Polymer Bulletin 44, 509–515 (2000)

Polymer Bulletin
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Preparation and electrochemical properties of nonwoven reinforced solid polymer electrolytes

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Received: 25 February 2000/Accepted: 14 April 2000

Summary

Reinforced PEO-based polymer electrolytes were prepared by UV curing method. In this study, nonwoven sheets which were polyethylene terephthalate and polypropylene were used for that purpose. To enhance the ionic conductivity of reinforced PEO-based polymer electrolytes, oligomeric poly(ethylene glycol) dimethyl ether was added as a plasticizer, which is a sort of nonvolatile chemicals. The reinforced PEO-based polymer electrolytes showed the ionic conductivity of around 1.2×10^{-4} S/cm at 30°C, which was a little bit lower than the value of not reinforced one, that is pristine UV cured SPE. Even though the reinforced PEO-based polymer electrolytes didn't have any organic solvent such as ethylene carbonate, lithium ionic type polymer cell containing the polymer electrolyte showed reasonable specific discharge capacity of 116 mAh/g at room temperature.

Introduction

Solid polymer electrolytes(SPEs) have been proposed in the past for use instead of liquid electrolyte which is widely used in lithium ion secondary battery. The advantages in the use of SPE are, in general, the elimination of possibility of leakage and the preclusion of the increment of internal pressure when volatile liquid electrolytes are present. Also such solid polymer electrolytes can be fabricated as a flexible polymer battery which permits space efficient battery to be designed.

Many types of solid polymer electrolytes have been suggested such as poly(ethylene oxide) (PEO) (1-3), poly(propylene oxide) (PPO) (4, 5), poly(ethylene imine) (PEI) (6) and so on. Although these SPEs have some significant properties such as electrochemical and chemical stability as well as easy fabrication characteristics, they have not met with any appreciable commercial success because the ionic conductivity at room temperature is poor.

A lot of attempts have been tried to increase the ionic conductivity at room temperature such as the blend of poly(ethylene glycol) dimethyl ether (PEGDMe) with PEO (7) or poly(vinylidene fluoride-co-hexafluoropropylene) (8). We also prepared crosslinked PEO polymer electrolyte containing PEGDMe for the purpose of enhancement of stability and ionic conductivity at ambient temperature (9). We got the ionic conductivity of 2.3 $\times 10^{-4}$ S/cm.

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In this study, we tried to make the reinforced PEO based SPE supported by nonwoven matrix with the reasonable ionic conductivity at room temperature. We investigated the effect of soaking time of nonwoven matrix in curable PEO solution on the ionic conductivity. We applied two types of nonwoven matrix, one was polypropylene (PP) and the other was poly(ethylene terephthalate) (PET).

Experimental

Materials and reagents

Methoxy poly(ethylene glycol) methacrylate (MPEGM, Mw=400, Poly Sciences Inc.) and poly(ethylene glycol) dimethacrylate (PEGDMA, Mw=400, Poly Sciences Inc.), crosslinking agent, were used as PEO matrix. They were dried in vacuum before use. Poly(ethylene glycol) dimethyl ether (PEGDMe, Mw=250, Aldrich Co.), oligomeric PEO, was used as a non-volatile plasticizer to increase the ionic conductivity of PEO SPE and it was distilled *in vacuo* for further purification. 2,2'-dimethoxy-2-phenylacetophenone (DMPA, Aldrich Co.), photoinitiator, and $LiCF_3SO_3$ (Aldrich Co.) were dried in vacuum before use. PP and PET nonwoven sheet were kindly supplied from XETEX Co., KOREA. Their thickness was around 80μm.

