Preparation and characterization of gel polymer electrolytes for solid state magnesium batteries

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Abstract

Magnesium-ion conducting gel polymer electrolytes (GPE) were prepared and their electrochemical properties were characterized. The composition of GPE containing P(VdF-*co*-HFP), $Mg(ClO_4)_2$–EC/PC and SiO_2 was optimized in consideration of ionic conductivity and mechanical stability. Solid state magnesium cell employing magnesium anode, GPE, and vanadium oxide cathode was assembled and its cycling characteristics were investigated. The $Mg/GPE/V_2O_5$ cell showed low initial discharge capacity of 58 mAh/g based on active V_2O_5 material and poor cycling characteristics. At present, the results show that the $Mg/GPE/V_2O_5$ cell has an inferior cycling performance in comparison with that of well-developed, lithium metal polymer cells.
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1. Introduction

There has been a lot of interests on research and development of solid state electrochemical devices such as rechargeable batteries, capacitors and sensors, which employ a thin film of solid polymer as an electrolyte material [1–4]. Among the electrochemical devices, polymer electrolytes have been widely studied and developed for battery applications over the past 25 years, because the use of a polymer electrolyte makes the fabrication of safe batteries possible and permits the development of thin batteries with design flexibility, which are mainly directed toward the rechargeable lithium battery systems. Although exploratory research has been made on monovalent salt systems, little attention has been given to the polymer electrolytes in which multivalent cations are the mobile species. In view of negligible hazards and enhanced safety, studies on rechargeable magnesium batteries are expected to have a wide scope in the future [5–7]. Magnesium metal possesses a number of characteristics which make it attractive as a negative electrode material for rechargeable batteries; highly negative standard potential (−2.375 V versus SHE), relatively low equivalent weight (12 g per Faraday), high melting point (649 °C), low cost, relative abundance, high safety, ease of handling, and low toxicity which allows for urban waste disposal. In resemblance to the rechargeable lithium battery system, the solid state rechargeable magnesium battery requires a Mg^{2+}-ion conducting polymer electrolyte.

In this work, we prepared the gel polymer electrolyte (GPE) in which magnesium ion is highly mobile. We will report the electrochemical properties of Mg^{2+}-ion conducting gel polymer electrolyte. With a GPE of optimum composition, solid state $Mg/GPE/V_2O_5$ cell is assembled, and its cycling performances will be briefly examined to evaluate the applicability of the gel polymer electrolyte to solid state rechargeable magnesium batteries.

2. Experimental

2.1. Preparation of gel polymer electrolyte

Poly(vinylidene fluoride-co-hexafluoropropylene) (P(VdF-*co*-HFP)), Kynar 2801 (Elf Atochem) was used as

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a matrix polymer for preparing the gel polymer electrolyte. The polymer was first dissolved in anhydrous acetone. After the polymer was completely dissolved, a predetermined amount of liquid electrolyte, 1 M $Mg(ClO_4)_2$ in EC (ethylene carbonate)/PC (propylene carbonate) (1:1 by volume) was added and the solution was further stirred. An appropriate amounts of high-purity silanized fumed silica (Cabot Co.) was then added, which had been treated with hexamethyldisilazane. When complete homogenization of the mixture was achieved, the resulting viscous solution was cast with a doctor blade onto a release paper, then left to evaporate the solvent slowly at room temperature. After evaporation of acetone, the film was separated from the release paper. The thickness of cast film was in the range of 60–100 μm. The polymer electrolyte was confirmed to be free of acetone by means of ^{1}H NMR. All procedures for preparing polymer electrolytes were carried out in a dry box filled with argon gas (99.999%). Tensile strength of gel polymer electrolytes was measured according to the ASTM 882 with a materials testing machine (Lloyd, LRX-PLUS).

2.2. Electrical measurements

Gel polymer electrolyte film was cut into 4 cm^2 squares and sandwiched between the two stainless steel (SS) electrodes for conductivity measurements. The sandwich was vacuum-packed in an aluminum plastic pouch in order to avoid contamination. The ac impedance measurement was then performed using Zahner Elektrik IM6 impedance analyzer over a frequency range of 100 Hz–1 MHz with an amplitude of 10 mV. The anodic decomposition voltage was determined by running linear sweep voltammetry on a stainless steel working electrode with magnesium electrodes as the counter and reference electrode at a scanning rate of 1 mV/s.

