Production and Characterization of carbon-free bi-functional cathodes for the use in lithium-air batteries with an aqueous alkaline electrolyte

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Germany

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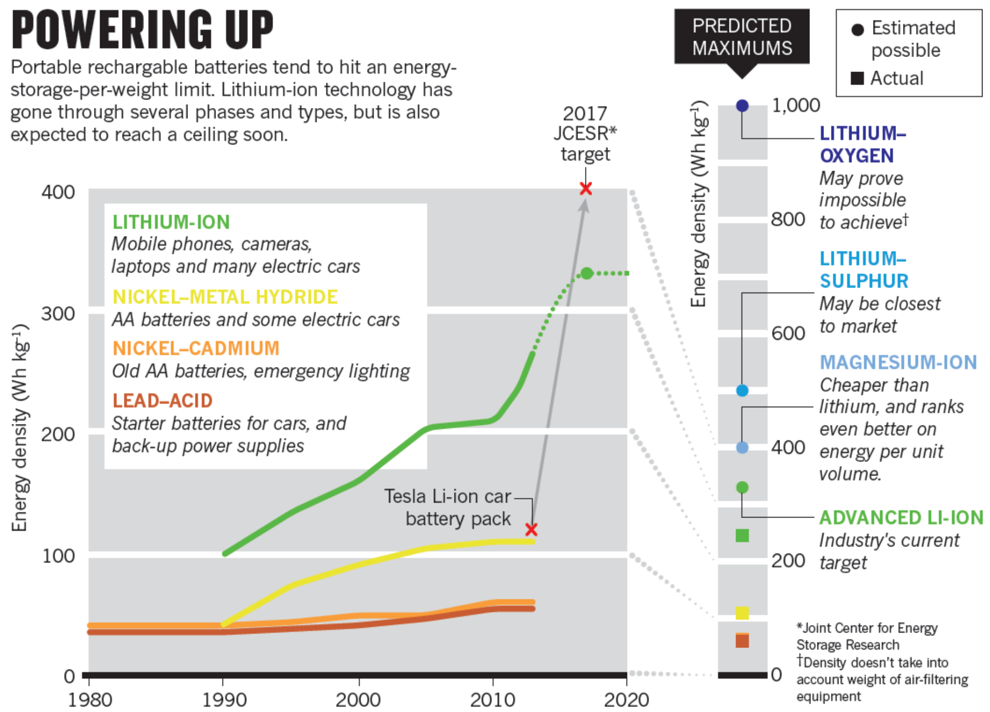
Presentation outline

- Application of EIS in battery research at DLR
    - Motivation Li-air batteries
- Electrode production techniques at the DLR
    - Cathode for the Li-air battery
- Influence of production parameter on electrode performance
- Conclusion and outlook

Activities of the „Batterietechnik“ team

Characterisation of
Li-ion batteries with
in-situ and ex-situ-methods

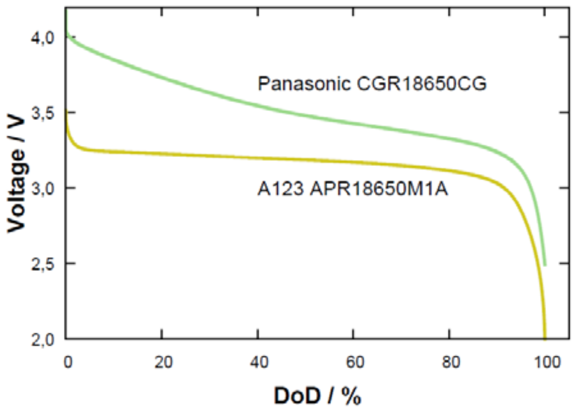
Production and Characterisation
of cathodes for
Lithium-Sulfur *and*
Lithium-air batteries

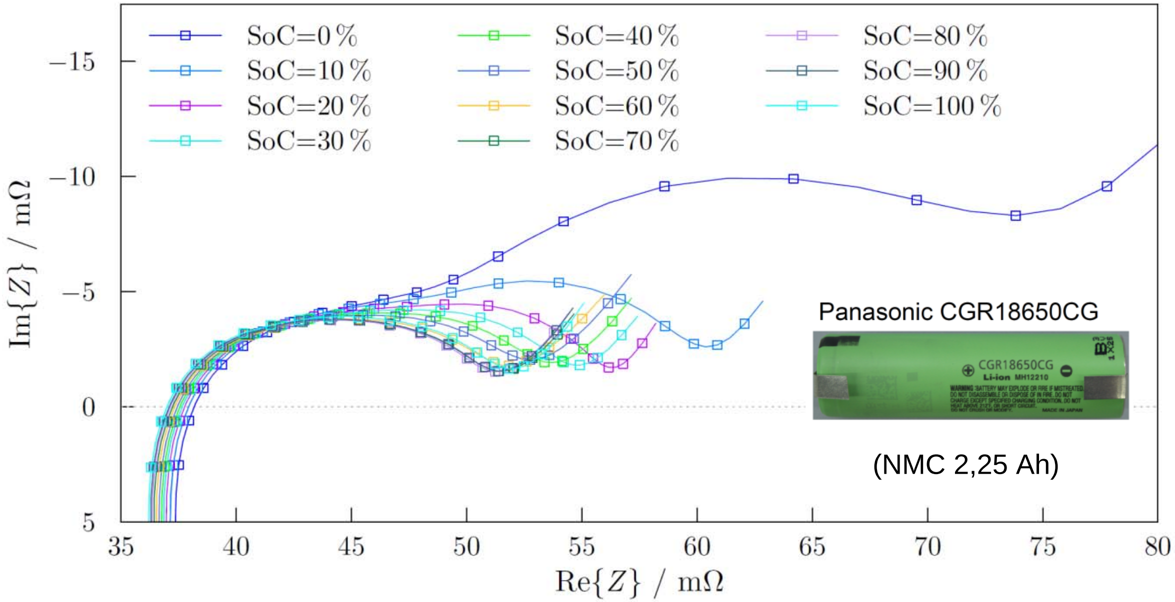


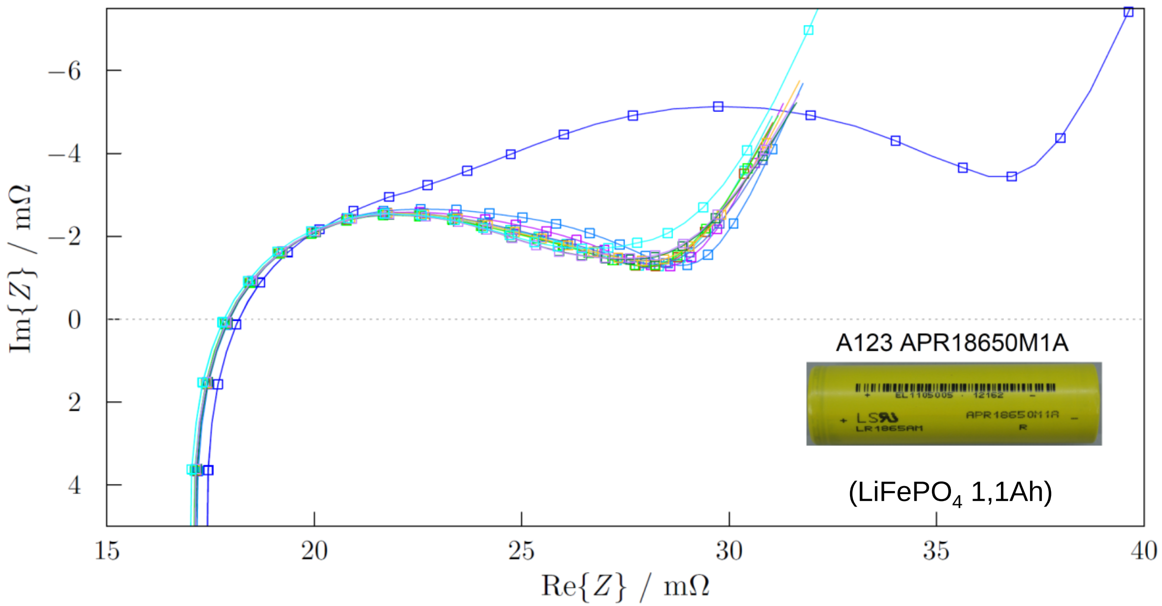
Source: N AT U R E | VO L 5 0 7 | 6 M A R C H 2 0 1 4

EIS measurement at different SOC

Discharge at 1C

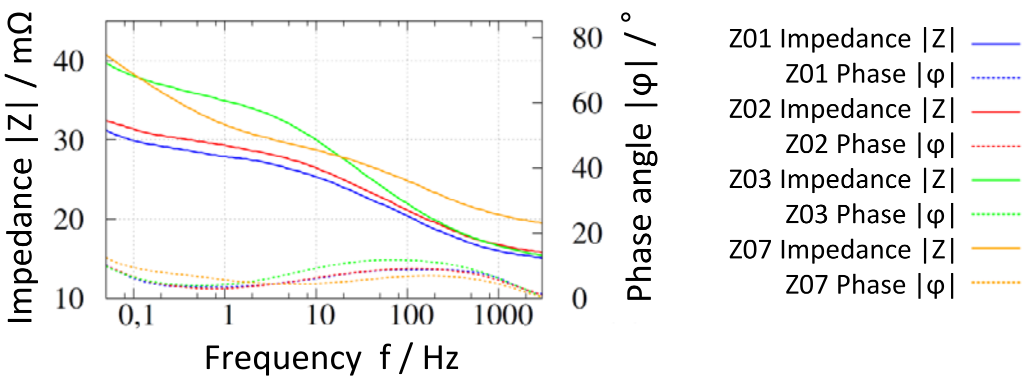


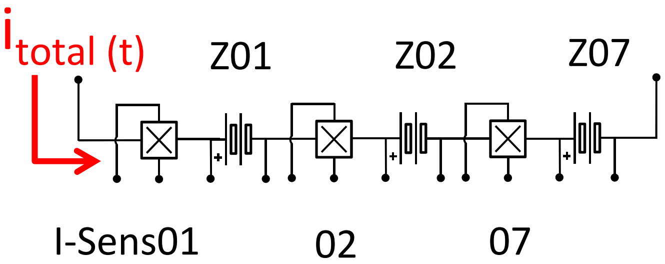


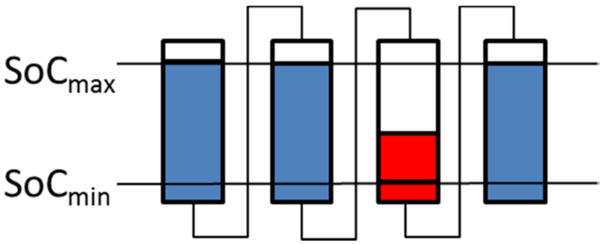


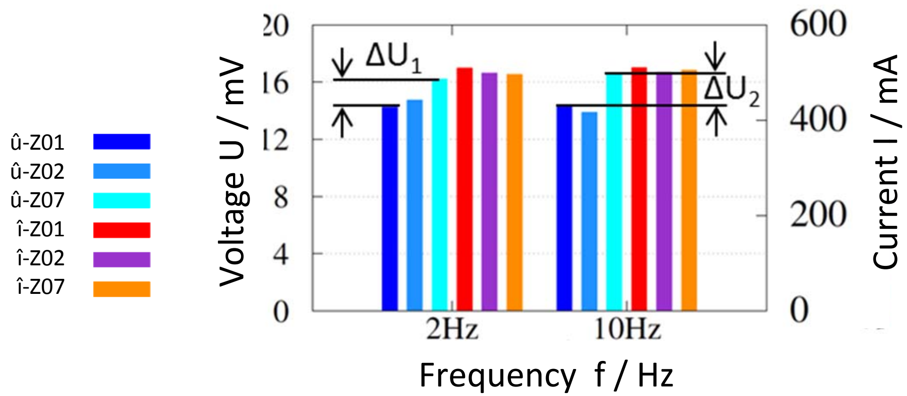
Discrimination of SOC and SOH of serial connected batteries

