An imide network polymer (INP), in which super acid groups arranged in high density by crosslinking with small molecules, has been proposed as a novel electrolyte that simultaneously allows high proton conductivity and water insolubility. The INP was synthesized by the reaction of tri-functional amide monomers and bi-functional sulfonyl fluoride monomers to form sulfonyl imide moieties as super acid groups within a polymer network. The INP had an acid group density that was more than four times higher than Nafion, a typical commercial electrolyte used for fuel cells. The INP also exhibited proton conductivity approximately 15 times higher than that of Nafion at 20% relative humidity (RH). The higher proton conductivity of the INP at low relative humidity is attributed to not only a high proton concentration but also enhanced proton diffusion due to high water uptake and water diffusion. These properties are due to the high acid group density of the INP. However, high water uptake causes the INP to undergo high dimensional change. To reduce this dimensional change for application as an electrolyte membrane of fuel cells, an INP electrolyte was synthesized in a porous film, which is not swelled with water. Reducing the dimensional change of the INP using a porous film, the composite membrane exhibited higher fuel cell performance at elevated temperature without humidification compared with Nafion.

**ABSTRACT**

An imide network polymer (INP), in which super acid groups arranged in high density by crosslinking with small molecules, has been proposed as a novel electrolyte that simultaneously allows high proton conductivity and water insolubility. The INP was synthesized by the reaction of tri-functional amide monomers and bi-functional sulfonyl fluoride monomers to form sulfonyl imide moieties as super acid groups within a polymer network. The INP had an acid group density that was more than four times higher than Nafion, a typical commercial electrolyte used for fuel cells. The INP also exhibited proton conductivity approximately 15 times higher than that of Nafion at 20% relative humidity (RH). The higher proton conductivity of the INP at low relative humidity is attributed to not only a high proton concentration but also enhanced proton diffusion due to high water uptake and water diffusion. These properties are due to the high acid group density of the INP. However, high water uptake causes the INP to undergo high dimensional change. To reduce this dimensional change for application as an electrolyte membrane of fuel cells, an INP electrolyte was synthesized in a porous film, which is not swelled with water. Reducing the dimensional change of the INP using a porous film, the composite membrane exhibited higher fuel cell performance at elevated temperature without humidification compared with Nafion.

**KEYWORDS**

Fuel Cell, Polymer Electrolyte, Proton Conductivity, Sulfonyl Imide, Composite Membrane

1. Introduction

Fuel cell vehicles that use hydrogen, produce zero emissions and have high energy efficiencies are becoming widespread with electric vehicles as eco-cars in response to increasing concerns regarding global energy supplies and environmental issues. However, a reduction in both the size and cost of fuel cell systems is required to promote the use of fuel cell vehicles. Operation at high temperature without humidification allows reduction of the heat radiator and elimination of the humidifier; however, this leads to issues regarding the electrolyte membranes, specifically the challenge in maintaining proton conductivity at low humidity and retaining water generated in the cell by diffusion.

To solve these issues, there are two approaches in the design of electrolyte membranes; thinning of the membrane and increasing the acid group density in the electrolyte. With a thin electrolyte membrane, it is possible to decrease the resistance due to both shortening of the proton transport distance and promoting water diffusion. On the other hand, thinning of the electrolyte membrane decreases its strength and increases the possibility for gas cross-leaks. The other approach, using an electrolyte membrane with a high acid group density, is expected to improve proton conductivity, water retention and diffusion due to an increase in proton density and the continuity of the conduction paths. High proton conductivity has been reported using perfluoro electrolyte membranes, of which the acid group density was above 1.7 meq/g (based on ion exchange capacity), through the use of short side chains or by increasing the acid units. However, an increase in the concentration of acid groups raises not only water absorption issues but also solubility and swelling of the conventional electrolyte in water due to reduced interaction of hydrophobic domains.

There have been attempts to introduce crosslinking to prevent dissolution in water and decrease swelling of
the electrolyte membrane.(3) For example, crosslinking of a perfluoro electrolyte using a diamine has been reported.(4) However, the introduction of crosslinks into the electrolyte by this method is considered to decrease both the acid group density and the proton conductivity. The introduction of sulfonyl imide crosslinking into an electrolyte is one approach to realize maintenance of the proton conductivity because sulfonyl imide moieties exhibit proton conductivity.(5–11)

In this work, a new approach is taken to realize both high acid group density and water insolubility of the electrolyte. Figure 1 shows a schematic design of a novel polymer electrolyte which is termed an imide network polymer (INP). The INP has a crosslinked network structure in which sulfonyl imide groups that act as super acids are distributed uniformly and with high density. Crosslinking with small molecules is employed in an attempt to make the electrolyte insoluble in water.

