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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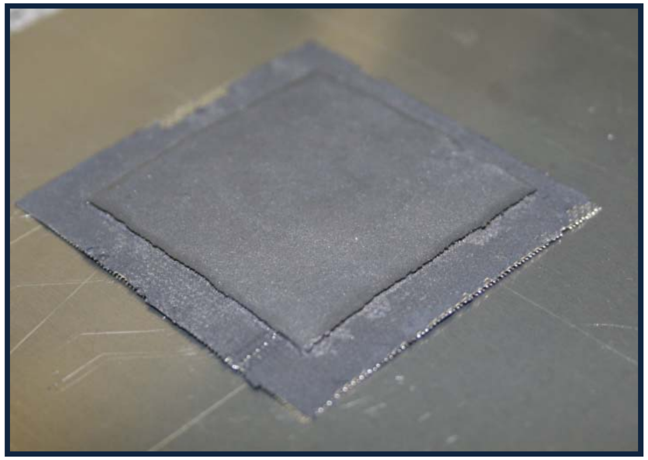
GDCh - Electrochemistry, 22.-24.09.2014, Mainz

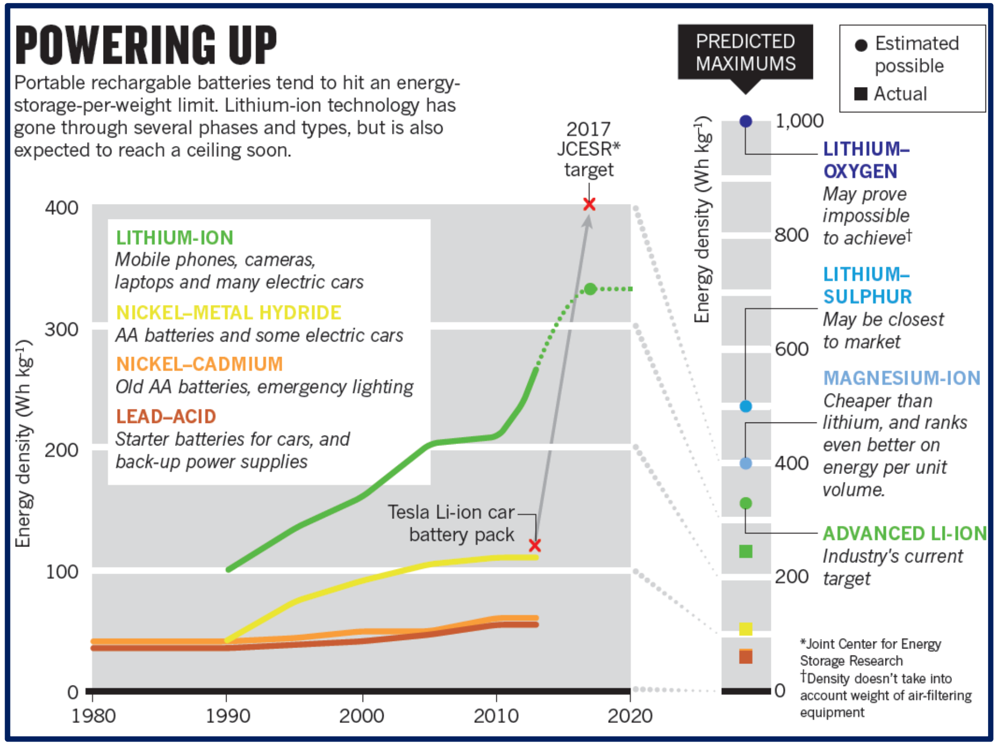
DLR

Outline

- Preparation methods
- Characterization methods
- Carbon-free electrodes
- Conclusion



Activities Battery-Group (DLR)



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- **11 Scientists, 2 Technicians, 6 Students**

Activities:

- **Characterization of state of the art Li - Ion Batteries (*in-* and *ex-situ*)**

Generation 4 batteries:

- **Lithium - Sulfur**
- **Lithium - Air**

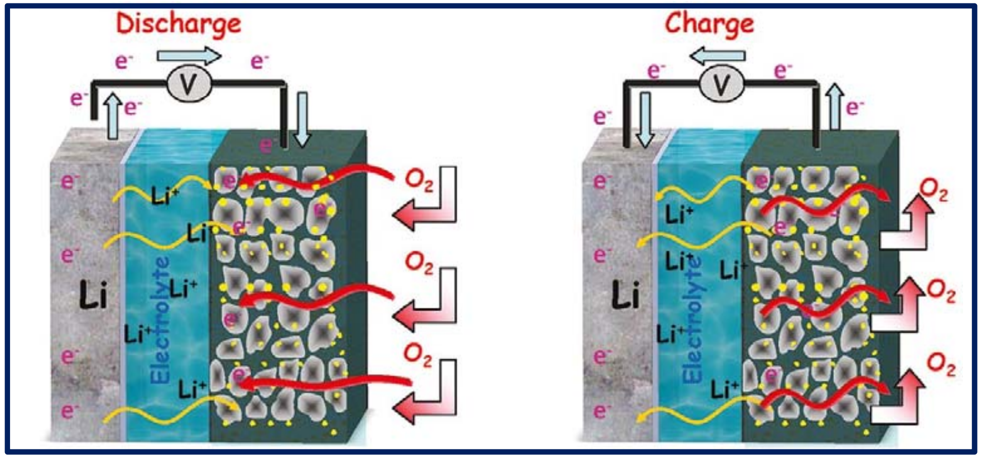
Preparation and characterization

DLR

Basic Concept Li-Air Battery

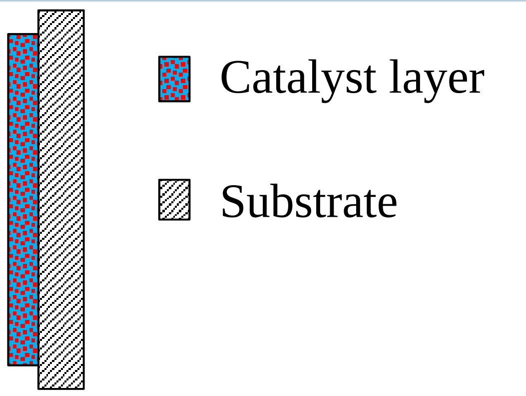
- Anode: Metallic lithium
- Cathode: Porous gas diffusion electrode (catalyst(s), binder, substrate and conductive agent)
- Battery reaction for aqueous alkaline Li-air battery:

$$4\ Li + O_2 + 2\ H_2O \leftrightarrow 4\ LiOH;\ E_0 = 3{,}45V$$



Ref.: G. Girishkumar, B. McCloskey, A. C. Luntz, S. Swanson, W. Wilcke, J. Phys. Chem. Lett. (2010) 1, 2193

- Highly porous, 3-dimensional bi-functional gas diffusion electrode (cathode)
- Bi-functional cathode catalizes battery reactions:
  - ORR = Oxygen reduction reaction – discharging
  - OER = Oxygen evolution reaction - charging

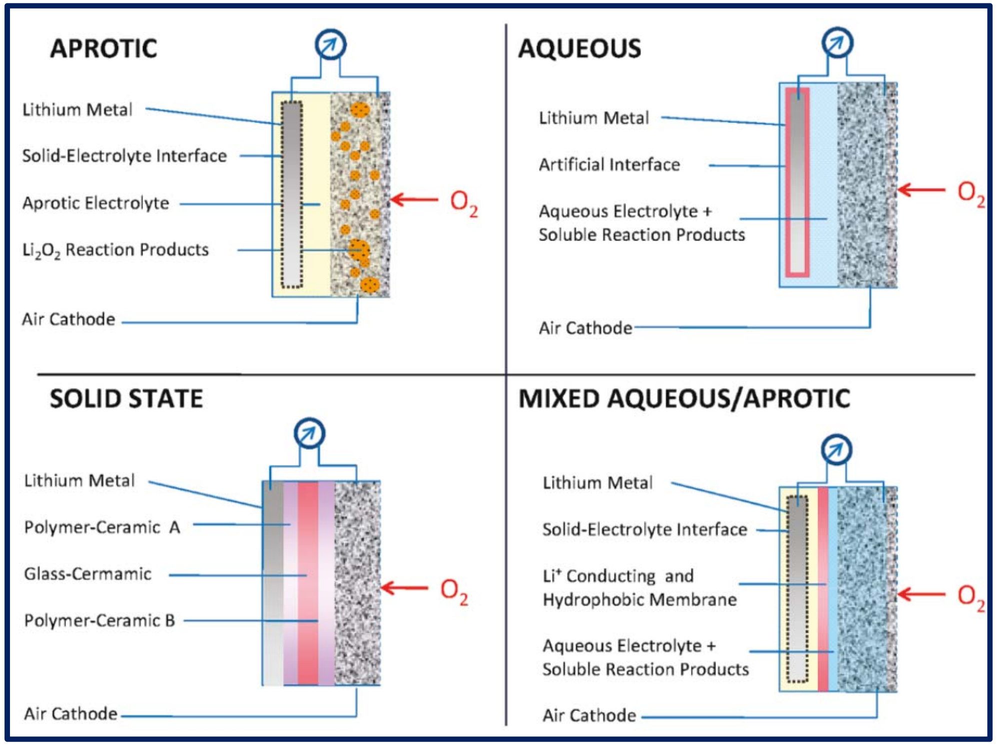


Sketch of gas diffusion electrode

Electrolyte Concepts Li-Air Battery

3 Basic electrolyte concepts :

- Aprotic electrolyte (water free)
- Aqueous electrolyte
- Solid state
- Mixed aqueous/aprotic hybrid



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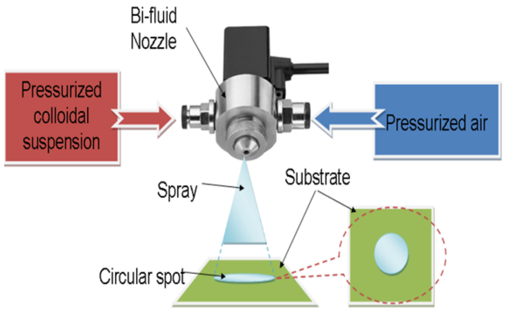
DLR Activities:

- **Bi-functional cathodes**
- **Aqueous alkaline electrolyte e.g. LiOH(aq.)**

DLR

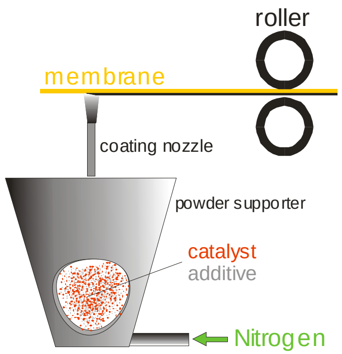
Preparation methods

Lab-scale | Mid-scale | Large-scale



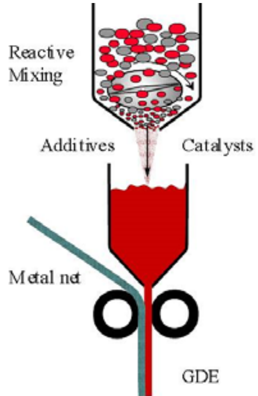
Colloidal Supension Spraying

Hydraulic Pressing



Dry Powder Spraying

Atmospheric Plasma Spraying (APS)

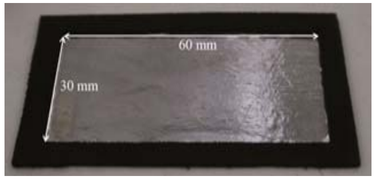


Reactive Rolling and Mixing

Preparation methods I: Hydraulic pressing

Hydraulic Pressing:

