

Synthesis of Cross-Linked Polyurethane-Based Gel Polymer Electrolyte and Its Electrochemical Properties

Hyun-Soo Kim[†], Sung-Il Kim, Gwan-Young Choi, Seong-In Moon, Mun-Soo Yun, and Sang-Pil Kim*

Korea Electrotechnology Research Institute, Changwon 641-120, KOREA

*Saehan Enertech Co., Chungju, Chungbuk 380-240, KOREA

(Received July 20, 2002; Accepted December 26, 2002)

Abstract. Urethane acrylate oligomer was synthesized and used in a gel polymer electrolyte (GPE) and then its electrochemical performances were evaluated. LiCoO₂/GPE/graphite cells were prepared and their performances depending on discharge currents and temperatures were evaluated. The precursor containing 5 vol% curable mixture had a low viscosity relatively. Ionic conductivity of the gel polymer electrolyte at room temperature and -20°C was ca. $5.9 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ and $1.4 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$, respectively. GPE showed good electrochemical stability up to potential of 4.5 V vs. Li/Li⁺. LiCoO₂/GPE/graphite cell showed a good high-rate and low-temperature performance.

Key words: Polyurethane acrylate, Lithium ion battery, Gel polymer electrolyte, Curable mixture, Ionic conductivity

1. Introduction

A lithium ion battery has a good high-rate and a low-temperature performance, but has a possibility of leakage of a liquid electrolyte. A probability of the leakage of lithium ion polymer battery is very low because of adopting a solid type or a gel type electrolyte, but the high-rate and the low-temperature performance decrease because its ionic conductivity is low. Therefore, a new type advanced lithium-ion battery with a gel polymer electrolyte is being developed to meet requirement of market, i. e. high power density and no leakage of electrolyte¹⁾.

A gel polymer electrolyte, especially membrane type, has been studied by many research groups and their results were reported. Kono et al.²⁾ prepared gel polymer electrolyte consisting of poly(alkylene oxide) macromonomer, LiClO₄, and propylene carbonate (PC). Its ionic conductivity was reported to be $10^{-5} \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$. And, many kinds of polymeric hosts such as polyacrylonitrile (PAN)³⁾, poly(vinylidene fluoride) (PVdF)¹⁾, poly(ethylene oxide) (PEO)¹⁾, poly(methylmethacrylate) (PMMA)¹⁾, poly(vinyl chloride) (PVC)⁴⁾ have been proposed as frameworks for gel polymer electrolyte. Their ionic conductivities were reported between 10^{-4} and $10^{-3} \text{ S} \cdot \text{cm}^{-1}$ at room temperature. Hybrid polymer electrolytes based on P(VdF-HFP)^{8,9)} copolymers exhibited high ionic conductivity and good mechanical performances.

Cross-linked polymers were found to reduce the solubility of the polymers with the organic solvents and also helped to trap the liquid electrolyte within the polymer matrix. Polyurethane has several merits as the polymer matrix; miscibil-

ity with an organic electrolyte, design flexibility of performances with a reactive modifier and amorphous structure with low glass transition temperature. M. L. Digar et al.¹⁰⁾ have prepared a PUA-based GPEs using by an UV radiation and their electrochemical and mechanical properties are different with reactive diluents. The ionic conductivity GPE was $1.01 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ at 25°C.

In present study, polyurethane acrylate (PUA) was designed and synthesized by two-step reaction. Precursor was prepared from PUA oligomer, reactive modifier, initiator and electrolyte and polymerized by a thermal reaction. The LiCoO₂/GPE/graphite cells were prepared and their electrochemical properties were evaluated at various current densities and temperatures.

2. Experimental

2.1 Synthesis of PUA

The PUA was synthesized by a two-step additional reaction. The prepolymer was prepared from the mixture of 4, 4'-methylene bis (phenyl isocyanate) (MDI) and a polyol. A polyol was consisted of ethylene oxide and propylene oxide and three OH groups at the end. The polyol (molecular weight = 3000, GP3000) was obtained from Hankook Polyol and dehydrated under reduced pressure at 80°C for 24 h before use. MDI was obtained from Aldrich and used as received. The mixture was reacted at 60°C for 2 h with stirring under a dried nitrogen blanket.