In the present work, the INP was synthesized by a new procedure, in which the sulfonyl imide groups are prepared by reacting tri-functional sulfonyl amide monomers as crosslinking points with bi-functional sulfonyl fluoride monomers. The bi-functional and tri-functional monomers were connected by formation of the sulfonyl imide groups between them to obtain the network polymer.(12) The proton conductivity and the diffusion coefficients of both water and protons in the INP were analyzed. From these results, the potential of this new polymer electrolyte is demonstrated and the mechanism for the high proton conductivity is clarified.

However, the use of an INP as an electrolyte membrane of a membrane electrode assembly (MEA) was not highly anticipated due to the excess dimensional change of the INP with high water absorption. Therefore, to suppress the swelling for fuel cell application, an INP electrolyte was synthesized in a porous film,(13) which is not swelled with water, and the fuel cell performance was then evaluated using the INP electrolyte composite membrane.

2. Experimental

2.1 Synthesis of the Imide Network Polymer (INP)

1,1,2,2,3,3-Hexafluoropropane-1,3-disulfonyl fluoride (C3F; Daikin Industries, Ltd.) was used as the bi-functional sulfonyl fluoride monomer. Benzene 1,3,5-trisulfonic acid triamide (BTSA) served as the tri-functional amide monomer and was synthesized as shown in Fig. 2 using 1,3,5-benzenetrisulfonyl chloride (NARD Institute, Ltd.). C3F and BTSA were used to synthesize the INP as shown in Fig. 3. BTSA was dispersed into anhydrous acetonitrile (CH3CN) under nitrogen followed by the addition of triethylamine (TEA) and stirring at room temperature. C3F was subsequently added to the BTSA solution and stirred, where 1.5 times as many moles of C3F as BTSA was employed. The solution was transferred to a petri dish and placed in an autoclave vessel filled

![Fig. 1 Molecular design of the INP.](image-url)
with nitrogen. After heating at 50°C for 70 h, the reaction mixture was heated for an additional 48 h at 90°C to continuously react and vaporize the solvent. The remaining solid was immersed in a mixed solvent consisting of ethanol and 15 wt% aqueous nitric acid (1 : 1 v/v) at 70°C for proton exchange and removal of the TEA salt. After soaking the resultant solid in ethanol, a transparent gel membrane was obtained by slow evaporation of the residual ethanol.

2.2 Preparation of the INP Composite Membrane

To adjust the length between the crosslinking points to maintain the flexibility of the network polymer, a bi-functional amide monomer that reacts with C3F was introduced into the INP structure. 1,1,2,2,3,3-Hexafluoropropane-1,3-disulfonic acid diamide (C3A) served as the bi-functional amide monomer and was synthesized by the same procedure as that for BTSA using C3F as a starting material.

A Solupor 5P09B (Lydall Performance Materials) membrane was used as a porous film in which to composite the INP. Figure 4 shows a schematic of the procedure for preparation of the INP composite membrane. This procedure was also performed under nitrogen. In this process, CH₃CN and the TEA were added to a mixture of BTSA and C3A in a reaction vessel, followed by stirring. The porous film was impregnated with the resultant mixture, irradiated with ultrasonic waves and then degassed by reducing pressure, after which C3F was added to the vessel followed by further sonication and then heating at 50°C for 96 h to gelate the solution. The vessel was heated to evaporate the solvent at 90°C over 24 h to obtain the product. The product was soaked in a mixed solvent of ethanol and sulfuric acid (9 : 1 v/v) at 25°C over 8 h to remove the TEA salt, which gave the gel and its composite membrane. Proton exchange was conducted by immersion of the membrane in 10 vol% sulfuric acid solution overnight, followed by stirring of the solution and washing with water at 25°C, each for several hours. Washing with water was repeated several times in the same procedure.

