



# Enhanced separator properties by thermal curing of poly(ethylene glycol)diacrylate-based gel polymer electrolytes for lithium-ion batteries



Kwang Man Kim<sup>a,\*</sup>, Beta Zenia Poliquit<sup>b</sup>, Young-Gi Lee<sup>a</sup>, Jeongha Won<sup>b</sup>, Jang Myoun Ko<sup>b</sup>, Won Il Cho<sup>c,1</sup>

<sup>a</sup> Research Section of Power Control Devices, Electronics and Telecommunications Research Institute (ETRI), Daejeon 305-700, Republic of Korea

<sup>b</sup> Department of Chemical and Biological Engineering, Hanbat National University, Daejeon 305-719, Republic of Korea

<sup>c</sup> Center for Energy Convergence, Korea Institute of Science and Technology (KIST), Seoul 136-791, Republic of Korea

## ARTICLE INFO

### Article history:

Received 2 September 2013

Received in revised form

13 December 2013

Accepted 13 December 2013

Available online 28 December 2013

### Keywords:

Poly(ethylene glycol)diacrylate

thermal polymerization

gel polymer electrolytes

lithium-ion batteries

## ABSTRACT

Porous polyethylene (PE) or nonwoven poly(vinylidene fluoride) (PVdF) separator-supported gel polymer electrolytes are realized by thermal polymerization of a precursor solution consisting of poly(ethylene glycol)diacrylate (PEGDA) and an electrolyte solution (1 M LiPF<sub>6</sub> in an equal-volume mixture of ethylene carbonate and dimethyl carbonate). The polymerization conditions are optimized to include a PEGDA content of 3 wt.% in the precursor solution and subsequent heat treatment at 80 °C for 10 min. Even though the gelled PEGDA electrolyte has a lower ionic conductivity than the electrolyte solution, a Li<sub>x</sub>CoO<sub>2</sub>/graphite full-cell that has a gel electrolyte with optimized PEGDA content on the PVdF separator achieves a battery performance superior to the one with PE. The best battery performances achieved are a high discharge capacity (116 mAh g<sup>-1</sup>), a good high-rate capability (95 mAh g<sup>-1</sup> at 5.0 C-rate), and a high capacity retention ratio (90%) after the 100th cycle. This enhancement is due to the incorporation of a polar electrolyte solution that is entrapped by the polar PEGDA matrix within the nonwoven PVdF separator, which is a more suitable host that is able to well absorb and preserve the gel electrolyte.

© 2013 Elsevier Ltd. All rights reserved.

## 1. Introduction

Lithium-ion batteries are rapidly acquiring a leading position as the power source of choice for a wide variety of portable electronic equipment such as cellular phones, digital cameras and laptop computers because of their high energy density, long cycle life and light weight advantages [1,2]. These batteries are also expected to be used in hybrid electric and fuel cell vehicles [3–6], which stimulates research on improving battery performance and safety. One of the trends in safety improvement studies is directed towards usage of a gel polymer electrolyte instead of conventional liquid electrolyte. This offers several advantages including lightness, shape design variety, no leakage system, and low volatility, which in turn improve cycle life and battery performance. For decades now, many polymers, such as poly(ethylene oxide), poly(acrylonitrile), poly(vinylidene fluoride) (PVdF), poly(methyl methacrylate), and poly(vinylidene fluoride-co-hexafluoropropylene), have been used as matrices for polymer electrolytes by soaking or swelling a

polymeric matrix with a liquid electrolyte [7]. However, the limit of this process lies in the poor stability and low electrolyte retention capability. Other research groups have focused on a gel-type polymer electrolyte formed by immobilizing an organic electrolyte within its polymer structure upon polymerization of cross-linkable monomers [7,8]. The mechanism of lithium-ion transport with this electrolyte system is facilitated by fragmental motions of polymeric chains, which greatly depend on its crystallinity [9].

On the other hand, a polymer electrolyte must have sufficient mechanical strength to withstand the stress between the anode and the cathode. However, gel-type polymer electrolytes do not meet this requirement. In order to overcome this problem, a porous polyolefin membrane, such as a polyethylene (PE) separator may be employed as a dimensional support to endow the gel polymer electrolyte with improved mechanical strength [8]. Another solution that addresses this problem is using nonwoven separators, which are usually made from poly(acrylonitrile) [10], poly(ethylene terephthalate) [11], PVdF [12], and poly(methyl methacrylate) [13], which are drawn to fibers via electrospinning methods fabricating multifibrous layers. Of these, PVdF is considered as the next generation separator candidate for high performance lithium-ion batteries [14] because of a high dielectric constant and a strong electron-withdrawing functional group (-CF-) [10] that provides

\* Corresponding author. Tel.: +82 42 860 6829; fax: +82 42 860 6836.

