

Electrochimica Acta 47 (2002) 4079-4084



www.elsevier.com/locate/electacta

Preparation of platinum-ruthenium onto solid polymer electrolyte membrane and the application to a DMFC anode

Naoko Fujiwara*, Kazuaki Yasuda, Tsutomu Ioroi, Zyun Siroma, Yoshinori Miyazaki

Special Division of Green Life Technology, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

Received 15 April 2002; received in revised form 2 July 2002

Abstract

The 'impregnation-reduction method' has been investigated as a tool for the preparation of a direct methanol fuel cell (DMFC) anode. In this method, PtRu electrocatalysts were directly bonded onto a polymer electrolyte membrane by the chemical reduction of a mixture of Pt and Ru complexes impregnated in the membrane. The deposited PtRu particles were embedded in the $3-4 \mu m$ region of the membrane surface to form a porous and hydrophilic layer. The PtRu layers turned out to be applicable to the DMFC anode, despite their small active surface areas compared to PtRu nanoparticles used in the conventional method. Approximately, 3 mg cm⁻² of the PtRu layer exhibited better catalyst utilization and facilitated the release of evolving CO₂. This preparation technique is attractive for the application of various solid polymer electrolyte materials with low heat-resistance or various shapes, etc.

© 2002 Elsevier Science Ltd. All rights reserved.

Keywords: PtRu electrocatalyst; Impregnation-reduction method; PtRu-polymer electrolyte composite; Membrane-electrode assembly; Direct methanol fuel cell

1. Introduction

A direct methanol fuel cell (DMFC) based on a polymer electrolyte membrane (PEM) is attractive for transport and portable applications. Despite a great number of research and development studies on DMFCs, several problems still prohibit their practical uses. In particular, it is urgently necessary to develop novel membranes with low methanol permeation [1-4]and anode catalysts with high catalytic activity for methanol oxidation [5,6]. Most of the fabrication methods for membrane-electrode assemblies (MEAs) for DMFCs were developed on the basis of those of gas diffusion electrodes for polymer electrolyte fuel cells (PEFCs). A typical method is the hot-pressing of catalyst layers, which were prepared separately by painting, spraving or printing catalyst inks containing catalyst particles and a polymer electrolyte suspension,

onto a PEM [7–9]. In this paper, we observed hydrophilic electrodes with the same structure as those for a polymer electrolyte water electrolyzer, from the point that liquid methanol aqueous solution is supplied to an anode in the DMFC.

In previous studies [10-12], the 'impregnation-reduction' (IR) method was developed for direct contact of a PEM and metal electrodes under wet conditions to apply to a polymer electrolyte water electrolyzer. In the IR method, the cation-exchange membrane with a preexchange cationic metal species, e.g. $[Pt(NH_3)_4]^{2+}$, is subsequently immersed in the reduction solution, which reduces and displaces the metal towards the outer surface of the membrane. All procedures can be conducted below 80 °C in a wet state, which are much milder conditions compared to the hot-pressing method. The characteristics of the electrodes prepared by this method are a few microns in thickness, hydrophilic and porous. In addition, they exhibit excellent adhesion and durability, due to the fact that the metal particles are embedded in the membrane surface. Indeed, the Pt-PEM composite prepared by the IR method was

0013-4686/02/\$ - see front matter \odot 2002 Elsevier Science Ltd. All rights reserved. PII: S 0 0 1 3 - 4 6 8 6 (0 2) 0 0 4 1 4 - 0

^{*} Corresponding author. Tel.: +81-727-51-9653; fax: +81-727-51-9629

E-mail address: n-fujiwara@aist.go.jp (N. Fujiwara).

supplied for solid polymer electrolyte water electrolysis and the electrolyzer was put into practical use as a hydrogen generator or a hydrogen station for a PEFC [13–16]. The scale-up of the electrolyzer has succeeded up to 0.75 m² with a six-cell module [16]. Pt electrodes have been durable during the vigorous gas evolution due to their adhesive property and porous structure.

The application of such a satisfactory IR method to the preparation of MEA for DMFC will facilitate the release of the evolving CO_2 [17] and decrease the risk of electrodes peeling from the PEM due to the swelling of the PEM on absorbing methanol. The IR method, which is conducted at low temperature under wet conditions, is applicable to polymer electrolyte materials with poor heat-resistance or various shapes (e.g. tubes or spheres).

