UiO : Department of Chemistry
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Electra

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fuel cells & hydrogen for sustainability

Characterization of double perovskite electrodes on ionic conductors with transport of more than one type of charge carriers

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SENTER FOR MATERIALVITENSKAP OG NANOTEKNOLOGI

FERMiO
Oslo Innovation Centre

BZCY: $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_3$

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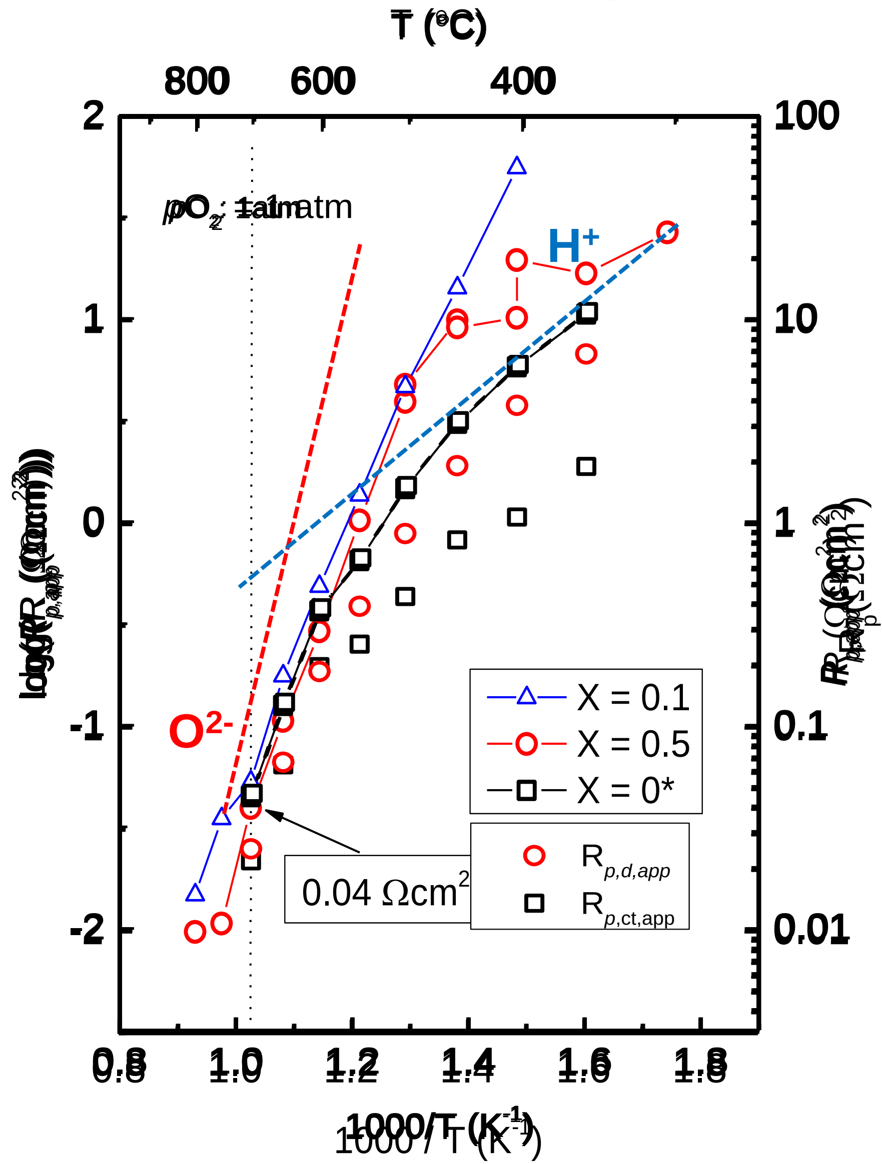
Double perovskite cathodes on BZCY electrolytes

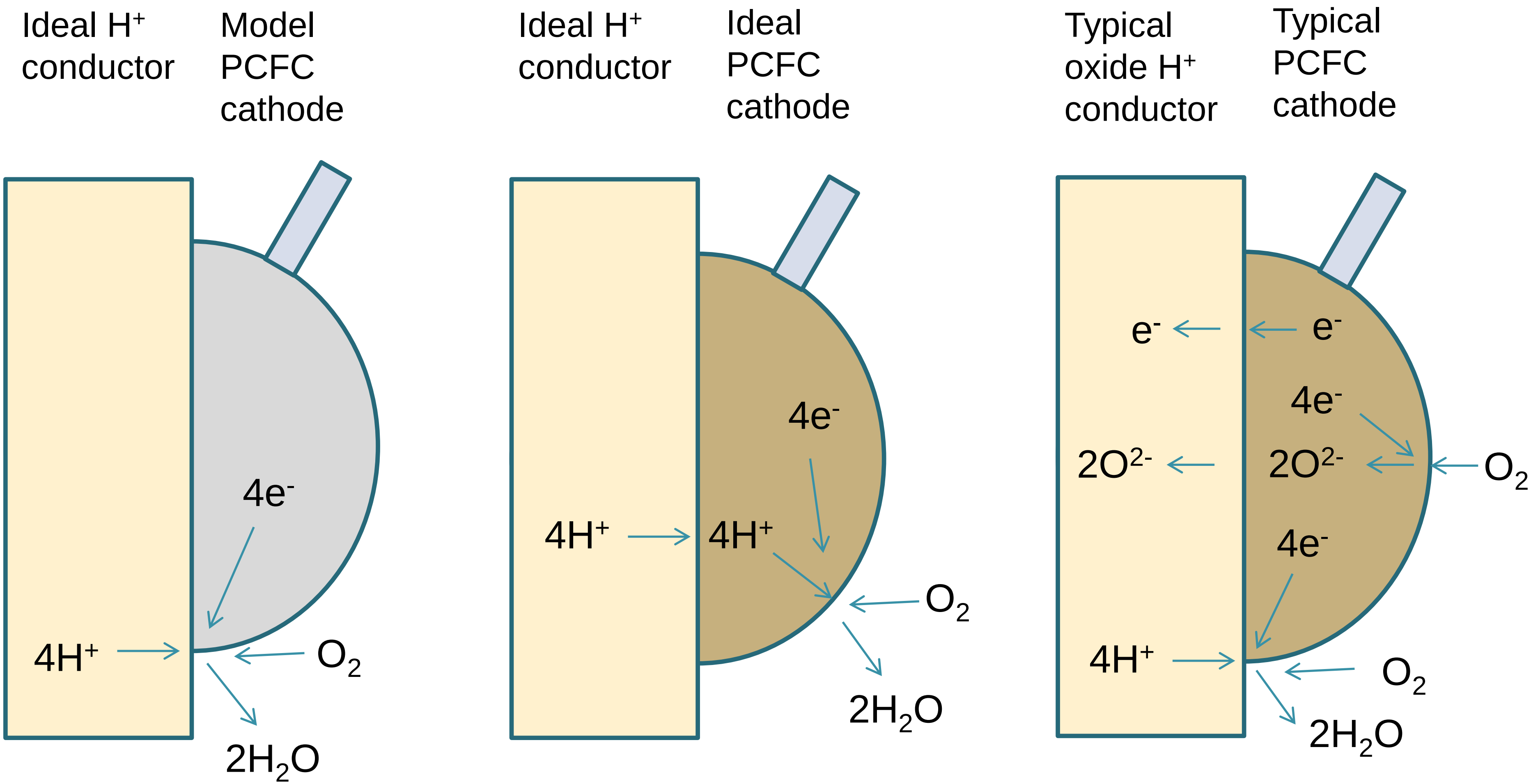
- Some apparent electrode polarisation resistances (in wet oxygen) from impedance spectroscopy

