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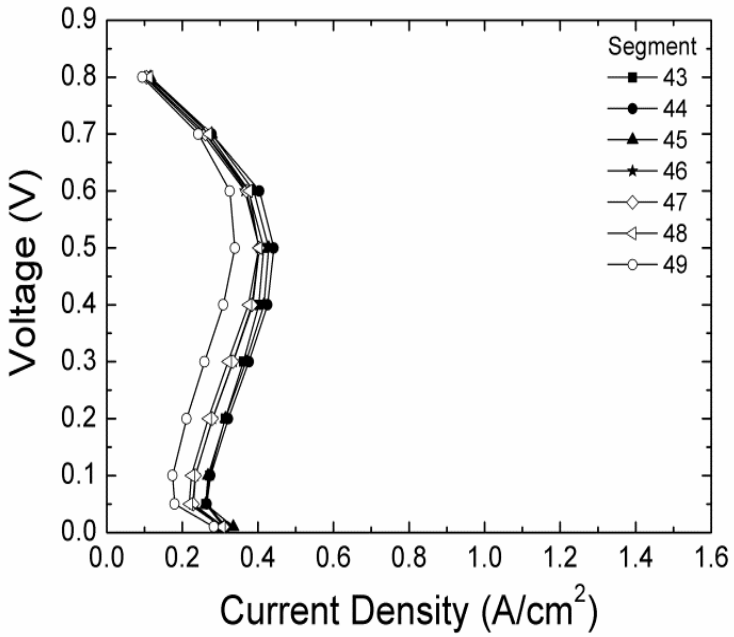
Relating the N-shaped polarization curve of a PEM fuel cell to local oxygen starvation and hydrogen evolution



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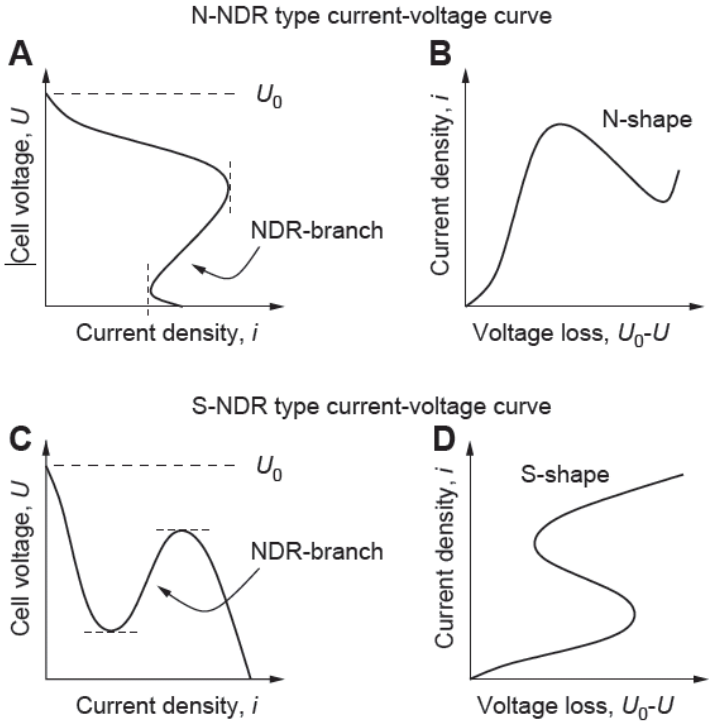
AGENDA

- Introduction
- Motivation
- Experimental Procedure
- Results
- Discussion
- Conclusions

