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Development of Inexpensive Metal Macrocyclic Complexes for Use in Fuel Cells

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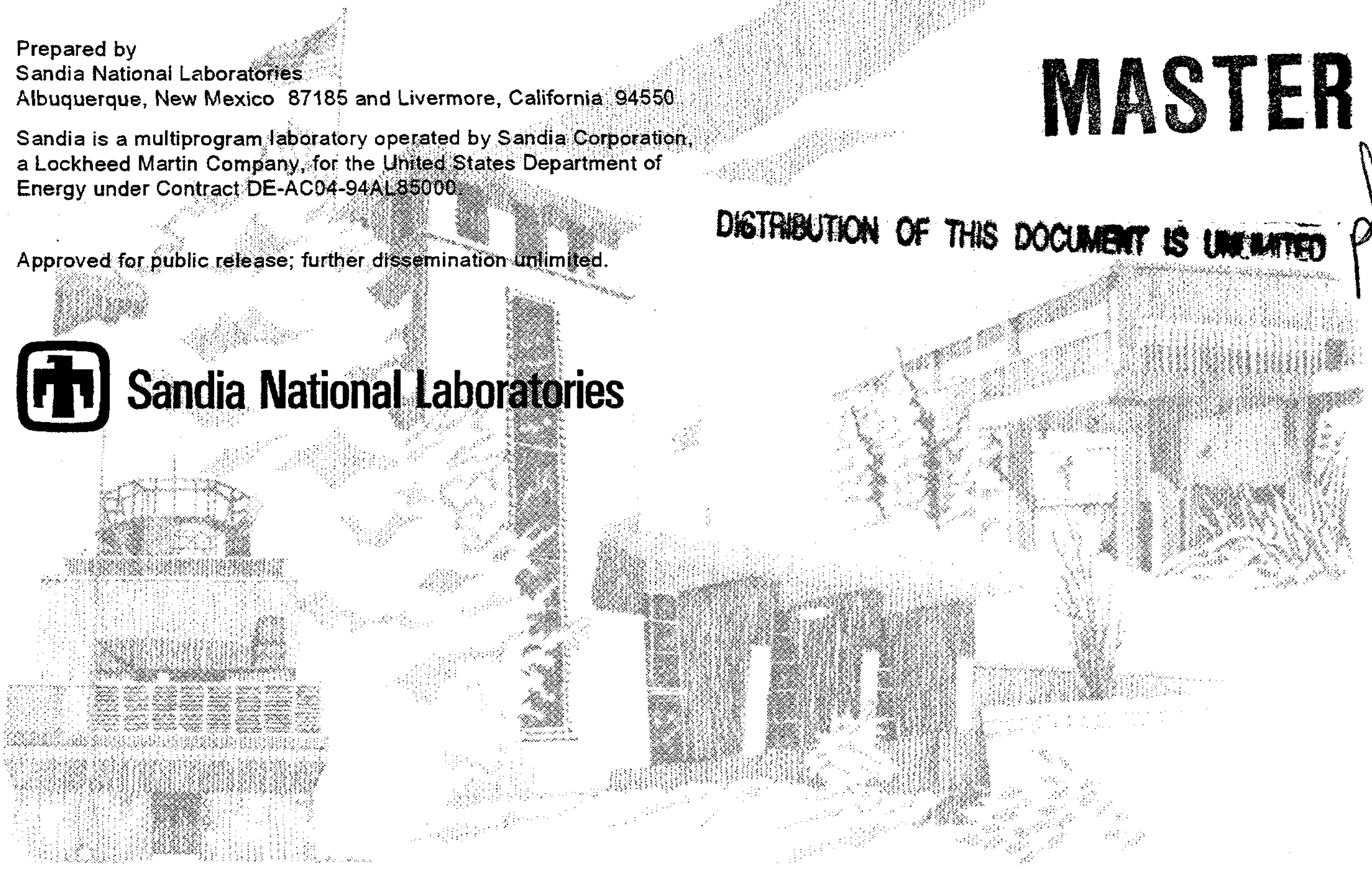

