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Simon Tschupp, S.E. Temmel, N. Poyatos Salguero, J. Herranz, T.J. Schmidt

Electrode Partitioning Model for the Koutecký-Levich Analysis of Electrochemical Flow Cells

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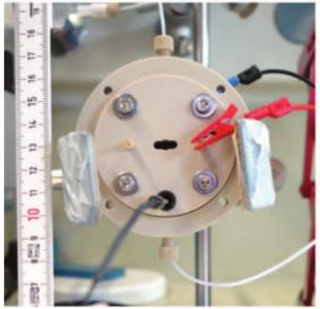
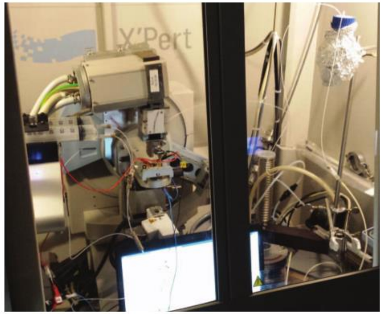
Fuel vs. Flow Cells

- Fuel Cells:
  - Energy conversion device
  - 2-electrode systems (bipolar setup)
  - Mass transport: gas diffusion
  - Complex system to study and model

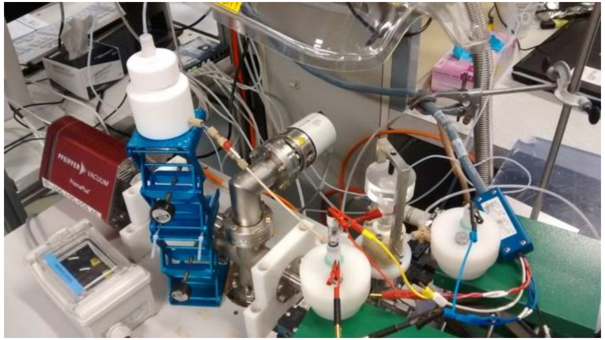
- Flow Cells:
  - 3-electrode setup (assess half-cell reactions)
  - Mass transport: gas dissolved in aqueous electrolyte, convection source
  - Combination with other experimental techniques:
    - X-ray techniques (XAS, SAXS, WAXS)
    - Mass spectrometry (OLEMS)
    - Optical (FT-IR, UV-Vis)
  - Unconventional sample properties



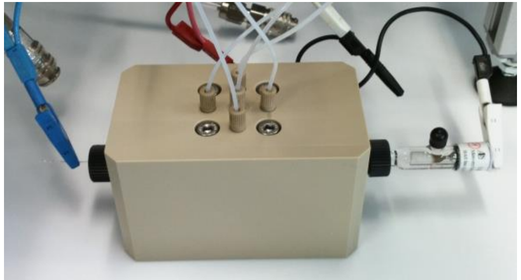
T. Binninger et al. *J. Electrochem. Soc.* **163** (2016) H906



J. Tillier et al., *J. Electrochem. Soc.* **163** (2016) H913

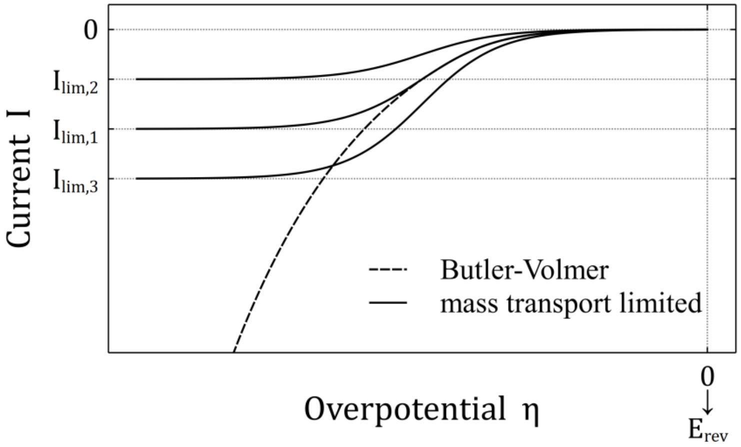


Y. Paratcha et al., *PSI Electrochemistry Laboratory - Annual Report* 2014 84

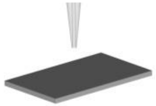


S.E. Temmel et al., *Rev. Sci. Instrum.* **87** (2016) 045115

Electrode Kinetics



Wall-jet electrodes: $\frac{1}{I_{tot}} = \frac{1.06}{I_{kin}} + \frac{1}{I_{lim}}$



