Catalysis Today 84 (2003) 223–229

www.elsevier.com/locate/cattod

Electrochemical oxidation of CO in sulfuric acid solution over Pt and PtRu catalysts modified with TaO_x and NbO_x

Atsushi Ueda*, Yusuke Yamada, Tsutomu Ioroi, Naoko Fujiwara, Kazuaki Yasuda, Yoshinori Miyazaki, Tetsuhiko Kobayashi

Special Division for Green Life Technology, National Institute of Advanced Industrial Science and Technology (AIST),
1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

Abstract

In order to survey new CO-tolerant anode for the PEFC application, the addition of TaO_x and NbO_x to the Pt catalyst was examined in the electrochemical oxidation of CO in a sulfuric acid solution. Voltammetric peak potentials for the oxidation of CO pre-adsorbed on the Pt surface shifted to lower potentials by these additives, indicating an enhancement of electro-catalysis of Pt for the CO oxidation. Both oxides of Ta or Nb also bring about an inhibition of the CO adsorption rate onto the Pt surface. Concerted effect of these oxides with Ru is discussed for the CO oxidation over the PtRu-TaO_x and the PtRu-NbO_x anodes.

Keywords: Electrochemical oxidation; Tantalum; Niobium; Electrocatalysis; Carbon monoxide; Platinum; Ruthenium; PEFC

1. Introduction

Polymer electrolyte fuel cells (PEFCs) have been attracting attention as new power sources for low emission vehicles (LEVs) as well as for household co-generation systems, in which hydrogen is used as fuel. Electrochemical hydrogen activation is then required on catalytic anodes. Platinum is widely used as the anodic electro-catalyst. When hydrogen is produced through reforming of natural gas, gasoline or methanol, a certain amount of carbon monoxide is inevitably contained in the hydrogen-rich gas from the hydrogen generators [1,2]. It is well known that even a small amount of CO, such as 0.01 vol.% in hydrogen, easily poisons the surface of the Pt anode [3]. Hydrogen activation ability of Pt deteriorates with time through the CO poisoning. Although water–gas-shift reaction and selective CO oxidation are employed to reduce the CO concentration in the hydrogen-rich fuel from the reformers, it is also important to enhance the CO-tolerance of the catalytic anode itself. For this purpose, a variety of Pt-based alloys have been extensively studied as the anodic catalysts. The PtRu alloy (1:1, atomic ratio) shows the highest performance among the catalysts examined so far [4,5]. However, much more durability of the anode catalysts is required for the practical PEFC application. In addition, the low fraction of Ru in the platinum-group resources is a serious drawback in its practical use. Therefore, it has been desired to develop new CO-tolerant anodes containing a low quantity of Ru or without Ru.

Besides the Pt-based alloys, the improvement of the CO-tolerance of Pt has been attempted by the addition of metal oxides such as WO_3 and MoO_3 to the

---

* Corresponding author. Tel.: +81-72-751-9656;
fax: +81-72-751-9630.
E-mail address: a-ueda@aist.go.jp (A. Ueda).

0920-5861/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0920-5861(03)00277-3

Pt/carbon (Pt/C) anode [6,7]. Recently, Ioroi et al. [8] showed a high performance of Pt/MoO_x/C anode under hydrogen containing 0.01 vol.% CO and this is almost comparable to the anodic performance of PtRu/C. Role of metal oxides for the CO-tolerance has been considered to create a new active site for the CO oxidation at the interface between Pt and metal oxide [9,10] and/or to modify the electronic band structure of Pt [11]. In the case of gas-phase CO oxidation by oxygen, the addition of SnO_2, TiO_2 or CeO_2-TiO_2 is also effective to avoid the CO poisoning of platinum-group metals [12]. In the present study, the addition of TaO_x and NbO_x to the Pt/C anode has been examined in the electrochemical CO oxidation. We report herein preliminary results on the enhancing effect of Pt and PtRu electro-catalysis by Ta- and Nb-oxide in the oxidation of CO.