After the prepolymer was synthesized, its contents of NCO groups were characterized with dibutyl amine back titration method. And required amount of hydroxyethyl acrylate (HEA) was slowly added to the NCO terminated prepolymer.

[†]E-mail: hskim@keri.re.kr

HEA was obtained from Aldrich and used as received. The reaction was allowed to continue for 3 hours and then it was terminated by addition of small amounts of methanol. The reaction scheme of synthesized PUA is shown in Figure 1. The functional group of PUA was examined using by FT-IR (Burker IFS 66/FRA 106). Specimen was prepared in the form of thin film and was scanned fifty times at wavenumber of 4 cm^{-1} .

2.2 Preparation of gel polymer electrolyte and cell

A precursor for the gel polymer electrolyte consisted of a liquid electrolyte, an oligomer, a reactive modifier and an initiator. Battery grade solution of 1.0 M $\text{LiPF}_6/\text{EC-DEC}$ (1:1 vol%) was obtained from Cheil Industries. Tri(ethylene glycol) dimethacrylate (TEGDMA) was used as a reactive modifier to improve mechanical properties of gel polymer electrolyte. Benzoyl peroxide (BPO) [$\text{C}_{14}\text{H}_{10}\text{O}_4$, Aldrich Chemical Co.] were used as a thermal initiator. A precursor was polymerized by a thermal reaction at 80°C for 40 minutes. All procedures for preparing the precursor were carried out in a dry-box filled with argon gas.

Lithium cobalt oxide electrodes were prepared by mixing 93 wt% LiCoO_2 (Osaka Gas Co.) with 4 wt% super P black and 3 wt% PVdF and coated on an aluminum foil. Graphite electrode were prepared using 95 wt% MCF (milled carbon fiber, Petoca Material Co.) and 5 wt% PVdF. Celgard 2500 was used as a separator. The electrodes were stacked and inserted into an aluminum laminated film. The precursor was filled into the assembled cell in a dry-box filled with argon gas and polymerized at the temperature of 80°C for 40 minutes in an oven.

2.3 Characterization of electrochemical properties of GPE and cell

Viscosity of the precursor was measured by a viscometer DV-II⁺ (Brookfield Co.). The ionic conductivity of gel polymer electrolyte was measured using an AC impedance analyzer (IM6, Zahner Elektrik) with a stainless steel blocking electrode cell. Ionic conductivity was measured for temperatures ranging from -20 to 60°C . A potential difference of 5 mV was applied to the sample for frequencies ranging from 100 to 2 MHz. The

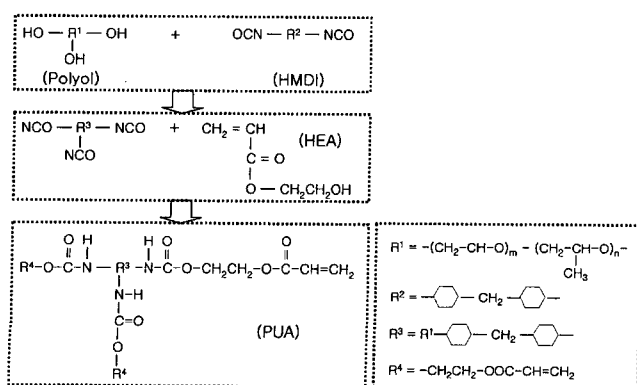


Fig. 1. Schematic representation of synthesis for polyurethane acrylate oligomer.

electrochemical stability of the GPE was studied using the cyclic voltammetry (CV). CV was carried out using a potentiostat (model 273, EG&G Co.). A three-electrode system was used for all measurement. A stainless steel electrode was used as working electrode and a lithium electrode was used as counter and reference electrode. A stainless steel electrode with an area of $3 \times 5\text{ cm}^2$ was swept in the potential range of -0.5 to 4.5 V vs. Li/Li^+ at a sweep rate of 5 mVs^{-1} .

