
PAST DEVELOPMENTS AND THE FUTURE OF NICKEL ELECTRODE CELL TECHNOLOGY

GERALD HALPERT

Jet Propulsion Laboratory, Pasadena, CA 91109 (U S A)

Introduction

The nickel hydroxide electrode has evolved over nearly 100 years from the pocket electrode structure through to the present design of a light weight, porous, plaque structure. Before discussing the historical aspects, it would be helpful to point out that there are basically two parts to the electrode: the active material and the current (electron) collector. Together they provide the essential properties for storing and converting the chemical energy into electrical energy and *vice versa*. The electrical energy is stored in the nickel hydroxide active material during charge, in which the electrode is oxidized. The chemical energy is converted back to electrical energy during discharge. The active material is itself initially non-conductive. Therefore it must be housed in a high conductivity metallic structure which serves as the current collector. This is, in turn, connected to another high conductivity metallic structure called the terminal.

History/background

According to Falk and Salkind [1], Desmazures [2], and Dun and Hasslacher [3] were the first (1887) to discuss the possible use of nickel oxide as a positive active material in alkaline cells. Jungner [4] and de Michalowski [5] described methods for preparing the compounds in the late 1890s. Jungner was joined in 1901 by Edison [6] in writing a series of patents related to electrochemical power sources and, in particular, to alkaline accumulators. The two became involved in several patent suits over the nickel-cadmium and nickel-iron cells.

The earliest nickel hydroxide electrodes were manufactured as pocket plates. The basic structure of these plates was flat, perforated conductive sheets containing indentations (pockets) into which the black nickel hydroxide powder was added. The active material powder, mixed with graphite for conductivity enhancement, was covered with a conductive, perforated metallic sheet. This structure with active material in the pockets was mounted in a nickel-plated steel frame which served as the current collector. With

time, the graphite presented a problem in that it oxidized and swelled, thus causing the pocket sheath to bulge. This was accompanied by the simultaneous loss of contact between the graphite and the steel pocket, resulting in a loss of capacity and polarization.

A further change came in 1908 when Edison replaced the pockets with a tubular construction. Several of the perforated steel tubes containing the active material were mounted in a steel frame which was connected to the terminal post. The ingenious change was a substitution of nickel flake for the graphite to improve conductivity. The process for producing the flake is described in ref. 1. The active material was added to each tube by placing alternate nickel hydroxide and nickel flake layers into the tube, then tamping (compacting) the powder with a solid rod after each layer was added.

The next advancement in technology was based on a 1928 patent by Pfleider *et al* [7] in which the process for producing sintered plate electrodes was described. Surprisingly, this process is much the same as that in use today, including the use of high purity nickel powder, produced by the carbonyl process, as the basis for the sintered nickel-plaque current collector. The carbonyl nickel powder is sintered in a reducing furnace at 900 °C over a nickel screen or perforated nickel-plated steel substrate to produce the high-porosity plaque. The substrate serves both as a support structure and central current collector. Tracy and Perks [8] described the variations in producing single plaques by loose sintering in a mold, typical of a batch process. A continuous plaque production process had been evaluated previously at Accumulator-Fabrik AG [9]. Later, the SAFT process [10] was licensed in the U.S.A. Referred to as the "slurry process", it involved placing a layer of nickel powder in a viscous binder (*e.g.*, carboxymethyl cellulose) on a continuous nickel-plated, thin, perforated steel sheet, burning off the binder, and sintering the plaque in a reducing atmosphere. The result was a continuous roll of 85% porous plaque material.

Porous plaques from the batch or continuous process are impregnated with the active material either by chemical deposition or galvanic precipitation from metal nitrate solution. The latter method was not applied commercially until the 1970s and became known as electrochemical impregnation. The Pfleider patent [7] also suggests the use of cobalt as an additive. Interestingly, the patent was aimed at the production of the iron electrode rather than the nickel electrode.

Although there is a record during the 1920s [11] of studies on sintered plate electrodes, it was not until the Second World War that the Germans produced sintered-plate electrodes for nickel-cadmium cells. The electrodes had high rate capability because of the larger active material surface area in contact with the electrolyte. In 1948 Fleischer [12] described in detail the process for producing and impregnating sintered-plate nickel hydroxide electrodes. Following the preparation of the porous plaque, the five step chemical deposition or impregnation process included

(1) submerging the plaque, and vacuum-filling the 85% porous structure with a nickel nitrate solution (acid pH),

(ii) placing the nitrate-filled plaque in NaOH, cathodically polarizing the plaque to form the $\text{Ni}(\text{OH})_2$,

(iii) washing;

(iv) drying,

(v) weighing.