2. Experimental

Platinum, platinum-tantalum oxide and platinum-niobium oxide catalysts without carbon support (Pt, Pt-TaO_x, Pt-NbO_x, respectively) were prepared by an addition of formaldehyde into the mixture solution of starting materials. The raw chemicals were $H_2PtCl_6\cdot 6H_2O$, $TaCl_5$ and $NbCl_5$ (Kishida Chemical). The 2-propanol solution containing the raw chemicals was heated to 323 K, and then the 2-propanol solution containing KOH was added. An aqueous solution of formaldehyde was dropped into the 2-propanol solution at 323 K. After washing with 2-propanol and then with the distilled water, the precursor obtained was filtrated and dried under vacuum for 12 h. Then it was heated at 523 K for 2 h under nitrogen flow, and reduced at 523 K for 2 h under H_2 (10 vol.%)/N_2 flow.

Carbon-supported platinum (Pt/C) catalyst was prepared by an impregnation method. In the present study, $Pt(NO_2)_2(NH_3)_2$ (Kishida Chemical) and carbon black powder (Vulcan XC-72, Cabot) were used as the precursors. The carbon powder was dispersed in an ethanol solution containing $Pt(NO_2)_2(NH_3)_2$. After evaporation to remove solvent, the precursor obtained was heated at 523 K for 2 h and 723 K for 2 h under nitrogen flow, and then it reduced at 723 K for 2 h under H_2 (10 vol.%)/N_2 flow. The metal loading of Pt in the catalysts was 20 wt.%. Tantalum oxide-loaded Pt/C (Pt-TaO_x/C) and niobium oxide-loaded Pt/C (Pt-NoO_x/C) were prepared by a similar impregnation procedure. The Pt/C powder was dispersed in an ethanol solution containing $TaCl_5$ or $NbCl_5$. The precursor was finally reduced at 725 K for 2 h under H_2 (10 vol.%)/N_2 flow. For comparison, a commercial catalyst of PtRu/C (Johnson–Mathesay, Pt = 20 wt.%, Ru = 10 wt.%) is used, and tantalum oxide-loaded PtRu/C (PtRu-TaO_x/C) and niobium oxide-loaded PtRu/C (PtRu-NbO_x/C) were also prepared by a similar preparation procedure.

Specific surface areas of the catalysts prepared were determined by the BET multi-points method using an automatic surface area analyzer (Shimadzu ASAP 2100). The X-ray diffraction pattern of the catalysts was measured using a Rigaku X-ray diffractometer (RINT 500). The crystallite size of Pt was calculated by using the Scherrer's equation. Morphology of the catalysts were analyzed by a TEM (Hitachi H-9000).

The electrochemical measurements of the catalysts in 0.5 M H_2SO_4 solution were carried out by following the method described by Schmidt et al. [13]. A suspension containing 10 mg of the catalyst in 5 ml of ethanol was ultrasonically dispersed for 15 min, and then 3 μl was dropped onto the polished surface of the glassy carbon disk electrode (0.28 cm^2). After heated at 343 K for 30 min, the electrode surface was covered with 10 μl Nafion solution (Aldrich, diluted to 1 wt.% solution with EtOH) and the electrode was heated at 423 K for 1 h to fix the catalyst onto the glassy carbon disk electrode.

Electrochemical measurements were carried out using a conventional three-electrode configuration after the electrode was immersed in 0.5 M H_2SO_4 solution. The cyclic voltamogram under Ar bubbling was done by a sweep rate of 20 mV/s. Pre-adsorption of CO was carried out under pure CO bubbling in the solution at the potential of 0.05 V versus RHE. The potential indicated in this paper was normalized against RHE.

3. Results and discussion

Unsupported Pt, Pt-TaO_x, and Pt-NbO_x catalysts were analyzed by XRD, TEM, and BET surface area analyzer. Table 1 shows the BET surface area and Pt particle size calculated from the XRD pattern with the Sherrer's equation. No XRD peak originated from oxides, hydroxides, alloys of Ta or Nb was observed. The

Table 1
Mean diameter of platinum particles and specific surface areas of platinum-tantalum oxide, platinum-niobium oxide and platinum

Catalyst	Surface area (m^2/g)	d_{Pt} (nm)[a]
Pt-TaO_x (Pt:Ta = 2:1, atomic ratio)	38.6	5.3
Pt-NbO_x (Pt:Nb = 2:1, atomic ratio)	75.9	5.1
Pt	35.0	7.2

[a] Crystallite size of platinum was calculated by using Scherrer's equation.

