

Determination of Properties of Ionomer Binder Using a Porous Plug Model for Preparation of Electrodes of Membrane-Electrode Assemblies for Polymer Electrolyte Fuel Cells

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Abstract : A new characterization method using a porous plug model was proposed to determine the degree of sulfonation (DS) of ionomer binder with respect to the membrane used in membrane-electrode assemblies (MEAs) and to analyze the fraction of proton pathways through ionomer-catalyst combined electrodes in MEAs for polymer electrolyte fuel cells (PEFCs). Sulfonated poly(ether ether ketone) was prepared to use a polymeric electrolyte and laboratory-made SPEEK solution (5wt.%, DMAc based) was added to catalyst slurry to form catalyst layers. In case of the SPEEK-based MEAs in this study, DS of ionomer binder for catalyst layers should be the same or higher than that of the SPEEK membrane used in the MEAs. The porous plug model suggested that most of protons were via the ionomer binder (~92.5%) bridging the catalyst surface to the polymeric electrolyte, compared with the pathways through the alternative between the interstitial water on the surface of ionomer binder or catalyst and the ionomer binder (~7.3%) and through only the interstitial water on the surface of ionomer or catalyst (~0.2%) in the electrode of the MEA comprising of the sulfonated poly(ether ether ketone) membrane and the 5wt.% SPEEK ionomer binder. As a result, it was believed that the majority of proton at both electrodes moves through ionomer binder until reaching to electrolyte membrane. The porous plug model of the electrodes of MEAs reemphasized the importance of well-optimized structure of ionomer binder and catalyst for fuel cells.

Keywords : Polymer electrolyte fuel cell; Porous plug model; Sulfonated poly(ether ether ketone); Membrane electrode assembly; Proton pathway

1. Introduction

Polymer electrolyte fuel cells (PEFCs) have been considered as the next energy generating device for mobile, transportation and stationary applications.¹⁻⁴⁾ A membrane-electrode assembly (MEA) is one of key components in PEFCs since it is an essential unit to make an energy conversion device that generates electricity and heat by electrochemically combining hydrogen and oxygen from the air. It is a composite of a polymer electrolyte membrane sandwiched between catalyzed electrode layers. The fabrication of the MEA has typically involved the following processes: The catalyst slurry for electrodes is prepared as the mixture of electrocatalyst (e.g., Pt/C or Pt/Ru/C) and perfluoro-sulfonated ionomer dispersed in lower alcohols (e.g., Nafion® solution). The catalyst slurry is applied to either the surface of a sheet of PTFE-impregnated carbon paper or polymer membrane (e.g., Nafion® membrane). The membrane is sandwiched between the carbon papers, and thereafter the sandwich is pressed at a temperature and a pressure. Recently, sulfonated aromatic

polymers such as sulfonated poly(ether ether ketone) (SPEEK), sulfonated poly(ether sulfone) (SPES), sulfonated polyimide (SPI) and so on are reported as electrolyte materials for PEFCs because these polymers are cheap and are relatively insensitive to a decrease in proton conductivity by dehydration at high temperature.⁵⁻⁹⁾

Much attention has been paid to develop optimized MEAs for PEFCs to reduce the amount of Pt loading without sacrificing their performances. For the fabrication of MEAs using newly prepared membranes,^{3,4)} optimization of the composition of catalyst slurry has to be made to satisfy other important criteria for PEFC operations, which are proton accessibility to proton-conducting membranes from the surface of catalyst layers, gas accessibility to catalysts as much as possible and electronic path continuity. Those criteria significantly depend on slurry composition, resulting in the configuration of catalyst layers.

