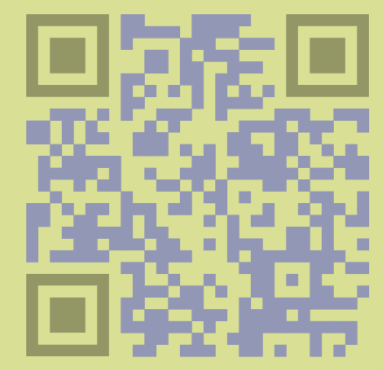




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HI ERN

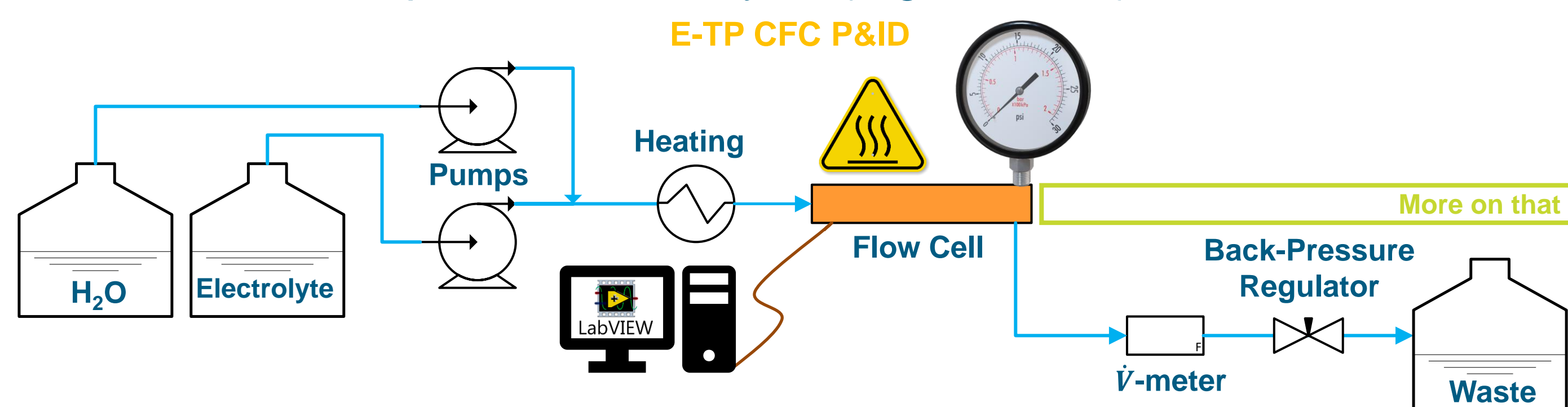
Helmholtz Institute
Erlangen-Nürnberg

Towards an Elevated Temperature and Pressure 3-Electrode Hydrodynamic Channel Flow Cell

