Investigation and prevention of anodic zinc passivation in alkaline zinc-air batteries

Cumulative Doctoral Thesis

to be awarded the degree

Doctor of Engineering (Dr.-Ing.)

submitted by

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Date of oral examination

21.06.2019

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D104

Abstract

The fluctuating character of regenerative energy sources requires the development of suitable energy storage systems to overcome the discrepancy between the availability of electrical energy and its demand. Electrochemical energy storage devices have a number of favorable properties such as flexible scalability, decentralization and high dynamic response, wherefore they will become an important component in the energy supply in future. Large-scale rechargeable metal-air batteries and specially the alkaline zinc-air batteries (ZAB) are of particular interest, despite the continuing demand of technological development of this system. They are characterized by a low safety risk and a high specific energy density. They are environmentally friendly, non-toxic and comparatively inexpensive. Despite the numerous advantages of the ZAB, these devices are still far from commercialization, primarily due to their poor cyclic stability and low efficiency. One of the reasons for the short service life of the ZAB is the anodic passivation of the zinc electrode during battery discharge. While anodic zinc dissolution, tetrahydrozincate ions are formed which tend to precipitate as zinc oxide or zinc hydroxide on the surface of the electrode. The resulting passive layer behaves like an insulator and stops the operation of the ZAB. A reactivation of the electrode is not possible according to the current state of knowledge.

The focus of the present work was on the development of a suitable in situ analysis method for the investigation of the passivation process on the zinc electrode. Based on a combination of electrochemical impedance spectroscopy and microscopy, it was possible to detect the starting point of passive film formation for the first time. On the basis of this result, a deeper understanding of the film formation could be gained and an overall mechanism of the complex passivation process could be suggested. Furthermore, the influence of the most important operating parameters of a ZAB, such as temperature, electrolyte composition and convection, on the passivation of the zinc electrode was studied. Therefore, it became possible to choose optimal operating conditions of a ZAB which allow a passivation-free operation of the system. This could also be confirmed within the present work by means of an in-house developed electrically rechargeable ZAB which had a significantly improved service life of over 600 cycles and showed no passivation phenomena due to optimization of operating conditions. Thus, it can be concluded, that this work represents an important step towards the realization of an electrically rechargeable zinc-air battery for energy storage applications.

Kurzfassung

Der fluktuierende Charakter der regenerativen Energieträger verlangt eine Entwicklung geeigneter Energiespeicher, um die Diskrepanz zwischen der Verfügbarkeit der elektrischen Energie und ihrer Nachfrage auszugleichen. Elektrochemische Energiespeicher besitzen eine Reihe günstiger Eigenschaften wie flexible Skalierbarkeit, Dezentralisierbarkeit und schnelles Ansprechverhalten, wodurch sie eine wichtige Rolle bei der Energieversorgung der Zukunft spielen werden. Dabei sind großskalige aufladbare Metall-Luft Batterien und im Speziellen die alkalische Zink-Luft Batterie (ZLB), trotz des weiterhin vorhandenen hohen Entwicklungsbedarfs, besonders interessant. Sie zeichnen sich durch ein geringes Sicherheitsrisiko und eine hohe spezifische Energiedichte aus und gelten als umweltverträglich, nicht toxisch und vergleichsweise kostengünstig. Trotz der zahlreichen Vorteile der ZLB sind diese Systeme noch weit entfernt von ihrer Kommerzialisierung, was in erster Linie an ihrer mangelnden Zyklenstabilität und zu geringen Effizienz liegt. Eine der Ursachen der kurzen Lebensdauer der ZLB ist die anodische Passivierung der Zink-Elektrode während des Entladevorgangs der Batterie. Bei der Auflösung der Elektrode entstehen Tetrahydrozinkat-Komplexe, die dazu tendieren, auf der Oberfläche des Zinks in Form von Zinkoxid oder Zinkhydroxid auszufallen. Die entstehende Passivschicht verhält sich wie ein Isolator und bringt den Betrieb der ZLB zum Erliegen. Eine Reaktivierung der Elektrode ist nach dem aktuellen Stand des Wissens nicht möglich.

