A mixture design approach to optimizing the cathodic compositions of proton exchange membrane fuel cell

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ABSTRACT

Cathodic catalyst layers for proton exchange membrane fuel cells (PEMFCs) are prepared according to a spraying technique, and the optimal composition of the catalyst layer is investigated by applying a mixture design approach, where the power density of the PEMFC is used as the response of the model. Based on the conventional experimental design, the optimal Nafion content of the electrocatalytic layers of a PEMFC is 35%, and a maximum power density (P_{max}) of 239.5 mW cm^{-2} is attained. Polytetrafluoroethylene (PTFE) is added to the cathodic catalyst layer to manage water, and the relationship between the P_{max} of the PEMFC (y) and the cathodic pseudo-compositions (Y_1 (Pt/C), Y_2 (Nafion) and Y_3 (PTFE)) is obtained:

$$y = 204.40Y_1 + 198.60Y_2 + 188.44Y_3 + 167.46Y_1Y_2 \ (R^2 = 0.9908)$$

Based on the constant power density contours of the cathodic compositions, the optimal weight fractions of Pt/C, Nafion and PTFE are 0.68, 0.29 and 0.03, respectively, and the corresponding P_{max} is 266.5 mW cm^{-2}.

1. Introduction

Proton exchange membrane fuel cell (PEMFC) is a promising green energy source due to its high energy efficiency, low operating temperatures and lack of greenhouse emissions. In the membrane assembly electrode (MEA) of a PEMFC, electrochemical reactions are used to generate electrical power. However, the sluggish kinetics of the cathodic oxygen reduction reaction (ORR) limit the performance of PEMFCs. Thus, a considerable amount of effort has been dedicated to the development of novel materials such as polymer electrolytes and highly electroactive cathodic ORR catalysts. Recently, the microstructure of an MEA is optimized by adjusting the composition of the catalytic layer. Therefore, procedures used for the preparation of MEAs have become of interest. For example, the ionic resistance and the mass transfer resistance of an MEA are affected by the content of the Nafion ionomer [1–3]. Moreover, methods [1,4–8] such as brush painting [9,10], spraying [11,12], decal transfer, doctor blade, screen printing and inkjet printing [13,14] have been developed for the preparation of MEAs. In the brush painting method, the paintability of an electrocatalyst slurry can be improved by adding a suitable amount of glycerol [10]. In general, indirect decal methods such as the gas diffusion layer (GDL)-based method and the membrane-based method have been developed for the preparation of MEAs [11]. Specially, an MEA with a current density of 830 mA cm^{-2} at 0.6 V is achieved by spraying catalyst ink on carbon cloth to form a GDL and hot pressing the GDL electrode assembly onto the membrane [11]. Moreover, the performances of DMFC (direct methanol fuel cell)-MEAs prepared by spraying and scraping techniques has been discussed in detail [15].

The addition of NH_4HCO_3 into the MEA of a PEMFC results in a uniform dispersion of the catalyst on the surface of the MEA and increases the porosity of the catalyst layer, which reduces gas diffusion resistance [9]. The performance of a MEA in a DMFC is affected by the Pt loading, Nafion content and cathodic porosity [16]. Moreover, in a PEMFC, superior MEA performance is achieved with a Pt loading of 0.1 mg cm^{-2} by mixing the Pt/C electrocatalyst and Nafion solution without additional organic solvent [17]. The optimal Nafion content in ultra-low Pt-loading MEAs for PEMFCs is 25% [18]. The performance and characteristics of fuel cells are generally affected by the composition of the MEAs [19–21]. For instance, PTFE is an important component for the management of water in MEAs for PEMFCs [22]. Therefore, Pt/C, Nafion and PTFE were selected as the components for the preparation of a cathodic MEA. The effect of the PTFE and Nafion content on the performance of a regenerative fuel cell is studied by conventional experimental techniques [23].

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To the best of our knowledge, the optimization of cathode compositions based on Pt/C, PTFE and Nafion according to the mixture design approach is seldom reported.

In general, the ORR and performance of a PEMFC are strongly affected by the cathodic composition of the MEA. However, for multi-component systems, conventional experimental approaches may not be efficient for identifying the full effects of the composition on the properties of the MEA. Moreover, experimental design and optimization strategies are useful tools for experimental situations [24]. The mixture design technique is based on statistical theory and uses a limited number of experiments to study the full range of a multi-component system. The properties of the system are examined with polynomial regression models and contour plots derived from the experimental data [25]. Approximate models of the logarithmic ionic conductivity versus the composition of PEO-LiCF$_3$SO$_3$-plasticizer polymer electrolytes are obtained in our previous study by applying a mixture design method [26]. In the present study, the effect of the cathodic composition of a MEA on the properties and performances of a PEMFC was investigated by applying a mixture design approach conducting polarization and AC impedance tests.

2. Experimental

2.1. Preparation of MEAs

To prepare the cathodic (anodic) slurry, appropriate amounts of Pt/C (20 wt%, E-TEK), Nafion (5 wt% Nafion solution, Aldrich) and PTFE (60 wt% PTFE suspension solution, Aldrich) (SiO$_2$ (5–15 nm, Aldrich)) were combined with isopropyl alcohol. The slurry was mixed with a magnetic stirrer and a supersonic agitator for 60 and 30 min, respectively. The agitation procedures were repeated, and well-mixed cathodic and anodic slurries were sprayed on 1 cm × 1 cm carbon paper (B1A10WP, E-TEK) to obtain anodic and cathodic catalyst layers with Pt loadings of 0.2 mg cm^{-2}. The catalyst layers were dried at room temperature and 100 °C in an oven for 30 min and 1 h, respectively.

