

Suppression of electrolyte creepage with polymer hydrogel electrolyte for nickel/metal hydride batteries

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1. Introduction

Several studies on solid or gel electrolytes have been made for nickel/metal hydride (Ni/MH) and related batteries [1–13]. We have studied polymer hydrogel electrolyte prepared by crosslinked potassium poly(acrylate) (PAAK) and a KOH aqueous solution [6–9], and have reported that (1) the polymer hydrogel electrolyte had almost comparable ionic conductivity to that of a KOH aqueous solution and (2) the experimental Ni/MH cells assembled with the polymer hydrogel electrolyte exhibited almost the same charge-discharge characteristics and much higher capacity retention, compared to those with KOH aqueous solution. However, from a practical point of view, there are still other important electrolyte characteristics that have not yet been clarified.

Considerable attention has been paid to sealing Ni/MH cells to avoid electrolyte leakage. Especially, creepage of alkaline electrolyte occurs easily along metal sealing surfaces connected with the negative electrode [14–17]. The following oxygen reduction reaction occurs on the metal surface covered with a thin creepage electrolyte layer.



This reaction causes a difference in alkali concentration between the electrolyte bulk and thin electrolyte layer, resulting in migration of water from the bulk to the thin layer. Thus, electrolyte creepage is facilitated on the negatively polarized metal surface connected with the negative electrode. It can be expected that electrolyte creepage is suppressed by using polymer hydrogel electrolyte containing PAAK with a high water-affinity. In this work, creeping behaviors along nonpolarized and negatively polarized metal surfaces were investigated for

the polymer hydrogel electrolyte, compared with those for 6 M KOH aqueous solution.

2. Experimental details

The polymer hydrogel electrolyte was prepared from PAAK (Aldrich, 43532-5) and a 6 M KOH aqueous solution in the same manner as described previously [6, 7]. The polymer hydrogel electrolyte consisted of 7 wt. % PAAK, 23 wt. % KOH and 70 wt. % H₂O.

Creep tests of the electrolytes were carried out in the following two ways at 25 °C. First, a nonpolarized copper rod (diameter: 6 mm) was vertically contacted with the surface of the polymer hydrogel electrolyte colored with Eriochrome black T (C₂₀H₁₂N₃Na₇O₇S), and then the creeping behavior of the electrolyte along the rod was measured in air. Second, as schematically shown in Figure 1, a nickel rod electrode (diameter: 5 mm) vertically contacted with the polymer hydrogel electrolyte surface was negatively polarized to –0.9 V vs. Hg/HgO, and the oxygen reduction current was measured with time under an Ar rich atmosphere, assuming that the current would be mainly proportional to the wetted surface area of the electrode. For comparison, these measurements were also carried out in a 6 M KOH aqueous solution.

3. Results and discussion

Figure 2 shows creeping behaviors of the two electrolytes along a nonpolarized copper rod. In case of the 6 M KOH aqueous solution, the solution crept a little just after the rod was contacted with the solution surface, and the creepage was clearly observed to high level after 2 h as can be seen from Figure 2. Because

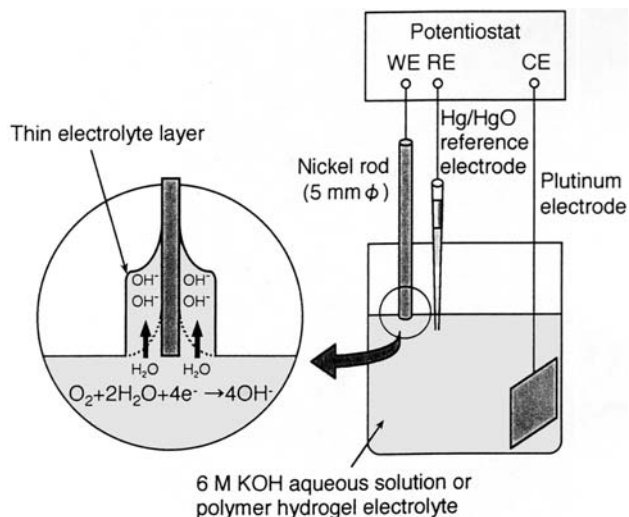


Fig. 1. Schematic representation of the cell for the electrochemical creep test.

