Continuum Thermodynamic Models for Electrochemical Interfaces

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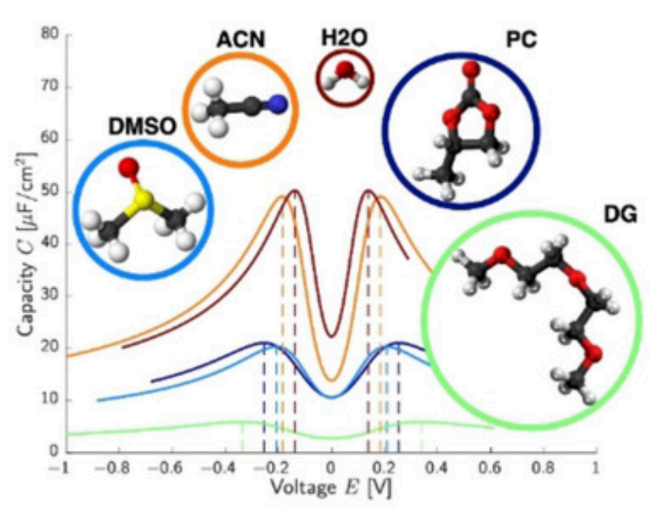
Leibniz
Association

IPAM

Workshop II: Bridging Scales from Atomistic to Continuum in Electrochemical Systems

08.10.2025



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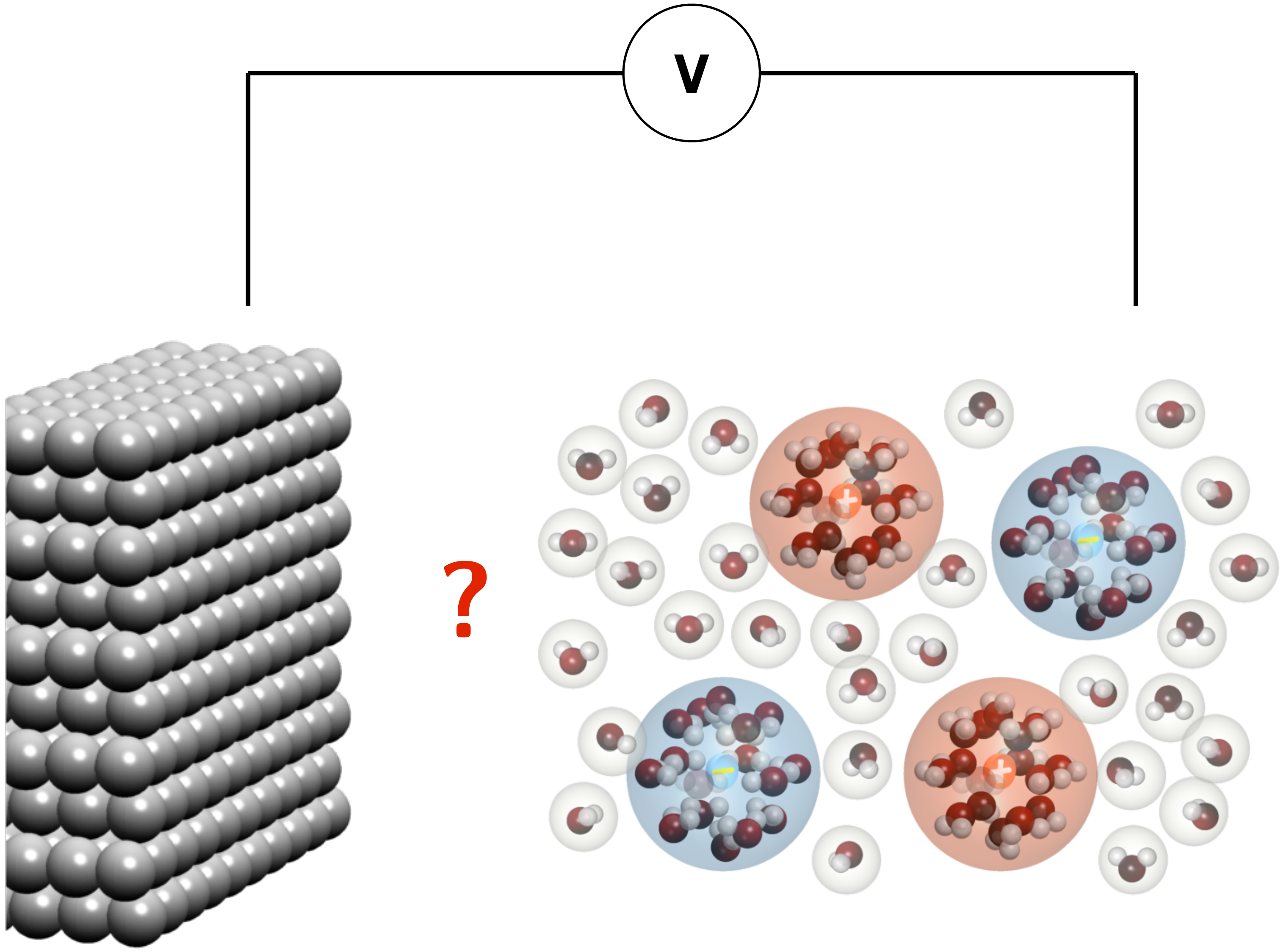
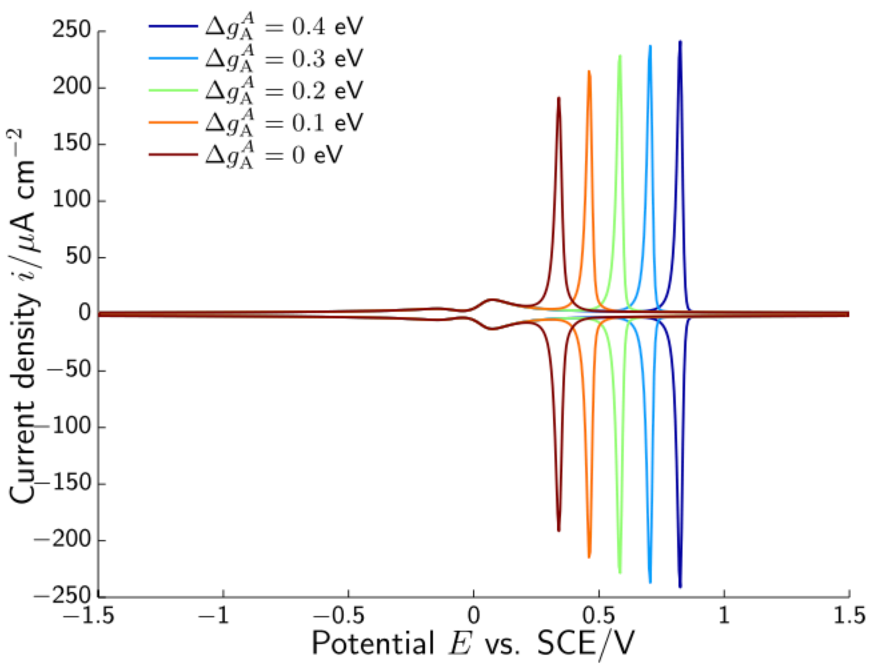
Electrode-Electrolyte Interfaces



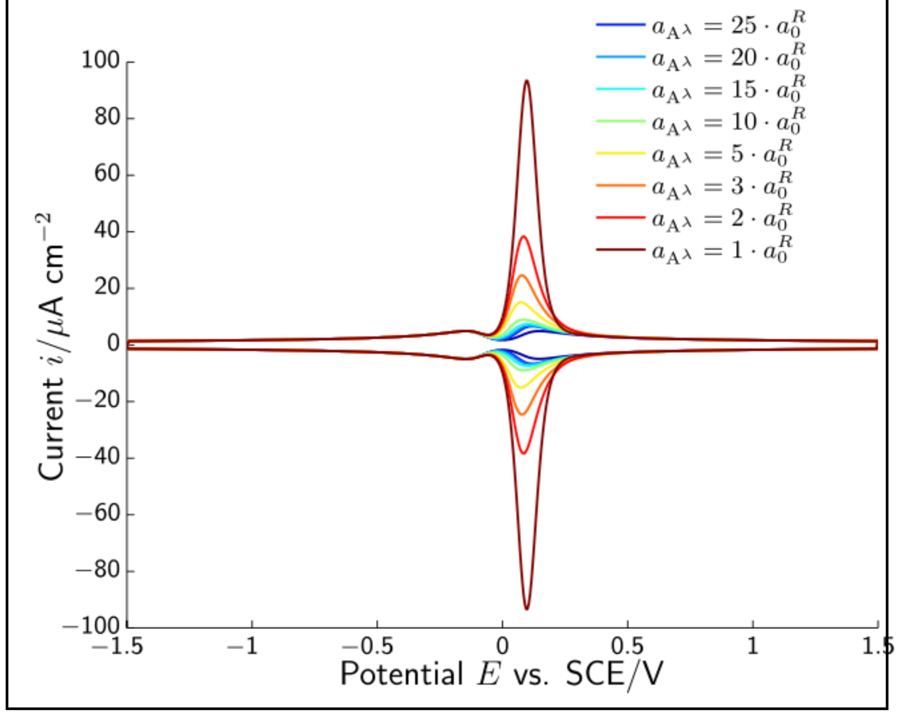
Goal — Develop a rigorous, thermodynamically consistent modeling framework for liquid electrolytes and charged interfaces.

What we can do … predict CVs

Pseudo-capacitance

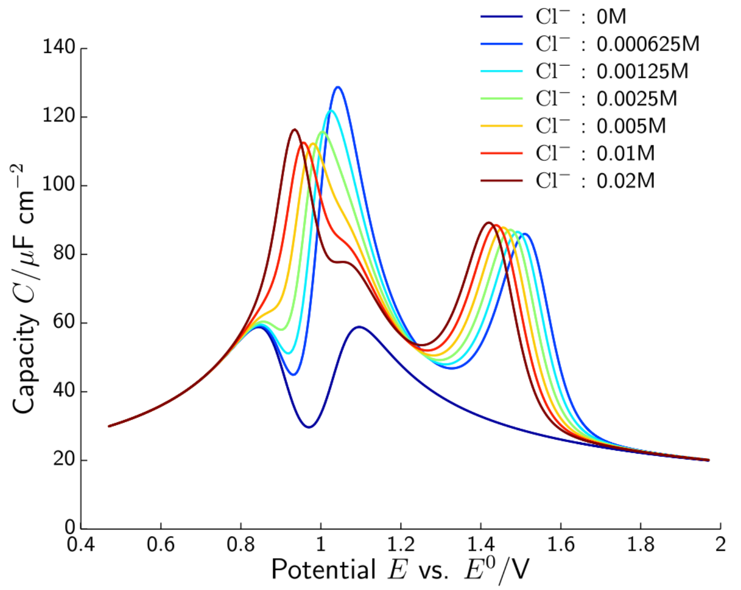


Partial charge transfer

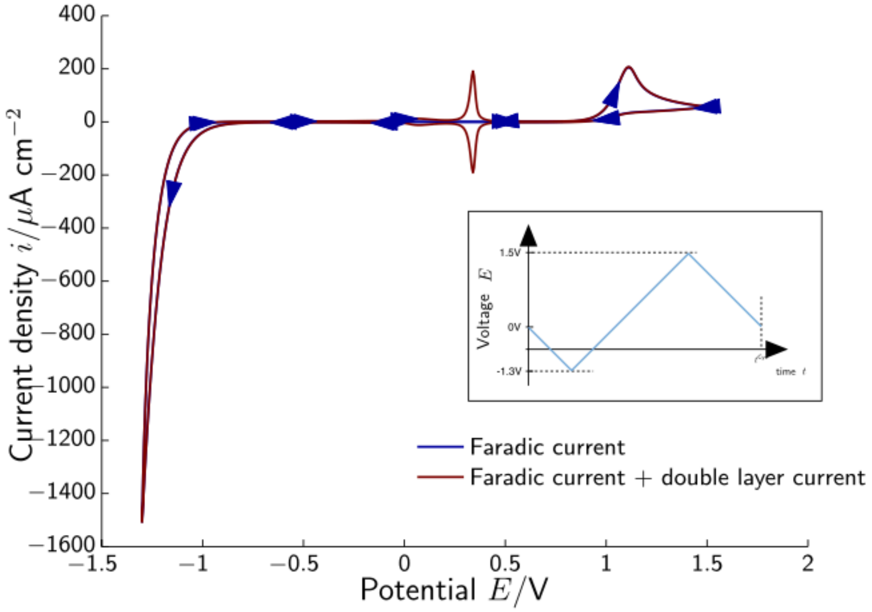


Solutions mixtures

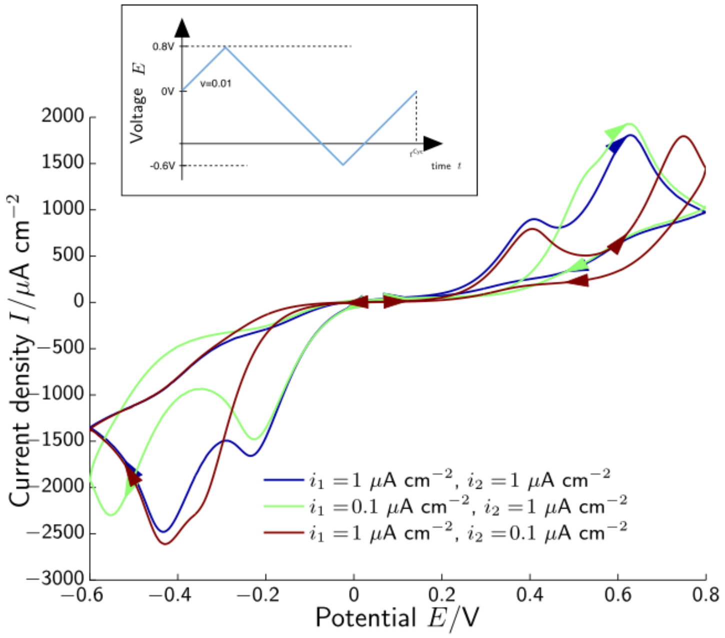
$Ag(110)—xM KCl + (0.02 - x)M KPF_6$



CVs of charge transfer

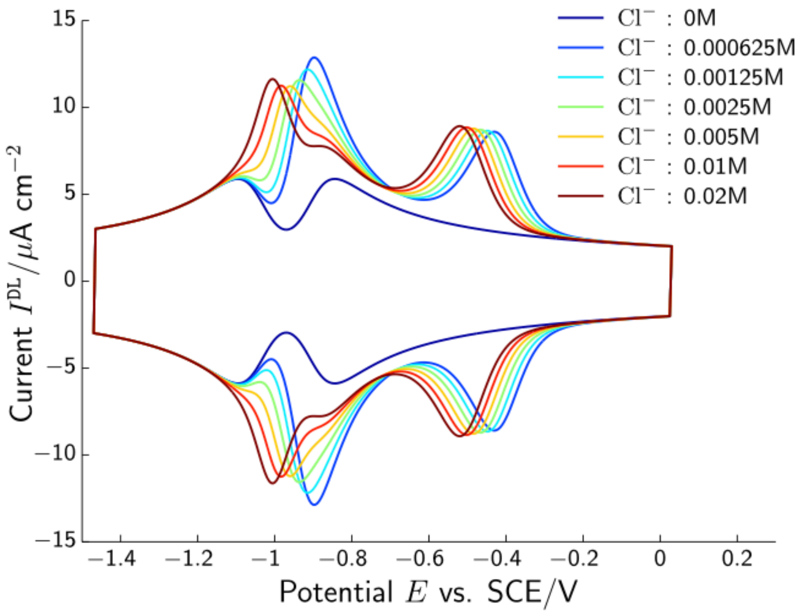


2-step reactions

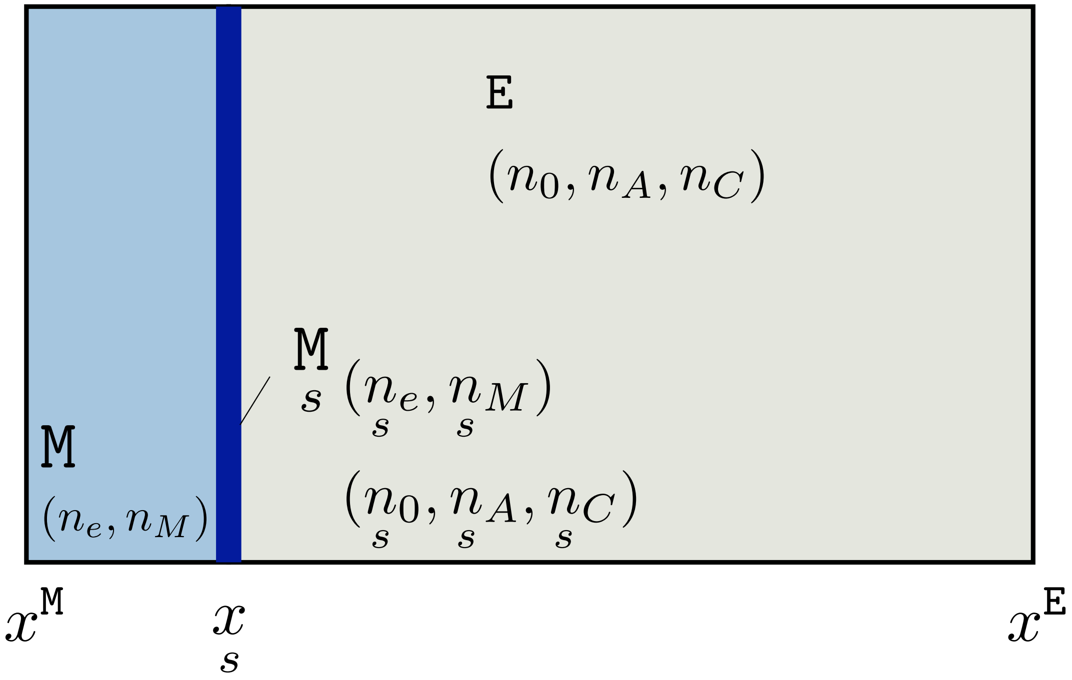


Solutions mixtures

$Ag(110)—xM KCl + (0.02 - x)M KPF_6$



The metal/electrolyte interface - general modeling

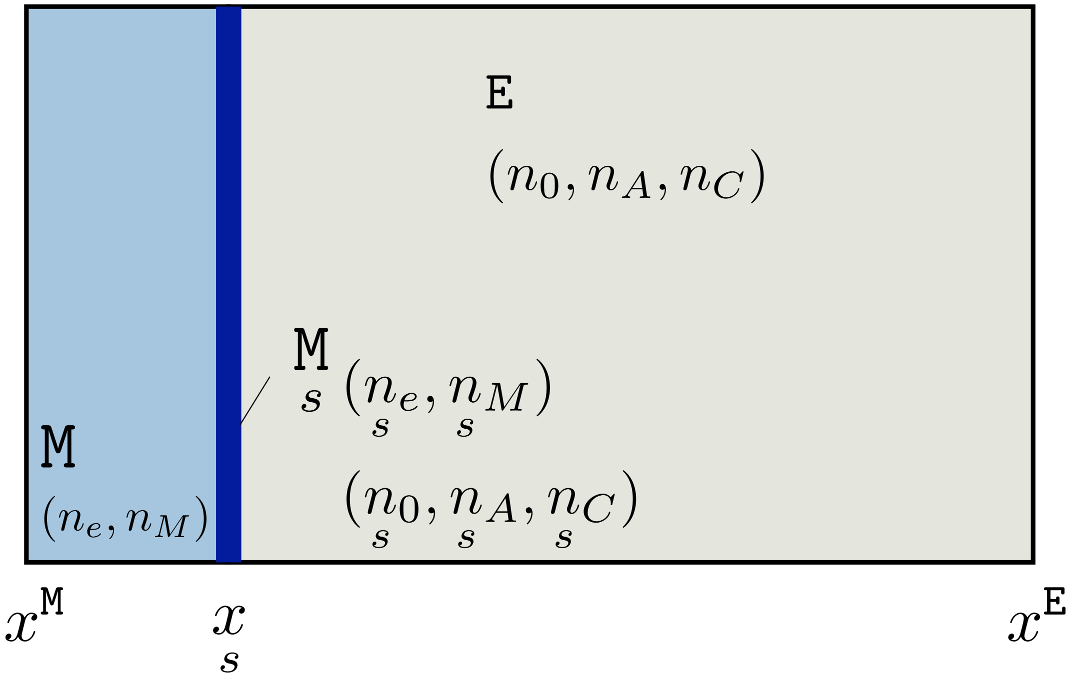


General field theory of the coupled non-equilibrium thermo-electrodynamics for volumes and surfaces

Literature selection

J. Meixner, *Annalen der Physik*, **1943**, 435, 244–270.
S. de Groot and P. Mazur, Non-Eq. Thermodynamics, Dover **1984**.
I. Müller, Thermodynamics, Pitman, **1985**.
M. Landstorfer, *Dissertation*, Universität Ulm, **2013**
C. Guhlke, *Dissertation*, TU Berlin, **2015**
D. Bothe and W. Dreyer, *Acta Mechanica*, **2014**, 1–49
R. Müller and M. Landstorfer, *Entropy, **2023,*** 416

The metal/electrolyte interface - general modeling



Volume and Surface species densities

Volume Ω_V considered as mixture of species densities $n_\alpha(\mathbf{x}, t), \;\; \alpha \in I_V \;\; [\text{mol}/\text{m}^3]$

Surface S considered as mixture of surface species densities $\underset{\text{s}}{n}_\alpha(\underset{\text{s}}{\mathbf{x}}, t), \;\; \alpha \in I_S \;\; [\text{mol}/\text{m}^2]$

Volume and Surface species densities

Volume Ω_V considered as mixture of species densities $n_\alpha(\mathbf{x},t),\ \alpha \in I_V \ \left[\,\mathrm{mol/m^3}\,\right]$

Surface S considered as mixture of surface species densities $\underset{s}{n}_\alpha(\underset{s}{\mathbf{x}},t),\ \alpha \in I_S \ \left[\,\mathrm{mol/m^2}\,\right]$

Free energy densities and chemical potentials

Free energy density of the volume Ω_V $\quad \rho\psi(n_0,\dots,n_{N_V}) \ \left[\,\mathrm{J/m^3}\,\right]$

Chemical potential of constituent A_α

$$\boxed{\mu_\alpha = \frac{\partial \rho\psi}{\partial n_\alpha} \ [\,\mathrm{J}\,]}$$

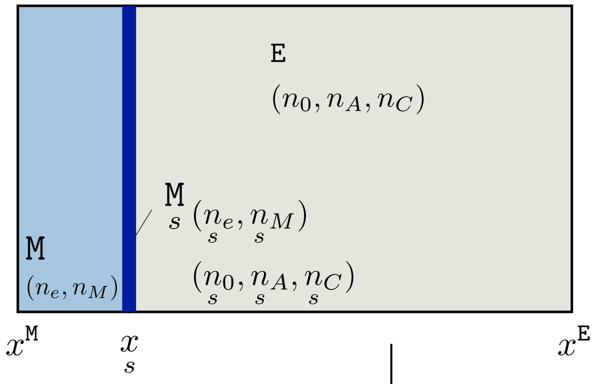
Free energy density of the surface S $\quad \underset{s}{\psi}(\underset{s}{n}_0,\dots,\underset{s}{n}_{N_S}) \ \left[\,\mathrm{J/m^2}\,\right]$

Surface chemical potential of $\underset{s}{\mathrm{A}}_\alpha$

$$\boxed{\underset{s}{\mu}_\alpha = \frac{\partial \underset{s}{\psi}}{\partial \underset{s}{n}_\alpha} \ [\,\mathrm{J}\,]}$$

The metal/electrolyte interface - General modeling

Volume $\Omega^{\pm}$



Surface S

Material Modeling - Electrolyte

Task: Chemical potentials μ_α of all species derived from a free energy density

$$\rho\psi = \rho\psi^{\mathsf{Mix}} + \rho\psi^{\mathsf{Ref}} + \rho\psi^{\mathsf{Mech}} + \ldots$$

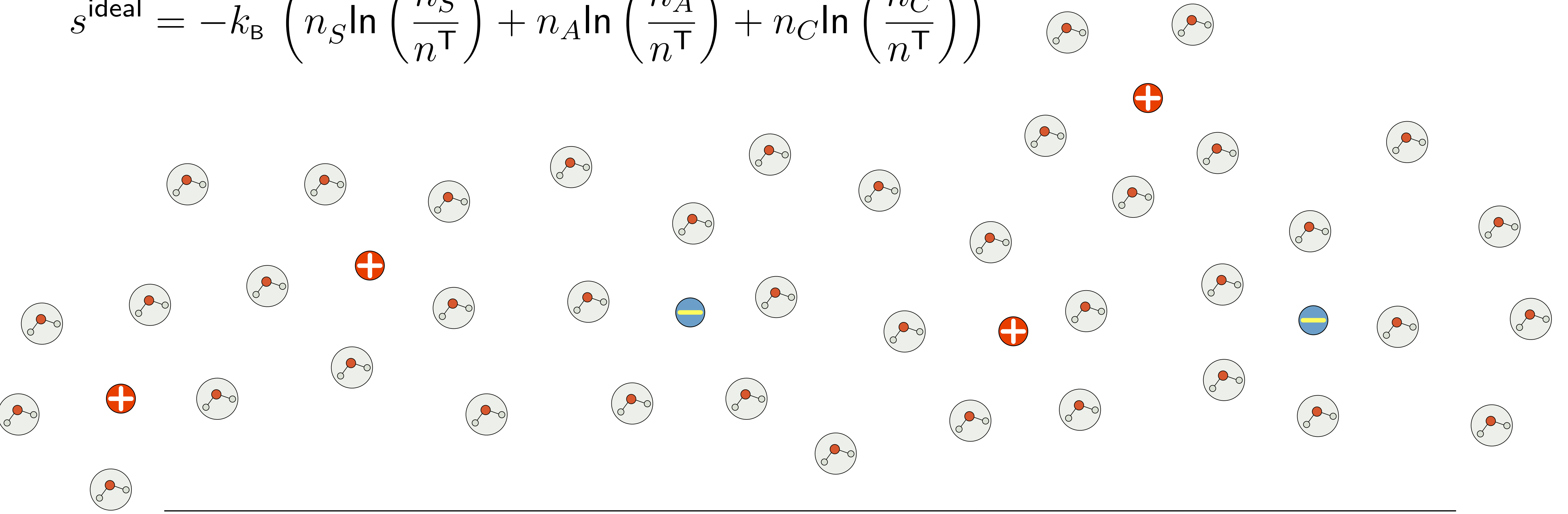
- Entropy of mixing
- Mechanical contributions
- Reference contributions
- Debye Hückel
- ... (e.g. Polarization)

$$\boxed{\mu_\alpha = \frac{\partial \rho\psi}{\partial n_\alpha} \ [\,\mathsf{J}\,]}$$

Material Modeling - Electrolyte - Entropy of mixing

$$\mu_\alpha = \frac{\partial \rho\psi}{\partial n_\alpha} \quad [\,\mathsf{J}\,]$$

$$s^{\text{ideal}} = -k_{\text{B}} \left(n_S \ln\left(\frac{n_S}{n^{\text{T}}}\right) + n_A \ln\left(\frac{n_A}{n^{\text{T}}}\right) + n_C \ln\left(\frac{n_C}{n^{\text{T}}}\right) \right)$$



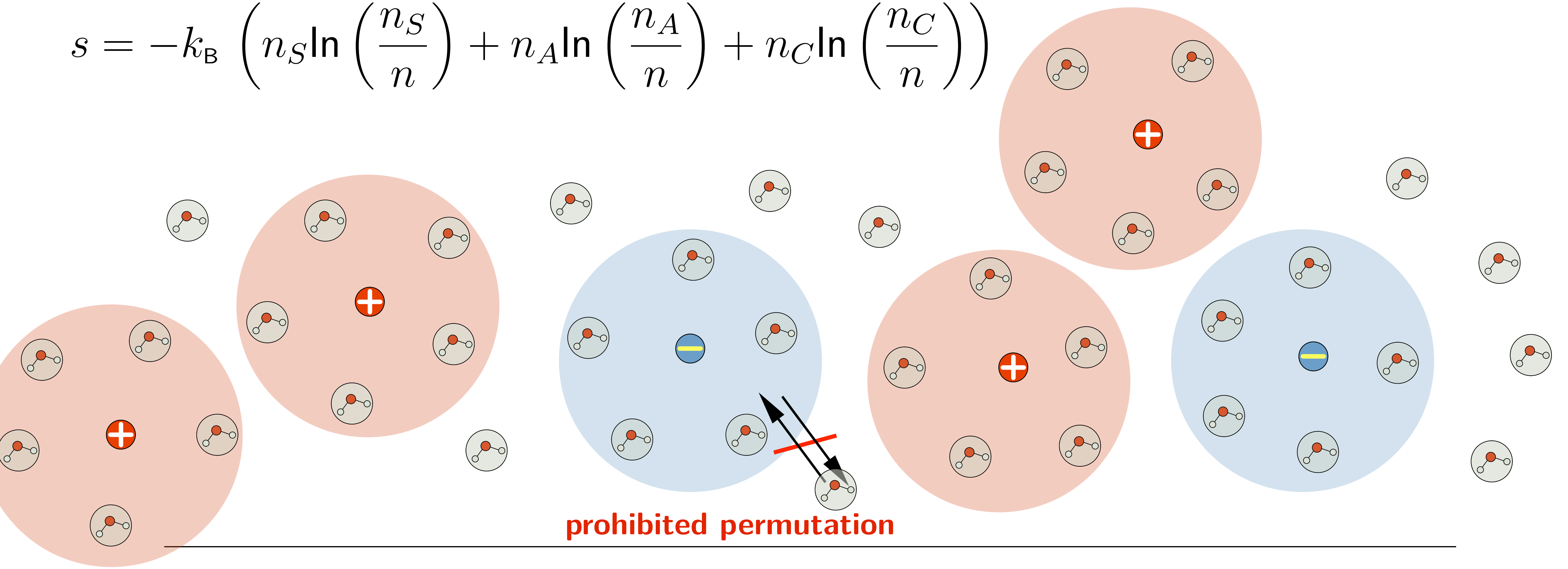
Basic idea: Count the number of permutations in the mixture

... common basis for ideal mixtures etc.

