Short Communication
Pd/C Catalyst with High Activity for Methanol Electrooxidation

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The Pd/C catalysts (carbon supported Pd nanoparticles) were synthesized using a polyol process by quickly heating using microwave. The research results revealed that the Pd nanoparticles with small size were successfully deposited on the carbon support. Moreover, the surfaces of the Pd nanoparticles contain abundant (100) planes, which was of benefit to the improvement of their electrochemical activity. Furthermore, the actually Pd loadings for all the Pd/C catalysts were closed to the theoretical loading (20 wt%), indicating the high efficiency of this preparation method for the Pd nanoparticles depositing on the carbon. The transmission electron microscope and electrochemical test results indicated that the average diameter and the dispersity of the Pd nanoparticles in the Pd/C catalysts, as well as the electrochemical activity of the Pd/C catalysts were becoming firstly better, and then worse with the amount of the adding KOH solution, suggesting the mean size and dispersity of the Pd nanoparticles in the Pd/C catalyst were the key factors affecting its electrochemical activity. The highest anodic mass-specific current densities of the Pd/C catalyst for the methanol electrooxidation in the 0.1 M KOH solution with 1 M CH_3OH reached to 655.2 mA mg^{-1} Pd, showing that the microwave-assisted polyol process was a suitable method for synthesizing the Pd/C catalyst with good activity.

1. INTRODUCTION

Proton exchange membrane fuel cell (PEMFC) was a kind of perfect energy conversion device, which efficiently converted the chemical energy of a fuel and an oxidant into electricity energy with low pollution [1,2]. Moreover, the PEMFCs using liquid fuels, such as methanol, ethanol, and formic acid etc., had wide application prospects in many portable power sources [3-6]. Therefore, the researches about PEMFCs fed by liquid fuels were attracted widely attentions, especially for the direct methanol fuel cells (DMFCs), due to the simple molecular structure and high energy density of methanol [6,7].

For achieving the commercialized application of DMFCs, a great effort was made in recent years, especially for the investigation of the anodic catalyst with excellent electrochemical activity towards the oxidation of methanol as well as the high CO-tolerance ability [8-15]. Generally, Pt based catalysts had the best electrochemical activity for the methanol oxidation [8-10]. However, the CO-like toxic species adsorbed on the Pt catalysts decreased their electrochemical performance [8-12]. Moreover, the high cost and limited resource of Pt were other reasons that DMFCs had not been commercialized on a large scale [16-22]. Therefore, more and more researchers focused on studying the inexpensive catalysts to replace Pt catalysts in recent.

Pd, as another platinum group metal, had similar electronic configuration compared with Pt. Furthermore, the Pd catalysts with low price were widely applied in industry [21-23]. Moreover, numerous Pd catalysts with good electrocatalytic activity in alkaline medium were reported in recent [8-15,19,24-26]. Therefore, Pd and Pd based catalysts employed as the electrocatalysts for the oxidation of methanol were intensively researched and developed in recent years [8-15,19,24-26]. It was reported that, many Pd nanocatalysts with excellent electrochemical activities were synthesized using plasma sputtering technique [9], electrostatic self-assembly and in situ reduction method [11], galvanic replacement method [27], electrodeposition method [28], chemical reduction method [12,22,24,29,30], polyol process [31,32] and colloid method [33], etc. In general, the electrochemical activities of the precious metal nanocatalyst were closely related to the inherent properties of the precious metal nanoparticles in the catalyst, such as the average size, structure and composition of the precious metal nanoparticles [34-38]. Furthermore, these inherent properties were often associated with the preparation methods. Among these synthesis methods, the polyol process aroused great interest in recent years, since many nanocatalysts with high activity were prepared easily by this process without any surfactant [39-43]. In terms of this synthesis method, ethylene glycol was decomposed to generate reducing species (CH_3CHO) in an alkaline medium under microwave irradiation [39-41].

In this work, a series of Pd/C catalysts (carbon supported Pd nanoparticles) were synthesized by a microwave-assisted polyol process to investigate their electrochemical performance for the methanol oxidation.

