

Fabrication of Industrial Ni-Zn Pocket-Type Secondary Battery

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Abstract

We fabricated the industrial-scale high-capacity Ni-Zn pocket-type secondary batteries with 100-Ah capacity, and connected in parallel to produce 300-Ah and optimized the performances. The pocket-type battery, which has a high capacity, has various advantages, however, due to a flooded-type structure containing a large volume of electrolytes, operational problems such as evaporation of the electrolyte and dissolution of active materials including zinc have been noted. To resolve these problems, we formulated different compositions of active materials and fabricated 100-Ah batteries and constructed 300-Ah large-capacity system through various pretreatments. In the 100-Ah battery, we identified the effects of binders—ingredients of the active material—and different electrolyte compositions. For the 300-Ah system, the effect of coating the membranes with polymer gel is tested. Binders and electrolytes play critical roles in enhancing the pocket-type battery performance; and thus we tried various mixtures of binders and electrolytes and optimized this battery for industrial applications. The 300-Ah pocket-type system coated with a gel polymer achieved the performance maintaining 75% retention capacity at 80% DOD for 350 cycles and showing sufficient performance for commercialization.

Key words : Ni-Zn secondary battery, pocket-type, fabrication, industrial-scale

1. Introduction

The Ni-Zn secondary battery, a type of alkaline aqueous solution battery like Ni-Fe, Ni-Cd, and Ni-MH batteries, has a long lifetime and wide variability in its charge and discharge rates. Depending on the type of anode, this battery has prominent advantages in terms of the voltage, size, weight, price and performance including the charge and discharge rate and the storage lifetime. The open-circuit voltage of the Ni-Zn battery is 1.73 V, which is greater than 1.2 V of Ni-Cd and Ni-MH batteries. Because this advantage provides a high energy density and reduces the number of the cells in a high-voltage battery, both the battery price and internal battery resistance can be greatly reduced [1, 2]. On the other hand, recent

studies on nickel secondary batteries have only focused on the development of sealed-type, square, and maintenance-free (MF) batteries, considering the interest in environmental friendly, high-density, and high-performance batteries [3, 4]. Few studies on the industrial pocket-type battery considered in this article have been performed. Park constructed the Ni-MH based pocket-type high-capacity battery [5], and ENER-GREEN, Inc. commercialized the first environmental friendly pocket-type Ni-MH battery [6, 7]. The pocket-type Ni-Zn secondary battery with the 440-V/600-Ah high-capacity for railcars, which was first developed by Drumm in 1931, had been used until 1949, but then essentially disappeared in the market due to the advent of the fossil-fueled engine [8, 9].

In this work, we reconsidered the Ni-Zn pocket-type battery to overcome the sealed-type and MF batteries with capacity limitations. The PowerGenix

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battery, which is represented as a sealed-type paste battery at the current technological level, has a considerably limited capacity of 80 Ah [10], but the pocket-type battery can be produced with a capacity higher than 200 Ah. Hence, it is necessary to develop the technologies related to the Ni-Zn pocket-type battery and commercialize an environmental friendly, low-cost, high-capacity, and high-output battery in order to actively respond to the replacement of existing lead and cadmium batteries.

The largest problems with the Ni-Zn battery are that the cathode materials, including zinc or zinc oxide, dissolve in alkaline electrolytes [11] and that this phenomenon generates dendrite electro deposition on the surface of the cathode plates [12]. In particular, the plates of the pocket-type battery are of the flooded type, where the plates are completely submerged in the alkaline electrolyte; thus, zinc, the electrode active material, is likely to be dissolved in the electrolyte. Moreover, the powder-type active material in the cathode plates is leaked through the pores on the plates, causing various battery performance failures, including capacity and lifetime reduction.

The electrodes of the pocket-type battery consist of a porous metal strip with artificial micro pores, making their surfaces very rough. These porous strips become the path through which ions are conducted for the active material and for the electrolyte and current collector at the same time; thus, it is highly possible that the zinc and zinc oxide, which are dissolved into the electrolyte, could be randomly precipitated on the surface of the current collector. The dendrite stemmed from the precipitation causes a short inside circuit, and this is inevitably to resolve in battery development. Various techniques, including not only reforming the cathode material but also adding a variety of additives [13] and enlarging the grains of the cathode material to prevent the cathode material from easily leaking from the strip, have been applied to fabricate battery plates. In addition, rectangular pellets (hereinafter called "square chips"), which were produced by pressing mixes of powdered active materials and binders in a mold, were selected for the plates in order to increase the collectivity of the cathode material,

To deal with the contact problem between the current collector and the electrolyte, including dendrite generation, gas releases, and erosion of the current collector, the electrode surfaces were coated with the high-cohesive polymer or a gel polymer that was sprayed on the electrode surfaces and the gaps between the membranes. Additionally, the composition of the electrolyte was controlled to improve the battery reaction, and to cope with the increased solubility of the charge material in a highly concentrated electrolyte solution. Appropriate pretreatments, including selections of a proper buffer material, additives, and membranes, were conducted [14, 15, 16, 17].