Material Modeling - Electrolyte - Entropy of mixing

$$\mu_\alpha = \frac{\partial \rho\psi}{\partial n_\alpha} \quad [\,\mathrm{J}\,]$$

$$s = -k_{\mathrm{B}} \left(n_S \ln\left(\frac{n_S}{n}\right) + n_A \ln\left(\frac{n_A}{n}\right) + n_C \ln\left(\frac{n_C}{n}\right) \right)$$



Basic idea: Count the number of permutations in the mixture

Each ion *bounds* κ_α solvent molecules

Note: *solvation impacts (implicitly) the mole fraction in solution!*

$$\boxed{y_\alpha = \frac{n_\alpha}{n}} \quad \text{with} \quad \boxed{n = n_S + n_A + n_C}$$

$$\boxed{n_S = n_S^{\mathrm{R}} - \kappa_A \cdot n_A - \kappa_C \cdot n_C}$$

dependent on the solvation number

Material Modeling - Electrolyte - Mechanical contribution

Volume occupied by the mixture at the reference pressure p^R

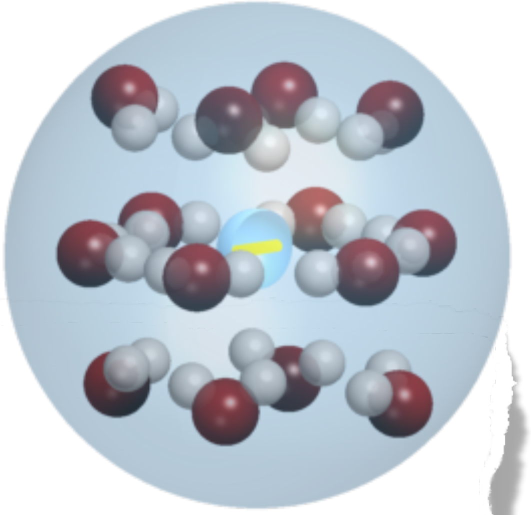
$$V_{p^R} = \sum_{\alpha=0}^{\mathrm{n}} v_\alpha^R N_\alpha$$

Note: Other mechanical models possible

solvent

$v_0^R \neq v_\alpha^R$

solvated ion



Tait equation of state

$$p = p^R + K \left(\left(\frac{V_{p^R}}{V} \right)^m - 1 \right)$$

with m=7 and K = 0.32 GPa

leads to the mechanical free energy contribution

$$\rho\psi^M = (K - p^R) \left(1 - \left(\sum_{\alpha=0}^{\mathrm{n}} v_\alpha^R n_\alpha \right) \right) - K \frac{1}{1-m} \left(\left(\sum_{\alpha=0}^{\mathrm{n}} v_\alpha^R n_\alpha \right)^m - \sum_{\alpha=0}^{\mathrm{n}} v_\alpha^R n_\alpha \right)$$

Goal: Incompressible limit $K \to \infty$

Material Modeling - Electrolyte

Chemical potentials

Incompressible limit $K \to \infty$: (entails pressure p as variable)

$$\mu_\alpha = \psi_\alpha^R + k_B T \ln(y_\alpha) + v_\alpha^R p \qquad \alpha = 0, 1, \ldots, n$$

and

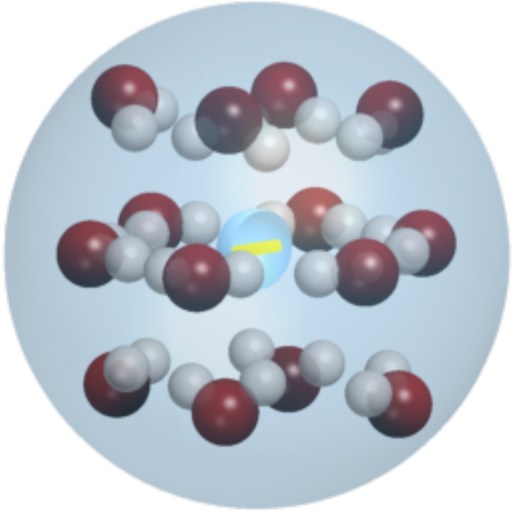
$$\sum_{\alpha=0}^{n} v_\alpha^R y_\alpha = \frac{1}{n}$$

Incompressibility constraint

solvent

$v_0^R \neq v_\alpha^R$

solvated ion



Impact of solvation

- Entropically: (implicitly) via the mole fraction
- Mechanically: via the pressure and the partial molar volume

$$y_\alpha = \frac{n_\alpha}{n}$$

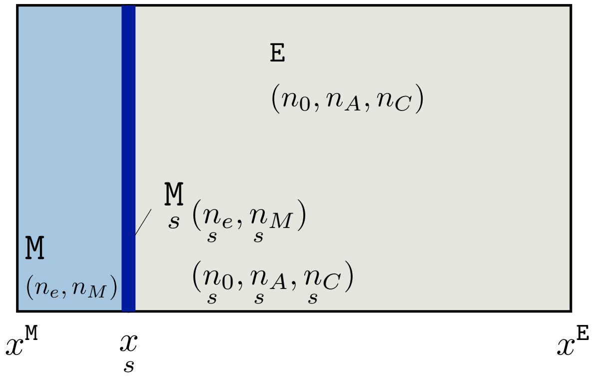
with

$$n = n_S + n_A + n_C$$

$$n_S = n_S^R - \kappa_A \cdot n_A - \kappa_C \cdot n_C$$

W. Dreyer, C. Guhlke and M. Landstorfer, Electrochemistry Communications, 2014, **43**, 75 – 78.

The metal/electrolyte interface - Modeling



- Diffusional equilibrium in $\Omega^{\pm}$

$$\nabla \mu_\alpha + e_0 z_\alpha \nabla \varphi = \mathbf{0} \qquad \alpha = 1, \ldots, N$$

which can be integrated as

$$\mu_\alpha(\mathbf{x}) + e_0 z_\alpha \varphi(\mathbf{x}) = \mu_\alpha^{\pm} + e_0 z_\alpha \varphi^{\pm}$$

Balance equations for $\rho_\alpha, \ \alpha = 1, \ldots, \mathrm{N}$

$$\frac{\partial \rho_\alpha}{\partial t} = -\mathrm{div}\, (\rho_\alpha \mathbf{v} + \mathbf{J}_\alpha) + r_\alpha$$

with

$$\mathbf{J}_\alpha \propto \nabla(\mu_\alpha - \mu_{\mathrm{N}}) + e_0 (\frac{z_\alpha}{m_\alpha} - \frac{z_{\mathrm{N}}}{m_{\mathrm{N}}}) \nabla \varphi$$

- Electrical equilibrium in $\Omega^{\pm}$

$$-\varepsilon_0 \mathrm{div}\, (\nabla \varphi) = q \qquad \text{with} \qquad q = \sum_{\alpha=0}^{N} z_\alpha e_0 n_\alpha$$

- Mechanical equilibrium in $\Omega^{\pm}$

$$\nabla p = -q \nabla \varphi$$

$$\frac{\partial \rho \mathbf{v}}{\partial t} + \mathrm{Div}\, (\rho \mathbf{v} \otimes \mathbf{v}) = \eta \Delta \mathbf{v} + \nabla p + q \nabla \varphi$$

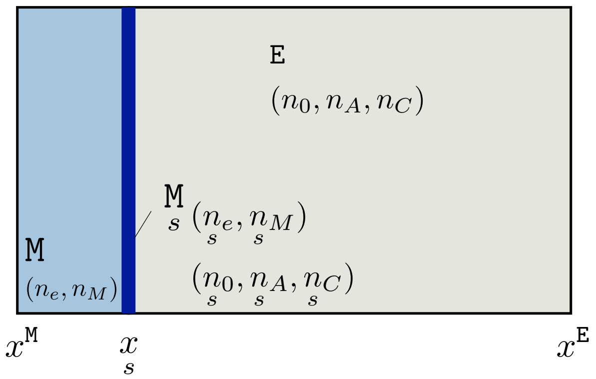
thermodynamic closure relations

$$\mu_\alpha = \psi_\alpha^R + k_{\mathrm{B}} T \ln (y_\alpha) + v_\alpha^R \, p \qquad \alpha = 0, 1, \ldots, \mathrm{n}$$

$$\sum_{\alpha=0}^{\mathrm{n}} v_\alpha^R y_\alpha = \frac{1}{n}$$

Incompressibility constraint

The metal/electrolyte interface - Modeling



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which can be integrated as

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General modeling framework for various salts, solvents, surfaces

- Electrical equilibrium in $\Omega^{\pm}$

$$-\varepsilon_0 \text{div}\,(\nabla\varphi) = q \qquad \text{with} \qquad q = \sum_{\alpha=0}^{N} z_\alpha e_0 n_\alpha$$

- Mechanical equilibrium in $\Omega^{\pm}$

$$\nabla p = -q\nabla\varphi$$

thermodynamic closure relations

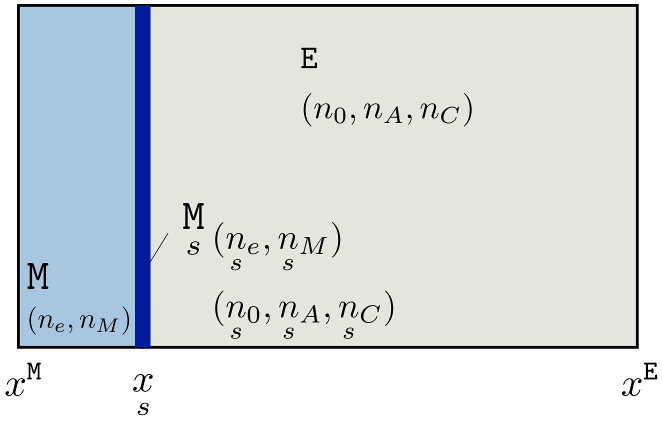
$$\boxed{\mu_\alpha = \psi_\alpha^R + k_{\text{B}} T \ln\left(y_\alpha\right) + v_\alpha^R\, p} \qquad \alpha = 0, 1, \ldots, \text{n}$$

$$\boxed{\sum_{\alpha=0}^{\text{n}} v_\alpha^R y_\alpha = \frac{1}{n}}$$

Incompressibility constraint

Electrolyte - Charge density in equilibrium

$$\nabla \mu_\alpha - e_0 z_\alpha \nabla \varphi = \mathbf{0} \qquad \alpha = 1, \ldots, \mathrm{n}$$



$$q^F = e_0 \frac{\sum_{\alpha=1}^{\mathrm{n}} z_\alpha \cdot \underline{y_\alpha(\varphi, p)}}{\sum_{\alpha=0}^{\mathrm{n}} v_\alpha^R \cdot \underline{y_\alpha(\varphi, p)}} = \underline{q^F(\varphi, p)}$$

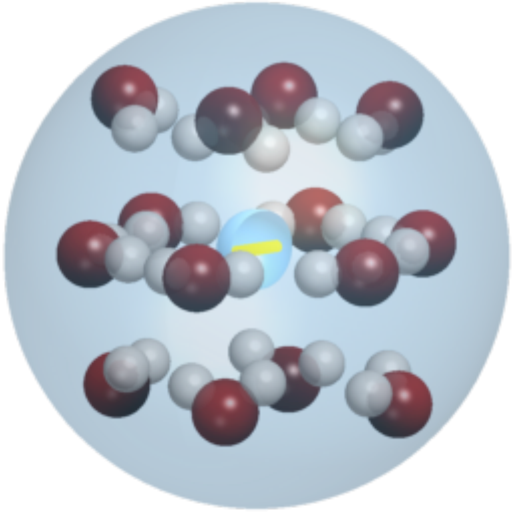
solvent

$$v_0^R \neq v_\alpha^R$$

Charge density is pressure ***and*** *potential dependent*

Pressure term covers the actual ***size*** *of the species*

solvated ion



Consequence: Poisson equation and momentum balance do **not** decouple

$$\varepsilon_0(1+\chi)\mathrm{div}\,\nabla\varphi = -q^{\mathrm{F}}(\varphi, p)$$
$$\nabla p = -q^{\mathrm{F}}(\varphi, p)\nabla\varphi$$

W. Dreyer, C. Guhlke, R. Müller, *PCCP*, 2013, **15**, 7075–7086

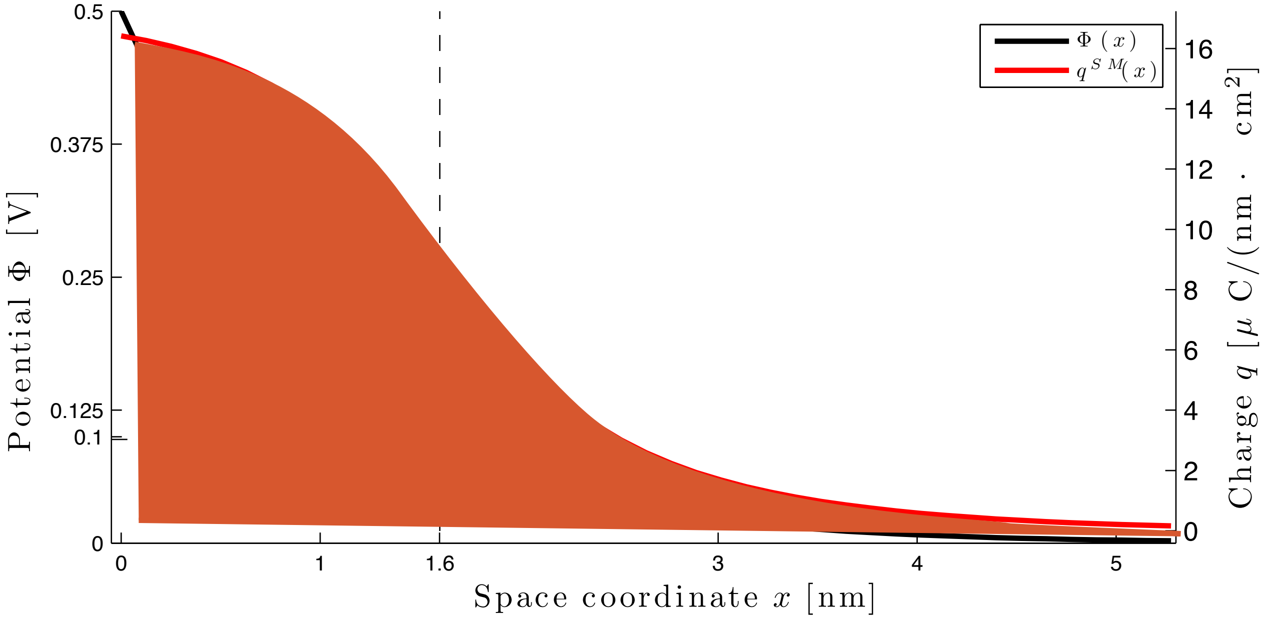
W. Dreyer, C. Guhlke and M. Landstorfer, Electrochem. Comm., 2014, **43**, 75 – 78.

Validation: Charge and Capacity of the double layer

Measured current: $I = \dfrac{dQ}{dt}$

Interface charge: $Q = Q_{\mathtt{E}} \;+ \underset{s}{q_{\mathtt{E}}}$ with $Q_{\mathtt{E}} = \displaystyle\int_0^{x_{\mathtt{E}}} q\, dx$

Interface capacity: $C = \dfrac{dQ}{dU}$



Based on our constitutive chemical potentials and the equilibrium conditions we derived expressions for the capacity

Charge density representation in equilibrium

experiment

$Q \approx \pm 100 \mu\mathsf{C}/\mathsf{cm}^2$

$C \approx 80 \mu\mathsf{F}/\mathsf{cm}^2$

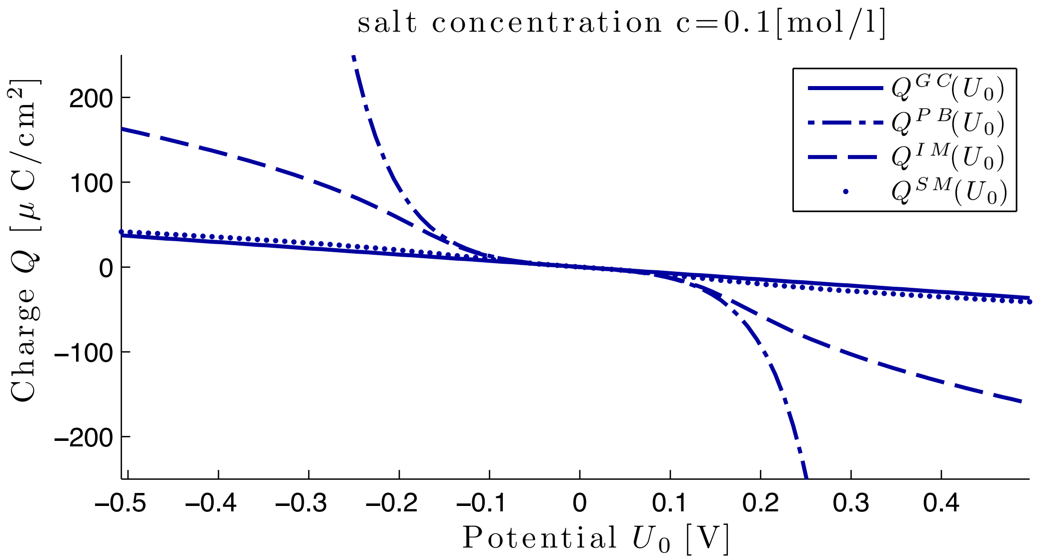
- Poisson–Boltzmann approximation ($p = p^B$):

$$q^{\mathsf{PB}} = \sum_{\alpha=1}^{\mathsf{n}} z_\alpha n_\alpha^B \cdot \mathsf{e}^{-z_\alpha \frac{e_0}{k_{\mathsf{B}} T} \Phi} = q^{\mathsf{PB}}(\Phi)$$

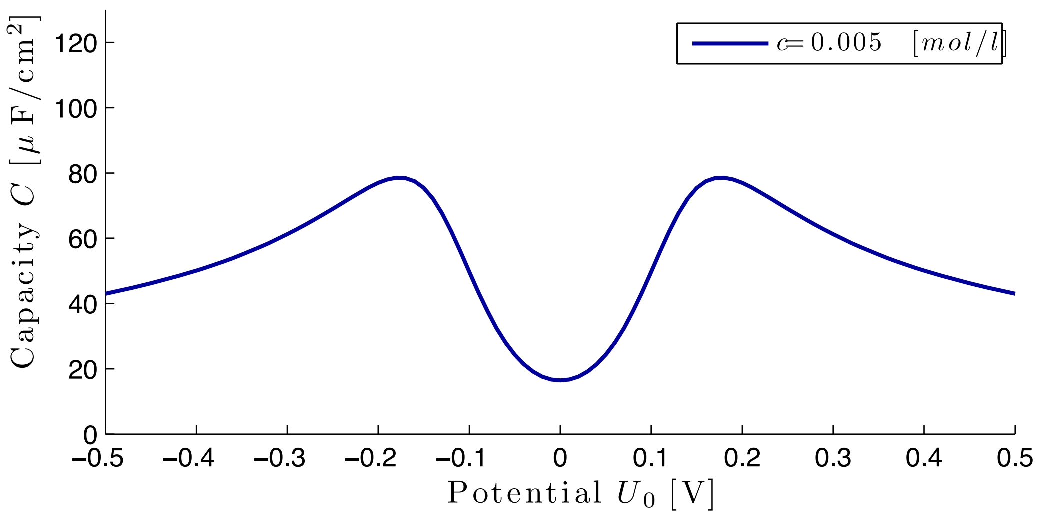
- Gouy–Chapman approximation ($\mathsf{e}^x \approx 1 + x$):

$$q^{\mathsf{GC}} = -\left(\frac{e_0}{k_{\mathsf{B}} T} \sum_{\alpha=1}^{\mathsf{n}} z_\alpha^2 n_\alpha^B\right) \cdot \Phi = q^{\mathsf{GC}}(\Phi)$$

Charge



Capacity



Validation: Ag(abc)|KPF_6 – non-adsorbing salt - Capacity

Experimental data

- Capacity of single crystal Ag(111)|$KPF_6(H_2O)$
- Variation of the salt concentration
- Capacity depends non-linear on the applied voltage

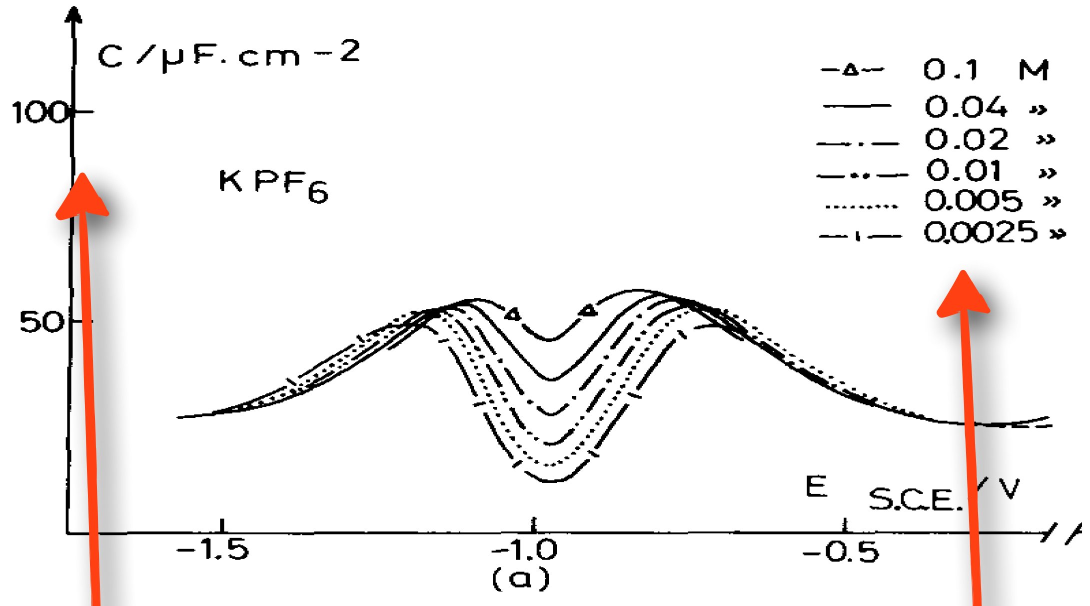
Mathematical model

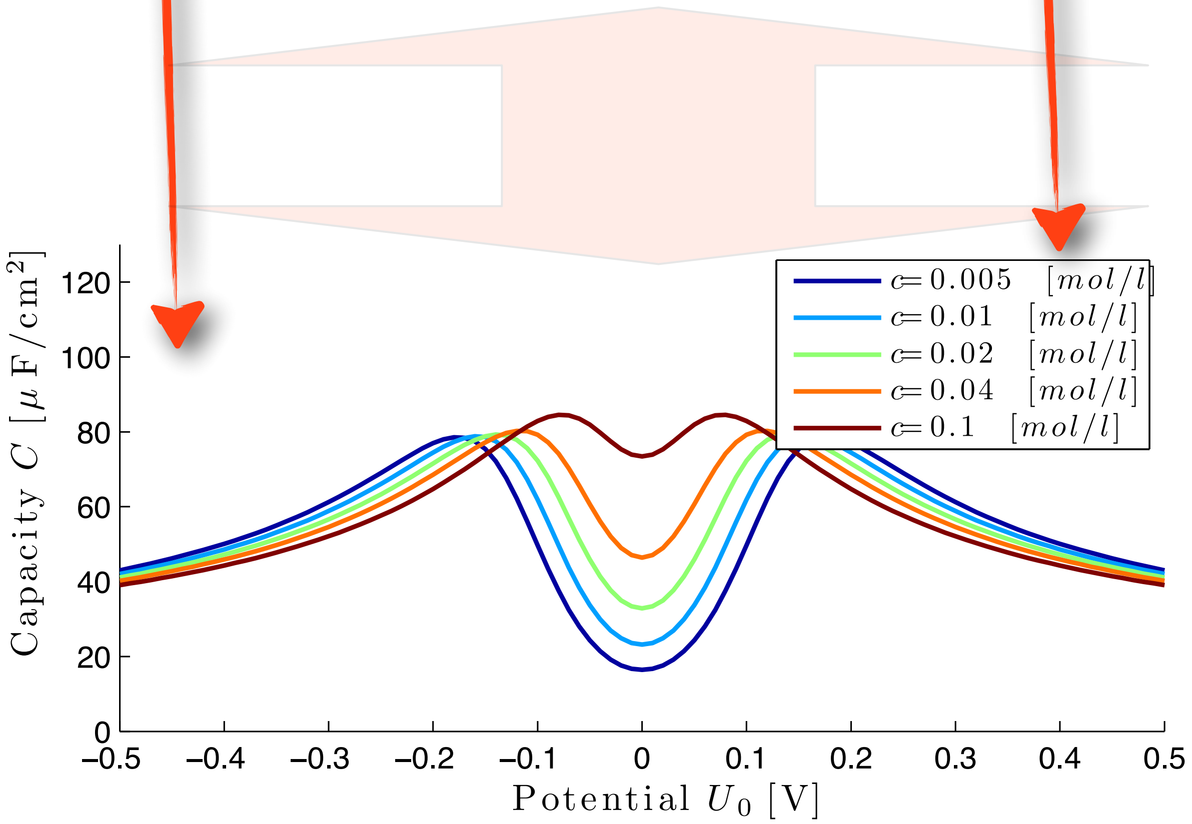
- Qualitative agreement
  - 1V potential range
- Quantitative agreement
  - of a **single** capacity curve (-0.5V - 0.5V)
  - regarding the salt variation

No parameter adjustment

self consistent prediction of capacity data

Fig. 3 of G. Valette, *J. of Electroanal. Chem.*, 1981, **122**, 285 – 297.





