Short communication

Synthesis and characterization of PtN$_x$/C as methanol-tolerant oxygen reduction electrocatalysts for a direct methanol fuel cell

Jong-Gil Oh, Hansung Kim*

Department of Chemical Engineering, Yonsei University, 134 Shinchon-Dong, Seodaemun-gu, 120-749 Seoul, Republic of Korea

ABSTRACT

Platinum nitride supported on carbon (PtN$_x$/C) is synthesized by the novel strategy of chelating the Pt precursor followed by pyrolysis and is characterized as a possible cathode electrocatalyst for direct methanol fuel cells (DMFCs). The prepared PtN$_x$/C is shown to possess high methanol tolerance and catalytic activity for the oxygen reduction reaction (ORR). The results indicate that the temperature of the heat treatment and the molar ratio of Pt to N in the precursor solution play important roles in the catalytic performance. A sample of PtN$_x$/C prepared at 700 °C with a Pt:N ratio of 1:2 shows a significant decrease in the potential loss associated with the mixed potential and the poisoning effect by adsorbed methanol, and this results in a high power density of 180 mW cm^{-2}. The performance is 30% higher than that of Pt/C under 4 M of methanol concentration.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The direct methanol fuel cell (DMFC) is an attractive candidate as a power source for future portable electronics [1–3]. However, in spite of significant progress in DMFC research and technology there are still some problems that need to be addressed in terms of efficiency and power density of both the anodic [3] and the cathodic reactions [4]. Methanol crossover from the anode to the cathode through the polymer electrolyte membrane remains one of the major obstacles in DMFC technology [5,6]. It has been observed that due to the presence of a concentration gradient and electroosmotic drag, the methanol transported to the cathode is absorbed on to the catalyst and gives rise to a mixed potential by virtue of the oxygen reduction and methanol oxidation reactions occurring simultaneously. This results in a substantial decrease in both the voltage efficiency and the performance of the DMFC [7,8]. In order to overcome the methanol crossover problem in the DMFC, much attention has been devoted to the development of membranes that are less permeable to methanol [9,10]. Nevertheless, it is still difficult to prevent completely methanol crossover. An alternative method that can be used to attack this problem is to develop selective electrocatalysts for the oxygen reduction reaction (ORR) that are tolerant to methanol oxidation.

Depending on the material used, most methanol-tolerant electrocatalysts can be placed in three categories. The first group consists of Pt alloyed with one of several different transition metals. Platinum-based binary alloys such as PtFe [11], PtCo [12], PtNi [13] and PtCr [14] have been found to exhibit higher methanol tolerance during oxygen reduction than pure Pt. However, the stability of the transition metal in the acidic environments of fuel cells still remains uncertain. The second approach is to use chalcogenide compounds. The Chevrel-type compounds of the ruthenium molybdenum chalcogenides prepared by decarboxylation of metal-carbonyl clusters under an inert gas at low temperature have been found to possess oxygen reduction ability as well as methanol tolerance [15–18]. The third category of electrocatalysts uses a transition metal macrocyclic complex catalyst (TMMC) with N-based ligands, such as porphyrins and phthalocyanines [19–21]. It has been reported that the electrocatalytic activity of a TMMC is affected by the type of transition metal; also the metal-N4 moiety formed by heat treatment increases the activity towards ORR. Although these non-Pt catalysts show better methanol tolerance than that of Pt, their intrinsic catalytic activity towards ORR is relatively low. Considering these deficiencies, researchers have tried to combine Pt with macrocycles. Pt dispersed on to cobalt phthalocyanine (CoPc) supported on carbon has been used as a cathodic catalyst in DMFCs and improves the electrocatalytic activity for ORR and methanol resistance [22]. However, macrocycles are as expensive as Pt, so this is not favourable in terms of cost.