2.3. Mg/GPE/V$_2$O$_5$ cell

The V$_2$O$_5$ cathode on an aluminium foil consisted of V$_2$O$_5$ with PVdF and super-P carbon at the proportions of 85:5:10 by weight percent. The Mg/GPE/V$_2$O$_5$ cell was assembled by sandwiching the gel polymer electrolyte (GPE) between the magnesium anode and V$_2$O$_5$ cathode. The cell was then enclosed in a metallized plastic bag and vacuum sealed. All assemblies of the cell were carried out in a dry box filled with argon gas. The cycle test of Mg/GPE/V$_2$O$_5$ cell was conducted in the voltage range of 0.5–4.0 V at constant current with galvanostatically controlled equipment.

3. Results and discussion

Fig. 1 shows the temperature dependence of ionic conductivities for the gel polymer electrolyte containing P(VdF-co-HFP), Mg(ClO$_4$)$_2$ and silica with different proportions. In every system, the temperature dependence is found to be non-Arrhenius, exhibiting slight curvature, and it may
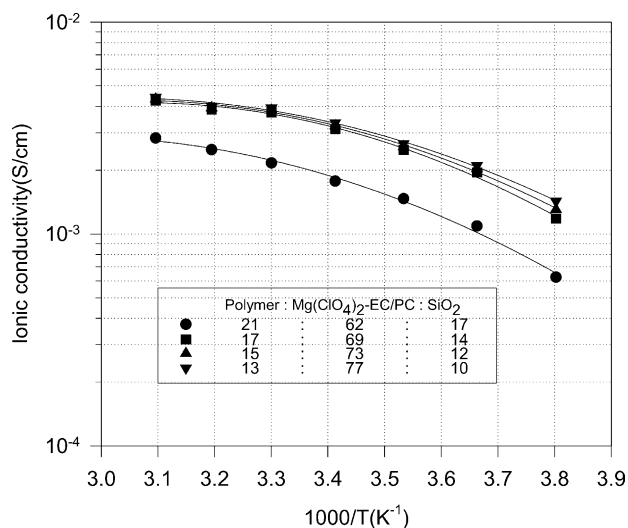

Fig. 1. Temperature dependence of ionic conductivity for Mg^{2+}-ion conducting gel polymer electrolytes.

be described by a Vogel–Tamman–Fulcher (VTF) equation over the temperature range measured. The ionic conductivity increases with the amount of electrolyte solution in the gel polymer electrolyte. The improved ionic conductivity is due to both the enhancement of the ionic mobility and the increase of carrier ions. Addition of the finely divided SiO$_2$ powder was shown to reinforce the physical strength of the film. The gel polymer electrolyte containing 17% silica shows a higher tensile strength (2.6 MPa) as compared to that (0.2 MPa) of the gel polymer electrolyte without silica. Over 14 wt.% of silica in the gel polymer electrolyte, the addition of silica powder decreases ionic conductivity due to the restriction of ionic motion. For the systems under study, the optimum SiO$_2$ content is believed to be 12% in terms of both ionic conductivity and mechanical stability. For this system, the ionic conductivity reaches the order of 3.2 × 10^{-3} S/cm at room temperature to give free-standing films sufficient to prepare thin film. In further discussions, the composition of gel polymer electrolyte will thus be restricted to 15:73:12 (polymer:liquid electrolyte:SiO$_2$) by weight percent.

For Mg/V$_2$O$_5$ cell, the potential can be as high as 4.0 V versus Mg/Mg^{2+} [6], implying that the gel polymer electrolyte should be electrochemically stable up to at least 4.0 V. The electrochemical stability of gel polymer electrolyte was evaluated by linear sweep voltammetric measurement. The voltage was swept from the open circuit potential of cell towards more anodic values until a large current due to the electrolyte decomposition at the inert electrode interface occurred. Fig. 2 shows the linear sweep voltammetry curve of the cell prepared with gel polymer electrolyte. As can be seen, the decomposition voltage is found to be higher than 4.3 V, which suggests that the gel polymer electrolyte is acceptable for magnesium cell using a V$_2$O$_5$ as an active cathode material.
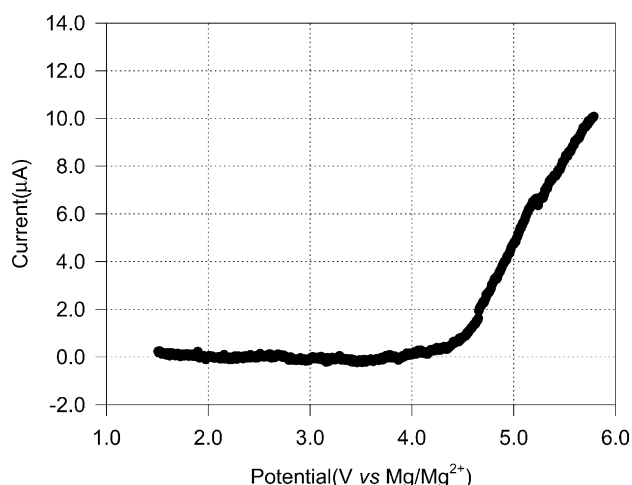
Fig. 2. Linear sweep voltammogram of Mg/GPE/SS cell (scan rate = 1 mV/s).

