Virtual Design of Next-Generation Zinc-Air Batteries

Dissertation zur Erlangung des Doktorgrades Dr. rer. nat. der Fakultät für Naturwissenschaften der Universität Ulm

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05.07.2019
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Abstract

In the on-going search for post-lithium-ion battery technologies, metal-air batteries stand out as promising candidates with high energy density. Zinc-air batteries (ZABs) in particular are the most advanced metal-air chemistry, and are based on cheap, abundant, and safe materials. With a theoretical energy density over 6000 Wh L\(^{-1}\), ZABs could play a pivotal role in grid-scale renewable energy storage and electric mobility applications. Unfortunately, both the electrical rechargeability and calendar lifetime of ZABs are limited. New electrolyte materials are needed to overcome these challenges. The application of physics-based numerical modeling and simulation can accelerate the development of ZAB materials and cell architectures.

Over the course of this work, I derive a new quasi-particle framework for continuum modeling of aqueous electrolytes. This method significantly improves the computational effort required to simulate electrolyte transport in aqueous ZABs and opens new complex electrolytes to model-based investigation.

Thermodynamic speciation models and 1D continuum models are applied to evaluate the performance of ZABs with a range of electrolyte compositions. These models allow the equilibrium composition of aqueous electrolytes and the solubility of various precipitates to be determined. I then simulate the dynamic and spatially resolved 1D concentration and multi-phase volume fraction profiles that develop in a ZAB cell during operation. This method can be applied to better understand the performance of current alkaline and near-neutral ZABs and envision next-generation designs.

Industry-standard primary ZABs currently contain aqueous alkaline KOH electrolytes. These batteries have good discharge characteristics, but the Zn electrode changes shape when cycled and the electrolyte slowly degrades as it absorbs CO\(_2\) from air. The lifetime of these cells is limited to just a few months. Aqueous near-neutral electrolytes have been proposed to address these challenges. ZABs with pH-adjusted NH\(_4\)Cl–ZnCl\(_2\) (LeClanché electrolyte) have shown good cycleability and are not subject to carbonation. But the strongly oxidizing nature of chlorine and the precipitation of unwanted solids hinders the development of a robust and high
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energy-density battery. In spite of these challenges, aqueous near-neutral ZABs are beginning to be commercialized for some large-scale stationary applications.

In this dissertation I present a theory-based method for evaluating the performance of current systems and designing new aqueous electrolytes for next-generation ZABs. Beginning with fundamental thermodynamics and moving up to cell-level engineering, I identify the important characteristics required for new electrolyte materials and highlight an example of electrolyte design in action. By applying a rational design method, I show the promising potential for long-life rechargeable ZABs based on abundant and non-toxic materials and indicate topics for future research.
Peer-Reviewed Publications

This dissertation forms the basis for the following peer-reviewed publications available in the literature:


Acknowledgement

This work is the result of a long collaborative research effort, and I would like to thank those who helped bring it to fruition.

First and foremost I thank my Doktorvater Prof. Dr. Arnulf Latz, supervisor Dr. Birger Horstmann, and all my colleagues from the German Aerospace Center (DLR) and Helmholtz Institute Ulm (HIU). It has truly been an honor and a pleasure learn from you and work with you. I thank the all the partners of the ZAS! project consortium for the successful collaboration and the members of the Examination Board for their time and guidance.

Finally, I thank my family and friends, whose encouragement made this work possible.

This work has received funding from the European Union Horizon 2020 research and innovation program under grant agreement No. 646186 (ZAS! project). The support of the bwHPC initiative through the use of the JUSTUS HPC facility at Ulm University is gratefully acknowledged.
1 Motivation and Introduction

The modern energy outlook is changing.

Over the last 200 years, society has gone through multiple energy transitions: progressing from primary sources of traditional biomass (e.g. wood, charcoal, etc.) in the 19th century, towards coal in the early 20th century, to oil and natural gas at the turn of the 21st century (Figure 1.1) [247, 30]. As our demand for energy grows, so too does innovation and the ability to harness new energy sources.

![Global annual primary energy consumption from 1800 - 2015. Data sources: [247, 30, 267, 78].](image)

This ingenuity has led to unprecedented advances in human achievement and comfort, but the industrial-scale combustion of hydrocarbon fuels is adversely altering the composition of our planet's atmosphere [219] and consuming resources faster than they can be replenished [112, 236]. Mitigating the effects of climate change...
and pursuing sustainable energy independence are two of the world’s major scientific and policy goals of the 21st century.

To achieve these goals, a new transition away from centralized Carnot-cycle heat engines towards distributed generation with alternative energy carriers is underway. For the first time in decades, the ways in which we produce, store, and consume energy are experiencing a fundamental shift.

Over the last 10 years, a combination of research breakthroughs, efficient production, and growing demand have contributed to a rapid drop in the cost of renewable energy sources and an increase in installed capacity around the world. However, the inherent instability of renewable energy supply (e.g. changes in wind speed or solar irradiation) complicates large-scale deployment into the electric grid.

In this chapter, I explore the integration of renewable energy sources into our electric grid and transportation network. New concepts for both stationary and mobile energy storage are needed to support the transition towards a clean, sustainable, and high-performance energy infrastructure.

1.1 Renewable Energy and Electric Mobility

Renewable energy is defined as being naturally replenished on a human timescale and encompasses wind, hydro, solar, biomass, and geothermal sources. Historically, the exploitation of renewables has focused heavily on hydroelectricity, which is a relatively cheap and high-power source of energy. Only in the last 20-30 years have alternative sources like wind and solar PV moved into the mainstream market.

There is wide disparity in the adoption of renewable energy sources in national electricity grids, especially within Europe. For example, Norway is 96% hydroelectric while 78% of France’s electricity comes from nuclear plants [268]. Germany offers a good case study for the integration of renewables into a mixed-infrastructure electric grid.

Figure 1.2 shows the share of electricity generation in Germany by source. Renewable electricity production (excluding hydro) grew from about 2% of the grid mix in 2000 to over 27% in 2015. While this growth was accelerated by the Energiewende (Energy Transition) policy adopted after the Fukushima nuclear disaster of 2011, Figure 1.2 indicates that the long-term trend towards increased renewable production has been steadily progressing since about the year 2000.
Motivation and Introduction

Figure 1.2: Share of annual electricity generation in Germany from 1960 - 2015. Data source: [268].

As the levelized cost of renewables becomes competitive with traditional fossil fuel sources, there has been a boom in newly installed renewable capacity around the world. Between 2010 and 2016 the cost of new solar photovoltaics (PV) dropped by 70%, wind by 25%, and battery costs by 40% [124]. Global consumer spending on electricity approached parity with spending on oil products in 2016 [124].

Data collected by the International Renewable Energy Agency (IREA) shows that the total amount of electric energy generated from wind and solar PV sources grew from 31.5 TWh (roughly the yearly electricity consumption of Munich) in 2000 to over 1000 TWh (roughly the yearly electricity consumption of Germany, Belgium, and the Netherlands) in 2015 (Figure 1.3). The International Energy Agency (IEA) projects that shortly after 2030, renewables will account for 80% of new capacity in the European Union, due to the growth of both onshore and offshore wind [124].

The growth of renewable energy generation is a positive sign for both energy independence and environmental well-being. But as renewables become a greater share of the electric grid mix, the need for large-scale energy storage becomes more urgent.

For the electric grid to function properly, the AC frequency must be kept constant at 50 Hz (60 Hz in the Americas and parts of Asia). Unanticipated changes in
power generation or consumption cause the frequency to vary around it’s stable point. If this variation becomes too large, cascade failures can lead to wide-scale blackouts [210]. To give an anecdotal example of just how sensitive the electric grid is to supply-and-demand fluctuations, even social events like the half-time pause of World Cup soccer games can cause observable grid instability [44]. If renewables become a significant share of the grid mix, then the inherent variations in local solar irradiation and wind speed could create a big problem for electric grid stability [238]. Large-scale energy storage is needed to buffer these fluctuations.

Historically, pumped hydro plants have been the gold standard for grid-scale energy storage. These plants consist of two water reservoirs: one in a valley (low) and one on a hill (high). In cases of an over-supply, water is pumped from the low reservoir up to the high reservoir; in cases of under-supply, water flows from the high reservoir down to the low reservoir, turning a turbine in the process. In 2016, the global installed power of pumped hydro storage plants exceeded 85 GW [228]. By contrast, the installed power of the closest alternative energy storage technology (thermal storage) was just 3.2 GW [228]. Pumped hydro plants are simple and
Motivation and Introduction

Figure 1.4: Global battery electric vehicles (BEVs) in use between 2012 - 2017. The worldwide number of BEVs grew from around 100,000 in 2012 to nearly 2,000,000 five years later. Data source: [228, 125].

effective, but they require a lot of space and hilly or mountainous terrain.

Electrochemical energy storage plants (including batteries, electrolyzers, and fuel cells) are an energy-dense and simple alternative. Unlike pumped hydro storage, most grid-scale electrochemical plants have architectures comparable to shipping containers [38, 39]. These kinds of modular units can be easily transported and stacked on-site. During the exponential growth of installed wind and solar PV capacity in the early 2000s, the installed power of electrochemical energy storage plants grew comparably from around 0.01 GW in 2000 to over 1.5 GW in 2016, as shown in Figure 1.4. The market for grid-scale battery storage is expected to be worth tens of billions of dollars in the next 10 years [5].

Electric vehicles (EVs) are another growing market for battery technology. Battery electric vehicles (BEVs) have grown from a niche concept ten years ago to mainstream success, with nearly 2 million units on the road in 2017 [125]. The much-publicized electric car manufacturer Tesla Motors recently exceeded its production target of 5000 battery-powered sedans (Model 3) per week [28], and has plans to expand its production facilities into China and Europe [29, 27]. However, Tesla has yet to achieve sustained profitability. More traditional auto-manufacturers are also pivoting their production towards EVs, driven by increasingly strict efficiency and air-quality standards [31] and some national plans to ban sales of internal combustion engine vehicles outright between 2025 and 2040 [125]. The IEA forecasts that the number of EVs on the road will hit 125 million by 2030 [125].

BEVs require batteries with both high power for acceleration and high energy for
distance, that are also small and cheap. These are very strict requirements, which can currently only be met by Li-ion batteries (LIBs) or hydrogen fuel cells. The stellar growth of the BEV market is largely linked with reductions in Li-ion costs to around 200 USD/kWh [125]. Efficient mass-production is likely to contribute to further cost reductions in the near-future [27, 198]; the tipping point for wide-spread commercialization of BEVs is generally considered to be 150 USD/kWh [198].

Currently, Li-ion batteries for high-performance applications require cobalt alloys as cathode materials. The Earth’s known cobalt reserves are highly concentrated in the Democratic Republic of the Congo (3.5 million tons) and Australia (1.2 million tons) [273], and recent supply-demand fluctuations have contributed to wild variations in the commodity market [289]. The price of cobalt has more than doubled since 2016, and analysts predict it could double again by 2025 [217].

The demand for high-performance batteries continues to increase. Although LIBs presently enjoy significant advantages in cost, power density, and cycleability, they are also at risk of catastrophic thermal runaway failure [169], difficult to recycle, and are dependent on a tenuous material supply chain [274].

Alternative battery chemistries are needed to supplement LIBs if we are to safely and effectively meet our energy storage needs.

1.2 Energy Storage Beyond Li-Ion Batteries

There are over over 17 GWh of grid-scale battery storage projects in the world today (operational and announced) with a combined power of 4.8 GW (Figure 1.5) [228].

Among those projects, the most energy is provided by vanadium redox-flow batteries (VRBs) and the most power is provided by lithium-ion batteries. VRBs have some characteristics that make them stand out for electric grid leveling applications. They have a high capacity, can maintain their state-of-charge over long intervals of inactivity, and can be reliably cycled to very deep depths-of-discharge (DoD). Although their energy density is very low (circa 20 Wh/L), this is often irrelevant when incorporated into a power plant. Another limitation is the cost of maintenance of the pumps, tanks, and ion-exchange membrane, which must be replaced from time-to-time [312].

Table 1.1 lists the global reserves and prices of common battery materials including Zn, V, Li, and Co. Among these materials, Zn is by far the cheapest and most
1 Motivation and Introduction

Figure 1.5: Energy (a) and power (b) of operational and announced stationary electrochemical energy storage projects worldwide, as compiled by the US DOE in 2018. Zn-based batteries (including Zn-Br flow and Zn—air) cover a significant share of both the energy and power of grid-scale storage. Data source: [228].

abundant metal. Cathode materials in Zn-based batteries often contain manganese or nickel, which are also abundant and cost-effective materials.

Zinc-based batteries, including Zn-Br flow and Zn-air, are the third-most common chemistry. The advantages of zinc-based batteries - particularly zinc-air - are that they are safe and based on abundant and cheap materials. Figure 1.6 shows the distribution of Zn reserves around the world. The wide availability of Zn metal simplifies the establishment of a reliable supply chain, in sharp contrast to Li and Co.

Zn-Br flow batteries operate with a similar basic concept as vanadium redox-flow batteries, but Zn-air batteries are unique. Zn-air batteries stand alone as the only successfully commercialized metal-air battery: a promising class of batteries with very high energy densities and the potential to be a game changer in both stationary and mobile electrochemical energy storage.

Metal-air batteries comprise a metal electrode (e.g. Zn, Li, Mg, Al, etc.), electrolyte (aqueous or non-aqueous), and an air electrode. The basic operating principle is to electrochemically reduce O₂ from air and oxidize the metal electrode to reversibly form solid metal-oxides. In this way, both the volume and the weight of the battery can be significantly reduced compared to Li-ion systems.

Research into a variety of metal-air chemistries is ongoing. The homogeneous deposition of Mg metal makes Mg-air systems appealing [160, 155, 45], but aqueous Mg-air batteries are severely limited by the corrosion of the Mg electrode. Ionic liquid electrolytes have been proposed for Mg-air systems, but they also suffer from
1 Motivation and Introduction

Table 1.1: Reserves and Prices of Common Battery Materials. Data source: [273].

<table>
<thead>
<tr>
<th>Material</th>
<th>World Reserves / metric tons</th>
<th>2017 Price / USD per metric ton</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manganese</td>
<td>680 000 000</td>
<td>$290¹</td>
</tr>
<tr>
<td>Zinc</td>
<td>230 000 000</td>
<td>$2,778</td>
</tr>
<tr>
<td>Nickel</td>
<td>74 000 000</td>
<td>$10,410</td>
</tr>
<tr>
<td>Vanadium</td>
<td>20 000 000</td>
<td>$11,464²</td>
</tr>
<tr>
<td>Lithium</td>
<td>16 000 000</td>
<td>$13,900³</td>
</tr>
<tr>
<td>Cobalt</td>
<td>7 100 000</td>
<td>$58,643</td>
</tr>
</tbody>
</table>

¹ Manganese Ore $2.90 per dtmu [193]
² Vanadium Pentoxide
³ US Lithium Carbonate

electrochemical instability, particularly during charging, and the reversibility of the cell is limited [275]. Another interesting contender is Al-air. Al is an abundant and safe material, and Al-air batteries with high theoretical energy density and specific energy values [189, 314, 84]. However these systems are susceptible to corrosion and have not demonstrated adequate cycling stability. The natural abundance and safety of sodium combined with its comparable properties with lithium have driven research into Na-air [2, 104, 134]. These systems are still in a very early stage of research. Si-air batteries have also attracted attention [72]. They have a high theoretical energy density and are stable in aqueous electrolytes. Experimental studies of Si-air systems have been performed in both ionic liquid [58] and alkaline electrolytes [73], but they currently face challenges with the reversibility of the solid discharge product, precipitation, and pore blockage. Among the metal-air systems under development, Li-air and Zn-air are the most promising [91, 150, 158].

Li-air batteries (LABs) have been researched for decades [24], but have only become a widely-pursued topic since the early 2000s. The electrolyte has proved to be a limiting factor in LAB development. The most common electrolyte configurations of Li-air systems are aprotic (non-aqueous) and aqueous. Mixed electrolyte systems have also been proposed. The beginning of the LAB research wave focused on aprotic electrolytes. The first work on the aprotic Li-air system (LiPF₆ in ethylene carbonate (EC)) was performed in 1996 by Abraham, et al. [1], who pro-
posed an overall reaction forming Li$_2$O$_2$ or Li$_2$O. Early aprotic Li-air cells were based on a carbonate solvent, but it has since been shown that carbonate solvents are unstable, producing lithium-carbonates during discharging and evolving CO$_2$ during charging [295, 181, 82, 183]. These days, carbonate electrolytes have been abandoned in favor of ether and ester solvents with lithium salts. A second challenge for LABs in aprotic electrolytes relates to the precipitation of Li$_2$O$_2$. When this solid precipitates in the cathode, it can form a dense layer over the carbon surface and inhibit the transfer of electrons. As precipitation continues, entire pores in the cathode may become blocked, passivating the electrode and limiting the cell capacity. Finally, it has been noted that oxygen transport in aprotic electrolytes can be a challenging factor in LAB performance, especially at higher current densities [6, 191]. This has motivated researches to learn from the success of the gas diffusion electrode in fuel cells and pursue investigations of LABs with aqueous electrolytes.

It is well known that Li metal reacts violently with water, which had previously limited the use of aqueous electrolytes for Li-air systems. Then in 2004, a glass ceramic layer over the Li electrode was successfully proposed to protect the metal electrode while still allowing the electrochemical reaction to proceed [280, 281]. In alkaline aqueous electrolytes, the discharge product is LiOH·H$_2$O instead of Li$_2$O$_2$. In these systems, LiOH·H$_2$O tends to precipitate at the separator-anode interface [115], which reduces the risk of pore clogging in the cathode as observed in aprotic LABs.
1 Motivation and Introduction

Figure 1.7: Overview of the energy density and specific energy of some common metal-air chemistries. Reproduced from Ref. [54] with permission from MDPI.

However, when aqueous alkaline electrolytes are exposed to air, dissolved CO$_2$ reacts with OH$^-$ to form carbonates, which slowly reduces the conductivity of the electrolyte and limits the lifetime of the cell.

In the recent wave of interest in the development of Li-air batteries, many theoretical studies have highlighted the impressive possibilities of these systems [121, 227, 317, 226, 115, 116, 61] and the company IBM pursued Li-air systems for commercial applications [91]. Although significant challenges remain [170, 131, 182, 279], the future of Li-air batteries is promising.

Zn-air batteries (ZABs) are the only fully mature metal-air system and have been successfully commercialized as primary cells for many years. But their calendar life and electrical rechargeability is limited [207]. One major advantage of Zn as an electrode material is that, unlike Li, it is practically stable in water and can be used with cheap aqueous electrolytes.

The development of secondary ZABs has progressed to the point that they are feasible for stationary storage applications, and some start-up companies like Eos Energy Storage [7] and Fluidic Energy [83] have begun to commercialize the technology, although some hurdles remain. Zn-air systems offer the most immediate and reliable pathway to a viable secondary metal-air battery.
1.3 Scope of This Work

The focus of this dissertation is the derivation and implementation of theory-based models to assist the development of next-generation aqueous zinc-air batteries. By following a rational process encompassing fundamental (electro)chemical thermodynamics, cell-level battery modeling, and the principles of engineering design, I show how new electrolyte materials can be developed to improve the performance of rechargeable ZABs.

I begin by discussing the fundamental operating principles of zinc-air cells and reviewing the progress of state-of-the-art rechargeable ZABs. I then review classical model-based design tools for electrochemical systems. Special emphasis is given to a new method of continuum modeling for aqueous metal-air batteries, which I derived over the course of my doctoral research. The quasi-particle method of continuum modeling allows the intricate behavior of pH-buffered aqueous electrolytes to be simulated with significantly reduced computational effort. The thoughtful application of the models presented in this work could open the theory-based development of many diverse aqueous electrochemical systems.

With these models in hand, I simulate the performance of ZABs with standard alkaline KOH electrolyte and a recently proposed near-neutral alternative, ZnCl₂−NH₄Cl (LeClanché electrolyte). Based on the results of the simulations, I make predictions regarding the suitability of LeClanché electrolytes for ZAB applications and highlight some potential challenges. After experimentally validating the results of the simulations, it is clear that neither KOH nor ZnCl₂−NH₄Cl electrolytes are ideal candidates for rechargeable ZABs.

The remainder of this dissertation is devoted to the design of new electrolyte materials for aqueous rechargeable ZABs. After defining a design method and selection criteria, I screen over 100 organic molecules for their suitability in aqueous zinc electrolytes and present some possible aqueous organic electrolyte formulations. The performance of a ZAB with one possible embodiment of an aqueous organic electrolyte is simulated and experimentally validated. The results show that aqueous near-neutral electrolytes containing organic molecules are suitable for ZAB applications, and are in some ways superior to LeClanché electrolytes.

This work is intended to define a promising framework for ZAB continuum modeling and electrolyte design, and provide a validated proof-of-concept example. Many topics for future research and development remain, as discussed in the closing outlook.
2 Zinc-Air Batteries: From Fundamentals to State of the Art

Zinc-air batteries (ZABs) are a promising technology to supplement lithium-ion batteries (LIBs) in future energy storage systems. ZABs have a long and successful history as primary (non-rechargeable) batteries, most notably for low current electronics.

Limitations including electrolyte degradation and Zn electrode shape change have traditionally restricted the electric rechargeability of ZABs. Because of their low cost and use of cheap, abundant, and safe materials, the development of a long-life and reliably cycleable ZAB could be a game-changer in the electrochemical energy storage market.

In this chapter, I review the history and operating principle of zinc-air batteries and discuss some challenges limiting their development. I then present a brief overview of state-of-the-art materials, electrodes, and system designs for ZAB applications.

2.1 History

Zinc-air batteries are one of the oldest and most commercially-successful batteries on the market.

Already in the 19th century, there were significant research activities devoted towards both zinc-carbon batteries and fuel cells, the precursors of zinc-air batteries. The first mention of the concept came around 1840 with the contemporary work of William Robert Grove in Great Britain and Robert Bunsen (of Bunsen burner fame) in Germany [35]. The Grove Cell, developed in 1839, consisted of Zn and Pt electrodes in dilute solutions of sulfuric and nitric acid, separated by a ceramic porous-pot construction. In 1841, Bunsen replaced the Pt electrode with a cheaper carbon cathode [35]. Both the Grove and Bunsen cells suffered from the disadvantage of evolving the noxious gas NO₂ during discharge. Between 1838 and 1842,
Grove was also at work developing the first $\text{H}_2$-$\text{O}_2$ fuel cell (Figure 2.1) [93, 94], paving the way for the development of the air electrode.

In 1866, Georges LeClanché introduced $\text{MnO}_2$ into the carbon cathode and used a single aqueous electrolyte, $\text{NH}_4\text{Cl}$ [146]. The LeClanché battery had some success powering early telegraphs and telephones. At the time, LeClanché noted that the performance of the battery was improved if the jar was only half-full (or half-empty) with electrolyte, thus allowing the solution to be saturated with oxygen [90]. In 1878, Maiche replaced the $\text{MnO}_2$ electrode of the LeClanché cell with a platinized carbon electrode, which was considered to be the first true zinc-air battery [172, 90]. Fifty-five years later, in 1933, a commercial zinc-air cell was patented by George Heise and Erwin Schumacher of the National Carbon Company [111, 109]. Heise and Schumacher treated the porous air electrode with wax to prevent flooding. Since then, the basic design has remained largely unchanged.

Primary ZABs for commercial applications started to become widely available in the 1930s. Initially, the market for ZABs comprised low current industrial electronics like railway signals and navigational buoys [220]. Beginning in the 1960s, advances in gas diffusion electrode development opened ZABs to new applications. In 1977 ZAB button cells were integrated into wearable hearing aids [90], which has contributed to a steady demand for ZABs over the past 40 years. In 2017, the global market for primary ZABs exceeded $3$ billion [127].
Efforts to develop zinc-air energy storage for electric vehicle applications have been going on since the 1960s. Concept cars containing ZABs were demonstrated by Gulf General Atomics (mini-moke jeep with a 20 kWh battery) and General Motors (35 kWh battery in a 1350 kg vehicle) [88], but were not further developed. Beginning in the 1990s, pilot EV projects were undertaken featuring mechanically-rechargeable zinc-air fuel cells (ZAFCs) - in which the discharged paste is physically removed from the cell and replaced with fresh zinc paste. In 1991, the Electric 200, a 200 km race for electric cars, was won by a Honda CRX modified with a 45 kWh zinc-air battery [59]. The car averaged 69 mph (111 kmh) and only used about 66% of its capacity. Serbian inventor Milo Zoric and Singapore Polytechnic demonstrated a ZAFC bus fleet in Singapore in 1997. At the end of the 1990s, the German company ZOXY demonstrated a van in Utah with a driving range of 760 km at temperatures below freezing and 1650 km at higher temperatures [88]. 64 vans of the German Post were fitted with mechanically-rechargeable ZAFCs in 1995; the vehicles had a range of 300 km [88, 225, 136]. Today, the Israeli company Electric Fuel continues to pursue zinc-air electric vehicles. although ZABs are clearly feasible for EV applications, these solutions have yet to be adopted on a large scale due to the considerable zinc paste supply and processing infrastructure they require and concerns about battery lifetime. Recent proposals suggest developing ZABs as electric vehicle range-extenders to supplement lithium-ion battery packs [239].

Grid-scale energy storage has become a main focus of ZAB development. In 2010, the United States Department of Energy initiated an ARPA-E project for the development of electrically rechargeable ZABs, and American companies Eos Energy Storage and Fluidic Energy are attempting to commercialize ZABs for stationary storage applications. Fluidic Energy is developing ZABs with ionic liquid electrolytes [99] and claims over 1 million commercial cycles [79]. Eos Energy Storage uses an aqueous LeClanché-type electrolyte in a flow configuration and advertises their technology at system-level price of $212 per kWh [77, 7]. In Europe, there have been a handful of recent research projects pursing rechargeable ZABs for stationary applications including the EU projects ZAS! [304] and ZAESS [303], and the German BMBF project LuZi.

The future of ZABs for both stationary and mobile applications is promising, but technical hurdles remain. In the following sections I review the operating principle of alkaline ZABs and discuss some of the main challenges in detail. With a solid understanding of the (electro)chemical processes that govern ZAB performance, I then review the current state-of-the-art ZAB technology.
2.2 Operating Principle and Challenges

2.2.1 In Alkaline Electrolytes

Figure 2.2 presents an operational schematic of an idealized alkaline ZAB discharge. In its simplest form, a rechargeable ZAB comprises a Zn metal electrode, aqueous electrolyte (e.g. KOH), and a bi-functional air electrode (BAE). The BAE consists of a porous substrate (e.g. carbon paper) loaded with a bi-functional air catalyst (e.g. MnO₂). The hydrophilic and hydrophobic properties of the BAE substrate and adjusted through the addition of PTFE to allow for the formation of a so-called three phase boundary between the electrolyte, air, and catalyst. In some configurations, a porous separator may be included between the Zn and air electrodes to prevent an internal short-circuit and manage the diffusion of aqueous zinc species.

When the ZAB is discharged, oxygen from the surrounding air absorbs into the electrolyte through the air electrode and is electrochemically reduced to form hydroxide ions, OH⁻. In the Zn electrode, the zinc metal is oxidized to create Zn²⁺ ions, which then form complexes with the excess OH⁻ in the electrolyte. The dominant complex in strongly alkaline electrolytes is the zincate ion, Zn(OH)₄²⁻. When the solubility...
limit of Zn\(^{2+}\) in the electrolyte is exceeded, a zinc solid phase dominated by ZnO precipitates on or near the Zn electrode. The elementary and overall cell reactions for an ideal Zn–O\(_2\) cell with alkaline electrolyte are listed below.

\[
0.5 \text{O}_2(g) \rightleftharpoons 0.5 \text{O}_2(aq) \tag{2.1}
\]

\[
0.5 \text{O}_2(aq) + \text{H}_2\text{O} + 2 e^- \rightleftharpoons 2 \text{OH}^- \tag{2.2}
\]

\[
\text{Zn} + 4 \text{OH}^- \rightleftharpoons \text{Zn(OH)}_4^{2-} + 2 e^- \tag{2.3}
\]

\[
\text{Zn(OH)}_4^{2-} \rightleftharpoons \text{ZnO} + 2 \text{OH}^- + \text{H}_2\text{O} \tag{2.4}
\]

Overall : \[\text{Zn} + 0.5 \text{O}_2(g) \rightleftharpoons \text{ZnO} \tag{2.5}\]

The half-cell reaction potentials are derived from fundamental thermodynamics. They are calculated using the generalized Nernst equation,

\[
E = -\left(\frac{\Delta_r G^o}{nF} + \frac{RT}{nF} \ln\left(\frac{a_{\text{red}}}{a_{\text{ox}}}\right)\right). \tag{2.6}
\]

Using the thermodynamic data available in Table 2.1, the equilibrium potentials of the major electrochemical reactions (as described above) are expressed as,

\[
E_{\text{Zn/Zn}^{2+}} = -0.762 - \frac{RT}{2F} \ln([\text{Zn}^{2+}]^{-1}), \tag{2.7}
\]

\[
E_{\text{H}_2\text{O}/\text{O}_2} = 1.229 - \frac{RT}{F} \left(\ln\left(\sqrt{\frac{[\text{O}_2]\text{[a]}}{[\text{O}_2]}}\right) + 2.303\text{pH}\right). \tag{2.8}
\]

In addition, the parasitic hydrogen gas evolution reaction (HER) can occur on the Zn electrode. This reaction and its equilibrium potential is expressed as,

\[
2 \text{H}^+ + 2 e^- \rightleftharpoons \text{H}_2(g), \quad E_{\text{H}_2/\text{H}^+} = 0 - 2.303\frac{RT}{F} \text{pH}. \tag{2.9}
\]

For a Zn–O\(_2\) cell in strongly alkaline electrolytes, the open-circuit voltage of the cell (\(U_{\text{OCV}}\)) is 1.65 V, and the nominal discharge voltage is 1.2 V. The theoretical specific capacity (\(Q\)), specific energy (\(N_{\text{mass}}\)), and energy density (\(N_{\text{vol}}\)) of the ZAB
Table 2.1: Thermodynamic quantities for selected chemicals in alkaline ZABs [164].

<table>
<thead>
<tr>
<th>Substance</th>
<th>State</th>
<th>Molar Mass</th>
<th>$\Delta H_f^\circ$</th>
<th>$S^\circ$</th>
<th>$\Delta G_f^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>[kJ mol$^{-1}$]</td>
<td>[J mol$^{-1}$ K$^{-1}$]</td>
<td>[kJ mol$^{-1}$]</td>
</tr>
<tr>
<td>Zn</td>
<td>cr</td>
<td>65.37</td>
<td>0</td>
<td>1.15</td>
<td>0</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>aq</td>
<td>65.37</td>
<td>-153.89</td>
<td>-122.21</td>
<td>-147.03</td>
</tr>
<tr>
<td>Zn(OH)$_4^{2-}$</td>
<td>aq</td>
<td>133.399</td>
<td>-</td>
<td>-</td>
<td>-859.26</td>
</tr>
<tr>
<td>ZnO</td>
<td>cr</td>
<td>81.369</td>
<td>-348.51</td>
<td>43.67</td>
<td>-318.53</td>
</tr>
<tr>
<td>O$_2$</td>
<td>g</td>
<td>31.998</td>
<td>0</td>
<td>205.2</td>
<td>0</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>l</td>
<td>18.0153</td>
<td>-286.02</td>
<td>69.96</td>
<td>-237.34</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>aq</td>
<td>17.0074</td>
<td>-230.15</td>
<td>-10.76</td>
<td>-149.02</td>
</tr>
<tr>
<td>H$^+$</td>
<td>aq</td>
<td>1.0080</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

are calculated as,

$$Q = \frac{nF}{M_{Zn}} = \frac{2 \cdot 26801}{65.38} = 819 \text{ mAh g}^{-1} \text{Zn}$$  \hspace{1cm} (2.10)

$$N_{mass} = \frac{U_{OCV} \cdot Q \cdot M_{Zn}}{M_{ZnO}} = \frac{1.65 \cdot 819 \cdot 65.38}{81.38} = 1086 \text{ Wh kg}^{-1} \text{ZnO}$$ \hspace{1cm} (2.11)

$$N_{vol} = N_{mass} \cdot \rho_{ZnO} = 1086 \cdot 5.61 = 6093 \text{ Wh L}^{-1} \text{ZnO}$$ \hspace{1cm} (2.12)

The main advantages of ZABs are that they can achieve a high theoretical energy density (6093 Wh L$^{-1}$ ZnO) and specific energy (1086 Wh kg$^{-1}$ ZnO) using simple materials. But they suffer from some disadvantages that have traditionally limited both their cycleability and calendar lifetime.

