

Report Title:

Synthesis and Characterization of CO- and H<sub>2</sub>S-Tolerant  
Electrocatalysts for PEM Fuel Cell

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Principal Author(s): Shamsuddin Ilias

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Name and Address of Submitting Organization:

North Carolina A&T State University  
Department of Mechanical and Chemical Engineering  
Greensboro, NC 27411

E-mail: [ilias@ncat.edu](mailto:ilias@ncat.edu)  
Tel: (336) 334-7564 ext. 317  
Fax: (336) 334-7904

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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<sub>2</sub>-fuel used or may be introduced during the fuel processing. Presence of trace amount of CO and H<sub>2</sub>S in the H<sub>2</sub>-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<sub>2</sub>S concentrations typical of those found in reformed fuel gas with coal/natural gas/methanol feedstocks.

During this reporting period we synthesized several tri-metallic electrocatalysts catalysts (Pt/Ru/Mo, Pt/Ru/Ir, Pt/Ru/W, Pt/Ru/Co, and Pt/Ru/Se on Vulcan XG72 Carbon) by ultrasonication method. These catalysts were tested in MEAs for CO tolerance at 20 and 100 ppm CO concentrations. From Galvonstatic study the catalytic activity was found in the order of: Pt/Ru/Mo/C > Pt/Ru/Ir/C > Pt/Ru/W/C > Pt/Ru/Co/C > and Pt/Ru/Se. The catalysts performed very well at 20 ppm CO but at 100 ppm CO performance dropped significantly.

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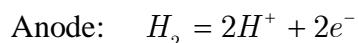
## EXECUTIVE SUMMARY

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<sub>2</sub>S in H<sub>2</sub>-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<sub>2</sub>S 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<sub>2</sub>S concentrations typical of those found in reformed fuel gas with coal/natural gas/methanol feedstocks.

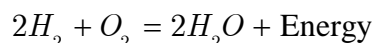
In our lab we synthesized several tri-metallic electrocatalysts (Pt/Ru/Mo, Pt/Ru/Ir, Pt/Ru/W, Pt/Ru/Co, and Pt/Ru/Se on Carbon) by ultrasonication process. The catalysts were evaluated for CO tolerance in PEMFC. It appears that Pt/Ru/Mo combination worked very well at 20 ppm CO contamination in the H<sub>2</sub>-fuel. At 100 ppm CO, the catalysts showed some co-catalytic activity but the voltage drop was significant which is expected. Work is in progress to further study these catalysts in quaternary form.

## 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<sub>2</sub>-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:



The over all fuel cell reaction is:



This Pt-catalyst is highly active but susceptible to poisoning by fuel impurities such as, H<sub>2</sub>S and CO, which may be present in the H<sub>2</sub>-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<sub>2</sub>-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<sub>2</sub>S-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<sub>2</sub>S-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 OBJECTIVES

The objectives of this research are to:

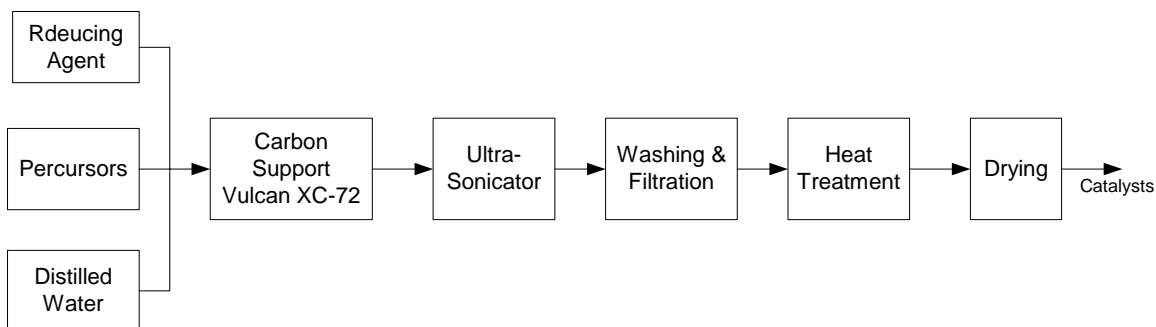
- Synthesize novel candidate electrocatalyst materials
- Characterize the electro-catalytic activity in pure hydrogen half-cell studies
- Demonstrate electrocatalyst feasibility in contaminated hydrogen half-cell studies
- Demonstrate H<sub>2</sub>/O<sub>2</sub> fuel cell performance with the improved 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 150°C, 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 electrocatalysts 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.



