

Electrochemical Characterization Techniques to Systematically Study Mechanically
Rechargeable Zinc Air Battery

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ABSTRACT

The mechanically rechargeable zinc-air battery (MRZAB) shows great potential for the next generation of batteries, suitable for both grid-scale long-duration energy storage and electric vehicle applications. Recently, high battery performance has been demonstrated on a lab scale using novel slurry electrode materials and a new cell configuration. However, further efforts are required to understand the limiting factors that contribute to performance losses in the cell. This understanding is essential for identifying which components need immediate engineering and optimization. In the first study, we systematically analyzed and decomposed the electrochemical losses of MRZABs through polarization curves, utilizing a pseudo-reference electrode. By varying the position of this pseudo-reference electrode between different components within the cell, we could isolate specific components or electrochemical losses of interest. It was found that the zinc slurry electrode is more limited in the mass transport region, while the air electrode shows more sluggish behavior in the kinetic region. In the second study, we explored the lack in zinc utilization within MRZABs. Zinc utilization can be improved by optimizing the zinc slurry composition, specifically through adjustments to KOH concentration and zinc loading. In-situ three-electrode electrochemical impedance spectroscopy (EIS) revealed that the specific resistance of the zinc slurry initially increases and then decreases during the discharge process. This suggests slurry viscosity, passivation layer growth and morphologic effects plays the important roles. An empirical model was developed to account for the conductivity in low-percolation slurries, capturing the phenomenon where zinc particles are sparsely distributed in suspension. Additionally, cell-scale MRZAB design advancements have shown promising directions towards achieving practically complete removal of discharged zinc slurry. Finally, a stopped-flow experiment, combined with potential step measurements as a new approach to

characterizing mass transport within porous electrodes in a vanadium redox flow battery, demonstrated its effectiveness in characterizing quasi-stable diffusion-controlled currents.

TABLE OF CONTENTS

CHAPTER 1. INTRODUCTION	1
Rechargeable zinc air battery	6
Definition of zinc air battery performance metrics in open system.....	8
Development of mechanically rechargeable zinc air battery	13
<i>Zinc anode</i>	14
Zinc slurry Modeling developments	19
Zinc electrochemistry, mechanisms, passivation.....	20
CHAPTER 2. MATERIALS AND METHODS.....	28
Methodology	29
Polarization curve	31
Utilization curve.....	32
Resistance as a function of SOC	32
Symmetric cell testing.....	33
Conductivity measurement	33
Zinc slurry air full cell components preparation.....	33
CHAPTER 3. ELECTROCHEMICAL CHARACTERIZATION IN A SYSTEMATIC CELL TO IMPROVE PERFORMANCE OF MECHANICALLY RECHARGEABLE ZINC SLURRY AIR BATTERY	35
Introduction.....	37
Methods and materials	39
<i>Cell construction</i>	39
<i>Zinc slurry and air electrode preparation</i>	41

<i>Electrochemical measurements</i>	42
Results and discussion	45
<i>Baseline Study</i>	45
<i>Cell parameter Effects</i>	51
Conclusion	57
CHAPTER 4. NEW APPROACH TO INVESTIGATE LOW-PERCOLATION SLURRY CHARACTERISTICS TO IMPROVE ZINC UTILIZATION IN MECHANICALLY RECHARGEABLE ZINC SLURRY AIR BATTERY	58
Abstract	60
Introduction.....	60
Materials and methods	62
<i>Cell design</i>	62
<i>Slurry compositions</i>	62
<i>Electrochemical characterization</i>	63
Results and discussion	63
Conclusion	81
CHAPTER 5. DEVELOPMENT OF LAB-CELL MRZABs FOR FUTURE PROTOTYPE TECHNOLOGY AND OTHER CONSIDERATIONS	82
Motivation.....	83
<i>Design progress towards lab-scale mechanically rechargeable zinc slurry air battery</i>	83
<i>Regeneration of zinc slurry – a test in symmetric cell</i>	86
<i>Corrosion effects</i>	90

CHAPTER 6. APPLYING POTENTIAL STEPS TO CHARACTERIZE MASS

TRANSPORT OF POROUS ELECTRODE IN VANADIUM REDOX FLOW BATTERY

.....	93
Abstract	94
Background	95
<i>Fundamentals of VRFB</i>	96
<i>Developments of membrane in VRFB</i>	99
<i>Development of electrodes for VRFB</i>	101
Approach	104
<i>Battery Testing</i>	104
<i>Theory</i>	104
<i>Details of Electrochemical Tests</i>	108
Results and Discussions	109
Impact of work	121
CHAPTER 7. CONCLUSIONS	122
REFERENCES	128
VITA	139

LIST OF FIGURES

Figure 1: Reproduced comparison of different types of battery in energy density ¹⁹	4
Figure 2: Schematic of an aqueous rechargeable zinc–air battery ²⁶	7
Figure 3: Reproduced types of mechanically rechargeable zinc air battery ²⁸	9
Figure 4: Reproduced diagram of porous electrode compositions ⁴⁷	16
Figure 5: Reproduced galvanostatic discharging profile of zinc electrode with 70 mA/cm ² and three passivation steps were presented ⁶⁸	22
Figure 6: Reproduced schematic of development of zinc passivation films. a) zinc dissolution; b) zinc polymerization (due to low zincate diffusivity); c) formation of passivation film type 1; d) formation of passivation film type 2 ⁷²	23
Figure 7: Reproduced Zn ²⁺ as a function of concentration of KOH from Zhang ⁷³	25
Figure 8: Pourbaix diagram of Zn, reprinted from Yadav et al ⁷⁴	26
Figure 9: A diagram of house-made zinc slurry air battery.	30
Figure 10: a). Flow design: Modified anode bipolar plate serpentine design with width of 2 mm flow channels and other cell components adapted from alkaline fuel cell; b) Injection design: In-house made 3D printed parts for current collector holder and slurry holders and other cell components adapted from alkaline fuel cell.	40
Figure 11: A schematic of zinc slurry air battery in injection mode to assist demonstrates location of pseudo reference electrode.	43
Figure 12: a) modified serpentine flow field in graphite bi-polar plate; b) flowing zinc slurry; c) polarization curve in zinc slurry air flow battery.....	46
Figure 13: a). A photo for newly designed experimental cell; b). Polarization curves, Blue - carbon felt with MPL; Red - carbon felt without MPL.	48

Figure 14: a). Separated polarization curves (in blue Zinc anode polarization, in red Air cathode polarization) with a pseudo reference wire. ; b). Detailed separated losses between each component in the Zinc-air battery.....	50
Figure 15: a) gas-through-side, b) gas-through-middle	52
Figure 16: a) non-IR-corrected Cell polarization curves; b). Separated polarization curves by varying the concentration of KOH.....	54
Figure 17: Effects of gas flow configuration on performance of cell.....	56
Figure 18: An illustration of mechanically rechargeable zinc air battery in semi-batch mode with 1 cm thick high-capacity anode and carbon light-weight air cathode with house-made CLAM. 65	
Figure 19: Galvanostatic discharging profile under different conditions, a) pre-screening the membrane and operational mode for the cell utilization testing; investigating effects of b) zinc loading in slurry, c) discharging rate, d) KOH concentration on the cell performance.....	67
Figure 20: Discharged zinc slurry in holder view and carbon paper view with 25.3wt%, 33.6wt%, and 37.2 wt% compositions.	69
Figure 21: a) High frequency resistance as a function of thickness measured by house-made slurry symmetric cell. b) The validation analysis of contact resistance through this conductivity measurements.....	72
Figure 22:. a) Resistance as a function of (state of charge) SOC in discharging direction with three electrodes assisted to isolate cathode part. b) Derived corresponding specific resistance and conductivity values as a function of SOC. c) Illustration of EIS slurry model, highlighting the three major processes: 1. electron transfer between zinc particles; 2. Ionic transfer from mobility of hydroxide ion; 3. Interfacial charge transfer between zinc particle and KOH. d) Its	

corresponding equivalent circuit model presents R_e , R_{ion} , and R_{ct} to describe these three processes	73
Figure 23: a) SEM images for pristine manufactured Spectrum zinc powders, b) Inverted stage microscope images on pristine zinc slurry with 33 wt% zinc loading in 10x resolution, c) same microscope with focus on ‘virtually closed-enough’ particles on same slurry in 20x resolution, d) Statistical results of simulated zinc particles in slurry with fixed range diameter from 1 μm to 60 μm , e) The results of 30 Monte Carlo runs for simulated conductivity of zinc slurry based on our developed model, f) a interactive view of representative volume element (RVE in 1 mm x 1 mm x 1 mm) that captured neighbors and isolated particles with different color, g) a slice view of RVE with dimension of 400 μm x 400 μm x 100 μm	78
Figure 24: A scheme shows the volume expansion of zinc particles during discharging. Assuming no major morphologic change on zinc particle. The expansion is solely from the zinc oxide layer uniform deposition.	80
Figure 25: Design of device perspective for slurry anode in development practically viable MRZAB, a) serpentine design of flow field adapted from alkaline fuel cell that allows dual phases operation (gas and liquid); b) Modified flow field design with 2 mm width of channel for pumping slurry; c) Initial slurry injection design with 5 cm^2 and 1 cm thickness; d) Knob assisted injection design for removal purpose manually; e) A illustration of modified nickel plate holder to allow slurry injection through multichannel; f) A modified slurry multichannel holder with 2 mm thickness to hold slurry while operating the cell.	84
Figure 26: A symmetric cell testing with Zn CLAM Zn setup plating and stripping under 40 mA/cm^2 , and 100 mA/cm^2 for 12 mins current holding (6 mins for charging, and 6 mins for discharging) each cycle until 50 cycles.	87

Figure 27: A symmetric cell testing with Zn CLAM Zn setup plating and stripping under and 100 mA/cm ² for 120 mins current holding (60 mins for charging, and 60 mins for discharging) each cycle until 20 cycles.....	89
Figure 28: Discharging profile for air-exposed zinc slurry after 6 hours in full cell testing.	92
Figure 29: A sketch for general lab-scale VRFB.....	97
Figure 30: A schematic VRFB detailed setup (reproduced) ⁷³	98
Figure 31: A schematic of the battery for a stopped flow experiment.....	105
Figure 32: A general pathway of electrode electrochemical reactions.	106
Figure 33: E vs. i in 50% SOC uncorrected stopped flow in 39AA (280um)	110
Figure 34: E vs. i in 50% SOC uncorrected stopped flow in 39AA, 36AA, 29AA.....	112
Figure 35: A potential step at controlled voltage 1.51 V and monitoring current verses time with fitting after 80 seconds in 39AA (280um). Note that this process V ⁴⁺ is electrochemically oxidized to V ⁵⁺	115
Figure 36: A potential step at controlled voltage 1.304 V and monitoring current verses time with fitting after 80 seconds in 39AA (280um). Note that this process V ⁵⁺ is electrochemically reduced to V ⁴⁺	116
Figure 37: A potential step at controlled voltage 1.62 V and monitoring current verses time with fitting after 80 seconds in 39AA (280um). Note that this process V ⁴⁺ is electrochemically oxidized to V ⁵⁺ . Higher overpotential allows diffusion-controlled process reaches faster, which benefits our model fitting.....	117
Figure 38: A potential step at controlled voltage 1.22 V and monitoring current verses time with fitting after 80 seconds in 39AA (280um). Note that this process V ⁵⁺ is electrochemically reduced to V ⁴⁺	118

Figure 39: A potential step at controlled voltage 1.52 V and monitoring current verses time with fitting after 80 seconds in 29AA (180um). Note that this process V^{4+} is electrochemically oxidized to V^{5+}	119
Figure 40: A potential step at controlled voltage 1.22 V and monitoring current verses time with fitting after 80 seconds in 29AA (180um). Note that this process V^{5+} is electrochemically reduced to V^{4+}	120

CHAPTER 1. INTRODUCTION

Producing less CO₂ is an important mission in the 21st century. However, there exists a contradiction between electricity generation and CO₂ emission. Hydrocarbon resources are often burned to generate electricity, which emits a considerable quantity of CO₂ into the atmosphere. Therefore, it is critical to deploy renewable energy sources, such as wind energy, solar energy, and other forms of renewable energy sources to substitute for fossil fuels in electricity generation. These sources all have some degree of intermittency—the sun does not always shine and wind is variable. Therefore, energy storage is needed to smooth out the peaks and valleys of available electricity. There are many energy storage system (ESS) technologies available today for storing renewable energy, including pumped hydroelectric power, flywheels, fuel cells, redox flow batteries, metal air batteries, solid state batteries, and many more^{1, 2}. ESS technologies can serve as large-scale energy storage system (LSESS), which store and supply the various energy resources into grid power. One important way to manage the variability and intermittency is by using a battery energy storage system (BESS).³ The reliability of the vanadium redox flow battery makes it a notable and well-established energy storage solution for large grid plants. However, its high upfront cost and low energy density compel researchers to seek other technologies, e.g. zinc air battery. In short, electrochemical energy storage systems offer a variety of desired properties, such as CO₂-free operation, high round-trip efficiency, a long-life cycle, minimal maintenance, and energy characteristics such as rapid reaction to satisfy various grid functions in the event of an emergency.

On the other hand, about 15% of global CO₂ emissions are produced by the transportation sector⁴. Most carbon dioxide emissions in this sector are created by conventional gasoline-powered automobiles. The use of electric vehicles has the potential to resolve this issue at its core. The battery that is applied in an EV needs both high energy density and power density.

High energy density is advantageous for extended driving range, whereas high power density is excellent for rapid acceleration⁵. Lead acid batteries were the most prevalent kind of battery used in electric cars in the 1990s, despite their poor energy density⁶. Other innovative batteries, including nickel-metal hybrid, lithium-polymer, sodium-sulfur, and sodium chloride, are also being studied for use in electric vehicles^{7, 8}. Lithium-ion batteries are used in most modern EVs because they have a broad working temperature range, low self-discharge rates, high power densities, and excellent capacity retention⁹. However, lithium-ion batteries have a modest energy density of 100-200 Wh/kg, and its estimated driving range is limited to 84-249 miles per charge depending on the cathode material characteristics claimed by different companies⁹⁻¹³. For comparison, one kilogram of gasoline has a theoretical energy density of 13,000 Wh. A vehicle can travel at least 350 miles even though it only has a 12.6% practical efficiency and a real energy density of 1700 Wh/kg which is still much higher than any type of lithium-ion batteries. Consequently, it is important to the overall goal to investigate various new batteries that pack more energy.

In addition to lithium-ion batteries' poor energy density, lithium is neither a common nor cheap metal, despite its commercial dominance in a number of applications such as large energy storage systems (LESS)¹⁴, electrical vehicles (EV)¹⁵ and mobile devices¹⁶. Metal air batteries use atmospheric oxygen, decreasing battery mass and allowing for greater energy storage capacity. Due to the apparent energy density of metal air batteries, researchers have begun examining these devices¹⁷. In addition to possessing double the energy density of lithium ion, as seen in **Figure 1**, zinc is affordable (\$1.85/kg compared with \$2.75/kg of Mg-air, and \$68/kg of Li-air¹⁸), abundant, safe, and ecologically benign in comparison to other metals such as Li, Al, and Mg¹⁹. A lithium air battery has a theoretical energy density that is equivalent to that of gasoline.

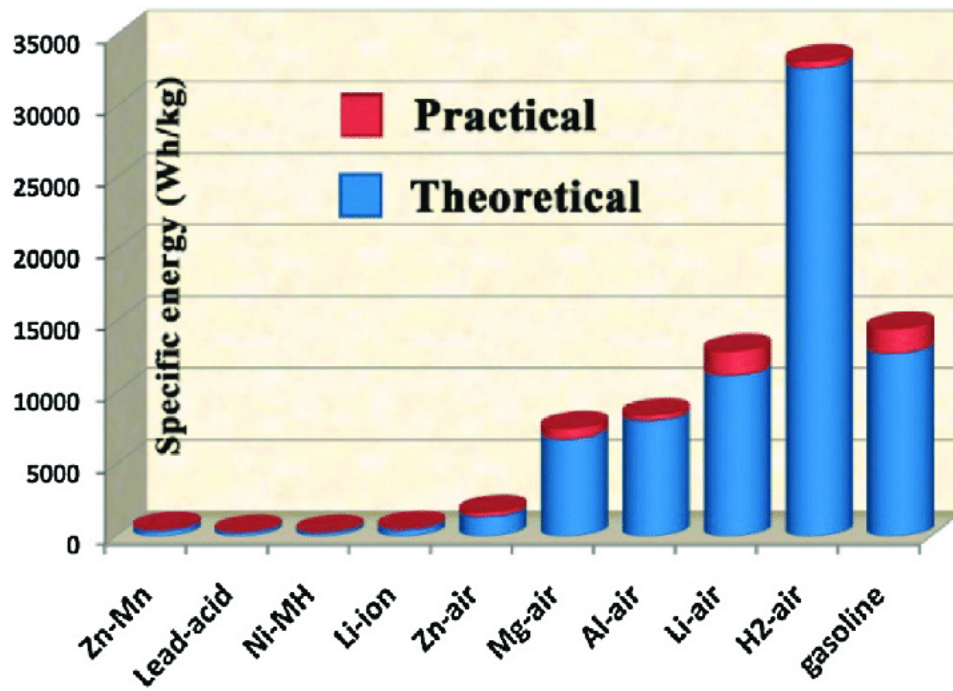


Figure 1: Reproduced comparison of different types of battery in energy density¹⁹.

However, progress in lithium air is hampered by many obstacles, including crossover of cathode product, intolerance of moisture, electrolyte degradation, and poor electrical efficiency etc^{20, 21}. Both aluminum and magnesium air batteries face the essential problem of metal corrosion, and the Al-air battery is practically irreversible. These two battery types are still in their infancy of development. It has been reported that rechargeable Mg batteries have an operating voltage in the range of 1.0 to 1.2 V and a core energy density of approximately 80 Wh/kg²². However, in terms of energy density and high operational voltage, these Mg-air batteries cannot compare to any type of Li-ion batteries.

Among all rechargeable metal air batteries, Zn air is the most commercially viable and suitable for broad application¹⁸. Zinc batteries were first realized by an invention of the Leclanché cell in 1868. It contains a zinc anode and manganese dioxide as a cathode. Over the course of a century, the primary zinc-air battery was successfully marketed in numerous applications, such as hearing aid button cells, in 1970s based on the development of thin electrodes from fuel cell research²³. The potential energy density of zinc air batteries is 1086 Wh/kg, which is approximately 5 times greater than the energy density of lithium-ion batteries currently in use. They also have the ability to be produced at costs (<\$10/kWh²⁴) that are more than an order of magnitude cheaper than lithium ion batteries. They have been hailed as the most technically and ecologically viable option to replace lithium-ion batteries in future electric vehicle applications²⁵. Despite their early origins and commercial maturity of primary cells, zinc air batteries have many challenges from the zinc anode and air catalyst cathode that inhibits development of the battery to substantially realize the theoretical energy density.

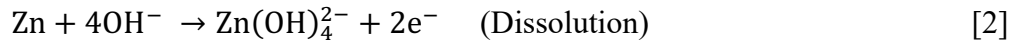
Rechargeable zinc air battery

Generally, a zinc air battery is an electrochemical cell with four main components (**Figure 2**): a zinc electrode, an air electrode made with a gas diffusion layer coated with catalysts, alkaline electrolyte, and a membrane as a separator. The cell uses oxygen from the air as an active ingredient on the cathode/positive side and, in alkaline versions, reduces it to hydroxide ions during discharging via the ORR (oxygen reduction reaction, eq. 1). The hydroxide ions moving across the membrane complex with positively charged Zn^{2+} at the zinc electrode surface to produce zincate ($\text{Zn}(\text{OH})_4^{2-}$) (eq. 2). When zincate hits its saturation concentration, it decouples into zinc oxide and water (eq. 3). Zinc oxide was formed by discharging Zn and oxygen, as illustrated in eq. 4, which represents the whole cell process.

Cathode reaction: $E = 0.4 \text{ V}$



Anode reaction: $E = -1.25 \text{ V}$



Overall reaction: $E = 1.65 \text{ V}$



The zinc air battery usually was adopted in alkaline condition because of the following benefits: 1. High conductivity of potassium hydroxide; 2. Stable operating potential; 3. High performance achieved by improving the efficiency of zinc and oxygen reactions; 4. Alternative, inexpensive catalysts (analogy from development of alkaline fuel cell) for the ORR.

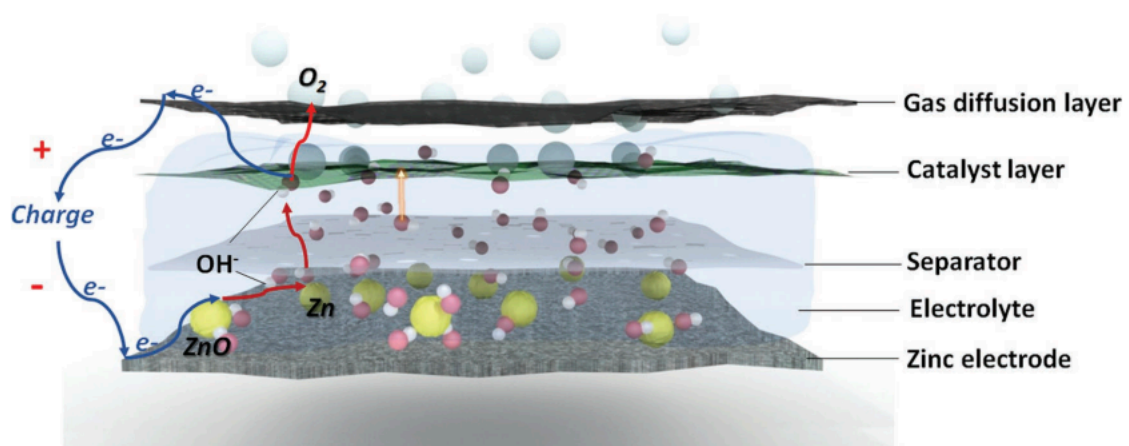


Figure 2: Schematic of an aqueous rechargeable zinc–air battery²⁶.

Secondary/rechargeable batteries can be classified into two categories in more detail: electrically rechargeable and mechanically rechargeable. An electrically rechargeable zinc air battery is recharged by using electricity. This can be achieved by developing an air electrode using bi-functional catalysts. These catalysts need to have the capability of activating both oxygen reduction (discharging) and oxygen evolution (charging). However, poor energy efficiency owing to the positive electrode and unstable zinc reversibility greatly hinders its development in a sealed cell²⁷. A mechanically rechargeable zinc air battery is recharged by mechanically replacing zinc anodes after each discharge cycle. The used zinc anode material can be recycled in a separate charging cell. The recharging or recycling of zinc oxide process is challenging and thus it is desirable to control the reaction to favor zincate formation. Known strategies that successfully handle the zinc oxide rechargeability have been patented. Two typical companies in the state-of-the-art market that focus on zinc as energy storage refillable fuel are zinc8 and ezinc. A mechanically/hydraulically rechargeable²⁸ system, as shown in **Figure 3** below, is unique in metal air batteries. I will focus on this type of battery in the remainder of my thesis. Additionally, due to the fact that our approach centers on mechanically rechargeable systems, we also only focus on discharge process. In this case, the air electrode is always the cathode, and zinc electrode is always anode.

Definition of zinc air battery performance metrics in open system

In the battery field it is quite common that researchers report ‘improved performance’, ‘higher peak power’, or ‘optimal energy density’ for specific applications. However, these battery performance metrics must be carefully defined before usage as a comparison between different technologies. For example, a mechanically rechargeable zinc air battery (an open

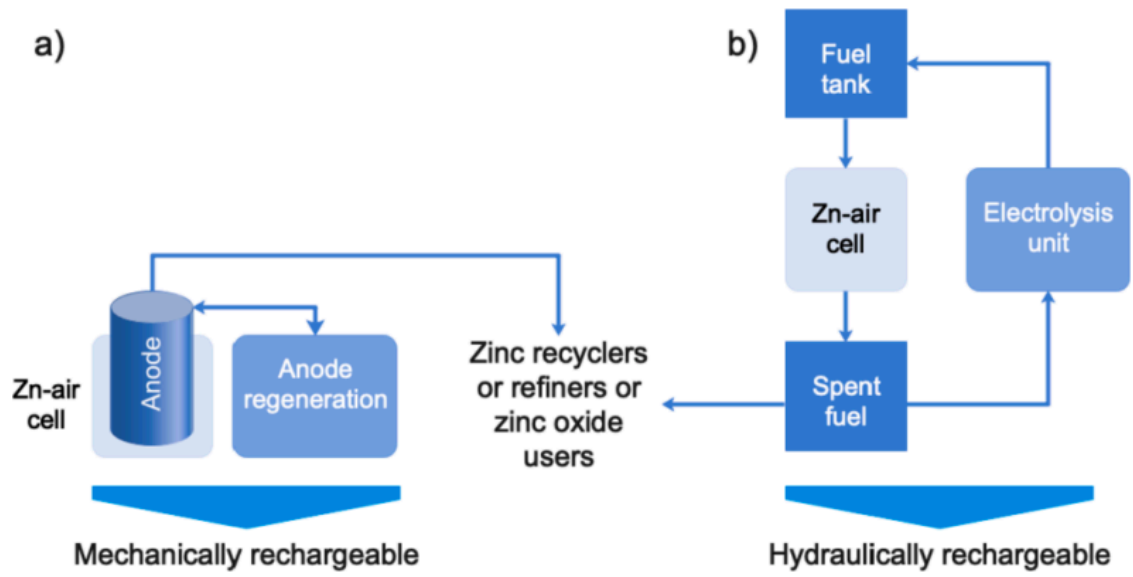


Figure 3: Reproduced types of mechanically rechargeable zinc air battery²⁸.

system summarized in **Table 1**) emphasizes the single pass discharging process. Thus, it is vital to maximize the practical capacity that can be delivered from theoretical specific capacity ($820 \text{ mAh/g}_{\text{Zn}}$) as well as the achievable current density to minimize the cost of parts in a stack. However, given that the value of specific capacity is normalized per grams of zinc (active material), the reported specific capacity or current is only a suitable metric for fundamental studies. It does not reflect practical systems because of other components in the cell level including current collector, membrane, air electrode, and gaskets that also contribute to the total weight of the cell. Also, there are other system components. Thus, specific capacity is usually not sufficient or facile to specify energy density for a new open system.

On the other hand, lithium-ion batteries (as summarized in **Table 2**) are available in commercial formats such as coin cells, cylindrical 18650 cells, and pouch cells. These designs prioritize tightly compressing all cell components, making lithium-ion batteries closed systems, which allows for relatively straightforward estimation of their energy density (Wh/kg). A key focus of these batteries is their cycle life, specifically how many cycles they can undergo before their capacity drops below 80%. This is particularly relevant for everyday applications, such as batteries used in mobile phones and electric vehicles.

To bridge the performance metrics between different batteries, a sensitivity study by the levelized cost of storage (LCOS), a key indicator for techno-economic analysis is strongly encouraged in the mechanically rechargeable zinc air battery field. However, such analyses have not yet been systematically reported in the literature, likely due to the relatively new nature of the concept, which presents challenges related to immature cell design and material selection for accurate LCOS modeling.

Table 1: A summary metric of zinc in mechanically rechargeable battery (open system)

Aspect	Performance metrics in Mechanically Rechargeable Zinc Air Battery (Open System)
Electrode Material	Zinc (Zn)
Operating Environment	Open system, often using zinc-air or zinc matrix approach in alkaline
Recharge Mechanism	Mechanical replacement of zinc anode
Specific Capacity (mAh/g)	820 mAh/g (theoretical)
Volumetric Capacity (Ah/L)	5850 Ah/L (Zn, based on density $\sim 7.14 \text{ g/cm}^3$)
Power Density (mW/cm ²)	Typically 50-100 mW/cm² (zinc-air)
Cycle Life	Long cycle life with mechanical recharging (avoiding electrochemical degradation)
Energy Density (Wh/kg)	200-470 Wh/kg (practical)
Dendrite Formation	Zinc can form dendrites in liquid electrolytes, but mechanical recharging avoids accumulation
Passivation Layer	Zinc forms ZnO/Zn(OH)₂ layers ; stable in alkaline solutions
System Type	Open system (air or external gas can interact with the battery)
Maintenance	Requires periodic mechanical replacement of zinc anode
Safety	Generally safer; non-flammable electrolyte (aqueous)
Environmental Impact	Zinc is abundant, less toxic, and easier to recycle
Cost	Lower cost, due to abundant zinc materials
Applications	Suitable for grid storage , backup power, and large-scale applications due to mechanical recharge

Table 2: A summary metric of lithium-ion battery (closed system)

Aspect	Performance metrics in lithium-ion Battery (Closed System)
Electrode Material	Lithium (Li) or graphite (anode) and transition metals (cathode)
Operating Environment	Closed system with controlled internal electrolyte (organic solvents in Li-ion batteries)
Recharge Mechanism	Electrochemical charging (Li^+ ions move between electrodes)
Specific Capacity (mAh/g)	372 mAh/g (graphite) for the anode; up to 150-200 mAh/g for the cathode (e.g., NMC)
Volumetric Capacity (Ah/L)	760 Ah/L for graphite anodes; ~1400-2000 Ah/L for NMC or LiFePO_4 cathodes
Power Density (mW/cm ²)	Typically, 150-200 mW/cm² for lithium-ion
Cycle Life	Moderate to high cycle life, but depends on managing degradation processes (dendrites, SEI, etc.)
Energy Density (Wh/kg)	250-500 Wh/kg (commercialized Li-ion)
Dendrite Formation	Lithium dendrites can form over cycles, leading to short circuits and failure
Passivation Layer	Li-ion forms a solid-electrolyte interphase (SEI); needs careful management
System Type	Closed system (sealed, no gas exchange with the environment)
Maintenance	No mechanical replacement needed; degradation handled by system design and electrolyte management
Safety	Flammable organic electrolytes pose risks of thermal runaway and fires
Environmental Impact	Li-ion has environmental challenges due to mining and disposal of rare materials
Cost	Higher cost, due to expensive and scarce materials like cobalt, lithium, and nickel
Applications	Portable electronics, EVs, and high energy density applications in a compact form factor

Development of mechanically rechargeable zinc air battery

The idea of the mechanically rechargeable Zn–Air battery was put forth from early 1986²⁹⁻³². In this kind of battery, the exhausted negative electrodes are replaced at the end of the discharge process. Compared to zinc-air batteries that are electrically rechargeable, this type of battery is capable of addressing the following two main issues: 1. Preventing or avoiding the OER during charging process; 2. avoiding the poor cyclability of zinc electrodes. In this way, the discharged zinc electrode can be regenerated electrically in a separate cell. The approach of replacing the zinc anode in a zinc air battery after discharging has been referred to as a zinc air fuel cell³². Compared with completely changing the entire negative compartment, many companies found it more practical to use a fuel cell concept with flowing Zn slurry and developed their own technology. These companies include Compagnie Generale d'Electricite (CGE), Sony, Power air, Metallic Power Inc. (MPI), and Zinc8³³⁻³⁷. However, the volumetric capacities of these technologies are limited by the large excess amount of electrolyte, the solubility of zincate and formation of zinc oxide. Less than 3% of the theoretical volumetric capacity of 5800 Ah/L was actually reached³⁵. Consequently, it is essential to conduct research into innovative patterns that can be included into this technology, allowing for greater energy density for industrial applications.

A semi-solid battery was first proposed by M Duduta et al in a lithium flow battery in 2011. The semi-solid electrode with flowability is often referred to as a slurry and it contains redox-active particles, electrolyte, and conductive material. Afterwards, many groups have exploited slurries in different redox flow batteries, such as Zn-nickel³⁸, all iron³⁹ and Zn-air,^{40, 41} because of higher energy density of the semi-solid electrode compared to that of dissolved ions. The slurry can be tuned from flowable to non-flowable by increasing the active particles

loadings, adding more gelling agent for good suspension, and mixing more conductive material to ensure electrical network percolation. A flowable slurry has less capacity and lower utilization but simpler design towards manufacturing. Recent MIT research reveals that 30% of zinc was utilized in a zinc slurry air flow battery for a total discharge time of 30 days⁴¹. Additionally, a relatively poor specific capacity of 40 Ah/L (3% utilization) was reported in a Zn-Nickel semi-solid flow battery by Zhu et al⁴². A non-flowable slurry has higher capacity and utilization because of an optimal percolation network within the slurry but it is not pumpable. Perez-Antolin et al reported non/semi-flowable zinc slurry can achieve 67–77% (546–633 mAh/g_{Zn}) zinc utilization under a discharging value (relative to areal capacity) of 13 mAh/cm² in a stagnant cell⁴³. Due to the reliability and quality of a non-flowable slurry, it is logical to build a novel mode of operation for the non-flowable mechanically rechargeable zinc air battery. This innovation has the potential to significantly expand the scope of applications.

Zinc anode

In this context, a zinc slurry is presently favored for the most promising of practical zinc air mechanically rechargeable batteries. Over several decades, many attempts have been made to build a bifunctional air electrode for zinc air electrically rechargeable batteries. These works were evaluated in comparison to a zinc foil or plate. It should be emphasized that planar zinc electrodes have a very low discharge capacity, making their use in commercial applications unfeasible. Therefore, a zinc slurry electrode with much higher surface area is suggested to replace the planar zinc foil or plate for future studies. The zinc anode of some commercial zinc-air batteries is a zinc slurry (high viscosity) in which the large weight of zinc participates in the electrochemical process. However, this zinc slurry must be reformulated to a favorable recipe of zinc slurry with lower viscosity for mechanically rechargeable zinc air batteries.

