We have attempted to combine a typical gel (hybrid liquid-solid system) and a typical solvent-free polymer electrolyte (solid system) through the concept of the pore-filling polymer electrolyte; instead of organic solvents, a viscous polymer complexed with a Li salt is filled into the pores of a porous membrane. The viscous polymer, poly(ethylene oxide-ethylene carbonate) copolymer [P(EO-EC)] with a low molecular weight (Mw = 1800) and amorphous nature is synthesized using ethylene carbonate (EC) and its viscosity is found to be independent of shear rate, which is a characteristic of a Newtonian fluid. Porous membranes consisting of poly(vinylidene fluoride-co-hexafluoropropylene) [PVdF-HFP] and P(EO-EC) are prepared by a phase inversion method and examined by means of 1H solid-state nuclear magnetic resonance and field emission-scanning electron microscopy. From these results, it is confirmed that they are homogeneous on a scale of a few tens of nanometers and the existence of P(EO-EC) in membranes makes much larger pore size and higher porosity than the pure PVdF-HFP membrane. This implies that the relative composition of P(EO-EC) plays a critical role in determining the membrane’s morphology and porosity. The temperature dependence of the ionic conductivity for the polymer electrolytes is well fitted to the Arrhenius equation. The highest conductivity of 3.7 × 10^{-3} S cm^{-1} at 25°C and 1.6 × 10^{-4} S cm^{-1} at 55°C is obtained for E-VdE4. Cyclic voltammetry on stainless steel electrodes shows that the polymer electrolyte is electrochemically stable up to at least 5.0 V vs Li/Li+.

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Preparation of porous membranes and polymer electrolytes. — Porous membranes were prepared by a phase inversion
Conducting electrochemical measurements, porous membranes were removed the residual acetone and water away from the electrolyte, was dried and stored in vacuum at 80°C for 48 h to completely evaporate at room temperature. Then, the highly viscous solution was added and slowly stirred at 50°C for 1 h. To prepare porous membranes with structural rigidity and high uptake of electrolyte, ethylene glycol was warmed and degassed at 50°C for 2 h. The resulting viscous solution, subsequently, was cast with a doctor blade on a glass plate and left to evaporate the solvent slowly at 35°C for 10 h. Ethylene glycol was removed by washing the membrane with methanol. The porous membranes were finally dried under vacuum at 50°C for 24 h. The resultant membranes had a thickness of 180-190 μm.

To prepare polymer electrolytes, P(EO-EC) was first dissolved in acetone (a volatile solvent) and then heated at 50°C. After the polymers were completely dissolved, an appropriate amount of ethylene glycol (a nonvolatile solvent) was added and slowly stirred at 50°C for 1 h. To prepare porous membranes, structural rigidity and high uptake of electrolyte, the weight ratio of polymers, a solvent, and a nonvolatile solvent was optimized at 10:80:10. The composition of polymers was [(10-x)wt%P(VdF-HFP)-xwt%P(EO-EC)] where x = 0, 1, 2, 3, 4, and 5. The proportion of a nonvolatile solvent was low enough to allow the dissolution and high enough to allow phase separation during evaporation. The resulting viscous solution degassed at 50°C for 2 h was cast with a doctor blade on a glass plate and left to evaporate the solvent slowly at 35°C for 10 h. Ethylene glycol was removed by washing the membrane with methanol. The porous membranes were finally dried under vacuum at 50°C for 24 h. The resultant membranes had a thickness of 180-190 μm.

To prepare polymer electrolytes, P(EO-EC) was first dissolved in acetone. After a homogenous solution was obtained, a reasonable amount of lithium trifluoromethane sulfonate (LiCF₂SO₃, Aldrich Chemicals) was added and then the solution was further stirred until the salt was completely dissolved. The solution was then spread thinly on a glass plate. The acetone was first allowed to slowly evaporate at room temperature. Then, the highly viscous solution was dried and stored in vacuum at 80°C for 48 h to completely remove the residual acetone and water away from the electrolyte, consequently producing a P(EO-EC)/LiCF₂SO₃ mixture. Before conducting electrochemical measurements, porous membranes were activated in a dry room by filling a viscous P(EO-EC)/LiCF₂SO₃ mixture heated at 80°C using porous vacuum filter equipment, thereby producing solvent-free polymer electrolytes (Fig. 1). The mixture remaining on the surface was wiped with a filter paper. All the preparation procedures for the polymer electrolytes were carried out in a dry room (relative humidity <0.2%). In this study, M-VxEy and E-VxEy denote the porous membrane with blend composition of P(VdF-HFP)/P(EO-EC) (x/y by wt %) and the polymer electrolyte filled with the P(EO-EC)/LiCF₂SO₃ mixture inside the pores of its membrane, respectively.