A 2.5 cm × 2.5 cm Nafion 117 film was placed into a boiling solution of 3 wt% H$_2$O$_2$ for 1 h to remove residual organic material. Upon completion, the film was washed with deionized (DI) water and was placed in boiling DI water for 1 h to completely remove residual H$_2$O$_2$. Inorganic contaminants were removed by submerging the Nafion film in a boiling solution of 0.5 M H$_2$SO$_4$ for 1 h. To remove residual H$_2$SO$_4$ within the Nafion film, the same procedure used to remove residual H$_2$O$_2$ was applied. The MEAs were prepared by hot pressing the catalytic layers onto the Nafion film under the desired conditions. The surface morphologies of the MEAs were analyzed by FESEM (JEOL JSM-7000F).

2.2. Polarization curves of the PEMFC

The MEA, Teflon gasket, graphite flowfield and current collector were assembled into a commercial PEMFC single cell house. The electrochemical characteristics of the PEMFC single cell were determined with a fuel cell testing system (PRODIGIT 3315D). When the gas flow control system and the electrical circuit were established, H$_2$ and O$_2$ were flowed through the cathodic and anodic humidifiers at a flow rate of 30 ml min^{-1} and were introduced into the cathodic and anodic chambers, respectively. The PEMFC was activated at 0.6 V until a steady current was obtained. Next, the polarization curves of the activated PEMFC were obtained according to the constant potential model. The electrochemical impedance spectra of the PEMFCs were obtained with an electrochemical analyzer (CHI 604A) at a frequency of 0.01 Hz to 100 kHz and an amplitude of 10 mV.

3. Results and discussion

3.1. Effect of the Nafion content in the electrocatalyst layers

3.1.1. Polarization curves and power densities

A suitable amount of Nafion in the electrocatalyst layer can increase the area of the three-phase reactive zone by increasing the proton transfer channels. However, due to its hydrophilic nature, excess Nafion can reduce the electroactive three-phase area. to determine the optimal composition of the catalyst layer, the Nafion content was varied at a constant Pt loadings of 0.2 mg cm^{-2}, and the polarization curves of the PEMFC were obtained, as illustrated in Fig. 1. At a Nafion content of 20 wt%, the potential decreased from the open circuit potential (OCP) (0.882 V) to 0.690 V (i.e. the kinetic control region) as the current density increased from 0 to 65.50 mA cm^{-2}. Alternatively, at current density greater than 65.50 mA cm^{-2}, electrochemical reactions on the electrodes of the PEMFC were affected by the electrochemical kinetics and the mass transfer of the reactants from the bulk phase to electroactive sites (mixed control).

When the PEMFCs were operated under kinetic control, the output current density increased with an increase in the Nafion content of the electrocatalyst layer. Specially, as the Nafion content increased from 20 to 50 wt%, the current density at 0.801 V increased from 11.0 to 40.0 mA cm^{-2}, as shown in Fig. 1. Thus, an increase in the Nafion content increased the contact and utility of the Pt/C electrocatalysts, which increased the current density of the PEMFC in the kinetic control region. However, when the PEMFC was operated in the mixed control region, excess Nafion blocked some micro-channels within the electrocatalyst layer, which resulted in water flooding conditions. Thus, when excess Nafion was applied, the mass transfer rate of gaseous reactants (H$_2$ and O$_2$) from the
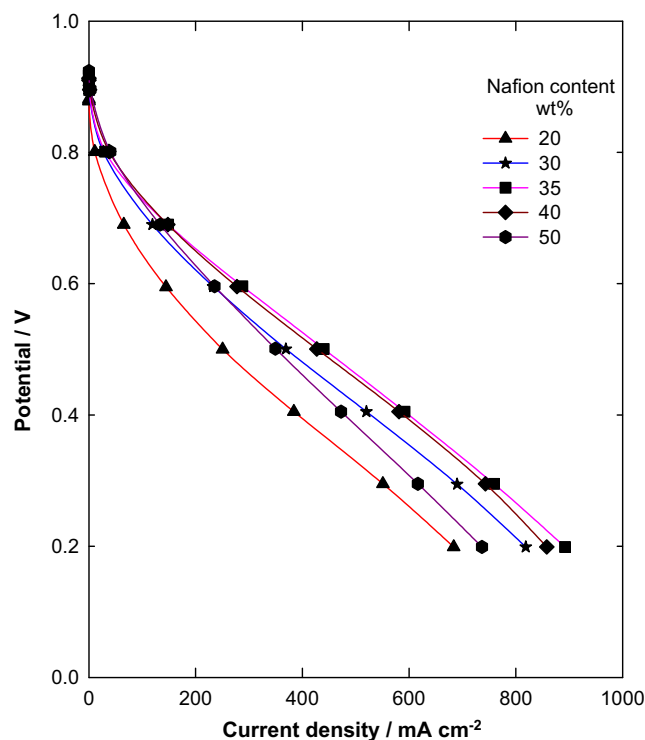