- Simple and fast process
- Dry process
- Solvent free
- Almost every powder processible
- Any shape of electrode
- Variable thickness
- Suitable for carbon-free electrodes



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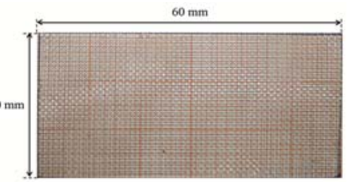

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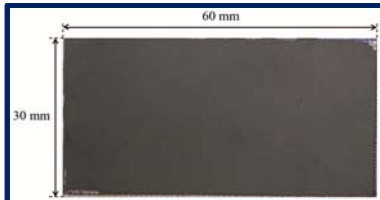
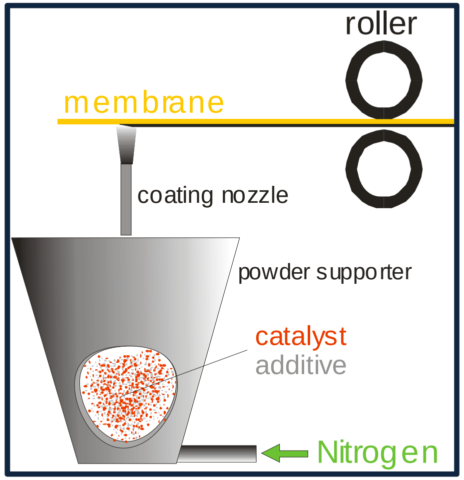
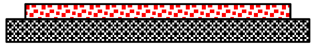


Preparation methods II: Dry spraying

Dry Spraying:

- Dry process
- Solvent free
- Coated substrates e.g. macroporous Rhodius metal mesh, metal foams
- Variable thickness
- Especially suitable for carbon contenting

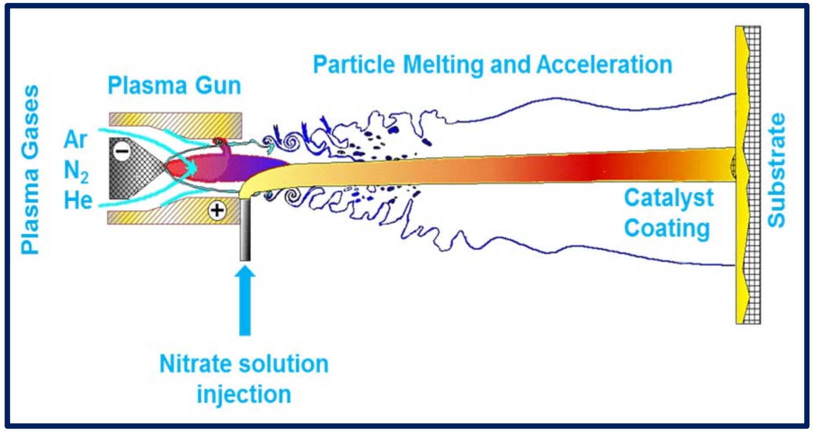


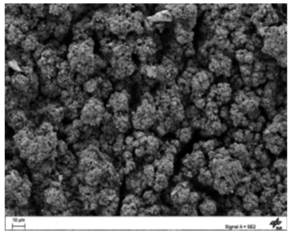


Preparation methods III: APS

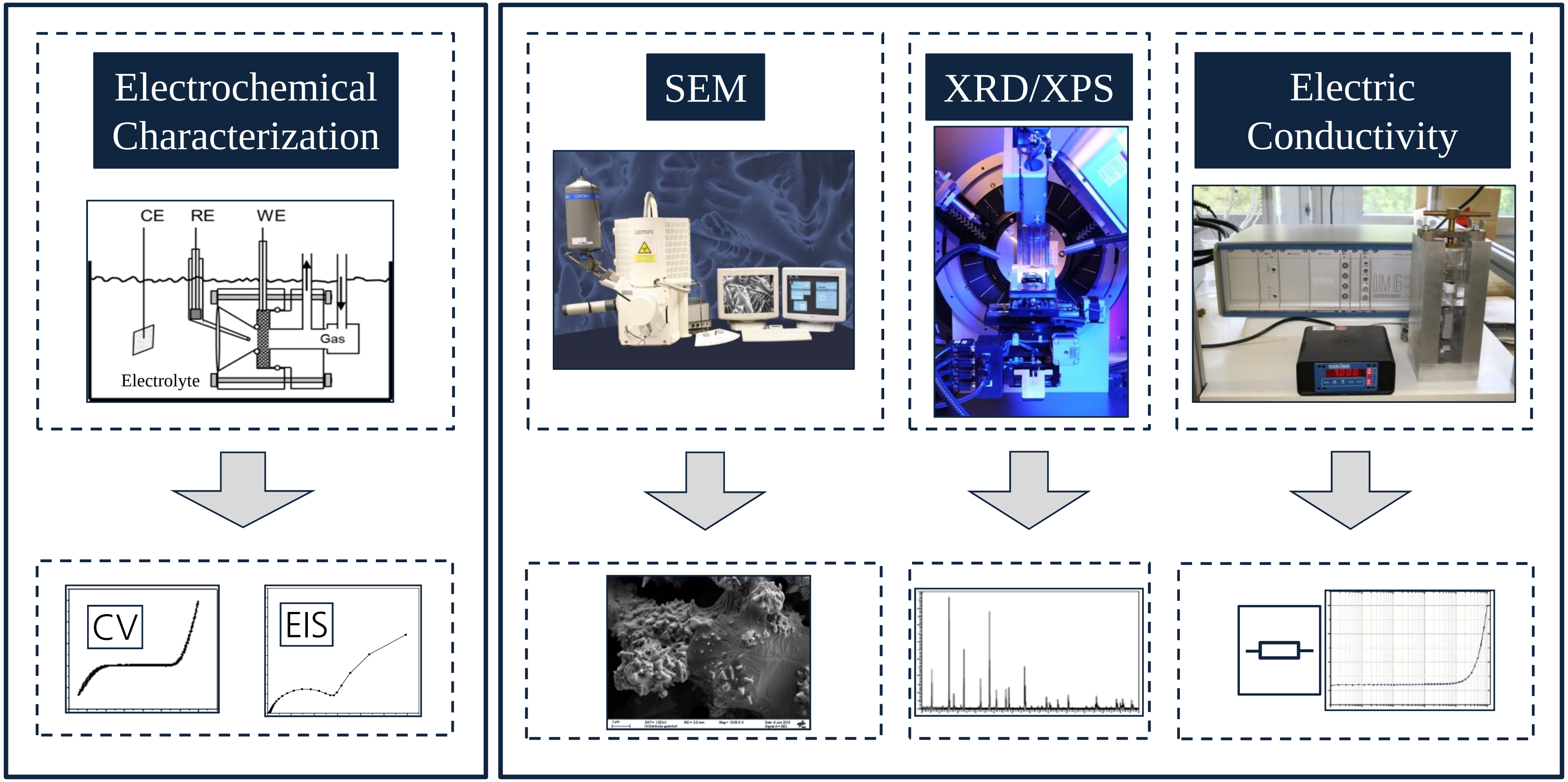
Atmosheric Plasma Spraying (APS):

