# State of the Art of Batteries of the 4th Generation

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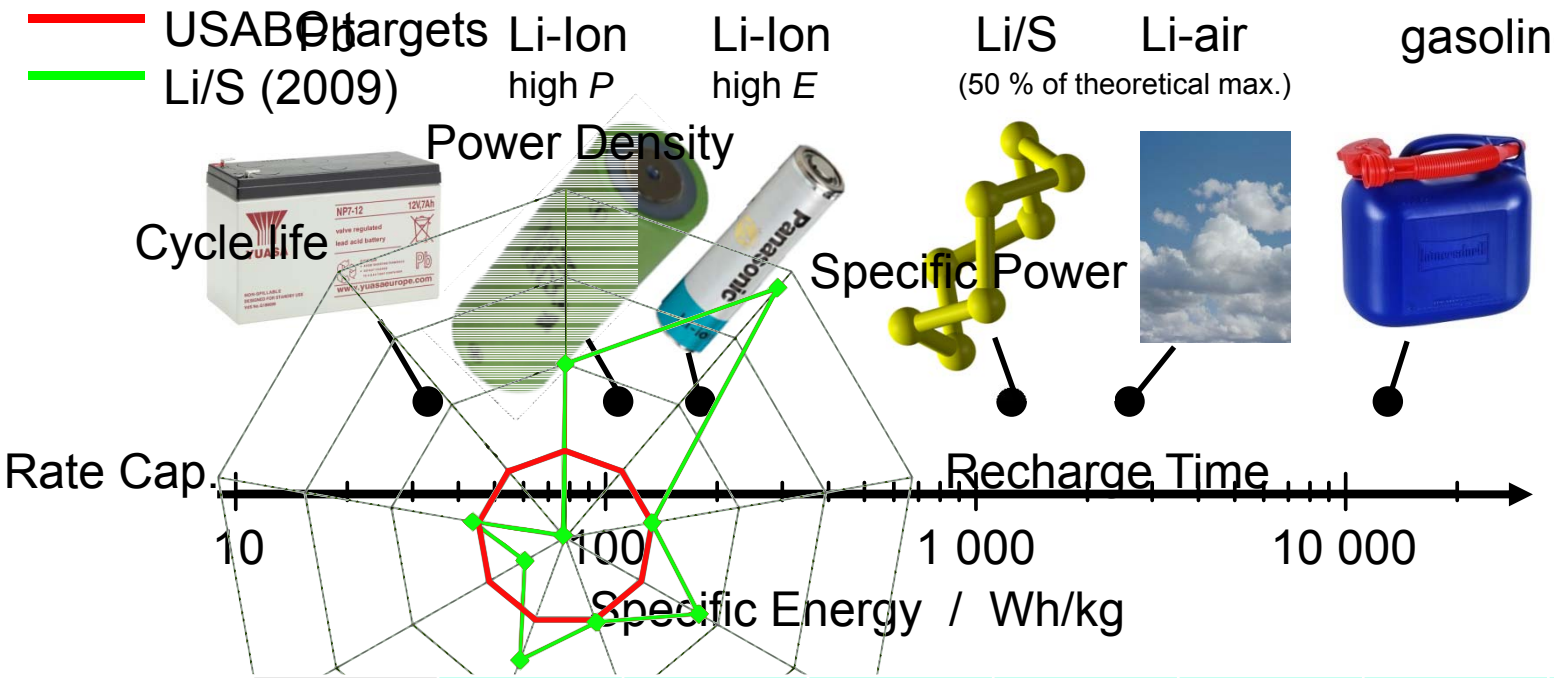
8th International Workshop on Impedance Spectroscopy (IWIS)
23-25 September, Chemnitz, Germany

# Presentation outline

- Introduction and motivation
  - Definition 4th generation batteries
  - Examples of batteries and applications
- Metal-Sulfur Batteries
  - Li-Sulfur and Mg-Sulfur Batteries
  - Production technique
  - Characterization
- Metal-Air Batteries
  - Li-Air and Zn-Air Batteries
  - Production techniques at the DLR
  - Characterization
- Outlook

# Novel Battery Concepts – Specific Energy Potentials



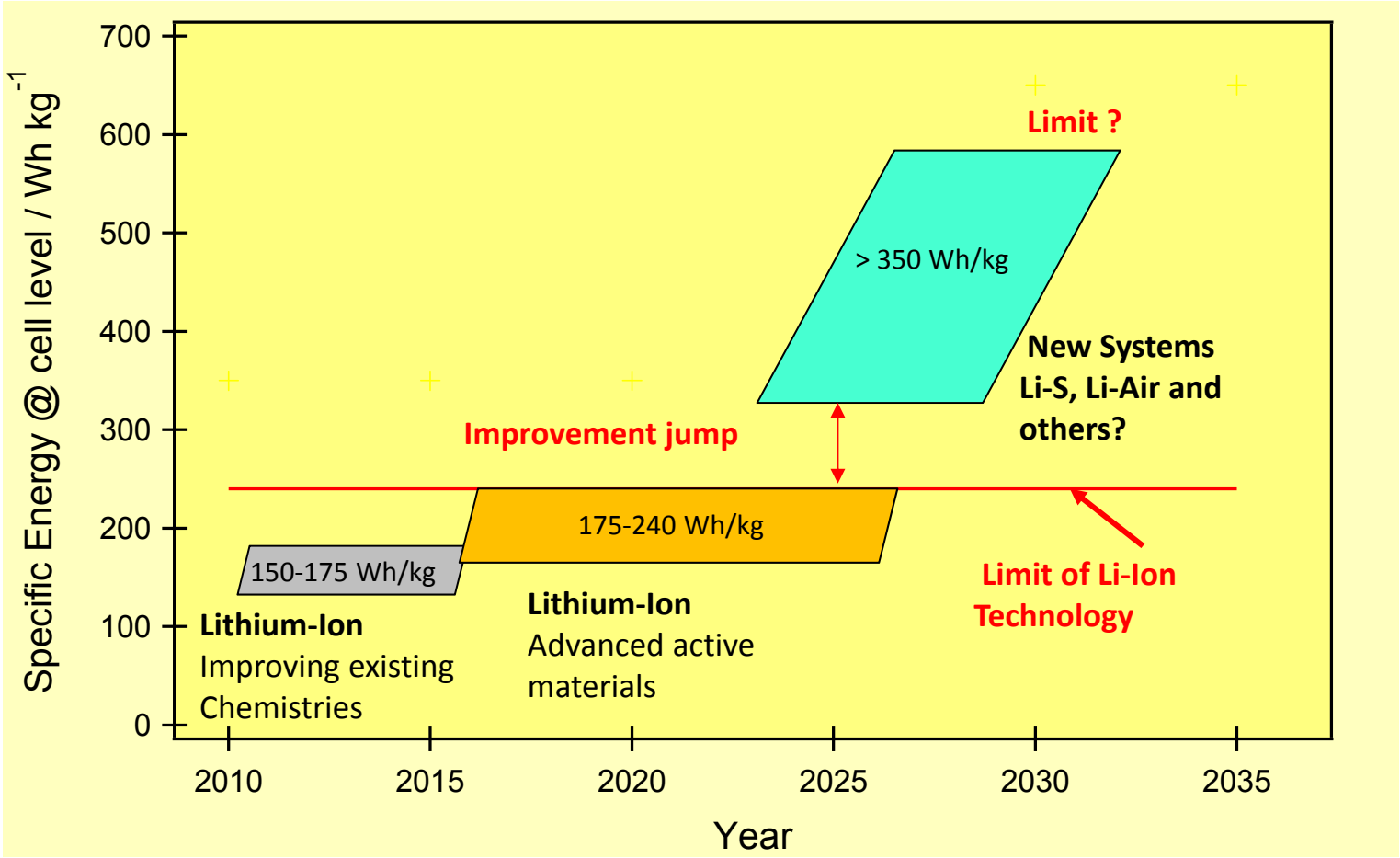

Upper T

| Chemistry | Cell size | Wh/L *theory | Wh/L actual | % achieved | Wh/kg *theory | Wh/kg actual | % achieved |
|---|---|---|---|---|---|---|---|
| $LiFePO_4$ | 54208 | 1980 | 292 | 14.8 | 587 | 156 | 26.6 |
| $LiFePO_4$ | 16650 | 1980 | 223 | 11.3 | 587 | 113 | 19.3 |
| $LiMn_2O_4$ | 26700 | 2060 | 296 | 14.4 | 500 | 109 | 21.8 |
| $LiCoO_2$ | 18650 | 2950 | 570 | 19.3 | 1000 | 250 | 25 |
| Si-$LiMO_2$ Panasonic | 18650 | 2950 | 919 | 31.2 | 1000 | 252 | 25.2 |

ation, 2009.

DLR

# Technical Progress: Improvement of Energy Density

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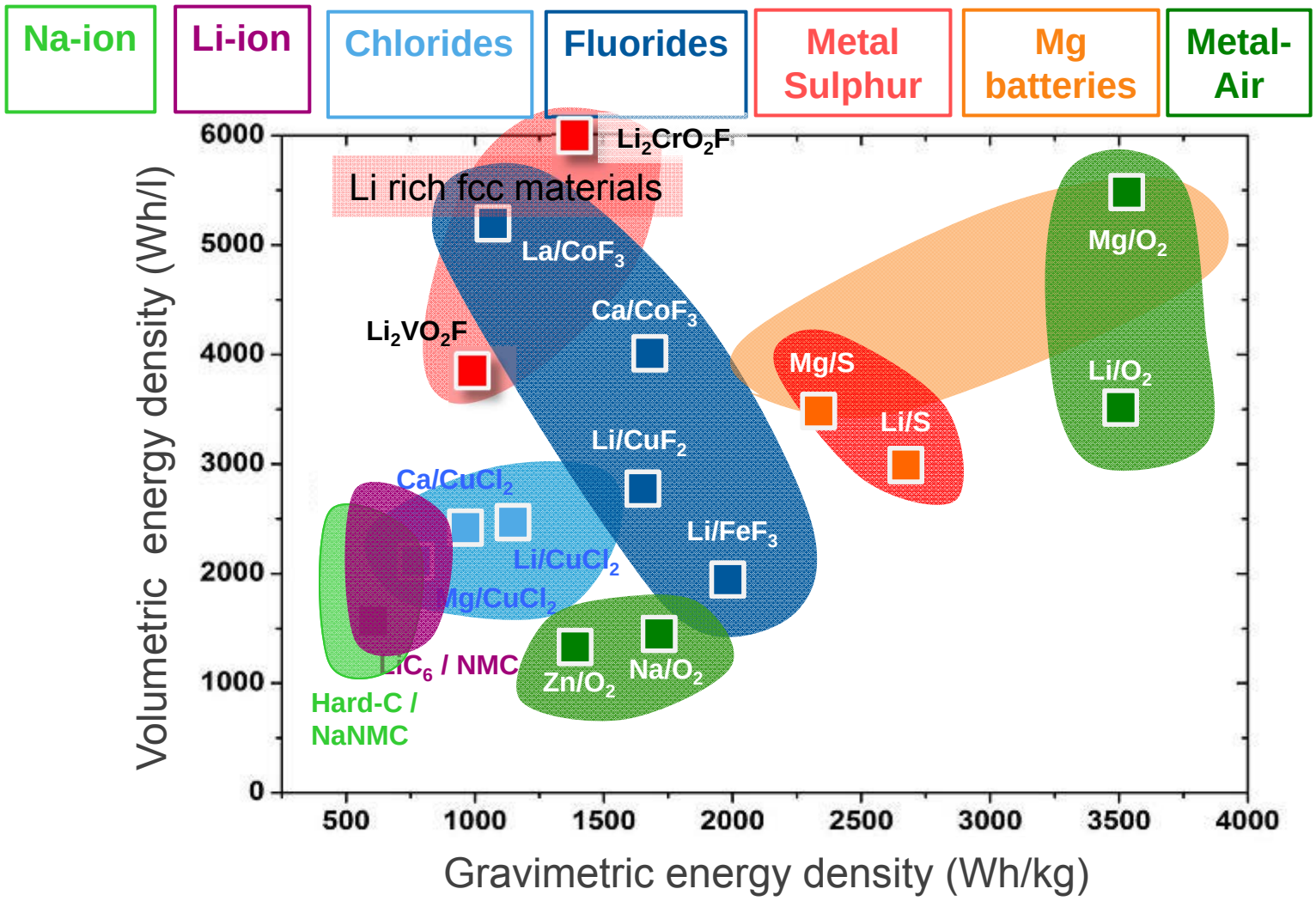
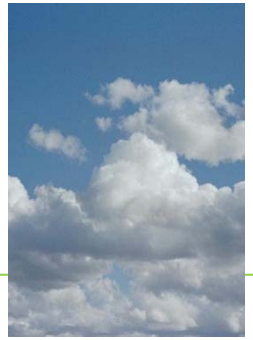

Na-ion
Li-ion
Chlorides
Fluorides
Metal Sulphur
Mg batteries
Metal-Air
Li rich fcc materials
$Li_2CrO_2F$
$La/CoF_3$
$Ca/CoF_3$
$Li_2VO_2F$
$Li/CuF_2$
$Li/FeF_3$
Mg/S
Li/S
$Mg/O_2$
$Li/O_2$
$Ca/CuCl_2$
$Li/CuCl_2$
$Mg/CuCl_2$
$LiC_6$ / NMC
Hard-C / NaNMC
$Zn/O_2$
$Na/O_2$
Volumetric energy density (Wh/l)
Gravimetric energy density (Wh/kg)
0
1000
2000
3000
4000
5000
6000
500
1000
1500
2000
2500
3000
3500
4000

DLR

# Chemistry of Fuel Cells and Batteries

$2H_2 + O_2 \rightarrow 2H_2O$



| 1 | | | | | | | | | | | | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 H 1.008 | 2 | | | | | | | | | | | | | | | | 2 He 4.0026 |
| 3 Li 6.94 | 4 Be 9.0122 | | | | | | | | | | | 5 B 10.81 | 6 C 12.011 | 7 N 14.007 | 8 O 15.999 | 9 F 18.998 | 10 Ne 20.180 |
| 11 Na 22.990 | 12 Mg 24.305 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 Al 26.982 | 14 Si 28.085 | 15 P 30.974 | 16 S 32.06 | 17 Cl 35.45 | 18 Ar 39.948 |
| 19 K 39.098 | 20 Ca 40.078 | 21 Sc 44.956 | 22 Ti 47.867 | 23 V 50.942 | 24 Cr 51.996 | 25 Mn 54.938 | 26 Fe 55.845 | 27 Co 58.933 | 28 Ni 58.693 | 29 Cu 63.546 | 30 Zn 65.38 | 31 Ga 69.723 | 32 Ge 72.63 | 33 As 74.922 | 34 Se 78.96 | 35 Br 79.904 | 36 Kr 83.798 |
| 37 Rb 85.468 | 38 Sr 87.62 | 39 Y 88.906 | 40 Zr 91.224 | 41 Nb 92.906 | 42 Mo 95.96 | 43 Tc (98) | 44 Ru 101.07 | 45 Rh 102.91 | 46 Pd 106.42 | 47 Ag 107.87 | 48 Cd 112.41 | 49 In 114.82 | 50 Sn 118.71 | 51 Sb 121.76 | 52 Te 127.60 | 53 I 126.90 | 54 Xe 131.29 |
| 55 Cs 132.91 | 56 Ba 137.33 | 57-71 * | 72 Hf 178.49 | 73 Ta 180.95 | 74 W 183.84 | 75 Re 186.21 | 76 Os 190.23 | 77 Ir 192.22 | 78 Pt 195.08 | 79 Au 196.97 | 80 Hg 200.59 | 81 Tl 204.38 | 82 Pb 207.2 | 83 Bi 208.98 | 84 Po (209) | 85 At (210) | 86 Rn (222) |
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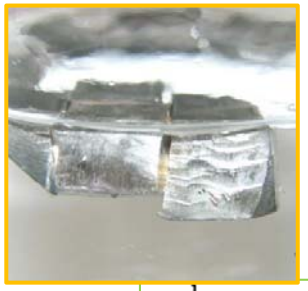
← Heavy Light →

Electropositive

Electronegative

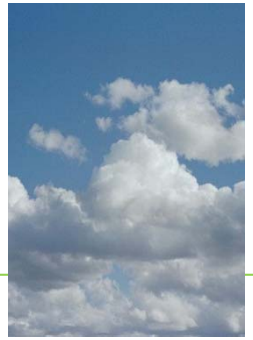
DLR

# Chemistry of Fuel Cells and Batteries



$2H_2 + O_2 \rightarrow 2H_2O$

$2Li + O_2 \rightarrow Li_2O\ (Li_2O_2),\ LiOH$



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← Heavy Light →

Electropositive

Electronegative

DLR

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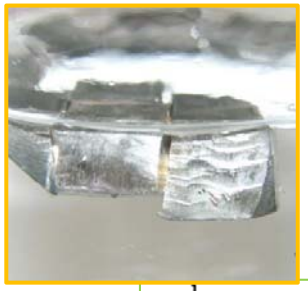
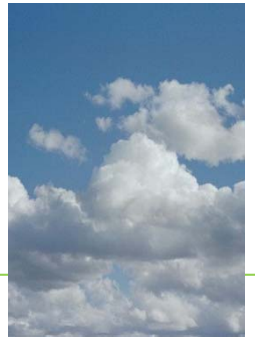