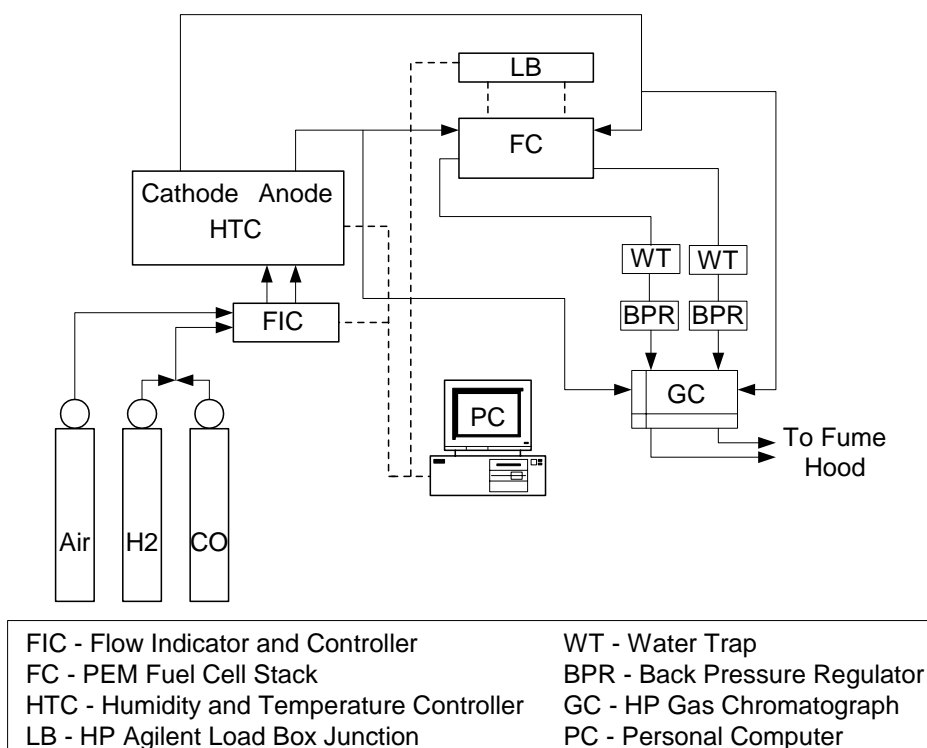
**Figure 1:** Schematic of the electrocatalysts synthesis method

### 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°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°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 0.4mg/cm<sup>2</sup> 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°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<sup>2</sup> 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 method for use in MEAs and were evaluated for CO tolerance in PEMFC:

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

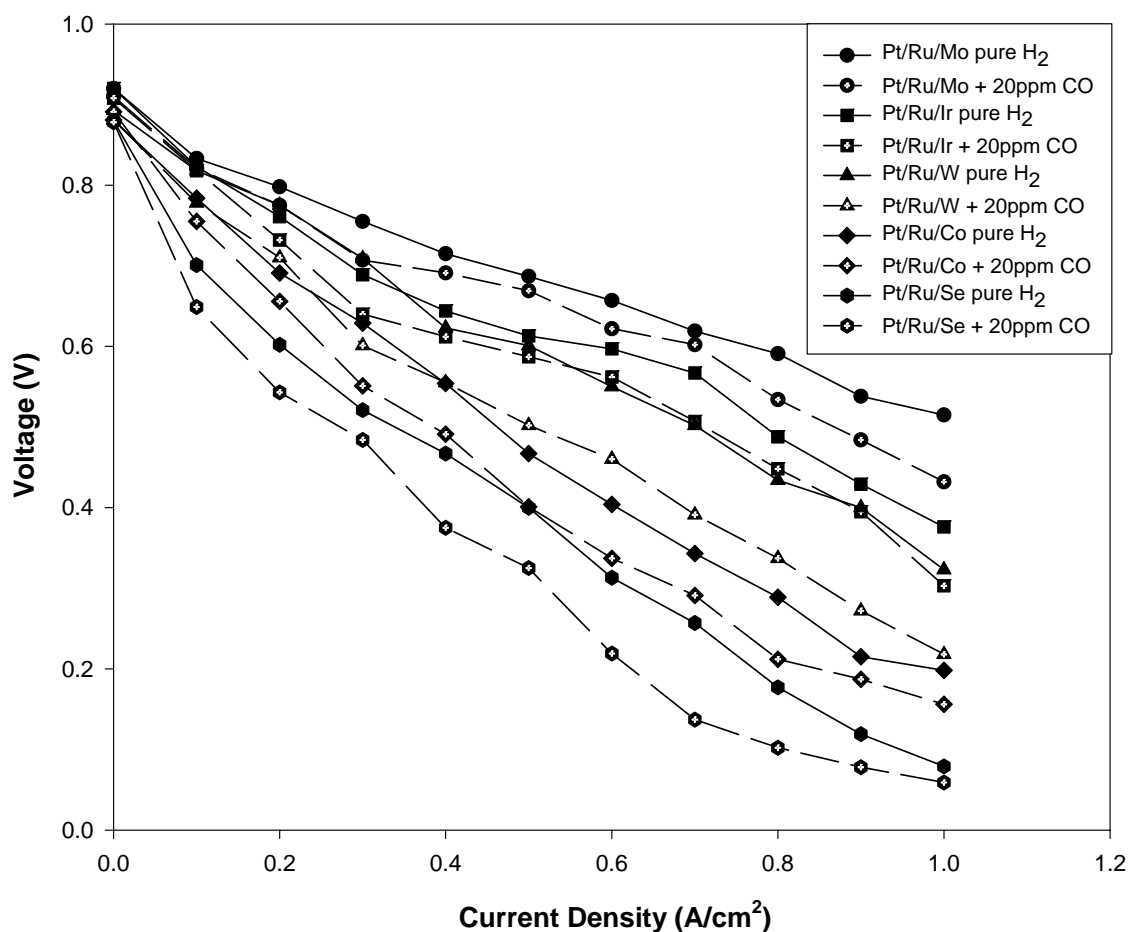
20 wt% Pt/Ru/Co on Carbon Vulcan XG72

20 wt% Pt/Ru/Se on Carbon Vulcan XG72



In order to make PEMFC more suitable for practical commercial applications a robust electrocatalyst for the MEA must be developed. While fuel cells operating on hydrogen produced from a reformer may be more practical, their performance decreases dramatically because of the inclusion of a few parts per million of carbon monoxide in the stream. Carbon monoxide chemisorbs onto the surface of the platinum in the electrocatalyst, poisoning the surface for H<sub>2</sub> oxidation and greatly reducing the electrical output of the cell. Research in the area of hydrocarbon reforming is geared toward developing catalysts which can convert the hydrocarbons into hydrogen with little to no CO at a relatively low temperature [5]. But developing CO tolerant electrocatalysts can help alleviate some of the burden in reforming while also lowering the total platinum loading in the catalysts.

The ternary metal candidates which were tested with pure H<sub>2</sub> as fuel to PEMFC were evaluated for CO tolerance. Two CO concentrations (20 ppm and 100 ppm in H<sub>2</sub> feed) were used in this study to simulate the operation from reformat gas. Figure 3 displays the polarization curves for the ternary catalysts with pure H<sub>2</sub> and 20 ppm CO in the feed.

