Institute of Engineering Thermodynamics

Highly Stable Carbon-Free Cathodes for Li-Air Batteries with Aqueous Alkaline Electrolyte: Electrochemical and Structural Investigations

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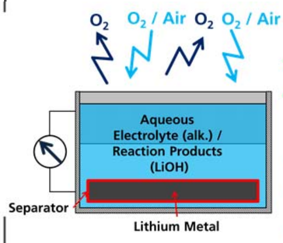
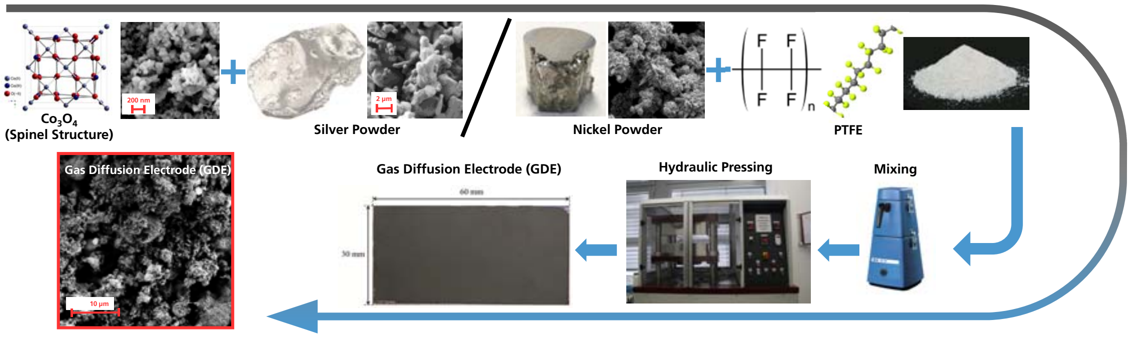
Motivation/Challenges



- \+ High theoretical energy density and capacity of Lithium-Air Batteries - 12931 Wh kg^{-1}
- \+ Oxygen is abundant, inexpensive and nontoxic
- − High overpotential during oxygen evolution reaction (OER, charge reac.) and oxygen reduction reaction (ORR, discharge reac.)
- − Low cyclability due to widely used carbon materials in potential ranges above 1.35 V vs. RHE (Carbon Corrosion)
- − Low solubility of reaction products

Electrode Fabrication



- **Electrode Composition:**

  Co_3O_4 (Sigma Aldrich) 5 – 40 wt.-%

  \+ **Silver** (Ferro AG) or Nickel powder 50 – 85 wt.-%

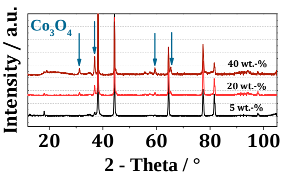
  \+ PTFE 10 wt.-%

- **Cell Configuration:**

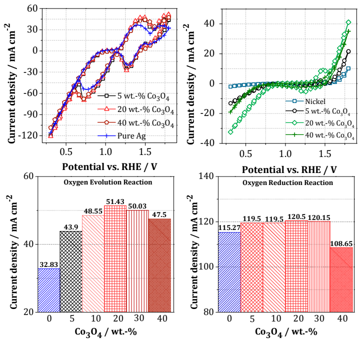
  Half-Cell with RHE Electrolyte 1 M LiOH(aq.)

Silver/Tricobalttetraoxid (Co_3O_4) - Electrodes

X-Ray Diffraction (XRD)

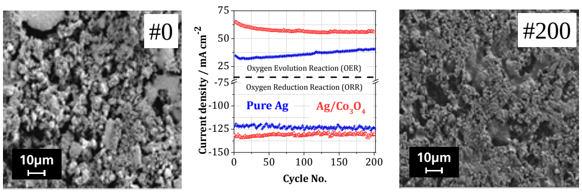


Cyclic Voltammetry (CV)



- Ag: Crystalline structure, particle size 10 – 30 µm; Ni: Crystalline structure, particle size 3 – 9 µm
- Co_3O_4: Amorphous structure, particle size < 50 nm
- Increasing intensity of Co_3O_4 peaks with higher Co_3O_4 content
- CV carried out in half-cell (potential range 0.3 – 1.8 V vs. RHE,1 M LiOH solution, 25 °C, platinum counter electrode).
- Surface area of bi-metal electrodes (Ag and Ni based) increasing with Co_3O_4 content
- High current density for ORR is due to high catalytic activity of Ag; Ni electrodes are less active for ORR
- Addition of Co_3O_4 has synergetic effect in ORR resulting in higher current densities compared to pure Ag or Ni electrodes.
- For OER addition of Co_3O_4 increases current density compared to pure Ag or Ni electrodes; Ag based electrodes show higher overall performance

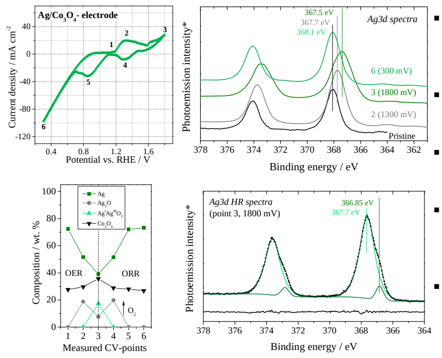
Cyclability/SEM Ag/Co_3O_4 electrodes



- Both, pure Ag and Ag/Co_3O_4 show good long-term behavior
- Surface area is increasing due to cycling

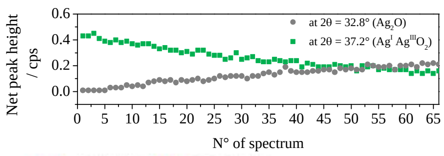
Structural / Surface Characteristics

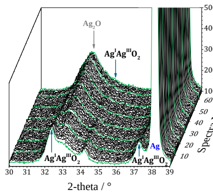
Oxidation States Ag/Co_3O_4 electrodes

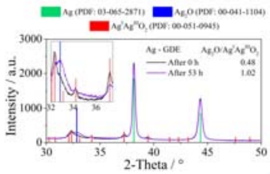


- Ag oxides: Proof of $Ag^{I}Ag^{III}O_2$ instead of $Ag^{II}O$ at high potentials of OER
- HR-XPS shows shoulder of Ag-III-oxide
- $Ag^{I}Ag^{III}O_2$ is reduced back to Ag_2O and Ag during cycling
- $Ag^{I}Ag^{III}O_2$ decomposes homogeneously to Ag_2O under ambient conditions
- After 53 hours more than 50 % of $Ag^{I}Ag^{III}O_2$ is decomposed to Ag_2O

Decomposition $Ag^{I}Ag^{III}O_2$







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Wissen für Morgen

DLR Deutsches Zentrum für Luft- und Raumfahrt

Federal Ministry of Education and Research

PtJ Projektträger Jülich Forschungszentrum Jülich

We thank the Federal Ministry of Education and Research for funding this work. FKZ:03X4624C