

Novel preparation of nanocomposite polymer electrolyte and its application to lithium polymer batteries

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Abstract

Gel nanocomposite polymer electrolyte (NCPE) was prepared by UV polymerization and thermal polymerization, respectively in the presence of liquid electrolyte with nanosize SiO₂-contained poly(ethylene glycol) diacrylate (PEGDA) as the monomer. Nanosize SiO₂-contained PEGDA was synthesized using aqueous colloidal silica as one of starting materials and its viscosity was very low. The partial silanol surface groups of SiO₂ were modified to acrylic group by employing of methacryloxypropyl-trimethoxysilane (MAPTMS), which made the dispersion of nanosize SiO₂ in PEGDA uniform and stable. Compared with the gel polymer electrolyte (GPE) based on PEGDA without nanosize SiO₂, the ionic conductivity of the gel NCPE was higher and the electrochemical stability and interfacial stability were better, whether it was prepared by UV polymerization or thermal polymerization. It showed oxidation stability up to 5.0 V versus Li/Li⁺ and lithium deposition/dissolution on the stainless steel electrode highly reversible. The applicability of the gel NCPE to lithium polymer batteries was demonstrated by graphite/SPE/LiCoO₂ cell, which was prepared by in situ thermal polymerization. It showed that the discharge capacity was stable with charge–discharge cycling.

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Keywords: Nanocomposite polymer electrolyte; Poly(ethylene glycol) diacrylate; Lithium polymer batteries; Colloidal silica; Nanosize SiO₂

1. Introduction

In the past three decades, many efforts have been made to employ solid polymer electrolyte (SPE) to rechargeable lithium batteries since the discovery of polymer electrolytes based on poly(ethylene oxide) (PEO) [1]. SPE can potentially eliminate leakage, negate the need for a separator and be amendable to low cost manufacturing technologies. However, conventional PEO-based SPE shows low conductivity ($\sigma < 10^{-5} \text{ S cm}^{-1}$) at ambient temperature and poor mechanical properties at temperature above 60 °C although the conductivity is above $10^{-4} \text{ S cm}^{-1}$ under that condition [2].

To overcome these problems, efforts have focused on two kinds of SPEs. One is composite polymer electrolyte (CPE) whose conventional preparation is by dispersing ceramic

fillers into polymer matrix. When the ceramic fillers size is nanometer scale, material thus formed is called nanocomposite polymer electrolyte (NCPE) [3,4]. The fillers not only contribute to enhanced mechanical properties but also lead to higher ionic conductivity due to the enhanced segmental motion of amorphous regions, and superior interfacial stability for the electrolyte in contact with lithium metal [5,6].

The other is gel polymer electrolyte (GPE), which consists of a liquid electrolyte immobilized in a polymer matrix and exhibits high ionic conductivity (10^{-3} to $10^{-4} \text{ S cm}^{-1}$ at room temperature) [7]. GPE can be obtained with three distinct approaches: (i) loading of a liquid electrolyte in a microporous matrix, such as porous P(VdF-HFP) [8–10]; (ii) increasing the viscosity of a liquid electrolyte by the addition of a soluble polymer until gel consistency is achieved [11,12]; and (iii) mixing a liquid electrolyte with monomers of relatively low molecular weight, then curing the mixture by means, such as UV polymerization, thermal polymerization

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and electron beam radiation polymerization [13–15]. When an acrylate or a methacrylate monomer is used in a gel polymer electrolyte, the precursor can be easily infiltrated into the electrodes and the separator because it has relatively low viscosity, which is beneficial to the fabrication of rechargeable lithium polymer batteries by in situ polymerization [16]. However, GPE has some drawbacks, such as weak mechanical strength and poor interracial properties [17].

Several reports have indicated that the introduction of ceramic fillers into gel polymer electrolyte led to improvement of physical properties, such as dimensional stability and liquid uptake, and electrochemical properties, such as ionic conductivity, electrochemical stability and compatibility with lithium electrode by approaches (i) and (ii) mentioned above [18,19]. But few reports are about introducing ceramic fillers into GPE by approach (iii). In my opinion, it is probably because the ceramic fillers will deposit for the low viscosity of the precursor, and/or because the addition of ceramic filler will increase the viscosity of the precursor greatly due to the great surface area of superfine particles [20].

In this study, gel NCPE was prepared by UV polymerization and thermal polymerization, respectively. The monomer was nanosize SiO₂-contained poly(ethylene glycol) diacrylate (PEGDA), which was synthesized using aqueous colloidal silica as one of starting materials. In the synthesis, a silane coupler was used to modify the surface group of SiO₂. The precursor for the gel NCPE consisted of nanosize SiO₂-contained PEGDA, a liquid electrolyte and an initiator. The electrochemical properties of gel NCPE, such as ionic conductivity, electrochemical stability and interfacial stability were investigated. The results had also been compared with those of filler-free PEGDA-based GPE. Moreover, the gel NCPE was attempted to apply to a complete lithium polymer battery of graphite/SPE/LiCoO₂, which was prepared by in situ thermal polymerization. And the electrochemical properties of the battery were evaluated.

