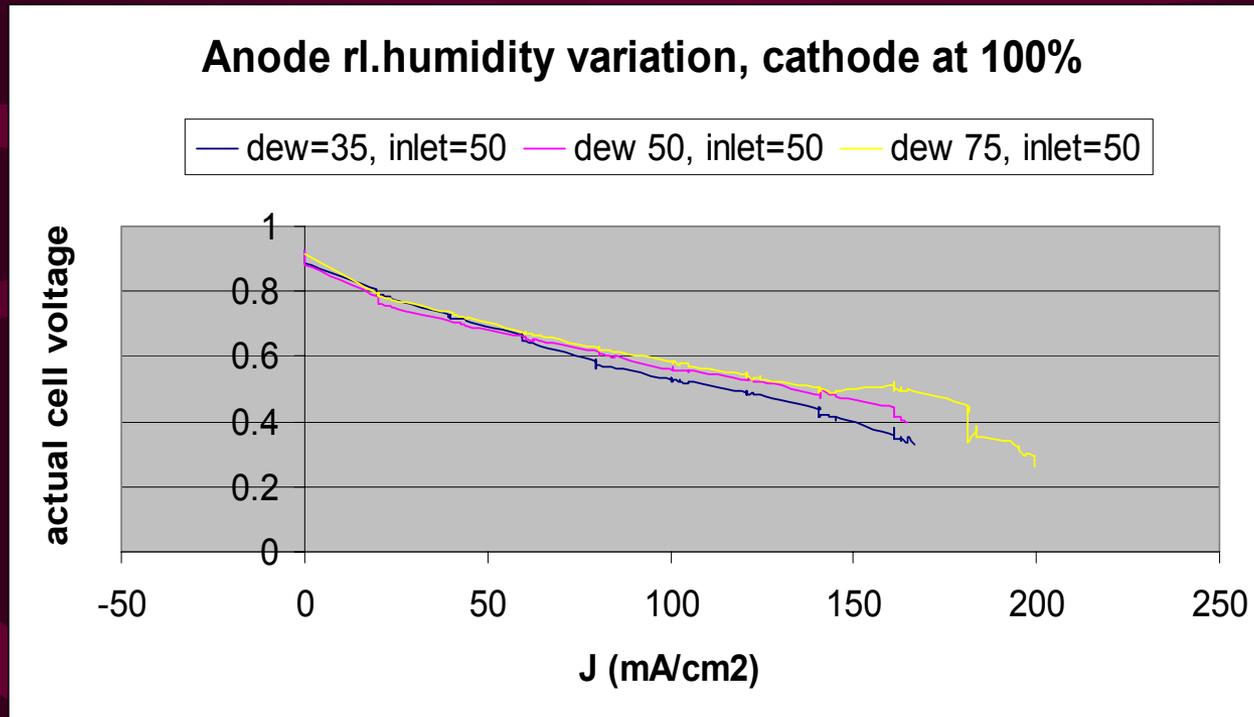


Humidification Variation

Cell Orientation- 45 inclined

Cell Shaking- At each current increment

Anode water removal – cathode side saturated with water vapor



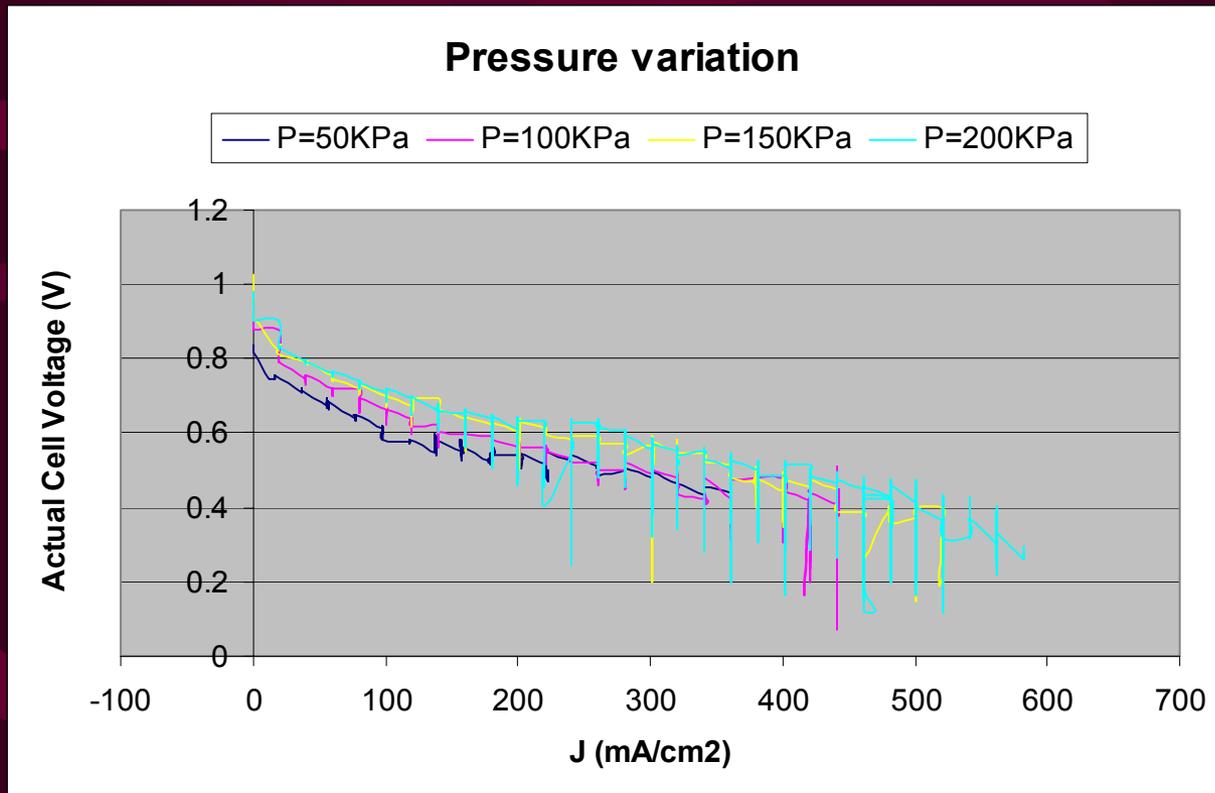
Pressure Variation

Cell Orientation- 45 inclined

Cell Shaking- each current increment

Anode water removal – cathode side saturated with water

Hydraulic Permeation – Anode pressure. 10 KPa < Cathode pressure.



AC Impedance Spectroscopy:

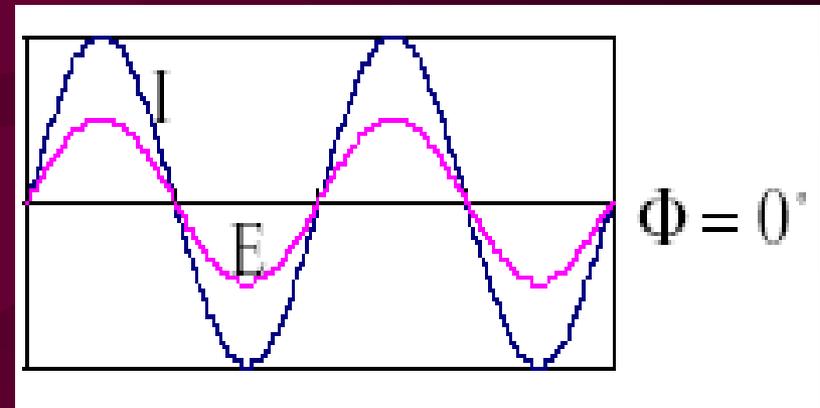
- AC impedance gives information about following as these change with load;
 - Membrane resistance
 - Kinetic and mass transport
 - Overall mechanism of operation
- Method
 - Application:
 - Small perturbation of the potential or the current. (constant voltage or constant current)
 - A single sine wave with different frequencies
 - Result determination by;
 - magnitude of the impedance
 - phase shift.
- Spectroscopy:
 - Parameters are measured as a function of the frequency of the applied perturbation.

