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

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

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EIS measurement at different SOC

Discharge at 1C
Discrimination of SOC and SOH of serial connected batteries

### Serial connection V2

<table>
<thead>
<tr>
<th>Component</th>
<th>Voltage (V)</th>
<th>State of Health</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z01</td>
<td>3.25</td>
<td>100</td>
</tr>
<tr>
<td>Z02</td>
<td>3.25</td>
<td>100</td>
</tr>
<tr>
<td>Z07</td>
<td>3.25</td>
<td>60</td>
</tr>
</tbody>
</table>

- $i_{\text{total}}(t)$
- $Z01$  
- $Z02$  
- $Z07$

- $\text{SoC}_{\text{max}}$
- $\text{SoC}_{\text{min}}$

![Graph showing impedance and phase angle vs. frequency](image)

![Bar graph showing voltage and current vs. frequency](image)
Electrochemical Model of Li-S Battery

<table>
<thead>
<tr>
<th>Model</th>
<th>Chemical and physical cause</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_0$</td>
<td>Ohmic resistance</td>
</tr>
<tr>
<td>$R_1$-CPE$_1$</td>
<td>Anode charge transfer</td>
</tr>
<tr>
<td>$R_2$-CPE$_2$</td>
<td>Cathode process: charge transfer of sulfur intermediates</td>
</tr>
<tr>
<td>$R_3$-CPE$_3$</td>
<td>Cathode process: reaction and formation of S$_8$ and Li$_2$S</td>
</tr>
<tr>
<td>$R_4$-CPE$_4$</td>
<td>Diffusion</td>
</tr>
</tbody>
</table>
Motivation

Why Li-air batteries?

- Highest theoretical specific energy density (11.425 Wh/kg)
  Cathodic reactant, O₂ 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
Motivation

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Schematically representation of a Li-air battery
Architectures of Li-air Batteries

Non-aqueous electrolyte:

\[ \text{2Li}^+ + \text{O}_2 + 2e^- \rightleftharpoons \text{Li}_2\text{O}_2 \quad E_{\text{rev}} = 2,959 \text{ V} \]

\[ \text{2Li}^+ + 2e^- + (1/2) \text{O}_2 \rightleftharpoons \text{Li}_2\text{O} \quad E_{\text{rev}} = 2,913 \text{ V} \]

Aqueous electrolyte:

\[ \text{4Li} + \text{O}_2 + 2\text{H}_2\text{O} \rightleftharpoons 4\text{LiOH} \quad \text{(alkaline media)} \quad E_{\text{rev}} = 3,446 \text{ V} \]

\[ \text{4Li} + \text{O}_2 + 4\text{H}^+ \rightleftharpoons 2\text{H}_2\text{O} + 4\text{Li}^+ \quad \text{(acidic media)} \quad E_{\text{rev}} = 4,274 \text{ V} \]
Schematically representation of Lithium-Air Battery with Aqueous Electrolyte

Interlayer

Lithium
Solid Li⁺-conductor

Reaction - products
Aqueous electrolyte solution
O₂-Reduction

Reaction equation (alkaline Electrolyte):
\[ 4 \text{Li} + \text{O}_2 + 2\text{H}_2\text{O} \leftrightarrow 4\text{LiOH}; \text{E} = 3.45 \text{V} \]
Bi-functional Oxygen-Electrodes: Design

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

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

- Different manufacturing 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
Manufacturing 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 = catalyst + carbon/graphite + binder

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

Catalyst layer = catalyst + carbon/graphite + binder

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

Catalyst layer = catalyst + carbon/graphite + binder

Graphite GDE substrate

Sigracet® GDL35 DC
Impedance Measurements during ORR in 10 N NaOH, on Silver Electrodes at Different Current Densities, \( i < -50 \text{ mAcm}^{-2} \)

Bode representation

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

\[ Z_q = \]

Diagram showing a model with components such as electrolyte, pores, and current collector GDL.
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
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
Potential dependency of total resistance during ORR at different electrodes, 1 N LiOH

![Graph showing the relationship between potential OCV minus x (in mV) and resistance (in Ω) for different electrodes and conditions. The graph includes lines for Electrode 1 (high pressure) at 25°C and 50°C, Electrode 2 (low pressure) at 25°C and 50°C, and their resistance values plotted against potential OCV minus x.](image_url)
Potential dependency of charge transfer resistance during OER

Potential OCV plus x / mV

Resistance / Ω

R₂ OER (charge transfer)
- Electrode 1 (high pressure) 25c
- Electrode 1 (high pressure) 50c
- Electrode 2 (high pressure) 25c
- Electrode 2 (low pressure) 50c
Potential dependency of charge transfer resistance in oxide layer potential region (OER)
CV of a polished Ag electrode, 25% KOH, O₂ sat.

Ag-Electrode (polished)
25% KOH, 18°C
v = 1 mVs⁻¹

Potential vs. Hg/HgO
Conclusion

• From the catalyst screening, a new bifunctional catalyst 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 mA cm⁻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
Reactions pathways for the cathodic oxygen reduction in alkaline solution

Direct-X 4e\(^{-}\) - path: \(2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^{-} \rightarrow 4\text{OH}^{-}\)

\(\text{O}_2 + 2\text{M} \leftrightarrow 2\text{M}...\text{O}\)

2 (M...O + e\(^{-}\) → MO\(^{-}\))
2 (MO\(^{-}\) + H\(_2\)O ↔ MOH + OH\(^{-}\))
2 (MOH + e\(^{-}\) ↔ OH\(^{-}\) + M)

Peroxid - Path: \(\text{H}_2\text{O} + \text{O}_2 + 2\text{e}^{-} \leftrightarrow \text{HO}_2^{-} + \text{OH}^{-}\)

\(\text{O}_2 + \text{M} \leftrightarrow \text{M}...\text{O}_2\)
\(\text{M}...\text{O}_2 + \text{e}^{-} \rightarrow \text{MO}_2^{-}\)
\(\text{MO}_2^{-} + \text{H}_2\text{O} \leftrightarrow \text{MHO}_2 + \text{OH}^{-}\)
\(\text{MHO}_2 + \text{e}^{-} \leftrightarrow \text{HO}_2^{-} + \text{M}\)

Peroxid-Reduction: \(\text{HO}_2^{-} + \text{H}_2\text{O} + 2\text{e}^{-} \rightarrow 3\text{OH}^{-}\)

\(\text{HO}_2^{-} + \text{M} \leftrightarrow \text{MHO}_2^{-}\)
\(\text{MHO}_2^{-} + \text{H}_2\text{O} \leftrightarrow \text{MH}_2\text{O}_2 + \text{OH}^{-}\)
\(\text{MH}_2\text{O}_2 + \text{e}^{-} \rightarrow \text{MOH} + \text{OH}^{-}\)
\(\text{MOH} + \text{e}^{-} \leftrightarrow \text{M} + \text{OH}^{-}\)

Catalytically Peroxid-decomposition: \(2\text{HO}_2^{-} \rightarrow \text{O}_2 + 2\text{OH}^{-}\)

\(\text{HO}_2^{-} + \text{M} \leftrightarrow \text{MHO}_2^{-}\)
\(\text{MHO}_2^{-} \rightarrow \text{MO} + \text{OH}^{-}\)
\(\text{MO} + \text{HO}_2^{-} \rightarrow \text{O}_2 + \text{OH}^{-} + \text{M}\)
SEM pictures of Ag-GDE, produced by the RMR technique (Ag$_2$O+PTFE)

Ag-GDE, unused part

Ag-GDE, used