COMSOL CONFERENCE 2016 MUNICH

Rotating Disk Electrode in Ionic Liquids: Difference between Water and Ionic Liquids

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INSTM

Industrial interest

Integrated FEA & Experimental approach

Results from FEA

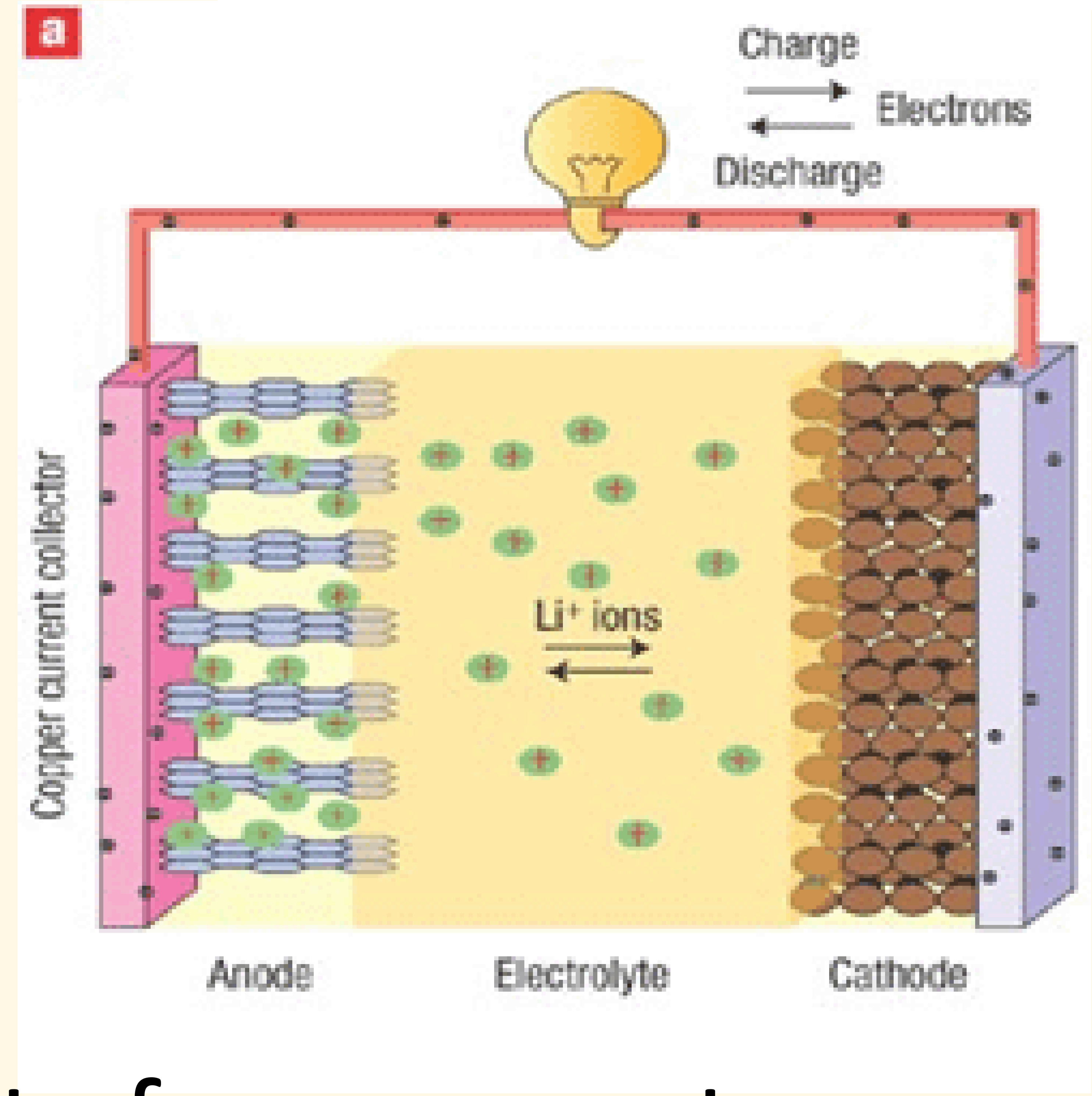
Approximations on Levich’s law

Conclusion

Industrial interest

Greener electrolyte for Ag electroplating

Electroplating of Al



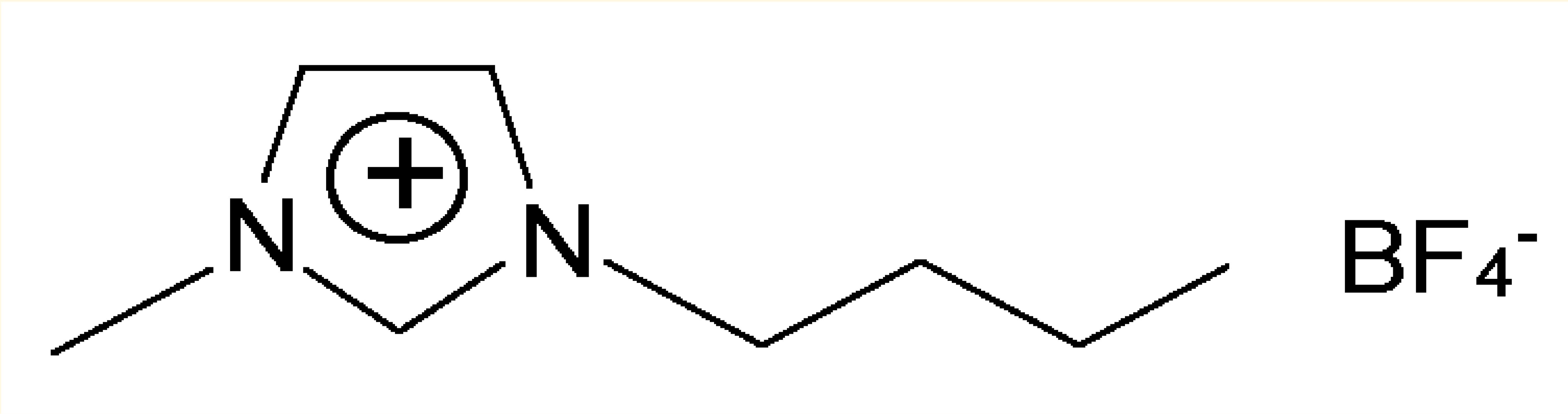
Electrolyte for energy storage

Industrial interest: $BMImBF_4$

The term «Ionic Liquid (IL)» describes salts characterized by a melting temperature below 100 °C, thus we can refer to these substances as «Room Temperature Molten Salts». (RTMS) Some ILs can be used **outside** a glovebox ($BMImBF_4$).

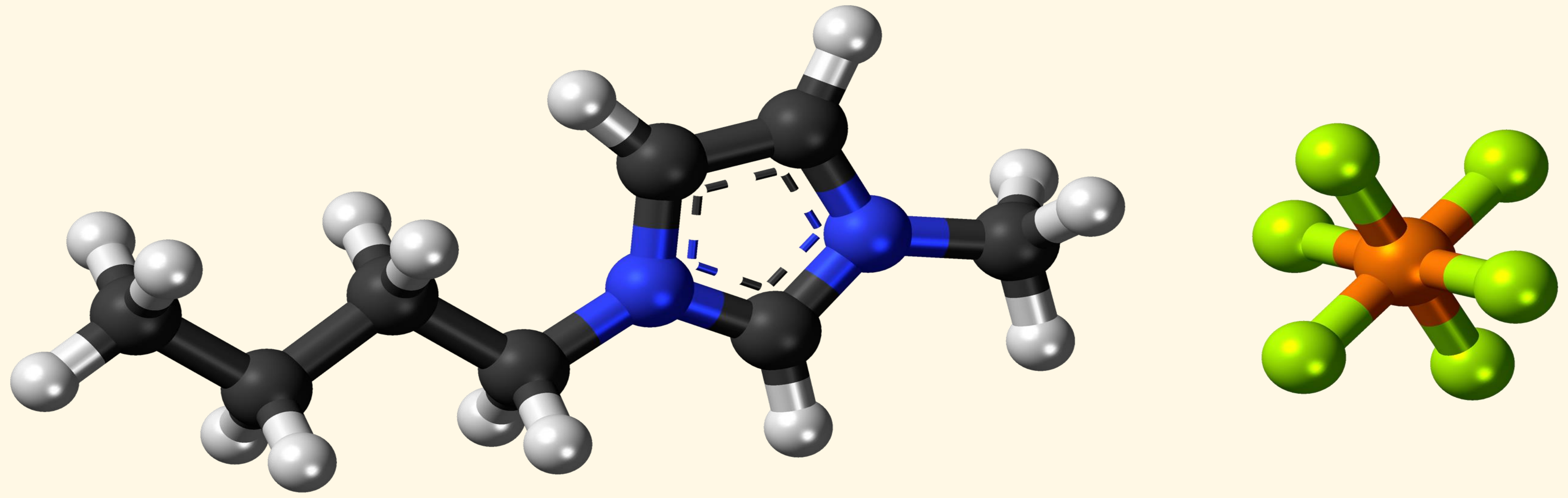
Their main features are:

•Low vapour pressure
•Low flammability
•Wide electrochemical window
•**Higher viscosity (two order of magnitude higher than water-based electrolytes)**



