FINAL REPORT

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1. Project Objectives

The objectives of the project are to elucidate science issues intrinsic to high energy density electricity storage (battery) systems for smart-grid applications, research improvements in such systems to enable scale-up to grid-scale and demonstrate a large 200 kWh battery to facilitate transfer of the technology to industry.

2. Background

Complex and difficult to control interfacial phenomena are intrinsic to high energy density electrical energy storage systems, since they are typically operated far from equilibrium. One example of such phenomena is the formation of dendrites. Such dendrites occur on battery electrodes as they cycle, and can lead to internal short circuits, reducing cycle life. An improved understanding of the formation of dendrites and their control can improve the cycle life and safety of many energy storage systems, including rechargeable lithium and zinc batteries.

Another area where improved understanding is desirable is the application of ionic liquids as electrolytes in energy storage systems. An ionic liquid is typically thought of as a material that is fully ionized (consisting only of anions and cations) and is fluid at or near room temperature. Some features of ionic liquids include a generally high thermal stability (up to 450 °C), a high electrochemical window (up to 6 V) and relatively high intrinsic conductivities. Such features make them attractive as battery or capacitor electrolytes, and may enable batteries which are safer (due to the good thermal stability) and of much higher energy density (due to the higher voltage electrode materials which may be employed) than state of the art secondary (rechargeable) batteries. Of particular interest is the use of such liquids as electrolytes in metal air batteries, where energy densities on the order of 1-2,000 Wh / kg are possible; this is 5-10 times that of existing state of the art lithium battery technology.

The Energy Institute has been engaged in the development of flow-assisted nickel zinc battery technology. This technology has the promise of enabling low-cost (<\$250 / kWh) energy storage, while overcoming the historical poor cycle-life drawback. To date, the results have been promising, with a cycle life of 1,500 cycles demonstrated in small laboratory cells – an improvement of approximately 400%. Prior state of the art nickel zinc batteries have only demonstrated about 400 cycles to failure.

3. Accomplishments

Milestones	Accomplishments
Task 1.0 Project Management and Planning	
Subtask 1.1 Maintain Project Management Plan	
Subtask 1.2 Reporting and Briefings	10th progress report submitted
Task 2.0 Fundamental Science Related to Electrochemical Energy Storage	
Subtask 2.1 Fundamental studies of the formation of dendrites, in aqueous, organic, or ionic liquid electrolytes	completed 3/31/13
Subtask 2.2 Examination of the behavior of ionic liquids in the context of metal/air batteries	completed 12/31/12
Task 3.0 Research leading to enable battery technology scale-up	
Subtask 3.1 Investigate potential improvements to nickel zinc and other metal anode battery technology	completed 3/31/12
Subtask 3.2 Fundamental studies of flow on the performance of rechargeable nickel zinc cells	completed 3/31/13
Task 4.0 Demonstration of flow-assisted nickel zinc battery technology	
Subtask 4.1 Preparation of a preliminary design study of a battery for grid-scale applications sized at approximately 8MWh	completed 6/30/12
Subtask 4.2 Construction and test of a battery module, using the flow-assisted nickel-zinc battery approach	completed 3/31/13

4. Progress and Status

Executive Summary

A **30 kWh battery string** appropriate for grid scale applications such as peak shaving and load leveling was constructed and operated at **The CUNY Energy Institute**, which

is located at The City College of New York in Hamilton Heights, New York City. The location of the battery string is the cellar level of Steinman Hall at the corner of Convent Avenue and 140th Street, home of the Grove School of Engineering.

The string consists of 30 1 kWh nickel-zinc (Ni-Zn) flowing electrolyte battery cells. At this writing, the string is nearing 800 deep cycles and operating at ~95% coulombic efficiency.

This project involved overcoming many technical challenges that have traditionally limited Ni-Zn battery cycle

life. Chief among these is zinc dendrite formation, which we mitigate using the dual **innovations** of *electrolyte flow* and periodic *cleaning cycles* to strip nascent dendrites. We have used both experiment and mathematical modeling to study the fundamentals of dendrite formation and the effect of electrolyte flow on dendrites. This has led to a novel phase field model of electrodeposited dendrite growth and new understanding of the mechanism by which zinc atoms deposit during battery charging.

We developed Ni-Zn battery prototypes at several sizes: 6.5 Wh research batteries, 35 Wh small scale “workhorse” batteries, and 1 kWh “monstero” batteries. The 1 kWh size cells were used for string construction, along with the **innovations** of *propeller electrolyte drive* and a novel *bottom-of-charge-balancing battery management system* (BMS), developed at CUNY. The project has been a success, and the battery string operates with excellent efficiency. A modular battery design such as this could be scale to arbitrary size for business, building, or utility-scale applications.

Task 2.0 Fundamental Science Related to Electrochemical Energy Storage

Summary and background

NETL funded work at the CUNY Energy Institute has dealt with plated metal anodes for secondary battery systems. These systems are well suited for large scale electrical storage because of the high energy density of metals and the appealing design of an open, flowing electrolyte configuration. Electrodeposition of metals from dissolved salts in electrolyte has one major drawback, which is dendrite formation.

A dendrite is one possible morphology of an electrodeposited metal layer. Morphology of these metal layers is variable from metal to metal, but is universally a function of the metal growth rate (current density or reaction rate) and the velocity of the flowing electrolyte. Figure 1 below shows the variation of electrodeposited zinc morphology as a function of current density, with electrolyte velocity fixed at one value. The panels show equivalent amounts of zinc deposited on an electrode at the top of the panel.

In panel a of Figure 1 mossy, porous zinc is seen. An increased current density in panel b results in a compact metal layer, which has the characteristic shiny appearance of a crystalline metal. In panel c, dendrites have resulted from an even higher current density. In fact, a large dendrite to the left has crossed the electrolyte channel as will soon short the cell. This illustrates the challenge dendrites present, as a short circuit in a battery causes failure and in some cases thermal runaway and an uncontrolled condition. In panels d and e, further increased current density results in forked dendrites and sword-like dendrites.

Figure 1. Zinc morphologies grown in a flow channel with an electrolyte flow velocity of 0.3 cm/s. a: mossy zinc, b: compact zinc, c: dendrites, d: forked dendrites, e: sword-like dendrites. The electrode substrate is copper.

The zinc morphologies in panels c, d, and e of Figure 1 can be seen in batteries if locally high current densities are inadvertently caused. However, the morphologies in panels a and b are more typical. Mossy zinc is less dense than compact zinc, which means lower energy density. On the other hand, compact zinc is less reactive and more prone to passivation, which can lead to a battery only able to discharge at slow rates. CUNY EI batteries tend to operate in a regime producing mossy zinc.

When batteries based on mossy zinc are cycled, another type of dendrite can be provoked over time, which is a mossy dendrite. In Figure 2, a relatively flat mossy zinc layer (panel a) is shown as it is repeatedly charged and discharged. Incomplete

discharge over many cycles results in a positive feedback situation, in which high aspect ratio mossy dendrites are formed as in panel c. These dendrites will soon short the cell, as in the case of crystalline dendrites presented above.

Figure 2. The growth of mossy dendrites shown from a: 1st cycle, b: 5th cycle, c: 9th cycle. Current density is a 1C rate and flow velocity is 2 cm/s.