A microscopic view of electrodes of MEAs can be suggested as illustrated in Fig. 1. It is assumed that there are three different pathways for proton conduction bridging from the surface of catalysts to the electrolyte membrane at anode and vice versa at cathode: i) alternating layers of ionomer binder and interstitial solution (Path I), ii) the channel

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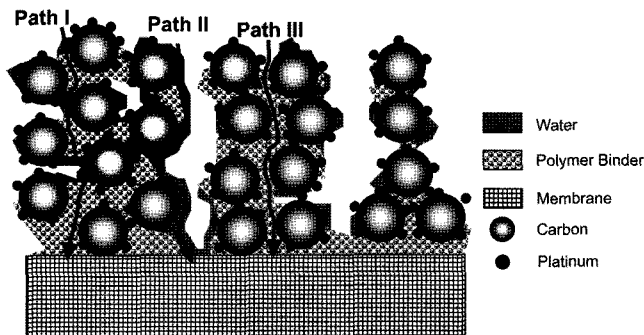


Fig. 1. Schematic illustration of three different proton conducting paths in catalyst layers of MEAs.

through the interstitial solution (Path II), iii) well-connected ionomer binder (Path III) (see Fig. 1). In this study, a new characterization method for MEAs was investigated using a "porous plug" model.^{10,11)} The porous plug model was used for accurate calculations of electric conductivities and potential difference in ion-exchange beds when the interstitial solution conductivity in the ion-exchange beds is very low. Spiegler et al.¹⁰⁾ proposed the new simple model to calculate electrochemical properties from empirical geometrical parameters. In fact, the configuration between the ion-exchange beds and the electrodes of MEAs is fairly analogous in that only movable ion, proton, is transported through ion-exchangeable ionomer binder which swells by water like ion-exchange resin. In this study, catalyst layers of MEAs can be analyzed and discussed by means of the porous plug model to determine the properties of ionomer binder on fabrication of MEAs using newly prepared sulfonated polymers (i.e., SPEEK in this study).

2. Experimental

2.1 Materials

Poly(ether ether ketone) (PEEK) from Victrex was dried overnight at 110°C under vacuum and used for the reaction. *N, N'*-dimethylacetamide (99%) and sulphuric acid (95%) from Junsei Chemicals Co, Ltd, Japan were used as received without further purification.

2.2 Sulfonation of PEEK

Sulfonation of PEEK was carried out by the reported literature procedure.^{3,7,9)} The reaction was carried out in a four neck round bottom flask fitted with a mechanical stirrer. About 500 mL of 95% H₂SO₄ was transferred to the reaction flask and heated over water bath to 50°C under N₂ atmosphere. Then, 25 g of PEEK was slowly added under stirring. The mass remained heterogeneous initially, the polymer completely dissolved in 0.5 h and the reaction was continued for further 50 h. Polymer solution was cooled down to room temperature to arrest the reaction and dropped over ice cold demineralised (DM) water through a separating funnel as thin stream. The fibers were then washed with DM water until neutral pH of the washing water was obtained and further stirred overnight with DM water to remove residual acid

if present. Sulfonated polymer obtained was dried at 60°C for 12 h and followed by overnight drying at 110°C under vacuum.

For preparation of SPEEK membranes, the dry SPEEK polymer was soaked in 1 M NaCl solution for 24 h, ion-exchanged by Na⁺ and was washed with DM water several times. The polymers were dried at the same condition as drying SPEEK. The 10wt.% SPEEK solution in *N, N*-dimethylacetamide (DMAc) filtered through a 0.45 μm filter was prepared. The resulting solutions prepared using Na⁺-form SPEEK were cast onto flat Petri dishes and were dried in an oven at 75°C for 4 h. The oven temperature was raised to 110°C for 24 h under vacuum to remove residual solvent. The membranes were cooled to room temperature and were then peeled off from the Petri dishes. Afterwards, the membranes were protonated by being soaked in 1M H₂SO₄ solution for 24 h at room temperature and were rinsed to remove the residual H₂SO₄ from the surface of membrane. Thickness range of the membranes was 65~90 μm. For preparation of ionomer binder used for preparation of catalyst coated membranes (CCMs), the H⁺-substituted SPEEK membranes were dried at 80°C for 48 h under vacuum and dissolved in DMAc to make a 5wt.% solution.