The charge and discharge cycling tests of $\text{LiCoO}_2/\text{gel polymer electrolyte/graphite}$ cells were conducted galvanostatically using Toyo battery test system (TOSCAT-3100K). The discharge curves were obtained at different current rates to get the rate capability of the cell and also at various temperatures.

3. Results and discussion

IR spectrum obtained from polyurethane acrylate was shown in Figure 2. There are many peaks such as NH bond peak at wavenumber of ca. $4,000\text{ cm}^{-1}$, aliphatic CH peak at wavenumber of ca. $3,000\sim 2,900\text{ cm}^{-1}$, and carbonyl group's peak at wavenumber of ca. $1,700\sim 1,600\text{ cm}^{-1}$ on the spectrum. It is thought that NH bond peak is attributed to urethane functional group.

Figure 3 showed the relationship between the contents of the electrolyte and the viscosity of the curable mixture. Curable mixture consisted of PUA oligomer, a reactive modifier and an initiator. TEGDMA (50 wt%) was used as the reactive modifier here. The viscosity of the precursor containing 50 vol% monomer was ca. 51 mPas, and decreased with decreasing the contents of curable mixture. The viscosity of the precursor containing 5 vol% curable mixture was around 4.8 mPas and its value was nearly same in a liquid electrolyte. In this study, 5 vol% curable mixture and 95 vol% electrolyte system was used at all test.

Ionic conductivity is one of the important factors in the gel polymer electrolyte. The ionic conductivity of gel polymer electrolyte was measured using an AC impedance analyzer with a stainless steel blocking electrode. Figure 4 showed the AC impedance spectra of the gel polymer electrolytes polymerized at temperature of 80°C for 40 minutes. There was only

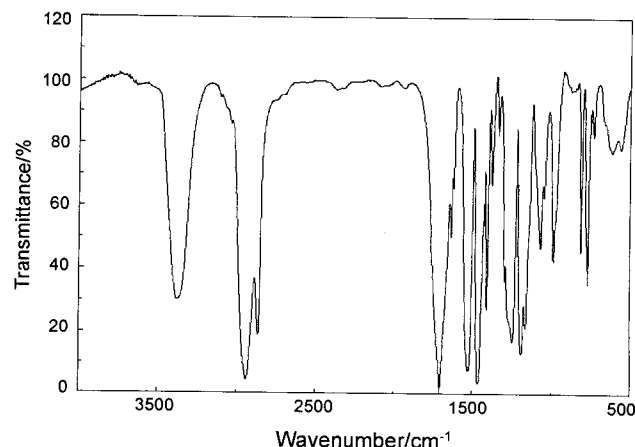


Fig. 2. FTIR spectrum of polyurethane acrylate oligomer.

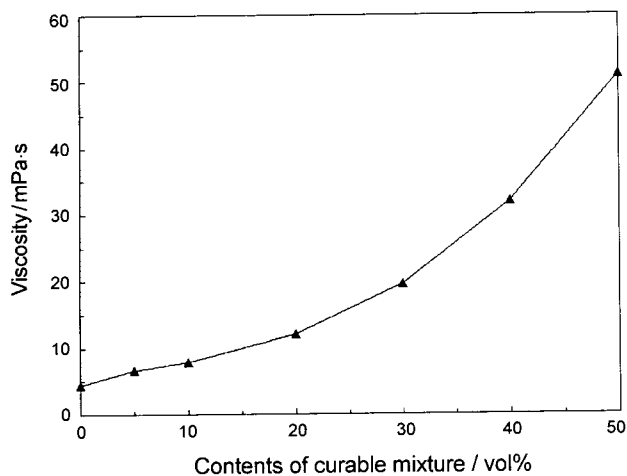


Fig. 3. Relationship between the viscosity of the precursor and the contents of the curable mixture.