We have recently reported on a new platinum nitride electrocatalyst supported on carbon (PtN$_x$/C) for use as a methanol-tolerant

* Corresponding author. Tel.: +82 2 2123 5753; fax: +82 2 312 6401.
E-mail address: elchem@yonsei.ac.kr (H. Kim).

catalyst for DMFCs and which is synthesized by using a chelating agent followed by heat treatment [23]. The chelating agent, which is considerably cheaper than macrocyclic complexes, is used to modify the surface of Pt with nitrogen. This approach is supposed to mimic the N-ligand structure of metal macrocycles. The PtN$_x$/C catalysts prepared in this way show significantly greater methanol tolerance compared with commercial Pt/C while maintaining high activity with respect to the ORR. The objective of this study is to examine the preparation conditions that produce optimization of the performance of these PtN$_x$/C catalysts.

2. Experimental

2.1. Preparation of the catalysts

Platinum(IV) chloride (PtCl$_4$ Alfa Aesar) was dissolved in 100 ml of de-ionized water and stirred for 20 min. A previously calculated volume of the chelating agent (1,3-propylendiamine) targetting the number of N atoms available to one Pt atom was added dropwise to the aqueous solution with vigorous stirring. The change in colour of the solution from clear to cloudy yellow indicated the chelation of Pt(IV) ions. The calculated amount of the carbon support (Ketjen black 300J) for a target 40 wt.% of Pt was added to the solution and the mixture was then kept overnight on reflux. Following the reflux, the mixture of the Pt complex adsorbed on the carbon support was dried in a rotary evaporator at 50 °C in a vacuum. The dried powder was then collected and heat-treated at various temperatures in a continuous flow of argon.

2.2. Electrochemical and physical characterization

The electrochemical characterizations were carried out in a three-electrode electrochemical cell. 0.5 M H$_2$SO$_4$ was used as the electrolyte and the experiments were carried out in the presence and absence of methanol at room temperature. A bi-potentiostat (CH-instruments) controlled a working electrode that consisted of a glassy carbon (GC) disc and a Pt ring. A spiral Pt wires was used as the counter electrode and Hg|HgSO$_4$ was used as the reference electrode. All the potentials reported in this work are with respect to the standard hydrogen electrode (SHE). For the preparation of the electrodes, the catalyst powder was mixed with a Nafion (5 wt.%) solution in isopropyl alcohol and water and then mixed ultrasonically for 15 min. The resulting suspension (12 μL) was dropped on to the glassy carbon electrode and dried in a nitrogen chamber. The size and distribution of the metal particles were determined by means of high-resolution transmission electron microscopy (HR-TEM, model JEM-30100).

2.3. Single cell test

Commercial PtRu black (E-TEK, 4 mg cm^{-2}) was used as the anode for fuel cell testing. For the cathode material, either the prepared PtN$_x$/C or a commercial Pt/C (E-TEK, 40 wt.%) catalyst was used. The amount of catalyst used in the cathode was fixed at 1 mg cm^{-1}. The pretreated Nafion 112 membrane was positioned between the two electrodes and hot pressed at a pressure of 60 kg cm^{-2} at 120 °C for 3 min to form the one-piece membrane electrode assembly (MEA). The performance of the cell was evaluated by measuring the current density against the cell voltage in a commercial fuel cell testing system (Wonatech). The polarization curves were recorded at 70 °C by circulating different methanol concentrations through the anode at a rate of 1 mL min^{-1}. Humidified oxygen gas was provided to the cathode at a pressure of 1 atm.

