

Investigation of Enhanced CO Tolerance in Proton Exchange Membrane Fuel Cells by Carbon Supported PtMo Alloy Catalyst

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We report a two- to threefold enhancement of CO tolerance in a proton exchange membrane (PEM) fuel cell, exhibited by carbon supported nanocrystalline PtMo/C as compared to the current state of the art PtRu/C electrocatalysts. The bulk of these nanocrystals were comprised of Pt alloyed with Mo in the ratio 8.7:1.3 as shown by both X-ray diffraction and in situ extended X-ray absorption fine structure measurements. Rotating disk electrode measurements and cyclic voltammetry in a PEM fuel cell indicate the onset of CO oxidation at potentials as low as 0.1 V. Further, the oxidation of CO exhibits two distinct peaks, indicating redox behavior involving oxyhydroxides of Mo. This is supported by in situ X-ray absorption near edge structure measurements at the Mo K edge.

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CO tolerance in reformer-based low and medium temperature H₂/O₂ proton exchange membrane fuel cells (PEMFC) is crucial for the viability of this technology for applications in transportation and portable power generation applications. The choice of an appropriate anode electrocatalyst with low susceptibility to CO poisoning and a high kinetic rate for hydrogen oxidation is therefore paramount. The most commonly used anode electrocatalyst, Pt/C, is susceptible to poisoning by CO, leading to high overpotentials. Alternate binary electrocatalysts containing a more oxidizable element with ability to activate oxygenated species at lower potentials and hence initiate CO oxidation on the surface with lower overpotentials have been the focus of several decades of research. Prior literature is replete with investigations on alloys such as PtSn,¹⁻² PtRh,³ PtRu,⁴⁻⁶ and Pt with oxygen adsorbing adatoms such as Ge, Sb, and Sn⁷⁻⁸ etc. In recent years PtRu alloys have received renewed attention as promising candidates for CO oxidation in PEM fuel cells.⁹⁻¹¹ A recent report by Oetjen et al.¹² indicates a fourfold performance enhancement with highly dispersed PtRu as compared to Pt at 80°C with CO concentrations up to 250 ppm. Despite these improvements the overpotential with CO concentrations of 100 ppm at moderate temperatures such as 85°C is substantial, resulting in a loss of 270 mV at 1 A/cm².¹²

Recently, the electro-oxidation kinetics of H₂, CO, and an H₂/CO mixture were studied on smooth and well-characterized PtMo surfaces in 0.5 M H₂SO₄ at 60°C.^{13,14} Grgur et al. proposed that the oxidation states of Mo surface atoms as well as the nature of Mo surface oxides are determining factors in the electrocatalysis of H₂, CO, and H₂/CO mixtures on these alloys. It was suggested that the oxyhydroxide state of Mo [predominantly as MoO(OH)₂] is reactive for oxidative removal of CO, but this state can also reduce the availability of adjacent Pt surface atoms for the dissociative adsorption of molecular hydrogen.^{15,16} This work also indicated that a surface composition of 20-25 atom % Mo was optimum for the rate of oxidative removal of CO and the rate of H₂ adsorption.¹³⁻¹⁶ It was assumed that, unlike bulk alloys, there is no surface segregation of Pt on the small PtMo/C particles. Accordingly, a 4:1 (Pt:Mo) PtMo/C catalyst was selected.

In this paper, we present measurements for electro-oxidation of H₂, CO, and H₂/CO mixtures on bimetallic PtMo-4:1 catalyst supported on Vulcan carbon black (PtMo/C). First, we present kinetic measurements using a thin catalyst layer in the rotating disk configuration (RDE) and, then, the cyclic voltammetry and the polarization data for an anode in a proton exchange membrane fuel cell. In addition,

preliminary efforts to understand the role of Mo in these alloys using in situ X-ray absorption spectroscopy (XAS) are included.

