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Development of Novel Electrocatalysts 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 electro catalysts 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 few parts per million (ppm). In this work, we have synthesized several novel elctrocatalysts (Pt/C, Pt/Ru/C, Pt/Mo/C, Pt/Ir and Pt/Ru/Mo) for PEMFCs. These catalysts have been 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 were also studied. It was found that at 70 ^{o}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 spraying method was better than the brushing technique for the preparation of electrode film.

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EXECUTIVE SUMMARY

In this work, novel electrocatalysts for PEMFCs has been developed. The catalysts were evaluated in a H_2/air fuel cell. The effects of temperature, and catalyst compositions on PEMFCs performance were studied. Several Pt-alloy catalysts (alloyed with Ru, Mo and ,Ir) were tested for CO-tolerance in the 20 ppm to 100 ppm range. The newly synthesized 20 wt% Pt/Ru/C electro catalyst 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 electro catalyst 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 one needs to include metals like Ru and Mo in combination with Pt in the catalyst formulation. For optimum cell performance, fine-tuning of these metal compositions in the catalyst would be necessary.

INTRODUCTION

The fundamental chemical reaction to produce water from oxygen and hydrogen is given as:

$$2H_2 + O_2 = 2H_2O + Energy$$

Fuel cells are electrochemical devices that convert the available chemical free energy directly into electrical energy, without going through the heat exchange process [1,2]. 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 growing interest 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 motor vehicles.

The present state-of-art Proton Exchange Membrane Fuel Cell (PEMFC) technology is based on Pt as a catalyst for both the fuel and air electrodes. This catalyst is highly active but susceptible to fuel impurities such as, S and CO, which may be present in the fuel used or may be introduced during fuel processing such as, reforming. These impurities poison the anode irreversibly and decrease the performance of the PEMFCs. Work is still needed to reduce system costs and to enhance operating life before the fuel cell can become commercially competitive with conventional power systems.

In this work, we plan to develop novel electrocatalysts for PEM fuel cells and will demonstrate the feasibility of a H_2/O_2 fuel cell based on these materials. Part of the work would be focused on developing procedure for preparing metal catalysts loaded on carbon matrix. Novel catalysts will combine with the known high activity of the Pt and other noble metals, such as Ru, Pt/Mo, Pt/Ru/Mo, Pt/W, Pt/Ru/W, Pt/W/C, Pt/Ru/W/C. Other possible metals may include Sn and Ir. Successful development of these electrocatalysts will lead to several advantages:

- It will eliminate the need for expensive treatment of the fuel feed stream to remove these contaminants as presently required
- It will reduce weight and result in compact fuel cell power system with improved energy efficiency
- It will lower the costs due to reduce Pt catalyst loading or use of non-precious metal catalyst and will have direct application in commercial and private sector.

The major tasks of this project may be summarized as follows.

Task 1: Synthesis of candidate electrocatalyst materials.

Task 2: Half-cell evaluation of electrocatalysts with pure Hydrogen.

Task 3: Half-cell evaluation of electrocatalysts with contaminated hydrogen.

Task 4: Electrode performance evaluation in a H_2/O_2 fuel cell.

Task 5: Final report preparation.

Based on above tasks, the project work is planned as follows.

- Set up a single cell Hydrogen/Oxygen fuel cell system

  Obtain commercially available fuel cell components.

  Familiarized with fuel cell operation and performance evaluation.

  Compare performance with H_2 contaminated with CO.

  Synthesized MEAs using commercially available catalysts and other components.

  Compare fuel cell performance with commercial MEA Vs synthesized MEAs.

- Develop procedure for preparing metal catalyst loaded on carbon

  Synthesize Pt and Pt/Ru catalysts and load on carbon.

  Prepare electrode as well as MEAs using the synthesized electrodes.

  Compare fuel cell performance with commercial MEAs Vs synthesized MEAs.

- Complete literature search to determine candidate catalysts to evaluate

  Pt/Mo, Pt/Ru/Mo, Pt/W, Pt/Ru/W, Pt/WC, Pt/Ru/WC are likely candidates.

  Other possible metals may include Sn and Ir.

- Evaluation of candidate catalyst materials.

  Determine performance with pure hydrogen as well as contaminated hydrogen.

EXPERIMENTAL: MATERIALS AND METHODS

The major objective of this work was to develop low-cost CO-tolerant electro-catalysts 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 procedure for preparing metal catalysts loaded on 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 powered 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 ^{o}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 slurry containing Nafion, Teflon, and catalyzed carbon. This 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 side of a Nafion 112 membrane by brushing. Electrodes were then placed on both sides of a Nafion 112 membrane and then assembly was hot pressed at 120 ^{o}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 then finally rinsed several times in de-ionized water.

Membrane electrode assemblies were also prepared by spraying method. Slurry preparation technique was the same as described above. Instead of brushing, the slurry was sprayed on both sides of the Nafion 112 membrane and the substrate was maintained at 120 ^{o}C to evaporate the solvents and to insure the homogeneity of the active layer. Then the assemblies were hot pressed for 2 minutes at 138 bars and 120 ^{o}C. The advantage of spraying is that it produces thinner membrane than the brushing and requires 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 Figure 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. Ultra pure carrier grade compressed air (UN 1002) was used 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 a transducer (model 8272) was used to control the flow of these gases and to mix CO with hydrogen in different proportion for the fuel cell. A HP GC 5890 was used to crosscheck the CO/H_2 composition.

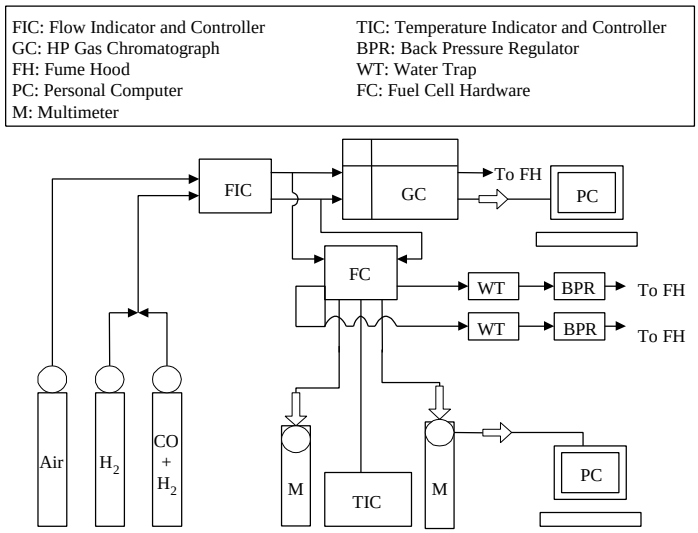

Figure 1: Schematic of PEMFC experimental set-up for evaluation of catalysts and MEAs

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 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 Figure 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 multi-meters.

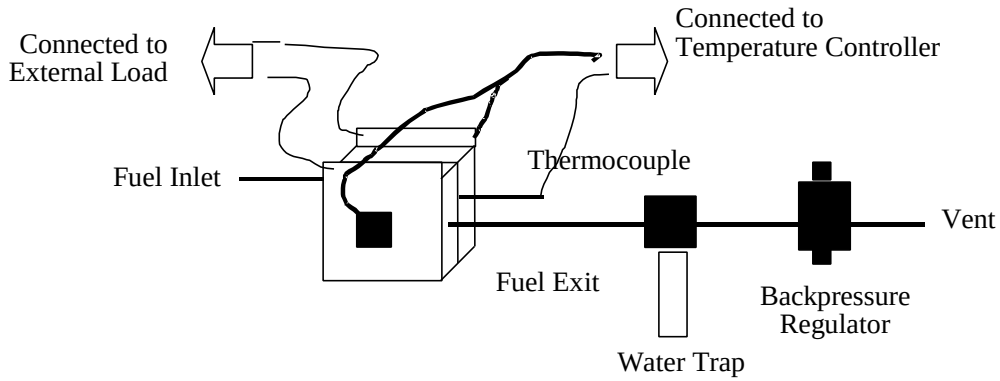

Figure 2: Schematic of laboratory PEM fuel cell (FC05-01SP) for MEA study

The MEA was placed in a graphite cell with the carbon cloth current collector pressed against the MEA. Carbon cloths were wet-proofed by treatment with a 10% Teflon suspension, followed by heating at 270 ^{o}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 assists a 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 ^{o}C and the pressure on cathode and anode sides were 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 DISCUSSIONS

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

10 wt% Pt on Carbon	20 wt% Pt on Carbon
10 wt% Pt/Ru (1:1) on Carbon	20 wt% Pt/Ru (1:1) on Carbon
20 wt% Pt/Ir (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 ^{o}C without humidification. All runs were made at a lower temperature, i.e., 70 ^{o}C. In 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 the literature that gave better performance on PEMFC. With an airflow rate of 1900 sccm and 70 ^{o}C, the performance curve of the cell is similar to that of a typical commercial PEMFC. This is shown in Figure 3 as the baseline case for pure hydrogen fuel.

The commercial MEA (20 wt% Pt/C) was exposed to contaminant CO in hydrogen fuel in PEMFC. The performance curves at two CO concentration levels (20 ppm and 100 ppm) are also shown in Figure 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 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 trace amount of CO would compromise the fuel cell performance.

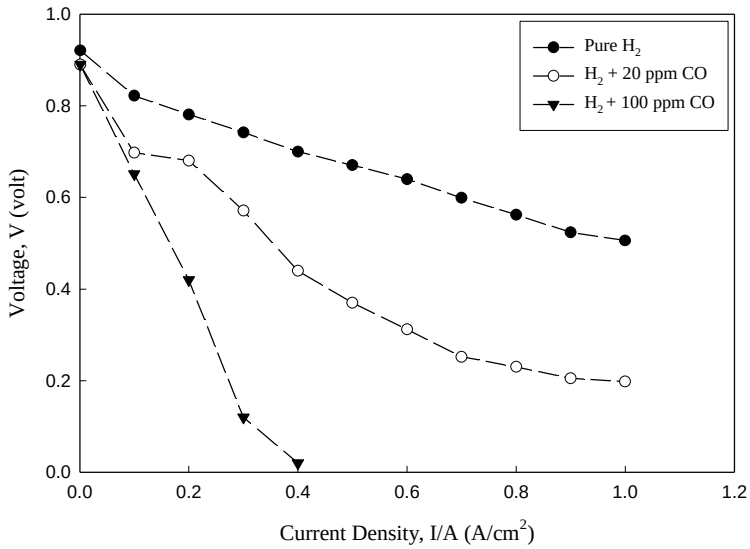

Figure 3: Effect of carbon monoxide composition in commercial MEA (20 wt% Pt/C) compared with baseline case.

Membrane Electrode Assemblies (MEAs) 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 brushing technique, having 10 wt% and 20 wt% Pt/C are shown in Figure 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 electro-catalyst at two CO concentration levels (20 ppm and 100 ppm) are shown in Figure 4. With increasing CO concentration, the cell performance decreases very rapidly. Compared with baseline performance curve, 100 ppm CO contaminated H_2 had 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, 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 reduce active catalyst sites (active surface area) at lower catalyst loading. As a result, one would expect rapid loss of active sites by CO poisoning. With increasing Pt loading, better cell performance may be achieved but CO poisoning remains a problem.

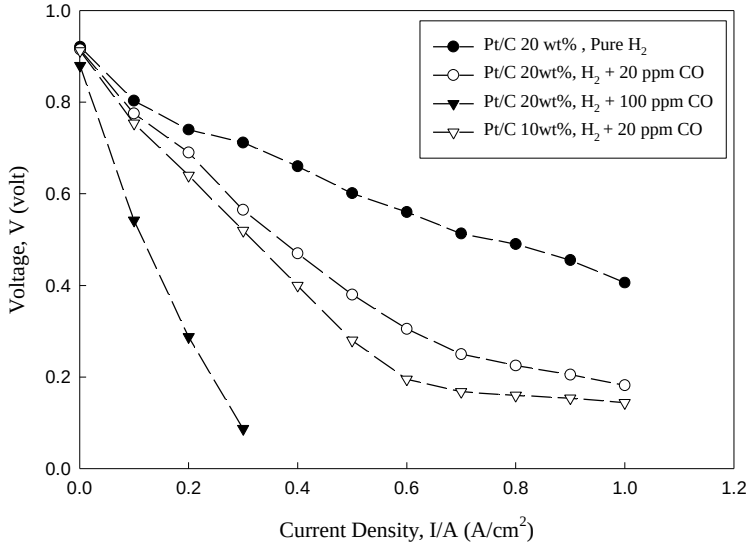

Figure 4: Performance curves of synthesized MEAs with commercial catalysts (10 wt% Pt/C and 20 wt% Pt/C) prepared by brushing technique.

In Figure 5, performance of the PEMFC with MEAs prepared by spraying technique, with 10 wt% and 20 wt% Pt/C are shown. The materials used in these MEAs are exactly 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 electro-catalyst at two CO concentration levels (20 ppm and 100 ppm) are shown in Figure 5. A comparison of the performance curves in Figure 4 with that in Figure 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 spraying method yielded better 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 Figure 6. When compared with Pt/C MEAs (Figure 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 low CO concentration, one may opt to use Ru in place of Pt to reduce Pt loading in the catalyst.

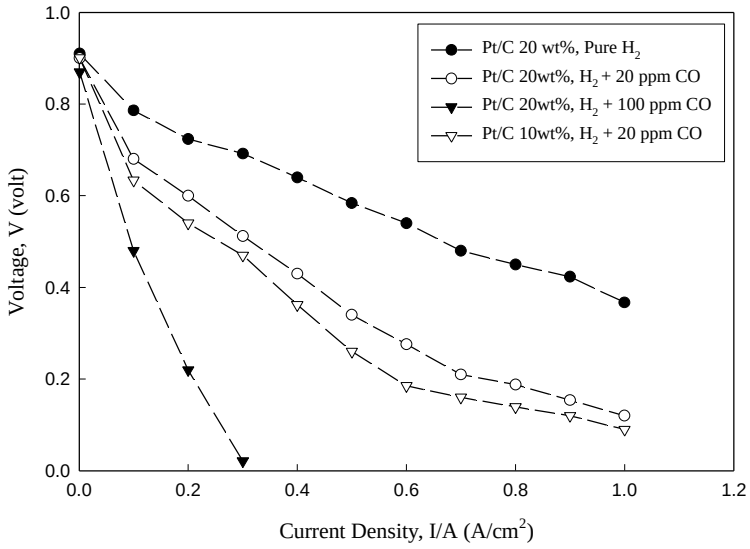

Figure 5: Performance curves of synthesized MEAs with commercial catalysts (10 wt% Pt/C and 20 wt% Pt/C) prepared by spraying technique.

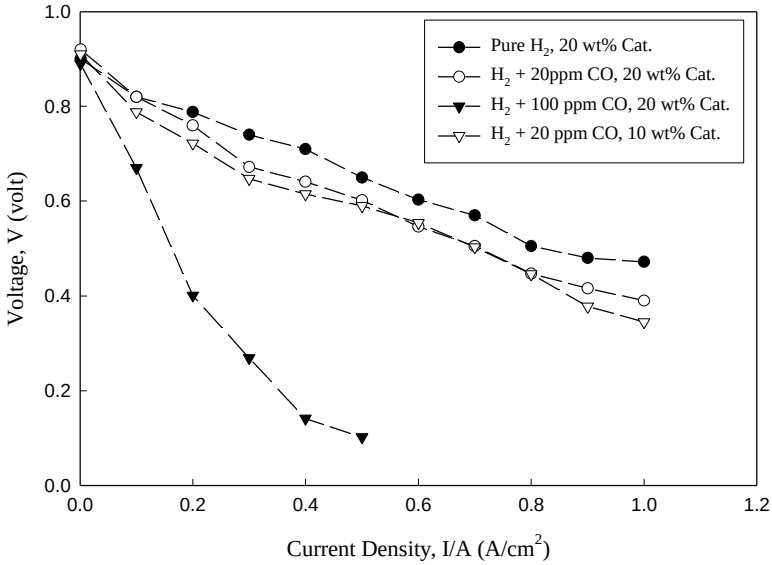

Figure 6: CO tolerance of MEAs prepared by spraying technique using 10 and 20 wt% Pt/Ru/C (1:1) synthesized catalysts.

In an effort to find CO-tolerant catalyst, a number of bi- and tri-metallic 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 Fisher Scientific. The MEAs were prepared by spraying method as stated earlier. 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 ^{o}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 Figure 7. The performance of our synthesized MEA was very much similar to that we obtained from a commercial vendor (ElectroChem, Inc.,), which can be seen by comparing the performance curves of Figure 3 with that of Figure 7.

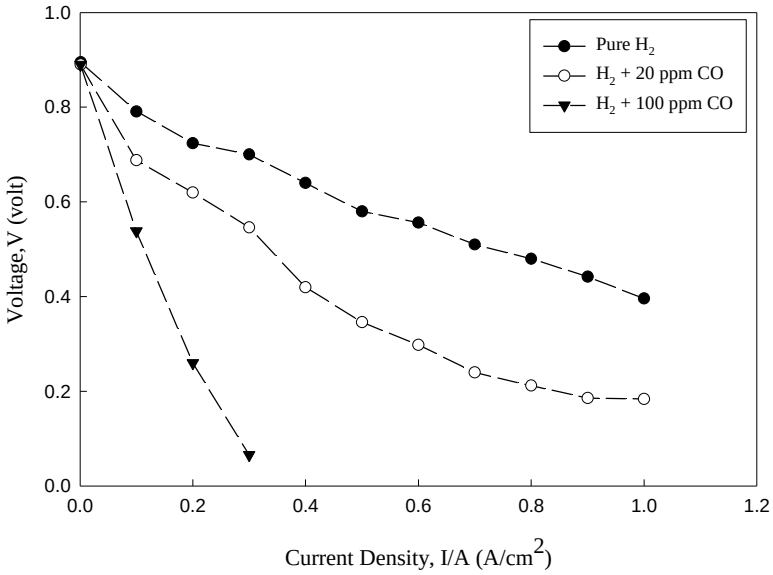

Figure 7: Effect of CO concentration on the performance of synthesized MEAs using synthesized 20 wt% Pt/C catalyst in PEMFC.

The performance curve of the 1:1 Pt/Ru 20 wt% MEA is shown in Figure 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 Figure 7 with that of Figure 8 clearly demonstrate that Pt/Ru/C 20wt% 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 Figure 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.

Electrocatlyst 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 Figure 9. This MEA is also sensitive to CO contaminant. A comparison of Figure 7 with that of Figure 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 Figure 9 with that of Pt/Ru/C 20 wt% MEA in Figure 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 to substitute for platinum for reduced Pt-loading in catalyst formulation. From 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.

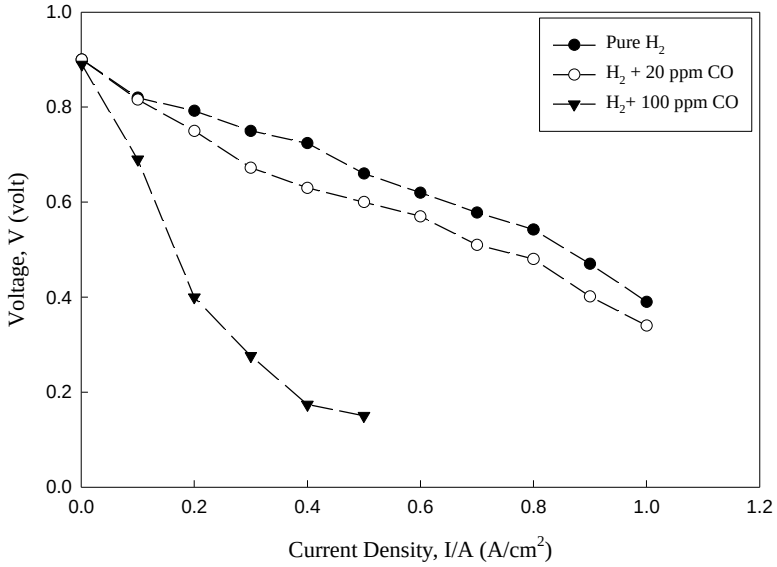

Figure 8: Effect of CO concentration on the performance of synthesized MEAs using synthesized 20 wt% Pt//Ru/C catalyst in PEMFC.

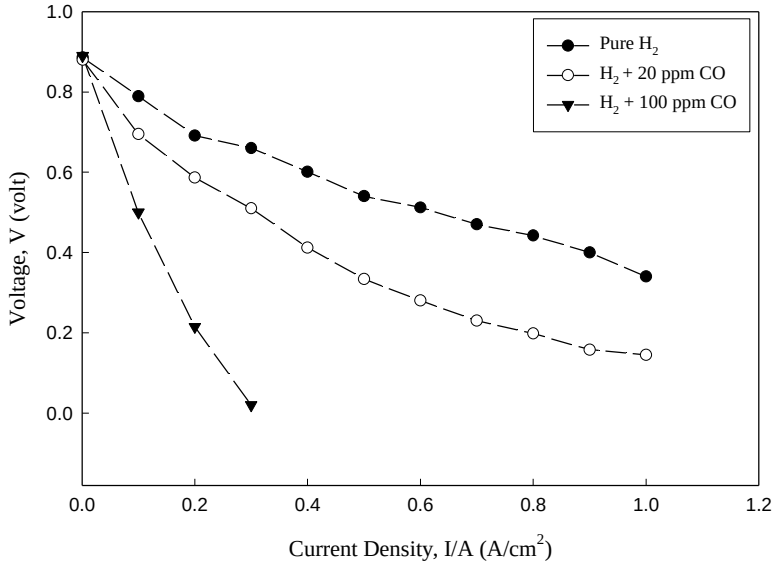

Figure 9: Effect of CO concentration on the performance of synthesized MEAs using synthesized 20 wt% Pt/Ir/C catalyst in PEMFC.

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 Figure 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 about the same level in terms of baseline voltage/current density and CO tolerance. By 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.

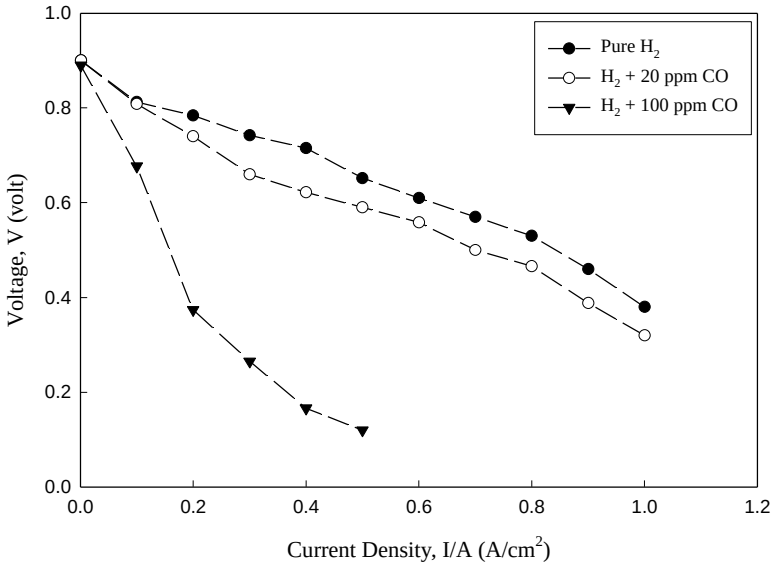

Figure 10: Effect of CO concentration on the performance of synthesized MEAs using synthesized 20 wt% Pt/Ru/Mo/C catalyst in PEMFC.

CONCLUSIONS

Both synthesized and commercial Pt catalysts in the MEAs are susceptible to CO poisoning. From limited experimentation, we observed that for MEA preparation, spraying method is more effective than brushing. 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 electro catalyst 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.

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