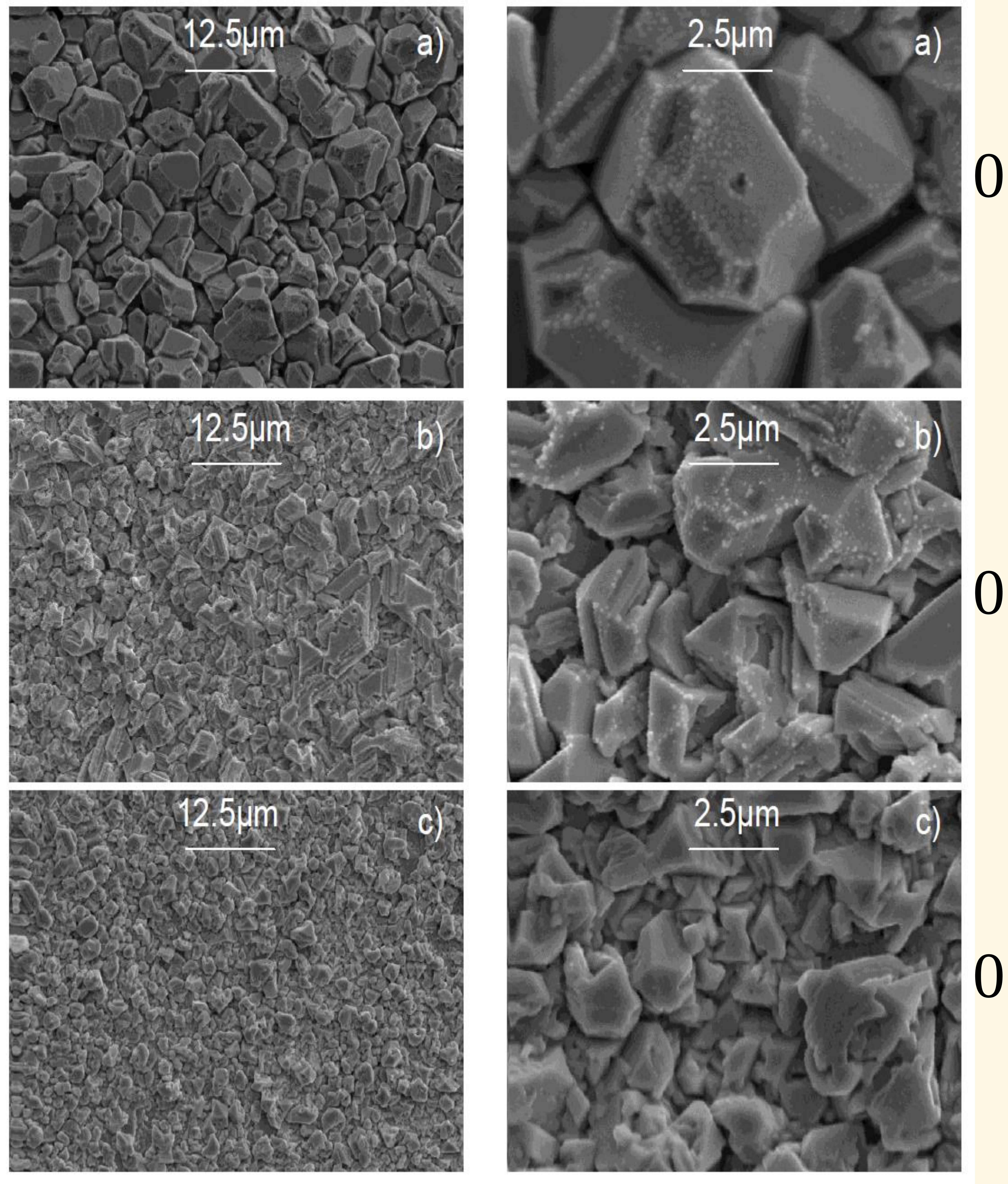
	Water	$BMImBF_4$
Viscosity(20°C)	0.894mPa s	132mPa s
Density(20°C)	1000 kg m^{-3}	1211 kg m^{-3}

$BMImBF_4$



Industrial interest: Motivation

$AgBF_4$ $BMImBF_4$



0.05 A/dm^{-2}

0.1 A/dm^{-2}

0.2 A/ dm^{-2}

2000X 10000X

- Low deposition rates
- Roughness of the coatings

TRANSPORT PROPRIETIES

$$Sc = \frac{\nu}{D}$$

1.17×10^2 $Ag(CN)_2^-$ in Water

1.43×10^5 $AgBF_4$ in $BMImBF_4$

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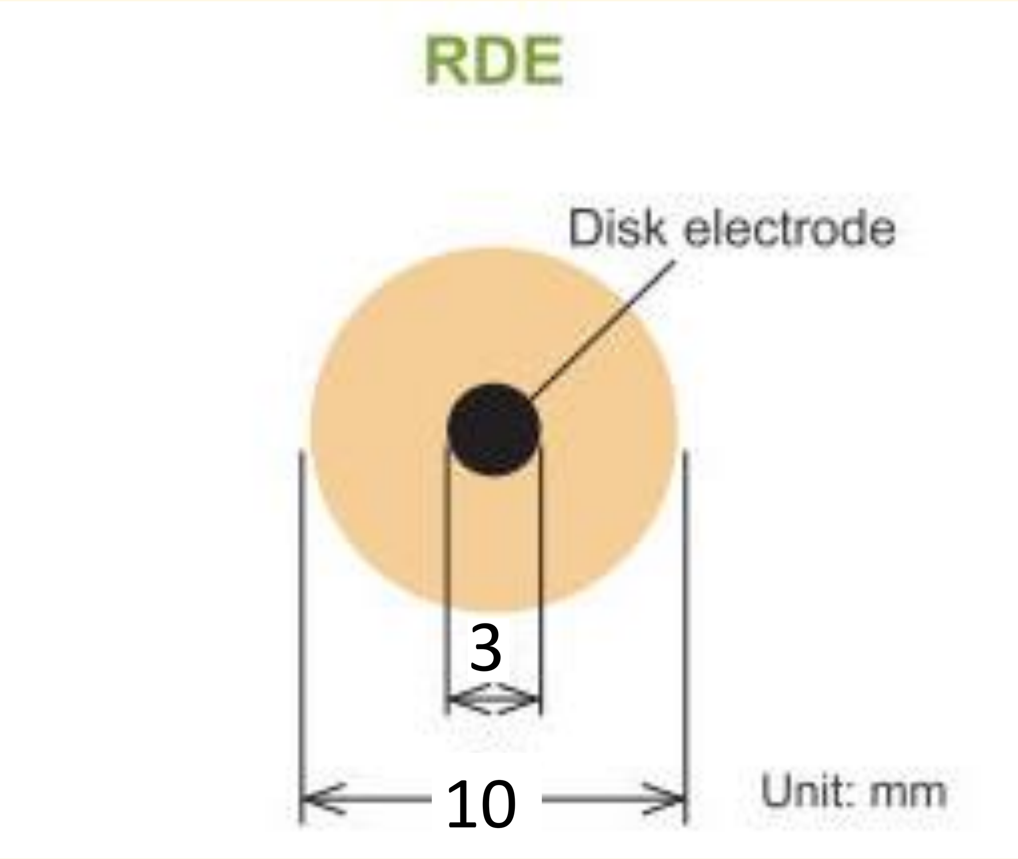
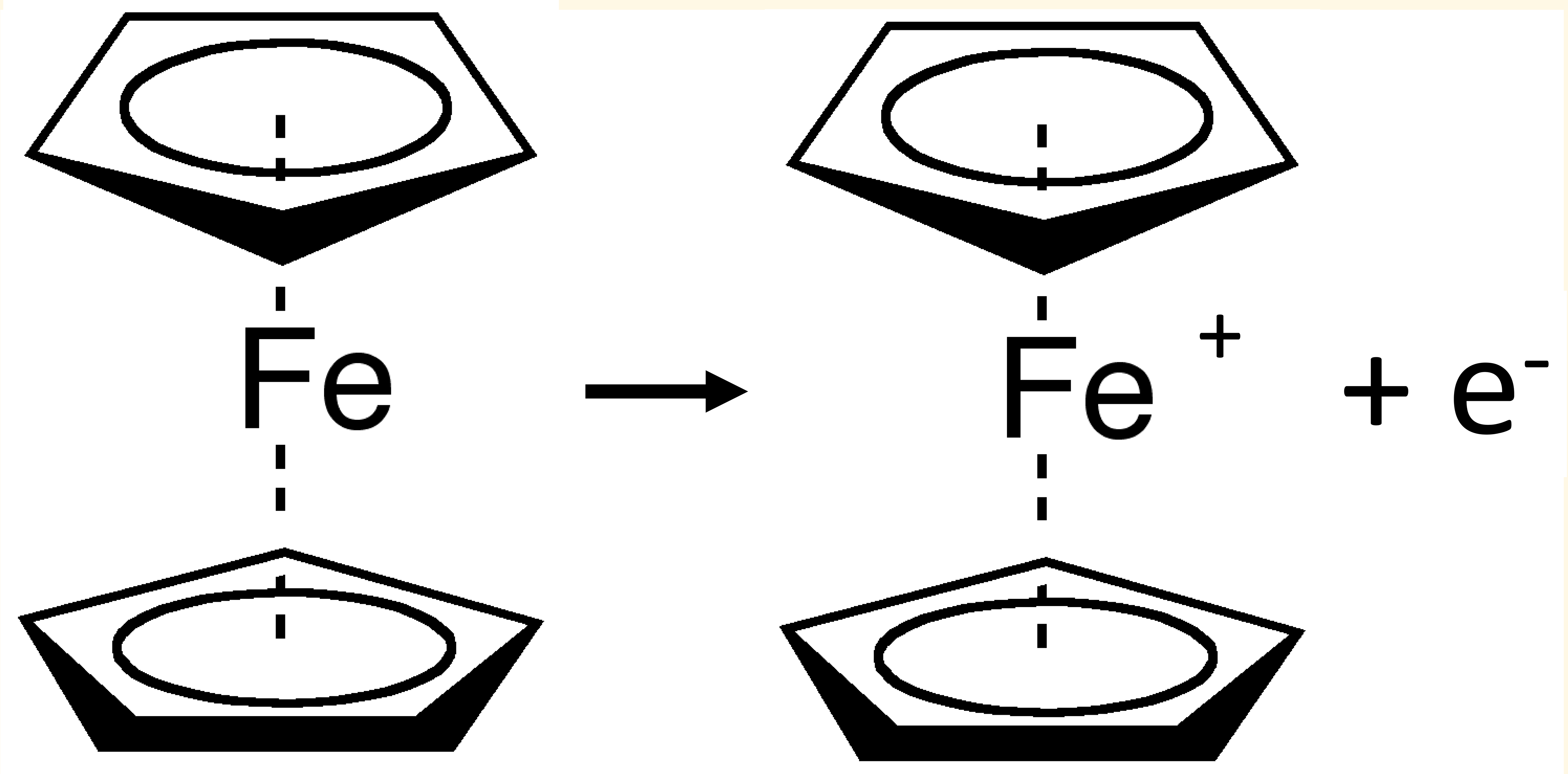
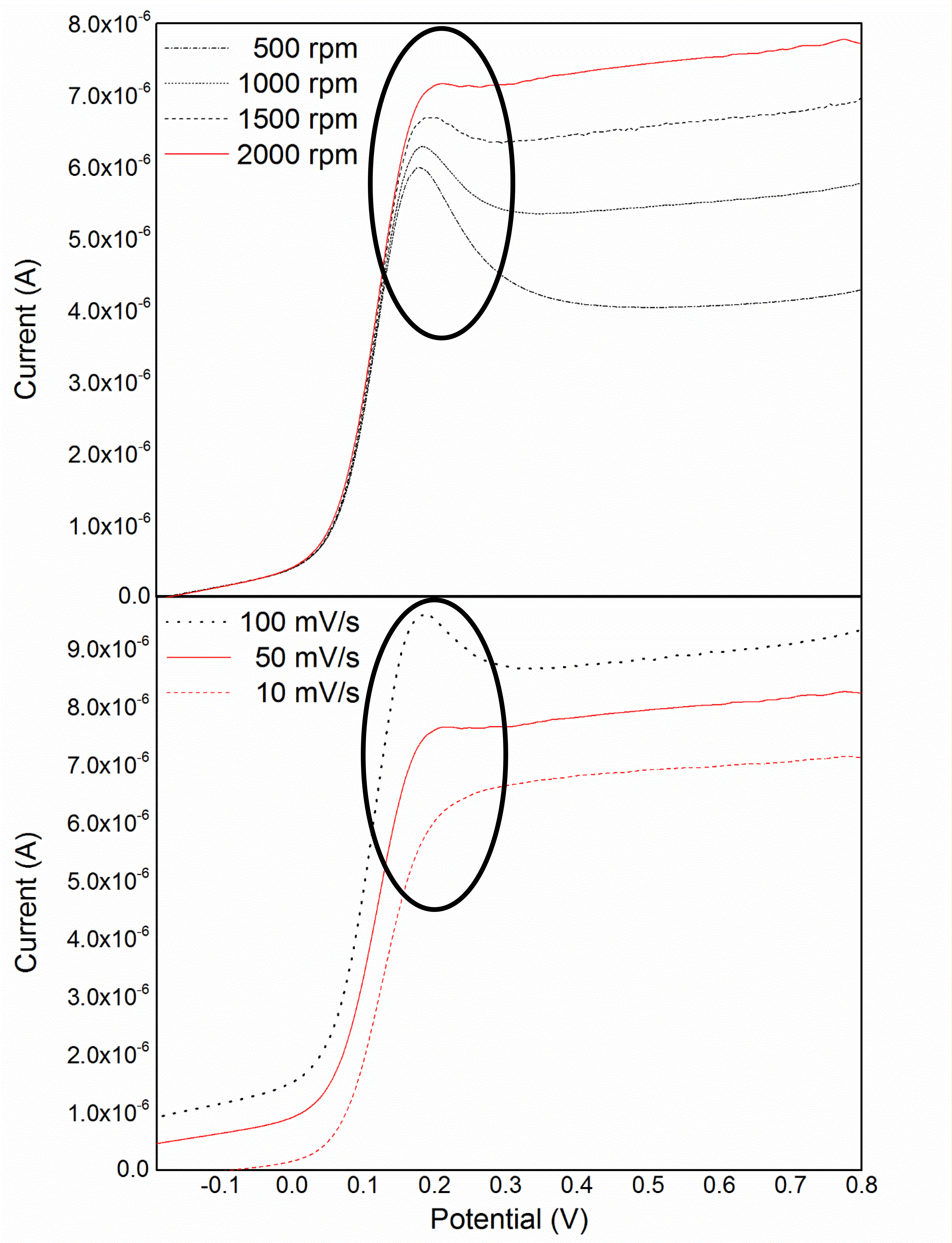
FEA & Exp: RDE of a model system

