Mechanism of CO Tolerance at Pt-Alloy Anode Catalysts for Polymer Electrolyte Fuel Cells

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We have found an excellent CO tolerance at Pt anodes alloyed with the second metals in spite of the formation of Pt skin layer (*ca.* 1-2 nm in thickness) over the alloy surfaces due to the dissolution of the second metals and proposed a new mechanism for the catalysis. In this study, ATR-SEIRAS, coupled with CV measurement, was used to observe the oxidation process of adsorbed CO on the typical Pt-Fe alloy. The alloy anode exhibits a lower saturated coverage with CO than that of pure Pt. Linear CO is observed predominantly on the alloy electrode, differing from both of linear and bridged CO besides COOH on the pure Pt. The negative-shift of the wavenumber for the linear CO stretching and the broadening of the half-wave width at the alloy also indicate the weakening of metal-CO bonding and the increased mobility of the adsorbed CO, respectively. As a presumable effect of the electronic structure change at the Pt skin, the dissociation/oxidation of adsorbed water as well as a formation of adsorbed HOOH species are clearly observed beyond 0.6 V in the electrolyte solution without CO. The mechanism of CO tolerance at the Pt skin on top of the alloy surface with an increased d-band vacancy, proposed previously by us, is supported by the present SEIRAS data as the "detoxification mechanism", featured by an increased mobility of the adsorbed CO with suppressed coverage.

Key Words : Fuel Cell, CO Tolerance, Pt Alloy Electrocatalysts, FTIR

1 Introduction

Polymer electrolyte fuel cell (PEFC) is an attractive power source for electric vehicles (EV), because of its high efficiency and cleanness as well as light weight by the high power density even at a low operating temperature.¹⁻³⁾ PEFCs, however, usually require platinum or its alloy as anode catalysts which have a high electrocatalytic activity for H₂ oxidation at such a temperature. For the EV use, it is desirable to operate the PEFC with reformed fuels from methanol or natural gas, but the performance of the conventional PEFC with pure Pt anode catalyst operating on reformates is seriously depressed by CO poisoning of Pt sites.³⁾ Watanabe and Motoo found previously an enhancement of CO tolerance at Pt electrode with ad-atoms such as Ru, Sn or As for H₂ oxidation.⁵⁻⁷) Recently, we found new CO-tolerant catalysts by alloying Pt with the second non-precious metals for PEFCs and proposed a new mechanism for the CO tolerance, based on the electronic structure change of the catalyst surface by the alloying.⁸⁻¹⁰⁾ This paper reviews the results and discusses the mechanism further with new experimental data of surface-enhanced IR reflection absorption spectroscopy with attenuated total reflection technique (ATR-SEIRAS).

2 Experimental

Water and 0.1 M (M = mol dm⁻³) HClO₄ used were purified with the conventional methods.⁷) Thin film Pt alloy electrodes were formed at room temperature by Arsputtering Pt and the second metal targets simultaneously onto Pyrex glass substrate for the measurement of electrocatalytic property^{8 -13)} and onto a flat plane of silicon hemi-cylinder for the ATR-SEIRAS measurement.^{14,15)} The resulting alloy composition was determined by gravimetry and fluorescent X-ray analysis. A crystallographic structure of the alloy was examined with a grazing angle X-ray diffraction. XRDs of the alloys indicated the formation of a solid solution phase with a face-centered cubic (fcc) crystal structure.

A usual set of rotating disk electrode equipment with a gas-tight Pyrex cell was used for the experiment of CO adsorption and H₂ oxidation on the prepared electrodes. Before the measurement of activities for the electrooxidation of H₂, a pretreatment of the alloy electrode was carried out by 10 times potential sweeps (10 V s⁻¹) from 0.05 to 1.2 V in the electrolyte solution (0.1 M HClO₄). During the pretreatment, the second non-precious metals were all dissolved out from the surface, resulting in the formation of a Pt skin layer, as mentioned later. Then, the electrolyte was saturated with each reactant gas of H_2 or 100 ppm CO/H_2 mixture. Then, hydrodynamic voltammograms for the H₂ oxidation were collected at room temperature as the potential was scanned from 0 to 0.2 V with the sweep rate of 10 mV s⁻¹ at different rotating rates for the disk electrode.^{8 - 10} Kinetic current values of H₂ oxidation for clean and CO adsorbed Pt alloy electrodes were evaluated from Levich-Koutecky plots.¹⁶⁾ After the RDE experiments, voltammograms (CV) were taken to determine the CO coverage by the first potential sweep (10 V s⁻¹) from 0.05 to 1.2 V on the electrode covered with CO, resulting in the oxidative stripping of CO during the sweep, and then by the second sweep on the clean electrode. According to previous works, ^{5,17)} CO coverage of alloy electrodes is determined by using the charge required to oxidize hydrogen adsorbed on a clean electrode and that with adsorbed CO.

