


PEM Fuel Cell Diagnostics
as Design Tool

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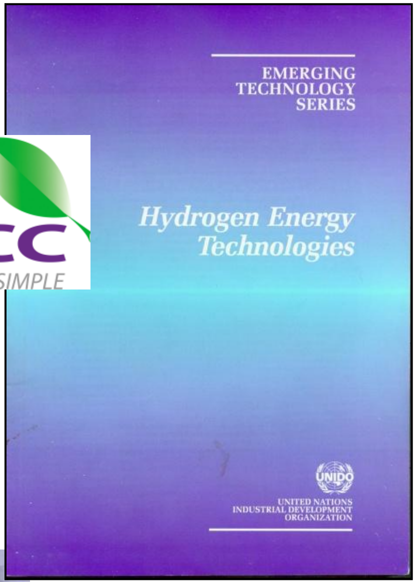
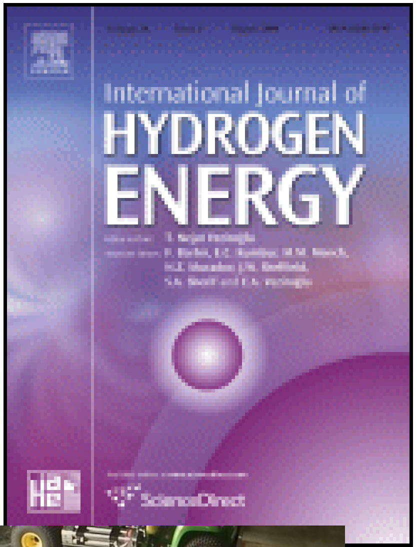
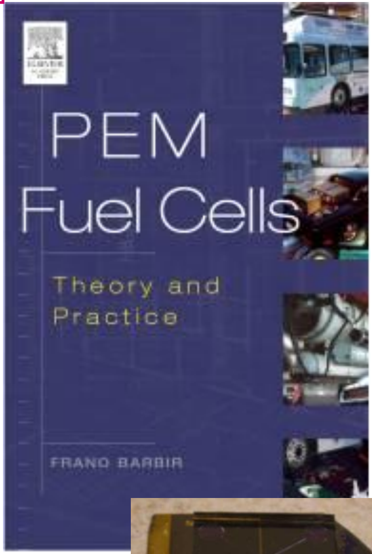
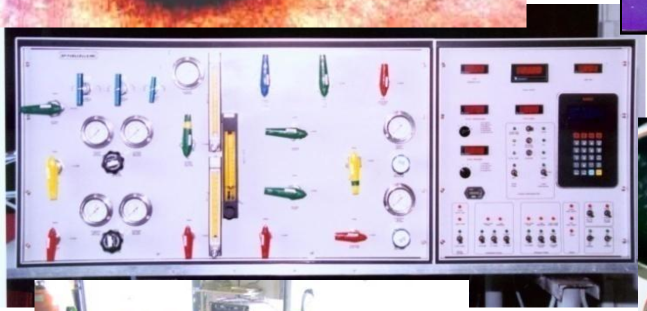
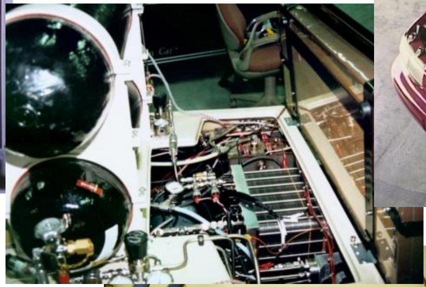
Frano Barbir
Pictorial Resume

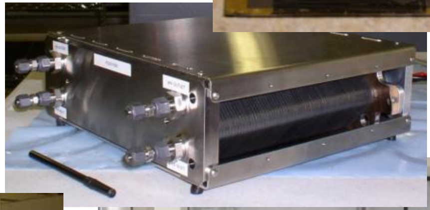


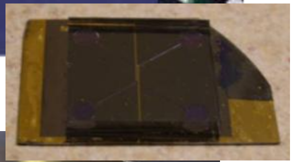












Diagnostic(s)

noun

the art or practice of diagnosis

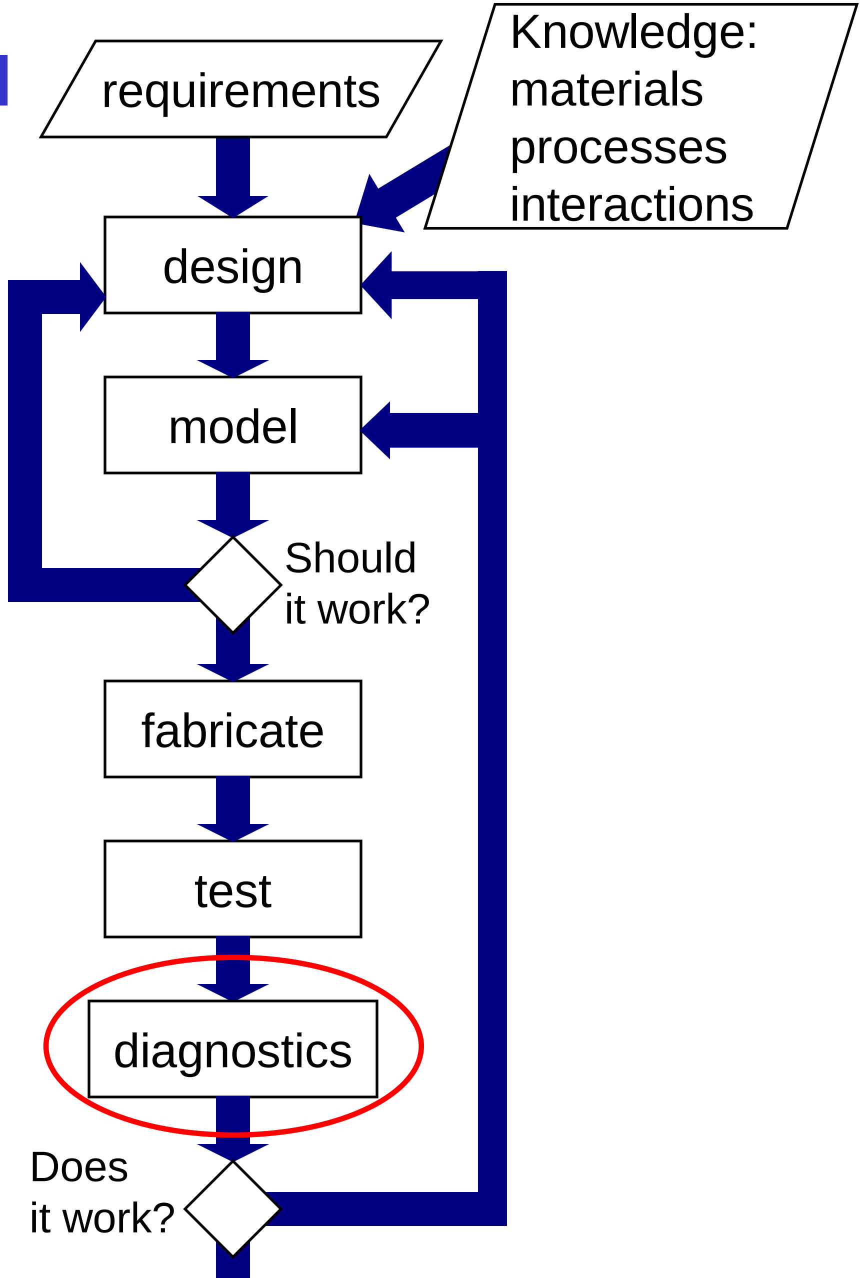
Diagnosis

noun

Investigation or analysis of the cause or nature of a condition, situation or problem

Purpose of Fuel Cell Diagnostics

- Diagnostics in fuel cell development process



requirements
Knowledge:
materials
processes
interactions
design
model
Should
it work?
fabricate
test
diagnostics
Does
it work?

Purpose of Fuel Cell Diagnostics

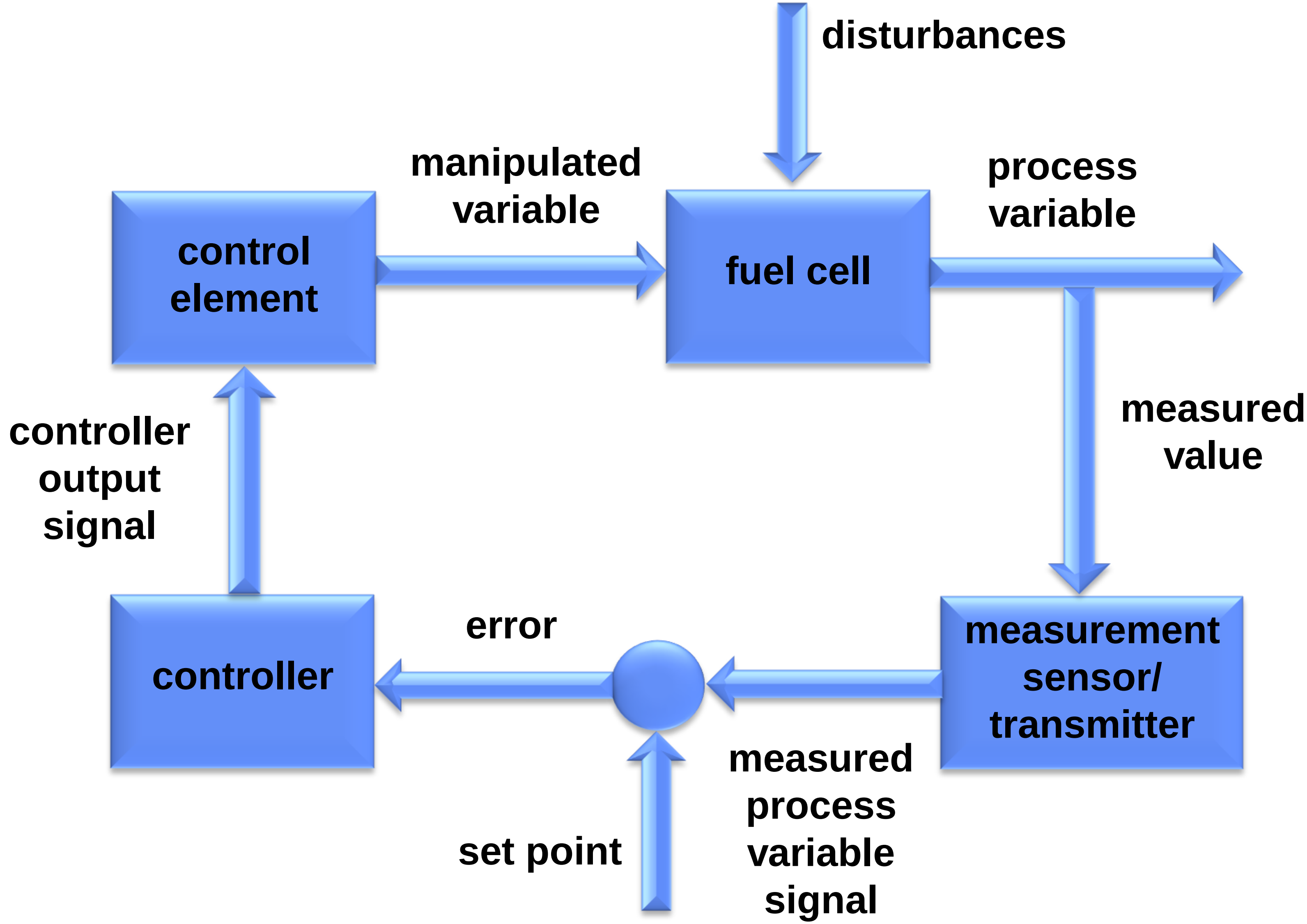
- Diagnostics in fuel cell development process

- Diagnostics in control development process

Purpose of Fuel Cell Diagnostics

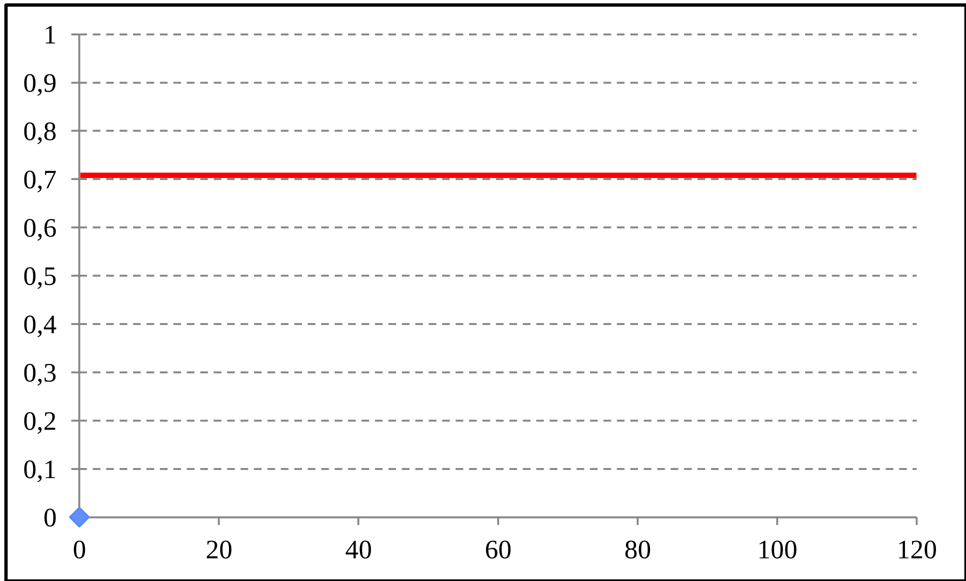
- Diagnostics in fuel cell development process
- Diagnostics in control development process
- **Diagnostics in operation**

Generic Control Loop



Fuel Cell Diagnostic Methods

- **Observe**
  (voltage/current, pressure drop, temperature)



Fuel Cell Diagnostic Methods

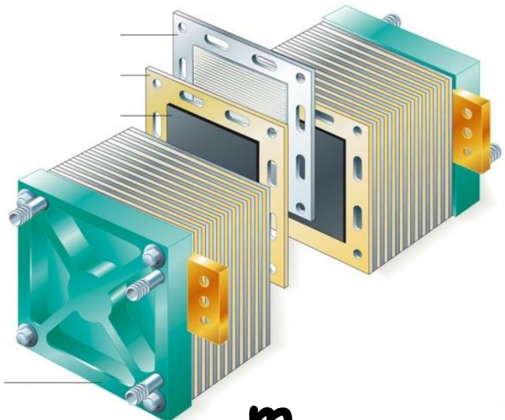
- **Observe**
  (voltage/current, pressure drop, temperature)
- **Change a parameter and compare**

First fuel cell law:

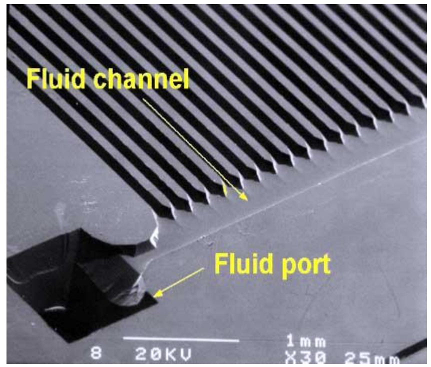
One cannot change only one parameter in a fuel cell — change of one parameter causes a change in at least two other parameters, and at least one of them has an opposite effect of the one expected to be seen.

F. Barbir, *PEM Fuel Cells Theory and Practice*, Elsevier/Academic Press, 2005

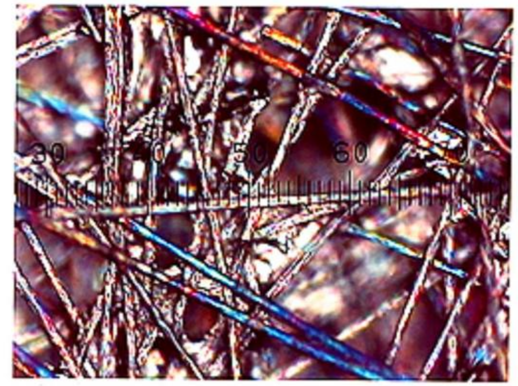
Fuel cells: Problems at different scales



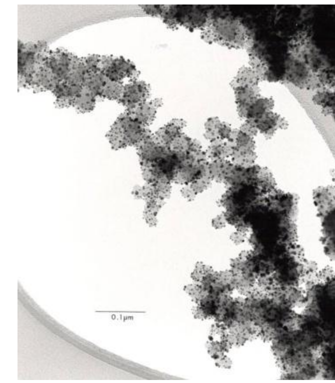
m



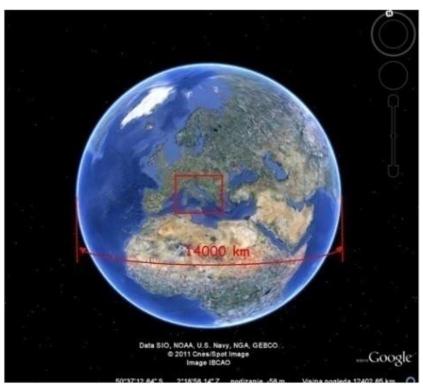
mm



μm



nm



12700 km

12.7 km

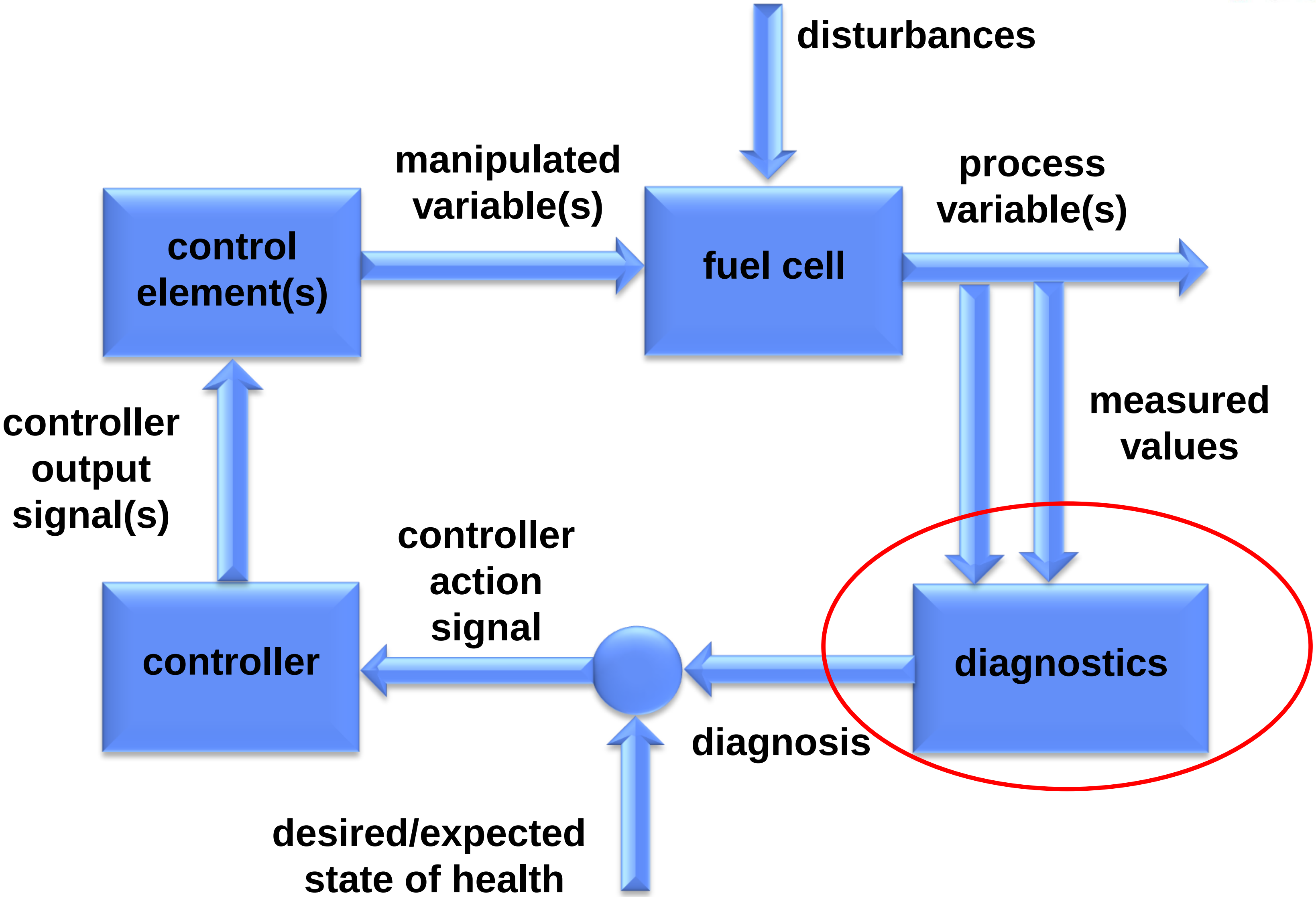
12.7 m

12.7 mm

Fuel Cell Diagnostic Methods

- **Observe**
  (voltage/current, pressure drop, temperature)
- **Change a parameter and compare**
- **Disturb and observe**
  - **Small disturbances**
  - **Large disturbances (exaggerate or accelerate)**

