

Improvement of Properties in Solid Polymer Electrolyte Using New Preparation Method

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새로운 막 제조 방법에 의한 고분자 전해질막의 특성 향상

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ABSTRACT

높은 이온전도도와 충분한 기계적 강도, 전해질 누수가 적은 새로운 형태의 고분자 전해질막 (pore-gel SPE)을 연구 개발하였다. 다공성 PVDF-HFP 고분자막의 기공 내에 전해질 용액을 흡수시킨 후 막 내에서 젤화를 진행시켰다. 전해질 용액은 2:2:1의 비를 갖는 PC/EC/DMA에 1M SA (Salicylic acid)를 용해하고 여기에 고분자막을 용해시킬 수 있는 아세톤을 첨가하였다. 초음파를 이용함으로써 고분자막의 용액 흡수율을 증가시키고 또 고분자막에서 젤화를 촉진시킬 수 있었다. 이렇게 젤화한 막의 이온전도도는 젤화 전 막보다 1~2.2 배 향상되었고, 인장강도는 gel-type SPE 보다 40 배 증가하였으며, 전해질 누수실험결과 hybrid-type SPE는 13%의 누수를 보였으나 본 연구의 막(pore-gel SPE)은 6%로 감소함을 보였다.

KEY WORDS : solid polymer electrolyte(고체 고분자 전해질), gelation(젤화), conductivity(전도도), mechanical strength(기계적 강도), solution leakage(용매 누수)

1. Introduction

Solid polymer electrolyte (SPE) have received much attention because of their application to batteries, sensors, electrochemical capacitors and fuel cells.

For this application, SPEs should satisfy the

following requirements; a) high ionic conductivity, b) strong mechanical properties in a wide temperature range and c) no electrolyte solution leakage.

Solid polymer electrolyte (SPE) system can be classified into three types; pure (or dry) SPE, gel-type SPE and hybrid (or porous)-type SPE. Recently, the works about gel-type and hybrid-type SPEs are very popular due to their ability for application in batteries^{1,2)}.

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The pure polymer electrolyte system is generally prepared by mixing high molecular weight branched polymer and solid plasticizing salts (or acid). To improve the ionic conductivity of polymer electrolytes, gel-type SPE has liquid property by adding liquid electrolyte solution to solid polymer. Gel-type SPE consists of polymer, electrolyte salt and a liquid plasticizer. Some gel-type SPEs containing proton conducting acids have also been studied because of their usefulness in fuel cells, electrochromic devices and solid state batteries etc. Initial work, strong acids like H_3PO_4 and H_2SO_4 used for proton conduction which may degrade the polymer and hence are not suitable for practical application. So some weak acid like salicylic acid which is a proton conducting material and suitable for use over a wide temperature range have been studied in recent work^{3,4}). Gel-type SPEs generally have higher ionic conductivity, but their mechanical properties are not sufficient for practical application⁵).

Hybrid-type SPEs are generally prepared by injecting organic liquid electrolytes into the small pores of polymer matrices. After long -time usage, the organic liquid electrolyte can leak from the polymer matrices and it decrease the ionic conductivity because the organic liquid electrolyte acts as a medium for ion conduction through the polymer matrices.

In order to overcome the problems of mechanical properties in gel-type SPE and the leakage in hybrid-type SPE, we prepared the new type of proton conducting SPE using alternative preparation method. This new type of SPE can be obtained by gelation of electrolyte solution and polymer matrix in the pores of the polymer membrane after swelling with electrolyte solution. Hence, we designate this new SPE as pore-gel SPE.

Gel-type SPE, hybrid-type SPE ,and pore-gel are the same SPE that is composed of liquid phase and solid phase in macroscopic aspect. But there are differences between these SPEs in microscopic aspect. Gel-type SPE is prepared by homogeneous mixing of liquid and solid phase. Therefore there is not solid domains that act as a mechanical support in Gel-type SPE.

On the other hand hybrid-type SPE consists of two domains; the liquid domain has large amount of liquid electrolyte entrapped by solid wall, and the solid domain acts as a mechanical support which enhance the mechanical strength of SPE. Pore-gel SPE is developed to reduce the leakage of liquid in hybrid-type SPE by gelling process which protrudes solids from interface between solid and liquid in liquid domain.

