Nickel/zinc batteries

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Abstract

The nickel/zinc battery is very attractive for electric vehicle applications. Development is slow because of problems related to the solubility of the zinc electrode discharge products and the disparity in charging efficiencies between the nickel and zinc electrodes. Recent advances in solving these problems are reviewed.

Introduction

The nickel/zinc battery was first proposed in a Russian patent by Michaelowski in 1901 [1]. The first serious attempt to develop a battery was the work of Drumm in Ireland in the 1930s. In the late 1950s and early 1960s, there were several reports on nickel/zinc battery development in the former USSR. In the late 1960s, there was a resurgence of development efforts in the USA. The early work was privately funded. After the oil embargo of 1973, infusion of government funds in the USA led to major development programs on nickel/zinc batteries for electric vehicle applications. This work lasted for about ten years. There was also a major development effort on electric vehicle batteries at the General Motors Corporation. All of this work has been reviewed extensively [2–4]. Since the early 1970s, there has been a continuous series of reports in the Japanese patent literature on the development of small sealed nickel/zinc batteries. Jindra [5] has reviewed developments on sealed cells, up until 1990. This paper reviews recent progress and future prospects for the battery.

Operating principles

The cell

Overall cell reaction and thermodynamics

The overall reaction of the nickel/zinc cell is usually given as:

$$2NiOOH + H_2O + Zn \rightleftharpoons 2Ni(OH)_2 + ZnO \qquad (1)$$
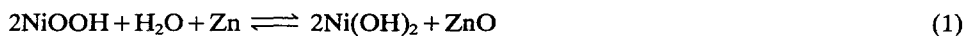
Sharma [6] has critically evaluated the thermodynamics of the cell reaction. He calculated a standard free energy ΔG^0 of $-80\,694$ cal at 298 K, a standard enthalpy change, ΔH^0, of $-85\,534$ cal and a standard entropy change, ΔS^0, of -16.239 cal/deg. This yields a thermoneutral voltage of 1.854 V, which is comparable to the value of 1.6 V

determined by Chen and Gibbard [7]. Under normal operating conditions, the battery is essentially isothermal on charge. On discharge, however, entropy contribution accounts for more than 40% of the heat generated in the cell. Sharma [6] has further calculated that the maximum temperature rise in a 150 Ah cell discharged adiabatically at 50 A at an average voltage of 1.6 V is 97 °C. If entropy effects are neglected, the calculated temperature rise is 62 °C.

General cell characteristics

In its simplest form, the nickel cell combines the positive electrode of the nickel/cadmium battery with the negative electrode of the silver/zinc battery. Initial development efforts in the former USSR and the USA were simply slight modifications of the designs developed by André for the silver/zinc battery [8]. The design of the silver/zinc battery was largely dictated by the requirements for suppressing the solubility of Ag_2O and preventing the migration of argentous species to the zinc electrode. This required the use of cellulosic separators and a 45% KOH electrolyte. The substitution of the nickel electrode for the silver electrode permitted the use of microporous separators and more dilute KOH electrolytes. Thus, electrolyte formulations that reduce the solubility of ZnO could be used. This mitigates some of problems with the zinc electrode, such as reducing the rate of zinc electrode shape change with cycling. Unlike the silver/zinc cell, however, there is a significant disparity between the charging efficiencies of the nickel and zinc electrodes. The zinc electrode is essentially 100% efficient on charge, whereas the nickel electrode is only 90 to 95% efficient on charge. Zinc electrodes typically contain three to four times the stoichiometric amount of ZnO. Because of the differences in charging efficiencies, this reserve of ZnO is rapidly consumed on cycling. So a vented cell rapidly becomes zinc limiting on charge, a condition that can lead to zinc dendritic growth and cell shorting. The development efforts on nickel/zinc batteries have focused on solving the problems due to the solubility of ZnO in the electrolyte and the disparity in charging efficiencies between the nickel and zinc electrodes. When cycling vented nickel/zinc cells, it is common practice to regenerate periodically the ZnO by draining the cell to 0 V and then shorting the terminals. In this way, the zinc completely discharges while hydrogen is evolved at the nickel electrodes. A more satisfactory solution is to seal the cell and depend on the oxygen recombination reaction to maintain a charge balance between the electrodes. The requirement of microporous separators to prevent zinc shorting reduces the rate of transport of oxygen to the negative electrode. In sealed zinc cells, there is always the possibility of hydrogen evolution on the zinc electrode. The kinetics of hydrogen recombination at the nickel electrode are slow. Several schemes using auxiliary electrodes for hydrogen recombination have been proposed. These have recently been reviewed [5].