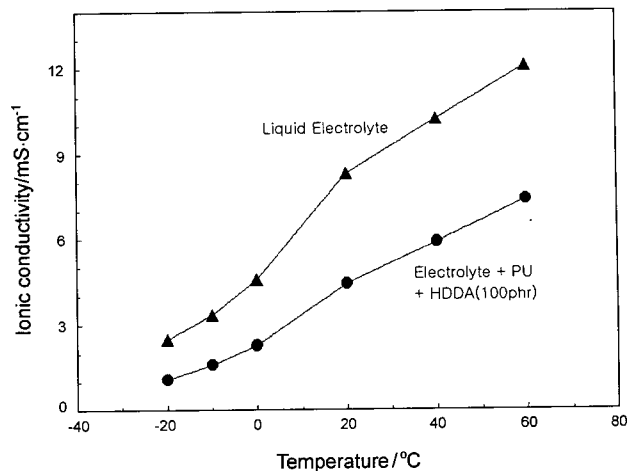


Fig. 5. Ionic conductivity of gel polymer electrolyte at various temperatures.

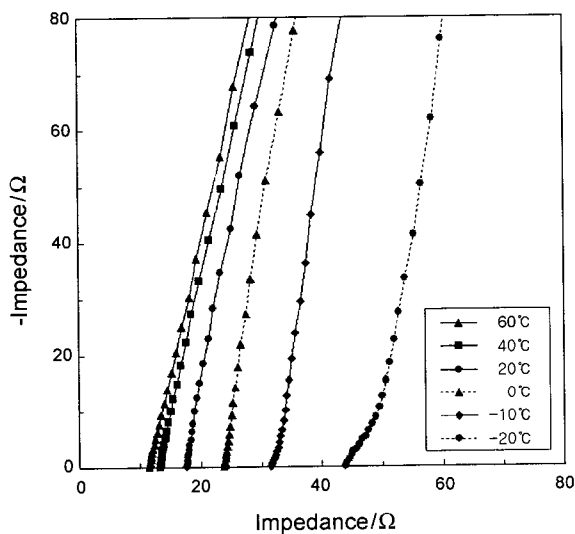


Fig. 4. AC impedance spectra of SS/GPE/SS cell with gel polymer electrolyte.

a spike, which represents a resistor in series with a capacitor, at the plot. The intercept on the real axis gives the resistance of the gel polymer electrolyte. The ionic conductivity at 20°C was calculated to be $5.9 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ from measured electrolyte resistance. Figure 5 showed the ionic conductivity of the gel polymer electrolyte containing 5 vol% curable mixture. It was measured for temperatures ranging from -20 to 60°C. The ionic conductivity at -20°C was around $1.4 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ and increased with increase in temperature. This behavior can be rationalized by recognizing the free-volume model¹¹⁾. As the temperature increases, the polymer can expand easily and produce free volume. Thus, ions, solvated molecules or polymer segments can move into the free volume. The resulting conductivity, represented by the overall mobility of ion and polymer, is determined by the free volume around the polymer chains. Therefore, as temperature increases, the free volume increases. This leads to an increase in ion mobility

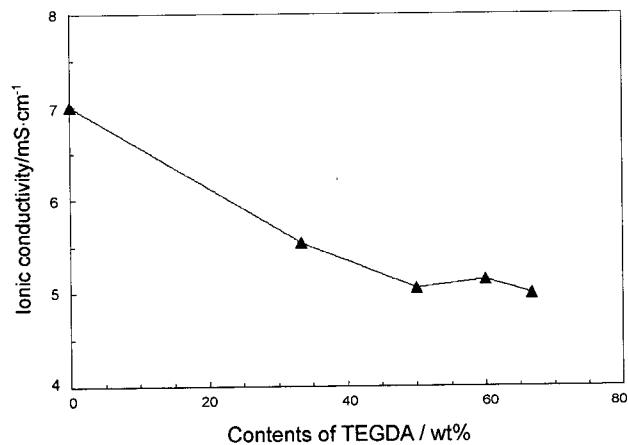


Fig. 6. Relationship between the ionic conductivity and the contents of TEGDMA.

and segmental mobility that will assist ion transport and virtually compensate for the retarding effect of the ion clouds¹¹⁾.

