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Journal of Power Sources 93 (2001) 151–155

JOURNAL OF
POWER
SOURCES

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Electrochemical characteristics of Li/LiMn₂O₄ cells using gel polymer electrolytes

Dong-Won Kim*, Jang-Myoun Ko, Jong-Han Chun

Department of Chemical Technology, Taejon National University of Technology, San 16-1, Dukmyung-Dong, Yuseong-Gu, Taejon 305-719, South Korea

Received 13 July 2000; accepted 18 August 2000

Abstract

Gel polymer electrolytes composed of acrylonitrile–methylmethacrylate (AM) copolymer and 1 M LiClO₄–ethylene carbonate (EC)/propylene carbonate (PC) are prepared. The ionic conductivity reaches $1.9 \times 10^{-3} \text{ S cm}^{-1}$ in a gel polymer electrolyte with 20 wt.% of AM copolymer and 80 wt.% of LiClO₄–EC/PC at room temperature. These systems showed no solvent exudation from the matrix polymer due to enhanced compatibility between AM copolymer and organic liquid electrolyte. A Li/gel polymer electrolyte/LiMn₂O₄ cell has a reversible capacity of 132 mAh g⁻¹ in the voltage range of 3.0–4.3 V at the C/5 rate and shows good cycling performance with a coulombic efficiency >99%. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cycling performance; Gel polymer electrolytes; Ionic conductivity; Lithium manganese oxide; Lithium polymer battery

1. Introduction

Polymer electrolytes are receiving considerable attention as solid electrolyte materials in advanced applications such as rechargeable lithium batteries because their use allows the fabrication of highly safe batteries and permits the development of thin batteries with design flexibility [1–3]. Conventional poly(ethyleneoxide) (PEO)-based polymer electrolytes are the most commonly studied. The electrolytes exhibit conductivities which range from 10^{-8} to $10^{-5} \text{ S cm}^{-1}$ at room temperature. This excludes practical application at ambient temperature [4]. In order to enhance conductivity at room temperature, several classes of gel polymer electrolytes have been developed and characterized. Such electrolytes are prepared by incorporating liquid electrolytes in a matrix polymer such as polyacrylonitrile (PAN), poly(vinylidene fluoride) (PVdF), poly(methylmethacrylate) (PMMA), poly(vinylchloride) (PVC), poly(vinylpyrrolidone) (PVP) and poly(vinylsulfone) (PVS) [5–9]. The ionic conductivities of these systems exceed $10^{-4} \text{ S cm}^{-1}$, which is necessary for battery applications. These plasticized polymer electrolytes combine the best features of both liquid and solid electrolytes [10]. In our previous study [11], the electrical properties of the gel polymer electrolytes based on acrylonitrile–methylmethacrylate (AM) copolymer were reported.

The ionic conductivity reached $2.0 \times 10^{-3} \text{ S cm}^{-1}$ in a gel electrolyte containing LiClO₄–EC/PC at room temperature. This paper is an extension of this research.

In this work, we have prepared gel polymer electrolytes (GPE) composed of AM copolymer and liquid electrolyte (LiClO₄–EC/PC). A composite cathode based on LiMn₂O₄ has also been prepared. LiMn₂O₄ was used as an active cathode material due to the low price and low toxicity of manganese. With these materials, we have assembled Li/GPE/LiMn₂O₄ cells and have investigated their electrochemical characteristics and cycling performance. In order to evaluate the electrochemical performance of gel polymer electrolytes with a LiMn₂O₄ cathode, Li metal was initially used as an anode. The lithium metal could later be replaced with an intercalation carbon anode, if necessary. The characteristics and electrochemical performance of Li/GPE/LiMn₂O₄ cells are presented and discussed.

