UiO : Department of Chemistry
University of Oslo

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CoorsTek MEMBRANE SCIENCES

PROTON CERAMIC ELECTRODICS

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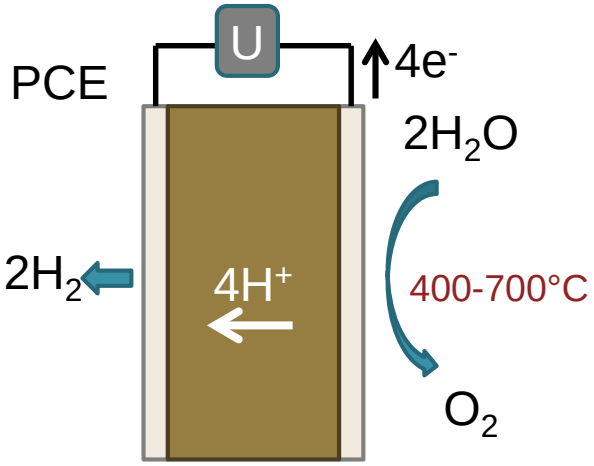
Electra

FCH FUEL CELLS AND HYDROGEN JOINT UNDERTAKING

FOXCET



- Hydration
- Redox electrode
- EIS: CT, MT
- SCL
- Mixed conduction
- Voltammetry

The electrolyte; example Y-doped $BaZrO_3$

- Doping reaction

$$2BaO + Y_2O_3 \xrightarrow{BaZrO_3} 2Y'_{Zr} + v_O^{\bullet\bullet} + 5O_O^x$$

- Hydration

$$H_2O(g) + v_O^{\bullet\bullet} + O_O^x = 2OH_O^{\bullet}$$

- Note: This is not an electrode redox reaction.
  - The charge carriers do not enter via an electrode reaction
  - They are present in equilibrium with $H_2O(g)$

Electrode redox reactions

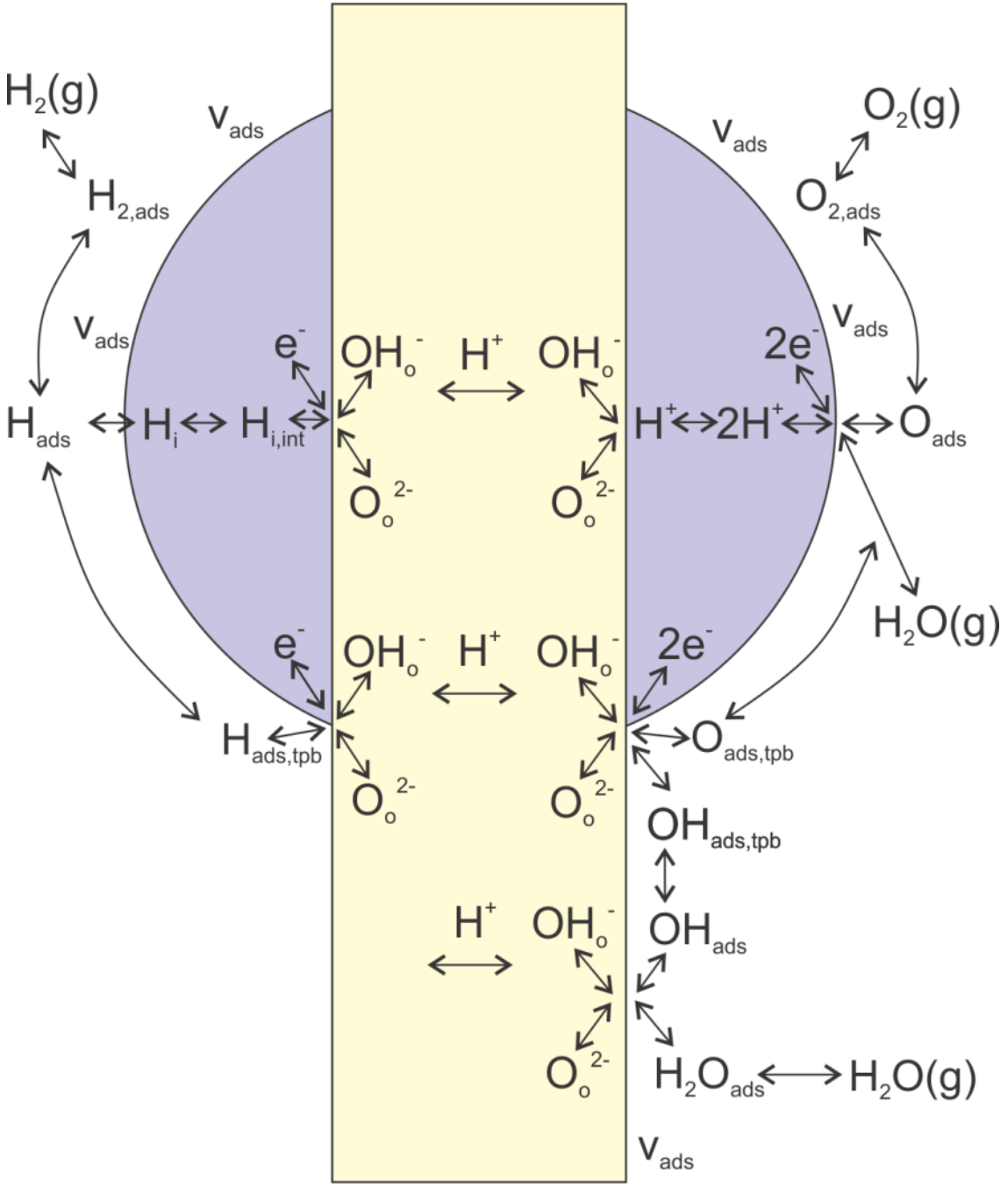
- H_2-side reaction

$$H_2(g) + 2O_O^{2-} \leftrightarrow 2OH_O^- + 2e^-$$

- O_2+H_2O-side reaction

$$O_2(g) + 4OH_O^- + 4e^- \leftrightarrow 2H_2O(g) + 4O_O^{2-}$$

Electrode reaction pathways



H_2-side

$$H_2(g) + v_{ads} \leftrightarrow H_{2,ads}$$

$$H_{2,ads} + v_{ads} \leftrightarrow 2H_{ads}$$

$$H_{ads} + v_i \leftrightarrow H_i + v_{ads} \quad |2$$

$$H_i \leftrightarrow H_{i,int} \quad |2$$

Diffusion

$$H_2(g) + v_{ads} \leftrightarrow H_{2,ads}$$

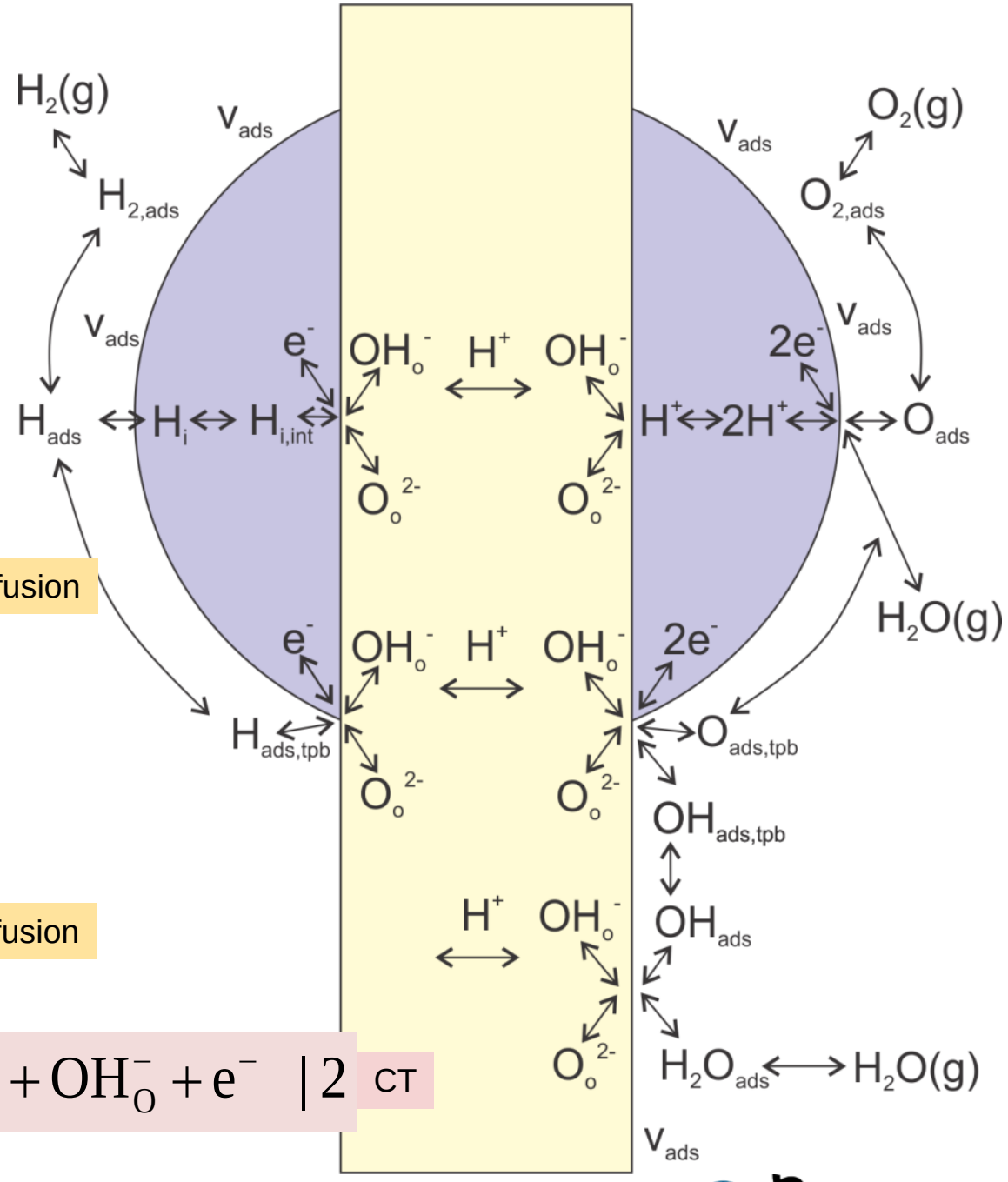
$$H_{2,ads} + v_{ads} \leftrightarrow 2H_{ads}$$

