

Progress in sealed Ni–Zn cells, 1991–1995

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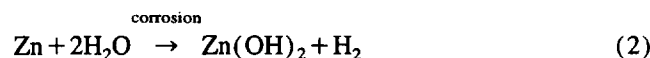
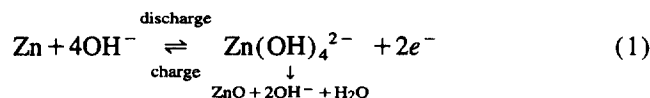
Abstract

Novelties in the development of sealed nickel–zinc cells are reviewed. The zinc electrodes remain the problem-limiting factors for long-operating cells and batteries. A tendency to light and inexpensive non-sintered nickel porous supports based on fibres at the positive electrodes in the Ni–Zn system is presented. Sealed Ni–Zn cells are discussed. The activity of the Far East Asian countries in this field is increasing continuously.

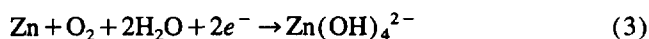
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1. Introduction

The nickel–zinc electrochemical system is a promising candidate for alkaline storage batteries. It exhibits good performances: (i) energy density of 55–85 Wh/kg; (ii) power density of 140–200 W/kg; (iii) open-circuit-voltage of 1.75 V, and (iv) a self-discharge rate of <0.8% per day. The electrode active materials used in the Ni–Zn system are low-toxic, inexpensive materials, and exist in abundance in nature. However, the cycle life of the system remains relatively low due to troubles with changes in the shape of the zinc electrodes, dendrite growth, and zinc corrosion. The zinc electrode operates as follows:



In these sealed systems the reduction of oxygen at the zinc electrode must occur



The system has often been studied and reviewed [1–5]. This paper deals with progress in R&D during the last five years.

2. Components of cells

2.1. Zinc electrodes

2.1.1. Preparation of electrodes

The preparation of the electrodes consists of pasting of the negative active mass to suitable metal collectors and/or slurry precipitation.

The main problems concerning the zinc electrode are: (i) shape changes of the electrode during cycling; (ii) formation of the zinc dendrites during charging; (iii) passivation of the electrode, and (iv) hydrogen evolution at the electrode.

The high solubility of the discharge products of the zinc electrode in strongly alkaline electrolytes is a common cause of the two first problems generally solved by adding suitable materials either to the active material or the electrolyte.

2.1.2. Additives to the active mass

The positive effect of the addition of acetylene black on the mechanical and electrochemical properties and the cycle life of zinc electrodes was evaluated potentiodynamically [6]. Jain et al. [7] investigated the influence of Ca(OH)₂ on the change in shape of the zinc electrodes and the cycle life of the Ni–Zn cell. Ca(OH)₂ reacts with zincate solutions, thus forming a crystalline calcium zincate compound during the discharge. The solubility of this complex is less than that of ZnO, and a lower solubility of zinc species leads to a slower rate of the zinc redistribution. Zinc electrodes with 25% Ca(OH)₂ solution showed the best performances; their lost capacity rate amounted to only 0.13% per cycle compared with 0.47% per cycle in calcium-free cells.

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The so-called stabilized Zn electrodes were used in Ni–Zn cells with improved cycle-life performance [8]. The anodes contained a small amount of CdO, the growth of zinc dendrites was therefore reduced, and no densification of the anodes occurred. The cells completed 130 cycles.

Suga et al. [9] proposed anodes comprising zinc-active material and a polymer layer permeable for oxygen formed in direct contact with the anode. Suitable polymers were: poly(dimethylsiloxane), poly(organosiloxane), poly(vinyl-triorganosiloxane), poly(alkylsulfone), poly(4-methyl-1-pentene), poly(2,6-dimethylphenylene oxide), and low-density poly(ethylene) or one of these polymers with more functional groups. The anodes suppress the occurrence of dendrites and the change in shape. The recommended positive additives to zinc-based and ZnO-based electrodes may be zinc alloys containing: (i) Cd, Pb, Bi, Sn, In, Ga, Tl [10]; (ii) alkaline-earth metal–zinc alloys M–Zn_x ($x \geq 1$) [11], or intermetallic (e.g. In–Tl) compounds [12], Cd and Tl oxides [13], In₂O₃ [14], Tl₂O₃ [15], and (iii) SnO, Sn(OH)₂, PbO or Pb(OH)₂ [16].

2.1.3. Additives to the electrolytes

Shivkumar et al. [17], using the potentiodynamic polarization and triangular potential sweep voltammetric techniques, studied the effect of V₂O₅, ZnO, PbO and (NH₄)₂CS on the reversibility of the redox couple. V₂O₅ cannot be used because it stimulates corrosion, despite a reduction in the cathodic oxygen overvoltage. PbO is not recommended because it leads to a reduction in open-circuit-voltage due to the deposition of lead. The additives ZnO and (NH₄)₂CS can be safely used as battery-electrolyte additives because they reduce the corrosion markedly, do not enhance passivation of the electrode in the electrolyte, and increase both the discharge capability and the cycle life. In the case of high-temperature performances additives, such as ZnO and (NH₄)₂CS, with endothermic adsorption is preferred. An optimum concentration of each additive (in the order of 10⁻³ to 10⁻² M) within the solubility limits was suggested for maximum protection.

Concerning the addition of carbonates to alkaline electrolytes [18], the beneficial role of CO₂ absorbed in zinc cells is confirmed; 0.5 M K₂CO₃ is regarded as the optimum concentration for a battery electrolyte [19].

Of the many organic additives one can mention in particular: (i) tetraethylammonium bromide in the concentration 10⁻⁴ M [20] which beneficially suppressed the formation of zinc dendrites and changes in the shape; (ii) alkylethers of poly(propyleneglycol) C_nH_{2n+1}(OC₃H₆)_mOH, where $n = 7–12$, $m = 10–20$ [21], or (iii) C_{10–16} fatty acid salts, mixed C_{19–20} fatty acid esters, C_{10–22} aliphatic alcohols, and C_{10–22} hydrocarbons [22].

2.1.4. Ionization of gases in sealed Ni–Zn cells

Since research into sealed cells carried out at the firm Samsung (Korea) being started only recently, several research groups studied the effect of the state-of-charge

(SOC) of the zinc electrode, corrosion inhibitors and the potential of the zinc electrode on the oxygen recombination rate during cycling of cells with a capacity of 25 Ah. The cells were equipped with manometers to measure the oxygen pressure during the three-stage charging and the one-stage discharging with a current corresponding to $C/3$. When the content of metallic zinc in the zinc electrodes increased to 40%, the rate of oxygen ionization increased linearly. The oxygen pressure after charging the cells influenced also the rate of oxygen ionization. The ionization current was 0.27 mA/cm² at 0.3 atm and 1–1.2 mA/cm² at 1 atm. The addition of Hg and PbO showed a higher current of oxygen ionization (0.5–8 mA/cm²). In₂O₃ enhanced also the oxygen ionization. When the potential of zinc electrodes was in a pre-passive or passive state (–1.0 to –0.6 V versus Hg/HgO), the rate of oxygen ionization decreased by three to five times. Thus, investigations of oxygen ionization in sealed Ni–Zn cells made it possible to define the influence of many factors on the rate of oxygen reduction and to find the optimum conditions for the effective oxygen ionization. The Samsung cells are apparently not provided with an auxiliary recombination electrode. During one cycle, the oxygen pressure in a cell charged with a constant current amounted to 0.9 to 1.4 atm; at rest and during discharging it fell almost to the initial value. The value of the oxygen pressure in a cell charged in the three-stage regime decreased by 50%. With large cells of a nominal capacity 180 Ah used to drive an electromobile the oxygen pressure continuously increased less with the three-stage, more with one-stage charging which is, therefore, evidence of insufficient rate of oxygen ionization on zinc electrodes. It is, therefore, necessary to use the three-stage charging till 90% SOC [23].

With smaller Samsung cells [24] the constant-current charge at a 0.1C rate caused an oxygen pressure of ~1 atm up to a 90% SOC. At higher SOC's the pressure rises considerably amounting to 5 atm at 120% SOC. The rate of oxygen ionization is, therefore, insufficient.

