PENNSTATE

Electrochemical Engine Center

Direct Methanol Fuel Cell Experimental and Model Validation Study

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URL: http://mtrl1.me.psu.edu

Overview

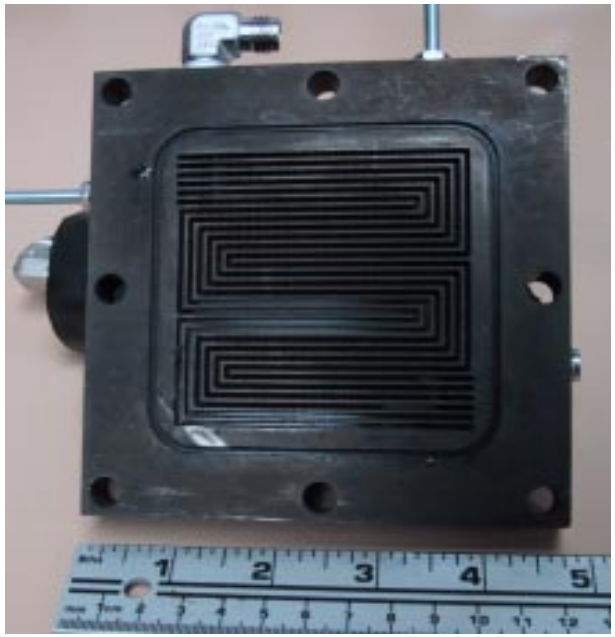
- Method of approach
- Results
  - Water management-cathode flooding performance boundary
  - Fuel cell performance
  - Current density distribution measurements
- Conclusions

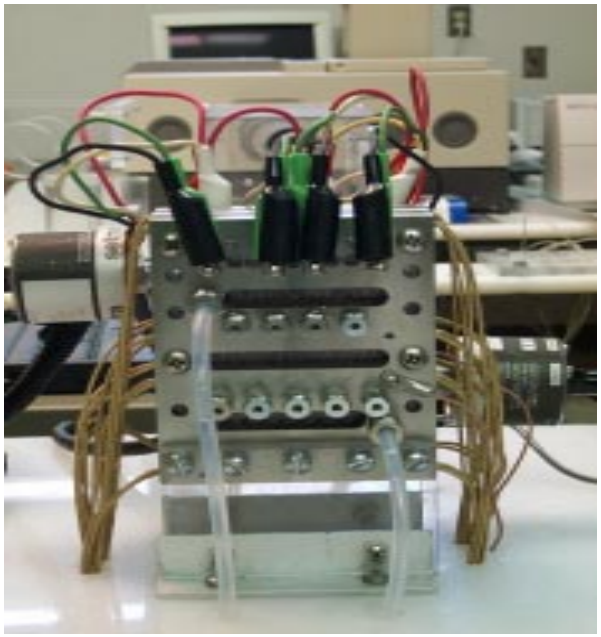
Method of Approach

Objective: to provide detailed experimental data for first principles model validation, develop diagnostic tools for DMFC characterization, and provide baseline data to support scale-up efforts.

Method of approach: Utilize two separate 50 cm^2 cells; a performance cell and a transparent, highly instrumented cell.