2.3 Characterization and Measurements

Samples were characterized using infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy. To confirm the formation of the sulfonyl imide groups after reaction of the monomers, the gel membranes obtained after acid treatment were assessed using the attenuated total reflectance (ATR) method with a Fourier transform IR instrument (FT-IR Avatar 360, Nicolet). Solid state ¹⁹F NMR (AVANCE400, Bruker BioSpin) measurements were also conducted on the gel membranes after treatment with acid. The crosslinked proportion was calculated from the ratio of the integrated values of the crosslinking and branching signals of the NMR spectrum. The gel and its composite membranes were measured using ATR to confirm the obtained composition.

The ion exchange capacity (IEC) and water uptake for each specimen were measured using a previously reported method. The dimensional change of the gel membrane was calculated from its water uptake value and density, while the composite membrane was assessed by measuring the differences in length and thickness between the dry and wet states. Water
Water self-diffusion coefficients ($D_{H_2O}$) were measured from the $^1$H pulsed field gradient (PFG) NMR method of samples (400 MHz, 12 T/m Avance400, Bruker BioSpin) at 25°C and under 10 to 100% RH conditions. The filling state of the composite membrane was confirmed by scanning electron microscopy (SEM) observations of the surface and cross-section prepared using a cross-section polisher (SM-09010, JEOL).

### 2.4 Fabrication of Membrane-electrode Assemblies (MEAs) and Cell Evaluation

MEAs with both the composite INP and Nafion membranes were fabricated by hot-pressing with catalyst layers, the details of which are shown in Table 1. Using MEAs with an active area of 13 cm$^2$, the proton conductivity of each membrane in the through-plane direction was measured using an electrical measurement cell and a frequency response analyzer.

![Fig. 4](image-url)
(SI 1280B, Solartron Analytical) by the AC impedance method at 80°C under 20% RH. The cell performance of the INP and Nafion MEAs with no humidification was evaluated by the following procedure. After the MEAs were operated at 0.5 A/cm² under 20% RH, the humidified gases supplied to both electrodes were changed to dry gases and the operating temperature was raised from 70 to 90°C in increments of 5°C. The cell voltage and resistance of the MEAs at 0.5 A/cm² were measured following operation for 1 h at each temperature. During these trials, the H₂ and air gases were supplied to the cell at fixed flow rates of 54 and 143 ml/min at 140 kPa, respectively.

3. Results and Discussion

3.1 Characterization and Properties of the INP

Figure 5 shows an IR spectrum of the gel membrane obtained after acid treatment following the reaction of tri-functional amide and bi-functional sulfonyl fluoride monomers. A sulfonyl imide peak was confirmed at 1100 cm⁻¹, which indicates progress of the desired reaction. Peaks attributed to sulfonic acid groups were also observed at 1050 cm⁻¹. As shown in Fig. 3, the unreacted sulfonyl fluoride groups are able to be substituted as sulfonic acid groups, which have proton conductivity as well as the sulfonyl imide groups, by acid hydrolysis. Figure 6 shows the solid-state ¹⁹F NMR spectrum of the INP. Four peaks were confirmed, which were assigned to correspond to two types of fluoride in the crosslinked units (A and C), while the B and D peaks correspond to two types of fluoride in the non-crosslinked units. From peak integration, the proportions of crosslinked and non-crosslinked units were calculated to be 76% and 24%, respectively.

Table 2 summarizes the properties of the INP and Nafion (a typical commercial perfluoride electrolyte, thickness 50 μm) membranes. The IEC value of the

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**Table 1** Composition of the catalyst layers.

<table>
<thead>
<tr>
<th>Ionomer</th>
<th>Catalyst (Pt/C)</th>
<th>I/C [a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product name</td>
<td>IEC (meq/g)</td>
<td>Pt loading (%)</td>
</tr>
<tr>
<td>Cathode</td>
<td>Aquision</td>
<td>1.20</td>
</tr>
<tr>
<td>Anode</td>
<td>DE2020</td>
<td>0.91</td>
</tr>
</tbody>
</table>

[a] Ionomer to carbon weight ratio.

**Table 2** Properties of INP and Nafion.

<table>
<thead>
<tr>
<th></th>
<th>IEC (meq/g)</th>
<th>Water uptake (%) [b]</th>
<th>Dimensional change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>INP</td>
<td></td>
<td>380</td>
<td>104 [c]</td>
</tr>
<tr>
<td>Nafion</td>
<td>4.0 (cal. 4.2 [a])</td>
<td>25</td>
<td>4</td>
</tr>
</tbody>
</table>

[a] Calculated from the ratio of crosslink and non-crosslink.  
[b] Measured using soaked samples in water.  
[c] Estimated using water uptake and polymer density.
INP indicates that the INP has an acid group density four times higher than Nafion. The INP shows high water uptake and dimensional change due to the increased acid group density; however, it is insoluble in water. It is considered that this insolubility, despite the high water uptake, results from the unique network structure of the INP.