XPS investigation was carried out on the sample before and after the electrochemical experiments.¹⁰⁻¹³

The thickness of the alloy film for the ATR-SEIRAS measurement was about 7 nm.^{14,15)} Before the collection of spectroelectrochemical data, fast potential sweeps (500 mV/s) between 0.05 and 1 V were applied to the electrode for the surface cleaning and for the evaluation of the active electrochemical surface area of the electrode. The surface area was typically about 3 times larger than the geometrical area. Infrared spectra were taken with a Bio-Rad FTS-6000 spectrometer. The spectral resolution was in 8 cm⁻¹. The electrolyte solution used was the 0.1 M HClO₄ solution saturated with high purity nitrogen. H_2 gas containing CO of 97.9 ppm was used to purge into the electrolyte solution at 0.05 V for 90 min in order to obtain an equilibrium adsorption of CO. Then, CO in the bulk solution was removed by purging with N₂ while keeping the potential constant for 1 hr.

3 Results and Discussion

3. 1 Development of CO tolerant Pt alloy catalysts and proposal of the mechanism

We have found that Pt-Fe alloys are excellent COtolerant anode catalysts as well as Pt-Ru, Pt-Co, Pt-Ni or Pt-Mo. Figure 1 shows an example of steady currentpotential curves for H₂ oxidation with and without CO contaminant on Pt₈₅Fe₁₅ and pure Pt. It is clear that the alloy shows almost the same catalytic activity regardless of the presence of CO although pure Pt loses completely the activity under the presence of CO. As shown in Figs. 1 and 2 of ref. 10, the kinetically controlled current at pure Pt, or the activity, declined to zero by the occupation of all Pt sites with CO. But, the CO tolerant alloys mentioned above showed no degradation in the activity and kept the CO-free sites more than 50% under the steady state in spite of the presence of pure Pt skin layer



Fig. 1 Steady polarization properties for H_2 oxidation at 20 mV vs. RHE on pure Pt and Pt-Fe alloy electrodes at 1500 rpm in 0.1 M HClO₄ saturated with H_2 or 100 ppm CO/H₂ balance at ambient temperature.



Fig. 2 Schematic explanation of CO tolerance on Pt alloys such as Pt-Fe with Pt skin having a modified electronic state (left) and on pure Pt (right).

over the alloy surface. The formation of this skin layer was inferred by the disappearance of the XPS signals corresponding to each non-precious metal in the Pt alloy after the potential cycling prior to the electrochemical measurements. The thickness of the skin was estimated to be ca. 1-2 nm corresponding to a few Pt monolayers, based on the reduction of the $2p_{3/2}$ peak for Fe atom during the penetration via the Pt skin layer.¹⁰⁾ In spite of the disappearance of Fe atoms at the alloy surface, the binding energies of 4d or 4f of the Pt skin shift to positive direction from those of pure bulk Pt as shown in Fig. 3 of reference 10, e. g., by about 0.65 and 0.75 eV for 4d_{3/2} and $4d_{5/2}$ at the present alloy composition, respectively. These positive chemical shifts corresponding to the less electronic population in the 4d- or 4f- orbital strongly indicate the increased 5d-vacancy or the lower Fermi level of the Pt skin. Since the back-donation of 5d electrons has been reported to play a dominant role for the CO chemisorption on bulk Pt,18,19) we have proposed a mechanism for the CO-tolerance as shown in the top of Fig. 2, *i. e.*, the lowered electron density of 5d orbital of Pt skin decreases an electron back-donation from the Pt 5d orbital to $2\pi^*$ orbital of CO, and consequently suppresses CO-Pt bonding, resulting in the lowered CO coverage and the increased CO tolerance.⁸⁻¹⁰⁾