Titanium Lynntech cell

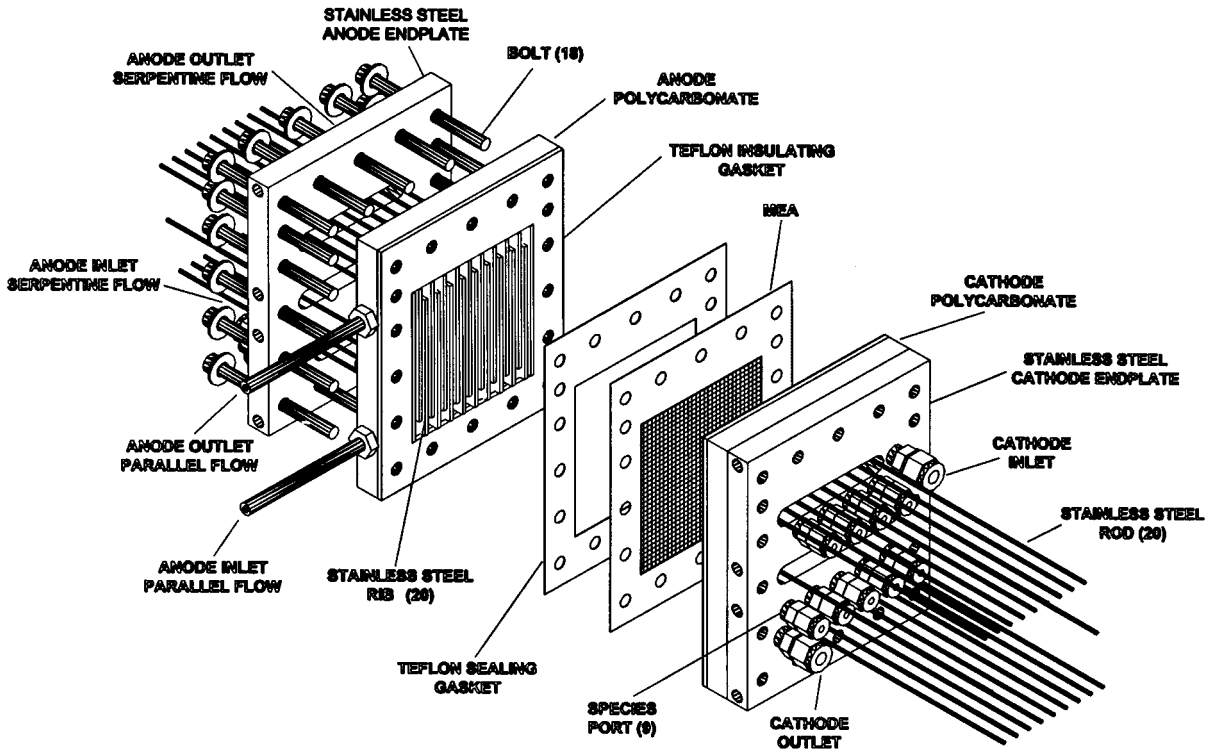


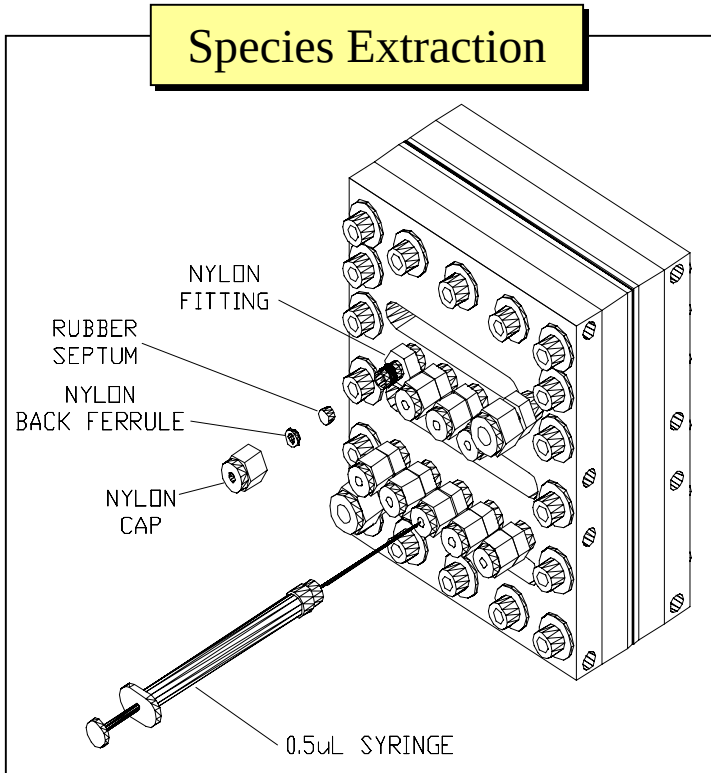


ECEC Transparent cell

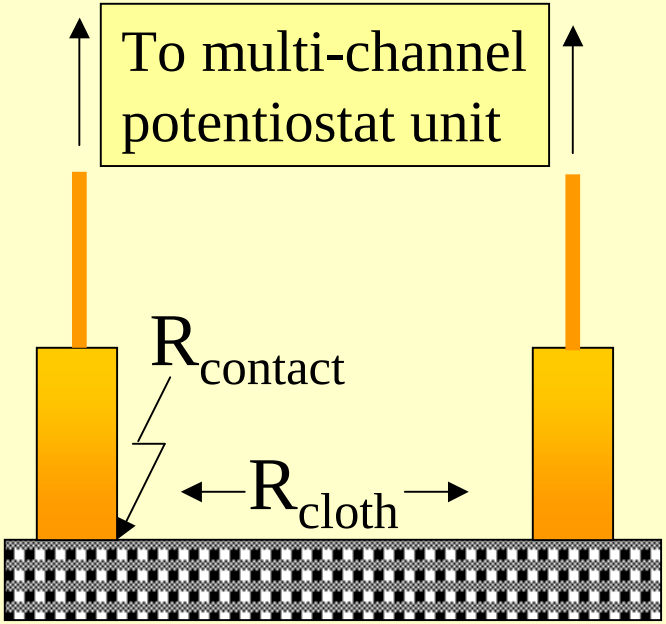
Highly Instrumented Cell Design

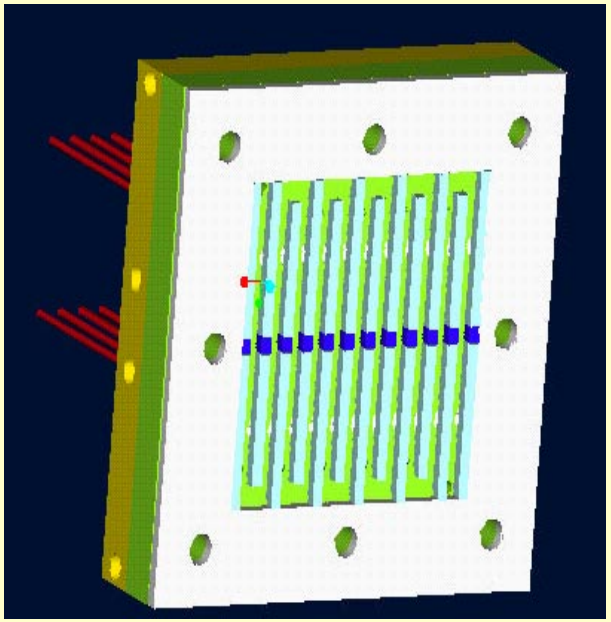
- Control of pressure, flow rate, species inlet and fuel cell temperature, and humidity.
- Transparent polycarbonate windows for flow visualization.
- Ports for *ex situ* FTIR study of species distribution at 18 locations along the anode and cathode flow paths.
- Segmented flow channel rib design, permitting current collection at 20 different locations on both the anode and cathode side.

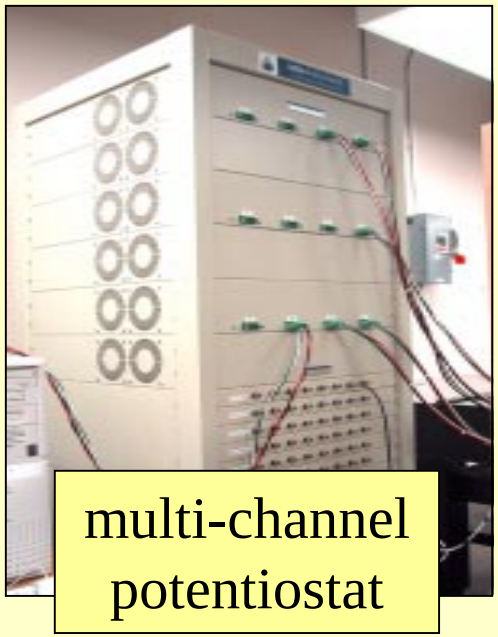




Current Density Distribution Measurements







Each rib is gold plated for low contact resistance and electrically isolated from the rest of the backing plate, allowing a real-time current density distribution with use of a multi-channel potentiostat without any segmentation of the MEA

Water transport/formation at the cathode

- Water is transported/created at the cathode in several ways.
  - Creation by cathode reaction:

$$6e^- + 6H^+ + 3/2\,O_2 \rightarrow 3H_2O \therefore 3H_2O / CH_3OH \text{ consumed} \qquad j_{\text{H2O, created}} = 3\frac{iA}{6F} = \frac{I}{2F}$$

  - Transport by electro-osmotic drag: $$j_{\text{H2O, drag}} = \frac{iA}{F}\lambda_{\text{drag}} \cong 2.5\frac{I}{F}$$

Cruickshank and Scott, (1998) or Ren and Gottesfeld (2001).

  - Transport by diffusion: $$j_{H2O} = -D\frac{\Delta C_{c-a}}{\Delta x}$$
  - Putting it all together, it can be modeled as:

$$j_{H2O,cathode} = -D\frac{\Delta C_{c-a}}{\Delta x} + \frac{iA}{F}\left(\lambda_{drag} + 0.5\right) - \frac{aK}{l}\Delta P_{c-a}$$

  - Pressure term is typically nearly negligible relative to drag and production. This also ignores creation from crossover reaction.

Water removal from the cathode

From basic thermo:

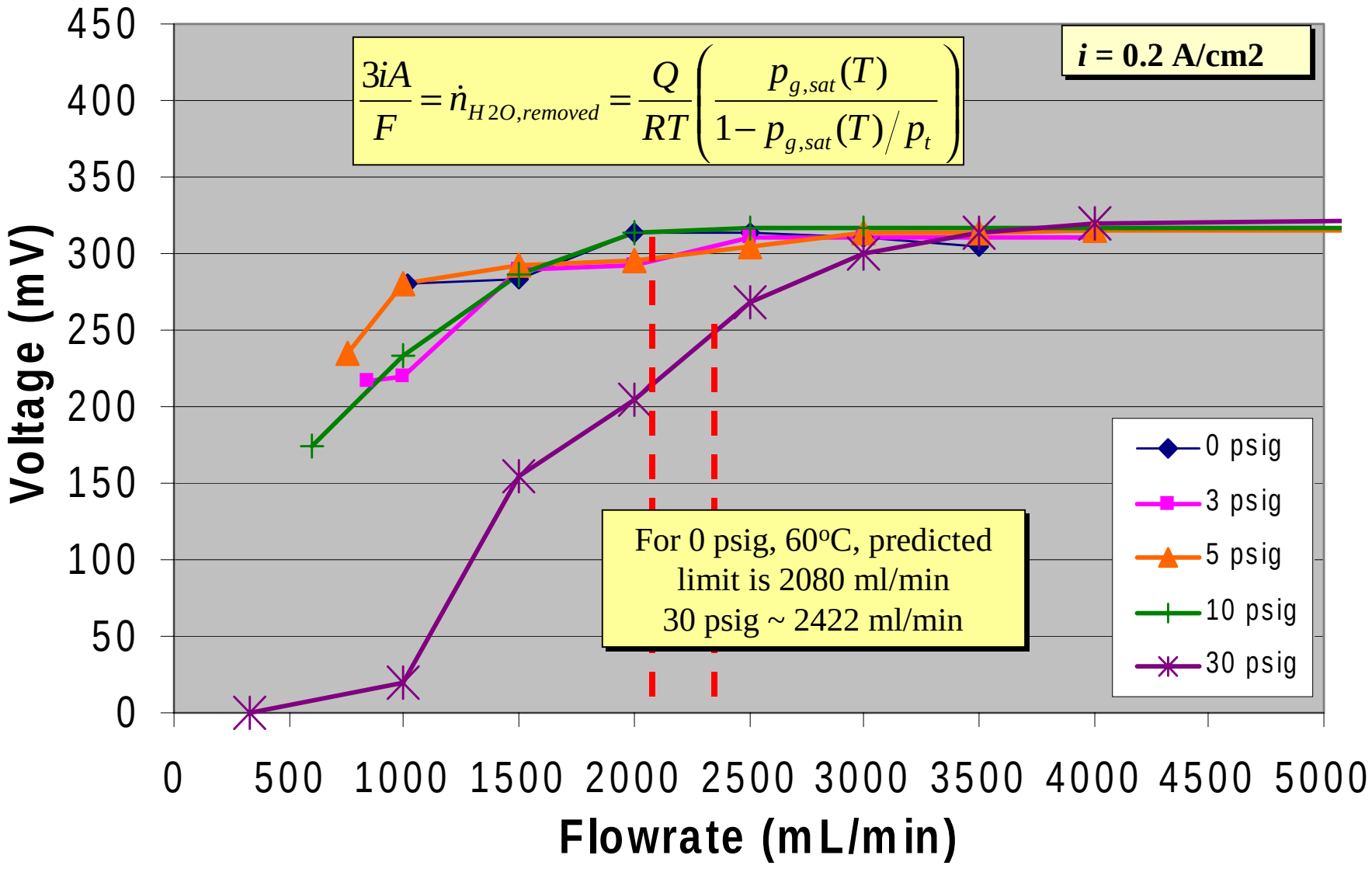
$$\phi = \frac{p_{v,H2O}}{p_{g,sat}(T)} \qquad p_{v,H2O} = y_{v,H2O} p_t = \frac{n_{v,H2O}}{n_{v,H2O} + n_{others}} p_t \qquad \phi = \frac{\frac{n_{v,H2O}}{n_{v,H2O} + n_{others}} p_t}{p_{g,sat}(T)}$$

