

## An improved nickel/zinc battery for ventricular assist systems

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### Abstract

Nickel/zinc batteries are currently being manufactured under contract to the National Institutes of Health (NIH) for a left ventricular assist device (LVAD). The nickel/zinc system is being developed to replace the current lead–acid battery in this application. First generation prototype cells provide  $60 \text{ Wh kg}^{-1}$ , which is a weight saving of more than 35% compared to the lead–acid battery in current use. Further optimization of this design will result in a projected energy density of  $70 \text{ Wh kg}^{-1}$  by reducing the cell weight by 15%. Cell characterization and accelerated testing are underway to establish cell performance as a function of cycle life.

*Keywords:* Zinc/nickel oxide secondary batteries; Applications/medical

### 1. Introduction

An improved nickel/zinc battery has been developed for the left ventricular assist device (LVAD). The LVAD is a surgically implanted pump which assists the heart in circulating blood throughout the body. It is designed primarily for interim usage by patients awaiting heart transplantation, though in some cases patients have been fitted with the device for more than 1 year. The LVAD system is designed to allow patients to return home while waiting for a donor heart, improving patient quality of life and reducing medical costs compared to a long-term in-hospital stay. The LVAD device is battery powered to allow increased mobility to the patient. Persons fitted with the device are restricted by the operating time provided by the lead–acid external battery pack which presently powers the device. Two 12 V lead–acid batteries provide approximately 5 to 8 h of runtime and weigh 1.27 kg. The battery is carried by the LVAD patient and therefore weight is an important consideration.

The first generation nickel/zinc battery being developed for the LVAD consists of seven series-connected nickel/zinc cells for a nominal battery discharge voltage of 11.6 V d.c. Each prototype cell weighs 60 g and provides 2.2 Ah of energy storage. The total battery package weighs about 440 g to yield an overall specific energy of  $60 \text{ Wh kg}^{-1}$ . Further weight reductions, with a resulting increase in specific energy, are possible by optimizing the cell design in next generation cells. The overall battery dimensions are 24.4

mm  $\times$  23.4 mm  $\times$  61.0 mm. Energy density is  $73 \text{ Wh dm}^3$ . This advanced nickel/zinc battery incorporates advanced design features such as a composite plastic-bonded nickel electrode and a unique, patented, reduced solubility, zinc electrode. The battery delivers more than 600 deep discharge cycles. A commercial-type battery charger is also being developed specifically for this nickel/zinc battery. This battery is being developed under a 2-year grant from the National Institutes of Health. The nickel/zinc battery technology being developed has important implications for both medical and non-medical applications.

#### 1.1. Advantages of nickel/zinc batteries

The general advantages of nickel/zinc batteries are well documented. The nickel/zinc battery provides the lowest cost, highest energy density option for alkaline rechargeable systems. The nickel electrode being equal in all nickel-based systems, zinc provides the highest specific energy, the lowest material cost and the least environmental impact of any potential anode material. Cadmium is environmentally undesirable for a number of reasons including worker exposure and waste material generation during manufacturing, plant effluent, and spent battery disposal and reclamation. Metal hydride alloys, although less toxic than cadmium, still contain heavy metals and are relatively expensive, even in large commercial quantities.

The specific advantages of the nickel/zinc technology developed at Energy Research Corporation (ERC) include:

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- plastic-bonded composite electrode technology
- lowest manufacturing cost of any alkaline rechargeable system
- environmentally friendly manufacturing process
- manufacturing process scaleable for high volume production
- very low attrition/scrap rates in electrode manufacturing
- improved insoluble zinc electrode structure
- improved electrolyte formulation which extends cycle life
- sealed maintenance-free cell construction.

ERC nickel/zinc battery technology provides the best overall performance versus cost benefit of any rechargeable alkaline system.

The nickel/zinc battery system has been under development for many years. Fairly large quantities of cells were manufactured for the military in the past. Nickel/zinc batteries have a high output voltage and have very high power density for high rate applications. Zinc is nearly the ideal battery electrode material. It is completely non-toxic, has a very high energy density, a high half-cell voltage, is naturally abundant and very low in cost.

