



Room temperature cross-linkable gel polymer electrolytes for lithium ion batteries by in situ cationic polymerization of divinyl ether

Seung Sik Hwang^{a,b}, Chang Gi Cho^c, Hansu Kim^{a,*}

^a Energy Lab, Samsung Advanced Institute of Technology, Samsung Electronics, Giheung-Gu, Yongin-Si, GyeongGi-Do, 446-712, Republic of Korea

^b Department of Advanced Materials and Chemical Engineering, Hanyang University, Haengdang-Dong, Seongdong-Gu, Seoul, 133-791, Republic of Korea

^c Department of Fiber and Polymer Engineering, Hanyang University, Haengdang-Dong, Seongdong-Gu, Seoul, 133-791, Republic of Korea

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ABSTRACT

We demonstrated room temperature cross-linkable gel polymer electrolytes (GPE) prepared by in situ cationic polymerization of tri(ethylene glycol) divinyl ether (TEGDVE) with LiBF_4 that yields protonic acid and Lewis acid as an acidic initiating system by the reaction with water as an impurity in the liquid electrolyte. FTIR analysis reveals that TEGDVE in the liquid electrolyte is successfully polymerized into gel polymer electrolyte. The resulting gel polymer electrolyte showed promising electrochemical properties including ionic conductivity, wide range in working potential and stable cycle performance as a lithium ion conducting medium.

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1. Introduction

Lithium ion batteries adopting gel polymer electrolyte have gained much attention as a potential power source for electric vehicles as well as mobile electronic devices due to their several advantages such as improved safety and reliability, compared to those with liquid electrolytes [1–6]. Various cross-linking methods such as thermal curing, UV radiation, and gamma-ray radiation have been suggested to improve mechanical and dimensional stability of gel polymer electrolyte [7–9]. Among them, thermal curing is one of the most promising methods and has been used for commercialized lithium ion battery with gel polymer electrolyte [10]. However, as pointed out by Lee et al. [11], thermal curing has been carried out at the elevated temperature, which might cause thermal decomposition of the salt and the unwanted side reactions including gas evolution owing to the use of the thermal initiators, thereby might degrade the battery performance. One can expect that these possible problems in thermal cross-linking for gel polymer electrolytes would be magnified with the scale-up of the battery for large scale applications including electric vehicle and electrical energy storage system. Therefore, it is of great interest to search for more stable cross-linking method for gel polymer electrolyte. In an attempt to lower cross-linking temperature and eliminate the gas formation during curing process, Lee et al. suggested in situ atom transfer radical polymerization (ATRP) as a more stable cross-linking method for lithium ion conducting gel polymer electro-

lyte [11]. They showed that gel polymer electrolyte could be successfully obtained by a result of in situ ATRP of methacrylates with liquid electrolyte at room temperature and the resulting gel polymer electrolyte showed promising electrochemical behavior for lithium ion batteries. However, ATRP needs a copper salt as a catalyst to trigger a polymerization, thus remaining copper cation in the polymer electrolyte. They reported that the remaining copper ions in the polymer electrolyte were found to have no obvious effect on the stability of the gel polymer electrolyte, however, one cannot rule out the possibility of the internal short-circuit caused by Cu particles that could be electrodeposited on the graphite anode during the first charge. As previously reported [12], metal particles in the cell might be one of the potential causes for the battery explosion. In this communication, we report room temperature cross-linkable gel polymer electrolyte without further curing process as well as metallic catalyst by in situ cationic polymerization of divinyl ethers in the liquid electrolyte.

2. Experimental

Gel polymer electrolytes were prepared by the mixing of the homogeneous precursor solution consisting of TEGDVE (Aldrich) and liquid electrolyte (1.0 M $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ (LiBETI) in ethylene carbonate/diethyl carbonate = 3/7 (v/v)) (Cheil Industries, Korea), with LiBF_4 (Cheil Industries, Korea) as a lithium salt and initiator at room temperature. Mixtures of the precursor solution with LiBF_4 were left in a dry room at room temperature without further curing process until gelation was completed. Note that no gaseous products were found during gelation. Concentration of the protonic acid in the liquid

* Corresponding author. Tel.: +82 31 280 9395; fax: +82 31 280 9359.
E-mail address: khansu@samsung.com (H. Kim).