2. Experimental

A mixture was heated to reflux for 5 min consisting of 60 parts of isopropanol, 10 parts of aqueous colloidal silica (SiO₂ content was 25 wt.% and average particle size was approximately 20 nm) and 0.5 part of methacryloxypropyltrimethoxysilane (MAPTMS). After cooling, 22 parts of PEGDA monomer (Sartomer Co. Inc., MW = 302) were added. After the solvent was distilled under reduced pressure, PEGDA monomer containing nanosize SiO₂ was obtained. Infrared spectra were recorded on a Nicolet MAGNA-IR 550 Fourier transform spectrometer.

Gel NCPE was prepared with a homogeneous mixture solution of the nanosize SiO₂-contained PEGDA, a liquid electrolyte and a photo-initiator or a thermal-initiator by UV polymerization or thermal polymerization, respectively. Battery grade solution of 1 M LiPF₆/EC:DEC:DMC (1:1:1 w/w) was obtained from Merck Co. 2-Hydroxy-2-methyl-1-phenyl

propane-1-one (Darocur 1173, Ciba Geigy) was used as a photo-initiator and 2,2'-azo-isobutyronitrile (AIBN, Aldrich Chemical Co.) as a thermal-initiator. The precursor was cross-linked by exposure to UV light from a high-pressure mercury lamp for 3 min or by thermal radiation at 70 °C for 120 min in an oven. All procedures for preparing the precursor were carried out in a glove box filled with dry argon gas. Filler-free PEGDA-based GPE was prepared by the same procedure.

The ionic conductivity of the gel polymer electrolytes at temperatures ranging –25 to 55 °C was obtained from the ac impedance spectra of 2016 button cells. These cells were assembled in a dry box by sandwiching the gel polymer electrolyte between two stainless steel (SS) blocking electrodes. The cells were thermally equilibrated for at least 1 h at operating temperature before the onset of measurement.

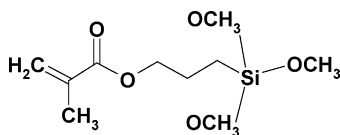
The stability of the lithium electrode and polymer electrolyte interface was evaluated by measuring the ac impedance of a Li/SPE/Li cell stored at 22 °C under open-circuit potential condition. The change of the impedance was continuously monitored after cell assembly.

The ac impedance of the cells was measured by using a Solartron 1260 frequency response analyzer connected to Solartron 1286 electrochemical interface. The 10 mV ac amplitude was applied with a frequency sweep of from 0.1 Hz to 1 MHz.

The electrochemical stability of the gel polymer electrolytes was studied using a cyclic voltammetry. It was carried out using Solartron 1286 electrochemical interface. The cells used for this study were 2016 button cells assembled by sandwiching the gel polymer electrolyte between stainless steel disc used as the working electrode and lithium metal disc used as the counter and reference electrodes. A stainless steel electrode with an area of 2.2 cm² was swept in the potential range of –0.5 to 5.0 V versus Li/Li⁺ at a sweep rate of 5 mV s^{–1}.

The applicability of the gel NCPE to lithium polymer batteries was demonstrated by fabricating and characterizing graphite/SPE/LiCoO₂ system. A precursor for the gel NCPE consisted of the nanosize SiO₂-contained PEGDA, a liquid electrolyte and a thermal-initiator. Battery grade solution of 1 M LiPF₆/EC:DEC:DMC (1:1:1 w/w) was obtained from Merck Co. AIBN was used as a thermal-initiator. Lithium cobalt oxide electrode was prepared by mixing 90 wt.% LiCoO₂ (Jinhe Industry Co. Ltd. China) with 5 wt.% super P black and 5 wt.% PVdF and coated on an aluminum foil. Graphite electrode was prepared using 92 wt.% graphite (Shanshan China Co.) and 8 wt.% PVdF. Celgard 2500 was used as a separator. The electrodes were stacked and inserted into an aluminum laminate film. The precursor was filled into the assembled cell in a glove box filled with dry argon gas and then it was vacuum-sealed. The assembled cell was polymerized at the temperature of 70 °C for 120 min in an oven.

The charge and discharge cycling test of the graphite/gel NCPE/LiCoO₂ cell was conducted galvanostatically between 3.0 and 4.2 V using battery program-control test system (Hangke Electron Co. China).



Scheme 1. Molecular structure of MAPTMS.

