Electrochemical Characterization of Silver Gas Diffusion Electrodes during Oxygen Reduction in Alkaline Solution

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Presentation outline

- Introduction and motivation
    - Examples of porous electrodes and some technical applications of the ORR in alkaline solution

        ✓Metal-(Li)-Air Battery
        ✓Cathode of the **A**lkaline **F**uel **C**ell (AFC)
        ✓ Silver-based gas-diffusion electrodes for chlor-alkali electrolysis with **o**xygen **d**epolarized **c**athodes (ODC)
        ✓ Electrode production techniques at the DLR

- Theory and model of the electrochemical impedance spectra (EIS) of porous electrodes

- Evaluation of EIS measured during oxygen reduction at Ag based GDE in 10 M NaOH at 80°C

- Conclusion

Motivation

Why Li-air batteries?

- Highest theoretical specific energy density (11.425 Wh/kg). Cathodic reactant, O_2 from ambient air, does not have to be stored

- Environmental friendliness

- Higher safety than Li-ion batteries

  (only one of the reactants contained in the battery)

- Potentially longer cycle and shelf lives

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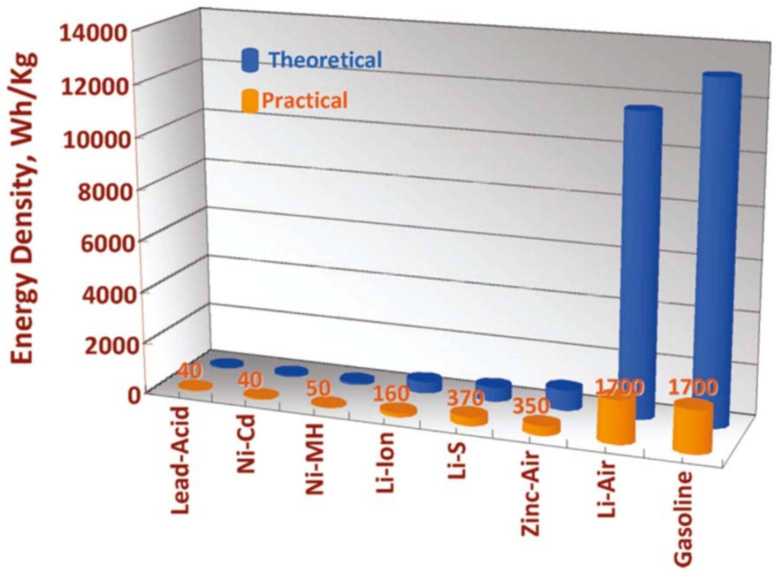
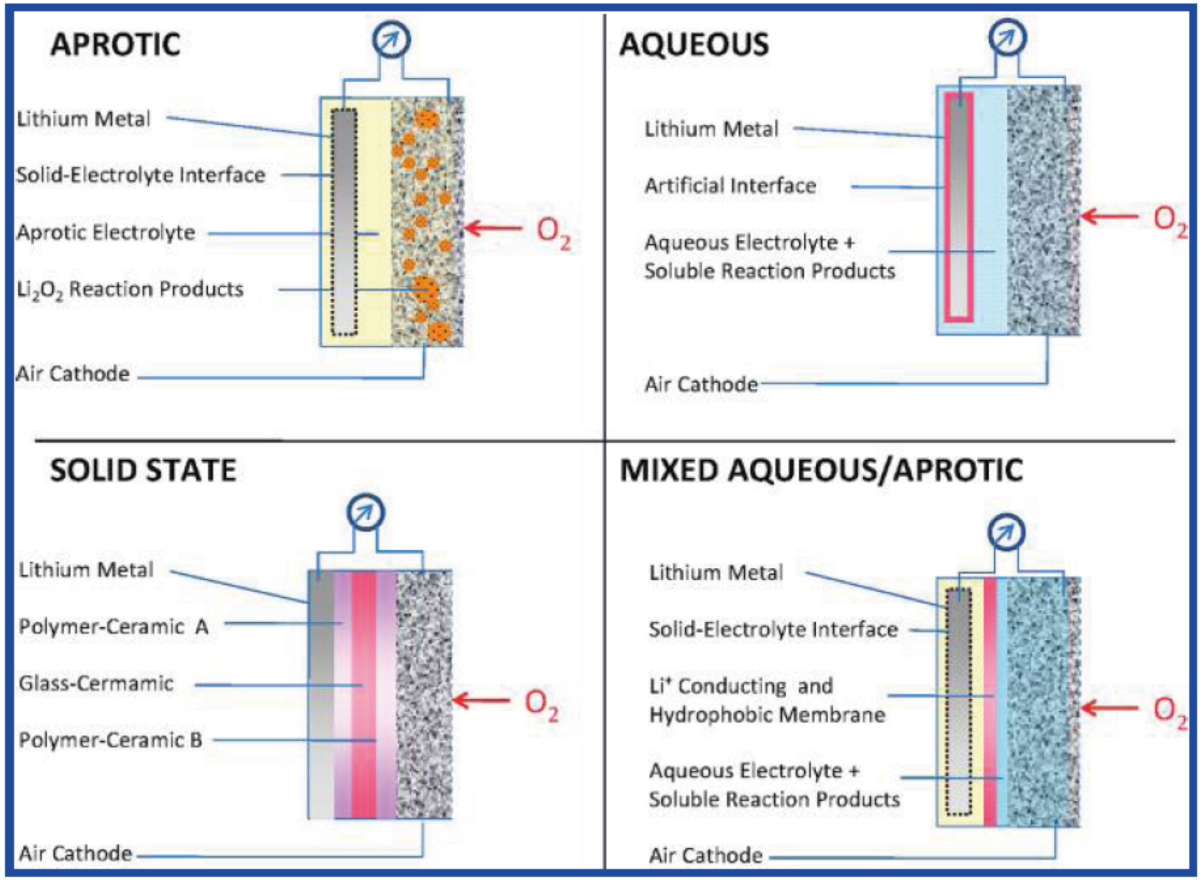


G. Girishkumar et al., J. Phys. Chem. Lett., **2010**, 1, 2193-2203

Architectures of Li-Air Batteries



Non-aqueous electrolyte:

$2Li^+ + O_2 + 2e^- \rightleftarrows Li_2O_2$ E_{rev}= 2,959 V

$2Li^+ + 2e^- + (1/2)\ O_2 \rightleftarrows Li_2O$ E_{rev}= 2,913 V

Aqueous electrolyte:

$4Li + O_2 + 2H_2O \rightleftarrows 4LiOH$ (alkaline media) E_{rev}= 3,446 V

$4Li + O_2 + 4H^+ \rightleftarrows 2H_2O + 4Li^+$ (acidic media) E_{rev}= 4,274 V

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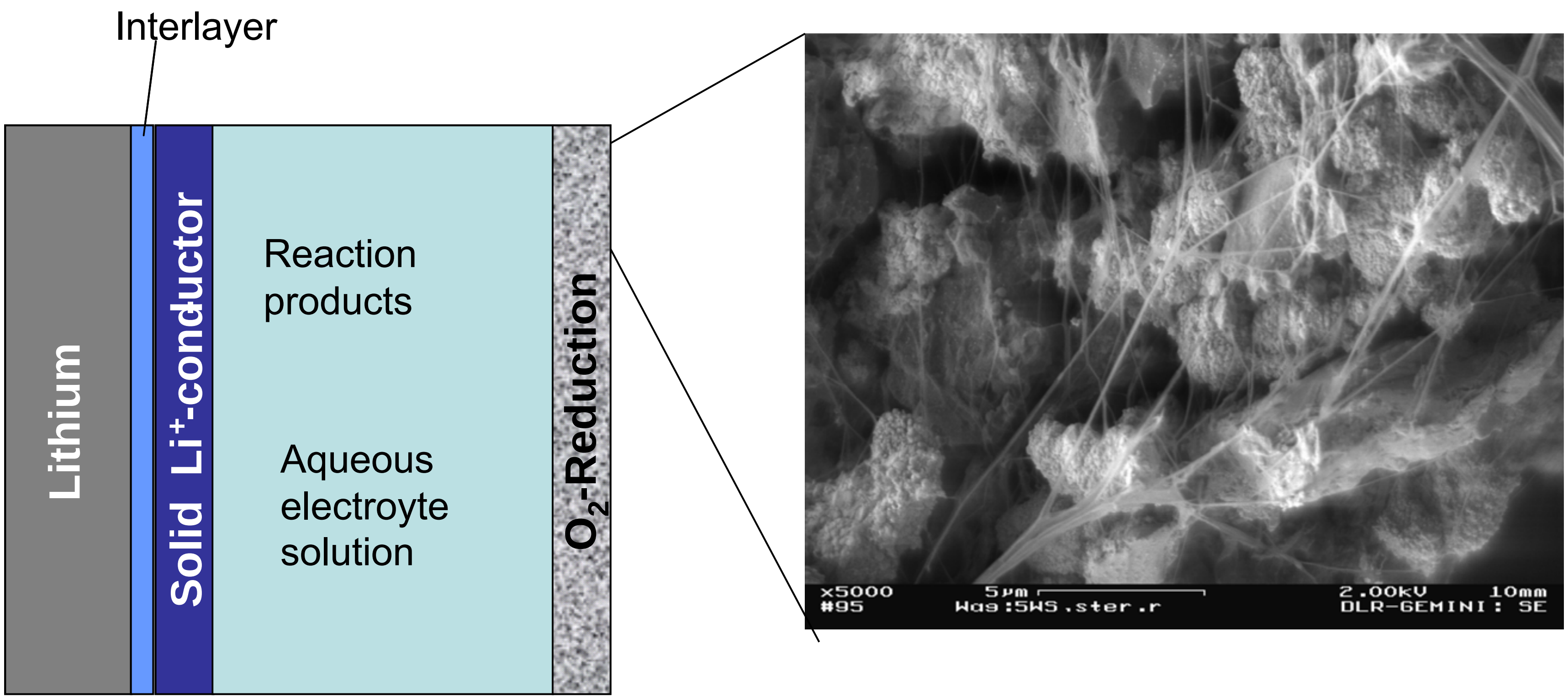
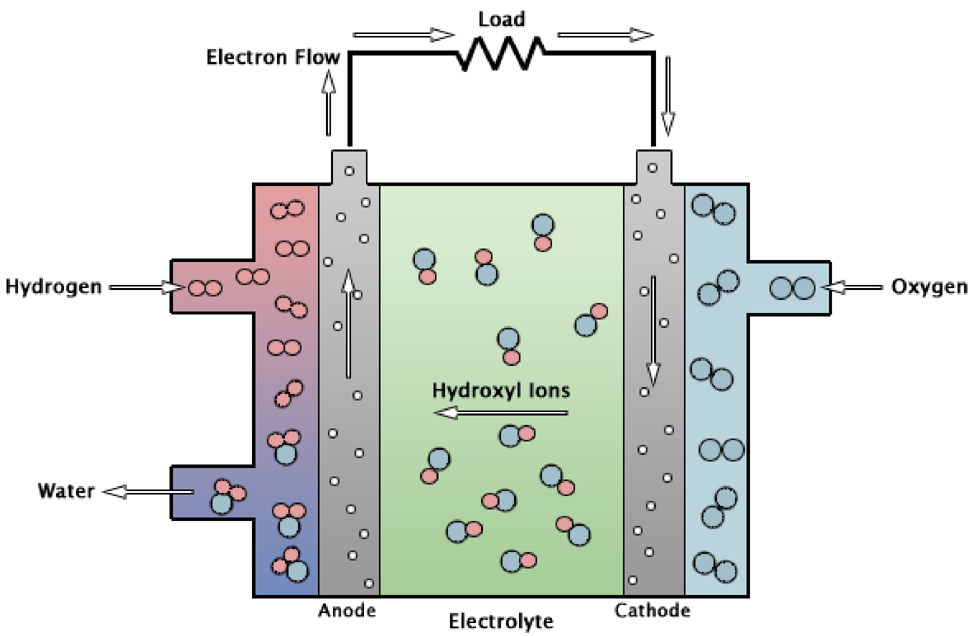
Schematic architecture of Lithium-air battery with aqueous alkaline electrolyte and GDE (OCR and OER)



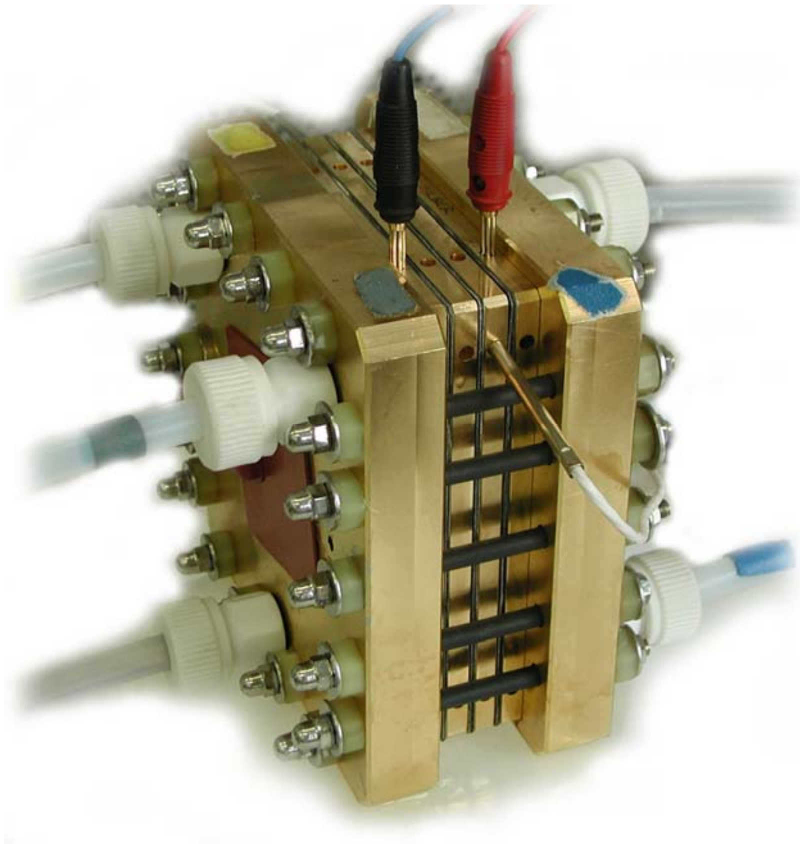
Reaction equation (alkaline electrolyte):

$4\ Li + O_2 + 2H_2O \leftrightarrow 4LiOH$; E = 3,45 V

Alkaline Fuel Cell (AFC) with Gas Diffusion Electrodes (Anode: Ni-GDE, Cathode: Ag-GDE)



Schematically representation of an AFC



DLR-Bipolar AFC stack

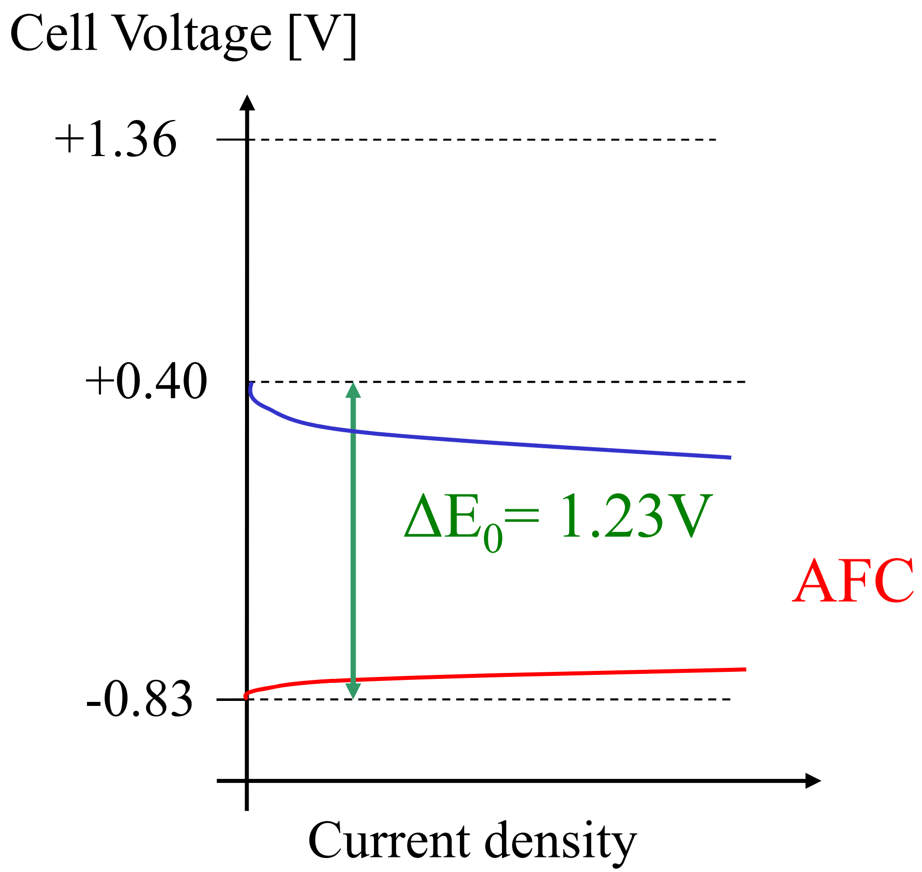
Schematically representation of cell voltage and potentials in an alkaline fuel cell, pH=14