2. Fabrication of the high-capacity Ni-Zn pocket-type battery

2.1. Fabrication of plates and 100-Ah batteries

It is crucial to determine the appropriate length, width, and depth of the plates for the battery because the capacity and properties of the electrode depend on them. In addition, when the number of laminated layers of the total plates changes, the energy density can vary according to the battery volume. Particularly, in the case of the pocket-type battery, different widths of the Ni strips and the current collectors could change the collectivity of the active material in the electrodes. Because a larger strip allows more active material to be charged, the energy density of the battery per weight increases, but in turn, the contact resistance between the current collector and the active material increases, which affects the discharge capacity and the rate capability. Thus we tested the electrode properties of commercial Ni strips in different sizes.

Fig. 1 depicts the images of the electrode components in sequence of the plate production processes as follows.

① Two perforated Ni strips ($T = 0.1$ mm, $W = 16, 23, 25$ mm) are corrugated in a U shape and put together to form a pocket type (the Ni strips are called "strips" hereinafter). Then, active materials are evenly injected into the pocket (Fig. 1 (a)).

② The active-material-filled strips are laminated in the direction of their sides to meet the designed

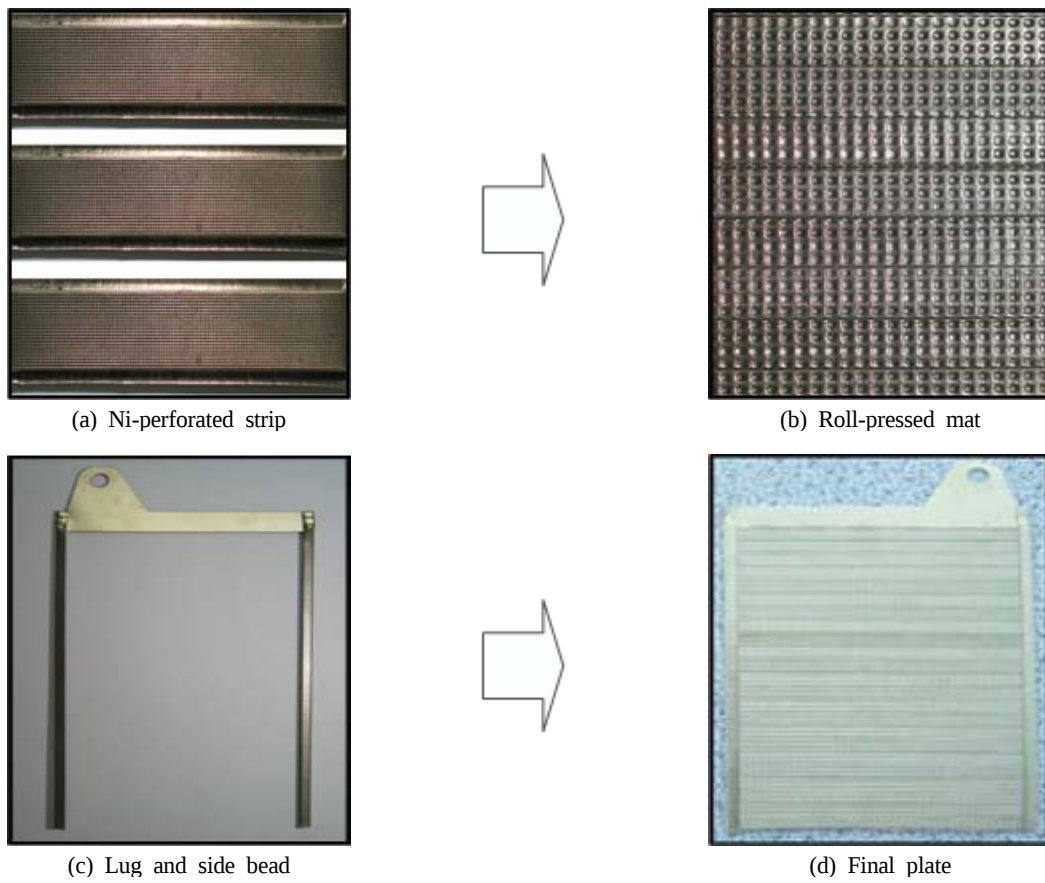


Fig. 1. Mimetic diagram of the plate production processes.

