Carbon-free bifunctional cathodes for the use in Lithium - Air Batteries with an aqueous alkaline electrolyte

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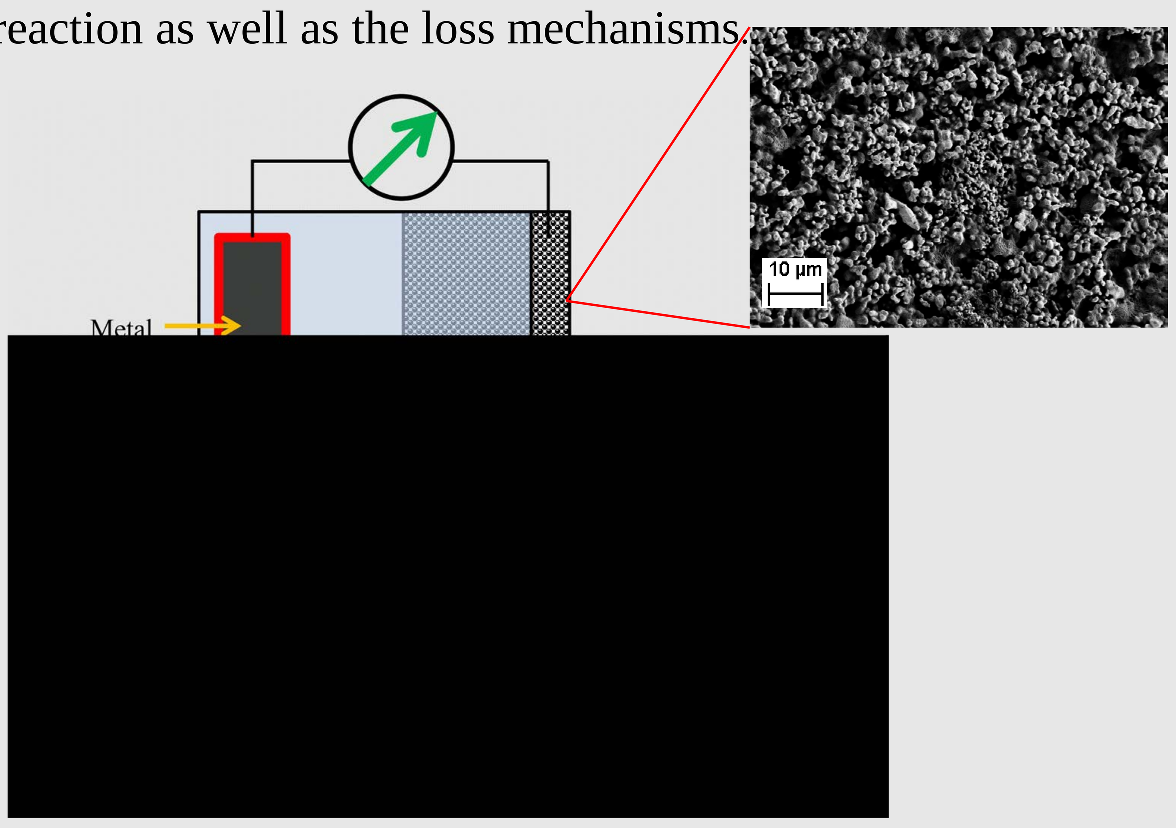
Introduction

Metal-Air Batteries

+ *High theoretical specific energy density and capacity*
+ *Oxygen is abundant, inexpensive and nontoxic*
- *High overpotentials during charging/discharging*
- *Low cyclability*
- *Low solubility of reaction products*

This poster shows carbon-free silver based gas diffusion electrodes for the use as cathodes in metal-air batteries. The electrodes were electrochemically investigated with cyclic voltammetry and electrochemical impedance spectroscopy to identify the behaviour during oxygen reduction and evolution reaction as well as the loss mechanisms.



