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Investigation of the Local Cathode Potential Evolution during Start-Up by Means of Embedded Reference Electrodes in a PEM Fuel Cell

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Air-air start-up (SU) events in proton exchange membrane fuel cells generate cathode potential overshoots exceeding 1.4 V, driving degradation through carbon corrosion and platinum dissolution. While the reverse-current mechanism is established, the influence of system-level pre-conditioning parameters on spatially resolved cathode potential transients remains insufficiently understood. This study employs a segmented along-the-channel cell with ten air-flushed reference electrodes to measure local cathode potentials during air-air SU events. Hydrogen flow rate and pre-conditioning parameters such as anode/cathode humidity and purge duration are investigated. Increasing hydrogen flow from 0.125 to 4 nl min^{-1} reduces SU duration (276–163 ms) and peak overshoot (1.56–1.45 V), though the effect does not scale linearly with residence time, indicating electrochemical process dominance. Anode humidity exerts minimal influence when the cathode remains fully humidified. In contrast, cathode dehydration fundamentally alters transient behavior: peak overshoots at the anode outlet decrease, while inlet segments develop pronounced overshoots with markedly slower decay rates. This is attributed to increased ohmic resistance and reduced double-layer capacitance under dehydrated conditions. The findings reveal that cathode hydration critically governs SU-induced degradation and that dehydration strategies may prolong exposure to corrosive potentials, providing guidance for optimizing shutdown protocols in automotive applications.

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Proton exchange membrane fuel cells (PEMFCs) are considered a key technology for sustainable energy conversion due to their high efficiency and zero local emissions. Despite these advantages, their commercialization success is lagging behind, primarily because the total cost of ownership is still too high. Reducing capital costs through manufacturing scale-up and lower platinum loading is one pathway toward improved competitiveness. Equally important is mitigating performance degradation for a lower fuel consumption due to higher efficiency and extend system lifetime. One key degradation effect is the start-up (SU) and shut-down (SD) event. Within the SU it needs to be distinguished between a start up from a H_2 environment (H_2 on anode and H_2 or air on the cathode) and the air-air SU in which both the anode and cathode compartments are initially filled with air. In an air-air SU, the cathode is exposed to extremely high potentials,[1–5] which can trigger carbon corrosion and platinum dissolution, leading to irreversible catalyst layer damage. This harmful type of SU is addressed in the following. Higher electrode potentials impose harsher conditions for Pt dissolution and carbon corrosion. The accelerated stress test (AST) protocols of the US Department of Energy (DOE)[6] propose a triangular potential sweep between 0.6–1.0 V to trigger catalyst degradation, and a triangular sweep between 1.0–1.5 V to trigger carbon support corrosion. Under adverse conditions, such high potentials of up to 1.5 V are known to occur during a SU event within a short time window.[2,4,7,8] Investigating this dynamic and local phenomenon under realistic conditions requires a cell with realistic channel length, since the simultaneous presence of air and hydrogen in the anode compartment is key to the overshoot behavior. As the resulting potential transients are highly inhomogeneous, spatially resolved characterization using segmented cells is equally essential, since single-cell measurements fail to capture this phenomenon.

Several mitigation strategies for SU/SD-induced degradation have been reported in the literature and are summarized by Zhang et al.[9] These range from catalyst-layer material selection, where highly graphitized carbon,[10] carbon nanotubes,[11,12] or alternative supports such as titanium carbide[13,14] or tungsten carbide[15,16] have shown promising results, to system-level control strategies that mitigate degradation during start-stop events through targeted gas management during operation, shutdown, or prior to start-up.[17] However, the effectiveness of such mitigation strategies inherently depends on a detailed understanding of the local cathode-potential evolution during air–air SU, which remains insufficiently resolved.

A deeper understanding of the operation parameters that influence the cathode potential during air–air SU is therefore essential.

Reiser et al.[18] proposed 2005 a mechanism during start up and shutdown event, called reverse-current mechanism, that cause accelerated performance decay. By means of a one-dimensional model they demonstrated that partial anode exposure to both hydrogen and oxygen during transient conditions causes electrolyte potential to drop from 0 to −0.59 V versus reversible hydrogen electrode, creating reverse current flow that raises cathode potential to 1.44 V and triggers severe carbon corrosion. Since the model does not account for transients, the reverse current is generated solely by oxygen reduction reaction (ORR), hydrogen oxidation reaction (HOR) and carbon corrosion. By connecting electrically two single cells in parallel, where one cell is operated with hydrogen at the anode and the other cell's anode with air, they confirmed significant electrochemically active surface area (ECSA) losses and cathode electrode thinning, establishing this mechanism as fundamental for SU and SD events or if hydrogen is starved. Gu et al.[19] advanced the modeling capabilities by incorporating electrode pseudo-capacitance effects, such as the reduction of oxidized Pt surface at the anode ($PtOH + 2H^+ + 2e^- \rightarrow PtH + H_2O$) or via further oxide formation at the cathode ($PtOH \rightarrow PtO + H^+ + e^-$) occurring during SU. Their model, validated through current density distribution maps of a single cell with serpentine flow field, revealed critical time-scale dependencies where capacitive effects reduce carbon corrosion by approximately 30% for application-relevant short residence times (1.3 s) compared to longer accelerated testing conditions, demonstrating excellent agreement with controlled start-stop experiments and spatially resolved degradation patterns. Chen et al.[20] developed a transient 1 + 1 D kinetic model that accounts for both pseudo-capacitance and double-layer capacitance, highlighting their

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Investigation of the local cathode potential evolution during start-up by means of embedded reference electrodes in a PEM fuel cell

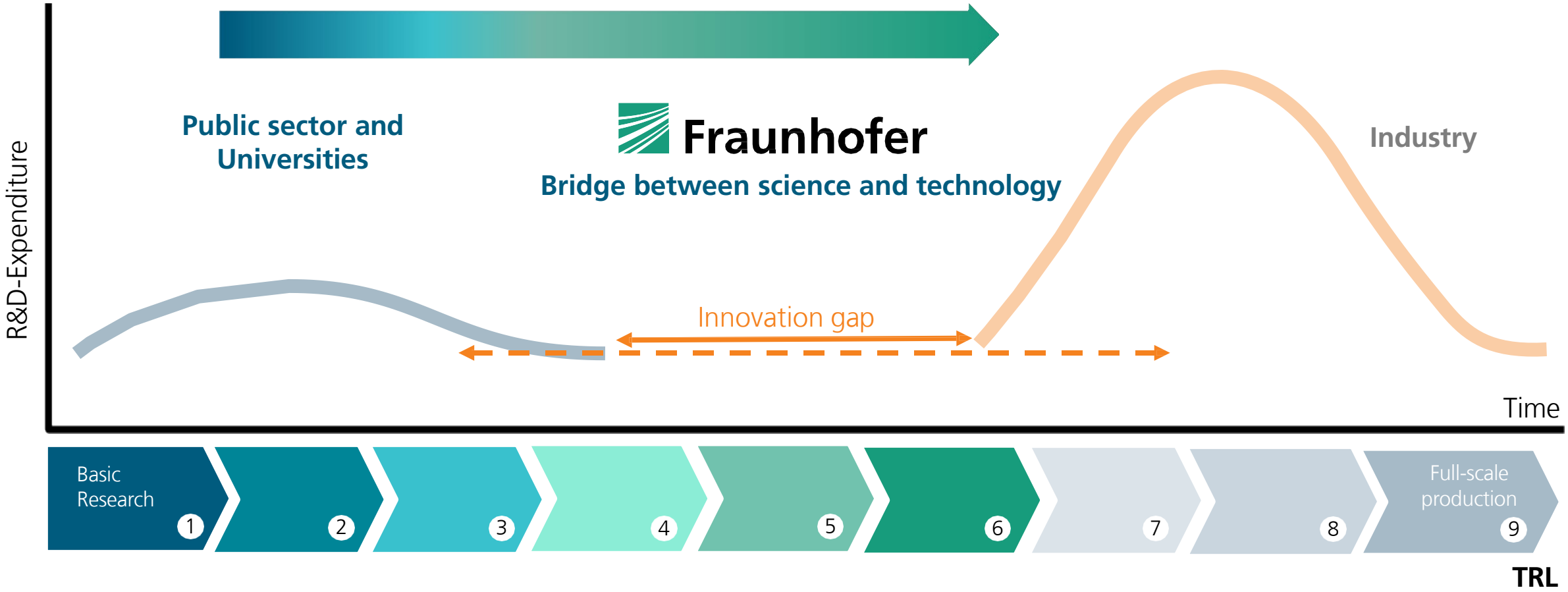
Speaker: Dr. Dietmar Gerteisen[1]
Co-authors: Johannes Schall[1]**, Pascal Gaus**[2]**, Dr. Timo Kurz**[1]
Fuel Cell Scientific Insights Series
Freiburg, Germany, 18.11.2026
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Our Mission in Our Department Fuel Cell

Assisting Global Industry with Scientifically Sound Services

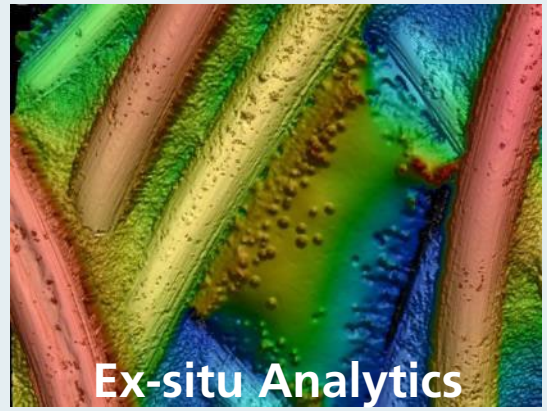
Understanding Fuel Cell Membrane Electrode Assemblies (MEAs)

Key Performance Indicators 2025:

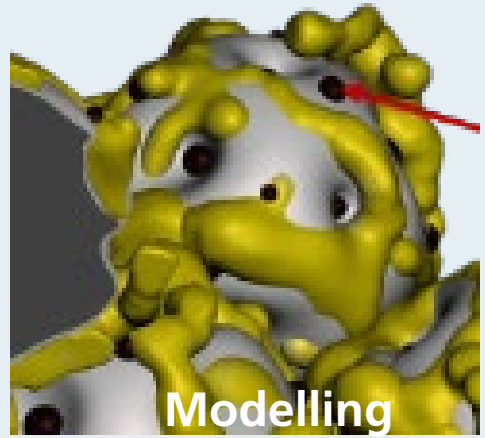
- 45 researchers plus students
- 9.4 Mio. € annual budget (w/o investments)
- 19% direct revenue by industry contract research
- > 500 m² laboratory area with 13 single cell test stations, 5 short stack test stations including temperature chamber (all fully automated for 24/7 operation)
- Focus on transport application

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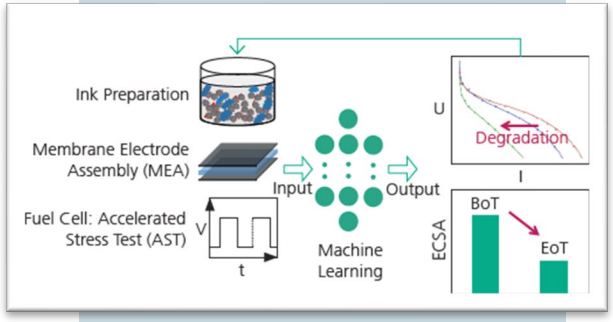
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Fuel Cell Modeling Team

Main Topics

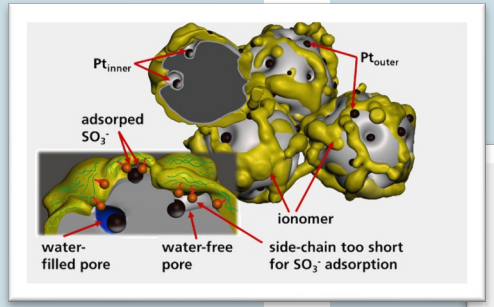
AI / Machine Learning

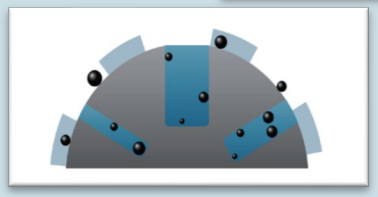
- CCM production



Electrode level

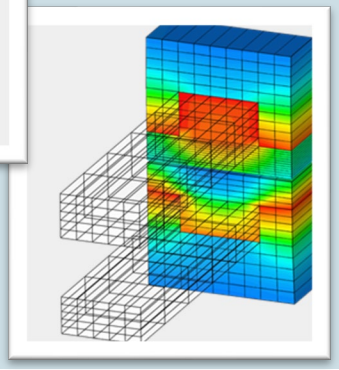
- Self developed codes, focus: Python
- Structure, performance degradation, transport processes





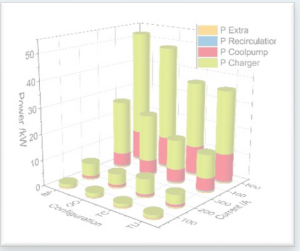
Cell level

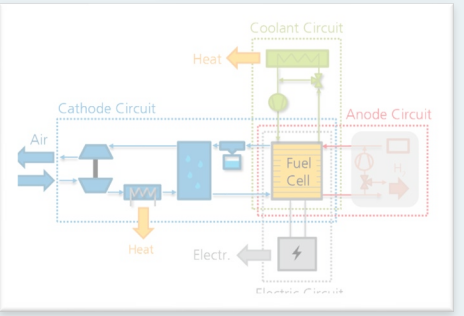
- Self developed codes (Python)
- Commercial CFD code (FireM)
- Local effects



System level

- Design and optimization





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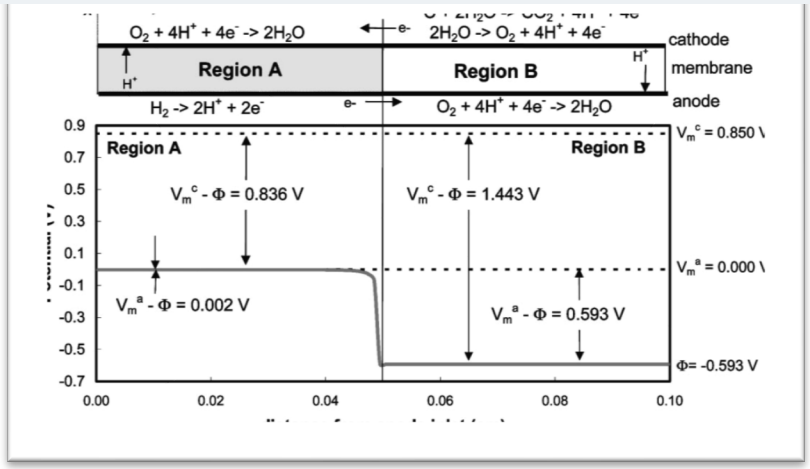
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Motivation for the air/air start-up investigation

