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Synthesis of Novel Electro-catalysts for Proton Exchange Membrane Fuel Cells

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ABSTRACT

The proton exchange membrane fuel cell (PEMFC) is one of the most promising power sources for stand-alone utility and electric vehicle applications. Platinum (Pt) catalyst is used for both fuel and air electrodes in PEMFCs. However, carbon monoxide (CO) contamination of H_2 greatly affects electrocatalysts used at the anode of PEMFCs and decreases cell performance. The irreversible poisoning of the anode can occur, even in CO concentrations as low as a few parts per million (ppm). In this work, we synthesized several novel electrocatalysts (Pt/C, Pt/Ru/C, Pt/Mo/C, Pt/Ir, and Pt/Ru/Mo) for PEMFCs. These catalysts were tested for CO tolerance in the H_2/air fuel cell, using CO concentrations in the H_2 fuel that varies from 10 to 100 ppm. The performance of the electrodes was evaluated by determining the cell potential against current density. The effects of catalyst composition and electrode film preparation method on the performance of PEM fuel cell

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were also studied. It was found that at 70°C and 3.5-atm pressure at the cathode, Pt-alloy catalyst (10 wt% Pt/Ru/C, 20 wt% Pt/Mo/C) were more CO tolerant than the 20 wt% Pt/C catalyst alone. It was also observed that the spraying method was better than the brushing technique for the preparation of electrode film.

Key Words: PEM fuel cells; Carbon support; Catalyst preparation; Pt/Ru/Mo catalyst; Non-noble metal catalyst.

INTRODUCTION

Fuel cells are electrochemical devices that convert the available chemical free energy directly into electrical energy, without going through the heat-exchange process. Earlier, it was thought that this type of energy would be used only for some special purposes, like space travel. In recent years, there have been growing interests in developing fuel cell technologies for down-to-earth applications. Because of the high efficiency and almost zero emission to the environment, these fuel cells are finding applications in chemical process industries (CPI) as stand-alone or on-site power generators and in vehicular transport. The present state-of-art proton exchange membrane fuel cell (PEMFC) technology is based on platinum (Pt) as a catalyst for both the fuel and air electrodes. This catalyst is highly active but susceptible to poisoning by fuel impurities, such as S and CO, which may be present in the fuel used or may be introduced during the fuel processing, such as reforming. These impurities poison the anode irreversibly and decrease the performance of the PEMFCs.[1] This irreversible poisoning of the anode can happen even in CO concentrations as low as few ppm and, therefore, require expensive scrubbing of the H_2 fuel to reduce the contaminant concentration to acceptable level.[2]

To reach full commercialization, cost reduction of the PEMFC stack and ancillary systems is required. For any commercial PEMFC, the fuel hydrogen has its source from the hydrocarbon fuels. These fuels, when combined with steam, give CO and H_2, where CO is converted to CO_2 in a shift reactor.[3] The residual CO concentration ($<1\%$) leaving the reactor is too high for the PEMFCs. The CO preferentially adsorbs on the platinum catalyst surface and blocks the access of hydrogen to the catalyst sites.[4] To reach optimum performance in commercial scale fuel cells, the optimization of electrochemical activity over the whole electrode is of prime importance.[2,5] The presence of CO as contaminant (>10 ppm) in the fuel H_2 is known to be detrimental to the Pt-catalysts in PEMFC. This impurity, causing large polarization loss, reduces the PEMFC efficiency and power output.[6,7]

To get an improved efficiency and output, development of a metal alloy catalyst for fuel cell electrodes (in particular, Pt/Mo catalysts) are of interest due to their high-CO-tolerance level relative to the Pt metal catalyst.[1] From economic considerations, there is renewed interest in preparing a fuel cell anode catalyst on conducting carbon support to minimize the amount of noble metal required in a working fuel cell. To commercialize this environmentally sound source of energy/power system, development of a suitable CO-tolerant catalyst is needed. The cost and reliability of the electrocatalyst in PEMFCs are major impediments in commercial application. Innovations are needed to reduce system costs and to enhance operating life before the fuel cell can become commercially competitive with conventional power generating systems.

In our laboratory, we synthesized several Pt-based bimetallic and trimetallic catalysts for PEMFC electrodes. In this article, we report our preliminary results on the performance of the membrane electrode assemblies (MEA) in CO-contaminated H_2 fuel.

MATERIALS AND METHODS

The major objective of this work was to develop low-cost, CO-tolerant electrocatalysts for PEMFCs and demonstrate the feasibility of a H_2/air fuel cell based on these materials. Part of the work was focused on developing a procedure for preparing metal catalysts loaded on a carbon matrix. Novel catalysts are combined with the known high activity of the Pt and other noble/transition metals, such as Pt/Ru, Pt/Mo, Pt/Ru/Mo, and Pt/Ir.

Catalyst Preparation

The metal catalysts were prepared by reducing the respective metallic chlorides. Chlorides of Pt, Ru, Mo, and Ir were obtained from ElectroChem, Inc. These salts of the respective metals chosen for the candidate electrocatalysts were mixed in appropriate proportion and dissolved in distilled water. Sodium bisulfite was added slowly in the solution to form metal sulfite colloids. Hydrogen peroxide was then added to the colloid suspension to convert sulfite species to respective oxides. High-surface area powdered carbon (Vulcan XC-72) was added to the oxide colloid suspension to load the metal oxide on the carbon. Then, hydrogen was bubbled through the suspension at 60°C to reduce the oxides to the respective metals. Primary variables of the electrocatalysts synthesis were the catalyst components, proportion of the various metals, and total metal loading on the carbon. The total metal loading on the carbon was up to 1 mg/cm^2 of the electrode surface area.

Preparation of MEA

The membrane electrode assemblies (MEAs) were fabricated by both brushing and spraying techniques. The brushing and spraying methods were judged most useful in electrode film laying.[8,9]

Thin-film MEA with a Nafion 112 membrane was prepared from a slurry containing Nafion, Teflon, and catalyzed carbon. The slurry was prepared by mixing catalyzed carbon with 5% Nafion solution and Teflon suspension. Thinning of the slurry to the required extent was accomplished by adding appropriate amounts of either 30 wt% t-butanol or distilled water. The Nafion content of the electrode was varied in the range 20 to 40 wt%. The Teflon loading was varied in the range 1 to 30 wt%. The catalyzed carbon slurry was coated on both sides of a Nafion 112 membrane by brushing. Electrodes were placed on both sides of a Nafion 112 membrane, and the assembly was hot pressed at 120°C and 138 bars for 2 minutes. Chemical treatment of the Nafion membrane prior to coating was done by boiling in 0.5-M sulfuric acid for 30 minutes and, finally, it was rinsed several times in deionized water.

Membrane electrode assemblies were also prepared by the spraying method. Slurry preparation technique was the same as described previously. Instead of brushing, the slurry was sprayed on both sides of the Nafion 112 membrane, and the substrate was maintained at 120°C to evaporate the solvents and to ensure the homogeneity of the active layer. The assemblies were hot pressed for 2 minutes at 138 bars and 120°C. The advantage of spraying is that it produces a thinner membrane than the brushing and requires a shorter time. The details of the brushing and spraying methods are given elsewhere.[10]

Experimental Set-up

The experimental set-up used for testing and evaluation of catalysts and MEAs in a PEMFC is shown schematically in Fig. 1. In the PEMFC, H_2/air electrodes were used. The gases used in this PEMFC evaluation work were obtained from Air Products. High-purity hydrogen (UN 1049) was used as fuel. Ultrapure carrier grade compressed air (UN 1002) was used as a source of oxygen. A 100-ppm CO in hydrogen (ID 40094) was used as a source of CO contaminant in the fuel. A Multiple Dyna-Blender (Matheson Model 8284), which consisted of a flow indicator and controller, a mixer (Model 8270), and

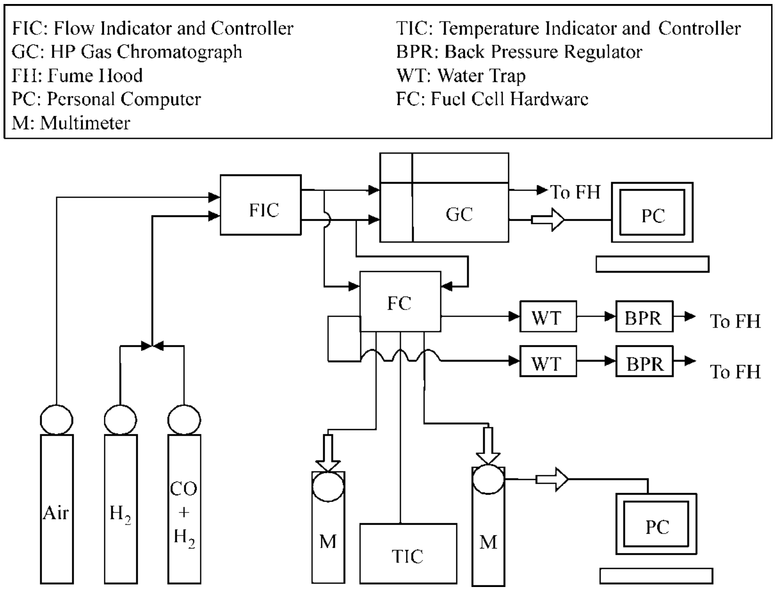

Figure 1. Schematic of PEMFC experimental set-up for evaluation of catalysts and MEAs.

a transducer (model 8272), were used to control the flow of these gases and to mix CO with hydrogen in different proportion for the fuel cell. An HP GC 5890 was used to cross check the CO/H_2 composition.

In the fuel cell, water is produced due to electrochemical reaction between hydrogen and oxygen. Two water traps (WT) were installed at the outlets of the fuel cell to remove water, as needed. Two back-pressure regulators (BPR) were used to maintain constant pressure in the fuel cell. Exit gases from the fuel cell (FC) were then taken to the fume hood (FH). As highly poisonous CO gas was used, the fuel cell system needed to be maintained in a negative-pressure environment in the fume hood. The fuel cell hardware used in the work was obtained from Electrochem, Inc., Model FC05-01SP. As shown in Fig. 2, this is a laboratory-scale fuel cell for the fundamental study of membrane electrode assembly (MEA) and fuel cell operation. Thermostats installed on each of the current collector plates prevented overheating of this type of fuel cell hardware. At each temperature, pressure, and flow rate and for all MEAs, the voltage and current were read and recorded using two multimeters.

The MEA was placed in a graphite cell with the carbon cloth current collector pressed against the MEA. Carbon cloths were wet proofed by

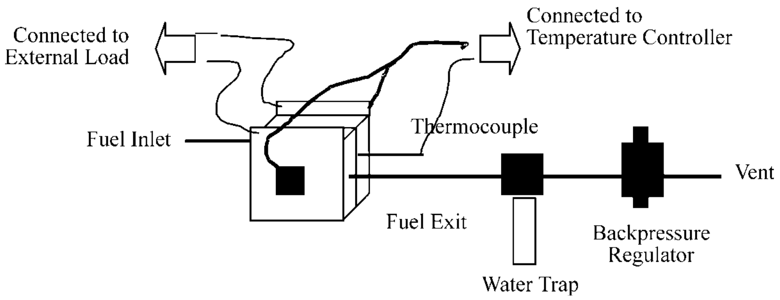

Figure 2. Schematic of laboratory PEM fuel cell (FC05-01SP) for MEA study.

treatment with a 10% Teflon suspension, followed by heating at 270°C for 20 minutes. This was done to facilitate gas diffusion and the rejection of water from the cathode. Graphite cell plates had grooves on one side to assist in uniform distribution of the reactant gases. The effective mass transfer area of the MEA was about 5 cm^2. The PEMFC was operated at 70°C and the pressure on cathode and anode sides was maintained at 3.5 atm and 2 atm, respectively. For each catalyst and/or MEA, the experiment was run for 72 hours. The cell performance was evaluated as a function of temperature, flow rate, composition of catalyst, and the MEA preparation method.

RESULTS AND DISCUSSION

A number of electrocatalysts were prepared and evaluated for CO tolerance in PEMFCs. The following catalysts were prepared by the codeposition method:

10 wt% Pt on Carbon
10 wt% Pt/Ru (1:1) on Carbon
20 wt% Pt/Ir (1:1) on Carbon
20 wt% Pt on Carbon
20 wt% Pt/Ru (1:1) on Carbon
20 wt% Pt/Ru/Mo (1/3:1/3:1/3) on Carbon

Each of the catalysts used in the MEA was tested in PEMFC with pure and CO-contaminated hydrogen fuel.

A commercial MEA obtained from ElectroChem, Inc., having 20 wt% Pt/C, was used to obtain the baseline performance curve of the PEMFC. The performance curve is a plot of voltage against current density at specified temperature and fuel/oxidant flow rates. In the experiment, the ratio of hydrogen to air was maintained at the stoichiometric proportions (2:1). Usually with increasing temperature, the cell performance improves. In the PEMFC, however, the operating temperature of the cell is dictated by the upper temperature limit of the polymer membrane used in the MEA. In this case, the upper limit was set to 75°C without humidification. All runs were made at a lower temperature (i.e., 70°C). In the PEMFC operation, the anode side was maintained at 2-atm pressure, while the cathode side operated at 3.5 atm. These values were taken from published research that reported better performance on PEMFC.[2] With an airflow rate of 1900 sccm and 70°C, the performance curve of the cell is similar to that of a typical commercial PEMFC. This is shown in Fig. 3 as the baseline case for pure hydrogen fuel.

The commercial MEA (20 wt% Pt/C) was exposed to the contaminant CO in hydrogen fuel in the PEMFC. The performance curves at two CO-concentration levels (20 ppm and 100 ppm) are also shown in Fig. 3. Although Pt is one of the most effective catalysts for electro-oxidation, it is susceptible to CO poisoning due to strong chemisorption. With increasing CO concentration, the cell performance deteriorates very rapidly. When compared with

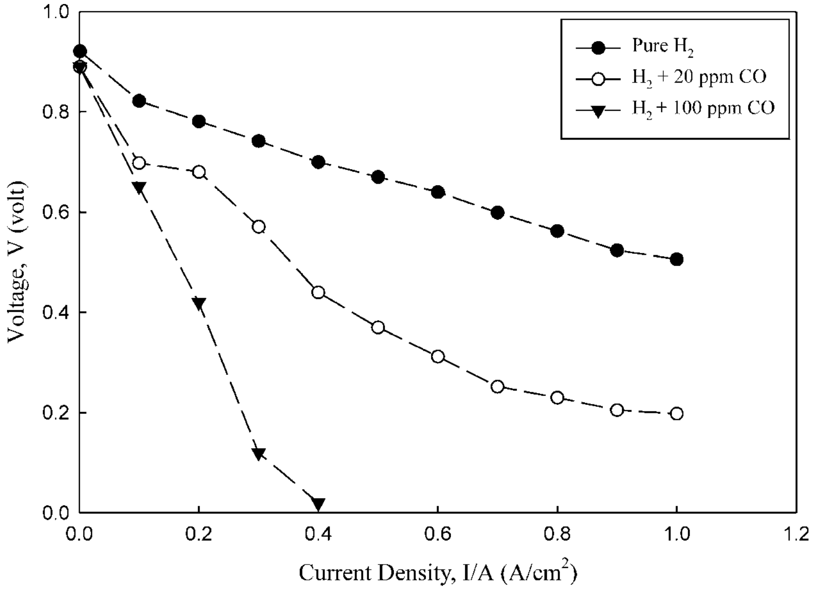

Figure 3. Effect of carbon monoxide composition in commercial MEA (20 wt% Pt/C) compared with baseline case.

the baseline performance curve (with pure H_2), 100-ppm CO-contaminated H_2 had more poisoning effect on Pt/C MEA than the 20-ppm CO-contaminated H_2. The results clearly show that the Pt catalyst cannot tolerate CO. Presence of a trace amount of CO would compromise the fuel cell performance.

Membrane electrode assemblies were prepared using commercial catalysts by brushing and spraying methods. The MEAs were prepared with catalyst loading of 20 wt% Pt/C and 10 wt% Pt/C. These MEAs were tested for cell performance in PEMFC with 20 and 100 ppm of CO-contaminated hydrogen. The baseline performance curve was also obtained with pure hydrogen fuel. The performance curves of the PEMFC with MEAs prepared by the brushing technique, having 10 wt% and 20 wt% Pt/C, are shown in Fig. 4. The baseline performance of PEMFC using 20 wt% Pt/C is similar to that of commercial MEA performance curves of 20 wt% Pt/C electrocatalyst at two CO concentration levels (20 ppm and 100 ppm) shown in Fig. 4. With increasing CO concentration, the cell performance decreases very rapidly. Compared with the baseline performance curve, 100-ppm CO-contaminated H_2 had a more pronounced poisoning effect on 20 wt% Pt/C MEA than the 20-ppm CO-contaminated H_2. It was also observed that in the presence of 20-ppm CO,

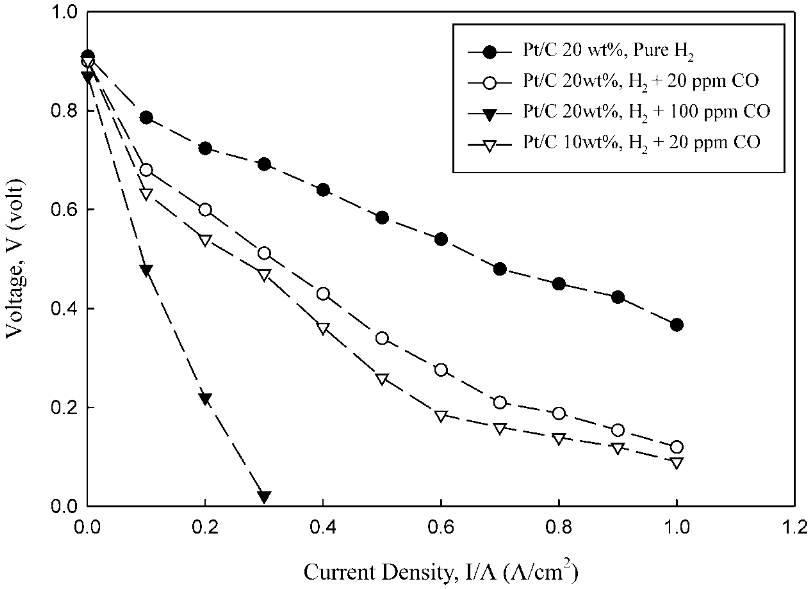

Figure 4. Performance curves of synthesized MEAs with commercial catalysts (10 wt% Pt/C and 20 wt% Pt/C) prepared by brushing technique.

the performance decreases with decreasing catalyst loading. A close review of the two performance curves for 20 and 10 wt% Pt/C MEAs operated with 20-ppm CO shows that low-catalyst loading leads to faster deterioration of cell performance. This may be attributed to reduced active catalyst sites (active surface area) at lower-catalyst loading. As a result, rapid loss of active sites by CO poisoning would be expected. With increased Pt loading, better cell performance may be achieved, but CO poisoning remains a problem.

In Fig. 5, performance of the PEMFC with MEAs prepared by the spraying technique with 10 wt% and 20 wt% Pt/C are shown. The materials used in these MEAs are exactly the same as before, but a spraying method was used in the laying of the electrode assembly. The baseline performance of the PEMFC with 20 wt% Pt/C in the synthesized MEA was similar to that of commercial MEA. Performance curves of 20 wt% Pt/C electrocatalyst at two CO-concentration levels (20 ppm and 100 ppm) are shown in Fig. 5. A comparison of the performance curves in Fig. 4 with that in Fig. 5 show that the characteristics of the curves are very similar both in presence of CO-contaminant hydrogen and pure hydrogen fuel in the PEMFC. However, a close look at each of the curves shows that the spraying method yielded a better

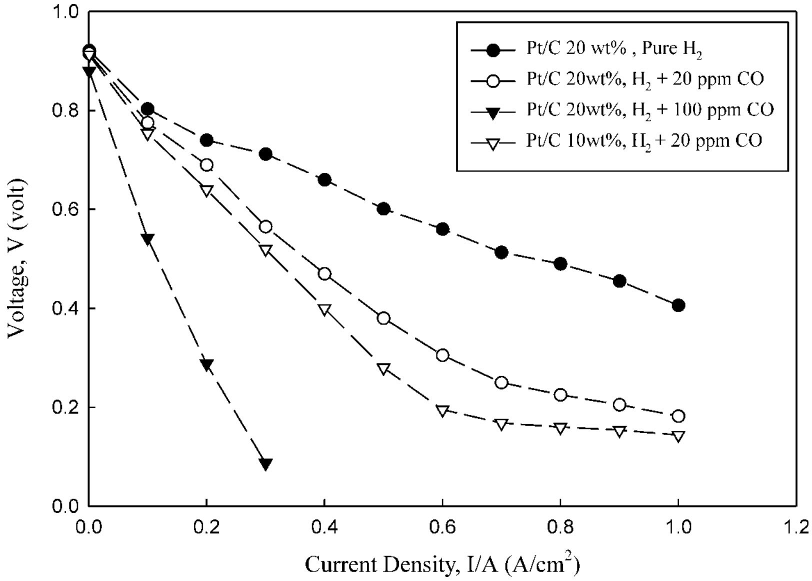

Figure 5. Performance curves of synthesized MEAs with commercial catalysts (10 wt% Pt/C and 20 wt% Pt/C) prepared by spraying technique.

performance curve than the brushing method in preparing MEAs. By using the spraying method, it is possible to lay a homogeneous active layer of catalyst with uniform particle distribution and thickness. This may account for the better performance of MEAs. In our subsequent work, the spraying method was consistently used in all MEA preparation.

Using the spraying technique, two MEAs were prepared with 10 and 20 wt% Pt/Ru/C catalysts. Performance curves of these MEAs in the PEMFC are shown in Fig. 6. When compared with Pt/C MEAs (See Fig. 3) with that of Pt/Ru/C MEAs, it appears that the presence of ruthenium (Ru) in the electrocatalysts provide improved CO tolerance. At high-CO concentration ($>$100 ppm), there is a significant drop in cell performance even with Pt/Ru/C catalyst. At low-CO concentration (20 ppm), MEAs with 10 wt% and 20 wt% Pt/Ru/C showed that the two formulations are equally good. Thus, it appears that at a low-CO concentration, one may opt to use Ru in place of Pt to reduce Pt loading in the catalyst.

In an effort to find a CO-tolerant catalyst, a number of bi- and trimetallic catalysts of Pt in combination with Ru, Ir, and Mo were synthesized for use in MEAs. The metal salts used in the catalyst synthesis were obtained from

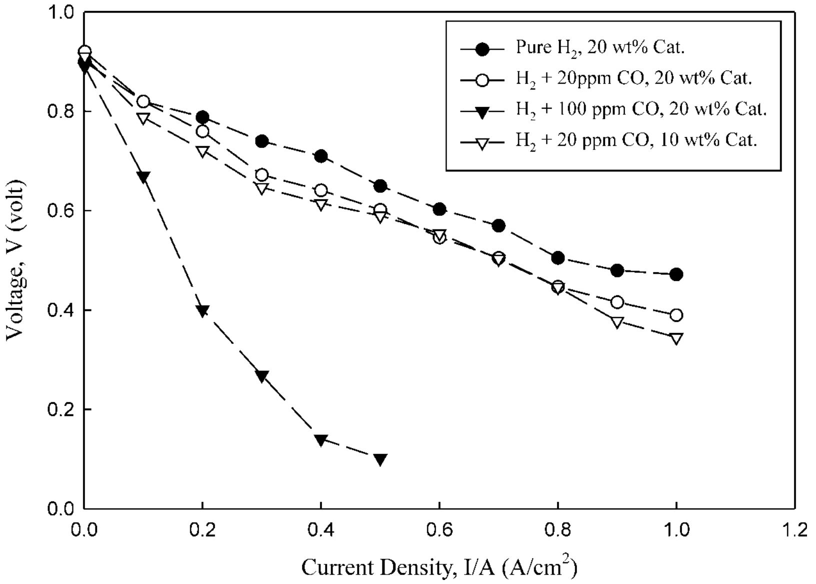

Figure 6. CO tolerance of MEAs prepared by spraying technique using 10 and 20 wt% Pt/Ru/C (1:1) synthesized catalysts.

Fisher Scientific. As stated earlier, the MEAs were prepared by the spraying method. All MEAs were evaluated in the PEMFC with pure hydrogen fuel and 20- and 100-ppm CO-contaminated hydrogen fuel, respectively. The fuel cell operated at 70°C with anode and cathode side gas pressure of 2 atm and 3.5 atm, respectively. The performance curve of the 20 wt% Pt/C MEA is shown in Fig. 7. The performance of the synthesized MEA was very similar to that we obtained from a commercial vendor (ElectroChem, Inc.), which can be seen by comparing the performance curves of Fig. 3 with that of Fig. 7.

The performance curve of the 1:1 Pt/Ru 20 wt% MEA is shown in Fig. 8. The MEAs were evaluated at 20- and 100-ppm CO-contamination in the hydrogen fuel. A comparison of the performance curves of Pt/C 20 wt% MEA in Fig. 7 with that of Fig. 8 clearly demonstrates that Pt/Ru/C 20 wt% MEA was tolerant to CO poisoning. In fact, Pt/Ru/C MEA yielded a better baseline performance when we compare that with Pt/C MEA of Fig. 7. Furthermore, we observed that at 20-ppm CO contamination, the performance of the Pt/Ru/C MEA was as good as the baseline performance curve of Pt/C MEA. This shows that ruthenium is a potent CO-tolerant catalyst and may be useful as a substitute of platinum for reduced Pt-catalyst loading.

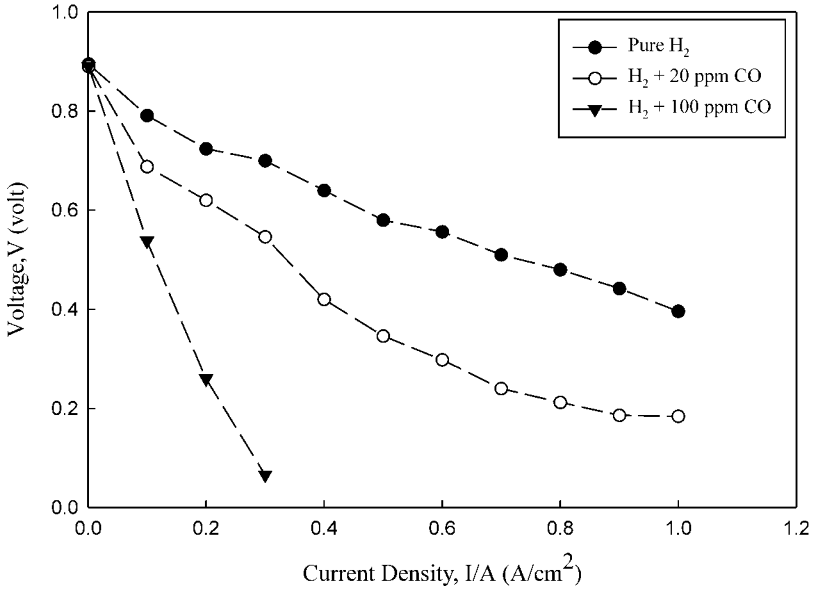

Figure 7. Effect of CO concentration on the performance of synthesized MEAs using synthesized 20 wt% Pt/C catalyst in PEMFC.

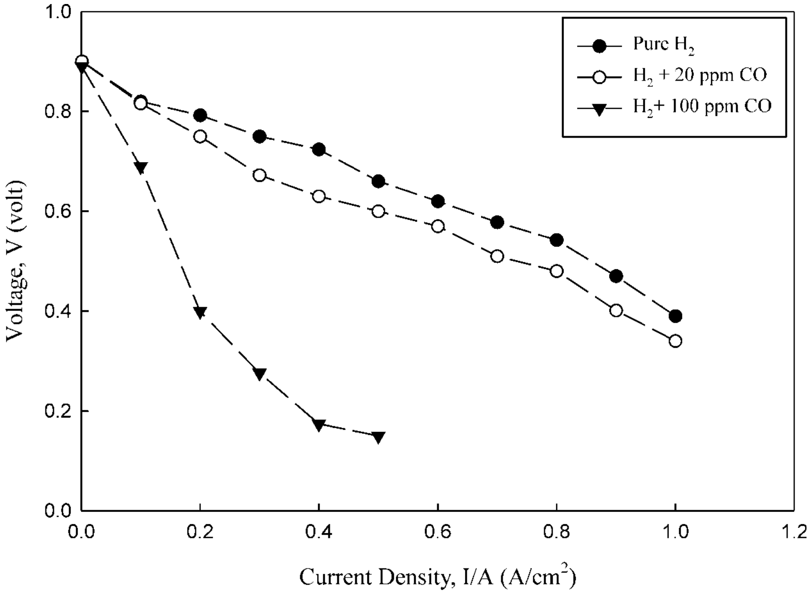

Figure 8. Effect of CO concentration on the performance of synthesized MEAs using synthesized 20 wt% Pt//Ru/C catalyst in PEMFC.

Electrocatalyst of Pt/Ir was synthesized in 1:1 ratio for preparation of Pt/Ir/C 20 wt% MEA. The performance curve of this MEA is shown in Fig. 9. This MEA is also sensitive to CO contaminant. A comparison of Fig. 7 with Fig. 9 reveals that Pt/Ir/C 20 wt% MEA performs better than Pt/C 20 wt% MEA, both in terms of baseline voltage/current density and CO tolerance. However, comparing the performance of Pt/Ir/C 20 wt% MEA in Fig. 9 with that of Pt/Ru/C 20 wt% MEA in Fig. 8, the later is found to have better performance characteristics. Like ruthenium, iridium could also be a choice of catalyst for CO tolerance and may be used as a substitute for platinum for reduced Pt-loading in catalyst formulation. From the CO tolerance point of view, it appears that both Pt/Ir/C and Pt/Ru/C 20 wt% MEAs are attractive options over Pt/C 20 wt% MEA in PEMFC operations.

A three-component catalyst of Pt, Ru, and Mo in the weight proportion of 1/3, 1/3, and 1/3, respectively was also synthesized. This catalyst was used to synthesize Pt/Ru/Mo/C 20 wt% MEA. The performance curve of this MEA is shown in Fig. 10. A comparison of the Pt/Ru/C 20 wt% MEA with that of Pt/Ru/Mo/C 20 wt% MEA show that both the MEAs perform at about the same level in terms of baseline voltage/current density and CO tolerance. By

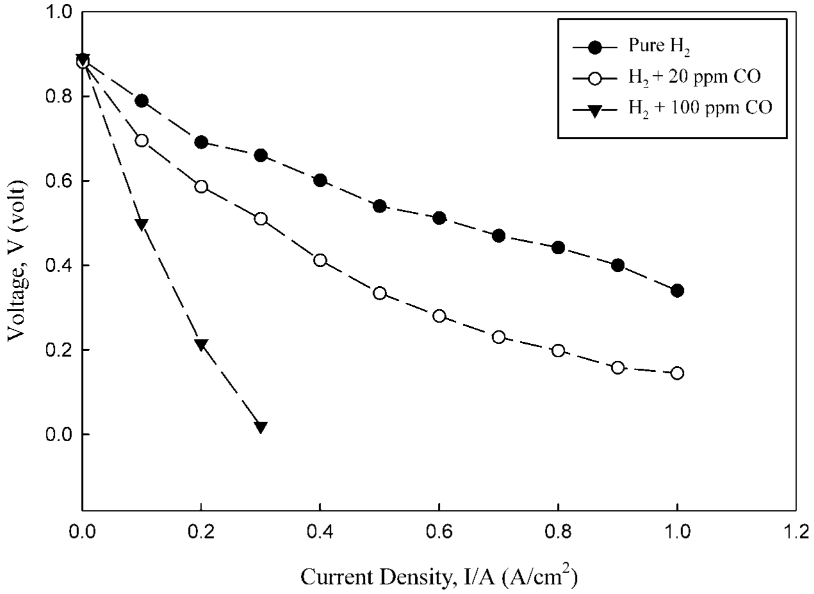

Figure 9. Effect of CO concentration on the performance of synthesized MEAs using synthesized 20 wt% Pt/Ir/C catalyst in PEMFC.

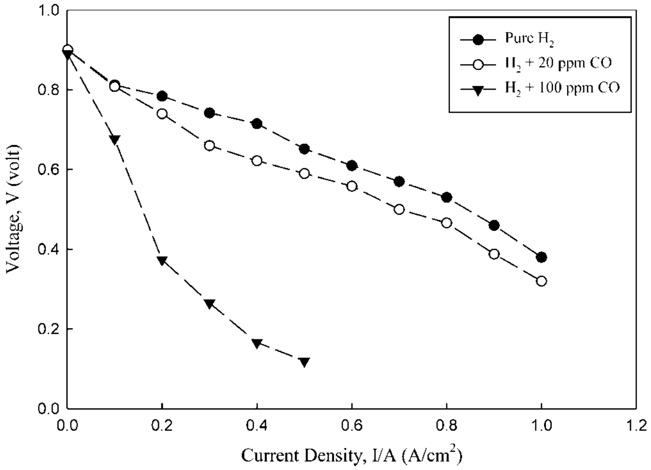

Figure 10. Effect of CO concentration on the performance of synthesized MEAs using synthesized 20 wt% Pt/Ru/Mo/C catalyst in PEMFC.

addition of molybdenum, fuel cell performance was not compromised but contributed to reduce Pt loading. Although we did not study sulfur poisoning of electrocatalysts, addition of Mo in catalyst formulation will provide added protection against sulfur poisoning.

CONCLUSION

Both synthesized and commercial Pt catalysts in the MEAs are susceptible to CO poisoning. From limited experimentation, we observed that for MEA preparation, the spraying method is more effective than the brushing method. The cell performance can be improved by incorporating Ru and Mo in catalyst formulation in combination with Pt. The metal Ir in combination with Pt in the catalyst did not have any significant impact on cell performance. The newly synthesized 20 wt% Pt/Ru/C electrocatalyst in MEA can tolerate CO poisoning in PEMFC at 20 ppm CO-contaminating H_2 fuel and outperforms commercial 20 wt% Pt/C in MEA. Our synthesized 20 wt% Pt/Ru/Mo/C electrocatlyst showed excellent CO tolerance in PEMFC and compared very favorably with 20 wt% Pt/Ru/C in CO-tolerance. Using Ru and/or Mo in combination with Pt in the electrocatalyst formulation, the loading of Pt can be reduced significantly without compromising cell performance. Furthermore, we conclude that to develop low-cost, CO-tolerant catalysts for use in MEAs, metals like Ru and Mo in combination with Pt need to be included in the catalyst formulation. For optimum cell performance, fine tuning of these metal compositions in the catalyst would be necessary.

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