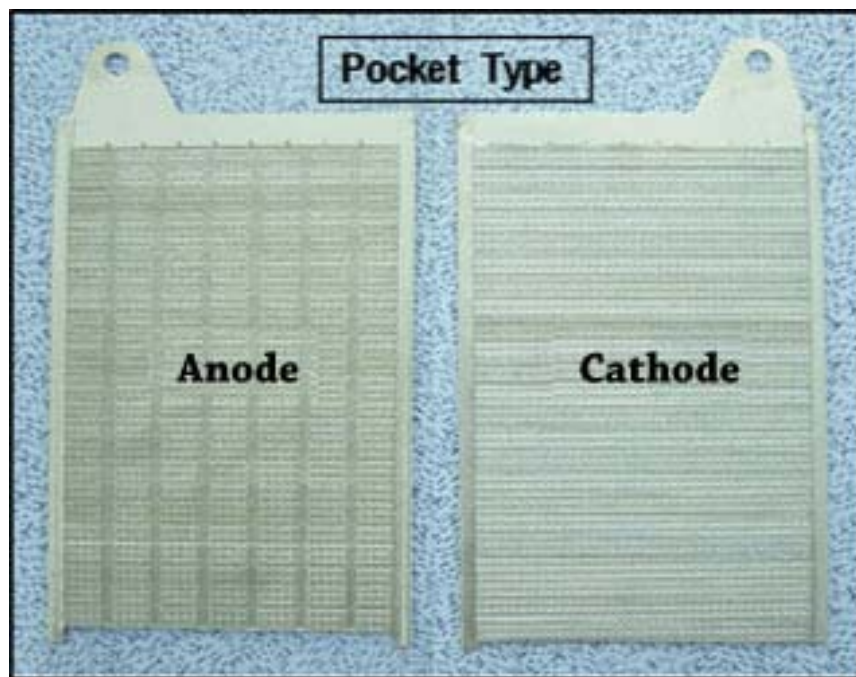


Fig. 2. Finished Ni-Zn pocket-type plates.



Fig. 3. Components of the Ni-Zn pocket-type battery and battery container.

capacity of the electrode. Prior to being connected with the side bead and lug (the connecting terminal), the strips are called the mat.

③ The produced mat is roll-pressed to enhance the bonding between the strips and the active materials and to smooth the burring surfaces due to the perforation. (Fig. 1 (b)).

④ Once the roll-pressing process is complete, the mat is inserted into the groove between the lug and side bead, and all are welded together (Fig. 1 (c)). The side bead and the mat are roll pressed to achieve an improved bonding and then welded, which completes the production of a plate (Fig. 1 (d)).

⑤ The plate is laminated at the cathode and the anode in accordance with the battery capacity, which is called the plate group, and the plate group is connected with the external terminal.

Fig. 2 and Fig. 3 show the finished plates of the cathode and anode, and the components of the battery and battery container, respectively

2.2. Production of the active materials

The plates for the Ni-Zn pocket-type battery are manufactured using active materials that are granulated to 500–700 μm . The active material grains have three advantages: (1) the loss rate is low, as the grains do not easily slip through the pores on the strips, (2) their excellent workability facilitates convenient plate production, and (3) the deviation of the plate decreases as the grains are evenly injected into the Ni strips. However, the grains of the cathode active material, ZnO , are so small that the rate of active materials that are slipped between the perforated Ni strips is high, and are also easily dissolved in the electrolyte and then lead to a high loss rate of active materials. Hence, in order to resolve these problems by enlarging the grain sizes of ZnO to fit the pore size of the anode plates, we fabricated the plates using the following methods: (1) reforming the cathode active material to granulate them at an even size, (2) granulating the slurry to an even size after heat-drying, and (3) producing an even size of square chips.

Table 1. Compositions of the active materials for the cathode and anode.