The *maximum* we can pick up in the fuel cell is:

$$\dot{n}_{H2O,removed} = \dot{n}_{others}\left(\frac{p_{g,sat}}{p_t - p_{g,sat}}\right) = Q\frac{p_t}{RT}\left(\frac{p_{g,sat}(T)}{p_t - p_{g,sat}(T)}\right) = \frac{Q}{RT}\left(\frac{p_{g,sat}(T)}{1 - p_{g,sat}(T)/p_t}\right)$$

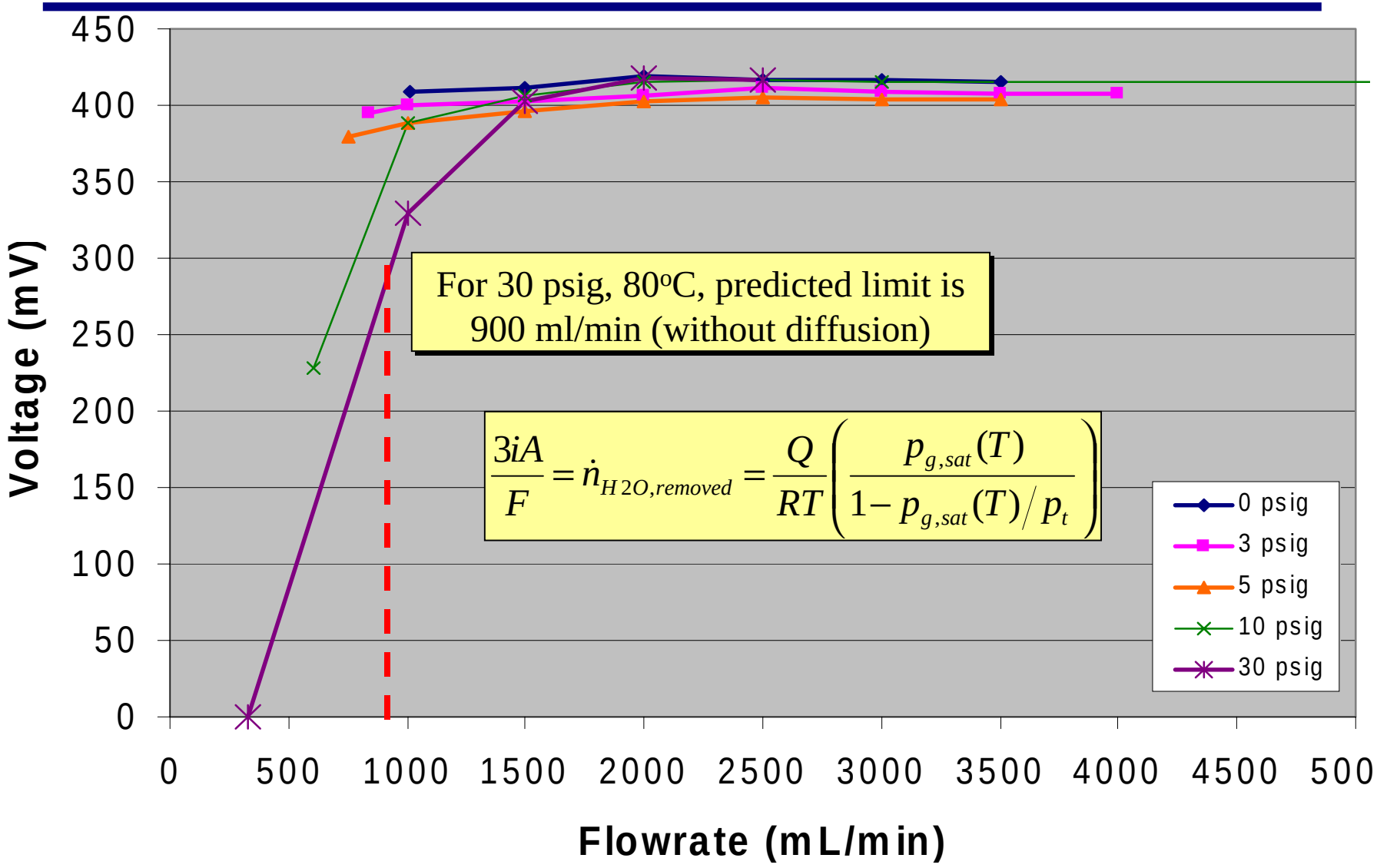
- So water removal is dominated by *flow rate* and *temperature*.
- This expression must balance the water transported/created at the cathode, or flooding will occur.
- Considering that the oxygen is consumed, the ability to remove water actually is not constant.

Evidence of Drying Boundary at 60 °C



Enhanced diffusion replaces excess water removed, leading to a performance plateau. This balance under predicts because of diffusion at inlet, consumption, and crossover.

Evidence of Drying Boundary at 80 °C



Note the peak is mainly a function of T, not pressure. For DMFC, the optimal flow rate may be determined by cathode drying requirements, not electrochemistry.

Minimum Stoichiometry

- For liquid water removal purposes, a ***minimum*** flow stoichiometry can be defined, below which, some liquid water will be formed.

$$j_{H2O,cathode} = -D\frac{\Delta C_{c-a}}{\Delta x} + \frac{i\mathrm{A}}{F}\left(\lambda_{drag} + 0.5\right) - \frac{aK}{l}\Delta P_{c-a}$$