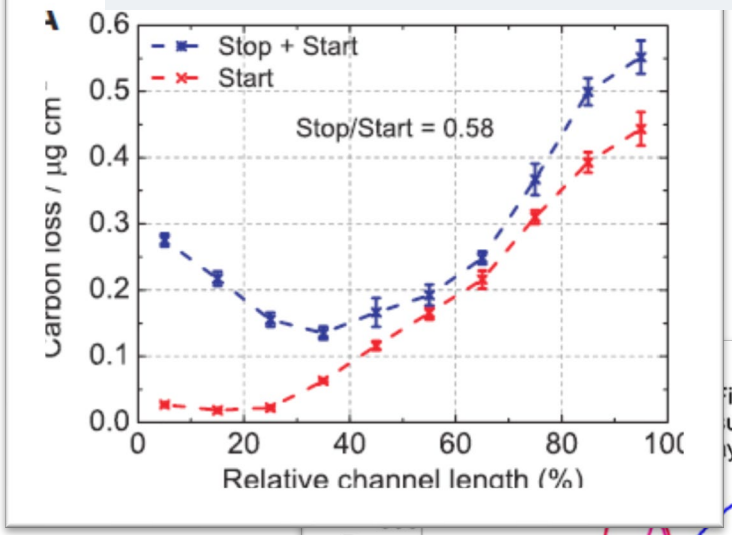
Question: What conditions before and during start-up (SU) are best to avoid high cathode potentials

- It is well known that an air/air start results in harmful cathode potentials
  - High potentials trigger degradation
  - Strong local phenomena → high cathode potential at anode outlet region

Reiser et al., Electrochemical and Solid-State Letters, 8 (6) A273-A276, 2005

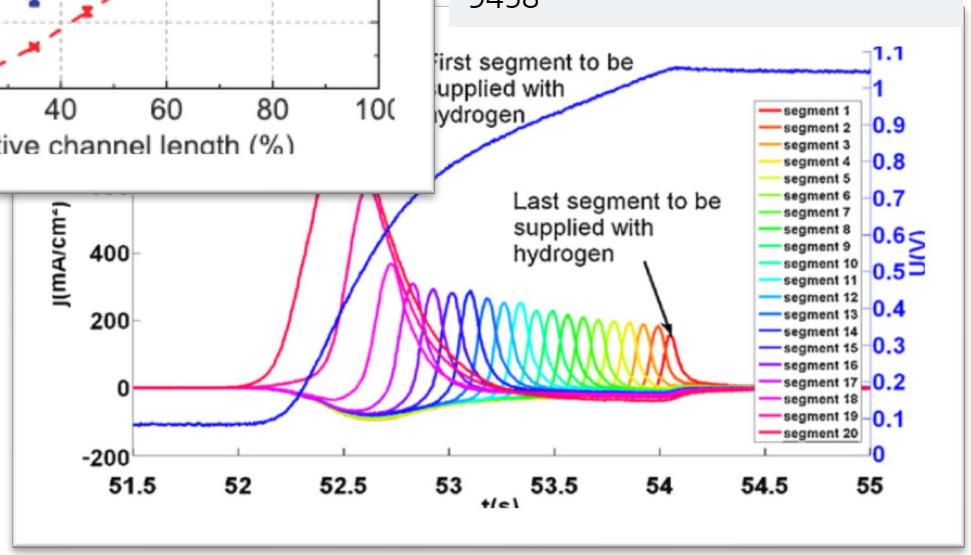


Kreitmeier et al., JES, 159 (11) F787-F793 (2012)



Spatially resolved measurements

A. Lamibrac et al. / Journal of Power Sources 196 (2011) 9451–9458



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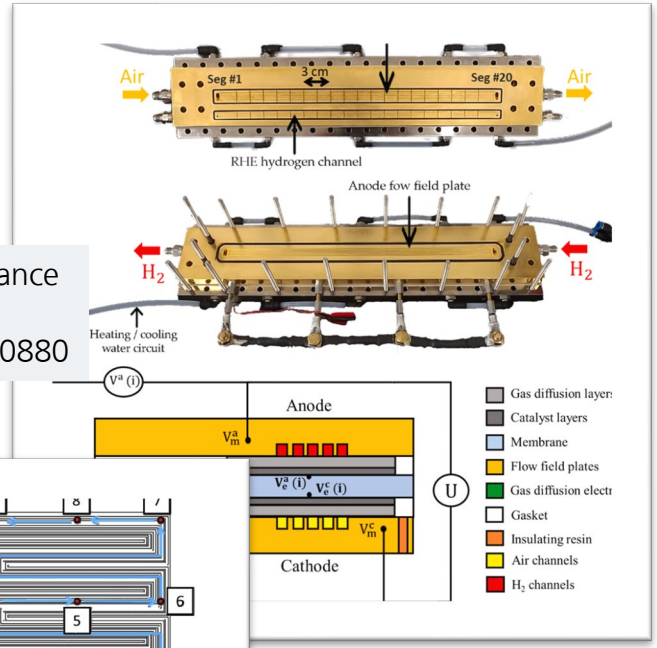
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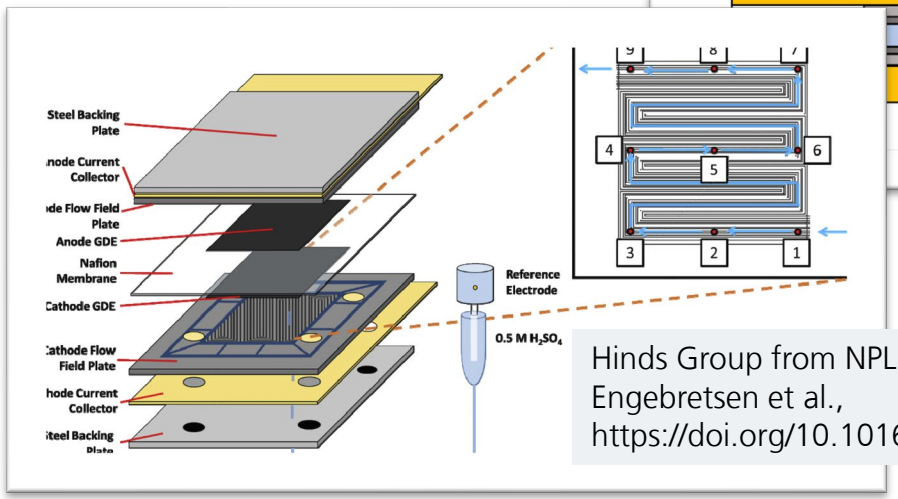
- It is well known that an air/air start results in harmful cathode potentials
  - High potentials trigger degradation
  - Strong local phenomena → high cathode potential at anode outlet region

- You can find several papers on this topic and they agreed on dynamic response dependencies
  - The cell / flow field design
  - On the material, especially the electrodes
  - The start conditions
  - The pre-conditioning conditions

Examples for local reference electrodes



Lottin group from Vandœuvre-lès-Nancy, France
Touhami et al.,
https://doi.org/10.1016/j.jpowsour.2021.230880



Hinds Group from NPL in Teddington (UK)
Engebretsen et al.,
https://doi.org/10.1016/j.jpowsour.2018.02.022

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Motivation for the air/air start-up investigation

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  - The cell / flow field design
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The phenomena of this cathode overshoot and the principle mechanism of air/air start-up are known and described in the literature but not specifically for the desired

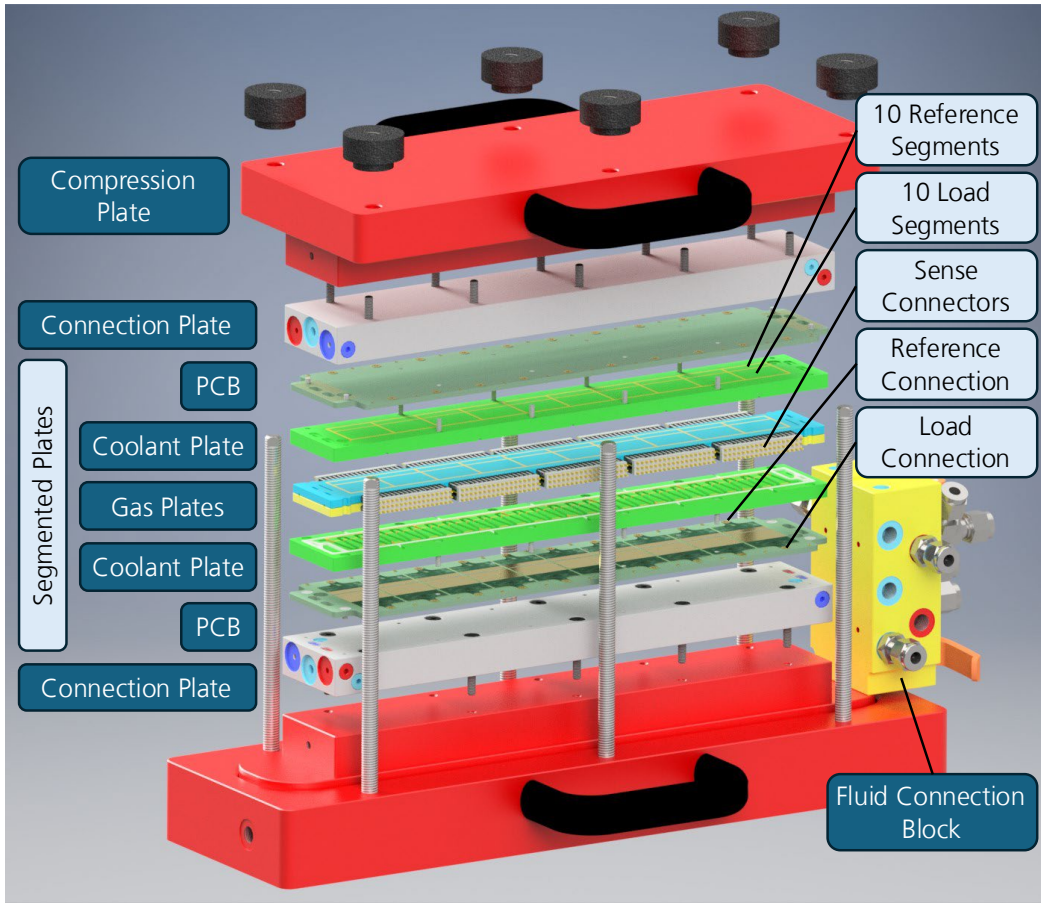
- flow field design
- material
- system limitations
- shut-down strategies
- start-up conditions

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Segmented Along-the-channel (ATC) cell: our working horse

Explosive view of the entire cell setup

- From outside to inside of the CAD rendering
  - Clamping pressure realized by air bladder system
  - Use of fluid connection blocks at anode and cathode inlet for a fast and reproducible setup
  - Connection plates for fluidic distribution and thermal isolation
  - PCBs act as interface to multichannel potentiostat system (EMA)
  - Segmented cooling plates
  - Segmented flow field plates
  - Non-segmented MEA (not shown)



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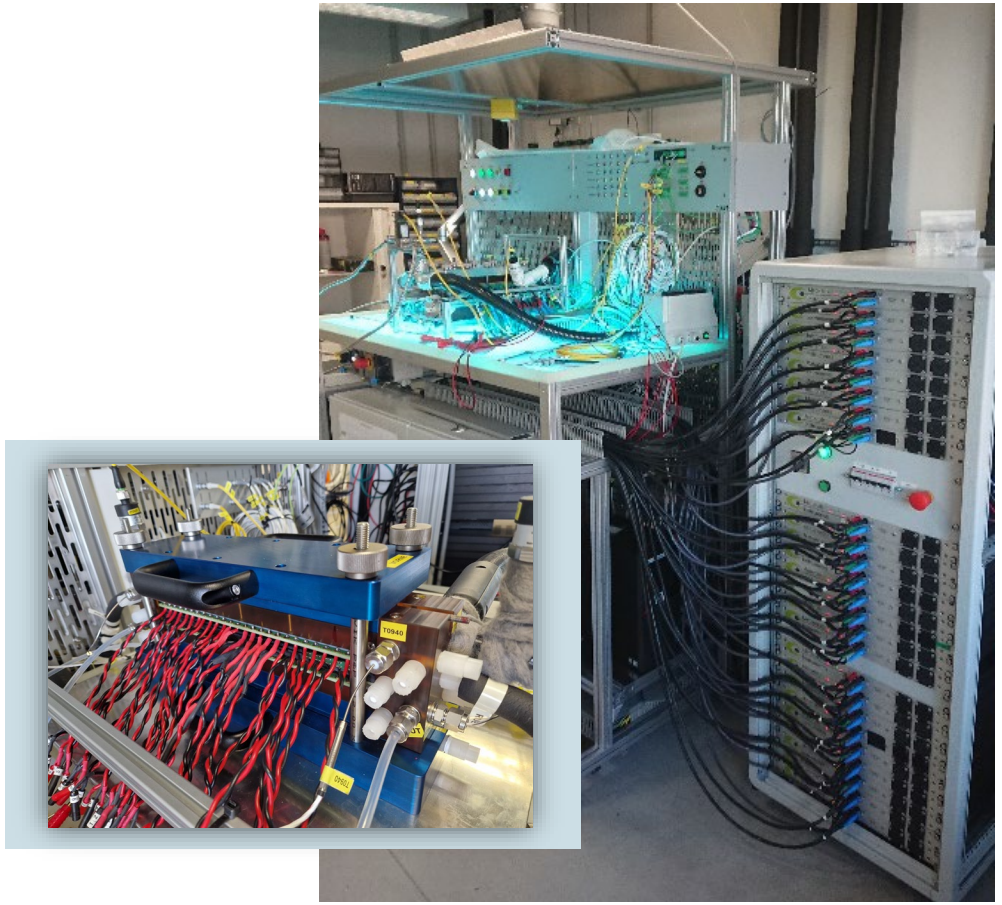
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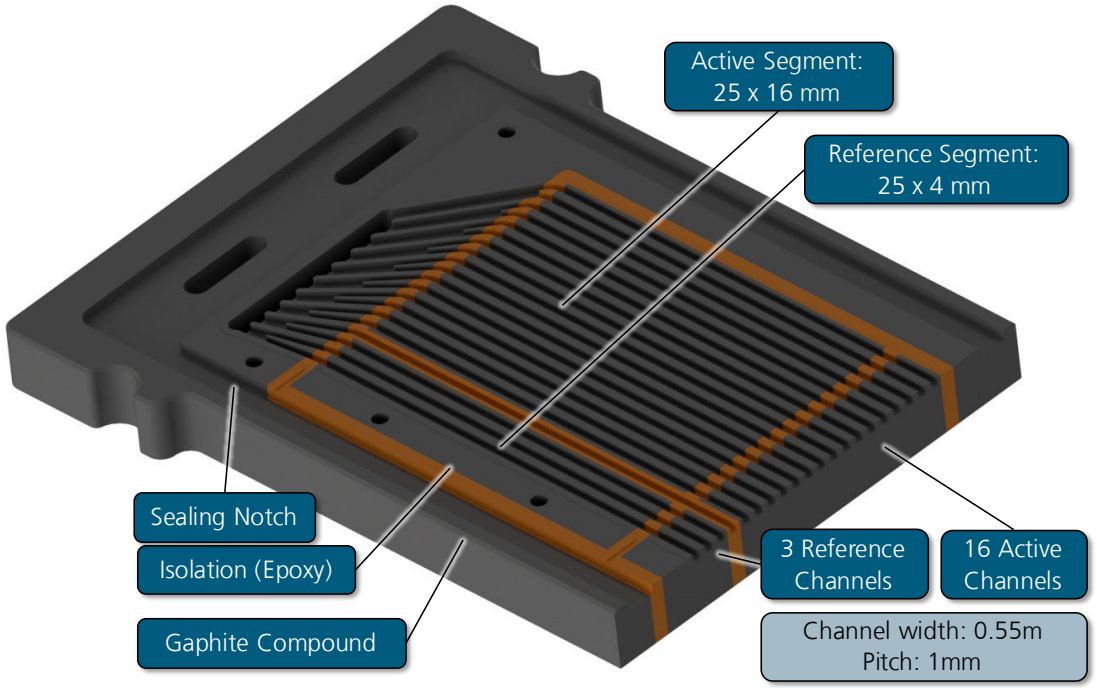
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Segmented Along-the-channel (ATC) cell: our working horse