Role of Diagnostics in Fuel Cell Control



Purpose of Fuel Cell Diagnostics

- Diagnostics in fuel cell development process
- Diagnostics in control development process
- Diagnostics in operation
- Post mortem diagnostics

Cathegorization of Diagnostic Methods

- Online
- Offline
- Post mortem

Fuel Cell Diagnostic Methods

Electrochemical techniques
- Polarization curve
- Current interruption
- Electrochemical Impedance Spectroscopy
- Cyclic Voltammetry
- CO Stripping Voltammetry
- Linear Sweep Voltammetry

Species Distribution Mapping
- Pressure Drop Measurements
- Gas Composition Analysis
- Neutron Imaging
- Magnetic Resonance Imaging
- X-ray Imaging
- Optically Transparent Fuel Cells
- Embedded Sensors

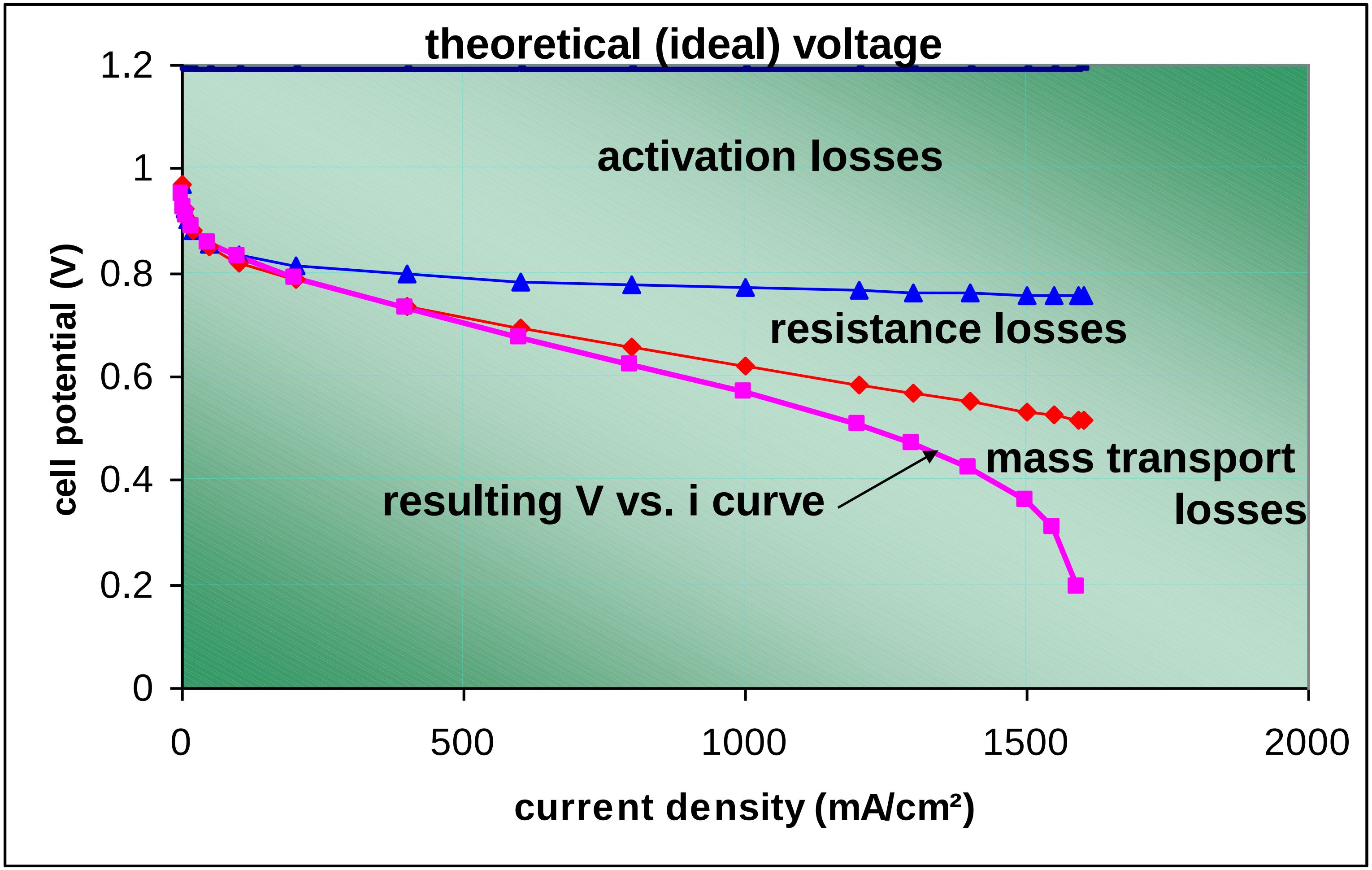
Current Distribution Mapping
- Partial MEA
- Segmented Cells

Temperature Distribution Mapping
- IR Transparent Fuel Cells
- Embedded Sensors

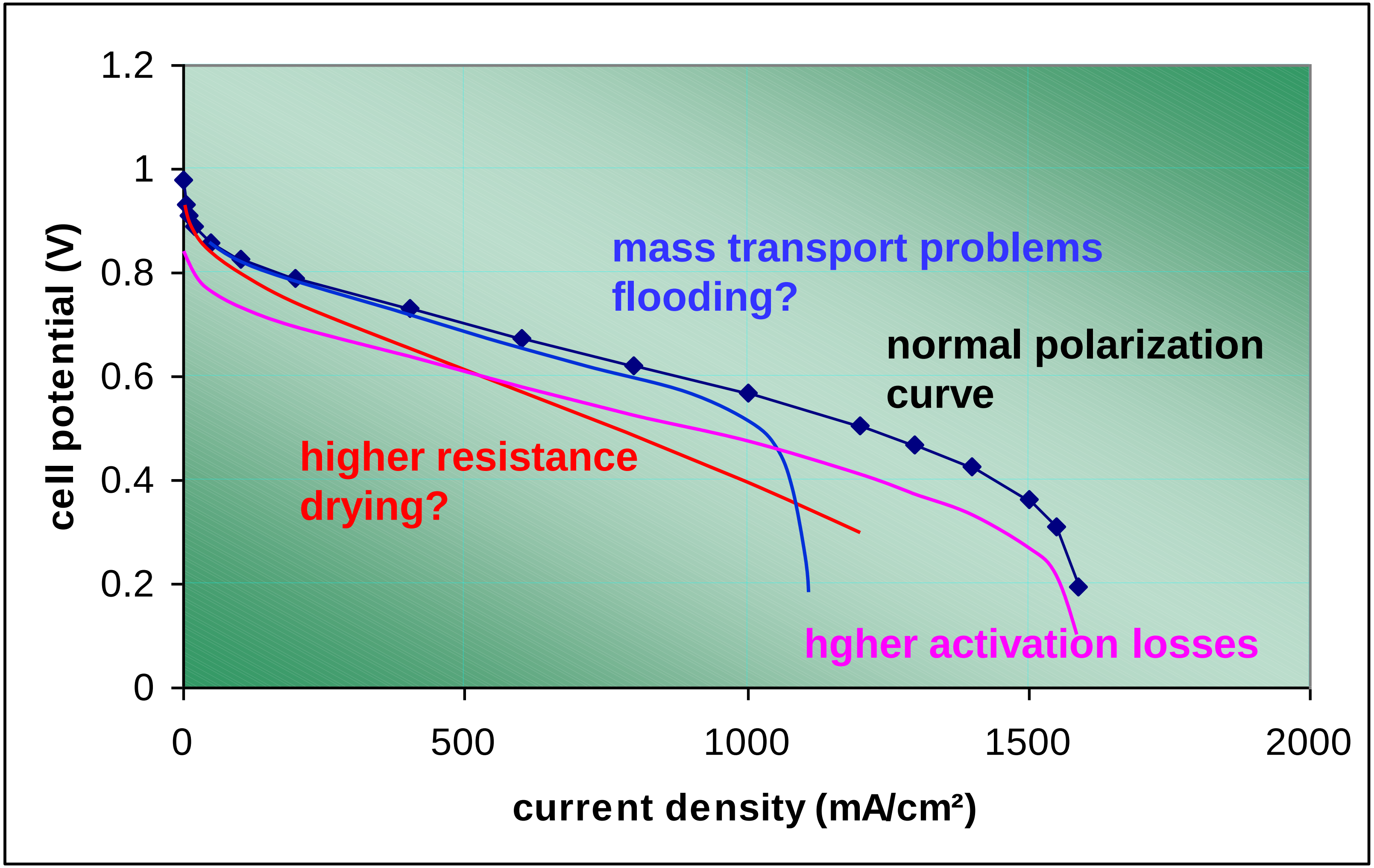
Diagnostics as a design tool

- Polarization curve
- Polarization curve hysteresis
- Comparative polarization curves
- Current interrupt
- AC impedance spectroscopy
- Pressure drop
- Current density mapping
- Temperature mapping
- Flow visualization
- Neutron/X-Ray imaging

Fuel cell polarization curve



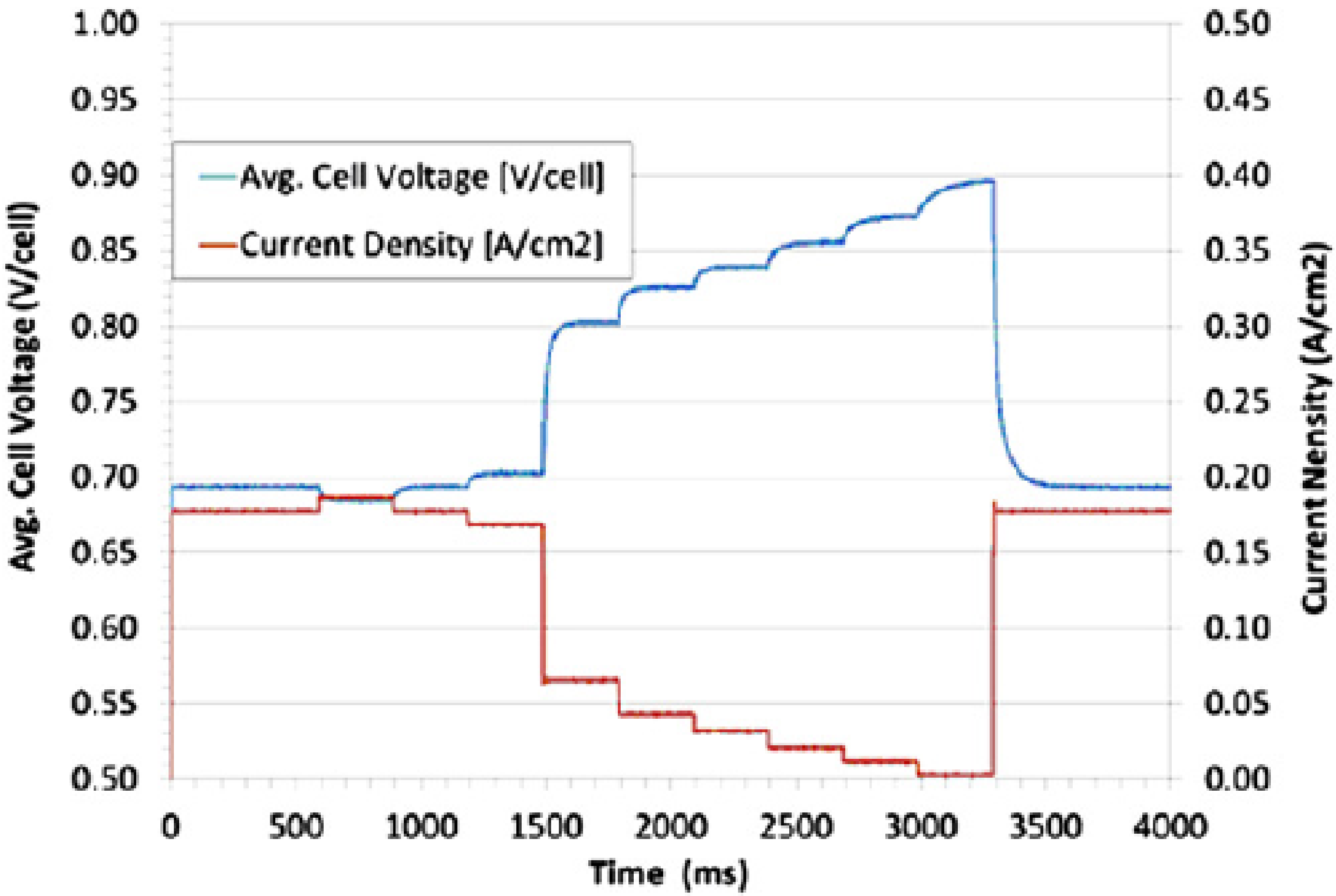
Fuel cell polarization curve



Fuel cell polarization curve

- Data should be taken at multiple current or voltage points.
- Typical points would be open circuit and 5 or 6 points between 600 mV/cell and 850 mV/cell,
- 15 minutes dwell at each point
- The data from the last five (5) minutes should be averaged and then plotted as average current versus average voltage.

Polarization curve sweep



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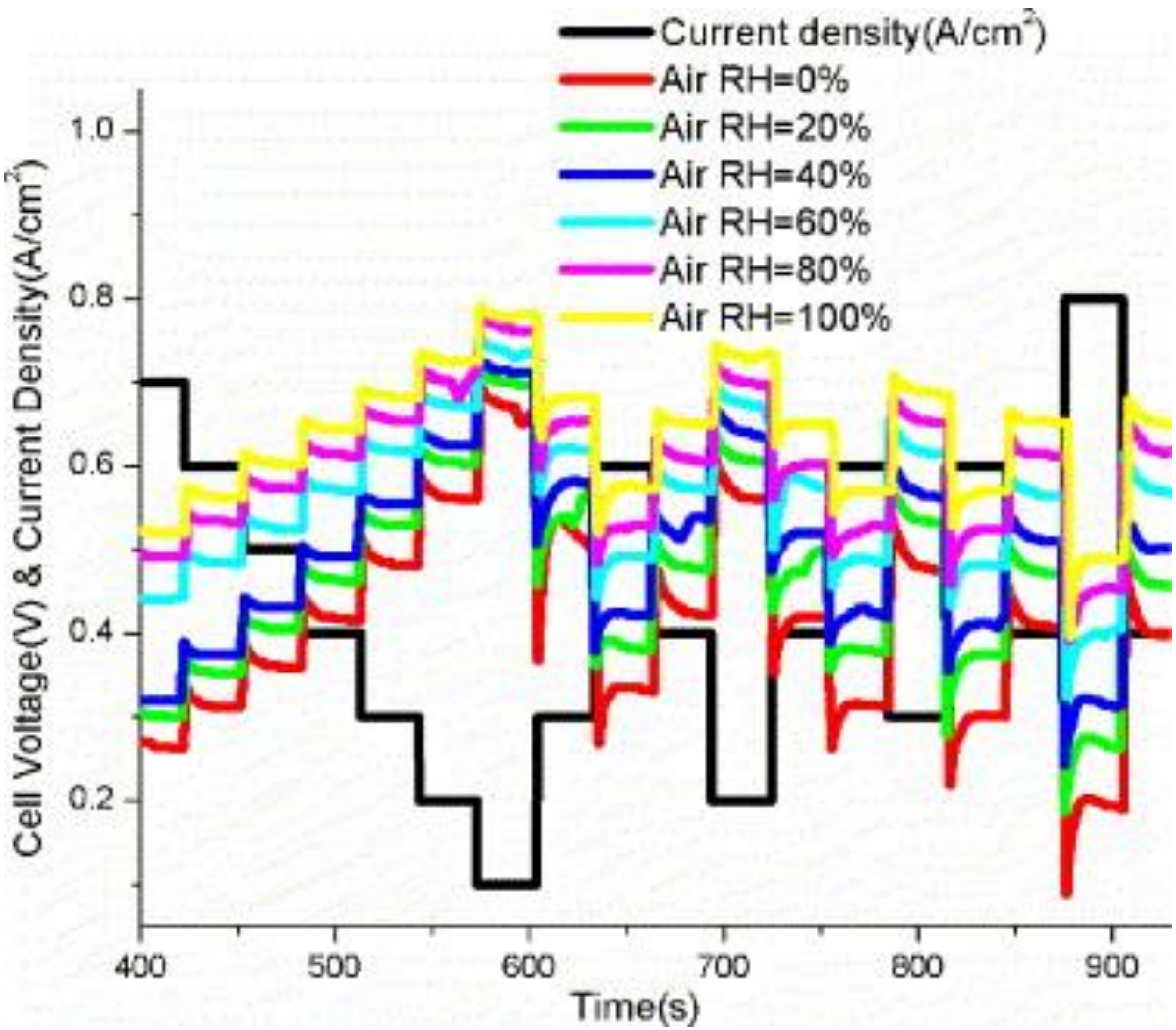
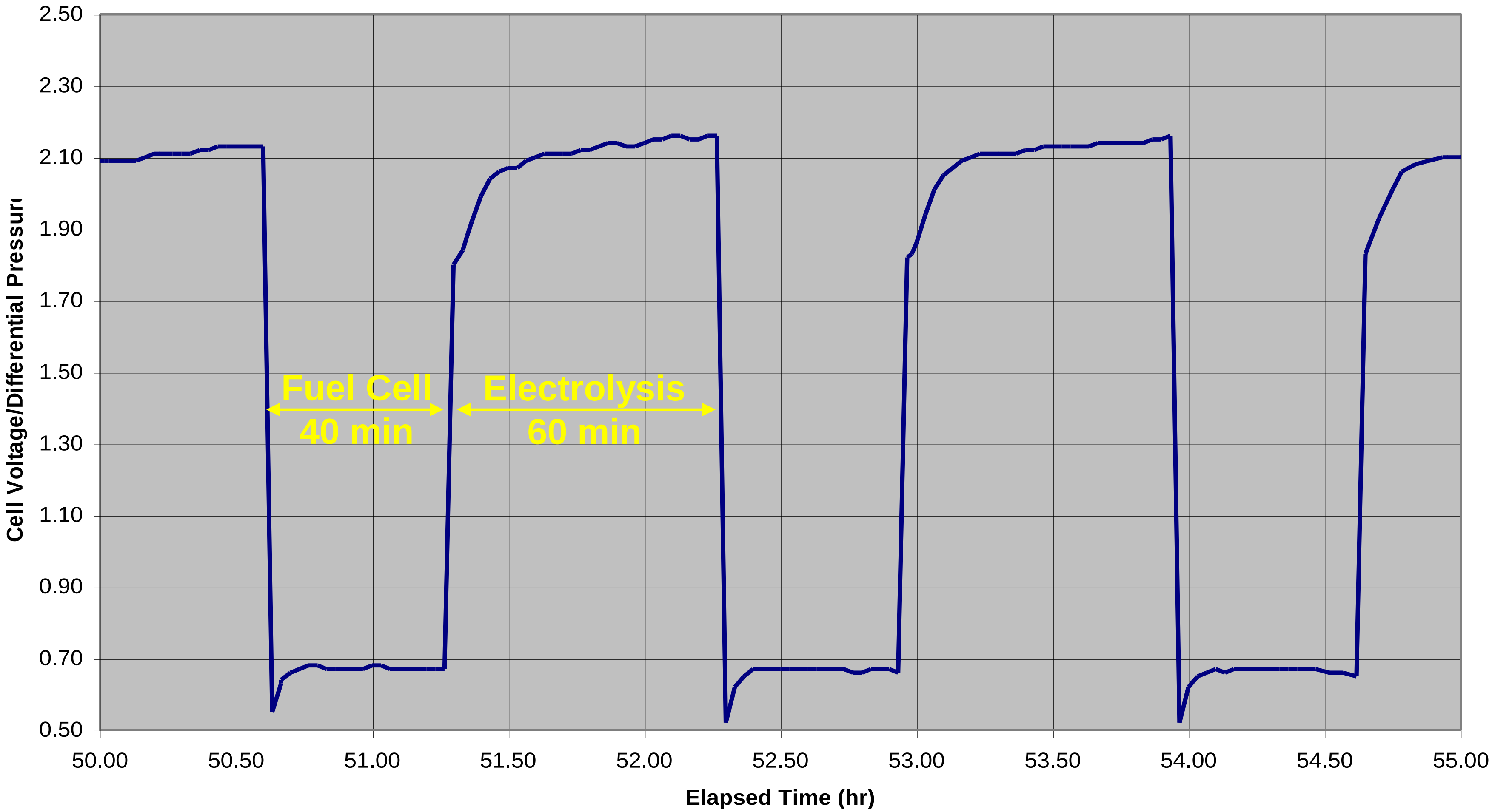
PEM Fuel cell transient response