Der Schwerpunkt der vorliegenden Arbeit lag auf der Entwicklung einer geeigneten in situ Analysemethode zur Untersuchung des Passivierungsprozesses auf der Zinkelektrode. Basierend auf einer Kombination aus elektrochemischer Impedanzspektroskopie und Mikroskopie ist es erstmalig gelungen, den Beginn der Passivfilmbildung zu beobachten. Anhand dieses Ergebnisses konnte darüber hinaus ein tieferes Verständnis der Schichtentstehung erarbeitet und ein umfassender Mechanismus für den Passivierungsprozess vorgeschlagen werden. Weiterhin wurde der Einfluss der wichtigsten Betriebsparameter einer ZLB wie Temperatur, Zusammensetzung und Strömungsgeschwindigkeit des Elektrolyten auf die Passivierung der Zinkelektrode untersucht. Dank dieser Untersuchung konnten optimale Betriebsbedingungen einer ZLB ermittelt werden, die eine passivierungsfreie Funktionsweise des Speichers ermöglichen. Dies konnte ebenfalls im Rahmen der vorliegenden Arbeit anhand einer eigenentwickelten elektrisch aufladbaren ZLB bestätigt werden, die unter optimalen Betriebsbedingungen eine deutlich verbesserte Lebensdauer von über 600 Zyklen aufwies und keine Passivierungserscheinungen zeigte. Diese Arbeit stellt deshalb einen wichtigen Schritt zur Realisierung einer elektrisch aufladbaren Zink-Luft Batterie als Energiespeicher dar.

Acknowledgements

Content

1   Introduction

Since some 10 years ago the Energiewende was initiated in Germany and although our energy needs today are still mainly covered by exhaustible energy sources, science is endeavoring to develop technologies to enable the use of wind and the sun as main energy sources and to put an end to environmentally harmful technologies such as fossil fuels or nuclear power plants. Among numerous advantages of wind and solar power, these technologies have one very decisive disadvantage: the electricity they supply is often wasted because of the mismatch between power generation and demand. This circumstance makes the development of suitable energy storage systems absolutely essential. In addition to systems that store electricity in the form of kinetic or potential energy like flywheels or compressed air energy storage systems, electrochemical systems are particularly beneficial. They have a high dynamic response, can be built decentralized and have no special environmental requirements. Most electrochemical energy storage systems for stationary use which are already commercially available are well known and widely adopted battery types as the lead-acid battery (Pb-A), the sodium-sulfur battery (NaS) or the lithium-ion battery (Li-ion). However, the so-called redox flow batteries (RFBs), such as the all-vanadium (VRFB), iron-chromium or the titanium-manganese RFBs, represent one of the most promising technologies and a highly auspicious choice for stationary energy storage [1-4]. In most cases, these batteries contain of aqueous solutions of metallic salts which can be stored in external electrolyte tanks and pumped through the cell, separated by a membrane, during the charging or the discharging process. The charge-carrying species at the two half cells change their valence through receiving or transmitting electrons and thus serve as active materials of the battery. Therefore, RFBs are able to store an energy quantity of several tens of megawatt hours and have the possibility of a separate scaling of the energy and the power density by the enlargement of the tank volumes or the cell stack size, respectively. Furthermore RFBs are nonflammable and have a lower hazardous potential than lithium-ion batteries [5]. However, power density and energy density of RFBs containing liquid active materials are low compared to other commercially available technologies such as lithium-ion batteries [6], making the initial costs of RFBs per kWh more expensive [7, 8] and this storage system therefore less attractive, despite the numerous advantages (Tab. 1.1). Rechargeable metal-air flow batteries (MAFBs) and particularly alkaline zinc-air flow systems (ZAFBs) could provide the solution for the described issue, as this battery type can

be regarded as a hybrid of RFBs and solid-state batteries, combining advantages of both technologies [9, 10]. A closer look at the functionality of an alkaline ZAFB (Fig. 1.1) explains the benefits of this system. It contains in its basic form of four main components: the solid zinc electrode on the negative side of the cell, the electrolyte, and of two different oxygen electrodes on the positive side of the cell. During the discharge of the battery, the zinc electrode electrochemically dissolves and generates complex zincate ions $Zn(OH)_4^{2-}$, which are removed by flowing electrolyte through the cell and stored in external electrolyte tank. Simultaneously, oxygen is reduced on the so-called oxygen depolarized cathode (ODC) to hydroxide ions on the positive half cell (Fig. 1.1). Since the solubility of oxygen in the electrolyte is low, a possibility of supplying oxygen from the gas phase is required. Thus, the ODC contains of a highly porous diffusion layer, which allows the diffusion of oxygen into the electrode and of a catalytic layer, where the electrochemical reduction of oxygen can take place. The occurred cell reactions during the discharging process can be expressed as follows and provide a theoretical cell voltage of 1.65 V.

