

Synthesis and electrochemical performances of di(trimethylolpropane) tetraacrylate-based gel polymer electrolyte

Hyun-Soo Kim*, Seong-In Moon

Battery Research Group, Korea Electrotechnology Research Institute, 28-1 Seongju-Dong, Changwon 641-120, Republic of Korea

Available online 2 June 2005

Abstract

The di(trimethylolpropane) tetraacrylate-based gel polymer electrolyte (GPE) was stable electrochemically up to 4.5 V versus Li/Li⁺ and showed the ionic conductivity of $6.2 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature. Lithium-ion polymer batteries with the GPE were prepared and their performances were also investigated. The battery showed good rate capability and low temperature performance. The cell delivered 95.1% of the initial discharge capacity at 1.0C rate after the 150th cycling. At the over-charged test, the temperature did not exceed 90 °C and neither leakage of electrolyte nor explosion was observed in the cell.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Gel polymer electrolyte; Cell; Di(trimethylolpropane) tetraacrylate; Initiator; Precursor; Lithium-ion polymer battery

1. Introduction

Lithium-ion battery has been widely used in portable IT equipments such as a cellular phone, PDA laptop computer, since it has good electrochemical performances. However, there is a possibility of electrolyte-leakage in the cells with a liquid electrolyte [1,2]. Therefore, new types of lithium battery with gel polymer electrolytes are under development in order to provide the leak-free characteristics [3].

Many kinds of polymeric hosts such as polyacrylonitrile (PAN) [4], poly(acrylonitrile-methyl methacrylate) (PAMMA) [5], poly(vinylidene fluoride) (PVdF) [6], poly(ethylene oxide) (PEO) [7] and poly(vinylidene fluoride)-hexafluoro propylene (PVdF-HFP) copolymer [8,9] have been proposed as frameworks for gel polymer electrolytes. We have also reported that many monomers and/or macromonomers such as urethane acrylate [10,11], tetraethylene glycol diacrylate [12] and triethylene glycol dimethacrylate [13] could be used to obtain the gel polymer electrolyte (GPE) for the lithium-ion polymer batteries. A linear sweep voltammetry confirmed that the GPE had good electrochemical stability up to around 4.8 V versus Li/Li⁺

[14]. Ionic conductivity of the gel polymer electrolyte was above $10^{-3} \text{ S cm}^{-1}$ at room temperature. It is required that the monomer for the GPE has a double bond at the end, a low molecular weight and oxide groups to get good a compatibility with the electrolyte and a high mechanical strength. Di(trimethylolpropane) tetraacrylate (DTPTA) has four vinyl bonds, low molecule weight and lots of oxide groups in the chain. It is, therefore, expected that the gel can be obtained even if a small quantity of DTPTA and has a good compatibility with the liquid electrolyte.

In this study, the GPE was prepared using DTPTA as a monomer and bis (4-*tert*-butylcyclohexyl) peroxydicarbonate (BBP) as a thermal initiator and its characteristics were measured. The LiCoO₂/GPE/graphite cells were prepared and their electrochemical properties were evaluated at various current densities and temperatures.

2. Experimental

The precursor for a gel polymer electrolyte in a lithium-ion cell consists of a liquid electrolyte, a monomer and an initiator. A battery grade solution of 1.1 M LiPF₆/ethylene carbonate (EC):propylene carbonate (PC):ethylmethyl carbonate (EMC):diethyl carbonate (DEC) (30:20:30:20 vol.%)

* Corresponding author. Tel.: +82 55 280 1663; fax: +82 55 280 1590.
E-mail address: hskim@keri.re.kr (H.-S. Kim).