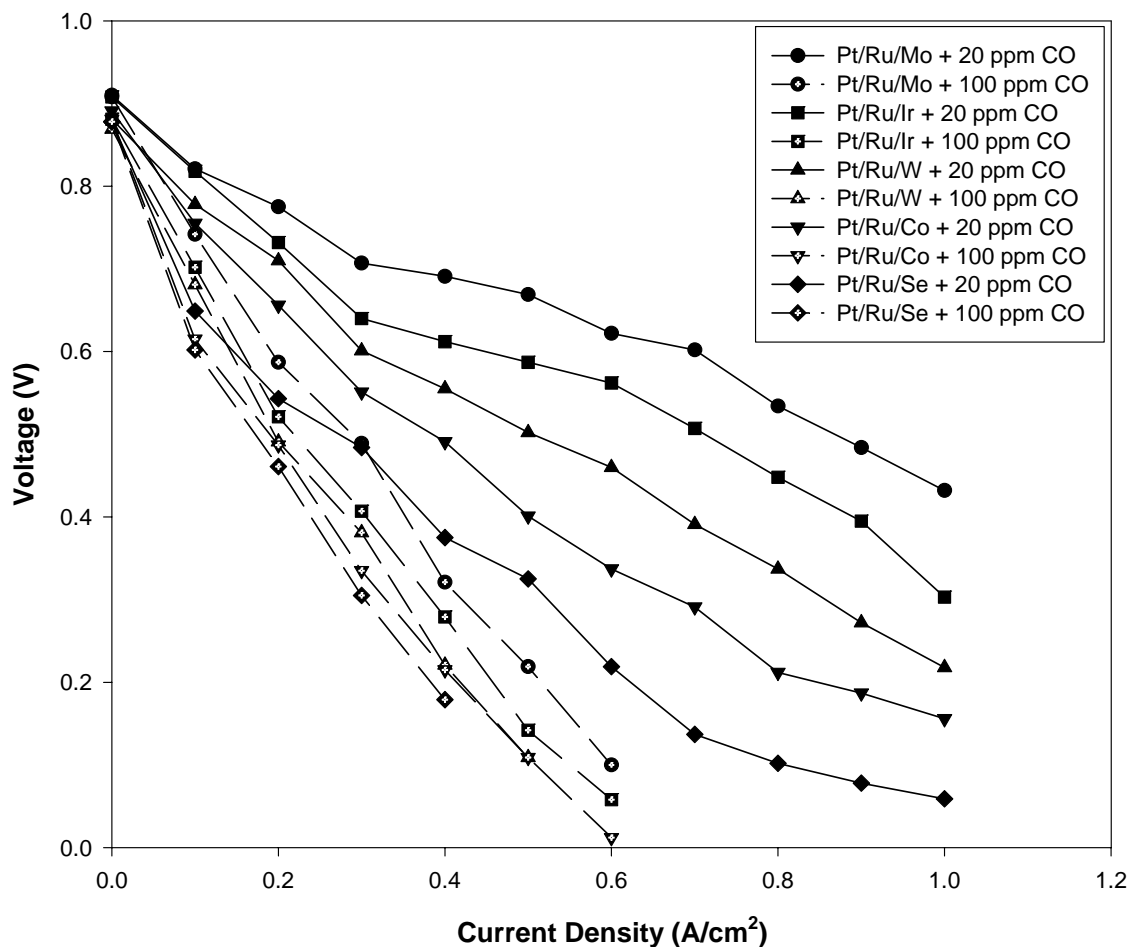


**Figure 3:** Current vs. Voltage curves for ternary electrocatalysts (20 wt%) with pure H<sub>2</sub> and 20 ppm CO in the feed.

The results show that Pt/Ru alloyed with Mo, Ir and W have very good co-catalytic activity towards carbon monoxide oxidation reaction in an MEA. The above figure also shows

that there was not much of a drop off in performance with the Pt/Ru/Mo, Pt/Ru/Ir and Pt/Ru/W catalysts when 20 ppm CO is added to the feed stream. The increased CO tolerance of the Pt/Ru/Mo catalyst can be attributed to the ability for Mo to promote the CO oxidation process at very low electrode potentials [6]. This was attributed to oxygen transfer from molybdenum oxyhydroxide species with only the OH species of the oxyhydroxide states, predominantly  $\text{MoO}(\text{OH})_2$ , being reactive with absorbed CO [7]. There was a significant loss in performance of the cell when 100 ppm of CO was added to the feed for all of the ternary catalysts.

Figure 4 shows the polarization curves for the ternary catalysts with 20 ppm and 100 ppm of CO in the  $\text{H}_2$  stream. Even the most active ternary catalysts at 20 ppm CO, the Pt/Ru/Mo catalyst, did not produce a significant voltage output beyond  $600 \text{ mA/cm}^2$  with 100 ppm CO in the feed.



**Figure 4:** Current vs. Voltage curves for ternary electrocatalysts (20 wt%) with 20 ppm and 100 ppm CO in the  $\text{H}_2$ -feed.

## CONCLUSIONS

The tri-metallic electro-catalysts that we synthesized in our lab for use in MEAs, it appears that Pt/Ru/Mo combination worked very well at 20 ppm CO contamination in the  $\text{H}_2$ -

fuel. At 100 ppm CO, the catalysts showed some co-catalytic activity but the voltage drop was significant which is expected. Work is in progress to further study these catalysts in quaternary form.

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