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DEVELOPMENT OF INEXPENSIVE METAL MACROCYCLIC COMPLEXES FOR USE IN FUEL CELLS

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Abstract

Several metal macrocyclic complexes were synthesized for use as catalysts in fuel cells. An initial evaluation of their ability to catalyze the fuel cell reactions was completed. Based on this initial evaluation, one metal macrocyclic catalyst was selected and long-term stability testing in a fuel cell was initiated. The fuel cell employing this catalyst was operated continuously for one year with little signs of catalyst degradation. The effect of synthetic reformates on the performance of the catalyst in the fuel cell environment also demonstrated high tolerance of this catalyst for common contaminants and poisons.

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Introduction

Fuel cells are being considered as alternative power sources for transportation and stationary applications. The degradation of commonly used electrode catalysts (*e.g.* Pt, Ag, and others) and corrosion of carbon substrates are making commercialization of fuel cells incorporating present day technologies economically problematic. Furthermore, due to the instability of the Pt catalyst, the performance of fuel cells declines on long-term operation. When methanol is used as the fuel, a voltage drop, as well as significant thermal management problems, can be encountered, the later being due to chemical oxidation of methanol at the platinized carbon at the cathode. Although extensive work was conducted on platinized electrodes (1-3) for both the oxidation and reduction reactions, due to the problems mentioned above, fuel cells have not been fully developed for widespread commercial use.

Several investigators have previously evaluated metal macrocyclic complexes as alternative catalysts to Pt and Pt/Ru in fuel cells (4). Unfortunately, though they have demonstrated catalytic activity, these materials were found to be unstable on long term use in the fuel cell environment. In order to improve the long-term stability of metal macrocylic complexes, we have chemically bonded these complexes to the carbon substrate, thereby enhancing their chemical stability in the fuel cell environment while still maintaining their catalytic activity. We have designed, synthesized, and evaluated these catalysts for O_2 reduction, H_2 oxidation, and direct methanol oxidation in Proton Exchange Membrane (PEM) and aqueous carbonate fuel cells. These catalysts exhibited both good catalytic activity and long-term stability. In this paper we focus on the performance results of some of these catalysts in H_2/O_2 PEM fuel cells, including their long-term stability characteristics as well their behavior in the presence of compounds known to be poisons on the precious metal catalytst, e.g. carbon monoxide.

Experimental

Several metal phthalocyanine polymer complexes $(MPc)_n$ having the structure shown in Figure 1 were synthesized in our laboratory. These catalysts were synthesized by heating a mixture of 3,3',4,4'-benzophenone tetracarboxylic dianhydride, metal chloride(s), and urea at 200 °C for 2 hours. The complexes prepared were $(CoPc)_n$, $(PtPc)_n$, $(Pt\text{-}RuPc)_n$, $(Pt\text{-}MoPc)_n$, and $(RuPc)_n$. A detailed description of the synthetic procedure of the catalysts and their impregnation onto the carbon substrate has been previously reported (5,6).

The method of attachment of the macrocyclic complex to the carbon has never been defenitively determined. However, it should be noted that these complexes become insoluble in common organic solvents and aqueous solutions of mineral acids after heat treatment. One possible explanation of this behavior is that when the carbon/catalyst mix is heat treated in an inert atmosphere to about 475 °C, a covalent linkage forms between the carbon substrate and the benzene ring of the complex, as shown in Figure 2.

