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Development of Novel Electrocatalysts for Proton Exchange
Membrane Fuel Cells

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ABSTRACT

Proton Exchange Membrane Fuel Cell (PEMFC) is one of the most promising power sources for space and electric vehicle applications. Platinum (Pt) catalyst is used for both fuel and air electrodes in PEMFCs. The carbon monoxide (CO) contamination of H₂ greatly affects electrocatalysts used at the anode of PEMFCs and decrease the cell performance. 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-tolerant catalyst is needed.

In this work, we have synthesized several novel electrocatalysts (Pt/C, Pt/Ru/C Pt/Mo/C, Pt/Ir and Pt/Ru/Mo) for PEMFCs. These catalysts have been tested for CO tolerance in the H₂/air fuel cell. The concentration of CO in the H₂ fuel varied from 10 ppm to 100 ppm. The performance of the electrodes was evaluated by determining the cell potential against current density. The effect of temperature, catalyst compositions, and electrode film preparation methods on the performance of PEM fuel cell has also been studied. It was found that at 70 °C and 3.5 atm pressure at the cathode, Pt-alloy catalysts (10 wt % Pt/Ru/C, 20 wt % Pt/Mo/C) were more CO-tolerant than 20 wt % Pt catalyst alone. It was also observed that spraying method is better for the preparation of electrode film than the brushing technique. Some of these results are summarized in this report

TABLE OF CONTENTS

Title page	i
Disclaimer	ii
Abstract	iii
Table of Contents	iv
Executive Summary	v
Introduction	1
Experimental	2
Results and Discussion	3
Conclusions	5
References	5

EXECUTIVE SUMMARY

The power generation in the Proton Exchange Membrane Fuel Cell (PEMFC) is based on Pt as a catalyst for both the fuel and air electrodes. This catalyst is highly active but susceptible to fuel impurities such as, S and CO, which may be present in the fuel used or may be introduced during fuel processing such as, reforming. These impurities poison the anode irreversibly and decrease the performance of the PEMFCs. Our work is to develop novel electro-catalysts for PEMFCs to reduce system costs and to enhance operating life before fuel cell can become commercially competitive with conventional means of power generation in the industrialized world.

In this work, novel electrocatalysts for PEMFCs has been developed. The catalysts were evaluated in a H₂/air fuel cell. The effects of temperature, and catalyst compositions on PEMFCs performance were studied. Several Pt-alloy catalysts (alloyed with Ru, Mo and ,Ir) were tested for CO-tolerance in the 20 ppm to 100 ppm range. From the PEMFC performance curve, it was concluded that catalysts formulated with Pt-Ru and Pt-Ru-Mo were more CO tolerant than Pt alone. By adding alloying metals like Ru and Mo in Pt, it is possible to reduce Pt loading significantly without compromising the cell performance. This would lead to low-cost PEMFC electro-catalysts.

INTRODUCTION

The fundamental chemical reaction to produce water from oxygen and hydrogen is given as:

Fuel cells are electrochemical devices that convert the available chemical free energy directly into electrical energy, without going through the heat exchange process [1,2]. Earlier, it was thought that, this type of energy would be used only for some special purposes like space travel. In recent years, there have growing interest in developing fuel cell technologies for down-to-earth applications. Because of the high efficiency and almost zero emission to the environment, these fuel cells are finding applications in chemical process industries (CPI) as stand-alone or on site power generators and in motor vehicles.

The present state-of-art Proton Exchange Membrane Fuel Cell (PEMFC) technology is based on Pt as a catalyst for both the fuel and air electrodes. This catalyst is highly active but susceptible to fuel impurities such as, S and CO, which may be present in the fuel used or may be introduced during fuel processing such as, reforming. These impurities poison the anode irreversibly and decrease the performance of the PEMFCs. Work is still needed to reduce system costs and to enhance operating life before the fuel cell can become commercially competitive with conventional power systems.

In this work, we plan to develop novel electrocatalysts for PEM fuel cells and will demonstrate the feasibility of a H₂/O₂ fuel cell based on these materials. Part of the work would be focussed on developing procedure for preparing metal catalysts loaded on carbon matrix. Novel catalysts will combine with the known high activity of the Pt and other noble metals, such as Ru, Pt/Mo, Pt/Ru/Mo, Pt/W, Pt/Ru/W, Pt/WC, Pt/Ru/WC. Other possible metals may include Sn and Ir. Successful development of these electrocatalysts will lead to several advantages:

- It will eliminate the need for expensive treatment of the fuel feed stream to remove these contaminants as presently required
- It will reduce weight and result in compact fuel cell power system with improved energy efficiency
- It will lower the costs due to reduce Pt catalyst loading or use of non-precious metal catalyst and will have direct application in commercial and private sector.

The major tasks of this project may be summarized as follows.

Task 1: Synthesis of candidate electrocatalyst materials.

Task 2: Half-cell evaluation of electrocatalysts with pure Hydrogen.

Task 3: Half-cell evaluation of electrocatalysts with contaminated hydrogen.

Task 4: Electrode performance evaluation in a H₂/O₂ fuel cell.

Task 5: Final report preparation.

Based on above tasks, the project work is planned as follows.