$Ba_{1-x}Gd_{0.8}La_{0.2+x}Co_2O_{6-\delta}$



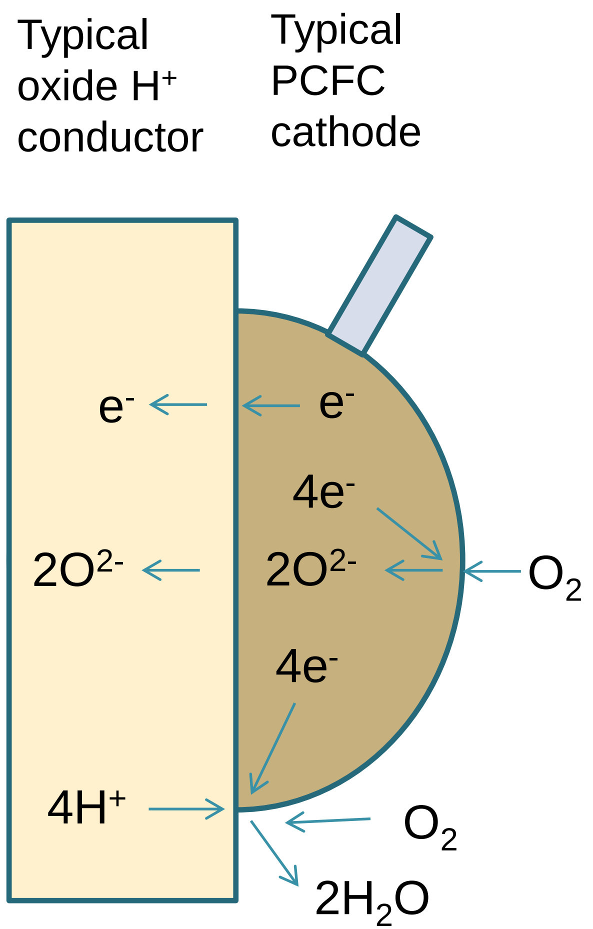
* Ragnar Strandbakke, Vladimir Cherepanov, Andrey Zuev, D. S. Tsvetkov, Christos Argirusis, Georgia Sourkouni-Argirusis, Stephan Prünte, Truls Norby, *"Gd- and Pr-based double perovskite cobaltites as oxygen side electrodes for proton ceramic fuel cells and electrolyser cells"*, under publication.

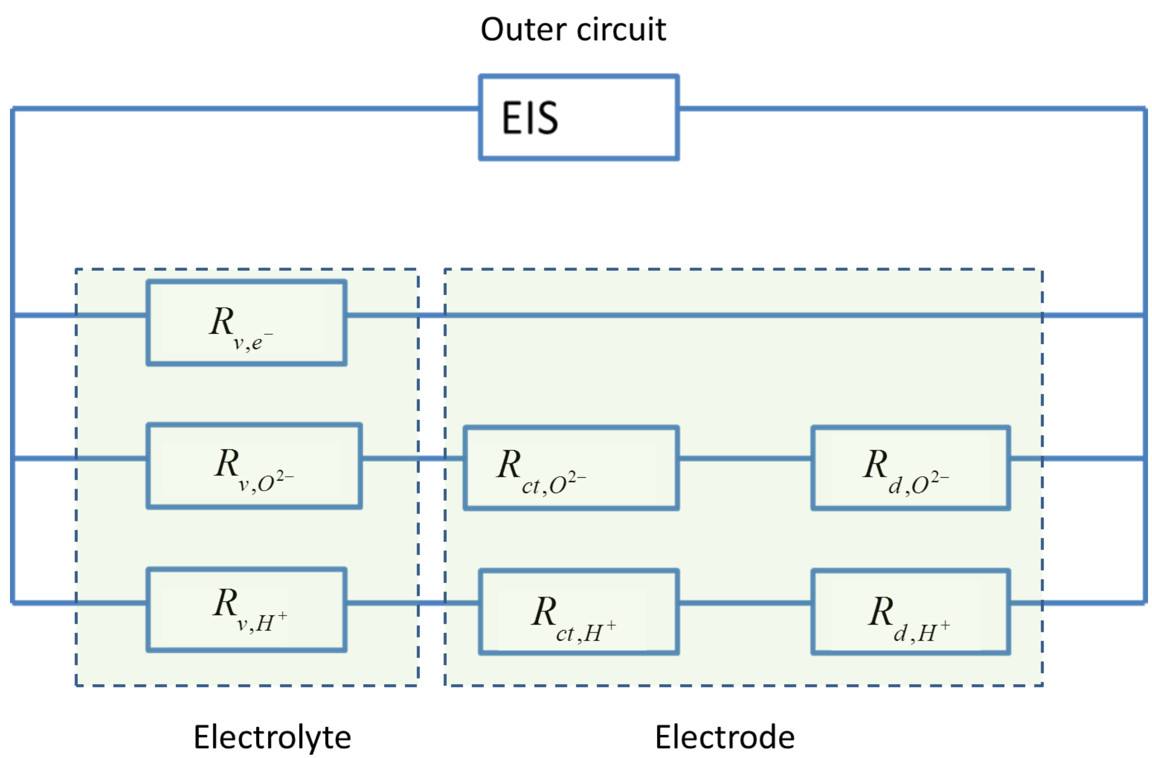
PCFC oxygen electrodes (cathodes)



PCFC oxygen electrodes (cathodes)

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





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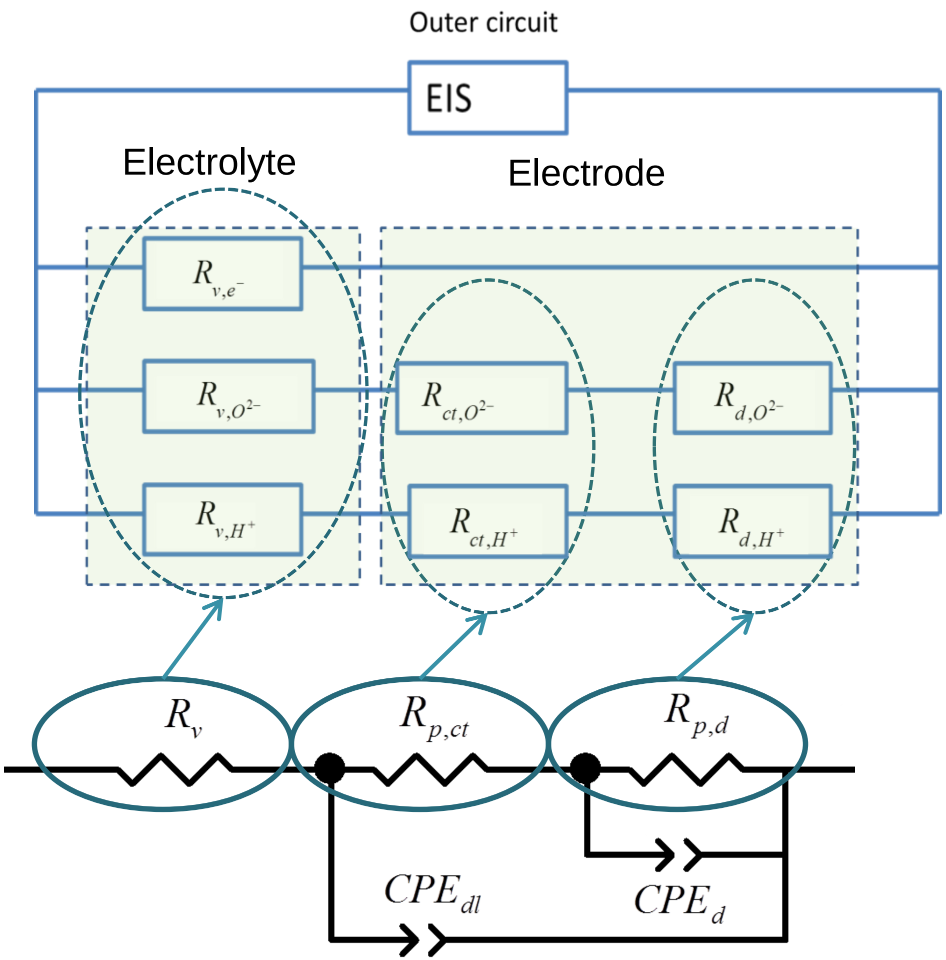
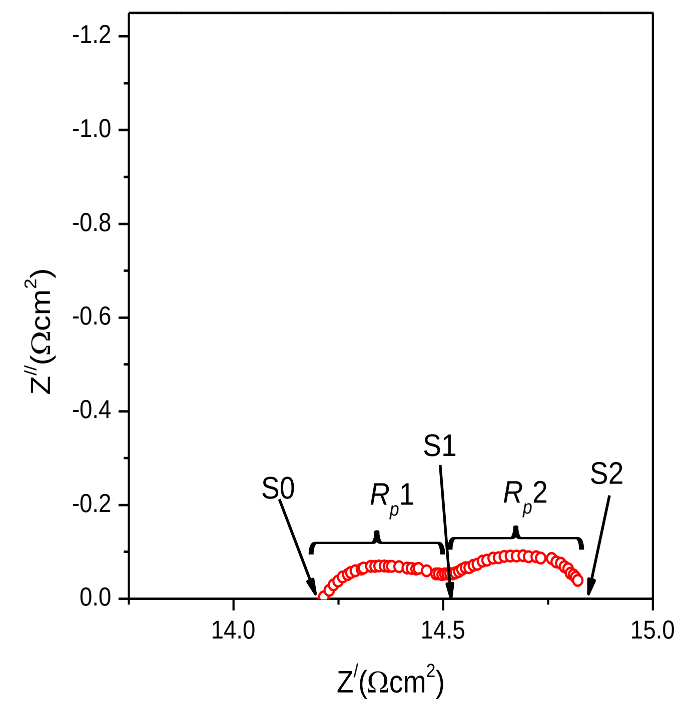
Perovskite electrode on $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_3$ (BZCY)