$2H_2 + O_2 \rightarrow 2H_2O$

$2Li + O_2 \rightarrow Li_2O\ (Li_2O_2)$, LiOH

$16Li + S_8 \rightarrow 8Li_2S$

$8Mg + S_8 \rightarrow 8MgS$



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← Heavy Light →

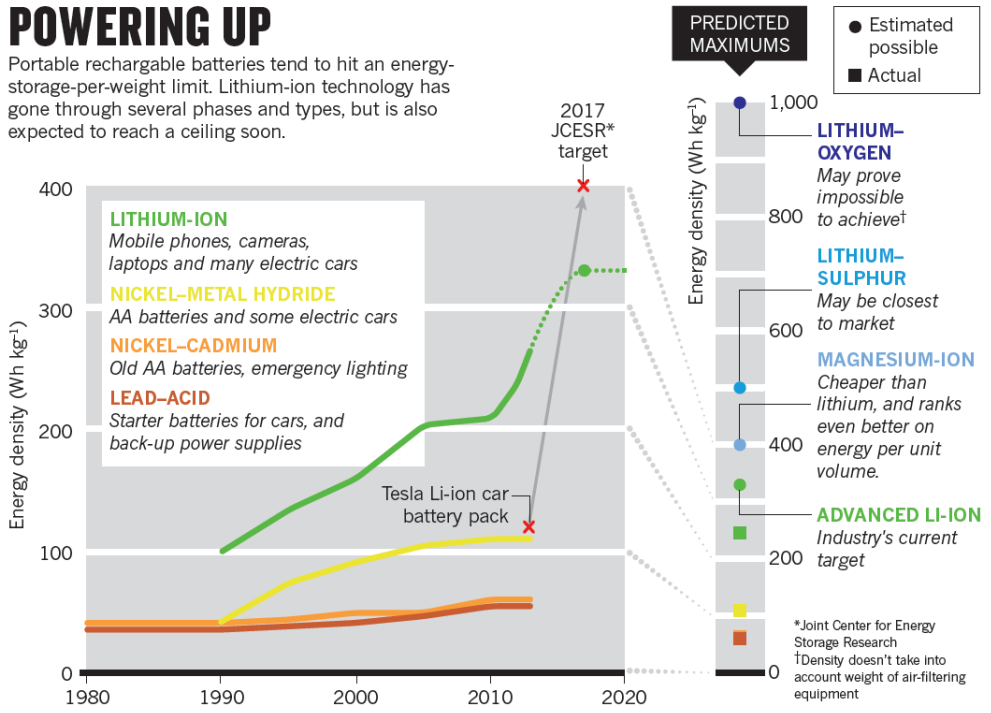
Electropositive

Electronegative

# Activities of the „Batterietechnik“ team at DLR

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

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




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

# Metal-Sulfur Batteries

# Metal-Sulfur Batteries: Overview

| Electrochemical Reaction | ΔG | Voltage | Capacity (Cathode) | Energy density | |
|---|---|---|---|---|---|
| | kJ/mol | V | mAh/g | Wh/kg | Wh/L |
| $Mg + S \leftrightarrow MgS$ | -341.8 | 1.771 | 1672 | 1684 | 3221 |
| $2Li + S \leftrightarrow Li_2S$ | -439.0 | 2.275 | 1672 | 2654 | 2856 |
| $2Na + 3S \leftrightarrow Na_2S_3$ | -405.2 | 2.100 | 558.4 | 791.7 | 1179 |
| $2Al + 3S \leftrightarrow Al_2S_3$ | -213.3 | 1.106 | 1672 | 1184 | 2676 |
| $Zn + S \leftrightarrow ZnS$ | -201.3 | 1.043 | 1672 | 573.6 | 2162 |
| $CoO_2 + LiC_6 \leftrightarrow LiCoO_2 + C_6$ | -347.4 | 3.600 | 273.8 | 567.8 | 1901 |

# Metal-Sulfur Batterie- Summary

| Electrochemical Reaction | ΔG | Voltage | Capacity (Cathode) | Energy density | |
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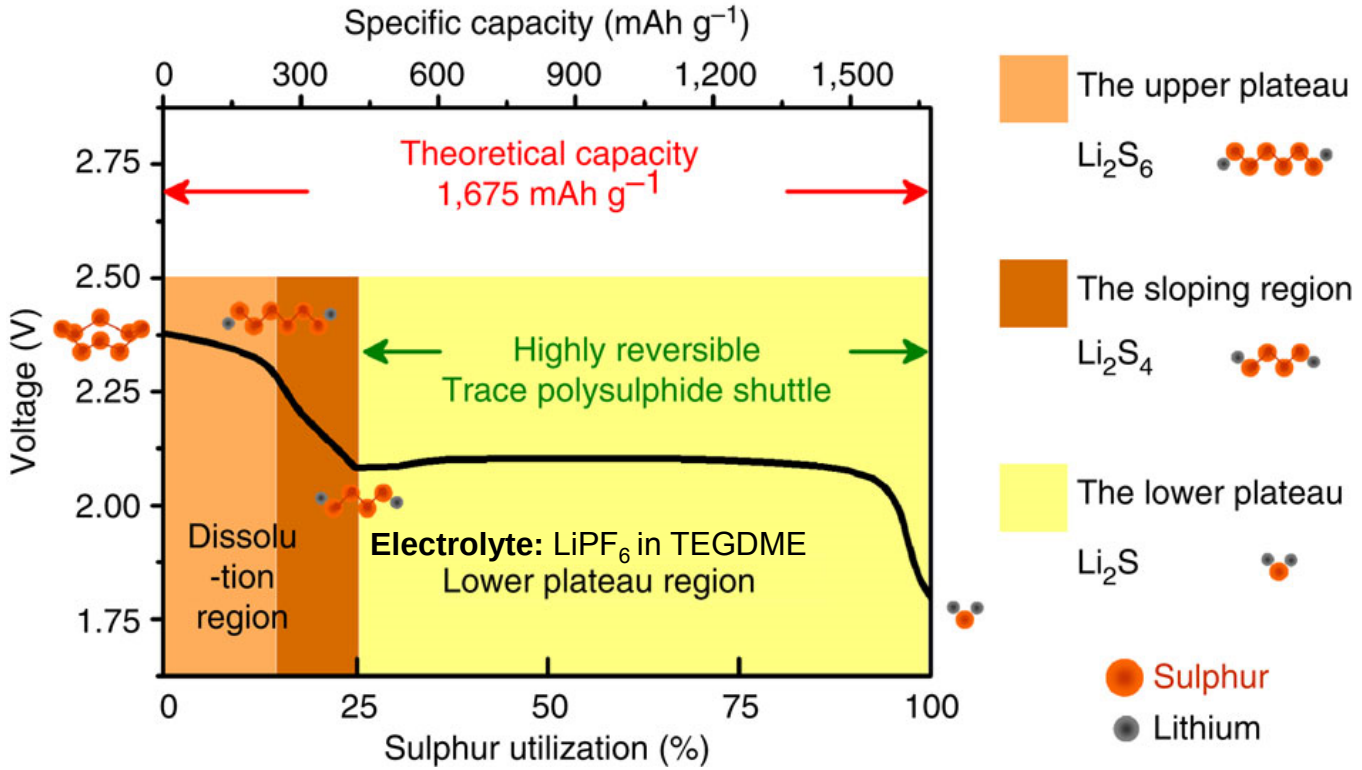
# Lithium-Sulfur Battery: Electrochemistry



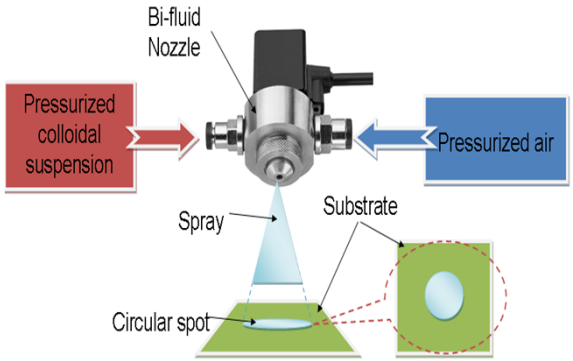

📖 **Y.-S. Su *et al.*, Nature (2013)**

Polysulfides ($Li_2S_x$) are intermediates in the transition of $S_8$ to $S^{2-}$

- gradual dissolution of sulfur form the cathode
- Self-discharge
- Different voltage plateaus

# Cathode production technique at DLR-TT

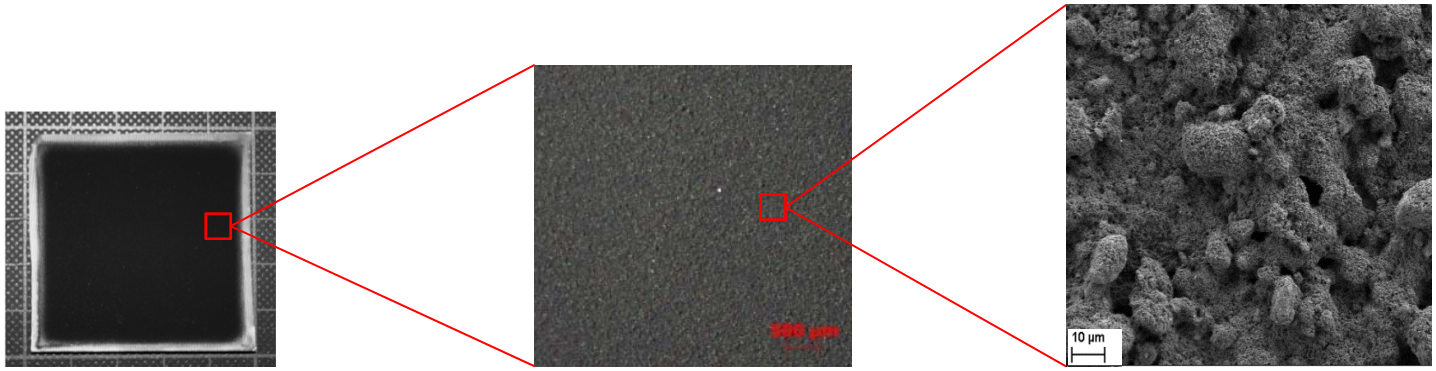
## Suspension–spray machine




- Nozzle with extern mixing of air and suspension
- Cathode mixture: Sulfur or Sulfur/Carbon composite, Carbon Black and PVDF (50:40:10, wt.%).

  Solvents: Ethanol and DMSO

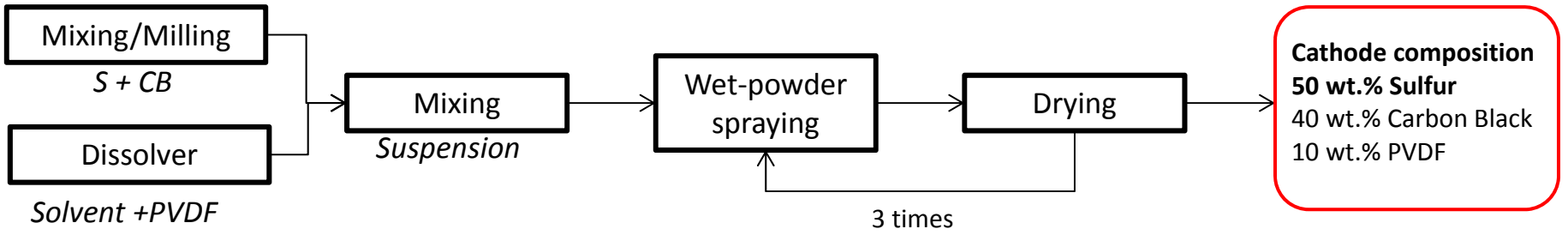
**Sprayed cathode**

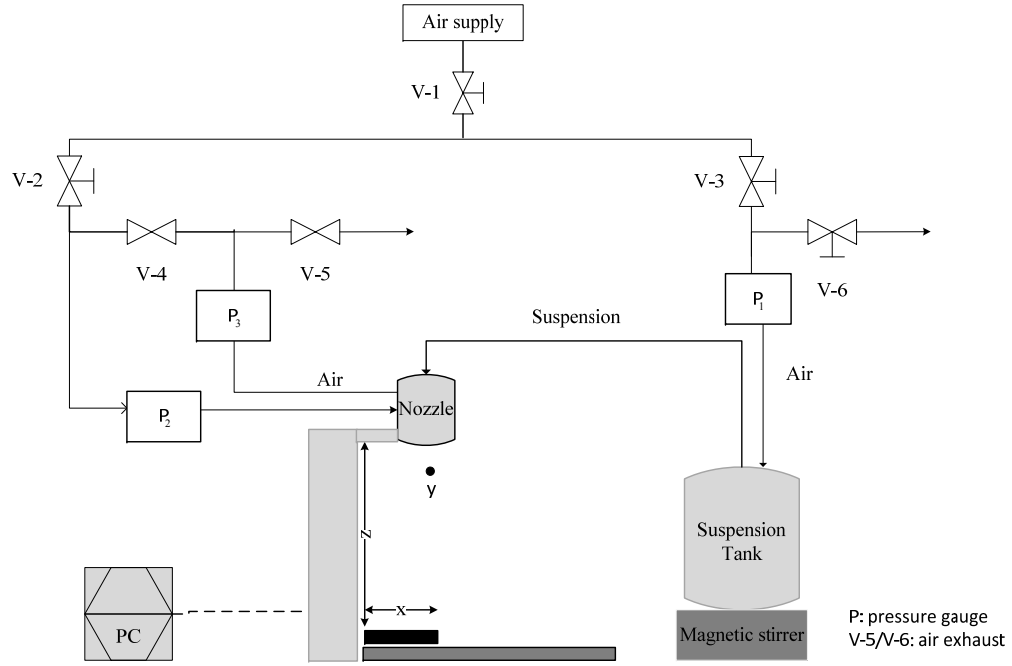



5 x 5 cm²

DLR

# Wet powder spraying for electrode fabrication




Air-atomizing external mixing nozzle controlled by a 3D axis robot

The axis with the nozzle moves in perpendicular direction (y) to the substrate holder

# Influence of cathode fabrication

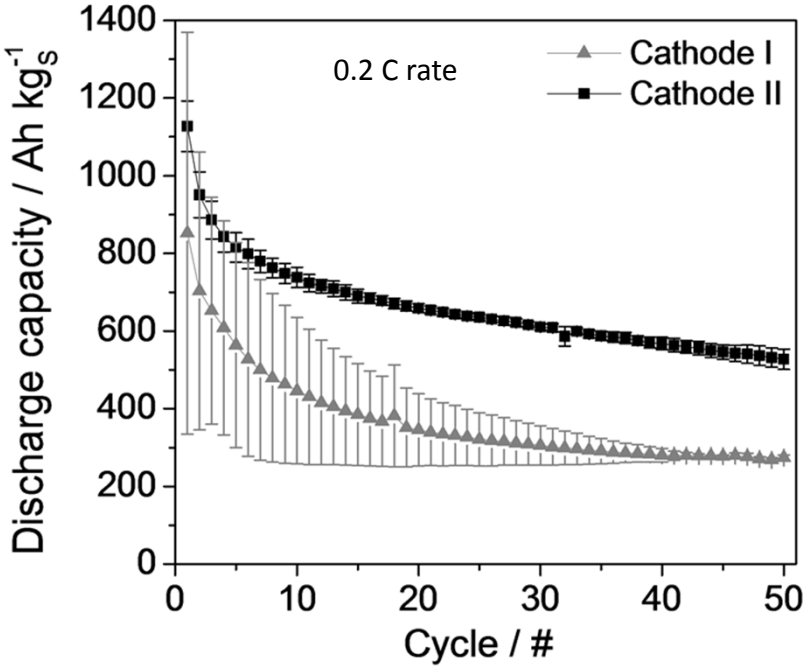
| Mixing/Milling | Coating | Drying |
|---|---|---|
| | Initial procedure (Cathode I) | |
| Roll mixer‡<br>1) Mix of S, CB and PVDF (5 rpm, t= 12 h)<br>2) Mix with solvents† (5 rpm, t= 12 h) | Suspension spray<br>– Internal mixing nozzle<br>– Coating in one step<br>– Heating plate under substrate (100 °C) | In vacuum oven<br>80 °C (48 h) |
| | New procedure (Cathode II) | |
| Tumbling mixer‡<br>1) Mix of S and CB (20 rpm, t= 24 h)<br>2) Dissolution of PVDF in solvents† (magnet stirring)<br>3) Mix of S and CB with dissolution (2) (20 rpm, t = 24 h) | Suspension spray<br>– External mixing nozzle<br>– Coating in 3 steps or more<br>– No heating plate<br>– Drying between each sprayed layer | In vacuum oven<br>Between sprayed layers, 60 °C (1.5-3 h)<br>At the end of coating: 60 °C (24 h)<br>In vacuum in the glove box |

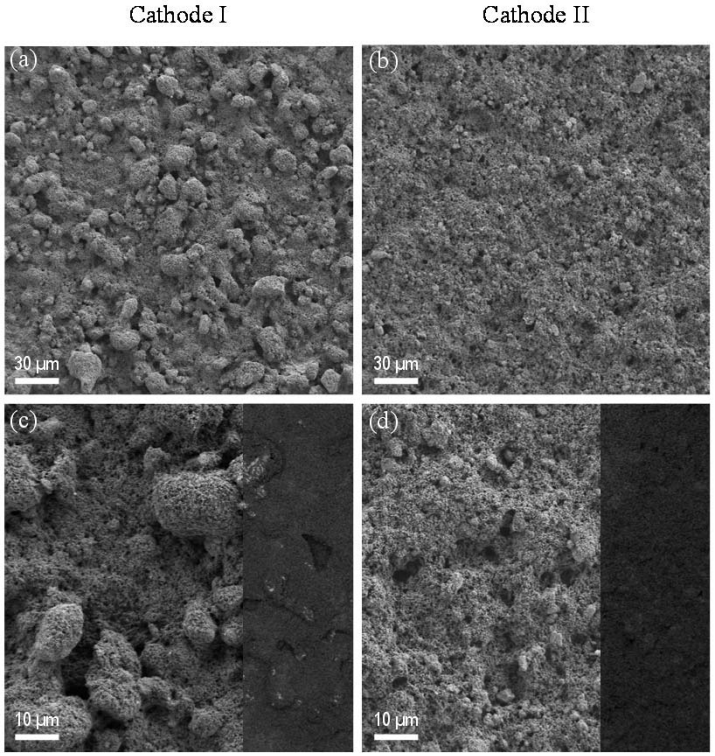
†Solvents: Ethanol/DMSO (50:50 wt.%). ‡In both cases ceramic balls were added in the mixing tank.