This section of the NETL project relates to the fundamental science needed for designing and operating metal anode batteries while eliminating the risk of battery shorting due to mossy dendrite structures as seen in Figure 2. These batteries will have to cycle many thousands of times without falling prey to this dangerous failure mechanism.

Figure 3 below shows a micro X-ray tomography of a typical mossy dendrite layer, which was collected early in the project to reveal general three dimensional characteristics of these structures. Table 1 highlights these properties, showing the structures can have a high closed porosity, which can result in blocking of the electrolyte flow and regions of the zinc that are inactivated. The obvious solution to this problem is to prevent the zinc layer from reaching this extremely dendritic state in the first place.

Figure 3. Three-dimensional reconstruction of zinc deposit using Micro X-ray Computed Tomography

In the Subtask 2.1 presented below, work at the CUNY EI has focused on the small-scale mesoscopic morphology of electrodeposited zinc. This is to understand the structures formed during the initial stages of zinc nucleation and growth, and how they lead to macro-scale dendrites that can result in battery failure. Results in this area revealed that more well-controlled zinc structures can be grown by changing the metal substrate on which they nucleate. This finding had implications on engineering and scale up in Task 4, where our nickel-coated current collectors were changed to tin-coated in late stages of the project.

Table 1. Computed characteristics of the mossy dendrite layer shown in Figure 3.

Degree of anisotropy	0.63-0.85
Fractal Dimension	2.22
Closed porosity	45-60%
Open porosity	2.5-13.5%

In Subtask 2.2 presented below, exploratory work was done on the use of non-aqueous, non-flammable ionic liquid electrolytes. This work showed an inexpensive, tri-valent metal, aluminum, can in principle be used in flowing electrolyte batteries. The results are promising, but the cycle life of these electrodes, which was hundreds of cycles rather than thousands, was not yet resilient enough for scale-up into tasks 3 and 4. The reason for lower cycle life was due to formation of a “black deposit” layer, and we established the phenomena leading to this formation using aluminum NMR techniques.

Subtask 2.1 Fundamental studies of the formation of dendrites, in aqueous, organic, or ionic liquid electrolytes

In this Subtask, we discovered several things about the fundamentals of zinc electrodeposition for battery applications.

- Transmission electron microscopy allowed us to observe the nucleation conditions that lead to the porous network of mossy zinc.
- Electron diffraction on just-nucleated zinc crystals allowed us to postulate an updated mechanism for the fundamental steps of zinc electrodeposition from an alkaline electrolyte.

This mechanism precluded the previous mechanism speculated in the literature.

- We used cyclic voltammetry of zinc electrodeposition on several metal substrates to observe that tin substrates lead to superior cycling compared to nickel ones.

This cyclic voltammetry work had direct implications in Task 4, as future versions of our scaled up battery are being produced with tin coated current collectors.

Effect of Current density on the mesoscopic morphology of zinc deposits

The operating condition of current and mass transfer have a strong effect on the deposition morphology, and hence performance. It is desirable to have zinc deposition to be compact, so as to prevent zinc redistribution, and dendrite growth. The dependence on morphology can be characterized by the ratio of the applied current to the mass transfer limiting current (i_L), or the current-density ratio (i/i_L). At low values of i/i_L , the deposition is kinetically controlled and growth is in the form of filamentous mossy zinc, shown in Figure 4 panel a. In the range of $0.3 < i/i_L < 1$, compact zinc is formed by the stacking of hexagonal zinc crystallites (panel b). At current densities in excess of the limiting current, mass transfer limiting dendrites are observed with secondary and tertiary side branching (panel c).

Figure 4. Zinc deposition morphology is (a) mossy at 13 mA/cm^2 , (b) compact at 80 mA/cm^2 and dendritic at 120 mA/cm^2 .

The effect of applied current on the deposition morphologies was investigated in a rotating cylinder Hull (RCH) cell. The primary current distribution varied across the length of a cylindrical Hull cell electrode, which means that the effect of current density could be analyzed parametrically in a single experiment. An Autolab HT cylindrical Hull cell (Autolab) was used to investigate the dependence of morphology on current density. The working electrode was a cylindrical brass rod 0.6 cm diameter, and 8 cm long. The zincate concentration in the electrolyte was varied from 0.49 M to 1.24 M and the rotational speed was varied in a manner such that the current density ratio changed in a prescribed manner across all the experiments. The surface morphology varied from mossy (dull grey), compact (bright gray) to dendritic (dark grey). The compact area fraction was computed using ImageJ, the results of which are shown in Figure 5. It is clear that a transition occurs from mossy to compact zinc at a current density ratio of $i/i_L = 0.3$. Further another transition occurs at the limiting current density ($i/i_L = 1$) due to rapid hydrogen evolution, causing dendritic zinc to be deposited.

The reason for the compact deposition is related to the charge transfer resistance (R_{ct}) associated with zinc deposition, and EIS experiments were performed to determine the dependence of R_{ct} on the overpotential, and hence current density. This part of the project showed the charge transfer resistance has a minimum at intermediate current density, typically between 0.4 - 0.5 i/i_L . We ascribe the formation of mossy zinc to the minimum in the charge transfer resistance, and it is important to have the zinc anode operating in this regime for optimal performance.

Figure 5. Effect of current density on compact area fraction for different zincate concentrations. The area fraction is highest in the region ($0.2 < i/i_L < 1$).

Transmission Electron Microscopy (TEM) to investigate early stages of zinc nucleation

Potentiostatic deposition experiments were performed to investigate the early stages of zinc nucleation and growth, providing us insight into how to create desired dense Zn deposit on plating in our batteries. Zn was electrodeposited on a 3 mm carbon-coated copper TEM grid. The grid was held in a pair of tweezers and lowered into a solution of 0.74 M ZnO dissolved in 45% KOH (electrolyte). The reference and counter electrodes were both zinc rods (99.9985% purity). Deposition time was varied from 200 ms to 16 s, and the nucleation potential varied from -50 mV to -150 mV (vs. Zn|KOH). This allowed the deposition to occur on an electron transparent substrate and the nucleation process could be imaged in a TEM. HRTEM images were obtained on a JEOL 2100F TEM operating at 200 kV.

Zinc was electrodeposited potentiostatically at a 50 mV overpotential ($\eta = -50$ mV) for 0.5 s, 0.8 s, 8 s and 16 s to investigate the evolution of zinc aggregates (Figure 6 panels a-d). A characteristic timescale for the process is the time corresponding to the peak nucleation current (t_m). At early times ($t < t_m$), first order aggregates about 50 nm in diameter were observed. Multiple such aggregates were deposited throughout the zinc surface. As $t \rightarrow t_m$ first order aggregates began to coalesce to initiate the formation of a networked structure. This is indicative of the fact that first order aggregates are the preferred sites of subsequent zinc nucleation. At later times ($t \gg t_m$), zinc deposited in the form of a highly branched three-dimensional network that covered the entire grid. This explains the process by which mossy zinc might be formed. Single crystal electrodeposits were investigated by potentiostatic deposition at $\eta = -150$ mV. A peak current was not observed, indicating instantaneous nucleation followed by diffusion-limited growth. The initial growth is isotropic, but the anisotropic surface energy of zinc forces larger crystals to form hexagonal crystallites up to 800 nm in size. Further growth leads to the formation of grain boundaries. A lighter 10 nm peripheral layer is observed surrounding the crystal, which was determined to be zinc oxide.