negative electrode: $Zn + 4\,OH^- \rightleftarrows Zn(OH)_4^{2-} + 2\,e^-$ $E^0 = -1.25$ V vs. NHE   (I)

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

positive electrode: $O_2 + 2\,H_2O + 4\,e- \rightleftarrows 4\,OH^-$ $E^0 = 0.40$ V vs. NHE   (III)

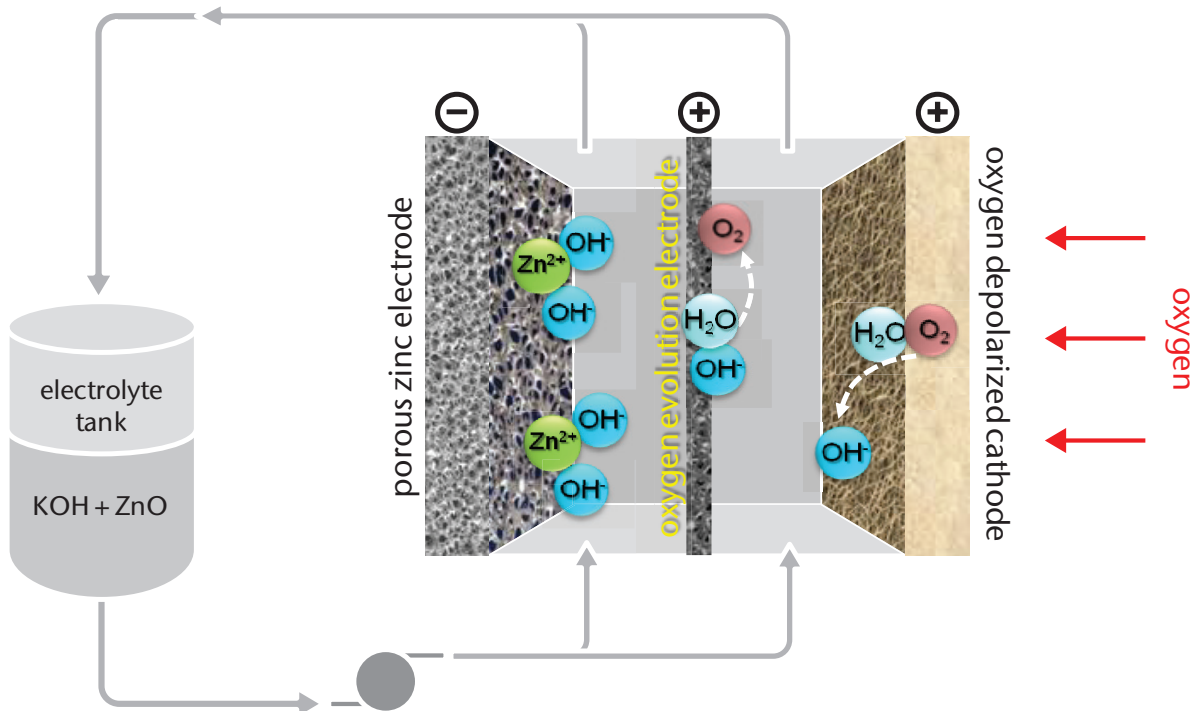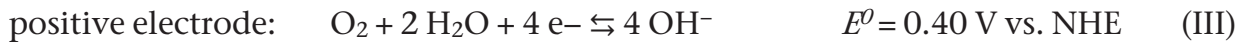cell reaction: $2\,Zn + O_2 \rightleftarrows 2\,ZnO$ $E^0 = 1.65$ V vs. NHE   (IV)

Fig. 1.1. Schematic illustration of an alkaline zinc-air flow battery in a three-electrode configuration.