Theory

- Ohm's law:
 - Relation b/w potential and current
- DC
 - $E = i R$
- AC-signals
 - $E_{ac} = I_{ac} Z$
 - where Z is the impedance

Fundamental Phenomena

- Pure resistance:
 - $Z = R$
 - $\Phi = 0$
- *Interpretation:*
 - Parts of a fuel cell resemble a resistance, e.g Membrane



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Basic elements

- Capacitor:
 - Interface:
 - Backing layer-Membrane
 - electrical double layer capacitance
 - Phase:
 - $\Phi = -90^\circ$

- PEMFC: R + C in series



- Inductor:
 - Catalyst
 - $fB(t) = L.i(t)$
 - Pt
 - $\Phi = +90^\circ$

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Resistor	Capacitor	Inductor
 R	 C	 L
Resistance	Capacitive reactance	Inductive reactance
$V_R/I = R$	$V_C/I = X_C = \frac{1}{\omega C}$	$V_L/I = X_L = \omega L$
V and I in phase	V lags I by $\pi/2$	V leads I by $\pi/2$

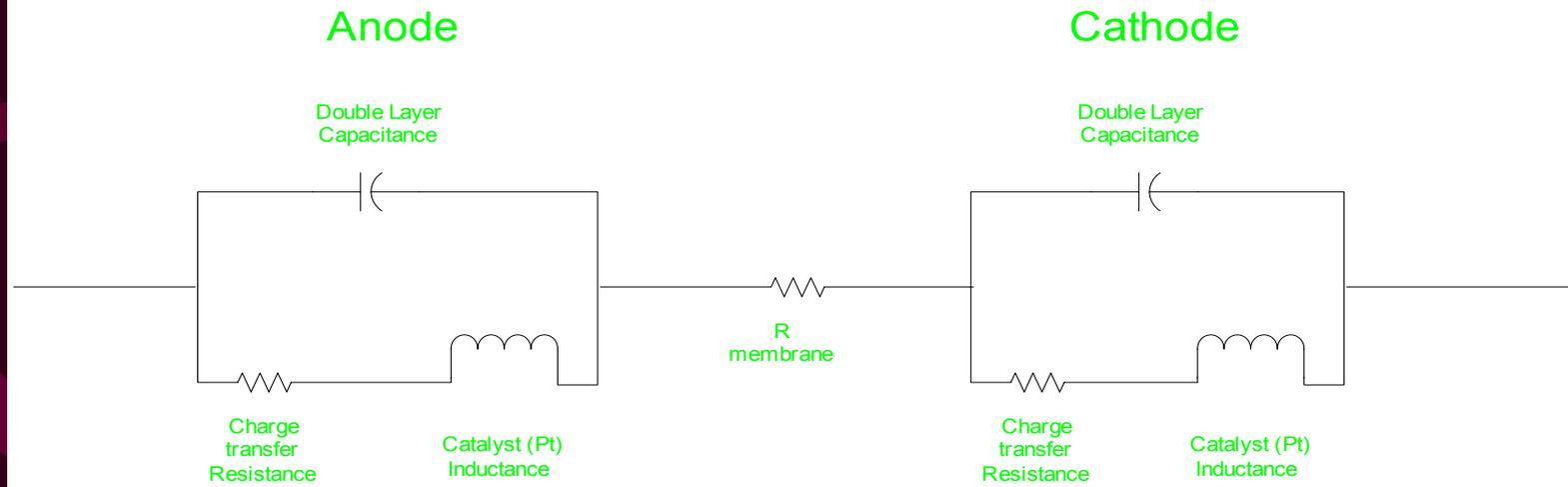
Impedance Plot

- R membrane: A resistance to the H^+ conduction offered by the membrane acts as a pure resistance
- C double layer capacitor: between the interface of membrane and Catalyst-GDL.
- L inductance corresponding to the Catalyst (Pt) activity referring adsorption process.
- Rct: Catalyst (Pt) activity, resistance of charge transfer mechanism. This resistance for electrochemical reaction to occur acts as a pure resistance in the impedance circuit and is in series with catalyst (Pt) adsorption process.