3. Results and discussion

3.1. Characterization of PEGDA monomer containing nanosize SiO₂

The nanosize SiO₂-contained PEGDA was prepared using aqueous colloidal silica as one of the starting materials. The preparation was actually the procedure of solvent exchange for nanosize SiO₂ from water to PEGDA with low molecular weight and at the same time the partial silanol surface groups of SiO₂ were modified into acrylic groups by employing of MAPTMS. MAPTMS is a silane coupler in common use, which has a functional group (–OCH₃) capable of hydrolytically condensing with a silanol group of the nanosize SiO₂. The molecular structure of MAPTMS is shown in Scheme 1 and FT-IR spectra of PEGDA and the nanosize SiO₂-contained PEGDA are shown in Fig. 1. In the spectrum of the latter, the intensity of the wide peak at 1110 cm^{–1} increases because the absorption peak of the Si–O–Si band of SiO₂ is at around 1110 cm^{–1}.

In the aqueous colloidal silica, the silica is hydrophilic with 100% silanol surface groups. During the distillation of water and isopropanol, dehydration reaction took place and most of silanol groups were translated into Si–O–Si. Only a few silanol groups including the isolated ones and the associated ones existed as indicated from Fig. 1. So, the surface groups of the nanosize SiO₂ modified by MAPTMS mainly

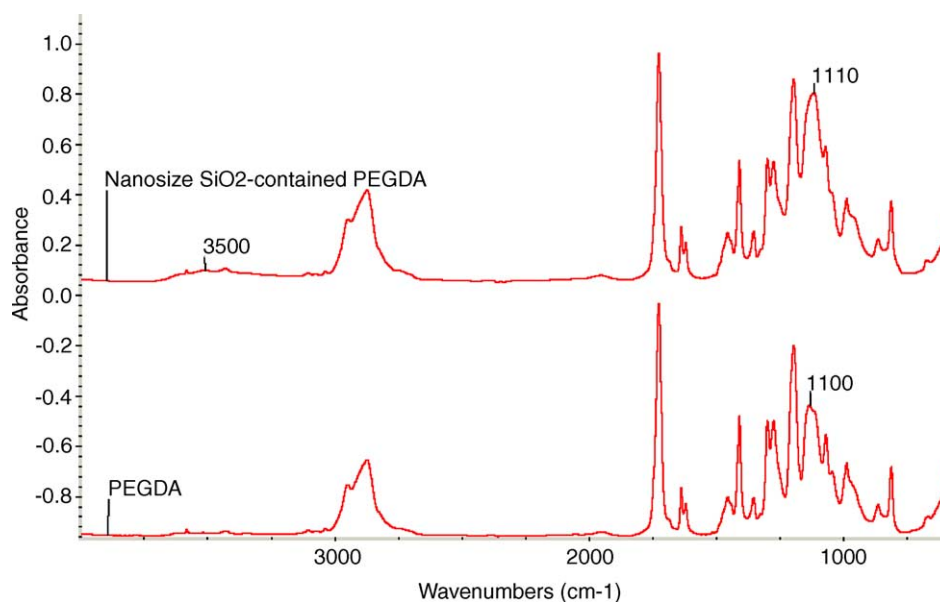
consisted of acrylic groups and silanol groups as shown in Scheme 2.

As the result of the surface modification of nanosize SiO₂, the nanosize SiO₂-contained PEGDA is so stable that no deposition is observed even after being stored for over six months. Moreover, the viscosity is still very low even if the SiO₂ content was up to 20 wt.%, and the liquid is clear and transparent too.

3.2. Ionic conductivity

The cross-linked polymer electrolytes were transparent and amorphous at room temperature. The nanosize SiO₂-contained PEGDA was freely blended with liquid electrolyte without phase separation.

The ionic conductivity of gel polymer electrolytes was measured using an ac impedance analyzer with a stainless steel blocking electrode. The comparison of ionic conductivity between the gel NCPE based on the nanosize SiO₂-contained PEGDA and the PEGDA-based GPE. These two kinds of GPEs were both prepared by UV polymerization considering its higher efficiency than thermal polymerization. The change in the measured conductivities as a function of liquid electrolyte content is shown in Fig. 2. The conductivity increases with an increase in the contents of liquid electrolyte. The trend is similar independent of ceramic particles. However, the conductivity of gel NCPE is a little higher than PEGDA-based gel polymer electrolyte without nanosize SiO₂ over the entire liquid electrolyte contents range. Although in gel polymer electrolytes, the ionic conductivity is dominated by the incorporated liquid electrolyte indicated by the previous studies [21], we feel confident on the observed difference since the conductivity values reported in this work were averages of at least five cells. The reason is

Fig. 1. FT-IR spectra of PEGDA and the nanosize SiO₂-contained PEGDA.

