JOURNAL OF MATERIALS SCIENCE **39** (2004) 703–705

Possible application of novel solid polymer membrane gel separator in nickel/metal hydride battery

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The sealed rechargeable nickel/metal hydride battery offers significant improvement over conventional rechargeable batteries in term of performance and environmental friendliness. The high energy density, excellent power density, and long cycle life of Ni/MH batteries also make them a leading technology as the battery source for electric vehicles. However, the greatest problem of Ni/MH batteries is their inherent high corrosion rate in aqueous solution. As a contribution to alkaline Ni/MH secondary battery technology, there has been a strong demand to present an original approach consisting of the replacement of the conventional aqueous electrolyte by a solid or gel polymer electrolyte [1, 2].

The concept of solid polymer electrolyte was first introduced by Armand [3], who discovered a new class of polymer electrolytes made conducting through dissolution of lithium salts. The discovery of polymeric "immobile solvents" became the basis of the lithium capable polymer battery. For the last 20 years, the polymer electrolyte used for lithium battery and fuel cell has been studied broadly and intensively, whereas, few reports on a solid or gel polymer electrolyte used for Ni/MH and related batteries have been presented.

The fast proton conductors, such as $Sb_2O_5 \cdot n\,H_2O$ [4] (protonic conductivity: 2.6×10^{-3} S cm^{-1} at 25 °C) and $HUO_2PO_4 \cdot 4H_2O$ [5] (protonic conductivity: 8×10^{-4} S cm^{-1} at 25 °C), have first been studied as solid electrolytes for Ni/MH related batteries. Kuriyama *et al.* [6] have reported research on a high proton conductivity of a clathrate hydrate, tetramethylammonian hydroxide penahydrate, $(CH_3)_4NOH \cdot 5H_2O$ (protonic conductivity: 4.5×10^{-3} S cm^{-1} 25 °C) and the performance of an all solid state type nickel/metal hydride (Ni/MH) battery, applying it as a solid electrolyte, e.g., $LaNi_{2.5}Co_{2.4}Al_{0.1}/(CH_3)_4NOH \cdot 5H_2O/NiOOH$. Vassal and Yang *et al.* [7–11] have investigated an original family of alkaline solid polymer electrolytes based on poly(ethylene oxide) PEO, poly(vinyl alcohol) PVA, potassium hydroxide KOH, and water H_2O.

The most commonly used separator in rechargeable cells is porous insulator film of polyolefin, nylon, or cellophane. Acrylic compounds may also be radiation-grafted onto these separators to make them more wettable and permeable to the electrolyte. Here, we develop a solid polymer membrane gel separator, which comprises a polymerization product of one or more monomers selected from the group of water-soluble ethylenically unsaturated amides and acid. The polymer-based gel also includes a water swellable polymer, which acts as a reinforcing element. In addition, ionic species are added to the solution and remain embedded in the polymer gel after polymerization.

The simple experimental Ni/MH cell for a preliminary investigation was assembled using solid polymer membrane gel separator and its charge-discharge characteristics were tested. A similar type of Ni/MH cell was also assembled using a 7.2 M KOH aqueous solution for comparison.

Electrode preparation: Pasted nickel electrodes were prepared as follows: nickel hydroxide powder was mixed with powder and Merhocel; a 1000 kg m^{-3} solution of cobalt sulfate and a suspension a 60 wt% polytetrafluroethylene (PTFE) were added and blended to obtained a paste, which was then loaded onto a nickel foam substrate having a porosity of about 90%. Subsequently, these electrodes were dried at 60 °C for 15 h and were finally shaped into a combat solid by pressing at 200 MPa. The composition was fixed at 66.8 wt% $Ni(OH)_2$, 8.3 wt% Ni, 1 wt% Methocel, 4 wt% dry PTFE, and 19.9 wt% $CoSO_4$ solution. These nickel electrodes had a theoretical capacity of 289 mAh g^{-1}.

The metal hydride material was a mish metal (Mm) of the AB_5 types, with the general composition $LaMmNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$. The metal hydride electrodes were prepared by a roller-pressing process, which involved spreading a blend of 90 wt% alloy powder, 5 wt% carbon black, and 5 wt% dry PTFE, with ethanol as a solvent. After drying for 15 h under vacuum at room temperature, the band was cut to suitable size and cold-pressed on nickel foam at 500 MPa to form

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the electrodes. The metal hydride electrodes had a theoretical capacity ranging from 250 to 300 mAh g^{-1}.

Solid polymer membrane gel separator preparation: The solid polymer membrane gel separator was prepared as the following procedure. 0.75 g methylenebisacrylamides, 0.56 g acrylamide, 4.70 g methylacrylic acid, and 0.25 g poly(sodium 4-styrenesulfonate) were dissolved in 10×10^{-6} m^3 water and then 20×10^{-6} m^3 40 wt% KOH was added to the resulting solution, which was maintained at room temperature. 0.05 g ammonium persulfate was then added to the solution. A piece of fabric was soaked in the resulting monomer solution and then sandwiched between a piece of glass and a piece of PET transparent film. This was heated on a 75 °C hotplate for 1 min and then irradiated under strong UV light for 5 min for each side.

The negative and positive electrodes were activated in a 7.2 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 ($LaMmNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$), solid polymer membrane gel separator (0.3 mm thick) and positive electrode (NiOOH) were stacked alternately as shown in the Fig. 1.

