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C.Y Wang

University of Wollongong, caiyun@uow.edu.au

J. Sun

Monash University

Hua-Kun Liu

University of Wollongong, hua@uow.edu.au

S. X. Dou

University of Wollongong, shi@uow.edu.au

D. MacFarlace

Monash University

See next page for additional authors

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Authors

C.Y Wang, J. Sun, Hua-Kun Liu, S. X. Dou, D. MacFarlace, and M. Forsyth

Potential Application of Solid Electrolyte P11OH in Ni/MH Batteries

C.Y. Wang*¹, J. Sun², H.K. Liu¹, S.X. Dou¹, D. MacFarlace² and M. Forsyth²

¹ Institute for Superconducting & Electronic Materials, University of Wollongong, NSW 2522, Australia

² School of Physics and Materials Engineering, Monash University, VIC 3800, Australia.

Abstract

N,N-Dimethylpyrrolidinium hydroxide (P11OH) with polymer poly(tetramethyl ammonium acrylate) (PTMA) was investigated as an electrolyte in Ni/MH cells in this work. The efficiency and the performance of the electrolyte was discussed and elucidated with the performance of the cell. Their electrochemical characteristics had been investigated at different temperatures (25°C and 50°C) and different discharge current (15 mA g⁻¹ and 30 mA g⁻¹). The results show that the cell with electrolyte polymer-P11OH is dischargeable at these two temperatures, and a discharge capacity of 142 mAh g⁻¹ at 25 °C has been obtained.

Keywords: polymer electrolyte, N,N-Dimethylpyrrolidinium hydroxide, Ni/MH cell, discharge capacity

1. Introduction

Nickel metal hydride (Ni/MH) battery is an alkaline storage secondary battery, and it has many significant advantages over other rechargeable batteries including cycle life, safety and nonhazardous materials. The electrolyte plays an important role in Ni/MH battery, particularly for nickel hydroxide electrode. It is involved in the material transfer to and away from the electrodes by the exchange of both OH⁻ ions and alkali. Moreover, it relates to charge acceptance, charge and discharge potentials, structural changes and electrode ageing [1]. Now the common accepted and used electrolyte in the battery industry is 30 wt. % KOH for its high conductivity. A small amount of LiOH is added to aid charge acceptance by the cathode. However, nickel hydroxide will transform into γ-NiOOH after long time charging or overcharging in KOH, and the formation of γ-NiOOH is thought to be the main cause of the deterioration of the service life of the battery. Solid or gel alkaline electrolytes are superior to liquid electrolyte (KOH) not only in the restraint of the formation of γ-NiOOH [2], but also in their reliability, safety and simple processibility [3–5].

For solid polymer or gel electrolytes, they must possess similar functions as liquid electrolytes to carry proton or hydrogen during the electrochemical process in Ni/MH batteries. In addition, mechanical strength, high ionic conductivity, fast charge transfer at the electrode interfaces and electrochemical stability are also essential

for their performance in the battery [6]. N,N-Dimethylpyrrolidinium hydroxide (P11OH.4H₂O, abbreviated as P11OH) was found to exhibit high ionic conductivity of 7×10⁻³ S cm⁻¹ at 25°C in its solid state [7], and such high ionic conductivity has attracted the authors' interest on its potential application as an electrolyte in Ni/MH battery. There has not been any report about it to date.

In order to decrease the melting point, polymer poly(tetramethyl ammonium acrylate, abbreviated as PTMA) was added in P11OH. Their schematic formulas are shown in Fig.1. In this work the electrochemical properties of Ni/MH cells with a polymer-P11OH electrolyte were investigated, and the efficiency and performance of the solid electrolyte were discussed and elucidated with the performance of the cell.

