ON THE MECHANISM OF CO-TOLERANCE OF PT-MO ALLOY ELECTROCATALYSTS

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ABSTRACT

A mechanism of action of Mo atoms in the Pt-Mo alloy surface for the electrooxidation of CO and H2/CO mixtures is proposed. The Mo atoms nucleate reactive OH groups which oxidize CO adsorbed at neighboring Pt sites at much lower overpotentials than on the pure Pt surface. In the case of H2/CO mixtures, the rate of oxidation of CO even at very low overpotential is sufficiently high such that the steady-state coverage by CO of Pt sites is significantly less than the saturation coverage, creating a steady-state level of vacant Pt sites for the oxidation of H2 to take place at a high rate. A mathematical model is derived which produces simulated i-E curves that are in reasonable agreement with experiment.

INTRODUCTION

Recent work from our laboratory (1, 2) has demonstrated that Pt-rich Pt-Mo alloy surfaces have shown the highest steady-state currents for the oxidation of H2 in the presence of CO at the operating conditions of a polymer electrolyte fuel cell, i.e. so-called CO-tolerance of the anode electrocatalyst. In the present communication, we report further more detailed studies on the mechanism of action of Mo atoms in the alloy surface. We show that in the potential range of stability of Pt-Mo alloys, Mo surface atoms have multiple oxygenated ligands, the stoichiometry of which varies with potential. The oxidation states of Mo surface atoms as well as the nature of Mo surface oxides is proposed to be determining factor in the electrocatalysis of H2, CO and H2/CO mixture on these alloys. A mathematical model is derived based on the proposed surface chemistry. The mathematical correctly simulates the potential dependence of the rate of CO electrooxidation on the alloy surface, and provides a reasonable mechanistic explanation for the enhancement in the rate of hydrogen electrooxidation of H2 in the presence of CO.

EXPERIMENTAL

The electrooxidation kinetics of H2, CO and H2/CO mixtures were studied on UHV-prepared, well-characterized solid Pt-Mo alloy surfaces in 0.5 M H2SO4 at 60° C as described previously (1,2). Surface compositions were determined by low energy ion...
scattering spectroscopy (LEIS) and were varied systematically by a combination of ion bombardment, thermal annealing and plasma deposition in UHV; the surface compositions reported here were 15, 23 and 33 at. % Mo. The chemical state of Mo in the surface as a function of potential was determined by ex-situ x-ray photoelectron spectroscopy (XPS). Following preparation and characterization in UHV, the solid alloy samples were transferred into the disk position of an insertable rotating ring-disk electrode arbor (Pine Instruments) as described in detail previously (3).

RESULTS

Oxidation States of Mo in the Alloy Surface in Electrolyte

The composition dependence of the base cyclic voltammetry of the Pt-Mo surfaces is shown in Fig. 1 in comparison to that of a pure Mo surface prepared in UHV and treated in the same way. In what follows, we try to resolve the transitions of Mo valence states in PtMo surface by comparing the electrochemical behavior of Mo metal with that of PtMo electrode in 0.5 M H2SO4. We take advantage of the reasonably complete knowledge of the surface chemistry of the pure Mo surface in acid electrolyte, and make use of the additional in-parallel characterization of both pure Mo and PtMo alloy surfaces by ex-situ XPS. We do not claim to make a definitive determination of the surface chemistry of Mo in PtMo alloy surfaces, but rather a determination that provides a reasonable explanation for the role of Mo in enhancing the kinetics of CO electrooxidation in the low overpotential region of interest for PEM fuel cells. The voltammetry in Figure 2 revealed that at least three anodic peaks are observed in the cyclic voltammetry of the Mo metal in 0.5 M H2SO4, e.g. on the positive sweep direction at 0.1 V, 0.22 V and 0.4V. These voltammetric features serve as an evidence for multiple higher valence-states of Mo surface atoms. At more positive potentials, e.g. just before the onset of Mo dissolution at 0.4 V, it seems likely that the surface is predominantly in the +VI state, as the dissolved state of Mo is identified as H2MoO4 (4). The fact that the dissolution of Mo at 0.4 V is mirrored with the broad peak at 0.4 - 0.45 V in the voltammetry for 23 and 33 % Mo alloys suggests that at this potential Mo atoms in the surface are also predominantly in the +VI valence state. In contrast to the pure Mo electrode, in the alloy Mo atoms are stabilized on the surface by Pt-Mo intermetallic bonding, a result we had seen previously (and even more dramatically) with Pt-Sn alloys (5). By further analogy, if the anodic peak in the voltammetry of Mo metal electrode at ca. 0.25 V corresponds to the transition of Mo+III to Mo+IV valence state, than it is also reasonable to suggest that a peak observed at 0.25 V in the voltammetry of Pt-Mo alloys may also be assigned to the oxidation of Mo atoms from Mo+III to Mo+IV. These valence state assignments are consistent with the ex-situ XPS analyses of both pure Mo electrodes (6) and Pt-Mo alloy electrodes (2). 