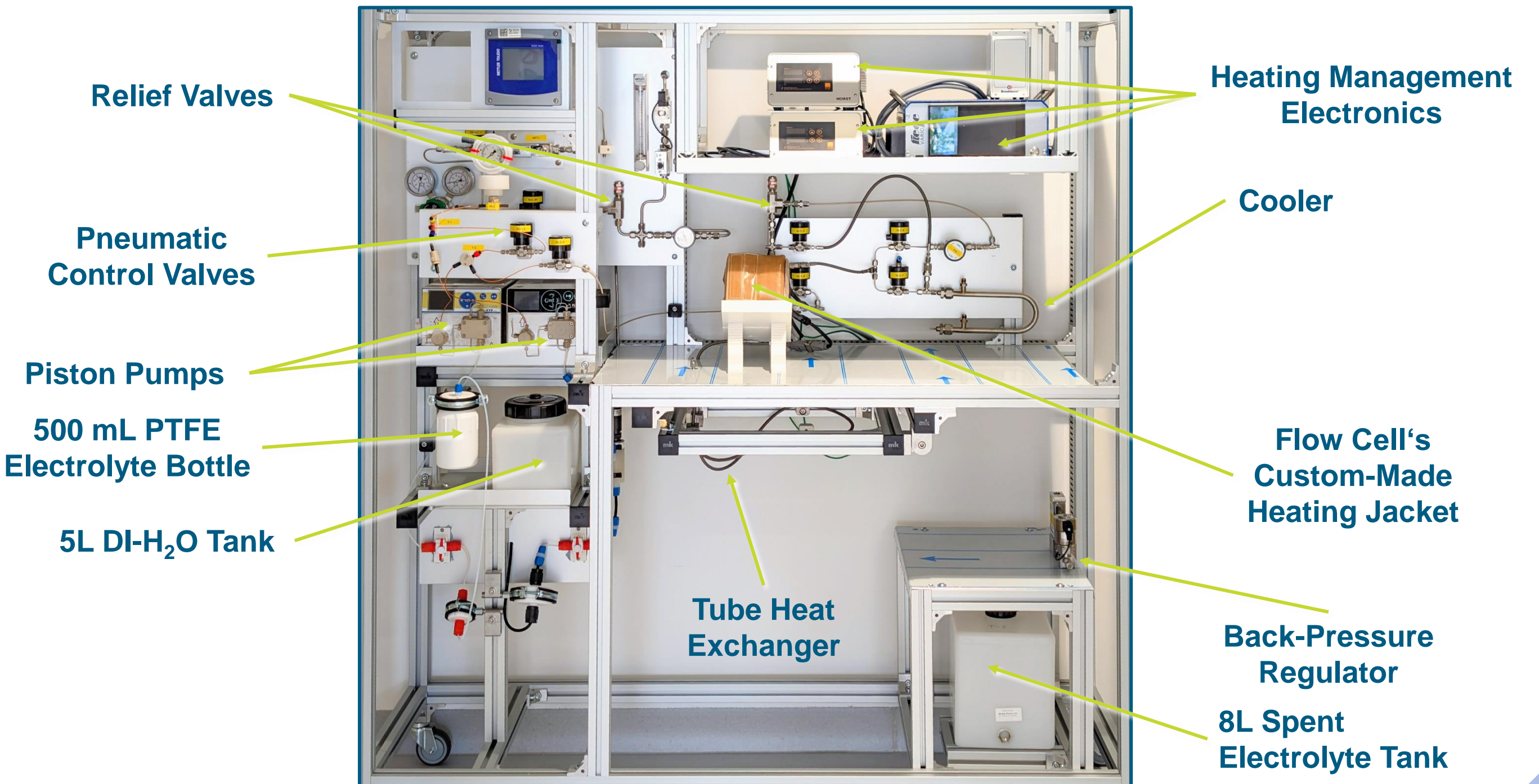
M. Martini, M. Bonanno, K.J.J. Mayrhofer. Forschungszentrum Jülich GmbH, Helmholtz Institute Erlangen-Nürnberg for Renewable Energy (IET-2), Germany

Motivation & Overall Goal

- Fundamental electrocatalyst characterization at **Elevated T&P**
- Desired conditions: $P \geq 10 \text{ bar}$ → increased gas solubility (reactant or product); $T = 150 \text{ °C}$ → kinetic & selectivity effects
- Flexible electrolyte composition and real-time pH tuning
- Possibility of future T -dependent catalyst dissolution & stability studies with coupled online analysis (e.g. ICP-MS)



