

Catalyst electrode preparation for PEM fuel cells by electrodeposition

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Abstract The preparation of catalyst electrodes by electrodeposition for the oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFCs) has been studied. This work looks at the potential to apply the electrodeposition technique, in the forms of direct current (DC) and pulse plating electrodepositions, to prepare Pt and Pt–Co alloy catalysts for membrane electrode assemblies (MEAs). The preparation of the non-catalyst layer was found to be important for the electrodeposition of Pt catalysts. The activities of the electrodeposited catalysts, both pure Pt and Pt–Co alloy, produced by pulse plating are substantially higher than that of the Pt catalyst produced by DC electrodeposition. The improvement in electroactivity towards the ORR of the electrodeposited catalysts produced by pulse plating is likely due to the finer structures of electrodeposited catalysts which contain smaller catalyst particles compared to those produced by DC electrodeposition. A maximum performance towards the ORR in PEMFCs was achieved from the catalysts prepared by pulse plating using a charge density of 2 C cm^{-2} , a pulse current density of 200 mA cm^{-2} , a 5% duty cycle and a pulse frequency of 1 Hz.

Keywords Pt catalyst · Pt–Co catalyst · PEMFC · Oxygen reduction reaction · Electrodeposition

1 Introduction

PEMFCs have shown a great promise as the alternative power generation for the future. However, there are still several technical issues that impede the commercialization of PEMFCs. One of the main challenges facing the development of PEMFCs is the preparation of catalyst layers for the cathodic reaction in PEMFCs, since the oxidation reaction of oxygen is significantly slower than the reduction reaction of the hydrogen fuel. This challenge can be approached in several ways; one such way is to invent alternative catalysts that have a higher electroactivity and, at the same time, a lower cost than the current one. Another approach would be to improve the fabrication process of the catalyst layers for membrane electrode assemblies MEAs. Platinum has commonly been used as the catalyst of choice for PEMFCs. Recently, however, it has been found that alloying Pt with Co achieves higher electrocatalytic activity in the oxygen reduction reaction (ORR) than do pure Pt or other Pt-based alloys [1–4]. It also has the potential to lower the cost of MEAs, since Pt is partially replaced by cheaper Co.

In the preparation process, there are various techniques for applying the catalyst layers onto the carbon electrodes for MEAs, such as impregnation, painting and spraying. In addition to these techniques, electrodeposition is also considered as an alternative for applying the catalyst layer onto the electrode [5–9], since it can produce metal particle uniform in size and uniform in metal distribution over the substrate [10]. It can be easily applied on different geometries and scales, from microscopic to macroscopic area [11]. It has various operating parameters for controlling the amount of deposited metal, the desired metal particle sizes and the desired metal structures. Moreover, it can be used to produce a thin layer of the metal alloy, with desired

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compositions, directly on the substrate in a single step at a lower operating temperature, a procedure that is relatively easy and more cost effective [12].

Although electrodeposition of Pt or Pt-based alloys has been studied by a number of researchers [13–18], only a few works have studied the electrodeposition for the preparation of the catalyst layers for PEMFCs [5, 8, 19, 20]. In this work, we study the preparation of a Pt catalyst layer onto a prepared carbon cloth using an electrodeposition technique for preparing MEAs by direct current (DC) and pulse plating electrodeposition. The influence of the hydrophilic layer has been studied, as has the influence of the electrodeposition mode—DC and pulse plating—and the effect of its operating parameters on the performance of the PEMFCs. Suitable deposition conditions for the preparation of the Pt catalyst layer were obtained based on fuel cell performance. Then, those preparation conditions were extended towards the preparation of a Pt–Co catalyst layer to investigate the feasibility of applying the Pt-based alloy prepared by electrodeposition for the electrocatalyst in PEMFCs. The catalyst layers prepared by electrodeposition were characterized by SEM and XRD (as well as EDX, in the case of the Pt–Co catalyst). The prepared catalyst electrodes were then used to fabricate the MEAs to test the performance of the PEMFCs.

2 Experimental

The preparation of the catalyst layer on the electrode by electrodeposition consisted of two steps: (i) preparation of the non-catalyst layer and (ii) electrodeposition of the catalyst onto the prepared non-catalyst electrode. Normally, the non-catalyst layer consists of 2 sub-layers—the hydrophobic and hydrophilic layers—formed on the carbon electrode. To form the hydrophobic sub-layer, a suitable amount of carbon black (Vulcan XC-72), PTFE (60 wt%) (Aldrich) and isopropanol (Fluka) mixture were mixed, painted onto the carbon cloth (Electrochem), and dried at 300 °C for 2 h. This sub-layer was prepared to have a total loading of 1.9 mg cm⁻² (with a carbon black to PTFE ratio of 30:70). The prepared electrode was subsequently painted with a mixture of Nafion and glycerol to form the hydrophilic sub-layer. The prepared non-catalyst electrode was then dried at 300 °C for 2 h. All non-catalyst layers had the same hydrophobic layers, but with different hydrophilic layers in which the loadings were varied.