Fig.1. The schematic formulas of P11OH and PTMA

* Corresponding author. Tel: +62-2-42213127; fax: +62-2-42213114; E-mail: cw16@uow.edu.au

2. Experimental

2.1 Synthesis of polymer-P11OH

Synthesis details of P11OH were described in reference [7]. PTMA was prepared by reaction of poly(acrylic acid) (Aldrich) with tetramethyl ammonium hydroxide (Aldrich, all chemicals were used as received) in a water solution. The samples of P11OH and PTMA were dried under vacuum at 60°C for 2 days before use, and the polymer-P11OH electrolyte was prepared by dissolving 10 wt % of PTMA in P11OH at about 50°C. To protect the sample from absorbing moisture from air, the polymer-P11OH electrolyte preparation was carried out in a glove box under a nitrogen atmosphere. It was found in this work that the PTMA-P11OH (10 wt % of PTMA) sample was solid at room temperature, but was a gel material at about 40°C, and conductivity of the PTMA-P11OH sample was close to that of pure P11OH.

2.2 Electrode fabrication and cell construction

The modular sealed cell was designed and made in the workshop of the Engineering Faculty in the University of Wollongong, and used to investigate the electrochemical properties of the electrolyte in Ni/MH cell. The main part of the cell was two polyethylene plates with screws to tighten them. The electrodes and separator were installed between these two plates. The epoxy resin was used to seal the modular cells and isolate the components of the cell from the moisture and oxygen in the air.

In the cell, the cathode electrode was nickel hydroxide electrode, the anode electrode was AB₅-type hydrogen storage alloy electrode, and the polypropylene non-woven fabric was used as separator. The cathode and alloy electrodes have the same size, but one cathode electrode is matched and inserted between two alloy electrodes to make the capacity of the alloy electrode larger than that of the cathode electrode. Both nickel hydroxide and alloy electrodes were activated in 6M KOH solutions in advance, and they were used to assemble the cells at their discharge state. The cells were assembled in the glove box with a stream of high purity argon. To obtain an intimate contact between the polymer-P11OH electrolyte and the electrodes, and hence reduce the resistance caused by grain boundaries of the PTMA-P11OH electrolyte powders, the PTMA-P11OH electrolyte was heated to homogeneous liquid state and all the electrodes and separators were impregnated into the liquid state electrolyte for 30 minutes to ensure the electrolyte had penetrated into their inner part.

2.3 Cell test

Cells were tested using a battery test device (Neware Electronic Co., China). In our experiments the cells were designed to be cathode-limited, the capacity of the cathode is much larger than that of the anode. The charge/discharge

capacity was calculated based on the amount of the active material (nickel hydroxide) in the cathode electrode.

The scheme to run the cell in this work is stated as follows: galvanostatically charged to 360 mAh g⁻¹, then discharged to the cut-off voltage of 0.9V. The experiment had been carried out under different temperatures of 25°C and 50°C. The temperature of 50°C was achieved by use of a thermostat water bath.

3. Results and Discussion

3.1 Charge/discharge properties

The charge/discharge properties of the cell with the PTMA-P11OH electrolyte were investigated at 25°C at the current of 15 mA g⁻¹. The relationship between the cell voltage and the capacity is shown in Fig.2 as a typical charge/discharge curves. In charge curve A, the cell voltage increased with the charge capacity. The discharge curve B (can be seen clearly in Fig.3) can be divided into three stages. The cell voltage dropped sharply from the beginning to 1.35V, and it was the first stage and the rate-determining step of the reaction at this stage is the proton diffusion. Then the voltage dropped gradually to 1.15V and the discharge plateau was formed. At this stage the rate-determining step is proton and charge transfer. The sharp drop of the cell voltage in the third stage is caused by the increased charge transfer resistance due to the increasing formation of semiconductor Ni(OH)₂.

Fig.2. Charge/discharge curve of Ni/MH cells with PTMA-P11OH as electrolyte at 25°C (current rate: 15mA g⁻¹)

A discharge capacity of 142 mAh g⁻¹ has been obtained for the cell with the PTMA-P11OH electrolyte. The results show that a Ni/MH cell with this electrolyte is dischargeable, and it also demonstrates that the PTMA-P11OH electrolyte possesses the function to carry proton or hydrogen during the electrochemical process. The performance of the cell with the PTMA-P11OH electrolyte was also investigated at a higher discharge

current of 30 mA g^{-1} , and the corresponding discharge curve (c) is shown in Fig. 3. It can be seen that the discharge capacity was much lower compared with that at the current of 15 mA g^{-1} ; only 43 mAh g^{-1} has been obtained. The cell shows poor performance at the higher discharge current. Perhaps the charge and proton transfer speed at the second stage cannot satisfy the faster reaction requirement at the high discharge current.

