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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 bi-metallic electrocatalysts were synthesized and tested in MEAs. From Galvonstatic study the catalytic activity was found in the order of: Pt/Ru/C > Pt/Mo/C > Pt/Ir/C > Pt/Ni/C > Pt/Cr/C. Work in progress to further study these catalysts for CO-tolerance in PEMFC and identify potential candidate metals for synthesis of tri-metallic electrocatalysts.

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 several bi-metallic electrocatalysts were synthesized and tested in MEAs. From Galvonstatic study the catalytic activity was found in the order of: Pt/Ru/C > Pt/Mo/C > Pt/Ir/C > Pt/Ni/C > Pt/Cr/C. These catalysts will be further tested for CO-tolerance in PEMFC and then identify potential candidate metals for synthesis of tri-metallic electrocatalysts.

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.

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 0.4mg/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 1. 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.

RESULTS AND DISCUSSIONS

A of Pt-based bi-metallic electro-catalysts were prepared and evaluated for their performance efficiency and CO tolerance in PEMFC. The cell performance was evaluated as a function of catalyst composition. The output from the PEMFC is measured at standard reaction conditions of 85^{o}C. Catalyst performances were evaluated through polarization studies. A polarization curve is a plot of cell voltage against current density at any given temperature and flow rate.

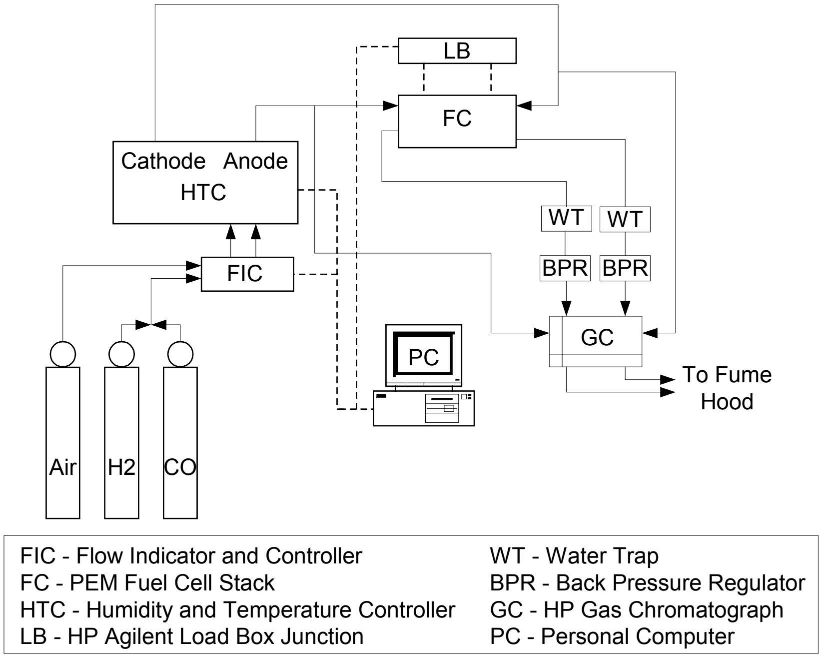

Figure 1: Schematic of Test Set-up of PEMFC for Evaluation of Electrocatalysts and MEASs.

The metal alloy catalysts prepared by co-deposition method for use in MEAs. The bimetallic catalysts prepared are: Pt/Ru/C; Pt/Mo/C; Pt/Ir/C; Pt/Ni/C; and Pt/Co/C. The metal ratios were maintained at equal atom wt% with a total metal loading of 20 wt%. A commercial MEA obtained from ElectroChem having 20 wt % Pt/C was used to obtain the baseline performance curve of the PEMFC.

Polarization experiments were carried out at 85^{o}C under constant stoichiometric flow of gases. A typical polarization curve of Pt/C (20 wt %) is shown in Figure 2, which has been used as standard reference curve (base case) for comparison of performance of electro catalysts. An open circuit voltage of 0.91V was measured at standard experimental conditions. Figure 2 shows the performance of the PEMFC with pure and CO-contaminated hydrogen at two concentration levels (10 and 100 ppm) as fuel. With increasing CO concentration, the cell performance deteriorates very rapidly. This deterioration of the catalyst activity can be explained by the chemisorptions of the CO molecules on the active sites of the Pt-catalyst.