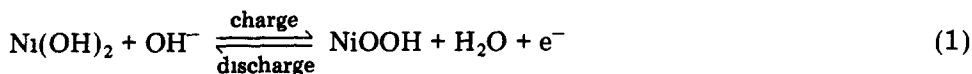
This process was repeated several times until the weight pickup of the active material provided the desired electrochemical capacity. The Fleischer method has been modified for commercialization of a continuous process by omitting the polarization step in the NaOH solution

A third method of impregnation adopted by Casey and co-workers [13, 14] utilized molten metal-nitrate solution produced by the thermal decomposition of the $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 85 - 125 °C in place of the aqueous $\text{Ni}(\text{NO}_3)_2$ solution. The plaques containing the melt are then roasted in air at 180 - 250 °C, producing what has been described as $\text{Ni}(\text{OH}) \cdot \text{NO}_3$. Conversion to the $\text{Ni}(\text{OH})_2$ occurs in 30% KOH solution

The latest methods of impregnation are referred to as the electrochemical impregnation or deposition methods. Hausler [15], initially, later Kandler [16] in more detail, recognized that nitrate, having a higher redox potential than nickel, was reduced in the pores of the plaques thus preventing metal deposition. The nitrate was reduced directly to the hydroxide thus depositing directly in the pore of the plaque. An extremely important adjunct is the existence of a pH gradient (higher inside the pores, lowest outside), thus providing deposition of the hydroxide from the inside of the plaque to its surface. McHenry [17] in 1967 was the first to utilize this method in the U.S.A. He also utilized LiOH in the active material. Takamura [18] identified the reaction and Beauchamp [19], recognizing the importance of controlling the pH, introduced sodium nitrate as a buffer to maintain the pH at 2. He also found greater loading at a higher impregnation temperature (>75 °C) which was due to improved efficiency of the deposition process. Others involved in the development included Seiger and Puglisi [20], and Pickett *et al.* [21], whose processes using alcohol to maintain pH are now utilized to produce nickel electrodes for nickel-hydrogen cells. The subject of electrochemical impregnation is thoroughly reviewed by Gross [22]

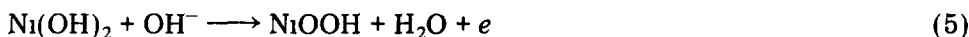
The reactions of the nickel hydroxide electrode

For many years the accepted oxidation/reduction reaction for the nickel hydroxide electrode was given by Glemser and Einerhand [23].



Complications were acknowledged by many, including Milner and Thomas who in their review [23a] suggested that.

(a) the oxidation state of nickel was not an integer value, *i.e.*, neither +2 in the discharged state, nor +3 in the charged state;



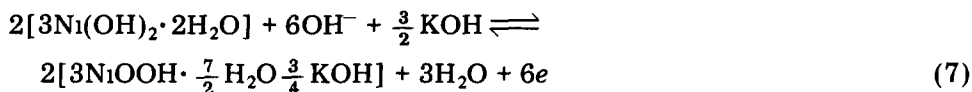
The first reaction (4) produces a peak, reflecting the conversion of Ni metal to the hydroxide. The active material in the cell is therefore increased, adding to the electrode capacity. This oxidation process is related to the corrosion of the nickel plaque substrate. Reaction (5) is the oxidation/reduction process occurring in the active material of the nickel hydroxide electrode. Reaction (6) occurs at significantly higher potentials where O_2 is evolved. The current resulting from these reactions masks the Ni^{3+} to Ni^{4+} reaction given by Lukovtsev and Slaiden [30] as having an efficiency of only 1 - 2%.

Briggs and Fleischmann [31] show that different oxidation processes take place simultaneously at the solid/liquid interface of $\text{Ni}(\text{OH})_2$. On discharge, NiOOH exists over a wide range of compositions which compete for reduction to the discharged species. It is suggested that electrochemical activity takes place at the interface between the conducting NiOOH and non-conducting $\text{Ni}(\text{OH})_2$.

An alternate concept, namely, of proton diffusion, has been discussed as a viable mechanism for the nickel hydroxide electrode by Lukovtsev and Slaiden [30]. They investigated the quantitative aspects of proton diffusion, and found that $\text{Ni}(\text{OH})_2$ is a good proton conductor but a poor electron conductor. Briggs and Fleischmann [31] also observed the reaction between $\alpha\text{-}3\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ and $\gamma\text{-NiOOH}$ and subsequent reduction. They reported that the discharge and recharge of full layers of NiOOH follows a composite pattern controlled by diffusion of a species through the layers. Salkind and Bruins [27] reported that $\text{Ni}(\text{OH})_2$ and $\beta\text{-NiOOH}$, during charge, form a solid solution.

Freshly prepared $\text{Ni}(\text{OH})_2$ electrodes are known to be both chemically and electrochemically more reactive than aged ones. Kober's [32] i.r. spectra showed that a sintered nickel oxide electrode on discharge has a hexagonal layered structure isomorphous with a D_{3d} structure. The OH^- ions are parallel to the c axis of the crystal and are free (H bonding is absent). A small amount of water is trapped in the lattice through coordinate covalent bonds. Upon charging, the structure develops a high degree of crystal symmetry. The relative intensity of H bonding in the charged state was shown to be a measure of the electrochemical capacity.