Zinc slurry electrodes (shown in **Figure 4**) are composed of active materials, binder/gelling agent, conductive material, and additives. Typically, the term "active material" refers to zinc powder. Nevertheless, secondary batteries are sometimes required to include substantial quantities of ZnO. During the discharging process, Zn ($9.15 \text{ cm}^3/\text{mol}$) is transformed to ZnO ($14.5 \text{ cm}^3/\text{mol}$), which greatly increases the volume of electrode⁴⁴. Thus, it was suggested to add zinc oxide at initial state of electrode for helping balance the cell's internal pressure⁴⁴. However, we must emphasize that adding zinc oxide reduces the initial state of charge of zinc anode which likely lowers the applied energy density of the open system. On the other hand, the rheology of the zinc slurry can also play an important role that affects the electrochemical performance of the zinc slurry in a cell. Besides these trades-off by adding zinc oxide in slurry, there is still no conclusion what ratio of Zn:ZnO best optimized the system currently.

On the other hand, the porosity of the zinc slurry impacts the performance of the zinc air battery significantly in aspects of electrode reaction kinetics and specific energy density. Changes in zinc morphology, such as shape shifts, dendritic development, and congregation, all of which lower capacity, are known to be linked to variations in porosity during the Zn slurry lifetime. For zinc particles in a slurry morphology changes leading to loss of active surface area are thought to be caused by, for example, uneven current density among the porous structure and concentration gradients in the interphase between electrode and electrolyte^{45, 46}. High surface area is needed to enhance the kinetics and utilization of zinc anode. However, it is usually challenging to optimize the applied current density to link to a specific morphology with highest porosity all the time. Even if this current density can be determined, zinc morphology still varies

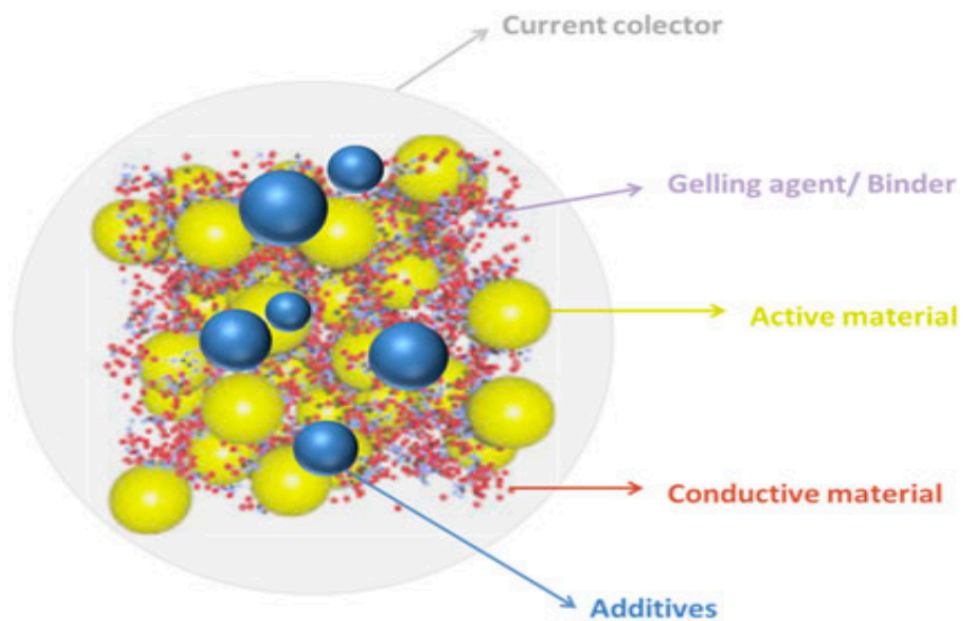


Figure 4: Reproduced diagram of zinc slurry electrode compositions⁴⁷.

with discharge time, as previously demonstrated in a SEM study by Faeph et al⁴⁸. They also reported that in a single pass of the discharge process, a zinc anode with a full state of charge has much lower porosity than the state in which the cell has already been discharging for a time, a natural process as the solid Zn is replaced by the Zn/ZnO composite electrode. Moreover, during the discharging process, under non-ideal conditions ZnO also forms on the surface of zinc, which may raise the resistance of the electrode and block a significant amount of its active surface area. Therefore, a fundamental study of the electrode evolution during discharge is needed to investigate the relationship between surface area, porosity, morphology, applied current, and discharging time within a zinc slurry electrode.

Usually, zinc foil⁴⁹/plate⁵⁰/granule⁵¹ electrodes require alkaline electrolyte constantly circulating around the zinc metal surface in the anode compartment. In contrast, the zinc slurry electrode directly carries the electrolyte. Zinc slurries are specifically formulated to include a gelling agent, such as poly acrylic acid (PAA)⁵², polyethylene oxide (PEO)⁵³, or carboxymethyl cellulose (CMC)⁵⁴. In comparison with binder, the function of gelling agent is to include zinc powders in a flowable system by suspending the particles in the electrolyte. A binder does not absorb the electrolyte whereas a gelling agent does hold the electrolyte. The gelling agent is a polymeric compound, usually present at around 1 wt%, that raises the viscosity of the electrolyte by a small amount which may greatly decrease the mobility of zinc particles to prevent dendrite formation caused by unequal current density. In addition, the ability of the gelling agent to maintain high ionic and electrical conductivity by stabilizing the zinc electrode is a further benefit. Yet it has been claimed that the gelling agent cannot sustain high current density, which causes the polymeric material to disintegrate⁵⁵. In addition, a loading of gelling agent more than 2 wt% may cause the zinc slurry to solidify and lose its flowability⁵⁶.

Zinc slurries are still in the early development stage, although they are presented as a very promising substitution of lithium-ion. Choi et al performed many studies of zinc slurry in a flow battery to optimize the current or power density. They found that including carbon additives in the slurry can improve the current density from 24 to 38 mA/cm² at 0.6 V and peak power density from 16 to 23 mW/cm² individually⁴⁰. Because adding carbon in slurry can improve the electrical conductivity through the slurry, carbon facilitates the electron transfer process in a more percolated slurry system by allowing access to more Zn. However, the trade-offs, such as decreased energy density, increased viscosity, parasitic reaction, and aggregation issues are barely discussed in this report. From an engineering standpoint, they also explore the implications of flow field and current collector material designs on battery performance. A maximum of 194 mW/cm² is produced by the combination of a serpentine flow field and a copper-nickel (70:30 alloy) current collector⁵⁷. Significant improvement has been achieved in performance from an engineering perspective. However, three electrode analysis is a must for this study to further understand why flow field design or current collector material selection matters. By using three electrode cells, we can potentially unveil more insights regarding how these engineering strategies improve specific electrochemical processes. Milian et al. evaluated zinc slurries using a rheology approach, and a 0.4 wt% optimum loading of PAA in zinc air flow batteries with adequate suspension and conductivity was identified⁵⁸. However, a flowable slurry often loads fewer zinc particles due to viscosity limitations and clogging issues. This results in less percolated zinc network that likely triggers more pronounced issues related to instability of suspension during discharging and mass transfer loss, which reduces zinc utilization. Recently, high viscosity zinc slurry was examined in a 3D printed cell, and 85% zinc utilization was achieved at 2 mm zinc anode thickness under 32 mA/cm² of discharging rate⁴³. However, as

indicated in the paper, the engineering strategy to scale up this cell has faced many challenges. Also, note that 2 mm thick zinc slurry is not practical in a mechanically rechargeable open system with only 30-40 wt% zinc as active material. Thus, to overcome the limitations in replacing a viscous zinc slurry, a systematic engineering strategy is required to overcome repeatability and scalability.

Zinc slurry Modeling developments

To achieve a homogeneous zinc suspension in harsh alkaline solution for better utilization, a high loading of zinc in a slurry, above 70wt.% of zinc, was typically used in zinc-air primary battery. Mao et al first proposed a mathematical 2D model to simulate primary zinc-air cell performance⁵⁹, and their model is aligned with experimental polarization curve data provided by MATSI, Inc. Ehsan et al reported work done with an *operando* primary zinc MnO₂ alkaline cell to reveal the different states of zinc particle morphology by scanning electron microscopy (SEM), and further modeled the conductivity of highly percolated zinc slurry anode by commercial software Geodict package⁶⁰. Mathematical models of static slurry anodes typically use results derived from percolation theory, for example, Bruggeman's approximation⁶¹ that correlates transport properties of porous media to its porosity in a comparatively simplistic assumption. However, recent advances were centered on the development of secondary zinc air battery, which potentially requires flowing zinc slurry in one side.

Wainright et al developed more experimentally connected models regarding flowing slurry behavior in an electrochemical cell⁶²⁻⁶⁴, specifically in iron slurry systems. Iron passivation is more severe than zinc in alkaline media due to iron's tendency to form a stable and dense hydroxide layer (Fe(OH)₂ and Fe(OH)₃), while Zn(OH)₂ typically exists as a porous layer. This suggests that zinc is potentially more effective for oxidation, allowing it to release capacity

more readily. Practically, the state of art zinc slurry composition for mechanically rechargeable systems is far below the percolation limit of particle loading to allow pumping or injection without considering clogging issues. Further modeling work is needed to assess the low-percolated zinc slurry conductivity and its intrinsic passivation mechanism during cell operation. A developed EIS model to characterize slurry electrode by Petek et al⁶⁵ also provides a very important link between the electrochemistry and slurry material itself. However, similar models of Zn slurries have not been reported.

Zinc electrochemistry, mechanisms, passivation

While the behavior of the zinc anode in alkaline solutions has been investigated for decades, no consensus exists about a particular mechanism. Today, there are two major processes that are used to explain the building of a passivation film: the "dissolution and precipitation" method and the "solid-state" reactions mechanism. These mechanisms emphasize different processes in the battery electrode and therefore capture different situations. The dissolution and precipitation process postulates that the zinc anode enables a reaction to occur until the zincate concentration reaches a threshold level and zinc oxide crystallizes on the electrode surface. The solid-state reaction mechanism argues that the zinc anodic performance change directly occurs with oxidation of zinc because of the formation of a solid film. These mechanisms only explain part of the passivation process. For example, the dissolution and precipitation process interprets galvanostatic test findings rationally but is not very useful to explain potentiodynamic^{66, 67} measurements due to the potential sweep process involving intricate and intermediate reaction mechanisms occurring within a limited time frame where the solid-state mechanism seems more applicable. In more details, according to the research of Liu et al, convection can prevent passivation as long as the critical concentration of zincate is not reached⁶⁸. Nonetheless,

potential-controlled measurements have demonstrated that passivation films are also produced even when the electrolyte is flowing, and that passive films form in a very short time. This result is believed to be explained by the solid-state oxidation mechanism in which direct oxidation of zinc in result of transformation to a zinc oxide film, as measurements of controlling onset potential reveal a sudden decrease in current density to zero.

The most important work on dissolution and precipitation mechanism was reported by Liu et al⁶⁸. They suggested that the passivation process can be broken down into three distinct steps (shown in **Figure 5**). During step A, the zincate starts to form with dissolution of Zn until the zincate reaches the critical saturation point. Afterwards, the agglomerated zincate transforms to zinc oxide and precipitates in a form of porous passivation film (Type 1 film) during step B. At step C, zinc oxide produces a dense film (Type 2 film) and does not allow the hydroxide ion to enter to the Zn electrode surface, fully restricting the mass transport. Previous groups determine the t_{pass} by recording the time where the potential jumps at the end of passivation process^{69, 70}. However, Liu et al proposed that it is more important to measure the t_{pass} where the passivation process starts to justify their passivation scheme above⁶⁸. They found it challenging to determine the time where critical zincate concentration is reached. Type 1 and 2 films build up because the zinc anode potential increases slightly during the galvanostatic discharging process.

Based on the dissolution and precipitation mechanism, Bockelmann et al represented the development of the passivation film in the scheme presented in **Figure 6**. By using in situ optical microscopy in conjunction with galvanostatic electrochemical impedance spectroscopy, they were able to determine the length of time required to produce so-called type 1 and 2 passivation

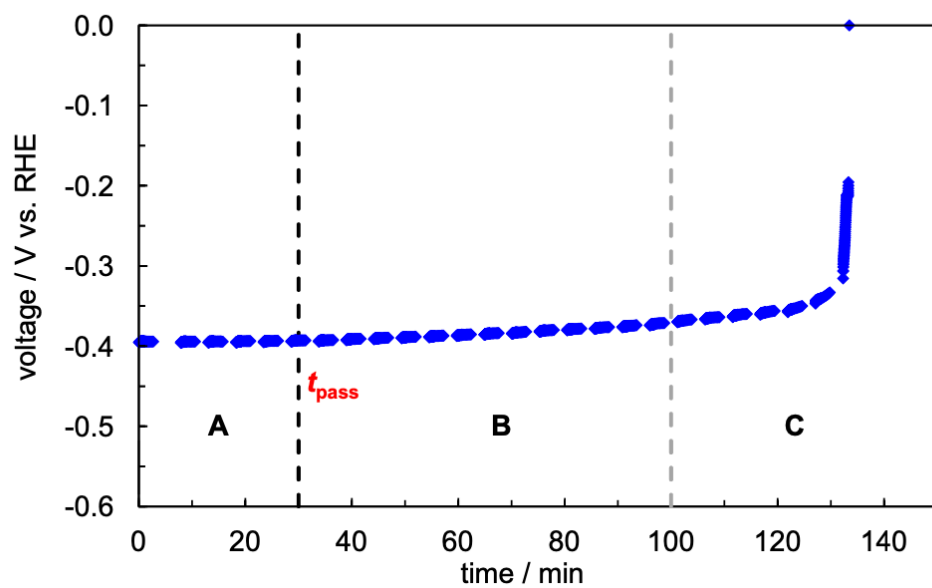


Figure 5: Reproduced galvanostatic discharging profile of zinc electrode with 70 mA/cm^2 and three passivation steps were presented according to Liu et al proposed mechanism⁶⁸.

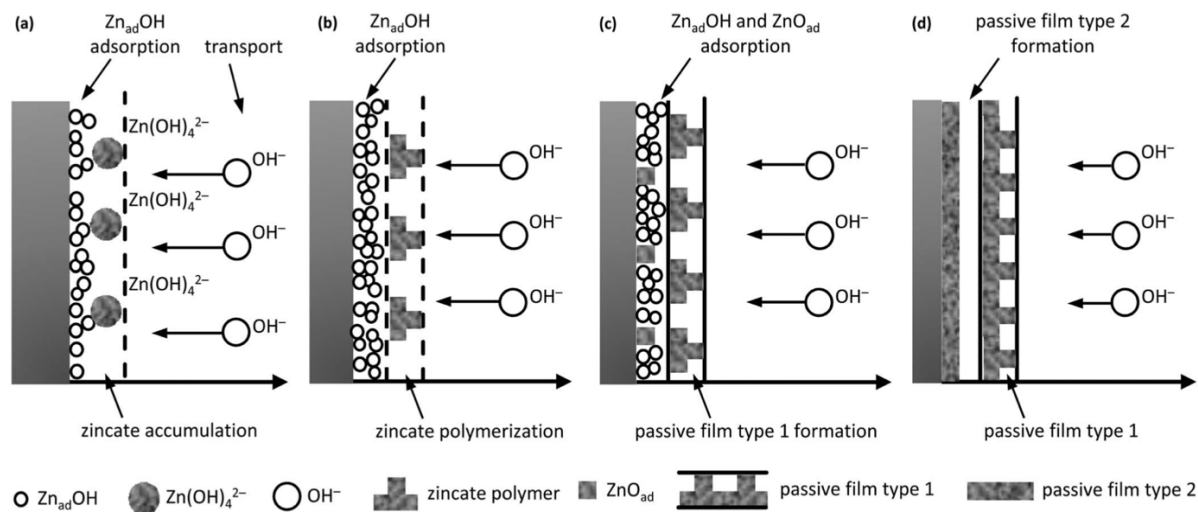


Figure 6: Reproduced schematic of development of zinc passivation films. a) zinc dissolution; b) zinc polymerization (due to low zincate diffusivity); c) formation of passivation film type 1; d) formation of passivation film type 2⁷¹.

films on a zinc planar electrode⁶⁶. In addition, in the current density range of 10-90 mA/cm², production of the so-called ‘type 1’ passivation film was shown to be independent of discharge current density. The type 1 film only occurs when zincate ions accumulate to a certain amount of $8.2 \times 10^{-4} \text{ mol cm}^{-2}$.

On the other hand, it is crucial to comprehend the general chemistry and electrochemistry governing zinc behavior in alkaline circumstances. The development of the type 1 film is directly proportional to the maximum zincate concentration in KOH, or the zinc solubility. As seen in the **Figure 7**, the solubility of Zn^{2+} in a 4M KOH solution is around 300 mM, whereas in a 12M KOH solution, it climbs to 1.5 M. By increasing the solubility of zincate, a higher concentration of KOH would delay the formation of so-called type 1 film in primary zinc air batteries, which is often preferred because it promotes high utilization of zinc.

The zinc Pourbaix diagram provides insight into the various zinc complexes and how they react to different potentials and pH levels (**Figure 8**). At >1M KOH solution (PH>14), the Zn(OH)_4^{2-} , called zincate, is the dominant product while zinc dissolves in the KOH, which was also confirmed using Raman spectroscopy by Fordyce and Baum⁷². The Pourbaix diagram is very useful to predict stable phases or complexes occurring as a result of electrochemical processes. For example, zinc in alkaline condition tends to form zincate and zinc oxide which prevents the corrosion. In acid, the hydrogen evolution side reaction is much more severe and zinc dissolves to form Zn^{2+} . To suppress the corrosion behavior and simplify the zinc medium product, zinc-air battery usually operates in strong alkaline condition (pH>14). Thus, it is very important to study zincate in any zinc-based alkaline batteries. An ex-situ method, the rotating disk electrode, was used to evaluate the diffusion coefficient of zincate ion by Pessine et al⁷³.

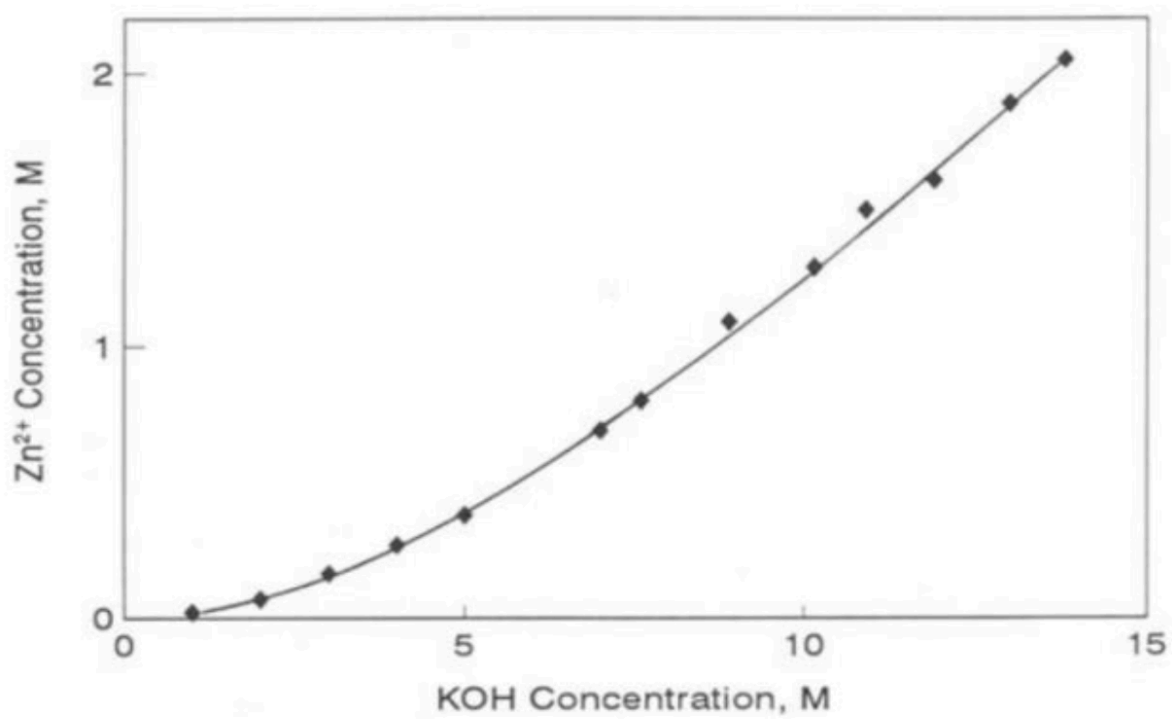


Figure 7: Reproduced Zn²⁺ as a function of concentration of KOH from X. Zhang⁷⁴.

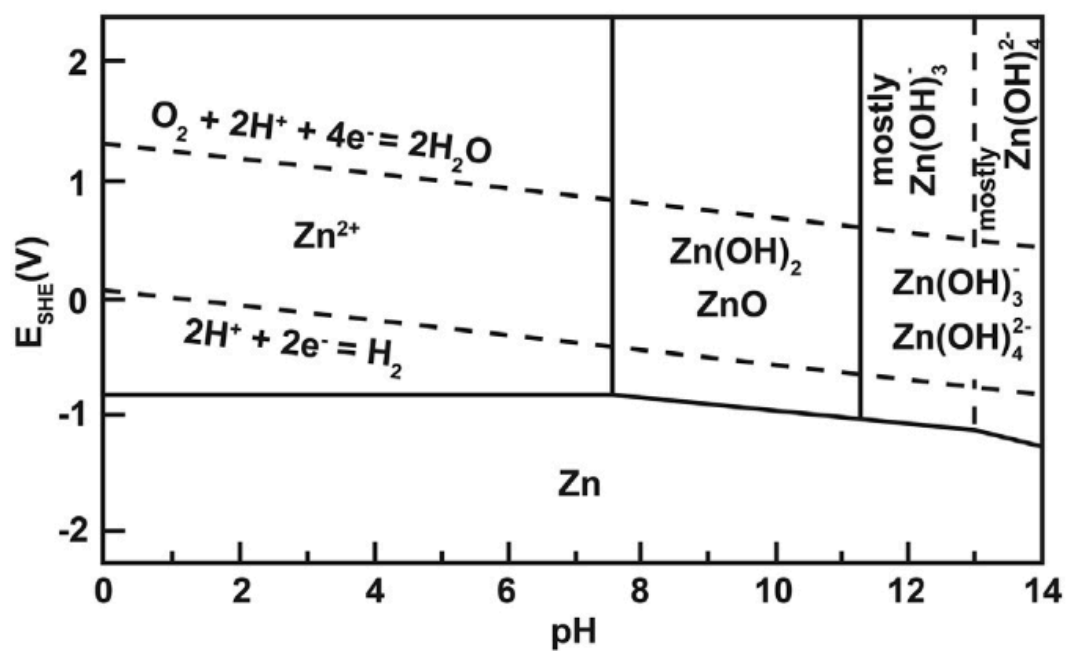


Figure 8: Pourbaix diagram of Zn, reprinted from Yadav et al⁷⁵.

At room temperature (25 °C), the diffusion coefficient of zincate is $4.8 \times 10^{-6} \text{ cm}^2/\text{s}$ at 1M NaOH, which significantly decreases to $2.9 \times 10^{-6} \text{ cm}^2/\text{s}$ at 4M NaOH because of the viscosity effect. As the diffusion rate of zincate ion was reported to be much slower than hydroxide ion (by an order of magnitude) the zincate is more likely congregated in the vicinity of electrode, which eventually causes the type 1 film.

CHAPTER 2. MATERIALS AND METHODS

Methodology

The research plan consists of detailed electrochemical characterization of zinc slurry in terms of power density (polarization curve), utilization (galvanostatic discharging profile), and resistance (Nyquist plot).

1. Synthesizing the basic or viable zinc slurry for MRZAB in flow mode.
2. Designing a new cell by deploying the injection mode for highly viscous slurry.
3. Determine the losses of individual components in the cell by implementing a pseudo reference electrode.
4. Determine the effects of KOH concentration and gas flow arrangement into the cell on overall performance of the battery.
5. Determine the zinc utilization in a symmetric and full cell under different discharging rate.
6. Determine the zinc slurry regeneration in a symmetric cell.
7. Determine the zinc slurry's resistance as a function of state of charge during discharging.

Using the zero-gap cell design as previously shown for a redox flow battery⁷⁶, a sketch for modified zinc slurry air cell is shown in **Figure 9**.

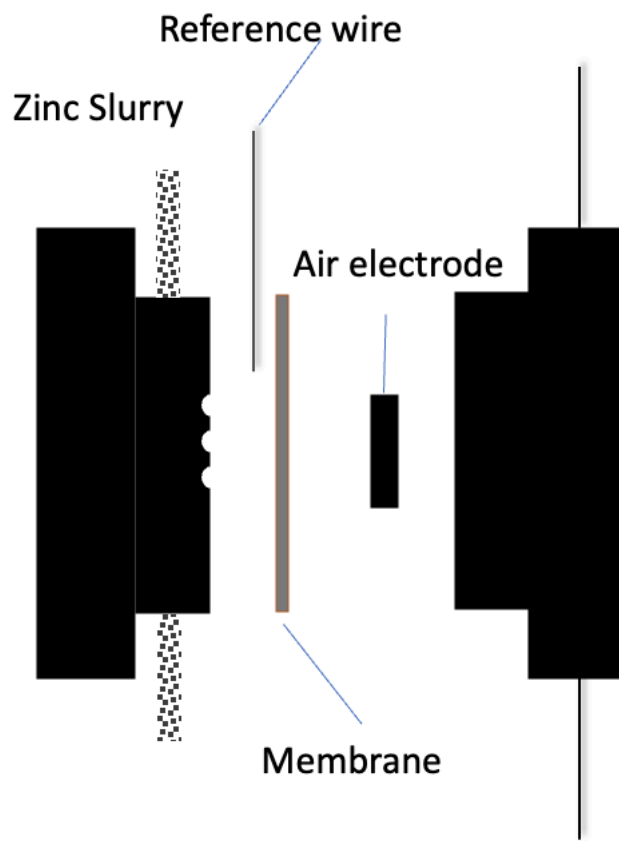


Figure 9: A diagram of house-made zinc slurry air battery.

Polarization curve

To measure the performance of the electrochemical cell, one typical method is the polarization curve, a steady-state determination of cell voltage or electrode potential as a function of applied current density. Experiments using the cell shown in Figure 9 and using the prepared components (electrodes, membrane) were performed using a house-made test stand and single cell hardware. A BioLogic SP-150 potentiostat with a 20 A booster was used to collect polarization curves and Nyquist plots through potentiostat-electrochemical impedance spectroscopy (PEIS). The cell featured a serpentine flow channel on the cathode and an active area of 5 cm².

The temperature was fixed at room temperature without any control, and no back pressure or relative humidity were controlled for all the experiments. Inlet gas on the cathode, whether oxygen or synthesized air, was fixed by a Masterflex flowmeter to a flow rate of 0.2 L/min. Electrolyte was induced into the cathode side for maintaining membrane wet with a slow flow rate of 6 rpm controlled by a master flex peristaltic pump. The battery was assembled with applied torque of 80 lb.

The polarization testing protocol was the following: A home-made pseudo reference electrode (Cu/Pd wire) was inserted in the cell for a three-electrode testing setup. Compared with a two-electrode setup for measuring polarization losses, it can separate the losses between anode and cathode, which makes the in-situ characterization of performance more accurate in each of components of the cell. After the cell was assembled, the cell was attached to leads and connected to a computer and a potentiostat. The OCV was monitored for 10 mins to ensure the battery stability. A polarization curve was obtained by decreasing the potential in steps of 25 mV from OCV to Ewe1 and 50 mV from Ewe1 to Ewe2, and each potential was held constant for 60

seconds for recording the current. Safety control was fixed by a pause when the total cell voltage dropped to 0.1 V.

Utilization curve

In a slurry, access to the full loading of active material is not guaranteed. Therefore, the utilization must be determined experimentally. The utilization testing protocol involved the following steps: After assembling the cell, it was connected to a probe, computer, and potentiostat in a two-electrode testing setup. The open-circuit voltage (OCV) was monitored for 10 minutes to ensure the battery's stability. A utilization curve was obtained by continuously discharging the battery at a constant current density and recording voltage shifts. A safety control was established by pausing when the total cell voltage dropped to 0.1 V.

Resistance as a function of SOC

In a MRZAB, the utilization is strongly connected to behavior of the zinc slurry during discharge. To understand its characteristics, we measure the resistance of slurry as a function of SOC during discharging process to gain more insights of the cell. The resistance testing protocol employed a custom-made pseudo reference electrode (Cu/Pd wire) inserted into the cell for a three-electrode testing setup. After assembling the cell, it was connected to leads, computer, and potentiostat. The OCV was monitored for 10 minutes to ensure the battery's stability. Resistance profiles were obtained by periodically discharging the battery using Chronopotentiometry (CP) and subsequently measuring the impedance through a frequency scan from 200 kHz to 1 Hz using Potentiostatic Electrochemical Impedance Spectroscopy (PEIS).

Symmetric cell testing

An in-house-customized symmetric cell was applied to measure the reversibility of the zinc cell. The symmetric cell was assembled in a 3D-printed plastic slurry holder, varying thickness from 10 mm to 20 mm, and area of 5 cm², with two nickel plates serving as current collector and a membrane as separator. Two types of membranes were used in this study: a porous membrane Celgard 3501 and a CLAM (cross-linked anion exchange membrane), a cross-linked KOH-loaded gel that was synthesized in house. The current density for stripping and plating was fixed at 10 mA/cm², 50 mA/cm², 100 mA/cm² to estimate its columbic efficiency.

Conductivity measurement

A modified design adapted from the symmetric cell, with no membrane and two nickel plates and one slurry holder for desired thickness, was applied to measure the impedance of the zinc slurry by EIS with 200 kHz to 1 Hz. The as-acquired Nyquist plot was obtained to calculate the high frequency resistance (R) for zinc slurry. The conductivity of slurry (σ) was derived from the following equation.

$$\sigma = \frac{L}{A * R}$$

[5]

Zinc slurry air full cell components preparation

Zinc slurry was prepared by mixing zinc powder (Spectrum, 325 mesh (50 μ m), ~95% purity), polyacrylic acid (Sigma-Aldrich, viscosity ~40,000-60,000 cP), and 4M KOH solution (Assay 85%) by following a recipe from Choi et al⁴⁰. The experimental procedure involved the following steps: 1) Pipetting 8 ml of 4M KOH into a 12 ml syringe; 2) Adding 0.112 g of polyacrylic acid and homogenizing for 2 minutes at a speed of 10,000 rpm to polymerize the KOH solution; 3) Adding 4.8 g of zinc powder and homogenizing for 2 minutes at the same

speed to ensure uniform and stable slurry mixing. The air electrode was fabricated by formulating inks and employing spray painting. The ink was prepared by mixing Pt on carbon powder, binder, polytetrafluoroethylene (PTFE), and isopropanol (IPA). We acknowledge Dr. Shane for providing the poly(phenylene oxide) (PPO)-based crosslinked anion exchange membranes for battery testing.

Note that all measurements were tested under room temperature without controlling (roughly 25 °C).

Other experimental methods were also used in the study related to vanadium redox flow battery which are discussed in the later context in Chapter 7.

CHAPTER 3. ELECTROCHEMICAL CHARACTERIZATION IN A
SYSTEMATIC CELL TO IMPROVE PERFORMANCE OF MECHANICALLY
RECHARGEABLE ZINC SLURRY AIR BATTERY

This chapter was adapted from paper entitled “Systematically Electrochemical Characterization to Improve Performance of Mechanically Rechargeable Zinc Slurry Air Battery” **under revision**, 2024.

In this study, we aim to enhance the performance of mechanically rechargeable zinc slurry-air batteries by analyzing and breaking down the sources of electrochemical losses. Using both flow and batch modes in a three-electrode setup with a pseudo-reference, we can isolate and quantify the contributions of each electrode to the overall losses. This targeted approach allows us to focus on optimizing individual processes within the cell, ultimately informing the redesign of the flow field and slurry chamber to improve efficiency and battery performance systematically.

Introduction

The demand for energy storage continues to escalate in both the transportation sector⁷⁷ and the stationary market⁷⁸. This surge is attributed to the burgeoning market for electric vehicle batteries and the need to establish gigawatt-hours (GWh) of storage capacity for grid-related applications in many global regions. Lithium-ion batteries are used in most modern electrical vehicles that dominates current EV market because they have a broad working temperature range, low self-discharge rates, high power densities, and excellent capacity retention⁹. However, lithium-ion batteries have a modest energy density of 100-200 Wh/kg, and its estimated driving range is limited, depending on the cathode material characteristics claimed by different companies⁹⁻¹³. The significant upfront cost of lithium-ion batteries, priced at \$152 per kWh in 2023, challenges their cost efficiency when considered for stationary storage applications. Accordingly, other energy storage devices such as vanadium redox flow batteries⁷⁹, organic redox flow batteries⁸⁰ and metal-air batteries⁸¹ have been evaluated to for application in long-duration energy storage and high energy density systems are sought for transportation applications.

Metal air batteries use atmospheric oxygen flowed into an open system, decreasing battery mass by removing the need for reagent storage, allowing for higher gravimetric energy storage capacity. Zinc-air batteries possess a theoretical energy density of 1086 Wh/kg, making them candidates for applications requiring high energy density. Also, Zinc-air batteries have been touted as the most technically and ecologically viable option to replace lithium-ion batteries in future electric vehicle applications²⁵, with economic and supply chain advantages.