2. Experimental

2.1. Preparation of gel polymer electrolytes

The copolymer used in this work, constituted by acrylonitrile (AN) and methylmethacrylate (MMA), was synthesized via emulsion polymerization with distilled water at 60°C. Potassium persulfate (K₂S₂O₈) was used as a free-radical water-soluble initiator, and sodium lauryl sulfate was

* Corresponding author. Tel. +82-42-821-1550; fax: +82-42-822-1562. E-mail address: dwkim@tnut.ac.kr (D.-W. Kim).

used as an emulsifier. From the ^1H NMR spectroscopy, the molar composition of AN and MMA was determined to be 56:44. For preparing gel polymer electrolytes with AM copolymer, polymer was first dissolved in anhydrous tetrahydrofuran (THF). After the polymer had completely dissolved, a predetermined amount of liquid electrolyte solution, 1 M LiClO_4 in ethylene carbonate (EC)/propylene carbonate (PC) (1:1 by volume), was added and the solution was further stirred. The added amount of electrolyte solution was 80 wt.% based on the total weight of the gel polymer electrolyte composed of matrix polymer and liquid electrolyte. The resulting viscous solution was cast with a doctor blade apparatus on to a release paper, then left so that the solvent evaporated slowly at room temperature. After complete evaporation of THF, the film was separated from the release paper. The resulting films were transparent, and the thickness of the cast film was in the range of 80–100 μm . All procedures for preparing the GPEs were carried out in a dry-box which was filled with argon gas.

2.2. Electrical measurements

The gel polymer electrolyte film was cut into 4 cm^2 squares and sandwiched between two stainless-steel (SS) electrodes for conductivity measurements. The sandwich was vacuum-packed in an aluminized polyethylene bag in order to avoid contamination. The ac impedance measurements were then performed with a Zahner Elektrik IM6 impedance analyzer over a frequency range of 100 Hz to ~ 1 MHz with an amplitude of 10 mV. The anodic decomposition voltage was determined by conducting linear sweep voltammetric studies on a stainless-steel working electrode with lithium electrodes as the counter and the reference electrode at a scanning rate of 1 mV s^{-1} .

2.3. Li/LiMn₂O₄ cell

The LiMn_2O_4 composite cathode on an aluminium foil consisted of LiMn_2O_4 with gel polymer electrolyte and super-P carbon in the proportions of 60:31:9 wt.%. The anode consisted of a 50- μm thick Li foil (Cyprus Foote Mineral Co.) pressed on to a copper current-collector. A Li/GPE/ LiMn_2O_4 cell was assembled by sandwiching the gel polymer electrolyte between the lithium anode and a composite LiMn_2O_4 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. Cycle tests of the Li/GPE/ LiMn_2O_4 cell were conducted in the voltage range of 3.0–4.3 V at different current densities with galvanostatically-controlled equipment.

3. Results and discussion

A copolymer comprising about 56 mol.% AN was used a matrix polymer for preparing the gel polymer electrolytes in

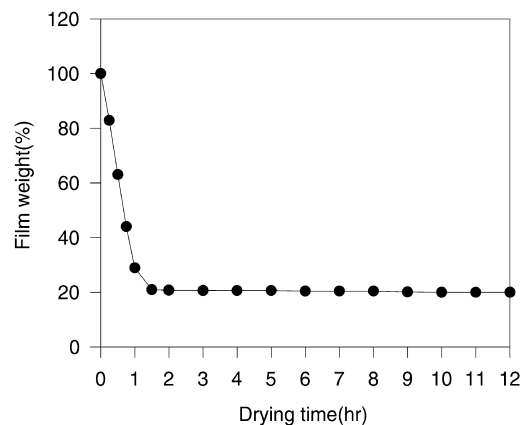


Fig. 1. Gel electrolyte film weight as a function of drying time at room temperature.