Serial connection V2		
Z01	U=3,25V	SoH100
Z02	U=3,25V	SoH100
Z07	U=3,25V	SoH60

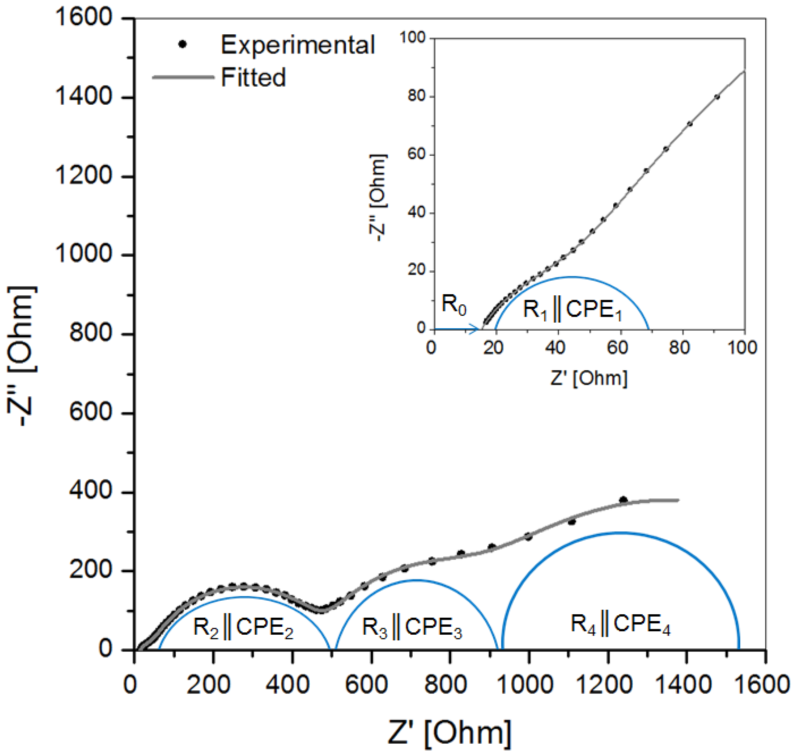




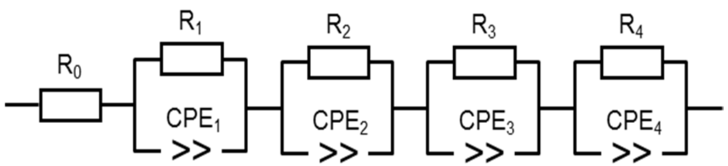




Electrochemical Model of Li-S Battery



Equivalent circuit



Model	Chemical and physical cause
R_0	Ohmic resistance
R_1-CPE_1	Anode charge transfer
R_2-CPE_2	Cathode process: charge transfer of sulfur intermediates
R_3-CPE_3	Cathode process: reaction and formation of S_8 and Li_2S
R_4-CPE_4	Diffusion

Motivation

Why Li-air batteries?

- Highest theoretical specific energy density (11.425 Wh/kg) Cathodic reactant, O_2 from 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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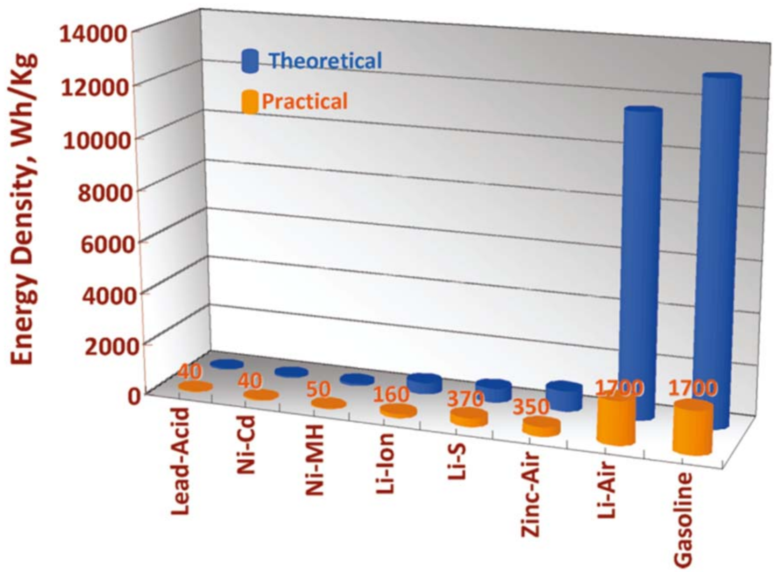

G. Girishkumar et al., J. Phys. Chem. Lett., **2010**, 1, 2193-2203

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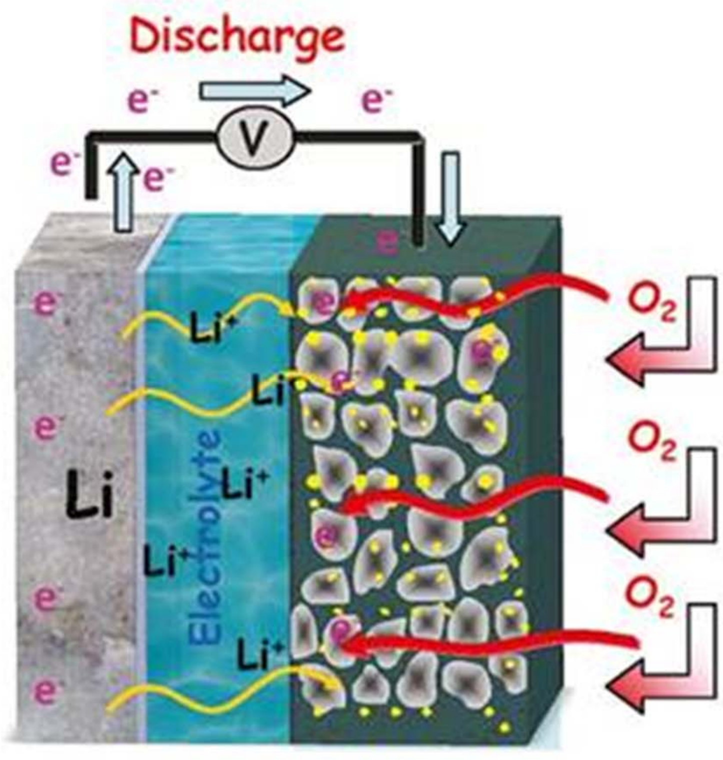
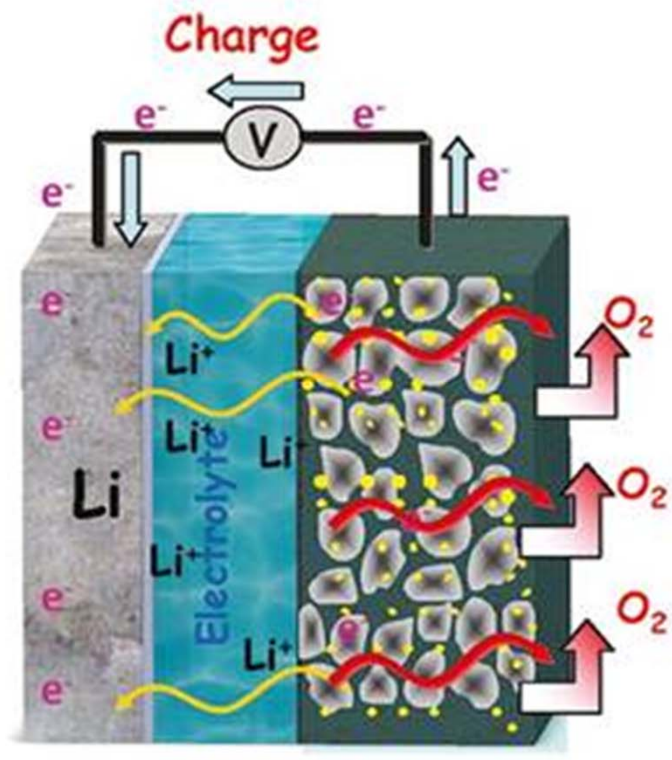
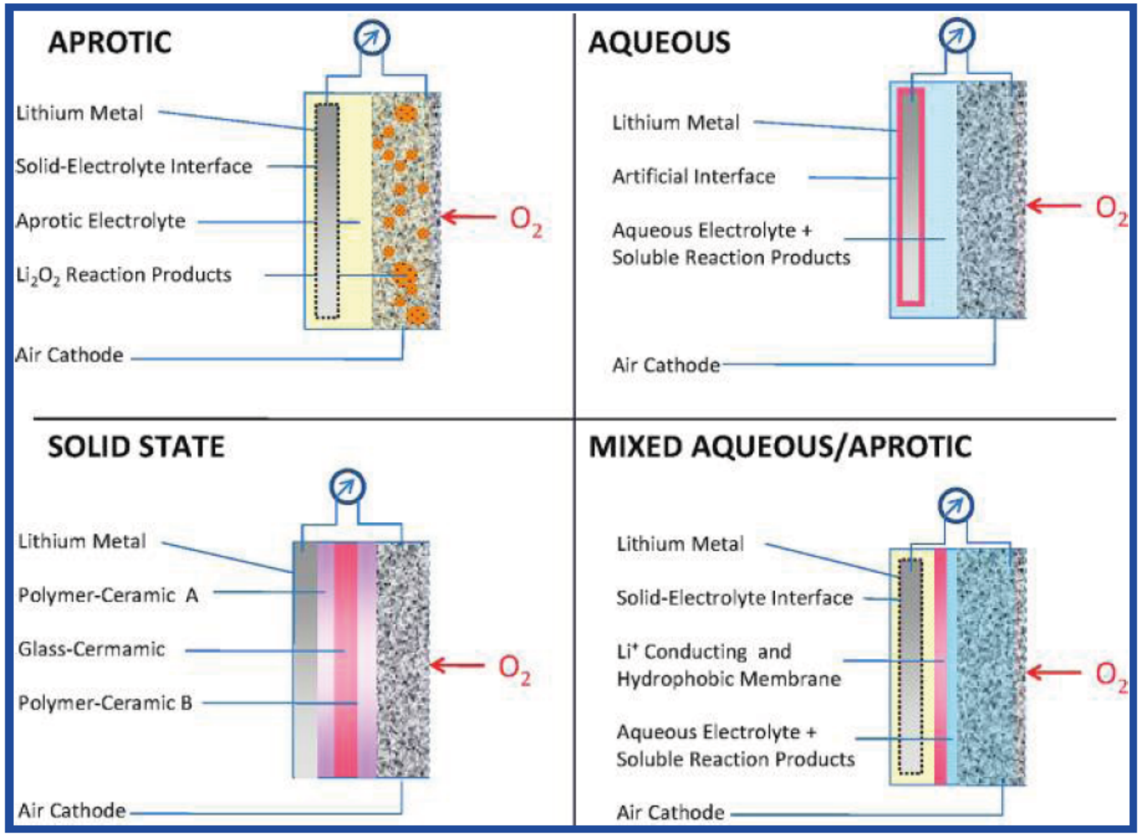
Schematically representation of a Li-air battery