① Anode composition (wt%)

Ingredients	Ni(OH) ₂	CoO	Carbon
Composition ratio	85	7	8

② Cathode composition (wt%)

Ingredients	ZnO(S)	AB	Acrylic	Ca(OH) ₂	Bi ₂ O ₃	PTFE	Binder b	Binder c	CMC
Composition ratio (A)	89.0	2.0	3.0	2.25	3.75	0	0	0	0
Composition ratio (B)	85.56	1.94	3.0	2.13	3.49	0.58	1.94	0.39	0.97
Basic composition ratio	88.2	2.0	0	2.2	3.6	0.6	2.0	0.4	1.0

- Composition ratio (A): A 3% acrylic binder was added instead of the existing binder.
- Composition ratio (B): Both the existing binders and a 3% acrylic binder were added.
- Binder b and c: trade secret

Table 2. Properties of the testing cells and the charge and discharge conditions.

Cell no.	Anode (No.)	Cathode (No.)	Anode: cathode mix ratio	Test purpose (tests by change of cathode active materials)	Charge and discharge conditions	Electrolyte
cell 1	10	12	1:3.44	Pocket battery TEST, 100 Ah, Dry mix	0.1-0.2 C, 80%/0.3 C	EG-EKNL
cell 2	10	12	1:3.44	Pocket battery TEST, 100 Ah, Dry mix	0.1-0.2 C, 80%/0.3 C	EG-EKNL
cell 3	10	12	1:3.51	Pocket battery TEST, 100 Ah, Wet mix	0.1-0.2 C, 80%/0.3 C	EG-EKNL
cell 4	10	12	1:4.10	Pocket battery TEST, 100 Ah, Standard power	0.1-0.2 C, 80%/0.3 C	EG-EKNL

Table 1 shows the compositions of the active materials of the cathode and anode. The slurry for the cathode active material was produced in accordance with the composition in Table 1, dried in a 90 °C oven for 24 h, ground to a certain grain size, and finally filtered through a 500-μm mesh.

The classified cathode active materials and binders were mixed together in reference to a dry mix (Composition A) or a wet mix (Composition B), which were pressed in a 0.8 cm × 5 cm mold, formed into square pellets (bonds), and finally

inserted into the 16-mm wide strips to make the bond. Then, the cathode and anode plates were fabricated by forming this bond into 14 cm × 21 cm mats according to the sequence of the electrodes production. At this time, the capacity of the anode was 15 Ah, and the capacity ratio of the cathode and anode plates was designed to be 3:1.

The produced 11 anode and 12 cathode plates were layered one on top of the other, which formed a 100-Ah plate group and were pressed and fixed together using a bending machine. For the anode

Table 3. Composition of the cathode of a 300-Ah battery.

	ZnO	AB	Ca(OH) ₂	Bi ₂ O ₃	Acrylic Binder
Composition (%)	89.0	2.0	4.0	3.0	2.0

Table 4. Charge and discharge conditions of the 100-Ah battery.

	Charge		Discharge	
Formation	3 step		0.1 C	1.2-V cut-off
Charge./Discharge.	0.2 C	2.4 h	0.3 C	
	0.1 C	3.2 h		

plates, two 90- μ m nonwoven fabrics, created by NKK, were inserted as the anode membranes, and for the cathode plates, two pieces of microporous polyolefin 3407 by Celgard were used as the cathode membranes. Ni-Zn pocket-type batteries were finally assembled with the battery components and case, and filled with the specific weight of the 1.226 ZnO saturated three-component electrolyte (EG-EKNL, KOH:NaOH:LiOH = 3:2:1) up to the upper part of the plates and the connecting terminal. We stabilized for six hours, and then tested for their charge and discharge capacities. A total of four testing cells were produced, and their general properties are shown in Table 2.

2.3. Fabrication of 300-Ah batteries

A 300-Ah battery was fabricated by connecting three aforementioned 100-Ah batteries in parallel, in which the testing cells uses the larger terminals and cases to prevent over-heating. The anode electrodes were the same as that of the 100-Ah battery, and the cathode electrodes, as shown in Table 3, consisted of a basic composition plus an acrylic binder. The excessive use of binder only results in the internal battery resistance, thus we reduced the binder in the active material of the testing cells. The membranes between the cathode and anode plates were coated with a 5% poly acrylic acid partial potassium salt (PAAK) polymer solution to prevent powder leakage.

