Structural Effects on Methanol Oxidation on Single Crystal Electrodes of Palladium

Nagahiro HOSHI,* Masashi NAKAMURA, and Hidenori HANEISHI

Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, 1-33 Yayoi, Inage-ku, Chiba 263-8522, Japan

* Corresponding author: hoshi@faculty.chiba-u.jp

ABSTRACT

Methanol oxidation reaction (MOR) has been studied on the low index planes of Pd (Pd(111), Pd(100) and Pd(110)) in 0.1 M HClO₄ using voltammogram. Onset potential of methanol oxidation increases as Pd(110)~Pd(100) < Pd(111). The activity for the MOR is estimated using anodic peak current density of the voltammograms. The order of the activity is Pd(111)~Pd(110) ≪ Pd(100): (100) surface enhances the activity for the MOR on Pd electrodes.

© The Electrochemical Society of Japan, All rights reserved.

Keywords : Methanol Oxidation, Single Crystal Electrodes, Palladium

1. Introduction

Methanol is one of the fuels of direct fuel cells that can be applied to batteries for mobile apparatuses such as cell phones and personal computers. The methanol oxidation reaction (MOR) has been studied widely since the report of Breiter et al.¹ It is important for the development of direct methanol fuel cell (DMFC) to find out electrocatalysts that have high activity for MOR.

Studies using Pt single crystal electrodes show that the activity for the oxidation of small organic molecules depends on surface structures strongly.^{2,3} In acidic solution, Clavilier et al. firstly reported structural effects on the MOR on single crystal electrodes of Pt in 0.5 M H₂SO₄ containing 0.1 M methanol.⁴ The activity for the MOR, which is estimated using anodic peak current density, increases as Pt(111) ≪ Pt(100) < Pt(110). (Bi)sulfate anions are adsorbed on Pt electrode surface strongly, resulting in the deactivation of the MOR. Therefore, the MOR has been also studied in HClO₄ solution in which perchloric anion is not adsorbed on Pt electrodes as strongly as (bi)sulfate anions. Some papers report the order of the activity for the MOR: Pt(111) < Pt(110) < Pt(100),^{3,5,6} whereas Wieckowski et al. report the activity series: Pt(111) < Pt(100) ≪ Pt(110).⁷ Pt(111) shows the lowest MOR activity in all the reports. However, there is no consensus on the surface structure that gives the highest activity for the MOR on Pt electrodes. The study was extended to the high index planes of Pt.^{8–10} PtOH enhances the activity for the MOR.⁸ The (110) structure on (111) terrace enhances the MOR activity,⁹ but (100) step on (111) terrace and (111) step on (100) terrace deactivate the MOR.^{8,10}

Pd(100) has higher activity for the formic acid oxidation^{11,12} and the oxygen reduction reaction^{13,14} than the low index planes of Pt. However, there has been no report on the MOR on single crystal electrodes of Pd. In this paper, we firstly report the structural effects on the MOR on the low index planes of Pd in 0.1 M HClO₄ containing 0.2 M methanol in which the highest activity for the MOR is reported on the low index planes of Pt.⁷

2. Experimental

A single crystal bead (about 3 mm in diameter) of Pd was prepared according to previous reports.^{15–17}

Electrolytic solutions were prepared from ultrapure water treated with Milli-Q Advantage A10 (Millipore) and suprapure grade chemicals (Merck). Voltammograms of the MOR were measured in

the hanging meniscus configuration. The potential was held at 0.3 V(RHE) in Ar saturated 0.1 M HClO₄ containing 0.2 M methanol and scanned to positive direction up to 1.2 V(RHE) at scanning rate 0.020 V s^{−1}, then swept negatively to 0.2 V(RHE). The potential was scanned successively to positive direction again up to 0.4 V(RHE). Anode stripping voltammogram of adsorbed CO (CO_{ad}) was measured according to the following procedure. CO was bubbled for 30 min. in 0.1 M HClO₄ and the dissolved CO was purged by Ar at 0.3 V(RHE). All the potential was referred to RHE.

3. Results and Discussion

Voltammograms of single crystal electrodes of Pd give sharp peaks characteristic of their orientation in H₂SO₄.^{15,16} we measured voltammograms of the low index planes of Pd in 0.5 M H₂SO₄ to confirm the quality of the electrodes (Fig. 1). Sharp redox peaks are observed around 0.25 V(RHE) on Pd(111) and Pd(100). These peaks are related to the adsorption/desorption of (bi)sulfate anions on the wide terrace according to the study of infrared reflection absorption spectroscopy (IRAS).¹⁸ No redox peaks on Pd(110) are attributed to the narrow terrace width of Pd(110) (1 × 1) structure¹⁹ where (bi)sulfate anions are hardly adsorbed at lower potentials.¹⁸ The onset potential of anodic peak of Pd oxides formation increases as Pd(110) (0.85 V) < Pd(100) (0.90 V) < Pd(111) (1.1 V). These results agree with the former reports.^{15,16,20}