Figure 7 shows the water adsorption isotherms of the INP and the Nafion membranes. The water uptake of the INP membrane was higher than that of the Nafion membrane at all RHs. The INP is able to retain much more water than Nafion because of its higher acid group density. Figure 8 plots the proton conductivities of the INP and Nafion as a function of RH. The INP exhibits higher proton conductivity than Nafion at all RHs. In particular, the INP has 10 to 15 times higher conductivity than Nafion in the range of 10 to 50% RH. As shown in Eq. (1), the proton conductivity ($\sigma$) is proportional to both the proton concentration ($N_H$) and the proton diffusion coefficient ($D_\sigma$). These values for both electrolytes at 20% RH are listed in Table 3, where $N_H$ was calculated by:

$$N_H = N_A(IEC/1000)/(1/\rho_{\text{polymer}} + \omega/\rho_{\text{H}_2\text{O}}). \tag{2}$$

$\rho_{\text{polymer}}$: Density of hydrated membrane
$\rho_{\text{H}_2\text{O}}$: Density of water
$\omega$: Water uptake
$N_A$: Avogadro’s number

The ratio (INP/Nafion) of $N_H$ is 2.7, while that of the proton conductivity is 15.1. From these values, the ratio of $D_\sigma$ estimated from Eq. (1) was 5.6. These results suggest that the high proton conductivity of the INP is dependent not only on $N_H$ but also on $D_\sigma$.

The diffusion of protons in a hydrated electrolyte occurs by either of two proposed mechanisms; the vehicle mechanism and the Grotthus mechanism.\(^{(14)}\) In the vehicle mechanism, protons diffuse with the water molecules, while in the Grotthus mechanism protons move through hydrogen bond networks formed by the water molecules.\(^{(15-17)}\) In both mechanisms, the mobility of the water molecules plays an important role in determining the mobility of the protons. Figure 9 shows $D_\sigma$ calculated from Eq. (1) and the water self-diffusion coefficients ($D_{\text{H}_2\text{O}}$) measured from $^1$H PFG NMR spectra of both electrolytes at each RH. The INP shows higher values of $D_\sigma$ and $D_{\text{H}_2\text{O}}$ than Nafion at all RHs.

The higher proton conductivity of the INP than Nafion at low RH appears to be due to its higher water uptake and $D_{\text{H}_2\text{O}}$. Higher water mobility enhances proton mobility expressed by $D_\sigma$. Possessing both higher $N_H$ and higher $D_\sigma$, which is influenced by water uptake and water mobility, results in the INP exhibiting superior proton conductivity compared to Nafion.

The morphologies of both electrolytes are also considered to affect these properties. It is well known

\begin{table}[h]
\centering
\caption{Properties of the INP and Nafion membranes at 20% RH.}
\begin{tabular}{lccc}
\hline
 & INP & Nafion & INP/Nafion \\
\hline
$\sigma$ (S cm$^{-1}$) & $3.75 \times 10^{-2}$ & $2.49 \times 10^{-3}$ & 15.1 \\
$N_H$ (10$^{27}$ m$^{-3}$) & 2.81 & 1.05 & 2.7 \\
$D_\sigma$ (m$^2$s$^{-1}$) & $2.14 \times 10^{-10}$ & $3.80 \times 10^{-11}$ & 5.6 \\
\hline
\end{tabular}
\end{table}
that the Nafion has a phase separated structure that is formed by hydrophobic domains of the fluoropolymer main chain and hydrophilic domains of acid groups and water.\(^{(18-21)}\) In contrast, the INP has a network structure in which sulfonil imide groups bonded with fluorocarbon (CF\(_2\)) and aromatic rings are uniformly dispersed. Figure 10 shows schematic illustrations of the primary and high order structures of both electrolytes at low humidity. In Nafion, the diffusion of water and protons is disturbed due to the presence of a bottleneck in the conduction path. However, the INP has a continuous conduction path, even at low humidity, due to the presence of acid groups in uniformly high density.

