Performance of zinc air batteries with added K₂CO₃ in the alkaline electrolyte

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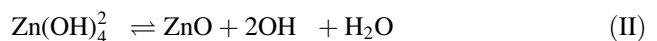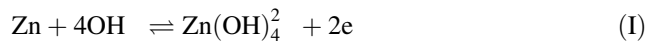
Abstract Intentionally adding potassium carbonate to the high molar alkaline electrolyte is one possibility to mitigate the negative impact of carbonation in zinc air batteries (ZABs) that were investigated in this novel study. In this work, an experimental analysis of the electrochemical performance of ZABs with added potassium carbonate in potassium hydroxide electrolyte was conducted. The experiments included polarization curve measurements, electrochemical impedance spectroscopy measurements, and constant current discharge with an in-house battery set-up. In addition, ionic conductivity was measured for mixtures of potassium hydroxide and potassium carbonate solutions. The results implied that up to 50 mol% of added potassium carbonate in the electrolyte had a weaker influence on the cell performance than a decreased amount of hydroxide ions in the electrolyte from 21.9 to 1.8 mol%. However, discharge measurements showed that the cell potential and the maximum state-of-discharge are decreased for the operation with 50.00 mol% of added potassium carbonate. The conductivity measurements revealed that solutions with 9 mol l⁻¹ K⁺ and added potassium carbonate possessed similar ionic conductivity, when compared to the standard 6 M KOH electrolyte. All in all, the analysis showed that it was acceptable to add potassium carbonate to the high molar potassium hydroxide electrolyte, while still obtaining stable cell potential under the premise to increase the practical energy density and the long-term stability of zinc air batteries. The here presented findings might help to establish the zinc air battery as next generation type battery.

1 Introduction

Zinc air batteries (ZABs) offer a comparably high theoretical energy density of 1353 Wh kg⁻¹ [1]. They are seen as one possible next generation battery for medium-sized portable and mobile devices, or for the energy storage of intermittent energy from wind or solar power. Zinc itself is a low-cost anode material and available in sufficient amounts; the needed oxygen is not stored within the ZAB and is supplied from the ambient air. Commonly, ZABs are composed of zinc electrode, air electrode, liquid electrolyte, and separator. The reactions at zinc and air electrode in alkaline electrolyte can be described as follows:

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

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

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightleftharpoons 2OH^- \qquad (III)$$

In theory the reactions are reversible, which gives the possibility for electrical recharge of ZABs.

The practical energy densities reported for ZABs range from 200 Wh kg⁻¹ for commercially available primary ZABs to 700 Wh kg⁻¹ for ZABs in lab-scale [1, 2]. To further increase the practical energy density, recent

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research is primarily focusing on the electrode materials applied in ZABs [3, 4]. In addition, the understanding of the diverse reaction and transport processes within full cell ZABs is of growing interest [5, 6]. Furthermore, the ambient air-composition with its relative humidity and carbon dioxide is investigated intensively, since it determines the maximum number of charge/discharge-cycles of secondary ZABs [7].

KOH solution has been widely used as electrolyte in ZABs because of its superior ionic conductivity when compared for example to NaOH solution [4]. A high molarity of 6 M is usually applied because its ionic conductivity is the highest with 620 mS cm^{-1} at this concentration [8]. However, alkaline KOH solution will form carbonate species when in contact with carbon dioxide from ambient air, according to the following irreversible carbonation reaction:

$$CO_2(diss) + 2OH^- \rightarrow CO_3^{2-} + H_2O \qquad (IV)$$
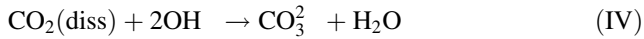
Reaction (IV) affects the long-term stability operation of ZABs, as was shown experimentally and by model-based analysis [7, 9]. The negative effect was explained by Drillet et al. by salt precipitation after electrolyte carbonation in the air electrode, which subsequently blocked gas diffusion pores and cuts off the O_2 supply at the air electrode [9]. Besides, the ionic conductivity of the electrolyte is diminished due to a replacement of OH^- by CO_3^{2-} if carbonation takes place during the operation of ZABs [7]. To avoid carbonation, scrubbed air, e.g. achieved with CO_2-filters, can be applied [9]. Changing the electrolyte after several hours of operation is another possibility to cope with the carbonation of the electrolyte [1, 10]. In addition, PTFE-membranes on top of the air electrode can help to reduce the absorption of CO_2 into the electrolyte [1]. All require additional components or efforts and might reduce the overall energy density of the battery.

Kucka et al. investigate the kinetics of the carbonation reaction in potassium hydroxide solution with a batch-operated stirred cell reactor and not with a full cell ZAB. They aim to determine the reaction rate constant of the carbonation reaction, k_{CO_2}, as a function of ionic strength of the electrolyte [11]. They report that the more CO_3^{2-} ions are present in the electrolyte, the slower the carbonation reaction rate will be. Taking this fact into account, another way to mitigate the carbonation reaction seems to be apparent: adding K_2CO_3, and thus increasing the concentration of K^+ and CO_3^{2-}, to the electrolyte.

The general possibility of adding carbonates to the electrolyte has initiated studies to investigate the effect of absorbed CO_2 on the performance of zinc electrodes [12, 13]. An electrolyte composed of 0.5 M K_2CO_3 and 5.3 M KOH is found to be suitable option as electrolyte for the zinc electrode reaction [13]. However, this work does not include a systematic variation of K_2CO_3 content and KOH molarity. Furthermore, Sato et al. investigate the passivisation of a zinc electrode in concentrated potassium hydroxide solutions (7.83, 7.86, and 8 M) with added carbonates [14]. They do not test the electrolyte solutions in a full cell ZAB. All in all, a systematic investigation of the electrochemical performance of a full cell ZAB with added amounts of carbonates in the electrolyte has not been reported yet.