Introduction
→ Defintion of the NDR i-U curves

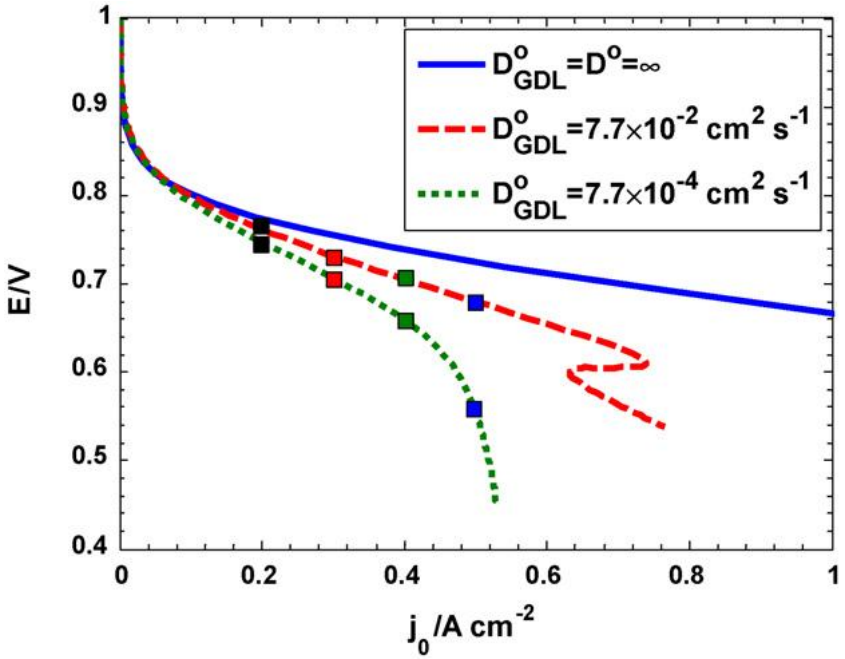
- (A) and (B) represent the so-called N-NDR type
  - Ends in two vertical tangets
- (C) and (D) represent the so-called S-NDR type
  - Ends in two horizontal tangents
- Behavior is typical of an electrochemical system going through oscillations



R. Hanke-Rauschenbach, M. Mangold, K. Sundmacher. Reviews in Chemical Engineering (2011) 27:23-52.

Introduction
→ N-NDR and Literature

- Occurs due to three main reasons:
  - Ion transport through the electrolyte[1,2]
  - Non-linear electrochemical surface kinetics[3,4]
  - Locality of the reaction within the catalyst layer (CL) thickness[5]
- Comma shaped polarization curves were measured under starvation modes in segmented fuel cells[6,7]



J. Liu, M. Eikerling. Electrochimica Acta (2008) 53:4435-4446

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2. J.B. Benziger, E. Chia, J.F. Moxley, I.G. Keyrekidis, Chemical Engineering Science, 60, 1743 (2005).
3. J. Zhang, et al. Journal of the Electrochemical Society (2004) 151:A689-A697.
4. J. Zhang, R. Datta. Journal of the Electrochemical Society (2002) 149:A1423-A1431.
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6. M.M. Mench and C.Y. Wang, Journal of the Electrochemical Society, 150, A79 (2003).
7. M.M. Mench, C.Y. Wang, M. Ishikawa, Journal of the Electrochemical Society, 150, A1052 (2003).

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Motivation

- Need to understand limiting phenomena in PEM fuel cells
  - Carry out comprehensive analysis to relate the behavior of measured polarization curves under dynamic and steady-state conditions
  - Special attention is given to the N-shaped characteristic