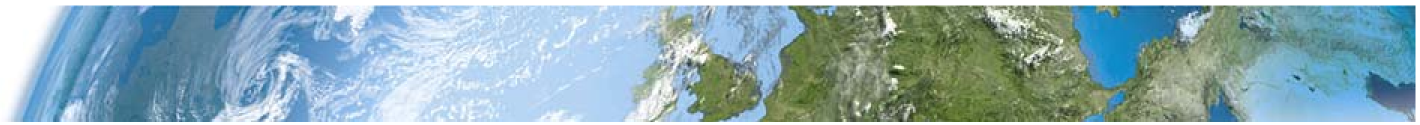
- Synthesis of catalysts via nitrate solution
- Oxide catalysts e.g. Co_3O_4, Mn_3O_4, NiO
- Coated substrates e.g. macroporous Rhodius metal mesh, metal foams
- Thin catalyst layer possible





Characterization methods: *In-* and *Ex-Situ*





Carbon-Free Bi-functional Electrodes

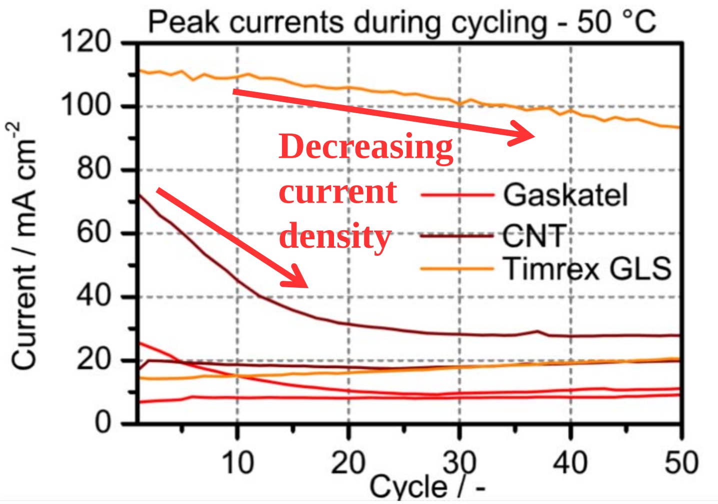
- Carbon is inexpensive, available, non-toxic, catalytic active for ORR and elec. conductive
- Most reported electrodes based on carbon material due to properties

! Problem of carbon material ! :

High carbon corrosion at potentials **> 1.35V** vs. RHE resulting in structural decomposition of electrodes and decreasing current densities due to the loss of active material **!**

DLR goal:

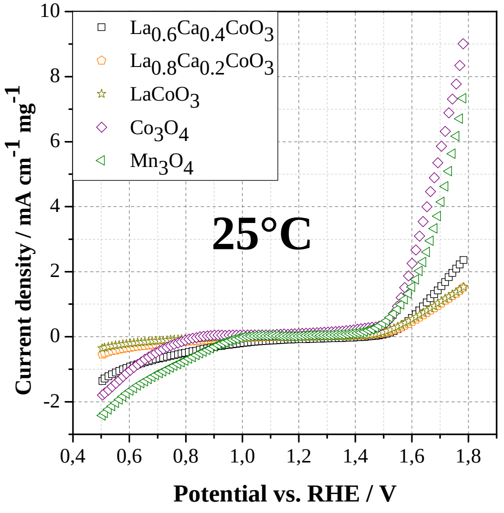
Complete substitution of carbon materials to enhance stability of electrodes **!**

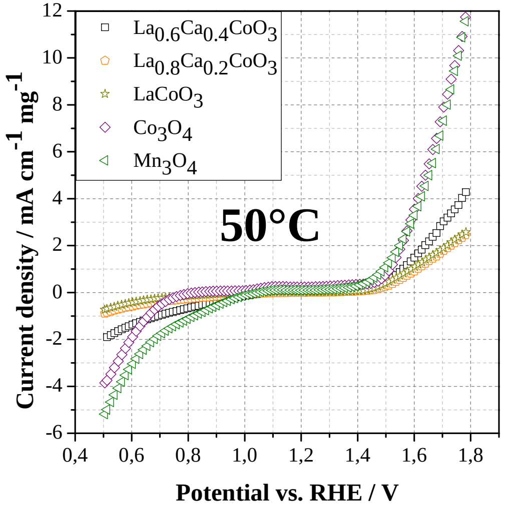


Carbon-Free Bi-functional Electrodes

- IrO_2, Co_3O_4, Mn_3O_4 and $La_{0.6}Ca_{0.4}CoO_3$ are most promising bi-functional catalysts
- Further investigations: **Co_3O_4** most promising oxide catalyst, comparable results to high cost catalyst IrO_2
  - D. Wittmaier, T. Danner, N. Wagner, K. A. Friedrich *Screening and further investigations on promising bi-functional catalysts for lithium-air batteries with an aqueous alkaline electrolyte*, Journal of Applied Electrochemistry (2014)