Each battery consisting of 34 anode and 32 cathode plates was filled with the two-component electrolyte (KOH:NaOH = 3.86:1) with a specific gravity of 1.31 and aged for 24 h at room temperature. The

supplementary liquid is the diluted two-component electrolyte with the specific gravity of 1.26.

3. Testing of the high-capacity Ni-Zn pocket-type battery

3.1. 100-Ah batteries

The charge and discharge conditions of the tested batteries are shown in Table 4.

The three step formation process was performed to activate the batteries: the batteries were charged to 91% for 11 h in the order of 0.15 C $\rightarrow$ 0.05 C $\rightarrow$ 0.03 C, discharged at 0.1 C, and stopped at 1.2 V. This formation process was repeated twice prior to beginning the charge and discharge tests. For the charging, the batteries were charged to 80% of their capacity by charging them for 2.4 h at 0.2 C and 3.2 h at 0.1 C, discharging them at 0.3 C, and stopping at 1.2 V.

Fig. 4 shows the charge and discharge behaviors of the four types of 100-Ah batteries. Cells 1 and 2 were fabricated with Composition (A), Cell 3 were fabricated with Composition (B), and Cell 4 were fabricated with a basic composition using the cathode active material. Cells 1 and 2, produced in accordance with the dry mix of the active materials, were added with an acrylic binder only, i.e., a basic composition. As a result, they showed very similar cell behaviors. In other words, deviation was unlikely to be found in the production process of the electrodes. On the contrary, Cell 4, using the basic

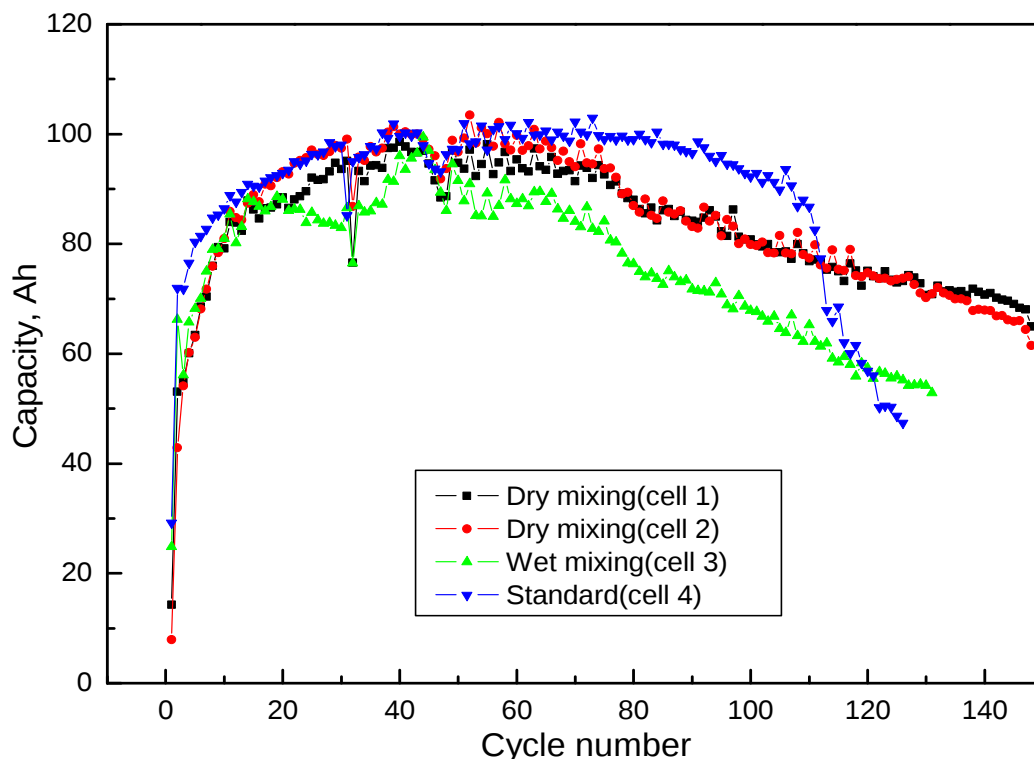


Fig. 4. Performances of the 100-Ah batteries by different cathode compositions.

binders in place of an acrylic binder, showed the most prominent capacity until Cycle 110, but its capacity abruptly dropped thereafter. It was analyzed that approximately 3% of the binder showed excellent performance with low internal battery resistance, but the capacity abruptly dropped due to the reduced performance of binders. Cell 3, added with excessive binder, approximately 6%, showed a low capacity in general due to high inner resistance but a longer lifetime in comparison with Cell 4.

