Comparison of CO on Carbon-supported Pt Catalysts Prepared by CO Gas Bubbling and Methanol Dehydrogenation

Kee Sung Han,[a] **Ki Ju Hwang, and Oc Hee Han**[*]

Analysis Research Division, Daegu Center, Korea Basic Science Institute, Daegu 702-701, Korea. [*]E-mail: ohhan@kbsi.re.kr
Received July 14, 2007

CO adsorbates on the surface of Pt supported on carbon catalysts (Pt/C) were investigated by CO stripping voltammetry. Three types of CO adsorbed samples were prepared: by methanol dehydrogenation only (CO_m), by CO gas bubbling only (CO_g), and by methanol dehydrogenation followed by CO gas bubbling (CO_{m+g}). Our coverage data show that CO gas can be adsorbed on Pt/C catalyst already saturated with CO adsorbates by methanol dehydrogenation. The CO_{m+g} sample showed the properties of both CO_m as well as CO_g samples in terms of the potential although the CO adsorbed by dehydrogenation was completely exchanged with CO in the electrolyte solution. Therefore, the oxidation pathways of CO on Pt/C were observed to depend on the initial adsorption conditions of CO more strongly than on the CO coverage. Our results imply that an initial CO poisoning condition in fuel cell operation is an important factor to determine the difficulty in removing the adsorbed CO and confirm that the properties of the adsorbed CO do not change even with chemical replacement with CO in different conditions. In addition, our results indicate a low CO surface mobility on the Pt in an electrolyte solution.

Key Words : Methanol dehydrogenation, CO gas adsorption, Pt supported on carbon, CO oxidation, CO coverage

Introduction

CO, which can be produced from methanol dehydrogenation in a direct methanol fuel cell (DMFC), is a poison for the fuel cell catalysts.[1,2] Therefore, the mechanisms of methanol dehydrogenation and/or oxidation and the properties of adsorbed CO on the surface of Pt catalysts have been studied extensively.[1-18] The methanol dehydrogenation mechanism was found to differ in liquid and gas phases.[3] Whereas the adsorbed CO is known to be very mobile on the Pt surface exposed to the gas phase,[4] the CO mobility on the Pt surface in an electrolyte solution has been controversial.[4-6,10] CO was observed to exchange rapidly with available CO not only in the gas phase but also in an electrolyte solution.[7-9] Regardless of the smaller desorption energy at higher coverage,[7-9] the adsorbed CO was reported not to desorb spontaneously even at saturation coverage in the absence of CO in the gas phase.[7-9] The CO oxidation mechanism in fuel cells has not been completely elucidated yet although the Langmuir-Hinshelwood mechanism has been generally accepted.[4-10]

There remains a discrepancy between the saturated CO coverage prepared by CO adsorption and that by methanol dehydrogenation. The CO coverage by direct CO adsorption is always about 0.1-0.2 ML higher than that from methanol dehydrogenation.[11,12] CO coverage is typically calculated with the peak areas of CO oxidation and the oxidation of adsorbed hydrogen measured from cyclic voltammo-grams.[12,14,15] Peak potentials of CO stripping voltammo-

[a]Present address: Department of Physics, Konkuk University, Seoul 143-701, Korea

grams have been used to investigate the activities of Pt-alloyed catalysts as well as Pt catalysts[1,2,11,16] while the number of electrons consumed to oxidize a single CO adsorbed on Pt has been used as an indicator of the strength of the CO bonding to Pt.[12]

In this work, three differently prepared samples of CO adsorbed on carbon-supported Pt catalysts were studied by CO stripping voltammetry, in order to compare the properties of CO adsorbates from methanol dehydrogenation and CO gas bubbling in an electrolyte solution.

Experimental

The three types of CO adsorbed samples were prepared by (1) methanol dehydrogenation only (CO_m), (2) CO gas bubbling to electrolyte solution only (CO_g), and (3) methanol dehydrogenation followed by CO gas bubbling (CO_{m+g}). A three electrode electrochemical cell consisting of a Pt boat working electrode, a Pt gauze counter electrode and a 1 M Ag|AgCl reference electrode[17] was used. All potentials were controlled with a model 263A potentiostat/galvanostat (Princeton Applied Research, USA) and experimentally measured versus a 1 M Ag|AgCl reference electrode but converted to the potential values against a reversible hydrogen electrode (RHE) by adding 222 mV.[19] The commercial electrocatalyst of 60% HP Pt on Vulcan XC-72 (E-Tek Inc., USA) was purchased and the catalyst was loaded onto the working electrode immersed in 0.5 M H_2SO_4 electrolyte solution. All samples were cleaned at the potential of 472 mV first[15,17,18] before CO adsorption on Pt. To prepare CO_m and CO_{m+g} samples methanol dehydrogenation was carried out at 222 mV to adsorb CO on about