Zinc-air batteries have evolved considerably over the decades, transitioning from primary to secondary forms. Secondary zinc-air batteries can be categorized into electrically and

mechanically rechargeable types²⁸. Extensive research has been dedicated to identifying highly efficient bi-functional catalysts that are active in both the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) to facilitate the development of electrically rechargeable zinc-air batteries⁸². However, pursuing catalysts for zinc-air batteries presents inherent challenges and can be time-intensive. Additionally, the growth of dendrites within the zinc anode poses a significant challenge, reducing the battery's lifespan during cycling. Based on these considerations, the mechanically rechargeable zinc-air battery (MRZAB) emerges as a more efficient approach because its operation centers primarily on discharge performance using stable ORR catalysts and manually replacing the discharged zinc anode. Many companies developed MRZABs based on this concept, such as Compagnie Generale d'Electricite (CGE), Sony, Power air, Metallic Power Inc. (MPI), and Zinc⁸³⁻³⁷. M. Duduta et al introduced a semi-solid electrode (i.e. slurry) in a redox flow battery, which further refined the concept of MRZAB⁸³. The slurry comprises active particles engaging in the redox reactions, along with the electrolyte and conductive additives. Several groups have exploited slurries in different redox flow batteries, such as Zn-nickel³⁸, all iron³⁹ and Zn-air,^{40, 41} because of the higher energy density of semi-solid electrode compared to that of dissolved ions. The practical flowability of slurry is directly determined by its rheology. D. Milian et al reported a systematic rheological study of the poly(acrylic acid) (PAA) loading effects on stability of the zinc slurry⁵⁸. They highlighted optimal performing slurry contains 0.4 wt% loading of PAA and its yield stress is 45 Pa. Further increasing binder loading can result in lower conductivity and sacrifice the electrochemical performance in a zinc slurry air flow cell. Thus, it should be emphasized that a flowable slurry with relatively low yield stress has less capacity but a simpler design for manufacturing. Recently, Choi et al found that introducing carbon additives into the slurry can improve the

current density from 24 to 38 mA/cm² at 0.6 V and the power density from 16 to 23 mW/cm² in zinc slurry-air flow cells⁴⁰. From an engineering standpoint, they also explored the implications of flow field and current collector material designs on battery performance. A maximum of 194 mW/cm² is produced by the combination of a serpentine flow field and a copper-nickel (70:30 alloy) current collector⁵⁷. Perez-Antolin et al used a cell area of 7 cm² with a zinc anode thickness of 0.2 cm to implement an injection mode for a ‘semi-flow’ zinc slurry, and they attained 100 mA/cm² with carbon loading of 80 mg/mL in this configuration⁴³. However, interpreting losses from individual components in the cell remains a challenge, complicating the assessment of zinc slurry performance across various designs.

In this study, we aim to dissect the losses from each component in a zinc slurry-air battery, whether operated in flow or injection mode. Current MRZAB designs utilizing zinc slurries present ambiguous loss contributions within the cell, leaving it uncertain as to which component predominantly contributes to this loss. To address this, we introduce a pseudo reference electrode in the zinc slurry air cell to separate distinct effects. Utilizing this approach, we further examined how various cell parameters, including zinc anode design, KOH concentration, orientation of gas flow, air electrode architecture, and catalyst choices, influence the performance of the cell.

Methods and materials

Cell construction

Two zinc air battery designs, shown in **Figure 10** (a-b), were used in this work for handling the zinc slurry. The first is a ‘flow design’, which is inspired by the redox flow battery that circulates zinc slurry through zinc anode compartments. To prevent the obstruction of zinc access to a current collector during circulation, the serpentine flow field was enhanced with

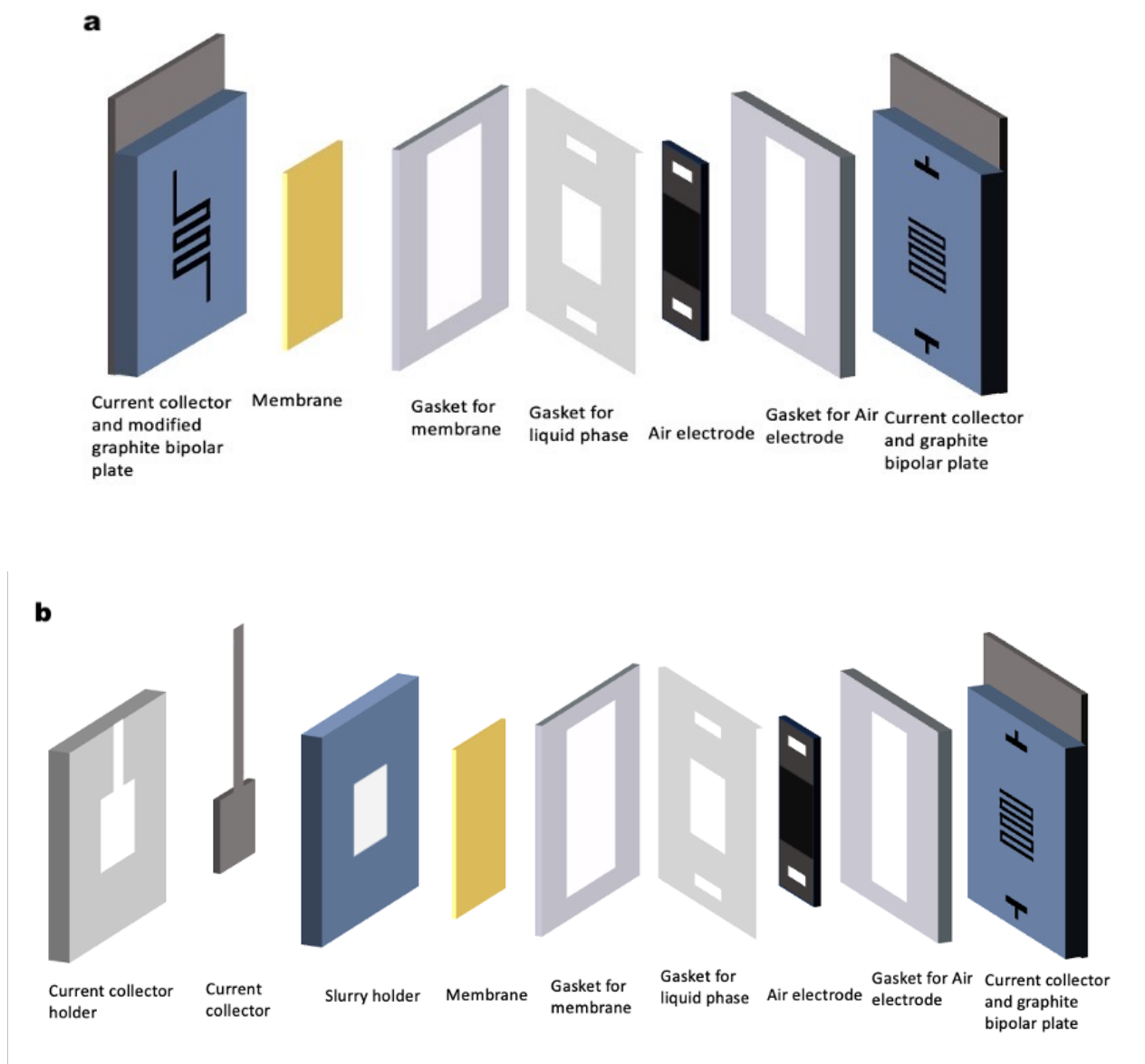


Figure 10: a). Flow design: Modified anode bipolar plate serpentine design with width of 2 mm flow channels and other cell components adapted from alkaline fuel cell; b) Injection design: In-house made 3D printed parts for current collector holder and slurry holders and other cell components adapted from alkaline fuel cell.

broader flow channels. A nickel plate, acting as the current collector, was coupled with a graphite bipolar plate. The second is the ‘injection design’. Using Autodesk Inventor®, we designed the current collector and slurry holders. These components were then fabricated using 3D printing with a 100% infill of (acrylonitrile butadiene styrene) ABS material. A precision-cut nickel plate, serving as the current collector, was positioned between the 3D printed parts. On the air side, a graphite bipolar plate was tailored to accommodate dual phases, and this was attached to the Nickel plate current collector. While the battery was in operation, the KOH electrolyte and gas were simultaneously introduced on the channel-side interface of the air electrode. Using the binary electrolyte-gas phase is necessary for supplying water for the ORR and preventing membrane dehydration. To ensure a leak-proof system and facilitate membrane wetting, Viton gaskets were strategically integrated and created a dedicated liquid phase gap.

Zinc slurry and air electrode preparation

Zinc slurries were prepared by mixing zinc powder (Spectrum, 325 mesh (~50 μm), ~95% purity), polyacrylic acid (Sigma-Aldrich, viscosity ~40,000-60,000 cP), and 4M KOH solution (Assay 85%), following the recipe from Choi et al⁴⁰. The experimental procedure was modified and involved the following steps: 1) Pipetting 8 ml of 4M KOH into a 12 ml syringe; 2) Adding 0.112 g of polyacrylic acid and homogenizing for 2 minutes at a speed of 10,000 rpm to make a gel form of the KOH solution; 3) Adding 4.8 g of zinc powder and homogenizing for 2 minutes at the same speed to ensure uniform and stable slurry mixing.

The air electrode was fabricated by formulating catalyst-containing inks and employing spray painting on a gas diffusion layer (GDL). The ink was prepared by Pt/C (HiSPEC 4000, Alfa Aesar) or an in-house made non-PGM catalyst, polytetrafluoroethylene (PTFE), Dimethyl-Imidazolium poly(p-phenylene oxide) (DmIm-PPO) (5 wt% sol in methanol), and isopropanol

(IPA). This non-PGM catalyst is obtained by pyrolysis of an iron salt, a nitrogen source and Kudzu leaves biomass (FeKudzu). Catalyst synthesis details are described in the SI. Additionally, a potential enhancement involved introducing thin carbon layer coated onto the GDL, functioning as a microporous layer (MPL). The spray-painting temperature was held at 80 °C. The details of fabricating steps are given in the SI.

CLAM membranes were prepared in house. A solution of 2-Methylimidazole (0.821 g, 0.01 mol) in NMP (5 mL) was stirred vigorously while NaH (60% wt, 0.02 g, 0.5 mmol) was added. The mixture was then stirred at 85 °C for half hour, followed by ultrasonic agitation in a sonic bath for additional half hour. Subsequently, 2.2 mL of this solution was then added to a stirred solution of bromomethylated polyphenylene oxide polymer in NMP (10% wt. obtained from Akron Polymers, 8 mL, 2.024 mol –Br). The combined solution was stirred for 3 minutes and then cast onto a glass plate using a doctor blade. The plate was heated at 95 °C for 2 hours in oven and then submerged in a deionized water bath to facilitate isolation of the CLAM membrane (100-110 µm). The membrane was soaked overnight in deionized water and then equilibrated with electrolyte before use.

Electrochemical measurements

To measure the performance of the electrochemical cell, a typical method used is the polarization curve, a steady-state determination of cell voltage or electrode potential as a function of applied current density. Experiments using the cell shown in **Figure 11** and using the prepared components (electrodes, membrane) were performed using a house-made test stand and single cell hardware. A BioLogic SP-150 potentiostat with a 20 A booster was used to collect polarization curves and Nyquist plots through potentiostat-electrochemical impedance

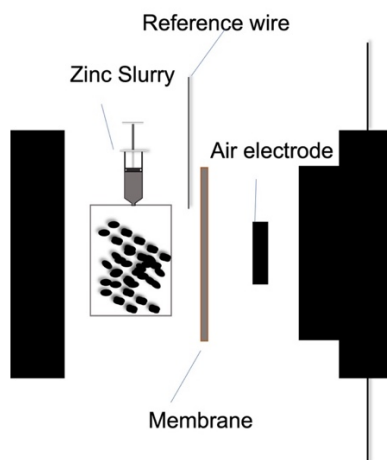


Figure 11: A schematic of zinc slurry air battery in injection mode to assist demonstrates location of pseudo reference electrode.

spectroscopy (PEIS). The cell featured a serpentine flow channel on the cathode and an active area of 5 cm².

The battery was operated at room temperature without any control, and neither back pressure or relative humidity were controlled for all the experiments. The inlet gas on the cathode, oxygen, was controlled using a Masterflex flowmeter to a flow rate of 0.2 L/min. Electrolyte was introduced into the cathode side to maintain a wet membrane with a slow flow rate of 6 rpm, controlled by a Masterflex peristaltic pump. The battery was assembled with applied torque of 80 lb.

The polarization testing protocol was as follows: A home-made pseudo reference electrode (Cu/Pd wire) was inserted in the cell for a three-electrode testing setup. Compared with a two-electrode setup for measuring polarization losses, the three-electrode system allows separation of the losses between anode and cathode, which enables the in-situ characterization of performance of each of the components of the cell. The OCV was monitored for 10 mins to ensure the battery's stability. The polarization curve was generated by reducing the potential in 25 mV increments from the open circuit voltage (OCV) to Ewe1 over 12 data points, and then continuing to decrease the potential in 50 mV steps from Ewe1 to Ewe2, taking 5 data points in this range. Each potential was held constant for 60 seconds, recording the current. A safety control was fixed by a pause when the total cell voltage dropped to 0.1 V.

Results and discussion

Baseline Study

Zinc slurry-air flow batteries provide the same benefits as redox flow batteries and store energy in external tanks. A zinc slurry packs much more energy density compared with traditional aqueous system because solubility of the redox active material is less of a limitation. Learning from the zero-gap design of redox flow batteries⁸⁴ and binary phase strategy from alkaline fuel cells, we used a similar approach to combine anode and cathode structures in cells to set up our zinc slurry air flow battery. However, we quickly realized that the channel of a typical serpentine flow field for all vanadium redox flow battery is too small to allow the viscous zinc slurry to flow in, which causes the anode flow channels to clog. We adjusted the channel as shown in **Figure 12a**, which partially resolved the clogging issues. Roughly 50 ml of zinc slurry (**Figure 12b**) was formulated for circulation inside the cell. **Figure 12c** depicts the polarization curve of the cell, which shows a reasonable open circuit voltage (OCV) of 1.45 V (thermodynamic potential or theoretical OCV is 1.65 V). In operation, the cell shows a significant kinetic loss (~ 0.15 V overpotential at 5 mA/cm²). The cell operates at 40 mA/cm² at 1 V under oxygen. This performance is comparable to that of a recent zinc slurry air flow battery presented by Choi et al⁴⁰. Nonetheless, the zinc slurry may still occasionally clog the cell, limiting the mass transport of Zn and drastically reducing cell performance. The clogging concerns at least partly arise from the stability and viscosity of the slurry during discharge. It is not yet clear how the mechanisms and characteristics of the discharging zinc slurry affect the stability of slurry. Thus, to deal with the viscous slurry, we switched the operating mode from pumping continuously to injection in semi-batch, which necessitates a redesign of the zinc-side cell structure.

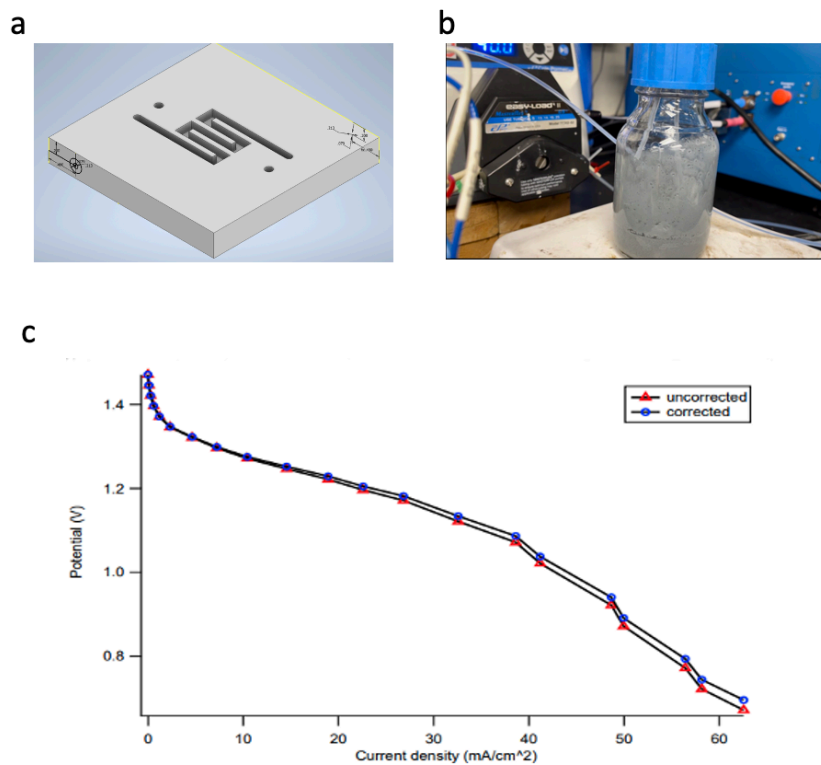
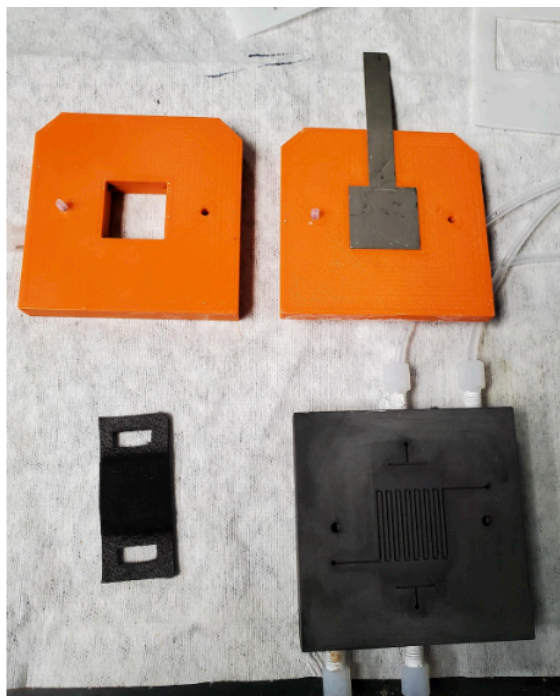


Figure 12: a) modified serpentine flow field in graphite bi-polar plate; b) flowing zinc slurry; c) polarization curve in zinc slurry air flow battery.

For optimizing the injection mode to fully address the clogging issue, a novel and straightforward design for the zinc side of the cell was developed utilizing 3D printing with (acrylonitrile butadiene styrene) ABS material. The two primary components are depicted in **Figure 13**. The left orange component is the slurry holder, featuring injection holes and channels on the upper left and right sides. The right orange component is the current collector holder, which contains a 1.5 mm thick nickel plate current collector. A rudimentary mechanically rechargeable zinc-air battery was assembled by placing the slurry holder onto the current collector holder. Practical testing demonstrated that the battery does not experience clogging during injection. Nonetheless, this does not allow for the complete removal of slurry at the end of the discharging cycle.

Polarization curves were obtained using the same two-electrode testing setup applied to cells with the new design. A comparable open-circuit voltage (OCV) of 1.42 V was observed with this configuration. With the injection design, we achieved a peak power density of 80 mW/cm² (corresponding to 100 mA/cm² at 0.8 V). Using an MPL-coated air electrode led to further increase of the power density, reaching 180 mW/cm² (equivalent to 200 mA/cm² at 0.9 V). In the polarization curve, an initial overpotential of 0.15 V was attributed to kinetic loss. Within a cell voltage range of 1.25 V to 0.8 V, the voltage-current (V-I) curve displays a linear trend. In this region, the primary losses are due to internal resistance and, to a lesser extent, residual mass transport. The ASR of air electrodes were measured as 1 ohm*cm² with MPL, and 0.865 ohm*cm² without MPL. This suggests the blue curve exhibits a larger internal resistance (IR) correction than the red curve, suggesting that the addition of a microporous layer (MPL) significantly enhances oxygen mass transport but also increases the internal resistance of the cathode. This observation is consistent with the fact that carbon felt with an MPL has a greater

a



b

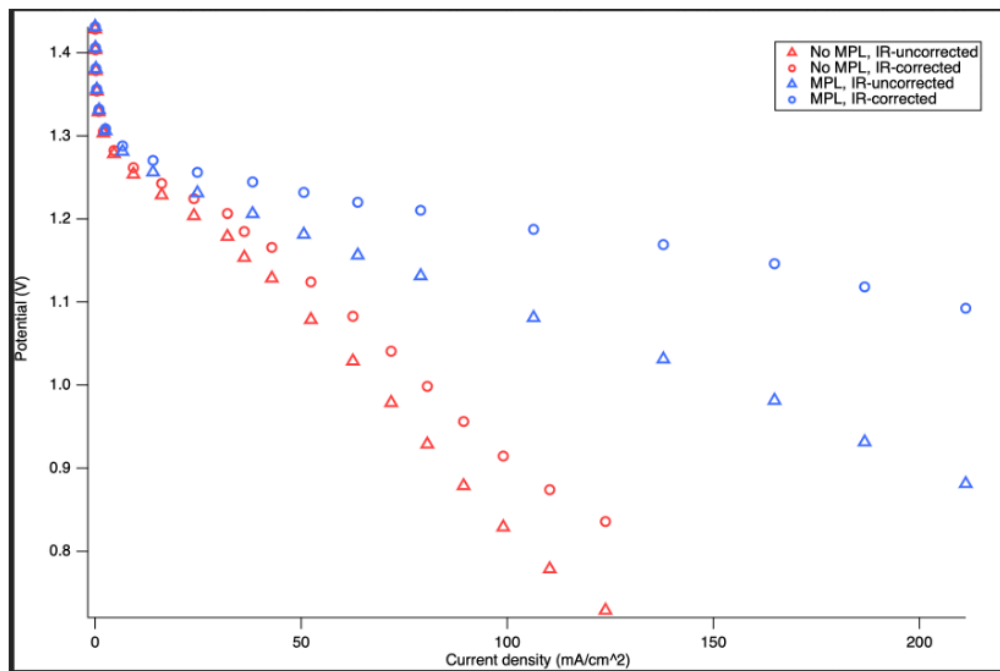


Figure 13: a). A photo for newly designed experimental cell; b). Polarization curves, Blue - carbon felt with MPL; Red - carbon felt without MPL.

thickness than carbon felt without an MPL. To further elucidate the contributions of various losses, it is necessary to incorporate a reference electrode into the cell to separtate these factors.

Contributions from the two electrodes to overall polarization were isolated by incorporating a pseudo-reference electrode (Pd coated Cu wire) into the system. Subsequently, polarization curves were obtained using this three-electrode setup. In **Figure 14a**, the red curve represents cathode performance, while the blue curve illustrates the voltage-current (V-I) responses of the zinc anode and membrane. In the region below 5 mA/cm², the red curve exhibits sharp overpotential losses compared to the relatively flat losses observed in the blue curve. This suggests that sluggish oxygen kinetics primarily contribute to the losses. As the current density is increased to 80 mA/cm², losses from the zinc side become more pronounced. According to results from Mao et al⁵⁹, they suggest that the major limiting factor is the depletion of hydroxide ions in the zinc slurry with a zinc loading of 27 vol%. Nonetheless, more tests are required to identify the limiting factors at a zinc loading of 7 vol% (33.6 wt%) in our scenario. In addition, as part of our investigation, we examined the impact of raising the KOH concentration from 4M to 8M on the cell's performance to determine if a higher concentration can counteract the hydroxide ion depletion.

The polarization curve is determined by measuring short-time steady-state steps. During each step, zinc dissolves rapidly to form zincate in the electrolyte. However, it has been reported that the zincate decomposition process (precipitating to ZnO) is considerably slower than dissolution⁵⁹. Consequently, it seems that the local depletion of hydroxide ions could contribute substantial concentration polarization, thus increasing the overpotential of the zinc anode.

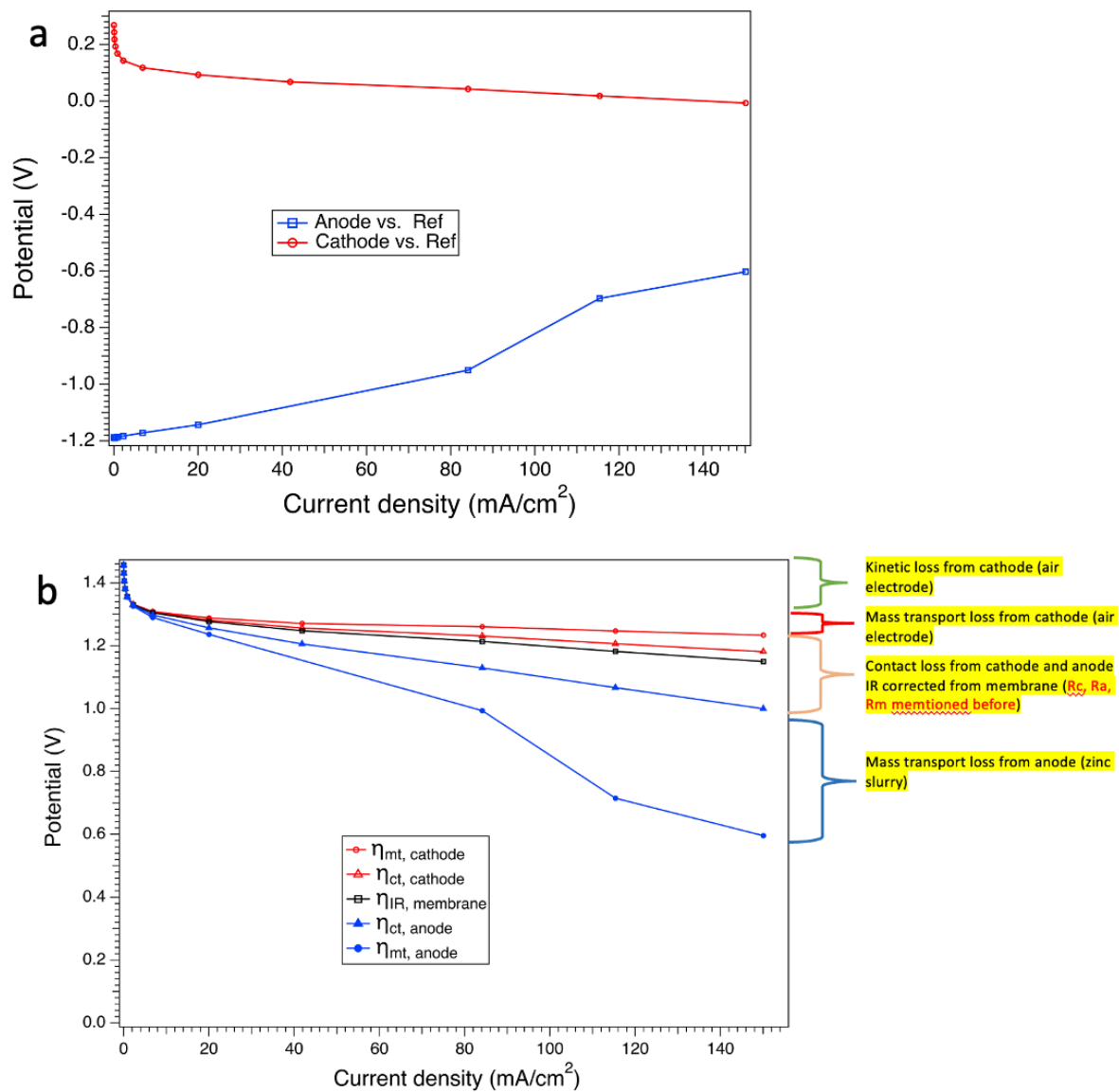


Figure 14: a). Separated polarization curves (in blue Zinc anode polarization, in red Air cathode polarization) with a pseudo reference wire; b). Detailed separated losses between each component in the Zinc-air battery.

In a more comprehensive measurement study, the areal-specific resistance (ASR) of each cell component was determined by relocating the reference electrode between compartments in figure 14b. In the legend, η_{mt} , η_{ct} , and η_{IR} , represent the overpotential for mass transport, contact loss, and internal resistance. R_c , R_a , and R_m denote the internal resistance of the cathode, anode, and membrane, respectively. Their respective values are $0.35 \Omega \cdot \text{cm}^2$, $1 \Omega \cdot \text{cm}^2$, and $0.21 \Omega \cdot \text{cm}^2$. Losses were characterized in greater detail, and the findings generally concur with previous results, indicating that mass transport in the zinc slurry is the predominant limiting factor within the typical cell operating voltage range of 0.8-1.2 V.

To enhance the performance of zinc-air batteries, a comprehensive parametric study was conducted to examine the mass transport loss from the zinc slurry and the resistive loss from the air electrode.

Cell parameter Effects

Two independent variables were investigated: the concentration of KOH (4M and 8M), and the orientation of gas flow in this particular design (side and middle) as shown in **Figure 15**. To clarify, the gas flowing through bipolar plate serpentine channels is defined as “gas through side” which is our baseline and is the typical experimental condition in most cases, with KOH flowing through liquid phase gap. Circulating gas through the gap is defined as “gas through middle”. In this study, we compared the air electrode performance of a standard high-performance catalyst to a much less costly alternative. The subsequent figures present polarization curves obtained for both platinum (Pt) on carbon and a in house-made non-PGM catalyst (FeKudzu).

For the FeKudzu catalyst deposited on carbon felt (depicted by red curves), the KOH concentration displayed no discernible impact on the air electrode performance, as shown in the top portion of the figure 16a. This potentially suggests that the mass transport losses in FeKudzu

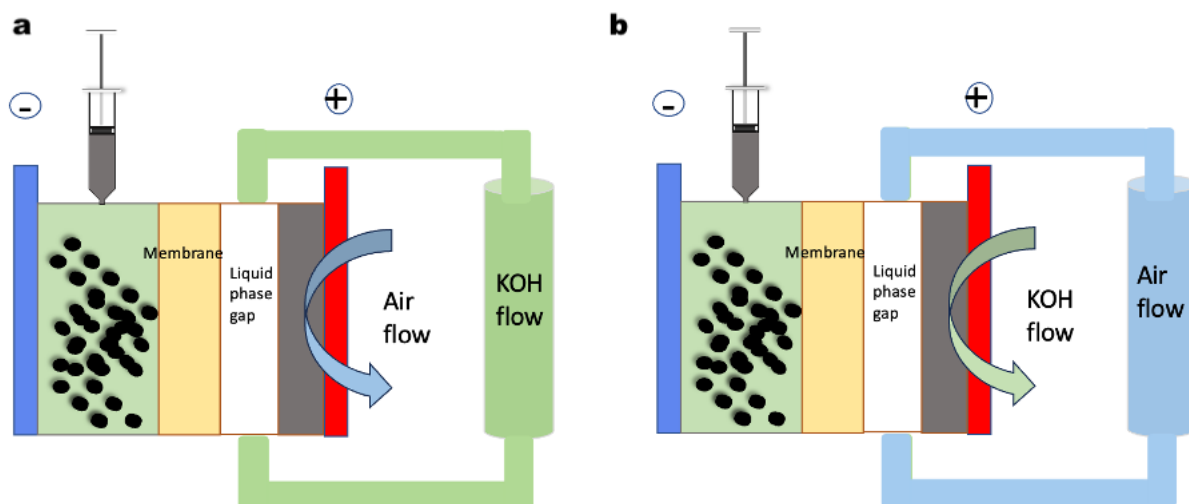


Figure 15: a) gas-through-side, b) gas-through-middle

catalyst layer of air electrode are not sensitive to the concentration of KOH (either 4M or 8M). However, the 8M KOH polarization was slightly more stable compared to the 4M KOH on the zinc slurry side, as demonstrated in the bottom portion of **Figure 16**. This finding implies superior performance of the zinc slurry with 8M KOH, particularly in high current density regions. In the case of Pt-based catalysts on carbon felt (represented by the blue symbols), an increase in the KOH concentration led to a slight increase in overpotential. This suggests that oxygen transport was hindered at higher KOH concentrations due to reduced oxygen solubility and diffusivity. It has been reported that both solubility and diffusion coefficient of oxygen decrease as the KOH concentration increases⁸⁵. The results obtained from both carbon felts qualitatively agree with the expected mass transport losses. No significant performance difference is observed in the total cell polarization upon varying KOH concentration in figure 16b. While literature suggests that 6M-8M KOH offers optimal ionic conductivity⁸⁶, the ideal KOH concentration for operating a cell truly hinges on the specific components within that cell.

From these polarization curves analyses, we found that the FeKudzu catalysts exhibit an open-circuit voltage (OCV) of approximately 0.45 V vs. the pseudo reference Pd/Cu electrode, while the Pt on carbon (Pt/C) catalysts display an OCV of roughly 0.3 V. Interestingly, both catalysts yield 5 mA/cm² at a potential of 0.15 V. The overpotential observed for the kudzu catalyst is double that of Pt/C in the given cell configuration. The oxygen reduction reaction (ORR) performance of Pt/C slightly outperforms the kudzu-derived catalysts in the kinetic region, but little difference is observed overall. This indicates that the FeKudzu catalysts could potentially replace Pt/C with little performance penalty, especially considering the high cost of this precious metal.

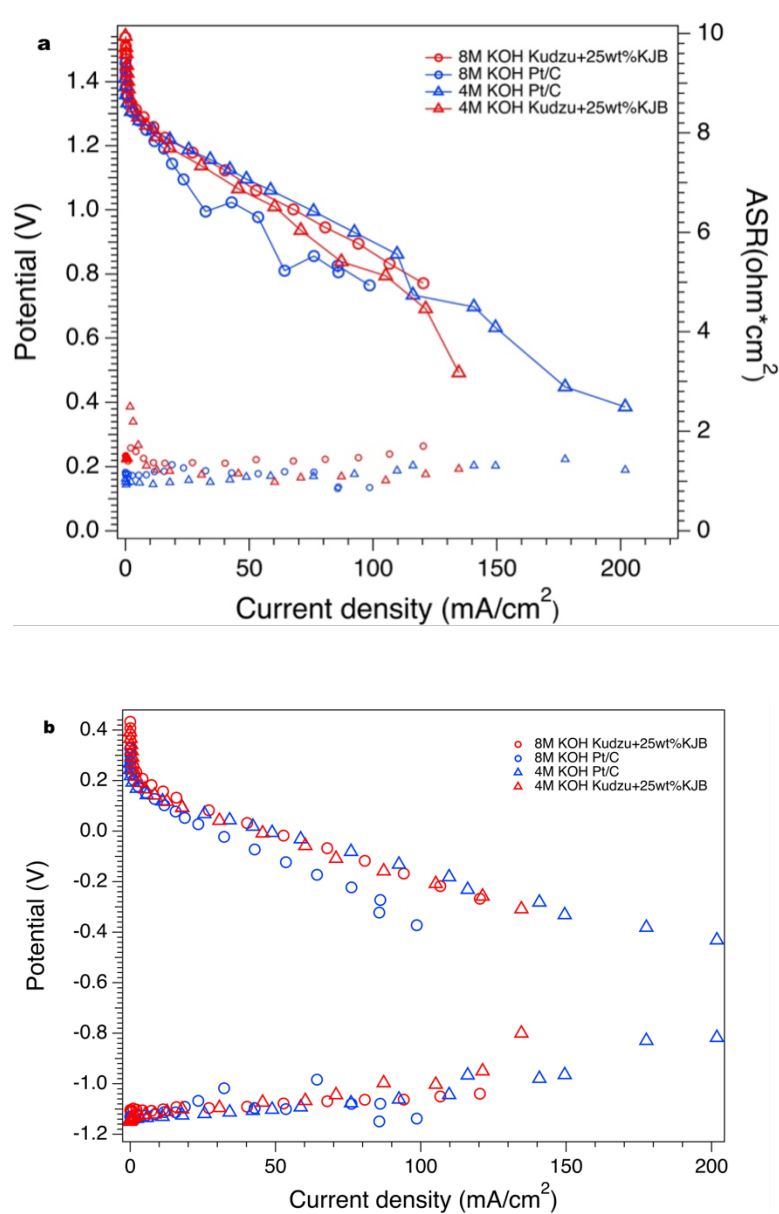


Figure 16: a) non-IR-corrected Cell polarization curves; b). Separated polarization curves by varying the concentration of KOH.

