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New Method for the Preparation of Solid Polymer Electrolyte Based on Poly(vinylidene fluoride-co-hexafluoropropylene)

Taehee Kim, Ik Joong Kang*, Gyoujin Cho and Kwon-pil Park†

Department of Chemical Engineering, Sunchon National University, 315 Maegok, Suncheon, Jeonnam 540-742, Korea
*Department of Chemical and Bio Engineering, Kyungwon University, Sungnam 461-701, Korea
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Abstract−A novel solid polymer electrolyte (pore-gel SPE) has been found to provide superior SPE having a high conductivity, good mechanical strength and low solution leakage. This pore-gel SPE was prepared from gelation in pores of polymer membrane with electrolyte solution including solvent. The conductivity of pore-gel type PVDF-HFP/ $TEABF_4$ (Tetraethylammomium tetrafluoroborate) membrane can reach 1.6×10^{-1} Scm^{-1}. The tensile strength of this membrane was 4,000 kPa, which is about 23 times larger than that of gel-type SPE with the same composition. Pore-gel SPE reduced solution leakage to 0%, compared with 2% of hybrid-type SPE after 2.0 hr leakage test in PVDF-HFP/$TEABF_4$ membrane.

Key words: Solid Polymer Electrolyte, Gelation, Conductivity, Mechanical Strength, PVDF-HFP

INTRODUCTION

Solid polymer electrolytes (SPE) have been extensively studied since Wright's discovery of ionic conductivity in a poly(ethylene oxide) (PEO)/Na^+ complex in 1973 [Fenton et al., 1973] and Armand's recognition of their application to batteries in 1978 [Armand et al., 1978]. SPEs have advantages of thin film fabrication, less flammability and low liquid leakage problem. They are used in batteries, sensors, electrochemical capacitors and fuel cells.

The SPE system can be classified into three types, namely pure SPE (or dry SPE), gel-type SPE and hybrid-type SPE (or porous SPE) [Murata et al., 2000; Chung et al., 2003]. The pure polymer electrolytes are generally prepared by mixing high molecular weight branched polymer and electrolyte salts. To improve ionic conductivity of polymer electrolytes, gel-type SPEs composed of a polymer electrolyte salt and a liquid plasticizer have been developed. Gel-type polymer electrolytes generally have higher ionic conductivity, but their mechanical properties are not sufficient for practical applications [Stephan et al., 2003]. Hybrid-type SPEs are generally prepared by injecting organic liquid electrolytes into small pores of the polymer matrices. After long time usage of hybrid-type polymer electrolytes, the leakage of organic liquid electrolytes can decrease the ionic conductivity.

In this study, we intended to prepare a new type of SPE by using an alternative preparation method, which injects gelled electrolytes into micro-pores of the polymer matrices to make SPE stronger than gel-type SPE and to reduce the leakage problem in hybrid-type SPE. This new type of polymer electrolyte could be obtained by gelling of electrolyte solution and polymer matrices in pores of the polymer membrane after electrolyte solution absorption. We designate this new SPE as pore-gel SPE.

EXPERIMENTAL

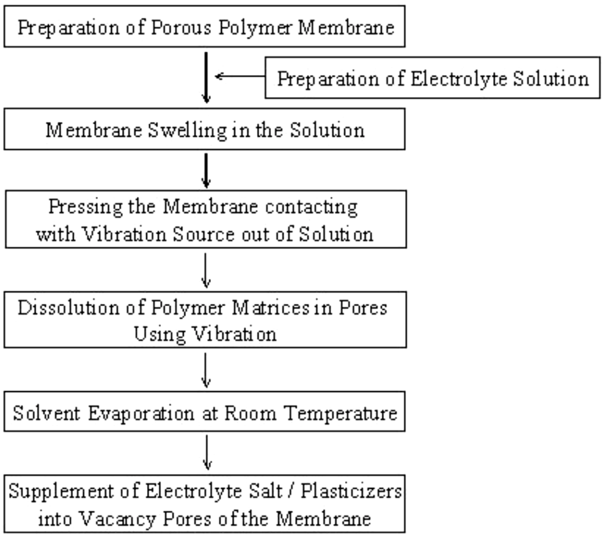

Fig. 1. The preparation procedure of solid polymer electrolyte.