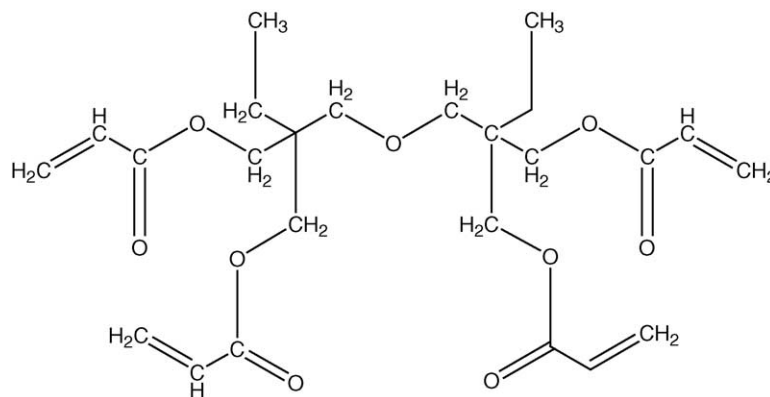


Fig. 1. The structural formula of di(trimethylolpropane) tetraacrylate.

was obtained from Cheil Industries. Di(trimethylolpropane) tetraacrylate $((\text{H}_2\text{C}=\text{CHCO}_2\text{CH}_2)_2\text{C}(\text{C}_2\text{H}_5)\text{CH}_2)_2\text{O}$ ($M_w = 467$, Aldrich Chemical Co.) and bis(4-*tert*-butylcyclohexyl) peroxydicarbonate ($\text{C}_{22}\text{H}_{38}\text{O}_6$, $M_w = 399$, Aldrich Chemical Co.) were used as the monomer and thermal initiator, respectively. Chemical structure of DTPTA is shown in Fig. 1. A precursor containing 98 vol.% electrolytes and 2 vol.% monomer was polymerized by thermal reaction. All procedures for preparing the precursor were carried out in a dry-box filled with argon gas.

The ionic conductivity, viscosity and electrochemical stability window of the gel polymer electrolyte were evaluated. The viscosity was measured by means of 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. The surface area and thickness of the sample was 3.14 mm^2 and 0.1 mm , respectively. 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 that ranged from 100 Hz to 2 MHz .

The cyclic voltammetry (CV) was conducted to investigate the electrochemical stability of the GPE using an IM6 instrument. Stainless steel was used as the working electrode and lithium was used for the counter and the reference electrodes, respectively. A stainless steel electrode with an area of $3 \text{ cm} \times 5 \text{ cm}$ was scanned at a potential range of -0.5 to 4.5 V versus Li/Li^+ at a sweep rate of 5 mV s^{-1} .

Cathodic electrodes were prepared by mixing 93 wt.% LiCoO_2 with 4 wt.% super P black and 3 wt.% PVdF and coated on an aluminum foil. Graphite electrode were prepared using 95 wt.% MCMB and 5 wt.% PVdF. The electrodes were stacked and inserted into an aluminum laminate film. The precursor was filled into the assembled cell in a dry-box filled with argon gas and then the cell was vacuum-sealed. Design capacity of the cell was 1400 mAh . The assembled cells were polymerized at 60°C for 120 min in an oven. The fabrication procedure of the cell has been described in our previous papers [15]. The electrochemical properties of the assembled cell were evaluated by means of an AC impedance analyzer. The AC impedance measurements were

performed with a Zahner Elektrik IM6 impedance analyzer over a frequency range of 700 mHz – 2 MHz . The charge and discharge cycling tests of the cells were conducted galvanostatically with a Maccor battery test system (MACCOR 4000). The discharge curves were obtained at various current rates and temperatures. Continuous cycling tests of the cells were carried out at 1.0C rate. Over-charge test was performed in a constant current regime at 1.0C rate for 150 min .

3. Results and discussion

The viscosity of the precursor increases a little because a monomer has higher viscosity than a liquid electrolyte. Fig. 2 showed the relationship between the contents of the liquid electrolyte and the viscosity of the precursor. The viscosity of the precursor containing a 10 vol.% monomer was ca. 32 mPa s and decreased with decreasing the contents of the curable mixture. The viscosity of the precursor containing a 2 vol.% curable mixture was as low as around 8.2 mPa s .