Figure 6. (panels a-d) TEM images of nanoclusters formed at $\eta = -50$ mV after (a) 0.5 s (b) 0.8 s (c) 8 s (d) 16 s. Adatoms grow on existing clusters, which coalesce to form a 3-D structure. (panels e-h) Single crystals are formed at $\eta = -150$ mV after (e) 0.2 s, (f) 0.5 s, (g) 1 s, (h) 4 s.

Selected area electron diffraction (SAD) of a hexagonal zinc nanocluster as in Figure 6 panel h is shown in Figure 7. Results show a speckled ring pattern indicative of a polycrystalline structure comprised with Zn and ZnO. The polycrystallinity occurs due to the twinning of $\langle 10\bar{4}0 \rangle$ Zn crystallites along 3 planes. The friable nature of mossy zinc is brought about by the polycrystalline structure. By comparison, the SAD of the hexagonal crystallite exactly matches (002) Zn. The thickness of the peripheral layer is 22 nm, and scatters light strongly. Lattice fringes from this region are about 2.80 Å apart, which matches (100) ZnO on (002) Zn. The phase boundary is quite well resolved as shown in Figure 8.

The presence of an oxide layer leads us to hypothesize a reaction pathway in which the zincate ion loses its hydroxide ions as it approaches the interface and precipitates as a $\text{Zn}(\text{OH})_2$ layer. The electron charge transfer reactions are at the $\text{Zn}|\text{ZnOH}$ and $\text{ZnOH}|\text{Zn}(\text{OH})_2$ interfaces which is a more feasible mechanism than reported earlier, where the charge-transfer reaction occurred in the Helmholtz plane [cf. the work of Bockris and Dirkse]. This has been represented in the reaction scheme below:

Figure 7. Mossy zinc is formed by the aggregation of zinc crystallites ~5 nm in size. SAD of a first order aggregate comprises polycrystalline zinc and zinc oxide. Lattice fringes show twinned crystals.

Figure 8. Anisotropic single crystal (0002) zinc is deposited at obtained at $\eta = -150$ mV, which has a single-crystal electron diffraction pattern. A 20 nm thick epitaxial (1010) ZnO layer is detected.

Effect of Substrate on zinc deposition:

Cyclic voltammograms were performed at 10 mV/s on disk electrodes of different substrate metals, shown in Figure 9. It is seen that nickel rapidly evolves hydrogen, and this is a potential cause for concern in batteries, especially during the first cycle. Uncontrolled gas evolution deteriorates cell performance by causing the anode and cathode to be imbalanced. An alloy phase is observed for deposition on copper and bismuth, evidenced by the anodic shoulder at ~ 1.1 V. This is attributed to the formation of a brass layer on Cu, and a Bi-Zn alloy on bismuth. By comparison, tin does not alloy with zinc. The dissolution current is highest on a tin substrate, followed by nickel, bismuth and copper.

Figure 9. Cyclic voltammograms at 10 mV/s on Ni, Cu, Bi and Sn respectively. Hydrogen evolved easily on Ni, and an alloy phase is detected on Cu and Bi.

The substrate metal has a strong effect on the performance of zinc anodes, especially at the earliest stages. Rotating disk electrodes were fabricated using 99.9%+ pure metal rods to investigate the performance of zinc deposition on silver, bismuth, copper, iron, nickel and tin substrates. Efficiency for a charging/discharging cycle on each is shown in Figure 10. The amount of charge passed in all the experiments was 5 C/cm^2 . Iron and nickel do not have desirable performance, due to hydrogen evolution. The hydrogen evolution on iron is rapid and soon covers the entire surface of the electrode. By comparison silver, bismuth and tin have desirable performance. The coulombic efficiency on each of these substrates is well in excess of 90% when deposited at -20 mA/cm^2 . Due to their relatively low cost, tin and bismuth are seen as promising choices of substrate metals in zinc anodes.

Figure 10. Coulombic efficiency of zinc deposition on different substrates for (a) single cycle, and (b) 50 cycles.

Subtask 2.2 Examination of the behavior of ionic liquids in the context of metal/air batteries

In this Subtask, we conducted research toward using aluminum as the cycled metal, to replace zinc which is used in all other Tasks. This would be beneficial as aluminum is a by far more abundant element than zinc, and aluminum is a trivalent rather than a divalent metal. For this reason it could in the future lead to even higher energy density batteries. However, aluminum is electrodeposited at a potential outside of the stability range of water. This necessitates the use of alternative electrolytes. In the past, work has been done using highly flammable organics as the electrolyte. Here, we study using room temperature ionic liquids, which are non-flammable and generally have a low vapor pressure, making them more desirable for use in batteries.

- We developed model aluminum-chlorine ionic liquid (ACIL) batteries to study cycling of the aluminum layer.

We found that optimizing the electrolyte composition could lead to approximately 100 cycles. However, further cycling was inhibited due to formation of a black deposit on the cycling metal. The further work in this Subtask aimed to identify the mechanism of formation for this black layer and to mitigate its formation.

- Using aluminum NMR we established formation of the black deposit is due to tetrahedral aluminum species with low symmetry such as Al_2Cl_7^- .
- From this knowledge we were able to improve aluminum cycleability >150% by employing a simple pre-treatment step.

This effort remains ripe for further development. However, because of far lower cycle life than our aqueous zinc electrodes, it was decided not to scale up aluminum anodes in Task 3 and Task 4.

Aluminum layer cycling in ionic liquids

Experiments to quantify anode performance were conducted using model aluminum-chlorine ionic liquid (ACIL) batteries. This was because the electrolyte could be used with a copper cathode current collector without modification as a chlorine electrode. Model ACIL batteries were constructed as test fixtures, with a reservoir of 0.5 mL size and two copper foil current collectors, as shown in Figure 11. The electrolyte for these cells consisted of the ionic liquid BMIM and aluminum chloride, AlCl_3 .

Figure 11. A model aluminum ionic liquid battery using for testing. Typical cycling results are shown as potential and current plots.

Room temperature chloroaluminate ionic liquids are known to vary in character depending on the relative mass fraction of its components. When AlCl_3 is in excess, the melt is acidic, and the principle aluminum species in equilibrium are Al_2Cl_7^- and AlCl_4^- . At 1:1 mass fraction of AlCl_3 :ionic liquid, the melt is neutral. In neutral and acidic electrolytes, aluminum was deposited on copper at the appropriate potential (~ 1.6 V). Formation of the aluminum metal anode film is indicated in Figure 11 by the circle. Stripping of the aluminum layer was observed on reversing the current, and repeated cycles were possible. This demonstrated the system was appropriate for use in storage batteries as an anode. In basic electrolytes (which have an excess of ionic liquid) aluminum deposition was not seen.

