

Dependence of optimum Nafion content in catalyst layer on platinum loading

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Abstract

In polymer electrolyte membrane fuel cells (PEMFC), Nafion is used not only as a membrane placed between the anode and the cathode, but also as an important component of the active layer in a gas diffusion electrode. The content of Nafion ionomer in the electrode affects simultaneously the gas permeability, the catalytic activity and the ionic resistance. Hence, an optimum Nafion content in the catalyst layer is necessary for good performance. This study examines the dependence of optimum Nafion content in the catalyst layer on platinum loading. Investigations are also made of the variation in cell impedance, electrochemical surface area (ESA) and percentage Pt utilization with change in Nafion loading in the catalyst layer. It has been generally reported that the optimum Nafion loading is in the range of 30–36 wt.%, irrespective of the platinum loading. The present study indicates that the optimum Nafion loading should in fact depend on the platinum loading. For electrodes with different platinum loadings of 0.5, 0.25 and 0.1 mg Pt cm⁻², the best performance was obtained at different Nafion loadings of 20, 40 and 50 wt.%, respectively. It is also found that the optimum Nafion loading does not depend on the membrane thickness.

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1. Introduction

Polymer electrolyte membrane fuel cell (PEMFC) technology has advanced considerably and a high level of performance has been achieved by adopting various strategies. Major progress in enhancing performance and reducing the platinum loading has been made possible by: (i) using platinum supported on high surface-area carbon as an electrocatalyst rather than pure platinum black; (ii) impregnation of a proton conductor (Nafion) into the catalyst layer of the gas-diffusion electrode [1–3]; (iii) depositing a thin layer of platinum on the front side of the electrode [4]; (iv) using thinner membranes [5,6]; (v) adopting different electrode preparation procedures such as spraying [7], rolling [8] and screen printing [9]; (vi) depositing a thin layer of supported electrocatalyst and a proton conductor on the proton conducting membrane [10–12] or on an uncatalyzed electrode [13,14]. Still further increase in fuel cell performance has been

achieved by using supported Nafion membranes developed by W.L. Gore and associates in the USA [15–17]. Gore membrane and membrane electrode assemblies (MEAs) have demonstrated the best fuel cell performance to date, and several of the fuel cell developers are using this technology [18].

In spite of the above advances, the most preferred catalyst in PEMFCs is still platinum, whose resources are both limited and costly [19]. Thus, to establish the commercialization of PEMFCs, it is important to improve platinum utilization [7,19] in the electrodes and enhance cell performance. One way to achieve these two objectives is through optimization of the electrode preparation parameters, such as the Nafion content in the electrodes.

A PEMFC electrode essentially consists of a gas-diffusion layer and a catalyst layer (active layer). The gas-diffusion layer is highly porous and hydrophobicized with PTFE polymer. The catalyst layer contains the electrocatalyst, usually platinum or platinum supported on carbon, Nafion ionomer, and sometimes PTFE. This layer is fabricated by mixing the electrocatalyst with the ionomer solution or by impregnation of an ionomer solution into a porous catalyst layer [2,20,21]. The presence of thin Nafion ionomer

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films that cover the catalyst particles is important for constructing highly reactive gas-diffusion electrodes [22,23]. Three-phase contact of the reactant gases, electrolyte (Nafion) and catalyst is required for electrochemical reaction to take place. Nafion ionomer in the catalyst layer also helps to retain moisture and prevent membrane dehydration, especially at high current densities. An optimum Nafion content in the catalyst layer is necessary for good performance.

Nafion loading [2] in the electrode is generally expressed as (mg cm^{-2}) (i.e., dry weight of Nafion ionomer divided by the geometric area of the electrode) or as wt.% of Nafion (dry weight of Nafion ionomer divided by the total weight of Pt/C catalyst and Nafion ionomer, multiplied by 100).