2. EXPERIMENTAL

2.1. Synthesis of Pd/C catalysts

The preparation procedure of the Pd/C catalyst was as follows. Firstly, a $PdCl_2$ solution (0.0564 M) was prepared by 1 g $PdCl_2$, 10 ml 12 M HCl solution and proper distilled water. Then, 24 mg Vulcan XC-72R carbon and 1 ml $PdCl_2$ solution were mixed with 20 ml ethylene glycol in a small beaker by ultrasonic agitation. After that, an excessive amount of 1 M KOH solution was employed to adjust the suspension to alkalescency. In this work, the volume of 1 M KOH aqueous solution was 1.7, 2.2, 2.7, 3.2 and 3.7 ml. Subsequently, the beaker was put in a Midea microwave oven (700 W, 2450 MHz) to heat for 1 or 2 min. The Pd/C catalyst was collected using vacuum filtration. Finally, the Pd/C catalyst was washed adequately with ethanol, deionized water and acetone, followed by dried in an oven for 6 h

at 80 ºC. The Pd/C catalysts were labeled as Pd/C#t-s, where "t" was the reaction time; "s" was the amount of the adding KOH solution.

2.2. Characterization of the Pd/C catalysts

The morphology, structure and Pd loading of the Pd/C catalyst were characterized using a JEM 1200EX transmission electron microscope (TEM), Bruker D8 advanced X-ray diffractometer and Agilent 7500ce inductively coupled plasma mass spectrometry (ICP-MS), respectively.

2.3. Electrochemical studies

The electrocatalytic activity of the Pd/C catalyst for the methanol oxidation was investigated by cyclic voltammetry using a CHI760E electrochemical workstation (Shanghai). The cyclic voltammograms (CVs) on the Pd/C catalysts were recorded at a scan rate of 50 mV s^{-1} in the nitrogen saturated 0.1 M KOH solution with 1 M CH$_3$OH at 25 ºC. The working electrode was fabricated according to the reported method [44-46]. The reference electrode and counter electrode were Ag|AgCl (c_{KCl} = 1 M) electrode and graphite electrode (2 cm^2), respectively.

3. RESULTS AND DISCUSSION

3.1. Catalyst characterization

The TEM images of the Pd/C catalysts synthesized using 1 min were shown in Figure 1. Its insets displayed the size distribution histograms of the Pd nanoparticles in the Pd/C catalysts. The TEM images revealed that the Pd nanoparticles in all the Pd/C catalysts were evenly deposited on the carbon support. It was found from Figure 1a, b, c and e that partial Pd nanoparticles were congregated to form some big Pd nanoparticles. Figure 1d showed that, however, the Pd nanoparticles in the Pd/C#1-3.2 catalyst were hardly gotten together. The insets in Figure 1 indicated that, moreover, the Pd nanoparticles in the Pd/C#1-3.2 catalyst had narrowest size distribution among the Pd/C catalysts prepared spending 1 min. Furthermore, the dispersity of the Pd nanoparticles became firstly better, and then worse with the amount of the KOH solution. Calculated from the insets in Figure 1, the mean sizes of the Pd nanoparticles in the Pd/C#1-1.7, Pd/C#1-2.2, Pd/C#1-2.7, Pd/C#1-3.2 and Pd/C#1-3.7 catalysts were respectively 5.1, 4.8, 4.5, 3.7 and 4.8 nm, implying that the average diameter of the Pd nanoparticles first decreased and then increased with the amount of the KOH solution. The changing trend of the mean size of the Pd nanoparticles in the Pd/C catalyst was closely related to the growth scheme of the Pd nanoparticles, which mainly involved the nucleation and growth of the Pd nanoparticles. Since the reducing species (CH$_3$CHO) was produced when ethylene glycol was heated in alkaline medium [39-41], the reducibility of the reaction system increased with the amount of KOH solution. The strong reducibility accelerated the nucleation rate of the Pd nanoparticles, increasing the amount of the Pd nanoparticles, which was similar to the effect of other reducing agents [46]. Therefore, the Pd nanoparticles in the Pd/C catalyst

