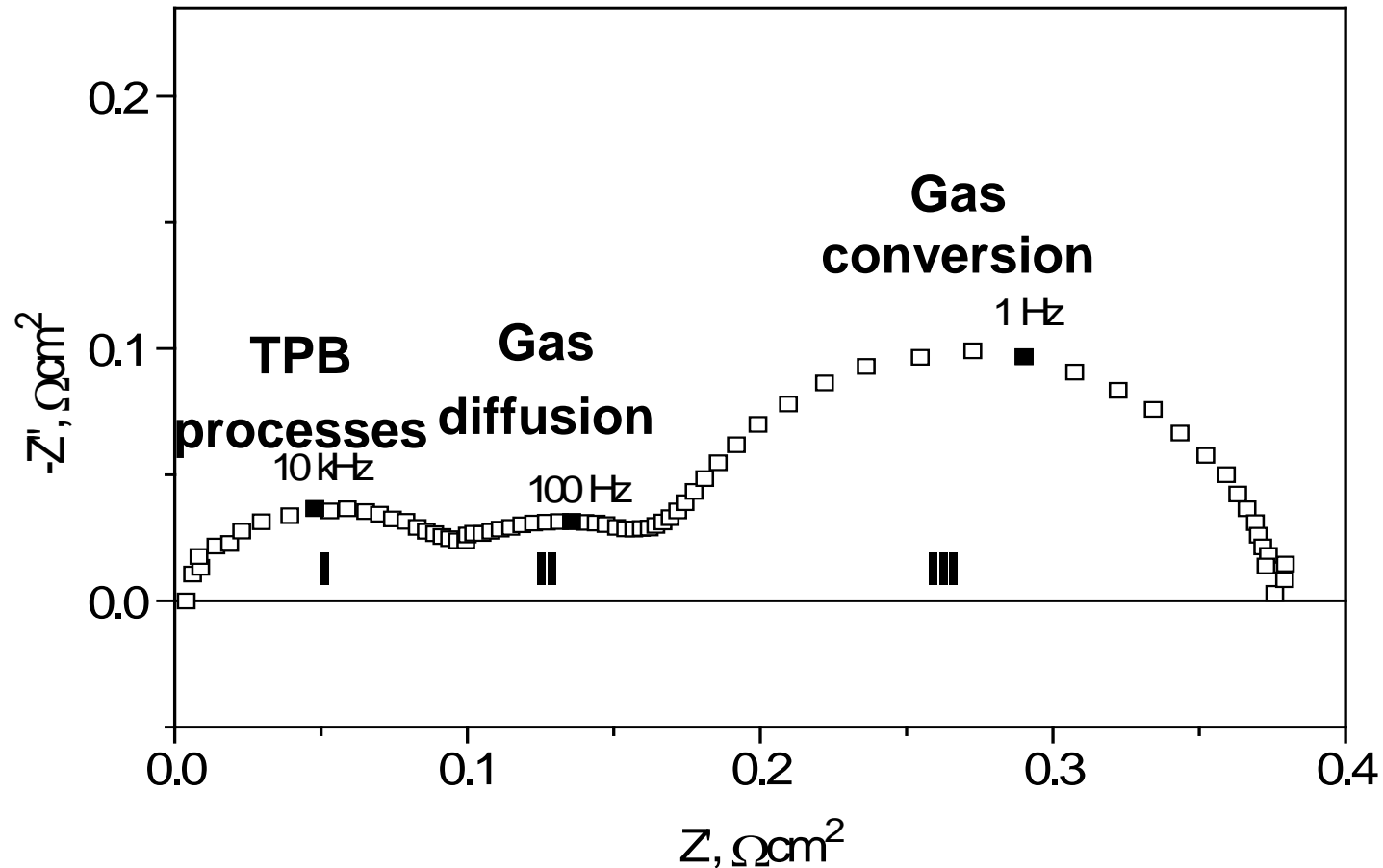


Outline

- 1. The disagreement in literature**
- 2. Electrode polarisation resistance and electrode reaction rate limitations**
- 3. What the Butler-Volmer equation describes**
- 4. i - V relationships for different impedance elements**
- 5. Concluding remarks**

Polarisation resistance



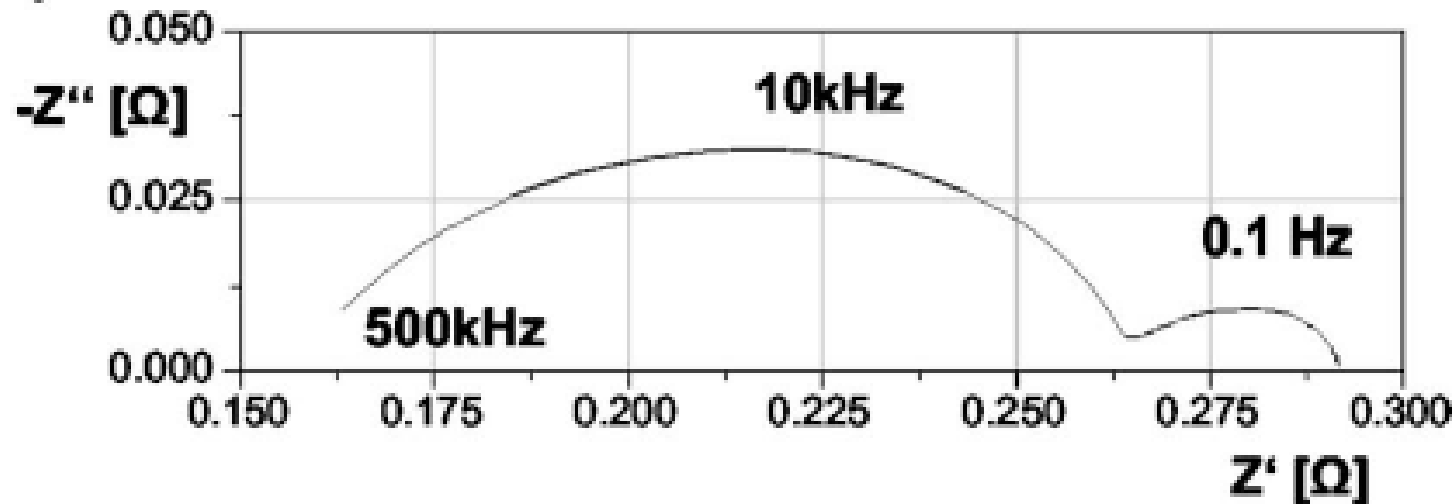
Impedance spectrum of a Ni-YSZ cermet in 3 electrode set-up at 1000 °C in $\text{H}_2 + 3\% \text{H}_2\text{O}$. Based on Primdahl and Mogensen, *J. Electrochem. Soc.*, **146 (1999) 2827**

Risø DTU

National Laboratory for Sustainable Energy

Polarisation resistance

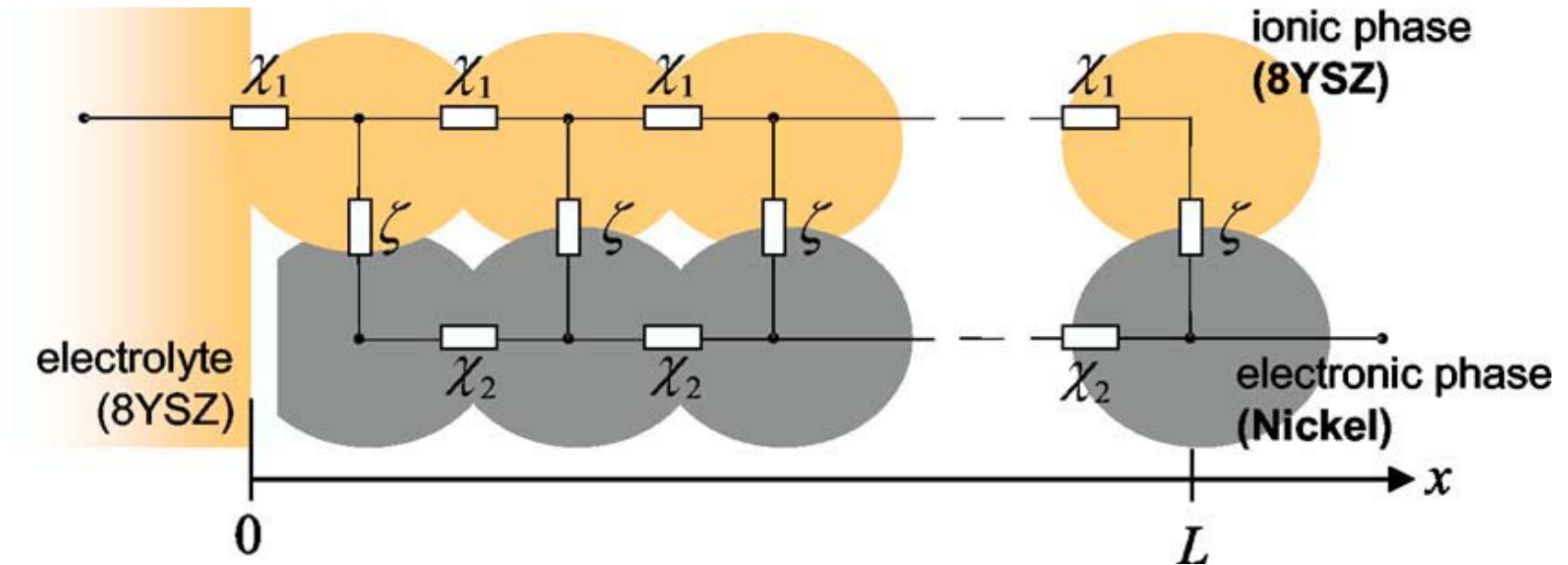
b)



Typical impedance spectrum of a of technical Ni/8YSZ cermet electrode at 950 °C in H₂ with 5 % H₂O. Electrode area is 1 cm². The anode consists of 47 vol % Ni and 53 vol % YSZ of solid content. From V. Sonn, A. Leonide, and E. Ivers-Tiffée, *J. Electrochem. Soc.*, 155 (2008) B675.