3. 2 Comparison of electrocatalytic behaviors of pure Pt with Pt-Fe

Vibrational spectroscopic techniques can provide information about the mechanism of the electrochemical oxidation of CO ad-layer on electrodes. However, most of the studies on the electrooxidation of the CO ad-layer using IR spectroscopy involved an external reflection set-up, in which the light beam has to pass through at least 10³ layers of electrolytes before striking the studying surface.^{20–27)} Very recently, Osawa and coworkers reported a series of IR spectra obtained on an evaporated gold electrode surface in aqueous electrolyte solution, utilizing ATR-SEIRAS.^{28–31)} Using this technique, we have successfully observed the electrooxidation of the CO adlayer involving adsorbed water at a pure Pt electrode¹⁴⁾ and Pt-Fe alloy.¹⁵⁾ In this paper, we report the potentialdependent adsorption and oxidation of CO at the Pt-Fe alloy electrode on a silicon prism surface. We will also report the dissociation behavior of the adsorbed water molecule.

3. 2. 1 Cyclic voltammometry on Pt-Fe with/with-Figure 3A shows a cyclic voltamout CO ad-layer mogram (CV) on the Pt skin of the Pt-Fe allov electrode (roughness factor = 3.5) in the solution saturated with and without CO. The CO coverage on the Pt skin was ca. 0.55, which is much lower than that of 1.0 saturated on a pure Pt electrode.¹⁴⁾ Figure 3B shows the similar CV on the pure Pt electrode (roughness factor = 3.2), where the total coverage with CO and the derivatives was controlled to the same level as the Pt-Fe alloy by exposing the electrode for a shorter time to the CO dissolved solution. Although the currents in y-axes in Figs. 3A and 3B were not shown by the current densities, the difference in the real surface areas of both electrodes is only ca. 10%.

It is clear that the blank anodic current on the Pt skin of the alloy electrode (solid line) commences to increase at about 0.6 V, which is *ca*. 0.2 V less positive than that of the pure Pt, and shows a larger current at more positive potentials in comparison with the blank CV on the pure Pt (solid line). This result infers that the Pt skin surface on the alloy has a larger affinity or an oxidative property to water molecules than the bulk pure Pt. On the alloy electrode with the saturated CO ad-layer, the anodic current for the CO oxidation commences to increase at about 0.6 V, corresponding to the onset of the water molecule oxidation or the adsorption of OH species, and shows only one anodic peak at 0.73 V without any shoulder peak (see Fig. 3A). On the other hand, as



Fig. 3 Cyclic voltammograms (20 mV/s) on a sputtered Pt₂₇ Fe₇₃ alloy film electrode (A), and on a pure Pt electrode (B) with (dashed line) and without (solid line) CO ad-layer of the total coverage of *ca*. 0.5 in 0.1 M HClO₄.

shown in Fig. 3B, the oxidation of the adsorbed CO on the pure Pt commences at the potential less positive than 0.55 V and shows a peak at *ca*. 0.7 V via a small preshoulder. The shoulder current and the less positive onset potential can be ascribed to oxidation of carboxyl radicals formed on the pure Pt surface.¹⁴⁾ Despite almost the same total CO ad-layer coverage on the Pt skin and the pure Pt, the electric charge (per real Pt surface area) for the CO ad-layer oxidation on the former is larger than that of the latter, which indicates that the former ad-layer involves CO species with a larger value of electrons per Pt sites, associated with the oxidation reaction, not like as carboxyl radical or multi-hold CO but linear CO.