became small with the amount of KOH solution firstly. However, the Pd nanoparticles became easy to reunite when the sizes of Pd nanoparticle was small enough, causing the Pd nanoparticles in the Pd/C#1-3.7 catalyst exhibited bigger mean size compared to the Pd/C#1-3.2 catalyst. Therefore, the Pd nanoparticles in the Pd/C#1-3.2 catalyst simultaneously had an excellent dispersity and a small mean diameter. This result was different to the report about Au/C catalyst [46], since the size of the big Pd nanoparticles was only about 10 nm, which were also efficiently deposited on the carbon support.
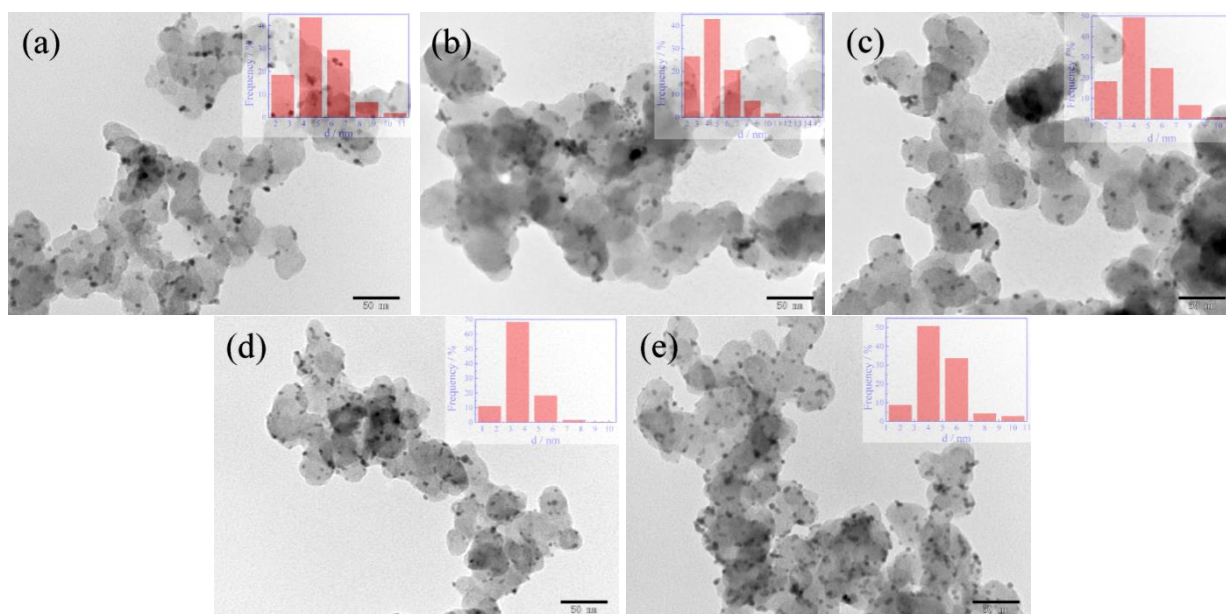

Figure 1. TEM images of the Pd/C#1-1.7 (a), Pd/C#1-2.2 (b), Pd/C#1-2.7 (c), Pd/C#1-3.2 (d) and Pd/C#1-3.7 (f) catalysts. Scale bar: 50 nm. The insets were the corresponding size distribution histograms of the Pd nanoparticles.

Figure 2 exhibited the morphology characteristics of the Pd/C catalysts prepared by 2 min. The insets in Figure 2 showed the size distribution histograms of the Pd nanoparticles in these catalysts. The average diameters of the Pd nanoparticles calculated based on the size distribution histograms for the Pd/C#2-1.7, Pd/C#2-2.2, Pd/C#2-2.7, Pd/C#2-3.2 and Pd/C#2-3.7 catalysts were 6.2, 5.7, 5.3, 5.0 and 5.0 nm, respectively. Compared Figure 2 with Figure 1, the changing trends of the mean diameter and dispersity of the Pd nanoparticles were similar, despite the preparation time was different. However, the dispersity of the Pd nanoparticles in the Pd/C#2-2.7 catalyst was best among the Pd/C catalysts prepared by 2 min. In other words, the dispersity of the Pd nanoparticles was best when the amount of KOH is 3.2 ml for the Pd/C catalyst prepared using 1 min; while the dispersity of the Pd nanoparticles was best when the amount of KOH was 2.7 ml for the Pd/C catalyst prepared by 2 min. This result implied that the reducing effect of the reaction system by adding 2.7 ml KOH solution and microwave heating for 2 min was close to that of the reaction system by adding 3.2 ml KOH solution and microwave heating for 1 min, suggesting that the reducibility of the reaction system enhances with the microwave heating time. However, the average diameter of the Pd nanoparticles in the Pd/C#2-2.7 catalyst (5.3 nm) was much larger compared to the Pd/C#1-3.2 catalyst (3.7 nm), showing that microwave heating with a long time