### 3. 2 Properties and Fuel Cell Performance of the INP Electrolyte Composite Membrane

Table 4 summarizes the properties of the INP, composite and Nafion membranes. The IEC of the composite membrane measured by titration is quite close to the theoretical value. The water uptake of the composite membrane was lower than that of the INP membrane, which indicates that the composition with the porous film restrains water absorption. The in-plane dimensional change of the composite membrane was 11\%, while that calculated for the INP membrane was 160\%. However, the dimensional change of the composite membrane in the through-plane direction was as high as 282\%; therefore, the

![Diffusion coefficients of the INP and Nafion membranes](image)

**Fig. 9** Diffusion coefficients of the INP and Nafion membranes (a) Proton diffusion coefficient (b) Water self-diffusion coefficient.

![Schematic illustrations of the INP and Nafion structures at low humidity](image)

**Fig. 10** Schematic illustrations of the INP and Nafion structures at low humidity.
Membrane swelling showed extreme anisotropy due to the layer structure of the porous film, as shown in Fig. 4. The proton conductivity of the INP composite membrane was 6.3 times higher than that of the Nafion membrane at 20% RH. The conductivity of the INP composite membrane in the through-plane direction was three times that of the Nafion membrane at 80°C and 20% RH. Therefore, the proton conductivity of the composite membrane was anisotropic. The porous film, which is used in the composite membrane, had a layered structure in cross-section, as shown in Fig. 4; therefore, this film inhibited proton conductivity in the through-plane direction of the membrane.

Figure 11 compares the cell performance of both the INP composite and Nafion MEAs operated without humidification. The voltage and cell resistance after operation for 1 h at each temperature are plotted. The Nafion MEA could be operated up to 75°C; however, it could not be operated at higher temperature, because of the increase in cell resistance. On the other hand, the INP MEA could be operated up to 85°C, which is 10°C higher than the Nafion MEA. This is considered to be due to the higher proton conductivity of the INP membrane than the Nafion membrane at low humidity, even though it is a composite membrane. In addition, the higher water diffusion of the INP membrane than the Nafion membrane enhances the back diffusion of water generated in the MEA.

Table 4 Properties of INP, INP composite membrane and Nafion.

<table>
<thead>
<tr>
<th></th>
<th>IEC (meq/g)</th>
<th>Water uptake (%)</th>
<th>Dimensional change (%)</th>
<th>Proton conductivity at 20% RH (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>In-plane direction</td>
<td>Through-plane direction</td>
</tr>
<tr>
<td>INP (5) [a]</td>
<td>4.0 cal. 4.0 [b]</td>
<td>870</td>
<td>(160 [d])</td>
<td>2.78 × 10⁻²</td>
</tr>
<tr>
<td>INP (5) composite membrane</td>
<td>2.5 cal. 2.6 [c]</td>
<td>440</td>
<td>11</td>
<td>2.02 × 10⁻¹ 1.52 × 10⁻²</td>
</tr>
<tr>
<td>Nafion</td>
<td>1.0</td>
<td>25</td>
<td>4</td>
<td>1.90 × 10⁻¹ 5.10 × 10⁻³</td>
</tr>
</tbody>
</table>

[a] INP (5) represents the number of C3 monomer units between the crosslinking is 5.
[b] Calculated from expected structure. [c] Calculated using filling rate and IEC value of the INP.

Fig. 11 Cell performance of the INP and Nafion MEAs with no humidification.
4. Conclusion

In this work, we synthesized a novel INP membrane that contains a high acid group density and is also insoluble in water. The INP has more than four times the acid group density than Nafion. This polymer also exhibits higher proton conductivity at all RH levels, and 10 to 15 times greater proton conductivity than Nafion over the range of 10 to 50% RH. This is attributed to both the elevated density of acid groups and the greater proton diffusion coefficient that results from improved water uptake and an improved water diffusion coefficient. The INP was used as the electrolyte membrane of a MEA by forming a composite membrane of the INP with a porous film to suppress in-plane dimensional change. A MEA with the INP composite membrane could be operated at higher temperature without humidification than a Nafion MEA due to the higher proton conductivity of the INP membrane.

Acknowledgements

Sample cross-sections were prepared with the cooperation of Mr. Yusuke Akimoto, Mrs. Kumi Amano and Mr. Yusuke Yagi at Toyota Central R&D Labs., Inc.

References


Fig. 10(right)

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