The electrochemical stability of the GPEs was investigated by cyclic voltammetry. It was designed to use stainless steel as working electrode and Li foil as both the counter and reference electrode. Fig. 3 shows the cyclic voltammogram

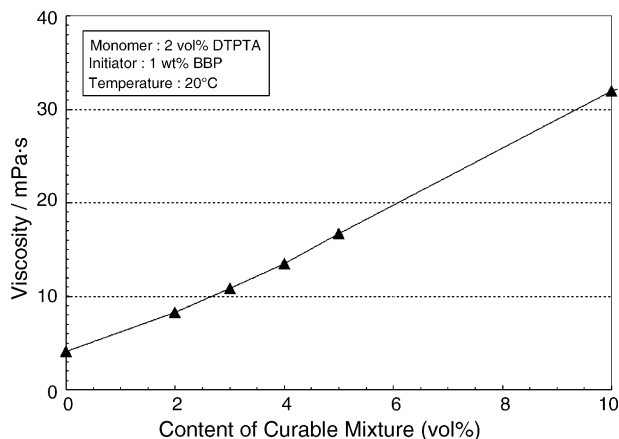


Fig. 2. Relationship between the viscosity of the precursor and the contents of the curable mixture.

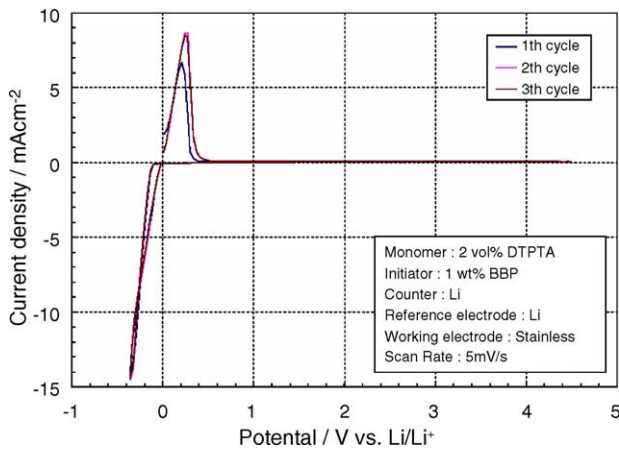


Fig. 3. Cyclic voltammograms of the gel polymer electrolyte on SS working electrode at potential scan rate of 5 mV s^{-1} .

of stainless steel/GPE/Li cell at a sweep rate of 5 mV s^{-1} and a voltage range of -0.5 to 4.5 V versus Li/Li^+ . It was observed that the cell system was electrochemically stable except for a peak relating to the oxidation–reduction reaction near 0 V . This GPE system shows no oxidation reaction up to around 4.5 V while currently commercially available carbonate-based liquid electrolyte system starts decomposition at above 4.5 V . The GPE system is, therefore, electrochemically stable, considering operating voltage for the cell system using LiCoO_2 as a cathode.

The ionic conductivity of the GPE was measured using AC impedance method. Fig. 4 shows the AC impedance spectra of the DTPTA-based gel polymer electrolyte. There was only a spike, which represents a resistor in a series with a capacitor. The intercept on the real axis provides the resistance for the gel polymer electrolyte. It was found that the bulk resistance increased with temperature rise. The ionic conduc-

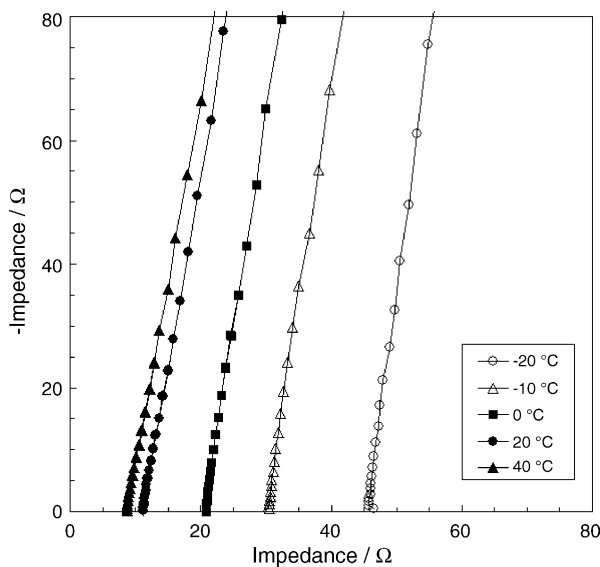


Fig. 4. AC impedance diagrams of SS/DTPTA-based GPE/SS cells with gel polymer electrolyte.

