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

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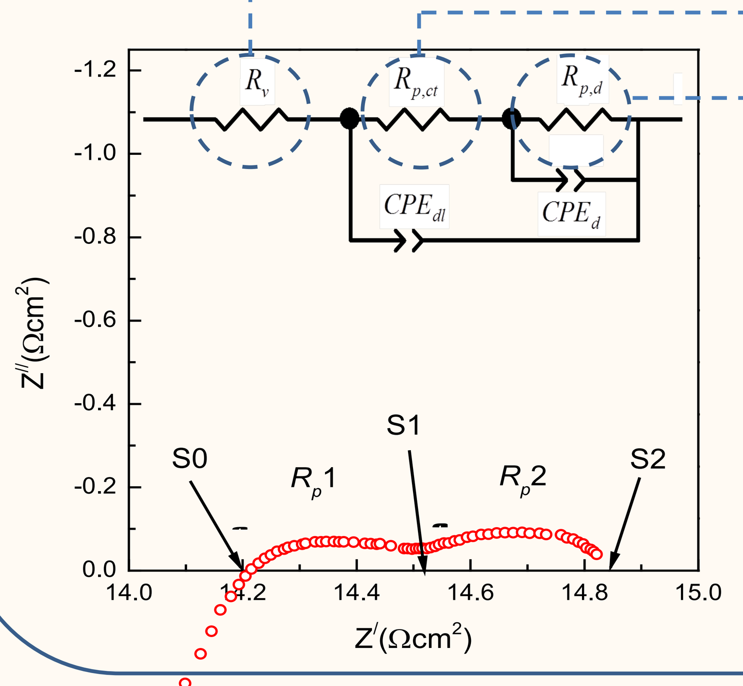
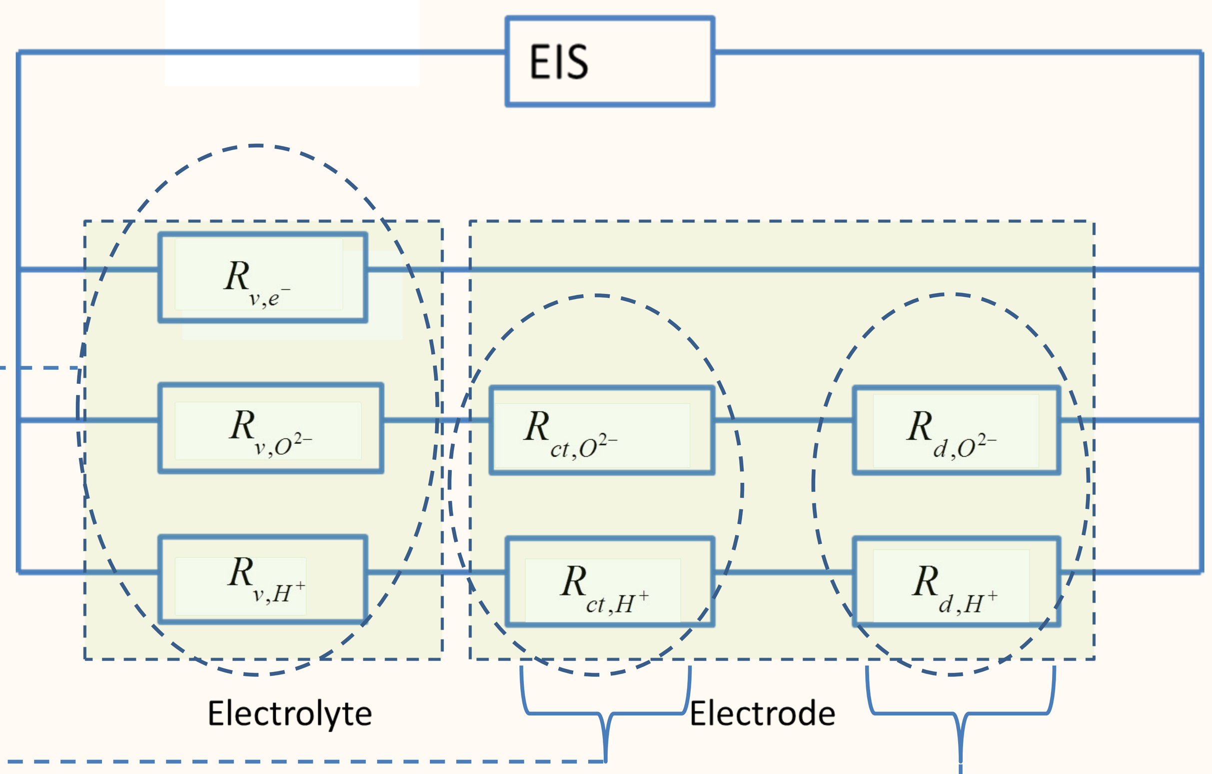
The work addresses characterization of electrodes on electrolytes with transport of more than one type of charge carriers, modelled in parallel “rails” where the resistances associated with electrolyte transport, charge exchange at the electrolyte / electrode interface and diffusion / adsorption at the electrode surface are connected in series in each rail. Using electrochemical impedance spectroscopy, deconvoluted electrolyte and electrode resistances are obtained and seen as parallel combinations of the processes undertaken by each individual charge carrier. By expressing these processes with Arrhenius-like equations, the resistances associated with each charge carrier can be parameterized and the total system can be modelled.

