Cation Effects on ORR Activity on Low-index Planes of Pd in Alkaline Solution

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ABSTRACT

The oxygen reduction reaction (ORR) has been studied on low-index planes of Pd in 0.05 M XOH (X = Li, Na, K, and Cs) solutions to determine the effects of cations on ORR activity. The order of ORR activity is Pd(110) < Pd(100) < Pd(111) in all solutions. This order differs from that in HClO₄: Pd(110) < Pd(111) < Pd(100). Cationic species do not affect the ORR activity on Pd(110) and Pd(100). In contrast, the ORR activity of Pd(111) increases in the order of Li⁺ < Na⁺ < K⁺ < Cs⁺. The lower the cation hydration energy, the higher the ORR activity on Pd(111), as is also the case on Pt(111). The ORR activity of Pd(111) in CsOH is 1.8 times higher than that of Pd(100) in HClO₄.

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Keywords : Oxygen Reduction Reaction, Alkaline Solutions, Low-index Planes of Pd, Structural Effects

1. Introduction

Pt is widely used as an electrocatalyst in polymer electrolyte fuel cells (PEFCs). Large amounts of expensive and rare Pt are loaded in an air electrode because of the high overpotential of the oxygen reduction reaction (ORR). It is necessary to develop new ORR-active electrocatalysts to reduce Pt loading.

The activity and selectivity of electrochemical reactions depend markedly on the surface structures of the electrodes.^{1–3} One method used to increase ORR activity is to adjust the surface structure on the atomic scale. Marković et al. reported that ORR activity increases in the order of Pt(100) < Pt(111) < Pt(110) in 0.1 M HClO₄.⁴ The ORR activity series of low-index planes of Pd differs from that of Pt: Pd(110) < Pd(111) < Pd(100).⁵ The ORR activity of Pd(100) is also three times higher than that of Pt(110).

In addition to the surface structure, surface oxides and ionic species at the solid–liquid interface affect the ORR activity.⁶ Alkali metal cations have stable hydration structure and exist as nonspecific adsorbed ions on the outer Helmholtz plane.^{6–10} The ORR activity of Pt(111) in 0.1 M XOH (X = Li, Na, K, and Cs) increases in the order of Li⁺ < Na⁺ < K⁺ < Cs⁺: low cation hydration energies yield higher activity. However, the ORR activity on single-crystal electrodes of Pd in alkaline solutions has not been reported. In this communication, we describe the ORR on the low-index planes of Pd (Pd(111), Pd(100) and Pd(110)) in XOH (X = Li, Na, K, and Cs) to clarify the cation effects on ORR activity.

2. Experimental

LiOH·H₂O (99.995 %), NaOH (≥98 %), KOH (99.99 %), and CsOH·H₂O (99.95 %) were purchased from Sigma-Aldrich. H₂SO₄ (Ultrapur) was purchased from Kanto Chemical Corporation. Ultrapure water was produced using Milli-Q Advantage A10 (Millipore). Ultrapure Ar gas (>99.9999 %) was used for cooling Pd single-crystal electrodes after annealing.

A single-crystal bead of Pd with a diameter of about 3 mm was prepared by a modified Clavilier method.^{11,12} The single crystal was oriented using the reflected beam of a He/Ne laser. Hard sphere

Figure 1. Hard sphere models of Pd(111), Pd(110), and Pd(100).

models of the single-crystal electrodes examined are shown in Fig. 1. The oriented single crystal was mechanically polished with a diamond slurry. Before electrochemical measurements, the single-crystal electrodes were annealed with a H₂–O₂ flame at approximately 1300 °C to remove distortions due to the mechanical polishing. After annealing, the single-crystal electrodes were cooled to room temperature in an Ar atmosphere, and their surfaces were protected with ultrapure water.

Electrochemical measurements were carried out using an electrochemical analyzer (ALS 701D). All potentials were referenced to the reversible hydrogen electrode (RHE).

Linear sweep voltammograms were measured using RRDE–3 (BAS) in the hanging meniscus rotating electrode (HMRDE) configuration.¹³ Potentials were scanned in the positive direction from 0.2 to 1.0 V (vs. RHE) at a rotation rate of 1600 rpm. ORR activity (j_K) was calculated at 0.90 V (vs. RHE) using the Koutecky–Levich equation.^{14,15}

$$\frac{1}{j} = \frac{1}{j_K} + \frac{1}{j_L},$$

where j , j_K , and j_L represent the total current density, kinetic current density, and limiting current density, respectively.