Electrode reaction rate limitations

- Often 2 concentration impedance arcs are observed, a small diffusion arc (summit freq. 10 – 100 Hz) arc and a larger conversion arc (1 -10 Hz).
- Often 2 TPB ion transfer process are seen for H₂/H₂O/Ni/YSZ cermet electrodes, see e.g. V. Sonn, A. Leonide, and E. Ivers-Tiffée, *J. Electrochem. Soc.*, 155 (2008) B675. An arc reflecting the parallel transport of O²⁻ and e⁻ in the region near the electrolyte, and an arc due to ion transfer across or around the TPB. Summit frequencies depend on temperature and structure.
- Activation energies from 0.5 - 1.7 eV have been reported
- Dependencies of R_p on partial pressures of water and hydrogen vary a lot. The H₂ anodic oxidation rate often increases with p_{H₂O}!! It seems very sensitive to impurities in materials as well as in the gas phase.



Modeling scheme for a porous two-phase composite electrode transmission line model.

Types of polarisation resistance



The area specific resistance, ASR, may be broken down into five contributing area specific polarisation resistances:

$$ASR = R_{\text{elyt}} + R_{\text{connect}} + R_{\text{p;elchem}} + R_{\text{p;diff}} + R_{\text{p;conver}}$$

Electrode reaction overvoltage or activation overvoltage

- *Activation overvoltage is an unspecific term used when you do not know what you have at hand. There may be many different reasons for electrode reaction rate limitations at an electrode. e.g.:*
- adsorption of reactant molecules at the electrode
- bond breaking in the reactant molecule
- surface diffusion of reaction intermediates from the catalytic sites to the three phase boundary (TPB) line
- diffusion of ions through the bulk of electrode particles with mixed conduction
- conduction through or around segregated phases at the surface/at the TPB
- desorption of reaction products
- transfer of ions across the electrode/electrolyte interface
- transfer of electrons from electrode to molecule

Activation overvoltage

The current density in **low temperature** electrochemistry is some times well described by the Butler - Volmer equation:

$$i = i_0 \cdot \left\{ \exp\left(\frac{(1 - \alpha_a)F \cdot \eta}{R \cdot T}\right) - \exp\left(\frac{-\alpha_c F \cdot \eta}{R \cdot T}\right) \right\} \quad \left[\frac{A}{cm^2} \right]$$

$\eta = E - E_0$, the difference between the actual, $E = \pi - \phi$, and the equilibrium, E_0 ($i = 0$), electrode potential; α_a and α_c are anodic and cathodic symmetry factors, $0 < \alpha < 1$

Activation overvoltage

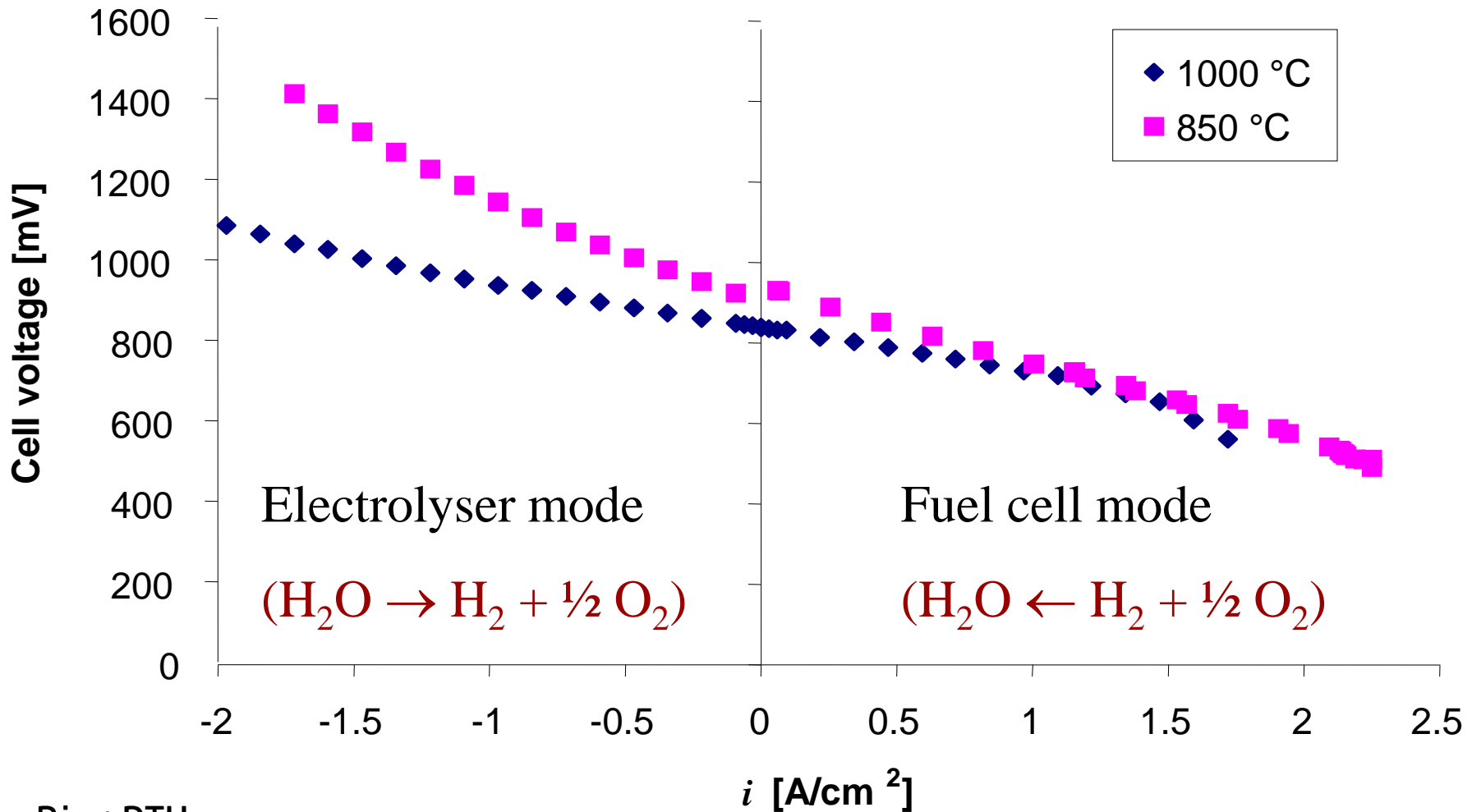
At low overvoltage the Butler-Volmer equation becomes linear

At high overvoltage it gets the same form as the Tafel equation:

$$\eta = a \pm b \times \log |i|$$

using the absolute value of the current density and the \pm sign for anodic and cathodic overpotentials, respectively.

i-V curves for a Risø SOC

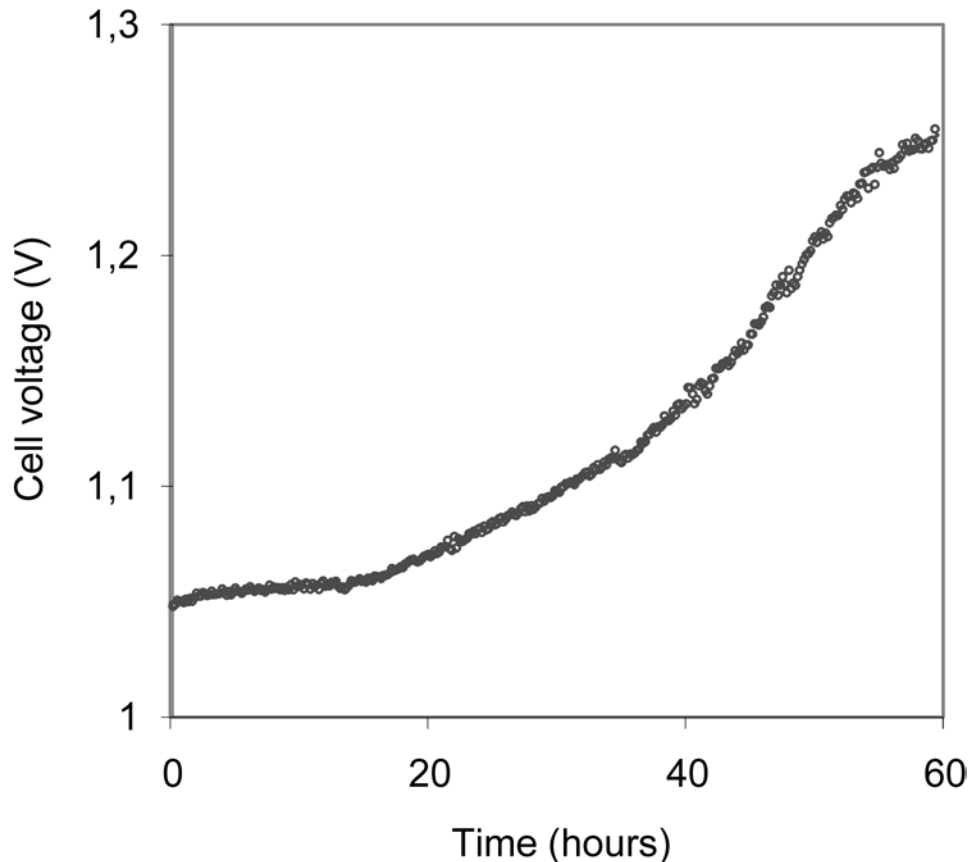


Activation overvoltage

- To my best knowledge there is **no experimental evidence** that charge transfer **as described by the Butler - Volmer equation** is rate limiting SOC electrode reactions above 700 °C!
- Further, the “bottle neck” theory - i.e. only one rate determining step is present at a given condition – is often taken for granted and is actually a prerequisite for the simple Tafel / Butler - Volmer analysis. This is very seldom seen in the case of SOCs and not common in electrochemistry.