Channel electrodes: $\frac{1}{I_{tot}} = \frac{1}{I_{kin}} + \frac{0.93}{I_{lim}}$

W.J. Albery, *J. Electroanal. Chem. Interfacial Electrochem.* **191** (1985) 1

- Polarization Experiments:
  - Irreversible reduction: $A + e^- \rightarrow A^-$
  - Cathodic current is described by Butler-Volmer equation:

$$I = I_0 \exp\left(\frac{-\alpha \cdot F}{R \cdot T}\eta\right)$$

  - Concentration of A at the electrode limited by mass transport
  - Steady-state obtained by application of controlled convection source

  - Separation of mass transport and electrode kinetics needed:
    - Koutecký-Levich equation for the rotating disk electrode (RDE)
    - Approximations for wall-jet and channel electrodes

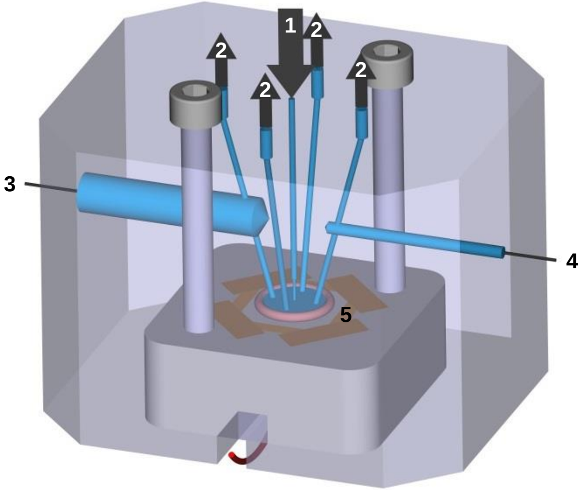
D.A. Scherson et al. *Electrochem. Solid-State Lett.* **11** (2008) F1

Cell Design, Geometry and Boundary Conditions

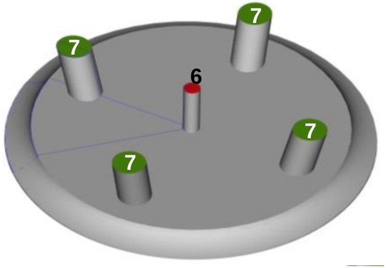
- Cell Design:
  - Designed for thin-film samples deposited on insulating substrates
  - Electrical contact from top of electrode
  - Wetted area defined by O-ring sandwiched between sample and fluidic part
  - Reference- and counter electrode situated downstream of reaction chamber to avoid contamination

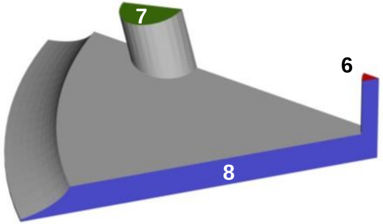
- Physics and Boundary Conditions:
  - Laminar single phase flow (Navier-Stokes)
  - Transport of diluted species (Nernst-Planck)
  - Equation based species flux (Butler-Volmer):

$$N = -\frac{I_0}{n \cdot F} \cdot \frac{c}{c_0} \cdot \exp\left(\frac{\alpha \cdot F}{R \cdot T}\eta\right)$$



(1) inlet
(2) outlets
(3) reference electrode
(4) counter electrode
(5) working electrode
(6) inflow boundary
(7) outflow boundary
(8) symmetry boundary