In our typical cell design adapted from an alkaline fuel cell, the gas is transported along the serpentine flow field and electrolyte is introduced into middle of the cell to wet the membrane. However, poor wet proofing of air electrodes can cause flooding while introducing electrolyte flowing between membrane and air electrode. This eventually blocks the gas penetrating the carbon felt GDL. One possible way to ameliorate this situation is to switch the flow configuration to deliver gas through the liquid phase gap of the cell. In **Figure 17**, the red and blue curves below represent Kudzu and Platinum on PTFE-treated carbon felt without MPL, while the green curve represents Platinum on non-PTFE-treated carbon felt with MPL. The comparison of red curves demonstrates that "gas through middle" performs better than "gas through side" in a Kudzu-based PTFE-treated carbon felt. This indicates that the electrode wettability is subpar, as there are significant transport losses on both sides. However, there is no significant relationship observed between PTFE-treated carbon felts without MPL when varying the gas flow configuration in a Pt on carbon electrode. This highlights the excellent morphology of Pt on carbon particles with PTFE coating for a consistent wettability. In comparison to Kudzu catalysts, the morphology of Pt on carbon layer coating ensures that the electrode porosity and the carbon structure of the gas diffusion layer permit efficient oxygen diffusion. Instead of pretreating carbon felt with PTFE, a further possible enhancement of wettability of electrode can be achieved by applying a MPL coating on GDLs. The green curve represents superior performance of the air electrode with MPL. Beyond 120 mA/cm² on this curve, we observe a rise in the overpotential for the zinc slurry when using the gas-through-middle setup compared to the gas-through-side, as illustrated by the lower curves. This rise potentially points to concentration polarization in the slurry, likely stemming from localized depletion of hydroxide ions at elevated current densities.

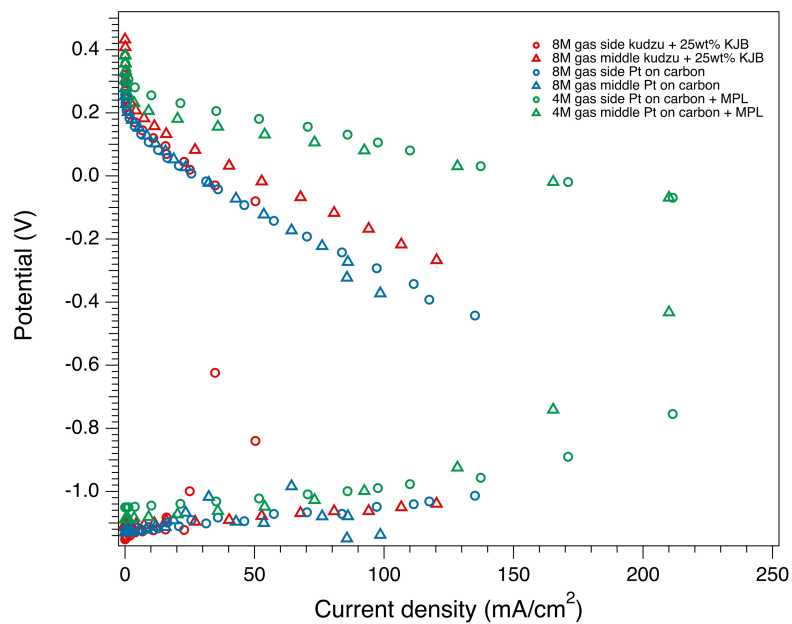


Figure 17: Effects of gas flow configuration on performance of cell.

Flowing KOH on the air side is primarily to ensure that the membrane remains hydrated. When gas flows between the air electrode and the membrane, a design referred to as 'gas-through-middle', this hydration is disrupted. This disruption leads to membrane dehydration, consequently restricting the movement of hydroxide ions from the cathode to the anode. Such a condition hampers the performance of the zinc slurry in systems with the 'gas-through-middle' configuration. We are still exploring effective methods to reduce the KOH flow on the air side while keeping the membrane well hydrated. The introduction of humidified air has been recognized as a viable solution in numerous alkaline fuel cell applications^{87, 88}. It remains to be determined if this level of humidification can adequately support the high discharge rates and moderate depth of discharge.

Conclusion

In summary, we examined mechanically rechargeable zinc-air batteries as potential successors to Lithium-ion technologies. Our investigations focused on the adoption of a three-electrode configuration with the integration of a pseudo reference electrode, which provided detailed insights into the losses experienced by different cell components. This approach facilitated a thorough assessment of electrodes of kinetics, internal resistances, and mass transport dynamics separately. By fine-tuning parameters such as operational modes, KOH concentrations, orientation of gas flow and air electrode designs, we substantially increased cell power density to 180 mW/cm². Our study underscores the promise of mechanically rechargeable zinc-air batteries as a technology for the next generation.

CHAPTER 4. NEW APPROACH TO INVESTIGATE LOW-PERCOLATION SLURRY
CHARACTERISTICS TO IMPROVE ZINC UTILIZATION IN MECHANICALLY
RECHARGEABLE ZINC SLURRY AIR BATTERY

For this chapter, we adapted the majority of a manuscript entitled “Systematic Parameters Study to Enhance Accessible Capacity of Low Percolated Zinc Slurry for Development of Mechanically Rechargeable Zinc Air Battery” **Under preparation.**

This study seeks to address the low utilization of zinc and the lack of comprehensive understanding of mechanically rechargeable zinc air batteries. By systematically exploring cell designs, operational modes, electrolyte concentration, zinc loading, and discharge rates, we aim to improve the zinc capacity utilization. We introduce a custom-designed cell, achieving a high areal capacity and optimized zinc utilization. Additionally, a novel model accurately simulates slurry conductivity, offering valuable insights for future advancements in zinc-air battery technologies.

Abstract

Mechanically rechargeable zinc-air batteries using a flowing slurry exhibit low utilization of zinc and are lacking in systematic study. To enhance accessible zinc capacity and focus on fundamental slurry composition, our investigations compared cell designs, operational modes, KOH concentration, zinc loading, and discharge rates and their effects on practical capacity of the cell. Additionally, we developed a unique model to interpret the conductivity of a low-percolation (low volumetric loading) slurry, potentially bridging a significant research gap in the study of flowing and semi-flowing slurries. Our customized cell with 1 cm thickness of anode achieves a theoretical areal capacity of 456 mA/cm² and 70.7% Zn utilization at a discharge rate of 10 mA/cm² with optimized conditions of 4M KOH and 33.6 wt% zinc loading. The model simulated a conductivity value of 1.02 S/cm in 30 Monte Carlo runs, which closely matches the experimentally measured data of 1 S/cm.

Introduction

The demand for high-capacity energy storage solutions is rapidly increasing. In today's energy landscape, there is a pressing need for efficient and reliable energy storage devices. Currently, lithium-ion batteries dominate the market due to their widespread use and proven performance. However, researchers are actively exploring alternative chemistries beyond lithium^{89, 90}, including solid-state batteries, redox flow batteries, fuel cells, and metal-air batteries. These alternatives aim to reduce the levelized cost of energy (LCOE) below 0.05 \$/kWh while enhancing safety and reliability in electricity supply⁹⁰.

Zinc air batteries (ZAB) are promising for some energy storage applications due to their high theoretical energy density at 1086 Wh/kg_{Zn}. The mechanically rechargeable zinc air battery (MRZAB) stands out among different types of ZAB owing to high discharge performance and

longer cycle life²⁸. This type of cell operates by manually replacing discharged zinc slurry with fresh slurry, and it can function in two modes: flowing or injection. N. H Choi et al studied a zinc slurry air battery in a flowing system^{40, 57}, with focus on optimizing cell design to increase the power density as indicated by the polarization curve. Additionally, Tsehaye et al⁹¹ reported a PO-6CH2-3x anion exchange membrane that has high ionic conductivity at 19 mS/cm. When applied in a zinc slurry-air flow cell, it produces a high peak power density of 153 mW/cm². D Milian synergizes the rheology and power density evaluation in flowing system to further elucidate slurry viscosity effects on the performance of cell⁵⁸. However, the practical energy density - utilization of slurry, is overlooked in these reports. MIT demonstrated that zinc foil pieces (1 – 5 cm² small-cut) suspension slurry⁴¹ in a flowing system achieve 30% utilization of capacity under 25 days continuous discharging current in a Zinc air battery cell. The inefficient and impractical utilization of slurry can be also seen in the other semi-solid redox flow batteries³⁹, which impedes their further commercialization. Daniel et al use an injection mode to operate zinc slurry air battery and achieve a promising high utilization of 85%⁴³, though it is found very challenging to scale up to a stack size.

Many factors, including cell design and slurry composition, can significantly affect the accessible capacity of zinc slurry in MRZAB. A critical aspect influencing this capacity is the conductivity of the slurry. A model that can be used to interpret zinc slurry is extremely helpful to guide experimental direction regarding optimizing compositions of slurry and elucidating mechanisms. J. Wainright et al established the EIS slurry model to interpret iron slurry resistance, and they highlighted slurry resistance is comprised by electronic resistance and ionic resistance. In the physics perspective, the conductivity of the composite electrode is often simulated through percolation theory by including Bruggeman's factor^{61, 92}. Mustain et al.

applied GeoDict to simulate slurry conductivity with a high percolated network at 30.5 vol.% zinc loading in operando primary zinc air cell. Their findings indicate that only a few particles are in contact with each zinc particle, demonstrating that the traditional Bruggeman approximation is not accurate for predicting our zinc slurry when particle contact must be considered. Thus, there is a research gap that no existing model can predict conductivity of low percolation zinc slurry.

In this work, we systematically investigate the effects of flow and injection designs on the performance of mechanically rechargeable zinc-air batteries (MRZAB), focusing on Zn utilization. Additionally, we explore two fundamental elements of slurry composition, the concentration of KOH and the zinc loading, to enhance the performance of MRZAB. By fine-tuning these parameters, we achieved 70.7% utilization at a discharge rate of 10 mA/cm² in an injection cell with 4M KOH and 33.6 wt% zinc loading. Furthermore, we developed an empirical model to simulate the conductivity of the slurry in a low-percolation state, which closely aligns with experimental observations.

Materials and methods

Cell design

Two major cell designs were examined in all electrochemical testing. 1) a graphite flow field, 2) a 3D printed slurry holder for injection. For each cell type, the cathode was constructed the same with binary (solution and gas) flow into graphite plate with flow, attached to Nickel plate as current collector. The cells were fastened with torque at 80 lb.

Slurry compositions

For the KOH concentration study, the slurry was prepared in 1M, 4M, and 8M KOH with 33.6wt% zinc particles (Spectrum, 325 mesh (~50 μ m), ~95% purity) with fixed 33.6 wt% zinc

and 0.112 g polyacrylic acid (PAA) from Sigma-Aldrich (viscosity ~40,000-60,000 cP). For the zinc loading study, the slurry was prepared with 25.3, 33.6, 37.2 wt.% zinc with fixed 8 ml 4M KOH and 0.112 g PAA. The slurry was prepared in two steps, first mixing PAA and KOH solution and then adding zinc powder and homogenizing the suspension by a high-speed homogenizer.

Electrochemical characterization

Galvanostatic discharge profile (E-Q), denoted as the utilization curve, was obtained through Chronopotentiometry (CP) in EC-Lab with a Biologic SP-150 with a 20A booster. A constant current of 10 mA/cm² was held until the cell voltage dropped to zero.

The slurry resistance was measured in a symmetric house-made cell. Holders with different slurry thickness (1 cm, 1.5 cm, 2 cm, and 2.5 cm) were used to measure the resistance or conductivity of a zinc slurry for thickness dependent resistance study. Two nickel plates were used as blocking electrodes and current collectors.

SOC-dependent EIS was performed by discharging the cell for 4 hrs with 1 min resting periodically, collecting impedance by EIS scans from 100 kHz to 10 Hz at the end of resting step.

Results and discussion

A mechanically rechargeable zinc-air cell was designed, and 3D printed using ABS material. We conducted a series of electrochemical characterizations using this cell, with a strong focus on the anode design and implementation in a semi-batch mode through slurry injection. The anode, with a functional area of 5 cm², was designed to match the established cathode side adapted from an alkaline fuel cell. To enable proper functioning of the syringe from the side for injecting the slurry, the optimized thickness was determined to be 1 cm. While this thick anode

could result in high resistance and practical challenges when mechanically removing used zinc slurry, it also presents new opportunities for large areal capacity applications. Notably, a 1 cm thick zinc slurry with 33 wt.% zinc loading equips the cell with an ultra-high areal capacity of 456 mAh/cm², which is 2.85 times higher than the highest reported areal capacity of 160 mAh/cm² in zinc-based batteries⁹³. The estimated areal capacity of 456 mAh/cm² corresponds to a volumetric capacity of 376.8 Ah/L, considering only the cell components with a membrane thickness of 0.1 mm and a carbon felt thickness of 2 mm. The gravimetric capacity is approximately 279.5 Ah/kg, calculated while neglecting the weight contributions of the carbon felt and membrane, as they comprise less than 2 wt% of the slurry. Based on this estimation, the injection mode of the mechanically rechargeable zinc-air battery (MRZAB-IM) achieves a practical energy density of 336 Wh/kg, excluding the weight of the current collector and gaskets.

Figure 18 depicts the core components of our cell, including the zinc slurry anode, membrane, and air cathode. The zinc slurry is prepared simply with three components: zinc particles as the anode active material, polyacrylic acid (PAA) as the binder/gelling agent, and 4M KOH as the electrolyte. While other studies^{40, 43} have incorporated carbon black as an additive to enhance the performance of zinc-based batteries, we have chosen to exclude carbon in our slurry. This decision was made to investigate the baseline performance of the mechanically rechargeable zinc-air battery (MRZAB), given the complex effects of carbon on both the viscosity and conductivity of the slurry.

The MRZAB is recharged by manually replacing discharged zinc slurry with fresh, fully charged slurry. Thus, its performance is highly dependent on how much zinc can be discharged in a single fill (defined as utilization). Quantitatively, the accessed capacity of zinc slurry

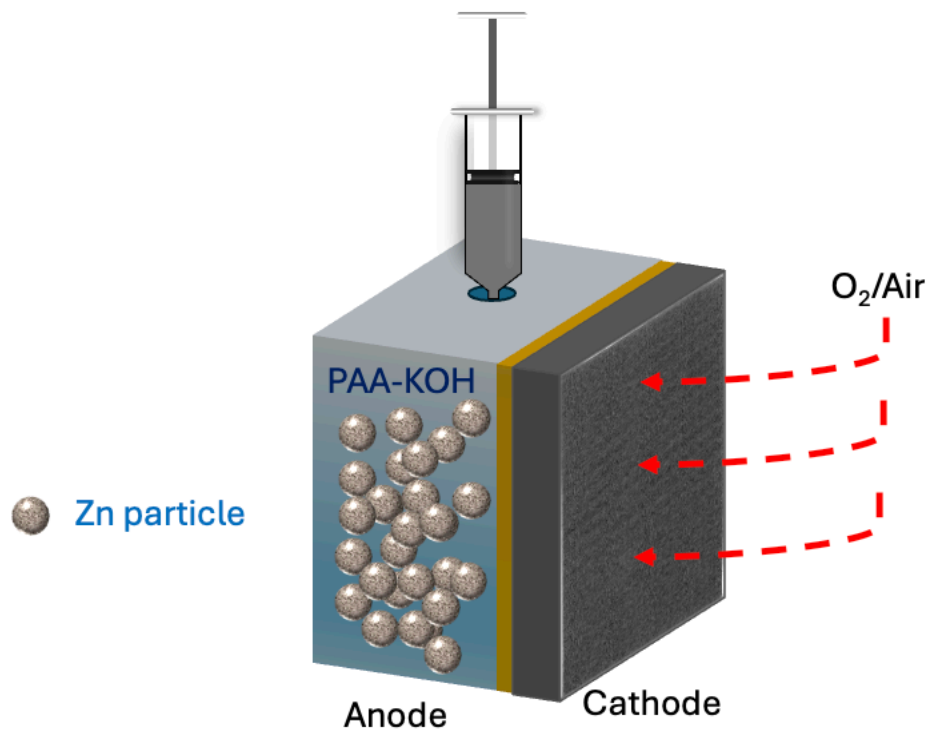


Figure 18: An illustration of mechanically rechargeable zinc air battery in semi-batch mode with 1 cm thick high-capacity anode and carbon light-weight air cathode with house-made CLAM.

dominates the efficiency of the MRZAB. To investigate the utilization of zinc slurry in our house made cell, galvanostatic discharge was performed while varying several aspects.

Figure 19a shows the cell tested with two different membranes (Celgard 3501 and CLAM) and in two different modes (flow, where the slurry is pumped continuously, and stagnant, where the slurry is injected in a semi-batch mode). The results indicate that the injection mode with the CLAM membrane delivers $568 \text{ mAh g}_{\text{Zn}}^{-1}$, which is 57.5% greater than the same mode with the commercial porous membrane Celgard 3501 (25 μm of thickness, 0.55 of porosity), documented as the benchmark membrane used in MRZAB⁹⁴. Additionally, the injection mode outperforms the flow mode in terms of delivered capacity ($365 \text{ mAh g}_{\text{Zn}}^{-1}$ vs. $125 \text{ mAh g}_{\text{Zn}}^{-1}$). This suggests that leveraging the flow-through mode with established infrastructure from redox flow batteries presents significant challenges due to the very low utilization of zinc in MRZAB, as also reported in a study using by MIT⁴¹ in which they use hand-cut small pieces of zinc foils (c.a. $1\text{-}5 \text{ cm}^2$) in the zinc slurry anode. Consequently, our focus turned to systematically studying the basic composition parameters of the slurry in the MRZAB-IM. Two variables, the loading of zinc and concentration of KOH, were selected to study on zinc slurry composition effects on performance of zinc slurry air cell. Studying high zinc loading and high KOH concentration is essential for maximizing zinc-air battery performance, as high zinc loading enhances the cell's theoretical capacity, providing a path to achieving higher energy densities and revealing potential limitations in zinc utilization. Simultaneously, high KOH concentration addresses hydroxide ion mass transport limitations and improves zinc solubility, ensuring efficient cell reactions and stable performance under high-demand conditions. **Figure 19b** reveals that 33.6% wt% zinc with porosity at 0.922 delivers the highest specific capacity at

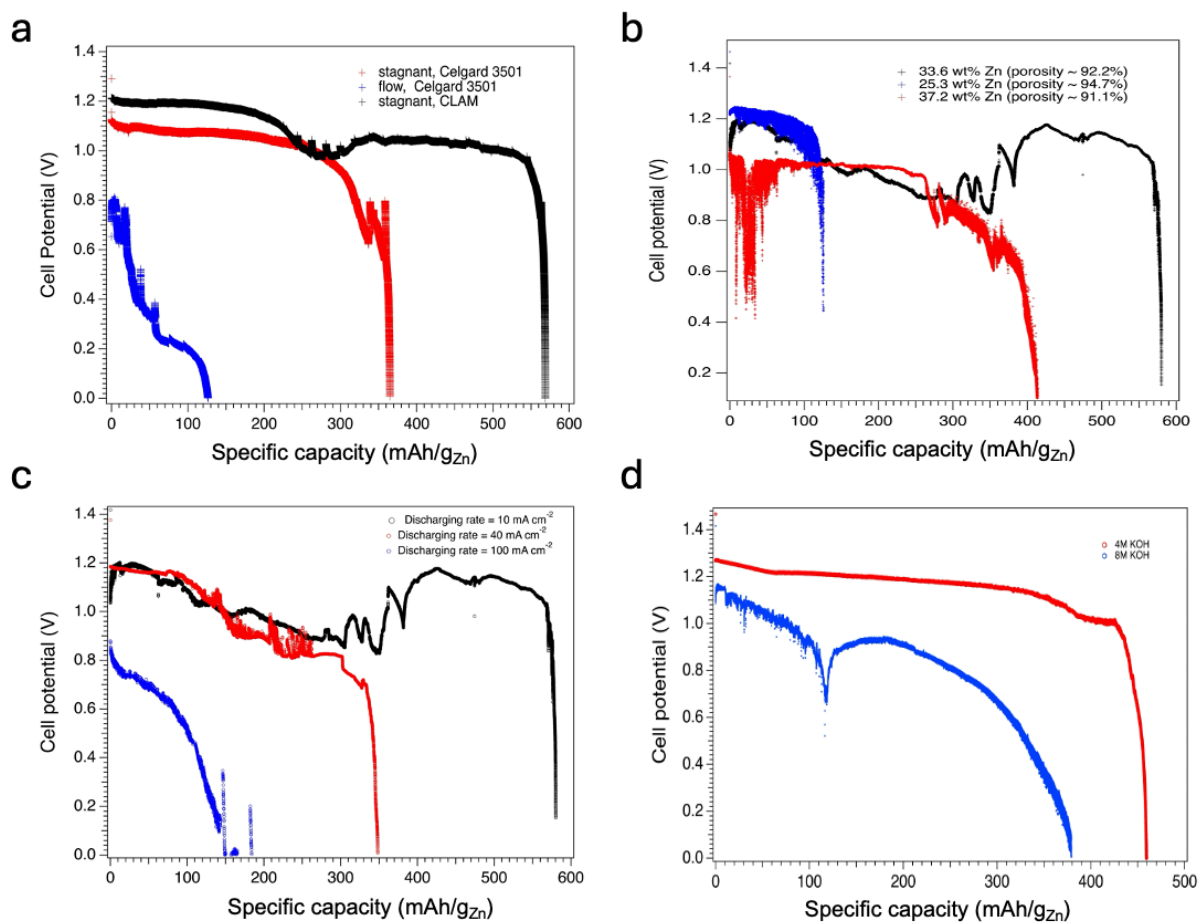


Figure 19: Galvanostatic discharging profile under different conditions, a) pre-screening the membrane and operational mode for the cell utilization testing; investigating effects of b) zinc loading in slurry, c) discharging rate, d) KOH concentration on the cell performance.

580 mAh g_{Zn}⁻¹ (corresponding to 70.7% utilization). However, further increasing the Zn loading to 37.2 wt% yields a 20.7% drop of utilization, which is attributed to thicker slurries with higher viscosity and lower diffusion rate of hydroxide ions. We observed large overpotential fluctuation (red curve) at the beginning of discharge, suggesting unstable slurry with high loading of zinc. Reducing the zinc loading to 25.3 wt% (blue curve) also contributes to massive utilization loss, determined to be 15.2 mAh g_{Zn}⁻¹, which is attributed to a poor percolation network amongst zinc particles. Note that the percolation threshold for zinc slurry is around 50 wt% loading of zinc²⁸. We are far below that requirement. Additionally, zinc slurry with 50 wt.% is found to be challenging to inject by syringe.

To characterize the post-discharge zinc slurry, we opened the cell and captured images of the fully discharged samples. **Figure 20** shows that with a 33.6 wt% zinc loading, the slurry exhibits uniform white particles, suggesting an optimal utilization scenario. In contrast, the 25.3 wt% loading retains its original slurry-like appearance, indicating that the zinc particles were not fully utilized. Moreover, the 37.2 wt% zinc loading displays a mixture of black and white particles, with black (zinc) particles closer to the current collector and white (zinc oxide) particles near the membrane. This suggests that zinc particles closer to the membrane react first. However, the higher viscosity of the high-zinc-loading slurry hinders complete utilization, particularly in the region near the current collector.

On the other hand, we hypothesized that the utilization of zinc is strongly dependent on the depletion of hydroxide ions. Initially, zinc reacts with hydroxide ions to form zincate ions. But as these hydroxide ions are depleted by the reaction, the reaction rate slows, leading to incomplete zinc utilization. This depletion also shifts the electrochemical potential, reducing the thermodynamic drive for zinc oxidation. Additionally, limited OH⁻ availability can cause ZnO to

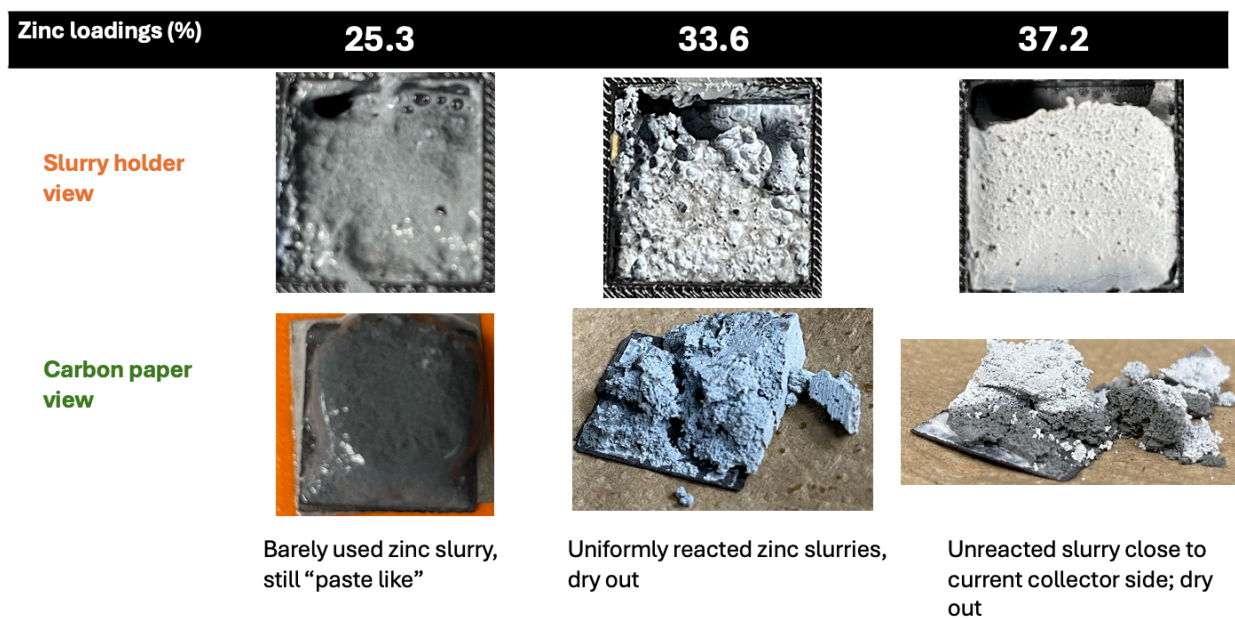


Figure 20: Discharged zinc slurry in holder view and carbon paper view with 25.3wt%, 33.6wt%, and 37.2 wt% compositions.

precipitate, forming a passive layer that blocks reactant access and limits further reactions. Mass transport limitations exacerbate this effect by restricting the supply of hydroxide ions to the reaction site, further hindering zinc utilization and overall discharge performance. Thus, we varied the concentration of KOH to 1M, 4M, and 8M (the highest ionic conductivity presented in the literature⁹⁵) to examine the OH⁻ depletion effect on slurry electrode discharge performance. 4M KOH was found to be the optimal concentration, delivering high utilization at 70.7%. Interestingly, the 1M KOH zinc slurry air cell shows an OCV of 1.2 V, which is lower than the typical zinc-air battery OCV of 1.4 V (at 4M or 8M KOH). This can be partially explained by differences calculated using the Nernst equation. The calculation shows that a 4M KOH zinc-air cell has roughly 0.02 V greater thermodynamic potential than a 1M KOH cell. The other portion of the OCV loss is attributed to poor electronic contact between zinc particles and the Ni current collector due to the unstable slurry suspension with low viscosity of the slurry. The 1M KOH zinc slurry instantly short-circuits with a constant discharge current density of 10mA/cm², which is potentially attributed to insufficient hydroxide ion conductivity to allow battery discharge at this rate. In contrast, the 8M zinc slurry air cell produces 17.3% less specific capacity than the 4M KOH cell. This contradicts our hypothesis that 8M KOH improves the solubility of zinc and provides twice as many hydroxide ions for producing capacity. The possible reason behind this is that the 8M KOH slurry's larger viscosity impedes OH⁻ diffusion. Additionally, 4M KOH benefits the cathode performance for the same reason. To further validate the mechanism, a systematic study is needed to synergize rheology and electrochemistry to characterize battery performance which has been done in lithium slurry battery⁹⁶.

We also investigated the impact of different discharge rates on the performance of the zinc slurry air cell. **Figure 19c** shows that with a large areal capacity of 456 mAh cm⁻², the cell

delivers 322.4 mAh cm⁻² (70.7% utilization) under a discharge rate of 10 mA cm⁻². As the discharge rate increases to 40 mA cm⁻², the cell delivers 194.6 mAh cm⁻² (42.6% utilization). The cell exhibits low utilization at a discharge rate of 100 mA cm⁻², as indicated by the blue line. Although the cell possesses significantly higher energy density due to the high thickness of the anode, the practical utilization is strongly dependent on discharging rate. Because the cell performance is sensitive to discharge current density, a future direction for this cell is to focus more on stationary energy storage systems, which require lower power density compared to electric vehicle (EV) systems that demand high power density and C rates to meet daily needs.

To characterize the anode resistance, EIS was used to monitor the resistance of slurry as a function of anode thickness. A house-made symmetric cell was employed to measure the impedance of slurry, with its thickness is controlled by the 3D printed slurry holder. As the thickness increases from 1 cm to 2.5 cm, the resistance increases from 0.185 to 0.45 Ohm as shown in **Figure 21a**. With a linear fit, we can extract the contact resistance if that is a significant contributor. **Figure 21b** reveals that no significant contact resistance was detected, indicating that our custom-made symmetric design provides reliable values for quantifying slurry resistance. Based on this, the specific conductivity of the slurry was calculated using the equation below. The calculated conductivity averages 1.1 S/cm, which aligns with results reported in other studies²⁸ with 33 wt.% zinc in the slurry.

To further understand how zinc slurry resistance evolves during cell discharge, SOC-dependent electrochemical impedance spectroscopy (EIS) was performed. Using a three-electrode setup to isolate the impedance of the anode, we captured the time-resolved resistance of the slurry in the full cell (in-situ EIS). **Figure 22a** depicts the Nyquist plot under different states of charge (SOC) from 100% to 29.2% (denoted as fully charged and discharged states).

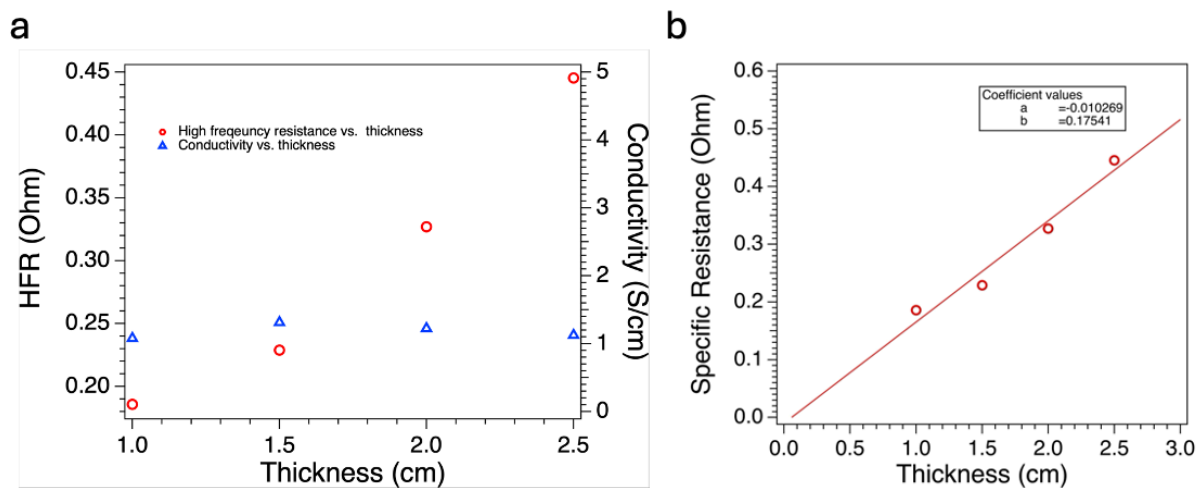


Figure 21: a) High frequency resistance as a function of thickness measured by house-made slurry symmetric cell. b) The validation analysis of contact resistance through this conductivity measurements.

