Model based quantification of air-composition impact on secondary zinc air batteries

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ABSTRACT

In this work we present an isothermal mathematical model of a secondary zinc air battery with alkaline liquid electrolyte. The model approach is flexible and allows to analyze the impact of surrounding air composition with its relative humidity, carbon dioxide and oxygen content on battery operation. We thereby apply an idealized approach to explore general limitations which give useful predictions for practical zinc air battery operation. Galvanostatic charge and discharge simulations show that air composition strongly impacts zinc air battery operation. Water level at anode and cathode, species concentrations and cell potential are shown to vary with air-composition impact during operation and may reach critical values which reduce battery lifetime. In detail, we deduce that intermediate relative humidity values of approximately 65%, carbon dioxide concentrations below 10 ppm and pure oxygen are beneficial for high performance and long term stable zinc air battery operation at 298 K with 6M potassium hydroxide as alkaline liquid electrolyte. The presented results will give useful information on operating strategies for zinc air batteries and electrochemical energy storage systems with open air electrode. The model might be adapted for other metal air batteries with aqueous electrolyte.

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1. Introduction

Zinc air batteries (ZABs) offer a high theoretical specific energy density and therefore are attractive for portable and mobile applications. In addition, non-platinum catalysts, such as perovskites, can be applied in air electrodes of secondary ZABs [1]. Research on ZABs is almost exclusively experimental and mainly focuses on material characterization of zinc electrode, air electrode or separator and on investigating performance and lifetime of entire ZABs [2–4]. It is of growing interest that ZAB operation is affected by environmental humidity [5,6]. This holds especially for secondary batteries as they are operated over a long period with charge and discharge cycles.

Mathematical models help to analyze to what extent environmental conditions can influence ZAB performance and its water and electrolyte balance. A better understanding of the latter is required to ensure long term stability and high efficiency. Relatively few models exist to describe parts of ZABs or entire ZABs: a zinc electrode model [7], a primary ZAB model [8] and a model for electrically rechargeable alkaline ZABs [9]. All are based on the one-dimensional macroscopic approach for porous battery electrodes by Newman and Tobias [10] and apply a system of coupled discretized non-linear differential and algebraic equations. In [9], a simplified air electrode is applied, so that the focus is mainly on zinc electrode description. This enables to analyze and optimize ZAB design parameters, such as separator thickness and zinc electrode thickness. A description of a battery with an air electrode open to the environment and the respective impact of air composition such as relative humidity, oxygen content and carbon dioxide content on battery operation is, to the authors knowledge, not introduced into ZAB modeling yet.

In this work we investigate the impact of surrounding air on ZAB operation. For this purpose, we introduce a flexible and expandable isothermal mathematical model of a secondary ZAB. We aim to investigate in an idealized way to observe general limitations due to the open air electrode which give useful predictions for practical ZAB operation. The introduced basic model is then modified to account for different scenarios with specific air-composition impacts. The main components in surrounding air concerning zinc air operation are $H_2O(g)$, CO_2 and O_2. Therefore the following scenarios are elucidated: (a) Reference scenario, (b) Relative humidity scenario, (c) Carbon dioxide scenario and (d) Oxygen scenario. Each scenario is evaluated with transient simulations for galvanostatic battery discharge and charge cycles. The conducted simulations give electrochemical information (e.g. the cell potential), chemical information (e.g. water and electrolyte content in each electrode) and volume information (e.g. solid and liquid volumes in the ZAB).

The following section describes the applied mathematical models, as well as the underlying assumptions. In section 3, simulation

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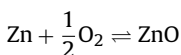u.krewer@tu-braunschweig.de (U. Krewer).

results for the different scenarios are presented and discussed. Finally, the results are summarized and conclusions are outlined in section 4.

2. Mathematical model

For this study, the considered electrically rechargeable ZAB consists of a zinc electrode, an air electrode and a porous separator with liquid electrolyte, here potassium hydroxide (KOH) solution. The ZAB is operated with air containing N_2, O_2, $H_2O(g)$ and CO_2. At the zinc electrode, solid zinc and hydroxide ions are electrochemically converted to zincate ions (reaction (I)) which are then precipitating to solid zinc oxide, water and hydroxide ions (reaction (II)). At the air electrode, oxygen and water are electrochemically converted to hydroxide ions (reaction (III)). All reactions are considered to be reversible. The occurring reactions, with the respective reaction rates r, in alkaline electrolyte are as follows

$$Zn + 4OH^- \overset{r_I}{\rightleftharpoons} Zn(OH)_4^{2-} + 2e^- \tag{I}$$

$$Zn(OH)_4^{2-} \overset{r_{II}}{\rightleftharpoons} ZnO + 2OH^- + H_2O \tag{II}$$

$$\frac{1}{2}O_2 + H_2O + 2e^- \overset{r_{III}}{\rightleftharpoons} 2OH^- \tag{III}$$

The overall reaction is

$$Zn + \frac{1}{2}O_2 \rightleftharpoons ZnO$$

It can be seen that the same amount of water and hydroxide ions are in each case provided and consumed at the respective electrode. Consequently, any loss or gain of these components by changing air composition, may influence ZAB operation.

One impact parameter is the relative humidity in the surrounding air. Loss or gain of gaseous water from the ZAB electrolyte may cause serious depletion or increase of the total water amount in the ZAB.