The standard electrolyte for ZABs is a concentrated aqueous alkaline electrolyte like 30 wt% KOH. Alkaline electrolytes have a high ionic conductivity, promote good oxygen reduction reaction (ORR) kinetics, and favor the precipitation of ZnO as the discharge product of the battery.

Dry air is about 21 mole% O$_2$ and contains roughly 300-400 ppm of CO$_2$. When the ZAB is operated in air, CO$_2$ co-absorbs in the electrolyte with O$_2$. Dissolved CO$_2$ slowly reacts with the excess OH$^-$ ions to form carbonates, CO$_3^{2-}$, via

$$CO_2(g) \rightleftharpoons CO_2(aq),$$ \hspace{1cm} (2.13)

$$CO_2(aq) + 2 \text{OH}^- \rightleftharpoons CO_3^{2-} + \text{H}_2\text{O}.$$ \hspace{1cm} (2.14)

This parasitic reaction lowers the conductivity of the electrolyte, slows the reac-
tion kinetics, and can block the pores of the BAE with solid precipitates. As a result, the shelf-life of alkaline ZABs is severely limited by just a few months of continuous exposure to air. To achieve shelf-life values required for rechargeable systems, the $\text{CO}_2$ concentration in the feed gas should be reduced by 2 orders-of-magnitude [253].

The changing shape of the Zn electrode as it is cycled between the charged and discharged state is another major obstacle to rechargeable ZAB development.

When the ZAB is discharged, the Zn metal electrode is converted into solid zinc oxide, ZnO. The volume of ZnO is about 60% larger than that of Zn metal. As a result, the volume of the zinc electrode can undergo significant expansion and contraction during cycling [81], with a few adverse effects for ZAB performance. First, the expansion of the Zn electrode induces a convective flux of the electrolyte and can flood the air electrode, possibly leading to a leakage of electrolyte out of the battery. On the other hand when the ZAB is charged, the shrinkage of the Zn electrode can "suck" electrolyte out of the air electrode and cause the cell to dry out. Therefore, in proper ZAB cell design, some accommodation for the expansion and contraction of the Zn electrode should be considered.

Second, ZnO does not always precipitate near the region of the original Zn metal dissolution. During discharge, Zn metal dissolves as the intermediate aqueous species $\text{Zn(OH)}_4^{2-}$, which can diffuse to new locations within (or even away from) the Zn electrode before it precipitates as ZnO. As a result, the distribution of material within the Zn electrode shifts as the cell is cycled. This can cause the electrode to become more dense and reduce the practically-achievable utilization of Zn metal in the electrode.

Another limitation has to do with the morphology of the electrochemically-deposited Zn metal during charging. It is know that Zn metal deposited from aqueous alkaline electrolytes is not smooth and homogeneous, rather it often takes on dendritic or mossy morphologies. The formation of zinc dendrites exacerbates electrode shape change and can lead to an internal short circuit. It’s worth noting that internal short circuits in zinc-air batteries do not lead to the same catastrophic thermal runaway that afflicts lithium-ion batteries, although the do result in the death of the battery.

Finally, the passivation of the Zn electrode (shown schematically in Figure 2.3) can limit the practically achievable energy density and lifetime of the cell. When ZnO precipitates in the Zn electrode, it forms a porous white film over the zinc metal (commonly called type I ZnO). This film acts as a barrier to mass transport, slowing both the transport of reactants to the electrode surface and the removal of products.
Figure 2.3: Schematic of Zn electrode passivation in aqueous alkaline electrolyte.

away from the electrode surface. At high current densities, the mass transport across the barrier cannot keep up with demand and the concentrations of reactants at the electrode surface are locally depleted. When that occurs a dense black ZnO film (commonly called type II ZnO) irreversibly forms over the zinc metal surface and kills the electrode.

In summary, Zn electrode design should (i) make accommodations for the volume expansion and contraction of the electrode, (ii) limit the formation of Zn dendrites, (iii) promote the homogeneous dissolution of Zn metal and precipitation of ZnO in a way that (iv) does not exacerbate the passivation of the electrode.

The kinetics of the electrochemical oxygen reduction and oxygen evolution reactions (ORR/OER) are one of the major factors limiting ZAB efficiency and lifetime. The bi-functional air electrode should be able to catalyze both the ORR and the OER. This is accomplished using either a single bi-functional air catalyst or two different catalysts for the ORR and OER. The most cost-effective and widely-used catalyst for this purpose is MnO$_2$.

The alternating reductive and oxidative environments during the ORR and OER a cause gradual and irreversible degradation to the air electrode, which often begins after just a few cycles [49, 48, 70, 132]. During charging, MnO$_2$ has a tendency to be oxidized to MnO$_4^{-}$ at potentials in the range of the OER. Furthermore, the oxidative corrosion of the carbon support to CO$_2$ also occurs at OER potentials [270]. To address these challenges, new bi-functional air electrode materials that are both active and stable are needed [158].
Some additional minor challenges complicate ZAB operation, but are not in-and-of-themselves detrimental to overall performance.

One such example is the parasitic hydrogen evolution reaction (HER). The equilibrium redox potential of the Zn electrode (-1.199 V in alkaline solution) is below the potential for H₂ evolution (-0.828 V in alkaline solution). Accordingly, the Zn electrode is thermodynamically unstable in water. The HER can occur either chemically or electrochemically via,

$$\text{Zn} + \text{H}_2\text{O} \rightleftharpoons \text{Zn(OH)}_2 + \text{H}_2(g), \quad (2.15)$$

$$2\text{H}_2\text{O} + 2e^- \rightleftharpoons \text{H}_2(g) + 2\text{OH}^- \quad (2.16)$$

Therefore, the HER contributes to both the self-discharge of the zinc electrode and a decrease in the Faradaic efficiency during charging. Fortunately the kinetics of H₂ gas evolution are slow and can be further reduced by the addition of dopants like Hg, In, or Bi on the surface of the Zn electrode.

The loss of electrolyte due to evaporation out of the air electrode is another challenge. Because the ZAB system is semi-open, unwanted mass transport into or out of the battery cannot be ruled out. The vapor pressure of water in KOH electrolytes is not negligible, and over time the water content in the cell will drop as it evaporates. This can be addressed by the appropriate humidification of the feed gas.

### 2.2.2 In Near-Neutral Electrolytes

Aqueous electrolytes with near-neutral pH values are not susceptible to carbonation and could improve ZAB lifetime. The most common near-neutral electrolyte (NNE) is ZnCl₂−NH₄Cl, which has been used in zinc-based LeClanché batteries for over 100 years [110, 87]. In this tradition, I refer to zinc-air batteries with aqueous ZnCl₂−NH₄Cl as LeClanché zinc-air batteries (L-ZABs) [55].

The L-ZAB concept was first proposed in the 1970s by Jindra et al. [130], but it has only recently become a broadly pursued topic in industry and research. The American company Eos Energy Storage has commercialized a variation of the L-ZAB for large-scale stationary storage [7], and recent experimental research [92, 259] has verified the favorable cycling stability and lifetime of these systems. In 2014, Goh et al. analyzed the cycling performance of L-ZABs and investigated the use of some electrolyte additives like polyethylene glycol (PEG) and thiourea to improve Zn deposition [92]. Two years later, Sumboja et al. demonstrated a manganese oxide
Figure 2.4: Schematic of idealized L-ZAB discharge. (I) The ORR occurs at the three-phase boundary of the air electrode. (II) The buffer reaction proceeds to stabilize the pH. (III) The zinc electrode dissolves to form Zn$^{2+}$, which (IV) then forms complexes with other solutes. (V) When the saturation limit of Zn$^{2+}$ is reached, zinc solids precipitate. Possible solid discharge products include ZnO, Zn(OH)$_2$, ZnCl$_2$·4Zn(OH)$_2$·H$_2$O, and ZnCl$_2$·2NH$_3$. Reproduced from Ref. [55] with permission from the Royal Society of Chemistry.

The operating principle of near-neutral L-ZABs is similar to that of alkaline ZABs, but the low concentrations of OH$^-$ and the presence of the weak acid NH$_4^+$ induce some modifications.

Figure 2.4 shows an operational schematic of an idealized L-ZAB. During discharge, the oxygen reduction reaction (ORR) occurs at the so-called three-phase boundary of the porous bi-functional air electrode (BAE) with the help of a catalyst like MnO$_2$. The ORR drives a change the concentration of H$^+$ at the air electrode, and the
pH is stabilized by the deprotonation of the weak acid NH$_4^+$. The Zn electrode is electrochemically oxidized to Zn$^{2+}$ ions, which can then form complexes with other solutes (Cl$^-$, NH$_3$, or OH$^-$). The equations and standard redox potentials for the electrochemical reactions in the L-ZAB are

$$Zn \leftrightarrow Zn^{2+} + 2e^-, \quad E^0 = -0.762 \text{ V},$$

$$0.5O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O, \quad E^0 = 1.229 \text{ V}.$$  

The stabilization of the electrolyte pH due to the weak acid buffer and the formation of zinc-amine complexes are described by the reactions,

$$NH_4^+ \rightleftharpoons NH_3 + H^+, \quad \text{and}$$  

$$Zn^{2+} + xNH_3 + yCl^- \rightleftharpoons Zn(NH_3)_xCl_y^{(2-y)}.$$  

When the solubility of Zn$^{2+}$ in the electrolyte is exceeded, zinc solids precipitate. For the system to function as a true zinc-air battery [53], ZnO should precipitate via

$$Zn^{2+} + H_2O \rightleftharpoons ZnO(s) + 2H^+,$$

and give an overall reaction of

$$Zn + 0.5O_2 \rightleftharpoons ZnO(s).$$

However, as I will discuss in later chapters, ZnO is not always the dominant solid product. Zinc-chloride salts are only sparingly soluble in aqueous electrolytes, and in some cases the discharge product can consist of a mix of ZnO, Zn(OH)$_2$, ZnCl$_2$ · 2NH$_3$, and ZnCl$_2$ · 4Zn(OH)$_2$ · H$_2$O [311, 141, 32]. The overall cell reactions for various products are shown in Table 2.2. The precipitation of non-ZnO solids consumes the electrolyte as an active material and reduces the energy density of the cell [53, 55].

The main advantage of near-neutral electrolytes (NNEs) like ZnCl$_2$－NH$_4$Cl is that they are not susceptible to the carbonation degradation that plagues alkaline electrolytes. But NNEs bring their own challenges. First, as mentioned above, the insolvency of some zinc salts consumes electrolyte during cell operation. This lowers the energy density of the battery and can exacerbate the passivation limitations discussed previously [316]. Second, near-neutral and slightly acidic pH values can increase the corrosion of the Zn metal and speed-up the evolution of H$_2$ gas. Finally, LeClanché electrolytes at pH values between 6 and 10 contain a significant concen-
Table 2.2: Overall cell reactions for different discharge products [55].

<table>
<thead>
<tr>
<th>Product</th>
<th>Overall Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>$\text{Zn} + 0.5 \text{O}_2 \rightleftharpoons \text{ZnO(s)}$</td>
</tr>
<tr>
<td>Zn(OH)$_2$</td>
<td>$\text{Zn} + 0.5 \text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Zn(OH)}_2(\text{s})$</td>
</tr>
<tr>
<td>ZnCl$_2$ · 2 NH$_3$</td>
<td>$\text{Zn} + 0.5 \text{O}_2 + 2 \text{NH}_4^+ + 2 \text{Cl}^- \rightleftharpoons \text{ZnCl}_2 \cdot 2 \text{NH}_3(\text{s}) + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>ZnCl$_2$ · 4 Zn(OH)$_2$ · H$_2$O</td>
<td>$\text{Zn} + 0.5 \text{O}_2 + 0.8 \text{H}_2\text{O} + 0.4 \text{NH}_4^+ + 0.4 \text{Cl}^- \rightleftharpoons 0.2 \text{ZnCl}_2 \cdot 4 \text{Zn(OH)}_2 \cdot \text{H}_2\text{O(s)} + 0.4 \text{NH}_3$</td>
</tr>
</tbody>
</table>

The vapor pressure of NH$_3$ is rather high, which leads to the loss of NH$_3$ by evaporation out of the air electrode. While the evaporation of water can be addressed by humidifying the feed-gas, the evaporation of ammonia is a more difficult challenge to address.

The performance of L-ZABs is governed by the delicate interplay between pH buffering, Zn$^{2+}$ chelation, and zinc salt precipitation. A firm understanding of the equilibrium and dynamic factors that affect those processes is paramount to making informed and appropriate design choices. In later chapters, I discuss how existing modeling methods can contribute to this understanding (Chapter 3), and I derive a new method of continuum-modeling to resolve some of the processes unique to pH-buffered aqueous electrolytes (Chapter 4). I then apply those models to study the challenges to L-ZAB operation and make suggestions for improvement (Chapter 5).

### 2.3 State-of-the-Art Design

The primary zinc-air battery is a mature technology, and there are decades of research investigating the challenges described in the previous section [85, 158]. As our understanding of battery design and capacity for materials innovation continue to improve, new technological solutions to ZAB lifetime and rechargeability challenges are quickly accumulating.

In this section, I review state-of-the-art innovations in ZAB design with a focus on the Zn electrode, air electrode, electrolyte, and cell architecture.


2 Zinc-Air Batteries: From Fundamentals to State of the Art

2.3.1 Electrolyte

When it comes to designing a high-performance ZAB with long cycle life, optimizing the electrolyte is one of the most crucial and difficult tasks [175, 176].

The electrolyte must be stable in the electrochemical window of the cell and facilitate the performance of both the Zn and the air electrodes. It should be conductive with a low viscosity and low vapor pressure. During discharge, $\text{Zn}^{2+}$ should be soluble enough to escape the electrode surface, but not so soluble as to diffuse far away. During discharging, $\text{ZnO}$ should be the dominate precipitated phase; during charging, the formation of Zn metal dendrites should be limited. It is easy to see why there has been so much research activity directed towards electrolyte optimization in recent decades [175].

The benchmark ZAB electrolyte in both industry and research is 30 wt% KOH saturated with ZnO. Some ZABs with alternative alkaline electrolytes like NaOH [229, 188] and LiOH [156] are described in the literature, but concentrated KOH solutions are generally preferred for their high ionic conductivity, moderate zinc solubility, and favorable electrochemical reaction kinetics [294]. The aqueous electrolyte is formulated with 30 wt% KOH because this represents an optimization of critical performance parameters (most notably conductivity) as described by comprehensive works in the literature [310, 311, 176].

The equivalent conductances at infinite dilution of $\text{K}^+$ (73.52 $\text{S} \cdot \text{cm}^2/\text{equiv}$) and $\text{OH}^-$ (197.6 $\text{S} \cdot \text{cm}^2/\text{equiv}$) are quite high [195]. Increasing the concentration of KOH in the solution correlates with an increase in ionic conductivity until the electrolyte becomes too viscous and the conductivity falls. Additionally, $\text{O}_2$ solubility is reduced in highly concentrated electrolytes (an effect known as salting-out) [139].

Because the optimum composition of KOH is a long-settled question, much of the prevailing research of alkaline electrolytes focuses on additives. Additives can be designed to serve a wide range of functions, but the most common functions of additives in zinc-air battery electrolytes are HER suppression, Zn dendrite inhibition, and $\text{Zn}^{2+}$ chelation. Both HER suppression and Zn dendrite inhibition serve to improve the lifetime of the battery, with $\text{Zn}^{2+}$ chelation can serve a few purposes including the dissolution of ZnO or improved rate capability. A list of some selected additives and their purposes is available in Table 2.4.

Unfortunately, the degradation of strongly alkaline electrolytes begins as soon as they are exposed to air due to the parasitic formation of carbonates. There are proposals to slow down electrolyte carbonation, but they often substantially increase
Table 2.3: Equivalent conductances and diffusion coefficients of selected ions at infinite dilution in water at 25°C [195].

<table>
<thead>
<tr>
<th>Ion</th>
<th>$z_i$</th>
<th>$\lambda_{0i}$ S cm$^2$/equiv</th>
<th>$D_i \times 10^5$ cm$^2$/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$</td>
<td>+1</td>
<td>349.8</td>
<td>9.312</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>+1</td>
<td>38.69</td>
<td>1.030</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>+1</td>
<td>50.11</td>
<td>1.334</td>
</tr>
<tr>
<td>K$^+$</td>
<td>+1</td>
<td>73.52</td>
<td>1.957</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>+1</td>
<td>73.4</td>
<td>1.954</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>+2</td>
<td>53</td>
<td>0.71</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>-1</td>
<td>197.6</td>
<td>5.260</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>-1</td>
<td>76.34</td>
<td>2.032</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>-1</td>
<td>71.44</td>
<td>1.902</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>-2</td>
<td>80</td>
<td>1.065</td>
</tr>
</tbody>
</table>

the cost and complexity of the system. To address this challenge on the materials-level, electrolytes with near-neutral pH values are considered.

Near-neutral ZABs were first proposed by Jindra et al. in 1973 [130]. They investigated the suitability of a variety of near-neutral aqueous electrolytes including NH$_4$Cl, KCl, (NH$_4$)$_2$SO$_4$, K$_2$SO$_4$, NH$_4$NO$_3$, and KNO$_3$. Their analysis found that the Zn electrode performed best in the chloride electrolytes, but underwent rapid corrosion in the nitrate electrolytes. Further investigating the chloride electrolytes, they found that both the volume and concentration have a significant impact on performance. ZABs with low volume of electrolyte degraded quicker than ZABs with large volume of electrolyte, due to accelerated and adverse precipitation of solids. They also found that a decrease in electrolyte concentration corresponded to a decrease in electrolyte conductivity and pH-buffering capacity, and confirmed that no formation of carbonates due to absorption of atmospheric CO$_2$ was observed. Since then, outside the work of Goh et al., Sumboja et al., and Clark et al. discussed in the previous section, there is a dearth of published research on near-neutral aqueous ZABs.

A handful of publications touch on ZABs with NNEs based on sulfate or nitrate. Wang et al. demonstrated a ZAB with a sulfate electrolyte while investigating the impact of magnetic fields on the Zn electrode [286]. An unrelated Wang et al. demonstrated a ZAB with a near-neutral Li$_2$SO$_4$–LiOH electrolyte [288]. Deng et al. [65] and Yu et al. [301] demonstrated mechanically-rechargeable zinc-air fuel
Table 2.4: Some selected additives used in alkaline electrolytes for zinc-battery or electroplating applications.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Purpose*</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alcohols</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>C</td>
<td>[117]</td>
</tr>
<tr>
<td>Polyvinylalcohol (PVA)</td>
<td>B</td>
<td>[200]</td>
</tr>
<tr>
<td>Polyethylene Glycol (PEG)</td>
<td>B</td>
<td>[21, 92]</td>
</tr>
<tr>
<td><strong>Amines</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(NH₄)₂CS</td>
<td>A</td>
<td>[240]</td>
</tr>
<tr>
<td>Glycine</td>
<td>C</td>
<td>[269, 199, 20, 292]</td>
</tr>
<tr>
<td>PA-Imid</td>
<td>B</td>
<td>[200]</td>
</tr>
<tr>
<td><strong>Carboxylic Acids</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>C</td>
<td>[151]</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>A B C</td>
<td>[262, 149, 140]</td>
</tr>
<tr>
<td>Tartaric Acid</td>
<td>A B C</td>
<td>[149]</td>
</tr>
<tr>
<td><strong>Other Organic Additives</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EDTA</td>
<td>A</td>
<td>[254]</td>
</tr>
<tr>
<td>MSA</td>
<td>B</td>
<td>[291]</td>
</tr>
<tr>
<td>Thiourea</td>
<td>B</td>
<td>[92]</td>
</tr>
<tr>
<td><strong>Other Inorganic Additives</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>A</td>
<td>[152]</td>
</tr>
<tr>
<td>CaO</td>
<td>A</td>
<td>[262]</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>A B C</td>
<td>[149]</td>
</tr>
<tr>
<td>SnO₂</td>
<td>A</td>
<td>[262]</td>
</tr>
</tbody>
</table>

*A = HER suppressor, B = Dendrite inhibitor, C = Zn²⁺ chelator

cells (ZAFC) based on KNO₃. These works speak to the general validity of ZABs with alternative near-neutral electrolytes, but do not conclusively investigate the performance of the electrolyte.

Acidic aqueous electrolytes are generally avoided in combination with metallic Zn electrodes due to the accelerated evolution of H₂ gas. On the other hand, acidic electrolytes are potentially desirable in the air electrode to reduce the threat of electrolyte carbonation and increase the cell voltage. For these reasons, there have been some efforts to develop dual-electrolyte ZABs.

Li et al. recently extended the dual-electrolyte concept from Li-air batteries [157] to create what they call an "acidic zinc-air battery (AZAB)" [156]. Their cell features
an alkaline LiOH–LiNO$_3$ anolyte on the Zn side and an acidic H$_3$PO$_4$–LiH$_2$PO$_4$ catholyte on the air side, separated by a solid Li$^+$-conducting membrane. The acidic electrolyte eliminates the problem of electrolyte carbonation in the air electrode, and the solid membrane helps limit diffusion of Zn(OH)$_4^{2-}$ out of the Zn electrode and improves reversibility. That study found that a dense passivating layer formed over the Zn electrode upon submersion in the anolyte. The authors attributed this to the strongly oxidative nature of LiNO$_3$, and the AZAB showed greatly improved performance in a nitrate-free LiOH electrolyte [156].

It is worth noting that ZABs with non-aqueous ionic liquid and deep-eutectic solvent electrolytes are presently widely-research topics, and have demonstrated some promising results. However, they are beyond the scope of this work.

### 2.3.2 Zinc Electrode

There are three typical configurations for the Zn electrode: foil, paste, and 3D matrix. Figure 2.5 shows examples of these electrodes. Foil electrodes are the simplest configuration; the Zn electrode is a dense metal sheet, which may be bent or molded into different shapes. This type of electrode is often used in lab-scale ZABs to study the kinetics of the Zn electrode reaction. Zn foils have also been used commercially (in the form of a Zn can) in zinc-carbon dry cells. Foil electrodes have the advantage of being very cheap and easy to produce, but the electrochemical surface area is low (limiting the rate-capability and increasing the risk of passivation) and the rechargeability is very poor.

Porous Zn paste electrodes are most commonly featured in commercial batteries like ZAB button cells [253, 17] and alkaline Zn/MnO$_2$ batteries [114]. The paste consists of a mixture of Zn metal particles, with electrolyte and a gelling agent [17, 114, 173]. Some recipes also call for the inclusion of ZnO [184, 148, 207]. The porous paste enhances the interface between the electrode and electrolyte, increases the active surface area, and helps to trap the intermediate species Zn(OH)$_4^{2-}$ from diffusing throughout the cell. Under normal operating conditions (e.g. 10 mA cm$^{-2}$), utilization of the Zn paste is nearly 100% [54, 253, 17], making them ideal for primary batteries. The composition of the Zn paste has a significant impact on cell performance, and a number of factors including porosity, the addition of a gelling agent, and Zn:ZnO ratio should be considered.

In paste electrodes, Zn particles must maintain contact with each other to conduct electrons throughout the electrode. Because of the tendency for the electrode to
physically expand/contract by as much as 60% during operation and the diminished conductivity of ZnO (a semiconductor), some Zn metal particles can get isolated from the bulk electrode and become electrochemically inactive [81]. The risk of this occurrence rises with increasing porosity. A high porosity is sometimes desirable, since it improves mass transport within the electrode and can increase rate-capability for high-power applications. To help mitigate the risk of inactive regions in porous electrodes, gelling agents are often included to hold the Zn particles together while improving transport within the electrode. Gelling agents include materials like polyacrylic acid (PAA), carboxymethyl cellulose (CMC), polyvinyl alcohol (PVA), and polyethylene glycol (PEG) in combination with PTFE [152, 133, 151, 106, 174]. They are generally considered to be necessary in Zn paste electrodes with porosity values between 60% - 70% [309]. To maintain adequate conductivity, the volume
fraction of Zn metal in the paste should not be less than 28% [309].

High-porosity electrodes are good for high-power applications, but a greater Zn content is needed to achieve high energy density. The maximum amount of Zn in the paste is determined by the precipitation of ZnO. Zn dissolution does not occur homogeneously throughout the Zn electrode, but begins at the separator and moves backwards towards the current collector [261, 17, 253]. This creates a barrier of ZnO which can exacerbate mass-transport limitations. Because ZnO precipitation increases the volume of the electrode by a factor of 1.6, Zn metal volume fractions greater than 50% run the risk of totally blocking the front of the electrode with ZnO. Considering these factors, the optimum volume fraction of Zn metal in the paste is circa 30% - 40%.

Powdered ZnO can also be added to the paste to improve voltage stability and reversibility. When pure Zn paste electrodes are first discharged, there is a characteristic steep drop in the cell voltage, which later recovers and stabilizes to a constant plateau (Figure 2.6) [253]. This initial drop is attributable to the nucleation of ZnO [253]. To address this issue, some recipes call for ZnO to be mixed into the electrode paste [184, 148, 207]. This eliminates the barrier for ZnO nucleation and leads to more homogeneous ZnO precipitation and improved cell perfor-
Table 2.5: Selected studies of Zn electrode performance and design in the literature.

<table>
<thead>
<tr>
<th>Aspect of Design</th>
<th>Details</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc Passivation</td>
<td>Mechanism</td>
<td>[211, 165]</td>
</tr>
<tr>
<td></td>
<td>Characterization</td>
<td>[100, 34, 69, 114]</td>
</tr>
<tr>
<td></td>
<td>Modeling</td>
<td>[43, 212, 165, 253]</td>
</tr>
<tr>
<td>Shape Change</td>
<td>Characterization</td>
<td>[180, 184]</td>
</tr>
<tr>
<td></td>
<td>Imaging</td>
<td>[201]</td>
</tr>
<tr>
<td></td>
<td>Engineering</td>
<td>[50, 168]</td>
</tr>
<tr>
<td></td>
<td>Modeling</td>
<td>[50, 261]</td>
</tr>
<tr>
<td>HER Suppression</td>
<td>Materials Modification</td>
<td>[262, 152]</td>
</tr>
<tr>
<td></td>
<td>Modeling</td>
<td>[171]</td>
</tr>
<tr>
<td>3D Electrode Design</td>
<td>Fibrous</td>
<td>[309]</td>
</tr>
<tr>
<td></td>
<td>Sponge</td>
<td>[205, 206]</td>
</tr>
<tr>
<td></td>
<td>Foam</td>
<td>[40, 256, 299]</td>
</tr>
<tr>
<td></td>
<td>Coatings</td>
<td>[232, 233, 187, 255]</td>
</tr>
</tbody>
</table>

The addition of ZnO in the electrode paste reduces the capacity of the electrode, therefore ZnO should comprise no more than circa 5 - 10 vol% of the initial paste composition.

3D Zn electrodes are a relatively new development [309, 42, 41], and can include various structures such as a matrix of Zn fibers or sponges. These electrodes generally consist of a 3D micro-porous structure, which may be either pure Zn or Zn plated onto a Cu or Ni substrate [309, 205, 298, 40, 206, 256, 255]. Electrodes based on a 3D Zn matrix offer a few significant advantages. First, the connectivity of the particles and the electrical conductivity of the electrode are improved. Unlike paste electrodes, where Zn particles can become isolated and electrochemically inactive, 3D fiber and sponge electrodes have a very good interconnectivity throughout the entire electrode that is not diminished by factors like volume expansion or ZnO precipitation [309]. Maintaining an uninterrupted conductive core in the electrode is paramount to achieving high Zn utilization [205, 71, 256]. 3D electrodes also allow for better control of porosity and specific surface area. These factors enhance both mass transport within the electrode and reaction kinetics, and boost performance for high-power applications [309].

Recent studies show the improved rechargeability of Zn sponge electrodes [205, 206]. Sponge electrodes consist of a Zn metal core containing a network of interconnected micro-pores. During discharge, the small volume of electrolyte in the
micro-pores quickly becomes saturated by \( \text{Zn(OH)}_2^{2-} \), causing \( \text{ZnO} \) to precipitate on the walls of the pores. In this way, the redistribution and densification of material is decreased and the electrode shows greater reversibility [205, 299, 40, 206, 255].

One proposal to decrease the parasitic evolution of \( \text{H}_2 \) gas and improve reversibility is to create an anion-conducting coating over the \( \text{Zn} \) metal surface. The idea is that the coating should limit direct contact between \( \text{Zn} \) metal \( \text{H}_2\text{O} \), and keep the intermediate species \( \text{Zn(OH)}_2^{2-} \) from diffusing away from the \( \text{Zn} \) particle. With the aqueous \( \text{Zn(OH)}_2^{2-} \) species and \( \text{ZnO} \) confined to a limited space in the immediate vicinity of the particle, the reversibility is improved. Proposed coating materials include bismuth- and silica-based glasses like \( \text{Bi}_2\text{O}_3-\text{ZnO-}\text{Li}_2\text{O} \), \( \text{Bi}_2\text{O}_3-\text{ZnO-}\text{CaO} \), \( \text{Bi}_2\text{O}_3-\text{ZnO-}\text{SiO}_2 \), and \( \text{SiO}_2 \) [232, 233, 187].

2.3.3 Bi-Functional Air Electrode

Figure 2.7 shows a conceptual diagram of a gas diffusion air electrode. The electrode consists of a porous gas diffusion layer (GDL) loaded with one or more catalysts for the oxygen reduction and oxygen evolution reactions (ORR/OER). The design of ZAB air electrodes draws heavily from progress made in gas diffusion electrodes (GDEs) of proton exchange membrane fuel cells (PEMFCs). However, bi-functional air electrodes (BAEs) differ from fuel cell GDEs in that they must be active towards both oxygen reduction and oxygen evolution and promote the formation of a three-phase boundary between the catalyst, air, and a liquid electrolyte. Many factors must be considered to optimize the performance and lifetime of the BAE, including phase management (i.e. electrolyte flooding/dry-out), material stability, and catalyst activity.

The kinetics of the ORR and OER are notoriously sluggish, and as a result, the BAE tends to limit both ZAB efficiency and rate capability. There is currently a boom in research of catalysts for zinc-air batteries. According to Web of Science [51], there were 99 publications on zinc-air catalysts in 2017 (up from 5 in 2010). Catalyst research largely focuses on the search for materials that are active for the ORR and OER, stable, cost-effective, and safe. There are two main lines of development for bi-functional air catalysts: (i) the use of a single catalyst that is active towards both the ORR and the OER or (ii) the use of two separate catalysts, each with its own separate preference to catalyze either the ORR or the OER.

Pt-based electro-catalysts are the benchmark for ORR performance in both acidic and alkaline media, and are normally dispersed on a high surface area carbon sup-
port like carbon black [62]. Unfortunately, Pt is also one of the most expensive and least-abundant metals on Earth. Although it is possible to reduce Pt loading with core-shell micro-structures (in which a Pt surface covers a less expensive substrate like copper), there is a concerted effort to develop non-Pt ORR catalysts. Recent research focuses on identifying alternative alloys, non-precious metals, or even nitrogen-doped carbon materials with ORR activity approaching that of Pt [62].

