Design and Performance of Large Format Nickel-Zinc Batteries

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Abstract

Nickel-Zinc batteries possess good characteristics in terms of energy density, cost and safety, but has typically suffered from poor cyclability, mainly due to the instability of the Zinc anode. ZAF Energy Systems has recently developed large format prismatic cells with capacities of 147Ah and 165Ah, respectively, that have energy densities between 70 Wh/kg to 90 Wh/kg. These cells have good cycle capability and recent testing also shows the versatility of the Nickel-Zinc system in terms of high rate discharges over a wide temperature range.

Keywords: Nickel-Zinc; batteries; rechargeable; large format.

Introduction

The energy and power density of the Nickel-Zinc (Ni-Zn) battery is very attractive to users looking for an alternative to Lead-Acid batteries. Its safety and relatively lower cost have also drawn the attention of those looking for an alternative to Lithium-Ion. Until recently, poor cycle life has limited the adaptation of Ni-Zn. The cycling issues have their roots in zinc migration and dendritic growth, causing cell shorting and loss in capacity. In addition, there has also been a tendency to have the cells dry out due to electrode gassing. In recent years there have been developments in the Ni-Zn community that have resolved these issues and shown that the cycle performance can match and even exceed those of Lead-Acid batteries[1,2,3]. The use of additives has been instrumental in this effort. Additives have been used both in the Zinc anode and the electrolyte and they have helped in stabilizing the zincate ions and reducing the migration of zinc. The additives also help to reduce hydrogen gassing, thus avoiding dry out conditions. This improvement in the electrolyte, combined with the use of a recombination coil, that recombines oxygen and hydrogen to form water and rehydrate the cell, allows for a sealed and maintenance free design with extensive cycle life. This paper will discuss some of these recent developments and show performance characteristics and cycle data collected as part of these efforts.

Historical Limitation and Mitigation Strategy

The main failure mode in Ni-Zn batteries is typically an accelerated capacity fade during long term cycling. This is usually related to the zinc in the negative electrode. Zinc is unstable in a potassium hydroxide solution and becomes a soluble ion that tends to migrate to the positive electrode on discharge and plate back on the negative electrode on charge. It typically does so unevenly, creating so-called shape change in the electrode structure, leading to uneven current density and even isolated regions of zinc that causes an unrecoverable capacity loss. In addition, the zinc solubility process tends to drive dendritic growth that will create shorts and, subsequently, capacity loss during cycling. ZAF Energy Systems utilizes several mitigation strategies to contain the zinc to the negative electrode. One is the use of additives in the anode that works to control the distribution of the nucleation sites and distribute the zinc evenly, thus limiting the potential growth sites for dendrites. Other additives are included in the electrolyte and works to stabilize the zinc, lowering the propensity of the zinc to migrate away from the anode. These additives also lower the molarity of the electrolyte. Lower molarity is better in terms of stability; however, this must be balanced with other performance requirements.

The separator design is also critical in inhibiting the migration of zinc and the dendritic growth. The tortuosity and the pore size of the separator are key factors in the design tradeoff between performance and zinc containment. Typically, there is a multicomponent separator system that works both as a zinc barrier and an electrolyte reservoir.

Another typical failure mode often seen in Ni-Zn cells is cell dry-out due to electrode gassing. During overcharge and severe over-discharge, the electrolyte will gas on the electrodes. Repeated occurrences will dehydrate the cell, increase impedance, and cause loss of performance. ZAF has approached this issue with additives to the anode material, minimizing the gassing, as well as the use of a recombination coil, which recombines the oxygen and hydrogen to form water that goes back into the electrolyte. This allows for a sealed and maintenance free design.

Large Format Cells

In recent years ZAF Energy System has taken these developments from the small lab scale cell level and incorporated these improvements into large G31 format cells and batteries. A single G31 cell is 4.6 cm thick, with a height of 23.7 cm and a width of 17.1 cm. The cell can be seen in Figure 1. It has a nominal voltage of 1.7V and seven cells are connected in series to make up a 12V G31 battery. ZAF is currently building and testing two different Generation 1 versions in this geometric format. One is a 147Ah hybrid power cell, targeted mainly for the heavy truck market, with a design that balances both power and energy. With a weight of 3.42 kg per cell, it has a nominal energy density of about 73 Wh/kg at a C/3-rate. The other is a 165Ah energy cell, targeted mainly for deep cycle applications, with an energy density of 81 Wh/kg at a C/3-rate.

Figure 1: G31 format cell and battery. Each battery contains 7 cells.

