



# Modified carbon-free silver electrodes for the use as cathodes in lithium–air batteries with an aqueous alkaline electrolyte

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## HIGHLIGHTS

- High activity bi-functional catalyst combination for ORR and OER.
- An optimum ratio of high active bi-functional catalysts was found.
- Novel electrodes without carbon to avoid carbon corrosion during OER mode.
- EIS models for ORR and OER describe influence of a growing oxide layers.
- Long-term test exhibited an excellent long-term stability over 200 cycles.

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## ABSTRACT

Gas diffusion electrodes with silver catalysts show a high activity towards oxygen reduction reaction in alkaline media but a rather poor activity towards oxygen evolution reaction. For the use in future lithium–air batteries with an aqueous alkaline electrolyte the activity of such electrodes must be improved significantly. As  $\text{Co}_3\text{O}_4$  is a promising metal oxide catalyst for oxygen evolution in alkaline media, silver electrodes were modified with  $\text{Co}_3\text{O}_4$ . For comparison silver electrodes were also modified with  $\text{IrO}_2$ . Due to the poor stability of carbon materials at high anodic potentials these gas diffusion electrodes were prepared without carbon support to improve especially the long-term stability. Gas diffusion electrodes were electrochemically investigated in an electrochemical half-cell arrangement. In addition to cyclic voltammograms electrochemical impedance spectroscopy (EIS) was carried out. SEM and XRD were used for the physical and morphological investigations. Investigations showed that silver electrodes containing 20 wt.%  $\text{Co}_3\text{O}_4$  exhibited the highest performance and highest long-term stability. For comparison, rotating – ring – disc – electrode experiments have been performed using model electrodes with thin catalyst layers, showing that the amount of hydrogen peroxide evolved is negligible.

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## 1. Introduction

Today's lithium-ion batteries (LIB) are limited in their capacity due to their active materials used as anode and cathode. The theoretical energy density of LIB's is only 75 to 200 Wh  $\text{kg}^{-1}$  [1,2]. For future applications in electric vehicles (EV), plug-in hybrid vehicles (PHEV) or in storage devices for renewable energy batteries

with far higher energy densities are required to reduce costs, weight and constructed space. The lithium–air battery (LAB) with a metallic lithium anode and an aqueous electrolyte has the theoretical energy density of 12,931 Wh  $\text{kg}^{-1}$  [3], which is almost as high as the theoretical energy density of gasoline with approximately 13,200 Wh  $\text{kg}^{-1}$ . Due to limitations in a real cell this theoretical energy density cannot be achieved in practice but still the practical energy density is predicted to increase by factor 5 to 10 compared to today's LIB's. Girishkumar et al. estimate a practical energy density of 1700 Wh  $\text{kg}^{-1}$  on cell level. This corresponds to 13% of the theoretical value of an aqueous LAB and would be the same as for gasoline [1].

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**Table 1**  
Composition of silver- or iridium/cobalt oxide electrodes.

		Ag/wt.%	PTFE/wt.%	Co <sub>3</sub> O <sub>4</sub> /wt.%	IrO <sub>2</sub> /wt.%
Electrode	Pure Ag	90	10	0	0
	5 wt.%	85	10	5	5
	10 wt.%	80	10	10	10
	20 wt.%	70	10	20	20
	30 wt.%	60	10	30	30
	40 wt.%	50	10	40	x

Before LAB cells can be used still some limiting factors must be overcome as reported in literature [1,2,4–23]. Main limiting factors are high overpotentials during charge and discharge resulting mostly from deficient catalytic activity of catalysts used on the cathode side of the battery. Catalysts must catalyze the oxygen reduction reaction (ORR) while discharging as well as the oxygen evolution reaction (OER) while charging the battery. Furthermore LAB's suffer from low cyclability and the decomposition of electrode materials. Especially carbon, mostly used in electrodes for metal–air batteries with aqueous alkaline electrolyte, is not stable under oxygen evolution conditions in alkaline media [24–26]. To overcome these limiting factors the main focus of research has to be on sufficient catalysts and a stable electronic conducting support for the cathodes. Co<sub>3</sub>O<sub>4</sub> was shown to be a good bi-functional catalyst with high activity towards both reactions [27] and a more inexpensive alternative to noble metal catalysts for future lithium–air batteries with an aqueous alkaline electrolyte. In this paper modified carbon-free bi-functional electrodes with Co<sub>3</sub>O<sub>4</sub> and silver were prepared and tested in a half-cell arrangement to improve achieved current densities for ORR and OER compared to pure silver or Co<sub>3</sub>O<sub>4</sub> electrodes as well as higher long-term stability compared to common used carbon-based electrodes. The Co<sub>3</sub>O<sub>4</sub> content was varied from 5 to 40 wt.% to investigate the improvement of the bi-functional ability. As a benchmark silver electrodes with IrO<sub>2</sub>/TiO<sub>2</sub> were also investigated. It was observed that Ag/Co<sub>3</sub>O<sub>4</sub> electrodes show a significant improvement compared to pure silver or Co<sub>3</sub>O<sub>4</sub> electrodes.