3. Results and Discussion

Figures 2(a)–2(c) show voltammograms of the low-index planes of Pd in 0.5 M H₂SO₄ solution saturated with Ar. The voltammograms are identical to those reported previously;¹¹ the surface is

Figure 2. Voltammograms of Pd in Ar-saturated solutions. Upper panels show voltammograms of Pd(111) (a), Pd(110) (b), and Pd(100) (c) in 0.5 M H_2SO_4 at a scanning rate 0.020 V s^{-1} . Lower panels show voltammograms of Pd(111) (d), Pd(110) (e), and Pd(100) (f) in 0.05 M KOH at a scanning rate 0.01 V s^{-1} .

correctly oriented. In situ surface X-ray scattering (SXS) analysis showed that the Pd single crystal electrodes have (1×1) structures.^{16,17}

Figures 2(d)–2(f) show voltammograms of the low-index plane in 0.05 M KOH saturated with Ar. The anodic peak at 0.5 V (vs. RHE) of Pd(100) is due to the release of the absorbed hydrogen, and the other anodic peak is due to oxide formation.¹⁸ The anodic peaks above 0.6 V (vs. RHE) on Pd(111) and Pd(110) are also due to oxide formation.¹⁸ Similar voltammograms were obtained in other alkaline solutions. Detailed analyses of the peaks were reported previously.¹⁸

Linear sweep voltammograms in O_2 -saturated solutions are shown in Figs. 3(a)–3(d). The ORR activities (j_k) at 0.90 V (vs. RHE) are summarized in Fig. 3(e). The ORR activity increases in the order of Pd(110) < Pd(100) < Pd(111) in all the solutions. The order of the ORR activity of Pd(111) and Pd(100) in alkaline solutions is opposite to that in 0.1 M HClO_4 : Pd(110) < Pd(111) < Pd(100).⁵ The ORR activity of Pd(111) in CsOH, which is the highest in this study, was 1.8 times higher than that of Pd(100), which has the highest activity in HClO_4 . In the case of Pt electrodes, the orders of ORR activity were Pt(100) < Pt(111) < Pt(110) in 0.1 M HClO_4 ⁴ and Pt(100) < Pt(110) < Pt(111) in 0.1 M KOH.¹⁹ These orders differ from those of Pd. However, the ORR activity on the (111) plane is the highest in the low-index planes of Pd and Pt in alkaline solutions.

The ORR activity of Pd(111) increases in the order of $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$. The order is the same as that of Pt(111). The ORR activity increases with decreasing hydration energy of the cation, as is also the case on Pt(111).⁶ However, no such cation dependence is found on Pd(100) or (110).

On Pt electrodes, the ORR activity decreases with increasing coverage of Pt oxides.^{20–23} The charge of Pd oxides (Q) at 0.90 V (vs. RHE) was calculated from the orange areas of the voltammograms in Fig. S1. Currents generated from the release of absorbed hydrogen continued up to 0.6 V (vs. RHE); charges associated with Pd oxide formation were estimated from voltammograms between 0.5 and 1.2 V (vs. RHE) in this voltage range no hydrogen was absorbed. The ORR activity is plotted against Q in Fig. S2. No correlation was found between Q and ORR activity. On the low-

Figure 3. Linear sweep voltammograms of Pd in O_2 -saturated solutions at a rotation rate of 1600 rpm and sweep rate of 0.010 V s^{-1} . Plots (a), (b), (c), and (d) show the results in 0.05 M LiOH, NaOH, KOH and CsOH, respectively. Plot (e) shows ORR activities (j_k) at 0.90 V (vs. RHE).

index planes of Pt, PtOH is blocks the ORR.^{21,22} However, PtO hinders the ORR on only Pt(100).²³ No correlation was found between the band intensity of surface-enhanced Raman spectroscopy (SERS) of PtO and the ORR activity on Pt(111) and Pt(110).²³ It is likely that PdOH and PdO are both adsorbed at 0.90 V (vs. RHE). Only PdOH or PdO may affect the ORR on Pd electrodes. Vibrational spectroscopy is necessary to elucidate which Pd oxides deactivate the ORR.

Alkali metal cations affect the ORR on Pd(111), but not on Pd(100) and Pd(110). One of the factors other than Pd oxides that affect the ORR is the structure of adsorbed water. On the low-index planes of Pt modified with alkylamines, the cluster size of ice like water (multilayer of hexamer water) affects the ORR activity markedly.²⁴ According to studies in ultra-high vacuum (UHV), hexameric water molecules are found on Pt(111).²⁵ The hexamer water structure is also formed on Pd(111), the atomic arrangement of which is hexagonal.²⁶ On Pd(100) and Pd(110), hexameric water is hardly ever formed because the symmetry of the surface structures differs from that of hexameric water. The absence of hexameric water structure may be responsible for the absence of an alkali metal cation effect on Pd(100) and Pd(110).

Studies on Pd oxides and adsorbed water are now in progress in our laboratory using vibrational spectroscopy to elucidate the detailed mechanism underlying the alkali cation effects on the ORR.