The problem of catalytic oxygen reduction is often solved by incorporating an auxiliary electrode. Simon et al. [25] proposed an auxiliary three-layer electrode electrically connected to anodes in order to decrease the oxygen build-up in the secondary sealed alkaline batteries — including the Ni–Zn system. The auxiliary electrode consists of: (i) a hydrophobic electrically non-conductive layer of synthetic fibres promoting the access of oxygen; (ii) a hydrophilic second layer also containing synthetic fibres, and (iii) a third hydrophobic layer of active carbon. The idea of an oxygen-consuming layer on anodes appeared again [26]. In the preparation of the latter layer an aqueous dispersion of carbon black is mixed with a surfactant of the same type. The finished layer contains stabilized particles of polytetrafluoroethylene (PTFE) covered with carbon black particles. Pores and cracks between the carbon black particles increase the effective catalyst surface. The dispersion is applied on the anodes by dipping or spraying.

A very original solution to the problem of gases in sealed cells was presented by Tserter [27]. These cells comprise two compartments: one having zinc anodes and a first hydrogen electrode, and the other having nickel cathodes and a second hydrogen electrode electrically connected to the first hydrogen electrode. The two compartments share a common gas space. During discharge the battery acts as a conventional battery. However, during charging the evolved gases are immediately consumed allowing the entire battery to be sealed. Additionally, when the battery is fully charged, a noticeable voltage jump helps preventing overcharging and other detrimental effects.

2.1.5. Passivation of the zinc electrodes

Pyun et al. [28] studied the influence of the addition of HgO, PbO, CdO and In₂O₃ in sealed 3.5 Ah cells on the passivation of zinc electrodes. It was found that even with a higher concentration of KOH the zinc electrode could be saved from passivation; a relatively thick (> 500 Å) passive film was created in a 7 M KOH solution whereas in a 1 M KOH solution a less thick (< 100 Å) film was formed. Zincate concentration also affected the reaction. When it increased up to 80 g/l, the limiting current was radically decreased, so that the passivation occurred actively. Obviously, 4 wt.% Hg is beneficial to retard passivation. Higher temperatures can also slow the passivation but thicken the film.

The passivation characteristics of zinc planar electrodes have been examined in 2 M KOH electrolytes containing a variety of additives [29]. The time prior to passivation was measured. Cationic zincate species are not effective in reducing the time taken to passivate the zinc electrode. With zinc anion species it was found that the concentration of the additive was critical, an excessive amount causing spontaneous passivation. Borate and chromate were found to be the most effective anions. Auger analysis of the passivated electrode surfaces suggested that these two additives functioned by different mechanisms. Borate reduced the free hydroxyl species in solution and thus reducing the zincate solubility. Chromate was causing passivation due to its strong oxidizing nature.

The electrochemical characterization of passive zinc was carried out only very recently [30] by potential sweep and impedance spectroscopy methods. These results still must be verified.

2.1.6. Other problems with zinc electrodes

The nature of dissolved zinc species should also be studied in order to improve the performance of zinc alkaline batteries. That is why the structure of zincate complexes in concentrated aqueous hydroxide solutions was studied by Pandya et al. [31]. Results by extended X-ray absorption fine structure analysis (EXAFS) show that the Zn²⁺ ions are in the tetrahedral configuration and the average Zn–O bond distance is 1.97 Å. No evidence of bridging between the tetrahedra was found. In order to determine the structure beyond the first

coordination, EXAFS analysis must include the contribution of the multiple scattering process.

The kinetic analysis of cathodic deposition of zinc in alkaline electrolyte was carried out by Cachet et al. [32], using impedance spectroscopy. This method was used also by Doo et al. [33] for the characterization of roll-pressed porous zinc electrodes in Ni–Zn battery. Jindra and Becker–Roes [34] also studied zinc electrodes by impedance spectroscopy. They found that starved electrolyte conditions had a very little effect on the impedance spectroscopic parameters of the electrode (compared with those of the flooded electrode).

Krejčí et al. [35] studied the transport of zincate ions across a polyolefin microporous membranes (Celgard) using polarography and conductometry. Membranes hinder the diffusion of Zn(OH)₄²⁻ ions to the cathodes. Soluble Nafion, as an ion-exchange modifying agent, was applied to the membranes to increase ionic selectivity. Inverse dependence of membrane conductivity and the flux of Zn(OH)₄²⁻ ions through the microporous membrane was found experimentally. By adjusting suitable coatings it is possible to prepare membranes with optimized resistance and ion-exchange properties, i.e. with desired zinc ion barrier properties.

2.2. Nickel oxide electrodes

These electrodes are still a problem of alkaline accumulators, Ni–Cd, Ni–Fe, Ni–H₂ and Ni–Zn system. Today, two types of electrodes are utilized: sintered and non-sintered. The first type is generally known and described very often in monographs. Sintered-type nickel oxide electrodes are used in Samsung Ni–Zn cells [24], Lawrence Berkeley Laboratory cells [36,37], and Sanyo cells [38,39], whereas the latter type in cells of General Motors [40], Yuasa [41–51], Matsushita [52–56], Japan Storage Battery [57–61] and Sanyo [62,63]. The non-sintered electrodes are provided with various porous nickel supports (mesh, metallic fibres [64], nickel-coated carbon fibres [65], foam metal, hollow metallic fibres [66], etc). The purpose is to substitute an expensive and heavy porous sintered nickel support with a light-weight and cheaper one. At the same time, non-sintered electrodes show small volume changes during cycling. Often non-sintered electrodes are paste-type ones using PTFE as a binder [67,68].

In a subsequent part of this review devoted to practical sealed cells, the various additives to the positive active mass are mentioned. Further, the nickel cathodes for Matsushita alkaline secondary batteries ensuring the prevention of expansion of active masses are described [69]. These electrodes consist of alkaline-resistant metal support and active mass mixtures (powdered spherical nickel hydroxide, containing 0.5–2 wt.% Zn hydroxide).

Due to the high solubility of zinc in alkaline electrolytes the presence of zinc ions at the nickel oxide electrodes in Ni–Zn systems must be assumed. The effect of zinc ions on the electrochemistry of nickel oxide electrodes was studied by slow cyclic voltammetry [70]. It was found that the presence

of zinc ions added to the electrolyte resulted in a decrease of the electrode charging ability. Removing ions which had been added, but leaving lithium ions partially restores the electrode properties. However, zinc ions when incorporated into the lattice structure of nickel oxide improve the performance of porous nickel oxide electrodes [71]. The presence of cobalt in the electrode material diminished substantially the influence of zinc ions on the electrode properties. Cobalt increases the reversibility of the electrochemical reaction.

2.3. Electrolyte

In open or sealed Ni–Zn systems, a ~30% KOH solution which has a maximum ionic conductivity must be used [19,72–75]. In view of problems with changes in the shape of zinc electrodes an electrolyte with a lower KOH concentration [40] is often used as well as various additives: inorganic [17,19,36,76–82] or organic additives [21,22,83,84].

These modified electrolytes are based on KOH solutions with a lower KOH level. Frequently, a 1% LiOH additive is used in the electrolyte to improve the NiOOH electrode charge acceptance. Doddapaneni and Ingersoll [84] recommend a new electrolyte: a KOH solution (15 or 20%) with alkali metal salts of 1,3,5-phenyltrisulfonic acid (29%). These novel electrolyte additives enhance the cycle life of Ni–Zn cells, reduce also the zincate formation, and thereby increase the zinc electrode cycle life. They also seem to coat the surface of the zinc electrode, preventing or inhibiting the shape changes of the zinc electrodes. These additives dramatically reduce the self-discharge rate of the cells.

A quite new electrolyte used in Ni–Zn batteries was reported by Fauvarque and co-workers [85,86]. This electrolyte is an alkaline solid polymer electrolyte (SPE) consisting of poly(ethylene oxide) (PEO) (40–80%), KOH (8–50%) and water (0–20%). Two classes of electrolyte compositions were tested: PEO–KOH–H₂O and PEO–KOH–H₂O with additives (Ca(OH)₂ and several pure or mixed metal oxides). The solid electrolytes were tested in experimental Ni–Zn cells of capacities 80 or 640 mAh. Despite the intermediate values of the faradaic efficiency, it was possible to perform approximately 60 cycles with smaller Ni/SPE/Zn cells without any dendritic growth and shape change. A decrease in capacity was observed during the 47th cycle. The main problem of SPE cells, namely a significant self-discharge, is being intensively solved. As for the quantity of electrolytes in a sealed system, Pyun et al. [87] state that the optimal amount is 1.3 ml KOH/Ah of zinc whereas Nakagawa et al. [72] give the amount 0.2–1 ml KOH/mAh of cathode capacity at the anode side and 0.4–2 ml KOH/Ah of cathode capacity at the cathode side. Onda et al. [88] recommend that the volume of electrolytes be 98–110% of the total free space of the electrode set. Doniat and Bronoel [73] mentioned 250–300 ml of 6–10 M KOH to 55–65 Ah batteries.