Figure 2 shows that voltammetric peak(s) recorded on Mo electrode at potentials negative of ca. E < 0.2 V indicate an even more reduced state of Mo than + III may exist at these potentials. However, these peaks are not clearly resolved in the voltammetry of the alloys, due to the extensive hydrogen evolution reaction (HER) on Pt sites in the same potential...
range. As a consequence, a similar processes may also occur on Mo in the Pt-Mo surface, but these processes are masked by the HER which occur in the same potential range. Because of this uncertainty, we shall not use the +II state in our subsequent modeling.

The above analysis indicates that under our experimental conditions, Mo surface atoms in the PtMo alloy have multiple O and/or OH ligands on them at all potentials of interest, the stoichiometry of which varies with electrode potential. We will assume that at a constant pH of ≈ 1 that any change in the valence state is charge compensated by change in surface protonation that retain the net surface charge. The surface redox processes on the Mo sites are then postulated to be represented by the following reactions: the Mo(+III)/Mo(+IV) at the surface is represented as

$$\text{MoOOH} \rightarrow \text{MoO}_2 + H^+ + e^-$$  [1]

while the Mo(+IV)/Mo(+VI) equilibrium is represented as

$$\text{MoO}_2 + 2H_2O \rightarrow \text{MoO}_3(OH)_2 + 2H^+ + 2e^-$$  [2]

The $\Delta G$'s (and thus the $E_o$'s) for rxns. 1&2 on the alloy surfaces may not be the same as those for pure Mo, but for the present purposes we shall use the values given in Pourbaix (7) for bulk Mo. In the latter case, MoOOH does not actually exist as a bulk phase, and we assume this state exists as a surface (2D phase) having an $E_o$ approximately equal to that for the $\text{Mo}^{3+/2}/\text{MoO}_2$ equilibrium, 0.311 V. For simplicity, we neglect any non-ideality and use purely Nernstian relations for the surface activities of the various species,

$$n(E - E_o)F / RT = \ln \Gamma_o / \Gamma_R$$  [3]

where $\Gamma_o$ and $\Gamma_R$ are the surface concentrations of the oxidized and reduced forms, respectively. For kinetic analysis, it is convenient to use relative coverages of the total surface by a particular species, $\Theta_j$, which are obtained by the normalization

$$\Theta_j = \Gamma_j / \sum \Gamma_j$$  [4]

The resulting "isotherms" for the various oxy/hydroxide species are shown in Figure 2. The isotherms from eqns. 1-4 clearly show in a quantitative way what we had deduced from the voltammetry and XPS results described above: that a mixture of both different oxidation states and different oxide phases of Mo surface atoms coexist over the potential range of interest; a significant change in the state of oxidation of Mo and the surface concentration of OH species occurs in the 0.3 < E < 0.5 V potential region. As we discuss further below, the oxidation state of Mo surface atoms as well as the nature of Mo surface oxides with nominally the same valence state of Mo, are postulated to be the determining factors in the electrocatalysis of CO and H$_2$/CO mixture on PtMo alloys. More specifically, we postulate that only the OH species of the oxyhydroxide states (for example, MoO(OH)$_2$) are reactive with CO, but because of its size oxyhydroxide states...
may reduce the availability of adjacent Pt surface atoms for the dissociative adsorption of molecular hydrogen. De-protonated oxide states (for example, MoO$_3$) are proposed to have a lesser screening effect on the adjacent Pt surface atoms, but are inactive for reaction with CO$_{ads}$. Translated to the development of PtMo catalyst, the surface concentration of Mo atoms should be such as to be capable both to provide (continuously) reactive oxyhydroxide species, but not to screen adjacent Pt sites on which the HOR (when not covered by CO$_{ads}$) takes place.