Cathode with ORR

$O_2 + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$

Anode

$2\ H_2 + 4\ OH^- \rightarrow 4\ H_2O + 4\ e^-$



Cell voltage and potentials in an electrolyzer for chlorine production with ODC (Oxygen Depolarised Cathode)

Anode

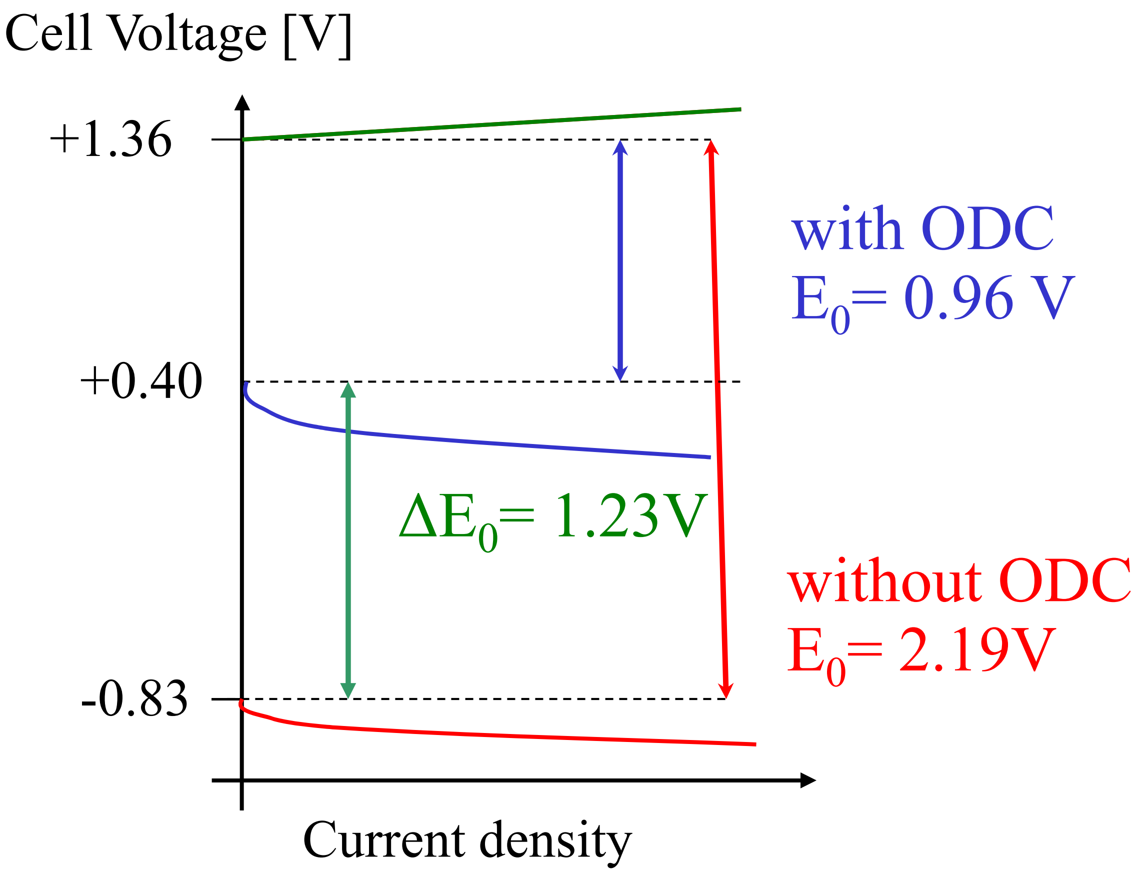
$4\,Cl^- \rightarrow 2\,\mathbf{Cl_2} + 4\,e^-$

Cathode with ORR

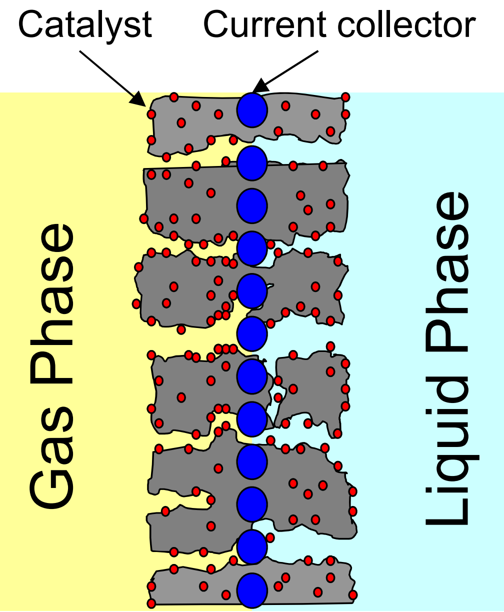
$\mathbf{O_2} + 2\,H_2O + 4\,e^- \rightarrow 4\,OH^-$

Cathode (conventional)

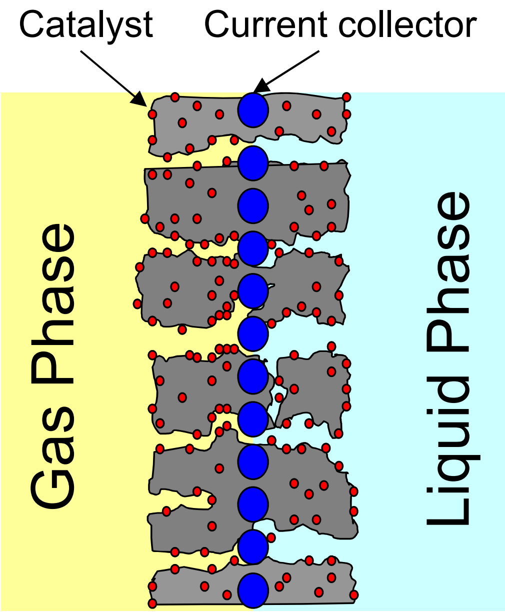
$4\,H_2O + 4\,e^- \rightarrow 4\,OH^- + 2\,\mathbf{H_2}$

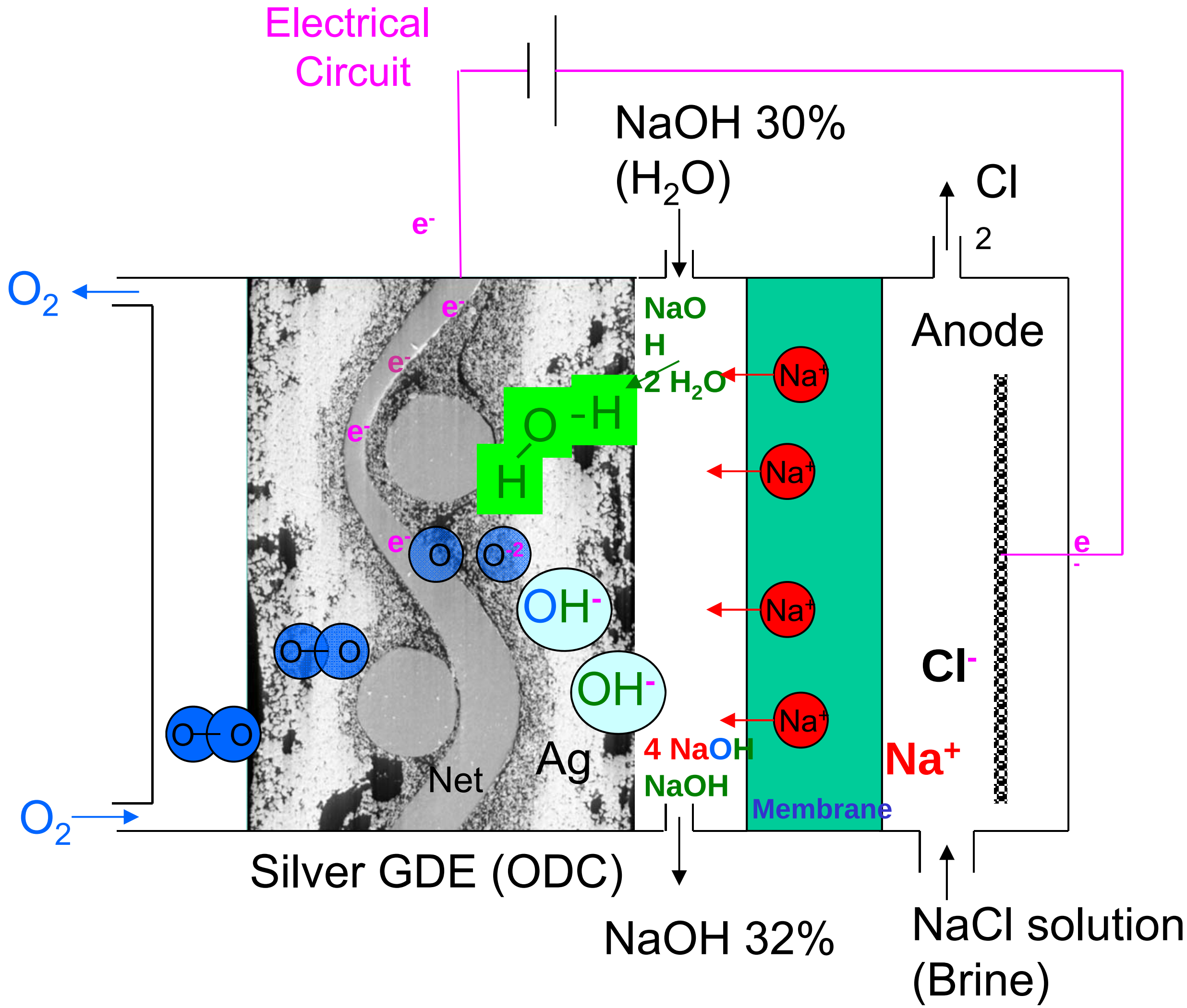


Schemtically representation of an electrolyzer for chlorine production with ODC (Oxygen Depolarised Cathode)



Schemtically representation of an electrolyzer for chlorine production with ODC (Oxygen Depolarised Cathode)





Chlorine production with ODC (Oxygen Depolarized Cathode)

Chlorine production unit with ODC technique at Bayer in Ürdingen (20,000 t/y) since May 2011

European Chlorine Production 2012 : 12.6 mio. t

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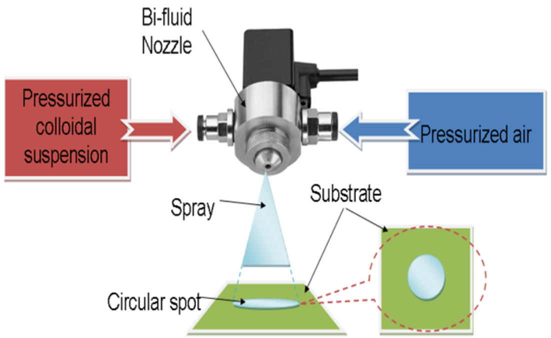
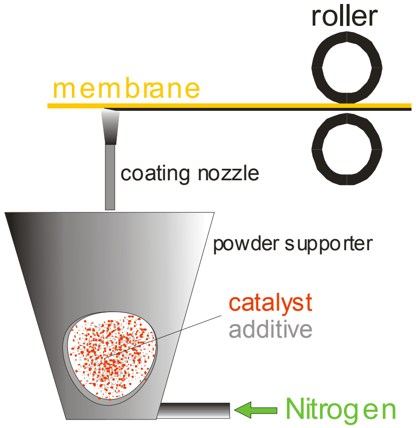
Overview of production techniques for electrodes at DLR-TT

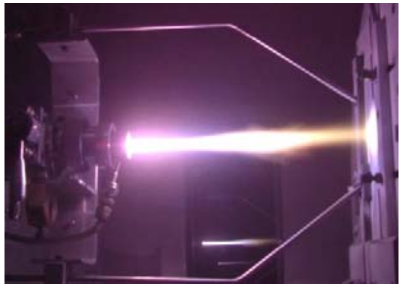
Small-scale production | Mid-scale production | Large-scale production



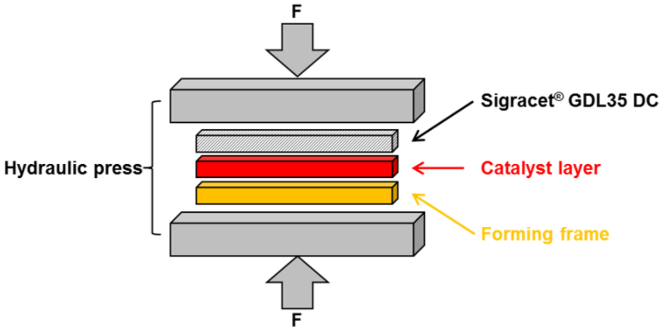
Colloidal Suspension Spraying



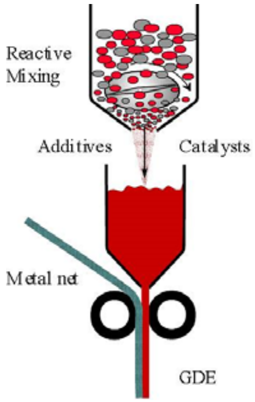
Dry Powder Spraying



Vacuum or Atmospheric Plasma Spraying



Pressing



Reactive Rolling and Mixing (RMR)

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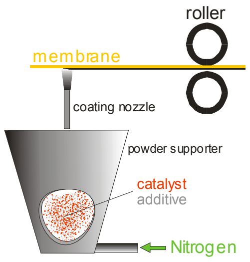
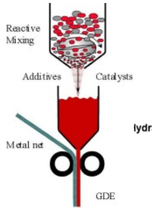
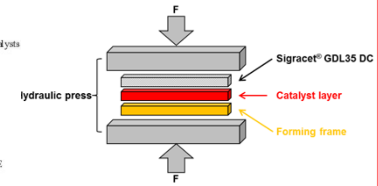
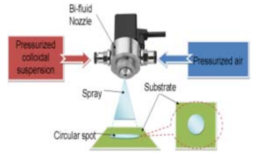
Overview of production techniques for electrodes at DLR-TT



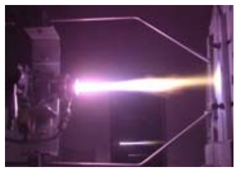


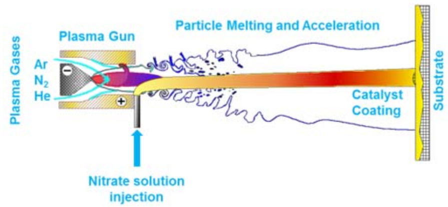


+ Solvent-free production techniques
+ Almost all kind of catalysts and conductive agents can be processed
+ Possible wide-range electrode thickness
- Production technique dependend from for example density or particle size
- Processing at room temperature