To apply the catalyst layer onto the pretreated non-catalyst electrode, the electrodeposition was conducted in a plating bath containing a solution of 0.02 M H₂PtCl₆·6H₂O in 0.5 M H₂SO₄. In the case of the Pt–Co alloy catalyst preparation, CoSO₄·7H₂O was added such that the plating bath contained 0.02 M H₂PtCl₆·6H₂O and 0.1 M

CoSO₄·7H₂O. The pretreated electrode was placed in an electrode holder having an exposed area of 5 cm² for the electrodeposition. Titanium gauze was used as the counter electrode. An Autolab PGSTAT 10 potentiostat (Eco Chemie) was used to perform both the DC electrodeposition and the pulse plating. During the electrodeposition, the plating solution was stirred by a magnetic stirrer at 300 rpm. After the electrodeposition, the electrode was dried at 80 °C for 2 h. The catalyst loadings were estimated from the weight difference before and after the electrodeposition. The catalyst electrodes prepared by electrodeposition were characterized by SEM (JEOL JSM-6400) equipped with EDX (JEOL JSM-6400) and XRD (JEOL JDX-3530). The average particle size of the prepared catalyst was estimated from Scherrer equation [21, 22], based on the broadening of the Pt(111) diffraction peak in the XRD data.

To test the performance of the prepared catalyst, the catalyst prepared by the electrodeposition was used as a cathode whereas a commercial carbon paper electrode by Electrochem (10 wt% Pt/C, 0.5 mg cm⁻²) was used as the anode for the fabrication of the MEA. Both the electrodeposited catalyst electrode and the commercial electrode were painted with 5 wt% Nafion 117 solution (Fluka) to get a Nafion loading of 0.8 mg cm⁻² on each electrode. Then, Nafion-impregnated electrodes and a Nafion 115 membrane were hot pressed at 137 °C for 2.5 min with a pressure of 65 kg cm⁻² to form the MEA. The performance test was conducted using a 5 cm² single cell fuel cell (Electrochem, Inc.) operated at 60 °C under ambient pressure. Hydrogen (99.999%, Praxair) and oxygen (99.999%, Praxair) were fed at the anode and cathode, respectively, both at flow rates of 100 cm³ min⁻¹ and at 100% relative humidity.

3 Results and discussion

3.1 Non-catalyst layer preparation

All non-catalyst layers had a fixed amount of hydrophobic loading, but the amount of hydrophilic loading—which consisted of Nafion and glycerol in a 1:1 ratio—was varied from 0 to 1.2 mg cm⁻². Pt was applied on the electrodes via DC electrodeposition at a current density of 20 mA cm⁻² and a charge density of 4 C cm⁻². The performances of the Pt electrodeposited electrodes with different hydrophilic loadings are shown in Fig. 1.

Figure 1 indicates that the hydrophilic layer is very important for electrode preparation using the electrodeposition technique, since the Pt catalyst electrode with no hydrophilic layer performed the worst. The hydrophilic layer is expected to play a major role in the electrodeposition process and is important in helping transfer protons from the membrane electrolyte to the catalyst sites on the cathode.

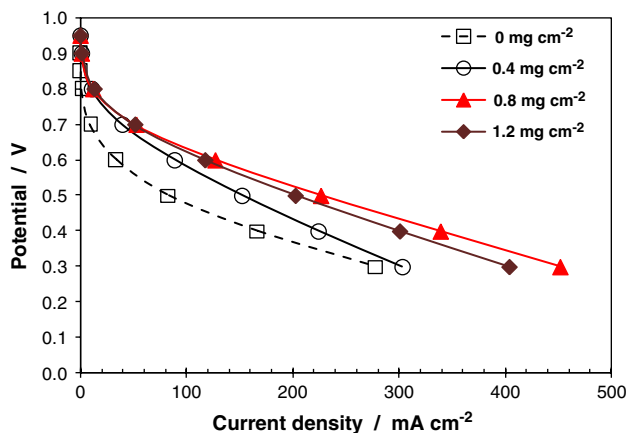


Fig. 1 Polarization curves of H₂/O₂ PEMFC with Pt catalyst electrodes having different amounts of hydrophilic loadings. All electrodes were prepared by DC electrodeposition at 20 mA cm⁻² and 4 C cm⁻²

When the amount of hydrophilic layer was increased, the fuel cell performance improved. A suitable amount of hydrophilic loading resulted in the improvement in the three-phase contact among the carbon electrode, the Pt catalyst particles and the Nafion electrolyte. However, too thick of a hydrophilic layer obstructed the penetration of the Pt compound ions from the bulk solution to react and form catalyst particles on the electrode during electrodeposition. In addition, a thicker hydrophilic layer led to an increase in the resistance and an ohmic drop in the MEA. Fuel cell performance tended to decline after the hydrophilic loading reached 0.8 mg cm⁻². As shown in Fig. 1, the Pt catalyst electrode with a hydrophilic loading of 1.2 mg cm⁻² had an activity polarization as high as the one with a hydrophilic loading of 0.8 mg cm⁻², but it had a substantially higher ohmic polarization than the one with a hydrophilic loading of 0.8 mg cm⁻².