The nickel/zinc battery has superior performance to both lead/acid and nickel/iron batteries. Specific energies of 55 to 75 Wh kg^{-1} and a specific power in excess of 200 W kg^{-1} have been demonstrated. The overall charge/discharge energy efficiency is good (>70%). The battery has excellent low-temperature performance. Work by Heitbrink et al. [9] has shown that a 150 Ah cell discharged at −18 °C delivered 80% of the energy available at 25 °C. This compares with only 50% for lead/acid batteries. The main problem is limited cycle life. In compact lightweight designs, cycle lives of 500 to 600 cycles have been routinely demonstrated [10]. The best cycle life obtained on an electric-vehicle battery was 300 cycles on a bench test at General Motors. Somewhat lower cycle life was found in actual vehicle tests [9].

Electrodes

The zinc electrode

The zinc electrode has been reviewed extensively [4, 11]. Recent fundamental work on the zinc electrode in alkaline electrolyte has focused on methods for reducing the solubility of ZnO, the mechanisms of formation and decomposition of supersaturated zincate electrolytes, the growth of mossy deposits on charge at low current densities, and the effect of additives and pulsed charging on the morphology of the zinc electrode.

Electrodes of limited solubility

The equilibrium solubility of ZnO in KOH depends on the KOH concentration and increases from 6 g l^{-1} in 10% KOH to 53 g l^{-1} in 30% KOH. One approach to minimizing problems at the zinc electrode is to reformulate the electrode or electrolyte composition so as to reduce the ZnO solubility. This can be done either by incorporating $Ca(OH)_2$ in the zinc electrodes or by use of electrolytes with minimal hydroxyl content containing highly soluble salts such as phosphate, borate, carbonate or fluoride. The benefits of these approaches have been reviewed by Bass *et al.* [12].

The most extensive work on the use of $Ca(OH)_2$ was done by General Motors [6, 13–18]. The addition of $Ca(OH)_2$ reduces the solubility of ZnO through the formation of calcium zincate $(CaZn_2(OH)_6 \cdot 2H_2O)$. A key finding of this work was that there is no suppression of the ZnO solubility at concentrations above 34% KOH. Also the kinetics of calcium zincate formation is very slow at concentrations above 25% KOH. The use of $Ca(OH)_2$ is effective only if a rigorous set of conditions are followed. The important aspects in applying this approach are the use 20% KOH, elimination of carbonate contamination of the electrolyte, and the use of microporous separators. The latter was first pointed out by Van der Grinten [19]; the microporous separator may prevent increases KOH concentration in the zinc electrode due to electroosmotic effects. Reduction of the zincate solubility increases the tendency for the zinc to passivate during discharge. The addition of a lead additive mitigates the problem. Another key ingredient is the incorporation of a wicking material such as cellulosic fibres in the electrode [20]. As in any zinc cell, careful attention has to be paid to stacking tolerances in the cell pack.

Cairns and co-workers [21] have performed extensive work on electrolytes with low zincate solubility. The best results were obtained with an electrolyte of the composition 3.2 M KOH + 1.8 M KF + 1.8 M K_2CO_3. Eisenberg [22, 23] has developed a series of mixed electrolytes for reducing the zincate solubility. A typical electrolyte composition is 3 M KOH + 3 M K_3PO_4 [23].

Supersaturated zincate electrolytes

When a zinc electrode is discharged in an alkaline electrolyte supersaturated zincate electrolytes can be formed. The zincate solubility can be as much as three times the equilibrium solubility. These solutions, however, are not supersaturated in the ordinary sense of the term. Neither seeding or shock causes precipitation of ZnO. Instead, the ZnO is precipitated slowly in a manner resembling a decomposition reaction. The presence of Li^+, SiO_2^{2-} or sorbitol retards the process. Depending on the conditions, it can take anything from hundreds-of-hours to a year to reach the equilibrium solubility. Developers, such as Sorapec Corporation in France [24], have taken advantage of this and have developed nickel/zinc batteries with the discharged products completely dissolved in the electrolyte. The most systematic study of the decomposition kinetics of supersaturated zincate solutions has been conducted by Debiemme-Chouvy and Vedel [25]. They found that the decomposition kinetics of the

supersaturated solution was autocatalytic, in that the precipitated ZnO accelerated the precipitation reaction. It was also shown that adsorption of silicate on the ZnO inhibited the precipitation reaction. Kinetic measurements indicated that the kinetics for the precipitation reaction had a second order relationship with respect to the zincate concentration. Thus, it was proposed that the supersaturated species are bridged zincate dimers.