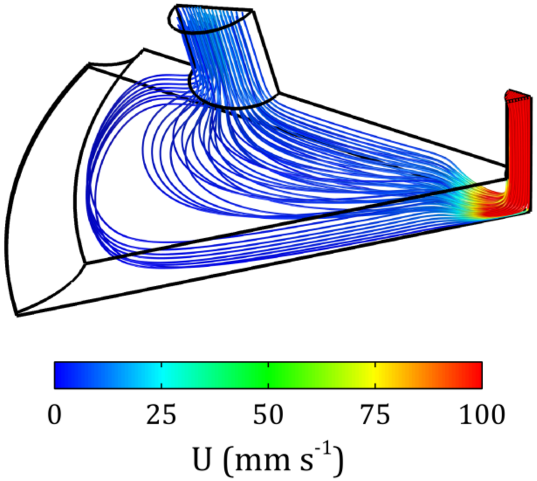


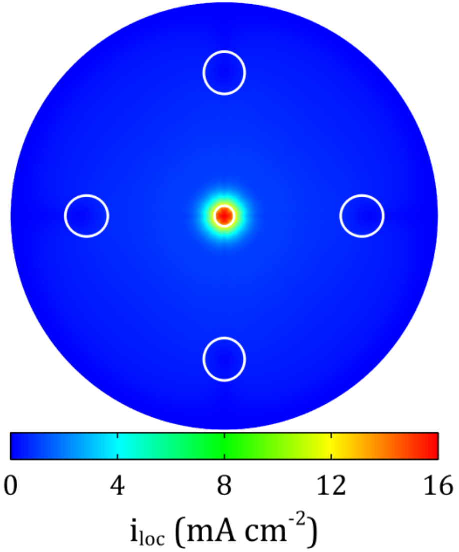
Flow Profile and Mass Transport

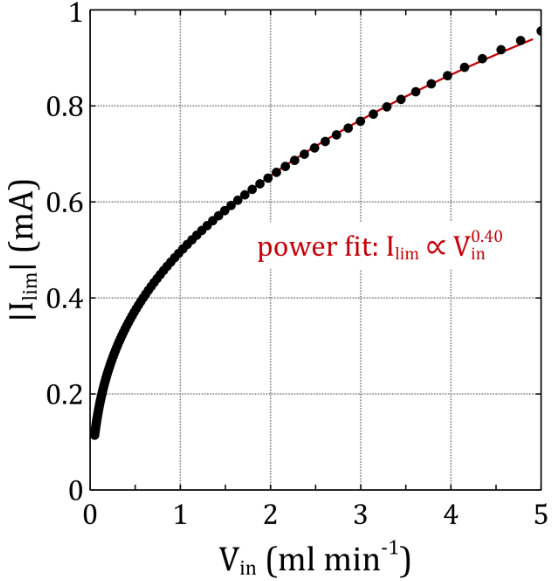
- Velocity Distribution:
  - Inlet flow rate V_{in} = 2 ml min^{-1}

- Local Current Density:
  - V_{in} = 2 ml min^{-1}
  - Overpotential η = 1 V
    (→ mass transport limited)