3. Results and discussion

Fig. 1 shows HR-TEM images of the PtN$_x$/C powder heat-treated at 500, 700 and 900 °C, respectively. As expected, the PtN$_x$/C catalyst
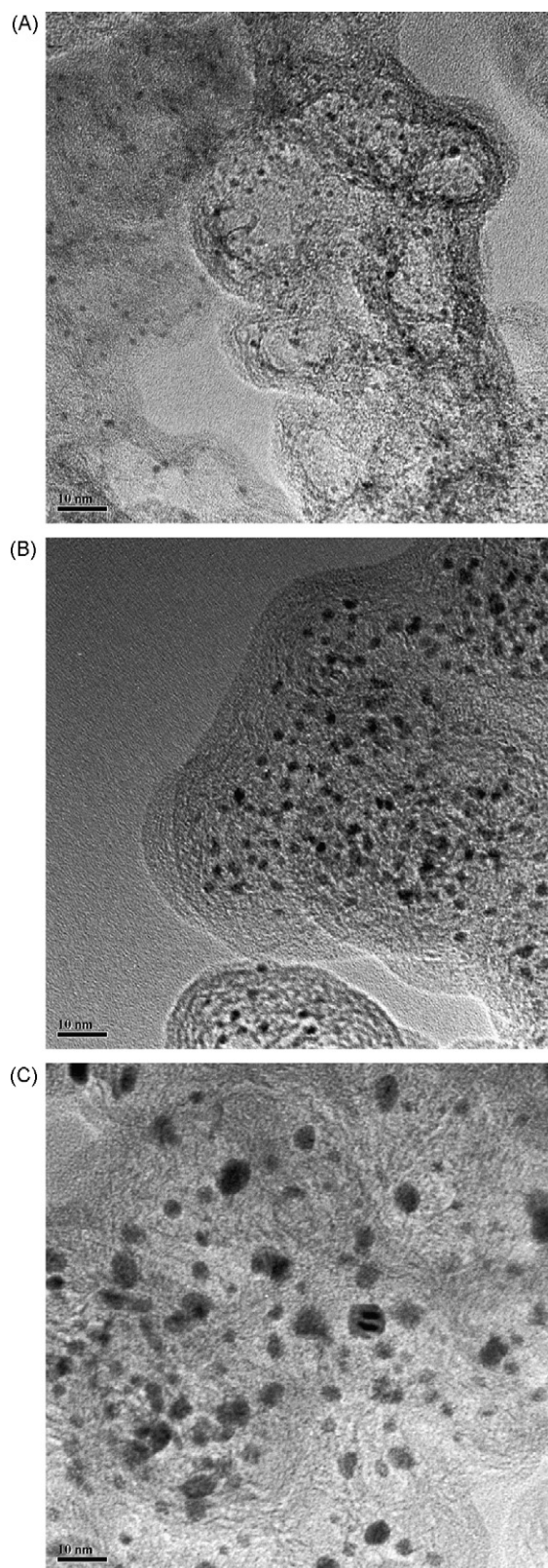

Fig. 1. HR-TEM images of PtN$_x$/C catalyst prepared at (A) 500 °C, (B) 700 °C and (C) 900 °C. Bar indicates 10 nm scale.
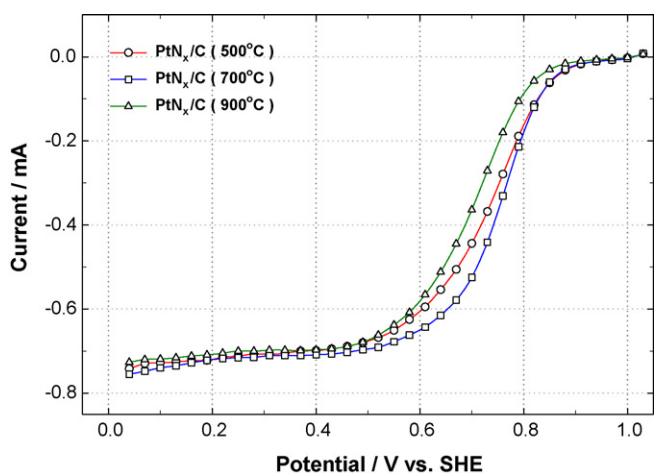
Fig. 2. Linear sweep voltammograms of PtN$_x$/C prepared at different temperatures using RDE in 0.5 M H$_2$SO$_4$ solution saturated with oxygen at scan rate of 5 mV s^{-1} and rotating speed of 1200 rpm.
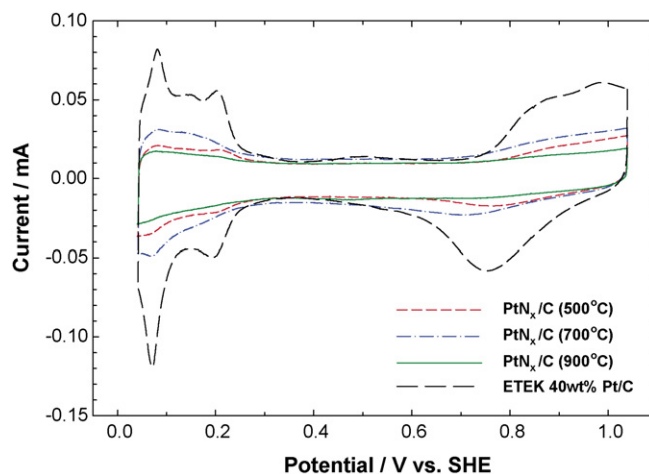