2.3. Characterizations

2.3.1. Ion-exchange capacity and the degree of sulfonation

Polymer samples were analyzed for ion exchange capacity (IEC) by a titration method. Weighed quantity (1-2 g) of the polymer was kept in 1.0 M NaCl solution under stirring for 24 h and titrated with 0.001 M NaOH using phenolphthalein indicator. The IEC was calculated as the ratio of total charge to dry polymer weight. The DS was calculated from IEC as

$$DS = \frac{M_{w,p}}{1 - M_{w,p}} \frac{IEC}{IEC} \times 100 \quad (1)$$

where $M_{w,p}$ is the molecular weight of non functional polymer repeat unit and $M_{w,f}$ the molecular weight of functional group with counter ion (-SO₃Na). The degree of sulfonation (DS) of SPEEK membranes with different sulfonation time is summarized in Table 1.

2.3.2. Water uptake

Water uptake of the membranes at different temperatures was determined from the difference in weight before and after hydration. Membrane samples were dried at 110°C under vacuum until constant weight which is recorded as W_{dry} . The samples were then immersed in DM water for 4 h at a given temperature, removed from water, surface attached water was wiped out with filter paper and immediately weighed (W_{wet}). Water uptake was reported as absorbed water weight percent with respect to dry membranes:

$$\text{Water uptake}(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (2)$$

2.3.3. Proton conductivity

Membrane samples (2 cm length, 1 cm wide) were dipped in water filled Petri dishes overnight before the measurement. Proton conductivity of the membranes was measured by ac impedance spectroscopy using a Solartron 1260 gain

Table 1. Degree of sulfonation of SPEEKs and ionic conductivity of SPEEK membranes (or SPEEK ionomer binder) (k) and catalyst layers (k_b) with 35wt.% of dry ionomer binder as a function of sulfonation time

Sulfonation time (h)	Degree of sulfonation (%)	Proton conductivity of SPEEK membranes	Proton conductivity of catalyst layers
		(S cm ⁻¹) $k (\times 10^{-4})$	(S cm ⁻¹) $k_{b, measured} (\times 10^{-4})$
0.5	18.2	2.30	1.99
1	19.7	5.90	4.80
3	20.9	15.0	13.5
6	23.1	32.0	29.0
12	28.8	61.0	50.4
24	38.9	130	105
36	47.9	190	158

phase analyzer interfaced to Solartron 1480 multistat. The measurement was carried out in a potentiostatic mode over the frequency range 0.1 Hz to 10 MHz with 5 mV of oscillating voltage. A laboratory-made four-probe conductivity cell configuration and detail information on a measurement procedure are found elsewhere.^{3,7,9} Proton conductivity of the samples was calculated from impedance data using the relation:

$$\sigma = \frac{L}{RWd} \quad (3)$$

where σ is the proton conductivity, L the length between two potential sensing platinum wires, R the membrane resistance derived from the impedance value at zero phase angle, W the width of the potential sensing platinum wire and d the membrane thickness. The proton conductivity of SPEEK membranes with different sulfonation time is summarized in Table 1.

2.4. Fabrication of MEAs

Pt/C (40wt%, Vulcan XC72, E-Tek, USA) was employed as a catalyst. The platinum loading for both anode and cathode was respectively 0.4 mg cm⁻². The catalyst slurries for SPEEK-based CCMs were prepared by mixing SPEEK ionomer solution (5wt%, laboratory-made) in DMAc with the catalyst powder. The properties of solutions are summarized in Table 2. The mixtures were then sonicated for 1 h and were kept being mixed on a stirrer for 3 days. Each catalyst slurry was applied to the surface of SPEEK membranes by a spraying method. The CCMs were dried in the oven at

100°C to determine the amount of catalyst loading under pressure. For fabrication of MEAs, the carbon papers used in this study were PTFE-impregnated Toray 250 carbon paper (waterproof by 8wt.% PTFE). The carbon papers sandwiched the membranes by hot pressing at 135°C and 50 kgf cm⁻² for 5 min.

3. Results and discussion

In this study, a new characterization method for MEAs was investigated using the "porous plug" model. The performance of MEA for PEFCs is highly dependent on the composition of catalyst, ionomer solution as a binder, solvent as a dispersant, etc. in catalyst slurry. The dependence arises from different ionic transport pathways of proton which is moving into or out of an electrolyte membrane.