- Impedance spectra yield apparent electrode polarisation resistances

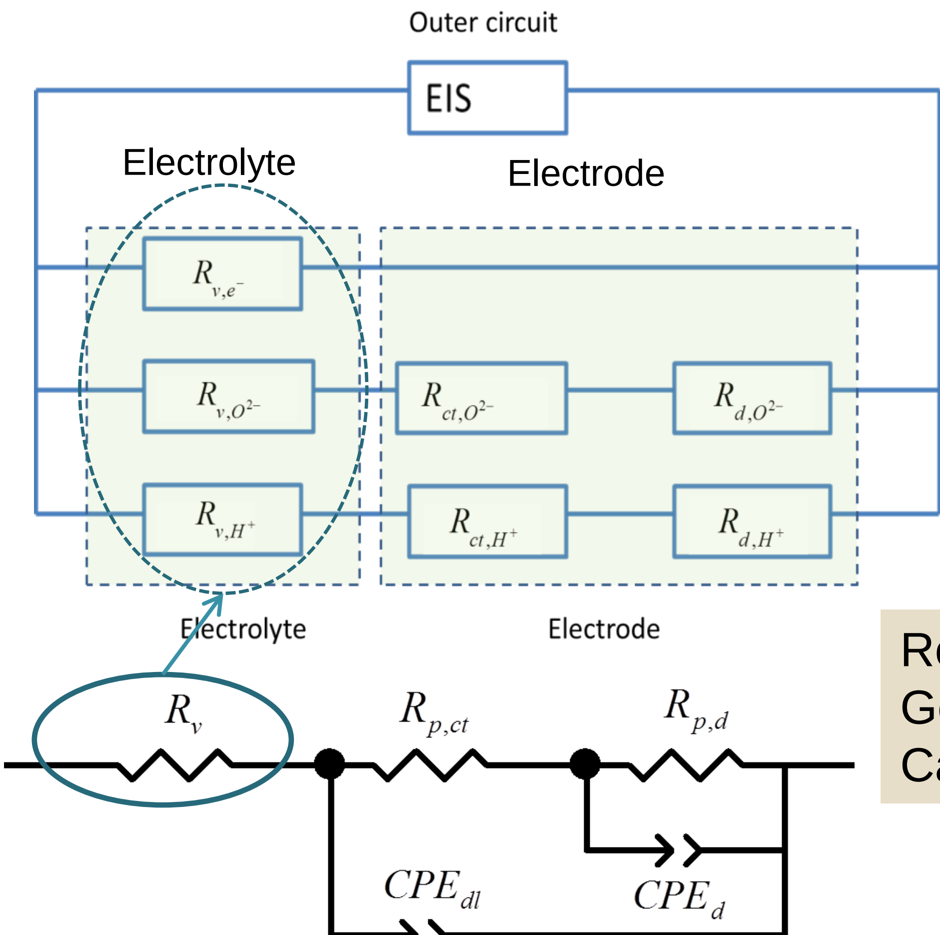


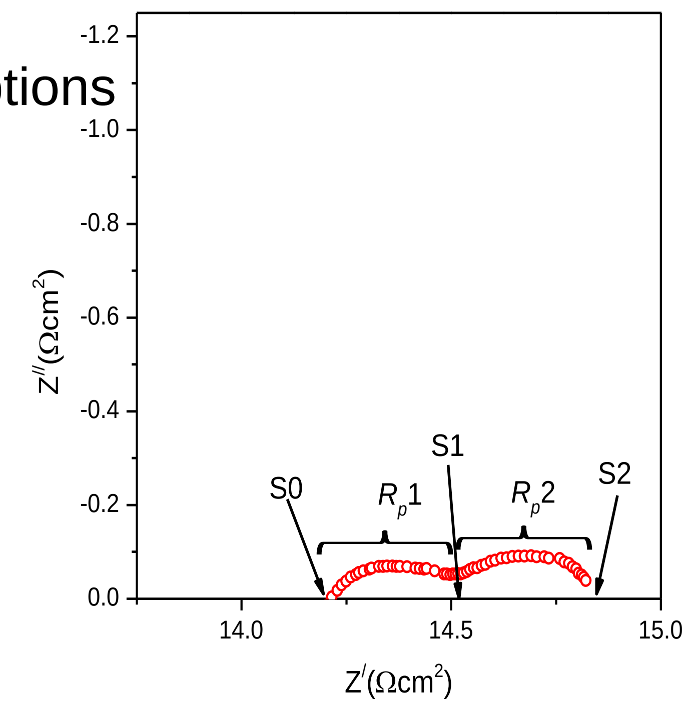


Not enough information

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





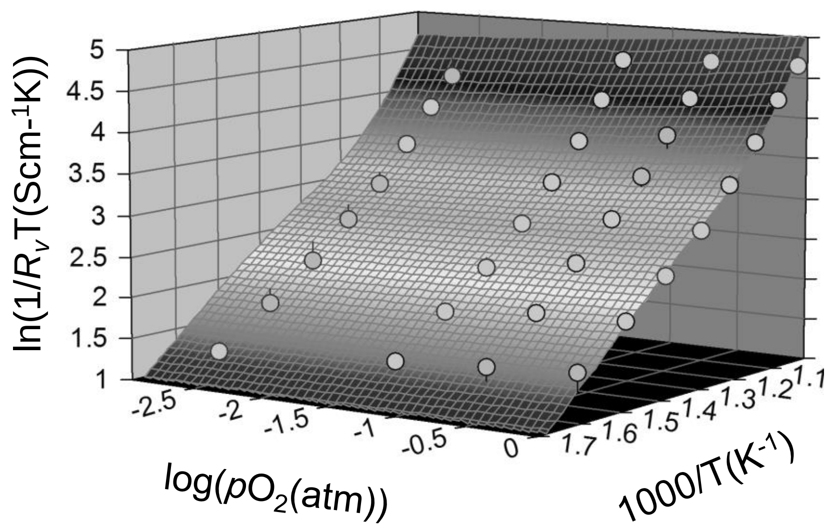
Recipe:
Get individual R_v's from conductivity data
Calibrate to R_v at S0

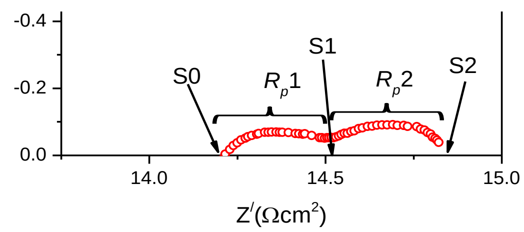
R_v at S0 is fitted to

$$R_{S0} = R_v = \frac{1}{\frac{1}{R_{v,e^-}} + \frac{1}{R_{v,H^+}} + \frac{1}{R_{v,O^{2-}}}}$$

$$1/R_{v,H^+} = \sigma_{H^+} = F\mu_{H^+}c_{H^+}z_{H^+} = F\left[OH_O^{\bullet}\right]d_m \frac{1}{T}\mu_{H^+}^0 \exp\left(\frac{-\Delta H_{mob,H^+}}{RT}\right)$$