The major problem which stalled nickel/zinc development for many years is the relatively short cycle life obtained. This limitation was due to zinc dissolution and 'shape change' associated with the zinc electrode. This problem has been solved through a unique reduced solubility zinc electrode technology and sealed cell design patented by ERC in 1995 (US Patent 5 460 899). The development and application of this technology, in conjunction with other advances, has made nickel/zinc a commercially viable battery system.

## 2. Cell design

A sealed nickel/zinc cell design was developed for the LVAD application. The cell incorporates several unique design features, including the electrode components and certain aspects of the mechanical design.

### 2.1. Roll-bonded electrode technology

Energy Research Corporation has developed a unique, patented, manufacturing process for nickel and zinc electrodes [1–4]. The process, known as 'roll-bonding', produces an

electrode structure with 40–50% less metallic nickel than conventional sintered or pasted electrodes. This not only reduces the usage of metallic nickel, thereby reducing cost, but also yields a substantially higher energy density by increasing the ratio of active material to inactive material in the electrode.

In the manufacturing process, outlined in Fig. 1, the nickel-hydroxide active material is mixed with conductive graphite, additives, polytetrafluoroethylene (PTFE) binder, and solvent. The solvent is an environmentally benign mineral oil. The mixture is then extruded in a continuous sheet to produce the nickel electrode material. This extrusion process was developed by ERC. The electrode sheet material is then roll-calendered to achieve the finished thickness. The finished electrode sheet of active material is air dried to remove the solvent, which can be reclaimed. The extruded sheet is then laminated to a foil current collector to produce the finished electrode.

A critical aspect of the roll-bonded electrode design is achieving a fibrillated three-dimensional matrix within the finished electrode structure. This is achieved by working the PTFE through a combination of the extrusion process and the roll-calender finishing process. Also, laminating the electrode sheet to the current collector involves a pressing operation which further sets the nickel hydroxide/binder matrix. The fibrillated active material/PTFE structure fixes the nickel hydroxide in place within the electrode which minimizes active material loss or extrusion from the electrode during cycling. The unique fibrillated active material/PTFE matrix also has a porosity and pore structure which maximizes electrolyte access within the electrode. This provides a maximum electrode–electrolyte interfacial area which reduces electrode concentration polarization.

### 2.2. Reduced solubility zinc electrode

Zinc electrodes are fabricated by a similar roll-bonded process as that described above for the nickel electrode. The 'shape change' that occurs in the zinc electrode during charge/discharge cycling is due to the formation of the intermediate zincate ion. The zinc active material passes through this soluble phase during oxidation and reduction in alkaline solution. Mitigation of zincate ion formation would correspondingly decrease zinc dissolution and reduce shape

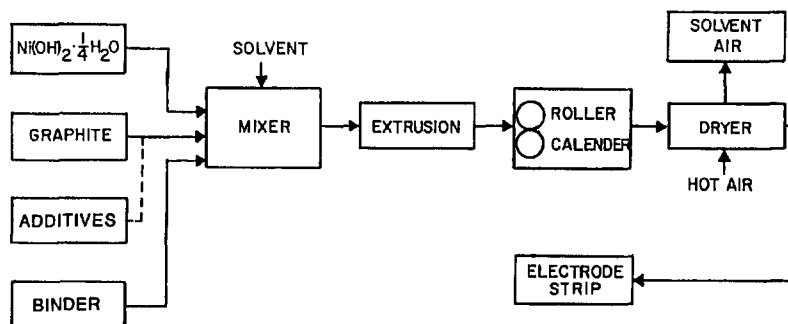


Fig. 1. Process diagram for the manufacture of plastic-bonded composite electrodes.

change. ERC has developed technology which reduces zincate formation through a combination of zinc electrode additives and electrolyte formulations and concentration (discussed in the paragraph below). This technology has recently been awarded a US Patent [5].