3.2 Pt catalyst electrodes prepared by electrodeposition

The Pt catalyst loadings and particle sizes of deposited catalysts prepared by DC electrodeposition under various conditions are summarized in Table 1. At fixed charge density of 4 C cm⁻², the Pt catalyst loadings obtained at high current densities were lower than those obtained at low current densities since the hydrogen evolution becomes more intense at higher current densities. The performances of the electrodes fabricated by DC electrodeposition at various applied current densities with a fixed charge density of 4 C cm⁻² are shown in Fig. 2. Figure 3 shows the SEM images of the Pt catalysts obtained at these current densities. As shown in Fig. 2, the best performance was obtained from the electrode prepared at a current density of 10 mA cm⁻², whereas the Pt catalyst electrodes prepared at the lowest and highest current densities studied provided

Table 1 Pt catalyst loadings and particle sizes of the Pt catalyst electrodes prepared by DC electrodeposition under various conditions

Charge density (C cm ⁻²)	Current density (mA cm ⁻²)	Pt loading (mg cm ⁻²)	Particle size (nm)
4	5	1.24	46.40
4	10	0.62	33.40
4	20	0.39	35.78
4	40	0.27	39.52
2	10	0.37	31.28
4	10	0.62	33.40
6	10	1.44	46.30

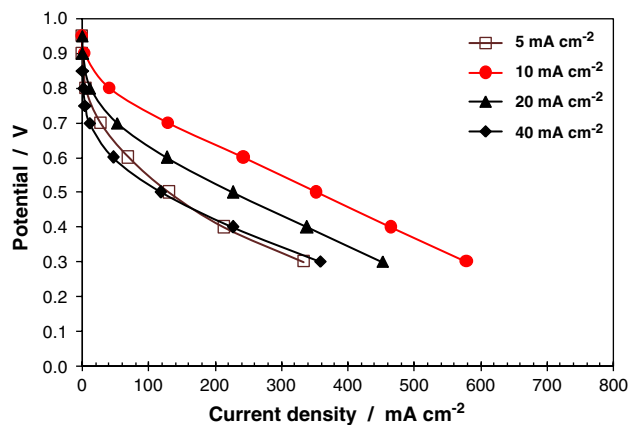


Fig. 2 Polarization curves of H₂/O₂ PEMFC with the Pt catalyst electrodes prepared by DC electrodeposition using 4 C cm⁻² at different current densities

the worst fuel cell performance. The poor performance of those electrodes was likely the result of their large catalyst particles, as shown in Fig. 3 and Table 1, which are resulted from the applied current density.

Although the Pt catalyst obtained at 5 mA cm⁻² has the highest amount of catalyst loading, it yielded very low fuel cell performance compared to those obtained at the higher current densities. This indicated low catalyst utilization of the catalyst prepared at 5 mA cm⁻² due to its large catalyst particles. Normally, electrodeposition using low current density enhances the grain growth process during electrocrystallization, leading to large deposit particles. On the other hand, electrodeposition using high current density favors the nucleation process, leading to small deposit particles. Thus, the Pt catalyst particles obtained at the 10 mA cm⁻² were smaller than those obtained at 5 mA cm⁻², as shown in Fig. 3a, b and Table 1. Small catalyst particles have a higher active surface area compared to large catalyst particles, and they provide for better fuel cell performance, as shown in Fig. 2. However, if the applied current density was higher than 10 mA cm⁻², the electrodeposition tended to take place closer to mass

Fig. 3 SEM images ($\times 15,000$) of the Pt catalyst electrodes prepared by DC electrodeposition using 4 C cm^{-2} at different current densities: **a** 5 mA cm^{-2} ; **b** 10 mA cm^{-2} ; **c** 20 mA cm^{-2} ; **d** 40 mA cm^{-2}