For the OER, Ir and Ru-based catalysts show very good activity, but these noble metals are also very expensive and can suffer from stability issues after cycling [221]. One less-expensive alternative is the use of a separate stainless steel mesh to catalyze the OER [10]. The activity of stainless steel towards water oxidation in alkaline electrolytes is further enhanced by a thin Ni, Fe oxide layer on the electrode surface [231].

Bi-functional ORR/OER catalysts must have exceptional stability to survive the alternating oxidative and reductive environments in the BAE. Common bi-functional catalysts include transition metal oxides like MnOₓ and CoOₓ. Among these materials, MnOₓ is the most common and has been used for many years in Zn-air hearing aid batteries [158]. Recent research shows that modifications to the phase...
2 Zinc-Air Batteries: From Fundamentals to State of the Art

Figure 2.8: Various zinc-air battery architectures including (a) the button cell, (b) flow battery (reprinted by permission from Springer Ref. [8]), and (c) flexible battery (reproduced from Ref. [204] with permission from WILEY).

and carbon-substrate can improve the lifetime and performance of rechargeable ZABs [48, 259, 260]. Research into other bi-functional transition metal oxides including mixed spinels and perovskites is on-going [62].

The gas diffusion layer (GDL) must promote good mixing between the catalyst, air, and liquid electrolyte and remain stable at high OER potentials. GDL research focuses on the development of stabilized or non-carbon materials to improve resistance to carbon oxidation [37], as well as the optimum tuning of hydrophilic-hydrophobic properties by including PTFE [61, 60].

2.3.4 Cell Architecture

There are a wide variety of zinc-air cell architectures currently in use in both industry and research. The design of the cell is modified according to the need, but for the purpose of this review I group them into 3 categories: static cells, flow cells, and fuel cells. Some examples are shown in Figure 2.8.
I define static cells as battery architectures in which mass neither enters nor leaves the main reaction chamber (aside from \( \text{O}_2 \)). The most common type of static cell is the ZAB button cell. ZAB button cells (Figures 2.8(a) & 2.5(b)) comprises a “can” containing about 1.3 g of Zn paste, layered with a separator and a gas diffusion electrode. In the can, an empty void at the back of the Zn electrode accommodates the expansion of the paste as it is discharged. ZAB button cells like the commercially-available VARTA PowerOne p675 battery achieve very high energy densities (around 1000 Wh/L) for the first discharge [253, 276], but they cannot be recharged. Furthermore, button cells contain only a small amount of electrolyte, which leaves them vulnerable to electrolyte carbonation and dry-out failure. Nonetheless, the low cost and first-discharge reliability of ZAB button cells has made them the battery of choice for low-current electronics like hearing-aids. Prismatic cells are scaled-up versions of the button cell architecture for higher-current industrial applications. Energizer briefly sold a consumer prismatic ZAB with a capacity of 1800 mAh in 2008 (the PP355), but it was discontinued shortly thereafter [76].

Flexible ZABs (Figure 2.8(c)) with novel architectures have gained research attention in recent years [265, 106, 161, 154]. There is hope that these batteries could serve some applications in the fields of medical devices or wearable electronics. Zinc-air batteries are particularly good for flexible applications because of their inherent safety [85]. Because flexible ZABs are semi-open systems subject to mechanical stress, there is a high risk of electrolyte leakage. Therefore, much research is dedicated to the development of flexible solid-state electrolytes [86, 315].

Zinc-air flow batteries (ZAFBs) are systems in which excess electrolyte is stored in a tank and allowed to flow (driven either by gravity or a pump) through the reaction chamber (Figure 2.8(b)) [15]. The flow cell architecture helps to stabilize the composition of the electrolyte and improves the rate capability of the battery (by reducing passivation due to ZnO precipitation). Recent experiments show that alkaline ZAFBs are able to operate at very high current densities of up to 600 mA/cm\(^2\) [25]. It is also suggested that flowing electrolyte inhibits the formation of Zn dendrites [222, 287] and helps to remove \( \text{O}_2 \) bubbles during charging [208]. Ethanol has been proposed as an additive to further enhance the dissolution of the Zn electrode [117]. The goal of ZAFBs is to provide a safe and cost-effective solution for grid-scale energy storage [251]. A pilot plant for an 1 kW, 4 kWh alkaline ZAFB plant demonstrated 2000 cycles and a round-trip energy efficiency of 40% [8]. Gravity-fed flow systems have also been proposed for grid-scale LeClanché-type ZAFBs [7].
Finally, zinc-air fuel cells (ZAFCs) address many lifetime challenges by mechanically replacing the discharged Zn and electrolyte with fresh material (Figure 2.9) [229, 318]. ZAFC designs tend to focus on either the use of interchangeable Zn electrodes or pumping through a slurry of Zn pellets (Figure 2.9(b)).

There are several design challenges for ZAFCs. First of all, it is not a trivial task to replace the Zn electrode. After discharging, the electrode is a slurry of corrosive electrolyte, ZnO, and unreacted Zn particles. It is easy for the reaction chamber to become clogged with old material. The tapered-end ZAFC structure was developed to address the clogging issue. In that setup, the electrolyte is constantly circulated and unreacted material is swept out of the bottom of the reaction chamber. However, the unreacted material will still collect somewhere in the system and the danger of clogging feed lines or electrolyte tanks remains. Furthermore, the spent Zn slurry must be collected and transported to a regeneration station. This would require additional infrastructure, compounding both the cost and the complexity of the system. Finally, the process of continuously replacing the Zn electrode puts the
air electrode and separator under additional stress. Advanced materials with high
durability are needed to improve the overall lifetime of ZAFCs.

2.4 Summary

Zinc-air batteries are the focus of decades of research and development. The fund-
damentals of ZABs were researched as early as the 19th century, and modern cell
design and engineering has been going on for at least 80 years. As such, there is
a wealth of literature on ZAB theory and operation.

Industry-standard primary ZABs feature a strongly alkaline KOH electrolyte. This
is ideal for non-rechargeable applications, but the performance of KOH slowly de-
grades upon contact with carbon dioxide in air, and the shape of the Zn electrode
changes when it is electrically recharged. A variety of solutions from the materials-
level up through cell architecture and design have been proposed to address these
challenges.

Aqueous pH-buffered near-neutral electrolytes are one possible solution to the elec-
trolyte carbonation limitation. In these electrolytes, there is no parasitic formation of
carbonates and Zn electro-deposition is more homogeneous than in alkllaine elec-
trolytes. However, the composition and performance of these systems is signifi-
cantly more complex than their KOH counterparts. Unwanted zinc-salts - not ZnO
- likely dominate the ZAB discharge product, lowering the energy density of the
battery and increasing the risk of Zn electrode passivation.

The design of the Zn electrode is another major area of research. Traditionally,
zinc-based batteries have utilized a Zn foil or paste as the anode material. These
solutions are simple and effective, but they are not ammenable to electrical recharg-
ing. Zn metal has a tendency to form dendritic or mossy structures, while Zn paste
becomes more and more dense as it is cycles. New Zn electrode designs featuring
metal fibres, foams, and sponges have been proposed, and experimental results
have shown good improvement the electrical cycleability.

Catalyst development is the major focus of air electrode development. There are
two approaches to secondary ZAB air electrodes: a single electrode that is active
towards both the ORR and the OER, or two electrodes dedicated towards either the
ORR or the OER. The kinetics of oxygen redox are notoriously slow, and limit ZAB
efficiency and rate-capability. Furthermore, at potentials near the OER the carbon
support becomes unstable and can oxidize to CO$_2$. Current research also focuses on the development of stabilized or non-carbon support materials.

Finally, many aspects of ZAB performance can be improved with thoughtful cell architecture. There are a range of architectures in use today including static cells, flow cells, and mechanically-rechargeable fuel cells. Static cells - like hearing aid button cells - are advantageous for their simplicity, high energy density, and self-contained design (i.e. no external infrastructure is required), but the electrical reversibility is limited. Flow cells pump electrolyte through the reaction chamber as the battery is operated. This has the advantage of reducing concentration gradients in the cell and Zn electrode passivation, but it requires significant supporting infrastructure like electrolyte tanks and pumps. These systems are more expensive and have a reduced energy density. Mechanically rechargeable zinc-air fuel cells seek to address the limited rechargeability of ZABs by simply replacing the spent Zn electrode and electrolyte with fresh material. In principle, this method works well and has been demonstrated in some pilot electric vehicle projects. However, it is not trivial to efficiently replace the Zn electrode and a complex network of zinc processing facilities are required to support the mechanically-rechargeable scheme.

The future of zinc-air batteries is promising, but more research and development is needed to make electrically rechargeable ZABs commercially feasible. In the following chapter, I discuss how physics-based models can be applied to advance and accelerate ZAB development.
3 Model-Based Design Tools for Metal-Air Batteries

Experimental research and development is absolutely essential to successful battery design, but it is also expensive and time consuming. The thoughtful application of theory-based models can save valuable resources, help guide experiments down the most promising paths, and identify materials or other aspects of design that may be otherwise overlooked.

In this chapter, I review some of the main model-based design tools researchers have at their disposal when designing next-generation batteries [54]. The review is setup to begin with materials modeling, and move up in space and time scales towards electrode and full-cell models. Many of these modeling methods have been derived and applied to study a variety of metal-air systems (including Zn-air, Li-air, Mg-air, and Si-air), and are largely interchangeable among the different chemistries.

This review lays the foundation for the derivation of a novel method of continuum modeling, presented in Chapter 4.

3.1 Materials Modeling

Appropriate screening of battery materials is one of the most fundamental and important aspects of design. The theory-based evaluation and selection of materials to promote high-performance and stable operation can save untold time and money during the design process.

Unfortunately this is not a straightforward task, since battery performance is governed by the synergy of anode, cathode, and electrolyte materials in conjunction with each other, rather than each material in isolation. Researchers of metal-air batteries have a number of tools at their disposal to investigate these questions. In this section, I review two of the most common and useful modeling methods: density functional theory (DFT) and thermodynamic speciation models.
3.1.1 Density Functional Theory

Catalyst development is one of the most expensive and time consuming aspects of material research in metal-air systems. Bi-functional air catalysts can take on a wide range of compositions, often include expensive or toxic metals (e.g. Pt, Ag, Co, etc.), and are labor intensive to produce and test. Atomic-scale modeling methods can be applied early in the design process to screen potential catalysts.

Density functional theory (DFT) uses quantum mechanical calculations to make predictions about the electronic structure of multi-atom systems [244]. This method allows researchers to investigate the properties of materials considering the influence of things like surface structures and local coordination of atoms. The basic approach of DFT is to analyze a multi-atom system as the movement of electrons through a fixed array of atomic nuclei. Using the Born-Oppenheimer approximation, the state of the nuclei and the electrons can be split into separate mathematical expressions [179]. In this way the adiabatic potential energy surface of the atoms can be calculated and used to investigate the characteristics of the material [244]. Due to the complexity of the calculations involved, the method is confined to considering a limited number of atoms. Nonetheless it has been shown to be effective at screening the properties of metal alloys for a variety of applications [113].

Beginning with the work of Norskov et al. [197], there have been a wealth of DFT studies investigating the reaction pathway, activity, and stability of materials in metal-air systems. Viswanathan et al. have utilized DFT to predict the activity of different pure and alloyed metals [283, 102]. This group has also applied DFT calculations to investigate a range of phenomena in Li-air batteries [282, 3]. In 2010, Keith and Jacob clarified a multi-pathway electrochemical mechanism for the ORR, which showed good agreement with experimental data. Eberle and Horstmann correlated the change in reaction pathway to an observed change in the Tafel slope [75]. In 2017, Tripkovic and Vegge elucidated the mechanism of the ORR on Pt(111), and used their results to investigate the high activity of Pt-alloys [271]. Non-metallic catalysts, such as nitrogen-doped graphene, are desirable due to their safety and low cost. A multi-scale model featuring DFT of such systems was recently presented by Vazquez-Arenas et al. [277], and used to investigate the rate-determining step for the ORR in KOH electrolyte.

DFT simulations can also be applied to investigate metal electrode materials and solid precipitants. Siahrostami et al. modeled the effect of surface structure on zinc dissolution [245]. They applied their model to simulate the dissolution of a Zn kink atom, highlighting the potential steps of the dissolution process and predicting
the overpotential of the reaction. For electro-deposition, Jäckle and Gross propose that surface diffusion processes are key to understanding the formation of metallic surface structures [128]. They utilized a DFT model to evaluate a range of metal anode materials for their tendency to form dendrites. In the case of non-aqueous Li-air batteries, the precipitation of Li₂O₂ can electrically insulate the cathode. DFT simulations have been applied to investigate the growth and electronic structure of Li₂O₂ [120, 121, 215, 216, 213], in an attempt to mitigate the risk of passivation.

DFT is also used to screen properties of electrolytes and their suitability for metal-air applications. One of the major challenges in aprotic LABs is the development of a solvent that is stable and facilitates oxygen solubility and transport. In 2015, Husch and Korth presented a study of non-aqueous LAB electrolytes [122]. In a wide-ranging work requiring about 2 million CPU hours, they integrated DFT calculations into a larger framework to screen 927,000 potential electrolyte solvents for high Li⁺ and O₂ solubilities and low viscosity. An illustration of their work is shown in Figure 3.1. By strategically applying modeling methods, Husch et al. were able to bypass the trial-and-error approach and directly highlight electrolyte solvents with the highest chances of success.

### 3.1.2 Thermodynamic Speciation Models

The behavior of aqueous electrolytes in electrochemical systems can be quite complex and has a deciding influence on overall cell performance. The first step in determining the dynamic performance and suitability of an electrolyte for a given system is to understand its equilibrium composition.

The speciation of ions, solubility of solids, and equilibrium potential of electrodes in an electrolyte is strongly dependent on pH and solute species concentration [66, 141, 311]. For some systems like KOH–ZnO–H₂O this behavior is rather straightforward and well-documented [313, 311], while for others like ZnCl₂–NH₄Cl it is very complex and sensitive to even small changes [52, 53]. The equilibrium properties of the electrolyte system are directly derived from fundamental thermodynamics.

According to the law of mass action, for a system at equilibrium with a constant temperature, the value of the reaction quotient is constant. For the formation of a complex between a metal, M, and a ligand, L, this concept is expressed as,

\[
M + L \rightleftharpoons ML, \quad \frac{[ML]}{[M][L]} = K_{eq} \tag{3.1}
\]
Figure 3.1: Chemical potentials for Li\(^{+}\) vs. chemical potentials for O\(_{2}\) in the bulk candidate compound are plotted for all 927,000 compounds. Black dots indicate compounds with a viscosity below 3 cP, grey dots indicate compounds with a viscosity below 6 cP. Reproduced from Ref. [122] with permission from the PCCP Owner Societies.

The value of the constant, \(\beta\), is referred to as the equilibrium constant (sometimes also called the formation or stability constant). The equilibrium constant is an expression of the Gibbs free energy change of the reaction,

\[
\log_{10} \beta = -\frac{\Delta_r G^0}{2.303RT}.
\]  

(3.2)

One special case of the equilibrium constant is the association (or binding constant), \(K_a\). While the equilibrium constant describes the formation of compounds between different particles, the association constant describes the propensity of a compound to dissociate into its constituent particles and reversibly associate. This is often used to describe the behavior of weak acids and bases. Likewise, the equilibrium constant for a solid substance dissolving or precipitating in an aqueous solution is
Table 3.1: Homogeneous electrolyte reactions in the simplified KOH–Zn(II)–H₂O system [311, 248].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium Constant $(\log_{10} β)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$</td>
<td>13.96</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + \text{OH}^- \rightleftharpoons \text{Zn(OH)}^+$</td>
<td>6.31</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 2 \text{OH}^- \rightleftharpoons \text{Zn(OH)}_2$</td>
<td>11.19</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 3 \text{OH}^- \rightleftharpoons \text{Zn(OH)}_3^-$</td>
<td>14.31</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 4 \text{OH}^- \rightleftharpoons \text{Zn(OH)}_4^{2-}$</td>
<td>17.70</td>
</tr>
</tbody>
</table>

described by the solubility product constant, $K_{\text{sp}}$:

$$M + aL \rightleftharpoons ML_a(s), \quad [M][L]^a = K_{\text{sp}}. \quad (3.3)$$

In the 1970s, Smith and Martell assembled an exhaustive compilation of thermodynamic stability constants of metal-ligand complexes, $pK_a$ values of acids, and solubility products of solids for a myriad of both inorganic and organic molecules [248, 249, 178, 67]. By incorporating these equilibrium expressions for every electrolyte reaction into simple equations for the conservation of mass and charge, the equilibrium composition of the electrolyte and the solubility of solids can be predicted as a function of pH and solute concentration.

A framework for such a model [162, 163] was presented by Limpo et al. in the 1990s and expanded upon in more recent research [278, 313]. Later in this work, I develop speciation and solubility models for a variety of complex zinc electrolytes. These models are described in the appendices of this work. For the purpose of introducing the modeling method, I consider the simple system KOH–Zn(II)–H₂O.

The homogeneous electrolyte reactions in the simplified KOH–Zn(II)–H₂O system, along with their corresponding equilibrium constants, are listed in Table 3.1. Consider an electrolyte that contains some arbitrary composition of mixture of KOH and ZnO. In order to describe the distribution of solute species in that system, we first note that, within the electrolyte, the conservation of mass and local charge neutrality
conditions must hold:

\[
[Zn]_T = [Zn^{2+}] + \sum_i [Zn(OH)_{i(2-i)}],
\]

\[
0 = [H^+] + 2[Zn^{2+}] + [K^+] - ([OH^-] + \sum_i [Zn(OH)_{i(2-i)}]),
\]

where \([Zn]_T\) is the total concentration of zinc in the electrolyte with units \(\text{mol L}^{-1}\).

Setting up the equilibrium expressions of the homogeneous reactions in Table 3.1 according to Equation A.1, there are 7 equations to describe the system. If the pH and total zinc concentration of the electrolyte are known quantities, then the solution has 7 unknown solute concentrations, and a solution to the system of equations (SoE) can be easily obtained. The solubility of \(\text{ZnO}\) in the electrolyte is given according to its solubility product constant expression:

\[
[Zn^{2+}][OH^-]^2 = K_{sp}^{\text{ZnO}}.
\]

Models of equilibrium thermodynamics can be extended to generate potential-pH, or Pourbaix, diagrams [224]. The Nernst equation describes the relationship between solute concentration and the equilibrium electrode redox potential [195]. Taking this into consideration, researchers can predict the influence of shifts in pH or solute concentration on electrode potential. Aside from describing the voltage of the cell, this is also useful for identifying possible parasitic reactions like \(H_2\) evolution or redox shuttles.

### 3.2 Electrode Modeling

#### 3.2.1 Lattice Boltzmann Method

The BAE in Zn-air batteries is comprised of a porous structure (usually carbon fibers and binder) with mixed hydrophilic and hydrophobic properties. The idea is to encourage the formation of the so-called three-phase boundary without either over-saturating (flooding) or under-saturating (drying out) the pores. When the cell is cycled, pressure gradients are induced in the battery due to the precipitation and dissolution of solid products, which can change the saturation of the BAE. To simulate this behavior, a method of predicting the pressure-saturation characteristics of the BAE structure is needed.
The Lattice Boltzmann Method (LBM) is useful for simulating multi-phase flow in porous media. This approach uses the Boltzmann equation to simulate the flow of fluids as a combination of collision and streaming events of particles on a discrete lattice [47, 272]. Particle positions are confined to the nodes of the lattice and it is assumed that they can move between their current position and adjacent nodes in discrete lattice directions. The probability to find particles at a lattice node with a velocity component in any of the discrete directions is described by a distribution function [4]. If solid boundaries are present in the system, no-slip boundary conditions can be introduced by a simple bounce back scheme. Implementation of the basic LBM equations is straightforward, and there are a variety of open-source codes available [258].

In electrochemical research [105], Lattice Boltzmann models have been applied to investigate the transport of water in the GDL of PEM fuel cells [196, 103, 190, 135]. One significant benefit of LBM is the ability to simulate flow in complex geometries. Using X-ray tomography [202] or FIB-SEM images [60], real electrode structures can be modeled in 3D and their transport properties evaluated. Recently, Danner et al. presented a LBM model to predict the pressure-saturation parameters of BAES in metal-air batteries [60]. Figure 3.2 shows pressure-saturation curves calculated with LBM for both 2D and 3D simulations of real BAE structures. Their simulations show that the pressure-saturation characteristics of air electrode substrates vary according to whether the electrolyte is draining from the structure (configuration I) or imbibing the structure (configuration II). They proposed this is because the structure contains some pores that can be filled with electrolyte, but are not easily emptied.

### 3.2.2 Metal Electrode Passivation

The design of the metal electrode is determined mostly by effects linked to passivation and shape change. For Zn-air batteries, the precipitation of ZnO on the electrode surface can isolate it from the electrolyte and slow down the reaction kinetics, eventually killing the electrode. It has been shown that ZnO can take on a porous white morphology (type I) that is reversible, or a dense black morphology (type II) that is irreversible. To simulate the effects of these precipitants on electrode performance, various models have been developed.

As discussed in Chapter 2, type I ZnO is formed when the dissolved zinc concentration in the electrolyte exceeds the saturation limit, and it precipitates on or near
the electrode surface. This layer of porous ZnO is generally modeled as an additional mass transport barrier [253], slowing diffusion and migration of OH$^-$ to the electrode surface. Early models determined the passivation characteristics using the so-called Sand equation, an empirical expression linking current density, $i$, and passivation time, $t$, with constants, $k$ and $i_e$:

$$i = k t^{0.5} + i_e.$$ \hfill (3.7) 

In 1981, Liu et al. expanded this concept taking into account the mechanism for type I ZnO precipitation. They proposed that the passivation due to type I ZnO occurs via a dissolution-saturation-precipitation mechanism. Put simply, the Zn electrode dissolves until the concentration of Zn(OH)$_2^{2-}$ exceeds the saturation limit for nucleation, and the ZnO phase grows as the precipitation reaction proceeds. In their model, they calculate the time required to saturate the electrolyte with Zn(OH)$_2^{2-}$ ($t_a$), the time to precipitate type I ZnO ($t_b$), and the time to precipitate type II ZnO ($t_c$), and define the passivation time as $t = t_a + t_b + t_c$ [165]. The resulting 0D model is a helpful predictor of Zn electrode performance, but is not suitable for use in continuum modeling.

In the continuum model of Zn electrodes developed by Sunu and Bennion in 1980, they considered passivation by assuming that the precipitation of ZnO reduced the active surface area available for the Zn dissolution reaction [261]. More recently in 2017, Stamm et al. implemented the effect of type I ZnO passivation in a continuum model by calculating the thickness of the ZnO shell and numerically solving for
the species concentration at the surface [253], assuming Nernst-Planck transport across the barrier. These values were then used to calculate the Nernst potential and exchange current density of the Zn dissolution reaction.

While models for passivation due to type I ZnO are rather well developed, there are fewer models for type II ZnO passivation. In 1991, Prentice et al. [212] proposed that type II ZnO forms directly on the surface of the Zn electrode, and does not follow the dissolution-saturation-precipitation mechanism of type I. By calculating the fractional surface coverage of various zinc-hydroxides as a function of concentration and electrode potential, they were able to simulate rotating disk experiments. Their simulations agreed well with experimental measurements. The model was recreated and the results are shown in Figure 3.3.

Valdes et al. proposed the following elementary reactions and rate-determining steps (rds) to describe the dissolution of Zn metal electrodes in alkaline electrolytes:

\[
\begin{align*}
\text{Zn} + \text{OH}^- & \rightleftharpoons \text{ZnOH} + \text{e}, \\
\text{Zn(OH)} + 2 \text{OH}^- & \rightleftharpoons \text{Zn(OH)}_3^- + \text{e}^- \quad \text{(rds)}, \\
\text{Zn(OH)}_3^- + \text{OH}^- & \rightleftharpoons \text{Zn(OH)}_4^-.
\end{align*}
\]
Prentice et al. postulated that a less soluble film forms at higher potentials via:

\[
\begin{align*}
\text{Zn}(\text{OH}) + \text{OH}^- & \rightleftharpoons \text{Zn}(\text{OH})_2 + \text{e}^- , \quad (3.11) \\
\text{Zn}(\text{OH})_2 + \text{OH}^- & \rightleftharpoons \text{Zn}(\text{OH})_3^- \quad \text{(rds)}, \quad (3.12)
\end{align*}
\]

and that electrode passivation is caused by the presence of type II ZnO on the electrode surface,

\[
\begin{align*}
\text{Zn} + \text{Zn}(\text{OH})_2 + 2 \text{OH}^- & \rightleftharpoons \text{Zn}(\text{OH})_3^- + \text{Zn}(\text{OH}) + \text{e}^- \quad \text{(rds)} \quad (3.13) \\
\text{Zn} + \text{Zn}(\text{OH})_2 + 2 \text{OH}^- & \rightleftharpoons 2 \text{ZnO} + 2 \text{H}_2\text{O} + 2 \text{e}^- . \quad (3.14)
\end{align*}
\]

To create a model for Zn electrode dissolution and passivation, Prentice et al assume that the rate determining steps control the overall reaction rate and that in the remaining steps, the reactions are fast enough that the species are essentially at equilibrium.

For reactions assumed to be at equilibrium, the fractional surface coverages can be expressed in terms of the equilibrium constants of the relevant reactions,

\[
\begin{align*}
\theta_{\text{ZnOH}} &= \theta_{\text{Zn}[\text{OH}^-]} K_2 \exp\left(\frac{FV}{RT}\right) , \quad (3.15) \\
\theta_{\text{Zn(OH)}_2} &= \theta_{\text{ZnOH}[\text{OH}^-]} K_3 \exp\left(\frac{FV}{RT}\right) , \quad (3.16) \\
\theta_{\text{ZnO}} &= \theta_{\text{Zn(OH)}_2[\text{OH}^-]} K_4 \exp\left(\frac{FV}{RT}\right) , \quad (3.17) \\
\theta_{\text{Zn}} &= 1 - (\theta_{\text{ZnOH}} + \theta_{\text{Zn(OH)}_2} + \theta_{\text{ZnO}}). \quad (3.18)
\end{align*}
\]

Values for the equilibrium constants are given in Table 3.2. This approach is analogous to the thermodynamic electrolyte speciation models discussed in the previous section, considering the additional influence of the electrode potential.

While much progress has been made in understanding the mechanisms of Zn passivation, work remains to be done. A more unified theory of type I and type II passivation, along with implementation in a continuum model, could be an area for future research. A dedicated review of experimental and modeling studies of Zn electrode passivation was presented by Bockelman et al. in 2017 [26].
Table 3.2: Thermodynamic equilibrium constants for the elementary reaction steps of Zn dissolution [212].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium Constant (ln K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn + OH$^-$ ⇌ ZnOH + e</td>
<td>47.7</td>
</tr>
<tr>
<td>Zn(OH) + 2 OH$^-$ ⇌ Zn(OH)$_3^-$ + e$^-$</td>
<td>42.3</td>
</tr>
<tr>
<td>Zn(OH)$_3^-$ + OH$^-$ ⇌ Zn(OH)$_4^-$</td>
<td>2.37</td>
</tr>
<tr>
<td>Zn(OH) + OH$^-$ ⇌ Zn(OH)$_2^+$ + e$^-$</td>
<td>50.0</td>
</tr>
<tr>
<td>Zn(OH)$_2^+$ + OH$^-$ ⇌ Zn(OH)$_3^-$</td>
<td>-7.77</td>
</tr>
<tr>
<td>Zn + Zn(OH)$_2^+$ + 2 OH$^-$ ⇌ Zn(OH)$_3^-$ + Zn(OH) + e$^-$</td>
<td>39.9</td>
</tr>
<tr>
<td>Zn + Zn(OH)$_2^+$ + 2 OH$^-$ ⇌ 2 ZnO + 2 H$_2$O + 2 e$^-$</td>
<td>97</td>
</tr>
</tbody>
</table>

3.3 Full Cell Modeling

The modeling methods described above are very useful for evaluating the properties of individual materials or components, but researchers often need to know how these components will interact with each other in a real electrochemical cell.

Continuum models are among the most useful and widely-applied methods for studying the cell-level performance of metal-air batteries. This approach applies the mass and charge continuity equations to describe the transient characteristics of spatially discretized systems [194, 266]. For most applications, a 1D model is sufficient to describe the cell. However, 2D and 3D [108, 107] finite volume models of batteries can give more in-depth information for detailed analysis.

3.3.1 Continuity of Mass and Charge

The mass and charge continuity equations are expressed in generic terms as,

\[
\begin{align*}
\text{Mass Continuity:} & \quad \frac{\partial (c_i \varepsilon_i)}{\partial t} = -\nabla \cdot \hat{N}_i^{D,M} - \hat{j} \cdot \hat{N}_i^{C} + \hat{\dot{s}}_i, \\
\text{Charge Continuity:} & \quad 0 = -\nabla \cdot \hat{j} + \sum_i z_i \hat{\dot{s}}_i,
\end{align*}
\]

(3.19) (3.20)
where $c_i$ is the concentration of solute $i$, $\varepsilon_e$ is the electrolyte volume fraction, $\vec{N}^{D,M}_i$ is the diffusion-migration flux, $\vec{N}^C_i$ is the convective flux, $\dot{s}_i$ is the reaction source term, $\vec{j}$ is the electrolyte current density and $z_i$ is the solute charge number. A detailed derivation of these terms based on non-equilibrium thermodynamics and their applicability to metal-air systems can be found in existing works [142, 253, 53, 115].

In their most general form, the continuity equations describe the local conservation of mass and charge due to transport across the boundaries of a control volume and the presence of a source/sink within the bulk of the control volume. To successfully implement these equations physical models for electrolyte transport and (electro)chemical reactions are needed.

Chemical reaction models feature a term describing the thermodynamic driving force and an expression of the kinetics [23]. In the case of electrochemical reactions, the most widely-used model is the Butler-Volmer approximation [143],

$$k = k_0 \left( \exp \left[ \frac{\alpha RT}{nF} \eta \right] - \exp \left[ - \frac{(1 - \alpha)RT}{nF} \eta \right] \right), \quad (3.21)$$

where $k_0$ is the rate constant (linked to the exchange current density), $\alpha$ is the symmetry factor, $\eta$ is the surface overpotential, and the other variables take on their usual meaning. The surface overpotential is defined as the difference between the potential drop at the electrode surface and the equilibrium half-cell potential (as defined by the Nernst equation), $\eta = \phi_{elde} - \phi_{elyte} - U_{eq}$.

While the Butler-Volmer approximation is sufficient to describe simple electrodes, the precipitation of solid metal-oxides on the surface of the metal electrode forms an insulating layer and can cause the kinetics of the electrode to deviate from idealized models [69, 68, 33]. Special models of metal-electrode kinetics considering the effects of passivation have been developed [165, 212, 26] and implemented [253] in continuum simulations.

The Marcus theory of charge transfer reaction kinetics is a more accurate alternative to the Butler-Volmer approximation [19, 306, 305]. The Marcus model builds on an Arrhenius approach, in that the pre-exponential factor is described by the electronic coupling element, $H_{ab}$, and the reorganization free energy, $\lambda$, and the exponential term containing the activation energy. In its quantum mechanical form, the Marcus theory is expressed as

$$k_{ct} = \frac{2\pi}{\hbar} \frac{|H_{ab}|^2}{\sqrt{4\pi k_B T \lambda}} \exp \left[ - \frac{(\lambda + \Delta G^0)^2}{4k_B T \lambda} \right]. \quad (3.22)$$
Marcus theory results naturally from quantum mechanics, and can be more easily linked to simulations like DFT [186]. While this approach has been applied in some continuum models, it is difficult to parameterize.

The dissolution of oxygen into the electrolyte from the gas phase is described in existing works [253, 115]. The solubility of oxygen in the electrolyte is determined by Henry’s law, $[O_2^{\text{sat}}] = H_{P_{O_2}}$. The kinetics of the reaction are defined using the Hertz-Knudsen equation, $k_s = 0.01(2\pi M_{O_2} RT)^{-0.5}$, assuming that 1% of the particles hitting the phase boundary absorb in the liquid. The rate of the reaction is given as $k_{O_2} = k_s(H_{P_{O_2}} - [O_2])$. For cell operation at low current density, it is assumed that the pressure of oxygen in the air electrode remains constant [115], indicating a state of equilibrium.