Fundamental studies for the oxidation of methanol were reported on Pt alloy electrodes bonded to a PEM by the reduction permeation (RP) method developed by Takenaka and Torikai [18,19]. A mixture of H_2PtCl_6 and a second metal chloride solution, and a reducing solution (e.g. NaBH₄, NH₂NH₂) were placed on both sides of the membrane, respectively. Pt alloy layers were formed on the surface of the membrane by permeation of reducing agents into the other side of the membrane. Ru or Sn alloyed with Pt increased the activity of methanol electro-oxidation in a sulfuric acid solution [20–22].

In this paper, the PtRu electrode, which is currently known to be the most active anode catalyst for methanol oxidation [2,23–25] was bonded directly onto a PEM by the IR method. The possibilities of a PtRu anode prepared by the IR method were investigated with the DMFC operation.

2. Experimental

2.1. Preparation of PtRu onto PEM by IR method

Fig. 1 is a schematic representation of the IR method for direct plating of PtRu onto a Nafion membrane. PtRu loading was performed on Nafion[®]117 (Du Pont), which is a typical perfluorocarbon sulfonic acid cationexchange membrane with an ion-exchange capacity of 0.909×10^{-3} eq. g⁻¹ and 180 µm thickness in the dry state. Tetraammineplatinum(II)chloride ([Pt(NH₃)₄]Cl₂ from Tanaka Precious Metals) and chloro pentaammineruthenium(III)chloride $([RuCl(NH_3)_5]Cl_2)$ from Johnson-Matthey) were used as PtRu precursors. Cation-exchange (impregnation) was carried out by immersing the H^+ form of the Nafion in aqueous solutions $(10^{-3}-10^{-2} \text{ M})$ of these Pt and Ru complexes overnight at room temperature (Fig. 1(i)). The membrane was washed with distilled water to remove the excess metal species. Subsequently, the membrane was immersed in 10^{-2} - 10^{-1} M of sodium borohydride $(NaBH_{4})$ solution at 60 °C for 5 h to precipitate PtRu (Fig. 1(ii)) on the surface of Nafion membrane. After the treatment in 1 M HCl aq. solution and distilled water at 80 °C, the Nafion-PtRu composite was successfully fabricated.

2.2. Characterization of PtRu layers of the composites

The concentration change in the precursor solution used for the impregnation step was monitored by ICP (Nippon Jarrell-Ash, ICAP-575 II) to determine the incorporated amounts of Pt and Ru complexes in the membrane. ICP analysis was also carried out to obtain the concentration of Pt and Ru eluted in the reduction or HCl solution. The chemical composition and loading amount of PtRu in the prepared composite were calculated by subtracting the eluting amount in the reduction step and HCl treatment from the incorporated amount in the ion-exchange step.



Fig. 1. Schematic representation of the PtRu-PEM composite prepared by the IR method: (i) the ion-exchange step; (ii) the reduction step.

4081

The X-ray diffraction (XRD) patterns for the PtRu layers were obtained on a JEOL X-ray diffractometer JDX-8020S using CuK α radiation source operating at 40 kV and 30 mA. The prepared composites were examined with a scanning electron microscope, SEM (Hitachi, S-2500), and the distribution of the PtRu layers was analyzed by an energy-dispersive spectrometer, EDS (Horiba, EMAX-3700).

2.3. Preparation of MEAs for DMFC

PtRu was deposited on only one side of a Nafion membrane by the same IR method described above and was applied to an anode in a DMFC. On the other hand, unsupported Pt black (from Johnson–Matthey, specific surface area 27 m² g⁻¹) was used as a cathode catalyst. The Pt black powders were polytetrafluor-oethylene (PTFE)-bonded (7 wt.%) by mixing with a PTFE dispersion and were suspended in 5 wt.% Nafion solution (Aldrich) to prepare the catalyst inks. The catalyst inks were spread onto PTFE blanks to form 4 mg cm⁻² loadings of Pt. The MEAs were prepared by the decal transfer [26,27] of the catalyst layer onto the opposite side of a PtRu layer of the Nafion–PtRu composite.