1. Membrane Preparation

Fig. 1 shows the membrane preparation procedure. Porous polymer membrane based on PVDF-HFP, which has excellent electrochemical stability, stronger mechanical strength and combustion-resistant properties, was prepared as follows. The PVDF-HFP copolymer (Kynar 2801, Elf. Atochem, Japan) was dissolved in acetone with agitation at 40 °C. The homogeneous solutions were cast on a glass substrate and solvent allowed to evaporate at ambient temperature. After evaporation of acetone, strong and self-supporting thin films were formed. Electrolyte solutions were prepared by first mixing $TEABF_4$ (99%, Aldrich) in acetone and plasticizer propylene carbonate (PC)/Ethylene carbonate (EC). The solutions consisted of 75% 1 M $TEABF_4$ in 1 : 1 mixture solutions of PC/EC and 25% acetone. The polymer films were then soaked in the electrolyte solution. To enhance velocity of the solution absorption into micro-pores of the films, we used ultrasonication (ultrasonic cleaner

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[†] To whom correspondence should be addressed.
E-mail: parkkp@sunchon.ac.kr

3210, Branson) adjusted at a frequency of 47 kHz. After absorption of the solution for a certain time, the swelling membrane was withdrawn from the solution and then put into a sealed bag. Gelling process in micro-pores of the membrane was made by using ultrasonic vibration on the membrane, which was contacted with a part of vibration source by weight. After drying of the membrane at room temperature, finally the liquid electrolyte was supplemented in vacant pores to enhance the conductivity of the membrane.

2. Measurements

For ionic conductivity measurements of the polymer electrolyte membranes, two stainless steel electrode cell configurations were used. The resistance of the membrane was measured from a frequency response analyzer (Solatron HF 1260) in the frequency range of 0.1 Hz-100 kHz [Kim et al., 2004]. The ionic conductivity (σ) was calculated from the resistance (R) by using the equation $\sigma = l/(R \times A)$, where l and A were the thickness of the polymer electrolyte membrane and the cell area, respectively.

The surface morphology of films was observed by using a Focused Ion Beam (FIB) imaging system (SMI 2050, Seiko). The tensile strength was measured at room temperature by means of a Texture analyzer (TA-XT2, England) at a full-out velocity of 4 mm/min. Measurements were performed five times for each sample and the average value was calculated.

The liquid electrolyte uptake of polymer films was measured by a gravimetric method. Prior to measurement of the weight of liquid absorbed by the film, light-patting with a filter paper was done several times to remove the surface liquid.

Solution leakages were measured with the method used by Shi et al. [2002]. Swelled membrane of 1 cm^2 area was put into 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 certain time pressing.

RESULTS AND DISCUSSION

1. Morphology

Generally, absorption components of hybrid-type SPE consist of electrolyte salt and plasticizers, but we added polymer solvent (acetone) to the absorption components. The absorbed solvent in pores dissolves the polymer matrices wall with vibration and then forms a solution including salt, plasticizers and polymer in membrane. After the polymer dissolution step, the size of the remaining polymer matrices depends on dissolution time and solvent content. As the acetone evaporates in the drying process, the polymer concentration becomes richer in solution and the polymer precipitates in the salt/plasticizers phase, resulting in gel formation. It seems that fine precipitates form due to fast evaporation of acetone.

Fig. 2(a) displays a scanning image by FIB of the PVDF-HFP membrane which swelled with PC/EC/TEABF$_4$/acetone. Fig. 2(b) and (c) show FIB images of the membrane treated with ultrasonication, respectively, for 10 min and 40 min after swelling. When the ultrasonication was applied to the swelled membrane, the surface morphology showed a more homogeneous phase, as shown in Fig. 2(b) and (c). There was a strong effect of the vibration method on the mixing, diffusion and gelling in micro-pores of membrane.