The "porous plug" model^{10,11} estimates the electrochemical properties from empirical and geometrical parameters of the catalyst layer in MEAs, which constitutes a continuous and discontinuous phase. In case of ion-exchange resin bed systems, the ionic conductivity of a bed as a function of the ionic conductivity of the interstitial solution provided main electrochemical behaviour of the resin bed systems such as an equiconductance point. Thus, waters with lower ionic conductivity than the equiconductance point can be applicable using the resin bed. Otherwise, non ion-exchanged ionic substances pass through the resin bed. In other words, in case of MEAs, the ionic conductivity of ionomer binder varies with the degree of sulfonation. Instead of the interstitial solution in case of the resin bed systems, the ionic conduc-

Table 2. Composition of catalyst slurries with different content of ionomer binder and ionic conductivity of the interstitial solution (\bar{k})

Loading amount of dry ionomer (%)	15	25	35	45
5wt.% SPEEK solution (g)	1.06	2.00	3.23	4.91
40wt.% Pt/C (on Vulcan XC72, E-Tek) (g)	0.30	0.30	0.30	0.30
DMAc (g)	8.64	7.70	6.47	4.79
Titration result* (mL of 0.001 M NaOH)	1.0	0.8	1.2	0.9
Ionic conductivity of interstitial solution** (S cm ⁻¹)	2.49×10^{-5}	1.49×10^{-5}	3.49×10^{-5}	1.99×10^{-5}

*Average volume of consumed NaOH as a function of DS at the same amount of ionomer binder; Consumed volume of 0.01 M NaCl for blank : 0.5 mL

**Average ionic conductivity of the interstitial solutions inside electrodes of MEAs including ionomer binder as a function of DS at the same amount of ionomer binder; Converting universal constant of consumed NaOH volume into solution conductivity, $349.64 \times 10^{-4} \text{ m}^2 \text{ S mol}^{-1}$

tivity relationship between the ionomer binder and the catalyst layer can be obtained. From this analysis, the degree of sulfonation for ionomer binder can be determined to make catalyst layers and the fraction of proton conducting pathways in catalyst layers of MEAs can be provided.

As is discussed, the ionic conductivity of the catalyst layer of MEAs is represented as follow:

$$k_b = k_1 + k_2 + k_3 = \frac{ak\bar{k}}{dk + e\bar{k}} + b\bar{k} + ck$$

$$(a + b + c, d + e = 1) \quad (4)$$

where k_b is the total ionic conductivity of the catalyst layers, \bar{k} the ionic conductivity of the interstitial solution, k the ionic conductivity of ionomer binder, k_1 the ionic conductivity through alternating layers of ionomer binder and interstitial solution, k_2 the ionic conductivity through the interstitial solution and k_3 the ionic conductivity through the ionomer binder.

The determination of a , b , c , d and e was made by fitting the experimentally measured ionic conductivity data of the catalyst layers (k_b) and the ionomer binder (k) using Eq. (4). The k values as a function of DS were determined as summarized in Table 1. Assuming that the entire proton is easily ion-exchanged by free proton in interstitial water generated by hydrogen oxidation at anode and transported from anode, the determination of \bar{k} is required to measure the amount of proton ion-exchangeable by the ionomer binder and the

amount of interstitial water at both electrodes. The former amount was determined by the NaOH titration of the NaCl solutions in which the CCMs were immersed for 24 h (see 2.3.1) and the subtraction of the amount of total proton from SPEEK membranes, and the latter amount by the steady-state weight difference between the dry and humidified (see Fig. 2, flowing humidified N_2 for 24 h under 100% relative humidity) single cell including the CCMs (~ 7 g for all cases). The former and latter amount were converted into ionic conductivity of the interstitial solution using a proton molar conductivity constant. As a result (see Table 2), the \bar{k} values were roughly not dependent on the dry amount of ionomer binder and the DS. Thus, the \bar{k} can be represented by $2.365 \times 10^{-5} \pm 0.625 \times 10^{-5} \text{ S cm}^{-1}$ and used as a constant. The k_b values as a function of DS were determined by measuring the through-plane impedance of MEAs which the steady-state weight was attained during flowing humidified N_2 for 24 h under 100% relative humidity and then subtracting the impedance of the wet respective SPEEK membranes. The measurement results are summarized in Table 1. As can be expected, k and k_b values were proportionally dependent on DS of SPEEK polymer.