- Substitution of carbon by electrochem. stable, elec. conductive + catalytic active material to support Co_3O_4 + maintain elec. conductivity
- Possible materials due to alk. electrolyte: Ag and Ni
- Combinations Ag/Co_3O_4 and Ni/Co_3O_4



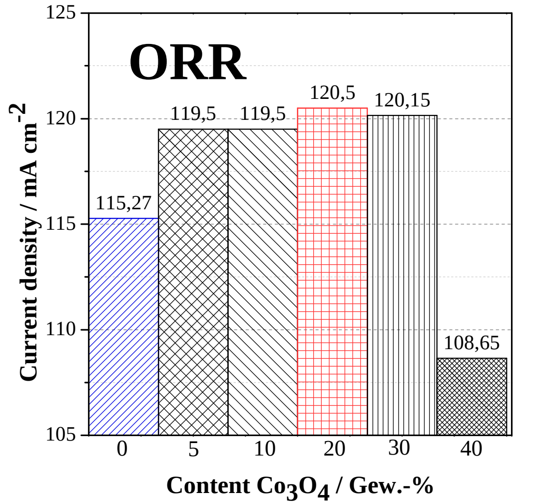


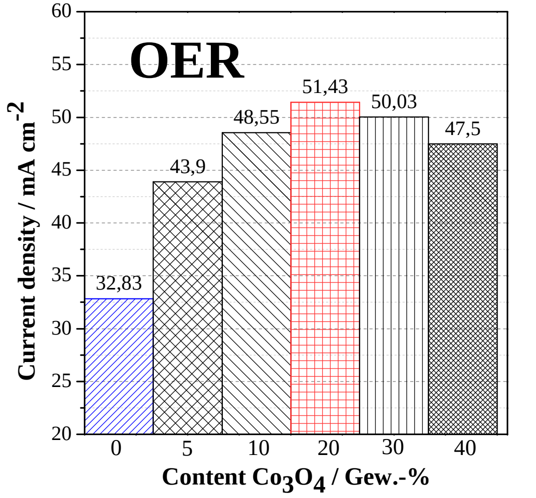
Basic concept Li-air battery: Type I (Ag)

- Combination exhibits high current densities
- Variation of Ag/Co_3O_4 ratio to find optimum composition; Binder content 10 wt.-% constant
- 20 wt.-% Co_3O_4 optimum catalyst content

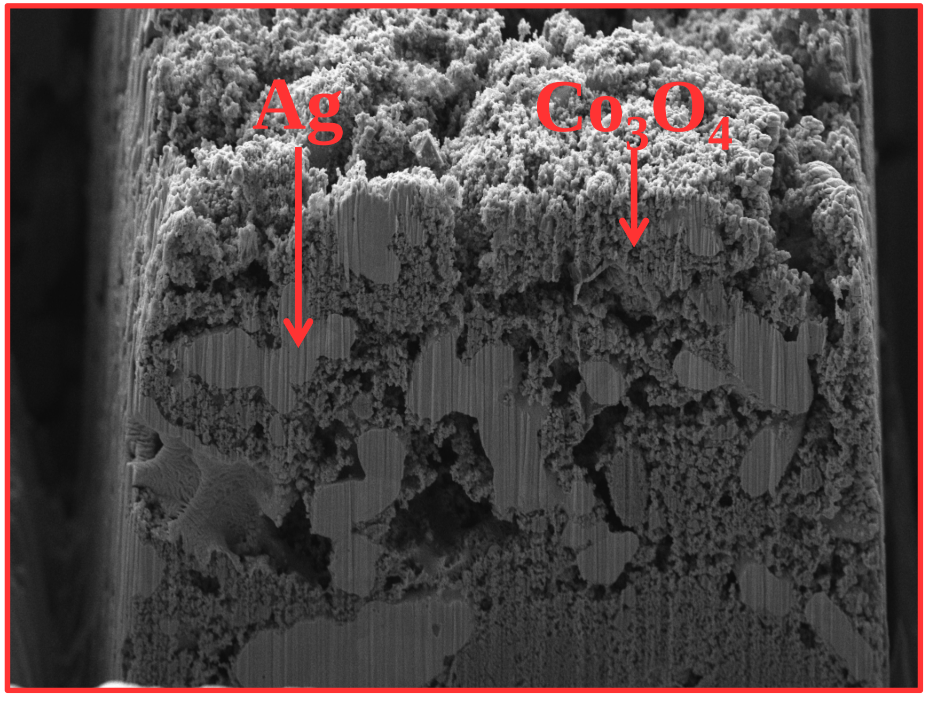
- High current densities + synergetic effect of Ag and Co_3O_4 leads to higher current densities for ORR + OER compared to pure Ag or Co_3O_4 electrodes (not completely understood yet)

- D. Wittmaier, N. Wagner, K. A. Friedrich, H. M. A. Amin, H. Baltruschat *Modified carbon-free silver electrodes for the use as cathodes in lithium-air batteries with an aqueous alkaline electrolyte*, Journal of Power Sources (2014)
- D. Wittmaier, N. Wagner, H. M. A. Amin, H. Baltruschat *Bifunktioneller Katalysator als Kathodenmaterial für die Metall-Luft-Batterie, Patentnummer* 10 2014 102 304.8 (2014)

