Report Title:

Synthesis and Characterization of CO- and H_2S-Tolerant Electrocatalysts for PEM Fuel Cell

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ABSTRACT

The present state-of-art Proton Exchange Membrane Fuel Cell (PEMFC) technology is based on platinum (Pt) as a catalyst for both the fuel (anode) and air (cathode) electrodes. This catalyst is highly active but susceptible to poisoning by CO, which may be present in the H_2-fuel used or may be introduced during the fuel processing. Presence of trace amount of CO and H_2S in the H_2-fuel poisons the anode irreversibly and decreases the performance of the PEMFCs. In an effort to reduce the Pt-loading and improve the PEMFC performance, we propose to synthesize a number of Pt-based binary, ternary, and quaternary electrocatalysts using Ru, Mo, Ir, Ni, and Co as a substitute for Pt. By fine-tuning the metal loadings and compositions of candidate electrocatalysts, we plan to minimize the cost and optimize the catalyst activity and performance in PEMFC. The feasibility of the novel electrocatalysts will be demonstrated in the proposed effort with gas phase CO and H_2S concentrations typical of those found in reformed fuel gas with coal/natural gas/methanol feedstocks.

During this reporting period several tri-metallic electrocatalysts were synthesized using both ultra-sonication and conventional method. These catalysts (Pt/Ru/Mo, Pt/Ru/Ir, Pt/Ru/W, Ptr/Ru/Co, and Pt/Ru/Se on carbon) were tested in MEAs. From Galvonstatic study the catalytic activity was found in the order of: Pt/Ru/Mo/C > Pt/Ru/Ir/C > Pt/Ru/W/C > Ptr/Ru/Co/C > and Pt/Ru/Se. It appears that electrocatalysts prepared by ultra-sonication process are more active compared to the conventional technique. Work is in progress to further study these catalysts for CO-tolerance in PEMFC.

TABLE OF CONTENTS

EXECUTIVE SUMMARY

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, presence of CO and H_2S in H_2-fuel as contaminants greatly affects electrocatalysts used at the anode of PEMFCs and decreases cell performance. The irreversible poisoning of the anode can occur even in CO and H_2S concentrations as low as few parts per million (ppm). In an effort to reduce the Pt-loading and improve the PEMFC performance, we propose to synthesize a number of Pt-based bi-metallic, tri-metallic electrocatalysts using Ru, Mo, Ir, Ni, and Co as a substitute for Pt. By fine-tuning the metal loadings and compositions of candidate electrocatalysts, we plan to minimize the cost and optimize the catalyst activity and performance in PEMFC. The feasibility of the novel electrocatalysts will be demonstrated in the proposed effort with gas phase CO and H_2S concentrations typical of those found in reformed fuel gas with coal/natural gas/methanol feedstocks.

In our lab we synthesized several tri-metallic electrocatalysts using both ultra-sonication and conventional method. These catalysts (Pt/Ru/Mo, Pt/Ru/Ir, Pt/Ru/W, Ptr/Ru/Co, and Pt/Ru/Se on carbon) were tested in MEAs. From Galvonstatic study it appears that electrocatalysts prepared by ultra-sonication process are more active compared to the conventional technique. Work is in progress to further study these catalysts for CO-tolerance in PEMFC.

INTRODUCTION

In recent years, there has been growing interest in Proton Exchange Membrane Fuel Cell (PEMFC) technologies for down-to-earth applications because of its high power density, high efficiency and almost zero emission to the environment. The major focus on PEMFC technology is to develop fuel cell system for transportation applications, which require development of low cost cell components and reliable, high-purity H_2-fuel source [1, 2]. The PEMFC technology is attractive because of its low operating temperature and ease of start-up. Reformed methanol and liquid hydrocarbons are expected to be major fuel source in PEMFCs for terrestrial transportation application as envisioned in Vision 21 for the 21st century. The present state-of-art PEMFC technology is based on platinum (Pt) as a catalyst for both the fuel (anode) and air (cathode) electrodes. The electrochemical reactions that occur at the Pt-electrodes are:

$$\text{Anode:} \quad H_2 = 2H^+ + 2e^-$$

$$\text{Cathode:} \quad O_2 + 4H^+ + 4e^- = 2H_2O$$

The over all fuel cell reaction is:

$$2H_2 + O_2 = 2H_2O + \text{Energy}$$

This Pt-catalyst is highly active but susceptible to poisoning by fuel impurities such as, H_2S and CO, which may be present in the H_2-fuel used or may be introduced during the fuel processing. These impurities poison the anode irreversibly and decrease the performance of the PEMFCs. 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. In order to commercialize this environmentally sound source of energy/power system, development of suitable CO- and H_2S-tolerant catalyst is needed. The cost and reliability of electrocatalyst in PEMFCs are major impediments in commercial application [2, 3]. Innovations are needed to reduce system costs and to enhance operating life before fuel cell can become commercially competitive with conventional power generating systems.

In this work we propose to develop CO- and H_2S-tolerant electrocatalysts for PEMFC anode by combining platinum with additional metallic components. Ruthenium, a noble metal catalyst, is the preferred choice for providing CO tolerance. The sulfur tolerance may be imparted by a number of transition metals with molybdenum, cobalt, and tungsten as the leading candidates. Based on our current understanding and experience in the Pt-based bi-metallic and tri-metallic PEMFC electrocatalysts, we propose to further develop these electrocatalysts by fine-tuning the metal loadings and compositions to minimize the cost and optimize the catalyst activity and performance

RESEARCH OJECTIVES

The objectives of this research are to:

- Synthesize novel candidate electrocatalyst materials
- Characterize the electro-catalytic activity in pure hydrogen half-cell studies
- Demonstrate electrocatalyst feasibility in contaminated hydrogen half-cell studies
- Demonstrate H_2/O_2 fuel cell performance with the improved electrodes in contaminated hydrogen environment

EXPERIMENTAL: MATERIALS & METHODS

Catalysts Preparation

The metal catalysts were prepared by the reduction of respective metallic chlorides. The details of the preparation technique have been reported elsewhere [4]. Chlorides of metal salts of Pt, Co, Mo, Ru, and Ir as precursors obtained from Fisher Scientific were used in this work. Precursors were weighed stoichiometrically to maintain equal atom wt% and dissolved in distilled water. Sodium bisulfite was added slowly in the solution to form metal sulfite colloids. A solution of hydrogen peroxide was added to this slurry to obtain a colloidal solution of respective metal oxides. High surface area powdered carbon (VULCAN XC72) was dispersed into this metal colloid solution with a dry weight ratio of 2:3 to load the metal particles on to it. This powder was heated in the oven overnight at 150ºC, which was followed by the passage of hydrogen for the reduction of metal oxides to respective metals.

To improve the dispersion of catalysts on support material, ultra-sonication was introduced as a step in the electrocatlysts synthesis steps, as shown by the block diagram in Figure 1. A Misonix 3000 Ultra-sonicator was used for mixing and even dispersion active metals on carbon.