200 mg of the precleaned catalyst in 0.6 M CH$_3$OH/0.5 M H$_2$SO$_4$ until the oxidation current was reduced below +200 μA.[15,17,18] The electrochemical cell was rinsed several times with 0.5 M H$_2$SO$_4$ solution to remove excess methanol after which about 100 mg of the catalyst was transferred to another electrochemical cell to adsorb CO by CO gas (minimum purity 99.5%, Airtech Co. LTD, Republic of Korea) bubbling at an open circuit voltage. CO gas at the flow rate of ~50 mL/min was bubbled directly into the catalysts immersed in 0.5 M H$_2$SO$_4$ electrolyte solution for about 60-90 minutes to prepare the CO$_{m+g}$ sample. The remained ~100 mg of the catalysts in the first electro-chemical cell was the CO$_m$ sample. The CO$_g$ sample was prepared by CO gas bubbling at the flow rate of ~50 mL/min directly onto about 100 mg of the catalysts immersed in 0.5 M H$_2$SO$_4$ electrolyte solution right after cleaning.

All CO stripping voltammograms starting at 222 mV and covering the potential range of −8 and 922 mV were obtained at ambient temperature with a scanning speed of 0.2 mV/s in 0.5 M H$_2$SO$_4$ electrolyte solution under purging of the ultrapure Ar gas which had been moisture-saturated by passing through water.

Results and Discussion

Representative CO stripping voltammograms are shown in Figure 1 and the CO coverage measured from the CO stripping voltammograms is presented in Table 1. Extensive study has examined the calculation of CO coverage based on the peak areas of CO oxidation and the oxidation of adsorbed hydrogen in cyclic voltammograms.[12,14,15] We used the simple method using cyclic voltammograms including both peak regions.[15] The coverage of the CO$_m$ sample was ~0.7 ML, which was about 0.2 ML less than ~0.9 ML for CO$_{m+g}$ and CO$_g$ samples. When a 0.25 M methanol solution was used, the coverage was not different from that of the sample prepared with a 0.6 M methanol solution. This no effect of the methanol concentration on the coverage was
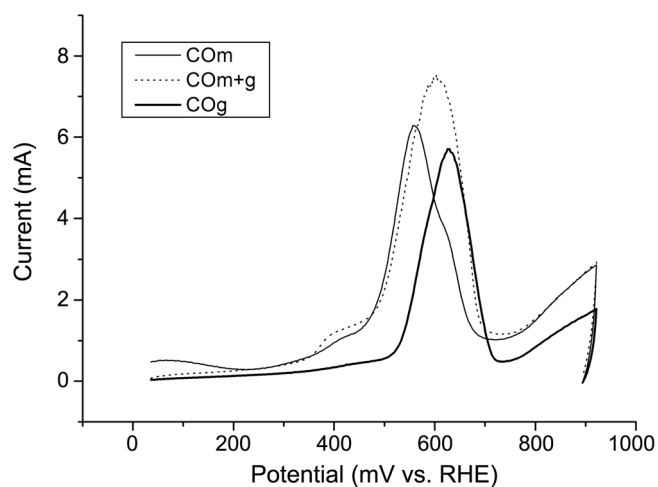
expected as long as the amount of methanol to react on the Pt surface was enough. The coverage of CO$_m$ and CO$_g$ samples has been reported previously[11,12] and was consistent with our data, which indicate that, in general, more CO gas is adsorbed on Pt than the CO produced from methanol dehydrogenation. The reason for this different saturation coverage is that methanol needs more than one adsorption site nearby while CO gas molecules need only one.[12,13,16] Our coverage data mean the presence of adsorption sites, on which CO gas could be adsorbed even after the Pt surface was already CO saturated by methanol dehydrogenation. This result experimentally supports the previous explanation that methanol needs more than one adsorption sites nearby for dehydrogenation to CO. In addition, our coverage data imply that the COs adsorbed by dehydrogenation do not move on the Pt surface rapidly enough to produce additional adsorption sites for CO by dehydrogenation. While the mobility of CO adsorbed on the Pt surface in vacuum or gas phase was reported to be very high,[4] the surface mobility of the CO adsorbed on the Pt surface in an electrolyte solution must be sufficiently slow to be neglected as previously reported.[5,6]