FeCen/FeCin is well characterized. It has been chose as model for the transport proprieties in IL.







FEA & Exp: theoretical methods

In the case of electroanalytical model, the conductivity is considered to be infinitly high, so the ohic drop across the electrolyte can be neglected and the electric potential is homogeneously distributed in the electrolyte. Only Nernst-Planck equation is needed to model the CV.

1. Solve for the steady state of the Navier-Stokes equations (stationaty velocity field)

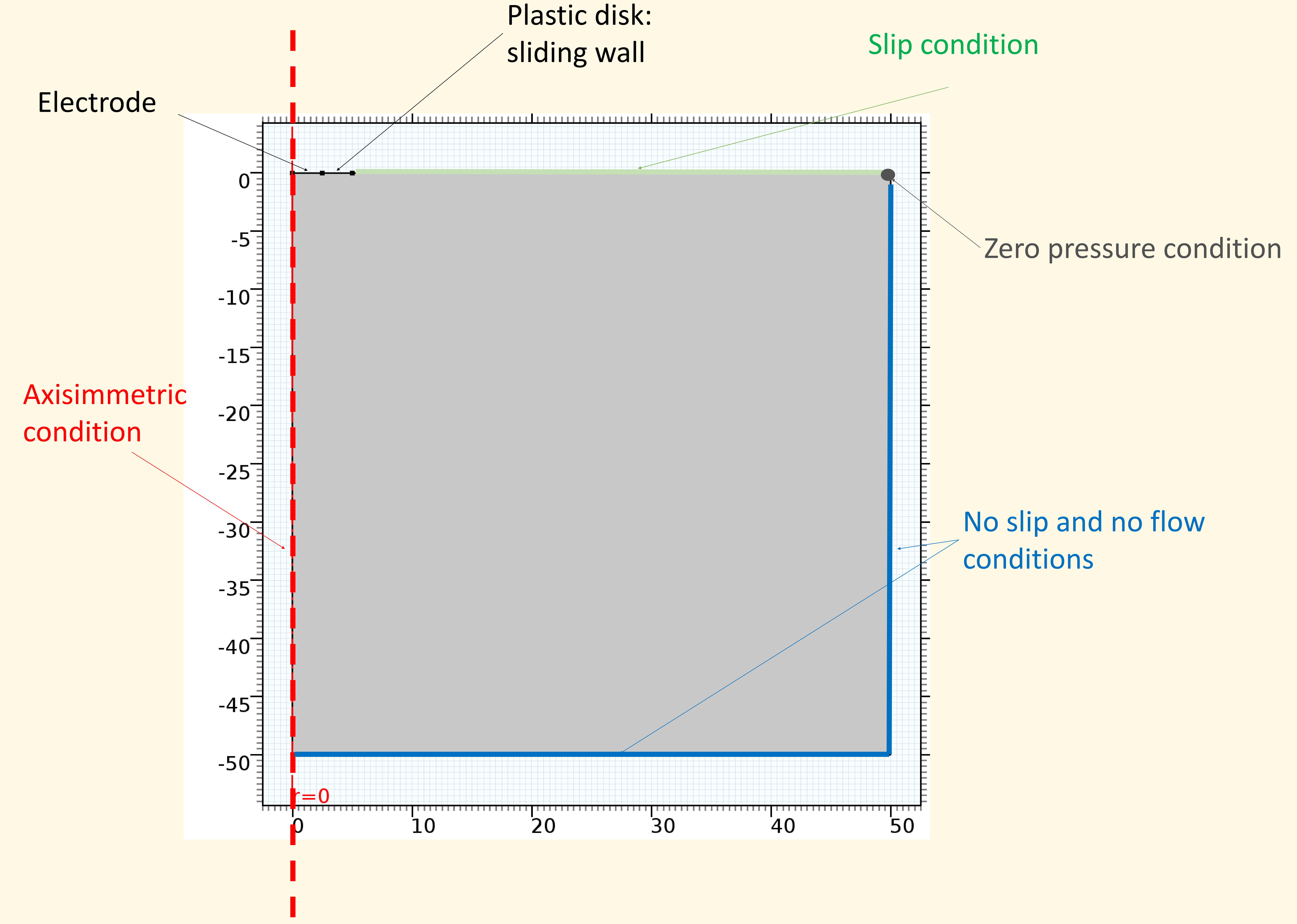
$$\begin{cases} k\boldsymbol{\nabla}^2\boldsymbol{v} - \rho(\boldsymbol{v}\cdot\boldsymbol{\nabla}\,\boldsymbol{v}) - \boldsymbol{\nabla}\,P = 0 \\ \boldsymbol{\nabla}\cdot\boldsymbol{v} = 0 \end{cases}$$

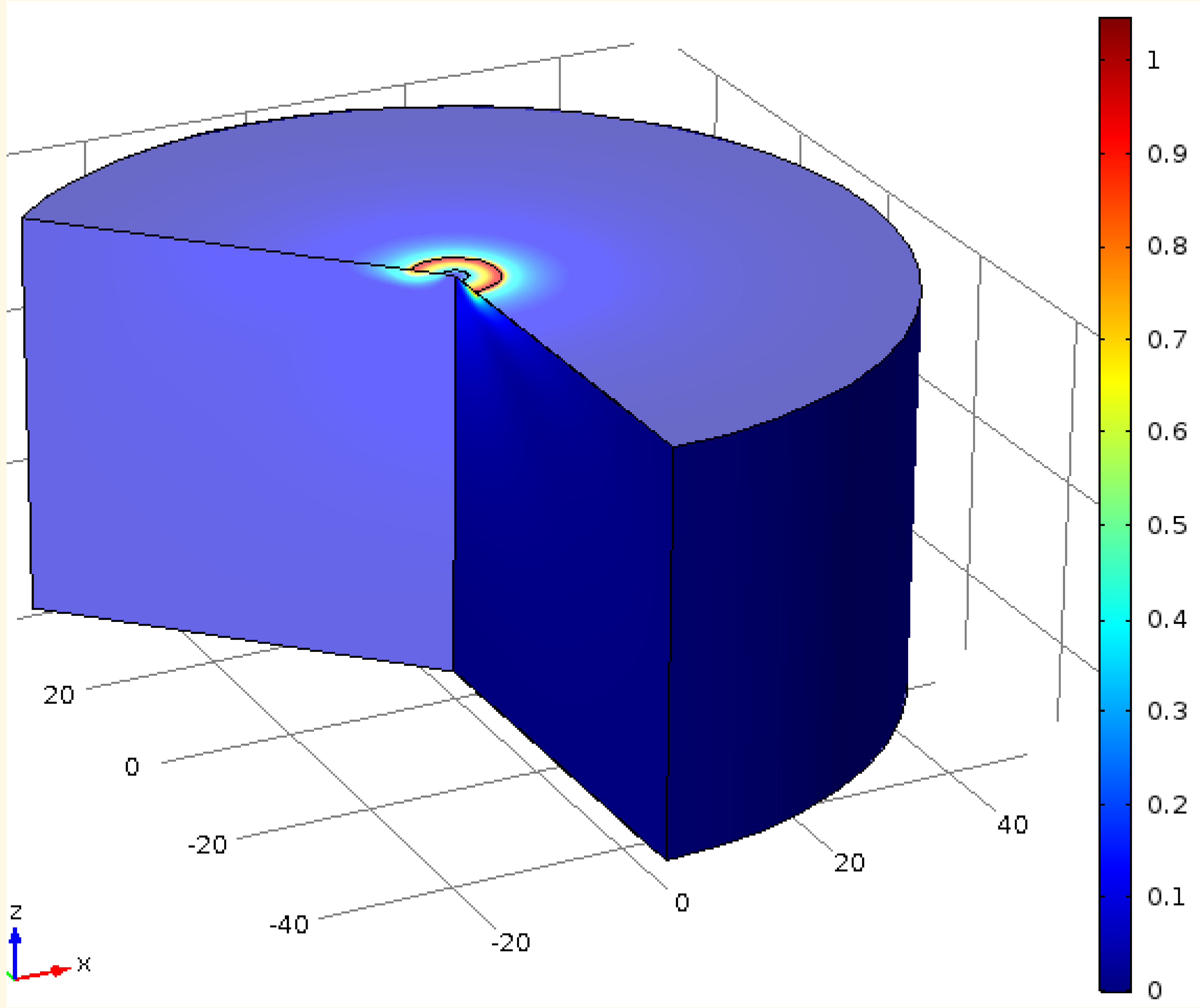
2. Solve the time dependent Nernst-Planck equation (with velocity field from 1) in order to solve for the characteristic curve of the RDE voltammetry

$$\begin{cases} \dfrac{\partial \boldsymbol{C_i}}{\partial t} + \boldsymbol{\nabla}\cdot\boldsymbol{N_i} = R_i \\ -\boldsymbol{\nabla}\cdot(\sigma_{\boldsymbol{l}}\boldsymbol{\nabla}\phi_l) = \rho \end{cases}$$

