GHT33-2
Calorimetric Measurements and Electrode Reactions in the PEM Fuel Cell

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18 November 2009
2009 Fuel Cell Seminar & Exposition, November 16-19, 2009
Palm Springs Convention Center, Palm Springs, CA, USA

SINTEF NTNU QUEEN'S-RMC FCRC IFE

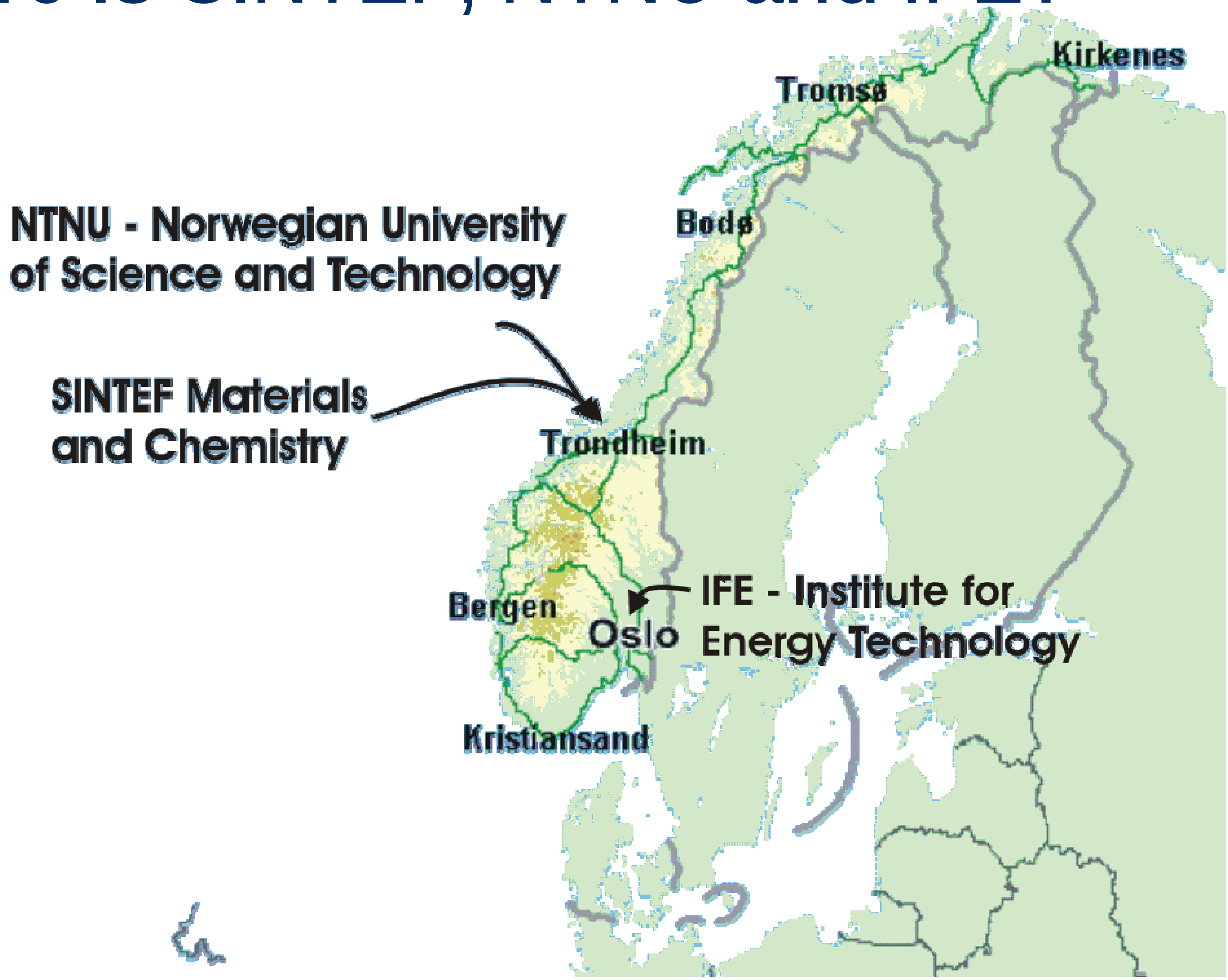
Outline

- Thermal Effects in PEMFC
- Heat and power generation in fuel cells
- Calorimetry
- Apparatus
- Experimental set-up and conditions
- Results
- Conclusions

Thermal Effects in PEM fuel cells

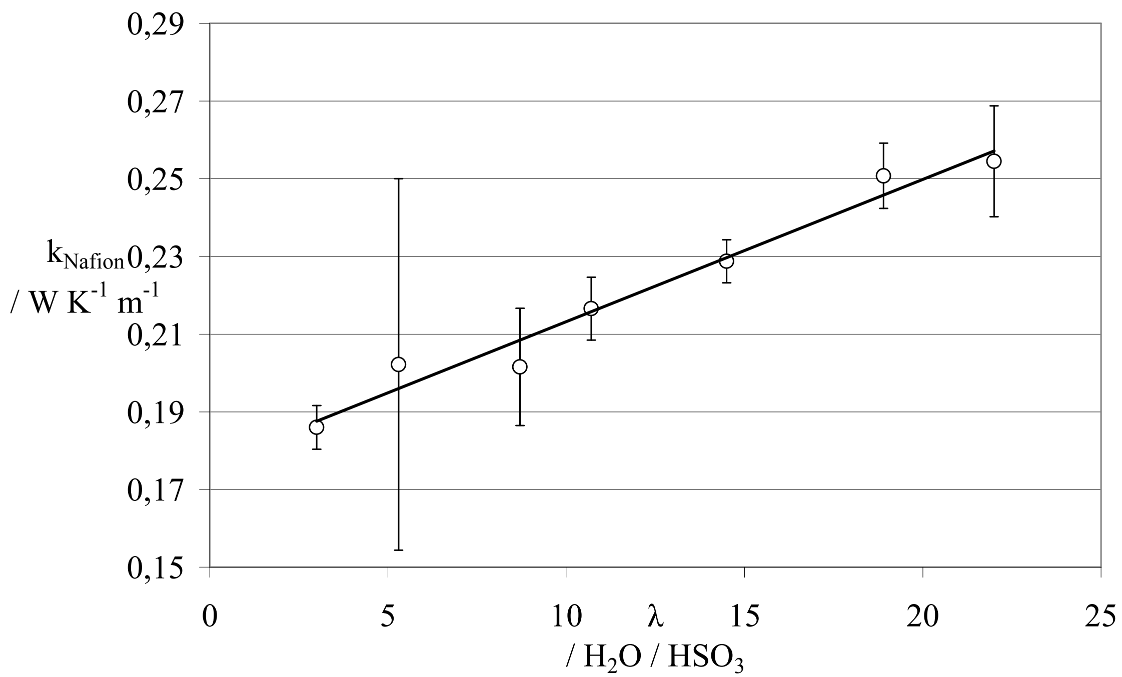
- Collaborative project:
  - Norwegian University of Science and Technology, Trondheim
  - SINTEF Materials and Chemistry
  - Institute for Energy Technology
- Thermal conductivites
  - Membranes
  - Porous Transport Layers (PTL/GDL)
- Local temperatures
- Calorimetry

Where is SINTEF, NTNU and IFE?



