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Life-Cycle Optimization and Flow Control in a Nickel-Zinc Flow Assisted Battery

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Life-Cycle Optimization and Flow Control in a Nickel-Zinc Flow Assisted Battery

Thesis
Submitted in partial fulfillment of the requirement for the degree

Master of Engineering (Chemical)
at
The City College of New York
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City University of New York

by
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Abstract

Nickel-Zinc flow-assisted rechargeable batteries are currently being explored as a potential new generation of large-scale, low-cost energy storage devices. The viability of a commercial nickel-zinc battery has been hindered by the well-known phenomena of dendrite formation and zinc morphology variation over time. Applying electrolyte flow to traditional nickel-zinc battery systems has demonstrated significant life cycle performance improvements by reducing both dendrite formation and morphological variation. It has also been demonstrated that periodic low-current reconditioning discharge further improves cycle life. This thesis examines the effect of eliminating electrolyte flow during discharge of nickel-zinc flow assisted batteries, which would allow a much broader range of applications for these novel batteries, particularly transportation-based applications such as electric vehicle applications. Experiments were further designed to determine the optimal periodicity for low-current reconditioning discharge, examining the effects of reconditioning after 7, 12, 20 and 30 charge-discharge cycles. The results of these experiments demonstrate that electrolyte flow during discharge does provide performance benefits, but it is possible to operate a nickel-zinc flow assisted battery without flow during discharge, when low-charge reconditioning is applied every 7 cycles. It was further found that when electrolyte is flowing continuously, nickel-zinc flow-assisted batteries can operate at high efficiency and minimal performance degradation with periodic reconditioning after 30 cycles.
1. INTRODUCTION

As global demand for energy increases, the need for more advanced energy storage devices is becoming paramount. Researchers are expending great efforts to design batteries, especially rechargeable (secondary) batteries that are cheaper, more reliable, safer, and last 1000’s of cycles. One of the most immediate and largest-growing markets requiring advances in rechargeable battery technology lies in the emergence of electric vehicles as commercially viable alternatives to traditional internal combustion engines.¹ The primary goal of current electric vehicle (EV) battery research is to drastically increase vehicle range per charge (increased capacity) while reducing the physical size, weight and expense of the batteries. As cities and municipalities embrace “greener,” or more sustainable energy consumption habits and practices, interest and adoption of commercial electric vehicles has also skyrocketed, especially in cities that employ significant bus-based mass transit systems. Municipal bus-based transit systems are particularly well-suited to electric vehicle adoption since a city bus does not have as stringent a size and weight limitation (for its battery) as a consumer vehicle. Also, bus routes are generally highly predictable, repeatable and adaptable and are thus well-suited for an electric vehicle that may have limited range but highly predictable and accessible charging locations (e.g. a bus depot or charging station at route end-points).

The Energy Institute of The City College at the City University of New York is developing a flow-assisted nickel-zinc alkaline battery for large-scale energy storage.² The Energy Institute is developing this novel battery system primarily for use as a grid-scale energy storage system in conjunction with power plant sized electricity generation facilities such as wind and solar farms, with a capacity of up to 10 megawatts. Any useful energy storage system of this scale must of course have the required capacity, but must also possess consistent, long-
lasting recharging (cycling) capabilities. The Energy Institute’s nickel-zinc flow-assisted battery has already demonstrated >1500 deep cycles (>80% discharge).\(^3\) Although nickel-zinc batteries have been generally dismissed due to short cycle life, the cost structure and potential for high cycle-life demonstrated by these new batteries suggest that the nickel-zinc flow assisted battery may be a viable candidate for stationary large-scale storage. However, as a flow assisted battery, the ancillary components of the entire system, notably the pump and associated apparatus make this technology seemingly unsuitable for EV applications. The following work provides an in-depth study of the practicality of off-loading the pump and associated electrolyte flow apparatus from the main battery components, thereby allowing nickel-zinc flow assisted battery development for EV applications.

1.1 History of Nickel-Zinc Batteries
Nickel-Zinc batteries have been known since at least the early 1900’s, and have undergone various periods of developmental interest ever since.\(^4\) There are numerous well-known advantages to nickel-zinc battery systems including fast recharge capability, good cycle life, low environmental impact, abundant, inexpensive raw materials and low cost per Watt-hour.\(^5\) In addition, Nickel-Zinc batteries exhibit relatively high specific energy densities (55-85 Wh/kg) and high specific power densities (>130 W/kg), making them a viable candidate for electric vehicle and grid-scale storage applications.\(^6,7,8\)

Despite these known benefits, nickel-zinc batteries still have higher overall costs than traditional lead-acid batteries, relatively low volumetric energy density and, perhaps most importantly, limited cycle life for applications requiring thousands of charge cycles.\(^9\) This last limitation has been the subject of extensive research as the need for low cost, high capacity, high cycle life batteries has become more prevalent. The primary cause for the limited cycle life of
Ni-Zn batteries is two-fold: the growth of zinc dendrites during charge leading to internal shorting; and zinc electrode shape change and morphological variation associated with non-uniform current distribution.\textsuperscript{10,11,12} Over time, zinc dendrites grow and accumulate from one cycle to the next until the anode and cathode become electrically connected, thus creating an internal short. Efforts to overcome this short cycle life have resulted in various cell designs and configurations such as vented static-electrolyte cells,\textsuperscript{13} sealed static-electrolyte cells\textsuperscript{14,15,16,17} and flowing electrolyte cells.\textsuperscript{12,18,19} Efforts to limit Zn dendrite formation have also focused on the development of electrode membranes and separators that reduce dendrite formation while allowing ion transport during the charge and discharge of the cells.\textsuperscript{20,21,22}

During the late 1960’s, R. D. Naybour examined the effect of electrolyte flow on electrodeposited zinc morphology in an effort to better understand the effects of zinc dendrite growth on zinc-based secondary battery performance. Using an aqueous alkaline electrolyte containing zincate ions, Naybour correlated distinct zinc dendrite morphologies with varied electrolyte flow velocities, Reynold’s number, and current density, demonstrating that electrolyte flow conditions have a direct impact on deposited zinc morphology.\textsuperscript{23}

Following Naybour’s work, electrolyte flow and other attempts to understand and improve Zn deposition in electrochemical systems had been made, and in 1991, Frank McLarnon and Elton Cairns published a general review of nickel-zinc battery development for the period from 1975-1990\textsuperscript{10}, providing a general overview of various approaches to developing commercially viable secondary nickel-zinc batteries. While flow and flow-assisted techniques had been explored to improve cycle life and overall performance, it had been concluded at that time that such techniques were either too complex or otherwise impractical for commercial applications that required extensive cycle life.
Then in the 2000’s, as interest in safe, inexpensive energy storage again began to gain traction due to increased interest in electric vehicle development and overall increased use of portable electronic devices, another wave of nickel-zinc battery research followed, due to the high energy density and high power density of nickel-zinc battery systems. In 2006, Wang et al expanded on Naybour’s and others’ earlier zinc morphology studies correlating zinc dendrite morphology to electrolyte composition, current density and other deposition conditions. In 2010, Gallaway et al. reported on zinc morphology in a microfluidic electrode cell, studying the relationship between zinc dendrite morphology and flow rate and current distribution. Gallaway et al concluded that while electrolyte flow rate can affect zinc deposition density and morphology, once zinc dendrite growth reached a critical near-shorting stage, flow rate cannot be increased to reduce zinc dendrite growth.

In 2007, Cheng et al. proposed a novel Zinc-Nickel oxyhydroxide (NiOOH) single flow rechargeable battery, reportedly achieving >1000 cycles while maintaining high average coulombic and energy efficiencies. This experimental cell employed sintered nickel hydroxide as positive electrodes, inert metal current collectors (cadmium-plated nickel plate) as anodes, and an alkaline electrolyte (concentrated 10M KOH) into which ZnO was dissolved, yielding a 1M ZnO in 10M KOH electrolyte. Cheng further reported 96% average coulombic efficiency and 86% average energy efficiency with no deterioration over 1000 charge-discharge cycles. This basic cell construction was further examined by Zhang et al., reporting average coulombic efficiency of about 98% and average energy efficiency of about 88%.

In 2011, Ito et al published preliminary results of a novel zinc-nickel flow assisted battery that showed stable cycling of a 3.7 Ah battery for over 1500 cycles, maintaining coulombic efficiencies over 90% and energy efficiencies greater than 80%. This cell was
constructed using sintered nickel oxide plates for positive electrodes, and zinc deposited on polished copper foil as negative electrodes. Ito et al compared several charge-discharge regimes, varying flow rate (1.6-25.7 cm/s) and galvanostatic charge/discharge rate (C/4-1.5C), ending charge when the cell reached full capacity of 3.7 Ah, based on the sintered nickel electrode capacity, and ending discharge when the cell reached 1.2V. The procedure further included a reconditioning procedure every 15 charge-discharge cycles. This reconditioning procedure consisted of a slow discharge following every 15th discharge at a rate of C/15 until the cell reached a voltage of 0.6V.