Preparation of UV curing type SPE

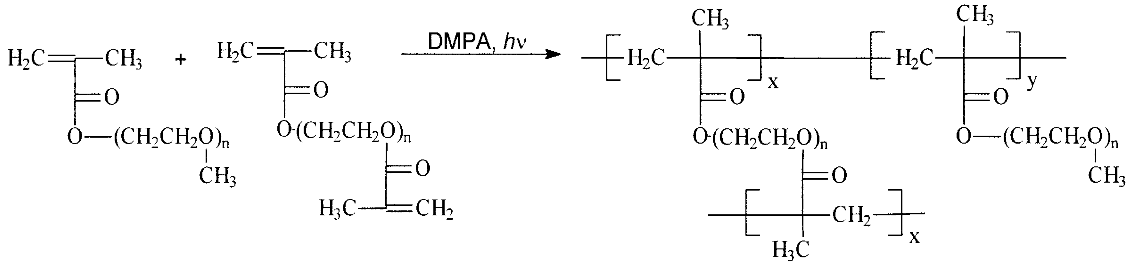
A solution of MPEGM, PEGDMA, PEGDMe and $LiCF_3SO_3$ was prepared by mixing them for 5hrs with magnetic stirrer, and the amount of the above compounds was 20.00g, 4.80g, 24.80g and 6.65g, respectively. The ratio of [EO]/[Li] was adjusted to 20. To this solution, DMPA was added and stirred to make transparent solution. Nonwoven sheets were dipped into the final curing solution in a certain time such as 1min, 1hr, 2hrs and 3hrs. The nonwoven sheets containing the curing solution were placed between glass plates and irradiated by UV (365nm, 30W) for 30min. Flexible films around 90μm were finally prepared and all freestanding. The morphology of the reinforced SPEs was observed by SEM. The brief curing reaction mechanism is shown in Scheme 1.

Electrochemical analysis

The ionic conductivity measurement was carried out with SUS/reinforced SPE/SUS cell. The a.c. complex impedance was recorded using impedance analyzer (Zahner Elektrik, model IM5d) in the frequency range of 1Hz to 1MHz. The temperature of the sample was controlled by means of the programmable hot plate (Mattler, model FP82HT). All samples were prepared in argon gas filled glove box.

The electrochemical stability of the SPEs was measured by means of cyclic voltammography using EG&G model 270 potentiostat. A stainless steel was used as working electrode and lithium foil was used as counter and reference electrodes.

Battery test was carried out with TOYO battery cycler. A rechargeable lithium ionic type polymer cell was assembled by sandwiching the reinforced SPE between MCF carbon anode and $LiCoO_2$ cathode. The composition of electrodes is listed in Table 1.



Scheme 1. Brief mechanism of UV curing reaction of MPEGM and PEGDMA.

Table 1. The composition of MCF carbon anode and $LiCoO_2$ cathode

[wt%]

Electrode	MCF	$LiCoO_2$	Super-P carbon	PVdF*	Liquid electrolyte**
Cathode	-	69.0	2.3	3.7	25.0
Anode	63.0	-	-	7.0	30.0

* PVdF = poly(vinylidene fluoride)

** 1.15M LiPF6 in EC/DMC/EMC was used here as an ionic conducting medium in electrodes.

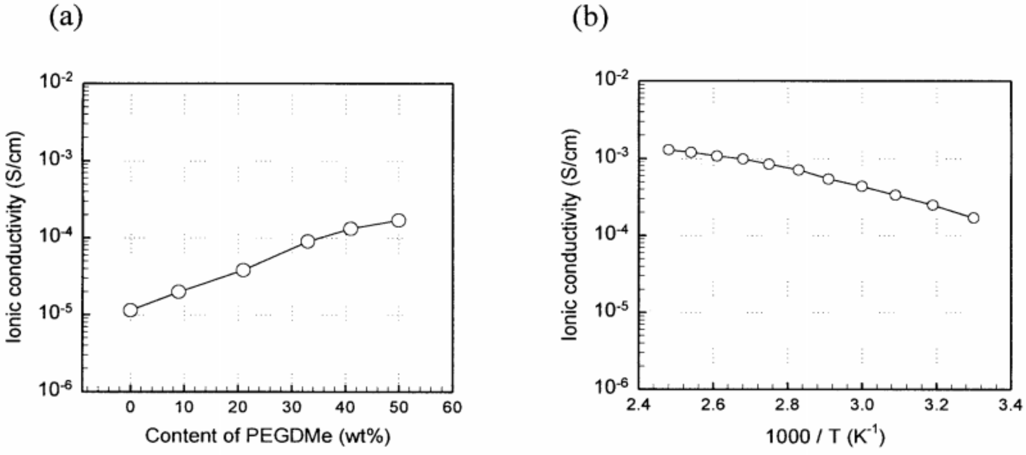


Fig. 1. Result of ionic conductivities of pristine SPEs, that is MPEGM/PEGDMA/ PEGDMe system, without nonwoven, where is a) the effect of the content of PEGDMe and b) the temperature dependency in the case of 50wt% of PEGDMe system.