Though many studies have been reported on the effect of Nafion content in the catalyst layer, the best results have been obtained at different loadings by different researchers. Antolini et al. [24] has suggested an empirical equation to calculate optimum loading, i.e.

$$\text{optimum Nafion loading (mg cm}^{-2}\text{)} = 56 \times \frac{L_{\text{Pt}}}{P_{\text{Pt}}} \quad (1)$$

where L_{Pt} is the platinum loading (mg cm^{-2}) and P_{Pt} the wt.% of Pt supported on carbon. The optimum Nafion loading calculated using this equation, expressed in wt.%, is 36 wt.% for all platinum loadings. Passalacqua et al. [25] are of the view that the optimum Nafion content is 33 wt.%, as are Gamburzev and Appleby [26]. On the other hand, Qi and Kaufman [27] have reported an optimum Nafion content of 30 wt.%. Thus, the optimum Nafion content reported is generally in the range of 30–36 wt.%, irrespective of the platinum loading in the electrodes. A problem may arise, however, if a fixed wt.% of Nafion is used without consideration of the platinum loading. In the case of electrodes with high platinum loadings, the Nafion layer thickness will be too high, which may cause high mass transport resistance. Alternatively, in electrodes with low platinum loadings the Nafion ionomer film thickness will be too small and the ionomer quantity will be insufficient to establish a three-phase contact. Thus, there must be an optimum thickness of the ionomer film for good performance, as suggested elsewhere [28]. Watanabe has reported that $0.2 \mu\text{m}$ is the critical thickness of the Nafion film on the catalyst surface up to which the diffusion process of reactant gases to the catalyst sites is not the rate-determining step [29]. In other words, the optimum Nafion content required for high electrode performance should depend on the platinum loading.

This paper examines the dependence of optimum Nafion content in the catalyst layer on platinum loading. Investigations are also made of the variation in cell impedance, electrochemical surface area (ESA) and percentage Pt utilization with change in Nafion loading in the catalyst layer.

Table 1
Typical characteristics of SIGRACET gas-diffusion media

Property	Typical values for GDL 10BB grade
Areal weight (g m^{-2})	120
Porosity (%)	84
Electrical resistance (Ωcm^2)	10
Air permeability ($\text{cm}^3 \text{cm}^{-2} \text{s}^{-1}$)	2.5
Thickness (mm)	0.42

2. Experimental

2.1. Preparation of PEMFC electrodes

Commercially available SIGRACET gas-diffusion media (GDL 10BB grade) from SGL Carbon Japan Ltd. was used for the preparation of the fuel cell electrode. Typical characteristics of this material are given in Table 1. The electrocatalyst used for the preparation of electrode was 20 wt.% Pt on Vulcan XC-72, from E-TEK Division of De Nora, Inc., USA, with a surface area of $100 \text{ m}^2 \text{ g}^{-1}$. A 5 wt.% Nafion solution supplied by DuPont, Inc., USA was used as the binder in the catalyst layer. The Nafion content was checked by evaporating a known volume of the solution to dryness. Analytical grade solvent were used for the preparation of the catalyst slurry.

For the preparation of the electrode, the required quantity of 20 wt.% Pt/C was placed in a beaker and wetted with a few drops of water. The required quantity of 5 wt.% Nafion solution and isopropyl alcohol were added and ultrasonicated for 30 min. The catalyst ink thus obtained was coated on the SIGRACET gas-diffusion media by a brush method and dried at 80°C for 30 min. Electrodes were prepared with a platinum loading of 0.5, 0.25 and $0.1 \text{ mg Pt cm}^{-2}$ with various percentages of Nafion ionomer in the catalyst layer.