TEM observation revealed that the calculated size of Pt particles is appropriate one. Amorphous phase containing Ta or Nb was observed by TEM in the Pt-TaO_x and Pt-NbO_x samples, respectively. It is estimated that amorphous hydroxides or hydrous oxides of Ta or Nb coexists with Pt particles in these catalysts.

Figs. 1 and 2 show typical cyclic voltammograms of the Pt-TaO_x and Pt-NbO_x catalysts. Under Ar atmosphere, symmetric waves attributed to cathodic adsorption and anodic desorption of hydrogen atoms on Pt are clearly observed at potentials below 0.3 V versus RHE. In the first anodic potential scan after pre-adsorption of CO at 0.05 V versus RHE for 60 min, the anodic waves of hydrogen desorption disappear and a new anodic peak attributed to the oxidation of CO pre-adsorbed on Pt appears at 0.66 and 0.75 V versus RHE for Pt-TaO_x and Pt-NbO_x, respectively. The anodic current pattern of the second potential scan in the CO atmosphere is restored to its original one observed in the Ar atmosphere.

Fig. 3 shows a growth of the CO oxidation peaks with an increase in the exposure time of the Pt-TaO_x catalyst toward CO at 0.05 V versus RHE. Hydrogen adsorption site correspond to the voltammetric waves at below 0.3 V versus RHE decreases with increasing CO oxidation current. Pre-adsorption time longer than 30 min is needed for the saturation of the CO peak growth on the Pt-TaO_x catalysts. Almost same pre-adsorption time was required for the case of the Pt-NbO_x catalysts. However, only 5 min was enough for the CO peak saturation on the Pt and the PtRu catalysts as shown in Figs. 4 and 5. It is evident that the CO adsorption on the Pt surface is inhibited by the presence of TaO_x and NbO_x, which may weaken the Pt–CO bond, and also indicates that the adsorption step of CO, thus poisoning of Pt, is not a very rapid one.

Table 2 summarizes the anodic peak potentials of the oxidation of CO pre-adsorbed on various Pt-based catalysts. These values are qualitative measure of the electro-catalytic activity for the CO oxidation. The

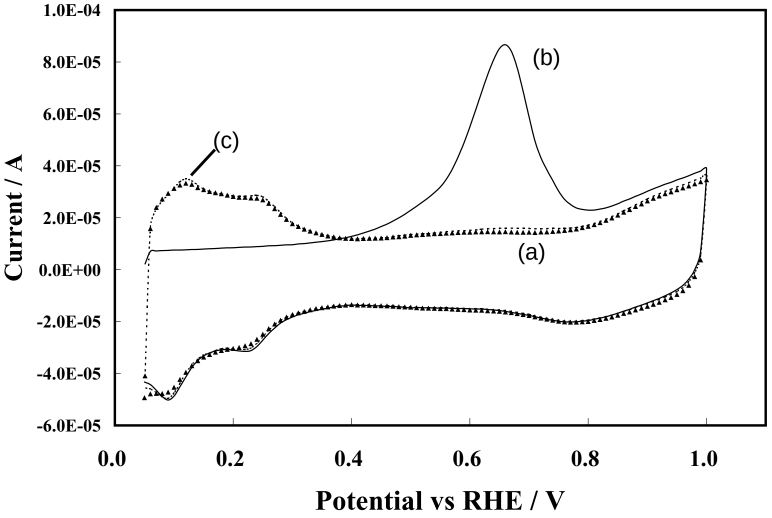

Fig. 1. Cyclic voltammograms of the Pt-TaO_x (Pt:Ta = 2:1, atomic ratio) catalyst: (a) under Ar atmosphere; (b) the first potential scan after pre-adsorption of CO at 0.05 V vs. RHE; (c) the second potential scan; in 0.5 M H_2SO_4 solution; sweep rate was 20 mV/s; temperature was 298 K.