Thermal conductivity measurements

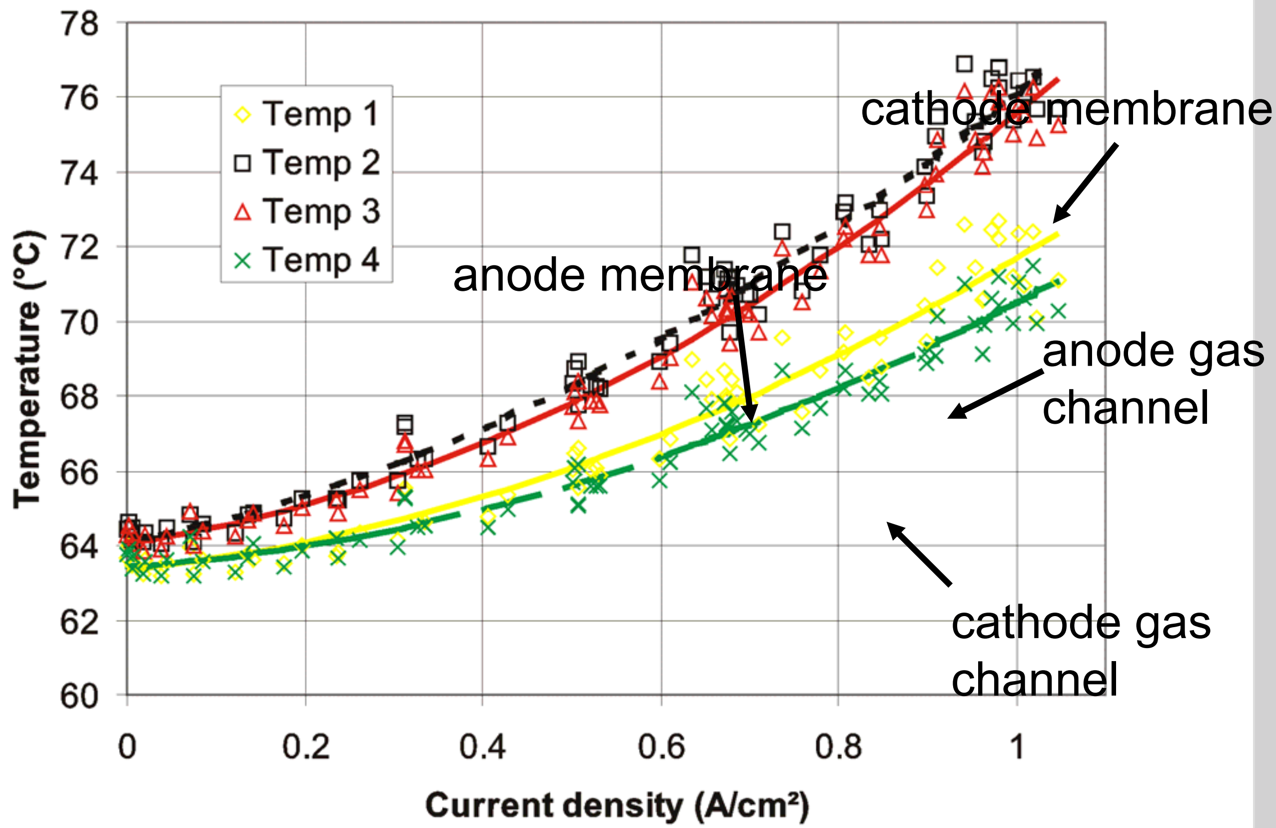
- Compression of samples
- Thickness measurements
- Varying humidity
- Measure contact resistances
- Nafion membranes
- Porous Transport layers (PTL/GDL)



Burheim, O., Vie, P.J.S., Pharoah, J.G., and Kjelstrup, S., Journal of Power Sources, 2010. **195**(1): p. 249-256.

Local temperatures

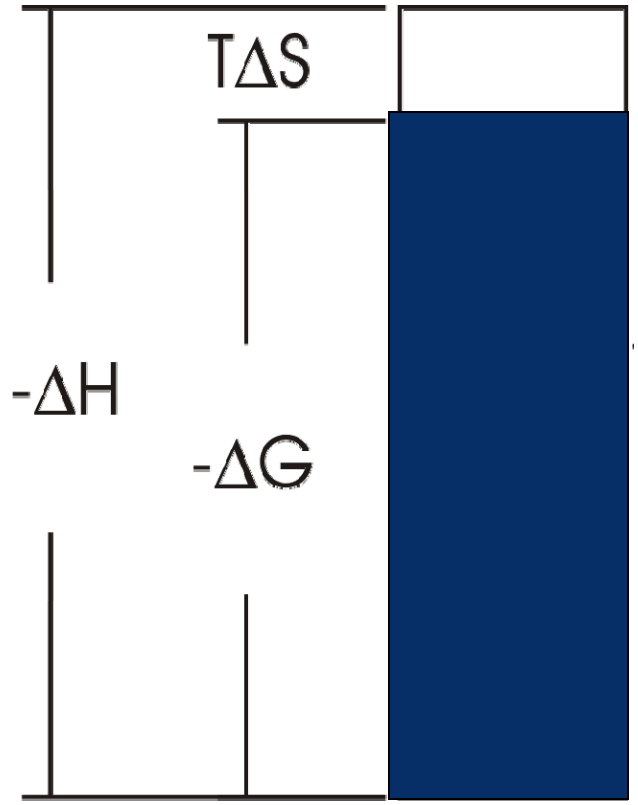
- 3.5 barg, H_2/O_2,
- stoich 2
- 0.1 mg/cm² Pt,
- 35 wt% Nafion
- Nafion 115
- 80°C humidification of gases



Vie, P.J.S. and Kjelstrup, S., Electrochimica Acta, 2004. **49**(7): p. 1069-1077.

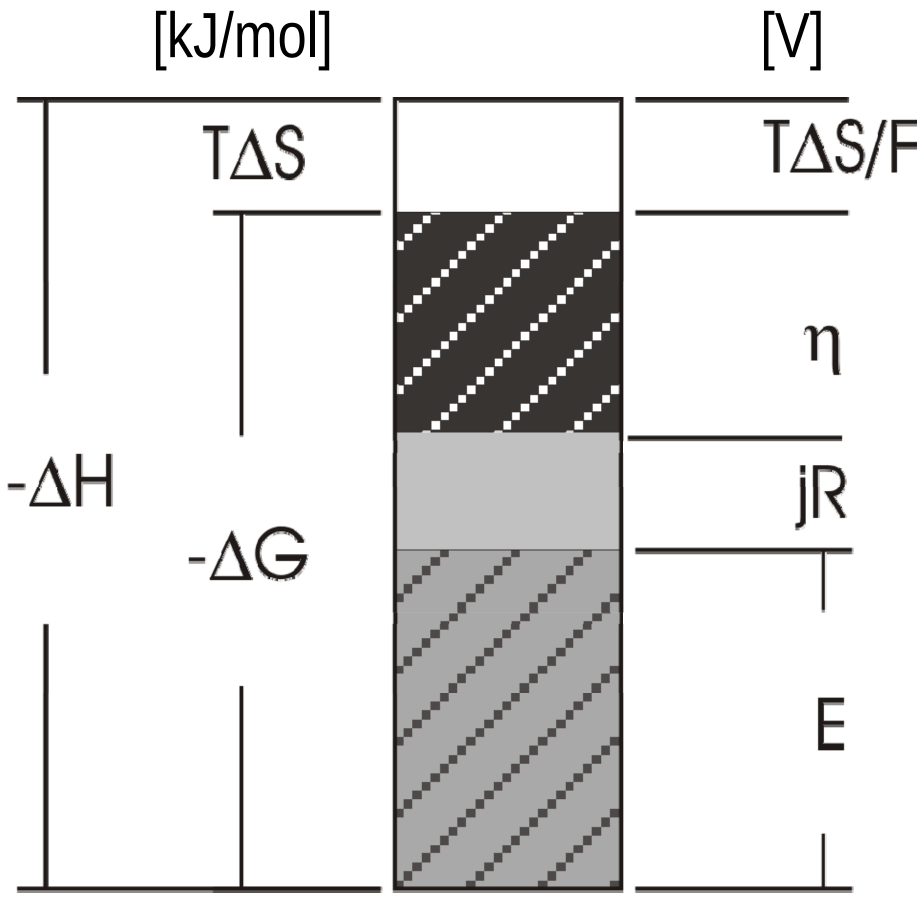
Thermodynamic properties

- Fuel cell reaction
  - ½H_2(g) + ¼O_2(g) = ½H_2O(l)
- Available electric energy
  - ΔG = -118.6 kJ/mol
  - $E_{rev} = -\Delta G/nF = -\Delta G/F$
  - E_{rev}=1.23 V, 25°C,1 bar
- Total energy change
  - $\Delta H = \Delta G + T\Delta S = T\Delta S - E_{rev}F$
  - ΔH = -142.9 kJ/mol = 1.48 V
- Reversible heat change
  - $T\Delta S$ = -24.4 kJ/mol = 0.25 V