+ Very thin layers
- Processing at room temperature

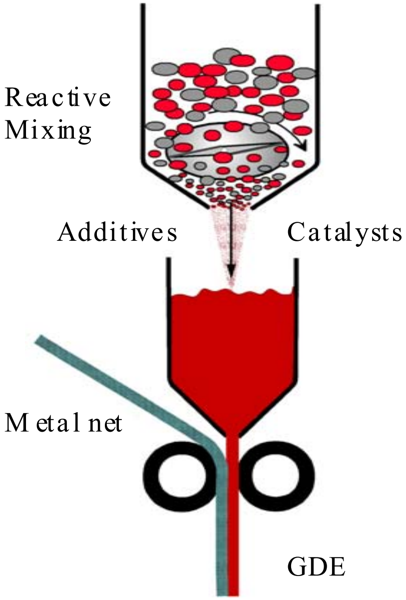


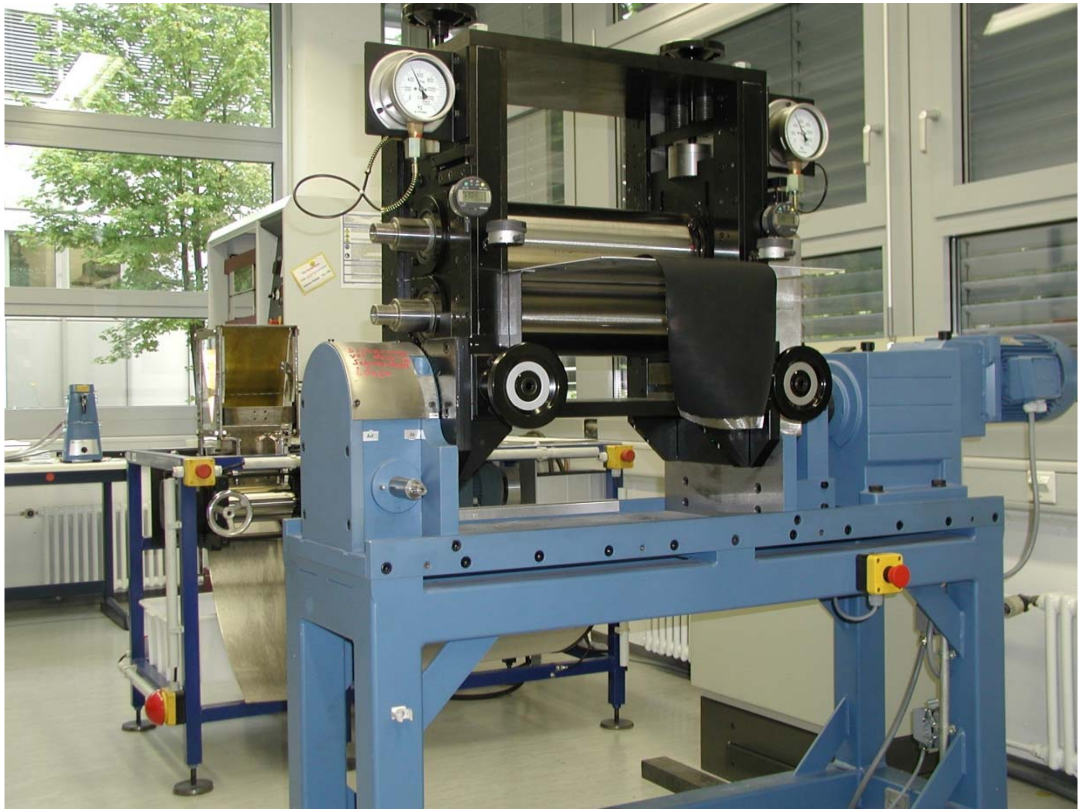


+ Solvent-free production techniques
+ Catalysts can be sythesized from nitrate solutions
+ Metal substrates can be coated
- Heat resistant materials required

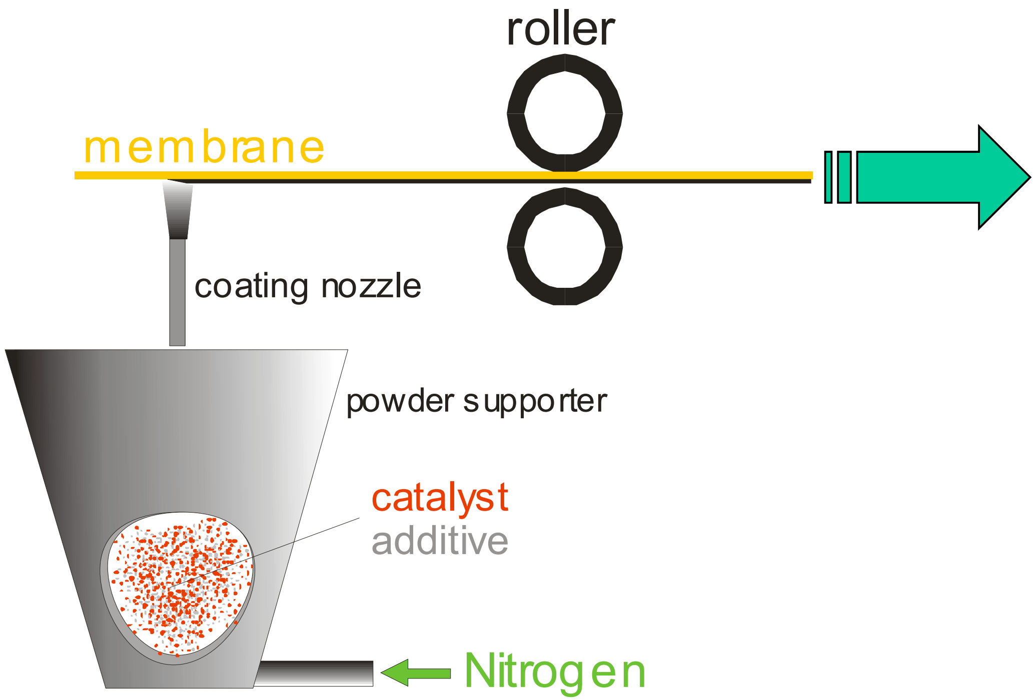
Production Techniques

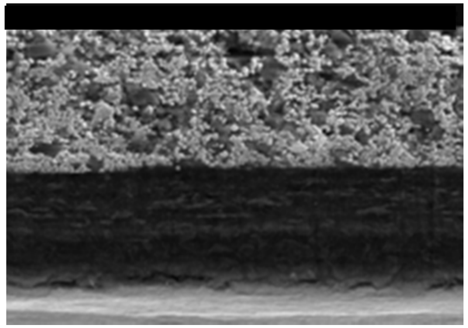
-Dry Spraying Technique
-Wet Spraying Techniquen
- Reactive Mixing
and Rolling (RMR)
-Screen printing
-…





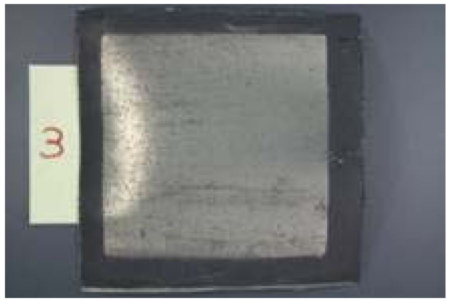
Dry Powder Spraying Technique





RMR (Substrat)