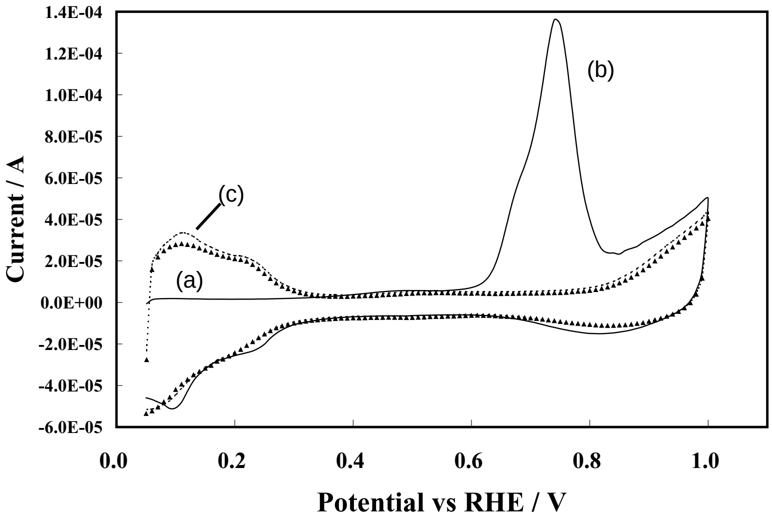

Fig. 2. Cyclic voltammograms of the Pt-NbO$_x$ (Pt:Nb = 2:1, atomic ratio) catalyst: (a) under Ar atmosphere; (b) the first potential scan after pre-adsorption of CO at 0.05 V vs. RHE; (c) the second potential scan; in 0.5 M H_2SO_4 solution; sweep rate was 20 mV/s; temperature was 298 K.

additive-free Pt shows the highest overpotential or the lowest activity for the electrochemical oxidation of CO. As has been reported [14], a good performance of the PtRu catalyst is noticeable. The addition of TaO$_x$ or NbO$_x$ to Pt brings about an enhancement of the CO oxidation activity of Pt. Table 3 summarized the quantity of electricity for the oxidation of H adsorbed on metal (Q_H), that for CO pre-adsorbed (Q_{CO}) and

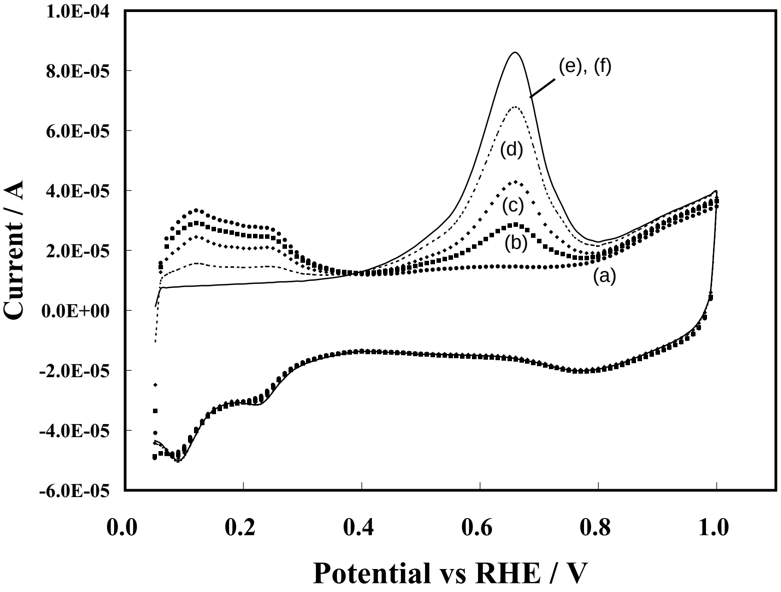

Fig. 3. Cyclic voltammograms of the Pt-TaO$_x$ (Pt:Ta = 2:1, atomic ratio) catalyst as a function of exposure time toward CO at 0.05 V vs. RHE: (a) under Ar atmosphere; (b) 5 min; (c) 10 min; (d) 20 min; (e) 30 min; (f) 60 min; in 0.5 M H_2SO_4 solution; sweep rate was 20 mV/s; temperature was 298 K.