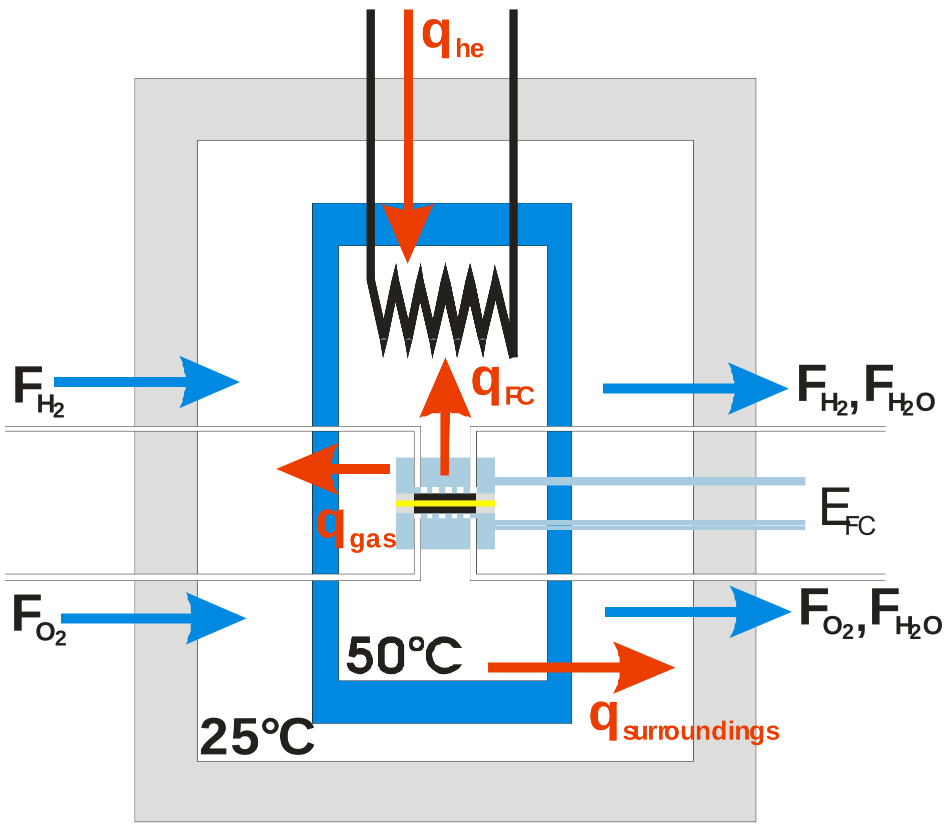
Heat and Power Generation

- Cell voltage at constant T
  - $E = E_{rev} - \eta^a + \eta^c - r \cdot j$
  - $E = \frac{-\Delta H}{F} + \frac{T\Delta S}{F} - \eta^{tot} - r \cdot j$
- Electric power [W]
  - $P_{FC} = E\,j = P_{tot} - P_{heat}$
  - $P_{heat} = -\,q_{FC}$
  - $P_{FC} = -\Delta H \frac{j}{F} + T\Delta S \frac{j}{F} - \eta^{tot} j - r \cdot j^2$
- Total power [W]
  - $P_{tot} = j\Delta H/F$
- Heat flow [W] at constant T
  - $q_{FC} = T\Delta S\, j/F - \eta^{tot} j - r\, j^2$

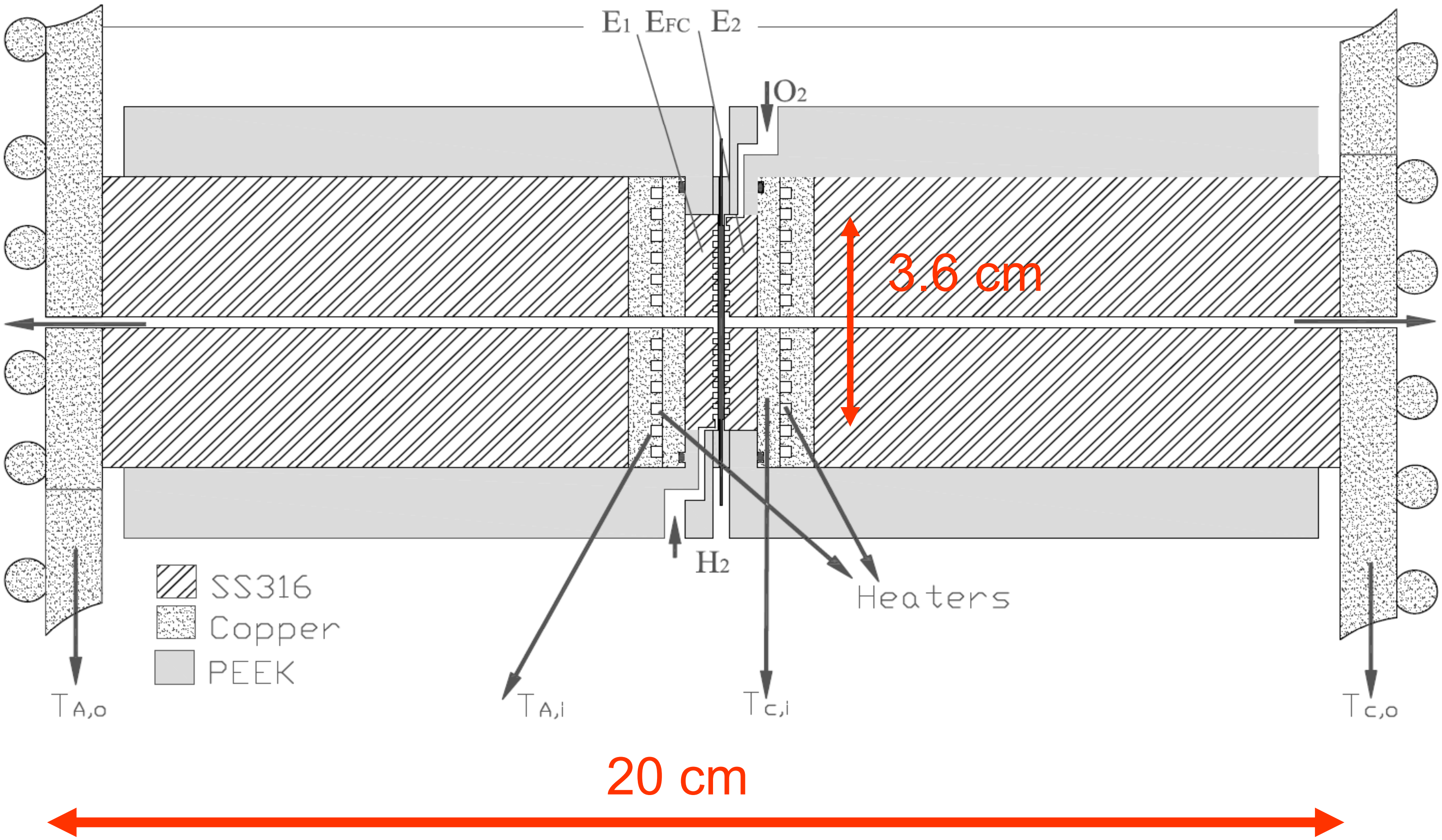


Isothermal calorimetry

- Reference case
  - No flow
  - No FC current
  - $q_{he,ref} + q_{surroundings} = 0$
- Flow case
  - No FC current
  - $q_{he,flow} + q_{surroundings} + q_{gas} = 0$
  - $- q_{he,flow} = q_{surroundings} + q_{gas}$
- FC operation case
  - $q_{FC} + q_{he,FC} + q_{surroundings} + q_{gas} =$
  - $q_{FC} + q_{he,FC} - q_{he,flow} = 0$
  - $q_{FC} = q_{he,flow} – q_{he,FC}$