We measured the MOR in 0.1 M HClO₄. Solid lines of Fig. 2(a) present the voltammograms of the MOR on the low index planes of Pd. All the voltammograms are the first cycle after the anneal. Hydrogen adsorption/desorption peaks disappear completely after holding the potential at 0.3 V. Potential scan from 0.3 to 0.2 V gave no current of hydrogen absorption. Surface enhanced infrared absorption spectroscopy (SEIRAS) shows that CO_{ad} is formed on Pd electrode at lower potentials in methanol containing solution²¹ as is the case of Pt.²² These facts show that methanol is dissociated to CO_{ad} at lower potentials on Pd electrodes: CH₃OH → CO_{ad} + 4H⁺ + 4e[−]. Large anodic peaks are found above 0.75 V. These peaks are composed of the oxidation of CO_{ad}, formate ion and direct oxidation of methanol.²¹ The MOR stops around 1.1 V. The charges of Pd oxides formation were larger than those of full coverage of PdOH at 1.1 V in methanol free solution (dotted lines), suggesting that the production of higher order oxide species such as PdO prevents the MOR. When the potential is scanned negatively from 1.2 V, no MOR occurs until part of Pd oxides are reduced around

Figure 1. Voltammograms of the low index planes of Pd in 0.5 M H_2SO_4 saturated with Ar. Scanning rate: 0.020 V s^{-1} . Inserts show the hard sphere models of the low index planes of Pd.

Figure 2. (a) Solid line: voltammograms of the low index planes of Pd in 0.1 M HClO_4 containing 0.2 M methanol. Dotted line: voltammograms in 0.1 M HClO_4 without methanol. (b) Anode stripping voltammograms of CO adsorbed on the low index planes of Pd in 0.1 M HClO_4 . Scanning rate: 0.020 V s^{-1} .

0.8 V on Pd(100) and Pd(110). These facts also indicate that the higher order of Pd oxides block the MOR. The hydrogen adsorption/desorption peaks appear between 0.2 and 0.4 V after the scan to 1.2 V on Pd(111) and Pd(100), showing slow rate of dissociative oxidation of methanol to CO_{ad} .

Table 1. Comparison of the onset potential (E_{onset}) and anodic peak current density of methanol oxidation (j_p) in 0.1 M HClO_4 (1 M in Ref. 5).

	$E_{\text{onset}}/\text{V(RHE)}$			$j_p/\text{mA cm}^{-2}$		
[methanol]/M	Pd(100)	Pd(110)	Pd(111)	Pd(100)	Pd(110)	Pd(111)
0.2 (this work)	0.76	0.75	0.83	0.60	0.12	0.12
	Pt(100)	Pt(110)	Pt(111)	Pt(100)	Pt(110)	Pt(111)
0.1 (Ref. 2)	0.60	0.55	0.45	21	20	1
0.26 (Ref. 5)	0.70	0.50	0.45	0.35	0.12	0.13
0.2 (Ref. 7)	0.70	0.56	0.40	2.0	35	1.4

Table 2. Onset potential of oxidation (E_{onset}) and saturated coverage of adsorbed CO (θ_{CO}) on the low index planes of Pd in 0.1 M HClO_4 .

	$E_{\text{onset}}/\text{V}$	θ_{CO}
Pd(111)	0.92	0.55
Pd(110)	1.0	0.80
Pd(100)	0.82	0.60

The onset potentials (E_{onset}) and anodic peak current densities of the MOR (j_p) in the positive scan are summarized in Table 1. The value of E_{onset} increases as $\text{Pd(110)} \sim \text{Pd(100)} < \text{Pd(111)}$. The value of j_p gives the activity series: $\text{Pd(110)} \sim \text{Pd(111)} \ll \text{Pd(100)}$. These facts show that Pd(100) surface has the highest activity for the MOR on Pd electrodes as is the case of formic acid oxidation.^{11,12}

The values of E_{onset} of Pd oxides formation are nearly identical with those of the MOR in the positive scan as shown in Fig. 2(a), showing that Pd oxides promote the MOR. The current of MOR changes in harmony with that of Pd oxides formation on Pd(100). However, the potentials of j_p on Pd(111) and Pd(110) do not correlate with the peaks of the Pd oxides formation in 0.1 M HClO_4 without methanol. The MOR on Pd(111) gives a peak at more negative potential than the peak of Pd oxides formation. The peak of the MOR on Pd(110) appears immediately after the positive end of the sharp anodic peak of Pd oxides at 0.85 V of which charge is almost identical with that of PdOH formation on all the step atoms of Pd(110) (1×1).