$$H_{ads} \leftrightarrow H_{ads,tpb} \quad |2$$

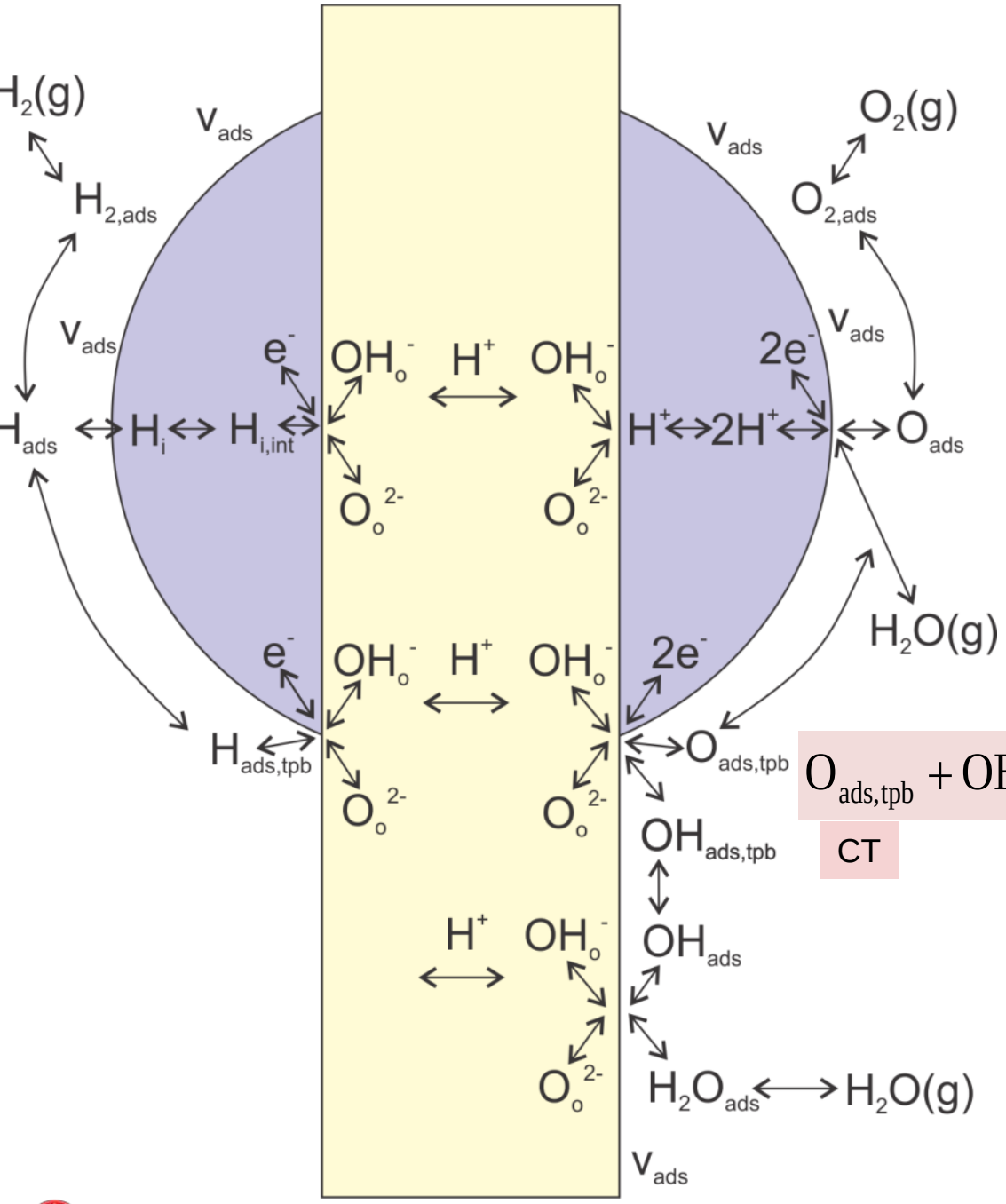
Diffusion

$$H_{ads,tpb/i,int} + O_O^{2-} \leftrightarrow v_{ads,tpb/i,int} + OH_O^- + e^- \quad |2$$

CT



O_2+H_2O side



$$O_2(g) + v_{ads} \leftrightarrow O_{2,ads}$$

$$O_{2,ads} + v_{ads} \leftrightarrow 2O_{ads}$$

$$O_{ads} \leftrightarrow O_{ads,tpb} \quad \text{Diffusion} \quad |2$$

$$O_{ads,tpb} + OH_O^- + 2e^- \leftrightarrow v_{ads,tpb} + OH_{ads,tpb}^- + O_O^{2-} \quad |2$$

CT

$$OH_{ads,tpb}^- \leftrightarrow OH_{ads}^- \quad \text{Diffusion} \quad |2$$

$$OH_{ads}^- + OH_O^- \leftrightarrow O_O^{2-} + H_2O_{ads} \quad |2$$

$$H_2O_{ads} \leftrightarrow H_2O(g) + v_{ads} \quad |2$$

Charge transfer (CT)

$$\mathrm{H}_{\mathrm{ads,tpb/i,int}} + \mathrm{O}_{\mathrm{O}}^{2-} \leftrightarrow \mathrm{v}_{\mathrm{ads,tpb/i,int}} + \mathrm{OH}_{\mathrm{O}}^{-} + \mathrm{e}^{-}$$

$$G_{ct,red}^{eq} = \frac{n_{red} F i_{0,red}}{RT} = \frac{(n_{red} F)^2}{RT} k_{ct,red}^{0} Q_{react,red}^{\beta_{red}} Q_{prod,red}^{1-\beta_{red}}$$

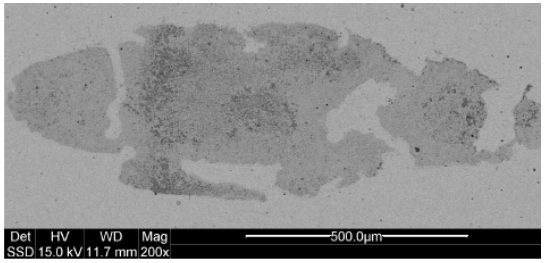
$p\mathrm{H}_2$- (and $p\mathrm{H}_2\mathrm{O}$?)-dependencies

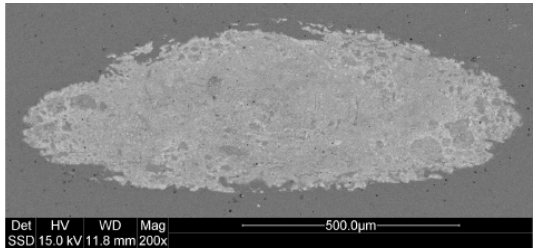
$$\mathrm{O}_{\mathrm{ads,tpb}} + \mathrm{OH}_{\mathrm{O}}^{-} + 2\mathrm{e}^{-} \leftrightarrow \mathrm{v}_{\mathrm{ads,tpb}} + \mathrm{OH}_{\mathrm{ads,tpb}}^{-} + \mathrm{O}_{\mathrm{O}}^{2-}$$

$$G_{ct,ox}^{eq} = \frac{n_{ox} F i_{0,ox}}{RT} = \frac{(n_{ox} F)^2}{RT} k_{ct,ox}^{0} Q_{react,ox}^{\beta_{ox}} Q_{prod,ox}^{1-\beta_{ox}}$$