Embedding of local reference electrodes in existing ATC cell setup

- Our boundary conditions for this project
  - Limited in space in the flow field area and for the gas distribution
- Challenge: How to embed reference electrodes
  - Without sealing between active and reference area
  - Without having extra gas supply to feed reference electrodes
- Our answer:
  - Anode changes gas composition @ SU: air → H2
  - **Cathode side must be our reference!**



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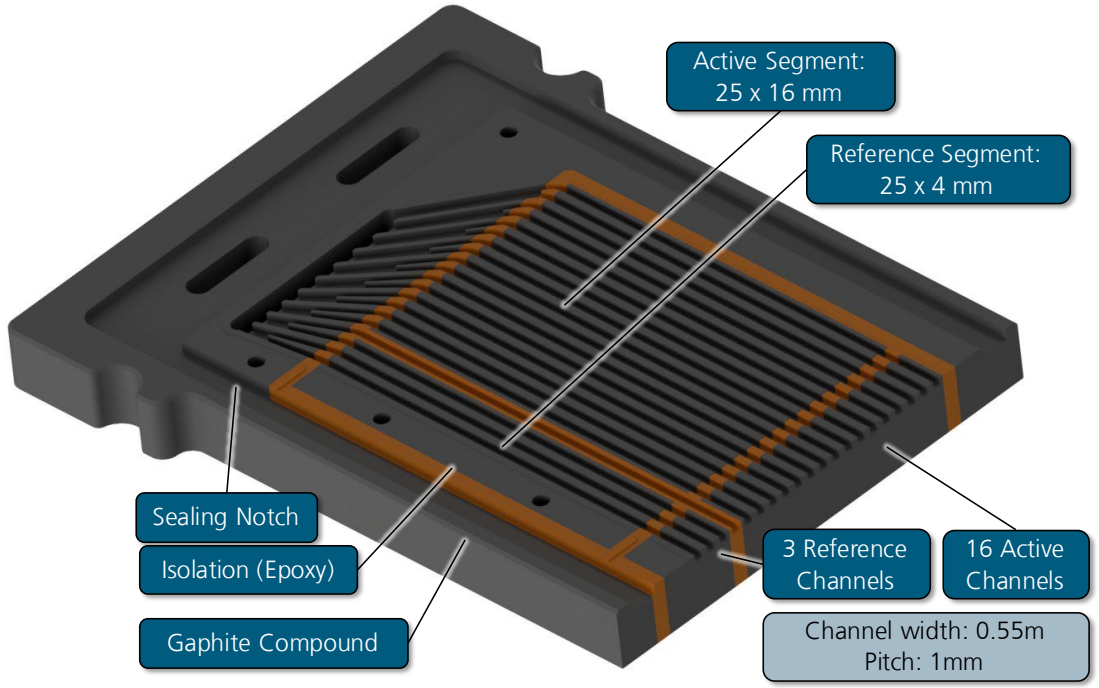
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Segmented Along-the-channel (ATC) cell: our working horse

Embedding of local reference electrodes in existing ATC cell setup

- Design
  - 10 active load segments (each 4cm^2)
  - 10 corresponding reference segments (each 1cm^2) separated by 1mm wide epoxy gap
  - Flow field consists of 20 channels (300/500µm) anode/cathode, width 550µm, channel pitch 1mm
    - No channels on anode side in the reference region



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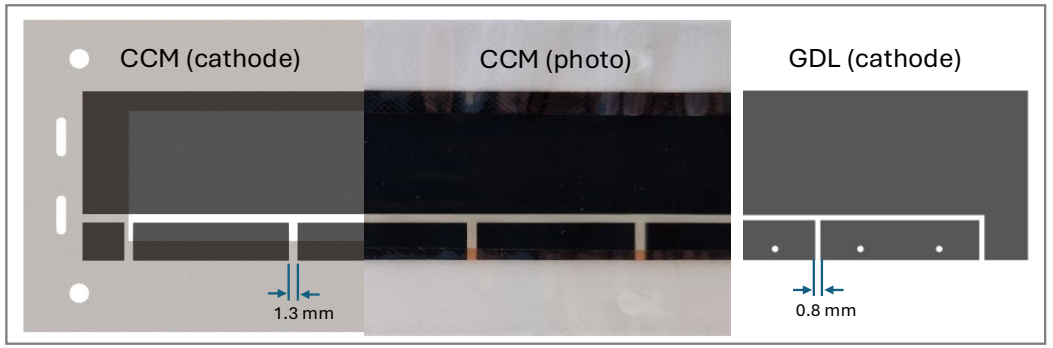
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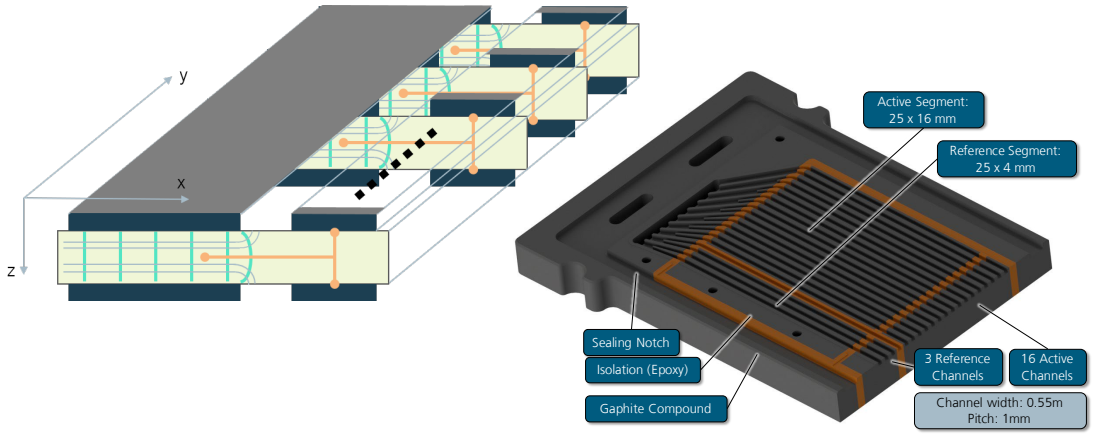
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Segmented Along-the-channel (ATC) cell: our working horse

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  - Separation of active catalyst layer (CL) to reference CL realized by Laser ablation
  - Active area covered with one piece of GDL
  - Reference electrodes separate GDL pieces with gaps of 800µm





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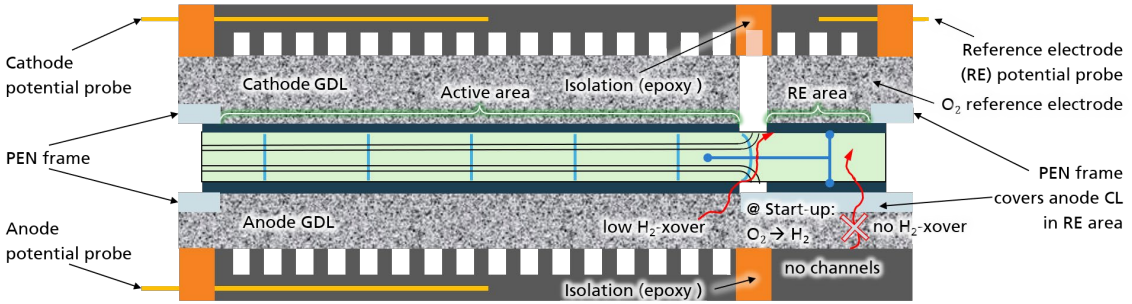
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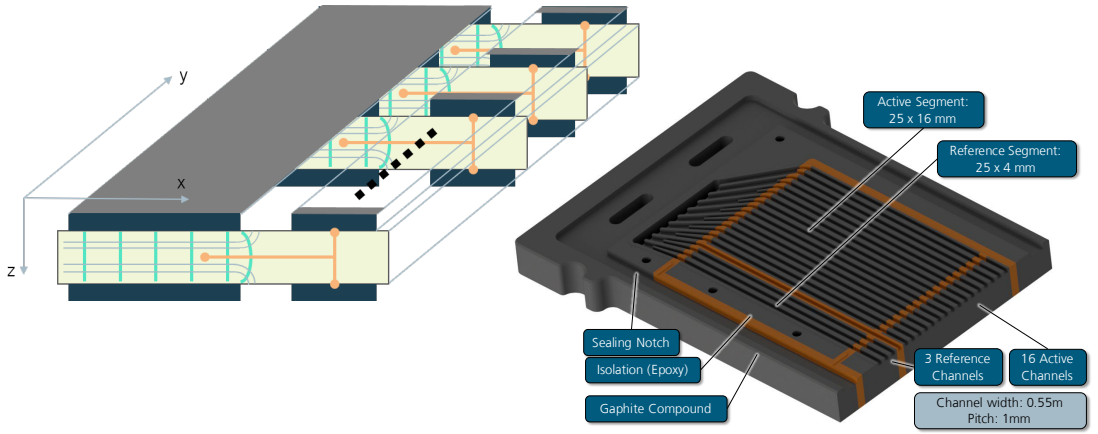
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  - Separation of active catalyst layer (CL) to reference CL realized by Laser ablation
  - Active area covered with one piece of GDL
  - Reference electrodes separate GDL pieces with gaps of 800µm
  - Enlarged PEM-frame at anode reference side minimizes H_2-xover





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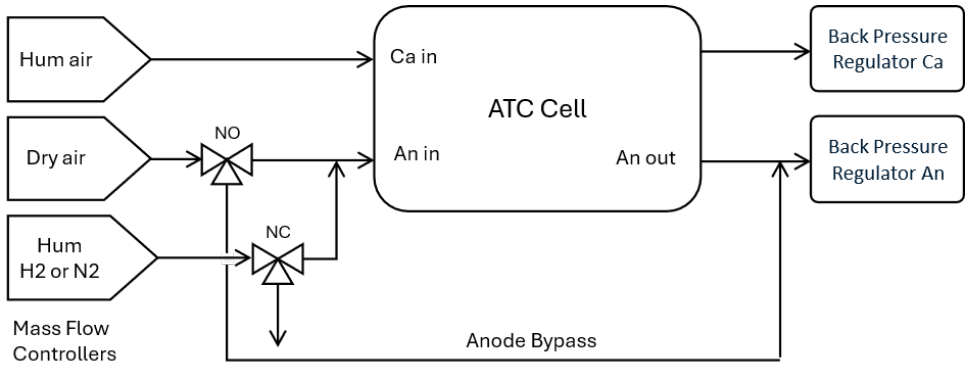
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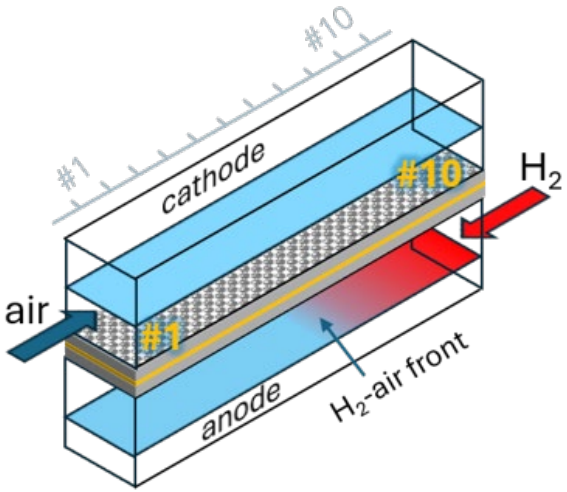
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Segmented Along-the-channel (ATC) cell

Experimental setup

- Material
  - GDL : Freudenberg H14CX653
  - CCM : Greenerity H520 Gen.8, anode/cathode loading 0.1/0.5 mg/cm^2, membrane thickness 15µm
- Cell compression
  - 1MPa
- DC data recording during SU experiment
  - 1 kHz
- Fluidic
  - Counter-flow configuration
  - Bypass realizes gas switch with minimized pressure spikes





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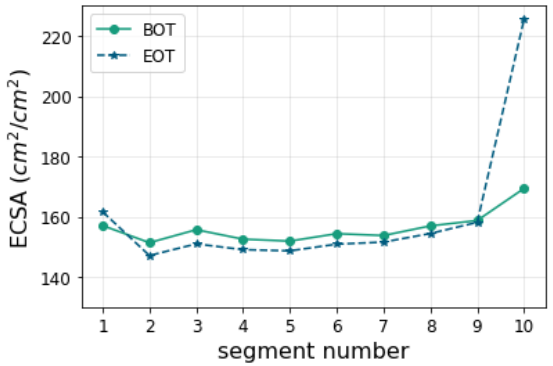
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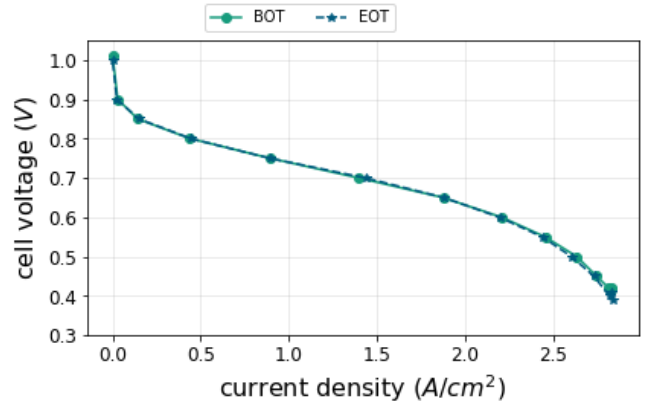
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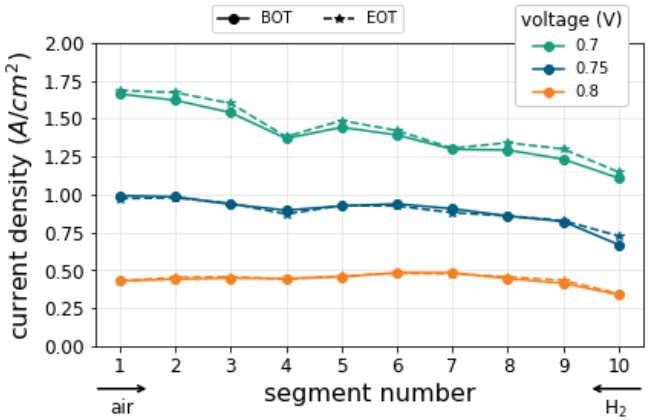
Testing protocol

- Break-in procedure @ T_{cell}=80°C and RH=100%
  - 2h at 600mV
  - 4h voltage cycling: OCV → 0.6V → 0.4V
  - @ anode/cathode flow of 2/5 nl/min
  - @ pressure of 2 bara
- Spatially resolved characterization
  - Polarization curves with HFR
  - CV
- SU experiments
  - atmospheric pressure
  - Cathode flow at 12nl/min for stable reference electrodes
  - T_{cell}=20°C → to avoid degradation





"Begin-of-test" and "End-of-test" characterization confirm that the electrode is intact and not altered