Qiangu Yan, J. Power Sources, Vol 161, 2006, pp 492–502

Unitized Regenerative Fuel Cell Cyclic Operation

> 100 LEO cycles

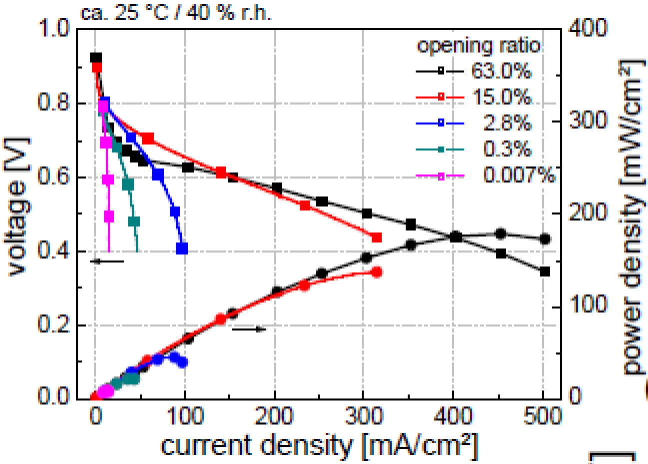


Presented at IECEC, Portsmouth, VA, August 12, 2003

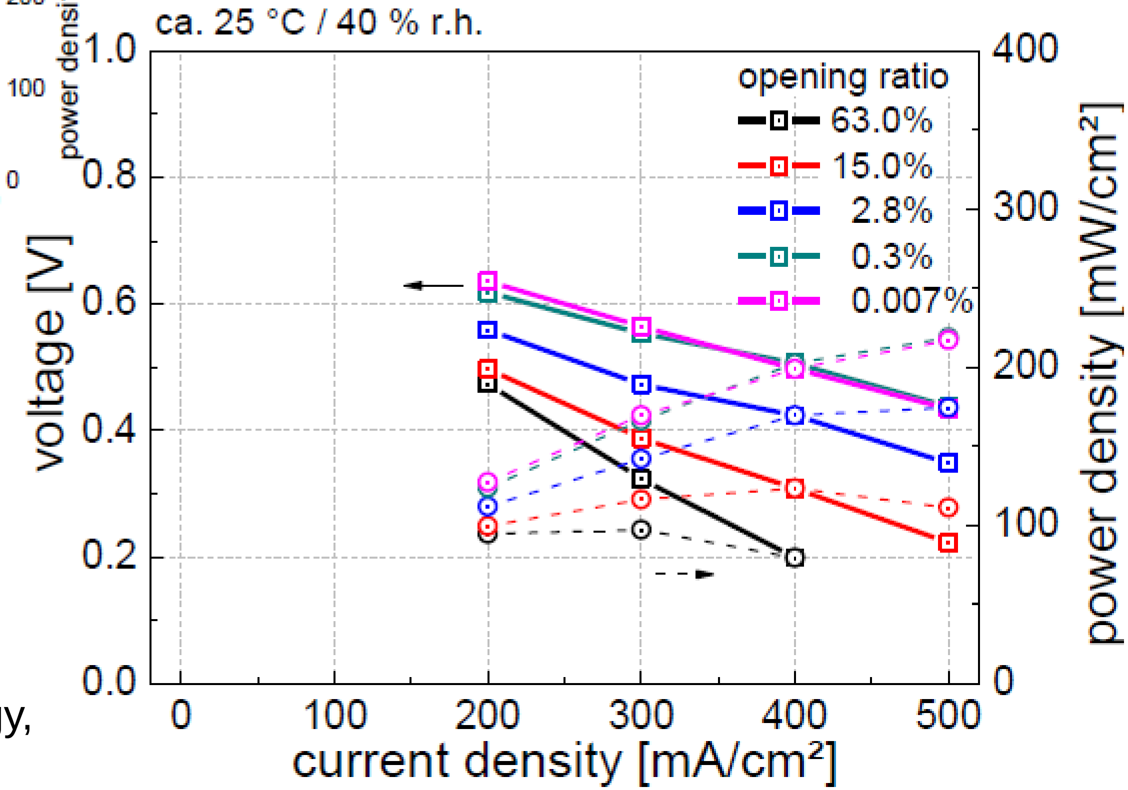
Passive Self-Breathing Micro PEM Fuel Cell

UI Curve

constant load



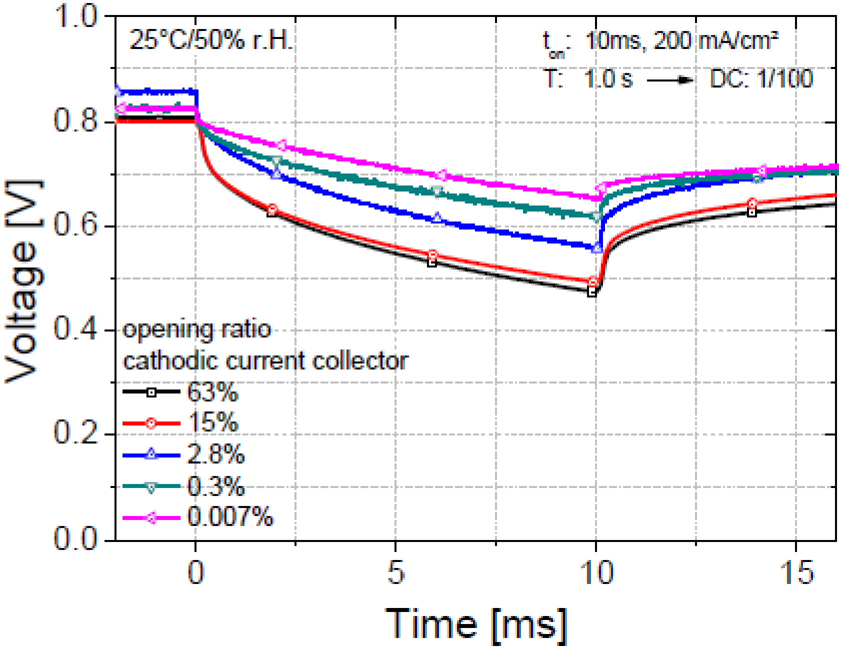
pulse load, 10 ms, 1s

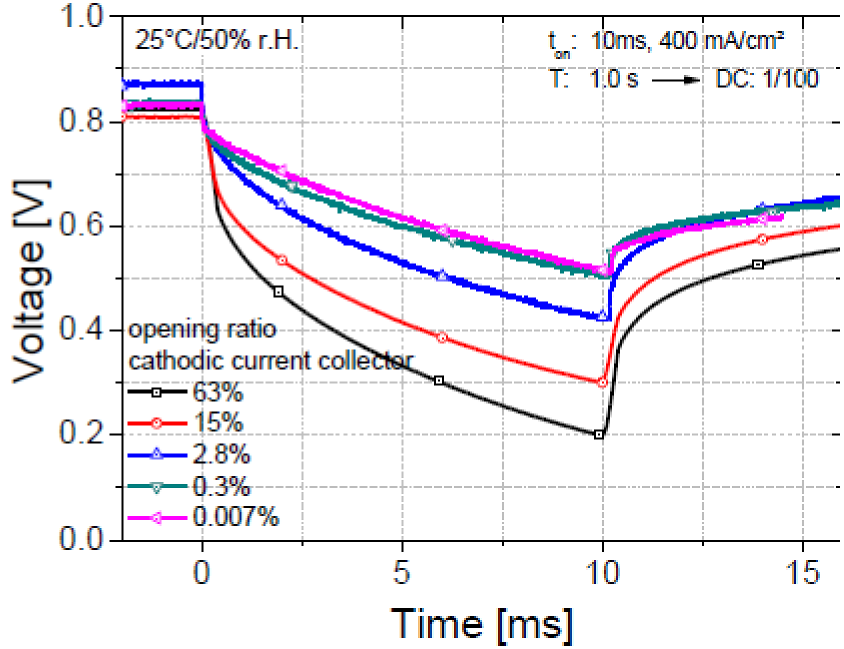


M. Weiland, Int. J. Hydrogen Energy, 2012, in print

Passive Self-Breathing Micro PEM Fuel Cell

Transient Voltage



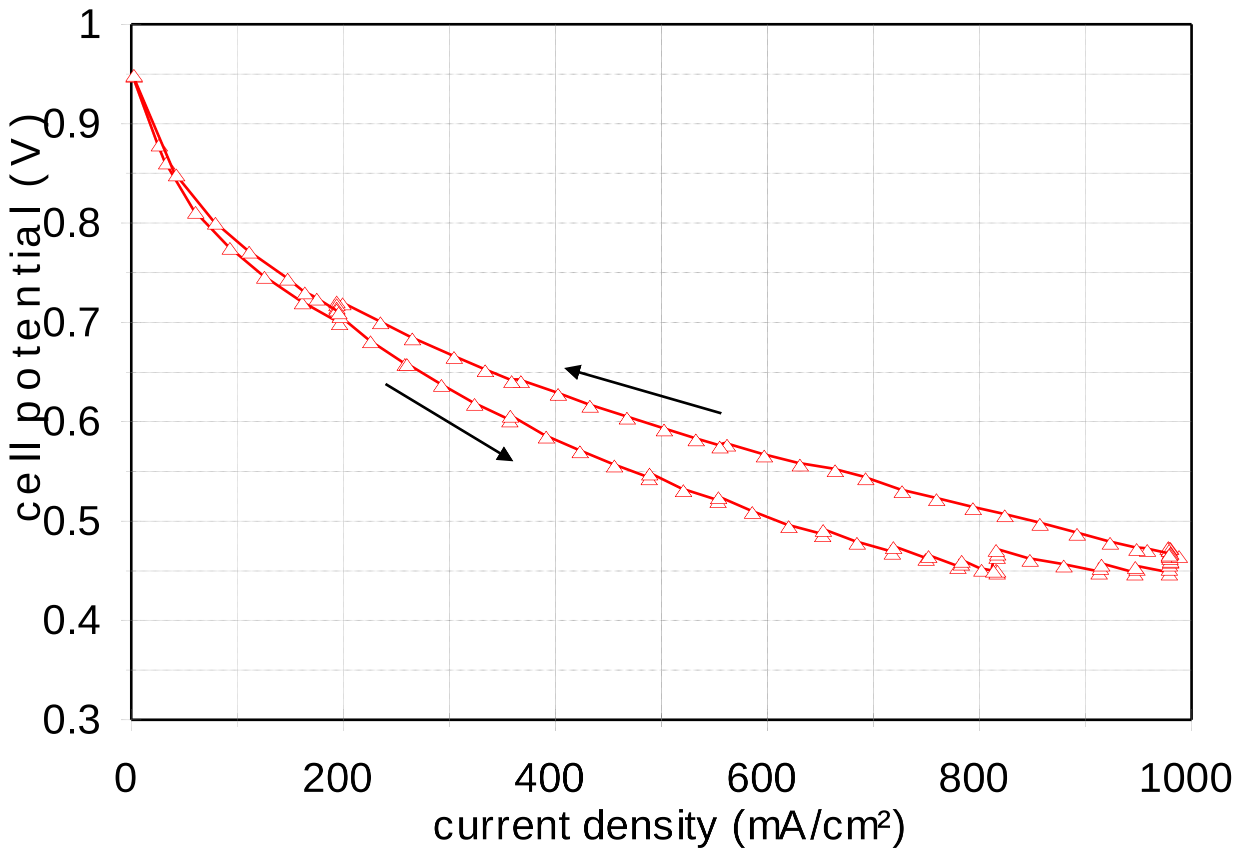


- after 120 min significant difference in between structures visible
- closed current collectors result in higher voltages
- higher differences with higher current densities
- voltage difference for pin-hole structure smaller at 400 mA/cm²
  → reduced concentrations ?

Diagnostics as a design tool

- Polarization curve
- Polarization curve hysteresis
- Comparative polarization curves
- Current interrupt
- AC impedance spectroscopy
- Pressure drop
- Current density mapping
- Temperature mapping
- Flow visualization
- Neutron/X-Ray imaging

Polarization Curve Hysteresis



Polarization curve at cell temperature 80°C
anode/cathode humidifier temperatures 80/60°C
hydrogen/air, 30 psig, H_2 stoich 1.5, air stoich 5.0

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Comparative polarization curves

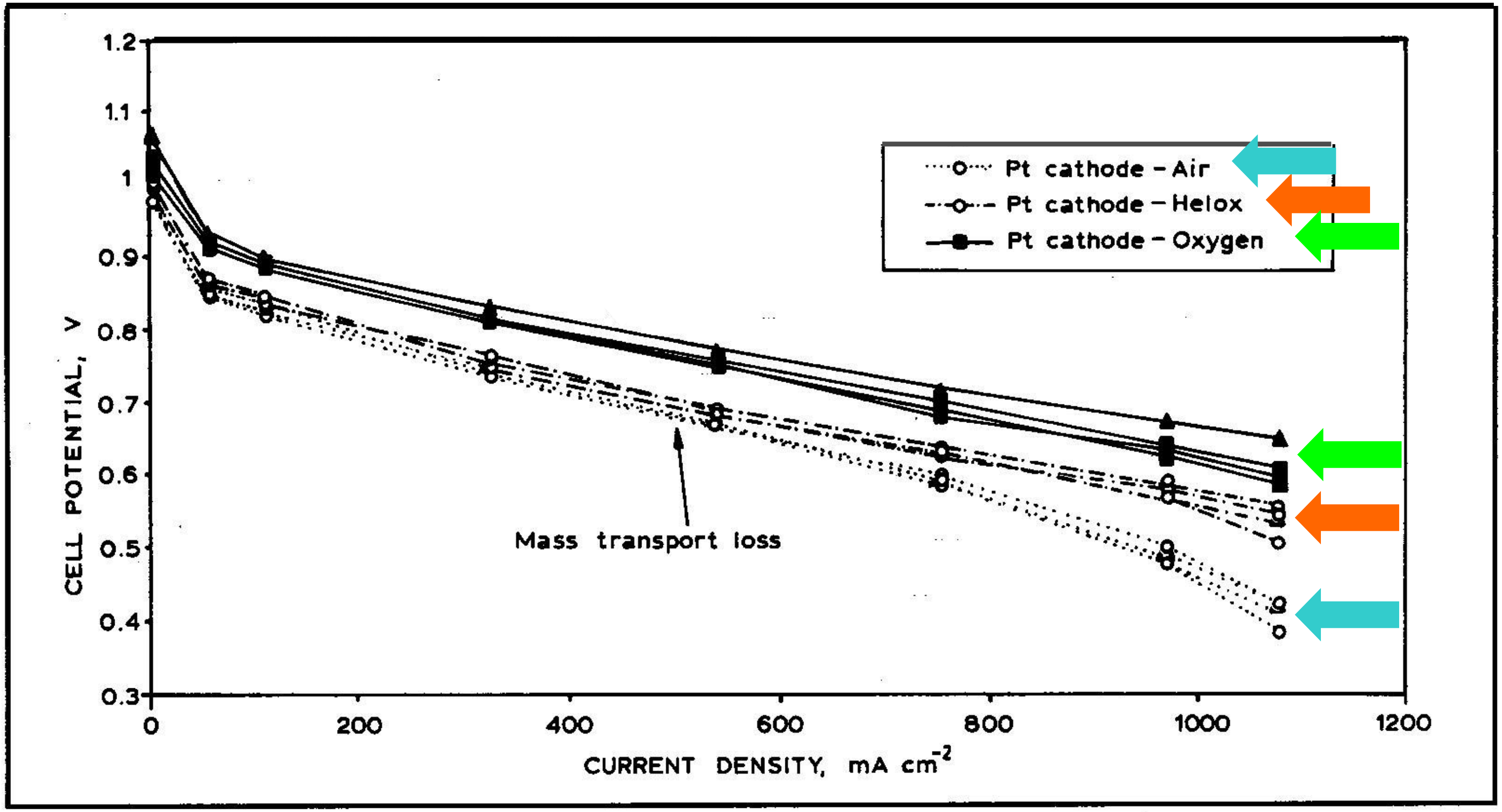

Fig. 5 For air operation, in Ballard Mark 5E hardware, the kinetic benefit of a PtCr alloy cathode is masked by mass transport losses. The comparative performance of the PtCr alloy and a pure Pt cathode electrocatalyst is shown using air, helox (21% O_2 in helium) and O_2 as oxidants and H_2 as fuel. The MEAs (< 1 mg Pt cm^{-2}) are based on catalysed substrates bonded to Nafion 115 membrane electrolyte. The cell is operated at 80°C, in hydrogen/air, helox, oxygen, 308/308 kPa, 1.5/2, 2, 10 stoichiometry, full internal membrane humidification

Source: T.P. Ralph and M.P. Hogarth, *Platinum Metals Review*, Vol. **46**, No. 1, pp. 3-14, 2002

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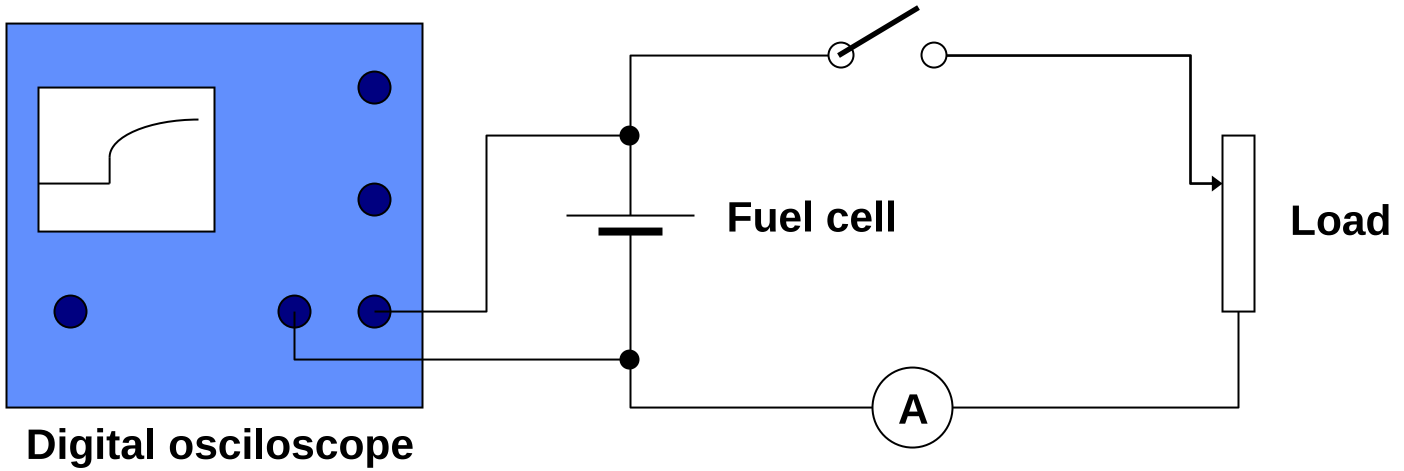
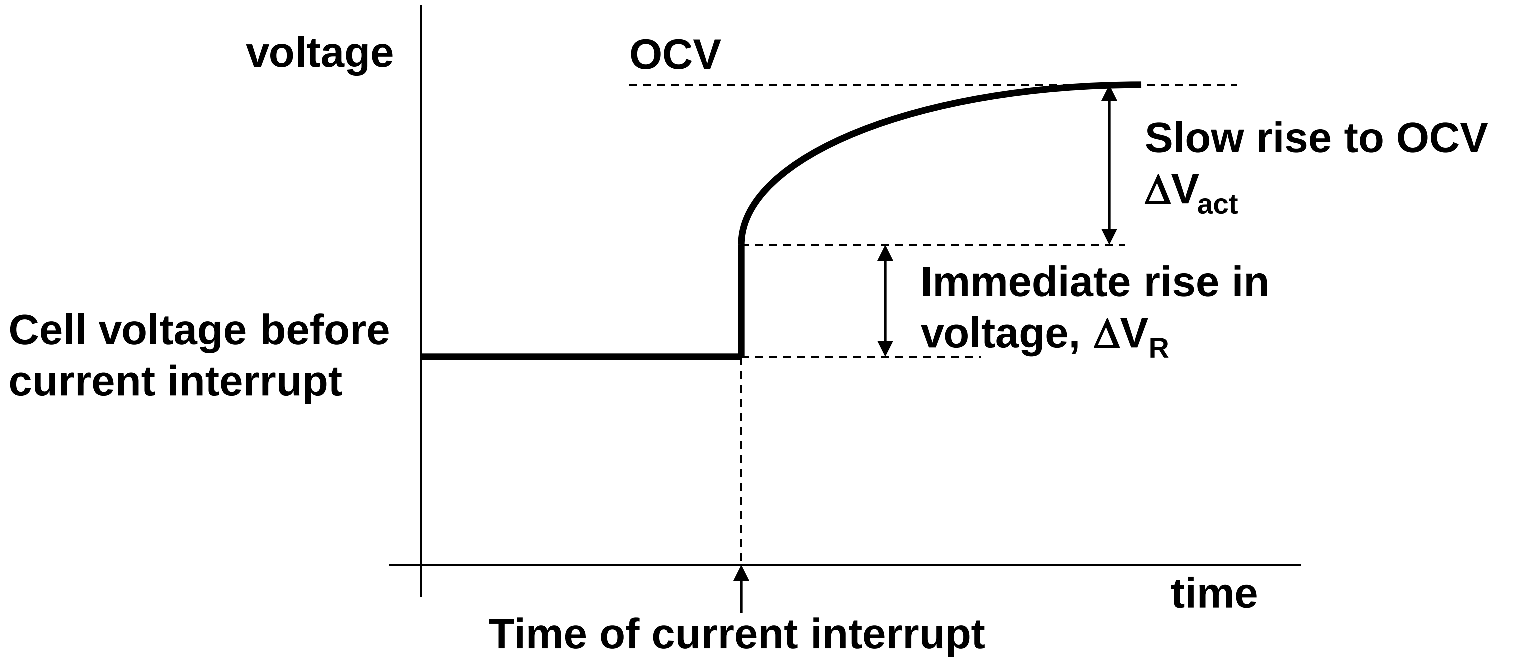
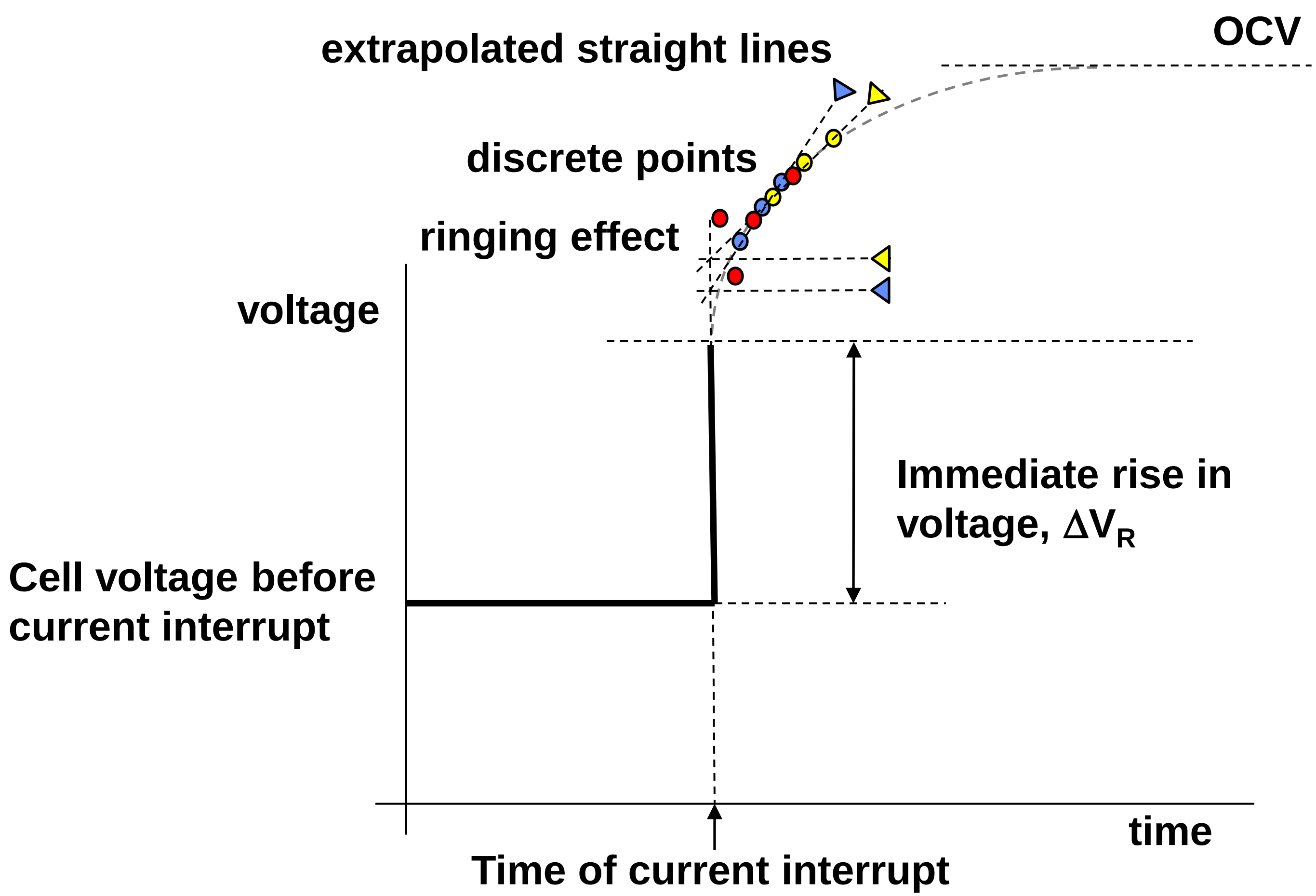
Current interrupt method for measurement of fuel cell resistance