3. 2. 2 In situ IR spectra of the interfacial water at the Pt-Fe electrode Figure 4 shows a series of IR reflectance spectra for (A) the Pt-Fe alloy electrode and (B) the pure Pt electrode in 0.1 M HClO_4 solution, which is simultaneously recorded with the linear potential sweep from 0.05 to 1.00 V at a rate of 20 mV/s (corresponding to the solid line in Fig. 3). Each spectrum was obtained by integrating 14 interferograms to improve the signal-to-noise radio of the spectrum. The acquisition time was about 2.5 s per spectrum. Therefore, the potentials shown in the figure are the averages of every 50 mV interval. The first single-beam spectrum at 0.075 V is chosen as the reference spectrum. The negative-going band near 3350 cm⁻¹ is observed on the Pt skin of the alloy at potentials less positive than 0.6 V, which is assigned to the OH stretching of the adsorbed water.²⁸⁻³¹⁾ The band shifts with increasing potential from a higher to a lower wavenumber, corresponding to a weakening of the OH bond. Negative sign of the band may indicate the reduction of the adsorbed water due to its consumption to form some O-species.

Beyond about 0.6 V, however, some new positive-going bands around 3450, 3250, 2960, 1720 and 1640 cm⁻¹ can be observed on the Pt skin of the alloy. They may not be assigned to the adsorbed water, since the bands around $3250 \sim 2960$ and $1720 \sim 1640$ cm⁻¹ are not only too sharp compared with the conventional ones for the adsorbed water, but also split into two sharp bands, and moreover they are independent of the electrode potential unlike the conventional H₂O. The fact of the simultaneous increase of these band intensities presumably indicates that the bands correspond to a single species, which may be assigned to a peroxide species.³²⁻³⁴⁾ The assignment to the OH or H_2O_2 could be confirmed by the fact that the absorption bands, attributed to HOOH, were clearly seen in the same mid-IR region when H₂O₂ was added into the blank electrolyte (see Fig. 3 of ref. 15). However, only the small sharp band around 2960 cm^{-1} cannot fully exclude the assignment to the CH impurity located between the Si and Pt surfaces, even though the increase in the band intensity with the potential results from its oxidation. On the pure Pt electrode, the potentialdependent bands near 3400 and 1620 cm⁻¹ appear, which can be assigned to the OH stretching and HOH bending vibrations of the adsorbed water. However, bands of 3450, 3250, 1720 and 1640 cm⁻¹ were not discernible on the



Fig. 4 In situ IR spectra taken in 0.1 M HClO₄ on the Pt₂₇ Fe₇₃ (A) and on the Pt (B) during a slow anodic potential scan (20 mV/s). The reference spectrum was the first singlebeam spectrum at $E_{ref}(IR)=0.075$ V during the potential sweep. (1)vOH in H₂O, (2)vOH in H₂O₂, (3) δ OH in H₂O₂/H₂O, (4) δ OH in H₂O.

pure Pt electrode. The different adsorption property implies that there is a distinctive difference in the electronic structures between the pure Pt and the Pt skin on the top of the alloy. Obviously, the Pt skin of the Pt-Fe alloy favors the dissociation/oxidation of the adsorbed water beyond 0.6 V. Correspondingly, the anodic current commenced to increase at the same potential as seen in Fig. 3. The Pt skin with less d-electron density may be highly active for the oxidation of the adsorbed water, described by the following sequence of reactions:

$$Pt-OH_{2} \longrightarrow Pt-OH + H^{+} + e^{-}$$
(1)
2Pt-OH $\longrightarrow Pt-O_{2}H_{2}-Pt$ (2)

A metal-molecule interaction may generally lead to an intramolecular bond weakening or dissociation,¹¹⁻¹³⁾ in particular for the oxygen element in water molecule, by the lateral interaction of the π -orbital of O with empty d_{z^2} orbital of the surface Pt atom or with empty d_{xy} and d_{yz} orbital of dual Pt atoms, respectively. The less 5d electron density of the surface Pt leads to an increased 2π -donation to the surface, which strengthens its ability

withdrawing electrons from the O in the adsorbed water molecule and in turn from the H in the adsorbed water. With sweeping potential towards positive, this effect increases. Consequently, the dissociation/oxidation of the adsorbed water molecule becomes easier at the alloy electrode than at the pure Pt electrode. Thus, *in situ* SEIRAS confirms the perturbation of the electronic structure in the Pt skin by the bulk alloy in electrochemical environment.