- Set up a single cell Hydrogen/Oxygen fuel cell system

- Obtain commercially available fuel cell components.
- Familiarized with fuel cell operation and performance evaluation.
- Compare performance with H₂ contaminated with CO.
- Synthesized MEAs using commercially available catalysts and other components.
- Compare fuel cell performance with commercial MEA Vs synthesized MEAs.
- Develop procedure for preparing metal catalyst loaded on carbon
 - Synthesize Pt and Pt/Ru catalysts and load on carbon.
 - Prepare electrode as well as MEAs using the synthesized electrodes.
 - Compare fuel cell performance with commercial MEAs Vs synthesized MEAs.
- Complete literature search to determine candidate catalysts to evaluate
 - Pt/Mo, Pt/Ru/Mo, Pt/W, Pt/Ru/W, Pt/WC, Pt/Ru/WC are likely candidates.
 - Other possible metals may include Sn and Ir.
- Evaluation of candidate catalyst materials.
 - Determine performance with pure hydrogen as well as contaminated hydrogen.

EXPERIMENTAL: MATERIALS AND METHODS

In this membrane electrode catalyst development, work several candidate metal and metal-alloy were considered. Chlorides of Pt, Ru, Mo and Ir were obtained from ElectroChem, Inc. These salts of the respective metals chosen for the candidate electrocatalysts were mixed in appropriate proportion and dissolved in distilled water. Sodium bisulfite was added slowly in the solution to form metal sulfite colloids. Hydrogen peroxide was then added to the colloid suspension to convert sulfite species to respective oxides. High surface area powdered carbon (Vulcan XC-72) obtained from ElectroChem, Inc., was added to the oxide colloid suspension to load the metal oxide on the carbon. Then hydrogen was bubbled through the suspension at 60 °C to reduce the oxides to the respective metals. Primary variables of the electrocatalysts synthesis were the catalyst components, proportion of the various metals, and total metal loading on the carbon. The total metal loading on the carbon was up to 1 mg/cm² of the electrode surface area.

The experimental set-up for testing and evaluation of catalysts and MEAs in PEMFC is given in the schematic diagram, Figure 1. In the PEMFC, H₂/air electrodes were used. The gases used in this PEMFC evaluation work were obtained from Air Products. The hydrogen (research grade, UN 1049) is used as fuel. As a source of oxygen compressed air (ultra pure carrier grade, UN 1002) is used. A mixture of hydrogen with 100 ppm CO was used as a source of CO contaminant in the fuel (Air Product Mixed ID 40094). A Multiple Dyna-Blender (Matheson, model 8284), basically a combination of a flow indicator and controller, and a mixer (model 8270), and transducer (model 8272) was used to control the flow of these gases and to mix CO with hydrogen in different proportion for the fuel cell. A HP GC 5890 was used to crosscheck the CO/H₂ composition.

Figure 1: Schematic of PEMFC for evaluation of catalysts and MEAs

RESULTS AND DISCUSSIONS

This annual report covers the first year of the project ending August 31, 2000. We have synthesized several novel electrocatalysts (Pt/C, Pt/Ru/C, Pt/Mo/C, Pt/Ir and Pt/Ru/Mo) for PEMFCs. These catalysts have been tested for CO tolerance in the H₂/air fuel cell. We also have compared the performance of our synthesized electrocatalysts with the commercial catalysts. The concentration of CO in the H₂-fuel varied from 10 ppm to 100 ppm.

The performance of the electrodes was evaluated by determining the cell potential against current density. The effect of temperature, catalyst compositions, and electrode film preparation methods on the performance of PEM fuel cell has also been studied. It was found that at 70 °C and 3.5 atm pressure at the cathode, Pt-alloy catalysts (10 wt % Pt/Ru/C, 20 wt % Pt/Mo/C) were more CO tolerant than 20 wt. % Pt catalyst alone.

To show the significance of the new electrocatalysts that we have synthesized and used in the membrane electrode assemblies (MEAs) along with commercial MEAs obtained from ElectroChem, Inc., the performance summary of the MEAs in the PEMFC are given in Figures (2) and (3).

From the results of this preliminary study we conclude that to develop low cost CO-tolerant catalysts for MEAs in PEMFC, one needs include metals like Ru and Mo in combination with Pt in the catalyst formulation. The metal Ir in combination with Pt in the catalyst did not

have any significant impact on cell performance. For optimum cell performance, fine-tuning of these metal compositions in the catalyst would be necessary.

Figure 2: Evaluation of commercial MEA (20 wt% Pt/C) and synthesized MEAs using commercial catalysts (10 and 20 wt% Pt/C, and Pt/Ru/C). Performance curves are for 20 ppm CO contaminated H₂-fuel on PEMFC

Figure 3: Evaluation of commercial MEA (20 wt% Pt/C) and synthesized MEAs using synthesized catalysts (1Pt/C, Pt/Ir/C, Pt/Ru/C, and Pt/Ru/Mo/C). Performance curves are for 20 ppm CO contaminated H₂-fuel in PEMFC

CONCLUSIONS

We have designed and built an experimental set-up to run PEMFC for testing and evaluation of its performance under various operating conditions and also with varied catalyst loading and compositions. To this date, we have synthesized Pt/C, Pt/Ru/C, Pt/Ir/C and Pt/Ru/Mo/C electrocatalysts and used them in MEAs to evaluate PEMFC performance. These MEAs were tested in PEMFC both in presence of CO contaminated hydrogen and pure hydrogen fuel. Commercial MEAs were also used for cell performance comparison. From this preliminary data we conclude that, to develop low cost, CO-tolerant catalysts for use in MEAs one needs to include metals like Ru and Mo in combination with Pt in the catalyst formulation. For optimum cell performance, fine-tuning of these metal compositions in the catalyst would be necessary.

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