Short communication

Charge–discharge characteristics of nickel/zinc battery with polymer hydrogel electrolyte

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Abstract

A new nickel/zinc (Ni/Zn) battery was assembled by using polymer hydrogel electrolyte prepared from cross-linked potassium poly(acrylate) and KOH aqueous solution, and its charge–discharge characteristics were investigated. The experimental Ni/Zn cell with the polymer hydrogel electrolyte exhibited well-defined charge–discharge curves and remarkably improved charge–discharge cycle performance, compared to that with a KOH aqueous solution. Moreover, it was found that dendritic growth hardly occurred on the zinc electrode surface during charge–discharge cycles in the polymer hydrogel electrolyte. These results indicate that the polymer hydrogel electrolyte can successfully be used in Ni/Zn batteries as an electrolyte with excellent performance.
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1. Introduction

In recent years, the application of solid or gel electrolytes to batteries and other electrochemical devices has attracted the increasing attention especially in terms of the reliability, safety, flexibility and processibility. Several systems of solid or gel electrolytes has been studied for an intended use in alkaline secondary batteries such as nickel/metal hydride (Ni/MH), nickel/cadmium (Ni/Cd) and nickel/zinc (Ni/Zn) batteries. For example, Fauvarque et al. reported solid polymer electrolytes based on poly(ethylene oxide) (PEO), KOH and water for the alkaline batteries [1–3]. Iwakura et al. prepared polymer hydrogel electrolyte from cross-linked potassium poly(acrylate) (PAAK) and a KOH aqueous solution, which had very high ionic conductivity (ca. $6 \times 10^{-1}\,S\,cm^{-1}$ at room temperature) [4,5] and markedly suppressed electrolyte creepage behavior [6]. Ni/MH cells using the polymer hydrogel electrolyte exhibited good charge–discharge characteristics and fairly improved

capacity retention [4,5,7,8]. Very recently, alkaline polymer electrolytes based on poly(vinyl alcohol) (PVA) with KOH were studied by some groups [9–11].

The Ni/Zn battery has attractive advantages of high energy and power densities, low cost and so on. However, widespread commercialization of the Ni/Zn battery using liquid electrolytes has been prevented due to the serious problems such as dendritic growth, shape change and high dissolution of the zinc electrode. Many attempts have been made to overcome the problems [12–16], and many organic additives have been reported to be effective in suppressing the dendritic growth [12,14,17–19]. Moreover, several groups have applied the alkaline polymer electrolyte to the Ni/Zn battery [1,2,11] and/or other batteries based on the zinc electrode [10,20–23]. In our previous papers [4,5], the polymer hydrogel electrolyte containing PAAK was found to suppress dissolution and diffusion of metal species such as aluminum and manganese. Thus, it can be expected that application of the polymer hydrogel electrolyte to the Ni/Zn battery would restrain the dissolution of zinc, leading to an improvement in the battery performance. In this study, a new Ni/Zn cell was assembled using the polymer hydrogel electrolyte prepared from PAAK

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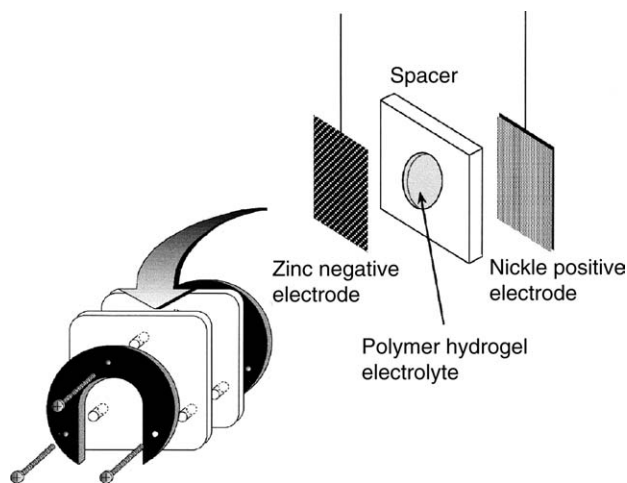*E-mail address:* iwakura@chem.osakafu-u.ac.jp (C. Iwakura).