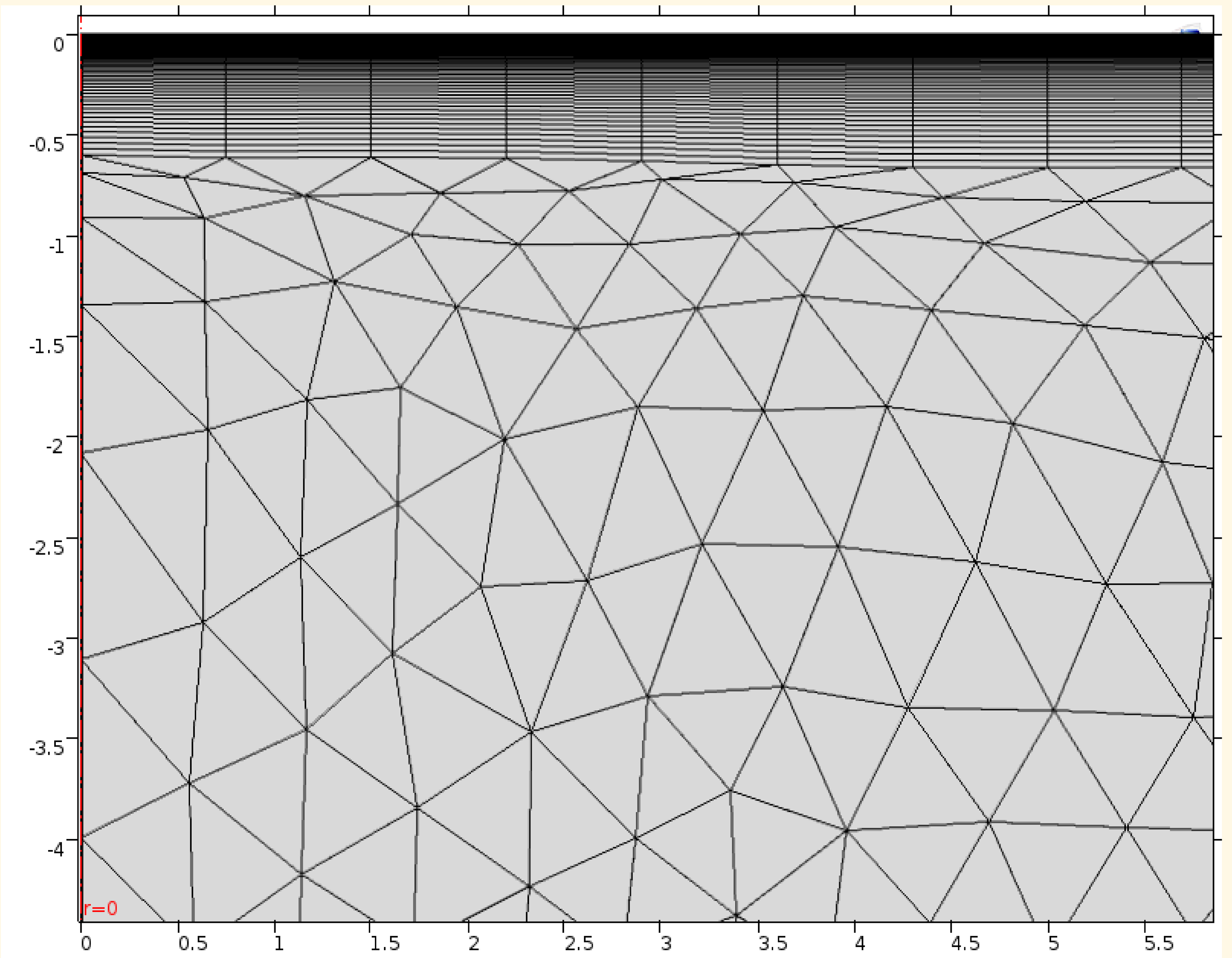
FEA & Exp: geometry and boundary conditions

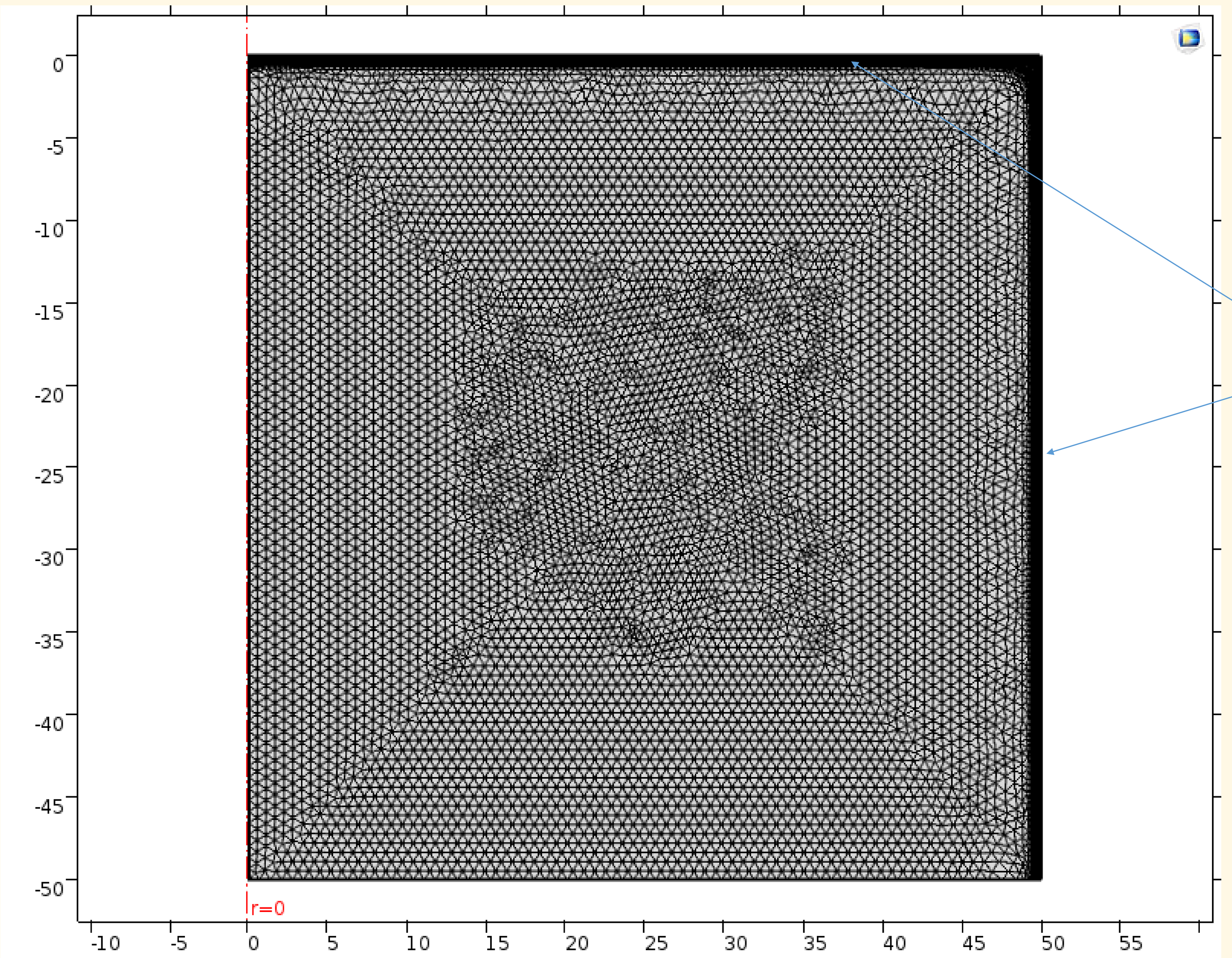
$$i_{loc} = i_0\left(\frac{C_R}{C_R^0} e^{\frac{\alpha_a F\eta}{RT}} - \frac{C_O}{C_O^0} e^{\frac{-\alpha_c F\eta}{RT}}\right)$$