E-TP CFC Plant: **Work in Progress!!!**



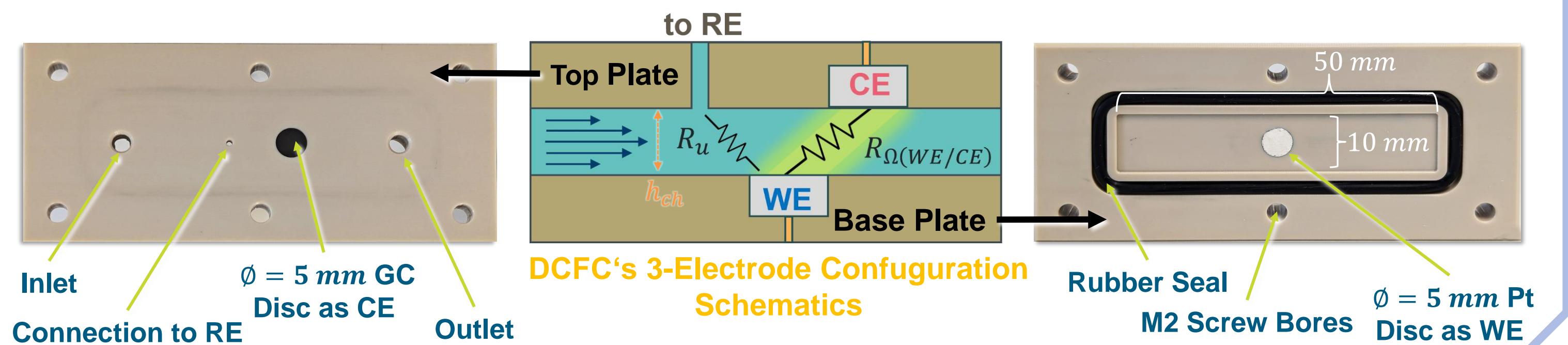
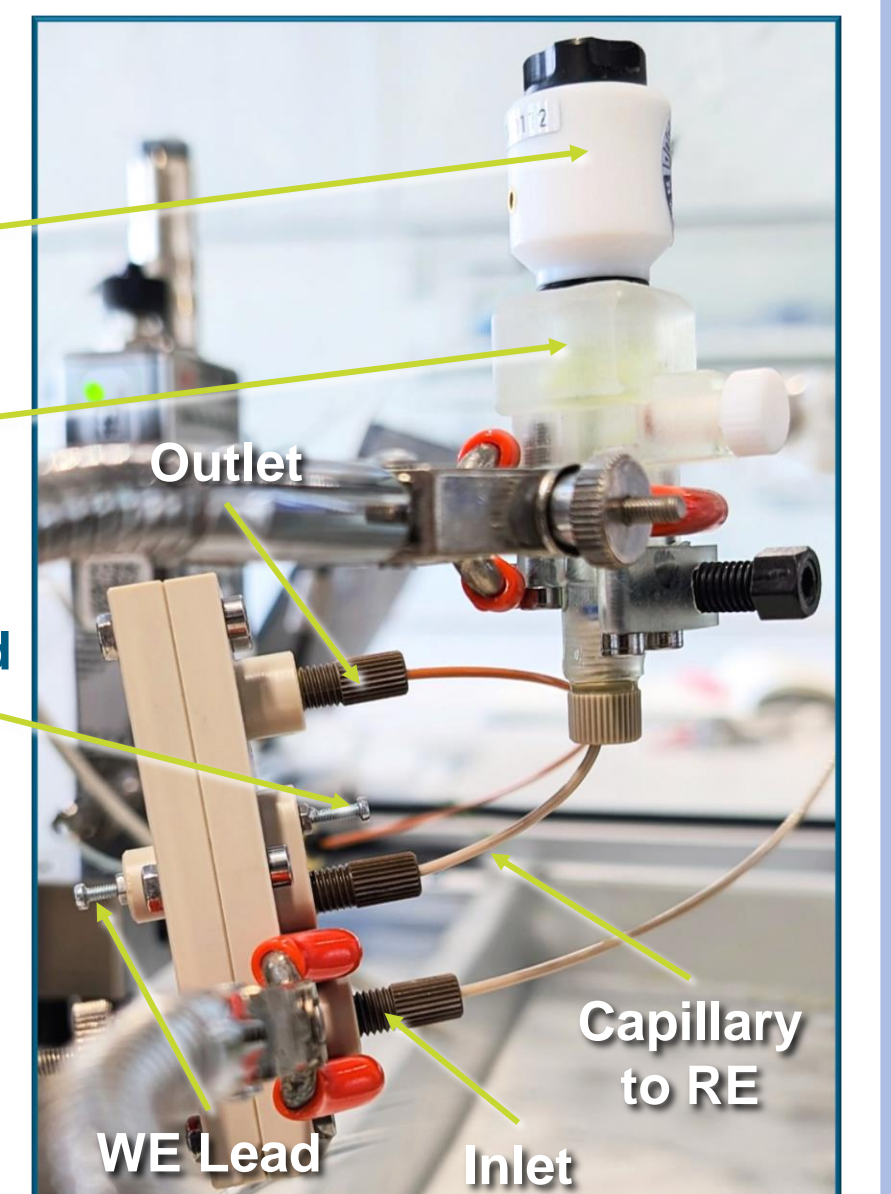
The Elevated T&P Channel Flow Cell (E-TP CFC)

