



Bifunctional, Carbon-Free Nickel/Cobalt-Oxide Cathodes for Lithium-Air Batteries with an Aqueous Alkaline Electrolyte



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ABSTRACT

Lithium-air batteries with an aqueous alkaline electrolyte promise a very high practical energy density and capacity. These batteries are mainly limited by high overpotentials on the bifunctional cathode during charge and discharge. To reduce overpotentials the bifunctional cathode of such batteries must be improved significantly. Nickel is relatively inexpensive and has a good catalytic activity in alkaline media. Co_3O_4 was found to be a promising metal oxide catalyst for oxygen evolution in alkaline media but it has a low electronic conductivity. On the other hand since nickel has a good electronic conductivity Co_3O_4 can be added to pure nickel electrodes to enhance performance due to a synergetic effect. Due to the poor stability of carbon materials at high anodic potentials, gas diffusion electrodes were prepared without carbon to improve especially long-term stability. Gas diffusion electrodes were electrochemically investigated in a half cell. In addition, cyclic voltammogrammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out. SEM was used for the physical and morphological investigations. Investigations showed that electrodes containing 20 wt.% Co_3O_4 exhibited the highest performance.

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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 state of the art LIBs is only 75 to 200 Wh kg^{-1} [1,2]. For future applications in electric vehicles (EV), plug-in hybrid vehicles (PHEV) or in storage devices for renewable energy, batteries are required to have a far higher energy density. In addition, costs and weight must be reduced. The theoretical energy density of lithium-air battery (LAB) is much higher than the LIBs. An aqueous LAB with metal lithium as an anode has a theoretical energy density of 12,931 Wh kg^{-1} [3], almost as high as gasoline (~ 13200 Wh kg^{-1}). Although the theoretical energy density cannot be achieved due to limitations of real batteries, the practical energy density is predicted to increase at least by a factor of 5 compared to LIBs. Girishkumar et al. [1] estimate a practical energy density of 1700 Wh kg^{-1} on cell level, corresponding to 13% of the theoretical value of an aqueous LAB. This would be the same value as for gasoline with conversion by internal combustion engine.

Some limiting factors of LAB must be overcome as reported in literature [1,2,4–24]. One of the them is the low performance of the cathode during charge and discharge, resulting mostly from deficient catalytic activity of the catalysts used so far. LABs also suffer from low cyclability, instable separators, and decomposition of electrode materials and the electrolyte. Especially carbon materials, the mostly used material for LAB electrodes in aqueous alkaline electrolyte, are not stable under oxygen evolution conditions in alkaline media [25–27]. In our previous publications, we presented Co_3O_4 as a bi-functional catalyst with high activity towards ORR and OER [28,29]. Particularly, the combination of Co_3O_4 and Ag in a carbon-free gas diffusion electrode (GDE) exhibits high current densities. In this work, Ag was substituted by low cost nickel to obtain a carbon-free bi-functional electrodes with nickel and Co_3O_4 . Electrodes were prepared and tested in a half-cell arrangement to evaluate this combination as bifunctional air electrodes for future LABs. The Co_3O_4 content was varied from 5 to 40 wt.-% to investigate the improvement of the bi-functional activity. In addition, the long-term stability of pure nickel electrodes was tested over 1200 cycles. The influence of the electrode thickness and binder content was also investigated. It was observed that the addition of Co_3O_4 to pure nickel electrodes leads to a significant improvement for ORR and OER current densities.

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Table 1
Composition of nickel-cobalt oxide electrodes with different Co_3O_4 -content.

Co_3O_4		Ni/wt.-%	Co_3O_4 /wt.-%	PTFE/wt.-%
Electrode	pure Ni	90	0	10
	5 wt.-%	85	5	10
	10 wt.-%	80	10	10
	20 wt.-%	70	20	10
	30 wt.-%	60	30	10
	40 wt.-%	50	40	10

2. Experimental

The Co_3O_4 powder (99.5%, < 50 nm, Sigma Aldrich) was first hand mixed with nickel (99.9%, 3–7 μm , Strem Chem Inc.) and PTFE (Hostafon TF 9207, 3 M) as a binder. Table 1 shows the individual content of Ni, PTFE, and Co_3O_4 for the optimization of electrode composition; Table 2, the composition of the electrodes with varying binder content. After, an electric double knife mill was used to get a homogeneous mixture of the powders. The mixture was filled in a flexible forming frame and covered afterwards with a stainless steel net. This net is used as current collector and mechanical strength enhancer of the electrode. Forming frames with different height were used to variate the electrode thickness. Standard frame had a thickness of 1 mm, the others, 1.5 and 2 mm. The filled forming frame was placed between two metal plates and pressed with a defined static pressure in a hydraulic press resulting in a gas diffusion electrode. To fix the catalyst layer, a heat treatment of the electrodes followed in an oven for 1 hour at 340 °C in ambient air.