Fig. 3. Cyclic voltammograms of PtN$_x$/C prepared at different temperatures together with commercial Pt/C in 0.5 M H$_2$SO$_4$ solution purged with nitrogen at scan rate of 5 mV s^{-1}.

at 500 °C shows very fine particles that have dimensions mostly less than 2 nm. As the temperature increases to 700 °C the particle size of the catalyst supported on carbon is observed to increase slightly to around 3 nm. It is obvious that further increase in firing temperature to 900 °C accelerates the increase in the particle size of the metal to more than 7 nm. This is associated with the deleterious effect of agglomeration.

The activities of the ORR for the PtN$_x$/C catalysts prepared at different annealing temperatures were evaluated by measuring the polarization curves on a rotating disc electrode (RDE) in the absence of methanol. These are given in Fig. 2. The electrochemical measurements were performed in 0.5 M H$_2$SO$_4$ solution saturated with oxygen and the scan rate was fixed at 5 mV s^{-1} with a rotation speed of 1200 rpm. The curves in Fig. 2 clearly show that the onset potential for PtN$_x$/C treated at 700 °C is more positive than that treated at 900 °C. This is due to difference in the roughness factor, the ratio between the actual reactive surface area, and in the geometrical electrode area. The polarization curves are fitted to the Tafel equation, which considers mass transfer effects in order to determine the Tafel slope.

$$E = E^0 - b \log \frac{ii_L}{i_L - i} \tag{1}$$

$$E^0 = E_r + b \log i^0 \tag{2}$$

where E and i are the experimentally measured potential and current density normalized to the disc area of the RDE, E_r is the reversible cell voltage, i_L the limiting current density, i^0 the exchange current density, and b is the Tafel slope for the ORR. The Tafel slopes of PtN$_x$/C prepared at 700 and 900 °C are calculated to be 63.6 and 64.0 mV dec^{-1}, respectively, which are close to the typical value of 60 mV dec^{-1} for Pt electrodes [24]. The similar values of the Tafel slope indicate that there is no difference in the O$_2$ reduction mechanism on the chelate modified PtN$_x$/C catalysts. In the case of PtN$_x$/C prepared at 500 °C, however, the Tafel slope is 75 mV dec^{-1}. The increase of Tafel slope does not favour the kinetics of the oxygen reduction reaction. This result also indicates that the oxygen reduction mechanism occurring on the surface of PtN$_x$/C prepared at 500 °C is different from that on the other two samples.

The cyclic voltammograms of PtN$_x$/C prepared at different temperatures, together with that for the commercial Pt/C catalyst for comparison, are shown in Fig. 3. All measurements were recorded at scan rate of 5 mV s^{-1} in 0.5 M H$_2$SO$_4$ saturated with nitrogen gas. The active surface area of the catalysts was determined from