2.4. Evaluation of DMFC performance

The MEA was hot-pressed between carbon cloth current collectors and assembled in a 10 cm² single cell. Aqueous methanol solution (1.0 M) was delivered to the anode at 4 ml min⁻¹, while humidified oxygen was delivered to the cathode (300 ml min⁻¹). Current–voltage (I-V) curves were obtained using a current pulse generator (Hokuto Denko HC-114) and a digital multimeter.

 Table 1

 PtRu amount and the compositions deposited by the IR method

Denotation	Deposited metal weight, mg cm ^{-2} (mole × 10 ^{-6} , mol cm ^{-2})	Pt:Ru (atom- ic %)
Pt	0.96 (4.9)	100:0
Pt _{0.85} Ru _{0.15}	0.93 (5.2)	85:15
Pt _{0.71} Ru _{0.29}	0.80 (4.8)	71:29
Pt _{0.63} Ru _{0.37}	0.82 (5.1)	63:37
$Pt_{0.44}Ru_{0.56}$	0.68 (4.8)	44:56
Pt _{0.28} Ru _{0.72}	0.59 (4.6)	28:72
Ru	0.36 (3.6)	0:100

3. Results and discussion

3.1. Preparation and characterization of Nafion–PtRu composites

Table 1 summarizes the deposited PtRu amount and the composition of the PtRu layers in the Nafion-PtRu composites prepared by the IR method. The stoichiometrically incorporated amounts of $[Pt(NH_3)_4]^{2+}$ and $[RuCl(NH_3)_5]^{2+}$ were calculated to be 5.8×10^{-6} mol cm^{-2} . ICP analyses showed that theoretical amounts of the Pt and Ru precursors were impregnated in the ionexchange step and more than 80% of the incorporated complexes were precipitated to PtRu except for Ru in this method. PtRu compositions deposited on the surface of the Nafion membrane were changeable according to the ratios of $[Pt(NH_3)_4]^{2+}$ and $[RuCl(NH_3)_5]^{2+}$ in the solution used in the ion-exchange step. The incorporation rates and the selectivity of the incorporation of $[Pt(NH_3)_4]^{2+}$ and $[RuCl(NH_3)_5]^{2+}$ in the Nafion membrane are thought to be similar, because the complexes have the same charge (2+) and similar structure. As a result, the PtRu ratios impregnated in the Nafion membrane and deposited on the surface were equal to those in the ion-exchange solution.

The examples of plating PEM with multiple metals by the IR method have already been reported for the preparation of MEAs used in a PEM water electrolyzer



Fig. 2. XRD patterns of various PtRu layers prepared by the IR method: (a) Pt; (b) $Pt_{0.85}Ru_{0.15}$; (c) $Pt_{0.71}Ru_{0.29}$; (d) $Pt_{0.63}Ru_{0.37}$; (e) $Pt_{0.44}Ru_{0.56}$; (f) $Pt_{0.28}Ru_{0.72}$; (g) Ru.

[10,13,28,29]. However, in the most cases, the first layer, which was first deposited by the IR method, was covered with the second metal layer by electro- or electroless plating. Ru or Ir deposited as the second metal is known to be active for oxygen evolution in the previous studies. Contrary to this case, co-deposited PtRu or PtRu alloy is thought to be appropriate for methanol oxidation [2,23–25].

XRD patterns of the PtRu layers of various Nafion-PtRu composites are shown in Fig. 2. The pattern of the Pt layer (a) displays the (111), (200), (220), (311) and (222) reflections characteristic of the face-centered cubic (fcc) crystal structure. The Ru pattern (g) corresponds to the (100), (101), (110), (103), and (201) reflection characteristic of its hexagonal close-packed (hcp) crystal structure. Peak patterns of the composites with less than 37% Ru content (b, c and d) were similar to those of pure Pt, although those peaks were broadened and shifted to the large angle side compared to those of pure Pt [30–32]. This implies the incorporation of Ru into the fcc structure. On the other hand, the (101) peak of Ru hcp was overlapped with fcc in the patterns of the composites with more than 56% Ru content (e, f), suggesting a mixture of fcc and hcp PtRu alloy phases. Similar results were reported for the unsupported PtRu



Fig. 3. SEM photograph of composite cross-sections prepared by the IR method.

alloy electrocatalysts prepared by an arc-melting [30] or thermal decomposition of H_2PtCl_6 and $RuCl_3$ [31].