Architectures of Li-air Batteries



Non-aqueous electrolyte:

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

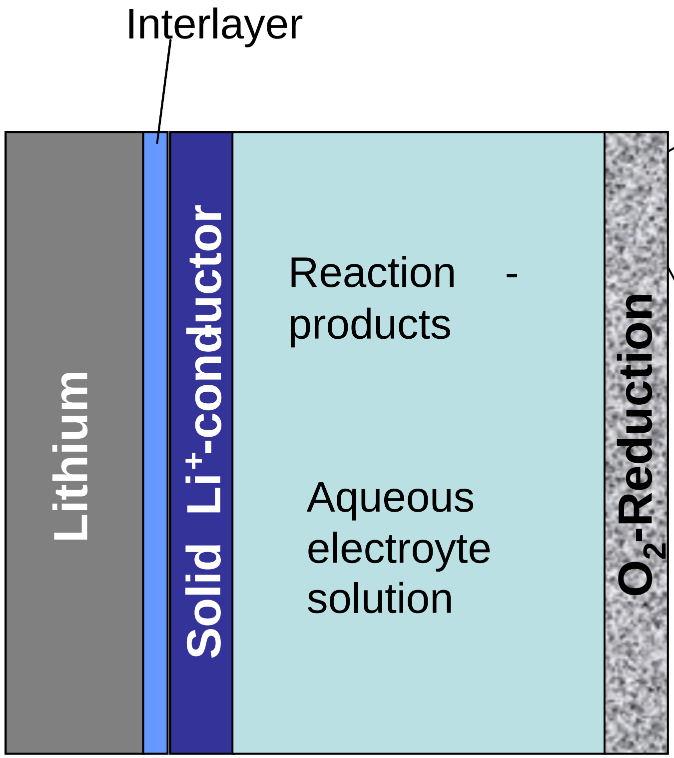
$2Li^+ + 2e^- + (1/2)\ O_2 \rightleftarrows Li_2O$ E_{rev}= 2,913 V

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

Schematically representation of Lithium-Air Battery with Aqueous Electrolyte



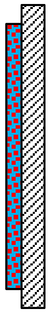
Reaction equation (alkaline Electrolyte):

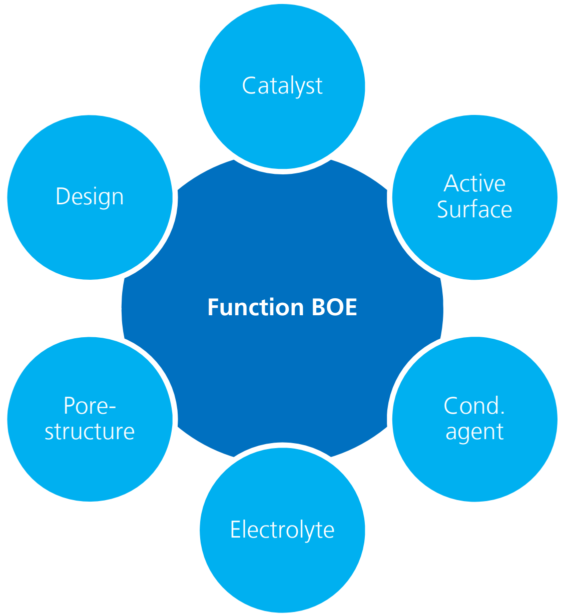
$4\ Li + O_2 + 2H_2O \leftrightarrow 4LiOH$; E = 3,45 V

Bi-functional Oxygen-Electrodes: Design

- Bi-functional Oxygen-Electrodes = catalizes ORR and OER

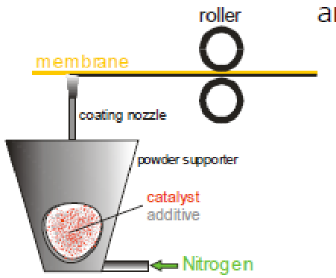
- Depending on manufactoring process every electrode consists of:
    - Catalyst(s)
    - Conductive agent (C, Graphit…)
    - Binder (PTFE, PVdF…)
    - Substrate (Metal mesh,…)



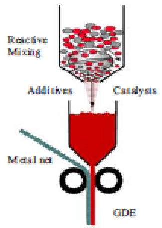


- Different manufactoring processes used at DLR: Dry Powder Spraying, Reactive Rolling an Mixing, Pressing and APS

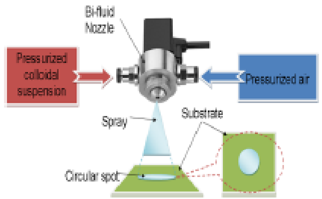
Dry Powder Spraying



Reactive Rolling and Mixing (RMR)



Colloidal Suspension Spraying



Atmospheric Plasma Spraying

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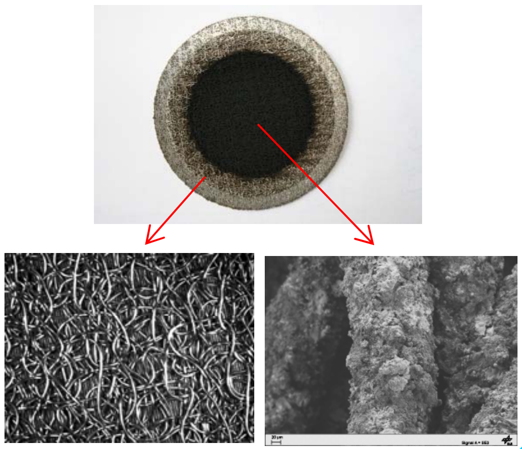
Manufactoring of bifunctional gas diffusion electrodes

Oxide catalysts
($La_{0.6}Ca_{0.4}CoO_{3...}$) can be sprayed on for example a Rhodius substrate with APS

Catalyst layer

Rhodius substrate



Manufactoring of bifunctional gas diffusion electrodes

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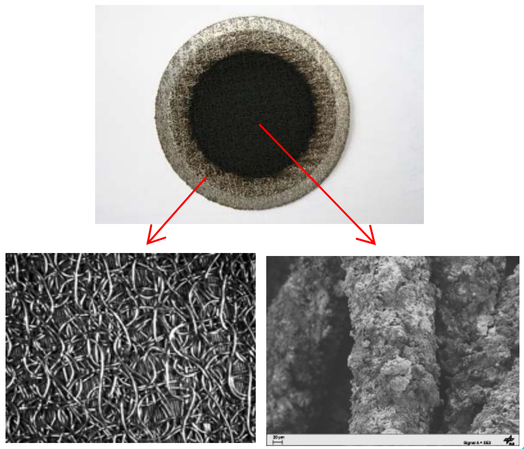
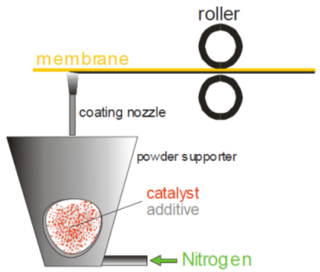
Catalyst layer

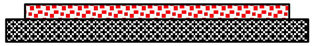
Rhodius substrate



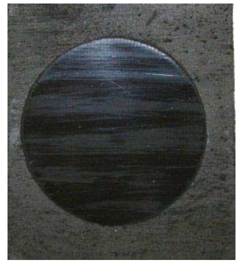
Electrodes with noble metal and other catalysts can be made with dry power spraying technique



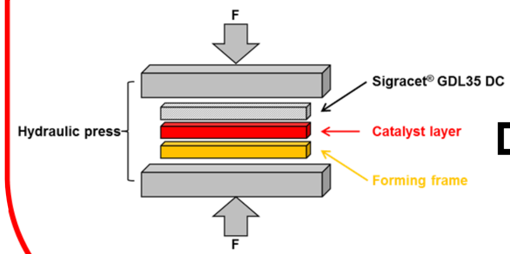
Catalyst layer = catalyst+carbon/ graphite+binder



