

The application of impedance spectroscopy to solid oxide fuel cells and their components

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Contents

Introduction and Theory

- Anatomy of the solid oxide fuel cell (SOFC)
- IS/EIS experiments, configurations, ranges
- Equivalent circuit elements and their significance
- Elaboration on the constant phase element (CPE)
- Other circuit elements in brief

Examples from the world of SOFC

- Ordinary fitting and the extraction of $C_{\text{near equivalent}}$
- Distributed Relaxation Time analysis
- Constrained fitting
- New directions
- Summing up

Overview a solid oxide fuel cell

Active components

- Electrolyte: stabilised zirconia
e.g. $Zr_{1-x}Y_xO_{2-x/2}$ (YSZ)
- Anode: Ni/ $Zr_{1-x}Y_xO_{2-x/2}$ cermet
- Cathode: el. conducting oxide
e.g. $La_{1-x}Sr_xMnO_\xi$ (LSM)
- Interconnect: metal or electronically conducting oxide

Other components

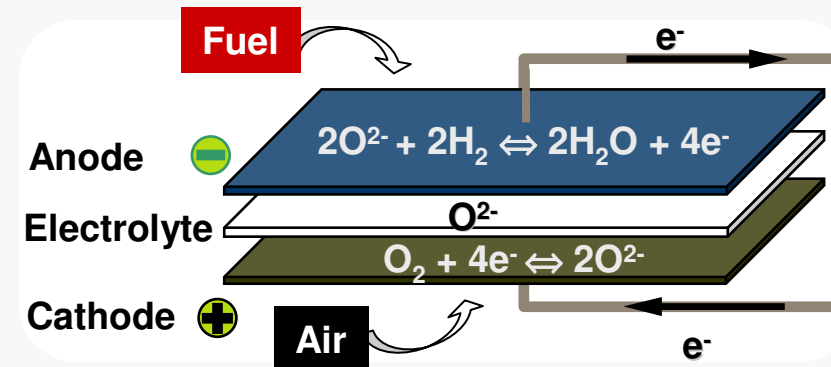
- Seals: glass/ceramic
- Current collector layers
- Gas distributor structures

Fuels

- H_2 , CO/ H_2 , reformed HC

Operating temperature

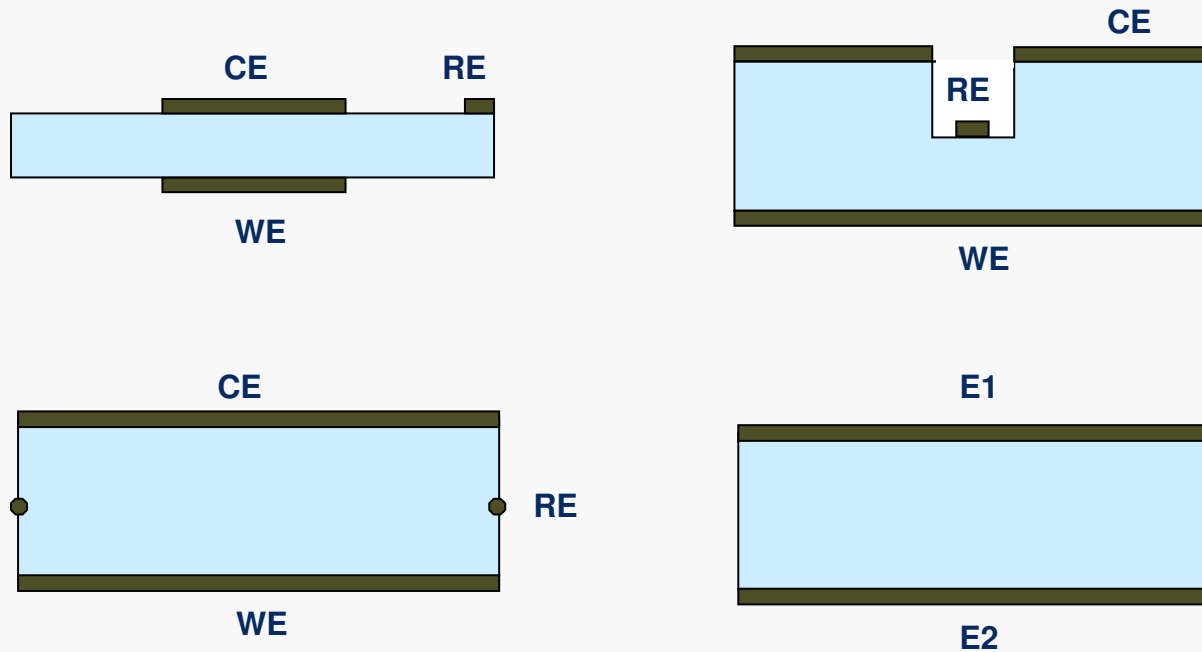
- 600 – 850 °C



Objective of SOFC studies

- Electrochemical characterisation with breakdown of losses.
- Gain extra insight into behaviour of individual cell components
- Phenomenological approach

Cell configurations for studying SOFC components

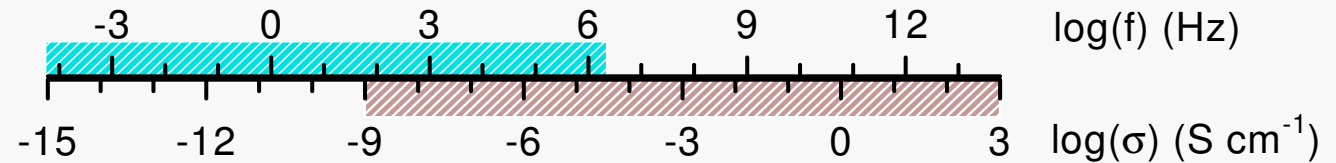


- DC polarisation – apply or not apply?
- Advantages of different geometries
- Issues of instrumentation and frequency range

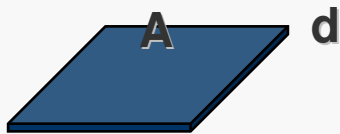


Frequency, conductance and capacitance ranges

Uniform medium $\kappa = 30$

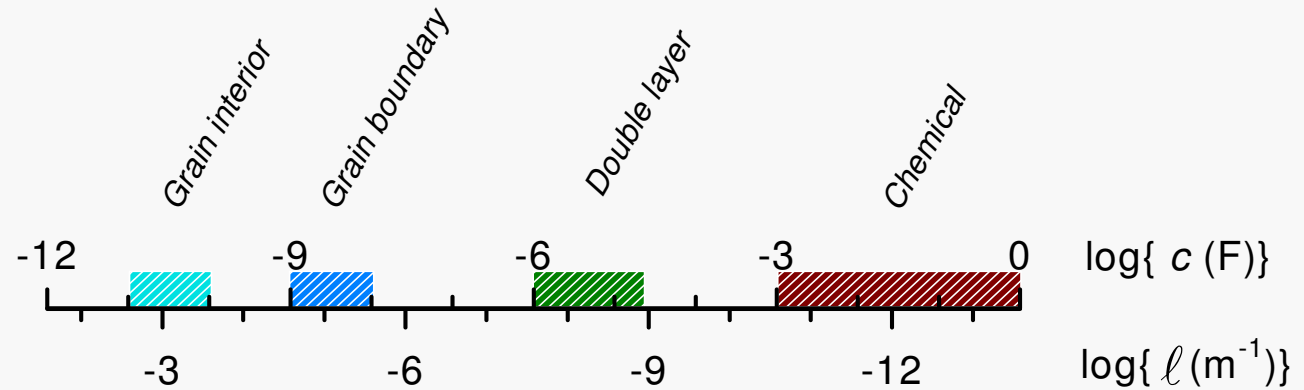


Typical SOFC system

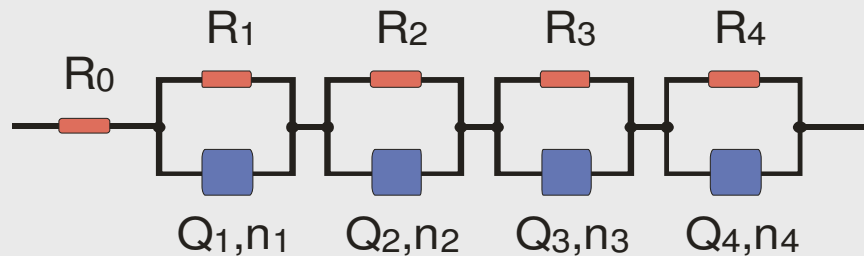
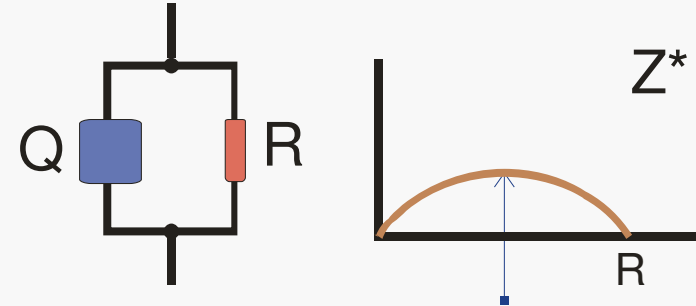
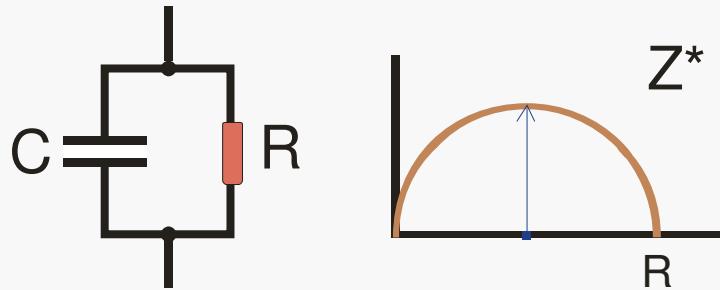


$d = 1 \text{ mm}$

$A = 1 \text{ cm}^2$



Elements, models and physical significance



Voigt circuit and reasons for preference.