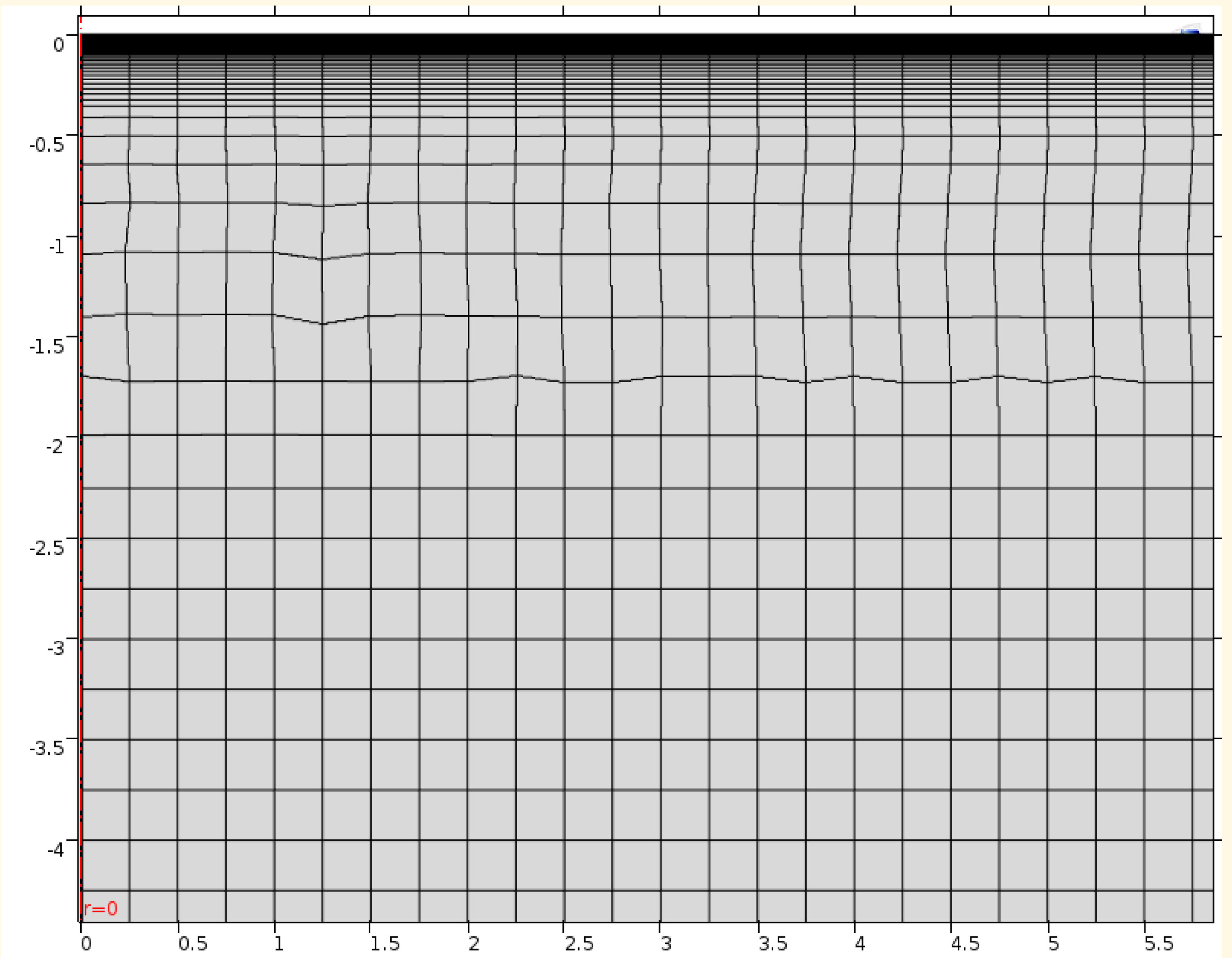


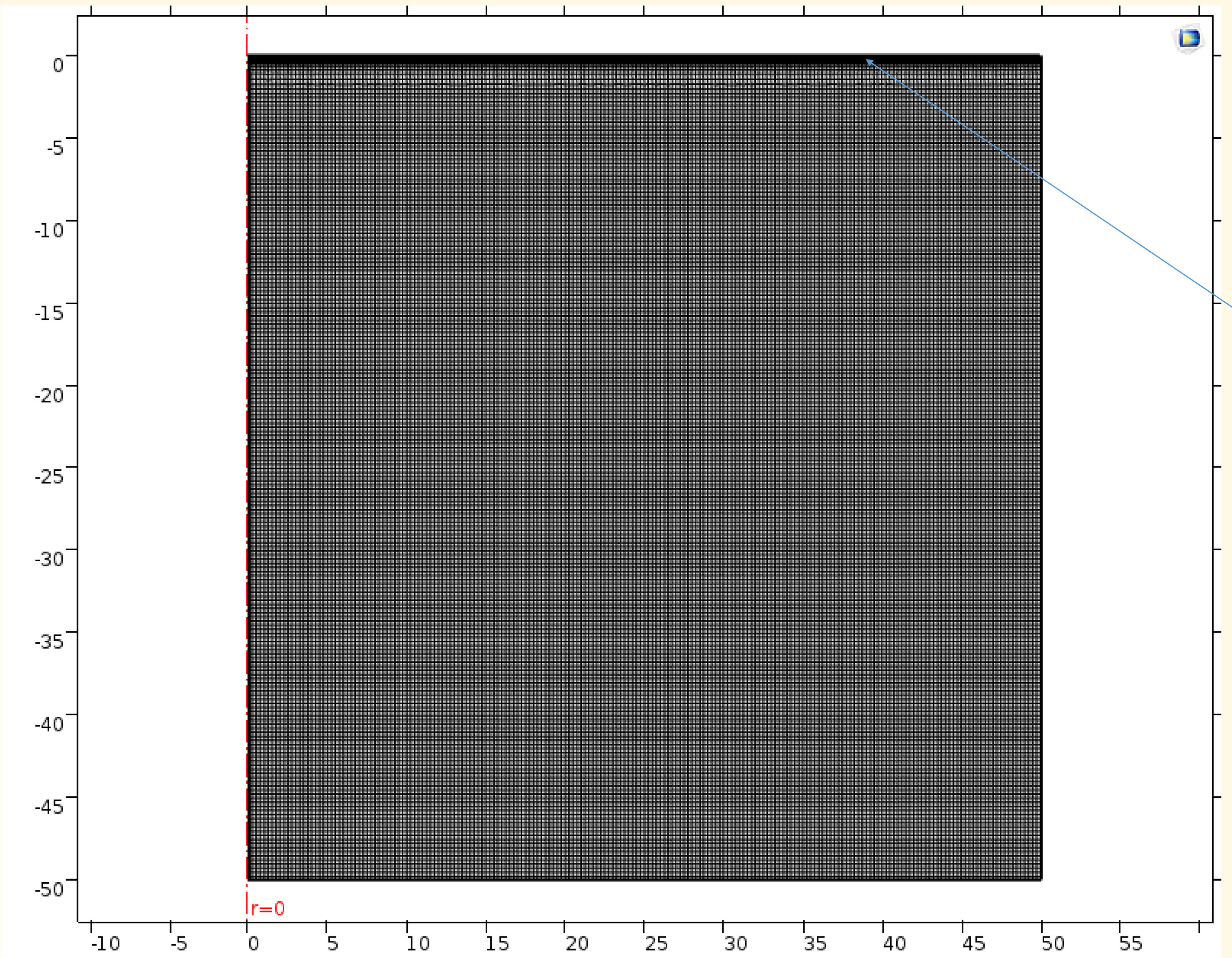
FEA & Exp: Physics-dependent meshing





Steady state - Navier-Stokes
- Triangular
- Boundary layer: 50 layers starting from 10 μm.





Time dependent - Nernst-Planck
- Mapped
- Boundary layer: 100 layer starting from 100 nm.

Industrial interest

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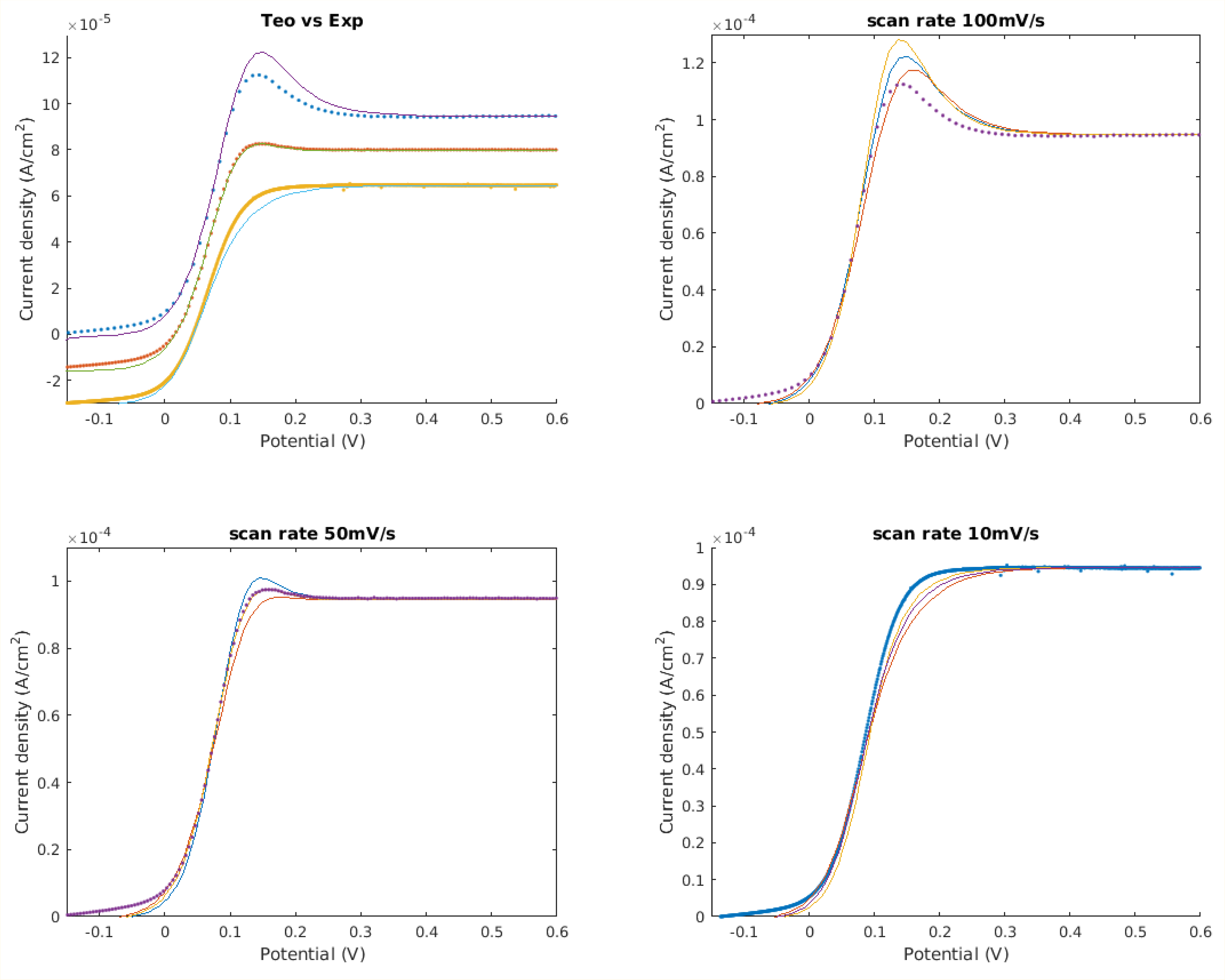
Results from FEA: validation

S. Eisele, M. Schwarz, B. Speiser, C. Tittel, Electrochim. Acta. 51 (2006) 5304–5306.

	Water	BMImBF4
Viscosity(25°C)	0.894mPa s	132mPa s
Density(25°C)	1000 kg m^{-3}	1211 kg m^{-3}
Diffusion coefficient	1.3x10^{-9} m^2/s	1.3x10^{-11} m^2/s
Exchange current density	0.18 A/m^2	0.18 A/m^2