Fig. 1. The polarization curves of PEMFC with various contents of Nafion. Pt loadings of cathode and anode = 0.2 mg cm^{-2}, geometric area of electrocatalyst layer = 1.0 cm^2. Hot pressing conditions: pressure = 10 kg cm^{-2}, T = 160 °C, t = 2 min. Operating conditions of PEMFC: T_{cell} = 60 °C, H$_2$ flow rate = 30 ml min^{-1}, O$_2$ flow rate = 30 ml min^{-1}, temperature of cathodic humidifier = 60 °C, temperature of anodic humidifier = 65 °C.
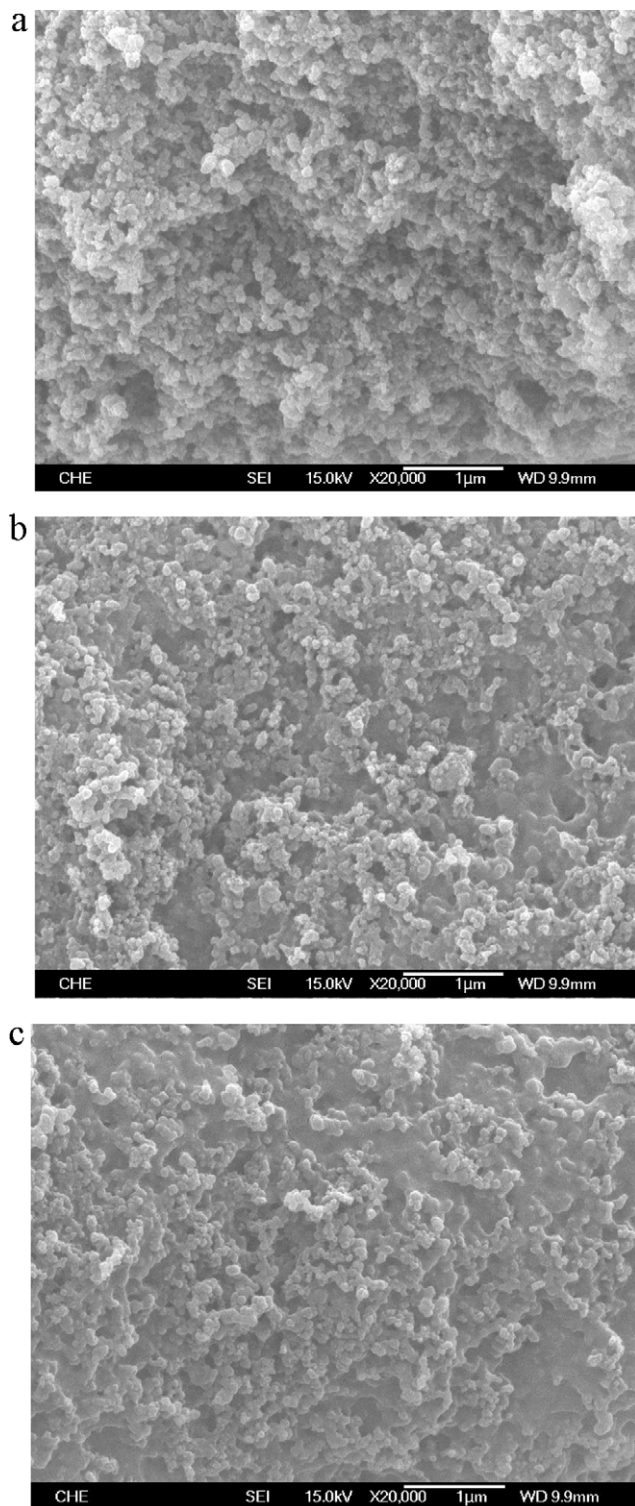
Fig. 2. SEM images of electrocatalyst layers for various Nafion contents. Nafion content within electrocatalyst layer (a) 20, (b) 35, and (c) 50 wt%.

Fig. 3. Effect of current density on power density of PEMFC with the various contents of Nafion. Pt loadings of cathode and anode = 0.2 mg cm^{-2}, geometric area of electrocatalyst layer = 1.0 cm^2. Hot pressing conditions: pressure = 10 kg cm^{-2}, T = 160 °C, t = 2 min. Operating conditions of PEMFC: T_{cell} = 60 °C, H$_2$ flow rate = 30 ml min^{-1}, O$_2$ flow rate = 30 ml min^{-1}, temperature of cathodic humidifier = 60 °C, temperature of anodic humidifier = 65 °C.

bulk phase to electroactive sites decreased. Moreover, as shown in Fig. 2, the porosity of the electrocatalyst layer decreased with an increase in the Nafion content of the electrocatalyst layer. When the electrocatalyst layer contained 20 wt% Nafion (Fig. 2(a)), the structure of the electrocatalyst layer was relatively loose. Alternatively, at a Nafion content of 50 wt%, some of the micropores and channels were blocked by excess Nafion (Fig. 2(c)). Neverthe-
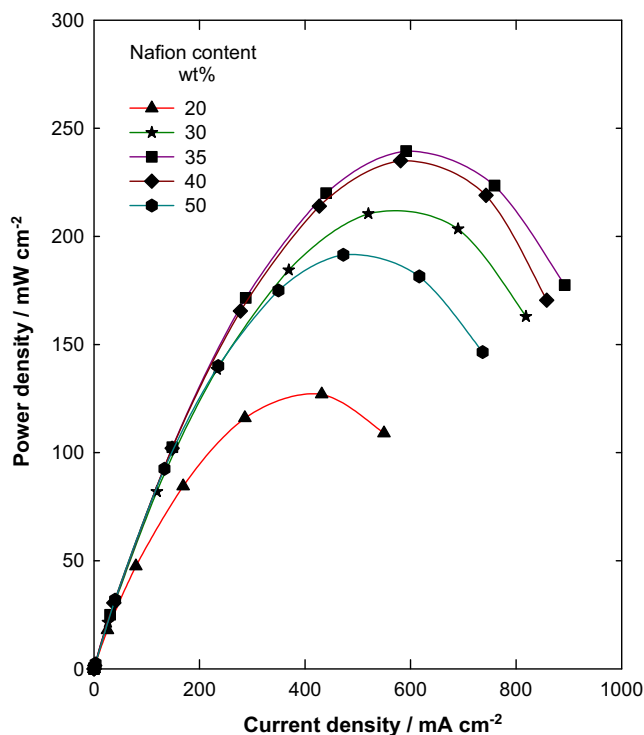
less, at 0.405 V (mixed control), the current density increased from 384.0 to a maximum value of 591.5 mA cm^{-2} as the Nafion content increased from 20 to 35 wt% (Fig. 1). However, as the Nafion content was further increased to 50 wt%, the current density decreased to 472.5 mA cm^{-2}.