Measurement models

- Built by regression of line shapes to the data.
- Allow us to identify character of a data set and facilitate the selection of a process model.

see Agarwal et al. *J. Electrochem. Soc.* 139, 1917 (1992)

Q!

The constant phase element (CPE), commonly known as 'Q'

- Definition and pedigree
- Parallel with R: ZARC
- Maximum frequency
- Distribution of time constants
- Nearly equivalent capacitance
- Transient response

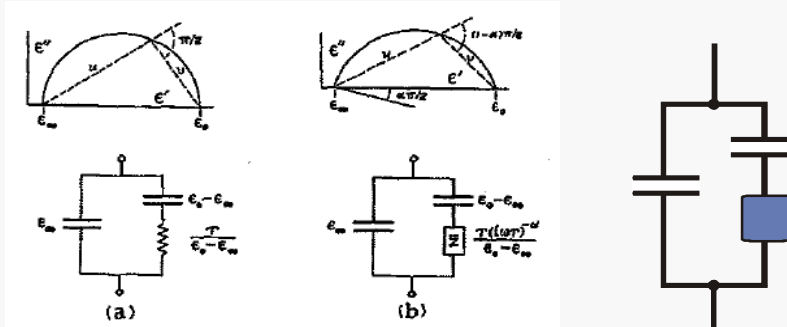
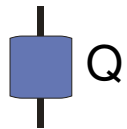
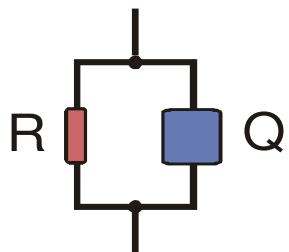


FIG. 2. Theoretical complex plane loci of the complex dielectric constant and equivalent circuits for dielectrics; (a) Debye theory, (b) as required by experimental evidence.

K.S. Cole and R.H. Cole, Dispersion and absorption in dielectrics, J. Chem. Phys. 9, 341-351 (1941).



$$Y(\omega) = Q \cdot (i\omega)^n$$

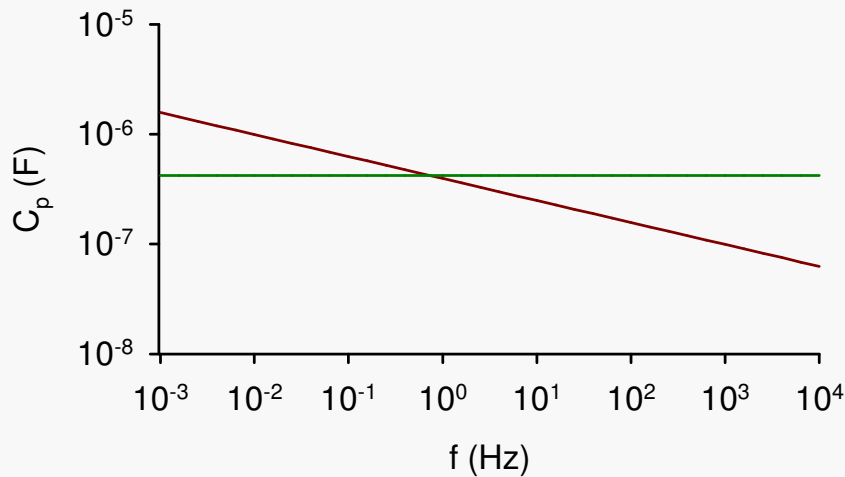
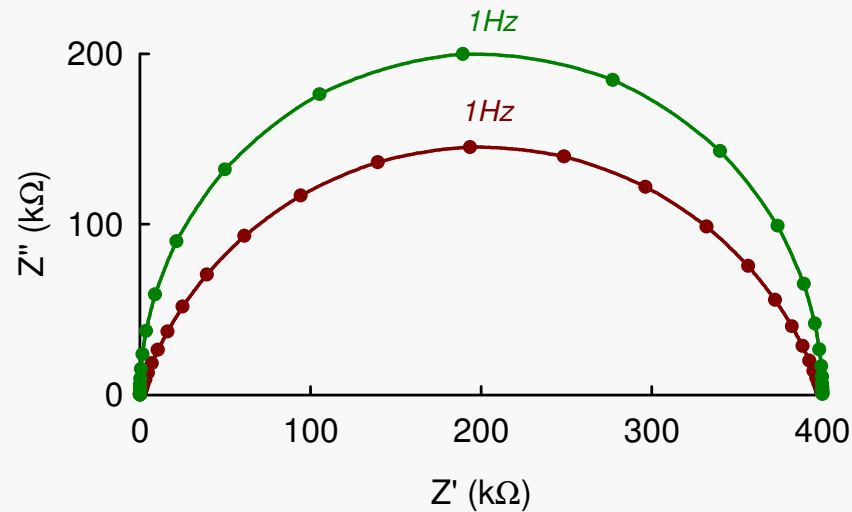


$$Y(\omega) = R^{-1} + Q \cdot (i\omega)^n$$

$$Z(\omega) = \left(R^{-1} + Q \cdot (i\omega)^n \right)^{-1}$$

ZARC

Properties of ZARC impedance function (1)



From derivative of $Z_{im}(\omega)$

$$\omega_{\max} = (RC)^{-1}$$

$$\omega_{\max} = (RQ)^{-\frac{1}{n}}$$

Near-equivalent capacitance

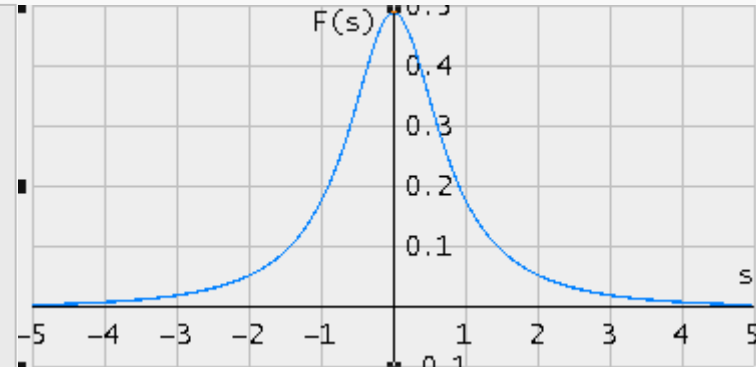
$$C_{ne} = \frac{(RQ)^{\frac{1}{n}}}{R}$$

J. R. Macdonald, *Solid State Ionics* 13,147 (1984)
 C. H. Hsu & F. Mansfeld, *Corrosion* 57, 747 (2001)
 Probably has been discovered many times ...