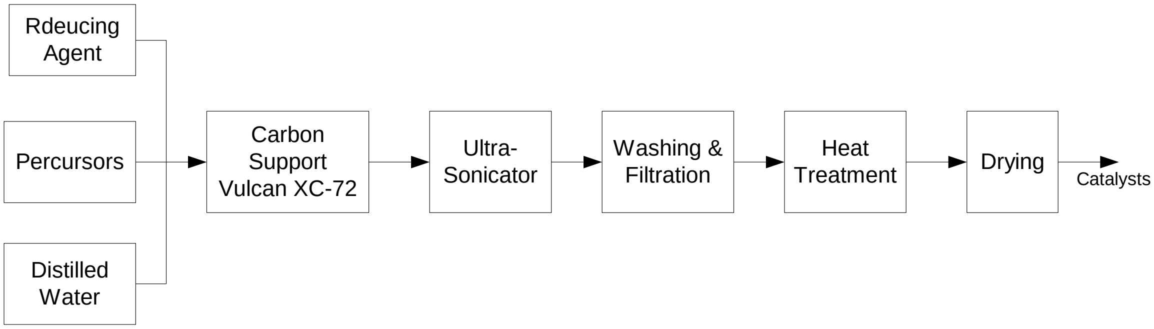

Figure 1: Schematic of the electrocatlysts synthesis method

MEA preparation

MEAs were prepared using brushing technique. Nafion112 was used as the proton conducting membrane electrolyte. Thick slurry was made out of the prepared catalyst powder, 5% Nafion solution and Teflon in 2-butanol. The slurry was stirred well and maintained at 70^{o}C. It was then loaded on the pretreated hydrophobic carbon paper by brushing technique, and the substrate was maintained at a relatively high temperature of 120^{o}C to evaporate the solvents. Spraying yields a slightly better performance than brushing, but brushing avoids wastage of catalyst powders by clogging. The catalyst loading of the thin film electrode was maintained at $0.4 mg/cm^2$ throughout the study. The loading was achieved using controlled weight and complete application of the slurry on to the hydrophobic carbon paper. The gas diffusion electrode thus prepared was hot pressed at a temperature of 110^{o}C at 130 bars for 2 minutes.

Experimental Setup

The experimental set-up used for testing and evaluation of the membrane electrode assemblies (MEAs) in the PEMFC is shown in Figure 2. Galvanostatic polarization measurements are carried out using the FUEL CELL TEST Station obtained from Fuel Cell Technologies, Inc, NM. A single cell of 5cm^2 area will be used for evaluating MEA in PEMFC. The DC current through the fuel cell is controlled by a HP 6060B Agilent power source. It is interfaced to a computer and data was collected using National Instrument's Data acquisition card. A LABVIEW program is used to interface and control these components and the mass flow controllers. Humidification is achieved using a dual humidification bottle subsystem and was read through the LABVIEW program.

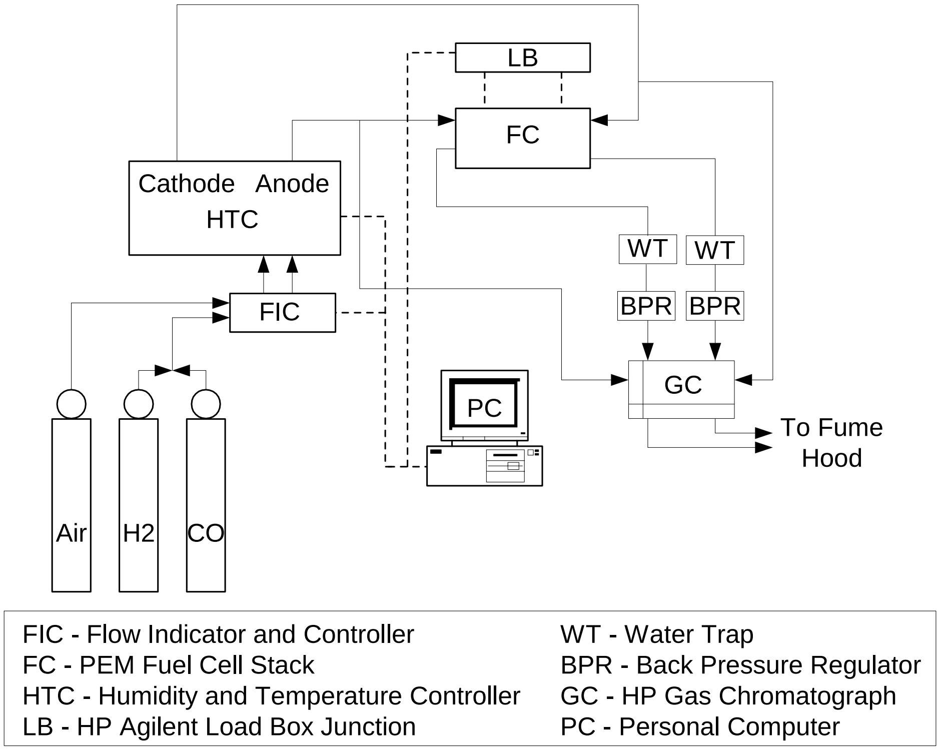

Figure 2: Schematic of Test Set-up of PEMFC for Evaluation of Electrocatalysts and MEASs.