$p\mathrm{O}_2$- and $p\mathrm{H}_2\mathrm{O}$-dependencies

Cu and Pt point electrodes on BZCY in H_2+H_2O





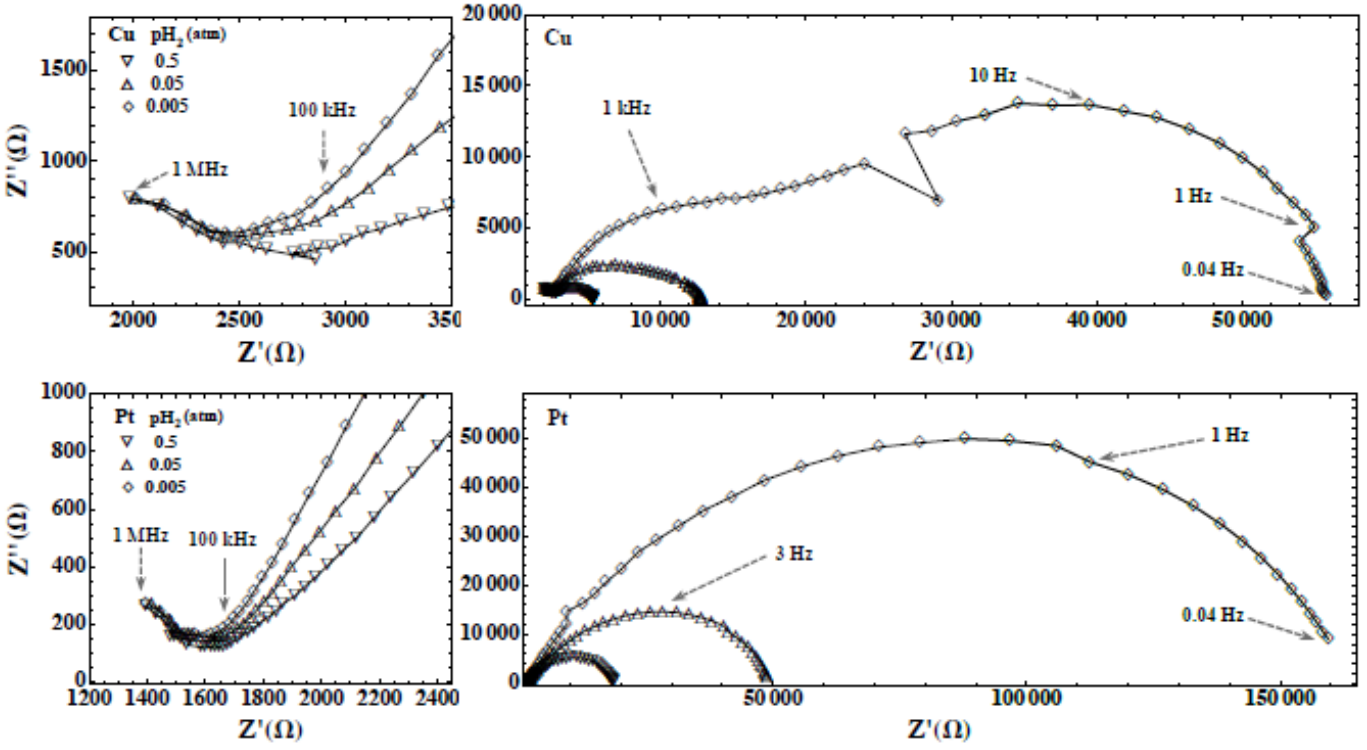
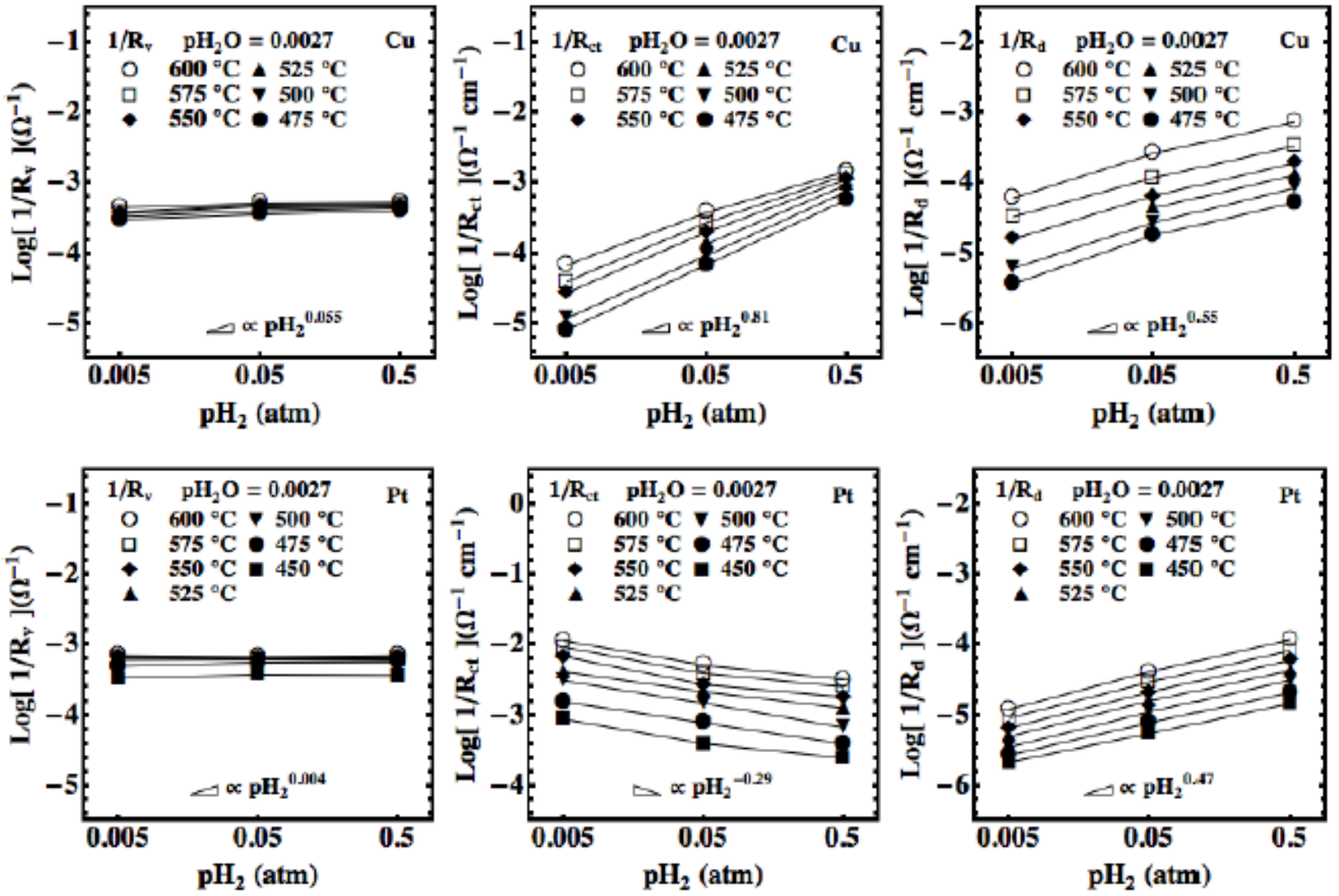


Figure 4: Representative impedance spectra for the Cu (*top*), and Pt (*bottom*) point electrodes, showing high (*left*) and low (*right*) frequency components. Spectra were obtained at 600°C by varying pH_2 in a pH_2O = 0.0027 atm.

S.A. Robinson, C. Kjølseth, T. Norby, "Comparison of Cu and Pt point-contact electrodes on proton conducting $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-d}$", in pub.