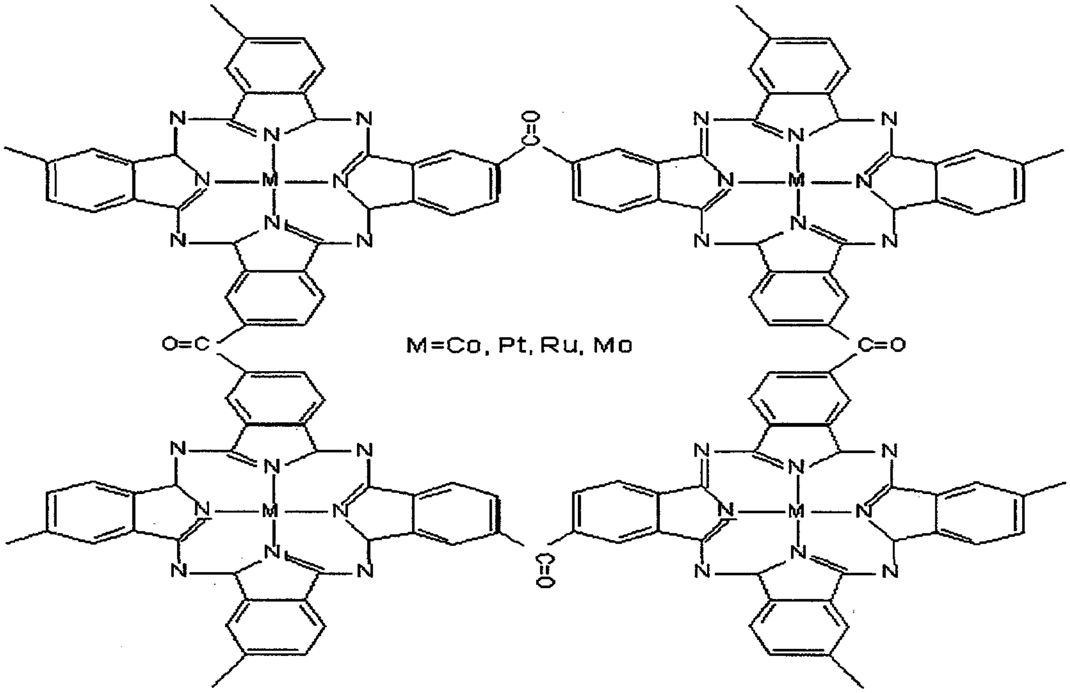

Figure 1

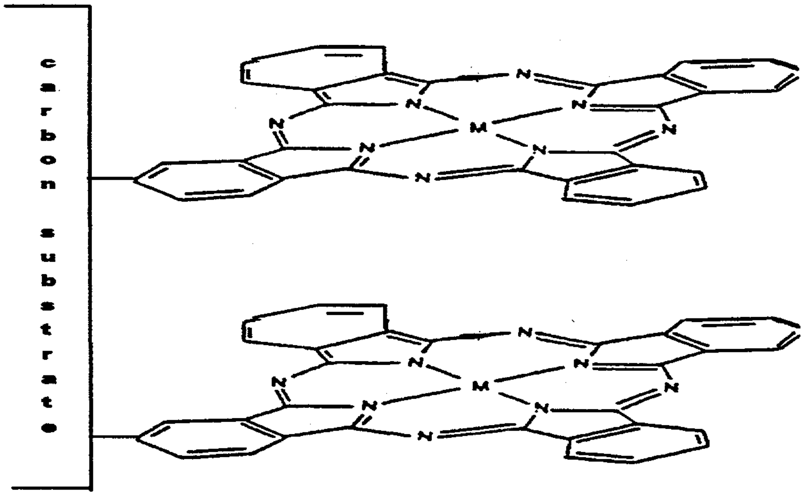

Figure 2.

The membrane electrode assemblies (MEAs) used in this work were prepared by Giner, Inc., Waltham MA. All electrodes, exceept those composed of Pt-black, contain 20% Nafion 117, and were cast onto Teflonized carbon fiber paper. Fuel cells were constructed having cathodes composed of either Pt-black (4 mg Pt/cm^2) or 20% Pt/Vulcan (0.5 mg Pt/cm^2). The anodes used in these cells consisted of either Pt-black, 10% Pt/Vulcan (0.25 mg Pt/cm^2), 20%Pt/Vulcan (0.5 mg Pt/cm^2), or 15% (Pt-RuPc)$_n$/Vulcan (0.035 mg Pt/cm^2 and 0.018 mg Ru/cm^2). All MEAs had active areas of 40 cm^2 and were evaluated at 80°C with 30 psig H_2 and either 30 or 60 psig O_2. The electrochemical screening of these complexes for the oxidation of hydrogen and reduction of oxygen in acid media was carried out in our laboratory. In order to provide independent evaluation of the performance of these inexpensive catalysts, PEM fuel cell fabrication and testing was carried out at Giner, Inc.