terms of ionic conductivity and capacity to retain organic liquid electrolyte, as described in the previous work [11]. The electrolyte was prepared by film-casting from a homogeneous solution which contained 4 wt.% AM copolymer, 16 wt.% 1 M LiClO_4 -EC/PC and 80 wt.% THF. After the solution was cast, the film weight was measured as a function of drying time until the free-standing gel polymer electrolyte film was obtained. Fig. 1 shows the variation of film weight with drying time a dry-box filled with argon gas at room temperature. As the volatile THF solvent evaporates, the weight of casting film decreases. After about 2 h the film weight does not show any change and has a constant value of 20 wt.%. The calculated weight of AM copolymer and liquid electrolyte (1 M LiClO_4 in EC/PC) without THF is 20 wt.%. This result means that THF is completely removed and non-volatile EC or PC is not lost during evaporation of THF in preparing the gel polymer electrolyte at room temperature. Given this result, 3 h is thought to be sufficient time to prepare a gel polymer electrolyte with a desirable GPE composition. From quantitative analysis by ^1H NMR, the gel polymer electrolyte obtained after 3 h was confirmed to be free of THF and to have a composition of about 80 wt.% liquid electrolyte. Fig. 2 shows an ac impedance spectrum of the SS/GPE/SS cell at room temperature. The intercept on the real axis gives the electrolyte resistance, viz. 1.3Ω . From this value, the ionic conductivity was calculated to be $1.9 \times 10^{-3} \text{ S cm}^{-1}$.

Gel polymer electrolytes may undergo solvent exudation upon long storage. This phenomenon, known as the syneresis effect, has been encountered in many gel polymer electrolyte systems [12,13]. The solvent exudation results in a rise in the electrolyte resistance, and finally leads to a gradual degradation of performance rechargeable lithium battery. In order to investigate the solvent exudation upon long storage in AM-based gel polymer electrolyte, the ionic conductivity was measured as a function of storage time. Fig. 3 illustrates the time dependence of ionic conductivities for GPE prepared with AM copolymer. The ionic conduc-

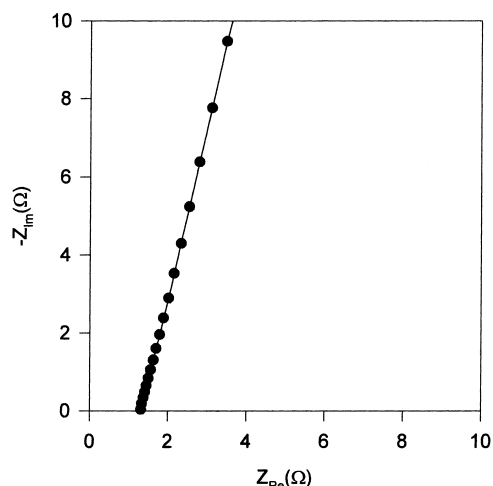


Fig. 2. The ac impedance spectrum of SS/GPE/SS cell with gel polymer electrolyte consisting of 20 wt.% AM and 80 wt.% LiClO₄-EC/PC at 25°C.

tivity remains nearly constant, which means no loss of liquid electrolyte encapsulated in matrix polymer. Since the MMA unit in the copolymer has carbonyl group (–COO–) in the side chain, it can be assumed that the MMA unit is compatible with the carbonate-based electrolyte such as EC and PC. A strong specific interaction between a MMA unit and carbonate-based solvent makes the organic solvent with high boiling point difficult to phase-separate from a matrix polymer. Even though these gel polymer electrolytes contain a large amount of organic liquids, they can behave like dry polymer electrolytes at ambient temperature. The stability of ionic conductivity with storage is also consistent with the previous result given in Fig. 1.