Current interrupt method for measurement of fuel cell resistance



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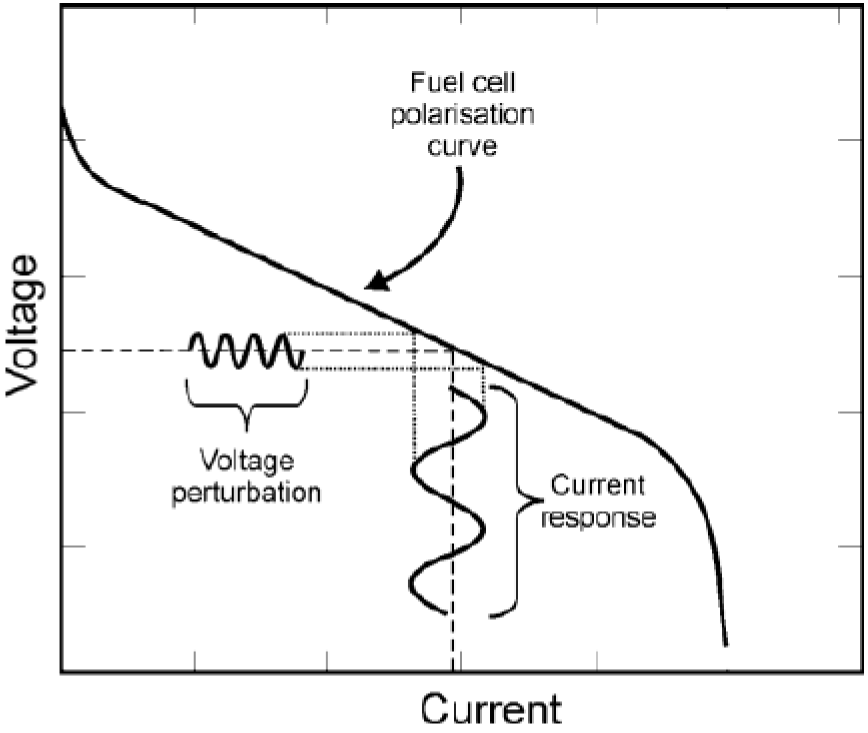
Electrochemical Impedance Spectroscopy

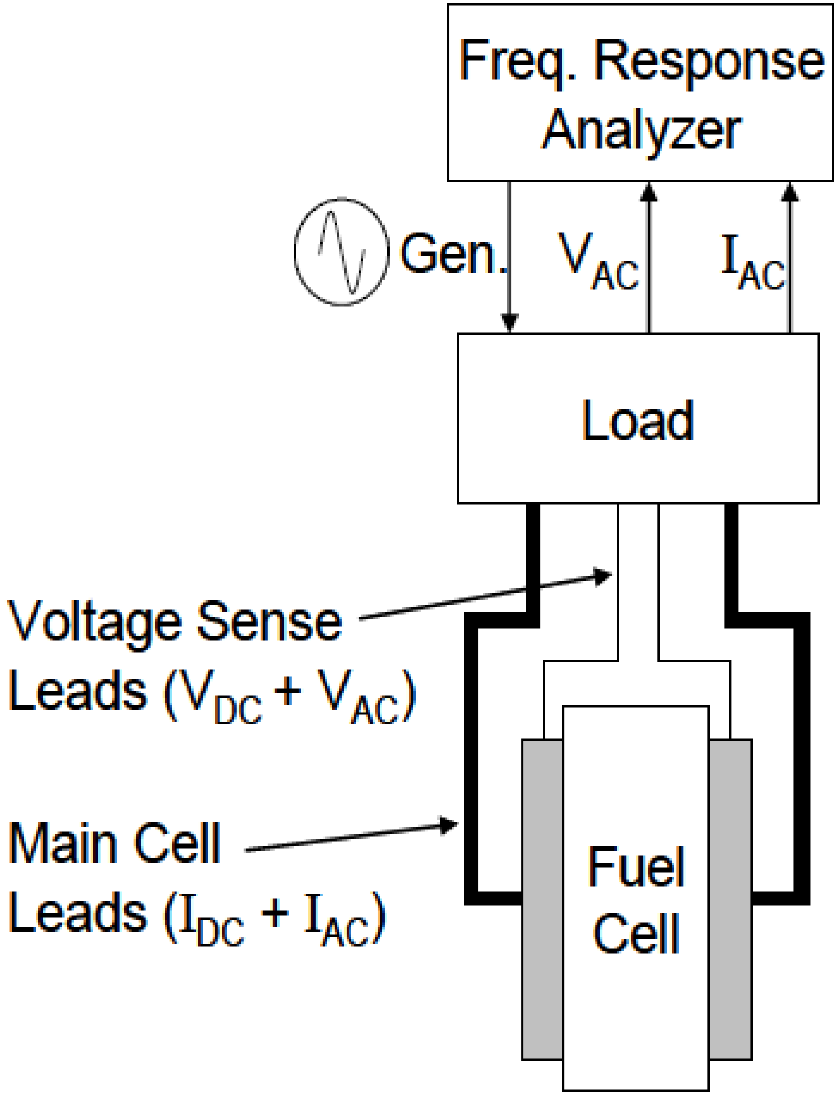
- Each of the losses has their own rate (time constant)
- Apply an AC stimulus (on top of DC) and observe consequent AC result (amplitude and phase)
- Deconvolute the impedance associated with each process.

$$Z(\omega) = \frac{E(\omega)}{i(\omega)}$$

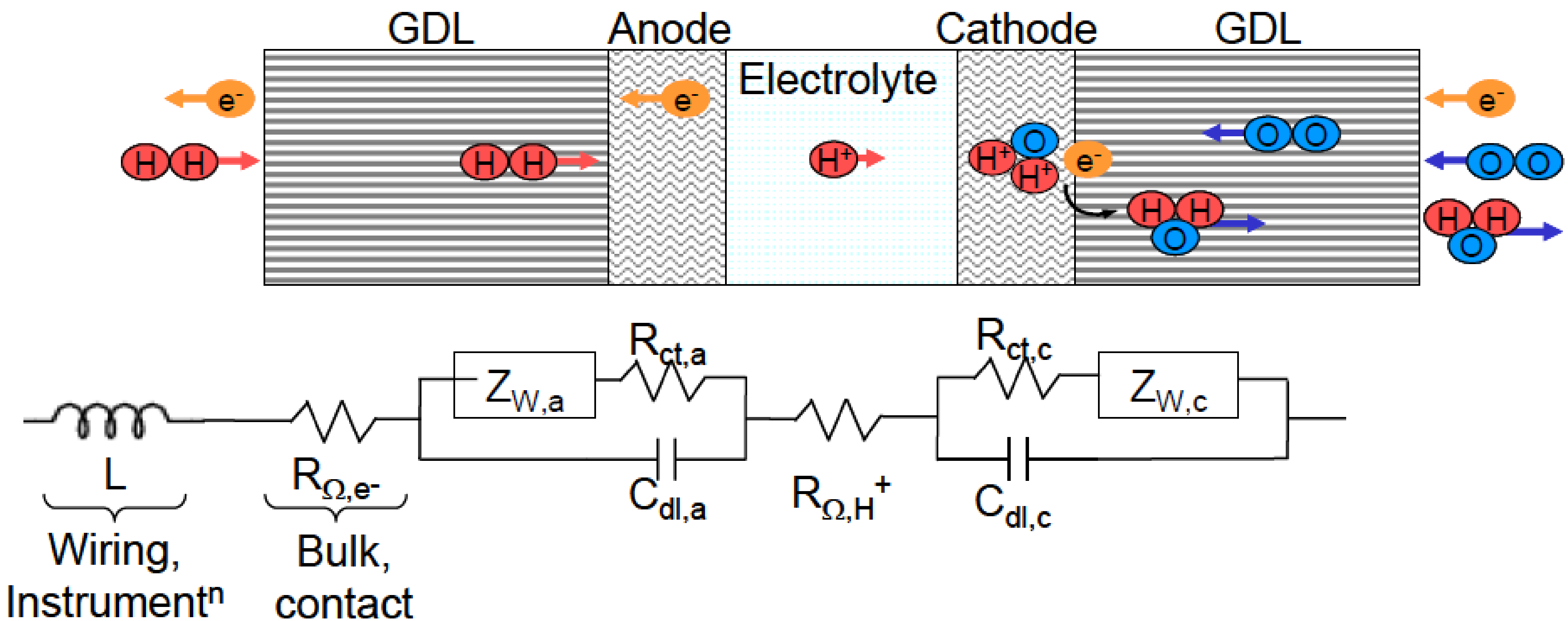


Electrochemical Impedance Spectroscopy

Set-up



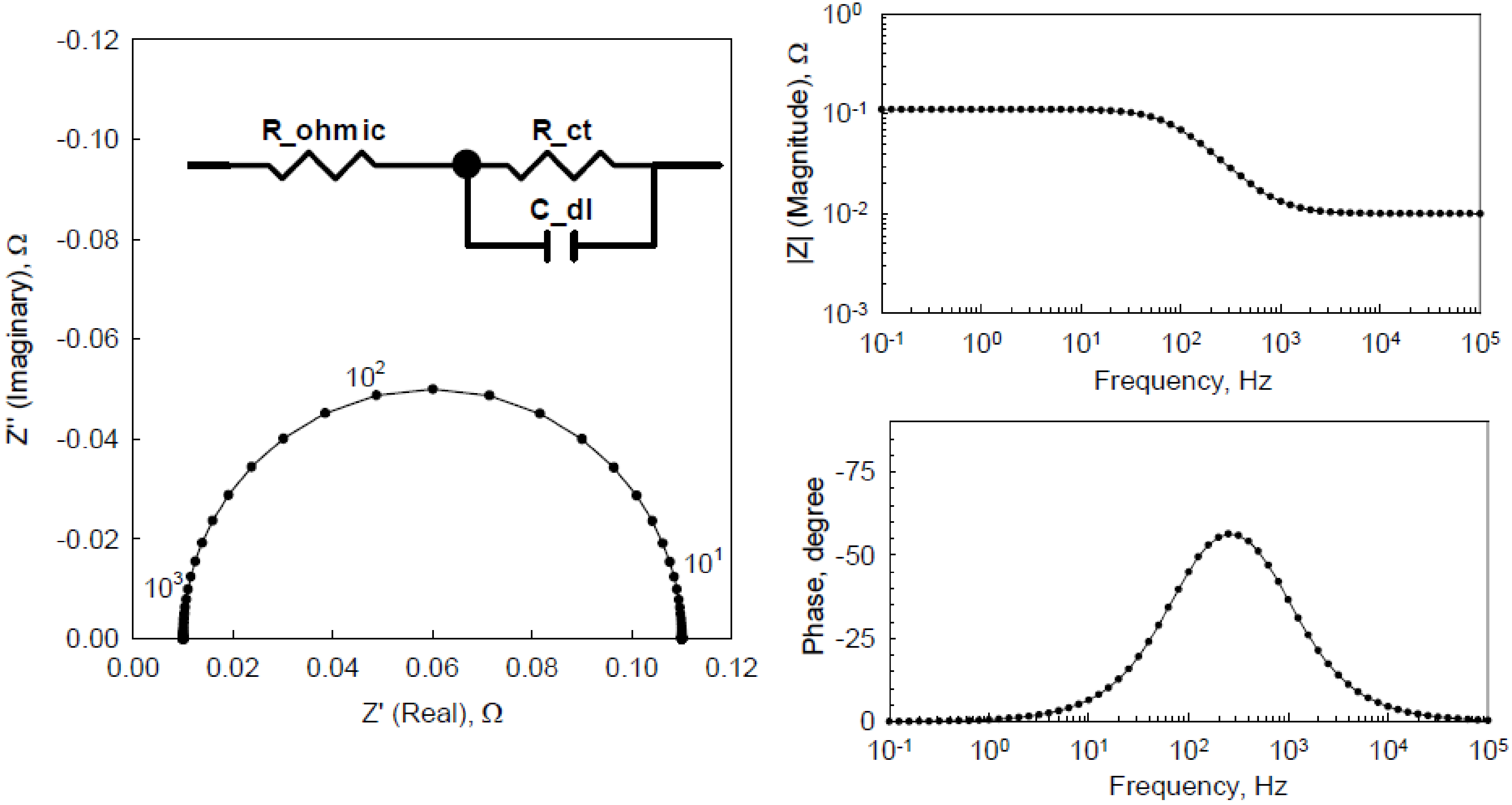
Fuel Cell Equivalent Circuit



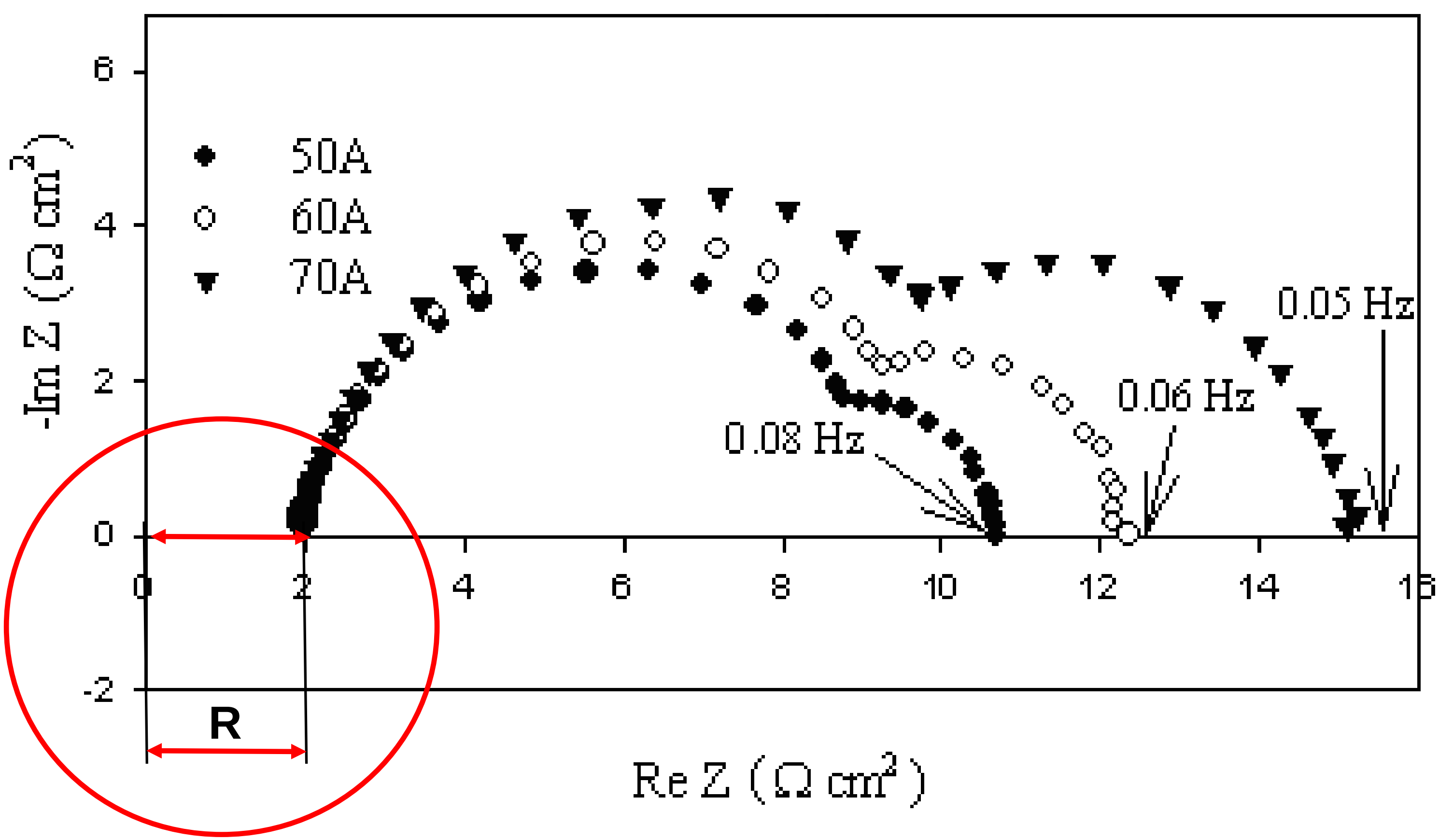
Key: GDL = gas diffusion layer, dl = double layer, ct = charge transfer, a = anode, c = cathode.

Two ways of showing the same results:

Nyquist and Bode plots



Fuel Cell EIS – Typical Results



HF Resistance

The high, medium and low-frequency features of PEFC EIS

- In a H_2/O_2 (air) fuel cell, the spectra often have **three features**, which are denoted as high-frequency, medium-frequency, and low-frequency.

- **High-frequency** – internal ohmic resistance and the contact capacitance in the granular electrode structure.
- **Medium-frequency** – charge transfer (kinetic) resistance.
- **Low-frequency** – mass transport resistance.

Advantages and limitations of EIS for fuel cells

- Studying the entire frequency response can give information on:
  - Interfacial **charge transfer** resistance
  - **Ohmic** losses
    - Electronic
    - Ionic conductivity of electrolyte membranes
  - Oxidant and fuel **mass transport** resistance
  - **Double-layer** capacitance
  - **Water management**
  - **Adsorption** processes
- Measurement is relatively fast (slower than current interrupt).
- Applicable across the whole current-voltage operating range.
- Does not perturb the system (much) (cf. current interrupt).
- Simple equivalent circuits can be used for analysis.