The technical approach to zinc electrode design is to reduce the formation of the soluble zincate intermediate reaction product by proceeding directly from the metallic oxidation state to an insoluble phase, such as  $\text{Zn}(\text{OH})_2$ .  $\text{Ca}(\text{OH})_2$  is used as an additive to the electrode in a substantial amount (15–40%) in order to promote the formation of calcium zincate. Calcium zincate is thermodynamically stable and remains substantially insoluble in the electrolyte. This effectively ties up the zinc, reducing zinc dissolution and subsequent migration into the separator. Zinc dissolution is mitigated by formation of a passivating layer of  $\text{ZnO}/\text{Zn}(\text{OH})_2$  at the electrode/electrolyte interface. A potential concern is electronic conduction through this passivating, insoluble film on the zinc electrode. This is addressed by doping the electrode with an electronically conductive metallic oxide species such as  $\text{PbO}$  or  $\text{Bi}_2\text{O}_3$  and by plating the current collector with metallic lead or bismuth.

### 2.3. Separator

The separator system in the nickel/zinc battery is relatively volume inefficient due to the requirements of having both an absorbent electrolyte reservoir and a zinc migration barrier. This is accomplished in current cell designs by using two layers of a non-woven nylon material, such as Pellon<sup>®</sup>, and several layers of a zinc migration barrier separator such as Celgard<sup>®</sup>. Celgard<sup>®</sup> is a hydrophobic polymer which must be treated with a wetting agent in order to wet in aqueous solution. The separation system used is a performance and life limiting component in the cell. Development work is continuing in evaluating alternative separator materials.

### 2.4. Improved electrolyte formulation and additives

Cells are activated with electrolyte consisting of an aqueous solution typically containing 20 wt% potassium hydroxide, with 1 wt% of lithium hydroxide added. This concentration of potassium hydroxide is used because of reduced zincate solubility in lower potassium hydroxide concentrations. A considerable amount of work has been done in studying the effect of various electrolyte additives for the nickel/zinc system. Research at ERC, and in conjunction with work done at Lawrence Berkeley National Laboratory and under a Cooperative Research and Development Agreement (CRADA), has shown that significant benefit can also be achieved with ternary electrolyte solutions based on the  $\text{KOH-KF-K}_2\text{CO}_3$  system [6].

### 2.5. Balanced cell design

One of the major limitations in the specific energy and energy density of the nickel/zinc cell is the requirement to

use excess zinc active material. Standard nickel/zinc cell designs use a zinc electrode active material to nickel electrode active material ratio of about three to one, calculated on an ampere-hour basis. This means that nearly three times as much zinc is used as that actually required to provide the energy storage capacity of the cell. This reduces the specific energy and energy density by a significant factor. Excess zinc is used to provide a buffer of uncharged zinc material to reduce hydrogen evolution at the end-of-charge and to compensate for the capacity degradation which occurs as the result of zinc solubility in the electrolyte. Hydrogen evolution management is an important issue in sealed cell designs. Development work is underway to reduce this excess zinc capacity which will substantially improve the specific energy of the system.

### 2.6. Mechanical cell design

The cell design developed for the LVAD application is a 2.2 Ah sealed nickel/zinc cell. A cut-away drawing of the cell is shown in Fig. 2. The cell case is moulded polysulfone and measures 24.4 mm × 23.4 mm and 61 mm in overall height. A lip is provided around the top edge to accept the cell cover and provide an optimum sealing arrangement. The cell case cover is also moulded polysulfone with two integral cell terminals moulded in place. The solder-type terminals are flush with the top of the cell to provide a low overall cell profile. A spring-loaded resealable vent is located in the cell case cover. The vent housing is also moulded integral to the cover and projects into the headspace of the cell. The vent is designed to operate at 270 kPascals. The cell case burst pressure is 760 kPascals minimum. This provides a worst case