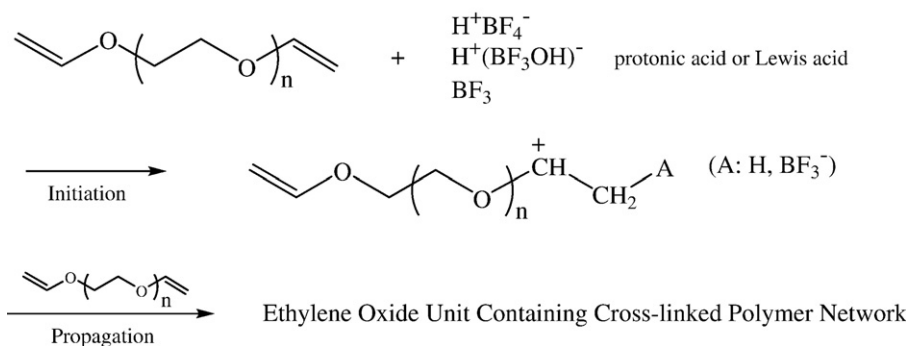


Fig. 1. Schematic diagram of cationic polymerization of divinyl ethers.

electrolyte was determined by acid-base titration using 0.01 N NaOH solution. Water content in the liquid electrolyte was found to be 20 ± 5 ppm by Karl Fisher method (831 KF Coulometer, Metrohm). The

resulting gel polymer electrolytes were characterized using FTIR spectroscopy (Bio-RAD FTS-6000 equipped with MCT detector). Electrochemical impedance spectroscopy was performed using the