2. Experimental

2.1 Membrane preparation

New type of SPEs were obtained through the following three steps. At a first step, we prepared the porous polymer films as the matrix for SPEs.

Polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP, Kynar Flex 2801, Elf Atochem, Japan) was directly dissolved in acetone with agitation at 40°C. The mixing solutions were cast on a glass plate and dried to evaporate solvent at ambient temperature. This copolymer does not precipitate homogeneously due to fast acetone evaporation. Therefore micro-pores may be formed at the site of evaporated acetone. After evaporation of acetone, strong and porous thin films were formed. At a second step, the electrolyte solution were prepared by mixing salicylic acid(SA), acetone and plasticizer mixture propylene carbonate (PC)/ethylene carbonate

(EC)/N,N-dimethylacetamide (DMA) (plasticizer). The solution was consisting of 85% 1M SA (99+%, Aldrich) in 2:2:1 plasticizer mixture of PC (99.7%, Aldrich), EC (98%, Aldrich) and DMA (99%, Aldrich) and 15% acetone. The polymer films were immersed into the electrolyte solution. To enhance velocity of the electrolyte solution impregnation into micro-pores of the films, we used ultrasonic vibration (Ultrasonic cleaner, Branson) adjusted at the frequency of 47 kHz. After impregnation of the electrolyte solution for a certain time, the swollen membrane was taken out of the solution and then put into a sealed bag. Finally, gelling process in micro-pores of the membrane was made using ultrasonic vibration on the membrane, which was contacted with part of vibration source by weight.

2.2 Measurements

For measurements of ionic conductivities, the polymer electrolyte membranes were put between two stainless steel electrodes and measured the resistance from a frequency response analyser (Solatron HF 1225) in the frequency range of 0.1Hz-100k Hz. The ionic conductivity (σ) was calculated from the resistance (R) using a equation $\sigma = l/(R \times A)$, Where l and A were the thickness and the area of the polymer electrolyte membrane, respectively.

Membrane morphology was observed by Scanning electron microscope (HITACHI, S-3500N) at 20 kV. Samples were dried in vacuum oven at 60°C for 24 hr and broken in liquid nitrogen in order to observe the membrane cross-sections. Their sections were coated by sputtering gold for 180 s.

Tensile tests were carried out with a Texture

Analyzer (TA-XT2, England) at a full-out velocity of 4 mm/min. The test specimens were 2 cm wide and 6 cm long. Measurements were performed five times for each samples and the average value was calculated.

Liquid electrolyte uptake of the polymer film was measured by a gravimetric method. Prior to measure the weight of swollen films, the solution on their surfaces was removed by light-patting with a filter paper.

The solution leakage was measured with the method used by Qiao et al⁽⁶⁾. Swollen membrane of 1 cm² area was put between filter papers and then a weight of 1 kg was put on top of the assembly. Mass of the membrane was measured before and after a certain time pressing.

3. Results and discussion

3.1 Morphology

Generally, impregnation components of hybrid-type SPE are consisting of electrolyte salt (or acid) and plasticizers. But we added a polymer solvent (acetone) for the polymer to the impregnation components. The impregnated solvent in pores dissolves the polymer matrices wall and then forms the solution including acid, plasticizers and polymer in membrane. At this step, polymer dissolution was promoted by vibration and heat. It was difficult to increase mass transfer of solution in micro-pores. And then we used the ultrasonic vibration to enhance the mass transfer rate of acetone. It has been well known that the cause of the accelerating effect of ultrasonic vibration was improvement of mass transfer of reactants and /or product in the pore^{7,8)}.

After polymer dissolution step, the size of the remained polymer matrices depends on dissolution time and solvent content. As acetone

evaporates in drying process, polymer concentration becomes richer in solution and polymer precipitate in the acid/plasticizers phase, resulting in gel formation. Due to fast evaporation of acetone, fine precipitates seems to form in the entire membrane.