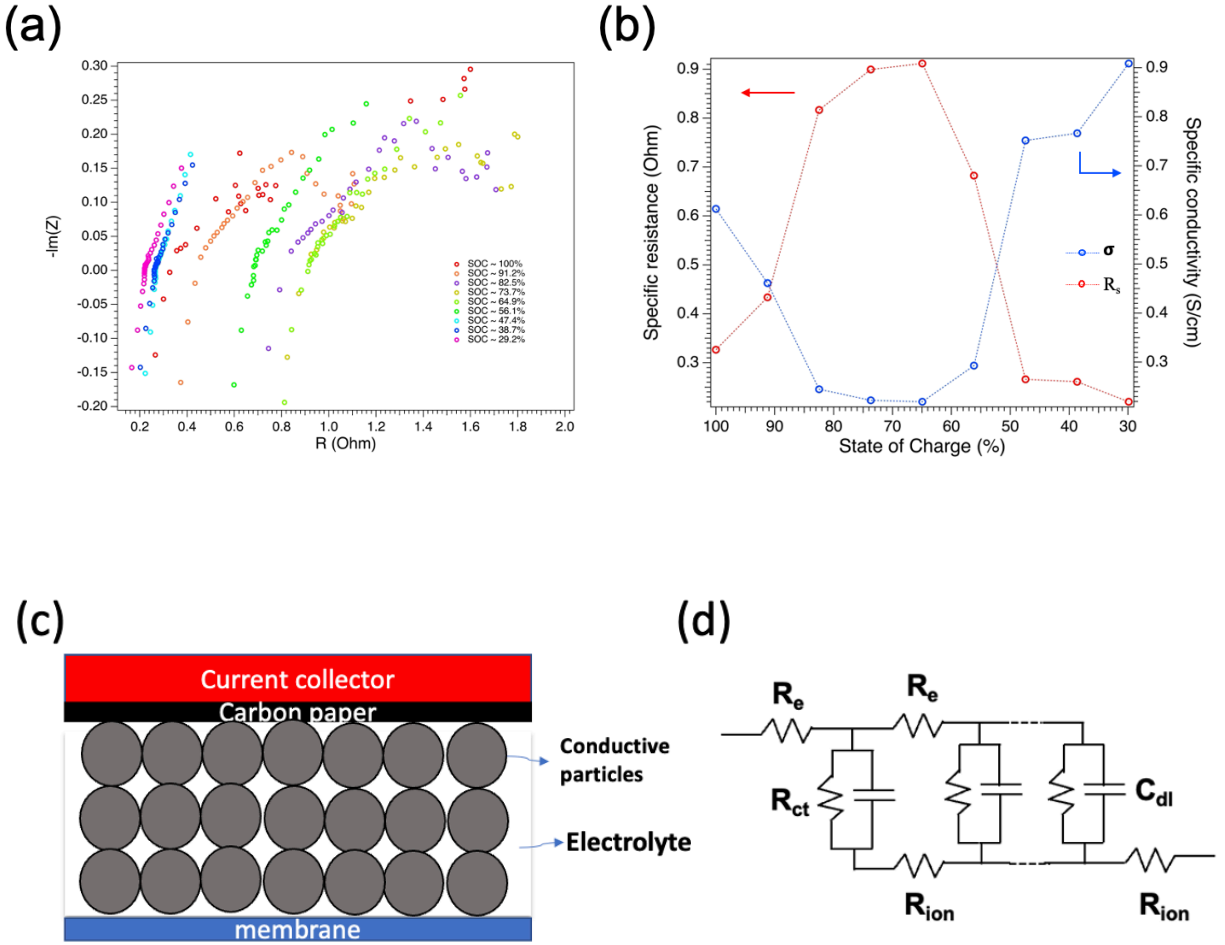


Figure 22: a) Resistance as a function of (state of charge) SOC in discharging direction with three electrodes assisted to isolate cathode part. b) Derived corresponding specific resistance and conductivity values as a function of SOC. c) Illustration of EIS slurry model, highlighting the three major processes: 1. electron transfer between zinc particles; 2. Ionic transfer from mobility of hydroxide ion; 3. Interfacial charge transfer between zinc particle and KOH. d) Its corresponding equivalent circuit model presents R_e , R_{ion} , and R_{ct} to describe these three processes

Note that the Nyquist plot shifts to the right as SOC approaches 64.9% and shifts back to the left as SOC approaches 29.2%. These overall horizontal shifts reflect a time-dependent change in zinc slurry resistance under different SOC. Specifically, from the data in **Figure 22b** we extracted the specific resistance of the slurry (R_s) from the x-axis intercept (HFR) and its corresponding specific conductivity (σ_s). It was found that the resistance of the slurry initially increases, reaching a maximum value of 0.9 Ohms at 70% SOC, then decreases sharply, reaching a low value of resistance at 47.4% SOC; thereafter, the slurry resistance maintains a plateau until SOC drops to 29.2%. The corresponding specific conductivity trend behaves oppositely to the resistance trend

To further elucidate the mechanism of slurry dynamic change during cell discharge, we first examine the slurry-EIS model developed by Wainright et al⁶⁵. Assuming that the slurry system is macro-homogeneous phase, similar to a porous electrode. Its directly derived impedance equation is complex, especially including the low frequency term (Z_{LF}) which is dependent on impedance of interface⁶⁵ ($\hat{Z}_\zeta$) as shown below. The first term (high frequency) is solely dependent on intrinsic properties of zinc slurry. The second and third terms are dependent on the impedance of solid liquid interphase. One of key parameter in the interphase impedance is charge transfer resistance (R_{ct}) in eq. 8. Its physical meaning is dependent on surface area or morphologic of zinc particles in our case. When impedance approaches low frequency, Z_{LF} includes R_{HF} , R_{ct} , and distribution resistance (R_{dist}), where R_{dist} accounts for additional impedance to minimize the overpotential arises when passing ionic or electronic current.

$$Z = \frac{r_e r_{ion}}{r_e + r_{ion}} \delta + \frac{r_e r_{ion}}{r_e + r_{ion}} \frac{2\lambda}{\sinh\left(\frac{\delta}{\lambda}\right)} + \lambda \frac{r_e^2 + r_{ion}^2}{r_e + r_{ion}} \coth\left(\frac{\delta}{\lambda}\right)$$

[6]

$$\lambda = \left(\frac{\hat{Z}_\zeta}{r_e + r_{ion}} \right)^{1/2} \quad [7]$$

$$\hat{Z}_\zeta = \frac{\bar{r}_{ct}}{1 + j\omega\bar{r}_{ct}c_{dl}} \quad [8]$$

$$Z_{LF} = R_{HF} + R_{ct} + R_{dist} \quad [9]$$

Where r_e , r_{ion} are the length average resistance of electronic and ionic phases,

δ is slurry electrode thickness,

$\hat{Z}_\zeta$ represents interaction between electronic and ionic phase when redox couple exists

$\bar{r}_{ct}$ is length average charge transfer resistance

c_{dl} is capacitance of double layer

The high frequency range is of specific interests since it can be applied in our zinc slurry study. At this range, the impedance of the interphase approaches to zero, which simplifies the equation to eq. 10. Thus, the specific resistance of the slurry at high frequency is represented by parallel ionic resistance (R_i) and electronic resistance (R_e). These parameters represent the mobility of hydroxide ions in the electrolyte and particle to particle contact resistance, respectively. On the other hand, charge transfer resistance and distributed resistance were not specifically applied to zinc slurry testing in the full cell due to non-obvious Randle's semi-circle formed in this frequency range for our case. Thus, R_{HF} , also called R_s , should be more of interest to interpret the possible zinc slurry charging mechanisms.

$$R_{HF} = R_s = \frac{R_{ion} * R_e}{R_{ion} + R_e} \quad [10]$$

$$\sigma_s = \sigma_i + \sigma_e \quad [11]$$

Assuming $\sigma_i = 0.55$ S/cm from literature reports⁹⁵, and σ_e as the electronic conductivity of zinc metal, which is $1.66 * 10^5$ S/cm, the derived σ_s is five orders of magnitude higher than the experimental value. This large discrepancy is attributed to two factors: 1) the porosity effects on conductivity, and 2) the particle contact. To account for the first factor, researchers apply the Bruggeman approximation to model the porous composite anode. Specifically, Bharatkumar Suthar et al. point out that a Bruggeman coefficient of 1.5 is commonly used for composite anodes with uniform spherical particles⁶¹. Based on this, our conductivity model equation is developed to include the effects of porosity:

$$\sigma_{eff} = \sigma_{Zn} \varepsilon_{Zn}^{1.5} + \sigma_{KOH} \varepsilon_{KOH}^{1.5} \quad [12]$$

The calculated effective conductivity is 3574 S/cm. The error is greatly reduced but there is still a three orders of magnitude gap in comparison to the experimental value. To overcome this, the second factor – particle contact must be considered. We propose the slurry (low percolation) composite electrode should adopt the following empirical model:

$$\sigma_{eff} = \sigma_{Zn} (f \varepsilon)_{Zn}^{1.5} + \sigma_{KOH} \varepsilon_{KOH}^{1.5} \quad [13]$$

Where f is the fraction of particles with neighborhood.

To clarify, the slurry we are dealing with contains 33 wt.% zinc loading, which is far below the percolation limit. This indicates that our particles do not all directly contact each other to form a percolation network. To characterize particle contact, we employed Python to simulate a representative volume element (RVE) of 1 mm³ with 7.7 vol.% zinc (33.6 wt.%). Scanning electron microscopy (SEM) was used to determine the particle size distribution of the zinc powder, with a D₅₀ of 44 μm, as shown in **Figure 23a**. Furthermore, we assume that particles are distributed with a range of 1 μm to 60 μm with a Gaussian distribution centered at 44 μm. The micron-sized particles were placed into the unit, and any particles that are 'close enough' (< 50 nm) were assumed to be neighbors, allowing electron transfer through quantum tunneling. Additionally, nano-sized zinc particles (D₅₀ < 100 nm) may serve as secondary support by filling electrical percolation gaps between the larger, micron-sized particles, ensuring consistent conductivity when quantum tunneling alone is insufficient. **Figure 23d** shows the simulated particle size, numbers, and volume fraction of the unit. **Figure 23f** visualizes this RVE with red and blue particles to distinguish those that conduct electrons. In 30 Monte Carlo simulations, the average conductivity was found to be 1.02 S/cm, which aligns with our experimental findings. The simulated conductivity ranges from 0.5 to 3 S/cm for random sampling of multiple volume elements.

To further validate our findings that zinc particles are highly scattered in the slurry, an inverted microscope was utilized to visualize the zinc particles in the slurry, as shown in **Figure 23b and 23c**. It was confirmed that the focused particles do not exhibit close contact with each other in either resolution image. The small dots in the background are believed to be PAA media

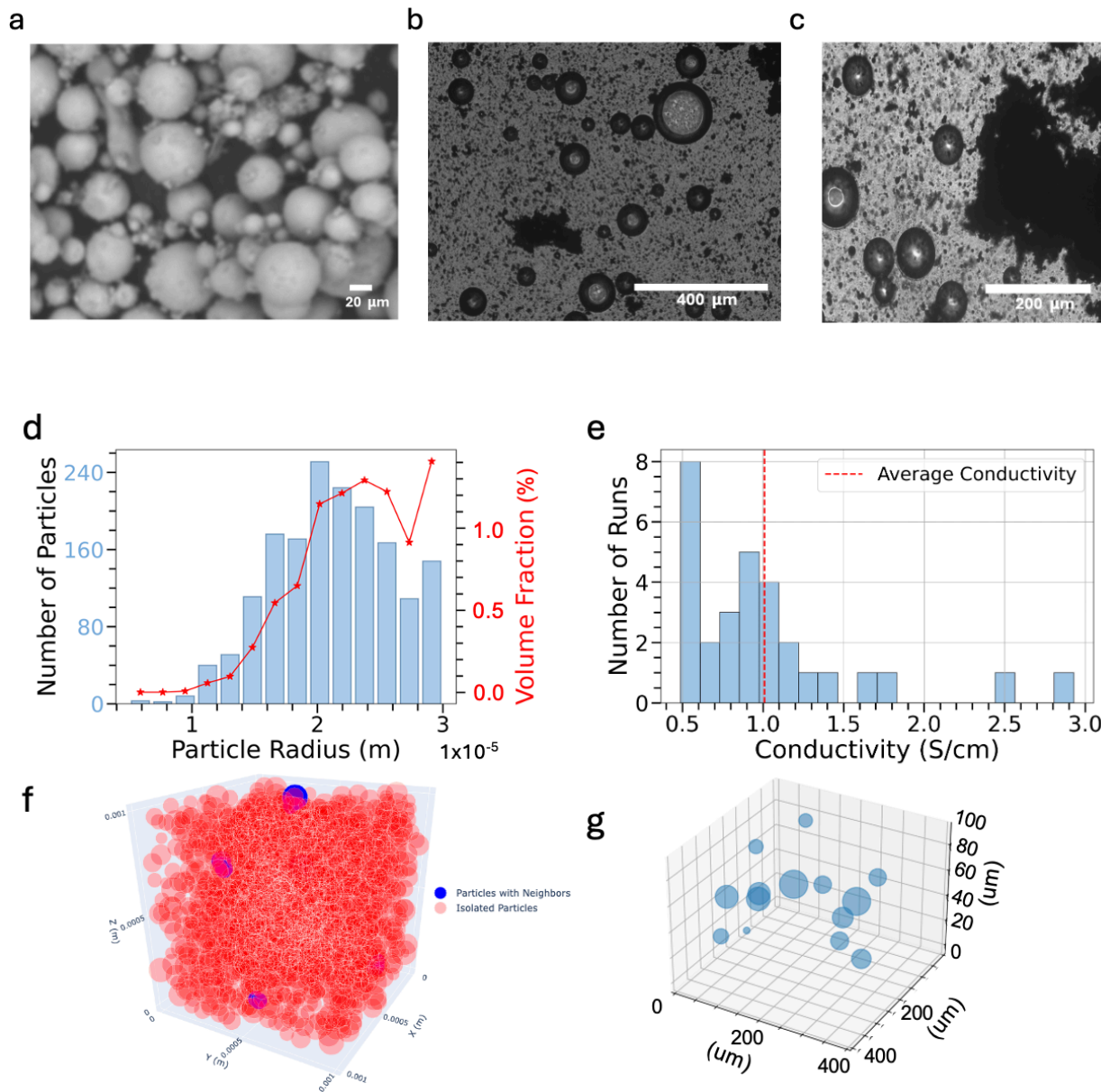


Figure 23: a) SEM images for pristine manufactured Spectrum zinc powders, b) Inverted stage microscope images on pristine zinc slurry with 33 wt% zinc loading in 10x resolution, c) same microscope with focus on 'virtually closed-enough' particles on same slurry in 20x resolution, d) Statistical results of simulated zinc particles in slurry with fixed range diameter from 1 μm to 60 μm , e) The results of 30 Monte Carlo runs for simulated conductivity of zinc slurry based on our developed model, f) a 3D interactive view of representative volume element (RVE in 1 mm x 1 mm x 1 mm) that captured neighbors and isolated particles with different color, g) a 3D slice view of RVE with dimension of 400 μm x 400 μm x 100 μm .

or small zinc particles, which could not be further distinguished. In the model, **Figure 23g** also depicts scattered zinc particles in the slide view of the RVE. Thus, we believe that the hypothesized empirical slurry model is aligned with experimental findings, emphasizing that zinc particles are in a scattered distribution.

Although the empirical model can be used to stimulate pristine zinc slurry, it is limited in its ability to predict dynamics of resistance change of zinc slurry in discharging process. For example, we found it a challenge to predict the conductivity of the slurry at 70% SOC, which relates to interpreting which possible reasons contribute to highest resistance (Fig 22b) in the entire discharge process. It has been reported that 4M KOH has 0.3 M saturated zincate solubility⁷⁵. Based on a calculation, at 70% SOC, 0.83g zinc in 5 ml 33.6 wt.% zinc slurry was consumed to yield the corresponding SOC, which is roughly 9 times greater than the saturated zincate solubility at 0.0975g. Thus, the formation and precipitation of zinc oxide happens in principle. Assuming that 1). 30% zinc transforms to zinc oxide during discharging (zinc to zinc oxide volume expansion is equal to 1.6); 2) considering corrosion rate referenced from Perez-Antolin et al⁴³, 5.46 wt% of zinc depleted due to parasitic reaction. KOH consumption results from the reaction with zinc particles. We also assume that all formed zinc oxide is well covered on the zinc particle surface without considering precipitation or major morphologic effects. Mathematically, we calculated particles size (D_{50}) expansion from 44 μm to 47.6 μm at 70% SOC as presented in **Figure 24**. Through same stimulation, the average conductivity is 1.37 S/cm based on 30 runs, which does not align our experimental finding on slurry resistance of 70% SOC. The limitation of this model is that we lack supporting evidence to quantify the conductivity of zinc oxide covered zinc particles, and its morphological impacts. This model can be potentially further evolved by considering many other factors, such as the large quantity of

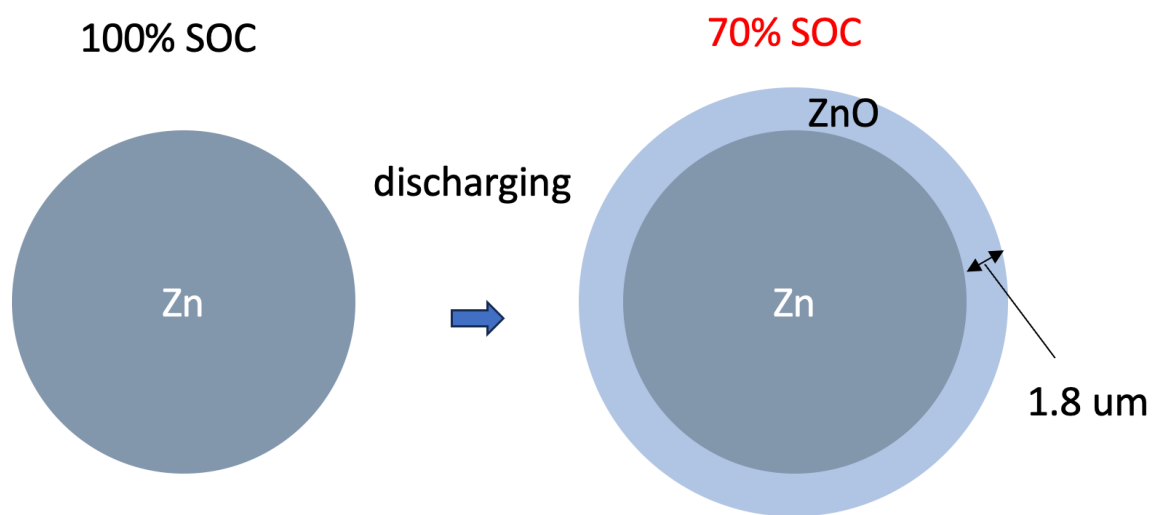


Figure 24: A scheme shows the volume expansion of zinc particles during discharging. Assuming no major morphologic change on zinc particle. The expansion is solely from the zinc oxide layer uniform deposition.

small zinc particles ($<1\mu\text{m}$), aggregation (discharging), introducing Multiphysics (including thermal and stress effects), and morphologic characterizations.

Conclusion

In this work, we successfully fabricated a zinc slurry-air cell with an ultra-high areal capacity of 456 mAh/cm^2 . We systematically studied the effects of zinc slurry compositions on the utilization of the MRZAB. Our findings indicate that a slurry composition of 4M KOH and 33 wt.% zinc achieves optimal utilization of 70.7%. Additionally, we investigated the slurry conductivity from both experimental and theoretical perspectives. This led to the development of a specific low-percolation slurry empirical conductivity model, which is particularly meaningful to the slurry or semi-solid electrode cell community. This model provides critical insights in considering particle contact, addressing challenges related to explanation of physics of low percolated slurry. By optimizing slurry composition, our study enhances the understanding and efficiency of zinc slurry air cells, paving the way for future innovations in energy storage technology.

CHAPTER 5. DEVELOPMENT OF LAB-CELL MRZABs FOR FUTURE PROTOTYPE
TECHNOLOGY AND OTHER CONSIDERATIONS

Motivation

The technical operational mode transition from flow to semi-batch injection was previously demonstrated as necessary to improve both power density and energy density. However, the design of the injection slurry is still in its infancy as it does not allow completely removal of discharged zinc slurry. Also, the self-discharge of zinc slurry (corrosion) and the capability for regeneration of fresh zinc slurry from used zinc slurry are also two major challenges which further impede the development of MRZAB. Thus, in this chapter, we aim to discuss our efforts to cope with these obstacles

Design progress towards lab-scale mechanically rechargeable zinc slurry air battery

To fully support the development of the injection mode in MRZAB, we systematically designed the following 3D-printed mold using Inventor to demonstrate a ‘completely removable’ prototype. **Figure 25a** depicts the classical serpentine flow field design widely applied in alkaline fuel cells to handle gas and liquid phases simultaneously. However, this design struggles with viscous zinc slurry due to clogging issues. We observed that zinc slurry immediately became lodged in the flow field and could not be manually forced out, leading to an initial practical failure with this setup. Subsequently, we modified the flow field channel by increasing the width to 2 mm, as shown in **Figure 25b**. This adjustment successfully mitigated many clogging issues during the initial injection stage, allowing us to obtain initial test results. However, we noticed that clogging could still occur during cell discharge because the zinc slurry slowly dries out and its viscosity increases significantly.

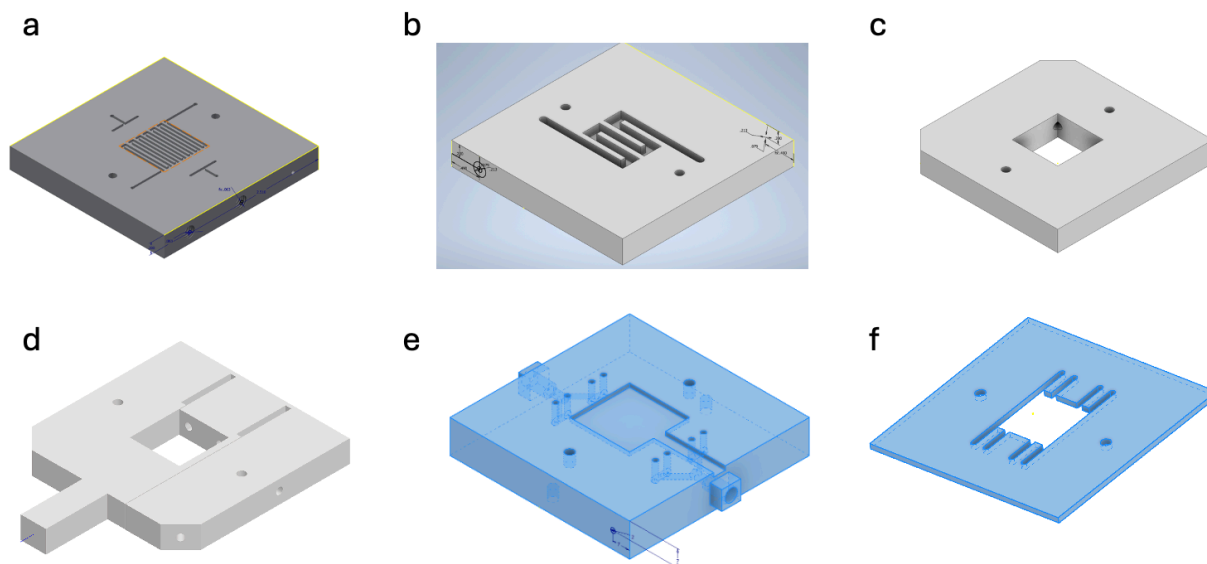


Figure 25: Design of device perspective for slurry anode in development practically viable MRZAB, a) serpentine design of flow field adapted from alkaline fuel cell that allows dual phases operation (gas and liquid); b) Modified flow field design with 2 mm width of channel for pumping slurry; c) Initial slurry injection design with 5 cm² and 1 cm thickness; d) Knob assisted injection design for removal purpose manually; e) A illustration of modified nickel plate holder to allow slurry injection through multichannel; f) A modified slurry multichannel holder with 2 mm thickness to hold slurry while operating the cell.

While a pumping slurry system appears more industrially viable for scaling up, as it can leverage the existing infrastructure of redox flow battery stack designs, the inherent problem of clogging remains unresolved. Consequently, we designed an injection mold through 3D printing using 100% infill ABS plastic (**Figure 25c**). This mold allows for side injection and enables verification that the slurry is fully filled. This design shifts the process from continuous flow to a semi-batch mode, with manual intervention required at the initial and final stages of slurry injection and removal, thereby reducing the risk of clogging during continuous flow. However, we identified a limitation in completely removing the slurry after the end of discharge with this design. Thus, subsequent efforts were focused on optimizing the removal process, which theoretically can be achieved in two ways.

Initially, we considered incorporating a central knob to push the slurry out after use without disassembling the battery (**Figure 25d**). However, a practical issue quickly emerged: after assembly, the knob-assisted slurry holder was tightly sandwiched between the current collector holder and the gasket with zero gap and secured with high torque. This resulted in impractically high friction between components, leading us to abandon this design.

The second method focused on a multi-channel concept. This design was inspired by the limitations of the baseline design in **Figure 25c**. Instead of injecting through a single hole, which is inefficient for complete slurry removal, we redesigned the current collector holder to allow slurry to pass through four channels (**Figure 25e**). Additionally, the upper and lower channels are joined into a single channel to simplify the external connection to tubing. Figure 16f illustrates the thin slurry holder, enabling a practical mechanically rechargeable concept. This multi-channel design successfully addressed the challenge of efficient slurry replacement. However, we observed leakage issues, likely due to the limitations of ABS, the material used for

3D printing. Although marketed as 100% infill, ABS plastic may be too porous during manufacture for this prototype design. Therefore, more advanced materials, such as PEEK, should be considered in the future.

Regeneration of zinc slurry – a test in symmetric cell

Although a major driving force of MRZAB is focused on development of a one- pass zinc discharge process, the discharged zinc must be technically recyclable. To explore the reversibility of zinc slurry in mechanically rechargeable zinc air battery, a symmetric zinc stripping and plating experiment was identified as most effective electrochemical method to characterize the zinc reversibility in terms of columbic efficiency (CE). An informed nature energy paper regarding a discussion of CE of zinc batteries was published by Lin Ma et al⁹⁷. They highlighted that standardized galvanostatic protocols should replace cyclic voltammetry (CV) in CE determination because CV lacks control over critical parameters such as current density and areal capacity, leading to inconsistent and unreliable results that don't reflect real battery conditions. Additionally, CV often uses unrealistic potential ranges, resulting in overly optimistic CE values. The ambiguous measurement of electrode surface area in CV further compromises accuracy. Therefore, galvanostatic protocols provide a more reliable and relevant approach to assessing CE. They also reported that many reports show close to 100% CE but unpractical utilization of zinc stripping and plating at below 1% of capacity, which is far below the commercial target of a rechargeable zinc metal battery at 80% utilization, 5 mAh/cm² of areal capacity, and 10 mA/cm² of current density.

Herein, we utilized our house-designed symmetrical cell with 1 cm cathode and anode thickness for stripping and plating the zinc slurry at 40 mA/cm², and 100 mA/cm². In **Figure 26**,

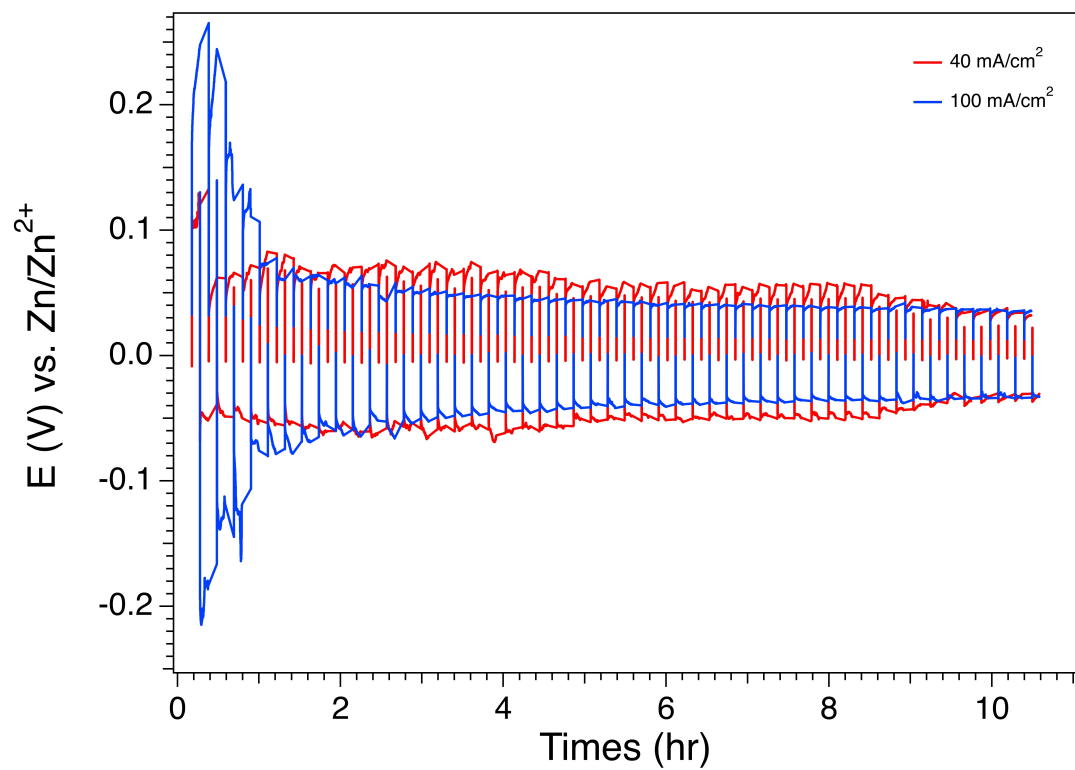


Figure 26: A symmetric cell testing with Zn|CLAM|Zn setup plating and stripping under 40 mA/cm², and 100 mA/cm² for 12 mins current holding (6 mins for charging, and 6 mins for discharging) each cycle until 50 cycles.

we observed roughly 0.25 V of overpotential over the first two cycles at 100 mA/cm². In contrast, 0.1 V of overpotential was observed when current density was decreased to 40 mA/cm². This is reasonable due to larger overpotential originating from IR drop when larger current is applied. Furthermore, we also noticed at roughly one hour cycling, the voltage response stabilizes in both cases. Interestingly, a smaller overpotential was detected at 100 mA/cm² in comparison to 40 mA/cm². This indicates that higher current density during formation cycles potentially benefits the zinc slurry percolation network formation due to enhanced electrodeposition dynamics. Higher current density accelerates the nucleation and growth of zinc particles. This promotes the formation of a more interconnected, robust percolation network within the slurry. This is crucial for ensuring good electrical conductivity during subsequent cycling. Another possible explanation is that the larger current density facilitates more heterogeneous surfaces of zinc particles, which ensures a larger surface area of active material can be utilized for long term cycling. Thus, based on this symmetric cell zinc slurry stripping and plating, we show that the optimal reversibility of zinc slurry occurs with 98.4% CE and around 2% utilization in our preliminary testing. Note that 2% utilization is very low, which is not practical compared to 100% utilization in commercialized batteries, such VRFB and lithium-ion battery. Thus, efforts must be made to improve the utilization in stripping and plating tests.

To increase the maximum utilization during striping and plating zinc slurry testing, we further investigated whether the slurry can be cycled with a deeper utilization in a symmetric cell. **Figure 27** proves that 20% zinc utilization cycling was achieved without shorting in this symmetric cell testing for 20 cycles while maintaining 98.4% CE under 100 mA/cm² current density and practical areal capacity of 91.2 mAh/cm². Recalling the benchmark, we are still far

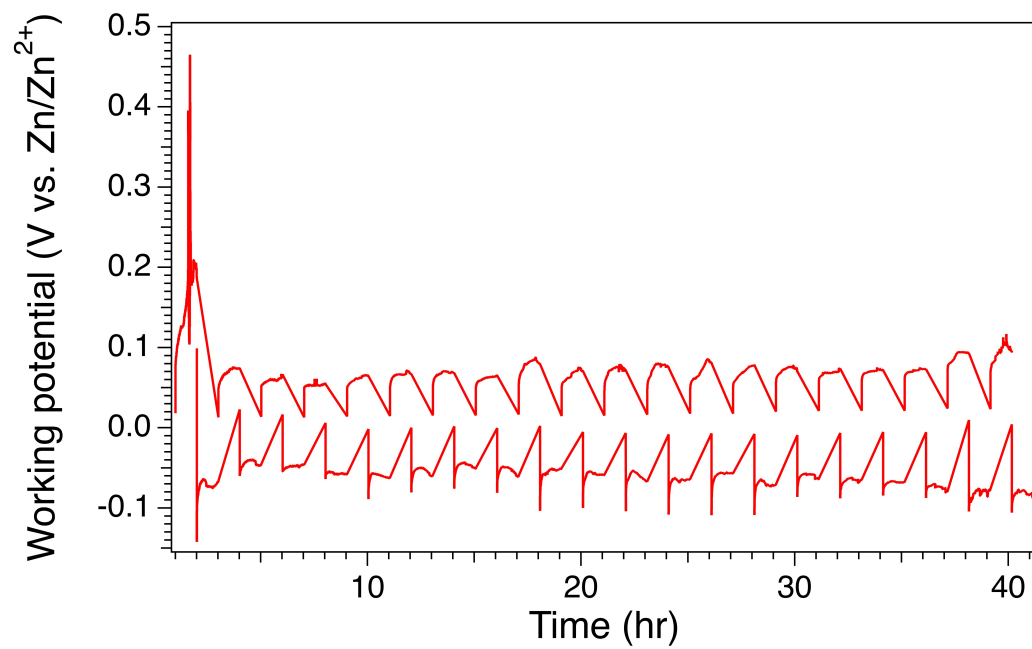


Figure 27: A symmetric cell testing with Zn|CLAM|Zn setup plating and stripping under and 100 mA/cm² for 120 mins current holding (60 mins for charging, and 60 mins for discharging) each cycle until 20 cycles.

below target of 80% utilization for Zn battery cycling. However, eighteen times higher areal capacity still makes this technology appealing, which benefits from thick slurry anode design. In this symmetric cell testing, we demonstrated comparable CE with 20% utilization of zinc during cycling in symmetric cell. It is still far below the commercial line but the progress of this still shows promising. To improve utilization of zinc during cycling, further experiments will be needed to systematically explore zinc anode parameters, such as the KOH starvation effects, *in-situ* measurement of slurry suspension stability, and zinc particle morphologic changes. Similarly, a corresponding OER catalysts or bi-functional catalysts needs to be utilized to achieve the regeneration of the used zinc slurry practically. Lastly, the design of this regeneration system also needs to be optimized in a larger stack scale. Usually this is a limiting and challenging step with issues that cannot be foreseen. All of these must be considered in future development of MRZAB.