Results and Discussion

Fuel cells of varying combinations of anodes and cathodes were evaluated using H_2 and these results are shown in Figure 3. As seen, the fuel cell having the (Pt-Ru Pc)$_n$/Vulcan anode had slightly lower voltage than the other electrode combinations. However, the initial performance of this system is very promising, considering the unoptimzed nature of this MEA and significantly lower noble metal loadings. At 500 mA/cm^2, this fuel cell with a Pt-black cathode exhibited a terminal cell voltage of 650 mV. A fuel cell built with an anode and a cathode both composed of 20% Pt/Vulcan exhibited a terminal voltage of 610 mV. In comparison to this, the fuel cell built with a 15% (Pt-RuPc)$_n$ /Vulcan anode and a 20% Pt/Vulcan cathode has a terminal voltage only 60 mV lower, namely 550 mV *vs* 610 mV. We have also evaluated the performance of the cobalt transition metal phthalocycanine complex ((CoPc)$_n$) on heat treated Black Peal 2000. The catalyst exhibits good catalytic activity for hydrogen oxidation.

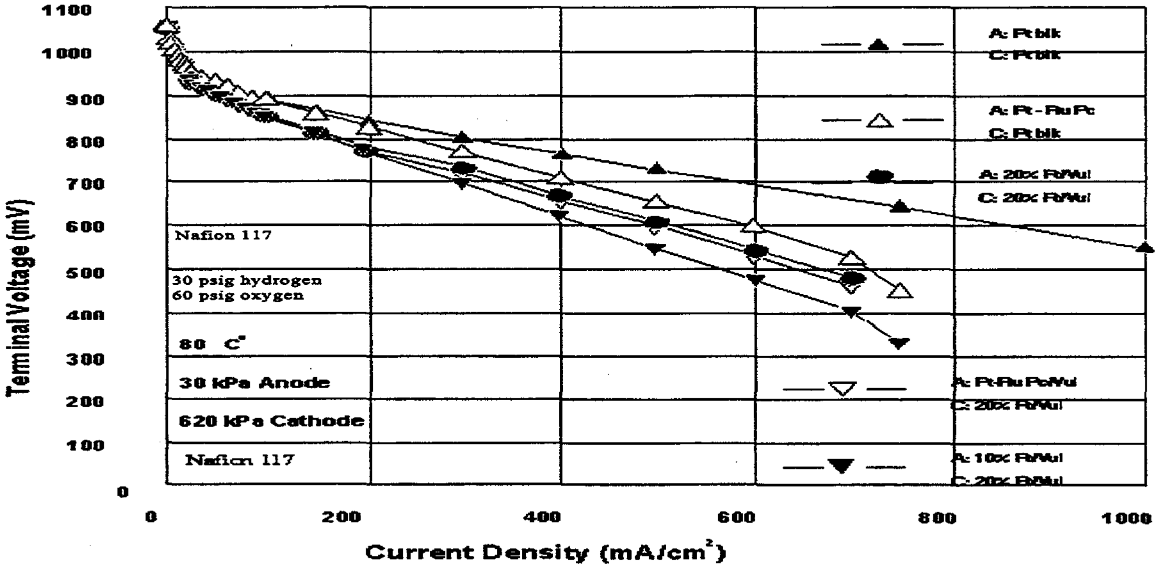

Figure 3. Comparison of PEMFC Performance of PtRuPc/vulcan with State-of-the-Art catalysts.

Based on this performance, preliminary stability characteristics of a PEM fuel cell using a 40 cm^2 MEA were evaluated at 80°C and 500 mA/cm^2 using one of the marcocyclic catalysts. The catalyst selected for this initial stability testing consisted of 25 wt% Pt-Ru phthalocyanine (Pc), with a Pt-Ru weight ratio of 54Pt:46Ru, deposited on Vulcan XC-72 carbon, a high-surface-area carbon commonly used as an electrocatalyst support. The noble metal content of this catalyst was 0.7 wt%, yielding a noble metal loading of 0.035 mg/cm^2 in the electrode structure developed for use with this catalyst. This noble metal loading is two orders of magnitude lower than that used by Ballard Power Systems in their commercial 5-kW PEMFCs.