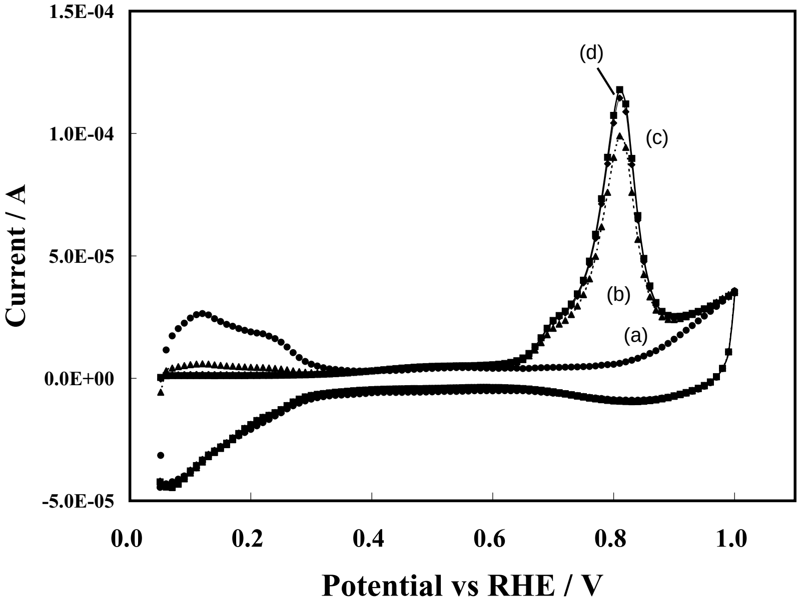

Fig. 4. Cyclic voltammograms of the Pt catalyst as a function of exposure time toward CO at 0.05 V vs. RHE: (a) under Ar atmosphere; (b) 2 min; (c) 5 min; (d) 30 min; in 0.5 M H_2SO_4 solution; sweep rate was 20 mV/s; temperature was 298 K.

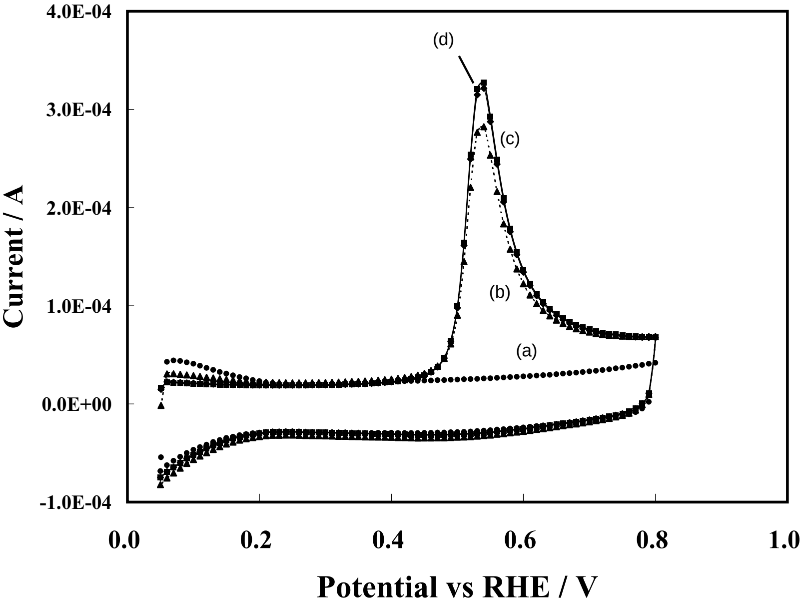

Fig. 5. Cyclic voltammograms of the PtRu (Pt:Ru = 1:1, atomic ratio) catalyst as a function of exposure time toward CO at 0.05 V vs. RHE: (a) under Ar atmosphere; (b) 2 min; (c) 5 min; (d) 30 min; in 0.5 M H_2SO_4 solution; sweep rate was 20 mV/s; temperature was 298 K.

Table 2
Anodic pea potentials of the oxidation of CO pre-adsorbed on various Pt-based catalysts

Catalyst	Peak potential of pre-adsorbed CO oxidation vs. RHE (V)		
Pt-TaO$_x$ (Pt:Ta, atomic ratio)	0.66 (2:1)	0.70 (1:1)	0.69 (1:2)
Pt-NbO$_x$ (Pt:Nb, atomic ratio)	0.75 (2:1)	0.78 (1:1)	0.77 (1:2)
PtRu (Pt:Ru, atomic ratio)		0.54 (1:1)	
Pt		0.81	

Pre-adsorption of CO was carried out under pure CO bubbling for 60 min in 0.5 M H_2SO_4 solution at the potential of 0.05 V vs. RHE; sweep rate was 20 mV/s; temperature was 298 K.