As a result, since the \bar{k} can be regarded as constant, the data relationship between ionic conductivity of the ionomer binder (k) and catalyst layers (k_b) can be fitted using Eq. (4). The data relationship and fitting result are shown in Fig. 3. The ionic conductivity of ionomer binder is lower than the ionic conductivity of catalyst layer in the entire range. It is believed that the ionomer binder-connected catalyst layers are likely to be favorable to proton conducting and the SPEEK-based ionomer binder with the same DS to the SPEEK membrane used in SPEEK-based MEAs can be used to make catalyst layers. However, up to 23% of DS, the curve is very close to the equiconductance line. In this range, it can be inferred that ionomer binder with a little higher DS is preferred to make catalyst layers.

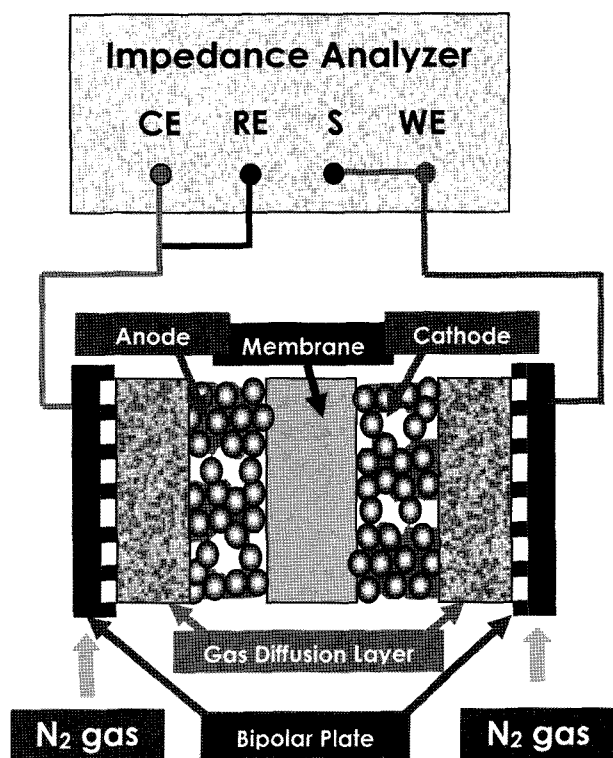


Fig. 2. Schematic illustration of a single cell for interstitial water uptake of MEAs and for ionic conductivity of catalyst layers of MEAs (k_b) (frequency range, $10^7 \sim 10^1$ Hz; amplitude, 5 mV; CE, counter electrode; RE, reference electrode; S, sensor; WE, working electrode).

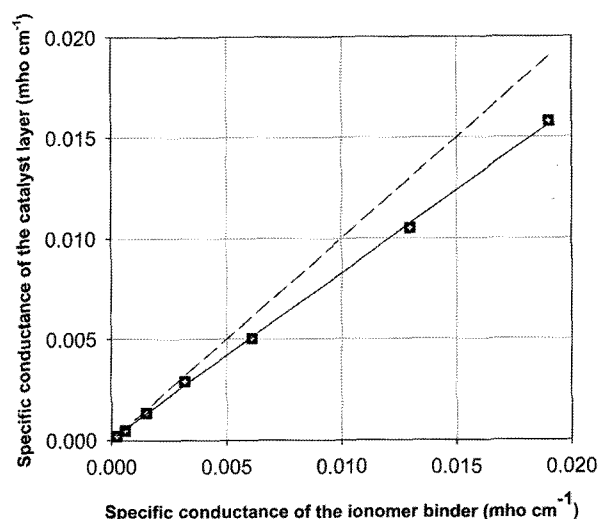
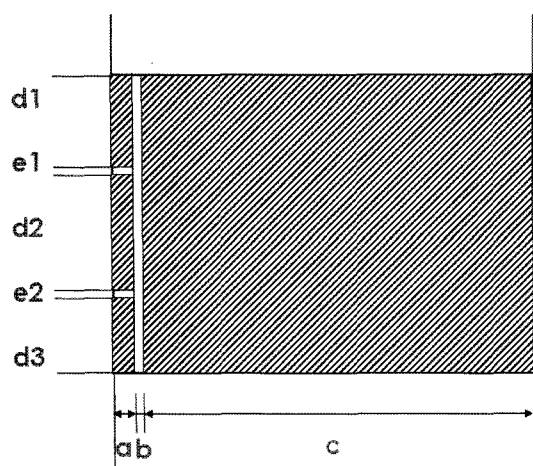