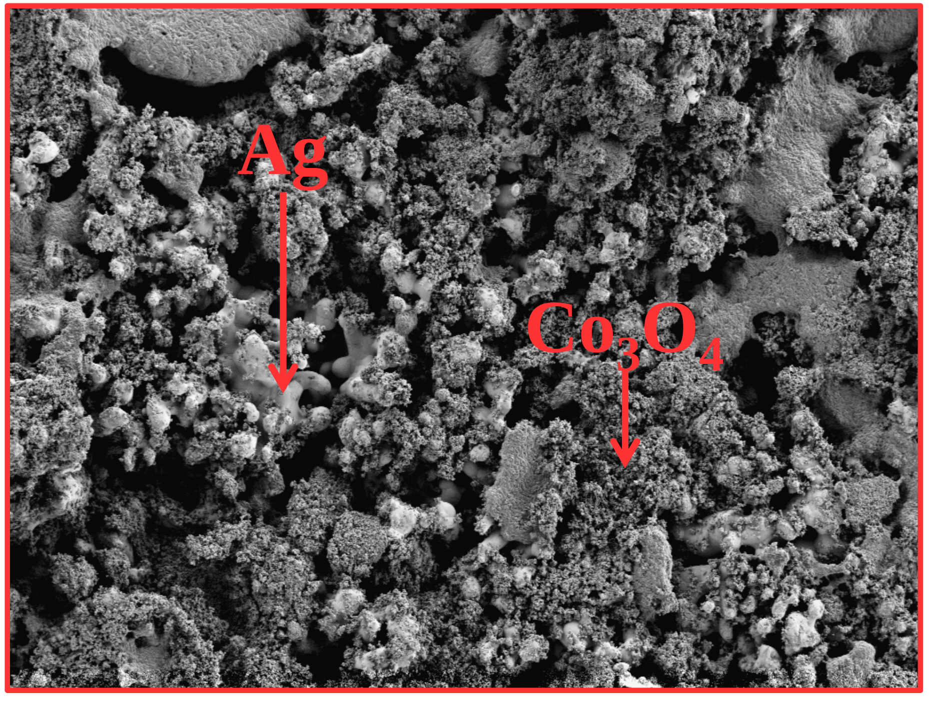




Carbon-Free Bi-functional Electrodes: Type I (Ag)



FIB-SEM Ag / Co_3O_4, 20 wt.-%
[University of Ulm]

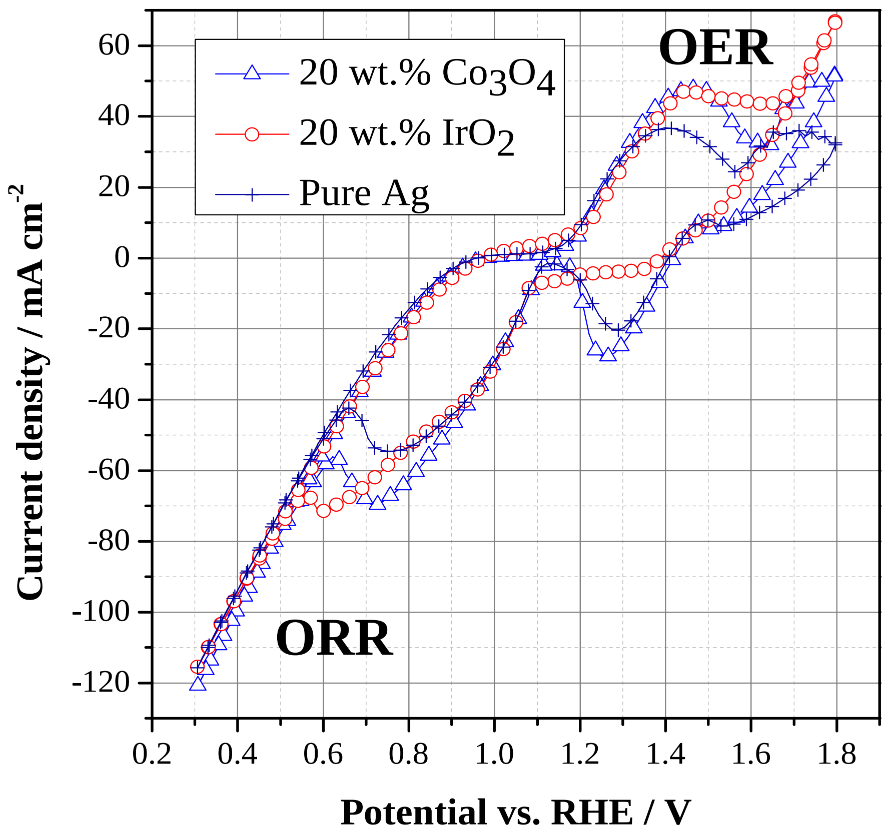


SEM Ag / Co_3O_4, 20 wt.-%
[DLR]

Carbon-Free Bi-functional Electrodes: Type I (Ag)

- Comparision of Ag/Co_3O_4 electrodes to high cost Ag/IrO_2 combination (benchmark)
- <u>20 wt.-% IrO_2</u> also highest current density
- <u>High improvement</u> over pure Ag;
- Ag/Co_3O_4 combination improves ORR activity
- Comparison shows only slight advantage of Ag/IrO_2 electrodes (in OER) but much higher costs