4. Conclusions

The ORR activity in 0.05 M XOH ($X = \text{Li}, \text{Na}, \text{K}, \text{Cs}$) increases in the order of $\text{Pd}(110) < \text{Pd}(100) < \text{Pd}(111)$. This order differs from that in HClO_4 : $\text{Pd}(110) < \text{Pd}(111) < \text{Pd}(100)$. The ORR activity of Pd(111) in CsOH is 1.8 times higher than that of Pd(100) in HClO_4 . Alkali metal cations affect the ORR activity of Pd(111): $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$. In contrast, there is no effect of cations on Pd(110) and Pd(100). No correlation is found between the ORR activity and the total charge of Pd oxide formation at 0.90 V (vs. RHE).

Supporting Information

The Supporting Information is available on the website at DOI: <https://doi.org/10.5796/electrochemistry.21-00008>.

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References

1. C. Lamy and J. M. Leger, *J. Chim. Phys.*, **88**, 1649 (1991).
2. N. M. Marković and P. N. Ross, Jr., *Surf. Sci. Rep.*, **45**, 117 (2002).
3. S. Ye, T. Kondo, N. Hoshi, J. Inukai, S. Yoshimoto, M. Osawa, and K. Itaya, *Electrochemistry*, **77**, 2 (2009).
4. N. M. Marković, R. R. Adžić, B. D. Cahan, and E. B. Yeager, *J. Electroanal. Chem.*, **377**, 249 (1994).
5. S. Kondo, M. Nakamura, N. Maki, and N. Hoshi, *J. Phys. Chem. C*, **113**, 12625 (2009).
6. D. Strmcnik, K. Kodama, D. van der Vliet, J. Greeley, V. R. Stamenkovic, and N. M. Marković, *Nat. Chem.*, **1**, 466 (2009).
7. D. Strmcnik, D. F. Van Der Vliet, K. C. Chang, V. Komanicky, K. Kodama, H. You, V. R. Stamenkovic, and N. M. Marković, *J. Phys. Chem. Lett.*, **2**, 2733 (2011).
8. W. Jin, H. Du, S. Zheng, H. Xu, and Y. Zhang, *J. Phys. Chem. B*, **114**, 6542 (2010).
9. D. J. Miller and J. M. Lisy, *J. Am. Chem. Soc.*, **130**, 15393 (2008).
10. D. J. Miller and J. M. Lisy, *J. Am. Chem. Soc.*, **130**, 15381 (2008).
11. N. Hoshi, K. Kagaya, and Y. Hori, *J. Electroanal. Chem.*, **485**, 55 (2000).
12. J. Clavilier, R. Faure, G. Guinet, and R. Durand, *J. Electroanal. Chem.*, **107**, 205 (1980).
13. B. D. Cahan and H. M. Villullas, *J. Electroanal. Chem.*, **307**, 263 (1991).
14. H. M. Villullas and M. L. Teijelo, *J. Electroanal. Chem.*, **384**, 25 (1995).
15. H. M. Villullas and M. L. Teijelo, *J. Electroanal. Chem.*, **385**, 39 (1995).
16. K. Naito, M. Nakamura, O. Sakata, and N. Hoshi, *Electrochemistry*, **79**, 256 (2011).
17. N. Hoshi, K. Naito, M. Nakamura, and O. Sakata, *Electrochemistry*, **82**, 351 (2014).
18. N. Hoshi, M. Nakamura, N. Maki, S. Yamaguchi, and A. Kitajima, *J. Electroanal. Chem.*, **624**, 134 (2008).
19. N. M. Marković, H. A. Gasteiger, and P. N. Ross, *J. Phys. Chem.*, **100**, 6715 (1996).
20. N. M. Marković, H. A. Gasteiger, B. N. Grgur, and P. N. Ross, *J. Electroanal. Chem.*, **467**, 157 (1999).
21. H. Tanaka, S. Sugawara, K. Shinohara, T. Ueno, S. Suzuki, N. Hoshi, and M. Nakamura, *Electrocatalysis*, **6**, 295 (2015).
22. T. Ueno, H. Tanaka, S. Sugawara, K. Shinohara, A. Ohma, N. Hoshi, and M. Nakamura, *J. Electroanal. Chem.*, **800**, 162 (2017).
23. F. Sugimura, N. Sakai, T. Nakamura, M. Nakamura, K. Ikeda, T. Sakai, and N. Hoshi, *Phys. Chem. Chem. Phys.*, **19**, 27570 (2017).
24. K. Saikawa, M. Nakamura, and N. Hoshi, *Electrochem. Commun.*, **87**, 5 (2018).
25. M. Nakamura and M. Ito, *Chem. Phys. Lett.*, **404**, 346 (2005).
26. T. Mitsui, M. K. Rose, E. Fomin, D. F. Ogletree, and M. Salmeron, *Science*, **297**, 1850 (2002).