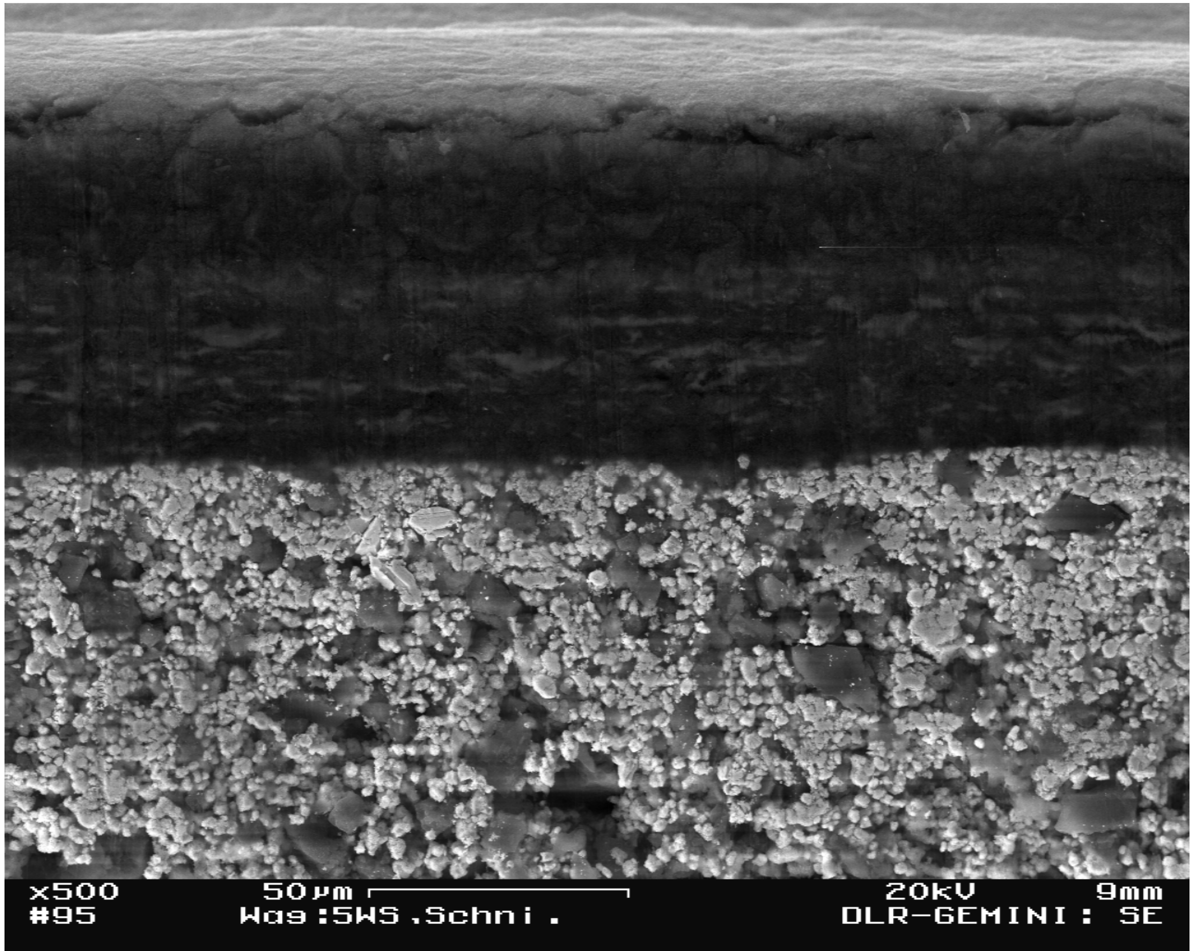
Dry sprayed layer



Top view

Multi-layer Gas Diffusion Electrodes

with different porous layers

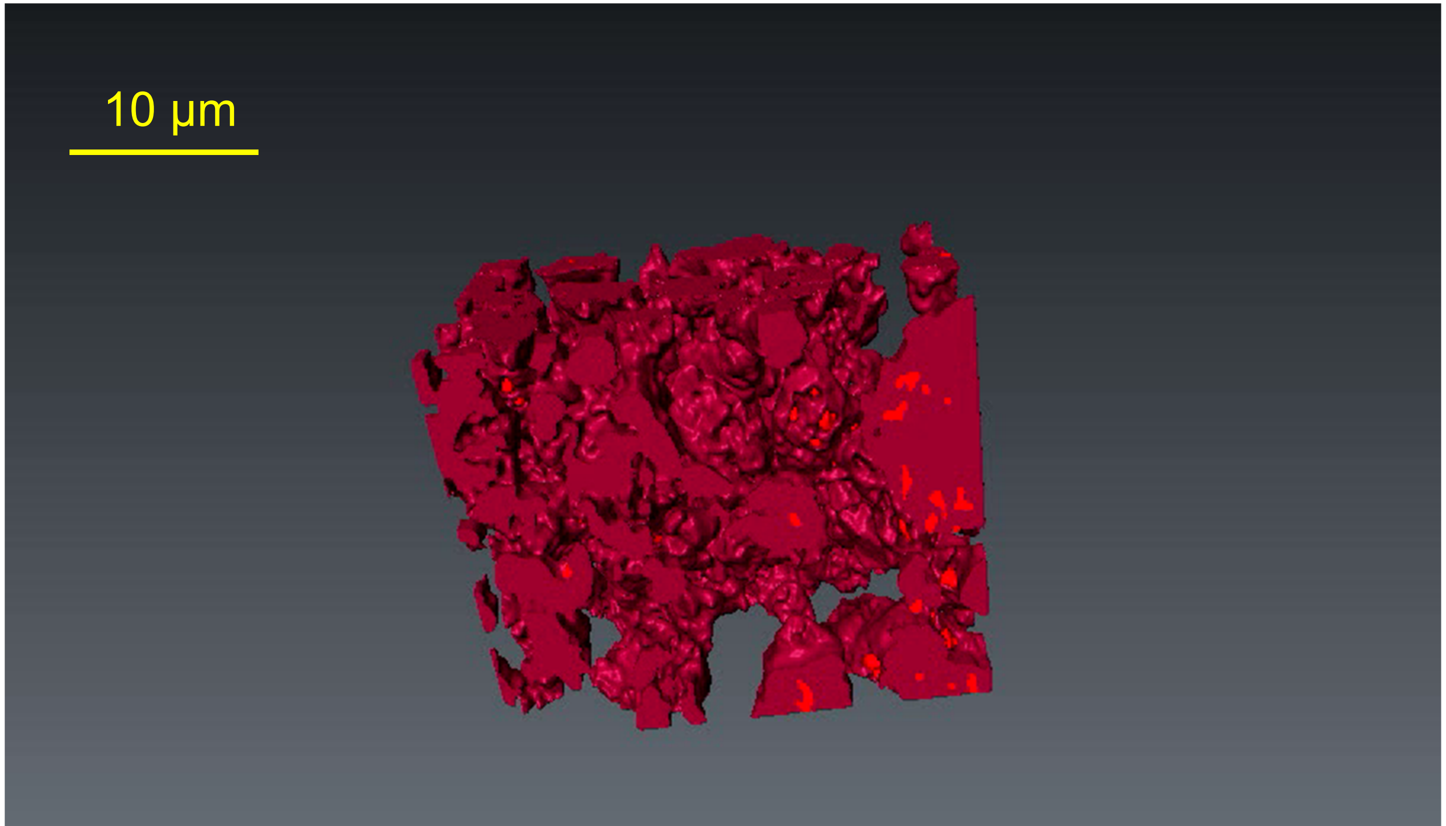


Dry sprayed
C/PTFE

Reactive Mixing
and Rolling
Ag-PTFE

N. Wagner, T. Kaz, DE 101 12 232 A1, 2002

3D reconstruction (TEM+FIB) of Ag-PTFE based Gas Diffusion Electrode



P. Balasubramanian, S. Eswara Moorthy, J. Bernhard, U. Kaiser, Uni Ulm (unpublished result).

3D reconstruction of CT pictures of the reduced Ag-GDE in the xz-plane

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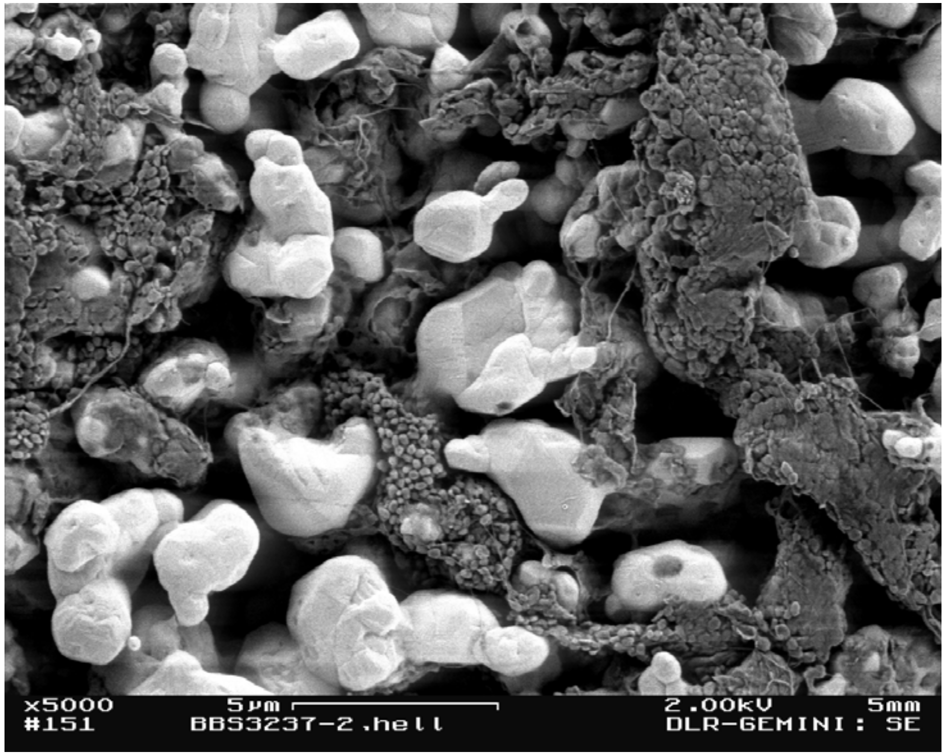
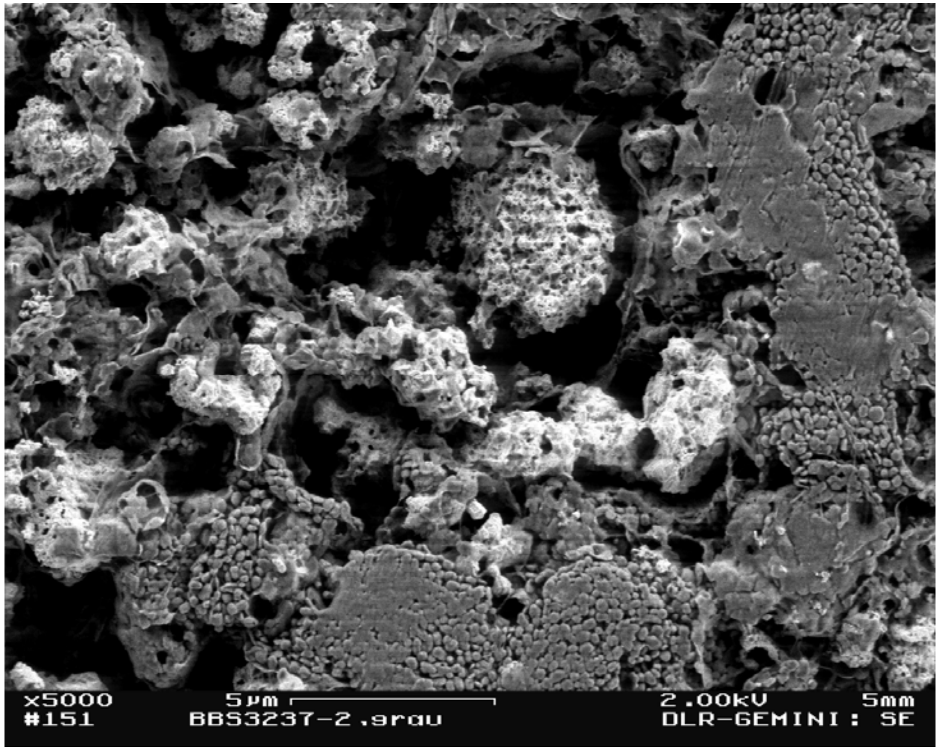
SEM pictures of Ag-GDE, produced by the RMR technique (Ag_2O+PTFE)



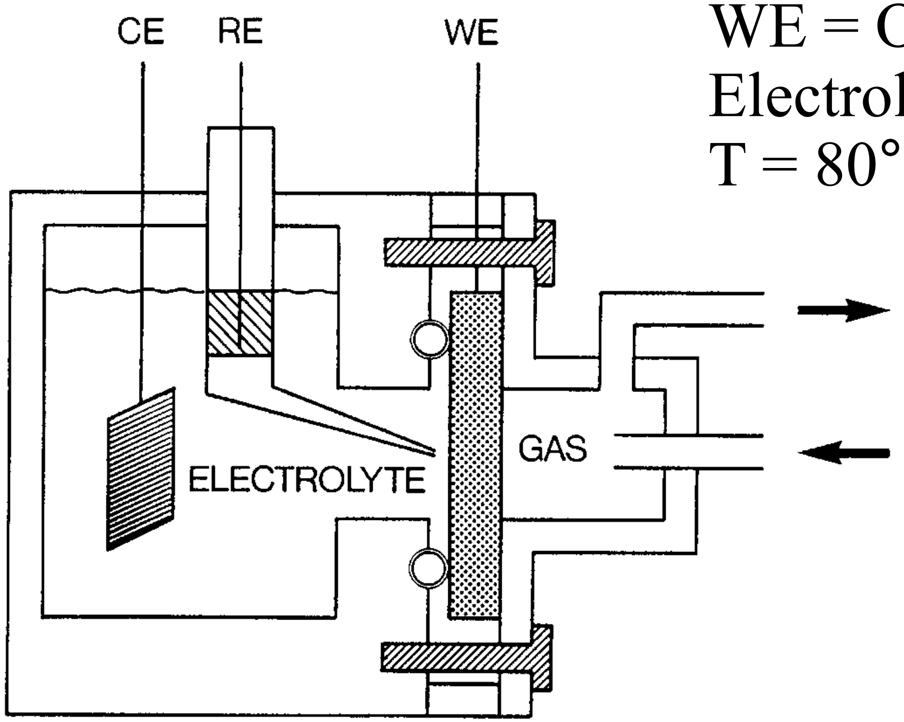
Ag-GDE, unused part



Ag-GDE, used

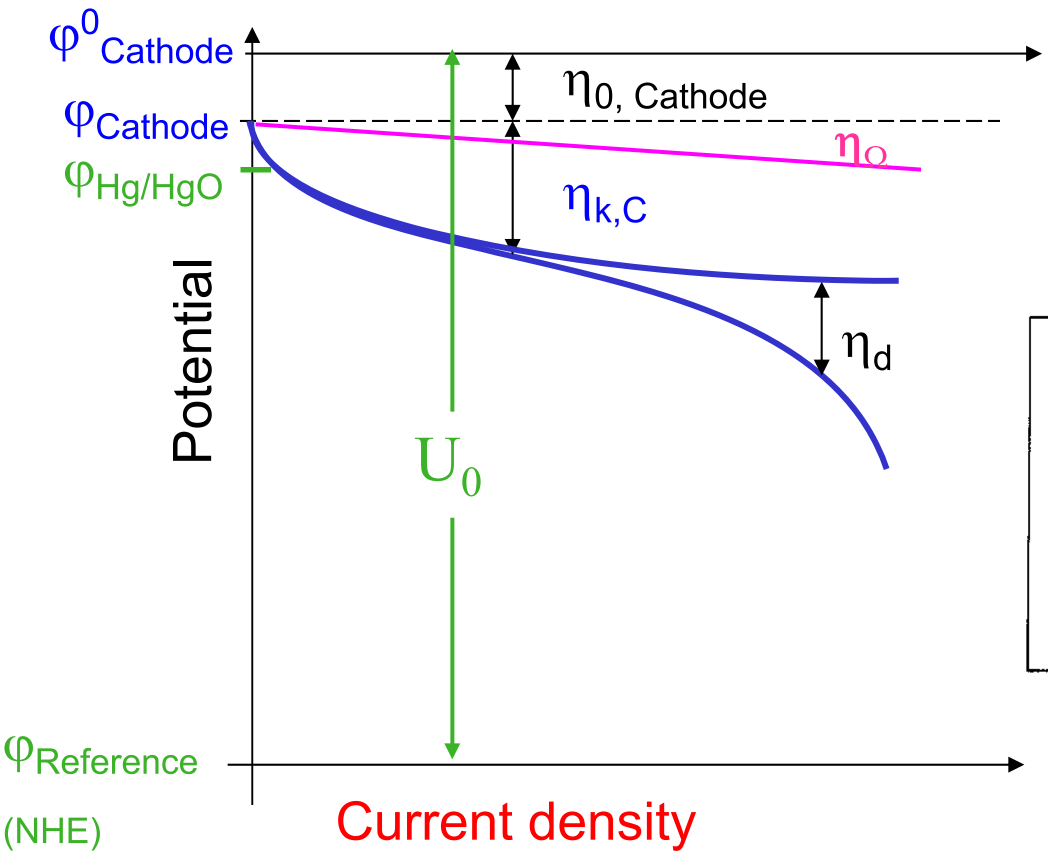
Schematically representation of measuring cell and experimental conditions

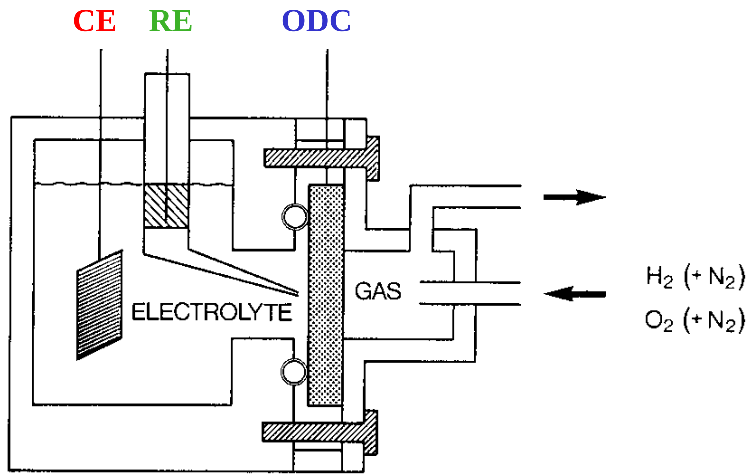
CE = Pt or Ni
RE = Hg/HgO or Hydroflex®
WE = ODC
Electrolyte = MOH (M: Li, K, Na)
T = 80°C (60, 40 and 20°C)



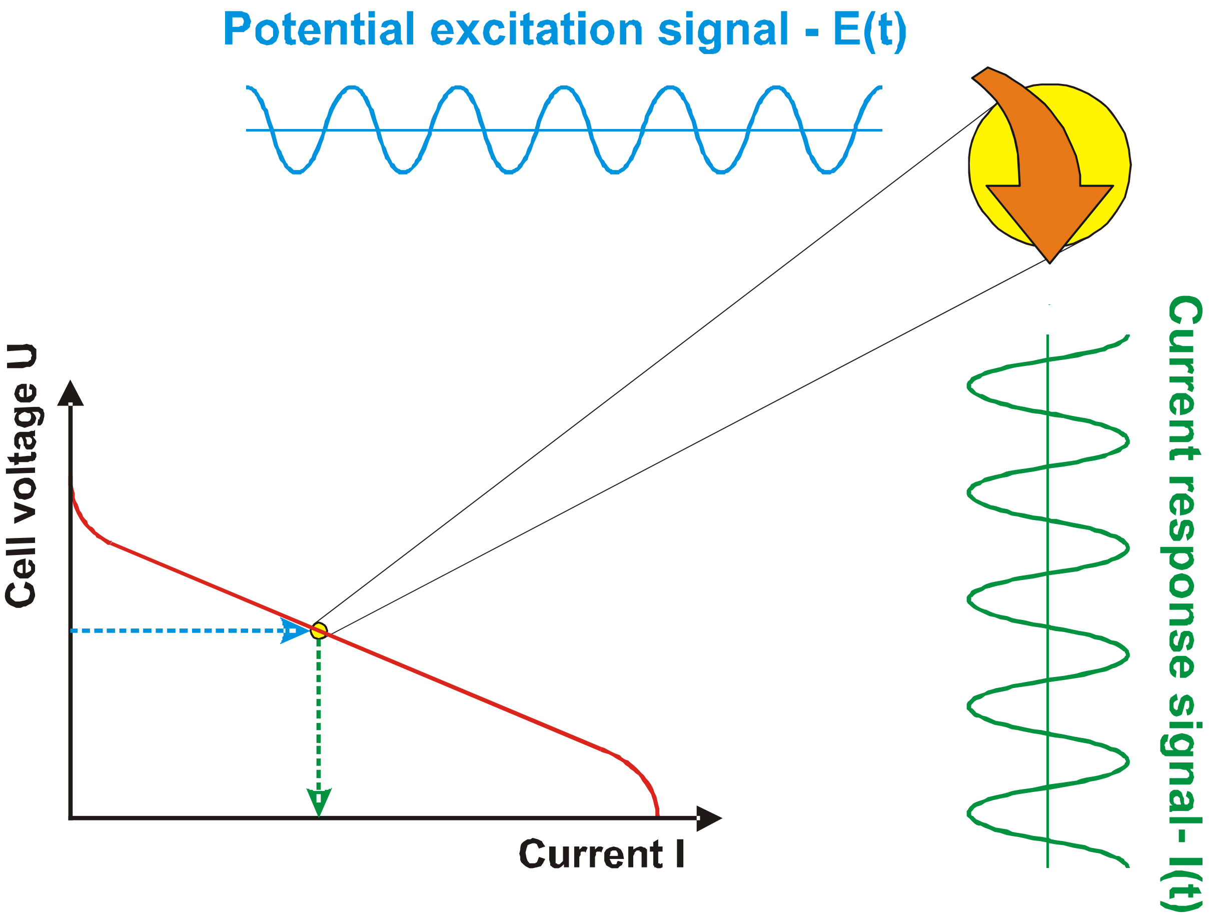
O_2
O_2-mixtures with
N_2 or He

Current density / potential characteristic

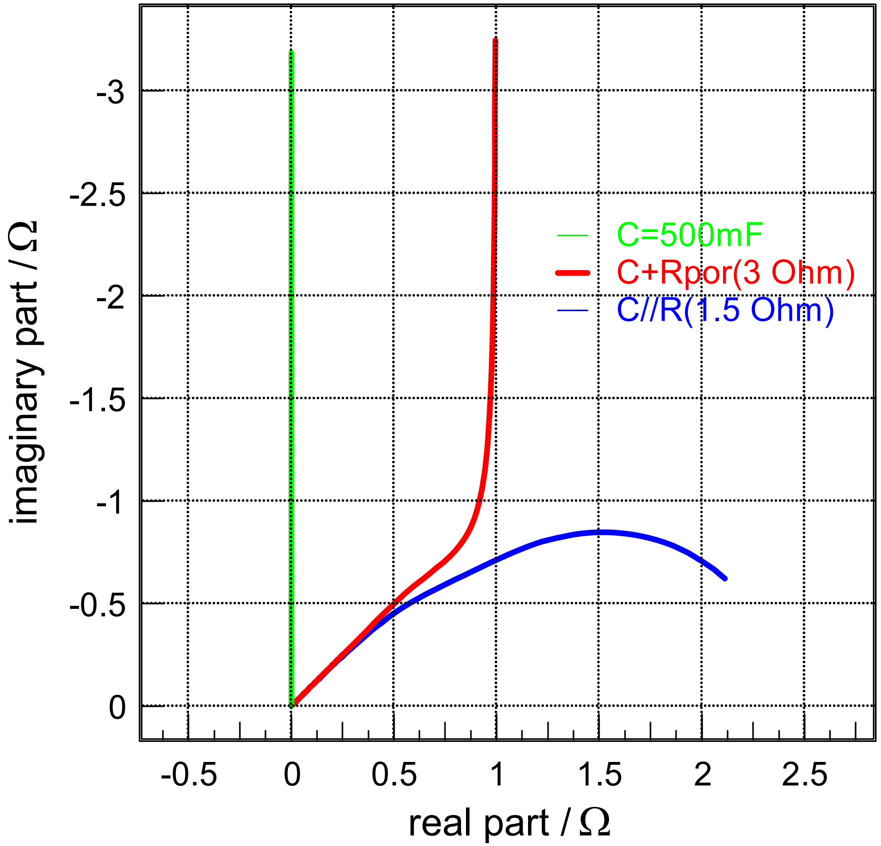


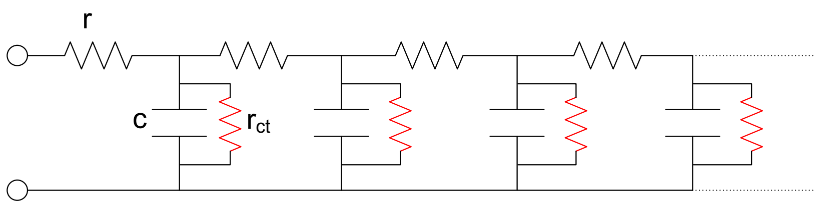


Electrochemical Impedance Spectroscopy



Nyquist representation of porous electrode impedance with faradaic impedance element