For a Li/LiMn₂O₄ cell, the potential can be as high as 4.3 V versus Li/Li⁺. This implies that the gel polymer electrolyte should be electrochemically stable up to at least 4.3 V. The electrochemical stability was evaluated by linear

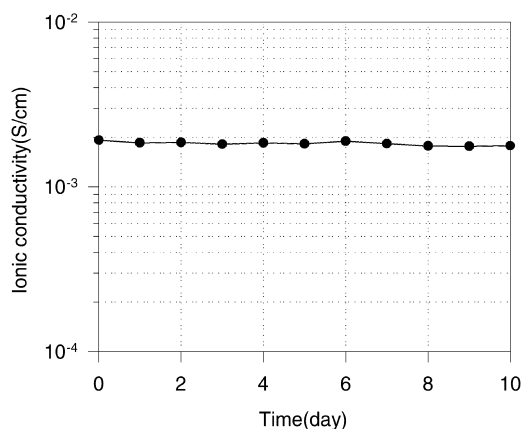


Fig. 3. Ionic conductivities of gel polymer electrolytes as a function of storage time at 25°C.

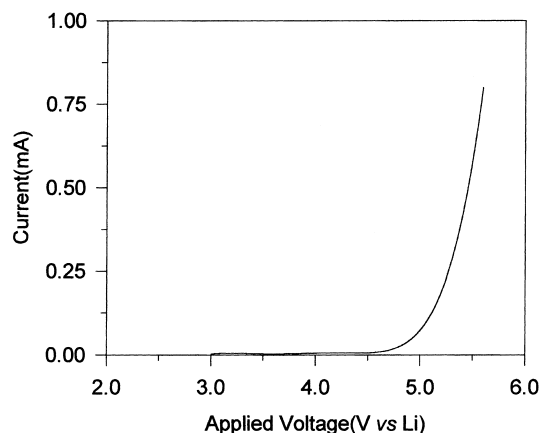


Fig. 4. Current–voltage curve of Li/GPE/SS cell (scan rate: 1 mV s⁻¹).

sweep voltammetric measurements. Experiments were performed by applying an anodic voltage to a cell which consisted of a GPE sandwiched between a lithium electrode and an inert SS electrode. The voltage was swept from the open-circuit potential (3.0 V) of cell towards more positive values until a large current due to the electrolyte decomposition at the inert electrode interface occurred. A voltammogram is given in Fig. 4. For such a curve, the decomposition voltage, is defined as the potential at which a rapid rise in current is observed. In Fig. 4, the decomposition voltage is higher than 4.5 V, which suggests that the AM-based gel polymer electrolyte is acceptable for a LiMn₂O₄ cathode.

Li/GPE/LiMn₂O₄ cells were fabricated with the above electrolytes. Fig. 5 shows the charge–discharge curves of a cell at a constant current density of 0.1 mA cm⁻², which corresponds to a charging (or discharging) time of 5 h (0.2C). It is seen that the charge–discharge curves have two distant plateaux, which are characteristics of the manganese oxide spinel structure [14,15]. It has been reported that each plateau delivered half the total capacity. This

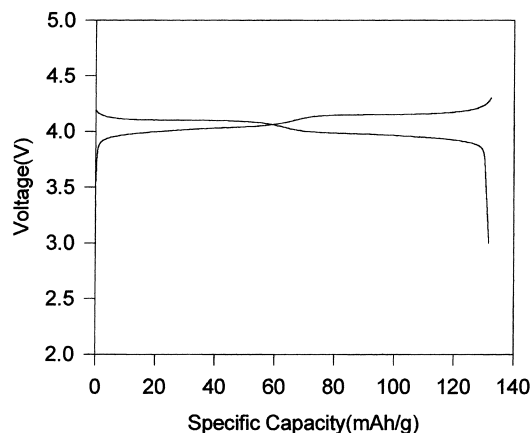


Fig. 5. Charge–discharge curves of Li/GPE/LiMn₂O₄ cell at a constant current density of 0.1 mA cm⁻² (0.2C rate).