**Characterization.**—¹H NMR (300 MHz) spectra were obtained by using a Bruker DPX 300 spectrometer with CDCl₃ as a solvent. Fourier transform infrared (FTIR) measurements were conducted using a Perkin-Elmer GX IR spectrometer within the range of 400-4000 cm⁻¹. Molecular weights and molecular weight distribution were obtained using a Waters model 410 gel permeation chromatography instrument (GPC) connected to a Waters 410 differential refractometer. Steady-shear viscosity measurements were performed with a TA instruments AR 2000 constant-stress rheometer using a cone-and-plate geometry with a 2° angle and 6 cm diameter cone. The temperature was controlled by a Peltier lower plate with a precision of 0.1°C. Measurements were performed between the temperatures ranging from 30 to 80°C at regular intervals of 10°C. In order to minimize the effect of the thermal expansion of the rheometer, the gap between the cone and the plate was automatically regulated to be 56 μm. The shear range from 0.1 to 100 s⁻¹. The proton spin-lattice relaxation time measurements were carried out a Bruker mq20 Minispec system with proton resonance frequency of 20 MHz at 30°C. Inversion-recovery pulse sequence (180°-τ-90°) with 2 μs 90° pulse width, 1 ms dead time, 40 number of scans, and 0.3 s recycle delay time was employed to determine the spin-lattice relaxation time, T₁(H). Morphological examination was made by using a field emission scanning electron microscope (FE-SEM, JEOL, JSM-6330F).

The ionic conductivity of the polymer electrolyte was measured using an ac impedance analyzer (IM6, Zahner Electrik) within a temperature range of 5 to 95°C and frequency range of 0.1 Hz to 1 MHz. The specimens were prepared by sandwiching the polymer electrolytes between two stainless steel (SS) electrodes. Each sample was allowed to equilibrate for 30 min at each temperature before the measurement was taken. The electrochemical stability window was evaluated by cyclic voltammetry at a scan rate of 1 mV s⁻¹ within the potential range of ~0.5 to 5.0 V (vs Li/Li⁺) using a lithium/polymer electrolyte/SS cell where lithium served as both the counter and reference electrodes. All assemblies and testing operations of samples were performed in a dry room (relative humidity <0.2%).

**Results and Discussion**

P(EO-EC) copolymer.—1 mol of EC was bulk polymerized with 1 mol of CH₃OK at 180°C for 15 h. From the beginning of the reaction, CO₂ gas was evolved vigorously from the reaction mixture and gas evolution continued for 15 h. This produced some mixture remaining on the surface was wiped with a filter paper. All the preparation procedures for the polymer electrolytes were carried out in a dry room (relative humidity <0.2%). In this study, M-VxEy and E-VxEy denote the porous membrane with blend composition of P(VdF-HFP)/P(EO-EC) (x/y by wt %) and the polymer electrolyte filled with the P(EO-EC)/LiCF₂SO₃ mixture inside the pores of its membrane, respectively.
of the integrations from NMR spectra, the monomer conversion and P(EO-EC) composition can be calculated using the following equations:\(^14\)

\[
\text{conversion} = \left( \frac{A_b + A_c + A_d}{A_o + A_b + A_c + A_d} \right) \times 100
\]

\[
\text{EC content (mol\%)} = \left( \frac{A_b + A_d}{A_b + A_c + A_d} \right) \times 100
\]

\[
\text{EO content (mol\%)} = 100 - \text{EC content (mol\%)}
\]

