

Report Title:

Synthesis and Characterization of CO- and H₂S-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 H₂-fuel used or may be introduced during the fuel processing. Presence of trace amount of CO and H₂S in the H₂-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 H₂S concentrations typical of those found in reformed fuel gas with coal/natural gas/methanol feedstocks.

In this work binary, ternary, and quaternary platinum-based electrocatalysts were synthesized for the purpose of lowering the cost and increasing the CO tolerance of the membrane electrode assembly (MEA) in the fuel cell. The metals Ru, Mo, W, Ir, Co and Se were alloyed with platinum on a carbon support using a modified reduction method. These catalysts were fabricated into MEAs and evaluated for electrical performance and CO tolerance with polarization experiments. The quaternary system Pt/Ru/Mo/Ir system is the most CO tolerant in the PEMFC and has a low total metal loading of 0.4 mg/cm² in the electrode of the cell.

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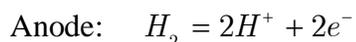
EXECUTIVE SUMMARY

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 H₂S in H₂-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 H₂S 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 H₂S concentrations typical of those found in reformed fuel gas with coal/natural gas/methanol feedstocks.

In this work we used a modified synthesis method to prepare Pt-based binary, ternary and quaternary electrocatalysts on carbon support. Non-noble metals that we investigated include Ir, Mo, W, Co and Se. The addition of ultrasonication in the synthesis step improved the electrical performance of the fuel cell as observed from polarization study. The synthesized Pt-based electrocatalysts were well dispersed on the carbon support as confirmed by SEM. The Pt/Ru/Mo/C and Pt/Ru/Mo/Ir/C catalysts showed a better CO tolerance when compared to the other in-house catalysts with 20 ppm of CO in the feed stream.

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 H₂-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, H₂S and CO, which may be present in the H₂-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 H₂-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 H₂S-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 H₂S-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 H₂/O₂ fuel cell performance with the improved electrodes in contaminated hydrogen environment

EXPERIMENTAL: MATERIALS & METHODS

In our previous report, methods used for electrocatalysts and MEA preparations, experimental methods MEA performance study have been discussed and are not repeated here. During this reporting period, we synthesized several Pt-based quaternary catalysts for MEA.

RESULTS AND DISCUSSIONS

Using both conventional and ultrasonication method, we synthesized Pt-based binary, ternary and quaternary catalysts on XG72 carbon support. The metals that were alloyed with Pt in binary, ternary and quaternary combinations include Ru, Mo, W, Ir, Co and Se. From a large number of experiments, the catalytic activity of the synthesized catalysts were found to be in the order of Pt/Ru/Mo/Ir > Pt/Ru/Mo > Pt/Ru > Pt.

Figure 1 shows the comparison of the binary, ternary, and quaternary catalysts made in this work to a commercial Pt/C catalyst. Not only was the amount of platinum loading decreased in the MEA but the overall performance of the fuel cell was enhanced. It can be observed that the synthesis method employed successfully dispersed the active metals on the carbon support and increased the electrical performance of the cell while maintaining a platinum loading less than 0.4 mg/cm^2 for each catalyst.

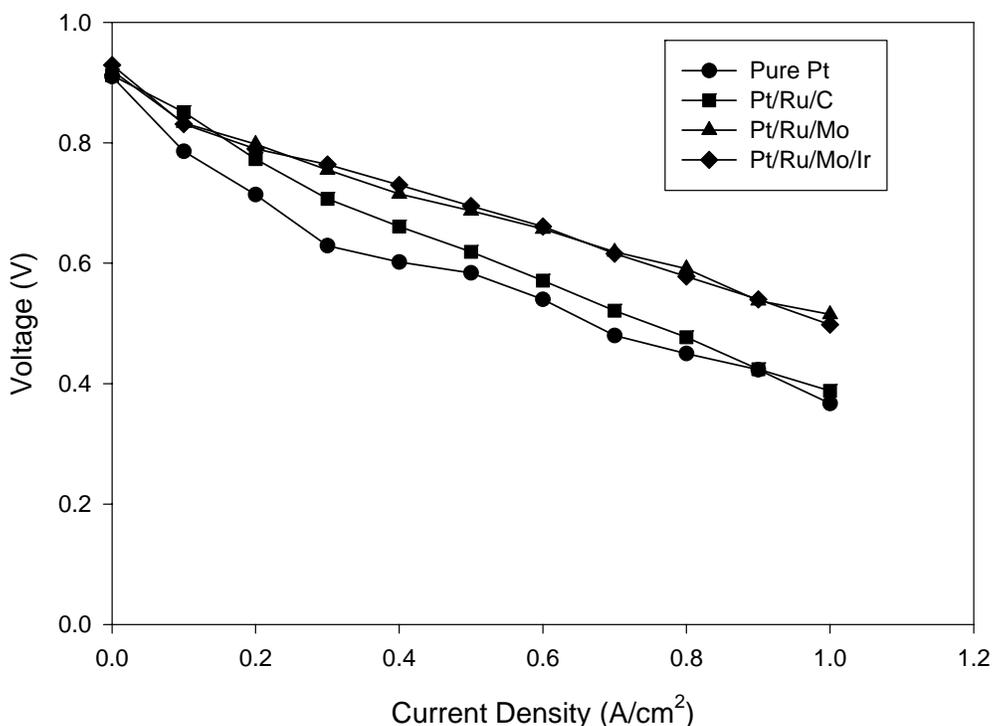


Figure 1: Comparison of current vs. voltage curves for in-house binary, ternary and quaternary (20 wt%) catalysts and a commercial Pt-based MEA.