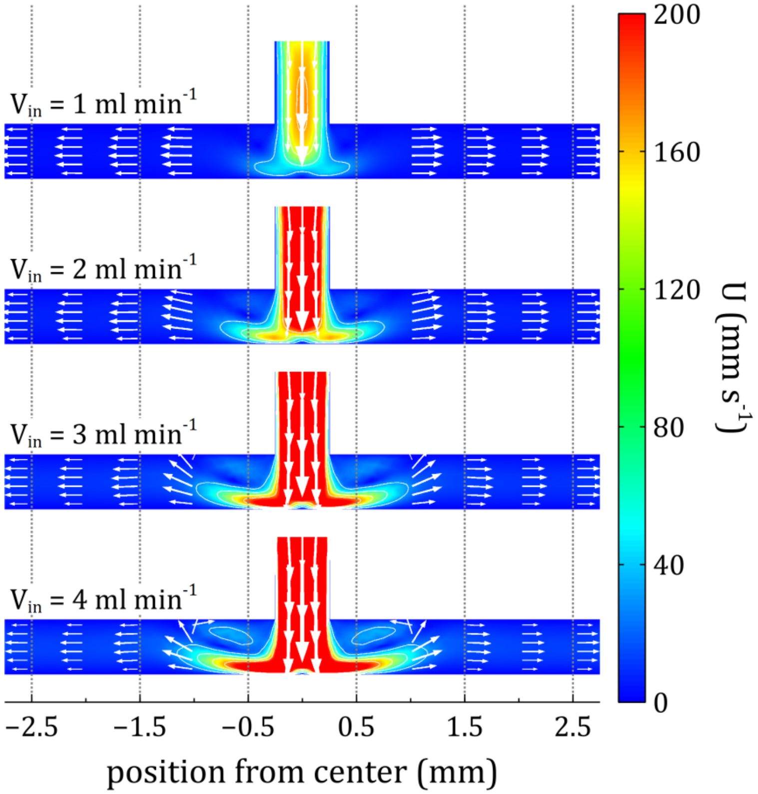
- I_{lim} vs. V_{in} Correlation:
  - Exponent of power fit: 0.40
  - Ideal channel flow: 0.33
  - Ideal wall-jet flow: 0.75



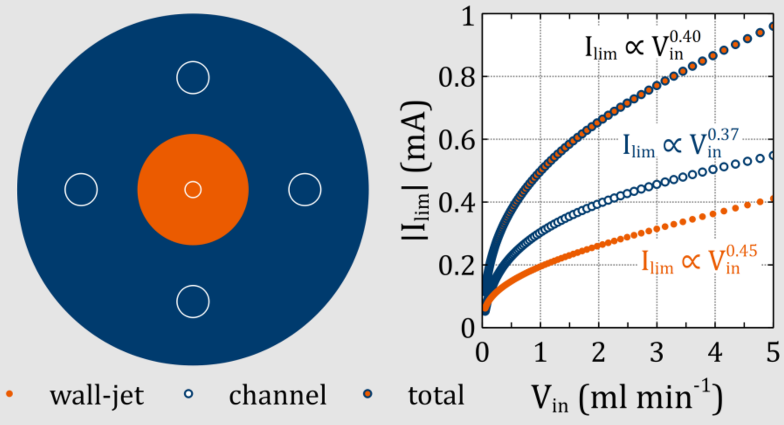




Electrode Partitioning: Motivation and Principle



- Velocity Distribution in Centre Slice:
  - Flow velocity profile composed of elements of wall-jet profile and channel profiles
  - Ratio of wall-jet to channel depends on V_{in}
- Electrode Partitioning:
  - Virtual separation of electrode surface

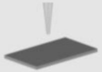


Electrode Partitioning: Results

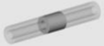
- Electrode Partitioning:
  - Power fit exponent for wall-jet and channel parts plotted as function of ratio
  - Reasonable match between channel and wall-jet parts with their idealized flow profiles
  - Superposition of two ideal flow profiles in first approximation

- Corresponding Koutecký-Levich eq.:

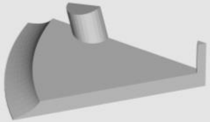
$$\frac{1}{I_{tot}} = \frac{1.06}{I_{kin}} + \frac{1}{I_{lim}}$$