The center of gravity of the CO stripping peak for the CO$_m$ sample was lower than that of our CO$_g$ sample in the same CO stripping cyclic voltammetry condition as shown in Table 1 and as previously reported.[12] This suggested that the CO adsorbed from the CO gas had inherently stronger binding than the CO from methanol or that the higher CO coverage retards the CO oxidation by reducing the available sites for oxygen sources.[14] The coverage of the CO$_{m+g}$ and CO$_g$ samples was the same. However, there was no recognizable retardation of the onset potential, ~250 mV, for the CO oxidation of the CO$_{m+g}$ sample compared to that for the CO$_m$ sample, as shown in Figure 1. Therefore, the CO coverage close to 0.9 ML does not necessarily retard CO oxidation. The CO stripping peak of the CO$_{m+g}$ sample covers the peak regions of both CO$_m$ and CO$_g$ samples. As a result, the linewidth of the CO stripping voltammoram of the CO$_{m+g}$ sample is wider than those of CO$_m$ and CO$_g$, as shown in Table 1. All these CO stripping peak properties of the CO$_{m+g}$ sample indicate that the CO adsorbates of the CO$_{m+g}$ sample maintain both characteristics of CO prepared by methanol dehydrogenation or by CO gas bubbling. This could be from the CO adsorption potential difference during methanol dehydrogenation and CO gas bubbling. The CO stripping peak potentials of the sample prepared by CO gas in an electrolyte solution were previously reported to depend

Figure 1. Representative CO stripping voltammograms of CO$_m$, CO$_g$, and CO$_{m+g}$ samples. Vertical intensities of the voltammograms are not to scale.

Table 1. Linewidth and peak potential of CO stripping voltammogram and CO coverage

Sample	Linewidth^a (mV)	E$_G$^{b} (mV)	CO coverage (ML)
CO$_m$	127 ± 10	564 ± 5	0.72 ± 0.04
CO$_{m+g}$.	140 ± 5	596 ± 5	0.91 ± 0.04
CO$_g$	110 ± 5	621 ± 5	0.85 ± 0.05

^{a}Full width at half maximum of the CO stripping peak in the voltammogram. ^{b}Center of gravity of the CO stripping peak in the voltammogram.

on the adsorption potential.[14]

In our CO gas bubbled electrolyte solution, the CO adsorbates of CO_{m+g} must have been exchanged completely with the CO in the solution within the given CO gas adsorption duration of about an hour.[8,9] Thus our data indicate that even though CO adsorbates were completely exchanged with CO in an electrolyte solution, the properties of the adsorbed CO were associated with how the CO was adsorbed initially. The adsorbed CO of the CO_{m+g} sample was observed to have the properties of the CO adsorbed from methanol dehydrogenation and from CO gas bubbling in the solution as well. Their contributions to the total properties were proportional to the relative populations of the CO initially from dehydrogenation and the additional CO adsorption from CO in the solution. CO adsorption energy is known to increase with increasing CO coverage[7,10] and CO oxidation is retarded at higher CO coverage.[14] However, our data suggest that the oxidation of the CO adsorbates is more strongly influenced by the initial adsorption condition than the CO coverage. The initial adsorption condition difference might have resulted from the adsorption potential rather than the reagent and/or adsorption mechanism.

Conclusion

Our cyclic voltammetry results confirm the previous report that the methanol oxidation process requires more than one adsorption site at the initial stage. Our data also imply that the CO mobility on the Pt surface in an electrolyte solution is sufficiently slow so as not to produce additional CO adsorption sites during methanol dehydrogenation after the CO coverage reaches ~0.7 ML. The CO adsorbed on Pt/C adsorbed by CO gas bubbling in an electrolyte solution had a higher onset potential to be oxidized to CO_2 than the CO adsorbed by methanol dehydrogenation.