Fig. 3 shows the cross-sectional view of the composite (Nafion–Pt_{0.71}Ru_{0.29}) obtained by SEM. Metallic Pt or Ru concentration profiles across the membrane analyzed by EDS are represented by the lower traces. This photograph shows that both Pt and Ru particles are selectively deposited near the membrane surface to form $3-4 \mu m$ thickness layers. Similar PtRu distributions were observed for all composites listed in Table 1.

A few previous studies have investigated such a curious distribution of metal particles, in terms of the mechanism of the ion-exchange and precipitation process in the IR method [33-35]. The preparation of Pt-Nafion [33,34] or Au-Nafion [35] composites have been used as examples in the literature. When the permeation of a reducing agent is much faster than diffusion of the metal complex, metal particles were deposited inside the membrane. In contrast, if diffusion of the metal complex is much faster than reductant permeation, metal particles will precipitate in the solution. Therefore, it is thought that the selective precipitation of PtRu on the surface resulted from the suitably balanced diffusion rates of the precursor complexes and reducing agents.

3.2. DMFC performance

The IR method was conducted on only one side of the Nafion membrane to deposit 1.6 mg cm⁻² PtRu alloy. The performance of DMFCs was evaluated with the PtRu (1.6 mg cm⁻²) deposited by the IR method as an anode and Pt (4.0 mg cm⁻²) as a cathode. Figs. 4 and 5 compare the cell performance with various PtRu compositions (pure Pt, Pt_{0.7}Ru_{0.3}, Pt_{0.5}Ru_{0.5}, Pt_{0.3}Ru_{0.7}) as



Fig. 4. I-V curves for DMFCs with different PtRu compositions at 60 °C and 0.2 MPa: \bullet , pure Pt; \blacktriangle , Pt_{0.7}Ru_{0.3}; \blacksquare , Pt_{0.5}Ru_{0.5}; and \checkmark , Pt_{0.3}Ru_{0.7}.



Fig. 5. I-V curves for DMFCs with different PtRu compositions at 120 °C and 0.3 MPa: \bullet , pure Pt; \blacktriangle , Pt_{0.7}Ru_{0.3}; \blacksquare , Pt_{0.5}Ru_{0.5}; and \checkmark , Pt_{0.3}Ru_{0.7}.

anodes at 60 °C, 0.1 MPa and at 120 °C, 0.2 MPa, respectively. The cell voltages (both open circuit voltage and at higher current densities) were significantly improved on the PtRu anode, compared to the pure Pt anode from 40 to 120 °C. The difference in the cell voltages increased with increasing temperature. It is thought that the activity of Ru toward the dissociative adsorption of methanol was increased at higher temperature [36]. The comparison of electrocatalytic activities of the different compositions of PtRu alloys are more complicated. Pt_{0.7}Ru_{0.3} performed the best activity at higher current densities in both 60 and 120 °C, although the cell voltages at low current densities below



Fig. 6. I-V curves for DMFCs at 60 °C and 0.2 MPa with various PtRu loadings (Pt:Ru = 7:3 in molar ratio): \bullet , 1.6; \blacktriangle , 3.2; \blacksquare , 4.8 mg cm⁻².



Fig. 7. I-V curves for DMFCs at 120 °C and 0.3 MPa with various PtRu loadings (Pt:Ru = 7:3 in molar ratio): \bullet , 1.6; \blacktriangle , 3.2; \blacksquare , 4.8 mg cm⁻².

0.02 A cm⁻² increased in the order of $Pt_{0.7}Ru_{0.3} < Pt_{0.3}Ru_{0.7} < Pt_{0.5}Ru_{0.5}$. In most studies, the PtRu alloys with 1:1 molar ratio were used as practical electrocatalysts for DMFC anodes. However, in the case of the PtRu prepared by the IR method, 7:3 molar ratio exhibited the optimum electrocatalytic activity for the methanol oxidation, which is consistent with the results on the well-structured PtRu alloy prepared by arc-melting [36].