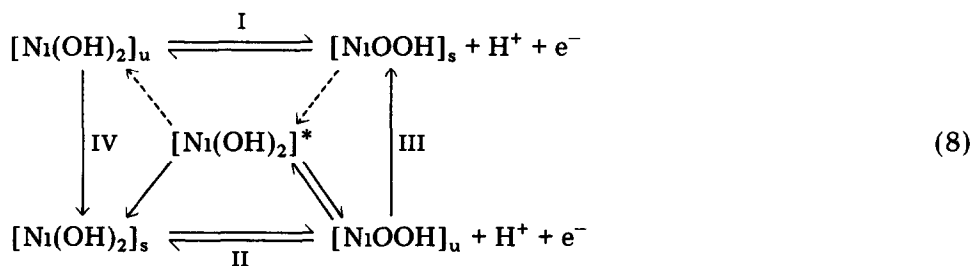
Several others, including Bourgault and Conway [33], Zedner [34], Foerster [35] and Kornfeil [36], have suggested reaction mechanisms similar to those already discussed. MacArthur [37], using Linear Scan Voltammetry prepared nickel hydroxide electrochemically on a 1 cm^2 nickel disc and suggested the following half cell reactions



In this work he used a model for the reaction in the nickel hydroxide electrode including a reversible charge transfer step at the nickel ion site in the lattice. During charge, a proton is released at the site and diffuses to the surface. During discharge, the proton returns to the nickel site. The proton diffusion is suggested as the limiting step in the reaction. In a later work MacArthur [38] determined the proton diffusion coefficient at 25 °C to be 3.1×10^{-10} cm²/s during charge (oxidation), and 4.6×10^{-11} cm²/s during discharge (reduction). He suggested that the movement of the proton in the lattice was due to thermal diffusion.

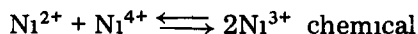
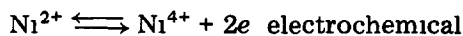
Proton diffusion as a limiting mechanism in the oxidation of Ni(OH)₂ to NiOOH was initially suggested by Jones and Wynne-Jones [39]. Others concurring in this mechanism included Lukovtsev and Slaiden [30], who measured the diffusion rate through a nickel oxide film and found it to increase with potential. Ewe and Kalberlah [40] suggested that the electric current was carried by the ions of the electrolyte in the electrode pores and the charge transported by proton diffusion to the surface.

In a recent series of papers, Schrebler-Guzman *et al* [41] suggested further modification of the Bode reaction mechanism,



where $[\text{Ni}(\text{OH})_2]^*$ is a hypothetical intermediate bridging both main electrochemical and chemical processes. The subscripts "u" and "s" refer to unstable and stable states. When the intermediate is omitted the box-like reactions are similar to those suggested by Bode [25], where $[\text{Ni}(\text{OH})_2]_{\text{u}}$ is the α form and $[\text{Ni}(\text{OH})_2]_{\text{s}}$ is the β form. $[\text{NiOOH}]_{\text{s}}$ is the γ form and $[\text{NiOOH}]_{\text{u}}$ is the β form.

In a recent development, Halpert and May [42] utilizing cyclic linear scan voltammetry and aqueous solution theory suggested that the nickel electrode reaction involved a two-electron change and that the charge mechanism was consistent with a quasi-reversible reaction. The results followed the pattern of a two-step reaction — electrochemical followed by chemical. The combined reaction suggested was



This would explain the wide range of oxidation states ranging from 2+ to 4+.

Cell types

The nickel electrode has been utilized as the positive electrode (cathode on discharge/anode on charge) in conjunction with four well-known negative electrode chemistries, *i.e.*, nickel-iron (Ni-Fe), nickel-cadmium (Ni-Cd), nickel-zinc (Ni-Zn) and nickel-hydrogen (Ni-H₂) cells. A description of these electrochemical systems and their characteristics is reviewed by Halpert [43]. The four systems utilize aqueous potassium hydroxide electrolyte and a separator material for physical separation of the plates. The plates of the nickel-iron, nickel-cadmium (non-sealed type) and nickel-zinc cells are flooded with electrolyte and therefore these cells are vented to release gas pressure. Sealed nickel-cadmium and all nickel-hydrogen cells are manufactured so that most of the electrolyte is absorbed in the separator and plates, thus allowing the oxygen which is produced during overcharge on the nickel electrode to be rapidly recombined at the opposing negative electrode.

The nickel-iron cell

Constructed of rugged tubular or pocket-plate electrodes, these cells have extremely long cycle-life (to 25 years) and are used for fork-lift trucks, railroad-cars, and other heavy-duty operations with relatively low depth of discharge. They are capable of moderate discharge rates. Their poor (high) self-discharge properties and low-temperature performance characteristics are disadvantages. However, they can be rebuilt, flushed with fresh electrolyte, and returned to service for many years. Lithium hydroxide in the electrolyte has a profound influence on the cell life.