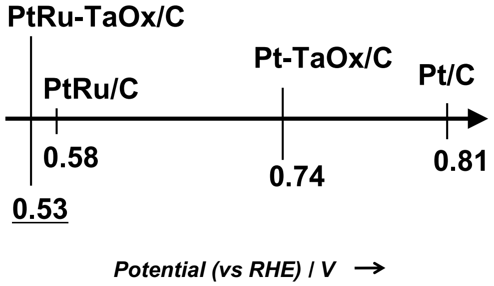

Fig. 6. Anodic peak potentials of the CO oxidation after CO pre-adsorption at 0.05 V vs. RHE over TaO$_x$-addition Pt/C and PtRu/C catalysts. In 0.5 M H_2SO_4 solution; sweep rate was 20 mV/s; temperature was 298 K.

Q_{CO}/Q_H values on various Pt-based catalysts. These quantities of electricity were calculated from the cyclic voltamogram under Ar bubbling and CO pre-adsorbed on metal catalyst conditions. If the number of adsorption sites for H adsorbed on metal (N_H) is same to that of CO adsorbed on metal (N_{CO}), the value of Q_{CO}/Q_H becomes two. Q_{CO}/Q_H value is 2.10 for Pt catalyst. This experimental result is strongly suggested that N_H are almost same to N_{CO} for Pt catalyst. In contrast, Q_{CO}/Q_H value (4.81) is much higher than two for PtRu catalyst, because the surface Ru attributes to the site for CO adsorption. The Pt-NbO$_x$ catalyst shows almost same values of Q_H and Q_{CO} compared to that of catalyst. In contrast, Pt-TaO$_x$ catalyst gives lower value of Q_{CO}/Q_H (1.71) than that of Pt-NbO$_x$ and Pt catalysts. It is also evident that the CO adsorption on the Pt surface is inhibited by the presence of TaO$_x$ which should weaken the Pt–CO bond.

Since carbon-supported catalysts are usually used in the PEFC application, the addition of TaO$_x$ and NbO$_x$ to the Pt/C and also the PtRu/C catalytic anode was examined. Figs. 6 and 7 show the anodic peak potentials of the CO oxidation after the CO pre-adsorption. The enhancing effect by the TaO$_x$- and NbO$_x$-addition is qualitatively reproducible in the CO oxidation on the Pt/C anode. Although the TaO$_x$-addition was slightly more effective than the NbO$_x$-addition in the case of the unsupported catalysts, the Pt-NbO$_x$/C anode is more active than the Pt-TaO$_x$/C catalysts. It is possible that some morphological difference related to the contact between Pt and Ta- or Nb-oxides causes such

Table 3
Quantity of electricity for the oxidation of H pre-adsorbed (Pt-H) and CO pre-adsorbed on various Pt-based catalysts

Catalyst	Q_H (C)[a]	Q_{CO} (C)[b]	Q_{CO}/Q_H
Pt-TaO$_x$ (Pt:Ta = 2:1, atomic ratio)	2.64×10^{-4}	4.52×10^{-4}	1.71
Pt-NbO$_x$ (Pt:Nb = 2:1, atomic ratio)	2.24×10^{-4}	4.85×10^{-4}	2.17
PtRu (Pt:Ru = 1:1, atomic ratio)	1.82×10^{-4}	8.75×10^{-4}	4.81
Pt	2.27×10^{-4}	4.75×10^{-4}	2.10

[a] Quantity of electricity for the oxidation of H pre-adsorbed (Pt-H) on metal catalyst was calculated from the cyclic voltamogram; under Ar bubbling in 0.5 M H_2SO_4 solution; sweep rate was 20 mV/s; temperature was 298 K.

[b] Quantity of electricity for the oxidation of CO pre-adsorbed on metal catalyst was calculated from the cyclic voltamogram; pre-adsorption of CO was carried out under pure CO bubbling for 60 min in 0.5 M H_2SO_4 solution at the potential of 0.05 V vs. RHE; sweep rate was 20 mV/s; temperature was 298 K.

