



Towards zinc-oxygen batteries with enhanced cycling stability: The benefit of anion-exchange ionomer for zinc sponge anodes

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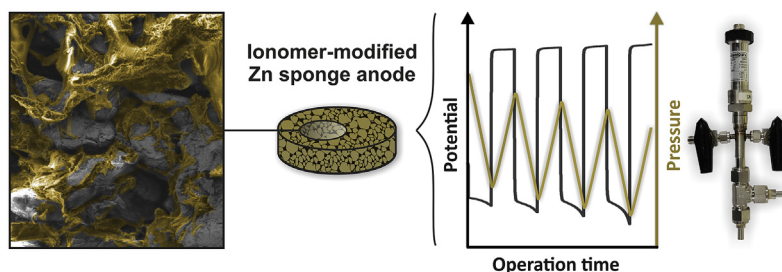
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HIGHLIGHTS

- Novel zinc anode with 3D pore system and incorporated anion-exchange ionomer.
- Energy-saving preparation method and enhanced cycling stability.
- Incorporation of anion-exchange ionomer yields promising zinc–oxygen batteries.
- Oxygen evolution and reduction proven by parallel pressure monitoring.

GRAPHICAL ABSTRACT



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ABSTRACT

Electrically rechargeable zinc-oxygen batteries are promising for sustainable and resource-uncritical energy storage with high energy density. Their commercialization is hindered by the limited cycling stability – especially due to the zinc anode. In this study, we present a zinc anode that stands out with two advantages: The use of an energy-saving and low temperature preparation method, and the mechanical stabilization of the pore system with a lightweight anion-exchange ionomer.

Our approach increases cycling stability for both the zinc-nickel oxide hydroxide cell and the zinc-oxygen cell: Electrochemical analysis in combination with operando X-ray diffraction measurements prove that the novel zinc anode is electrically rechargeable and can be cycled up to five times more often than zinc sponge anodes without anion-exchange ionomer to a depth of discharge of 35%. Scanning electron microscopy is used to evidence that the anion-exchange ionomer stabilises the entire pore system during cycling. We furthermore analyse zinc-oxygen batteries with anion-exchange ionomer at all parts – inside the zinc sponge anode, as separator and at the cathode. These cells can be electrically recharged with unprecedented high utilization of active material, and thus highlight the benefit of introducing an ion-selective coating into alkaline batteries with zinc anode.

1. Introduction

Zinc-based secondary batteries offer appealing advantages including environmental friendliness, abundance and safe operation [1,2]. Over

the last decades several primary and secondary batteries with zinc (Zn) anode have been investigated (Zn/Ag₂O, Zn/MnO₂, Zn/NiOOH, Zn/O₂) [3–7]. Secondary zinc-oxygen (Zn/O₂) batteries become a promising candidate for energy storage in electronic applications combining large

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theoretical specific capacity and cheap recyclable materials.

However, only primary Zn/O₂ batteries are successfully commercialized so far, which mainly results from limited cycling stability due to complex and related issues at both the Zn electrode and the gas diffusion electrode (GDE) [2,3]. The limited cycling life of the Zn anode mainly originates from the high solubility of oxidized Zn species in alkaline electrolytes [8,9]: During discharge Zn metal forms zincate ions ([Zn(OH)₄]²⁻), which can form insoluble zinc oxide (ZnO) once the electrolyte is locally saturated; the formation of a ZnO film then might lead to irreversible passivation of the active material Zn [10–12].

One recent approach by Parker et al. is to control the complex dissolution/precipitation dynamics of the Zn anode by introducing a three-dimensional pore system into the anode [13–15]. Their Zn sponge anodes showed highly promising charge-discharge cycle numbers with considerable Zn utilization and large specific capacity density without dendrite formation. However, the Zn sponge preparation protocol by Parker et al. requires a heat treatment process at temperatures above 650 °C and an additional, energy intensive (electro)reduction process of the Zn sponges to obtain an anode in charge state [13,16].

In this work, we present a preparation method for Zn sponge anodes that is energy-saving and is performed at lower temperature. We then advance the Zn sponge concept by incorporating anion-exchange ionomer (AEI) into the pore system. With adding the AEI, we aim to increase the mechanical stability of the porous network and thus of the entire anode. In addition, applying an AEI to the Zn anode is especially appealing because its properties fulfill all requirements to keep up the working principle for discharge and charge of Zn electrodes: The AEI is permeable for hydroxide ions (OH⁻), is mechanical flexible to accommodate the expected volume change due to Zn/ZnO conversion in the pore system [17], is electrically insulating [18], and is adequately stable in alkaline electrolyte [19–21]. In addition, Miyazaki et al. applied an AEI to a slurry-based Zn anode and showed suppressed dendrite growth of Zn anodes due to the advantage of selective ion permeation through the AEI [21]. Recently, we demonstrated that a homogeneous coating with AEI on a Zn anode (based on a Zn wire/foil model electrode) can indeed confine [Zn(OH)₄]²⁻ near the Zn anode surface – retaining the active material at the Zn/AEI interface [22]. With this, it was possible to enhance the cycling stability of the Zn model electrodes.

In this work, we investigate the cycling stability focusing on maximal utilization of the active material of the herein proposed Zn sponge anodes with incorporated AEI (referred to as AEI-modified Zn sponge anodes) in electrochemical cells with nickel oxide hydroxide (Zn/NiOOH) as cathode, and evaluate the induced morphology change inside the pore system after cycling by means of scanning electron microscopy. Beyond, we apply AEI-modified Zn sponges as anode in Zn/O₂ coin-type cells consisting of an AEI-modified GDE with anion-exchange membrane (AEM) and Sr₂CoO₃Cl as catalyst. We demonstrate that prepared zinc-oxygen cells with ionomer-modified zinc sponge anode can be cycled with almost ideal cell chemistry due to negligible impact of side reactions proven by parallel monitoring of the pressure in the oxygen reservoir of the cathode.