where \(A_o, A_b, A_c,\) and \(A_d\) are the intensities of the \(a, b, c,\) and \(d\) proton peaks, respectively. From these results, it was found that monomer conversion was about 100\% and P(EO-EC) is a mixture of monomeric unit (EC units) and the corresponding EO units. Soga et al.\(^16-18\) reported that EC can be polymerized using Lewis acids, trans esterification catalysts, or bases as initiators or catalysts. When Lewis acids or trans esterification catalysts were used, the resultant polymers generally contained ca. 40-50 mol\% of EC units (150-170°C, 70-100 h). When bases were used, the resultant polymers contained ca. 10-20 mol\% of EC units (ca. 150°C, 72-98 h). In this study, EC was polymerized using CH\(_3\)OK as a base at 180°C for 15 h, resulting in a P(EO-EC) copolymer consisting of ca. 30 mol\% of EC units and ca. 70 mol\% of EO units.

Additional evidence for polymerization was provided by FTIR spectroscopy. The characteristic band (ca. 1850 cm\(^{-1}\)) of carbonate five-membered ring disappeared completely after the reaction. These results provide reliable evidence for the ring-opening polymerization. The number average molecular weight and molecular weight distribution of P(EO-EC) were 1800 g mol\(^{-1}\) and 2.39, respectively.

An interesting feature of P(EO-EC) distribution of P(EO-EC) is the amorphous nature allows the P(EO-EC) material to be successfully used as an ion-conducting polymer electrolyte. Therefore, this amorphous nature allows the P(EO-EC) to be independent of shear rate, which is a characteristic of Newtonian fluid. Furthermore, the viscosity (ca. 5 Pa s) measured at 80°C was much lower than that (ca. 71 Pa s) measured at 30°C, suggesting that viscous P(EO-EC) heated at 80°C may be easily penetrated into the pores of a membrane. The temperature dependence of the viscosity of P(EO-EC) is illustrated in Fig. 3b. From this figure, it can be confirmed that P(EO-EC) exhibits good linear relationship between ln \(\eta\) and 1000/\(T\) within the temperature range employed, namely, an Arrhenius behavior.

Miscibility of porous membranes.—The most common method used in studying miscibility in polymer-polymer blends is by determining their \(T_g\) values. A miscible blend system shows generally a single \(T_g\) between those of the pure components with a sharpness of the transition.\(^19\) For the P(VdF-HFP)/P(EO-EC) blend membrane, however, it was difficult to detect its intermediate \(T_g\) by differential scanning calorimetry (DSC) due to the semicrystallinity of P(VdF-HFP). It was also reported\(^20\) that the intermediate \(T_g\) for the P(VdF-HFP)/polyacrylonitrile (PAN) blend membrane could not be observed because P(VdF-HFP) is a semicrystalline. Landis and Moore\(^21\) reported that the origin of miscibility between PVdF and some polar polymers is attributed to strong dipole-dipole interactions between the polar carbon-fluorine bonds in PVdF and the carbonyl groups of the ester-containing polymers. Therefore, the P(VdF-HFP)/P(EO-EC) blend system is expected to be miscible due to the high polarity of the carbonyl groups in P(EO-EC).

The degree to which polymers are mixed in binary blends is often determined via solid-state NMR relaxation methods. For instance, by measuring the proton relaxation times in the rotating frame, \(T_1(H)\), and in the laboratory frame, \(T_1(H)\), for a blend in comparison with the proton relaxation time values for the pure poly-
where $M$ is the chemically different constituents and blend membranes are calculated by the following equation:

$$D = \frac{L_s}{\langle L \rangle (T_1(H))^2}$$

where $L_s$ is the average diffusive path length for the effective spin diffusion, and $D$ is the effective spin diffusion coefficient determined by the average proton-proton distance and the strength of the dipolar interaction. A typical value of $D$ for an ordinary polymer is of the order of $10^{-16}$ m$^2$ s$^{-1}$. $T_1$ is the relaxation time, $T_1(H)$ or $T_1(\eta)$, according to the type of relaxation measurements and has the $T_1(\eta)$ value in this study. Using Eq. 5 and considering the $T_1(\eta)$ values of membranes, the average diffusive path length, viz. domain size of the M-V8E2 and M-V6E4, was calculated to be about 14–16 nm (Table I) and thus, it was concluded that two components [i.e., P(Vdf-HFP) and P(EO-EC)] in the blend were intimately mixed on the scale of a few tens of nanometers.