Figure 3 shows the co-catalytic activity of each of Ru, Mo, Ir, Ni and Co towards the oxidation reaction along with Pt at 20-wt%. Pt/Ru/C shows the highest activity and it can also be noted that Pt/Mo/C binary system competes with the Pt/Ru/C system with its performance imparting almost the same performance of Pt/Ru/C. This suggests that Ru and Mo impart strongest co-catalytic activity for the oxidation reaction, than by Ir, Ni and Co. Although Pt/Ru/C shows the lowest polarization at low current densities, it shows higher polarization at larger current densities. On the other hand Pt/Ir/C and Pt/Co/C show optimal performance with lower polarization. From cell performance, the catalytic activity of the binary catalysts was found as:

Pt/Ru/C > Pt/Mo/C > Pt/Ir/C > Pt/Ni/C > Pt/Cr/C. These results will be used as a basis to formulate tri-metallic catalysts as we make progress.

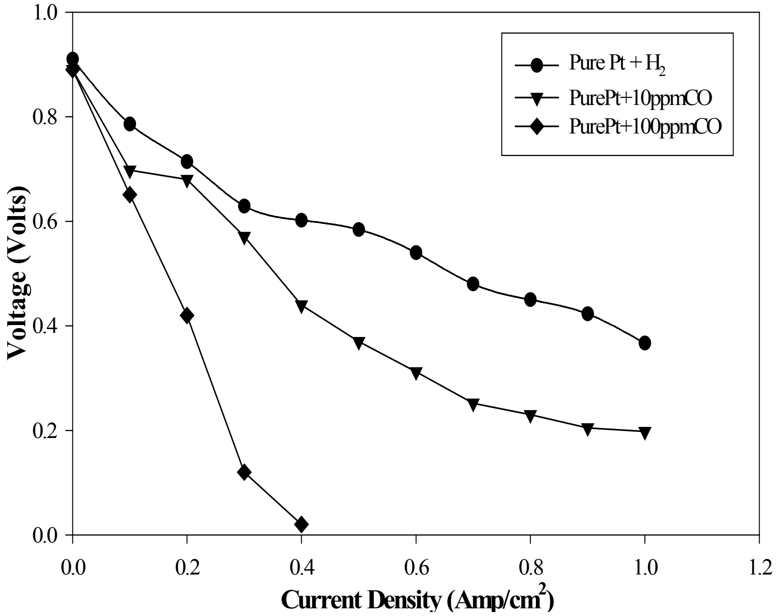

Figure 2: Current-Voltage curves of pure Pt (20wt%) catalyst with pure H2 and with 10 and 100ppmCO with the fuel.

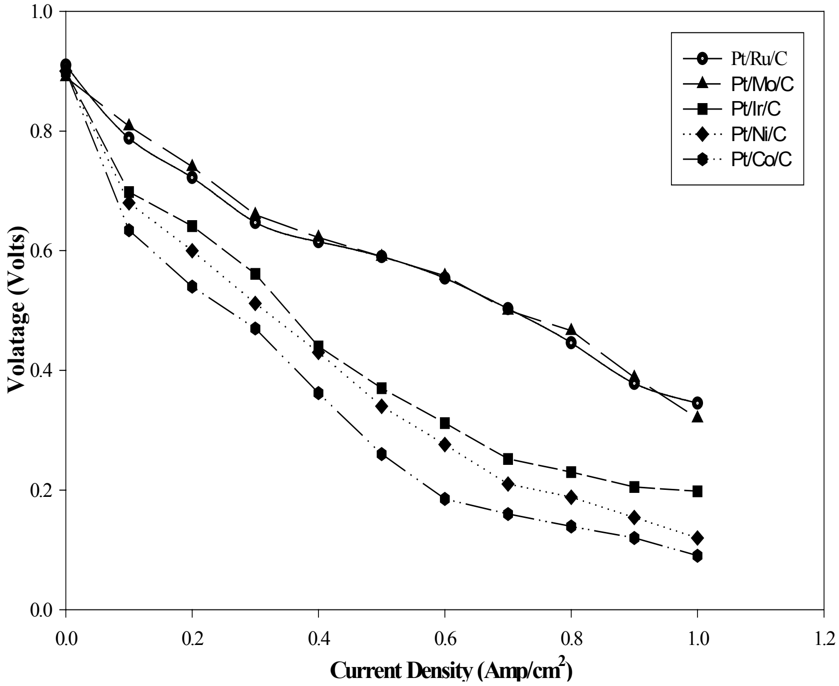

Figure 3: Performance curves of the MEAs prepared using in-house binary metal catalysts, (Atomic metal ratios 1:1).

CONCLUSIONS

Several bi-metallic electrocatalysts were synthesized and tested in MEAs. From Galvonstatic study the catalytic activity was found in the order of: Pt/Ru/C > Pt/Mo/C > Pt/Ir/C > Pt/Ni/C > Pt/Cr/C. Work in progress to further study these catalysts for CO-tolerance in PEMFC and identify potential candidate metals for synthesis of tri-metallic electrocatalysts.

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