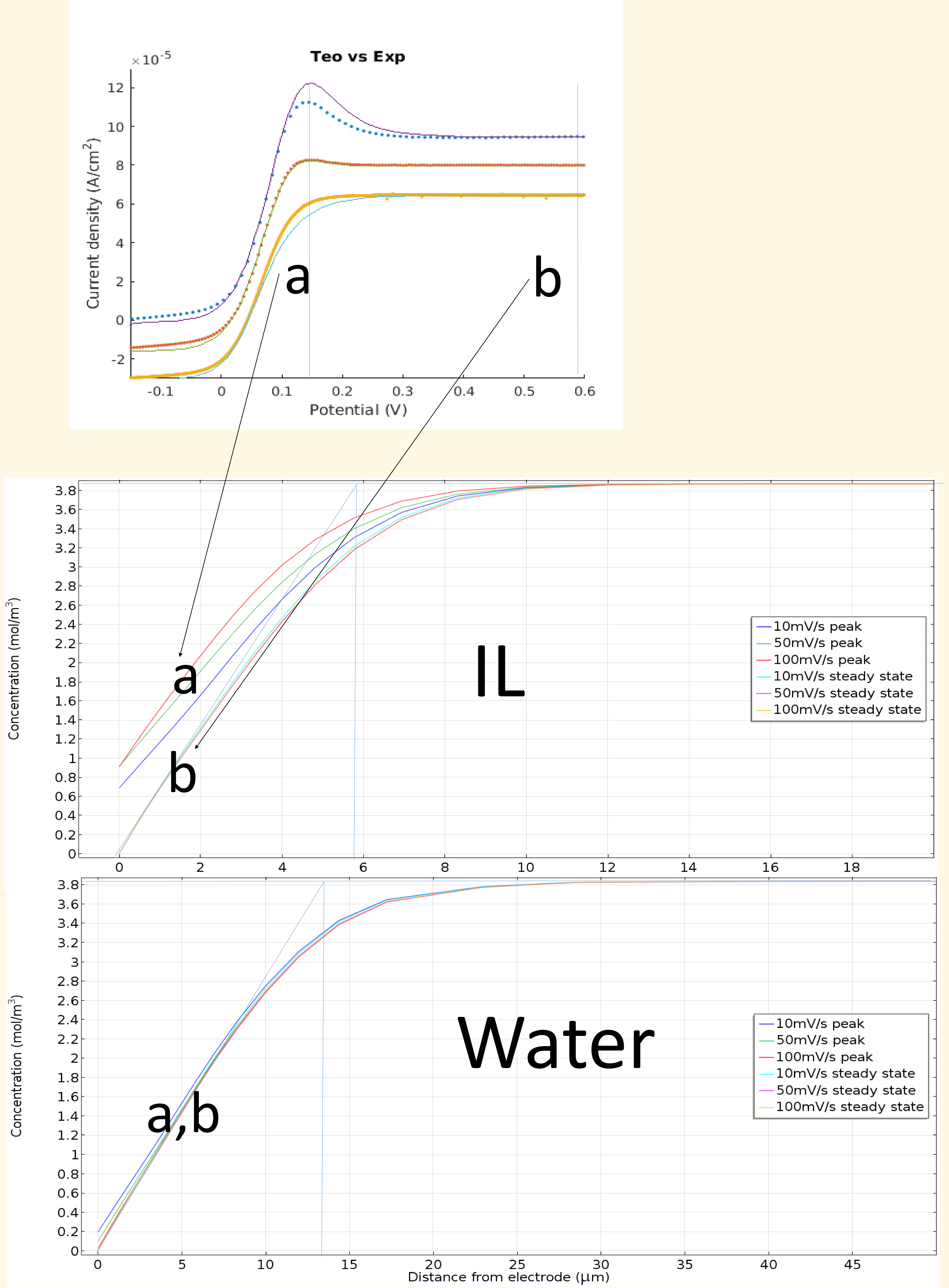
Rotating Speed is 2000 rpm

Inverse problem for the determination of the exchange current densities.

Good correspondance between experimental and theoretical results.

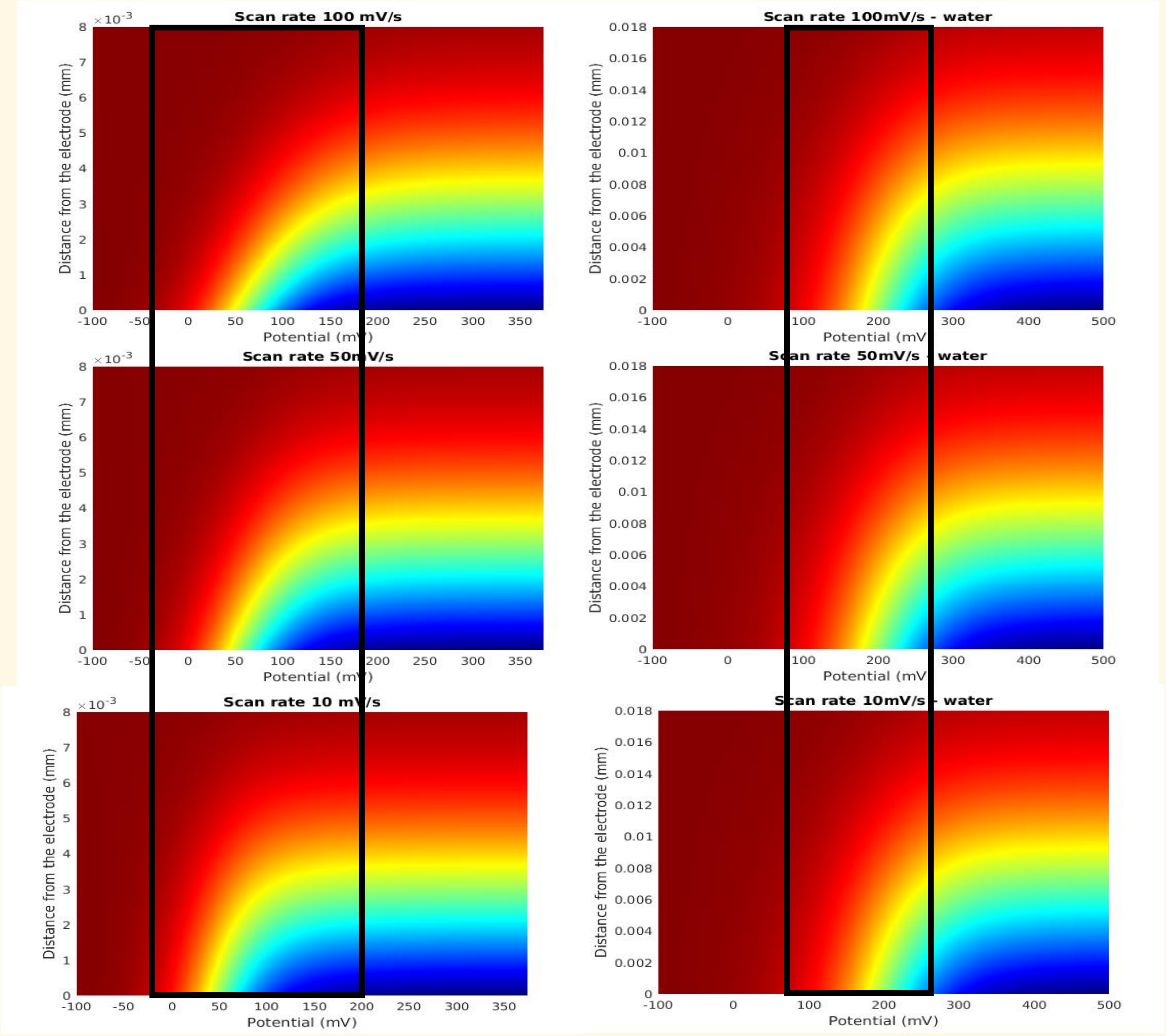
Perfect match between the limit currents.

Results from FEA: convection layers



The convection layer it is not well developped at the potential corresponding to the peak

IL Water

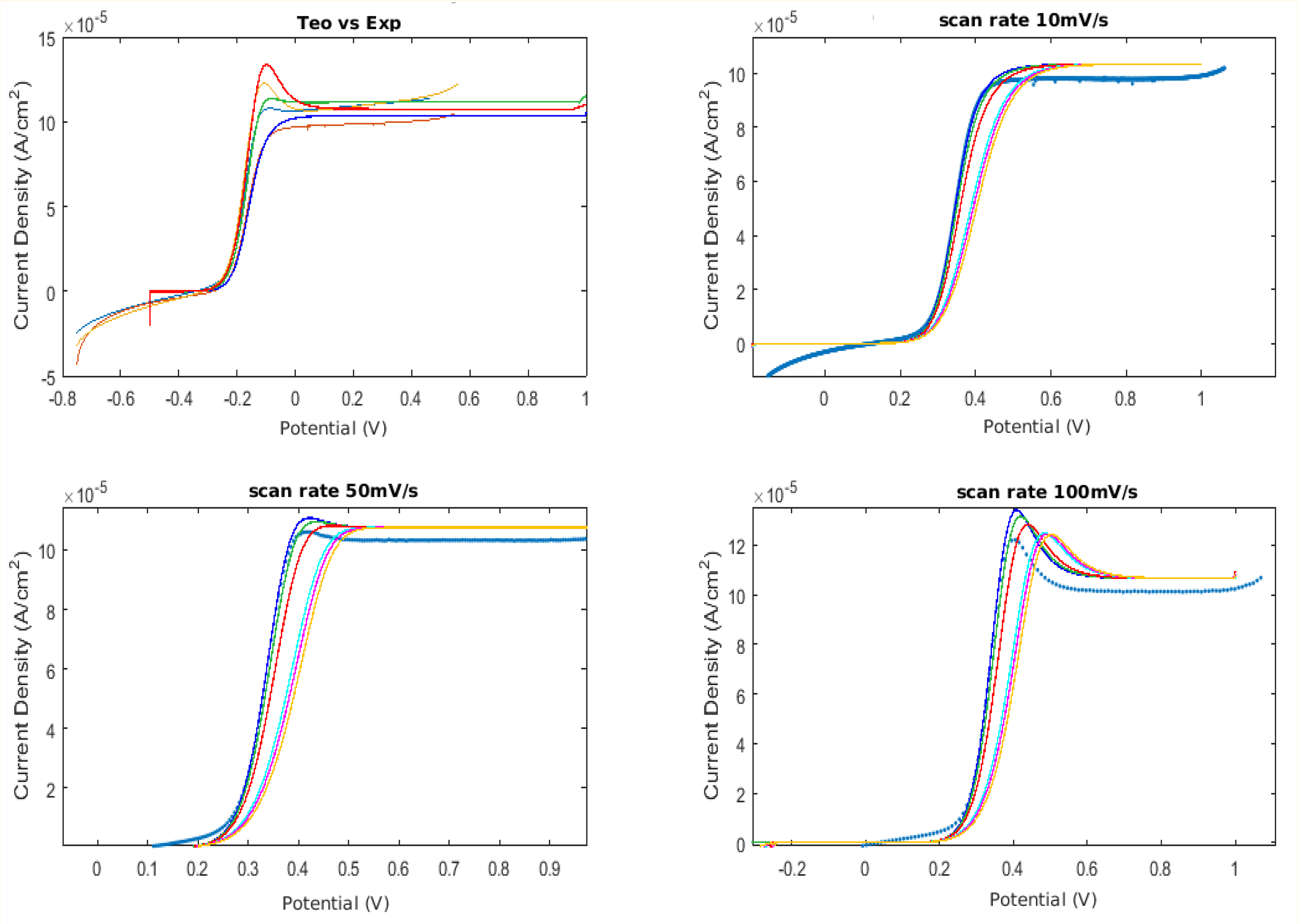


Results from FEA: Breaking of the Levich's law

S. Eisele, M. Schwarz, B. Speiser, C. Tittel, Electrochim. Acta. 51 (2006) 5304–5306.

Static electrochemical measurements →

Diffusion coefficient	**1.3×10^{-11} m²/s**



	BMImBF4
Viscosity(25°C)	132mPa s
Density(25°C)	1211 kg m^{-3}
Diffusion coefficient	**1.6×10^{-11} m²/s**