Example: Solid Oxide Electrolyser Cell

Performance decreases during electrolysis operation (Søren Højgaard Jensen PhD work)



Operating conditions:

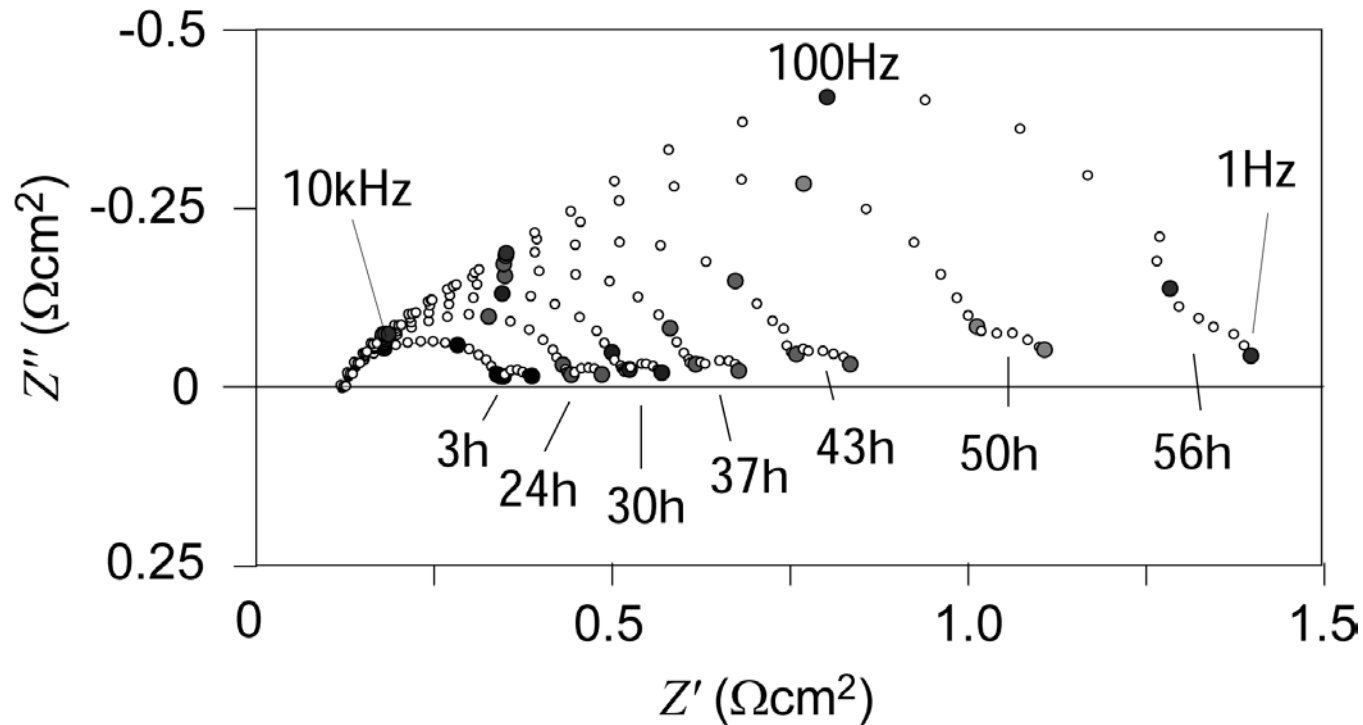
750 °C
-0.25 A/cm²

gas to LSM-electrode:
O₂ (10 l/h)

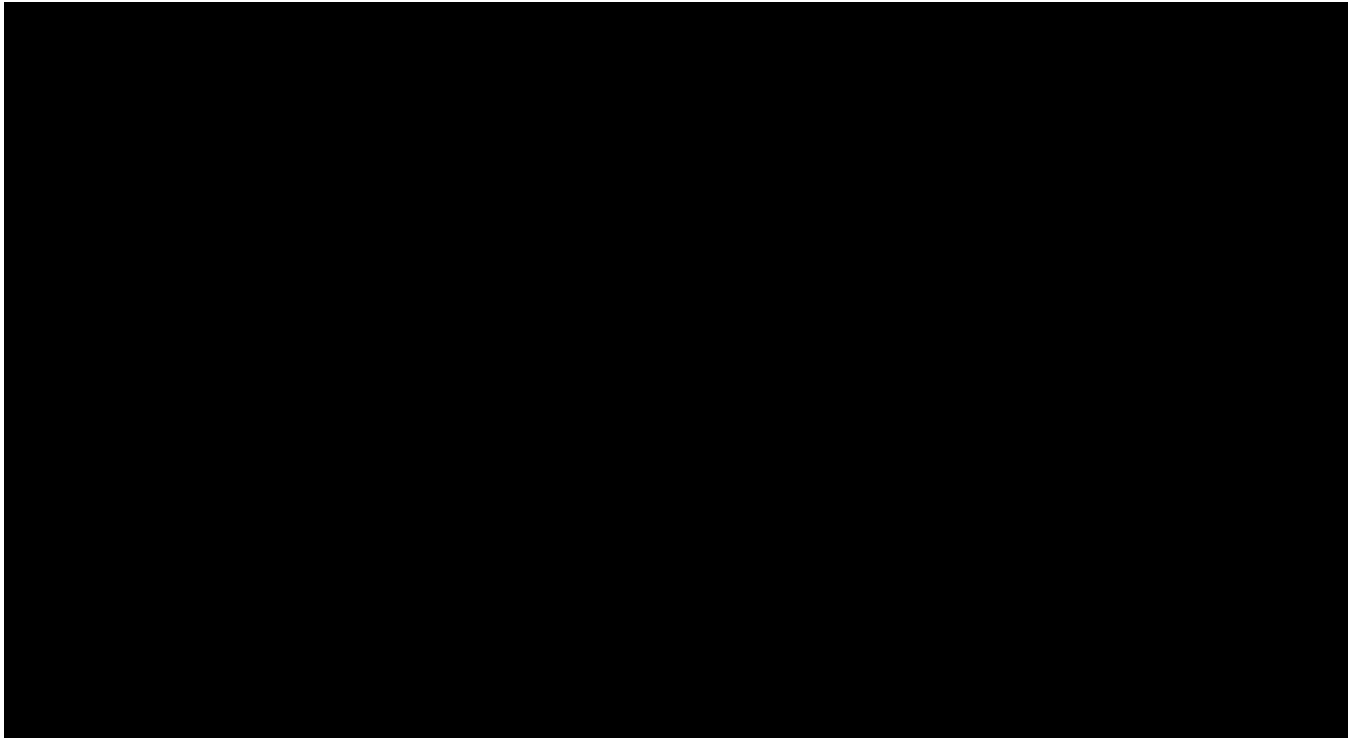
gas to Ni-electrode:
70% H₂O + 30 % H₂ (18 l/h)

Cell area:
16 cm²

Impedance Spectra Measured During Electrolysis Operation



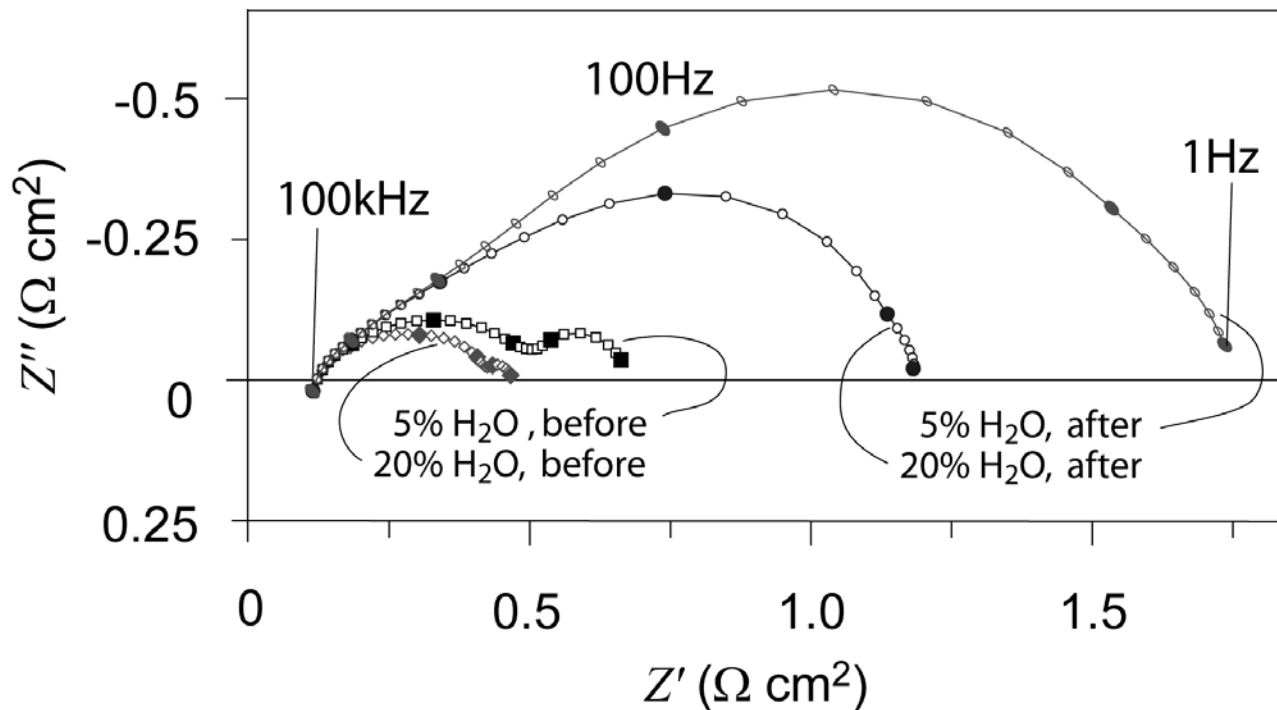
DRT of Impedance Spectra Measured During Electrolysis Operation