From these experiments, Ito et al demonstrated that this cell is capable of exceptionally long cycle life as long a minimal flow rate of 15 cm/s was maintained. Ito concluded that this threshold flow rate distorted the direction of Zn dendrite formation, thus suppressing internal shorts that have been known to drastically reduce the cycling capability of Ni-Zn battery systems. Additionally, the reconditioning procedure renews the zinc anode providing a relatively flat and uniform surface for zinc electrodeposition for the following cycles.

While past research, from Naybour to Ito and Gallaway, has demonstrated the effects and advantages of electrolyte flow, the examination of the beneficial impact of electrolyte flow has been focused on zinc dendrite formation and electrodeposition morphology during charge. For stationary applications such as grid-scale energy storage, continuous electrolyte flow does not pose any significant logistical problems, since pumps and related equipment can be incorporated into the overall battery design. But if the benefits of electrolyte flow-assistance reside primarily in the zinc dendrite formation phase, it is reasonable to consider a charge-discharge regime whereby flow is induced during charge, but then eliminated during discharge, allowing the pump and related flow apparatus to be segregated from the actual cell. Such a system would allow for
a much wider array of potential applications, as well as a system-wide increase in energy efficiency from the reduced energy loss required for pump operation. In addition, operating under the assumption that reconditioning is indeed beneficial to Ni-Zn battery cycle life, a more systematic approach to optimizing periodic reconditioning would further increase the longevity and overall efficiency of the system. Thus, the focus of these experiments is to investigate the effect of eliminating electrolyte flow during cell discharge, and to determine how a reconditioning discharge can be applied to optimize the cycle life of a Ni-Zn flow assisted battery system.

Given the cycling success demonstrated by Ito, Zhang, and Cheng, particularly the extended cycling benefits achieved by flowing electrolyte and periodic reconditioning, studies were undertaken to evaluate the performance of a Ni-Zn cell whereby flow was implemented during charge to minimize Zn dendrite formation, but then eliminating the flow during cell discharge. If the benefits of flowing electrolyte in a Ni-Zn battery system are related primarily to dendrite growth and morphology during formation, and thus limited to the charging phase, then the pump, reservoir, and any other extraneous equipment and apparatus required to implement flow can be off-loaded as part of a distinct charging station or apparatus. This in turn would allow these cells to be used as a power source for electric vehicles or any number of additional mobile applications where the physical separation of charging and discharging conditions may be practical.

1.2 Nickel-Zinc Battery Chemistry

As discussed above, the high energy density and higher open-circuit voltage of Nickel-Zinc batteries are among the chief benefits that make Ni-Zn chemistry attractive for new energy
storage devices. The basic electrochemical reactions during discharge (forward) and charge (reverse) for this system are:\(^7,^{25}\):

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
<th>Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positive electrode</td>
<td>(2 \text{NiOOH} + 2 \text{H}_2\text{O} + 2 \text{e}^- \leftrightarrow 2 \text{Ni(OH)}_2 + 2 \text{OH}^-)</td>
<td>0.49 V</td>
</tr>
<tr>
<td>Negative electrode</td>
<td>(\text{Zn} + 4 \text{OH}^- \leftrightarrow \text{Zn(OH)}_4^{2-} + 2 \text{e}^-)</td>
<td>1.20 V</td>
</tr>
<tr>
<td>Overall reaction</td>
<td>(2 \text{NiOOH} + 2 \text{H}_2\text{O} + \text{Zn} \leftrightarrow 2 \text{Ni(OH)}_2 + \text{Zn(OH)}_4^{2-})</td>
<td>1.69 V</td>
</tr>
</tbody>
</table>

However, when these cells are overcharged, hydrolysis occurs and the following set of reactions prevails:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positive electrode</td>
<td>(2 \text{OH}^- \rightarrow \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2 \text{e}^-)</td>
</tr>
<tr>
<td>Negative electrode</td>
<td>(2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2 + 2 \text{OH}^-)</td>
</tr>
<tr>
<td></td>
<td>(\text{Zn} + \frac{1}{2} \text{O}_2 \rightarrow \text{ZnO}) (Recombination of oxygen from the positive electrode)</td>
</tr>
<tr>
<td>Overall reaction</td>
<td>(\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2)</td>
</tr>
</tbody>
</table>

Overcharging presents several problems in a Ni-Zn battery system. Most obviously, coulombic efficiency is lost as electrons are used in side-reaction gas formation instead of contributing to zincate (Zn\(^{2+}\)) reduction for Zn deposition. Also, depending on the specific cell configuration and end-use application, generation of hydrogen or oxygen gas can pose significant safety concerns.

The relationship between gas generation at the NiOOH cathode and cell potential can be understood by examining the Pourbaix diagram for Nickel metal (or Ni(OH))\(_2\), as seen in Figure 1.\(^{26}\) For highly alkaline Ni-Zn battery systems, operating at pH greater than 14, the Pourbaix diagram demonstrates that such systems are operating near the equilibrium conditions between Ni(OH)\(_2\) and NiOOH\(^-\)(HNiO\(_2\)^-) denoted by reaction [1]. This is desirable for encouraging the appropriate charge-discharge reaction at the sintered nickel cathode, thereby minimizing unwanted gas formation (reaction [4]). However, as the cell potential drifts higher during charge, conditions at the electrode surface can be pushed away from Zn formation (or zincate reduction) at the anode and NiOOH oxidation at the cathode in favor of gas evolution.
Similarly at the anode, the thermodynamic conditions for solid metallic zinc stability do not coincide with water stability. Thus, zincate reduction to zinc metal competes with hydrogen formation from hydrolysis of water, which also reduces the efficiency and potential capacity of the cell. As the NiOOH is increasingly converted to Ni(OH)$_2$, (as the cell approaches maximum capacity), zinc dendrite growth accelerates, creating a thermodynamic shift towards gas production, which in turn results in diminished battery efficiency.

### 1.3 Nickel-Zinc Reaction Kinetics

The above thermodynamic analysis demonstrates that a nickel-zinc battery is thermodynamically viable, but for the reasons discussed above, side reactions and dendritic growth greatly limit long term stability and performance. Ito and Chang both demonstrated that flowing electrolyte in a nickel zinc system greatly improves overall performance by limiting dendritic growth, but the mechanism by which growth is reduced is a complex combination of interfacial ion concentrations, local current density and limiting current density. The impact of flow on limiting current density, $i_L$, can be understood by the relationship between limiting current density and mass transfer at the electrode surface where
\[ i_L = nFm_0C_0 \] \[ \text{[8]} \]

where \( m_0 \) is the mass-transfer coefficient of the electroactive material in solution, and \( C_0 \) is the bulk concentration.\(^{28}\)

A system of flowing electrolyte across an electrode surface is analogous to the hydrodynamic impact of an RDE apparatus. As with an RDE, imposing electrolyte flow increases mass transport at the electrode surface, thus increasing \( i_L \). Since limiting current density is defined as the current at which the electrode processes are limited entirely by mass transfer (as opposed to charge-transfer or potential),\(^{28}\) increasing the limiting current density can have the effect of increasing the amount of electrode material involved in the charge transfer reaction (i.e. reduction of zincate ion into zinc metal).

### 1.4 Overpotential

Another essential aspect of electrochemical process analysis is an understanding of overpotential and its impact on overall battery health and performance. Overpotential, \( \eta \), is defined as the additional potential required to drive an electrochemical reaction above what is thermodynamically required, or:

\[ \eta = E - E_{\text{eq}} \] \[ \text{[9]} \]

where \( E \) is the actual cell potential and \( E_{\text{eq}} \) is the equilibrium cell potential.\(^{28}\) The relevant electrochemical reactions for any battery can be limited by any of 3 stepwise processes: mass transfer, charge transfer and the surface reaction chemistry itself. Each of these processes have their own associated overpotentials such that the total overpotential of a given cell, \( \eta_T \) can be defined as:

\[ \eta_T = \eta_{MT} + \eta_{RXN} + \eta_{CT} \] \[ \text{[10]} \]

Each component of overpotential has an associated current such that the total current, \( i \), passed through a cell can be expressed as:
or, in terms of limiting current density, the Koutecky-Levich equation,

\[
\frac{1}{i} = \frac{1}{i_K} + \frac{1}{i_R} + \frac{1}{i_C} \tag{11}
\]

where \(i_K\) represents the current in the absence of any mass-transfer effects.\(^{28}\) Thus, galvanostatic experimental cycling conditions can be selected to isolate specific causes for changes in cell overpotential over time. In a typical battery without flow-induced convection, ion mass transfer at the surface of the electrode varies, and is dependent on the state of charge of the electrode. As the electrode SOC increases, the availability of reactant decreases, resulting in an eventual increase in observed overpotential. In the case of the Ni-Zn flow assisted battery, where the zinc anode is present as saturated zincate ion in solution, zincate reactant is continuously replenished by convective electrolyte flow, reducing (or, depending on zincate concentration, eliminating) the overpotential dependence on ion mass transfer at the zinc electrode.