Levich's law

Speed ($mV\ s^{-1}$)	**FEA ($mA\ cm^{-1}$)**	**Exp ($mA\ cm^{-1}$)**	
10	103.3	98	5.4 %
50	107.5	103.5	5.4 %
100	106.7	101.3	3.9 %

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Approximations on Levich's law: How to Levich's law

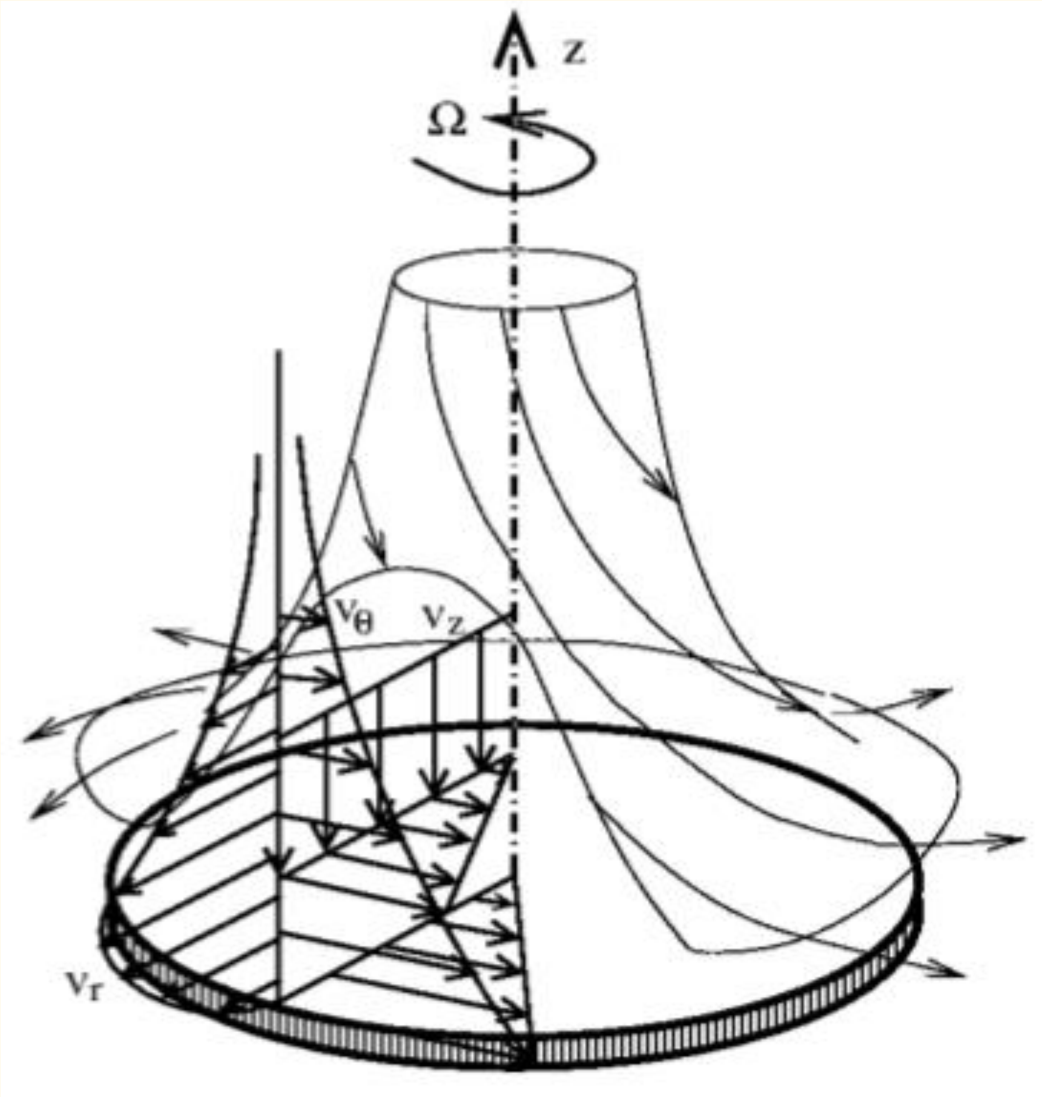
$$z^* = z\sqrt{\frac{\omega}{\nu}} \qquad G(z^*) = \frac{v_\theta}{r\omega} \quad H(z^*) = \frac{v_z}{\sqrt{\nu\omega}} \quad F(z^*) = \frac{v_r}{r\omega}$$

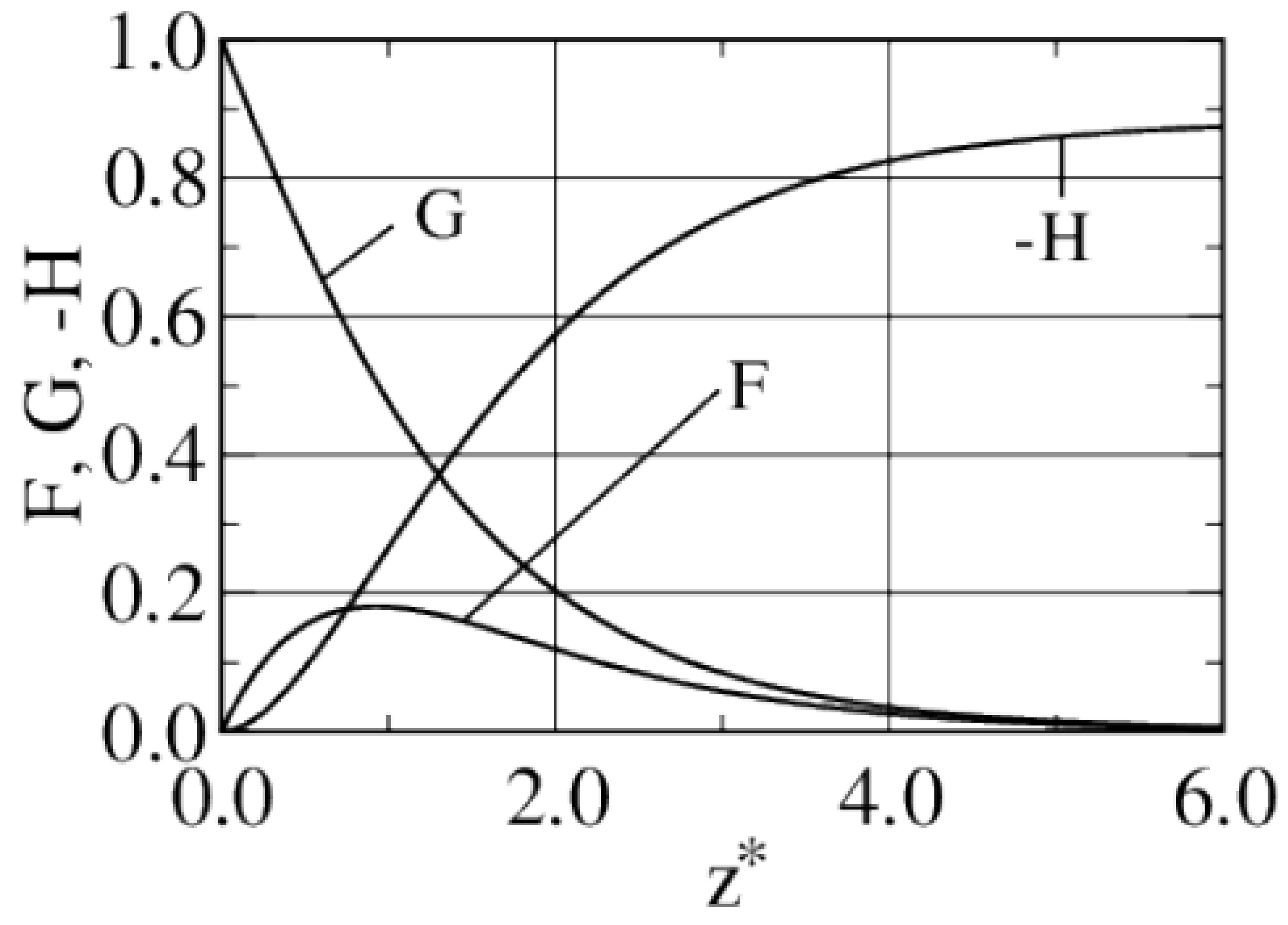
Von Karman's PDEs

$$\begin{cases} 2F + H' = 0 \\ F'' - HF' - F^2 + G^2 = 0 \\ G'' - HG' - 2FG = 0 \\ H'' - HH' - P' = 0 \\ \\ H = F = P = 0, G = 1 \; at \; z^* = 0 \\ F = G = 0 \; at \; z^* = \infty \end{cases}$$

Cochran's solution

$$\begin{cases} F = az^* - \frac{z^{*2}}{2} - b\frac{z^{*3}}{3} \; \ldots \\ G = 1 + b\,z^* + a\frac{z^{*3}}{3} \; \ldots \\ H = -a\,z^2 + \frac{z^{*3}}{3} + b\frac{z^{*4}}{6} \ldots \end{cases}$$