Cu and Pt point electrodes on BZCY in H_2+H_2O



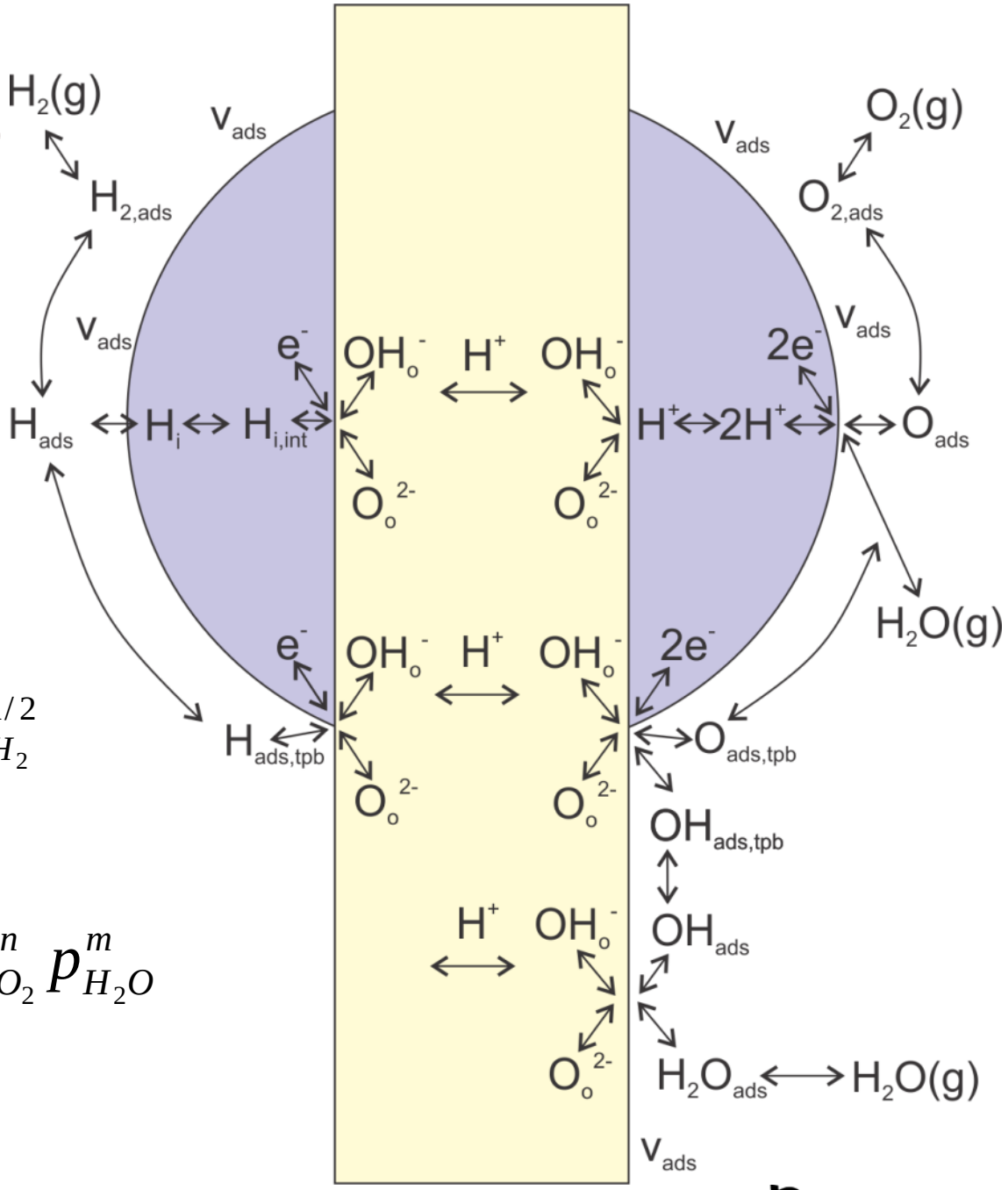
S.A. Robinson, C. Kjølseth, T. Norby, "Comparison of Cu and Pt point-contact electrodes on proton conducting $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-d}$", in pub.

Mass transfer (MT)

- Adsorption
- Dissociation
- Dissolution
- Diffusion

$$G_{mt,red}^{eq} = \frac{(2F)^2}{RT} K_{mt,red}^{0} p_{H_2}^{1/2}$$

$$G_{mt,ox}^{eq} = \frac{(4F)^2}{RT} K_{mt,ox}^{0} p_{O_2}^{n} p_{H_2O}^{m}$$



Cu and Pt point electrodes on BZCY in H_2+H_2O

$$H_{ads,tpb/i,int} + O_O^{2-} \leftrightarrow v_{ads,tpb/i,int} + OH_O^- + e^-$$

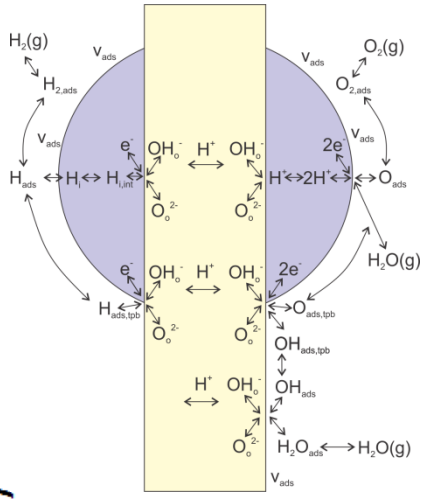
$$G_{ct,red}^{eq} = \frac{n_{red} F i_{0,red}}{RT} = \frac{(n_{red} F)^2}{RT} k_{ct,red}^0 Q_{react,red}^{\beta_{red}} Q_{prod,red}^{1-\beta_{red}}$$

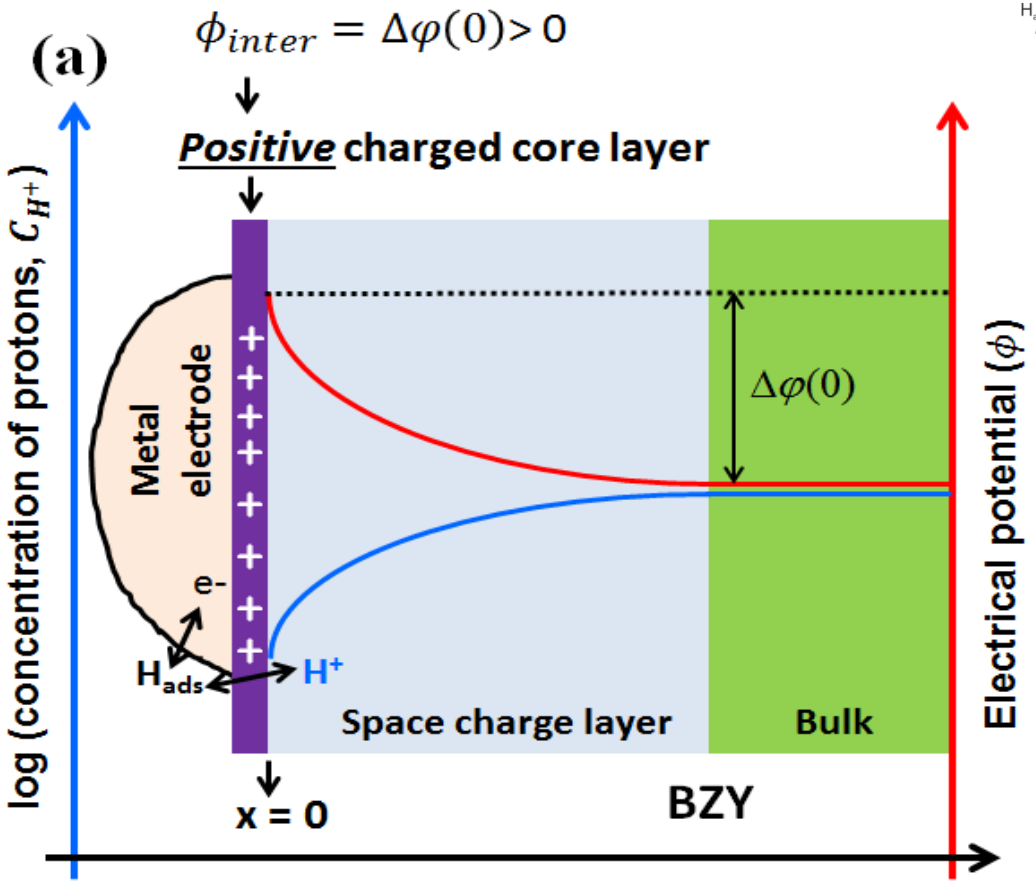
	$\overline{x_i} \pm \sigma_i$	Cu	Pt
CT	n_{ct}	0.77 ± 0.09	-0.30 ± 0.04
	m_{ct}	-0.02 ± 0.12	0.08 ± 0.08
	ΔH_{ct} (eV)	0.82 ± 0.21	0.93 ± 0.09
	$\mathrm{Log}(A_{0,ct}(\Omega^{-1}cm^{-1}))$	2.21 ± 0.10	3.00 ± 0.06
MT	n_d	0.53 ± 0.04	0.46 ± 0.02
	m_d	0.04 ± 0.04	0.01 ± 0.03
	ΔH_d (eV)	1.21 ± 0.09	0.73 ± 0.05
	$\mathrm{Log}(A_{0,d}(\Omega^{-1}cm^{-1}))$	4.00 ± 0.13	0.42 ± 0.04

$$G_{mt,red}^{eq} = \frac{(2F)^2}{RT} K_{mt,red}^0 p_{H_2}^{1/2}$$

S.A. Robinson, C. Kjølseth, T. Norby, "Comparison of Cu and Pt point-contact electrodes on proton conducting $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-d}$", in pub.