Equivalent Circuit

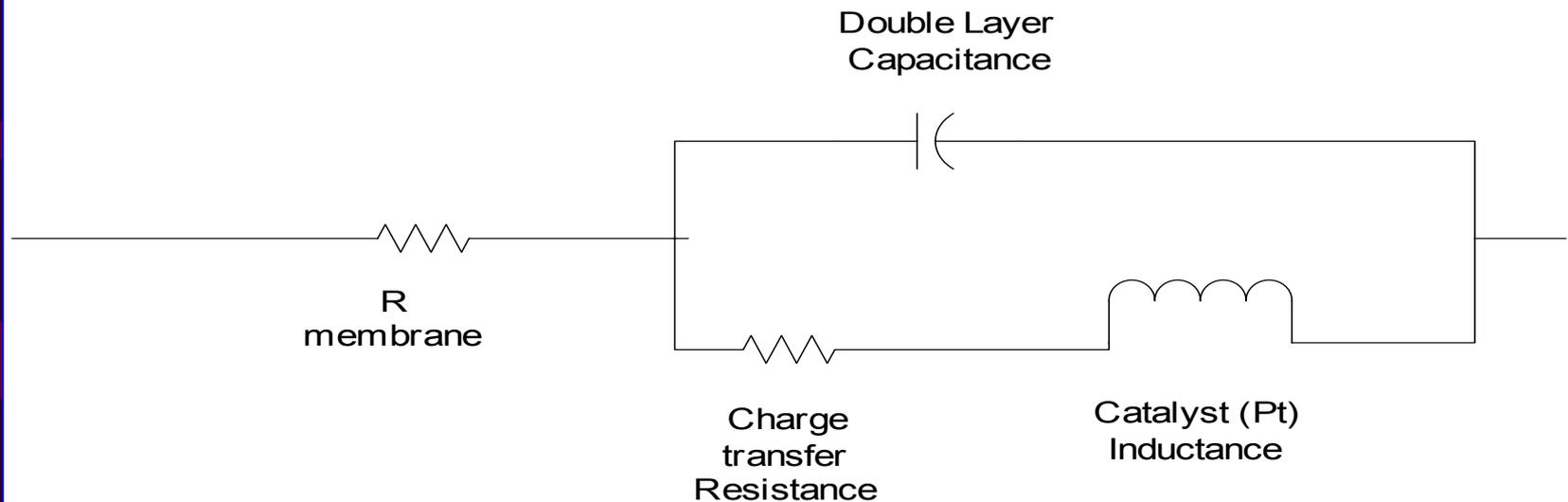
- PEMFC

PEMFC Equivalent Elements Circuit



Circuit for Analysis

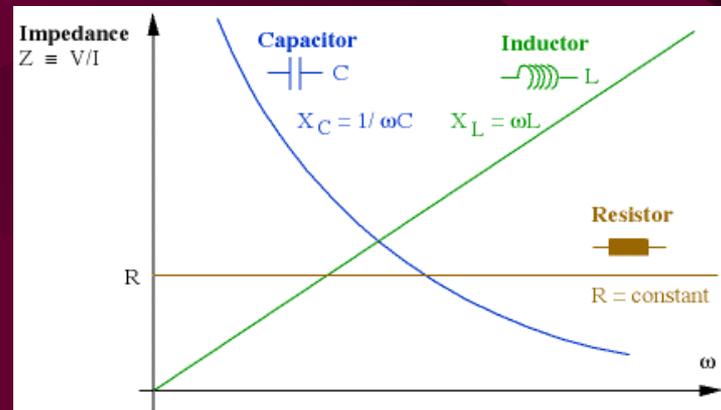
PEMFC Equivalent Elements



Application to PEMFC

- When electrochemical reaction occurs
 - charge transfer resistance R_{ct} in parallel to double layer appear
- At high frequencies:
 - phase angle of 0°
 - Magnitude of the $Z = R$ membrane
- At low frequencies:
 - Impedance will be frequency-dependent and the phase angle will be 90° .
- Intermediate frequencies
