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Screen printed bifunctional gas diffusion electrodes for aqueous metal-air batteries: Combining the best of the catalyst and binder world

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ABSTRACT

The oxygen reactions in a metal-air battery during discharge (oxygen reduction reaction: ORR) and charge (oxygen evolution reaction: OER) take place on accessible catalyst sites at the gas diffusion electrode (GDE or air-cathode). Typical low-cost catalysts only have function for *either* the ORR (e.g. MnO₂) or the OER (e.g. NiCo₂O₄). To overcome this issue, either a bifunctional catalyst or a bifunctional GDE is needed. Herein, we focus on the development of such a bifunctional GDE. One key is the use of a carefully tuned binder which allows optimal wetting of the GDE. The combination of carboxymethyl cellulose (CMC) and styrene-butadiene rubber (SBR) can replace conventional binders such as polytetrafluoroethylene (PTFE). Using this binder system, two different approaches to combine the two catalysts γ -MnO₂ and NiCo₂O₄ in one cathode are employed. The first is to mix the ORR catalyst γ -MnO₂ and the OER catalyst NiCo₂O₄ for integration in the same reactive layer. The second is to build a GDE with two reactive layers which are screen printed on top of each other. The reactive layer facing the air side consists of the ORR catalyst γ -MnO₂ and the binders CMC/SBR. The second reactive layer, facing the electrolyte, consists of the hydrophilic binder CMC and the OER catalyst NiCo₂O₄. This double-layer design with two different catalyst species results in a better cycling behavior.

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1. Introduction

For today's mobile communication devices, a mobile energy supply is of utmost importance. As the devices we use are getting more and more sophisticated, the demand for battery systems with high energy densities increases continuously. Lithium-ion batteries have a theoretical energy density of around 387 Wh kg⁻¹ (for a LiCoO₂ – graphite lithium-ion battery) [1]. In order to increase these values, metal-air batteries with very high theoretical energy densities of 3582 Wh kg⁻¹ for Li–O₂ (aq) and 1086 Wh kg⁻¹ for Zn-air [1] have moved into the focus of current research. Metal-air batteries generally consist of a gas diffusion electrode (GDE), also

known as air-cathode, a metal as anode and in-between a separator which is soaked with electrolyte and serves to separate the two electrodes [2]. Depending on the choice of metal anode or configuration, different electrolytes can be used, e. g. aprotic or solid state electrolytes for Li-air batteries or aqueous electrolytes for Zn-air batteries. Further concepts include a hybrid electrolyte or a solid state electrolyte, as reported in literature by Lee et al. [3].

In the present work, we focus on an aqueous Zn-air system. During discharge, oxygen from the ambient air is reduced and forms hydroxide ions at the GDE (oxygen reduction reaction, ORR), while zinc is oxidized to ZnO or Zn(OH)₂. The reverse reaction takes place during charging [4]. The formation of oxygen at the GDE during charging is called oxygen evolution reaction (OER). Both reactions (ORR and OER) suffer from high overpotentials. However, these overpotentials can be reduced by the use of suitable catalysts like noble metals, perovskites, spinels, transition metal oxides or carbon materials [3,5,6]. Another important way to reduce the overpotential is tailoring the three-phase boundary. In the area of

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the three-phase boundary, gaseous oxygen is reduced at the solid catalyst and the formed hydroxide ions are released into the liquid electrolyte. To reduce the overpotential, the surface area of the three-phase boundary should be as large as possible. A promising way to achieve this is by the choice of a suitable binder. Conventionally, a hydrophobic binder like polytetrafluoroethylene (PTFE) will be used for such systems [7,8].

In this work, we implement carboxymethyl cellulose (CMC) and styrene butadiene rubber (SBR) binders which are well known from their use in electrodes for lithium-ion batteries [9,10]. We employ these binders to tailor the wettability of the GDE and enhance the number of accessible three-phase boundaries to reduce the overpotential of the oxygen reactions. Furthermore, we aim to overcome the disadvantage that most catalysts are optimized for only one of the oxygen reactions, i.e., either the OER or the ORR but not for both at the same time. To solve this problem, either bifunctional catalysts [11,12] have to be used or an ORR catalyst has to be combined with an OER catalyst to obtain a bifunctional GDE [13–16]. Herein, we focus on the concept of a bifunctional GDE using CMC and SBR binders to adjust the wettability of the GDE.

In Fig. 1 the two intended constructions of bifunctional GDEs are depicted. In a first approach (Fig. 1a) ORR and OER catalysts are mixed and integrated into one hydrophobic reactive layer. In the second approach (Fig. 1b), the GDE consists of a reactive ORR layer on the air-facing side and an OER layer on the electrolyte-facing side. In the ORR layer, a combination of the SBR and CMC binders is used to tailor the hydrophobic contact angle to result in a partial wetting behavior. This wetting behavior, the position of the layer close to the oxygen supply and the use of the ORR catalyst $\gamma\text{-MnO}_2$ set up the ORR reactive layer. On top of the ORR layer, a second layer that consists of only CMC as binder and NiCo_2O_4 as catalyst is screen printed. This layer is designed to have a hydrophilic behavior in order to allow flooding of the layer with electrolyte. The proposed system should not only allow the electrolyte to reach the ORR layer, but also foster the OER at the catalyst sites in the OER layer.