During the charging of a ZAFB zincate ions electrochemically reduce back to metallic zinc and deposit on the negative electrode, while oxygen evolution reaction takes place on the second positive electrode, the so-called oxygen evolution electrode (OEE). As it can be seen from Fig. 1.1, the active material of a ZAFB can also be stored in external electrolyte tank and oxygen reservoir, similar to all-liquid RFBs, enabling separate scaling of the energy and power output. However, contrary to all-liquid RFBs, both half cells of the ZAFB can be operated with the same electrolyte and the use of a membrane is not required. This leads to a significant cost saving through the elimination of one electrolyte tank and the expensive membrane [11]. Furthermore, the ODC can be operated in self-breathing mode by consumption of oxygen from ambient air, so that no external oxygen supply is needed; a CO_2 filter [12-14] is, however, required in this case. Zinc is the cheapest and most available metal of all the battery types [15]. ZAFBs are non toxic, inherently short-circuit proof and can be shut down in an emergency by shutting off the oxygen supply.

Since zinc-air batteries are currently under development and far from commercialization, it is difficult to estimate the technically possible energy density of a ZAFB system. The energy density of zinc-air cells cited in literature ranges from 970 Wh L^{-1} for a button cell [19], over 200 Wh L^{-1} for a zinc-air traction battery [19] to 48 Wh L^{-1} for a 16-cell ZAFB-stack [17] (Tab. 1.1). Despite the first zinc-air battery was already developed in 1878 [20], the rechargeable system is still very far from technical usability. Secondary alkaline zinc-air batteries are still characterized by electrically low efficiency and insufficient cyclic stability, mainly caused by dendritic growth of zinc, resulting in morphology and shape change, passivation of the zinc electrode during discharge as well as low catalytic activity and lifetime of oxygen electrodes [15]. However, these technical difficulties, which will be

Tab. 1.1. Comparative data for rechargeable battery technologies [8].

Techno-logy	Lifetime years	Cycling times	Energy density Wh/L	Power density W/kg	Energy efficiency %	Energy capital cost €/kWh
Pb-A	25	3,000	60-90	26-125	87-92	145-450
Li-ion	> 30	> 10,000	200-400	< 5500	90-98	850-950
NaS	> 10	4,500	180-280	150-230 [6]	75-90 [6]	< 300
VRFB	20-25	unlimited	15-22	250^1 [16]	75-85 [6]	600-1200
ZAFB	---	---	48 [17]	24 [17]	---	~ 100 [18]

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[1] Related only to the weight of the cell stack.

discussed in more detail below, can be overcome by further development, so that the ZAFB has the potential to become a promising energy storage system.

As already mentioned, two different oxygen electrodes are commonly used for the operation of a rechargeable ZAFB, which is rather disadvantageous with regard to cell design, weight and cost. However, strong irreversibility of electrochemical reactions of oxygen leads to electrode potential changes of about 1 V between oxygen reduction and oxygen evolution reaction and therefore to high degradation rates of the catalyst [21]. In order to prolong the service life of the ZAFB, the cell design with two separated oxygen electrodes was proposed. The most active catalysts for the oxygen reduction reaction are platinum and platinum family metals, silver, some metal oxides and perovskite materials [21, 22]. Due to the comparatively low price, good catalytic activity and satisfying electrochemical stability of silver, technically established ODCs usually contain silver catalyst [23]. The use of the ODC also for the oxygen evolution reaction would lead (in addition to the already mentioned electrochemical degradation) to high mechanical stress within the electrode due to formation of oxygen bubbles in the pores of the ODC and oxidation of silver, which would cause volumetric expansion of silver particles within the electrode.

For the oxygen evolution reaction platinum family metal oxides like IrO_2, RuO_2, some spinel type oxides like $NiCo_2O_4$ or perovskite like $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ show excellent catalytic activity [21, 24, 25]. Spinel materials $NiCo_2O_4$, La-Sr-CoO$_3$ and Co_3O_4 currently represent the best compromise between activity, stability and cost which makes them the first choice catalysts for the oxygen evolution reaction [26, 27]. Nonetheless, scientists are aimed at development of highly catalytic active and stable bifunctional oxygen electrodes (BOE). Already known catalysts for the oxygen evolution reaction $NiCo_2O_4$ and Co_3O_4 are reported to show also promising activity towards the oxygen reduction reaction [28-32]; however, no detailed and satisfactory information concerning the cyclic stability of these electrodes is available. Consequently, a great research effort is still needed in order to enable the use of bifunctional oxygen electrodes in ZAFBs.