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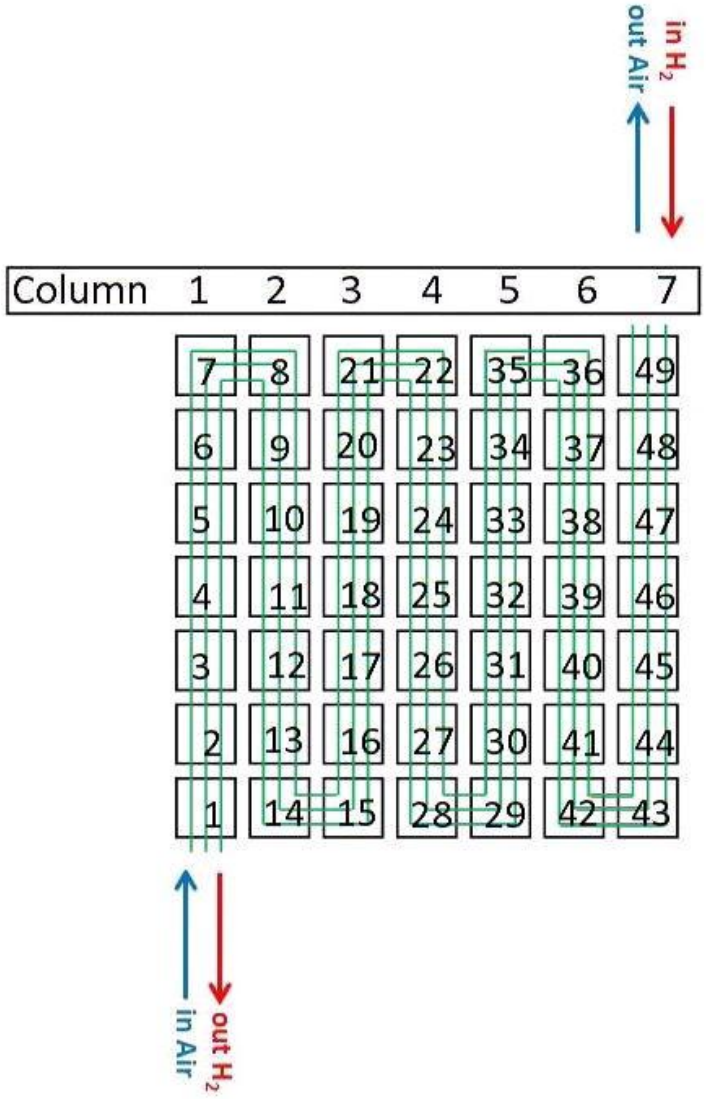
Experimental procedure
→ Multi-channel characterization system enables the spatially resolved polarization curves

- 50 potentiostats / 50 FRAs
- current range +/- 5 A per segment
- ultra-low inductive cabling
- current / voltage mapping

Experimental procedure
→ The cell

- Active cell area: 49 cm^2 (7 x 7 square matrix)
- Insulation by epoxy
- Serpentine flow field
- Counter flow configuration
- Gore membrane with a SIGRACET GDL 25-BC



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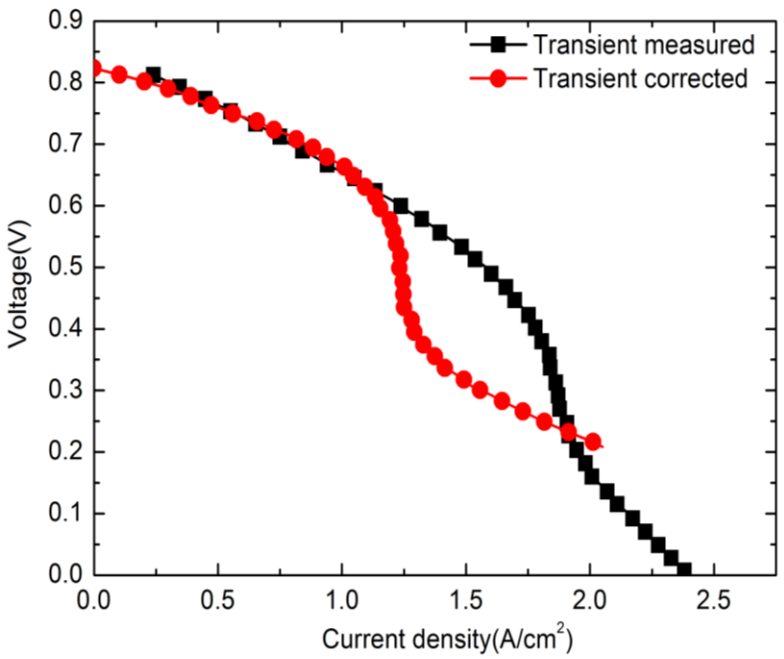
Experimental procedure
→ Experimental conditions