M. Landstorfer, C. Guhlke and W. Dreyer, Electrochim. Acta., 2016, **201**, 187 – 219.

Remarks: Charge and Capacity of the double layer

Interface capacity: $\boxed{C = \frac{dQ}{dU}}$ with $C_{\mathtt{M}} = \frac{dQ_{\mathtt{M}}}{dU}$

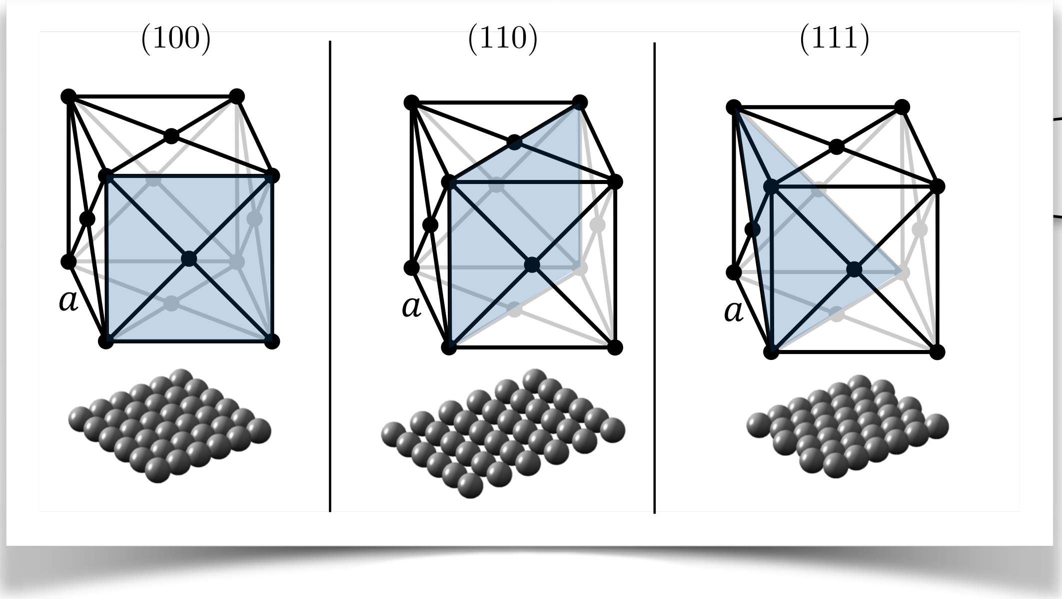
Note: No single equation, but an algebraic equation system

$$C_{\mathtt{M}} = \frac{\varepsilon_0(1+\chi)}{\sqrt{2(p-p^{\mathtt{E}})}} \cdot q_{\mathtt{E}}(U^{\mathtt{M,E}}, p - p^{\mathtt{E}}) \quad \text{and} \quad g(U^{\mathtt{M,E}}, p - p^{\mathtt{E}}) = 0$$

... originates from the Poisson-momentum coupling due to solvation effect

Note: Relation between metal-surface/bulk-electrolyte potential drop $U^{M,E}$ to the applied/measured voltage U

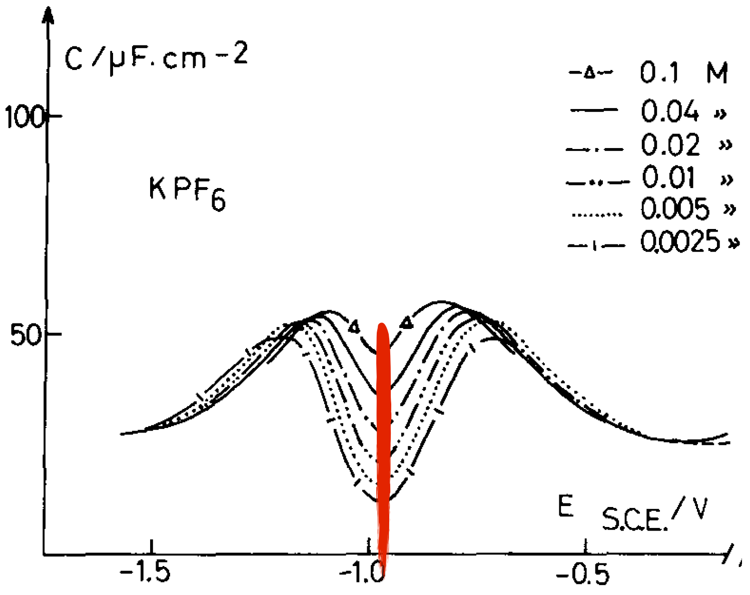
$$U^{\mathtt{M,E}} = U - U^{\mathtt{R}} \quad \text{with } U^{\mathtt{R}} = \text{const. and dependent on } \underset{s}{\mu_e^{\mathtt{M}}}$$



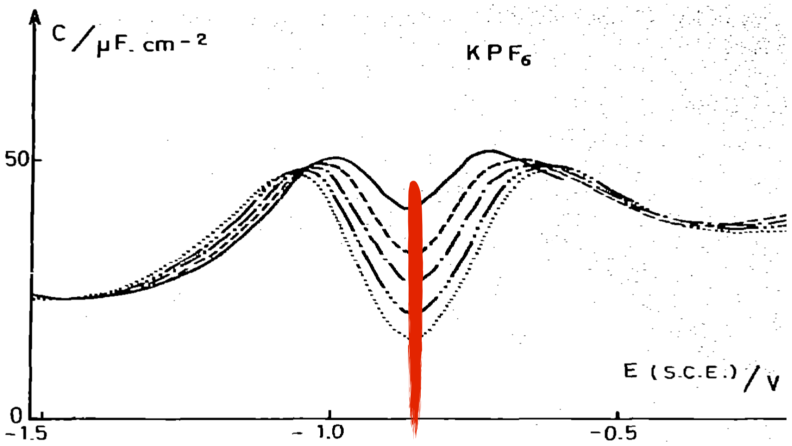
surface chemical potential of electrons

Validation: Ag(abc)|KPF$_6$ – non-adsorbing salt - work function

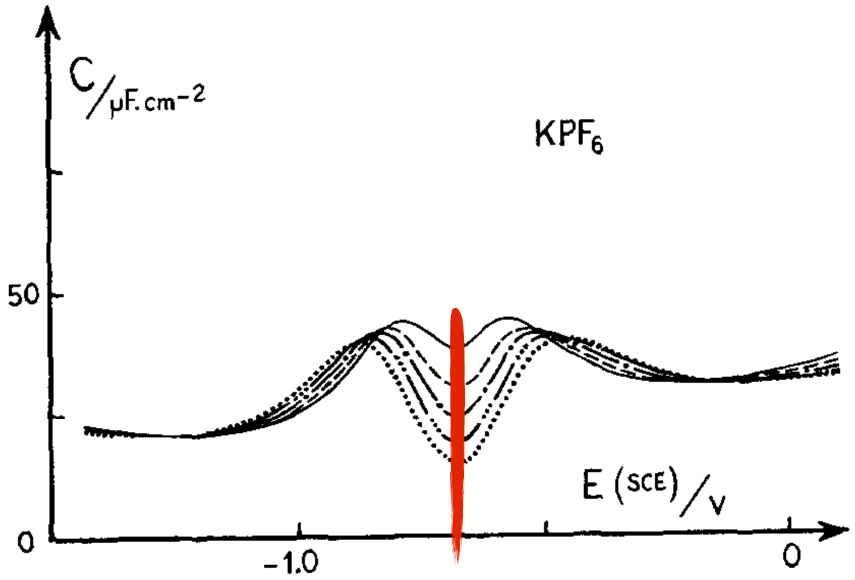
Ag(110)



Ag(100)



Ag(111)



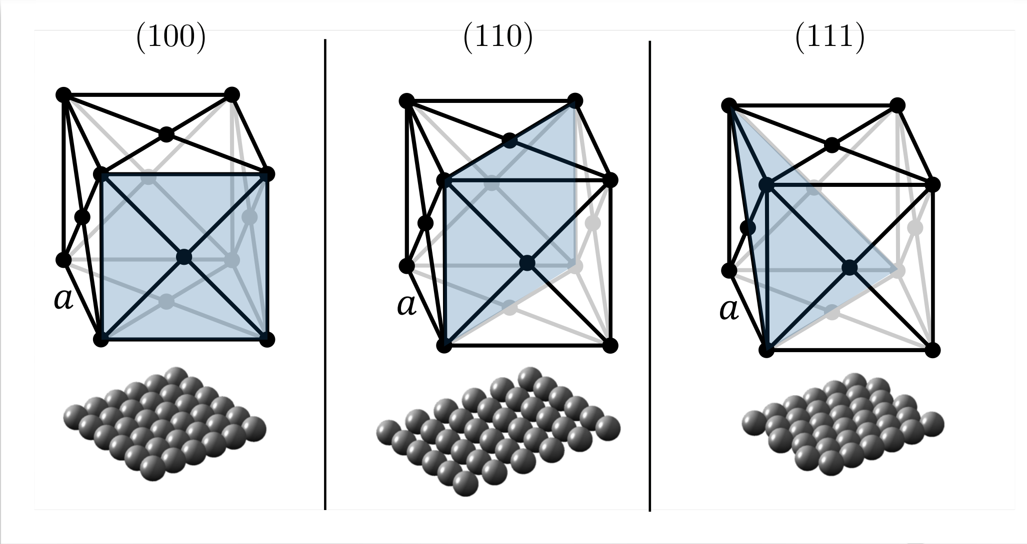
Data of G. Valette

Capacity minimum (Potential of zero charge for a non-adsorbing salt *E^0*) dependent on the

- metal surface orientation
- work function

A. Frumkin, A. Gorodetzkaya, *Z. Phys. Chem.*, **136** (1928) 215.

	(110)	**(100)**	**(110)**
	$\underset{s}{\mu_e}$	$\underset{s}{\mu_e}$	$\underset{s}{\mu_e}$
Ag	4.52	4.64	4.74

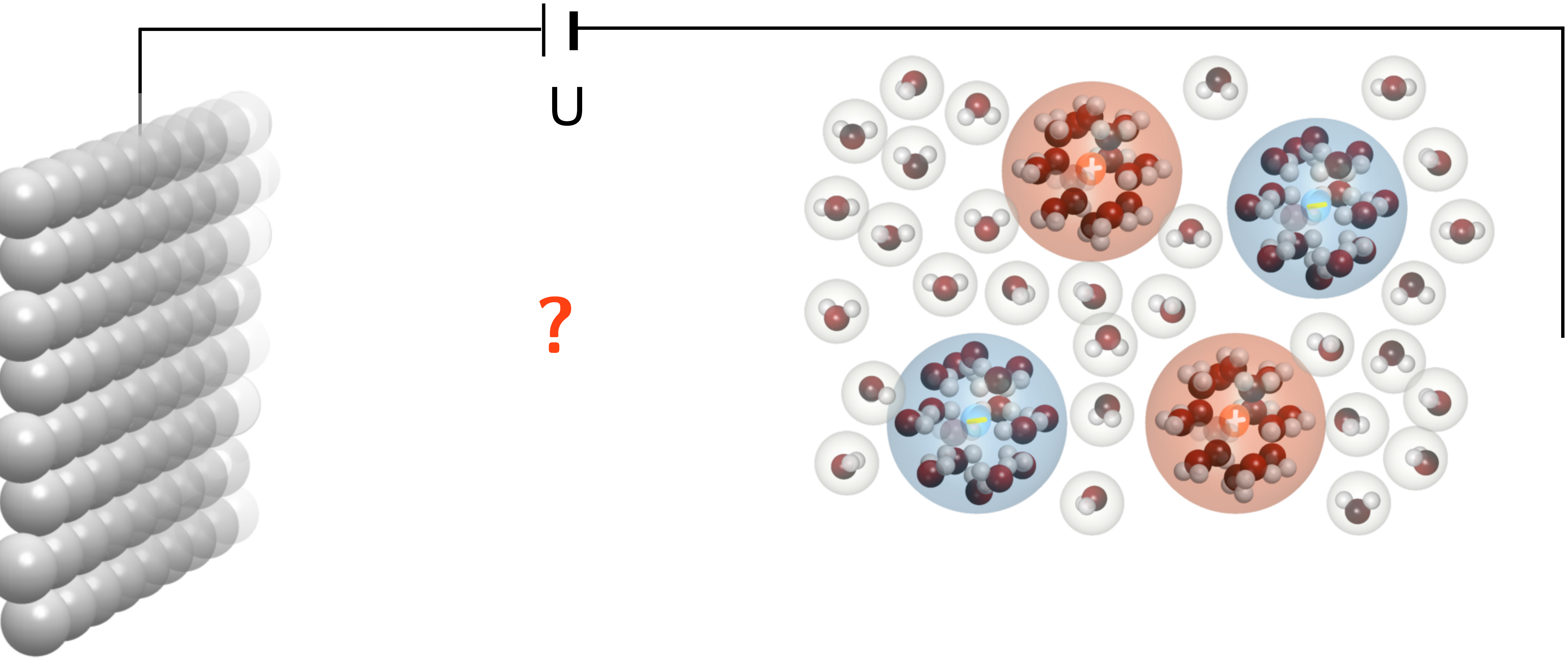


Our model predicts:

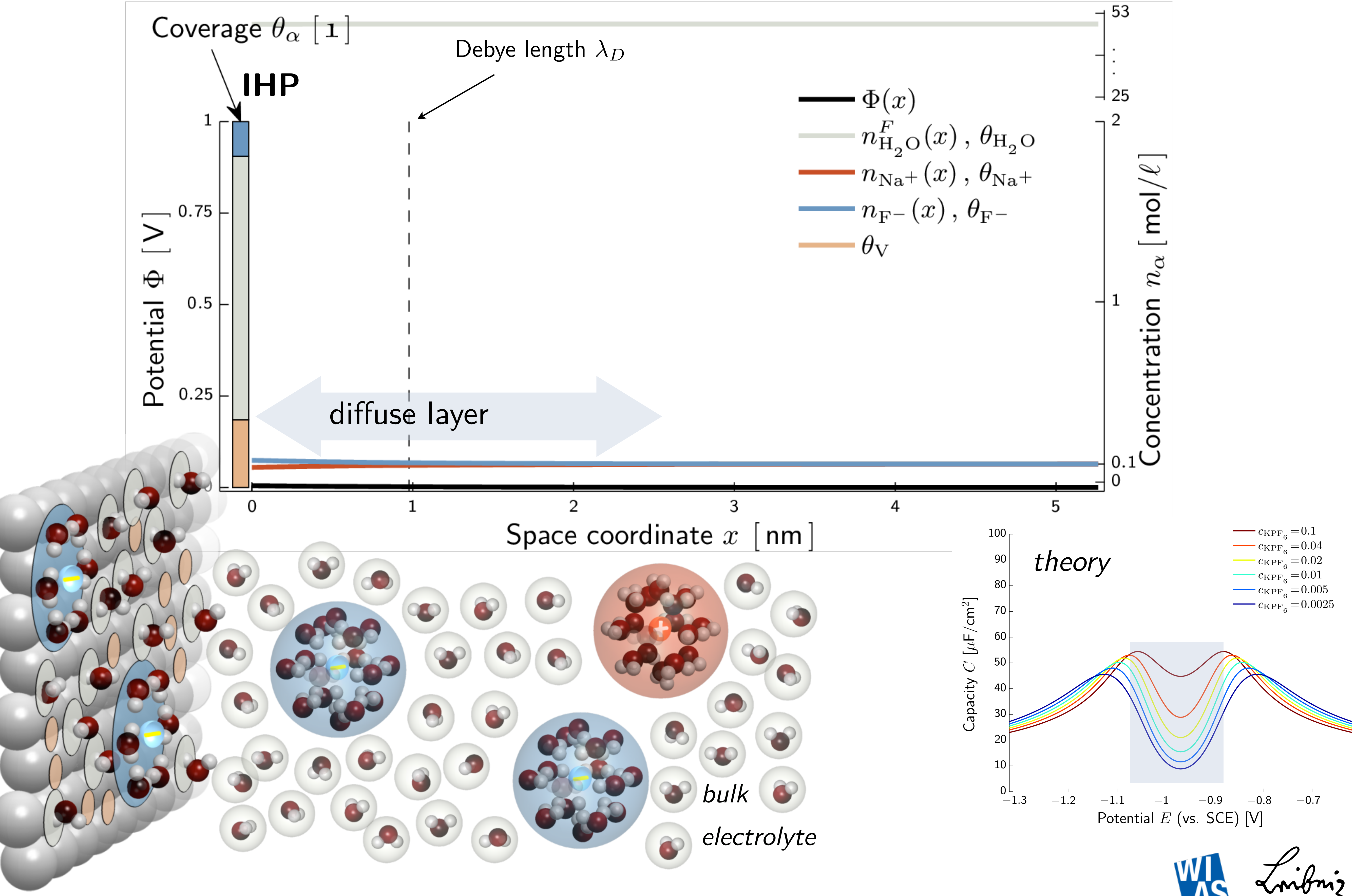
$$E^0 \propto -\underset{s}{\mu_e^{\mathtt{M}}}$$

self consistent incorporation of the PZC in the model

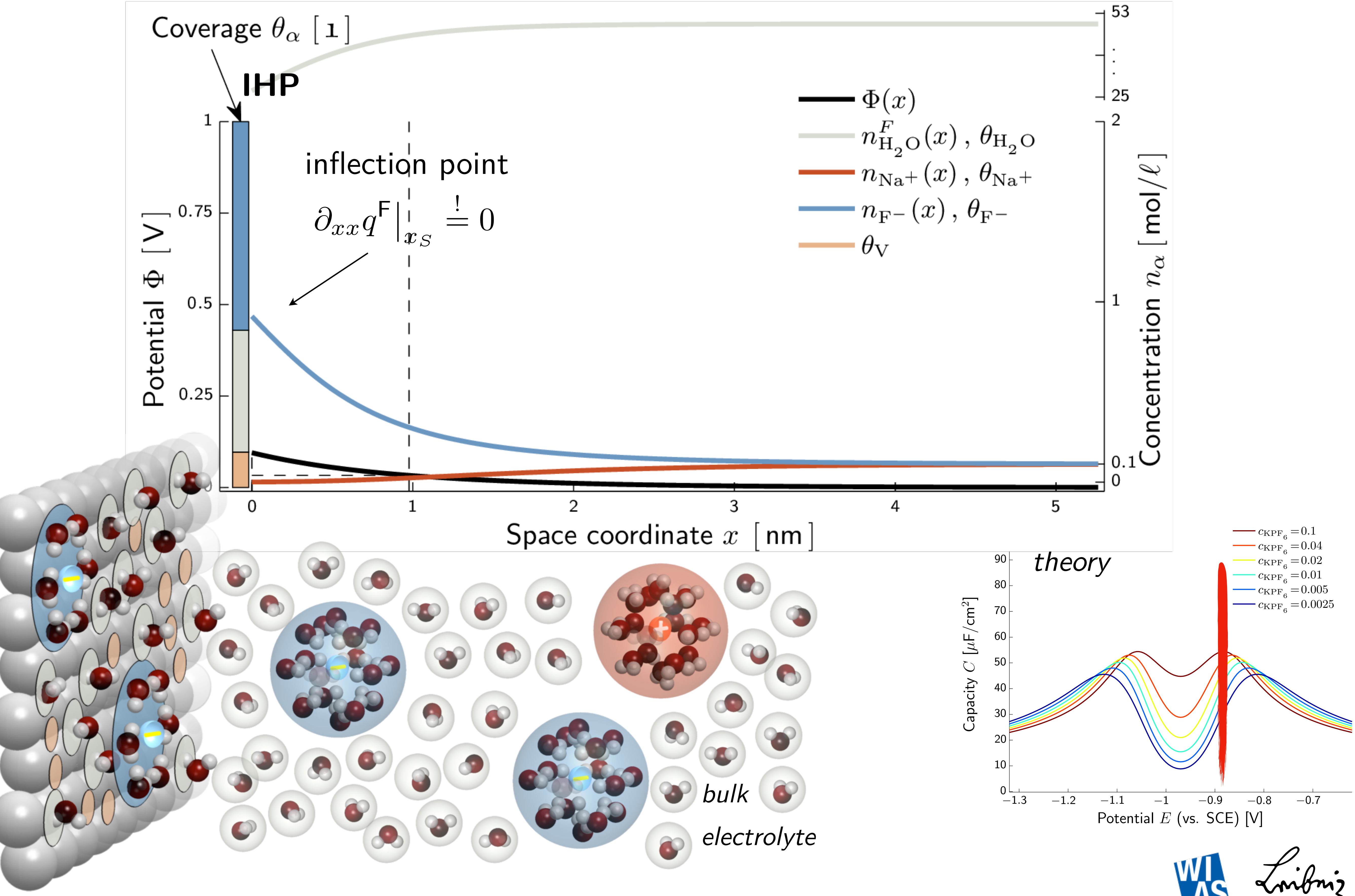
Structure of the double layer



Low potential regime (±~60mV)



Stern layer potential Φ_S~60mV



Definition of the Stern layer

IUPAC Definition

Stern layer
Counter and co-ions in immediate contact with a surface are said to be located in the Stern layer, and form with the fixed charge a molecular capacitor.

Our new definition

Stern layer
the domain $[0, x^S]$, where x^S is the inflection point of the free charge density q^{F}, *i.e.* $\partial_{xx} q^{\mathsf{F}}\big|_{x=x^S} = 0$. If no inflection point is present, no Stern layer is formed.

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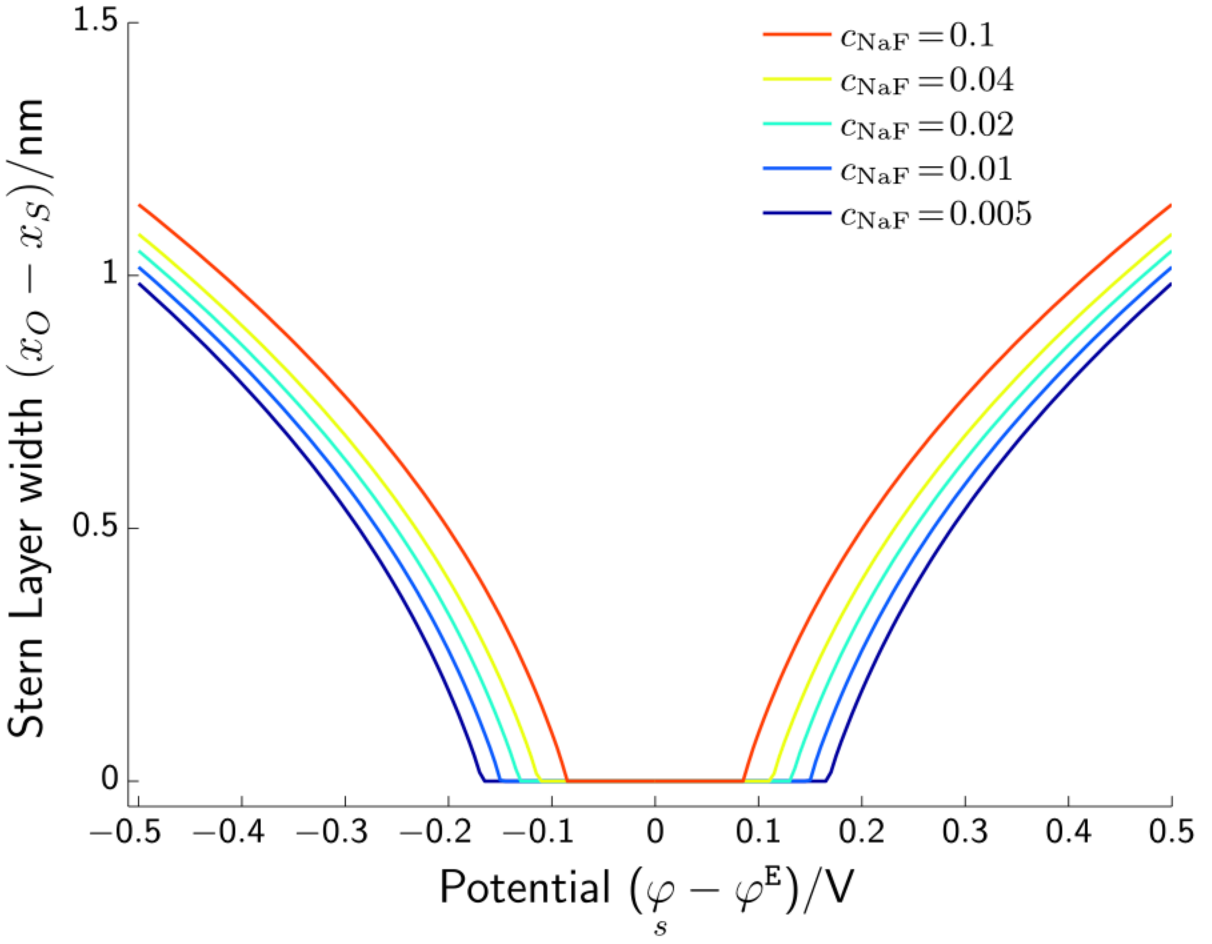
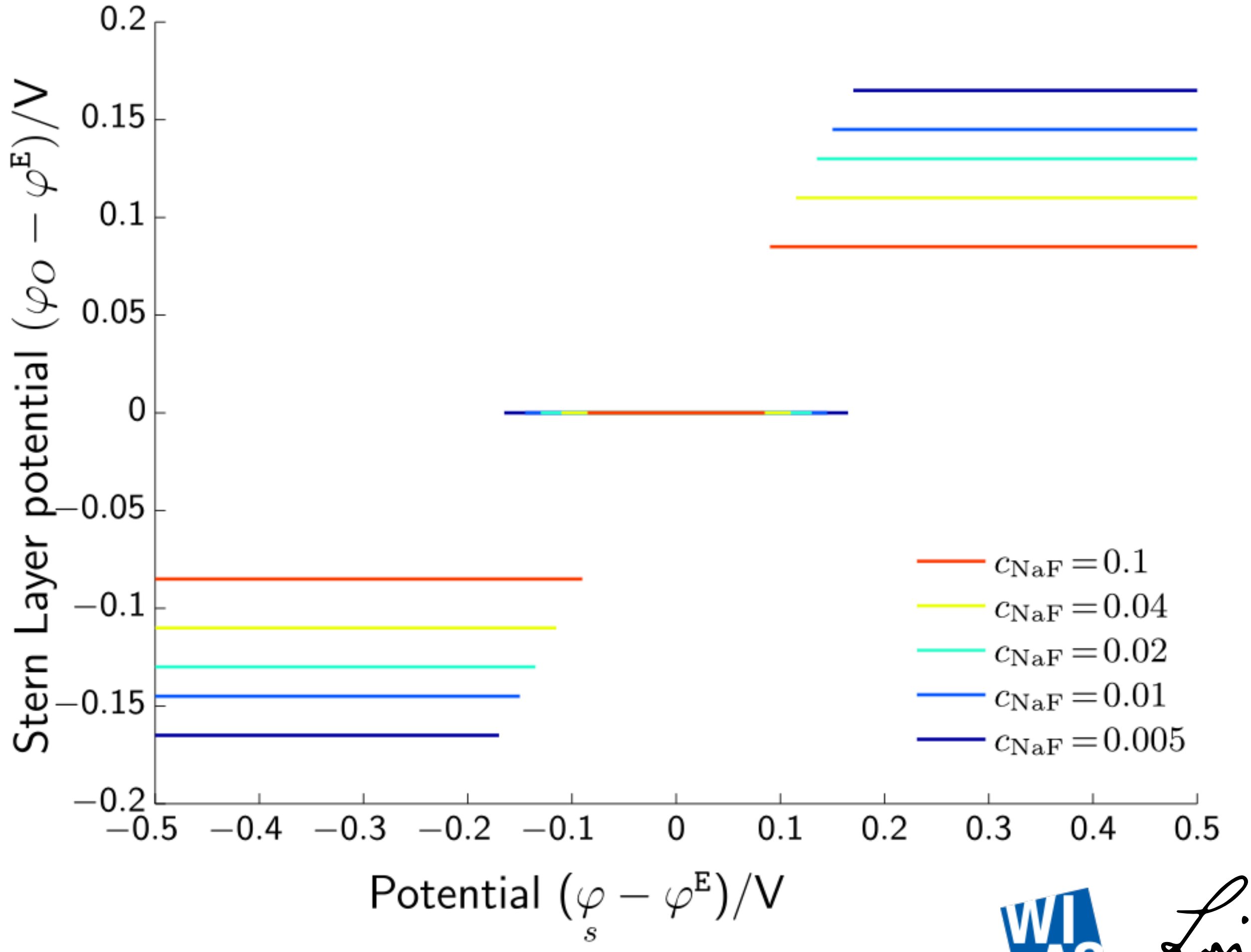
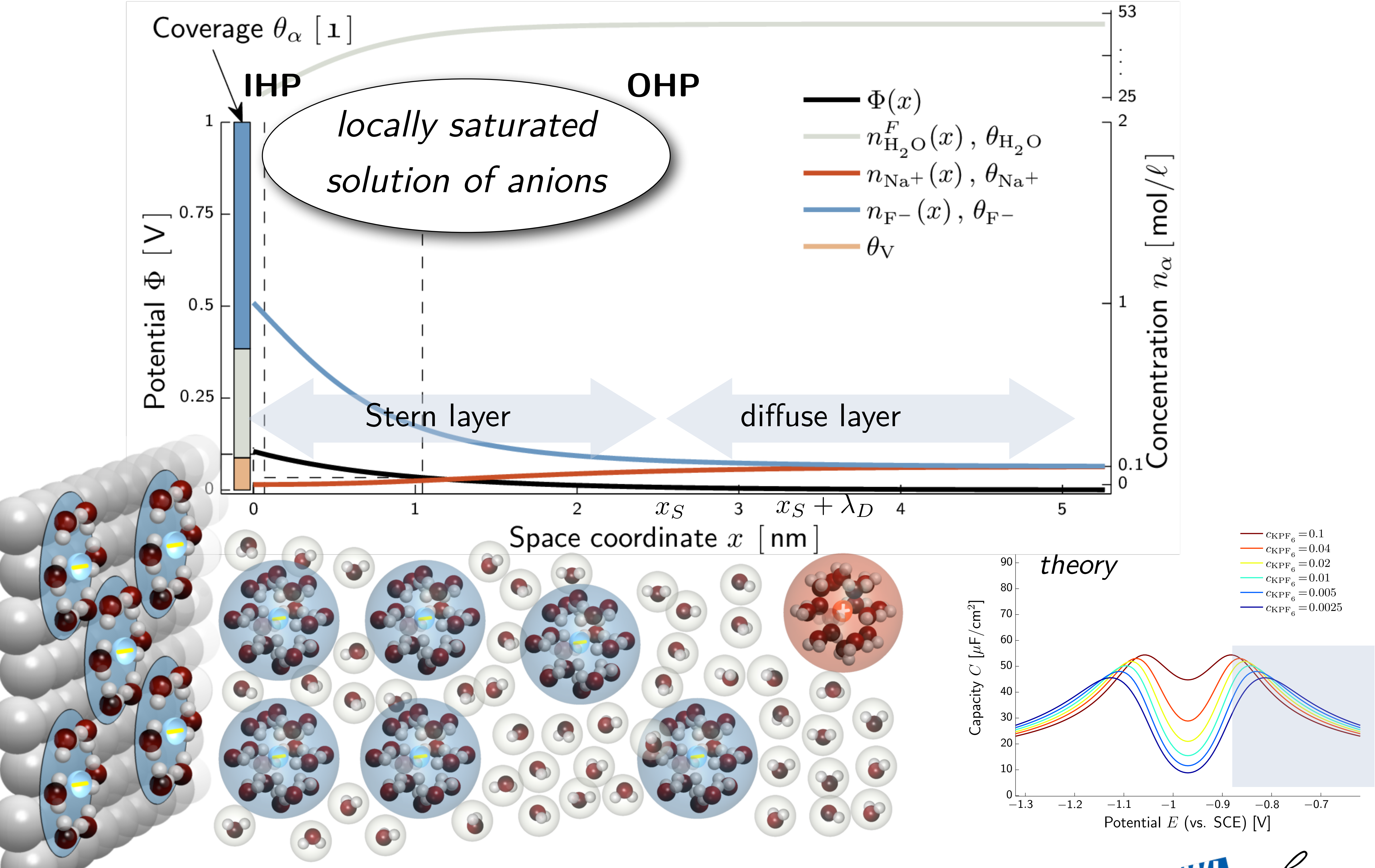