Fig. 1(a) displays a SEM photograph of the PVdF-HFP membrane swollen in PC/EC/DMA/SA solution without acetone. It can be seen that membrane consists of solution domain and polymer matrix domain similar to hybrid-type SPE⁹⁾. Fig. 1(b) and Fig. 1(c) show SEM images of the membrane treated with ultrasonic vibration respectively for 30 min and 60 min after swelling in solution with acetone. When the ultrasonic vibration was applied to the membrane, the large polymer matrices disappear and homogeneous gel phase exists in entire membrane as shown Fig. 1 (c), that is, there was a strong effect of the vibration method on the mixing, diffusion and gelling in micro-pores of the membrane.

3.2 Ionic conductivity

The results of conductivity measurements for pore-gel SPE (curve B) and hybrid-type SPE (curve A) are presented in Fig. 2. Because of the contact resistance between stainless steel electrodes and SPE during ionic conductivity measurement, the ionic conductivities are lower than other studies used SA^{3,4)}. But clearly we improved the ionic conductivity by gelation in same SA/PC/EC/DMA uptake as shown in Fig. 2. In case of gel SPE, a mechanism consisting of two conduction paths has been postulated by other researchers^{10,11)}.

By this mechanism, the effective higher conductivity pathway decreases with increasing polymer content. And the resistance due to the

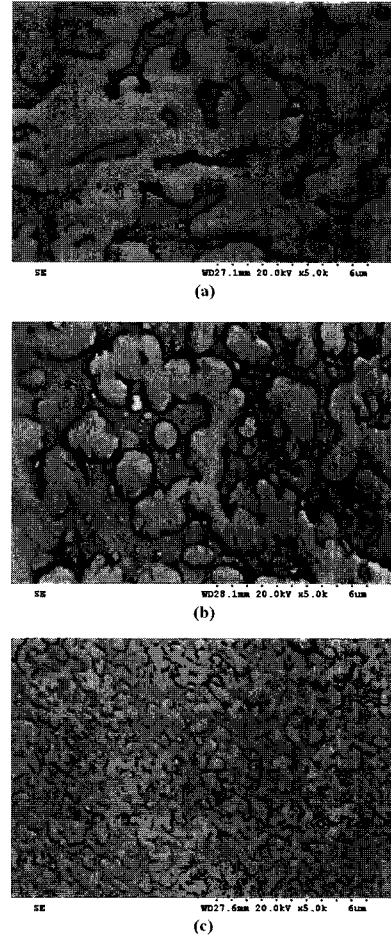


Fig. 1 SEM photographs of the membrane just swollen in electrolyte solution (a) and treated with ultrasonication for 30 min (b) and 60 min (c) after swelling

membrane is linked to its porosity (ϵ) and tortuosity (T) by the following formula⁹⁾:

$$R_{\text{membrane+liquid electrolyte}} = R_{\text{liquid electrolyte}} \times (T/\epsilon)$$

When pore-gel SPE is compared with hybrid-type SPE having same electrolyte uptake in Fig. 2, the fact that the conductivity of pore-gel SPE is higher than that of hybrid-type SPE can be explained by the tortuosity decrease of pore-gel SPE by gelling process. This would be due to

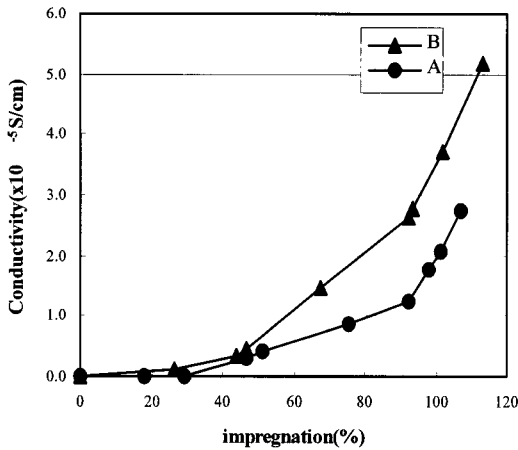


Fig. 2 The ionic conductivity of the membrane swollen in solution (A) and treated with ultrasonication (B) for 60 min after swelling

smooth movement of the solution into the polymer from the retained pores, resulting in homogeneous three-dimensional network chains appropriate for carrier migration¹²⁾.