could increase the Pd particle size.
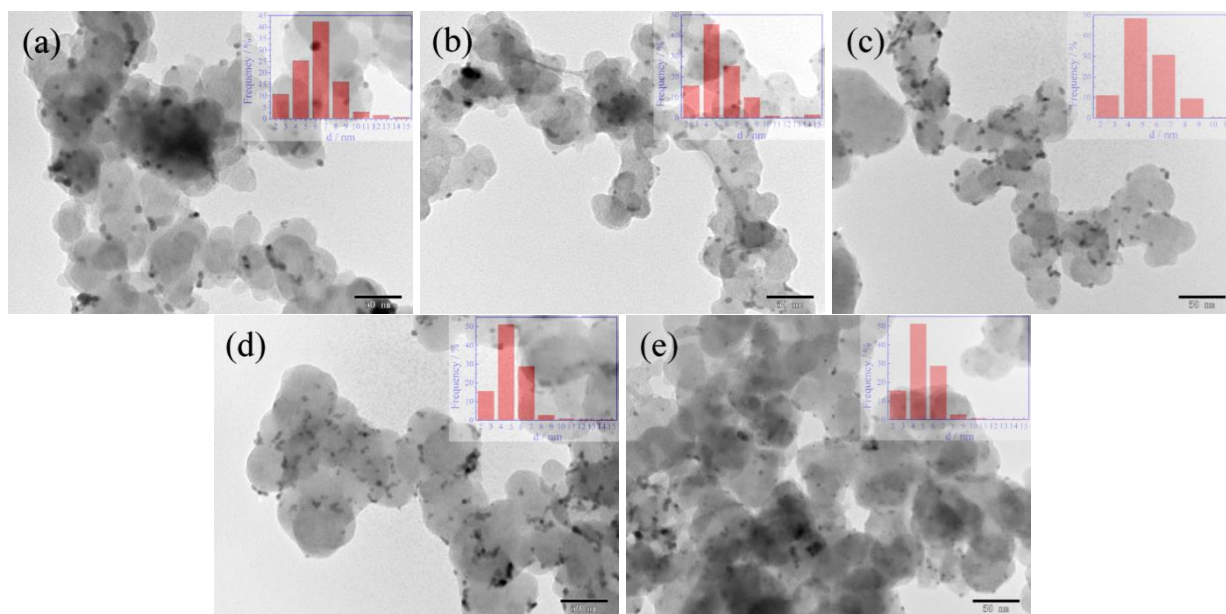
Figure 2. TEM images of the Pd/C#2-1.7 (a), Pd/C#2-2.2 (b), Pd/C#2-2.7 (c), Pd/C#2-3.2 (d) and Pd/C#2-3.7 (f) catalysts. Scale bar: 50 nm. The insets were the corresponding size distribution histograms of the Pd nanoparticles.
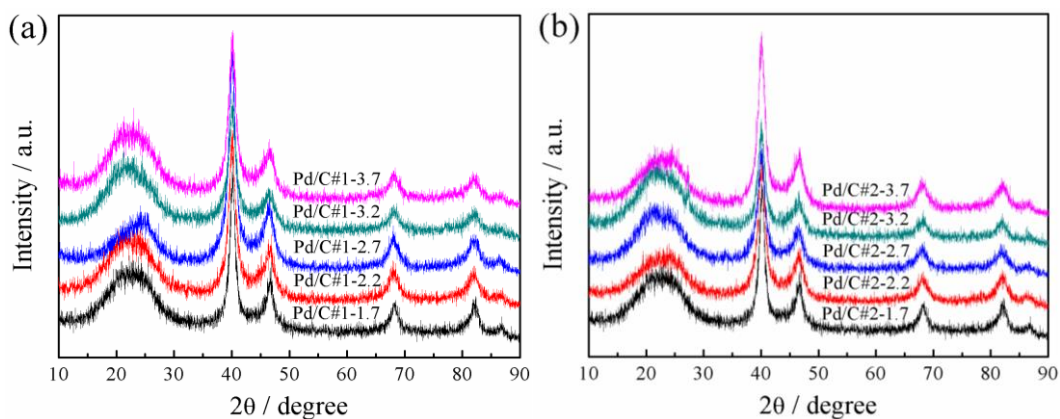
Figure 3. XRD patterns of the Pd/C catalysts synthesized using 1 min (a) and 2 min (b).