2.4. Separation system

The separation system in Ni–Zn cells functions as a barrier to discharged zincate species whilst it allows the passage of charge and oxygen (in the case of sealed systems). The system consists of: (i) a separator for the anode; (ii) a separator for the cathode, and (iii) an electrolyte retainer. The new materials are generally complex, often laminated in structure, forming a separator system rather than a single layer; most frequently used are microporous polyolefines, mainly of poly(propylene) or poly(ethylene). These compounds are also used in other types of alkaline battery [89–91]. In some cases, the membranes are modified: composite sheets consisting of polyolefin porous membranes and polyolefin fibre non-woven fabrics containing oxygen-functional groups. These membranes have a thickness of 10–100 μm, polyolefin fibres of a diameter of 0.1–3 μm, non-woven fabrics of a weight of 20–200 g/m² and thickness 30–500 μm [92]. Polyolefin fibres are coated with a carboxyl group-containing acrylonitrile–styrene copolymer are patented by Ikeda [93–95]. (For more detailed information on poly(propylene), as the most frequently-used material in separation systems of Ni–Zn batteries, refer to the following Refs. [72,96–101]; on cellulose [72,74,96,101–104]; on the less frequently-used polyamide [105–107]; on cellophane [8,108] and on Nylon [72,106,109].) Nakagawa et al. [101] report on sealed secondary zinc batteries with laminated electrolyte retainer–separators consisting of glass fibres or non-woven cellulosic fabrics. Even earlier Nagaro and Uramoto [110] announced separators based on silicate glass fibres and poly(ethylene). Recently, Bronoel and Rouget patented [111] separators mainly composed largely of an ion-exchange material, and to a lesser extent of an oxygen-permeable hydrophobic material. The separators consist of a hydrophobic porous of fibrous material impregnated or filled with an ion-exchange material to prevent migration of zinc.

3. Practical sealed cells

3.1. SAIT (South Korea)

Very recently, the data on sealed Ni–Zn batteries for electric vehicles were published by Pyun et al. of the Samsung Advanced Institute of Technology, South Korea [24]. The Institute has developed two types of sealed cells, namely those with nominal capacities of either 50 or 180 Ah, for electric traction purposes. In the case of the 180 Ah battery, the authors used 15 sets of nickel oxide sintered double electrodes with a total capacity of 201 Ah, and 16 sets of plastic-bonded zinc electrodes with a total capacity of 576 Ah. The separator system consisted of a poly(propylene) non-woven fabric (cathodes) and another kind of poly(propylene) non-woven fabric (anodes). The zinc electrodes were covered with three layers of microporous poly(propylene) membrane (Celgard 3401). The following parameters of the 180 Ah

battery were presented (weight: 300 kg, total voltage: 180 V, specific energy: 65 Wh/kg, specific power: 220 W/kg, and cycle life: 300 cycles). The battery was used in electric-powered vehicles (the Hyundai Excel), weight: 940 kg. Its run was 200 km per single charge. A smaller type — SAIT NZ 50 — capacity: 50 Ah, total voltage: 48 V and weight: 33 kg, was used in an electric-powered scooter (weight: 65 kg, run: 120 km/single charge). For the charging of batteries a three-step charge was suggested:

- step 1: 0.15 C till 60% SOC;
- step 2: 0.05 C till 85% SOC, and
- step 3: 0.03 C till 90% SOC.

Using this three-step regime one can keep the oxygen over-pressure below 1 atm during cycling. At the same time, the discharge capacity (155 Ah) is practically the same as that when using a constant-current charging with 0.1 or 0.2 C as well as for the charge efficiency (97%). The maximum charge voltages and cell pressures are, of course, different: 1.90 or 1.96 V and 0.48 or 0.64 atm at 0.1 or 0.2 C charging, whereas 1.89 V and 0.34 atm at the three-step charging. The three-step charging method is considered valuable for application in existing sealed Ni–Zn batteries for electric vehicles because it enables one to maintain cell pressure below 1 atm, in order to provide a complete sealing of the cell and to maintain a discharge capacity of cells as high as by using conventional charging methods.

This 180 Ah battery is probably the largest at present.

3.2. General Motors

General Motors [40] developed cells containing three full-size zinc electrodes (16 cm × 16 cm × 0.14 cm) composed of ZnO, Ca(OH)₂, Pb₃O₄, and super-wettable poly(ethylene) fibres as a binder. The copper current collector is plated with a Pb–Sn alloy. All the zinc electrodes are pressure-sealed with a talc–CaAc₂ separator. The nickel oxide electrodes (two full-capacity and two half-capacity electrodes with dimensions of 16 cm × 15.6 cm × 0.11 cm) are non-sintered; they contain a nickel brick distex current collector and are preformed in an alkaline electrolyte. All the nickel oxide electrodes are heat-sealed in one layer of Al₂O₃-treated Pellon. The cells have an average capacity of 23.5 Ah and an average coulometric Zn/NiOOH ratio of 3.14 and operate either in starved or flooded electrolyte. They were cycled (charge at 3.92 A for 6 h or to a 2.25 V cut off, discharge at 11.75 A to a 1 V cutoff) to determine the effect of a lower KOH concentration on cell performance. It was found that the decrease in cell capacity, early in cycling, seemed to be the same as for cells with flooded or starved electrolyte, and with 10 or 20 w/o KOH solution; however, cells with 10 w/o KOH solution tended to plateau-off at about 70% of the theoretical capacity late in cycling (after almost 300 cycles). The shape changes of the zinc electrodes were reduced by going from 20 to 10 w/o KOH solutions and by operating in a starved electrolyte condition; however, the low-

temperature properties of 10 w/o KOH solutions are not as favourable as those of the 20 w/o KOH solution.

3.3. Lawrence Berkeley Laboratory

Research on sealed Ni–Zn batteries has been carried out at Lawrence Berkeley Laboratory [36,37] since the 1980s, with particular attention to their application in electromobility.

In order to determine the effect of low-solubility electrolytes on cycle-life performance, experimental Ni–Zn cells were constructed, cycled for extended periods, and then examined in detail. A cell consisted of a zinc electrode (70 mm × 62 mm × 0.76 mm) held between two nickel oxide electrodes. The capacity of each positive electrode was 50% of that of the 1.35 Ah cell design capacity, and the zinc electrode capacity was 4.05 Ah (3:1 ratio). The zinc electrodes consisted of ZnO 93, PbO₂ 2, newsprint (internal wick) 1, and PTFE 4 w/o were provided with the expanded-metal copper mesh electroplated with lead as a current collector. The final porosity of zinc electrodes was about 70%. All zinc electrodes were wrapped with three layers of microporous poly(propylene) membrane (Celgard 3401). At the same time, each layer was individually heat-sealed, when possible, to the edges of the electrode. As positives, the commercial sintered nickel oxide electrodes of a thickness of 0.56 mm and wrapped in a layer of Pellon 2524 (non-woven Nylon wick material) were used in the tested cells. In the sealed, starved-electrolyte cells there was no excess of electrolyte. The cells were subjected to regular cycling performed at a 6 h charge rate of 0.22 A and a 2.7 h discharge rate of 0.5 A, respectively. Cycling continued until the cell capacity dropped and remained below 60% of its original value. Novel electrolytes (KOH–KF, KOH–K₂CO₃, and KOH–KF–K₂CO₃) were used in cells to determine their effect on the change in shape of the zinc electrodes and cell cycle-life performances. The solubility of zinc species in novel electrolytes are 20–25% of that in strong alkaline electrolytes. The changes in shape of the zinc electrodes (after 575 cycles) operating with novel electrolytes were significantly less than those operating in highly alkaline ones. The limited shape change is primarily responsible for the extended cycle-life performance of the cells. A capacity-loss rate of 0.09% per cycle was found. It was again confirmed that sealing the cell eliminates the dendrite formation. Any zinc dendrite produced is quickly oxidized by the oxygen present in the cells. Certain problems appeared in small cells with the evolution of hydrogen. Hydrogen must be recombined with available oxygen, otherwise it accumulates in the cell gasket. In larger cells (20 Ah) a small fuel cell electrode with a platinum catalyst is placed. The nickel oxide electrode limits the life time of these cells and, in order to extend cell cycle life from approximately 500 to 1000 cycles, better nickel electrodes will be required.