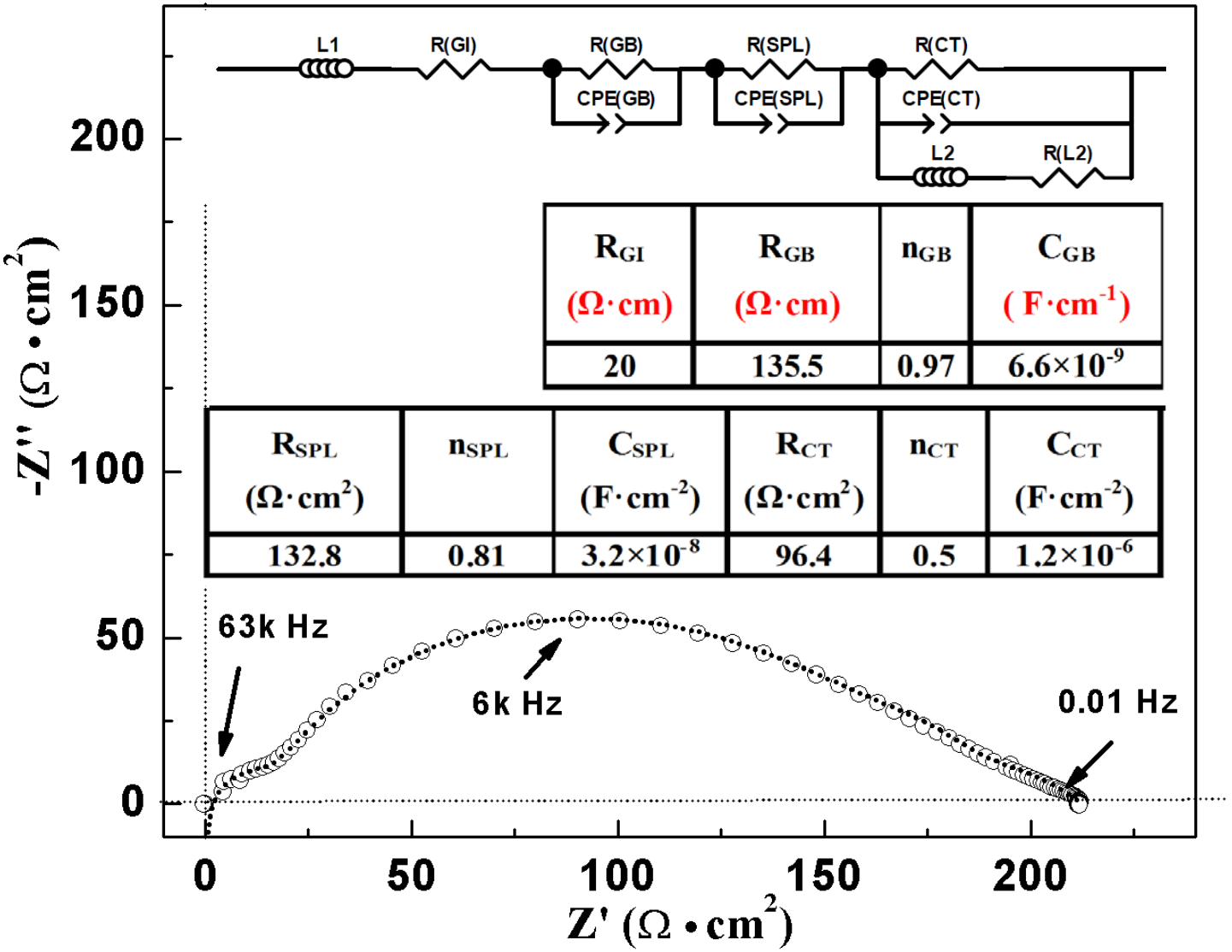
Electrode space charge layer (SCL)





$$G_{scl,red}^{eq} = \frac{Fc_{H^+}u_{H^+}}{\int_0^{\lambda} \exp\left(\frac{F\Delta\varphi(x)}{RT}\right)dx} \approx \frac{Fc_{H^+}u_{H^+}\frac{2F\Delta\varphi(0)_{red}}{RT}}{\lambda \exp\left(\frac{F\Delta\varphi(0)_{red}}{RT}\right)}$$

B+GB+SCL+CT for nanograined Ni on BZY in H_2+H_2O

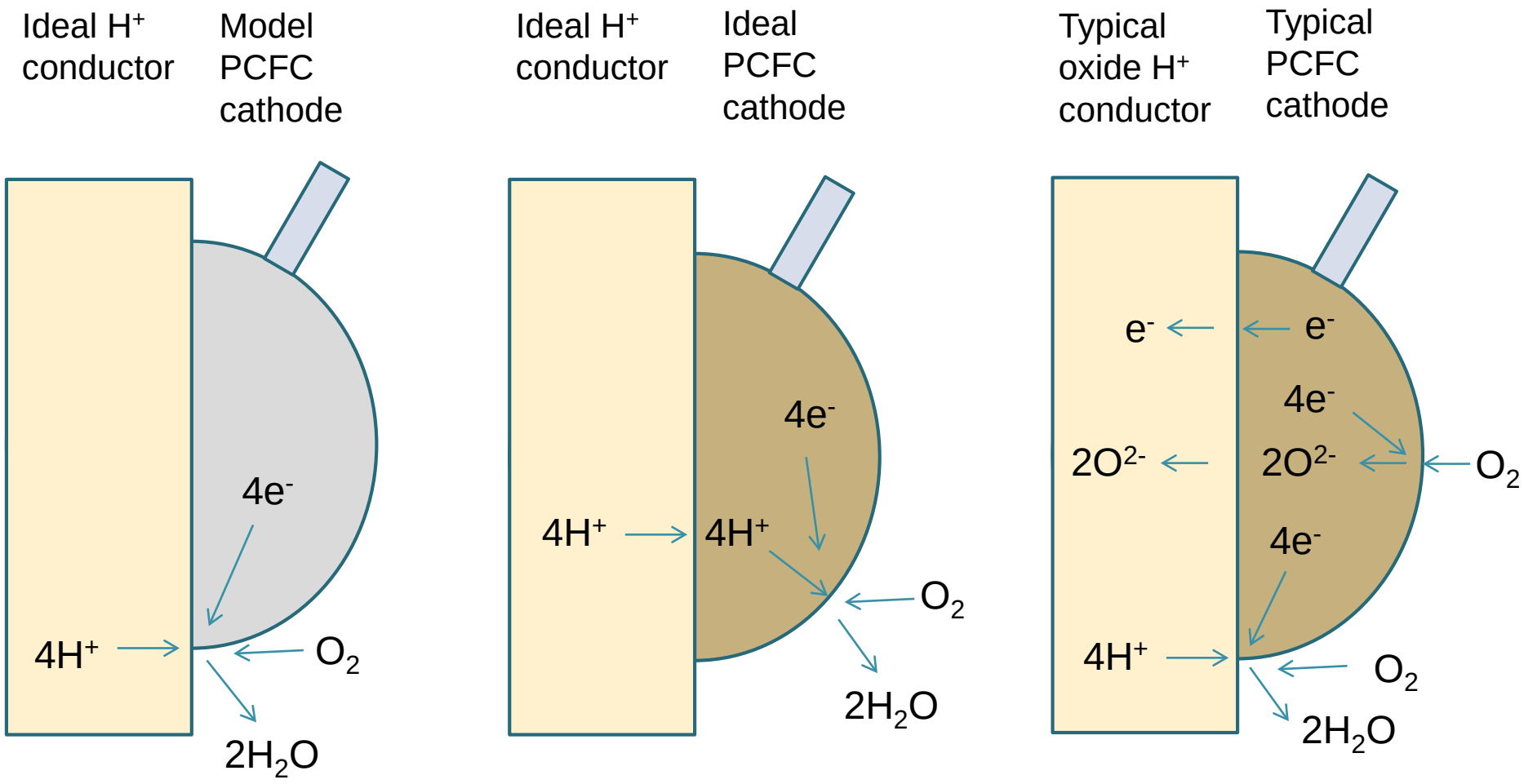


R_{GI} (Ω·cm)	R_{GB} (Ω·cm)	n_{GB}	C_{GB} (F·cm^{-1})
20	135.5	0.97	6.6×10^{-9}

R_{SPL} (Ω·cm^2)	n_{SPL}	C_{SPL} (F·cm^{-2})	R_{CT} (Ω·cm^2)	n_{CT}	C_{CT} (F·cm^{-2})
132.8	0.81	3.2×10^{-8}	96.4	0.5	1.2×10^{-6}