Experimental

PtMo/C supported catalyst in the RDE configuration.—The PtMo/C bimetallic catalysts with a 30% loading, prepared by using a proprietary method, were obtained from E-TEK, Inc. (Natick, MA). The carbon black support was Vulcan XC-72. For comparison, high surface area supported (Vulcan XC 72) Pt/C and PtRu/C (50 atom % Ru) catalysts, each with a 20% loading, were also obtained from E-TEK. The preparation of PtMo/C supported catalyst into the RDE closely followed the method recently described by Schmidt et al.¹⁷ A suspension of 2 mg of the PtMo/C in 1 mL of C₂H₅OH was redispersed ultrasonically for 15 min, and then 10 μL (6 μg/PtMo) was pipetted onto the polished surface of glassy carbon disk electrode (0.283 cm²) imbedded into a Pine Instruments interchangeable arbor. After evaporation of alcohol at 354 K in a furnace under an argon atmosphere (ca. 5 min), the electrode surface was covered with 10 μL of Nafion (5% solution CH₃OH/H₂O) and returned to the furnace where the electrode was heated in an argon atmosphere at 374 K for ca. 10 min. The prepared electrode had a catalyst loading of ca. 6 μg of PtMo alloy/cm², corresponding to a catalyst layer thickness close to 1 μm.¹⁵ The RDE was immersed in the solution under potential control at ca. 0.05 V. All potentials in this paper are referred to the reversible hydrogen electrode (RHE) at the same temperature.

The PtMo/C catalyst was characterized by X-ray diffraction (XRD) analysis by methods described elsewhere.^{13,14} The results indicated a single metallic face-centered cubic (fcc) phase for PtMo/C with a lattice constant of 0.391 ± 0.005 nm. The surface area, as determined from line broadening, was close to 68 m²/g.

The electrolyte (0.5 M H₂SO₄, Baker Ultrex), prepared with triply pyrodistilled water was thermostated at 333 K, in a standard three-compartment electrochemical cell. The reference electrode was a standard calomel electrode (SCE) separated by a bridge from the reference compartment. The CO/H₂ mixtures as well as pure H₂ and CO (6 N H₂, 4 N CO) were purchased from Matheson; the purity of the argon was 5N8 (Air Products). Data from the rotating disk electrode setup was acquired using a Pine Instruments bipotentiostat interfaced with an IBM PC using Lab View for Windows.

X-ray absorption spectroscopy.—XAS measurements were conducted at beam line X11A at the National Synchrotron Light Source (NSLS), both at the Pt L (L₃ and L₂) and Mo K edges. Details of the beam line optics, monochromator and detuning, etc. are given elsewhere.¹⁸ Electrodes for XAS measurements were prepared according to the methodology described elsewhere,¹⁸ the catalyst loading on the electrode was ~10 mg of PtMo alloy/cm². All electrodes were

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soaked in 1 M HClO₄ for 48 h and wetted by a vacuum procedure prior to XAS experiments. Details of the spectroelectrochemical cells, data acquisition, and X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analysis are given elsewhere.¹⁸⁻²⁰

PEM fuel cell measurements.—Anode electrodes were prepared by a brushing/rolling technique developed in-house. They were comprised of a carbon cloth substrate (E-TEK, Carbon Cloth), with a diffusion layer of Teflonized carbon [35 wt % polytetrafluoroethylene (PTFE)] with average thickness of 35 μm, which was presintered at 320°C under Ar. The reaction layer was comprised of the catalyst (0.4 mg/cm² of Pt or Pt alloy loading) + Nafion. The gas diffusion side of the electrode had a thinner diffusion layer of C/PTFE (30 wt %) of ~15 μm thickness. Membrane electrode assemblies were made for anodes Pt/C, PtRu/C, and PtMo/C while keeping the cathode electrode the same (Pt/C, E-TEK electrode, 0.4 mg/cm² Pt loading). The Nafion loading [solubilized Nafion (Aldrich Chemicals)] in the reaction layer of the electrodes was ~1.9 mg/cm² and the assembly was made by hot pressing at 1000 kg_f/cm², 140°C for 3 min. The membrane was Nafion 115 which was cleaned by a procedure described in detail elsewhere.²¹

Steady-state polarization measurements on CO tolerance were carried out in a fuel cell test station using a cell fixture for a 5 cm² membrane-electrode assembly which allowed for both single and half-cell polarization measurements. The test station was built in-house and had provisions for controlling temperature, pressure, humidification, and flow (mass flow) of reactant gases. The bipolar plates made of carbon with resin impregnation (Poco graphite) had conventional ribbed flow channels and the anode chamber had a built-in hydrogen reference electrode with separate flow channels allowing for simultaneous half-cell measurements. Details of the fuel cell test station and the single-cell test fixture are given elsewhere.²¹ Simultaneous measurements of single- and half-cell performance were made at 85°C, with respective anode/cathode pressures and humidification temperatures of 16/11 psig and 100/90°C. For H₂/CO mixtures, premixed gas cylinders were used (Matheson, NJ).