RESULTS AND DISCUSSIONS

The following tri-metallic catalysts were prepared by both ultra-sonication and without ultrasonication step for use in MEAs:

20 wt% Pt/Ru/Mo on Carbon Vulcan XG72
20 wt% Pt/Ru/Ir on Carbon Vulcan XG72
20 wt% Pt/Ru/W on Carbon Vulcan XG72
20 wt% Pt/Ru/Co on Carbon Vulcan XG72
20 wt% Pt/Ru/Se on Carbon Vulcan XG72

The polarization curves for the above materials are shown in Figure 3. This graph shows that molybdenum alloyed with Pt/Ru is the most active catalyst followed by iridium and tungsten. This trend also follows those of other research findings. In some cases tungsten has been found to be more active than molybdenum in a ternary metal catalyst system [5]. The difference in the findings here may be due to the synthesis method employed in order to deposit the active metals onto the carbon support. Proprietary reduction methods have been used in order to deposit nanometer sized active metals onto their supports which could cause the active metals in a ternary metal catalyst to alloy differently from the method employed in this work. Figure 3 also shows that Pt/Ru alloyed with Mo, Ir, and W exhibit a similar voltage reading at a current density of 200 mA/cm^2. However, at higher current densities Pt/Ru/Mo has the better voltage reading than the other two metals.

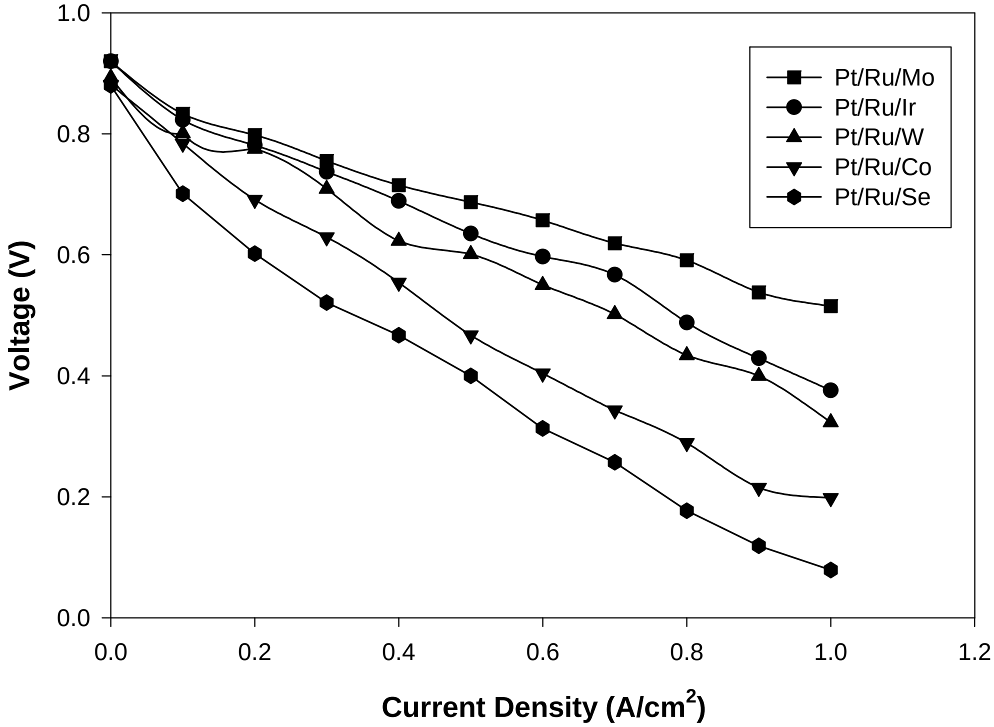

Figure 3: Current vs. Voltage curves for ternary electrocatalysts (20 wt%) with pure H_2 in the anode feed stream.

Figure 4 displays a comparison of the ternary catalysts synthesized by the method described in this work and those same ternary catalysts synthesized by a similar method without the sonication step. Once again, those catalysts with the sonication step exhibited a slightly higher voltage at the same current density for those without sonication. Better dispersion of the three active metals on the carbon support leads to a better voltage reading from the MEAs. The sonication step allows the reducing agent to successfully deposit the active metals Pt, Ru, Ir, Mo, and Co in their elemental form from their precursors on the support and allow for better co-catalytic activity in the fuel cell.