Advantages and limitations of EIS for fuel cells

- Relatively sophisticated instrumentation required.
  - Care must be taken with the measurement and the interpretation of the data.
  - Robust EIS measurements must show:
    - Linearity – the AC signal must be low enough to ensure that the electrochemical response is linear. I.e. response from the system must be a linear function of the applied perturbation for meaningful mathematical analysis.

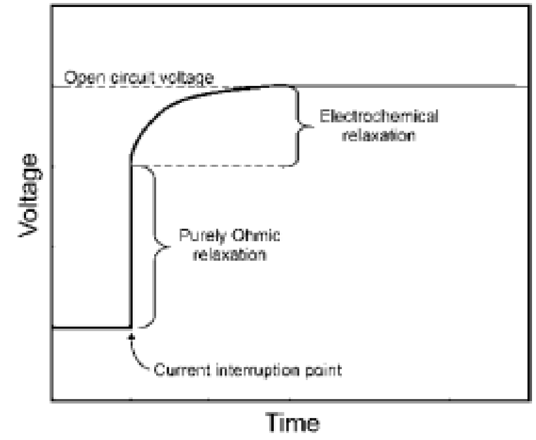
$$\Delta V = \Delta i R$$

    - For a non-linear system, the change in current is not proportional to the voltage change

$$\Delta V \neq \Delta i R$$

  - in practice we use small signals (ca. 10 mV) to ensure that the system behaves approximately linearly.
    - Small signals lead to lower accuracy
    - In practice we have to consider a trade-off between linearity and accuracy.

Comparison with Current Interrupt



Electrochemical Impedance Spectroscopy	Current Interrupt
Advantages *Provides information on the various losses in a fuel cell.* *No significant perturbation to fuel cell.*	***Advantages*** **Rapid** measurement. **Low cost**. Easy to apply to cells in a stack. Applicable to high current operation
Disadvantages *For **high current** systems a **load is required** that has the ability to accept ac input and operate over the bandwidth of the measurement.* ***High cost** instrumentation required.* *Difficult to apply to all cells in a stack simultaneously.*	***Disadvantages*** **Significant perturbation** to fuel cell. Requires interruption of the fuel cell current delivery. **Current must be flowing** for measurement to be taken (cannot measure at open circuit conditions). Low signal-to-noise when measuring at low current density.

Diagnostics as a design tool

- Polarization curve
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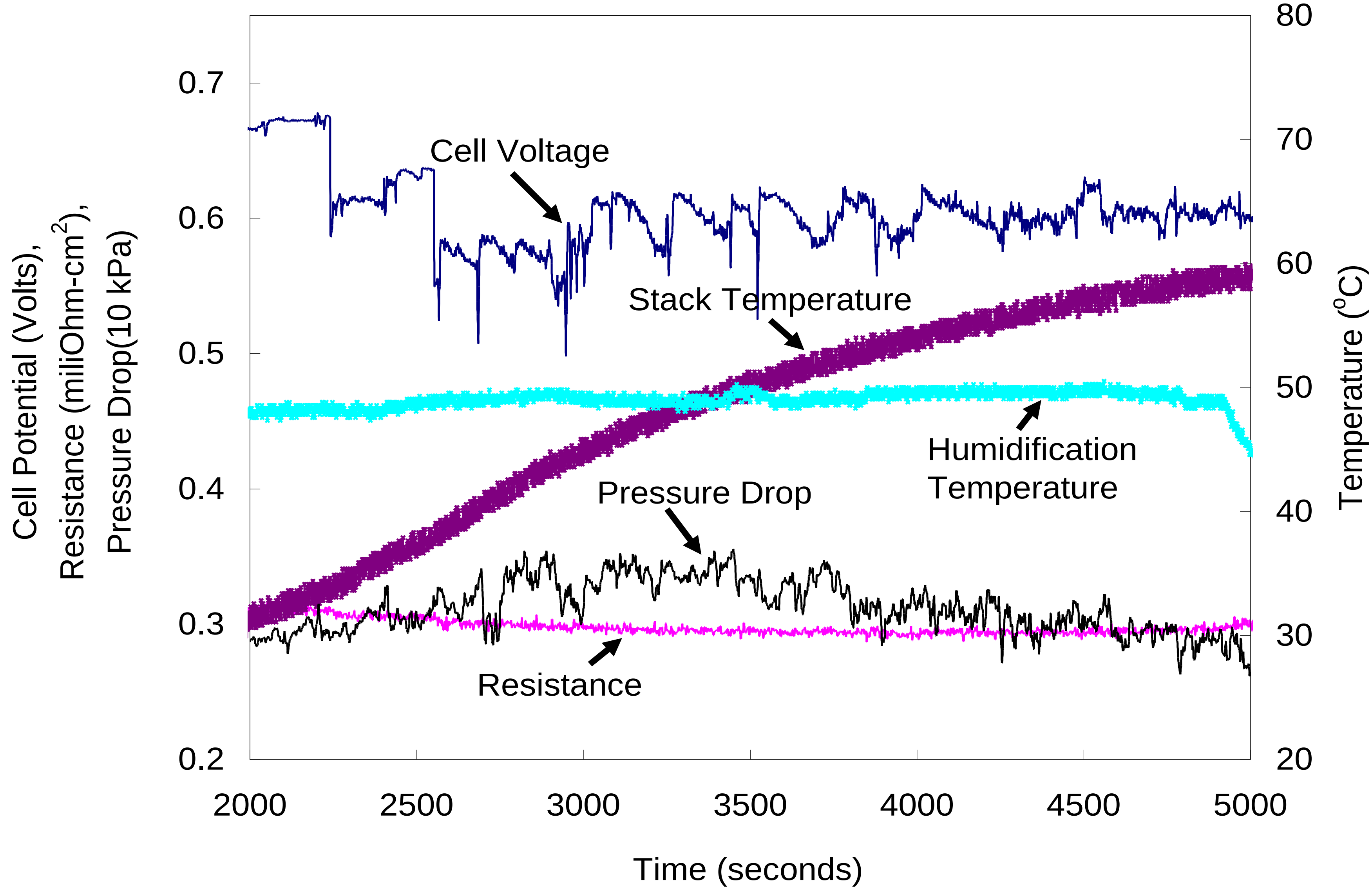
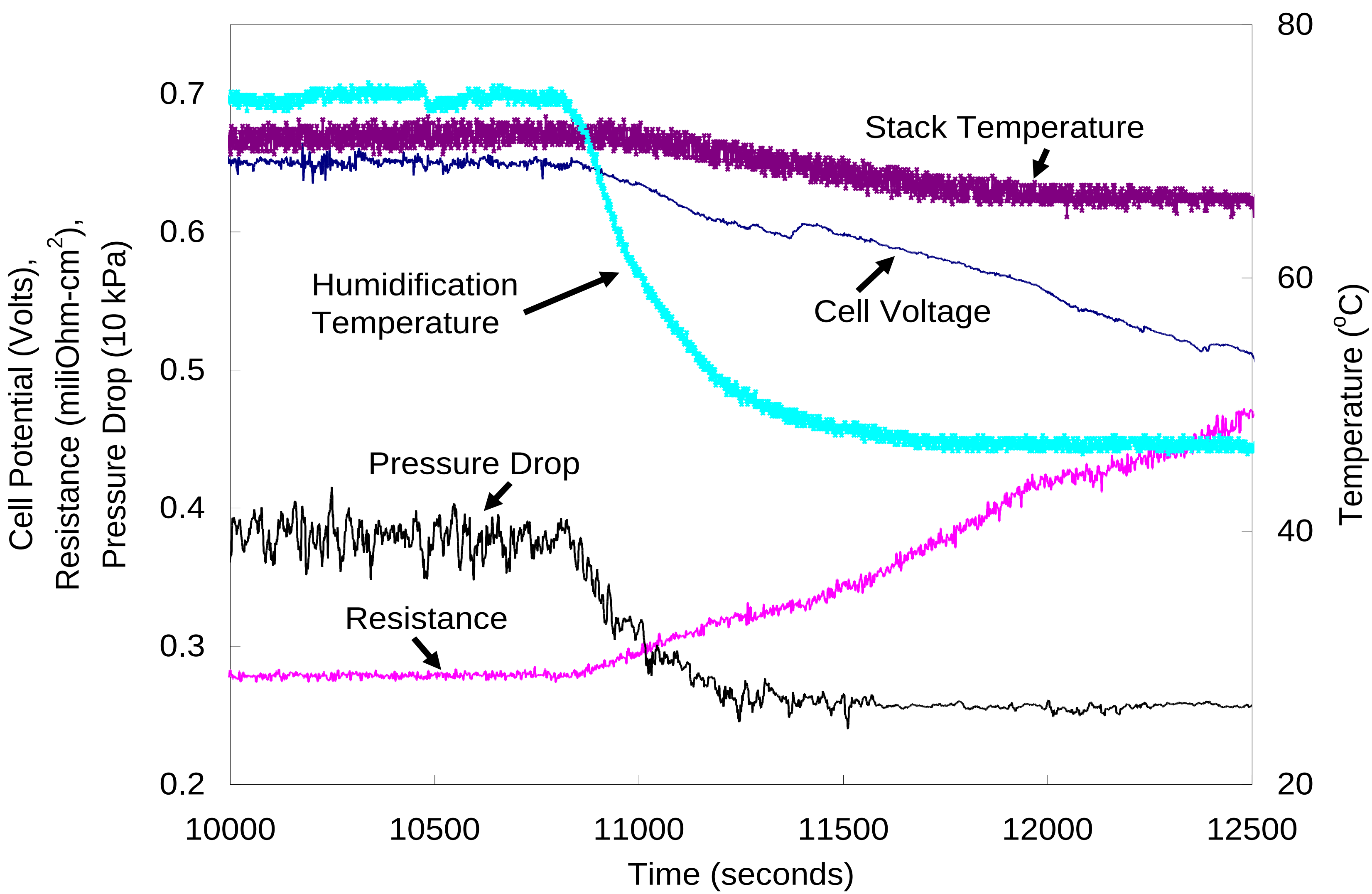
Stack Flooding and Recovery



Stack Drying



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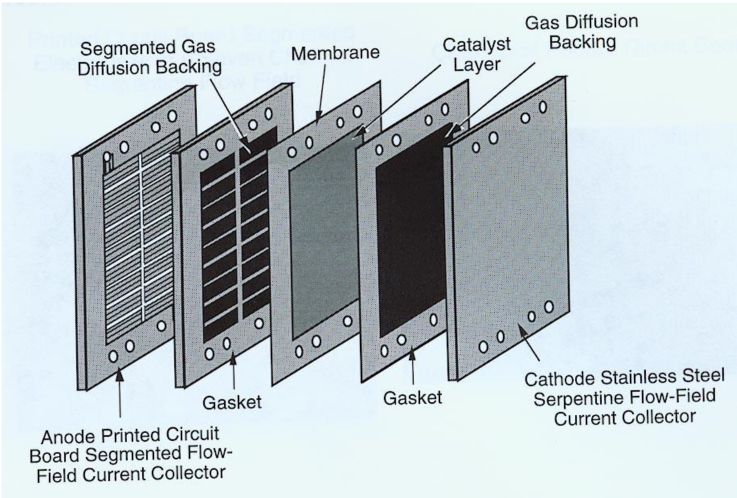
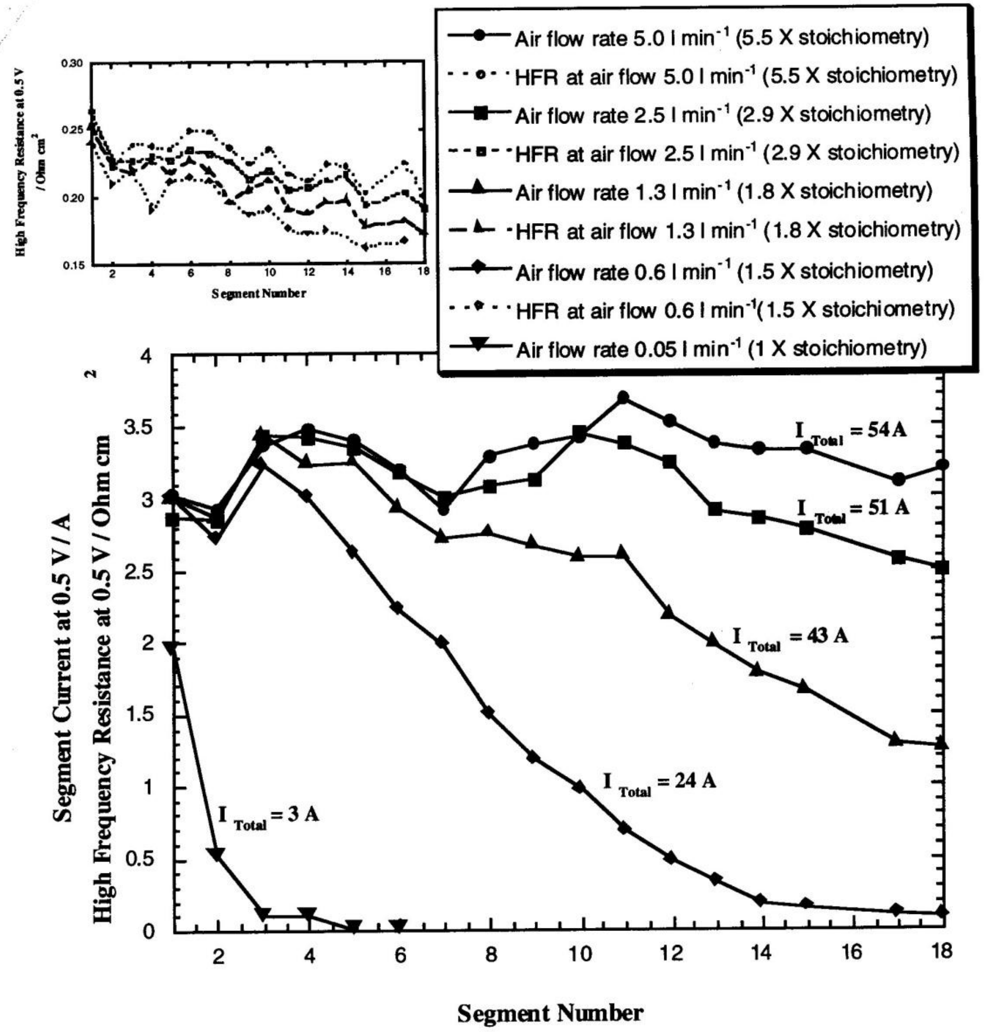
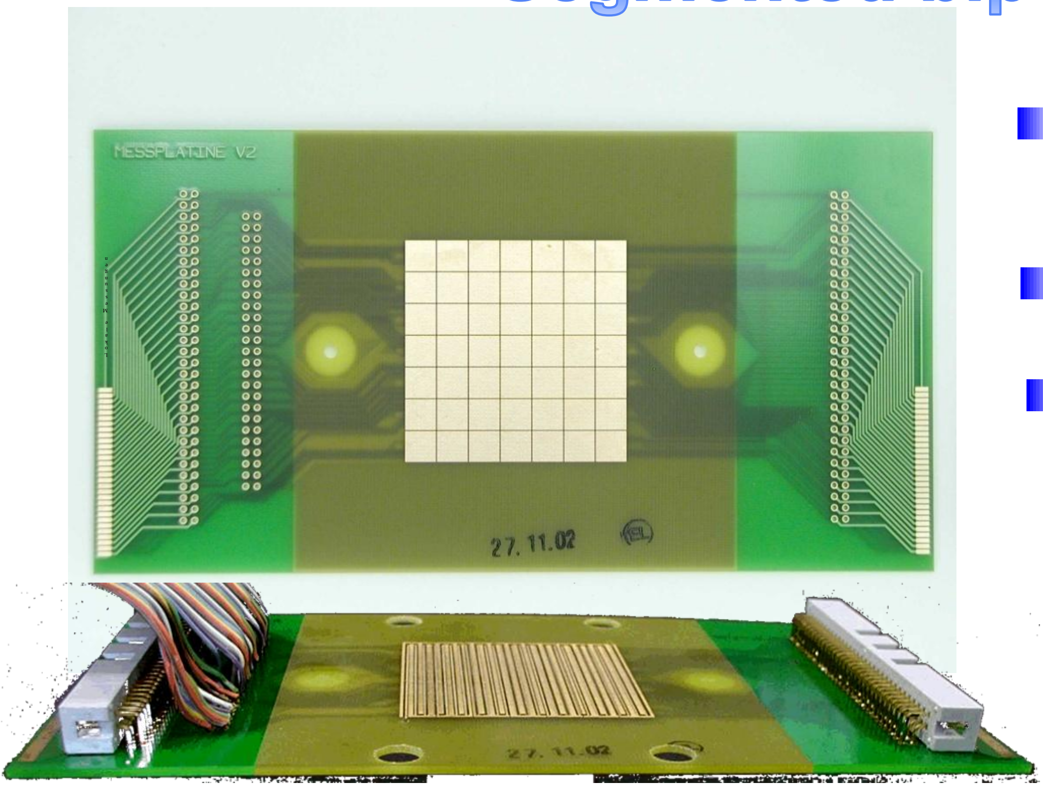
Current density mapping with segmented cell



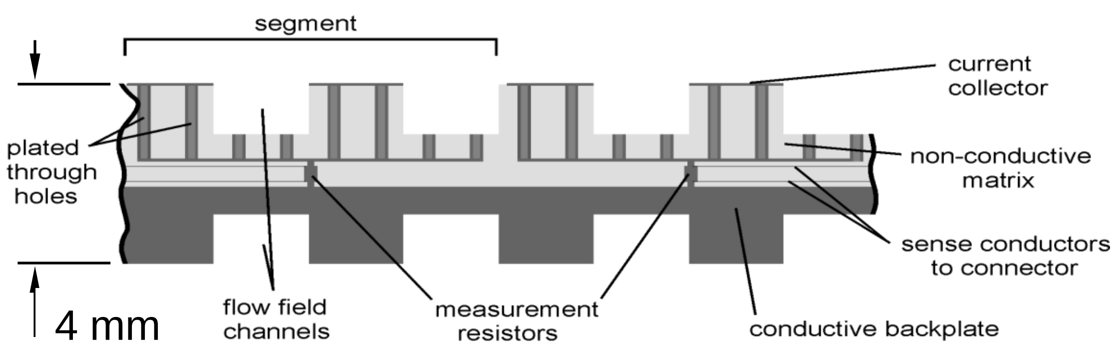


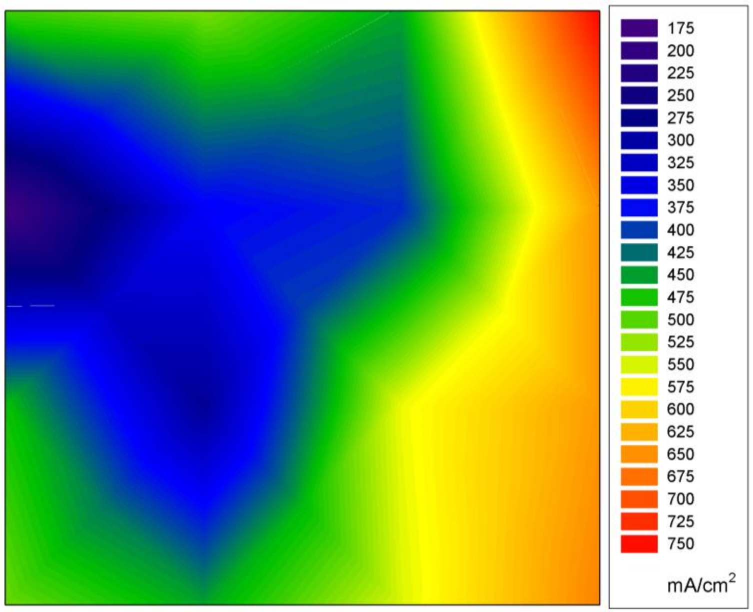
S.J.C. Cleghorn, C.R. Derouin, M.S. Wilson, and S. Gottesfeld, A Printed Circuit Board Approach to Measuring Current Distribution in a Fuel Cell, J. Appl. Electrochem., 1997