The battery performances greatly depended on different binder mixes for the cathode plates. In general, a higher binder prevalence resulted in less battery capacity, but a longer battery lifetime. In conclusion, our findings suggest that the volume of an acrylic binder, rather than other factors, optimizes the lifetime and a battery capacity. However, our batteries, which were specifically produced for the study, dropped up to 75% of their initial capacities in less than approximately 120 cycles; thus, their performances were far from that of an industrial battery, and additional measures are needed to enhance their performances.

Another critical parameter that affects the performance of a battery is the electrolyte. The electrolyte becomes the path through which ions move when the active materials of the anode and cathode react with each other, and the efficiency and lifetime of a battery can be optimized by controlling the ion conductivity, which can be performed by controlling the composition and specific gravity of the electrolyte. In general, an electrolyte with a higher specific gravity results in a higher ion conductivity, but if the specific gravity exceeds a certain degree, it negatively affects the ion conductivity. Because of this critical problem with the Ni-Zn secondary battery, i.e., the dissolution of the zinc cathode charge materials into the electrolyte, an electrolyte with a low specific gravity is more common, but it is more desirable to enhance the ion conductivity with a higher specific gravity and to minimize the dissolution by adding a buffer or using a zinc-saturated electrolyte.

Fig. 5 shows the cycles of cells, which were produced with the active material of Composition (A). Cells 1 and 2 were both produced by the same active material composition with both dry mixes, but with different electrolytes. We tested Cell 1 with

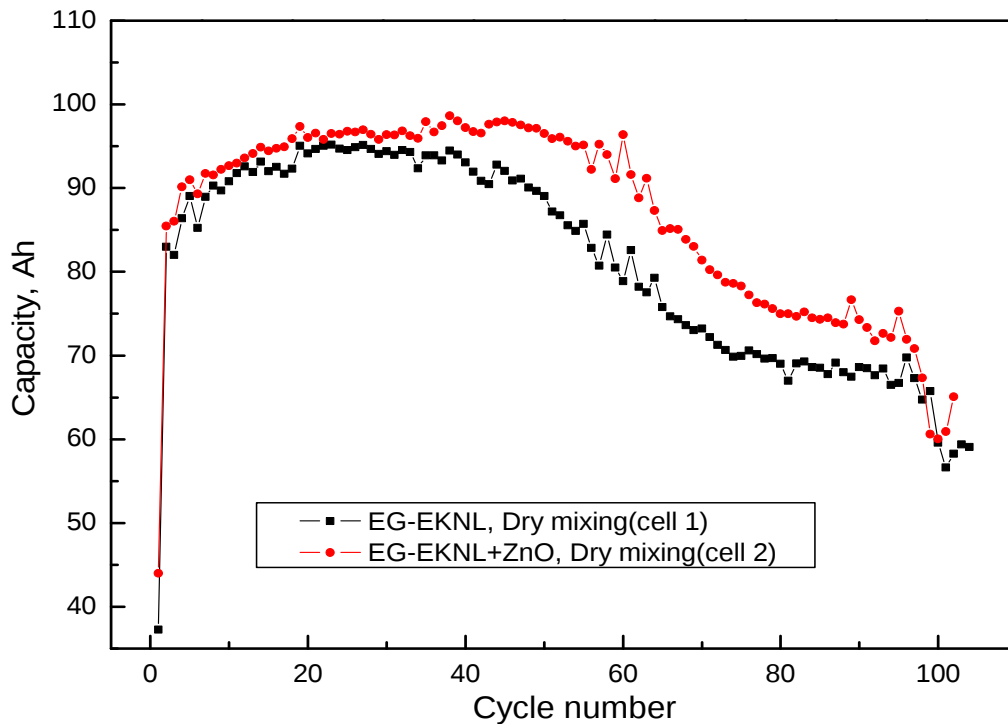


Fig. 5. Evaluation of properties of the 100-Ah batteries according to different electrolytes.

EG-EKNL and Cell 2 with ZnO saturated EG-EKNL, which are mixed with three electrolytes and have the same density.

As a result, the ZnO-saturated electrolyte showed an excellent result in terms of the volume and lifetime of the electrolyte because ZnO, saturated in the electrolyte, made the less dissolution in the cathode plates, and the mitigated dissolution of the cathode substantially enhanced the efficiency and lifetime of the battery. ZnO-saturated electrolyte certainly helped the zinc electrode to be stabilized to a certain degree, but the sudden drop in the battery capacity after 50 cycles explains that adding only the saturated liquid was insufficient to prevent the zinc electrode from being dissolved.