2.2. Preparation of membrane electrode assembly (MEA)

Nafion 115 and Nafion 1035 (DuPont, Inc., USA) were used as the polymer electrolyte membrane. Prior to use, each membrane was boiled in 3% hydrogen peroxide to remove any organic impurities, washed with water, and then boiled in 1 M sulfuric acid to remove any metallic impurities as well as to convert the membrane fully to the H^+ form [2]. Finally, it was boiled in distilled water. The MEA was prepared by placing two electrodes (active area: 5 cm^2), with the same platinum loading on both sides of a Nafion membrane and hot pressing at 130°C and 1000 psig for 2 min. A flexible silicone sheet was placed on the bottom platen of the hot press to obtain uniform MEA thickness, good electrode to membrane bonding, and good reproducibility.

2.3. Assembly of PEMFC

The MEA was placed between two silicone gaskets of thickness 0.24 mm and inserted between two graphite plates

with serpentine grooves, in a single cell test fixture supplied by Electrochem, Inc., USA. A uniform torque of 75 kgf·cm was applied to the eight bolts that were used to assemble the PEMFC.

2.4. Evaluation of electrodes/MEA

2.4.1. Current–voltage characteristics

The fuel cell was connected to the test station (Nara Cell Tech Corp., Korea) that was equipped with a gas humidifier, a mass flow controller, and a temperature indicator controller. Humidified hydrogen and oxygen gases were fed to the cell at a flow rate of $200 \text{ cm}^3 \text{ min}^{-1}$. The current–voltage (I – V) characteristics of the cell were evaluated at 80°C and 1 atm pressure by means of a potentiostat–galvanostat (HPCS1) along with a WBCS3000 battery cyler system supplied by WonA Tech, Korea.

2.4.2. Cell impedance

Cell impedance was measured using an EG&G PARC potentiostat–galvanostat (model 263A) along with a lock-in amplifier (model 5210). The impedance was determined at open-circuit at 25°C , with hydrogen and oxygen at ambient pressure.

2.4.3. Cyclic voltammetry

Cyclic voltammetry (CV) was carried out with an EG&G potentiostat–galvanostat in order to determine the ESA. For CV studies, argon was passed through the test electrode and hydrogen was passed through the counter electrode chamber. The counter electrode was also used as the reference electrode because of the negligible overpotential for hydrogen oxidation and reduction on platinum. The potential was then scanned between 50 and 800 mV versus the reversible

hydrogen electrode (RHE) at a rate of 20 mV s^{-1} . The ESA of the Pt catalyst was evaluated from the voltammogram by dividing the charge (in μC) that corresponded to the area under the hydrogen desorption region by $210 \mu\text{C}$ [4,24,29]. The roughness factor (RF) was calculated by dividing the ESA by the geometric area (5 cm^2) of the electrode. Utilization of the Pt catalyst was evaluated by dividing the RF of the electrode by the theoretical RF (250) for 20% Pt/C, which had a surface area of $100 \text{ m}^2 \text{ g}^{-1}$ and was used in the present study.

3. Results and discussion

Electrodes with a platinum loading of 0.25 mg cm^{-2} were prepared and tested at 80°C as described earlier. The current–voltage characteristics of electrodes with different Nafion contents in the catalyst layer and using a Nafion 115 membrane are presented in Fig. 1. The electrode performance improves with increase in Nafion content up to 40%, but then slightly decreases with further increase in Nafion content. This latter behaviour may be due to blocking of the catalyst sites, reduced gas permeability, and increased mass transport polarization. The transport limitation results from an increase in the distance through which the gas has to permeate, diffuse, or migrate. By contrast, the poor electrode performance at low Nafion content may be the result of: (i) higher cell impedance, since proton-conducting Nafion ionomer fragments may be discontinuous [27]; (ii) poor contact of the electrolyte with the catalyst, i.e. a smaller number of three-phase interfaces and hence a lower ESA/Pt utilization.

Impedance studies were performed to examine the variation of cell impedance with change in Nafion loading.