In this work, a novel experimental analysis of the electrochemical performance of ZABs with added potassium carbonate in potassium hydroxide electrolyte will be presented. It will be elucidated to what extent the electrolyte composition affects the ion transport, the polarization behavior, the reaction kinetics at both electrodes, and thus the discharge behavior of a full cell ZAB. The main focus is thereby to systematically and quantitatively investigate the effect of adding K_2CO_3 to the alkaline electrolyte in ZABs with special focus on a wide range of K_2CO_3 content and KOH molarity. For this purpose, full cell measurements with various electrolyte compositions are performed with an in-house ZAB set-up. Polarization curve measurements and electrochemical impedance spectroscopy (EIS) are applied on the set-up to evaluate cell potential and cell impedance of ZABs with different alkaline electrolyte compositions. Subsequently, constant current discharge is applied to investigate the discharge behavior of as-prepared batteries with and without added K_2CO_3. The investigations presented identify a suitable amount of K_2CO_3 additive, with the aim to increase the practical energy density and the long-term stability of ZABs.

In addition, we present ionic conductivity measurements for mixtures of KOH and K_2CO_3 as a basis for the interpretation of the aforementioned electrochemical analysis. We extend the available data set on ionic conductivity for carbonated KOH solution by Ko and Juang [15]. We investigate a wider range for solutions with $3-9$ mol l^{-1} K^+. Conductivity values for the applied mixtures of KOH solution and K_2CO_3 are of particular importance, since they are used to determine whether sufficient ionic conductivity is maintained in the electrolyte for ZAB operation at elevated current densities.

2 Methods

2.1 Preparation of electrolyte

Two different KOH solutions were initially prepared using KOH flakes (Sigma-Aldrich, 90 % purity, reagent grade) and pure water with a resistivity of 18.2 MΩ cm

(Millipore). Approximately 20 wt% excess of flakes was added to ensure defined concentration of OH. The molarity of these two solutions was measured by performing titration, and the values found out were 6.07 and 10.03 M, respectively. These solutions were then diluted with pure water to get defined amounts of solutions of lower concentrations, which were then used for conductivity measurements as described in Sect. 1 in the appendix.

The preparation of the solutions with various amounts of carbonate ions was performed by using K_2CO_3 (Sigma-Aldrich) as follows. First, a solution of KOH with defined molarity was prepared and titrated to determine the actual concentration of OH. After titration, a molar amount of K_2CO_3 was added to achieve the desired concentration of K^+. The molar amount added per molecule containing K^+ is expressed as molar percentage of potassium carbonate, $x_{K_2CO_3}$, and is given by the following relation:

$$x_{K_2CO_3} = \frac{n_{K_2CO_3}}{n_{K_2CO_3} + n_{KOH}} \times 100 \tag{1}$$

The molar percentage of K_2CO_3 was checked with titration measurements as described in Sect. 1 in the appendix.

2.2 Battery design and electrode preparation

An in-house battery set-up was used to prepare batteries with various compositions of electrolyte. The set-up is depicted in Fig. 1. It consists of a two-piece housing, made of polyvinyl chloride (PVC), a PVC union nut, two gold-plated copper parts as current-collectors, and a separator between the zinc and air electrode. The zinc electrode current-collector was provided with a 1.3 cm diameter cylindrical indentation. Consequently, the cross-sectional area of the active material was 1.32 cm^2, which is used in this work to express the current densities adjusted. The cylindrical indentation is adjustable in depth and was set to 0.15 cm for measurements with various amounts of K_2CO_3 in the electrolyte and to 0.17 cm for measurements with pure KOH electrolyte, respectively. A paste, containing the active material Zn, was filled into the cavity given by the indentation in the zinc electrode current-collector. The paste consisted of Zn and ZnO (Grillo), Bi and cellulose-fibers (Sigma-Aldrich), and appropriate amount of electrolyte, so that a porous zinc electrode was obtained. The solid constituents of the mixture were chosen in the weight-ratio of 10:1:1:1 (Zn:ZnO:Bi:cellulose). The weight-ratio of solid and liquid in the paste was chosen as approximately 1:1. Pure KOH solution and KOH solution with intentionally added K_2CO_3 were used, respectively. New batteries were prepared each time by filling the above-mentioned paste in the cavity of the indentation (approximately 450 and 550 mg resulting in a battery capacity of approximately 200 and 250 mAh, respectively) and assembling all components of the set-up. The

battery separator applied, Celgard 3401 by Celgard LLC, was soaked with the respective electrolyte before assembly, had a diameter of 3.40 cm and a thickness of 25 μm.

The air electrode (1.40 cm diameter) was a commercially available gas diffusion layer (GDL) with Pt/C catalyst purchased from Johnson Matthey (ELE0132 W19216). It was placed on top of the air electrode current-collector which was provided with a 0.05 cm wide single-flow-channel for the active supply of air. Oil-free air was supplied with a mass flow controller Smart Trak 100 from Sierra Instruments with a constant flow rate of 2.00 ml min^{-1} to ensure sufficient supply and solubility of oxygen in the liquid electrolyte at the air electrode. All measurements were conducted at a temperature of 298 K.

2.3 Electrochemical measurements

Electrochemical measurements were conducted with a Gamry Reference 3000 Potentiostat/Galvanostat/ZRA. Each battery was initialized by subjecting it to a polarization for which current density was drawn from the battery in steps of 1.88 mA cm^{-2}, with each current density being held for a period of 10 s, until the current density of 30.13 mA cm^{-2} was reached. Subsequently, the actual polarization curve was measured, where current density was drawn from the battery with increasing steps of 1.88 mA cm^{-2} held for a period of 30 s. The state-of-discharge (SOD) was thereby decreased marginally so that approximately 1 % of the initial capacity was discharged for the entire procedure. Only the cell potential every 30 s and the set current density were taken to depict the polarization curves presented in Sect. 3.2. EIS was conducted at 0.75 mA cm^{-2} DC discharge current density and a 0.08 mA cm^{-2} AC amplitude to obtain the frequency response of the ZAB set-up. Each electrochemical procedure was repeated at least three times to obtain a measurement error by averaging and calculating the standard deviation, except for the EIS measurements for various amounts of added K_2CO_3, where the measurement was conducted once. Subsequently, batteries with pure 6.07 M KOH electrolyte, and electrolyte with 6 mol l^{-1} K^+ and 16.70 and 50.00 mol% of added K_2CO_3 were discharged at a constant current density of 3.76 mA cm^{-2} to monitor their cell potential with increasing SOD.