Cyclic voltammetry was carried out using the same single-cell setup at 55°C. To investigate catalyst behavior with respect to the CO oxidation process, H₂ containing 100 ppm of CO was passed through the electrode for at least 1 h while maintaining a constant potential (0.05 V vs. RHE). At the same time pure hydrogen was passed through the counter electrode which also served as a RHE reference electrode. After passing the CO mixed gas, the anode compartment were purged with N₂ for about 30 min to remove residual H₂ gas and nonadsorbed CO.

Results and Discussion

H₂, CO, and H₂/CO electrocatalysis on PtMo/C supported catalyst.—Voltammetric profiles of 4:1 PtMo/C thin catalyst layer electrode in 0.5 M H₂SO₄ along with the polarization curves of both oxidation of pure H₂ and 0.1% CO/H₂ mixture are shown in Fig. 1. A distinguishing characteristic in the voltammetry of 4:1 PtMo/C high surface area catalyst was a H_{upd} region that is not well defined and which overlaps with the pseudocapacitive feature associated with the oxidation/reduction of Mo atoms on the surface.¹³⁻¹⁶ As in the case for Pt₇₇Mo₂₃ surface in the bulk alloy catalyst,^{13,14} the polarization curve for the oxidation of pure H₂ on 4:1 PtMo/C high surface area catalyst is identical with that for pure Pt/C^{15,16} (Fig. 1). Figure 1 also shows that the electro-oxidation reaction of H₂ on 4:1 PtMo/C catalyst is somewhat poisoned if solution contains 0.1% CO/H₂ mixture. Inset (a) of Fig. 1 shows representative results for the oxidation of pure CO on the 4:1 PtMo/C catalyst. The polarization curve for the continuous oxidation of CO dissolved in solution revealed an initially slow oxidation rate, which begins as low as 0.1 V, followed by relatively fast kinetics at potentials positive to ≈0.25 V. It is important to note that the enhanced activity of the PtMo surface toward the electro-oxidation of CO is observed at a potential where a Mo(IV) oxyhydroxide state is probably created on the surface.^{13,14}

On solid bulk electrodes, the steady-state measurements for the electro-oxidation of CO/H₂ mixtures can be obtained potentiody-

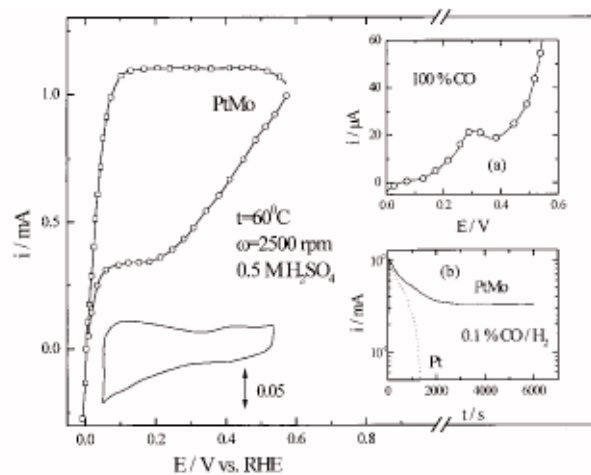


Figure 1. (Bottom) Cyclic voltammetry (1 mV/s) of the 4:1 PtMo/C high surface area catalyst in the RDE configuration. (Top) Polarization curves of the HOR on the 4:1 PtMo/C catalyst; in solution containing pure hydrogen (—□—); in solution containing a mixture of 0.1% CO/H₂ (—○—). (Top inset) Quasi-steady-state *i*-*E* curve for CO oxidation on the 4:1 PtMo/C catalyst. (Bottom inset) Potentiostatic transient (*E* = 0.05 V vs. RHE) on the Pt and 4:1 PtMo/C high surface area catalyst for oxidation of H₂/CO mixture.