Fig. 1. Experimental cell assembly for the polymer hydrogel electrolyte-based Ni/Zn cell.

and 7.3 M KOH aqueous solution, and the charge–discharge characteristics were investigated.

2. Experimental

The alkaline polymer hydrogel electrolyte was prepared from one gram of PAAK and $0.01\,dm^3$ of a 7.3 M KOH aqueous solution in the same manner as described in our previous papers [4,5]. Zinc negative electrodes were prepared by electrodeposition of zinc on porous carbon paper (TORAY, TGP-H-060) in a 7.3 M KOH/0.7 M ZnO aqueous solution (25 °C) at $60\,mA\,cm^{-2}$ for 1 h. Experimental cell assembly for the polymer hydrogel electrolyte-based Ni/Zn cell is shown in Fig. 1 The polymer hydrogel electrolyte and a polypropylene spacer (1 mm thick) are stacked between the zinc negative electrode and a commercially used nickel positive electrode. A similar type cell was also assembled using a 7.3 M KOH aqueous solution as an electrolyte for comparison.

In charge–discharge cycle tests, the negative electrode was charged at $100\,mA\,g^{-1}$ for 1 h and discharged at $100\,mA\,g^{-1}$ to the cell voltage of 1.2 V. After each charging, the circuit was kept open for 10 min. The charge–discharge cycle tests were carried out at 25 °C. The discharge capacity was calculated based on the mass of zinc electrodeposited on the carbon paper. After charging at 50th cycle, surface morphology of the zinc negative electrode was observed by SEM.

3. Results and discussion

Fig. 2 shows charge–discharge curves at 2nd and 10th cycles of experimental Ni/Zn cells with a 7.3 M KOH aqueous solution and the polymer hydrogel electrolyte. At the second charge–discharge cycle, a well-defined charge curve was obtained for each cell. In the discharge curve at second cycle, a plateau of the cell voltage was seen in the range approx-
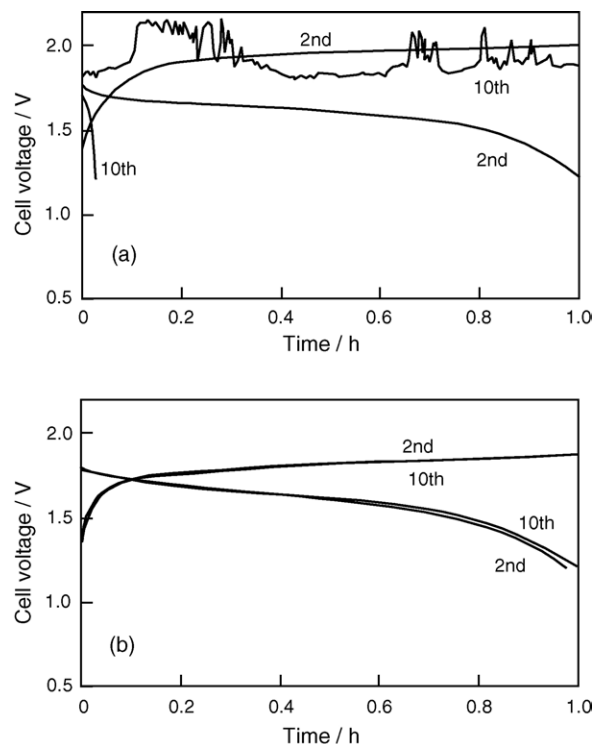

Fig. 2. Charge–discharge curves (2nd and 10th cycles) of the Ni/Zn cells with (a) a 7.3 M KOH aqueous solution and (b) the polymer hydrogel electrolyte.