Mechanical property is also important factor in lithium ion polymer batteries using a gel polymer electrolyte. Polyurethane acrylate has a design flexibility that its property can be easily modified from blending with reactive modifier. Figure 6 shows the relationship between the ionic conductivity of lithium ions and the contents of TEGDMA. TEGDMA could act as a crosslinking agent to improve mechanical stability. The ionic conductivity, however, decreased a little because the ionic conductivity and the mechanical stability was in trade-off relationship.

The electrochemical stability of the gel polymer electrolyte was studied using a cyclic voltammetry. Figure 7 showed the cyclic voltammograms of the gel polymer electrolyte on the stainless steel electrodes measured between -0.5 and 4.5 V vs. Li/Li⁺. No peak was observed up to 4.5 V except at potential range of -0.5~0.5 V. There is no problem in the electrochemical stability, because charging voltage for lithium ion battery using lithium cobalt oxide is about 4.2 V. On scan-

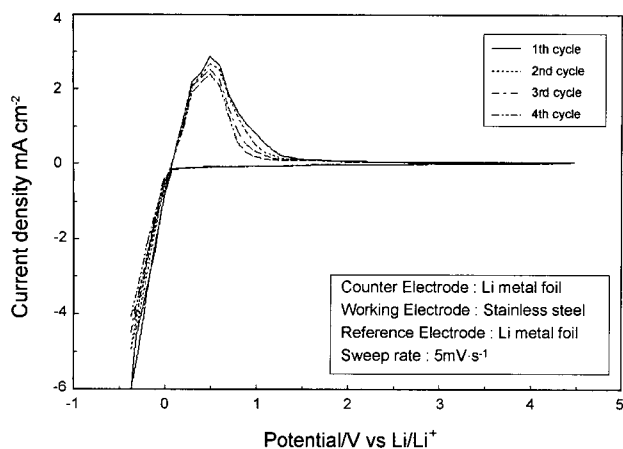


Fig. 7. Cyclic voltammogram of stainless steel/GPE/Li cell at 25°C.

ning the electrode in a negative direction, a cathodic peak is observed at about -0.45 V, which corresponds to the plating of lithium on to the Ni electrode. On the reverse scan, stripping of lithium is observed at about 0.37 V. The voltammograms ascribed to lithium deposition/dissolution are highly reversible, because the peak currents remain fairly constant with repeated cycling.

In order to evaluate the electrochemical performance of a lithium-ion polymer cell using the gel polymer electrolyte, LiCoO₂/GPE/graphite cell was fabricated. The gel polymer electrolyte consisted of 5 vol% curable mixture and 95 vol% 1.0 M LiPF₆/EC-DEC electrolyte. The assembled cell was preconditioned with a cut-off voltage of 4.2 V for the upper limit and 3.0 V for the lower limit at the 0.2C rate (1.5 mAcm⁻²). An irreversible capacity was observed in the 1st cycle and this is caused by the formation of passivation film on the surface of the carbon electrode due to the decomposition of electrolyte, as reported previously by other authors^{12,13}. The process of passivation film on the surface during the initial cycling is referred to as the formation period. The film can prevent the electrolyte from further reduction by the active lithium and thus limits the degradation of electrolytes. The cell was charged at a given current density up to cell voltage of 4.2 V. This was followed by a constant-voltage charge with a decline in current until the final value has reached 20% of the charging current. And then the cell was discharged to a cut-off voltage of 3.0 V at the same current density. Charge and discharge curve of the cells was shown in Figure 8. It showed well-defined charge-discharge voltage profile, which indicates a reversible cycling process. The small voltage drop, obtained from the cycle test, confirms the low internal resistance of the lithium-ion polymer cell. The coulombic efficiency in the preconditioning cycle is calculated to be ca. 100%.