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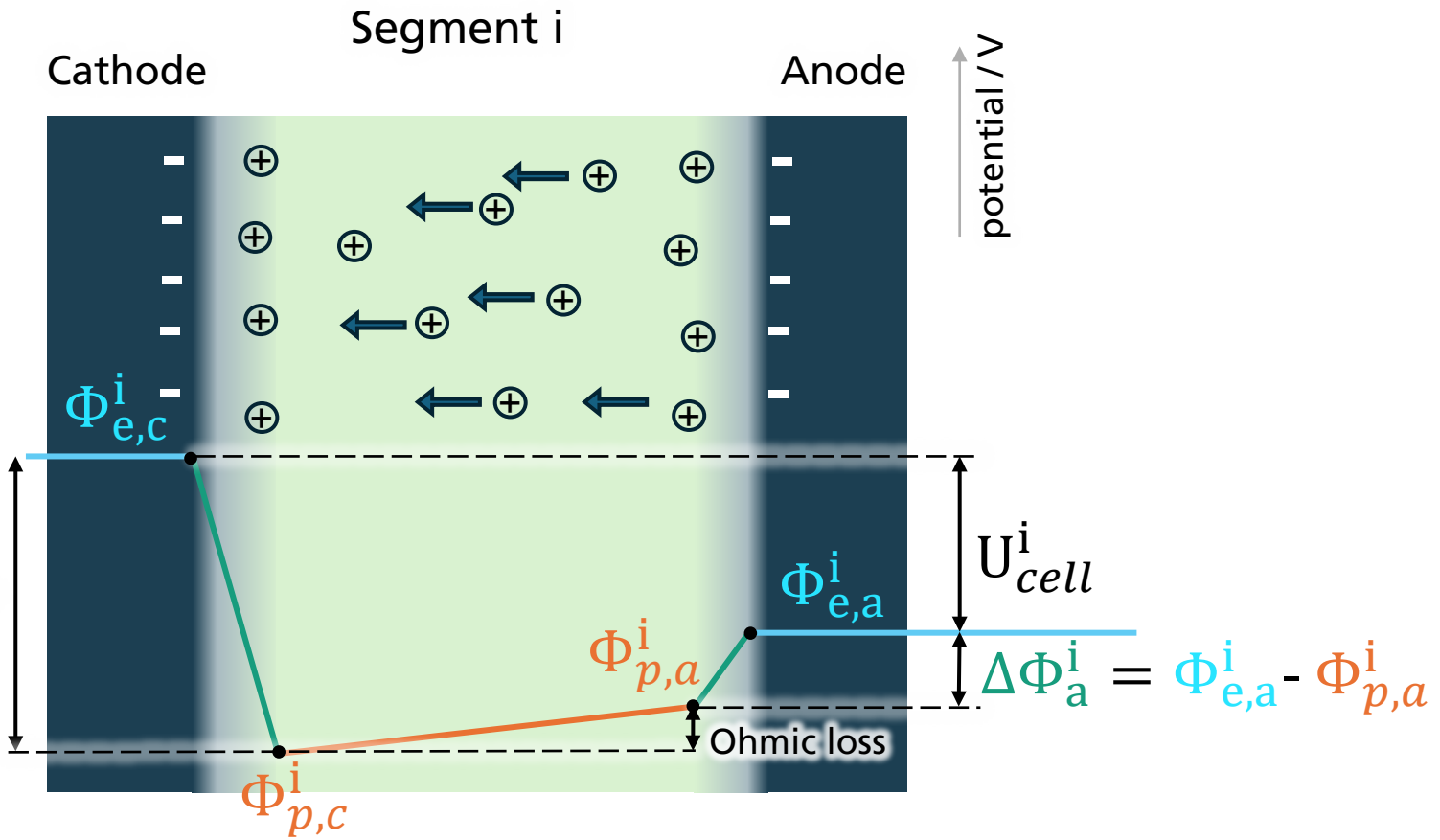
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Brief excursion into the basics of reference electrodes

Through-plane schematic of a fuel cell

- Simplified potential distribution
  - Electrode potential $\Delta\Phi$ defined as difference between metal Φ_e and electrolyte Φ_p potential
  - Potential gradients in CL neglected
  - Ohmic drop in membrane will be relevant for connecting reference electrode



$$\Delta\Phi^{i}_{c} = \Phi^{i}_{e,c} - \Phi^{i}_{p,c}$$

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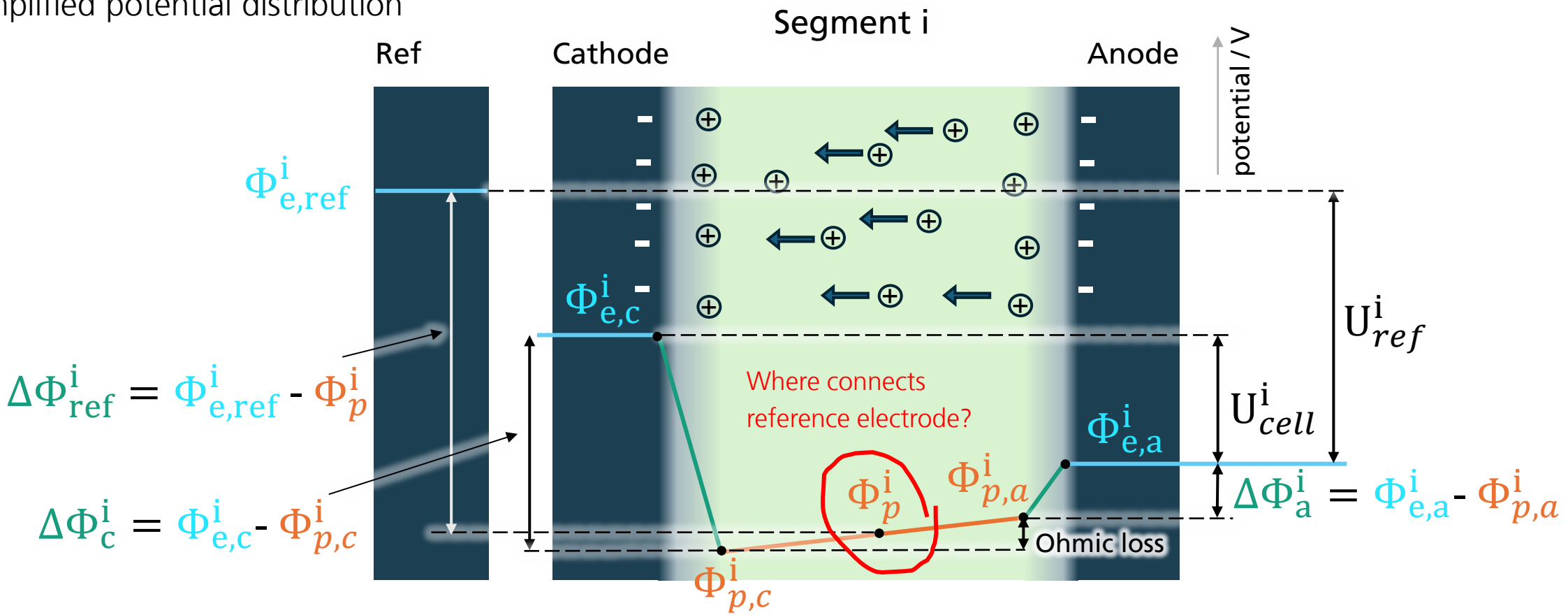
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Brief excursion into the basics of reference electrodes

Simplified through-plane schematic of a fuel cell

- Simplified potential distribution



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Brief excursion into the basics of reference electrodes

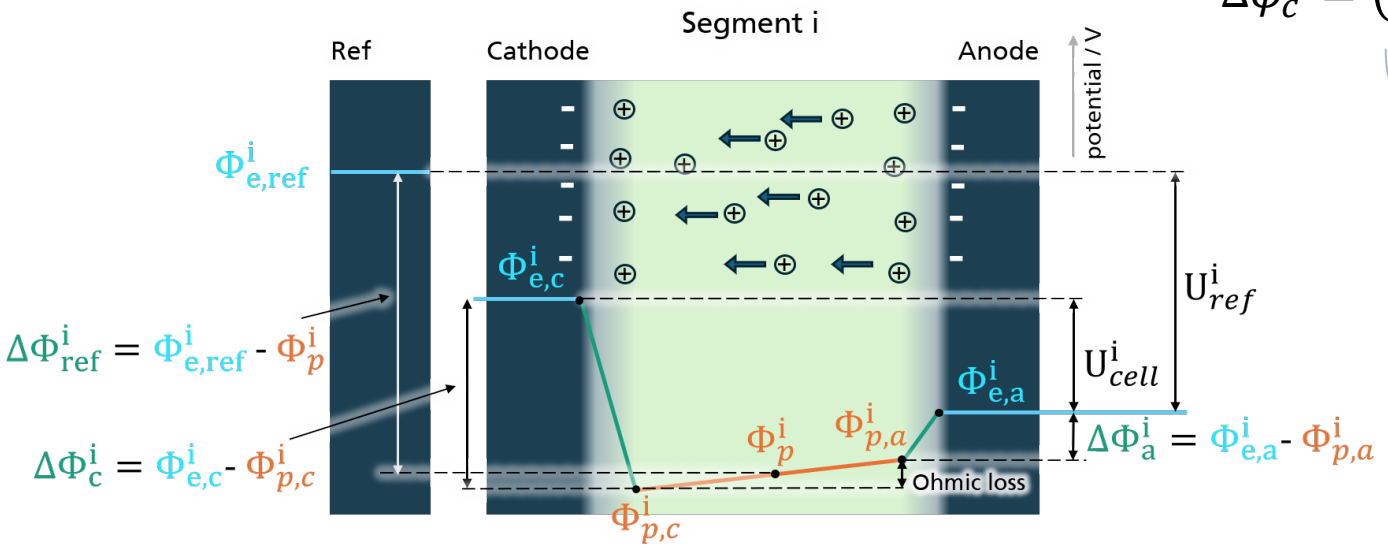
Simplified through-plane schematic of a fuel cell

- Simplified potential distribution
  - Cathode potential is of interest
  - Measured indirectly via U^i_{cell}, U^i_{ref} by assuming $\Delta\phi^i_{ref}$ is stable during SU

$$\Delta\phi_c^i = \phi_{e,c}^i - \phi_{p,c}^i$$

$$\Delta\phi_c^i = \phi_{e,c}^i - \phi_{e,a}^i + \phi_{e,a}^i - \phi_{p,c}^i + \phi_{e,ref}^i - \phi_{e,ref}^i$$

$$\Delta\phi_c^i = \underbrace{(\phi_{e,c}^i - \phi_{e,a}^i)}_{U_{cell}^i} + \underbrace{(\phi_e^{ref\,i} - \phi_{p,c}^i)}_{\Delta\phi_{ref}^i} - \underbrace{(\phi_e^{ref\,i} - \phi_{e,a}^i)}_{U_{ref}^i}$$



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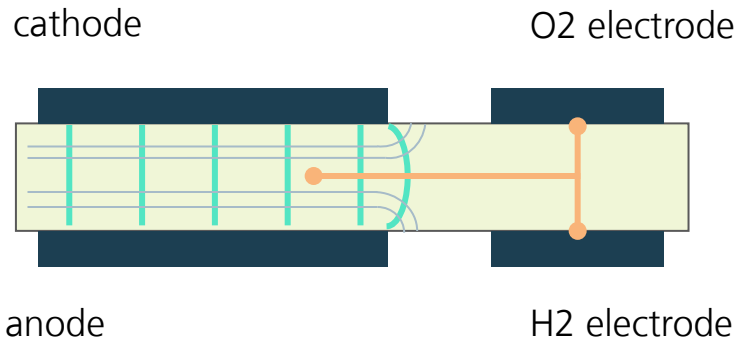
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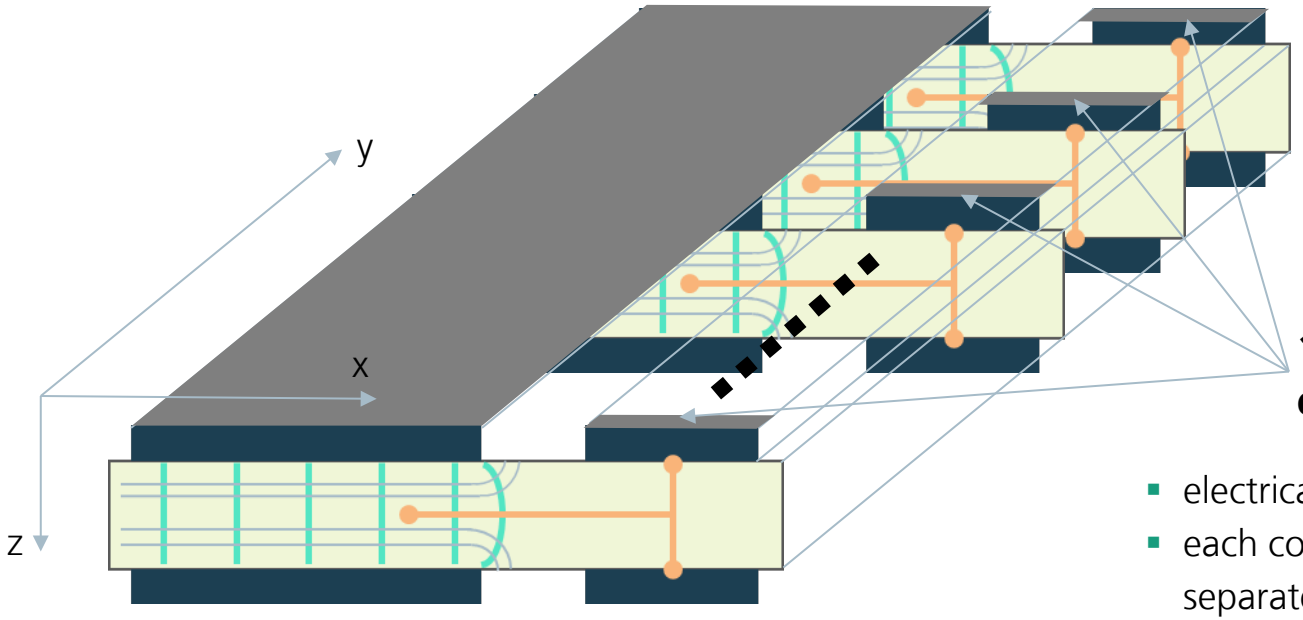
Measuring spatially resolved electrode potential

Via local reference electrodes

Assumptions

- Reference potential stable during start-up experiment (several 100ms)
- Neglecting ohmic drop in z-direction





10x reference electrodes

- electrically isolated
- each covered with separate GDL

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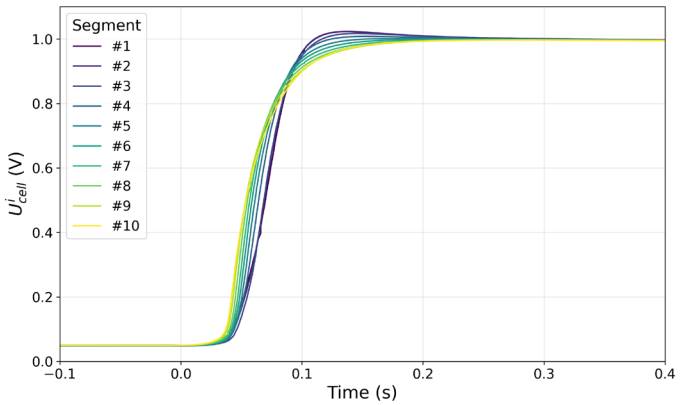
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What do we really measure during SU?