In recent years, there has been some effort to utilize batteries of this type in electric vehicles. For the 80 kW range, a projection of 1500 deep discharge cycles appears reasonable. The problems with the use of these cells for transportation are (a) low efficiency — 50%, (b) H₂ evolution — cannot be sealed, and (c) high self-discharge rate (10% capacity loss in 100 h). Efforts to improve this technology are being continued.

Nickel-cadmium pocket plate cells

These cells are capable of higher rates than the nickel-iron cells and their capacities are less sensitive to the discharge rate. Their charge retention is also better than the nickel-iron cells. Because of their construction, they are also used for applications where rugged handling is the norm. In addition, they cost less than nickel-iron cells. Nickel-cadmium pocket plate cells can be used at temperatures to as low as -25 °C and to as high as +30 °C without damage. It is of interest to note that the cell voltage changes inversely with temperature, but the effect is so small it is practically immeasurable.

Sintered plate nickel-cadmium cells

These cells, first utilized in Germany during the Second World War, have the advantage of a very high (2 - 10 C)* charge and discharge rate

capability over a wide temperature range. The sealed cells have the further advantage of being maintenance free. Although the cost for these cells is generally higher than the pocket plate cells, they have wide use in aerospace, remote, and consumer applications. They are also available in a wide variety of configurations such as button, cylindrical, and prismatic cells. The fact that the oxygen evolved at the nickel hydroxide electrode during overcharge is recombined at the cadmium electrode, provides a means of maintaining balance between the relative states of charge of the two electrodes and avoids pressure buildup.

The fact that the sintered plate cells are (a) resistant to vibration and shock, (b) hermetically sealed, (c) efficient, and (d) relatively stable over many thousands of charge/discharge cycles makes them ideally suited for use as power sources in satellites.

The nickel-zinc cell

The interest in the nickel-zinc (Ni-Zn) cell after many years of study was brought about by the desire to find a higher energy-density battery for electric vehicles to replace the lead-acid system. The 1.65 V discharge voltage offered almost a 30% increase over the nickel-iron cells. The nickel electrodes were sintered but the zinc electrodes, either electrodeposited or pasted, are life limiting. The capacity associated with the requirement for high depth of discharge for vehicle applications was difficult to achieve. A new construction using vibrating electrodes to minimize the dendrite growth has been utilized with limited success. The flooded, vented nickel-zinc cells are capable of high-rate discharge. However, there is a disparity between the charge efficiencies of the charged nickel and zinc electrodes. This, together with the loss of O_2 by venting, results in the zinc species being depleted relatively quickly, favoring zinc shape-change and dendrite formation. The multilayer separator system used in the silver-zinc (Ag-Zn) cell must be utilized in this system as well, to prevent shorting and to minimize shape-change.

The lower cost-projections for the Ni-Zn cell require a reduction in cost of the nickel electrodes. Several attempts have been made to produce plastic bonded plates, which is one way to reduce costs. Graphite in place of nickel is utilized to enhance the conductivity of the electrode. Thus far, cycle life at high depth of discharge (DOD) has been adversely affected. The low cost approach results in a reduction in gravimetric energy density because additional active material is required to offset the reduced usable energy density.

The nickel-hydrogen cell

The newest of the technologies is the Ni- H_2 cell, utilizing the electrochemically impregnated nickel hydroxide positive electrode and a fuel cell

*C is the nominal ampere hour capacity removed in 1 hour

negative electrode During charge, H_2 is evolved at the negative electrode. The gas pressure continues to increase during the charge process When the positive electrode reaches the overcharge condition, the oxygen generated reacts with the hydrogen from the negative at the fuel cell electrode An equilibrium is reached and the pressure levels off, typically at 450 psi (31.6 kgf/cm²) in present designs By using a transducer to measure pressure, the state-of-charge can be monitored Another advantage is that this cell is also unaffected by overdischarge because hydrogen gas liberated from the nickel electrode is recombined at the negative electrode

To date, the most direct application is in satellite power systems Although baseline Ni-H₂ cell test data are limited, claims of high depth of discharge capability and longer life than the nickel-cadmium systems have been predicted, but not yet achieved The longer life is anticipated because of the absence of the cadmium electrode, thought to be the life-limiting electrode in the Ni-Cd cell This Ni-H₂ cell has a somewhat higher gravimetric energy-density than the nickel-cadmium cell but because of its higher depth of discharge, it yields a significantly higher usable energy-density than Ni-Cd

There are two drawbacks to the system aside from the cost factor One is the higher volumetric energy-density and the other that of electrolyte management The high volumetric energy-density of the Ni-H₂ cell is due to the large volume required to contain and store the high pressure gas in each cell. This results in a large electrochemically "inefficient" volume There has been a considerable effort to develop a Common Pressure Vessel (CPV) cell A bipolar plate nickel-hydrogen cell has been under development at NASA-Lewis Research Center [44] This design not only affords a significant reduction in volume but is capable of very high discharge rates because of the low internal impedance