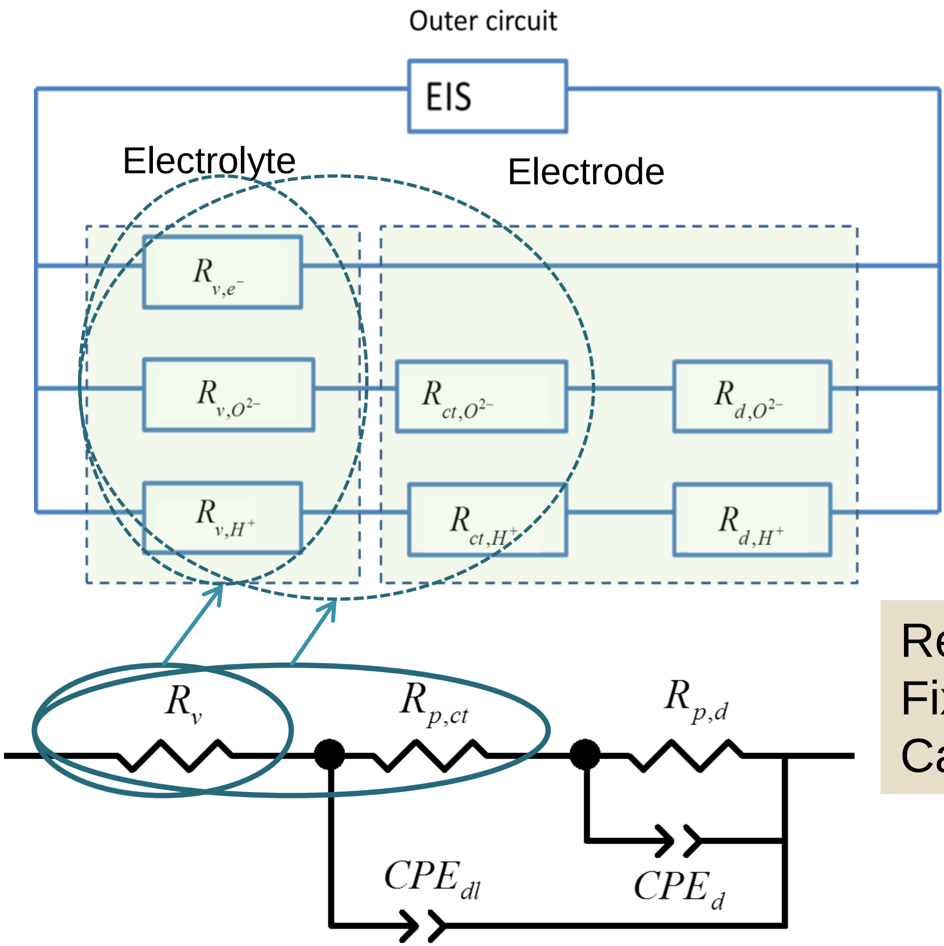
$$1/R_{v,e^-} = \sigma_h = \sigma_h^0 \frac{1}{T}\exp\left(\frac{-E_{A,h}}{RT}\right)pO_2^{1/4}$$

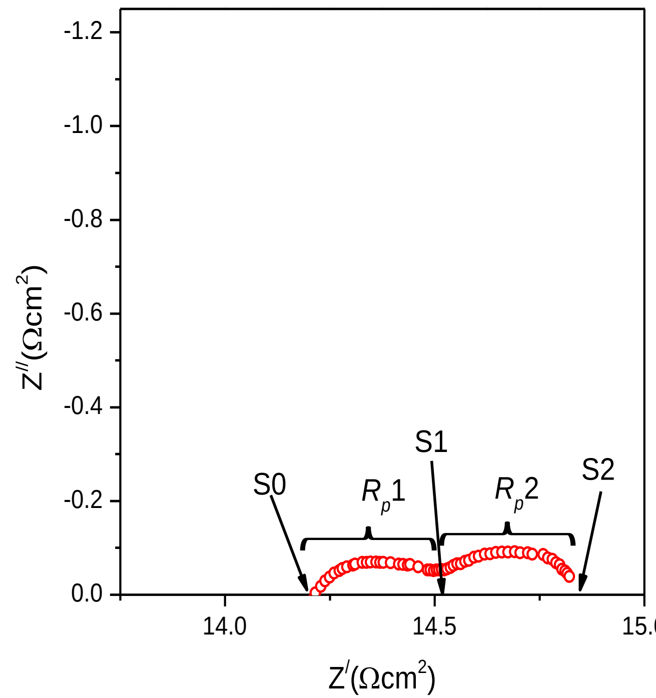




Perovskite electrode on $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_3$ (BZCY)

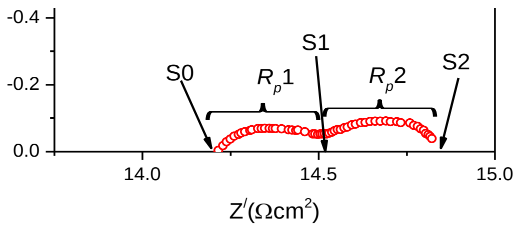
- …and now the charge transfer resistance:



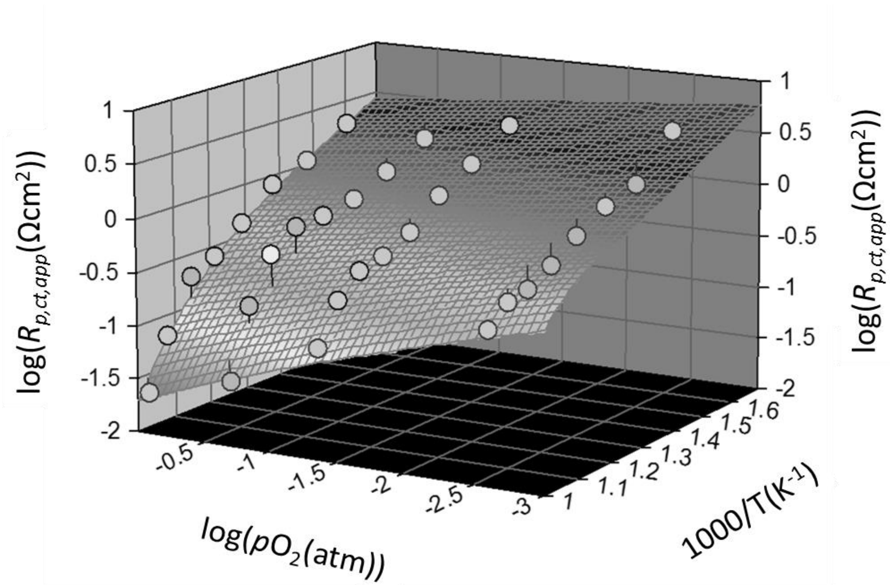


Recipe:
Fix conductivity values at S0
Calculate properly $R_v+R_{p,1}$ at S1

R_v +Rp,ct,app at S1 is fitted to



$$R_{S1} = R_v + R_{p,ct,app} = \frac{1}{\frac{1}{R_{v,e^-}} + \frac{1}{R_{v,H^+} + R_{p,ct,H^+}} + \frac{1}{R_{v,O^{2-}} + R_{p,ct,O^{2-}}}}$$