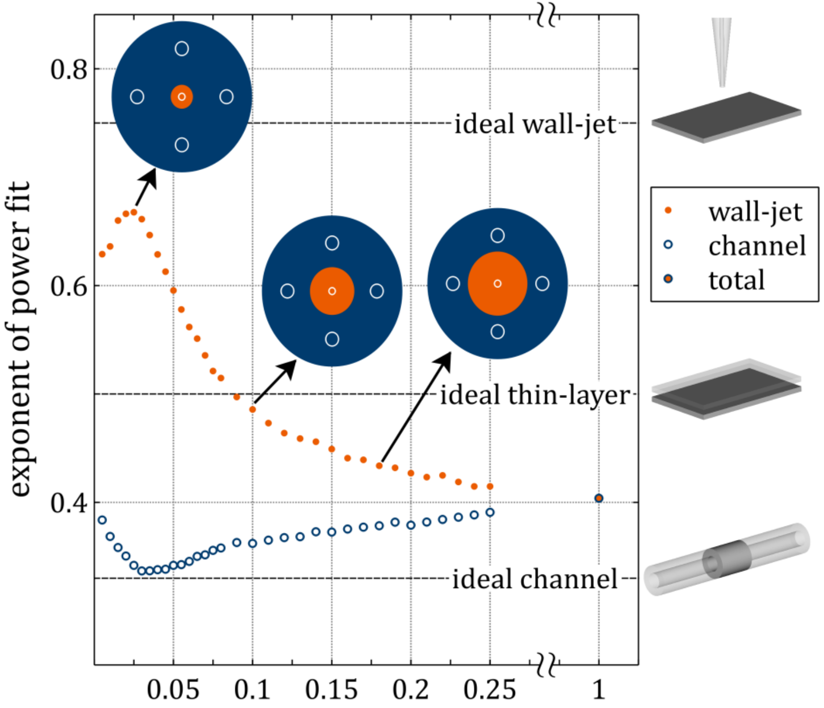


$$\frac{1}{I_{tot}} = \frac{1}{I_{kin}} + \frac{0.93}{I_{lim}}$$



$$\frac{1}{I_{tot}} = \frac{1 + 0.06 \cdot R}{I_{kin}} + \frac{0.93 + 0.07 \cdot R}{I_{lim}}$$





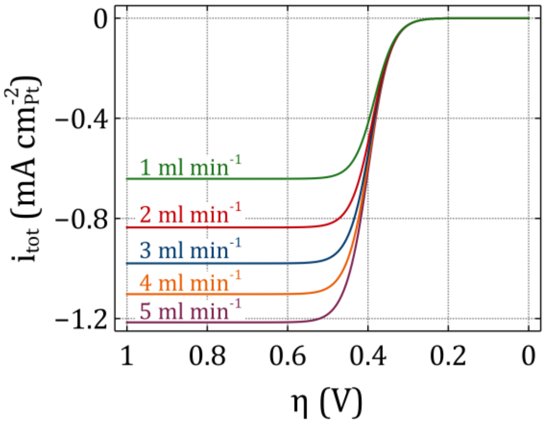
$$R = \frac{A_{\text{wall-jet}}}{A_{\text{wall-jet}} + A_{\text{channel}}}$$

Verification: Polarization Curves and Tafel plots

- Polarization Curves:
  - Oxygen reduction reaction on polycrystalline Platinum
  - Electrode kinetics:

$$i = i_0 \cdot \exp\left(\frac{-\alpha \cdot F}{R \cdot T}\eta\right)$$

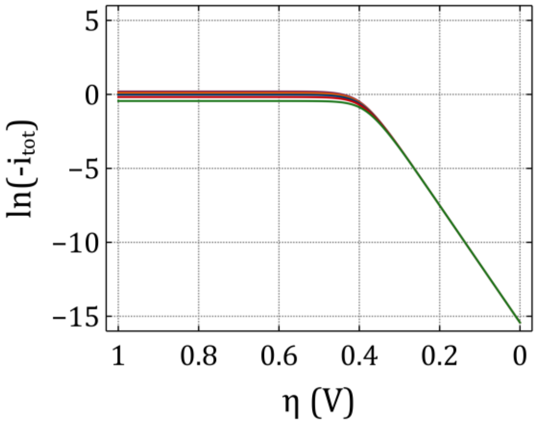
$i_0 = 2 \cdot 10^{-6}$ A m_{Pt}^{2} $b_{Tafel} = 39.6$ V^{-1}