Materials and Methods

Cathode catalysts/materials

- Silver powder (Ferro AG)
- Co_3O_4 powder (Sigma Aldrich)
- IrO_2/TiO_2 powder (Umicore)
- PTFE powder (3M)

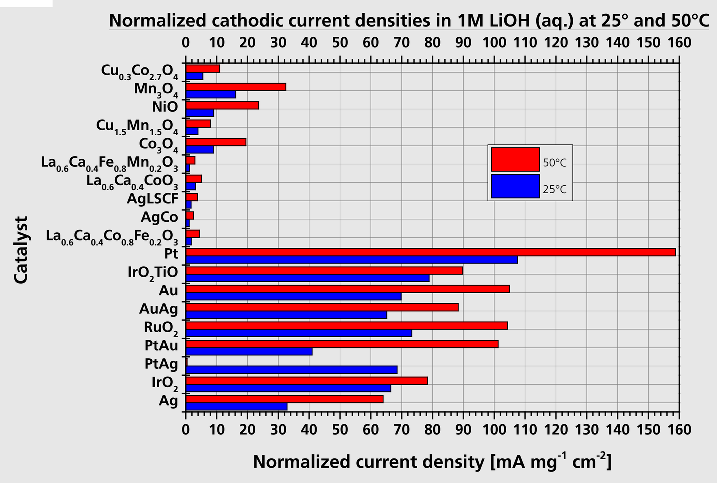
Cathode preparation

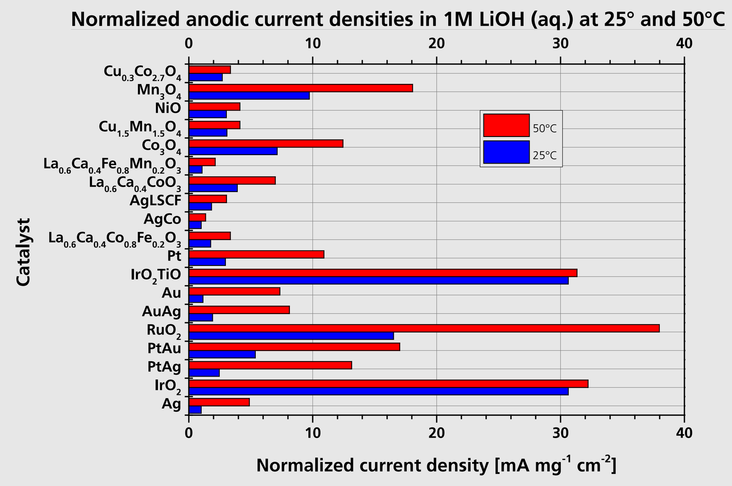
- Ag/Co_3O_4 or $Ag/(IrO_2/TiO_2)$ powders and binder were mixed in a double knife mill
- Powders were filled in a forming frame covered with a stainless steel net and afterwards grouted to an electrode
- A heat treatment at 340°C for 1h enhances mechanical strength
- Thickness 330-397 µm

Experimental

- Cyclic Voltammetry was carried out in a half cell with 1 M LiOH, a potential range from 0.3 V to 1.8 V vs. RHE and at 25° C.
- Polarization curves were carried out at 0.3 V and 1.8 V vs. RHE for 15 min and 25°C
- Long-term tests were also carried out at 25° C and 200 cycles.
- Potentiostatic EIS was carried out in the at OCV and at OCV ± 100 mV, ± 300 mV, ± 500 mV, ± 700 mV in the frequency range of 100 mHz to 100 kHz.