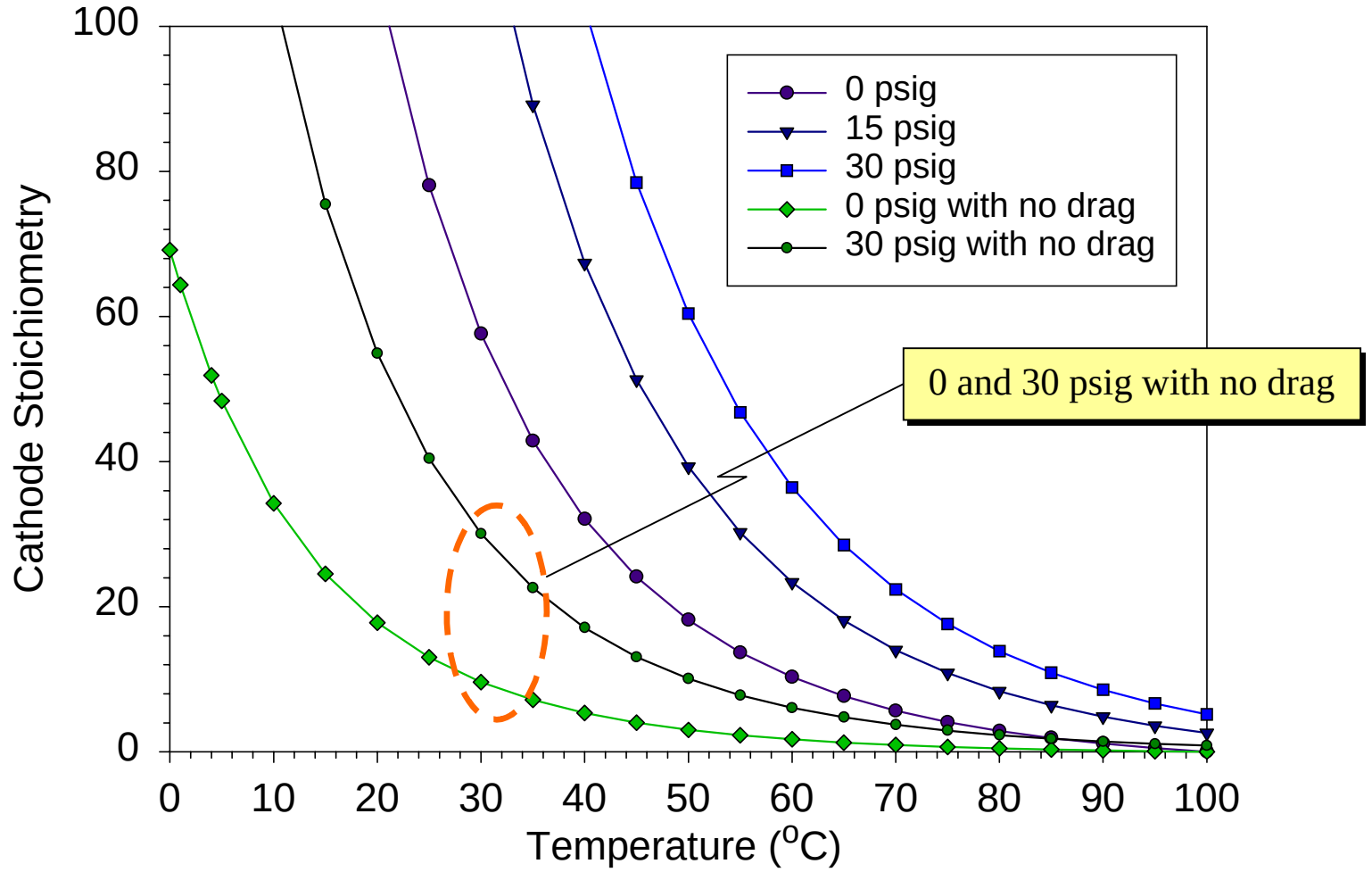
- Divide the minimum H2O removed from cathode by what is required for reaction with air:

$$\approx 3\frac{i\mathrm{A}}{F} = \dot{n}_{H2O,removed,\min} = \dot{n}_{others}\left(\frac{p_{g,sat}}{p_t - p_{g,sat}}\right) \Rightarrow \dot{n}_{others} = \frac{3\frac{i\mathrm{A}}{F}}{\left(\frac{p_{g,sat}}{p_t - p_{g,sat}}\right)}$$

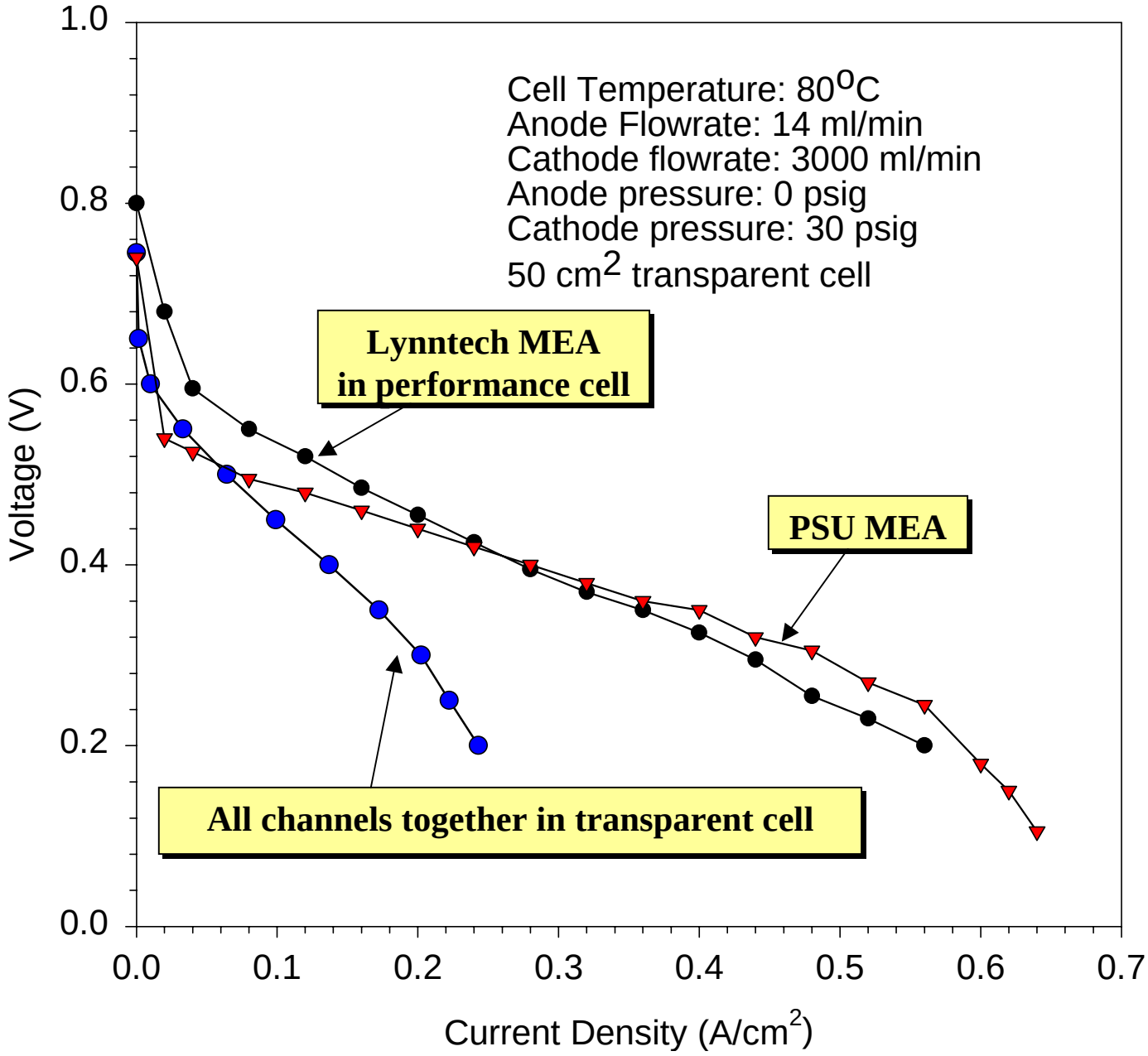
$$\lambda_{cathode} = \frac{\dot{n}_{others}}{\dot{n}_{required}} = \frac{3\frac{i\mathrm{A}}{F}}{\left(\frac{p_{g,sat}}{p_t - p_{g,sat}}\right)}\frac{0.21\cdot 4F}{i\mathrm{A}} \approx \frac{2.52}{\left(\frac{p_{g,sat}}{p_t - p_{g,sat}}\right)} \text{ in air}, \frac{12}{\left(\frac{p_{g,sat}}{p_t - p_{g,sat}}\right)} \text{ in } O_2$$