Electrolyte flow serves the additional functions of removing heat generated at the electrode and carrying gas microbubbles away from the electrode surface. Both heat generation and gas generation (\(H_2\) and \(O_2\)) are inevitable contributions to lower energy efficiency. A comparison of otherwise identical cells where flow is varied is expected to give further insight into any benefits of electrolyte flow.
2. **EXPERIMENTAL**

2.1 **Cell Construction**
To obtain a preliminary understanding of the effect of eliminating electrolyte flow during discharge, and to determine an optimal number of cycles between reconditioning discharges, 8 identical Nickel-Zinc flow-assisted batteries and flow systems were constructed. Each cell consisted of 3 sintered nickel oxy-hydroxide (NiOOH) sheets (Jiangsu Highstar Battery Mfrg. Co., Ltd) as positive electrodes placed between 4 nickel-plated copper negative electrodes cut from source sheet metal (Orbel Corp.). The sintered nickel electrodes were prepared from stock sheet sintered nickel and cut to a $\frac{7}{8} \times \frac{7}{8}$ square, leaving a $\frac{1}{2} \times \frac{1}{4}$ inch tab exposed above the primary plating surface. A $3 \times \frac{1}{2}$ inch tab of sheet nickel metal was welded to the exposed tab of each sintered nickel electrode to allow for flexibility when positioning the electrodes in the cell casing. Once the electrodes were properly arranged, the tabs were then attached to a single positive terminal made of nickel-plated stainless steel, providing an electric coupling between each of the positive electrodes. Similarly, each of the nickel-plated copper negative electrodes were cut such that a rectangular tab protruded out from the square electrode surface. These tabs were similarly jointly connected to a negative terminal of the cell. Figure 2. The square surface area of the electrodes were $2 \frac{7}{8} \times 2 \frac{7}{8}$ inches, providing a total plating surface area of 8.25 in$^2$ and a manufacturer’s rated theoretical capacity of 4.46 – 4.70 Ah, based on the sintered nickel energy density of 0.18-19 Ah/in$^2$ provided by the manufacturer multiplied by the available surface area.
As discussed above, to prevent electrode warping or deformation, various spacers or supporting structures have been used. For these experiments, a custom acrylic spacer was designed to provide maximum structural support while at the same time minimizing interference with electrolyte flow and ion transport between the plates. Acrylic frames were cut from 1/8 inch thick acrylic sheets using a laser cutter as shown in Figure 3. Three channels were then etched at the top and bottom edges of the frame to approximately 1.0 mm to allow as little flow resistance as possible through the 3 channels. Figure 4. These acrylic spacers were then inserted between each electrode, creating a 0.125” (3mm) distance between each electrode. Figure 5.

The electrodes were attached to the terminals using standard stainless steel nuts, bolts and lock washers. Once the electrode assembly was completed, it was placed in an unsealed 3 ¼ x 6 ¼ x 1 ¼ polysulfone case (Yardney Technical Products). Figure 6. To prevent the spacers from moving, and to provide additional support, polypropylene sheets were inserted between the
outer-most electrode face and the casing wall, exerting additional pressure against the electrodes and spacers to maintain their original configuration. An inlet and outlet hole was drilled into the bottom and top of each acrylic case before the electrode assembly was inserted. Chemically inert tube fittings and tubing were then connected between the battery casing and pump to allow electrolyte circulation.

Figure 5. Electrode-terminal assembly.

Figure 6. Fully assembled cell
Consistent with similar Ni-Zn flow-assisted battery designs of Ito, 60g/L ZnO was dissolved into 8.9M KOH, which was used as the electrolyte for each of the cells, providing an excess of zincate ion during plating (charge). Each cell was initially filled with 350mL KOH solution, providing a maximum hypothetical availability of 16.9g Zn.

2.2 Flow system
With the electrode assembly firmly in place within the battery casing, ¼ inch tygon tubing was attached from the inlet fitting at the bottom of the case to the outlet of a the chemically inert pump with a stainless steel pump head (Fluid-O-Tech, MG204XD0PT00000). Another length of tubing was attached to the outlet fitting located above the electrodes, with the other end inserted into the top of an acrylic electrolyte reservoir, ensuring that the electrodes would be completely immersed in electrolyte. The reservoir was then connected to the pump inlet such that when the pump operates, electrolyte is forced up through the bottom of the cell, flowing parallel to the electrode surface out of the top into the electrolyte reservoir, ensuring that the electrodes would be completely immersed in electrolyte. An additional valve was inserted near the reservoir outlet to facilitate any modifications to the flow system. Each system for which the pump would be turned off at any point during the test, an additional chemically resistant one-way check valve was inserted near the cell inlet to prevent back flow or cell drainage when the pump was disengaged. A general schematic of the flow-assisted battery apparatus and control circuit is shown in Figure 7.
2.3 Test cells
To accurately control the electrolyte pumps, each pump operating a test cell was electrically connected to a custom-programmed Arduino-based control circuit. The pumps used with the control cells were directly connected to a constant 5V power supply since they require continuous, constant electrolyte flow. The control circuit, properly programmed, automatically controlled power to the pump, keeping the pump on to effectuate electrolyte flow except when the cell was discharging. When the cell switched to discharge, the control circuit cut power to the pump, eliminating electrolyte flow until discharge was completed.

2.4 Circuit design/control program
A customizable program was written to control electrolyte flow for each of the test cells. A primary goal of this experiment was to determine the effect of eliminating electrolyte flow of a Ni-Zn flow-assisted battery during battery discharge. To achieve this goal, a basic software program and control circuit were designed to turn the pump off when the battery entered a state of discharge, and then resume electrolyte flow when discharge was completed. Since the

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The term “test cells” are used herein to identify those cells being cycled without flow during the discharge step of the cycle. “Control cells” refer to the correlating cells being cycled with electrolyte flowing continuously.
available battery testing systems do not have the capability to communicate with external
devices, an analog input on an Arduino was connected to the positive terminal of the test cell.
The negative terminal was connected to a ground on the circuit board to maintain a consistent
voltage reference. An electronic relay was then connected to a digital output pin on the Arduino,
which was then in turn connected directly to the pump.

The Duemilanove has an operating voltage of 5V, with analog input pin connections
capable of 1024 ‘states,’ which automatically scales the input voltage of the cell, translating the
actual cell voltage into an analog numerical equivalent with an accuracy of ± 5 mV. Since the
specific change in cell voltage is also measured and reported by the Battery Testing System
(BTS) in real-time, it was possible to create a correlation between the actual voltage and the
scaled analog state. When the cells switch to discharge, the cell experiences a measurable and
repeatable drop in voltage. A short script was implemented that takes advantage of this initial
voltage drop by regularly measuring the cell voltage and reporting the scaled analog equivalent.
When the pre-determined voltage drop correlating to the beginning of a discharge is observed, a
signal is sent to the digitally connected relay, cutting power to the pump. As the cell discharges
in a galvanostatic cycle, the voltage drops continuously until the cell reaches 1.0V, at which
point the BTS procedure switches to an open circuit voltage (OCV) rest state, ending the
discharge cycle. When this OCV state begins, a noticeable and repeatable increase in cell
voltage is observed, and a digital signal is sent to the relay to resume power supply to the pump,
thereby resuming electrolyte flow until the next discharge occurs. Several modifications were
required during the course of the experiments as individual cell variations were observed and to
compensate for hardware compatibility requirements of the battery testing systems used to implement the cycling schedules. These scripts are included in Appendix A.