ACIL battery cycling was observed at acidic and neutral conditions, making these regimes suitable for secondary aluminum batteries. Optimum electrolyte composition for cycling was the neutral case. Results were collected by charging at 10 mA/cm^2 for 15 minutes, followed by discharge at 5 mA/cm^2 for 10 minutes. In 1:1 electrolyte, charging has a cell potential of 2.8 V, and discharge proceeds at ~ 1 V. Discharge capacities as a function of cycle number for ACIL batteries with electrolyte compositions of 2:1, 1.2:1, and 1:1 were determined. In acidic ACIL batteries, charging potential suggested CuCl_2 formation at the cathode. While acidic electrolytes resulted in a higher discharge capacity during initial cycles, device cycle life was poor. In the case of 2:1 electrolyte, no more than 10 cycles were achieved. In contrast, 1:1 electrolyte, while resulting in a lower discharge capacity initially, could be cycled in a stable fashion greater than 100 times.

With the ultimate goal being development of an aluminum-air battery, further work focused on understanding the cycle life limitation of the aluminum electrode. We believe that if aluminum can be successfully cycled, it can be combined with an oxygen cathode. The cycleability of the O_2/O_2^- couple has been examined in similar ionic liquids to BMIM (e.g. EMI, TMSI) although it has not yet been attempted in the exact system used in figure 11.

Extending aluminum layer cycle life beyond hundreds of cycles

Aluminum cycling was found to be hindered by formation of a deposition product over time. This layer was black in appearance. We wished to learn how to prevent or mitigate formation of the black layer.

To study the electrodeposited Al as the rechargeable electrode, galvanostatic cycling was carried out with a 3-electrode system. The Al electrodeposited from an acidic mixture of $AlCl_3$ and 1-ethyl-3-methyl imidazolium chloride (EMImCl) with composition 1.5:1 was deep cycled at 12 mA/cm^2 for 70 cycles of deposition and stripping with an energy efficiency of 84%. The charge storage capacity of the deposited Al was 2900 mAh/g (comparable to its theoretical charge storage capacity). Further cycling was limited due to the formation of a black deposit of uncertain structure but known composition. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDAX) were used to analyze the elemental composition of the black material as shown in Figure 12.

Figure 12. EDAX analysis of the black deposit after galvanostatic cycling

This black deposit consisted of Cl and Al. A small Cu peak was also seen which was due to the Cu current collector. To assess whether the black deposit was caused by

copper, a stainless steel working electrode was also used. The black deposition was observed which had a similar EDAX profile. Therefore, the formation of the black deposit was not dependant on the working electrode used. We hypothesize that due to the modified composition in the electrolyte solution over many cycles, the electrodeposited Al metal layer becomes oxidized. The oxidation product is the black layer.

For 70 cycles with 100% Depth of Discharge (DOD), pure Al was deposited and stripped during cycling. But after that the concentration of Cl in the deposit increased and rising voltage was observed during stripping. This indicated the deposited Al had reacted in the electrolyte solution possibly forming Al-Cl complexes as seen from the black appearance of the deposit and its elemental EDAX analysis. As the concentration of Cl in the deposit increased, composition of the electrolyte changed and the electrolyte solution was depleted of the electroactive species. Hence, the cycling of deposited Al failed after 70 cycles and deposition of pure Al was difficult due to depletion of Al_2Cl_7^- in the solution and the continuous build up of Al and Cl in the deposit which was not cycleable.

Direct evidence of changes in electrolyte composition upon cycling were obtained by ^{27}Al NMR. ^{27}Al is a highly sensitive nucleus that resonates over a wide chemical shift range with the shift ranges for 6, 5 and 4-coordinated Al being well separated. ^{27}Al is a quadrupolar nucleus with spin $I = 5/2$ and thus often gives broad lines. The ^{27}Al NMR spectra of various compositions of AlCl_3 and EMImCl were recorded and are shown as in Figure 13.

Figure 13. ^{27}Al NMR spectra (in ppm) of AlCl_3 :EMImCl at AlCl_3 mole ratios of (a) 1:1 (b) 1.33:1 (c) 1.5:1 (d) 2:1

The single and sharp resonance observed at around 103 ppm in the 1:1 composition of the electrolyte is consistent with the symmetric four-coordinated aluminum species, AlCl_4^- . The resonances take on additional width and intensity at lower chemical shift with increase of AlCl_3 composition, which is consistent with the presence of other tetrahedral aluminum species with lower symmetry such as Al_2Cl_7^- . Additional contributions to the linewidth arise from exchange between species on the NMR timescale. The presence of tetrahedral aluminum species, AlCl_4^- and Al_2Cl_7^- are also observed in electrolytes harvested from cycled cells.

Figure 14. ^{27}Al NMR spectra (in ppm) of 1.5:1 ($\text{AlCl}_3\text{:EMImCl}$) (a) 0 cycles (b) 20 cycles (c) 50 cycles

The 1.5:1 composition of the electrolyte was used to study galvanostatic cycling. The samples were collected after 20 and 50 cycles and the NMR spectra were recorded and that spectrum is as shown in Figure 14. Distinct changes in linewidth and lineshape occur upon cycling as shown for the cases of 20 cycles and 50 cycles. The cycled electrolytes reveal a resolved spectral component associated with AlCl_4^- . The enhanced broadening of the 50-cycle sample could arise from the aforementioned chemical exchange. Other factors such as changes in viscosity may contribute, but these results indicate unambiguously that the concentration of chloroaluminate species in the electrolyte changes as a function of cycling.

To improve the cycle life of the deposited Al electrode, pre-treatment of the deposited Al was done. In the pre-treatment process, the first 15 galvanostatic cycles have been carried out at 12 mA/cm^2 with 40% DOD and further cycles were carried with 100% DOD at same current density. This resulted into increased cycle life to 150 cycles

compared to 70 cycles previously as shown in Figure 15. For 180 cycles, the deposited Al electrode was cycled with 2900 mAh/g capacity.

Figure 15. Effect of pretreatment on the charge and discharge capacities of the deposited Al electrode. Green circle indicates the pretreatment stage.

Task 3.0 Research leading to enable battery technology scale-up

Summary and background

In Task 3 we developed various Ni-Zn batteries for small and medium scale testing, the most important of which was the 35 Wh Ni-Zn flowing electrolyte workhorse battery cell. Several workhorses are pictured in Figure 16. The deep discharge cleaning cycles which enable long cycle life were extensively explored using this size cell.

Figure 16. 35 Wh workhorse batteries with electrode packs removed.

Subtask 3.1 Investigate potential improvements to nickel zinc and other metal anode battery technology

In this Subtask, 6.5 Wh cells were used to benchmark the performance of flow-assisted Ni-Zn batteries. To achieve good cycle life, deep discharge cleaning cycles were developed to periodically eliminate mossy zinc dendrites.

Most importantly in this Subtask, we developed a platform to test conditions in flowing electrolyte Ni-Zn batteries:

- The 35 Wh “workhorse” cell for use with an external pump was developed.

- Cell parameters such as electrolyte composition, charging rate, flow channel design, and nature of the deep discharge cleaning cycles were explored using the workhorse platform.

Small-scale Ni-Zn cell development and deep discharge cleaning cycles

The initial CUNY Ni-Zn cell design was a parallel plate battery, in which a single anode and a single cathode were separated by a serpentine flow channel, defined by a 3 mm Teflon spacer. There was an external reservoir for electrolyte storage, and electrolyte flow through the cell was driven by an external pump. Capacity of these cells was 3.7 Ah (~6.5 Wh). A cell with the NiOOH cathode plate removed is shown in Figure 17.