The structures in the Pd/C catalysts were displayed by the X-ray diffraction (XRD) patterns shown in Figure 3. For the XRD patterns of all the catalysts, there were a broadened diffraction peak from $2\theta = 15$ to $33°$, which related to the diffraction of the carbon support (JCPDS, No. 50-926) [44-46]. The diffraction peaks corresponding to the Pd (111), (200), (220), (311) and (222) lattice planes were respectively located at about $2\theta = 40.2, 46.8, 68.2, 81.9$ and $86.6°$ [47-49]. The lattice structure of the Pd nanoparticles could be identified by the intensity ratios between the diffraction peaks [47]. According to Figure 3, the average intensity ratio between the Pd (200) and (111) lattice planes for the Pd/C catalysts was about 0.414, which was close to the intensity ratio (≈ 0.42) calculated from the standard Pd XRD card (JCPDS, No. 5-0681) [47]. This result suggested that the Pd (100) planes on the surfaces of the Pd

nanoparticles were scarcely reduced [47], which was favorable for the improvement of their electrochemical activity [47-50].

The Pd loading of the Pd/C catalyst was tested by an Agilent 7500ce ICP-MS. The corresponding test results indicated the Pd loadings were 20.9, 21.2, 21.4, 20.5, 19.2, 20.7, 20.8, 20.7, 19.3 and 19.4 wt% respectively for the Pd/C#1-1.7, Pd/C#1-2.2, Pd/C#1-2.7, Pd/C#1-3.2, Pd/C#1-3.7, Pd/C#2-1.7, Pd/C#2-2.2, Pd/C#2-2.7, Pd/C#2-3.2 and Pd/C#2-3.7 catalysts. It was found that the measured Pd loadings of all the Pd/C catalysts were closed to the theoretical loading (20 wt%), indicating that this preparation method had high efficiency for the Pd nanoparticles depositing on the carbon. The high loading efficiency of the Pd nanoparticles sufficiently attested that the microwave-assisted polyol process was an excellent synthesis method for the preparation of the Pd/C catalysts.

3.2. Electrochemical studies

The CVs on the Pd/C catalysts in deoxygenated 0.1 M KOH + 1 M CH$_3$OH mixed solution at 25 °C were shown in Figure 4, in which all the scan rates were 50 mV s^{-1}. All the current densities in Figure 4 were normalized by the actual Pd loadings measured using ICP-MS. According to Figure 4, methanol was oxidized initially at about -0.5 V, and the anodic current densities reached to a maximum at around -0.02 V [8,12,13,24]. The peak of the anodic current densities were 348.9, 374.8, 391.7, 655.2, 530.1, 303.9, 423.6, 588.5, 399.9 and 375.7 mA mg^{-1} Pd respectively on the Pd/C#1-1.7, Pd/C#1-2.2, Pd/C#1-2.7, Pd/C#1-3.2, Pd/C#2-3.7, Pd/C#2-1.7, Pd/C#2-2.2, Pd/C#2-2.7, Pd/C#2-3.2 and Pd/C#2-3.7 catalysts. It was found that the electrochemical activities of the Pd/C catalysts synthesized by microwave heating for 1 and 2 min for the methanol oxidation had the same trend with the increase in the KOH solution. Namely, the activity of the Pd/C catalyst first became better and then worse with the amount of the KOH solution. This trend was same to that of the mean diameter and dispersity of the Pd nanoparticles observed from TEM images, suggesting the effect of the mean size and dispersity of the Pd nanoparticles on the activity of Pd/C catalyst was very important.
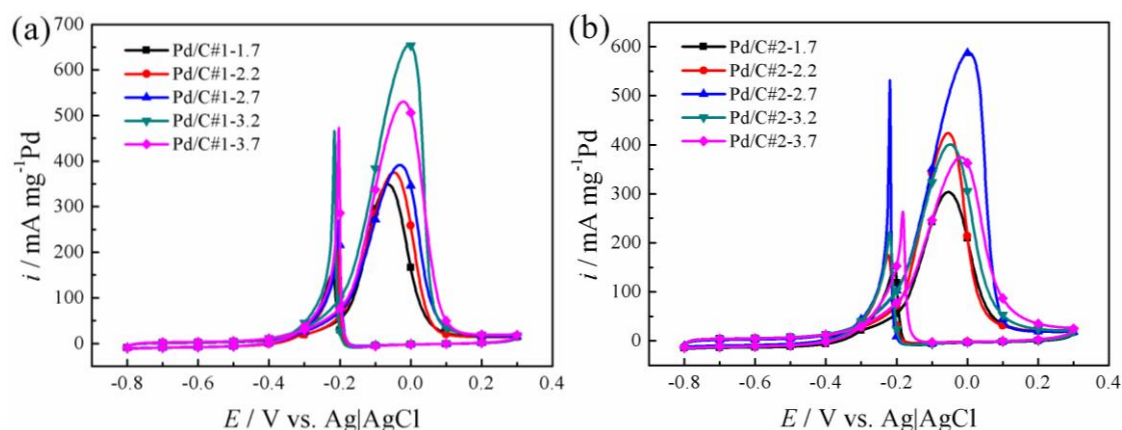
Figure 4. CVs on the Pd/C catalysts synthesized using 1 min (a) and 2 min (b) in deoxygenated 0.1 M KOH + 1 M CH$_3$OH mixed solution at 25 °C. Scan rate: 50 mV s^{-1}.