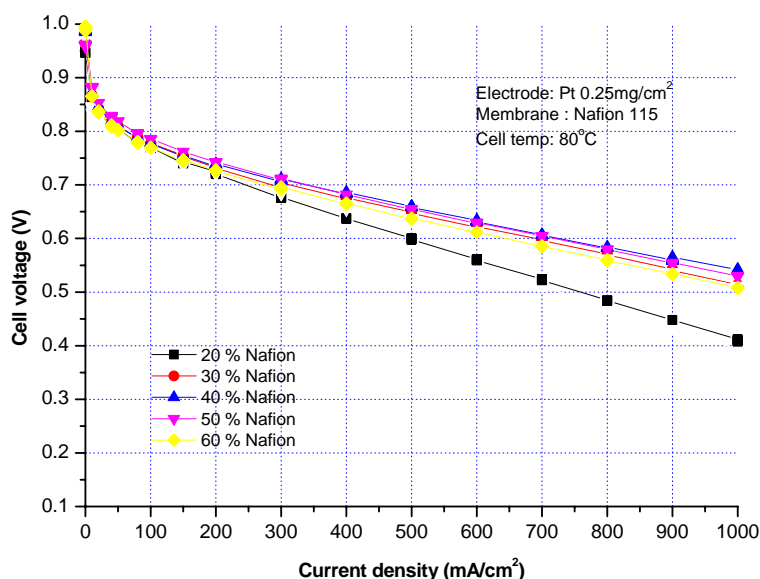


Fig. 1. Current–voltage characteristics of electrodes with 0.25 mg cm^{-2} of Pt and various Nafion contents in catalyst layer, using Nafion 115, at 80°C , 1 atm.

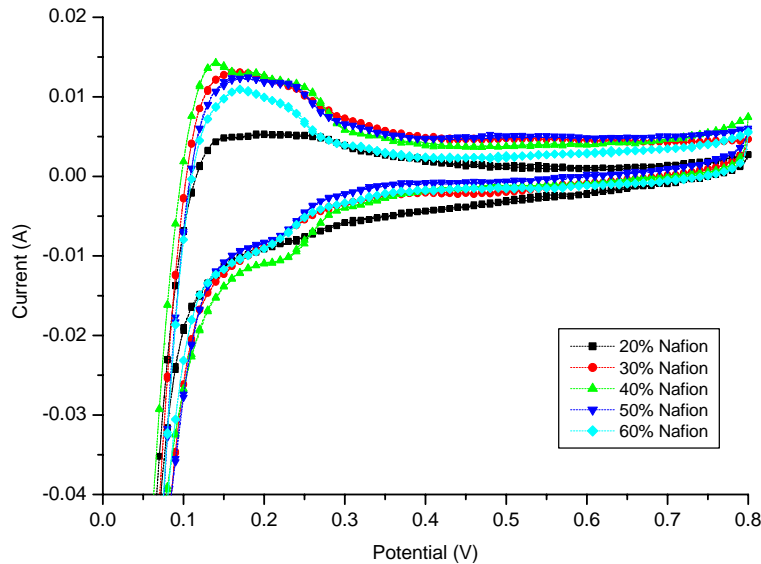


Fig. 2. Cyclic voltammograms of electrodes with 0.25 mg cm^{-2} of Pt and various Nafion contents in catalyst layer, at a scan rate of 20 mV s^{-1} .

The impedance of cells with a Nafion 115 membrane electrolyte and electrodes containing 20, 30, 40, 50 and 60 wt.% Nafion ionomer was found to be 65, 63, 57, 59 and 60 $\text{m}\Omega$, respectively. The cell impedance decreases with increase in Nafion loading, reaches a minimum, and then increases with further addition of Nafion. The lowest cell impedance was observed at 40 wt.% Nafion, which may be one of the reasons for the highest I - V performance observed at this value.