The role of the surface concentration of Mo atoms on the availability of Pt surface sites can be assessed from its effects on the electrooxidation of pure H$_2$ (no CO) on Pt-Mo alloys, as shown in Figure 3. The alloy surfaces containing 15 and 23 at. % Mo have polarization curves indicative of pure diffusion control, i.e. equivalent to a pure Pt RDE. Increasing the Mo surface concentration from 23 up to 33 at. % produced a dramatic reduction in the activity of Pt-Mo alloy surfaces for the oxidation pure H$_2$, even exhibiting a reaction limiting current (no dependence on the rotation rate) below 0.4 V. Interestingly, above 0.4 V, the 33% Mo surface becomes re-activated for the oxidation pure H$_2$, apparently due to a change in the oxidation state of Mo atoms in the surface as we have discussed above. Note that the deactivating effect of too much Mo in the surface is not a simple blocking relation, i.e. the effect is much bigger than the change in 1 - x$_{Mo}$. For that reason, we will not attempt to model the blocking effect in this work, and only model the two surfaces where the blocking effect appears to be negligible, the 15 and 23 at. % Mo surfaces.

**The Electrooxidation of Adsorbed CO and Dissolved CO in Solution**

We had suggested in previous studies (1,2) of the oxidation of H$_2$ in the presence of CO that the superior kinetic properties of the Pt-Mo alloy surface relative to Pt or any other Pt alloy surface (such as Pt-Ru) was due to the oxidation of both adsorbed CO and CO dissolved in solution in the low overpotential region. We illustrate independent physical evidence for this process with kinetic studies on the 15 % Mo surface summarized in Figure 3. The quasi-steady-state electrooxidation (1 mV/s) polarization curves for CO in argon show a positive reaction order in CO partial pressure, and clearly indicates that a continuous oxidation of CO occurs at a finite rate even at potentials < 0.2 V. The anodic stripping of CO$_{ads}$ is also shown in this figure. There are three states of CO$_{ads}$ on the Pt-Mo surface, only two of which are observed in anodic stripping (at 0.2 - 0.5 V and 0.6 - 0.8 V), which we call the “strongly” adsorbed states (2), while the “weakly” adsorbed state is oxidized when CO is purged from solution. Below 0.2 V, oxidation of CO (gas) occurs via this weakly adsorbed state, which as we show below constitutes about 10 % of the saturation coverage of CO$_{ads}$. This weakly adsorbed state of CO is created by strong repulsive interaction between CO$_{ads}$ molecules on the Pt sites, which has been clearly demonstrated with Pt(hkl) low index single crystal surfaces (8), but in our kinetic modeling we find that it is characteristic of all Pt and most Pt alloy surfaces. What is unique about Pt-Mo is not the occurrence of the weakly adsorbed state, or the amount of it, but that it is oxidized at potentials < 0.2 V, and this appears to be due to unique reactivity of the OH$_{ads}$ on the Mo sites in this potential region.
We derive here a quantitative mathematical model for the CO electrooxidation process in terms of the concepts enunciated above. The elementary steps are assumed to be

\[
\text{CO} \leftrightarrow \text{CO}_{\text{ads}} \quad [5]
\]

\[
\text{CO}_{\text{ads}} + \text{Mo(OH)}_n \Rightarrow \text{CO}_2 + \text{Mo(OH)}_{n-1} + \text{H}^+ + 1 \text{e}^- \quad [6]
\]

\[
\text{Mo(OH)}_{n-1} + \text{H}_2\text{O} \leftrightarrow \text{Mo(OH)}_n + \text{H}^+ + 1 \text{e}^- \quad [7]
\]

where the second step is assumed to be rate determining. We are interested primarily in simulating the shape of the polarization curve, rather than the absolute value of the current, we will assume Tafel kinetics of the form

\[
i = nFk\Theta_{\text{ott}}\Theta_{\text{CO}} \exp\left(\frac{FE}{RT}\right) \quad [8]
\]

where \(\Theta_{\text{ott}}\) as a function of potential is given by eqns. 3&4. Following from the discussion above of the concepts of “weakly adsorbed” and “strongly adsorbed” states of CO, the chemical rate constant, \(k\), is a function of \(\Theta_{\text{CO}}\), and \(\Theta_{\text{CO}}\) is a function of potential. We will use semi-empirical relations for both \(k(\Theta_{\text{CO}})\) and \(\Theta_{\text{CO}}(E)\) that captures what we know (or have postulated) about the chemistry of adsorbed CO. It is known from careful studies in UHV (9) that the heat of adsorption of CO on Pt decreases linearly with coverage as the coverage approaches saturation. This decrease in the heat of adsorption is caused by strong repulsive interaction between adsorbed CO molecules and in effect creates the “weakly bonded” state. We will assume that a similar repulsive interaction exists near saturation coverage for CO on Pt in solution. This linear decrease in the heat of adsorption can then be related to a linear decrease in the activation energy for CO electrooxidation through the Bronsted relation,