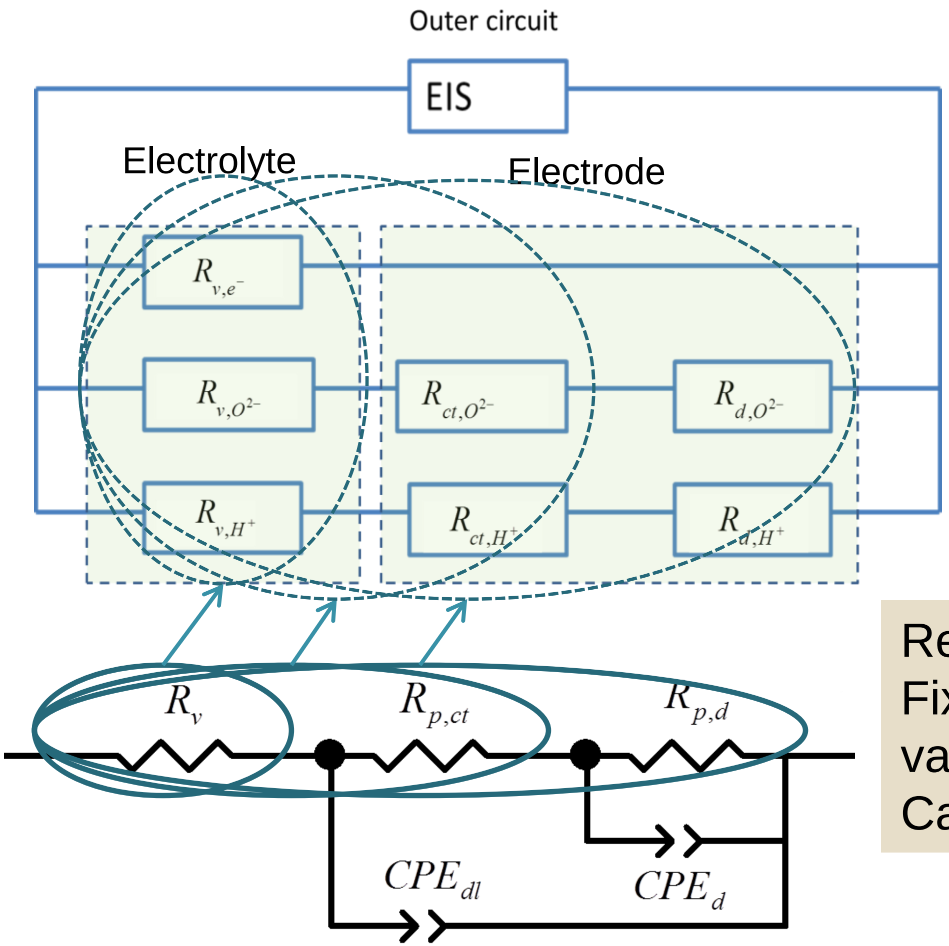


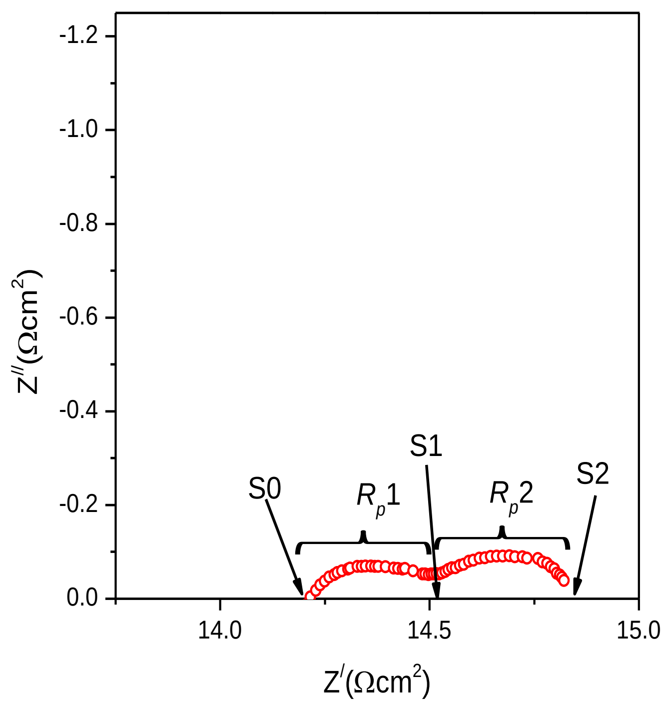
where

$$\frac{1}{R_{p,ct,H^+/O^{2-}}} = F pO_2^n \, pH_2O^m A^0 \exp\left(\frac{-E_A}{RT}\right)$$

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

- …and the diffusion resistance

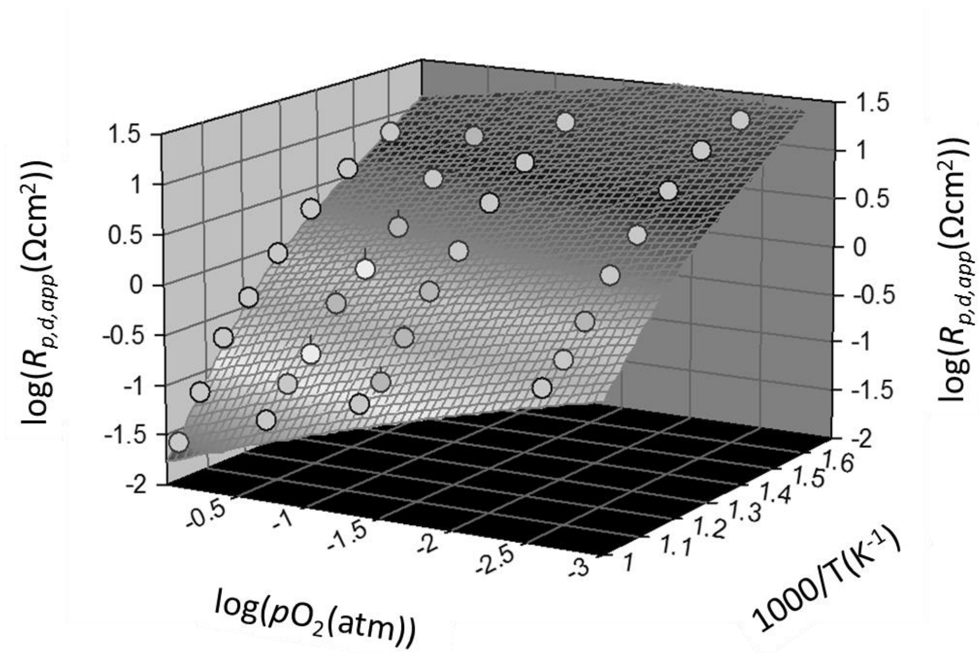




Recipe:
Fix conductivity + charge transfer valuesat S1
Calculate properly R_v+$R_{p,1}$+$R_{p,2}$ at S2

R_v + $R_{p,ct,app}$ + $R_{p,d,app}$ at S2 is fitted to

$$R_{S2} = R_v + R_{p,ct,app} + R_{p,d,app} = \frac{1}{\frac{1}{R_{v,e^-}} + \frac{1}{R_{v,H^+} + R_{p,ct,H^+} + R_{p,d,H^+}} + \frac{1}{R_{v,O^{2-}} + R_{p,ct,O^{2-}} + R_{p,d,O^{2-}}}}$$