The SOD is estimated in this work as follows

$$SOD = \frac{C_{Ah}(t)}{C_{Ah,initial}} \times 100 = \frac{I^{cell} \times t}{m_{Zn} \times 819 \text{ mA h g}^{-1}} \times 100, \tag{2}$$

where m_{Zn} is the mass of zinc particles filled into the zinc electrode and 819 mA h g^{-1} is the theoretical capacity for one gram of Zn [1].
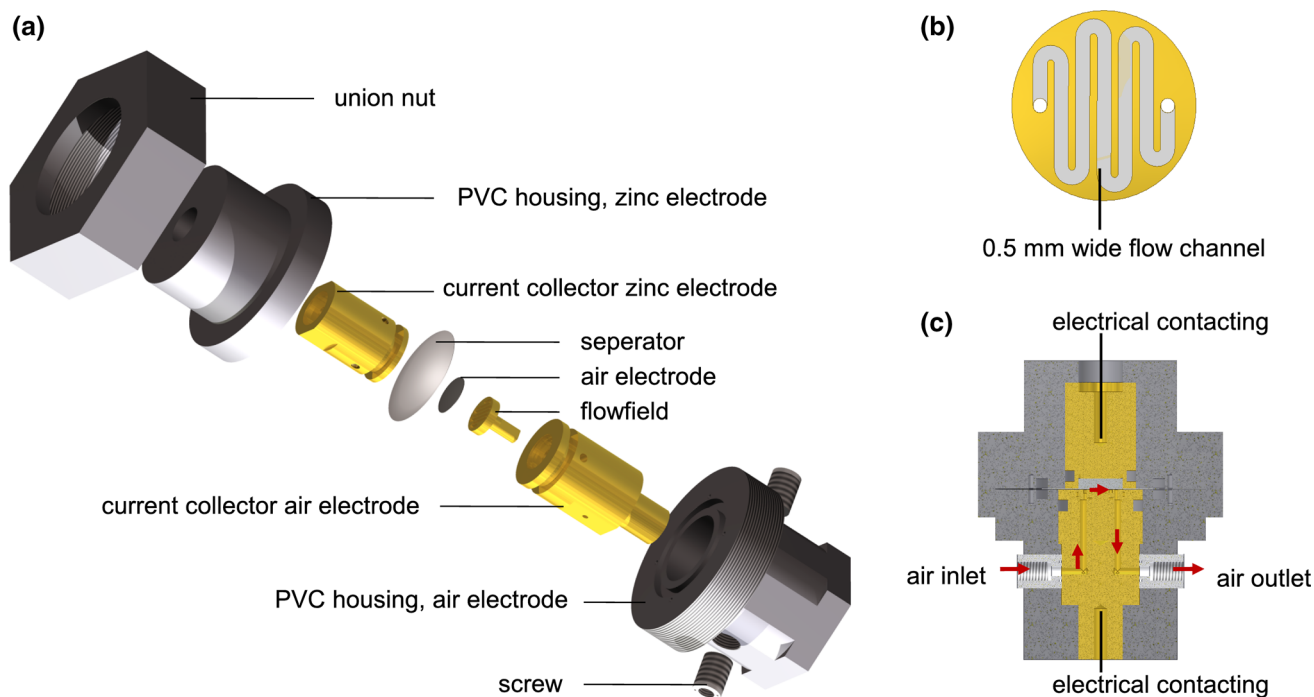
Fig. 1 Zinc air battery set up for the electrochemical analysis: **a** exploded view of the battery with PVC housings, union nut, current collectors, separator and air electrode; **b** top view of the flow field applied at the air electrode; **c** cross sectional view of the assembled battery

3 Results and discussion

The various electrolyte compositions adjusted for the measurements in this work, affect the electrochemical state of the ZABs investigated and their operation behavior. To gain a detailed understanding of the impact of the electrolyte composition on ZABs, it is elucidated in this section to what extent the electrolyte composition influences the ion transport, the polarization behavior of the ZAB, the reaction kinetics at both electrodes, and thus the discharge behavior of an entire ZAB. In particular, the results obtained for the battery polarization, the electrochemical impedance spectroscopy, and the discharge behavior with different electrolyte compositions, and the ionic conductivity of various electrolyte compositions are presented and discussed in the following.

3.1 Ion transport

The results for the conductivity measurements conducted are shown and discussed in this subsection to identify, which electrolyte composition might be adjusted to ensure sufficient ionic conductivity for the transport of OH$^-$ in ZABs.

3.1.1 Impact of KOH molarity

Figure 2a depicts the ionic conductivity measured for various KOH molarities (dark filled circles). In the range of 0.1 3 M KOH, the ionic conductivity increases linearly with increasing molarity. For concentrations higher than 3 M, the ionic conductivity increases until a local maximum is obtained. Fitting a quadratic function to the measured conductivities, reveals a maximum conductivity of 650 ms cm^{-1} at 6.73 mol l^{-1}. For further increasing molarity, the ionic conductivity decreases again. In addition, Fig. 2a shows ionic conductivity values reported in literature [8, 16]. They are in good agreement with the values obtained in this work.

The measured conductivities reveal one reason why usually KOH electrolytes with a molarity of 5 8 are applied in ZABs: the ionic conductivity is superior, which ensures optimal OH$^-$ transport through the separator of ZABs [4].