\[
\Delta G^0 = \beta\Delta H_{\text{ads}}
\]

where \(\beta\) is the symmetry factor. The higher reactivity of the weakly adsorbed state is then clearly seen as a consequence of a lowered free-energy of activation for its oxidation, \(\Delta G^0\), which will then be represented mathematically by a Temkin-type relation

\[
\Delta G^0 = \Delta G^0_{\text{w}} - r\Theta_{\text{CO}} \quad [9]
\]

where \(r\) is the interaction parameter (\(r>0\) is repulsive). For the purposes of obtaining an expression for free-energy of activation as a function of potential, we shall assume that \(\Theta_{\text{CO}}\) varies linearly with potential in the region of interest, e.g. 0 - 0.4 V, and we will neglect the contribution of this potential-dependence of \(\Theta_{\text{CO}}\) in the pre-exponential term, but we will include a \(P_{\text{CO}}\) dependence as indicated by the experimental data. After rearranging, the final form for simulation of the i-E curve is
where $\Delta G^\circ_0$ and $\gamma$ are semi-empirical parameters, the reaction order ($m$) in CO is experimentally approximately 0.5 and $k_o$ is essentially a scale factor. $\Delta G^\circ_0$ can be obtained independently from the experimental temperature dependence of the current, $(\partial \log i / \partial T)_E$, while $\gamma$ is best obtained by fitting the simulated i-E curve to experiment. The simulated i-E curve for CO electrooxidation on PtMo alloy for $\Delta G^\circ_0 = 80$ kJmol$^{-1}$ and $\gamma = 34$ kJmol$^{-1}$V$^{-1}$ is shown in Figure 5, along with the observed i-E curve on the 23 at. % Mo alloy surface. The simulated curve reproduces both the shape of the observed curve, and captures the physical concepts described, i.e. it is not just “curve-fitting”. In the low overpotential region, $< 0.2$ V, the oxidation proceeds through the “weakly adsorbed” state of CO, which produces the lowest activation energy; OH groups are provided exclusively by the MoOOH state on the Mo surface atoms. With increasing potential, the weakly adsorbed state is depleted, increasing the activation energy, and causing the current to increase much less than the Tafel factor, $(F/RT)$. Above about 0.3 V, there is a significant change in the OH population on the surface, as seen in Figure 2, where the decrease in OH from the deprotonation of the MoOOH state is more than compensated for by the production of OH from the MoO$_2$(OH)$_2$ state. Again, the slope of the i-E curve in this region matches the experimental slope extremely well, but the potential where the transition occurs is not well represented by the $E_o$'s used in eqn. 3, i.e. the values for pure Mo. It is not unreasonable to use adjusted values for the effect of Pt-Mo intermetallic bonding on the O and OH formation chemistry. Note that such adjustments would be physically in the right direction, i.e. increasing the values of $E_o$ corresponds to bonding with Pt stabilizing the more reduced states of Mo. If we make the $E_o$'s about 0.1 V more positive, the agreement with experiment is essentially perfect (!).

Oxidation of Hydrogen in the Presence of CO

A basic hypothesis of this work is that the model for the electrooxidation of CO contains all the ingredients necessary to understand the oxidation of H$_2$ in the presence of CO. The physical concept is that the electrooxidation of CO creates vacancies on Pt surface atoms on which H$_2$ oxidation occurs. We assume that for very high coverages of CO, where we are concerned with only the weakly adsorbed state of CO, the oxidation takes place via the Heyrovski-Volmer single-site mechanism (9). This is a different mechanism than we found in our previous study of H$_2$ oxidation on pure Pt covered only by the irreversibly or strongly adsorbed state of CO (2), which was the Tafel-Volmer dual-site mechanism. Mathematically, we represent the single-site mechanism by the simple site-blocking model,