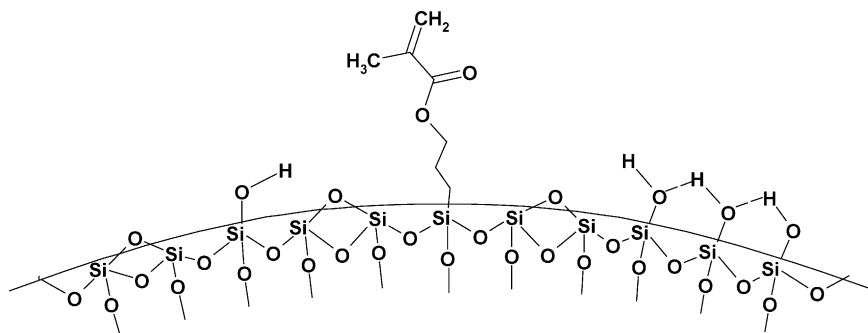
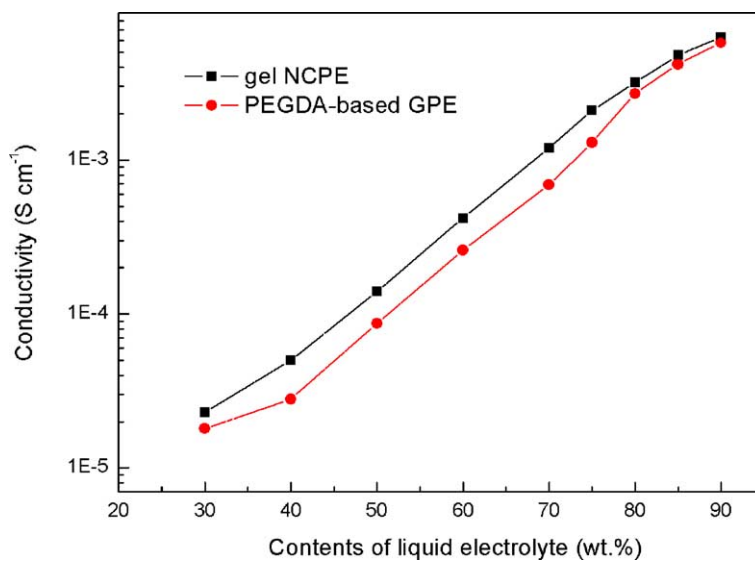
Scheme 2. Schematic model for the surface of nanosize SiO₂ modified by MAPTMS.

Fig. 2. Relationship between the conductivity and the contents of liquid electrolyte in the GPEs.

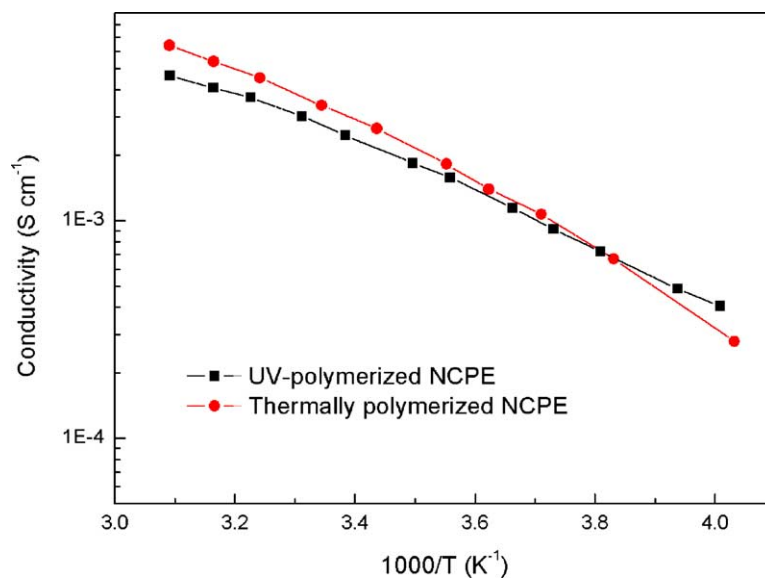


Fig. 3. Temperature dependence of ionic conductivity of the gel NCPEs prepared by UV polymerization and thermal polymerization, respectively.