In Figure 4 the terminal voltage as a function of time for continuous operation over 800 hours is shown. As seen, the voltage observed is relatively constant at about 600 mV. The minor variations in voltage are attributed to changes in the degree of membrane hydration. A second cell was built and tested under similar conditions in order to evaluate the performance reproducibility. This cell was continuously operated at 500 mA/cm^2 for 102 hours and was then shut-down for 48 hours. The cell was then restarted and the testing continued for another 98 hours, for a total testing time of 200 hours. It should be noted that this discontinuous operation of the cell did not adversely affect its performance. The cell also displayed stable operating characteristics, and this can be seen in the polarization behavior of this cell measured before and after 200 hours of operation. These results are shown in Figure 5 on the following page. One thing that can be seen upon examination of this data is that fuel cell terminal voltage has increased after operation. This improved performance could be the result of increased hydration of the assembly.

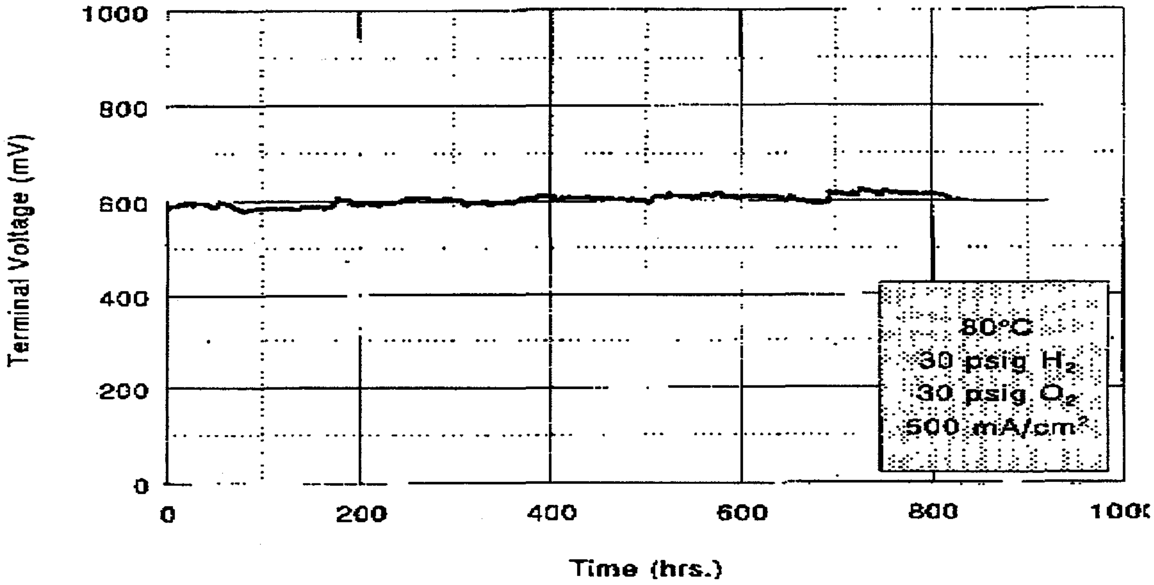

Figure 4. Life Test of Pt-RuPc/Vulcan Catalyst in PEMFC.