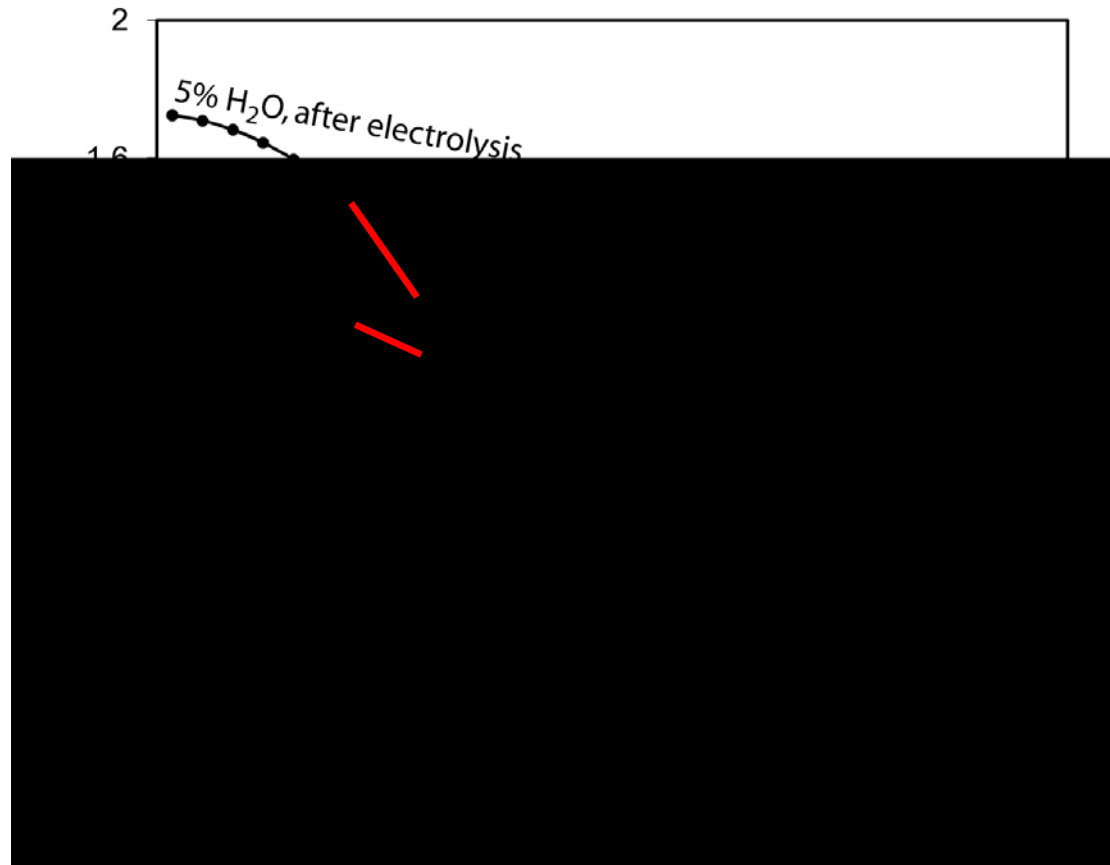
Impedance Spectra Measured Before and After Electrolysis Operation at OCV

gas to Ni-electrode: H₂ with either 5% or 20% H₂O

gas to LSM-electrode: air before electrolysis and O₂ after electrolysis

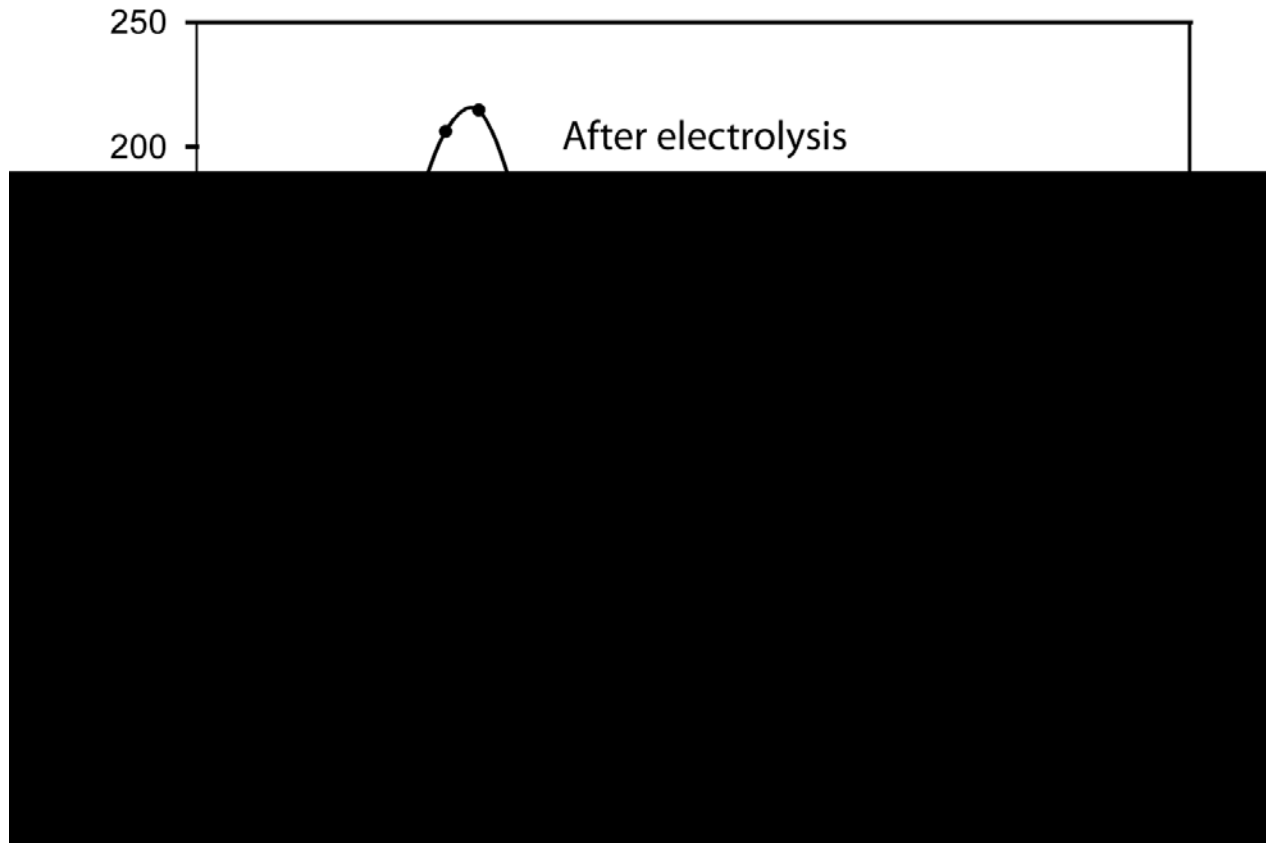


Impedance Spectra Measured Before and After Electrolysis Operation



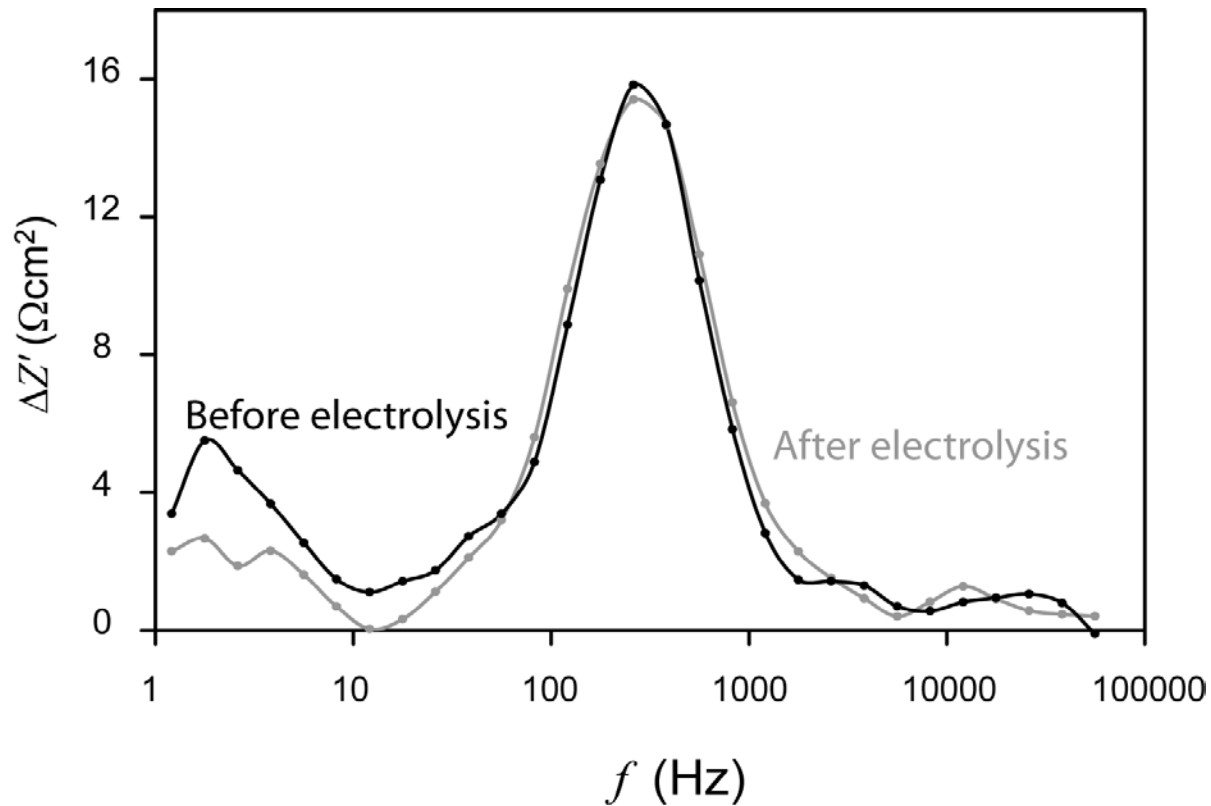
*between the two slopes
impedance characteristic*