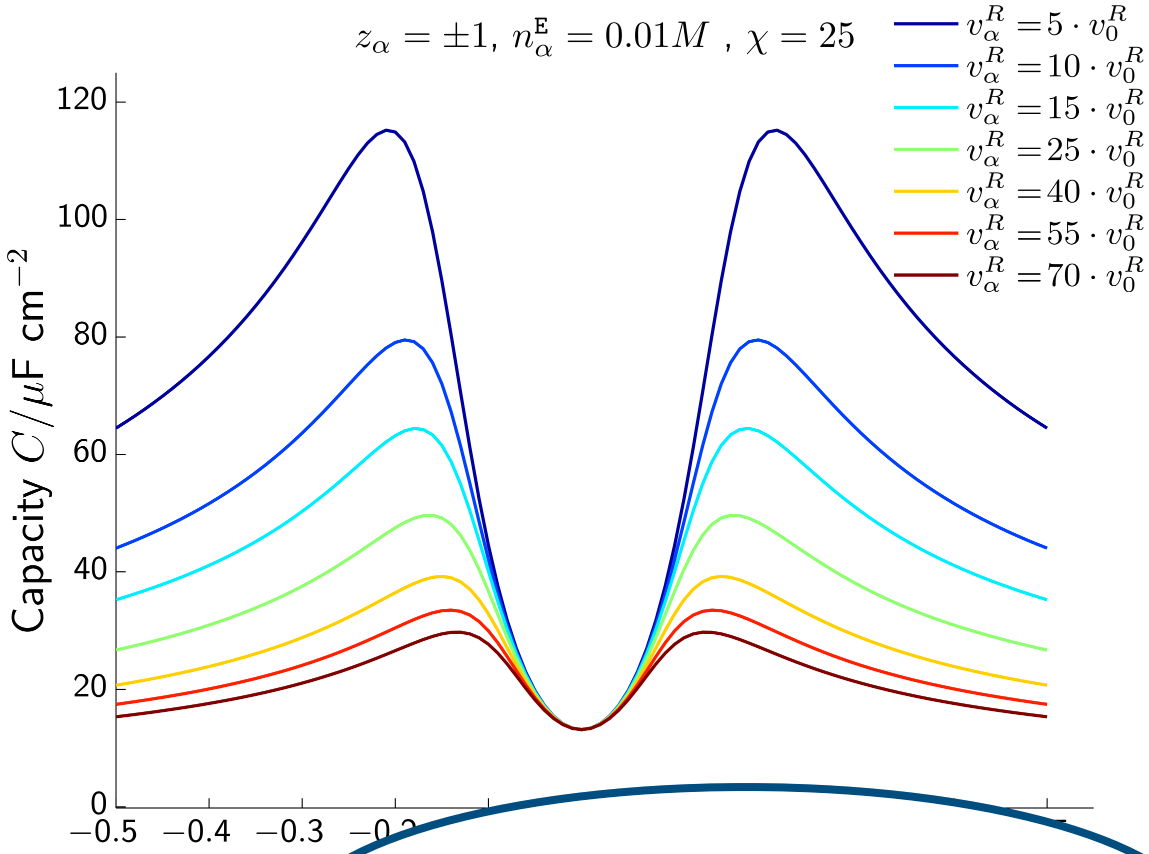
High potential regime (>60mV)

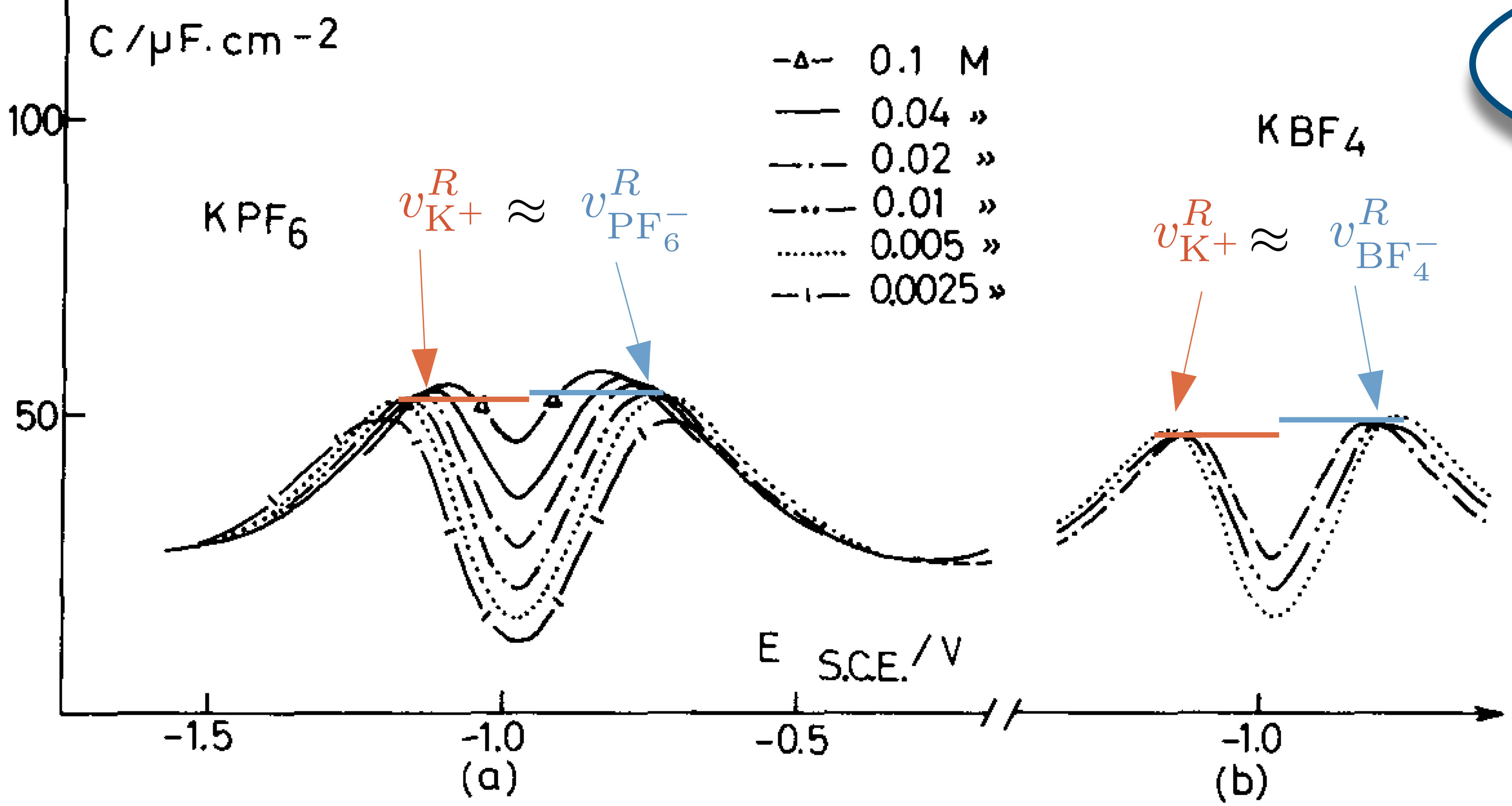


Some consequences

Capacity maximum is proportional to ionic partial molar volume

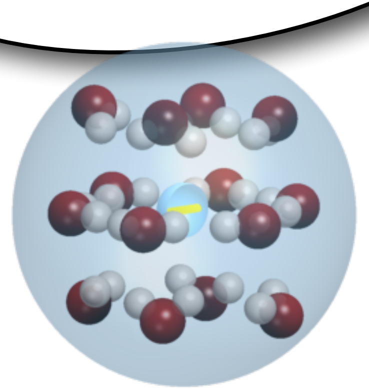
$$\boxed{C^{\mathrm{max}} \propto v^{\mathrm{R}}_{A,C}}$$



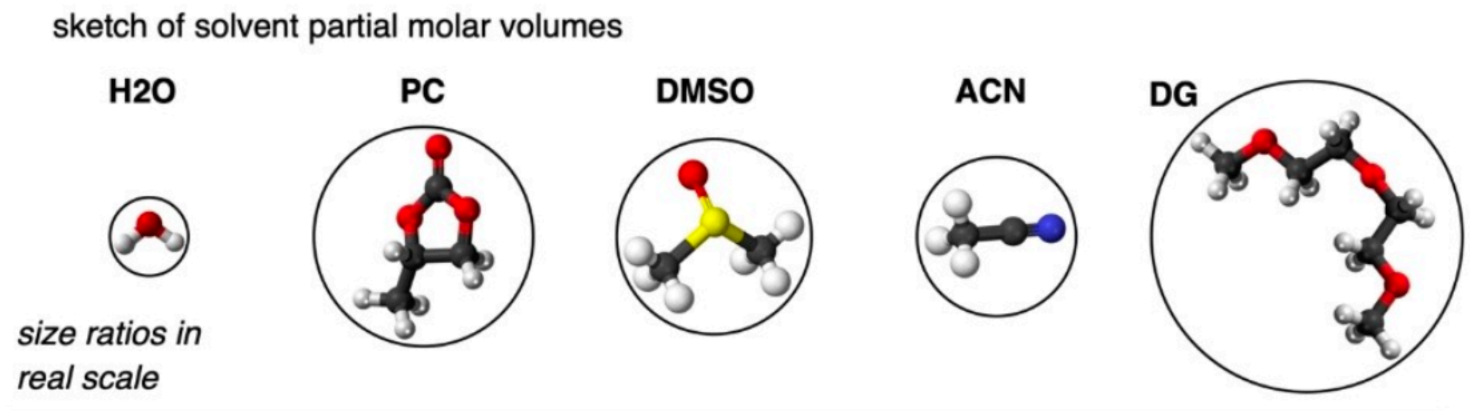


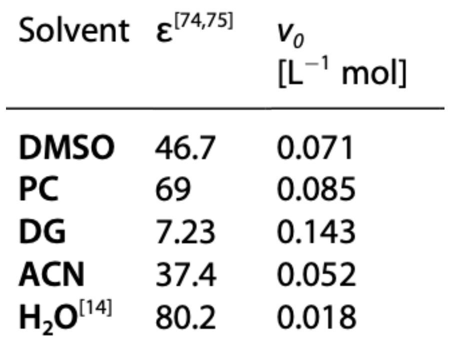
Does this apply to different solvents as well?

monovalent cations and anions have equal partial molar volumes



Various solvents, equal ions (KPF_6)

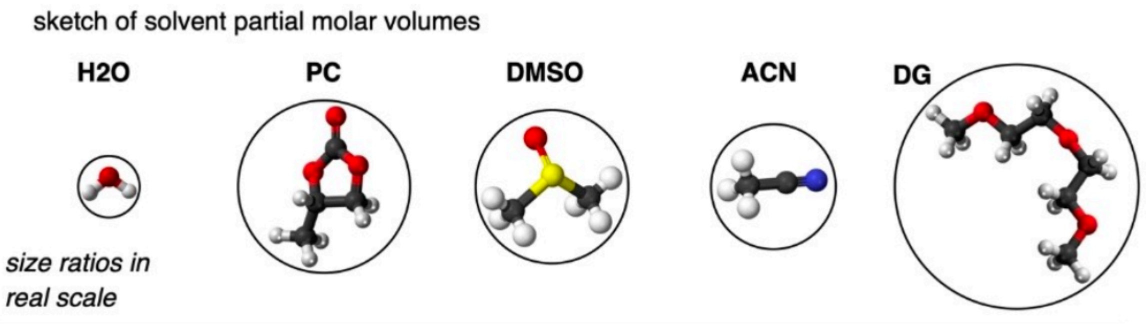


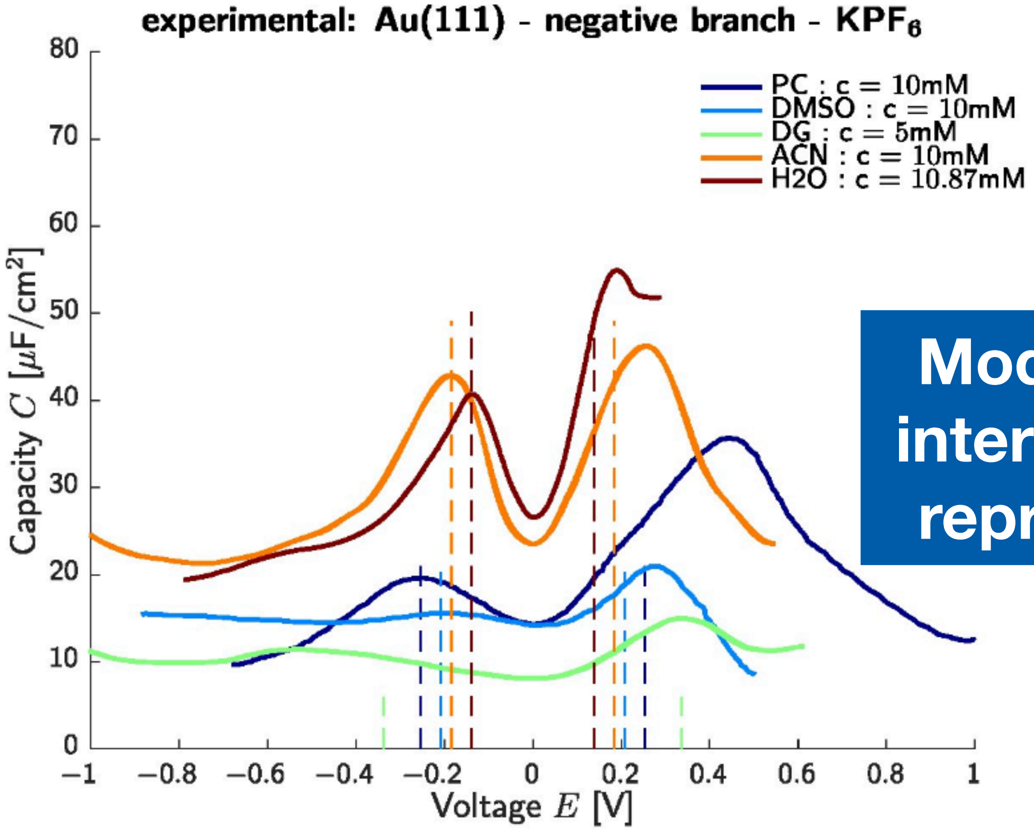


Solvent	ε[74,75]	v_0 [L^{-1} mol]
DMSO	46.7	0.071
PC	69	0.085
DG	7.23	0.143
ACN	37.4	0.052
H_2O[14]	80.2	0.018

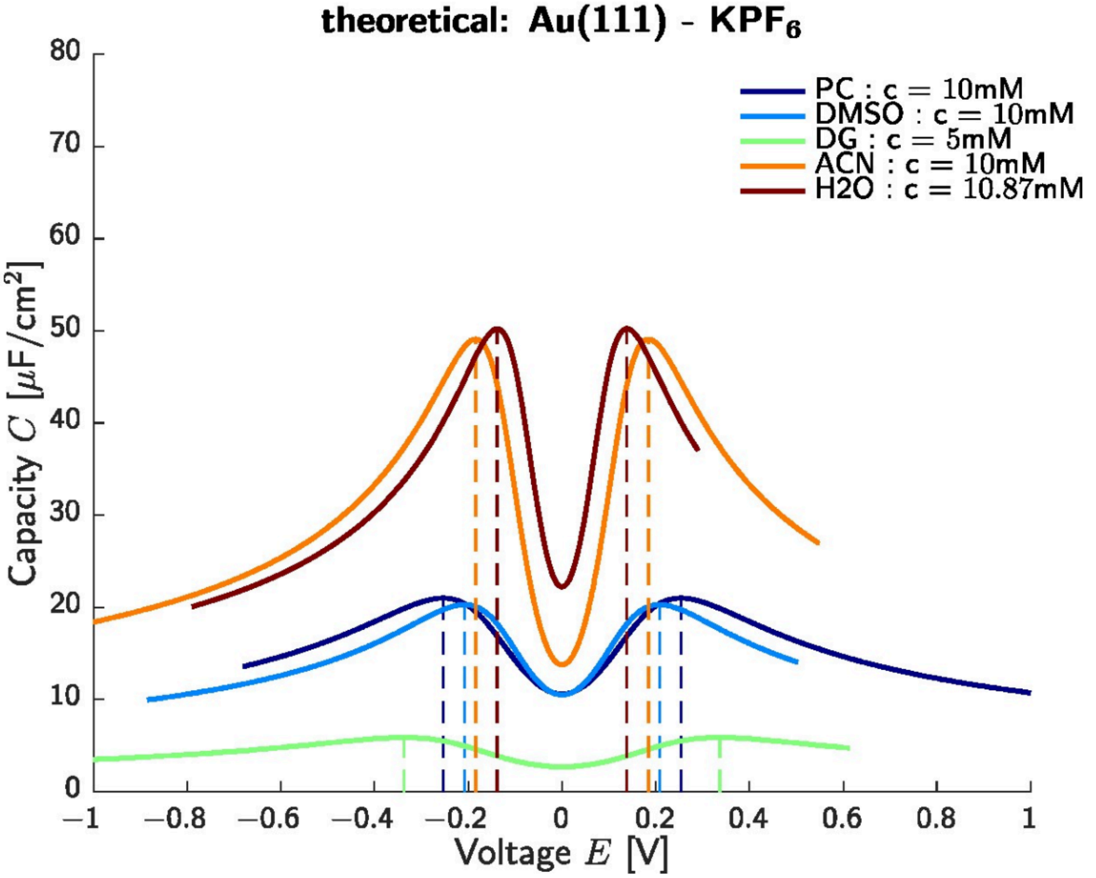
A. S. Shatla, M. Landstorfer, and H. Baltruschat. *ChemElectroChem*, **8** (2021)

Various solvents, equal ions (KPF$_6$)





Model based interpretation/ reproduction



solvated ions →

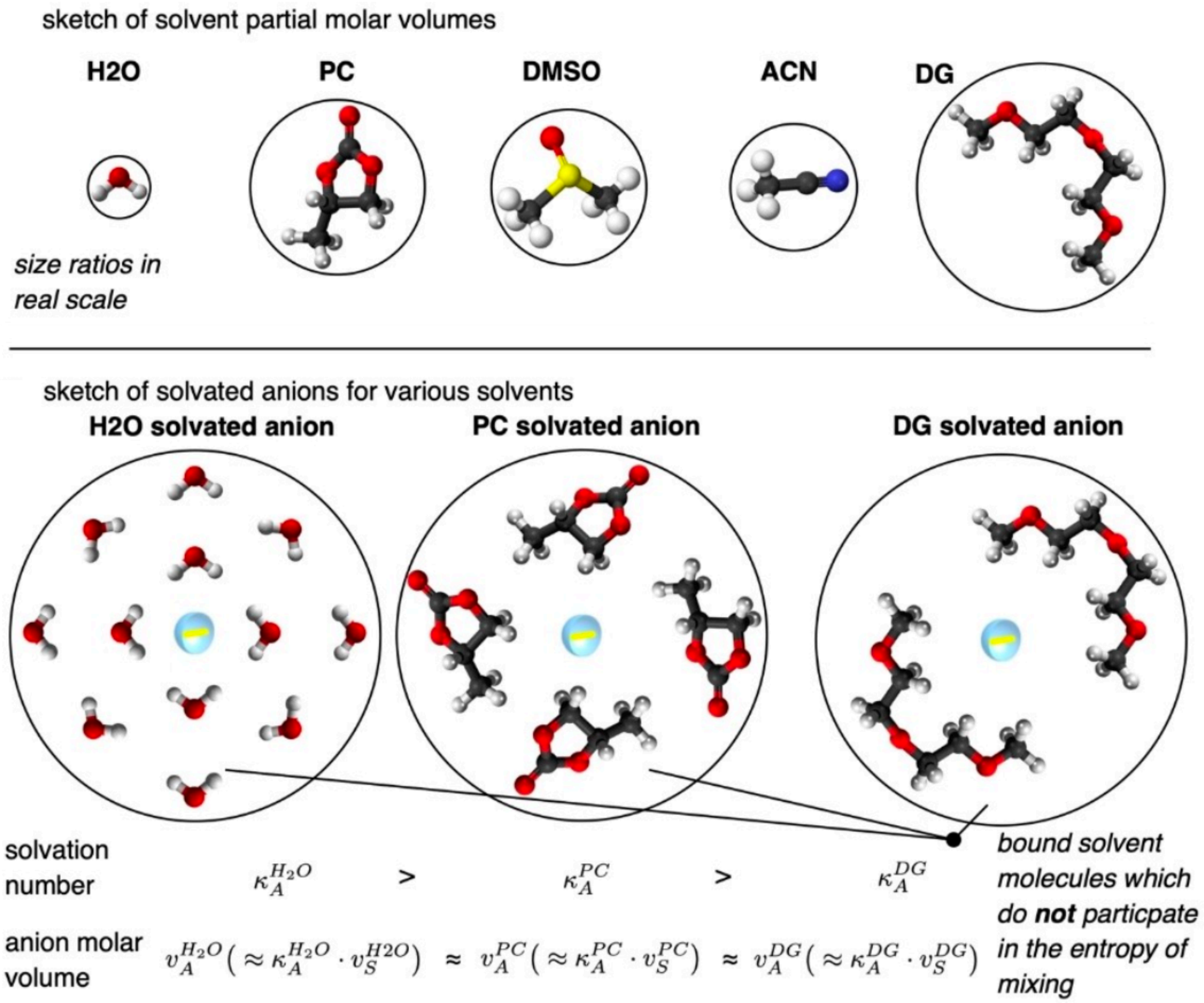
Estimated properties for some organic solvents at 25 °C (KPF$_6$).

	PC	DMSO	DG	ACN	H$_2$O
$\frac{v_{A/C}}{v_S}$	20	25	10	10	70
$v_{A/C}$	1.7/L mol^{-1}	1.8/L mol^{-1}	1.4/L mol^{-1}	0.52/L mol^{-1}	1.3/mol L^{-1}
$\widehat{r}_{A/C}$	8.76 Å	8.93 Å	8.22 Å	5.91 Å	8 Å
ϑ_S	0.51/ V	0.41/V	0.64/V	0.37/V	0.28/V
η_S	1.02	0.68	1.56	0.15	0.03

$$v_{A/C} = \frac{4\pi}{3}\,\widehat{r}_{A/C}^{\,3}$$

A. S. Shatla, M. Landstorfer, and H. Baltruschat. *ChemElectroChem*, **8** (2021)

Various solvents, equal ions (KPF_6)



solvation number $\kappa_A^{H_2O} > \kappa_A^{PC} > \kappa_A^{DG}$

anion molar volume $v_A^{H_2O}(\approx \kappa_A^{H_2O} \cdot v_S^{H2O}) \approx v_A^{PC}(\approx \kappa_A^{PC} \cdot v_S^{PC}) \approx v_A^{DG}(\approx \kappa_A^{DG} \cdot v_S^{DG})$

*bound solvent molecules which do **not** particpate in the entropy of mixing*

Solvent	ε[74,75]	v_0 [L^{-1} mol]	$\frac{v_{A/C}}{v_S}$	$v_{A/C}$ [L^{-1} mol]
DMSO	46.7	0.071	25	1.7
PC	69	0.085	20	1.8
DG	7.23	0.143	10	1.4
ACN	37.4	0.052	10	0.52
H_2O[14]	80.2	0.018	50-70	1.3

Well, Au(111) …

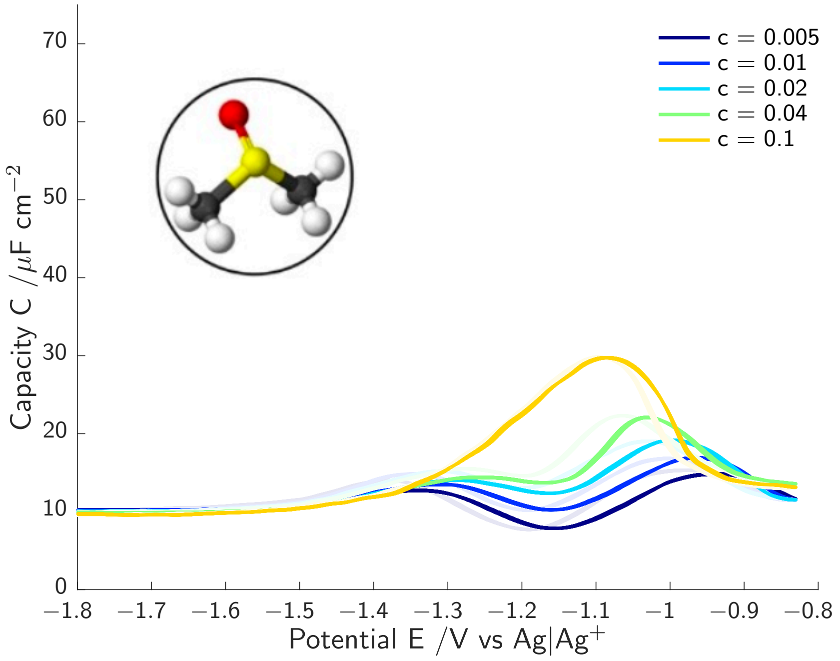
@Helmut: What about Ag(111) and complete the dataset of Valette for various solvents?