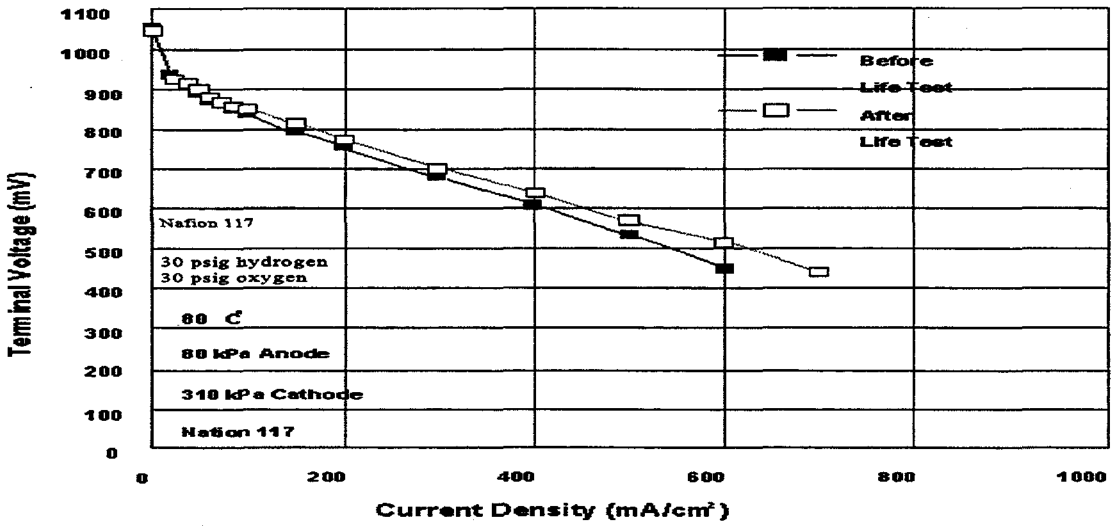

Figure 5. Polarization of Pt-RuPc/Vulcan Catalyst in PEMFC Before and After 200 hr LifeTest

The anode structure previously developed for use with the SNL-008 catalyst provided performance within 10% of that of the Ballard PEMFC. However, long-term stability in the PEMFC environment was a concern with the SNL-008 catalyst since phthalocyanine and other macrocyclic catalysts developed by other research groups demonstrated poor stability (Lalande, 1995). Although the catalyst demonstrated stable performance in a PEMFC over 200 hours of testing, practical fuel cell operation will require catalysts that are stable for thousands of hours. Consequently, long-term stability studies were initiated.

A membrane-electrode assembly (MEA) having the SNL Pt-RuPc/Vulcan catalyst designated -008, as the anode catalyst was fabricated. In this MEA, the anode consisted of 5 mg/cm^2 of the SNL-008 catalyst, coated with 20 wt% Nafion®[1], cast onto wetproofed carbon fiber paper. Due to the low noble metal content of the SNL catalyst, the anode noble metal loading was 0.035 mg/cm^2. This electrode was bonded to Nafion 117 along with a cathode consisting of 5 mg/cm^2 of 20 wt% Pt/Vulcan (1 mg Pt/cm^2), also coated with Nafion and supported on wetproofed carbon fiber paper.

This MEA was continuously run in standard Giner, Inc. PEMFC laboratory hardware, shown in Figure 6, with an active area of 40 cm^2. The fuel cell was operated at 80°C with humidified H_2 and O_2 at 30 psig at a current density of 500 mA/cm^2. The gas flow rates were 6-8 times the stoichiometric requirements. Periodic polarization scans with O_2 and air as the oxidants were taken.

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[1] Nafion is a registered trademark of E.I. DuPont de Nemours & Co.

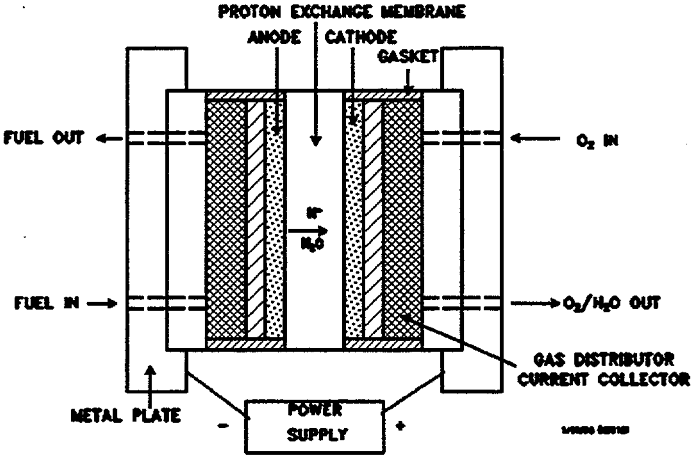

Figure 6. Schematic Cross-Section of Giner, Inc. PEMFC Hardware

During fuel cell operation, the liquid water in the effluent anode and cathode streams was collected in separate traps, which were emptied weekly. The collected water from each trap was analyzed weekly for the presence of F^-, using a calibrated F^- ion-selective electrode. Fluoride in the collected water is an indication of degradation of the proton-exchange membrane. This testing was conducted to determine whether the Pt-RuPc catalyst accelerated membrane degradation.