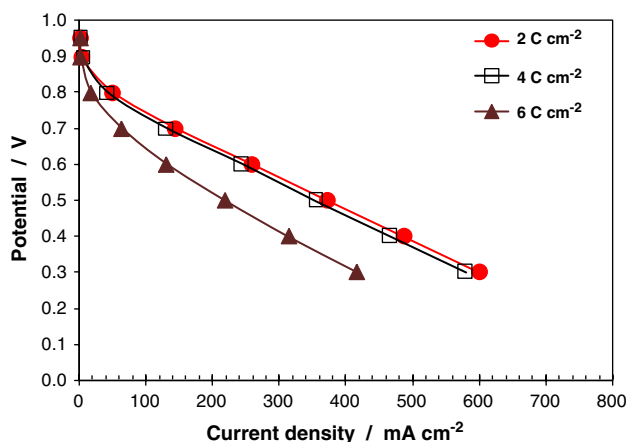
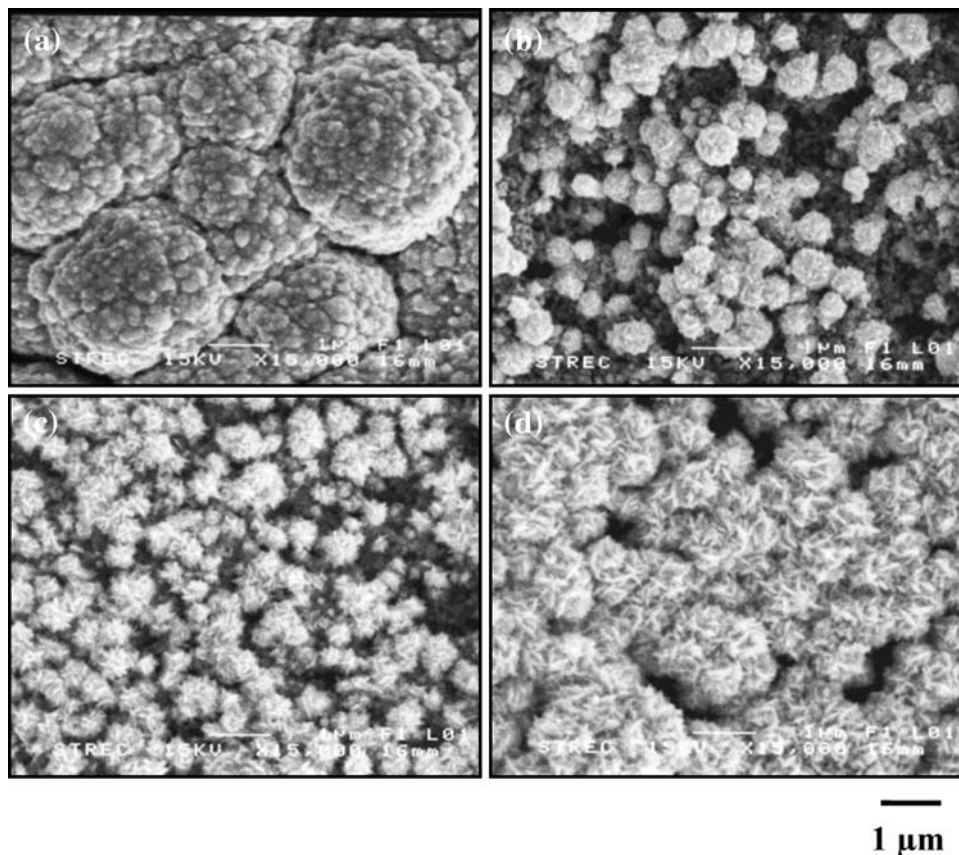


Fig. 4 Polarization curves of H_2/O_2 PEMFC with the Pt catalyst electrodes prepared by DC electrodeposition using 10 mA cm^{-2} at different charge densities

transport control resulting in lower Pt catalyst loadings and big-grained and coarse structures, as shown in Fig. 3c, d and Table 1. As a result, the fuel cell performance became lower for the Pt catalyst electrode obtained at 20 mA cm^{-2} and even worse for Pt catalyst electrode obtained at 40 mA cm^{-2} (Fig. 2).

The performances of the electrodes fabricated by DC electrodeposition at various applied charge densities with a

fixed current density of 10 mA cm^{-2} are shown in Fig. 4. The best performance was obtained from the electrode produced at 2 C cm^{-2} . The Pt catalyst electrode obtained at 2 C cm^{-2} provided slightly better performance than the one obtained at 4 C cm^{-2} , and substantially better performance than the one obtained at 6 C cm^{-2} . As expected, the charge density applied for the electrodeposition of the Pt catalyst layer affects the amount of Pt loading and particle size of the deposited catalysts, as shown in Table 1. From Table 1, it can be seen that the electrode obtained at a charge density of 6 C cm^{-2} had significantly greater Pt loading than those obtained at lower charge densities, but it had the poorest performance. Figure 5 shows the SEM images of the Pt catalysts electrodeposited at the various charge densities. Figure 5a reveals that the electrodeposited surface obtained at the charge density of 2 C cm^{-2} consisted of small Pt particles that almost completely covered the entire electrode surface. When the charge current density was increased to 4 C cm^{-2} , the Pt particles grew larger (Fig. 5b, Table 1). The relatively bigger particles of the Pt catalyst led to a slight decrease in the fuel cell performance of the electrode prepared at 4 C cm^{-2} , as shown in Fig. 4. When the charge current density was further increased to 6 C cm^{-2} , the Pt particles grew even larger (Table 1) and covered the entire surface of the electrode (Fig. 5c). The significant decline in the fuel cell

Fig. 5 SEM images ($\times 5,000$) of the Pt catalyst electrodes prepared by DC electrodeposition using 10 mA cm^{-2} at different charge densities: **a** 2 C cm^{-2} ; **b** 4 C cm^{-2} ; **c** 6 C cm^{-2}