Minimum Stoichiometry

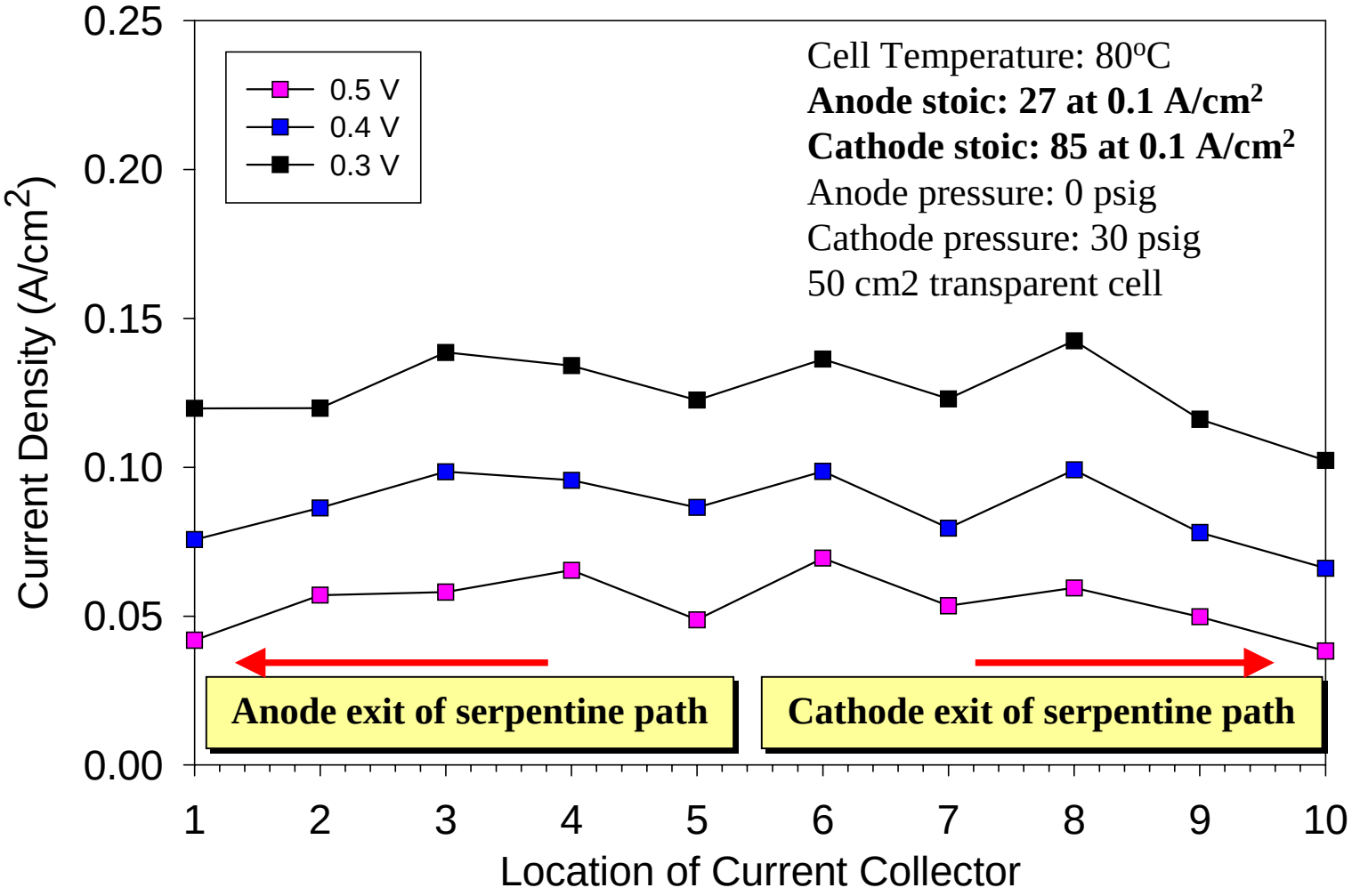
- Diffusion from the anode and crossover will increase this minimum requirement, while a large pressure differential may decrease it. This assumed drag coefficient is constant at 2.5 with no methanol crossover water production.