Electrolyte transport is modeled using a combination of expressions for diffusion, migration and convective mass flux [195], as well as a source term stemming from the chemical reactions described above [302, 11]. While the fundamental components of electrolyte transport models are universal, their exact form can vary based on the ionic strength [195] and pH [53] of the electrolyte. For low ionic strength electrolytes, a simplified dilute solution theory (DST) approach can be applied to model the diffusion and migration transport of solutes [195]. According to DST, the diffusion and migration fluxes of a solute are expressed as,

$$
\vec{N}_i^D = -D_i \nabla c_i, \quad \text{(3.23)}
$$

$$
\vec{N}_i^M = \frac{D_i c_i z_i F}{RT} \nabla \phi_e. \quad \text{(3.24)}
$$

For high ionic strength electrolytes, a more complete concentrated solution theory (CST) is needed. In this case, a coupled expression for diffusion-migration flux can be derived from non-equilibrium thermodynamics [192, 142, 144]. According to CST, the coupled diffusion-migration flux and electrolyte current density are defined as,

$$
\vec{N}_i^{D,M} = -D_i \nabla c_i - \frac{t_i}{z_i F} \vec{j}, \quad \text{(3.25)}
$$

$$
\vec{j} = -\kappa \nabla \phi_e + \frac{\kappa}{F} \sum_i \frac{t_i}{z_i} \frac{\partial \mu_i}{\partial c_i} \nabla c_i, \quad \text{(3.26)}
$$

where $\kappa$ is the conductivity of the electrolyte, $t_i$ is the transport number of the solute, and $\mu_i$ is the chemical potential of the solute.

When metal-air batteries are operated, a convective flux of electrolyte also con-
tributes to mass transport in the cell \[ 115 \]. In general terms, the convective flux is expressed as

$$\vec{N}_i^C = c_i \vec{v}_e,$$

(3.27)

where $\vec{v}_e$ is the center-of-mass velocity of the electrolyte. This adds an additional level of complexity to metal-air battery models over closed systems like Li-ion, which often apply a simpler Nernst-Planck model. A method for considering multi-phase convective flow in continuum models was presented by Horstmann et al. \[ 115 \]. The electrolyte velocity is driven by a pressure gradient. The flow is assumed to be incompressible, isothermal and laminar. A Darcy approach \[ 194 \] is therefore sufficient to describe the flow. The center-of-mass velocity of the electrolyte is defined as

$$\vec{v}_e = -\frac{B_e}{\mu_e} \nabla p_e,$$

(3.28)

where $B_e$ is the permeability of the porous medium and $\mu_e$ is the viscosity of the electrolyte \[ 53 \].

The coupled relationship between electrolyte velocity, pressure, and the saturation of porous media is described in existing works \[ 194, 115, 253, 61 \] and discussed in more detail in the following section.

### 3.3.2 Continuum Models of Metal-Air Batteries

Continuum models can be invaluable for investigating a range of phenomena in electrochemical cells, from the effects of discharge product precipitation to the electrolyte stability. Through the development of theory-based models, side-by-side with experimental investigation and validation, researchers can identify and pursue the most promising paths towards advanced metal-air batteries. Here I review some continuum modeling studies of Zn-air and Li-air batteries published in the literature.

**Zinc-Air Batteries**

Continuum models of ZABs have been developed intermittently since the 1980s. The first 1D continuum model of a Zn electrode in an alkaline ZAB was developed in 1980 by Sunu and Bennion \[ 261 \]. It was based on the general 1D model for concentrated transport in porous electrodes outlined by Newman \[ 195 \]. Their simulations showed the inhomogeneous precipitation of ZnO and investigated the shape
change of the Zn electrode during cycling. In 1992, Mao and White [177] developed an extended model that also resolved the separator and air electrode. They found that $K_2\text{Zn(OH)}_4$ does not precipitate and compared simulated cell voltages with experimental measurements. Ten years later, Deiss et al. [64] performed ZAB cycling simulations with a 1D model of the Zn electrode and separator based on dilute solution theory. They studied the redistribution of Zn and the development of concentration gradients in the cell.

More recent Zn-air modeling studies provide insight into challenges like electrolyte carbonation, Zn electrode passivation, and improved cell design. In 2014, Schröder et al. published a framework for a 0D ZAB continuum model, which they utilized to study the effect of air composition on cell performance [234]. Examining the effects of the relative humidity (RH) and carbon dioxide content of air, they found that
controlling the RH can help reduce electrolyte loss and that the presence of CO\(_2\) can dramatically limit the lifetime of the cell. In a separate paper, they combined this model with x-ray tomography measurements of a primary button cell to monitor the state-of-charge during discharge [17].

Experimental tests of ZAB button cells have shown a voltage step in the middle of discharge, particularly at high current densities [253]. In 2017, Stamm et al. presented a model to clarify the mechanism behind this observation. Concentration profiles from their model are shown in Figure 3.4. The nucleation of ZnO requires an over-saturation of Zn(OH)_4^{2-} in the electrolyte. For high current densities, the electrolyte concentration gradients that develop in the cell are strong enough that Zn(OH)_4^{2-} does not reach the critical super-saturation for nucleation in the anode-separator interface and ZnO does not nucleate. As a result, the surface concentration of OH\(^-\) in this region is much higher than in areas of the electrode covered by a ZnO film, as shown in Figure 3.4(c). When the uninhibited Zn near the separator is completely utilized, the overpotential of the dissolution reaction increases, causing the observed drop in cell voltage. For this reason, they proposed that Zn electrodes should contain a small amount of ZnO powder. In this way, the effects of inhomogeneous ZnO nucleation can be avoided. Stamm et al. also considered the effects of CO\(_2\) dissolution in the KOH electrolyte. They found that after about 2 months, the carbonation of the electrolyte becomes so severe that the cell can no longer function. To address this issue, they propose employing either carbon dioxide filters or neutral electrolytes [54].

**Lithium-Air Batteries**

In recent years, there has been a boom in continuum modeling frameworks for both Zn-air and Li-air systems, with some areas of overlap. In 2012, Neidhardt et al. presented a flexible continuum modeling framework for multi-phase management, with direct application to a variety of electrochemical systems [194]. In their work, they applied this framework to simulate a range of fuel cells and batteries to demonstrate the versatility of the approach. In their simulations of non-aqueous Li-O\(_2\) batteries, they noted that the system is limited by a combination of slow oxygen transport and blockage of cathode pores with Li\(_2\)O\(_2\).

To address the oxygen transport and passivation challenges associated with aprotic lithium-air batteries (LABs), Horstmann et al. were motivated to examine precipitation in alkaline aqueous LABs [115]. Their model featured two important developments. The first was the introduction of pressure-saturation expression to simulate
the electrolyte flooding and drying-out of the BAE. The saturation of porous structures was described with a so-called Leverett approach, which had previously been applied in models of fuel cells.

The second development was the implementation of a model for LiOH \cdot H_2O precipitation based on the classical theory of nucleation and growth. By defining terms for the reaction enthalpy of formation for both the bulk and surface of the nucleus, they identified the critical formation energy and nucleus size. Considering a diffusion limited precipitation mechanism and the supersaturation of Li$^+$ as the driving force for nucleation and growth, they were able to simulate the spatially resolved precipitation of LiOH \cdot H_2O. The results indicate that LiOH \cdot H_2O does not block the cathode pores; rather, it precipitates mostly near the separator-anode interface, thereby addressing the passivation challenge in aprotic LABs.
In 2015, the model of Horstmann et al. extended by Gröbl and Bessler to engineer seven variants of aqueous alkaline LAB systems [96]. They identified improvements to the glass separator and the development of lighter electrode materials as areas for further research. While the potential advantages of aqueous LABs are clear, most recent modeling studies have focused on non-aqueous systems.

One of the first continuum models for non-aqueous LABs was presented by Andrei et al. in 2010 [12]. Their simulations considered the effects of cell architecture and operational conditions on concentration profiles and cell voltage, and provided a solid foundation for further development. Recent multi-scale modeling studies of non-aqueous LABs focus heavily on the nucleation and growth of solids, and their affect on cell performance. A 1D continuum model of a LAB was developed by Albertus et al. in 2011 [6]. They found that although O\textsubscript{2} transport can be limiting for high current densities, the main limitation in LABs relates to the precipitation of solids. For carbonate solvents, the dominant discharge product is Li\textsubscript{2}CO\textsubscript{3}, which, along with Li\textsubscript{2}O\textsubscript{2}, poses a strong passivation risk to the cathode. The model was based on a CST approach for electrolyte transport. It did not consider the effects of electrolyte convection or cathode saturation, which was identified as an area for future development.

With the shift to non-carbonate electrolytes, the morphology of Li\textsubscript{2}O\textsubscript{2} precipitated during discharge became the subject of research. Knowing that pore blockage was a challenge in LAB performance, Xue et al. developed a continuum model to investigate Li\textsubscript{2}O\textsubscript{2} precipitation considering the pore size distributions of cathode materials [297]. They later extended their model to determine the effect of both electrolyte solvent and applied current density on Li\textsubscript{2}O\textsubscript{2} morphology [296]. A nanoscale continuum model to study the rate-dependent growth of Li\textsubscript{2}O\textsubscript{2} was presented by Horstmann et al. [116]. They found that the morphology of Li\textsubscript{2}O\textsubscript{2} shifts from discrete particles at low discharge rates to an electronically insulating film at high current densities. This line of research was then expanded to consider the effects of Li\textsubscript{2}O\textsubscript{2} precipitation on the charging process. Yin et al. presented a continuum model for non-aqueous LABs that links the size of the Li\textsubscript{2}O\textsubscript{2} particles created during discharging to the two-step voltage profile observed during charging [300]. The effect of the Li\textsubscript{2}O\textsubscript{2} reaction mechanism on the discharge/charge characteristics was investigated by Grübl et al. [95]. They found that the reaction mechanism is partially irreversible, and considered the effects of adding a redox mediator to the electrolyte. Finally, some researchers have highlighted not only the effects of Li\textsubscript{2}O\textsubscript{2} morphology, but also its electronic properties. Radin et al. integrated a DFT simulation of Li\textsubscript{2}O\textsubscript{2} with charge carrying dopants into a simple Nernst-Planck continuum model to study
ways to promote the OER [214]. They found that dopants like Co and Ni could enhance the OER and improve the rechargeability of non-aqueous LABs.

Applying continuum modeling methods to both aqueous and non-aqueous LAB development has illuminated the challenges and the opportunities inherent to these systems. Further research is needed into the effects of solid precipitation and oxygen transport in non-aqueous LABs and the long-term electrolyte stability of aqueous LABs. But the modeling studies highlighted above have shown promising paths for further investigation.

3.4 Summary

A variety of modeling and simulation methods can be applied to aid the development of zinc-air and other metal-air battery systems. While many metal-air systems are currently under development, Li-air batteries (LABs) and Zn-air batteries (ZABs) are the most promising systems [54].

On the material level, density functional theory (DFT) can be applied to investigate the electronic properties of catalysts and metals. This could help to screen new catalysts for properties like activity, stability, and selectivity and to elucidate the effect of surface structures on metal dissolution and deposition. Furthermore, equilibrium thermodynamic models can be used to predict the speciation of electrolytes and the solubility of precipitants. This can help determine not only the state of the electrolyte for different pH and concentration mixtures, but also its stability within the electrochemical window of the cell.

When it comes to electrode design, one challenge is to develop a bi-functional air electrode (BAE) that maintains an optimum level of saturation (neither flooding nor drying out) during battery operation. Lattice-Boltzmann-Methods (LBM) can be developed to investigate the pressure-saturation characteristics of real BAE structures in 2D or 3D.

Physics-based continuum modeling is the most useful and widely-utilized method for simulating the cell-level performance of metal-air batteries. Models constructed with this method are able to give researchers insight into a range of phenomena including the coupled effects of electrolyte concentrations, precipitation of solids, electrode kinetics, and cell voltage. The versatility of continuum modeling and the wide array of existing literature on the subject make it a good tool to advance the development of metal-air batteries.
Numerical modeling and simulation studies have shown that the performance LABs with non-aqueous electrolytes is encouraging but limited by slow oxygen transport and pore blockage by Li$_2$O$_2$. DFT simulations have been applied to elucidate the electronic structure and reaction mechanisms of Li$_2$O$_2$ and investigate possible alternative non-aqueous electrolyte solvents. Continuum models have highlighted the cell-level effects of Li$_2$O$_2$ precipitation and O$_2$ transport. The nucleation and growth of Li$_2$O$_2$ particles and films and its effect on the reversibility and performance of non-alkaline LABs is a major topic of research. Aqueous LABs improve oxygen transport in the air electrode and facilitate more favorable precipitation, but the long-term stability of the electrolyte is limited when exposed to CO$_2$. Continuum models developed for aqueous LABs have provided a framework for integrating the multi-phase flow in the air electrode into models of other metal-air systems.

ZABs stand alone as the only successfully commercialized primary metal-air system so far. Modeling studies of these systems highlight the performance of the alkaline electrolyte in air, passivation and shape change of the Zn electrode, and cell-level engineering. Because of its historical dominance, there is a long history of Zn-air continuum models, going back to the 1980s. Implementing these modeling tools in the design process brings researchers closer to the goal of building high-performance and electrically rechargeable zinc-air batteries [54].
4 Quasi-Particle Continuum Modeling Framework

Traditional continuum models offer a very effective way to simulate the behavior of aqueous electrolytes with a moderate quantity of solute species and source terms that are driven mainly by heterogeneous (electro)chemical reactions (e.g. charge-transfer or chemical precipitation reactions). But in cases where homogeneous electrolyte reactions rapidly change the concentrations of solute species by orders-of-magnitude (e.g. metal complex formation or weak acid (de)protonation), solutions to the mass and charge continuity equations become unstable and computationally expensive [36, 237]. A new approach is needed to open such systems to reliable and computationally cost-effective simulations.

In this section, I derive a new framework for the continuum modeling of aqueous electrolytes. Beginning with an understanding of the thermodynamic equilibrium in the electrolyte, I identify the minimum number of concentrations required to describe the state of the system. I then define a set of quasi-particles to express those concentrations in terms of the quantities of mass and charge that are conserved in the homogeneous electrolyte reactions. In this way, the equations required to describe the system are simplified and the computational effort to obtain a solution is significantly improved.

4.1 General Form

As discussed in the previous chapter, the concentrations of aqueous metal complexes is rather stable for strongly alkaline or acidic pH values, but can swing by orders-of-magnitude in the weakly acidic to weakly alkaline regime [311]. These concentration swings are driven by the homogeneous reactions in the electrolyte. For example, the homogeneous reactions in a simplified aqueous zinc electrolyte are listed in Table 4.1. In this section, I discuss in general terms how quasi-particles
4 Quasi-Particle Continuum Modeling Framework

Table 4.1: Homogeneous electrolyte reactions in the KOH–ZnO–H₂O system [311, 248, 55, 56]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\log_{10} \beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$</td>
<td>13.96</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + \text{OH}^- \rightleftharpoons \text{Zn(OH)}^+$</td>
<td>6.31</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 2 \text{OH}^- \rightleftharpoons \text{Zn(OH)}_2$</td>
<td>11.19</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 3 \text{OH}^- \rightleftharpoons \text{Zn(OH)}_3^-$</td>
<td>14.31</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 4 \text{OH}^- \rightleftharpoons \text{Zn(OH)}_4^{2-}$</td>
<td>17.70</td>
</tr>
</tbody>
</table>

can be defined to incorporate such reactions into an efficient continuum modeling framework. The special forms for zinc electrolytes are defined later in the chapter.

4.1.1 Definitions

The quasi-particles are specified to represent the quantities of mass and charge that are conserved in the homogeneous electrolyte reactions. The concentrations of the quasi-particles are defined in terms of their constituent components,

$$c_q = \sum_i \tau_{i,q} c_{i,q},$$  \hspace{1cm} (4.1)

where $\tau_{i,q}$ describes the stoichiometry of solute $i$ in quasi-particle $q$. The solute source term attributable to the homogeneous reactions is defined as

$$s^h_i = \sum_r k^h_r \nu_{i,r},$$  \hspace{1cm} (4.2)

where $k^h_r$ is the rate of the homogeneous reaction $r$ and $\nu_{i,r}$ is the stoichiometric coefficient of solute $i$ in homogeneous reaction $r$. Using the stoichiometric coefficient for the quasi-particle ($\tau_{i,q}$), the solute source term is converted into a source term for the quasi-particles,

$$s^h_q = \sum_{i,r} k^h_r \nu_{i,r} \tau_{i,q}.$$  \hspace{1cm} (4.3)
By demanding that the relation \( \sum_i \nu_{i,r} \tau_{i,q} = 0 \) holds, it is apparent that for any value of \( k^h_r \), the quasi-particle source term due to the homogeneous reactions is zero:

\[
\dot{s}^h_q = 0. \tag{4.4}
\]

Thus, the homogeneous reactions do not contribute to the quasi-particle source term.

Mathematically speaking, the quasi-particles are defined such that the vectors \( \vec{\tau}_i = \sum_q \tau_{i,q} \vec{e}_q \) span the kernel of the matrix \( \nu^T \). Considering that the electrolyte is locally charge-neutral, the number of quasi-particles needed to describe the system \( n_q \) is one less than the difference of the number of solutes \( n_s \) and the number of homogeneous reactions \( n_h \),

\[
n_q = n_s - n_h - 1. \]

By assuming that the kinetics of the homogeneous electrolyte reactions are fast, the concentrations of all the individual solutes are calculated from a few quasi-particle concentrations.

### 4.1.2 Source Terms

Because the quasi-particles represent quantities that are conserved in the homogeneous electrolyte reactions, only the heterogeneous (electro)chemical reactions contribute to the quasi-particle source terms [53].

The kinetics of the electrochemical reactions are described by the Butler-Volmer approximation,

\[
k_e = k_0 \left( \exp \left[ \frac{\alpha RT}{nF} \eta \right] - \exp \left[ - \frac{(1 - \alpha) RT}{nF} \eta \right] \right), \tag{4.5}
\]

where \( k_0 \) is the rate constant (linked to the exchange current density), \( \alpha \) is the symmetry factor, \( \eta \) is the surface overpotential, and the other variables take on their usual meaning.

The kinetics of the precipitation reactions are assumed to be diffusion-limited, and are described by the equation:

\[
k_p = \frac{D}{\delta} \frac{[Zn^{2+}] - [Zn^{2+}]_{sat}}{[Zn^{2+}]_0}. \tag{4.6}
\]

The source term for quasi-particle \( q \) due to all heterogeneous (electro)chemical
reactions \( r \) is given by,
\[
\dot{s}_q = \sum_r \sum_i \tau_{i,q} \nu_{i,r} k_r A_{r}^{sp}.
\] (4.7)

The specific surface area available for the reaction, \( A_{r}^{sp} \), is fixed for the air-electrode electrochemical reaction (given by the active area of the catalyst) and is calculated for all other reactions as:
\[
A_{r}^{sp} = \frac{6}{a_0} (\varepsilon_s (1 - \varepsilon_s)),
\] (4.8)
where \( \varepsilon_s \) is the appropriate solid volume fraction, and \( a_0 \) is the diameter of the solid phase pores.

Table 4.2: Kinetic parameters for the electrochemical reactions [64, 118].

<table>
<thead>
<tr>
<th>Parameter ( k_{0}^{Zn} )</th>
<th>Alkaline Media</th>
<th>Near-Neutral Media</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_{Zn} )</td>
<td>5 \times 10^{-8}</td>
<td>8 \times 10^{-6}</td>
<td>mol \cdot m^{-2} \cdot s^{-1}</td>
</tr>
<tr>
<td>( \alpha_{Zn}^{c} )</td>
<td>0.5</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>( A_{Zn}^{sp} )</td>
<td></td>
<td>( f(\varepsilon_{Zn}) )</td>
<td>m^{-2} \cdot m^{-3}</td>
</tr>
<tr>
<td>( k_{0}^{GDE} )</td>
<td>1 \times 10^{-11}</td>
<td>4 \times 10^{-10}</td>
<td>mol \cdot m^{-2} \cdot s^{-1}</td>
</tr>
<tr>
<td>( \alpha_{GDE} )</td>
<td>0.5</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>( \alpha_{GDE}^{c} )</td>
<td>0.5</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>( A_{GDE}^{sp} )</td>
<td>4.5 \times 10^{3}</td>
<td>4.5 \times 10^{3}</td>
<td>m^{-2} \cdot m^{-3}</td>
</tr>
</tbody>
</table>

4.1.3 Transport

There are two types of mass flux that can contribute to transport in metal-air batteries: diffusion-migration flux, \( \vec{N}^{DM}_q \), and convective flux, \( \vec{N}^{C}_q \) [54]. The diffusion-migration flux of the quasi-particles is given as,
\[
\vec{N}^{DM}_q = \sum_i \tau_{i,q} \vec{N}^{DM}_i = c^\beta_e \sum_i (\tau_{i,q} D_i \vec{\nabla} c_i) + \sum_i (\tau_{i,q} \frac{t_i}{z_i F} \vec{j}).
\] (4.9)

The electrolyte current density, \( \vec{j} \), is given by,
\[
\vec{j} = \varepsilon_e \beta_e \vec{\nabla} \phi_e - \sum_i \frac{k t_i}{z_i F} \frac{\partial \mu_i}{\partial \vec{c}_i} \vec{\nabla} c_i,
\] (4.10)
where $\varepsilon_e$ is the electrolyte volume fraction, $\tilde{\beta}$ is the Bruggeman coefficient, $t_i$ is the transference number and $z_i$ is the charge number of the solute species, $\kappa$ is the electrolyte conductivity, $\phi_e$ is the electrolyte potential, and $\mu_i$ is the chemical potential of the solute species.

The convective flux is given by,

$$\vec{N}_q^C = \varepsilon_e \tilde{\beta} c_i \vec{v}_e,$$

(4.11)

where $\vec{v}_e$ is the mass-average velocity of the electrolyte, which is calculated using a Darcy approach:

$$\vec{v}_e = -\frac{B_e}{\tilde{\mu} e} \nabla p_e.$$  

(4.12)

$\tilde{\mu}_e$ is the viscosity of the electolyte. The pressure in the electrolyte is calculated as described in existing works [194, 115, 253, 53]. The equation of state for the electrolyte is,

$$\sum_i V_i c_i = 1,$$

(4.13)

where $V_i$ is the partial molar volume of the species $i$, and is defined as a material parameter. The link between electrolyte volume fraction and pressure is given through a Leverett-approach. I define the electrolyte saturation of the porous phase as,

$$\tilde{s} = \frac{\varepsilon_e}{1 - \varepsilon_a}.$$  

(4.14)

The capillary pressure is then defined according to the Leverett function,

$$p_c = p_g - p_e = J(\tilde{s}).$$  

(4.15)

The dimensionless Leverett function is used to model the pressure saturation characteristics of the porous media. This function takes the form

$$J(\tilde{s}) = A + B e^{C(s-0.5)} - D e^{-E(s-0.5)} = \frac{p_c}{\sigma} \sqrt{\frac{B_0}{\varepsilon_0}},$$  

(4.16)

where $p_c$ is the capillary pressure, $\sigma$ is the surface tension of the electrolyte, $B_0$ is the permeability, and $\varepsilon_0$ is the porosity of the air electrode. The coefficients of the Leverett function, listed in Table 4.3, were determined using a Lattice Boltzmann simulation of a reconstructed GDE structure [60]. I assume that the gas pressure is constant. For more information, please refer to existing works in the literature [194, 115, 253].
Table 4.3: Leverett function parameters.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.1872</td>
</tr>
<tr>
<td>B</td>
<td>0.02523</td>
</tr>
<tr>
<td>C</td>
<td>8.707</td>
</tr>
<tr>
<td>D</td>
<td>0.09515</td>
</tr>
<tr>
<td>E</td>
<td>5.622</td>
</tr>
</tbody>
</table>

4.1.4 Continuity Equations

Considering the quasi-particle definitions, source terms, and transport equations derived above, the equations for mass and charge continuity are

\[
\frac{\partial (c_q \varepsilon_e)}{\partial t} = -\nabla \cdot N^D_M - \nabla \cdot N^C_q + s_q
\] (4.17)

\[
0 = -\nabla \cdot j + \sum_{i} z_i F \nu_{i,e} k_e A_{sp}^e, \tag{4.18}
\]

where \( \nu_{i,e} \) is the stoichiometric coefficient of solute \( i \) in the electrochemical reaction \( e \).

The quasi-particle formulation offers a simple method for modeling a series of coupled chemical reactions, taking advantage of the conservation of atom numbers and charge. In the following section, I expand upon these definitions to create a special quasi-particle description of aqueous zinc electrolytes.

4.2 Special Form for Aqueous Zinc Electrolytes

Later in this dissertation, simulations of ZABs with various electrolyte compositions are presented. These electrolytes include the industry standard KOH—ZnO—H\(_2\)O, LeClanché electrolyte ZnCl\(_2\)—NH\(_4\)Cl—NH\(_4\)OH—H\(_2\)O, and a new class of aqueous organic electrolytes - including carboxylic acids (e.g. citric acid) and amino acids (e.g. glycine) - which were invented over the course of this dissertation. To show how the quasi-particle method of continuum modeling is applied to aqueous ZABs, I start with the simplest electrolyte composition (KOH—ZnO—H\(_2\)O) and demonstrate how that foundation is expanded to model more complex systems.
4.2.1 Alkaline Electrolytes

To obtain a generalized form of the quasi-particle framework, I first consider a simple aqueous electrolyte composed of KOH–ZnO–H₂O [56]. The electrolyte contains the elementary species K⁺, OH⁻, H⁺, Zn²⁺, and complexes formed between Zn²⁺ and OH⁻. The homogeneous reactions of the system are listed in Table 4.1.

There are a total of 8 solutes (K⁺, OH⁻, H⁺, Zn²⁺, Zn(OH)⁺, Zn(OH)₂, Zn(OH)₃⁻, and Zn(OH)₄²⁻) and 5 homogeneous reaction equations. The total number of quasi-particles required to describe the system is one less than the difference between the number of solutes and the number of homogeneous electrolyte reactions, 

\[ n_q = n_s - n_{hr} - 1 = 2 \]

In this case, the state of the system can be described by the concentration of Zn²⁺ and the pH, and two quasi-particles, \( \sim Zn \) and \( \sim HOH \), are needed. \( \sim Zn \) is defined as the sum of all Zn²⁺ (both free and complexed) and \( \sim HOH \) is the sum of all H⁺ less the sum of all OH⁻ in the solution. Mathematically, this is expressed as:

\[
\begin{align*}
[\sim Zn] &= [Zn^{2+}] + \sum_{i=1}^{4} [Zn(OH)_{i-1}^2] \\
[\sim HOH] &= [H^+] - \left( [OH^-] + \sum_{i=1}^{4} i[Zn(OH)_{i-1}^2] \right).
\end{align*}
\]  

(4.19)  
(4.20)

The conservation of mass and charge in the system are:

\[
\begin{align*}
[Zn]_T &= [\sim Zn] \\
[K]_T &= -2[\sim Zn] - [\sim HOH].
\end{align*}
\]  

(4.21)  
(4.22)

This is the simplest form of the quasi-particle description of aqueous zinc electrolytes, and it is sufficient to describe the standard alkaline KOH–ZnO–H₂O system. These definitions provide a foundation that can be expanded to model more complex systems [55].

I now add some generic weak acid HA, and an additional quasi-particle, \( \sim A \), is
4 Quasi-Particle Continuum Modeling Framework

Figure 4.1: Schematic depiction of the quasi-particle definitions in a simple alkaline zinc electrolyte. $\tilde{Zn}$ is defined as the sum of all the zinc atoms in the electrolyte, while $\tilde{HOH}$ is defined as the sum of all the $H^+$ in the electrolyte less the sum of all the $OH^-$. In this depiction, $Zn^{2+}$ is gray, $H^+$ is white, and $O^{2-}$ is red.

needed. With this extra component, the quasi-particle definitions become:

\[
\tilde{Zn} = [Zn^{2+}] + \sum_{i=1}^{4} [Zn(OH)_{i}^{2-j}] + \sum_{j} [Zn(A)_{j}^{2-j}] + \\
\sum_{k} \sum_{l} [Zn(OH)_{k}(A)_{l}^{2-(k+l)}],
\]

(4.23)

\[
\tilde{A} = [A^-] + [HA] + \sum_{j} j[Zn(A)_{j}^{2-j}] + \sum_{k} \sum_{l} l[Zn(OH)_{k}(A)_{l}^{2-(k+l)}],
\]

(4.24)

\[
\tilde{HOH} = \left( [H^+] + [HA] \right) - \left( [OH^-] + \sum_{i=1}^{4} i[Zn(OH)_{i}^{2-i}] + \\
\sum_{k} \sum_{l} k[Zn(OH)_{k}(A)_{l}^{2-(k+l)}] \right).
\]

(4.25)
The conservation of mass and charge in the system are:

\[ [\text{Zn}]_T = [\tilde{\text{Zn}}] \]  
\[ [\text{A}]_T = [\tilde{\text{A}}] \]  
\[ [\text{K}]_T = [\tilde{\text{A}}] - 2[\tilde{\text{Zn}}] - [\text{HOH}] . \]

These generic definitions assume a weak acid with a single proton and negatively-charged conjugate base. They can be easily modified to accommodate weak acids with other properties. Further components can be added to the electrolyte through the inclusion of additional quasi-particles [55, 56].

### 4.2.2 LeClanché Electrolytes

In the LeClanché zinc-air battery (L-ZAB) system, I consider 24 homogeneous reactions and 28 solute species [55]. Therefore, 3 quasi-particles are required. A list of the homogeneous reactions and corresponding equilibrium constants is given in the appendix. The transport parameters for the continuum model are listed in Table 4.4.

The concentrations of the quasi-particles are defined as the sum of their constituent components, weighted by the stoichiometric coefficient \( \tau_{i,q} \) for solute species \( i \) in quasi-particle \( q \). In this case, we make the following definitions:

\[
[\tilde{\text{Zn}}] = [\text{Zn}^{2+}] + \sum_{i=1}^{4} [\text{ZnCl}_{2-i}^{2-}] + [\text{ZnCl}_3\text{NH}_3] + [\text{ZnCl}(\text{NH}_3)_3] + \]
\[ \sum_{j=1}^{4} [\text{Zn}(\text{NH}_3)_j^{2+}] + \sum_{k=1}^{4} [\text{Zn}(\text{OH})_k^{2-k}] + \sum_{l=1}^{3} [\text{Zn}(\text{OH})(\text{NH}_3)_l^{1+}] + \]
\[ \sum_{m=1}^{2} [\text{Zn}(\text{OH})_2(\text{NH}_3)_m] + [\text{Zn}(\text{OH})_3\text{NH}_3] + [\text{ZnOHCl}] \quad (4.29) \]

\[
[\tilde{\text{NH}_3}] = [\text{NH}_3] + [\text{NH}_4^+] + [\text{ZnCl}_3\text{NH}_3] + 3[\text{ZnCl}(\text{NH}_3)_3] + \sum_{j=1}^{4} j[\text{Zn}(\text{NH}_3)_j^{2+}] + \]
\[ \sum_{l=1}^{3} l[\text{Zn}(\text{OH})(\text{NH}_3)_l^{1+}] + \sum_{m=1}^{2} m[\text{Zn}(\text{OH})_2(\text{NH}_3)_m] + [\text{Zn}(\text{OH})_3\text{NH}_3] \quad (4.30) \]
Table 4.4: Transport parameters of aqueous species [195, 241, 243, 242, 80, 18, 218, 263].