### Porosity and morphology of porous membranes.

The porosity was measured by immersing the porous membranes into n-butanol for 1 h and then calculated by the following equation:

$$\text{porosity} = \frac{W_p}{W_s} \times 100$$

where $W_p$ is the weight of dry membranes, $W_s$ is the weight of n-butanol absorbed in the wet membranes, $p_s$ is the density of n-butanol, and $p_d$ is the density of membranes. The porosity generally increased with increasing P(EO-EC) composition in membranes. These results are listed in Table I. This indicates that the introduction of P(EO-EC) in membranes results in high porosity because the evaporation of a nonvolatile in flexible membranes is easier than that in rigid membranes. Therefore, highly porous membranes can be obtained by adding viscous P(EO-EC) in membranes and their maximum porosity reaches up to 65% for M-V6E4. Also, this high porosity led to the increase in the uptake amount of the electrolyte [i.e., P(EO-EC)/LiCF$_3$SO$_3$ mixture], which is associated with ionic conductivity as shown in Table I. Despite the addition of a large amount of P(EO-EC), M-V5E5 showed a slightly low porosity compared to that of M-V6E4. This is probably due to P(EO-EC) conglomeration ascribed to the inversion effect of the host matrix from a P(Vdf-HFP)-rich phase to a P(EO-EC)-rich phase. The porous membranes with above 50 wt% of P(EO-EC) in P(Vdf-HFP)/P(EO-EC) composition exhibited a sticky property, making it impossible to obtain a self-supporting film. From these results, we concluded that the M-V6E4 is the most promising matrix in terms of porosity as well as uptake, and thus focused our attention to M-V6E4 in our evaluation tests.

Typical FE-SEM micrographs of the surface of a few porous membranes and a polymer electrolyte are presented in Fig. 5. From the FE-SEM images, the pore diameter was estimated to be 1–10 μm. The results showed that the surface pore size of membranes increased gradually with the increase of P(EO-EC) composition in membranes. Interestingly, the image of M-V5E5 containing 50 wt% P(EO-EC) showed a conglomeration feature of P(EO-EC) near pores (Fig. 5d). As mentioned above, this conglomeration has a tendency to decrease its porosity. Figure 5e shows that a viscous P(EO-EC)/Li-salt mixture is well filled into the pores of M-V6E4, thereby producing a solvent-free polymer electrolyte, E-V6E4, with no visible signs of leakage.

### Ionic conductivity and electrochemical stability of polymer electrolytes.

In order to determine the optimum Li-salt concentration of polymer electrolytes, ionic conductivity, $\sigma$, of the polymer electrolyte with different LiCF$_3$SO$_3$ concentration was measured through impedance measurements. Figure 6a shows a typical impedance spectrum of the stainless steel (SS)/E-V6E4/SS cell at 30°C. In this figure, the intercept on the real axis gives the electrolyte resistance. Thus, the ionic conductivity was calculated from the measured resistance for surface area of the electrode and thickness of the polymer electrolyte. Figure 6b shows the relationship between LiCF$_3$SO$_3$ concentration and log $\sigma$ for E-V8E2 and E-V6E4. Regarding LiCF$_3$SO$_3$ concentration, both polymer electrolytes showed

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**Table I. NMR characteristics, porosity, and uptake of porous membranes.**