N.A. Cañas, A.L.P. Baltazar, M.A.P. Morais, T.O. Freitag, N. Wagner, K.A. Friedrich, *Electrochim. Acta*, **157** (2015) 351-358

# Influence of cathode fabrication

**Cathode I ▸▸▸ Cathode II**



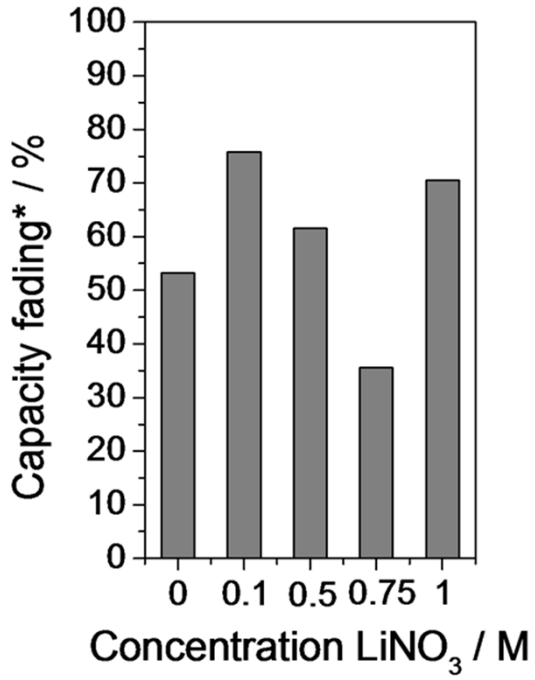

Optimization of suspension spraying and mixing processes

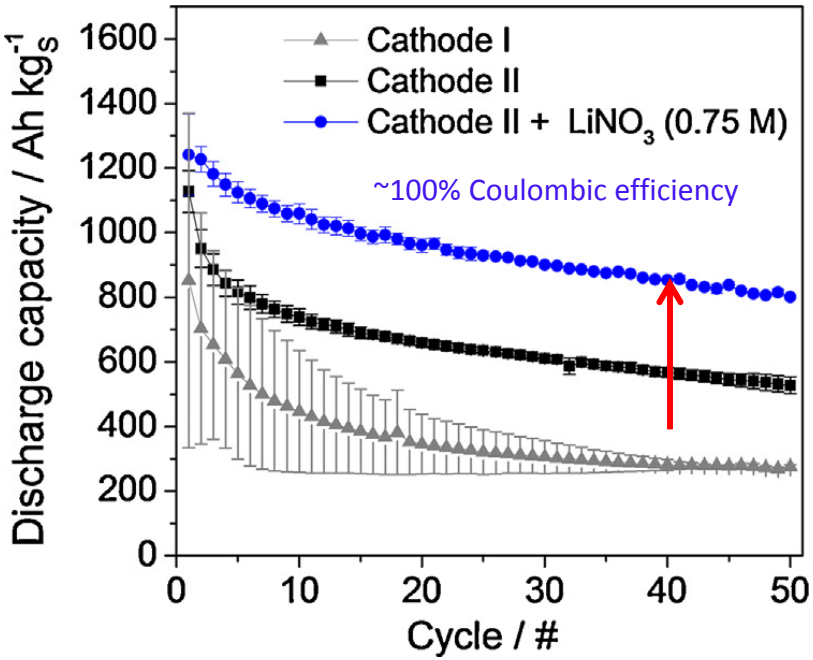
- Improved dispersion of S particles
- Reduction of S particle size

Electrolyte: 1M $LiPF_6$ in TEGDME

# Influence of $LiNO_3$ as co-salt

Capacity fading and coulombic efficiency is affected by the concentration of the co-salt



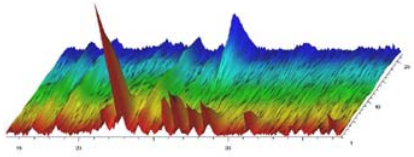




Considering both the capacity fading and the Coloumbic efficiency:
the optimal concentration of $LiNO_3$ was found to be 0.75M for this cell configuration/components

Electrolyte= 1M $LiPF_6$ in TEGDME

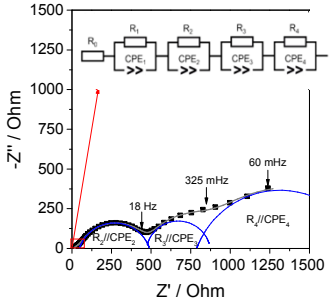
N. A. Cañas, A. L.P. Baltazar, M.A.P. Morais, T.O. Freitag, N. Wagner, K.A. Friedrich. *Electrochimica Acta* 157 (2015) 351-358

# Main *in situ* and *ex situ* characterization techniques



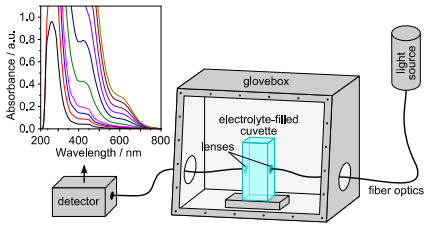
In-situ x-ray diffraction (XRD)

Crystalline end products $S_8$ and $Li_2S$




Electrochemical impedance spectroscopy (EIS)

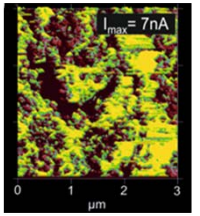
Impedance contributions of processes




Ultraviolet-Visible spectroscopy

Intermediates products $Li_2S_x$

BATTERY FABRICATION

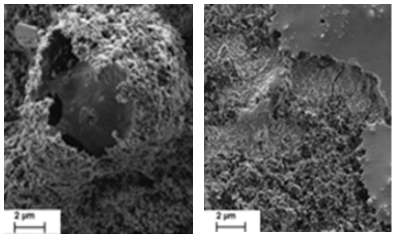



Atomic force microscopy (AFM)

Formation of isolating layers

Thermal analysis and mass spectroscopy

Stability of binding and structural changes



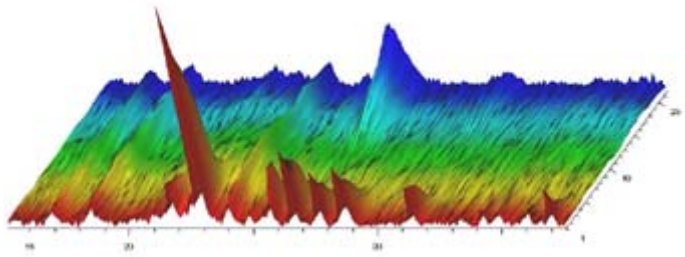
Scanning electron microscopy (SEM)

Morphological changes

Modeling and simulation

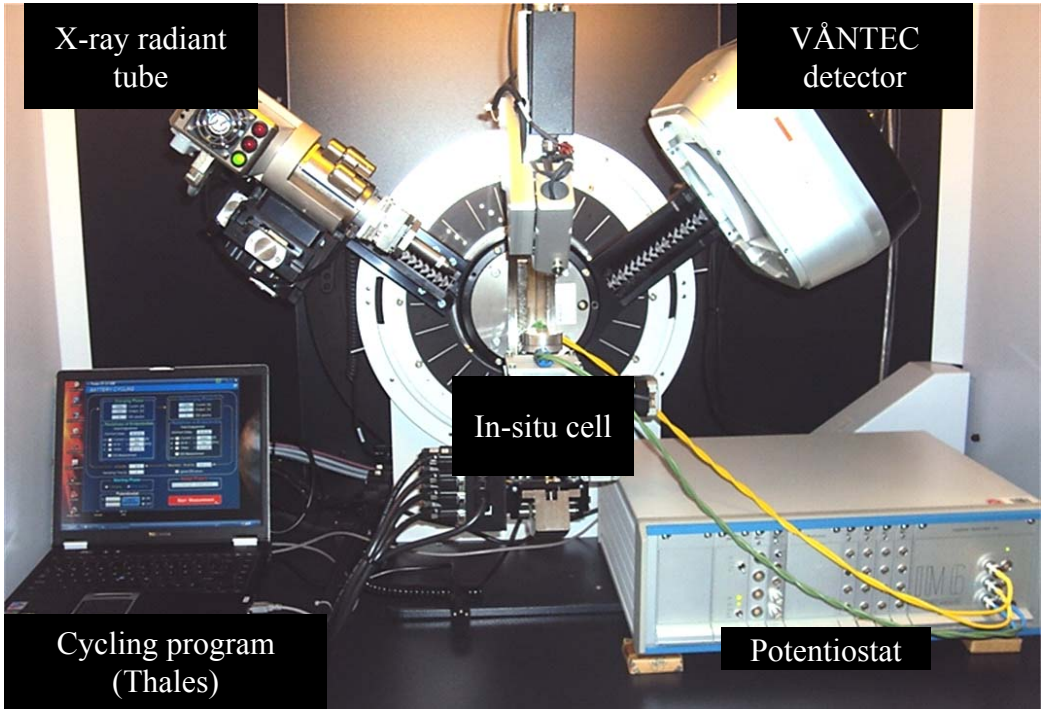
Fundamental understanding

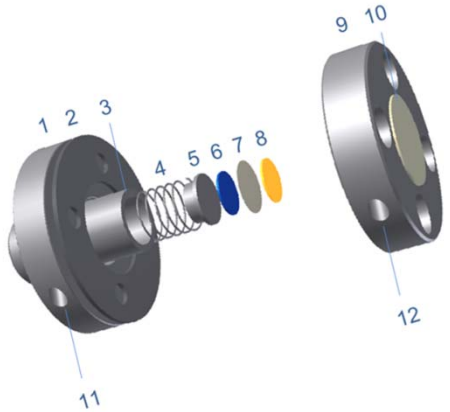
# *In situ* X-Ray diffraction



**Objective:**

- Monitoring of crystalline reaction products of the cathode
- identification of structural changes during cycling



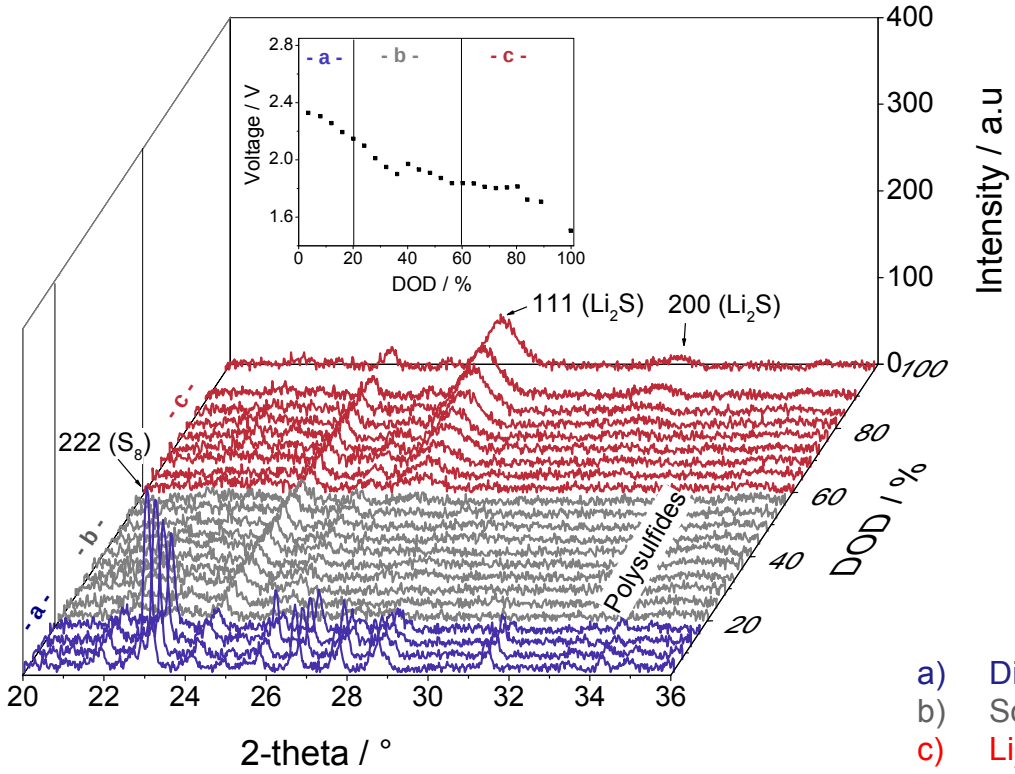




1) anode plate
2) polymer gasket
3) insulator plastic tube
4) spring
5) stainless steel anode collector
6) anode
7) separator
8) cathode
9) cathode plate
10) Al-window
11) holes for connecting the banana jacks

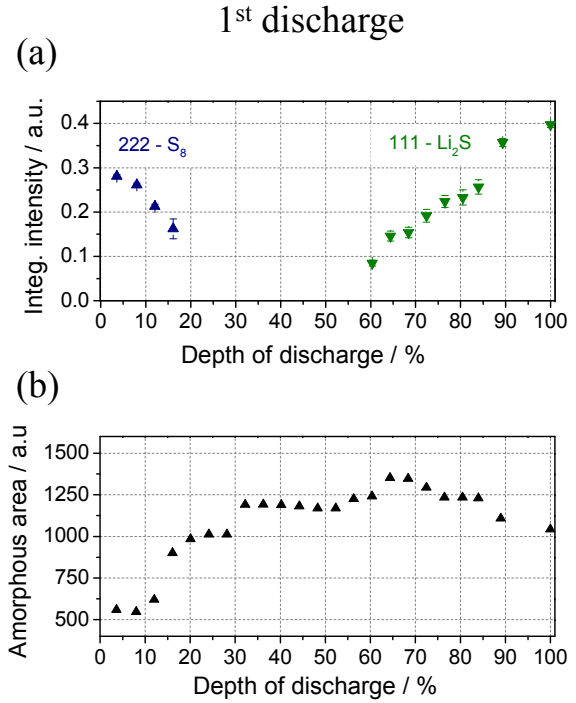
N. A. Cañas, S. Wolf, N. Wagner, K. A. Friedrich. J. of Power Sources, 226 (2013) 313-319.