Properties of ZARC impedance function (2)

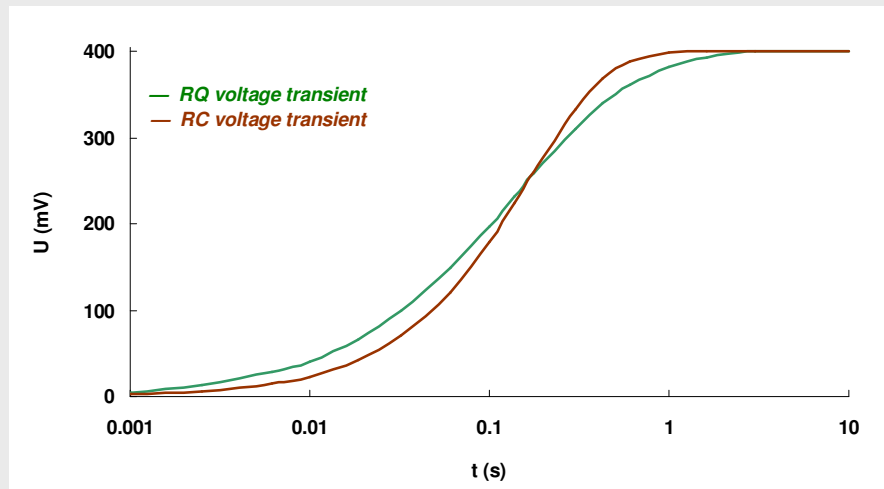
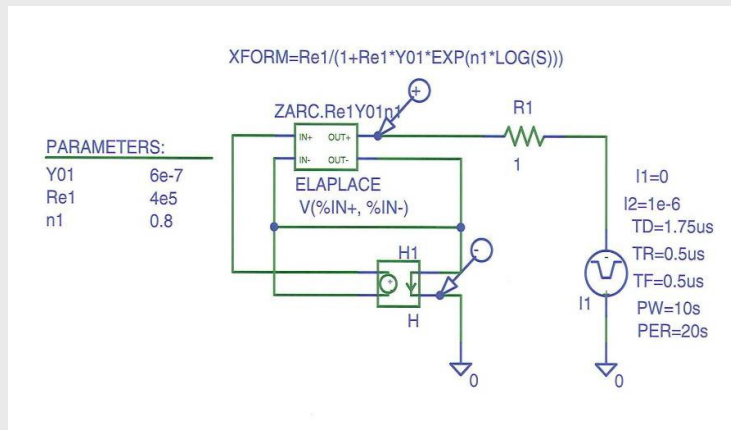
Distribution of time constants

$$F(s)ds = \frac{1}{2\pi} \frac{\sin\{(1-n)\pi\}}{\cosh(ns) - \cos\{(1-n)\pi\}}$$

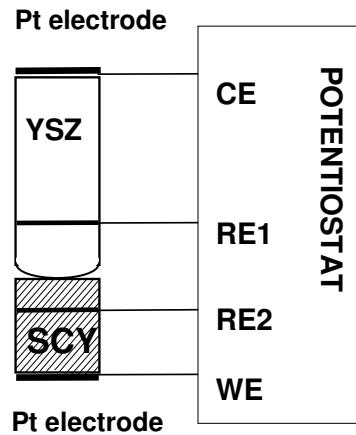


The transient response of a ZARC is not trivial, see van Heuveln, J. Electrochem. Soc. 141, 3423 (1994).

Voltage transient calculated using PSPICE software.



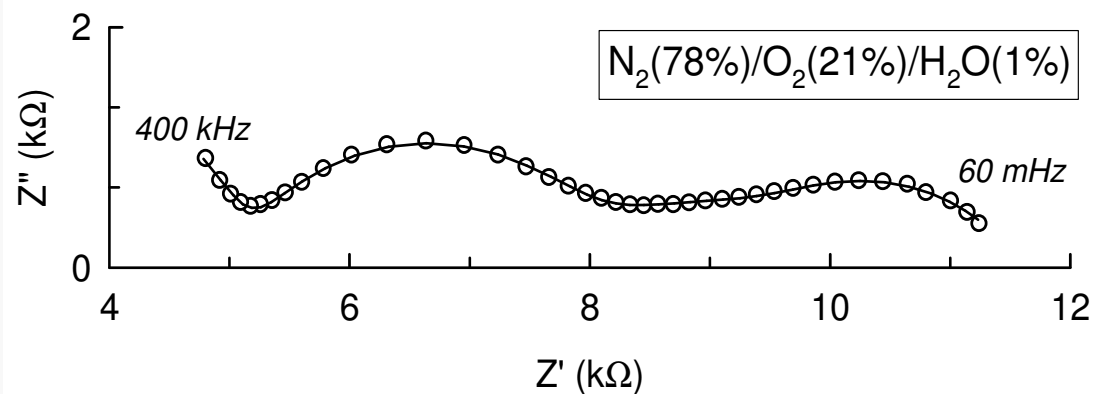
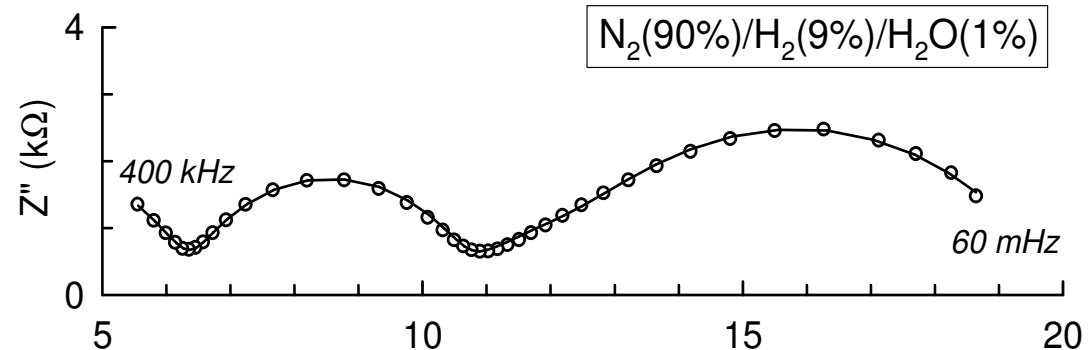
Case (1): Junction between two solid electrolytes



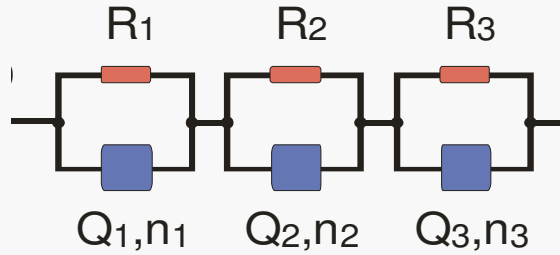
YSZ: Ytria stabilised zirconia (oxide ion conductor)

SCY: Yttrium doped strontium cerate $\text{SrCe}_{1-y}\text{Y}_y\text{O}_\xi$ (partial protonic conductor)

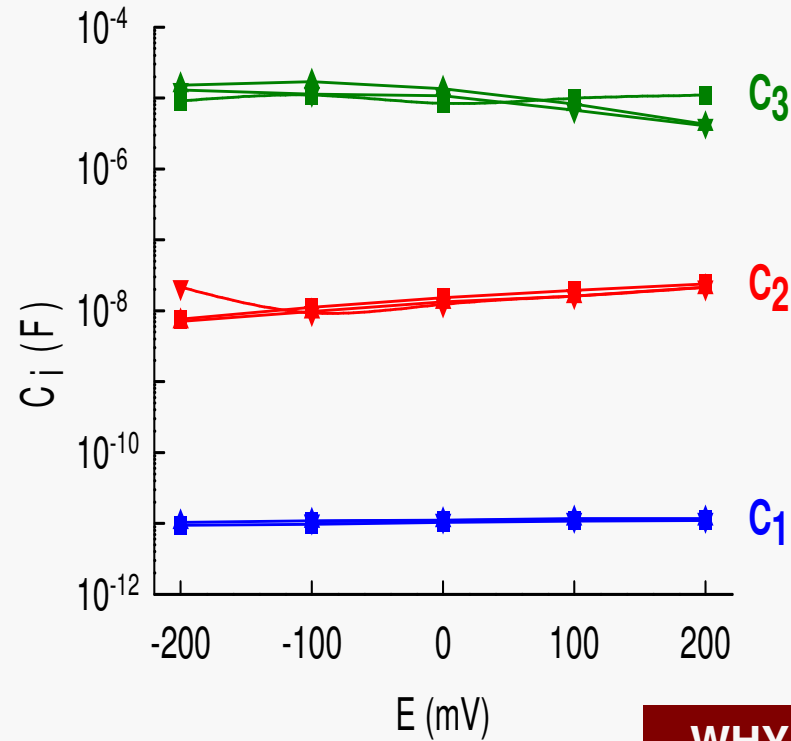
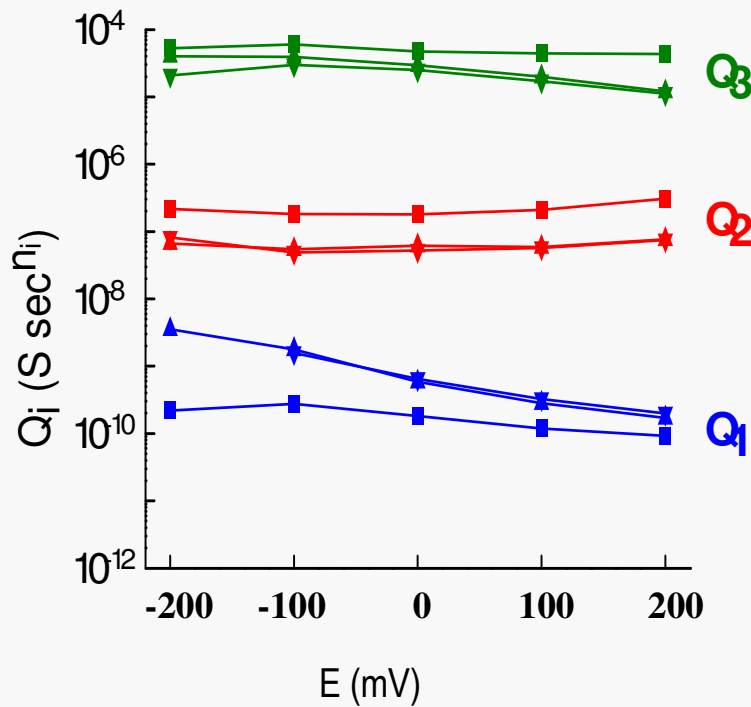
Impedance of junction at zero dc bias (small signal response)



