Nickel/Metal Hydride Cells Using an Alkaline Polymer Gel Electrolyte Based on Potassium Salt of Crosslinked Poly(acrylic acid)

Chiaki IWAKURA,* Naoji FURUKAWA, Toshiyuki OHNISHI,
Kouichi SAKAMOTO, Shinji NOHARA, and Hiroshi INOUE

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University (1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan)

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Alkaline polymer gel electrolyte with high ionic conductivity was prepared from potassium salt of crosslinked poly(acrylic acid) and KOH aqueous solution in order to investigate the applicability of the polymer gel electrolyte to alkaline secondary batteries such as nickel/metal hydride (Ni/MH) battery. An experimental Ni/MH cell was assembled using the polymer gel electrolyte and its charge-discharge and capacity retention characteristics were tested. A similar type of Ni/MH cell was also assembled using a 6 M KOH aqueous solution for comparison. The former cell was found to exhibit rather better charge-discharge and capacity retention characteristics than the latter cell.

Key Words : Polymer Gel Electrolyte, Ionic Conductivity, Ni/MH Battery, Charge-discharge Characteristics

1 Introduction

There has been a strong demand for rechargeable batteries to use a solid or gel electrolyte instead of a liquid electrolyte.¹⁻⁴⁾ Nickel/metal hydride (Ni/MH) battery with a solid or gel electrolyte would be attractive especially in terms of its reliability, safety, designing and processibility. Properties such as electrode/electrolyte interface, ionic conductivity, electrochemical stability, thermal stability and mechanical strength of the electrolyte would become important factors to realize all-solid-state Ni/MH and related batteries. However, there have been only a few reports on a solid or gel electrolyte with high ionic conductivity for use in the Ni/MH and related batteries.

Mohri *et al.*^{5, 6)} have first reported Ni/MH related batteries using $\text{Sb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ as a solid electrolyte; *e.g.* $\text{TiNi} : \text{MmH}_x$ ($\text{Mm} = 1 \text{ wt } \%$) / $\text{Sb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ / MnO_2 . Kuriyama *et al.*⁷⁻⁹⁾ have investigated Ni/MH and related batteries using tetramethylammonium hydroxide pentahydrate, $(\text{CH}_3)_4\text{NOH} \cdot 5\text{H}_2\text{O}$ as a solid electrolyte with proton conductivity; *e.g.* $\text{LaNi}_{2.5}\text{Co}_{2.4}\text{Al}_{0.1}\text{H}_x$ / $(\text{CH}_3)_4\text{NOH} \cdot 5\text{H}_2\text{O}$ / NiOOH or MnO_2 . Very recently Ni/MH batteries with an alkaline solid polymer electrolyte based on poly(ethylene oxide) (PEO), KOH and water have been reported by Vassal *et al.*^{10, 11)}; *e.g.* $\text{LaMmNi}_{3.55}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Co}_{0.75}\text{H}_x$ / $\text{PEO-KOH-H}_2\text{O}$ / NiOOH . These batteries showed long charge-discharge cycle life but rather small current density to be drawn because of low ionic conductivity of the electrolytes, as compared with aqueous electrolyte-based Ni/MH batteries.

Poly(acrylic acid) is a well-known polymer that has a high water-absorbing capacity, a high water-holding capacity, a high gel strength and a relatively low cost. So, in this work, alkaline polymer gel electrolyte was prepared from potassium salt of crosslinked poly(acrylic

acid) and KOH aqueous solution in order to investigate the applicability of the polymer gel electrolyte to alkaline secondary batteries such as Ni/MH battery. The simple experimental Ni/MH cell for a preliminary investigation was assembled using the polymer gel electrolyte and its charge-discharge and capacity retention characteristics were tested under several conditions. The main purpose of this preliminary work was to compare roughly the electrochemical characteristics between the polymer gel electrolyte-based cell and the KOH aqueous solution-based cell under the same conditions.

2 Experimental

2.1 Preparation of polymer gel electrolyte

The alkaline polymer gel electrolyte was prepared according to the following steps. One gram of potassium salt of poly(acrylic acid) having lightly crosslinked network (Aldrich, #43532-5) was added to 0.01 dm³ of KOH aqueous solution in concentration from 2 to 20 M ($\text{M} = \text{mol dm}^{-3}$) with stirring in a beaker at room temperature. The resulting initial gel was allowed to stand for over 70 h at 25°C in an airtight glass vessel to avoid water evaporation and absorption of carbon dioxide. After the gel formation was completed, air bubbles in the gel were removed under vacuum. The resulting transparent gel was stored at 25°C.