imately from 1.7 to 1.5 V in each case. Discharge capacities for both the cells were close to the charged electricity, $100\,mAh\,g^{-1}$. These results indicate that the experimental cells successfully worked as Ni/Zn batteries during the early cycles. The polymer hydrogel electrolyte used in this study has very high ionic conductivity of ca. $6 \times 10^{-1}\,S\,cm^{-1}$ at 25 °C, nearly comparable to that of the 7.3 M KOH aqueous solution, due to a high water-absorbing capacity of PAAK [4,5]. This may lead to the smooth charge–discharge reactions in the polymer hydrogel electrolyte as well as the KOH aqueous solution. However, remarkable differences between
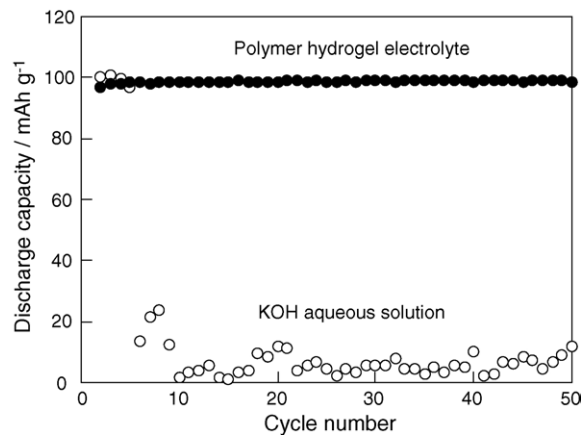

Fig. 3. Discharge capacities as a function of cycle number for the Ni/Zn cells with a 7.3 M KOH aqueous solution and the polymer hydrogel electrolyte.
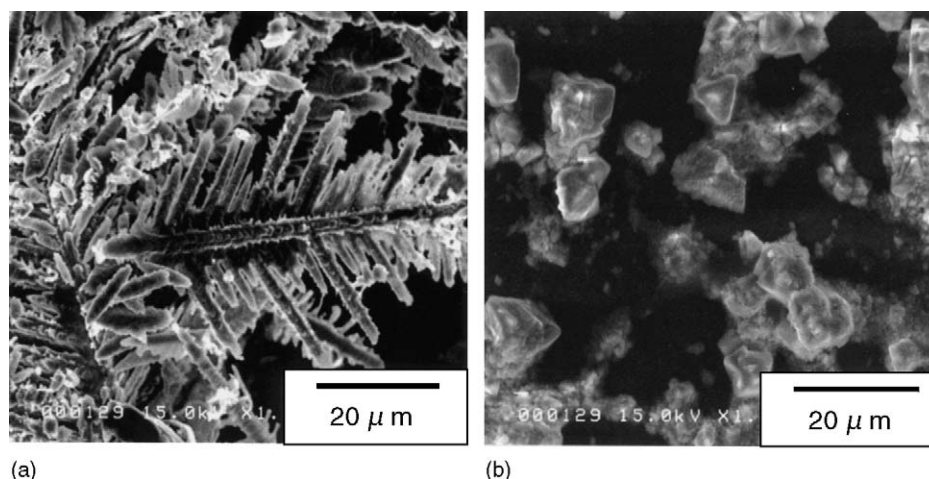
Fig. 4. SEM photographs of negative electrodes in the Ni/Zn cells with (a) a 7.3 M KOH aqueous solution and (b) the polymer hydrogel electrolyte after charging at 50th cycle.

the two electrolytes were seen at 10th cycle. In case of the KOH aqueous solution, the cell voltage was oscillated during charging and the charge curve was quite unstable under the present condition. As can be seen from the discharge curve at 10th cycle, the discharge capacity for the KOH aqueous solution was quite low. In this case, it is inferred that the experimental Ni/Zn cell was controlled by the zinc negative electrode. On the other hand, the charge and discharge curves for the polymer hydrogel electrolyte were very stable even at 10th cycle, almost the same as those at second cycle.