the area of the hydrogen desorption peak between 0.02 and 0.39 V vs. SHE after subtracting the contribution from the double-layer charge. It was then converted into the specific active surface area using a factor of 210 μC cm^{-2} for a monolayer of hydrogen adsorbed on the surface of polycrystalline Pt. According to the CV measurements, the hydrogen adsorption and desorption peak areas decrease after modifying the Pt surface with the chelating agent. It is assumed that hydrogen can be adsorbed only on the free Pt surface. Therefore, the decrease in the active surface area is considered to be due to the surface coverage of Pt with nitrogen. It is also interesting to note that the hydrogen adsorption and desorption peaks of the PtN$_x$/C prepared at 500 °C appear smaller than those of PtN$_x$/C prepared at 700 °C. From the HR-TEM images shown in Fig. 1, the particle size of PtN$_x$ treated at 500 °C is smaller than that prepared at 700 °C. Generally, a smaller particle size should create a higher specific surface area. This inconsistency implies that the surface condition of PtN$_x$/C treated at 500 °C is different. This is in good agreement with the analysis of the Tafel slope from the rotating disc electrode experiment. Based on these observations, it is concluded that 500 °C is not sufficiently high to modify completely the Pt surface with the chelating agent.

In addition to the heat-treatment temperature, the content of nitrogen in PtN$_x$/C is a critical factor for effective catalytic activity. It is varied by using different molar ratios of Pt to N in the precursor solution for the synthesis of the PtN$_x$/C. Note that the Pt/N ratio used represents the molar ratio of Pt to N in the precursor solution not the actual atomic ratio between Pt and N. Fig. 4 shows the linear sweep voltammograms of PtN$_x$/C and the commercially available Pt/C catalyst. The molar ratio of N to Pt changes from 0.5 to 15 using different amounts of chelating agent in the solution. The experimental conditions are the same as those used in Fig. 2. From this result, the ORR activity of the PtN$_x$/C catalyst is found to increase as the molar ratio of N to Pt decreases from 15 to 2. With further decrease of the ratio to 0.5, no distinct activity change is observed. This behaviour is not in accordance with the results on RuN$_x$/C reported by Popov and coworkers [25]. They synthesized RuN$_x$/C supported on carbon as electrocatalysts for the ORR using a chelating agent. The N coordinated Ru clusters enhanced the catalytic activity towards the ORR. The activity of ORR increased with increase in the ratio of N and the highest activity was found with a Ru:N ratio of 1:20. Since Ru is not active towards the ORR, the N coordinated Ru serves as an active site of oxygen reaction. As a consequence, a high ratio of the N precursor is required in
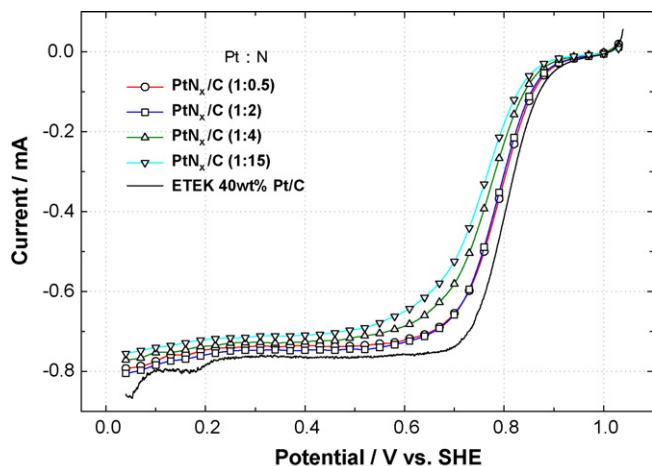
Fig. 4. Polarization curves obtained on RDE for commercial Pt/C and PtN$_x$/C catalysts prepared using different molar ratios of Pt to N in precursor solution. Measurements performed in 0.5 M H$_2$SO$_4$ solution saturated with oxygen at scan rate of 5 mV s^{-1} and rotating speed of 1200 rpm.

the preparation process. In the case of PtN$_x$/C, Pt is already a very active catalyst for the ORR. The surface of Pt is modified with N not to enhance the activity of ORR but to suppress the adsorption of methanol. It is well established that at least three neighbouring Pt atoms in a proper crystallographic orientation are required to initiate the chemisorption of methanol [13,26,27]. Therefore, the optimum metal:N ratio for PtN$_x$/C in the ORR in the absence of methanol is much smaller than that for RuN$_x$/C.