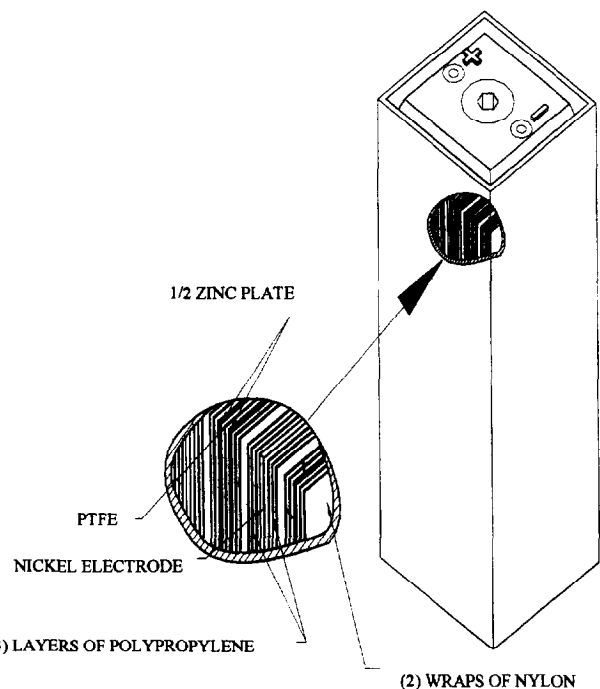


Fig. 2. A prototype 2.2 Ah nickel/zinc cell design for the left ventricular assist device showing the arrangement of the internal components.

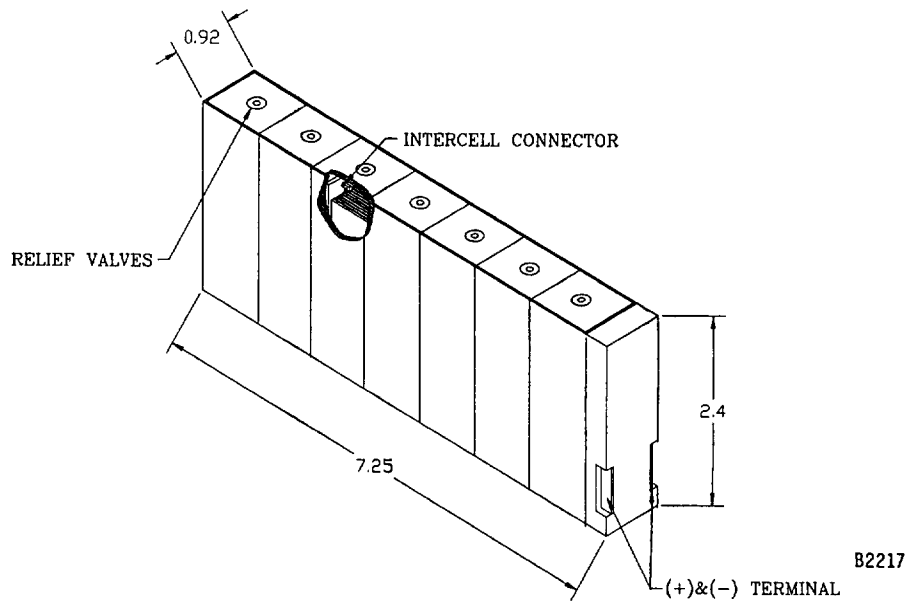


Fig. 3. 12 V nickel/zinc battery package for the left ventricular assist device.

safety factor of 2.5 to 1. The vent does not open under normal operating conditions (including moderate overcharge) and is provided only as a safety feature. The cover is bevelled, which allows a fillet of epoxy resin to provide a redundant seal around the full perimeter of the case/cover joint. An electrolyte fill port is provided which allows the introduction of electrolyte after the case/cover seal is made. This prevents contamination of the case/cover seal by the potassium hydroxide electrolyte. After electrolyte activation this opening is sealed with a polysulfone plug which is solvent-bonded and epoxied in place.

### 3. Battery design

The battery design consists of seven of the above described cells configured into a compact package as shown in Fig. 3. The cells are connected electrically in series. Nominal output voltage of the battery pack is 11.6. The LVAD device is designed to operate to a cut-off voltage of 10.5. The device draws an average current of approximately 0.7 A (about the 3 h rate). At this current drain the cell is able to deliver more than 90% of its rated capacity above the required voltage cut-off.

Two models of the LVAD device are manufactured by Thermo Cardiosystems, Inc., Woburn, MA [7]. One device uses two batteries connected electrically in series and the other is configured to operate either with two batteries or with four batteries to provide an extended operating time. In either case the nickel/zinc battery provides an equivalent run-time with substantially reduced weight (approximately 35% less than the lead-acid currently in use). The current nickel/zinc battery is designed to fit the same overall volume as the lead-

acid battery. Another approach would be to design a battery with the same weight as the lead-acid battery which would provide a 35% increase in operating time. This would substantially increase the benefit to the patient.