<table>
<thead>
<tr>
<th>Membrane</th>
<th>$T_1(H)$ (s)</th>
<th>Domain size, $L_s$ (nm)</th>
<th>Porosity (%)</th>
<th>Uptake (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-V10E0</td>
<td>0.78</td>
<td>21.6</td>
<td>54.3</td>
<td>36.4</td>
</tr>
<tr>
<td>M-V9E1</td>
<td>0.42</td>
<td>15.9</td>
<td>57.4</td>
<td>44.4</td>
</tr>
<tr>
<td>M-V8E2</td>
<td>0.35</td>
<td>14.5</td>
<td>61.8</td>
<td>56.3</td>
</tr>
<tr>
<td>M-V7E3</td>
<td>0.35</td>
<td>14.5</td>
<td>64.6</td>
<td>61.3</td>
</tr>
<tr>
<td>M-V6E4</td>
<td>0.35</td>
<td>14.5</td>
<td>62.9</td>
<td>55.2</td>
</tr>
<tr>
<td>M-V5E5</td>
<td>0.35</td>
<td>14.5</td>
<td>62.9</td>
<td>55.2</td>
</tr>
</tbody>
</table>

$^a$ Determined as $(W_f - W_d)/W_f \times 100$, where $W_f$ and $W_d$ are the weights of the filled (by a P(EO-EC)/LiCF$_3$SO$_3$ mixture) and dried membranes, respectively.

---

**Figure 4.** Logarithmic plots of resonance intensity vs delay time for M-V10E0, M-V8E2, and M-V6E4 at 30°C. The slope yields the proton spin-lattice relaxation time in the laboratory frame, $T_1(H)$.
the highest conductivity at 1.5 mmol-LiCF₃SO₃/g-P/EO-EC/H₂O. The conductivity of polymer electrolytes increased with increasing salt concentration up to 1.5 mmol-LiCF₃SO₃/g-P/EO-EC/H₂O, but further addition of the salt caused the conductivity to decrease. It is reported that the conductivity increases initially with increasing salt concentration as the number of charge carriers increases, but at higher salt concentration, the conductivity decreases due to the increasing influence of ion pairs, ion triplets, and higher ion aggregations, which reduces the overall mobility and the number of effective charge carriers. This behavior is also similar to most of the salt concentration dependence of polymer electrolytes. Consequently, the optimum salt concentration was 1.5 mmol-LiCF₃SO₃/g-P/EO-EC/H₂O and was used throughout the subsequent series of measurements.

The temperature dependence of various SS/solid polymer electrolyte/SS cells with different content of a P/(EO-EC)/LiCF₃SO₃ mixture was studied by conducting impedance measurements between 5 and 95°C at regular intervals of 10°C. Figure 7 shows typical Arrhenius plots for the ionic conductivity of the polymer electrolytes. Interestingly, all polymer electrolytes showed a linear enhancement of the conductivity by increasing the temperature, namely, Arrhenius behavior, although there was a slight curvature in some of the plots, but less than in similar plots for conventional solid polymer electrolytes. This behavior suggests a liquid-like conduction of the LiCF₃SO₃ in the viscous P/(EO-EC) with amorphous nature, which is in good agreement with linear relationship between ln η and 1000/T for P/(EO-EC), as described in steady-shear viscosity measurements. Further investigation through ⁷Li NMR is in progress to better understand the conductive environment of Li ions in this system.

As shown in Fig. 7, the ionic conductivity increased with an increase in temperature. This behavior is attributed to the free volume model. As the temperature increases, the polymer can expand easily and produce free volume. Thus, ions, solvated molecules, or polymer segments can move into the free volume, causing it to increase. This in turn enhances ion and polymer segmental mobility. Therefore, as the temperature increases, the ionic conductivity...
where the slopes of the Arrhenius plots covered the range of 41-50 kJ mol\(^{-1}\).

The ionic conductivity of polymer electrolytes also increased with the increase of the P(EO-EC) content in polymer electrolytes. This difference in conductivity is due to the different content of P(EO-EC) in polymer electrolytes, implying that the incorporation of polar groups in amorphous P(EO-EC) significantly improves conductivity. That is, the higher the porosity of the membranes, the higher the ionic conductivity will be. Thus, E-V6E4 with the highest P(EO-EC) content showed a maximum conductivity value of 3.7 \(\times 10^{-5}\) Sc m\(^{-1}\) at 25°C. This is still lower than that of most gel electrolytes based on an amorphous polymer of a low molecular weight. This difference in conductivity is due to the pore-filling system prepared by filling the pores of a membrane with P(EO-EC) complexed with LiCF\(_3\)SO\(_3\), which plays an effective role as an ion conductor. To compare pore-filling and blend systems, blend-based polymer electrolytes of P(Vdf-HFP) and P(EO-EC) complexed with LiCF\(_3\)SO\(_3\) were prepared by a solvent casting method. Ionic conductivity of pore-filling systems was much higher than that of blend systems by nearly an order of magnitude for the same composition. This implies that Li ions in the pores of a membrane have high mobility. Further research with the aim of improving the ionic conductivity of the polymer electrolyte by adding various Li salts and nanoparticles is now in progress and a more detailed report will be published in the near future.

