Poly(acrylamide-co-acrylic acid) Gel Electrolytes for Ni-Zn Secondary Batteries

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Recently, there is growing concern about energy crisis and efficient controlling energy. The nickel-zinc (Ni-Zn) rechargeable battery is the one of the most attractive power source for various electric devices and large-scaled energy storage systems because it has high specific energy density (373 Wh·kg^{-1}), high specific power density, high open-circuit voltage (1.75 V), low toxicity and so on.[1-5] Despite all the advantages of Ni-Zn rechargeable battery, there are inherent critical problems, such as zinc shape change, dendrite formation and high dissolution of the zinc electrode, arising from zinc electrode itself.[1,2] As a result, a zinc-based rechargeable battery usually shows short cycle life, and it prevents the commercialization of zinc-based energy storage system.[6] These problems for zinc-based system have grown serious as an increase in the number of charge/discharge cycles.[5] In order to enhance the cell performance and overcome these problems originating from zinc redistribution and the solubility of zinc electrode in an alkaline medium, one of the possible ways is to use gel polymer electrolyte instead an alkaline solution.[6-8] Several researchers demonstrated the enhanced cell performance and the suppression of zinc dendrite formation even if they also reported some disadvantages.[6-11] In the present study, the gel polymer electrolyte was prepared using poly(acrylamide-co-acrylic acid) (P(AAm-co-AAc)). The electrochemical performances of the Ni-Zn cell with the gel polymer electrolyte and the morphology of the zinc electrode during charge-discharge cycles were investigated.

The anode (Zn electrode) was prepared by pasting a mixture consisting of the pristine or modified ZnO powder (82 wt %), Ketjen Black (KB; 10 wt %), Ca(OH)$_2$ (1 wt %), Bi$_2$O$_3$ (3 wt %), and polytetrafluoroethylene (PTFE; 4 wt %) on a porous Ni foam. The addition of Ca(OH)$_2$ reduces the shape change of the zinc electrode and improves the cycle stability of the Ni-Zn batteries,[12] and Bi$_2$O$_3$ suppresses the hydrogen evolution.[13] The electrode was dried at 70 °C and pressed (700 kgf·cm^{-2}) to a thickness of ~0.3 mm. The Ni electrode consists of Ni(OH)$_2$ powder (86 wt %), Ni powder (3 wt %), Co(OH)$_2$ (3 wt %), polyethylene (PE; 7 wt %), and PTFE (1 wt %). It has been reported that the addition of cobalt to the active material improves the reversibility of the electrochemical reaction.[2] The standard electrolyte is an aqueous solution consisting of 3.8 M KOH, 2.5 M NaOH, and 1.2 M LiOH because this composition has a maximum

ionic conductivity and suppresses the shape change of zinc electrode.[14,15] The gel polymer electrolyte was prepared by the following steps. P(AAm-co-AAc) was added to alkaline solution, and the mixture was stirred until they form a homogeneous solution. Then, the solution was poured onto an airtight glass vessel to avoid water evaporation and absorption of carbon dioxide. The conductivities of gel polymer electrolyte and normal alkaline electrolyte were measured by IM6 impedance analyzer (Zahner elcktrik). The morphologies of ZnO electrode and the microstructure of ZnO powders were investigated by field emission scanning electron microscopy (FE-SEM, Hitachi S-4300, Japan) with energy dispersive spectroscopy (EDS, Horiba EX-200). The electrochemical performances of the various compounds were evaluated using a WBCS 3000 instrument (WonA Tech., Korea). The three-step charge regime[2,5] from Samsung advanced institute of technology was used and the discharge rates were 0.1 C (until the 3rd cycle) and 0.3 C (after the 3rd cycle).

The gel polymer electrolyte is a viscous liquid mixture. As increase in the concentration of P(AAm-co-AAc) the viscosity of the electrolyte increases. The conductivity of the gel polymer electrolytes as a function of the concentration of P(AAm-co-AAc) was measured at room temperature. The ionic conductivity of gel polymer electrolyte slightly decreases with an increase in the concentration of P(AAm-co-AAc). Considering the conductivity and the viscosity of the gel polymer electrolyte, the concentration of P(AAm-co-AAc) is fixed to 6 wt % and the conductivity is 4.8×10^{-1} S·cm^{-1}.