Solvated ions have *similar* partial molar volumes in the various solvents

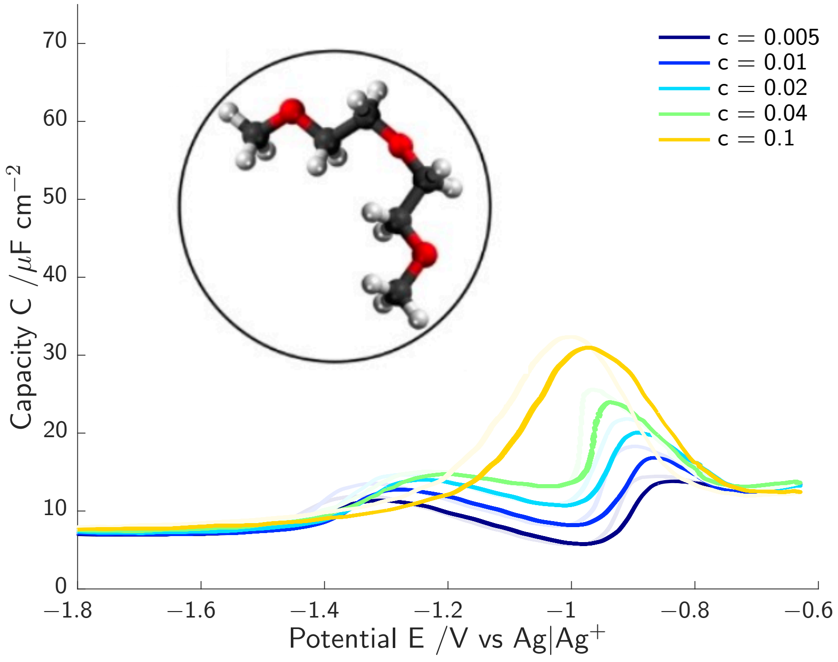
A. S. Shatla, M. Landstorfer, and H. Baltruschat. *ChemElectroChem*, **8** (2021)

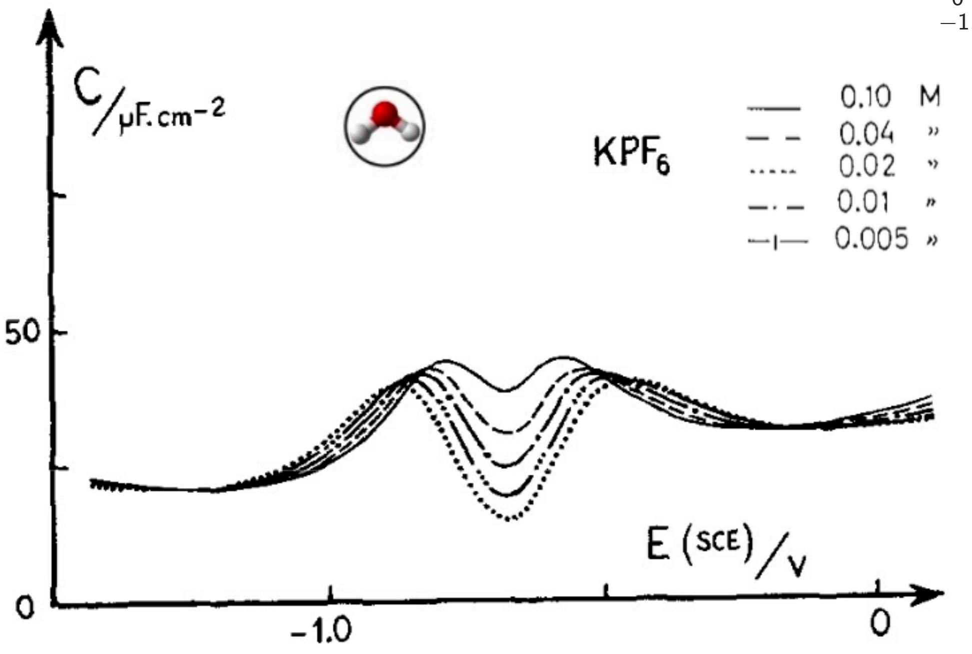
Ag(111) - KPF6

Ag(111) in DMSO + KPF6



Ag(111) in DG + KPF6





G. Valette, J. Electroanal. Chem., **269** (1989), 191 – 203.

agreement among various solvents

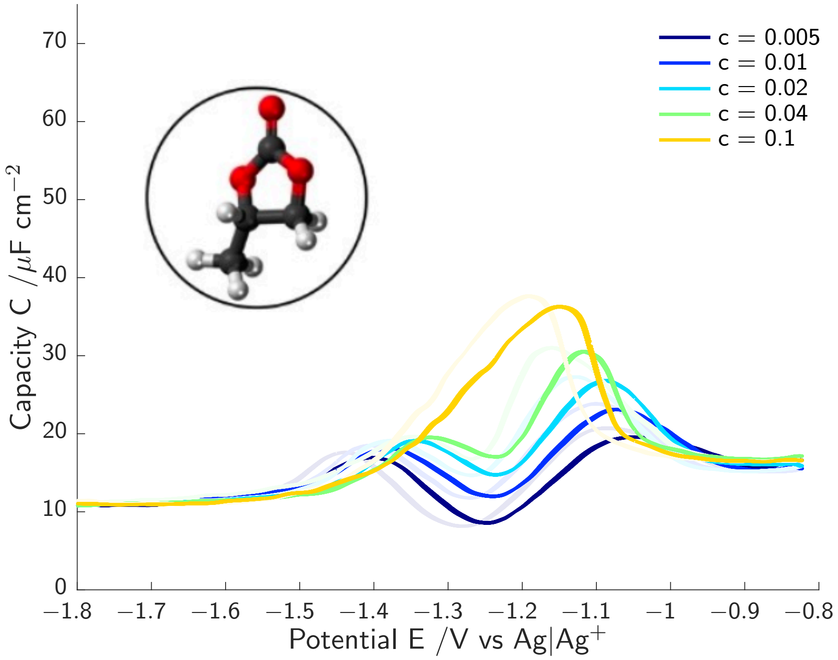
work in progress

A. S. Shatla, M. Landstorfer, H. Baltruschat. *ChemElectroChem*, **8** (2021)

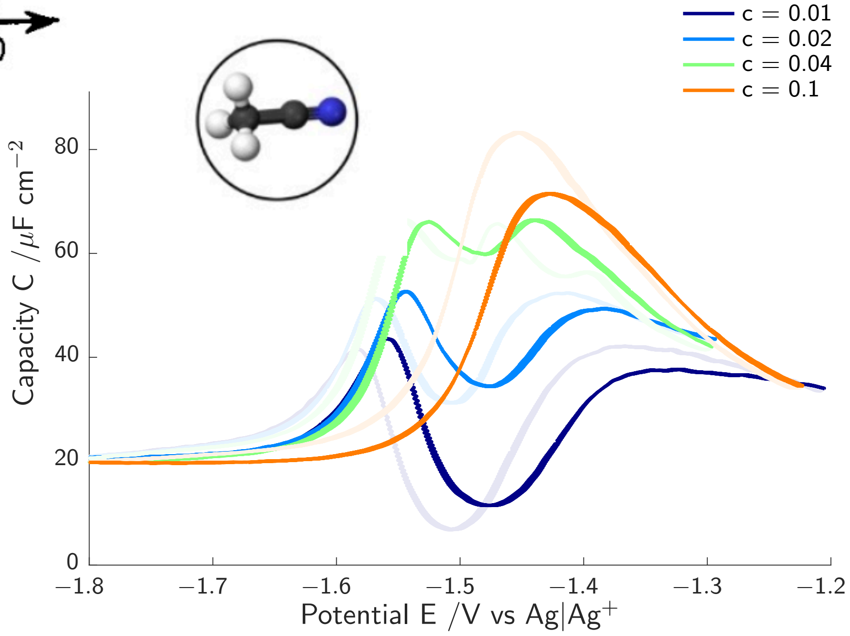
M. Landstorfer, H. Baltruschat, *in preparation*

M. Landstorfer, C. Guhlke and W. Dreyer, Electrochim. Acta., 2016, **201**, 187 – 219.

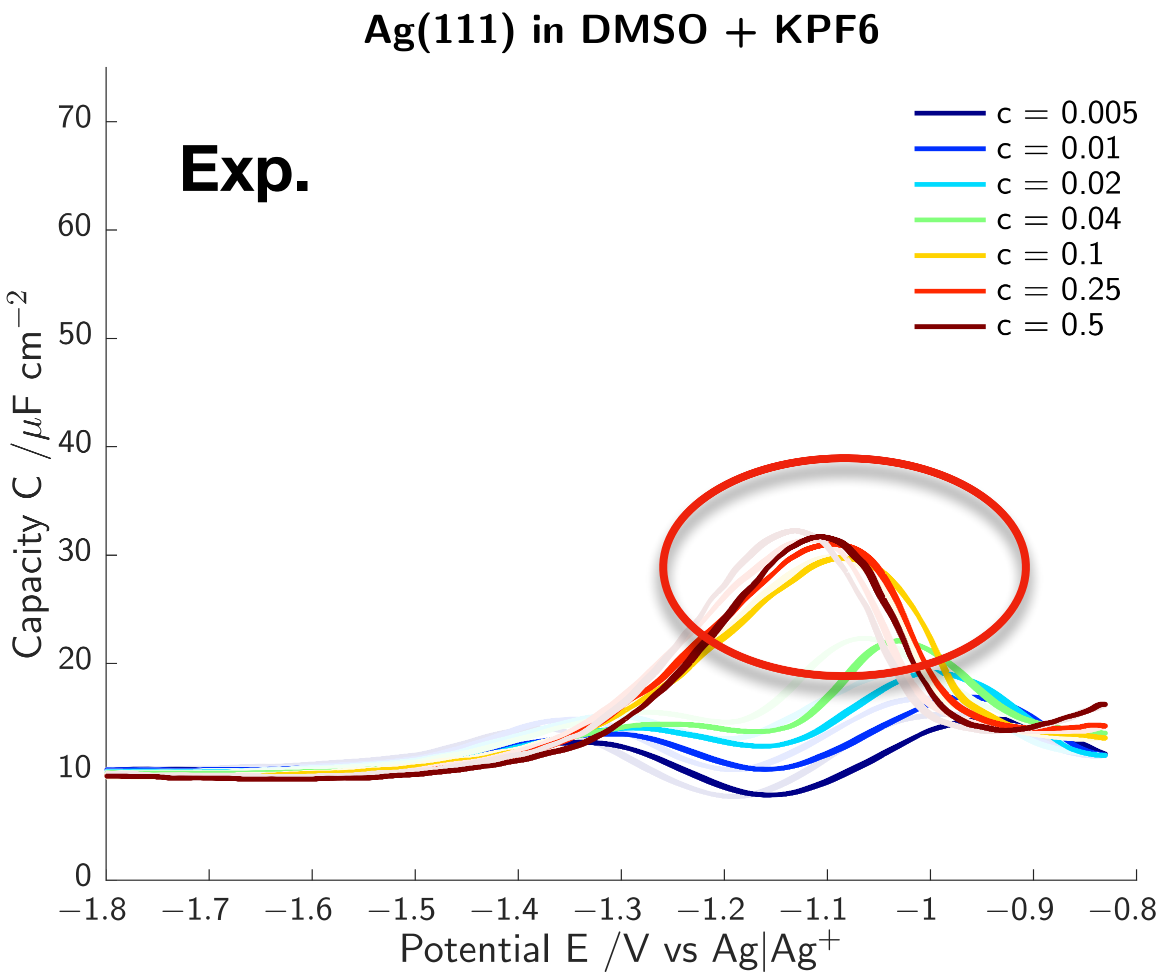
Ag(111) in PC + KPF6



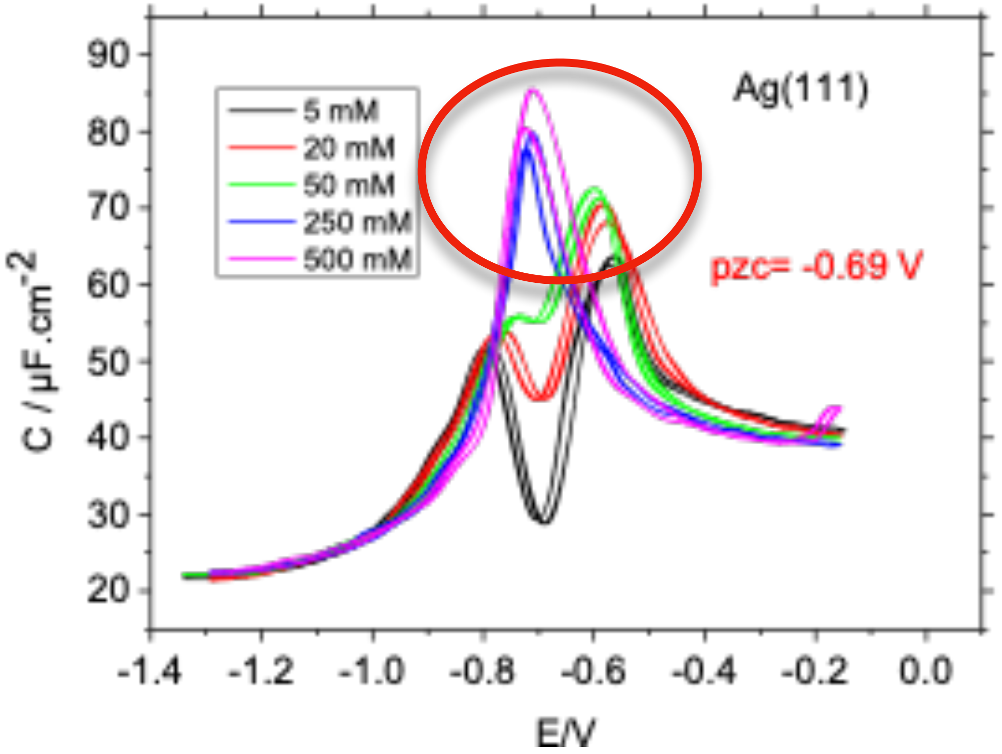
Ag(111) in ACN + KPF6



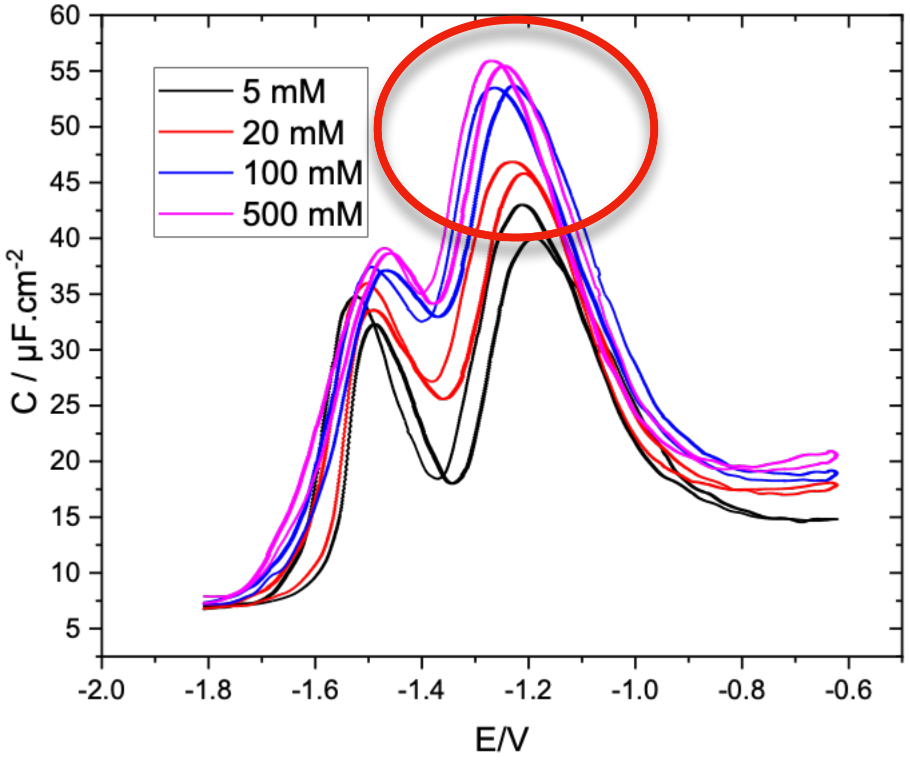
Ag(111) - KPF6 - Higher concentrations



Ag(111) | Ca(ClO_4)$_2$ in Water



Ag(111) | $NaClO_4$ + 0.1 mM NaBr in DG



Beyond a certain concentration $c > c^{max}$ the capacity becomes *independent of c*

?

Incomplete dissocation due to solvation effects

M.Landstorfer, On the dissociation degree of ionic solutions considering solvation effects. *Electrochemistry Communications*, **2018**

A. S. Shatla, M. Landstorfer, and H. Baltruschat. *ChemElectroChem*, **8** (2021)

Discussion - Dissociation degree

Consider **1** mol/L **AC** solution

common assumption: **complete dissociation**

justified ?

Consequence: re-question dissociation reaction $\boxed{\left.\mathrm{AC}\right|^{\mathtt{R}} \rightleftharpoons \mathrm{A}^- + \mathrm{C}^+}$

1. Step: dissolution of the **ion pair**

$$\boxed{\left.\mathrm{AC}\right|^{\mathtt{R}} \rightleftharpoons \mathrm{AC}}$$

2. Step: dissociation of the **ion pair** with **solvation effect**

$$\boxed{\mathrm{AC} + (\kappa_A + \kappa_C)\mathrm{S} \rightleftharpoons \mathrm{A}^- + \mathrm{C}^+}$$

TD equilibrium condition: $\mu_{\mathrm{AC}} + (\kappa_A + \kappa_C)\mu_S = \mu_A + \mu_C$.

same chemical potential functions as previously!

Discussion - Dissociation degree

same chemical potential functions as for the double layer capacity computation

TD equilibrium condition: $\mu_{\mathrm{AC}} + (\kappa_A + \kappa_C)\mu_S = \mu_A + \mu_C \ .$

Dissociation degree: $n_A = n_C = \delta \cdot c$ and $n_{\mathrm{AC}} = (1-\delta)c$

TD equilibrium condition:

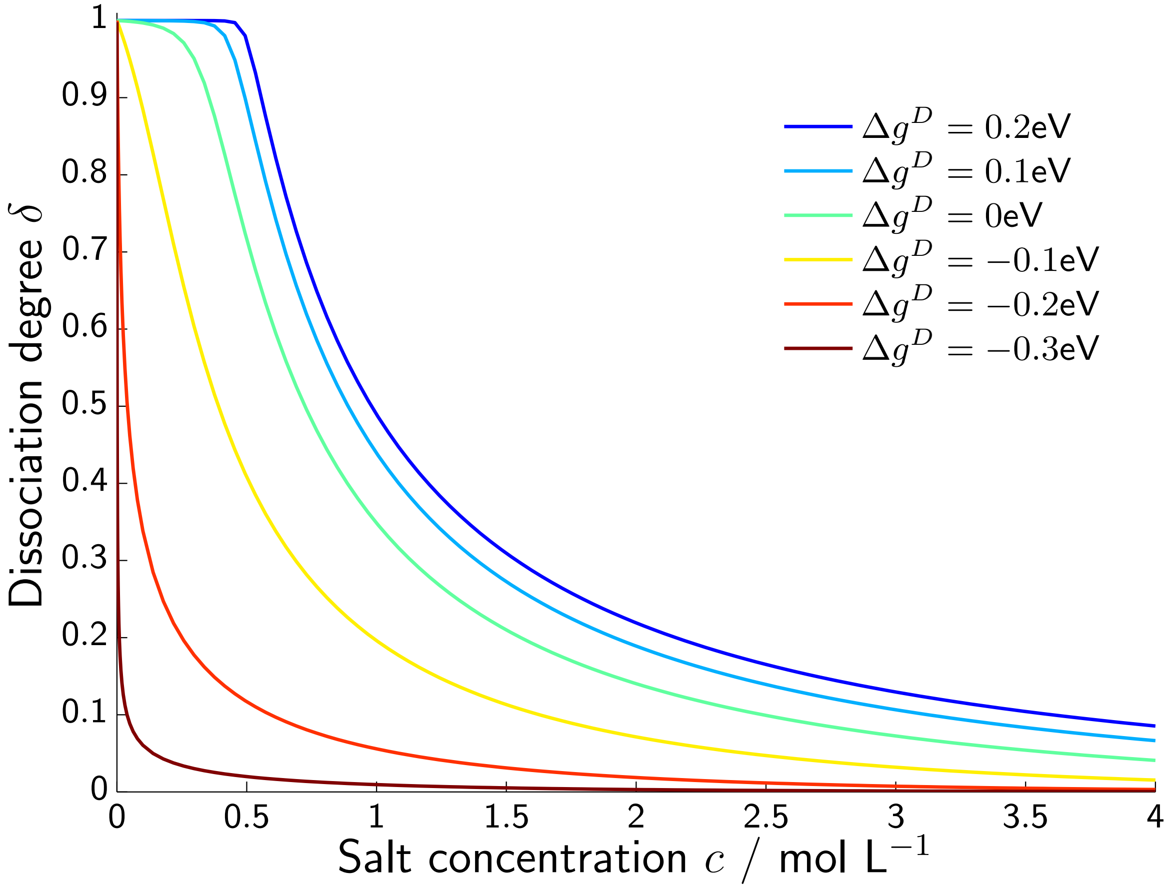
$$\frac{\delta^2}{(1-\delta)} \cdot \frac{c}{n_S^{\mathtt{R}} + 2(1-\kappa)\delta \cdot c + (1-\delta) \cdot c} \cdot \left(\frac{n_S^{\mathtt{R}} + 2(1-\kappa)\delta \cdot c + (1-\delta) \cdot c}{n_S^{\mathtt{R}} - 2\kappa\,\delta \cdot c} \right)^{2\kappa} - \mathrm{e}^{\frac{\Delta g^D}{k_{\mathrm{B}} T}} = 0$$

Ostwald's dilution law: (*commonly used to compute diss. degree*)

$$\frac{\delta^2}{1-\delta} \cdot \frac{c}{n_S^{\mathtt{R}}} - \mathrm{e}^{\frac{\Delta g^D}{k_{\mathrm{B}} T}} = 0$$

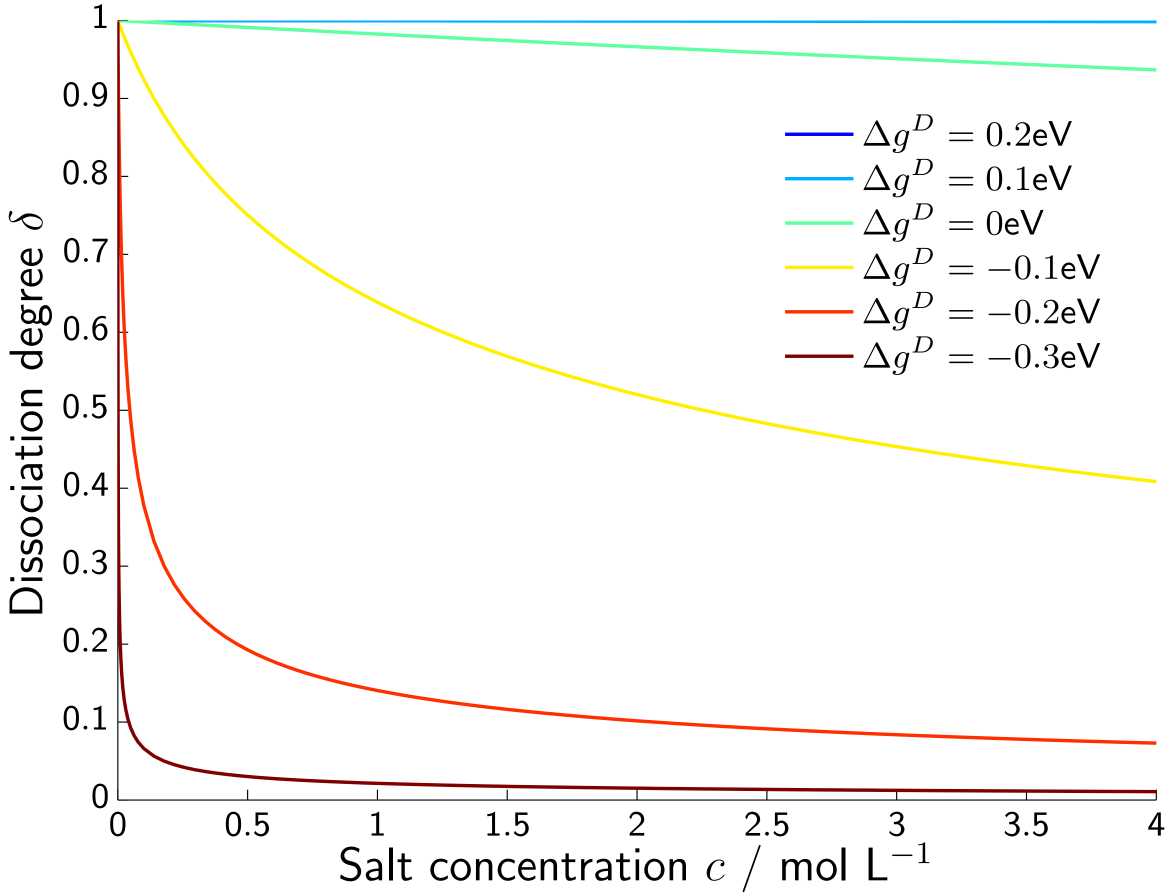
Discussion - Dissociation degree

Solvation mixture: $(\kappa = 30)$



Ostwald's dilution law:

Capacity at PZC



complete dissociation is **impossible** when solvation effects are considered!

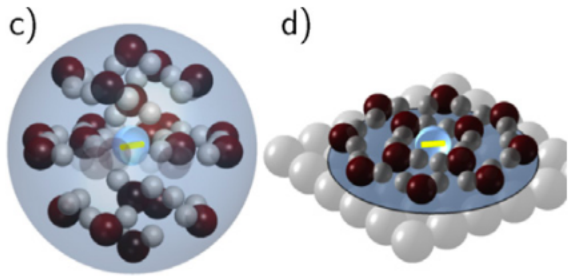
M. Landstorfer, *Electrochem. Comm.*, 2018, **59**, 56 – 59.

Beyond a certain concentration c > c^{max} the capacity becomes *independent of c*

c^{max} can be estimated from capacity measurements and implicitly be used to determine solvation numbers

Ag(110)|NaClO4 – *adsorbing* solvated ions

- Capacity of single crystal Ag(111)|NaClO4(H_2O)
- Variation of the salt concentration
- Capacity depends non-linear on the applied voltage
- Unsymmetric capactiy hump



Experimental data

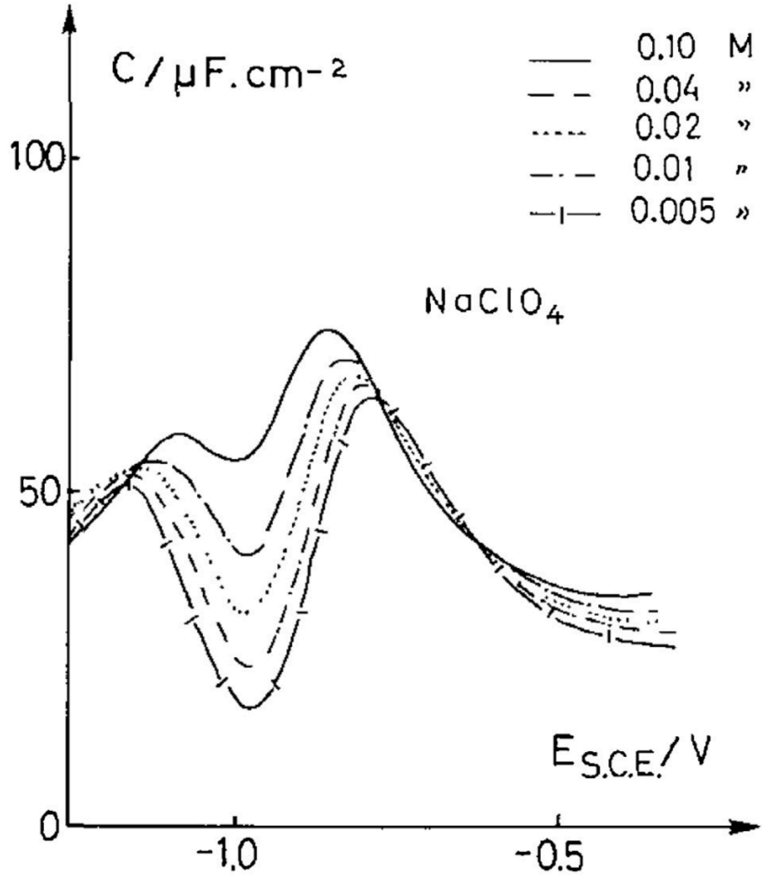
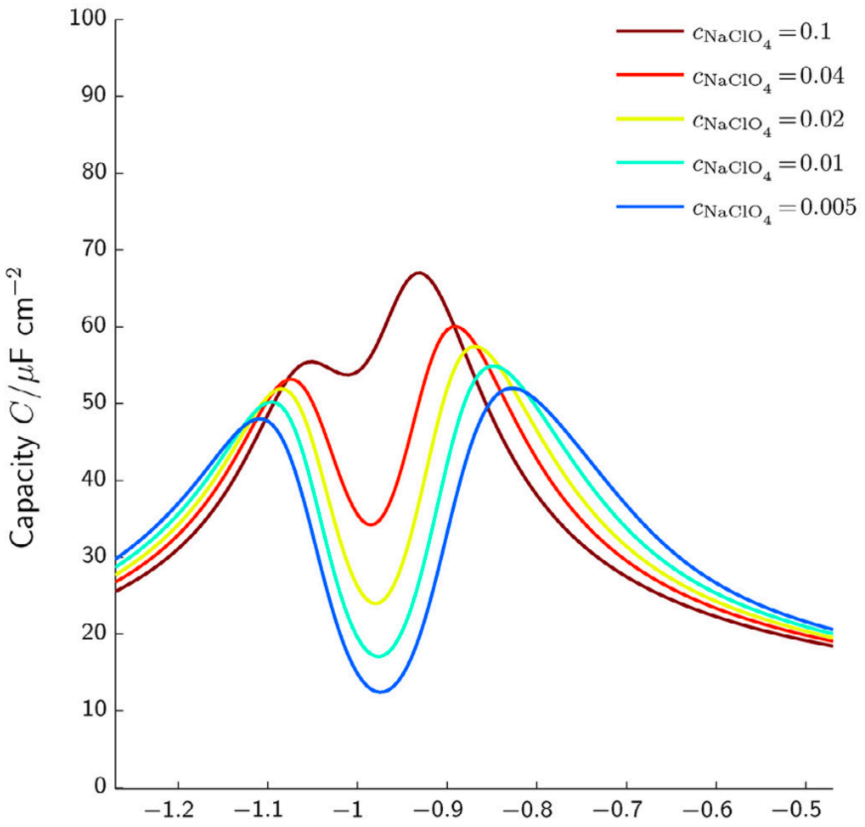


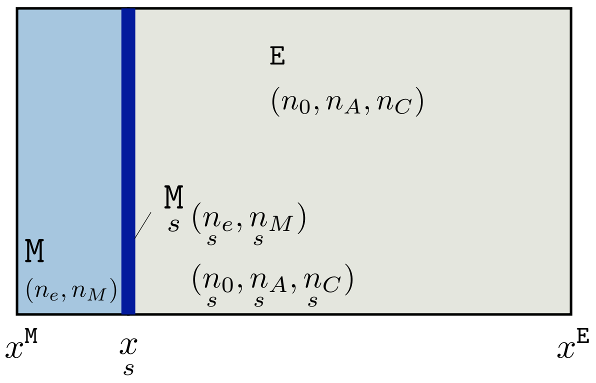
Fig. 5 of G. Valette, *J. of Electroanal. Chem.*, 1981, **122**, 285 – 297.