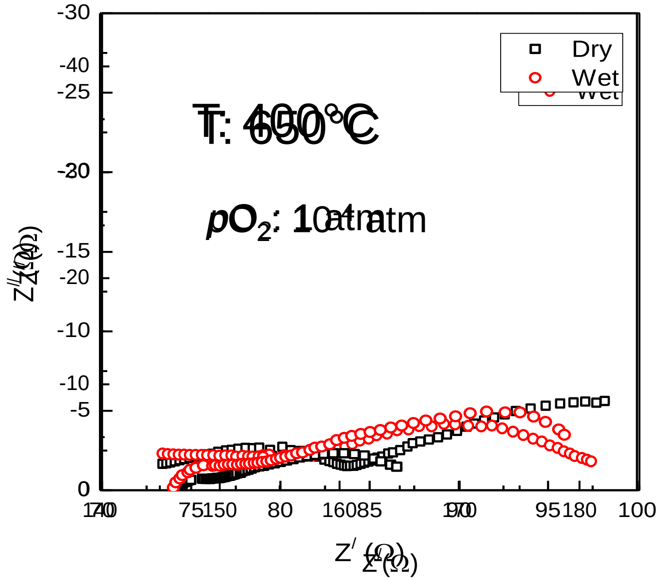
where

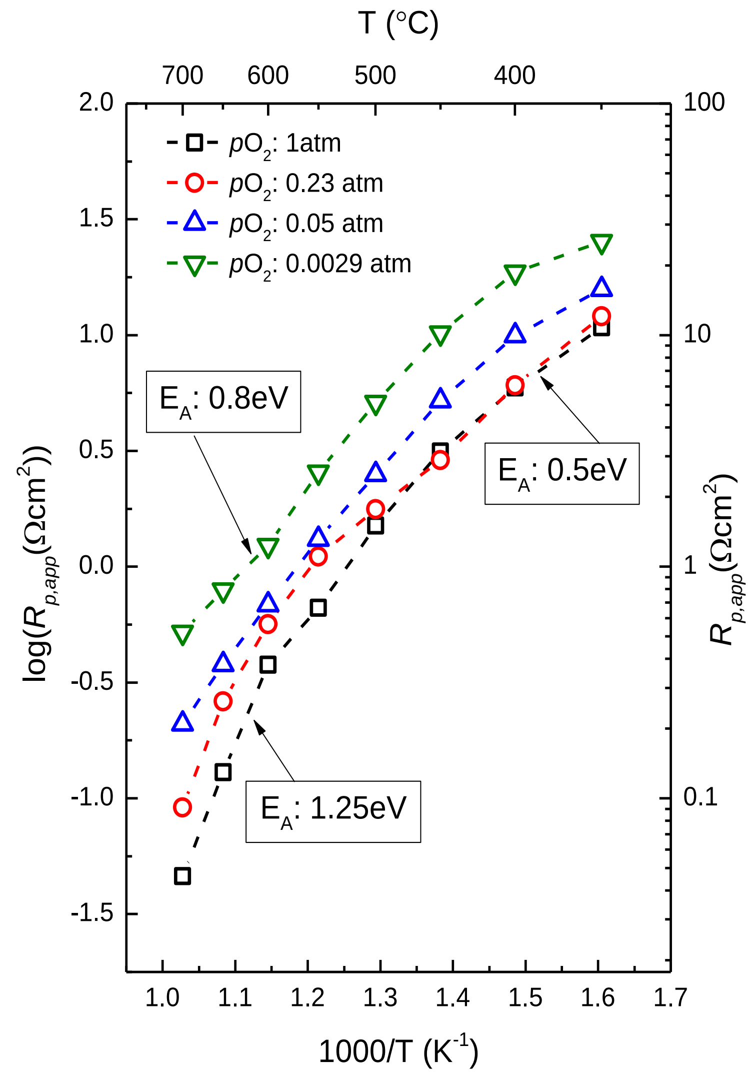
$$\frac{1}{R_{p,d,H^+/O^{2-}}} = F pO_2^n \, pH_2O^m A^0 \exp\left(\frac{-E_A}{RT}\right)$$

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

- Dependencies on
  - Temperature
  - pO_2
  - pH_2O

give input to interpretation and modelling

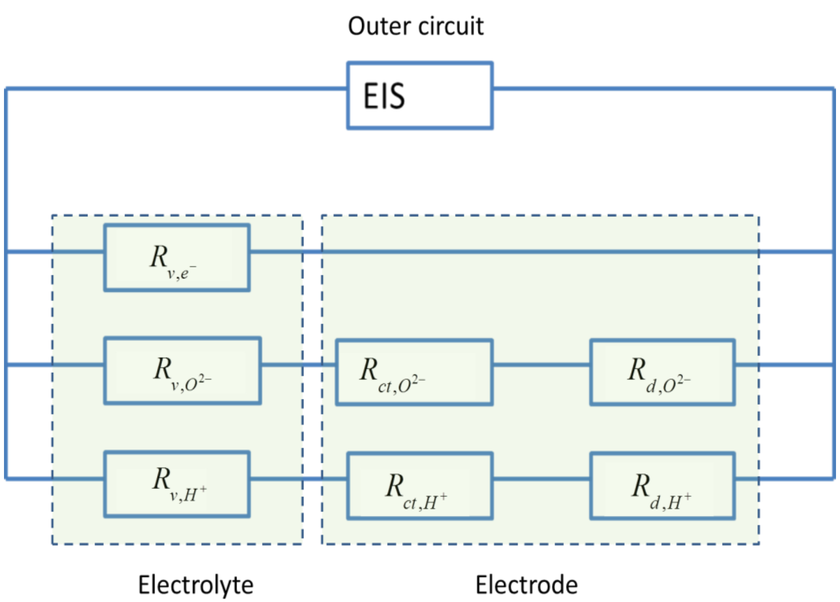


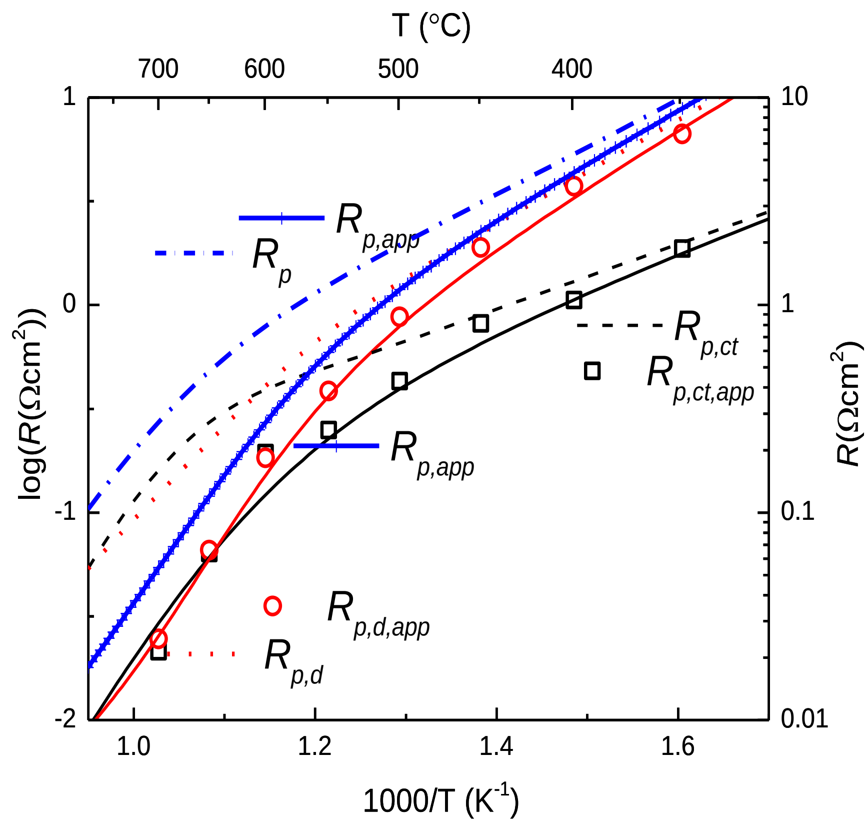


$BaGd_{0.8}La_{0.2}Co_2O_{6-\delta}$

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

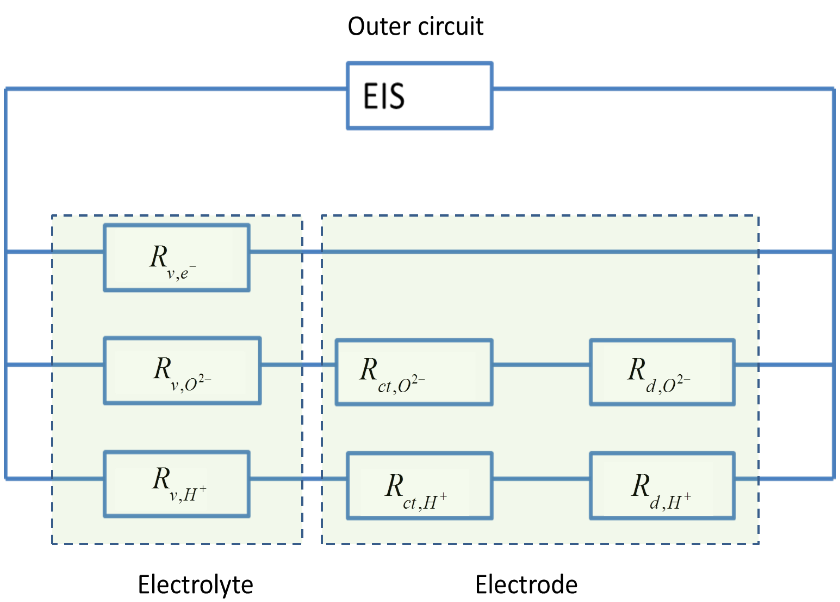
- Modelling by fitting all data
- Charge transfer vs diffusion
- Effect of electronic conduction