Characteristics

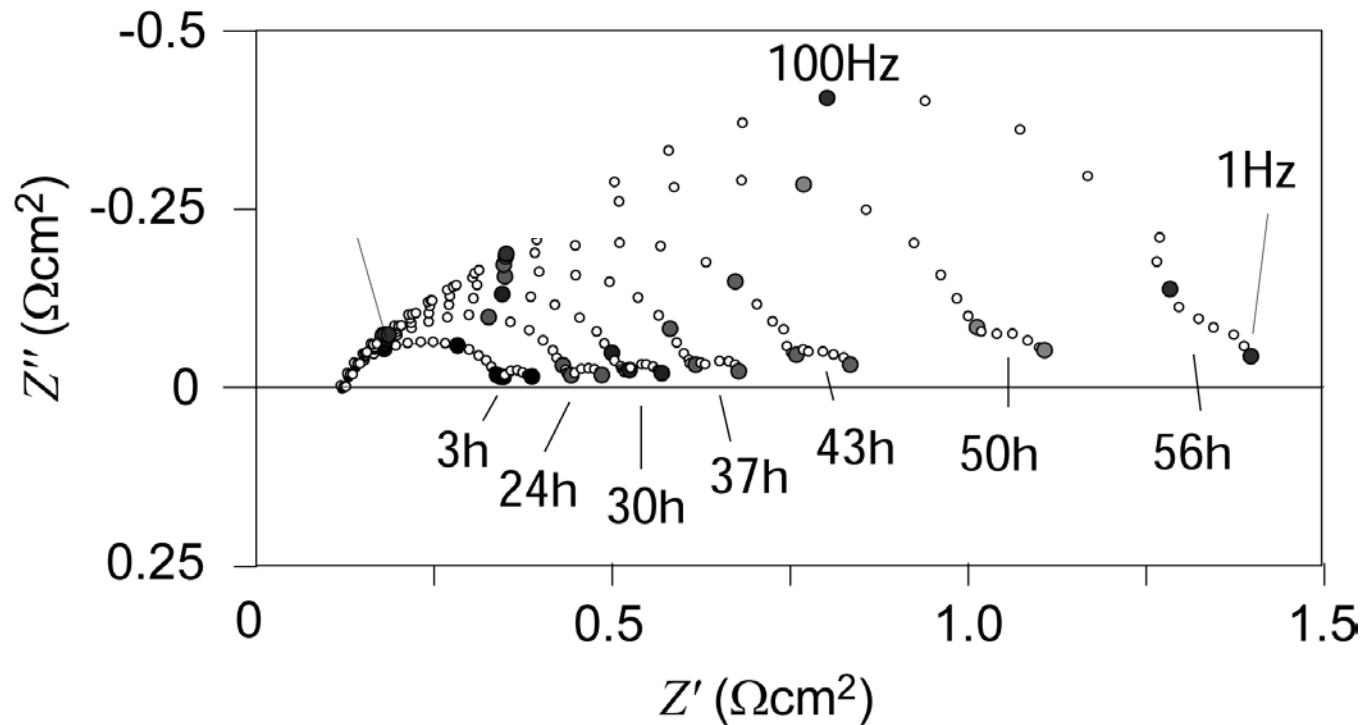


Characteristics

...based on gas shifts at the LSM-electrode from air to O₂



Impedance Spectra Measured During Electrolysis Operation



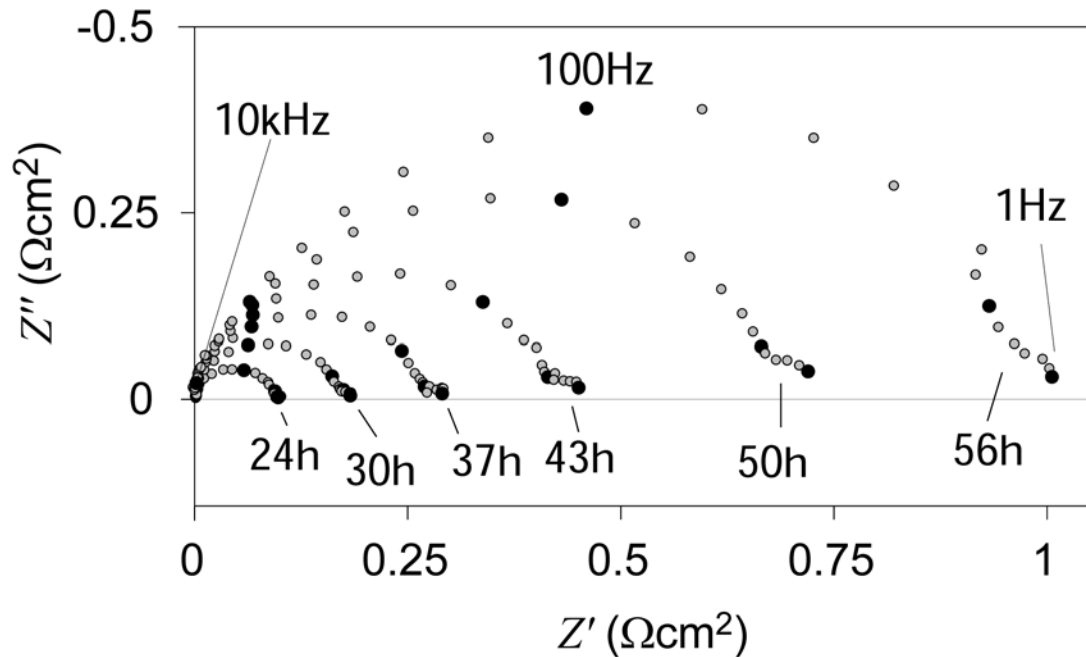
What contribute to these impedance spectra?

...LSM-electrode, Ni-electrode, Electrolyte and Wire inductance

...too many variables in an equivalent circuit model

Difference spectra (x h – 3 h)

...the spectra reflect changes in the Ni-electrode impedance



...fewer variables to model the spectra.

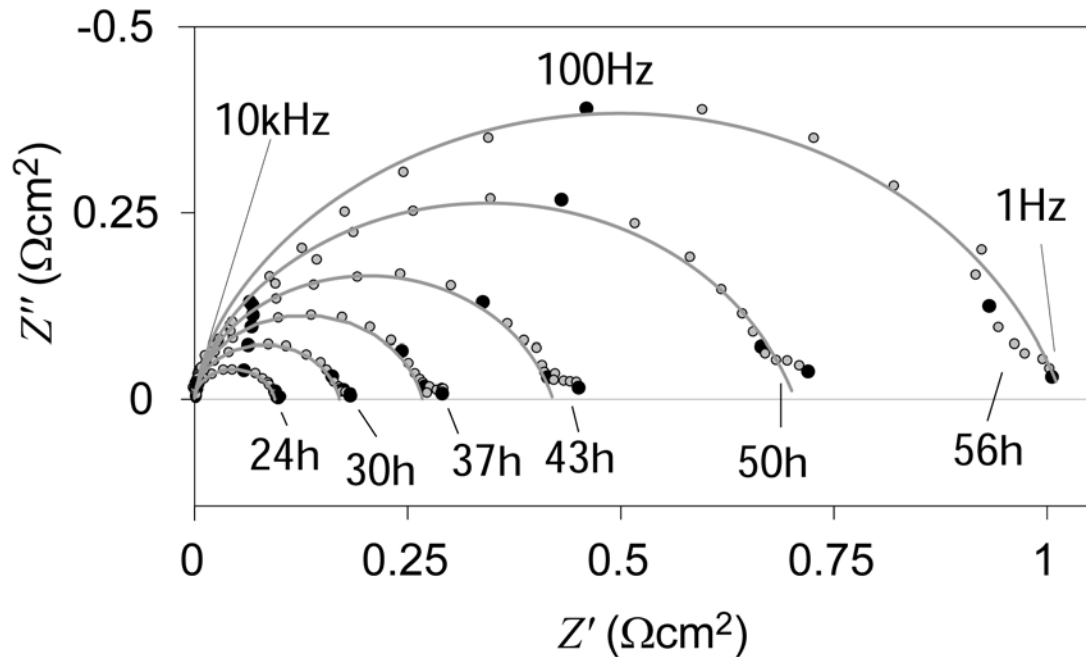
Which Impedance Element do Best Model the Ni-electrode Impedance?



$$Z_{(RQ)} = \frac{R_{(RQ)}}{1 + (j\omega/\omega_0)^n} \quad ?$$

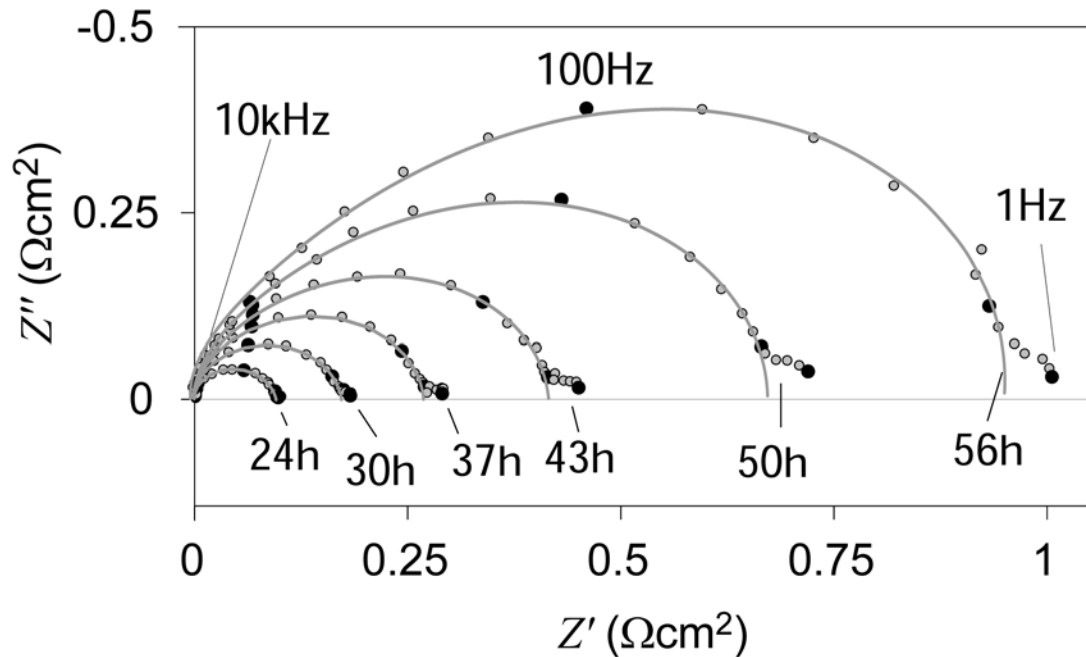
$$Z_{Ge} = \frac{R_{Ge}}{\sqrt{1 + (j\omega/\omega_0)^n}} \quad ?$$