namically by using a relatively slow sweep rate, e.g., 1 mV/s.^{1,6,9} In the case of high surface area catalysts, however, the sweep rate of 1 mV/s is not slow enough to bring the system to the steady-state condition. Therefore, to measure true activities of supported catalysts for electro-oxidation of H₂/CO mixtures (especially for partial pressure of CO less than 0.1 %), the kinetics were monitored under potentiostatic conditions. Inset (b) in Fig. 1 shows a set of potentiostatic data (*E* = 0.05 V) for the electro-oxidation of 0.1% CO/H₂ mixture on pure Pt/C and PtMo/C high surface area catalysts under otherwise identical conditions. The pure Pt/C shows a relatively fast rate of poisoning, e.g., within 1200 s the hydrogen-oxygen reaction (HOR) is completely inhibited due to poisoning of active platinum sites with CO_{ad}. A much slower rate of poisoning is observed on the PtMo/C alloy, i.e., initially the rate of the reaction decreases sharply, but after ca. 3000 s a steady-state current for the HOR is observed. The approach to steady state requires that the rate of CO adsorption (*v*_{ad}) and continuous CO oxidation (*v*_{ox}) be in equilibrium, i.e., *v*_{ad} = *v*_{ox}. Therefore, it is reasonable to suggest that at this electrode potential the high activity of 4:1 PtMo/C alloy for the oxidation of H₂/CO mixtures arise due to the continuous oxidation of CO and subsequent formation of bare platinum sites which are required for the dissociative adsorption of molecular H₂.

Figure 2 shows the cyclic voltammograms for dispersed PtMo/C and Pt/C in the PEM fuel cell at 55°C in absence and presence of CO. Results for PtMo/C in absence of CO show evidence for both Pt and Mo features, although the Pt-H_{upd} region is not as well defined as on the Pt/C or PtRu/C electrodes.²² However, the Pt features are evident from the peaks for hydrogen desorption for an electrode polarized at 0.0 V (N₂ purge) for 1 h (not shown). In addition to this, the voltammograms of PtMo/C show a redox behavior at potentials of 0.4 V vs. RHE involving Mo in agreement with the cyclic voltammogram from RDE (Fig. 1). Comparison with the Pourbaix diagram²³ for Mo indicates that this redox behavior is most likely due to Mo⁴⁺ ↔ Mo⁶⁺ oxidation states. Repeated cycling between 0.05 and 1.2 V for 50 cycles showed no changes indicating minimal dissolution of Mo from these electrocatalysts.

Figure 2 shows a cyclic voltammogram that was taken on a PtMo/C electrode in a PEM fuel cell, at 55°C, after the electrode was previously subjected to a purge with H₂/CO [100 ppm] for 1 h (electrode polarized at 0.05 V), followed by a N₂ purge for 30 min to remove residual H₂/CO. The voltammogram shows two CO stripping peaks, one at 0.45 V and the other at 0.65 V. In accordance with

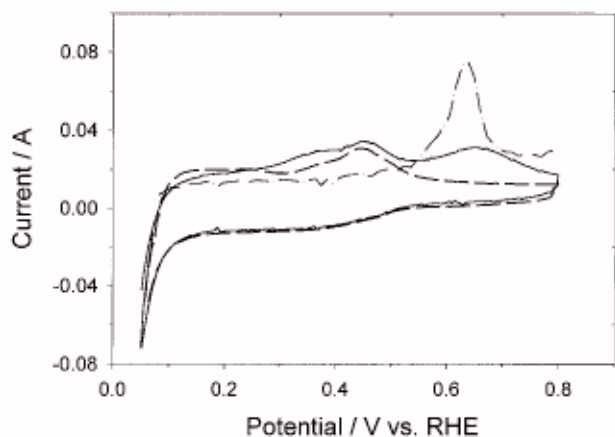


Figure 2. Cyclic voltammograms at 20 mV/s on PEM fuel cell anodes at 55°C (humidification temperatures 65/60°C for working/counter) in a PEM fuel cell (5 cm² membrane electrode assembly); PtMo/C with N₂ purge (---) and no contact with CO. Pt/C (- · - ·) and PtMo/C (—) with a N₂ purge, after the anode was contacted with CO (100 ppm)/H₂ for ca. 1 h at 0.05 V.

