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 we synthesized four Pt-based electrocatalysts catalysts (Pt/Ru/Mo/Se, Pt/Ru/Mo/Ir, Pt/Ru/Mo/W, Ptr/Ru/Mo/Co) on Vulcan XG72 Carbon support by both conventional and ultra-sonication method. From current-voltage performance study, the catalytic activity was found in the increasing order of Pt/Ru/Mo/Ir > Pt/Ru/Mo/W > Pt/Ru/Mo/Co > Pt/Ru/MO/Se. Sonication method appears to provide better dispersion of catalysts on carbon support.

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 four Pt-based electrocatalysts catalysts (Pt/Ru/Mo/Se, Pt/Ru/Mo/Ir, Pt/Ru/Mo/W, Ptr/Ru/Mo/Co) on Vulcan XG72 Carbon support by both conventional and ultra-sonication method. From current-voltage performance study, the catalytic activity was found in the increasing order of Pt/Ru/Mo/Ir > Pt/Ru/Mo/W > Pt/Ru/Mo/Co > Pt/Ru/MO/Se. Sonication method appears to provide better dispersion of catalysts on carbon support. Work is in progress to further study these quaternary catalysts for CO-tolerance in PEM Fuel Cell.

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:

Anode: $H_2 = 2H^+ + 2e^-$

Cathode: $O_2 + 4H^+ + 4e^- = 2H_2O$

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

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

Not much work has been published on the study of platinum-based quaternary catalysts for PEM fuel cells. As discussed in the previous reports, our Pt-based ternary metal catalysts appear to out-perform Pt-catalysts in presence of CO. With these encouraging results, we investigated Pt-base quaternary metal catalysts. As with the previous tri-metallic and bi-metallic catalysts, an atomic ratio of 1:1:1:1 of active metal on the carbon support was used for the candidate catalysts. This would not only allow for the reduction in platinum loading, but it would also give a better dispersion of the active material on the support. Better dispersion would lead to more co-catalytic activity of the alloyed catalysts in the MEA of the fuel cell.

The better performing alloyed catalysts from the ternary and binary systems were chosen to be studied as quaternary catalysts:

- Pt/Ru/Mo/Ir on carbon
- Pt/Ru/Mo/W on carbon
- Pt/Ru/Mo/Co on carbon
- Pt/Ru/Mo/Se on carbon

Figure 1 shows the current-voltage performance plots for these quaternary catalysts with pure hydrogen in the feed. This graph shows that the Pt/Ru/Mo/Ir/C electrocatalyst gave the best performance of the candidates followed by Pt/Ru/Mo/W/C. While the overall electrical output of the fuel cell may not have increased significantly when compared to the ternary catalysts, the additions of Ir and W allowed for lower platinum loading in the MEA and thus reduced the overall cost of the fuel cell.

Figure 2 shows the comparison of quaternary metal catalysts made in this study and those made in a previous study from a similar method. The materials developed with sonication show a slightly better performance in the MEA for a given current density. With similar metal loadings, the sonication step dispersed the active metals more evenly along the active carbon support allowing for more active sites on the catalyst, thus giving a better electrical performance in the fuel cell.

CONCLUSIONS

Four quaternary catalysts were synthesized in our lab for use in MEAs using both conventional and sonication methods. From current-voltage performance study, the catalytic activity was found in the increasing order of Pt/Ru/Mo/Ir > Pt/Ru/Mo/W > Pt/Ru/Mo/Co > Pt/Ru/MO/Se. Sonication method appears to provide better dispersion of catalysts on carbon support.