Figs. 6 and 7 show I-V curves for MEAs with $Pt_{0.7}Ru_{0.3}$ (Pt-Ru = 7:3 in molar ratio) anode prepared by the IR method. The loading amount of PtRu was 1.6, 3.2 and 4.8 mg cm⁻² corresponding to one, two and three repetitions of the IR method, respectively. Although an increase in the PtRu loading from 1.6 to 3.2 mg cm^{-2} improved the cell voltage, 4.8 mg cm^{-2} loading of PtRu had the opposite effect. The deterioration in the cell voltage with the anode having the highest PtRu loading was much more prominent at 120 °C. The second or third metal layers prepared by the repeated IR method widely spread into the membrane, because the reduction of the metal precursors diffusing from the inside the membrane occurs catalytically on the first metal layer. This tendency suggests that PtRu particles electrically isolated from the electrode exist in the multiply-plated PtRu layers. Therefore, PtRu deposited inside a Nafion membrane poorly performs the three functions of proton conductivity, electrical conductivity, and fuel accessibility [37]. In addition to decreasing the catalyst utilization, it is thought to be fatal because thicker anode layers prohibited the release of the evolving CO₂ [17], especially in operation at higher temperature or higher current density.

The maximum power density was 0.14 W cm⁻² at 0.6 A cm⁻² with the Pt_{0.7}Ru_{0.3} anode in the DMFC

operation at 120 °C, 0.3 MPa. The performance obtained in this study did not reach the highest level [9,38,39]. This is due to the small active surface area of the PtRu anode prepared by the IR method compared to PtRu black or PtRu nanoparticles dispersed on carbon black. However, the morphologies of the deposited PtRu prepared by the IR method might be optimized, in terms of the selection of precursor complexes and reduction agents, concentration and temperature in the reduction solution, pretreatment of the membrane, etc.

Recently, many studies have been conducted on the development of novel PEMs for attaining high proton conductivity, low methanol permeability and low cost [40]. Despite their poor chemical stabilities, hydrocarbon-based membranes have been attractive especially for utilization at low temperature, because they are easily synthesized at low price compared to commercialized perfluorinated polymers (e.g. Nafion, Flemion, Aciplex). Additionally, a recent paper proposed a tubular design for a PEFC in order to optimize air access to the cathode [41]. The IR method should be a powerful tool for applying polymer electrolyte materials with poor heat-resistance or various shapes to the PEFC system.

4. Conclusions

In this work, a PtRu alloy was successfully deposited directly on a PEM by the IR method using $[Pt(NH_3)_4]^{2+}$ and $[RuCl(NH_3)_5]^{2+}$ with NaBH₄, as PtRu precursors and reducing agents, respectively. Porous and hydrophilic PtRu layers were selectively formed on the surface of the membrane. The feasibility of the MEA with the prepared PtRu for the DMFC anode was also demonstrated. Despite the small active surface area of the PtRu layer, the DMFC with a 3.2 mg cm⁻² PtRu (Pt:Ru = 7:3 in molar ratio) anode exhibited a power density of 0.14 W cm⁻² in operation at 120 °C and 0.3 MPa. We propose the IR method, which can be conducted under wet conditions at low temperature, as a preparation method for DMFC anodes.

Acknowledgements

The authors acknowledge Yumiko Hayashi, Yoshiko Murai and Takako Tanjo for their kind experimental support.

References

[1] A. Heinzel, V.M. Barragán, J. Power Sources 84 (1999) 70.