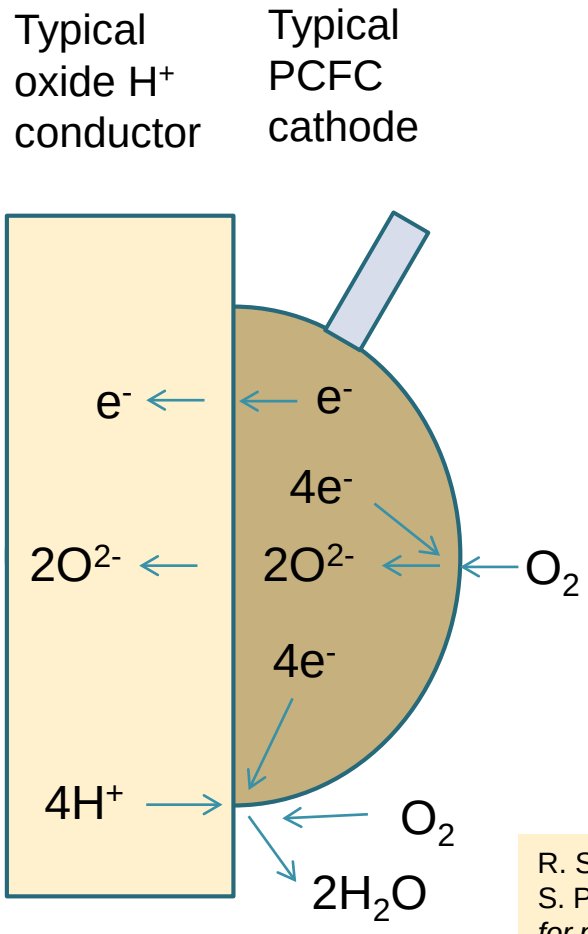
Min Chen, T. Norby, “Space Charge Layer Effect at the Ni/$BaZr_{0.9}Y_{0.1}O_{3-\delta}$ Electrode Interface in Proton Ceramic Electrochemical Cells”, under publication

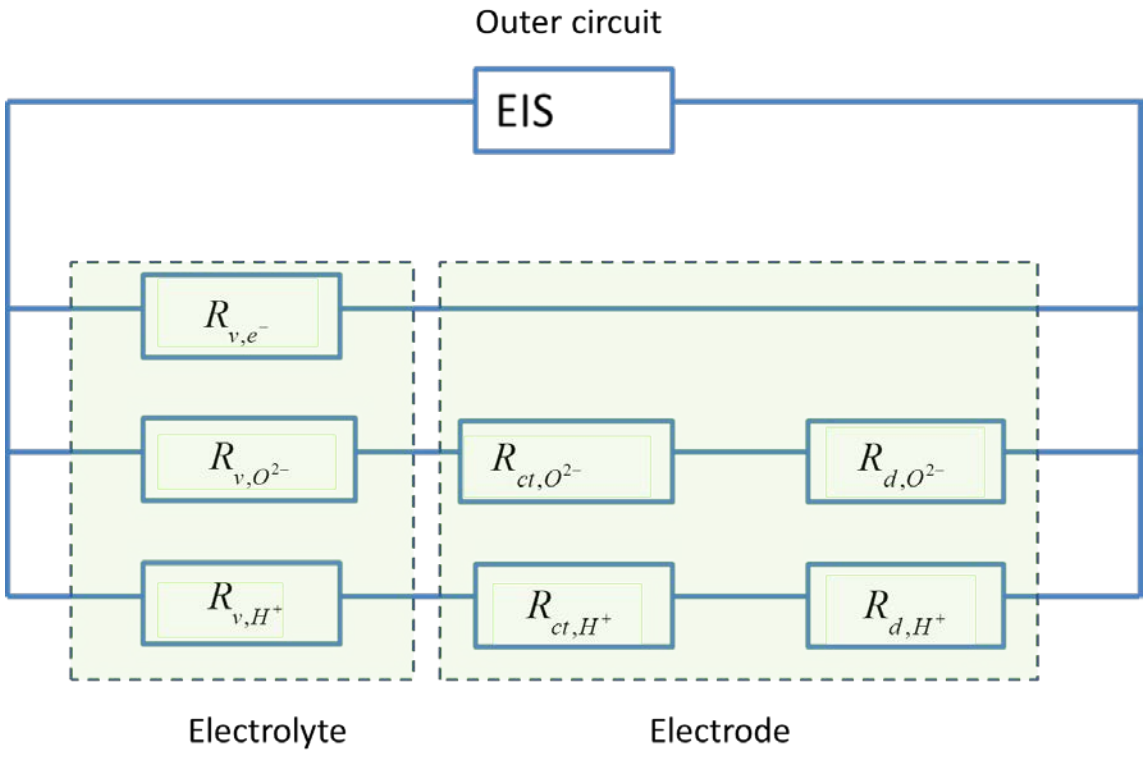
Mixed conduction – example O_2+H_2O-side electrode



PCFC oxygen electrodes (cathodes)

- Mixed conductivity: protons, oxide ions, electrons (holes)

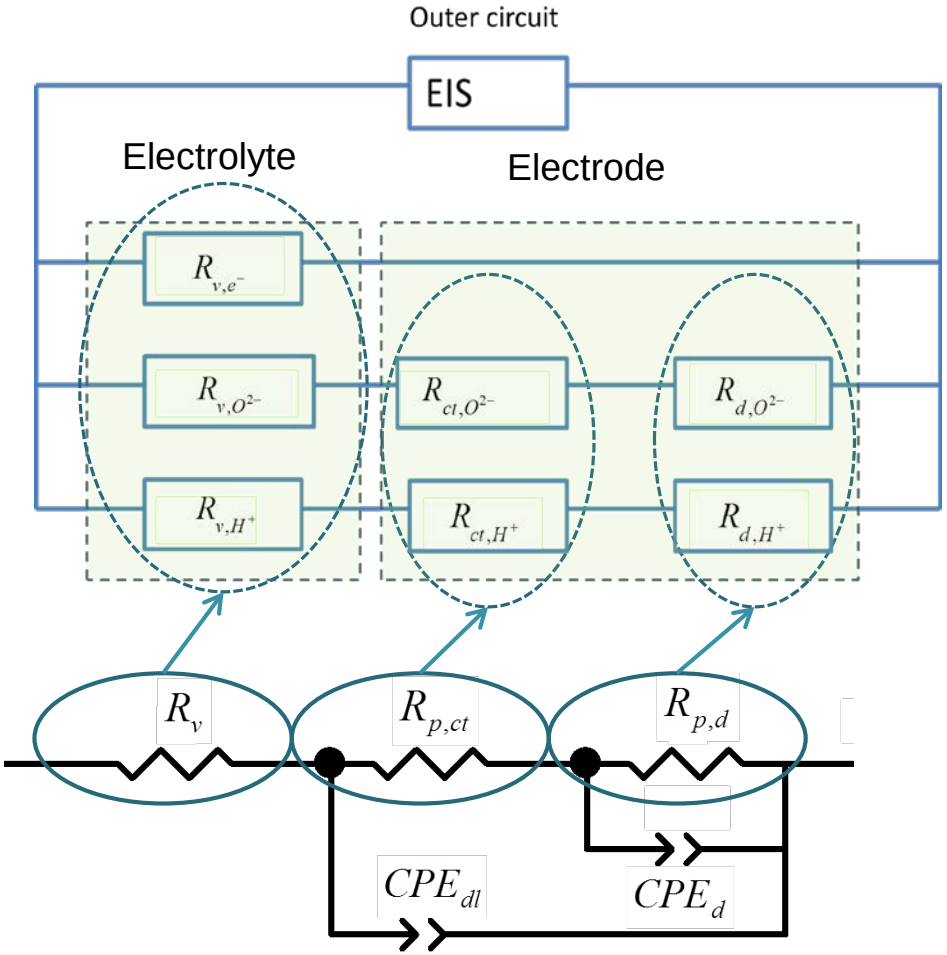


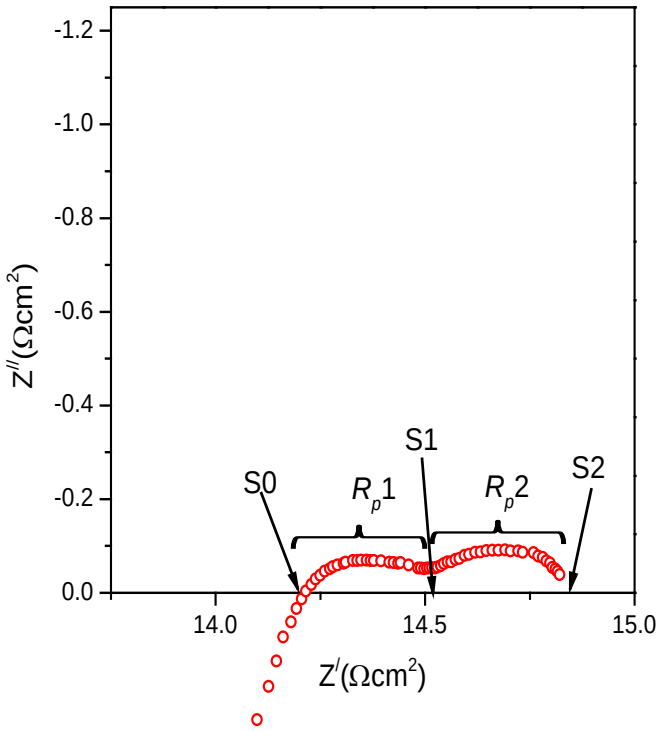


R. Strandbakke, V. Cherepanov, A. Zuev, D.S. Tsvetkov, C. Argirusis, G. Sourkouni-Argirusis, S. Prünte, T. Norby, *"Gd- and Pr-based double perovskite cobaltites as oxygen side electrodes for proton ceramic fuel cells and electrolyser cells", Solid State Ionics*, **278** (2015) 120.