Graphite GDE substrate



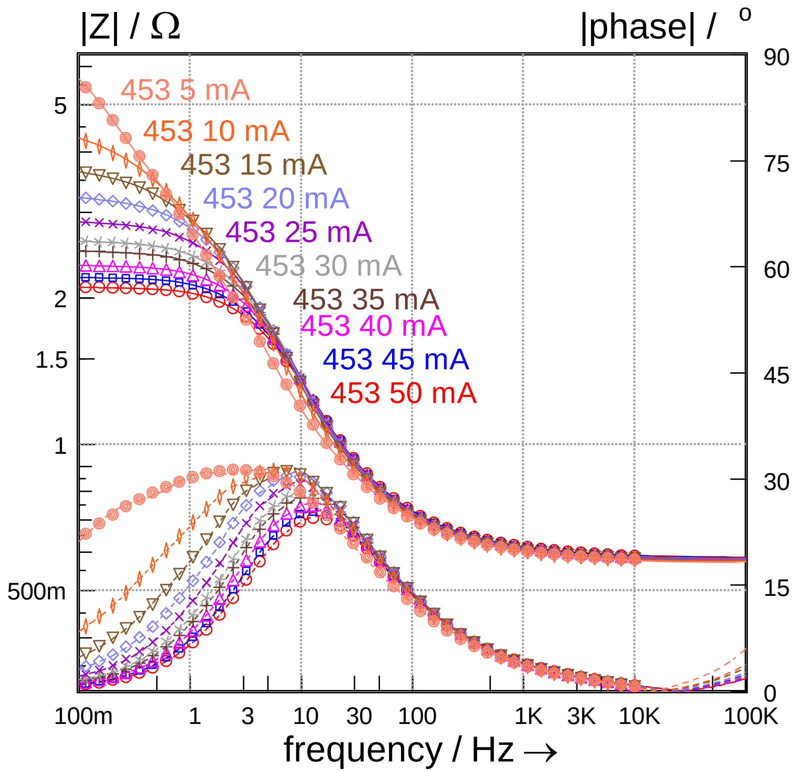
or by pressing the catalyst layer on for example a Sigracet® GDL 35 DC with a hydraulic press



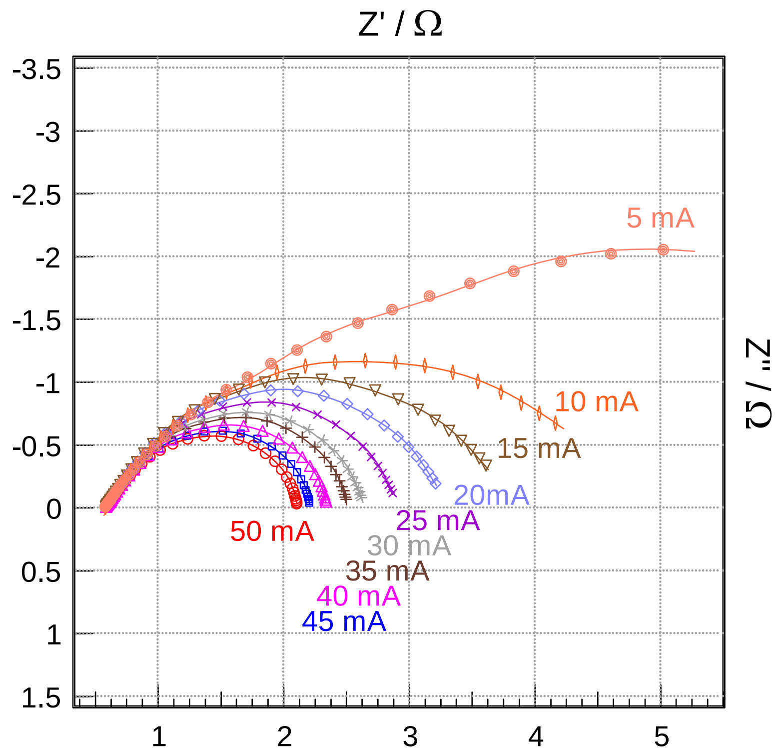
Catalyst layer = catalyst+carbon/ graphite+binder

Sigracet® GDL35 DC

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



Bode representation



Nyquist representation

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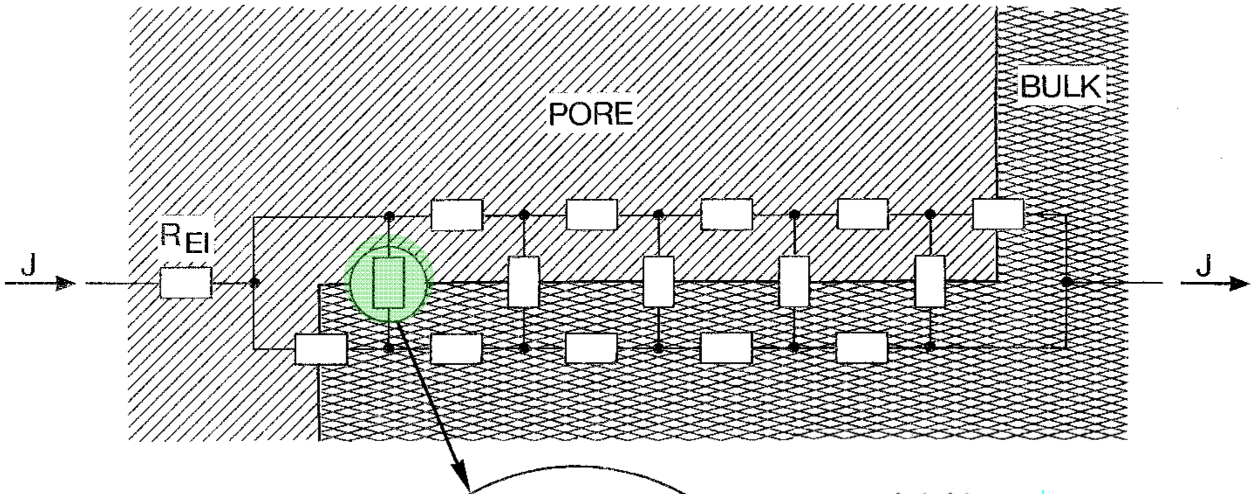
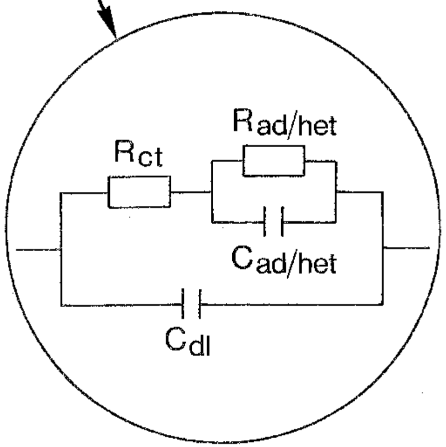
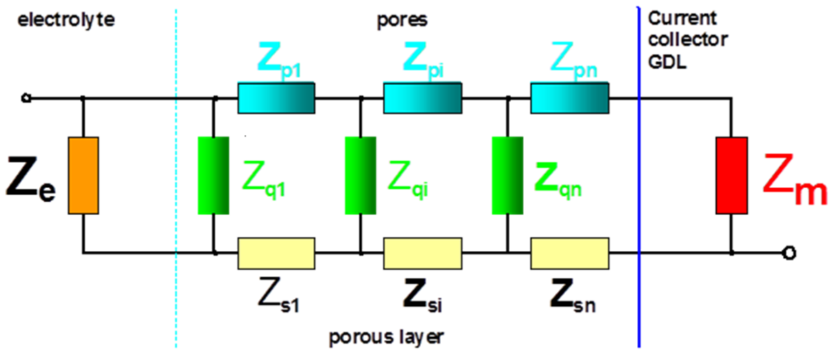
Electrode Model with cylindrical , homogeneous pores and complex Faraday-impedance