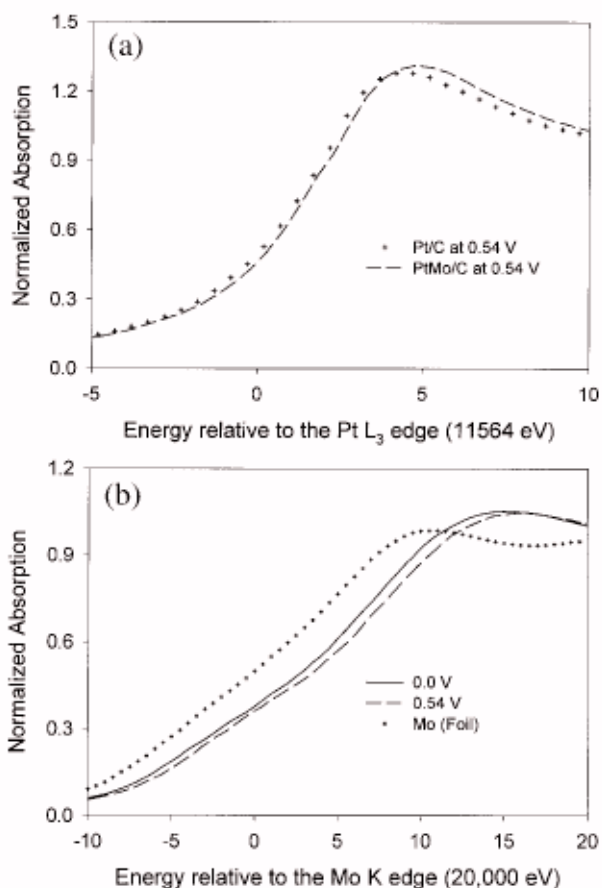


Figure 3. XAS in 1 M HClO₄ showing (a) XANES spectra at the Pt L₃ edge for PtMo/C (---) and Pt/C (+) at 0.54 V and (b) XANES at the Mo K edge for PtMo/C at 0.0 (—) and 0.54 (---) V, data for a Mo foil reference standard shown for comparison (+).

the previous interpretation of the reaction mechanism for the electro-oxidation of CO on PtMo bulk alloy,¹⁶ it is proposed that at low overpotentials, $E < 0.2$ V, the electro-oxidation of CO is consistent with a Langmuir-Hinshelwood mechanism. Here the CO adsorbed on Pt sites is oxidized by oxygenated species, which are activated at the neighboring Mo atoms. In this potential region preadsorbed CO

cannot be completely removed and the surface remains blocked to a large extent by adsorbed CO. Complete stripping can only be achieved at a significantly higher overpotential, $E > 0.55$ V and this reaction takes place on Pt sites between the CO and Pt-OH. The latter is apparent since the CO stripping peak for the PtMo/C alloy is similar to that observed on Pt/C (Fig. 2). A more remote possibility is that the presence of two distinct CO oxidation peaks is due to the CO adsorption on both Pt and Mo atoms, probably indicating the presence of some phase segregation. Detailed in situ XAS investigation of these electrocatalysts at Pt L and Mo K edges with and without CO may provide further insights into this issue.

In situ XAS results at Pt L and Mo K edge.—The ratio of Pt to Mo atoms in the dispersed electrocatalyst was determined from the edge jumps at the Pt L₃ (1.005) and Mo K (0.0972) edges using the methodology described elsewhere¹⁸ and indicated 87 atom % Pt. Examination of the Pt-Pt phase corrected Fourier transforms at the Pt L₃ edge EXAFS indicated alloy formation in PtMo/C (not shown). The Pt L₃ edge XANES at 0.54 V (Fig. 3a) comparing Pt/C with PtMo/C at 0.54 V, in 1 M HClO₄ shows an increased white line intensity for PtMo/C relative to Pt/C. This indicates an increase in the Pt 5 d-band vacancies in PtMo/C due to alloying. A significant change in the Pt d-band vacancies is normally expected in the case of formation of an alloy as shown previously.¹⁸⁻²⁰ Detailed analysis of changes in the short-range atomic order and electronic structure around Pt and Mo (in situ XAS analysis) as a function of potential and CO adsorption will be described in detail in the full version of this paper.

The Mo K edge XANES spectra for PtMo/C in 1 M HClO₄ at 0.0 and 0.54 V show that some of the Mo is oxidized with the edge positions shifted positive to the Mo reference foil. Preliminary analysis of the spectrum with known standards have shown the spectra to be close to an oxidation state of (+IV) at potentials as low as 0.0 V (not shown) which is in agreement with XPS data reported previously.^{13,14} This suggests the presence on the electrocatalyst surface of some sort of a hydrated oxide close to Mo(OH)₂²⁺. Comparison of the spectra at 0.0 and 0.54 V shows a change in oxidation state (Fig. 3b), which corresponds to the cyclic voltammograms (Fig. 2). These changes in the oxidation state were reversible. Further experiments are in progress to determine the nature of these oxidation states at these potentials by comparison with known standards.