### 4. Test results

The NIH contract under which this work is being done is in progress. Initial testing on prototype cells is still underway. Cells are being characterized for discharge capacity, charge and discharge rate performance, charge retention, charge efficiency and cycle life.

#### 4.1. Electrical characterization

Fig. 4 shows a typical charge curve for a single cell at the 5 h rate (400 mA). Cell voltage is plotted as a function of

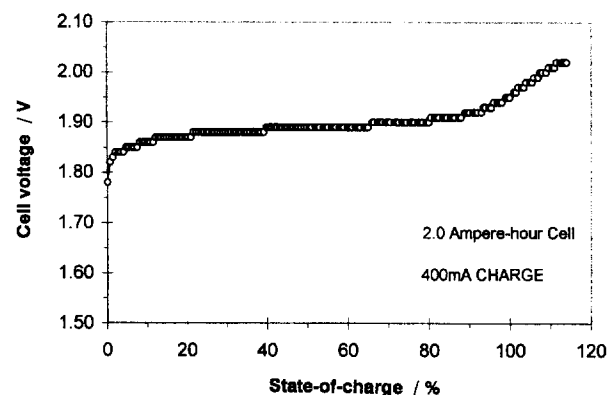


Fig. 4. Nickel/zinc cell voltage vs. state of charge (expressed as a percentage of cell discharge capacity) for a typical 5 h charge rate.

the cell state-of-charge (SOC), expressed as a percentage of the nominal capacity of this cell (2.1 Ah) at the 3 h discharge rate. The cell is operating at ambient room temperature with no active cooling. At this low rate the increase in cell temperature during charging is negligible, even at the end of charge. The mid-point voltage of the charge plateau is 1.89. This value increases only slightly to 1.93 V upon achieving 100% SOC. If the charge is terminated at this point, the cell will deliver 1.97 Ah upon subsequent discharge. This translates into an Ah charge efficiency of 94%. If charging is continued to a standard 10% overcharge, the cell will then deliver its nominal 2.1 Ah. This corresponds to a coulometric efficiency of 91%. Overcharging the cell clearly results in a point of diminishing return. Watt-hour efficiency is 82% at 100% SOC and 79% at 110% SOC, taking into account the difference in charge and discharge mid-point voltages.

Upon reaching 100% SOC, the nickel electrode is essentially fully charged and is evolving oxygen gas. This oxygen gas is consumed at the zinc electrode which prevents a significant rise in cell internal pressure. Also, the cell has a resealable safety vent which opens well below the burst pressure of the cell container. The transition to oxygen evolution results in a significant rise in the cell voltage as is apparent in Fig. 4. The oxygen evolution reaction results in a cell voltage plateau of 2.02 (at this current and temperature). This rapid rise in cell voltage at the end of charge (approximately 90 mV) provides for convenient charge termination detection.

#### 4.2. Discharge capacity and specific energy

Fig. 5 shows the cell voltage as a function of discharge capacity at three rates, ranging up to the 1 h rate (2.2 A). The cell will operate in the LVAD device at an average discharge current corresponding to the 0.33C rate (3 h discharge rate). Cell voltage and discharge capacity are unaffected by increased discharge current up to the 2 h rate. At the 1 h rate or higher, the cell impedance begins to show an effect in the discharge plateau voltage. This is normal operation for any battery and corresponds to an  $IR$  voltage drop according to Ohm's Law. The actual discharge capacity is

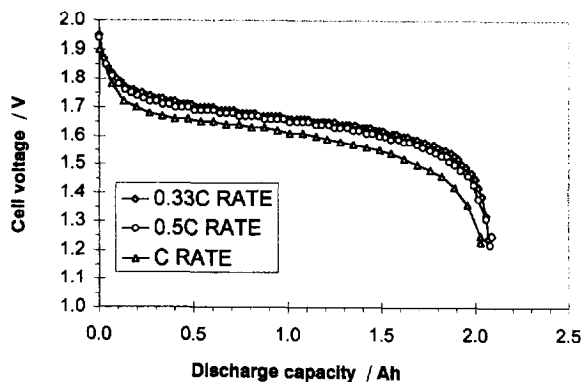


Fig. 5. Nickel/zinc cell voltage and discharge capacity as a function of discharge rate.