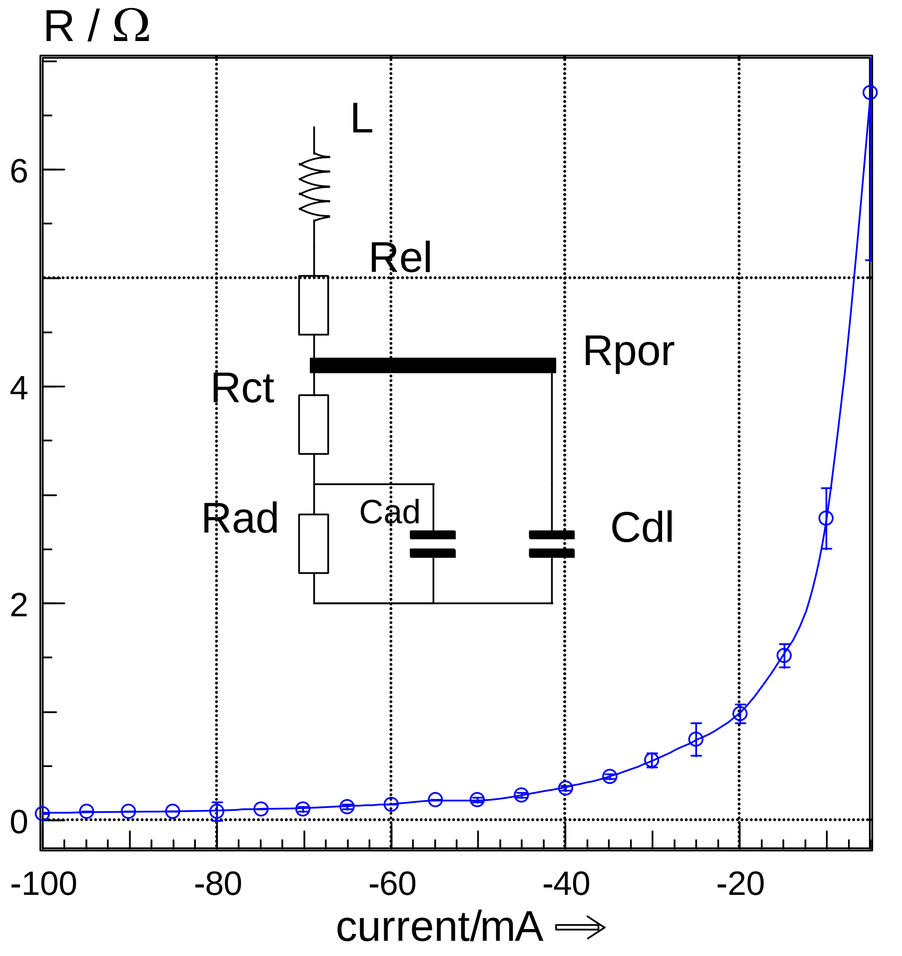


Zq=

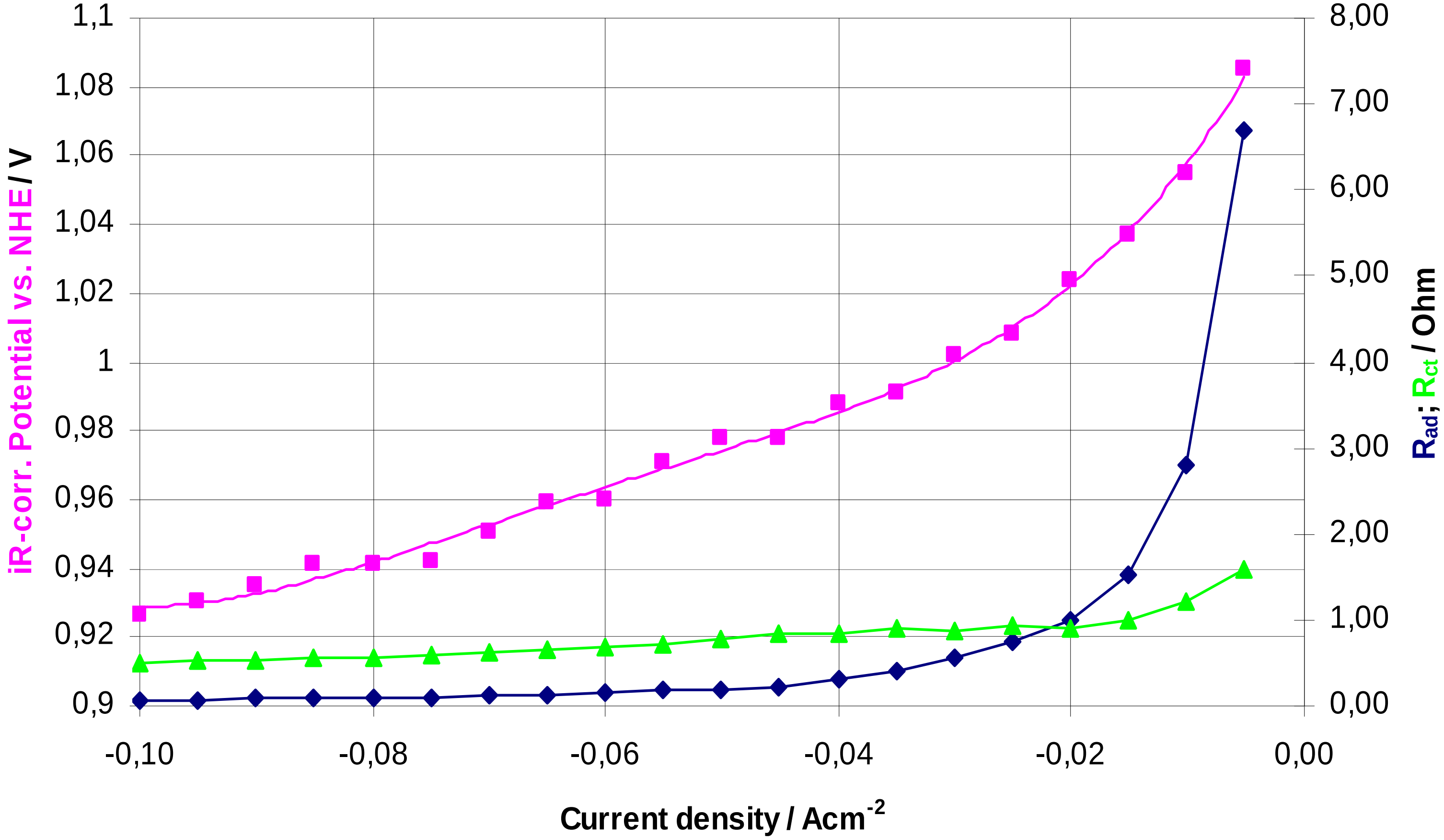




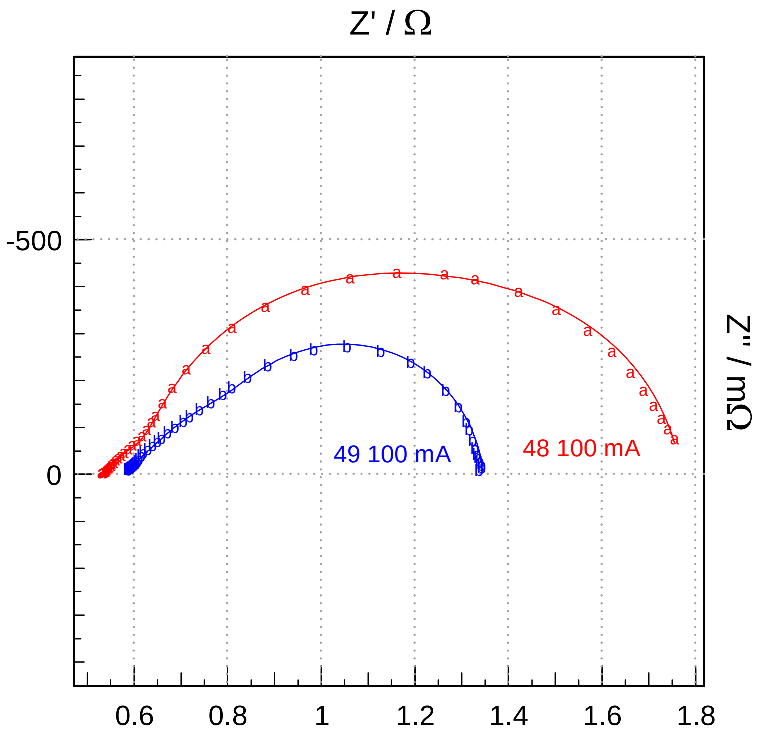
Evaluation of EIS measured during ORR Equivalent circuit and R_{ad} = f(i)

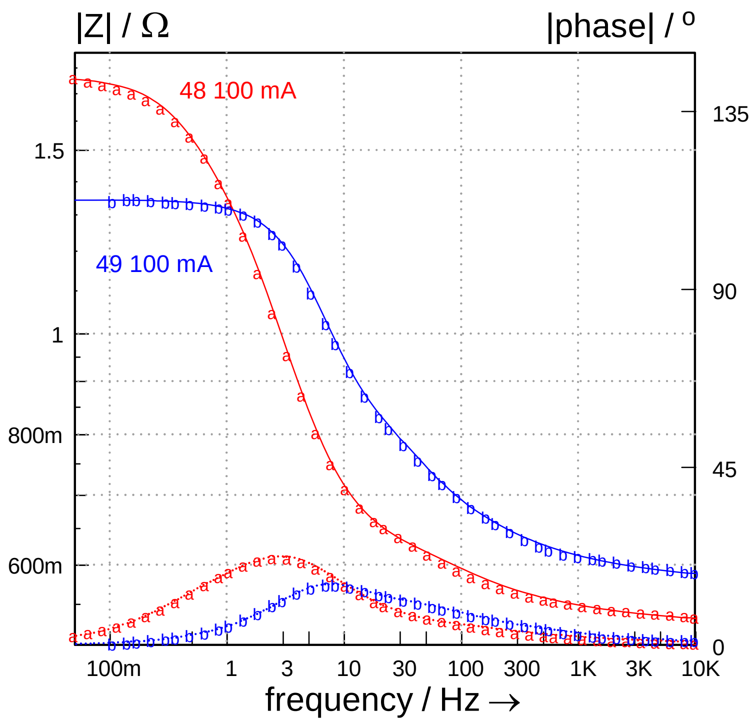


U-i characteristic and current density dependency of impedance elements R_{ad} and R_{ct}



Influence of compacting pressure: Evaluation of EIS measured during OCR, -100 mA, 80°C, 10 N NaOH





Sample	R_{ct}	R_{por}	R_{el}
48 (High pressure)	940Ω	287mΩ	524mΩ
49 (Low pressure)	534Ω	727mΩ	577mΩ