- Steady-state:
  - Potentiostatic mode
  - Cell temperature kept at 60°C
  - i-U curve collected for a voltage range of 800 mV – 50 mV
  - 30 minutes at each voltage increment
  - Air/hydrogen flow rates 600/600
  - Inlet relative humidity of air/hydrogen 80%
- Dynamic:
  - Atmospheric pressure and cell temperature of 60°C
  - i-U curves collected for a voltage sweep of 800 mV – 50 mV in 120 ms
  - Prior to measurements a good hydration of the membrane is achieved and the cell is run at 800 mV for 5 seconds to homogenize oxygen distribution

Experimental Procedure
→ Data analysis

- The effects of the double layer charging and the Ohmic drop on the measured current density and the measured voltage were taken into account
- The Faradaic current (i_f) is:
  $i_f = i_m + i_c$
- The charging current (i_c) is:
  $i_c = C_{dl} \frac{d\Delta\varphi_c}{dt}$
- The double layer voltage ($\Delta\varphi_c$) is:
  $\Delta\varphi_c = i_m \times R_{ohm} + V_m$



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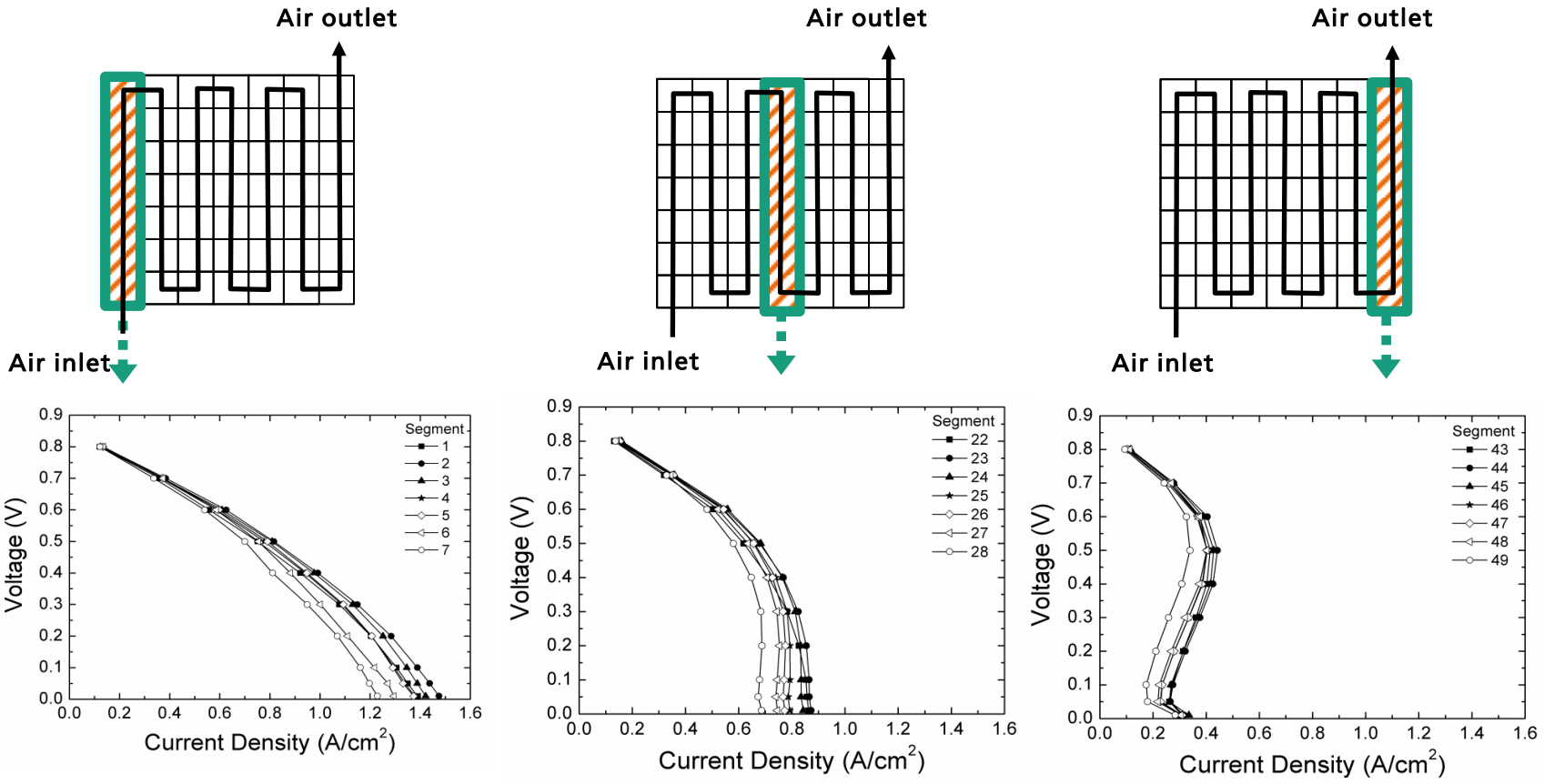
Results
→ Steady-state condition