The cathode potential needs calculations

$$\underbrace{\left(\phi_{e,c}^{i} - \phi_{e,a}^{i}\right)}_{U_{cell}^{i}}$$



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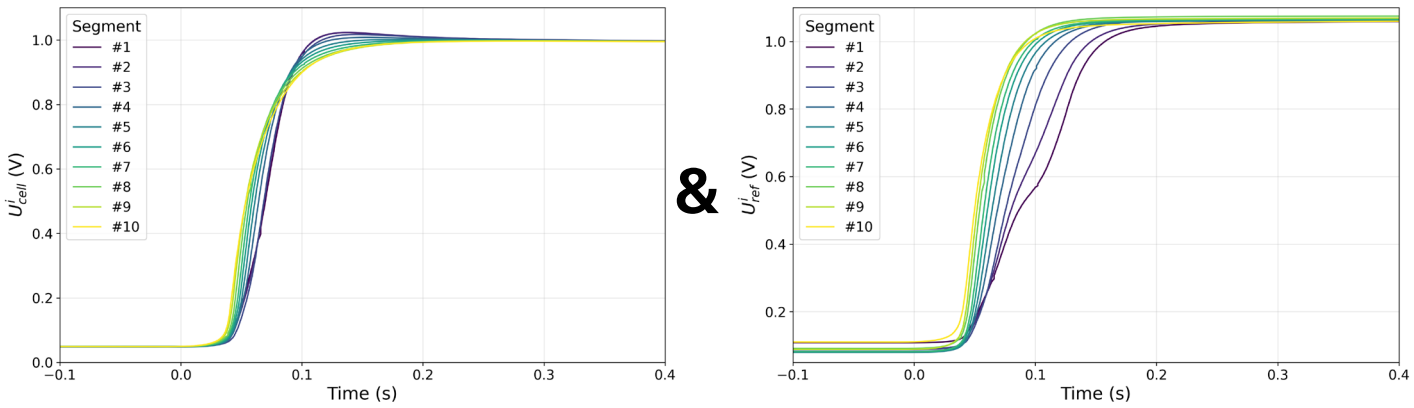
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What do we really measure during SU?

The cathode potential needs calculations

$$\underbrace{\left(\phi_{e,c}^{i} - \phi_{e,a}^{i}\right)}_{U_{cell}^{i}} - \underbrace{\left(\phi_{e}^{ref\ i} - \phi_{e,a}^{i}\right)}_{U_{ref}^{i}}$$



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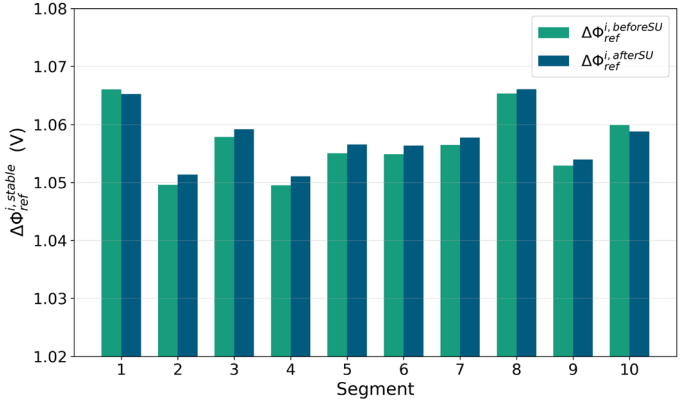
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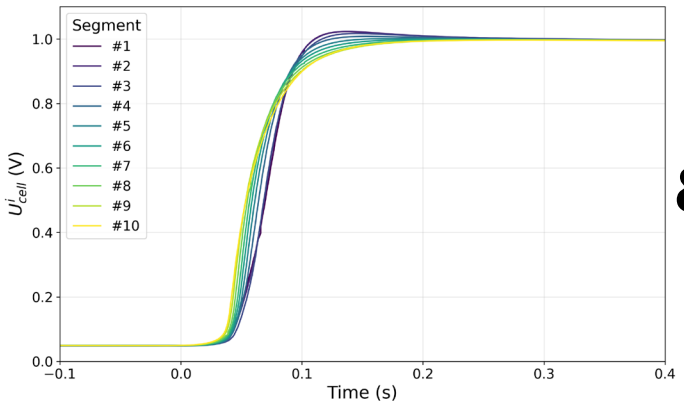
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What do we really measure during SU?

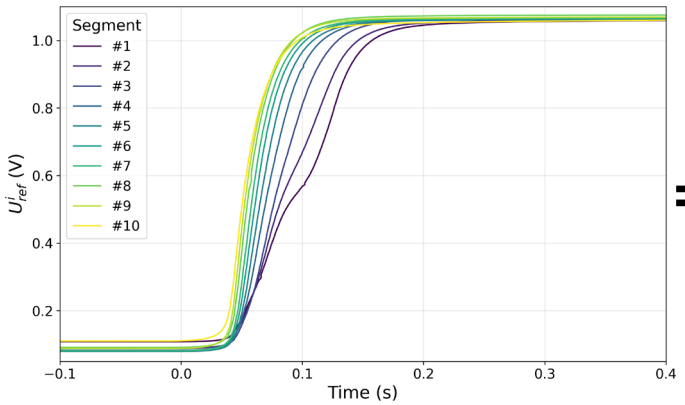
The cathode potential needs calculations

$$\Delta\phi_c^i = \underbrace{\left(\phi_{e,c}^i - \phi_{e,a}^i\right)}_{U_{cell}^i} - \underbrace{\left(\phi_e^{ref\,i} - \phi_{e,a}^i\right)}_{U_{ref}^i} + \underbrace{\left(\phi_e^{ref\,i} - \phi_{p,c}^i\right)}_{\Delta\phi_{ref}^i}$$

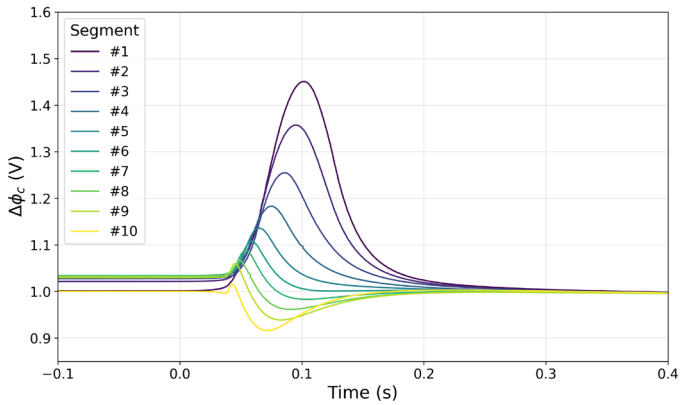




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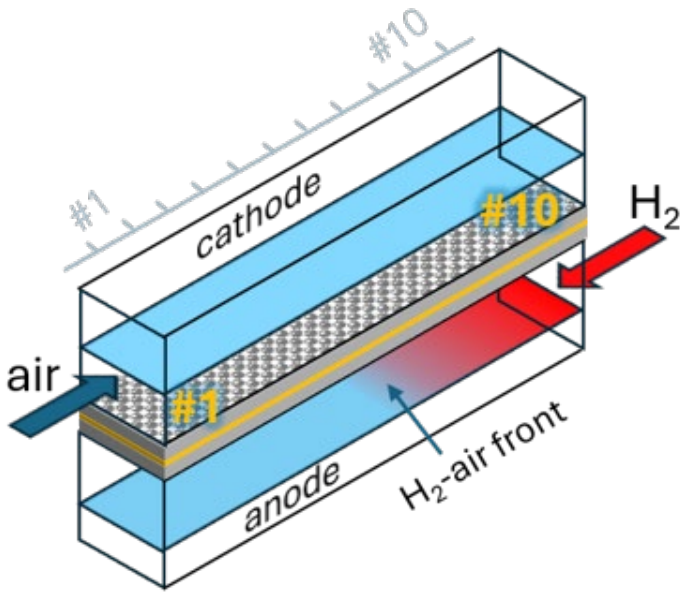
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Start-up experiment

In Slow-motion

- Air inlet at segment #1
- H_2 inlet at segment #10



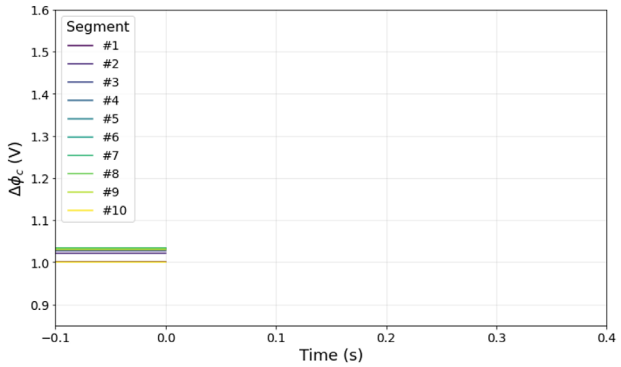
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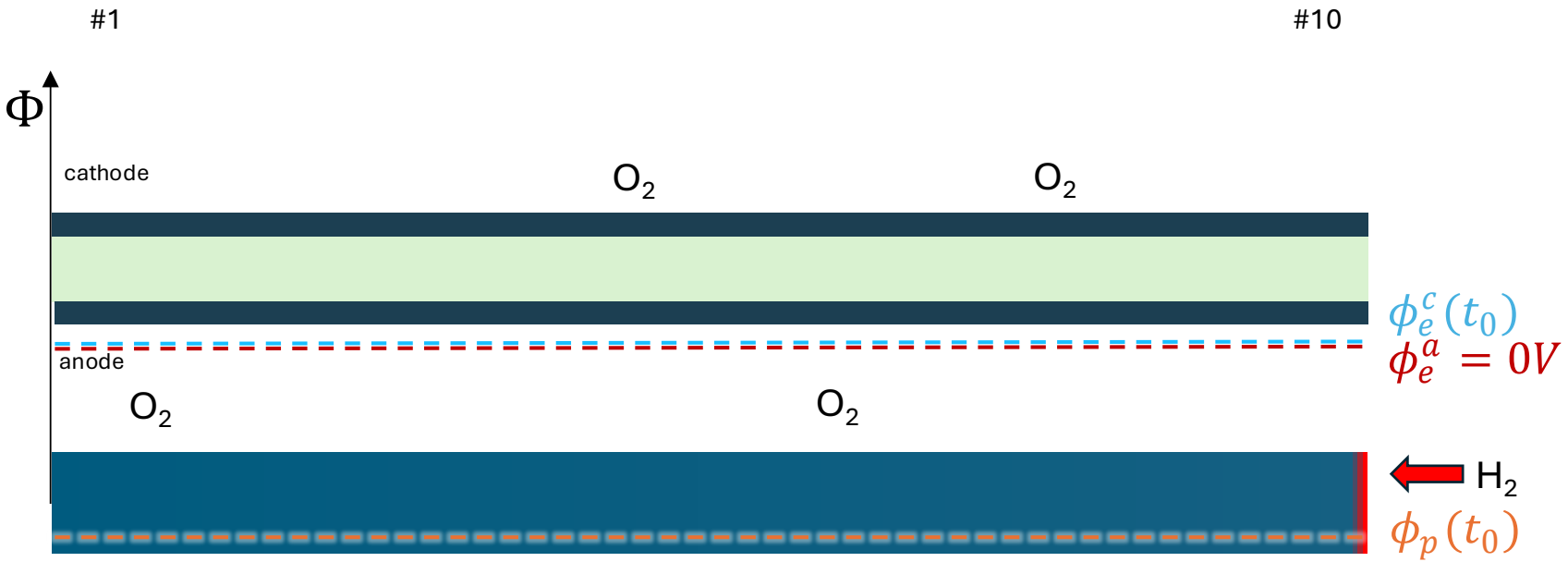
Start-up experiment

Step-by-step

Cathode and anode compartment filled with air

- Both electrodes at Φ_{ORR}^{eq}
- $U_{cell} = 0V$





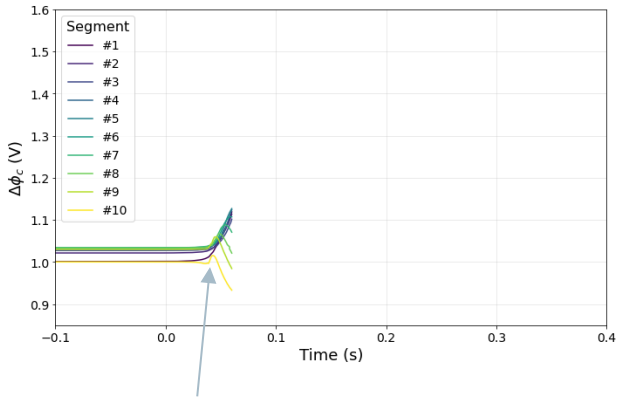
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Start-up experiment

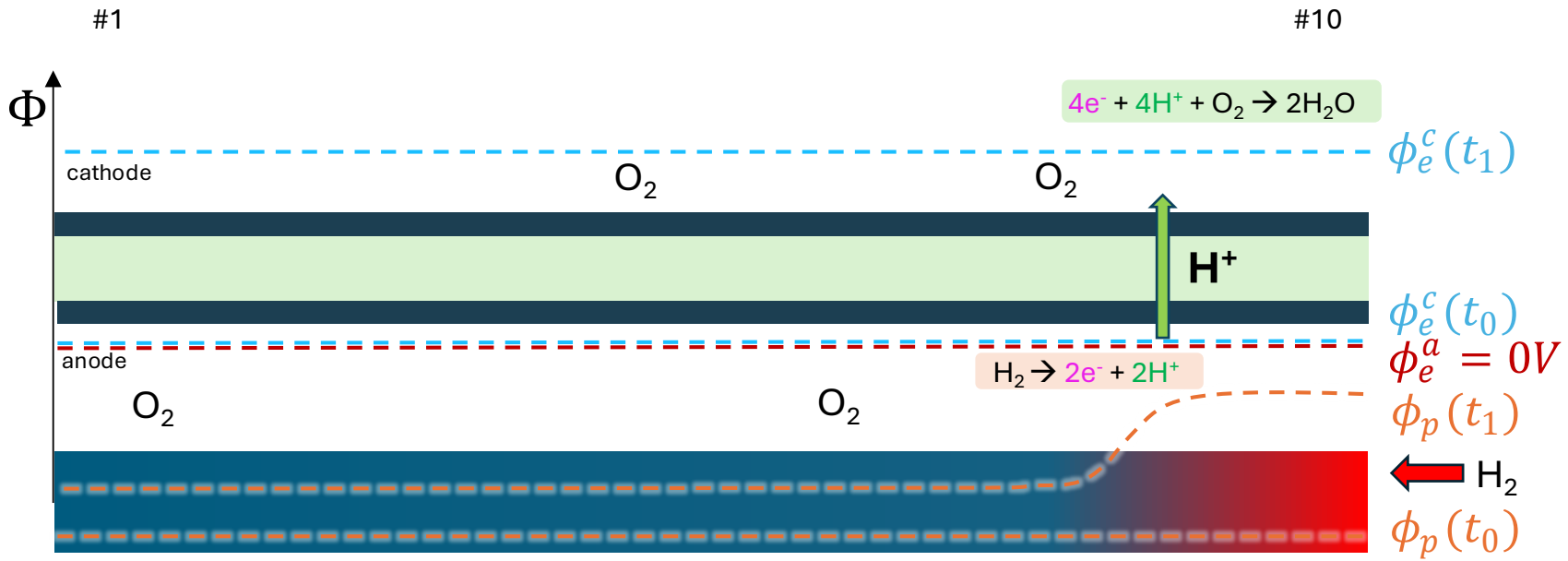
Step-by-step

Hydrogen enters the cell

- HOR kicks in
  - reduces anode potential
  - ORR starts at cathode
    - But also at anode