- [2] M.K. Ravikumar, A.K. Shukla, J. Electrochem. Soc. 143 (1996) 2601.
- [3] K. Scotto, W.M. Taama, P.A. Argyropoulos, K. Sundmacher, J. Power Sources 83 (1999) 204.
- [4] X. Ren, T.E. Springer, S. Gottesfeld, J. Electrochem. Soc. 147 (2000) 92.
- [5] W.T. Napporn, H. Laborde, J.-M. Lèger, C. Lamy, J. Electroanal. Chem. 404 (1996) 153.
- [6] A.S. Aricò, Z. Poltarzewski, H. Kim, A. Morana, N. Giordano, V. Antonucci, J. Power Sources 55 (1995) 159.
- [7] E.A. Ticianelli, C.R. Derouin, S. Srinivasan, J. Electroanal. Chem. 251 (1988) 275.
- [8] M.S. Wilson, S. Gottesfeld, J. Electrochem. Soc. 139 (1992) L28.
- [9] X. Ren, M.S. Wilson, S. Gottesfeld, J. Electrochem. Soc. 143 (1996) L12.
- [10] E. Torikai, H. Takenaka, Kokai Tokkyo Koho, Jpn. Patent no. 57-134586, 1982.
- [11] P.S. Fedkiw, W.-H. Her, J. Electrochem. Soc. 136 (1989) 899.
- [12] R. Liu, W.-H. Her, P.S. Fedkiw, J. Electrochem. Soc. 139 (1992) 15.
- [13] T. Sakai, Y. Kawami, H. Takenaka, E. Torikai, J. Electrochem. Soc. 137 (1990) 3777.
- [14] P. Millet, F. Andolfatto, R. Durand, Int. J. Hydrogen Energy 21 (1996) 87.
- [15] Y. Nishimura, K. Yasuda, Z. Siroma, K. Asaka, Denki Kagaku (presently Electrochemistry) 65 (1997) 1122(in Japanese).
- [16] M. Kondoh, N. Yokoyama, C. Inazumi, S. Maezawa, N. Fujiwara, Y. Nishimura, K. Oguro, H. Takenaka, J. New Mat. Electrochem. Systems 3 (2000) 61.
- [17] P. Argyropoulos, K. Scott, W.M. Taama, J. Appl. Electrochem. 29 (1999) 661.
- [18] H. Takenaka, E. Torikai, Kokai Tokkyo Koho, Jpn. Patent no. 55-38934, 1980.
- [19] H. Takenaka, E. Torikai, Y. Kawami, N. Wakabayashi, Int. J. Hydrogen Energy 7 (1982) 397.
- [20] A. Aramata, T. Kodera, M. Masuda, J. Appl. Electrochem. 18 (1988) 577.
- [21] A. Aramata, M. Masuda, J. Electrochem. Soc. 138 (1991) 1949.
- [22] G. Méli, J.-M. Léger, C. Lamy, R. Durand, J. Appl. Electrochem. 23 (1993) 197.
- [23] S. Surampudi, S.R. Narayanan, E. Vamos, H. Frank, G. Halpert, A. LaConti, J. Kosek, G.K. Surya Prakash, G.A. Olah, J. Power Sources 47 (1994) 377.
- [24] K. Scott, W.M. Taama, P. Argyropoulos, J. Appl. Electrochem. 28 (1998) 1389.
- [25] J.S. Wainright, J.-T. Wang, D. Weng, R.F. Savinell, M. Litt, J. Electrochem. Soc. 142 (1995) L121.
- [26] M.S. Wilson, S. Gottesfeld, J. Appl. Electrochem. 22 (1992) 1.
- [27] S.C. Thomas, X. Ren, S. Gottesfeld, J. Electrochem. Soc. 146 (1999) 4354.
- [28] E. Torikai, H. Takenaka, Y. Kawami, Y. Naka, K. Nagaya, Kokai Tokkyo Koho, Jpn. Patent no. 60-162780, 1985.
- [29] P. Millet, R. Durand, M. Pineri, Int. J. Hydrogen Energy 15 (1990) 245.
- [30] H.A. Gasteiger, P.N. Ross, Jr., E.J. Cairns, Surf. Sci. 293 (1993) 67.
- [31] D. Chu, S. Gilman, J. Electrochem. Soc. 143 (1996) 1685.
- [32] Y. Takasu, T. Fujiwara, Y. Murakami, K. Sasaki, M. Oguri, T. Asaki, W. Sugimoto, J. Electrochem. Soc. 147 (2000) 4421.
- [33] P. Millet, F. Andolfatto, R. Durand, J. Appl. Electrochem. 25 (1995) 227.
- [34] P. Millet, F. Andolfatto, R. Durand, J. Appl. Electrochem. 25 (1995) 233.
- [35] N. Fujiwara, K. Asaka, Y. Nishimura, K. Oguro, E. Torikai, Chem. Mater. 12 (2000) 1750.
- [36] H.A. Gasteiger, N. Marković, P.N. Ross, Jr., E.J. Cairns, J. Electrochem. Soc. 141 (1994) 1795.