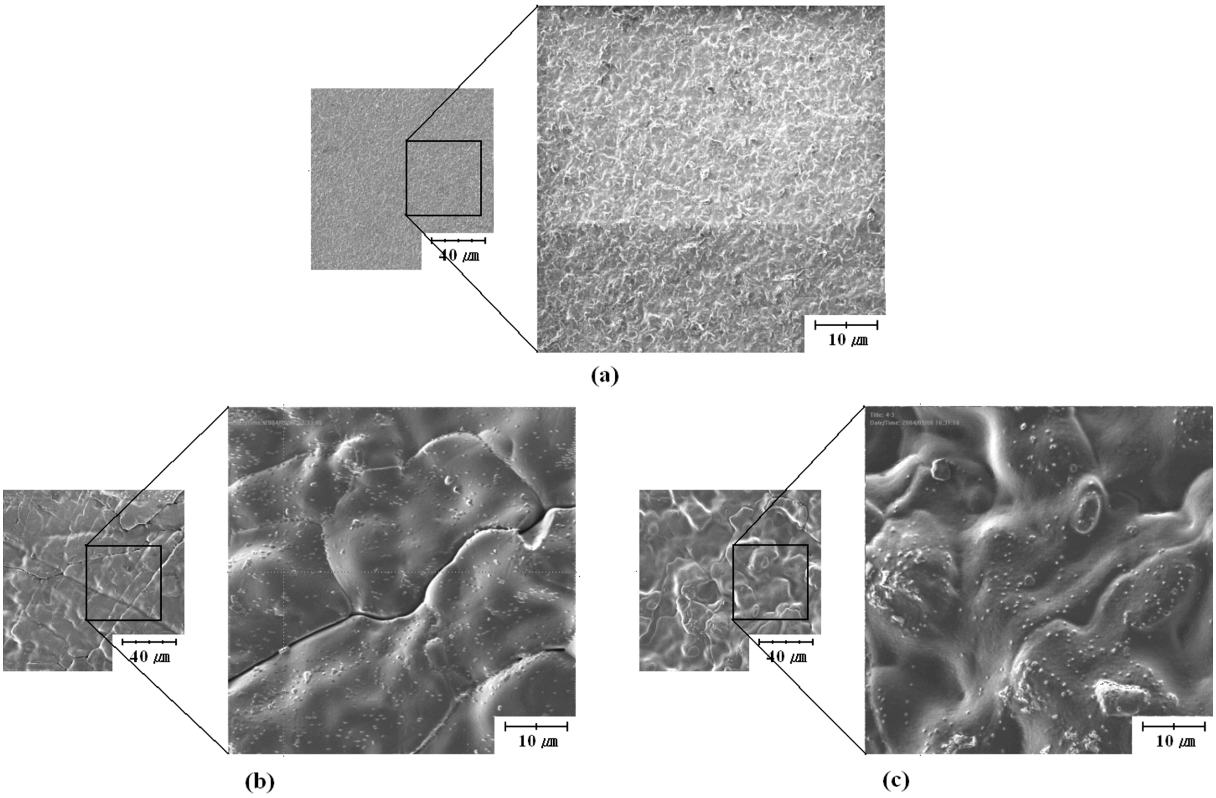

Fig. 2. FIB images of SPEs swelled with PC/EC/TEABF$_4$/acetone (a) and treated with ultrasonication for 10 min (b) and 40 min (c) after swelling.

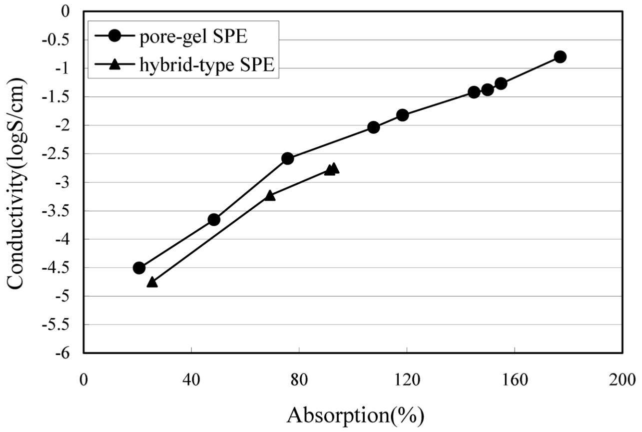

Fig. 3. The conductivities of pore-gel type and hybrid-type SPE.

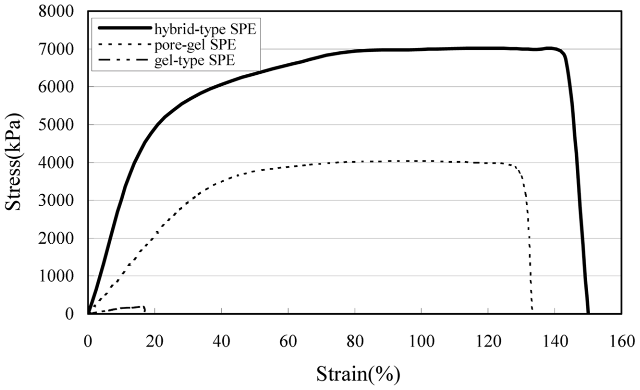

Fig. 4. The stress-strain behaviors of gel-type, pore-gel type and hybrid-type SPE.