A second approach is to deconvolute the impedance data in a three-rail equivalent circuit, enabling more precise deconvolution and a more elaborate utilization of the information contained in the data. The ratio between electrolyte charge carriers must be known and fixed in the deconvolution

Approach I : Standard deconvolution + 3 rail modelling

Impedance spectroscopy and “standard” deconvolution model





Fitting of partial resistances for electronic, proton and oxide ion rail

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

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

$$1/R_{p,d,H^+/O^{2-}} = FpO_2^n pH_2O^m A^0\exp\left(\frac{-E_A}{RT}\right)$$

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

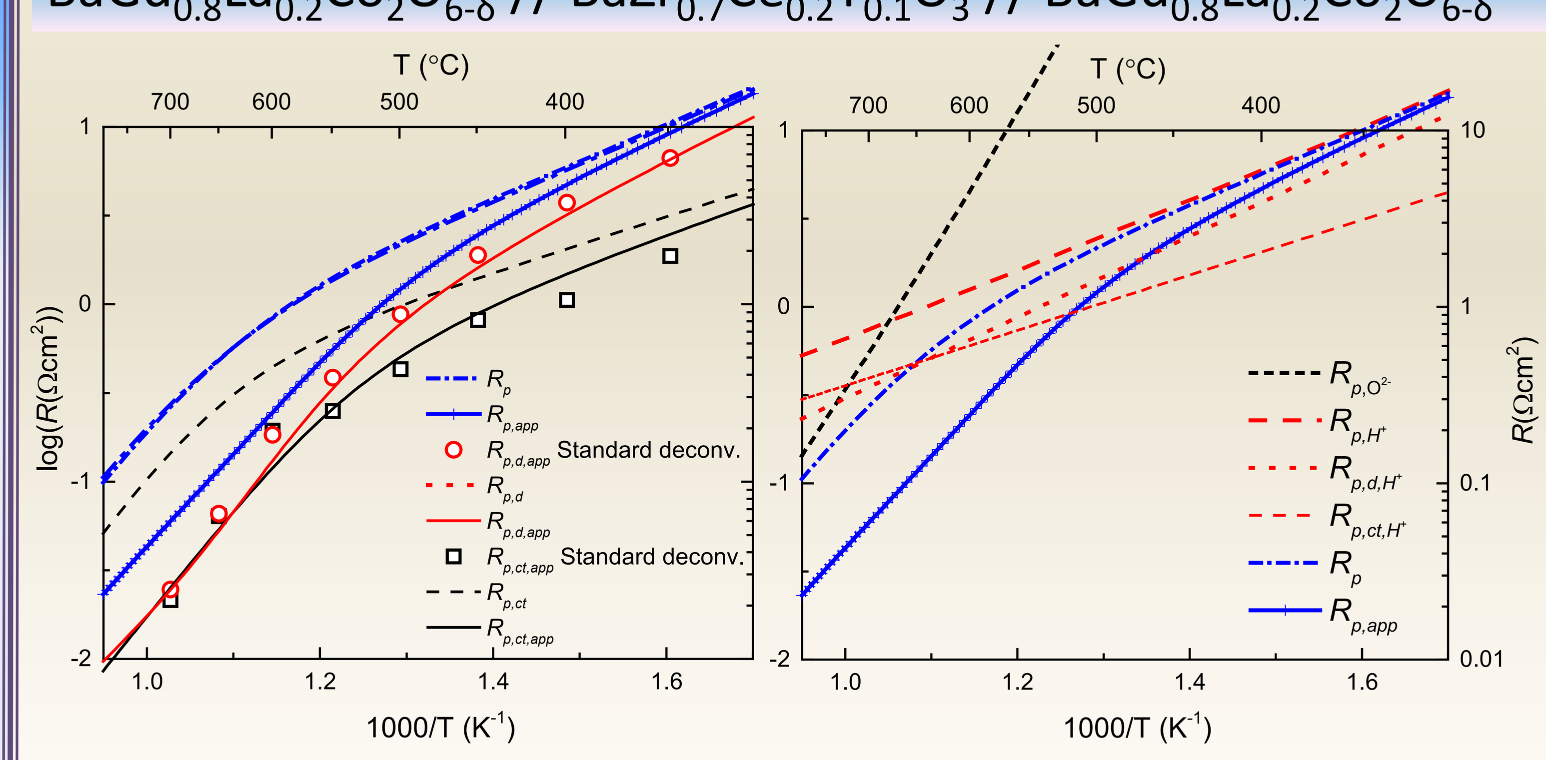
Stepwise fitting:

1

2

3

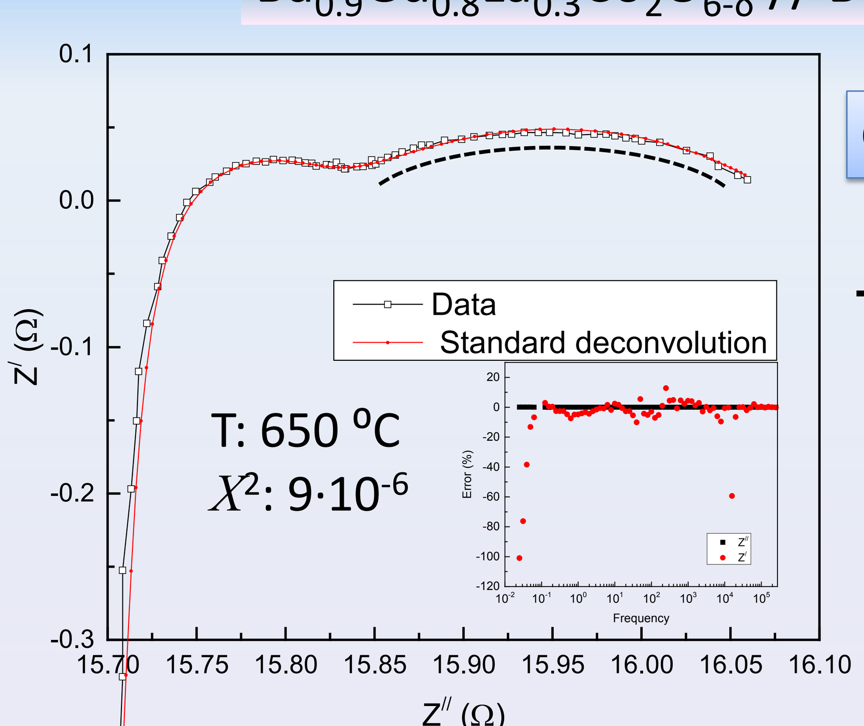
$BaGd_{0.8}La_{0.2}Co_2O_{6-\delta}$ // $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_3$ // $BaGd_{0.8}La_{0.2}Co_2O_{6-\delta}$



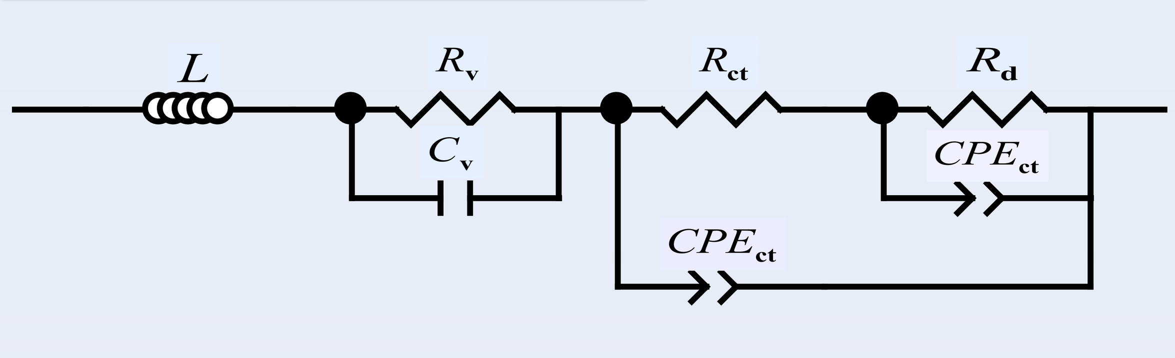
Results of modelling according to approach I