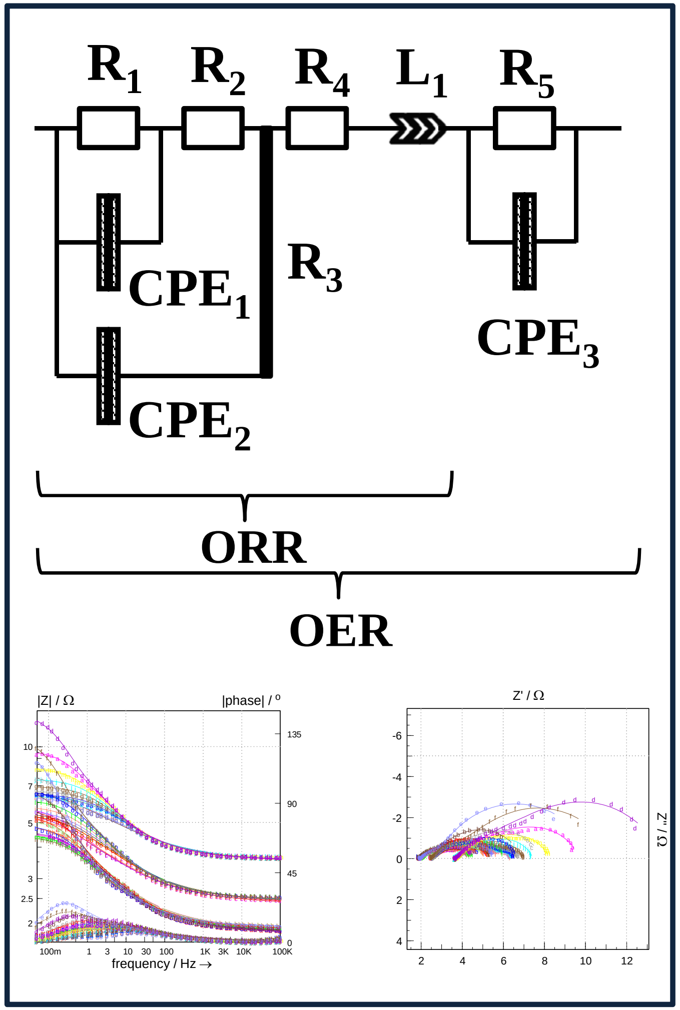
Ag/Co_3O_4 most promising combination for future investigations



➢D. Wittmaier, N. Wagner, K. A. Friedrich, H. M. A. Amin, H. Baltruschat *Modified carbon-free silver electrodes for the use as cathodes in lithium-air batteries with an aqueous alkaline electrolyte*, Journal of Power Sources (2014)

Carbon-Free Bi-functional Electrodes: EIS, Type I (Ag)

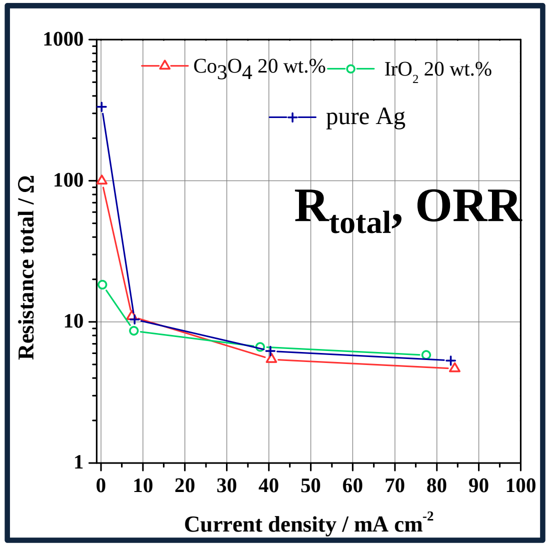
- Recorded impedance spectra were modeled with equivalent circuit model
- Different models for ORR and OER
- OER model takes into account growing oxide layer on surface of electrode while electrode operating in OER mode
- Evaluation of important resistances R_{total} for ORR and OER and R_5 (oxide layer)



Carbon-Free Bi-functional Electrodes: EIS, Type I (Ag)

Resistances gained from simulation of impedance model:

- Current densities for ORR only slight difference, this corresponds to values for R_{total}, ORR
- Current densities for pure Ag electrodes in OER much lower than for also corresponds to R_{total}, OER
- Best combintion for OER exhibits lowest resistance R_5 for oxide layer
- Ag electrodes have highest resistances for OER