2.5 Experimental Design
To obtain an initial empirical understanding of the number of cycles the experimental Ni-Zn flow-assisted batteries can complete before requiring a low-current deep discharge reconditioning to rejuvenate the electrodes, removing residual Zn deposits that may have accumulated over time, 4 different cycling schedules were implemented. These schedules were identical in all respects except for the number of completed cycles before a reconditioning discharge was applied. The 4 cycling schedules chosen were 7-, 12-, 20-, and 30-cycles between deep discharges. Each schedule was applied to 2 of the 8 cells, with each pair of cells corresponding to a “test” cell, with pump connected to the control circuit, and a “control” cell, employing continuous electrolyte flow. By implementing this 4x2 experimental matrix, an initial understanding of both experimental objectives could be gained with minimal duplication and repetition of the experiments.

Due to the nature of the electrodes, an initial electrode formation period was required before useful cycling data could be obtained. Since the negative electrodes were cut from nickel-plated copper sheet metal, copper metal was exposed at the electrode edges. If these copper edges remain exposed and unprotected, copper ions can leach into the electrolyte contaminating the cell. Also, the sintered nickel positive electrodes are initially porous and provide a highly non-uniform surface for zinc plating. Before the cycling schedules were implemented, a low-current, extended duration cell formation charge was applied to the cells at a current of 50mA for a period of 8 hours.

Because two battery testing systems (BTS) were used over the course of these experiments, each required implementing slightly different pump control scripts.
2.6 Cycle Schedule

As mentioned above, the experiments were conducted using a galvanostatic cycling schedule. An initial run of 60 cycles were conducted whereby all 8 cells charged and discharged with the control circuit disabled, allowing the electrolyte to flow continuously. These 60 cycles, shown in Figure 8, provided an initial baseline that served two purposes: first, to determine the actual capacity of each of the cells, which was necessary to determine an appropriate current at which the galvanostatic cycling should be implemented; and second to provide initial cell efficiency data to compensate for natural cell-to-cell variations.

![Coulombic Efficiency vs. Cycle (Start-up Comparison)](chart)

Figure 8. Coulombic Efficiency at cell start-up

Final cycling conditions targeted a C/2 charge rate to maximize the number of cycles that would be completed given experimental time constraints while maintaining practical real-world

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\(^{c}\) Due to a software malfunction, all data for cycles 1-97 from the 7-cycle control cell were inadvertently lost and thus could not be included in the baseline analysis.

\(^{d}\) While it is expected that the round-trip cycle efficiencies of the cells would naturally evolve over time, the initial efficiency data points provided a preliminary view of actual cell-to-cell variations that can be used to reduce overall experimental uncertainty.
Based on the sintered nickel plate manufacturer’s stated capacity of ~0.18 Ah/in$^2$ and an 8.266 in$^2$ surface area, the total expected theoretical capacity was 4.46 Ah.

To ensure maximum charge and complete nickel utilization, a charge rate slightly higher than the maximum rated capacity was used to estimate the actual cell capacity. An initial cycling schedule of a constant current charge at 2.23 A for 2 hours, followed by a 20 minute “rest” period, followed by a constant current discharge at 2.23 A was implemented. The discharge continued until the cell voltage dropped below 1.0 V at which point another OCV rest period was applied such that the discharge + rest period equaled 2h20minutes. An additional 5 minute rest period was inserted to enhance the BTS synchronicity between pairs of cells under the same cycle algorithm. After this additional 5 minute rest, the next charge cycle began until the requisite number of cycles (7, 12, 20, or 30) had been completed at which point the BTS would impose a low, constant current deep discharge at 0.50A until the cell reached a potential of -0.2V$^f$, ensuring complete de-plating of Zn at the negative electrodes. The deep discharges were followed by a rest period such that the deep discharge + rest period equaled 3h 30min. A simplified schematic of the charging algorithm is shown in Figures 9 and 10.

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$^e$ “C-rating” is often used to describe galvanostatic battery cycling conditions. A “C” charge rate defines the current that is applied to the cell that will charge the cell to full capacity in 1 hour. Thus, a C/2 charge rate will charge the cell to maximum capacity in 2 hours.

$^f$ Because the Maccor 4600 BTS cannot process “negative” potential, for those cells using the Maccor BTS, a limit of 0.15V was applied to indicate complete zinc dissolution.

---

**Figure 9.** Charge-discharge algorithm for each control cell, where X=7, 12, 20 and 30.
Figure 10. Charge-discharge algorithm for each test cell where X=7, 12, 20 and 30.

The charge-discharge curves for the initial 60 cycles for each of the cells are presented in Figure 8 above. The charge rate was increased during the initial capacity determination cycles until a significant voltage increase at the end of charge indicated complete utilization of the sintered nickel cathode. Based on these initial cycles, an actual capacity of 4.9Ah and final charge rate of 2.45 A over 2 hours was used to ensure complete utilization of the sintered nickel electrode, utilizing an appropriate approximation of a C/2 charge schedule, which was implemented for the remainder of the experiment.

Initially, the pairs of cells subject to the 7-cycle algorithm and 12-cycle algorithm were connected to the Maccor BTS, while the 20- and 30-cycle algorithm cells were connected to the Arbin BT2000 BTS. However due unforeseen hardware limitations, the 12-cycle algorithm test and control cells were transferred to the Arbin BTS after 117 and 160 cycles respectively.
3 RESULTS

The 8 experimental nickel-zinc flow-assisted batteries will continue to be cycled until the discharge efficiency drops below 30% for continuous cycles, however, as of this writing, only one of the 8 cells has met this condition. The 20-cycle test cell was disassembled after 467 cycles, while each of the other cells continues to cycle, with the longest-running cell, the 7-cycle test cell, at 1024 cycles. Table 1 shows the status of each of the 8 experimental batteries as of this writing:

Table 1. Status of all experimental flow-assisted cells as of this writing.

<table>
<thead>
<tr>
<th>Cycling Algorithm</th>
<th>Number of Cycles Completed</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test Cells</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7-cycle reconditioning</td>
<td>790</td>
<td>88% Coulombic Efficiency; consistent cycling</td>
</tr>
<tr>
<td>12-cycle reconditioning</td>
<td>840</td>
<td>87% Coulombic Efficiency; decreasing cycle-to-cycle; rejuvenated after reconditioning</td>
</tr>
<tr>
<td>20-cycle reconditioning</td>
<td>467</td>
<td>Test ended</td>
</tr>
<tr>
<td>30-cycle reconditioning</td>
<td>863</td>
<td>85-50% Coulombic Efficiency; rapid decrease cycle-to-cycle; rejuvenated after reconditioning</td>
</tr>
<tr>
<td>Control Cells</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7-cycle reconditioning</td>
<td>731</td>
<td>86% Coulombic Efficiency; consistent cycling; exceptionally weak Zn metal adhesion on charge (thick black electrolyte, slowly lightening over 7-cycle set)</td>
</tr>
<tr>
<td>12-cycle reconditioning</td>
<td>902</td>
<td>81% Coulombic Efficiency; slowly decreasing cycle-to-cycle; rejuvenated after reconditioning</td>
</tr>
<tr>
<td>20-cycle reconditioning</td>
<td>1024</td>
<td>87% Coulombic Efficiency; consistent cycling</td>
</tr>
<tr>
<td>30-cycle reconditioning</td>
<td>858</td>
<td>86% Coulombic Efficiency; consistent cycling</td>
</tr>
</tbody>
</table>

Since the primary benchmark used in this study is cycle efficiency, both coulombic and energy efficiency are reported. However, because the reconditioning discharge and first-cycle
after reconditioning are not representative of typical or expected battery usage, these cycles were excluded from average efficiency trend analyses, allowing a normalized comparison between cells. The following Figures 11-14 show the coulombic efficiency over time for each test cell compared to the corresponding control cell for each of the reconditioning algorithms:

**Figure 11.** Coulombic Efficiency comparison of 7-cycle reconditioning cells.

**Figure 12.** Efficiency comparison of 12-cycle reconditioning cells. Region I: cell startup conditions. Regions II: irregular cycling due to Maccor equipment interference with the pump control circuit. Region III: erratic cycling due to electrolyte leakage.
Figure 13. Efficiency comparison of 20-cycle reconditioning cells. Region I: cell start-up conditions. Region II: cell operation failures due to valve and pump control circuit failures.

From the above comparisons, several trends are observed. Most notably, the cells subjected to the 30-cycle reconditioning algorithm demonstrate a clear effect from electrolyte flow during discharge. The 30-cycle test cell experiences a consistent, roughly linear efficiency degradation from cycle-to-cycle, and is then rejuvenated during each reconditioning discharge.
This cell experienced a coulombic efficiency drop from roughly 85% efficiency after reconditioning to as low as 50% efficiency immediately prior to reconditioning, whereas the control cell with continuous electrolyte flow during discharge experienced minimal cycle-to-cycle efficiency drops. This trend is in stark contrast with the cells subjected to the 7-cycle reconditioning algorithm. When reconditioned every 7 cycles, the test cell performs more consistently, and at a higher overall efficiency than the control cell, with minimal cycle-to-cycle efficiency degradation. Over the final 300 cycles, the 7-cycle control cell has been operating at roughly 77-82% coulombic efficiency, whereas over the same period, the 7-cycle test cell ran at roughly 85-92% coulombic efficiency, with minimal cycle-to-cycle degradation.