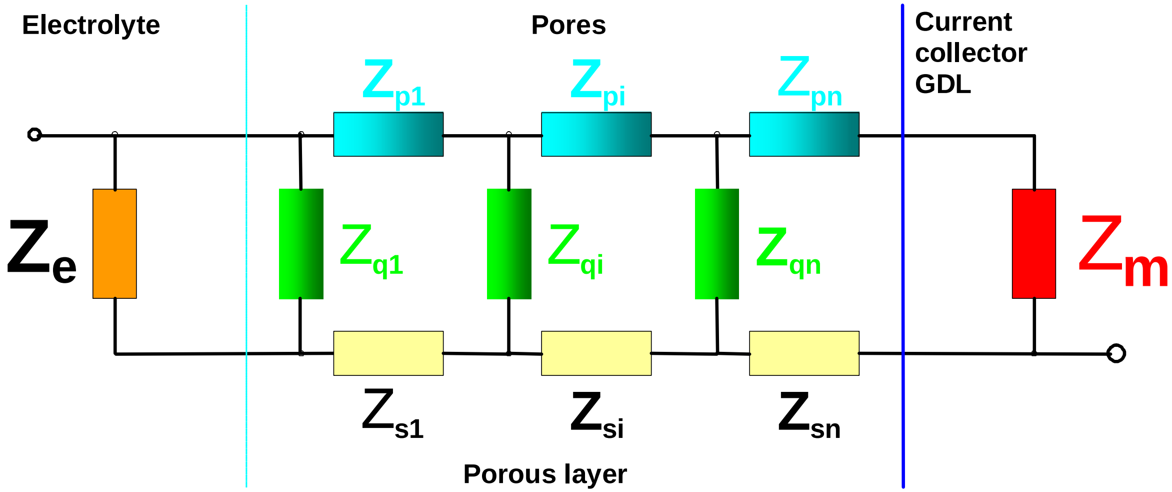


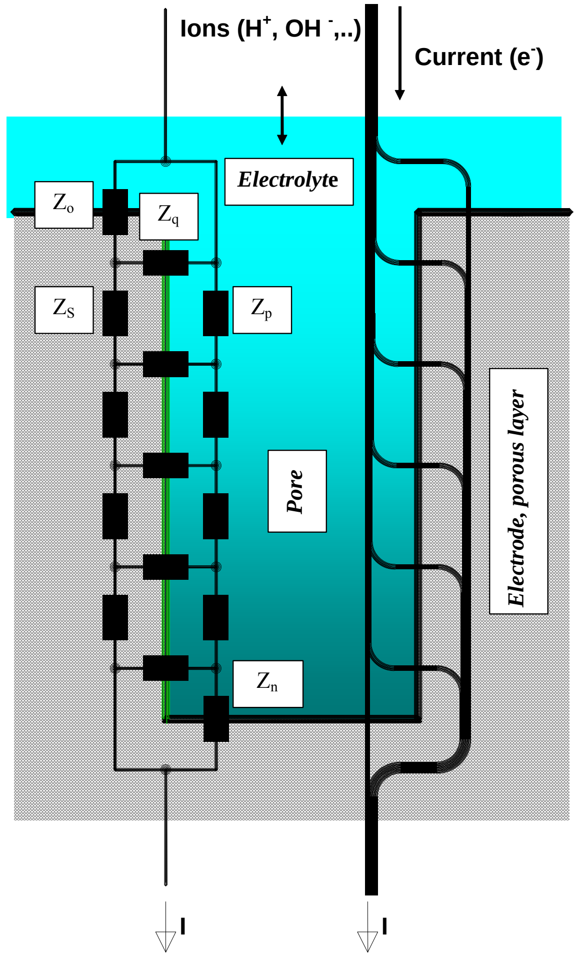
$r = 3\ \Omega$

$c = 500\ \text{mF}$

$r_{ct} = 1.5\ \Omega$

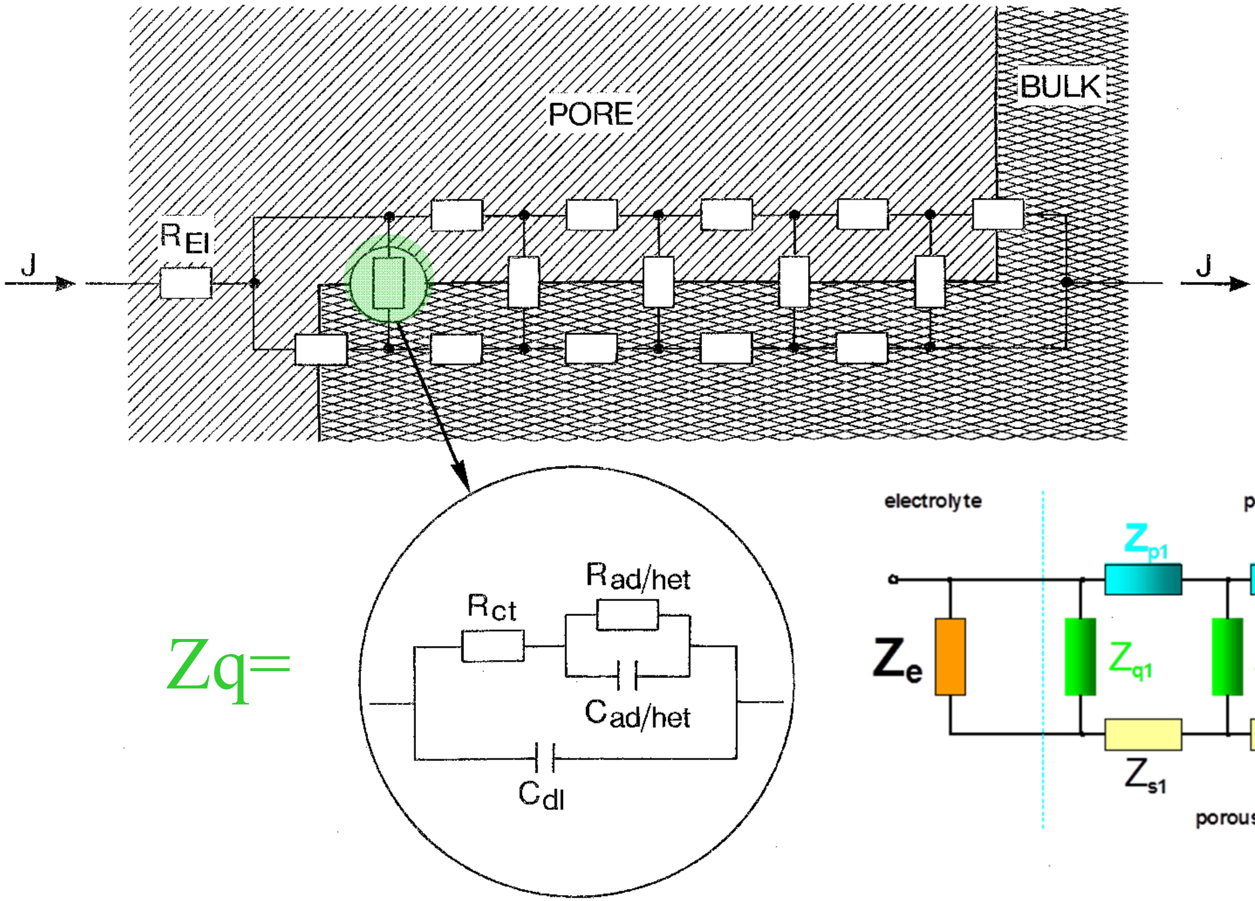
Cylindrical homogeneous porous electrode model (H. Göhr)



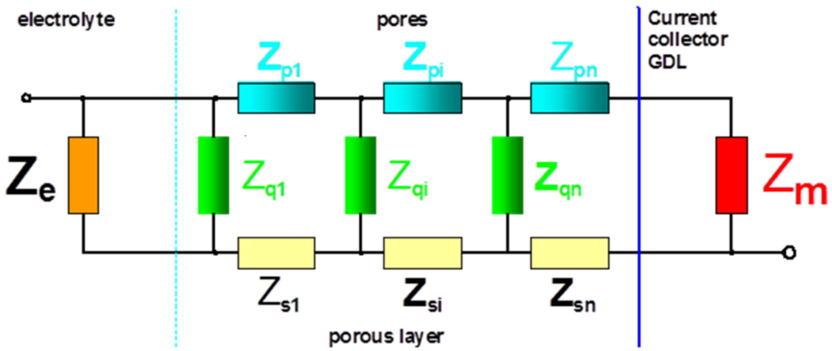


H. Göhr in *Electrochemical Applications/97*, www.zahner.de

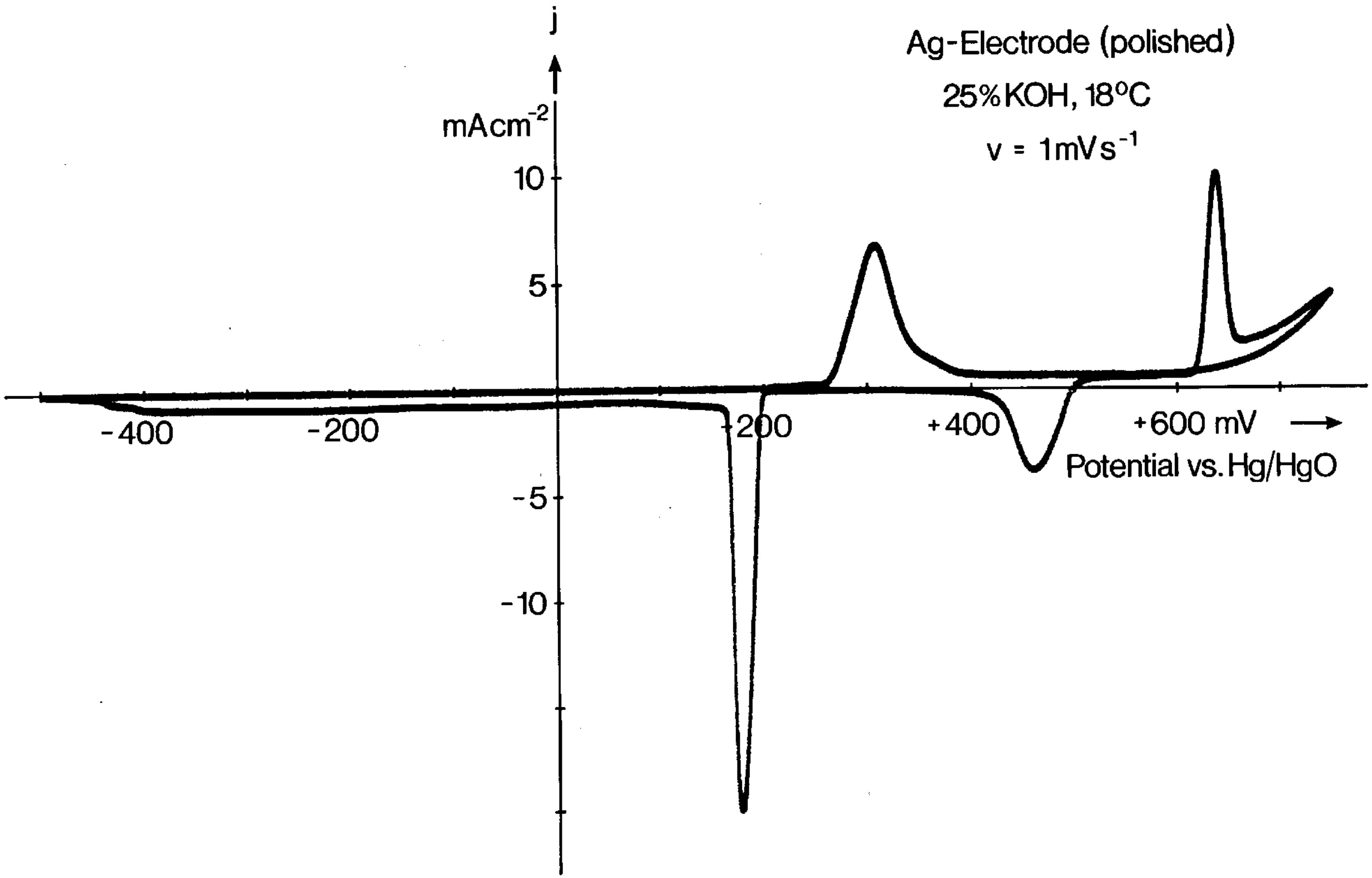
Electrode Model with cylindrical , homogeneous pores and complex Faraday-impedance



Zq=

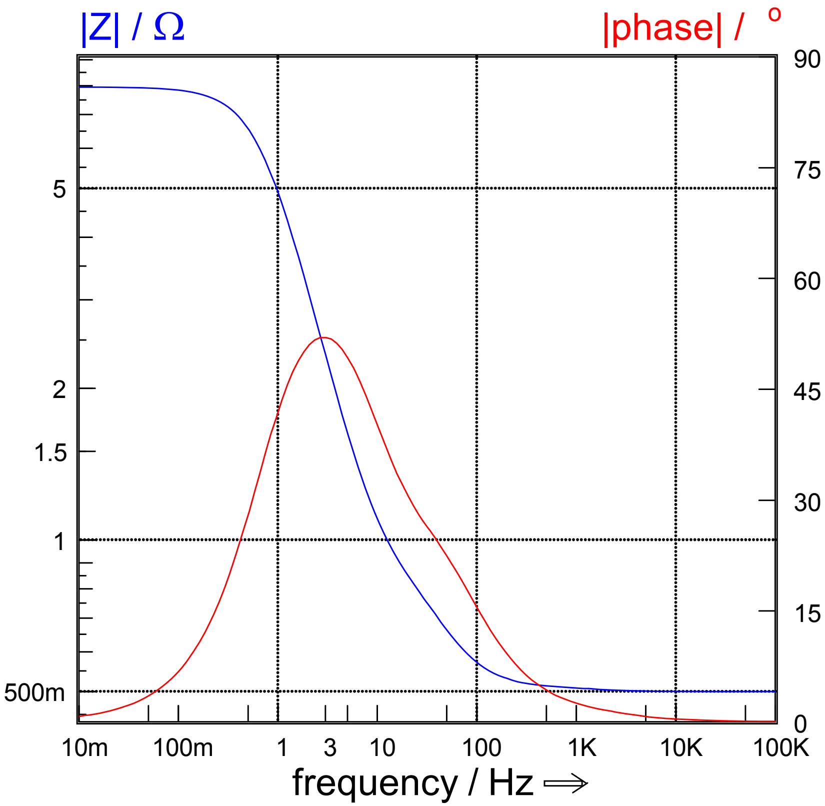


CV of a polished Ag electrode, 25% KOH, O_2 sat.