Impedance spectra measured before and after electrolysis operation



$$\Delta Z_{(RQ)_{xh}} = \frac{R_{xh}}{1 + (j\omega/\omega_{0xh})^{n_{xh}}} - \frac{R_{3h}}{1 + (j\omega/\omega_{03h})^{n_{3h}}}$$

Impedance spectra measured before and after electrolysis operation

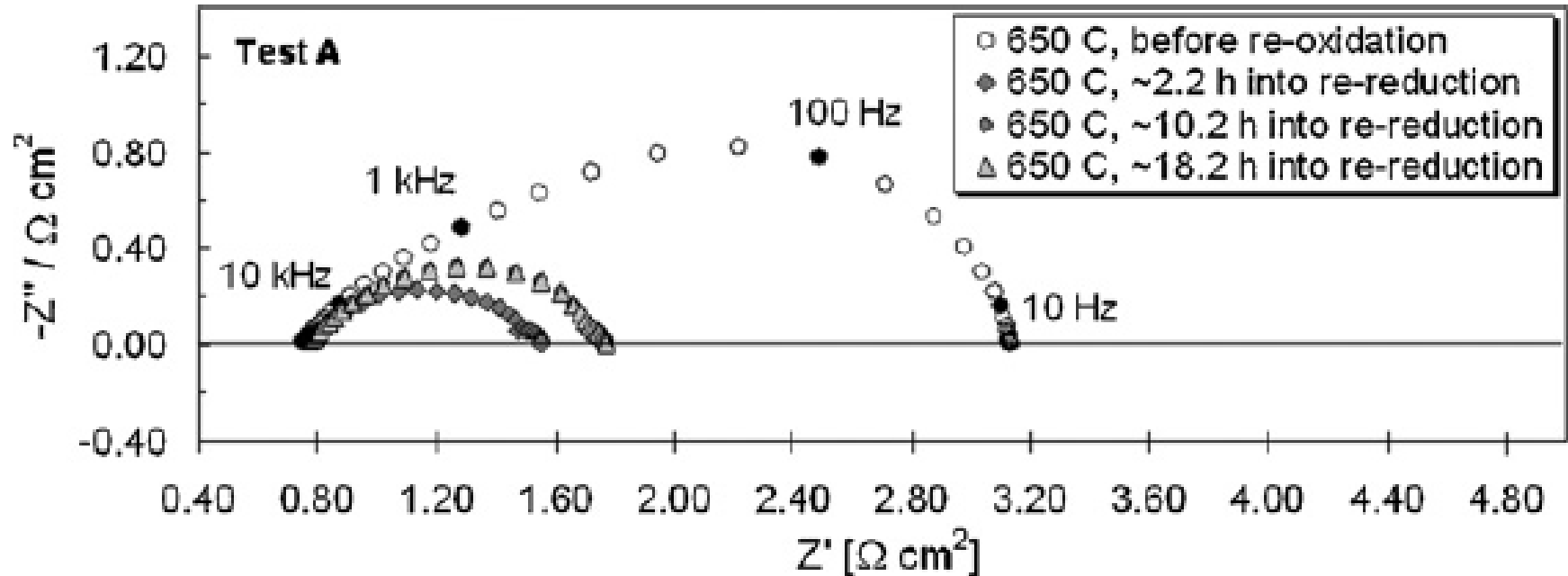


$$\Delta Z_{Ge\ xh} = \frac{R_{Ge\ xh}}{\sqrt{1 + \left(j\omega / \omega_{0\ xh} \right)^{n_{xh}}}} - \frac{R_{Ge\ 3h}}{\sqrt{1 + \left(j\omega / \omega_{0\ 3h} \right)^{n_{3h}}}}$$

Conclusion on impedance model

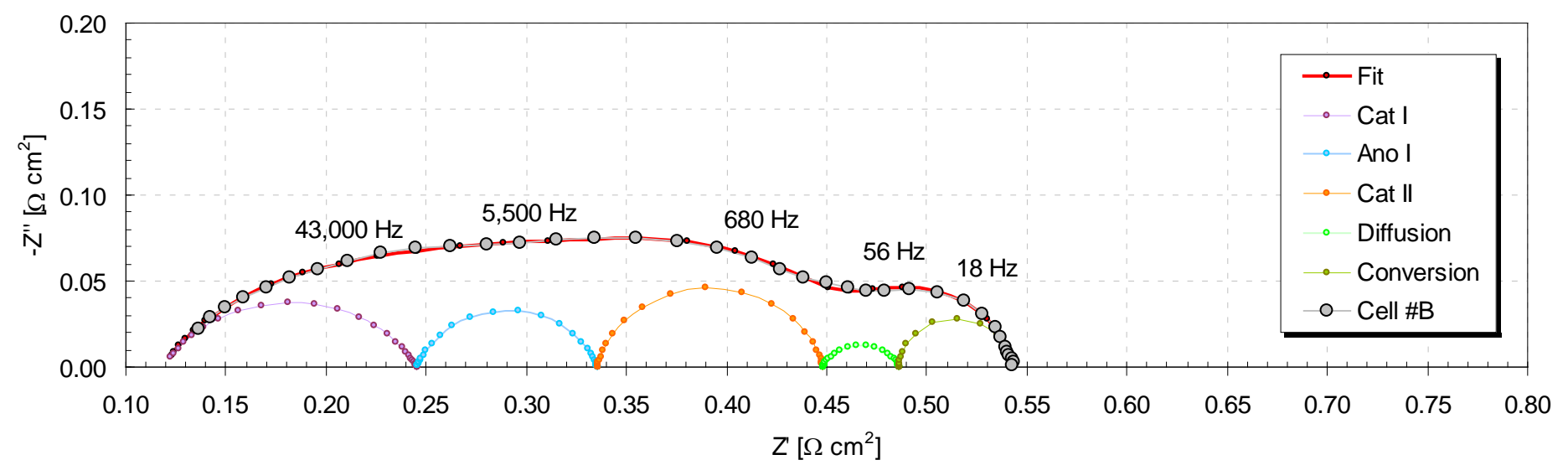
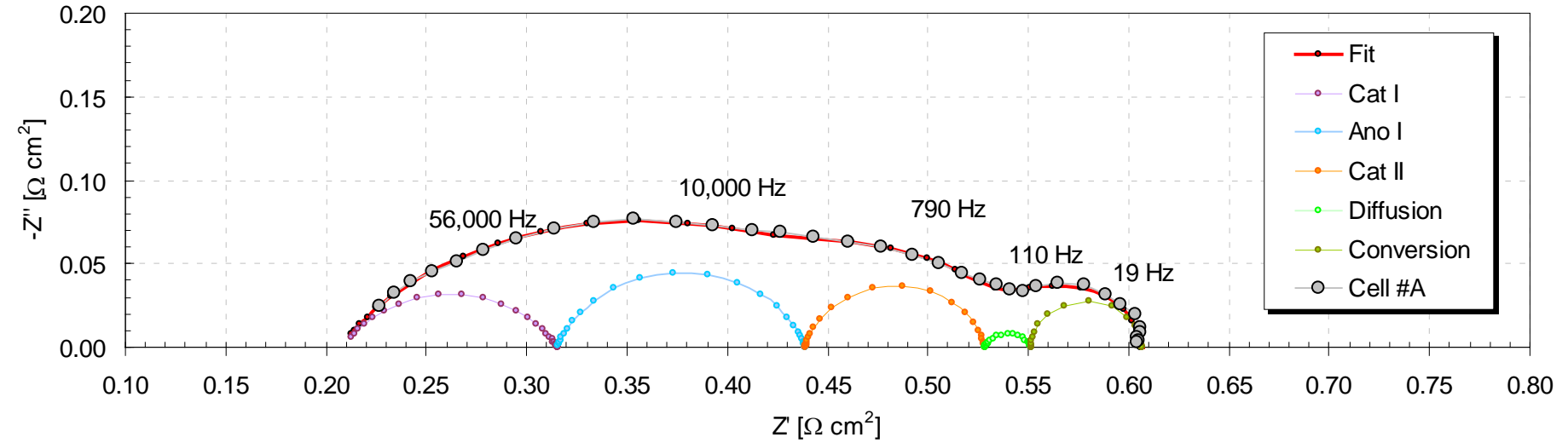
- Analysis of differences in impedance spectra before and after an operation period can be used to determine how much the electrodes are affected by the operation period
- Modeling of differences in impedance spectra may reduce the number of model variables. This can enhance the modeling accuracy
- A Gerischer impedance element model the Solid Oxide Fuel Cell Ni/YSZ-electrode impedance more precise than a (RQ)-element