These moderately alkaline cells exhibit peak power in the region of 200–300 W/kg throughout cycle life; this is sufficient for electric-vehicle applications.

Later Striebel et al. [37] referred to Ni–Zn (sealed) batteries used in electric vehicles. The cells operated with 17 wt.% KOH electrolyte containing about 27 wt.% supporting electrolyte (2 M K_2CO_3 and 2 M KF) pre-saturated with ZnO. Single cells (1.27 Ah) were charged and discharged with a constant current and with controlled-power discharge profiles, scaled to the predicted mass of a full-size battery. Cells were able to meet the requirements for power discharge specified by the Simplified Federal Urban Driving Schedule (SFUDS) early in cycle life (the first 15 cycles) and achieved 51 SFUDS repetitions (5.1 h) per discharge. Therefore, preliminary results indicate that cells are capable of providing the power for electric-vehicle applications.

3.4. Yuasa

The Japanese firm, a producer of alkaline accumulators, has long been concerned with development of Ni–Zn accumulators, including sealed versions. In recent years, however, they have not published any data on size, capacity, life or other parameters of the batteries. The patent literature, however, contains some particular problems which were studied.

The Yuasa sealed Ni–Zn batteries can probably replace lead/acid batteries in electric vehicles: their weight is only 60% that of lead/acid batteries and they have a better discharge performance at high current drain and a longer cycle life (both of which are even better at low ambient temperatures) [112,113]. At the same time, a special charger for Ni–Zn batteries was developed [112,113]. The charging is completed when a charging voltage of 1.85–2.0 V/cell is reached [114].

At Yuasa, the problem of cooling batteries is also being solved: the battery is formed by alternately stacking heat-collecting plates and plurality of cells to form an integrated body. Heat-releasing plates in cells are connected to heat-collecting plates near the outside of the body-forming coolant passage outside of the heat-releasing plates [115].

A number of Yuasa's patents are concerned with the problem of zinc electrodes. Zinc electrodes based on zinc and ZnO mixed with zinc alloy containing Cd, Pb, Bi, Sn, In, Ga and/or Tl [10] are usually wrapped in non-conducting and alkali-resistant microporous sheets [116]. The particle size of zinc powder is 10–25 and that of ZnO powder is $\geq 0.3 \mu\text{m}$, respectively [117]. Zinc anodes may be provided with a metal current collector of 40–70% porosity [118] made of 10–40wt.%Cu–Sn alloy [119]. At the same time, the shape of a collector may be a honeycomb [120], preferably of the same thickness as the anodes, or a porous mat of sintered copper alloy fibres or copper-coated plastic foams [121]. The copper alloy fibres may have a length of 6–10 mm. The porous mats have a porosity of 80–90%. In another patent [122] it is mentioned that anodes resistant to dendrite growth comprise fatty acid esters having a sorbitan structure [122]. Elsewhere it was proposed to divide zinc anodes in batteries into sections by gas-permeable alkali-resistant resin partitions (Teflon) [123].

In view of internal arrangement, the batteries have an electrode stack comprising cathodes and zinc or ZnO anodes surrounded individually with an electrolyte retainer layer and a separator. The anodes and the stack ends and additional zinc or ZnO anodes fill the spaces between end anodes in the stack and the inner wall of the battery case. The additional anodes may be covered with a separator on the side facing the end anodes and hydrophobic net-shaped spacer on the side facing the case wall [124]. Another patent mentions batteries with a stack of unit cells, each comprising a framed cathode held between a framed anode and an insulating plate with a packing between the cathode and anode frames. The anodes have a zinc plate covered by separators on both sides with retainers between the plate and the separators [125]. Special attention is paid to the electrolyte retainer and separation system, e.g. a retainer composed of cellulose fibres having a diameter of 5–10 μm and length of 0.5–50 mm [102] or a glass fibre retainer [101] surrounding the electrode stack.

Electrolyte-retaining gaps are also mentioned [126]. The voids in the gaps are 15–70% filled with carboxymethyl cellulose which enhances the electrolyte retention, stabilizes electrolyte distribution, and prevents the dendrite formation as well as the deformation of electrodes. The batteries preferably contain non-woven fabrics or poly(propylene) fibres and/or Nylon fibres as an anode electrolyte retainer, non-woven fabrics containing cellulose fibres and optionally synthetic fibres for the cathode electrolyte retainers [72].

Yuasa patented also a relatively complicated separator system: the batteries have a plurality of anode–cathode pairs with a hydrophilic layer between the electrodes and a hydrophobic layer between neighbouring electrode pairs. The hydrophilic layer may be a separator or separator–electrolyte retainer laminate, and the hydrophobic layer may consist of laminates having electrolyte retainer layers in contact with electrodes [127]. A very interesting idea of an oxygen-absorption inhibitor (preferably SnO) in the electrolyte retainer–separator system of anodes has been patented by Nakagawa et al. [107].

Recently, Yuasa has published data on the amount of electrolyte used in sealed batteries: the volume of electrolyte is 98–110% of the total voids in the electrode stack [88], 0.2–1 ml/mAh of anode capacity or 0.4–2 ml/mAh of cathode capacity [72]. The application of a microporous separator in secondary zinc batteries, e.g. made of poly(propylene), is nothing new; Yuasa [100], however, proposed three-layer microporous separators having a thickness of $\leq 100 \mu\text{m}$ and average pore diameter of $\leq 1 \mu\text{m}$. At the same time, one of the layers has a different thermal expansion coefficient compared with that of other separators.

According to another patent [99] the separators for zinc batteries should be alkaline-resistant microporous films with hydrophilic portions for suppression of ZnO deposition which easily-permeate oxygen. Particularly for sealed zinc batteries the addition of poly(ethylene imine) with a mol. wt. $\leq 10\,000$ is recommended [83]. The polymer may exist

either in the electrolyte and the anode or in the electrolyte retainers.

Yuasa is also devoting great efforts to nickel cathodes for alkaline accumulators. Unfortunately, it is rarely stated which of the patent cathodes are suitable for Ni–Zn batteries, and never stated those suitable for sealed Ni–Zn batteries.

What is certain, however, is that in batteries non-sintered cathodes are used. Yuasa patents contain a number of fascinating ideas. For example, according to one patent [41], the cathodes have an electrochemically irreversible conductor layer at the interface between the current collector and active-mass layer. The layer is preferably cobalt oxyhydroxide and is formed from cobalt which has been plated onto the collector (thickness of cobalt layer 2–5 μm [42]) or a cobalt compound electrolytically precipitated onto the collector. The collector may be a nickel foil or mesh, sintered metal fibres or metal foam [41,128]. It was recommended to use the active material particles covered with surface layers of a solid solution of $\text{Ni}(\text{OH})_2$ and $\geq 20\%$ cobalt hydroxide. This surface layer probably prevents permeation of alkali cations and water into particles and lowers the swelling of electrodes [43,44]. The addition of cobalt compounds into the positive active mass is frequently recommended [45–47]. Even a definite internal pore volume (≤ 0.14 ml/g) of powdered $\text{Ni}(\text{OH})_2$ for cathodes is mentioned for nickel cathodes for alkaline batteries [50,51].