Perovskite electrode on $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_3$ (BZCY)

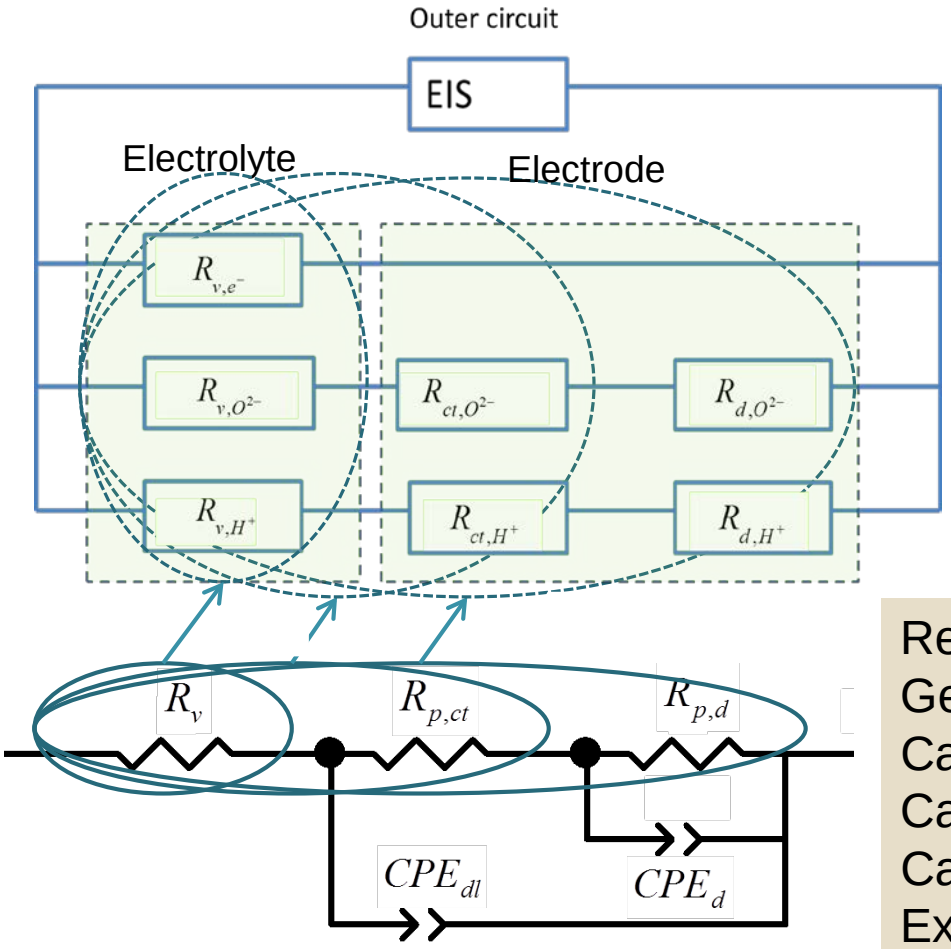
- Impedance spectra yield apparent electrode polarisation resistances

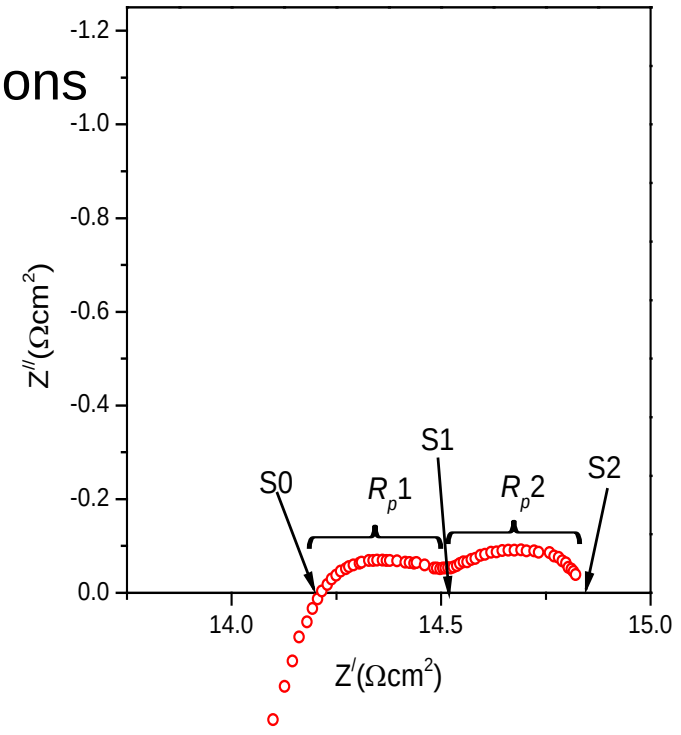




Perovskite electrode on $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_3$ (BZCY)

- …but a more correct treatment is required
- needs more input parameters and assumptions