<table>
<thead>
<tr>
<th>Species</th>
<th>$M_i / g \cdot mol^{-1}$</th>
<th>$\bar{z}_i$</th>
<th>$D_i \times 10^9 / m^2 \cdot s^{-1}$</th>
<th>$\lambda_i \times 10^4 / S \cdot m^2 \cdot equiv^{-1}$</th>
<th>$V_i \times 10^6 / m^3 \cdot mol^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H^+$</td>
<td>1.0</td>
<td>+1</td>
<td>9.31</td>
<td>349.8</td>
<td>0</td>
</tr>
<tr>
<td>$OH^-$</td>
<td>17.0</td>
<td>-1</td>
<td>5.26</td>
<td>197.6</td>
<td>-4.18</td>
</tr>
<tr>
<td>$NH_4^+$</td>
<td>18</td>
<td>+1</td>
<td>1.95</td>
<td>73.4</td>
<td>18.13</td>
</tr>
<tr>
<td>$NH_3$</td>
<td>17</td>
<td>0</td>
<td>1.94</td>
<td>-</td>
<td>24.43</td>
</tr>
<tr>
<td>$Cl^-$</td>
<td>35.5</td>
<td>-1</td>
<td>2.03</td>
<td>76.34</td>
<td>17.79</td>
</tr>
<tr>
<td>$Zn^{2+}$</td>
<td>65.4</td>
<td>+2</td>
<td>0.71</td>
<td>53</td>
<td>-24.3</td>
</tr>
<tr>
<td>$O_2^{aq}$</td>
<td>32</td>
<td>0</td>
<td>1.5*</td>
<td>-</td>
<td>30.38</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>18</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>18</td>
</tr>
<tr>
<td>$ZnCl^+$</td>
<td>100.8</td>
<td>+1</td>
<td>1.10</td>
<td>35*</td>
<td>-1.28</td>
</tr>
<tr>
<td>$ZnCl_2$</td>
<td>136.3</td>
<td>0</td>
<td>1.10</td>
<td>-</td>
<td>24.82</td>
</tr>
<tr>
<td>$ZnCl_3^-$</td>
<td>171.7</td>
<td>-1</td>
<td>1.10</td>
<td>35</td>
<td>53.9</td>
</tr>
<tr>
<td>$ZnCl_4^{2-}$</td>
<td>207.2</td>
<td>-2</td>
<td>1.10</td>
<td>55</td>
<td>81*</td>
</tr>
<tr>
<td>$Zn(NH_3)^{2+}$</td>
<td>82.4</td>
<td>+2</td>
<td>1.12*</td>
<td>84.2*</td>
<td>7.5*</td>
</tr>
<tr>
<td>$Zn(NH_3)_{2/3}^{2+}$</td>
<td>99.4</td>
<td>+2</td>
<td>1.14*</td>
<td>85.7*</td>
<td>39.2*</td>
</tr>
<tr>
<td>$Zn(NH_3)_{3/2}^{2+}$</td>
<td>116.5</td>
<td>+2</td>
<td>1.09*</td>
<td>81.5*</td>
<td>70.9*</td>
</tr>
<tr>
<td>$Zn(NH_3)_4^{2+}$</td>
<td>133.5</td>
<td>+2</td>
<td>0.83*</td>
<td>62.7*</td>
<td>102.6*</td>
</tr>
<tr>
<td>$ZnCl_2(NH_3)^-$</td>
<td>188.8</td>
<td>-1</td>
<td>1.10*</td>
<td>41.3*</td>
<td>86.4*</td>
</tr>
<tr>
<td>$ZnCl(NH_3)_{3/2}^+$</td>
<td>151.9</td>
<td>+1</td>
<td>1.10*</td>
<td>41.3*</td>
<td>97.2*</td>
</tr>
<tr>
<td>$ZnOH(NH_3)^+$</td>
<td>99.4</td>
<td>+1</td>
<td>1.0*</td>
<td>50*</td>
<td>10*</td>
</tr>
<tr>
<td>$ZnOH(NH_3)_{2/3}^+$</td>
<td>116.4</td>
<td>+1</td>
<td>1.0*</td>
<td>50*</td>
<td>40*</td>
</tr>
<tr>
<td>$ZnOH(NH_3)_{3/2}^+$</td>
<td>133.4</td>
<td>+1</td>
<td>1.0*</td>
<td>50*</td>
<td>60*</td>
</tr>
<tr>
<td>$Zn(OH)_{2}(NH_3)$</td>
<td>116.4</td>
<td>0</td>
<td>1.0*</td>
<td>-</td>
<td>40*</td>
</tr>
<tr>
<td>$Zn(OH)<em>{2}(NH_3)</em>{2}$</td>
<td>133.4</td>
<td>0</td>
<td>1.0*</td>
<td>-</td>
<td>40*</td>
</tr>
<tr>
<td>$Zn(OH)_{3}(NH_3)^-$</td>
<td>113.4</td>
<td>-1</td>
<td>1.0*</td>
<td>30*</td>
<td>20*</td>
</tr>
<tr>
<td>$Zn(OH)Cl$</td>
<td>6.51</td>
<td>0</td>
<td>1.0*</td>
<td>-</td>
<td>1*</td>
</tr>
<tr>
<td>$Zn(OH)^+$</td>
<td>82.4</td>
<td>+1</td>
<td>0.50</td>
<td>90.35</td>
<td>1</td>
</tr>
<tr>
<td>$Zn(OH)_{2}$</td>
<td>99.4</td>
<td>0</td>
<td>0.50</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>$Zn(OH)_3^-$</td>
<td>116.4</td>
<td>-1</td>
<td>0.50</td>
<td>90.35</td>
<td>40</td>
</tr>
<tr>
<td>$Zn(OH)_{4}^{2-}$</td>
<td>133.4</td>
<td>-2</td>
<td>0.50</td>
<td>90.35</td>
<td>60</td>
</tr>
</tbody>
</table>

*Estimated
\[
\hat{\text{HOH}} = \left( [\text{H}^+] + [\text{NH}_4^+] + [\text{HCl}] \right) - \\
\left( [\text{OH}^-] + \sum_{k=1}^{4} k[\text{Zn(OH)}_{k}^{2-k}] + \sum_{l=1}^{3} [\text{Zn(OH)}(\text{NH}_3)_{l}^{1+}] + \sum_{m=1}^{2} 2[\text{Zn(OH)}_{2}(\text{NH}_3)_{m}] + \\
3[\text{Zn(OH)}_{3}\text{NH}_3] + [\text{ZnOHCl}] \right)
\] (4.31)

The conservations of mass and charge in this system are:

\[
[Zn]_T = [\hat{\text{Zn}}] \tag{4.32}
\]

\[
[\text{NH}_3]_T = [\hat{\text{NH}}_3] \tag{4.33}
\]

\[
[\text{Cl}]_T = 2[\hat{\text{Zn}}] + [\hat{\text{HOH}}]. \tag{4.34}
\]

These definitions are valid for the entire pH regime.

There is some flexibility in the definition of the quasi-particles for any given system. An alternative quasi-particle formulaulation LeClanché electrolytes in the acidic to near-neutral pH regime where the concentration of OH\(^{-}\) is very low and the formation of zinc-hydroxide complexes is negligible is as follows [53]:

\[
[\hat{\text{NH}}_3] = [\text{NH}_3] + \sum_{n=1}^{4} n[\text{Zn(NH}_3)_n^{2+}] + [\text{Zn(NH}_3)_3\text{Cl}_3^-] + 3[\text{Zn(NH}_3)_3\text{Cl}^+] - [\text{H}^+] + [\text{OH}^-], \tag{4.35}
\]

\[
[\hat{\text{Zn}}] = [\text{Zn}^{2+}] + \sum_{n=1}^{4} [\text{Zn(NH}_3)_n^{2+}] + \sum_{m=1}^{4} [\text{ZnCl}_{m}^{(2-m)}] + [\text{Zn(NH}_3)\text{Cl}_3^-] + [\text{Zn(NH}_3)_3\text{Cl}^+]. \tag{4.36}
\]

\[
[\hat{\text{NH}}_4] = [\text{NH}_4^+] + [\text{H}^+] - [\text{OH}^-]. \tag{4.37}
\]
4.2.3 Aqueous Organic Electrolytes

Here I consider an aqueous electrolyte consisting of a mixture of citric acid, glycine, and zinc oxide, with the pH adjusted through the addition of KOH [56]. A list of the homogeneous electrolyte reactions in this system and the corresponding equilibrium constants are given in the appendix. There are 21 total solutes and 16 homogeneous reactions; therefore, 4 quasi-particles are needed to describe the system.

Following the convention laid out in the general form, the quasi-particles are $\tilde{Zn}$, $\tilde{Cit}$, $\tilde{Gly}$, and $\tilde{HOH}$, and they are defined as:

\[
[\tilde{Zn}] = [Zn^{2+}] + \sum_{i=1}^{4} [Zn(OH)_i^{2-}] + [ZnHCit] + \sum_{j=1}^{2} [Zn(Cit)_j^{2-3j}] + \sum_{k=1}^{3} [Zn(Gly)_k^{2-k}], \quad (4.38)
\]

\[
[\tilde{Cit}] = [Cit^{3-}] + \sum_{l=1}^{3} [H_lCit^{(3-l)}] + [ZnHCit] + \sum_{j=1}^{2} [Zn(Cit)_j^{2-3j}], \quad (4.39)
\]

\[
[\tilde{Gly}] = [Gly^{-}] + \sum_{m=1}^{2} [H_mGly^{(1-m)}] + \sum_{k=1}^{3} [Zn(Gly)_k^{2-k}], \quad (4.40)
\]

\[
[\tilde{HOH}] = \left( [H^+] + \sum_{l=1}^{3} [H_lCit^{(3-l)}] + [ZnHCit] + \sum_{m=1}^{2} [H_mGly^{(1-m)}] \right) - \left( [OH^-] + \sum_{i=1}^{4} [Zn(OH)_i^{2-1}] \right). \quad (4.41)
\]

The conservations of mass and charge in this system are:

\[
[Zn]_T = [\tilde{Zn}] \quad (4.42)
\]

\[
[Cit]_T = [\tilde{Cit}] \quad (4.43)
\]

\[
[Gly]_T = [\tilde{Gly}] \quad (4.44)
\]

\[
[K]_T = -2[Zn] + 3[Cit] + [\tilde{Gly}] - [\tilde{HOH}]. \quad (4.45)
\]
Transport parameters used in the continuum model are listed in Table 4.5. Transport parameters of citric acid species are compiled by Apelblat [13]. Transport parameters for glycine are estimated according to those reported by Hamborg, et al. [98]. Other transport parameters have yet to be investigated in existing experimental studies, and are chosen to reflect the order of magnitude. Detailed experimental determination of these transport parameters could be a topic for further research [56].

4.2.4 Summary

This chapter describes the novel quasi-particle method of continuum modeling. The method simplifies the modeling of complex near-neutral aqueous electrolytes by defining a series of quasi-particles, which can be used to describe the thermodynamic equilibrium state of the electrolyte. The quasi-particles represent quantities of mass and charge that are conserved in the homogeneous electrolyte reactions. For the first time, this allows the thermodynamic chemical speciation of the electrolyte to be considered in a continuum model.

There is some flexibility in the quasi-particle definitions. This chapter presents three applied examples of the method: alkaline KOH, near-neutral ZnCl$_2$–NH$_4$Cl, and a novel aqueous electrolyte containing organic molecules. In the following chapters, these models are applied to simulate the performance of ZABs based on the various electrolyte compositions.
Table 4.5: Estimated transport parameters of aqueous citrate and glycine species.

<table>
<thead>
<tr>
<th>Species</th>
<th>$M_i$ / g · mol⁻¹</th>
<th>$z_i$ / -</th>
<th>$D_i \times 10^9$ / m² · s⁻¹</th>
<th>$\lambda_i \times 10^4$ / S · m² · equiv⁻¹</th>
<th>$V_i \times 10^6$ / m³ · mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_3$Cit</td>
<td>192.1</td>
<td>0</td>
<td>0.66</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>$H_2$Cit⁻</td>
<td>191.1</td>
<td>-1</td>
<td>0.81</td>
<td>35.87</td>
<td>100</td>
</tr>
<tr>
<td>HCit²⁻</td>
<td>190.1</td>
<td>-2</td>
<td>0.81</td>
<td>50.38</td>
<td>100</td>
</tr>
<tr>
<td>Cit³⁻</td>
<td>189.1</td>
<td>-3</td>
<td>0.76</td>
<td>72.05</td>
<td>100</td>
</tr>
<tr>
<td>$H_2$Gly⁺</td>
<td>76.1</td>
<td>+1</td>
<td>1.11</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>HGly</td>
<td>75.1</td>
<td>0</td>
<td>1.11</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>Gly⁻</td>
<td>74.1</td>
<td>-1</td>
<td>1.11</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>ZnHCit</td>
<td>254.5</td>
<td>0</td>
<td>0.2</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>ZnCit⁻</td>
<td>253.5</td>
<td>-1</td>
<td>0.2</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>ZnCit₂⁴⁻</td>
<td>442.6</td>
<td>-4</td>
<td>0.2</td>
<td>80</td>
<td>150</td>
</tr>
<tr>
<td>ZnGly⁺</td>
<td>139.4</td>
<td>+1</td>
<td>0.5</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>ZnGly₂</td>
<td>213.5</td>
<td>0</td>
<td>0.5</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>ZnGly₃⁻</td>
<td>287.6</td>
<td>-1</td>
<td>0.5</td>
<td>30</td>
<td>40</td>
</tr>
</tbody>
</table>
5 Alkaline Zinc-Air Battery Simulations

In this chapter, I apply the modeling methods discussed previously to simulate the equilibrium characteristics and dynamic performance of state-of-the-art alkaline ZABs.

I begin by simulating the thermodynamic properties of alkaline ZABs and introduce concepts like the speciation of the zinc ion and the solubility of zinc solids that will be important when we move on to near-neutral and next-generation electrolytes. I then simulate the galvanostatic operation of alkaline ZABs, conduct an optimization of the Zn electrode design, and show how these simulations can be applied to support experimental design. Finally, I perform a feasibility study of alkaline ZABs for stationary energy applications using real data from a PV power plant in Spain (generously provided by our ZAS! project partner Abengoa).

Applying both 0D thermodynamic equilibrium models and the novel 1D cell-level continuum models derived in the previous chapter, I establish the performance characteristics of alkaline ZABs. There is no shortage of both experimental and model-based studies of alkaline ZABs in the literature, and they offer a good opportunity to establish a foundation for the more advanced simulations to come.

5.1 Electrolyte Thermodynamics

To understand the overall performance of ZABs it is helpful to first look to the thermodynamics of the system: the speciation of the Zn$^{2+}$ ion, the solubility of zinc precipitates, and the equilibrium redox potentials of the various electrochemical cell reactions.

Figure 5.1 shows the simplified speciation diagram for the Zn$^{2+}$ ion in aqueous solution as a function of pH. As discussed in Chapter 3, the stability of the various zinc
complexes is governed by both the concentrations of species in the solution, and the thermodynamic formation constant of the complex (an expression of the Gibbs free energy). For low pH values, the solution is dominated by solvated Zn$^{2+}$. When the solution approaches pH-neutral values, more OH$^{-}$ is available to form complexes and Zn(OH)$^{+}$ dominates the solution. As the pH becomes more alkaline, the zinc complex passes through various degrees of coordination (Zn(OH)$_2$ and Zn(OH)$_3$), until the electrolyte is dominated by the zincate species (Zn(OH)$_4^{2-}$) for strongly alkaline pH values. The thermodynamics of these simple aqueous zinc solutions are extensively discussed in the literature [195, 311]. Although this behavior may seem trivial it demonstrates a significant characteristic of Zn$^{2+}$ in aqueous solutions: by complexing with OH$^{-}$, it has the potential to act as a pH-buffer in the near-neutral to alkaline range. This will become important when we expand or analysis to near-neutral electrolytes in the coming chapters.

The equilibrium composition of the electrolyte is determined not only by the speciation of the Zn$^{2+}$ ion but also by the solubility of various zinc solids which may precipitate from the solution.

Figure 5.2 shows a 2D thermodynamic landscape of the KOH–ZnO–H$_2$O system, as a function of pH and total aqueous zinc concentration, [Zn]$_T$. The colored regions indicate the dominant aqueous zinc species (e.g. Zn(OH)$_4^{2-}$, Zn(OH)$_3^-$, etc.), the solid colored lines indicate the solubility limits of ZnO and Zn(OH)$_2$ in the electrolyte, and the gray lines show paths of constant K$^+$ concentration (which indicate paths the electrolyte would follow as the cell is discharged or charged, according to increases or decreases in the total aqueous zinc concentration). Creating diagrams like this
allows us to know the equilibrium composition of various electrolyte recipes and predict how the composition will shift during ZAB operation.

For example, a standard alkaline ZAB electrolyte might have a pH of 14.8 and a total zinc concentration of 0.5 M. Locating this position on the diagram, we see that the dominant zinc species is Zn(OH)$_4^{2-}$ and it is very close to the solubility limit of ZnO. Following the gray path of constant K$^+$ concentration, we see that during discharging (when [Zn]$^+$ rises), the electrolyte crosses the solubility limits of ZnO and Zn(OH)$_2$ and these solids would precipitate. On the other hand, during charging, the values of [Zn]$^+$ drops and the precipitated ZnO and Zn(OH)$_2$ phases would dissolve. In this way we can predict the general behavior of the electrolyte before performing dynamic simulations.

Finally, with information about the Zn$^{2+}$ speciation and ZnO and Zn(OH)$_2$ solubility known, we can extend the analysis to include the equilibrium redox potentials of the electrochemical reactions.

Figure 5.3 shows the Pourbaix diagram of the KOH−ZnO−H$_2$O system. The colored regions indicate the dominant state of zinc in the system; the lines show the
Figure 5.3: Pourbaix diagram for the simplified aqueous ZAB system.

equilibrium redox potentials for the various electrochemical reactions that may occur. In aqueous alkaline ZABs, there are three important electrochemical reactions: the ORR/OER, the HER, and the electro-dissolution/deposition of Zn.

The diagram shows that while the potentials of the oxygen and hydrogen electrodes vary linearly with pH, the potential of the Zn electrode is non-linear in the pH domain. This is determined by the shifting concentration of non-complexed Zn\(^{2+}\) in the electrolyte as the dominant complex transitions from Zn(OH)\(^+\) to Zn(OH)\(^{2-}\). Another important aspect of this diagram is that the potential of the zinc electrode is always below the potential of the hydrogen electrode, indicating the metallic Zn is thermodynamically unstable in water. This is a known effect, and the evolution of H\(_2\) gas can be kinetically suppressed by doping the surface of the Zn metal with Hg, In, or Bi.

Additionally, the Pourbaix diagram gives an indication of the expected open-circuit voltage of the cell. Comparing the potential difference between the oxygen and zinc electrodes, we would expect the OCV for alkaline (1.62 V) or acidic pH values (1.93 V) to be higher than the OCV for neutral pH values (1.58 V).

It is important to note that these diagrams give information about the thermodynamics of the system, assuming equilibrium. In a real cell, the kinetics of the various reactions and mass transport play an important role and cause the behavior to deviate from predictions based exclusively on thermodynamics. This is discussed in
5.2 Cell-Level Simulations

In this section, I apply the quasi-particle method of continuum modeling to simulate the dynamic performance of alkaline ZAB cells. An overview of the parameterization and computational details used in the models is given in the appendix.

5.2.1 Computational Domain

Figure 5.4 shows the computational domain of the ZAB model and the initial volume fractions of the various components. For the purpose of these simulations, I consider a cell architecture based on a button cell with a Zn paste electrode.

The left side of the domain (corresponding to $x = 0\text{mm}$) contains an expansion zone to accommodate the electrolyte (dark blue) pushed out of the Zn electrode.
5 Alkaline Zinc-Air Battery Simulations

Figure 5.5: Electrolyte concentration and volume fraction profiles for a ZAB discharged at 20 mA cm$^{-2}$ at (a) 20% DoD and (b) 100% DoD.

as ZnO precipitates. Next comes the Zn electrode (gray), contained by two porous separators (black), and the air-electrode (black) at the right of the domain ($x = 6$ mm). The cell depicted in the figure contains a Zn electrode that is 4 mm thick and containing a paste that is 35 vol% Zn particles and 5 vol% ZnO. This is a starting point for the simulations. The exact dimensions and composition of the Zn electrode will be adjusted in the section on cell optimization.

5.2.2 Galvanostatic Discharge

Figure 5.5 shows the concentrations of electrolyte species and volume fraction profiles in a ZAB cell discharged at 20 mA cm$^{-2}$ to a cutoff voltage of 1 V. The profiles are shown at (a-b) 20% DoD and (c-d) 100% DoD.

When the ZAB is discharged, the pH in the air electrode rises as OH$^-$ is produced from the ORR (Figure 5.5a). On the other side, the pH in the Zn electrode falls as free OH$^-$ is consumed to form Zn(OH)$_4^{2-}$ complexes with the new Zn$^{2+}$ ions produced from the electro-oxidation of the zinc metal electrode. The resulting concen-
tration and electric potential gradients in the electrolyte drive a diffusion-migration flux of OH\(^-\) from the air electrode towards the Zn electrode. But for the OH\(^-\) to reach the electrode surface, it must first diffuse across the porous ZnO film. For shallow DoDs and low current densities, the difference between bulk and surface OH\(^-\) concentration is small because the ZnO film is still rather thin (Figure 5.5b).

Although the Zn electrode initially contains 5 vol% of ZnO evenly distributed throughout the electrode, Figure 5.5b shows that the ZnO profile begins to become inhomogeneous as the cell is discharged. Starting at the interface to the separator/air electrode (ca. \(x = 5.5\) mm), we see that the ZnO volume fraction is reduced at the separator, peaks shortly thereafter (\(x = 5\) mm), and tapers off towards the back of the Zn electrode (\(x = 1.7\) mm). Figure 5.2 helps to understand this behavior.

Figure 5.2 shows that when the pH increases, the solubility of zinc in the electrolyte can significantly increase (even so much as double). The pH increase in the air electrode due to the ORR also raises the pH in the front of the Zn electrode (Figure 5.5a). Therefore, even though the concentration of Zn(OH)\(_4\)^{2-} in the front of the Zn electrode is high, there is actually a tendency for ZnO to dissolve rather than precipitate. But as we move deeper into the Zn electrode, the pH value falls and the excess Zn(OH)\(_4\)^{2-} precipitates out of the solution.

At the end of discharge (Figure 5.5c-d), the precipitated ZnO layer becomes so thick that it creates a significant mass-transport barrier between the electrode surface and the bulk electrolyte. As a result, the concentration of OH\(^-\) at the Zn electrode surface rapidly falls and electrode passivation sets in. Again, we see that the ZnO at the front of the Zn electrode dissolves due to the high pH in the air electrode and peaks about 1 mm back from the interface.

The passivation of the Zn electrode due to ZnO precipitation is strongly influenced by the design of the electrode and the applied current density.

Figure 5.6 shows the cell voltage profiles for a ZAB discharged at current densities ranging from 1 to 50 mA cm\(^{-2}\). The results show that the cell can be discharged at rates up to about 20 mA cm\(^{-2}\) with only minimal capacity loss. However, as current density increases, the cell can see up to a 20% loss in capacity due to the passivation of the Zn electrode. Therefore when designing a ZAB for a given application, care should be taken to optimize the design of the Zn electrode to avoid passivation.
5.2.3 Zinc Electrode Optimization

The design of the Zn electrode is one of the most important properties governing ZAB performance and lifetime. In this analysis, I optimize the thickness and volume fraction of the zinc electrode to maximize the capacity of the cell while avoiding the unwanted effects of passivation [54]. The initial composition of the electrolyte is 7M KOH, saturated with ZnO. The BAE and separator are both 0.5 mm in length and the Zn electrode is varied. The cell is galvanostatically discharged at current densities ranging from 0.1 to 50 mA·cm$^{-2}$.

Figure 5.7(a) shows the magnitude of the KOH concentration drop across the cell at the end of charging. As the thickness of the Zn electrode and the magnitude of the current density increase, the long transport paths and large source terms induce significant concentration gradients in the cell. This is important because KOH gradients can affect the solubility of ZnO and increase the risk of passivation in the Zn electrode.

Figure 5.7(b) presents the utilization of zinc metal in the battery. The results show that for current densities less than circa 20 mA·cm$^{-2}$, the active Zn in the electrode is essentially completely utilized (over 90%) for all Zn electrode thicknesses. But for higher current densities, passivation of the electrode occurs due to two compet-
Figure 5.7: (a) Magnitude of the KOH concentration gradient across the cell at the end of discharge, (b) Zn utilization, and (c) discharged capacity as a function of Zn electrode thickness and current density. Zn volume fraction is constant 0.35. Reproduced from Ref. [54] with permission from MDPI.

...ing factors. The ZnO that precipitates in the electrode acts as a barrier to mass transport. For thick Zn electrodes, this barrier to transport is so large that the bulk concentration of KOH in the Zn electrode drops to the point that there is insufficient hydroxide present to form Zn(OH)$_2^-$ complexes, and Zn utilization drops to circa 50%. For thin electrodes, the ZnO transport barrier remains relatively small and the bulk KOH concentration remains in an acceptable range. However, in these electrodes there is less active surface area available for the reaction, which leads to a higher flux term at the surface of the Zn particles. For current densities over 30 mA cm$^{-2}$ and electrodes less than 2 mm, the magnitude of the flux term is large enough to locally deplete OH$^-$ at the electrode surface and passivate the electrode. The Zn utilization drops to circa 80%.

Figure 5.7(c) shows the discharged capacity of the battery. Increasing the thickness of the Zn electrode increases the amount of active material in the cell and the theoretically achievable capacity. However, the passivation of thick electrodes at higher current densities limits the amount of Zn that can be utilized, as shown in the previous figure. The result is that a battery with a 5 mm Zn electrode discharged at 10 mA cm$^{-2}$ has roughly the same capacity as a battery with a 10 mm Zn electrode discharged at 50 mA cm$^{-2}$.

The design of the Zn electrode is also affected by the volume fraction of Zn metal in the paste. Figure 5.8 shows the same ZAB performance metrics for Zn volume fractions ranging from 0.1 to 0.5 at current densities between 0.1 - 50 mA cm$^{-2}$. The thickness of the Zn electrode is kept constant at 4 mm.
5 Alkaline Zinc-Air Battery Simulations

Figure 5.8: (a) Magnitude of the KOH concentration gradient across the cell at the end of discharge, (b) Zn utilization, and (c) discharged capacity as a function of Zn volume fraction and current density. Zn electrode thickness is constant 4 mm.

For electrodes with very low Zn volume fractions (e.g. 0.1), there is good electrolyte transport and the Zn utilization is high, but the overall capacity of the cell is very low owing to the absence of active material. As the Zn volume fraction increases, the capacity of the cell rises but the electrolyte transport and Zn utilization become increasingly limited. These limitations are strongest for Zn volume fractions of 0.5, where full Zn utilization is only possible at low current densities.

Figure 5.8c shows an interesting feature. The practical capacity of the cell peaks as a function of Zn volume fraction. For example a cell that is discharged at very low current densities achieves its highest practical capacity with a Zn volume fraction of 0.5. For a ZAB discharged at 25 mA cm$^{-2}$, the peak occurs with a volume fraction of 0.4, which drops further to about 0.35 for 50 mA cm$^{-2}$.

The main finding of this analysis is that Zn electrodes can be designed for either high power (e.g. a 2 mm electrode that retains 90% Zn utilization at 50 mA cm$^{-2}$) or high energy (e.g. a 10 mm electrode with a capacity of nearly 2 Ah cm$^{-2}$ at 10 mA cm$^{-2}$), but it is not trivial to design an electrode that is both.

When designing an alkaline ZAB, care should be taken to size the Zn electrode considering the current requirement and the desired capacity. With this information, an informed decision can be taken regarding how much Zn paste should be included in the battery to obtain the optimum performance.
5 Alkaline Zinc-Air Battery Simulations

Figure 5.9: (a) Time required to cycle a ZAB 200 times for various Zn electrode thickness and current density combinations, (b) passivation time, and (c) operational window for a model ZAB. Reproduced from Ref. [54] with permission from MDPI.

5.2.4 Experiment Design

Simulations like those described above help to understand ZAB performance and suggest directions for further development, but experimental research is essential to developing functional and feasible batteries. Model-based engineering can also be applied in the testing phase of development to design experiments with the highest chance of success.

Zn electrodes have a very high capacity and can only be discharged at limited rates. Therefore, it takes a very long time to experimentally study their cycling characteristics. Often, the solution is to perform "accelerated" tests with smaller electrodes or at higher current densities, both of which increase the risk of irreversible passivation.

Consider the case in which a researcher wants to cycle a ZAB 200 times in less than 3 months. One cycle is defined as moving between 70% and 30% state-of-charge (SOC), and the electrode consists of a paste that is 50 vol% Zn and 50 vol% electrolyte. Figure 5.9(a) shows the time required to complete 200 cycles under these conditions for different combinations of current density and Zn electrode thickness.

Figure 5.9(b) shows the time required to passivate the Zn electrode. By comparing the passivation time with the cycling time and applying an engineering safety factor of 1.3, we can mark the passivation limitations of the system. This region is shaded in black in Figure 5.9(c). Combinations in the red zone of the figure exceed the time limitation, and we assume that electrodes smaller than 100 microns are impractical to manufacture (orange). With these factors in mind, we define a region of combinations (green) which could fit the researcher’s needs.
5.2.5 Stationary Energy Storage Feasibility

Continuum ZAB models are not only useful for the development of lab-scale cells, but can also be applied to study the feasibility of grid-scale storage systems. Stationary energy storage is one of the most promising applications for ZABs. In this analysis, I use real data from a PV power plant in Spain to simulate the cell-level performance of one cycle.

Figure 5.10 shows both the power produced by the PV plant and the load demand over the course of a single day. This plot clearly highlights one of the main challenges to the large-scale integration of renewable energy sources into the power grid: the demand for power remains high in the evening, but the PV plant only produces power during the day. To address this issue, energy storage is needed to shift the excess energy produced during the day to cover the load during the night.

One potential configuration for a load-shifting ZAB system was developed by the ZAS! project consortium. The ZAB system must be sized such that it can cover the load all night and efficiently store the surplus power produced during the day. The cell, module, and system properties of the proposed ZAB are listed in Table 5.1.

ZAB cycle limitations are often a function of depth-of-discharge (DoD), i.e. the
Table 5.1: Stationary ZAB module and cell properties

<table>
<thead>
<tr>
<th></th>
<th>Cell</th>
<th>Module</th>
<th>System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy (Wh)</td>
<td>172.8</td>
<td>8.64</td>
<td>4147.2</td>
</tr>
<tr>
<td>Power (W)</td>
<td>4.32</td>
<td>0.216</td>
<td>103.68</td>
</tr>
<tr>
<td>Nominal Voltage (V)</td>
<td>1.2</td>
<td>60</td>
<td>480</td>
</tr>
<tr>
<td>Maximum Current (A)</td>
<td>3.6</td>
<td>3.6</td>
<td>216</td>
</tr>
<tr>
<td>Zn Electrode Thickness (mm)</td>
<td>7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zn Volume Fraction</td>
<td>0.35</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

deeper the DoD the more severe the cell aging. Therefore, the overall system is sized such that the battery should only be cycled at about 20% of its capacity per day. Therefore, the cell should have a high capacity and be able to be cycled at moderate current densities. Reviewing the Zn electrode optimization in the previous section, an electrode that is 7 mm thick and 35 vol% Zn could meet these needs. With the parameters of the cell known, the cycling performance can be simulated.

Figure 5.11 shows the concentrations of OH\(^{-}\) in the electrolyte and volume fractions at the end of (a-b) discharging and (c-d) charging. The results show that the proposed cycling procedure is well within the limitations of the ZAB cell. The system is over-sized such that, even though the system level power is quite high, the power supplied by each individual ZAB cell is fairly mild.