Moreover, Figure 4a presented that the Pd/C#1-3.2 catalyst had the highest activity (655.2 mA

mg^{-1} Pd) for the electrochemical oxidation of methanol among the Pd/C catalysts prepared by 1 min; while Figure 4b indicates that the Pd/C#2-2.7 catalyst had the best electrochemical activity (588.5 mA mg^{-1} Pd) among the Pd/C catalysts synthesized using 2 min. This result proved again that the heating time and the amount of KOH solution worked together to affect the reducibility of the reaction system. The reason that the Pd/C#1-3.2 and Pd/C#2-2.7 catalysts had the best electrochemical activities respectively among the Pd/C catalysts prepared using 1 and 2 min was the Pd nanoparticles in the Pd/C#1-3.2 and Pd/C#2-2.7 catalysts both had small mean size and excellent dispersion, simultaneously. Otherwise, this result revealed that the Pd/C catalyst with excellent activity could be prepared by microwave heating for 1 or 2 min using proper KOH solution. For evaluating the methanol electrooxidation activity of the as-prepared Pd/C catalysts, numerous Pd catalysts reported in literatures were collected and listed in Table 1 [10,11,19,25]. Compared to the Pd catalysts listed in Table 1, both the Pd/C#1-3.2 and Pd/C#2-2.7 catalysts exhibited good activity for the electrochemical oxidation of methanol.

Table 1. Pd catalysts reported in literatures.

Catalyst	Mass activity (mA mg^{-1} Pd)	Electrolyte solution
Pd/rGO-CNT [10]	255.68	1.0 M KOH + 1.0 M CH$_3$OH
Pd/GS [11]	222.0	1.0 M KOH + 1.0 M CH$_3$OH
Pd/RGO [19]	358.5	1.0 M KOH + 1.0 M CH$_3$OH
Pd/Vulcan [25]	205.41	0.5 M KOH + 1.0 M CH$_3$OH
Pd/MWCNTs [25]	288.65	0.5 M KOH + 1.0 M CH$_3$OH

Figure 4 revealed that, furthermore, all the CVs on the Pd/C catalysts showed a peak from about -0.2 to -0.4 V in the reverse scan. These peaks were associated with the electrochemical oxidation of the CO-like toxic species adsorbed on the Pd/C catalysts, which were yielded during the positive scan, due to the incomplete oxidation of methanol [11,12,19]. For an electrochemical catalyst, the peak related to the methanol electro-oxidation indicated its activity; while the peak about the CO-like intermediates revealed its CO tolerance. At present, the ratio between the (i_f) and (i_b), i_f/i_b, was usually employed an index to gauge the CO tolerance of the electrochemical catalyst [13,14,25]. The i_f/i_b values calculated from the Figure 4 for the Pd/C#1-1.7, Pd/C#1-2.2, Pd/C#1-2.7, Pd/C#1-3.2, Pd/C#2-3.7, Pd/C#2-1.7, Pd/C#2-2.2, Pd/C#2-2.7, Pd/C#2-3.2 and Pd/C#2-3.7 catalysts were 2.33, 1.64, 1.46, 1.43, 1.14, 1.98, 2.42, 1.12, 1.82, 1.41, respectively. All the i_f/i_b values were more than 1, showing the good CO tolerance of the Pd/C catalyst. Moreover, the microwave-assisted polyol process was simple, fast, and highly efficient. Therefore, this method provided a suitable process for synthesizing the Pd/C catalyst with good activity and excellent CO tolerance on an industrial scale.