Figure 17. A CUNY Ni-Zn 6.5 Wh cell with the NiOOH cathode removed, revealing the serpentine channel and deposited zinc.

Cells such as that shown in Figure 17 would display incomplete removal of the zinc layer upon discharge. On the subsequent charge cycle, deposition would begin from the resulting sinusoidal profile of remaining zinc. Due to positive feedback, mossy dendrites would build up to a high significant enough to cause cell shorting during charging. Depending on cycling parameters and electrolyte flow velocity, this would occur anywhere from the 5th to the 20th cycle. Capacity fade would occur due to this shorting.

Deep discharge cleaning cycles were introduced to order to eliminate this capacity fade. The batteries were subjected to a reconditioning procedure periodically. The reconditioning procedure consisted of a very slow discharge at a C/10 rate to a low cell voltage. Figure 18 shows the action of a deep discharge cleaning cycle performed in a

transparent cell. This cell was charged at a 1C rate, and had electrolyte flow velocity of 1.6 cm/s. After the 15th discharge, substantial mossy dendrites remained. The cell was deep discharged to 0.6 V. After the reconditioning cycle, the anode surface was renewed to a flat state. The electrodeposition of the 16th charge cycle proceeded as in the first cycle, beginning from a flat surface. This is as though the battery were “reset” to its original state.

Figure 18. A deep discharge cleaning cycle. a: Mossy dendrites remaining after the 15th discharge cycle. **b, c:** The cell is discharged at C/15 to a cell voltage of 0.6 V. **d:** After the deep discharge cleaning cycle, no zinc remains on the anode current collector. **e:** The 16th charge cycle results in a relatively flat zinc layer.

The CUNY 35 Wh workhorse research scale Ni-Zn battery

The CUNY 6.5 Wh cells were scaled up to a more practical size to assess battery performance in a form factor that could be used as a production-ready battery. This battery had multiple parallel electrodes, resulting an electrode pack. Flow between the parallel electrodes depended on equal distribution of the electrolyte from a common reservoir, which was completely enclosed within the cell containment. The cell was

closed to the atmosphere to discourage carbonate formation. The only external balance of plant to this cell was the electrolyte pump, which could consist of several designs interchangeably. The size of this cell was fixed at 35 Wh, and it is referred to generally as a “workhorse” cell.

Figure 19. The workhorse 35 Wh research scale Ni-Zn test battery developed at the CUNY EI. a: Electrode pack concept and rendering. b: Final design with electrode pack removed. c: Final design assembled.

In Q3 we first reported the 19 Ah, 35 Wh workhorse Ni-Zn research scale battery. This cell was developed for conducting cell optimization experiments, the first of which began using the workhorse platform in July 2011. The benefit of the workhorse design was that it could be constructed rapidly, but was large enough to involve all elements that would be important in a grid-scale cell: multiple anode and cathode plates in an electrode

pack, current distributions, electrolyte flow on long length scales, a significant electrolyte volume, heat dissipation, pump losses, significant gas generation, etc. The general design and form factor of the workhorse is shown in Figure 19.

35 Wh workhorse design iterations

Initial designs of the workhorse were refined for several months. The most significant refinement was assembly of the electrode pack. Three designs for electrode pack assembly are detailed below: drilled design, rod-channel design, and dogbone design. All designs had electrolyte flow driven by a high efficiency gear pump.

The first workhorse design had the electrode plates mounted on cylindrical acrylic bars, with rubber o-rings to space the electrodes and create the flow channels. This is the drilled design. This was labor-intensive, as all electrodes (cathodes and anode current collectors) had to be drilled to accommodate the acrylic bars. More critically, this cell failed after ~50 cycles due to warping of the electrodes and accumulation of precipitated zinc on the rods. This accumulation led to short-circuiting and cell failure.

The next design, the rod-channel design, had no holes drilled in the electrodes, but rather several plastic rods laying between each pair of electrodes. The plastic rods were oriented vertically so that no zinc precipitate could accumulate and cause short-circuiting. Warping of the electrodes was less dangerous because the electrodes had more room to grow and shrink without touching each other. This design was built at the 35 Wh scale in roughly fifteen separate experiments. This design was also built at the large-scale in 5 or 6 prototypes up to 1.6 kWh per cell, as mentioned in Task 4.

The rod-channel design was replaced by the final dogbone design in order to better mask inactive electrode area (those areas occluded by the channel spacers), to provide channels with a rectangular cross-section, and to restrict flow at the top of the flow channels. The desire to restrict flow was to make flow more uniform in the electrode pack. This was because the flow jets created by the pump resulted in uneven flow in the channels, and by restricting the top this uneven distribution would be smoothed. Thus the channel spacers were flat with a dogbone shape, giving the design its name.

35 Wh workhorse experimental findings

Many dozens of workhorse cells were assembled and tested to decide on basic battery parameters, such as charge and discharge rate, flow velocity, electrolyte composition, and deep discharge cleaning cycle protocol. The results were generally reported between Q3 and Q10 of this NETL funded work.

Cycle life, coulombic efficiency, and energy efficiency were used as metrics for evaluating cell performance. Many of the early cells encountered poor coulombic efficiency within the first 200 cycles. A Ni-Zn cell running without problems was defined as coulombic efficiency in the $95\% \pm 2\%$ range. Poor performing cells typically had coulombic efficiency going below 80% within the first 150 cycles.

We present here an abbreviated account of the workhorse experimental findings, with a series of electrolyte composition experiments as an illustrative example. Figure 20 panel a shows the coulombic and energy efficiency of a control workhorse cell, which had an electrolyte composition of 37% KOH and 60 g/L ZnO. Two experimental deviations are shown in panels b and c: 37% KOH and 40 g/L ZnO and 45% KOH and 40 g/L ZnO respectively.

This series of experiments showed that the base-case concentration of 37% KOH and 60 g/L zinc were optimal, achieving 2900 cycles before being decommissioned. Evaluated by coulombic efficiency, this cell shown in panel a began at $96\% \pm 1\%$, dipped to $93\% \pm 2\%$ around 600 cycles, recovered to 96%, and maintained $88\% \pm 3\%$ at 2000 cycles. In contrast, the battery in panel b fell to $87\% \pm 5\%$ with poor stability by cycle 300. However, this cell did attain ~1800 cycles before being decommissioned. The highly alkaline cell in panel c fell to $83\% \pm 5\%$ at 300 and faded to 65% by cycle 600. This cell was decommissioned early. This series of experiments led, through a decision-tree analysis, to maintaining the cell electrolyte composition at the base case. Similar multiple-cell experiments were used to screen electrolyte flow, flow channel restriction type, charge and discharge rates, pump types, etc.

In the experiments shown in Figure 20, regular deep discharge cleaning steps can be seen periodically, shown as efficiency briefly dropping to a value of 0 as the zinc was removed from the anode current collector as described in the section above. During the workhorse experiments, the nature of the electrode cleaning was modified in ways that carried over to the cell scale up in Subtask 4.2, discussed later. The experiments described next outline these changes.