There is good electrolyte transport in the cell. Figures 5.11(a) and (c) show that the maximum concentration gradient of OH\(^{-}\) in the bulk electrolyte is about 1 mol L\(^{-1}\) from one side of the cell to the other. Figure 5.11(b) shows that there is some inhomogeneity in the ZnO profile, as discussed previously. However, the discharged capacity is so small relative to the capacity of the cell, that this does not lead to any adverse passivation effects.

Figure 5.11(d) shows that when the cell is charged there is some minor re-distribution of material. There is some slight inhomogeneity in the ZnO profile and the electrodeposited Zn tends to gather at the front of the electrode. Again, the charge transferred relative to the battery capacity is so small that this re-distribution will not seriously affect the performance of the battery.

This analysis provides an example of how continuum models can be applied to aid the design of large projects and provide some insight into system performance prior to construction. In this case, the cycling loads are well within the limits of the proposed battery.
Modeling of both electrolyte materials and full cells helps to understand the fundamental process that govern ZAB performance and build better batteries.

0D thermodynamic models offer a quick and cost-effective way to study the state of the zinc ion and solubility of zinc oxides/hydroxides in aqueous electrolytes. The thoughtful application of these models can give some insight into the general trends of electrolyte behavior during full cell cycling. Furthermore, the construction of Pourbaix diagrams helps to identify optimum electrolyte compositions to facilitate the electrochemical performance of the cell and highlight possible challenges (like H₂ gas evolution). While these tools are very useful, it is important to remember that they make statements based on the thermodynamics of the system. In real cells, reaction kinetics and mass-transport limitations also strongly affect ZAB performance.

Cell-level continuum models provide an opportunity to simulate cell performance considering wide-ranging phenomena. The continuum simulations presented in section 5.2.2 elucidate some of the mechanisms behind ZAB limitations like Zn
5 Alkaline Zinc-Air Battery Simulations

electrode passivation and shape-change, and air electrode flooding and dry-out. The usefulness of these models extends beyond fundamental understanding to also address questions of cell design and optimization.

In the section 5.2.3, I show that the performance of the zinc electrode is determined by the electrode thickness, Zn volume fraction, and the applied current density. The results of the simulations show that Zn electrodes can be designed for either high power or high energy, but designing an electrode with both is non-trivial. In many cases, the Zn utilization and practical capacity of the cell become limited by Zn electrode passivation.

ZAB continuum models can be extended to investigate real-world questions like effective experiment design or proper sizing of grid-scale energy storage systems. In sections 5.2.4 and 5.2.5, I show examples of how these models can be applied to practical engineering challenges.

The simulations presented in this chapter utilize the novel quasi-particle method (QPM) of continuum modeling. The results are in agreement with existing models of alkaline ZABs [253], which supports the validity of the method. The QPM is not strictly necessary to model alkaline ZABs, but it greatly simplifies and improves the modeling of more complex systems that are investigated in the following chapters.

Cell optimization can only take the development of alkaline ZABs so far. To achieve the lifetimes necessary for electrically-rechargeable applications, the issue of electrolyte carbonation must be addressed. The use of aqueous near-neutral electrolytes has been suggested as one solution to this challenge.
6 LeClanchè Zinc-Air Battery Simulations

Aqueous electrolytes with near-neutral pH values have been proposed as one possible solution to the parasitic carbonation of alkaline ZABs [53, 55]. Recent attention in industry [7] and research [130, 92, 259] has focused on the so-called LeClanchè electrolyte (ZnCl$_2$–NH$_4$Cl). In spite of this interest, there are no modeling studies of zinc-air batteries with LeClanchè electrolytes prior to this work.

In this chapter, I simulate the performance of LeClanchè zinc-air batteries (L-ZABs). The findings presented in this dissertation (and the associated publications [52, 53, 54, 55, 56]) comprise the first model-based study of L-ZABs.

To begin, I consider the equilibrium composition of the electrolyte and highlight important factors that govern L-ZAB operation, including pH buffering, Zn$^{2+}$ speciation, and zinc salt solubility. I then predict the dynamic performance characteristics of L-ZAB cells, validate the results with experimental measurements, and discuss means of optimization.

6.1 Electrolyte Thermodynamics

L-ZABs utilize an electrolyte of mixed ZnCl$_2$–NH$_4$Cl with the pH adjusted through the addition of NH$_4$OH. The equilibrium composition of the LeClanchè electrolyte is substantially more complex than the alkaline electrolyte. The steady-state composition is calculated with the help of 0D thermodynamic models. These models also highlight properties of the electrolyte like pH buffering, zinc salt solubility, and Zn$^{2+}$ speciation, which are vital for optimum L-ZAB performance. The models applied in this analysis are derived and validated in existing works [162, 163, 313, 278, 53, 252] and described in the appendix. In the text, square brackets are used to denote concentration, e.g. $[\text{NH}_3] = c_{\text{NH}_3}$ with units mol L$^{-1}$.
In aqueous solutions, the Zn$^{2+}$ ion forms complexes with other solutes \[311\]. The dominant zinc complex \[311\] in strongly alkaline electrolytes is the zincate ion, Zn(OH)$_4^{2-}$; the dominant zinc complex in acidic chloride electrolytes is the tetra-chlorozincate ion, ZnCl$_4^{2-}$. But between the strongly acidic and strongly alkaline pH regions, the state of the Zn$^{2+}$ is very sensitive to changes in electrolyte composition.

Figure 6.1(a) shows the speciation diagram of Zn$^{2+}$ in aqueous ZnCl$_2$–NH$_4$Cl–NH$_4$OH–H$_2$O electrolyte. The pH is adjusted through the addition of NH$_4$OH, which gives the effect of mixing the weak acid NH$_4^+$ with its conjugate base, NH$_3$. The concentrations of NH$_4^+$, non-complexed NH$_3$, and total NH$_3$ are shown in Figure 6.1(b). In these diagrams, it is important to note the relationship between NH$_4^+$, NH$_3$, and the zinc-
amine complexes. For acidic pH values, the solution is dominated by zinc-chloride complexes because the concentration of NH$_3$ is very low. The NH$_3$ concentration rises with increasing pH values, leading to the formation of ternary zinc-chloride-amine complexes. When the concentrations of NH$_3$ and NH$_4^+$ approach the equivalence point at pH 9.8, the solution is dominated by Zn(NH$_3$)$_3^{2+}$ [53, 55].

During L-ZAB operation, the pH of the electrolyte is maintained by the buffer reaction NH$_4^+$ $\rightleftharpoons$ NH$_3$ + H$^+$ and is defined in terms of the buffering species concentrations as

$$pH = pK_a - \log_{10} \frac{[NH_4^+]}{[NH_3]}.$$  \hspace{1cm} (6.1)

The capacity and reversibility of the buffer are described by the ratio $[NH_4^+] : [NH_3]$. First I consider the capacity of the pH buffer. To achieve a stable operational pH,
the value of the ratio $[\text{NH}_4^+] : [\text{NH}_3]$ should be kept as constant as possible,

$$\frac{\partial [\text{NH}_4^+]}{\partial t} \approx 0, \quad \frac{\partial [\text{NH}_3]}{\partial x} \approx 0.$$  \hspace{1cm} (6.2)

The buffer reaction consumes $\text{NH}_4^+$ and produces $\text{NH}_3$ as it proceeds, causing the value of $[\text{NH}_4^+] : [\text{NH}_3]$ to fall and creating a slow and steady increase in pH. Fortunately, the formation of complexes between $\text{NH}_3$ and $\text{Zn}^{2+}$ allows the buffer reaction to proceed while the concentration of free $\text{NH}_3$ remains relatively constant. In this way, the time-rate-of-change of $[\text{NH}_4^+] : [\text{NH}_3]$ is reduced and the capacity of the buffer to stabilize the pH is enhanced [55].

The reversibility of the buffer is described by the magnitude of $[\text{NH}_4^+] : [\text{NH}_3]$. For most compositions in the near-neutral pH range, the concentration of $\text{NH}_4^+$ is much higher than $\text{NH}_3$ (see Figure 6.1(b)). This allows $\text{NH}_4^+$ to act as a proton donor and effectively buffer pH shifts in the alkaline direction. But if the pH becomes more acidic, there is only a small amount of $\text{NH}_3$ available to act as proton acceptors. Although some excess $\text{NH}_3$ can be supplied from $\text{Zn(NH}_3)_2^{2+}$ complexes, the reaction is very susceptible to any concentration gradients that could develop. Therefore, the buffer reaction can manage pH shifts in the alkaline direction, but the practical reversibility of the reaction to manage similar shifts in the acidic direction is limited. Because of this, there is a risk that the electrolyte could become acidic when the L-ZAB is charged [53, 55].

The formation of $\text{Zn(NH}_3)_n^{2+}$ complexes also has an important effect on the solubility of zinc solids. $\text{ZnO}$ and $\text{Zn(OH)}_2$ are normally insoluble in the near-neutral pH regime. However, $\text{NH}_3$ is able to act as a chelator for $\text{Zn}^{2+}$ ions, thereby increasing the solubility of zinc solids. To examine this effect, I expand the zinc speciation analysis into two dimensions.

Figure 6.2(a) and (b) show 2D zinc speciation and solubility landscapes for the $\text{ZnCl}_2—\text{NH}_4\text{Cl—NH}_4\text{OH—H}_2\text{O}$ system as a function of the pH and total concentration of zinc in solution, $[\text{Zn}]_T$, for a fixed total chloride concentration, $[\text{Cl}]_T$. The colored regions identify the dominant $\text{Zn}^{2+}$ complex, and the colored solid lines represent the solubility of various zinc solids. The gray dashed lines represent fixed total $\text{NH}_3$ concentrations (complexed $\text{NH}_3$, non-complexed $\text{NH}_3$, and $\text{NH}_4^+$) and indicate paths the electrolyte follows as the ZAB is operated, as indicated by increases or decreases in the total zinc concentration [53, 55].

Figure 6.2(a) shows that in the acidic pH regime, $\text{Zn}^{2+}$ is very soluble. As the pH approaches the near-neutral regime, the solubility falls sharply until the increasing
NH₃ concentration becomes high enough to chelate the Zn²⁺ ions. The solubility levels off and subsequently increases as the solution becomes saturated with NH₃. This diagram can also be used to predict how electrolyte composition affects the stable working point of the battery. An electrolyte with an initial total zinc concentration of 0.5 M and pH of 4 will follow the gray dashed line until the solubility limit of ZnCl₂ · 4 Zn(OH)₂ · H₂O is reached around pH 6, and the battery achieves a stable working point. On the other hand, an electrolyte with the same initial total zinc concentration but with an initial pH of 9 will reach its stable working point around pH 8 and Zn(OH)₂ is the first solid to precipitate. Increasing the total chloride content of the electrolyte, as shown in Figure 6.2(b), decreases the solubility of zinc-chloride solids like ZnCl₂ · 2 NH₃ [53, 55].

Figure 6.3 shows a three dimensional analysis of zinc speciation and solubility as a function of pH, NH₄Cl, and ZnCl₂ concentrations. Using this diagram, it is possible to identify electrolyte compositions that yield the desired precipitant and find a mixing pathway that avoids the precipitation of unwanted solids during preparation [53, 55].

Finally, I examine the equilibrium potentials of the electrochemical reactions. Figure 6.4 shows a Pourbaix diagram for the L-ZAB system. The equilibrium redox poten-
The equilibrium properties of the system are predicted from thermodynamics, but the real performance of L-ZAB cells deviate due to kinetics and mass transport limitations. In the following section, I apply a dynamic model to consider these effects.
6.2 Cell-Level Simulations

The performance of L-ZAB cells is rather complex, and strongly affected by both cell architecture and electrolyte composition. The simulations presented in this section are organized in a step-by-step approach.

First, I build upon the equilibrium electrolyte composition in the previous section to show how the composition of the electrolyte changes due to the dynamic effects of galvanostatic cell cycling. This provides a foundational understanding of the trends that occur during L-ZAB operation.

Next, I simulate the performance of some L-ZAB cells reported in the literature. There are currently 3 published studies that present experimentally obtained results [130, 92, 259]. The most recent publications by Goh et al. [92] and Sumboja et al. [259] offer a good opportunity for initial model validation. I simulate the cells presented in these works, discuss the modifications in electrolyte composition and cell architecture, and compare and contrast the results.

Finally, I perform an elementary optimization of L-ZAB design and electrolyte composition. The optimization highlights some aspects that can be improved and some fundamental limitations to L-ZAB operation that could be unavoidable. The insights obtained from these simulations lay the groundwork for designing next-generation electrolytes, as presented in the next chapter.

6.2.1 L-ZAB Dynamics

To simulate the dynamic performance of the L-ZAB electrolyte, I implement a 1D quasi-particle continuum model of the system and examine the performance over a single shallow discharge-charge cycle (2 mAh cm$^{-2}$). The electrolyte pH and dominant aqueous zinc complex are shown in Figure 6.5.

The dynamic pH profile (Figure 6.5(a)) indicates that that the pH in the BAE trends alkaline during discharging; on the other hand, the pH in the BAE trends acidic during charging. In both cases, the buffer reaction $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$ stabilizes the pH in the near-neutral regime. At the Zn electrode, the pH trends acidic during discharging. This is because the excess Zn$^{2+}$ takes up what small amount of NH$_3$ is present. When the cell is charged, Zn$^{2+}$ is redeposited and releases NH$_3$ into the electrolyte, causing the pH to trend alkaline [55].
Figure 6.5: Dynamic profiles of (a) electrolyte pH and (b) dominant Zn$^{2+}$ complex in a L-ZAB cell over one discharge-charge cycle. The electrolyte is 0.5M ZnCl$_2$ - 1.6 M NH$_4$Cl at pH 8. The cell is operated with current density $j_d = j_c = 1 \text{ mA cm}^{-2}$. Reproduced from Ref. [55] with permission from the Royal Society of Chemistry.

Figure 6.5(b) shows the dominant Zn$^{2+}$ complex in the solution. Initially the dominant complex over the entire cell domain is ZnCl(NH$_3$)$_3^+$, but as the pH shifts and concentration gradients build up in the cell, the dominant complex becomes Zn(NH$_3$)$_4^{2+}$ in the air electrode and ZnCl$_3$(NH$_3$)$_-$ in the Zn electrode. Comparing the dynamic Zn speciation with the equilibrium values calculated in Figure 6.2 shows how cell operation can affect the inhomogeneous behavior of the electrolyte [55].

These results provide a foundation for understanding the performance of real lab-scale L-ZABs, simulated in the following section.
6.2.2 Cell Cycling

In this section, I simulate the performance of two lab-scale L-ZABs reported in the literature [92, 259]. The first cell is described by Goh et al., and consists of a Zn foil electrode and MnO$_2$-catalyzed air electrode separated by an electrolyte bath 28 mm thick. The electrolyte is 0.51 M ZnCl$_2$ - 2.34 M NH$_4$Cl$_2$ at pH 6. This cell is referred to in the text as Cell A.

Cell A is discharged at 5 mA cm$^{-2}$ for 4 hours and charged at 2.5 mA cm$^{-2}$ for 8 hours. This corresponds to a cycled capacity of 20 mAh cm$^{-2}$.

The second cell is described by Sumboja et al. [259]. The cell comprises a Zn foil electrode and MnO$_2$-catalyzed air electrode separated by an electrolyte bath 24 mm thick. The electrolyte is 0.26 M ZnCl$_2$ - 5 M NH$_4$Cl$_2$ at pH 7. This cell is referred to in the text as Cell B.

Cell B is discharged at 1 mA cm$^{-2}$ for 2 hours and charged at 1 mA cm$^{-2}$ for 2 hours. This corresponds to a cycled capacity of 2 mAh cm$^{-2}$.

Cell A Simulations

First, I investigate the basic processes that occur in Cell A during galvanostatic cycling. Figures 6.6(a), (c), and (e) show the concentration profiles of zinc, NH$_3$ and pH as the cell is discharged.

When the discharge of Cell A begins, the metallic Zn electrode dissolves to form aqueous species, which may exist as either zinc-ligand complexes or solvated Zn$^{2+}$ ions. At the BAE, the ORR consumes H$^+$, and the NH$_4^+ \rightarrow$ NH$_3$ + H$^+$ reaction (combined with the uptake of NH$_3$ by the zinc-ligand complexes) acts to stabilize the electrolyte pH.

Figure 6.6(a) shows that at the end of discharge, aqueous zinc in the BAE exists mostly as complexes with NH$_3$. Once the aqueous zinc exists exclusively as Zn(NH$_3$)$_4$$^{2+}$, then its capacity to take up excess NH$_3$ is exhausted and the concentration of NH$_3$ rises as shown in Figure 6.6(c). When the concentration of NH$_3$ approaches its equivalence point with NH$_4^+$, the pH becomes steadily more alkaline in the BAE, as shown in Figure 6.6(e). At the Zn electrode, what small amount of NH$_3$ is present is taken up by the excess Zn$^{2+}$ ions and the pH becomes slightly more acidic.
Figure 6.6: Electrolyte composition of near-neutral ZAB in during discharging and charging. During discharging, the aqueous zinc concentration shifts, comprising mostly zinc-chlorides at the Zn electrode and zinc-amines at the air electrode (a). The concentration of non-complexed NH$_3$ in the BAE increases (c), driving a rise in pH (e). During charging, NH$_3$ in the BAE is consumed by the pH buffer and aqueous zinc is dominated by zinc-chlorides (b) and (d). The slow transport of NH$_3$ from the bulk to the BAE limits the pH-buffer and the pH in the BAE becomes acidic (f). Reproduced from Ref. [53] with permission from WILEY.
Figure 6.7: Cell A simulated voltage profile over 3 charge-discharge cycles, compared with experimental results (Goh, et al. [92]). $j_d = 5 \, \text{mA cm}^{-2}$, $t_d = 4 \, \text{hours}$. $j_c = 2.5 \, \text{mA cm}^{-2}$, $t_c = 8 \, \text{hours}$. Reproduced from Ref. [53] with permission from WILEY.

Figures 6.6(b), (d), and (f) show the concentration profiles in the cell during charging. When the cell is charged, aqueous zinc is redeposited at the Zn electrode. At the BAE, the OER produces $\text{H}^+$, and the $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$ reaction moves towards $\text{NH}_4^+$. The $\text{NH}_3$ that had formed complexes with $\text{Zn}^{2+}$ during discharge is now released back into the solution to stabilize the equilibrium with $\text{NH}_4^+$. Figure 6.6(b) shows that at the end of charging, aqueous zinc in the BAE has donated all of the available $\text{NH}_3$ and exists exclusively as zinc chloride complexes. Figure 6.6(d) shows that during the OER, the concentration of $\text{NH}_3$ in the BAE steadily falls as it is converted into $\text{NH}_4^+$. Once the $\text{NH}_3$ donated from the locally-available zinc complexes is exhausted, additional $\text{NH}_3$ must diffuse into the BAE from the separator. However, some of the zinc-amine complexes produced during discharge diffuse far into the bulk electrolyte and they cannot be quickly transported to the BAE. These effects have significant consequences for the pH in the cell. Because the amount of $\text{NH}_3$ in the BAE is no longer sufficient to convert the protons produced by the OER into $\text{NH}_4^+$, the pH becomes acidic at the end of charging. This effect is shown in Figure 6.6(f). Conversely, the rise in the concentration of $\text{NH}_3$ at the Zn electrode causes the pH in that region to become slightly more alkaline.

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MnO$_2$ is often used as an OER catalyst in alkaline and neutral solutions, but it is known to be unstable under acidic conditions due to the dissolution of Mn[123, 264, 209]. If the pH in the BAE drops to a value of 1 or below, as occurs during the charging of Cell A (Figure 6.6(f)), the risk of accelerated catalyst degradation is increased.

Figure 6.7 compares the simulated cell voltage over three cycles with experimental data. During discharge, there is a slight negative slope in the cell potential, which can be attributed to the pH shift in the BAE. Between the first and second discharges there is a positive shift in cell potential. In our model it is ca. 100 mV; in the experimental data it is ca. 250 mV. This shift in discharge voltage is due partly to the increase in the active surface area of the Zn electrode.

Initially, the Zn electrode is a polished sheet, but when zinc is electro-deposited, it takes on a porous morphology. This leads to an increase in the active surface area of the Zn electrode and a decrease in the overpotential of the electrochemical
reaction (Figure 6.8). The model considers this effect by altering the pore size of the deposited zinc. However, the overpotential of the zinc reaction cannot be solely responsible for a 250 mV voltage shift. There may be other mechanisms (such as activation of the MnO₂ catalyst) occurring simultaneously, which could increase the magnitude of the voltage shift between the first and second discharge. Further experimental data is needed to accurately characterize this effect.

As noted in the previous sections, the final product has a significant effect on cell performance. In the case of Cell A, however, the discharged capacity is rather small and the cell is operated with an excess of electrolyte. Few solids precipitate, and they have little effect on the cell performance.

In summary, Cell A shows that a zinc-air battery can be reliably cycled in the ZnCl₂−NH₄Cl electrolyte. However, the shift towards acidic pH values in the BAE can limit the material stability and cell lifetime.

**Cell B Simulations**

Cell B addresses one of the challenges observed in Cell A. The results of the simulations indicate that the performance of the two cells are very similar, with one notable exception: the pH in Cell B remains in the near-neutral regime when cycled. By avoiding the drop to acidic pH values, the stability of the catalyst and BAE is maintained, and the cell lifetime is improved. The pH profile of the cell at the end of discharge and end of charge are shown in Figure 6.9.

There are a few factors which contribute to the gain in pH stability. First, Cell B is charged at a lower current density, which reduces the NH₃ concentration gradient and allows more of the capacity of the buffer solution to be utilized. Second, the initial pH of the electrolyte is 7 instead of 6. That means there is initially more NH₃ in solution, and the state of the aqueous zinc ion is dominated by zinc-ammine complexes. As the pH drops to more acidic values, these complexes can donate NH₃ to the electrolyte. Third, the separator length is shorter, which reduces the magnitude of the NH₃ concentration gradient and limits the distance NH₃ can diffuse away from the BAE.

Figure 6.10 shows the aqueous zinc speciation profiles in Cell B at (a) the end of discharging and (b) the end of charging. Because of the shallow DoD and stable pH, the distribution of the zinc complexes does not change much during cell cycling. The dominant species in both discharging and charging are variations of ternary zinc-ammine-chloride complexes.
Figure 6.9: Cell B pH profiles at the end of the first discharge and end of the first charge. Reproduced from Ref. [53] with permission from WILEY.

Although Cell B does show a dramatic gain in lifetime and pH stability over Cell A, it is operated at a lower current density and to a shallower depth of discharge (DoD). The simulations show that the zinc solubility in the electrolyte is barely breached, and few solids precipitate.

Cell B represents another important step towards designing a practical neutral zinc-air cell, but questions remain. In the following simulations I show what happens when the cell is discharged to states at which significant amounts of solids precipitate, and investigate how the electrolyte composition and cell design may be optimized.

6.2.3 Optimization

The experimental studies modeled in the previous section show the general viability of the neutral electrolyte for secondary zinc-air battery applications. However, these cells are operated at relatively shallow DoDs, thereby avoiding complications that could arise due to the precipitation of chloride-containing solids.

Cells A and B feature a bath of excess electrolyte. This ensures that the cell always has sufficient amounts of electrolyte available, but it can lead to strong concentration
gradients, increase the internal resistance of the cell and lower the overall energy density. It is beneficial to design the cell with a thinner separator.

Figure 6.11 shows the pH profile across the cell for various separator thicknesses at the end of charging. Reducing the thickness of the separator improves the performance of the battery in three notable ways. First, it reduces the length of the transport paths in the battery, allowing for the more efficient utilization of NH\textsubscript{3}. Second, the reduced volume of the electrolyte accelerates the precipitation of solids, which stabilize the buffer solution. Third, the reduction of excess volume increases the energy density of the cell. The simulations show that for low current densities, separator lengths less than 2 mm are sufficient to maintain a stable pH at 1 mA cm\textsuperscript{−2}. As the energy density is inversely proportional to the separator length, I choose a 0.5 mm separator for the remainder of the optimizations.

With the optimum size of the separator defined, I turn our attention to the electrolyte composition. I define a standard test architecture to evaluate the effects of different electrolytes on battery performance. Our standard cell consists of a Zn electrode 5 mm in length, a 0.5 mm separator, and a 0.5 mm BAE. The cell is operated at 1 mA cm\textsuperscript{−2}. I first search for electrolyte compositions that thermodynamically favor the desired discharge product. Then I evaluate the stability of the electrolytes during cell operation.

From existing studies of zinc-carbon batteries and the thermodynamic analysis presented previously, it is known that the thermodynamically favored discharge product in most cases is either ZnCl\textsubscript{2} · 2 NH\textsubscript{3} or ZnCl\textsubscript{2} · 4 Zn(OH)\textsubscript{2} · H\textsubscript{2}O. As these solids
precipitate, the aqueous chloride concentration decreases, altering the properties of the electrolyte. For the system to function as a zinc-air battery, the discharge product should be ZnO, or alternatively Zn(OH)$_2$.

To predict an electrolyte composition that features a stable chloride concentration in the near-neutral pH regime and precipitates either ZnO or Zn(OH)$_2$, I revisit the thermodynamic analysis. The risk of precipitating chloride-containing solids increases with increasing total chloride concentration. For total chloride concentrations of ca. 3 M and pH values above 7.5, Zn(OH)$_2$ is the thermodynamically favored product. The initial electrolyte composition should be formulated such that it is at the solubility limit of Zn(OH)$_2$ to facilitate precipitation. I therefore propose an electrolyte composition of 0.5 M ZnCl$_2$ - 1.6 M NH$_4$Cl with the pH adjusted to 8 (referred to in the text as Electrolyte C). Evaporation of NH$_3$ through the BAE is not considered in this analysis and should be a topic for further research.

I evaluate the performance of Electrolytes A, B, and C by simulating the complete discharge of the test cell architecture to a cut-off voltage of 0.6 V. Figure 6.13(a) shows the total volume fractions of solid precipitants in the cell and the total chloride concentration versus discharged capacity, and Figure 6.13(d) shows the cell voltage.
Figure 6.12: Thermodynamic stability diagram for a fixed total zinc concentration of (a) 0.5 M and (b) 1 M. For slightly alkaline pH values (e.g. 8), Zn(OH)$_2$ is the thermodynamically favored precipitant. Reproduced from Ref. [53] with permission from WILEY.

and average pH in the BAE for Electrolyte A. The discharge occurs in 3 stages. In the first stage, the total chloride concentration falls as ZnCl$_2$ · 4Zn(OH)$_2$ · H$_2$O precipitates. The pH in the BAE becomes steadily more alkaline. This is because the precipitation of ZnCl$_2$ · 4Zn(OH)$_2$ · H$_2$O only removes 1.6 OH$^-$ for every Zn$^{2+}$ precipitated. In stage 2, the chloride concentration falls to the lower solubility limit of ZnCl$_2$ · 4Zn(OH)$_2$ · H$_2$O and the dominant discharge product shifts to Zn(OH)$_2$. The pH in the BAE begins to stabilize, because the precipitation of Zn(OH)$_2$ removes 2 OH$^-$ for every Zn$^{2+}$ precipitated. In the final stage, the capacity of the buffer solution is exhausted and the pH in the BAE becomes alkaline. Small amounts of ZnO precipitate.

Figures 6.13(b) and (e) show the discharge characteristics of a test cell with Electrolyte B. Again, the discharge occurs in 3 stages. In the first stage, the total chloride concentration falls rapidly as ZnCl$_2$ · 2NH$_3$ precipitates and the pH remains stable. In the second stage begins when the total chloride concentration falls to a level at which ZnCl$_2$ · 4Zn(OH)$_2$ · H$_2$O precipitation is favored. The pH becomes steadily alkaline due to the inadequate removal of OH$^-$. In the final stage, the discharge product shifts to Zn(OH)$_2$ and the total chloride concentration and pH stabilize.

Figures 6.13(c) and (f) show the discharge characteristics of a test cell with Electrolyte C. The composition of this electrolyte is tuned to favor only Zn(OH)$_2$ precipitation. The results show that both total chloride concentration and pH remain stable throughout the discharge of the cell. The end of discharge occurs when the Zn electrode is passivated by Zn(OH)$_2$. 

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Figure 6.13: Stability of the total chloride concentration and pH ZAB cells with different electrolytes. For electrolytes with high chloride concentrations (a,d) and (b,e), the precipitation of chloride-containing solids reduces the total chloride concentration in until $\text{Zn(OH)}_2$ begins to precipitate. In electrolytes with lower total chloride contents (c,f), the discharge product becomes exclusively $\text{Zn(OH)}_2$. Reproduced from Ref. [53] with permission from WILEY.

The shift in the solid discharge product observed in these simulations can be clarified by re-examining the thermodynamic stability plots in Figures 6.2 and 6.12. For high chloride concentrations, neutral pH values, and total zinc concentrations less than 1M, the battery discharge follows a path which takes it directly into the region of $\text{ZnCl}_2 \cdot 2\text{NH}_3$ insolvency, as shown in Figure 6.2(b). When the total chloride concentration in the electrolyte is reduced, as shown in Figure 6.2(a), the dominant discharge product becomes $\text{ZnCl}_2 \cdot 4\text{Zn(OH)}_2 \cdot \text{H}_2\text{O}$ for slightly acidic-neutral pH values and $\text{Zn(OH)}_2$ for slightly alkaline pH values.

This analysis yields a few significant takeaways for zinc-air battery design. First, $\text{ZnCl}_2 \cdot 2\text{NH}_3$ and $\text{ZnCl}_2 \cdot 4\text{Zn(OH)}_2 \cdot \text{H}_2\text{O}$ are not desirable discharge products. The precipitation of these solids consumes chloride from the electrolyte and reduces the effectiveness of the pH buffer. Second, electrolytes featuring a high initial chloride concentration will eventually converge to a steady-state chloride concentration at or near the solubility limit of $\text{ZnCl}_2 \cdot 2\text{NH}_3$ and $\text{ZnCl}_2 \cdot 4\text{Zn(OH)}_2 \cdot \text{H}_2\text{O}$. Therefore, it should be noted that any advantages of high chloride concentration (e.g. improved...
conductivity) are only valid for shallow discharges. Third, it is possible to tune the initial concentration of the electrolyte to exclusively precipitate Zn(OH)$_2$ as demonstrated by our proposed Electrolyte C composition. Favoring the precipitation of Zn(OH)$_2$ over chloride-containing solids is a modest improvement for cell operation. However, a means to thermodynamically or kinetically favor ZnO precipitation should be a topic for ongoing research.

Finally, I consider the design of the Zn electrode, which strongly influences the capacity and energy density of the battery. It is well-known that passivation due to the precipitation of solid products on the electrode surface is perhaps the biggest challenge limiting the full utilization of zinc in batteries. In alkaline zinc batteries, a shell of ZnO or Zn(OH)$_2$ forms around the zinc particles [114]. This shell isolates the surface of the zinc particle from the electrolyte and limits the transport of aqueous species to and from the electrode surface. When the thickness of the ZnO shell surpasses a critical value, the resistance to mass transport becomes so great that the concentrations of aqueous species at the zinc surface are depleted and the reaction cannot proceed. When this occurs, the electrode is said to be passivated.

Although this effect has been extensively studied in alkaline electrolytes, there is little research dedicated to the passivation process in the ZnCl$_2$–NH$_4$Cl system. It
is thought that ZnCl$_2$·2NH$_3$ is crystalline and dense and therefore presents a high resistance to the transport of solutes between the electrolyte and electrode. On the other hand, ZnCl$_2$·4Zn(OH)$_2$·H$_2$O is amorphous and porous and presents a lower resistance to mass transport [316]. Therefore, it is likely that ZnCl$_2$·4Zn(OH)$_2$·H$_2$O is less passivating than ZnCl$_2$·2NH$_3$ and could help achieve a higher zinc utilization in the battery. This should be the subject of a more in-depth study. For the purpose of this optimization, I assume that the zinc particles are spheres with an initial diameter of 100 µm. When the thickness of solid precipitants around the particle exceeds 5 µm, the particle is considered to be passivated.