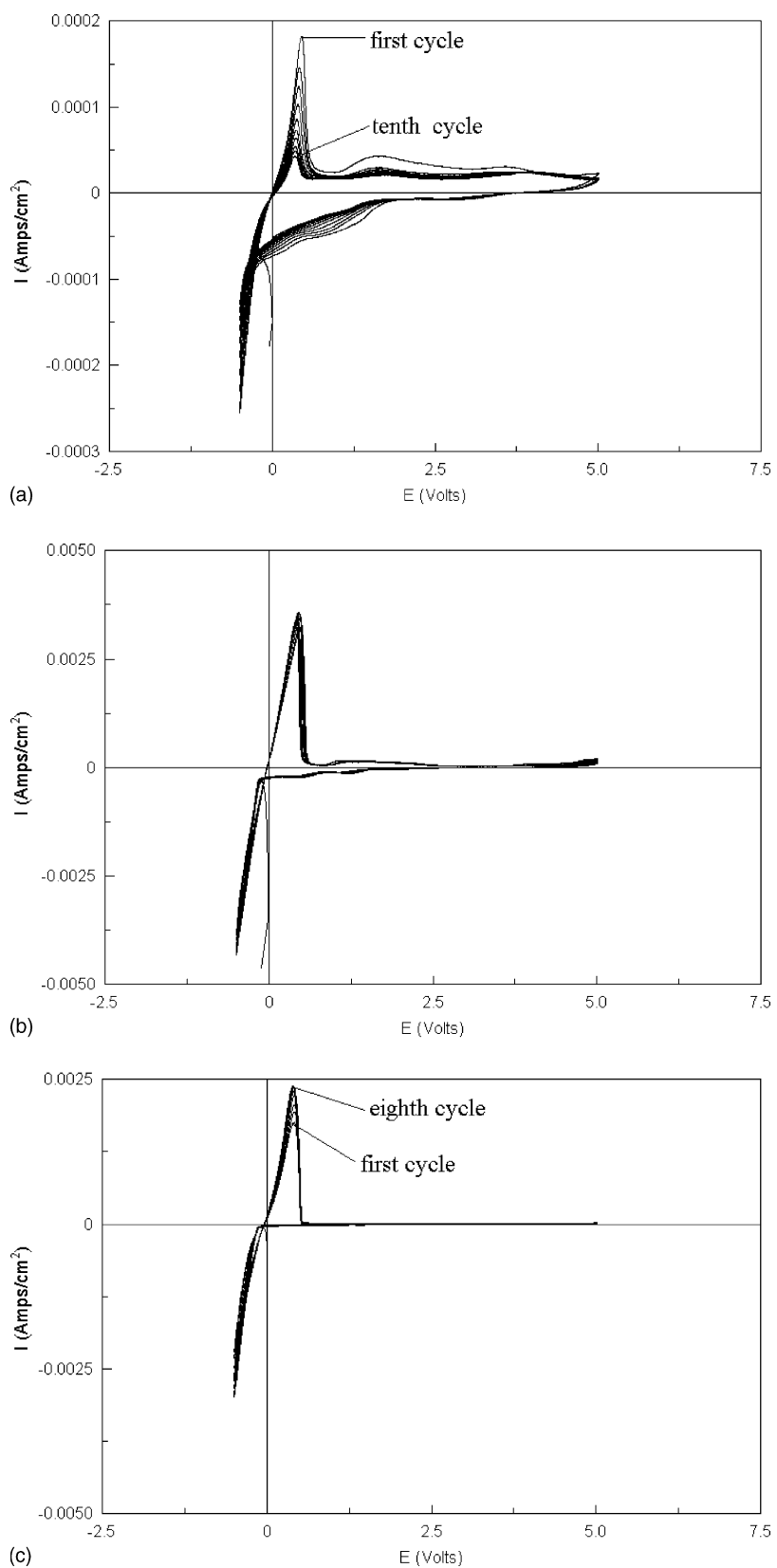


Fig. 4. Cyclic voltammograms of the GPEs containing 80 wt.% liquid electrolyte. These GPEs contain 80 wt.% liquid electrolytes, respectively: (a) PEGDA-based GPE prepared by UV polymerization; (b) gel NCPE prepared by UV polymerization; and (c) gel NCPE prepared by thermal polymerization.

maybe that nanosize SiO_2 can decrease the glass transport temperature and liquid retention ability of the polymer host.

The gel NCPE was also prepared by thermal polymerization at the temperature of 70°C for 120 min. Its ionic conductivity is around $4.0 \times 10^{-3} \text{ S cm}^{-1}$ with the liquid electrolyte content of 90 wt.% and $3.0 \times 10^{-3} \text{ S cm}^{-1}$ with the liquid electrolyte content of 80 wt.% at ambient temperature. The ionic conductivity of the thermally polymerized NCPE is a little smaller than that of UV-polymerized one.

Fig. 3 shows the ionic conductivity (σ) for the gel NCPEs prepared by UV polymerization and thermal polymerization, respectively at various temperatures. The ionic conductivity increases with increase in temperature. Both of the curves show a typical Vogel–Tamman–Fulcher (VTF) relationship (Eq. (1)) in the temperatures from -25 to 55°C , i.e.

$$\sigma = AT^{-1/2} \exp \left[\frac{-B}{T - T_0} \right] \quad (1)$$

where A , B and T_0 are fitted parameters which are related to the carrier density, pseudo activation energy and zero configuration entropy of the polymer chain, respectively. The VTF expression implies that the main mechanism of ion conduction may be related to the free volume theory [22].