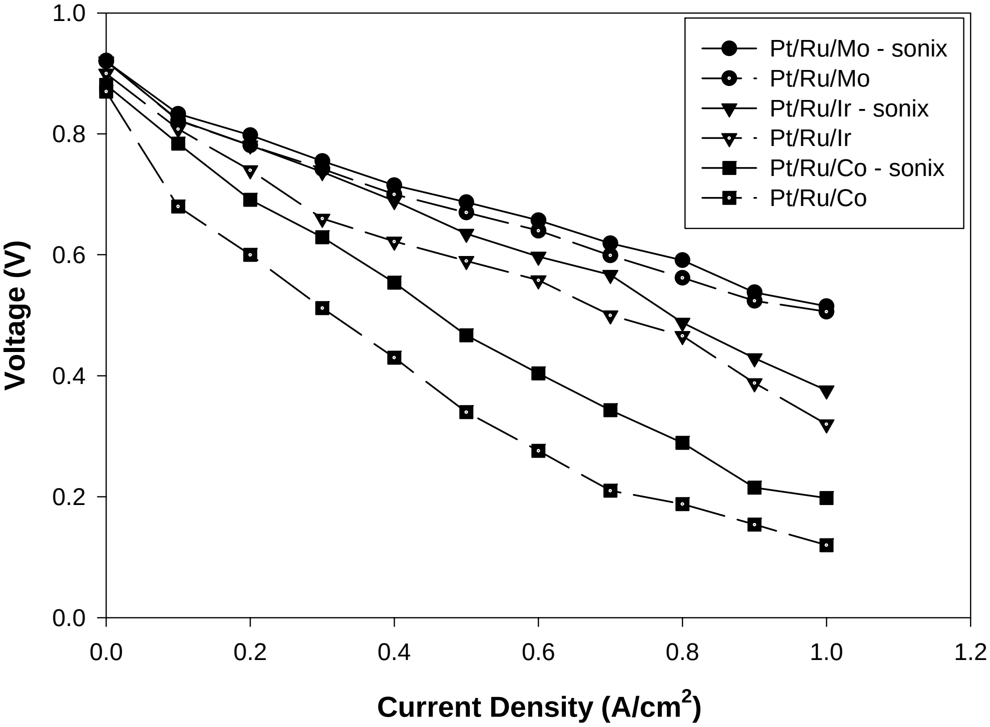

Figure 4: Performance comparison of in-house ternary metal catalysts (20 wt%) synthesized with sonication and without sonication with pure H_2 in the feed.

CONCLUSIONS

Based on the performance of bi-metallic catalysts, several tri-metallic electrocatalysts were prepared both by with and without ultra-sonication method. From polarization study, it appears that electrocatalysts prepared by ultra-sonication process are more active compared to the conventional technique. Work is in progress to further study these catalysts for CO-tolerance in PEMFC.

REFERENCES

1. Prater, K. B., "Solid Polymer Fuel Cell Developments at Ballard," *J. Power Sources*, **37**, 181 (1992).
2. Ralph, T., “Proton Exchange Membrane Fuel Cell: Progress in Costs Reduction of the Key Components,” *Platinum Metal Review*, **41**, 102 (1997).
3. Hirschenhofer, J. H., Stauffer, D. B., Engleman, R. R., and Klett, M. G., Fuel Cell Handbook, 4th Edition, DOE, DE-AC21-94MC31166, 1999.
4. Sharmin, S., S. Irulappan, and S. Ilias, “Synthesis of Novel Electrocatalysts for Proton Exchange Membrane Fuel Cells (PEMFC),” *Sep. Sci. Tech.*, **38**, 2963 (2003).
5. M. Götz, H. Wendt. “Binary and ternary anode catalyst formulations including the elements W, Sn and Mo for PEMFCs operated on methanol or reformate gas.” Electrochimica Acta, **43**, 3637 (1998).