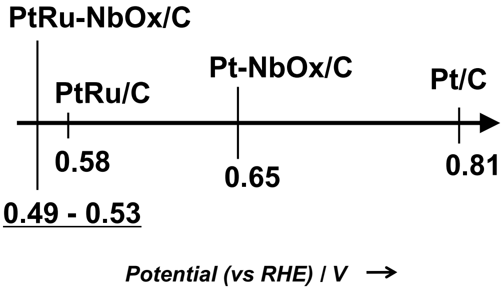

Fig. 7. Anodic peak potentials of the CO oxidation after CO pre-adsorption at 0.05 V vs. RHE over NbO$_x$-addition Pt/C and PtRu/C catalysts. In 0.5 M H_2SO_4 solution; sweep rate was 20 mV/s; temperature was 298 K.

a slight difference in the activating effect by TaO_x and NbO_x.

It is noteworthy that the CO oxidation activity of the PtRu/C is evidently enhanced by the addition of TaO_x or NbO_x. A plausible explanation for the role of Ru in the PtRu-catalyzed oxidation of CO is to provide active oxygen species as an oxidized form of water molecule [15]. The CO adsorped on the platinum site is effectively oxidized and removed by the oxygen species supplied from the ruthenium site adjacent to the platinum site. As proposed in this study, the role of TaO_x and NbO_x might be to inhibit or to weaken the Pt-CO adsorption. Thus, it is probable that the high activity of the TaO_x-modified or the NbO_x-modified PtRu/C anode in the CO oxidation is brought about concertedly by the activation of water molecule by Ru and the relaxation of the Pt-CO adsorption by TaO_x or NbO_x. Further study in connection with strong-metal-support-interaction (SMSI) in the catalysis of the supported platinum-group metals [16] will give a deeper understanding of the enhancing effect observed in the present study.

In conclusion, it has been found through this study that the addition of TaO_x and NbO_x to the catalytic Pt anode as well as to the PtRu anode enhances the electrochemical oxidation of CO in a sulfuric acid solution. Role of TaO_x and NbO_x is proposed to relax the strong CO adsorption on the surface of Pt. A concerted mechanism for the enhancement of the CO oxidation activity of Pt is also proposed in which the relaxation of the strong CO adsorption and the supply of activated oxygen species are assumed.

References

[1] C.E. Thomas, B.D. James, F.D. Lomax, I.F. Kuhn, Int. J. Hydrogen Energy 25 (2000) 551.

[2] O. Korotkikh, R. Farrauto, Catal. Today 62 (2000) 249.

[3] S. Gotesfeld, J. Pafford, J. Electrochem. Soc. 135 (1988) 2651.

[4] H.-F. Oetjen, V.M. Schmidt, U. Stimming, F. Trila, J. Electrochem. Soc. 143 (1996) 3838.

[5] M. Götz, H. Wendt, Electrochem. Acta 43 (1998) 3637.

[6] P.K. Shen, A.C.C. Tseung, J. Electrochm. Soc. 141 (1994) 3082.

[7] Y. Wang, E.R. Fachini, G. Cruz, Y. Zhu, Y. Ishikawa, J.A. Colucci, C.R. Cabrera, J. Electrochem. Soc. 148 (2001) C222.

[8] T. Ioroi, N. Fujiwara, Z. Shiroma, K. Yasuda, Y. Miyazaki, Electrochem. Commun. 4 (2002) 442.

[9] A. Hamnett, in: A. Wieckowski (Ed.), Interfacial Electrochemistry: Theory, Experiment, and Applications, Marcel Dekker, New York, 1999, p. 843.

[10] N.M. Markovic, H.A. Gasteiger, P.N. Ross Jr., X. Jiang, I. Villegas, M.J. Weaver, J. Electrochem. Acta 40 (1995) 91.

[11] T. Frelink, W. Visscher, J.A.R. van Veen, Langumir 12 (1996) 3702.

[12] M. Okumura, N. Masuyama, E. Konishi, S. Ichikawa, T. Akita, J. Catal. 208 (2002) 485.

[13] T.J. Schmidt, H.A. Gasteiger, G.D. Stäb, P.M. Urban, D.M. Kolb, R.J. Behm, J. Electrochem. Soc. 145 (1998) 2345.

[14] H.F. Oetjen, V.M. Schmidt, U. Stimming, F. Trila, J. Electrochem. Soc. 143 (1996) 3838.

[15] M. Watanabe, S. Motoo, J. Electroanal. Chem. 60 (1975) 267.

[16] A.J. Tauster, S.C. Fung, R.L. Garten, J. Am. Chem. Soc. 100 (1978) 170.