Fig. 3. Discharge curves of Ni/MH cells with PTMA-P11OH as electrolyte

The performance of the cell with the PTMA-P11OH electrolyte was also investigated at the higher temperature of 50°C , and the charge curves obtained at the current of 15 mA g^{-1} are shown in Fig. 4. It can be seen that the charge voltage was lower than that of 25°C . The final charging voltage was 1.41 V at 25°C , while only 1.35 V for the temperature of 50°C . There are two reasons to explain the charge voltage drop: 1), the ionic conductivity of the PTMA-P11OH electrolyte becomes higher and thus reduce the proton and charge transfer resistance at the high temperature; 2), the oxygen overpotential of the nickel electrode drops rapidly at high temperature [8]. It needs further experiments to investigate the main cause for this drop.

The discharge properties of the cell at 50°C was also investigated in this work, and the discharge curve is shown in (curve D) Fig. 3. The discharge current is 15 mA g^{-1} , and a discharge capacity of 46 mAh g^{-1} has been obtained. It indicates that the PTMA-P11OH electrolyte still possess the function to carry proton and hydrogen during the electrochemical process at 50°C .

Fig. 4. Charge curves of Ni/MH cells with the PTMA-P11OH electrolyte at 25°C and 50°C (current: 15 mA g^{-1})

3.2 Cycle life

The cycle ability of the cell was investigated at 25°C , and the discharge capacities as a function of the cycle number are shown in Fig. 5. The curve A is obtained at the discharge current density of 15 mA g^{-1} , and the curve B shows the cell's performance at 30 mA g^{-1} . It can be seen that the discharge capacity of the cell dropped slowly at these conditions, which means that the cell with the polymer-P11OH electrolyte possess good cycle life. It also indicates that polymer-P11OH is suitable to be used in Ni/MH battery. However, the discharge capacity of the cell is still lower than that with KOH electrolyte (usually about 260 mAh g^{-1}). Perhaps it is caused by the low ionic conductivity of the electrolyte PTMA-P11OH.

Fig. 5. Cycle life of Ni/MH cells with the PTMA-P11OH electrolyte at 25°C

4. Conclusions

The charge and discharge curves have been obtained for the Ni/MH cell with the PTMA-P11OH electrolyte. An obvious discharge plateau has been shown in the discharge curve at the current density of 15 mA g^{-1} and 25°C , and it can be divided into three stages. The rate-determining step for the first two stages are proton diffusion, proton and charge transfer. A discharge capacity of 142 mAh g^{-1} has been obtained. At the discharge current density of 30 mA g^{-1} the discharge capacity decreased to 43 mAh g^{-1} . Perhaps it is because the charge and proton transfer speed cannot match the increased electrochemical reaction speed at the higher discharge current.

Different charge characteristics have been shown for the cell with the PTMA-P11OH electrolyte at 25°C and 50°C . The charge voltage became lower at the higher temperature. At 50°C , a discharge capacity of 46 mAh g^{-1} has been obtained at the discharge current density of 15 mA g^{-1} . The cell also demonstrates a promising cycle life at the discharge current density of 15 mA g^{-1} and 30 mA g^{-1} .

All the results show that the Ni/MH cell with the PTMA-P11OH electrolyte is dischargeable at the temperature from 25°C to 50°C . It also indicates that the PTMA-P11OH electrolyte possesses the function to carry proton or hydrogen at the temperature range from 25°C to 50°C , and is a promising alkaline polymer electrolyte in Ni/MH battery industry. However, a lot of work needs to be

done for commercializing this promising solid electrolytes in the Ni/MH battery industry.

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