Comparison of Different Cell Overall Performance

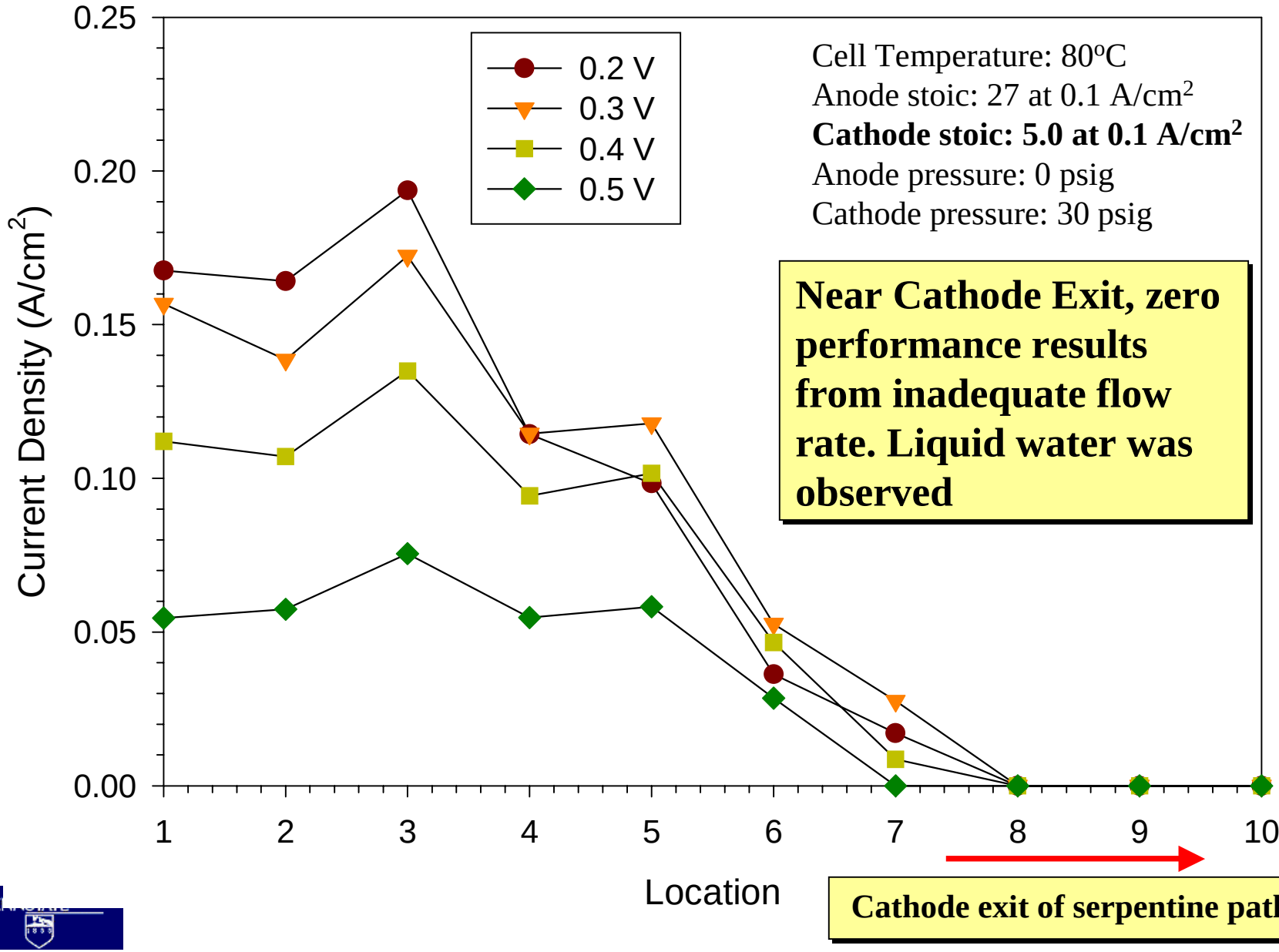


Current Density Distribution for High Flow Rates

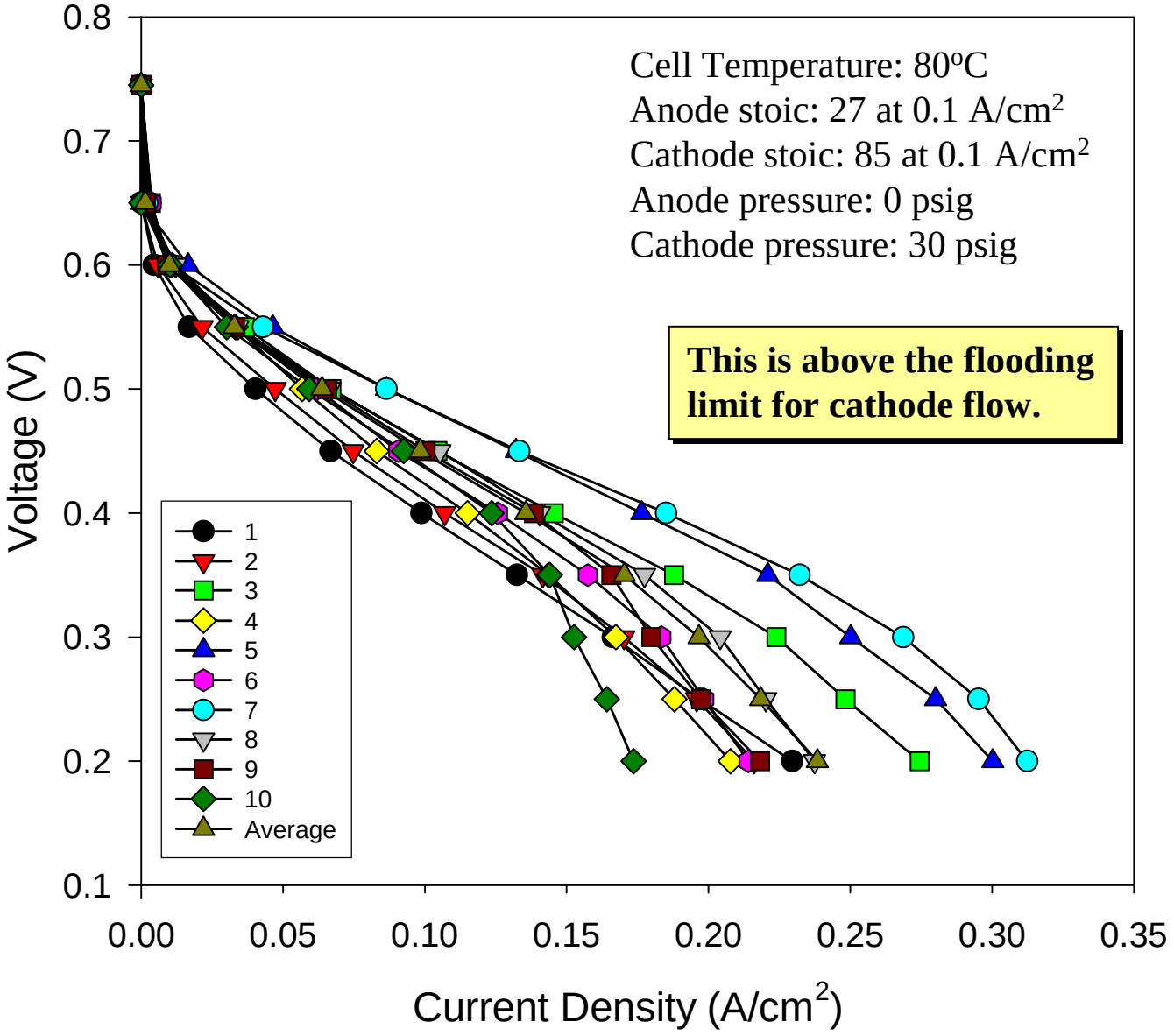


We see a slight increase in performance from the inlet location of dry air. Then, essentially homogeneous distribution

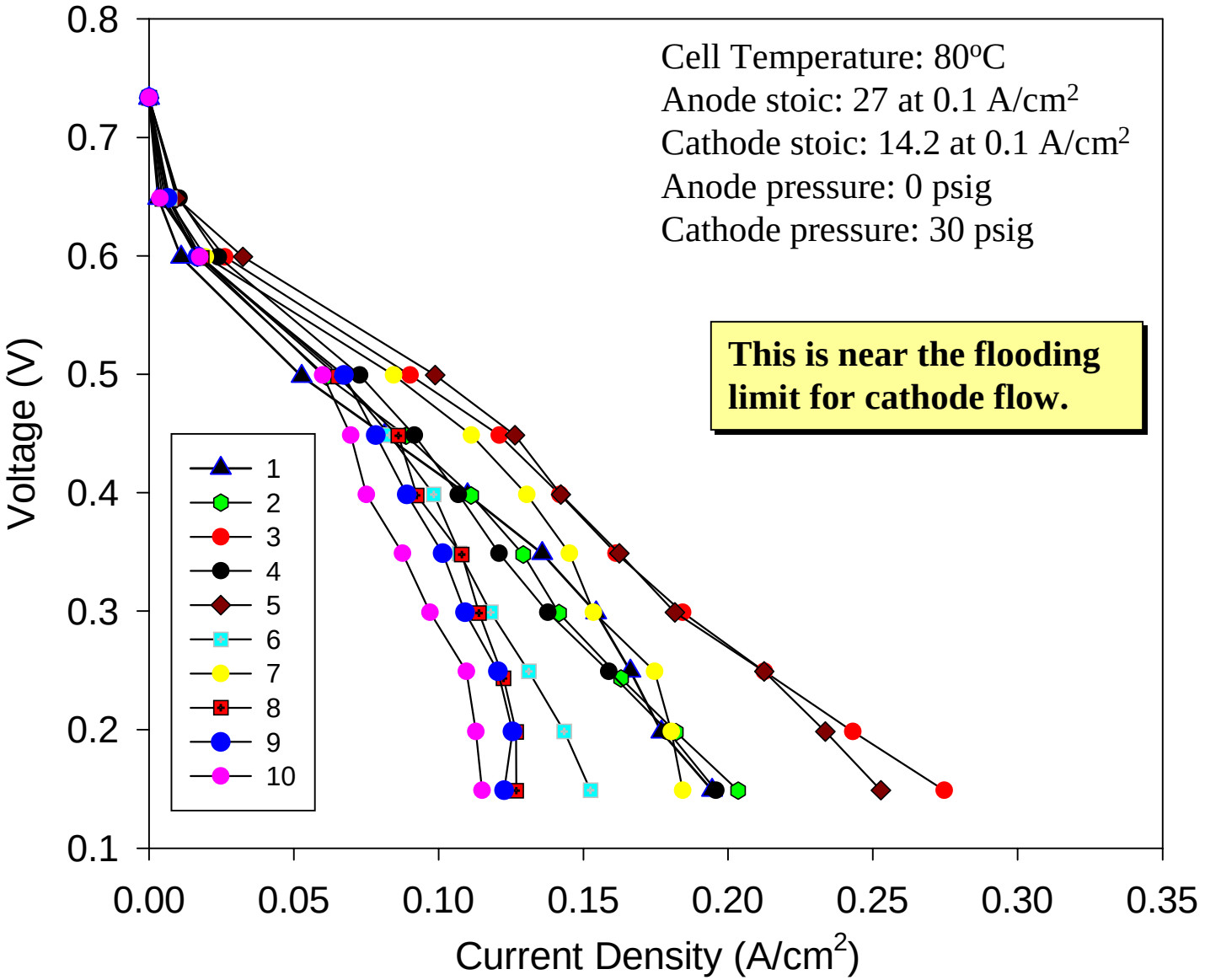
Current Density Distribution for Low Flow Rates