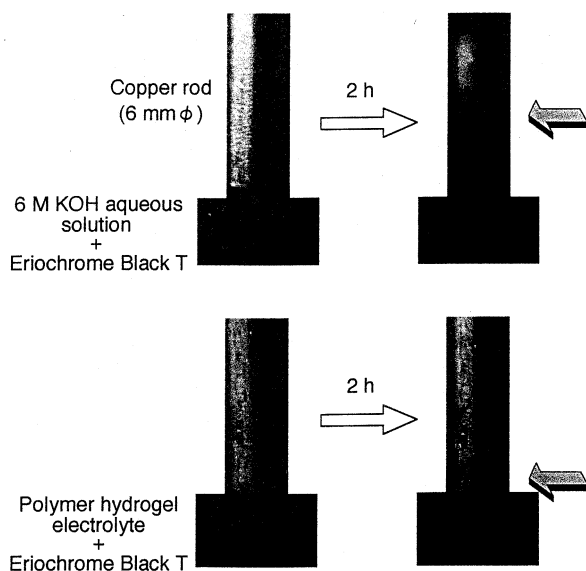


Fig. 2. Photographs of copper rods contacted with a 6 M KOH aqueous solution and the polymer hydrogel electrolyte at 25 °C.

water has a strong surface tension, the KOH aqueous solution creeps easily along the copper rod surface. On the other hand, in the case of the polymer hydrogel electrolyte, creepage was not observed just after contact and then hardly observed even after 2 h. It is clear that the electrolyte creepage could be suppressed by using the polymer hydrogel electrolyte instead of an aqueous KOH solution. It is suggested that the high water-affinity of PAAK led to the suppression of electrolyte creepage.

Time courses of currents for the two electrolytes contacted with a negatively polarized nickel rod are shown in Figure 3. The cathodic currents observed under the present condition can be ascribed to the oxygen reduction according to Equation 1 in the presence of oxygen [14, 16]. In the case of a 6 M KOH aqueous solution, an oxygen reduction current was

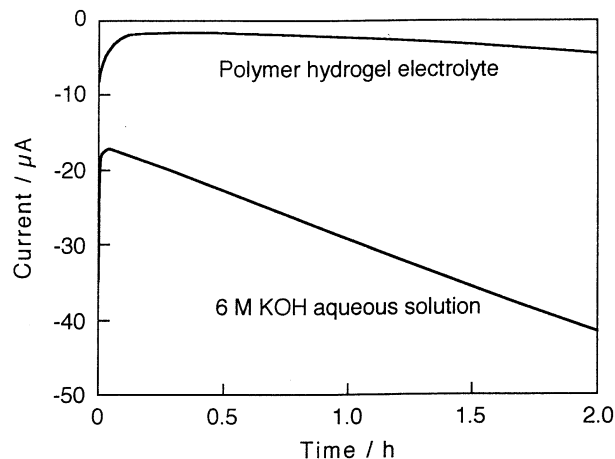


Fig. 3. Time courses of currents at -0.9 V vs. Hg/HgO for a 6 M KOH aqueous solution and the polymer hydrogel electrolyte at 25 °C.

observed even under Ar rich atmosphere as seen from Figure 3. It is suggested that residual oxygen in the gas phase was dissolved into the thin electrolyte layer covering the electrode and then reduced on the electrode surface. Moreover, the current increased with time. Since the oxygen reduction current should be mainly proportional to the area of thin electrolyte layer, the increase in the current can be ascribed to an increase in the area of thin electrolyte layer due to the electrolyte creepage. On the other hand, the oxygen reduction current for the polymer hydrogel electrolyte was small, and the rate of increase in the current was also markedly suppressed by using the polymer hydrogel electrolyte. The current after 2 h for the polymer hydrogel electrolyte was ca. a tenth as small as that for the 6 M KOH aqueous solution. This implies that creepage of the thin electrolyte layer along the negatively polarized metal surface was largely suppressed. PAAK with high water-affinity can work effectively in suppressing electrolyte creepage, even if the creepage is facilitated by negative polarization of the electrode.

From the results of the creep tests, it can be expected that the suppression of creepage with the polymer hydrogel electrolyte leads to reduction of sealing materials and improvement in the reliability for prevention of electrolyte leakage. In previous papers [8, 9], it was reported that experimental Ni/MH cells with polymer hydrogel electrolyte exhibited much higher capacity retention than those with KOH solution aqueous. The suppressed creepage of the polymer hydrogel electrolyte is a significant advantage together with the high capacity retention for application in practical sealed-type Ni/MH batteries.

4. Conclusions

In this work, creeping behavior of the polymer hydrogel electrolyte prepared from PAAK and a 6 M KOH aqueous solution was examined and compared to a 6 M aqueous KOH solution. The electrolyte creepage along a

nonpolarized metal surface was markedly suppressed by using the polymer hydrogel electrolyte. In addition, from the measurement of oxygen reduction current, it was also found that utilization of the polymer hydrogel electrolyte suppressed the electrolyte creepage along a negatively polarized metal surface. The improvements are due to the high water-affinity of PAAK. These results indicate that the creeping behavior can be very important advantage of polymer hydrogel electrolyte for use in practical sealed-type Ni/MH batteries.

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