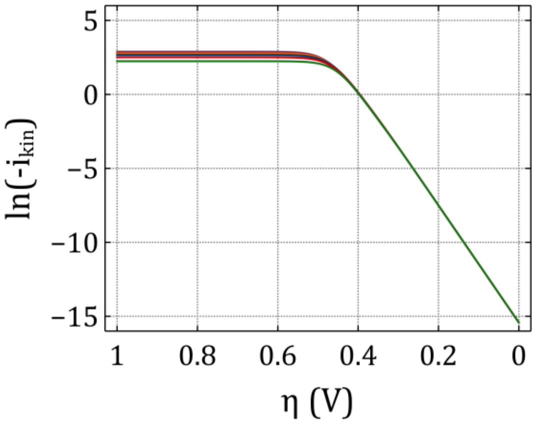
- Tafel Plot for i_{tot}:
  - Linearized Butler-Volmer eq.

$$\ln(i_x) = \frac{-\alpha \cdot F}{R \cdot T}\eta + \ln(i_0)$$

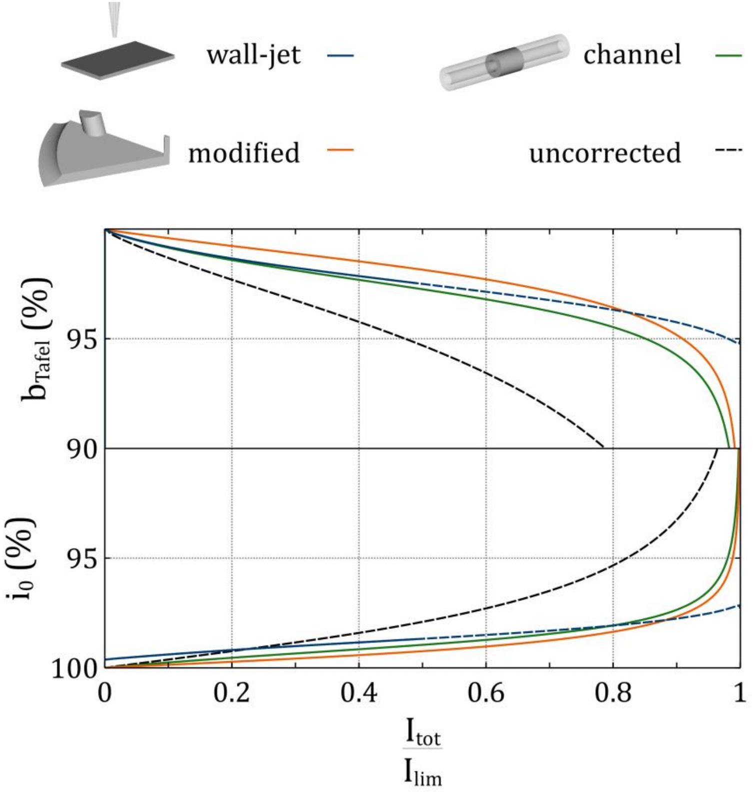
  - i_{tot} contains mass transport currents → error upon determination of i_0 and b_{Tafel}



- Tafel Plot for i_{kin}:
  - Apply Koutecký-Levich eq. to subtract mass transport currents
  - i_{kin} is free from mass transport losses and yields more accurate kinetic information



Verification: Precision across Fitting Range

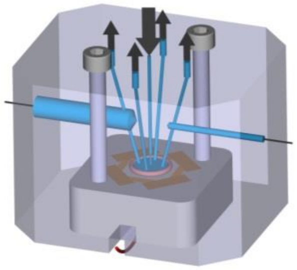


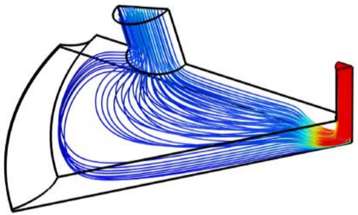
- Comparison with Input Values:
  - Tafel slope b_{Tafel} and exchange current density i_0 are known for the model data
  - Assess precision of mass transport correction for different fitting regimes for the Butler-Volmer equation
  - Notable improvement in comparison with uncorrected current densities (i_{tot})