3.1.2 Impact of K$_2$CO$_3$ as additive

Figure 2b shows the ionic conductivity for solutions with 3, 6 and 9 mol l^{-1} K$^+$ with increasing molar percentage of added K$_2$CO$_3$. The ionic conductivity for all solutions measured decreases almost linearly with increasing molar percentage of added K$_2$CO$_3$. In general, it can be observed that solutions with 6 mol l^{-1} K$^+$ possess the highest ionic conductivity over the entire range of molar percentage of added K$_2$CO$_3$. However, the ionic conductivity of solutions with 9 mol l^{-1} K$^+$ is only marginally lower than that of solutions with 6 mol l^{-1} K$^+$. This yields one major
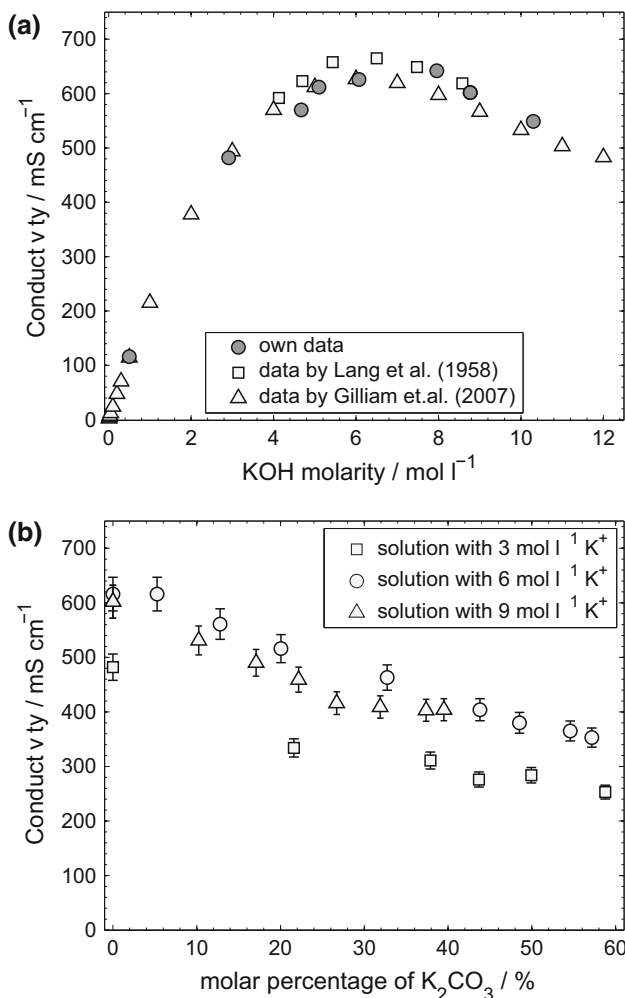
Fig. 2 Measured conductivity for **a** various KOH molarities, own measurements including error bar compared to literature data at 298 K [8, 16] and **b** various molar percentages of added K_2CO_3 in mixtures of KOH and K_2CO_3 solution with different concentrations of K^+ at 298 K

Fig. 3 Polarization curve measurement results including *error bars* for **a** three different molarities of KOH and **b** mixtures of KOH and K_2CO_3 with 6 mol l^{-1} K^+, indicated by the molar percentage of added K_2CO_3, and measurement with pure K_2CO_3 solution (100 %)

implication for ZAB operation: if ZABs are polarized in the region of ohmic losses where ionic conductivity might be predominant, solutions with 9 mol l^{-1} K^+ and added K_2CO_3 might be an acceptable option compared to the standard 6 M KOH electrolyte.

All in all, these measurement results have shown that the ionic conductivity for solutions with 9 mol l^{-1} K^+ and added K_2CO_3 is only marginally lower than that of solutions with 6 mol l^{-1} K^+ for the entire range of added K_2CO_3 investigated.

3.2 Polarization behavior for various electrolyte compositions

Figure 3 shows the results for the polarization curve measurements with pure KOH electrolyte and with
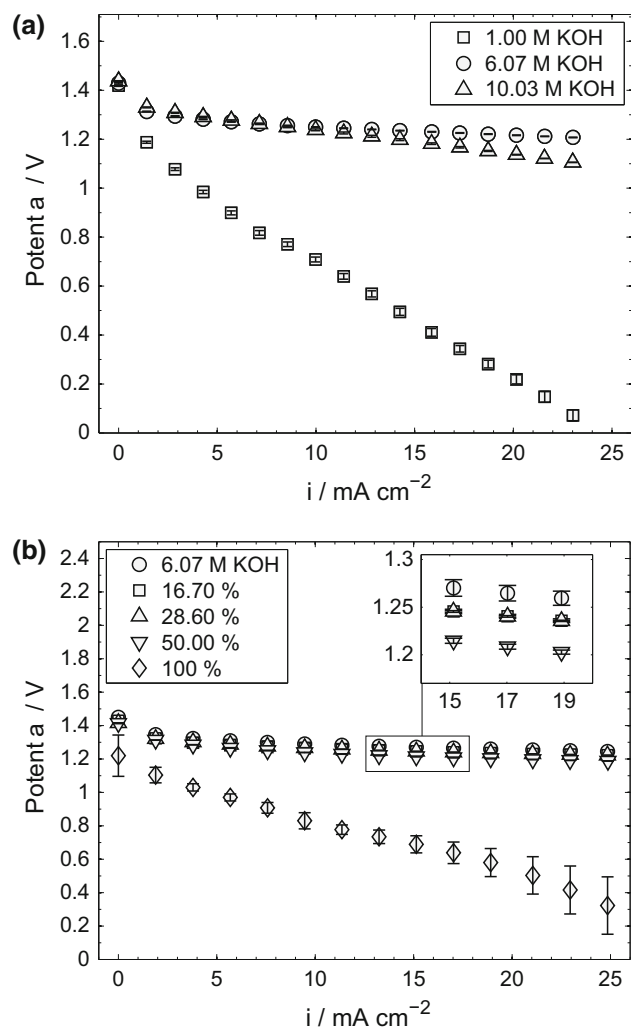
mixtures of KOH and K_2CO_3 solution. In general, all measured polarization curves possess an offset of around 0.20 V to the theoretical open circuit potential of 1.67 V. A linear decline of the cell potential with increasing current density can be observed in the ohmic region of all polarization curves.