E-mail addresses: [kwang@etri.re.kr](mailto:kwang@etri.re.kr) (K.M. Kim), [wonic@kist.re.kr](mailto:wonic@kist.re.kr) (W.I. Cho).

<sup>1</sup> Tel.: +82 2 958 5223; fax: +82 2 958 5478

as good polarity as with a battery liquid electrolyte. Utilizing the nonwoven separators, previous reports emphasized their superiority over conventional polyolefin separators in terms of excellent thermal properties, high porosity, improved electrolyte wettability, and even cost competitiveness [15]. In this study, the PE and PVdF separators are used as the support for a gel polymer electrolyte.

To prepare the gel polymer electrolyte on the separator, the cross-linkable precursor is mixed with a liquid electrolyte containing lithium salt. The cross-linking and gelation can be started by the thermal polymerization of a precursor oligomer. Due to the high water sensitivity of lithium salt, the whole process should be done in a moisture-free environment. In this study, the gel polymer electrolyte on the separator (PE or PVdF) is prepared by in situ polymerization of the gel precursor solution within battery packages, which is also called preparing an *active separator* [7,16–18]. A solution of the liquid electrolyte, cross-linking oligomer, and thermal initiator is injected into the pouch, and then the pouch is heated at a certain temperature. This process aims to obtain easy fabrication of a gel polymer battery for large scale production. Here, poly(ethylene glycol)diacrylate (PEGDA) is utilized as a gelating agent for preparing a gel polymer electrolyte. The PEGDA contains cross-linkable double bonds that easily react with radicals for polymerization. In addition, the PEGDA can gain the advantage of lower molecular weight, almost the same as with its monomer, for easy absorption in the porous membrane. The problem lies in the heating process which may destroy the electrodes and other components in the battery. Thus, the main purpose of this study is to prepare easily a safe lithium-ion polymer battery based on a separator-supported PEGDA-based gel electrolyte using in situ polymerization and to look for the optimized conditions where the battery properties are at their best.

## 2. Experimental

Commercialized porous PE (K2045, 20  $\mu\text{m}$  thick, porosity 45%, Celgard) and nonwoven PVdF (30–40  $\mu\text{m}$  thick, porosity 67%, Amotech) separators were used as received. The PVdF separator consisted of 3-dimensionally stacked electro-spun fibers with a diameter of 300–500 nm. PEGDA (Aldrich,  $M_n = 258$ ) as an gelating oligomer, benzoyl peroxide as an initiator, and an liquid electrolyte (1 M  $\text{LiPF}_6$  dissolved in an equal-volume mixture of ethylene carbonate and dimethyl carbonate, Panax E-Tech) were also used. The  $\text{Li}_x\text{CoO}_2$  cathode and graphite anode were generously provided by Kokam Company. Prior to usage, all materials were dried using molecular sieves 3A or a vacuum oven.

Prior to preparing the gel precursor solution, a pouch-type stacking full-cell was first assembled and dried in a vacuum oven overnight. The cell was composed of a  $\text{Li}_x\text{CoO}_2$  cathode (2.0  $\times$  2.0  $\text{cm}^2$ ) and a graphite anode (2.2  $\times$  2.2  $\text{cm}^2$ ) with the PE or PVdF separator (3.0  $\times$  3.0  $\text{cm}^2$ ) between the cathode and anode. The gel precursor solution was prepared by mixing for 30 min the PEGDA, benzoyl peroxide, and the liquid electrolyte. The composition ratio of the liquid electrolyte to PEGDA was varied in the range of 98:2–94:6 w/w to optimize it, while the amount of benzoyl peroxide initiator added was fixed at 1 wt.% of PEGDA in the solution. After stirring, 1.0 mL of precursor solution was directly loaded to the pre-dried full-cell, and then the aluminum pouch was completely sealed using a vacuum sealer to yield a lithium-ion full-cell before gelation. Absorption of the precursor solution into the separator was estimated to occur within 1 h. Gelation was done by heat treating the full-cell at a temperature range of 80–90  $^\circ\text{C}$  for 10 min and cooling it for 1 h (see Fig. 1). All the processes were done inside an argon-filled glove box because of the sensitivity of the materials to water. Gelation was first tested by heat treatment to the sealed aluminum pouch full-cell. The changes and degradation of the active materials