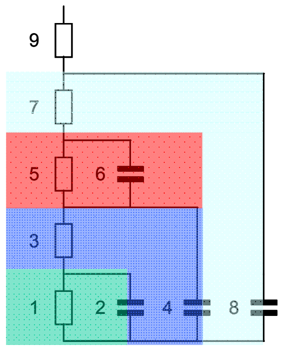
Model of the oxygen reduction

Simulated Impedance Spectra



Data for -20 $mAcm^{-2}$, 6 N KOH, 25°C

1	5.9	Ω	O_2-diffusion
2	20	mF^{α}	
	990	m	
3	660	mΩ	-heterogeneous reaction
4	4	mF^{α}	
	950	m	
5	840	mΩ	
6	50	mF^{α}	OH- diffusion (into solution)
	950	m	
7	50	mΩ	Charge transfer resistance
8	5	mF^{α}	Double layer capacity
	950	m	
9	500	mΩ	Electrolyte resistance



D.W. Wabner, Metalloberfläche Angew. Elektrochemie, Band 28 (1974) 21-25

Adsorptions- and heterogeous reaction impedance

Definition of $Z_{ad/het}$:

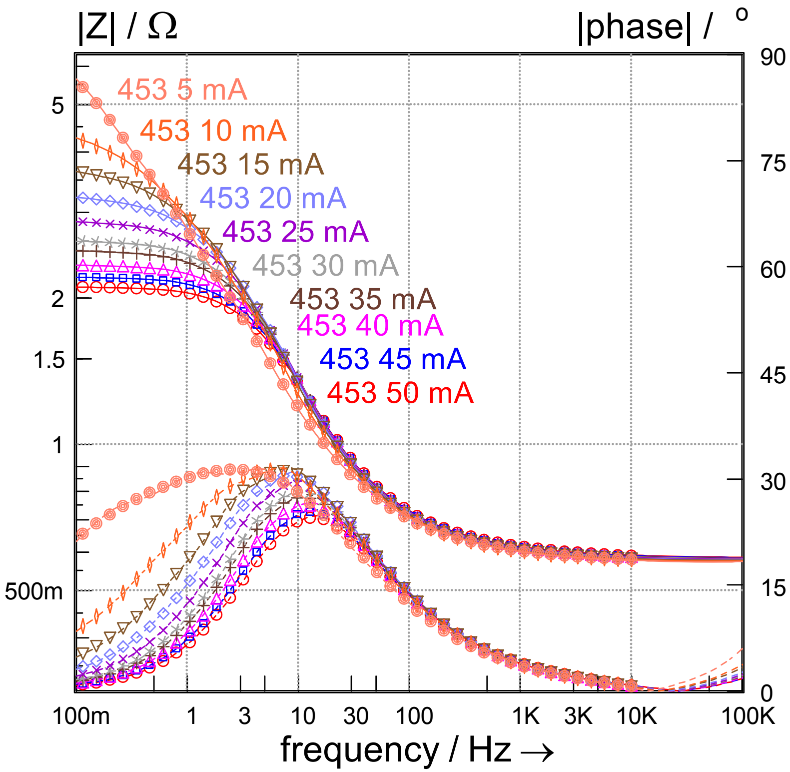
$$Z_{ad/het} = RT(k-\omega i)/n^2F^2c_sA(k^2+\omega^2)$$

With A=electrode surface, k= first order reactions rate, F=Faraday constant, c_s=surface concentration and angular frequency $\omega=2\pi f$.
The heterogenous reaction impedance can be converted into a parallel combination of $R_{ad/het}$ and $C_{ad/het}$:

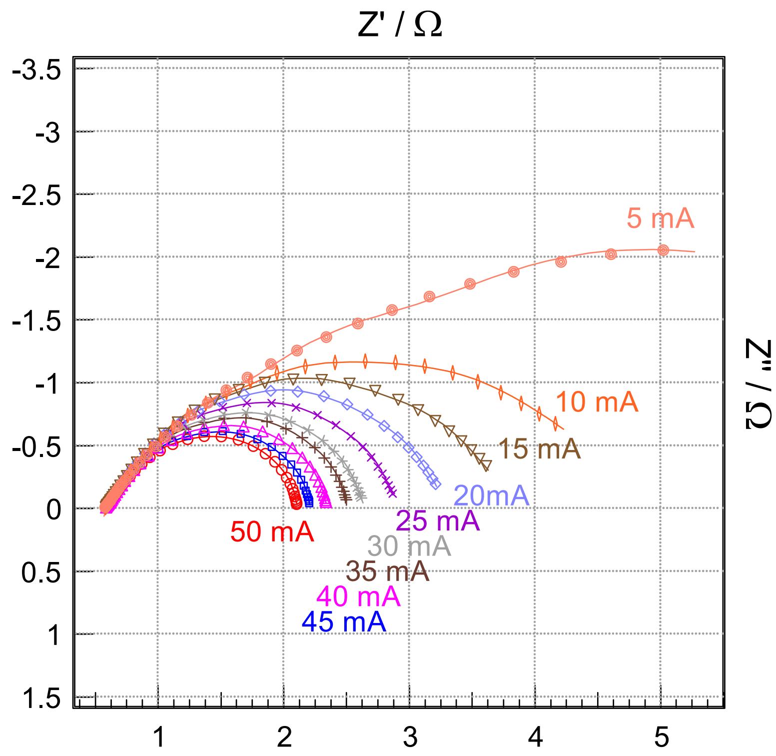
$$R_{ad/het} = RT/(n^2F^2c_sA\mathbf{k})$$

$$C_{ad/het} = n^2F^2c_sA/(RT)$$

Impedance Measurements during ORR in 10 N NaOH, on Silver Electrodes at Different Current Densities, i< -50 $mAcm^{-2}$

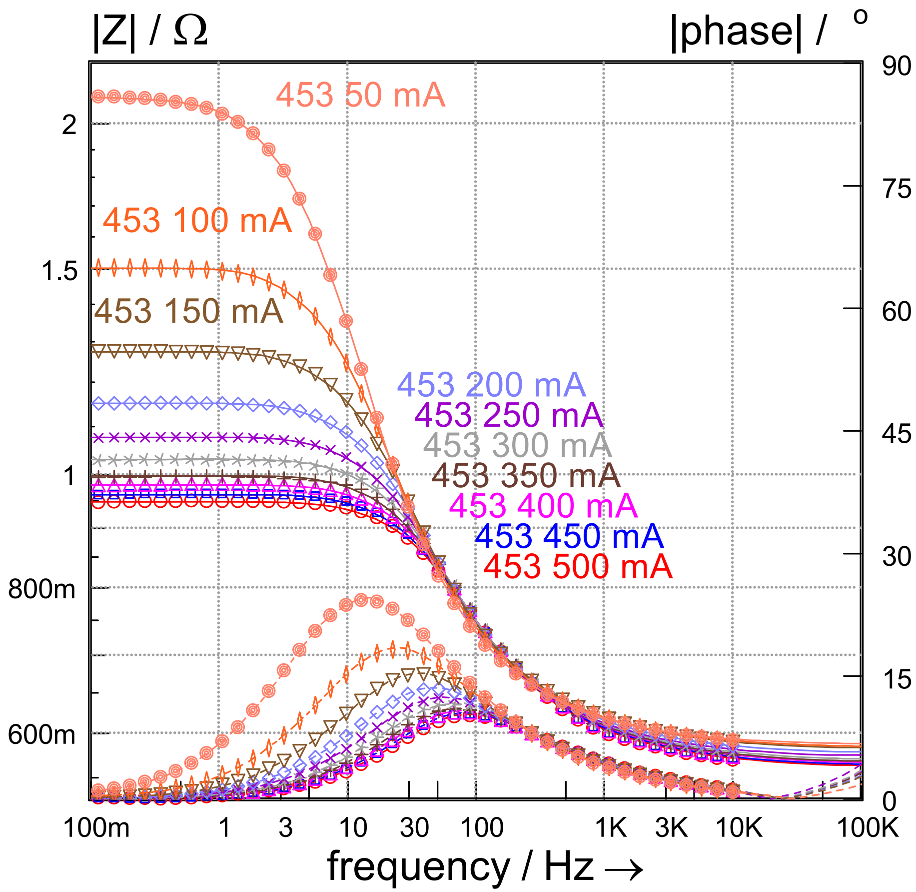


Bode representation

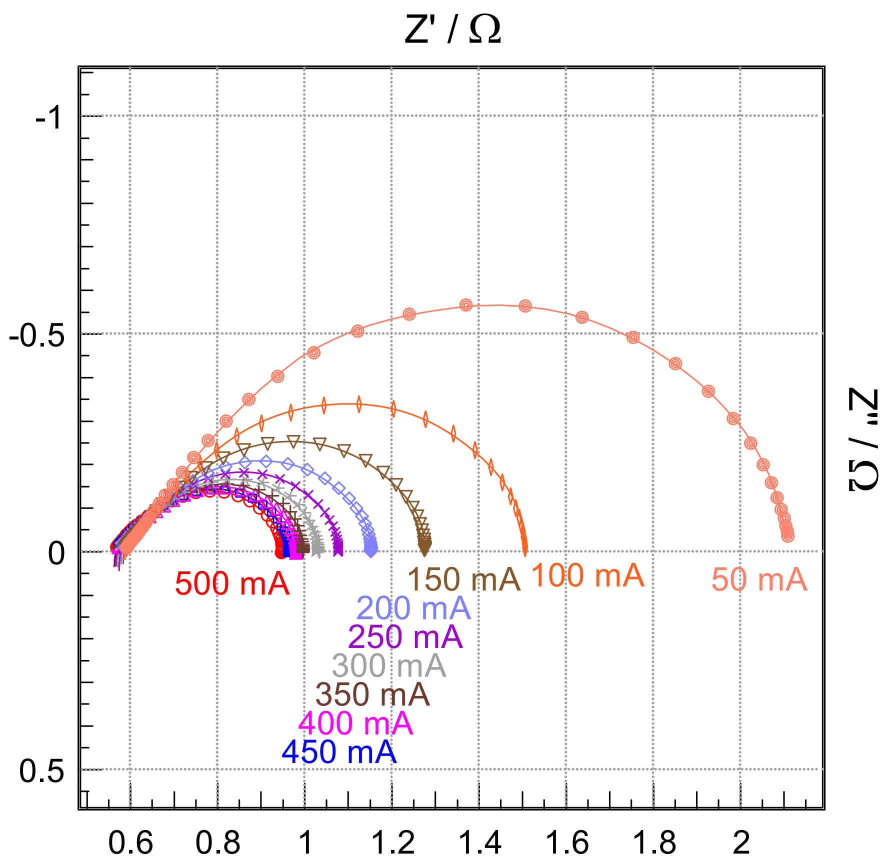


Nyquist representation

Impedance Measurements during ORR in 10 N NaOH, on Silver Electrodes at Different Current Densities, i> -50 mAcm^{-2}

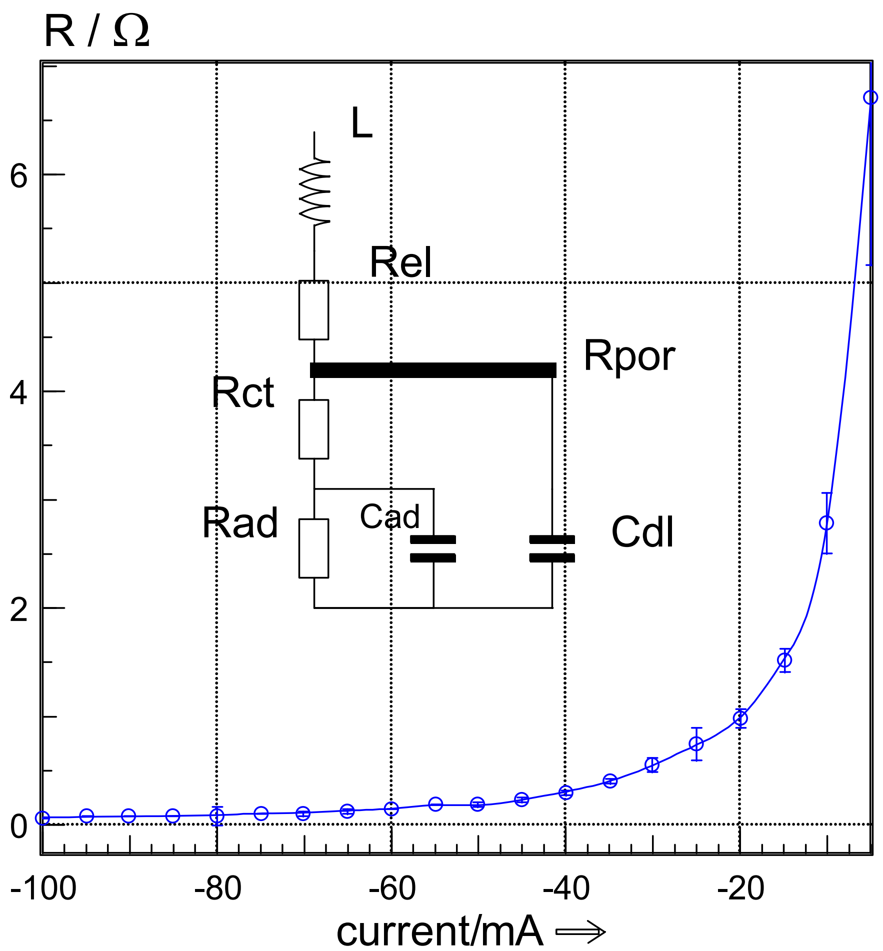


Bode representation

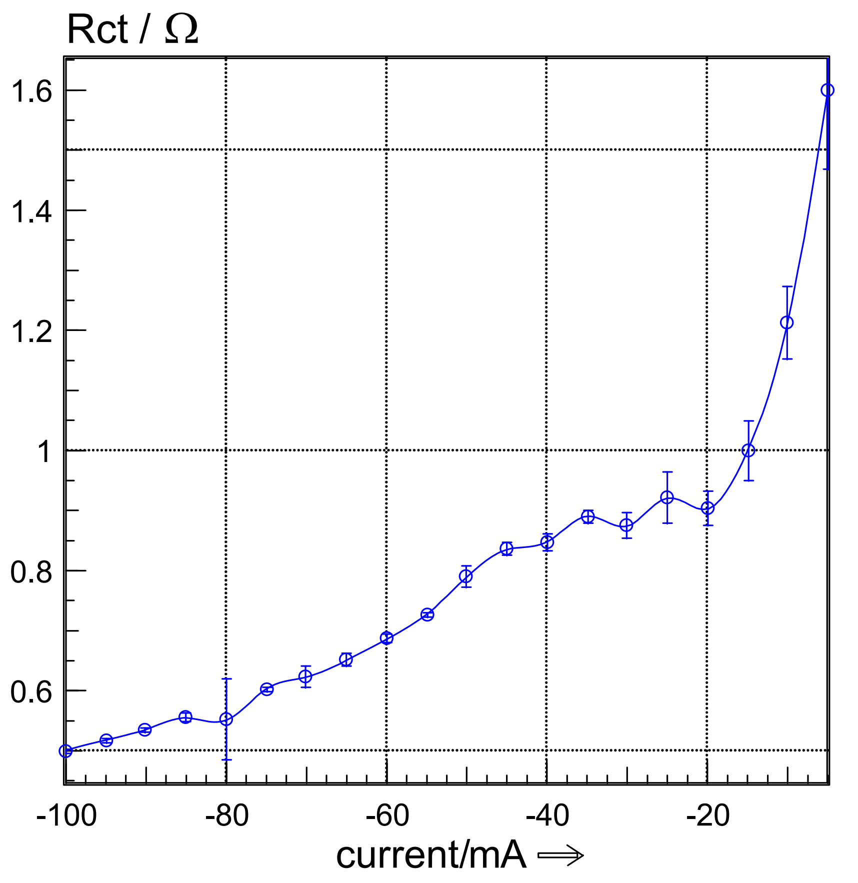


Nyquist representation

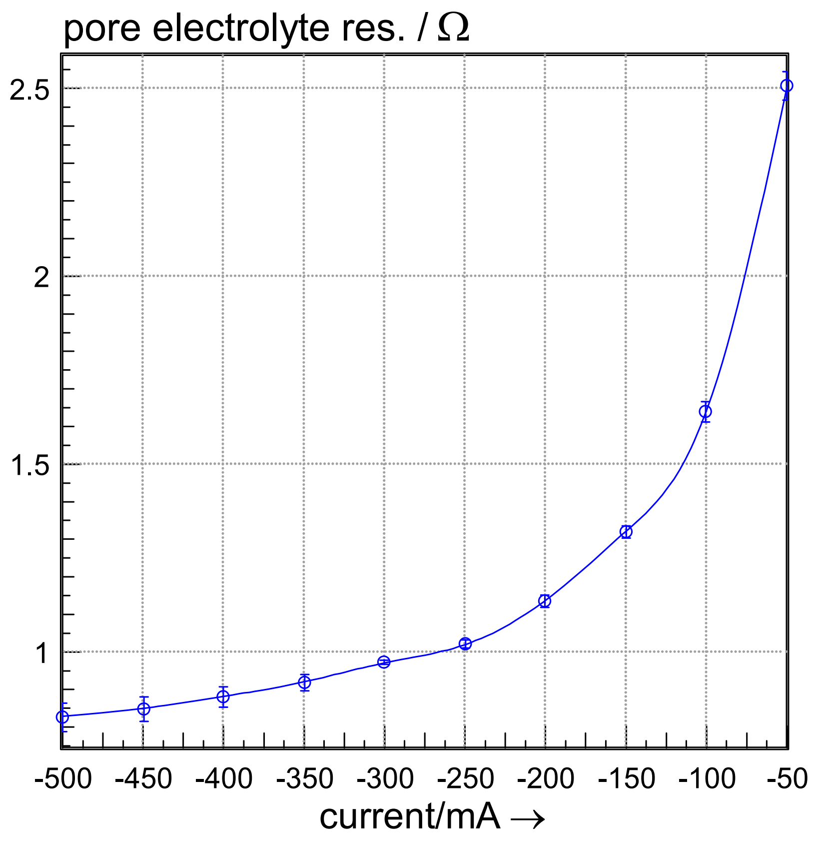
Evaluation of EIS measured during ORR Equivalent circuit and $R_{ad} = f(i)$