Fig. 3. Data relationship between specific conductance of ionomer binder and catalyst layer (square dot), fitting result (solid line) and equiconductance line (dotted line).

Table 3. Fitted parameters (a , b , c , d and e) of Eq. (4) and k_b calculated using predetermined a , b , c , d , e , k and \bar{k} as a function of DS.

Fitted parameter of Eq. (4)				
a	b	c	d	e
0.073	0.002	0.925	0.98	0.02
SPEEK DS (%)	$k_1 (\times 10^{-6})$	$k_2 (\times 10^{-8})$	$k_3 (\times 10^{-4})$	$k_b, \text{calculated} (\times 10^{-4})$
18.2	1.7617	4.74	2.127	2.146
19.7	1.7640	4.74	5.457	5.476
20.9	1.7648	4.74	13.87	13.89
23.1	1.7651	4.74	29.60	29.62
28.8	1.7653	4.74	56.42	56.44
38.9	1.7653	4.74	120.2	120.3
47.9	1.7654	4.74	175.7	175.8

**Fig. 4. Schematic illustration of the fraction of proton conducting paths in catalyst layers of the SPEEK-based MEAs investigated in this study using the result of fitted parameters in Table 3.**

Fraction of proton conducting pathways in catalyst layers of MEAs is illustrated in Fig. 4 using the fitted parameter result as summarized in Table 3. It is believed that most of proton in catalyst layers of the MEAs is transported using the pathway via ionomer binder bridging the catalyst surface to the polymeric electrolyte rather than the pathways through the alternative layers between the interstitial water on the surface of ionomer binder or catalyst and ionomer binder or through the interstitial water on the surface of ionomer or catalyst in the electrode of the MEAs.

The measured and calculated k_b values show a little discrepancy in Table 1 and 3. This discrepancy might arise from the different configuration between ion-exchange resin bed and catalyst layer. Originally, the porous plug model is the empirical model for spherical resin packed systems, but the shape of ionomer binder packed in catalyst layers is amorphous. However, the range of deviation of the calculated values from the measured ones was still in 6.7~7.5%, which was quite small.

4. Conclusions

In this study, a porous plug model was proposed as a new characterization method of determining the degree of sulfonation of ionomer binder to make catalyst layers of mem-

brane-electrode assemblies and evaluating the fraction of proton conducting pathways in catalyst layers of membrane-electrode assemblies. In case of fabrication of MEAs using SPEEK polymers, DS of ionomer binder for catalyst layers should be the same or higher than that of the SPEEK membrane used in the MEAs. As a fitting result, most of proton in catalyst layers of the MEAs was transported using the pathway via ionomer binder (~92.5%) bridging the catalyst surface to the polymeric electrolyte.

Using the porous plug model proposed in this study, the minimum ionic conductivity of ionomer binder with respect to the electrolyte membrane used in MEAs can be determined. Generally, higher DS of ionomer binder brings about lower cell resistance of MEAs and finally better performance, but higher DS of ionomer binder is weak to humidified gas environment due to high water uptake and consequently low mechanical strength and/or continuous dissolution of ionomer binder. In addition, using the pathway via ionomer binder means well-configured catalyst layers. Thus, in case of MEA fabrication using newly prepared electrolyte membranes and ionomer binder, it is believed that the porous plug model enables to provide the good electrochemical guideline.

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