3. 2. 3 In situ IR spectra for the oxidation of CO ad-layer on Pt-Fe Infrared reflection spectra for the CO ad-layer on the Pt-Fe alloy are shown in Fig. 5 (top), which are simultaneously recorded with the linear potential sweep from 0.05 to 1 V. The first single-beam spectrum at 0.075 V (CO₂-free surface) or the last singlebeam spectrum at 0.975 V (CO-free surface) during potential sweep from 0.05 to 1 V were chosen as the reference spectrum for observing CO_2 or CO_2 , respectively. The absorption bands around 2000 cm⁻¹ and 2360 cm⁻¹ could be assigned to the stretch mode of linearly (atop) bound CO and CO₂, respectively.^{14, 20-22, 35, 36)} The alteration of these absorption bands with the increase of electrode potential indicates the CO oxidation and the CO2 production. It is obvious that linear CO (COL) is dominantly observed around 2000 cm⁻¹, which is distinctive from that linear CO (also around 2000 cm⁻¹) and bridged CO (around 1850 cm⁻¹) besides COOH co-exist at the pure Pt electrode even at the same coverage of CO.¹⁴⁾ The electronic structure of the metal determines which adsorption sites, i. e., on-top, twofold and threefold bridges, are occupied for the different metal sites. The predominant presence of the linear CO indicates that there is a smaller back-donation of d-electrons at the alloy electrode than that at the pure Pt electrode, which may suppress the formation of multi-fold CO, the total coverage of the multi-fold CO and the COOH as a CO derivative. The result is well consistent with our previously proposed mechanism that the strong modification in the electronic structure of the Pt skin by the underlying alloy lowers the Fermi level at the electrode surface, which results in deactivation of the Pt skin towards the CO chemisorption, *i. e.*, $(\theta_{co} = 0.55 \text{ (see Fig. 2 (bottom))})$.

The O-H stretching band near 3400 cm⁻¹ of the adsorbed water is observed below ca. 0.75 V (see Fig. 5 (bottom)), which is slightly potential-dependent. The increased negative peak of the absorption band infers the decrease in the amount of the adsorbed water due to the strong interaction between the water molecule and metal, which also leads to the negative shift of the wavenumber for the stretching. The corresponding O-H bending band between 1600 and 1750 cm⁻¹ is too weak to observe below 0.75 V. The reduction of COL band and the growth of CO_2 band commence beyond 0.625 V in Fig. 5. Whereas the adsorbed HOOH species has been detected at least beyond 0.625 V in the blank solution (see Fig. 4A), it cannot be detected until the linear CO is almost removed beyond 0.75 V by the oxidation to CO₂. Thus, it is considered that the linear CO on the Pt skin underlain by the Pt-Fe alloy must be oxidized by the reaction with the peroxide species via the so-called "bi-functional mecha-



Fig. 5 *In situ* IR spectra taken in 0.1 M HClO₄ on the Pt₂₇-Fe₇₃ film electrode for the saturation coverage of CO (θ co = 0.55); the positive-going scan rate: 20 mV/s $\textcircled{1}\nu$ OH in H₂O, $\textcircled{2}\nu$ OH in H₂O₂/H₂O, $\textcircled{3}\delta$ OH in H₂O₂/H₂O, 5CO₂, 6linear CO, and 7CO₃²⁻. *E*_{ref}(IR) = 0.075 V except 6 (no CO at *E*_{ref}(IR) = 0.975 V).

nism" proposed by Watanabe and Motoo,⁵⁾ where HOOH species are considered as the limiting reactant in the CO oxidation reaction.

$$Pt-OH + Pt-CO \longrightarrow 2Pt + CO_2 + H^+ + e^- \qquad (3)$$

Accompanied with the production of CO_2 , new bands around 1450, 1380 and 1310 cm⁻¹ appear. The bands could be assigned to carbonate species.^{37,38)} The carbonate species may be formed through the subsequent steps as in the following,

$$Pt-(CO_2) + Pt-OH_2 \longrightarrow Pt-CO_3^{2^-} + Pt + 2H^+$$
(4)

where the (CO_2) represents a weakly bonded or nonbonded CO_2 on the Pt skin surface.