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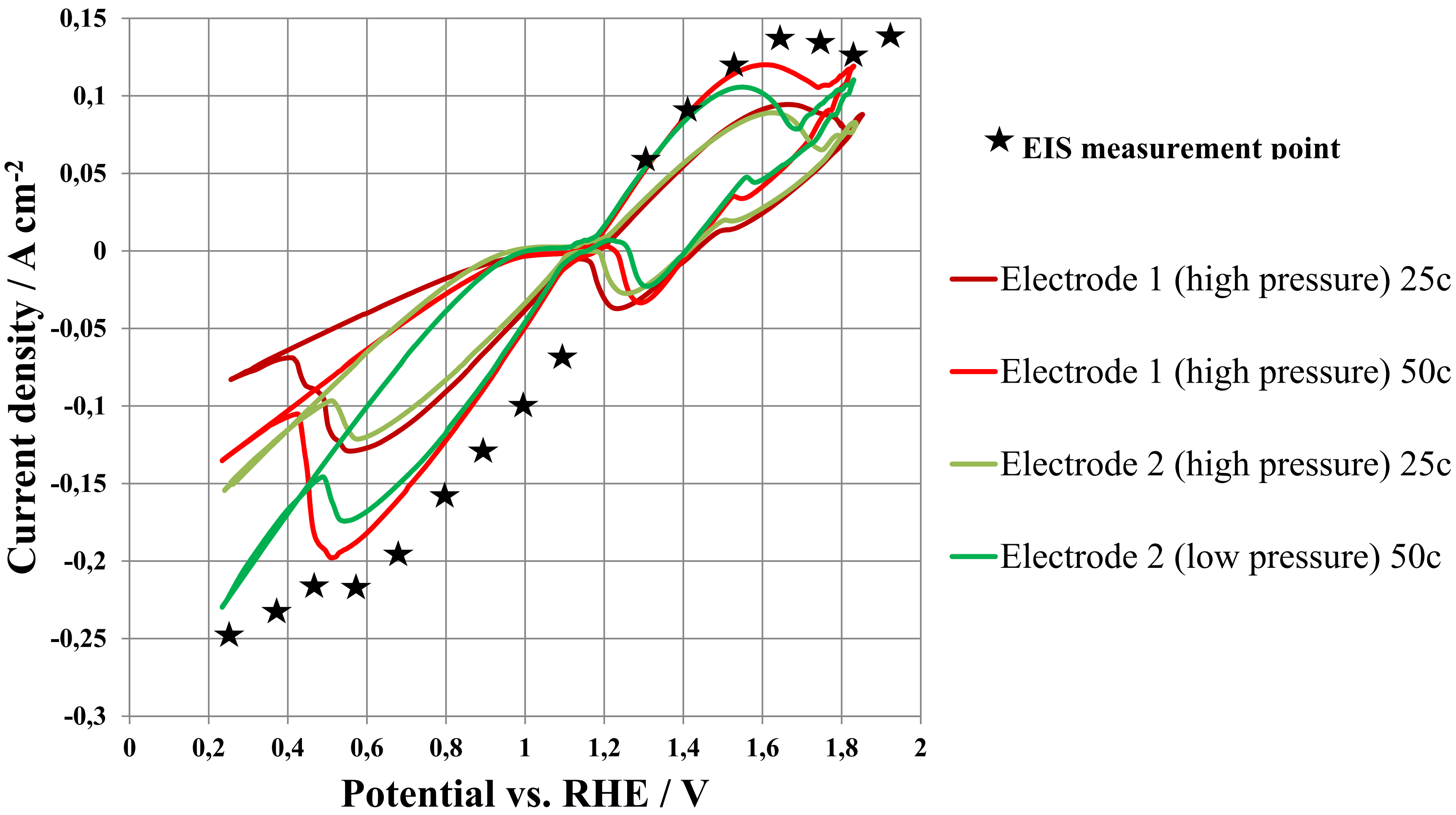
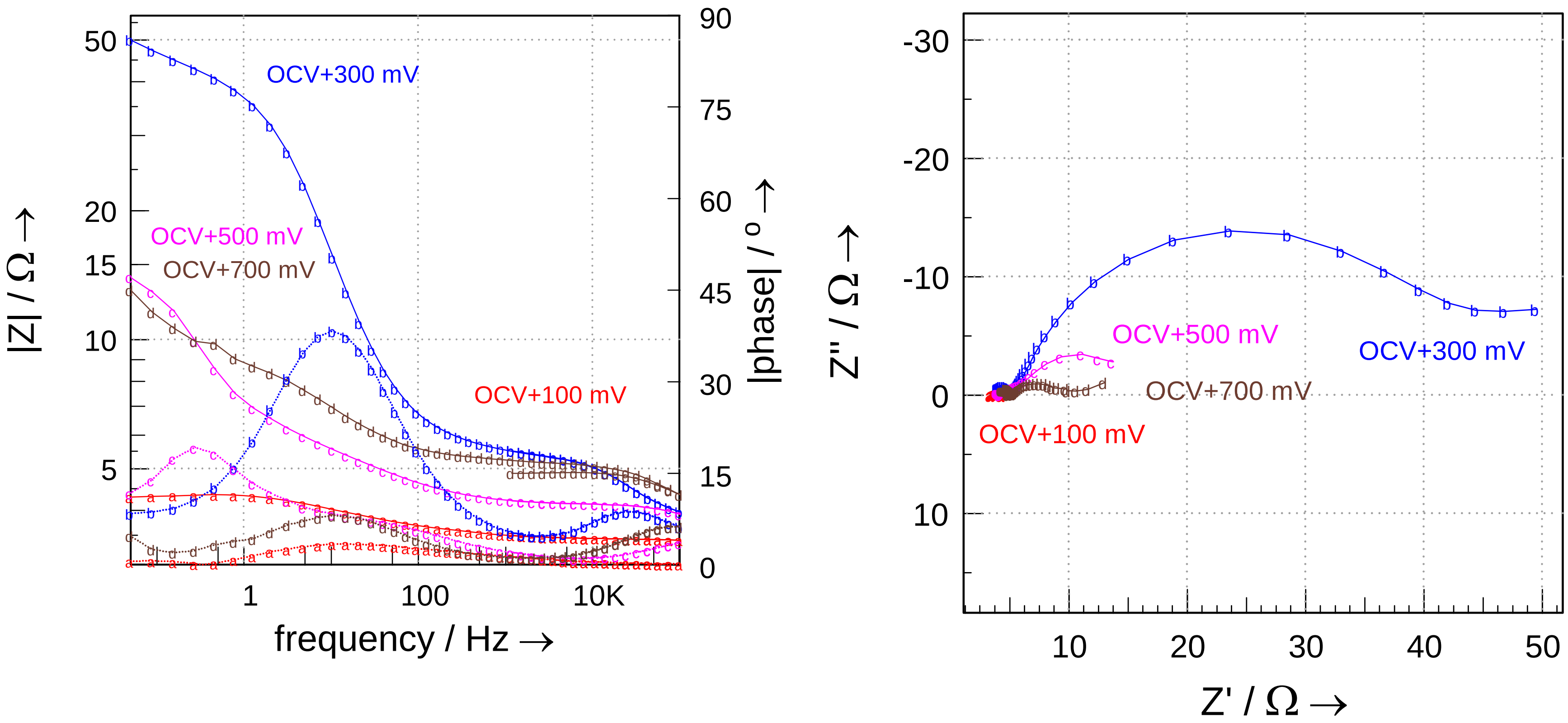
Overview EIS measurement points and CV with 1 mV/s at RT, 1 N LiOH , Ag-GDE



Impedance measurements during Oxygen evolution on Ag-GDE (high pressure), 1 N LiOH, 25°C



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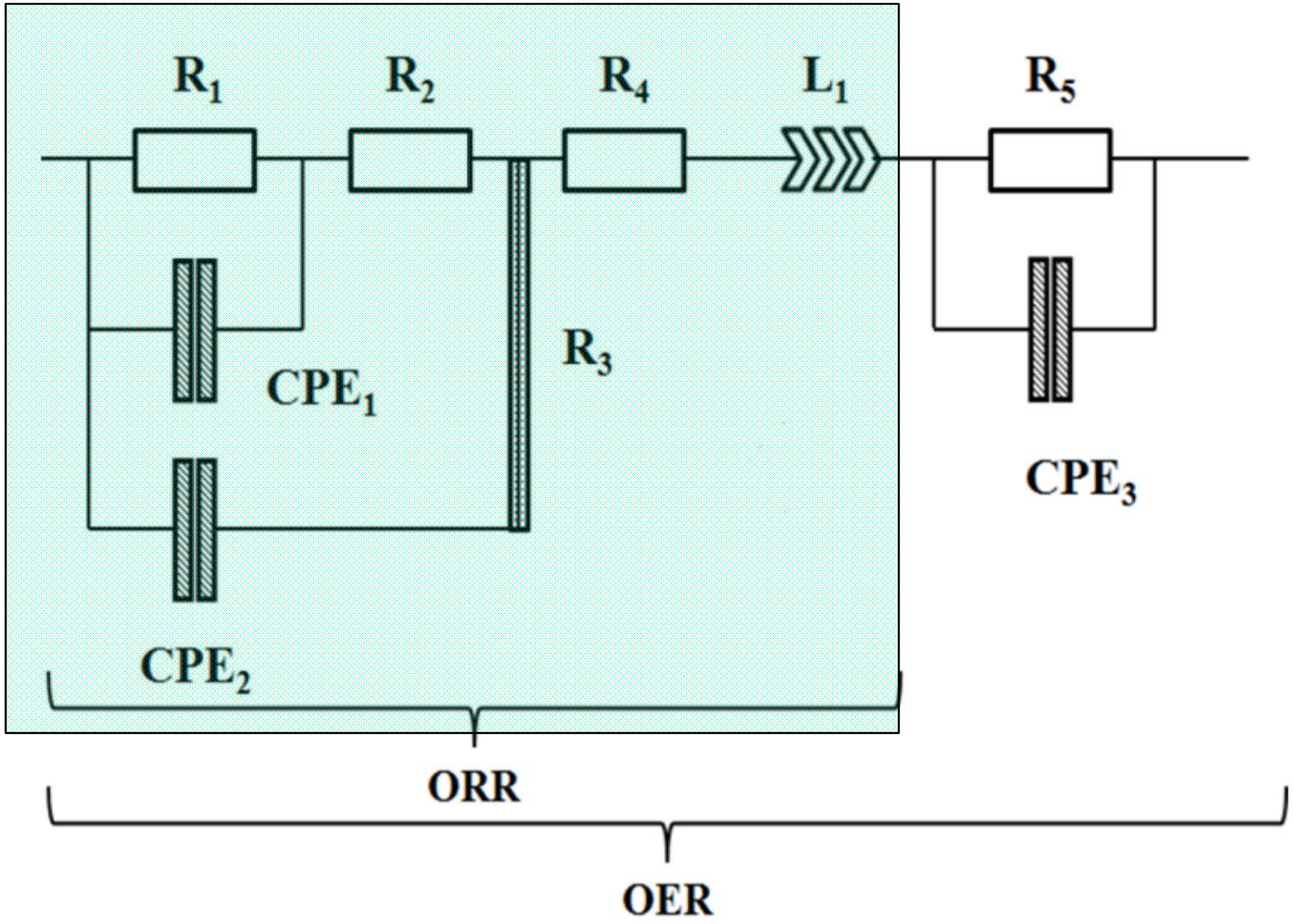
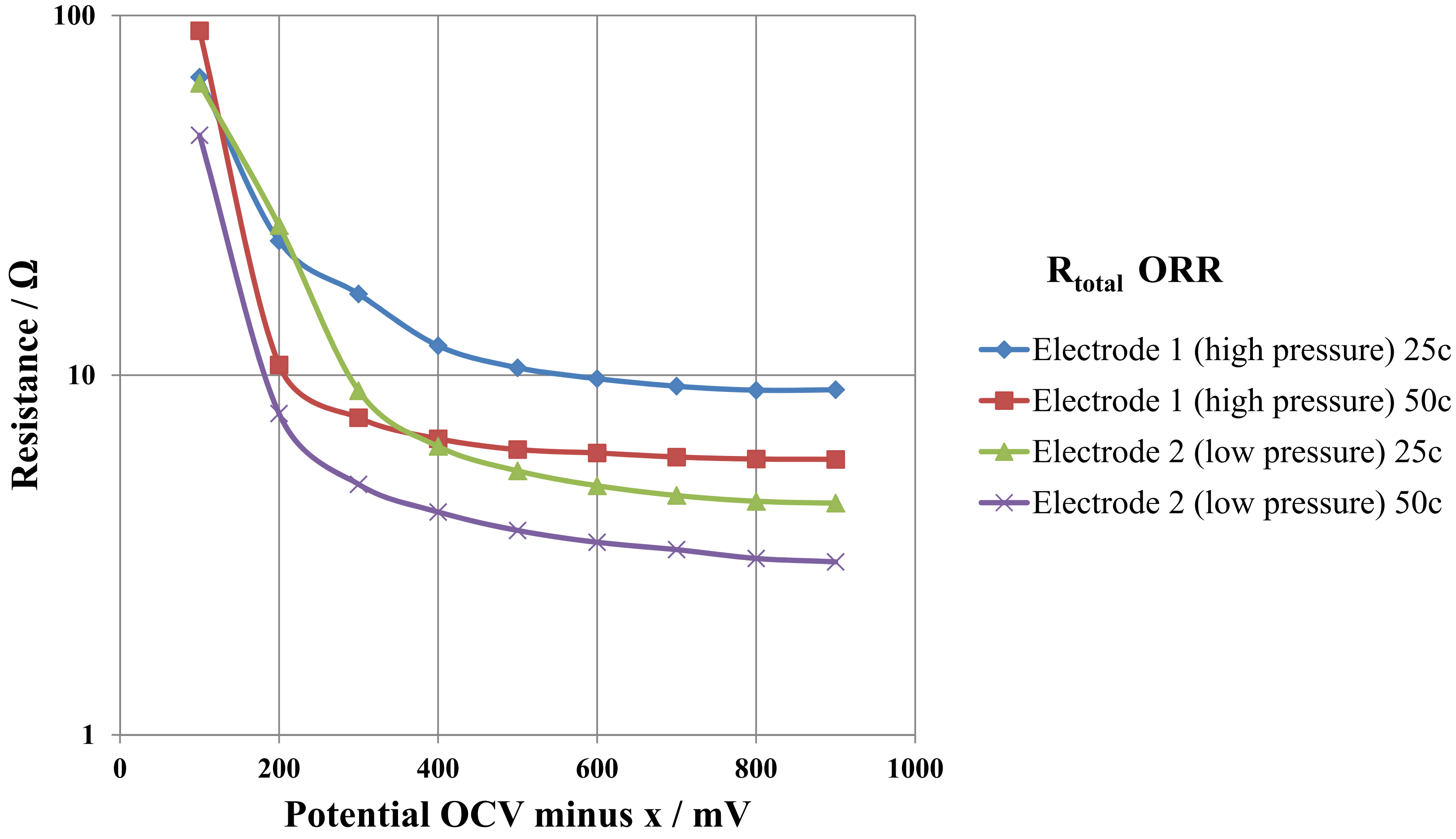
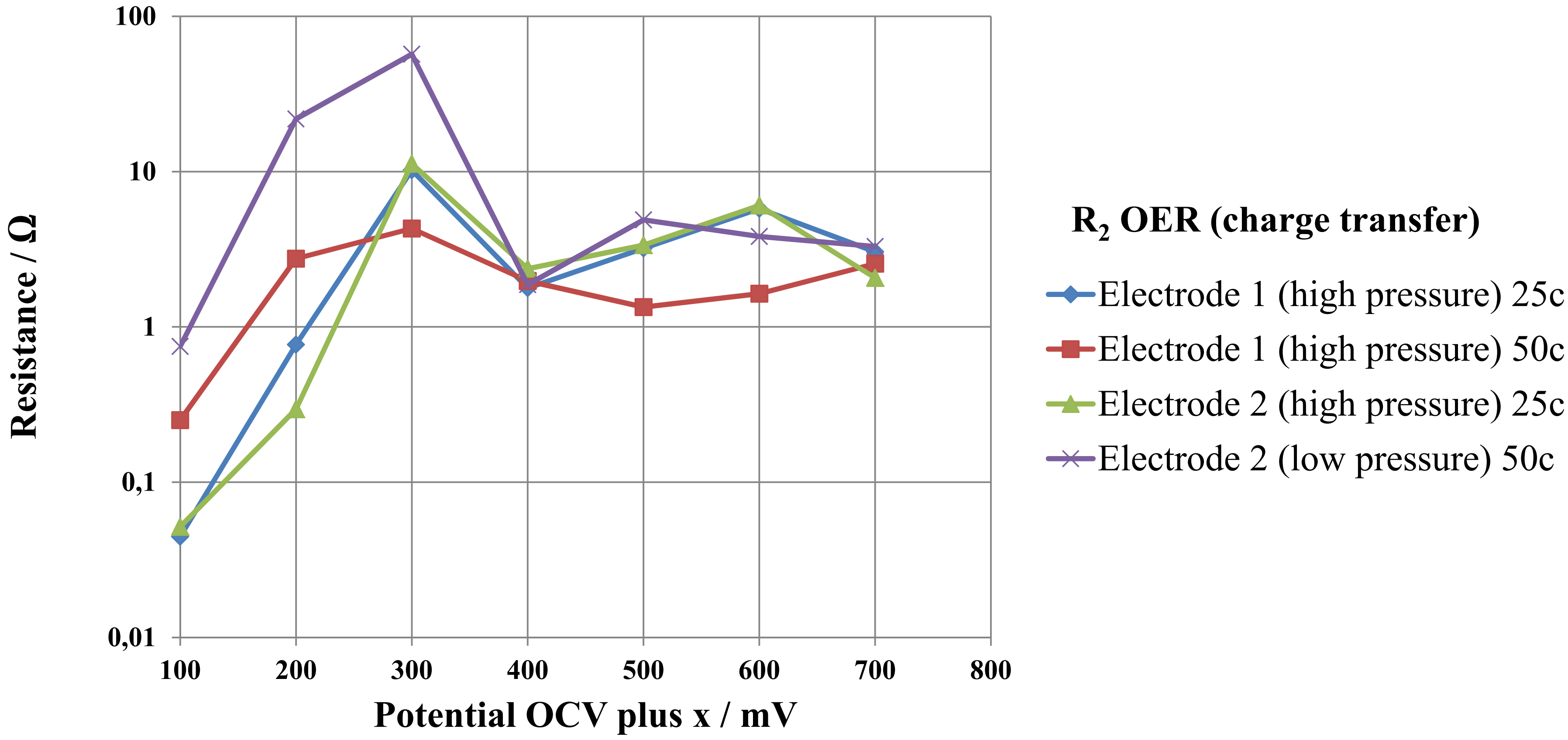
Equivalent circuit used for evaluation of EIS during OCR and OER at different electrodes for Lithium-Air batteries