Case (1): Conversion of CPE to near-equivalent capacitances



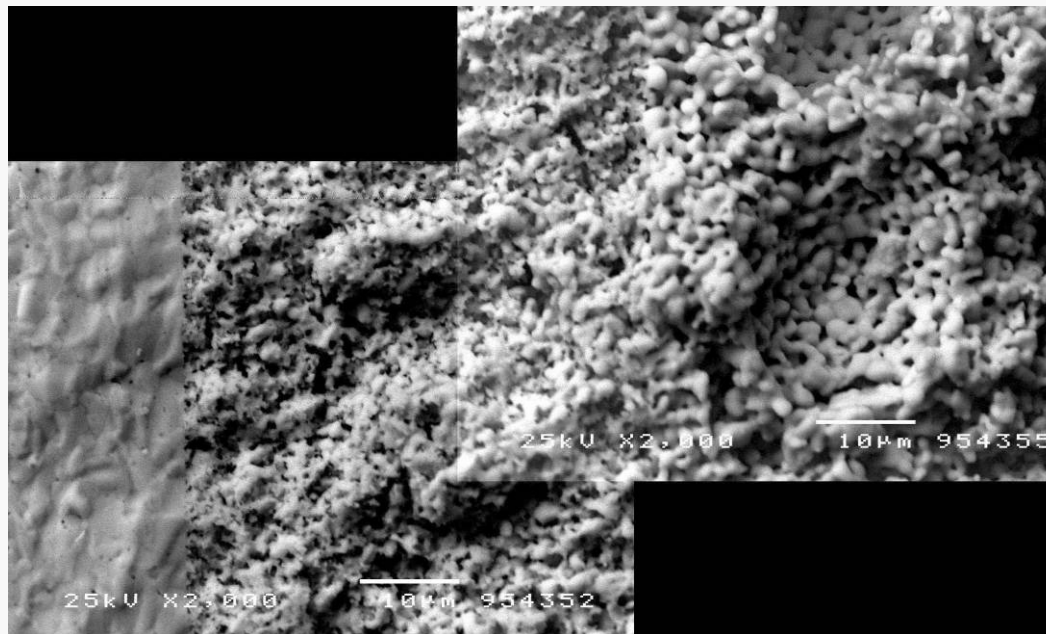
- ◆ N₂ (90%) / H₂ (9%) / H₂O (1%),
- ◆ N₂ (98%) / H₂ (1%) / H₂O (1%)
- N₂ (78%) / O₂ (21%) / H₂O (1%)



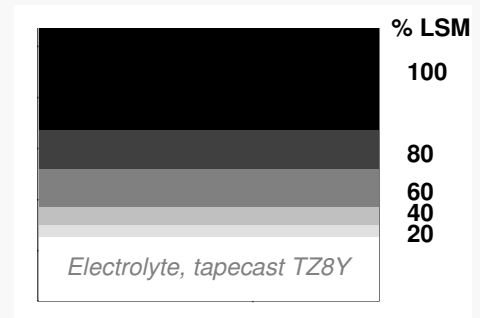
WHY?

Case (2) Ordinary fitting

- Symmetr. cell, YSZ, with ‘cathode’ on either side
- Five-layer graded cathodes based on LSM, YSZ
- Polarisation resistance $< 100 \text{ m}\Omega \text{ cm}^2$, air, 850°C



L1 5 μm L2 7 μm L3 15 μm L4 15 μm L5 40 μm



Microstructure/performance

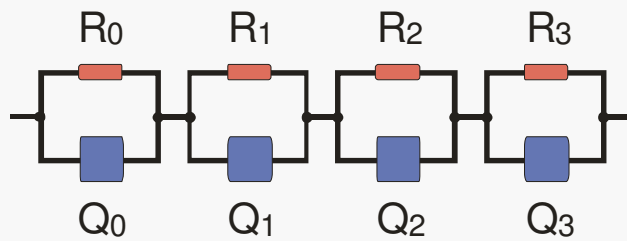
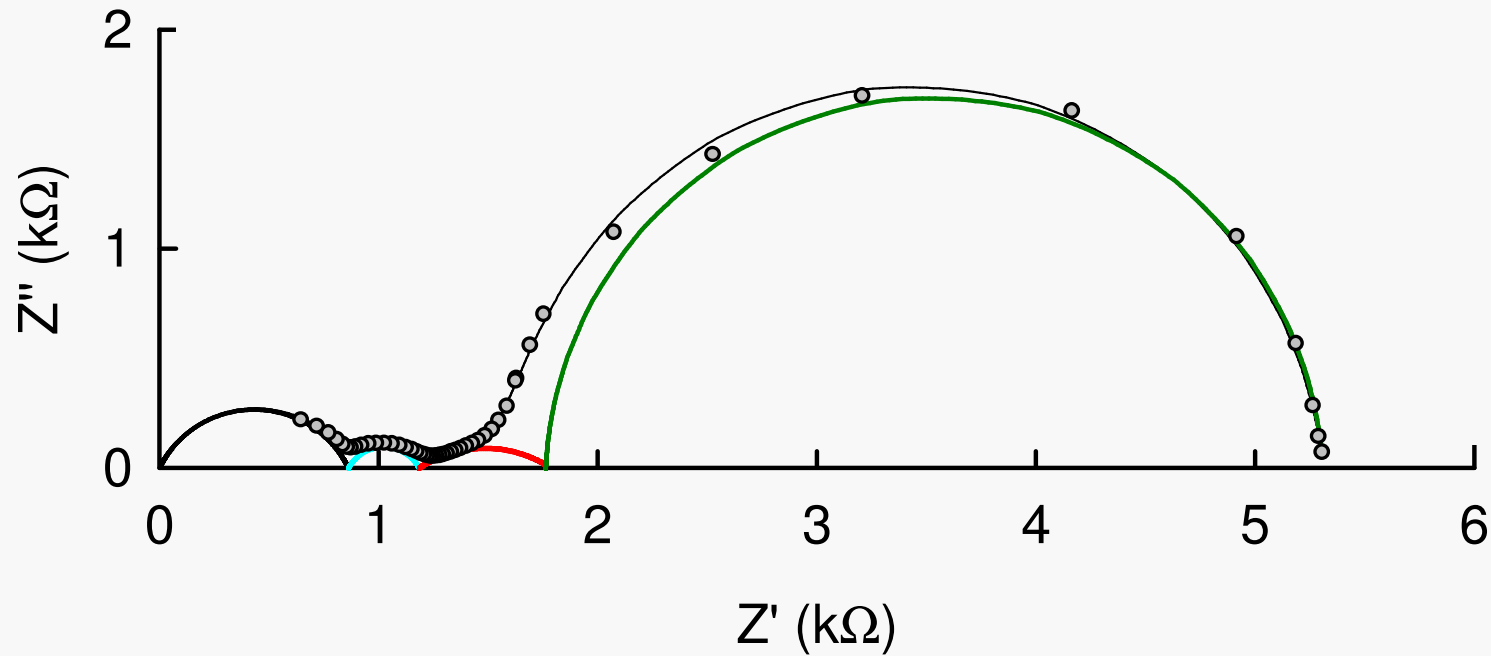
P. Holtappels and C. Bagger, J. Europ. Ceram. Soc. 22, 41, (2002).

Re-evaluation of impedance

N. Bonanos, P. Holtappels and M.J. Jørgensen, 5th European SOFC Forum, Science and Engineering of SOFC, 01-05 July 2002, Luzern, Switzerland.