The more significant technical problem, that of electrolyte management, is of concern for the long term use of this cell The electrolyte forced out of the separator and plates during charge must find its way back during the discharge process since drying out of the interelectrode spaces would lead to an increase in resistance and ultimate failure

Satellite use of Ni-Cd and Ni-H₂ power sources

The first documented in-space use of a cell containing nickel electrodes was in Explorer VI launched Aug. 7, 1959 A 142 lb. (64.4 kg) spheroid with four solar paddles, this satellite contained two 14-cell Ni-Cd batteries which ultimately degraded because of loss in solar array power The cells were Sonotone cylindrical F size (5 A h) with paper separators and glass-to-metal seals It lasted 2 months in the highly elliptical orbit

The quality of Ni-Cd cells has improved significantly since those days. Cells are now manufactured to high reliability specifications [45] with numerous quality-control steps and procedures The present state of the art uses prismatic cells, stainless-steel cases, ceramic/metal seals and a non-woven nylon separator Life in the Low Earth Orbit (LEO) has achieved 8 years of cycling in a 100 min (65 min charge/35 min discharge) orbit at

15 °C, and 10 years in Geosynchronous Orbit with a maximum depth of discharge of 60% at 10 °C. The cell sizes have increased to the point that 20 and 50 A h cells have become typical as the spacecraft power levels have increased.

Both 20 and 50 A h General Electric cells manufactured to the Goddard Space Flight Center Specification [45], which have been designated NASA Standard Cells, have completed 5 years of testing at the Naval Weapons Support Center, Crane, Indiana at 25% DOD and 20 °C without incident. These Standard Cells have also been successfully tested at 40% Depth of Discharge at 20, 30 and 40 °C as part of the qualification [46].

Twenty-two Standard Cells have been assembled into the NASA Standard Battery by McDonnell Douglas and have been in orbit for more than 4 years on the Solar Max Mission (SMM) Satellite. The Standard Batteries are required to meet test requirements of 28 g acceleration in addition to high levels of random and sine vibrations and a number of capacity test requirements before acceptance, according to the NASA Specifications for the Standard Battery (S-711-16). The high degree of sampling, testing, analysis, and quality control of the plates, separators, electrolyte, and seals have provided an amazingly consistent product over the past several years. The product has been consistent enough to match and select cells for the Standard Battery from the manufacturer's data alone, without undergoing a separate and costly selection test. The results on the NASA standard 20 and 50 A h battery have been reported at the Annual NASA Battery Workshop [47].

The future of nickel electrode cells and batteries

Continued advances in technology will provide opportunities for improvements in life, cost, weight, and energy density of nickel electrode cells. Although the nature of the nickel electrode reaction is complex, progress can be made through improvements in materials technology methods of operation and modelling that will have an impact on the state of the art.

Energy density

Given a specific quantity of active material, the potential and ampere hour capacity define the number of watt hours available from a given cell. Therefore, the only means of improving the gravimetric energy density of a cell or battery is to reduce the weight of the structural components of the cell. The typical weight breakdown for a 20 ampere hour, sealed, sintered-plate, flight-qualified nickel-cadmium cell is

case	173 g
header	33 g
separator and liner	18 g
negative electrodes	305 g

positive electrodes	261 g
electrolyte (31% KOH)	104 g
	<hr/>
Total weight	894 g

The nickel hydroxide active material in the positive electrode to produce 24 ampere hours at the *C/2* rate at 20 °C in a sealed condition is approximately 90 g. The cell also contains cadmium hydroxide in the negative electrode having twice the positive electrode capacity or approximately 160 g of active material. The remainder of the plate comprises the plaque and perforated steel current collector. Including the electrolyte and separator, all but 372 g (or 58% of the cell) is in the weight of the structural components. The theoretical energy density of the active materials is 211 W h/kg. In practice, at 100% depth of discharge, the energy density of the above cell is approximately 33 W h/kg (assuming a 1.25 V discharge voltage cutoff).

Actually, there has been an effort to reduce cell-case weight through the use of thinner-walled cases. However, the larger cells must be sturdy enough to withstand internal pressures of 100 psi (7.03 kgf/cm²) as specified [45]. The larger the cell, the greater the strength necessary to withstand the pressure on the broader surfaces. Although the sealed aerospace cell has been shown to withstand internal pressures of several hundred psi, expansion at the edges (the large, flat surfaces are structurally restrained in a battery) would produce a distortion of the case, affecting the reliability and operational characteristics. In a recent development, the edges of a thin (19 mil) cell case were strengthened with ridges pressed into the stainless steel. These provided the strength to withstand 100 psi (7.03 kgf/cm²) without distortion and a significant improvement in weight. The lighter weight case, together with a compressed polymeric seal, and electrochemically-impregnated plates, decreased the weight of a nominal 50 A h cell (60 A h of positive electrode capacity) from 2100 g to 1600 g — a 24% weight saving. This resulted in an energy density of 46.9 W h/kg compared with the 35.7 W h/kg of the flight-qualified cell.