Results and Discussion

Ionic conductivity of pristine UV cured SPEs

Fig. 1a shows the ionic conductivity of pristine UV cured SPEs, that is not reinforced by nonwoven sheet. The SPEs were transparent and amorphous at room temperature. The T_g was well described in our previous report (9) and clearly decreased in proportion to the content of PEGDMe. The weight ratio of MPEGM/PEGDMA was always fixed as noted in experimental section. It was thought that the addition of nonvolatile oligomeric PEO, PEGDMe, could give enough plasticizing effect to improve the ionic conductivity at ambient temperature. The ionic conductivity is, thus, increased as increasing the content of PEGDMe.

The ionic conductivity of pristine UV cured SPEs which have 50% of PEGDMe are also significantly dependent upon the temperature as shown in Fig. 1b. A typical Vogel-Tamman-Fulcher (VTF) type of ionic conductivity-temperature relationship is observed in the temperature range of 30~ 120°C. This trend implies that the main mechanism of ion transport could be explained by free volume theory (10).

Preparation of nonwoven reinforced SPEs

Fig. 2 shows the surface SEM morphologies of PET nonwoven reinforced SPEs according to the nonwoven soaking time in UV curing solution. From the experiment of pristine UV cured SPEs, we adapted the composition of 50% of PEGDMe, and the amount of MPEGM and PEGDMA was the same as described in experimental section.

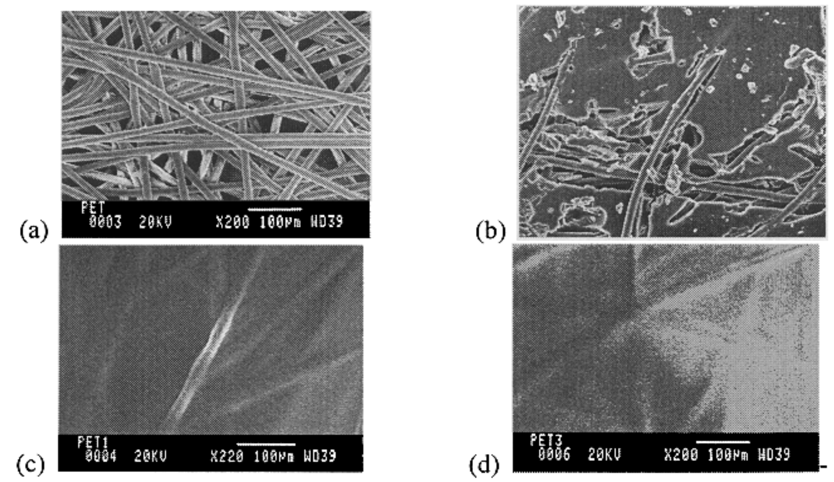


Fig. 2. Surface SEM morphologies of PET nonwoven reinforced SPEs according to the nonwoven soaking time in UV curing solution, and soaking time is a) 0 min, b) 1 min, c) 1hr and d) 2hrs, respectively.

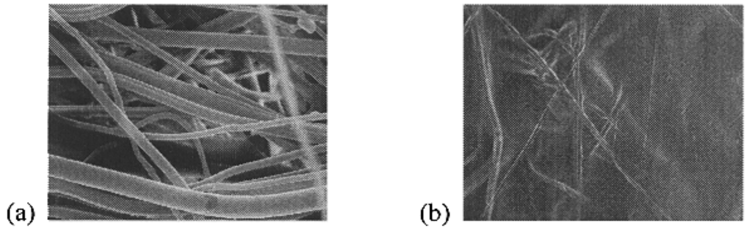


Fig. 3. Surface SEM morphologies of PP nonwoven reinforced SPE. Soaking time is a) 0 min and b) 2hrs, respectively

It could be found that the whole area of nonwoven is covered by SPE after the soaking time of 1hr and just dip-in-and-out, that is the soaking time of 1min, is not enough time to make homogeneous nonwoven reinforced SPE. We also tried to prepare a reinforced SPE by using PP nonwoven sheet (see Fig. 3). In the case of PP, it was needed 2hrs of soaking to make a homogeneously reinforced SPE. It is thought that PP is more hydrophobic than PET and that requires more time to be fully soaked state.