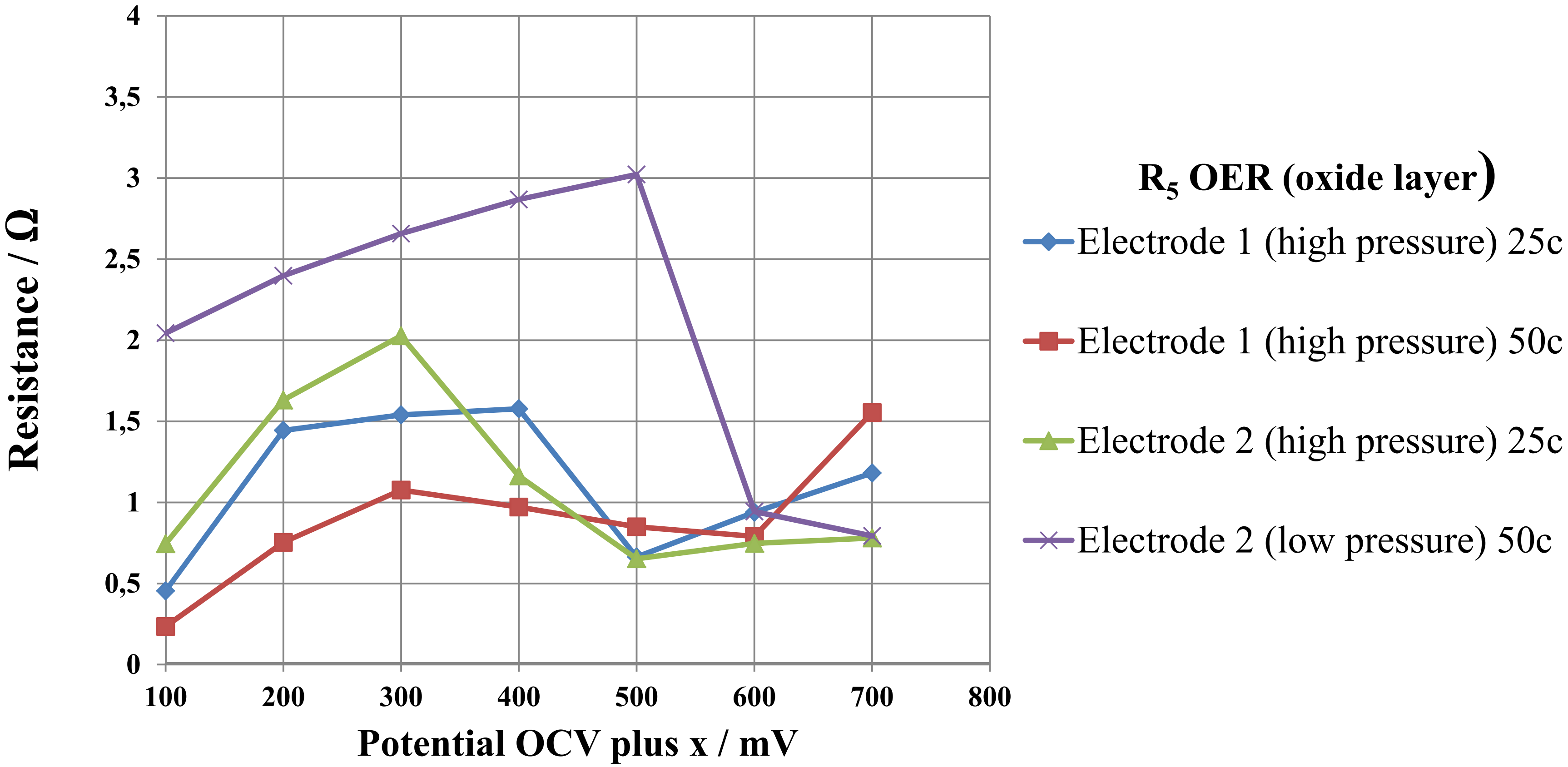
Potential dependency of total resistance during ORR at different electrodes, 1 N LiOH