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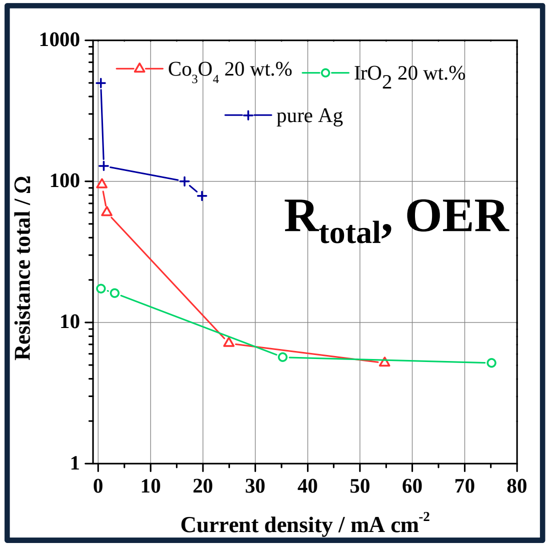
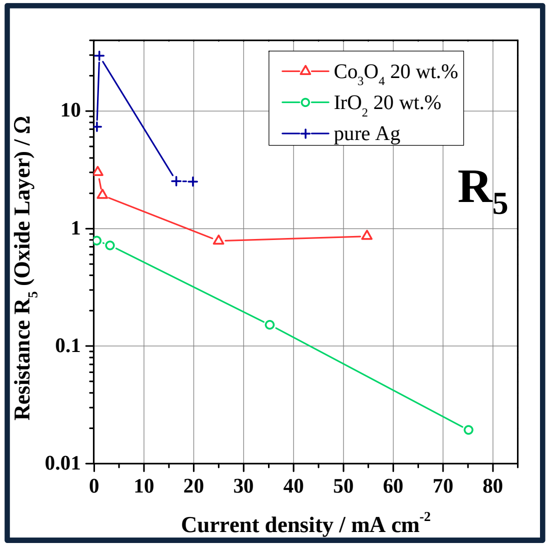
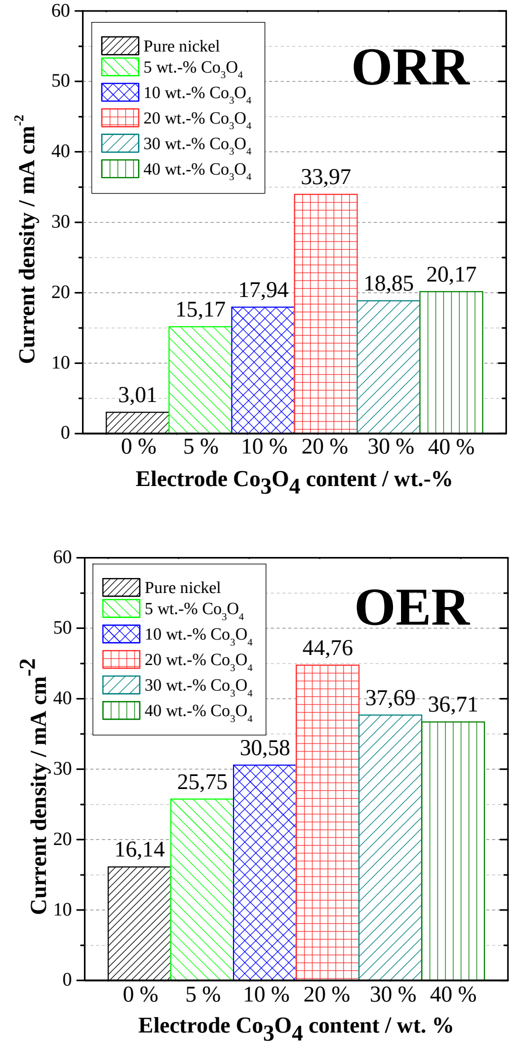




Carbon-Free Bi-functional Electrodes: Type II (Ni)

- Combination exhibits high current densities and high stability
- Variation of Ni/Co_3O_4 ratio to find optimum composition; Binder content 10 wt.-% constant
- <u>20 wt.-% Co_3O_4</u> optimum catalyst content (as for Ag and IrO_2)



- High current densities + synergetic effect of Ni + Co_3O_4 leads to higher current densities for ORR + OER compared to pure Ni or Co_3O_4 electrodes (not completely understood yet)
- Higher current densities for OER than ORR but lower than Ag/Co_3O_4

- D. Wittmaier, S. Aisenbrey, N. Wagner, K. A. Friedrich
Carbon-free nickel/cobalt-oxide cathodes for lithium-air batteries with an aqueous alkaline electrolyte, Electrochim. Acta (2014), submitted
- D. Wittmaier, N. Wagner
Bifunktioneller Katalysator und Leitzusatz als Kathodenmaterial für die Metall-Luft-Batterie, Patentnummer 10 2014 111 701.8 (2014)

Publications

Peer-reviewed publications:

- D. Wittmaier, T. Danner, N. Wagner, K. A. Friedrich
  Screening and further investigations on promising bi-functional catalysts for lithium-air batteries with an aqueous alkaline electrolyte, Journal of Applied Electrochemistry (2014)
- D. Wittmaier, N. Wagner, K. A. Friedrich, H. M. A. Amin, H. Baltruschat
  Modified carbon-free silver electrodes for the use as cathodes in lithium-air batteries with an aqueous alkaline electrolyte, Journal of Power Sources (2014)
- D. Wittmaier, S. Aisenbrey, N. Wagner, K. A. Friedrich
  Carbon-free nickel/cobalt-oxide cathodes for lithium-air batteries with an aqueous alkaline electrolyte, Electrochim. Acta (2014), submitted
- T. Danner, B. Horstmann, D. Wittmaier, N. Wagner, W. G. Bessler
  Reaction and transport in Ag/Ag2O gas diffusion electrodes of aqueous Li-O2 batteries; Experiments and modeling, Journal of Power Sources (2014)
- H. M. A. Amin, H. Baltruschat, D. Wittmaier, K.A. Friedrich
  Highly efficient bifunctional catalyst for alkaline oxygen-electrodes based on a Ag and spinel Co3O4 hybrid: RRDE and online DEMS insights, Angewandte Chemie (2014) submitted

Patents:

- D. Wittmaier, N. Wagner, H. M. A. Amin, H. Baltruschat
  Bifunktioneller Katalysator als Kathodenmaterial für die Metall-Luft-Batterie, Patentnummer 10 2014 102 304.8 (2014)
- D. Wittmaier, N. Wagner
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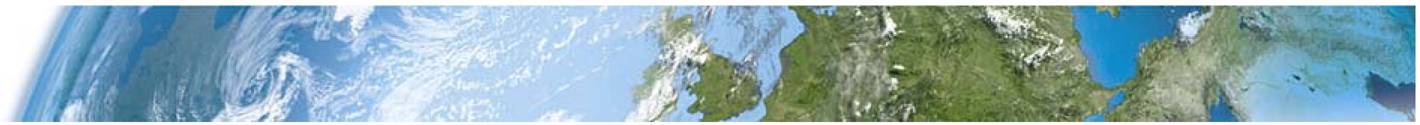

Conclusion

- Most promising bi-functional catalysts Co_3O_4 and IrO_2
- Due to carbon corrosion carbon-free electrodes promise higher (long-term) stability
- Substituion of carbon by Ag and Ni. Electrodes prepared with in comparision to IrO_2 low cost Co_3O_4
- 20 wt.-% Co_3O_4 carbon-free electrodes show highest current densities

Thank you for your attention!

DLR

Thank you to

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Luft Li

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