3.2.1 Impact of KOH molarity

For the results in Fig. 3a, the battery set-up was operated with 1.00, 6.07, and 10.03 M KOH solutions as electrolyte, respectively. It can be observed that batteries with 6.07 M and 10.03 M possess about the same cell potential. The curve for 10.03 M is showing slightly lower cell potential at current densities above 15 mA cm^{-2}. The measurement for 1.00 M electrolyte reveals a much steeper decline of

cell potential with increasing current density than for the other measurements. This is presumably due to the low concentration of 1.00 M OH. On the one hand it might cause a higher *IR*-drop due to the lower ionic conductivity at this concentration, and on the other hand it might slow down the reactions at both electrodes and consequently causes a higher polarization overpotential. A better distinction of these two effects will be provided with the analysis of the EIS measurements in Sect. 3.3.

All batteries were operated with active supply of air with a high flow rate to ensure sufficient O_2 supply and solubility with the aim to minimize the impact of the air electrode on the polarization behavior. The O_2 solubility is roughly six times higher in 1.00 M KOH solution than in 6.07 M KOH solution under presence of ambient air [17]. However, the higher O_2 solubility for the measurement with 1.00 M electrolyte can apparently not compensate the observed loss in potential. Thus, other effects must cause the comparably low cell potential at this electrolyte concentration.

3.2.2 Impact of K_2CO_3 as additive

For the results in Fig. 3b, the battery set-up was operated with 6.07 M KOH electrolyte without added K_2CO_3, with 16.70, 28.60, and 50.00 mol% of intentionally added K_2CO_3, and with pure K_2CO_3 solution. The polarization curves measured with 16.70 mol% up to 50.00 mol% of added K_2CO_3 only marginally deviate from the results obtained for pure 6.07 M KOH electrolyte, although the cell potential for the battery with 6.07 M KOH solution is the highest over the entire range of current densities (see enlargement).

It becomes evident that operation with pure K_2CO_3 electrolyte is not favorable since the cell potential is much lower, possesses a higher measurement error than for the other batteries, and decays gradually with increasing current density. This is due to the fact that the reactions (I) and (III) do not hold for pure K_2CO_3 electrolytes where only marginal amounts of OH are present as impurity or from the solvent water. As such, a different reaction mechanism might occur.

Compared to the results in Fig. 3a, it is suggested that adding K_2CO_3 has a weaker influence on the cell potential of ZABs than changing the amount of OH in the electrolyte. This implies that adding molar percentages of K_2CO_3 of up to 50.00 mol% to a high molar KOH electrolyte may still result in acceptable short-term performance. This has to be confirmed with the discharge measurements shown in Sect. 3.4.

3.3 Reaction kinetics for various electrolyte compositions

The following EIS results are used to further elucidate the reason for the aforementioned polarization behavior trends,

as well as to interpret the impact of KOH concentration and added K_2CO_3 on the reaction kinetics of both electrodes.

It can be expected that the impedance response of porous electrodes behaves significantly different than the impedance response of flat electrodes [18]. In particular, the electrolyte concentration in the porous zinc electrode influences the overall impedance at high frequencies and is solely an ionic contribution [19].

3.3.1 Impact of KOH molarity

Figure 4a depicts the Nyquist-plot of the impedance response of ZABs prepared with 1.00, 6.07, and 10.03 M KOH solution. In all measurements, there is one pronounced arc in the low frequency region, and there is another smaller, less pronounced arc in the high frequency region (see enlargement). The curves strongly deviate from each other above $Z_{real} > 10\ \Omega\ cm^2$, possessing a higher impedance for
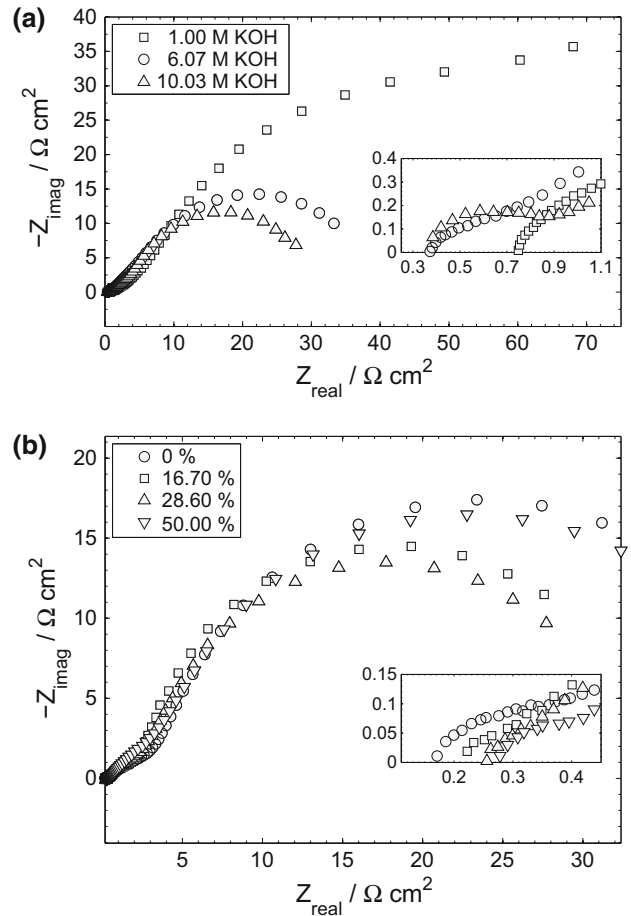

Fig. 4 Nyquist plot for batteries with **a** 1.00, 6.07, and 10.03 M KOH solution applied and **b** 6.07 M KOH solution without added K_2CO_3 in the electrolyte, 16.70, 28.60, and 50.00 mol% added K_2CO_3; obtained at 0.75 mA cm^{-2} DC discharge current and a 0.08 mA cm^{-2} AC amplitude at a frequency of f 10^{-2} 10^5 Hz

decreasing electrolyte concentrations of KOH. This is particularly distinct for the measurement result with 1.00 M KOH solution.

The enlargement in Fig. 4a shows the impedance response in the high frequency region. The area specific ohmic resistance at the highest frequency is $0.7481\,\Omega\,cm^2$ for a battery with 1.00 M KOH solution, $0.3723\,\Omega\,cm^2$ for 6.07 M, and $0.3844\,\Omega\,cm^2$ for 10.03 M. These values can be seen as internal battery resistances. The internal battery resistance is the highest at 1.00 M KOH electrolyte and the lowest for 6.07 M KOH electrolyte, which is in line with the trend for the ionic conductivity presented in Fig. 2a.