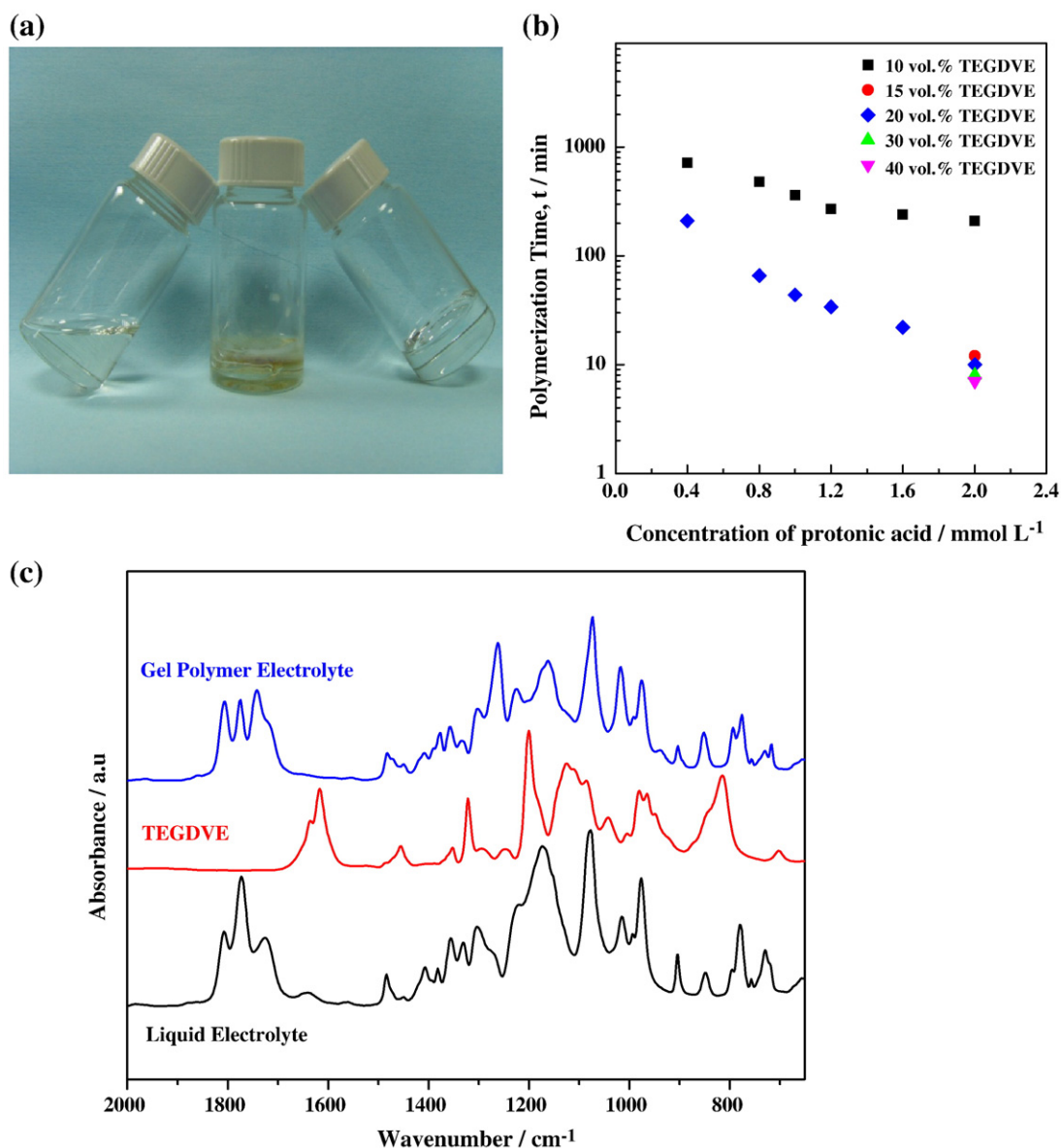


Fig. 2. (a) Photographs of the mixture of 20 vol.% of TEGDVE and 1.0 M LiBETI in EC:DEC (3:7, by volume) without protonic acid (left-hand image), 1.0 M LiBETI in EC:DEC (3:7, by volume) of 2 mmol L^{-1} of protonic acid derived from deliberately added 0.5 M LiBF_4 (right-hand image), and 1.3 M LiPF_6 in EC:DEC (3:7, by volume) (center image). (b) time needed for complete gelation with respect to different amounts of the protonic acid and TEGDVE in the liquid electrolyte. (c) FTIR spectra of liquid electrolyte, TEGDVE and gel polymer electrolyte (1.0 M LiBETI in EC:DEC (3:7, by volume) + 0.5 M LiBF_4 with 20 vol.% of TEGDVE) by cationic polymerization of TEGDVE.

blocking type cell of stainless steel/gel polymer electrolyte/stainless steel to measure the ionic conductivity of the gel polymer electrolytes using impedance analyzer (Electrochemical interface 1260 with frequency response analyzer 1255, Solartron Analytical) over the frequency range of 1 MHz to 100 kHz with an amplitude of 5 mV. Cyclic voltammetry was performed using sandwich type cell of Ni(working electrode)/GPE/Li(counter and reference electrode) at a sweep rate of 1.0 mV s^{-1} over the potential range of 0 to 5 V (vs. Li/Li⁺).

Graphite and LiCoO₂ electrodes were prepared by coating the slurries (active material (90 wt.%), carbon black (5 wt.%, Super P) and polyvinylidene fluoride (5 wt.%) as a binder mixed in *N*-methyl-2-pyrrolidone) on a Cu and Al substrate, respectively. After the coating, the electrodes were dried for 2 h at 120 °C under vacuum and then cut into disks (12 mm in diameter and about 0.06 mm in thickness). Gel polymer electrolytes were prepared by direct addition of the precursor solution with LiBF₄ on to the electrode and their thickness was about 10 μm. Coin type cells (CR2016) were assembled in a dry room using Celgard 3501 as a separator and Li metal foil as a counter and reference electrode and tested at a constant current of 30 mA g⁻¹ for graphite electrode, and 15 mA g⁻¹ for LiCoO₂ electrode within a fixed voltage window (graphite: 0.001–1.5 V, LiCoO₂: 3.0–4.3 V).

3. Results and discussion

Divinyl ethers with acidic initiator can be polymerized into ethylene oxide (EO) unit containing polymer network as shown in Fig. 1. However, cationic polymerization of divinyl ethers has some disadvantages for the preparation of gel polymer electrolyte. First, cationic polymerization involves acidic initiator such as a protonic acid, Lewis acid and their mixture that is mostly harmful to the electrochemical performance of gel polymer electrolyte [13–17]. Another problem of cationic polymerization of divinyl ethers is its extremely rapid reaction kinetics that might cause inhomogeneous gel polymer electrolyte. To obtain homogeneous and electrochemically stable gel polymer electrolyte by in situ cationic polymerization of divinyl ether, acidic initiating system should be carefully chosen and its concentration should be also controlled in trace level. In this work, we used trace level of (H⁺BF₄⁻) as an initiating system, which was in situ obtained from by the addition of LiBF₄ into the mixture of liquid electrolyte and divinyl ether. LiBF₄ brings about proton and fluorine-containing inorganic anion as BF₄⁻, from its hydrolysis by trace amount of water in the liquid electrolyte. One cannot rule out that LiBF₄ may bring about another initiating system, H⁺(BF₃OH⁻), which