# *In situ* X-Ray diffraction

## Spectra collected during discharge




## Quantification of crystalline and amorphous phase

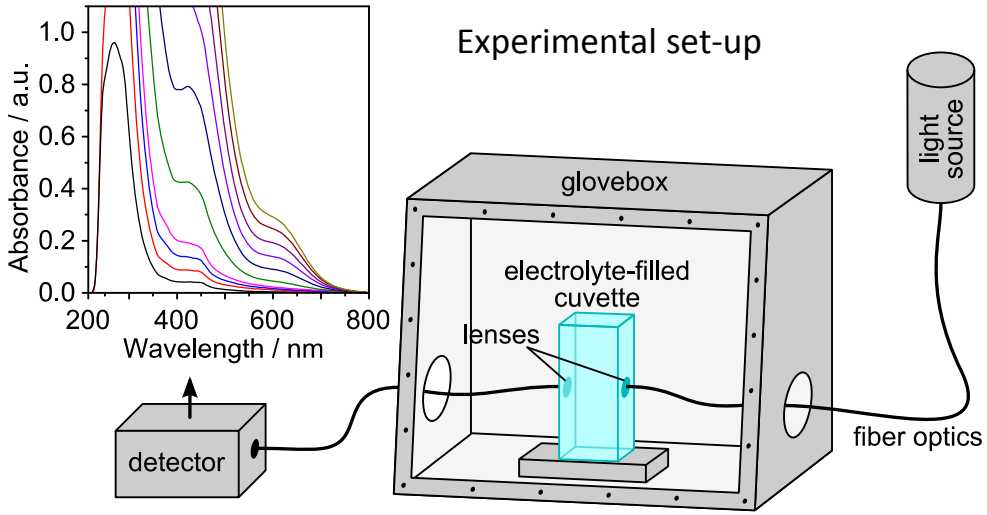



a) Dissolution of sulfur and reduction to soluble polysulfides
b) Soluble polysulfides
c) $Li_2S$ formation

N. A. Cañas, S. Wolf, N. Wagner, K. A. Friedrich. J. of Power Sources, 226 (2013) 313-319.

# UV-vis spectroscopy

## Investigation and quantification of reaction intermediates (polysulfides)





| Wavelength /nm | Species (in TEGDME) |
|---|---|
| 245,255, 282 | $S^-$ ($Li_2S$) |
| 243, 265, 289 | cyclo $S_8$ |
| 332 | $S_6^{2-}$ |
| 425 | $S_4^{2-}$ |
| 615 | $S_3^{\bullet-}$ |

References:

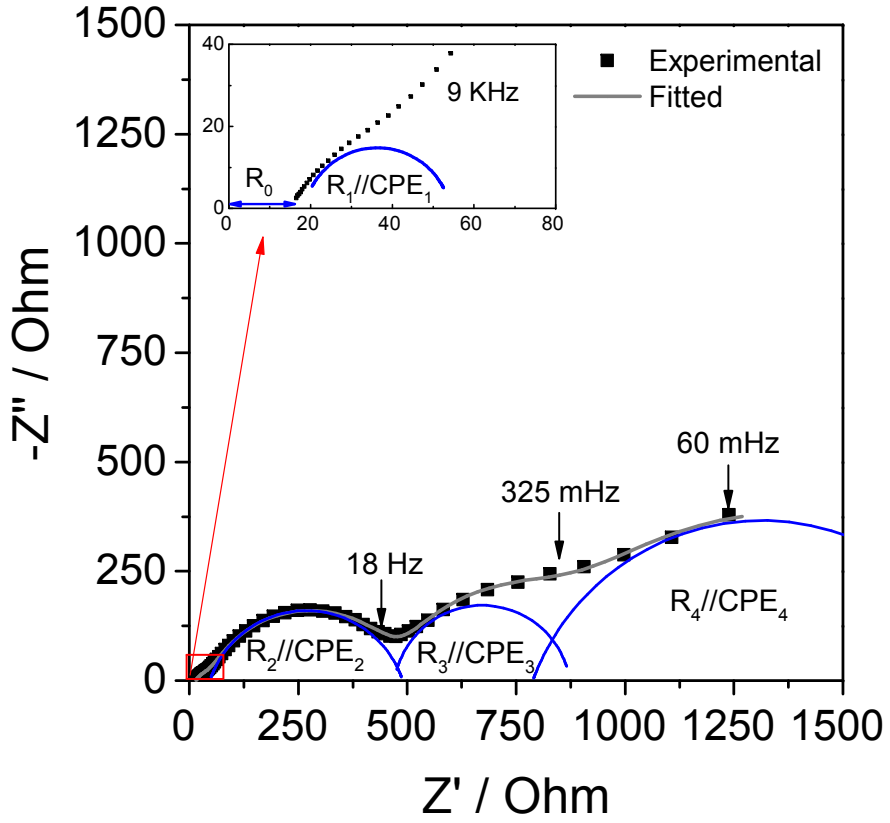
a) Stoichiometric mixture of $Li_2S$ and $S_8$ in TEGDME*
b) $Li_2S$ in TEGDME
c) $S_8$ in TEGDME

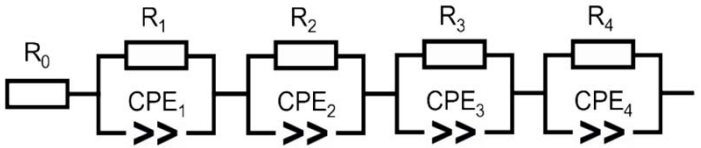
*TEGDME:Tetraethylene glycol dimethyl ether

N. A. Cañas, D. N. Fronczek, N. Wagner, A. Latz, K. A. Friedrich. J. Phys. Chem. C, 2014, 118, 12106–12114.

# Electrochemical Impedance spectroscopy (EIS)

## Investigation of physical and chemical processes during cycling



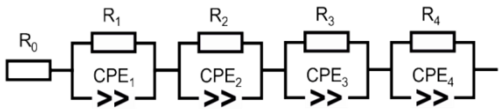



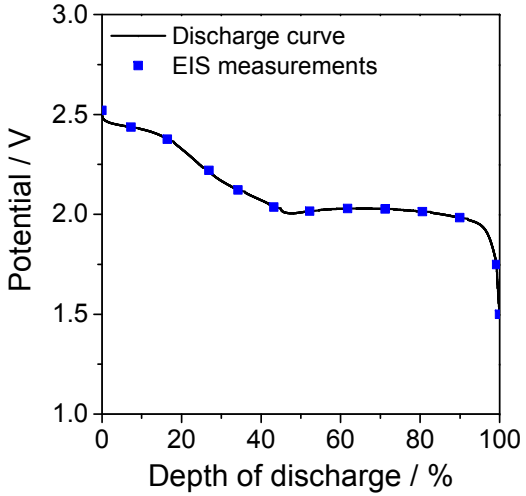

### Assignment of processes to the elements of the EC

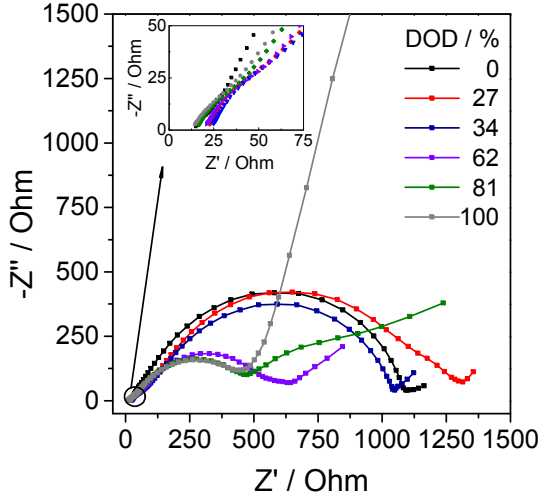
| Model | Chemical and physical cause |
|---|---|
| $R_0$ | Ohmic resistance |
| $R_1$-$CPE_1$ | Anode charge transfer |
| $R_2$-$CPE_2$ | Cathode process: charge transfer of sulfur intermediates |
| $R_3$-$CPE_3$ | Cathode process: reaction and formation of $S_8$ and $Li_2S$ |
| $R_4$-$CPE_4$ | Diffusion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

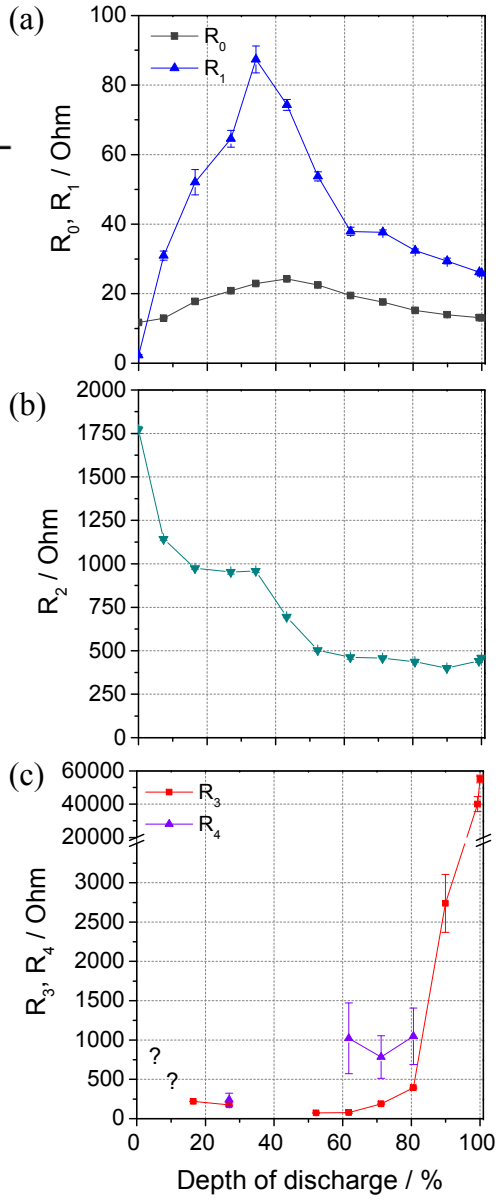
N. A. Cañas, K. Hirose, B. Pascucci, N. Wagner K. A. Friedrich, R. Hiesgen, Electrochim. Acta, 2013, 97, 42–51.

# EIS during 1st discharging cycle




$R_0$: Increase of resistance due to dissolution of $Li_2S_x$

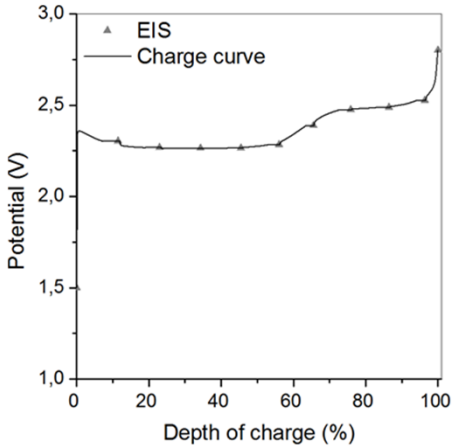
$R_1$: Anodic charage transfer resistance influenced by $Li_2S_x$

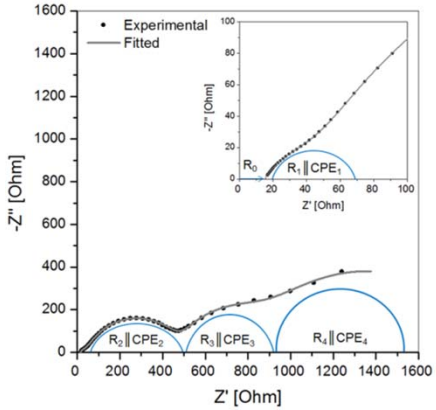
$R_2$: Cathodic charge transfer resistance diminishes with order or polysulfide

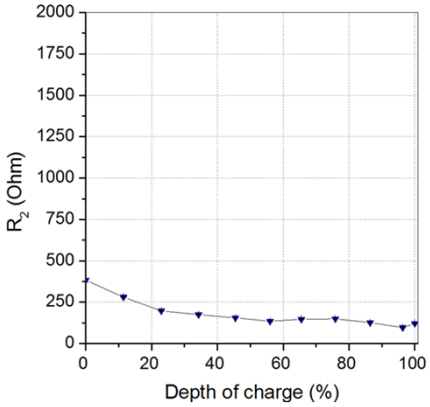
$R_3$: Proportional to formation of isolating products ($Li_2S$ and $S_8$)

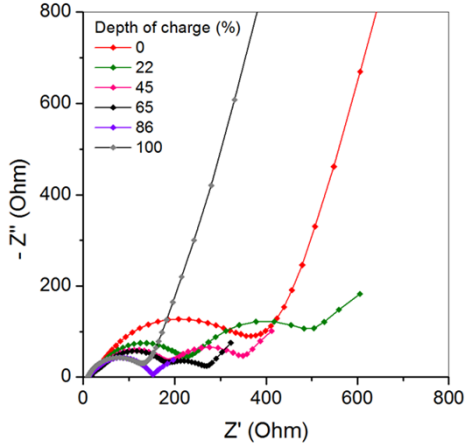
$R_4$: Diffusion hindered by formation of $Li_2S$ and $S_8$

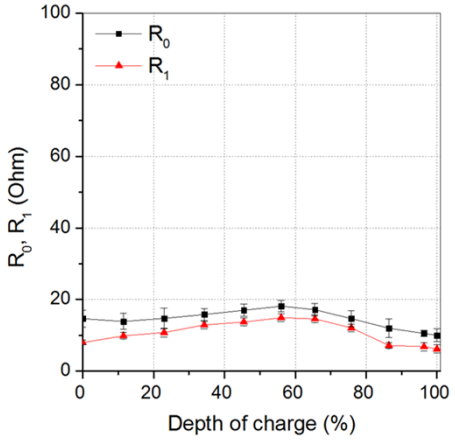
# Variation of the equivalent circuit elements during first charging determined by EIS analysis

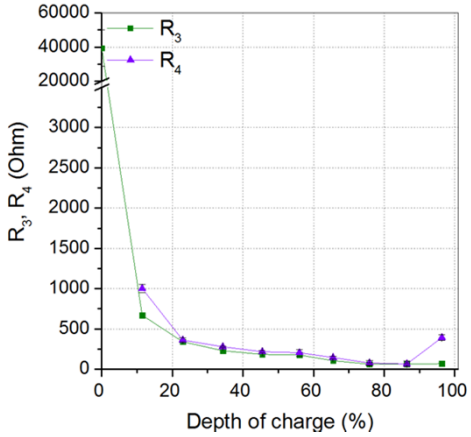


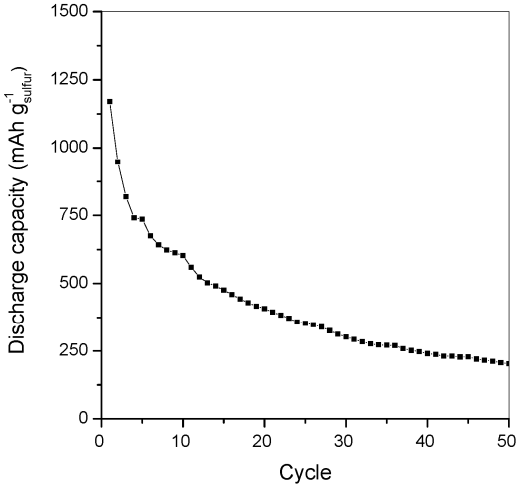



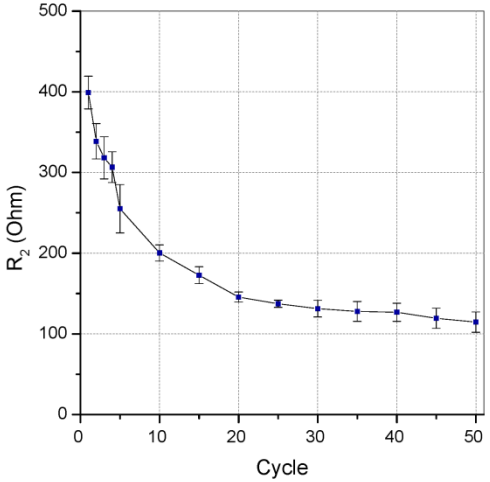




# EIS during 50 charging/ discharging cycle



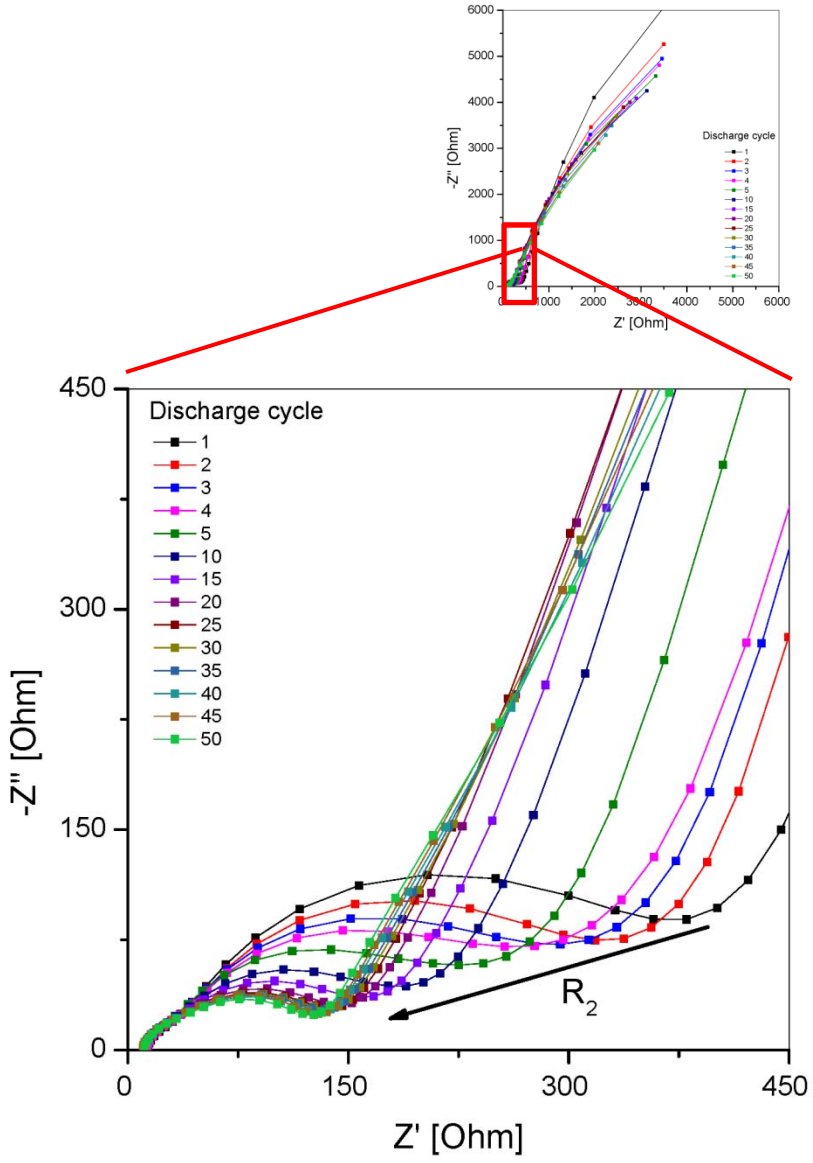

Strong discharge capacity fading

↓

Decrease of cathodic charge transfer ($R_2$)