Based on the polarization curves of the PEMFC, the power densities of electrocatalysts with various Nafion contents were calculated, and the results were provided in Fig. 3. As shown in the figure, the maximum power density of the PEMFC (P_{max}) occurred in the mixed control region. Namely, as the Nafion content increased from 20 to 35 wt%, the P_{max} increased from 127 to a maximum value of 239.5 mW cm^{-2}. However, as the Nafion content was further increased to 50 wt%, the value of P_{max} decreased to 191.5 mW cm^{-2}.

3.1.2. EIS of PEMFC

Electrochemical impedance spectra (EIS) of a PEMFC containing an electrocatalyst layer with a Nafion content of 35 and 50 wt% at 0.6 V were illustrated in Fig. 4. Two semi-circles in the EIS spectra were attributed to the parallel combination of charge transfer resistances at the anode and the cathode (Rct(A) and Rct(C), respectively) and the electrical double layer capacitances at the anode and the cathode, which were represented by CPE(A) and CPE(C) to correlate the nonhomogeneity of the rough surface. The left intercept on the x-axis was attributed to the resistance of the electrolyte (Re), which was associated with the resistance of proton transfer from the electroactive sites of the anode through the anodic catalyst layer, the Nafion film and the cathodic catalyst layer to the active sites of cathode. Almost the same Re values obtained for 35 and 50 wt% Nafion content (Table 1) revealed that the effect of the Nafion content on the high frequency resis-

Table 1
Effect of Nafion content in the electrocatalyst layers on the parameters of the equivalent circuit of PEMFC.

Nafion content wt%	Rct(A) $\Omega\,cm^2$	Re $\Omega\,cm^2$	Rct(C) $\Omega\,cm^2$	W $\times 10^{-3}\,\Omega\,cm^2$
35	0.07	0.81	0.32	1.69
50	0.15	0.74	0.40	3.35

Pt loadings of cathode and anode = 0.2 mg cm^{-2}, geometric area of electrocatalyst layer = 1.0 cm^2. Hot pressing conditions: pressure = 10 kg cm^{-2}, T = 160 °C, t = 2 min. Operating conditions of PEMFC: T_{cell} = 60 °C, H$_2$ flow rate = 30 ml min^{-1}, O$_2$ flow rate = 30 ml min^{-1}, temperature of cathodic humidifier = 60 °C, temperature of anodic humidifier = 65 °C. Ac impedance conditions: f = 0.01–10^5 Hz, amplitude = 10 mV, dc bias = 0.6 V.

tance Re was insignificant. The equivalent electrical circuit of the PEMFC single cell is illustrated in the inset of Fig. 4. In general, the mass transfer rate of H$_2$ within the anodic catalyst layer was faster than the mass transfer rate of O$_2$ through the cathodic catalyst layer. Hence, only the mass transfer resistance within cathode (i.e. the Warburge impedance (W)) was considered and was connected with the cathodic charge transfer resistance in series.

As shown in Fig. 4, the small semi-circle at higher frequency in the EIS spectra, which could be found from the change in the curvature indicated by the dashed circle, was attributed to the anodic oxidation of H$_2$. Alternatively, the large semi-circle in the low frequency region of the spectra was attributed to the cathodic reduction of O$_2$ at high charge transfer resistance and CPE(C). According to the equivalent circuit, the fitted curves of electrocatalyst layers with various Nafion contents were in agreement with the experimental results, as shown in Fig. 4. At a potential of 0.6 V, the anodic and cathodic charge transfer resistances of an electrocatalyst layer with a Nafion content of 35 wt% were lower than that of 50 wt% (Table 1). The obscure infinite diffusion impedance (45° straight line) for 50% Nafion content might cause by the adsorption of trace species (such as CO, H$_2$S and NH$_3$) existed in the hydrogen fuel [27,28]. The Warburge impedance (the mass transfer resistance within the cathode) of an electrocatalyst layer with a Nafion content of 35 wt% was 1.69 × 10^{-3} Ω cm^2 and was lower than that of Nafion content of 50 wt% (3.35 × 10^{-3} Ω cm^2). The aforementioned results were correlated well with those obtained from the polarization curves (Fig. 1) and the surface morphology experiments (Fig. 2).
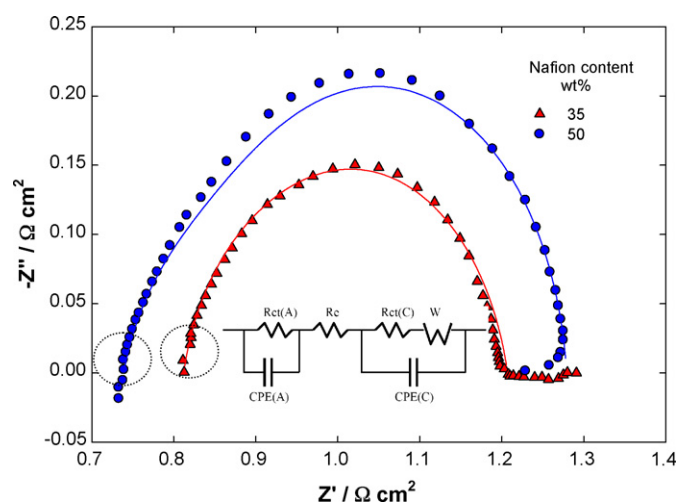
3.2. Optimization of the composition of the cathodic electrocatalyst layer