Figure 20. Workhorse cell results evaluating electrolyte composition

Several clues led us to conclude that zinc short-circuiting caused the common reduction in coulombic efficiency observed in poor performing cells. Clues were:

- fluctuations in the voltage time series curves
- bubbling rates during rest periods increased by 2x to 5x, as observed by eye
- balls of zinc the size of marbles or large grapes forming along the underside of electrode stack
- bubbles emitted by the cathode during rest periods after deep discharging
- rectangular tubes of zinc that fall out of the channels after the cell is vibrated
- increased electrolyte temperature to 40 °C during periods of poor performance
- decrease of electrolyte temperature to 30 °C during periods of good performance
- much increased coulombic efficiency after zinc chunks were removed from the channels by vibrating or 24 hour rest periods.

It was decided most of this short-circuiting formed during deep discharging periods when the most zinc was shed from the anodes.

In response to these findings, the deep cleaning step was changed from a C/10 rate to C/40. A soft cleaning step was added to the end of every discharge period, to bring the voltage of the cell down to ~1.45 V at a C/40 hour rate. The coulombic efficiency of all cells responded overwhelmingly favorably and coulombic efficiency recovered to 95% in many cells and to 85% or better in all cells. In response to later findings, the protocol was made more cautious to avoid zinc clogs: 4 hour rest periods followed every discharge, 16 hour rest periods followed deep cleaning, and deep cleaning brought the cell voltage down to only 0.8 V. This is illustrated in an example detailed below.

Figure 21. Workhorse cell data showing capacity loss due to detached zinc particulate build up in the flow channels (highlighted by the red arrow).

Charge and discharge energy for a workhorse cell are shown in Figure 21. Cell efficiency was acceptable when new, but faded rapidly around cycle 120. This was due to the cleaning stage being too vigorous, which lead to channel clogging and short circuiting by detached zinc. After slowing the deep-cleaning phase and slowly raising the capacity back to the nominal value, the cell recovered to 90% coulombic efficiency by cycle 600 and ultimately ran for 1300 cycles.

Another innovation developed at this stage was a “recovery plate” mesh in the bottom of the cell, which served as a current collector to anodically dissolve detached zinc particles and return them to the electrolyte phase. This prevented zinc particulate buildup in the bottom of the cell, and therefore prevented the associated loss in capacity.

Subtask 3.2 Fundamental studies of flow on the performance of rechargeable nickel zinc cells

In this Subtask we explored specifically the effect of electrolyte velocity on Ni-Zn battery performance. As detailed above, the chief consequence of flow is on the morphology of electrodeposited zinc.

Figure 22. 6.5 Wh Ni-Zn battery performance as a function of charge rate and electrolyte velocity. X = Poor performance; O = Good performance

Performance of the 6.5 Wh cells detailed in Subtask 3.1 was characterized as a function of electrolyte velocity and charging rate, as shown in Figure 22. Dendrite formation is a function of these two parameters, making them critical for battery lifetime.

- As seen in Figure 22, high reaction (charging) rates lead to early battery failure. However, with increased electrolyte flow, higher rates are possible. This is due to battery shorting.

In the sections that follow, findings on the action of dendrites in flow are detailed.

- A novel phase-field model has been built to predict dendrite shape and growth rate in flow.
- Zinc morphology in flow has been analyzed for battery innovations such as reduced area current collectors. In all cases we find flowrate and current density still determine zinc morphology.

Novel mathematical modeling of electrodeposited dendritic structures

The growth of dendritic structures in flow involves several factors, as the growing metal interface exerts a force on the electrolyte. In turn, the interface is constantly in shear due to viscous forces. To understand their importance, modeling was performed. The

mathematical modeling of dendritic growth was carried out using a coupled approach of numerical methods:

- phase-field method (PFM) to track the growing electrode and
- lattice Boltzmann method (LBM) to compute the electric-field and flow-field.

During the electrodeposition phenomena, the electrode grows due to the surface reaction and subsequent deposition of the metal ions from the electrolyte. Hence, electrode configuration (dendritic or mushy or compact) is thus a function of time and tracked using a parameter (a phase-field variable) to distinguish between the two participating phases (electrode & electrolyte) with a diffuse interface. The concentration of the positively charged specie is evolved along with the phase-field variable. These governing equations are coupled and highly non-linear in nature.

A finite-difference scheme is used to discretize the governing equations. Ohm's law gives the potential in the solid and liquid phase with variable conductivity values and the governing equation is an elliptic PDE. The solution of the elliptic equation is challenging with the traditional finite-difference scheme and hence we have incorporated the lattice Boltzmann method. The method is advantageous over other methods due to the parallelizability so that large computational mesh points become feasible for an accurate solution.

Initial studies on the solidification of binary alloys have been carried out to understand the growth of primary and secondary branches when the driving force is under-cooling or super-saturation using PFM. Shown in Figure 23 (panels a-d) are the contour plots of the phase-field variable for the solidification simulations from an initial circular seed placed at the center of the periodic domain. From these models, we studied how the temperature/concentration, degree of anisotropy, and other parameters influence the pattern formation.

Figure 23. Contour plot for the phase-field variable. a: Instantaneous plot using Kobayashi [1] model for pure-melt solidification. b: Time-evolution using the

Karma-Rappel [2] model. c: Instantaneous plot using the Wheeler-Boettinger-McFadden [3,4] model for binary alloy solidification. d: Instantaneous plot using the Kim-Kim-Suzuki [5] model.

The advancement of solidification (or deposition) front exerts a displacement force on the solvent/electrolyte. This is modeled using an additional set of equations for the fluid flow and solved using LBM with a variable viscosity depending on the phases [6]. Our results in Figure 24 show that the solidification front computed using the Karma-Rappel model [2] grows into the flow-direction and this result is quantitatively agreed with the observation in the literature [7].

Figure 24. Time-evolution from the initial centrally placed seed using the Karma-Rappel [2] model with 4-fold symmetry. a: Solidification without flow of a pure melt. b: Solidification under the unidirectional flow along +x co-ordinate axis.

The coupled PFM-LBM code is first applied to understand the electro-deposition in one-dimensional domain. Figure 25 shows the variation of growth velocity with respect to applied voltage and for various values of initial solute concentration. It is seen that for a saturated system ($C_0 = 0.0183$) and with no applied voltage, deposition or dissolution does not occur. Next, a certain degree of under-saturation necessitates the use of external forcing via the imposed electric field (electro-migration flux).

Figure 25. Comparison of the computed growth velocity for different initial composition ratios; lines represent results from present approach (one-dimensional simulations); symbols represent earlier numerical data [8].

Further, we extended the one-dimensional domain to two-dimensions and imposed periodic boundary condition in the y-direction. We studied two initial configurations corresponding to the initial electrode placement as shown in Figure 26, namely, (a) flat-sheet, (b) circular or wire electrode. A certain degree of random noise is added to generate secondary branching. It is seen that the deposition proceed generating dendritic-like structures in both the configurations. The structures are denser in a direction lateral to the electric field.

Figure 26. Instantaneous contour plots of the phase-field variable for the electro-deposition process in two-dimensions. Simulation parameters: 700x350 nodes, applied voltage on right boundary, ratio of conductivity values for two-phases = 100.