- CNC-machined polyether-ether ketone (PEEK)
- Chemically & mechanically stable
- Internal (pseudo)reference electrode
- Interchangeable electrode discs
- Glue & sealant free



The „Dummy“ Channel Flow Cell

- Room temperature; $P \propto \dot{V}$
- Completely metal-free structure
- Same internal geometry as the E-TP CFC
- Uses a commercial reference electrode (RHE)
- Validation of the fluid-dynamics assumptions
- Probing of the electrodes configuration' electrochemical features (distance, position, etc)
- Simpler troubleshooting & system development (bubbles management, electrical contact, leak-tightness, etc)



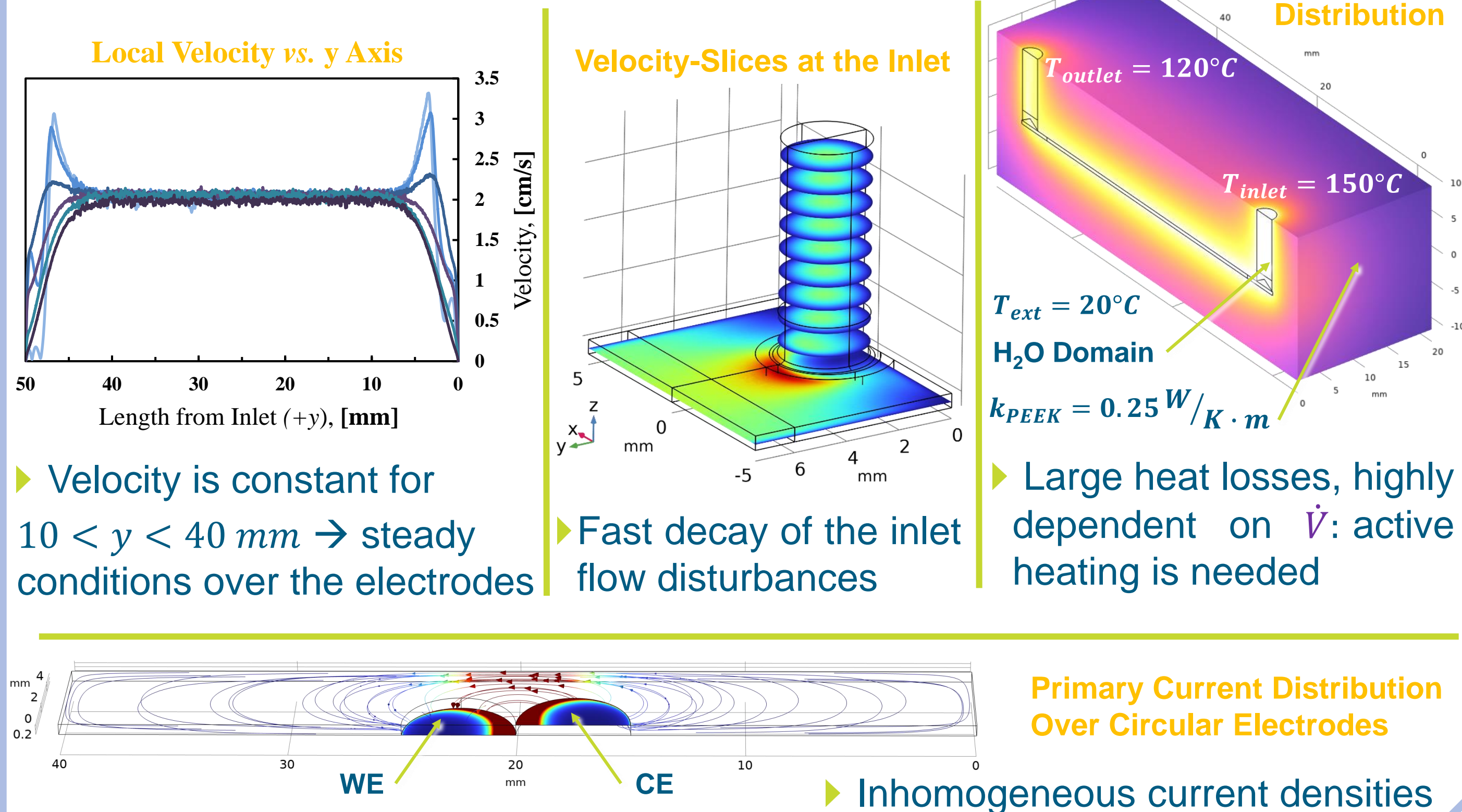
The Physical Electrochemistry of Channel Flow Cells