The slope of the Arrhenius plots is related to the activation energy, \(E_a\), for ion transport. Therefore, \(E_a\) for polymer electrolytes can be determined by the Arrhenius equation

\[
\sigma = \sigma_0 \exp\left(-\frac{E_a}{RT}\right)
\]

where \(T\) is temperature on the Kelvin scale, \(\sigma_0\) is a pre-exponential factor, and \(R\) is the ideal gas constant. \(E_a\) values calculated from the slopes of the Arrhenius plots covered the range of 41-50 kJ mol\(^{-1}\). Also, \(E_a\) values decreased with increasing P(EO-EC) content, giving a lowered temperature dependence of conductivity. It is noteworthy that pore-filling polymer electrolytes with high P(EO-EC) content are more advantageous because of their low dependence on temperature and consequent uniform response over a wide temperature range. These results are listed in Table II.

The electrochemical stability window of polymer electrolytes was evaluated by cyclic voltammetry of cells using a SS electrode, a lithium counter, and a lithium reference electrode. Figure 8 shows the results obtained on a cell using an E-V6E4 sample at 55°C. On scanning the electrode in a negative direction, a cathodic peak was observed at about -0.48 V, which corresponds to the plating of lithium onto the SS electrode. On the reverse scan, stripping of lithium was observed at about 0.31 V. Reversible electrochemical plating/stripping of lithium was also observed in the potential range of -0.5 to 0.6 V on the SS electrode. Furthermore, further sweeping the electrode up to 5.0 V resulted in no additional oxidation peaks related to the decomposition of the polymer electrolyte, implying that the polymer electrolyte is electrochemically stable up to at least 5.0 V vs Li/Li\(^+\). Consequently, the electrochemical stability window of the resulting pore-filling polymer electrolyte was good enough to be used for the rechargeable lithium battery.

### Conclusions

P(EO-EC) was synthesized through the ring-opening polymerization of an EC monomer and used to prepare a porous membrane and an electrolyte mixture. The resulting P(EO-EC) with a low molecular weight (Mw = 1800) was a viscous copolymer (ca. 71 Pa s at 30°C), which consisted of ca. 70 mol % EO units and ca. 30 mol % EC units. The amorphous nature of the P(EO-EC) allowed this material to be successfully used as an ion-conducting polymer electrolyte with no detrimental effects by crystallization. P(Vdf-HFP)/P(EO-EC)-based porous membranes having a pore diameter of 1–10 \(\mu\)m were prepared by a phase inversion method and they were homogeneous on the scale of a few tens of nanometers. The existence of viscous P(EO-EC) in membranes not only contributed to the flexibility but also led to the increase in the pore size and porosity. Polymer electrolytes were fabricated by filling the pores of a membrane with viscous P(EO-EC) complexed with LiCF\(_3\)SO\(_3\). The introduction of the P(EO-EC) component in membranes led to an increase in the uptake of a P(EO-EC)/LiCF\(_3\)SO\(_3\) mixture from 36.4 to 61.3%, and a corresponding increase in ionic conductivity of the polymer electrolytes at 25°C from 5.4 \(\times 10^{-6}\) to 3.7 \(\times 10^{-5}\) Sc m\(^{-1}\). Cyclic voltammetry on stainless steel electrodes showed that the polymer electrolyte was electrochemically stable up to at least 5.0 V vs Li/Li\(^+\). With further efforts to improve the cell performance, the polymer electrolyte based on a pore-filling system is expected to be a good candidate in rechargeable lithium batteries, and this approach may offer the opportunity to design solvent-free polymer electrolytes.

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