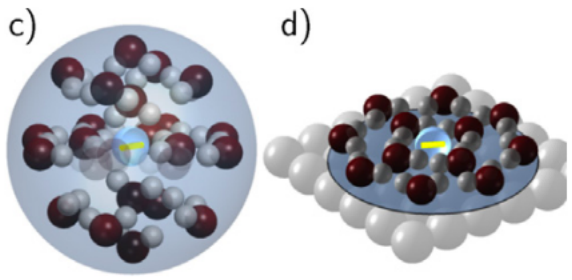
Mathematical model



M. Landstorfer, C. Guhlke and W. Dreyer, Electrochim. Acta., 2016, **201**, 187 – 219.

Ag(110)|NaClO4 – *adsorbing* solvated ions





- Diffusional equilibrium in $\Omega^\pm$

$$\nabla\mu_\alpha + e_0 z_\alpha \nabla\varphi = \mathbf{0} \qquad \alpha = 1, \dots, N$$

- Electrical equilibrium in $\Omega^\pm$

$$-\varepsilon_0 \mathrm{div}\,(\nabla\varphi) = q$$

- Mechanical equilibrium in $\Omega^\pm$

$$\nabla p = -q\nabla\varphi \qquad \text{with} \qquad q = \sum_{\alpha=0}^{N} z_\alpha e_0 n_\alpha$$

- Adsorption equilibrium at S

$$\underset{s}{\mu_\alpha} = \mu_\alpha|_{\underset{s}{x}} = \mu_\alpha|_{x^{\mathrm{E}}} + e_0 z\alpha(\underset{s}{\varphi} - \varphi|_{x^{\mathrm{E}}})$$

thermodynamic closure relations

$$\underset{s}{\mu_\alpha} = \underset{s}{\psi^R_\alpha} + k_BT\ln(\underset{s}{y_\alpha}) - \omega_\alpha k_BT\ln(\underset{s}{y_V}).$$

$$\frac{1}{\underset{s}{n}} = a^R_V \underset{s}{y_V} + \sum_{\alpha=0}^{N_S-2} a^R_\alpha \underset{s}{y_\alpha}$$

Constant number of adsorption sites

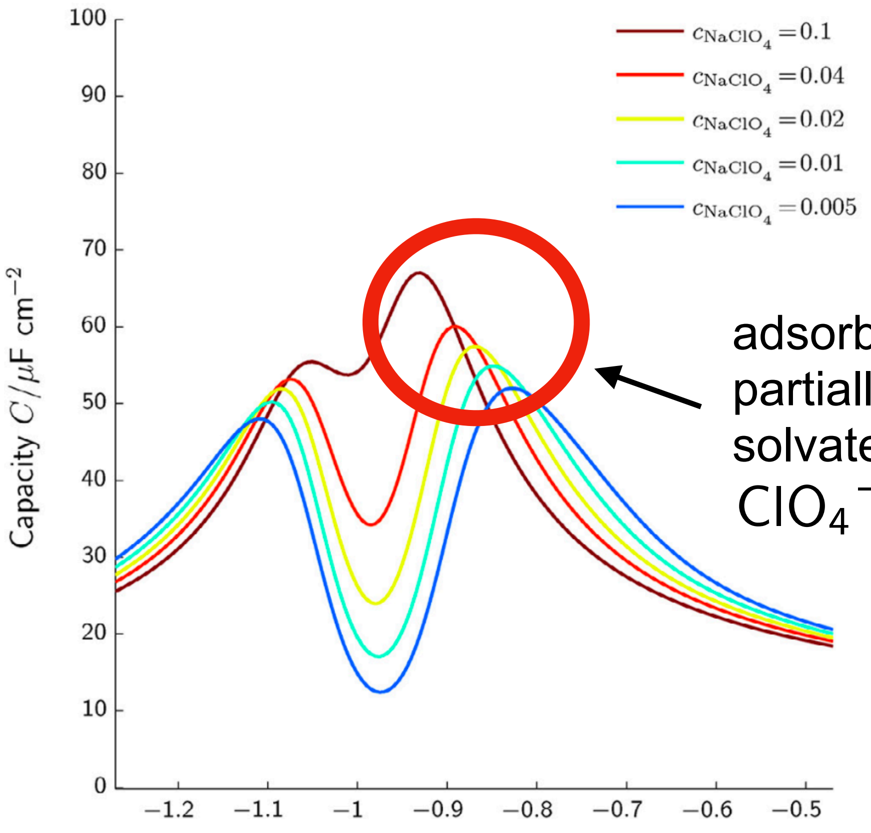
Interface charge: $Q = Q_{\mathrm{E}} + \underset{s}{q_{\mathrm{E}}}$

with $Q_{\mathrm{E}} = \int_0^{x_{\mathrm{E}}} q\,dx$

Interface capacity: $C = C_{\mathrm{E}} + \underset{s}{C}$

with $C_{\mathrm{E}} = \frac{dQ_{\mathrm{E}}}{dU}$, $\underset{s}{C} = \frac{\underset{s}{q_{\mathrm{E}}}}{dU}$

Mathematical model

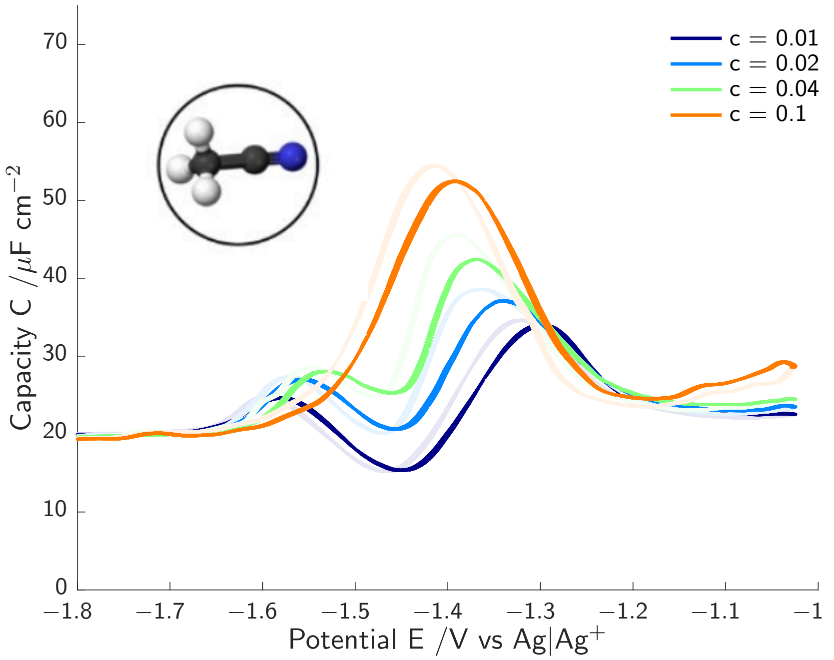


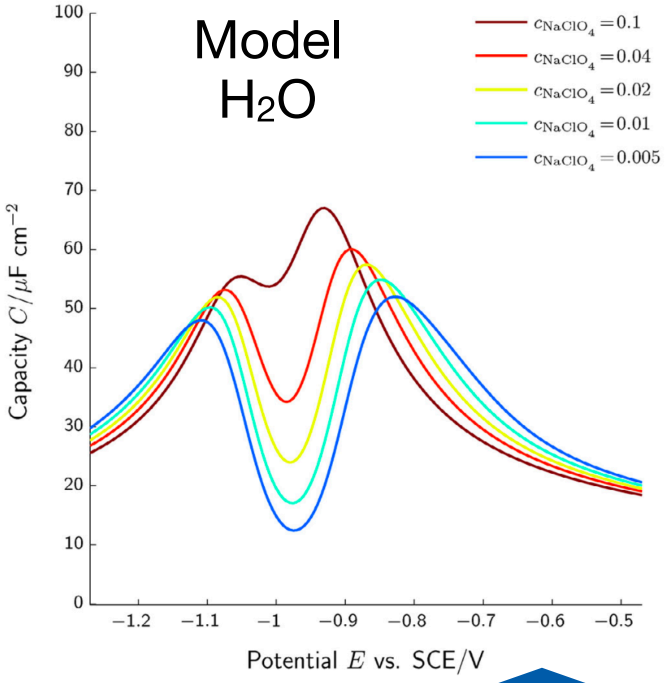
adsorbed, partially solvated $\mathrm{ClO_4}^-$

M. Landstorfer, C. Guhlke and W. Dreyer, Electrochim. Acta., 2016, **201**, 187 – 219.

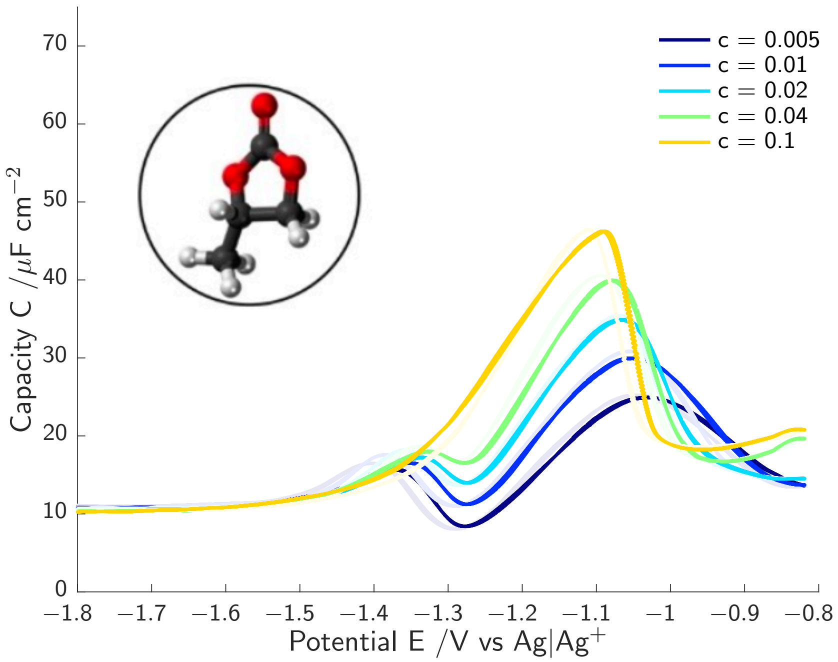
Ag(111) | NaClO4

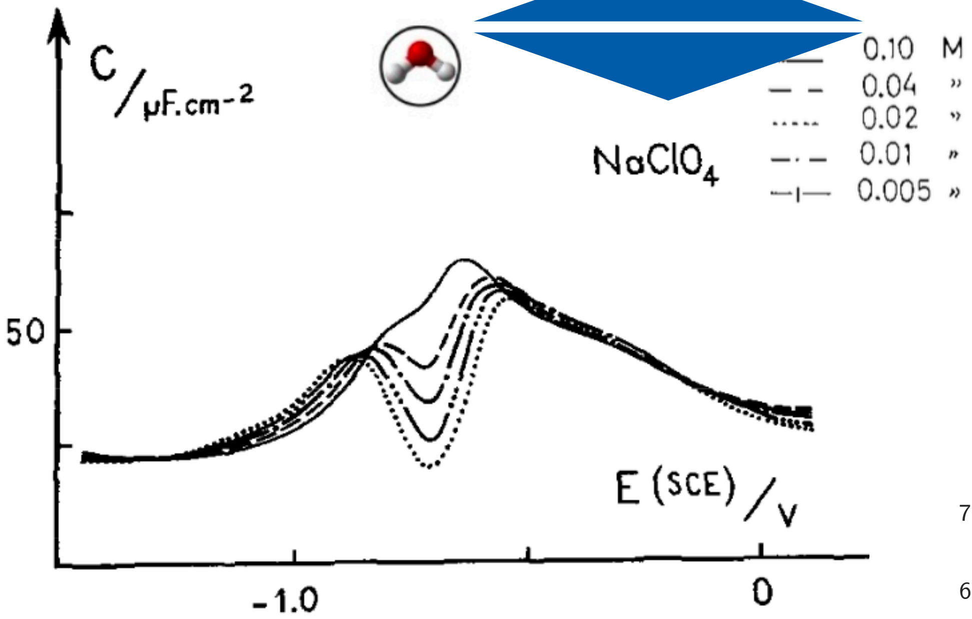
Ag(111) in ACN + NaClO4





Ag(111) in PC + NaClO4



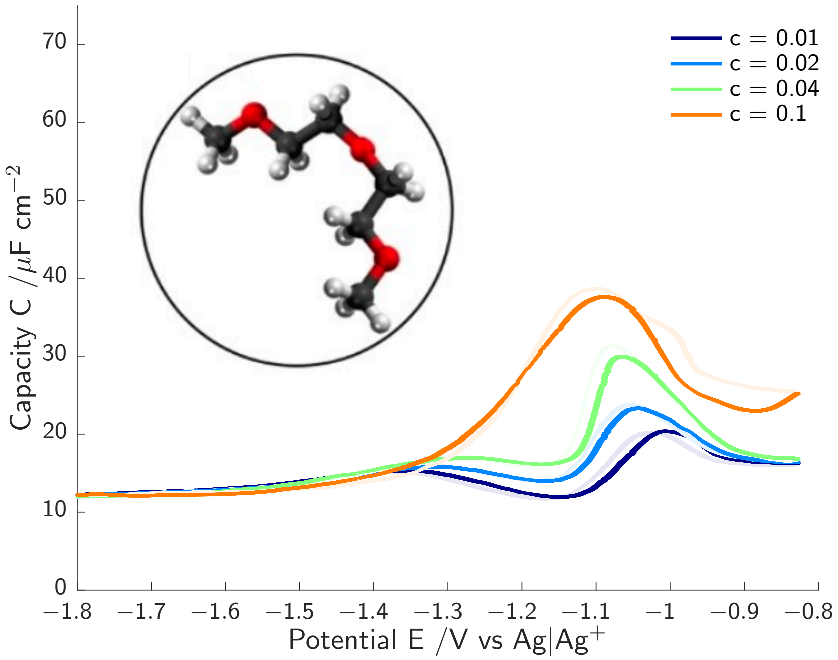


G. Valette, J. Electroanal. Chem., **269** (1989), 191 – 203.

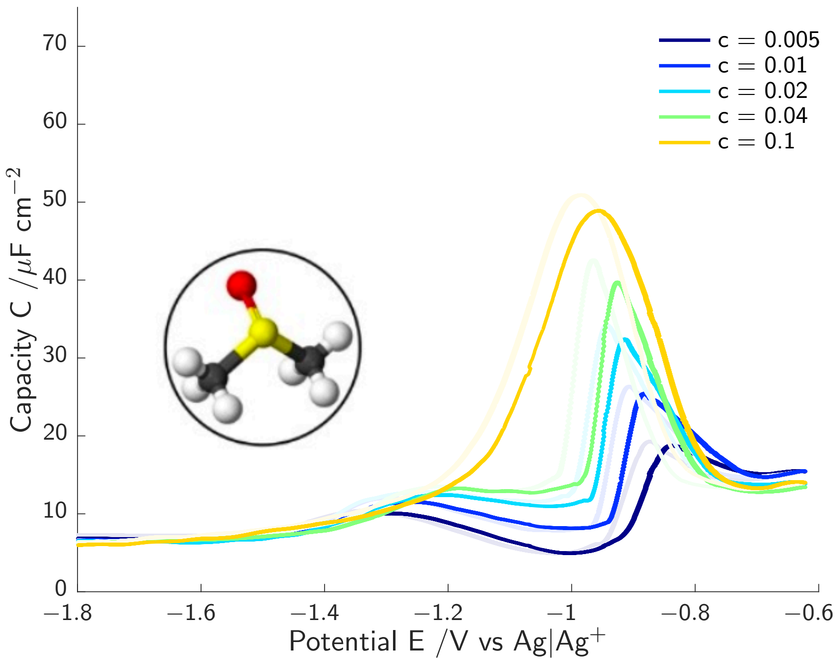
Simulation/Validation
work in progress

Simulation/Validation
work in progress

Ag(111) in DMSO + NaClO4



Ag(111) in DG + NaClO4



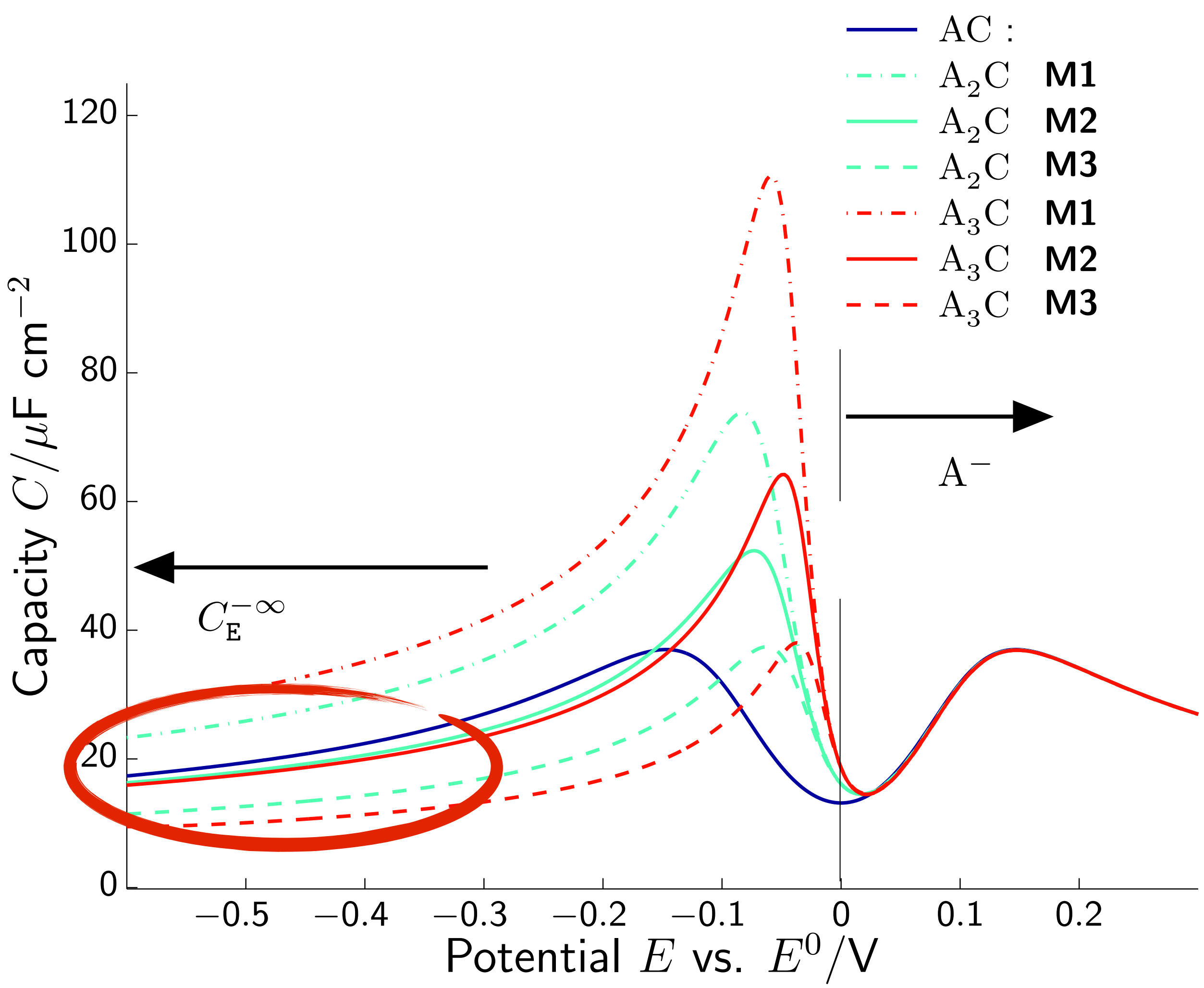
M. Landstorfer, H. Baltruschat, *in preparation*

Discussion - multivalent ions

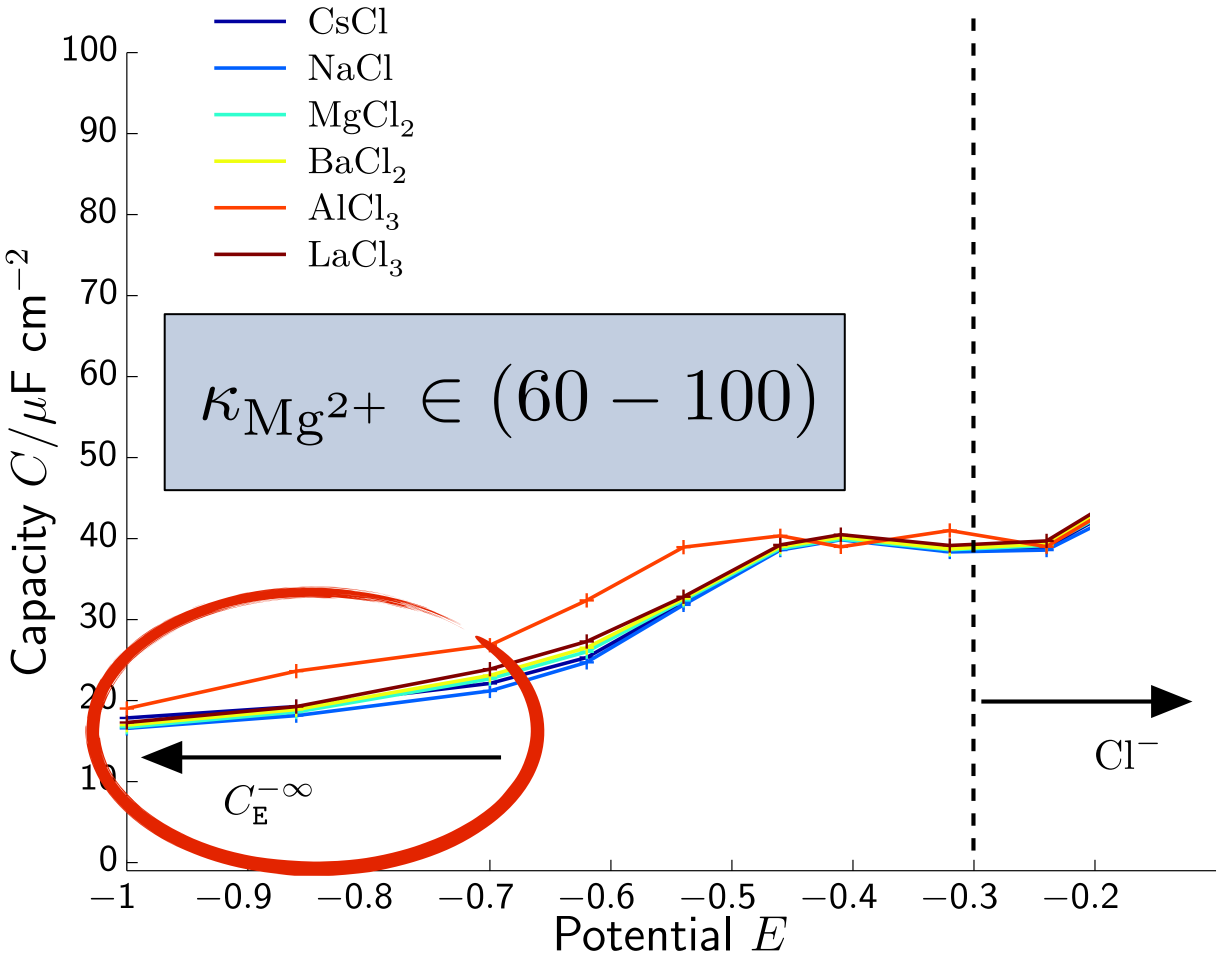
Consider solutions 0.1M **AC**, 0.5M **A_2C**, 0.33M **A_3C**

what is the relationship between partial molar volume and charge number ?

$$\mathbf{M1} : \kappa_\alpha = \kappa \qquad \boxed{\mathbf{M2} : \kappa_\alpha = |z_\alpha| \cdot \kappa} \qquad \mathbf{M3} : \kappa_\alpha = |z_\alpha|^2 \cdot \kappa$$



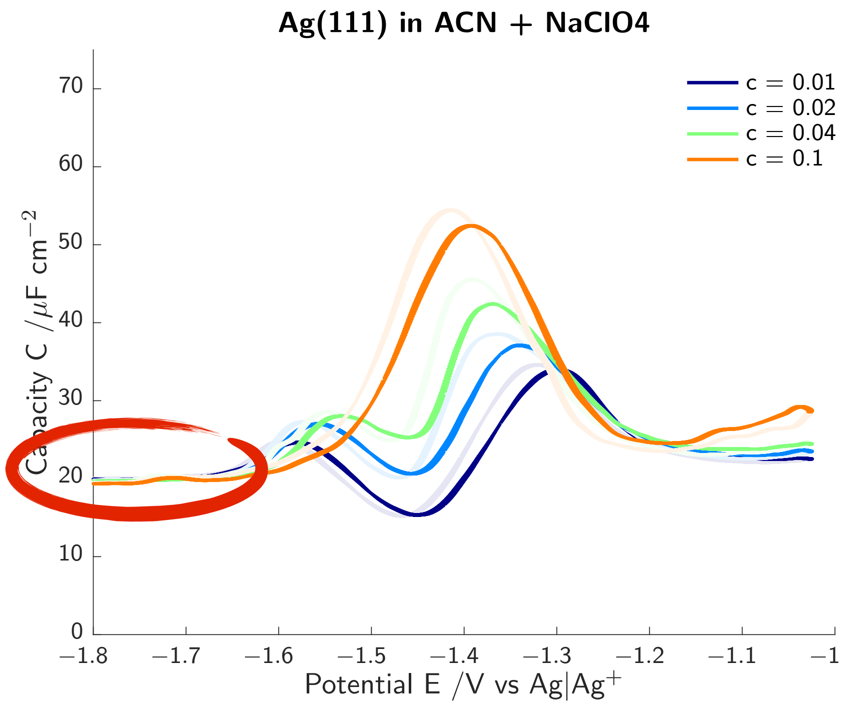
measured data (Grahame)