Corrosion effects

The corrosion of zinc anodes in ZABs, is primarily driven by the hydrogen evolution reaction (HER), which severely hampers the battery's performance and efficiency. The thermodynamically favorable potential at which these batteries operate exacerbates this issue (HER at -0.83 V vs. SHE; Zn/ZnO at -1.26 V vs. SHE in PH= 14)⁹⁸. Various strategies have been proposed to mitigate this corrosion, such as incorporating metal oxides or surfactants into the electrolyte. For example, Subramaniam et al⁹⁹ investigated the use of nanofluid electrolytes to mitigate the hydrogen evolution reaction and zinc corrosion in electrically rechargeable zinc-air batteries recently, enhancing their cyclic performance and stability. They found that nano-size SiO_x and ZnO are two effective additives in 6 M KOH electrolyte to increase the HER onset potential. Similarly, In₂O₃ and Bi₂O₃ were also explored to improve the utilization of zinc in

other groups^{100, 101}. On the other hand, Hosseini et al reported various surfactants effectively suppressing the zinc corrosion in zinc air flow battery^{51, 102, 103}, such as ethanol, sodium dodecyl sulfate, pluronic F-127, and dimethyl sulfoxide.

However, most of these approaches have been tested with solid zinc plates or prefilled zinc granules as the anode. In contrast, a zinc slurry, which has a significantly higher surface area, could potentially experience even more severe corrosion, which is not explored. To establish a baseline understanding, corrosion behavior in thick slurry anodes was assessed in the absence of additives designed to suppress corrosion, offering insights into future improvement strategies. **Figure 28** below exhibited zinc slurry air battery discharge profile after six hours of air exposure for zinc slurry. It almost delivers 70 mAh/g_{Zn} capacity, which is 88% less than benchmark that using as-prepared zinc slurry. This large capacity loss is likely attributed to two major factors. First, different side reactions can occur. For example, the zinc reacts with water to release hydrogen. The intermediate product Zn(OH)₂ further reacts with CO₂ from air to undesired ZnCO₃. These result in the loss of the active amount of zinc we can assess during cell discharging. Second, the formation of side products alters the rheology of the zinc slurry, which affects the stability of suspension. Although storing the zinc slurry under Argon seems a promising solution, the study of chemo-mechanics of zinc slurry is still at very early stage. It is crucial to optimize slurry stability in different stages in the battery life cycle: storage stage, cell discharging process, and regeneration.

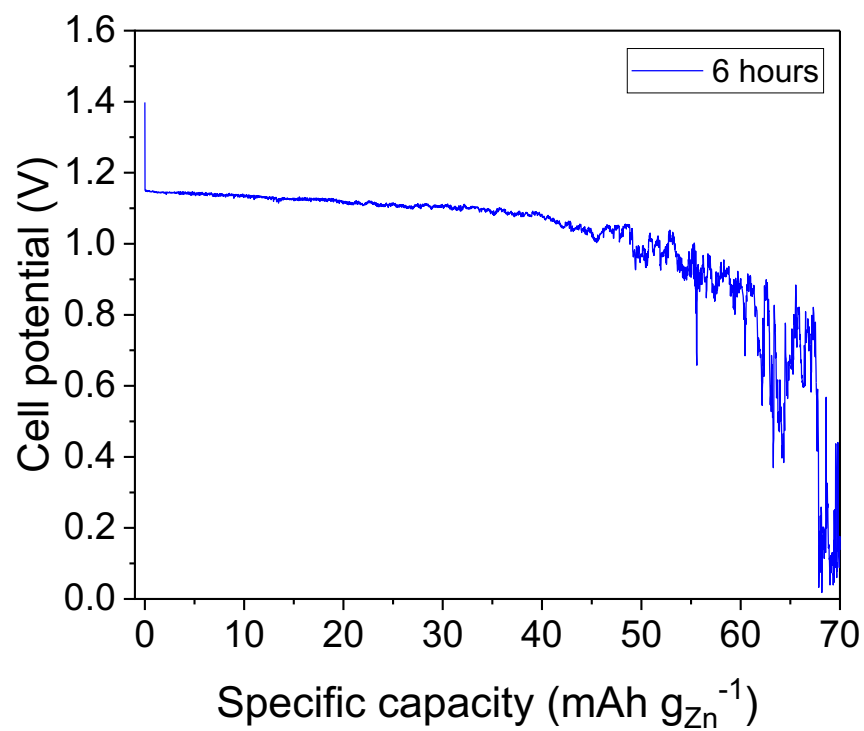


Figure 28: Discharging profile for air-exposed zinc slurry after 6 hours in full cell testing.

CHAPTER 6. APPLYING POTENTIAL STEPS TO CHARACTERIZE MASS TRANSPORT
OF POROUS ELECTRODE IN VANADIUM REDOX FLOW BATTERY

Abstract

This work is to implement a new experimental method to study the flux of redox-active materials through electrodes used in redox flow batteries (RFBs). Methods have already been established to study other components in such cells. Permeability and conductivity tests are two essential methods to investigate the performance and intrinsic properties of a membrane. Polarization and cycling are two general methods to study the overall performance and stability of a cell. Although the classical polarization experiment can be applied to investigate the performance of cells, how to explain the limiting current, the most important factor in polarization curve, is still a big challenge. To go beyond that, to characterize the flux regarding limiting current in the electrode, a new stopped flow experiment is employed to access the fundamental understanding of mass transport phenomena in various materials that serve as electrodes. The new stopped flow experiment is applied to a vanadium RFB and is conducted by combining voltametric techniques and impedance spectroscopy in one cell with only a total of 75 mL vanadium electrolyte needed in each run. The potential benefit of this method is that we will measure a basic quantity that can be analyzed in the diffusion and migration process to characterize the flux in the redox flow battery.

Background

Recently, there are increasing amounts of sustainable and renewable energy coming from wind power, solar energy, and other non-fossil fuel sources to which we need to have access. However, such renewable electrical energy sources have the properties of variability and intermittency, and it can be mitigated using a battery energy storage system (BESS).³ An energy storage system (ESS) is needed to store a large amount of ‘clean’ electrical energy from these intermittent sources. There are many types of ESS technologies: pumped hydroelectric storage, flywheels, reversible fuel cells, redox flow battery, solid state battery etc.^{1, 2} ESS technologies serve as the large-scale energy storage system (LSESS), to store and supply the various energy resources into grid power. Thus, the BESS has the potential to be applied into the grid power for residential dwelling and commercial houses as a small-scale energy integration.³ Although pumped hydroelectric is now dominant in grid energy storage, there are more opportunities found in the BESS. The redox-flow battery can offer low cost, and the lithium-ion battery serves as ‘mobile energy’ applying into commercial electronics.¹⁰⁴

The all-vanadium redox flow battery (VRFB) has served as one of our most mature stable and reliable LSESS for many years. At the early stage of development of VRFB, the V^{2+}/V^{3+} couple was first investigated with glassy carbon electrode using cyclic voltammetry (CV) by Skylas-Kazacos's group in 1985.¹⁰⁵ VRFB was then proposed by them formally at the University of New South Wales in 1986.¹⁰⁶ VRFB was characterized in construction and performance including the basic cycling hours and fundamentals of the cell in 1987.¹⁰⁷ VRFB was then shown as an efficient storage unit for photovoltaic systems in 2000.¹⁰⁸ In recent years, many researchers and engineers were putting efforts to transform the lab-scale cell into the industrial-scale working station as LSESS.¹⁰⁹⁻¹¹¹ Recent efforts have dramatically advanced in developing extremely large

capacities from VRFB as large storage power applications. The variable generation energy from solar or wind power is possibly averaged out by these applications. Some of the largest vanadium grid batteries were constructed successfully worldwide in the following countries: Japan, Germany, China, USA. An 800 MWh VRFB is expected to finish construction in China by 2018¹¹². And there are many great companies funding and developing VRFB, such as Invinity Energy Systems in USA, Renewable Energy Dynamics Technology in Europe, and Rongke power in China.

Fundamentals of VRFB

Compared with traditional batteries, the VRFB has its unique properties. The energy is stored in the electrolyte, and the electrode, porous carbon paper, or carbon felt, provides a large surface area where the redox reaction takes place. Nitrogen is pumped in the negative electrolyte tank to avoid oxidation while the battery is working. A membrane serves as a separator and is used to allow proton exchange but minimize vanadium ion crossover functionally.

The critical components of the battery setup include an electrode, membrane, electrolyte solution reservation tanks, and pumps circulating the electrolyte, as is shown in **Figure 29**. Negative and positive electrolytes were stored in two different tanks, small bottles at lab scale, and circulated through the cell by the pump. The membrane for the following measurement was 3M 825 EW (thickness 50 μm). The positive half redox reaction is $VO_2^+ + 2H^+ + e^- \leftrightarrow VO^{2+} + H_2O$. And the negative electrode redox reaction is $V^{3+} + e^- \leftrightarrow V^{2+}$.

The most advanced, high-performance cell was designed in a non-gap structure found in the Mench and Zawodzinski groups^{76, 113}, and details of components were shown in **Figure 30**. The gasket was made with 70% thickness of the electrode to ensure good compression and avoid leakage. The copper wire coated with palladium serves as our reference electrode to isolate the

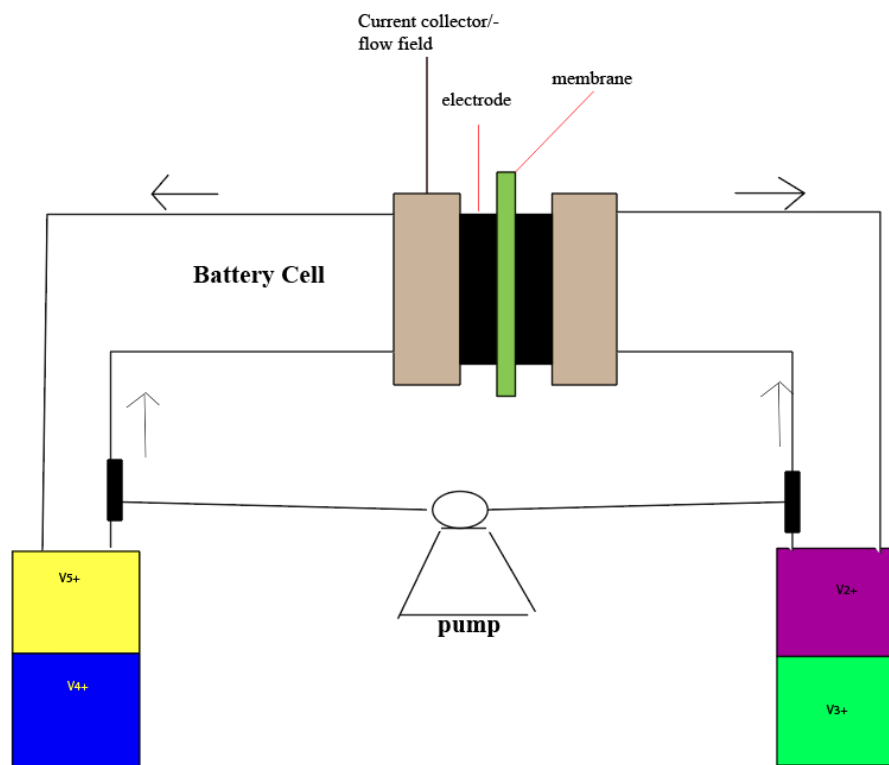


Figure 29: A sketch for general lab-scale VRFB

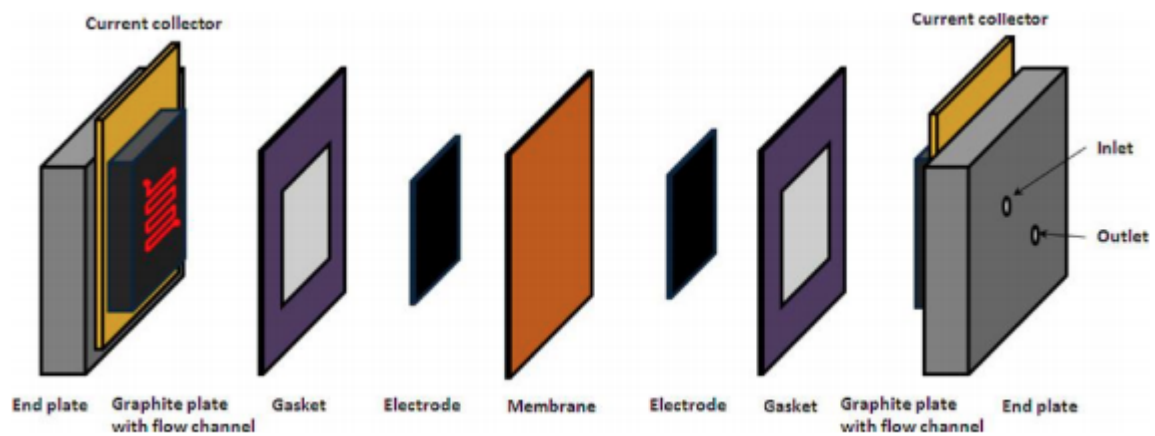


Figure 30: A schematic VRFB detailed setup (reproduced)⁷⁶

performance of each electrode. It was sandwiched by two pieces of membranes. SGL carbon paper 39AA (280 μm) and 29AA (180 μm) were conducted in the experiment as the electrode.

Developments of membrane in VRFB

To improve the performance of VRFB, several components need to be improved. Membranes, serving as a separator, plays an important role in VRFB to allow proton exchange but preventing vanadium or other ions crossover in an ideal case. The ideal membrane should have high conductivity, high ionic exchange capacity, low vanadium ions permeability, low swelling ratio, low area internal resistance, good chemical stability and low cost. To target suitable membranes in different cells, different materials and technologies were developed in recent years.

To determine whether it is a good membrane in the cell, measurements of membrane are inevitably conducted to obtain the membrane performance and properties. In a single cell with discharge and charge experiment, the coulombic efficiency (CE), voltage efficiency (VE), the energy efficiency (EE) can be determined by the equations in the literature¹¹⁴. Ionic exchange capacity can be measured by titration method¹¹⁵. Standard experiments were conducted to obtain water uptake¹¹⁶, swelling ratio¹¹⁶, and water transport parameters¹¹⁷. The internal areal resistance can be derived as a part of a polarization experiment, allowing making correction of the V-I curve¹¹³ for DC resistive losses. The proton conductivity can be measured through experiments conducted in a home-made cell in our group¹¹⁸. Permeability and selectivity can be measured through UV-visible spectroscopy in a standard permeability test¹¹⁹. Chemical stability can be tested in several methods¹²⁰ in a long term.

In the research study of membranes, the fabrication process plays an important role, because it does not only affect the internal structure of the membranes as well as the needed pretreatments before applying in experiments but also impacts the cost of the membranes. VRFB

membranes are classified in two large groups: ionic exchange membrane (IEM) and non-ionic exchange membrane (NIEM). In the IEM, cation exchange membrane (CEM) were studied most frequently in the early time till now. Nafion membranes, the famous membrane product by Dupont¹²¹, contains the sulfonic acid group which can ionize to liberate protons and exchange the ions in the solution. There are many preparation methods to change the physical or chemical properties of membranes, such as radiation grafting method¹²², casting method¹²³, sol-gel method¹²⁴ or a layer-by-layer self-assembly method¹²⁵.

Researchers put a lot of efforts on Nafion series membranes for VRFB over time. Many literature studies compare these membranes including N115, N117, N112, N1135, N1100^{123, 126}. Membranes thickness, the main factor, determines the performance of the cell as they are produced by the same material. The membrane with higher thickness will have higher area resistance but lower permeability. In order to balance these two factors, the N117 was measured to be found that it provides better performance among Nafion series. However, when these membranes apply to the VRFB applications in the long term at all climates, the research showed that N115 was found that it was the best because it had better chemical stability and lower crossover rate.

Although Nafion based membranes provide high chemical stability and great electrochemical properties, it still has high permeability and cost. Sulfonated poly (ether ketone) membrane (SPEEK) and sulfonated polyimide (SPI) are two other types of CEM, which have been extensively studied^{127, 128}. SPEEK showed a lower permeability and higher CE, VE, EE than Nafion. SPI, a low-cost polymer, has a lower crossover issue and excellent chemical stability. Both SPEEK and SPI offer a lower permeability but lower conductivity and stability compared to Nafion. Thus, these CEM were studied to be modified to improve the performance of VRFB by adding lower swelling ratio matrix. CEM is still the most used membrane in VRFB.

Development of electrodes for VRFB

Electrodes perform a very important role in providing active sites where redox reactions take place. During any process of VRFB applications, the energy efficiency is mainly dependent on the activation and concentration polarization, which are governed by the electrode. The ideal electrodes require the following characteristics: 1. the electrode must be chemically stable in the highly acidic environment; 2. the electrode must be durable and electrochemically stable in any operative potentials; 3. the electrode must be inert, and it cannot participate in any redox reactions; 4. the electrode must have high electronic conductivity to ensure charge transfer is fast. To fulfill the requirements in VRFB, efforts were advanced in studying the material of electrode and surface treatments for understanding the mechanisms of the reactions and the mass transport of the electrode.

In the research of VRFB electrode, the understanding of mechanism of redox reaction is extremely important, because it not only determines the activation loss but also provides a characterized method for the electrode. There were many mechanisms hypothesized and developed in last 30 years. To best of my knowledge, the general mechanism of $\text{VO}_2^+/\text{VO}^{2+}$ and $\text{V}^{3+}/\text{V}^{2+}$ couples can be summarized as following: First, the vanadium ions which diffuses in the electrolyte solution is absorbed to the electrode surface. In the second step, the V ions and protons of functional groups containing nitrogen, carbon, and oxygen are undergoing ion exchange; next, oxygen and electron transfer reactions take place in the positive redox couple. In the final step, an ion exchange process takes place between V ions on the surface of electrode and protons existing in the electrolyte. Then, the produced reactants diffuse back to the bulk solution. In the following paragraph, the detailed summary of developments of VRFB reactions mechanism is given with several important findings. To improve the redox reactions, the electrical conductivity of the

electrode must be high, and the presence of abundant oxygen or nitrogen functional groups must exist on the surface of the electrode.

In the early stage, Skyllas-Kazacos investigated the kinetics of $\text{VO}_2^+/\text{VO}_2^+$ couple by rotating disc voltammetry and Tafel plots at different types of graphite and carbon electrodes¹²⁹. They found that the kinetics of the $\text{VO}_2^+/\text{VO}_2^+$ is limited by the number of active sites on the graphite and carbon surfaces rather than the surface area. Li *et al.* indicated that the carbon paper electrode with hydroxyl functional groups had a better performance on the $\text{V}^{3+}/\text{V}^{2+}$ couple reaction kinetics¹³⁰. In a later study, Wu *et al.* reported that the standard reaction rate constant k was determined by investigating the kinetics of redox couple reactions¹³¹. Other efforts have been devoted to building the kinetics of the new materials or catalysts such as carbon nanofibers, carbon nanotubes, graphene oxide besides graphite felt and carbon felt electrodes. Zhang *et al.* offers a nitrogen doping method to modify the GO electrode to create abundant active sites¹³². Moreover, although most of studies refer to the improvements of the $\text{VO}_2^+/\text{VO}_2^+$ redox reaction in cathode, in recent study, Santamaria *et al.* investigated the importance of preventing hydrogen evolution to further enhance the reversibility of the $\text{V}^{3+}/\text{V}^{2+}$ couple¹³³.

In this phase, although many efforts were devoted to investigating the mechanisms of redox reactions on the surface of electrode, many researchers were mainly focused on discovering suitable materials of electrode or the surface treatment method to improve the surface oxide groups shown to provide active sites for VRFB reactions. In the early stage, the carbon cloth electrode material was first studied by Skyllas-Kazacos's group. During the charging, mechanical degradation was observed, and the vanadium ion diffusion was limited because of low surface area. Next improvement was the study of Carbon-polymer composite electrode. This type of electrode was not suitable to be applied as electroactive material in VRFB, but it can be developed as the

electrode substrate. The PAN-type carbon or graphite felt has been used most frequently up to now, because it provides large surface area, high conductivity, and offers excellent chemical and electrochemical stability. Carbon paper electrodes have promising properties such as porosity, thin thickness, low density, and low electrical resistance, leading to the trend that most of researchers have a great of interest in studying it in VRFB. Ever since a non-gap cell architecture^{76, 134} was developed by our group, which significantly improves the battery performance, the thin carbon papers are the top choices in this non-gap cell and studied extensively.

Researchers also made impressive methods to characterize the battery potential losses and stability of cycle, as known as polarization and cycling experiments.¹¹³ The polarization curve indicates the performance of the battery. This method provides researchers a tool to analyze the losses in the whole process. There are three types of losses such as activation loss, Ohmic loss, and transport loss. The activation loss occurs in the beginning part of polarization in discharging process, which is governed by the mechanisms of the redox reactions and charge transfer on the surface of electrode. The Tafel plot was used as a method to analyze the kinetics in the activation polarization. The Ohmic loss is associated with contact and ionic resistances, and internal resistances. The mass transport loss is related to the reactants in electrolyte delivery to the electrode, where the limiting current reaches because of starvation of reactants on the electrode surface.

Although the polarization method provides an excellent view of performance of the cell, there is still a lack of methods which can indicate the stability and durability of the battery. Cycling experiments provides this information, and it can monitor the battery working in many cycles. Cycling experiments indicate whether the battery is suffering severe crossover issue which causes the capacity decay, and whether the battery has the excellent chemical and electrochemical stability in the long-time operation. However, there is a significant gap in the analytical methods

to analyze the limiting current governing the transport loss. We seek to fill the gap to allow fundamental understanding of the limiting current where reactants on the electrode surface reaches ‘starvation.’ It is extremely important, because the limiting current affects the ultimate performance of the cell.

Approach

The stopped flow experiment can be outlined in the three aspects: the battery setup, the supporting theory, and the details of electrochemical tests. The battery setup offers the overview of how to design our experiment. The theory provides the analytical reasons behind the measurements we have done. The details of electrochemical tests indicate the general idea of how to measure the information we need.

Battery Testing

To improve our understanding of mass transport through the electrode, we need to isolate that component. This can be achieved, in principle, by adapting the cell in **Figure 31** for a ‘stopped flow’ experiment. The core design of this experiment is that we adopt two pieces of membrane, and the reference electrode was inserted in between the two membranes. To isolate the testing electrode or the working electrode in our experiment, we control the working potential only to characterize the testing electrode by various electrochemical techniques. The details of electrochemical techniques and general procedures will be introduced later.

Theory

There are many factors affecting the electrode reaction rate and current. The rate of processes governs the current or the electrode reaction. The general pathway of processes reaction taking place is shown in **Figure 32**. Mass transfer, electron transfer, and surface reactions control electrode reaction rate.

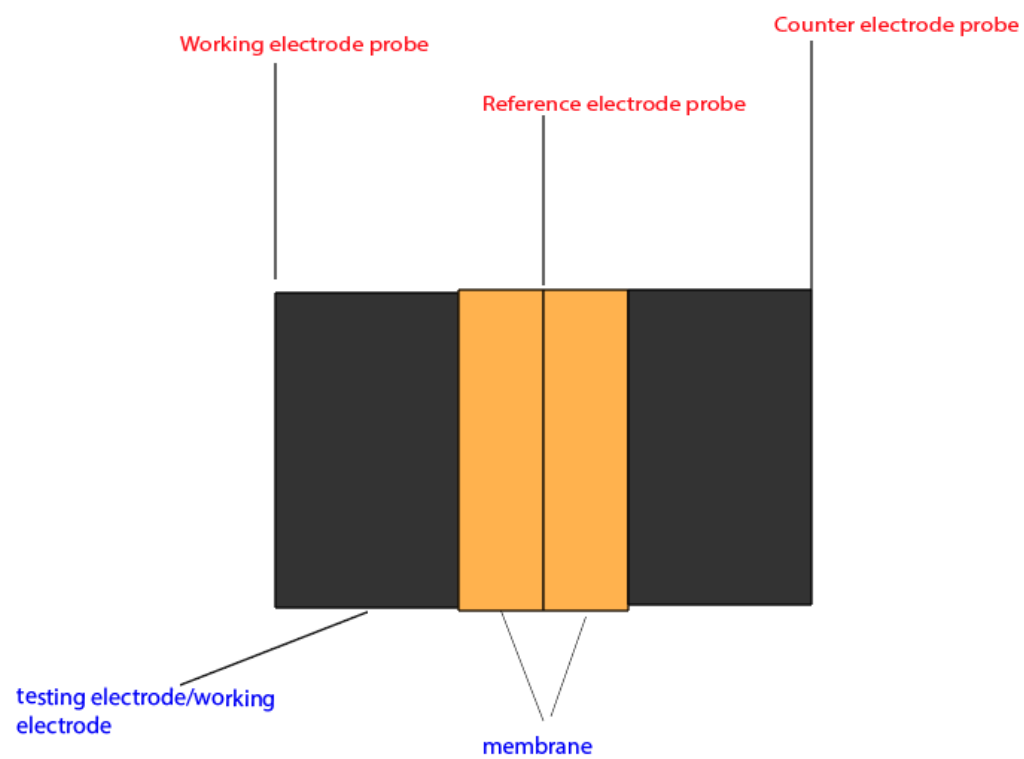


Figure 31: A schematic of the battery for a stopped flow experiment

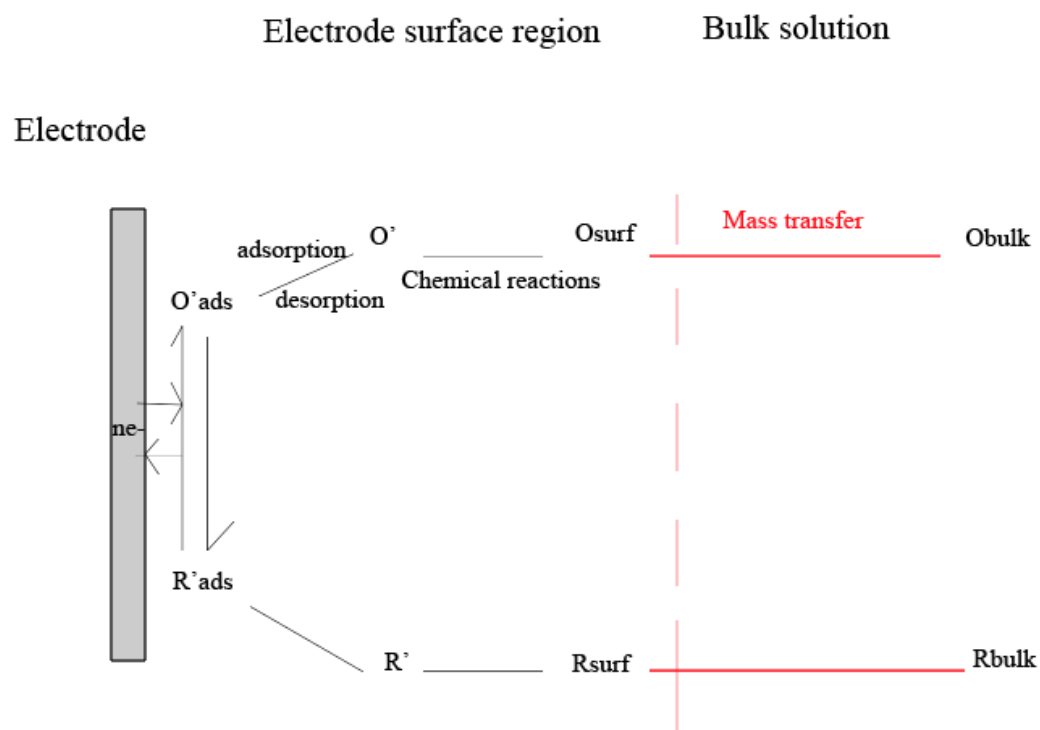


Figure 32: A general pathway of electrode electrochemical reactions.

In VRFB, the electrode kinetics can be very fast, so the electron transfer and other surface reactions can be neglected. This limit of such a process is called reversible or Nernstian process. The limiting current is mainly controlled by the mass transfer in VRFB. Mass transfer includes three factors: migration (electrical gradient), diffusion (concentration gradient), convection (stir velocity).

Mass transfer to the electrode is governed by the Nernst-Plank equation, written in one-dimension as:

$$J_i(x) = -\frac{D_i \partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i * \frac{\partial \phi(x)}{\partial x} + C_i v(x) \quad [14]$$

Where $J_i(x)$ is the flux of species i, D_i is the diffusion coefficient, $\partial C_i(x)/\partial x$ is the gradient of concentration, $z_i C_i$ represents the charge, and concentration of species i, $v(x)$ is the convection or stir velocity, F is the faraday's constant. In this stopped flow experiment, the convection can be neglected because of the stagnant electrolyte solution in the small pores of the electrode. Thus, only migration and diffusion contribute to the mass transfer flux.

The diffusion can be analyzed by semiempirical treatment and it was governed by the Nernst equation. When the SOC is not 100%, the oxidant and reductant both exist. The concentrations of both depend on SOC. The equation can be written in the following:

$$E = E^{0'} - \frac{RT}{nF} * \ln \frac{m_o}{m_R} + \frac{RT}{nF} * \ln \frac{i_l, c - i}{i - i_l, a} \quad [15]$$

Where i_l, c and i_l, a are limiting current when starvation of electrolyte on the electrode surface occurs (eg. $i_l, a = -nFAm_R C_R^*$), m_o, m_R are mass transport numbers for the oxide and reductant.

The migration is governed or characterized by the transference number of species ion in the electrolyte. In VRFB, the mobility of $VO_2^+, V^{2+}, V^{3+}, VO^{2+}, SO_4^{2-}, H^+$ can affect the migration. The transference number of vanadium ion, t_V , is related to the following equation:

$$t_V = \frac{u_V C_V}{u_V C_V + u_- C_- + u_+ C_+} \quad [16]$$

Where u_V, u_-, u_+ are the mobility of vanadium ion, sulfate ion, proton, and C_V, C_-, C_+ are the concentration of vanadium ion, sulfate ion, proton. The mobilities of ions in VRFB were reported in the paper¹³⁵. A similar analysis for migration in the membrane was reported by Elgammal et al¹³⁶. The effect of migration in the electrochemical cell is minimized by the presence of supporting electrolyte. In the VRFB, sulfuric acid is the supporting electrolyte. To minimize the migration effect, we can either increase the concentration of sulfuric acid or decrease the concentration of $VOSO_4$ in a specific volume of electrolyte, which can be easily analyzed by the transference equation showing above.

Details of Electrochemical Tests

All measurements were conducted in potentiostat/galvanostat SP-150. In the two steps charging process, Chronoamperometry (CA) technique was performed with electrode potential set at 1.8 V to avoid battery overcharge. Battery capacity (Q) was estimated and modified for a given SOC in the second charging step. To start our stopped flow experiment, Open circuit voltage (OCV) and Potentiostatic Electrochemical Impedance Spectroscopy (PEIS) techniques were used in the method. The settings for the stopped flow experiment is similar to the polarization experimental.¹¹³

However, the OCV and PEIS were measured while we turned off the pump and the flow was stopped. The general procedure is that we were setting PEIS -0.05 V vs. E_{ctrl} (potential observed in OCV) and then we turned on the pump and to allow flow for 5 sec to make sure the concentration returns to the original state. Next, we continued to modify PEIS for different potential steps to various potentials to get observe corresponding limiting currents. As the cell was assembled as a three-electrode system, the working potential was simply controlled, and the testing electrode was isolated.

Results and Discussions

In this experiment, the electrolytes were made by mixing $VOSO_4 \cdot H_2O$ (Alfa Aesar), sulfuric acid, and deionized water. In this experiment, the vanadium electrolyte solution were prepared in 1M $VOSO_4$ and 4M H_2SO_4 . Following the two-step charging protocol, two 25mL electrolytes were transported by the pipette in two different bottles which serves as positive and negative electrolytes and then charged with 1.8 V to a certain state of charge (SOC) which is ready for the following experiment. It was indicated that the battery referred to ‘fully charged’ as the current was below 20 mA. Then 25 mL electrolyte was transported into the third bottle and the charged positive electrolyte bottle was replaced by the third bottle. One more charging step was conducted to ensure the battery reaching to a certain SOC.

Below is the plot for E vs. i in 50% SOC of 1M vanadium/4M sulfuric acid stopped flow experiment as **Figure 33**. The limiting current is approached as we are running out of the electrolyte reactant at the electrolyte surface. As in 50% SOC, $[V^{5+}]/[V^{4+}]$ is 1:1. The symmetric shape of the plot proves limiting currents for anolyte and catholyte are essentially the

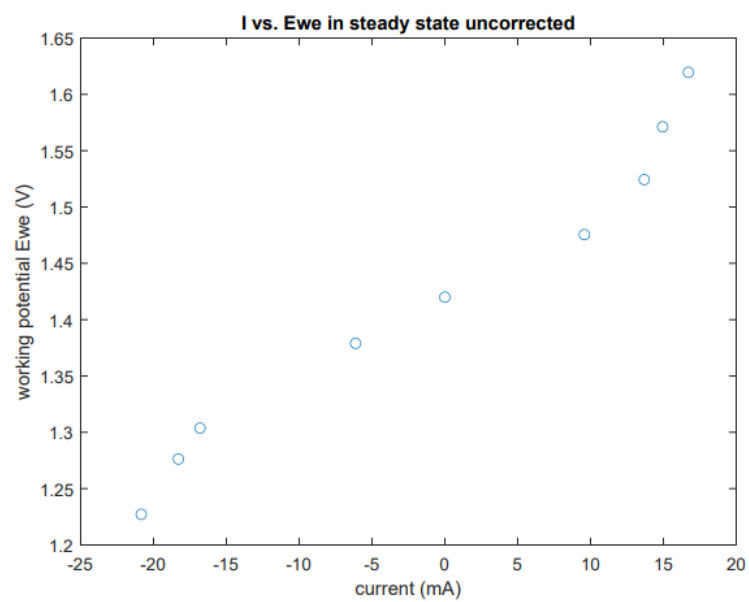


Figure 33: E vs. i in 50% SOC uncorrected stopped flow in 39AA (280um)

same. In the migration part, a simple calculation for t_v was obtained as 0.04. Only 4% of the current is carried by vanadium with these assumptions.