3.5. Matsushita

The activity of this firm in the 1990s in the area of sealed Ni–Zn batteries is great. Sealed secondary alkaline zinc batteries of Matsushita contain a material capable of ionizing hydrogen attached to their electrodes at areas exposed to the gas phase in the battery case or to their electrode leads. The material may be platinum-group metals or hydrogen-absorbing alloys [129]. The cylindrical batteries comprise thin nickel cathodes prepared by forming a mixture of (i) nickel hydroxide, a conducting agent, (ii) a rubber binder into sheets, and (iii) a thin zinc anode prepared by forming a mixture of ZnO-based powder and rubber binder into sheets. The electrodes and separators are wound into a cylindrical shape [130]. The Matsushita sealed batteries use separators comprising a non-woven electrolyte retainer laminated with a microporous film. These batteries using non-woven Nylon–poly(alkyl sulfone) laminate separators had low internal pressure during charging and a long cycle life [106]. The cathodes are prepared by pressing a two-dimensional conductive porous sheet (e.g. screen, punched metal, expanded metal) between two spongy nickel plates cutting the integrated body to desired size by laser, and filling with the active mass. These cathodes have improved discharging properties and are suitable for all alkali batteries including Ni–Zn [52]. Their active mass comprises nickel hydroxide, a synthetic elastomeric binder, and a fibrous graphite conductor [53]. The improved nickel cathodes have a layer of $\text{Ni}(\text{OH})_2$ with

a binder on a porous conductive core attached to the layer, a fine carbon powder layer on the active mass layer, and a hydrophobic polymer layer on the carbon layer (graphite). The binder may be carboxymethyl cellulose, poly(vinyl alcohol), fluoro polymers, rubber [54], water glass [55] or vinyl chloride–vinyl acetate copolymer [56]. The batteries of Matsushita are apparently provided with a H–O recombination catalyst mixture comprising 1 volume of catalyst powder and 1–300 volumes of powdered hydrophobic resin. The catalyst mixture may be on top of the electrode stack in the battery case or on the inside wall of the case [131]. Matsushita has patented sealed alkaline batteries in which anodes are coated with water-repellent resin powders; a separator is prepared by adding a surfactant to a polyolefin porous material treated with a sulfate-containing acid. Preferably, poly(propylene) and PTFE–hexafluoropropene copolymer are used. The battery with these components shows excellent gas absorbance [98].

3.6. Cells of Japan Storage Battery

Two development programs were carried out [132]. One program concerned a large-size sealed battery for electric vehicles, and the other dealt with a small-size prismatic sealed battery for portable electronic devices. In the former, an energy density of 72 Wh/kg and cycle life of 180 cycles (at 80% depth-of-discharge) were demonstrated. In the latter, an Ni–Zn battery with rated capacity of 550 mAh was commercialized.

Most of the new patents of Japan Storage Battery concerning sealed Ni–Zn batteries are devoted to positive nickel oxide electrodes and separators for these batteries. For example, graphite or carbon in the form of short fibres resistant to oxidation and dissolution are recommended as a conducting agent in $\text{Ni}(\text{OH})_2$ cathodes. In this case, the weight ratio of ZnO in anodes to $\text{Ni}(\text{OH})_2$ in cathodes has to be ≤ 0.52 [57]. To support the absorption of hydrogen into cathodes, lanthanides and cobalt hydroxide may be added to the $\text{Ni}(\text{OH})_2$ cathodes. Batteries using these cathodes show long cycle life and good reliability [58].

The active material of the Japan Storage Battery cathodes contains 10–20 wt.% Co based on the sum of nickel and cobalt. The cathode grid is made of sintered carbonyl nickel powder and has a porosity of 86–98%. The 1–4 mm thick cathodes have a residual porosity of 30–40%. The particles of the $\text{Ni}(\text{OH})_2$ active material are spherical [59]. The cathodes are manufactured by applying $\text{Ni}(\text{OH})_2$ to the nickel substrates which are immersed in a mixed solution containing Co and 10–80 mol% Cd, then treated with aqueous alkali solutions, and then dried. These cathodes have suppressed swelling properties [60,61]. The batteries have plastic cases, safety valves operating at ≤ 4 kg/cm², electrolytes of mixed NaOH and KOH solutions, and zinc anodes. The batteries show high performance at $> 0^\circ\text{C}$ as well as at $\geq 50^\circ\text{C}$ [59]. The batteries comprise fine porous film separators made of e.g. polysulfone (gas permeability 2–500 s/100 ml)

[97,133] covered with nickel layers (thickness 20–180 Å, porosity 50–85%) on their surfaces. The battery may also have cellulose separators [96,134]. The anodes for secondary alkaline batteries contain ZnO, 10–90 wt.% (based on ZnO) powdered Cd, and Tl oxides [13]. They have a copper current collector uniformly surrounded with fine copper powder, or use an active mass containing fine copper particles. These anode plates are resistant to shape change and growth of dendrites [135]. In an Ni–Zn battery, the total thickness of electrodes and separators ought to be 85–90% of the battery case thickness. Microshort circuits are prevented even when a sponge made of a felt-like three-dimensional porous metal body is used as a support for the active mass of a zinc electrode [136].

3.7. Sanyo

From the open literature it can be seen that Sanyo is intensely involved in developing secondary alkaline batteries including Ni–Zn systems. There is no mention, however, whether these are sealed-type batteries.

Sanyo's nickel cathodes are either sintered-type [38,39] with cobalt oxide coatings on the substrate or non-sintered-type [62,63] with the active mass containing nickel hydroxide particles with average particle size 7–12 µm formed with conductive layers of Ca(OH)₂ and/or Zn(OH)₂ and Co(OH)₂. These cathodes comprise three-dimensional porous grids [62,63,137].

Sanyo's zinc anodes are pasted; at the same time, powdered zinc is treated with additives containing elements with a larger hydrogen over-voltage and a more noble redox potential than zinc or ZnO. The additives are uniformly distributed in the anodes and the dendrite formation is effectively suppressed [14]. Also, alkaline earth metal–zinc alloys suppress dendrite formation [11]. Electrodes are prepared by reacting zinc powder with thallium compounds in water, kneading the product with binder and applying the paste on a collector. For example, a mixture of ZnO, Zn, and Tl₂O₃ is mixed with water and kneaded with fluoropolymer powder and applied to a copper collector [15]. Thallium may be a component in the form of an intermetallic compound, e.g. In–Tl [12]. To suppress the dissolution of zinc in electrolytes, the addition of a small amount of phosphate esters is recommended [138].

Sanyo's batteries use multilayered separators containing non-woven Nylon fabrics and hydrophobic microporous films of poly(propylene) partially coated with surfactant films (poly(oxyethylene alkyl aliphatic acid amide)) [109].

3.8. Energy Research Corporation

According to a patent by Charkey [139] it appears that the activity of the Energy Research Corporation in the area of sealed zinc batteries has not yet been achieved. According to this patent the anodes of a battery are comprised of a zinc-

active material together with Ca(OH)₂ and a conductive matrix including a metallic oxide (PbO, Bi₂O₃, CdO, Ga₂O₃, Tl₂O₃) which is more electropositive than zinc. In order to promote gas recombination, the zinc electrode is configured as a split electrode to provide good access of oxygen generated in the battery. In addition, the gas-recombination element based on CdO is included. A sealed rechargeable Ni–Zn battery with a rated capacity of 15 Ah was constructed with seven zinc and six nickel oxide electrodes and with 20% KOH electrolyte. During cycling (charge with 3.83 A for 3.6 h, discharge with 5 A for 2.4 h, i.e. 80% depth-of-discharge) the capacity of the battery remained over 100% of rated for over 400 cycles. Even after 500 cycles the capacity was still at 85%. A maximum pressure of about 20 psig after charge and a pressure of less than 5 psig after discharge was measured. No evidence of a change in the shape was seen at the edges of the zinc electrode.

4. Conclusions

During the last five years, there has been no significant progress in the area of sealed Ni–Zn cells. Judging from great number of patents from this period, it can be said that intensive research has been carried out in view of ecological requirements, because the Ni–Zn system is a suitable substitute for the Ni–Cd system. Ni–Zn accumulators remain a serious candidate for electromobility. The biggest problem with zinc electrodes is their shape changes during cycling. With positive electrodes there appears to be a slight tendency to light and inexpensive non-sintered nickel porous supports based on fibres.

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References

- [1] F.R. McLarnon and E.J. Cairns, *J. Electrochem. Soc.*, 138 (1991) 645–664.
- [2] K. Bass, P.J. Mitchell, G.D. Wilcox and J. Smith, *J. Power Sources*, 35 (1991) 333–351.
- [3] J. Jindra, *J. Power Sources*, 37 (1992) 297–313.
- [4] J. McBreen, *J. Power Sources*, 51 (1994) 37–44.
- [5] J. McBreen, *Ext. Abstr., 188th Meet. The Electrochemical Society, Proc. Vol. 95-2*, 1995, p. 32.
- [6] E. Frackowiak, *Power Sources*, 13 (1991) 225–235.