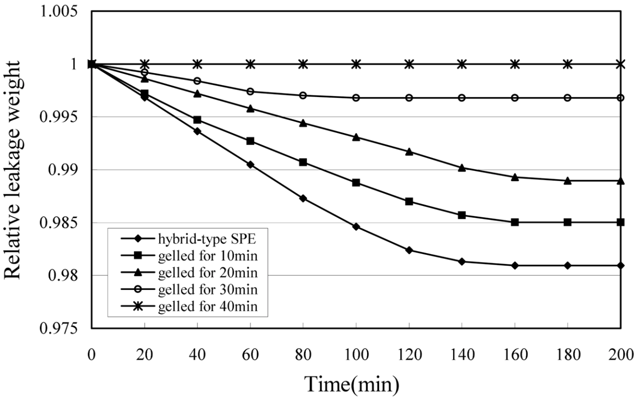

Fig. 5. Relative leakage weight of samples gelled in different times.

2. Ionic Conductivity

The results of conductivity measurements for the pore-gel SPE are given in Fig. 3 and compared with that of hybrid-type SPE. Curve of pore-gel SPE results from conductivity measurement of the membrane soaked in electrolyte solution containing acetone in $TEABF_4$/PC/EC. The process of general hybrid-type SPE did not use acetone in the absorption process. Absorption of solution $TEABF_4$/PC/EC in PVDF-HFP film was not achieved over 95% without acetone, but in case of pore-gel SPE, absorption was achieved up to 177% using acetone. For the same $TEABF_4$/PC/EC uptake, the conductivity increases by gelling as shown in Fig. 3. In case of gel SPE, a mechanism consisting of two conduction paths has been postulated [Christie et al., 1998; Bohnke et al., 1993]. By this mechanism, the effective higher conductivity pathway decreases with increasing polymer content. And the resistance due to the membrane is linked to its porosity (ε) and tortuosity (T) by the following formula [Boudin et al., 1999]:

$$R_{membrance+liquid\ electrolyte}=R_{liquid\ electrolyte}\times(T/\varepsilon)$$

When pore-gel SPE is compared with hybrid-type SPE having the same electrolyte uptake in Fig. 3, 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 smooth movement of the solution into the polymer from the retained pores, resulting in homogeneous three-dimensional network chains appropriate for carrier migration [Saito et al., 2003].

By combining enhancement of electrolyte absorption and gelling effect, pore-gel SPE ($TEABF_4$/PC/EC in PVDF-HFP) can offer ionic conductivity of $\cong 1\times10^{-1}$ Scm^{-1}, which is about 50 times larger than that of Osaka's work (5×10^{-3} Scm^{-1}) [Osaka et al., 1999].

3. Mechanical Properties

The stress-strain behaviors of the polymer electrolyte membranes consisting of the same composition with different preparation method are presented in Fig. 4.The tensile strengths of gel-type, pore-gel type and hybrid-type polymer electrolyte are 170, 4,000 and 7,000 kPa, respectively. Even though the modulus and tensile strength are lower than those of porous type polymer electrolyte membrane, the pore-gel type membrane can enhance mechanical strength about 20 times larger than the gel-type electrolyte membrane. The pore-gel type electrolyte membrane is mechanically so stable that it can be used when stretched to 1.3 times its original length, but the gel type membrane broke when it reached to 17% strain.

4. Solution Leakage Properties

Relative leakage weights of samples gelled in different time were presented in Fig. 5. The relative leakage weight, R_w, is defined as following.

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

where m_i, m_f are the mass of absorbed electrolyte solution before and after solution leakage test, respectively. The relative leakage weights of gelled samples are increasing along with their gelling time, that is, solution leakage decreases. Qiao Shi et al. reported that small pore diameter is needed to prevent solution leakage in porous polymer electrolyte [Shi et al., 2002]. That is to say, big pores easily result in solution leakage. In our experiment, it seems that gelling reduced the solution leakage owing to pore size's decrease during gelling process, as shown in Fig. 2.

CONCLUSION

In this work, a novel pore-gel type SPE was prepared by using a new manufacturing method based on the PVDF-HFP/$TEABF_4$ system. The pore-gel type SPEs are obtained by gelling in pores of the polymer membrane after electrolyte solution absorption.

Homogeneous gelation in micro-pores of the membrane enhanced conductivity and mechanical strength of membrane and reduced solution leakage. It was found that the conductivity of pore-gel SPE was about 2-3 times larger than that of hybrid-type SPE, and tensile strength of the pore-gel SPE was about 24 times larger than that of the gel-type SPE. Solution leakage decreases with increasing the degree of gelation in pores of the membrane. Solution leakage of the pore-gel SPE sample gelled for 40 min reached to 0% compared with 2% of porous SPE under same condition.

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