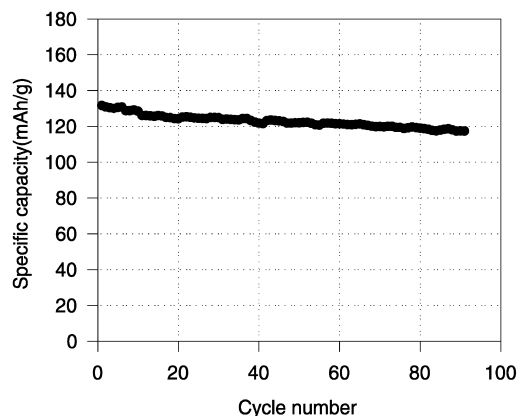


Fig. 6. Discharge capacities of Li/GPE/LiMn₂O₄ cell as a function of cycle number at 0.1 mA cm⁻².

confirms the hypothesis that there are two binary equilibrium states during Li⁺ intercalation [14]. The coulombic efficiency of the cell was 99.5%. The Li/GPE/LiMn₂O₄ cell delivered 132 mAh g⁻¹ based on LiMn₂O₄ active material. Fig. 6 shows the discharge capacity as a function of cycle number. The capacity is about 117 mAh g⁻¹ at the 90th cycle, which is 89% of the initial capacity. The coulombic efficiency of the cell is more than 99% through cut cycling. In the previous work [11], the passivation of lithium metal in these gel polymer electrolytes was proven to be stable with time. Thus, the capacity decline of the Li/GPE/LiMn₂O₄ cell may be mainly related to the deterioration of interfacial contacts at the composite cathode, as a result of a lattice change of the cathode active material during charge–discharge cycling. A considerable strain on the interface of a composite cathode is believed to degrade the electrical contact between the surfaces of the insertion particles, and hence to decrease the capacity of the cathode during repeated cycling.

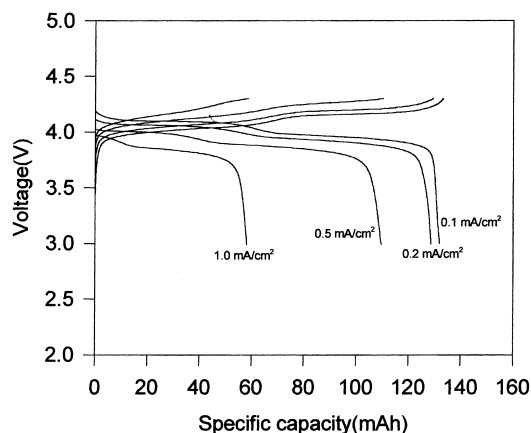


Fig. 7. Charge–discharge curves of Li/GPE/LiMn₂O₄ cell obtained at different current rates.

With these gel polymer electrolytes, an attempt was made to obtain the rate capability of Li/GPE/LiMn₂O₄ cells. Fig. 7 gives the charge–discharge curves obtained at different current rates. It is found that polarization increases as the current rate increases, which results in a decrease in capacity. The discharge capacity falls to 58 mAh g⁻¹ at a current density of 1.0 mA cm⁻². The reduced capacity at a high current rate is due to the high value of resistance of gel polymer electrolyte. The larger resistance of gel polymer electrolyte due to the thick film (~100 μm) as compared with that of a separator with a liquid electrolyte (~25 μm) may limit the cycling rate of Li/LiMn₂O₄ cells. More efforts to improve the high-rate performance, such as incorporation of highly conductive liquid electrolyte into the AM copolymer, minimization of the GPE film thickness, and preparation of a composite cathode with optimum LiMn₂O₄/conducting carbon/gel polymer electrolyte composition, are in progress.

4. Conclusions

A gel polymer electrolyte composed of AM copolymer and LiClO₄–EC/PC shows high ionic conductivity and sufficient electrochemical stability to allow safe operation in Li/LiMn₂O₄ cells. A strong specific interaction between the MMA unit and the carbonate-based solvent makes the organic solvent difficult to exude from a matrix polymer. A Li/GPE/LiMn₂O₄ cell shows a stable discharge capacity of about 130 mAh g⁻¹.

Acknowledgements

This work was supported in part by the Korea Science and Engineering Foundation (KOSEF) through the Advanced Materials Research Center for Better Environment (AMAREN) at Taejon National University of Technology (TNUT).

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