The typical charge-discharge curves of the assembled Ni/MH cell with the solid polymer membrane gel separator and a 7.2 M KOH aqueous solution at 25 °C are shown in Fig. 2. It appears the similarity in the voltage performance, which exhibits a well-defined plateau at 1.1 V for discharge and at 1.35 V for charge. As a whole, the charge-discharge characteristics of both Ni/MH cells are quite similar to each other.

The electrochemical behavior of the solid polymer membrane gel was examined by cyclic voltammetry using a smooth platinum electrode. The experiment was performed in the solid polymer membrane gel separator and a 7.2 M KOH aqueous solution under argon atmosphere at a scan rate of 100 mV s^{-1}. As can be seen in Fig. 3, there are well-known reaction currents in the KOH aqueous solution in the potential ranges −1.0 to +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 also have been found in the cyclic voltammogram for the solid polymer membrane gel separator, however, no significant currents for extra reactions were seen in the voltammogram. From these results, it has been found that no decomposition of the solid polymer membrane gel separator of potassium salt of cross-linked poly(methylacrylic acid) occurred in the potential ranges (−1.0 to +0.5 V vs. Hg/HgO) for charge and discharge of the Ni/MH cell. Since this solid polymer membrane gel separator has a high conductivity and wide potential window, it could become a potential candidate as an electrolyte of alkaline secondary batteries such as a Ni/MH battery.

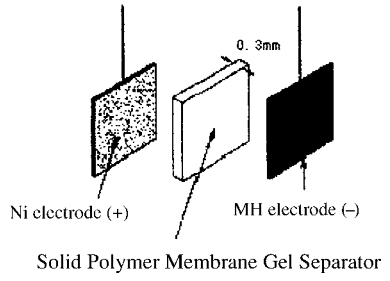

Figure 1 Schematic cell design of experimental Ni/MH cell using the solid polymer membrane gel separator.

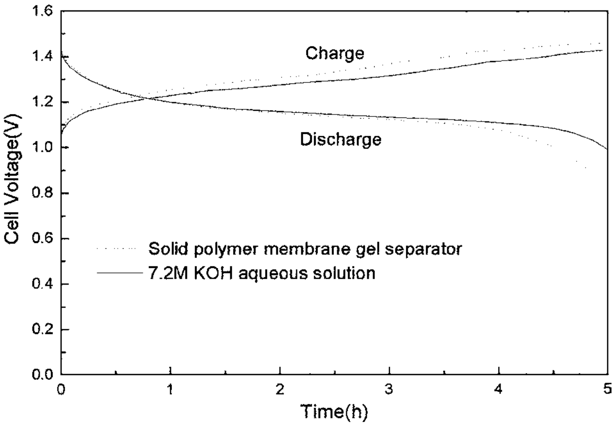

Figure 2 Typical charge-discharge curves of Ni/MH cells with the solid polymer membrane gel separator and a 7.2 M KOH aqueous solution at 25 °C, 0.2 C charge and discharge rate.

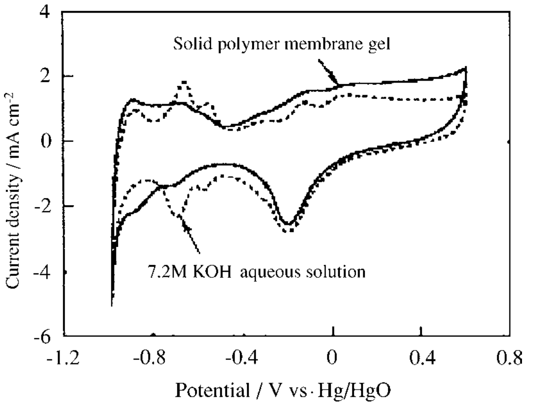

Figure 3 Cyclic voltammograms of Pt electrode in the solid polymer membrane gel separator and a 7.2 M KOH aqueous solution at 25 °C. Scan rate: 100 mV s^{-1}.

The ionic conductivity at room temperature of the solid polymer membrane gel separator is about 3.6×10^{-1} S cm^{-1}, which is the same degree that of the 7.2 M KOH aqueous solution (6×10^{-1} S cm^{-1}) but much higher than that of PEO-based solid polymer electrolyte (at best 10^{-3} S cm^{-1} [7]). In Ni/MH batteries, the charge-discharge involves the hydrogen ion shuttled between the positive and the negative electrodes. Poly(methylacrylic acid) is a well-known polymer that has a high water-absorbing capacity, a high water-holding capacity. The poly(methylacrylic acid) grafted onto the separator make it can hold more KOH aqueous solution in gel state. Moreover, the copolymerization of poly(sodium 4-styrenesulfonate) can improve the ion movement and prevent the diffusion of reaction products such as metal oxides to remaining parts of the cell which is a key factor affecting the cycle life of the Ni/MH batteries.

The results presented here have been shown that the use of solid polymer membrane gel separator may be a good alternative in order to avoid problems of leakage or electrode corrosion related to the high convection occurring in an aqueous solution of potassium hydroxide. Moreover, the addition of poly(sodium 4-styrenesulfonate) may lead to a decrease of the self-discharge rate. Nowadays, more and more nickel/metal hydride batteries of bipolar design are being developed because they offer some advantages for applications as power storage system for electric and hybrid vehicles. The solid polymer membrane gel separator could be very useful for such an application in bipolar design, avoiding short-circuits occurring in liquid-electrolyte system.

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Received 8 May
and accepted 18 August 2003