tivity (σ) at 20°C was calculated to be $6.2 \times 10^{-3} \text{ S cm}^{-1}$ from the electrolyte resistance with the thickness and surface area of the gel polymer electrolyte. As a reference, the ionic conductivity of the liquid electrolyte was $8.3 \times 10^{-3} \text{ S cm}^{-1}$ in the same stainless steel blocking electrode system. Thus, there is no big difference for the ionic conductivity between the GPE and liquid electrolyte. The electrolyte of the cell should also allow low temperature performances because the commercial batteries are sometimes used at low temperature. It is especially pointed out that the performance of the lithium-ion polymer batteries at low temperature and high current is lower compared to lithium-ion batteries having the liquid electrolyte. The ionic conductivity (σ) was ranged in $1.8\sim 8.3 \times 10^{-3} \text{ S cm}^{-1}$ at -20 to 40°C . The ionic conductivity of the DTPTA-based gel polymer electrolyte increased with an increase in temperature. The ionic conductivity of the DTPTA-based GPE was higher than TMPTA-based GPE due to the relatively flexible molecular structure of the DTPTA monomer [16]. This is also associated with the interfacial adhesion between electrode and electrolyte and chain length of the GPE. The DTPTA-based GPE has lower interfacial resistance and good mobility due to longer chain length. The polymer matrix of the GPE retains liquid electrolyte, compared with the solid type polymer electrolyte. We found through this study that the chain mobility of the polymer matrix and compatibility with the liquid electrolyte are associated with ion movements.

The LiCoO_2 /GPE/graphite cells optimized 2 vol.% of curable mixture, 1 wt.% of initiator and 3 ml of precursor were fabricated to evaluate the electrochemical. The assembled cell was pre-conditioned with a cut-off voltage of 4.2 V as the upper limit and 2.75 V as the lower limit at $0.2C$ rate. An irreversible capacity was observed in the first cycle and this is caused by the formation of a passivation film on the surface of the carbon electrode due to the decomposition of electrolytes, as reported previously by other authors [17,18]. The development of a passivation film on the surface during initial cycling is referred to as the formation period. The film can prevent the electrolyte from further reduction and thus limits the degradation of electrolytes. After the pre-conditioning cycle, the cell was charged and discharged at various current densities and temperatures. The electrochemical properties of the LIPB using the GPE were evaluated by rate capability, low temperature performance and cycle life. Fig. 5 shows the discharge capacity of gel polymer electrolyte battery at various current densities. The cells were discharged at 0.2 , 0.5 , 1.0 and $2.0C$ against initial discharge capacity, respectively. The initial discharge capacity was maintained well in low current rate, but reduced at high current rate like $2.0C$. This might be attributed to internal resistance due to high cross-linking density at high current rate. The cell shows 92.9% of discharge capacity retention at $2.0C$ rate when compared with $0.2C$ rate, and this performance is similar to the LIB.

The LIB's performance evaluation upon temperature change is important because the LIB is used at room temperature or various temperature environments. Fig. 6 shows

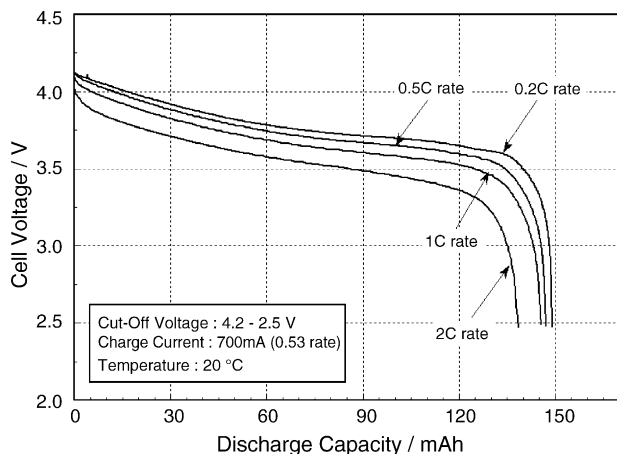


Fig. 5. Discharge curves for LiCoO₂/DTPTA-based GPE/graphite cells at various current densities at 20 °C.

the discharge capacity of gel polymer electrolyte battery at various temperatures. The charge is processed at room temperature and the current rate was 0.5C, respectively, in both charge and discharge. The discharge capacity decreased with decreasing temperature, especially sharply decreased due to decrease of the ionic conductivity at -20 °C. The discharge capacity at -20 °C against room temperature was about 123.7 mAh g⁻¹. It means that the cell delivered 83.0% of the discharge capacity at room temperature.