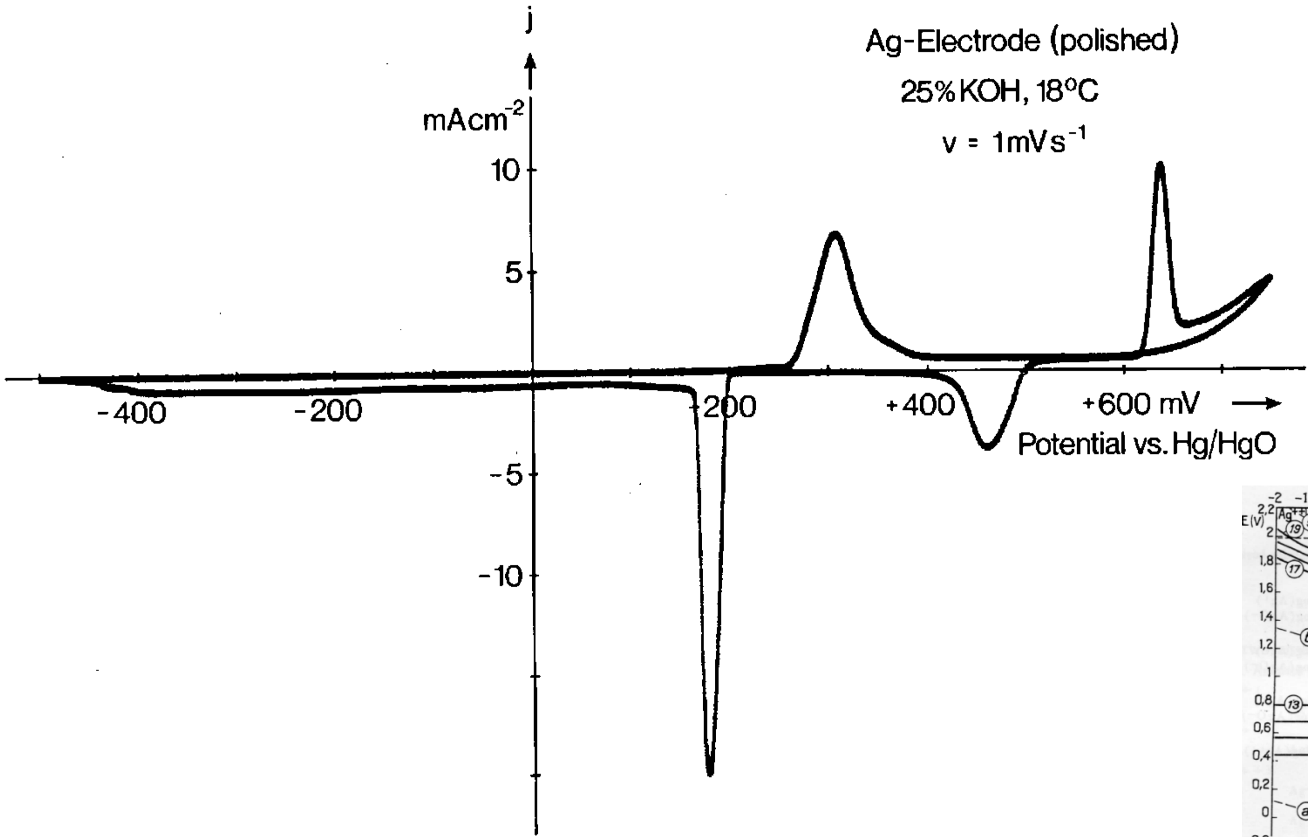
Potential dependency of charge transfer resistance during OER



Potential dependency of charge transfer resistance in oxide layer potential region (OER)



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



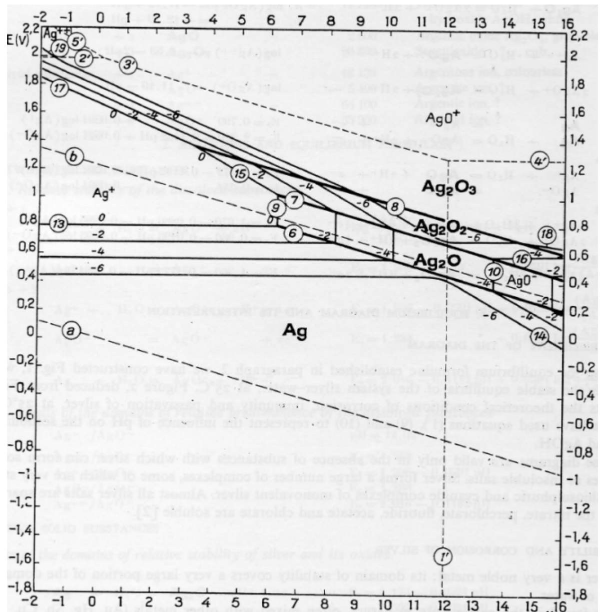


FIG. 1. Potential–pH equilibrium diagram for the system silver–water, at 25°C.

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Conclusion

- From the catalyst screening, a new bifunctionall catalysts system for the cathode of a Li-air battery was found
- 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
- Silver electrodes are not stable during OER

Thank you for your Attention !

Acknowledgment

Bundesministerium für Bildung und Forschung

luft li

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Reactions pathways for the cathodic oxygen reduction in alkaline solution

Direct-X $4e^-$ - path: $\mathbf{2H_2O + O_2 + 4e^- \rightarrow 4OH^-}$

$O_2 + 2M \leftrightarrow 2M\ldots O$

$2\,(M\ldots O + e^- \rightarrow MO^-)$

$2\,(MO^- + H_2O \leftrightarrow MOH + OH^-)$

$2\,(MOH + e^- \leftrightarrow OH^- + M)$

Peroxid - Path: $\mathbf{H_2O + O_2 + 2e^- \leftrightarrow HO_2^- + OH^-}$

$O_2 + M \leftrightarrow M\ldots O_2$

$M\ldots O_2 + e^- \rightarrow MO_2^-$

$MO_2^- + H_2O \leftrightarrow MHO_2 + OH^-$

$MHO_2 + e^- \leftrightarrow HO_2^- + M$

Peroxid-Reduction: $\mathbf{HO_2^- + H_2O + 2e^- \rightarrow 3OH^-}$

$HO_2^- + M \leftrightarrow MHO_2^-$

$MHO_2^- + H_2O \leftrightarrow MH_2O_2 + OH^-$

$MH_2O_2 + e^- \rightarrow MOH + OH^-$

$MOH + e^- \leftrightarrow M + OH^-$

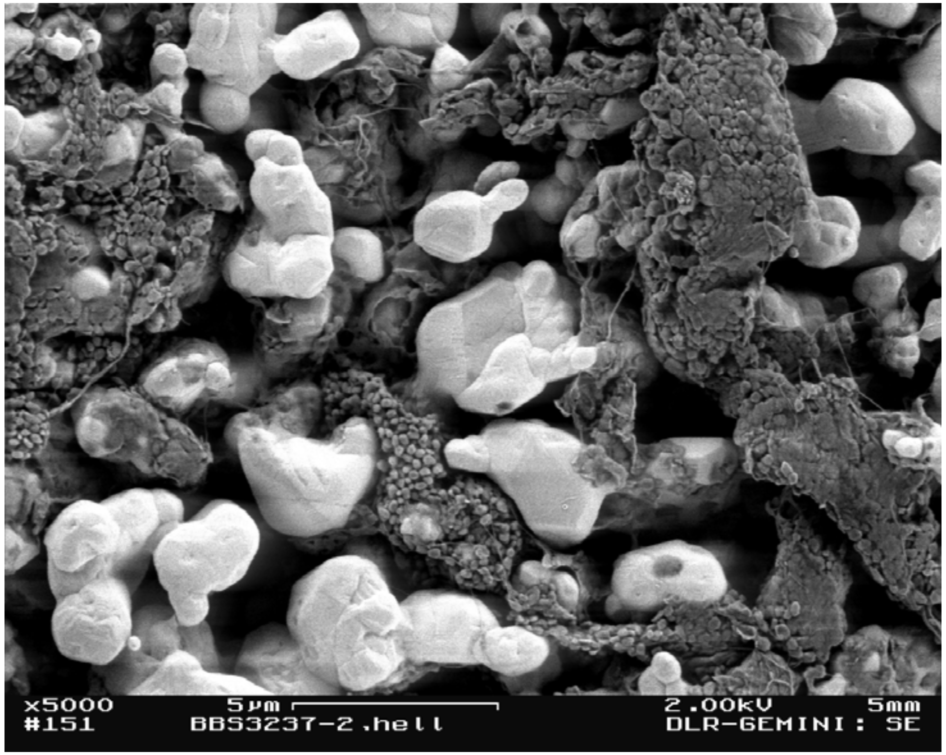
Catalytically Peroxid-decomposition: $\mathbf{2HO_2^- \rightarrow O_2 + 2OH^-}$

$HO_2^- + M \leftrightarrow MHO_2^-$

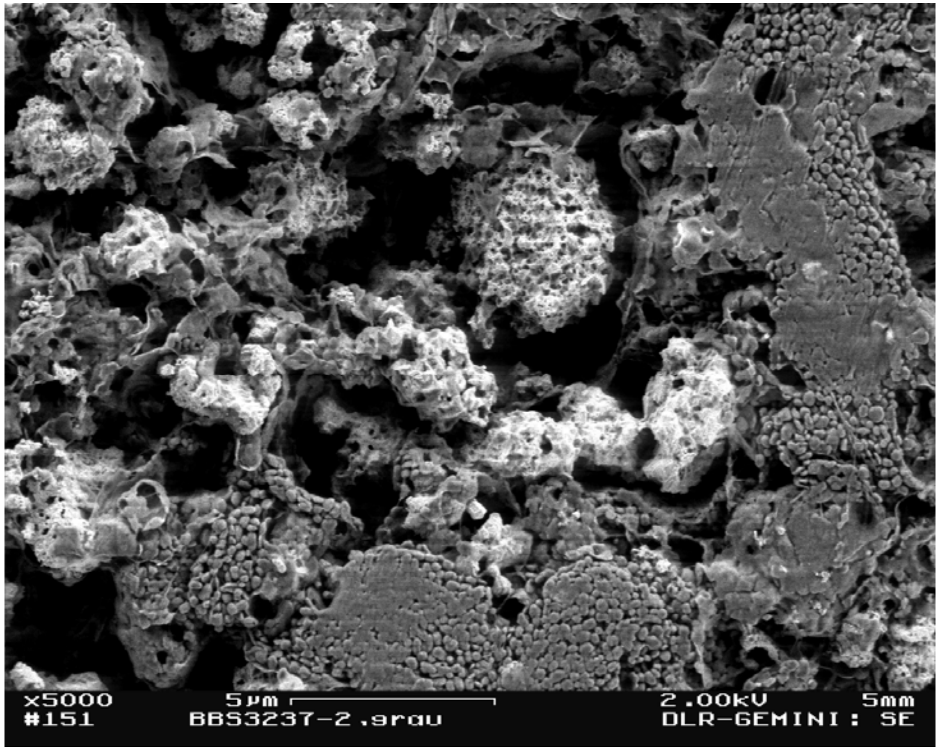
$MHO_2^- \rightarrow MO + OH^-$

$MO + HO_2^- \rightarrow O_2 + OH^- + M$

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



Ag-GDE, unused part



Ag-GDE, used