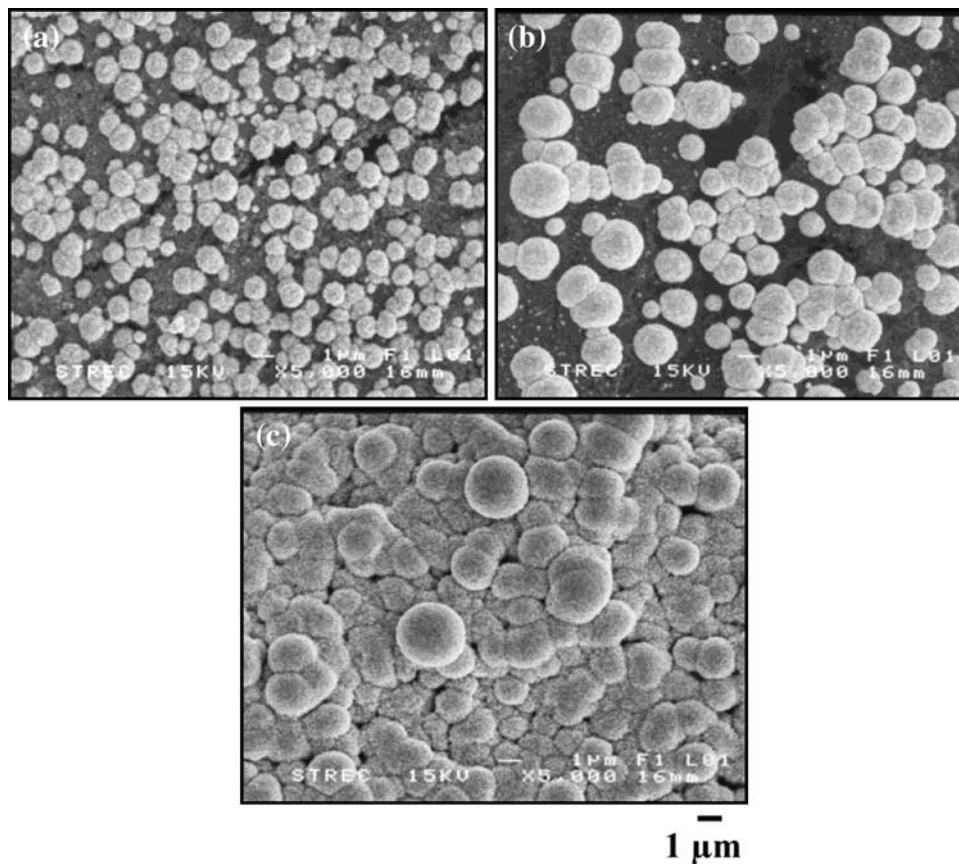


Table 2 Summary of pulse plating conditions, Pt catalyst loadings, and particle sizes of the prepared Pt catalysts

Pulse conditions			Pt loading (mg cm^{-2})	Particle size (nm)
Pulse frequency	Peak current (mA cm^{-2})	Duty cycle (%)		
DC	10	–	0.37	31.28
1 Hz	200	5	0.32	23.30
10 Hz	20	50	0.48	33.38
		20	0.42	27.39
	200	5	0.38	24.00
100 Hz	200	5	0.41	25.70

performance of the electrode prepared at 6 C cm^{-2} , as shown in Fig. 4, should be due to the substantial decrease in the active surface area of the large-grained particles. The large-grained and coarse structure may cause the inhomogeneous Nafion distribution, which can lead to low proton conductivity and low three-phase contact. In addition, the high charge density used for catalyst electrodeposition led to an excessive amount of catalyst loading on the electrode. The catalyst particles then blocked each other, resulting in a decrease in the accessibility of reactant gas to the catalyst sites. The combination of these effects thus led to a low fuel cell performance.

The results obtained from DC electrodeposition show that the Pt catalyst electrode prepared at 2 C cm^{-2} and 10 mA cm^{-2} provided the best fuel cell performance. To study the preparation of Pt catalyst electrodes by pulse plating, the applied charge density of 2 C cm^{-2} was used and the time-average current density (i_{avg}) was fixed at 10 mA cm^{-2} . The pulse plating conditions as well as information about the particle sizes and loadings of Pt catalysts are summarized in Table 2. The polarization curves of the Pt catalysts prepared using the pulse plating conditions are shown in Fig. 6.