The other two carbon papers have the same carbon c-fibers milled from Sigracet manufacture reported size at 80-150 μm length and 7 μm diameter microtubes. They were tested in the same conditions with different manufactured thickness. Below is the plot of data for three carbon papers for a stopped flow experiment using 50% SOC of 1M vanadium/4M sulfuric acid as in figure 5, suggesting 0.5 M of VO_2^- or VO_2^+ as the catholyte. From the plot, 39AA delivers larger residual current than 36AA and 29AA. Notably, 29AA seems to experience an intrinsic issue during this potential holding experiment as a sharply increasing slope is observed where overpotential is less than 0.15V. This possibly indicates 29AA possess limited surface area to hold enough redox electrolyte for allowing rapid current exchange during the potential step at very early stage (< 60 seconds). Figure 34 represents an ‘isolated diffusion process’ polarization curve, which helps directly identifying the optimal porous electrode semi-quantitatively. We successfully designed the stopped flow to isolate the convection that contributes to the limiting current. Also based on the optimized vanadium ion to sulfuric acid ratio, we were able to minimize migration effects. However, the Nernst-Planck equation has its own limitation to quantify diffusion process: 1. It is in differential form; 2. A limiting current is usually challenging to obtain since stopped flow breaks the steady state that can be achieved during constant flow. Thus, we need seek other models to interpret the diffusion processes among different carbon papers more accurately.

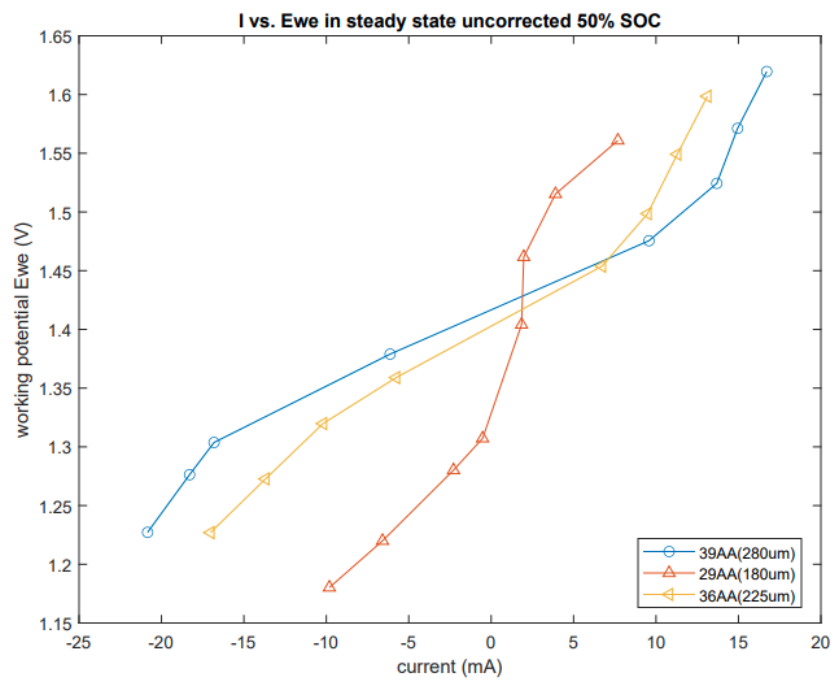


Figure 34: E vs. i in 50% SOC uncorrected stopped flow in 39AA, 36AA, 29AA.

There are many methods to characterize diffusion in an electrode, with the ultimate goal of quantifying the diffusion coefficient. Common ex-situ methods, eg. NMR (nuclear magnetic resonance) spectroscopy are powerful due to its ability of deliver absolute diffusion coefficient. Determining apparent diffusion coefficients can be achieved in galvanotactic intermittent titration technique (GITT), cyclic voltammetry (CV), and EIS. However, these techniques are not our focus and have been reported.

To corroborate our stopped flow design, the most efficient analysis method for potential step is Cottrell's equation for diffusion-controlled process.

$$i = \frac{nFAc_j^0 \sqrt{D_j}}{\sqrt{\pi t}} \quad [17]$$

Where i is the current (A); n is number of electrons transferred during the process; F is Faraday constant, 96485 C/mol; A is the area of electrode in cm^2 , C_j^0 is the initial concentration of species; D_j is the diffusion coefficient for species j ; t is time (s).

Due to utilizing porous electrode in VRFB, the Cottrell equation transform to eq. 18.

$$i = \frac{nFAc_j^0 \sqrt{D_{eff}}}{\sqrt{\pi t}} \quad [18]$$

Where $D_{eff} = D/\tau^2$ (this relation can found in Yong et al's model paper¹³⁷, where D is the diffusion coefficient across the fluid media, and τ is the tortuosity of porous media structure).

As previously presented, we applied multiple potential holds at different voltage to extract the current verse time profile. To explore the diffusion coefficient of VO_2^+ and VO^{2+} (denoted as V^{5+} and V^{4+}) in the stopped flow experiment, we used the Cottrell equation fit to the

I-V profiles for each of the electrodes. **Figure 35** reveals potential holding for 39AA carbon paper and its corresponding current versus time profile. Before 80 seconds, we suggest the sharply current drop is attributed to depletion of local V^{4+} species around surface of carbon paper. After 80 seconds, due to concentration gradient of V^{4+} forms a distance from bulk to surface of electrode, the residual current is more representative as solely diffusion-controlled process and mass transport limited. $D_{\text{eff}}(V^{4+})$ was calculated as $1.33 \times 10^{-6} \text{ cm}^2/\text{s}$ at $E = 1.51 \text{ V}$ with R square equals to 89.8%. Similarly, overpotential for quantifying $D_{\text{eff}}(V^{5+})$, we exhibited $1.93 \times 10^{-6} \text{ cm}^2/\text{s}$ at $E = 1.304 \text{ V}$ in **Figure 36**. Notably, V^{5+} has a higher diffusion coefficient than V^{4+} , which is aligned to literature reported values^{129, 138}, $2.1 \times 10^{-6} \text{ cm}^2/\text{s}$ for V^{4+} and $2.8 \times 10^{-6} \text{ cm}^2/\text{s}$ for V^{5+} .

To improve the accuracy of fitting, larger overpotential was applied to overcome two factors: 1. allowing faster time to reach the diffusion-controlled process; 2. stepping further away from kinetics overpotential region. We determined values of $1.84 \times 10^{-6} \text{ cm}^2/\text{s}$ for V^{4+} at $E = 1.62 \text{ V}$ and $2.81 \times 10^{-6} \text{ cm}^2/\text{s}$ for V^{5+} at $E = 1.22 \text{ V}$ as shown in **Figure 37-38**. Also higher R square values were associated with these plots, suggesting that the data is better fit into the model. These values are closer to literatures value.

Figure 39-40 presents the 29AA potential steps current versus time profiles. The model fitting is not reliable due to low R square value. However, generally, we observed a much lower diffusion controlled limiting current. And the calculated diffusion coefficient value suggests that we are at least one magnitude value of D_{eff} for vanadium ions less than 39AA carbon paper. The

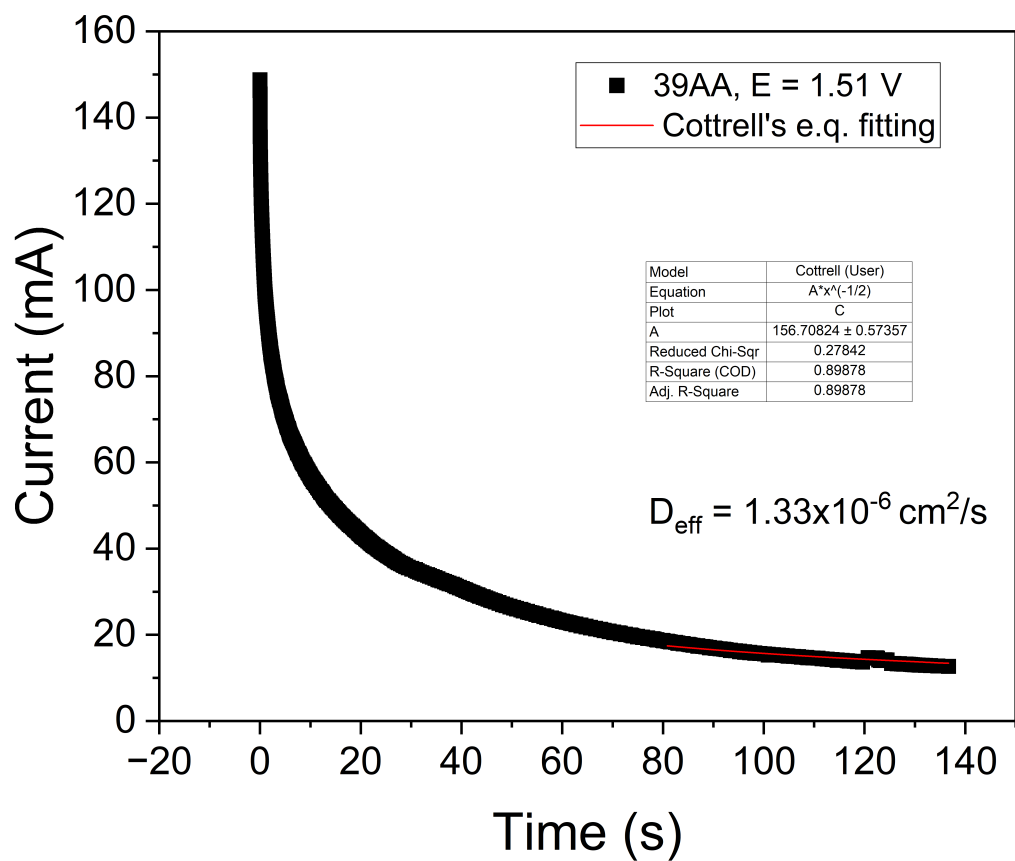


Figure 35: A potential step at controlled voltage 1.51 V and monitoring current verses time with fitting after 80 seconds in 39AA (280um). Note that this process V^{4+} is electrochemically oxidized to V^{5+} .

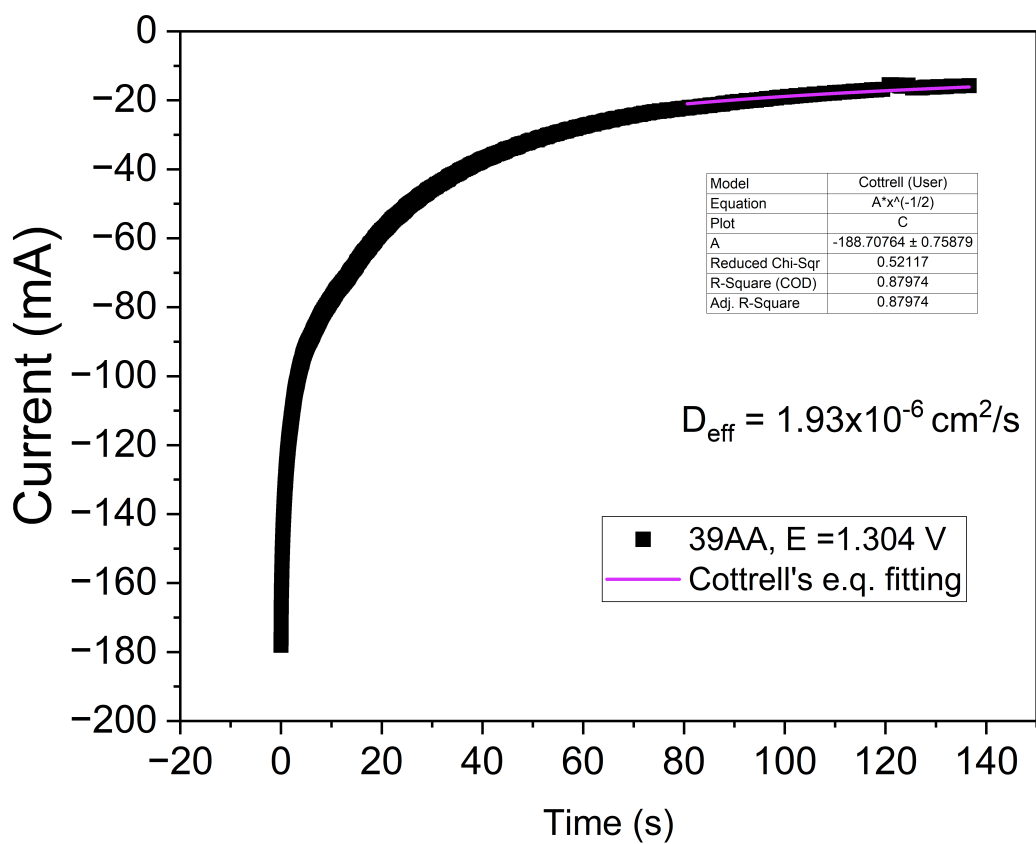


Figure 36: A potential step at controlled voltage 1.304 V and monitoring current verses time with fitting after 80 seconds in 39AA (280um). Note that this process V^{5+} is electrochemically reduced to V^{4+} .

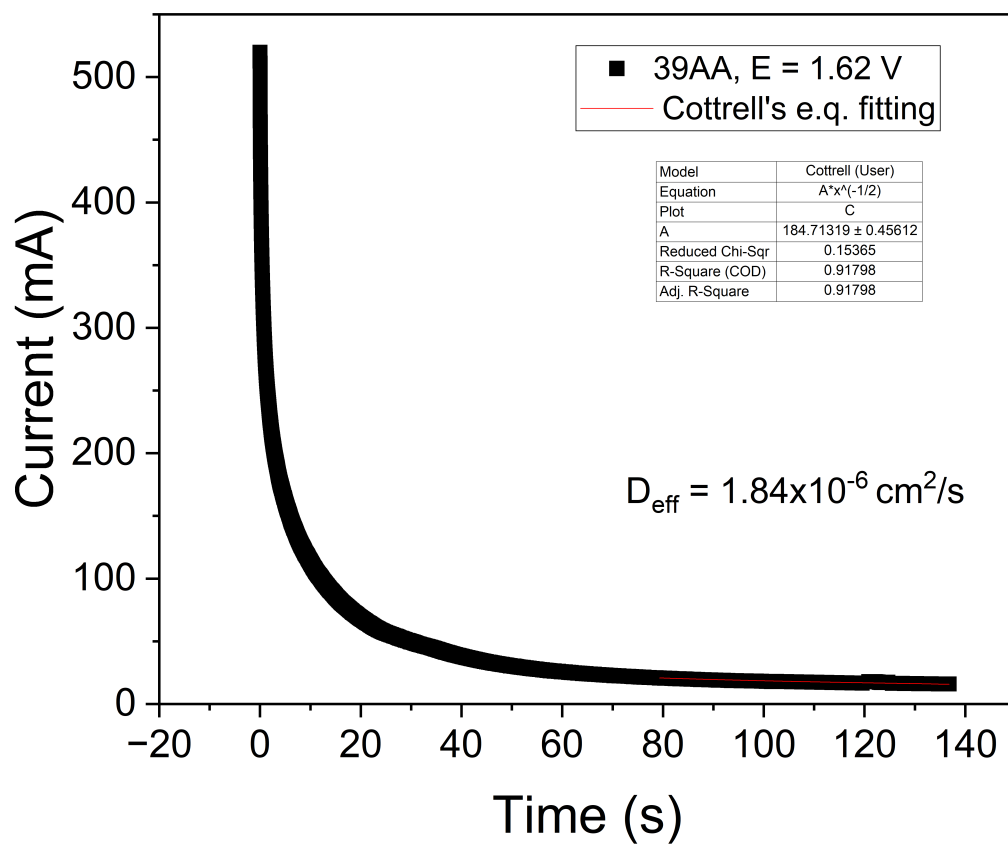


Figure 37: A potential step at controlled voltage 1.62 V and monitoring current verses time with fitting after 80 seconds in 39AA (280um). Note that this process V^{4+} is electrochemically oxidized to V^{5+} . Higher overpotential allows diffusion-controlled process reaches faster, which benefits our model fitting.

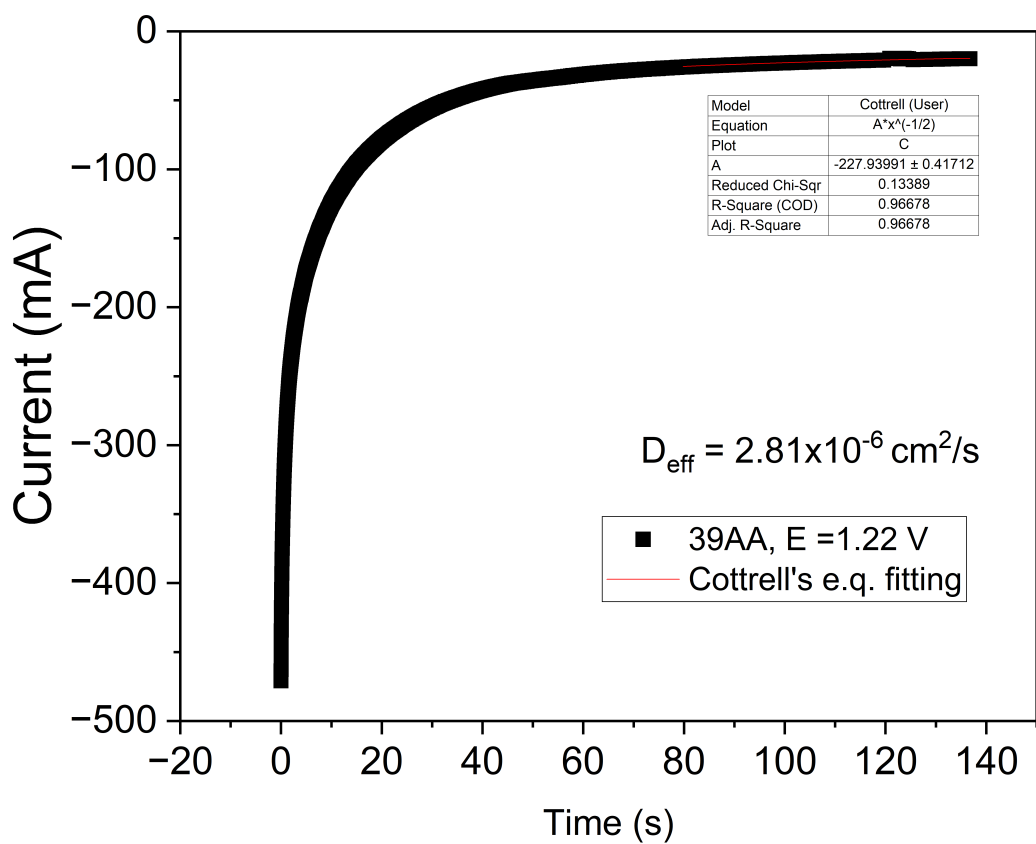


Figure 38: A potential step at controlled voltage 1.22 V and monitoring current verses time with fitting after 80 seconds in 39AA (280um). Note that this process V^{5+} is electrochemically reduced to V^{4+} .

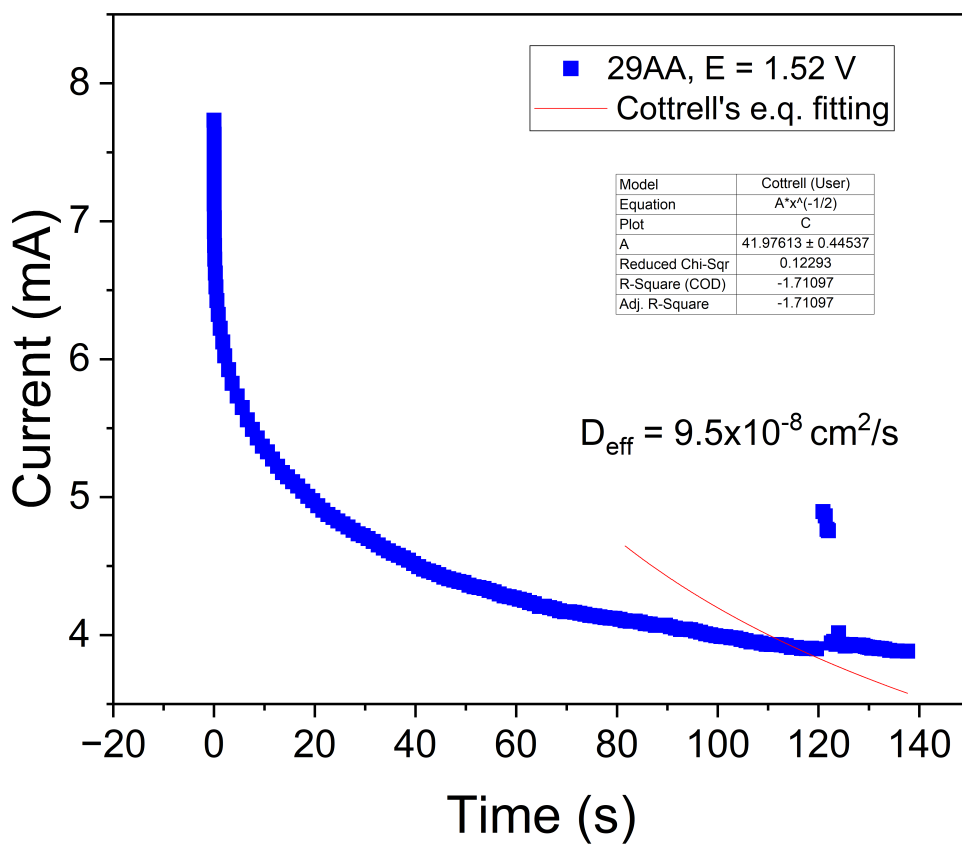


Figure 39: A potential step at controlled voltage 1.52 V and monitoring current verses time with fitting after 80 seconds in 29AA (180um). Note that this process V^{4+} is electrochemically oxidized to V^{5+} .

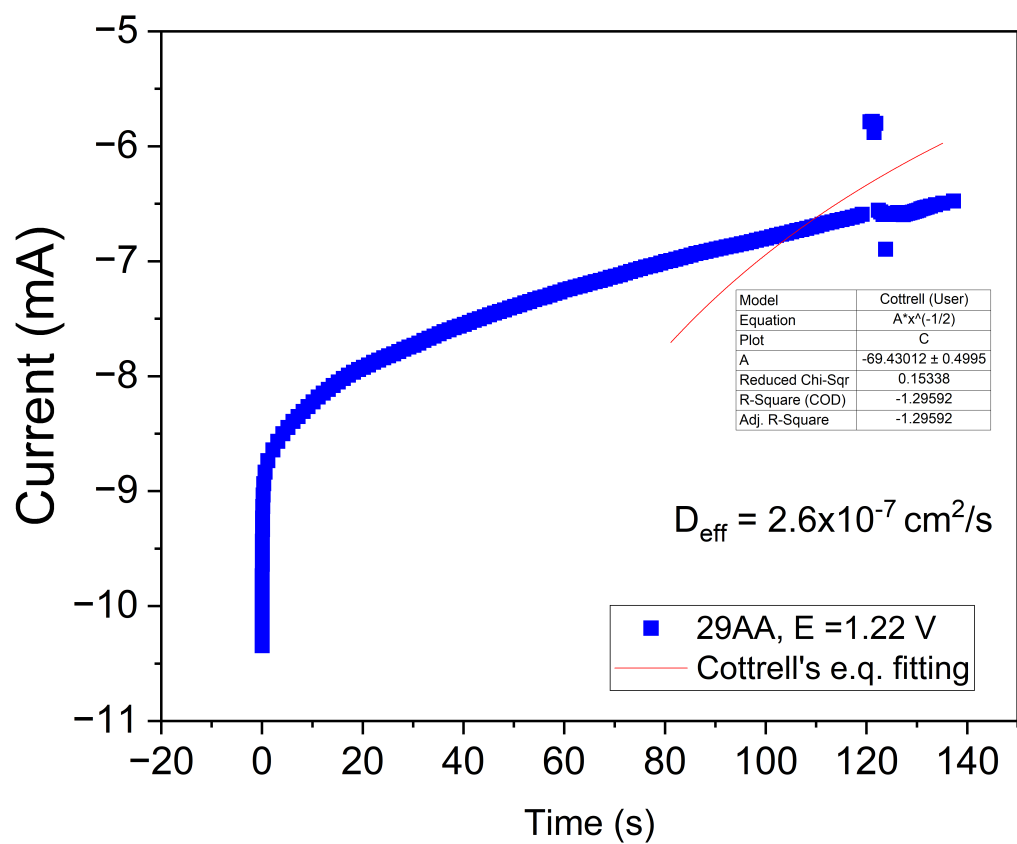


Figure 40: A potential step at controlled voltage 1.22 V and monitoring current verses time with fitting after 80 seconds in 29AA (180um). Note that this process V^{5+} is electrochemically reduced to V^{4+} .

reason behind this is possibly due to 29AA carbon fiber structure defects. More importantly, 29AA has lower thickness that is more brittle, and will become denser after cell assembly compression. This further makes diffusion path inside of 29AA more challenging, as the tortuosity of carbon fiber electrode is linked to its porosity. Lower porosity of porous electrode can significantly alter its tortuosity.

Impact of work

The ‘stopped flow’ experiment is a general method to characterize the electrode material. It is mainly focused on diffusion controlled current where bulk reactants are depleted on the electrode surface and the flux has to come from an infusion of bulk species. Porous carbon paper provides large surface area where redox reactions take place. Also, electrochemically accessible surface area is highly important during our experiment. Abundant wettability allows the carbon paper carries more electrolyte solution and reactants, which can significantly improve the performance of battery.

In future applications, this method can be applied to other processes, such as organic electrosynthesis, and serve as the initial characterization method for the electrode material. To improve the efficiency of production of the organics, efforts are devoted to study the mechanisms of various reactions on the electrode surface.

CHAPTER 7. CONCLUSIONS

1. Systematically Electrochemical Characterization to Improve Performance of Mechanically Rechargeable Zinc Slurry Air Battery

In this study, we aimed to enhance performance of MRZAB by using zinc slurry with larger surface area, which provides higher energy density than traditional zinc-air systems, addressing dendrite formation and cycling limitations by manually replacing zinc anode after discharging. Drawing from redox flow battery designs, we encountered flow issues due to slurry viscosity but resolved some clogging by modifying the flow channels. To further tackle clogging, we shifted from continuous pumping to an injection mode and redesigned the zinc-side cell with 3D-printed components. This new setup prevented clogging, achieving a peak power density of 180 mW/cm² with an MPL on the air electrode.

Next, we systematically analyzed and separated losses from each electrode by adding a pseudo-reference electrode. Probing the pseudo-reference electrode position between each component of the cell can help decoupling the internal resistance of each component. This allows us more accurately to separate differences effects, particularly separating mass transport residual loss in medium current region based on polarization curve. We observed that oxygen reduction at the cathode was a primary loss factor at low currents. This is associated with ORR sluggish kinetics issue. In contrast, zinc slurry transport limitations became more significant at higher currents. These insights highlighted the need to optimize KOH concentration and slurry composition. Moreover, a parametric study on KOH concentration and gas flow orientation revealed that a higher KOH concentration stabilized slurry performance at high currents but hindered oxygen transport. Switching to a ‘gas-through-middle’ flow configuration improved performance with FeKudzu catalysts, while MPL coating further boosted oxygen transport despite raising internal resistance.

Finally, we compared the performance of FeKudzu and Pt/C catalysts, finding FeKudzu to be a viable, cost-effective alternative. Further, using humidified air instead of KOH flow on the air side could maintain membrane hydration, enhancing performance in high-discharge applications.

2. New Approach to Investigate Low-Percolation Slurry Characteristics to Improve Zinc Utilization in Mechanically Rechargeable Zinc Slurry Air Battery

This study presents a novel mechanically rechargeable zinc-air battery (MRZAB) designed using 3D-printed ABS components. The cell's anode, optimized for high-capacity, semi-batch operation through slurry injection, achieved an ultra-high areal capacity of 456 mAh/cm². Our analysis revealed that utilizing a thick anode with 33 wt% zinc slurry significantly enhances energy density, though it also presents practical challenges in mechanical slurry removal, paving the way for large areal capacity applications.

To improve zinc utilization, we systematically investigated key parameters, including membrane type, operational mode, zinc loading, and KOH concentration. Results indicate that the injection mode outperforms continuous flow, particularly when using the CLAM membrane, which delivered 57.5% higher utilization compared to commercial membranes. Additionally, optimizing KOH concentration at 4M achieved an ideal balance by providing 70.7% zinc utilization; higher concentrations increased viscosity, impeding hydroxide ion diffusion. Through *in-situ* EIS, we observed that zinc slurry resistance changes dynamically with the state of charge (SOC), likely due to zinc particle aggregation, passive layer formation, and viscosity fluctuations in the slurry. We applied an impedance-based model to characterize the specific conductivity of the slurry, which decomposes the high-frequency impedance into contributions

from ionic resistance (R_i) and electronic resistance (R_e), representing hydroxide ion mobility and particle-particle contact, respectively.

To account for conductivity variations due to particle distribution, we employed the Bruggeman approximation, adjusting for porosity effects and validating against a simulated RVE for zinc particle distribution. This RVE model, based on Monte Carlo simulations and informed by SEM-derived particle size distributions, predicted a conductivity range aligned with experimental values (around 1.02 S/cm). The model revealed that zinc particles are highly scattered in the slurry, preventing the formation of a percolation network, which is essential for continuous electronic pathways. This scattering effect, confirmed via microscopy, highlighted the importance of particle contact probability in conductivity calculations.

3. Development of Lab-Cell MRZABs for Future Prototype Technology and Other

Considerations

The transition from continuous flow to semi-batch injection in MRZABs has proven necessary to improve power and energy density. However, the injection mode design still faces challenges, such as incomplete slurry removal, zinc slurry corrosion (self-discharge), and the potential to regenerate fresh zinc slurry from used material. These challenges underscore the need for innovations in slurry injection and removal, as well as methods to enhance slurry stability and reusability.

To address these issues, we systematically designed a 3D-printed MRZAB prototype aimed at achieving complete slurry removal post-discharge. Initial tests using a serpentine flow field inspired by fuel cells revealed severe clogging, necessitating a flow field modification with a 2 mm channel width, which partially alleviated clogging but still presented issues during cell

discharge due to viscosity increases. Shifting to an injection-based approach with multi-channel configurations improved slurry replacement efficiency. Although this design allowed more thorough slurry removal, material limitations in 3D-printed ABS led to leakage issues, highlighting the need for more advanced materials like PEEK for future prototypes.

Zinc slurry regeneration is essential for the economic viability of MRZABs. Using a symmetrical cell setup, we conducted zinc stripping and plating tests to evaluate reversibility and coulombic efficiency (CE). By operating at 40 mA/cm² and 100 mA/cm², we observed stable voltage responses and overpotential reduction at higher current densities, suggesting enhanced percolation network formation. This setup achieved a CE of 98.4% with around 2% utilization, while extended tests under deeper cycling showed potential for higher utilization. Future work will focus on optimizing conditions for increased zinc utilization and exploring in-situ measurements to monitor slurry stability and zinc particle morphology changes during cycling.

Zinc corrosion, primarily due to the hydrogen evolution reaction (HER), remains a significant obstacle, particularly for high-surface-area zinc slurry anodes. Preliminary tests without corrosion-suppressing additives showed an 88% capacity loss in 6 hours air-exposed slurry, attributed to side reactions (e.g., Zn(OH)₂ and ZnCO₃ formation) and rheological changes that compromise slurry stability. This highlights the need for slurry optimization across storage, discharge, and regeneration stages. Future studies will examine corrosion inhibitors and investigate zinc slurry stabilization in air-free environments to mitigate these effects.

4. Applying Potential Steps to Characterize Mass Transport of Porous Electrode in Vanadium Redox Flow Battery

This study aims to advance electrochemical characterization techniques tailored to vanadium redox flow batteries (VRFBs), specifically targeting mass transport effects in porous electrodes.

Traditional polarization curves are often limited in explaining limiting current, the most important factor that governing a cell's performance. To address this, we developed a refined method incorporating a stopped flow setup with applying potential steps, which enables fundamentally understanding of limiting current related to diffusion-controlled process in porous electrode for VRFB.

In stopped flow conditions with prepared VRFB charged to 50% SOC. We performed potential steps in different overpotential values among three carbon papers (39AA, 36AA, and 29AA). During potential holding, the voltage differences forces electrolyte depletion on electrode surface, and a small quasi-stable current has to come from diffusion from bulk with concentration gradient. This quasi-stable diffusion-controlled current was treated as limiting current in this study, while real limiting current in stagnant system without convection to replenish the reactants is always zero. Results showed that 39AA exhibited the highest limiting current, suggesting better surface area and mass transport capability. Conversely, 29AA displayed much smaller limiting current at same overpotential, possibly due to limited active surface area and compression effects reducing its porosity. We applied a modified Cottrell equation that considers porous media by introducing an effective diffusion coefficient (D_{eff}). Current versus time profiles for each electrode were fitted to this model, revealing D_{eff} values of $1.33 \times 10^{-6} \text{ cm}^2/\text{s}$ for VO_2^+ and $1.93 \times 10^{-6} \text{ cm}^2/\text{s}$ for VO_2^+ on 39AA carbon paper. The higher diffusion coefficient for VO_2^+ aligns with literature, suggesting reliability of this new stopped flow approach.