Results and Discussion

ZAF has been able to scale the performance and the characteristics seen in small R&D pouch cells up to large format prismatic cells with capacities greater than 150Ah. These cells are now manufactured in a production environment and are undergoing extensive testing that shows the characteristics of what current Ni-Zn technology can do in a practical cell. Following is a brief overview of some of the key performance features of these Ni-Zn cells.

General Rate Characterization: A 147Ah hybrid power cell was discharged at various C-rates while at room temperature. The nominal rate for this cell is C/3, or 49A, with a nominal voltage of 1.7V. Typical cut-off voltage is about 1.25V, but when discharged at rates above 3C, the cut-off is typically lowered to 1.0V. Discharging below 1.0V is not recommended, mainly to optimize cycle life. However, there is generally no safety risk in doing so, although at very low voltages there is a chance for gassing. The various voltage curves can be seen in Figure 2. While this cell is not optimized for truly high rates, it still delivers about 90% of nameplate capacity at a 6C rate (882A). In a constant power mode, this cell can deliver 1200W for more than 5 minutes down to 1.0V.

Cycle Life: Cycle life has long been the Achilles heel of the Ni-Zn battery. Rooted in the developments in the early 2000s to stabilize the zinc in the electrolyte and thereby reducing its solubility[3], ZAF's recent R&D effort and technology transfer to a large format practical cell have demonstrated the cycle potential of the Ni-Zn system. Ongoing cycle testing shows cycle life performance that makes Ni-Zn viable for many applications in terms of life cycle cost.

Figure 3 shows the 10% depth-of-discharge (DOD) cycle performance data of a 100Ah prototype cell. It was first discharged to a 50% state-of-charge (SOC), then discharged 10 Ah and charged 10Ah at a 1C-rate repeatedly, only allowed to top charge after every 1000th cycle. No overcharge was allowed during the 10% charge segments. After about 8000 cycles a significant degradation in performance can be seen. After 8500 cycles the reduction in mass was measured to be only 1.07%, indicating insignificant loss of electrolyte during cycling and the ability of the cell design to control gassing and prevent dry out.

Figure 4 shows the cycle life performance of a 165Ah energy cell after about 100 cycles. This test is ongoing at a C/3 charge and discharge rate with a 100% DOD while at room temperature. The discharge capacity, shown in blue, indicate only a slight degradation of 2-3 Ah at this point and the discharge efficiency (Ah out/Ah in) has been above 0.98. This data underscores the ability of the Ni-Zn cell to handle deep cycles well, something that makes it a viable option in numerous Lead-Acid applications.

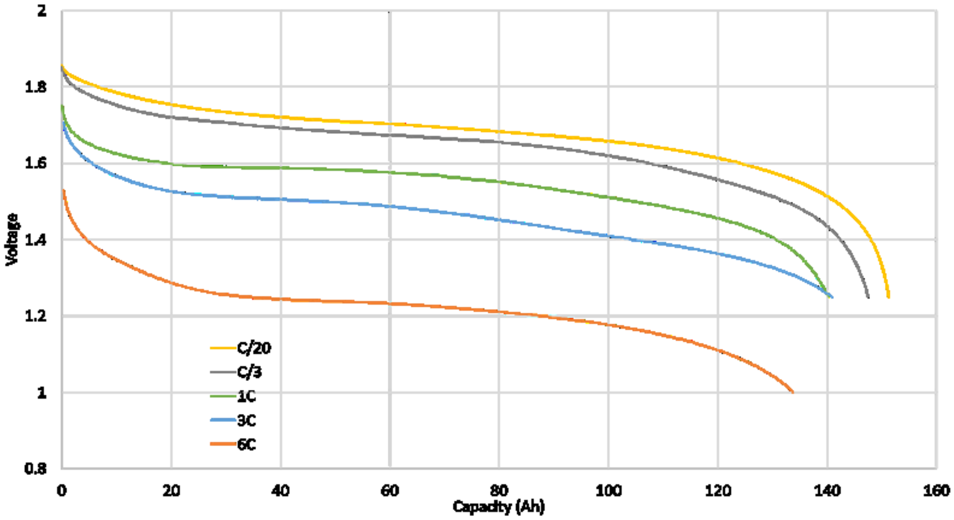

Figure 2: Voltage versus capacity at various discharge rates while at room temperature.