Fig. 5 shows the methanol-tolerant properties of the PtN$_x$/C catalysts in terms of polarization in an N$_2$-saturated 0.5 M H$_2$SO$_4$ solution containing 0.1 M methanol. The methanol oxidation peak for the PtN$_x$/C is more than ten times smaller than that obtained for the commercial Pt/C catalyst. This result proves that the chelate modified Pt surface is less active towards methanol oxidation and thus results in a high methanol tolerance during the ORR. With increasing N content, methanol oxidation is inhibited further and shows almost constant methanol tolerance when the molar ratio of N to Pt is higher than 4. Therefore, the optimum N:Pt ratio in the precursor solution should be between 0.5 and 4.

Fig. 6 shows a comparison of the DMFC polarization curves obtained for the PtN$_x$/C catalyst and commercial Pt/C at 70 °C and
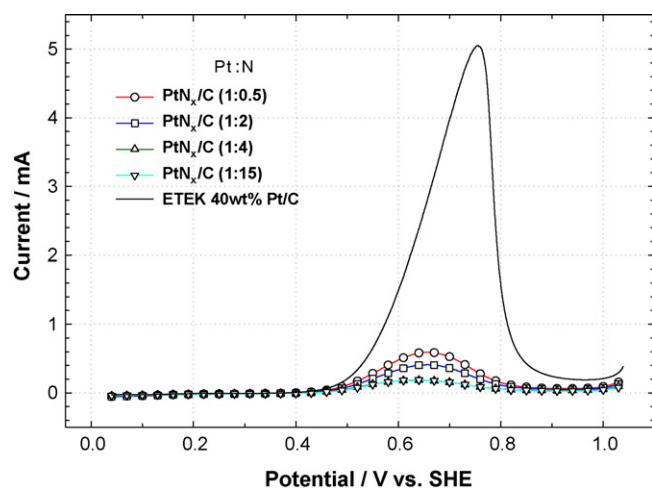

Fig. 5. Linear sweep voltammogram for methanol oxidation on PtN$_x$/C and commercial Pt/C catalysts in 0.5 M H$_2$SO$_4$ + 0.1 M CH$_3$OH solution saturated with nitrogen at scan rate of 5 mV s^{-1}.
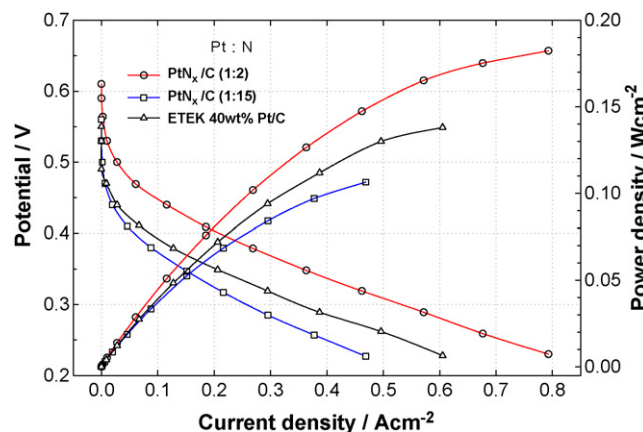

Fig. 6. Polarization curves in single DMFC using PtN$_x$/C and Pt/C as cathode electrodes. Anode: PtRu black 4 mg cm^{-2}; cathode: PtN$_x$/C or commercial Pt/C 1 mg cm^{-2}; electrolyte: Nafion 112; methanol (4 M) flow rate: 1 mL min^{-1}; O$_2$ pressure: 1 atm; cell temperature: 70 °C.

1 atm. A PtRu black catalyst (4 mg cm^{-2}) is used for the anode in all cases. The membrane is Nafion 112 and the concentration of methanol is 4 M to create a severe methanol crossover environment. It is seen that the surface modified PtN$_x$/C (Pt:N = 1:2 in the precursor solution) gives improved performance, as much as 180 mW cm^{-2}, compared with the commercial Pt/C value of 138 mW cm^{-2}. The improved performance is attributed to the high oxygen reduction activity and the enhanced tolerance towards the oxidation of methanol transferred from the anode to the cathode through the Nafion membrane. In addition, the open-circuit voltage for PtN$_x$/C is higher than that for Pt/C and signifies the fact that the surface modified PtN$_x$/C electrode alleviates the formation of a mixed potential.