As previously mentioned, the optimal Nafion content of the electrocatalyst layers was 35 wt%. Moreover, 10 wt% 5–15 nm SiO$_2$ powder was added to the anodic catalyst slurry (at a weight ratio of 20 wt% Pt/C and Nafion = 0.65/0.35) to prevent the loss of humidity [29–31]. However, humidity produced via ORR on the cathode of a PEMFC might cause water flooding conditions in the micropores of the catalyst layer. Hence, the PTFE was added to the cathodic catalyst layer and to suppress water flooding effects. The optimal composition of the cathodic catalyst layer was studied by applying the mixture design method.

Based on the results described in Section 3.1, the lower limit of Pt/C (20 wt%) content and the upper limit of the Nafion and PTFE content were set to 0.5. Furthermore, to ensure proton transfer, the lower limit of the Nafion content was set to 0.2. Therefore, as illustrated in Fig. 5, the weight fractions of Pt/C (20 wt%), Nafion and PTFE ranged between 0.5 and 0.8, 0.2 and 0.5, and 0 and 0.3, respectively. In the mixture design approach, the actual amount of a single ingredient does not affect the outcome of the procedure. Rather, the relative proportion of the ingredients is varied to optimize the composition of a material. The sum of the fractions of all of the ingredients was equal to 1.

The cathodic catalyst layers were prepared based on the weight fractions illustrated in Table 2, and the MEA was prepared from the anodic catalyst layer, the cathodic catalyst layer and Nafion film, according to a hot pressing procedure. Based on the polarization curves of the PEMFC single cell, the relationship between the power density and the current density was evaluated, as shown in Fig. 6. The maximum power densities (P_{max}) of various cathodic compositions were used as the response of the mixture design approach, as shown in the last column of Table 2 (y). The P_{max} values (y values in

Fig. 4. Electrochemical impedance spectroscopies of PEMFC at 0.6 V with various Nafion content in the electrocatalyst layers. Pt loadings of cathode and anode = 0.2 mg cm^{-2}, geometric area of electrocatalyst layer = 1.0 cm^2. Hot pressing conditions: pressure = 10 kg cm^{-2}, T = 160 °C, t = 2 min. Operating conditions of PEMFC: T_{cell} = 60 °C, H$_2$ flow rate = 30 ml min^{-1}, O$_2$ flow rate = 30 ml min^{-1}, temperature of cathodic humidifier = 60 °C, temperature of anodic humidifier = 65 °C. Ac impedance conditions: f = 0.01–10^5 Hz, amplitude = 10 mV.
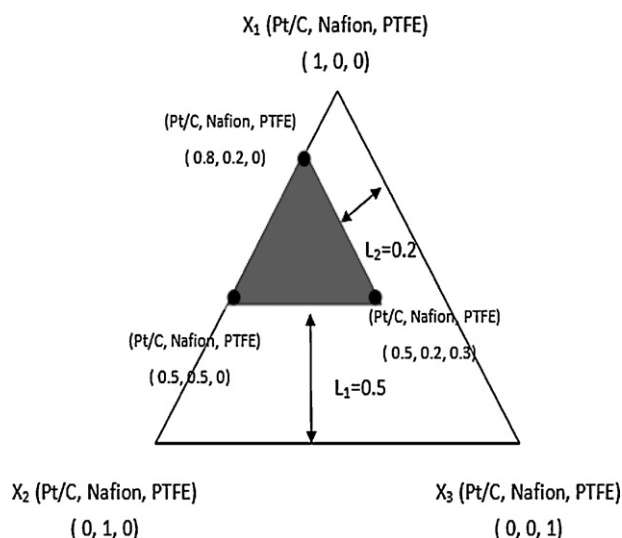

Fig. 5. Mixture design of ternary compositions of cathodic catalyst layer.

Table 2
Mixture design matrix and experimental responses of cathodic catalyst layer of PEMFC.

Run	Real composition[a]			Pseudo-composition[a]			Response (y)mW cm^{-2}
	X_1	X_2	X_3	Y_1	Y_2	Y_3	
1	0.8	0.2	0	1	0	0	195.4 ± 13.1
2	0.5	0.5	0	0	1	0	193.3 ± 17.5
3	0.5	0.2	0.3	0	0	1	198.5 ± 14.1
4	0.7	0.3	0	2/3	1/3	0	242.0 ± 13.3
5	0.6	0.4	0	1/3	2/3	0	228.0 ± 15.3
6	0.5	0.4	0.1	0	2/3	1/3	201.1 ± 16.4
7	0.5	0.3	0.2	0	1/3	2/3	198.4 ± 14.1
8	0.7	0.2	0.1	2/3	0	1/3	231.7 ± 18.1
9	0.6	0.2	0.2	1/3	0	2/3	145.6 ± 15.2
10	0.6	0.3	0.1	1/3	1/3	1/3	230.3 ± 11.0

Pt loadings of cathode and anode = 0.2 mg cm^{-2}, geometric area of electrocatalyst layer = 1.0 cm^2, anodic catalyst layer compositions: (Pt/C, dry Nafion, SiO$_2$) = (0.585, 0.315, 0.100). Hot pressing conditions: pressure = 10 kg cm^{-2}, T = 160 °C, t = 2 min. Operating conditions of PEMFC: T_{cell} = 60 °C, H$_2$ flow rate = 30 ml min^{-1}, O$_2$ flow rate = 30 ml min^{-1}, temperature of cathodic humidifier = 60 °C, temperature of anodic humidifier = 60 °C.