2.2 Preparation of negative electrode

An ingot of $\text{MmNi}_{3.6}\text{Mn}_{0.4}\text{Al}_{0.3}\text{Co}_{0.7}$ alloy was prepared by arc melting under an argon atmosphere in a water-cooled copper crucible. The alloy was pulverized mechanically being passed through graded sieves to obtain alloy particles in the range of 106 to 125 μm .

Roll-compacted metal hydride electrodes were prepared according to the following steps. The alloy powder (95 wt%), acetylene black (4 wt%) and PTFE powder (1

wt%) were mixed thoroughly with using 0.001 dm^3 of ethanol as a solvent, followed by roll-pressing the paste to form its sheet on a flat plate. The resulting disc of the sheet (thickness: *ca.* $200 \mu\text{m}$, surface area: 0.58 cm^2) containing *ca.* 30 mg of the alloy was placed onto a porous nickel substrate followed by pressing it at $3 \times 10^7 \text{ kg m}^{-2}$ for 5 min to prepare paste-type negative electrode.

2.3 Cell assembly

Experimental cell assembly for the polymer gel electrolyte-based Ni/MH cell is shown in Fig. 1. In this work, the simple type cell was used to obtain basic electrochemical data. A similar type of Ni/MH cell was also assembled using a 6 M KOH aqueous solution as an electrolyte for comparison. The negative and positive electrodes were activated in a 6 M KOH aqueous solution in a glass beaker at 30°C prior to the setting of the electrodes in the test cell. The paste-type negative electrode ($\text{MmNi}_{3.6}\text{Mn}_{0.4}\text{Al}_{0.3}\text{Co}_{0.7}\text{H}_x$), a disc of polymer gel electrolyte (3 mm thick, 1.54 cm^2), positive electrode (NiOOH) used in commercial batteries and a polypropylene sheet with a circular hole (3 mm thick, 1.54 cm^2) as a spacer were stacked alternately as shown in the figure. No separator was used in this cell for simplification. The polymer gel electrolyte consisted of 7 wt% potassium salt of crosslinked poly(acrylic acid), 23 wt% KOH and 70 wt% H_2O was used as the electrolyte for the test battery. The battery was deaerated under vacuum, and then stored in an argon atmosphere taking care of avoiding water evaporation. Total thickness of the battery in this work was about 5 mm.

2.4 Electrochemical measurements

In charge-discharge cycle tests, the negative electrode was charged at 50 mA g^{-1} for 4 h (200 mAh g^{-1}) and discharged at various currents to 0.8 V of the cut-off cell voltage. After each charging, the circuit was kept open for 10 min. Charge-discharge cycle tests were performed using galvanostatic charge-discharge unit (Hokuto Denko HJ-101 SN 6). Capacity retention was evaluated as a function of storage time at the charge and discharge currents of 50 mA g^{-1} .

The conductivity of the polymer gel electrolyte was measured by AC impedance spectroscopy between 10 Hz and 10 kHz. A small glass beaker (5 cm^3) with two plati-

nized platinum electrodes placed in 1 cm distance was used for the conductivity cell. Voltammetric study was carried out to examine the electrochemical stability of the polymer gel electrolyte using a Pt working electrode.

3 Results and Discussion

3.1 Electrochemical characteristics of polymer gel electrolyte

Figure 2 shows the conductivity of polymer gel electrolytes and KOH aqueous solutions at 25°C . It can be seen from this figure that the conductivity of the polymer gel electrolytes is very high because of its high content of a 6 M KOH aqueous solution, compared with the PEO-KOH- H_2O (typically 60-30-10 wt%) electrolyte reported by Vassal *et al.*^{10,11} The conductive behavior of the polymer gel electrolytes bears a striking resemblance to KOH aqueous solutions. Maximal conductivity can be seen at intermediate KOH concentration in both electrolytes. This phenomenon is qualitatively interpreted as follows; at low KOH concentrations, conductivity decreases due to a low number of charge carriers, whereas at high KOH concentrations, conductivity decreases due to restriction of ionic mobility.

Figure 3 shows Arrhenius plots of the conductivity for the polymer gel electrolyte and a 6 M KOH aqueous solution. An approximately linear dependency can be seen from this figure over the temperature range of -40 to 80°C . Activation energies for ionic conduction in the polymer gel electrolyte and a 6 M KOH aqueous solution were calculated to be 13.7 and 13.4 kJ mol^{-1} , respectively. The ion conduction mechanism of both electrolytes may be quite similar over the entire concentration of KOH and the temperature range measured in this work. No deterioration or decomposition of the polymer gel was found even in concentrated alkaline media.