Case (2) Impedance spectrum

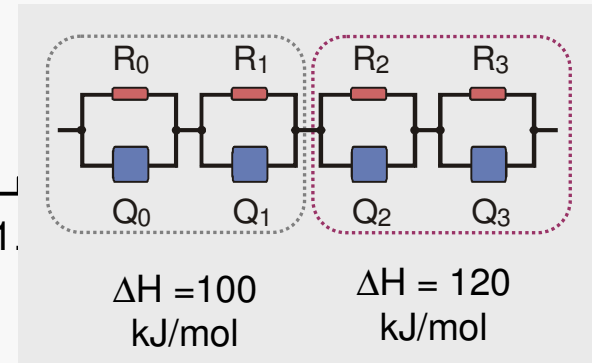
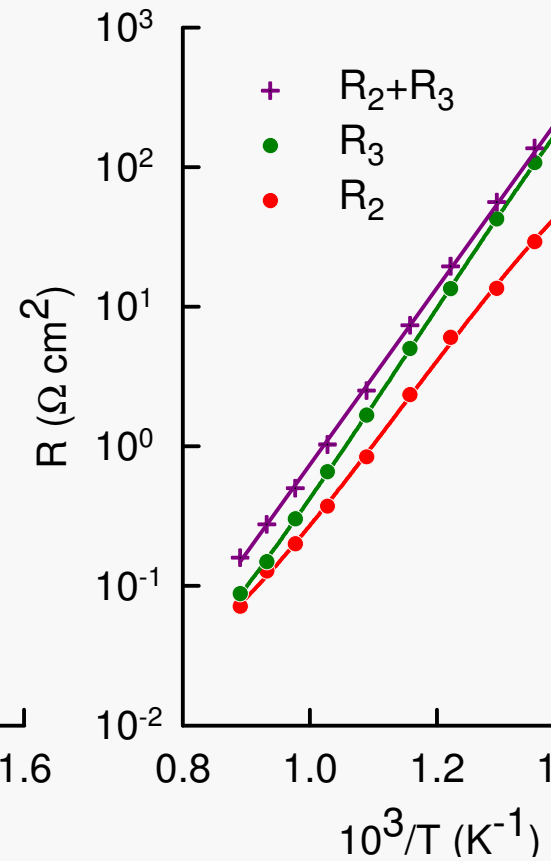
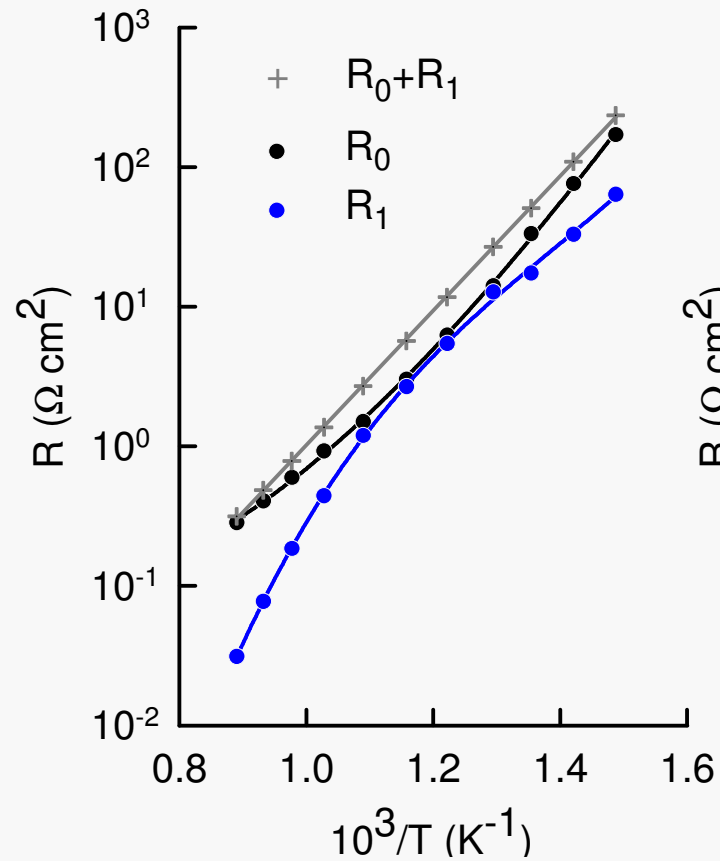
Impedance for symmetrical cell, measured in air at 400°C



T var

Case (2) Arrhenius analysis of resistive elements

Temperature dependence of the resolved resistances and some combinations thereof

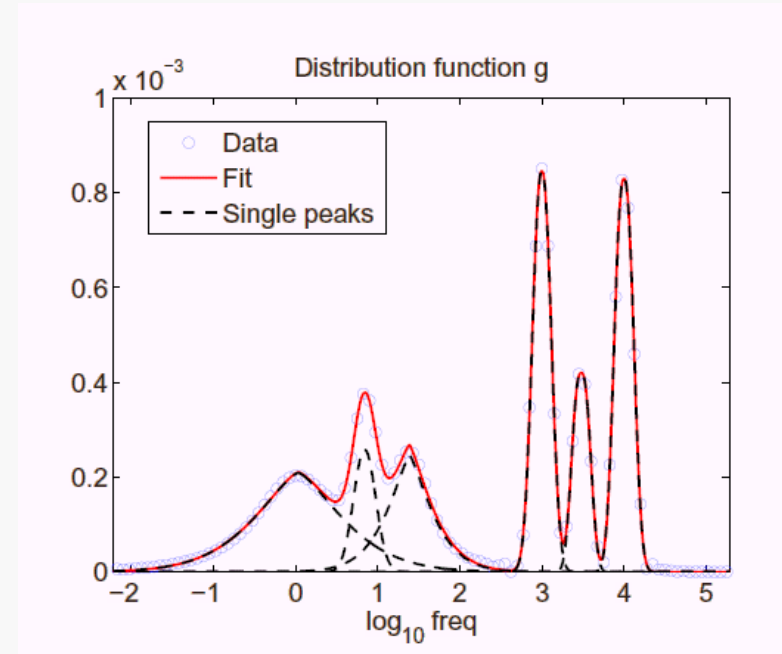


Deconvolution analysis

$$Z(\omega) = R_0 \int_0^{\infty} \frac{\gamma(t)}{1 + i\omega\tau} d\tau$$

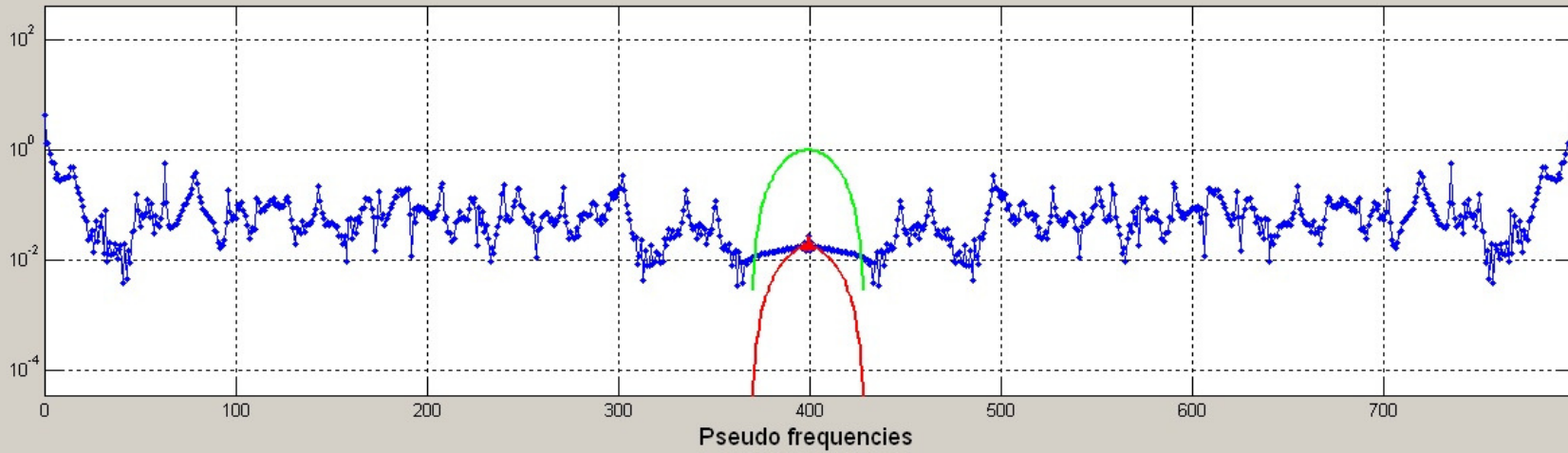
Method involves:

Fourier transform and
filtering of frequencies

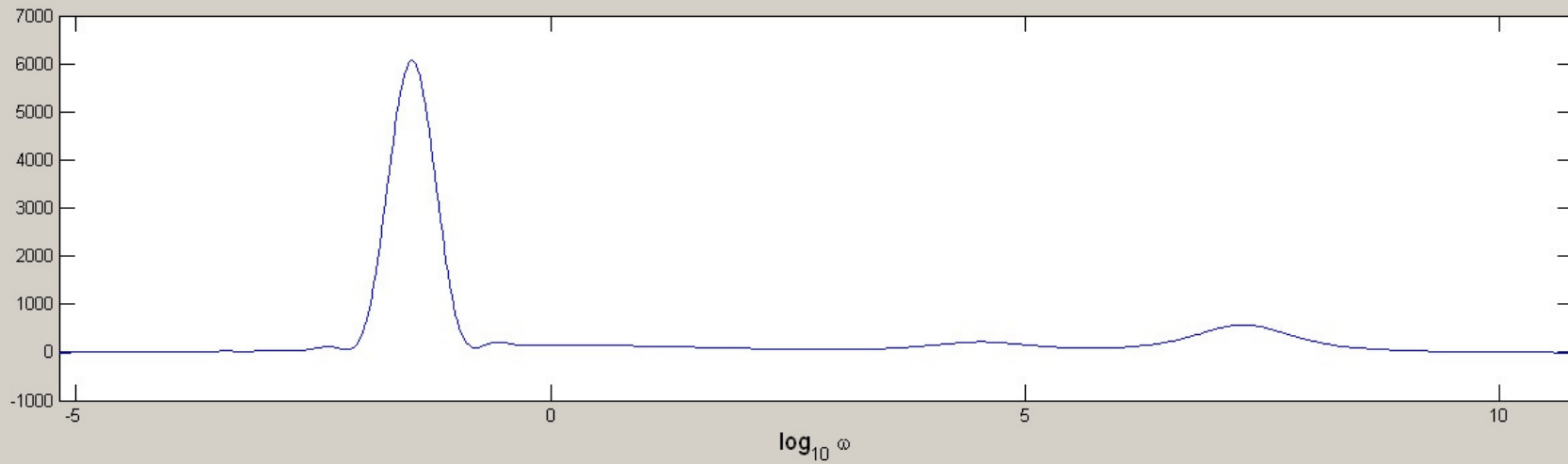


- Method first used on dielectrics by Misell & Shephard in 70s (QEC, London).
- Revived in early 80s by A.D. Franklin and H.J. de Bruin (Australia).
- Adapted by H. Schichlein *et al.* (Karlsruhe), see *J. Applied Electrochem.* 32, A610 (2001).
- Present implementation made at Risø-DTU by Jakob H. Jørgensen (2007).

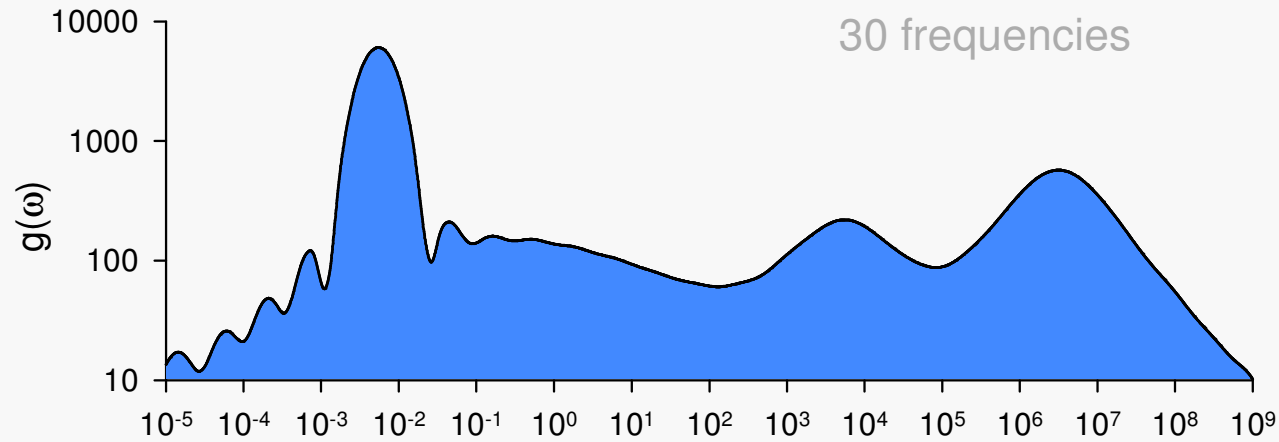
Filtering and the resulting distribution function



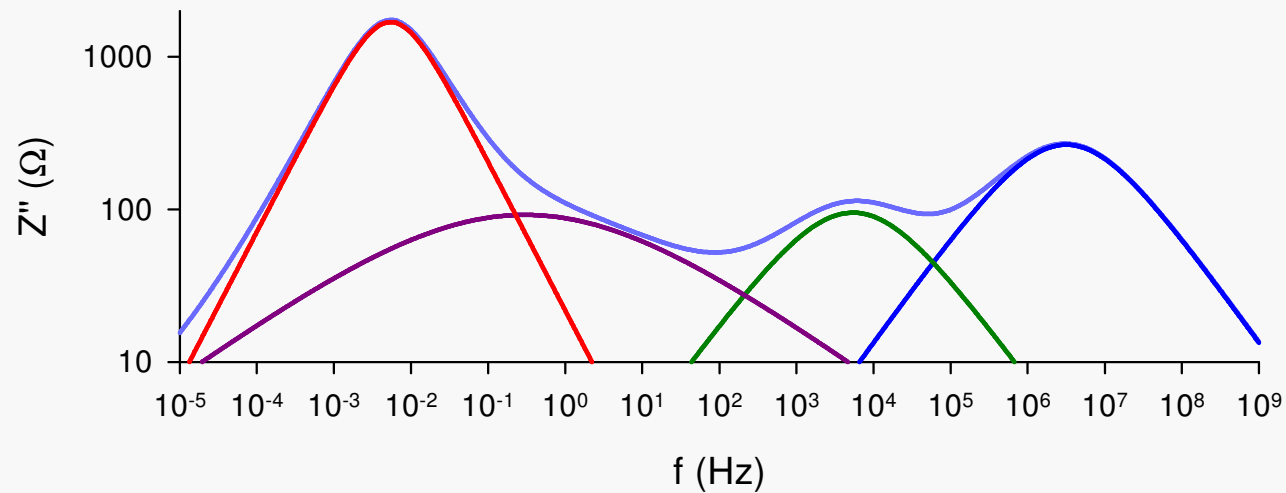
Distribution function for selected nfil



Deconvolution analysis



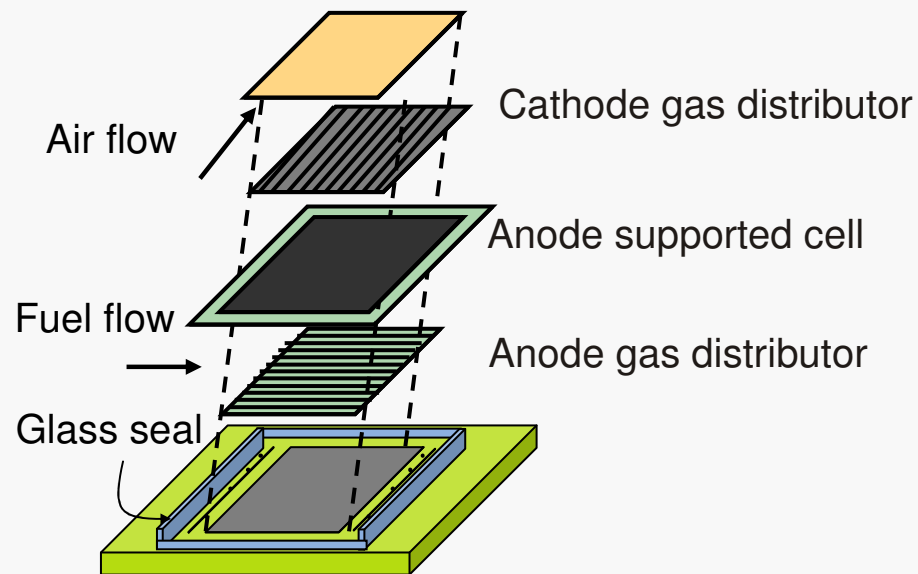
Deconvoluted
distribution function
(note log scale in y)