In Figures 15-18, the cycle-averaged coulombic efficiency per completed cycle set (signified by a reconditioning discharge) for each reconditioning algorithm is provided. By comparing cycle-averaged coulombic efficiency, long-term trends are more readily apparent.

![Graph](image)

*Figure 15. Cycle-averaged coulombic efficiency for 7-cycle reconditioning cells.*

---

*Cycle-averaged efficiency is the weighted mean-efficiency of the cell from one reconditioning discharge to the next, excluding the actual reconditioning cycle and first cycle following reconditioning. Thus, for the 7-cycle algorithm cells, cycles 2-6 are averaged and plotted over time; for the 12-cycle algorithm, cycles 2-11 are averaged and plotted; etc....
Figure 16. Cycle-averaged coulombic efficiency for 12-cycle reconditioning cells.

Figure 17. Cycle-averaged coulombic efficiency for 20-cycle reconditioning cells.
Figure 18. Cycle-averaged coulombic efficiency for 30-cycle reconditioning cells.

Once again, the apparent benefits of continuous electrolyte flow are clear for the cells subjected to the 30-cycle reconditioning algorithm. The control cell shows an overall drop in coulombic efficiency of about 10% after 850 cycles, whereas the test cell experienced an efficiency drop of over 30%. This 10% efficiency loss in the continuous-flow control cells is consistent regardless of reconditioning frequency (see “Control Cell Comparison” Discussion below). Each of the control cells began cycling at roughly 95% coulombic efficiency, and as of this writing, each cell has experienced a roughly 10% drop. This contrasts with the test cells, where no clear trend is apparent. The test cells subject to 12-, 20-, and 30-cycle reconditioning algorithms have demonstrated significant detrimental effects from eliminating electrolyte flow during discharge, but the 7-cycle test cell appears relatively unaffected.

3.1 30-cycle test cell

Due to an unexpected and inadvertent pump control circuit failure, the 30-cycle reconditioning test cell operated with continuous electrolyte flow from cycle 614-650. Figure 19.
During the complete 30-cycle set between reconditioning, the test cell maintained a coulombic efficiency range of 84.1-86.0%, similar to that of the control cell, which operated at a coulombic efficiency range of 87.0-89.0%. Figure 20. When the pump control circuit resumed proper operation (eliminating electrolyte flow during discharge), the next 30-cycle set demonstrated decreased, albeit sporadic, coulombic efficiency, ranging from 89% to 49.9% (Figure 21), with an overall average going from 85.1% for continuous electrolyte flow to 71.1% when flow is halted during discharge. As shown in Figure 18, as the cell cycled, the linear decrease in cell efficiency between reconditioning discharges resumed.
3.2 7-cycle reconditioning algorithm

The two cells subjected to the 7-cycle reconditioning algorithm exhibited starkly contrasting behavior. The long-term cycle-averaged efficiency demonstrated in Figure 15 shows the 7-cycle test cell operating at roughly 84-91% coulombic efficiency over the last 300 cycles, whereas the 7-cycle control cell operated more inconsistently, and generally poorer, at roughly 76-86% coulombic efficiency over the same cycle range. The poor performance of the 7-cycle control cell was further observed in the electrolyte itself. After roughly 400 cycles, the electrolyte turned from clear to a dark black, indicating significant amounts of undisolved Zn suspended in the electrolyte, whereas the 7-cycle test cell electrolyte remained relatively clear over the course of the experiment, with only occasional zinc precipitate settling at the bottom of the reservoir and cell.

3.3 20-cycle test cell

As mentioned above, the 20-cycle reconditioning test cell was terminated after only 476 cycles due to repeated discharge inefficiencies, or fundamental cell failure with repeated coulombic efficiencies below 30%. While valuable data had been collected, the electrolyte flow system suffered from repeated failures due to faulty control circuit operation and check-valve operation. After numerous cycles where the electrolyte would either flow continuously during
charge and discharge, or more serious failures where the check-valve would fail, allowing the electrolyte to drain out of the cell during discharge, the 20-cycle test cell became sufficiently corrupt that valid comparative data could not be collected.

Various rehabilitative attempts, including redesigning the reservoir itself to prevent excess precipitate from clogging the pump and valves, failed to prevent sporadic and unpredictable cycle errors. These errors culminated in the cell meeting the <30% coulombic efficiency end condition after 476 cycles at which point the cell was disconnected.
4 DISCUSSION

4.1 Coulombic vs. Energy Efficiency
While a measure of coulombic charge-discharge efficiency is a valuable benchmark to determine basic relative cell performance, energy efficiency gives a more accurate performance-based metric by which batteries can be compared. As discussed above, observed changes in overpotential can act as an informative proxy for inefficiencies and deterioration in battery performance. Changes in cell overpotential can be seen in changes in the ratio of energy vs. coulombic efficiency. Coulombic efficiency is fundamentally a coulomb counter and does not take into account changes in potential caused by side reactions, increased cell impedance or other inefficiencies. Because the cycling procedure employed a constant and equal current throughout charge and discharge, coulombic efficiency cannot account for cell deterioration or inefficiencies in the charging phase. Since changes in energy efficiency will account for any increases in overpotential, the ratio of energy vs. coulombic efficiency provides additional insight into the cause of observed inefficiency. Figures 22-29 shows a comparison between coulombic and energy efficiency for each of the 8 experimental cells, including an overlayed plot of the ratio between energy and coulombic efficiency over time.

Figure 22. Coulombic vs. Energy Efficiency for 7-cycle control cell with EE:CE Ratio overlay.
Figure 23. Coulombic vs. Energy Efficiency for 7-cycle test cell with EE:CE Ratio overlay.

Figure 24. Coulombic vs. Energy Efficiency for 12-cycle control cell with EE:CE Ratio overlay.
Figure 25. Coulombic vs. Energy Efficiency for 12-cycle test cell with EE:CE Ratio overlay.

Figure 26. Coulombic vs. Energy Efficiency for 20-cycle control cell with EE:CE Ratio overlay.
Figure 27. Coulombic vs. Energy Efficiency for 20-cycle test cell with EE:CE Ratio overlay.

Figure 28. Coulombic vs. Energy Efficiency for 30-cycle control cell with EE:CE Ratio overlay.
Figure 29. Coulombic vs. Energy Efficiency for 30-cycle test cell with EE:CE Ratio overlay.

As shown in Figures 22-29, the efficiency ratio for all of the control cells and the 7-, and 20-cycle reconditioning test cell remained flat over time, suggesting that coulombic efficiency is a valid metric by which cell performance can be measured and compared. Coupled with the fact that the charge energy for each of these cells remained relatively constant over time, this suggests that the total cell overpotential, $\eta_T$, or more precisely, the difference in overpotential on charge and discharge, remained relatively constant even though the overall efficiency dropped by roughly 10% in each of these cells. Each of the 4 pump-controlled test cells did show slight long-term decreases in efficiency ratio such that, if extrapolated over thousands of cycles, this decrease can become significant, but additional long-term cycling experiments are required to verify this trend.

The 12-, and 30-cycle test cells, however, show stark decreases in EE:CE ratio at various points during the cycling experiments suggesting that a further examination of experimental conditions may provide useful insight into eventual cell deterioration. The 12-cycle test cell demonstrated a consistently longer recovery time after reconditioning than the other cells demonstrated by the lower efficiency even 2 and 3 cycles after reconditioning. The EE:CE ratio
showed a similar pattern. This suggests that the reconditioning cycle had a specific, direct impact on the overpotential of the cell for the initial few cycles after reconditioning, but then recovered until the next reconditioning cycle.

The 30-cycle test cell demonstrated a different, more experimentally isolated effect. As discussed above, from cycles 614-650, the pump control circuit failed leaving the pump on at all times. When the pump control circuit was recalibrated to turn off during discharge, the recalibration efforts had the unexpected effect of keeping the pump off during various charge cycles, as well as discharge cycles. In addition, valve failures caused simultaneous slow, partial electrolyte drainage when the pump was off. At cycle 680, these calibration efforts were corrected, but it appears there was a permanent effect on the cell. The EE:CE ratio became erratic, and the energy efficiency degraded more rapidly than the coulombic efficiency. This suggests that the overpotential on charge increased at a higher rate than on discharge, confirming the hypothesis that the earlier calibration efforts damaged either the nickel electrode or zinc-containing electrolyte, pushing the overpotential higher during charge, resulting in a cumulative, rapidly decreasing coulombic and energy efficiency of the cell that could not be repaired by additional cycling or reconditioning.