3.3 Mechanical Properties

The stress-strain behaviors of the SPEs consisting of same composition are presented in Fig. 3. The tensile strengths of gel-type SPE, pore-gel SPE and hybrid-type SPE are 170, 6715 and 6620 kPa, respectively. In spite of gelation, the modulus and tensile strength of pore-gel SPE is similar to that of the hybrid-type SPE and about 40 times larger than that of the gel-type SPE. The pore-gel type electrolyte membrane is mechanically so stable that can be used when stretched to 1.4 times its origin length, but gel-type membrane are broken when it reached to 25% strain.

3.4 Solution leakage properties

Relative leakage weight of the samples prepared

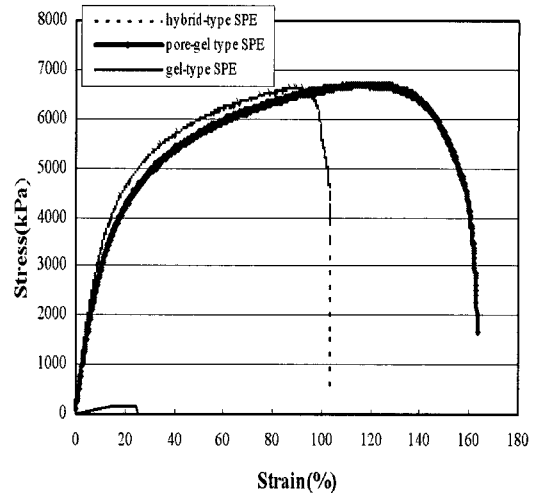


Fig. 3 The stress-strain behaviors of membrane prepared with different preparation method

with different preparation method were presented in Fig. 4. The relative leakage weight, R_w , is defined as following.

$$R_w = \frac{m_f}{m_i}$$

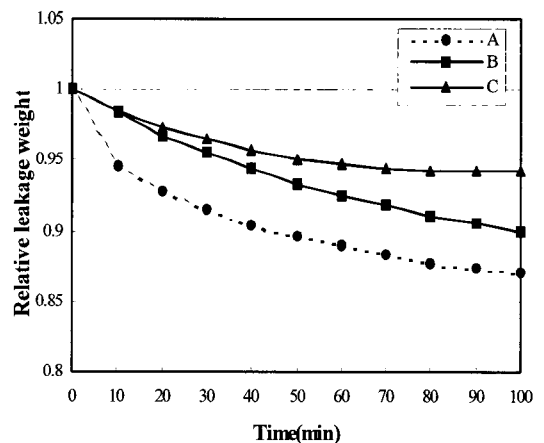


Fig. 4 The relative leakage weight of membrane just swollen in solution (A) and treated with ultrasonication for 30 min (B) and 60 min (C) after swelling

where m_i , m_f are the mass of impregnated electrolyte solution before and after solution leakage test, respectively. The solution leakage decreases by gelation the membrane. Qiao Shi et al. reported that small pore diameter reduced the solution leakage in porous polymer electrolyte⁶⁾. That is to say, solution leakage increases in big pores of membrane easily. In our experiment, it seems that gelation reduces the solution leakage owing to pore size's decrease during gelation process as shown in Fig. 1(b) and Fig. 1(c).

4. Conclusion

In this work, we prepared a new proton conducting pore-gel type SPE using a new manufacturing method. This pore-gel SPE is obtained by gelation in pores of polymer membrane after electrolyte solution impregnation.

Homogeneous gelation by vibration in micropores of the membrane enhanced conductivity and mechanical strength and also reduced solution leakage of the membrane. The ionic conductivity of the gelled membrane enhanced 1~2.2 times higher than that of the membrane without gelation. And the tensile strength of pore-gel SPE was about 40 times larger than that of gel-type SPE. Solution leakage of pore-gel SPE gelled for 60 min reduced to 6%, which is smaller than 13% of hybrid-type SPE under the same condition.

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