Selected samples of the collected anode trap water were sent to an outside laboratory for analysis of Pt and Ru content to determine if the catalyst was dissolving or otherwise being lost in the water during fuel cell operation.

A life plot showing fuel cell performance as a function of operating lifetime is shown in Figure 7. Stable performance was observed throughout the nearly 10,000-hour life test. During this time, the fuel cell operated continuously, except for minor shutdowns to replace malfunctioning test stand equipment and a 2-week shutdown during the Christmas holidays. The fuel cell had a decay rate of 2.2 mV/1000 hours, comparable to that obtained with PEMFCs having two orders of magnitude higher anode catalyst loadings. Much of this decay was likely due to the cathode, not the anode; evidence of cathode flooding was observed during the life test. Briefly increasing the O_2 flow rate through the cathode compartment typically resulted in a 30- to 100-mV increase in fuel cell performance. Cathode flooding was also the reason for the performance decrease observed at the approximately 9000-hour mark.

Because of the excellent performance of this catalyst in these tests, the life test is being continued to the 10,000-hour mark under NSF funding, at which time the test will be voluntarily terminated.

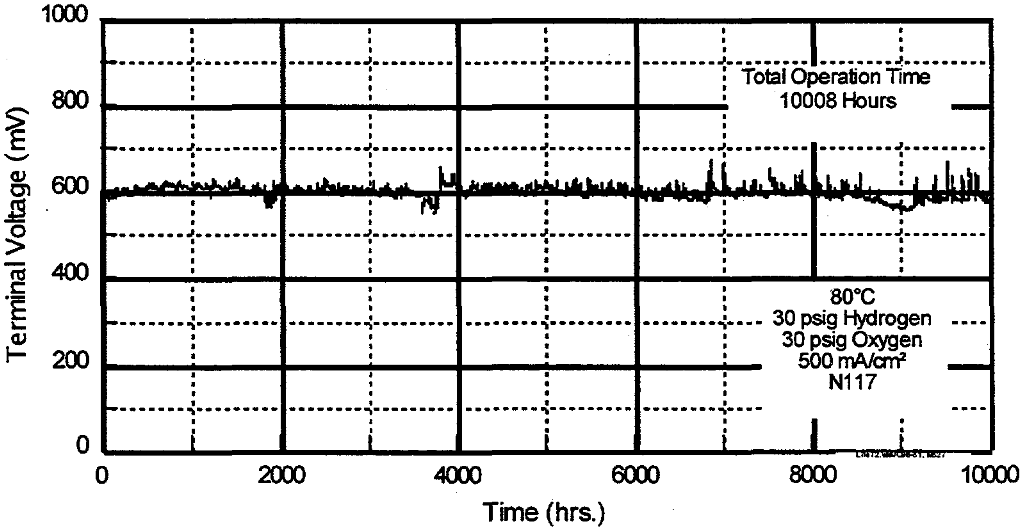

Figure 7. Life Plot of PEMFC Containing SNL-008 Catalyst on Anode

The Nafion membrane used as the fuel cell electrolyte is a fully fluorinated material. Likewise, both the anode and cathode catalysts were imbibed with Nafion for proton conductivity. Therefore, to monitor for the effects of any long-term membrane or electrode structure degradation, fluoride contents of both the anode and cathode effluent water were checked on a weekly basis; results are plotted in Figure 8.

Over approximately the first month of fuel cell operation, the amount of fluoride ion collected in the cathode trap over a one-week period was between 2 and 3 mg. From the data in Figure 7, no detrimental effects on fuel cell performance were observed. Cathode fluoride levels were higher than those on the anode, suggesting cross-membrane transport from the anode or degradation of a fluoride-containing species on the cathode. After the 2000-hour mark, anode fluoride levels were extremely low, averaging approximately 0.1-0.2 mg fluoride/week. From this data and from fuel cell performance data, the anode catalyst does not appear to contribute to membrane degradation.