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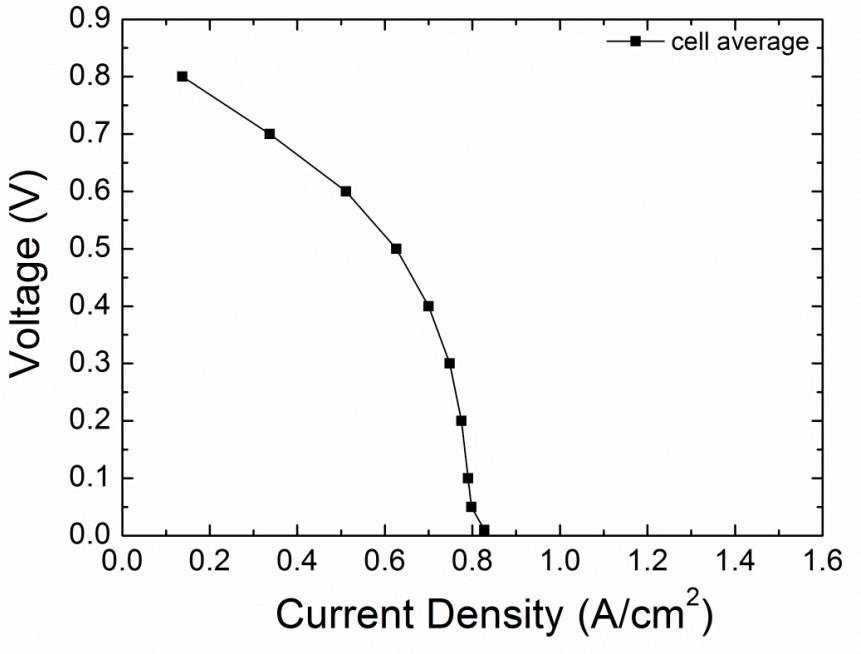
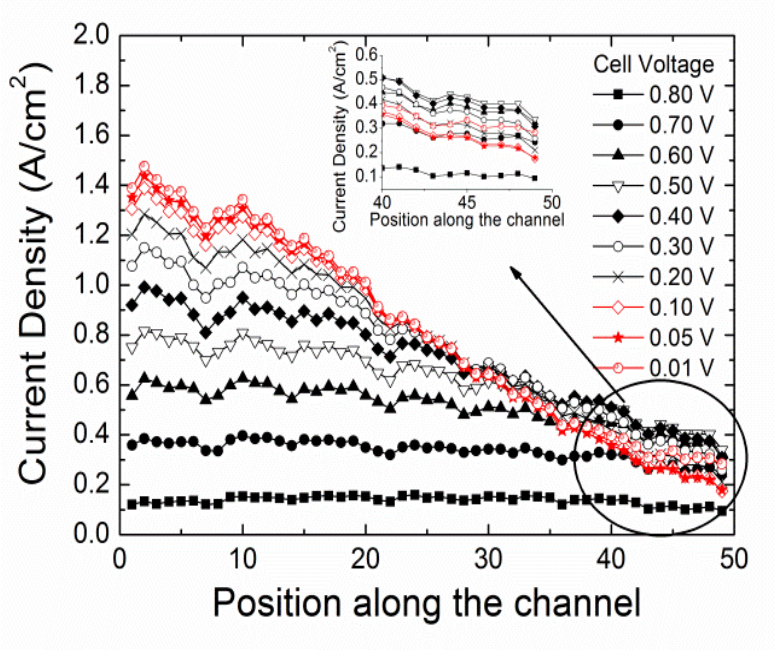
Results
→ Steady-state condition
→ Total cell performance clearly shows an increase in current