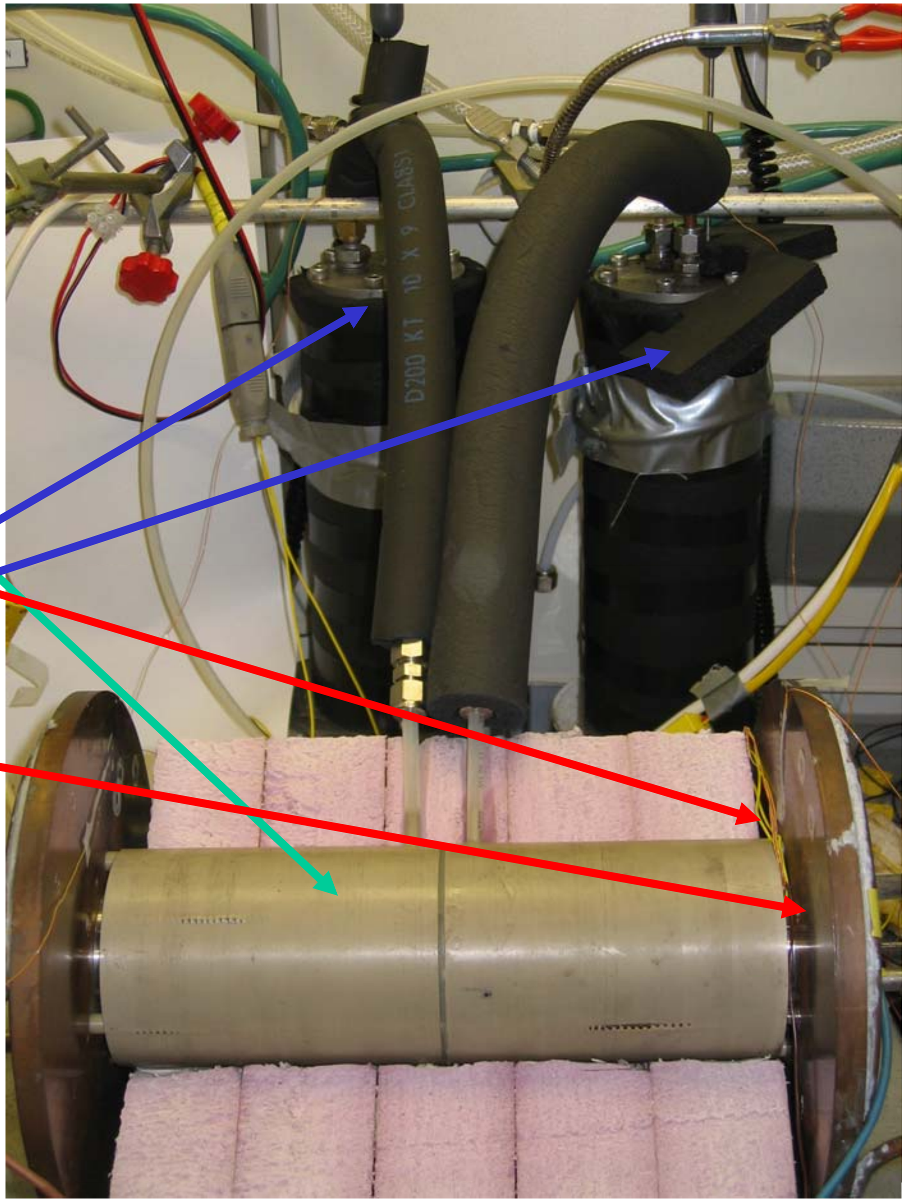


Apparatus
Fuel Cell and Calorimeter

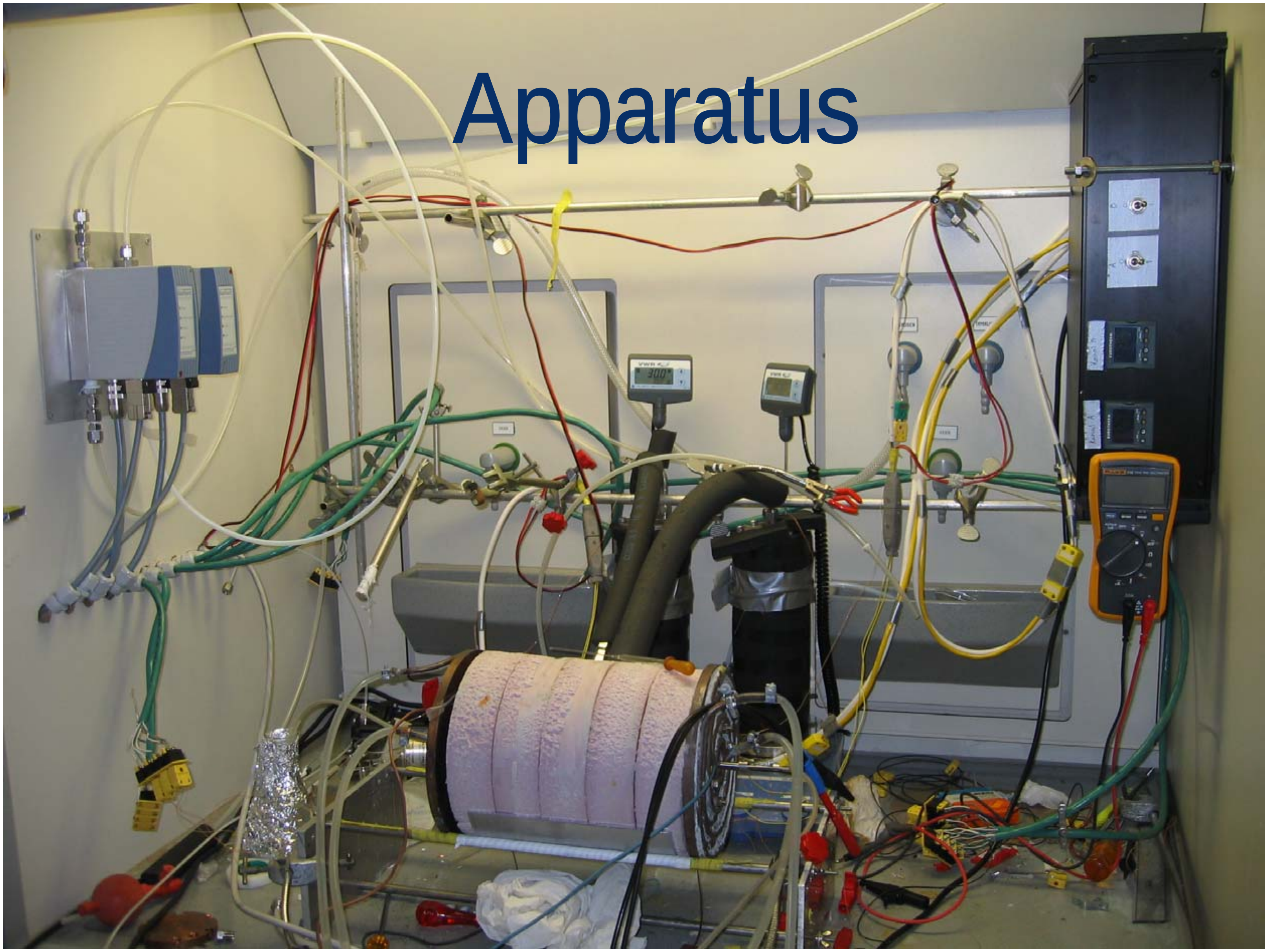


Apparatus

- Fuel Cell housing
- Thermocouples
- Gas humidifiers
- Cell housing heaters



Apparatus



Apparatus

- Instruments:
  - Electronic Load (Agilent 6060B)
  - Power supply (Agilent EE3633A)
  - High Frequency Ohm meter (HFO) (Agilent 4338B)
  - Gas flow controllers (Bürkert, CMOSensTM)
  - Temperature control: Eurotherm PID-controllers
  - LabVIEW based control system
    - Compact Field Point modules