Fig. 7 showed the discharge capacity with cycling for LiCoO₂/GPE/graphite cell at 1.0C rate. Discharge capacity of the cell was stable and decreased slightly with charge–discharge cycling. As seen from the figure, capacity fading was low during the discharge with cycles. The cell delivered the discharge capacity of ca. 145.3 mAh g⁻¹ after the 150th cycling. It means that the cell delivered 95.1% of the initial discharge capacity after the 150th cycling. This is attributed to the excellent mechanical properties of the polymer matrix of DTPTA-based GPE.

Safety of the lithium secondary cell is one of the important factors; especially over-charge test is indispensable to

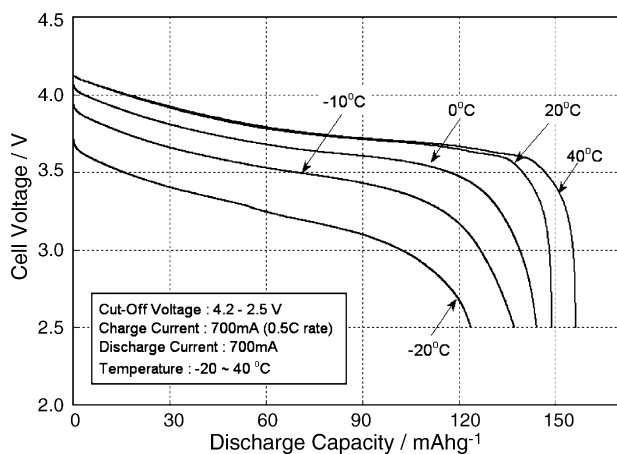


Fig. 6. Typical discharge curves for LiCoO₂/DTPTA-based GPE/graphite cells at 0.5C rate at various temperatures.

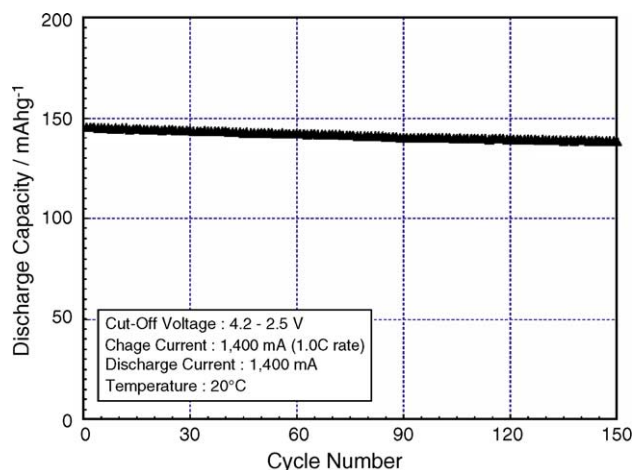


Fig. 7. Discharge capacity upon cycling at 1.0C rate for LiCoO₂/DTPTA-based GPE/graphite cell at 20 °C.

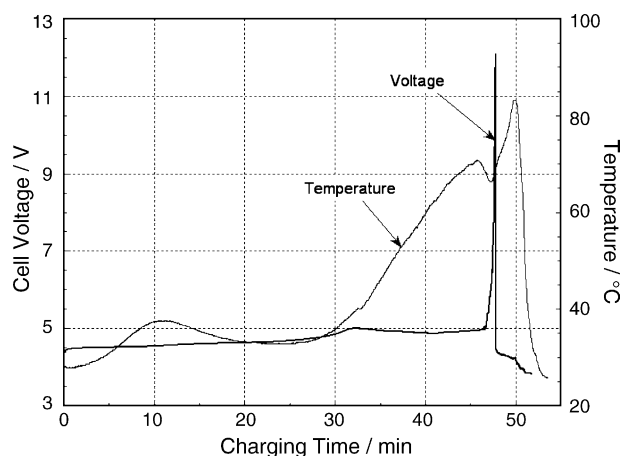


Fig. 8. Voltage and temperature profile with over-charge test for LiCoO₂/DTPTA-based GPE/graphite cell.

a lithium-ion battery. The cell was charged with 1.0C rate for 150 min in fully discharged state. The cell voltage and temperature profiles are shown in Fig. 8. The cell voltage increased gradually up to ca. 4.8 V with charging, but increased rapidly from 4.8 V to around 6 V and then decreased again. During over-charging, metallic lithium would deposit on the surface of anode and might cause a micro-short (soft-short). However, the temperature did not exceed over than 90 °C and no leakage of electrolyte nor an explosion was observed in the cell.