Ionic conductivity of nonwoven reinforced SPEs

We investigated the change of the ionic conductivity of nonwoven reinforced SPEs with the function of soaking time (see Fig. 4). The tendency of Fig. 4 can be explained with the morphology change as it can be seen in Fig. 2 and 3. That means the stable ionic conductivity can be only acquired when the nonwoven sheets are fully soaked by UV curing solution. If not, there might be occurred the disconnected channel for ionic conduction that would reduce the ionic conductivity. We could get the ionic conductivities of over 1.2 x 10^{-4} S/cm for the reinforced SPEs at 30°C with enough mechanical strength for battery application, and those are closed values to that of pristine SPE, that is without nonwoven sheet, which is 2.3 x 10^{-4} S/cm. In the case of reported SPEs for near room temperature application which had PEGDMe as a plasticizer and $LiCF_3SO_3$, their ionic conductivities were below 2.0 x 10^{-4} S/cm (7, 8) at 30 °C. It is concluded that the mechanically reinforced SPEs in this study show reasonable ionic conductivities at near room temperature regardless the sort of nonwoven sheets.

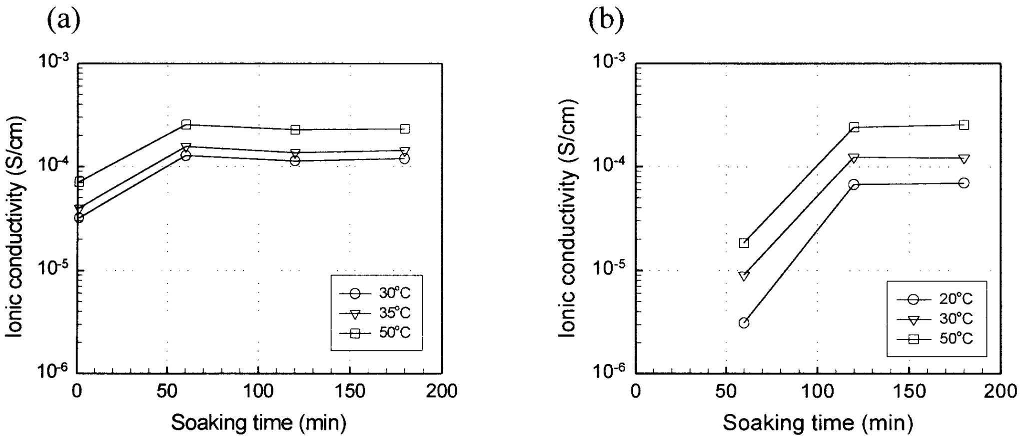


Fig. 4. Result of ionic conductivities of a) PET nonwoven reinforced SPEs and b) PP nonwoven reinforced SPEs according to the temperature and soaking time.

Electrochemical stability and battery performance

We examined the electrochemical stability window for the reinforced SPEs to check their possibility to apply as a separator for lithium polymer cell adapting lithium metal oxide as cathode active material such as $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$ and so on. As we used $LiCoO_2$ as a cathode material in this study, the SPE should have over 4.5V of stability window (11). The result is shown in Fig. 5. PET nonwoven reinforced SPE shows enough electrochemical stability window over 4.5V. The SPE reinforced with PP nonwoven shows more higher stability than PET reinforced SPE. It is because that PP has more stable chemical structure than PET, there is no carbon-oxygen single bond.

We also investigated the battery performance of MCF carbon anode/PET nonwoven reinforced SPE/$LiCoO_2$ cathode cell at 30°C. The important point was the near room temperature application by using solid polymer electrolyte without any volatile solvent. We could get a specific discharge capacity of about 116mAh/g at a current density of 0.15mA/cm^2. There was no significant decrease of discharge capacity with cycles although it was just 5 cycle test (See Fig. 6a).