The area specific ohmic resistance is 50 % lower for the measurement with 6.07 M KOH solution than for 1.00 M KOH, which will be explained in the following. For the ZABs investigated, the internal battery resistance is composed of the electrical resistance of the metal parts of the battery set-up (current-collectors, catalyst layer), contact resistances, the ionic resistance of the separator, and the electrical and ionic resistances of the porous zinc electrode. The ionic resistance is the dominant contribution and is determined by the electrolyte concentration in the porous zinc electrode [19]. The ionic contribution of the separator to the internal battery resistance is approximated with Eq. (3) in the appendix. If the separator is soaked with 6.07 M KOH electrolyte and possesses a thickness of 25 μm (for Celgard 3401), its contribution to the overall battery resistance would be 1 %. On the contrary, the ionic contribution of the porous zinc electrode (paste with 6.07 M KOH electrolyte, 0.17 cm thick) to the internal battery resistance would be 74 %, as approximated with Eq. (4) in the appendix. This shows that the changes observed in the area specific ohmic resistance at high frequencies between the different electrolyte molarities applied must be primarily evoked by the contribution of the porous zinc electrode and the constant contribution of the air electrode catalyst layer and GDL.

Figure 5a shows the Bode-plot of the aforementioned EIS measurements. The modulus of the impedance is similar for all frequencies for 6.07 and 10.03 M KOH, but is higher for the battery with 1.00 M KOH electrolyte. A minimum value for the phase angle is observed for all molarities at 10^{-1} Hz. Close to these frequencies, presumably the slower processes, such as the sluggish oxygen reduction reaction and the oxygen diffusion in the liquid electrolyte, are predominant. Since the frequency for this minimum is not shifting with molarity, it is suggested that the air electrode is not significantly affected by the change of electrolyte molarity.

Processes at the porous zinc electrode usually occur at frequencies higher than 10^2 Hz [20]. In the frequency region from 10^2 to 10^4 Hz, we observe that the frequency at which a local maximum in phase angle is emerging, increases with increasing molarity of KOH. This is in particular distinct for the measurement with 10.03 M KOH electrolyte, where the local maximum of the phase angle shifts to a higher frequency of approximately 6×10^2 Hz. This can presumably be attributed to improved zinc electrode kinetics, since the reaction rate at the zinc electrode is enhanced at higher molarities of KOH [21].

3.3.2 Impact of K_2CO_3 as additive

Figure 4b depicts the Nyquist-plot of the impedance response of ZABs prepared with various molar percentages of added K_2CO_3. All possess one pronounced arc in the low frequency region, and another smaller, less pronounced arc in the high frequency region (see enlargement). The arc at low frequencies first decreases and then increases in size with increasing amounts of K_2CO_3. Adding K_2CO_3 to the electrolyte might enhance the kinetics of the oxygen reduction reaction for small portions added. This might be explained as follows: if the amount of carbonates is increased in the electrolyte, the amount of hydroxide ions is decreased analogously. The lower amount of hydroxide ions can on the one hand favor reaction (III) at the air electrode, since less of the product, OH^-, is present. On the other hand, the presence of more carbonates will decrease the oxygen solubility because the carbonate ion is larger than the hydroxide ion, and hinder reaction (III), since less oxygen is available. It follows that for 16.70 and 28.60 mol% of added carbonates, reaction (III) might be favored predominantly and thus lower impedance values can be observed, and that for 50.00 mol% the diminished oxygen solubility might become predominant and shifts the impedance again to higher values.

The enlargement in Fig. 4b shows the impedance response in the high frequency region. The area specific ohmic resistance at the highest frequency is $0.1711\,\Omega\,cm^2$ for a battery with no added K_2CO_3, $0.2223\,\Omega\,cm^2$ for 16.70 mol% added K_2CO_3, $0.2557\,\Omega\,cm^2$ for 28.60 mol% added K_2CO_3, and $0.2781\,\Omega\,cm^2$ for 50.00 mol% added K_2CO_3. The internal battery resistance depends predominately on the ionic conductivity of the electrolyte molarity applied; more K_2CO_3 added implies a lower ionic conductivity, which is in line with the findings in Fig. 2b, and consequently a higher internal battery resistance.

It is to be noted that the ohmic resistances for the two measurements presented with pure 6.07 M KOH differ (0.1711 and $0.3723\,\Omega\,cm^2$, respectively). This can be explained by the fact that the as-prepared zinc paste was different in amount and that the indentation depth in the current-collector of the zinc electrode was different (see Sect. 2), which consequently results in a different impedance response of the zinc electrode. The same holds for observations in the Bode-plots presented in Fig. 5.
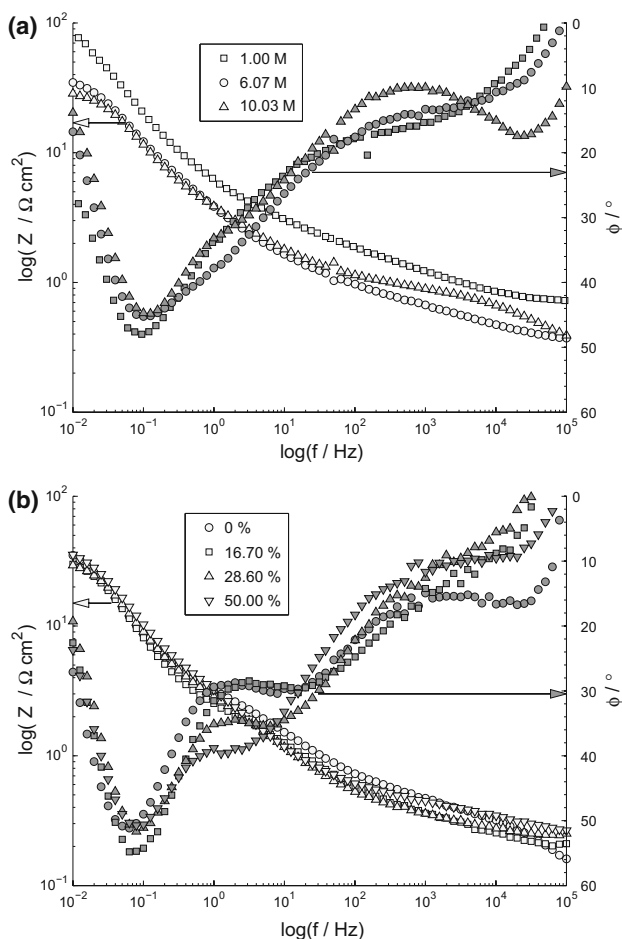
Fig. 5 Bode plots for **a** batteries with 1.00, 6.07, and 10.03 M KOH solution applied and **b** batteries with no added K_2CO_3 in the electrolyte, 16.70, 28.60, and 50.00 mol% added K_2CO_3; shown for $f = 10^{-2} - 10^5$ Hz, measurement conditions as in Fig. 4