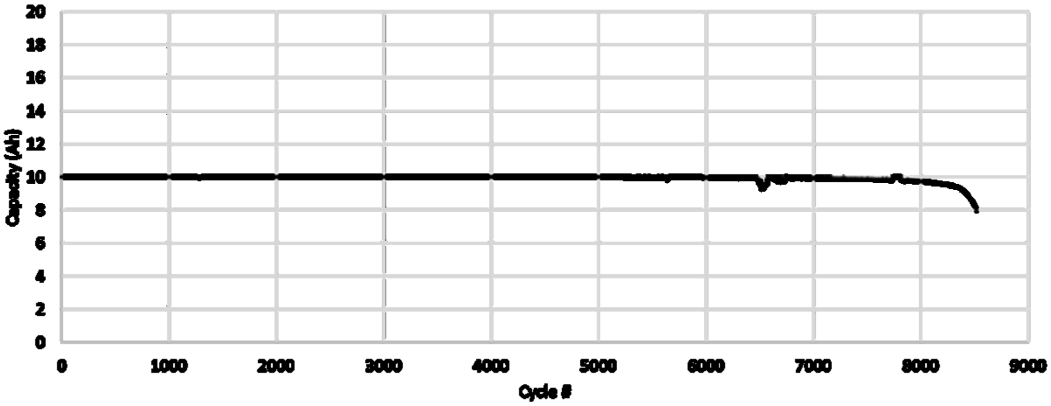

Figure 3:10% DOD cycle test performance at 1C charge and discharge rate.

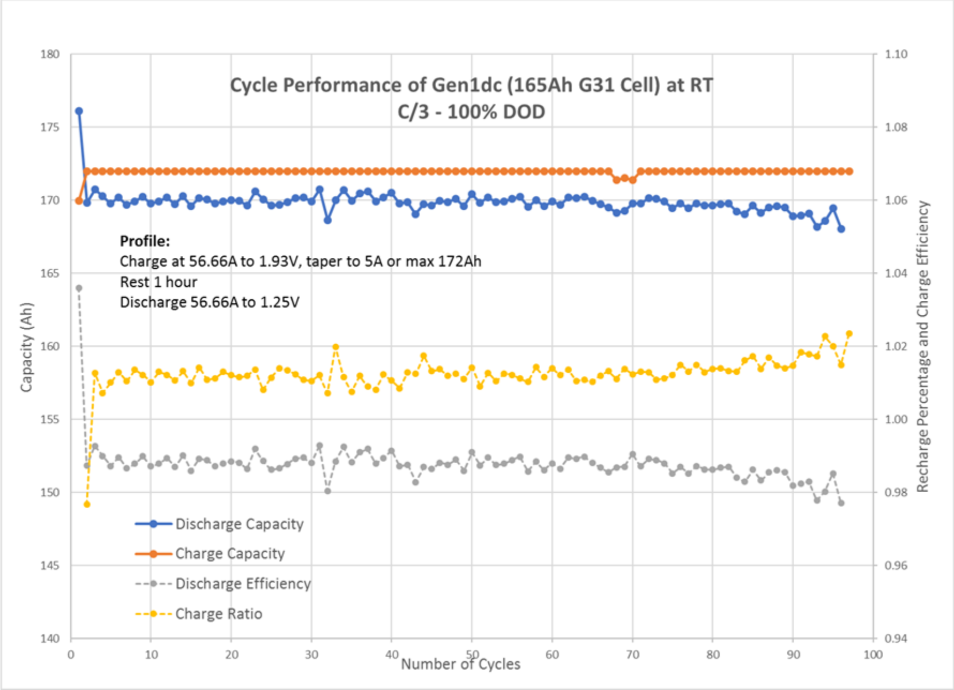

Figure 4: 100% DOD cycle test performance at C/3 charge and discharge rate.

Temperature Effect: The Ni-Zn cell has a wide operating temperature range from -30°C to 75°C. General characteristics at a nominal C/3 rate is shown in Figure 5. At -30°C the cell will deliver about 60% of nameplate capacity. At higher rates, like those considered in cold crank applications (CCA), the Ni-Zn system can deliver useful power for significant time. Figure 6 shows CCA data at -18°C, where it can deliver 900A for about 50 seconds. At -30°C, the cell can deliver 700A for more than 30 seconds, as seen in Figure 7. This is a very attractive capability in a cell package that nominally exceeds 70 Wh/kg. The cold soak was for 24 hours and no heaters or warm-up current were allowed before the 700A load was applied. The same cell can also operate at 75°C. Cells are currently undergoing the SAE J2801 cycle test, performed continuously at 75°C. This test is intended to test batteries to some of the harshest conditions under the hood of a car. After 12 weeks of cycling there is still not any significant degradation in the voltage profiles. It is noteworthy that the cell design being cycled at 75°C, is the same cell design that performed the CCA results in Figures 6 and 7. There has been no modifications to the electrolyte or other cell components, underscoring the versatility and the wide operating environment of this design. ZAF believes that similar CCA results can be achieved at -40°C with its forthcoming Generation 2 technology.