Experimental conditions

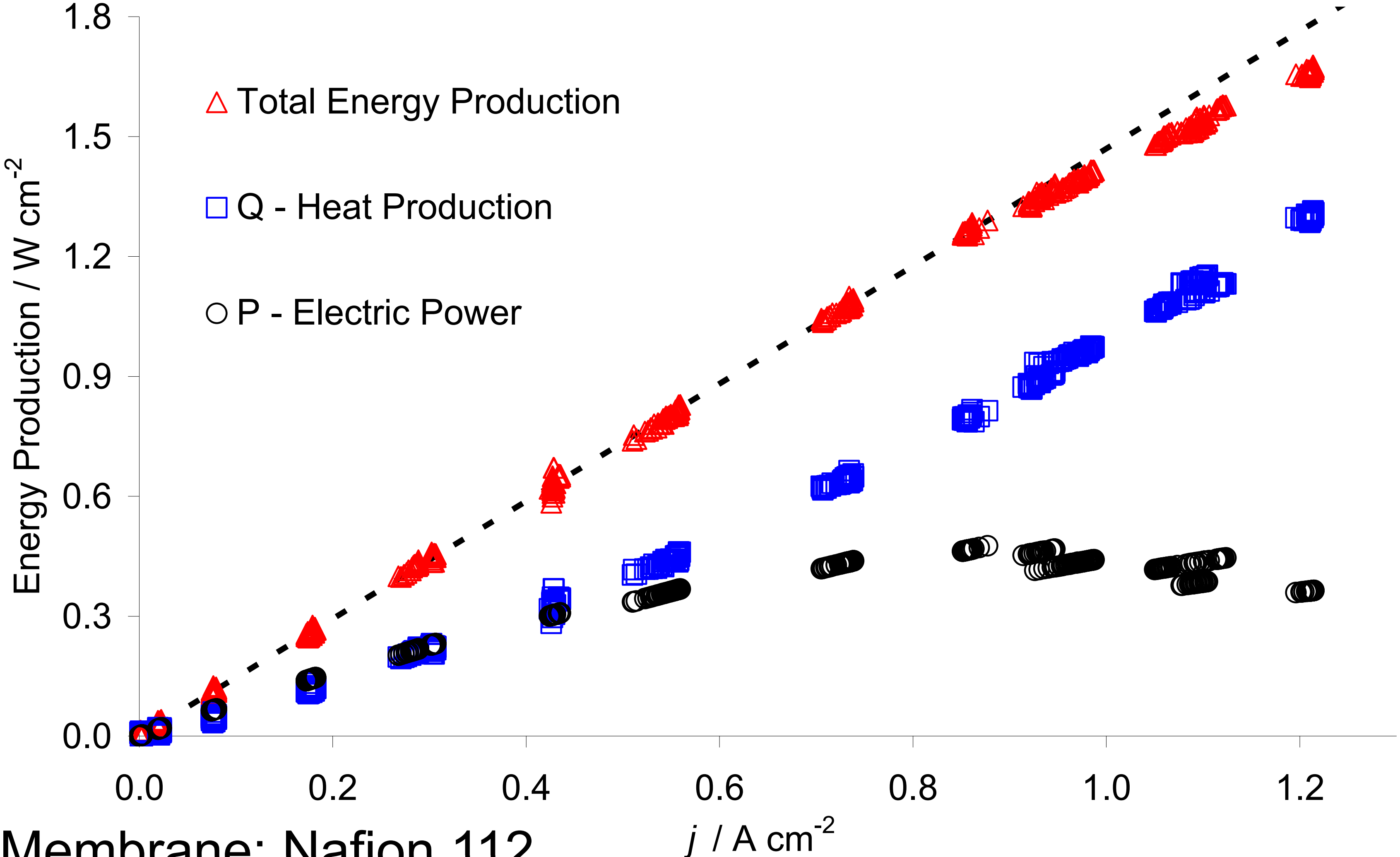
- Fuel cell:
  - Membrane:
    - Nafion 112, 115 or 117
  - Electrodes (with PTL):
    - SolviCore Catalyst Coated Backings (Batch Number # 205-07-1)
  - Active area:
    - 10.2 cm²

- Experimental conditions:
  - Pressure: 1 bar
  - Operating temperature:
    - 50 °C (323 K)
  - Humidifier temperature:
    - 40 °C (313 K)
  - H_2 and O_2:
  - Stoichimetric flow rates:
    - O_2: 3
    - H_2: 1.5

Procedure

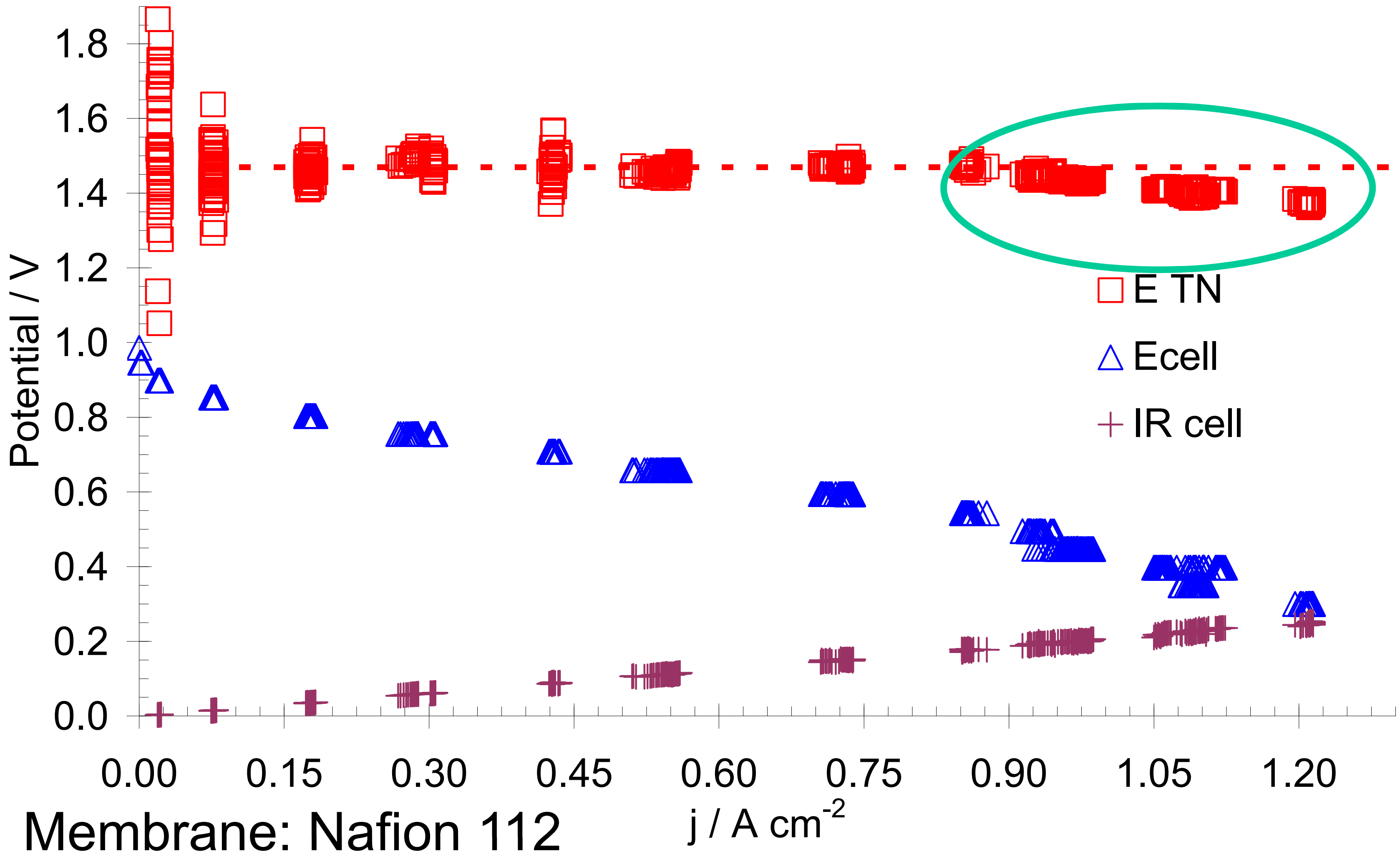
- Measure $Q_{he,j=0}$ at OCV and no flow
- Measure Q_{gas} at OCV with flow
- Measure $Q_{he,j}$ in steps of 0.05 V from 0.2 V to OCV (polarisation curves)
- Measure potential drop in FC housing – Q_{house}