Further, CV studies were carried out to understand the variation of ESA and percentage Pt utilization with Nafion loading. The voltammograms of electrodes, each with a Pt loading of 0.25 mg cm^{-2} but with a different Nafion content in the catalyst layer, are presented in Fig. 2. The ESA, RF and percentage Pt utilization were calculated from the CV

Table 2

ESA, RF and percentage Pt utilization of electrodes with 0.25 mg cm^{-2} Pt loading

Nafion percentage	ESA (cm^2)	Roughness factor	Percentage Pt utilization
20	266	53	21
30	628	126	50
40	648	130	52
50	586	117	47
60	457	91	37

data and the results are given in Table 2. All three parameters increase as the Nafion content increases, reach maximum values at 40 wt.% Nafion, and then decrease with further increase in Nafion content. At 40 wt.% Nafion, the RF is 130

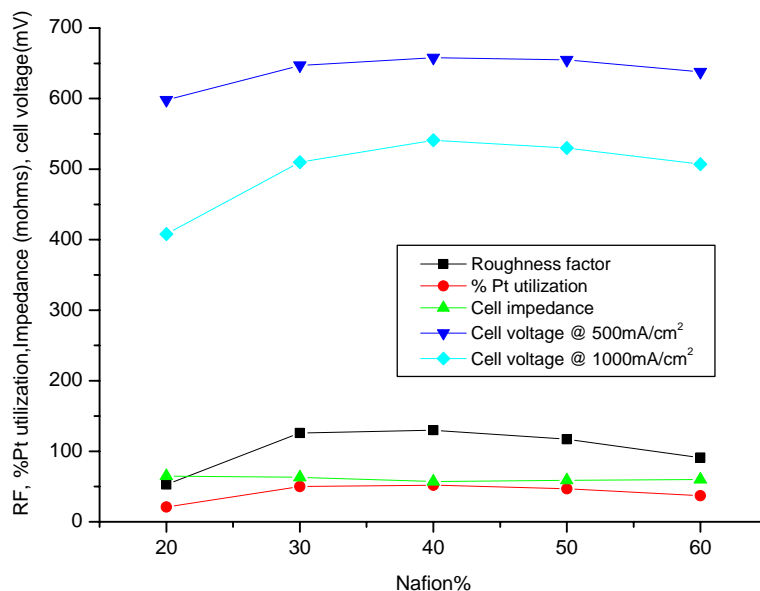


Fig. 3. Effect of Nafion content (wt.%) in catalyst layer on RF, percentage Pt utilization, impedance and current-voltage characteristics.

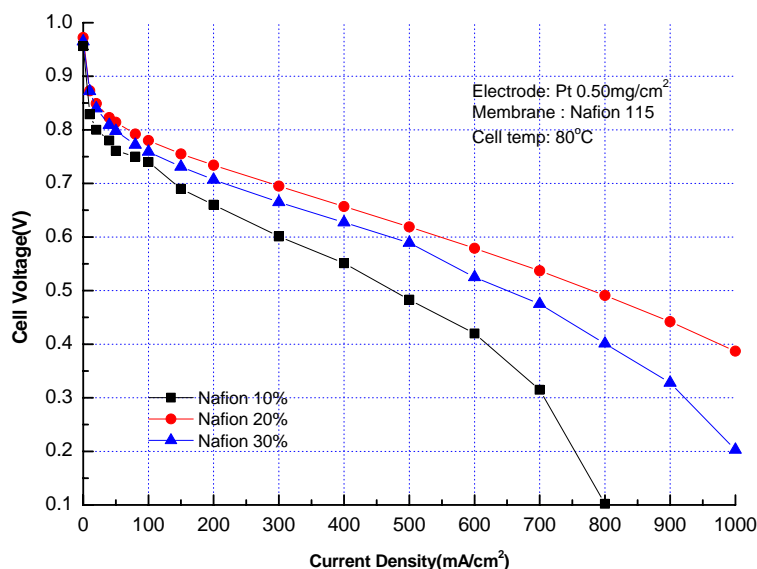


Fig. 4. Current–voltage characteristics of electrodes with 0.5 mg cm^{-2} of Pt and various Nafion contents in catalyst layer, using Nafion 115, at 80°C , 1 atm.

and the Pt utilization is 52%. The correlation of I – V performance with RF, percentage Pt utilization and impedance can be clearly seen in Fig. 3.