- [7] R. Jain, T.C. Adler, F.R. McLarnon and E.J. Cairns, *J. Appl. Electrochem.*, 22 (1992) 1039–1048.
- [8] A. Renuka, A. Veluchamy, N. Venkatakrishnan, S.S. Begun, V.R. Chidambaram and R. Sabapathi, *J. Appl. Electrochem.*, 22 (1992) 182–184.
- [9] M. Suga, N. Kuroda and S. Akita, *Eur. Patent Applic. EP No. 578 501* (1994); *Chem. Abstr.*, 120 (1994) 139 222.
- [10] T. Onda, K. Okabe, K. Fujii and M. Yamane, *Jpn. Patent JP No. 0 428 160* (1992); *Chem. Abstr.*, 117 (1992) 30 534.
- [11] S. Furukawa, M. Nogami and M. Tadokoro, *Jpn. Patent JP No. 03 122 235* (1991); *Chem. Abstr.*, 115 (1991) 23 6319.
- [12] S. Furukawa, M. Nogami and M. Todokoro, *Jpn. Patent JP No. 03 297 057* (1991); *Chem. Abstr.*, 116 (1992) 177 762.
- [13] K. Nishama, *Jpn. Patent No. 04 179 051* (1992); *Chem. Abstr.*, 117 (1992) 195 236.
- [14] S. Furukawa, M. Tadokoro and M. Nogami, *Jpn. Patent JP No. 03 127 451* (1991); *Chem. Abstr.*, 115 (1991) 139 629.
- [15] Y. Fujiwara and Y. Ishikura, *Jpn. Patent JP No. 03 152 869* (1991); *Chem. Abstr.*, 115 (1991) 186 784.
- [16] K. Okabe, Y. Eguchi, T. Atsuda and K. Fujii, *Jpn. Patent JP No. 04 126 356* (1992); *Chem. Abstr.*, 117 (1992) 154 561.
- [17] R. Shivkumar, G. Paruthimal Kalaignam and T. Vasudevan, *J. Power Sources*, 55 (1995) 53–62.
- [18] E.M. Jost, *US Patent No. 3 485 673* (1969).
- [19] A. Renuka, A. Veluchamy and N. Venkatakrishnan, *J. Power Sources*, 34 (1991) 381–385.
- [20] Z. Baohong, Ch. Meng, Xu Dongari and W. Yindong, *Ext. Abstr., 46th ISE Meet., Xiamen, P.R. China, 1995*, Vol. 2, Abstr. No. 5-43.
- [21] V.V. Bocharov, V.E. Dmitrenko, Yu.M. Volkov, V.V. Berendt, V.D. Sudejchenko, A.E. Frolov, T.V. Balashova, E.A. Ranneva and V.M. Zlobin, *USSR SU Patent No. 1 311 553* (1992); *Chem. Abstr.*, 119 (1993) 52 899.
- [22] V.V. Bocharov, V.E. Dmitrenko, M.K. Ostrovskii, V.V. Berendt, V.D. Budajchenko, A.E. Frolov, T.V. Balashova, V.M. Zlobin and N.I. Maznichenko, *USSR SU Patent No. 1 457 760* (1992); *Chem. Abstr.*, 118 (1993) 258 137.
- [23] Y.B. Pyun, H. Chang and M.E. Alexeeva, *Ext. Abstr., 188th Meet. The Electrochemical Society, 1995*, Vol. 95-2, Abstr. No. 39.
- [24] Y.B. Pyun, H. Chang and B.H. Jung, *Ext. Abstr., 46th ISE Meet., Xiamen, China, 1995*, Vol. 2, Abstr. No. 5-36.
- [25] G. Simon, K. Kleinsorgen and U. Koehler, *Ger. Offen. DE NO. 3 929 304* (1991); *Chem. Abstr.*, 114 (1991) 210 630; *US Patent No. 5 122 426* (1992); *Chem. Abstr.*, 117 (1992) 216 250.
- [26] Ch. Klaus, *Ger. Offen. DE No. 4 326 944* (1995); *Chem. Abstr.*, 122 (1995) 165 607.
- [27] B. Tsenler, *US Patent No. 5 143 799* (1992); *Chem. Abstr.*, 117 (1992) 254 904.
- [28] Y.B. Pryun, H. Chang and M.E. Alexeeva, *Ext. Abstr., 188th Meet. The Electrochemical Society, 1995*, Vol. 95-2, Abstr. No. 37.
- [29] K. Bass, P.J. Mitchell, G.D. Wilcox and J. Smith, *J. Power Sources*, 39 (1992) 273–284.
- [30] K.M. Ismail and D.D. Macdonald, *Ext. Abstr., 188th Meet. The Electrochemical Society, 1995*, Vol. 95-2, Abstr. Nos. 22 and 23, pp. 37–40.
- [31] K.I. Pandya, A.E. Russell, D.E. Sayers, J. McBreen and W.E. O'Grady, *Ext. Abstr., 188th Meet. The Electrochemical Society, 1995*, Vol. 95-2, Abstr. No. 21, pp. 35–36.
- [32] C. Cachet, B. Saidami and R. Wiert, *J. Electrochem. Soc.*, 138 (1991) 678.
- [33] S.G. Doo, H.B. Lee and J.Y. Oh, *Ext. Abstr., 188th Meet. The Electrochemical Society, 1995*, Vol. 95-2, Abstr. No. 36, p. 59.
- [34] J. Jindra and D. Becker-Roes, *J. Power Sources*, 45 (1993) 55–60.
- [35] I. Krejčí, P. Vanýsek and A. Trojánek, *J. Electrochem. Soc.*, 140 (1993) 2279–2284.
- [36] T.C. Adler, F.R. McLarnon and E.J. Cairns, *J. Electrochem. Soc.*, 140 (1993) 289–294.
- [37] K.A. Striebel, F.R. McLarnon and E.J. Cairns, *J. Power Sources*, 47 (1994) 1–11.
- [38] K. Otsuki and N. Ikeda, *Jpn. Patent JP No. 0 475 257* (1992); *Chem. Abstr.*, 117 (1992) 93 791.
- [39] K. Otsuki, *Jpn. Patent JP No. 0 475 255* (1992); *Chem. Abstr.*, 117 (1992) 115 192.
- [40] E.G. Gagnon, *J. Electrochem. Soc.*, 128 (1991) 3173–3176.
- [41] M. Oonishi, M. Watada and M. Oshitani, *Jpn. Patent JP No. 02 265 165* (1990); *Chem. Abstr.*, 114 (1991) 232 044.
- [42] M. Oonishi and M. Oshitani, *Jpn. Patent JP No. 0 378 966* (1991); *Chem. Abstr.*, 115 (1991) 53 461.
- [43] M. Oshitani and M. Watada, *Jpn. Patent JP No. 0 362 457* (1991); *Chem. Abstr.*, 115 (1991) 124 102.
- [44] M. Watada, M. Oonishi and M. Oshitani, *Jpn. Patent JP No. 0 378 965* (1991); *Chem. Abstr.*, 115 (1991) 139 634.
- [45] Y. Eguchi and M. Yamane, *Jpn. Patent JP No. 0 426 058* (1992); *Chem. Abstr.*, 117 (1992) 30 532.
- [46] M. Oonishi, T. Horii and M. Oshitani, *Jpn. Patent JP No. 04 215 248* (1992); *Chem. Abstr.*, 118 (1993) 94 000.
- [47] Y. Eguchi and M. Yamana, *Jpn. Patent JP No. 0 439 861* (1992); *Chem. Abstr.*, 117 (1992) 52 463.
- [48] Y. Eguchi, T. Onda, H. Yufu and M. Yamana, *Jpn. Patent JP No. 0 355 758* (1991); *Chem. Abstr.*, 115 (1991) 139 606.
- [49] M. Watada, J. Matsumara, N. Myake and M. Oshitani, *Jpn. Patent JP No. 06 260 166* (1994); *Chem. Abstr.*, 122 (1995) 60 177.
- [50] M. Oonishi and M. Oshitani, *Jpn. Patent JP No. 05 182 662* (1993); *Chem. Abstr.*, 120 (1994) 195 901.
- [51] S. Mukai, M. Watada and M. Oshitani, *Jpn. Patent JP No. 0 613 075* (1994); *Chem. Abstr.*, 120 (1994) 275 454.
- [52] T. Iwaki, Y. Moriwaki and A. Shintani, *Jpn. Patent JP No. 04 126 359* (1992); *Chem. Abstr.*, 117 (1992) 154 514.
- [53] T. Iwaki, Y. Morikawa and A. Shintani, *Jpn. Patent JP No. 03 149 753* (1991); *Chem. Abstr.*, 116 (1992) 177 702.
- [54] T. Iwaki, K. Yamamura, H. Sera, Y. Tsuji and N. Maekawa, *Jpn. Patent JP No. 06 275 261* (1994); *Chem. Abstr.*, 122 (1995) 352 252.
- [55] H. Matsuda, K. Oota, T. Kimura, K. Komori and Y. Toyoguchi, *Jpn. Patent JP No. 05 314 981* (1993); *Chem. Abstr.*, 120 (1994) 195 948.
- [56] Y. Toyoguchi, H. Matsuda, K. Oota, K. Komori and T. Kimura, *Jpn. Patent JP No. 05 314 980* (1993); *Chem. Abstr.*, 120 (1994) 195 947.
- [57] K. Nishiyama, *Jpn. Patent JP No. 03 171 565* (1991); *Chem. Abstr.*, 115 (1991) 259 917.
- [58] H. Yasuda, *Jpn. Patent JP No. 04 366 553* (1992); *Chem. Abstr.*, 118 (1993) 216 637.
- [59] T. Sonoda and H. Yasuda, *Eur. Patent Applic. EP No. 512 565* (1992); *Chem. Abstr.*, 118 (1993) 128 385.
- [60] A. Kawakami, Y. Ito and H. Yasuda, *Jpn. Patent JP No. 0 613 076* (1994); *Chem. Abstr.*, 120 (1994) 222 485.
- [61] K. Nishiyama and H. Yasuda, *Jpn. Patent JP No. 04 337 246* (1992); *Chem. Abstr.*, 118 (1993) 172 567.
- [62] S. Yasuoka, M. Nogami, M. Yano, K. Nishio and T. Saiko, *Jpn. Patent JP No. 07 201 326* (1995); *Chem. Abstr.*, 123 (1995) 291 861.
- [63] S. Yasuoka, M. Nogami, K. Nishio and T. Saito, *Jpn. Patent JP No. 07 201 327* (1995); *Chem. Abstr.*, 123 (1995) 291 862.
- [64] W. Taucher, T.C. Adler, F.R. McLarnon and E.J. Cairns, *Ext. Abstr., 188th Meet. The Electrochemical Society, 1995*, Vol. 95-2, Abstr. No. 132.
- [65] M. Eisenberg, *Proc. 34th Int. Power Sources Symp., 1990*, pp. 232–234.
- [66] M. Konishi and M. Koseki, *Jpn. Patent JP No. 0 495 347* (1992); *Chem. Abstr.*, 117 (1992) 115 203.
- [67] K. Watanabe, H. Inamura and M. Koseki, *Jpn. Patent JP No. 06 140 037* (1994); *Chem. Abstr.*, 121 (1994) 113 350.