The measured heat and work



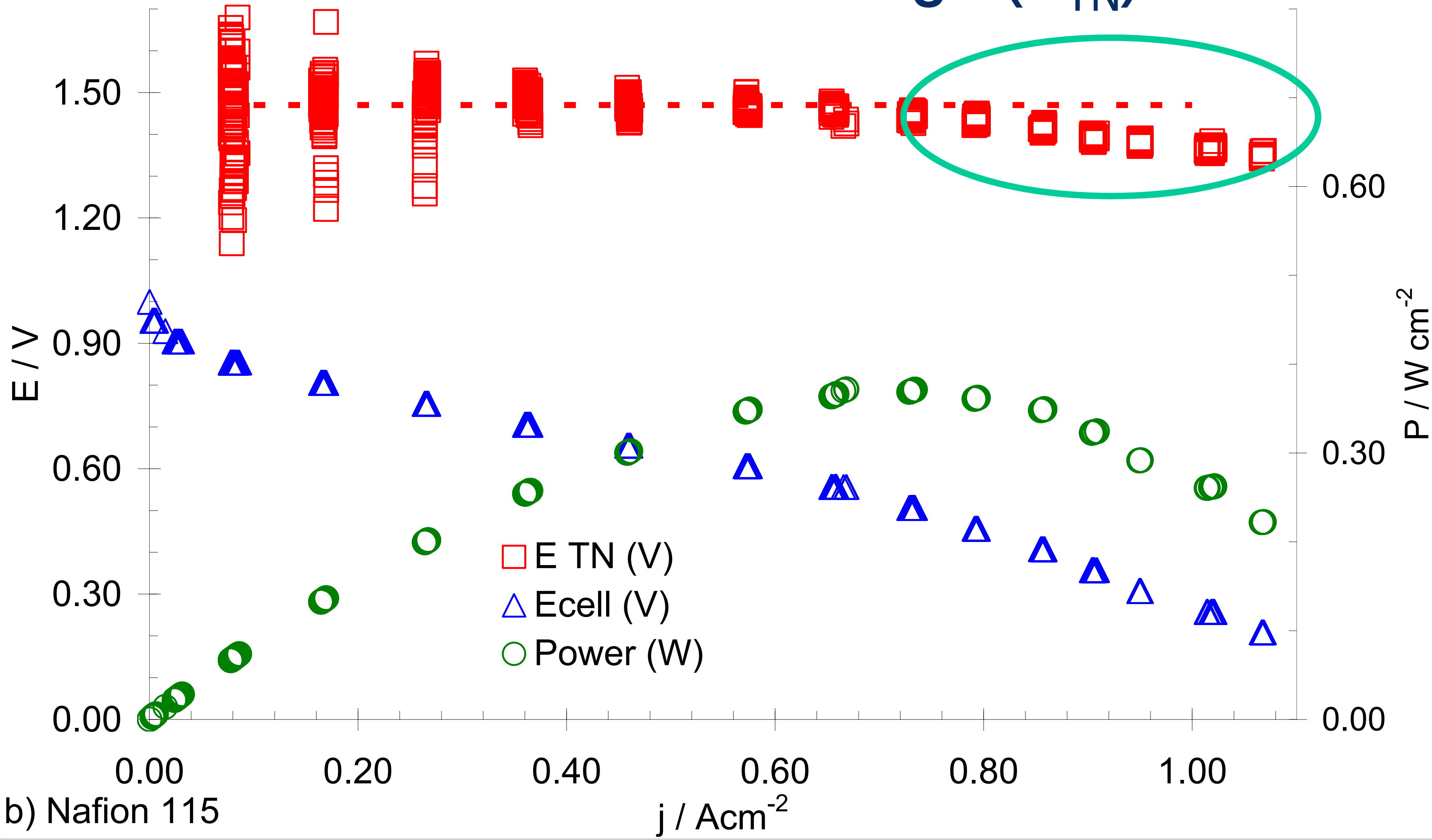
Membrane: Nafion 112

Polarisation curve

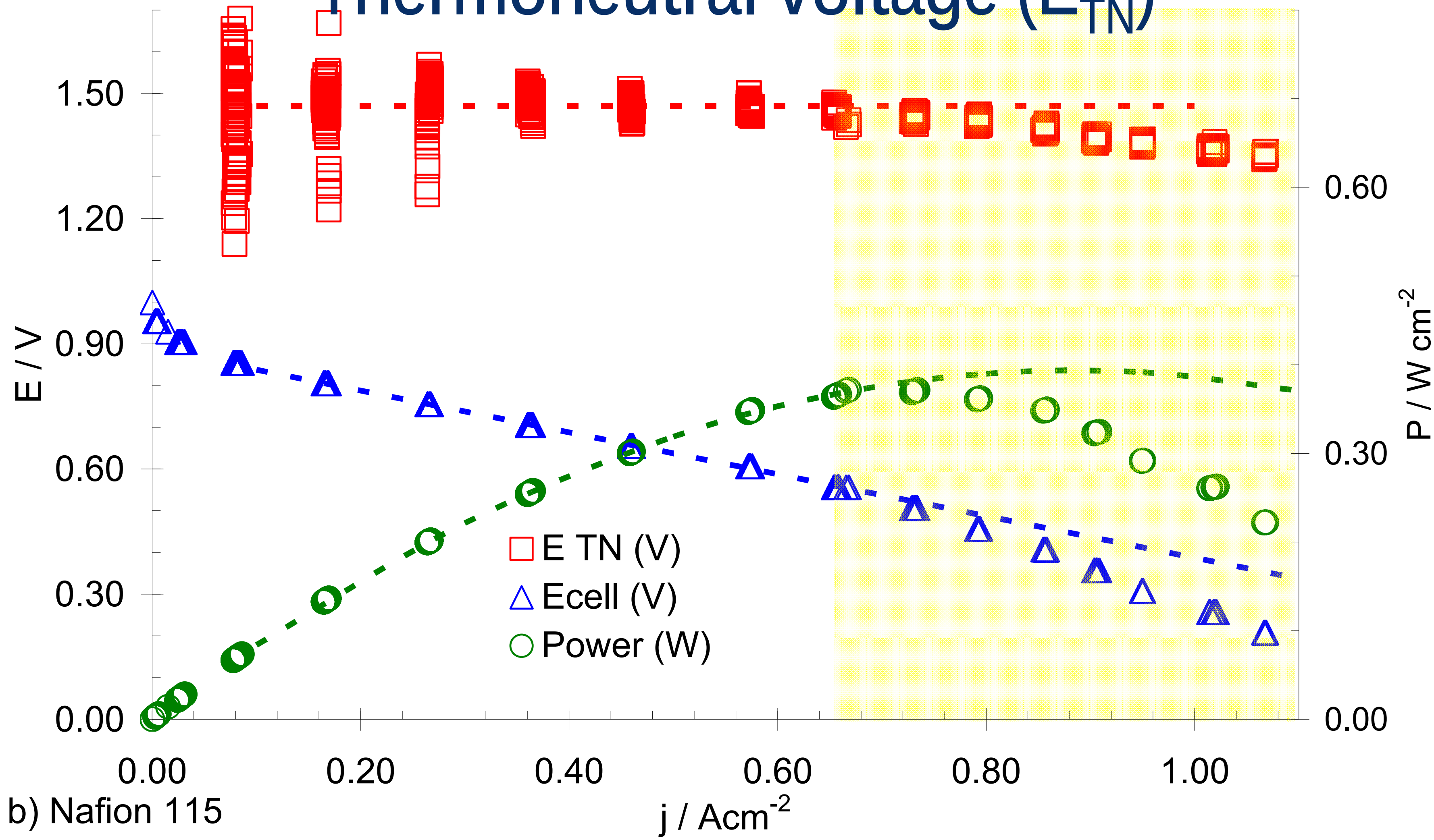


Membrane: Nafion 112

Measure Enthalpy through Thermoneutral voltage (E_{TN})



Measure Enthalpy through Thermoneutral voltage (E_{TN})