 - Phase angle will have a value between 0° and -90°

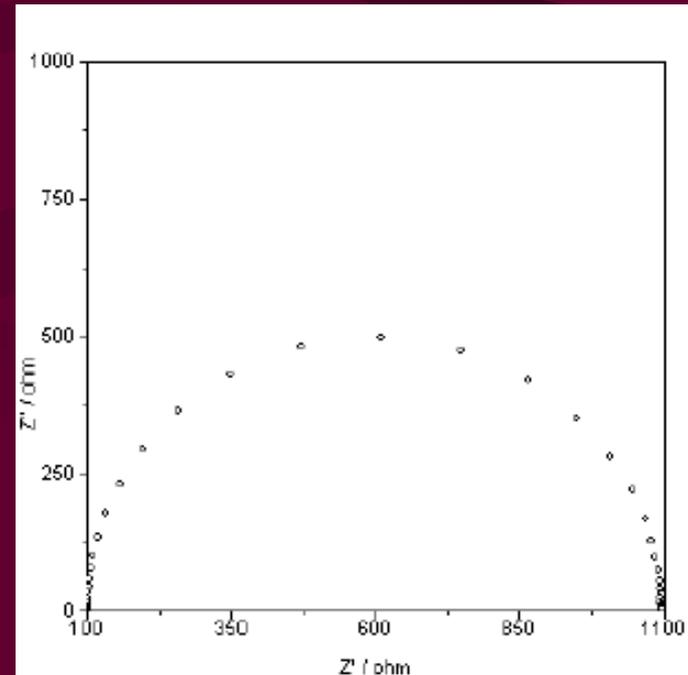
Equivalent circuit for a simple electrochemical cell



Impedance Plot

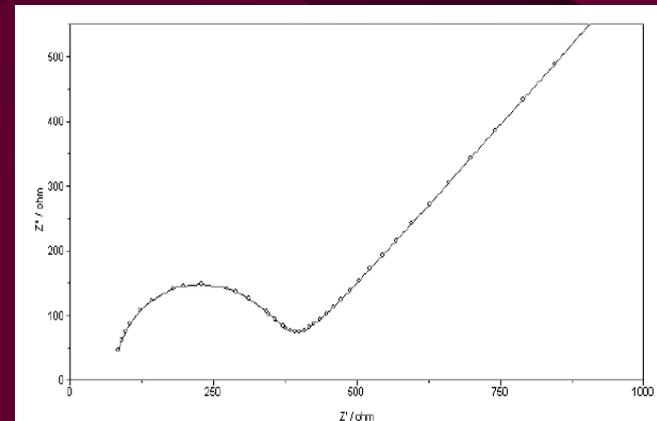
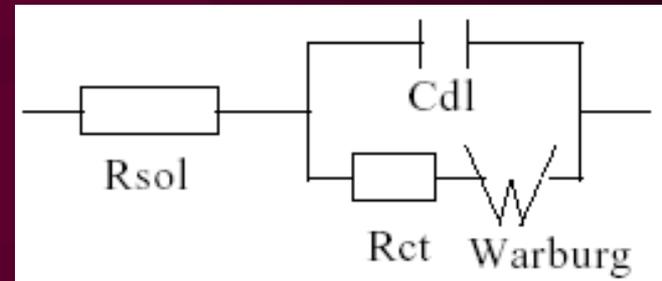
- At high frequencies:
 - impedance is determined by the solution resistance R_{sol} .
- At very low frequencies:
 - impedance is equal to $R_{sol} + R_{ct}$. Both limits show a phase shift equal to 0° .
- Intermediate frequencies:
 - The cell impedance is influenced by the value of the double layer capacitance C_{dl} .