[a] The subscripts 1, 2 and 3 represent 20 wt% Pt/C, Nafion and PTFE, respectively.

Table 2) of the catalyst layers were between 145.6 mW cm^{-2} ((X_1, X_2, X_3) = (0.6, 0.2, 0.2)) and 242.0 mW cm^{-2} ((X_1, X_2, X_3) = (0.7, 0.3, 0)).

To achieve a statistically significant regression equation of the experimental results, the actual compositions of the three components (X_1, X_2, X_3) were linearly transformed to pseudo-compositions (Y_1, Y_2, Y_3), according to the following equation:

$$Y_i = \frac{X_i - L_i}{1 - L} \qquad (1)$$

where L_i is the lower limit of the constraints (L_1 = 0.5, L_2 = 0.2, L_3 = 0) (Fig. 5), and L is the sum of L_i (=0.7). The actual weight fractions and pseudo-compositions are provided in columns 2 and 3 of Table 2.
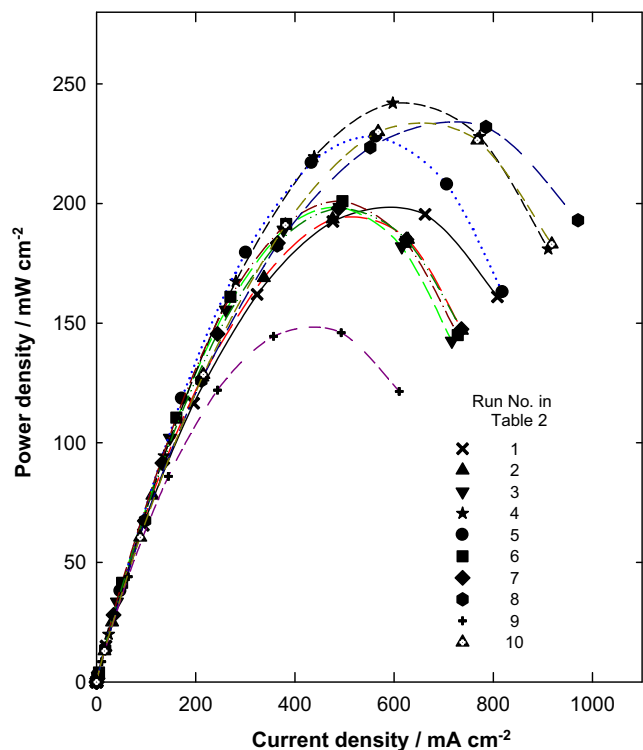

Fig. 6. Effect of current density on the power density of PEMFCs for various compositions of cathodic catalyst layer illustrated in Table 2. Pt loadings of cathode and anode = 0.2 mg cm^{-2}, geometric area of electrocatalyst layer = 1.0 cm^2, anodic catalyst layer compositions: (Pt/C, dry Nafion, SiO$_2$) = (0.585, 0.315, 0.100). Hot pressing conditions: pressure = 10 kg cm^{-2}, T = 160 °C, t = 2 min. Operating conditions of PEMFC: T_{cell} = 60 °C, H$_2$ flow rate = 30 ml min^{-1}, O$_2$ flow rate = 30 ml min^{-1}, temperature of cathodic humidifier = 60 °C, temperature of anodic humidifier = 60 °C.

Using P_{max} as the response (y) (last column of Table 2), the approximate model was evaluated with Statistical Analysis System (SAS) software. The coefficients of the regression equation were calculated using the appropriate formulas.

$$y = 204.4Y_1 + 198.6Y_2 + 188.4Y_3 + 167.5Y_1Y_2 \,(R^2 = 0.99) \qquad (2)$$

R^2 is a statistical measure of the fit of a regression equation to the experimental data. The regression model provided a good fit of the experimental data, and R^2 value of 0.99 was obtained [32]. The regression equation (Eq. (2)) and the constraint of $Y_1 + Y_2 + Y_3 = 1$ were used to construct contour plots of P_{max} versus the composition of the cathodic catalyst layer, as shown in Fig. 7. The results indicated that the value of P_{max} decreased with an increase in the pseudo-composition of PTFE (Y_3) (Fig. 7). Moreover, a relatively high P_{max} (240–260 mW cm^{-2}) was obtained when the pseudo-composition of PTFE was between 0 and 0.3 (or a weight fraction (X_3) of 0–0.09). Due to its hydrophobic nature, a suitable amount of PTFE increased the three-phase areas and pathways in the cathodic catalyst layer, which improved the power density of the PEMFC. However, because PTFE was an electric and ionic insulator, excess PTFE depressed the performance of the PEMFC.

3.2.1. Verification of the mixture design model

To verify the appropriate model of Eq. (2), three sets of compositions located in the uppermost P_{max} region of Fig. 7 were selected and used to assemble several MEAs and PEMFCs. As illustrated in Table 3, the experimental P_{max} of the PEMFCs was 246.0–266.5 mW cm^{-2}, which was in agreement with the predictions of the model (239.6–256.6 mW cm^{-2}).