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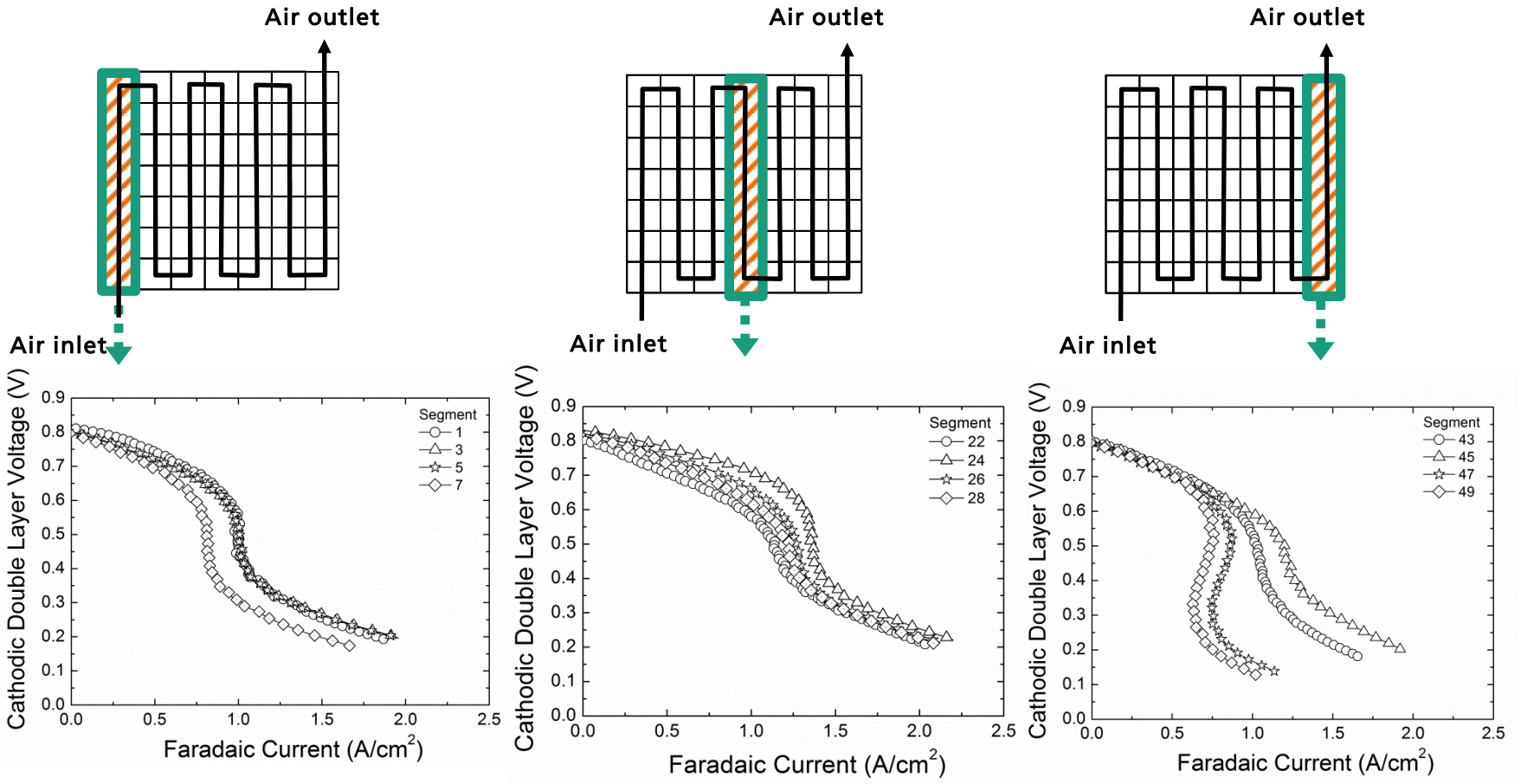
Results
→ Dynamic condition