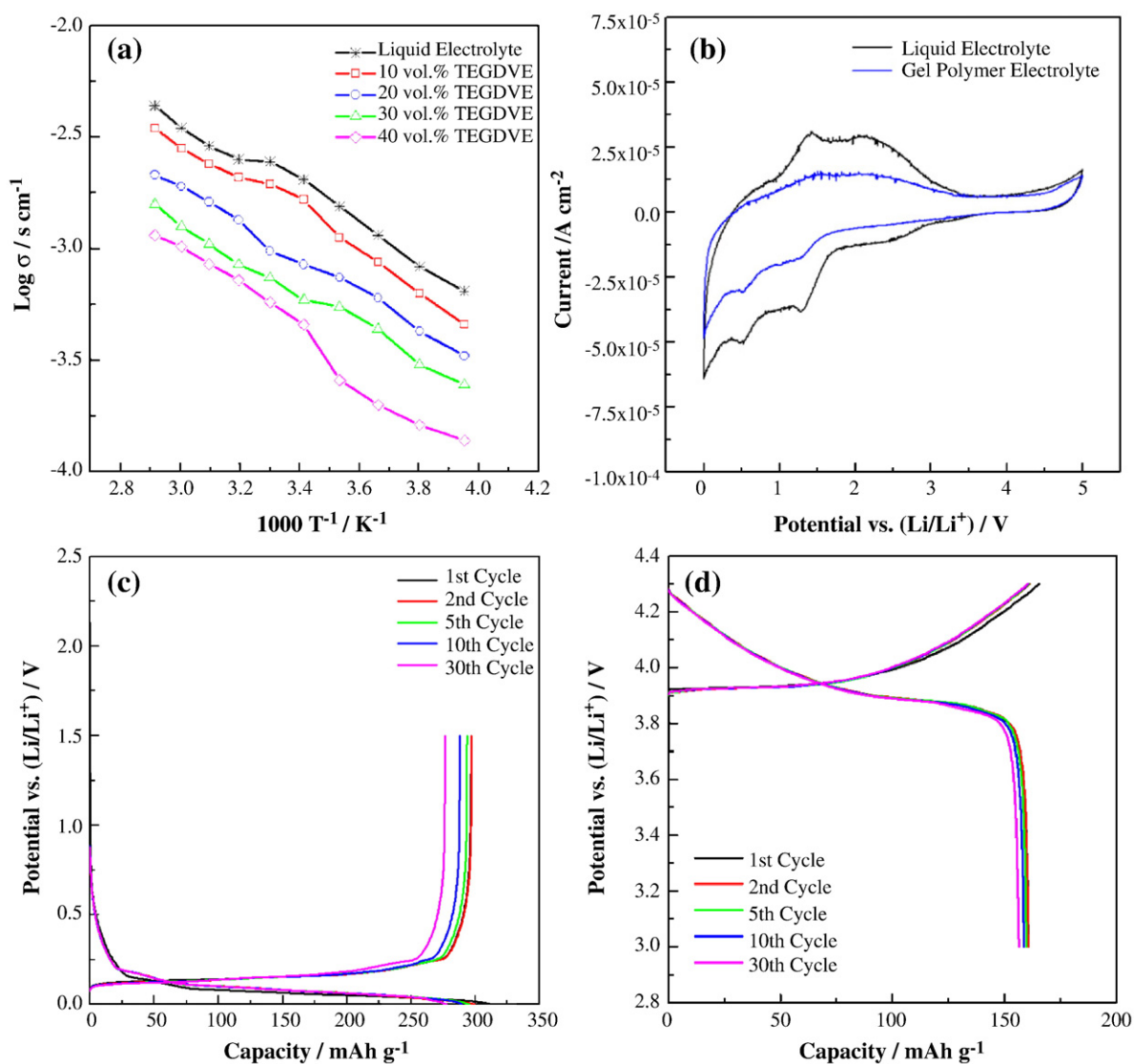


Fig. 3. (a) Arrhenius plots of conductivities of the gel polymer electrolyte prepared with various concentrations of TEGDVE, (b) cyclic voltammograms of liquid electrolyte (1.0 M LiBETI in EC:DEC (3:7, by volume) + 0.5 M LiBF₄) and gel polymer electrolyte prepared by 10 volume percent of TEGDVE with the same liquid electrolyte, voltage profiles of (c) graphite electrode/GPE/Li half cell, (d) LiCo₂ electrode/GPE/Li half cell.