4. Conclusions

The cross-linked GPEs using DTPTA and the cells were prepared and their performances were measured. The GPE had the electrochemical stability up to 4.5 V versus Li/Li⁺. The ionic conductivity of the GPEs increased with increasing temperature, and showed 1.8~8.3 × 10⁻³ S cm⁻¹ at -20 to 40 °C. We also investigated the cell performance of the gel

polymer electrolyte battery. The battery showed good rate capability and temperature performance. The discharge capacity of DTPTA-based battery at 2.0C rate showed 92.9% against 0.2C rate at room temperature. The cell at -20°C also delivered 83.0% of the discharge capacity at room temperature. The DTPTA-based battery showed better cycle life due to excellent mechanical properties. The cell delivered 95.1% of the initial discharge capacity at 1.0C rate after the 150th cycling. At the over-charged test with 1C rate, the temperature did not exceed above 90°C . Neither leakage of electrolyte nor explosion was observed in the cell.

Acknowledgements

This research was supported by a grant (code#: 04K1501-02010) from ‘Center for Nanostructured Materials Technology’ under ‘21st Century Frontier R&D Programs’ of the Ministry of Science and Technology, Korea.

References

- [1] F.B. Dias, L. Plomp, J.B.J. Veldhuis, *J. Power Sources* 88 (2000) 169.
- [2] H. Kim, J. Shin, S. Moon, S. Kim, *Electrochim. Acta* 48 (2003) 1573.
- [3] H. Kim, S. Kim, G. Choi, S. Moon, M. Yun, S. Kim, *J. Korean Electrochem. Soc.* 6 (2003) 98.
- [4] K.M. Abraham, M. Alamgir, *J. Electrochem. Soc.* 136 (1990) 1657.
- [5] S.S. Zhang, K. Xu, T.R. Jow, *Solid State Ionics* 158 (2003) 375.
- [6] F. Boudin, X. Andrieu, C. Jehoulet, I.I. Olsen, *J. Power Sources* 81–82 (1999) 804.
- [7] B. Scrosati, F. Croce, L. Persi, *J. Electrochem. Soc.* 147 (2000) 1718.
- [8] V. Arcella, A. Sanguineti, E. Quartane, P. Mustarelli, *J. Power Sources* 81–82 (1999) 790.
- [9] H. Huang, S.L. Wunder, *J. Electrochem. Soc.* 148 (2001) A279.
- [10] H. Kim, G. Choi, S. Moon, S. Kim, *J. Appl. Electrochem.* 33 (2003) 491.
- [11] H. Kim, J. Shin, S. Moon, M. Yun, S. Kim, *Chem. Eng. Sci.* 58 (2003) 1715.
- [12] H. Kim, J. Shin, S. Moon, M. Yun, *J. Power Sources* 119–121 (2003) 482.
- [13] H. Kim, J. Shin, C. Doh, S. Moon, S. Kim, *J. Power Sources* 112 (2002) 469.
- [14] H. Kim, J. Shin, S. Na, S. Eom, S. Moon, S. Kim, *J. Korea Inst. Electr. Electron. Mater. Eng.* 16 (2003) 994.
- [15] H. Kim, S. Kim, G. Choi, S. Moon, S. Kim, *J. Korean Electrochem. Soc.* 5 (2002) 197.
- [16] S. Kim, H. Kim, S. Na, S. Moon, S. Kim, N. Jo, *Electrochim. Acta* 50 (2004) 317.
- [17] R. Fong, U. von Sacken, J.R. Dahn, *J. Electrochem. Soc.* 137 (1990) 2009.
- [18] J.M. Tarascon, D. Guyomard, *J. Electrochem. Soc.* 138 (1991) 2864.