4. CONCLUSIONS

The Pd/C catalysts were successfully synthesized using a simple method and investigated their

electrochemical activity for the oxidation of methanol. The TEM research result indicated that the Pd/C catalysts could be synthesized by microwave heating for 1 and 2 min. The XRD result revealed that the surface of the Pd nanoparticles in the Pd/C catalysts exited abundant (100) planes that could improve the electrochemical activity. With the increase in the amount of the KOH solution, moreover, the average diameter and dispersity of the Pd nanoparticles, as well as the electrochemical activity of the Pd/C catalyst were becoming firstly better, and then worse. This suggested the mean size and dispersity of the Pd nanoparticles were the key factors affecting the electrochemical activity. Furthermore, the Pd/C#1-3.2 and Pd/C#2-2.7 catalysts had the best electrochemical activities among the Pd/C catalysts synthesized respectively using 1 and 2 min, due to their Pd nanoparticles with the small mean size and excellent dispersion. The anodic mass-specific peak current densities of the Pd/C#1-3.2 and Pd/C#2-2.7 catalysts for the methanol electrooxidation reached to 655.2 and 588.5 mA mg^{-1} Pd, respectively. Therefore, this preparation method was a promising process for the synthesis of Pd/C catalysts with high activity on an industrial scale.

References

1. M. Oezaslan, P. Strasser, *J. Power Sources*, 196 (2011) 5240.
2. M. Ku. Jeon, Y. Zhang, P. J. McGinn, *Electrochim. Acta*, 55 (2010) 5318.
3. A. S. Aricò, S. Srinivasan, V. Antonucci, *Fuel Cells*, 1 (2001) 133.
4. E. Sarwar, T. Noor, N. Iqbal, Y. Mehmood, S. Ahmed, R. Mehek, *Fuel Cells*, 18 (2018) 189.
5. A. Bach Delpeuch, T. Asset, M. Chatenet, C. Cremers, *Fuel Cells*, 15 (2015) 352.
6. S. K. Hassaninejad-Darzi, M. Rahimnejad, M. Gholami-Esfidvajani, *Fuel Cells*, 16 (2016) 89.
7. L. M. Zhang, Z. B.Wang, J. J. Zhang, X. L. Sui, L. Zhao, J. C. Han, *Fuel Cells*, 15 (2015) 619.
8. J. S. Moon, Y. W. Lee, S. B. Han, K. W. Park, *Int. J. Hydrogen Energy*, 39 (2014) 7798.
9. J. Zhang, X. Hu, B. Yang, N. Su, H. Huang, J. Cheng, H. Yang, N. Saito, *J. Alloy. Compd.*, 709 (2017) 588.
10. M. Wang, Z. Ma, R. Li, B. Tang, X. Q. Bao, Z. Zhang, X. Wang, *Electrochim. Acta*, 227 (2017) 330.
11. S. Guo, S. Li, T. Hu, G. Gou, R. Ren, J. Huang, M. Xie, J. Jin, J. Ma, *Electrochim. Acta*, 109 (2013) 276.
12. Y. Zhang, H. Shu, G. Chang, K. Ji, M. Oyama, X. Liu, Y. He, *Electrochim. Acta*, 109 (2013) 570.
13. Z. P. Sun, X. G. Zhang, R. L. Liu, Y. Y. Liang, H. L. Li, *J. Power Sources*, 185 (2008) 801.
14. H. Huang, H. Chen, D. Sun, X. Wang, *J. Power Sources*, 204 (2012) 46.
15. P. Kannan, T. Maiyalagan, M. Opallo, *Nano Energy*, 2 (2013) 677.
16. J. N. Zheng, M. Zhang, F. F. Li, S. S. Li, A. J. Wang, J. J. Feng, *Electrochim. Acta*, 130 (2014) 446.
17. F. Benseba, A. A. Farah, D. S. Wang, C. Bock, X. M. Du, J. Kung, Y. L. Page, *J. Phys. Chem. B*, 109 (2005) 15339.
18. W. Wei, W. Chen, *J. Power Sources*, 204 (2012) 85.
19. H. Y. Na, L. Zhang, H. X. Qiu, T. Wu, M. X. Chen, N. Yang, L. Z. Li, F. B. Xing, J. P. Gao, *J. Power Sources*, 288 (2015) 160.