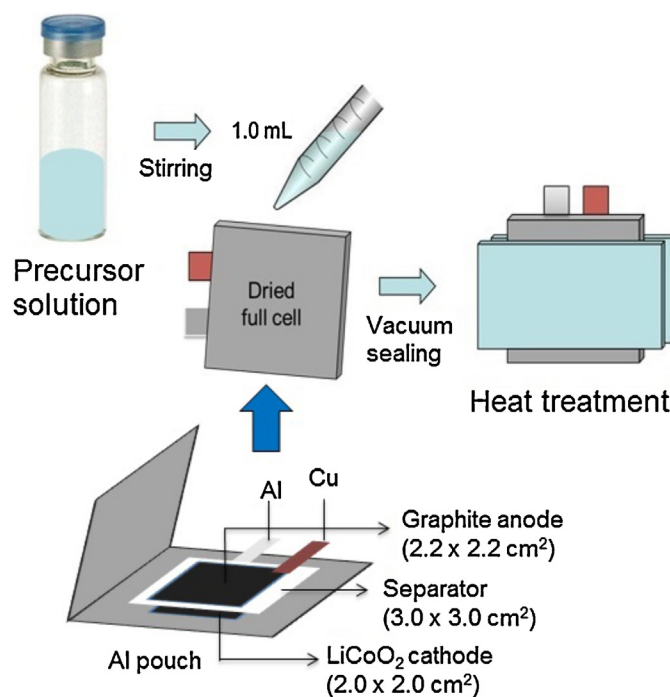


Fig. 1. Schematic diagrams of gelation procedures from the full-cell fabrication to its heat treatment via a droplet insertion of the precursor solution.

were carefully examined after the gelation process to determine the optimized temperature. To determine the optimized PEGDA content, the aluminum pouch containing the excess content of the precursor solution with different PEGDA content was heated at the optimized temperature for 10 min to examine the gelation state. To examine the separator state according to the gelation, the surface and/or cross-section morphologies were also observed using a field-emission scanning electron microscope (Hitachi S-4800) after the heat treatment for the precursor-coated PE and PVdF separators.

The electrochemical stability of the liquid electrolyte and the separator-supported gel electrolytes was determined via linear sweep voltammetry over a potential range of 0–8 V at a scan rate of 10  $\text{mV s}^{-1}$  using an Autolab instrument (Eco Chemie, PGstat 100). The ionic conductivity of the separator-supported gel electrolyte was measured by an impedance technique. The separator was sandwiched between two Ti electrodes ( $A = 1 \times 1 \text{ cm}^2$ ) and assembled in an aluminum pouch. After drying, the pouch was loaded with the precursor solution and then heat treated for the gelation process. Measurement was carried out using an Autolab (Eco Chemie, PGstat 100) instrument and data were collected in a frequency range of  $10^{-1}$ – $10^6$  Hz. Ionic conductivity was calculated using  $\sigma = d/(RA)$ , where  $\sigma$  is the ionic conductivity,  $d$  the distance between two electrodes,  $A$  the area of the electrode and  $R$  the value of the solution resistance acquired from the impedance data. The galvanostatic charge/discharge performance and high-rate capability of the lithium-ion batteries containing the liquid electrolyte and gel electrolytes coated on the separators were investigated using a cycler (Toscat-3000, Toyo Systems) in a voltage range of 3.0–4.2 V at various C-rates, 0.1, 0.2, 0.5, 1.0, 2.0 and 5.0. A cycle performance test was also performed 100 times at a 1.0 C-rate to determine the life span and retention of the electrolytes within the polymer matrix. The impedance spectra after the initial charge-discharge at 0.1 C-rate were obtained for the lithium-ion cells adopting the PE- and PVdF-based gel polymer electrolytes using the an Autolab (Eco Chemie, PGstat 100) instrument in the frequency range of  $10^{-2}$ – $10^5$  Hz.

Download English Version:

<https://daneshyari.com/en/article/6613788>

Download Persian Version:

<https://daneshyari.com/article/6613788>

[Daneshyari.com](https://daneshyari.com)