2. Experimental

2.1. Synthesis of catalysts

The co-precipitation synthesis of $\gamma\text{-MnO}_2$ is based on the publications of Xi et al. [17], Li et al. [18] and described in detail by Flegler et al. [19].

For the synthesis of NiCo_2O_4 , cobalt acetate tetrahydrate ($\text{C}_4\text{H}_6\text{CoO}_4 \cdot 4\text{H}_2\text{O}$) was refluxed in ethoxyacetic acid for half an hour and solvent/water was removed with a rotary evaporator at 160°C and 20 mbar. Meanwhile, nickel acetate tetrahydrate ($\text{C}_4\text{H}_6\text{NiO}_4 \cdot 4\text{H}_2\text{O}$) was dissolved in propionic acid at 110°C . Both reactants were mixed and dissolved at 140°C . After stirring for 1 h

under reflux, the solution was reduced on a rotary evaporator at 160°C and 30 mbar. The product was tempered at 375°C for 5 h in ambient air and ground with a ball mill.

2.2. Preparation of gas diffusion electrodes (GDE)

The preparation process of GDEs (or air-cathodes) was started by creating a gas diffusion layer (GDL, Freudenberg H2315C2) as substrate. The GDL consisted of carbon fibers with a microporous carbon layer on top of them. To enhance the electrical contact of the GDE, a nickel mesh was hot-pressed onto the microporous layer of the GDL. On top of this, the reactive layer was applied via screen printing (Ekra X1-SL) and dried at 100°C for 1 h. The dried reactive layer exhibited a layer thickness of $19 \pm 2 \mu\text{m}$. The slurry for this purpose consisted of 20 wt % catalyst, 45 wt % conductive carbon black (Super C 65, Imerys), 20 wt % activated carbon (Kuraray YP 50F, Kuraray) and 15 wt % binder and solvent. Three different binder/solvent combinations were used: The first combination was 15 wt % PTFE (Sigma Aldrich, $\leq 12 \mu\text{m}$) and terpineol as solvent (Fluka Chemie, 65% α -terpineol, 10% β -terpineol, 20% γ -terpineol) [19]. The second combination was 15 wt % carboxymethyl cellulose (CMC, Sigma Aldrich) and deionized water as solvent. The third composition consisted of a mixture of 7.5 wt % CMC and 7.5 wt % styrene-butadiene rubber (SBR, Tagray) and deionized water as solvent. All slurries were mixed in a speedmixer (Hauschild DAC 150 FVZ). It should be noted that every GDE with one reactive layer had the same mass load of catalyst.

The double-layer GDEs were prepared with the same slurries as described above. After screen printing the first reactive layer and drying it at 100°C for 1 h in air, the second reactive layer was screen printed on top of the first one and dried again at 100°C for 1 h. Every double-layer GDE had the same catalyst mass load, i. e. twice the catalyst mass load of a single layer GDE.

2.3. Materials characterization

The structural properties of the catalysts were analyzed by powder X-ray diffraction (XRD, Cu- K_α radiation, Philips PW 1730/10) at a step rate of 0.02 s^{-1} in a range from $2\theta = 10^\circ\text{--}80^\circ$ and by scanning electron microscopy (SEM, Zeiss Supra 25). The specific surface area of the catalysts was measured by N_2 adsorption/desorption isotherms (Quantachrome Autosorb-3B) and calculated according to the Brunauer-Emmett-Teller (BET) method.

The contact angle between reactive layer and electrolyte (6 M KOH_{aq}), and therefore the wetting behavior of the GDE with different binders, was determined by an optical method (drop shape analyzer, DSA 100, Krüss). The cross sections of the GDEs were prepared with an ion beam cross section polisher (CSP) and the distribution of the catalyst particles was detected by Energy

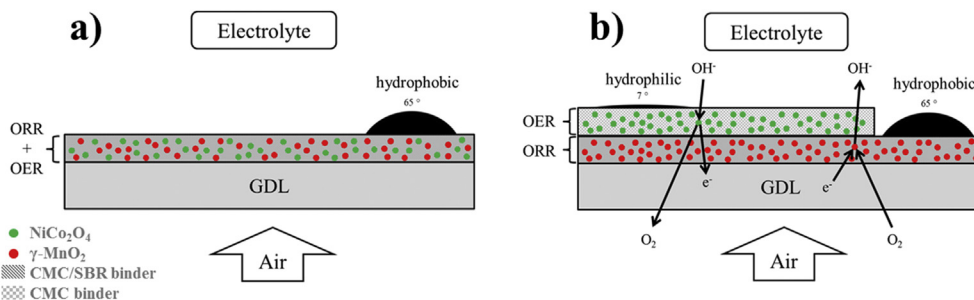


Fig. 1. Schematic construction of the intended bifunctional GDEs. (a) GDE with a mixture of ORR and OER catalysts in one reactive layer with a hydrophobic binder. (b) GDE consisting of two reactive layers printed on top of each other. The upper layer includes a hydrophilic binder and is especially active for the OER during charge. The binder system used in the lower layer is hydrophobic and thus it is conducive for the ORR.

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