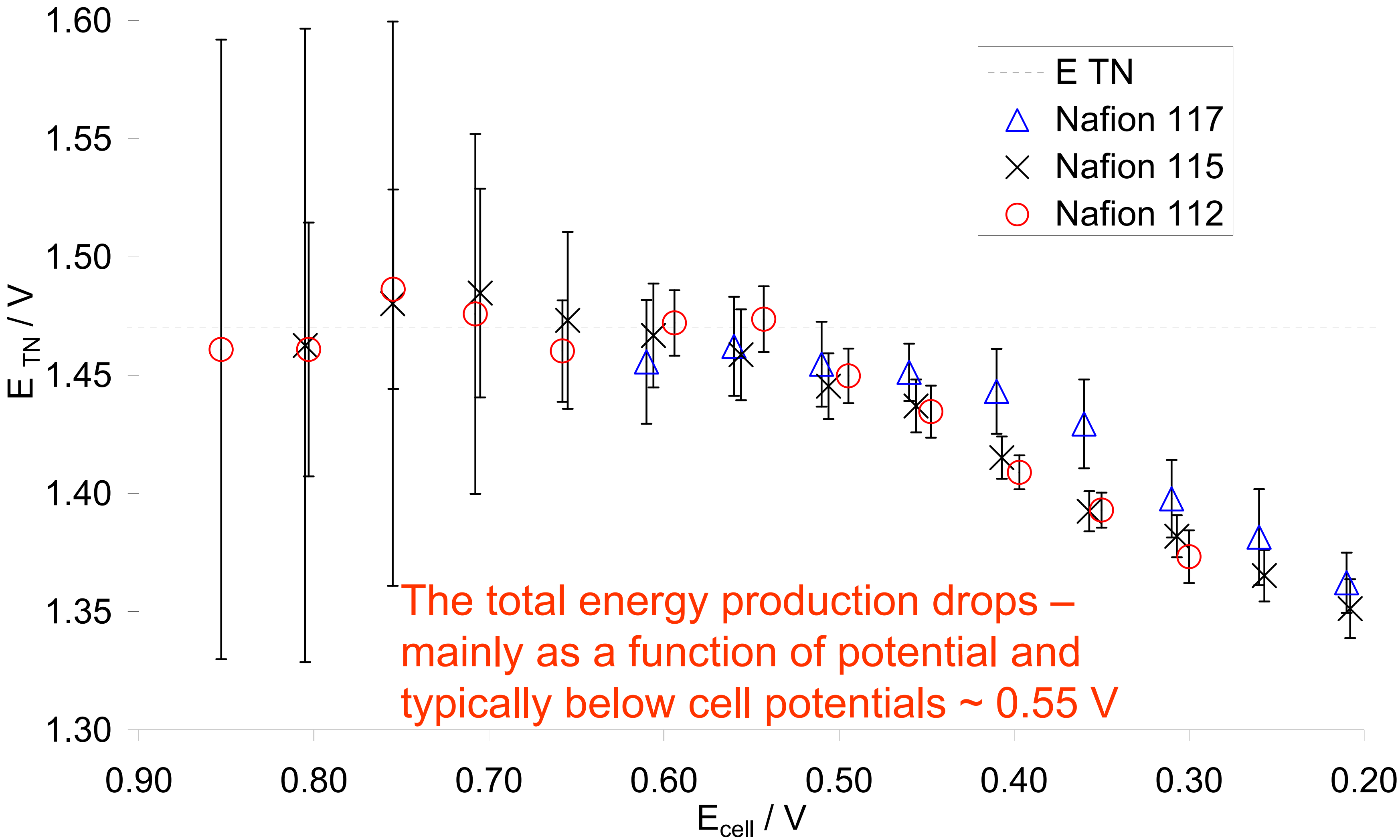


Why is the E_{TN} (ΔH) reduced at higher current densities?

- Diffusion limitations?

	E_{cell} / V	j / A cm^{-2}	E_{TN} / V
Nafion 112	0.30	1.19 ± 0.10	1.37 ± 0.01
Nafion 115	0.31	0.950 ± 0.001	1.38 ± 0.01
Nafion 117	0.31	0.602	1.40 ± 0.02

Thermoneutrol voltage vs Cell voltage



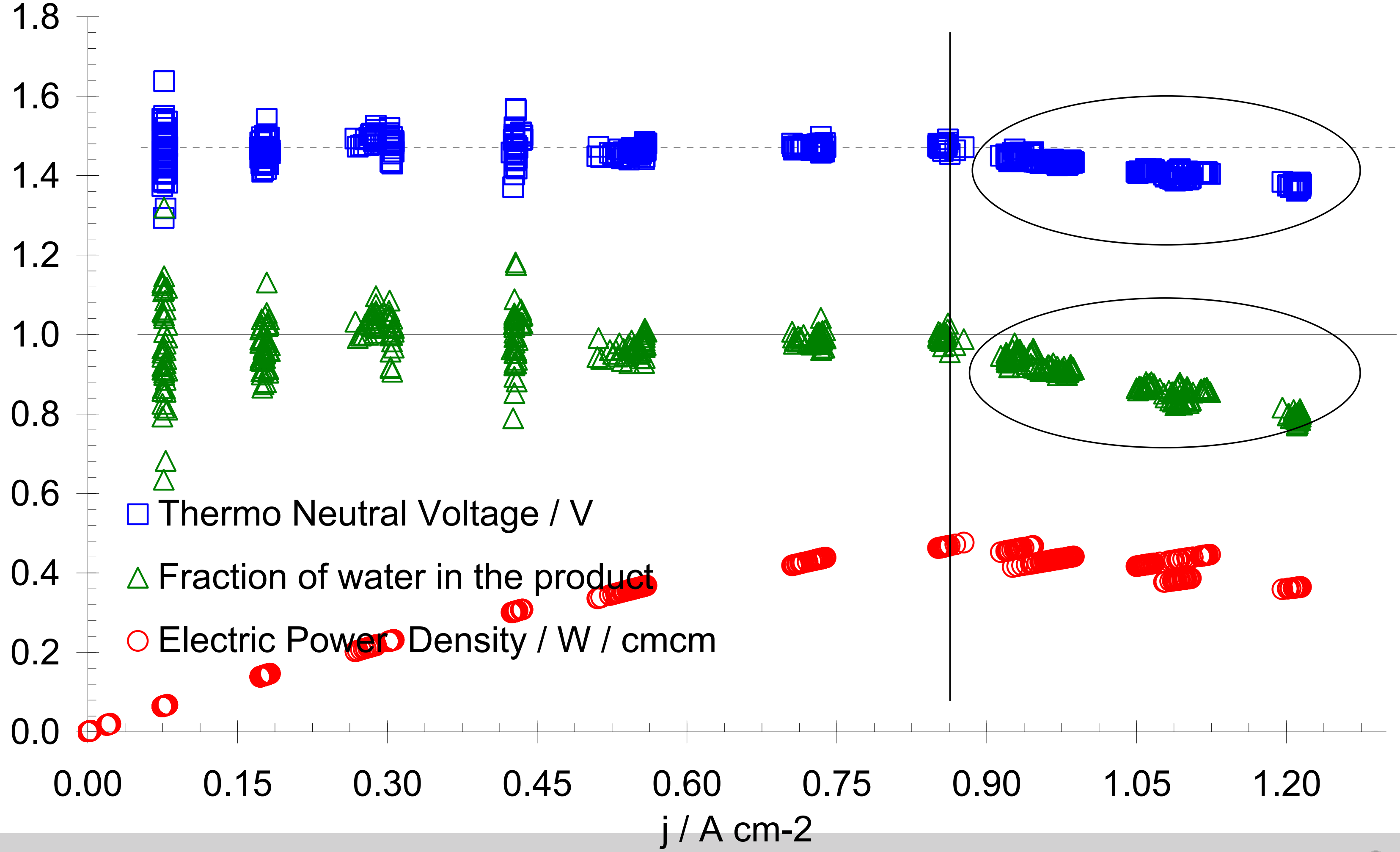
Why is the E_{TN} (ΔH) reduced at higher current densities?

- Competing reactions?

	ΔG^o / kJ mol^{-1}	E^o / V	ΔH^o / kJ mol^{-1}	E_{TN} / V
$H_2(g)+\frac{1}{2}O_2(g) \rightarrow H_2O(l)$	-237	1.23	-286	1.48
$H_2(g)+\frac{1}{2}O_2(g) \rightarrow H_2O(g)$	-229	1.19	-242	1.25
$H_2(g)+O_2(g) \rightarrow H_2O_2(l)$	-120 / -134*	0.62 / 0.69*	-188 / -191*	0.97 / 0.99*