- **Nyquist Plot**



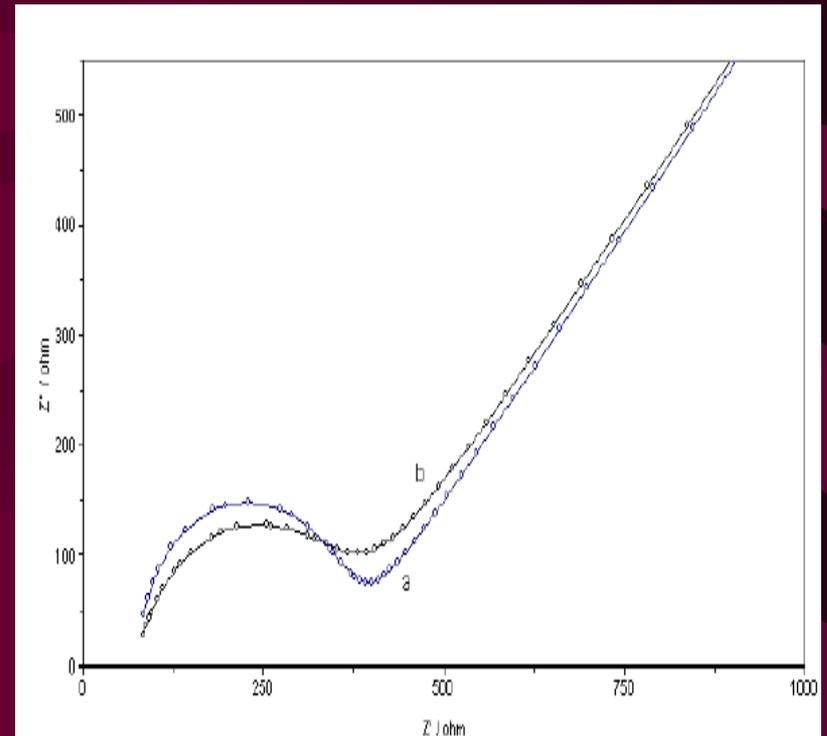
Modifications

- Randles' circuit:
 - The Warburg element
 - an angle of 45° in the lower frequency region.
 - Solution resistance,
 - Double layer capacitance,
 - Charge transfer resistance
 - Warburg impedance



Deviations

- Constant Phase Element (CPE):
 - Phase angle of less than 90° .
The impedance of such a non-ideal double layer
 - $Z = -j / (\omega Q)^n$.
 - For ideal electrodes, Q is equal to Cdl and $n = 1$.
 - Usually $n = 0.5 - 1$.
 - This effect is supposed to be due to surface roughness or caused by heterogeneity of the surface.