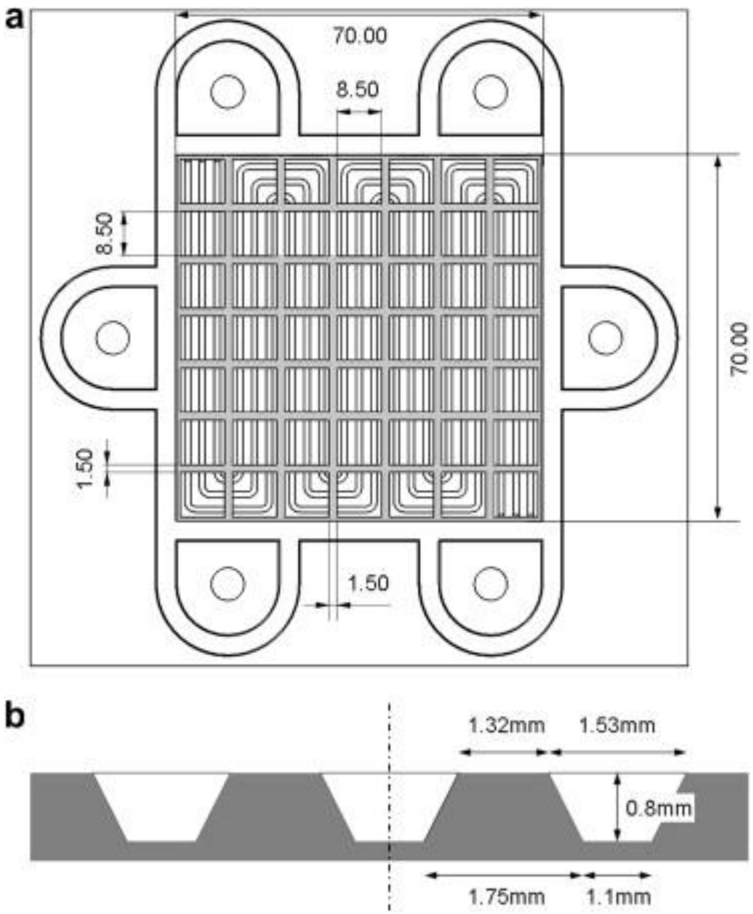
Segmented bipolar plates

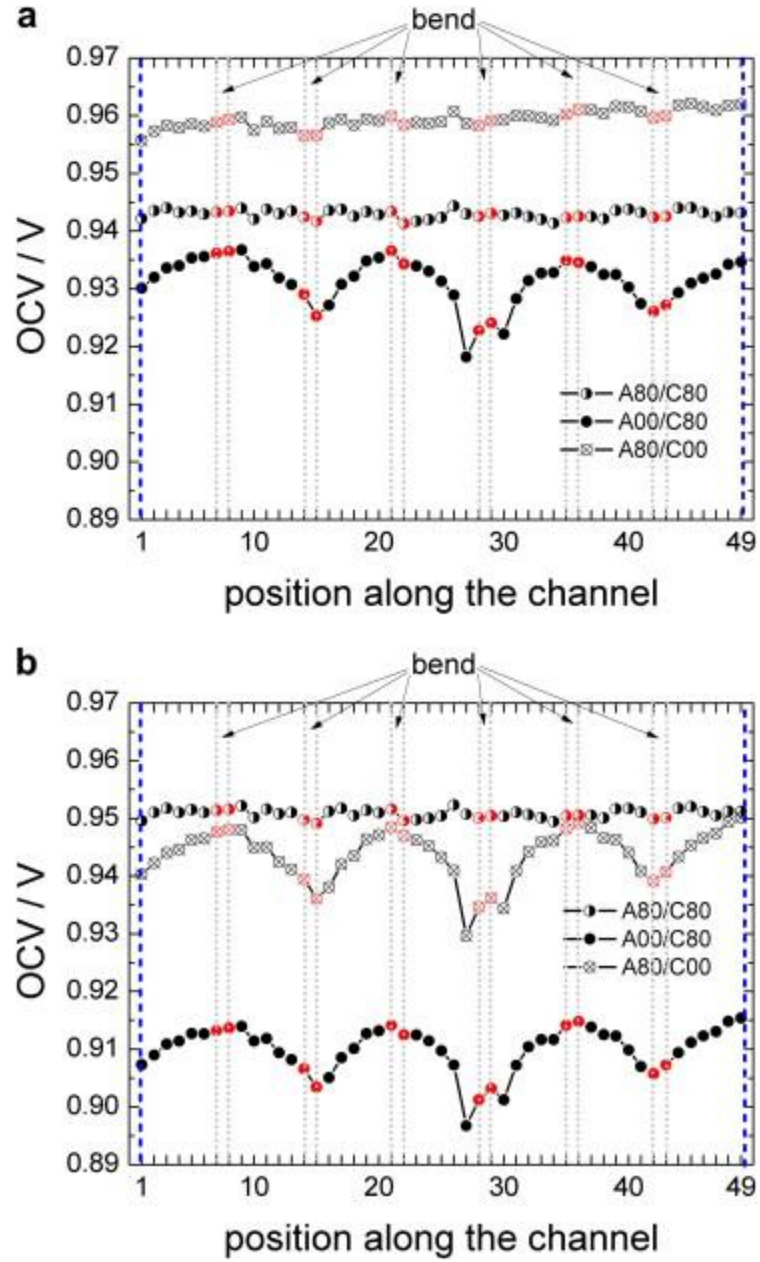


- local current density measurement
  dynamic > 2000 measurement /s
- local temperature measurement
- local electrochemical
  impedance spectroscopy (EIS)

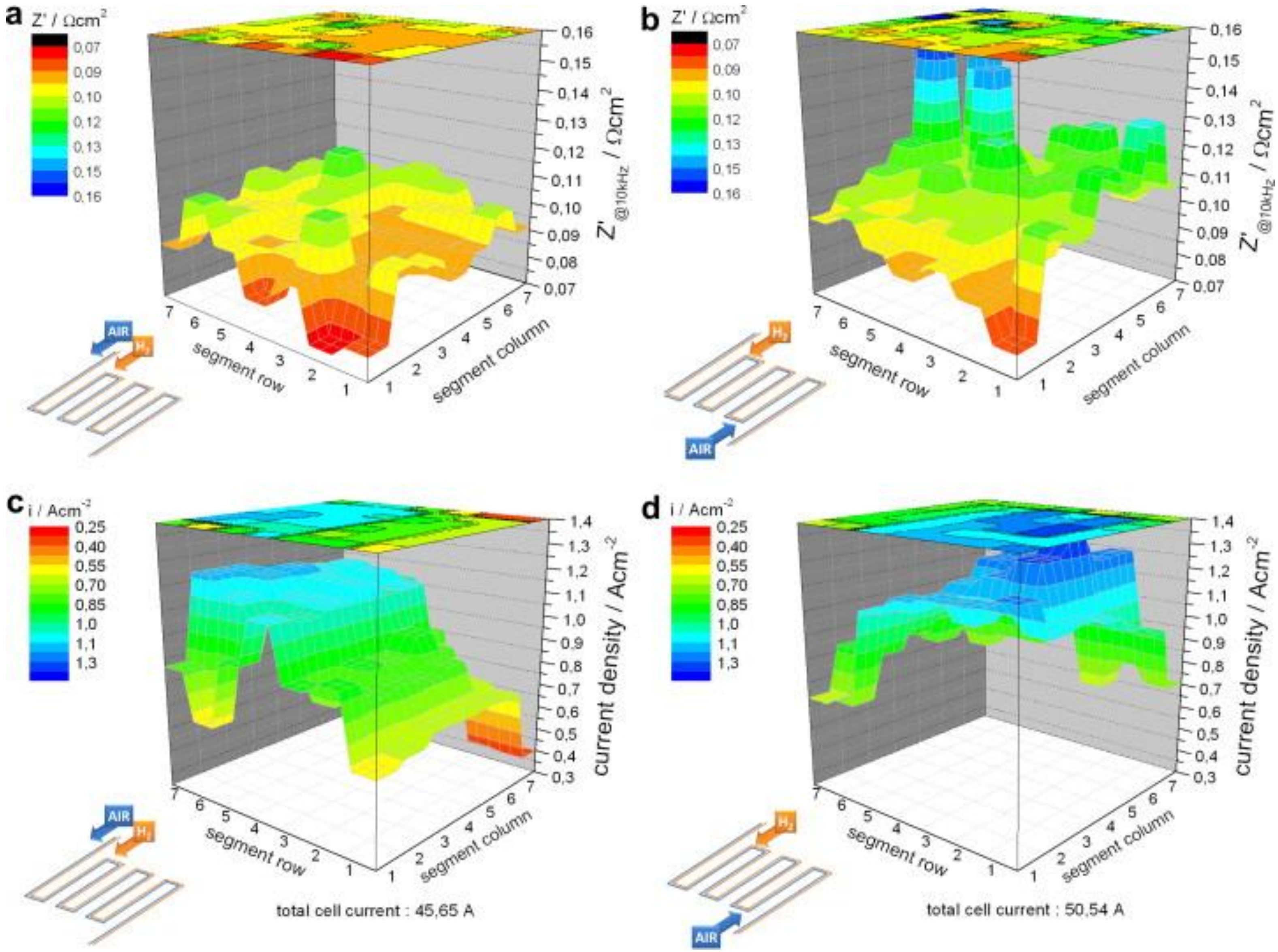








D. Derteisen et al., Int. J. Hydrogen Energy, Vol 37, 2012, pp. 7736–7744



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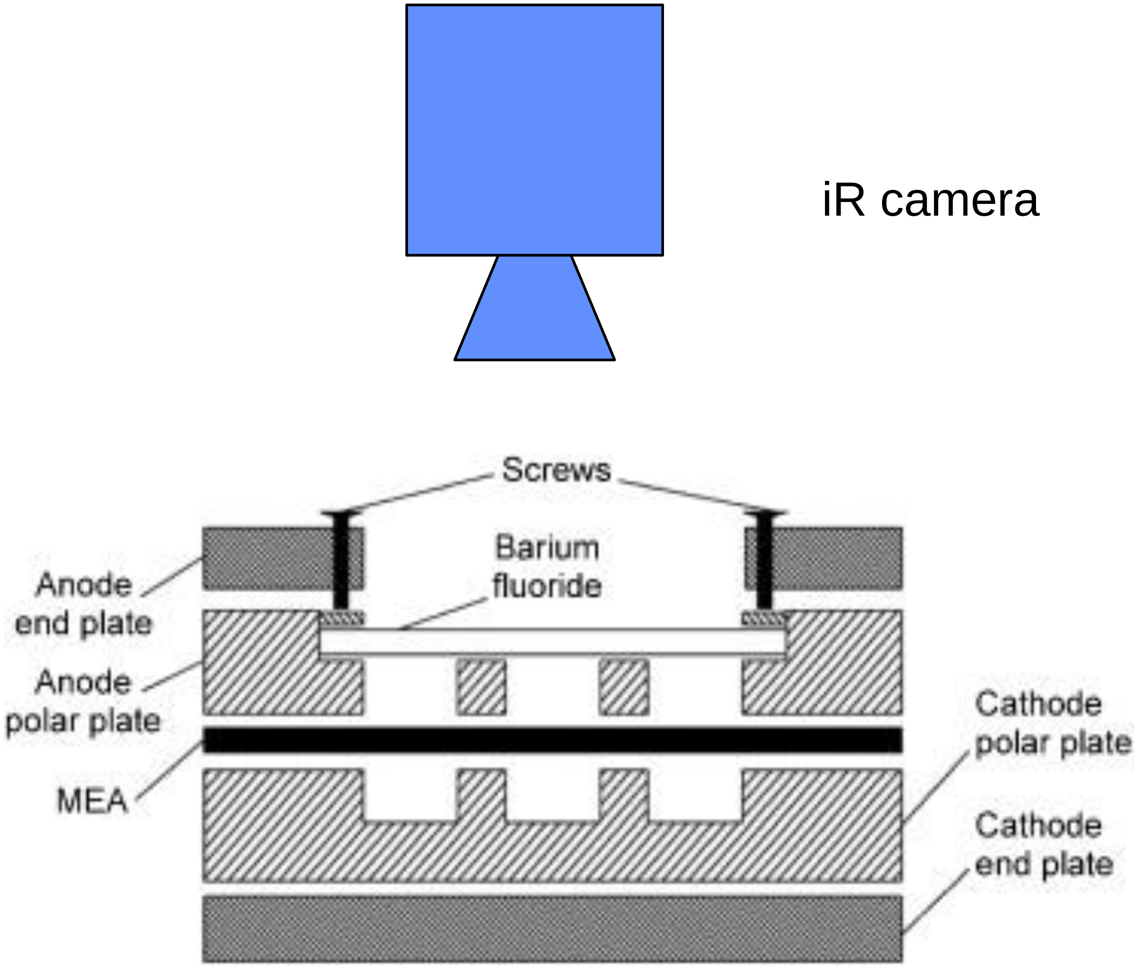
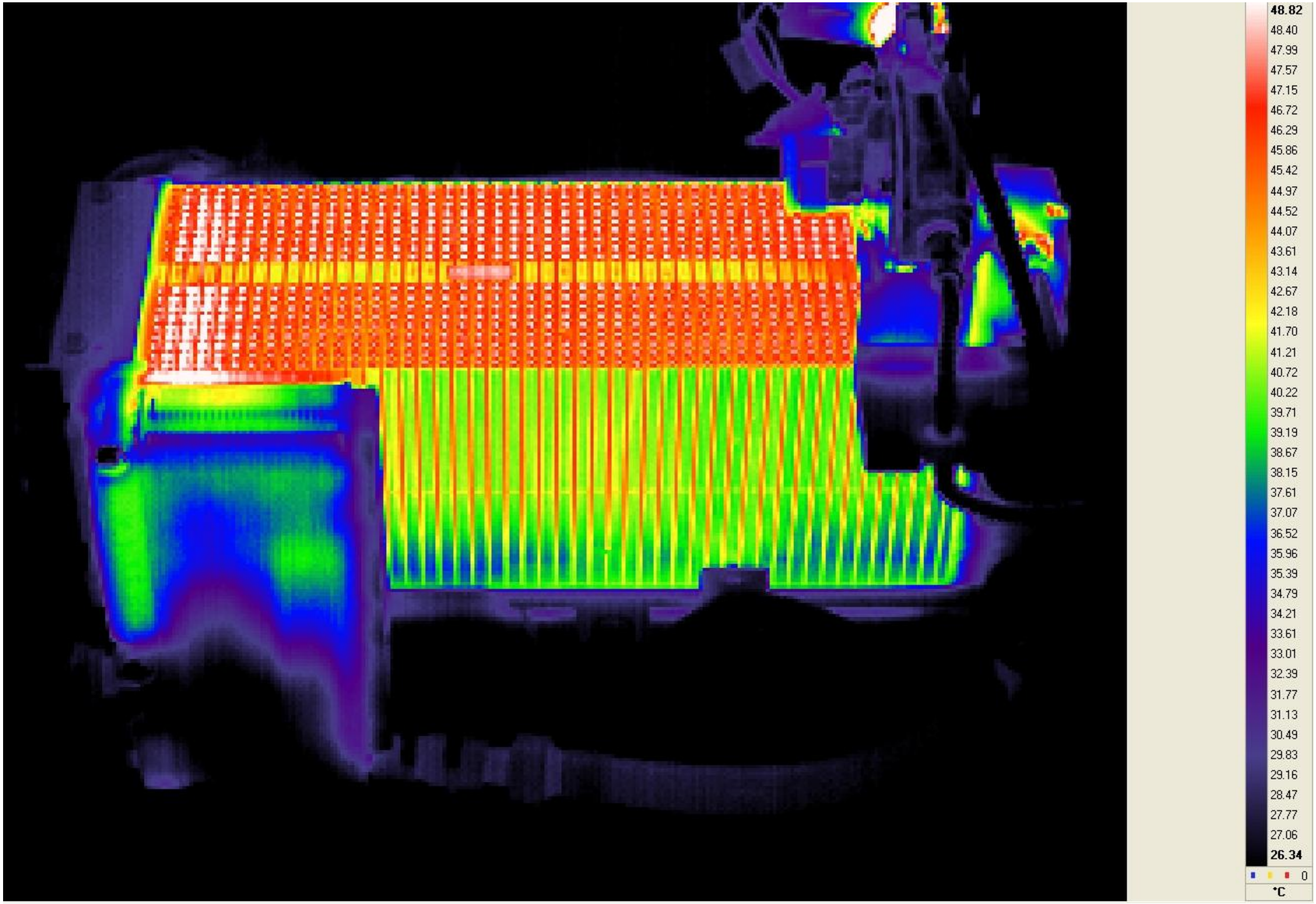
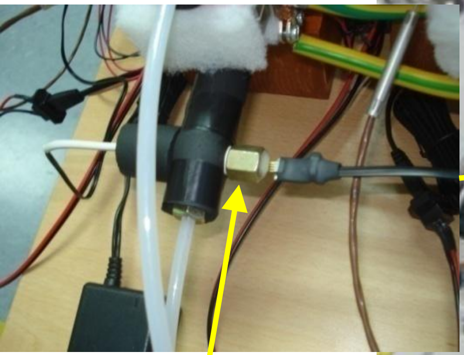
Temperature Mapping with iR Camera

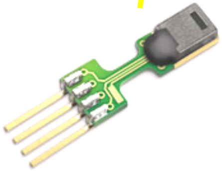


Temperature Mapping with iR Camera



Segmented fuel cell with separate temperature control





smallest sensor
on the market
Sensirion SHT 71

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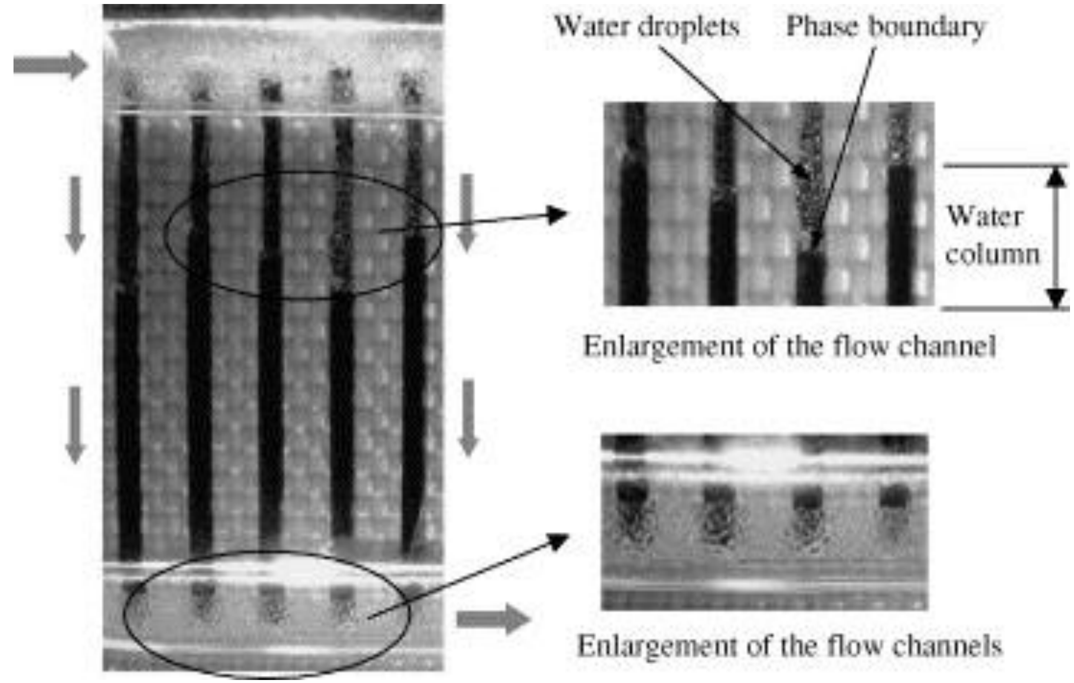
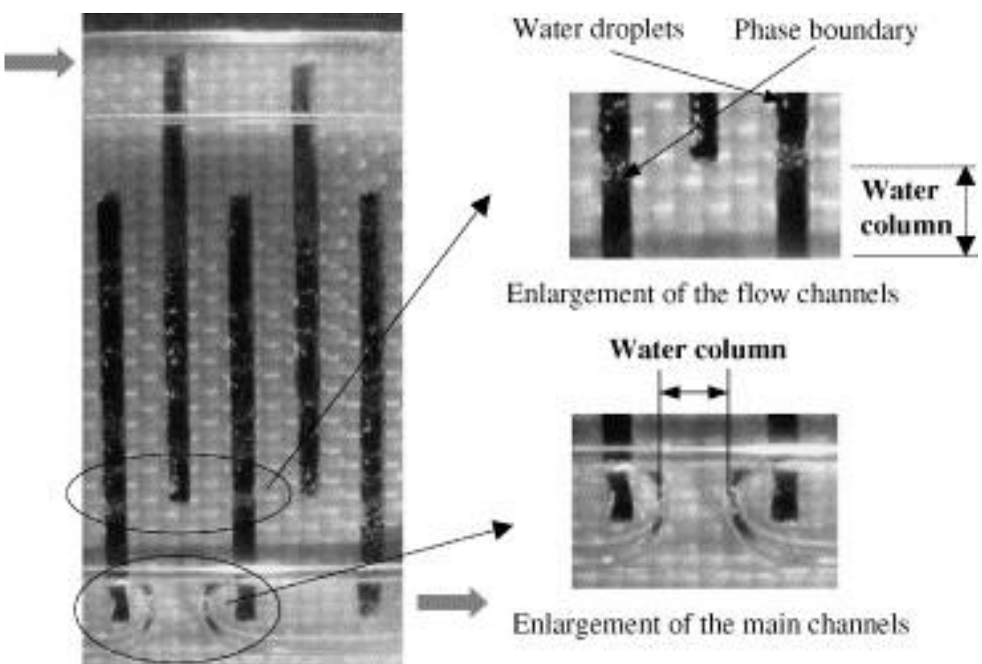
- Comparative polarization curves
- Current interrupt
- AC impedance spectroscopy
- Pressure drop
- Current density mapping
- Temperature mapping
- Flow visualization
- Neutron/X-Ray imaging