As shown in Fig. 6, in most cases the Pt catalyst electrodes prepared by pulse plating had better performance than that prepared by DC electrodeposition. The enhancement of performance was likely due to the decrease in the Pt particle sizes, as indicated by the XRD results shown in Table 2. The decrease in the particles size was likely influenced from the substantially higher applied peak current densities in pulse plating compared to the lower constant current density applied in DC electrodeposition. In general, the current density applied during the on-time (i.e., peak current density, i_p) in pulse plating can be significantly higher than that applied in DC electrodeposition without violation of mass transfer limitation. By applying the current in pulse waveform pattern, the Pt ions consumed on the

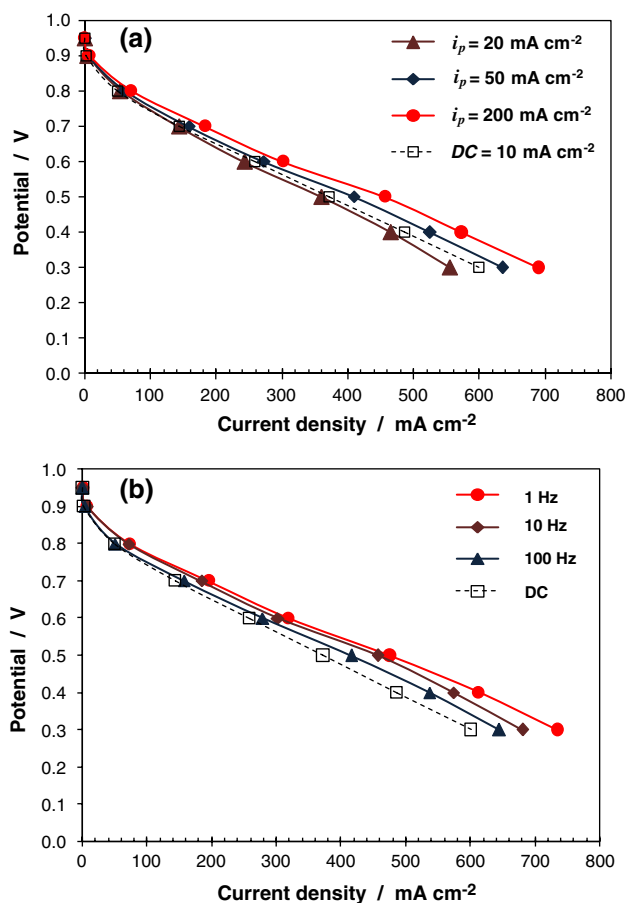


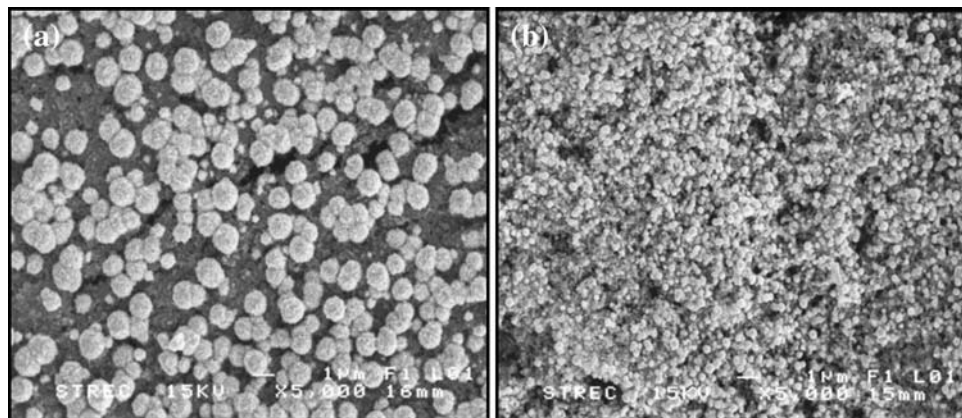
Fig. 6 Polarization curves of H₂/O₂ PEMFC with the Pt catalyst electrodes prepared by pulse plating using the average current density of 10 mA cm⁻² and **a** 10 Hz and different pulse current densities; **b** a pulse current density of 200 mA cm⁻² (5% duty cycle) and different pulse frequencies

electrode surface during the on-time were compensated by the Pt ions transported from the bulk solution during the off-time (when no current was applied). Then, the peak current

density applied in pulse plating can substantially exceed the current density used in DC electrodeposition. The higher level of the applied current density led to an enhancement of the nucleation process, such that the formation of new Pt nuclei was faster compared to the growth of existing Pt particles to form bigger grained-particles. As a result, Pt catalysts having smaller grained-particles with fine structures were produced by pulse plating. Figure 7 shows the SEM image of the Pt catalyst prepared by pulse plating at the pulse current density of 200 mA cm⁻² and pulse frequency of 1 Hz, compared to that prepared by DC electrodeposition. SEM images (Fig. 7) and particle size estimations obtained from XRD (Table 2) clearly show that the Pt catalyst produced at the highest pulse current density of 200 mA cm⁻² consists of substantially smaller particles, compared to that produced by DC electrodeposition. The smaller Pt particles provide the catalyst with a higher surface area, which leads to better fuel cell performance.

Figure 6a shows that, at the same average current density of 10 mA cm⁻² and the fixed pulse frequency of 10 Hz, the Pt catalysts produced at higher applied current densities tended to increase fuel cell performance. Figure 6b shows that at the same pulse current density of 200 mA cm⁻², the fuel cell performance gradually worsened as the applied pulse frequency was increased. This observation is likely due to the effect of the electrical double layer capacitance, which is considered to be important in pulse plating, especially at high frequencies. When the pulse frequency is increased, the electrical double layer capacitance can affect the set pulse waveform [23, 24] and eventually can distort the set pulse waveform to a ripple DC signal at very high pulse frequencies. Then, as the applied pulse frequency is increased to levels high enough, the deposit morphology approaches that produced by DC electrodeposition. This might explain the decrease in fuel cell performance of the Pt catalyst with the applied pulse frequency.