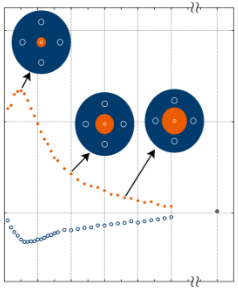
- Comparison with equations for ideal wall-jet and channel flow profiles:
  - Improvement over channel electrodes
  - Koutecký-Levich equation for wall-jet electrodes needs further investigation

Summary and Conclusions

- Model:
  - Model can be set up with the base COMSOL Multiphysics® module
  - Equation-based electrode reaction
- Method:
  - Partition flow profile virtually in two parts and correlate with ideal (= well established) cases
  - Obtain Koutecký-Levich equation based on above correlation
- Verification:
  - Compute polarization curves and apply equation to subtract mass transport currents
  - Comparison of precision across the whole fitting range



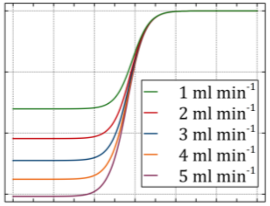


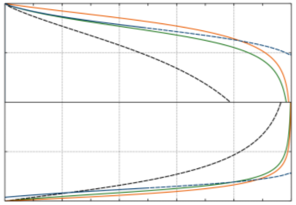


$$\frac{1}{I_{tot}} = \frac{1.06}{I_{kin}} + \frac{1}{I_{lim}}$$

$$\frac{1}{I_{tot}} = \frac{1}{I_{kin}} + \frac{0.93}{I_{lim}}$$

$$\frac{1}{I_{tot}} = \frac{1 + 0.06 \cdot R}{I_{kin}} + \frac{0.93 + 0.07 \cdot R}{I_{lim}}$$





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- the Electrochemistry Laboratory (ECL)
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Appendix

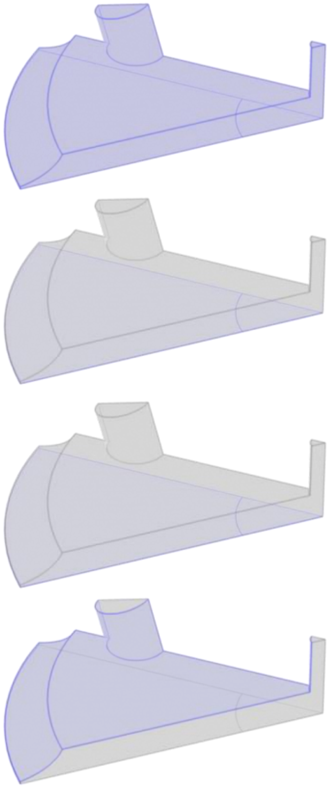
- Input Values and Meshing Sequence

Table I. Input Parameters for 5% H_2SO_4

Parameter	Symbol	Value (ORR)
Temperature	T	293 K
Electrolyte density	ρ	1032 kg m^{-3}
Dynamic viscosity	μ	$1.112 \cdot 10^{-3}$ Pa s
Inlet concentration	c_{in}	1 mol m^{-3}
Diffusion coefficient	D	$2.01 \cdot 10^{-9}$ m^2 s^{-1}
Exchange current density	i_o	$2 \cdot 10^{-6}$ A $m_{Pt}{}^2$
Transfer coefficient	α	1
Transferred electrons	n	4
Overpotential for I_{lim}	η	1 V