The electrochemical behavior of the polymer gel electrolyte was examined by cyclic voltammetry using a smooth platinum electrode. The experiment was performed in the polymer gel electrolyte and a 6 M KOH aqueous solution under argon atmosphere at a scan rate of 100 mV s^{-1} . As can be seen from Fig. 4, there are well-known reaction currents in the KOH aqueous solution in

Fig. 1 Experimental cell assembly for the polymer gel electrolyte-based Ni/MH cell.

Fig. 2 Effect of the KOH concentration on the conductivity of polymer gel electrolytes and KOH aqueous solutions at 25°C .

Fig. 3 Arrhenius plots of the conductivity for the polymer gel electrolyte and a 6 M KOH aqueous solution.

the potential ranges $-1.0 \sim +0.6$ V vs. Hg/HgO : formation of adsorbed hydrogen, oxidation of the adsorbed hydrogen, formation of adsorbed oxygen or platinum oxide layer, reduction of the oxide. Similar reaction currents have been also found in the cyclic voltammogram for the polymer gel electrolyte, however, no significant currents for extra reactions were seen in the voltammogram. From these results, it has been found that no decomposition of the gel electrolyte of potassium salt of crosslinked poly(acrylic acid) occurred in the potential ranges ($-1.0 \sim +0.5$ V vs. Hg/HgO) for charge and discharge of the Ni/MH cell.

Since this polymer gel electrolyte have high conductivity and rather wide potential window, it could become a potential candidate as an electrolyte of alkaline secondary batteries such as a Ni/MH battery.

3. 2 Charge-discharge characteristics

Figure 5 shows typical charge-discharge curves (at 1st, 10th and 50th cycles) of the Ni/MH cells with the polymer gel and a 6 M KOH aqueous solution at 25°C. Well-defined charge and discharge curves were obtained in either case. A plateau of the cell voltage is seen in the discharge curves ranging from 1.3 to 1.1 V. At the first cycle, discharge capacity was about 160 mAh g^{-1} . After the second cycle, stationary discharge capacity of *ca.* $170\text{--}180 \text{ mAh g}^{-1}$ was obtained which corresponds to *ca.* 85-90% of the charged quantity of electricity (200 mAh g^{-1}) of the negative electrode.

The voltage at the last stage of discharge for the Ni/MH cell with the polymer gel electrolyte is rather high, compared to the Ni/MH cell with a 6 M KOH aqueous solution. In the Ni/MH cell of this work, the polymer gel electrolyte and a 6 M KOH aqueous solution were 3 mm thick and no separator was used. As difference of the conductivity between both electrolytes was so small (*ca.* 0.6 S cm^{-1} in Fig. 3), difference of the voltage drops across through the gel and aqueous electrolytes of 3 mm in thickness can be neglected. Although active materials were impregnated in the foamed nickel substrate under high pressure, the active materials might be partially re-

Fig. 4 Cyclic voltammograms of Pt electrode in the polymer gel electrolyte and a 6 M KOH aqueous solution at 25°C. Scan rate : 100 mV s^{-1} .

Fig. 5 Typical charge-discharge curves (at 1st, 10th and 50th cycles) of the Ni/MH cells with the polymer gel electrolyte and a 6 M KOH aqueous solution at 25°C. Quantity of electricity is expressed by the charge passed per unit weight of the alloy used in negative electrode.

leased from the electrode during the charge-discharge process. But, as a whole, charge-discharge characteristics of both Ni/MH cells are quite similar to each other.

Relationships between charged quantity of electricity and discharge capacity are shown in Fig. 6 for the Ni/MH cells with the polymer gel electrolyte and a 6 M

KOH aqueous solution. The discharge capacity was 85~90% of the charged quantity of electricity. The electrochemical reaction of potassium salt of crosslinked poly (acrylic acid) seemed not to occur during charging process (Fig. 4). Decrease of discharge capacity from the nominal capacity might be caused by hydrogen release from the negative electrode because the experimental cell was of an open type.