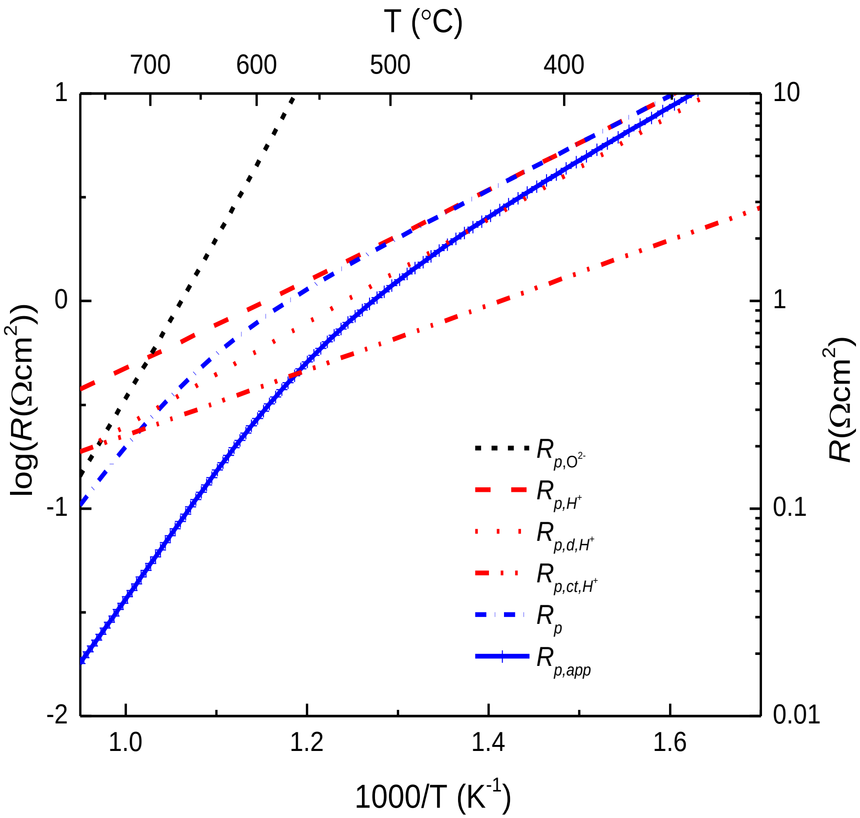




Perovskite electrode on $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_3$ (BZCY)

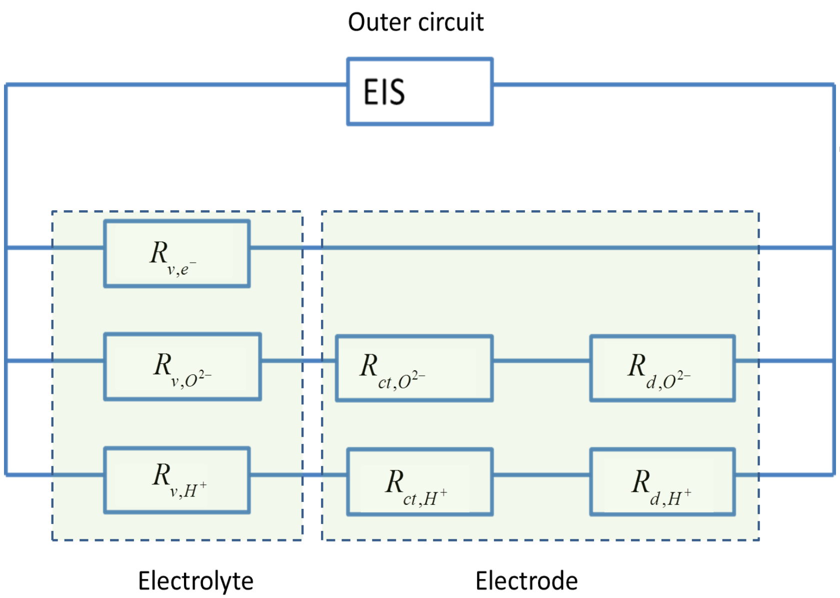
- Modelling by fitting all data
- Protons vs oxide ions
- Effect of electronic conduction

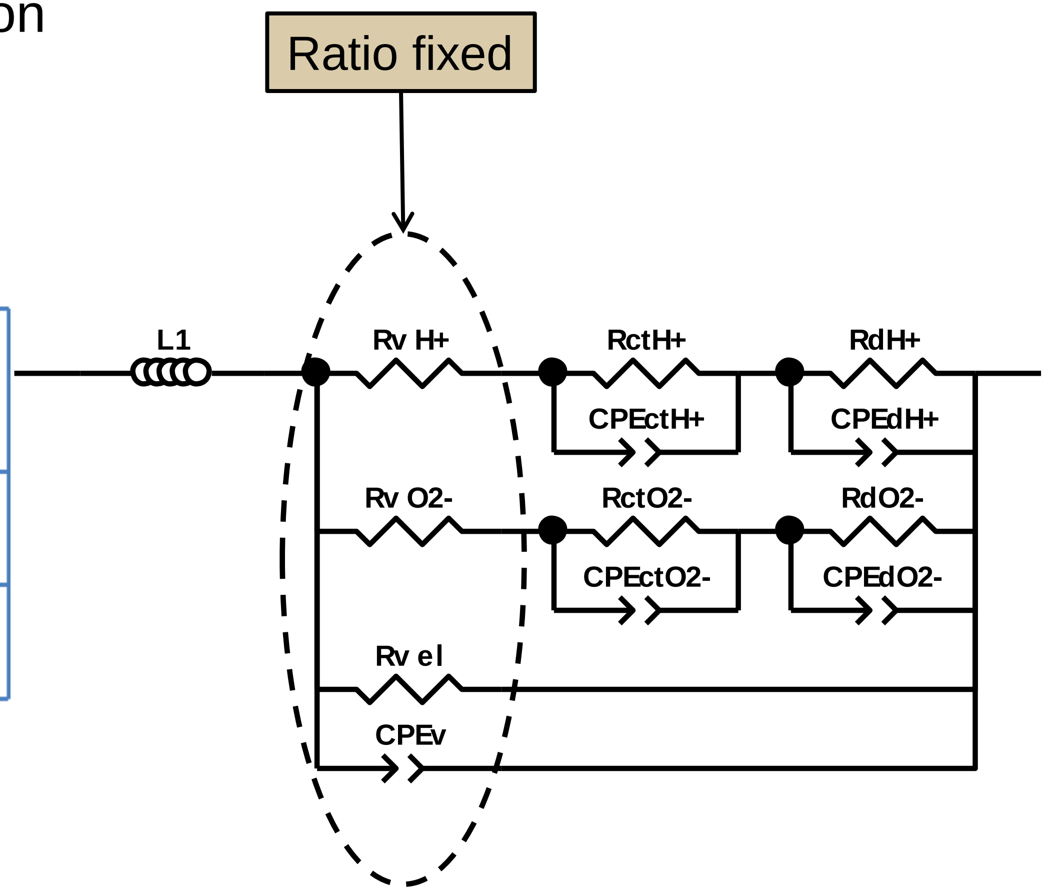




Perovskite electrode on $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_3$ (BZCY)

- Direct deconvolution of three rails
- Protons vs oxide ions
- Effect of electronic conduction



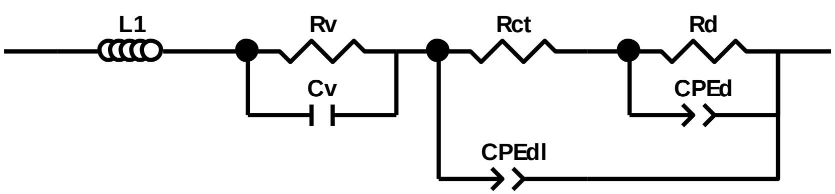


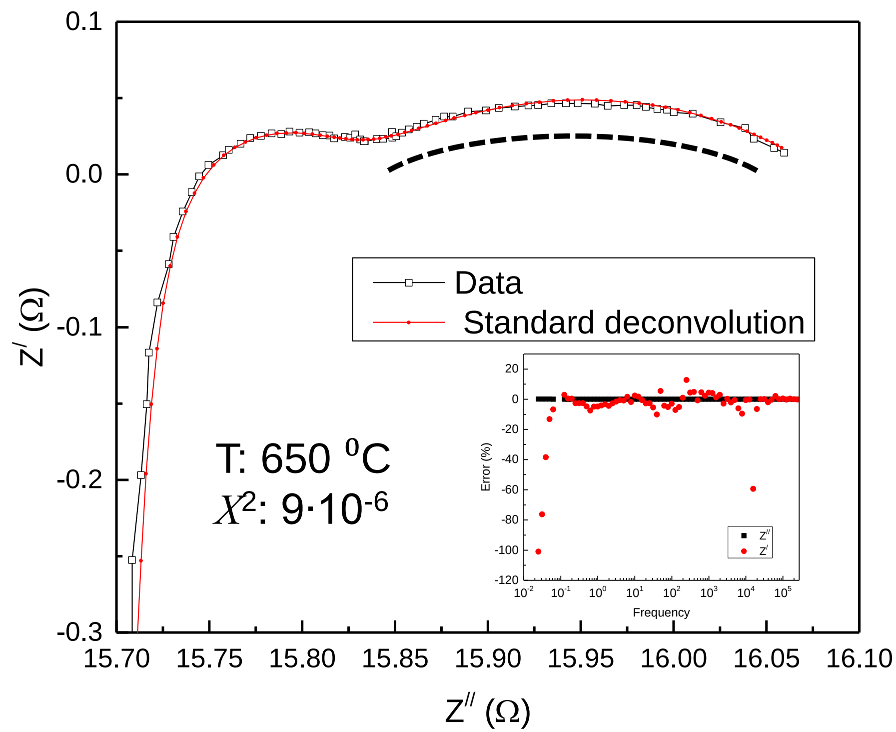
Perovskite electrode on $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_3$ (BZCY)