Electrodes with higher (0.5 mg cm^{-2}) and lower (0.1 mg cm^{-2}) Pt loadings were prepared and tested to examine the variation of optimum Nafion content with Pt loading.

The current–voltage characteristics of the electrodes with a Pt loading of 0.5 mg cm^{-2} and 10, 20 or 30 wt.% Nafion in the catalyst layer, and tested using a Nafion 115 membrane are presented in Fig. 4. The performance is found to increase as the Nafion content is increased from 10 to 20 wt.%. Further increase to 30 wt.% Nafion results in a decrease in cell performance. The best electrode performance is obtained at

20 wt.% Nafion. Thus, when the Pt loading is increased from 0.25 to 0.5 mg cm^{-2} , the optimum Nafion content decreases.

The current–voltage characteristics of a fuel cell with 0.1 mg cm^{-2} of Pt, but with different Nafion contents are given in Fig. 5. The electrode performance increases with increase in Nafion content and maximum performance is obtained at 50 wt.%. Further increase in Nafion content causes a slight decrease in cell performance, but no sharp decline is observed even at 60 wt.% Nafion. Thus, when the Pt loading is decreased from 0.25 to 0.1 mg cm^{-2} , the optimum Nafion content increases.

From the above results, it can be seen that the optimum Nafion content depends on the platinum loading. For electrodes with 0.5, 0.25 and 0.1 mg cm^{-2} of Pt, the best

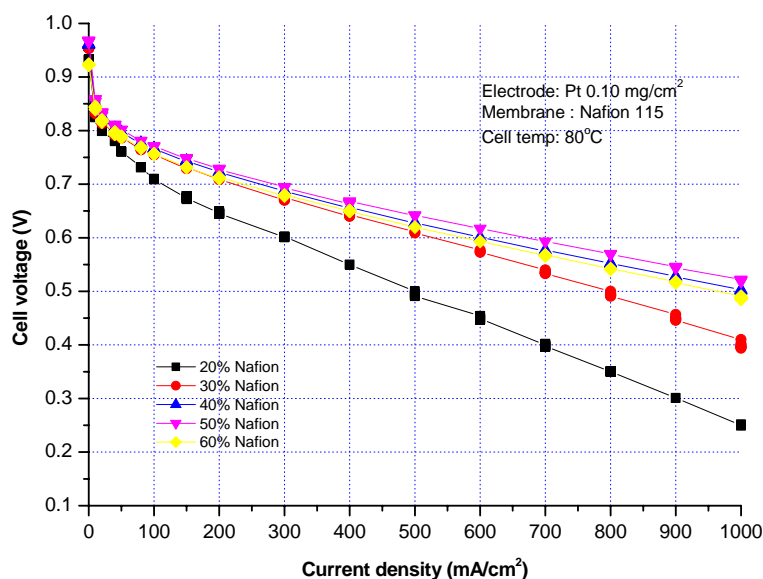


Fig. 5. Current–voltage characteristics of electrodes with 0.1 mg cm^{-2} of Pt and various Nafion contents in catalyst layer, using Nafion 115, at 80°C , 1 atm.