Polarisation resistance

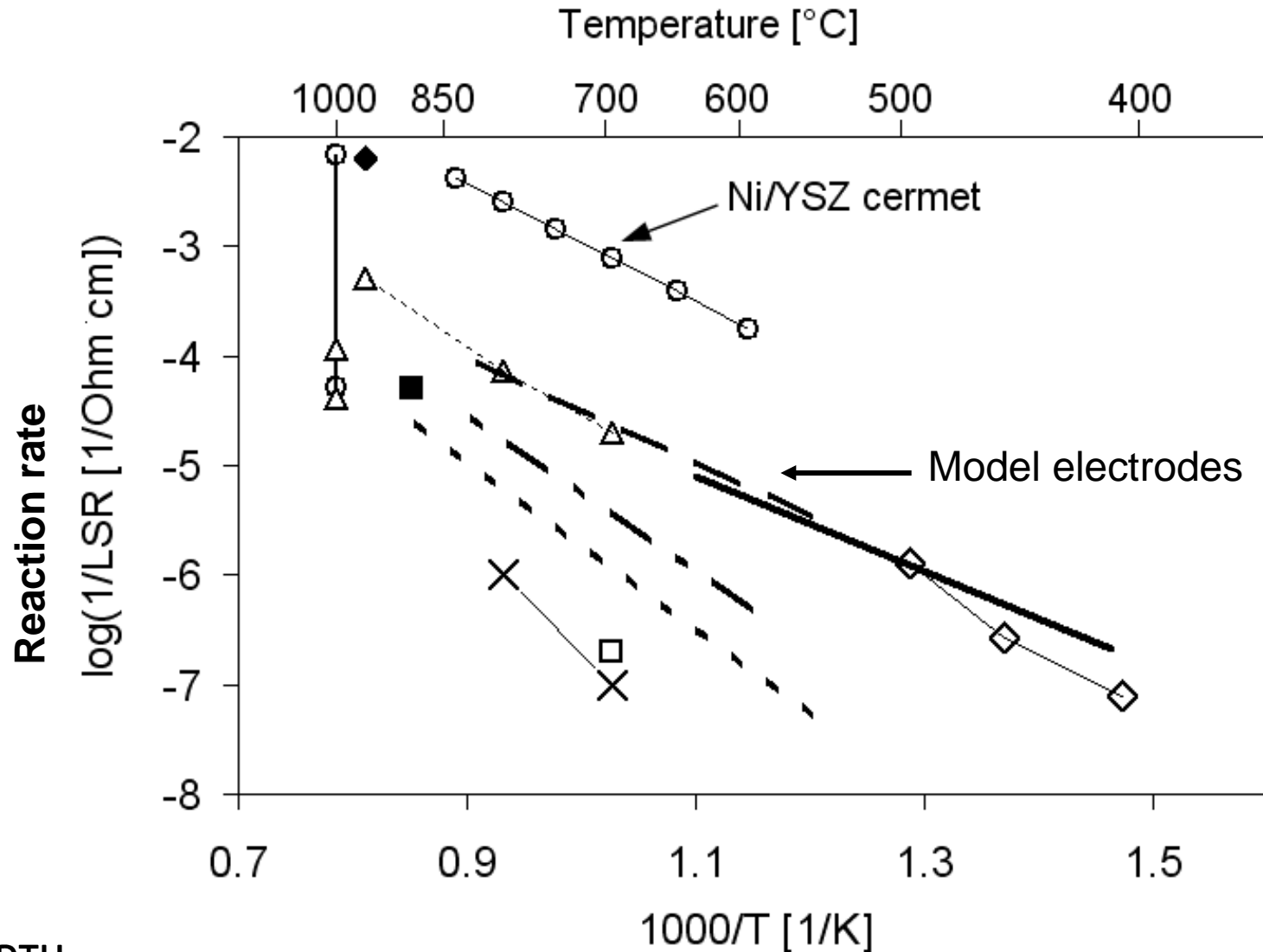


Nyquist plots of impedance spectra obtained for a symmetric cell (Ni-ScYZ/ScYZ/Ni-ScYZ) as a function of re-reduction time at 650 °C after a re-oxidation period of 12 h at the same nominal temperature. From Pihlatie et al., J. Power Sources **193** (2009) 322.

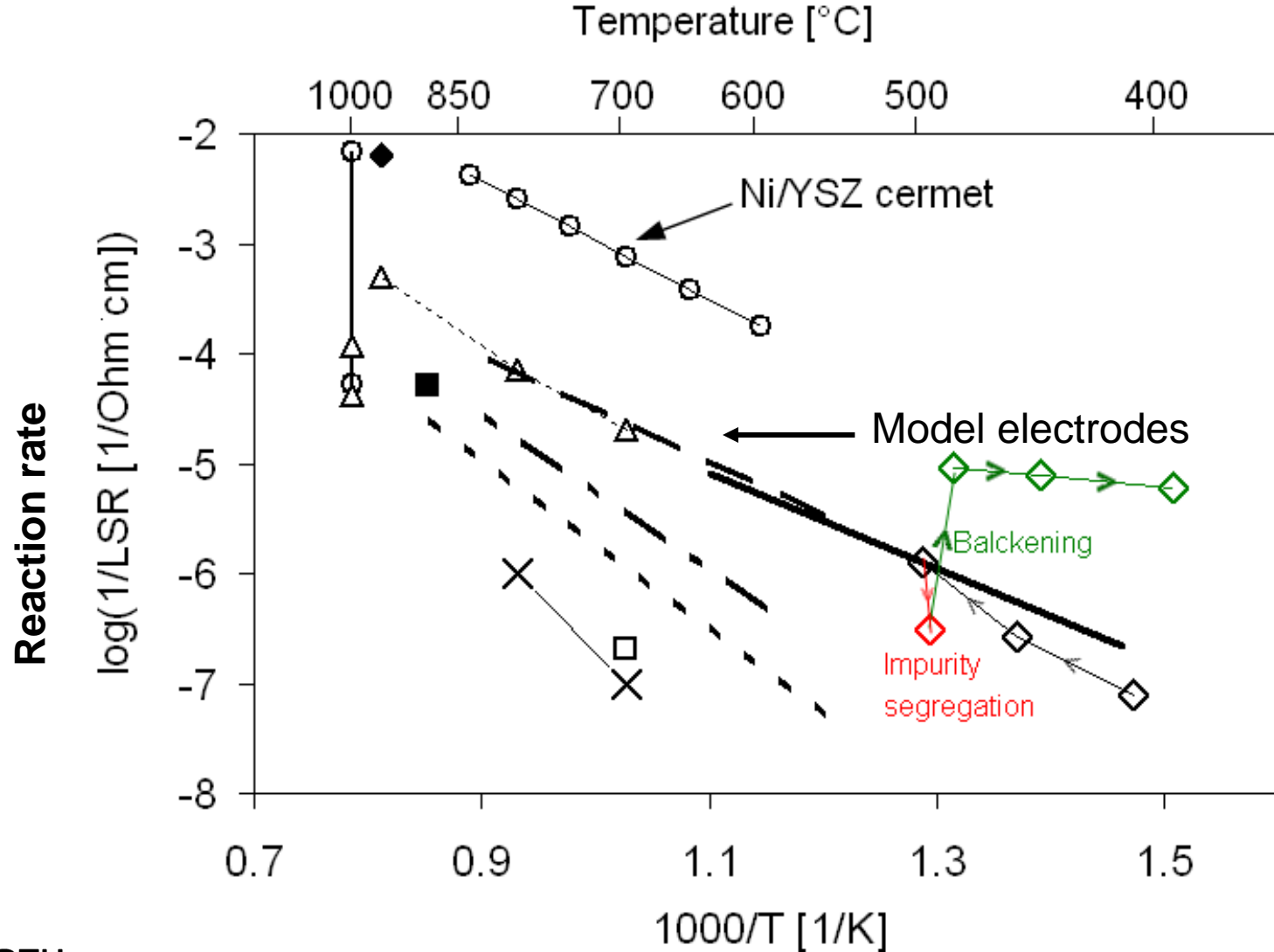
Electrochemical model validation: 750°C, 20% H₂O, air