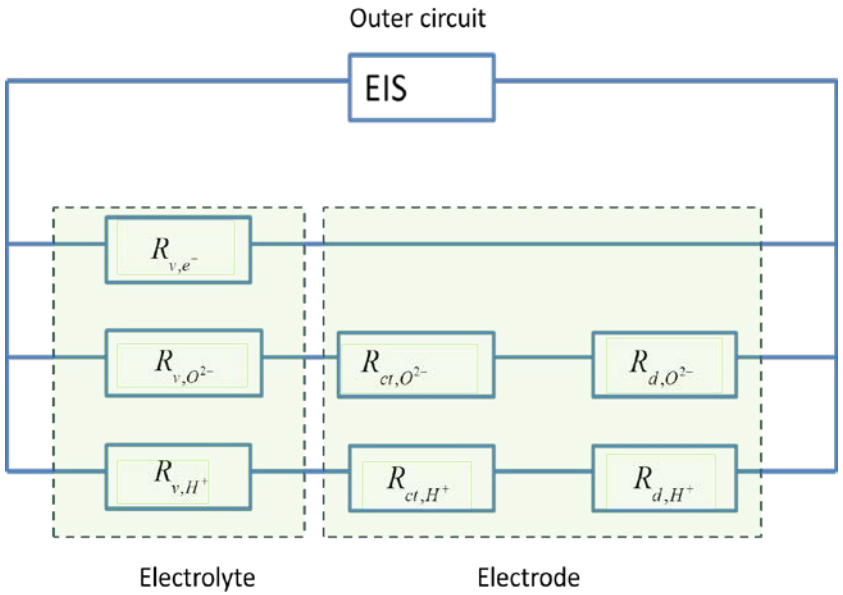


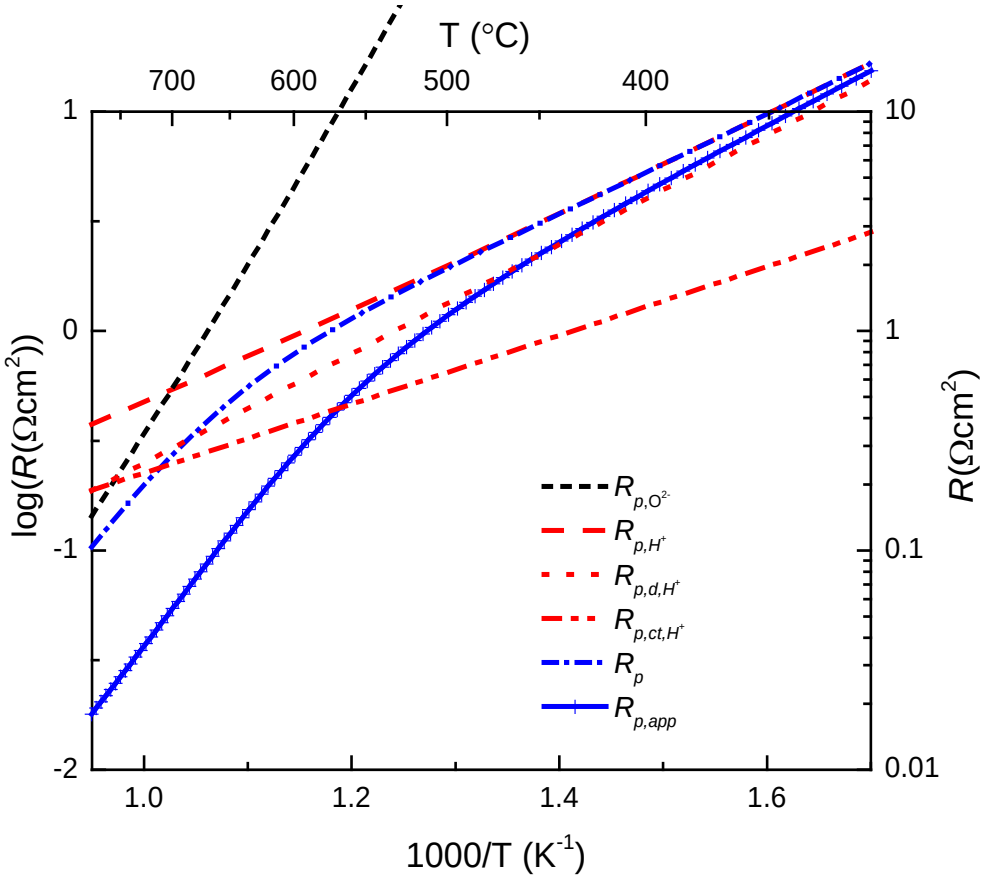


Recipe:
Get individual R_v's from conductivity data
Calibrate to R_v at S0
Calculate properly R_v+$R_{p,1}$ at S1
Calculate properly R_v+$R_{p,1}$+$R_{p,2}$ at S2
Express and fit 4 unknown R_p's to variations in T, pO_2, pH_2O

Perovskite electrode on $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_3$ (BZCY)

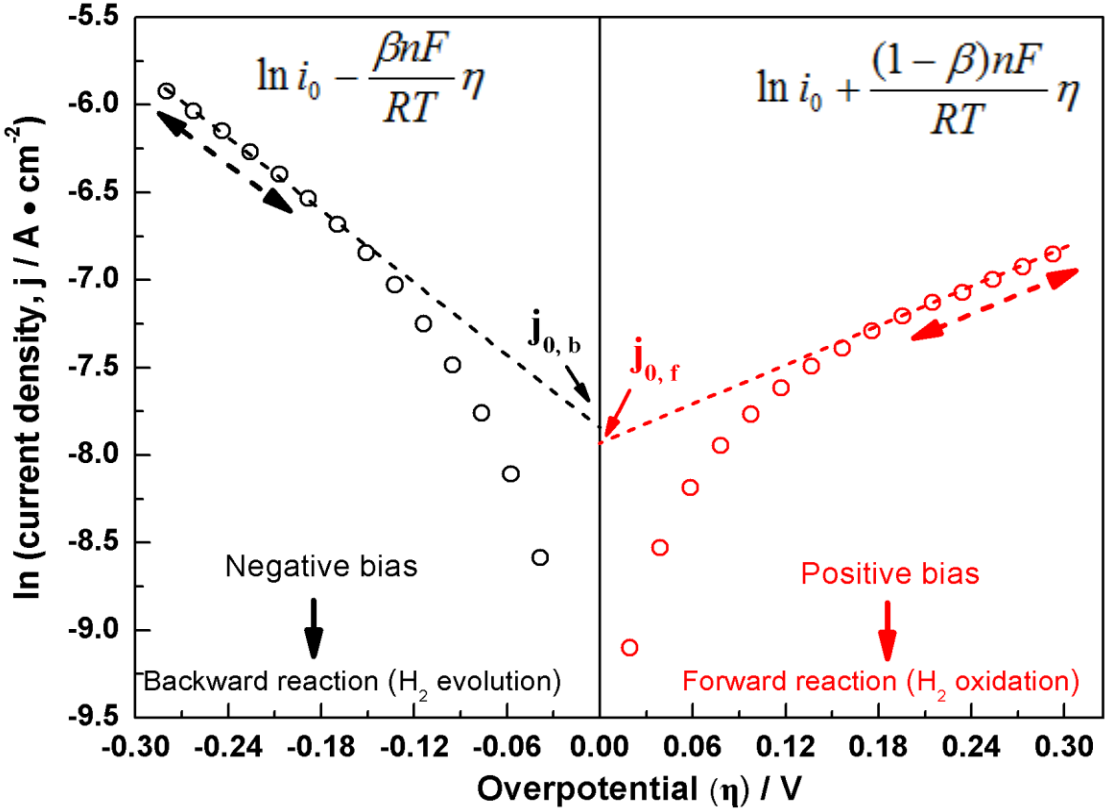
- Modelling by fitting all data
- Protons vs oxide ions
- Effect of electronic conduction
- CT and MT(d)





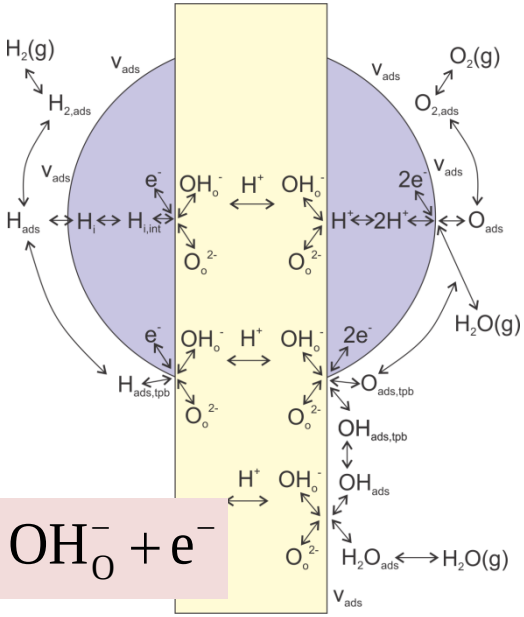
Voltammetry

- Tafel plot displays the kinetics of only the forward or backward reaction
- Yields β, n, i_0
- May require EIS to deconvolute R's and η's
- Example: Ni on BZY

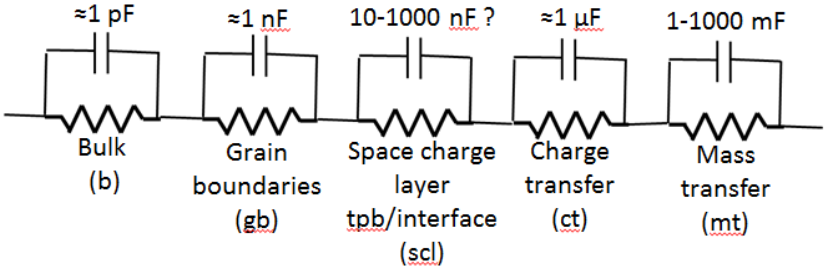


Summary

- Hydration $H_2O(g) + v_O^{\bullet\bullet} + O_O^x = 2OH_O^{\bullet}$
- Redox-reactions $H_2(g) + 2O_O^{2-} \leftrightarrow 2OH_O^- + 2e^-$
- Reaction paths and CT $H_{ads,tpb/i,int} + O_O^{2-} \leftrightarrow v_{ads,tpb/i,int} + OH_O^- + e^-$

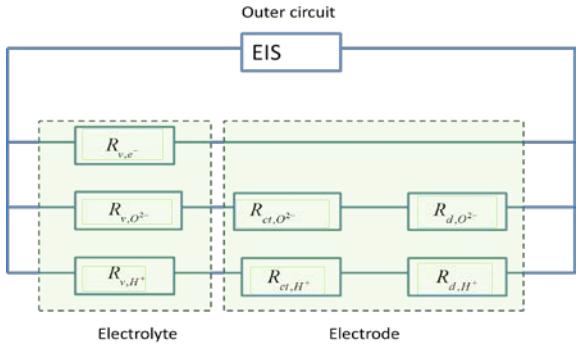


- EIS
  - Separate into G+GB, (SCL?), CT, MT
  - Pre-exponential: Microstructure
  - Activation energy: Kinetics
  - pH_2, pH_2O, pO_2 dependencies: Mechanistics



D. Poetzsch, R. Merkle, J. Maier, *J. Electrochem. Soc.*, **162** [9] (2015) F939.

- Mixed conduction
- Voltammetry



Acknowledgements

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