CO_{ad} is produced at lower potential during MOR; CO_{ad} oxidation should be studied for the elucidation of MOR. We measured anode stripping voltammogram of CO_{ad} to investigate the correlation of CO_{ad} oxidation and MOR (Fig. 2(b)). We assume that CO_{ad} is fully covered the surface of Pd single crystal surfaces, because no hydrogen adsorption/desorption peak is observed after holding the potential at 0.3 V in methanol containing solution. Coverage of CO_{ad} (θ_{CO}) is calculated using the following equation: $\theta_{\text{CO}} = (Q_{\text{CO}}/2)/e/d$, where Q_{CO} , e and d are charge per unit area of CO_{ad} oxidation, the elementary charge and density of atoms at the first layer of single crystal electrode, respectively. The values of E_{onset} of CO_{ad} oxidation and θ_{CO} are summarized in Table 2. The value of E_{onset} generally gets lower as θ_{CO} gets lower. However, the value of E_{onset} is the lowest on Pd(100) of which θ_{CO} is higher than that of Pd(111). This fact shows that Pd(100) has high activity for CO_{ad} oxidation. The E_{onset} of the MOR is similar to that of CO_{ad} oxidation on Pd(100). The higher activity for CO_{ad} oxidation may be the cause of the highest MOR activity on Pd(100). However, the MOR starts at more negative potentials than CO_{ad} oxidation on Pd(111) and Pd(110). Pd surfaces are not fully occupied by adsorbed CO as shown in Table 2; direct MOR may proceed at the vacant sites without CO on Pd(111) and Pd(110).

Table 1 summarizes the E_{onset} and j_p of MOR on the low index planes of Pd and Pt. The values of E_{onset} on Pt are lower than those on Pd. This is because the values of E_{onset} of CO_{ad} oxidation on Pt are lower than those on Pd.^{23–25} The MOR activity of Pd, which is estimated by j_p , is lower than that of Pt except the case of Ref. 5 where 1 M HClO_4 is used. The (111) structure has the lowest activity for the MOR on both Pd and Pt electrodes.

Acknowledgments

This work was supported by New Energy and Industrial Technology Development Organization (NEDO).

References

1. M. W. Breiter and S. Gilman, *J. Electroanal. Chem.*, **109**, 622 (1962).
2. C. Lamy, J. M. Leger, J. Clavilier, and R. Parsons, *J. Electroanal. Chem.*, **150**, 71 (1983).
3. S. Motoo and N. Furuya, *Ber. Bunsenges. Phys. Chem.*, **91**, 457 (1987).
4. J. Clavilier, C. Lamy, and J. M. Leger, *J. Electroanal. Chem.*, **125**, 249 (1981).
5. R. R. Adzic, A. V. Tripkovic, and W. E. O'Grad, *Nature*, **296**, 137 (1982).
6. S. C. S. Lai, N. P. Lebedeva, T. H. M. Housmans, and M. T. M. Koper, *Top. Catal.*, **46**, 320 (2007).
7. E. Herrero, K. Franaszczuk, and A. Wieckowski, *J. Phys. Chem.*, **98**, 5074 (1994).
8. A. V. Tripkovic and K. D. Popovic, *Electrochim. Acta*, **41**, 2385 (1996).
9. T. H. M. Housmans and M. T. M. Koper, *J. Phys. Chem. B*, **107**, 8557 (2003).
10. V. Grozovski, V. Climent, E. Herrero, and J. M. Feliu, *J. Electroanal. Chem.*, **662**, 43 (2011).
11. N. Hoshi, K. Kida, M. Nakamura, M. Nakada, and K. Osada, *J. Phys. Chem. B*, **110**, 12480 (2006).
12. N. Hoshi, M. Nakamura, and K. Kida, *Electrochem. Commun.*, **9**, 279 (2007).
13. S. Kondo, M. Nakamura, N. Maki, and N. Hoshi, *J. Phys. Chem. C*, **113**, 12625 (2009).
14. A. Hitotsuyanagi, S. Kondo, M. Nakamura, and N. Hoshi, *J. Electroanal. Chem.*, **657**, 123 (2011).
15. N. Hoshi, K. Kagaya, and Y. Hori, *J. Electroanal. Chem.*, **485**, 55 (2000).
16. N. Hoshi, M. Kuroda, and Y. Hori, *J. Electroanal. Chem.*, **521**, 155 (2002).
17. N. Furuya and S. Koide, *Surf. Sci.*, **220**, 18 (1989).
18. N. Hoshi, M. Kuroda, O. Koga, and Y. Hori, *J. Phys. Chem. B*, **106**, 9107 (2002).
19. N. Hoshi, K. Naito, M. Nakamura, and O. Sakata, *Electrochemistry*, **82**, 351 (2014).
20. M. Hara, U. Linke, and T. Wandlowski, *Electrochim. Acta*, **52**, 5733 (2007).
21. Y. Y. Yang, J. Ren, H. X. Zhang, Z. Y. Zhou, S. G. Sun, and W. B. Cai, *Langmuir*, **29**, 1709 (2013).
22. Y. X. Chen, A. Miki, S. Ye, H. Sakai, and M. Osawa, *J. Am. Chem. Soc.*, **125**, 3680 (2003).
23. J. M. Orts, A. Fernandez-Vega, J. M. Feliu, A. Aldaz, and J. Clavilier, *J. Electroanal. Chem.*, **327**, 261 (1992).
24. S. C. Chang and M. J. Weaver, *J. Phys. Chem.*, **94**, 5095 (1990).
25. N. M. Markovic, B. N. Grgur, C. A. Lucas, and P. N. Ross, *Surf. Sci.*, **384**, L805 (1997).