3. 2. 4 Dependence of the absorption band for the CO ad-layer on the electrode potential

The wavenumber of the linear CO band in the saturated coverage ($\theta_{CO} = 0.55$) on the Pt-Fe alloy electrode is plotted (\diamondsuit) as a function of the potential(Fig. 6B). It was found that the wavenumbers exhibit extremely small

values, *e. g.*, *ca*. 1980 cm⁻¹ at 0.05 V, which is 60 cm⁻¹ smaller than that of the pure Pt with the saturated coverage CO, *i. e.*, $\theta_{\rm CO} = 1.0^{14}$ As the potential is swept to positive direction between 0.075 and about 0.7 V, the CO band linearly shifts to higher wavenumbers with the slope of about 54 cm⁻¹/V. The slope is larger than that (ca. $30 \text{ cm}^{-1}/\text{V}$) of the pure Pt electrode with the saturated coverage of CO, *i. e.*, $\theta_{\rm CO} = 1.0^{14, 20, 21, 39}$ Generally, the slope increases with the decrease of the coverage.⁴⁰⁾ The present large slope is apparently reflecting the suppressed saturating CO coverage on the alloy surface. Two models have been proposed in order to explain such a linear potential dependence on the wavenumber for the CO ad-layer, i. e., a first-order "Stark effect" assuming a rigid dipole oscillator in a variable electric field⁴¹⁾ and a "chemical" model of the potential-dependent surface bonding.⁴²⁾ In addition to the electric field in the inner Helmholtz layer, other physical parameters may also influence the wavenumber of the CO ad-layer, e.g., the adsorbate coverage and the adsorbate binding geometry. If these physical parameters are constant, the linear frequency-potential relationship can be observed as in the present work on the skin of the Pt-Fe alloy. This linear relationship is quite different not only in the shape but also in the wavenumber location from the nonmonotonous relationship obtained on the pure Pt with the same coverage of CO ad-layer, which is shown in Fig. 6B, cited from ref. 14. The non-monotonous relationship on the pure Pt is due to the transition of the bridged CO to the linear CO and maybe due to the effect of the



Fig. 6 (A) Potential dependencies of the normalized intensities of the linear and bridged CO or CO₂ absorption bands, on the Pt₂₇Fe₇₃ ($\theta_{CO} = 0.55$) and on the pure Pt ($\theta_{CO} = 0.48$), (B) The potential dependence of the stretching vibration wavenumber, of the linear CO on the Pt₂₇Fe₇₃ ($\theta_{CO} = 0.55$) and on the pure Pt ($\theta_{CO} = 0.48$). \triangle , \bigcirc , \diamondsuit : Pt₂₇Fe₇₃, \blacktriangle , \blacktriangledown , \blacksquare : pure Pt.

COOH species.¹⁴⁾ The less d-electron density of the Pt skin on the alloy electrode leads to the decrease of the electron back-donation to $2\pi^*$ orbital of the CO, which is one of the dominant factors for the Pt-CO bonding formation,¹⁹⁾ and thus only linear CO may be formed unlike the pure Pt electrode. The decrease of the back-donation might increase the wavenumber for the C-O stretching. In fact, however, a lower C-O wavenumber is observed as shown in Fig. 6B. The observed low wavenumber for the C-O stretching indicates that another factor should be considered to understand the present experimental fact. For example, the metal-CO molecule interaction must be important. Here, it should also be noted that the half width (40 cm⁻¹) of the linear CO band on the Pt skin is broader than that (30 cm⁻¹ at $\theta_{co} = 0.5$ and 20 cm⁻¹ at $\theta_{co} = 1.0$) on the pure Pt.¹⁴⁾ The band broadening mainly reflects the increase in mobility of the adsorbed CO molecules. Regarding the vibrational frequency of CO adsorbed on metal site, the following theoretical equation has been accepted,⁴³⁾

$$v_{a} = v_{0} (1 + k_{1} \mu^{2} / 2k_{0} M_{C}^{2})$$
 (5)

where k_1 and k_0 represent the force constant of the metal-C and the C-O stretching, respectively. v_a and v_0 are the vibrational frequency in the adsorbed state and in the gas phase. μ is the reduced mass of the CO molecule and M_C is the mass of carbon. Since k_0 is constant, the negative shift of the CO_L wave number indicates the reduction of the force constant k_1 at the metal-C or the increase of the bond length between Pt and C. Thus, the observed low wavenumber of the CO ad-layer confirms the weakening of bond strength between Pt and C on the Pt skin of the alloy.