Additional improvements in weight can be achieved with a lighter weight terminal and the use of pressed powder electrodes. The pressed powder electrodes would provide a significant saving in manufacturing cost as well. The improved utilization of electrochemically-impregnated electrodes would result in the requirement for less active material to achieve the same capacity.

Multiple cells are usually assembled into a structure to produce a battery. The battery structure itself adds weight, which also reduces the energy density. The battery case or frame is required to maintain mechanical integrity during overcharge when the cell pressure is at its maximum, and to remove heat (16 - 18% of the power) generated during discharge. These two requirements are diametrically opposed to reducing weight. The best battery-to-cell weight ratio achieved has been 1.15, which must be taken into account when considering the usable energy-density.

Finally, the most significant improvement in usable energy-density can be achieved by increasing the depth of discharge. The Ni-Cd cell in a Low Earth Orbit (LEO) application is generally restricted to 25% depth of discharge (DOD) for a long-life, high-reliability application. The Ni-H₂ cell, it is claimed, can operate at 50% DOD with long life. This would more than double the usable energy-density of the Ni-H₂ cell compared with the Ni-Cd cell even though their theoretical energy densities are not too different. An important consideration is that for a fixed period of discharge, as in the LEO orbit, doubling the DOD results in doubling the discharge rate. This would require additional heat removal capabilities of the battery and associated hardware thus increasing the weight and reducing the usable energy density.

The Ni-Zn, Ni-Fe and vented Ni-Cd cells are not optimized for energy density in the same manner because they operate with flooded electrolyte. However, the Ni-Zn and Ni-Fe cells have been considered for electric vehicle applications where the DOD is high (80%) and the number of cells is quite large. A weight saving in the structure would have an impact on the size of the cells and, even more importantly, the range and performance of the vehicle.

One of the drawbacks to the Ni-H₂ cell has been its volumetric energy-density because of the larger volume and configuration required to withstand the high pressures (~ 500 psi) (35.15 kgf/cm²). Gas storage space must be provided. The volumetric energy-density of a single nickel-hydrogen cell is 1.2 times that of a nickel-cadmium cell. However, two advances are being made to improve the volumetric energy-density. A common pressure vessel (CPV) battery comprising several cells has been developed [48] which eliminates a significant volume. Further, the development of a bipolar nickel-hydrogen pack [49] further reduces the volume, while significantly improving the power density.

Modelling

Among the areas attracting a great deal of attention in recent years is the development of models for predicting cell performance and life. The ability to predict the effect of operation on life and performance can result in a cost-effective reduction of testing. With regard to the aerospace, sintered plate Ni-Cd cell, NASA several years ago [50] attempted to establish a means for predicting life using a simplified linear regression technique on the first computer-operated cell test. The test included 12 packs operated in a related manner but did not accurately simulate orbital operations. The equations produced were found to be only applicable to the cells in each test sequence. Later, an attempt was made to predict life, not after years of testing, but from only a short period (1 - 2 months) of operation. The accelerated test program [51] at the Naval Weapons Support Center, Crane, Indiana, was planned statistically with five variable operating parameters

(Depth of Discharge (DOD), temperature, charge and discharge current, and overcharge) and three manufacturing parameters (precharge, electrolyte volume, and electrolyte concentration) A significant effort was put into developing the relationship between the variables.

McDermott [52] has spent several years evaluating the accelerated test data and performing computations using these data. Among the results has been an equation predicting life, and equations relating the effect of operating conditions on life. Recently, he has been able to describe mathematically the equations for discharge voltage using all empirical methods. This effort, together with the failure analysis of the cells from the earlier program, was able to identify failure modes such as swelling of the positive plate, electrolyte redistribution, and cadmium migration [53].

JPL developed a unique approach in evaluating the accelerated test data using the Weibull distribution and flaw theory. They assumed that there is an initial distribution of flaws in the cell and they were growing at a given rate. Fedors *et al* [54] developed an equation which related the generating variables (DOD, temperature, etc.) to the probability of survival. In so doing they were able to develop an equation for the number of cycles to failure which was in close agreement with McDermott's equation. However, the NASA accelerated test data described above were generated under severe non-orbital conditions. Hafen and Corbett [55] showed, however, that the theory could be applied to simulated orbital test data. They selected packs from LEO orbits and also developed a similar equation.

There are three very important applications of a model. The first will provide the information necessary to answer the question: "Is the product being tested consistent with the qualified or previously utilized cell design?" Years of testing have only proved that the test cells were good but, when the cell finally faded after several years, the chances of obtaining a repeat cell with the same internal construction, design, and material, was very poor. Therefore, the model must be capable of verifying that the samples being tested are as tested previously. It is necessary that the verification involves only a short-term test. Lengthy testing would provide the answers too late in the program.

Secondly, once the reproducibility of the hardware is verified, then the modelling needs to be useful for predicting cycle life under any number of specific operating sequences (DOD, temperature, current, orbit, etc.) In this way it can be universally applied. Most of the effort in modelling today is based on a specific sequence of operations which has only narrow applications.