↓

No complete conversion to $Li_2S$




# New batteries concepts

## Further cathode improvements

### Components

- Electrolyte/sulfur weight ratio: ≤ 3/1
- Mass loading higher than 2 mg $cm^{-2}$
- Sulfur utilization ≥ 70 %

### Different approaches or combination of them:

- **Additives:** hydrophilic inorganic additives (like $Me_xO_y$) for adsorption of polysulfides
- **Protective layers:** ion conductive interlayers for retention of active material
- **Binders:** replacement of conventional PVDF by ion /electric conductive additive

### Guideline for an optimized electrode and cell design:

- Modeling from a single active particle to full battery cells
- Mechanistic studies of degradation processes on both electrodes

DLR

# Main companies developing Li/S Batteries in industry

oxis ENERGY
Next Generation Battery Technology

*Abingdon, UK*

SION POWER®

*Tucson, USA*

POLYPLUS

*Berkeley, USA*

**Target for commercialization: ca. 500 Wh/kg**

Oxis Energy:
- 300 Wh/kg achieved at cell level in 2014
- 400 Wh/kg forecast in 2016

Sion Power:
- 250 Wh/kg and over 300 full depth of discharge cycles (now)
- 600 Wh/kg are in the foreseeable future


http://www.oxisenergy.com/technology/
http://www.sionpower.com/
http://www.polyplus.com/

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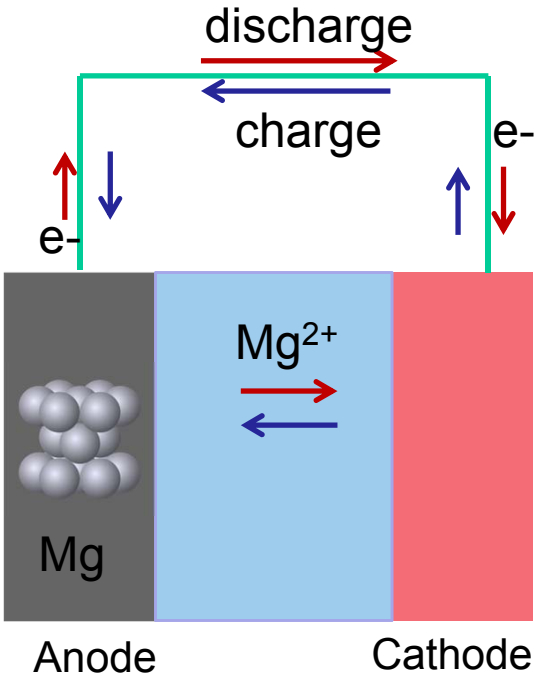
# Li-Sulfur vs. Mg-Sulfur Battery




| | Li | Mg |
|---|---|---|
| Atomic weight | 6.9 | 24.3 |
| Ionic radius | 90 pm | 86 pm |
| Ionic charge | + 1 | + 2 |
| Reduction potential | - 3.04 V | - 2.37 V |
| Density | 0.53 g/cm$^3$ | 1.74 g/cm$^3$ |
| Gravimetric capacity | 3861 mAh/g | 2205 mAh/g |
| Volumetric capacity | 2061 mAh/cm$^3$ | 3832 mAh/cm$^3$ |

- Good handling and operational safety
- No dendrite formation using Mg metal as anode
- Naturally abundant → low raw material cost (currently Li/25)
- Mg/S offers theoretical 4000 Wh/L while the gravimetric capacity is similar to that of $LiC_6$
- Sulfur cathode needs non-nucleophilic electrolyte

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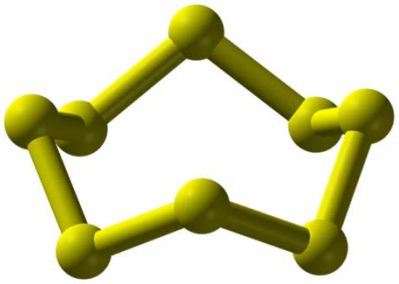
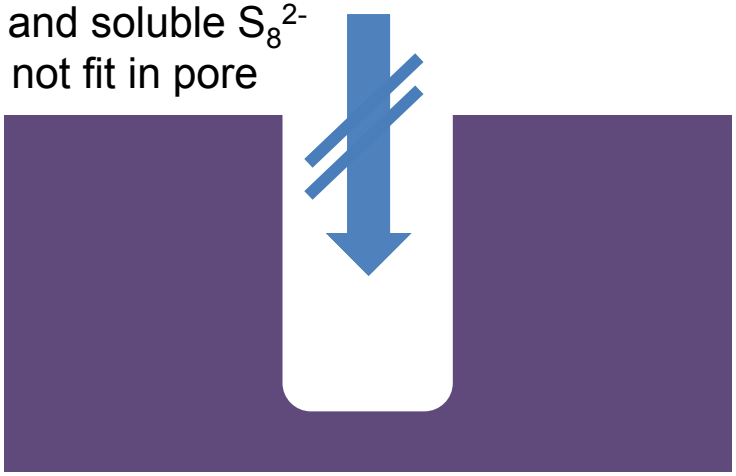
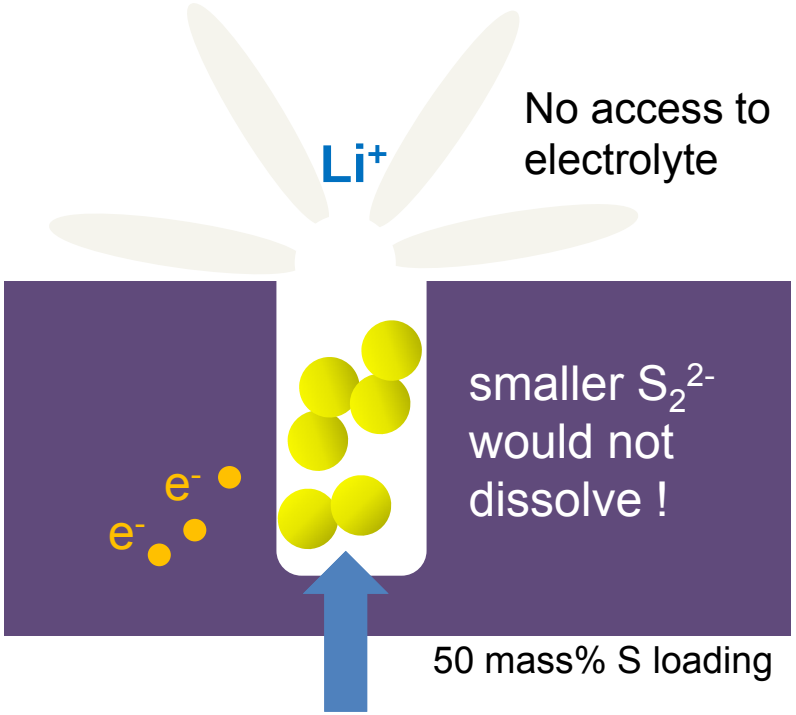
# Reduction of polysulfide shuttle



$S_8$ and soluble $S_8^{2-}$ do not fit in pore



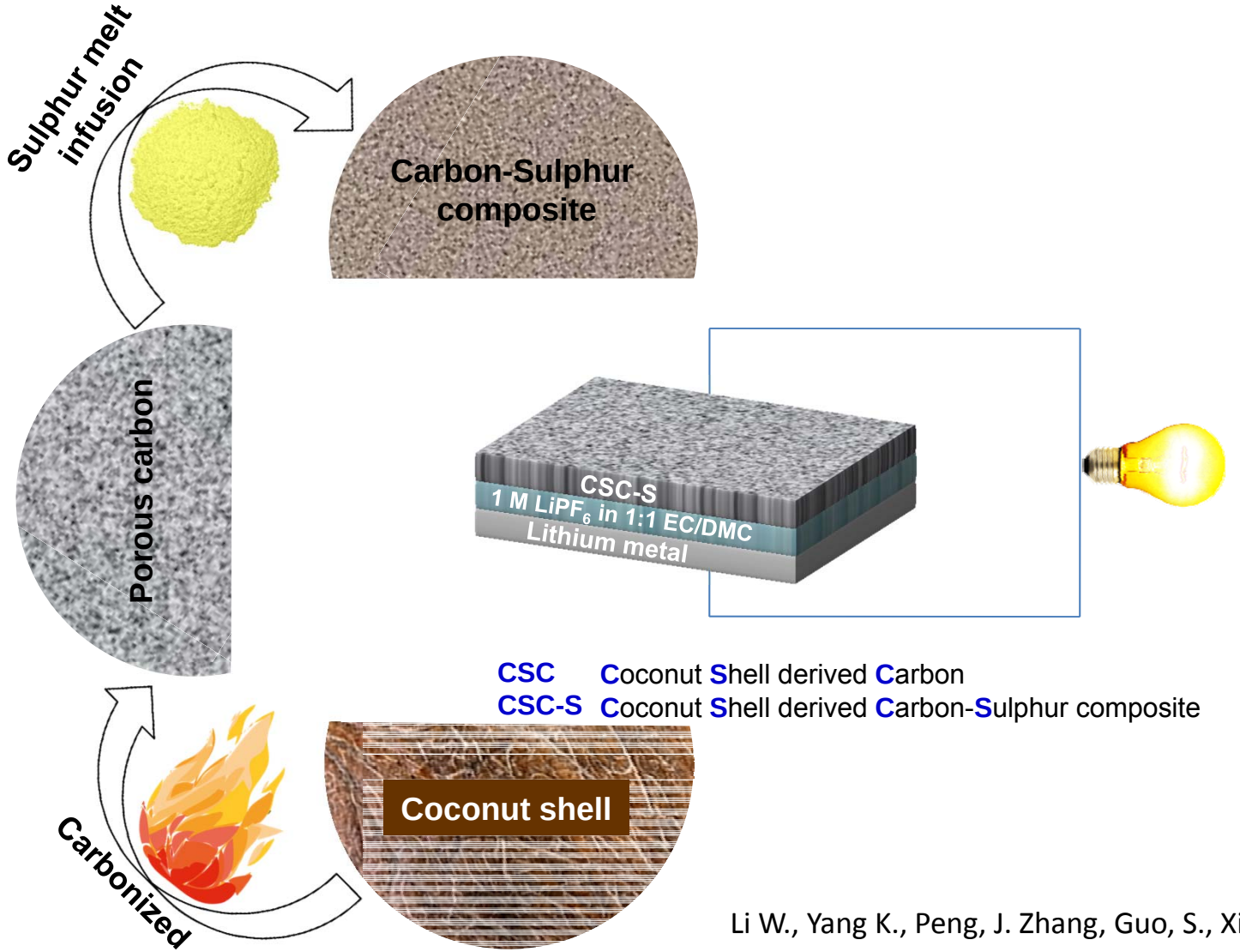
Ultramicroporous carbon made from coconut shells (inexpensive, scalable).
Pore ø ≈ 0.6 nm




Hypothesis:
direct transition of S to $Li_2S_2$ and $Li_2S$

**one reaction step → one plateau**

# Production of Carbon-Sulfur Composite




**CSC** **C**oconut **S**hell derived **C**arbon
**CSC-S** **C**oconut **S**hell derived **C**arbon-**S**ulphur composite

Li W., Yang K., Peng, J. Zhang, Guo, S., Xia, H. *Ind. Crop. Prod*. **28**, 190–198 (2008).

# Metal-air batteries

# 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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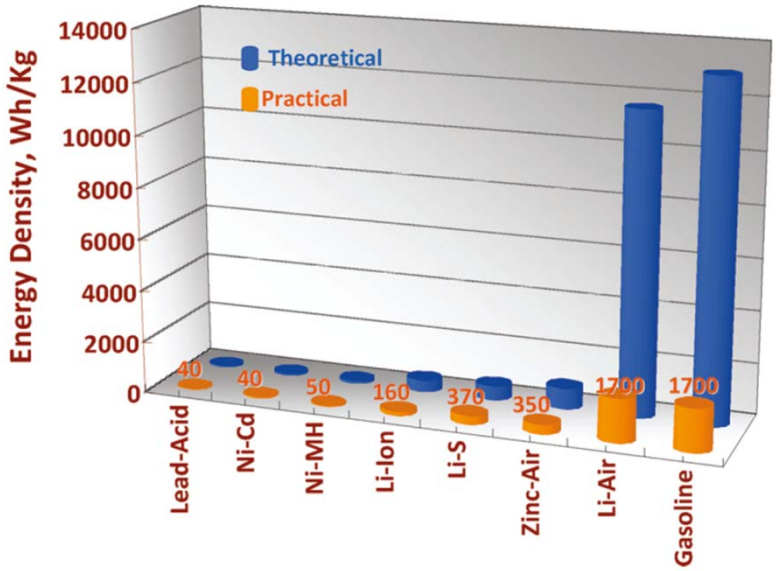


G. Girishkumar et al., J. Phys. Chem. Lett., **2010**, 1, 2193-2203

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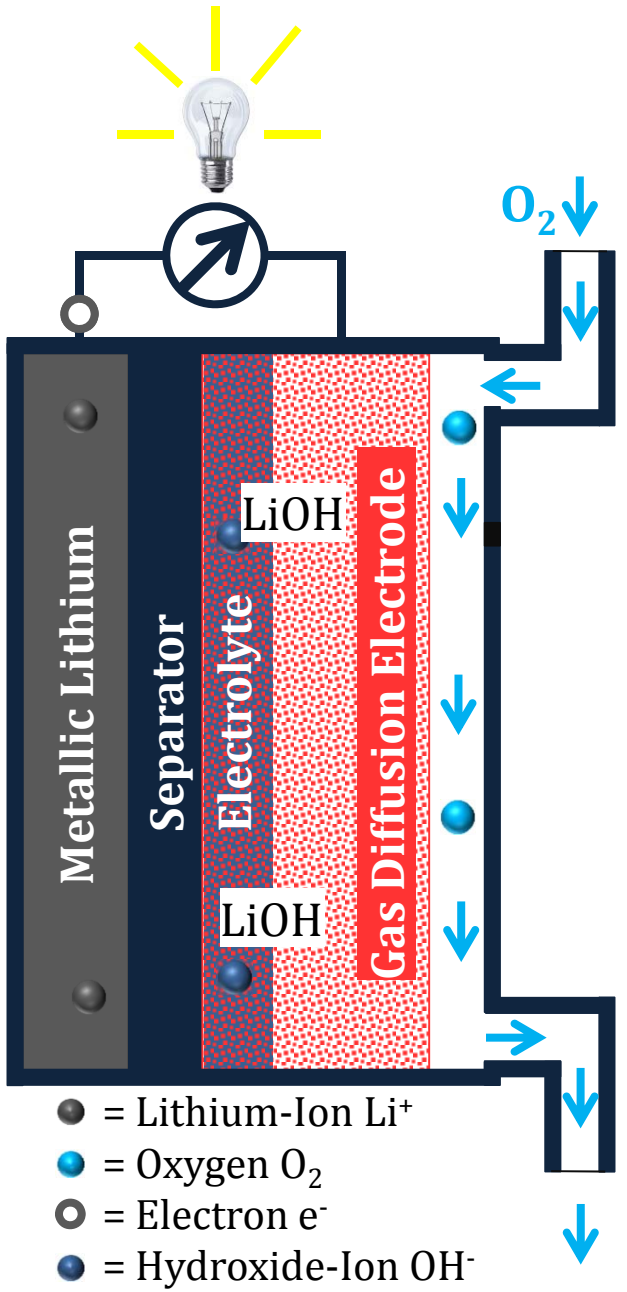
# Li-air battery: Functional scheme