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Zinc morphology on mesh substrates

We explored many possibilities to mitigate mossy dendrite formation in flow. One of these was reduced area electrodes for the anode, essentially consisting of a mesh with a pre-defined porosity. This results in higher current density initially, with current density decreasing as the pore fraction is reduced. We wanted this to encourage a compact zinc layer, followed by more mossy growth.

In the Q4 report, we reported that zinc morphology on flat substrates in potassium hydroxide solution is determined by the ratio between the applied current density and limiting current density (CD ratio, i/i_L). We also tested mesh-type anode current collectors as reduced-area current collectors. This enabled increasing the effective current density for the anodes while maintaining the same cathode area.

For these experiments the prismatic cell pack consisted of 2 positive and 1 negative plates alternately layered with a 3 mm gap. Zinc metal was deposited on a nickel-plated copper current collector. A nickel-coated expanded copper sheet was employed as the reduced-area current collector, which had 84% porosity.

Figure 27 shows zinc morphology mapped by the CD ratio and (a) the current density, (b) zincate concentration, and (c) flow velocity. The morphology was principally determined by the CD ratio regardless the current density, zincate concentration, flow velocity, and the substrates. When the CD ratio was less than 0.4, the morphology was mossy, becoming a mix of mossy and crystalline structures when $0.4 < \text{CD ratio} < 0.9$. Completely compact structure appeared only when the CD ratio was above 0.9.

Figure 27. Zinc morphology mapped by the CD ratio and (a) the current density, (b) zincate concentration, (c) flow velocity for deposition on an 84% mesh substrate. Blue circle: mossy; red triangle: mossy and crystalline; green square: crystalline.

Task 4.0 Demonstration of flow-assisted nickel zinc battery technology

Summary

A battery string was constructed and installed in the cellar level (room C11) of Steinman Hall at the corner of Convent Avenue and 140th Street on the campus of the City College of New York. Steinman Hall is the location of CCNY's Grove School of Engineering. In Q5 of the project it was decided this string would be approximately 30 kWh in capacity. This size was chosen as it is a reasonable module size for a larger grid-scale load-leveling system. The 30 kWh string is shown in Figure 28.

Figure 28. 30 kWh Ni-Zn flow-assisted battery string at the CUNY Energy Institute

This Ni-Zn battery string has achieved ~800 cycles with good efficiency and as of this writing is still in service. Build out of the string involved scale up of the workhorse cells developed in Subtask 3.1 and development of a novel battery management system (BSM). Details of the string development are discussed in the following sections.

Subtask 4.1 Preparation of a preliminary design study of a battery for grid-scale applications sized at approximately 8MWh

In this subtask we dealt with scale up issues from workhorse cells to cells appropriate for grid scale battery modules. This included:

- Racking and module concepts
- Development of a novel battery management system (BMS) specially designed for our flowing electrolyte Ni-Zn batteries.

String design and siting studies

The preliminary design study for a battery system for grid scale applications began with initial concepts for cell design and combination of cells into larger modules. The 35 Wh workhorse cell developed in Subtask 3.1 served as a starting point, and it was assumed individual cells would maintain their general character. A cell would have a potential defined by the Ni-Zn couple, approximately 1.8 V depending on current and state of charge. However, many variables are important for scale up, such as the length of electrolyte flow, the electrode 2D size, the nature of the pumps, etc.

Figure 29. Concept of 1 kWh cells combined into an 8 kWh module.

Figure 29 shows a concept rendering of 1 kWh cells, which retain the basic design of the workhorses, racked into an 8 kWh module. These concept cells are driven by external centrifugal pumps, which will occupy the open space on the racks. The cell containment for these cells are transparent acrylic tanks, with the cells only lightly sealed to allow service during research.

Further concepts stemming from Figure 29 were undertaken to envision the battery in a finished form as a production scale cell. Renderings of sealed, manufactured cells based on those in Figure 29 are shown in Figure 30. The cell is completely enclosed. The cutaway rendering shows the electrolyte flow drive tubing internal to the cell.

Figure 30. Production quality renderings of 1 kWh (560 Ah) cells based on the research models in Figure 29. Cutaway shows the flow tubing designed for even electrolyte distribution.

Figure 31 shows a production quality racking concept which holds the model cells in Figure 30. In panel a 24 kWh of storage is shown. Panel b shows a rendering of a 200 kWh module. Adding modules allows scale up to any size desired, easily attaining the 8 MWh scale.

Figure 31. a: 24 kWh concept, rack holding cells as in Figure 30. b: 200 kWh concept.

Ultimately the design concept in Figure 29 was altered for build out, as detailed in Subtask 4.2. This alteration was to use a different electrolyte flow method.

Battery management system (BMS) designs

Off the shelf BMS designs were not appropriate for the flowing electrolyte Ni-Zn cell. This is for many reasons, for example typical batteries are balanced by overcharging the entire string until all cells are at an equivalent state. In a battery with an electrodeposited metal anode, this is not possible. In the battery management system developed and described below, the cells are balanced at the bottom of their charge cycle, rather than the top. This BMS also has the capability to withdraw 15 W per cell. A wireless BMS module, which manages 4 cells, is shown in Figure 32 panel a. A later, ruggedized version of the BMS is shown in panel b.

The BMS accomplished two things for a battery string:

- Battery monitoring, by noting the voltage of every cell with 5 mV resolution. This data is compiled in real time, and therefore the string state is known in real time. From this voltage profile, information can be inferred, for example if a pump is down, a cell is clogged, there is abnormal performance.
- Battery balancing, by noting the real time difference in cell voltages and equalizing their capacities relative to each other. This is essential as the string will function at the level of the poorest cell in the string. This BMS has a passive balancing system: a load resistor is connected to every cell, and capacity is bled through this resistor at bottom of charge to equalize the cells within the 5 mV resolution. This is essentially a soft cleaning. This lessens the severity of the deep discharge cycles, which the BMS schedules approximately every ten cycles depending on string performance.

The BMS is designed to safeguard each battery during all its modes of operation and keep the string of cells balanced. Functions of the BMS include over current protection on charge and discharge. The BMS opens the circuit if the measured current is greater than a 1C rate. The BMS monitors individual cell voltage and stops charge or discharge in the event of over or under voltage conditions to prevent damage to the electrodes, polarity reversal, and excessive gas generation. Individual cell temperature is monitored to prevent thermal runaway. If the cell temperature begins to exceed 55 °C, the charge or discharge current is reduced. Battery operation ceases if the temperature exceeds 60 °C and will not resume until cell temperature has subsided below 50 °C.

Figure 32. a: Battery management system developed at the CUNY EI for monitoring and balancing flowing electrolyte Ni-Zn batteries. b: Later, ruggedized version of the BMS

A zinc recovery plate, as mentioned in Subtask 3.1, is integrated into every cell to dissolve precipitated zinc back into the electrolyte. The recovery plate is disconnected from the cathode by the BMS during charge in order to prevent deposition of zinc on its surface and uneven utilization of the cathode.

When cycling a series-connected battery string, the individual cells can become imbalanced. This results in cells having different states of charge and an overall lower available capacity in the string. The BMS has an integrated balancing system which equalizes the batteries during their discharge cycle. Cells with a higher state of charge are power bled off, maximizing the accessible power of the battery string. The balancing system serves in reconditioning the cells and removing zinc dendrites from the anodes.