Thirdly, and most important, is the ability of a model to describe not only the cycle life which is a finality, but the change in voltage and other measurable and operational characteristics with life. This kind of information will allow the capability to observe the degradation of a cell/battery in operation and provide indicators well in advance of failure, so that steps can be taken to (a) reduce the load, (b) increase or decrease the charge voltage or operate the power system on an orbit-by-orbit basis. Further, in

the event of a change in spacecraft power system operation due to equipment, instrument failure or change of orbital attitude, a well-designed model can predict even after years of cell/battery operation, how long and what the new characteristics will be in the abnormal operating condition.

Modelling has evolved mainly because of the ability of the computer to perform tests, store data, and perform a wide variety of complex calculations. With the improved uniformity of cells, it is only a matter of time before a universal model is available.

A new technique being applied to cell evaluation is the non-destructive complex impedance measurement [53]. Although not well understood yet, the derived parameters such as Warburg impedance, and relationships between frequency and the real and imaginary components of the impedance have been found to be related to processes occurring within a cell. Changes in these more subtle parameters occur with state of charge and cycle life. Although no definite model has been developed, the chances are that one can be developed with the use of sophisticated electronics. These characteristics may be measurable continuously during operation rather than just before and/or after operation.

Although the above has been directed at the sealed nickel cells, there is little doubt that modelling can be utilized for the other nickel electrode cell chemistries.

The use of the nickel electrode cell is going to continue to grow as the needs for portable power increase. The era of the electronics explosion has made the use of these systems even more suitable because of the miniaturization and lower drain losses from the cell. The nickel electrode is a proven, reliable, long life, predictable and reproducible electrode whose use will continue to grow for many years to come.

References

- 1 S G Falk and A J Salkind, *Alkaline Storage Batteries*, Wiley, New York, 1969
- 2 C Desmazures, *US Pat 402,006* (1889), *Fr Pat* (1887) cited in E J Wade, *Secondary Batteries*, The Electrician Printing and Publishing Co, London, 1902, p 130
- 3 A Dun and F Hesslacher, *Brit Pat 1862* (1887)
- 4 W Jungner, *Swed Pat 8,558* (1897), *10,177* (1899), *11,132* (1899), *11,487* (1899), *15,567* (1901)
- 5 T de Michalowski, *Brit Pat 15,370* (1899), *Ger Pat 112,351* (1899)
- 6 T A Edison, *Ger Pat 157,290* (1901), *US Pat 678,722* (1901), *692,507* (1902)
- 7 G Pfeider, F Spoun, P Gmelin and K Ackermann, *Ger Pat 491,498* (1928)
- 8 V A Tracy and R. P Perks, *Powder Metall*, 12 (1963) 54
- 9 Akumulatoren Fabrik AG (Varta), *Brit Pat 468,518* (1936)
- 10 Société des Accumulateurs Fixes et de Traction (SAFT), *US Pat 2,819,962* (1958), *Fr Pat 1,290,138* (1960)
- 11 F Sauerwald, *Z Elektrochem*, 30 (1924) 175
- 12 A Fleischer, *J Electrochem Soc*, 94 (1948) 289
- 13 E J Casey, *Proc Annu Battery Res Dev Conf*, 13 (1959) 75
- 14 P L Bourgault, P E Lake, E J Casey and A R Dubois, *Can J Technol*, 34 (1957) 495