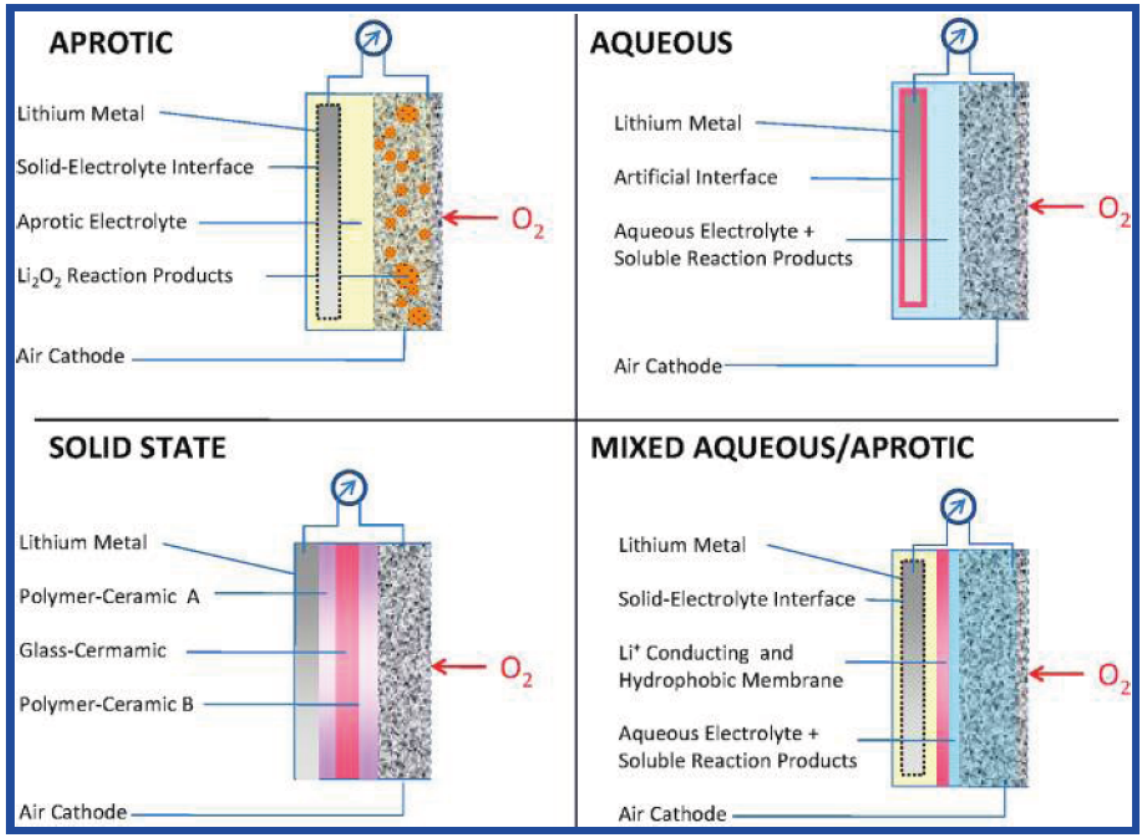
Structure:
- Anode, Lithium metal (foil)
- Cathode (Gas diffusion electrode = GDE)
- Separator

Reactions and products:
- During discharge: Oxygen Reduction Reaction (ORR)
- During charging: Oxygen Evolution Reaction (OER)
- Reaction product:
  - organic electrolyte: $Li_2O$, $Li_2O_2$
  - alkaline electrolyte: LiOH

DLR:
- Bifunctional Cathode (GDE) with alkaline electrolyte (LiOH)
- Global reaction: $4\ Li + O_2 + 2\ H_2O \leftrightarrow 4\ LiOH$ ; E=3.45V




# 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

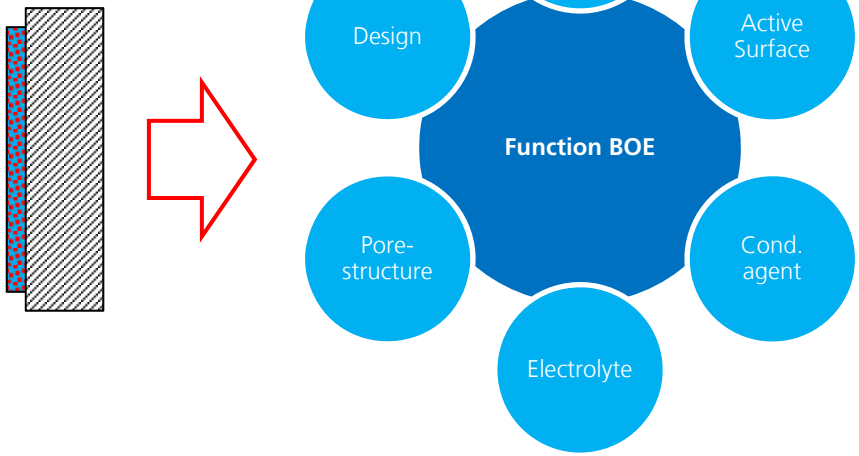
$4Li + O_2 + 4H^+ \rightleftarrows 2H_2O + 4Li^+$(acidic media) $E_{rev}$= 4,274 V

DLR

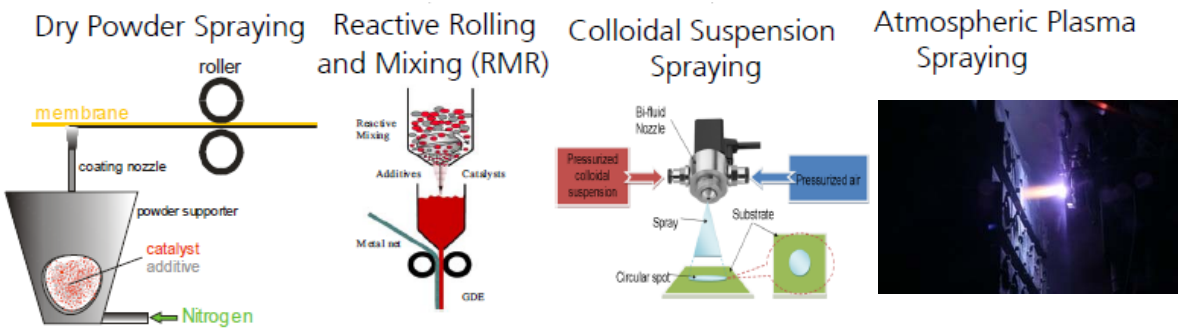
# Bi-functional Oxygen-Electrodes: Design

- 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,…)



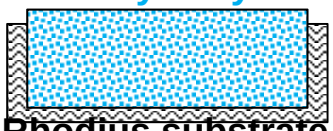

- Different manufactoring processes used at DLR: Dry Powder Spraying, Reactive Rolling an Mixing, Pressing and APS



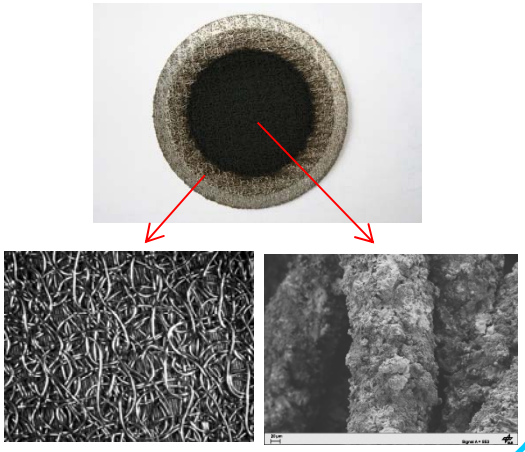

# Manufactoring of bifunctional gas diffusion electrodes

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

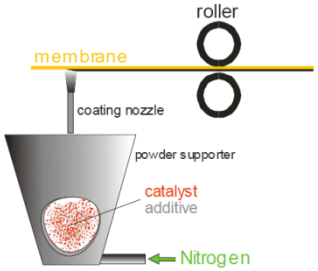
**Catalyst layer**



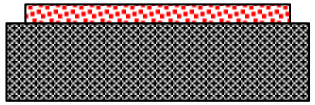
**Rhodius substrate**



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

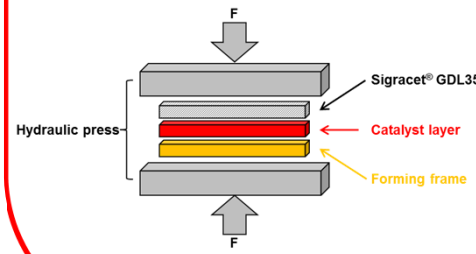



**Catalyst layer = catalyst+carbon/graphite+binder**

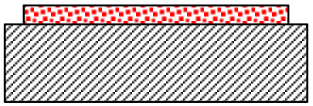


**Graphite GDE substrate**

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**

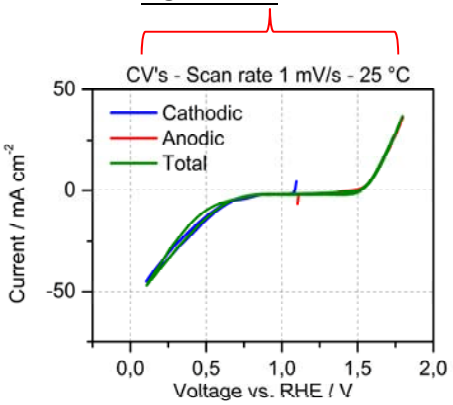
DLR

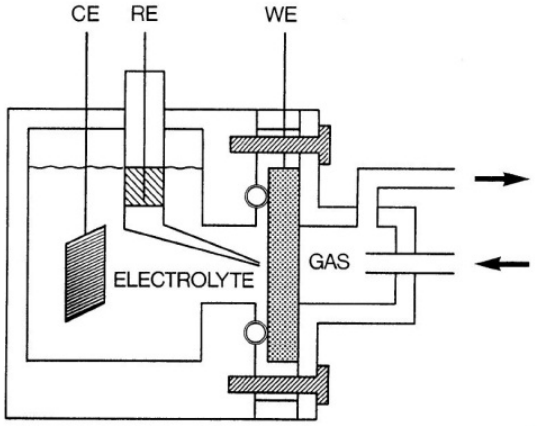
# Screening of bifunctional catalysts

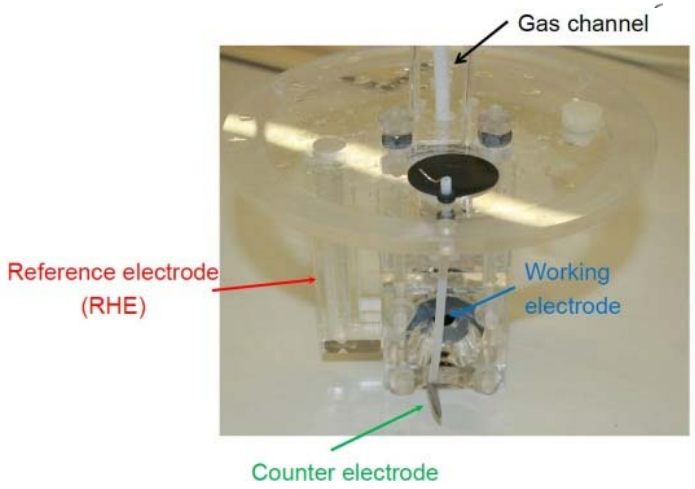
## Experimental

- Thin catalyst layers reduce the influence of the electrode structure
- Cyclic Voltammetrie was carried out at a half cell with 1M LiOH (aq.) and 25° C and 50° C
- Gas $O_2$, platinum counter electrode (CE), reversible hydrogen reference electrode (RE)

Potential range 0.1V - 1.8V vs. RHE

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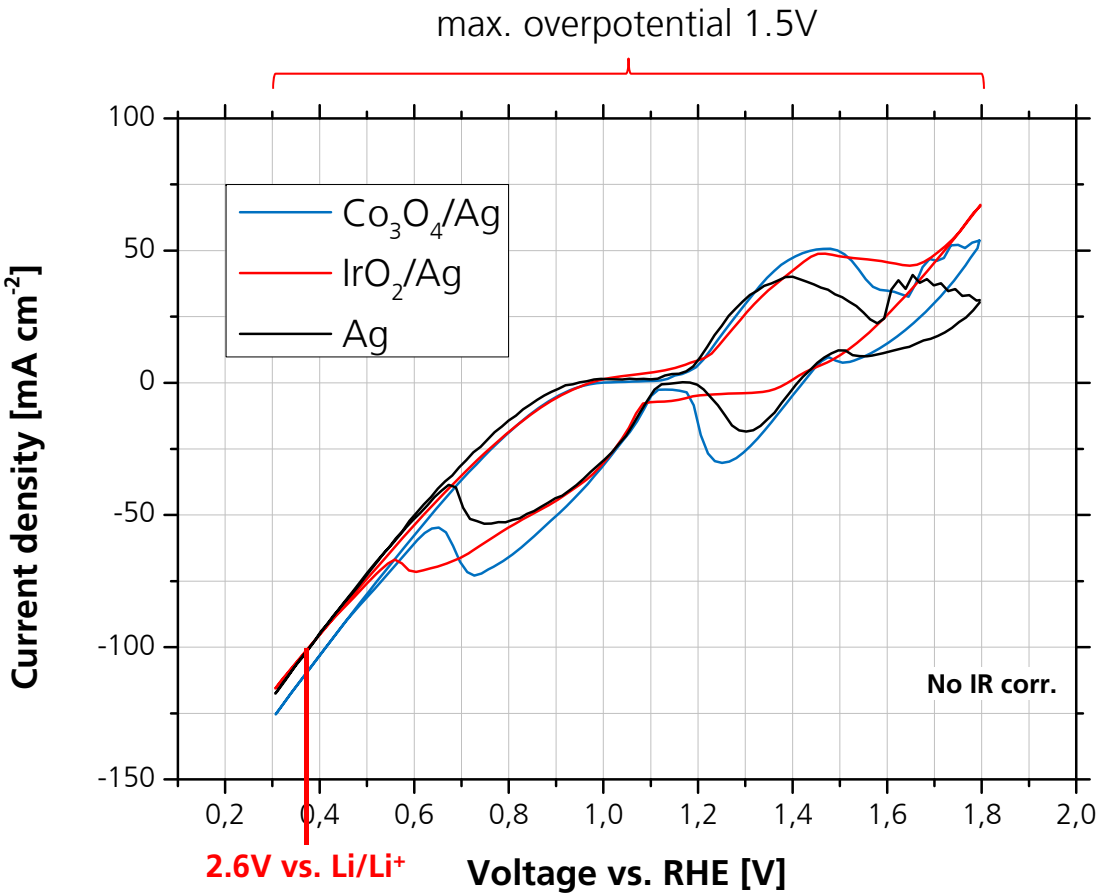
# Bi-functional Oxygen-Electrodes: $IrO_2$/- and $Co_3O_4$/Ag-electrodes

- CV´s electrodes 20 wt. % catalyst ($IrO_2$, $Co_3O_4$
- Improved cycling performance due to use of $IrO_2$ and $Co_3O_4$ compared to pure Ag

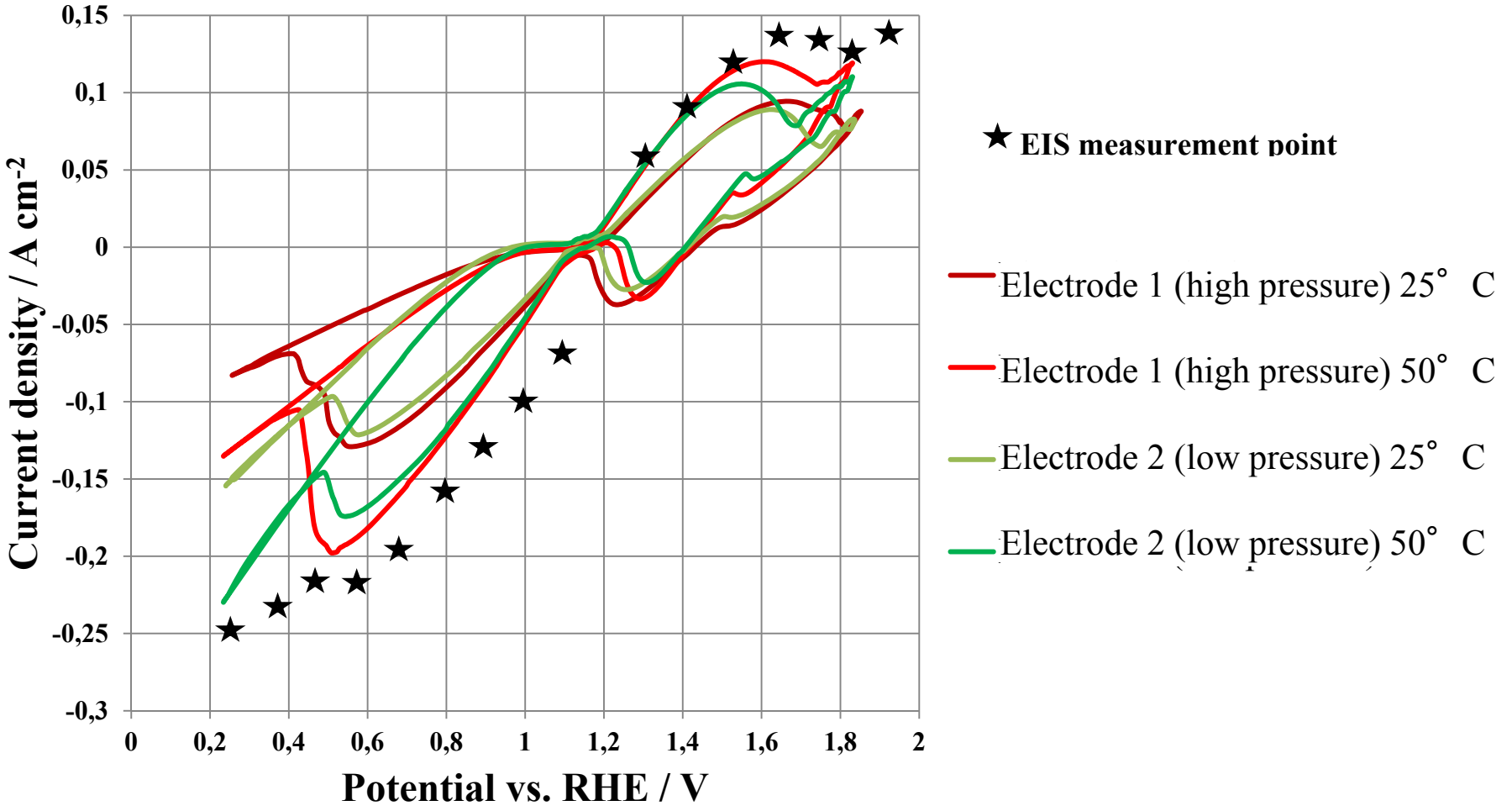
| Current density @ 2.6V vs. $Li/Li^+$ [mA $cm^{-2}$] | |
|---|---|
| $IrO_2$/Ag | 99,7 |
| $Co_3O_4$/Ag | 107 |