Fig. 7 Comparison between SEM images (×5,000) of Pt catalyst electrodes prepared by **a** DC electrodeposition and **b** pulse plating at a pulse current density of 200 mA cm⁻² and a pulse frequency of 1 Hz



1 μm

3.3 Pt–Co catalyst electrodes prepared by electrodeposition

The preparation of catalyst electrodes by electrodeposition can also extend to form Pt-based alloy catalysts used for PEMFC. In this study, the best conditions for the preparation of pure Pt catalyst electrodes were extended for the preparation of a Pt–Co catalyst electrode. The more thorough study on the preparation of the Pt–Co alloy catalyst is reported in a separate work [25].

Figure 8 shows the XRD pattern of the Pt–Co alloy catalyst obtained by pulse plating, using a charge density of 2 C cm^{-2} , a pulse current density of 200 mA cm^{-2} , a 5% duty cycle, and a pulse frequency of 1 Hz in a solution containing $0.02 \text{ M H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $0.1 \text{ M CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $0.5 \text{ M H}_2\text{SO}_4$, compared to the XRD pattern of the pure Pt catalyst obtained under the same pulse plating conditions, but in a solution containing no $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$. The XRD patterns clearly show the shift of the Pt(111) peak to a higher 2θ for the Pt–Co electrodeposited catalyst compared to the peak for the Pt electrodeposited catalyst. The shift indicates the alloy formation of Pt and Co due to a lowered lattice parameter of Pt in the Pt–Co catalyst as a result of the incorporation of Co into the fcc structure of Pt [3, 4, 26, 27] during Pt–Co electrodeposition. The XRD pattern shows no evidence of metallic Co (i.e., reflection of Co(111) is expected at $2\theta = 44.8^\circ$) or Co oxides, which implies that Co is incorporated into the Pt structure to form an alloy. The EDX result shows that the Pt:Co alloy composition is 88:12.

The performance of the Pt–Co catalyst electrode prepared by pulse plating compared to those of the pure Pt catalyst electrodes is shown in Fig. 9. The polarization results show that the Pt–Co catalyst prepared by pulse plating has substantially better performance than the Pt

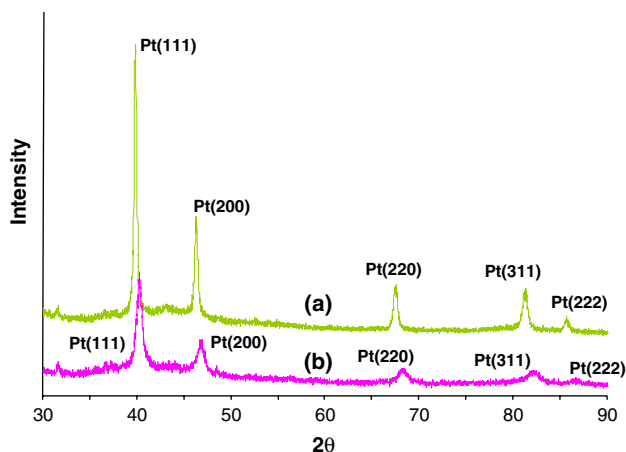


Fig. 8 X-ray diffraction patterns of the **a** Pt and **b** Pt–Co catalysts prepared by electrodeposition

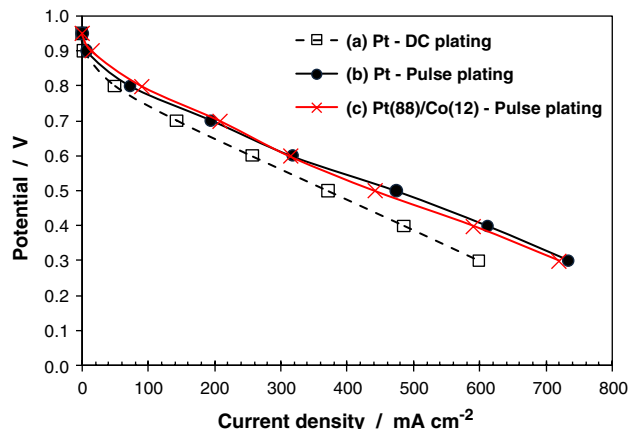


Fig. 9 Comparison of MEAs of the **a** Pt catalyst prepared by DC electrodeposition; **b** Pt catalyst prepared by pulse plating; **c** Pt–Co catalyst prepared by pulse plating