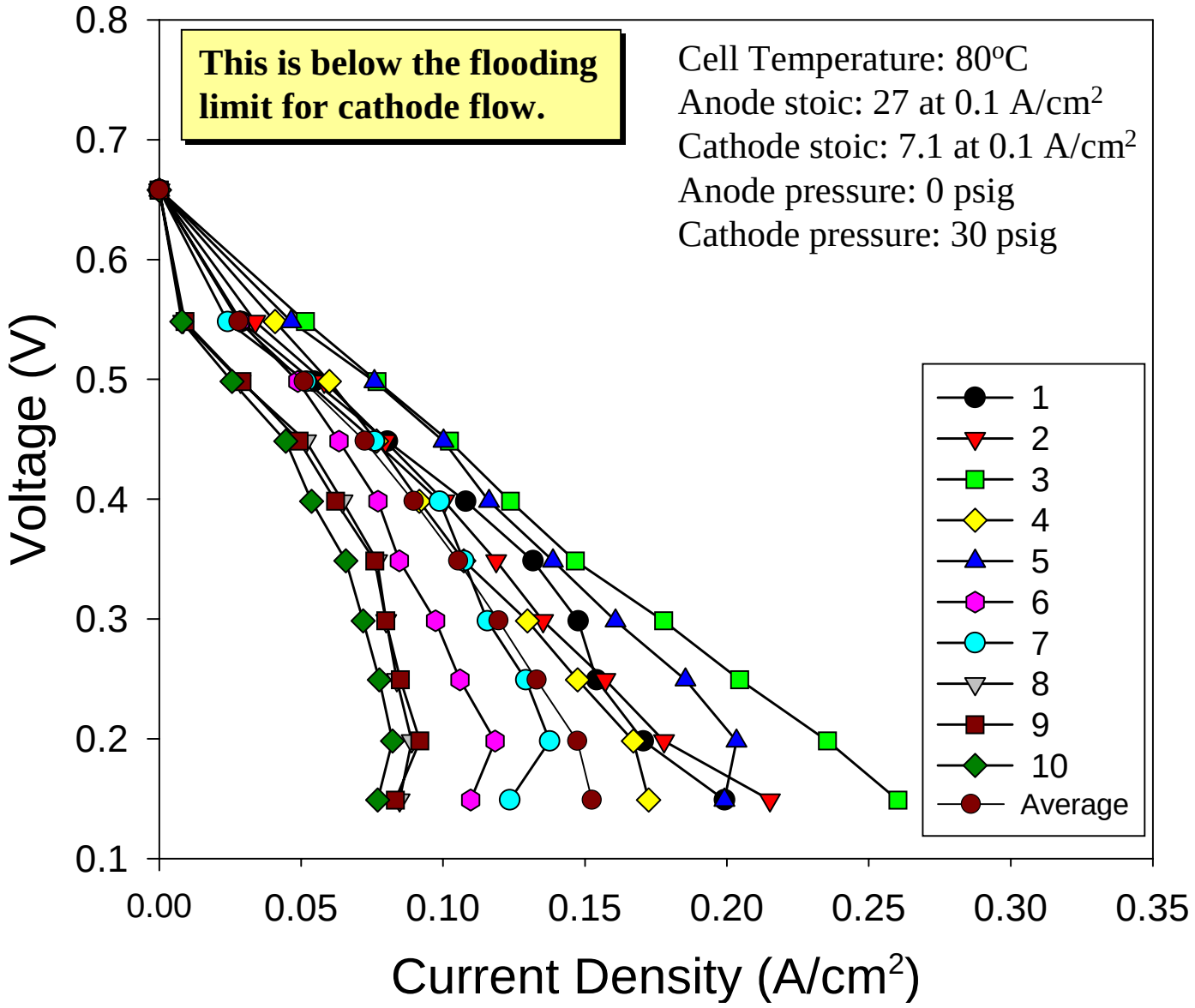
Current Density Distribution for 3000 ml/min



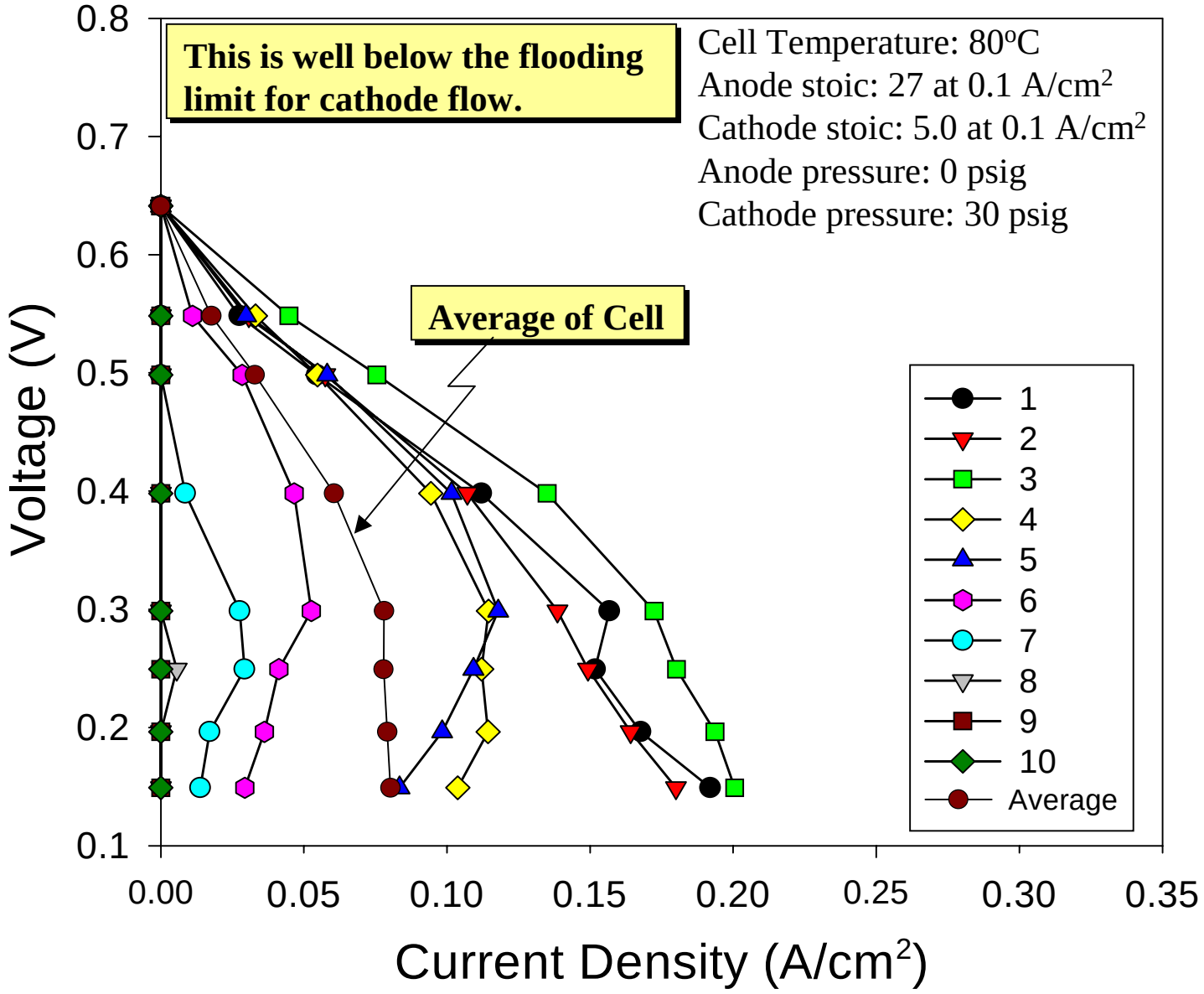
Current Density Distribution for 500 ml/min