Another influential impact factor is the concentration of surrounding oxygen. Depending on the electrolyte concentration, more or less oxygen can dissolve and participate in the air electrode reaction; consequently the limiting current density varies.

A further impact factor is the carbon dioxide concentration in the surrounding of the ZAB. Liquid electrolytes like KOH will form carbonate species when in contact with carbon dioxide. Due to the high pH value of the KOH electrolyte, the predominant carbonate species is the carbonate ion (CO_3^{2-}), so that the following irreversible reaction will be taken into account for this work:

$$CO_2(diss) + 2OH^- \overset{r_{IV}}{\rightarrow} CO_3^{2-} + H_2O \tag{IV}$$

Reaction (IV) is presumed to have several effects on ZAB operation [11]: if maximal solubility of K_2CO_3 is reached, precipitation occurs and solid particles of K_2CO_3 can reduce the electrolyte void volume in the catalyst layer of the air electrode which consequently reduces ZAB performance; besides, K_2CO_3 salt formation might block pores in the air electrode, reduce the active area and eventually cut off the oxygen supply; most importantly, the electrolyte conductivity is reduced due to replacement of OH^- by CO_3^{2-}. Only the latter is included in this work, because precipitation limits are not reached for our simulations.

2.1. Basic model

In this section the flexible and expandable ZAB basic model is derived which is later modified to account for certain scenarios of air-composition impacts.

2.1.1. Reaction rates

The reaction rate of reaction (I) at the zinc electrode is described with a Butler-Volmer approach. The reaction rate of reaction (II) is accounted for with a saturation approach. Both equations are adapted from [9] and [7], respectively, so that

$$
\begin{aligned}
r_I = \\
- \Bigg[& k_I^c \cdot \frac{c_{Zn(OH)_4^{2-}}^{zinc}}{c^{ref}} \cdot \exp\left(-\frac{(1-\alpha^{c,zinc}) \cdot \mathbf{F}}{\mathbf{R} \cdot T} \cdot \eta^{zinc} \right) \\
& - k_I^a \cdot \left(\frac{c_{OH^-}^{zinc}}{c^{ref}} \right)^4 \cdot \frac{n_{Zn}}{n^{ref}} \cdot \exp\left(\frac{\alpha^{a,zinc} \cdot \mathbf{F}}{\mathbf{R} \cdot T} \cdot \eta^{zinc} \right) \Bigg]
\end{aligned}
\tag{1}
$$

$$r_{II} = k_{II} \cdot \left(c_{Zn(OH)_4^{2-}}^{zinc} - c_{Zn(OH)_4^{2-}}^{sat} \right) \tag{2}$$

The reaction rate of reaction (III) at the air electrode is described with a Butler-Volmer approach as presented by [9]

$$
\begin{aligned}
r_{III} = \\
+ \Bigg[& k_{III}^a \cdot \frac{c_{H_2O}^{air}}{c^{ref}} \cdot \left(\frac{c_{O_2}^*}{c^{ref}} \right)^{\frac{1}{2}} \cdot \exp\left(-\frac{(1-\alpha^{c,air}) \cdot \mathbf{F}}{\mathbf{R} \cdot T} \cdot \eta^{air} \right) \\
& - k_{III}^c \cdot \left(\frac{c_{OH^-}^{air}}{c^{ref}} \right)^2 \cdot \exp\left(\frac{\alpha^{a,air} \cdot \mathbf{F}}{\mathbf{R} \cdot T} \cdot \eta^{air} \right) \Bigg]
\end{aligned}
\tag{3}
$$

Whereas $c_{O_2}^*$ is considered to be the concentration of dissolved oxygen present in the liquid electrolyte at the air electrode. Its usage is explained in more detail within section 2.3.

2.1.2. Mass balance equations

The molar concentration for species $k = OH^-$, H_2O and $Zn(OH)_4^{2-}$ in the liquid electrolyte within electrode j, indicating either zinc or air electrode, is applied as

$$c_k^j = \frac{n_k^j}{V_{electrolyte}^j} \tag{4}$$

Concentrations for species k in the liquid phase of the ZAB are calculated with the following mass balance in concentration form

$$
\begin{aligned}
\frac{dc_k^j}{dt} = & \frac{+J_k^{j,diff} + J_k^{j,mig} + J_k^{j,conv}}{V_{electrolyte}^j} \\
& + \frac{\sum_i \nu_{k,i} \cdot r_i}{V_{electrolyte}^j} \\
& - \frac{c_k^j}{V_{electrolyte}^j} \cdot \frac{dV_{electrolyte}^j}{dt}
\end{aligned}
\tag{5}
$$

with $\nu_{k,i}$ being the stoichiometric coefficient for species k in reaction i. Equation (5) requires the use of molar flow rates of exchange, J, between both ZAB electrodes, namely diffusion (diff), migration (mig) and convection (conv) molar flow rates. They are given by the Nernst-Planck equation in more detail with equations (A.8)-(A.10) in the appendix. For H_2O in the zinc electrode in equation (5), the migration molar flow rate of exchange, J^{mig}, is omitted because water molecules are considered with neutral charge. For the basic model, no gaseous water is allowed to be exchanged with the surrounding. Hence, H_2O in the air electrode appears in the