The discharge capacities of Ni-Zn cells with normal alkaline electrolyte and gel polymer electrolyte as a function of the number of charge-discharge cycles are presented in Figure 1. For a normal alkaline electrolyte, the discharge capacity rapidly decreases with increasing number of charge-discharge cycles. At 60 cycles, the retention ratio of discharge capacity is ~40% (125 mAh·g^{-1}). This is the typical phenomenon of ordinary Ni-Zn cells due to the formation of dendrite, shape change, and dissolution of zinc electrode. On the contrary, the initial discharge capacity of cell with the gel polymer electrolyte is above 350 mAh·g^{-1} after activation up to 40 cycles, and then gradually decreases with increasing number of cycles. The capacity retention of cell is ~88% at 60 cycles (310 mAh·g^{-1}) and remarkably increases in com-
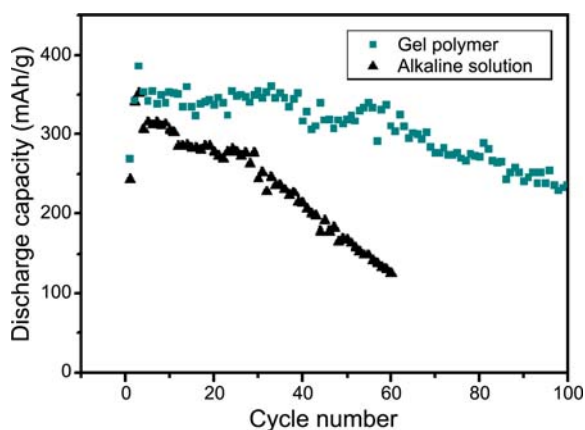
Figure 1. Discharge capacities of Ni-Zn cells with the normal alkaline and P(AAm-co-AAc) gel polymer electrolytes.
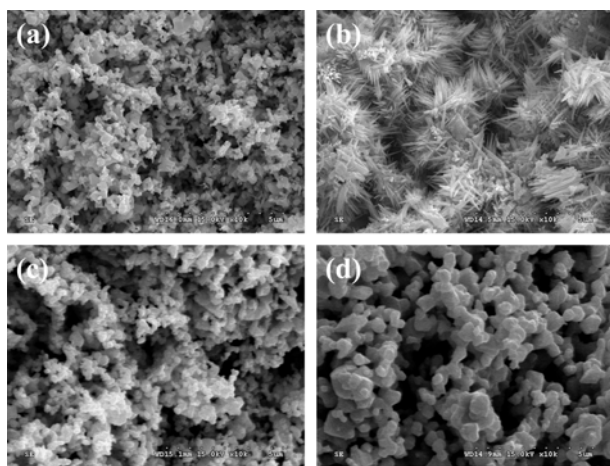
Figure 2. SEM images of (a) pristine ZnO electrode, (b) after 60 cycles with a normal alkaline electrolyte, (c) after 60 cycles with a gel polymer electrolyte, and (d) after 100 cycles with a gel polymer electrolyte.

parison with that with a normal alkaline electrolyte. It is reported that polymer electrolytes are expected to be less reactive than liquid electrolyte and the use of polymer electrolyte can suppress the problem of dendrite growth.[6-11] In addition, gel polymer electrolyte can reduce the zinc dissolution in an alkaline medium in Ni-Zn secondary battery.

The morphology of zinc electrode in the two electrolyte media after charge-discharge tests was investigated by SEM as shown in Figure 2. After the charging-discharging test, the zinc electrode was washed in distilled water, rinsed with ethanol and then dried. The initial morphology of the pristine ZnO has a characteristic hexagonal prismatic shape with a smooth surface as shown in Figure 2(a). As we

expected, the severe dendrite formation is observed on the cell with a normal alkaline electrolyte after 60 cycles of charging-discharging as shown in Figure 2(b). The Zn dendrite easily penetrates into the separator and results in an interior short circuit. However, Figure 2(c) and 2(d) show the morphology of the zinc electrode with the gel polymer electrolyte after 60 and 100 charge-discharge cycles, respectively. The morphology of the zinc electrode with the gel polymer electrolyte was not changed much after the charge-discharge cycles. Only the difference is that particle size slightly increases with increasing number of charge-discharge cycles. It is demonstrated that the gel polymer electrolyte effectively suppresses dendrite formation.

In summary, the gel polymer electrolyte has high ionic conductivity of good mechanical stability. The Ni-Zn cell with gel polymer electrolyte shows good charge-discharge characteristics and suppresses the shape change of the zinc electrode. The gel polymer electrolyte, P(AAm-co-AAc), is considered as a promising candidate for applications in rechargeable zinc-based rechargeable battery systems.

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