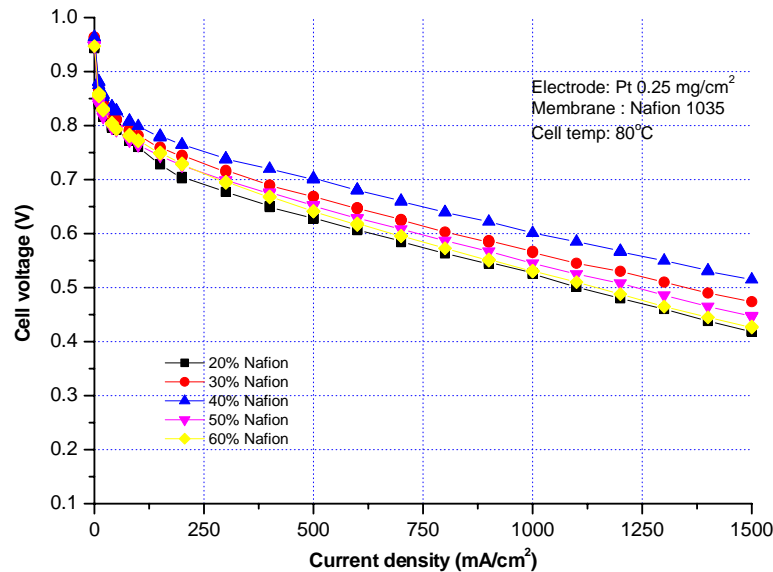


Fig. 6. Current–voltage characteristics of electrodes with 0.25 mg cm^{-2} of Pt and various Nafion content in catalyst layer, using Nafion 1035, at 80°C , 1 atm.

performance is obtained at 20, 40 and 50 wt.% Nafion, respectively.

Electrodes were also tested with a Nafion 1035 membrane to investigate whether the optimum Nafion requirement is influenced by the membrane thickness. The results obtained with Nafion 1035, using electrodes with a platinum loading of 0.25 mg cm^{-2} , are given in Fig. 6. The best performance is obtained at Nafion loading of 40 wt.%, as in the case of the Nafion 115 membrane. Thus, the optimum content of Nafion does not change with the membrane used. At 80°C , current densities of 500, 1000 and 1500 mA cm^{-2} were obtained at 0.7, 0.6 and 0.5 V, respectively. Some researchers have observed [30] the mass transport problem and a sudden drop in performance, even at 300 mA cm^{-2} , with electrodes that contain high contents of Nafion. In the present study, for electrodes with low Pt loadings, no sudden drop in performance has been observed even with 60 wt.% Nafion in the catalyst layer.

4. Conclusions

A proton-conducting ionomer is required in the catalyst layer of PEMFC electrodes to extend the three-phase contact between the reactant gases, the electrolyte and the catalyst so as to enhance the electrochemical reaction. Nafion ionomer in the catalyst layer also helps to retain moisture and prevent membrane dehydration, especially at high current densities. The content of Nafion ionomer affects simultaneously the gas permeability, the catalytic activity, and the ionic resistance. Hence, an optimum Nafion content in the catalyst layer is necessary for good performance.

The present study has established that the optimum Nafion content should depend on the platinum loading.

The numerical values of the optimum amounts of Nafion may, however, depend on the fabrication method [27]. For electrodes with different platinum loadings of 0.5, 0.25 and 0.1 mg cm^{-2} , the best performance is obtained at Nafion loadings of 20, 40 and 50 wt.%, respectively. From impedance and CV studies, it is found that cell impedance, ESA, roughness factor and percentage Pt utilization vary with the Nafion content in the electrode. At the optimum Nafion content, the value of the cell impedance is found to be the lowest and those for the ESA, the roughness factor and the Pt utilization are the highest. The present study also indicates that the optimum Nafion content does not depend on the membrane thickness. It is considered that there is scope for further improvement in both electrode performance and percentage Pt utilization by refining the optimum Nafion content, especially for electrodes with low Pt loadings.

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References

- [1] S. Srinivasan, E.A. Ticianelli, C.R. Derouin, A. Redondo, J. Power Sources 22 (1988) 359.
- [2] E.A. Ticianelli, C.R. Derouin, A. Redondo, S. Srinivasan, J. Electrochem. Soc. 135 (1988) 2209.