$$i = i_{H_2} (1 - \Theta_{CO})$$

where $i_{H_2}$ is the current in the absence of CO, and for our purposes here we will treat it as a scale factor for the current, i.e. the potential dependence of $i_{H_2}$ is neglected since it
reaches the diffusion limiting current above ca. 0.02 V. Thus, the i-E curve is given entirely by the potential dependence of the steady-state coverage by adsorbed CO. Thus, the more accurately this potential dependence is represented, the closer the simulation will be to experiment. To derive the most accurate representation of the steady-state coverage of CO, we return to the elementary steps represented by eqns. 5 & 6, and note that these are steps in series, and that a more accurate analysis would not assume the second is rate determining but that at steady-state the two steps proceed at equal rates, i.e. the rate of adsorption = rate of oxidation. Using \((i/nF)\) from eqn. 10 for the rate of oxidation, and using a simple form for the rate of adsorption of CO we have,

\[
k_{ad}P_{CO}(1 - \Theta_{CO}) = k_0P_{CO}^{0.5}\Theta_{OH} \exp[(\Delta G^0_{eq} - \gamma E) / RT]\exp(FE / RT)
\]

where \(k_{ad}\) is the rate constant for CO adsorption, and \(P_{CO}\) is the CO partial pressure. Then rearranging,

\[
(1 - \Theta_{CO}) = KP_{CO}^{-0.5}\Theta_{OH} \exp[(\Delta G^0_{eq} - \gamma E) / RT]\exp(FE / RT) \quad [12]
\]

Multiplying eqn 12 by the scale factor \(l_{H_2}\) is then the simulated i-E curve, which is shown in Figure 6 together with the observed curve on the 23 % Mo alloy surface with 0.1 % CO in \(H_2\). The potential dependence is extremely well represented by the simulated curve in the potential region 0.05 - 0.3 V, but the model overestimates the kinetic effect of oxidation of oxidizing the "strongly bonded" CO from the surface at \(E > 0.3\) V. There are two other pieces of experimental data, presented in our previous paper (2), that are also well represented by the model: the reaction order in CO, which is ca. - 0.5 both experimentally and in the model as well \((m \approx 0.5)\); and an apparent activation energy that increases linearly with potential in the region \(0.05 < E < 0.4\) by a nearly identical amount as in our simulation, 25 kJ/mol.

**SUMMARY**

A mechanism of action of Mo atoms in the Pt-Mo alloy surface for the electrooxidation of CO and \(H_2/CO\) mixtures is proposed. The Mo atoms nucleate reactive OH groups which oxidize CO adsorbed at neighboring Pt sites at much lower overpotentials than on the pure Pt surface. In the case of \(H_2/CO\) mixtures, the rate of oxidation of CO even at very low overpotential is sufficiently high such that the steady-state coverage by a specific state of adsorbed CO on the Pt sites, a state we term "weakly adsorbed, is significantly reduced, creating a steady-state level of vacant Pt sites for the oxidation of \(H_2\) to take place at a reasonably high rate. A mathematical model is derived which captures the proposed surface chemistry of both the OH groups on the Mo sites and the weakly adsorbed state of CO on the Pt sites. The mathematical model produces simulated i-E curves that are in reasonable agreement with experiment.
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Figure 1. Cyclic voltammetry of Pt-Mo alloy surfaces having surface concentrations of 15, 23 and 33 at. % Mo compared to that of a pure Mo surface pre-treated in an identical fashion (see text). 20 mV/s⁻¹, 0.05 M H₂SO₄, 333°K.

Figure 2. Plots of relative surface concentrations of various Mo oxide species as a function of potential according to eqns. 3 & 4.
Figure 3. Cyclic voltammetry of the three Pt-Mo alloy surfaces of Fig. 1 as RDE electrodes in H₂-saturated. Base voltammetry in Ar-purged solution shown for comparison. 20 mVs⁻¹, 0.05 M H₂SO₄, 333°K.

Figure 4. Quasi-steady-state i-E curves for CO oxidation on the 15 at. % Mo alloy electrode at different CO partial pressures. 2500 rpm, 1 mVs⁻¹; CO stripping voltammetry for CO adsorbed at 0.1 V, following Ar-purging. 20 mVs⁻¹, 0.05 M H₂SO₄, 333°K.
Figure 5. Simulated i-E curve for CO oxidation on a Pt-Mo alloy surface according to eqns. 3, 4 & 10. Open symbols denote contribution of OH in the +III and +VI oxide states, respectively. (insert) Experimental curve for 23 at. % Mo alloy electrode shown for comparison.

Figure 6. (solid) Simulated i-E curve for the oxidation of H₂ containing 0.1 % CO according to eqns. 3, 4 &12. (dashed) Experimental curve for the 23 at. % Mo alloy electrode shown for comparison.