20. C. Xu, H. Wang, P. K. Shen, S. P. Jiang, *Adv. Mater.*, 19 (2017) 4256.
21. R. M. Abdel Hameed, *Appl. Surf. Sci.*, 411 (2017) 91.
22. X. Chen, Z. Lin, T. Jia, Z. Cai, X. Huang, Y. Jiang, X. Chen, G. Chen, *Anal. Chim. Acta*, 650 (2009) 54.
23. S. Dutta, C. Ray, A. Roy, R. Sahoo, T. Pal, *Chem. – Eur. J.*, 22 (2016) 10017.
24. Z. P. Sun, X. G. Zhang, Y. Y. Liang, H. L. Li, *Electrochem. Commun.*, 11 (2009) 557.
25. Y. Zhao, L. Zhan, J. Tian, S. Nie, Z. Ning, *Int. J. Hydrogen Energy*, 35 (2010) 10522.
26. C. Xu, L. Cheng, P. Shen, Y. Liu, *Electrochem Commun.*, 9 (2007) 997.
27. A. A. Ensafi, M. Jafari-Asl, B. Rezaei, *J. Electroanal. Chem.*, 731 (2014) 20.
28. X. Lu, L. Zheng, M. Zhang, H. Tang, X. Li, S. Liao, *Electrochim. Acta*, 238 (2017) 194.
29. K. Jukk, N. Kongi, L. Matisen, T. Kallio, K. Kontturi, K. Tammeveski, *Electrochim. Acta*, 137 (2014) 206.
30. Z. P. Sun, X. G. Zhang, Y. Y. Liang, H. L. Li, *J. Power Sources*, 191 (2009) 366.
31. Y. Liu, W. Wang, Y. Yang, F. Wang, X. Zhao, Z. Lei, *Appl. Catal. A-Gen.*, 505 (2015) 410.
32. M. Zhang, J. Xie, Q. Sun, Z. Yan, M. Chen, J. Jing, , A.M. Showkot Hossain, *Electrochim. Acta*, 111 (2013) 855.
33. Y. Huang, X. Zhou, J. Liao, C. Liu, T. Lu, W. Xing, *Electrochem. Commun.*, 10 (2008) 621.
34. S. Yan, S. Zhang, *Int. J. Hydrogen Energy*, 36 (2011) 13392.
35. S Wang, N Kristian, S Jiang, X. Wang, *Nanotechnology*, 20 (2009) 025605.
36. S. Yan, S. Zhang, *Int. J. Hydrogen Energy*, 37 (2012) 9636.
37. J. Luo, L. Wang, D. Mott, P. N. Njoki, Y. Lin, T. He, Z. Xu, B. N. Wanjana, I. I. S. Lim, C. J. Zhong, *Adv. Mater.*, 20 (2008) 4342.
38. H. Tang, J. H. Chen, M. Y. Wang, L. H. Nie, Y. F. Kuang, S. Z. Yao, *Appl. Catal. A-Gen.*, 275 (2004) 43.
39. S. Yan, S. Zhang, W. Zhang, J. Li, L. Gao, Y. Yang, Y. Gao, *J. Phys. Chem. C*, 118 (2014) 29845.
40. Z. Liu, J. Y. Lee, W. Chen, M. Han, L. M. Gan, *Langmuir*, 20 (2004) 181.
41. X. Li, W. X. Chen, J. Zhao, W. Xing, Z. D. Xu, *Carbon*, 43 (2005) 2168.
42. Z. Liu, B. Guo, L. Hong, T. H. Lim, *Electrochem. Commun.*, 8 (2006) 83.
43. Z. Liu, L. Hong, M. P. Tham, T. H. Lim, H. Jiang, *J. Power Sources*, 161 (2006) 831.
44. L. Lu, S. Zhang, S. Yan, *Int. J. Electrochem. Sci.*, 10 (2015) 649.
45. S. Yan, L. Gao, S. Zhang, L. Gao, W. Zhang, Y. Li, *Int. J. Hydrogen Energy*, 38 (2013) 12838.
46. S. Yan, L. Gao, S. Zhang, W. Zhang, Y. Li, L. Gao, *Electrochim. Acta*, 94 (2013) 159.
47. C. Shang, W. Hong, Y. Guo, J. Wang, E. Wang, *Chem.-Eur. J.*, 23 (2017) 5799.
48. W. Hong, P. Bi, C. Shang, J. Wang, E. Wang, *J. Mater. Chem. A*, 4 (2016) 4485.
49. Y. Huang, X. Zhou, J. Liao, C. Liu, T. Lu, W. Xing, *Electrochem. Commun.*, 10 (2008) 1155.
50. N. Hoshi, M. Nakamura, H. Haneishi, *Electrochemistry*, 85 (2017) 634.