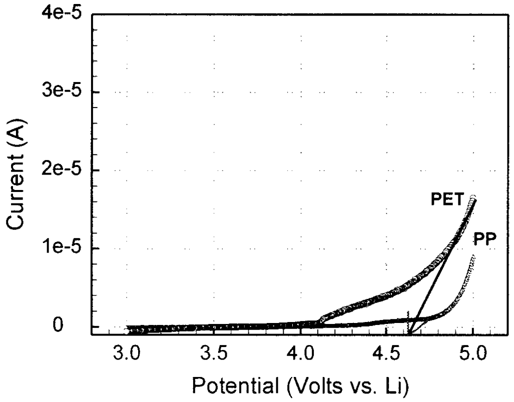


Fig. 5. Electrochemical stability window for nonwoven reinforced SPEs.

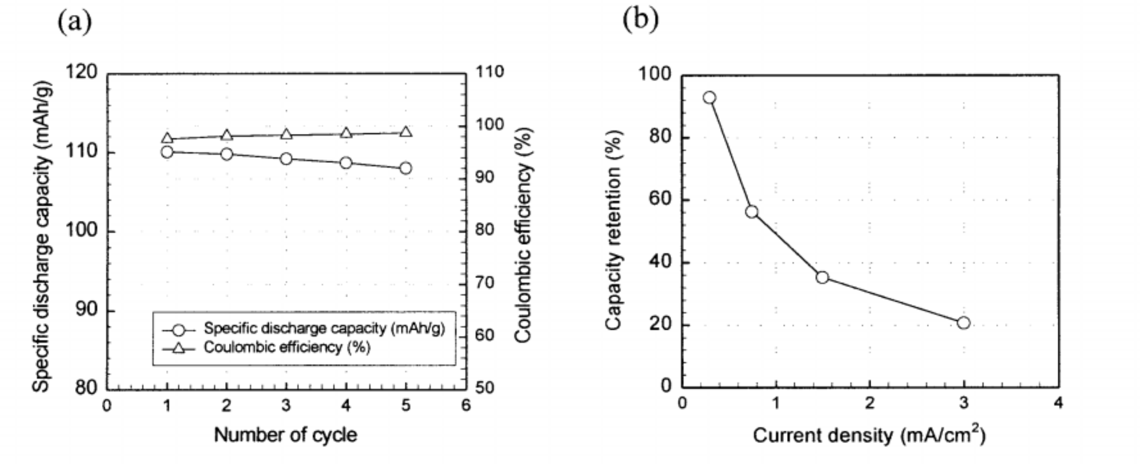


Fig. 6. Result of battery cell having PET reinforced SPE, where is a) cyclic test at 0.15 mA/cm^2 and b) rated capability with a different current density.

The rated capacity of the cell was, however, deeply sensitive to the granted current density (see Fig. 6b). We thought that there is the limitation of possible current density to operate with the ionic conductivity of 1~2 x 10^{-4} S/cm. K. Abraham also explained about the similar result as the moderate ionic conductivity of SPE (8).

Conclusions

We prepared the reinforced SPEs with nonwoven sheets to ensure enough mechanical strength. The reinforced SPEs showed closed ionic conductivities to that of pristine SPE and good electrochemical stability window of over 4.5V. The reinforced SPE with PP nonwoven showed better electrochemical stability than that with PET nonwoven but harder to make homogeneous SPE due to its less affinity toward UV curing solution. The lithium ionic type polymer cell with PET reinforced SPE showed promising cyclic performance at a low current density of 0.15 mA/cm^2 but its rated capacity was considerably dependant upon the granted current density due to its moderate ionic conductivity and the thickness of about 90$^{\mu}$m.

It is thought that one of the clues to reduce the rate sensitivity of the cell is to minimize the thickness of SPE with the same ionic conductivity, and it will reduce the resistance the ion conduction. We are going to further study about it.

Acknowledgement

This work was financially supported by MOST (Ministry of Science and Technology) through KISTEP under Contract 98-G-06-02-A-32.

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