3. 2. 5 CO tolerance mechanism on Pt-Fe alloys for the oxidation of H₂ containing CO impurity Figure 6A shows the relationships between the normalized intensity of CO or CO₂ bands and the potential. On the Pt skin of the alloy electrode, CO₂ (\bigcirc) increases monotonously by the oxidation of the linear CO (\triangle) beyond *ca*. 0.6 V. Thus, it was confirmed that the linear potential dependence of the vibration frequency for the linear CO appears below the onset potential of the apparent CO oxidation, presumably resulting from the change of the electric field in the inner Helmholtz layer.

The normalized intensities of the CO (\blacktriangle , \bigtriangledown), CO₂ (\bigcirc) absorption bands at $\theta_{CO} = ca$. 0.5 on the pure Pt electrode are shown in Fig. 6A.¹⁵⁾ Since IR spectra for the COOH, the presence of which was confirmed in our previous work,¹⁴⁾ were overlapping with those of CO₃²⁻ in some potential region, the similar quantitative potential-dependence to that on the Pt skin could not be shown in the figure. However, it is clear that after the internal transition of the bridged CO (\bigtriangledown) to linear CO (\bigstar) around 0.2 V, each of them keeps a steady value until their oxidation commences in the more positive potential region (see ref. 14). This result is well consistent with the dependence of the wavenumber for the stretching of the linear CO (\bigstar) on the potential, shown in Fig. 6B.

It should be emphasized that both of linear and

bridged CO (\blacktriangle , \checkmark) on the pure Pt begin to decrease and disappear almost at the same narrow potential region as that of the linear CO (\triangle) on the Pt skin of the alloy, *i. e.*, $0.60 \sim 0.75$ V, although the CO₂ production occurs at less-positive potential by more than 0.1 V on the pure Pt. This clearly shows two important points, *i. e.*, (1) the Pt skin surface on the alloy is not more active than that of the pure Pt for the direct oxidation both of linear and bridged CO, (2) the lower onset potential for the oxidation of the CO ad-layer on the pure Pt, found in the CV (see Fig. 3B) is not due to the direct oxidation of the linear and/or bridged CO but due to the adsorbed COOH, induced by the surface reaction between the adsorbed CO and H₂O, as proposed in our previous work.¹⁴⁾ Then, the question arises how the excellent CO tolerance for the oxidation of H₂ containing CO impurity can be achieved on the Pt-Fe alloys as well as Pt-Ru, Pt-Co, Pt-Ni or Pt-Mo.^{8 - 10)}

Recently, Ross and coworkers have worked extensively about the CO tolerance on Pt-Sn, Pt-Mo as well as Pt-Ru alloys, but the CO content in H_2 is really high (> 1 %) far from that in the practical fuel cell condition.⁴⁴⁻⁴⁶⁾ Gottesfeld and coworkers also studied the mechanism on the Pt-Ru alloy in the practical fuel cell by means of mathematical simulation.⁴⁷⁾ Both groups ascribed the CO tolerance to the formation of a few percent of CO-free sites, which were thought to be prepared by the direct CO oxidation on the exposing surface of both alloycomponent metals via the bi-functional mechanism originally proposed by Watanabe and Motoo.⁵⁾ But, the mechanism may not be applicable to the present CO tolerance to the anodic oxidation of H₂ containing CO, by two reasons. First, the H₂ oxidation occurs in less positive potential region near the equilibrium potential, where O or OH species required for the oxidation of CO may not be remaining on the neighbor surface sites due to the negligibly small equilibrium coverage and due to the reaction with H₂ existing around them in large excess. Second, there are no second element sites for O or OH adsorption, because of the formation of Pt skin as described above. Although the Pt sites at corrosion resistant Pt alloys such as a Pt-Ru have adjacent second element sites, O or OH adsorption on the latter may not occur also by the above first reason. The Pt skins on the Pt-alloys with different compositions had neither particularly high roughness nor exposure of particular crystalline facets in comparison with pure Pt, rather did they exhibit the modified electronic structure.⁸⁻¹³⁾ All of the SEIRAS data combined with the CVs in the present work well agree with the modification of the surface by the alloying in the electronic structure, e.g., the high activity to H₂O oxidation, the disappearance of the multi-fold CO or the weakened Pt-C bonding force, all of which must be brought about by the increased d-vacancy. No specific enhancement of direct CO oxidation, however, was found as shown in Fig. 6, in spite of the high activity for the formation of OH species, which may be involved in the bi-functional CO oxidation mechanism. Nevertheless, there remain a large number of CO free sites (mostly> 50%) on the Pt skin surfaces having no alloying met-