4.2 **30-cycle reconditioning**

Notable results from these long term cycling experiments were demonstrated by the two outer reconditioning schedules – the 7- and 30-cycle reconditioning algorithms. The test cell subjected to the 30-cycle reconditioning algorithm showed an immediate response when flow was eliminated during discharge. During the first 60 cycles, the pump remained on and electrolyte flow was imposed continuously to establish a benchmark efficiency level. The efficiencies of the control and test cell during these initial cycles are barely distinguishable,
averaging 95.3 % and 95.1% respectively. When the pump control circuit was activated for the 30-cycle test cell, the cycle-averaged coulombic efficiency immediately dropped to 89.6% for the next set of cycles, remaining relatively constant for approximately 150 cycles (see Figure 18), but as shown in Figure 14, the 30-cycle test cell began to immediately exhibit cycle-to-cycle degradation and cyclic rejuvenation after reconditioning as soon as the pump control circuit was activated.

The immediate efficiency decrease suggests that an excess amount of Zn remains at the anode after discharge compared to its electrolyte-flowing counterpart. The cycle-to-cycle efficiency drop is further evidence that this effect is cumulative and the linearity of the efficiency decrease suggests an equal amount of Zn accumulates at the anode after each successive discharge. This pattern was further supported by visual inspection of the cells from one cycle to the next. This pattern in the 30-cycle test cell suggests that electrolyte flow not only effects dendrite formation,21, 24 but also has an effect on dendrite dissolution. Because the electrolyte is deliberately oversaturated with zincate ion (Zn(OH)_{4}^{2-}) relative to the nickel cathode capacity, it is possible that the electrolyte flow decreases Zn(OH)_{4}^{2-} concentration locally, allowing the Zn metal to dissolve more uniformly across the anodic deposits during discharge. When the electrolyte flow is eliminated, local Zn(OH)_{4}^{2-} concentration is sufficiently high (see reactions [2], [6]) to discourage Zn dissolution in favor of side reactions such as hydrogen formation, reducing the overall efficiency of the cell. Alternatively, electrolyte convection sufficiently distributes both OH^{-} and Zn(OH)_{4}^{2-} to allow for more uniform current density distribution across the zinc electrode, resulting in more uniform Zn metal dissolution.

An unintended pump control circuit failure occurring at cycle 614 lends further support the effects of electrolyte flow during discharge. At cycle 614, the pump control circuit failed and
electrolyte flow was continuous for 37 cycles. As seen in Figure 19, the efficiency of the cell immediately stabilized at 85% cycle-to-cycle efficiency and was maintained until the next reconditioning discharge at cycle 650. The pump control circuit was then re-applied and the above-discussed efficiency loss resumed. The inconsistency of the degradation was due to difficulties in recalibrating the pump control circuit, which resulted in unanticipated pump control failures. The efficiency spikes shown between cycles 650-680 were due to continuous electrolyte flow during discharge, giving further support for the proposition that electrolyte flow during discharge does have an effect on overall cell efficiency.

4.3 20-cycle reconditioning
Although the 20-cycle test cell experiment was terminated after only 467 cycles, the efficiency data for this cell prior to termination demonstrated a similar pattern to that of the 30-cycle test cell. As shown in Figures 13 and 17, the 20-cycle test cell showed similar cycle-to-cycle degradation and rejuvenation after reconditioning, while the 20-cycle control cell exhibited fractional, but consistent, cycle-to-cycle degradation similar to the 30-cycle control cell, losing on average about 2-3% per 20-cycle set. Thus, the 20- and 30-cycle reconditioning data supports the conclusion that electrolyte flow has a direct impact on cell efficiency.

The 20-cycle test cell also experienced a pump control circuit failure during cycles 354-364. Figure 23 shows a focused view of the performance of this cell, demonstrating (similar to the 30-cycle test cell) that electrolyte flow during discharge has a direct beneficial impact on efficiency.
Figure 30. Focused comparison of 20-cycle reconditioning cells. At cycle 354, the pump control circuit failed, resulting in continuously flowing electrolyte until cycle 364. Region I: Test cell operating with continuous electrolyte flow due to pump control circuit failure. Region II: Irreversible cell failure at end-of-test conditions.

### 4.4 12-cycle reconditioning

While the 20- and 30-cycle reconditioning data provide compelling evidence supporting a conclusion that electrolyte flow has a direct impact on cell efficiency, this pattern was not observed across the other cycling algorithms. Focusing on the most recent data from the cells subjected to 12-cycle reconditioning, Figure 24 shows that the control cell also demonstrated cycle-to-cycle degradation, whereas the 12-cycle test cell has exhibited inconsistent performance, often showing cycle-to-cycle increases in efficiency until the next reconditioning discharge.
Figure 31. Focused comparison of 12-cycle reconditioning cells

4.5 7-cycle reconditioning

The cells subjected to the 7-cycle reconditioning algorithm showed consistent, and contrary, results relative to the 30-cycle reconditioning data. As noted above, the 7-cycle test cell has been among the most consistent, and highest-performing cells, maintaining a cycle-averaged efficiency of 85-92% over its last 300+ cycles. Within the 7-cycle sets, the test cell exhibits no cycle-to-cycle degradation, and in many cases, even slight increases in efficiency similar to that sporadically seen in the 12-cycle test cell described above. Figure 25 shows a gradual cycle-averaged degradation over time, but this degradation is matched by the cycle-averaged degradation of the control cell. Most notably, Figure 25 demonstrates that the 7-cycle test cell consistently performed at higher energy efficiency than the control cell, not taking into account any efficiency boost provided by the pump control circuit. An overall experimental mean energy efficiency of 80.7% vs. 78.8% (again, not taking into account energy losses due to continuous pump operation for the control cell), shows a small, but consistent outperformance by the 7-cycle test cell versus the control.
4.6 Control cell comparison

A second end-point of these experiments was to seek a better understanding of the effects of periodic reconditioning via slow, low-current (C/10) discharge. Figure 26 shows a comparison of coulombic efficiency across each control cell reconditioning algorithm. A consistent trend of decreasing efficiency is seen across all 4 control cells, suggesting a slow, steady efficiency loss over time. Each cell began cycling at roughly 95% coulombic efficiency, and has decreased to roughly 85% efficiency for the 7-, 20- and 30-cycle reconditioning algorithms, and 82% for the 12-cycle control cell as of this writing. As shown in Figure 26, each of the control cells show some cycle-to-cycle efficiency loss and subsequent rejuvenation upon reconditioning, but no clear trend is apparent to suggest the optimal number of cycles between reconditioning discharges. Figure 26 also demonstrates that after roughly 350 cycles, all of the cells experience a slight jump in efficiency loss before again leveling out into a linear decrease, suggesting that after 350 cycles there may be a specific physical effect or transition independent of reconditioning periodicity.
After 600 cycles, the 20- and 30-cycle control cells demonstrated losses of 1-3% over the course of a given cycle set, the 12-cycle control cell demonstrated losses of 1-10%, and the 7-cycle control cell demonstrated cycle-to-cycle efficiency gains between reconditioning discharges. This efficiency gain is attributed to the observation that the cell required more than 1 cycle to recover from each reconditioning cycle. The second cycle after reconditioning exhibited some lingering detrimental effects from reconditioning yielding a lower operating efficiency, although this effect was eventually mitigated before the next reconditioning cycle occurred.

Despite the variations in the effects of reconditioning, it is clear that periodic reconditioning does provide significant operational benefit. The 1-3% losses shown by 20- and 30-cycle control cells suggests that reconditioning may only be necessary after a certain (application-specific) threshold efficiency loss has been reached.

![Coulombic Efficiency vs. Cycle](image)

**Figure 33.** Comparison across all continuously flowing electrolyte control cells. The 7-cycle reconditioning cell suffered from extended recovery time after reconditioning, resulting in 2 low-efficiency cycles immediately after reconditioning.

### 4.6 Pump-related Energy Effects

The energy efficiency data collected by the BMS and plotted in Figure 22, accounts only for the actual cell (and associated overpotential) itself, and not the energy lost by the pump or
other peripheral system necessities. If the actual pump energy itself is taken into account, it is apparent that energy efficiency comparisons can be heavily skewed depending on the efficiency of the pump selected. To avoid such arbitrary skewing of the data while preserving the validity of the energy efficiency metric, a rough estimate of an approximate 3-8% energy loss is from an appropriately selected high-efficiency commercial pump. These losses must be imposed on any flow-assisted battery comparison, but must be equally credited to a system with an effective pump-management control procedure such as those employed by the test cells described herein.