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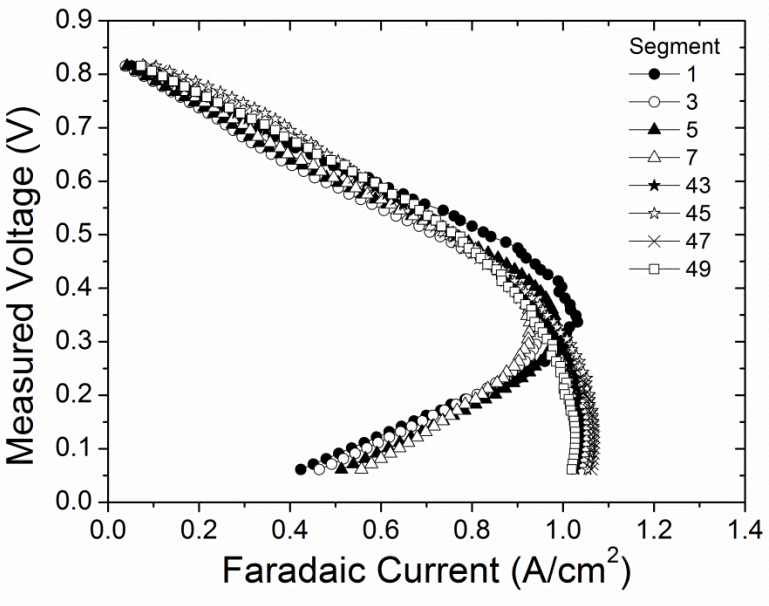
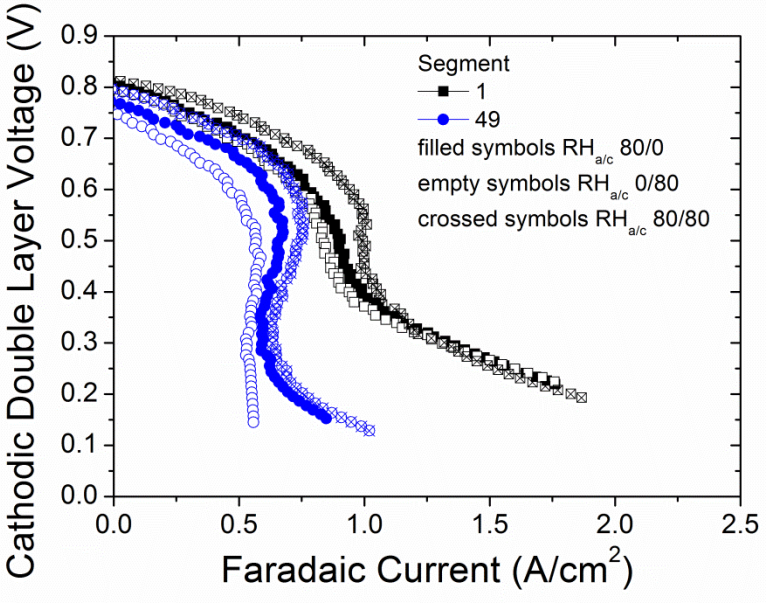
Results
→ Dynamic condition
→ Effect of anode losses