In order to examine the effect of methanol tolerance of the cathode electrode on the overall cell performance, it is desirable to know the exact potential of the cathode in the DMFC. Using a two-electrode configuration within the operating cell, the DMFC cathode potential is evaluated from ordinary cell polarization measurements using the following *iR*-corrected voltage–current density equation [28].

$$E_{O_2}^{MeOH}(i) - E_{HOR}(i) = V_{MeOH/O_2}^*(i) + V_{MeOH/H_2}^*(i) - V_{H_2/H_2}^*(i) \qquad (3)$$

where $E_{O_2}^{MeOH}(i)$ is the DMFC cathode potential at a current density of i, $E_{HOR}(i)$ is the potential of the hydrogen oxidation reaction,
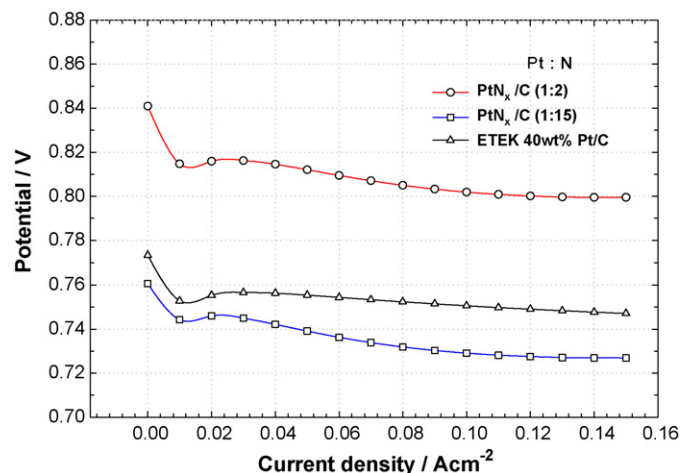

Fig. 7. Evaluation of cathode potential for PtN$_x$/C and commercial Pt/C in DMFCs.

$V^*_{\text{MeOH}/O_2}(i)$ is the cell potential from a methanol–oxygen cell, $V^*_{\text{MeOH}/H_2}(i)$ is the cell potential from a driven cell with the same methanol anode and a hydrogen evolving cathode, and $V^*_{H_2/H_2}(i)$ is the cell potential from a driven hydrogen pump cell with a hydrogen oxidizing anode and a hydrogen evolving cathode. Based on the assumption that the overpotentials of hydrogen oxidation and evolution are negligible, the cathode potential is calculated and presented in Fig. 7. According to the results, the cathode potential of PtN$_x$/C (Pt:N = 1:2) is higher than that of the Pt/C electrode. This is mainly due to the fact that the strong methanol tolerance of the PtN$_x$/C inhibits the poisoning of O_2 reduction by adsorbed methanol [7]. Under conditions of significant methanol crossover, the potential loss arising from the poisoning effect is higher than the overpotential of the oxygen reduction reaction. For PtN$_x$/C (Pt:N = 1:15), as shown in Fig. 4, the intrinsic oxygen reduction activity is so low that the cathode potential is lowest among the catalysts tested.

4. Conclusions

PtN$_x$/C is proposed as a novel catalyst with high methanol tolerance for a DMFC. By modifying the platinum surface with a chelating agent, the PtN$_x$/C catalysts are endowed with remarkable methanol tolerance while maintaining comparable ORR activity with the commercial Pt/C. The findings indicate that the heat-treatment temperature and the molar ratio of Pt to N play important roles in the performance of the catalysts. The heat-treatment temperature needs to be higher than 500 °C to modify the surface of the Pt. The ORR activity decreases with increase in the molar ratio of nitrogen, whereas the methanol tolerance increases up to the point where the molar ratio of N to Pt is 4. Since the surface of Pt is modified with N not to enhance the activity of ORR but to suppress the adsorption of methanol, it is necessary to decrease the content of N to the lowest possible value while maintaining the methanol tolerance. The higher cathode potential and OCV in fuel cell tests under severe methanol crossover conditions demonstrate that PtN$_x$/C is a promising methanol-tolerant electrocatalyst for DMFCs.