REFERENCES

1. Dell, R. M.; Rand, D., Energy storage - A key technology for global energy sustainability. *Journal of Power Sources* **2001**, *100*, 2-17.
2. Chen, H.; Cong, T. N.; Yang, W.; Tan, C.; Li, Y.; Ding, Y., Progress in electrical energy storage system: A critical review. *Progress in Natural Science* **2009**, *19* (3), 291-312.
3. Nair, N.-K. C.; Garimella, N., Battery energy storage systems: Assessment for small-scale renewable energy integration. *Energy and Buildings* **2010**, *42* (11), 2124-2130.
4. Awan, A.; Alnour, M.; Jahanger, A.; Onwe, J. C., Do technological innovation and urbanization mitigate carbon dioxide emissions from the transport sector? *Technology in society* **2022**, *71*, 102128.
5. Chau, K. T.; Wong, Y. S.; Chan, C. C., An overview of energy sources for electric vehicles. *Energy conversion and management* **1999**, *40* (10), 1021-1039.
6. Larminie, J.; Lowry, J., *Electric vehicle technology explained*. J. Wiley: Chichester, West Sussex, England ;, 2003.
7. Pesaran, A., Battery Thermal Management in EVs and HEVs: Issues and Solutions. *Battery Man* **2001**, *43*.
8. Rao, Z.; Wang, S., A review of power battery thermal energy management. *Renewable and Sustainable Energy Reviews* **2011**, *15* (9), 4554-4571.
9. Xiaopeng, C.; Weixiang, S.; Thanh Tu, V.; Zhenwei, C.; Kapoor, A. In *An overview of lithium-ion batteries for electric vehicles*, 2012; IEEE: pp 230-235.
10. Amine, K.; Chen, C. H.; Liu, J.; Hammond, M.; Jansen, A.; Dees, D.; Bloom, I.; Vissers, D.; Henriksen, G., Factors responsible for impedance rise in high power lithium ion batteries. *Journal of Power Sources* **2001**, *97-98*, 684-687.
11. Thackeray, M. M.; David, W. I. F.; Bruce, P. G.; Goodenough, J. B., Lithium insertion into manganese spinels. *Materials Research Bulletin* **1983**, *18* (4), 461-472.
12. Wang, J.; Sun, Z.; Wei, X. In *Performance and characteristic research in LiFePO4 battery for electric vehicle applications*, 2009 IEEE Vehicle Power and Propulsion Conference, 7-10 Sept. 2009; 2009; pp 1657-1661.
13. Omar, N.; Verbrugge, B.; Mulder, G.; Van Den Bossche, P.; Van Mierlo, J.; Daowd, M.; Dhaens, M.; Pauwels, S., Evaluation of performance characteristics of various lithium-ion batteries for use in BEV application. *2010 IEEE Vehicle Power and Propulsion Conference* **2010**, 1-6.

14. Steckel, T.; Kendall, A.; Ambrose, H., Applying levelized cost of storage methodology to utility-scale second-life lithium-ion battery energy storage systems. *Applied energy* **2021**, *300*, 117309.
15. Pesaran, A. A., *Lithium ion batteries in electric drive vehicles*. Society of Automotive Engineers: Warrendale, Pennsylvania (400 Commonwealth Dr., Wallendale PA USA), 2016.
16. Quintero-Almanza, D.; Gamiño-Arroyo, Z.; Sánchez-Cadena, L. E.; Gómez-Castro, F. I.; Uribe-Ramírez, A. R.; Aguilera-Alvarado, A. F.; Ocampo Carmona, L. M., Recovery of Cobalt from Spent Lithium-Ion Mobile Phone Batteries Using Liquid–Liquid Extraction. *Batteries (Basel)* **2019**, *5* (2), 44.
17. Rahman, M. A.; Wang, X.; Wen, C., High Energy Density Metal-Air Batteries: A Review. *Journal of the Electrochemical Society* **2013**, *160* (10), A1759-A1771.
18. Li, Y.; Dai, H., Recent advances in zinc-air batteries. *Chemical Society reviews* **2014**, *43* (15), 5257-5275.
19. Zhu, A. L.; Wilkinson, D. P.; Zhang, X.; Xing, Y.; Rozhin, A. G.; Kulinich, S. A., Zinc regeneration in rechargeable zinc-air fuel cells—A review. *Journal of energy storage* **2016**, *8*, 35-50.
20. Kraytsberg, A.; Ein-Eli, Y., Review on Li–air batteries—Opportunities, limitations and perspective. *Journal of Power Sources* **2011**, *196* (3), 886-893.
21. Rahman, M. A.; Wang, X.; Wen, C., High Energy Density Metal-Air Batteries: A Review. *Journal of The Electrochemical Society* **2013**, *160* (10), A1759.
22. Aurbach, D.; Gofer, Y.; Lu, Z.; Schechter, A.; Chusid, O.; Gizbar, H.; Cohen, Y.; Ashkenazi, V.; Moshkovich, M.; Turgeman, R.; Levi, E., A short review on the comparison between Li battery systems and rechargeable magnesium battery technology. *Journal of Power Sources* **2001**, *97-98*, 28-32.
23. David, L.; Thomas, B. R., Handbook of batteries. *United state of America, New York. McGraw-hill companies Inc* **2002**.
24. Li, Y.; Gong, M.; Liang, Y.; Feng, J.; Kim, J.-E.; Wang, H.; Hong, G.; Zhang, B.; Dai, H., Advanced zinc-air batteries based on high-performance hybrid electrocatalysts. *Nature Communications* **2013**, *4* (1), 1805.
25. Sherman, S. B.; Cano, Z. P.; Fowler, M.; Chen, Z., Range-extending Zinc-air battery for electric vehicle. *Aims Energy* **2018**, *6* (1), 121-145.
26. Fu, J.; Cano, Z. P.; Park, M. G.; Yu, A.; Fowler, M.; Chen, Z., Electrically Rechargeable Zinc–Air Batteries: Progress, Challenges, and Perspectives. *Advanced materials (Weinheim)* **2017**, *29* (7), 1604685-n/a.

27. Liu, Q.; Pan, Z.; Wang, E.; An, L.; Sun, G., Aqueous metal-air batteries: Fundamentals and applications. *Energy Storage Materials* **2020**, *27*, 478-505.
28. Mahlendorf, F.; Heinzl, A.; Mueller, C.; Fuchs, D., Chapter 6 - Secondary zinc-air batteries – mechanically rechargeable. In *Electrochemical Power Sources: Fundamentals, Systems, and Applications*, Arai, H.; Garche, J.; Colmenares, L., Eds. Elsevier: 2021; pp 99-123.
29. Cooper, J. F.; Fleming, D.; Keene, L.; Maimoni, A.; Peterman, K.; Koopman, R. In *Demonstration of zinc/air fuel battery to enhance the range and mission of fleet electric vehicles: Preliminary results in the refueling of a multicell module*, Presented at the 29th Intersociety Energy Conversion Engineering Conference, August 01, 1994; 1994; pp 7-12.
30. Foller, P. C., Improved slurry zinc/air systems as batteries for urban vehicle propulsion. *Journal of Applied Electrochemistry* **1986**, *16* (4), 527-543.
31. Goldstein, J.; Brown, I.; Koretz, B., New developments in the Electric Fuel Ltd. zinc/air system. *Journal of Power Sources* **1999**, *80* (1), 171-179.
32. Sapkota, P.; Kim, H., Zinc–air fuel cell, a potential candidate for alternative energy. *Journal of Industrial and Engineering Chemistry* **2009**, *15* (4), 445-450.
33. Appleby, A. J.; Jacquier, M., The C.G.E. circulating zinc/air battery - A practical vehicle power source. *Journal of Power Sources* **1976**, *1*, 17-34.
34. Smedley, S. I.; Zhang, X. G., A regenerative zinc-air fuel cell. *Journal of Power Sources* **2007**, *165*, 897-904.
35. Cherepy, N. J.; Kruegar, R.; Cooper, J. F. In *A zinc/air fuel cell for electric vehicles*, 1999; IEEE: pp 11-13.
36. Baba, H., A new zinc-air fuel battery system. *SAE technical paper series* **1971**.
37. Zinc8 technology. <https://www.zinc8energy.com/technology>.
38. Zhu, Y. G.; Narayanan, T. M.; Tulodziecki, M.; Sanchez-Casalongue, H.; Horn, Q. C.; Meda, L.; Yu, Y.; Sun, J.; Regier, T.; McKinley, G. H., High-energy and high-power Zn–Ni flow batteries with semi-solid electrodes. *Sustainable Energy & Fuels* **2020**, *4* (8), 4076-4085.
39. Petek, T. J.; Hoyt, N. C.; Savinell, R. F.; Wainright, J. S., Slurry electrodes for iron plating in an all-iron flow battery. *Journal of Power Sources* **2015**, *294*, 620-626.
40. Choi, N. H.; del Olmo, D.; Milian, D.; El Kissi, N.; Fischer, P.; Pinkwart, K.; Tübke, J., Use of carbon additives towards rechargeable zinc slurry air flow batteries. *Energies (Basel)* **2020**, *13* (17), 4482.
41. Fenton, A. M., Jr.; Ashraf Gandomi, Y.; Mallia, C. T.; Neyhouse, B. J.; Kpeglo, M. A.; Exson, W. E.; Wan, C. T.-C.; Brushett, F. R., Toward a Mechanically Rechargeable Solid Fuel Flow Battery Based on Earth-Abundant Materials. *ACS Omega* **2022**, *7* (44), 40540-40547.

42. Zhu, Y. G.; Narayanan, T. M.; Tulodziecki, M.; Sanchez-Casalongue, H.; Horn, Q. C.; Meda, L.; Yu, Y.; Sun, J.; Regier, T.; McKinley, G. H.; Shao-Horn, Y., High-energy and high-power Zn–Ni flow batteries with semi-solid electrodes. *Sustainable Energy & Fuels* **2020**, 4 (8), 4076-4085.
43. Perez-Antolin, D.; Schuhmann, W.; Palma, J.; Ventosa, E., Semi-flowable Zn semi-solid electrodes as renewable energy carrier for refillable Zn–Air batteries. *Journal of Power Sources* **2022**, 536, 231480.
44. Müller, S.; Holzer, F.; Haas, O., Optimized zinc electrode for the rechargeable zinc–air battery. *Journal of Applied Electrochemistry* **1998**, 28 (9), 895-898.
45. Haas, O.; Holzer, F.; Müller, K.; Müller, S., Metal/air batteries: the zinc/air case. *Handbook of Fuel Cells* **2010**.
46. Choi, K. W.; Hamby, D.; Bennion, D. N.; Newman, J., Engineering analysis of shape change in zinc secondary electrodes: II. Experimental. *Journal of the Electrochemical Society* **1976**, 123 (11), 1628.
47. Mainar, A. R.; Colmenares, L. C.; Blázquez, J. A.; Urdampilleta, I., A brief overview of secondary zinc anode development: The key of improving zinc-based energy storage systems. *International journal of energy research* **2018**, 42 (3), 903-918.
48. Faegh, E.; Omasta, T.; Hull, M.; Ferrin, S.; Shrestha, S.; Lechman, J.; Bolintineanu, D.; Zuraw, M.; Mustain, W. E., Understanding the Dynamics of Primary Zn–MnO₂ Alkaline Battery Gassing with Operando Visualization and Pressure Cells. *Journal of The Electrochemical Society* **2018**, 165 (11), A2528.
49. Chen, S.; Duan, J.; Bian, P.; Tang, Y.; Zheng, R.; Qiao, S. Z., Three-dimensional smart catalyst electrode for oxygen evolution reaction. *Advanced Energy Materials* **2015**, 5 (18), 1500936.
50. Meng, F.; Zhong, H.; Bao, D.; Yan, J.; Zhang, X., In situ coupling of strung Co₄N and intertwined N–C fibers toward free-standing bifunctional cathode for robust, efficient, and flexible Zn–air batteries. *Journal of the American Chemical Society* **2016**, 138 (32), 10226-10231.
51. Hosseini, S.; Han, S. J.; Arponwichanop, A.; Yonezawa, T.; Kheawhom, S., Ethanol as an electrolyte additive for alkaline zinc-air flow batteries. *Scientific reports* **2018**, 8 (1), 11273-11.
52. Lee, S.-M.; Kim, Y.-J.; Eom, S.-W.; Choi, N.-S.; Kim, K.-W.; Cho, S.-B., Improvement in self-discharge of Zn anode by applying surface modification for Zn–air batteries with high energy density. *Journal of Power Sources* **2013**, 227, 177-184.
53. Burchardt, T., Zinc electrode comprising an organic gelling agent and an organic binder. Google Patents: 2006.

54. Phillips, J.; Mohanta, S.; Maske, C.; Bose, D. C.; Wu, J. J.; McKinney, B. L., Pasted zinc electrode for rechargeable nickel-zinc batteries. Google Patents: 2013.
55. Burchardt, T.; Ngamga, R. F., Agglomerated zinc powder anode. Google Patents: 2011.
56. Malone, E.; Berry, M.; Lipson, H., Freeform fabrication and characterization of Zn-air batteries. *Rapid Prototyping Journal* **2008**, *14* (3), 128-140.
57. Choi, N. H.; Del Olmo, D.; Fischer, P.; Pinkwart, K.; Tübke, J., Development of flow fields for zinc slurry air flow batteries. *Batteries (Basel)* **2020**, *6* (1), 15.
58. Milian, D.; Choi, N. H.; Tsehaye, M. T.; Fischer, P.; Tübke, J.; Iojoiu, C.; Roux, D. C. D.; El Kissi, N., Formulation and characterization of zinc slurries for zinc slurry – Air redox flow battery: A rheological approach. *Journal of power sources* **2023**, *555*, 232331.
59. Mao, Z.; White, R. E., Mathematical modeling of a primary zinc/air battery. *Journal of the Electrochemical Society* **1992**, *139* (4), 1105-1114.
60. Faegh, E.; Omasta, T.; Hull, M.; Ferrin, S.; Shrestha, S.; Lechman, J.; Bolintineanu, D.; Zuraw, M.; Mustain, W. E., Understanding the Dynamics of Primary Zn-MnO₂ Alkaline Battery Gassing with Operando Visualization and Pressure Cells. *Journal of the Electrochemical Society* **2018**, *165* (11), A2528-A2535.
61. Suthar, B.; Northrop, P. W. C.; Rife, D.; Subramanian, V. R., Effect of Porosity, Thickness and Tortuosity on Capacity Fade of Anode. *Journal of The Electrochemical Society* **2015**, *162* (9), A1708.
62. Hoyt, N. C.; Agar, E.; Nagelli, E. A.; Savinell, R.; Wainright, J., Electrochemical impedance spectroscopy of flowing electrosorptive slurry electrodes. *Journal of the electrochemical society* **2018**, *165* (10), E439.
63. Hoyt, N. C.; Wainright, J. S.; Savinell, R. F., Mathematical modeling of electrochemical flow capacitors. *Journal of The Electrochemical Society* **2015**, *162* (4), A652.
64. Hoyt, N. C.; Savinell, R. F.; Wainright, J. S., Modeling of flowable slurry electrodes with combined faradaic and nonfaradaic currents. *Chemical Engineering Science* **2016**, *144*, 288-297.
65. Petek, T. J.; Hoyt, N. C.; Savinell, R. F.; Wainright, J. S., Characterizing Slurry Electrodes Using Electrochemical Impedance Spectroscopy. *Journal of the Electrochemical Society* **2016**, *163* (1), A5001-A5009.
66. Bockelmann, M.; Becker, M.; Reining, L.; Kunz, U.; Turek, T., Passivation of zinc anodes in alkaline electrolyte: Part i. determination of the starting point of passive film formation. *Journal of The Electrochemical Society* **2018**, *165* (13), A3048.

67. Bockelmann, M.; Reining, L.; Kunz, U.; Turek, T., Electrochemical characterization and mathematical modeling of zinc passivation in alkaline solutions: A review. *Electrochimica Acta* **2017**, *237*, 276-298.
68. Liu, M. B.; Cook, G. M.; Yao, N. P., Passivation of Zinc Anodes in KOH Electrolytes. *Journal of The Electrochemical Society* **1981**, *128* (8), 1663.
69. Powers, R.; Breiter, M., The anodic dissolution and passivation of zinc in concentrated potassium hydroxide solutions. *Journal of the Electrochemical Society* **1969**, *116* (6), 719.
70. Farmer, E.; Webb, A., Zinc passivation and the effect of mass transfer in flowing electrolyte. *Journal of Applied Electrochemistry* **1972**, *2*, 123-136.
71. Bockelmann, M.; Becker, M.; Reining, L.; Kunz, U.; Turek, T., Passivation of Zinc Anodes in Alkaline Electrolyte: Part I. Determination of the Starting Point of Passive Film Formation. *Journal of the Electrochemical Society* **2018**, *165* (13), A3048-A3055.
72. Fordyce, J. S.; Baum, R. L., Vibrational spectra of solutions of zinc oxide in potassium hydroxide. *The Journal of Chemical Physics* **1965**, *43* (3), 843-846.
73. Pessine, E. J.; Agostinho, S. M.; Chagas, H. C., Evaluation of the diffusion coefficient of the zincate ion using a rotating disk electrode. *Canadian journal of chemistry* **1986**, *64* (3), 523-527.
74. Zhang, X. G., *Corrosion and Electrochemistry of Zinc*. Springer US: Boston, MA, 1996.
75. Yadav, G. G.; Wei, X.; Meeus, M., Chapter 3 - Primary zinc-air batteries. In *Electrochemical Power Sources: Fundamentals, Systems, and Applications*, Arai, H.; Garche, J.; Colmenares, L., Eds. Elsevier: 2021; pp 23-45.
76. Aaron, D. S.; Liu, Q.; Tang, Z.; Grim, G. M.; Papandrew, A. B.; Turhan, A.; Zawodzinski, T. A.; Mench, M. M., Dramatic performance gains in vanadium redox flow batteries through modified cell architecture. *Journal of power sources* **2012**, *206*, 450-453.
77. IEA, Global EV Data Explorer. **2023**.
78. Henze, V., Energy Storage Investments Boom As Battery Costs Halve in the Next Decade. **2019**.
79. Lourenssen, K.; Williams, J.; Ahmadpour, F.; Clemmer, R.; Tasnim, S., Vanadium redox flow batteries: A comprehensive review. *Journal of Energy Storage* **2019**, *25*.
80. Leung, P.; Shah, A. A.; Sanz, L.; Flox, C.; Morante, J. R.; Xu, Q.; Mohamed, M. R.; de León, C. P.; Walsh, F. C., Recent developments in organic redox flow batteries: A critical review. *Journal of Power Sources* **2017**, *360*, 243-283.
81. Mainar, A. R.; Iruin, E.; Colmenares, L. C.; Kvasha, A.; de Meatza, I.; Bengoechea, M.; Leonet, O.; Boyano, I.; Zhang, Z. C.; Blazquez, J. A., An overview of progress in

electrolytes for secondary zinc-air batteries and other storage systems based on zinc. *Journal of Energy Storage* **2018**, *15*, 304-328.

82. Fu, J.; Cano, Z. P.; Park, M. G.; Yu, A.; Fowler, M.; Chen, Z., Electrically Rechargeable Zinc–Air Batteries: Progress, Challenges, and Perspectives. *Advanced Materials* **2017**, *29* (7), 1604685.

83. Duduta, M.; Ho, B.; Wood, V. C.; Limthongkul, P.; Brunini, V. E.; Carter, W. C.; Chiang, Y.-M., Semi-Solid Lithium Rechargeable Flow Battery. *Advanced energy materials* **2011**, *1* (4), 511-516.

84. Aaron, D.; Liu, Q.; Tang, Z.; Grim, G.; Papandrew, A. B.; Turhan, A.; Zawodzinski, T. A.; Mench, M. M., Dramatic performance gains in vanadium redox flow batteries through modified cell architecture. *Journal of Power Sources* **2012**, *206*, 450–453.

85. Davis, R. E.; Horvath, G. L.; Tobias, C. W., The solubility and diffusion coefficient of oxygen in potassium hydroxide solutions. *Electrochimica Acta* **1967**, *12* (3), 287-297.

86. Gilliam, R. J.; Graydon, J. W.; Kirk, D. W.; Thorpe, S. J., A review of specific conductivities of potassium hydroxide solutions for various concentrations and temperatures. *International Journal of Hydrogen Energy* **2007**, *32* (3), 359-364.

87. Truong, V. M.; Duong, N. B.; Wang, C. L.; Yang, H., Effects of Cell Temperature and Reactant Humidification on Anion Exchange Membrane Fuel Cells. *Materials (Basel)* **2019**, *12* (13).

88. Wang, J.; Wang, B.; Tongsh, C.; Miao, T.; Cheng, P.; Wang, Z.; Du, Q.; Jiao, K., Combining proton and anion exchange membrane fuel cells for enhancing the overall performance and self-humidification. *Chemical Engineering Journal* **2022**, *428*, 131969.

89. Zhang, C.; Chou, S.; Guo, Z.; Dou, S.-X., Beyond Lithium-Ion Batteries. *Advanced Functional Materials* **2024**, *34* (5), 2308001.

90. Trahey, L.; Brushett, F. R.; Balsara, N. P.; Ceder, G.; Cheng, L.; Chiang, Y. M.; Hahn, N. T.; Ingram, B. J.; Minter, S. D.; Moore, J. S.; Mueller, K. T.; Nazar, L. F.; Persson, K. A.; Siegel, D. J.; Xu, K.; Zavadil, K. R.; Srinivasan, V.; Crabtree, G. W., Energy storage emerging: A perspective from the Joint Center for Energy Storage Research. *Proc Natl Acad Sci U S A* **2020**, *117* (23), 12550-12557.

91. Tsehaye, M. T.; Choi, N. H.; Fischer, P.; Tübke, J.; Planes, E.; Alloin, F.; Iojoiu, C., Anion Exchange Membranes Incorporating Multi N-Spirocyclic Quaternary Ammonium Cations via Ultraviolet-Initiated Polymerization for Zinc Slurry-Air Flow Batteries. *ACS applied energy materials* **2022**, *5* (6), 7069-7080.

92. Sanyal, J.; Goldin, G. M.; Zhu, H.; Kee, R. J., A particle-based model for predicting the effective conductivities of composite electrodes. *Journal of Power Sources* **2010**, *195* (19), 6671-6679.

93. Wu, J.; Yuan, C.; Li, T.; Yuan, Z.; Zhang, H.; Li, X., Dendrite-Free Zinc-Based Battery with High Areal Capacity via the Region-Induced Deposition Effect of Turing Membrane. *Journal of the American Chemical Society* **2021**, *143* (33), 13135-13144.
94. Tsehay, M. T.; Gebreslassie, G. T.; Choi, N. H.; Milian, D.; Martin, V.; Fischer, P.; Tübke, J.; Kissi, N. E.; Donten, M. L.; Alloin, F.; Iojoiu, C., Pristine and modified porous membranes for zinc slurry–air flow battery. *Molecules (Basel, Switzerland)* **2021**, *26* (13), 4062.
95. Allebrod, F.; Chatzichristodoulou, C.; Mollerup, P. L.; Mogensen, M. B., Electrical conductivity measurements of aqueous and immobilized potassium hydroxide. *International Journal of Hydrogen Energy* **2012**, *37* (21), 16505-16514.
96. Su, P.; Zhang, H.; Yang, L.; Xing, C.; Pan, S.; Lu, W.; Zhang, S., Effects of conductive additives on the percolation networks and rheological properties of $\text{LiMn}_{0.7}\text{Fe}_{0.3}\text{PO}_4$ suspensions for lithium slurry battery. *Chemical Engineering Journal* **2022**, *433*, 133203.
97. Ma, L.; Schroeder, M. A.; Borodin, O.; Pollard, T. P.; Ding, M. S.; Wang, C.; Xu, K., Realizing high zinc reversibility in rechargeable batteries. *Nature Energy* **2020**, *5* (10), 743-749.
98. Davari, E.; Ivey, D. G., Bifunctional electrocatalysts for Zn–air batteries. *Sustainable Energy & Fuels* **2018**, *2* (1), 39-67.
99. Subramaniam, T.; Idris, M. B.; K.S, S.; K.S, R.; S, D., Mitigating hydrogen evolution reaction and corrosion of zinc in electrically rechargeable zinc-air batteries using nanofluid electrolytes. *Journal of Energy Storage* **2024**, *81*, 110457.
100. Park, D.-J.; Aremu, E. O.; Ryu, K.-S., Bismuth oxide as an excellent anode additive for inhibiting dendrite formation in zinc-air secondary batteries. *Applied Surface Science* **2018**, *456*, 507-514.
101. Zeng, D.; Yang, Z.; Wang, S.; Ni, X.; Ai, D.; Zhang, Q., Preparation and electrochemical performance of In-doped ZnO as anode material for Ni–Zn secondary cells. *Electrochimica Acta* **2011**, *56* (11), 4075-4080.
102. Hosseini, S.; Abbasi, A.; Uginet, L.-O.; Haustraete, N.; Praserthdam, S.; Yonezawa, T.; Kheawhom, S., The Influence of Dimethyl Sulfoxide as Electrolyte Additive on Anodic Dissolution of Alkaline Zinc-Air Flow Battery. *Scientific reports* **2019**, *9* (1), 14958-12.
103. Hosseini, S.; Lao-atiman, W.; Han, S. J.; Arpornwichanop, A.; Yonezawa, T.; Kheawhom, S., Discharge Performance of Zinc-Air Flow Batteries Under the Effects of Sodium Dodecyl Sulfate and Pluronic F-127. *Scientific reports* **2018**, *8* (1), 14909-13.
104. Dunn, B.; Kamath, H.; Tarascon, J.-M., Electrical Energy Storage for the Grid: A Battery of Choices. *Science (New York, N.Y.)* **2011**, *334*, 928-35.
105. Sum, E.; Skyllas-Kazacos, M., A study of the V(II)/V(III) redox couple for redox flow cell applications. *Journal of power sources* **1985**, *15* (2-3), 179-190.

106. Skyllas-Kazacos, M., New All-Vanadium Redox Flow Cell. *Journal of the Electrochemical Society* **1986**, *133* (5), 1057-1058.
107. Rychcik, M.; Skyllas-Kazacos, M., Characteristics of a new all-vanadium redox flow battery. *Journal of power sources* **1988**, *22* (1), 59-67.
108. Fabjan, C.; Garche, J.; Harrer, B.; Jörisen, L.; Kolbeck, C.; Philippi, F.; Tomazic, G.; Wagner, F., The vanadium redox-battery: an efficient storage unit for photovoltaic systems. *Electrochimica acta* **2001**, *47* (5), 825-831.
109. You, X.; Ye, Q.; Cheng, P., Scale-up of high power density redox flow batteries by introducing interdigitated flow fields. *International Communications in Heat and Mass Transfer* **2016**, *75*.
110. Guarnieri, M.; Trovò, A.; D'Anzi, A.; Alotto, P., Developing vanadium redox flow technology on a 9-kW 26-kWh industrial scale test facility: Design review and early experiments. *Applied Energy* **2018**, *230*, 1425-1434.
111. Trovò, A., Battery management system for industrial-scale vanadium redox flow batteries: Features and operation. *Journal of Power Sources* **2020**, *465*, 228229.
112. "It's Big and Long-Lived, and It Won't Catch Fire: The Vanadium Redox-Flow Battery".
113. Aaron, D.; Tang, Z.; Papandrew, A. B.; Zawodzinski, T. A., Polarization curve analysis of all-vanadium redox flow batteries. *Journal of Applied Electrochemistry* **2011**, *41* (10), 1175-1182.
114. Wei, Z.; Zhao, J.; Xiong, B., Dynamic electro-thermal modeling of all-vanadium redox flow battery with forced cooling strategies. *Applied Energy* **2014**, *135*, 1-10.
115. He, S. S.; Frank, C. W., Facilitating hydroxide transport in anion exchange membranes via hydrophilic grafts. *Journal of Materials Chemistry A* **2014**, *2* (39), 16489-16497.
116. Li, Z.; Dai, W.; Yu, L.; Liu, L.; Xi, J.; Qiu, X.; Chen, L., Properties Investigation of Sulfonated Poly(ether ether ketone)/Polyacrylonitrile Acid-Base Blend Membrane for Vanadium Redox Flow Battery Application. *ACS Applied Materials & Interfaces* **2014**, *6* (21), 18885-18893.
117. Zawodzinski, T. A.; Derouin, C.; Radzinski, S.; Sherman, R. J.; Smith, V. T.; Springer, T. E.; Gottesfeld, S., Water Uptake by and Transport Through Nafion® 117 Membranes. *Journal of The Electrochemical Society* **1993**, *140* (4), 1041-1047.
118. Tang, Z.; Svoboda, R.; Lawton, J.; Aaron, D.; Papandrew, A.; Zawodzinski, T., Composition and Conductivity of Membranes Equilibrated with Solutions of Sulfuric Acid and Vanadyl Sulfate. *Journal of the Electrochemical Society* **2013**, *160*, F1040-F1047.
119. Tang, Z.; Lawton, J. S.; Sun, C.-N.; Chen, J.; Bright, M. I.; Jones, A. M.; Papandrew, A. B.; Fujimoto, C. H.; Zawodzinski, T. A., Characterization of Sulfonated Diels-Alder

Poly(phenylene) Membranes for Electrolyte Separators in Vanadium Redox Flow Batteries. *Journal of the Electrochemical Society* **2014**, *161* (12), A1860-A1868.

120. Park, Y.; Kim, D., Chemical stability enhancement of Nafion membrane by impregnation of a novel organic ·OH radical scavenger, 3,4-dihydroxy-cinnamic acid. *Journal of Membrane Science* **2018**, *566*, 1-7.

121. Schwenzer, B.; Zhang, J.; Kim, S.; Li, L.; Liu, J.; Yang, Z., Membrane Development for Vanadium Redox Flow Batteries. *ChemSusChem* **2011**, *4* (10), 1388-1406.

122. Gaylord, N. G.; Adler, G., Radiation chemistry of polymeric systems high polymers, A. Chapiro, ed., interscience, New York, 1962, xvi + 712 pp. \$21.00. *Journal of Polymer Science Part A: General Papers* **1963**, *1* (6), 2237-2237.

123. Xing, D.; Zhang, S.; Yin, C.; Zhang, B.; Jian, X., Effect of amination agent on the properties of quaternized poly(phthalazinone ether sulfone) anion exchange membrane for vanadium redox flow battery application. *Journal of Membrane Science* **2010**, *354* (1), 68-73.

124. Roth, W.-M.; Tobin, K.; Ritchie, S., Chapter 1: Introduction. *Counterpoints* **2001**, *177*, 1-14.

125. Zhang, X.; Chen, H.; Zhang, H., Layer-by-layer assembly: from conventional to unconventional methods. *Chemical Communications* **2007**, (14), 1395-1405.

126. Jiang, B.; Wu, L.; Yu, L.; Qiu, X.; Xi, J., A comparative study of Nafion series membranes for vanadium redox flow batteries. *Journal of Membrane Science* **2016**, *510*, 18-26.

127. Pu, Y.; Huang, X.; Yang, P.; Zhou, Y.; Xuan, S.; Zhang, Y., Effect of non-sulfonated diamine monomer on branched sulfonated polyimide membrane for vanadium redox flow battery application. *Electrochimica Acta* **2017**, *241*, 50-62.

128. Winardi, S.; Raghu, S. C.; Oo, M. O.; Yan, Q.; Wai, N.; Lim, T. M.; Skyllas-Kazacos, M., Sulfonated poly (ether ether ketone)-based proton exchange membranes for vanadium redox battery applications. *Journal of Membrane Science* **2014**, *450*, 313-322.

129. Zhong, S.; Skyllas-Kazacos, M., Electrochemical behaviour of vanadium(V)/vanadium(IV) redox couple at graphite electrodes. *Journal of Power Sources* **1992**, *39* (1), 1-9.

130. Yue, L.; Li, W.; Sun, F.; Zhao, L.; Xing, L., Highly hydroxylated carbon fibres as electrode materials of all-vanadium redox flow battery. *Carbon* **2010**, *48* (11), 3079-3090.

131. Wu, X. W.; Yamamura, T.; Ohta, S.; Zhang, Q. X.; Lv, F. C.; Liu, C. M.; Shirasaki, K.; Satoh, I.; Shikama, T.; Lu, D.; Liu, S. Q., Acceleration of the redox kinetics of VO₂⁺/VO₂²⁺ and V³⁺/V²⁺ couples on carbon paper. *Journal of Applied Electrochemistry* **2011**, *41* (10), 1183.

132. Fu, S.; Zhu, C.; Song, J.; Engelhard, M. H.; Du, D.; Lin, Y., Three-dimensional Nitrogen-Doped Reduced Graphene Oxide/Carbon Nanotube Composite Catalysts for Vanadium Flow Batteries. *Electroanalysis* **2017**, 29 (5), 1469-1473.
133. Suárez, D. J.; González, Z.; Blanco, C.; Granda, M.; Menéndez, R.; Santamaría, R., Graphite Felt Modified with Bismuth Nanoparticles as Negative Electrode in a Vanadium Redox Flow Battery. *ChemSusChem* **2014**, 7 (3), 914-918.
134. Liu, Q. H.; Grim, G. M.; Papandrew, A. B.; Turhan, A.; Zawodzinski, T. A.; Mench, M. M., High Performance Vanadium Redox Flow Batteries with Optimized Electrode Configuration and Membrane Selection. *Journal of The Electrochemical Society* **2012**, 159 (8), A1246-A1252.
135. Zhou, X. L.; Zhao, T. S.; An, L.; Zeng, Y. K.; Yan, X. H., A vanadium redox flow battery model incorporating the effect of ion concentrations on ion mobility. *Applied Energy* **2015**, 158, 157-166.
136. Elgammal, R. A.; Tang, Z.; Sun, C.-N.; Lawton, J.; Zawodzinski, T. A., Species Uptake and Mass Transport in Membranes for Vanadium Redox Flow Batteries. *Electrochimica Acta* **2017**, 237, 1-11.
137. Yong, Y.; Lou, X.; Li, S.; Yang, C.; Yin, X., Direct simulation of the influence of the pore structure on the diffusion process in porous media. *Computers & Mathematics with Applications* **2014**, 67 (2), 412-423.
138. Yamamura, T.; Watanabe, N.; Yano, T.; Shiokawa, Y., Electron-Transfer Kinetics of $\text{Np}^{3+} / \text{Np}^{4+}$, $\text{NpO}_2^+ / \text{NpO}_2^{2+}$, $\text{V}^{2+} / \text{V}^{3+}$, and $\text{VO}_2^+ / \text{VO}_2^{2+}$ at Carbon Electrodes. *Journal of The Electrochemical Society* **2005**, 152 (4), A830.

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