catalyst prepared by DC electrodeposition and has a performance comparable to the Pt catalyst prepared by pulse plating electrodeposition. In fact, if we consider only the activation polarization (i.e., $E \leq 0.7 \text{ V}$), the Pt–Co catalyst prepared by pulse plating tends to show a slight improvement in fuel cell performance over the Pt catalyst prepared by pulse plating. This improvement should be due to the shorter Pt–Pt interatomic distance when cobalt atoms are introduced in the platinum structure [28] (i.e., a Pt–Pt distance of 0.2235 nm for the Pt–Co catalyst compared to a Pt–Pt distance of 0.2262 nm for the pure Pt catalyst). This result is considered as a possible alternative for catalysts used for PEMFCs. Alloying Pt with cheap Co, while the performance of the fuel cell still retains (or even improves) at the same level, has a potential to lower the amount of Pt loading, which will benefit the commercialization of fuel cells in the future. As Pt–Co alloy catalysts can be prepared by various methods from conventional high temperature multi-step methods to low/medium temperature methods [29], this study shows that the electrodeposition offers an alternative approach to prepare the thin layer of Pt–Co alloy catalyst, where the preparation can take place in one step at room temperature.

4 Conclusions

Electrodeposition technique was used to prepare Pt and Pt–Co alloy catalyst electrodes for the ORR in PEMFCs. First, the preparation of Pt catalysts was conducted using DC electrodeposition, where the hydrophilic layer was found to have an important effect on the performance of the fuel cell and the suitable applied current density and charge density were found to be 10 mA cm^{-2} and 2 C cm^{-2} , respectively. By applying the current in the pulse waveform pattern, the

applied pulse current density can be significantly high compared to the current density used in DC electrodeposition without violation of mass transfer limitation and thus the grain sizes of the electrodeposited catalysts can be reduced. Of the conditions studied, pulse plating using a pulse current density of 200 mA cm^{-2} at 1 Hz and 5% duty cycle was found to produce the best catalysts for PEMFC. The electrodeposited Pt–Co alloy catalyst obtained from pulse plating provides slightly better fuel cell performance than the electrodeposited Pt catalyst prepared by pulse plating under the same plating conditions.

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References

- Shukla K, Neergat M, Bera P, Jayaram V, Hegde MS (2001) *J Electroanal Chem* 504:111
- Xiong L, Kannan AM, Manthiram A (2002) *Electrochem Commun* 4:898
- Neergat M, Shukla AK, Gandhi KS (2001) *J Appl Electrochem* 31:373
- Travitsky N, Ripenbein T, Golodnitsky D, Rosenberg Y, Burshstein L, Peled E (2006) *J Power Sources* 161:782
- Taylor EJ, Anderson EB, Vilambi NRK (1992) *J Electrochem Soc* 139:L45
- Mikhaylova AA, Khazova OA, Bagotzky VS (2000) *J Electroanal Chem* 225:232
- Thompson SD, Jordan LR, Forsyth M (2001) *Electrochim Acta* 46:1657
- Kim H, Popov BN (2004) *Electrochem Solid-State Lett* 7:A71
- Duarte MME, Pilla AS, Sieben JM, Mayer CE (2006) *Electrochem Commun* 8:159
- Paunovic M, Schlesinger M (1998) *Fundamentals of electrochemical deposition*. Wiley, New York
- Datta M, Landolt D (2000) *Electrochim Acta* 45:2535
- Landolt D, Marlot A (2003) *Surf Coat Technol* 169–170:8
- Lin-Cai J, Pletcher D (1983) *J Electroanal Chem* 149:237
- Shimazu K, Weisshaar D, Kuwana T (1987) *J Electroanal Chem* 223:223
- Shimazu K, Uosaki K, Kita H (1988) *J Electroanal Chem* 256:481
- Cattaneo C, Sanchez de Pinto MI, Mishima H, López de Mishima BA, Lescano D, Cornaglia L (1999) *J Electroanal Chem* 461:32
- Selvaraju T, Ramaraj R (2005) *J Electroanal Chem* 585:290
- Domínguez-Domínguez S, Arias-Pardilla J, Berenguer-Murcia Á, Morallón E, Cazorla-Amorós D (2008) *J Appl Electrochem* 38:259
- Kim H, Subramanian NP, Popov BN (2004) *J Power Sources* 138:14
- Ra Y, Leeb J, Kim I, Bong S, Kim H (2009) *J Power Sources* 187:363
- Lu Y, Reddy RG (2007) *Electrochim Acta* 52:2562
- Warren BE (1996) *X-ray diffraction*. Addison-Wesley, Reading, MA
- Tantavichet N, Pritzker MD (2005) *Electrochim Acta* 50:1849
- Tantavichet N, Pritzker MD (2003) *J Electrochem Soc* 150:C665
- Saejeng Y, Tantavichet N (2009) *J Appl Electrochem* 39:123
- Lopes T, Antolini E, Colmati F, Gonzalez ER (2007) *J Power Sources* 164:111
- Zhang X, Chan KY (2002) *J Mater Chem* 12:1203
- Huang Q, Yang H, Tang Y, Lu T, Akins DL (2006) *Electrochem Commun* 8:1220
- Antolini E, Salgado JRC, da Silva RM, Gonzalez ER (2007) *Mater Chem Phys* 101:395