- Standard deconvolution

$Ba_{0.9}Gd_{0.8}La_{0.3}Co_2O_{6-\delta}$

Gives apparent R_p-values



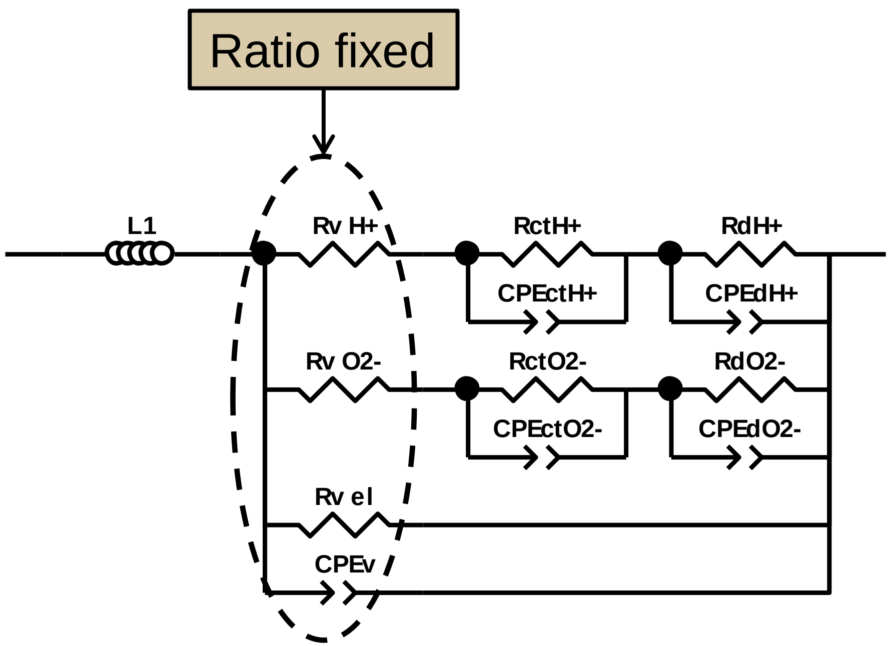


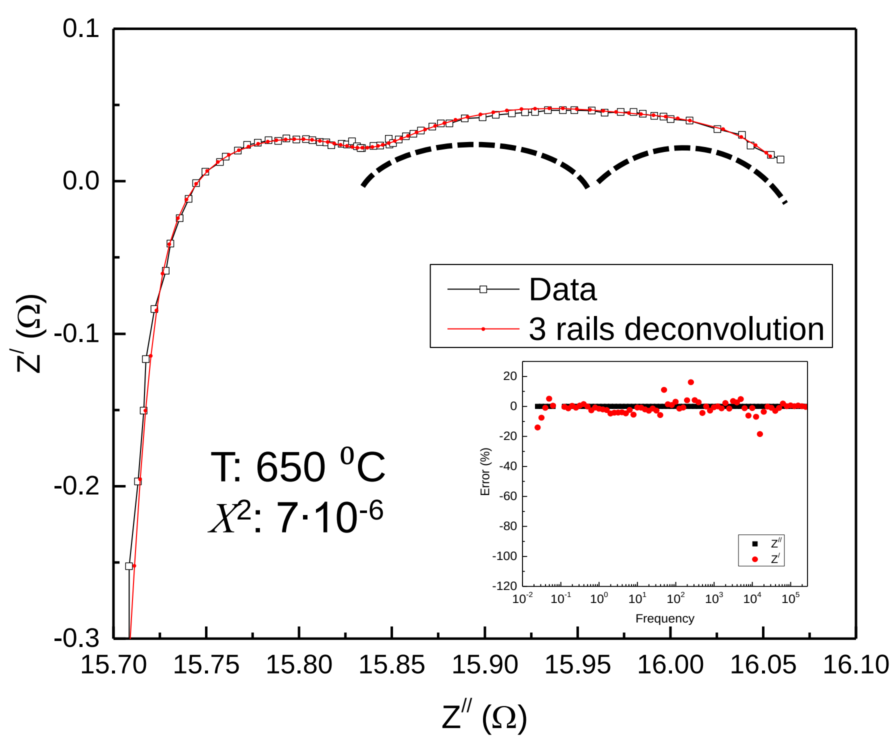
Perovskite electrode on $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_3$ (BZCY)

- Direct deconvolution of three rails
- Protons vs oxide ions
- Effect of electronic conduction

$Ba_{0.9}Gd_{0.8}La_{0.3}Co_2O_{6-\delta}$

Gives real R_p-values





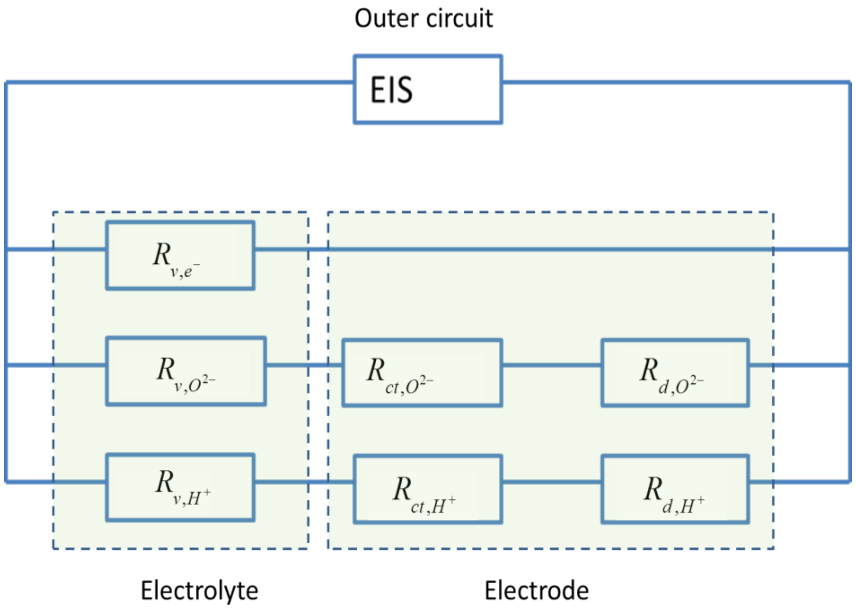
Perovskite electrode on $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_3$ (BZCY)

- Direct deconvolution of three rails
- Protons vs oxide ions
- Effect of electronic conduction

$Ba_{0.9}Gd_{0.8}La_{0.3}Co_2O_{6-\delta}$

Standard deconvolution		Approach II: 3 Rails		
$R_{ct}(\Omega cm^2)$	0.065	R_{ct}	$R_{ct}(H^+)$	0.13
			$R_{ct}(O^{2-})$	0.76
$R_d(\Omega cm^2)$	0.125	R_d	$R_d(H^+)$	0.27
			$R_d(O^{2-})$	1.9
$R_p(\Omega cm^2)$	0.19	R_p	0.35	

Conclusions



- Proton conducting oxides
  - Exhibit also some oxide ion conduction
    - especially at higher temperatures
  - Exhibit some electronic conduction,
    - especially at high or low pO_2 (p- or n-type)
    - affecting especially electrode studies
- Oxide-based oxygen electrodes
  - Tend to enhance oxide ion path over proton path
- Consequences for (oxygen) electrode studies
  - Impedance spectra must be interpreted accordingly
  - Conductivity data necessary as input
  - Go to lower temperatures!
  - Electrochemical impedances appear lower than they are