- [3] I.D. Raistrick, US Patent No. 4,876,115 (1989).
- [4] E.A. Ticianelli, C.R. Derouin, S. Srinivasan, J. Electroanal. Chem. 251 (1988) 275.
- [5] S. Srinivasan, D.J. Manko, H. Koch, E.A. Enayetullah, A.J. Appleby, J. Power Sources 29 (1990) 367.
- [6] S. Srinivasan, E.A. Ticianelli, M.A. Enayetullah, A. Parthasarathy, D.J. Manko, O. Velev, H.P. Dhar, C.R. Martin, A.J. Appleby, Fuel Cell Seminar Abstracts, Washington, DC, USA, 1990, p. 364.
- [7] G. Sasi Kumar, M. Raja, S. Parthasarathy, Electrochim. Acta 40 (1995) 285.
- [8] E. Gülzow, M. Schulze, N. Wagner, T. Kaz, A. Schneider, R. Reissner, Fuel Cells Bull. 2 (1999) 8.
- [9] C.S. Kim, Y.G. Chun, D.H. Peck, D.R. Shin, Int. J. Hydrogen Energy 23 (1998) 1045.
- [10] M.S. Wilson, S. Gottesfeld, J. Electrochem. Soc. 139 (1992) L28.
- [11] M.S. Wilson, S. Gottesfeld, J. Appl. Electrochem. 22 (1992) 1.
- [12] S. Gottesfeld, T.A. Zawodzinski, in: R.C. Alkire, H. Gerischer, D.M. Kolb, C.W. Tobias (Eds.), Advances in Electrochemical Science and Engineering, vol. 5, Wiley-VCH, Weinheim, Germany, 1997, p. 95.
- [13] H.P. Dhar, US Patent No. 5,313,863 (1994).
- [14] H.P. Dhar, J.H. Lee, K.A. Lewinski, in: Proceedings of Fuel Cell Seminar, Orlando, FL, USA, 1996, p. 583.
- [15] B. Bahar, A.R. Hobson, J.A. Kolde, US Patent No. 5,599,614 (1997).
- [16] H. Kato, US Patent No. 6,054,230 (2000).
- [17] V. Mehta, J.S. Cooper, J. Power Sources 114 (2003) 32.
- [18] P. Cosstamagna, S. Srinivasan, J. Power Sources 102 (2001) 242.
- [19] X. Cheng, B. Yi, M. Han, J. Zhang, Y. Qiao, J. Yu, J. Power Sources 79 (1999) 75.
- [20] Z. Poltarzewski, P. Staiti, V. Alderucci, W. Wieczorek, N. Giordano, J. Electrochem. Soc. 139 (1992) 761.
- [21] A. Pozio, M. De Francesco, A. Cemmi, F. Cardellini, L. Giorgi, J. Power Sources 105 (2002) 13.
- [22] G.G. Scherer, Solid State Ionics 94 (1997) 249.
- [23] M. Inaba, M. Uno, J. Maruyama, A. Tasaka, K. Katakura, Z. Ogumi, J. Electroanal. Chem. 417 (1996) 105.
- [24] E. Antolini, L. Giorgi, A. Pozio, E. Passalacqua, J. Power Sources 77 (1999) 136.
- [25] E. Passalacqua, F. Lufrano, G. Squadrito, A. Patti, L. Giorgi, Electrochim. Acta 46 (2001) 799.
- [26] S. Gamburgzev, A. Appleby, J. Power Sources 107 (2002) 5.
- [27] Z. Qi, A. Kaufman, J. Power Sources 113 (2003) 37.
- [28] Z. Siroma, T. Sasakura, K. Yasuda, M. Azuma, Y. Miyazaki, J. Electroanal. Chem. 546 (2003) 73.
- [29] M. Watanabe, H. Igarashi, K. Yosida, Electrochim. Acta 40 (1995) 329.
- [30] J.M. Song, S.Y. Cha, W.M. Lee, J. Power Sources 94 (2001) 78.