Discharge capacities as a function of cycle number for the two type cells are shown in Fig. 3. Although the discharge capacity for the KOH aqueous solution was close to $100 \, \text{mAh g}^{-1}$ only in some early cycles, the discharge capacity drastically decreased to the quite low value after that. In case of the cell with the polymer hydrogel electrolyte, the discharge capacity close to $100 \, \text{mAh g}^{-1}$ hardly changed with increasing cycle number. The stable cycle performance strongly suggests that the charge–discharge reactions occurred reversibly and uniformly at the interface between the polymer hydrogel electrolyte and zinc negative electrode.

The Ni/Zn cell is based on electrochemical and dissolution-precipitation reactions at the negative zinc electrode as follows [12]:

$$Zn + 4OH^- = Zn(OH)_4{}^{2-} + 2e^- \tag{1}$$

$$Zn(OH)_4{}^{2-} = ZnO + 2OH^- + H_2O \tag{2}$$
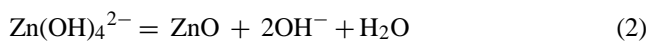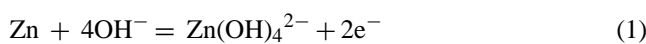
During charging, the electrodeposition of zinc on the negative electrode occurs according to the reverse reaction of Eq. (1). The unstable charge curve observed at 10th cycle for the KOH aqueous solution suggests that the electrodeposition proceeded heterogeneously on the electrode surface due to the non-uniform current distribution. The heterogeneous electrodeposition may lead to the formation of dendrites which cause the poor electrode performance and the short-circuit of the cell. Fig. 4 shows SEM photographs of

the negative electrode surface in the two electrolytes after charging at 50th cycle. As can be seen from Fig. 4(a), a large amount of dendrites were clearly observed in case of the KOH aqueous solution. For the polymer hydrogel electrolyte (Fig. 4(b)), granular zinc deposits were observed over the electrode surface and no dendrites were seen. Therefore, the unstable potential in the charge curve and the drastic decay in the discharge capacity for the KOH aqueous solution could be attributed to the dendritic growth.

The data as mentioned above indicates the polymer hydrogel electrolyte remarkably suppress the formation of dendrites and improved charge–discharge performance. PAAK would play an important role in the suppression. In our previous paper, it was reported that the polymer hydrogel electrolyte inhibited the dissolution and diffusion of metal species in the electrolyte [4,5]. Generally, the high solubility of $Zn(OH)_4{}^{2-}$ ions in alkaline solution results in the shape change of the zinc electrode, leading to the poor charge–discharge characteristics [13,16]. Thus, many attempts have been made to reduce the solubility. In this work, it is thought that a large amount of the zincate ions would dissolve and easily diffuse in the KOH aqueous solution with no other additives, while the polymer hydrogel electrolyte might restrain the dissolution and diffusion due to the PAAK. In addition, it is quite possible that high concentration of zincate ions in the neighborhood of electrode surface led to the smooth and uniform zinc deposition during charging. Along this line, further work is now in progress.

4. Conclusions

The polymer hydrogel electrolyte with high conductivity based on PAAK and 7.3 M KOH aqueous solution was applied to the Ni/Zn battery. The experimental Ni/Zn cell with a 7.3 M KOH aqueous solution with no other additives showed unstable and poor charge–discharge characteristics after sev-

eral cycles. This can be ascribed to the formation of dendrites on the zinc negative electrode. The charge–discharge characteristics were markedly improved using the polymer hydrogel electrolyte. This clearly indicates that charge and discharge reactions occurred smoothly and reversibly at the interface between the polymer hydrogel electrolyte and zinc electrode. No dendritic growth was observed on the negative electrode in the polymer hydrogel electrolyte. It is suggested that the improvements may be due to the suppression of dissolution and diffusion of $Zn(OH)_4^{2-}$ ions by PAAK.

Acknowledgements

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