Figure 5b shows the Bode-plot of the aforementioned EIS measurements with added K_2CO_3. The modulus of the impedance is almost identical for the entire range of frequencies for all electrolytes applied. A minimum value for the phase angle is observed for all molarities at 10^{-1} Hz (the same frequency as for the measurements with various KOH electrolytes), which is where the slower processes at the air electrode are expected.

For frequencies from 10^3 to 10^4 Hz, we observe that the frequency at which a local maximum in phase angle is emerging, is increasing slightly with increasing percentage of K_2CO_3 added. This is presumably due to the presence of an increased amount of CO_3^{2-} ions, which possibly enhance the formation of $ZnOH_4^{2-}$ in reaction (I) and slightly improve the kinetics of the reactions at the zinc electrode.

Additionally, the frequency at which a local maximum in phase angle can be observed in the range of $10^0 - 10^1$ Hz, is decreasing with increasing percentage of added K_2CO_3. The frequency observed is the lowest for

50.00 mol% of K_2CO_3. This observation might imply that another charge transfer, and thus another reaction, slower than reaction (I), takes place if high amounts of K_2CO_3 are added to the electrolyte. It is reported that $ZnCO_3$ and its accompanied precipitation species can be formed at elevated carbonate content in the electrolyte [14, 22]. The presence of these species might be the reason that another charge transfer reaction can occur. The presumed reactions are explained in more detail in the appendix in Eqs. (5) and (6).

Compared to the impedance measured for various KOH electrolytes, it can be concluded that the molar percentage of added K_2CO_3 affects the processes at the zinc electrode to a smaller amount than the concentration of OH^-. However, the added K_2CO_3 might affect the reaction mechanism at the zinc electrode significantly, which could change the discharge performance of the entire battery.

3.4 Discharge capacities for various electrolyte compositions

Selected electrolytes of 6.07 M KOH solution, and of solutions with 6 mol l^{-1} K^+ and 16.70 and 50.00 mol% of added K_2CO_3 are used to prepare batteries to identify which electrolyte composition is suitable to achieve high discharge capacities for ZABs. For this purpose, these batteries are discharged at a constant current density of 3.76 mA cm^{-2}. Figure 6 illustrates the cell potentials obtained.

The discharge curves for batteries with 6.07 M KOH solution and solution with 6 mol l^{-1} K^+ and 16.70 mol% added K_2CO_3 possess a flat cell potential at approximately 1.28 V until a SOD of 60 % is reached. Then the cell potential decays below 1.00 V, indicating the maximum SOD. The maximum SOD for the battery with 6.07 M KOH is 70 %, which is in line with other experimental findings for this current density [23]. The discharge for a battery with 6 mol l^{-1} K^+ electrolyte with 16.70 mol% added K_2CO_3 shows a maximum SOD of 62 %, and its cell potential progresses similar to the aforementioned.

On the contrary, the cell potential obtained for the battery with electrolyte containing 6 mol l^{-1} K^+ and added 50.00 mol% of K_2CO_3 behaves considerably different than for the case with pure KOH electrolyte. After an initial drop to 1.23 V, the cell potential recovers to approximately 1.28 V, and then decreases rapidly with a different shape with respect to the other curves until the cell potential is below 1.00 V. This leads to the conclusion that the high percentage of 50.00 mol% of added K_2CO_3 reduces the maximum SOD achievable at this current density by half. This is presumably caused by the participation of CO_3^{2-} in the electrode reactions, which was deduced from the EIS
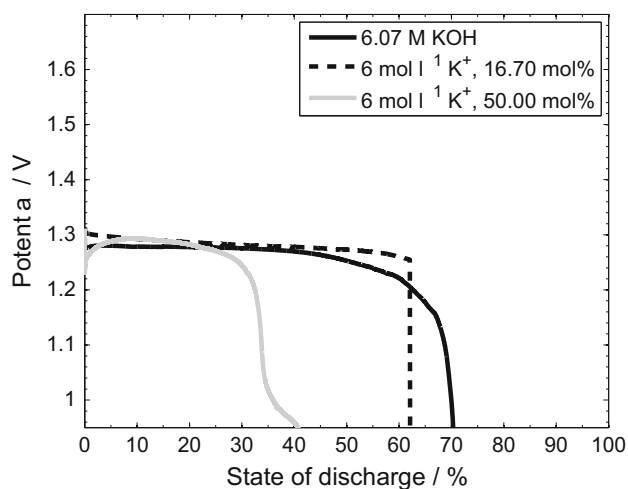
Fig. 6 Discharge measurement results at 3.76 mA cm^{-2} for batteries with various percentages of added K_2CO_3 in the electrolyte

measurements shown in Fig. 5b. To analyze the shape of the discharge curve and the underlying changes in the reaction mechanisms at both electrodes is out of the scope of this work, and remains an open issue for future work.

All in all, the discharge measurements indicate that for stable long-term operation of ZABs adding 50.00 mol% K_2CO_3 is not recommended, since only low discharge capacities can be obtained.