Mossy zinc deposits

Zinc deposition from alkaline zincate electrolytes is unusual in that finely-divided spongy or mossy deposits are formed at low current densities [26]. In the case of other metals, finely-divided deposits are only formed at very high current densities [27]. Three types of mechanisms have been proposed to explain the anomalies in zinc deposition. These are: (i) zinc deposition through surface oxide films [28–30]; (ii) instabilities due to multiple steady states caused by autocatalytic processes [31, 32], and (iii) stabilization of dendrites and superlattices by co-deposition of adsorbates such as hydrogen [33].

Deposition of mossy non-adherent deposits is undesirable in free-electrolyte systems such as those developed by Sorapec. The formation of mossy deposits can be prevented by pulsed charging [24, 34–36]. A combination of a pulsed-charging regime in combination with a Pb^{2+} additive is particularly effective [24].

The nickel electrode

The characteristics of the nickel electrode have been reviewed recently [37]. Early attempts to develop low-cost, non-sintered electrodes have been abandoned because of electrode swelling and decreases in high-rate capabilities on cycling [38]. A more recent approach is to incorporate the $Ni(OH)_2$ into nickel-fiber mats, mats of nickel-plated carbon, or foams. Ferrando [39] has described a process for doing this called the 'suspension impregnation method'. This has been used successfully in electrodes for nickel/zinc batteries [40].

Effect of zinc on the nickel electrode

In the past, there have been questions as to what is the effect of zinc species on the nickel electrode. Early work has been reviewed by McBreen [37]. At one time, zincate was considered to be a poison for the nickel electrode. More recent work, however, has shown that zinc is actually a beneficial additive for the nickel electrode, particularly when used in combination with a cobalt additive [41–43]. There are several recent claims in the Japanese patent literature on combinations of cobalt and zinc as an additive for the nickel electrode [44–46]. This combination of additives suppresses the formation of γ-NiOOH during battery overcharge [43]. In normal battery operation, large quantities of zinc material are incorporated in the pores of the nickel electrode. This can decrease the capacity of the electrode. The mechanism appears to be pore plugging by ZnO or $Zn(OH)_2$ rather than a chemical poisoning effect.

The separator

The separator is a very important element in determining cell performance and life. Its effects have been reviewed recently [12]. Lundquist [47] has pointed out that the cycle life of nickel/zinc cells varies inversely with the separator–electrolyte resistivity and/or porosity.

Current status

There has been no major development effort in nickel/zinc batteries in the USA since the early 1980s, when the program at General Motors was terminated. There have been two small development efforts, one at the Lawrence Berkeley Laboratory [21] and the other at Electrochimica Corporation [40]. Both developers used electrolytes with limited zincate solubility. Sorapec Corporation in France, has had a development effort on cells for electric-vehicle batteries using a system based on soluble zincate in a large excess of electrolyte [24]. There have been several efforts in Japan on the development of small, cylindrical, sealed nickel/zinc cells. This work has been reviewed by Jindra [5]. In Japan, Yuasa apparently marketed small ($\leqslant 10$ Ah) sealed cells [48]. More recently, Yuasa has reported on the development of a sealed nickel/zinc battery for powering electric lawn-mowers [49]. They claim it contains mercury-free zinc electrodes and weighs only 60% of a corresponding lead/acid battery.

Lawrence Berkeley Laboratory

Work at Lawrence Berkeley Laboratory has included work with both calcium zincate electrodes [50] and electrolytes with limited solubility for zincate [21, 51]. The best results were obtained in the cells with ternary electrolytes. Several mixed electrolytes were evaluated both in sealed and vented 1.35 Ah cells. Table 1 shows a comparison for results obtained in sealed cells with a conventional electrolyte (6.8 M KOH + 0.6 M LiOH) and a ternary electrolyte (3.2 M KOH + 1.8 M KF + 1.8 M K_2CO_3) with low zincate solubility. The cell with the ternary electrolyte exhibited no dendritic shorts after 575 cycles at 100% depth-of-discharge.