After the preconditioning cycle, the rate capability of the cells was evaluated. The discharge curves obtained at different current rates were given in Figure 9. The cell delivered a discharge capacity of ca. 63 mAh at current density of 1.5 mAcm⁻² (0.2C rate). The discharge capacity slowly decreased with current rate, which was due to polarization. A useful

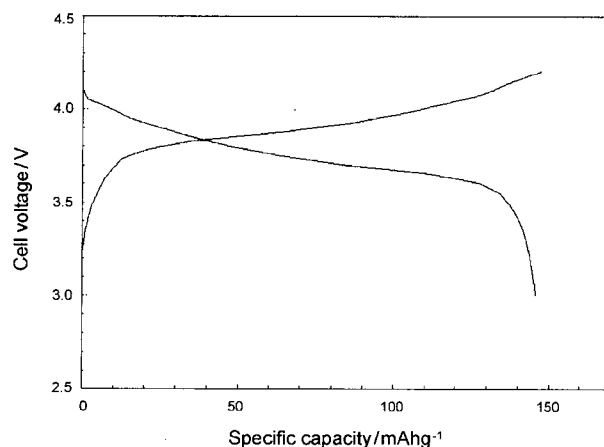


Fig. 8. Charge and discharge curve of LiCoO₂/GPE/MCF cell at current density of 0.6 mAcm⁻²

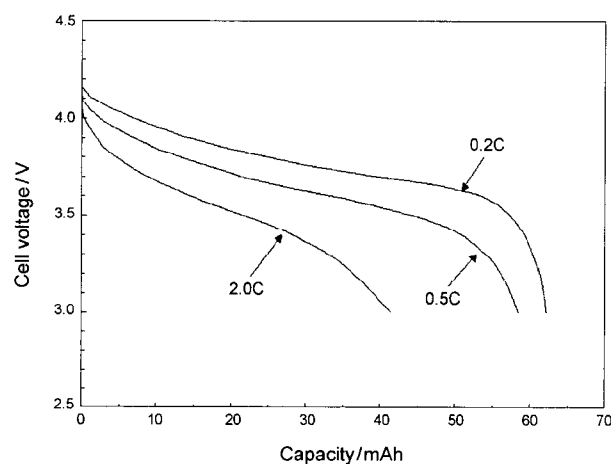


Fig. 9. Discharge curves for LiCoO₂/GPE/MCF cell at discharge rates.

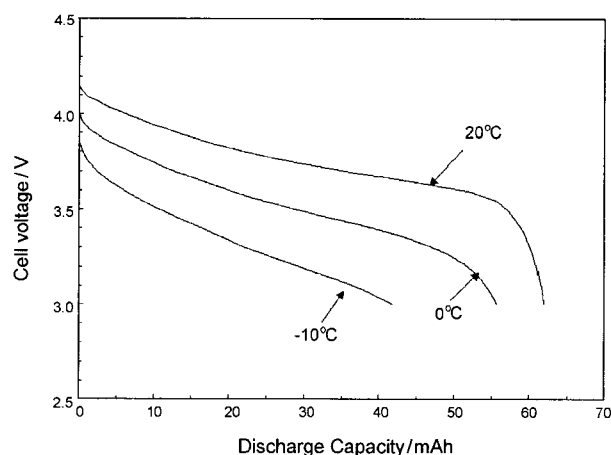


Fig. 10. Discharge curves for LiCoO₂/GPE/MCF cell at various temperatures.

capacity of ca. 57 mAh was obtained at 0.5C rate, which was 91% of the discharge capacity at 0.2C rate. The capacity of ca.