Inlet: Undershoot-overshoot-undershoot pattern



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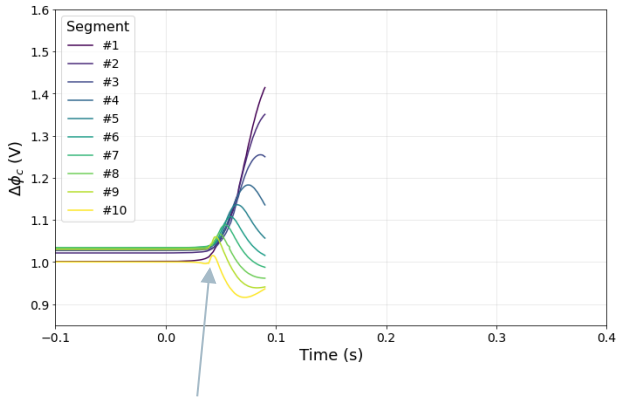
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Start-up experiment

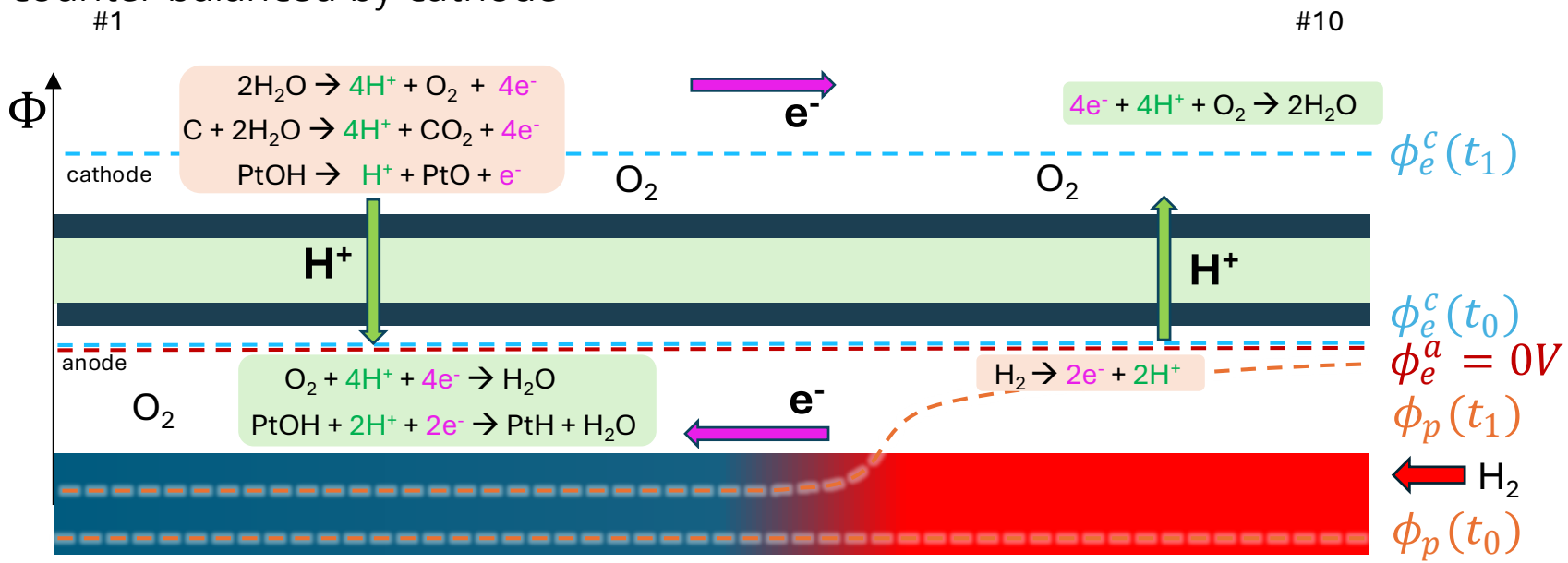
Step-by-step

Hydrogen-Air front moves deeper into cell

- ORR at anode has to be locally counter-balanced by cathode
  - Carbon corrosion
  - Oxide formation
  - Water splitting



Inlet: Undershoot-overshoot-undershoot pattern



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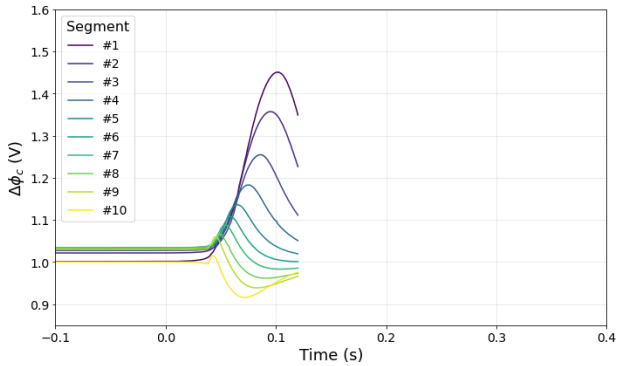
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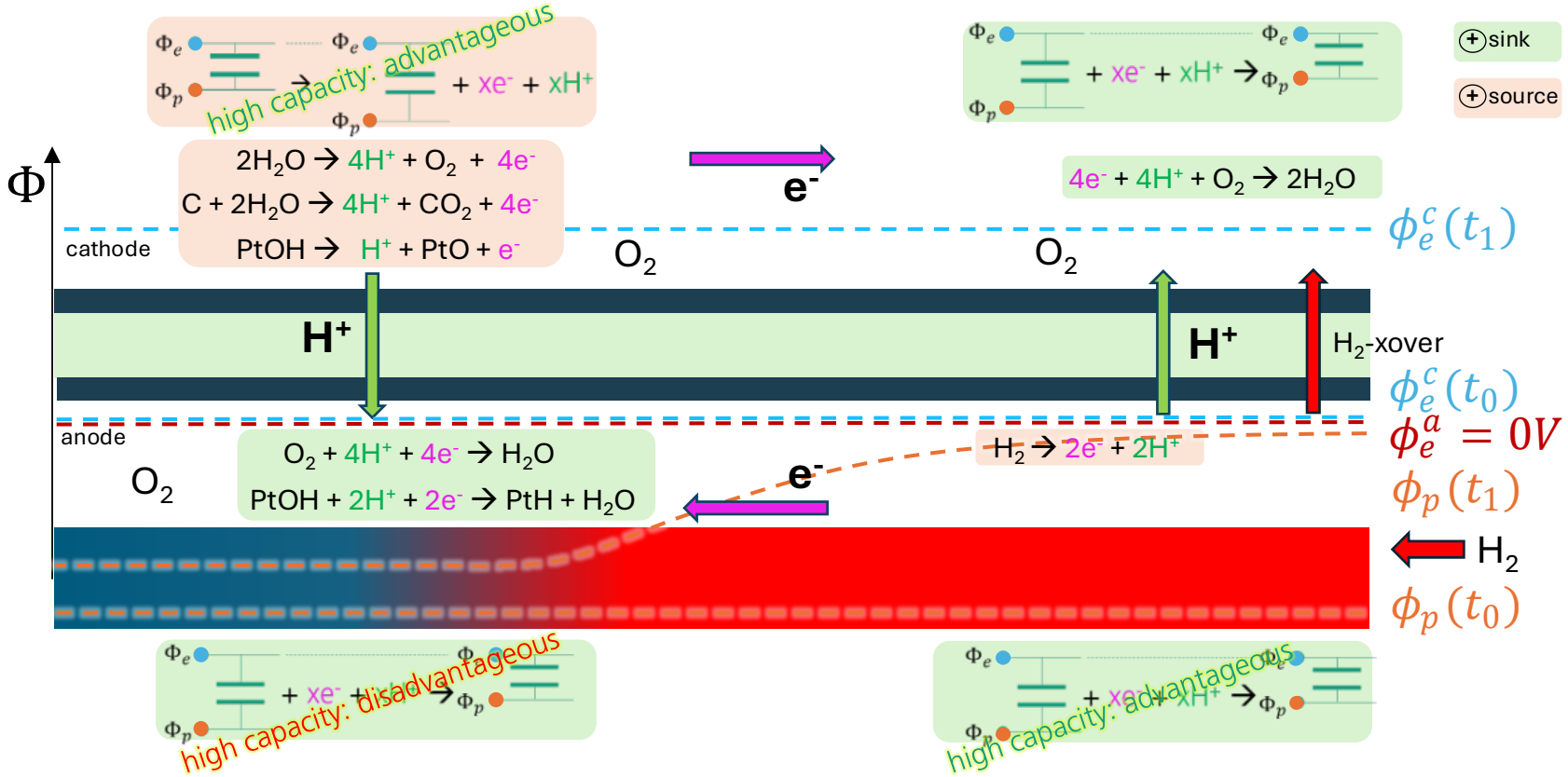
Start-up experiment

Step-by-step

Double-layer capacity charging

- Charging effects must be accounted for the charge balance





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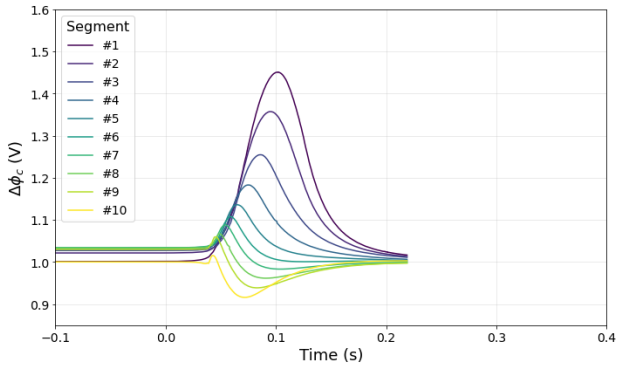
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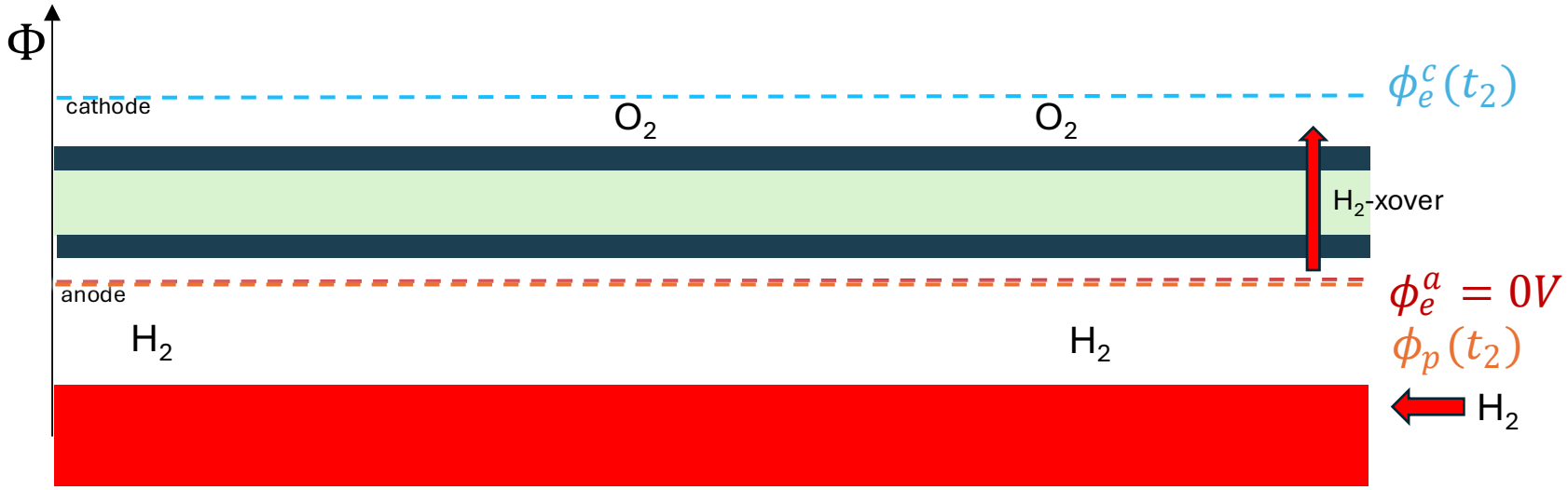
Start-up experiment

Step-by-step

Anode flooded with hydrogen

- Cathode potential relaxes back to Φ_{ORR}^{eq}





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Investigation of H_2 flow rate, $RH_{c/a}$ pre-conditioning and air purge time

Impact on cathode-potential overshoot height and duration

Each SU experiment followed a standardized five-step procedure

- **Conditioning phase**
  - 20min @ 750mV and 2 nl/min H_2
  - Continuous HFR (4kHz), monitoring membrane hydration
- **Load disconnection** (OCV for 30s)
- **Anode purge** with N_2
  - 2min duration with specified humidification
- **Anode purge** with air
  - 10s (or variable) of dry air to create air/air configuration
  - Adjust H_2 flow via bypass system
- **Start-up** initiation by H_2 purge
  - Introduce dry H_2 → generating H_2/air front

Table I. Flow parameters for the investigated SU test points (TP): flow rate and RH during conditioning (step 1) and air purge duration (step 4).

Test point (TP)	H_2 Flow (nl min^{-1})	RH_{An} (%)	RH_{Ca}(%)	Air purge time (s)
1	4.000	100	100	10
2	2.000	100	100	10
3	1.000	100	100	10
4	0.500	100	100	10
5	0.250	100	100	10
6	0.125	100	100	10
7	4.000	100	100	10
8	4.000	80	100	10
9	4.000	60	100	10
10	4.000	40	100	10
11	4.000	20	100	10
12	4.000	0	100	10
13	4.000	100	100	10
14	4.000	100	80	10
15	4.000	100	60	10
16	4.000	100	40	10
17	4.000	100	20	10
18	4.000	100	0	10
19	4.000	100	100	10
20	4.000	80	80	10
21	4.000	60	60	10
22	4.000	40	40	10
23	4.000	20	20	10
24	4.000	0	0	10
25	4.000	100	100	10
26	4.000	100	100	30
27	4.000	100	100	60
28	4.000	100	100	90
29	4.000	100	100	120
30	4.000	100	100	240