Fig. 7 Relationship between the steady kinetic currents at 20 mV vs. RHE for the oxidation of H_2 containing 100 ppm CO on various CO tolerant alloys having different compositions and the surface CO coverage. Dashed line is the similar relationship on pure Pt, cited from ref. 17. The numbers attached to data points indicate atomic percentage values of the second element contents in Pt alloys, and the data sets at zero CO coverage show initial activities of some alloys just after exposing them to CO containing H_2 .

als.^{8 - 10)} Thus, we conclude the mechanism for the COtolerance on the Pt-Fe alloy, *i. e.*, the lowered electron density of 5d orbital of Pt decreases an electron backdonation from the Pt 5d orbital to $2\pi^*$ orbital of CO, and consequently suppresses CO-Pt bonding, resulting in the lowered CO coverage and the sufficient H₂ oxidation rate on the CO-free sites. Although we have discussed the CO-tolerant alloy based only on the data for Pt₂₇Fe₇₃ in this paper, we have obtained the similar results on the other Fe compositions and believe that the results on this representative alloy can be extended to all of the CO-tolerant alloys.

Figure 7 shows the steady kinetic currents (I_k) on our various CO tolerant alloys as a function of the CO coverage in comparison with those obtained previously on pure Pt.¹⁷⁾ The I_k values on the pure Pt decrease with increasing CO coverage, *i. e.*, $I_k = k(1 - \theta_{CO})$ at $\theta < ca. 2/3$, and $I_k = k(1 - \theta_{co}^2)$ at $\theta > ca$. 2/3, as shown by dotted line.¹⁷⁾ The relations indicate that the adsorbed CO is not mobile on pure Pt and the dissociative H₂ adsorption followed by the ionization becomes the rate-determining step for the H_2 oxidation. On the other hand, it is clear that the I_k values scarcely depend on the CO coverage at the CO-tolerant alloys and keep the similar large currents to that of pure Pt without poisoning by CO regardless of the alloy combination as well as the composition. A suppressed CO coverage has been found on every our CO-tolerant alloy,¹⁰⁾ but the independency on this CO coverage distinctive from that of pure Pt may not be explained unless a high mobility of the adsorbed CO is taken into account so as the dissociative adsorption of H₂ molecules and the following charge transfer may not be disturbed. The weakening of Pt-C bond-strength and the increase of mobility are inferred by the negative-shift of COL band and the broadening of its half-width at ATR-

SEIRAS, as seen above. Thus, it is considered that the H_2 dissociation and the successive oxidation may not be disturbed on the alloy surface, even though there are some adsorbed CO molecules.

4 Conclusion

The electronic property of the metal was modified when they were alloyed with another metal. In situ ATR-SEIRAS was used to investigate the oxidation process of adsorbed CO on the Pt₂₇Fe₇₃ alloy, the surface of which was covered with the Pt skin and had the increased dvacancy. Linear CO with lowered saturated coverage was found predominantly on the skin of the alloy, which had a higher mobility by the weakened Pt-C bonding than on the pure Pt. An adsorbed HOOH species, which could not be observed at the pure Pt electrode, was clearly observed beyond 0.6 V in the electrolyte solution without CO. This formation could also be ascribed to the increased d-vacancy in the Pt skin. Carbonate species was also detected around $1300 \sim 1450 \text{ cm}^{-1}$, which were possibly produced by the surface reaction of CO_2 with water or OH species. However, it was found that the Pt skin had no specifically high activity for the direct CO oxidation. Thus, we can conclude that the CO tolerance on the Pt-Fe alloy surface is brought about by the lowering of the CO coverage as well as its bonding strength, i. e., "detoxification" by giving mobility to adsorbed CO with the low coverage, but not via facilitating the oxidation of CO.

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