3.2. 300-Ah batteries

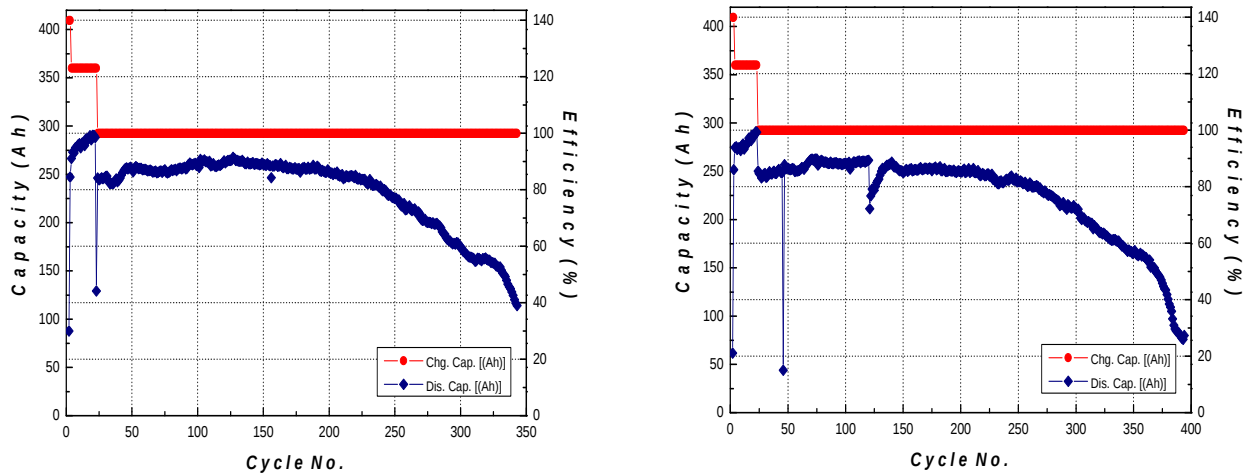
As shown in Table 5, the 300-Ah batteries also underwent a formation process prior to the charge and discharge tests. This process consisted of three steps: the batteries were charged to 91% for 11 h in the order of 0.15 C→0.05 C→0.03 C, discharged at 0.1 C, and stopped at 1.2 V. The formation process was repeated twice prior to beginning the charge and discharge tests. For the charging, until 22 cy-

cles, the batteries were charged to 80% of their capacity by charging them for 2.4 h at 0.2 C and 3.2 h at 0.1 C and discharging them at 0.3 C. For the cycles thereafter, the batteries were charged to 80% at 0.2 C. The discharging was stopped at 1.2 V and 0.3 C.

Cycle graphs that show the behaviors of the 300-Ah Ni-Zn pocket-type batteries are presented in Fig. 6., in which the red line depicts charge, and the blue line depicts discharge.

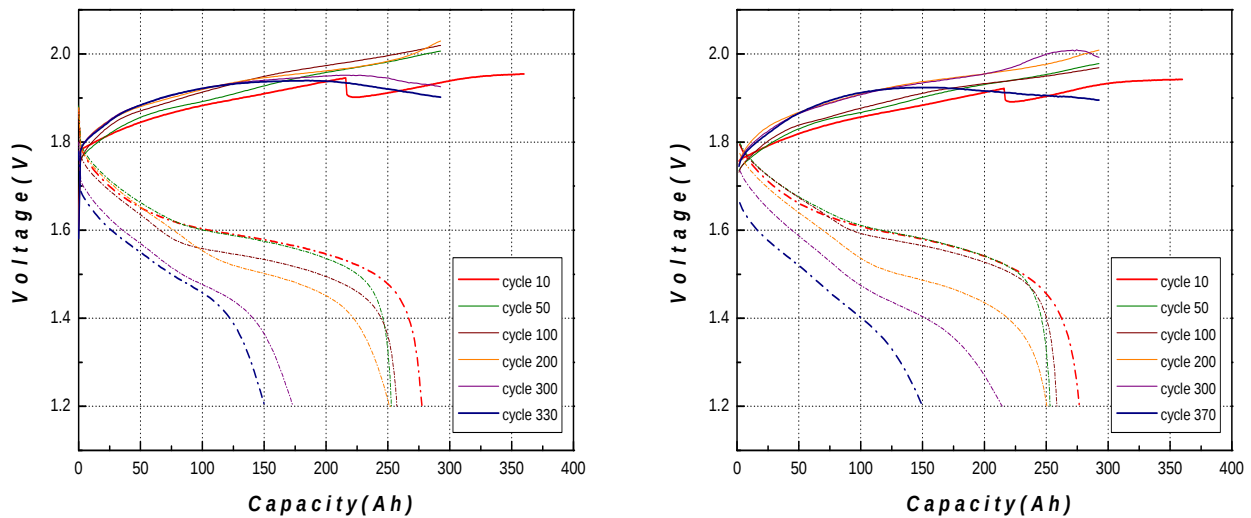
Because the charging was performed in multiple stages, according to the charge and discharge conditions in Table 5, the charge graphs are shown in a cascaded format. The formation processes of the initial two cycles charged the batteries to 400 Ah or more, which exceeded their designed capacity. From cycles 3 to 22, which were in the stage of battery activation, the batteries were charged to 350 Ah or greater. From 23 cycles onward, the batteries were charged to their designed capacity of 300 Ah.