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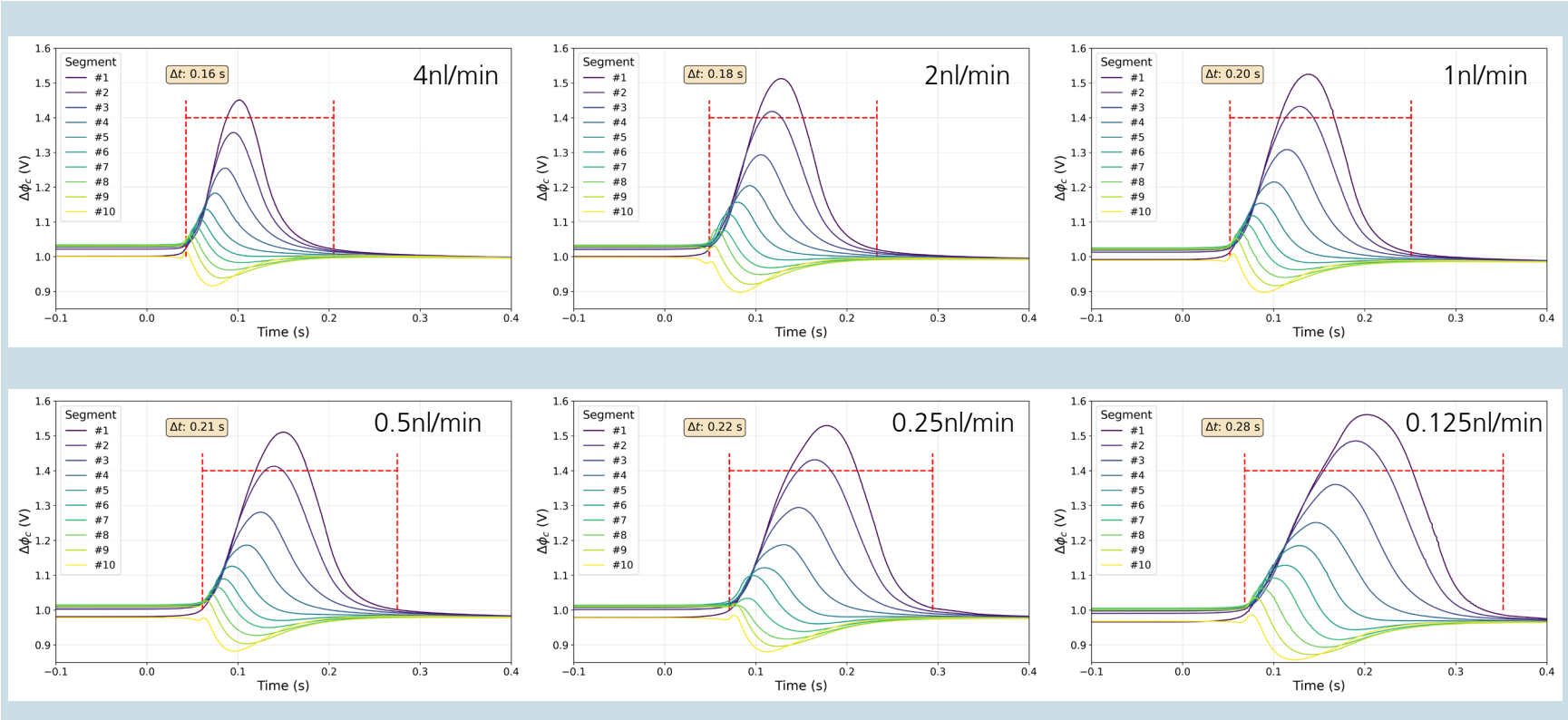
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Impact of anodic gas flow rates

Rate of oxygen displacement

- Investigated flow rates
  - 4, 2, 1, 0.5, 0.25, 0.125 nl/min
  - Ratio of highest to lowest flow rate is 32
- Duration changes from 0.16s to 0.28s
  - ratio ~1.7
  - Scales not linearly with residence time
- Overshoot voltage (#1) changes from ~1.45V to ~1.57V



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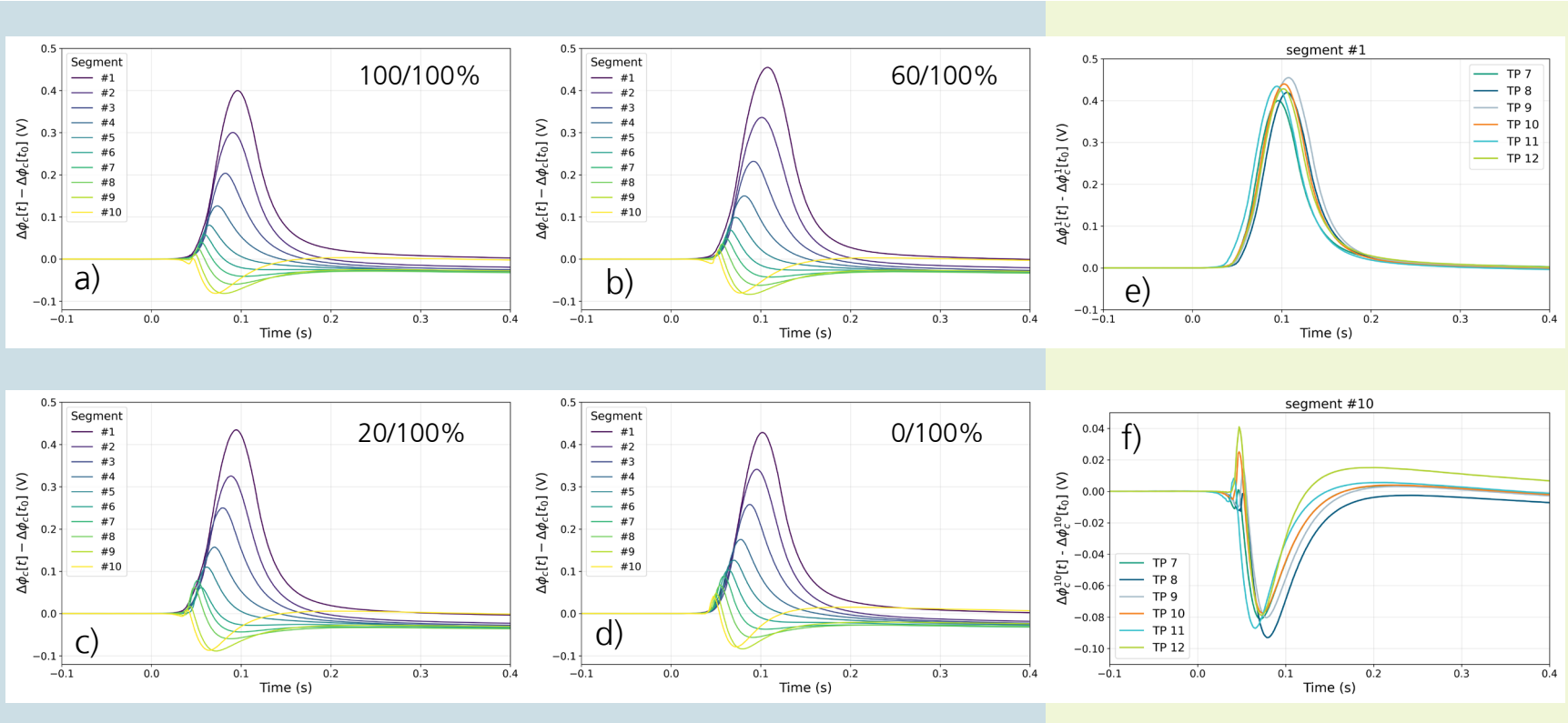
Impact of Anode humidity conditioning

with fully humidified cathode (RH_c=100%)

- Investigated humidity ($RH_{a/c}$)
  - 100/100 %
  - 60/100 %
  - 20/100 %
  - 0/100 %

- Nearly same overshoot behavior at segment #1
- Tiny differences at segment #10

- Note: conditioning phase @ 750mV → water production by ORR



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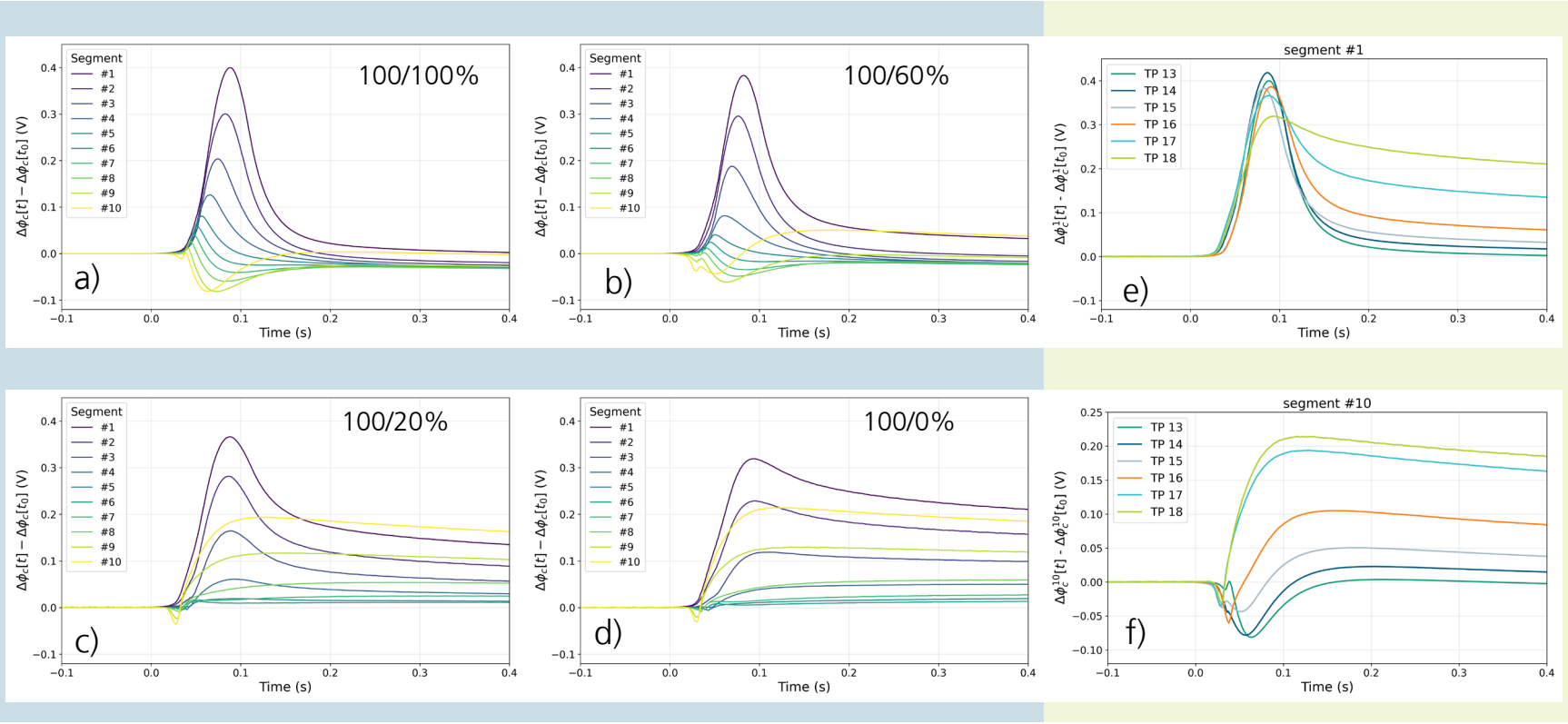
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Impact of cathode humidity conditioning

with fully humidified anode (Rh_a=100%)

- Investigated humidity ($RH_{a/c}$)
  - 100/100 %
  - 100/60 %
  - 100/20 %
  - 100/0 %
- High impact
  - Pattern changes
- Cathode inlet region (#1) reduces overshoot height but with slower relaxation (several seconds)
- Anode inlet region (#10) shows long-lasting lift in potential



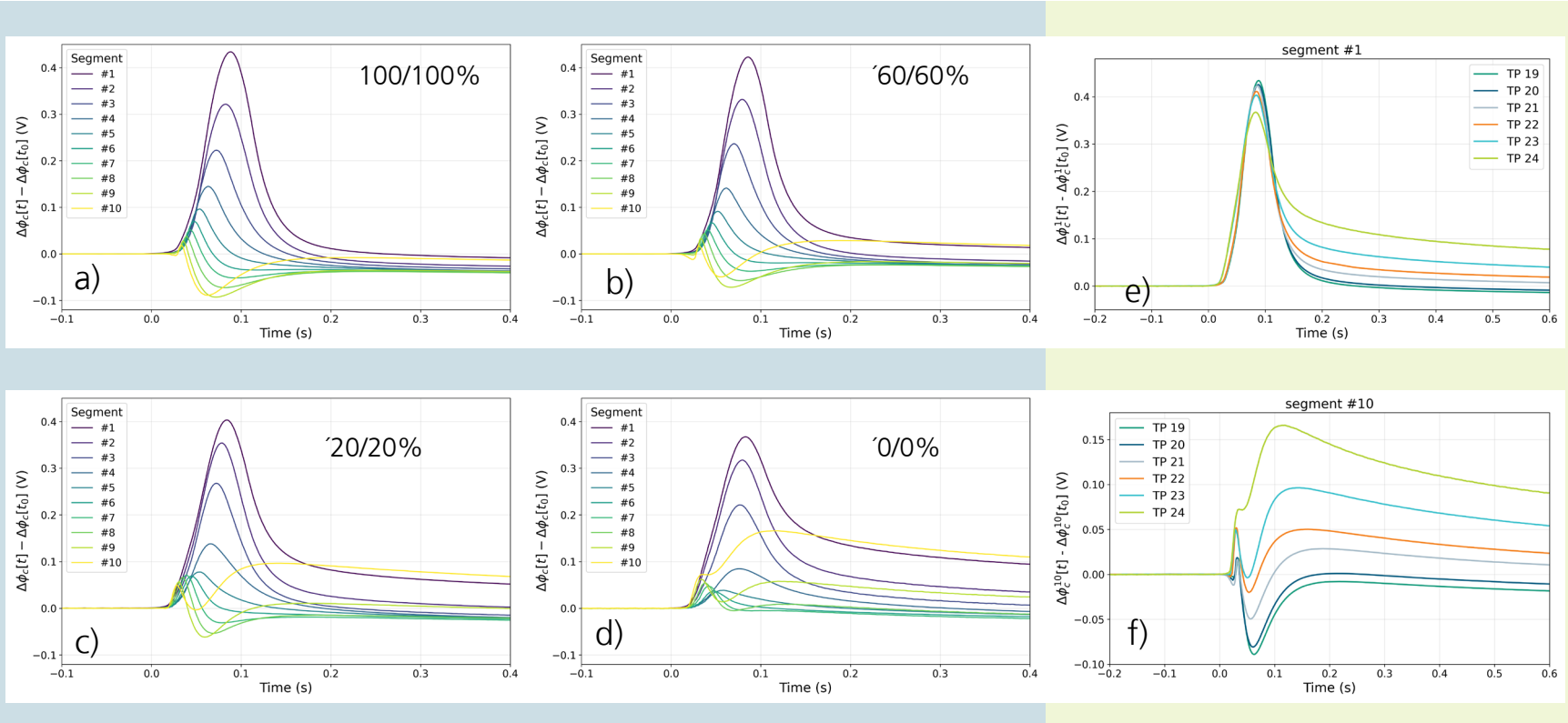
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Impact of symmetric RH conditioning at anode and cathode

- Investigated humidity ($RH_{a/c}$)
  - 100/100 %
  - 60/60 %
  - 20/20 %
  - 0/0 %
- High impact
  - Pattern changes
- Cathode inlet region (#1) reduces overshoot height but with slower relaxation (several seconds)
- Anode inlet region (#10) shows long-lasting lift in potential