42 mAh was available even at 2.0C rate, which was 67% of the discharge capacity at 0.2C rate. The cells showed good rate capability, compared to other membrane-type gel polymer electrolyte. The reduced capacity in the LiCoO₂/GPE/graphite cell at high rate may be primarily related and to a poor wetting and to a low diffusion rate of lithium ions in the gel polymer electrolyte¹⁴). The cells, furthermore, will be able to deliver discharge capacity much more, when discharge cut-off voltage become 2.7 or 2.5 V.

The performances of the LiCoO₂/GPE/graphite cells at various temperatures were also evaluated. The discharge curves obtained at current density of 1.5 mAcm⁻² at various temperatures were given in Figure 10. The discharge capacity of the cell was ca. 63 mAh at 20°C. The discharge capacity slowly decreased with decreasing the temperature. A useful capacity of ca. 57 mAh was obtained at 0°C, which was 90% of the discharge capacity at 20°C. The capacity of ca. 43 mAh was available even at temperature of -10°C, which was 68% of the discharge capacity at 20°C. The cells showed good low-temperature performance and will be, as mentioned above, able to deliver discharge capacity much more, when discharge cut-off voltage become 2.7 or 2.5 V. Recently, ethyl methyl carbonate (EMC) was found to be a useful co-solvent in binary solutions with propylene carbonate and ethylene carbonate because of its low freezing point (-55°C). Performances of the lithium-ion cells at low temperature, therefore, can be improved much more using such solvents having low freezing point.

4. Conclusions

Polyurethane acrylate was synthesized from polyol, HMDI and HEA using two-step reaction. Gel polymer electrolyte was obtained using liquid electrolyte, PUA oligomer, reactive modifier and initiator. The viscosity of the precursor con-

taining 5 vol% curable mixture was around 4.6 mPas. The ionic conductivity of the gel polymer electrolyte at 20°C was around 5.9×10^{-3} Scm⁻¹. The gel polymer electrolyte had good electro-chemical stability up to 4.5 V vs. Li/Li⁺. The capacity of the cell at 2.0C rate was 67% of the discharge capacity at 0.2C rate. The discharge capacity slowly decreased with decreasing the temperature. The capacity of the cell at temperature of -10°C was 68% of the discharge capacity at temperature of 20°C.

References

1. F. B. Dias, L. Plomp, and J. B. J. Veldhuis, *J. Power Sources*, **88**, 169 (2000).
2. M. Kono, E. Hayashi, and M. Watanabe, *J. Electrochem. Soc.*, **146**, 1626 (1999).
3. K. M. Abraham and M. Alamgir, *J. Electrochem. Soc.*, **136**, 1657 (1990).
4. F. Boudin, X. Andrieu, C. Jehoulet, and I. I. Olsen, *J. Power Sources*, **81**, 804 (1999).
5. B. Scrosati, F. Croce, and L. Persi, *J. Electrochem. Soc.*, **147**, 1718 (2000).
6. E. Quartarone, C. Tomasi, P. Mustarelli, G. B. Appetecchi, and F. Croce, *Electrochimica Acta*, **43**, 1435 (1998).
7. M. Alamgir, K.M. Abraham, *J. Electrochem. Soc.*, **140**, L96 (1993).
8. V. Arcella, A. Sanguineti, E. Quartane, and P. Mustarelli, *J. Power Sources*, **81**, 790 (1999).
9. H. Huang and S. L. Wunder, *J. Electrochem. Soc.*, **148**, A279 (2001).
10. M. L. Digar, S. L. Hung, T. C. Wen, and A. Gopalan, *Polymer*, **43**, 1615 (2002).
11. S. Rajendran and T. Uma, *J. Power Sources*, **88**, 282 (2000).
12. R. Fong, U. von Sacken, J. R. Dahn, *J. Electrochem. Soc.*, **137**, 2009 (1990).
13. J. M. Rarascon and D. Guyomard, *J. Electrochem. Soc.*, **138**, 2864 (1991).
14. D. W. Kim, *J. Power Sources*, **87**, 78 (2000).