Electrochimica Corporation

Reisner and Eisenberg [40] have reported on the use of various buffered electrolytes in nickel/zinc cells. The electrolyte compositions are described in two patents [22, 23]. Cycle lives of 600 cycles were achieved in 225 Ah vented cells cycled to 80% depth-of-discharge, whereas cells with conventional KOH electrolyte gave cycle lives of about 100 cycles. The 225 Ah cells were reconditioned about three times during cycling. Eisenberg [40, 52, 53] also reported on the development of several smaller sealed cells (2 to 12 Ah) using these electrolytes. He claimed specific energies of 56 Wh kg^{-1} and energy densities of 123 Wh l^{-1}. The cells had nickel electrodes prepared by the suspension impregnation of $Ni(OH)_2$ into nickel foams or sintered nickel-plated carbon fibers [40, 52].

TABLE 1

Comparison of performance of 1.35 Ah sealed nickel/zinc cells with a conventional KOH electrolyte (6.8 M KOH + 0.6 M LiOH) and with an electrolyte with low zincate solubility (3.2 M KOH + 1.8 M KF + 1.8 M K_2CO_3)

Parameter	Electrolyte	
	Conventional	Low solubility
Cycles (> 80% capacity)	60	380
Cycles (> 60% capacity)	190	575

Sorapec Corporation

Bronoel *et al.* [24] have given an extensive report on the development of nickel/ zinc cells at Sorapec. Their system was based on a large excess of 8 M KOH electrolyte with a 2% sodium silicate additive to stabilize supersaturated zincate solutions (200 g Zn l^{-1}). The zinc morphology was controlled by a Pb^{2+} additive and a pulsed-charging regime consisting of a charging pulse of 5 mA cm^{-2} for 2.75 s, followed by a discharge pulse of 5 mA cm^{-2} for 0.15 s with no open-circuit time between pulses. The cells were designed carefully to ensure good primary current distribution. Cells of 60 Ah capacity were built. These had a specific energy of 57 Wh kg^{-1} and cycle lives in excess of 1000 cycles. No report was given on how these cells performed on shallow cycling or whether reconditioning cycles were needed. They reported that the next step was scale-up to 140 Ah cells, where they expected specific energies of 70 Wh kg^{-1}.

Technical challenges

The technical problems are still related to zinc electrode shape change and the disparity in charging efficiency between the positive and negative electrodes. The latter can be overcome by sealed cell operation. This is more of a challenge in large cells. The nickel/zinc couple offers considerable leeway in the choice of electrolyte, separator and charging method that may be used. The proper choice of these together with combinations of additives may yield batteries with adequate cycle life. The disparity in charging efficiencies is a major challenge. Nevertheless, unlike many non-aqueous batteries, there is an obvious chemical route, via the oxygen cycle, for solving the problem.

Commercial impact

It now appears that production of nickel/cadmium batteries will eventually be phased out because of environmental problems. At present, the trend is to replace them with nickel/metal-hydride batteries in medium-rate applications ($C/4$ to C rate). An advantage of this approach is that the separator and the manufacturing processes are identical to those for nickel/cadmium. Metal-hydride batteries have specific energies that are similar to nickel/zinc. The active materials for nickel/zinc have lower cost, but this is not important in small battery sizes, so it is doubtful if nickel/zinc batteries could soon capture this market. In applications requiring limited power and cycle life, at modest cost, it is likely that rechargeable zinc/manganese dioxide batteries will also be a strong contender. If the technical problems can be overcome, nickel/zinc batteries could replace nickel/cadmium batteries in high-power applications (C rate and higher). Another application could be electric lawn-mowers. Pollution control laws may well outlaw gasoline-powered mowers. Nickel/zinc batteries have been proposed for engine-cranking in cold climates, but thin-film lead/acid batteries are a competing technology. Recent reports indicate excellent performance of nickel/metal-hydride batteries in electric vehicles. In large electric-vehicle batteries, nickel/zinc would have a substantial economic advantage over nickel/metal hydride. In vehicular applications, nickel/zinc offers excellent specific energy, high power, good efficiency and excellent low-temperature performance.

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