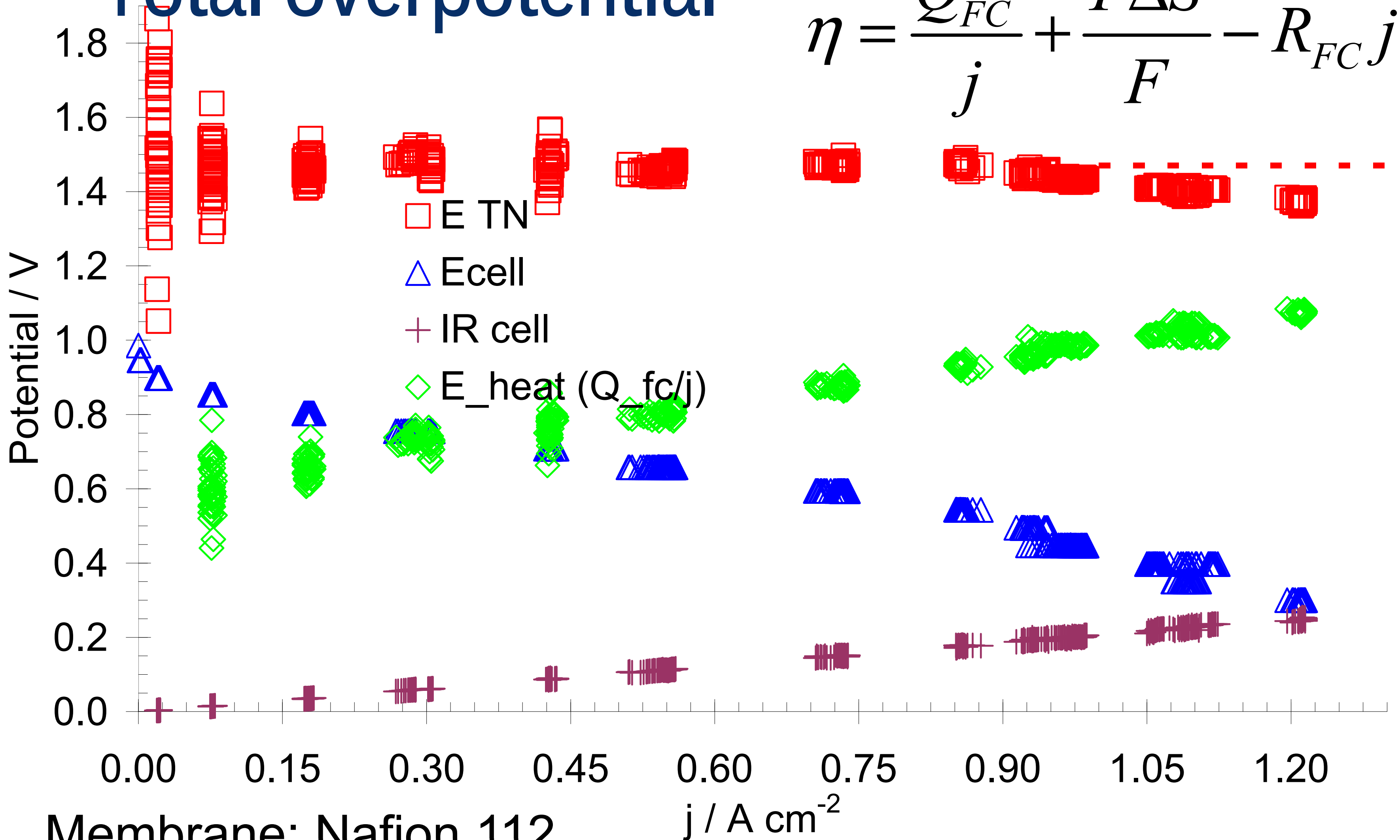
* Infinitely diluted hydrogen peroxide

Fraction of water in products



Total overpotential

$$\eta = \frac{Q_{FC}}{j} + \frac{T\Delta S}{F} - R_{FC}\, j$$

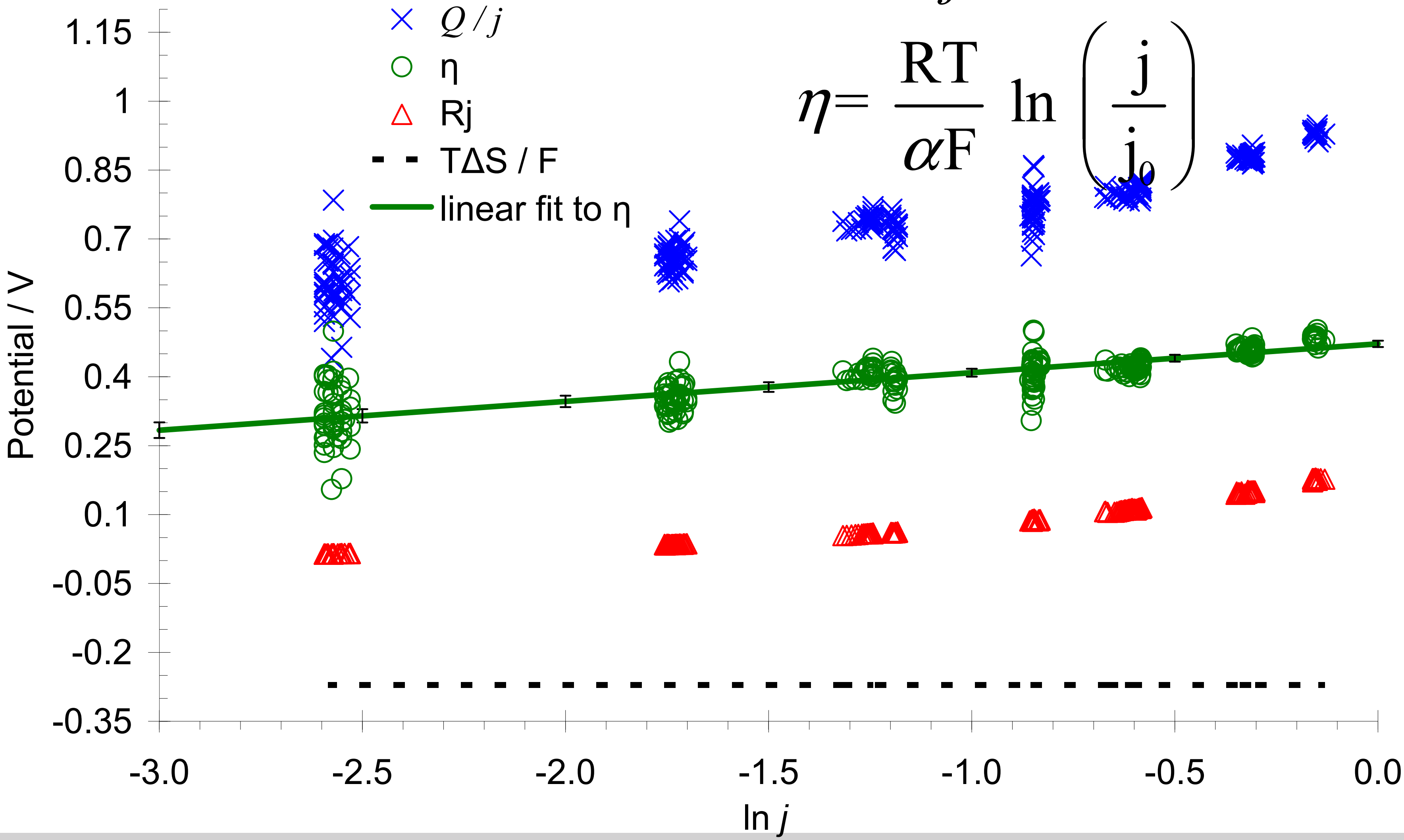


Membrane: Nafion 112

Total overpotential

$$\eta = \frac{Q_{FC}}{j} + \frac{T\Delta S}{F} - R_{FC}\, j$$

$$\eta = \frac{RT}{\alpha F} \ln\left(\frac{j}{j_0}\right)$$



Overpotential results

- Tafel equation: $$\eta = \frac{RT}{\alpha F}\ln\left(\frac{j}{j_0}\right) = \frac{RT}{\alpha F}\ln(j) - \frac{RT}{\alpha F}\ln(j_0)$$

- Heat measurements:

$$\eta_{thermal}\left(j/A\ cm^{-2}\right) = 0.472 + 0.063\ln j,\quad j_o = 5.36\cdot10^{-4}\ A/cm^2,\quad \alpha = 0.45$$

- Classic overpotential measurement:

$$\eta_{classic}\left(j/A\ cm^{-2}\right) = 0.447 + 0.0577\ln j,\quad j_o = 4.24\cdot10^{-4}\ A/cm^2,\quad \alpha = 0.483$$

Conclusions

- A calorimeter for PEM fuel cells was developed and verified
- The thermal signature of a PEM fuel cell was measured
- Enthalpy is lower than enthalpy for pure water production at cell voltages below 0.55 V
  - This can be explained by production of Hydrogen Peroxide on the cathode
- The total overpotential of the fuel cell can be determined from the thermal signatur

Acknowledgements

- Research Council of Norway is acknowledged for funding the research project: “Thermal Effects in Polymer Electrolyte Fuel Cells” grant number 164466/S30

Thank you for your attention !

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