3.3. Electrochemical stability

The electrochemical stability of the gel polymer electrolytes was studied using a cyclic voltammetry. Fig. 4 shows the cyclic voltammograms of the GPEs containing 80 wt.% liquid electrolytes on the stainless steel electrodes measured between -0.5 and 5.0 V versus Li/Li^+ . No peak is observed up to 5.0 V except the potential from -0.5 to 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 scanning the electrode in a negative direction, a cathodic peak is observed at about -0.5 V , which corresponds to the plating of lithium on to the stainless steel electrode. On the reverse scan, stripping of lithium is observed at about 0.45 V . For the gel NCPE whether prepared by UV polymerization or by thermal polymerization, the voltammograms ascribed to lithium deposition/dissolution are highly reversible because the peak currents remain fairly constant with repeated cycling. This indicates that the existence of SiO_2 can increase the electrochemical stability of gel polymer electrolytes.

3.4. Interfacial stability

The stability of the lithium electrode and polymer electrolyte interface was evaluated by measuring the ac impedance of $\text{Li}/\text{GPE}/\text{Li}$ cells stored at 22°C under open-circuit potential condition. The spectra are shown in Fig. 5. The first interception of data at a high frequency is related to bulk resistance (R_{bulk}). A semi-circle in the medium frequency range represents the interfacial resistance (R_{intf}).

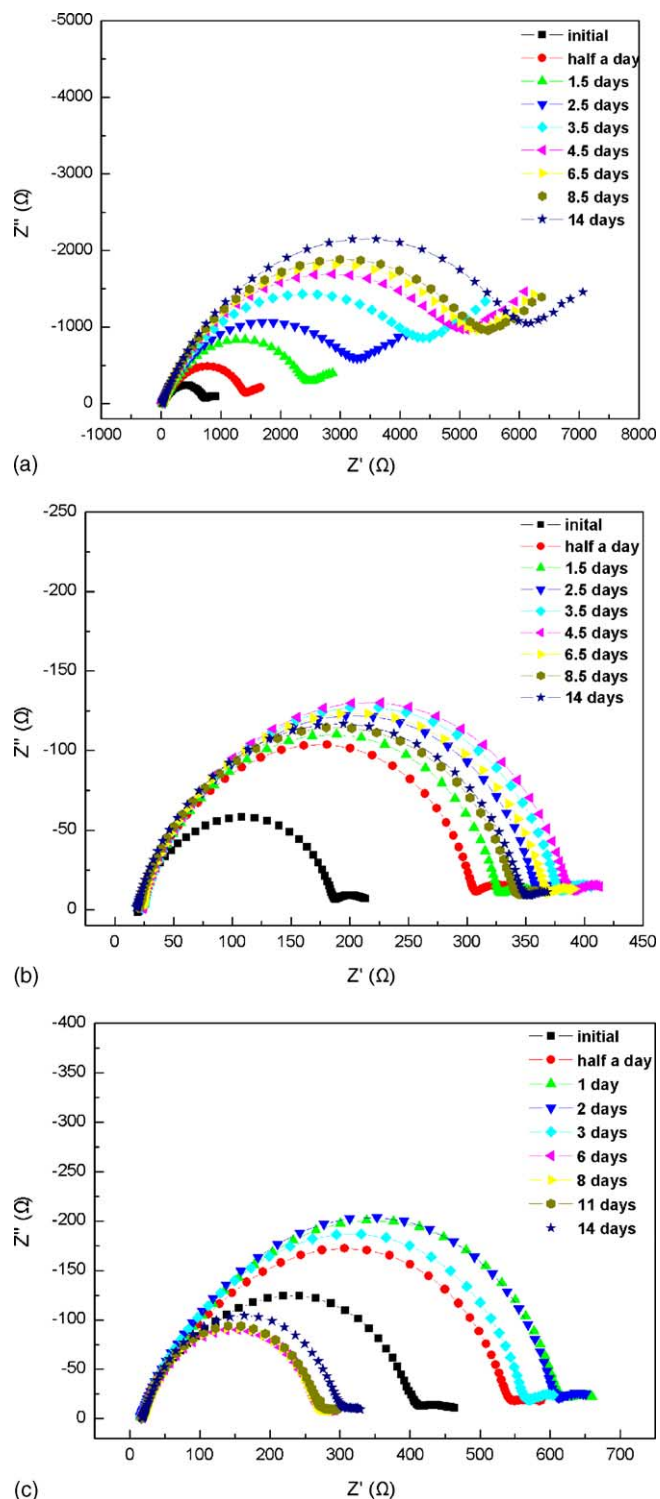


Fig. 5. Ac impedance spectra of $\text{Li}/\text{GPE}/\text{Li}$ cell with storage time at 22°C . The GPEs contain 80 wt.% liquid electrolytes, respectively. (a) PEGDA-based GPE prepared by UV polymerization; (b) gel NCPE prepared by UV polymerization; and (c) gel NCPE prepared by thermal polymerization.