Shape change is defined as irreversible zinc migration caused by inhomogeneous electrode dissolution and subsequent zinc deposition during the operation of the cell due to non-uniform electrolyte flow distribution through the cell. During the charging process, the concentration of zincate ions reaches quickly the critical value in areas with poor electrolyte exchange, resulting in enhanced formation of dendrites. These needle-shaped zinc structures can foremost cause short circuits within the cell. The next disadvantage of dendritic deposits is their low mechanical stability. It is mostly not possible to dissolve dendrites during the discharging process, because they tend to break off, leading to the loss of the active material. This effect is especially high in zinc-air cells without convection and it is expected that it will be less pronounced in optimized ZAFBs [33-35]. Additionally, it was

shown that the application of pulsed zinc deposition hampers the formation of dendrites and improves the cycling stability of zinc-air batteries [34, 35].

The last serious technical issue of ZAFBs is associated with the passivation of the zinc electrode during the discharge of the battery. Zincate ions, generated during the dissolution of the electrode (I), show low solubility in alkaline electrolytes [36, 37] and are known to form so-called type 1 passive films on the electrode surface containing zinc hydroxide and zinc oxide (II) after exceeding a critical surface concentration [38]. Apart from that, passivation of zinc was observed to proceed due to the direct oxidation of the electrode [39], forming type 2 passive film, which means that different mechanisms of zinc passivation can be present. However, no general consensus about the underlying mechanism could be achieved so far. The arisen passive film behaves as an insulator and prevents the electrode from further dissolution, stopping the discharging process of the battery. Besides this, the film cannot be removed electrochemically e.g. by reverse polarization of the electrode [40-43] and the deposition of zinc on passivated electrode is, accordingly, not possible. Thus, in order to develop rechargeable and high-power ZAFBs, it is essential to solve the problem of anodic zinc passivation. However, despite decades of research on zinc passivation, no viable strategies to prevent the appearance of passive films in alkaline batteries could be proposed. The definition of term "passivation" could be a possible reason for this unsatisfactory state. In the field of corrosion science, it is generally accepted that after a period of active zinc dissolution, the electrode becomes passive, leading to a sudden breakdown of the cell potential. From that moment on, the electrode is regarded as passivated. Thus, most work on passivation is focused on the potential jump as its indication. The same procedure was adapted to the field of the battery technology, which is not reasonable. Since the process of the passive film formation is rather irreversible and begins considerably before the potential breakdown, for the development of long-life zinc-based batteries it is highly important to investigate the starting point of the passive film formation and not its ending point. Some research groups have recognized the significance of this aspect [44, 45], but did not succeeded in observing the beginning film formation. It is known, that passivation is enhanced at higher current densities [19, 46]. Therefore, zinc electrodes with high specific surface area are supposed to show lower passivation impact. Moreover, similarly to the charging process, the effect of passive film formation is expected to decrease in presence of electrolyte convection due to limitation of the zincate concentration near the electrode [38, 47].

Regarding the described crucial problems of a ZAFB, which still have to be solved, it becomes apparent why the most powerful zinc–air systems developed so far are not electrically rechargeable, but mechanically refueled systems [19]. These batteries contain packed bed zinc anodes or zinc slurries which can be mechanically or hydraulically removed after the discharge and replaced with a fresh anode [18, 48-51]. The energy densities of mechanically rechargeable systems are estimated to be about 230 Wh L^{-1}, the periphery required for the regeneration of zinc particles

was, however, not taken into account [19]. Furthermore, the recharging process is rather complicated due to difficulties in removing the zinc electrode, cleaning the cell and insertion of the new electrode, making the handling of these batteries challenging. Consequently, the development of electrically rechargeable ZAFBs is the only way forward to establish zinc-based energy storage systems.

However, notwithstanding the concept of the rechargeability of a ZAFB, the passivation of zinc remains the most essential issue of this battery type, because it is not possible to discharge the storage system efficiently in case of occurring passivation. For that reason, passivation of zinc electrodes became the main subject of the present thesis. For a deeper understanding of the passivation process, a comprehensive literature research was done on this topic. Based on the gained knowledge, it was possible to find an appropriate in situ analyzing method for investigations of zinc passivation. With the help of a combination of electrochemical impedance spectroscopy and microscopy, it was possible to detect the starting point of the passive film formation and to propose a new mechanism of this complex process. Additionally, it was possible to study the influence of temperature, electrolyte composition and convection, as well as of interruptions of the current load during the discharge on the passivation process and to identify the optimal parameters, leading to passivation-free operation of a ZAFB. As the final result, a high power density, cyclically stable and electrically rechargeable ZAFB in a three-electrode configuration could be realized and showed no indications of passivation during more than 600 cycles.