Imposing an 85% average coulombic efficiency, and ignoring arbitrary interim rest-states, the pump would only be operating for 57.5% of any given operational cycle. Thus, when comparing the overall energy efficiency of the control cells to the test cells of otherwise identical systems, the test cells should be credited an additional 1.3-3.4% increase in overall energy efficiency relative to the corresponding control cell. Accumulated over 1000’s or tens of 1000’s of cycles, this energy savings can provide significant operational differences when multiplied over a mass implementation, such as a fleet vehicle operations.
5 CONCLUSIONS

A 4x2 experimental matrix was designed to examine two primary experimental endpoints. First, to determine the feasibility of operating a nickel-zinc flow assisted battery without electrolyte flow during discharge, and second, to determine the effects and necessity of a periodic reconditioning discharge cycle at low discharge rate. Eight identical cells were constructed and cycled until the cell’s coulombic discharge efficiency was below 30% for repeated cycles. To date, only one cell met this cell failure criteria, after 476 cycles. The other 7 cells continue to operate, having completed at least 750 cycles.

Using coulombic efficiency as a primary benchmark, it appears feasible to operate a Ni-Zn flow-assisted secondary battery without requiring electrolyte flow during discharge, allowing the entire flow apparatus to be separated from the actual electrode encasement and off-loaded to a centralized location, but such operation appears to require a more frequent reconditioning discharge algorithm. After nearly 800 cycles and implementing a reconditioning discharge every 7 cycles, a 4.9 Ah test cell operated continuously with a repeatable coulombic efficiency loss of 87% and a total efficiency loss of less than 10%.

It has also been confirmed that periodic reconditioning has a rejuvenating effect on the Ni-Zn electrode system, thus increasing the cell’s cycle life. The optimal number of cycles between reconditioning discharges may be application-specific, but reconditioning as infrequently as every 30 cycles has a restorative effect on the system, while suffering only 1-3% loss between reconditioning cycles.
6  FUTURE WORK

While these results demonstrate the feasibility and practicality of developing low-cost Ni-Zn flow-assisted batteries for transportation-based applications (as opposed to large-scale stationary applications), additional testing and experimentation is necessary. Most importantly, a more robust series of duplicative experiments will eliminate inherent cell-to-cell variability. It was noted early on during these experiments that the specific charge-discharge parameters employed lent themselves to systematic and repeated overcharging and excessive gas generation. This was due in part to the constant-current charge-discharge procedure employed. Combined constant-current/constant voltage charge parameters are known to provide higher overall cycling efficiency for Ni-Zn batteries and would provide a more realistic set of testing conditions from which more accurate and realistic efficiency comparisons can be made.

As an open system, atmospheric CO$_2$ was free to react with the electrolyte to form K$_2$CO$_3$, a known buffering agent. The quantitative effect of this carbonate formation and dissolution into the electrolyte is unknown, but is suspected to have a detrimental buffering effect on ion availability in the electrolyte over time. Additional experiments may be designed to quantitatively examine the effect of carbonate formation and carbonate poisoning of the electrolyte on cell performance. Alternatively, the cell design can be modified towards a closed system. This would accomplish the dual goal of reducing carbonate formation, while at the same time allowing gas production monitoring, which in turn will allow for more effective battery operational control. Such sealed, closed-cell Ni-Zn flow-assisted battery systems with gas monitoring and management systems are currently being designed and tested.

Finally, a reference electrode may be added to the cell design to allow more direct differentiation of the effects on the anode and cathode of given variables and observed phenomena.
Appendix A

12 cycle reconditioning test cell control pump-control script:

/*
 * Single-channel pump controller:

 Analog input, digital output, serial output

 Reads an analog input pin, maps the result to a range from 0 to 1023
 and uses the result to control a digital output pin.
 Also prints the results to the serial monitor.

 The circuit:
 * cell electrode connected to analog pin 5.
 * pump connected from digital pin 8 to ground

 */

// to the pins used:

const int analogInP1 = 5;  // Analog input pin for cell 1
const int digitalOutP1 = 8; // Digital output pin for pump 1

int firstanalog1 = 0;        // first analog voltage reading from cell 1
int secondanalog1 = 0;       // second (1min delayed) analog voltage reading from cell 1
int outputValue1 = HIGH;     // value output to Pump 1 (digital out)
int difference = 0;

float Time = 0;              //first value of timer = 0, counting by 1 min increments
void setup() {

  Serial.begin(57600);

  pinMode(digitalOutP1, OUTPUT);        //sets the digital pin as output
}

void loop() {

  // read the analog in value for FIRST cell at 1 minute increments:
  secondanalog1 = analogRead(analogInP1);
  //turn pump off on discharge: when cell potential (analog) drops by 6 (~30mV) or more:

  if((secondanalog1 - firstanalog1 <= -6) && (secondanalog1 >= 377) && (secondanalog1 <= 402))
    outputValue1 = LOW;

  //turn pump on when cellValue increases >= 15:
  if ((outputValue1 == LOW) &&

46
(secondanalog1 - firstanalog1 >= 15)) outputValue1 = HIGH;

// send outputValue1 to digital pin (pump):
  digitalWrite(digitalOutP1, outputValue1);
// print the results to the serial monitor:
  difference = secondanalog1 - firstanalog1;
  Serial.print("Analog Cell voltage = ");
  Serial.print(secondanalog1);
  Serial.print("t and the difference is ");
  Serial.print(difference);
  Serial.print("t output = ");
  Serial.print(outputValue1);
  Serial.print("t Time = ");
  Serial.println(Time);
  firstanalog1 = secondanalog1;

  delay(60000);

//increase timer by 1 minutes:
  Time = Time + 1.0;

}

30 cycle reconditioning test cell control pump-control script:

/* Single-channel pump controller:
   Analog input, digital output, serial output
   Reads an analog input pin, maps the result to a range from 0 to 1023
   and uses the result to control a digital output pin.
   Also prints the results to the serial monitor.
   The circuit:
     * cell electrode connected to analog pin 5.
     * pump connected from digital pin 8 to ground
   */

// to the pins used:

  const int analogInP1 = 4; // Analog input pin for cell 1
  const int digitalOutP1 = 6; // Digital output pin for pump 1
  int firstanalog1 = 0; // first analog voltage reading from cell 1
int secondanalog1 = 0; // second (1s delayed) analog voltage reading from cell 1
int outputValue1 = HIGH; // value output to Pump 1 (digital out)
int difference = 0;

float Time = 0; // first value of timer = 0, counting by 1 min increments
void setup() {
    Serial.begin(57600);
    pinMode(digitalOutP1, OUTPUT); // sets the digital pin as output
}

void loop() {
    // read the analog in value for FIRST cell at 1 minute increments:
    secondanalog1 = analogRead(analogInP1);
    // turn pump off on discharge: when cell potential (analog) drops by 15 or more:
    if((secondanalog1 == firstanalog1 <= -15) && (secondanalog1 >= 340) &&
      (secondanalog1 <= 375))
        outputValue1 = LOW;

    // turn pump on when cellValue increases >= 15:
    if ((outputValue1 == LOW) &&
        (secondanalog1 - firstanalog1 >= 25)) outputValue1 = HIGH;

    // send outputValue1 to digital pin (pump):
    digitalWrite(digitalOutP1, outputValue1);
    difference = secondanalog1 - firstanalog1;
    // print the results to the serial monitor:
    Serial.print("Analog Cell voltage = " );
    Serial.print(secondanalog1);
    Serial.print(" t and the difference is ");
    Serial.print(difference);
    Serial.print(" t output = ");
    Serial.print(outputValue1);
    Serial.print(" t Time = ");
    Serial.println(Time);

    firstanalog1 = secondanalog1;

    delay(60000);

    // increase timer by 1 minutes:
    Time = Time + 1.0;
}
Appendix B

Several experimental conditions have been regularly observed that have required pump control circuit recalibration or other manipulations to maintain the battery cycling continuity. The follow is a set of procedures in response to commonly observed experimental interruptions.

Maccor

Currently, only the 7-cycle control and test cells are running on the Maccor BTS. Due to equipment and software limitations, the Maccor cannot process zero, or below-zero voltages. Thus, at the end of reconditioning, it is common to observe a software error during cycling that issues a “problem” status at the end of reconditioning. This problem status will pause all data collection and places the cell in an OCV state. When this occurs, cycling can be simply resumed by clicking the “resume” button on the Maccor interface. It may be necessary to resume the channel numerous times until the measured voltage drop is within an acceptable range to advance the testing schedule to the next step.