Figure 6.14 shows the energy density of ZABs considering the electrolyte compositions A, B, and C discussed previously. An electrolyte composition that favors ZnO precipitation is not immediately apparent. However, it is commonly noted that Zn(OH)$_2$ can undergo a decomposition to ZnO. Therefore, we evaluate what the performance of a theoretical ideal electrolyte would be, if the precipitation of ZnO were achieved. We set the composition for this idealized electrolyte at 0.5 M ZnCl$_2$ - 2 M NH$_4$Cl pH 7. For this analysis the Zn electrode thicknesses varies from 0.5 mm to 20 mm. A cutoff voltage of 0.6 V is used as a reference.

For small Zn electrodes, the solid precipitants accumulate and passivate the electrode quickly. As the size of the electrode increases, the passivation risk becomes less severe and a higher fraction of the zinc is utilized, leading to a higher energy density. For thick Zn electrodes, the long transport path for the aqueous species destabilizes the pH in the BAE and reduces the energy density and lifetime of the cell. This is strongly the case in Electrolyte A. As shown in Figure 6.13(a), the precipitation of ZnCl$_2$·4Zn(OH)$_2$·H$_2$O is unable to stabilize the buffer solution and the pH becomes steadily more alkaline. This effect is exacerbated by the longer transport paths of thick Zn electrodes. The energy density of a cell with Electrolyte A peaks at 116 Wh L$^{-1}$. Electrolyte B shows increased pH stability, resulting in improved energy density up to Zn electrode thicknesses of about 10 mm. The energy density of a cell with Electrolyte B peaks at 132 Wh L$^{-1}$. Electrolyte C shows a modest improvement in energy density over Electrolytes A and B, peaking at 151 Wh L$^{-1}$. The simulations show that a theoretical ideal electrolyte which precipitates only ZnO could obtain an energy density of 952 Wh L$^{-1}$, comparable to commercial alkaline zinc-air button cells [253].
Table 6.1: Measured physicochemical properties of the four proposed electrolyte compositions compared with literature values for the standard alkaline ZAB electrolyte, 30 wt% KOH. Values for ionic conductivity (IC), mass density ($\rho$), dissolved oxygen concentration ([O$_2$]), and viscosity ($\mu$) are measured for each electrolyte. Reproduced from Ref. [55] with permission from the Royal Society of Chemistry.

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<th>[O$_2$] (mg L$^{-1}$)</th>
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<td>14.8</td>
<td>641[235]</td>
<td>2.52[63]</td>
<td>2.23[246]</td>
</tr>
</tbody>
</table>

6.2.4 Experimental Validation

The model-based analysis in the previous sections makes two important predictions about L-ZAB operation: the pH can become locally unstable (particularly in the air electrode during charging) and the dominant discharge product is not ZnO, rather some mix of zinc-hydroxide-chloride salts. To validate these predictions, operando pH measurements were carried out by ZAS! consortium partner Cidetec Energy Storage in San Sebastian, Spain.

The custom-built operando pH cell consists of a zinc foil anode and MnO$_2$-carbon cathode separated by an electrolyte bath 28 mm wide. Micro-pH meters were placed near the air and zinc electrodes to track locally resolved changes in the pH as the cell is cycled for 29 hours at 2 mA cm$^{-2}$.

Four different electrolyte compositions, listed in Table 6.1 were selected for experimental characterization. These electrolytes comprise an unadjusted mixture of ZnCl$_2$—NH$_4$Cl (E4) and those proposed by Goh et al. [92] (E6), Sumboja et al. [259] (E7), and Clark et al. [53] (E8). The model-based analysis predicts that initial electrolyte composition can have a significant impact on pH stability, particularly during charging. Characterizing a variety of electrolytes allows this hypothesis to be tested.

An overview of the physicochemical characterization of each electrolyte formulation is given in Table 6.1. To provide an adequate frame of reference for these values, I compare them with properties of the standard electrolyte for alkaline ZABs (30
wt% KOH) as reported in the literature. The ionic conductivity (IC) measurements indicate that electrolytes E4, E6, and E8 have comparable ionic conductivity values just above 200 mS cm\(^{-1}\), while E7 shows a substantially higher conductivity of 382 mS cm\(^{-1}\). This is likely due to the higher concentration of NH\(_4\)Cl in E7 as compared to the other electrolytes. Although the measured IC values are lower than that of KOH (641 mS cm\(^{-1}\)), they are still in a suitable range for battery electrolyte applications. Analysis of the dissolved oxygen content (DO) and viscosity (\(\mu\)) of the electrolytes also indicate their suitability for ZAB applications. The dissolved oxygen levels are over twice as high as those found in KOH, and the viscosity is roughly half that of KOH. Higher dissolved oxygen concentration is beneficial for the kinetics of the ORR, and the low viscosity helps achieve good transport and wetting behavior in the air electrode. On the other hand, lower electrolyte viscosity could increase the risk of flooding the air electrode. Care should be taken to adjust the hydrophilic/hydrophobic properties of the BAE substrate accordingly [61, 60].
According to our understanding of L-ZAB performance, the electrolyte in the air electrode can become strongly acidic during charging due to the slow diffusion of NH$_3$. Electrolyte E4 is the formulation most likely to become unstable because there is initially very little NH$_3$ in the solution and the composition is far from the stable working point of the cell. Therefore, an L-ZAB featuring E4 offers the best opportunity to observe the predicted behavior.

Figure 6.15(a) shows the measured pH profiles in an L-ZAB with electrolyte E4. These curves contain two features of interest. First, although the electrolyte is initially at pH 4, there is a rapid increase at the start of discharge that eventually approaches a steady-state value near pH 6. The pH increase begins at the air electrode followed by a delayed increase at the Zn electrode. Second, when the cell is charged the pH is initially stable but drops to strongly acidic values near the end of charging. This drop begins in the air electrode and is followed by the Zn electrode. The pH in the Zn electrode rebounds upward at the very end of charging. The L-ZAB model predicts this behavior [53]. An in-depth analysis of the simulation results can help elucidate the mechanism behind the observed pH swings.

Figure 6.15(b) shows the simulated pH values in a L-ZAB with electrolyte E4. As observed in the experiment, the model predicts that the pH will rapidly increases at the air electrode from the start of discharge until the cell reaches a stable working point in the near-neutral pH regime. A comparable shift is expected at the Zn electrode, but it is delayed due to slow mass transport across the electrolyte bath and the excess concentration of Zn$^{2+}$. As discharge continues, the rate of pH change stabilizes for both the BAE and the Zn electrode. When the cell is charged, the pH near the BAE begins to drop and is stabilized by the buffer reaction. On the other side, the pH near the Zn electrode becomes slightly more alkaline as Zn$^{2+}$ is deposited, releasing more NH$_3$ from zinc-amine complexes. Near the end of charging, a NH$_3$ mass transport limitation becomes dominant in the air electrode. With NH$_3$ locally depleted, the buffer reaction is no longer effective and the pH drops to acidic values.

Measured and simulated pH curves for the remaining L-ZAB electrolyte systems are compared in Figure 6.16. In contrast to electrolyte E4, the pH of the other systems remains more stable. There is no increase at the start of discharge because electrolytes E6, E7, and E8 are formulated at their stable working points. The drop to acidic values at the end of charging is not observed at the measurement location in these systems.

There is generally good agreement between the predicted and observed pH be-
Figure 6.16: pH profiles near the air electrode and the Zn electrode from (a) experiment and (b) simulation. For a single cycle at current density $j_d = j_c = 2\text{mA} \cdot \text{cm}^{-2}$. Reproduced from Ref. [55] with permission from the Royal Society of Chemistry.
Figure 6.17: Powder X-ray diffractograms for anode product phases obtained at 40% DoD in electrolytes E4, E6, E7, and E8. Data are scaled with the square-root of intensity to emphasize weak reflections. Samples were measured on the host Zn foil anode. Reproduced from Ref. [55] with permission from the Royal Society of Chemistry.
behavior. The model tends to overestimate pH changes than are measured in the experiment. This may be because the measurement is taken at a single point in three-dimensional space, while the simulation is simplified to one-dimension. Because the pH is measured near the electrodes, there is a delay between the onset of pH variations in the electrodes and when they can be observed in the measurement. Nonetheless, the major predictions of the model including pH increase to the stable working point during discharging and the rapid fall to acidic values during charging are experimentally observed.

The pH fluctuations that occur during cell cycling can have important consequences for L-ZAB lifetime and performance. As discussed previously, MnO$_2$ is known to be unstable in acidic solutions due to the dissolution of Mn$^{2+}$. The repeated exposure to strongly acidic conditions during charging is detrimental to the long-term stability of the air electrode.

The performance of the Zn electrode for the different L-ZAB electrolyte compositions is characterized with XRD and SEM measurements performed by ZAS! consortium partner SINTEF Industry in Trondheim, Norway.

Figure 6.17 shows the XRD spectra of Zn electrodes discharged to 40% depth-of-discharge at 1 mA cm$^{-2}$ in each electrolyte composition (E4 - E8). The results show that mixed zinc-hydroxide-chlorides and zinc-amine-chlorides are the dominant phases in all the measured electrolytes. No peaks directly attributable to ZnO or Zn(OH)$_2$ are observed. However for the electrolytes E7 and E8 - which are neutral and slightly alkaline - a significant peak is unattributable to either of the zinc-chloride phases. A similar peak is observed in existing studies of amino acid insertion into zinc-hydroxide-chlorides [16]. Considering the increasing concentration of NH$_3$ in the electrolyte for neutral and alkaline pH values, the unidentified phase is possibly a layered zinc-hydroxide-chloride intercalated with NH$_3$. Further characterization is needed to confirm this hypothesis.

Figure 6.18 shows (a) the cross-section of a Zn electrode discharged in electrolyte E6 and (b) the top-down view of the discharged-charged electrode. Both cross-section and top-down views of the SEM/EDS data are presented, so as to give a full insight into the sample microstructure. Figure 6.18(a) shows that there is a clear separation between layers of chlorine-rich and oxygen-rich phases during discharge. The observed phase layering supports the hypothesis that local changes in electrolyte concentration affect the composition of the precipitation product. In this case, the precipitation of a chlorine-rich phase reduces the local concentration of chlorides in the electrolyte, thus favoring the shift towards an oxygen-rich phase.
Figure 6.18: SEM and EDS analysis showing (a) the cross-section of a Zn electrode after discharge and (b) the surface of a Zn electrode discharged and charged in electrolyte E6. There is a separation of chloride and oxide phases in the discharged electrode. The charged electrode is covered by significant quantities of zinc precipitates. Reproduced from Ref. [55] with permission from the Royal Society of Chemistry.

This theory is supported by the thermodynamic analysis in Figures 6.1 and 6.2 and our existing work [53]. However, we note that the SEM cross-section indicates the distribution of the phases in space but not in time. Therefore, additional research investigating precipitation at various states of discharge could give further insight into the time-dependent phase formation.

Figure 6.18(b) shows that after charging, the products that precipitated during the discharge process are not redissolved and deposited as Zn metal, as would be expected for a reversible electrode reaction. Instead, additional material deposits on the Zn electrode which corresponds to the chemical composition of the simonkolleite phase. This is further supported by the cross-sectional image for the recharged cell using electrolyte E4 in Figure S3 of the supplementary information. The kinetics of ZnO dissolution are known to be sluggish in neutral electrolytes [311], but this cannot be solely responsible for the limited reversibility of the electrode.

Figure 6.19 shows the SEM and EDS measurements of Zn electrodes discharged and charged in electrolytes E4, E7, and E8. In electrolyte E4, the top view of the discharged electrode shows the separation of chlorine-rich and oxygen-rich phases. The chlorine-rich phase consists of a uniform crystalline domain, while the oxygen-rich phase precipitates as a conglomeration of platelets. The cross section of the charged electrode shows the oxygen-rich layer and chlorine-rich phases forming separate layers. In electrolyte E7, phase layering is also observed in the cross-
Figure 6.19: SEM and EDS analysis of Zn electrodes discharged and charged in electrolytes E4 (a & b), E7 (c & d), and E8 (e & f). Reproduced from Ref. [55] with permission from the Royal Society of Chemistry.
Table 6.2: EDS elemental characterization for positions labeled "1" and "2" in the SEM images. Reproduced from Ref. [55] with permission from the Royal Society of Chemistry.

<table>
<thead>
<tr>
<th></th>
<th>Discharged</th>
<th></th>
<th>Charged</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zn (at%)</td>
<td>Cl (at%)</td>
<td>O (at%)</td>
</tr>
<tr>
<td>E4 - Position 1</td>
<td>40.9</td>
<td>15.7</td>
<td>43.5</td>
</tr>
<tr>
<td>E4 - Position 2</td>
<td>18.8</td>
<td>37.4</td>
<td>0.0</td>
</tr>
<tr>
<td>E6 - Position 1</td>
<td>35.7</td>
<td>15.4</td>
<td>48.0</td>
</tr>
<tr>
<td>E6 - Position 2</td>
<td>16.1</td>
<td>56.5</td>
<td>13.4</td>
</tr>
<tr>
<td>E7 - Position 1</td>
<td>39.8</td>
<td>17.5</td>
<td>42.7</td>
</tr>
<tr>
<td>E7 - Position 2</td>
<td>25.6</td>
<td>49.8</td>
<td>9.2</td>
</tr>
<tr>
<td>E8 - Position 1</td>
<td>28.4</td>
<td>11.4</td>
<td>50.6</td>
</tr>
<tr>
<td>E8 - Position 2</td>
<td>21.1</td>
<td>40.8</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Section of the discharged electrode. In the charged electrode, the top-view measurement shows that the large domains of precipitated solids cover the surface of the electrode.

The EDS elemental analysis for positions labeled "1" and "2" in the SEM images are presented in Table 6.2. For electrolytes E6 and E7 after discharge, the atomic ratios for the chlorine-rich phase deviate somewhat from the expected 1:2:2 for Zn:Cl:N, and the phase appears to be more chlorine-rich than the ZnCl$_2$·2NH$_3$ identified by the XRD patterns for these samples. This may be due to the formation of additional amorphous or poorly crystalline chlorine-rich phases, or due to only a small quantity of a more chlorine-rich composition being present and thus being below the detection limit of XRD. For precipitates formed in electrolytes E4 and E8 after discharge, and in E4, E6 and E7 after charge, the measured compositions of both chlorine-rich and oxygen-rich phases correspond extremely well to the phases observed by XRD. It is interesting to note that for the samples which exhibit a modified layered phase by XRD, the Zn:Cl:O ratio agrees well with that of ZnCl$_2$·4Zn(OH)$_2$·H$_2$O, but that these samples are observed to contain a measurable quantity of nitrogen also, which is not the case for the samples in which ZnCl$_2$·4Zn(OH)$_2$·H$_2$O was observed.

The experimental validation presented in this section confirms the predictions of the model: (i) the pH in the air electrode can become strongly acidic during charging, and (ii) the solid discharge product is dominated by mixed zinc-chlorides - not ZnO. Although the proposed optimized E8 electrolyte does show more stable pH performance and more homogeneous precipitation of zinc-hydroxides, the results are still not ideal. Significant quantities of zinc-chlorides remain in the discharge product. This highlights the difficulty of designing halide-based electrolytes for zinc-air
batteries. An alternative approach is proposed in the next chapter.

6.3 Summary

This chapter presents the first model-based investigation of LeClanché zinc-air batteries [52, 53, 55].

The thermodynamics of L-ZABs are substantially more complex than strongly alkaline electrolytes and sensitive to even small changes in composition. L-ZAB operation is governed by the delicate interplay between Zn\(^{2+}\) chelation, pH-buffering, and the precipitation of zinc solids.

The results of the simulations show that LeClanché electrolytes are generally valid for zinc-air battery applications, but are subject to limitations. Some of these limitations can be addressed with adroit cell engineering, while others are inherent to the materials.

The simulations predict that the pH in the air electrode can become unstable during charging. This prediction is confirmed by operando pH measurements of a lab-scale cell. Achieving reasonably stable pH values in the cell requires both the efficient exploitation of the buffer reaction NH\(_4^+\) ↔ NH\(_3\) + H\(^+\) and the formation of zinc-ammine complexes, Zn(NH\(_3\))\(_n\)\(^{2+}\). The formulation of the electrolyte should be set such that there are adequate quantities of both NH\(_4^+\) and NH\(_3\) to promote good pH-buffering characteristics.

Furthermore, the simulations predict that mixed zinc-hydroxide-chloride salts - not ZnO - dominate the discharge product, with negative effects for energy density. Experimental XRD and SEM analyses confirm the presence of mixed zinc-hydroxide-chloride precipitates and support the predicted separation of phases during discharging. A means to favor ZnO precipitation, either thermodynamically or kinetically, should be a topic for future research.

The prospects of L-ZABs to address the electrolyte carbonation challenge are promising, but the electrolyte brings challenges of its own. Using LeClanché electrolytes in a flow cell configuration could improve the efficiency of the buffer solution and reduce the effect of unwanted precipitants. However, the energy densities of flow cells are very limited. Therefore, L-ZABs are most suitable for stationary energy storage applications.
7 Next-Generation Aqueous Electrolyte Design

In this chapter, I focus on the design of aqueous zinc electrolytes. First, I define some key performance criteria necessary to support ZAB operation. Next, I discuss the general formulation of aqueous electrolytes and identify possible components. I then evaluate some common systems and suggest a new aqueous organic electrolyte for evaluation.

7.1 Performance Criteria

An ideal aqueous electrolyte should meet some basic requirements to promote good ZAB operation [56]. These requirements are summarized in Figure 7.1. First, the pH of the electrolyte should be relatively stable during operation, either through the use of concentrated alkaline/acidic electrolytes or the incorporation of a pH-buffer solution. Second, Zn$^{2+}$ should be moderately soluble in the solution. The goal is to allow Zn$^{2+}$ to escape the surface of the Zn electrode (avoiding passivation), but not diffuse so far away as to contribute to Zn electrode shape change. When zinc precipitates do form, they should be dominated by a porous ZnO phase. On the air electrode side, the kinetics of the ORR/OER are the major limitation to ZAB efficiency and rate-capability. The electrolyte should not inhibit these reactions (e.g. by blocking active catalyst sites). Finally, to facilitate mass transport within the ZAB cell, the electrolyte should be conductive and non-viscous. An electrolyte with such properties could be useful for ZAB applications.

For rechargeable ZABs, we must also consider reversibility and lifetime limitations. For the battery to have a long lifetime, the electrolyte should be stable in air and within the electrochemical window of the cell. Furthermore, the vapor pressure of the electrolyte should be low to avoid evaporation losses out of the air electrode. Because ZABs are semi-open systems, human contact with the electrolyte can-
To design electrolytes that fulfill these criteria, we will focus on tuning the nominal pH of the electrolyte and choosing materials (inorganic and organic) that contribute to some or all of the criteria described above.

### 7.2 Electrolyte Components

An aqueous electrolyte is composed of a salt (e.g. KCl), acid (e.g. HCl), or base (e.g. KOH) dissolved in water. Alkaline ZABs often feature the strong base KOH, where K\(^+\) acts as a counterion while OH\(^-\) fulfills dual roles as both an active material in the ORR/OER and as a Zn\(^{2+}\) complexing agent. As already mentioned, OH\(^-\) reacts with CO\(_2\) in air to form carbonates that slowly degrade the electrolyte. Therefore, we avoid the use of strong bases as the sole electrolyte material. On the other extreme, strongly acidic electrolytes are often problematic for metallic Zn electrodes because of the increased danger of H\(_2\) gas evolution. For these reasons, we focus on weak acids and salts with pH values between circa 4 and 12. For the purpose of this work, we refer to these as near-neutral electrolytes (NNEs).
Table 7.1: Common electrolyte components. The feasibility of these materials for use in ZAB applications is discussed in the text. Many of the inorganic components have properties that exclude them from further consideration.

<table>
<thead>
<tr>
<th>Counterions</th>
<th>Inorganic pH Buffers</th>
<th>Organic pH Buffers</th>
</tr>
</thead>
<tbody>
<tr>
<td>K⁺, Na⁺, Li⁺,</td>
<td>NH₄⁺, PO₄³⁻</td>
<td>carboxylic acids,</td>
</tr>
<tr>
<td>Cl⁻, Br⁻, I⁻,</td>
<td>CO₃²⁻, BO₃³⁻</td>
<td>amino acids,</td>
</tr>
<tr>
<td>NO₃⁻, SO₄²⁻,</td>
<td>CN⁻</td>
<td>azoles, azines, etc.</td>
</tr>
<tr>
<td>BF₄⁻, PF₆⁻, TFSI⁻, OTf⁻</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Near-neutral electrolytes for ZAB applications require a buffer to stabilize the pH during operation, because of the pH shifts inherent to the ORR/OER. The weak acid ammonium, NH₄⁺, is among the most common pH buffers. NH₄⁺ and other quaternary ammonium cations are unique because the acid is positively charged and the conjugate base, e.g. NH₃, is charge-neutral. Thus, the solution requires a negatively-charged counterion, often a halide like Cl⁻ or Br⁻. Electrolytes containing NH₄Cl have been demonstrated for ZAB applications [130, 7, 92, 259], but there are some challenges. NH₄⁺ is able to donate only a single proton and buffer the pH at a single value. This is sufficient to stabilize the pH at low current densities, but strong concentration gradients can develop under some conditions and cause the pH to become unstable [53]. Furthermore, the vapor pressure of NH₃ in water is rather high [223], increasing the risk of electrolyte evaporation out of the air electrode. The use of halide counterions presents additional obstacles. The solubility of zinc-chloride-hydroxide salts in the near-neutral pH regime is low, leading to the consumption of electrolyte during ZAB discharge [162, 163, 141, 16].

One alternative would be to keep NH₄⁺ as the weak acid, but replace the halide counterion with another anion. A good counterion should be mobile, coordinate only weakly or not at all with Zn²⁺, and not form insoluble zinc salts. Two possible counterions for NH₄⁺ proposed in the literature are SO₄²⁻ or NO₃⁻ [130]. The advantages of NO₃⁻ are that it forms only weak complexes with Zn²⁺ and the solubility of zinc-nitrate salts is high [248, 57]. Unfortunately, NO₃⁻ is subject to a redox shuttle, as is known from Ni—MH batteries [87, 145]. Zn(SO₄)₂ electrolytes have recently attracted attention for use in Zn-ion batteries [203, 137, 138, 285]. SO₄²⁻ forms only weak complexes with Zn²⁺, but zinc-sulfate-hydroxide salts are insoluble for near-neutral pH values [147]. Other alternative anions could include...
molecules from ionic liquids, like hexafluorophosphate (PF$_6^-$) and tetrafluorooborate (BF$_4^-$), bistriflimide (TFSI$^-$) or triflate (OTf$^-$) [101]. There have been some studies of aqueous zinc electrolytes with these molecules [308]. They could be of interest for aqueous Zn-ion batteries, but their acute toxicity makes them undesirable for semi-open systems like Zn-air. It is difficult to identify a negatively-charged counterion that is non-toxic, stable, and soluble under ZAB conditions. We direct our attention towards alternative weak acids that can be utilized with positive alkali earth metal counterions (e.g. Li$^+$, Na$^+$, K$^+$).

Inorganic pH-buffers like H$_3$PO$_4$, H$_2$CO$_3$, H$_3$BO$_3$, or HCN could potentially address some of these challenges. In these examples, the acid is charge-neutral and the conjugate base is negatively charged, avoiding the need for a negative counterion. Furthermore, because of their polyprotic nature (excepting HCN), these acids can buffer pH at multiple levels, improving the resilience of the battery against unstable pH shifts. But the solubilities of zinc phosphates, carbonates, and borates are still very low and threaten the precipitation of ZnO as the dominant discharge product [248, 57]. Additionally, cyanide is highly toxic and unsuitable for a semi-open system. These materials do not offer an outstanding alternative to NH$_4^+$.

Organic weak acids like carboxylic or amino acids could serve as feasible alternatives to their inorganic counterparts, and have been studied as additives to aqueous zinc electrolytes. They are often polyprotic and buffer pH at multiple levels. The conjugate bases are negatively-charged and can be combined with a positive counterion. The solubilities of zinc-organic salts are often high enough so as not to threaten the precipitation of ZnO. Additionally, the wide variety of organic weak acids give a large degree of flexibility in electrolyte design. Disadvantages of organic acids are that the ionic conductivity is reduced and the redox properties are complex, due to the variety of possible intermediate products. Nonetheless, they are deserving of closer inspection to determine their feasibility as aqueous zinc electrolyte materials.

### 7.3 Thermodynamic Screening of Aqueous Organic Electrolytes

Figure 7.2 presents a visualization of pK$_a$ and logarithmic zinc complex stability constant data for a variety of organic weak acids. There are a plethora of acids that could be considered as ZAB pH buffers. To focus our search, we look for acids
Figure 7.2: Zinc complex stability constant and pKₐ values for a selection of weak organic acids. Dashed lines indicate the approximate region of interest for aqueous zinc electrolyte applications. Data compiled from Refs. [248, 249, 178].
with $pK_a$ values in the near-neutral pH range, whose conjugate bases form moderately strong complexes with $\text{Zn}^{2+}$ and have electrochemical heritage. Among the more promising candidates are carboxylic acids, amino acids, and azoles. These materials are discussed below.

Carboxylic acids refer broadly to organic compounds that contain a carboxyl group. Most carboxylic acids have $pK_a$ values in the range of 2-6, and are often polyprotic. The logarithmic stability constants of zinc carboxylate complexes fall mostly between 0 and 5. Because the pH of ZAB electrolytes is often near-neutral or alkaline, carboxylic acids exist in their deprotonated state. Carboxylate salts - particularly those of acetate, tartrate, and citrate - are often used as additives in ZAB electrolytes and zinc electroplating processes [89, 153, 307, 159, 151, 290, 185, 46, 166, 119, 97, 293, 7] for the purpose of suppressing both hydrogen evolution and Zn dendrite formation [149]. Although both acetate and citrate have strong electrochemical heritage, we select citrate for further investigation in this analysis because of its superior pH buffering and transport properties [195, 14].

Figures 7.4(a) and (b) show the dissociation and $\text{Zn}^{2+}$ speciation properties of citric acid. In Figure 7.4(a), citric acid dominates the solution at acidic values. As the pH increases, it passes through its various deprotonated states until citrate is the

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Figure 7.3: Structures acid dissociation constants for some organic molecules with promising characteristics for aqueous ZAB electrolytes.
Figure 7.4: Equilibrium speciation plots for aqueous solutions of citric acid and glycine. Dissociation diagrams for 1M solutions (a), (c) and with 0.1 M [Zn]** added (b), (d). Reproduced from Ref. [56].
sole species at pH values around 7 and above. When Zn$^{2+}$ ions are introduced to the solution in Fig. 7.4(b), they form complexes with the various citrate species in the solution, dominated by Zn(Cit)$_4^{4-}$ in the near-neutral pH domain. As the solution becomes more alkaline, the zinc-hydroxide complexes become dominant. This model of chemical equilibrium shows that pH-adjusted solutions of citric acid and zinc could stabilize the electrolyte pH between values of circa 3-6 due to citric acid dissociation and 11-14 due to the formation of zinc-hydroxide complexes.

Amino acids feature both amine and carboxyl functional groups. Although the pK$_a$ value of the carboxyl group is low (circa 2-6), the pK$_a$ of the amine group is much higher (circa 9-11). Therefore, amino acids are good candidates for near-neutral pH buffers. The simplest amino acid is glycine, and it has electrochemical heritage as an additive in battery [292] and electroplating electrolytes [269, 199, 20].

Fig. 7.4(c) & (d) show the dissociation and Zn$^{2+}$ speciation properties of glycine. Fig. 7.4c shows that, in aqueous solutions, glycine can exist in three states: the glycinium cation (H$_2$Gly$^+$), the glycine zwitterion (HGly), and the glycinate anion (Gly$^-$). When zinc is introduced in Fig. 7.4(d), it forms complexes with glycinate and the solution is dominated by Zn(Gly)$_3^{3-}$ between pH 9-12. The best option to obtain a stable pH under ZAB operating conditions to utilize the HGly/Gly$^-$ buffer between pH 8-12, which coincides with the domain of Zn(Gly)$_3^{3-}$ dominance and abuts the region of Zn(OH)$_4^{2-}$ dominance.

Imidazolium-based cations are currently widely researched for ionic liquid electrolytes, but they could also be of interest in aqueous electrolyte development [89, 167]. Imidazolium has a proton in the N-3 location with a pK$_a$ value of 7.31 (in an aqueous solution of 1.0 ionic strength [249]). The imidazolium ring can be modified to include a variety of functional groups. For example 4-(2-Aminoethyl)imidazolium is able to donate a second proton from the amine group with a pK$_a$ value of 9.88 [249]. Ionic liquid electrolytes often include 1-ethyl-3-methylimidazolium, but as the N-3 position is occupied by a methyl group, the pK$_a$ is outside the range that would be appropriate for aqueous ZAB pH buffering [9].

Figures 7.5(a) and (b) show the dissociation and Zn$^{2+}$ speciation properties of imidazolium. In aqueous solution, imidazolium can donate a single proton (pK$_a$ = 7.31) and become the charge-neutral species imidazole. Imidazole forms strong complexes with Zn$^{2+}$, which significantly increases the solubility of zinc oxide and hydroxide in the near-neutral pH regime (as shown in Figure 7.4(j)). The gray pathways indicate that the pH of the electrolyte is buffered between circa 7.5 and 12.5 during ZAB operation.
Figure 7.5: Equilibrium speciation plots for (a) the dissociation of imidazolium in a 1M solution and (b) the speciation of 0.1 M $[\text{Zn}]_T$ added. Reproduced from Ref. [56].

From the thermodynamic analysis, we can make a few statements regarding the practical uses of these materials for aqueous ZAB electrolyte applications. Imidazolium shows suitable pH buffering and Zn$^{2+}$ complexing properties, but the pKa value is slightly too low to adequately stabilize the pH during cell operation. Furthermore, because it can only donate a single proton, pH stability is susceptible to unfavorable concentration gradients that could occur during ZAB operation. Functional group modification (e.g. 4(2-Aminoethyl)imidazole) could address these challenges, but electrochemical oxidation of the electrolyte during charging could become a limiting factor [230]. We highlight imidazolium and its variants as materials of future interest, but do not consider them further in this work.

Glycine has good pH buffering properties in the appropriate domain, but its transport properties are insufficient [98, 74]. Additionally, even through its carboxyl group can act as a secondary proton acceptor, the pKa value is too low to be of practical use. In contrast, citric acid has a good conductivity and a large buffering capacity, but its pKa values are too low to act as the primary pH buffer. Therefore, we examine what properties a mixture of citric acid and glycine would have.

Fig. 7.6 shows the 2D solubility and speciation landscape of a mixed citric acid-glycine electrolyte with the pH adjusted through the addition of KOH. The total concentration of citrate in the solution is 2 mol dm$^{-3}$ ($[\text{Cit}^2^-] = 2\text{M}$) and glycine is 1 mol dm$^{-3}$ ($[\text{Gly}^-] = 2\text{M}$). The figure is interpreted as follows: the colored regions (labelled (i) - (vi)) represent the dominant zinc complexes in the electrolyte. The thick white lines show the solubility limits of ZnO (solid) and Zn(OH)$_2$ (dashed). The thick black line shows the solubility limit of Zn$_3$(Cit)$_2$. The dotted black lines...
trace paths of constant $[K^+]$ concentration, indicating how the composition of the electrolyte shifts as the cell is discharged ($[Zn]_T$ increases) or charged ($[Zn]_T$ decreases). Stable working points for the ZAB are located at positions where the dotted solid lines (iso-$[K^+]$ paths) cross the solid white line (ZnO solubility). Locating the position on the chart corresponding to a total zinc concentration of 0.5 M and pH of 9, the dotted pathway shows stable operation between pH values of 8 and 11, with mixed ZnO-Zn(OH)$_2$ dominating the discharge product. There is a risk of zinc citrate precipitation, but this can be avoided with proper electrolyte preparation. Therefore, we propose an electrolyte containing 2M $[\text{Cit}^{3-}]$, 1M $[\text{HGly}^-]$, saturated with ZnO and adjusted to pH 9 through the addition of KOH.