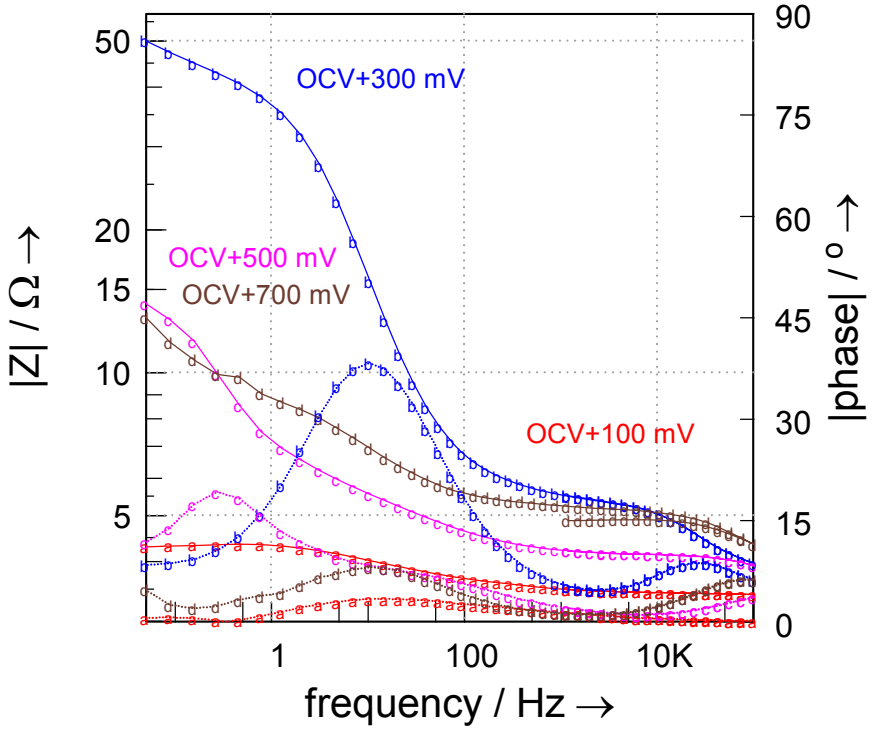

N. Wagner , D. Wittmaier, German Patent Application, 2014

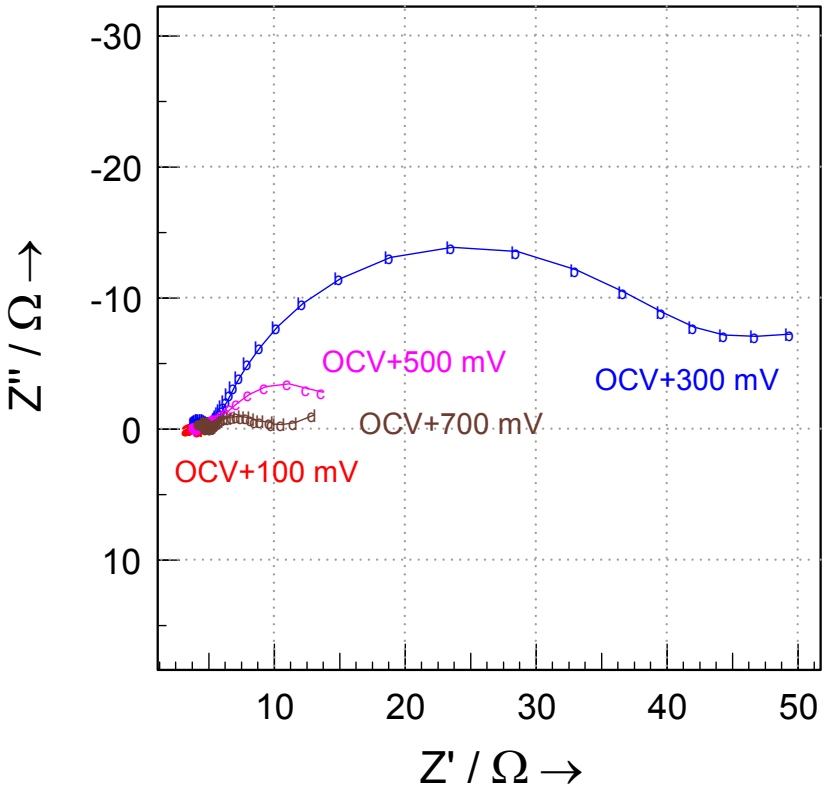
DLR

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

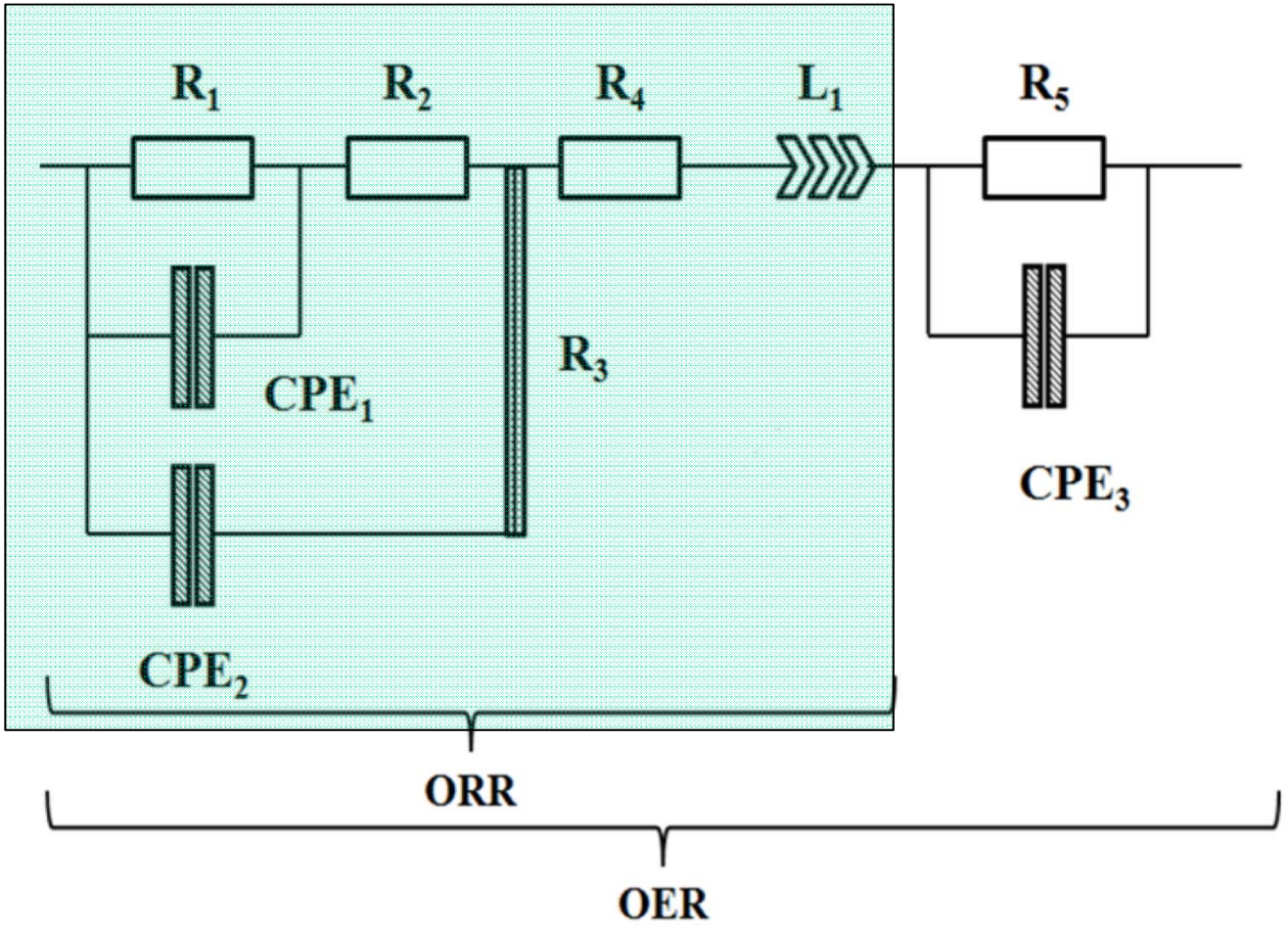



# Impedance measurements during Oxygen evolution on Ag-GDE (high pressure), 1 N LiOH, 25° C

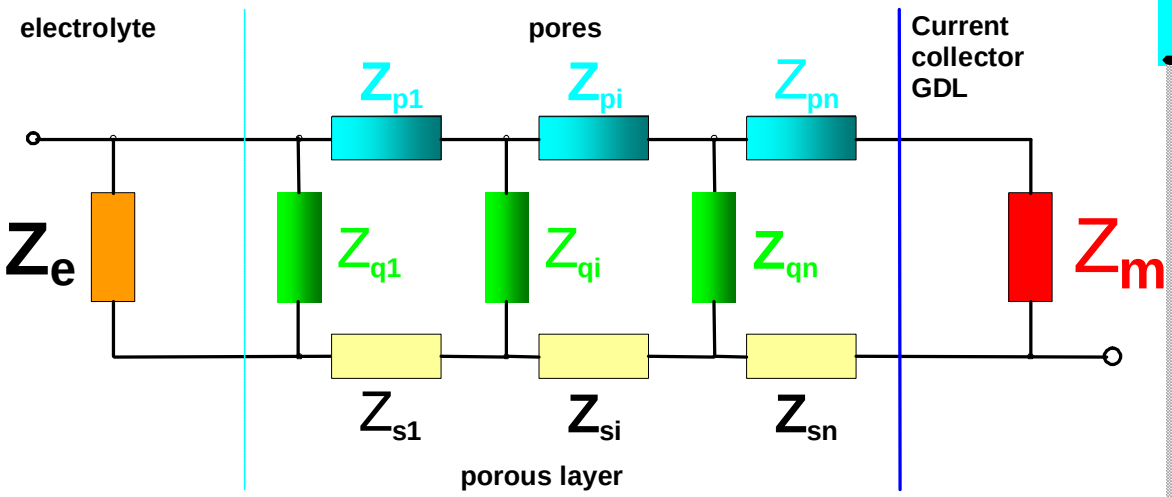


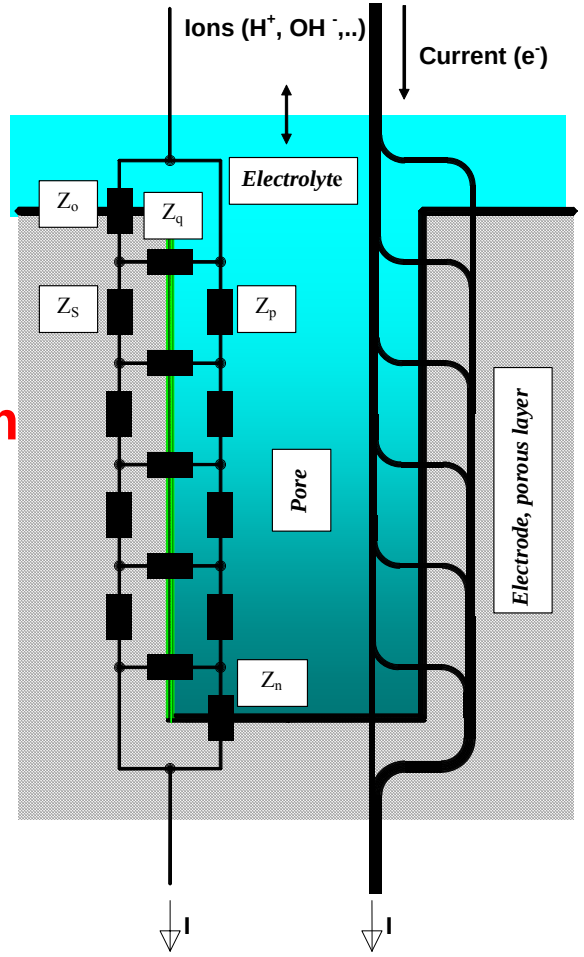




# Equivalent circuit used for evaluation of EIS during OCR and OER at different electrodes for Lithium-Air batteries



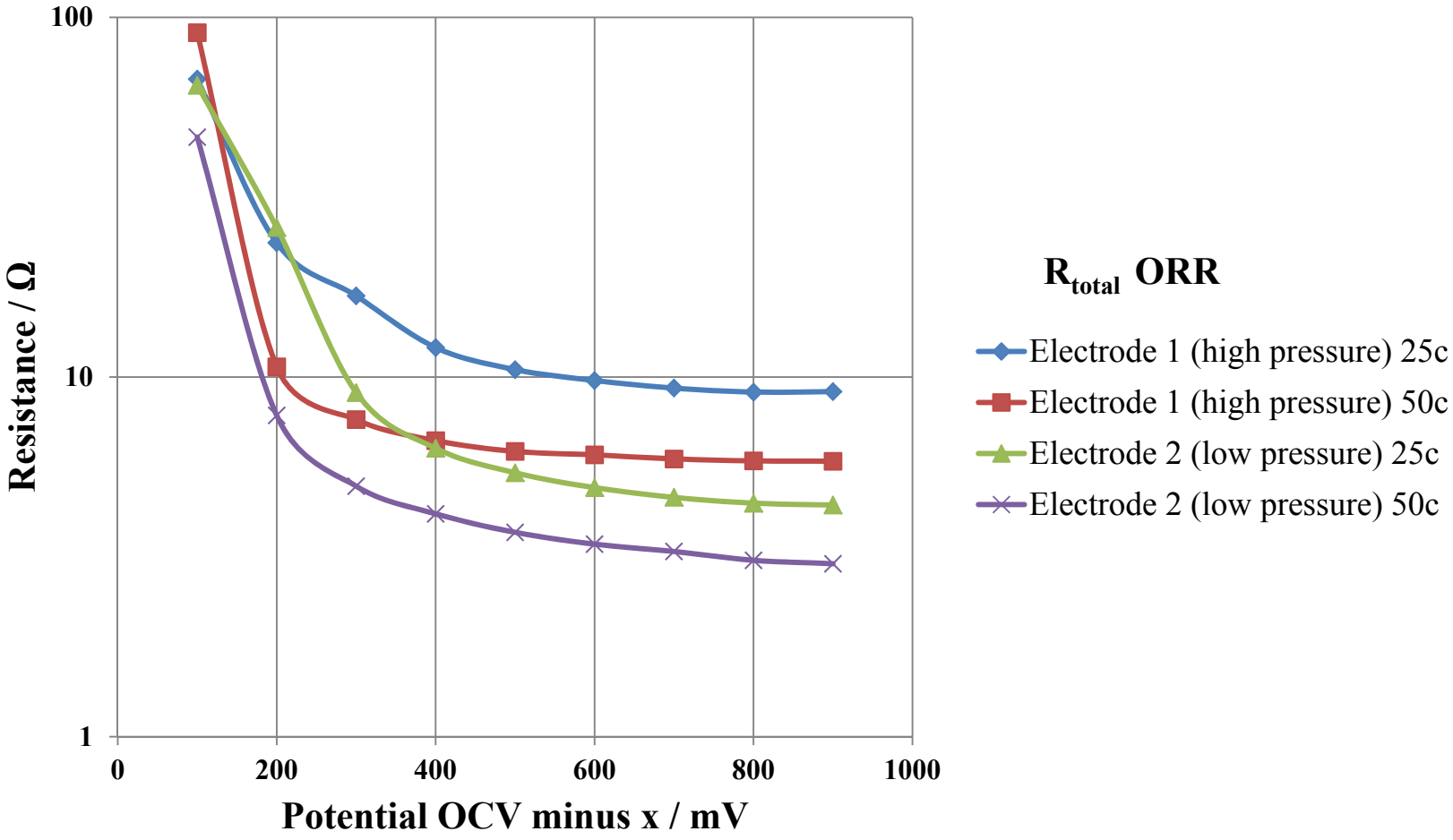

# Cylindrical homogeneous porous electrode model (H. Göhr)




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

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