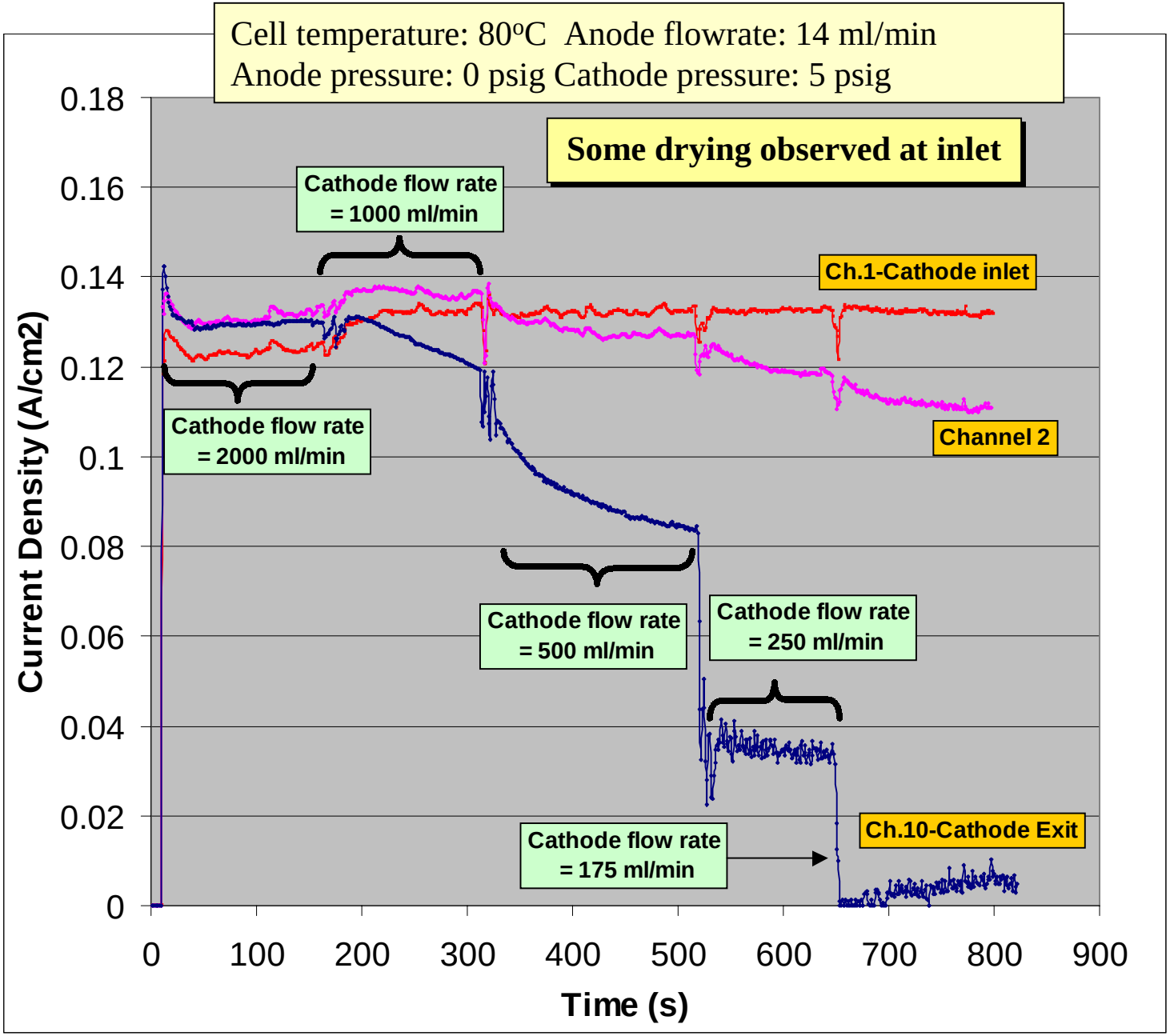
Current Density Distribution for 250 ml/min



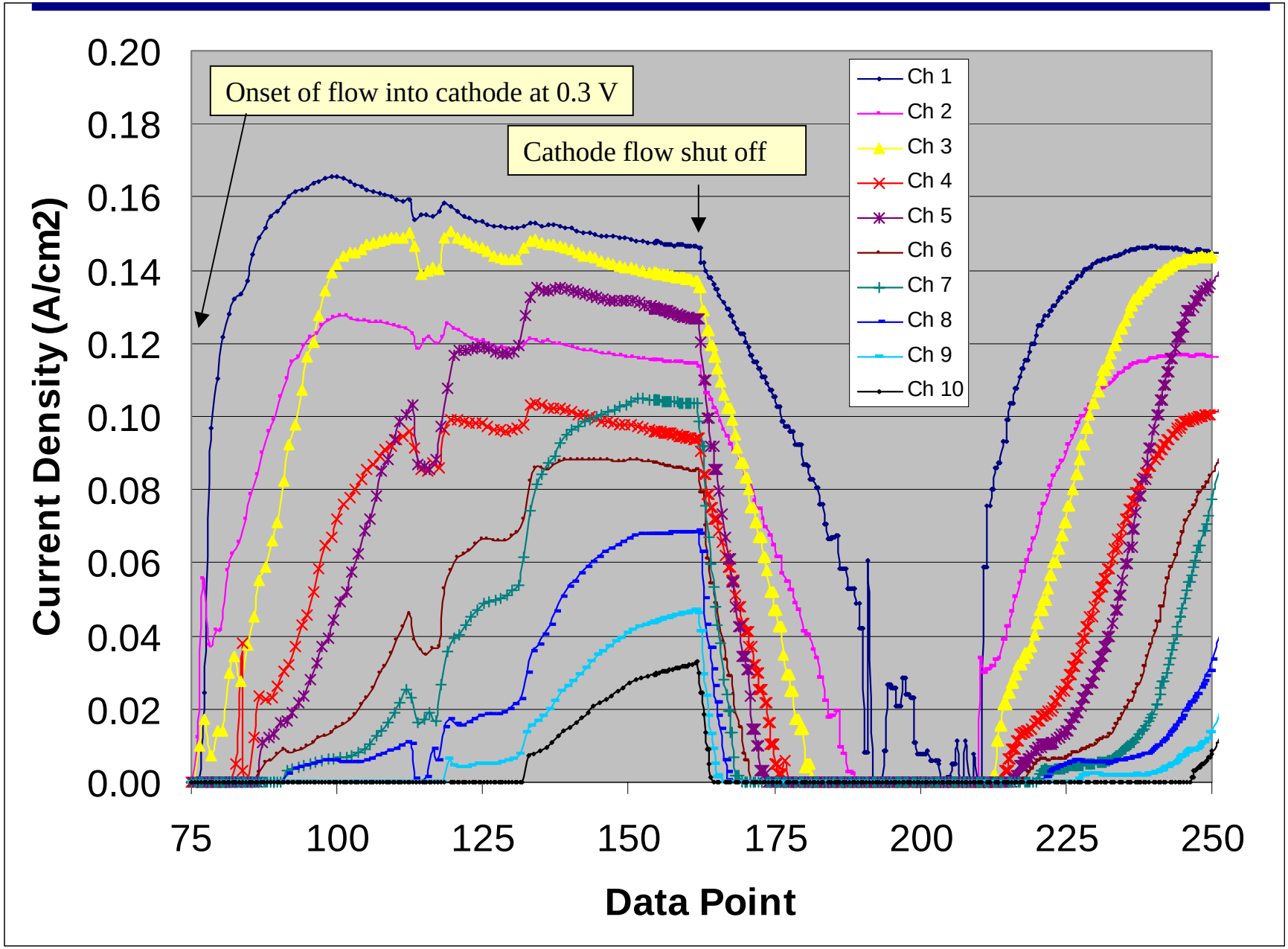
Current Density Distribution for 175 ml/min



Transient Response to Cathode Flow Rate Change



Onset of Cathode Flow Transient



Concluding Remarks

- A method for ***determination of current density distribution*** in a PEM fuel cell has been demonstrated utilizing a segmented current collector with off-the-shelf MEAs. These data are being used for detailed model validation of a first-principles 2-phase model.
- ***Transient performance data were obtained***, showing time transients for adjustment to cathode flow rate changes.
- A basic equation defining a ***lower limit for cathode stocihiometry*** to avoid flooding was defined that qualitatively matches experimental trends.
- ***Cathode flooding was observed*** for conditions of low flow rates, but sufficient stoichiometry for electrochemical reaction.
- ***Drying of Nafion was shown***, resulting in reduced performance near the inlet of a DMFC operating with high cathode flow rate.

Acknowledgements

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