D.R. Lide, ed., *CRC Handbook Chem. Phys.*, Internet Version 2016, CRC Press

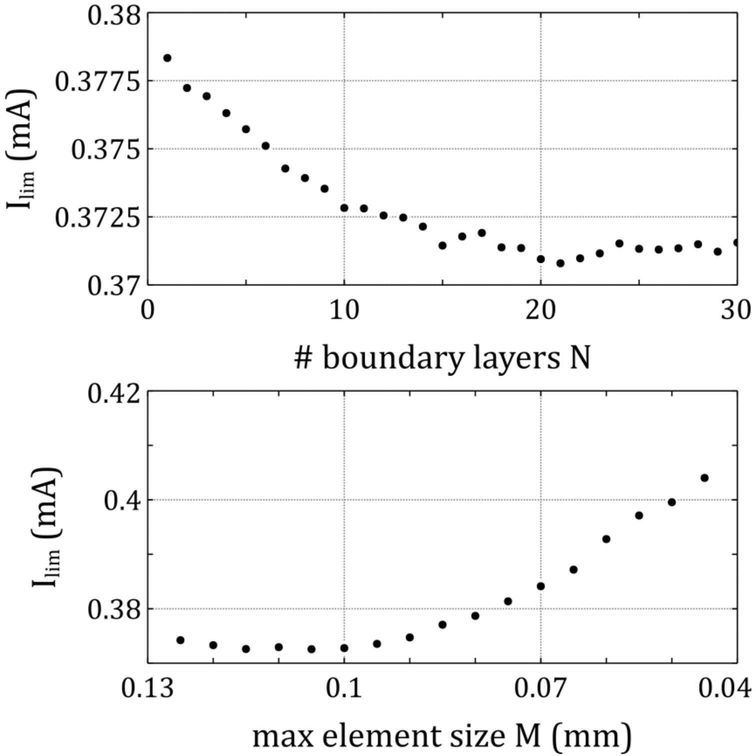
K.C. Neyerlin et al. *J. Electrochem. Soc.* **153** (2006) A1955



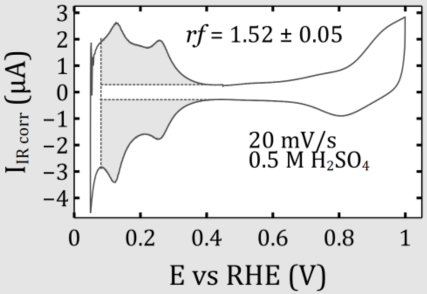
- Free Tetrahedral
  - Max element size = 2·M
  - Min element size = 0.2·M
  - Corner refinement
- Free Triangular
  - Max element size = M
  - Min element size = 0.1·M
- Fine Boundary Layers
  - Number of layers = N
  - Stretching factor = 1.25
  - Thickness = M / $1.25^{(N-1)}$
- Coarse Boundary Layers
  - Number of layers = 2
  - Stretching factor 1.25
  - Automatic adjustment

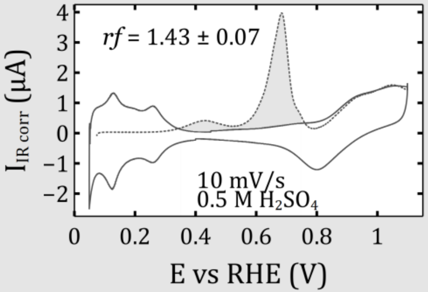
Mesh Refinement Study

- Number of boundary layers N:
  - M = 0.1 mm
  - Increasing number of boundary layers = finer boundary layer at the surface
  - Size of outermost boundary layer determined by mesh element size of tetrahedral mesh
  - More boundary layers = more accurate model
  - Current decreases with increasing N
  - No significant improvement after N = 15
- Maximum element size M:
  - N = 10
  - M determines lateral resolution on electrode, size of tetrahedral mesh elsewhere and thickness of boundary layers
  - Smaller M = more accurate model
  - Current increases with decreasing M
- But:
  - Differences in I_{lim} for different M and N are not significant upon comparison with experimental data!



- Comparison to Experimental Results
  - Hold potential while recording current I = f(t)
  - Run slow (= approach steady-state) linear ramp on pump driving the electrolyte
  - Correct experimental current for surface roughness determined by H_{upd} and CO monolayer oxidation:





- Results (Hydrogen Oxidation Reaction)
  - Comparison of V_{in} vs I_{lim} curves computed for different inlet concentrations of H_2: