

Pd–Co–Mo Electrocatalyst for the Oxygen Reduction Reaction in Proton Exchange Membrane Fuel Cells

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The catalytic activity of carbon supported Pd–Co–Mo for the oxygen reduction reaction (ORR) in a single cell proton exchange membrane fuel cell (PEMFC) has been investigated at 60 °C and compared with data from commercial Pt catalyst and our previously reported Pd–Co–Au and Pd–Ti catalysts. The Pd–Co–Mo catalyst with a Pd:Co:Mo atomic ratio of 70:20:10 exhibits slightly higher catalytic activity like the Pd–Co–Au catalyst than the commercial Pt catalyst, but with excellent chemical stability unlike the Pd–Co–Au catalyst. The Pd–Co–Mo catalyst also exhibits better tolerance to methanol poisoning than Pt. Investigation of the catalytic activity of the Pd–Co–Mo system with varying composition and heat treatment temperature reveals that a Pd:Co:Mo atomic ratio of 70:20:10 with a heat treatment temperature of 500 °C exhibits the highest catalytic activity. Although the degree of alloying increases with increasing temperature from 500 to 900 °C as indicated by the X-ray diffraction data, the catalytic activity decreases due to an increase in particle size and a decrease in surface area.

Platinum supported on carbon black is widely used as the electrocatalyst for the oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFC) due to its high catalytic activity and excellent chemical stability in the fuel cell environment. However, platinum is expensive and the limited world's supply of platinum poses serious problems for a widespread commercialization of the fuel cell technology. These difficulties have created enormous interest in the search for less expensive, more efficient electrocatalysts as well as in lowering the catalyst loading.^{1–9} With respect to identifying alternative electrocatalysts, non-platinum based metal combinations,^{10–13} metal oxides,^{14–16} carbides,¹⁷ chalcogenides,^{18,19} enzymes,^{20,21} inorganic and organometallic complexes,^{22,23} and porphyrins have been investigated over the years for ORR, but they generally exhibit lower catalytic activity than Pt.

Recently, we reported two palladium based electrocatalysts, Pd–Co–Au and Pd–Ti, that show essentially equal or slightly better performance than Pt for ORR in PEMFC at 60 °C.²⁴ The initial identification of these metal combinations employing scanning electrochemical microscopy (SECM) was based on simple thermodynamic principles recently reported by Fernandez et al.²⁵ that involve the pairing of a good oxygen-bond cleaving metal with a good oxygen-reducing metal.²⁵ However, the Pd–Co–Au catalyst was found to degrade after polarizing the cell at 200 mA/cm² for 12 h, while the Pd–Ti catalyst was stable.²⁴ On the other hand, the Pd–Co–Au system showed slightly better performance than the Pd–Ti system in PEMFC. With an aim to improve the stability of the Co-containing system while maximizing the electrochemical performance, we report here the investigation of another promising metal combination, Pd–Co–Mo (70:20:10 atom %), that exhibits not only better performance than Pt for ORR in PEMFC, but also good stability and better tolerance to methanol.

The carbon supported Pd–Co–Mo ternary catalyst with a metal loading of 20 wt % was prepared by reducing the Pd and Co precursors with sodium borohydride in the presence of the carbon support to form first Pd–Co/C followed by Mo incorporation by an impregnation method. To prepare Pd–Co/C, required amounts of ammonium hexachloropalladate (Aldrich, Milwaukee, WI) and cobalt nitrate (Aldrich) were added into a constantly stirred suspension of Vulcan XC-72R carbon black in deionized water and the mixture was agitated in an ultrasonic bath for 30 min. A few drops of 1 M NaOH solution was then added to this mixture to raise the pH to 10 before adding 5 wt % sodium borohydride. The resulting reaction mixture was stirred for 15 min, left standing overnight, filtered, washed with deionized water, and dried in air oven at 100 °C to form Pd–Co/C. To a known amount of Pd–Co/C thus obtained, the required amount of ammonium heptamolybdate (Aldrich) solution was added, then the mixture was ultrasonicated for 30 min and the solvent evaporated on a hot plate. The product was subsequently heat treated at various temperatures in a flowing 90% Ar–10% H₂ atmosphere to form the Pd–Co–Mo alloy catalyst. Compositional analysis of the Pd–Co–Mo/C samples by energy-dispersive X-ray spectroscopic (EDXS) analysis and X-ray photoelectron spectroscopy (XPS) indicated the composition to be very close to the nominal value.

Figure 1 compares the X-ray diffraction patterns of the Pd–Co–Mo/C (Pd:Co:Mo = 70:20:10 atom %) catalysts after heat treating at various temperatures. The diffraction peaks are characteristic of a face-centered cubic (FCC) lattice, but the reflections are shifted to higher angles compared to that of Pd metal, indicating a contraction of the lattice due to alloy formation. The extent of shifting increases and the lattice parameter decreases with increasing heat treatment temperature (Table 1), suggesting an increase in the degree of alloying. Although no reflections corresponding to bulk oxides of Co and Mo are seen, their presence may not be completely ruled out due to smaller quantity and possibly poor crystallinity. The alloy

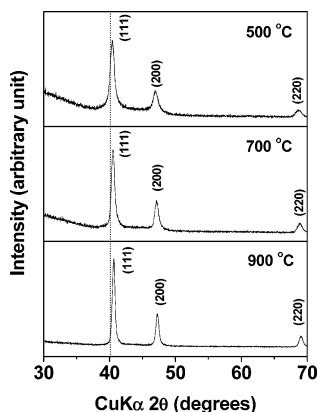
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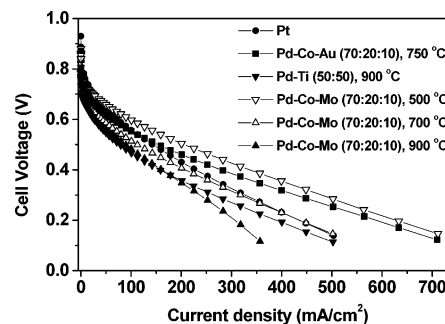
TABLE 1: Lattice Parameters and Grain Sizes of the Pd–Co–Mo Catalyst Heat Treated at Various Temperatures

catalyst	heat treatment temp (°C)	lattice parameter (nm)	crystallite size (nm)	XRD-determined surface area (m ² /g)	specific activity (A/m ² catalyst) at 0.7 V
Pd ^a		0.3879			
Pd–Co–Mo (70:20:10)	500	0.3862	24	22	4.5
Pd–Co–Mo (70:20:10)	700	0.3850	31	17	4.0
Pd–Co–Mo (70:20:10)	900	0.3844	42	13	1.5
commercial Pt (Johnson Matthey)	as-received	0.3921	3.8	74	2.0

^a JCPDS file no. 1-088-2335.**Figure 1.** X-ray diffraction patterns of the carbon supported Pd–Co–Mo (Pd:Co:Mo = 70:20:10 atom %) catalyst after heat treating in 90% Ar–10% H₂ at various temperatures. The dotted line refers to the standard 2θ value corresponding to the (111) reflection of Pd metal.

crystallite size as derived from the X-ray data with use of the Scherer equation increases with increasing temperature (Table 1). The surface area values calculated by using the equation $S = 6000/rd$ (r is the crystallite size in nm obtained from X-ray data and d is the density of the metal/alloy) are given in Table 1; the density values used are 21.5 and 11.2 g/cm³ respectively for Pt and Pd–Co–Mo (70:20:10 atom %). The XRD-determined surface area in Table 1 decreases with increasing heat treatment temperature for the Pd–Co–Mo alloy due to the increase in crystallite size and the values are smaller than those for the commercial Pt catalyst due to the much smaller crystallite size of Pt. The electrochemical active surface area could not be measured accurately because of the interference of the charge due to cobalt and molybdenum oxide formation in the hydrogen desorption potential region on the palladium surface of the Pd–Co–Mo alloy.

The gas diffusion electrodes for testing in single cell PEMFC were prepared as follows: The gas-diffusion layer was made by spraying a mixture consisting of carbon black powder (Vulcan XC-72R), 40 wt % poly(tetrafluoroethylene) (PTFE), and a solvent (mixture of water and isopropyl alcohol) onto a tefloned carbon cloth and drying in a vacuum at 300 °C for 2 h. On top of this gas diffusion layer, the catalyst layer was deposited by spraying a mixture consisting of the required amount of the carbon-supported metal(s) catalyst, solvent (mixture of water and isopropyl alcohol), and 33 wt % Nafion, followed by sintering in a vacuum at 90 °C for 1 h. All the electrodes had a uniform catalyst metal loading of 0.2 mg/cm². The membrane–electrode assembly (MEA) was obtained by sandwiching the Nafion 115 membrane between the cathode and anode (20 wt % Pt on carbon, Johnson Matthey) by hot pressing. The fuel cell testing was carried out at an operating temperature of 60 °C with hydrogen and oxygen pressures of respectively 18 and 20 psi and a humidifier temperature of 60 °C. Before the steady-state polarization curves were recorded, the cell was kept at a constant current density of 200 mA/cm²

**Figure 2.** Comparison of the steady-state polarization curves of the carbon supported Pd–Co–Mo (Pd:Co:Mo = 70:20:10 atom %) catalyst heat treated at various temperatures for ORR in single cell PEMFC at 60 °C with those of a commercial (Johnson–Matthey) Pt catalyst and our previously reported Pd–Co–Au (70:20:10) and Pd–Ti (50:50) catalysts with a metal(s) loading of 0.2 mg/cm². The current density values are with respect to the electrode geometrical area.

for several hours (~24 h) until the open circuit voltage (OCV) became steady and constant (MEA conditioning).

Figure 2 compares the electrochemical performances in a single cell PEMFC of the Pd–Co–Mo/C (Pd:Co:Mo = 70:20:10 atom %) cathode catalysts with those of commercial Pt/C (20 wt % Pt on carbon, Johnson Matthey) and our previously reported Pd–Co–Au and Pd–Ti cathodes.²⁴ The Pd–Co–Mo/C catalyst heat treated at 500 °C exhibits better performance with lower polarization loss than the commercial Pt and our previously reported Pd–Co–Au and Pd–Ti catalysts at the same loading. Pd–Co–Mo/C shows an open circuit voltage of ~0.9 V, which is close to that found with the commercial Pt catalyst. To have a better comparison of the catalytic activity for ORR, we give in Table 1 the specific activities (A/m² of metal/alloy), which are defined as the current per unit surface area of the catalyst at 0.7 V in the polarization curves given in Figure 2. It is interesting to note that the 500 and 700 °C treated Pd–Co–Mo samples show better specific activity for ORR than the commercial Pt. With the Pd–Co–Mo alloy, the specific activity decreases with increasing heat treatment temperature due to an increase in crystallite size and a consequent decrease in the surface area (Table 1). Although the actual electrochemical active surface area will be lower than the XRD-determined surface area given in Table 1, the specific activity data in Table 1 clearly reflect the influence of particle size on the catalytic activity. However, the increase in heat treatment temperature provides an important advantage of increasing the degree of alloying as indicated by the X-ray diffraction data (Figure 1) and lattice parameter values (Table 1). Therefore, synthetic approaches that can give a high degree of alloying and homogeneity at lower temperatures while keeping the crystallite size small have the possibility of improving the catalytic activity beyond what is seen in Figure 2.

Furthermore, the electrochemical performance will also depend strongly on the membrane–electrode assembly (MEA) fabrication procedures and parameters such as hot-pressing

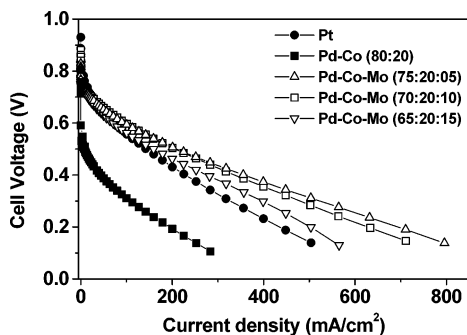


Figure 3. Comparison of the steady-state polarization curves of the carbon supported Pd–Co–Mo catalysts with various Pd:Co:Mo ratios after heat treating at 500 °C for ORR in a single cell PEMFC at 60 °C with that of a commercial Pt catalyst with a metal(s) loading of 0.2 mg/cm². The current density values are with respect to the electrode geometrical area.

temperature and pressure and catalyst ink composition. Although the performance of the commercial Pt catalyst in Figure 2 may be lower compared to that in some literature reports, we have kept the MEA fabrication procedure and parameters the same for all the samples in Figure 2, which allows a clear comparison of the new Pd–Co–Mo catalyst with the well-known Pt catalyst.

With an aim to study the effect of composition on the electrochemical performance, we prepared the Pd–Co–Mo catalysts with different Pd:Co:Mo ratios and evaluated their performance as a cathode in a single cell after heat treating at 500 °C (Figure 3). The samples with Pd:Co:Mo = 70:20:10 and 75:20:05 atom % exhibit higher catalytic activity than the Pd:Co = 80:20 sample without Mo and the Pd:Co:Mo = 65:20:15 sample, suggesting that an optimum Mo content of 5–10 atom % offers the highest catalytic activity.

In addition to high catalytic activity, the stability of the material in the fuel cell environment is critical for practical applications. A preliminary stability assessment was carried out with the 500 °C Pd–Co–Mo (Pd:Co:Mo = 70:20:10 atom %) cathode by recording the cell voltage with time (Figure 4a) and the polarization curves before and after polarizing the fuel cell at a constant current density of 200 mA/cm² for 80 h (Figure 4b). The cell exhibits stable voltage within this test period (Figure 4a) without any difference in the curves before and after polarizing the cell (Figure 4b) while our previously reported Pd–Co–Au/C catalyst degraded after 12 h of polarization, indicating excellent stability for the Pd–Co–Mo catalyst.

In direct methanol fuel cells (DMFC), the oxidation of methanol that crosses from the anode to the cathode compartment through the membrane causes a significant poisoning and degradation of the Pt cathode catalyst. Therefore, the tolerance of the cathode catalyst to methanol oxidation in the cathode compartment is an important parameter to achieve good cell performance and operational life in DMFC. Accordingly, to assess the tolerance toward methanol poisoning, we carried out the ORR in a half cell with 1 M sulfuric acid electrolyte in the presence and absence of methanol. Figure 5 compares the polarization curves recorded for ORR in the absence and presence of 1 M methanol (Figure 5a) and potential loss due to methanol poisoning at various methanol concentrations and current densities (Figure 5b) for the 500 °C Pd–Co–Mo/C (Pd:Co:Mo = 70:20:10 atom %) and commercial Pt catalysts. While the Pt/C catalyst exhibits a significant potential loss that increases with increasing methanol concentration, the Pd–Co–Mo/C catalyst exhibits a quite stable performance with only a small potential loss at high methanol concentrations, indicating remarkable tolerance to methanol poisoning. Also,

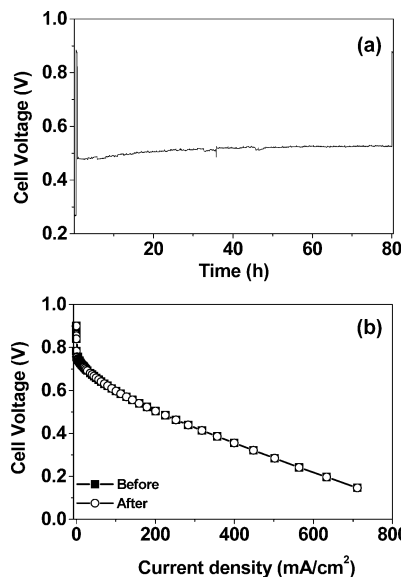


Figure 4. The stability evaluation of the 500 °C Pd–Co–Mo/C (Pd:Co:Mo = 70:20:10 atom %) cathode upon polarizing the cell at 200 mA/cm² for 80 h in a single cell PEMFC at 60 °C with a metal(s) loading of 0.2 mg/cm²: (a) cell voltage variation during the time of polarization and (b) steady-state polarization curves before and after polarization. The current density values are with respect to the geometrical area.

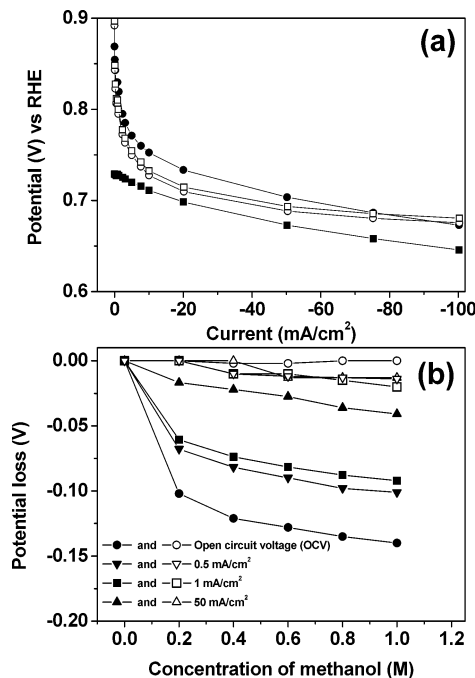


Figure 5. Comparison of 500 °C treated Pd–Co–Mo and Pt for ORR in 1 M H₂SO₄: (a) polarization curves recorded in the absence and presence of 1 M CH₃OH and (b) potential loss due to methanol poisoning at various methanol concentrations at different current densities. Closed and open symbols refer respectively to commercial (Johnson-Matthey) Pt catalyst and 500 °C Pd–Co–Mo (Pd:Co:Mo = 70:20:10 atom %) catalyst. Circles and squares in part (a) refer respectively to the absence and presence of methanol. The metal(s) loading in the electrode is 0.2 mg/cm².

the potential loss observed for the Pt catalyst is higher at lower current densities (Figure 5a,b), indicating that the methanol poisoning is significant in the activation overpotential region of the oxygen reduction kinetics.

In conclusion, we have shown that the Pd–Co–Mo ternary alloy catalyst with an optimum composition of around Pd:Co:

Mo = 70:20:10 exhibits high catalytic activity for ORR in PEMFC with good chemical stability and tolerance to methanol poisoning. Its catalytic activity at 60 °C is slightly better than that of commercial Pt catalyst. This study demonstrates the feasibility of designing new less expensive, more efficient non-platinum catalysts for PEMFC and DMFC, enhancing the commercialization prospects of the fuel cell technology.

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