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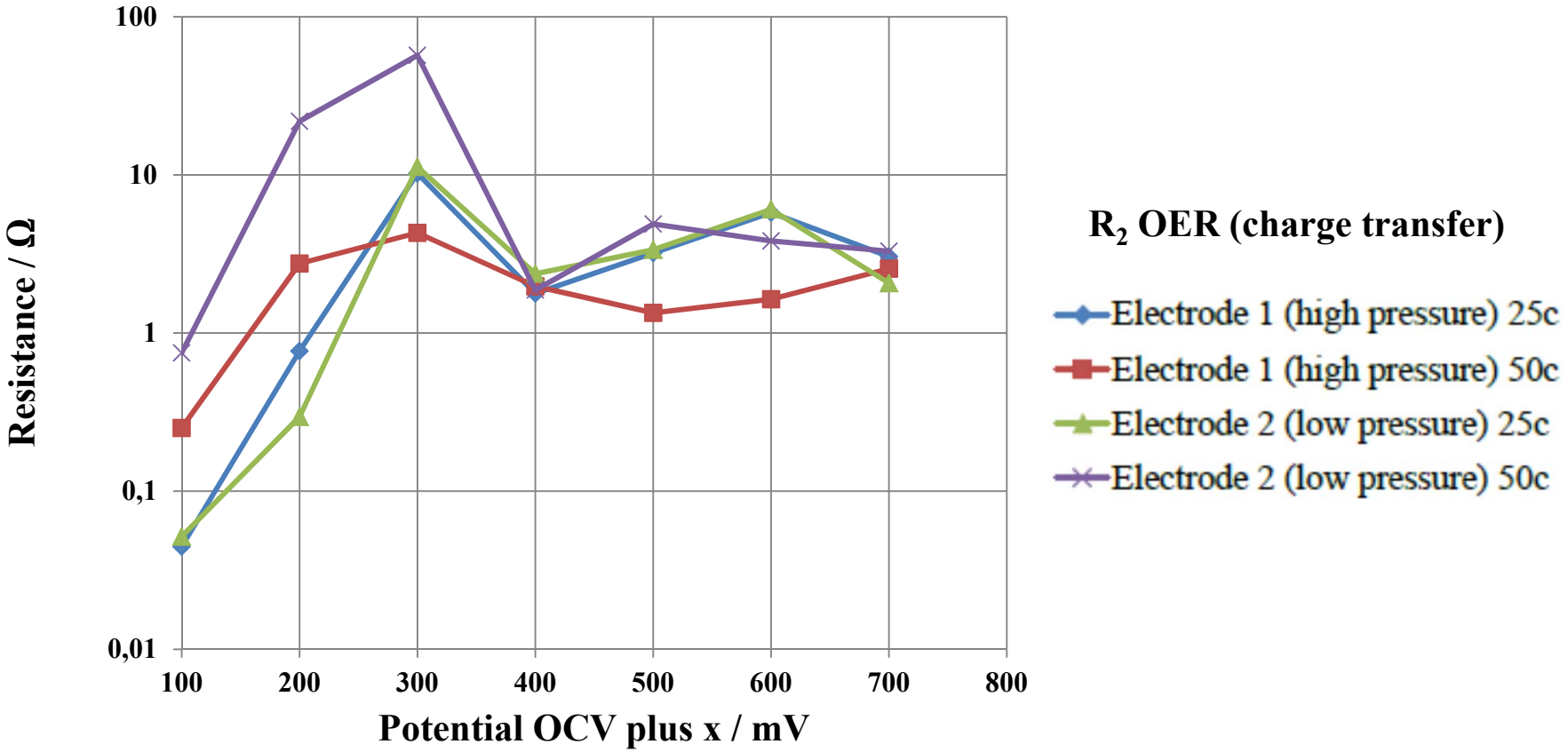
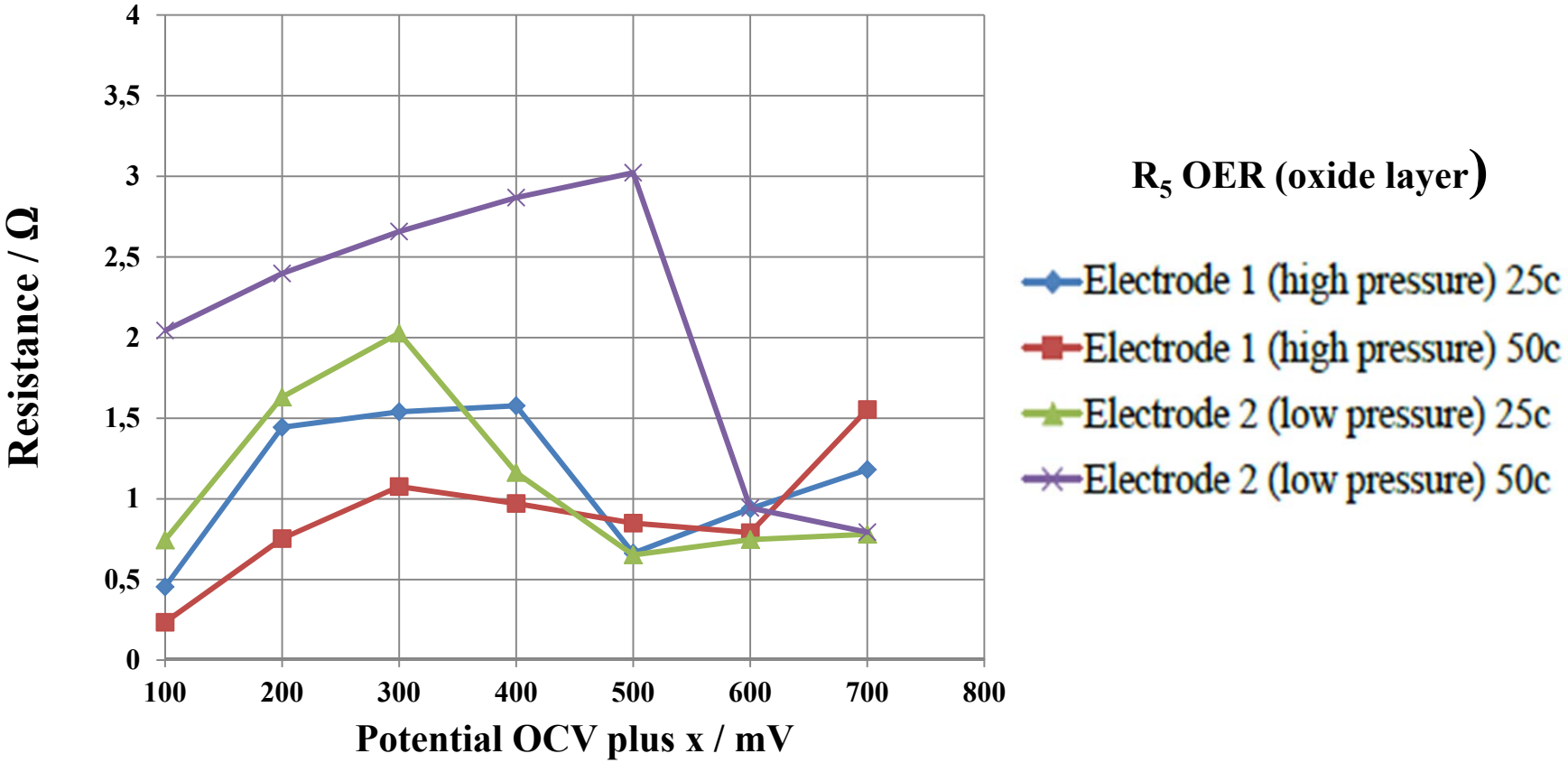
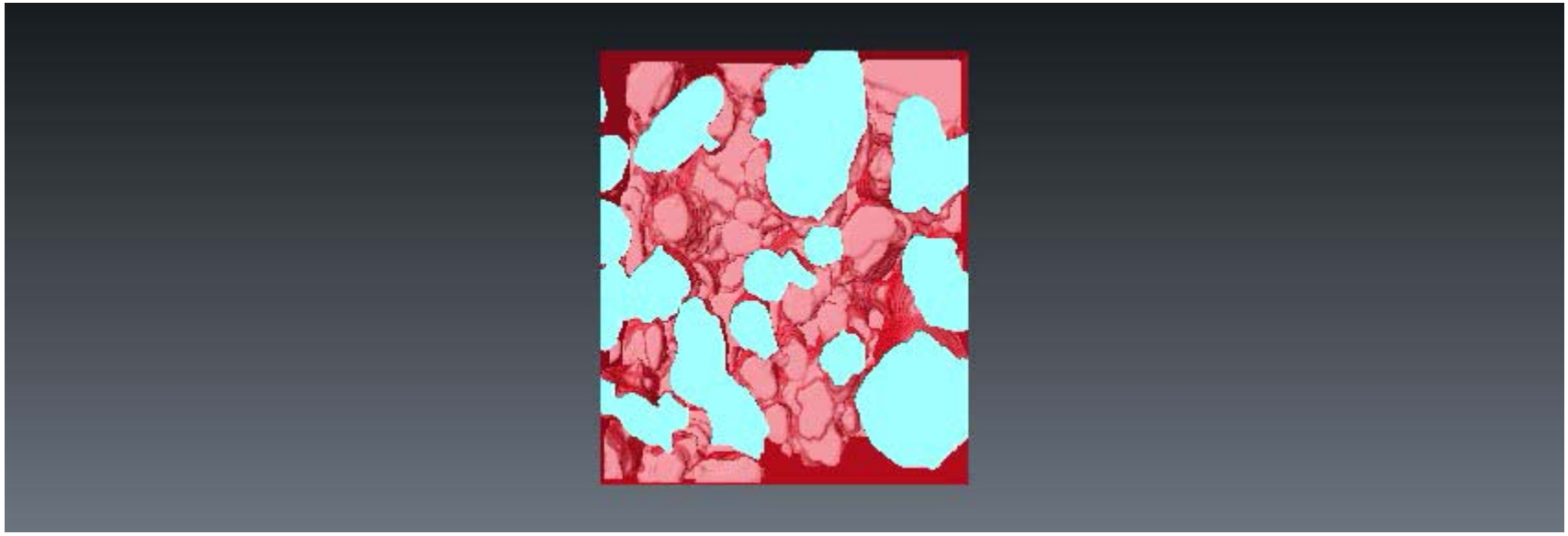
# Potential dependency of charge transfer resistance during OER




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

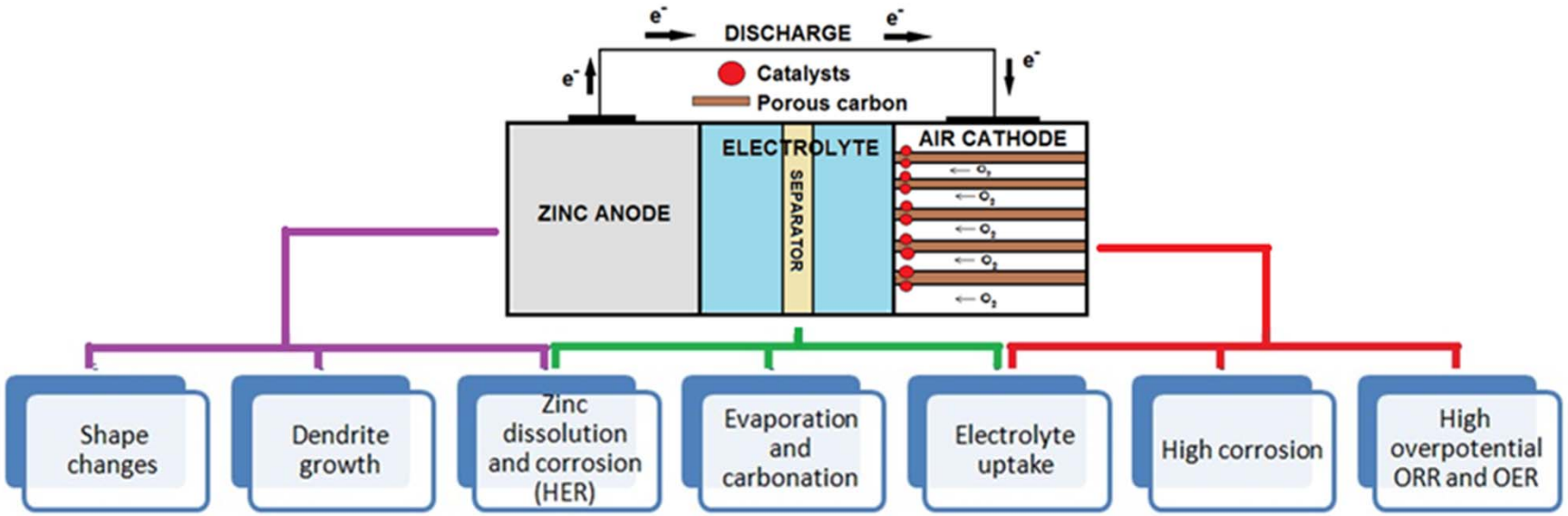



# FIB-TEM picture of a Silver gas diffusion electrode

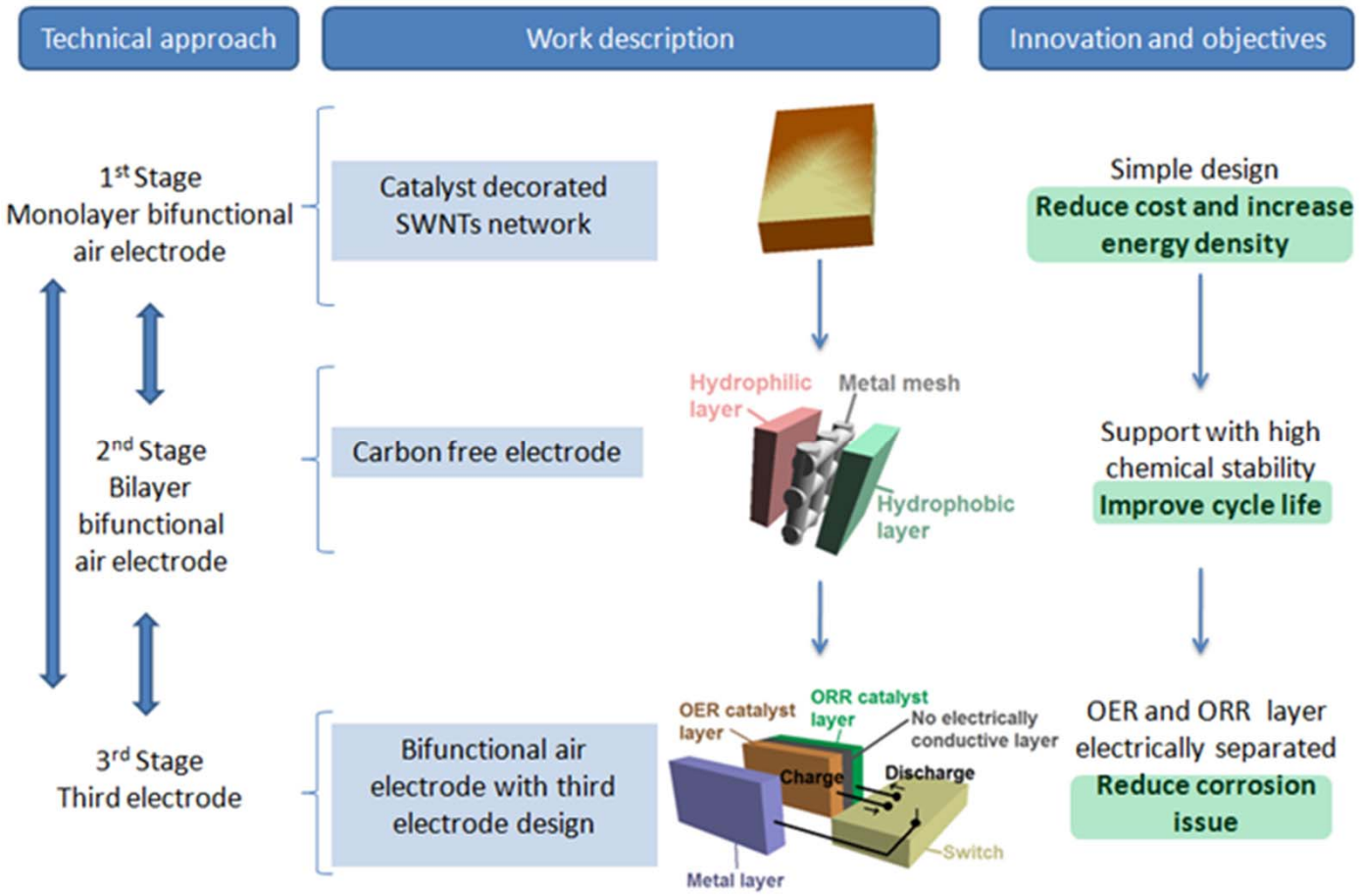


-8th IWIS 2015, Norbert Wagner

# Main Limitations of the Zinc-Air Battery



# “ZAS” innovation on the bifunctional air electrode




**German Aerospace Center (DLR)**

Institute of Engineering Thermodynamics

Battery group

# Thank you for your attention!

Vielen Dank für Ihre Aufmerksamkeit!

Gracias por su atención!

Multumesc pentru atentie!