3.2.2. Effect of the weight ratio of PTFE and Nafion

As shown in Table 3, the highest value of P_{max} (266.5 mW cm^{-2}) was obtained at a Pt(20%)/C weight fraction of 0.68. Thus, the optimal PTFE content was identified by varying the PTFE/Nafion ratio from 0 (0/0.32) to 0.23 (0.06/0.26) at a constant Pt(20%)/C ratio of 0.68. As shown in Fig. 8, the PEMFC displayed the highest potential at a PTFE/Nafion weight ratio of 0.10 (0.03/0.29). Moreover, electrochemical impedance spectra of PEMFCs containing cathodic catalyst layers with different PTFE/Nafion ratios were obtained via AC impedance analysis and were similar to those shown in Fig. 4. The parameters of the equivalent circuit under OCP and 0.6 V were provided in Table 4.

The charge transfer resistance Rct = RT/nFi_0 and the Warburg impedance can be expressed as [33]

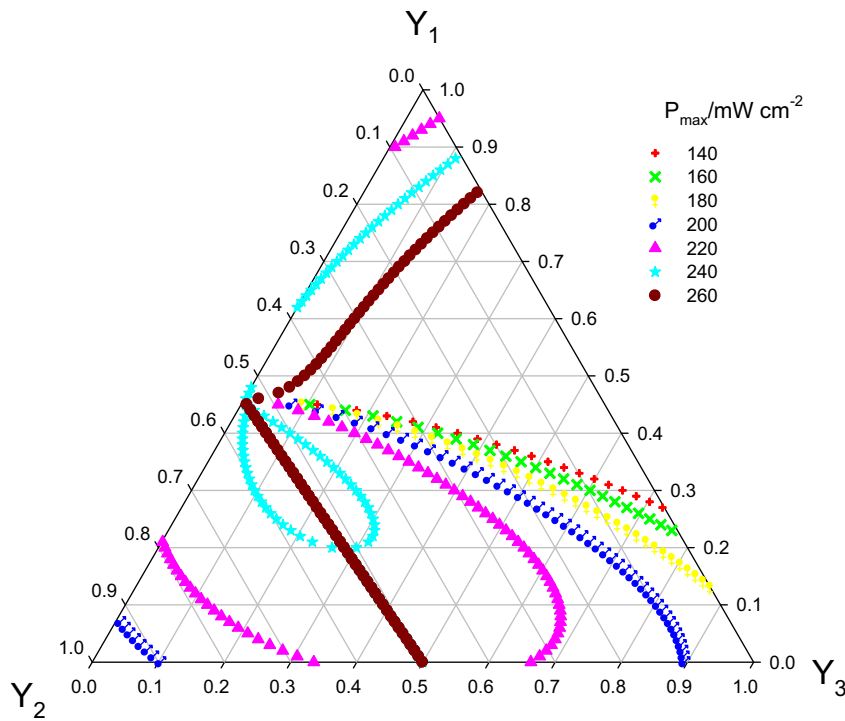$$W = \left(\frac{2}{\omega}\right)^{1/2} \sigma \qquad (3)$$

Fig. 7. Constant power density contour lines versus the compositions of cathodic catalyst layer.

Table 3
Effect of the compositions of cathodic catalyst layer on P_{max}.

Pseudo-composition			Real composition			P_{max}/mW cm^{-2}	
Y_1	Y_2	Y_3	X_1 (Pt/C)	X_2 (Nafion)	X_3 (PTFE)	Predict value[a]	Exp. data
0.73	0.10	0.17	0.72	0.23	0.05	239.6	246.0
0.60	0.30	0.10	0.68	0.29	0.03	252.8	266.5
0.53	0.43	0.03	0.66	0.33	0.01	256.6	256.0

Pt loadings of cathode and anode = 0.2 mg cm^{-2}, geometric area of electrocatalyst layer = 1.0 cm^2, anodic catalyst layer compositions: (Pt/C, dry Nafion, SiO$_2$) = (0.585, 0.315, 0.100) Hot pressing conditions: pressure = 10 kg cm^{-2}, T = 160 °C, t = 2 min. Operating conditions of PEMFC: T_{cell} = 60 °C, H$_2$ flow rate = 30 ml min^{-1}, O$_2$ flow rate = 30 ml min^{-1}, temperature of cathodic humidifier = 60 °C, temperature of anodic humidifier = 60 °C.

  [a] The predict values were calculated by using model equation of mixture design (Eq. (2)).

where ω is the frequency, and

$$\sigma = \left(\frac{RT}{2^{1/2} n^2 F^2 A} \right) (D_O^{-1/2} C_O^{-1} + D_R^{-1/2} C_R^{-1}) \qquad (4)$$

where T, n, F, A, D_O, D_R, C_O, and C_R are the temperature, number of electron transfer, Faraday constant, surface area, diffusivities of oxygen and water molecules, and concentration of oxygen and water molecules, respectively. As indicated in Eqs. (3) and (4), the Warburg impedance is proportional to $D_O^{-1/2}$ for the constant concentration of oxygen at OCP, i.e. a higher Warburg impedance is

obtained for a lower diffusivity of oxygen within the electrocatalyst layer.

As shown in the table, the mass transfer resistance (Warburg impedance) decreased with an increase in the PTFE/Nafion weight ratio due to the hydrophobic nature of PTFE, which increased the mass transfer rate of the reactants. Moreover, as the PTFE/Nafion ratio increased from 0 (0/0.32) to 0.23 (0.06/0.26), the Warburg impedance of the cathodic catalyst layer at OCP and 0.6 V decreased from 0.36 and 4.32 × 10^{-3} Ω cm^2 to 0.16 and 1.91 × 10^{-3} Ω cm^2, respectively. Compared with OCP, a higher Warburg resistance

Table 4
Effect of PTFE/Nafion weight ratio in the cathodic catalyst layer on the parameters of the equivalent circuit of PEMFC.