The electrochemical tests were carried out in half-cell arrangement with a three electrode setup (Fig. 1). The GDE is the working electrode (WE) and a platinum-electrode is used as counter electrode. The electrochemical potential is measured between the working electrode and a reversible hydrogen electrode RHE (HydroFlex, Gaskatel). The active area of the electrode in the half-cell was reduced to 1 cm^2 . To diminish the contact resistance between the current collector of the half-cell and the GDE, the GDE was additionally stacked with a Sigracet® GDL 35DC towards the gas inlet. For the measurements, the half-cell was placed in an electrolyte tank (1000 ml, 1 M LiOH (aq.)) and maintained at 25 °C. The feed gas was purified oxygen (O_2).

Cyclic voltammograms (CV), Chronoamperometry (CA), and electrochemical impedance spectra (EIS) were carried out with a Zahner IM6 Electrochemical Workstation. GDE's were cycled between 0.3 and 1.8 V versus RHE with a constant scan rate (1 mV s^{-1}). Pre-tests showed that after 20 cycles electrodes have a stable electrochemical behavior. Thus, before carrying out EIS and CA every electrode was cycled 20 times in CV mode. For CAs the GDEs were held for 15 minutes at fixed potentials of 0.3 or 1.8 V vs. RHE. Potentiostatic EIS was carried out at open cell voltage (OCV) and at $\text{OCV} \pm 100 \text{ mV}$, $\pm 300 \text{ mV}$, $\pm 500 \text{ mV}$, $\pm 700 \text{ mV}$. The frequency range for EIS was 100 mHz to 100 kHz with an amplitude of 5 mV, which corresponds to a peak-to-peak amplitude of 10 mV. For the long-term test, the electrode was cycled for 1200 cycles

Table 2
Composition of nickel-cobalt oxide electrodes with different PTFE-content.

Binder		Ni/wt.-%	Co_3O_4 /wt.-%	PTFE/wt.-%
Electrode	10 wt.-%	70	20	10
	8 wt.-%	72	20	8
	6 wt.-%	74	20	6
	4 wt.-%	76	20	4

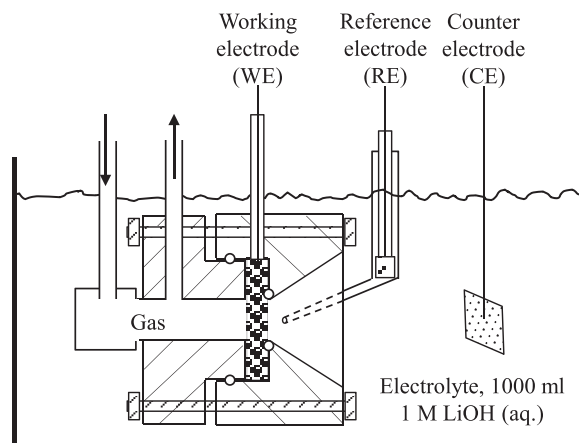


Fig. 1. Half-cell with a three electrode setup in electrolyte tank filled with 1 M LiOH (aq.).

with the same scan rate (1 mV s^{-1}), and the electrochemical test described before were applied. The morphology of the electrodes were examined with a Zeiss ULTRA plus SEM with charge compensation. Additionally, *ex-situ* electronic conductivity measurements of the electrodes were carried out with the 4-point probes method. For that purpose, the electrodes were stacked with a Sigracet® GDL 35DC as in the half cell, placed between two gold coated testing electrodes, and pressed with a load of 3 kg. The testing electrodes were connected to the Zahner IM6 and EIS spectra were carried out to observe the electronic resistance.

3. Results and discussion

First, the long-term stability and behavior of gas diffusion electrodes composed of pure nickel were tested. No degradation of pure nickel under the testing conditions was observed after 1200 cycles (Fig. 2a). In fact, OER and ORR current densities increase with the cycle number, which is even more beneficial than stability. The structure of pure nickel electrodes do not change over cycling (Fig. 2b); thus, the high OER and ORR current densities might be explained by an increase of the surface area of the electrode through cycling. The surface of the electrode shows an increase of roughness after cycling, this can be seen by comparing the SEM pictures before (Fig. 3a and b) and after cycling (Fig. 3c).

The long-term test proved that Ni is a suitable catalyst for LAB cathodes. However, Ni electrodes favor to catalyze OER over ORR. To further improve the ORR and OER current densities, Co_3O_4 was added to create a modified electrode. Previous publications showed that Co_3O_4 is an excellent OER catalyst as well as a good ORR catalyst in alkaline media [28–33]. As Co_3O_4 is an electric semiconductor, only modified electrodes with certain composition can lead to an enhanced electrochemical activity. The content of Co_3O_4 was varied from 5 to 40 wt.-%. The increasing Co_3O_4 content can also be confirmed by the higher intensity of the reflexes in the XRD spectrum (i.e. around 32°, 59° and 66°, Fig. 2b). Fig. 3d shows a modified electrode with 20 wt.-% Co_3O_4 ; the electrode has a structure with a high porosity. Co_3O_4 particles built up agglomerates and cover partially the larger Ni particles.

The Ag/ Co_3O_4 electrodes were measured in a half cell configuration as described before. The resulting not iR-corrected CVs are shown in Fig. 4a and compared with the one of Ag electrode. The addition of Co_3O_4 to the pure nickel electrode enhances the current density in OER as well as ORR significantly (Fig. 4b and c).

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