Relaxations, resolved
by conventional fitting

Case (3) Testing of a solid oxide fuel cell

Testing arrangement for anode – supported, thin electrolyte SOFC

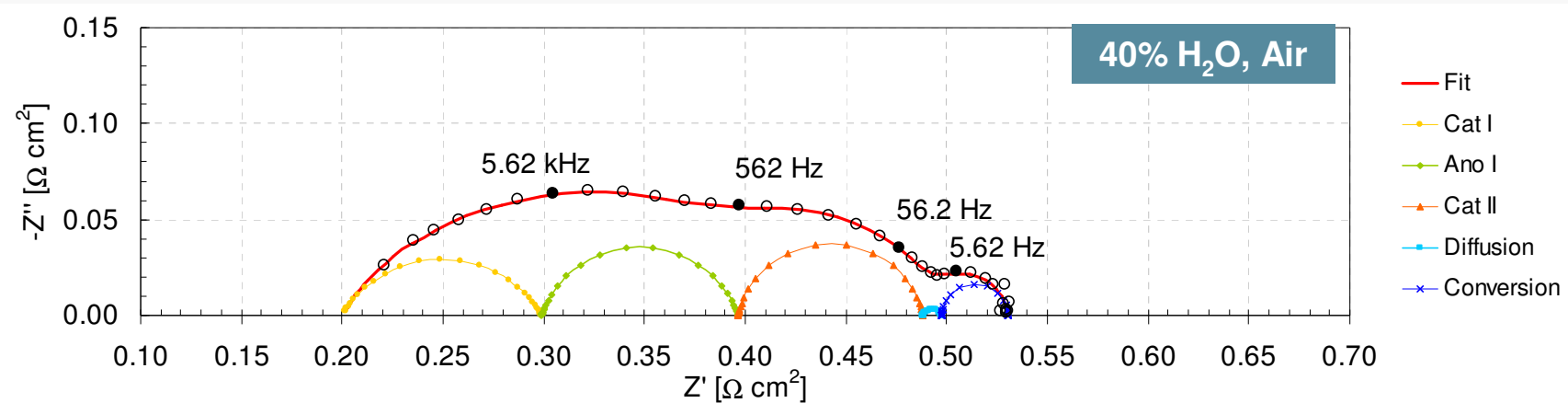
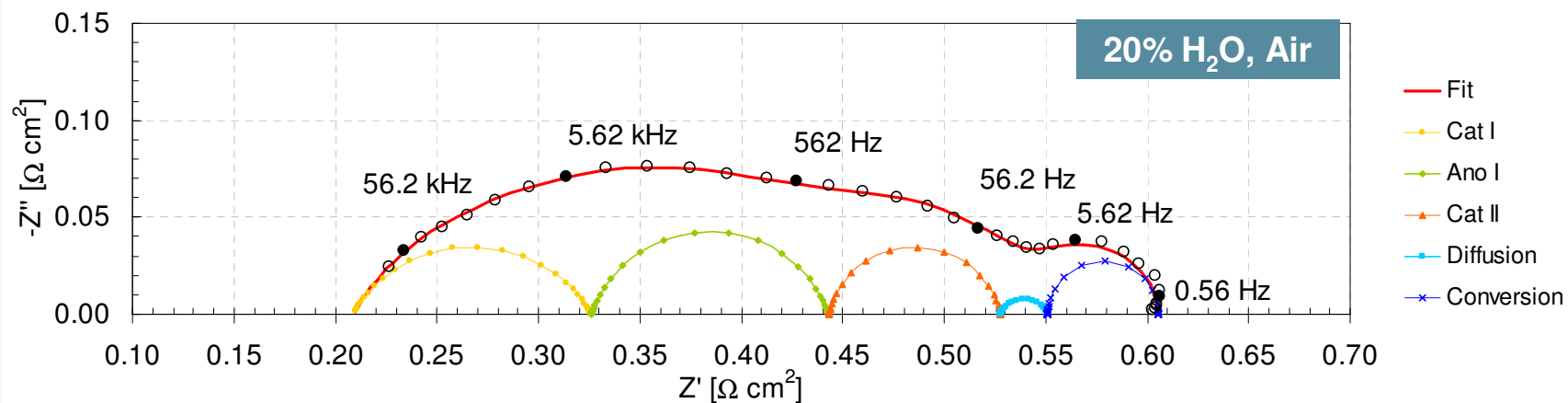


At least six relaxations associated with anode and cathode

- No ref. electrode
- Gas change method
- Anode compartment
- Cathode compartment

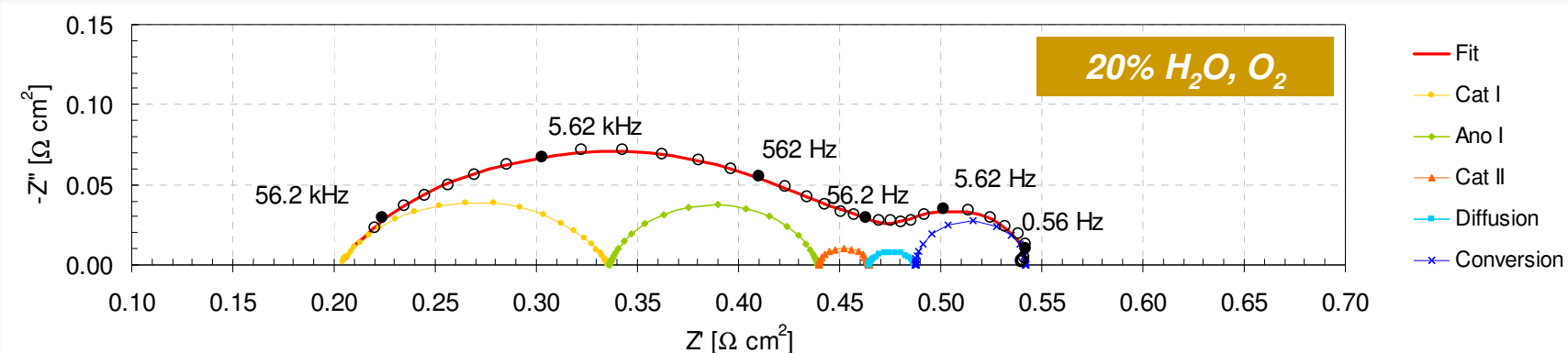
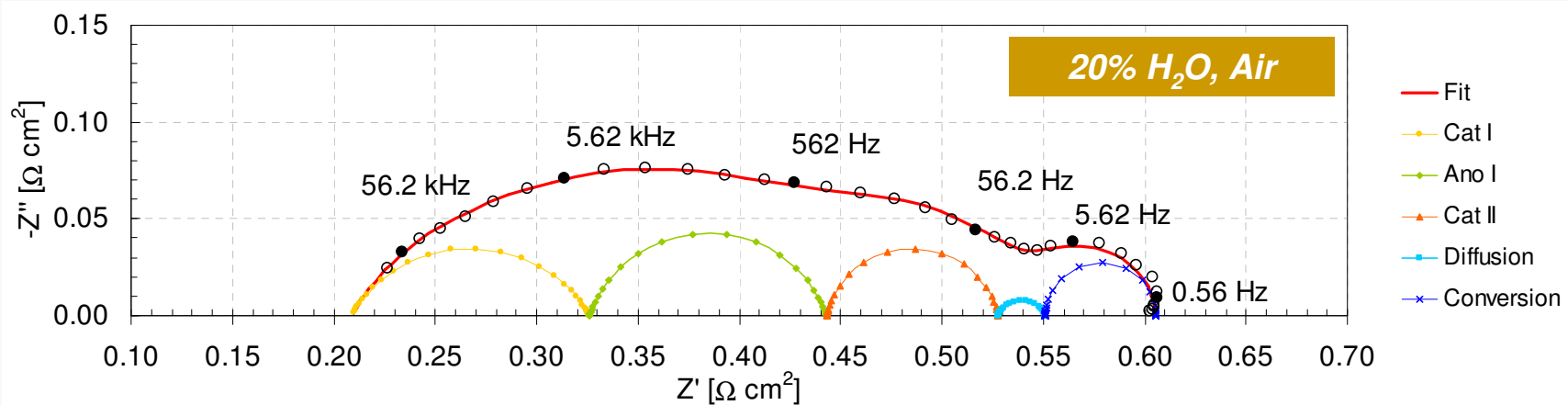
Case (3) Change of atmosphere in the anode compartment