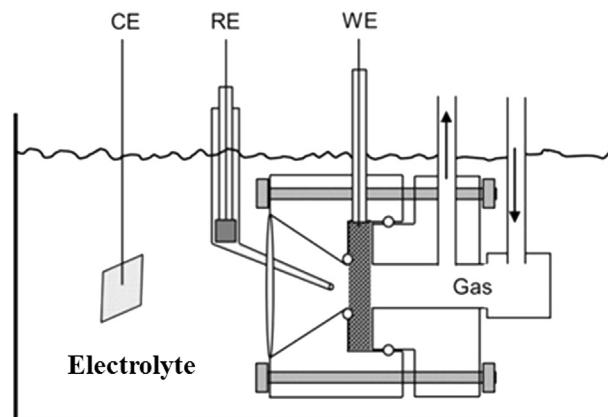
### 1.1. Lithium–air battery with aqueous alkaline electrolyte

A lithium–air battery with an aqueous electrolyte consists of a lithium metal anode and a porous gas diffusion electrode on the cathode that contains at least one catalyst for the battery reaction. Anode and cathode are separated by a lithium ion conducting separator that protects the lithium metal anode from oxygen and moisture. A protected lithium anode was recently proposed in literature by Visco et al. [28], Zhang and Nobuyuki [29] and Shimomishi et al. [30]. The electrochemistry at the cathode depends on the electrolyte which is used. In this paper cathodes for future LAB's with an aqueous alkaline electrolyte at the cathode were investigated. The fundamental battery reactions are:

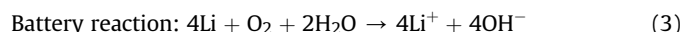


**Table 2**  
Thickness and loading of silver- or iridium/cobalt oxide electrodes.

		Loading Ag/mg cm <sup>-2</sup>	Loading Co <sub>3</sub> O <sub>4</sub> /mg cm <sup>-2</sup>	Thickness/μm	Electronic resistance/mΩ	Loading Ag/mg cm <sup>-2</sup>	Loading IrO <sub>2</sub> /mg cm <sup>-2</sup>	Thickness/μm
Electrode	Pure Ag	86.51	0	342	22.25	86.51	0	342
	5 wt.%	76.12	4.48	330	22.25	80.16	4.72	347
	10 wt.%	71.12	8.89	343	28.58	73.32	9.14	328
	20 wt.%	64.73	18.49	367	29.27	68.15	19.47	377
	30 wt.%	56.11	28.05	362	572	55.76	27.88	378
	40 wt.%	46.33	37.06	397	x	x	x	x



**Fig. 1.** Half-cell with a three electrode setup in electrolyte tank filled with 1 M LiOH (aq.).



$$E_0 = 3.45 \text{ V}$$

While discharging O<sub>2</sub> is reduced at the cathode according to Equation (1). Simultaneously lithium is oxidized at the anode liberating lithium ions and electrons (Equation (2)). Equation (3) represents the overall battery reaction taking place.

Three catalysts in two combinations were used to prepare electrodes and were tested in a half cell using cyclic voltammetry for analyzing the electrochemical performance of the catalysts. Long-term tests show the stability of the electrodes with these combinations. XRD and SEM were used to investigate the morphology of the catalysts and the electrodes respectively. Electrochemical impedance spectroscopy (EIS) was used to identify loss mechanisms.

## 2. Experimental

In this chapter the preparation of the electrodes is described as well as the electrochemical and physical characterization methods used in this publication.

### 2.1. Preparation of electrodes

The Co<sub>3</sub>O<sub>4</sub> catalyst powder (99.5%, <50 nm, Sigma Aldrich) was at first hand mixed with Ag (Ag311, Ferro Ag) and PTFE (Hostafion TF 9207Z, 3 M) as a binder. The IrO<sub>2</sub> catalyst powder (>99%, TiO<sub>2</sub> supported, Umicore) was mixed with Ag and PTFE in the same way. Table 1 shows the individual content of Ag, PTFE and Co<sub>3</sub>O<sub>4</sub> or IrO<sub>2</sub> of the prepared electrodes.

After mixing the three materials the compound was again mixed in an electric mill to get a homogeneous mixture. Afterwards the

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