Fig. 4. Discharge capacities of Mg/GPE/V_2O_5 cell as a function of cycle number.

Mg/GPE/V_2O_5 cell was fabricated with a GPE of optimum composition. Since the cell was assembled in charged condition, it was first subjected to discharge. Fig. 3 shows the first discharge-charge curves of Mg/GPE/V_2O_5 cell at a constant current density of 0.04 mA/cm^2. Potential plateaus were observed in both discharge and charge curves. That is, during the first discharge, Mg^{2+} ion is inserted into V_2O_5 structure from GPE, and deserted from V_2O_5 to GPE during the recharge. The specific discharge capacity of 58 mAh/ g based on V_2O_5 cathode material was obtained at the first discharge. In charge cycle, high overvoltage and poor rechargeablity could be observed. High interfacial resistance at Mg anode is thought to be responsible for high overvoltage and poor reversibility of the Mg/GPE/V_2O_5 cell, as the many previous workers have reported [8–11]. It is well known that the passivating layer coveri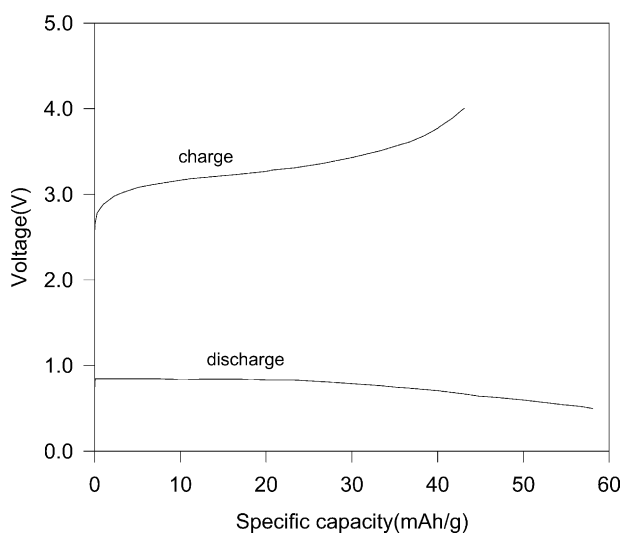ng the active lithium metal in the cells using a lithium metal as an anode are Li$^+$ ion conductors. In contrast, surface films formed on magnesium metal in the rechargeable magnesium cell can hardly conduct Mg^{2+} ions. This presumption was confirmed by ac impedance analysis. From the ac impedance measurements at Mg/GPE interface, it was observed that the interfacial resistance was about 3560 Ω cm^2, which was considerably higher than the value obtained from Li/GPE interface (163 Ω cm^2). For Li/GPE/V_2O_5 cells prepared with Li-ion conducting gel polymer electrolyte, the cycling performance was proven fairly good [12].

Fig. 4 shows the discharge capacity as a function of cycle number. The discharge capacity abruptly decreased at second cycle and gradually declined with subsequent cycling. Capacity decline with cycling is also attributed to the Mg/GPE interface, where the surface film grows in thickness during the repeated cycling. Surface films block the charge transfer reaction between Mg anode and gel polymer electrolyte, since the mobility of Mg^{2+} ions in the passivating films is extremely low. From these results, it is concluded that further research about Mg/GPE interface should be conducted to improve the cycling performances of solid state magnesium battery to practical level, which is progress in our laboratory.

4. Conclusions

Mg^{2+}-ion conducting gel polymer electrolytes have been prepared. Ionic conductivity reached 3.2 × 10^{-3} S/cm in the gel polymer electrolyte containing 15% P(VdF-*co*-HFP), 73% Mg(ClO$_4$)$_2$–EC/PC and 12% silanized fumed silica at room temperature, and use of this GPE assured an electrochemical stability of 4.3 V versus Mg/Mg^{2+}. Solid state Mg/GPE/V_2O_5 cell showed low initial discharge capacity and poor cycling performances, which are attributed to high interfacial resistance at Mg anode.

Fig. 3. First discharge and charge curve of Mg/GPE/V_2O_5 cell at 0.04 mA/ cm^2.

Acknowledgement

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