Arbin

Any cell running on the Arbin BTS can be resumed during a hardware or software error simply by resuming the paused/stopped channel into the current testing step.

If a channel experiences a cycle-terminating condition (“Rest8 – End Test”) for reasons other than <30% cycle-to-cycle efficiency, cycling can be “jumped” directly into the charge or discharge step immediately preceding the End Test condition.

The most commonly observed experimental anomaly for cells operating on the Arbin BTS has been sporadic cell drainage due to check-valve failure. If the one-way check-valve fails, the test cells may drain entirely into the reservoir during discharge, and both the discharge cycle and following charge cycle may be compromised and often leads to an “unsafe voltage” End Test condition. The most common cause for check-valve failure has been Zn particulate
clogging the valve preventing valve closure. If this is observed, the valve should be removed and cleaned using high-flow rate water, or simply replaced.

Another commonly observed experimental anomaly has been that transitions from rest (OCV) to discharge can occur at voltages outside the calibrated range of the pump control circuit. If this occurs, the pump will remain on during discharge, resulting in an invalid data point. This situation often requires a recalibration of the pump control circuit. The pump control circuit for each of the test cells is operating with a specifically calibrated control script (See Appendix A), whereby the actual cell potential is scaled to the 1024bit range of the Arduino analog input channel. The control circuit script requires that the rest-to-discharge transition occurs within a specifically calibrated scaled range.

When the discharge transition occurs outside the pre-determined scaled range, the script must be revised to reflect the recalibrated transition range. This is done by first collecting data from the control circuit using a USB cable and noting the discharge transition range from the serial output. Once the range is established, the corresponding operating script can be easily revised to reflect the new transition range. For those circuits using RBBB configurations, the RBBB must be manually reset immediately prior to re-loading the script. If the circuit is using a full Arduino, this is unnecessary. Once the recalibrated script is loaded, the channel can be resumed.
Appendix C

Summary of Invalid Data Points/Experimental Anomalies Due To Equipment Failure

<table>
<thead>
<tr>
<th>Data Point</th>
<th>Cycle</th>
<th>Cause</th>
</tr>
</thead>
<tbody>
<tr>
<td>7-cycle reconditioning test cell</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>171</td>
<td>Possible pump failure (particulate zn interfered with pump operation during charge) or internal short circuit; excess capacity carried over to next cycle</td>
</tr>
<tr>
<td>b</td>
<td>199-200</td>
<td>Likely internal short circuit at cycle 199; cycle 200 yielded &gt;100% efficiency from untapped capacity in cycle 199</td>
</tr>
<tr>
<td>c</td>
<td>276</td>
<td>Cell drained on discharge (clogged valve); excess capacity carried over to next cycle</td>
</tr>
<tr>
<td>d</td>
<td>341</td>
<td>Likely internal short; cleared on cycle 342 reconditioning cycle</td>
</tr>
<tr>
<td>e</td>
<td>361</td>
<td>Likely internal short; pump remained on during cycles 349-360; upon recalibration, cycle 361 discharge voltage dropped quickly leaving significant amounts of zinc at anode; excess capacity carried over to next cycle</td>
</tr>
<tr>
<td>f</td>
<td>645</td>
<td>Pump was off during charge. Copper buildup observed at pump control circuit wire connections</td>
</tr>
<tr>
<td>7-cycle reconditioning control cell</td>
<td></td>
<td></td>
</tr>
<tr>
<td>g</td>
<td>537</td>
<td>Charge cycle paused for 2 days due to unobserved (weekend) equipment error</td>
</tr>
<tr>
<td>h</td>
<td>642</td>
<td>Equipment anomaly on charge; no observed failure</td>
</tr>
<tr>
<td>12-cycle reconditioning test cell</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bb</td>
<td>58</td>
<td>Equipment failure: discharge capacity data carried over from previous cycle resulting in &gt;100% efficiency</td>
</tr>
<tr>
<td>i</td>
<td>71-117</td>
<td>Interference from shared power supply effected pump control circuit, turning pump off during charge sporadically, keeping pump on during discharge; frequent test pauses mid-cycle. Switched cell to Arbin at cycle 118.</td>
</tr>
<tr>
<td>j</td>
<td>427</td>
<td>No zinc deposition remained from charge cycle (visually observed ‘clean’ anode sheets) immediately upon discharge; e’lyte very dark, most likely due to particulate zinc not adhering to anode current collector</td>
</tr>
<tr>
<td>k</td>
<td>514-560</td>
<td>Observed slow e’lyte leakage, black discoloration; inconsistent pump operation.</td>
</tr>
<tr>
<td>l</td>
<td>674-676</td>
<td>Observed excessive gas production during charge at cycle 674-676; poor zinc adhesion for multiple cycles</td>
</tr>
<tr>
<td>m</td>
<td>767</td>
<td>Excessive gas production during charge coupled with high charge potential (&gt;2.05V)</td>
</tr>
<tr>
<td>12-cycle reconditioning test cell</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cc</td>
<td>528-529</td>
<td>Extended recovery after reconditioning; cell self-recovered.</td>
</tr>
<tr>
<td>dd</td>
<td>719</td>
<td>Arbin Equipment malfunction, test manually jumped to discharge after 0.89Ah of charge</td>
</tr>
<tr>
<td>20-cycle reconditioning test cell</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n</td>
<td>55</td>
<td>Voltage spike on charge triggered safety stoppage; cell remained in OCV mid-charge for 3 days</td>
</tr>
<tr>
<td>o</td>
<td>164-255</td>
<td>Cell experienced slow partial e’lyte drain during discharge cycles due to sporadic check-valve failure; zn accumulated during successive charge cycles resulting in &gt;100% discharge on following cycles until valve failure was corrected</td>
</tr>
<tr>
<td>p</td>
<td>288-291</td>
<td>Excessive gas production during charge coupled with high charge potential (&gt;2.10V)</td>
</tr>
<tr>
<td>q</td>
<td>459,466-467</td>
<td>Voltage dropped to 0.56V immediately into discharge (459); possible internal short; cell voltage dropped rapidly during discharge cycles 466-467 meeting end-test criteria.</td>
</tr>
<tr>
<td>30-cycle test cell</td>
<td></td>
<td></td>
</tr>
<tr>
<td>r</td>
<td>248-259</td>
<td>Cycles 248-252: pump control circuit failure; charge voltage &gt;2.05V; OCV for 3 days for recalibration (cycle 254), pump remained on during discharge yielding high efficiency; pump recalibrated and cell self-corrected after next reconditioning cycle (260)</td>
</tr>
<tr>
<td>s</td>
<td>614-650</td>
<td>Pump control circuit failed, continuous e’lyte flow during charge and discharge</td>
</tr>
<tr>
<td>t</td>
<td>653-680</td>
<td>Recalibration period for pump control circuit; pump control was erratic (flow stopped during charge or flow continued through discharge)</td>
</tr>
<tr>
<td>Cycle-averaged coulombic efficiency (12-cycle reconditioning)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>u</td>
<td>5-7</td>
<td>Corresponding to cycles 71-117</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Corresponding to cycles 330-340: poor discharge efficiency during entire set; cell self-corrected after reconditioning</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>v</td>
<td>25</td>
<td>Corresponding to cycles 514-560</td>
</tr>
<tr>
<td>w</td>
<td>43-45</td>
<td>Corresponding to cycle 767 gas production</td>
</tr>
<tr>
<td>x</td>
<td>60</td>
<td>Cycle-averaged coulombic efficiency (20-cycle reconditioning)</td>
</tr>
<tr>
<td>y</td>
<td></td>
<td>Corresponding to cycles 230-250, incorporating cell electrolyte drainage problems (valve failure)</td>
</tr>
<tr>
<td>z</td>
<td>21</td>
<td>Cycle-averaged coulombic efficiency (20-cycle reconditioning)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Corresponding to cycles 620-650; electrolyte flowed continuously during discharge</td>
</tr>
<tr>
<td>aa</td>
<td>27</td>
<td>20-cycle reconditioning control cell</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Test inadvertently and prematurely switched from charge directly to discharge after only 1.51Ah charge; residual Zn from previous cycle resulted in &gt;100% efficiency</td>
</tr>
</tbody>
</table>
REFERENCES

5. Linden at Table 31.1.
7. Shukla et al., *J. Power Sources*, 100 (2001) 146
8. Linden at Figure 22.3.
15. US Patent No. 4,552,821.
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21. US Patent No. 4,298,666