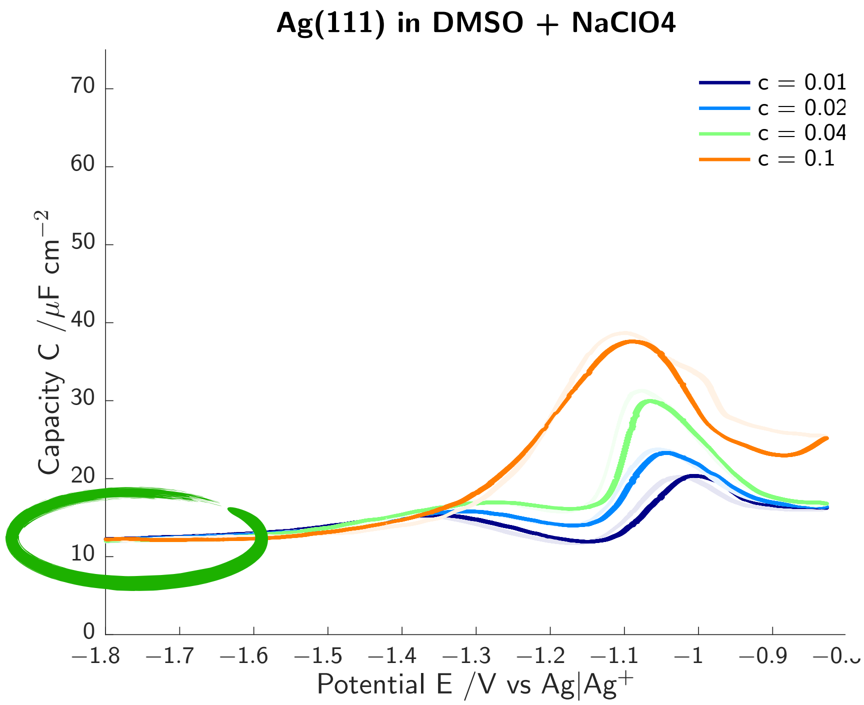
$$\kappa_{\mathrm{Mg}^{2+}} \in (60 - 100)$$

less reliable experimental data for multivalent ions available

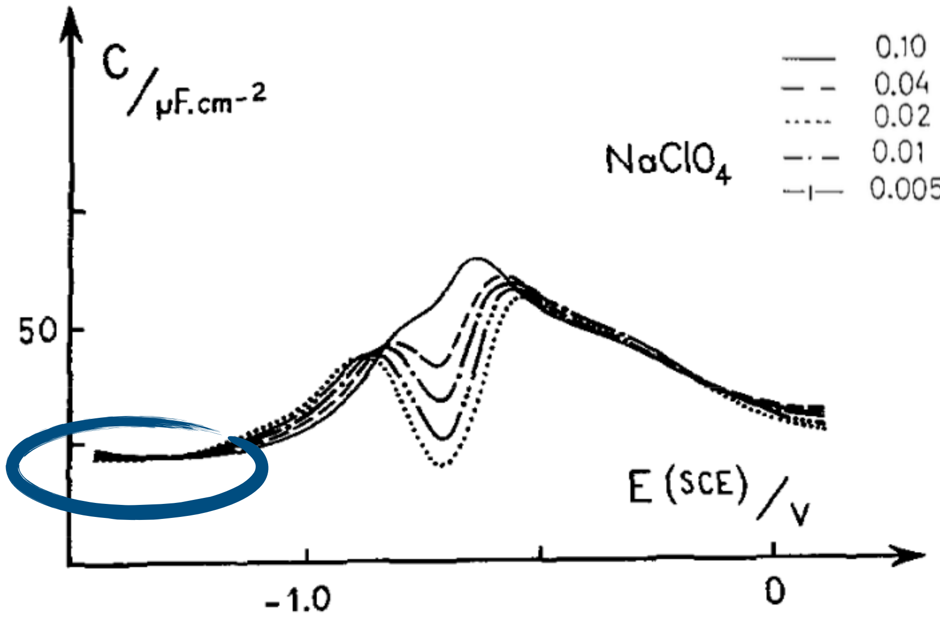
Multivalent ions



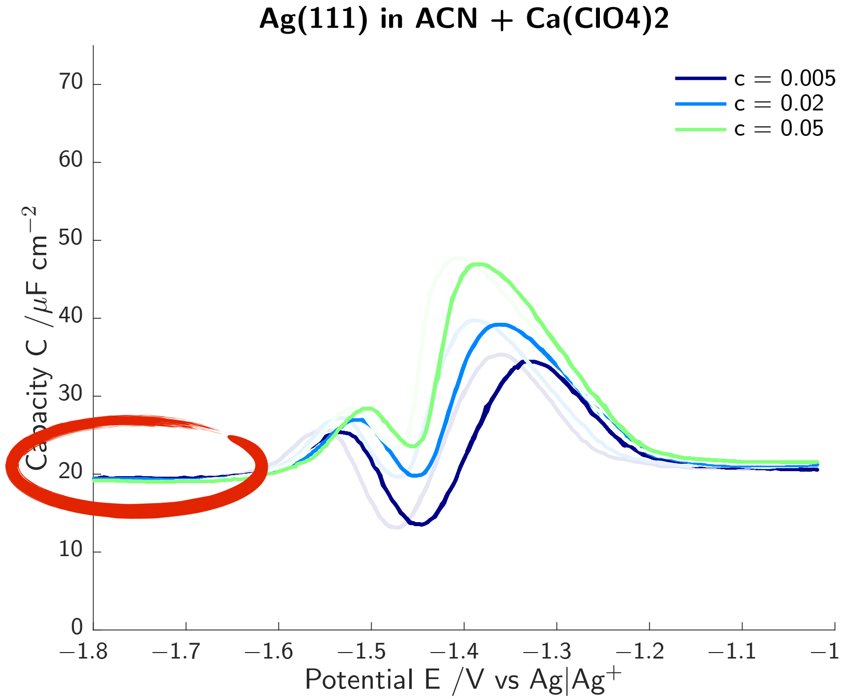
Ag(111) in ACN + NaClO4



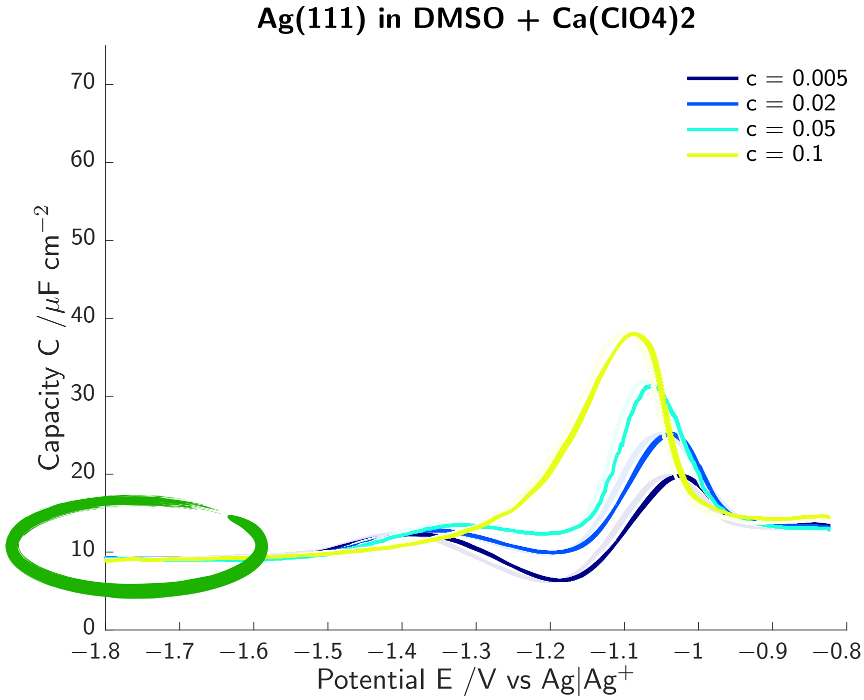
Ag(111) in DMSO + NaClO4



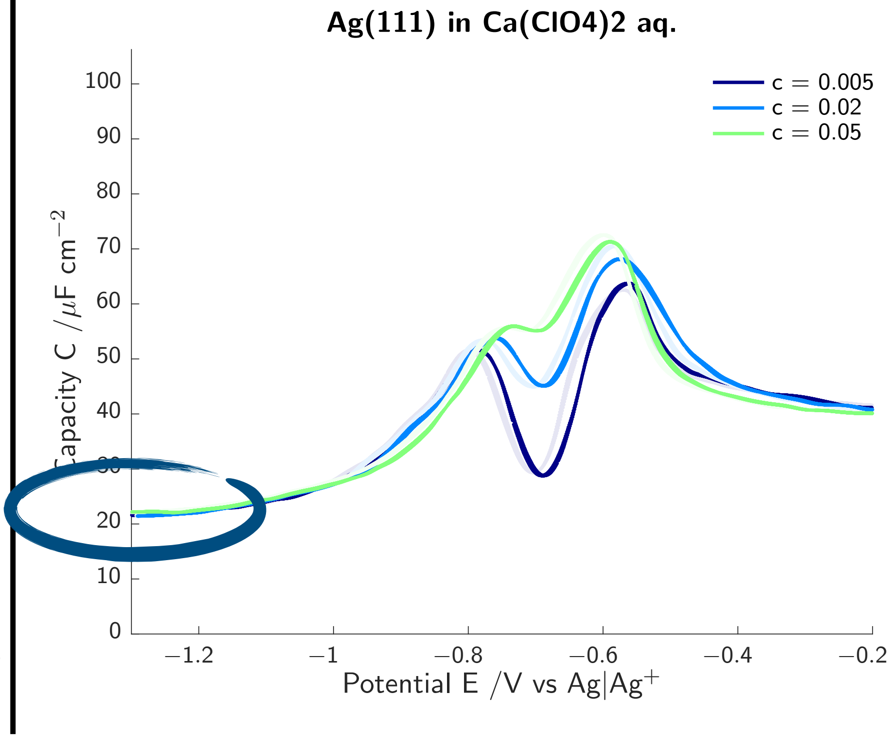
G. Valette, J. Electroanal. Chem., **269** (1989), 191 – 203.



Ag(111) in ACN + Ca(ClO4)2



Ag(111) in DMSO + Ca(ClO4)2



Ag(111) in Ca(ClO4)2 aq.

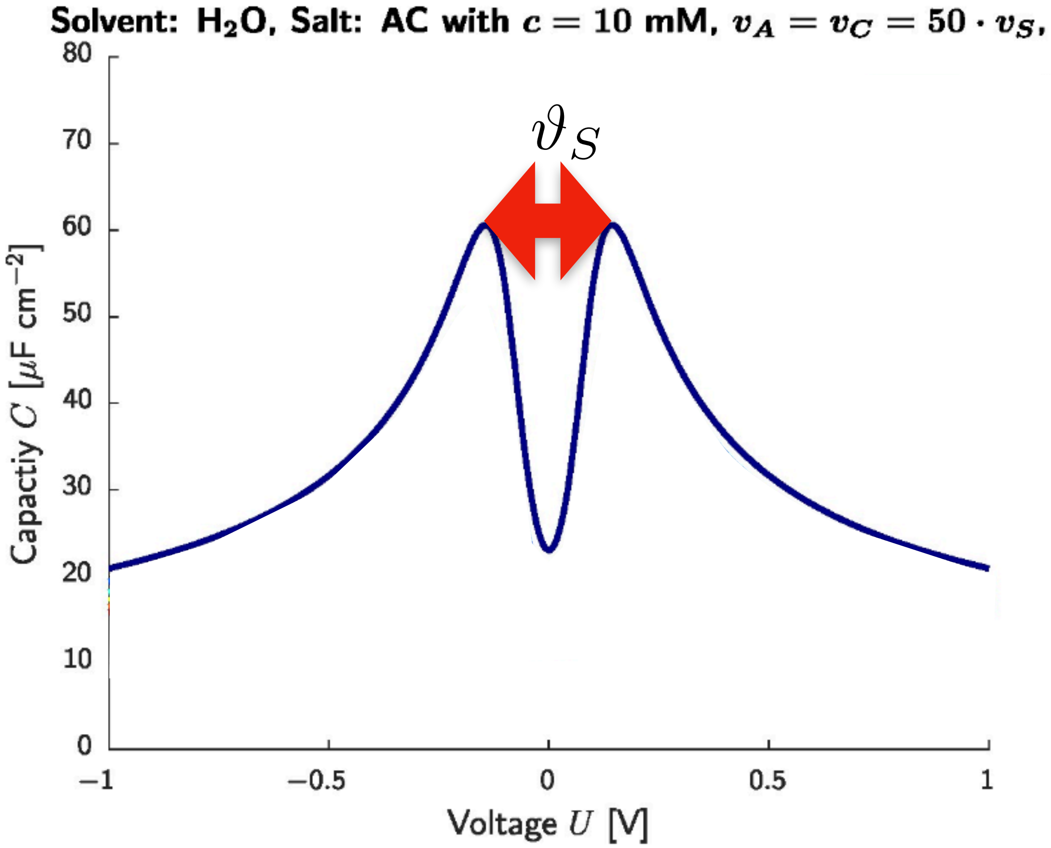
M2 : $\kappa_\alpha = |z_\alpha| \cdot \kappa$

Solvation numbers and partial molar volumes of solvated ions scale <u>linear</u> with charge number

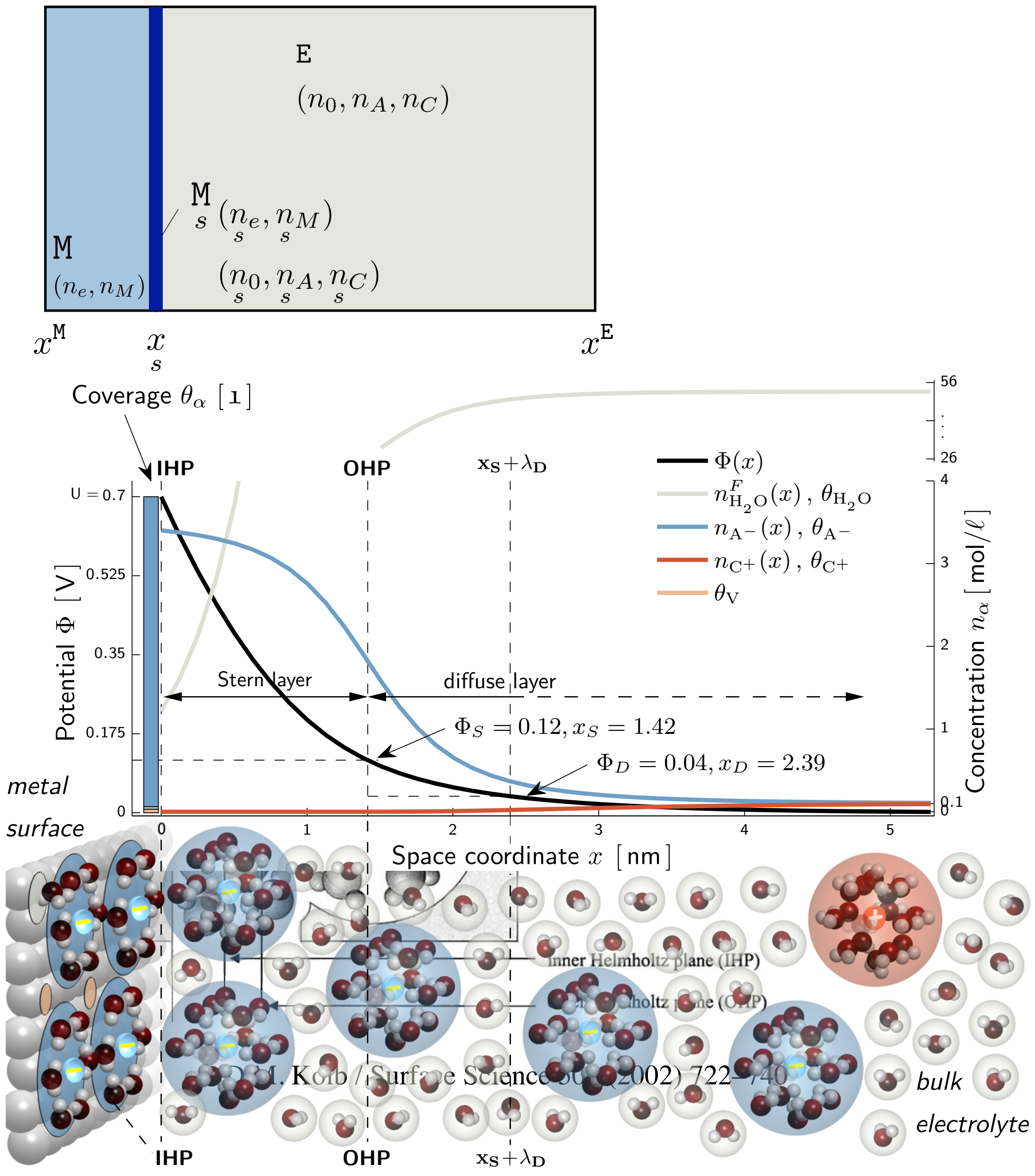
Adsorption of solvent molecules

Yet: Adsorption of surface species do **not** contribute to the overall potential drop

Main consequence: Capacity **maxima width** ϑ_S is equal for all solvents (fixed concentration, susceptibility, molar volumes)



Solvent: H_2O, Salt: AC with $c = 10$ mM, $v_A = v_C = 50 \cdot v_S$,



M. Landstorfer et. al, *Electrochim. Acta.*, 2016, **201**, 187 – 219.

work in progress

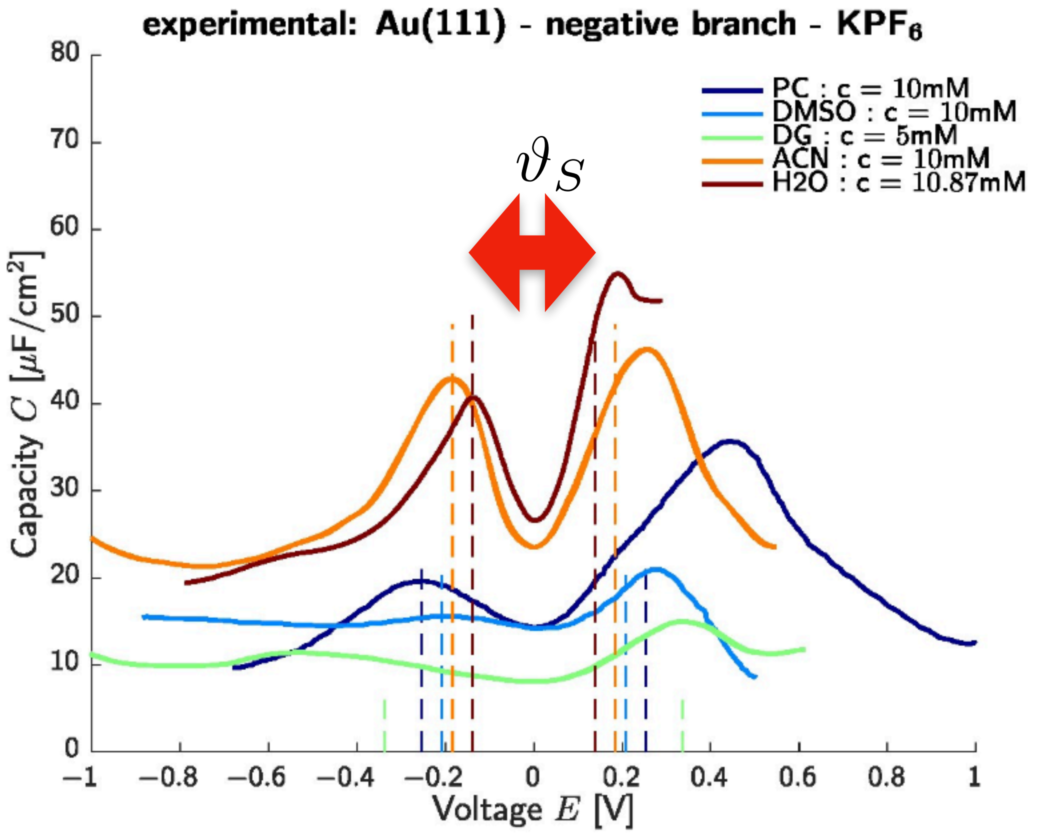
Adsorption of solvent molecules

Experimental: Capacity width ϑ_S dependent on the solvent adsorption

Requirement: Adsorption of (solvent) species contributes to the overall potential drop

$$U - U_{\text{pzc}} = U^S + U^{M,E} \approx (1+\eta_S)\cdot U^{M,E}$$

Linear potential drop across the solvent adsorption layer



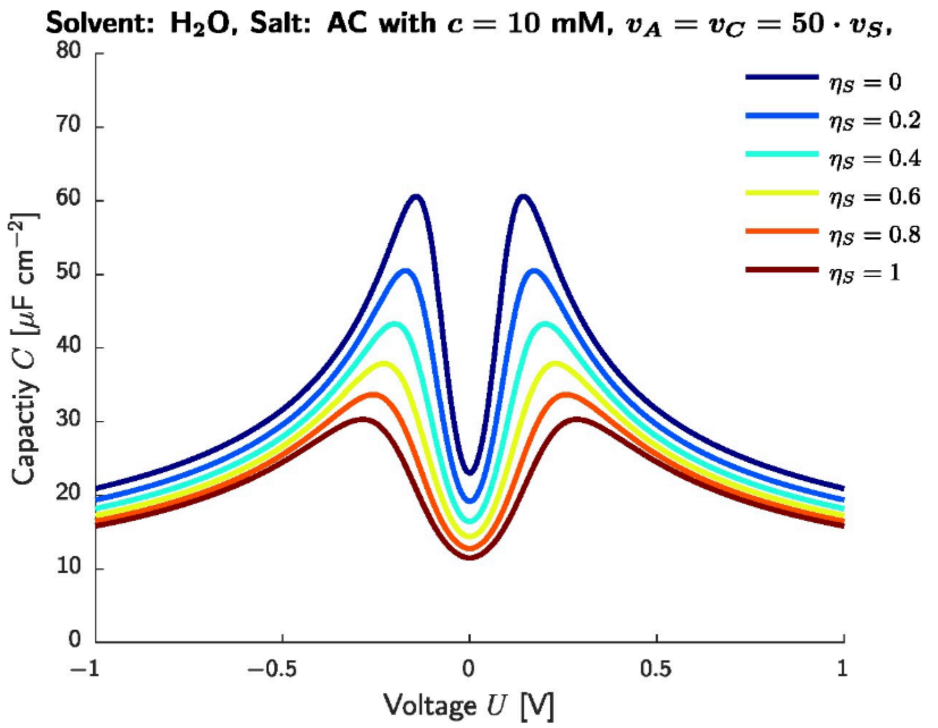
A. S. Shatla, M. Landstorfer, and H. Baltruschat. *ChemElectroChem*, **8(10)**, 2021.

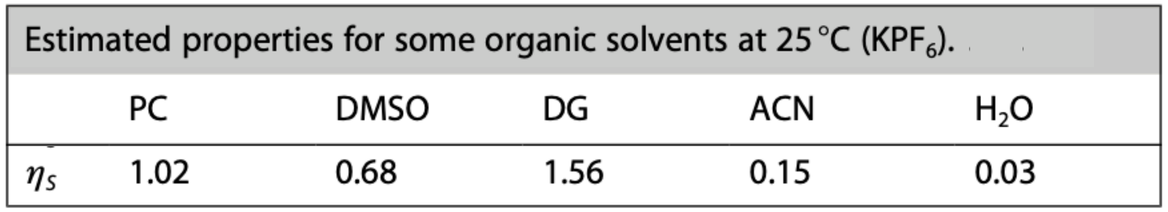
Consequences:

- Capacity **maxima width dependent** on the solvent coefficient η_S

- Capacity scales with η_S

$$C = \frac{dQ}{dU} = \frac{1}{1+\eta_S}\frac{dQ}{dU^{M,E}}$$





Estimated properties for some organic solvents at 25 °C (KPF$_6$).

	PC	DMSO	DG	ACN	H$_2$O
η_S	1.02	0.68	1.56	0.15	0.03

Polycrystalline Electrode - Electrolyte Interface

Charge stored in the interface: $Q_{\text{poly}}(E) = -\frac{1}{|\Sigma|}\int_{\Omega^{\mathrm{E}}} q(x)\,dx$

Double layer capacity (*measurable*): $C_{\text{poly}} = \frac{dQ_{\text{poly}}}{dE}$

thermodynamic equilibrium

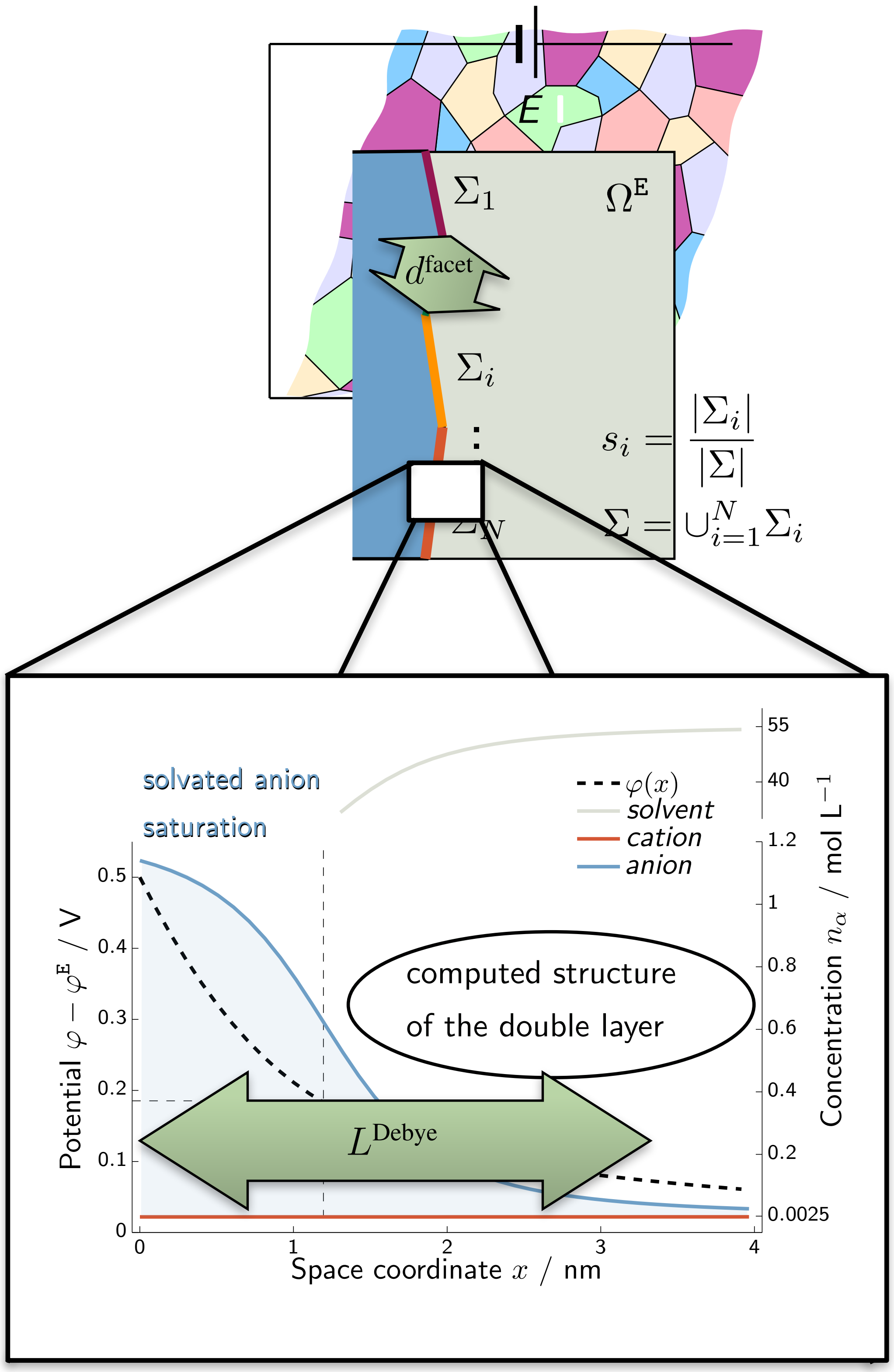
→ Single-crystal functions: $(\hat{Q}^{\text{BL}}(U), \hat{C}^{\text{BL}}(U))$

Two scaling parameters

- double layer width L^{Debye}
- faced diameter d^{facet}

some results

(M1) $$\frac{d^{\text{facet}}}{L^{\text{Debye}}} \to \infty \quad \begin{cases} Q_{\text{poly}} = \sum_{i=1}^{N} s_i \cdot \hat{Q}^{\text{BL}}\left(E + \frac{1}{e_0}\mu_{e}^{i}{}_{s} - E^{ref}\right) \\ E^{\text{PZC}}_{\text{poly},\infty} = E \quad \text{s.t.} \quad Q_{\text{poly},\infty}(E) \overset{!}{=} 0 \\ C_{\text{poly}} = \sum_{i=1}^{N} s_i \cdot \hat{C}^{\text{BL}}\left(E + \frac{1}{e_0}\mu_{e}^{i}{}_{s} - E^{ref}\right) \end{cases}$$



R. Müller, J. Fuhrmann and M. Landstorfer, *Journal of The Electrochemical Society*, 2020, **167**, 106512.

Polycrystalline Electrode - Electrolyte Interface

some results

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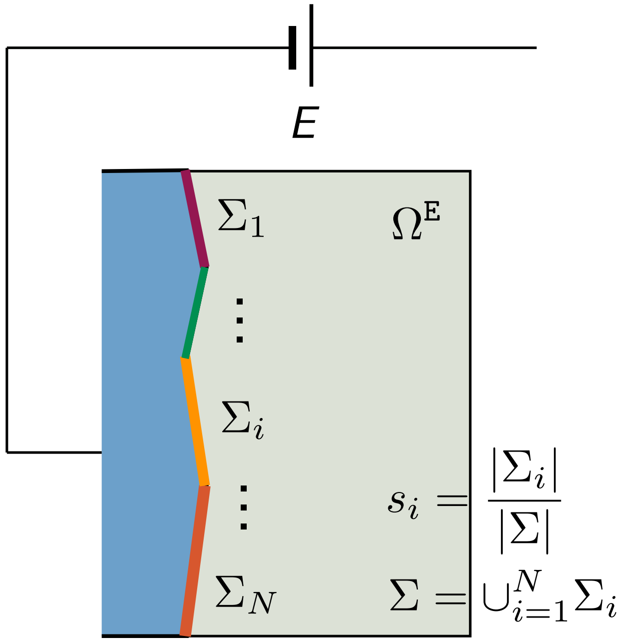
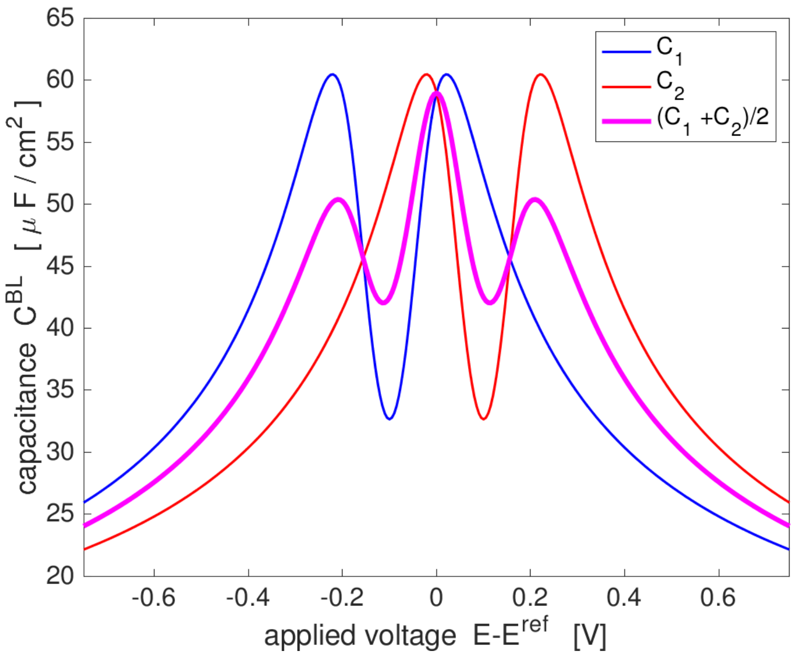


simple example: symmetric bi-crystal



R. Müller, J. Fuhrmann and M. Landstorfer, *Journal of The Electrochemical Society*, 2020, **167**, 106512.

Polycrystalline Electrode - Electrolyte Interface

some results

(M1)