- Hydrodynamic systems (alternative to rotating disc electrodes)^[1]
- The flowrate \dot{V} directly controls the mass transport and current I_{LIM}
- Submillimetric channel height h_{ch} → possible ohmic effects^[4]
- In laminar regimes:

$$|I_{LIM}|^{[2]} = n_e \cdot F \cdot k_{cell} \cdot C_{bulk} \left(\frac{A_{WE}^{geo} \cdot D}{h_{ch}} \right)^{2/3} \cdot \sqrt[3]{\dot{V}}$$

$$\begin{cases} k_{cell} = 1.467 \\ D^{[3]} = 3.47 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1} \\ h_{ch} = 0.055 \text{ cm} \\ A_{WE}^{geo} = 0.196 \text{ cm}^2 \\ C_{bulk} = 10^{-5} \text{ mol cm}^{-3} \end{cases}$$

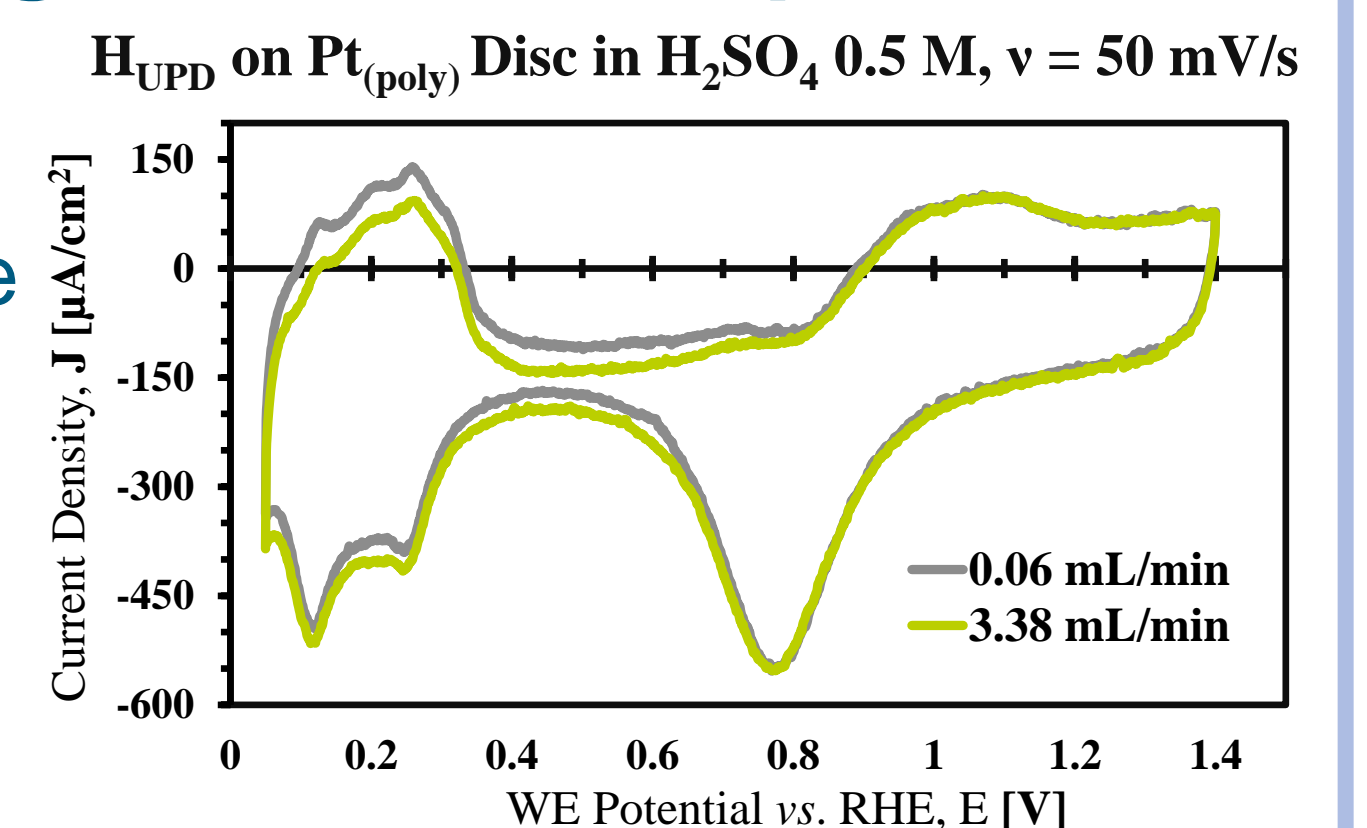
Finite-Element Simulations