Flow Visualization



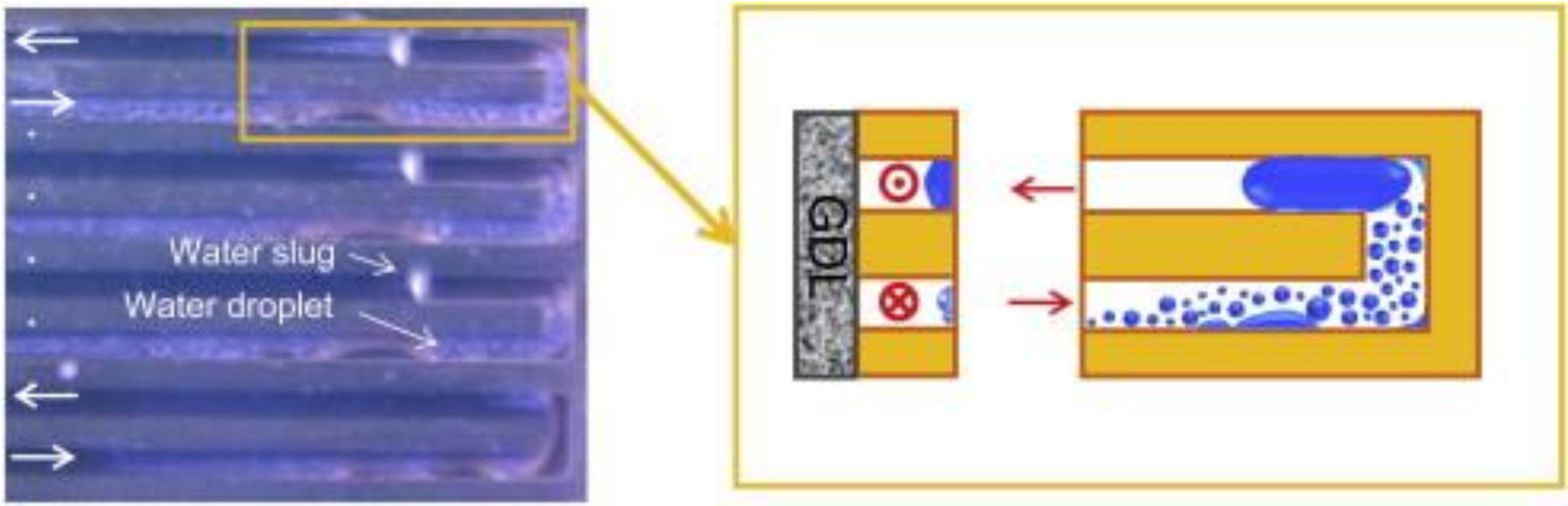
Interdigitated Flow Field

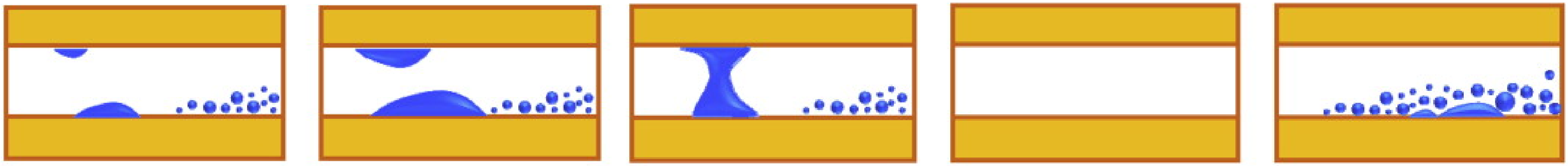


Straight Channels

X Liu, et al. **Water flooding and two-phase flow in cathode channels of proton exchange membrane fuel cells,** *Journal of Power Sources,*

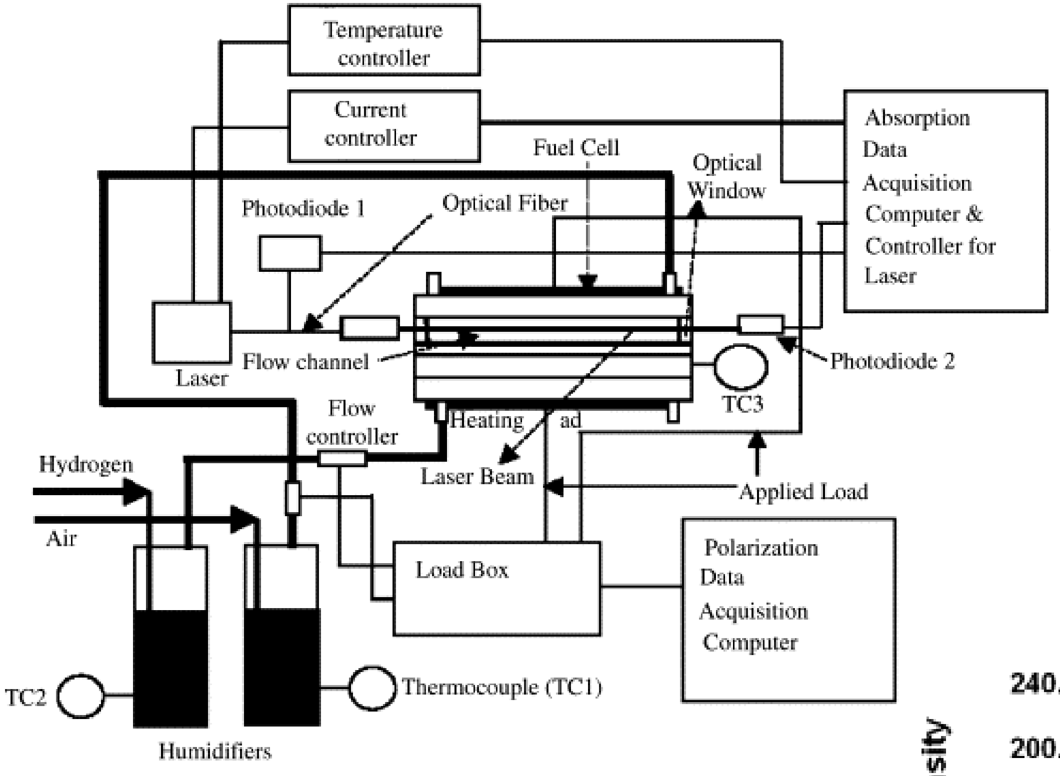
Flooding in Fuel Cell Channels

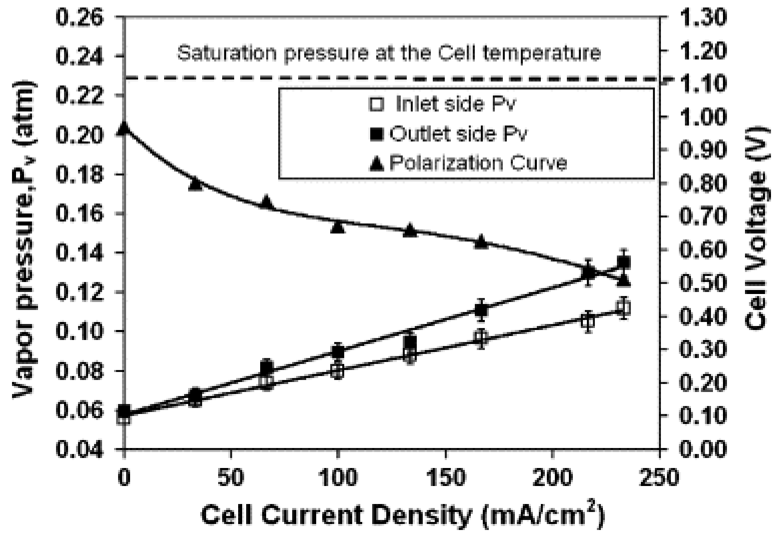


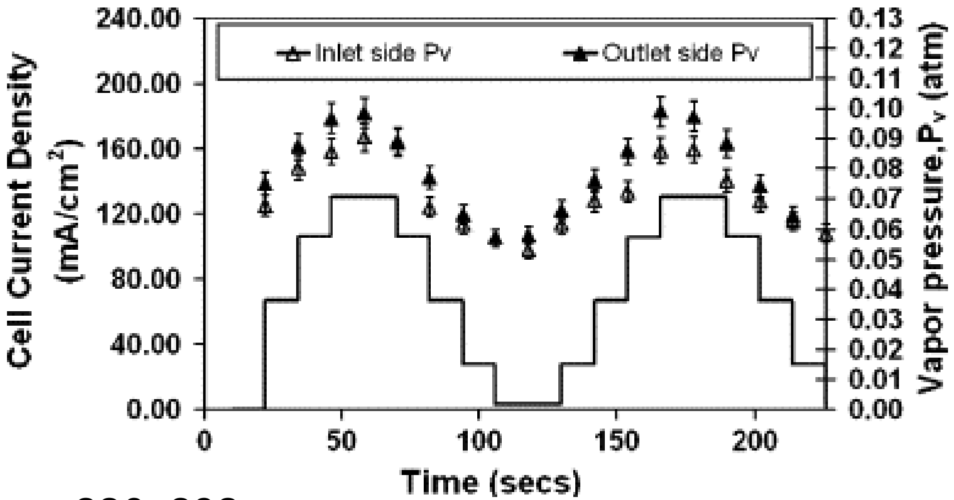


D. Lee, J. Bae, Visualization of flooding in a single cell and stacks by using a newly-designed transparent PEMFC International Journal of Hydrogen Energy, Vol. 37, No.1, 2012, pp 422–435

Optical measurements of water partial pressure

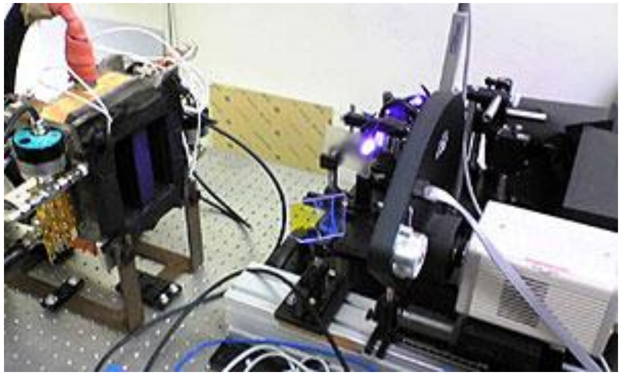


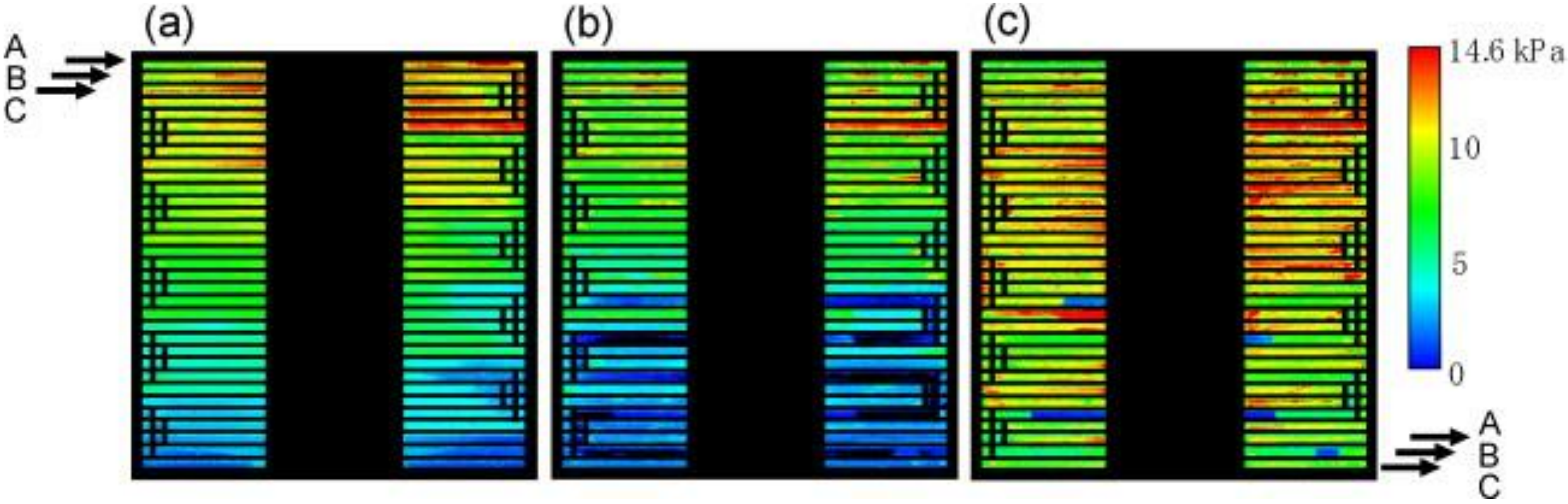




S Basu et al., J Power Sources, Vol 162, 2006, pp 286–293

Visualization of oxygen partial pressure





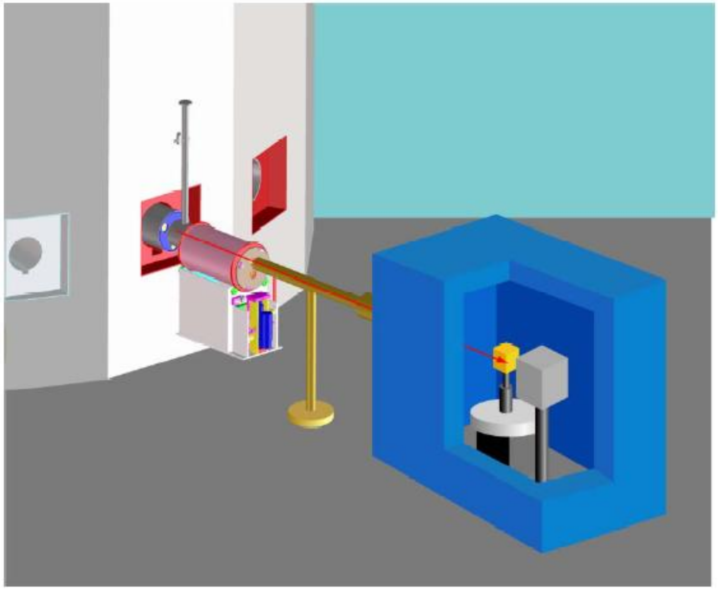
K Takada et al. J. Power Sources , Vol 196, 2011, Pages 2635–2639

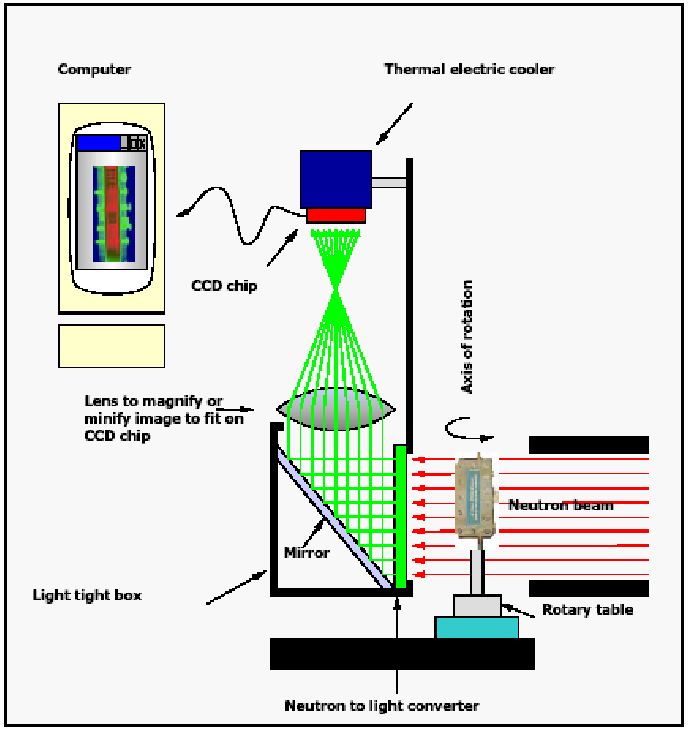
Inukai, J. *et al*. Direct Visualization of Oxygen Distribution in Operating Fuel Cells. Angew. Chem. Int. Ed. 47, 2792–2795 (2008).

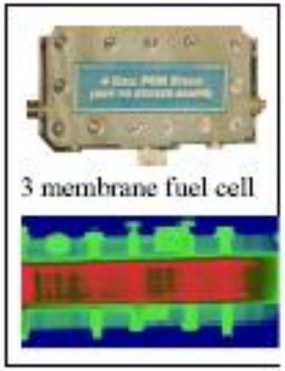
Diagnostics as a design tool

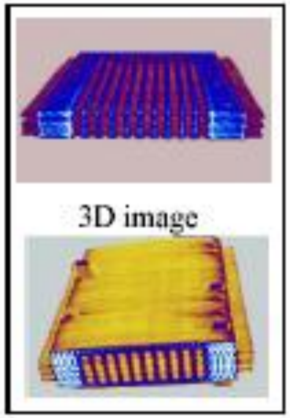
- Polarization curve
- Polarization curve hysteresis
- Comparative polarization curves
- Current interrupt
- AC impedance spectroscopy
- Pressure drop
- Current density mapping
- Temperature mapping
- Flow visualization
- Neutron/X-Ray imaging

Real time detection of liquid water inside an operating fuel cell

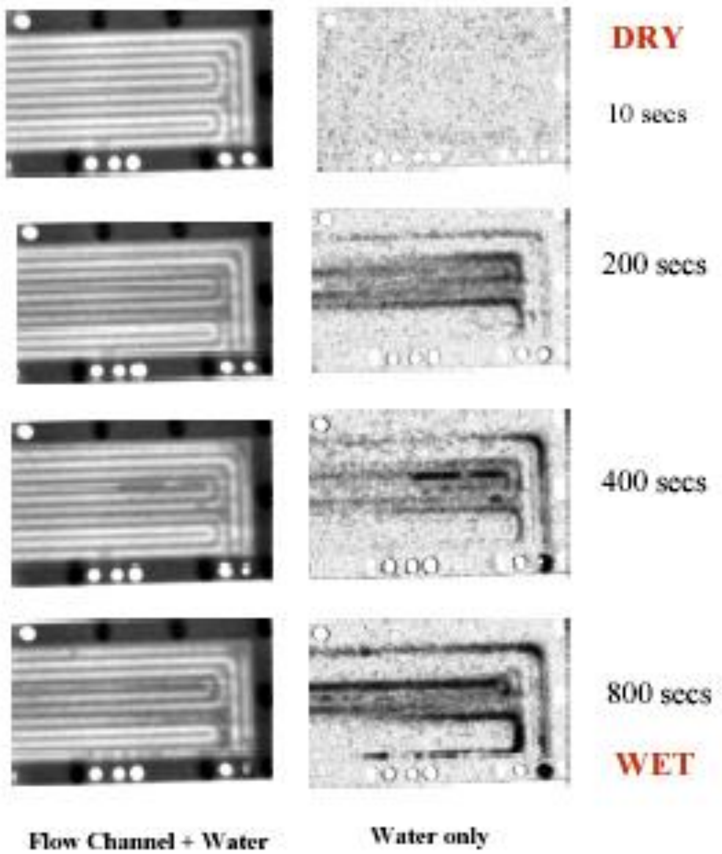








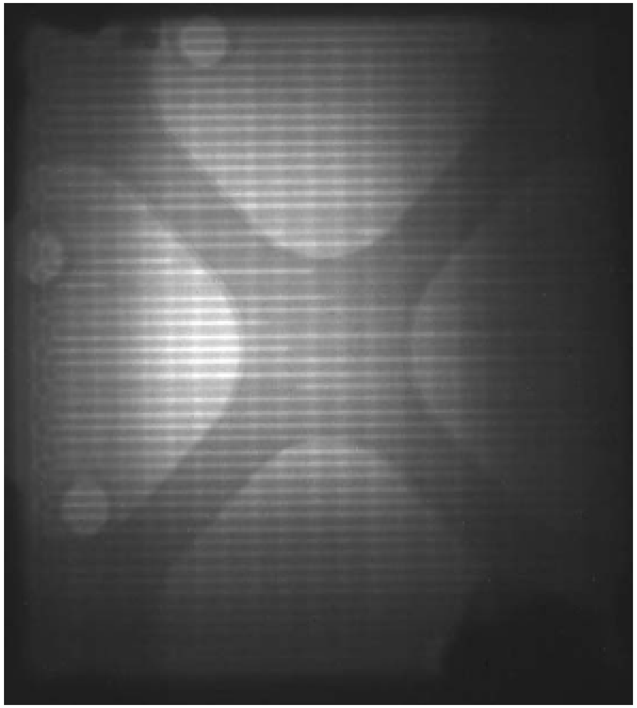
Water Distribution in flow channels vs. Time