The present thesis is structured in published manuscripts focusing on different aspects of this work:

➢ Chapter 3 demonstrates the comprehensive literature research on electrochemical characterization of zinc passivation in alkaline solution including the discussion of different approaches to the modeling of the passivation process.
➢ Chapter 4 introduces the developed in situ analyzing method which enables the detection of the starting point of passive film formation and illustrates the proposed overall mechanism of the passivation process.
➢ Chapter 5 concentrates on the influence of temperature, electrolyte composition and electrolyte convection on the passivation of zinc in order to find appropriate conditions for a passivation-free operation of a ZAFB.
➢ Chapter 6 describes the design and the electrochemical performance of a cyclically stable and electrically rechargeable ZAFB, which could be operated over 600 cycles without passivation appearances.

2 Overview of the publications

The following publication were submitted and published in "peer-reviewed" scientific journals and are an integral part of this doctoral thesis.

1. M. Bockelmann, L. Reining, U. Kunz, T. Turek, Electrochemical characterization and mathematical modeling of zinc passivation in alkaline solutions: A review, Electrochim. Acta, 237 (2017) 276-298.

   The actual impact factor of the journal Electrochemica Acta is 5.116 (2017). The contribution of the first author was the preparation of Chapters 1-5, 7, and of parts of Chapter 7 of the manuscript. This publication is reprinted in Chapter 3 of the thesis and summarizes the current state of knowledge concerning passivation of zinc anodes in alkaline electrolytes, achieved over the last 100 years, and critically discusses the existing experimental findings related to investigation of passive film formation as well as the state of the mathematical modeling of this process.

2. Bockelmann, M. Becker, L. Reining, U. Kunz, T. Turek, Passivation of zinc anodes in alkaline electrolyte: Part I. Determination of the starting point of passive film formation, J. Electrochem. Soc., 165 (2018) A3048-A3055.

   The actual impact factor of the Journal of the Electrochemical Society is 3.662 (2017). The contribution of the first author was to design and to perform the experiments as well as the preparation of the manuscript. This publication is reprinted in Chapter 4 of the thesis and demonstrates a new testing cell, which allows simultaneous in situ optical and electrochemical investigations of passivation processes on zinc anodes in alkaline electrolytes. By combination of microscopy and galvanostatic impedance spectroscopy it is possible to detect the starting point of passive film formation, which has not been achieved so far and which is a very important accomplishment for the further development of zinc-based batteries.

3. Bockelmann, M. Becker, L. Reining, U. Kunz, T. Turek, Passivation of zinc anodes in alkaline electrolyte: Part II. Influence of operation parameters, J. Electrochem. Soc., 166 (2019) A1132-A1139.

The actual impact factor of the journal Electrochemical Society is 3.662 (2017). The contribution of the first author was to design and to perform the experiments as well as the preparation of the manuscript. This publication is reprinted in Chapter 5 of the thesis and demonstrates an experimental approach, based on the previous work, which enables the study of the influence of different experimental parameters like interruptions of the current load, variation of temperature, electrolyte composition, and of the forced electrolyte convection on the passivation process on zinc electrodes. With the help of this work it became possible to select optimal operation conditions of zinc-based alkaline batteries which guarantee a long-term usage of zinc anodes due to the avoidance of their passivation.

4. M. Bockelmann, U. Kunz, T. Turek, Electrically rechargeable zinc-oxygen flow battery with high power density, Electrochem. Commun., 69 (2016) 24-27.

The actual impact factor of the journal Electrochemical Communications is 4.66 (2018). The contribution of the first author was to design and to perform the experiments as well as the preparation of the manuscript. This publication is reprinted in Chapter 6 of the thesis and demonstrates a zinc-oxygen battery with coherent zinc anode which is able to provide enormously high current and power densities of 6 kA m^{-2} and 2.7 kW m^{-2}, that were previously only reached with mechanically or hydraulically recharged systems. Furthermore, the developed cell shows unprecedented high cyclic stability over 600 cycles without the need for exchanging the zinc anode or the electrolyte. Moreover, the presented cell design is technically feasible, thus larger-scale rechargeable flow batteries could be developed on the basis of this work.