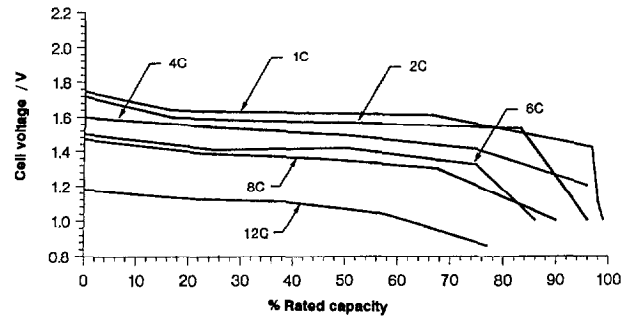


Fig. 6. Discharge rate capability for a 15 Ah nickel/zinc cell.

reduced by only 5% at the 1 h rate compared to lower discharge rates.

#### 4.3. Rate capability

Full discharge rate capability testing on the 2.2 Ah cell design is still underway. However, a large database exists for other nickel/zinc cell designs. Fig. 6 shows typical rate capability data for the nickel/zinc system. This testing was performed on a 15 Ah cell design. The NIH cell is essentially a scaled-down version of this cell although designed to operate at lower rates. A series of discharges was performed at rates from 1C up to 12C. The cell incorporates a lightweight plastic cell case and a resealable pressure vent. The cells were discharged up to the 12C rate (180 A) at ambient temperature with no active cooling. The cells perform extremely well up to the 8C rate and only start to significantly drop in voltage at the 12C rate. This data indicates the excellent pulse and high rate discharge capability of the nickel-zinc system. No cell venting was observed, even operating at these extremely high rates.

#### 4.4. Accelerated cycle life testing

Several 2.2 Ah cells are being cycle life tested under an accelerated regime at 28% depth-of-discharge, based on the cell nominal capacity at the 3 h rate. The cells are charged for 27.5 min at 1.30 A and then discharged for 17.5 min at 2.0 A. This corresponds to a charge/discharge Ah ratio of 1.03. The mid-point charge voltage is 1.93 V and the mid-point discharge voltage is 1.58. This corresponds to a Wh ratio of 1.25 (80% efficiency). The elapsed time per cycle is 45 min which results in a total of 32 cycles per day. This allows the rapid accumulation of cycles achieving an acceleration factor of 32 compared to one cycle per day in normal usage. Though in actual usage, 2 or 3 batteries are used alternately which effectively reduces the number of discharge cycles for each battery.

The typical discharge rate for the LVAD application is 0.60 A. The rapid discharge regime operates at 2.0 A which corresponds to a current density of 3.3 times the normal discharge rate. The battery would be normally discharged to 80–90% of its rated capacity in the device. The accelerated test is discharging to 28% of full capacity. Since the battery

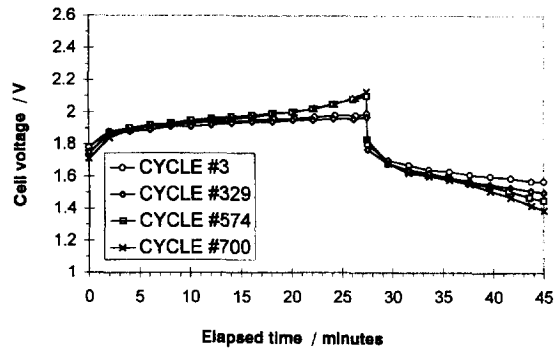


Fig. 7. Nickel/zinc cell voltage vs. elapsed time for an accelerated test regime comparing cell performance for an early cycle (no. 3) with later cycles (nos. 329, 574 and 700).

is operating at more than three times the current density and slightly less than one-third of the depth-of-discharge, these two factors essentially balance each other. The accelerated regime being used should nearly correspond to real-time usage at normal rates and depths-of-discharge, while allowing the rapid accumulation of data. As with any accelerated test, the results may not be completely linear but the information obtained is still useful.