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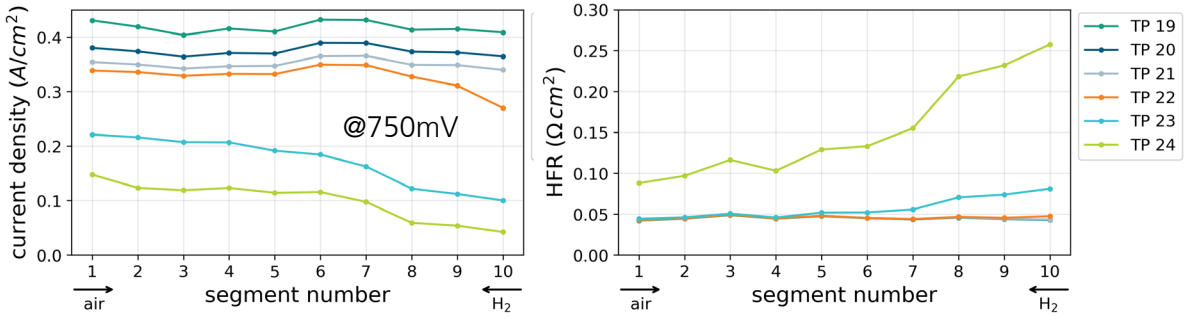
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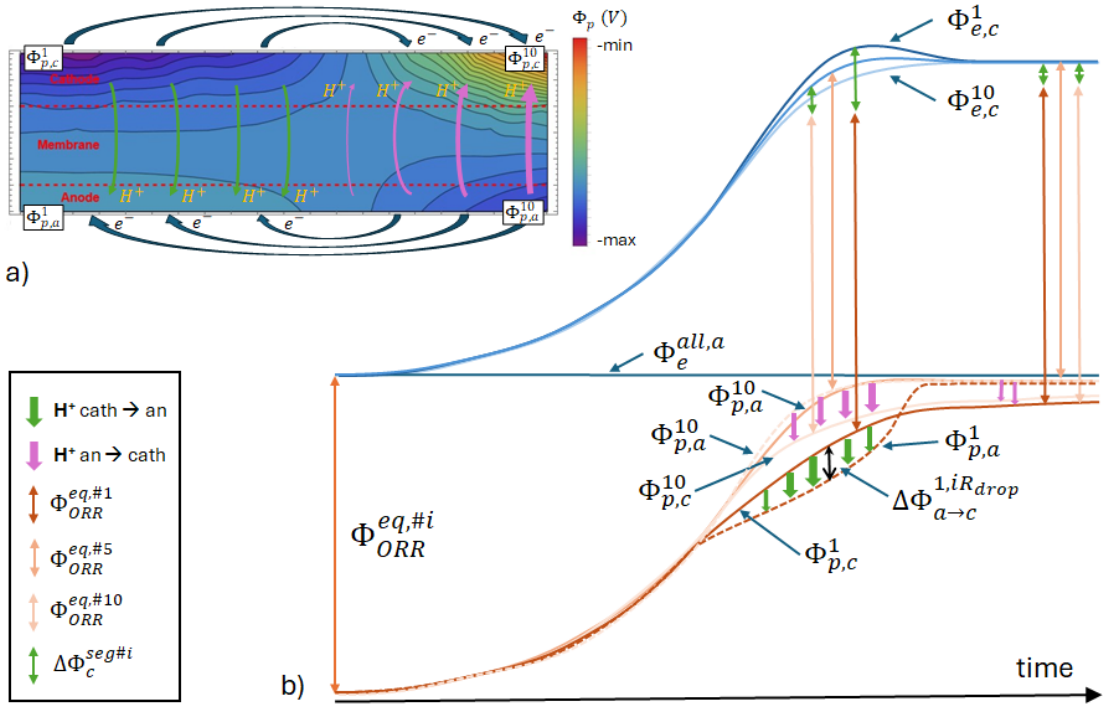
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Mechanistic explanation for the overshoot behavior at low humidity levels

Our hypothesis based on experimental observations

- Dehydrated cathode catalyst layer leads to high potential gradients at high current densities
  - Highest at H_2 inlet and outlet
- Continuous increase of common $\Phi_{e,c}$ charges cathode double-layer capacity above Φ_{ORR}^{eq}
- Reduced ionomer conductivity at dry conditions and the absence of proton sinks at high cathode potentials leads to slow discharge



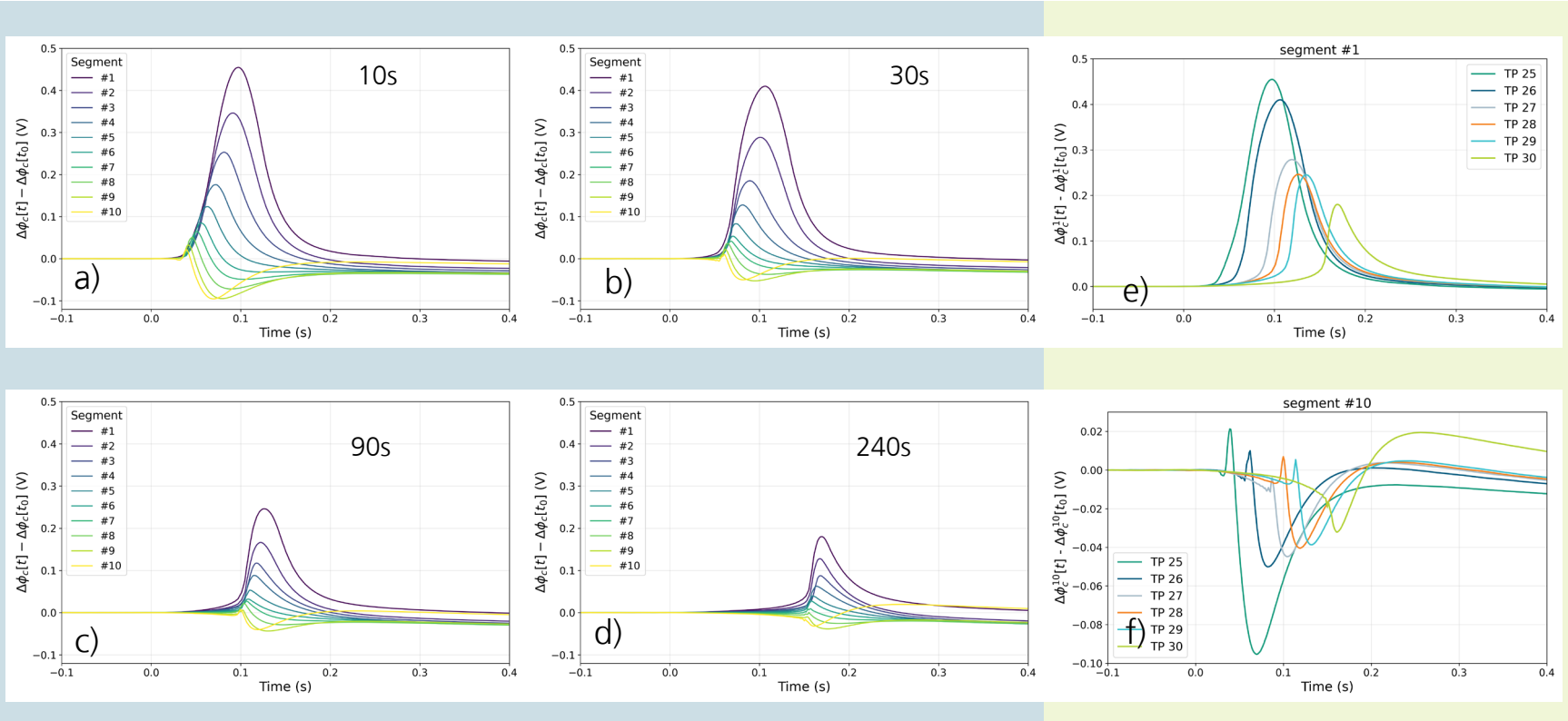


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Impact of anode purge duration with dry air (RH_a=0%)

After fully humidified conditioning ($RH_{c/a}$=100%)

- Purge duration with dry air
  - 10s
  - 30s
  - 90s
  - 240s
- High impact
  - Without pattern change
- Cathode overshoot markedly reduced
  - Delayed potential peak due to reduced dynamic of anode processes



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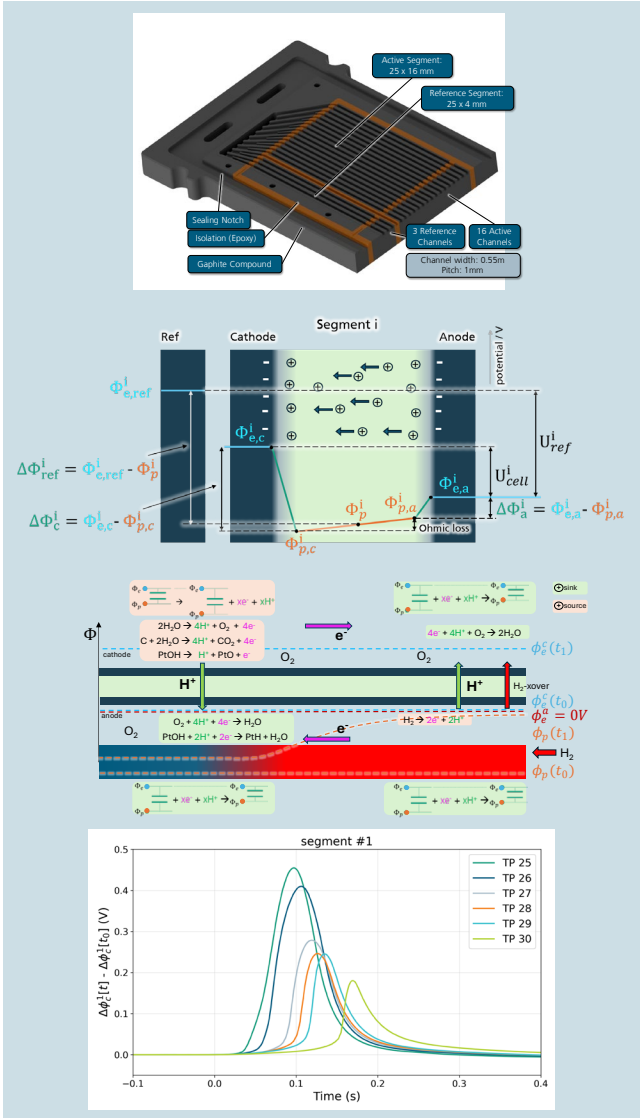
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Summary

Of start-up investigations

- Segmented ATC cell with embedded reference electrodes discussed
- Theory of
  - reference electrodes
  - SU phenomena
- Experimental SU results discussed
  - Strategies to reduce length and height of cathode overshoot
    - Fast H_2 purge
    - Pre-conditioning of cell at dry conditions (without current)
    - Loading the cell immediately after SU



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Investigation of the Local Cathode Potential Evolution during Start-Up by Means of Embedded Reference Electrodes in a PEM Fuel Cell

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[1]*Fraunhofer Institute for Solar Energy Systems ISE, 79110 Freiburg, Germany*
[2]*EKPO Fuel Cell Technologies GmbH, 72581 Dettingen/Erms, Germany*

Air-air start-up (SU) events in proton exchange membrane fuel cells generate cathode potential overshoots exceeding 1.4 V, driving degradation through carbon corrosion and platinum dissolution. While the reverse-current mechanism is established, the influence of system-level pre-conditioning parameters on spatially resolved cathode potential transients remains insufficiently understood. This study employs a segmented along-the-channel cell with ten air-flushed reference electrodes to measure local cathode potentials during air-air SU events. Hydrogen flow rate and pre-conditioning parameters such as anode/cathode humidity and purge duration are investigated. Increasing hydrogen flow from 0.125 to 4 nl min^{-1} reduces SU duration (276–163 ms) and peak overshoot (1.56–1.45 V), though the effect does not scale linearly with residence time, indicating electrochemical process dominance. Anode humidity exerts minimal influence when the cathode remains fully humidified. In contrast, cathode dehydration fundamentally alters transient behavior: peak overshoots at the anode outlet decrease, while inlet segments develop pronounced overshoots with markedly slower decay rates. This is attributed to increased ohmic resistance and reduced double-layer capacitance under dehydrated conditions. The findings reveal that cathode hydration critically governs SU-induced degradation and that dehydration strategies may prolong exposure to corrosive potentials, providing guidance for optimizing shutdown protocols in automotive applications.

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Proton exchange membrane fuel cells (PEMFCs) are considered a key technology for sustainable energy conversion due to their high efficiency and zero local emissions. Despite these advantages, their commercialization success is lagging behind, primarily because the total cost of ownership is still too high. Reducing capital costs through manufacturing scale-up and lower platinum loading is one pathway toward improved competitiveness. Equally important is mitigating performance degradation for a lower fuel consumption due to higher efficiency and extend system lifetime. One key degradation effect is the start-up (SU) and shut-down (SD) event. Within the SU it needs to be distinguished between a start up from a H_2 environment (H_2 on anode and H_2 or air on the cathode) and the air-air SU in which both the anode and cathode compartments are initially filled with air. In an air-air SU, the cathode is exposed to extremely high potentials,[1–5] which can trigger carbon corrosion and platinum dissolution, leading to irreversible catalyst layer damage. This harmful type of SU is addressed in the following. Higher electrode potentials impose harsher conditions for Pt dissolution and carbon corrosion. The accelerated stress test (AST) protocols of the US Department of Energy (DOE)[6] propose a triangular potential sweep between 0.6–1.0 V to trigger catalyst degradation, and a triangular sweep between 1.0–1.5 V to trigger carbon support corrosion. Under adverse conditions, such high potentials of up to 1.5 V are known to occur during a SU event within a short time window.[2,4,7,8] Investigating this dynamic and local phenomenon under realistic conditions requires a cell with realistic channel length, since the simultaneous presence of air and hydrogen in the anode compartment is key to the overshoot behavior. As the resulting potential transients are highly inhomogeneous, spatially resolved characterization using segmented cells is equally essential, since single-cell measurements fail to capture this phenomenon.

Several mitigation strategies for SU/SD-induced degradation have been reported in the literature and are summarized by Zhang et al.[9] These range from catalyst-layer material selection, where highly graphitized carbon,[10] carbon nanotubes,[11,12] or alternative supports such as titanium carbide[13,14] or tungsten carbide[15,16] have shown promising results, to system-level control strategies that mitigate degradation during start-stop events through targeted gas management during operation, shutdown, or prior to start-up.[17] However, the effectiveness of such mitigation strategies inherently depends on a detailed understanding of the local cathode-potential evolution during air–air SU, which remains insufficiently resolved.

A deeper understanding of the operation parameters that influence the cathode potential during air–air SU is therefore essential.

Reiser et al.[18] proposed 2005 a mechanism during start up and shutdown event, called reverse-current mechanism, that cause accelerated performance decay. By means of a one-dimensional model they demonstrated that partial anode exposure to both hydrogen and oxygen during transient conditions causes electrolyte potential to drop from 0 to −0.59 V versus reversible hydrogen electrode, creating reverse current flow that raises cathode potential to 1.44 V and triggers severe carbon corrosion. Since the model does not account for transients, the reverse current is generated solely by oxygen reduction reaction (ORR), hydrogen oxidation reaction (HOR) and carbon corrosion. By connecting electrically two single cells in parallel, where one cell is operated with hydrogen at the anode and the other cell's anode with air, they confirmed significant electrochemically active surface area (ECSA) losses and cathode electrode thinning, establishing this mechanism as fundamental for SU and SD events or if hydrogen is starved. Gu et al.[19] advanced the modeling capabilities by incorporating electrode pseudo-capacitance effects, such as the reduction of oxidized Pt surface at the anode ($PtOH + 2H^+ + 2e^- \rightarrow PtH + H_2O$) or via further oxide formation at the cathode ($PtOH \rightarrow PtO + H^+ + e^-$) occurring during SU. Their model, validated through current density distribution maps of a single cell with serpentine flow field, revealed critical time-scale dependencies where capacitive effects reduce carbon corrosion by approximately 30% for application-relevant short residence times (1.3 s) compared to longer accelerated testing conditions, demonstrating excellent agreement with controlled start-stop experiments and spatially resolved degradation patterns. Chen et al.[20] developed a transient 1 + 1 D kinetic model that accounts for both pseudo-capacitance and double-layer capacitance, highlighting their

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Thank You for Your Attention!

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