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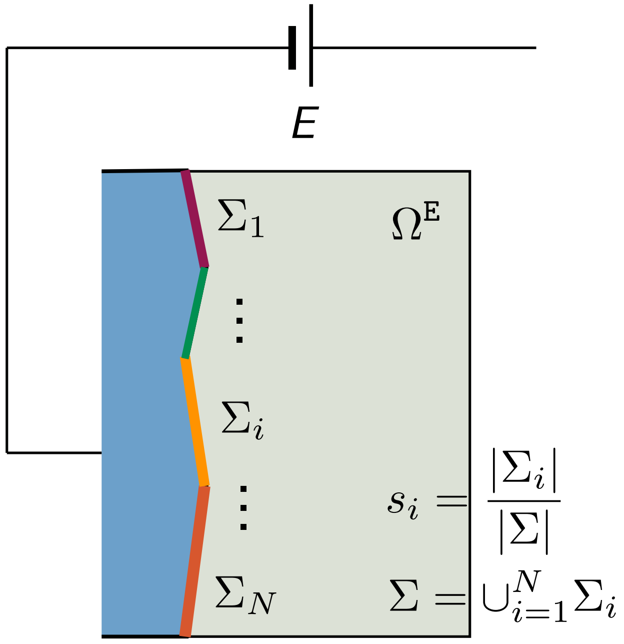

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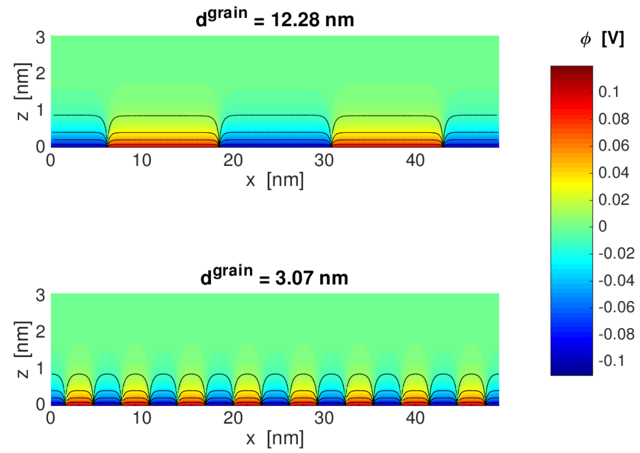
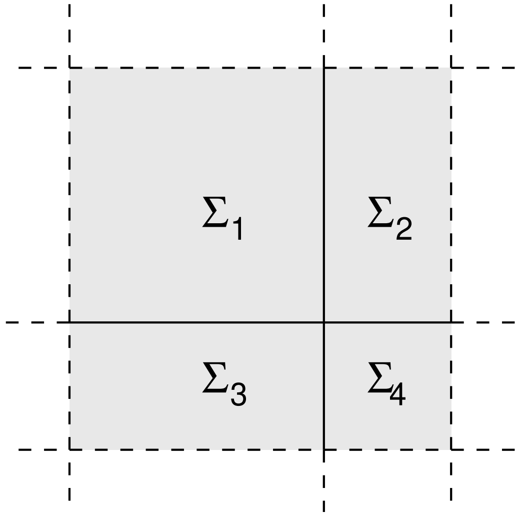
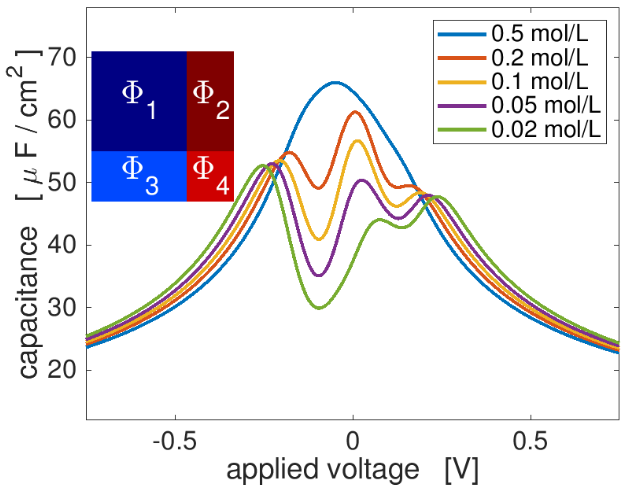
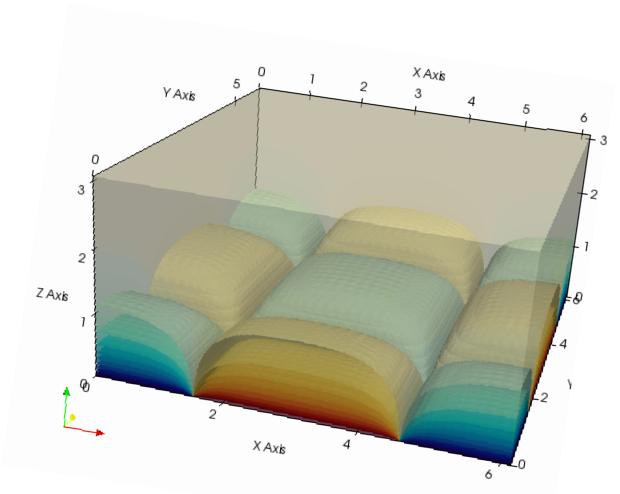
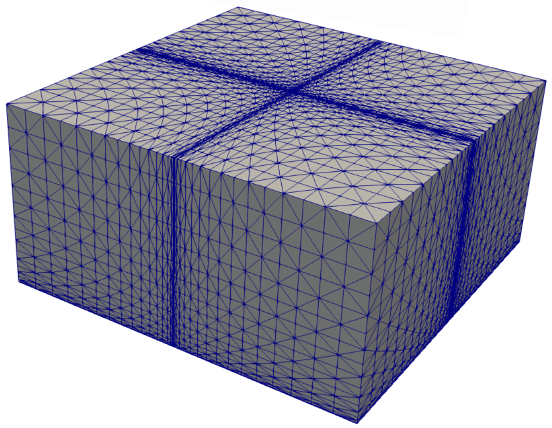
general case: *2D- and 3D-FEM implementation*









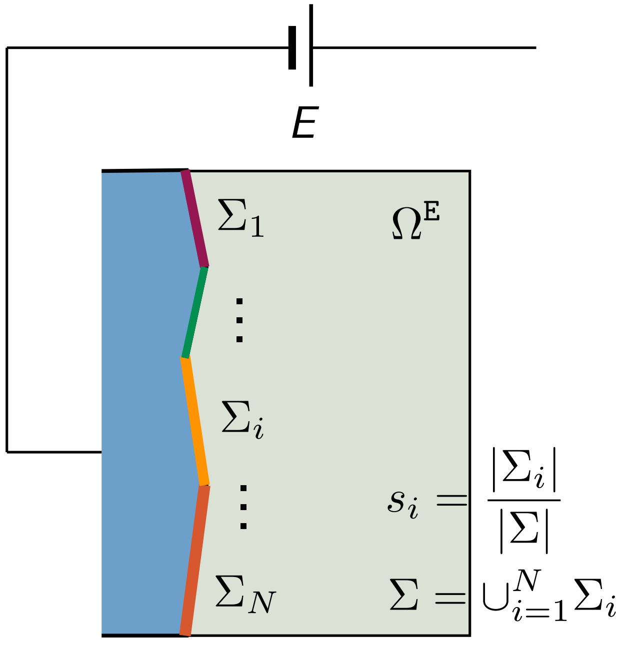


R. Müller, J. Fuhrmann and M. Landstorfer, *Journal of The Electrochemical Society*, 2020, **167**, 106512.

Polycrystalline Electrode - Electrolyte Interface

some results

(M1) $$\frac{d^{\text{facet}}}{L^{\text{Debye}}} \to \infty \quad \begin{cases} Q_{\text{poly}} = \sum_{i=1}^{N} s_i \cdot \hat{Q}^{\text{BL}}\left(E + \frac{1}{e_0}\underset{s}{\mu_e^i} - E^{ref}\right) \\ E^{\text{PZC}}_{\text{poly},\infty} = E \quad \text{s.t.} \quad Q^{\text{BL}}_{\text{poly},\infty}(E) \overset{!}{=} 0 \\ C_{\text{poly}} = \sum_{i=1}^{N} s_i \cdot \hat{C}^{\text{BL}}\left(E + \frac{1}{e_0}\underset{s}{\mu_e^i} - E^{ref}\right) \end{cases}$$



$$s_i = \frac{|\Sigma_i|}{|\Sigma|}$$

$$\Sigma = \cup_{i=1}^{N} \Sigma_i$$

transition to a labeling regarding work-function values ω

→ *introduction of a distribution function f(ω) of the surface fraction*
→ *stochastic description of polycrystalline surfaces*

$$\sum_{i=1}^{N} s_i = \int_{-\infty}^{\infty} f(\omega) d\omega = 1\,.$$

(M2) $$\frac{d^{\text{facet}}}{L^{\text{Debye}}} \to \infty \quad \begin{cases} Q_{\text{poly}} = (f * \hat{Q}^{\text{BL}})(E) \\ E^{\text{PZC}}_{\text{poly},\infty,f} = E \quad \text{s.t.} \quad Q^{\text{BL}}_{\text{poly},\infty,f}(E) \overset{!}{=} 0 \\ C_{\text{poly}} = (f * \hat{C}^{\text{BL}})(E) \end{cases}$$

R. Müller, J. Fuhrmann and M. Landstorfer, *Journal of The Electrochemical Society*, 2020, **167**, 106512.

Concentration and Field dependent Susceptibility

$$\begin{aligned} \varepsilon_0(1+\chi)\,\mathrm{div}\,\nabla\varphi &= -q^{\mathsf{F}}(\varphi,p) \\ \nabla p &= -q^{\mathsf{F}}(\varphi,p)\nabla\varphi \end{aligned}$$

$\chi \neq$ const.

How to model this ?

Concentration and Field dependent Susceptibility

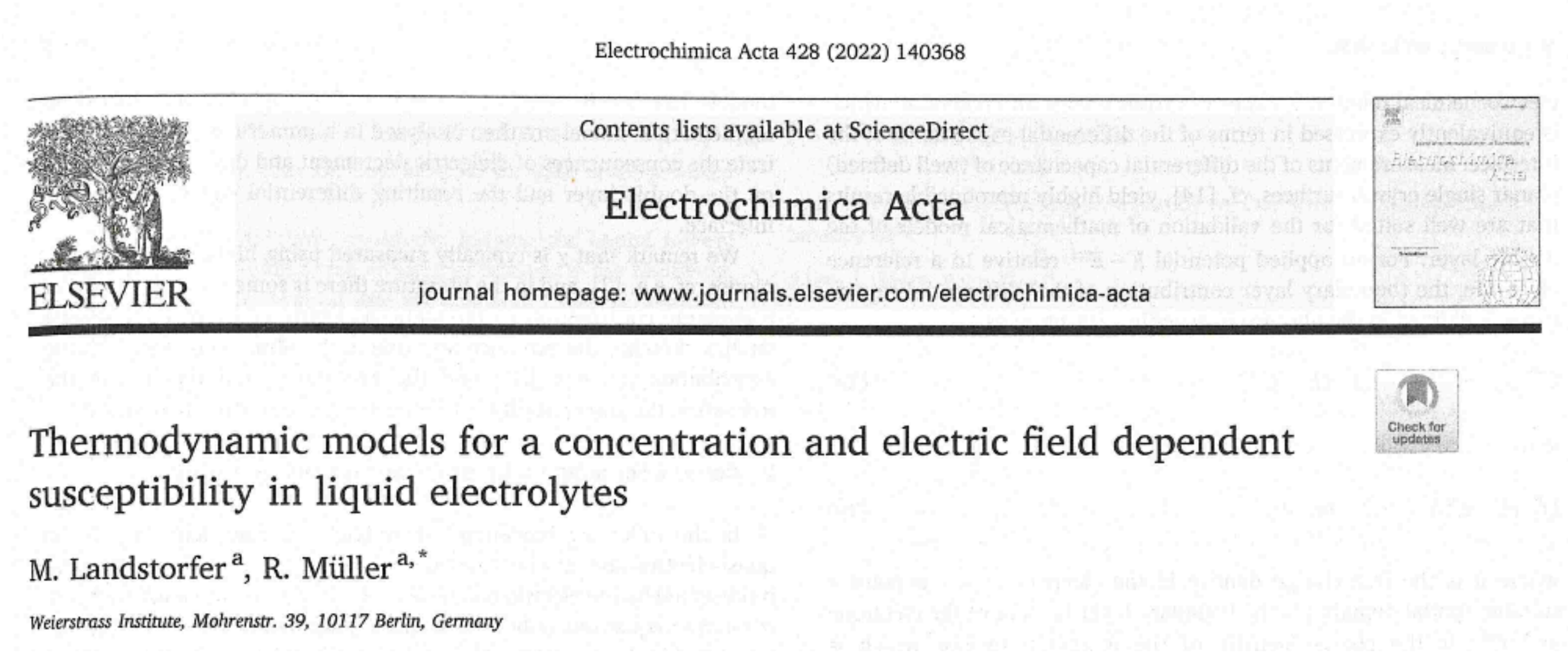
We seek a transition $\chi \to \chi((n_\alpha)_\alpha, |\boldsymbol{E}|^2)$

Can't we just insert our new $\chi((n_\alpha)_\alpha, |\boldsymbol{E}|^2)$ *in the Poisson equation ?*

$$-\mathrm{div}\,\big(\varepsilon_0(1+\chi)\nabla\varphi\big) = q(\varphi, p)$$

No, you can't

The whole equation system has to be re-derived in order to ensure overall thermodynamic consistently → contributions also to the chemical potential!



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Thermodynamic models for a concentration and electric field dependent susceptibility in liquid electrolytes

M. Landstorfer[a], R. Müller[a,*]

[a] Weierstrass Institute, Mohrenstr. 39, 10117 Berlin, Germany

Concentration and Field dependent Susceptibility

Concentration and field dependent susceptibility

$$\nabla p = q\,\boldsymbol{E} + \hat{\chi}^{(3)}((n_\alpha)_\alpha, |\boldsymbol{E}^2|)(\boldsymbol{\nabla} \boldsymbol{E})\boldsymbol{E}$$

$$\varepsilon_0\,\mathrm{div}((1 + \hat{\chi}^{(3)}((n_\alpha)_{\alpha\in\mathcal{I}}, |\boldsymbol{E}^2|))\boldsymbol{E}) = q\;.$$

$$q = q\,(\varphi, p^{\mathsf{mat}}, |\boldsymbol{E}|)$$

M. Landstorfer, R. Müller, Thermodynamic models for a concentration and electric field dependent susceptibility in liquid electrolytes, *Electrochimica Acta, 2022,* ***428***

Constant susceptibility

$$\varepsilon_0(1+\chi)\mathsf{div}\,\nabla\varphi = -q^{\mathsf{F}}(\varphi, p)$$

$$\nabla p = -q^{\mathsf{F}}(\varphi, p)\nabla\varphi$$

M. Landstorfer, C. Guhlke and W. Dreyer, Electrochimica Acta, 2016, **201**.

diffusional equilibrium

$$\nabla(\mu_\alpha + e_0 z_\alpha \varphi) = 0 \qquad \text{for all } \alpha \in \mathcal{I}$$

$$\mu_\alpha^{\mathsf{pol}} = -\tfrac{\varepsilon_0}{2} v_\alpha^{\mathrm{E}} X_\alpha(|\boldsymbol{E}|^2)$$

$$y_\alpha(x) = y_\alpha^{\mathsf{bulk}} \cdot \exp\Big(-\tfrac{e_0 z_\alpha}{k_B T}(\varphi(x) - \varphi^{\mathsf{bulk}}) - \tfrac{v_\alpha^{\mathrm{E}}}{k_B T}(p^{\mathsf{mat}}(x) - p^{\mathsf{bulk}}) + \tfrac{1}{k_B T}\mu_\alpha^{\mathsf{pol}}(|\boldsymbol{E}(x)|)\Big) \quad = \hat{y}_\alpha(\varphi, p^{\mathsf{mat}}, |\boldsymbol{E}|)$$

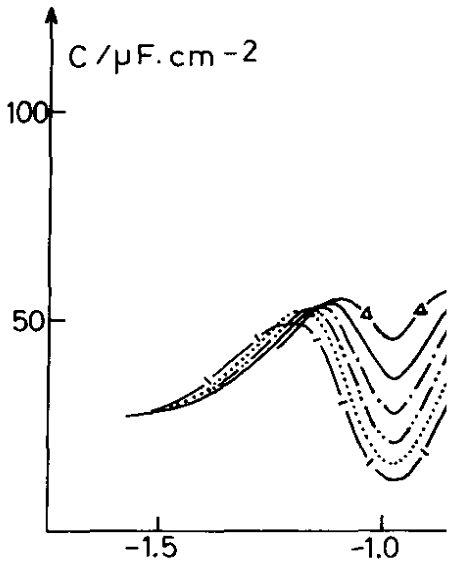
Modeling - Electrolyte - Transport

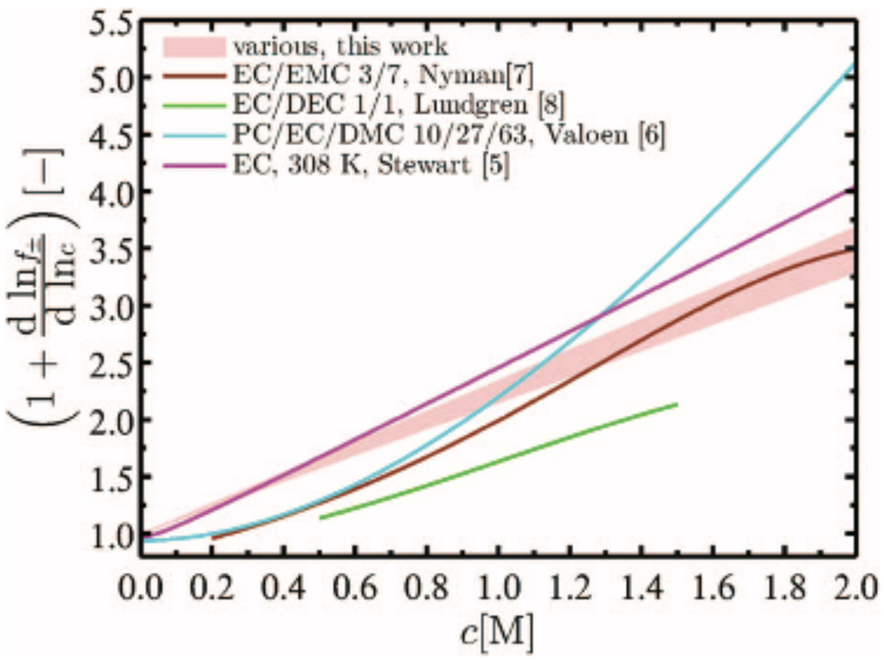
$$\boxed{\mu_\alpha = g_\alpha^{\mathrm{E}} + k_{\mathrm{B}}T\ln\left(\frac{n_\alpha}{\sum_\beta n_\beta}\right) + v_\alpha^{\mathrm{E}}(p - p^{\mathrm{E}})}$$

Ion flux $$\mathbf{J}_\alpha = D_\alpha \frac{n_\alpha}{k_{\mathrm{B}}T}(\nabla\hat{\mu}_\alpha + e_0 z_\alpha \nabla\varphi)$$ with $$\mu_\alpha - \frac{m_\alpha}{m_0}\mu_0 =: \hat{\mu}_\alpha$$

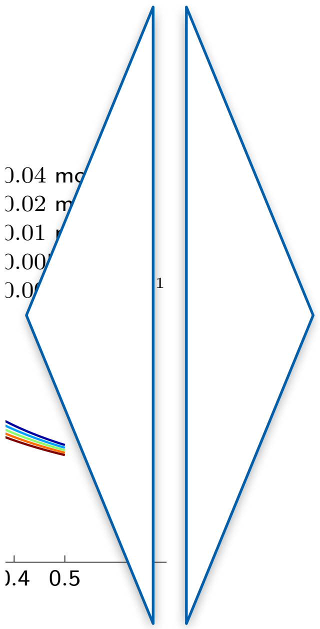
Thermodynamic factor $$\Gamma^{\mathrm{tf}} = \frac{n_\alpha}{k_{\mathrm{B}}T}\cdot\frac{d\hat{\mu}_\alpha}{dn_\alpha}$$

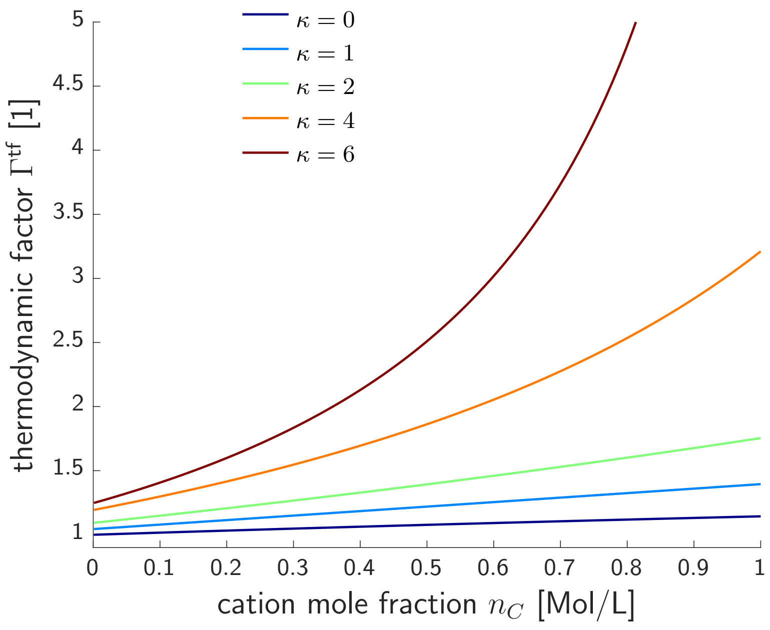
measurement





J. Landesfeind, A. Ehrl, M. Graf, W. A. Wall, H. A. Gasteiger. *J. Electrochem. Soc.*, **163**(7):A1254–A1264, 2016.





M. Landstorfer, WIAS Preprint, *in prep.*

Incompressible solvation mixture

Modeling - Electrolyte - Transport - Nernst-Planck

binary electrolyte without cross-diffusion coefficients

$$\boxed{q = 0}$$

$$\mathbf{J}_A = \frac{n_A}{k_B T}\mathbf{D}_A^E \nabla \hat{\mu}_A + \frac{z_A e_0}{k_B T} n_A \mathbf{D}_A^E \nabla \varphi$$

$$\mathbf{J}_C = \frac{n_C}{k_B T}\mathbf{D}_C^E \nabla \hat{\mu}_C + \frac{z_C e_0}{k_B T} n_C \mathbf{D}_C^E \nabla \varphi$$

$$\mathbf{J}_C = \Gamma^{\mathrm{tf}}(c)\,\overline{\mathbf{D}} \cdot \nabla c + \frac{\mathrm{t}_C}{e_0 z_C} \cdot \mathbf{J}_q$$

$$\mathbf{J}_q = e_0 z_A \mathbf{J}_A + e_0 z_A \mathbf{J}_C$$

with

validation: molar conductivity

$$\Lambda = \frac{e_0^2}{k_B T}(\mathbf{D}_A^E + \mathbf{D}_C^E)\ ,$$

$$\mathrm{t}_C = \frac{\mathbf{D}_C^E}{(\mathbf{D}_A^E + \mathbf{D}_C^E)}\ ,$$

$$\overline{\mathbf{D}} = \frac{2\mathbf{D}_C^E \mathbf{D}_A^E}{\mathbf{D}_A^E + \mathbf{D}_C^E}\ ,$$

$$\overline{\mathbf{S}} := e_0 z_C (\mathbf{D}_C^E - \mathbf{D}_A^E)$$

---

simple Nernst-Planck-flux leads to a **constant** molar conductivity (and transference number)

Experimentally it was found by Kohlrausch around 1900 that

$$\Lambda \approx \Lambda^0 - K \cdot \sqrt{c}$$

contradictory

Nernst-Planck type fluxes violate Kohlrausch' law

M. Landstorfer, WIAS Preprint, *in preparation*

Modeling - Electrolyte - Transport - Cross-diffusion

binary electrolyte with cross-diffusion coefficients

$$\mathbf{J}_A = \mathbf{M}_{A,A}\nabla\hat{\mu}_A + e_0 z_A \mathbf{M}_{A,A}\nabla\varphi$$
$$\mathbf{J}_C = \mathbf{M}_{C,C}\nabla\hat{\mu}_C + e_0 z_C \mathbf{M}_{C,C}\nabla\varphi$$

$$\boxed{\mathrm{M}_{A,A} = \frac{n_A}{k_\mathrm{B}T}\mathrm{D}^E_A} \qquad \boxed{\mathrm{M}_{C,C} = \frac{n_C}{k_\mathrm{B}T}\mathrm{D}^E_C} \qquad \boxed{\mathbf{M}_{A,C} = f(c)\cdot\mathbf{F}_{A,C}\frac{n_C}{k_\mathrm{B}T}}$$

$$\mathbf{J}_C = \Gamma^{\mathrm{tf}}(c)\,\overline{\mathbf{D}}\cdot\nabla c + \frac{\mathfrak{t}_C}{e_0 z_C}\cdot\mathbf{J}_q$$
$$\mathbf{J}_q = \Gamma^{\mathrm{tf}}(c)\,\overline{\mathbf{S}}\cdot\nabla c + c\,\boldsymbol{\Lambda}\nabla\varphi\ .$$

- molar conductivity $\boldsymbol{\Lambda} = \boldsymbol{\Lambda}^0$

$$\boldsymbol{\Lambda}^0 = \frac{e_0^2}{k_\mathrm{B}T}\left(\mathbf{D}^E_A + \mathbf{D}^E_C\right)$$

- Kohlrausch

$$\Lambda \approx \Lambda^0 - K\cdot\sqrt{c} \quad \Longrightarrow \quad f(c) = \sqrt{c}$$

cross-coefficients can simply explain Kohlrausch' law!

M. Landstorfer, WIAS Preprint, *in preparation*

Intercalation electrode - electrolyte interface

$$\mathrm{Li}^{+}\big|_{\mathtt{E}} + \mathrm{e}^{-}\big|_{\mathtt{A}} \rightleftharpoons \mathrm{Li}\big|_{\mathtt{A}} + \kappa_{\mathrm{E}}\cdot\mathrm{S}\big|_{\mathtt{E}}$$

Active phase transport equations and chemical potential functions

$$\mathbf{J}_{Li(A)} \propto \nabla\mu_{Li(A)}$$

$$E^{OCP} \propto \mu_{Li(A)}$$

$$\mathbf{J}_{e^-} \propto \nabla\varphi^{\mathtt{A}}$$

Surface reaction rate for intercalation reaction

$$\underset{s}{R} = \underset{s}{L}\cdot\left(\mathrm{e}^{\alpha\cdot\frac{1}{k_{\mathrm{B}}T}\underset{s}{\lambda}} - \mathrm{e}^{-(1-\alpha)\cdot\frac{1}{k_{\mathrm{B}}T}\underset{s}{\lambda}}\right)$$

with

$$\underset{s}{\lambda} = \mu_{Li(A)}\big|_{\Sigma} + \kappa_{\mathrm{E}}\,\mu_{S}\big|_{\Sigma} - \mu_{Li^+}\big|_{\Sigma} - \mu_{e^-}\big|_{\Sigma} + e_0\left(\varphi^{\mathtt{A}} - \varphi^{\mathtt{E}}\right)$$

Electrolyte transport equations and chemical potential functions

$$\mathbf{J}_{Li^+} \propto \nabla\mu_{Li^+}, \nabla\varphi^{\mathtt{E}}$$

$$\mathbf{J}_{S} \propto \nabla\mu_{S}$$

W. Dreyer, C. Guhlke, R. Müller. A new perspective on the electron transfer: recovering the butler-volmer equation in non-equilibrium thermodynamics. *Phys. Chem. Chem. Phys.*, **18** (2016), 24966–24983.

M. Landstorfer, Boundary conditions for electrochemical interfaces, *J. Electrochem. Soc.* **164**(2017), 3671–3685

2nd law of surface thermodynamics:

$$\underset{s}{L}\cdot\left(\mathrm{e}^{\alpha\cdot\frac{1}{k_{\mathrm{B}}T}\underset{s}{\lambda}} - \mathrm{e}^{-(1-\alpha)\cdot\frac{1}{k_{\mathrm{B}}T}\underset{s}{\lambda}}\right)\cdot\underset{s}{\lambda} \geq 0$$

Intercalation electrode - electrolyte interface

$$\mathrm{Li}^+\big|_{\mathtt{E}} + \mathrm{e}^-\big|_{\mathtt{A}} \rightleftharpoons \mathrm{Li}\big|_{\mathtt{A}} + \kappa_{\mathtt{E}}\cdot\mathrm{S}\big|_{\mathtt{E}}$$

Active phase transport equations and chemical potential functions

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$$\underset{s}{\lambda} = \mu_{Li(A)}\big|_{\Sigma} + \kappa_{\mathtt{E}}\mu_S\big|_{\Sigma} - \mu_{Li^+}\big|_{\Sigma} - \mu_{e^-}\big|_{\Sigma} + e_0\left(\varphi^{\mathtt{A}} - \varphi^{\mathtt{E}}\right)$$

Electrolyte transport equations and chemical potential functions

$$\mathbf{J}_{Li^+} \propto \nabla\mu_{Li^+}, \nabla\varphi^{\mathtt{E}}$$

$$\mathbf{J}_S \propto \nabla\mu_S$$

This coupling ensures overall thermodynamic consistency (and thus predictablility)

M. Landstorfer, M. Ohlberger, S. Rave, M. Tacke, *European Journal of Applied Mathematics,* **2022,** 1-38.

Questions

Thank you for your attention

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