Dummy Flow Cell Benchmarking at Room Temperature

Hydrogen Underpotential Deposition

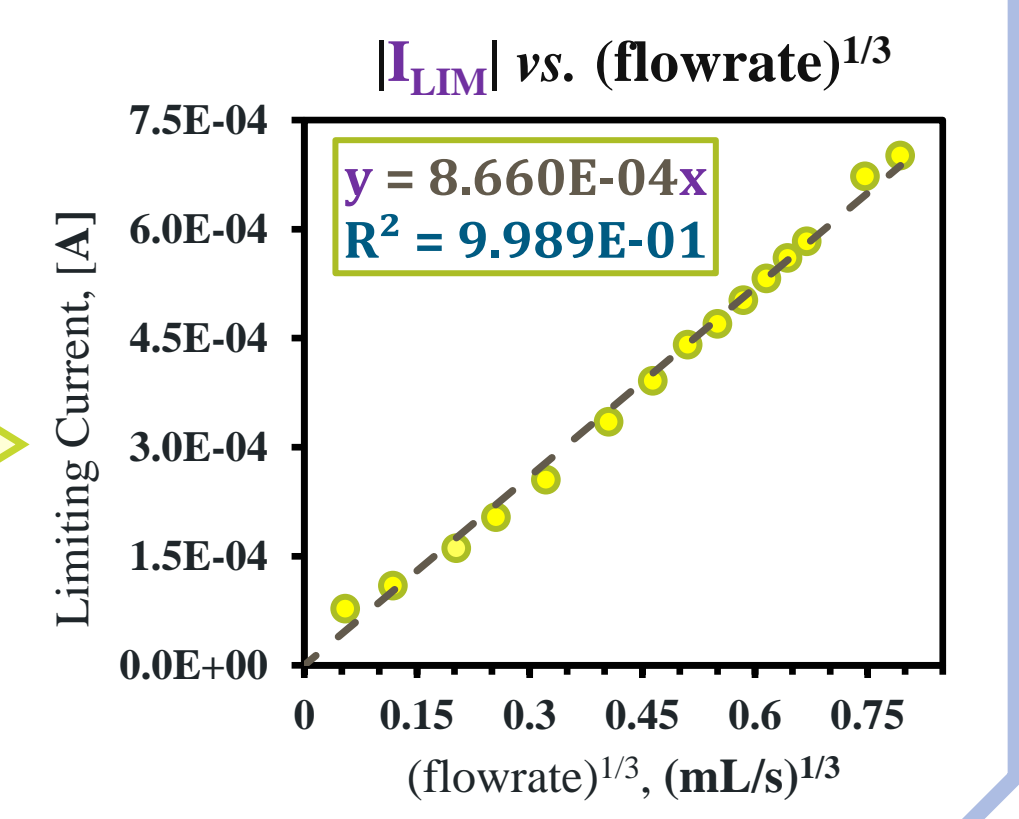
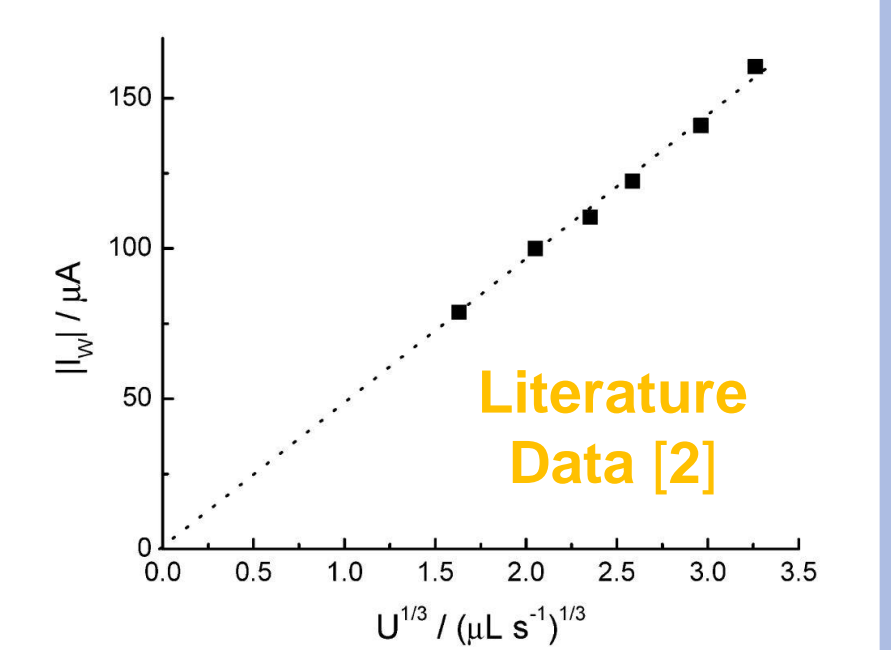
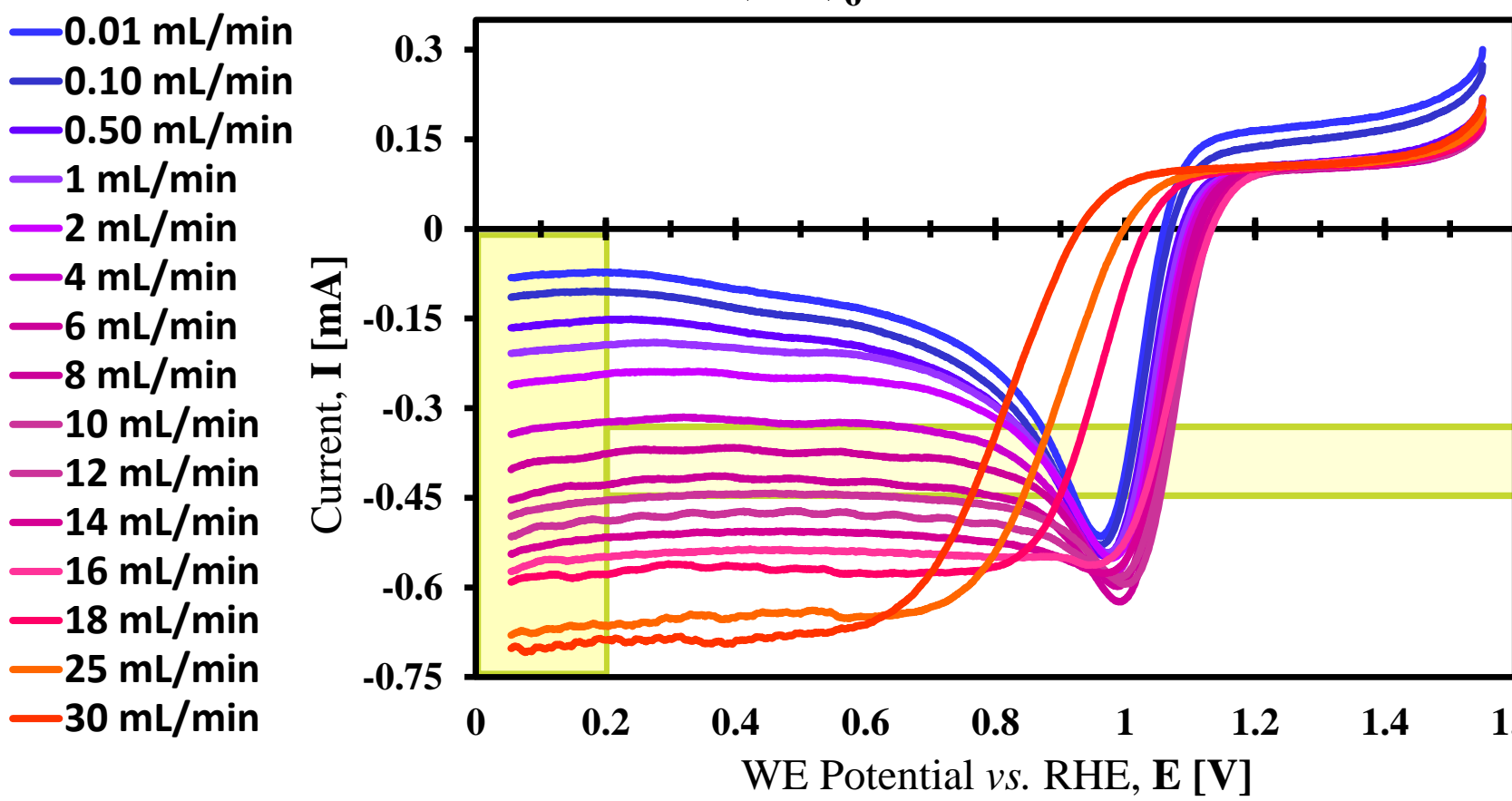
- Correct potential sensing, little resistance
- Potential values are independent on \dot{V}
- Traces of $O_2(liq)$ → negative current shift