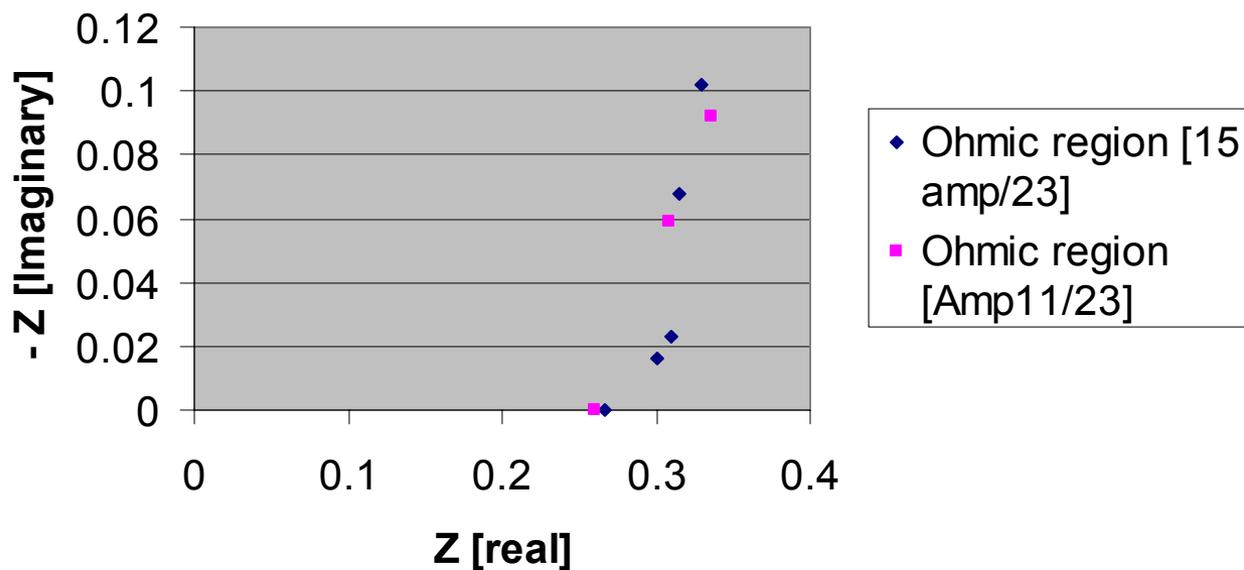
Method of Analysis

– Method:

- Impedance measurements are analyzed by fitting the impedance spectrum to an **equivalent circuit** that best fits.
- To **determine the values of its elements**.
- Commonly used elements for creating equivalent circuits are:
 - R: resistance
 - C: capacitance
 - L: Inductor
 - Q: constant phase element
 - W: Warburg element (diffusion element)

Result of Actual Measurement

Nyquist Plot, V cell=0.56 v, P=100 KPa,
Temp=50 C , Stoich: [H=2.4, Air=4.0]



Summary

- The water flooding produces inconsistency.
- The optimum cell orientation 45 degree inclined.
- Cell shaking at each load increment.
- Both the techniques showed consistent results for up to current density of 300 mA/cm².
- Variation of Cathode humidification was not possible due to test equipment problem.
- Fully saturated water vapor developed back diffusion.
- Water removal was possible with pressure difference between the Cathode and Anode inlet gases.
- In combination, produce consistent results up to limiting current density of 600 mA/cm².
- Performance =f (OCV) and recoverable.
- AC impedance result revealed insufficient membrane hydration despite 100 % relative humidity of anode and Cathode gases.

Conclusion

- **Conclusions:**

- Orientation of fuel cell leads to improve cell performance in ohmic and mass transport regions.
- Cell shaking improved overall cell performance
- Performance = f (ocv).
- OCV recoverable and hence the cell performance.
- Cell shaking improved performance.
- Fully saturated air improved Cell performance.
- Anode gas pressure 10 KPa lower than Cathode improved limiting current density.
- At fully saturated air flow at Cathode showed less than required hydration in membrane

Recommendations

- **Recommendations:**
 - Cell shaking may be done before taking any measurement.
 - OCV may be regained before conducting any test.
 - FCATS dew set point problem may be rectified to conduct tests on Cathode relative humidity variation.
 - FCATS may be upgrade to include more frequency points in order to get complete impedance spectrograph.
 - The effect of operating conditions may be explored with AC impedance to optimize the performance of PEMFC.
 - Relation of OCV to pressure may be investigated for further studies.
 - A filter in chiller water line of FCATS may be installed to prevent potential problems in cooling circuit due to supply line deposits and contamination.

Questions?