Cell "A", thin electrolyte, anode supported cell fed with H_2 /air 750°C



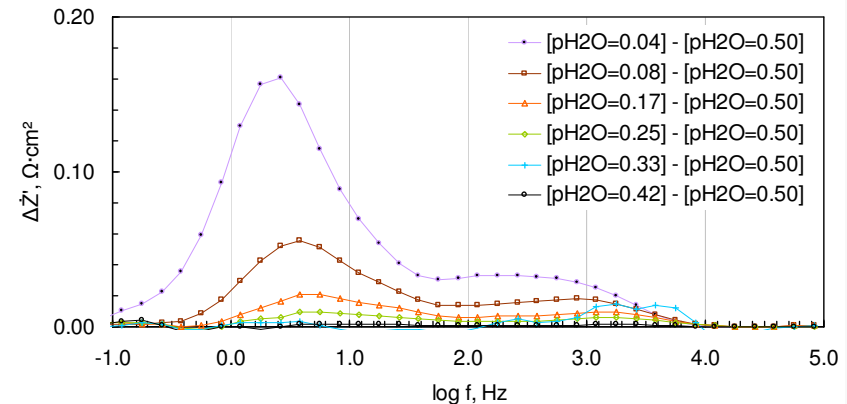
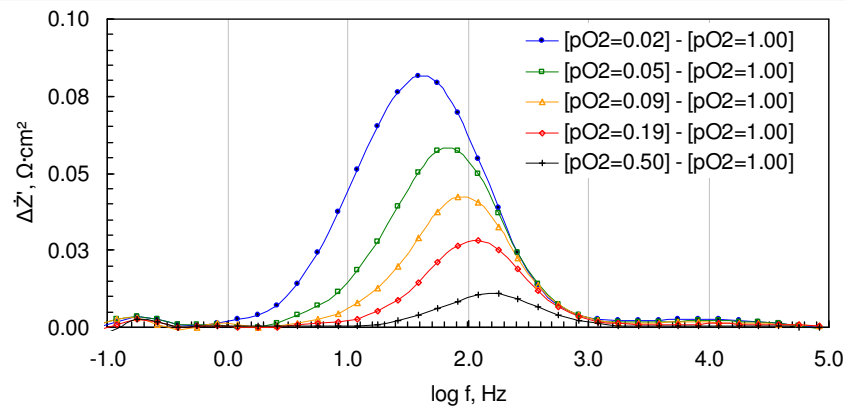
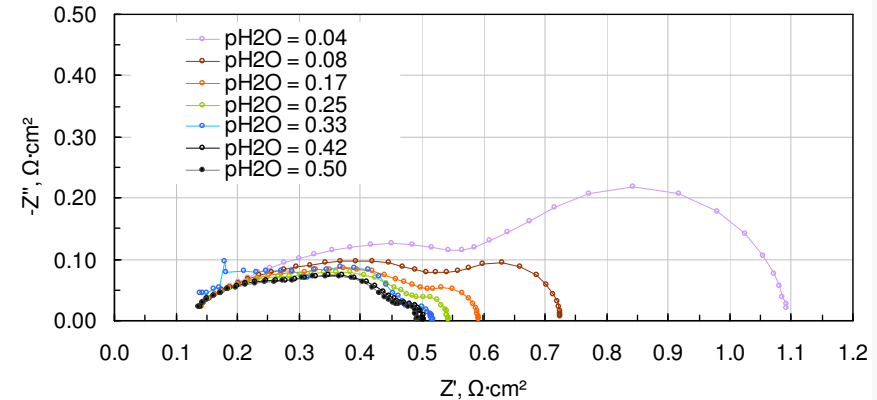
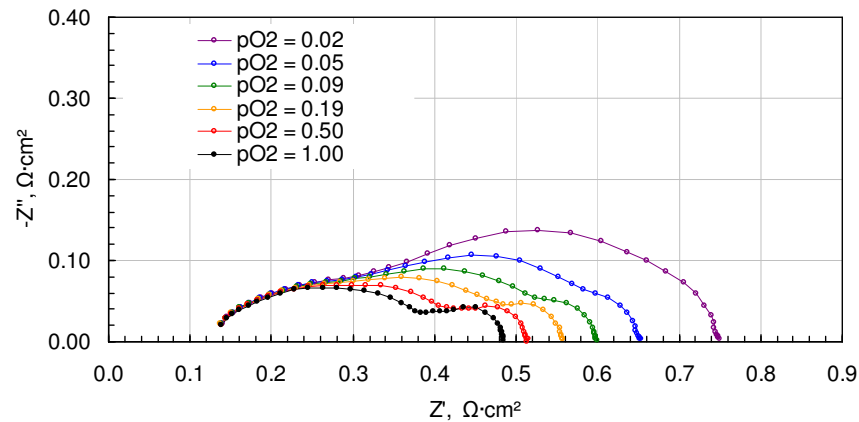
Case (3) Change of atmosphere in cathode compartment

Cell "A", thin electrolyte, anode supported cell fed with H_2 /air 750°C



Analysis of differences in impedance spectra (ADIS).

Example at 750°C employing p_{O_2} and p_{H_2O} variations on different cell from previous one.
Identify cathode or anode related processes by suitable variations of operating conditions

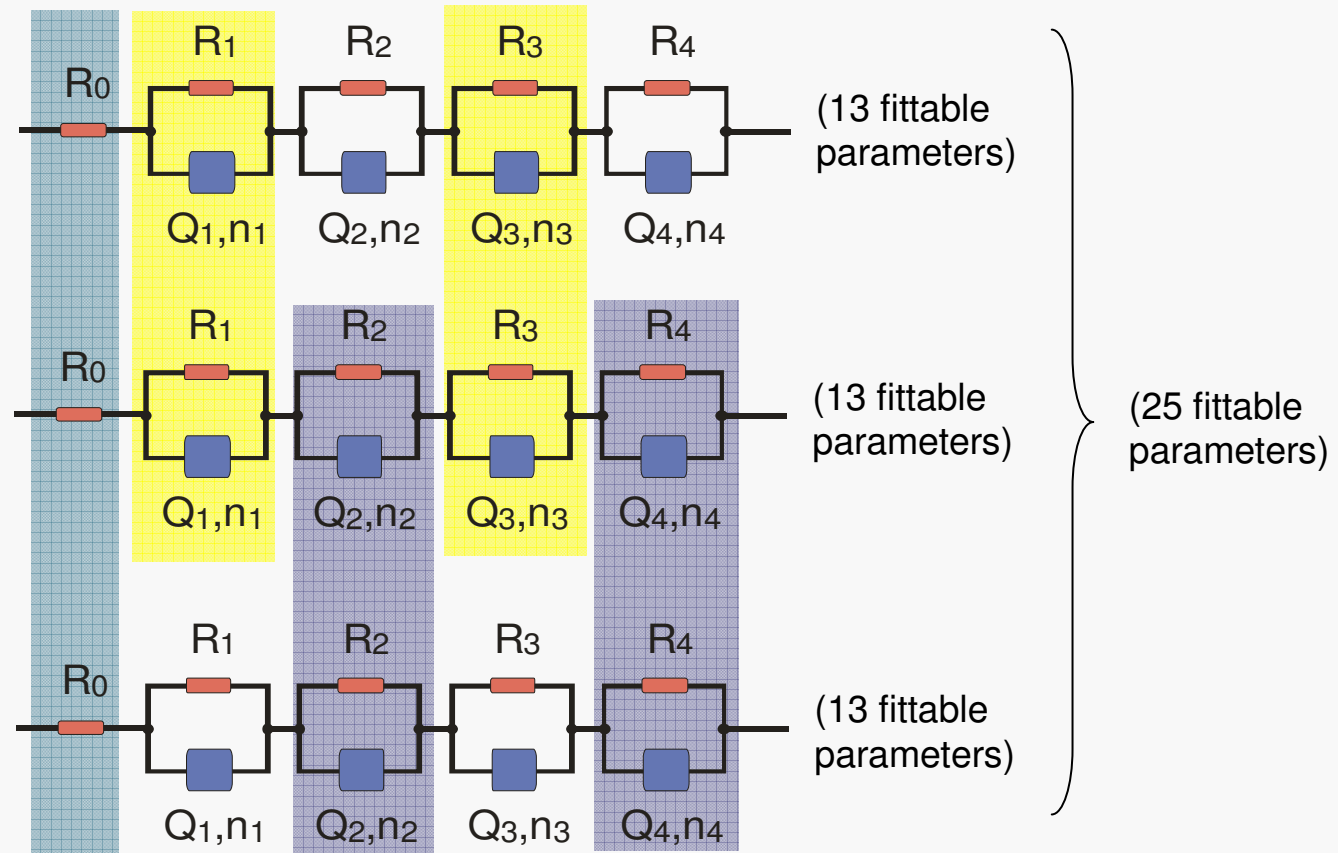


S.H. Jensen et al. J. Electrochem. Soc., 154, B1325-B1330 (2007)
see also *D. Vladikova et al. Solid State Ionics 176, 2005-2009 (2005)*

New direction: gas change studies with constrained multiple fits

Anode gas composition changed — cathode related relaxations unchanged

Cathode gas composition changed — anode related relaxations unchanged



With these constraints, the number of parameters is reduced.

Concluding remarks

- EIS can be applied to materials, cell components and complete cells.
- Can resolve... from relaxations of dielectric constant/conductivity to relaxations of chemical composition.
- Mainly by use of a Voight measurement model (series connection).
- Mainly R, Q, other elements introduced when strictly necessary.
- Background study of cell components to fix relaxation frequency ranges.
- Results would benefit from increased use of deconvolution techniques.
- Gas change methods are instrumental in achieving resolution.
- Phenomenological approach, but with mechanistic component.

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 - Torben Jacobsen and the above for useful discussions
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