- [68] K. Hata, K. Isawa, K. Miyamoto and H. Teraoka, *Jpn. Patent JP No. 04 160 755* (1992); *Chem. Abstr.*, 117 (1992) 154 585; *Jpn. Patent JP No. 04 160 756* (1992); *Chem. Abstr.*, 117 (1992) 154 586.
- [69] K. Ookawa, H. Mikurya, T. Akutsu, K. Aoki and H. Kaiza, *Jpn. Patent JP No. 07 192 732* (1995); *Chem. Abstr.*, 123 (1995) 261 772.
- [70] I. Krejčí and P. Vanýšek, *J. Power Sources*, 47 (1994) 79–88.
- [71] D.H. Fritts, in R.G. Gunther and S. Gross (eds.), *Proc. Symp. on the Ni Electrode*, Proc. Vol. 82-4, p. 175. The Electrochemical Society, Pennington, NJ, USA, 1982.
- [72] H. Nakagawa, T. Bogauchi and N. Kishimoto, *Jpn. Patent JP No. 06 283 194* (1994); *Chem. Abstr.*, 122 (1995) 85 425.
- [73] D. Doniat and G. Bronoel, *Eur. Patent Applic. EP No. 423 385* (1991).
- [74] R.R. Dzhuraev, M.S. Zubov and A.V. Kotov, *Zh. Prikl. Khim.* (St. Petersburg), 65 (1992) 2695–2699.
- [75] V.D. Gud, V.A. Nikolskii, Z.P. Arkhangel'skaya and G.N. Reshetova, *Zh. Prikl. Khim.* (Leningrad), 63 (1990) 2650–2653.
- [76] R.F. Plivelich, F.R. McLarnon and E.J. Cairns, *J. Appl Electrochem.*, 25 (1995) 433–440.
- [77] T. Adler, F.R. McLernon and E.J. Cairns, *US Patent No. 5 302 475* (1994).
- [78] M. Eisenberg, *US Patent No. 5 215 836* (1993).
- [79] G. Bronoel, A. Millot and N. Tassin, *J. Power Sources*, 34 (1991) 243–245.
- [80] K. Bass, P.J. Mitchell, G.D. Wilcox and J. Smith, *Int. Chem. Eng. Symp. Ser.*, (1992) 127; *Electrochem. Eng. Environ.*, 92 (1992) 269–281; *Chem. Abstr.*, 118 (1993) 42 222.
- [81] K. Bass, *Diss. Abstr. Int. B*, 53 (1992) 1521; *Chem. Abstr.*, 120 (1994) 275 306.
- [82] S. Müller, F. Holzer, Ch. Schlatter, C. Comminellis and O. Haas, *Ext. Abstr.*, 188th Meet. The Electrochemical Society, 1995, Vol. 95-2, p. 53–4.
- [83] K. Okabe, Y. Fujita, T. Onda and K. Fujii, *Jpn. Patent JP No. 06 275 310* (1994); *Chem. Abstr.*, 122 (1995) 85 412.
- [84] N. Doddapaneni and D. Ingersoll, *Ext. Abstr.*, 188th Meet. The Electrochemical Society, 1995, Vol. 95-2, Abstr. No. 61-2.
- [85] J.F. Fauvarque, S. Guinot, N. Bouzin, E. Salmon and J.F. Penneau, *Electrochim. Acta*, 40 (1995) 2449–2453.
- [86] S. Guinot, N. Bouzin, J.F. Penneau and J.F. Fauvarque, *Ext. Abstr.*, 188th Meet. The Electrochemical Society, 1995, Vol. 95-2, p. 57–58.
- [87] Y.B. Pyun, H. Chang and Y.S. Sou, *Han'guk Pustik Hekhoechi*, 24 (1995) 14–22; *Chem. Abstr.*, 123 (1995) 148 916.
- [88] T. Onda, K. Fujii and K. Okabe, *Jpn. Patent JP No. 0 696 795* (1994); *Chem. Abstr.*, 121 (1994) 39 215.
- [89] J.S. Chen, F.R. McLernon and E.J. Cairns, *J. Power Sources*, 39 (1992) 333–348.
- [90] R. Fleming, *Prog. Batteries Solar Cells*, 9 (1990) 58–66.
- [91] D. Hoffmann, *Prog. Batteries Solar Cells*, 9 (1990) 48–57.
- [92] I. Ichimukizaka and K. Ikeda, *Jpn. Patent JP No. 0 773 863* (1995); *Chem. Abstr.*, 122 (1995) 295 430.
- [93] K. Ikeda, *Jpn. Patent JP No. 06 187 964* (1994); *Chem. Abstr.*, 121 (1994) 234 708.
- [94] K. Ikeda, *Jpn. Patent JP No. 06 187 963* (1994); *Chem. Abstr.*, 121 (1994) 234 709.
- [95] K. Ikeda, *Jpn. Patent JP No. 06 187 962* (1994); *Chem. Abstr.*, 121 (1994) 234 710.
- [96] H. Yasuda and M. Ushio, *Jpn. Patent JP No. 05 343 096* (1993); *Chem. Abstr.*, 120 (1994) 196 006.
- [97] K. Nishama and M. Ushio, *Jpn. Patent JP No. 05 343 095* (1993); *Chem. Abstr.*, 120 (1994) 196 005.
- [98] T. Iwaki, K. Yamamura and H. Seri, *Jpn. Patent JP No. 06 181 068* (1994); *Chem. Abstr.*, 121 (1994) 209 250.
- [99] T. Kishimoto, M. Yamane, T. Bogauchi and Y. Eguchi, *PCT Int. Applic. WO No. 9 212 544* (1992); *Chem. Abstr.*, 117 (1992) 216 268.
- [100] K. Murata, K. Takeuchi and H. Mishima, *Jpn. Patent JP No. 04 294 054* (1992); *Chem. Abstr.*, 118 (1993) 42 332.
- [101] H. Nakagawa, S. Kimura, N. Kishimoto and T. Bogauchi, *Jpn. Patent JP No. 0 714 604* (1995); *Chem. Abstr.*, 122 (1995) 244 134.
- [102] T. Bogauchi, N. Kishimoto and M. Yamane, *Jpn. Patent JP No. 05 303 978* (1993); *Chem. Abstr.*, 120 (1994) 81 690.
- [103] H. Matsuda, K. Oota, T. Kimura, K. Komoti and Y. Toyoguchi, *Jpn. Patent JP No. 05 290 829* (1993); *Chem. Abstr.*, 121 (1994) 81 652.
- [104] T.N. Toroptseva, V.I. Baulov, M.S. Zubov, I.V. Sporykhina, T.V. Shcherbakova, Yu.V. Tikhomirov and L.A. Khazova, *USSR Patent SU No. 1 739 403* (1992); *Chem. Abstr.*, 119 (1993) 12 103.
- [105] H. Abe, *Jpn. Patent JP No. 04 163 857* (1992); *Chem. Abstr.*, 117 (1992) 154 604.
- [106] T. Senoo, I. Matsumoto and K. Yamasaka, *Jpn. Patent JP No. 04 206 456* (1992); *Chem. Abstr.*, 117 (1992) 237 209.
- [107] H. Nakagawa, S. Kimura, N. Kishimoto and T. Bogauchi, *Jpn. Patent JP No. 06 267 587* (1994).
- [108] K. Okabe, Y. Fujita, A. Matsuo and K. Fujii, *Jpn. Patent JP No. 0 722 028* (1995); *Chem. Abstr.*, 122 (1995) 244 135.
- [109] M. Yano, M. Nogami, K. Nishio, T. Saito and T. Ito, *Jpn. Patent JP No. 0 765 814* (1993); *Chem. Abstr.*, 122 (1995) 295 419.
- [110] H. Nagaro and H. Uramoto, *Jpn. Patent JP No. 03 196 459* (1991); *Chem. Abstr.*, 116 (1992) 87 683.
- [111] G. Bronoel and R. Rouget, *Fr. Pending Applic. FR No. 2 708 382* (1995); *Chem. Abstr.*, 122 (1995) 318 681.
- [112] T. Nukuda, K. Fujii and M. Yamane, *Yuasa Jiho*, 60 (1990) 19–23; *Chem. Abstr.*, 114 (1991) 105 661.
- [113] H. Nakagawa, K. Fujii and M. Yamane, *Yuasa Jiho*, 72 (1992) 13–22; *Chem. Abstr.*, 117 (1992) 93 641.
- [114] T. Atsuta, Y. Eguchi, K. Okabe and K. Fujii, *Jpn. Patent JP No. 03 134 968* (1991); *Chem. Abstr.*, 115 (1991) 139 652.
- [115] T. Oreda, K. Mori and K. Fujii, *Jpn. Patent JP No. 0 620 716* (1994); *Chem. Abstr.*, 120 (1994) 249 295.
- [116] K. Okabe, T. Onda and K. Fujii, *Jpn. Patent JP No. 0 689 719* (1994); *Chem. Abstr.*, 121 (1994) 61 551.
- [117] K. Okabe, K. Fujii and Y. Fujita, *Jpn. Patent JP No. 06 124 706* (1994); *Chem. Abstr.*, 121 (1994) 137 540.
- [118] K. Okabe, T. Onda and K. Fujii, *Jpn. Patent JP No. 05 182 686* (1993); *Chem. Abstr.*, 119 (1993) 164 135.
- [119] Y. Eguchi, T. Onda, H. Yufu and K. Fujii, *Jpn. Patent JP No. 0 304 449* (1991); *Chem. Abstr.*, 114 (1991) 189 171.
- [120] Y. Nakazawa, M. Yamane and T. Bogauchi, *Jpn. Patent JP No. 05 325 952* (1993); *Chem. Abstr.*, 120 (1994) 168 849.
- [121] H. Nakagawa, T. Bogauchi, N. Kishimoto and M. Yamane, *Jpn. Patent JP No. 0 706 758* (1995); *Chem. Abstr.*, 122 (1995) 192 529.
- [122] K. Okabe, T. Onda, K. Fujii, M. Yamane, N. Matoba, S. Nakajima, K. Rikihisa and K. Adachi, *Jpn. Patent JP No. 07 161 375* (1995); *Chem. Abstr.*, 123 (1995) 204 393.
- [123] H. Nakagawa, K. Okabe, K. Fujii and M. Yamane, *Jpn. Patent JP No. 04 206 468* (1992); *Chem. Abstr.*, 117 (1992) 237 212.
- [124] H. Nakagawa, S. Kimura, T. Bogauchi and N. Kishimoto, *Jpn. Patent JP No. 06 124 724* (1994); *Chem. Abstr.*, 121 (1994) 87 602.
- [125] M. Watada, M. Oonishi, K. Takeuchi, R. Okuyama, S. Yamada and K. Matsumura, *Jpn. Patent JP No. 04 296 468* (1992); *Chem. Abstr.*, 118 (1993) 63 279.
- [126] Y. Eguchi, K. Fujii, T. Atsuta and K. Okabe, *Jpn. Patent JP No. 03 230 480* (1991); *Chem. Abstr.*, 116 (1992) 44 150.
- [127] T. Bonochi, H. Nakagawa, N. Kishimoto and M. Yamane, *Jpn. Patent JP No. 0 696796* (1994); *Chem. Abstr.*, 121 (1994) 39 216.
- [128] Y. Harada, *Jpn. Patent JP No. 0 402 048* (1992); *Chem. Abstr.*, 116 (1992) 177 771.
- [129] T. Senoo, I. Matsumoto and K. Yamasaka, *Jpn. Patent JP No. 04 206 475* (1992); *Chem. Abstr.*, 117 (1992) 237 216.
- [130] T. Iwaki, K. Yamamura and Y. Tsuji, *Jpn. Patent JP No. 05 205 772* (1993); *Chem. Abstr.*, 119 (1993) 184 867.
- [131] E. Kadochi and I. Matsumoto, *Jpn. Patent JP No. 05 182 669* (1993); *Chem. Abstr.*, 120 (1994) 81 593.