- 15 E Hausler, in D H Collins (ed), *Power Sources 1*, Pergamon Press, London, 1967, p 287
- 16 W D Wabner, L Kanother and W Kroenke, *Z Elektrochem*, 26 (1972) 68 L Kandler, *US Pat* 3,214,355 (1965), 3,282,808 (1966), *West Ger Pat* T133,442 (1962)
- 17 E J McHenry, *Electrochem Technol*, 5 (1967) 275, D R Turner, W E Hamden, Y Okinaka and E J McHenry, in D H Collins (ed), *Power Sources 1*, Pergamon Press, London, 1967, p 349
- 18 T Takamura, T Shirogame and T Nakamura, *J Electrochem Soc Jpn*, 42 (1974) 582
- 19 R L Beauchamp, *The Electrochemical Society Meeting, Atlantic City, NJ, Oct, 1970*, Electrochem Soc, Pennington, NJ, Ext Abstr No 65, *Oct, 1971*, Ext Abstr No 23. *US Pat* 3,653,967 (1972)
- 20 H N Sieger, D F Pickett, v J Puglisi, P F Ritterman and R L Olver, *AFAPL-TR-74-56, Part II*, August, 1974.
- 21 D F Pickett, W S Bishop and R A Marsh, *AFAPL, TR 75-79*, Feb 1976, D F Pickett, *1971 - 73 Battery Workshop*, D F Pickett, *AFAPL, TR 75-34, Parts I and II*
- 22 S Gross, *Final Rep, JPL Contract 953 984*, Aug, 1977
- 23 O Glemser and J Eimerhand, *Z Anorg Chem*, 261 (1950) 26
- 23a P C Milner and U B Thomas, *Adv Electrochem Electrochem Eng*, 5 (1967) 1
- 24 D Tuomi, *J Electrochem Soc*, 112 (1965) 1, 115 (1968) 450, paper presented at the *Spring Meeting of the Electrochemical Society, May 1968*
- 25 H Bode, K Dehmelt and J Witte, *Electrochim Acta*, 11 (1966) 1079
- 26 J P Harival, B Morignat, J Labat and J F Laurent, in D H Collins (ed), *Power Sources 1*, Pergamon Press, London, 1967, p 239
- 27 J Weininger, *Fall Meeting of the Electrochemical Society, Denver, CO, Oct, 1981*, Electrochem Soc, Pennington, NJ, Ext Abstr No 20
- 28 A J Salkind and P F Bruins, *J Electrochem Soc*, 109 (1962) 356
- 29 J L Weininger and M W Breiter, *J Electrochem Soc*, 110 (1963) 484
- 30 P D Lukovtsev and G J Slaiden, *Electrochim Acta*, 6 (1962) 17
- 31 G W D Briggs and M Fleischmann, *Trans Faraday Soc*, 62 (1966) 3217, 67 (1971) 2397
- 32 F P Kober, *J Electrochem Soc*, 112 (1965) 1064, 114 (1967) 215
- 33 P L Bourgault and B E Conway, *Can J Chem*, 38 (1960) 1557
- 34 J Zedner, *Z Elektrochem*, 11 (1905) 809, 12 (1906) 463, 13 (1907) 752
- 35 F Foerster, *Z Elektrochem*, 13 (1907) 414, 14 (1908) 285
- 36 F Kornfeil, *Proc Am Power Sources Conf*, 12 (1958) 18
- 37 D M MacArthur, *J Electrochem Soc*, 117 (1970) 422
- 38 D M MacArthur, *J Electrochem Soc*, 117 (1970) 729
- 39 E Jones and W F K Wynne-Jones, *Trans Faraday Soc*, 52 (1956) 1260
- 40 H Ewe and A Kalberlah, *Electrochim Acta*, 15 (1970) 1185
- 41 R S Schrebler-Guzman, J R Vilche and A J Arvia, *J Appl Electrochem*, 9 (1979) 183, 9 (1979) 321, 8 (1978) 67 *J Electrochem Soc*, 125 (1978) 1578
- 42 G Halpert and L May, *Fall Meeting of the Electrochemical Society, Washington, DC, Oct, 1983*, Electrochem Soc, Pennington, NJ, Ext Abstr No 3 G Halpert, Effect of cadmium on the nickel hydroxide electrode, *Dissertation*, Catholic University, Washington, DC, April, 1982
- 43 G Halpert, A review of secondary batteries and evaluation techniques, Ch V, in E Yeager and A J Salkind (eds), *Techniques of Electrochemistry*, Vol 3, Wiley, New York, 1978
- 44 R L Cataldo and J J Smithrick, *Proc 17th IECEC Conf, New York, 1982*, Am Inst Chem Eng, New York, p 780
- 45 Goddard Space Flight Center (GSFC), *Hi Reliability Aerospace Nickel-Cadmium Cell Specification 74-15000*, January, 1974

- 46 *NASA Standard 20 Ah Nickel-Cadmium Cell Qualification Tests* NWSC, Crane Report WQEC/C 83-133, 7 June 1983, Naval Weapons Support Center, Crane, IN
- 47 R Broderick, *Proc 1981 NASA Battery Workshop, Nov, 1981*, NASA Conf Publ 2217, p 305
- 48 G Holleck, *AFWAL Rep TR-81-2097*, 1981
- 49 L H Thaller, *Fourth Estec Spacecraft Power Conditioning Seminar Sponsored by European Space Agency NASA Tech Mem 82946*, Nov 1982
- 50 G Halpert and J M Sherfey, *Nickel-Cadmium Battery Test Project Relationship between operation, life and failure mechanism Vol II, Battery Test Results, GSFC Doc X735-69-24*, March, 1969
- 51 L A Goodman, *Accelerated test program for sealed nickel-cadmium cells, NASA CR148209*, Feb, 1976
- 52 P M McDermott, *NASA Battery Workshop Proc 1978 - 1982*, Goddard Space Flight Center, Greenbelt, MD
- 53 S DeStefano, *Studies of life-limiting failure mechanism, JPL Report D991, Nov 1982*, Jet Propulsion Lab, Pasadena, CA
- 54 R F Fedors, S D Hong, A Gupta and J Moacanin, *J Power Sources*, 8 (1982) 369
- 55 D P Hafen and R E Corbett, *16th Intersoc Energy Conversion Engineering Conf, Atlanta, GA, Aug 1981*, Amer Inst Chem Eng, New York, Paper No 819112