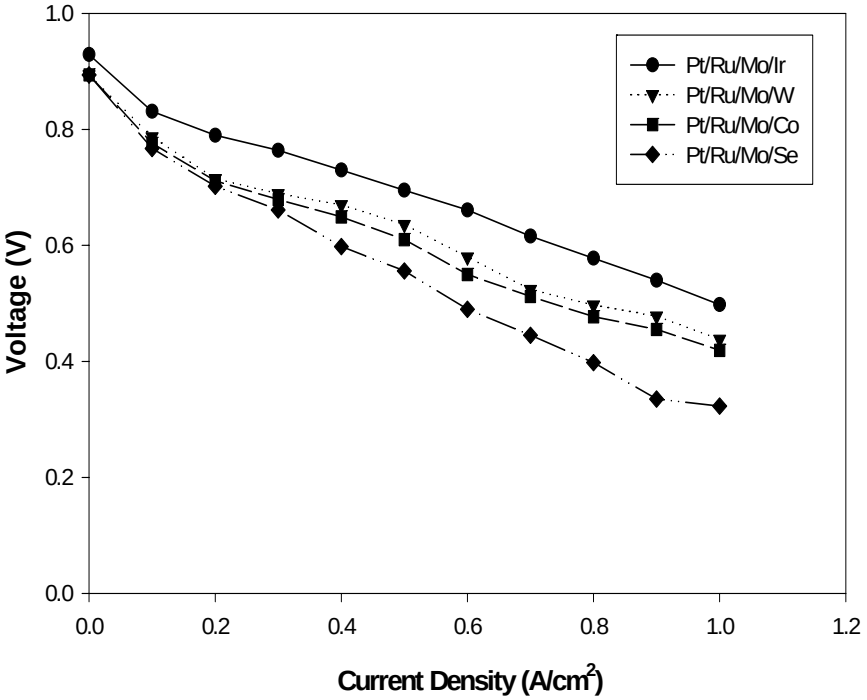

Figure 1: Current vs. Voltage curves for quaternary metal (20 wt%) catalysts with pure H_2 in the feed stream.

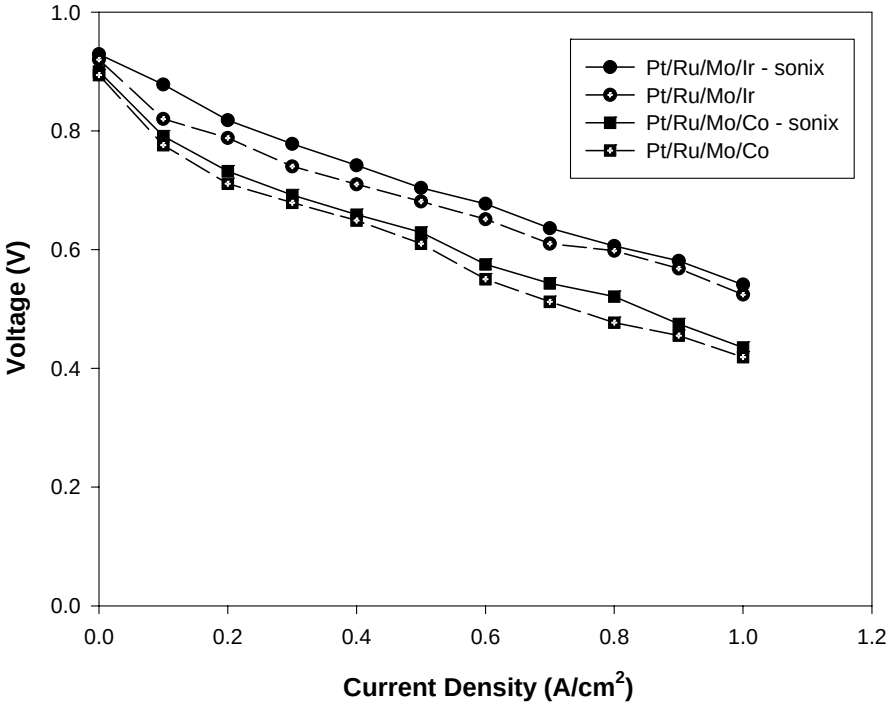

Figure 2: Performance comparison of current vs. voltage plots of quaternary metal (20 wt%) catalysts made with sonication and without sonication.

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