With increasing time, little changes are observed in the R_{bulk} whether for gel NCPEs or PEGDA-based GPE, thus, indicating the stability of the polymer electrolytes. On the other hand, it can be learned from Fig. 5(a) and (b) that R_{intf} of the PEGDA-based GPE increases with increase of storage time and it is significantly larger than that of NCPE when the values of R_{bulk} are similar. R_{intf} of the gel NCPE increases initially and reaches a steady value after two days while for. The initial increase in R_{intf} may be explained by the formation of a passive film on the surface of the lithium electrode caused by the reactivity of the electrode with polymer electrolyte or residual impurities in the polymer electrolyte [23–25]. This indicates that nanosize SiO_2 is helpful to quickly form a compact and stable passive film; and thereby, stabilizes the interface between gel polymer electrolyte and electrode. It has been suggested by previous research that ceramic fillers could trap trace impurities, such as water and oxygen, and protect surface from corrosion [26,27].

As to the thermally polymerized gel NCPE (see Fig. 5(c)), the interface was also very stable. The R_{intf} was up to a maximum value after one day and then decreased with the storage time until coming to a low and steady value after six days. Although the initial R_{intf} is a little larger than that of UV-polymerized gel NCPE in the case of similar R_{bulk} , it is far smaller than that of the PEGDA-based GPE. The larger initial R_{intf} of thermally polymerized gel NCPE probably results from the procedure of Li/SPE/Li cell preparation, in which the cell was assembled after the oligomer was added between two lithium slices, and then kept at 70°C for 2 h, so the passive film on the surface of the lithium electrode grew thicker.

A phenomenon can be observed either from Fig. 5(b) and (c) that the R_{intf} decreases with an increase of time after passing the maximum. It is probably because the passive film can renovate itself spontaneously and become thinner and more uniform and compact. The mechanism need more work.

3.5. Battery performances

The applicability of the gel NCPE to lithium cells was demonstrated by fabricating and characterizing graphite/gel NCPE/ LiCoO_2 system. The gel NCPE with the liquid electrolyte content of 90 wt.% was brittle and unfit to wind. So the graphite/gel NCPE/ LiCoO_2 cell was fabricated by in situ thermal polymerization. The precursor consisting of the nanosize SiO_2 -contained PEGDA, a liquid electrolyte and a thermal-initiator can be easily infiltrated into the electrodes and the separator due to its relatively low viscosity.

This cell was charged and discharged at the 0.2 C rate between 3.0 and 4.2 V. Discharge capacity and coulombic efficiency are shown in Fig. 6. The discharge capacity decreases very slowly during cycling and this cell retains over 97% of the initial discharge capacity after 30 cycles. The coulombic efficiency is better than 99%. According to the work Song et al. [17] had reported, however, the performance of the Li/ LiCoO_2 cell with PEGDA-based GPE was too bad to be applied practically, such as large irreversible capacity,

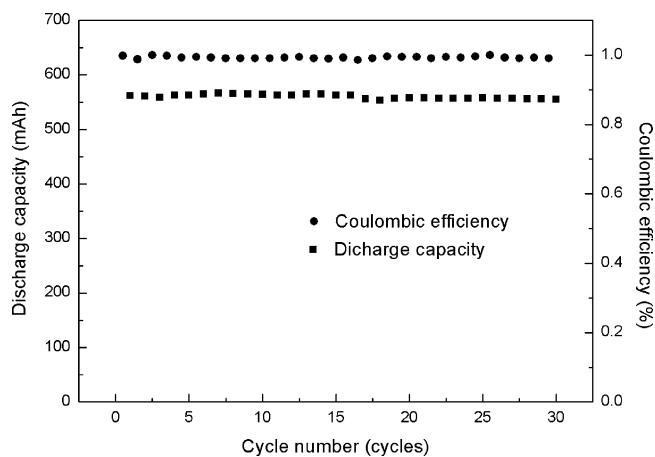


Fig. 6. Discharge capacity and coulombic efficiency change upon cycling at 0.2 C rate for graphite/gel NCPE/ LiCoO_2 cell at 22°C .

short cycle-life and poor coulombic efficiency, which primarily were ascribed to low ionic conductivity and poor interfacial properties.