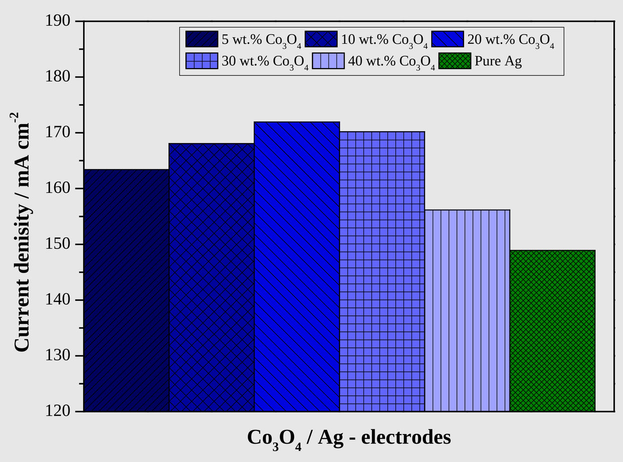
Experimental Results

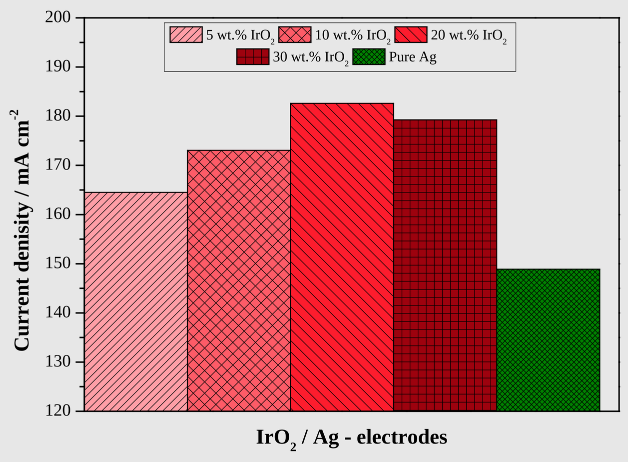


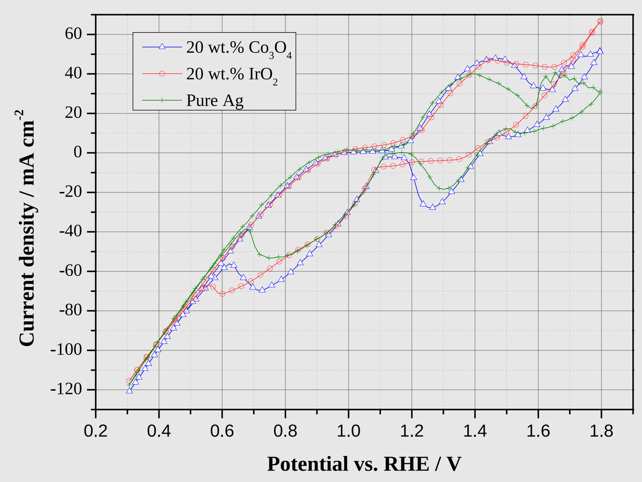


Catalyst screening showed that Co_3O_4 and IrO_2 are suitable catalysts for ORR and OER [1]. Even though carbon materials cause major issues due to their instability in OER (< 1350mV vs. RHE) they are mostly used in cathodes for aqueous Li-Air Batteries. A high degradation and therefor a low cycle life are the results for carbon based electrodes. This work shows carbon-free electrodes consisting of metal and metal oxides exhibiting high current densities at relatively low overpotentials and a high cycle life (< 200 cycles) [2].

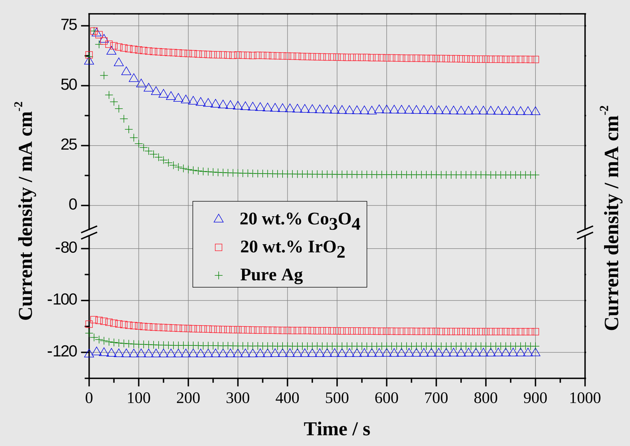
Both metal oxides Co_3O_4 and IrO_2 have low electric conductivities and can therefor not be used as single catalysts in gas diffusion electrodes causing high overpotentials during charge and discharge mode. Mixing one of these two metal oxides with pure silver enhances electric conductivity as well as catalytic activity of the gas diffusion electrodes significantly. ORR is dominated by the activity of silver, OER is dominated by Co_3O_4 or IrO_2. The metal oxides enhance OER current densities compared to pure silver electrodes [2] [3].