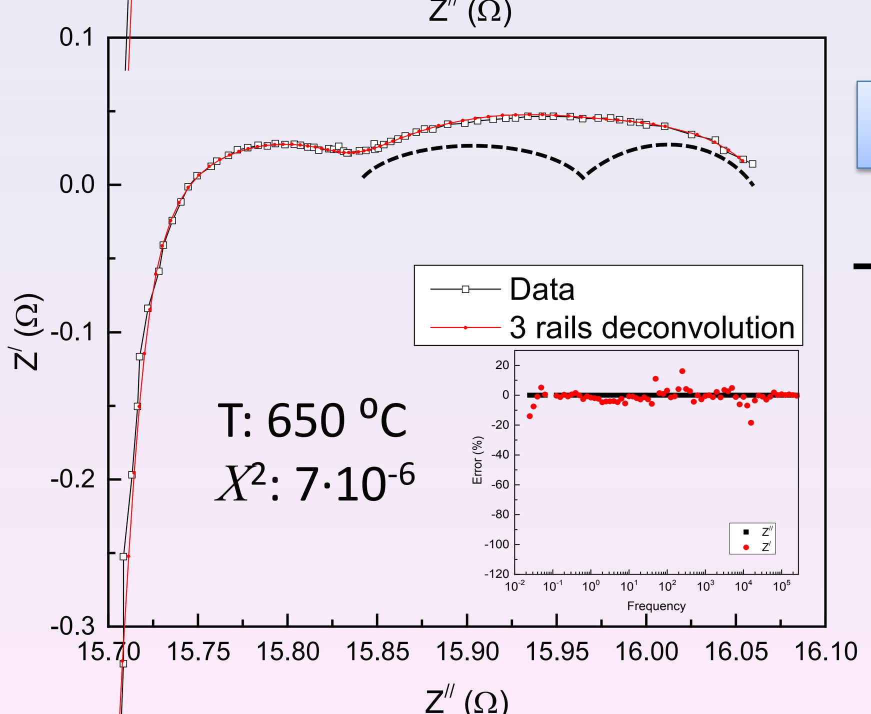
Approach II : 3 rail deconvolution

$Ba_{0.9}Gd_{0.8}La_{0.3}Co_2O_{6-\delta}$ // $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_3$ // $Ba_{0.9}Gd_{0.8}La_{0.3}Co_2O_{6-\delta}$

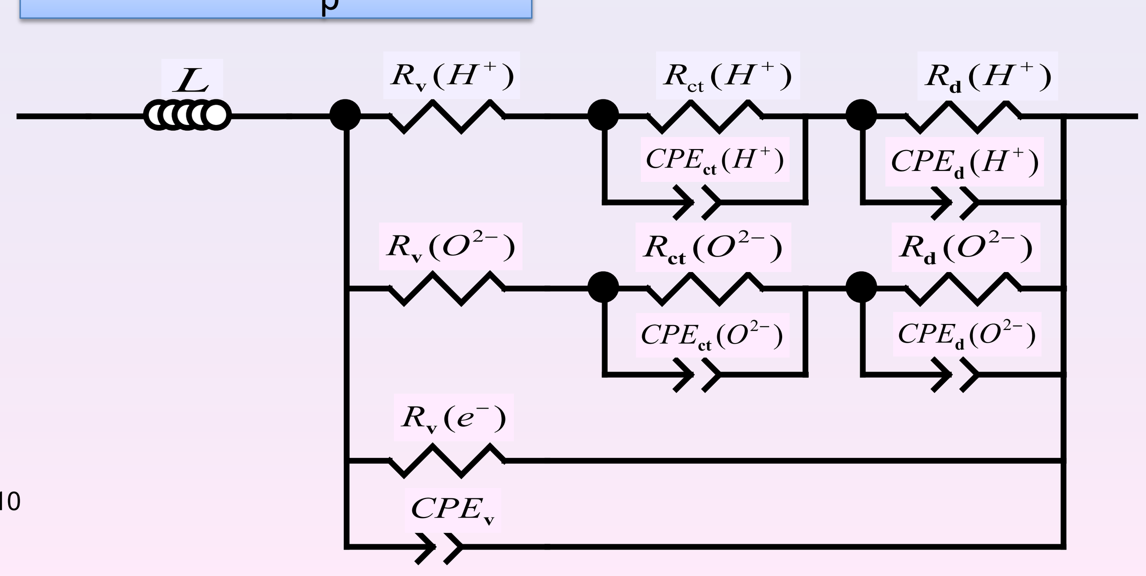


Gives apparent R_p-values





Gives real R_p-values



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

The polarization resistance of a system with multiple charge carriers across electrolyte and electrodes can be modelled with respect to the contribution to polarization resistance from each type of charge carrier. The partial electronic conductivity in $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_3$ contributes to an underrating of R_p of an order of magnitude at 700°C in oxidising conditions. Under conditions where more than one charge carrier contribute to multiple responses in the impedance spectra, the three rail deconvolution model can provide elaborate information about partial polarization resistances

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