PTFE/Nafion	Bias	Rct(A) Ω cm^2	Re Ω cm^2	Rct(C) Ω cm^2	W ×10^{-3} Ω cm^2
0 (0/0.32)	OCP	0.19	0.78	6.01	0.36
	0.6 V	0.05	0.84	0.37	4.32
0.10 (0.03/0.29)	OCP	0.17	1.31	3.59	0.19
	0.6 V	0.06	0.80	0.30	2.32
0.23 (0.06/0.26)	OCP	0.12	1.28	9.66	0.16
	0.6 V	0.05	0.82	0.40	1.91

Pt loadings of cathode and anode = 0.2 mg cm^{-2}, geometric area of electrocatalyst layer = 1.0 cm^2, anodic catalyst layer compositions: (Pt/C, dry Nafion, SiO$_2$) = (0.585, 0.315, 0.100). Hot pressing conditions: pressure = 10 kg cm^{-2}, T = 160 °C, t = 2 min. Operating conditions of PEMFC: T_{cell} = 60 °C, H$_2$ flow rate = 30 ml min^{-1}, O$_2$ flow rate = 30 ml min^{-1}, temperature of cathodic humidifier = 60 °C, temperature of anodic humidifier = 60 °C.
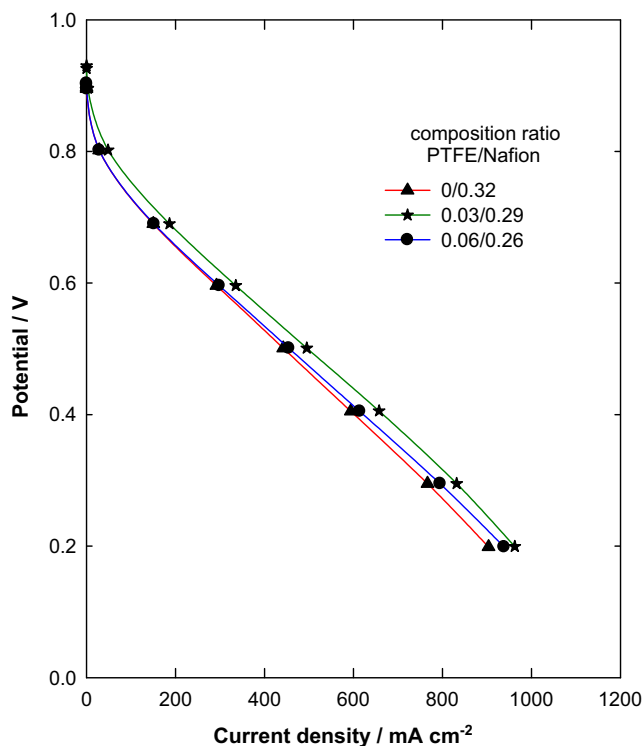
Fig. 8. Polarization curves of PEMFC for Pt/C weight fraction of 0.68 and various PTFE/Nafion composition ratios within the cathodic catalyst layer. Pt loadings of cathode and anode = 0.2 mg cm^{-2}, geometric area of electrocatalyst layer = 1.0 cm^2, anodic catalyst layer compositions: (Pt/C, dry Nafion, SiO$_2$) = (0.585, 0.315, 0.100). Hot pressing conditions: pressure = 10 kg cm^{-2}, T = 160 °C, t = 2 min. Operating conditions of PEMFC: T_{cell} = 60 °C, H$_2$ flow rate = 30 ml min^{-1}, O$_2$ flow rate = 30 ml min^{-1}, temperature of cathodic humidifier = 60 °C, temperature of anodic humidifier = 60 °C.

found for 0.6 V was deduced with the decrease in the O$_2$ diffusivity, which was due to the decrease in the porosity of cathodic catalyst layer by the water produced at a higher ORR rate. However, at a PTFE/Nafion ratio of 0.10 (0.03/0.29), the minimum cathodic charge transfer resistance (Rct(C)) at OCP and 0.6 V was 3.59 and 0.30 Ω cm^2, respectively. Hence, the optimal Pt(20%)/C, Nafion and PTFE weight fraction of the cathodic catalyst layer were 0.68, 0.29 and 0.03, respectively.

4. Conclusions

When the PEMFC was operated under kinetic control, the current density increased with an increase in the Nafion content of the electrocatalyst layer due to an increase in the contact and utility of the Pt/C electrocatalyst. Alternatively, when the PEMFC was operated under mixed control, the power density decreased to 191.5 mW cm^{-2} as the Nafion content increased to 50% because the micropores and channels of the electrocatalyst layer became blocked with excess Nafion. However, as the Nafion content of the electrocatalyst layers increased from 20 to 35 wt%, the power density of the PEMFC increased from 127 to a maximum value of 239.5 mW cm^{-2}. PTFE was added to the cathodic catalyst layer to improve water management, and the optimal cathodic catalyst layer composition was obtained by applying a mixture design approach, where the power density of the home-made PEMFC was used as the response. The results indicated that the optimal PTFE content of the cathodic catalyst layer was 0–0.09 wt%, and high P_{max} values (240–260 mW cm^{-2}) were achieved. Moreover, by fine tuning the weight ratios of PTFE and Nafion, the optimal composition of the cathodic catalyst layer was identified. Namely, the optimal

weight fraction of Pt(20%)/C, Nafion and PTFE was 0.68, 0.29 and 0.03, respectively, and a P_{max} of 266.5 mW cm^{-2} was obtained.

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