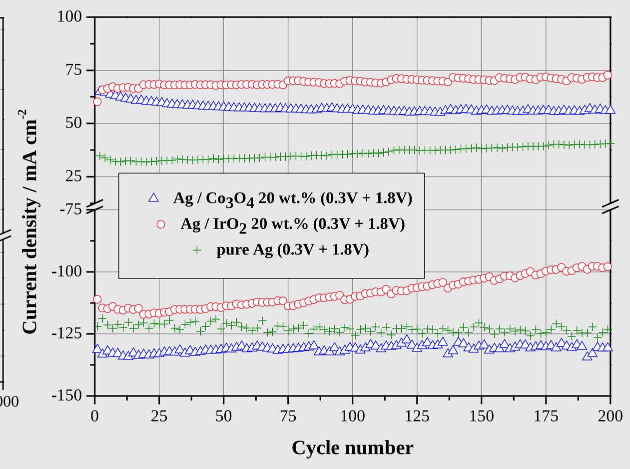


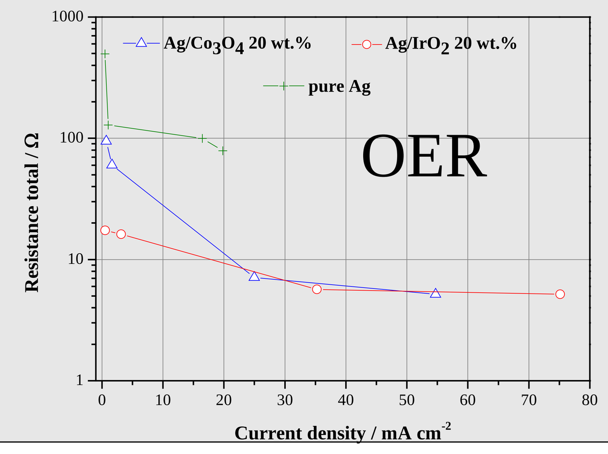


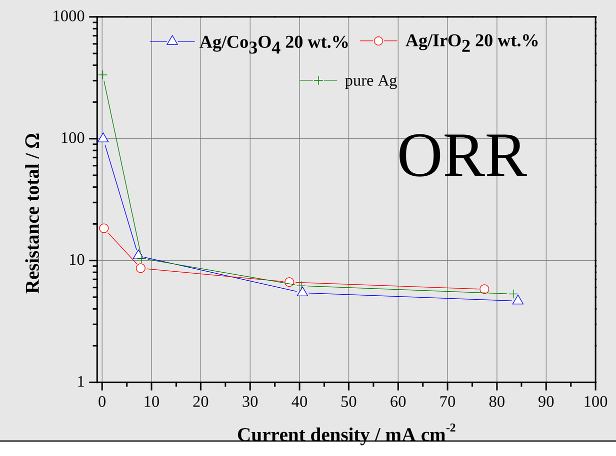


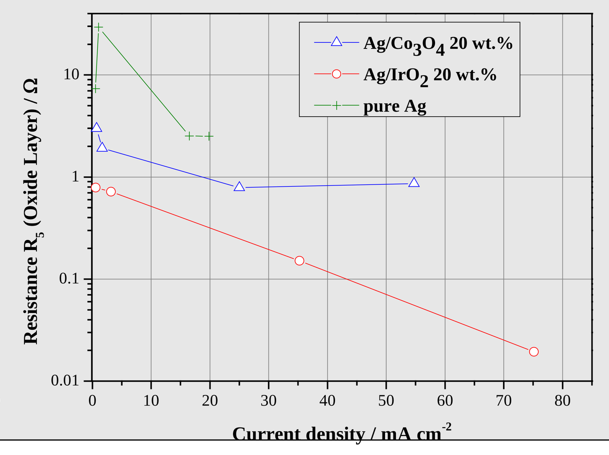
A mixture of silver and 20 wt.% Co_3O_4 or IrO_2 shows the highest current densities. Also potentiostatic polarization curves show enhanced current densities and a stable behavior after 200 s for ORR and OER. Especially the combination Co_3O_4 and silver shows also an excellent long-term stability over 200 cycles. Impedance spectra shows that total resistances in ORR and OER of the electrodes correlate to the achieved current densities [2].











Conclusions

- Carbon-free silver-based gas diffusion electrodes were developed
- GDE´s with 20 wt. % Co_3O_4 or IrO_2 exhibit the highest current densities and stable current densities in potentiostatic mode
- Ag/ Co_3O_4 -electrodes show an excellent long-term stability (< 200 cycles)
- Resistances calculated from impedance spectra correlate to achieved current densities

References

[1] D. Wittmaier, T. Danner, N. Wagner, K.A. Friedrich, J. Appl. Electrochem., (2014) 44:73 – 85

[2] D. Wittmaier, N.Wagner, K.A. Friedrich, H.M.A. Amin, H. Baltruschat, J. Power Sources (2014) submitted

[3] T. Danner, B. Horstmann, D. Wittmaier, N. Wagner, W.G. Bessler, J. Power Sources (2014) submitted

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