Limiting Current Analysis

- $[Fe^{III}(CN)_6]^{3-} + 1e^- \rightarrow [Fe^{II}(CN)_6]^{4-}$; $K_3Fe(CN)_6$ 10 mM + KNO_3 0.2 M
- 0.05 → 1.6 V, $v = 250 \text{ mV/s}$ CVs
- Pt & GC discs both work as WE (CE = GC)
- $|I_{LIM}|_{calc} = 7.54 \cdot 10^{-4} \cdot \sqrt[3]{\dot{V}} \rightarrow \Delta_{Exp/Calc} = +12.9 \%$
- No disturbances, laminar flow ($0.04 < Re < 114$)

10 mM $[Fe^{III}(CN)_6]^{3-}$ Cathodic Scans vs. Flowrate



References

- Fuhrmann, J., Zhao, H., Holzbecher, E., Langmach, H., Chojak, M., Halseid, R., Jusys, Z., Behm, J. *Phys. Chem. Chem. Phys.* (2008), 10, 3784-3795
- Jusys, Z., Kaiser, J., Behm, R.J. *Electrochimica Acta* 49 (2004) 1297-1305
- $D_{[Fe(CN)_6]^{3-/4-}}$ from Diakowski, P.M., Kraatz, H-B. *Chem. Commun.*, (2011), 47, 1431-1433, SI.
- Coles, B.A., Compton, R.G., Larsen, J.P., Spackman, R.A. *Electroanalysis* (1996), 8, No. 10

Conclusions & Future Perspectives

- The DCFC demonstrated the effectiveness of the geometry and design
- Completing the commissioning and optimization of the E-TP CFC plant
- Multiphysics modelling of P , T & \dot{V} effects and comparison with experiments
- Benchmark tests at the E-TP conditions, then "real" catalyst studies