Report Title:

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

Report Type: Semi-Annual Technical Report

Reporting Period Start Date: 10/01/2005 End Date: 03/31/2006

Principal Author(s): Shamsuddin Ilias

Report Issue Date: May 18, 2006 DOE Award No.: DE-FG26-02NT41673

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
Tel: (336) 334-7564 ext. 317
Fax: (336) 334-7417

DISCLAIMER

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 used four Pt-based electrocatalysts (Pt/Ru/Mo/Se, Pt/Ru/Mo/Ir, Pt/Ru/Mo/W, Ptr/Ru/Mo/Co) in MEAs and these were evaluated for CO-tolerance with 20 and 100 ppm CO concentration in H_2-fuel. 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. From preliminary cost analysis it appears that could of the catalyst metal loading can reduced by 40% to 60% depending on the selection of metal combinations without compromising the fuel cell performance.

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.

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 were evaluated for CO-tolerance in PEM Fuel Cell. The catalysts were found tolerant to CO at 20 and 100 ppm and from the 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.

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

Using ultrasonication method, we prepared following quaternary catalysts on Vulcan XG72 carbon support:

- Pt/Ru/Mo/Ir on XG72 Carbon support
- Pt/Ru/Mo/W on XG72 Carbon support
- Pt/Ru/Mo/Co on XG72 Carbon support
- Pt/Ru/Mo/Se on XG72 Carbon support

Based on our prior work on bi-metallic and tri-metallic electrocatalysts, an atomic ratio of 1:1:1:1 of active metal on the carbon support was used for these quaternary electrocatalysts. The ability of a few of the ternary catalysts to oxidize carbon monoxide in the MEA leads to better CO tolerance in the fuel cell [4]. The quaternary metal catalysts chosen in this study were based upon the success of the Pt/Ru/Mo system, and exhibited notable CO tolerance in the MEA. Figure 1 shows the CO tolerance of the catalysts with 20 ppm and 100 ppm of CO in the hydrogen feed stream. The overall performance of the fuel cell operating under reformate conditions did not increase significantly. The additions of the non noble metals Ir and W allowed for a lower platinum loading in the MEA. The transition metals Co and Se did not contribute to increasing the CO tolerance of the fuel cell. However, none of the MEAs made in this work exhibited a significant voltage output beyond 700 mA/cm^2 with 100 ppm of CO in the H_2 feed. However, when compared with Pt/C catalyst under similar CO-concentrations, the quaternary catalyst Pt/Ru/Mo/Ir/C out performed the reference Pt/C catalyst as seen from the current voltage study.

Given the electrochemical performance of the materials, it is important to analyze the cost of each catalyst in order to understand which candidate would be most economical to use in the PEM fuel cell. Table 1 shows the costs of producing 100 grams of the alloyed catalyst and the pure platinum on carbon catalyst. The cost of the Pt/C catalyst is more than any of the binary, ternary, or quaternary Pt-based electrocatalysts synthesized in-house. When comparing the cost and the performance of the materials, the ternary Pt/Ru/Mo/C catalyst would be the economical choice for use in the fuel cell because it combines performance with a relatively low cost. Cost savings could be 40 to 60% depending upon the selection of metal combinations.

CONCLUSIONS

Using ultrasonication method four quaternary catalysts were synthesized for use in MEAs to evaluate their CO-tolerance in PEM Fuel Cell. 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 and these results compare very favorably with Pt/C catalysts under similar operating conditions. By using this new electrocatalysts, it is is possible to reduce the cost of metal-loadings by 40 to 60% depending upon the choice of metal combinations.

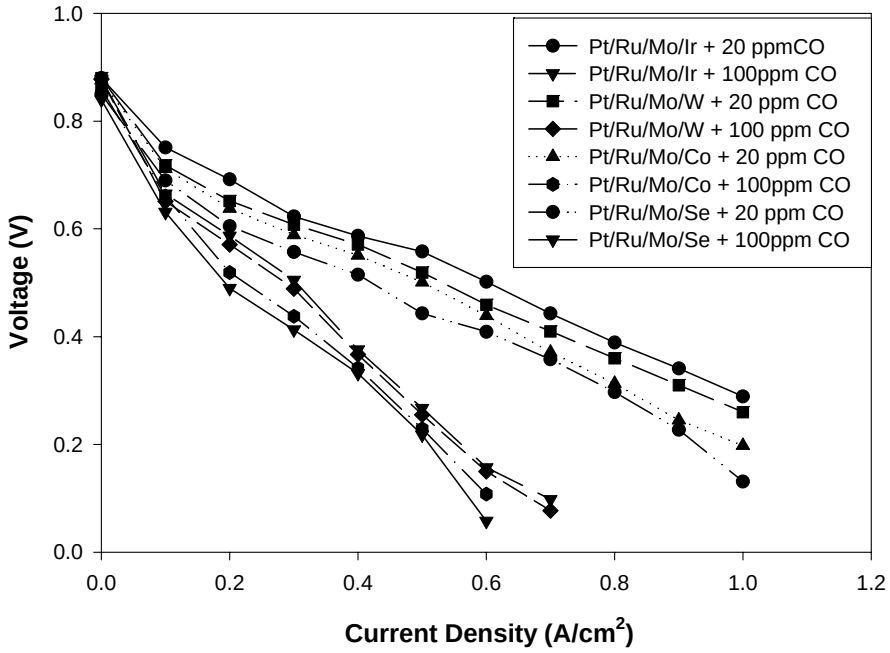

Figure 1: Current-voltage plots for quaternary metal catalysts at 20% metal loading with 20 and 100 ppm CO in H_2-fuel.

Table 1: Cost of Producing 100 g of catalysts

Pt/C Cost	Binary Catalyst	Cost	Ternary Catalyst	Cost	Quaternary catalyst	Cost
$20.16	Pt/Ru/C	$15.06	Pt/Ru/Mo/C	$10.16	Pt/Ru/Mo/Ir/C	$12.13
	Pt/Mo/C	$10.19	Pt/Ru/Ir/C	$16.18	Pt/Ru/Mo/W/C	$7.88
	Pt/Ir/C	$19.17	Pt/Ru/W/C	$10.48	Pt/Ru/Mo/Co/C	$8.43
	Pt/W/C	$10.66	Pt/Ru/Co/C	$11.22	Pt/Ru/Mo/Se/C	$8.05
	Pt/Se/C	$11.01	Pt/Ru/Se/C	$10.71		

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. Hou, Z., et al., "CO tolerance electrocatalyst of PtRu-H_xMeO_3/C (Me = W, Mo) made by composite support method." *Journal of Power Sources*, **123**, 116 (2003).