Figure 7 shows discharge capacities at 25°C as a function of cycle number for the Ni/MH cells with the polymer gel electrolyte and a 6 M KOH aqueous solution. As can be seen from this figure, cycle life of the cell with the polymer gel electrolyte was prolonged keeping discharge capacity of over 85% even at 50th cycle. The discharge capacity was about 70% of charged quantity of electricity at 300th cycle. Under the present conditions there may be no problems in the electrode/electrolyte interface, and then charge and discharge reactions might proceed smoothly. These were resulted from high water-holding capacity of potassium salt of crosslinked poly (acrylic acid). The polymer gel electrolyte might hold enough water for smooth progress of the charge-discharge reactions at the positive and negative electrodes. The polymer gel electrolyte used in this work was found to be so stable during charge-discharge cycling in a concentrated KOH aqueous solution. It had a strong adhesive force to the electrode materials, and thus contact discontinuity between electrode and gel electrolyte did not occur during the cycle test. Another type of negative electrode, which was covered with porous nickel plate to prevent degradation of alloy powder from the porous nickel substrate during the cycle test, was also used in the case of the Ni/MH cell with a 6 M KOH aqueous solution. It was found from Fig. 7 that the Ni/MH cell using the negative electrode covered with porous nickel plate showed better cycle performance than the cell without porous nickel plate in a 6 M KOH aqueous solution.

Fig. 6 Relationship between charged quantity of electricity and discharge capacity for the Ni/MH cells with the polymer gel electrolyte and a 6 M KOH aqueous solution at 25°C.

Figure 8 shows capacity retention obtained from the storage test for twelve days of the Ni/MH cells with the polymer gel electrolyte and a 6 M KOH aqueous solution at 25°C. The capacity retention of these experimental cells is lower than that of the commercial Ni/MH batteries. This is probably because these experimental cells were of an open type and assembled without using a separator for simplification. However, it is clear from this figure that the capacity retention of the Ni/MH cell with the polymer gel electrolyte was much higher than that of the Ni/MH cell with a 6 M KOH aqueous solution. Table 1 shows the surface composition of alloys in negative electrodes stored for eight days (Fig. 8) in the polymer gel electrolyte and a 6 M KOH aqueous solution. The composition of the alloys was determined by EPMA. No significant change was observed for the contents of Mn, Ni and Co of the alloys before and after the storage test. However, the contents of Mn and Al decreased for the alloys after the storage test in the polymer gel electrolyte and a 6 M KOH aqueous solution. This result is attributed to the dissolution of those metals in the electrolytes during storage of the cells, affecting the discharge capacity of the cells. It should be noted that the dissolution

Fig. 7 Discharge capacities at 25°C as a function of cycle number for the Ni/MH cells with the polymer gel electrolyte and a 6 M KOH aqueous solution. *negative electrode covered with porous Ni plate.

Fig. 8 Capacity retention characteristics of the Ni/MH cells with the polymer gel electrolyte and a 6 M KOH aqueous solution at 25°C.

Table 1 Surface composition of alloys in negative electrodes stored for eight days in the polymer gel electrolyte and a 6 M KOH aqueous solution.

Negative electrode	atom% (M/Mm ratio)				
	Mm	Ni	Mn	Al	Co
As prepared	18.6 (1.00)	60.8 (3.27)	5.3 (0.28)	4.0 (0.22)	11.2 (0.60)
Stored in the polymer gel electrolyte	18.2 (1.00)	61.6 (3.38)	5.1 (0.28)	2.8 (0.16)	11.2 (0.60)
Stored in a 6 M KOH aqueous solution	18.8 (1.00)	62.0 (3.30)	4.6 (0.24)	2.3 (0.12)	11.5 (0.61)

rates of those elements are larger in a 6 M KOH aqueous solution than the polymer gel electrolyte. This is probably due to the low solubility of alloy constituents in the polymer gel electrolyte. It seemed that inhibition of the dissolution of those metals resulted in high capacity retention of the Ni/MH cell with the polymer gel electrolyte. Work along this line is in progress.

4 Conclusion

The polymer gel electrolyte prepared from potassium salt of crosslinked poly(acrylic acid) and a KOH aqueous solution was found to have high ionic conductivity almost comparable to the KOH aqueous solution over the wide ranges of KOH concentration and temperature. The polymer gel electrolyte had enough potential windows for charge and discharge reactions of the Ni/MH battery. The experimental Ni/MH cell assembled using the polymer gel electrolyte exhibited equivalent or better charge-discharge and capacity retention characteristics at 25°C, compared with the cell assembled using a 6 M KOH aqueous solution. The polymer gel electrolyte has found to be stable in concentrated KOH aqueous solution and acted as an excellent electrolyte to avoid rapid evaporation of water from the gel. The polymer gel electrolyte used in this work therefore seems to have the applicability to alkaline secondary batteries such as a Ni/MH battery.

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