2. Experimental methods

Zinc sponge electrode preparation. Preparation of the emulsion for Zn sponge anodes was carried out following the procedure reported by Drillet et al. and Parker et al. [13,16,23]: First, both emulsifying agents carboxymethylcellulose (0.255 mg; Sigma-Aldrich) and sodium dodecyl sulfate (6 mg; Sigma-Aldrich) were added to a mixture of distilled water (1 g) and decane (1.67 g; Sigma-Aldrich) and stirred for 30 min. Second, Zn powder (6 g; #G-6-0 with 300 ppm In and 300 ppm Bi incorporated to suppress H₂ evolution; Grillo Werke GmbH) was added to the mixture and further stirred for 20 min. The resulting emulsion was poured into an in-house manufactured molding press out of polytetrafluoroethylene (PTFE), which allowed to produce Zn

sponges with variable thickness. The wet formulation was compressed into cylindrical Zn pellets with a diameter of 10.0 mm and a thickness of 0.6 mm.

After drying the formulation for 24 h, the Zn pellets were thermally treated in a tube furnace (Heraeus) following the described procedure: To obtain all-metal Zn sponges without ZnO (referred to as low temperature Zn sponge), Zn pellets were heated under Ar flow (75 sccm) at 120 °C/h to (409 ± 3) °C and held at temperature for 2 h to create sinter bridges between the Zn particles. Then the Zn pellets were heated at 120 °C/h to (419 ± 3) °C and held at temperature for 4.5 h. Likewise, Zn sponges, following the heat treatment protocol by Parker et al. were prepared as reference sample (referred to in this work as reference Zn sponge after Parker; see also Fig. S1 in the Supporting Information) [16]. In this case the Zn pellets were heated under Ar flow at 120 °C/h to (409 ± 3) °C and held at temperature for 2 h. Afterwards, the Zn pellets were calcined at (665 ± 3) °C in air for 2 h to obtain Zn sponges with ZnO encapsulation. To remove residuals out of the pore system, the heat treated Zn sponges were soaked in ethanol and dried afterwards.

The AEI was introduced into the pore system of low temperature Zn sponges by a vacuum infiltration technique: The samples were either infiltrated with AS4 (5 wt% in 1-propanol; Tokuyama) or KOH doped *meta*-polybenzimidazole (PBI; 2 wt% with 2.5 wt% KOH in ethanol; FumaTech). Approximately 12 mg of AEI, which corresponds to approximately 15% of the mass of the as-prepared sample without AEI, were incorporated for each anode (see also Supplementary Information). To ensure sufficient electronic connection between the AEI-modified Zn sponge anode and the tin (Sn) current collector, the backside of the AEI-modified Zn sponge was polished with SiC paper (5 μm, Buehler) to remove the electronic isolating AEI layer on one side of the AEI-modified Zn sponges; the as-prepared Zn sponges possessed a thickness of (0.50 ± 0.05) mm.

Gas diffusion electrode with Sr₂CoO₃Cl catalyst. Preparation of the GDE with the bifunctional Sr₂CoO₃Cl catalyst for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) was carried out using the following protocol: First, 0.450 g Sr₂CoO₃Cl catalyst [24], 0.450 g Vulcan XC-72 (Cabot Corporation) and 0.166 g PTFE (60% solution, Sigma Aldrich) were dispersed (45:45:10 wt%) in a 1:1 solution of N-methylpyrrolidone and water (by weight). After stirring, the dispersion was sprayed on carbon paper (PTFE-treated, Toray) and dried under vacuum at 80 °C over night. To ensure good electronic contact to the catalyst, the samples were pressed (9.8 kN cm⁻² for 1 min) and annealed for 20 min at 375 °C. The resulting GDE (10 mm diameter) was loaded with 2.7 mg cm⁻² Sr₂CoO₃Cl.

Assembly of Zn/NiOOH and Zn/O₂ cells. To obtain the OH⁻ form of the AEI, the AEI-modified Zn sponges were immersed in ZnO-saturated KOH solution (4 mol dm⁻³; Alfa Aesar) for 1 h and rinsed with ZnO-free aqueous KOH (4 mol dm⁻³) before cell assembly. We assume that the AEI was loaded fully with OH⁻ within this time, which should yield sufficient OH⁻-conductivity (KOH-doped PBI: ~30 mS cm⁻¹ and ion exchange capacity (IEC) of 0.97 mmol g⁻¹; AS4: 13 mS cm⁻¹ and IEC of 1.3 mmol g⁻¹ [25,26]). Recently, Hwang et al. found that 4 mol dm⁻³ KOH solution provides optimal properties for use in Zn-based battery operations, which is why this concentration was used for all experiments [27].

A two electrode commercial test cell casing (Toyo System) and the following cell assembly procedure were used for Zn/NiOOH cells: The soaked Zn sponge was placed on top of a Sn-disk acting as current collector (14 mm diameter, 125 μm thickness, > 99.99%, Chempur) [28,29]. Two laminated nonwoven separators (Celgard[®] 5550) were soaked in aqueous ZnO-saturated KOH (4 mol dm⁻³) and placed in between the Zn sponge anode and a commercial nickel oxide hydroxide/nickel hydroxide electrode (NiOOH/Ni(OH)₂; Panasonic). Before cell assembly, the NiOOH/Ni(OH)₂ electrode was charged in a separate procedure with a three-electrode measurement setup (SVC-3 Voltammetry cell with PTFE cap, ALS Co., Ltd) containing aqueous KOH

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