- Diluted hydrogen feed increases anode overpotential
  - → Recovery is not measured

- Low anode humidification increases losses
  - → Recovery is not measured

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Discussion
→ Hypothesis

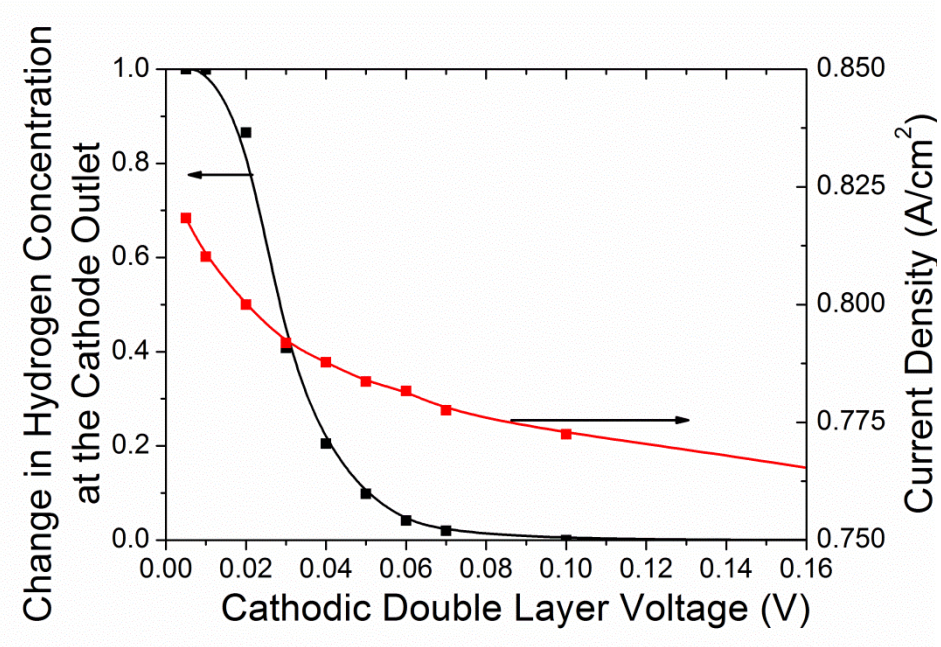
- Based on experimental measurements the following is true:
  - Vertical branch in the i-U curve of the cell corresponds to the stoichiometric possible current from the oxygen fed to the cell
  - Current density in the tail of the i-U curve lies a little bit above limiting current
- The following can then be concluded:
  - The NDR branch originates from a cathodic process
  - This tail originates from an unexpected second Faradaic process

Discussion
→ Hydrogen concentration at the cathode outlet

- The hydrogen evolution reaction occurs within the voltages measured here
- Hence in the CCL:

$$2H^+ + 2e^- \leftrightarrow H_2$$

- Protons and electrons from the HOR in the anode combine to create hydrogen in the cathode
- A shift in the reference Nernst potential allows for this combination to occur at positive voltages



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Conclusions

- Spatially resolved i-U curves in steady-state and dynamic conditions
- Comma-shaped polarization curves resembling oxygen starvation and depletion
- Upon reaching the theoretical limiting current density and with the further decrease of the cell potential, a recovery was subsequently measured
- This recovery is due to the hydrogen evolution reaction in the CCL
  - Large polarization resistance of the ORR at low cell voltages,
  - Occurrence of hydrogen at the outlet of the cell near the limiting oxygen current density (i_{O2}^{lim})
  - These findings are important for explaining degradation issues

Conclusions
→ Final thought

- A mathematical model has been developed to prove the hypothesis
- Further information can be found here
  - N. Zamel, R. Hanke-Rauschenbach, S. Kirsch, A. Bhattarai, D. Gerteisen. Relating the N-shaped polarization curve of a PEM fuel cell to local oxygen starvation and hydrogen evolution. Submitted to Journal of the Electrochemical Society.

Thank You Very Much for Your Attention!

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