There are a few aspects motivating our selection of a halide-free citrate-glycine electrolyte for further investigation. To our knowledge, this electrolyte mixture has not been previously proposed or investigated; it is therefore a suitable proof-of-concept for our electrolyte design rationale. Second, these materials are very safe and cheap (they are often used in dietary supplements), and these ZABs could per-
haps serve some niche applications. Finally, the dynamic behavior of this electrolyte is very complicated and serves as an excellent opportunity to further develop and validate our method of quasi-particle continuum modeling. Therefore, this selection should be seen as one step in the process of aqueous electrolyte development.

The analysis of the thermodynamics of organic weak acids shows that there are many contenders that could contribute to improved ZAB operation. By considering factors relating to pH buffering, Zn\(^{2+}\) chelation, and zinc solubility we have identified one electrolyte formulation from among many possibilities. In the following section, we discuss a method to simulate the cell-level dynamic performance of this aqueous organic electrolyte.

### 7.4 Cell Simulations of an Aqueous Organic ZAB

Figure 7.7 shows (a) the simulated electrolyte pH profile and (b) cell voltage during galvanostatic cycling. The current density is 0.5 mA cm\(^{-2}\) for discharging time = charging time = 4 hours. The Zn electrode is at the left of the domain, followed by an electrolyte bath 9mm thick, and the bi-functional air electrode is on the right of the domain. The initial pH of the electrolyte is 9.

At the start of discharge, the electrolyte becomes more alkaline in the BAE because of the effects of the ORR. The buffering capacity of the electrolyte stabilizes the pH at values around 11. As discharge continues, the electrolyte in the separator steadily trends alkaline due to the diffusion of spent buffer solution away from the air electrode. Because the electrolyte bath is relatively large, it takes time for this diffusion front to reach the Zn electrode. The pH in the Zn electrode varies only slightly (between circa 9-10.5) during cycling. To better understand the behavior of the electrolyte, we examine the distribution on zinc, glycine, and citrate in the electrolyte.

Figure 7.8 shows the anatomized concentration profiles of zinc, glycine, and citrate in the electrolyte at the end of the first discharge and end of the first charge. At the end of discharge (Figure 7.8(a)), aqueous zinc in the air electrode exists mostly as complexes with Gly\(^-\) with some zinc-hydroxides present. At the end of charge (Figure 7.8(b)), there are no zinc-hydroxides present in the air electrode, and instead the proportion of zinc-citrate complexes increases. This indicates that the alkaline shift that occurs during discharge is mostly stabilized by the uptake of OH\(^-\) by the Zn(OH)\(_x\) complexes. On the other hand, the acidic pH shift that occurs during
charge is stabilized by the buffering capacity of the organic molecules, namely the glycine.

This effect can also be seen in the glycine distributions shown in Figures 7.8(c) and (d). At the end of discharge, glycine in the air electrode exists only as complexes with zinc. But at the end of charging there is a significant increase in the proportion of glycine in its zwitterionic state. The concentration profiles of citrate (Figures 7.8(e) and (f)) show that it mostly acts as a background electrolyte. Citrate does form some complexes with zinc, but the pH of the electrolyte does not drop to low enough values to engage its buffering properties.

The cell-level simulations predict that a ZAB with the proposed citrate-glycine electrolyte can be reliably cycled at low current densities (e.g. 1 mA·cm$^{-2}$). The pH is anticipated to stabilize between circa 8.5 and 11.5 in the air electrode and circa 9 and 10.5 in the Zn electrode. The solid discharge product is dominated by ZnO, with the possibility for some Zn(OH)$_2$ to also be present. In the following sections, custom-built ZABs with the proposed electrolyte are experimentally characterized to investigate and validate these predictions.
Figure 7.8: Anatomized concentration profiles of zinc (a)-(b), glycine (c)-(d), and citrate (e)-(f) in the electrolyte at the end of discharging and charging. The presence of Zn(OH)$_x$ in the discharged electrolyte but not in the charged electrolyte indicates a shift in the dominant pH buffering mechanism between discharging and charging.
7.5 Experimental Validation

A range of experimental characterization methods - including full-cell cycling, rotating ring-disk electrode (RRDE) measurements of the air electrode, and x-ray diffraction (XRD) and scanning electron microscope (SEM) measurements of the Zn electrode - were performed to validate the model-based predictions. These measurements were carried out by ZASI consortium partners Cidetec Energy Storage in San Sebastian, Spain and SINTEF Industry in Trondheim, Norway. Additional support was provided by the Institute for Surface Chemistry and Catalysis (IOK) at Ulm University in Ulm, Germany.

Figure 7.9 shows RRDE measurements performed on glassy carbon (GC), EMD, carbon nano-tubes (CNT), and EMD+CNT in the same aqueous organic electrolyte. The results in oxygen-saturated electrolyte (solid lines) are compared with measurements from nitrogen-saturated electrolyte (dotted line). The results show very low disk current densities for both GC and EMD electrodes, while CNT and EMD+CNT
electrodes show much higher current densities. This may be due to the insertion of dissolved oxygen into the CNT structure. The ring shows no significant signal in the OER domain, but a clear peak for EMD-CNT is visible in the ORR domain. This indicates that the ORR follows the 2-electron pathway to form hydrogen peroxide, H$_2$O$_2$. The formation of H$_2$O$_2$ is not desirable from either an efficiency or material stability point of view, and this observation further highlights the need for appropriate catalyst selection. While the performance is not yet optimized, the RRDE measurements support the viability of oxygen redox chemistry in the proposed electrolyte.

The performance of the three catalyst materials were also evaluated in a full-cell configuration, as shown in Figure 7.10. The cell-level results reflect the findings of the RRDE measurements. EMD shows the lowest activity for both ORR and OER. CNT and EMD+CNT show comparable ORR behaviour, but the OER performance of EMD+CNT occurs at significantly lower overpotentials than just CNT, as indicated in Figure 7.9.

Figure 7.11 shows the long-term galvanostatic cycling of a ZAB cell with EMD+CNT catalyst, operated at 0.5 mA cm$^{-2}$. The results show that after the first few cycles, the discharging voltage of the cell stabilizes just over 1 V. There is little variation in
the discharging voltage until a sudden drop occurs after 500 hours. On the other hand, the charging voltage steadily increases over the cycle lifetime of the cell, indicating that some degradation occurs during the charging process. This can be attributed to carbon corrosion of the air electrode support and parasitic oxidation of the organic molecules, which occurs near OER potentials. The results of the long-term cycling experiment validate the feasibility of the system to be cycled over an extended period (500 hours), and highlight the need for further optimization of degradation processes in the air electrode.

Figure 7.12 shows the XRD spectrum of the Zn electrode after one discharge at 0.5 mA cm\(^{-2}\). The results clearly indicate the presence of both ZnO and Zn(OH)\(_2\) phases, in good agreement with the model-based predictions (see Figure 7.6). This is in strong contrast to the halide-based LeClanché electrolyte, in which the precipitate is dominated by zinc-chloride phases and no distinguishable ZnO. The XRD also shows peaks for an unidentified layered hydroxide phase, which could be a topic for additional research.

The formation of solid discharge products on the Zn electrode is further investigated under cycling conditions, as shown in Figure 7.13. In this analysis, the full
cell is cycled 13 times for 13.5 hours discharge and charge time at 0.5 mA cm$^{-2}$. The measurements are taken on a charged electrode. The XRD pattern in Figure 7.13(a) again shows peaks for both ZnO and Zn metal. However, in the cycled electrode there is no Zn(OH)$_2$ signal. Instead the presence of the unidentified layered hydroxide phase is increased.

Figure 7.13(b) shows the SEM measurement of the Zn electrode after 13 cycles. The results show that the precipitate is dominated by a phase rich in zinc and oxygen, with very little potassium from the electrolyte present. However, a significant quantity of precipitates remain on the electrode after charging. For a fully reversible Zn electrode, there should be mostly Zn metal and very few precipitates. There are a few initial explanations for this observation. First, the kinetics of ZnO dissolution are known to be slow in near-neutral electrolytes, due to the low concentration of OH$^-$ [311]. Second, the buffer solution stabilizes the pH near the solubility limit of the precipitates, reducing the driving force for dissolution. Finally, the parasitic evolution of H$_2$ gas during charging can cause the electrochemical formation of even more precipitated solids, possibly contributing to the observed increase in the layered hydroxide phase.
7 Next-Generation Aqueous Electrolyte Design

Figure 7.13: (a) Powder XRD pattern for anode products formed after 13 discharge-charge cycles at rate of 0.5 mA cm\(^{-2}\) and a charge-discharge cycle time of 27 hours per cycle. Cycling was stopped at the end of a charging step. Identified phases are fit and displayed in colour. (b) Backscattered electron image of an anode cross section after 13 discharge-charge cycles at a rate of 0.5 mA cm\(^{-2}\) and a discharge-charge time of 27 hours per cycle. Reproduced from Ref. [56].

The methods of experimental validation presented in this section confirm that the proposed ZAB electrolyte can (i) achieve stable full-cell cycling over long periods of time, (ii) allow for the occurrence of oxygen redox chemistry, and (iii) precipitate ZnO as the dominant discharge product. However, challenges remain regarding the electrochemical stability of the electrolyte, optimized catalyst selection, and the reversibility of ZnO precipitation.

7.6 Summary

The method of aqueous electrolyte design laid out in this chapter is used to propose and test novel electrolyte compositions for next-generation zinc-air batteries.

Inorganic materials for aqueous electrolytes often form insoluble salts with zinc in the near-neutral pH regime. This threatens the formation of ZnO as the final discharge product and reduces the energy density of the battery. Furthermore, many inorganic materials are acutely toxic and should be avoided in semi-open systems. On the other hand, many organic materials have very favorable Zn\(^{2+}\) chelation and pH-buffering properties, and they favor the formation of ZnO as the final discharge product.
Thermodynamic screening of potential organic molecules shows that there is a wide variety of materials with the appropriate properties for aqueous ZAB electrolytes. Carboxylic acids, amino acids, and azoles are particularly suitable. Through the application of theory-based models, we show that a halide-free electrolyte containing citrate and glycine is feasible for an electrically-rechargeable ZAB system. The viability of the proposed electrolyte is confirmed using experimental validation techniques including full-cell cycling, half-cell RRDE measurements, and XRD/SEM characterization. Challenges related to the electrochemical stability of the electrolyte, catalyst optimization, and Zn electrode reversibility remain.

The proposed halide-free aqueous organic electrolyte should be viewed as a proof-of-concept for the electrolyte design method, and as one manifestation of many possibilities. The favorable initial results validate both the modeling methods applied in the analysis and the underlying understanding that governs them. Continuing to apply these methods to investigate and optimize aqueous organic electrolytes assists the development of novel materials for zinc-based batteries.
8 Conclusion and Outlook

This dissertation presents a framework for the model-based design of next-generation zinc-air batteries (ZABs), advancing both the theory of electrochemical modeling and the design of real ZABs a step beyond the current state of the art.

Chapter 2 reviews state-of-the-art ZAB technology. Primary ZABs are a mature technology and there are decades of literature on the development and optimization of these systems. The rate-capability and efficiency of the battery is limited mainly by the air electrode, and the electrical rechargeability is generally limited by the Zn electrode. New secondary batteries utilize advanced air catalysts and Zn metal electrodes with sponge, fiber, or foam morphologies. The calendar lifetime of ZABs is limited by the parasitic carbonation of alkaline electrolytes, which cuts the life of the battery to just a few months. New materials and cell designs are required to address the carbonation challenge. Aqueous near-neutral LeClanché electrolytes have been proposed as one possible solution.

The thoughtful application of physics-based models can accelerate the development of batteries, saving time and money in the process. Chapter 3 reviews traditional model-based design tools for metal-air batteries. Appropriate battery design requires a knowledge of the intrinsic properties of materials, how those materials can be transformed into electrodes, and how the electrodes and electrolyte interact with each other in the dynamic cell environment. Tools to address each of these aspects of design are presented, along with their advantages and limitations. One of the most powerful design tools is cell-level continuum models.

Traditional continuum models very effectively simulate the transport of concentrated electrolytes that are strongly acidic or alkaline. But near-neutral electrolytes - like those proposed to improve ZAB lifetime - contain many possible dissolved species, whose concentrations can quickly change by orders-of-magnitude. This causes the solution to traditional continuum models to become numerically unstable.

Chapter 4 derives a novel quasi-particle method of continuum modeling. Rather than solving the continuity equations for each individual solvent, our novel method
defines a set of quasi-particles that represent quantities of mass and charge that are conserved in homogeneous electrolyte reactions and are sufficient to describe the state of the electrolyte. In this way, the computational effort required to obtain a solution is significantly improved.

The quasi-particle model is applied to study the performance of alkaline ZABs in Chapter 5. After discussing the general performance characteristics of alkaline ZABs, I show how continuum models can be applied to solve real cell engineering challenges. An optimization of the Zn electrode is presented. According to the needs of the battery, Zn electrodes can be designed with either high power or high energy, but it is difficult to design an electrode with both. Nonetheless model-based investigations can help identify promising electrode compositions. Furthermore, continuum models can be applied to help design everything from lab-scale experiments to grid-scale energy storage projects. However, no matter how much the design or performance of alkaline ZABs are optimized, they will always be subject to lifetime limitations due to the absorption of atmospheric CO$_2$ and subsequent formation of carbonates in the electrolyte.

Chapter 6 presents the first model-based investigation LeClanché zinc-air batteries (L-ZABs). L-ZABs, which feature the near-neutral ZnCl$_2$–NH$_4$Cl electrolyte, are not subject to carbonation when exposed to air. The analysis in this chapter traces the factors governing L-ZAB performance from fundamental thermodynamics up through cell architecture. The simulations confirm that LeClanché electrolytes are generally valid for ZAB applications, but bring some limitations of their own. Under some conditions, the electrolyte pH can become locally unstable. Our models predict that slow mass transport of NH$_3$ cause the pH in the air electrode to become strongly acidic during charging. This prediction is validated with operando pH measurements in a lab-scale L-ZAB. The models also predict that the final discharge product is not ZnO, rather a mix of zinc-hydroxide-chloride salts. This has potentially detrimental effects for the energy density of the cell and passivation of the Zn electrode. Utilizing LeClanché electrolytes in a flow cell architecture could improve the pH stability and reduce the effects of unwanted precipitation, but would also decrease the energy density of the system. Therefore, L-ZABs are most suitable for stationary energy storage applications.

Finally, Chapter 7 lays out a method for designing next-generation electrolytes for ZABs. After defining a set of electrolyte performance criteria and evaluating the suitability of a range of both inorganic materials, we see that there are a wide range of organic electrolyte materials that could promote good ZAB performance. In particular, carboxylic acids, amino acids, and azoles stand out for their pH-buffering
characteristics and the favorability of ZnO precipitation. One possible embodiment of an aqueous organic electrolyte containing citric acid and glycine is proposed and the cell-level performance is simulated. The results confirm the pH stability and give insight into the behavior of the electrolyte during cycling. This first analysis of aqueous organic ZABs confirms their validity and supports further research.

Zinc-air batteries have the potential to offer cheap, safe, and high-performance energy storage. The challenges that have so-far limited them to non-rechargeable applications can be overcome with adroit material development and cell design. In the future, research should be directed towards favoring the reversible precipitation of ZnO and improving pH stability in near-neutral aqueous electrolytes.
A Thermodynamic Speciation Models

Here I give an overview of the speciation models used to determine the equilibrium concentration of the electrolytes considered in this work.

As stated in the main text, according to the law of mass action, for a system at equilibrium with a constant temperature, the value of the reaction quotient is constant. For the formation of a complex between a metal, $M$, and a ligand, $L$, this concept is expressed as,

$$M + L \rightleftharpoons ML, \quad \frac{[ML]}{[M][L]} = K_{eq}. \quad (A.1)$$

The value of the constant, $\beta$, is referred to as the equilibrium constant (sometimes also called the formation or stability constant). The equilibrium constant is an expression of the Gibbs free energy change of the reaction,

$$\log_{10} \beta = \frac{-\Delta_r G^o}{2.303RT}. \quad (A.2)$$

One special case of the equilibrium constant is the association (or binding constant), $K_a$. While the equilibrium constant describes the formation of compounds between different particles, the association constant describes the propensity of a compound to dissociate into its constituent particles and reversibly associate. This is often used to describe the behavior of weak acids and bases. Likewise, the equilibrium constant for a solid substance dissolving or precipitating in an aqueous solution is described by the solubility product constant, $K_{sp}$:

$$M + aL \rightleftharpoons ML_a(s), \quad [M][L]^a = K_{sp}. \quad (A.3)$$
Alkaline Electrolytes

The equilibrium constants and solubility product constants for alkaline electrolytes are listed in Table A.1.

Table A.1: Reactions and corresponding equilibrium constants in alkaline electrolytes [313, 248].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\log_{10} K_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H^+ + OH^- \rightleftharpoons H_2O$</td>
<td>13.96</td>
</tr>
<tr>
<td>$Zn^{2+} + OH^- \rightleftharpoons Zn(OH)^+$</td>
<td>6.5</td>
</tr>
<tr>
<td>$Zn^{2+} + 2 OH^- \rightleftharpoons Zn(OH)_2^-$</td>
<td>11.6</td>
</tr>
<tr>
<td>$Zn^{2+} + 3 OH^- \rightleftharpoons Zn(OH)_3^{-}$</td>
<td>13.8</td>
</tr>
<tr>
<td>$Zn^{2+} + 4 OH^- \rightleftharpoons Zn(OH)_4^{2-}$</td>
<td>14.7</td>
</tr>
<tr>
<td>$Zn^{2+} + 2 OH^- \rightleftharpoons ZnO(s) + H_2O$</td>
<td>-16.65</td>
</tr>
<tr>
<td>$Zn^{2+} + 2 OH^- \rightleftharpoons Zn(OH)_2^-(s)$</td>
<td>-16.52</td>
</tr>
</tbody>
</table>

Assuming that the total amount of zinc in the solution ($[Zn]_T$) and the pH of the solution is known, the concentration of $[Zn^{2+}]$ and $[K^+]$ in the solution can be determined from the equations for mass and charge conservation

$$[H^+] = 10^{-pH} \quad (A.4)$$

$$[OH^-] = \frac{10^{-13.96}}{[H^+]} \quad (A.5)$$

$$[Zn]_T = [Zn^{2+}] + \sum_{i=1}^{4} [Zn(OH)_{i}^{2-i}] \quad (A.6)$$

$$[OH^-]_T = [OH^-] + \sum_{i=1}^{4} i[Zn(OH)_{i}^{2-i}] \quad (A.7)$$

$$0 = 2[Zn]_T + [K^+] - [OH^-]_T \quad (A.8)$$
LeClanché Electrolytes

The equilibrium constants and solubility product constants for LeClanché electrolytes are listed in Table A.2.

Assuming that the pH of the electrolyte, total zinc concentration ([Zn]_T), and total chloride concentration ([Cl]_T) are known, the concentrations of the fundamental solutes [H⁺], [OH⁻], [NH₃], [NH₄⁺], [Cl⁻], and [Zn²⁺] can be calculated from the equations for mass and charge conservation.

\[
[H^+] = 10^{-pH} \quad (A.9)
\]

\[
[OH^-] = \frac{10^{-13.96}}{[H^+]} \quad (A.10)
\]

\[
[NH_3] = \frac{[NH_4^+]10^{-9.8}}{[H^+]} \quad (A.11)
\]

\[
[Zn]_T = [Zn^{2+}] + \sum_{i=1}^{4} [Zn(OH)_{2-i}^2] \quad (A.12)
\]

\[
[O\,^H^-]_T = [O\,^H^-] + \sum_{i=1}^{4} i[Zn(OH)_{2-i}^2]. \quad (A.13)
\]

\[
[Zn]_T = [Zn^{2+}] + \sum_{i=1}^{4} [ZnCl_{2-i}^2] + [ZnCl_3NH_3] + [ZnCl(NH_3)_3]+
\]

\[
\sum_{j=1}^{4} [Zn(NH_3)_{2-j}^2] + \sum_{k=1}^{4} [Zn(OH)_{2-k}^2] + \sum_{l=1}^{3} [Zn(OH)(NH_3)_{1-l}] +
\]

\[
\sum_{m=1}^{2} [Zn(OH)_{2}(NH_3)_m] + [Zn(OH)_{3}NH_3] + [ZnOHCl] \quad (A.14)
\]
Table A.2: Homogeneous electrolyte reactions and corresponding equilibrium constants [162, 163, 311, 248].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log$_{10}$$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}^+ + \text{Cl}^- \rightleftharpoons \text{HCl}$</td>
<td>-7.00</td>
</tr>
<tr>
<td>$\text{H}^+ + \text{NH}_3 \rightleftharpoons \text{NH}_4^+$</td>
<td>9.80</td>
</tr>
<tr>
<td>$\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$</td>
<td>13.96</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + \text{Cl}^- \rightleftharpoons \text{ZnCl}^+$</td>
<td>0.72</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 2 \text{Cl}^- \rightleftharpoons \text{ZnCl}_2$</td>
<td>-0.49</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 3 \text{Cl}^- \rightleftharpoons \text{ZnCl}_3^-$</td>
<td>-0.19</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 4 \text{Cl}^- \rightleftharpoons \text{ZnCl}_4^{2-}$</td>
<td>-0.18</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 3 \text{Cl}^- + \text{NH}_3 \rightleftharpoons \text{ZnCl}_3\text{NH}_3^-$</td>
<td>3.70</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + \text{Cl}^- + 3 \text{NH}_3 \rightleftharpoons \text{ZnCl(NH}_3)_3^+$</td>
<td>7.90</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + \text{NH}_3 \rightleftharpoons \text{Zn(NH}_3)_2^{2+}$</td>
<td>2.38</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 2 \text{NH}_3 \rightleftharpoons \text{Zn(NH}_3)_2^{2+}$</td>
<td>4.88</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 3 \text{NH}_3 \rightleftharpoons \text{Zn(NH}_3)_3^{2+}$</td>
<td>7.43</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 4 \text{NH}_3 \rightleftharpoons \text{Zn(NH}_3)_4^{2+}$</td>
<td>9.65</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + \text{OH}^- + \text{NH}_3 \rightleftharpoons \text{ZnOH(NH}_3)_2^+$</td>
<td>9.23</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + \text{OH}^- + 2 \text{NH}_3 \rightleftharpoons \text{ZnOH(NH}_3)_2^+$</td>
<td>10.80</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + \text{OH}^- + 3 \text{NH}_3 \rightleftharpoons \text{ZnOH(NH}_3)_3^+$</td>
<td>12.00</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 2 \text{OH}^- + \text{NH}_3 \rightleftharpoons \text{Zn(OH)}_2(\text{NH}_3)$</td>
<td>13.00</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 2 \text{OH}^- + 2 \text{NH}_3 \rightleftharpoons \text{Zn(OH)}_2(\text{NH}_3)_2$</td>
<td>13.60</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 3 \text{OH}^- + \text{NH}_3 \rightleftharpoons \text{Zn(OH)}_3(\text{NH}_3)$</td>
<td>14.50</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + \text{OH}^- + 4 \text{Cl}^- \rightleftharpoons \text{Zn(OH)}\text{Cl}$</td>
<td>6.51</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + \text{OH}^- \rightleftharpoons \text{Zn(OH)}^+$</td>
<td>6.31</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 2 \text{OH}^- \rightleftharpoons \text{Zn(OH)}_2$</td>
<td>11.19</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 3 \text{OH}^- \rightleftharpoons \text{Zn(OH)}_3^-$</td>
<td>14.31</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 4 \text{OH}^- \rightleftharpoons \text{Zn(OH)}_4^{2-}$</td>
<td>17.70</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 2 \text{OH}^- \rightleftharpoons \text{ZnO(s)} + \text{H}_2\text{O}$</td>
<td>-16.83</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 2 \text{OH}^- \rightleftharpoons \text{Zn(OH)}_2(\text{H}_2\text{O})$</td>
<td>-17</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 1.6 \text{OH}^- + 0.4 \text{Cl}^- + \text{H}<em>2\text{O} \rightleftharpoons \text{Zn(OH)}</em>{1.6}\text{Cl}_{0.4} \cdot \text{H}_2\text{O(s)}$</td>
<td>-14.2</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 2 \text{Cl}^- + \text{NH}_3 \rightleftharpoons \text{Zn(NH}_3)_2\text{Cl}_2(\text{s})$</td>
<td>-6.42</td>
</tr>
</tbody>
</table>
\[ \text{[NH}_3\text{]}_T = [\text{NH}_3] + [\text{NH}_4^+] + [\text{ZnCl}_3\text{NH}_3] + 3[\text{ZnCl(NH}_3\text{)}_3] + \sum_{j=1}^{4} j[\text{Zn(NH}_3\text{)}_j^{2+}] + \sum_{l=1}^{3} l[\text{Zn(OH)(NH}_3\text{)}_l^{1+}] + \sum_{m=1}^{2} m[\text{Zn(OH)}_2(\text{NH}_3)_m] + [\text{Zn(OH)}_3\text{NH}_3] \] (A.15)

\[ \text{[OH}^-\text{]}_T = [\text{OH}^-] + \sum_{k=1}^{4} k[\text{Zn(OH)}_k^{2-k}] + \sum_{l=1}^{3} [\text{Zn(OH)}(\text{NH}_3)_l^{1+}] + \sum_{m=1}^{2} 2[\text{Zn(OH)}_2(\text{NH}_3)_m] + 3[\text{Zn(OH)}_3\text{NH}_3] + [\text{ZnOHCl}] \] (A.16)

\[ 0 = 2[Zn]_T + [\text{NH}_4^+] - [\text{Cl}^-] - [\text{OH}^-]_T \] (A.17)
Aqueous Organic Electrolytes

The equilibrium constants and solubility product constants for citric acid-glycine electrolytes are listed in Table A.2.

Assuming that the pH of the electrolyte, total zinc concentration ([Zn]_T), total citrate concentration ([Cit]_T), and total glycine concentration ([Gly]_T) are known, the concentrations of the fundamental solutes [H^+], [OH^-], [Cit^3-], [Gly^-], [K^+], and [Zn^{2+}] can be calculated from the equations for mass and charge conservation.

\[
\begin{align*}
[H^+] &= 10^{-pH} \quad \text{(A.18)} \\
[OH^-] &= 10^{-13.96} / [H^+] \quad \text{(A.19)} \\
[HCit^{2-}] &= [Cit^3-][H^+]10^{5.33} \quad \text{(A.20)} \\
[H_2Cit^-] &= [HCit^{2-}][H^+]10^{4.08} \quad \text{(A.21)} \\
[H_3Cit] &= [H_2Cit^-][H^+]10^{2.87} \quad \text{(A.22)} \\
[HGly] &= [Gly^-][H^+]10^{9.63} \quad \text{(A.23)} \\
[H_2Gly^+] &= [HGly][H^+]10^{2.37} \quad \text{(A.24)}
\end{align*}
\]

\[
[Zn]_T = [Zn^{2+}] + \sum_{i=1}^{4} [Zn(OH)^{2-i}] + [ZnHCit] + \sum_{j=1}^{2} [Zn(Cit)^{2-3j}] + \sum_{k=1}^{3} [Zn(Gly)^{2-k}], \quad \text{(A.25)}
\]

\[
[Cit]_T = [Cit^3-] + \sum_{l=1}^{3} [H_lCit^{(3-l)}] + [ZnHCit] + \sum_{j=1}^{2} [Zn(Cit)^{2-3j}], \quad \text{(A.26)}
\]

\[
[Gly]_T = [Gly^-] + \sum_{m=1}^{2} [H_mGly^{(1-m)}] + \sum_{k=1}^{3} [Zn(Gly)^{2-k}], \quad \text{(A.27)}
\]
Table A.3: Homogeneous electrolyte reactions in the H$_3$Cit–HGly–KOH–ZnO–H$_2$O system [311, 248, 249, 178, 250].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log$_{10}$$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$ + OH$^-$ ⇌ H$_2$O</td>
<td>13.96</td>
</tr>
<tr>
<td>H$^+$ + Cit$^{3-}$ ⇌ HCit$^{2-}$</td>
<td>5.33</td>
</tr>
<tr>
<td>H$^+$ + HCit$^{2-}$ ⇌ H$_2$Cit$^{-}$</td>
<td>4.08</td>
</tr>
<tr>
<td>H$^+$ + H$_2$Cit$^{-}$ ⇌ H$_3$Cit</td>
<td>2.87</td>
</tr>
<tr>
<td>H$^+$ + Gly$^-$ ⇌ HGly</td>
<td>9.63</td>
</tr>
<tr>
<td>H$^+$ + HGly ⇌ H$_2$Gly$^+$</td>
<td>2.37</td>
</tr>
<tr>
<td>Zn$^{2+}$ + HCit$^{2-}$ ⇌ ZnHCit</td>
<td>2.98</td>
</tr>
<tr>
<td>Zn$^{2+}$ + Cit$^{3-}$ ⇌ ZnCit$^{-}$</td>
<td>4.27</td>
</tr>
<tr>
<td>Zn$^{2+}$ + 2 Cit$^{3-}$ ⇌ ZnCit$_2^{4-}$</td>
<td>5.90</td>
</tr>
<tr>
<td>Zn$^{2+}$ + Gly$^-$ ⇌ ZnGly$^+$</td>
<td>4.90</td>
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<tr>
<td>Zn$^{2+}$ + 2 Gly$^-$ ⇌ ZnGly$_2$</td>
<td>8.98</td>
</tr>
<tr>
<td>Zn$^{2+}$ + 3 Gly$^-$ ⇌ ZnGly$_3$ $^{-}$</td>
<td>11.29</td>
</tr>
<tr>
<td>Zn$^{2+}$ + OH$^-$ ⇌ Zn(OH)$^+$</td>
<td>6.31</td>
</tr>
<tr>
<td>Zn$^{2+}$ + 2 OH$^-$ ⇌ Zn(OH)$_2$</td>
<td>11.19</td>
</tr>
<tr>
<td>Zn$^{2+}$ + 3 OH$^-$ ⇌ Zn(OH)$_3$ $^{-}$</td>
<td>14.31</td>
</tr>
<tr>
<td>Zn$^{2+}$ + 4 OH$^-$ ⇌ Zn(OH)$_4^{2-}$</td>
<td>17.70</td>
</tr>
<tr>
<td>Zn$^{2+}$ + 2 OH$^-$ ⇌ ZnO(s) + H$_2$O</td>
<td>-16.65</td>
</tr>
<tr>
<td>Zn$^{2+}$ + 2 OH$^-$ ⇌ Zn(OH)$_2$(s)</td>
<td>-16.52</td>
</tr>
<tr>
<td>3 Zn$^{2+}$ + 2 Cit$^{3-}$ ⇌ Zn$_3$(Cit)$_2$(s)</td>
<td>-10.98</td>
</tr>
</tbody>
</table>
\[ [\text{OH}^-]_T = \left( [\text{H}^+] + \sum_{l=1}^{3} [\text{H}_l\text{Cit}^{(3-l)}] + [\text{ZnHCit}] + \sum_{m=1}^{2} [\text{H}_m\text{Gly}^{(1-m)}] \right) - \\
\left( [\text{OH}^-] + \sum_{i=1}^{4} i [\text{Zn(OH)}^{2-i}_i] \right). \]  
(A.28)
B  Full List of Publications and Conferences

Publications


Patents


147
Conferences


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Germany  
August 2010 - August 2013
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<table>
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<th>Volume</th>
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Erklärung
Ich erkläre, dass ich die Arbeit selbständig verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel verwendet habe.

Ulm, den ..........................................................