arises from the reaction of water as a Lewis base with BF_3 coming from the decomposition reaction of LiBF_4 . These chemical reactions can be expressed as follows: [18–21]



It should be noted that our strategy in this work would not have any adverse influence on the electrochemical performance of the resulting gel polymer electrolyte, since LiBF_4 used in this work is frequently applied in the conventional liquid electrolyte and only the trace level of proton is generated.

Fig. 2a shows photographs of gel polymer electrolyte by in situ cationic polymerization of TEGDVE with different amounts of proton derived from LiBF_4 . We found that gelation of the liquid electrolyte with TEGDVE occurs in the presence of LiBF_4 . However, inhomogeneous gel polymer electrolyte, i.e., separated liquid electrolyte and polymer, was obtained with 14 mmol L^{-1} of the protonic acid (the center image in Fig. 2a), while homogeneous polymer electrolyte was prepared with about 2 mmol L^{-1} of the protonic acid (the right-hand image in Fig. 2a), implying that polymerization rate and homogeneity of the resulting gel polymer electrolyte depend on the amount of protonic acid arising from the addition of LiBF_4 . Fig. 2b shows the time needed for complete gelation with different amounts of the protonic acid and TEGDVE in the precursor solution. In the case of 0.4 mmol L^{-1} of protonic acid added 10 vol.% of TEGDVE solution, time needed for complete gelation was about 12 h, while 14 mmol L^{-1} of the protonic acid added solution was immediately cross-linked into inhomogeneous gel polymer electrolyte. FTIR analysis was carried out to confirm in situ cationic polymerization of divinyl ethers. We found that the IR absorption band observed at $1600\text{--}1660 \text{ cm}^{-1}$ ($\text{C}=\text{C}$) corresponding to vinyl functional group of TEGDVE almost disappeared after the completion of polymerization (Fig. 2c), suggesting that gelation of the liquid electrolyte was responsible for cationic polymerization of TEGDVE in the liquid with the protonic acid.

Fig. 3a shows Arrhenius plots of conductivities of the gel polymer electrolyte prepared with various concentrations of TEGDVE. Their ionic conductivities are on the order of magnitude of 10^{-3} Scm^{-1} at 303 K, which is similar to the typical ionic conductivity of gel polymer electrolytes and comparable to liquid electrolyte [21,22]. Ionic conductivity decreased with the increase of the amount of TEGDVE, which might be due that more rigid polymeric network formed by the increased amount of TEGDVE has a bad influence on the mobility of lithium ion and liquid solvents [23–25]. Fig. 3b compares cyclic voltammograms of TEGDVE based gel polymer electrolyte and liquid electrolyte, in which the gel polymer electrolyte shows highly stable between 0 and 5 V (vs. Li/Li^+) and comparable to liquid electrolyte. Fig. 3c and d shows voltage profile of graphite electrode and LiCoO_2 electrode with the gel polymer electrolyte, respectively, in which we did not find a voltage plateau associated with side reactions coming

from the acidic initiating system. In addition, they showed stable cycle performance during 30 cycles, indicating that cationic species arising from the hydrolysis of LiBF_4 did not degrade the electrochemical performance of the electrode, and TEGDVE based gel polymer electrolyte prepared at room temperature has the potential as an alternative gel polymer electrolyte for lithium ion batteries.

4. Conclusion

We demonstrated room temperature cross-linkable gel polymer electrolyte by in situ cationic polymerization of divinyl ether with protonic acid based initiating system prepared by the reaction of deliberately added LiBF_4 and water in the liquid electrolyte. The resulting gel polymer electrolyte showed promising electrochemical properties including ionic conductivity, wide range in working potential and cycle performance as a lithium ion conducting medium for lithium ion batteries. Besides the capability to reduce the cost of production by the elimination of curing process with the associated facility, such a room temperature cross-linkable gel polymer electrolyte can provide the opportunities to develop thermally reliable process for gel polymer electrolyte for lithium ion batteries and can be applied to other electrochemical devices such as dye sensitized solar cell and electrochromic devices [26,27], in which thermal stability as well as production cost would be one of the key factors for their fabrication processes.

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