Cells 1 and 2, which were coated with a gel electrolyte between the anode and cathode membranes, showed enhanced behaviors, compared to



(a) PAAK coating between anode membranes (Cell 1) (b) PAAK coating between cathode membranes (Cell 2)

Fig. 6. Cycle behaviors of 300-Ah Ni-Zn pocket-type batteries



(a) Charge/discharge graph (Cell 1)

(b) Charge/discharge graph (Cell 2)

Fig. 7. Charge/discharge graphs of the Ni-Zn pocket-type 300-Ah batteries.

Table 5. Charge and discharge conditions for the 300-Ah batteries.

	Charge	Discharge	
Formation	3 step	0.1 C	1.2-V cut-off
Charge./Discharge.(cycles 3-22)	0.2 C $\rightarrow$ 0.1 C	0.3 C	
Charge./Discharge.(cycle 23)	0.2 C		

those of the aforementioned 100-Ah batteries. In particular, the coating was more effective on the

cathode membranes than on the anode membranes. Cell 2, when its cathode membranes were coated,

showed a 75% preserved capacity at the condition of 80% DOD for 350 cycles, which approaches the performance of the existing paste-type battery.

Fig. 7 shows the charge/discharge graphs of the 300-Ah batteries. First, there were drops at cycle 10 (in red) on the charge graphs when the capacity was approximately 230 Ah because the charge current changed to 0.1 C from 0.2 C; thus, cycle 50 and above showed no drops as the charge current remained constant at 0.2 C. In general, with the above charge conditions, the batteries showed no overcharge or other failures. On the other hand, the discharge curves showed abrupt drops from 250 Ah, indicating the batteries work normally for approximately 300 cycles.

4. Conclusions

For the commercialization of the industrial high-capacity Ni-Zn pocket-type secondary battery, we fabricated 100-Ah batteries, which in turn were used to manufacture 300-Ah batteries by connecting them in parallel, and tested their performances. Because the pocket-type battery is also a flooded type containing a large volume of electrolytes, it can be used for a high-capacity battery system, but it generates various problems, including the evaporation of the electrolyte and dissolution of the active materials including Zn.

To solve these problems, we formulated different compositions of the active materials and designed the battery system for the production of the high-capacity battery and minimized problems through various pretreatments. Furthermore, we identified the effects of binders—ingredients of active materials—on 100-Ah batteries and tested the effect of coating the membranes of 300-Ah batteries with polymer gel. The test results indicated that the binders and electrolytes were crucial in enhancing the performance of the pocket-type batteries. It was found that the acrylic binder was more effective than other binders, that optimization with the appropriate level within 3% is required, and that the ZnO-saturated liquid was effective to extend the battery life. Our findings are that excess binder results in the increase of the battery resistance and that a saturated electrolyte restrains zinc dissolution.

Through a variety of pretests, the PAAK polymer coating showed better performance on the cathode membranes than the anode membranes, indicating that the coating prevents the active materials from desorbing in the cathode than the anode and also extend the battery lifetime. Our comprehensive conclusion is that when the 300-Ah pocket-type battery is coated with gel polymers, it can serve as a high-capacity battery that maintains a 75% retention capacity at 80% DOD for 350 cycles, thereby confirming its potential to be commercialized as a high-capacity battery.

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