- [132] H. Yasuda and K. Nakamitsu, *GS News Tech. Rep.*, 54 (1995) 83–88 (in Japanese); *Chem. Abstr.*, 124 (1996) 12 246.
- [133] K. Nishama, *Jpn. Patent JP No. 04 179 048* (1992); *Chem. Abstr.*, 117 (1992) 237 196.
- [134] H. Yasuda and M. Ushio, *Jpn. Patent JP No. 05 343 044* (1993); *Chem. Abstr.*, 120 (1994) 196 007.
- [135] H. Yasuda and K. Nishiyama, *Jpn. Patent No. 04 337 248* (1992); *Chem. Abstr.*, 118 (1993) 151 040.
- [136] K. Nishama and M. Ushio, *Jpn. Patent No. 05 343 094* (1993); *Chem. Abstr.*, 120 (1994) 168 891.
- [137] M. Nogami, M. Yeno, S. Yasuoka, K. Nishio and T. Saito, *Jpn. Patent JP No. 07 201 328* (1995); *Chem. Abstr.*, 123 (1995) 291 863.
- [138] M. Yano, M. Nogami, K. Nishio and T. Saito, *Jpn. Patent JP No. 07 161357* (1995); *Chem. Abstr.*, 123 (1995) 291 800.
- [139] A. Charkey, *US Patent No. 5 460 899* (1995); *Chem. Abstr.*, 124 (1996) 12 343.