Fig. 7 shows cell voltage versus elapsed time for an early cycle (no. 3) compared to later cycles (nos. 329, 574 and 700). Some degradation in discharge voltage is apparent resulting in a decrease in both the cell end-of-discharge voltage and the cell mid-point discharge voltage. The 700 cycles completed correspond to nearly 2 years of normal use. Extrapolation of this cell data to the battery level (seven series-connected cells) indicates that after 2 years the battery will still provide 75% of nominal capacity above the device cut-off voltage of 10.5. This is much better performance than that provided by the standard lead-acid battery. Part of the decrease in capacity with cycling is the result of decreased charge acceptance and increased cell impedance, which

makes achieving full charge difficult. Improved charging techniques will result in longer battery cycle life. Cell dry-out remains the ultimate long-term failure mechanism in the cell. Development of an improved separator will address this issue. The accelerated test data, based on initial prototype cells, predict a battery useful life of 2 years. This should be improved in next generation cell designs.

#### 4.5. Deep-discharge cycle life testing

Current nickel/zinc cell designs are capable of delivering more than 600 cycles at 80% depth-of-discharge. Fig. 8 shows the % rated capacity versus the number of cycles for a representative 15 Ah cell design. The cell was charged at the 0.25C rate and discharged at the 0.33C rate, amounting to 15% overcharge each cycle. The cell capacity to a 1.2 V cut-off was measured at 25 cycle intervals. This amounts to an additional 25 cycles at 100% DOD in addition to the standard 80% DOD cycles. The cell dropped to below 80% of its rated capacity after nearly 600 cycles. The primary failure mechanisms for this type of duty cycle are electrode swelling, and subsequent stack dry-out, and zinc dissolution. Although shape change and dendritic growth have been greatly diminished, changes in the zinc electrode with cycling cause a gradual degradation in discharge capacity. Also, cumulative charging (and overcharging) results in depletion of the reserve of uncharged zinc active material. This results in increased hydrogen evolution in the cell and correspondingly decreased charge efficiency.

## 5. Conclusions

The nickel/zinc battery system offers a number of advantages over competing systems including high performance, low cost and reduced environmental impact. First generation

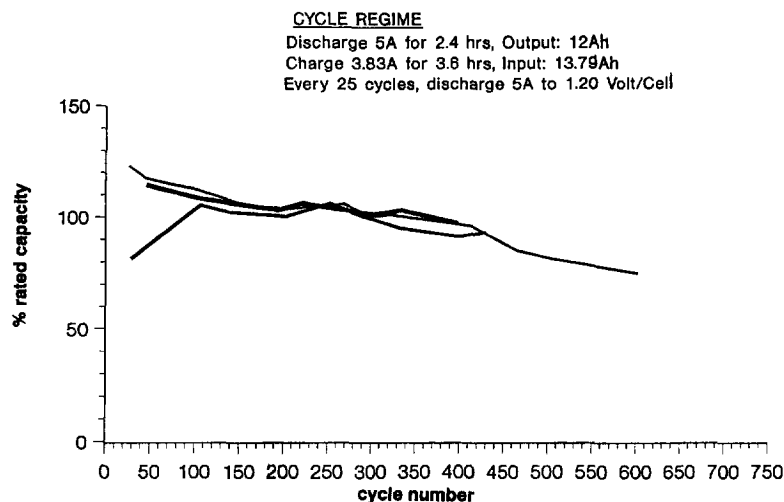


Fig. 8. Full-depth discharge capacity of a nickel/zinc cell as a function of cycle life when cycled at 80% depth-of-discharge.

prototype cells deliver  $60 \text{ Wh kg}^{-1}$ . This can be increased to  $70 \text{ Wh kg}^{-1}$  by further optimization of the cell design. Accelerated testing indicates that the cell will deliver more than 90% of initial rated capacity after 1 year of normal usage and approximately 75% of rated capacity after 2 years. The increased performance and reduced weight provided by the nickel/zinc battery is an important benefit for the LVAD patient. Another alternative is to provide significantly greater operating time for the equivalent weight of the lead–acid battery. Energy Research Corporation's unique manufacturing technology provides the potential for greatly reduced battery manufacturing costs. This provides an important economic benefit in a time of rapidly increasing medical costs.

### Acknowledgements

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