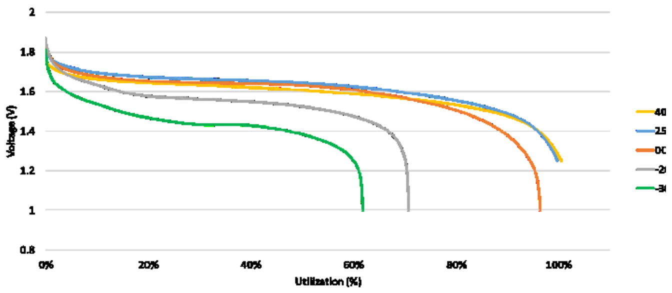

Figure 5: Capacity utilization as a function of temperature.

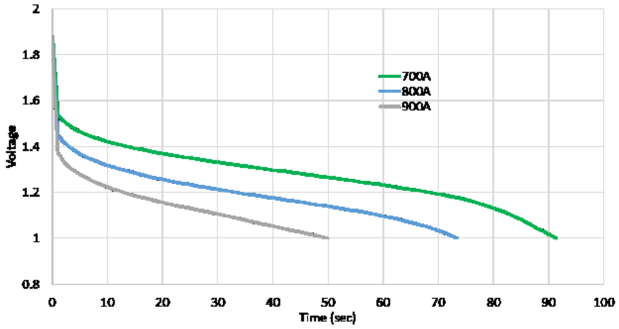

Figure 6: CCA data at -18°C

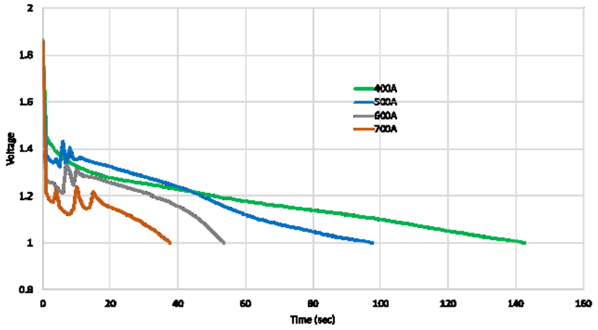

Figure 7: CCA data at -30°C

Charge acceptance: The constant current, constant voltage (CCCV) schedule is commonly used when charging nickel-zinc cells.. Figure 8 shows the charge profile at various C-rates for a G31 cell. If the current is 1C or less, the voltage is held at about 1.93V or lower. At higher charge rates, the voltage is allowed to increase during the constant current phase. During 2C and 3C charge the voltage is allowed to go to 2V. During the constant voltage portion the voltage is held at 1.93V or lower. While nominal charge rate for this specific cell design is C/3, the data shows that 80% SOC can be attained in less than 1.5 hours by charging at a 1C- or 2C-rate. The subsequent discharges give 100% of rated capacity at a C/3 rate. This charge acceptance rate separates Ni-Zn from typical Lead-Acid batteries and becomes very useful in industrial equipment applications, where it allows for faster turnaround time of equipment and maximized operating hours when using multiple shifts.

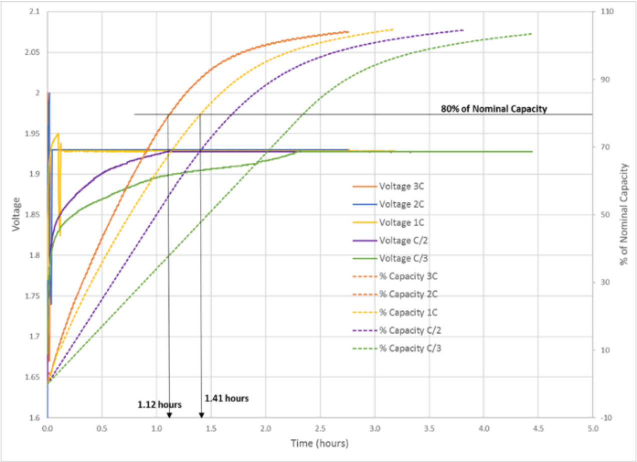

Figure 8: Charge profiles of a 147Ah G31 Ni-Zn cell at various C-rates.

Conclusion

Large format Ni-Zn cells have been built and tested, showing good cycle capability at 100% DOD and an operational temperature range from -30°C to 75°C. Particularly the CCA capability at -30°C indicates a versatile design, given a nominal density above 70Wh/kg. The ability to charge to 80% of nameplate capacity in less than 1.5 hours is also particularly attractive when turnaround time is critical. ZAF is currently in the process of building and testing their Generation 2 technology in the same cell format. Preliminary results show that 195Ah can be delivered at a nominal rate of C/3 in a G31 format cell. It is anticipated that these cells will have improved energy density, as well as better cycle life and rate capability.

References

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