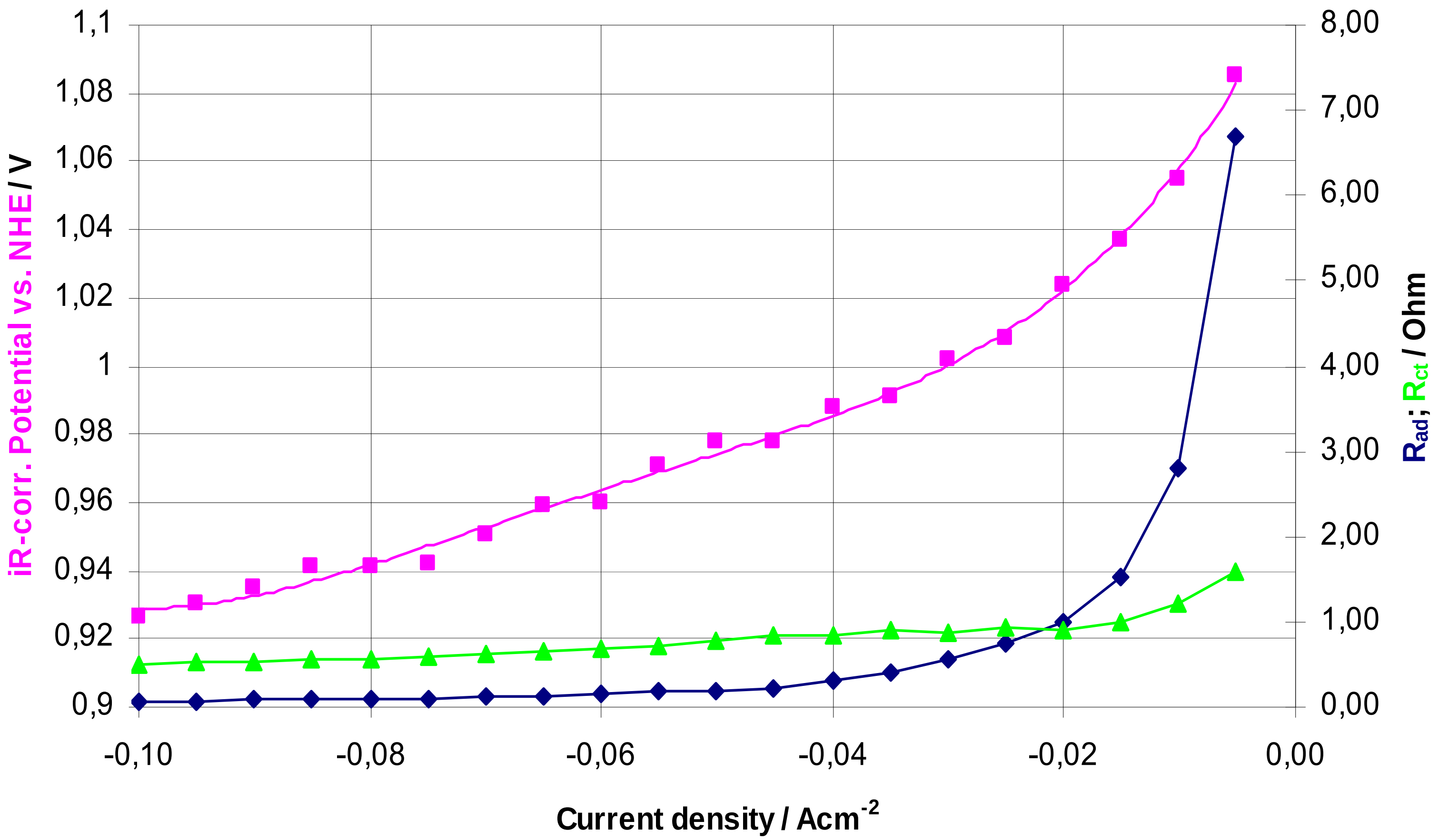
Current density dependency of the charge transfer resitance R_{ct}



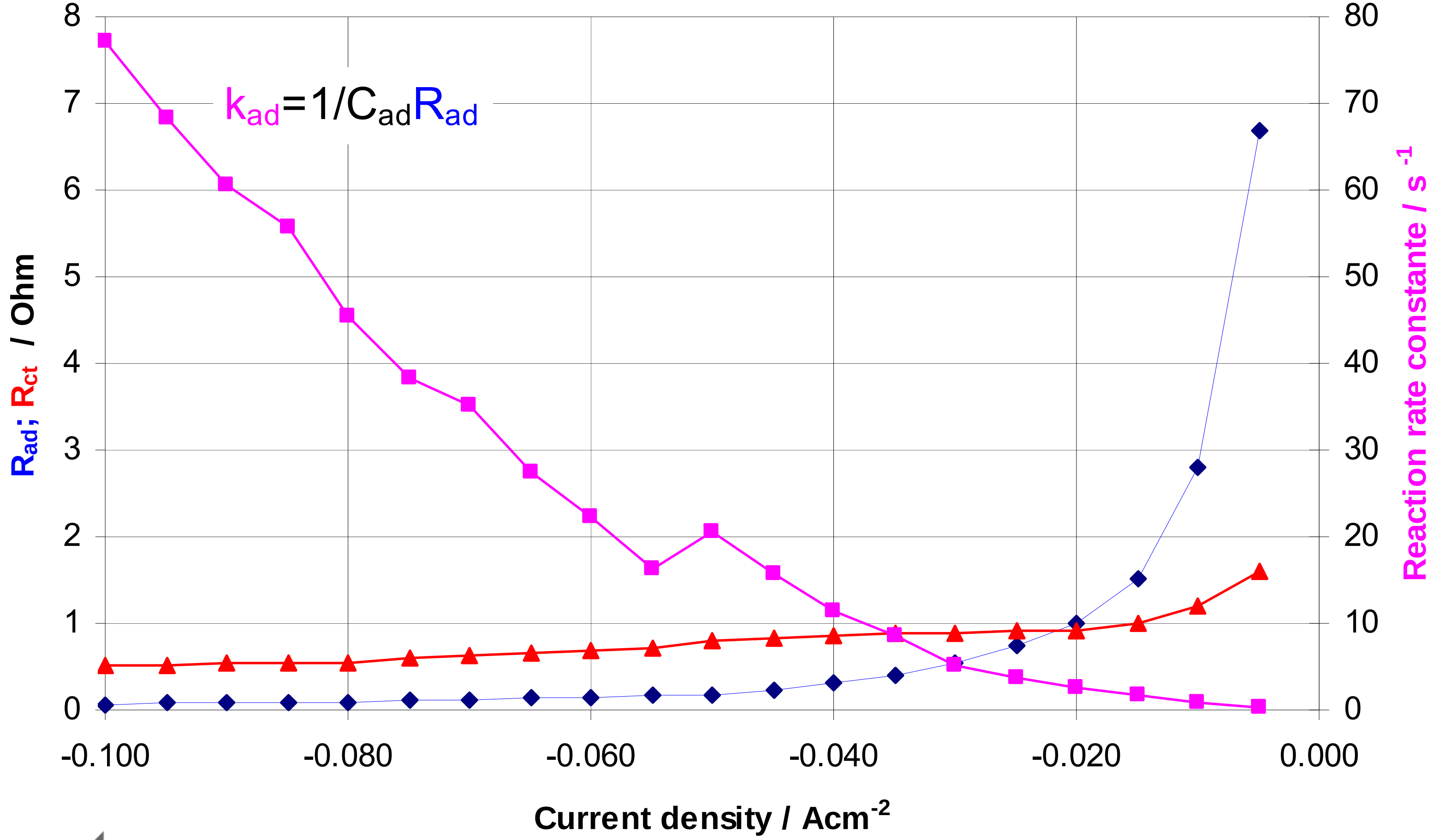
Current density dependency of electrolyte resistance inside the pore



U-i characteristic and current density dependency of impedance elements R_{ad} and R_{ct}

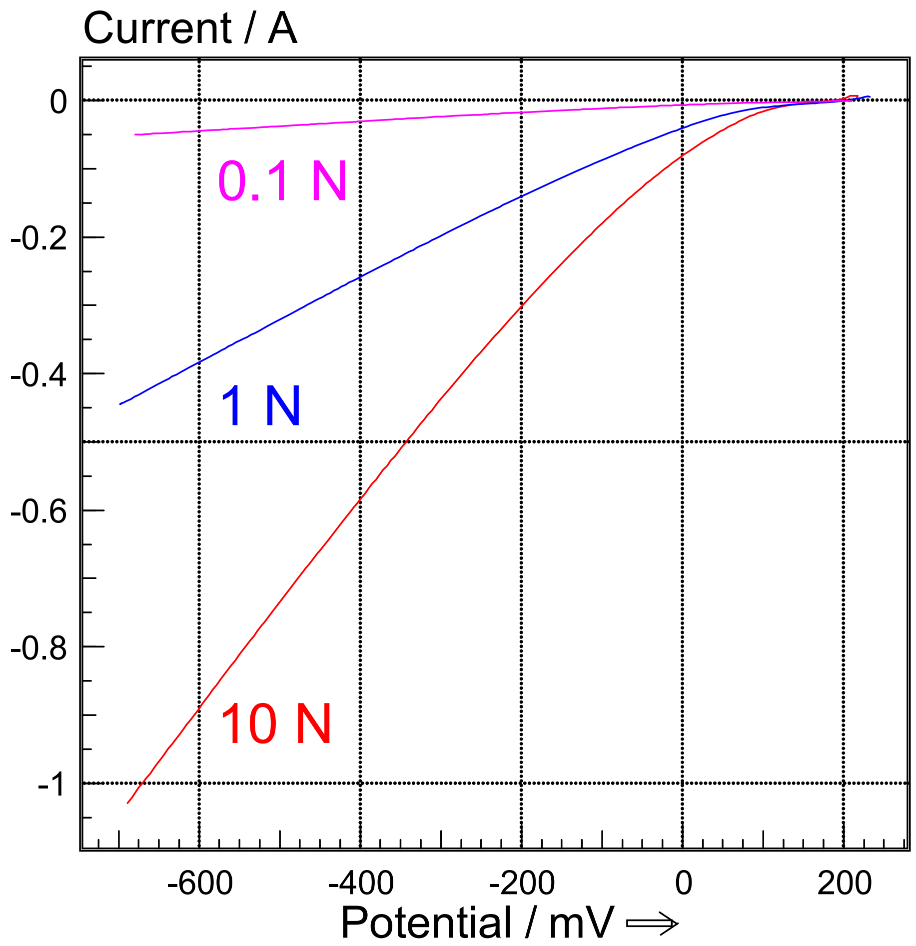


Current density dependency of k_{ad}, R_{ad} and R_{ct}, determined from EIS evaluation