The CO adsorbates in the CO_{m+g} sample were expected to have been completely exchanged with CO in the electrolyte solution during additional CO adsorption process by CO gas bubbling. However, the properties of the CO_{m+g} sample were observed to resemble those of CO adsorbates not only from the CO gas bubbling but also from the methanol dehydrogenation. In addition, the CO adsorbates of the CO_{m+g} sample initially passed through the same oxidation pathways as the CO adsorbates prepared by methanol dehydrogenation only during the cyclic voltammetry. This suggests that the oxidation pathways of CO on Pt/C depend on the initial condition of CO adsorption more strongly than on the CO coverage. Our results imply that an initial CO poisoning condition in fuel cell operation with an electrolyte solution (for example, methanol solution) is an important factor to determine the difficulty of CO removal and, further, that subsequent exchange of CO, even in different conditions, does not change the CO properties.

All the observed differences of oxidation properties of the

differently prepared CO adsorbates may have been caused by the CO adsorption potential difference rather than different CO sources. Although it is difficult in practice to control the CO gas adsorption potential of the Pt/C powder because of disconnection of Pt/C particles from the Pt boat electrode owing to the floating particles during CO gas bubbling in an electrochemical cell, it would be worthwhile to clarify the CO adsorption potential effect with newly designed electrochemical cells in the near future. Also informative would be further study on the dynamics, chemical bonding properties, and spatial distribution of CO on Pt from methanol and CO gas with ^{13}C NMR.

References

1. Ross, P. N., Jr. In *Electrocatalysis*; Lipkowski, J.; Ross, P. N., Eds.; Wiley-VCH: New York, 1988; Ch. 2 and references therein.
2. Arico, A. S.; Srinivasan, S.; Antonucci, V. *Fuel Cells* **2001**, *1*, 133 and references therein.
3. Franaszczuk, K.; Herrero, E.; Zelenay, P.; Wieckowski, A.; Wang, J.; Masel, R. I. *J. Phys. Chem.* **1992**, *96*, 8509.
4. Koper, M. T. M.; Jansen, A. P. J.; van Santen, R. A.; Lukkien, J. J.; Hilbers, P. A. J. *J. Chem. Phys.* **1998**, *109*, 6051 and references therein.
5. Feliu, J. M.; Orts, J. M.; Fernandez-Vega, A.; Aldaz, A. *J. Electroanal. Chem.* **1990**, *296*, 191.
6. de Becdelièvre, A. M.; de Becdelièvre, J.; Clavilier, J. *J. Electroanal. Chem.* **1990**, *296*, 97.
7. Davies, J. C.; Nielsen, R. M.; Thomsen, L. B.; Chorkendorff, I.; Logadóttir, A.; Lodziana, Z.; Nørskow, J. K.; Li, W. X.; Hammer, B.; Longwitz, S. R.; Schnadt, J.; Vestergaard, E. K.; Vang, R. T.; Besenbacher, F. *Fuel Cells* **2004**, *4*, 309.
8. McGovern, M. S.; Waszczuk, P.; Wieckowski, A. *Electrochim. Acta* **2006**, *51*, 1194.
9. Iwasita, T.; Vogel, U. *Electrochim. Acta* **1988**, *33*, 557.
10. Batista, E. A.; Iwasita, T.; Vielstich, W. *J. Phys. Chem. B* **2004**, *108*, 14216 and references therein.
11. Lu, C.; Rice, C.; Masel, R. I.; Babu, P. K.; Waszczuk, P.; Kim, H. S.; Oldfield, E.; Wieckowski, A. *J. Phys. Chem. B* **2002**, *106*, 9581 and references therein.
12. Seland, F.; Harrington, D. A.; Tunold, R. *Electrochim. Acta* **2006**, *52*, 773.
13. Wang, K.; Gasteiger, H. A.; Markovic, N. M.; Ross, P. N., Jr. *Electrochim. Acta* **1996**, *41*, 2587.
14. Rush, B. M.; Reimer, J. A.; Cairns, E. J. *J. Electrochem. Soc.* **2001**, *148*, A137.
15. Han, K. S.; Han, O. H. *Bull. Kor. Chem. Soc.* **2006**, *27*, 1121.
16. Markovic, N. M.; Gasteiger, H. A.; Ross, P. N., Jr.; Jiang, X.; Villegas, I.; Weaver, M. *J. Electrochim. Acta* **1995**, *40*, 91 and references therein.
17. Han, K. S.; Han, O. H. *Electrochim. Acta* **2001**, *47*, 519.
18. Han, K. S.; Han, O. H.; Babu, P. K. *J. Electrochem. Soc.* **2005**, *152*, J131.
19. Brett, C. M. A.; Brett, A. M. O. *Electrochemistry Principle, Methods, and Applications*; Oxford University Press: Oxford, 1993; p 24.