neutrons can 'see' water in fuel cells

normalization of images: water distribution map

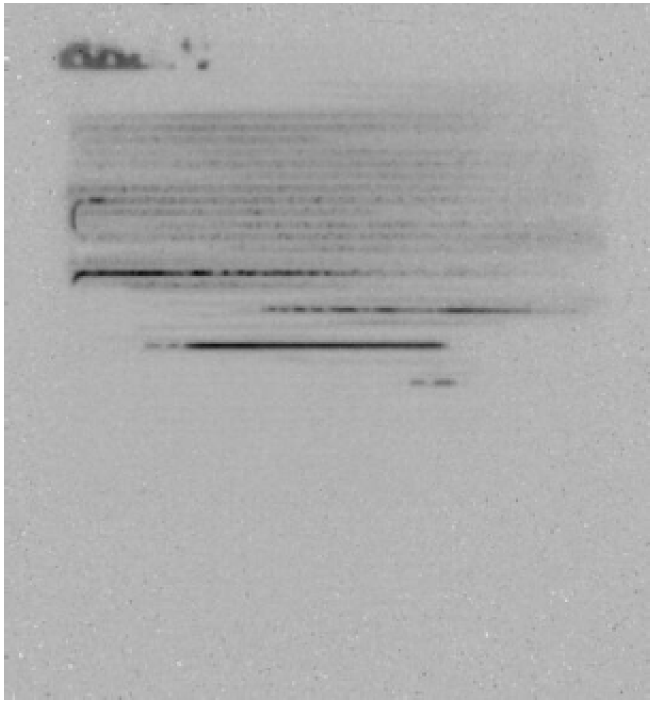
original radiography



← 100 mm →

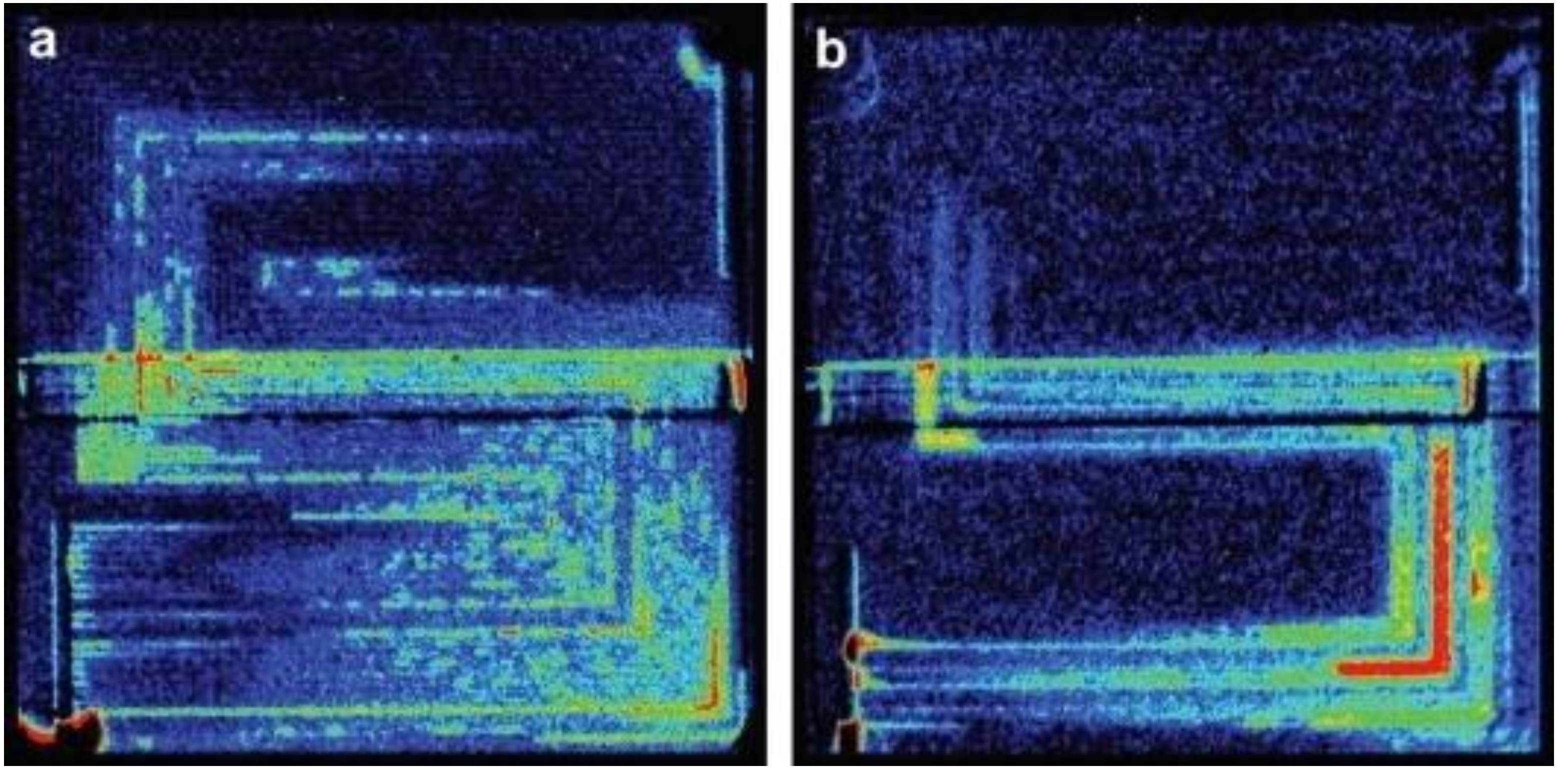
ratio: water filled cell /empty cell

water distribution



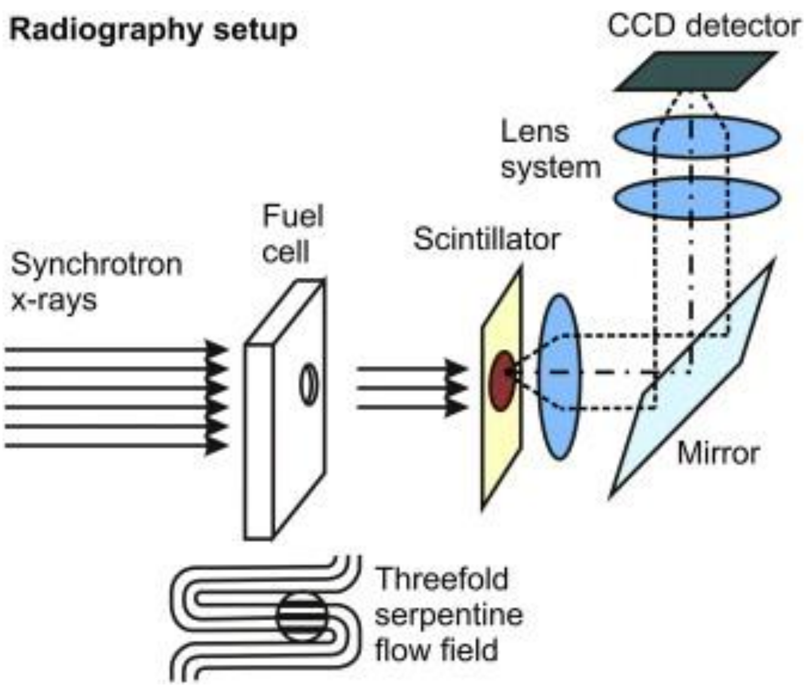
Liquid water distribution in PEMFC by neutron imaging

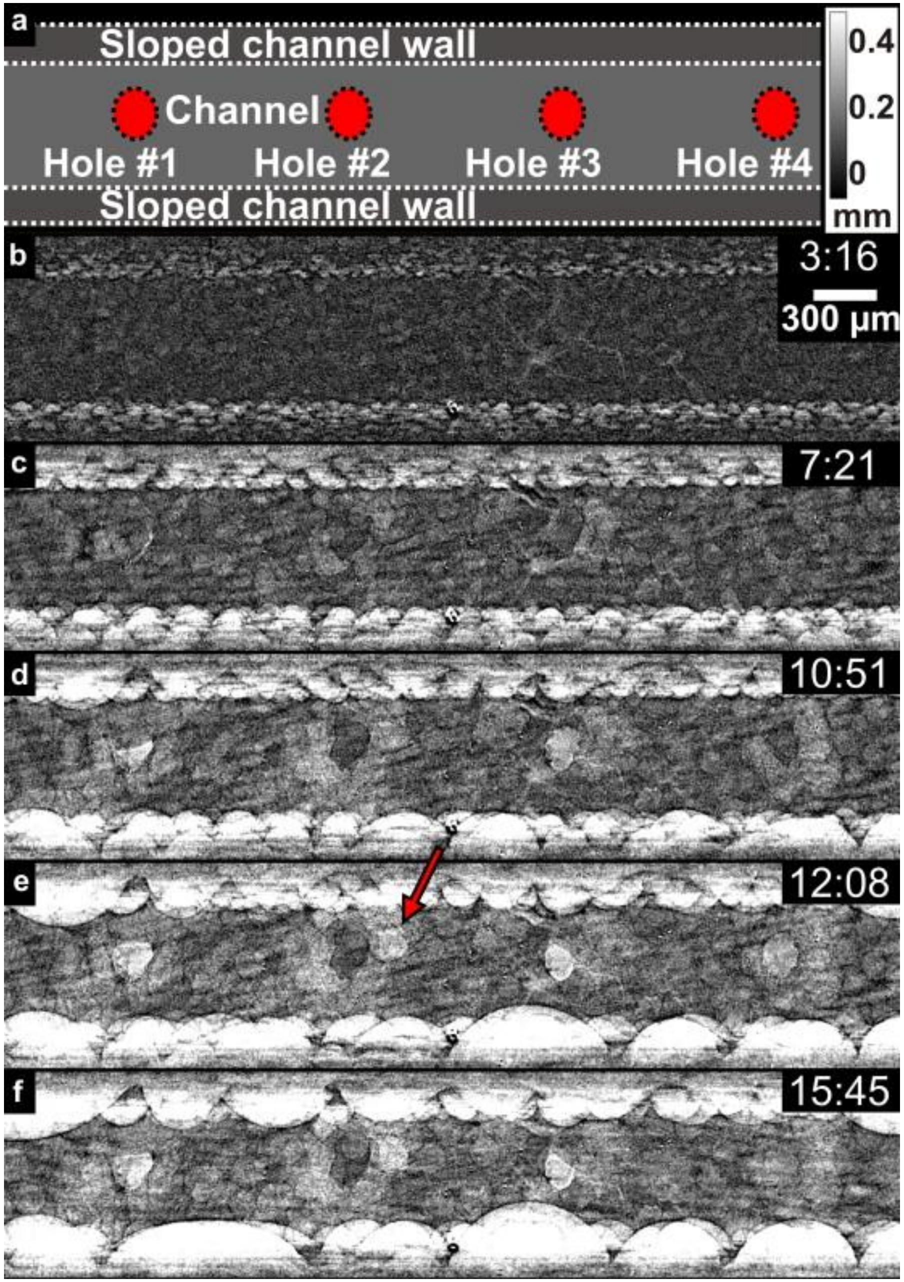
at Penn State University



A. Turhan, K. Heller, J.S. Brenizer and M.M. Mench, Passive control of liquid water storage and distribution in a PEFC through flow-field design, *Journal of Power Sources* 180 (2) (2008), pp. 773–783.

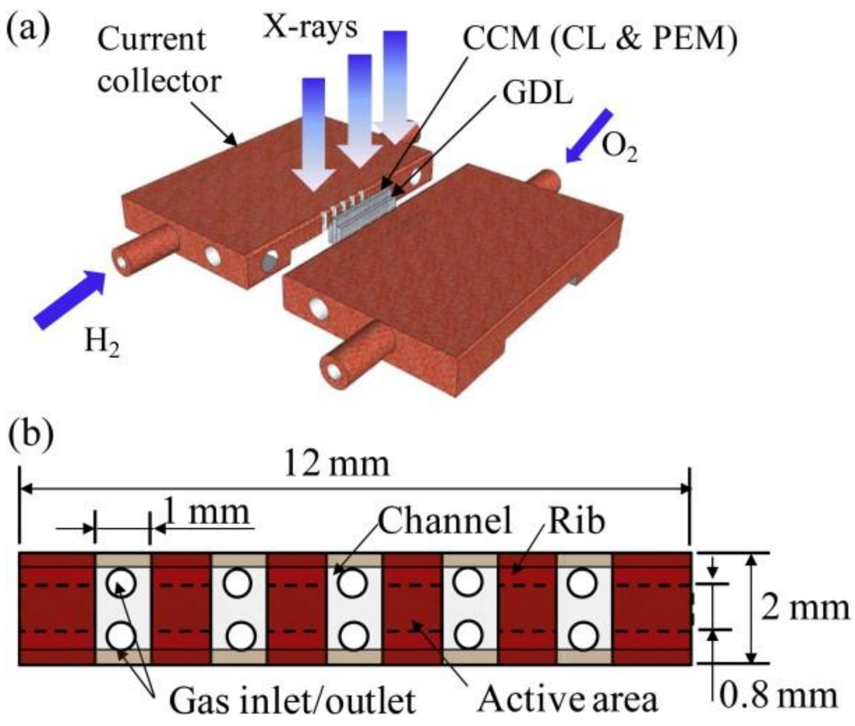
Synchrotron X-Ray Radigraphy

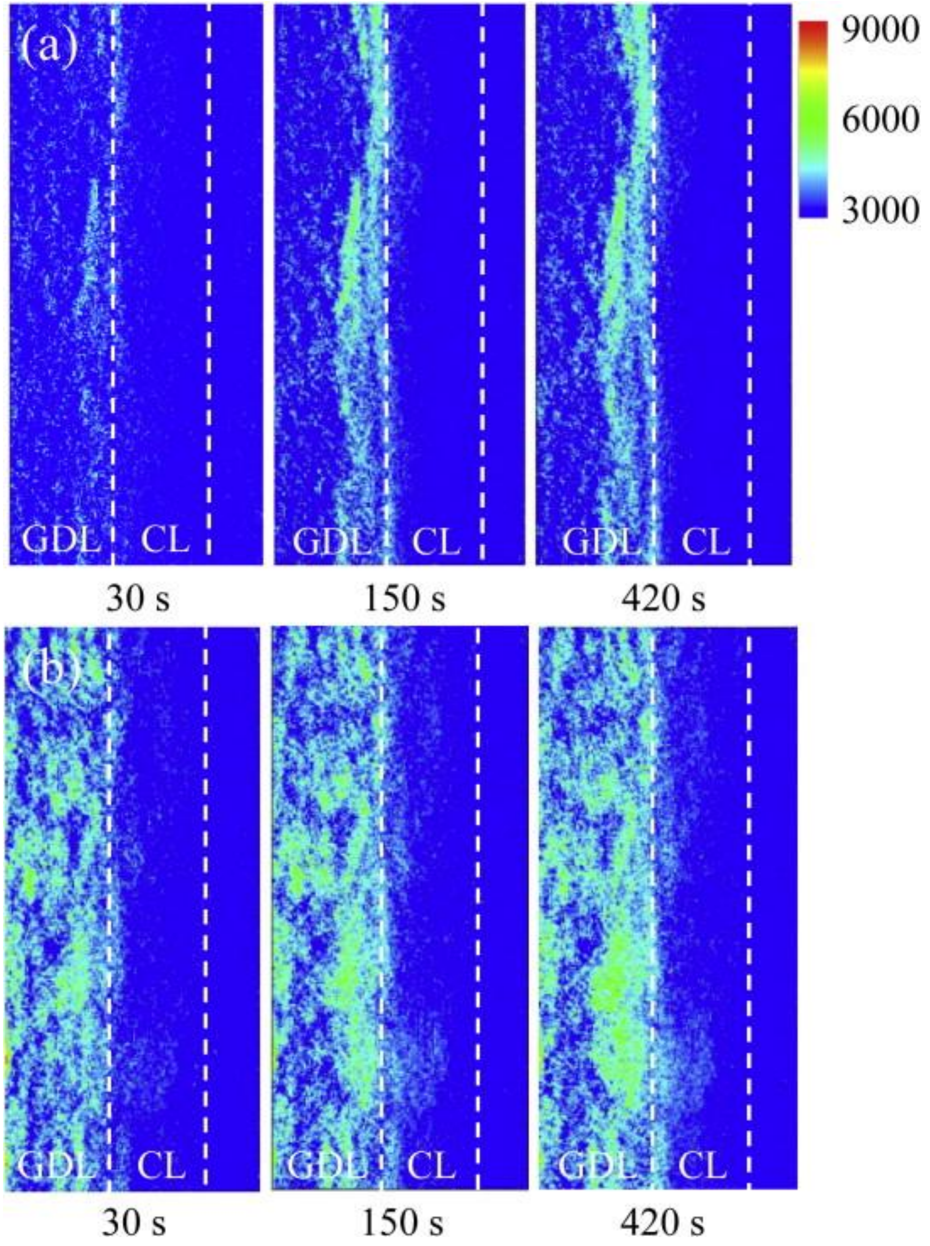




H. Markötter et al., Int. J. Hydrogen Energy, Vol 37, 2012, pp. 7757–7761

High-resolution Soft X-ray Radiography





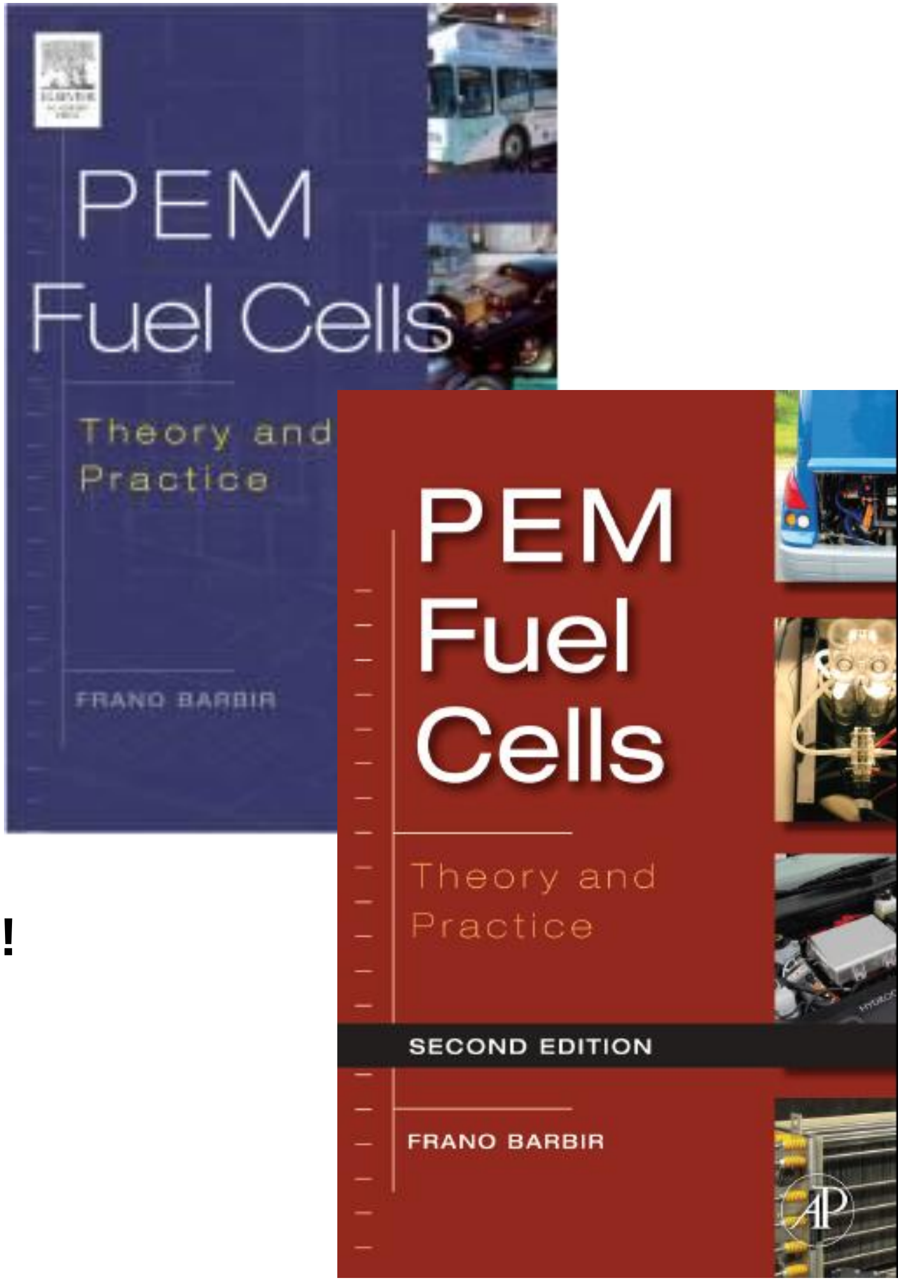
P. Deevanhxay, Electrochemistry Comm., 2012
http://dx.doi.org/10.1016/j.elecom.2012.05.028,

Conclusions

- Diagnostics – important aspect of fuel cell R&D
- Limited number of diagnostic methods applicable for fuel cell control purposes
- Definition of optimum performance must include life time
- In order to achieve optimum performance diagnostics is crucial for prognostics and health management

More information about PEM fuel cells:

Frano Barbir
PEM Fuel Cells: Theory and Practice
Elsevier/Academic Press, 2005
ISBN 978-0-12-078142-3



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