References

[1] A.S. Patil, T.G. Dubois, N. Sifer, E. Bostic, K. Gardner, M. Quah, C. Bolton, J. Power Sources 136 (2004) 220–225.
[2] B.D. McNicol, D.A.J. Rand, K.R. Williams, J. Power Sources 83 (1999) 15–31.
[3] R. Dillon, S. Srinivasan, A.S. Arico, V. Antonucci, J. Power Sources 127 (2004) 112–126.
[4] T.R. Ralph, M.P. Hogarth, Platinum Met. Rev. 46 (2002) 3–12.
[5] A. Kuver, W. Wielstih, J. Power Sources 74 (1998) 211–218.
[6] B. Gurau, E.S. Smotkin, J. Power Sources 112 (2002) 339–352.
[7] D. Chu, S. Gilman, J. Electrochem. Soc. 141 (1994) 1770–1773.
[8] P.S. Kauranen, E. Skou, J. Electroanal Chem. 408 (1996) 189–198.
[9] M. Miyake, J.S. Wainright, R.R. Savinell, J. Electrochem. Soc. 148 (2001) A905–A909.
[10] L.J. Hobson, Y. Nakano, H. Ozq, S. Hayase, J. Power Sources 104 (2002) 79–84.
[11] A.K. Shukla, R.K. Raman, N.A. Choudhury, K.R. Priolkar, P.R. Sarode, S. Emura, R. Kumashiro, J. Electroanal. Chem. 563 (2004) 181–190.
[12] J.R.C. Salgado, E. Antolini, E.R. Gonzalez, Appl. Catal. B 57 (2005) 283–290.
[13] H. Yang, C. Coutanceau, J.M. Leger, L. Alonso-Vante, C. Lamy, J. Electroanal. Chem. 576 (2005) 305–313.
[14] H. Yang, N. Alonso-Vante, C. Lamy, D.L. Akins, J. Electrochem. Soc. 152 (2005) A704–A709.
[15] R.W. Reeve, P.A. Christensen, A.J. Dickinson, A. Hamnett, K. Scott, Electrochem. Acta 45 (2000) 4237–4250.
[16] S.S. Ozenler, F. Kadirgan, J. Power Sources 154 (2006) 364–369.
[17] R.W. Reeve, P.A. Christensen, A. Hamnett, S.A. Haydock, S.C. Roy, J. Electrochem. Soc. 145 (1998) 3463–3471.
[18] A.K. Shukla, R.K. Raman, Annu. Rev. Mater. Res. 33 (2003) 155–168.
[19] R. Jiang, D. Chu, J. Electrochem. Soc. 147 (2000) 4605–4609.
[20] S. Baranton, C. Coutanceau, C. Roux, F. Hahn, J.M. Leger, J. Electroanal. Chem. 577 (2005) 223–234.
[21] P. Convert, C. Coutanceau, P. Crouigneau, F. Gloaguen, C. Lamy, J. Appl. Electrochem. 31 (2001) 945–952.
[22] Y. Lu, R. Reddy, Electrochem. Acta 52 (2007) 2562–2569.
[23] J.G.O.C.H. Lee, H. Kim, Electrochem. Commun. 9 (2007) 2629–2632.
[24] A. Parthasarathy, S. Srinivasan, A.J. Appleby, C.R. Martin, J. Electroanal. Chem. 339 (1992) 101–121.
[25] L. Liu, H. Kim, J.W. Lee, B.N. Popov, J. Electrochem. Soc. 154 (2007) A123–A128.
[26] H.A. Gasteiger, N. Markovic, P.N. Ross, E.J. Cairns, J. Electrochem. Soc. 141 (1994) 1795–1803.
[27] N.M. Markovic, P.N. Ross, Surf. Sci. Rep. 45 (2002) 117–229.
[28] S.C. Thomas, X. Ren, S. Gottesfeld, P. Zelenay, Electrochem. Acta 47 (2002) 3741–3748.