The CO tolerance of the MEA was also enhanced when compared to a commercial MEA as seen in Figure 2. The CO tolerance of the fuel cell at 20 ppm is considerably greater for the Pt/Ru/Mo and Pt/Ru/Mo/Ir catalysts developed in-house.

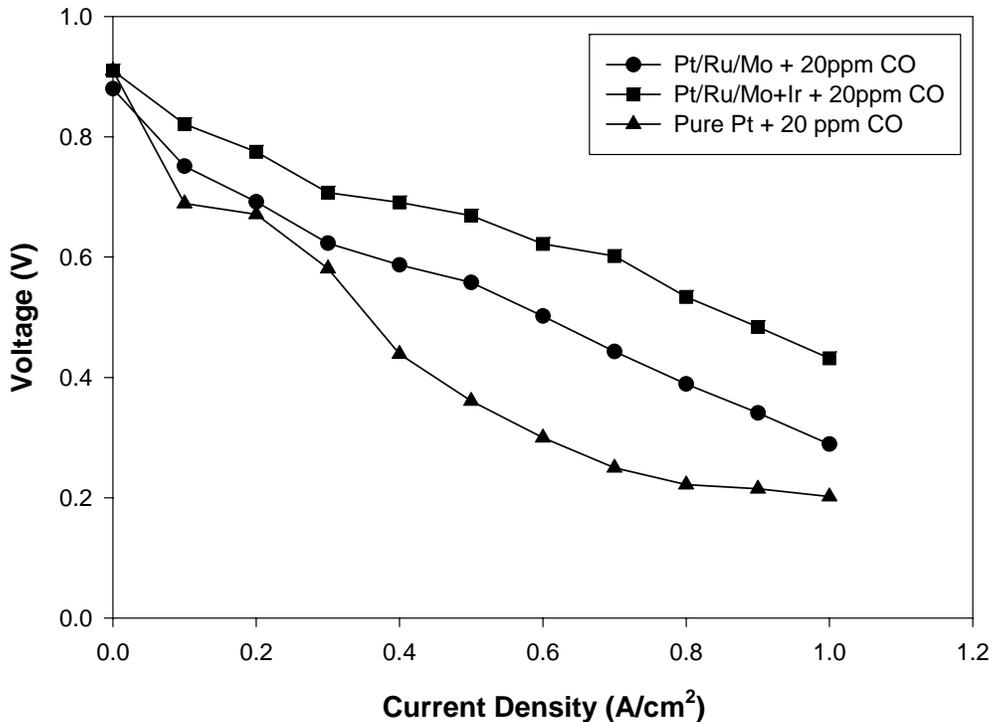


Figure 2: Comparison of current vs. voltage curves for in-house ternary and quaternary (20 wt%) catalysts and commercial Pt/C MEA with 20 ppm of CO in the feed stream.

The electrocatalysts synthesized in this work were examined by SEM for surface morphology. Figure 3 is a SEM image of an in-house Pt/Ir/C catalyst magnified at 30k. The SEM image shows that the platinum and iridium were successfully deposited onto the support with a nanometer size diameter. Small active metal size is important because the materials can be dispersed more evenly on the Vulcan XG72 carbon and thus more active sites will be available for the H₂ oxidation and O₂ reduction reactions in the MEA [4]. More available active sites due to dispersion will also allow for better CO tolerance of the fuel cell.

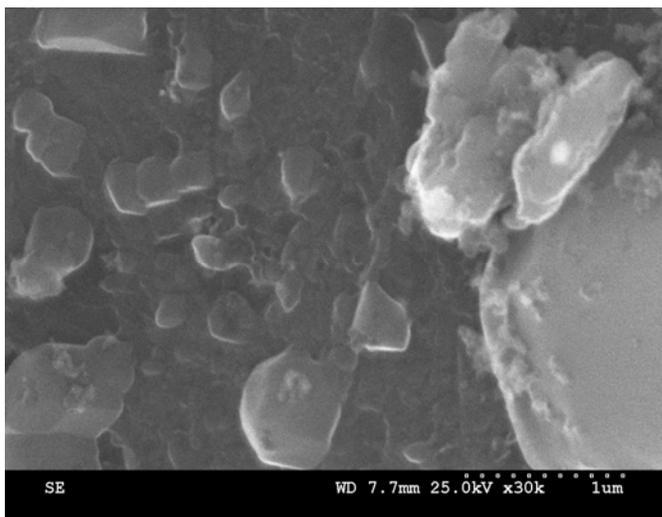


Figure 3: SEM image of in-house Pt/Ru/C catalyst (30K magnification).

CONCLUSIONS

The modified synthesis method successfully alloyed non-noble metals Ir, Mo, W, Co and Se with platinum and dispersed them more evenly along the active carbon support as confirmed by SEM. The addition of ultrasonication in the synthesis step improved the electrical performance of the fuel cell when compared to similar catalysts made in a previous work. The Pt/Ru/Mo/C and Pt/Ru/Mo/Ir/C catalysts showed a better CO tolerance when compared to the other in-house catalysts with 20 ppm of CO in the feed stream. The Pt/Ru/Mo/Ir/C and Pt/Ru/Mo/C catalysts exhibited superior performance in the fuel cell with pure H₂ and contaminated H₂ in the feed when compared to a commercial Pt/C MEA.

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