The BMS is wireless, meaning there is no possibility of interference between BMS modules. This also makes distributed installation possible. There is a master station which controls the individual slave elements shown in Figure 32. These in turn each balance four cells. A scheme of the BMS system is shown in Figure 33.

has achieved nearly 800 cycles and is still cycling as of this writing. The good performance of this string demonstrates it could serve as a module in a large grid scale peak shaving or load leveling storage system.

Cell scale up and string construction and performance

A battery string was constructed and installed in the cellar level (room C11) of Steinman Hall at the corner of Convent Avenue and 140th Street on the campus of the City College of New York. Steinman Hall is the location of CCNY's Grove School of Engineering. In Q5 of the project it was decided this string would be approximately 30 kWh in capacity. This size was chosen as it is a reasonable module size for a larger grid-scale load-leveling system. This size is slightly larger than the size needed to power a typical American household for one day (~1 kW for 24 hours), providing a relatable mental benchmark and point of reference. The completed string is shown in Figure 28.

The engineering designs from Task 3 of this project needed to be scaled up to provide single cells for this string. A single cell has a voltage defined by the Ni-Zn couple, approximately 1.8 V. Capacity of the cell is defined by the total area of NiOOH cathode plates and the total volume of zincate-containing electrolyte. The workhorse design from Task 3.1 had a 20 Ah (~35 Wh) capacity with essentially square electrode plates (3.5 x 4 in). Workhorse flow was accomplished with high efficiency gear pumps. However, clogging of these gear pumps by solid zinc particulates was a major issue, which required re-engineering during scale up to string-level size.

Large-scale monstero cell design iterations

These issues were addressed during this scale up stage:

- Scaled up cell size (capacity)
- Length scale in the direction of electrolyte flow
- Nature of the electrolyte pumps
- Spacer and manufacturing issues
- Nature of the deep discharge cleaning stage (discussed in Subtask 4.1)

The first scale up results were reported in Q3 with a 480 Wh design, pictured in Figure 34 panel a. This cell was commissioned in May 2011, and was the first cell tested on the CUNY EI 1000A Arbin cycler. This cell achieved over 100 cycles with good efficiency, but >100 cycles the cell lost efficiency precipitously as detached zinc

particulates accumulated at the bottom of the cell. These particulates also represented lost zinc capacity.

Figure 34. Initial monstero scale up cells. a: 480 Wh cell, May 2011. b: Two 1.6 kWh cells, September 2011.

In Q4 we reported two 1.6 kWh cells commissioned and tested on the CUNY EI 5V/300A Arbin cycler. These cells are pictured in Figure 34 panel b. Detailed cycling data are reported in the Q5 report. Briefly, it was found that by 100 cycles detached zinc had collected in the bottoms of the cells to the extent necessary to plug the channels and cause cell shorting. The temporary fix decided upon was slowing cell discharge by 33% and slowing the deep discharge cleaning stage by 5x. However, this reduction in rate was untenable for real-world cells. The long term solution of this problem led to development of the recovery plate innovation. This innovation was developed at the workhorse cell level, and has been detailed in Subtask 3.1.

The cells in Figure 34 allowed us to explore fabrication and electrode racking options at the scaled up level. At this point we explored the option of different drive systems for the electrolyte flow. Previously, gear pumps were used for the workhorse cells (Subtask 3.1), and centrifugal pumps were used for initial monstero designs. Figure 35 panel a shows a 1 kWh monstero design rendering equipped for a 24 V centrifugal pump. The tubing can be seen, and there is a side flow box to dissipate turbulence. Panel b shows a design with propeller driven flow, from an external 3.5 V motor.

Figure 35. a: 1 kWh monstero design equipped for a 24 V centrifugal pump. b: 1 kWh monstero design with propeller driven flow and an external 3.5 V motor.

Prototypes based on the renderings in Figure 35 were produced and tested for screening prior to string construction. Monstero quartero was a 200 Wh design with an external centrifugal pump as in Figure 35 panel a. Monstero claro was a full 1 kWh cell with the propeller drive. Cycling data from the cells is shown in Figure 36. Both has good efficiency and capacity. It can be seen that the monstero claro cell was started at half capacity and slowly walked to the full 1 kWh.

As both cells in Figure 36 performed well, selection of the final cell design was based on practical issues stemming from the pumps. The 24 V pump motors generated far more heat than the propeller motors, and required voltage higher than that supplied by the batteries themselves to run, meaning a voltage step-up was required. Also the 24 V (36 W) centrifugal pumps used in the monstero quartero cell required priming, which added complexity. Additionally they required the electrolyte to exit the cell containment through tubing, which was seen as a possible safety problem. A large fraction of the energy expenditure of these pumps went to waste heat, which elevated the temperature of the electrolyte returning to the cells. For these reasons, the monstero claro cell switched to a propeller drive for the electrolyte. This required a lower parasitic energy loss for electrolyte convection (8 W vs. 36 W) and also solved another problem by not requiring the electrolyte to leave the cell containment. As the propeller drive motor was outside the cell and never contacted the electrolyte, this design did not cause heating of the electrolyte.

Figure 36. Monstero cell data. a: efficiency. b: energy.

30 kWh string

The monstero claro design lead to the final cell design used in the 30 kWh string. Figure 37 shows a final concept rendering of the string with this design. Half of the final string size (16 kWh shown) are shown in the rendering. Compare to the initial concept shown

in Figure 29, and the final string seen in Figure 28. Note the BMS and gas recombiners added.

Figure 37. Final 30 kWh string concept. 16 kWh shown.

Figure 38 shows current cycling data for the 30 kWh string. It was operated at half capacity then walked to 30 kWh after ~75 cycles. Coulombic efficiency has been ~95%, with energy efficiency generally >80%. The string will soon attain 800 cycles. Operation has been excellent, and this bodes well for further Ni-Zn battery module construction.

Figure 38. Energy and efficiency of the 30 kWh Ni-Zn battery string pictured in Figure 28. The string is still under operation as of this writing.

Further developments stemming from this task

Lessons learned from the NETL funder project and the 30 kWh string construction and operation have encouraged us to further alter the basic Ni-Zn cell design. Figure 39 shows the next generation 140 Ah (250 Wh) cell.

Figure 39. The 140 Ah prototype flow drive module

This cell has tin-coated current collectors, which is an innovation from Subtask 2.1. Flow drive is from a magnetically coupled propeller and funnel distributor in the bottom of the cell. The electrode pack isn't as long as the monstero designs, requiring less power to drive the flow.

Cell size has been decreased from 560 Ah to 140 Ah due to current limitations and power limitation on off the shelf inverters. Inverters rated for 50-200 kW are typically

limited to 300 A. This limits the rate cells can be charged at. As one advantage of the Ni-Zn chemistry is the ability to handle high rates, switching to smaller cell size allows us to take advantage of this. The form factor of this cell is standard, often used for lead-acid and Ni-Cd cells, making our Ni-Zn appropriate as a replacement with a small footprint. The electrolyte reserve of this cell is close to that of a workhorse. The monster cells had overbuilt electrolyte reserve, which we believe is unnecessary in the future.