The CO tolerance and activity in PEM fuel cells.—Figure 4 compares the single-cell performance of Pt/C, PtRu/C, and PtMo/C (0.4 mg/cm²) as anode electrodes (cathode: Pt/C, 0.4 mg/cm²) in H₂/CO [100 ppm]/O₂ at 85°C with the respective anode/cathode pressures of 16/11 psig and humidification temperatures of 100/90°C. As evident from the polarization behavior relative to the data for Pt/C anode without CO, PtMo/C exhibits significantly higher CO tolerance than PtRu/C. Comparison of half-cell polarization (and the overall single-cell performance) behavior of these electrocatalysts in H₂/O₂ (without CO) shows negligible differences (not shown), indicating that, as in the RDE experiments, the hydrogen polarization characteristics without CO are unchanged. However, the polarization characteristics of the anodes in the presence of CO in H₂ (Fig. 4 inset) exhibits marked differences. Comparison of current densities at 50 and 100 mV using the polarization plot for hydrogen oxidation in the presence of 100 ppm CO indicates two- to threefold enhancement of anode electrode performance in going from PtRu/C (current state of the art) to PtMo/C.

The polarization data from the PEM fuel cell was compared with the RDE data extrapolated from 0.1% CO/H₂ mixture at 60°C (Fig. 1). The $(P_{CO})^{-1/2}$ data was used together with the potential dependent apparent activation energies previously observed on the solid bulk alloy RDE assuming pure kinetic control for the HOR¹⁴ and extrapolation of current in direct proportion to the mass of catalyst.¹⁵ Figure 4 (inset) shows that the projected polarization curve in the RDE configuration is in reasonable agreement with 4:1 PtMo/C alloy catalyst in the PEM single cell. Detailed assessment of these data as a function of catalyst composition, operating temperature, and pressure will be presented in the full version of this paper.

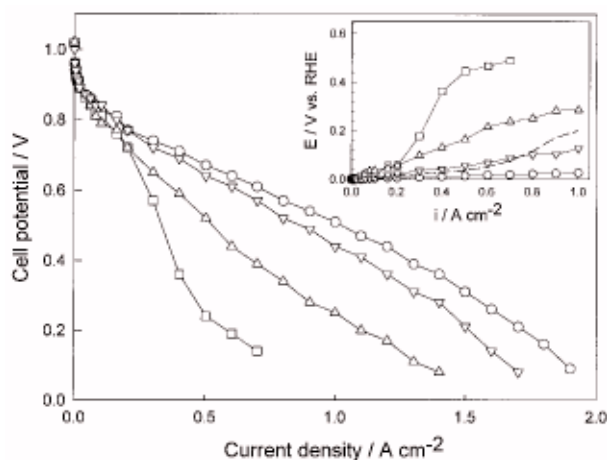


Figure 4. Performance of a 5 cm² cell with H₂/CO [100 ppm]/O₂ at 85°C, Nafion 115 membrane, respective anode/cathode pressures of 16/11 psig, and humidification temperature of 100/90°C. Cathode electrode: Pt/C (0.4 mg/cm²). Anodes were Pt/C {□}, PtRu/C {△}, 4:1 PtMo/C {▽}; data for Pt/C (H₂/O₂) {○} are shown for comparison. Inset: Corresponding linear polarization characteristics for the anodes showing the 4:1 PtMo/C polarization curve (---) projected from the RDE experiments. Polarization measurements were done galvanostatically. The current was varied manually, with 30 s or more stabilization time for each point.

Conclusions

Results of this investigation point to enhancements in CO tolerance in PEM fuel cells with 4:1 PtMo/C which show a two- to three-fold enhancement of activity at low overpotentials, compared to the current state of the art PtRu/C at 85°C with 100 ppm CO in H₂. Cyclic voltammograms show evidence of a redox couple involving Mo located around 0.4 V. Voltammograms for CO stripping on PtMo/C show two distinct peaks indicating that both Pt and Mo are active in the oxidative removal of CO. The onset of the CO oxidation occurs at very low potentials (~100 mV) and corresponds to the oxidation of CO adsorbed on Pt sites by oxygenated species which are activated at the neighboring Mo atoms. It is proposed that the high activity of the 4:1 PtMo/C alloy for the oxidation of H₂/CO mixtures is due to the continuous oxidation of CO and the subsequent formation of bare platinum sites which are required for the dissociative adsorption of molecular H₂.