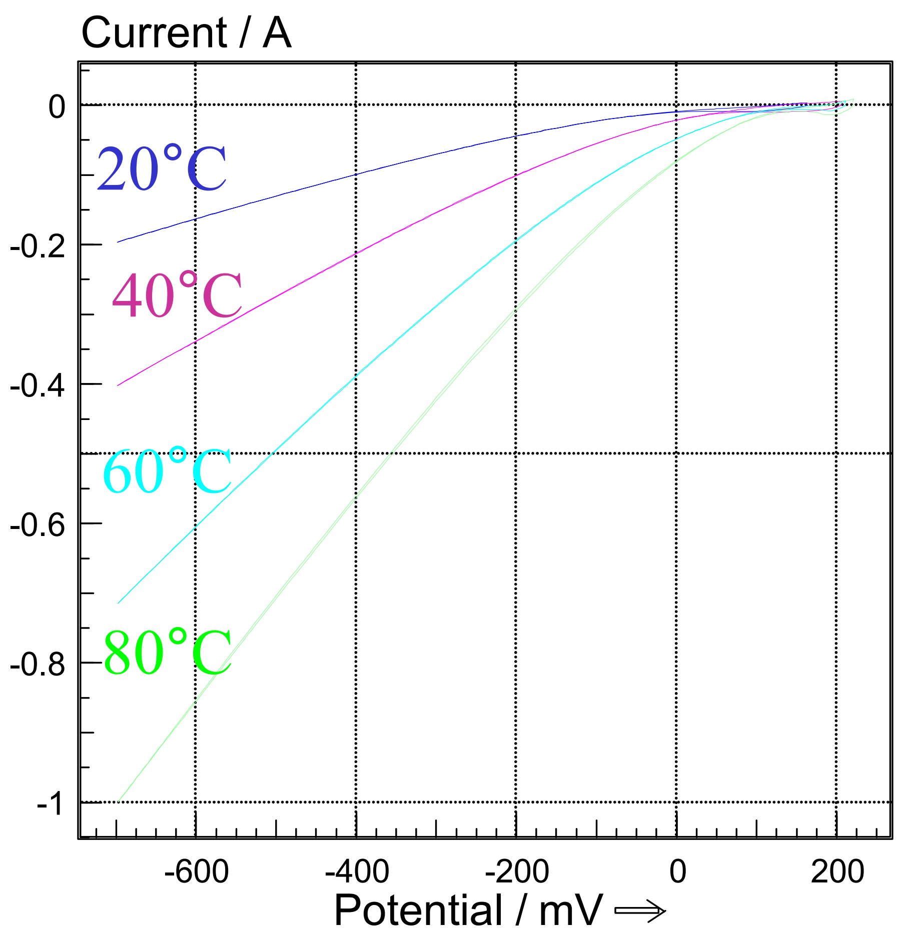


DLR

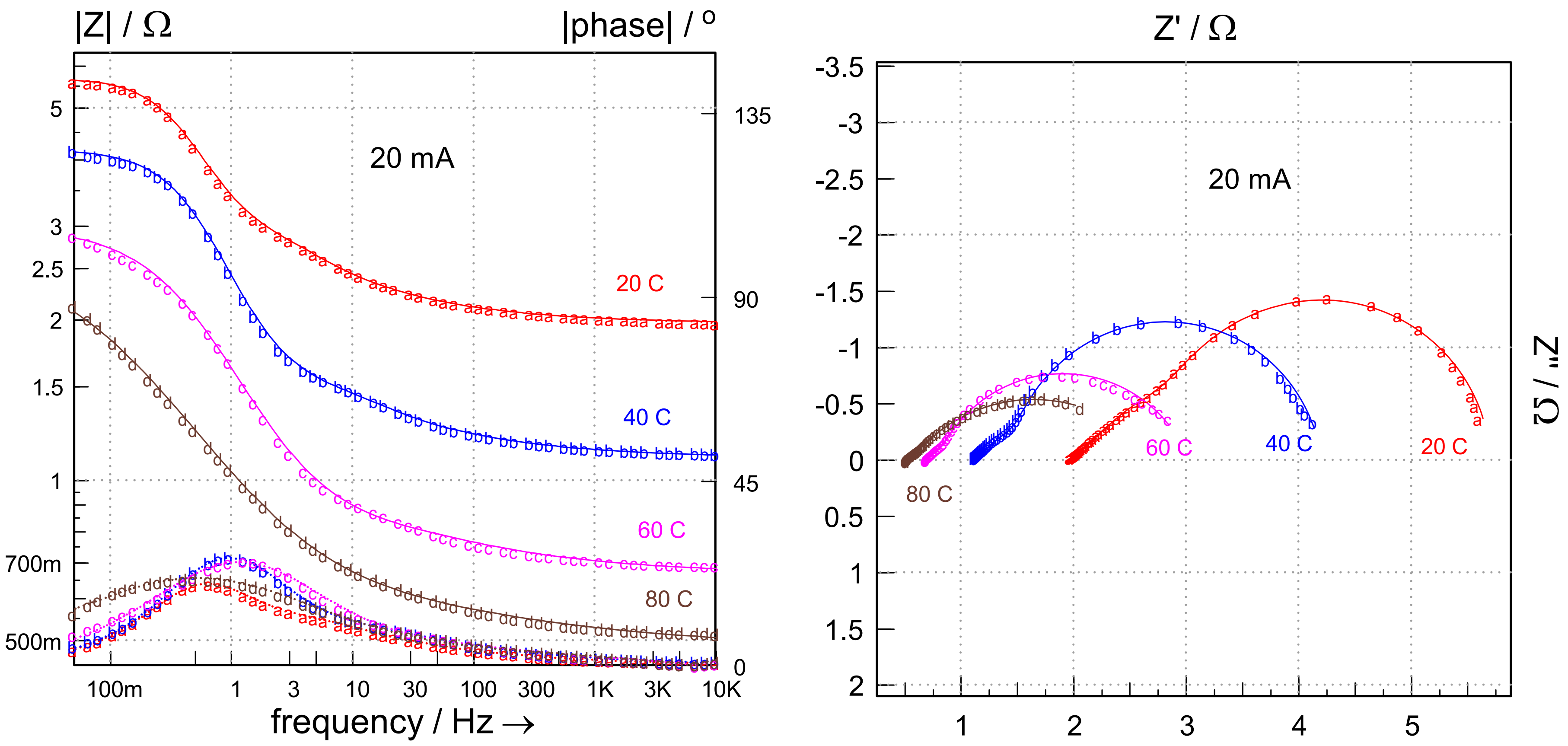
CVs measured from OCP+10 mV, 1 mVs^{-1} in different concentrated NaOH solutions, 80°, O_2



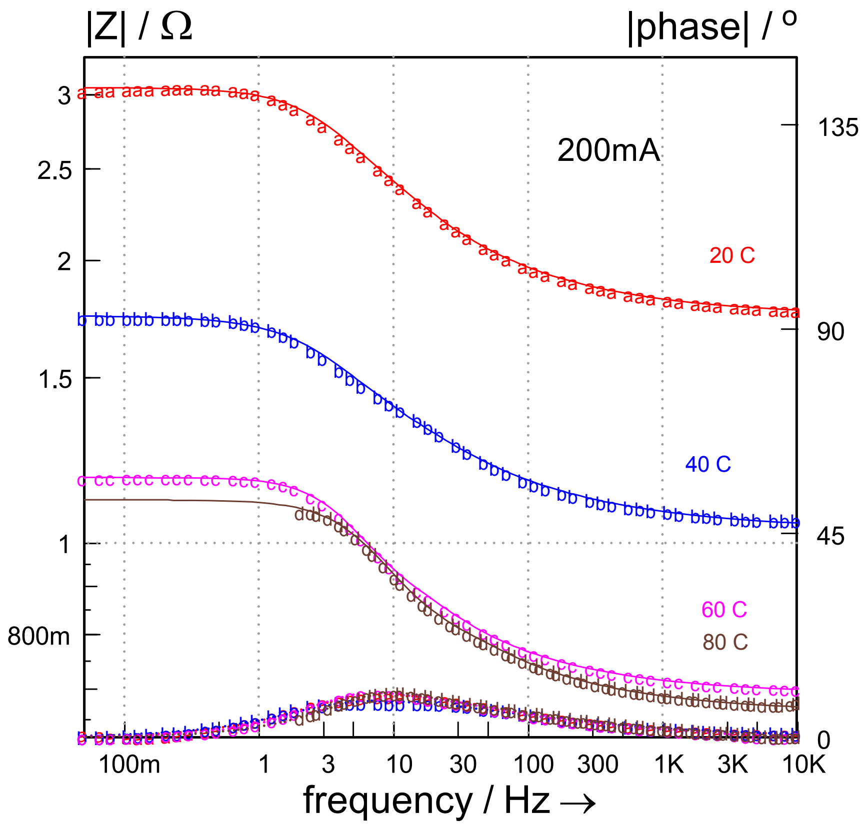
CVs measured from OCP+10 mV, 1 mVs^{-1} in 10 N NaOH, at different temperatures, O_2

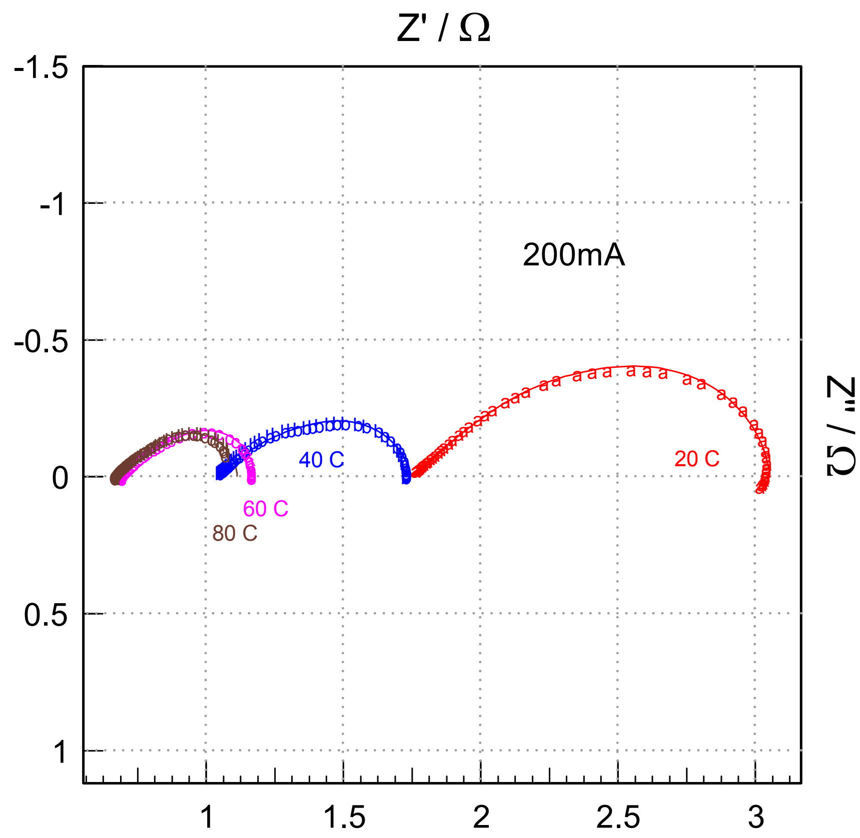


EIS measured at different temperatures during OCR 10 M NaOH, 20 mAcm^{-2}

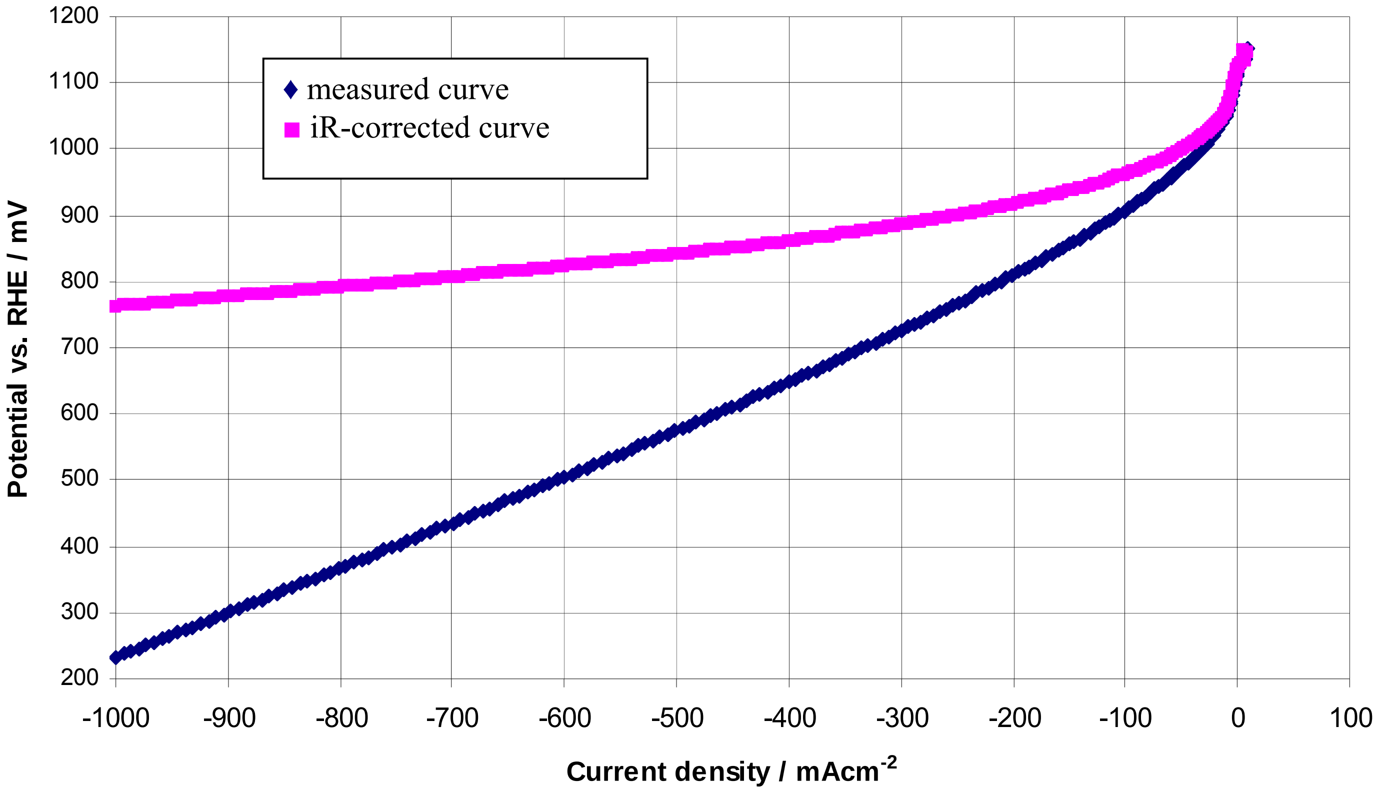


EIS measured at different temperatures during OCR 10 M NaOH, 200 mAcm^{-2}

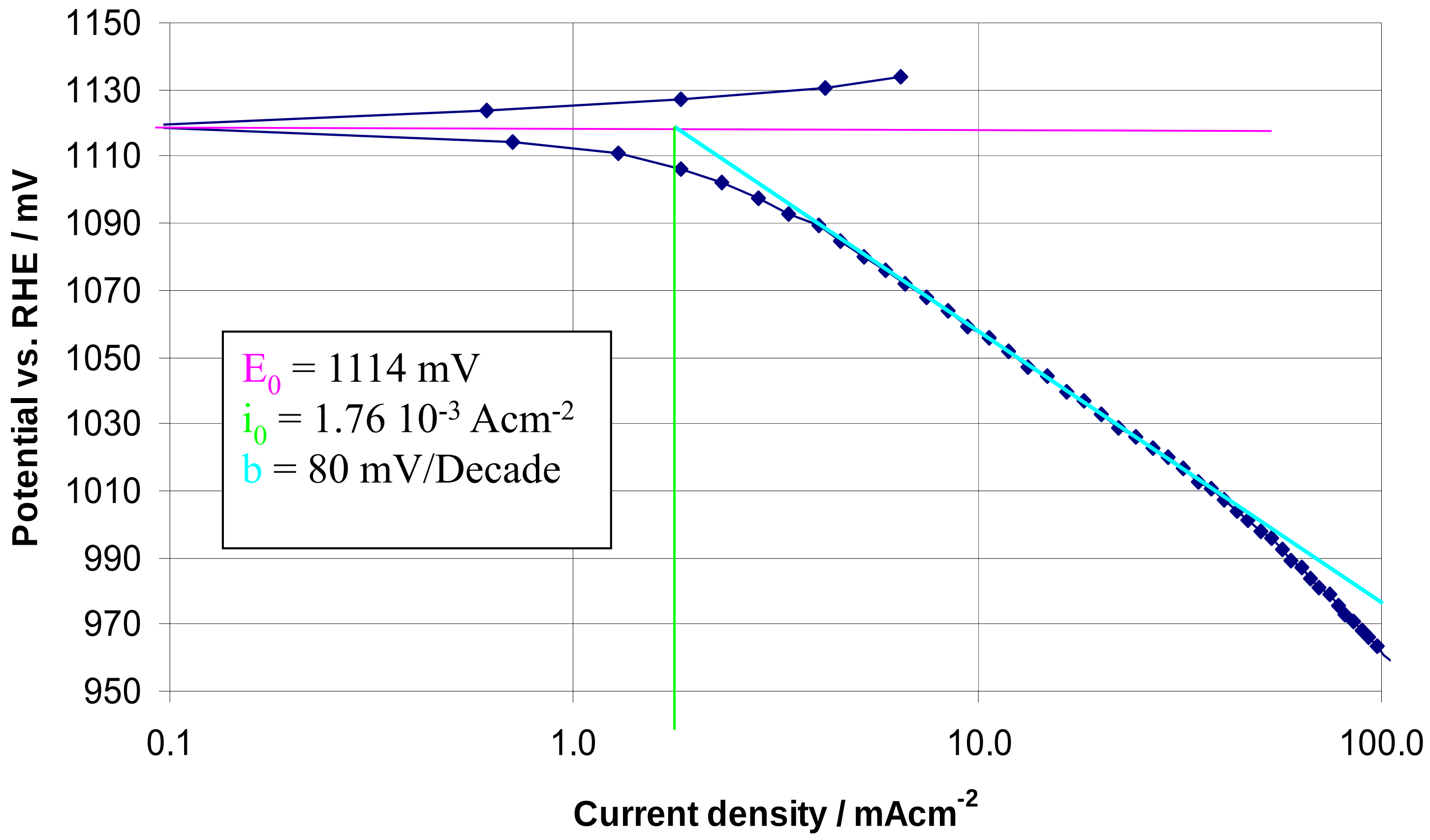




Determination of kinetic parameters from CV measurements : iR-correction



Determination of kinetic parameters from CV measurements : Tafel plot



Conclusion

- From the evaluation of the measured impedance spectra one can propose a reaction mechanism for the ORR:
  - ➢Adsorptions- / heterogeneous reactions and charge transfer reaction are consecutive reactions
  - ➢Reaction mechanism and rate determining step is changing at higher current densities at ca. 20 $mAcm^{-2}$
- Production parameters, composition and structure have a strong influence on electrode reactivity
- Change of reaction zone with current density

Thank you for your attention !

Acknowledgment

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