4 Conclusions

We have designed and operated an in-house set-up to characterize the electrochemical performance of ZABs with and without added amounts of K_2CO_3 in the KOH electrolyte in this work. Additionally, ionic conductivities for mixtures of KOH and K_2CO_3 solution were measured.

The ionic conductivity measurements have shown that solutions with 9 mol l^{-1} K$^+$ and added K_2CO_3 might be an acceptable option as electrolyte in zinc air batteries; their ionic conductivity is only marginally lower than that of solutions with 6 mol l^{-1} K$^+$ for the entire range of added K_2CO_3 investigated.

The polarization curve measurements imply that a variation of K_2CO_3 from 0 to 50.00 mol% does not impact the polarization behavior of ZABs as much as a variation of OH$^-$ from 1 M to 10 M KOH (or equivalent from 1.8 to 21.9 mol%). Additionally, these results have shown that it is not beneficial to operate ZABs with pure K_2CO_3 solution as electrolyte since it leads to an unwanted decrease in performance.

The EIS measurements applied reveal further information on the reactions and transport mechanisms in zinc air batteries. At high frequencies, the impedance is predominately determined by the zinc electrode and the electrolyte applied;

internal battery resistances obtained are then in good agreement with the ionic conductivity measured for the respective solutions. The impedance response of ZABs in the low frequency region is only slightly affected because sufficient air was provided during the battery operation, and thus the transport of the reactant oxygen was not limiting. Increasing amounts of K_2CO_3 in the electrolyte cause a change in the phase angle of the impedance responses obtained. The underlying process might be a change in the reaction mechanisms in the zinc electrode, which consequently affects the discharge behavior. This thought is supported by the discharge measurements presented, whereas no stable and reproducible discharge of ZABs at 3.76 mA cm^{-2} with 50.00 mol% of added K_2CO_3 in the electrolyte containing 6 mol l^{-1} K$^+$ was achieved.

In summary, the results presented extend the knowledge about zinc air battery operation with various electrolyte compositions. In detail, the results imply that it is acceptable to add approximately 28.6 mol% of K_2CO_3 to a high molar KOH electrolyte for stable ZAB operation with marginal losses in electrochemical performance, such as cell potential and maximum SOD. The ongoing exploration of ZABs as next generation battery can benefit from the here presented findings. They can also contribute to improve other electrochemical energy storage systems with aqueous electrolyte and the problem of carbonation.

Appendix

Conductivity measurements

The conductivity for various KOH molarities (as presented in Sect. 3.1) and added percentage of K_2CO_3 was measured with a Seven Compact conductivity meter (Mettler Toledo) in a conical flask at 298 K and under presence of ambient air; the conductivity measured was allowed to settle until it reached a stable value after approximately one minute. Each measurement was repeated three times.

Titration of the solution

The solutions were titrated to get the actual concentrations and these were verified to lie within one percent of the intended value. The indicator used for the titration was methyl orange (Sigma-Aldrich) and a 25 ml standard

burette with an accuracy of ± 0.5 ml was used to perform the titration.

Two different titrations were conducted: KOH solution and a mixture of KOH and K_2CO_3 solutions. For the titration of KOH solution, 0.5 M basic standard of potassium hydrogen pthalate (KHP) was used. For the titration of the mixture of KOH and K_2CO_3, a standard procedure was followed [24]: to determine the carbonate content in the solution, $BaCl_2$ solution was used to precipitate the carbonate ions and then the solution was titrated which gave the K^+ concentration excluding the carbonate ions. The carbonate content was determined by subtracting this value from the one obtained without the addition of $BaCl_2$.

Additional equations

The contribution of the separator, if soaked with 6 M KOH electrolyte and possessing a thickness of 25 μm (for Celgard 3401), to the overall battery resistance is approximated as

$$\frac{R_{separator}}{R_{measured}^{specific}} = \frac{\frac{d_{separator}}{\kappa_{6\,M\,KOH}}}{R_{measured}^{specific}} = \frac{\frac{0.0025 \text{ cm}}{616 \text{ mS cm}^{-1}}}{0.3723 \,\Omega \text{ cm}^2} = 0.01 \tag{3}$$

The contribution of the porous zinc electrode to the internal battery resistance is approximated as

$$\frac{R_{Zn}}{R_{measured}^{specific}} = \frac{\frac{d_{Zn}}{\kappa_{6\,M\,KOH}}}{R_{measured}^{specific}} = \frac{\frac{0.17 \text{ cm}}{616 \text{ mS cm}^{-1}}}{0.3723 \,\Omega \text{ cm}^2} = 0.74 \tag{4}$$

Sato et al. report the presence of $ZnCO_3$ in the carbonated alkaline electrolyte during zinc oxidation [14]. The proposed reaction is:

$$Zn(OH)_4^{2-} + CO_3^{2-} \leftrightarrow ZnCO_3 \downarrow + 4OH^- \tag{V}$$
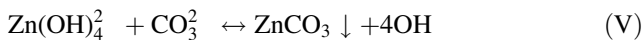
It is, similar to the zincate reaction (II), a precipitation reaction. Thereby, OH^- are produced on the one hand, which is beneficial for the zinc electrode reaction. On the other hand, the zinc atoms in $Zn(OH)_4^{2-}$ might be irreversibly lost to form $ZnCO_3$, which would diminish the battery capacity during cycling. Sato et al. state that $ZnCO_3$ is very soluble in the electrolyte and would not precipitate before ZnO [14]. However, it might still interfere with the zinc oxidation reaction. More importantly, Kannangara and Conway suggest that zinc is directly reacting with carbonates in an electron transfer reaction [22]. The proposed reaction is:

$$Zn(s) + CO_3^{2-} \rightleftharpoons ZnCO_3 + 2e^- \tag{VI}$$
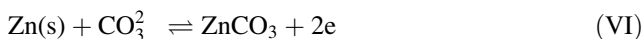
This reaction is accompanied by a multitude of subsequent reactions, which in their entirety might impact the impedance responses measured for ZABs with carbonates electrolyte.

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