The edge jumps at Pt L₃ and L₂ edges and Mo K edge show that the atomic ratio of Pt to Mo in these electrocatalysts is ~8.7:1.3. The short-range atomic order and d-band vacancies around Pt atoms in PtMo/C clearly show alloy formation as evidenced from XAS at the Pt L₃ edge. The Mo K edge XANES spectra at 0.0 V show that Mo is present as a hydrated oxide species with an approximate oxidation state of (+IV). The Mo K edge XANES spectra provide direct spectroscopic evidence of change in the oxidation state of Mo between 0.0 and 0.54 V confirming the results from the voltammograms.

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References

- H. A. Gasteiger, N. M. Markovic, and P. N. Ross, Jr., *J. Phys. Chem.*, **99**, 8945 (1995).
- M. R. Andrew, B. D. McNicol, R. T. Short, and J. S. Drury, *J. Appl. Electrochem.*, **7**, 153 (1977).
- P. N. Ross, Jr., K. Kinoshita, A. J. Scarpellino, and P. Stonehart, *J. Electroanal. Chem.*, **59**, 177 (1975).
- L. W. Niedrach, D. W. McKee, J. Paynter, and I. F. Danzig, *Electrochem. Technol.*, **4**, 318 (1967).
- P. N. Ross, Jr., K. Kinoshita, A. J. Scarpellino, and P. Stonehart, *J. Electroanal. Chem.*, **63**, 97 (1975).
- H. A. Gasteiger, N. M. Markovic, and P. N. Ross, Jr., *J. Phys. Chem.*, **99**, 16757 (1995).
- M. Watanabe, M. Shibata, and S. Motoo, *J. Electroanal. Chem.*, **187**, 161 (1985).
- M. Shibata and N. Furuya, *J. Electroanal. Chem.*, **269**, 217 (1989).
- H. A. Gasteiger, N. M. Markovic, P. N. Ross, Jr., and E. J. Cairns, *J. Phys. Chem.*, **98**, 617 (1994).
- R. Ianiello, V. M. Schmidt, U. Stimming, J. Stumper, and A. Wallau, *Electrochim. Acta*, **39**, 1863 (1994).
- T. Iwasita, R. Dalbeck, E. Pastor, and X. Xia, *Electrochim. Acta*, **39**, 1817 (1994).
- H.-F. Oetjen, V. M. Schmidt, U. Stimming, and F. Trila, *J. Electrochem. Soc.*, **143**, 3838 (1996).
- B. N. Grgur, G. Zhuang, N. M. Markovic, and P. N. Ross, Jr., *J. Phys. Chem.*, **101**, 3910 (1997).
- B. N. Grgur, G. Zhuang, N. M. Markovic, and P. N. Ross, Jr., *J. Phys. Chem.*, **102**, 2494 (1998).
- B. N. Grgur, G. Zhuang, N. M. Markovic, and P. N. Ross, Jr., *J. Electrochem. Soc.*, Submitted.
- B. N. Grgur, G. Zhuang, N. M. Markovic, and P. N. Ross, Jr., Abstract 1097, The Electrochemical Society Meeting Abstracts, VOL. 98-2, Boston, MA, Nov 1-6, 1998.
- T. J. Schmidt, H. A. Gasteiger, G. D. Stab, P. M. Urban, D. M. Kolb, and R. J. Behm, *J. Electrochem. Soc.*, **145**, 2354 (1998).
- J. McBreen and S. Mukerjee, *J. Electrochem. Soc.*, **142**, 3399 (1995).
- S. Mukerjee, S. Srinivasan, M. P. Soriaga, and J. McBreen, *J. Electrochem. Soc.*, **142**, 1409 (1995).
- J. McBreen, *J. Electroanal. Chem.*, **357**, 373 (1993).
- S. J. Lee, S. Mukerjee, J. McBreen, Y. W. Rho, and T. H. Lee, *Electrochim. Acta.*, **43**, 3693 (1998).
- C. He, H. R. Kunz, and J. M. Fenton, in *Electrode Materials and Processes for Energy Conversion and Storage IV*, J. McBreen, S. Mukerjee, and S. Srinivasan, Editors, PV 97-13, p. 52, The Electrochemical Society Proceedings Series, Pennington, NJ (1997).
- M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, p. 272, National Association of Corrosion Engineers, Houston, TX (1994).