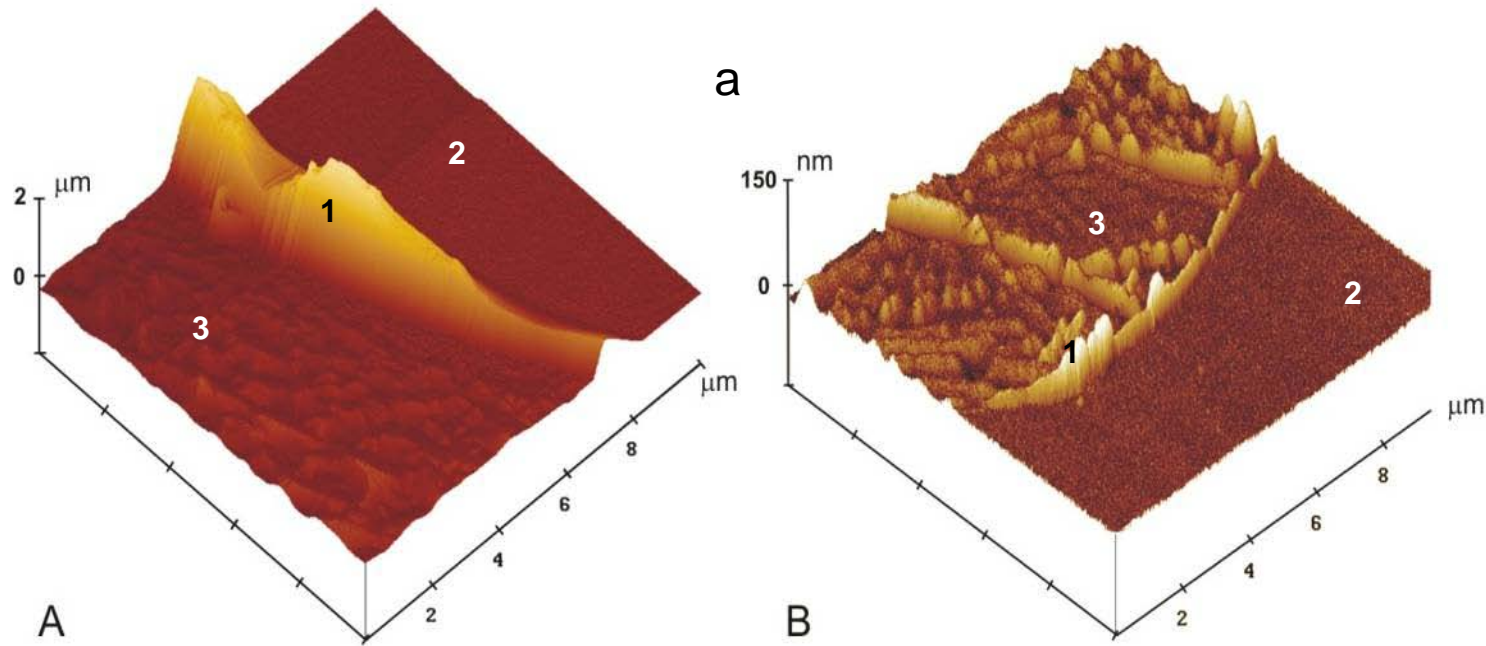
Effect of materials impurities



Effect of materials impurity



Effect of materials impurity



Atomic force microscope pictures of: rim ridge (1) of impurity phases at TPB of Ni point electrodes on a YSZ after ca. 1 week test and removal Ni. A. “Impure” Ni = 99.8% Ni. B. “Pure” Ni = 99.99% Ni. (2) the YSZ surface exposed to the H₂, and (3) the YSZ side of the YSZ-Ni. After K.V. Hansen, J. Electrochem. Soc., 151 (2004) A1436

Reaction mechanisms and sites



Concluding remarks

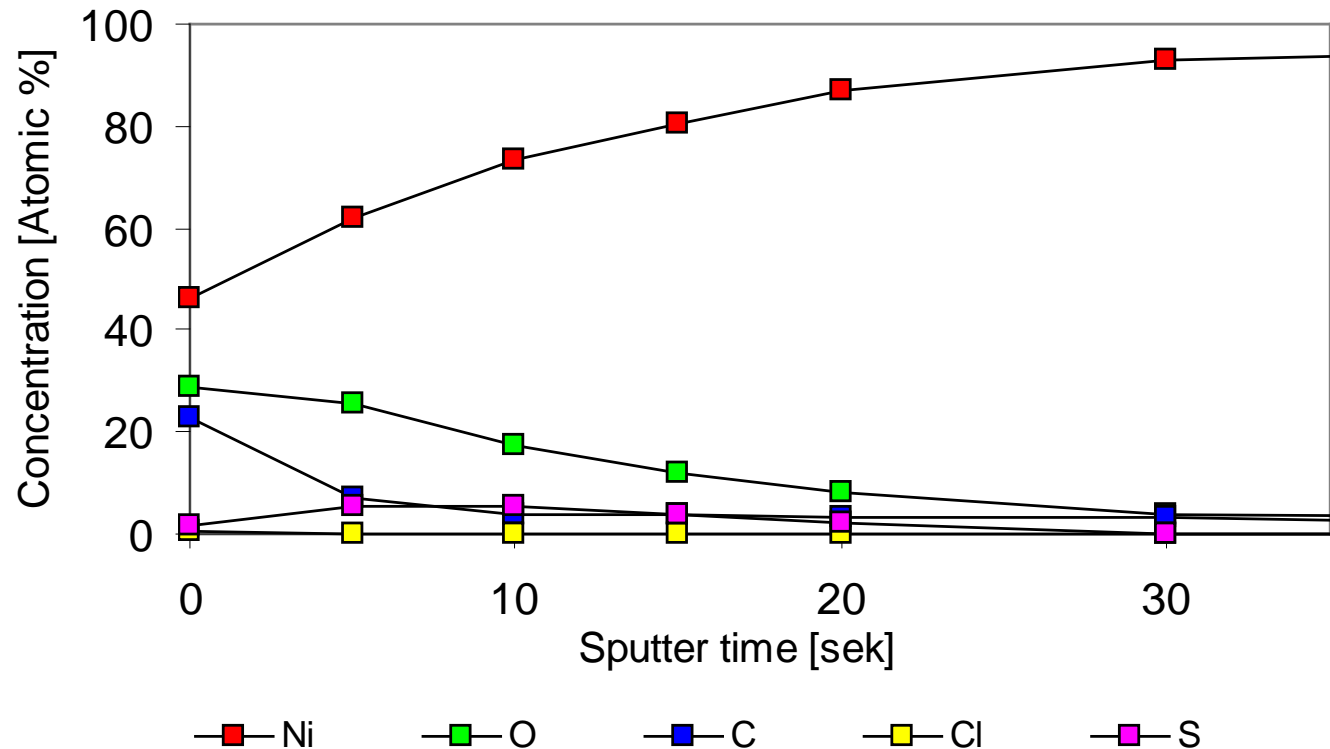
- **Some combination of the a) and d) pictures is probably the best basis for a description of the Ni-YSZ electrode**
- **There is no direct experimental evidences that the $i - V$ curves of the Ni-YSZ electrode is described by a simple Butler - Volmer equation**
- **The impedance of the main contribution seems be best described by a Gerischer impedance**
- **Can the resistance (i/V) of a Gerischer element be described by a Butter - Volmer expression? Probably no.**

Thank you for your attention

Ni surface

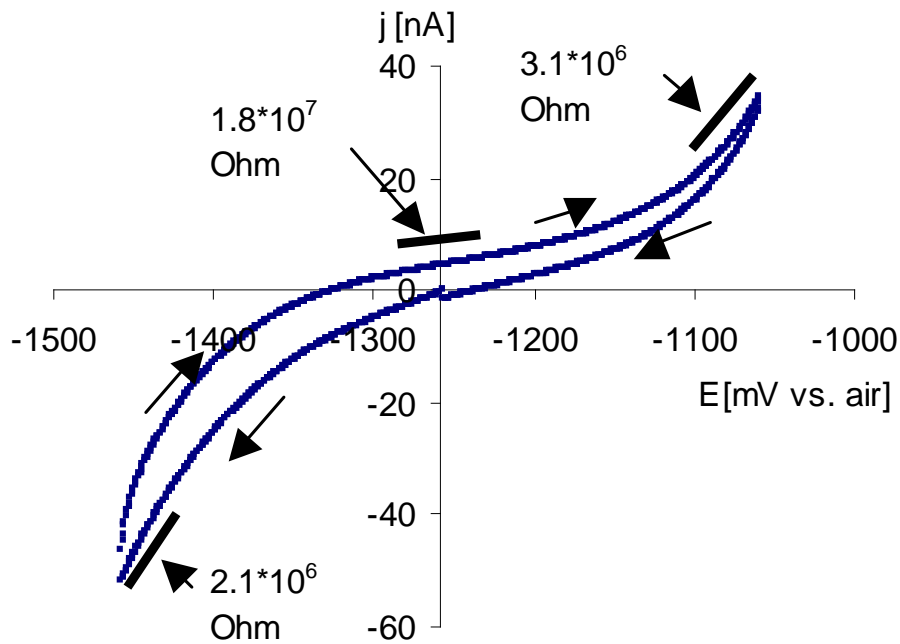
AES sputter profile on Ni-wire (1000°C, 8 days 9%H₂/N₂)

Depth profiling using AES



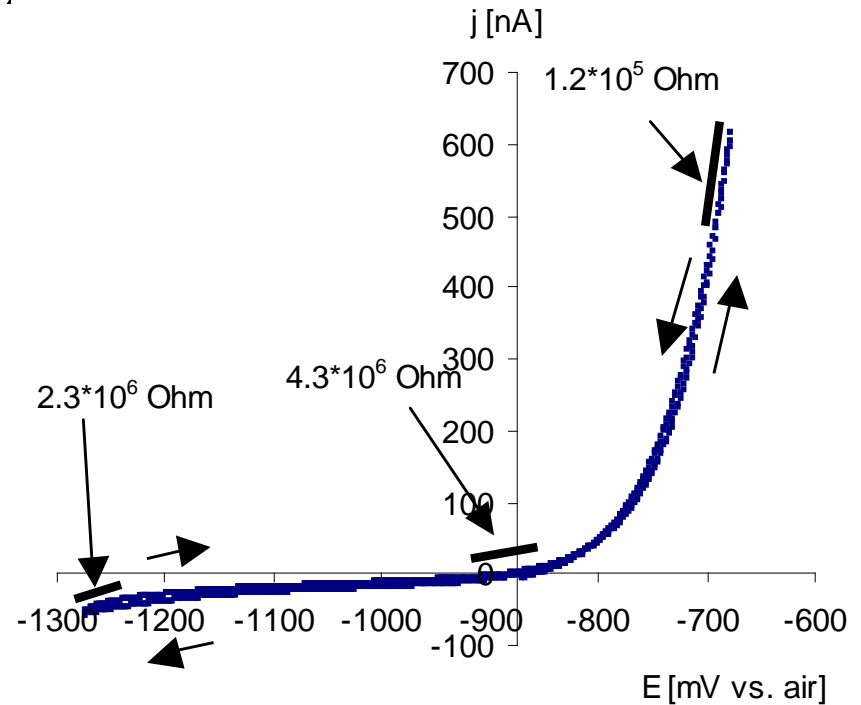
Ni Point Electrode

H₂/H₂O



Potential sweep (5 mV/s) at
700°C, H₂ = 99.9%, H₂O = 0.1%,

$\mathcal{E}_0 = -1259$ mV vs. air



Potential sweep (5 mV/s) at
700°C, H₂ = 2%, H₂O = 19.7%,

$\mathcal{E}_0 = -876$ mV vs. air

J. Høgh, K.V. Hansen and M. Mogensen, in *Proc. 26th Risø Internat. Symp. Mat. Science*, S. Linderoth et al., Editors, p. 235, Risø National Laboratory, Roskilde, Denmark (2005).