4. Conclusions

A gel nanocomposite polymer electrolyte was prepared by UV polymerization and thermal polymerization, respectively with the nanosize SiO_2 -contained PEGDA as the monomer in the presence of liquid electrolyte. The nanosize SiO_2 -contained PEGDA was synthesized using aqueous colloidal silica as one of the starting materials and the partial silanol surface groups of SiO_2 were modified into an acrylic group by employing of MAPTMS. The method was simple and the dispersion of nanosize SiO_2 in the monomer was uniform and stable. The electrochemical properties of the gel NCPE were similar whether it was prepared by UV polymerization or thermal polymerization. Compared with the gel polymer electrolyte (GPE) based on PEGDA without nanosize SiO_2 , the ionic conductivity of the gel NCPE was higher and especially the electrochemical stability and interfacial stability were better. It showed oxidation stability up to 5.0 V versus Li/Li^+ and lithium deposition/dissolution on the stainless steel electrode highly reversible. Impedance studies confirmed that the gel NCPE had better compatibility with lithium metal. A graphite/gel NCPE/ LiCoO_2 cell was prepared by in situ thermal polymerization and the discharge capacity was stable with charge–discharge cycling. Consequently, the synergetic performance of the gel NCPE based on the nanosize SiO_2 -contained PEGDA appears to be highly suitable for rechargeable lithium polymer batteries.

Acknowledgements

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References

- [1] D.E. Fenton, J.M. Parker, *Polymer* 14 (1973) 589.
- [2] S.R. Raghavan, M.W. Riley, P.S. Fedkiw, S.A. Khan, *Chem. Mater.* 10 (1998) 244.
- [3] W. Krawiec, L.G. Scanlon, J.P. Fellner, *J. Power Sources* 54 (1995) 310.
- [4] F. Croce, G.B. Appetecchi, L. Persi, *Nature* 394 (1998) 456.
- [5] Z.Y. Wen, T. Itoha, T. Uno, M. Kubo, O. Yamamoto, *Solid State Ionics* 160 (2003) 141.
- [6] K.S. Ji, H.S. Moon, J.W. Kim, J.W. Park, *J. Power Sources* 117 (2003) 124.
- [7] F.B. Dias, L. Plomp, J.B.J. Veldhuis, *J. Power Sources* 88 (2000) 169.
- [8] F. Boudin, X. Andrieu, C. Jehoulet, I.I. Olsen, *J. Power Sources* 81–82 (1999) 804.
- [9] J.M. Song, H.R. Kang, S.W. Kim, W.M. Lee, H.T. Kim, *Electrochim. Acta* 48 (2003) 1339.
- [10] Y. Saito, A.M. Stephan, H. Kataoka, *Solid State Ionics* 160 (2003) 149.
- [11] P.P. Prosini, S. Passerini, *Solid State Ionics* 146 (2002) 65.
- [12] C.S. Kim, S.M. Oh, *J. Power Sources* 109 (2002) 98.
- [13] B. Oh, W.I. Jung, D.U. Kim, H.W. Rhee, *Bull. Korea Chem. Soc.* 23 (2002) 683.
- [14] H.S. Kim, J.H. Shin, S.I. Moon, M.S. Yun, S.P. Kim, *Chem. Eng. Sci.* 58 (2003) 1715.
- [15] A. Reiche, R. Sandner, A. Weinkauff, B. Sandner, G. Fleischer, *Polymer* 41 (2000) 3821.
- [16] H.S. Kim, J.H. Shin, S.I. Moon, M.S. Yun, *J. Power Sources* 119–121 (2003) 482.
- [17] M.K. Song, J.Y. Cho, B.W. Cho, H.W. Rhee, *J. Power Sources* 110 (2002) 209.
- [18] A.Du. Pasquier, P.C. Warren, D. Culver, A.S. Gozdz, G.G. Amatucci, J.M. Tarascon, *Solid State Ionics* 135 (2000) 209.
- [19] K.M. Kim, N.G. Park, K.S. Ryu, S.H. Chang, *Polymer* 43 (2002) 3951.
- [20] Y.B. Fu, X.H. Ma, Q.H. Yang, X.F. Zong, *Mater. Lett.* 57 (2003) 1759.
- [21] Y. Matsuda, T. Fukushima, Y. Katoh, E. Ishiko, M. Nishiura, M. Kikuta, M. Kono, *J. Power Sources* 119–121 (2003) 473.
- [22] M.M. Armand, in: J.R. McCallum, C.A. Vincent (Eds.), *Polymer Electrolyte Reviews*, vol. 1, Elsevier, London, 1987, p. 1.
- [23] Y. Kang, H.J. Kim, E. Kim, B. Oh, J.H. Cho, *J. Power Sources* 92 (2001) 255.
- [24] Z. Florjanczyk, W. Bzducha, N. Langwald, J.R. Dygas, F. Krok, B. Misztal-Faraj, *Electrochim. Acta* 45 (2000) 3563.
- [25] C. Polo Fonseca, S. Neves, *J. Power Sources* 104 (2002) 85.
- [26] H.J. Walls, J. Zhou, J.A. Yerian, P.S. Fedkiw, S.A. Khan, M.K. Stowe, G.L. Baker, *J. Power Sources* 89 (2000) 156.
- [27] J. Zhou, P.S. Fedkiw, S.A. Khan, *J. Electrochem. Soc.* 149 (2002) 1121.