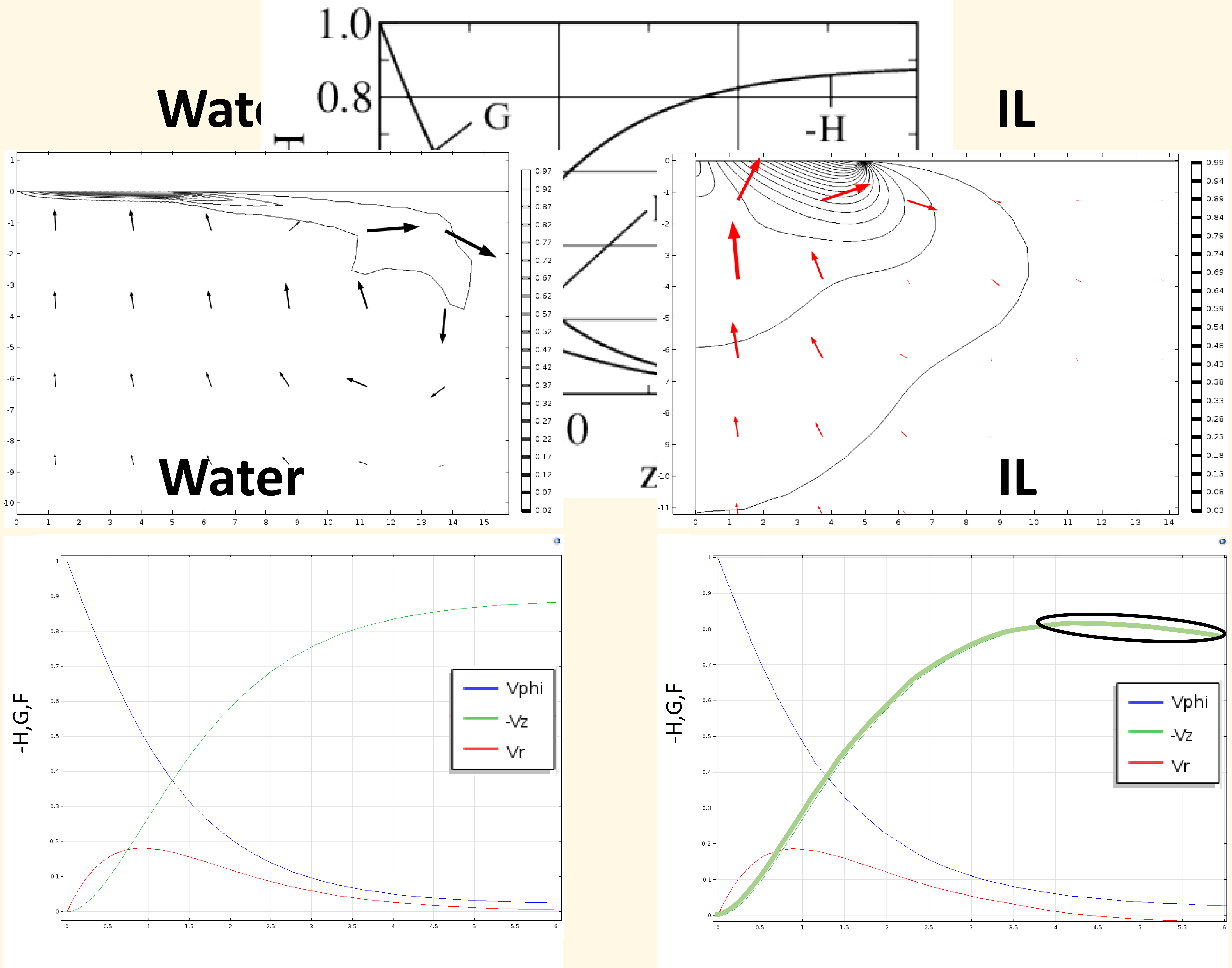


Levich's solution to N-P

$$\frac{\partial \boldsymbol{C_i}}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{N_i} = R_i$$

$$j_L = 0.6205\, n\, F D^{\frac{2}{3}} \omega^{\frac{1}{2}} \nu^{-\frac{1}{6}} C$$

Approximations on Levich’s law: the «dragged layer»



Dragged layer

$$\delta_h = 3.6\sqrt{\frac{\nu}{\omega}}$$

Water: 0.26 mm

IL: 2.6 mm

(JUST OF HALF OF CYLINDER RADIUS)

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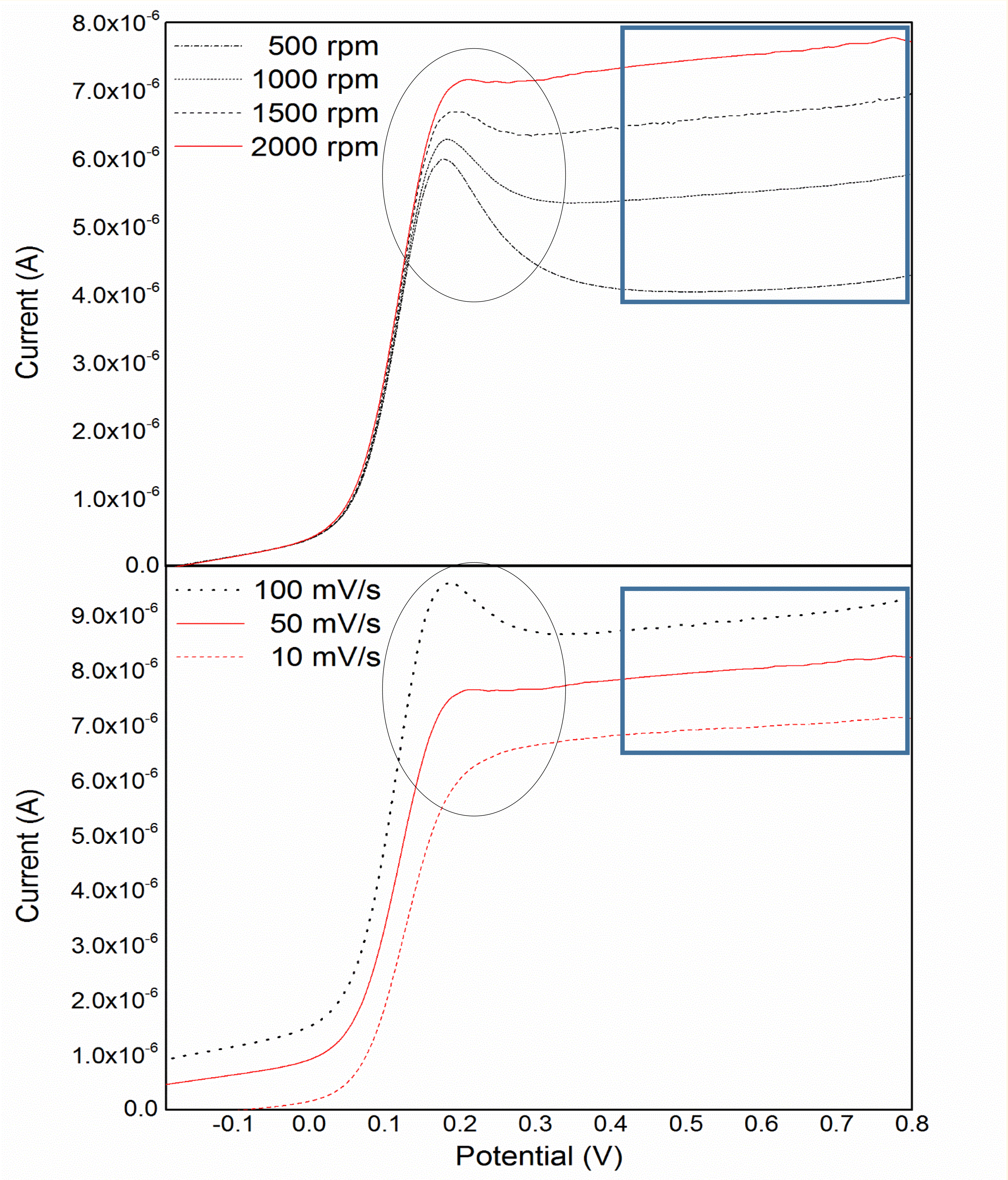
- Unexpected features found in the RDE voltammetries have been explained, they arise from the non developping of the convection layers.

- **A vessel comparable with the dragged layer impair the development of the velocity field.** Non completely developped velocity field are inconsistent with the Levich’s assumptions.

Conclusion: Take home message

Inefficent mixing of the electrolyte leads to peaks in the RDE voltammetry.

Inefficient mixing has also a more subtle effect, leading to the breaking of the Levich's Law.



That’s what happen when you don’t run a good simulation!

Thanks for your attention

Solute	Sc
Helium	120
Hydrogen	190
Nitrogen	280
Water	340
Nitric Oxide	350
Carbon monoxide	360
Oxygen	400
Ammonia	410
Carbon dioxide	420
Hydrogen sulfide	430
Ethylene	450
Methane	490
Nitrous oxide	490
Sulfur dioxide	520
Sodium chloride	540

Solute	Sc
Sodium hydroxide	590
Acetic acid	620
Acetone	630
Methanol	640
Ethanol	640
Chlorine	670
Benzene	720
Ethylene glycol	720
n-propanol	730
i-propanol	730
Propane	750
Aniline	800
Benzoic acid	830
Glycerol	1040
Sucrose	1670

Approximations on Levich’s law: the Schimdt number correction

Von Karman’s velocity field (H,F,G) → $\frac{\partial \boldsymbol{C_i}}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{N_i} = R_i$

After different approximations (taylor series)

Levich’s equation

$$j_L = 0.6205\, n\, F D^{\frac{2}{3}} \omega^{\frac{1}{2}} \nu^{-\frac{1}{6}} C$$

Newman’s equation

$$j_L = \frac{0.6205\, n\, F D^{\frac{2}{3}} \omega^{\frac{1}{2}} \nu^{-\frac{1}{6}} C}{1 + 0.2980\, Sc^{-\frac{1}{3}} + 0.1451\, Sc^{-\frac{2}{3}}}$$

Table I: Comparison of Values for $i(1 - t)/nF(c_\infty - c_0)\sqrt{\Omega\nu}$

Sc	"Exact"[a]	Newman	ϵ[b]	Gregory and Riddiford	ϵ[b]	Levich	ϵ[b]
100	0.026874	0.026892	0.069	0.026970	0.36	0.028799	7.16
200	0.017188	0.017194	0.038	0.017226	0.22	0.018137	5.52
500	0.009471	0.009472	0.015	0.009488	0.18	0.009850	4.00
800	0.006964	0.006965	0.010	0.006975	0.16	0.007200	3.39
1000	0.006016	0.006017	0.009	0.006024	0.14	0.006205	3.13
1200	0.005338	0.005338	0.007	0.005346	0.15	0.005495	2.94
1400	0.004824	0.004824	0.005	0.004830	0.14	0.004958	2.79

[a] "Exact" refers to a numerical evaluation of eq 1, and thus is still subject to error. [b] ϵ is per cent deviation.

Typical range in water: 160 < Sc < 1600

Typical range in Ionic Liquids: Sc > 1 x 10^4 Levich’s approximation very accurate for IL