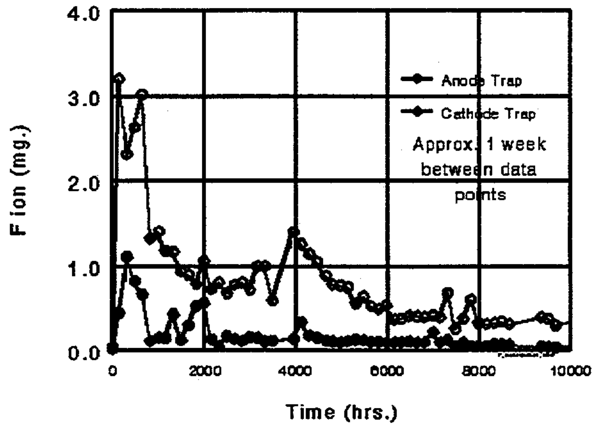

Figure 8. Fluoride Content of Anode and Cathode Effluent Water Over Time

To determine the chemical stability of the SNL-008 catalyst under operating fuel cell conditions, the anode effluent water was collected for 1-week intervals at the 300-hour mark and at the 8000-hour mark during the life test; the water was then analyzed for Pt and Ru content by a local contract analytical laboratory. Both the Pt and Ru levels were below the 0.1 mg/liter quantitation limit of the laboratory, indicating no detectable loss of Pt and Ru was occurring.

Preliminary studies of the effect of carbon monoxide contamination of the fuel have shown voltage drops of 25mV, 30mV, and 325mV for CO levels of 10ppm, 20ppm, and 100ppm in the H_2 fuel, respectively. Los Alamos National Laboratory (LANL) has reported (7) values of 90mV and 390-400mV for CO levels of 5ppm and 20ppm, respectively. No results were reported at higher CO levels. The LANL results were obtained using Pt/Vulcan anode formed into a thin-film having a Pt loading of 0.14 mg/cm^2. This is four times the noble metal loading of the $(PtRuPc)_n$/Vulcan. We believe that the voltage drop in the $(Pt\text{-}RuPc)_n$/Vulcan can be reduced by optimization of the electrode, including removal of the small amounts of uncomplexed noble metal which could be present.

Based on these promising results, it was decided to interrupt the long term life test to evaluate the effect of potential poisons on the fuel cell catalyst. This was done by briefly interrupting the life test after approximately 7500 hours of operation and again at approximately 9600 hours of operation to determine the performance of this cell on simulated methanol reformate, an alternative fuel to pure

H_2 for automotive and many other applications. The Pt catalysts typically used in PEMFCs are readily poisoned by CO in the reformate, requiring extensive cleanup of the reformate to reduce CO levels to below 10 ppm. The CO_2 in the reformate has also been demonstrated to reduce fuel cell performance below that expected due to dilution of H_2. In previous testing, the SNL Pt-RuPc/Vulcan catalyst demonstrated improved CO tolerance compared to Pt/Vulcan catalysts. The goal of this testing was to determine if the previous results were reproducible and if extensive reformate testing of the catalyst is warranted.

The effect of reformate containing various levels of CO on fuel cell performance is summarized in Table I, which lists the voltage loss at 300 mA/cm^2 due to 2 hours of operation on the reformate compared to operation on pure H_2, and Figure 9, polarization scans for reformate operation taken at 7500 hours. As previously reported for this Pt-RuPc/Vulcan catalyst, a performance loss greater than that due to dilution occurred when 25% CO_2 was added to the H_2. When tested at the 7500-hour mark, the dilution loss at 300 mA/cm^2 for addition of 25% N_2 was 8 mV, compared to 98 mV for addition of 25% CO_2. These values increased somewhat to 35 and 129 mV at the 9600-hour mark. The voltage losses are comparable to the 95-mV loss for operation on H_2-25% CO_2 obtained in a previous program.

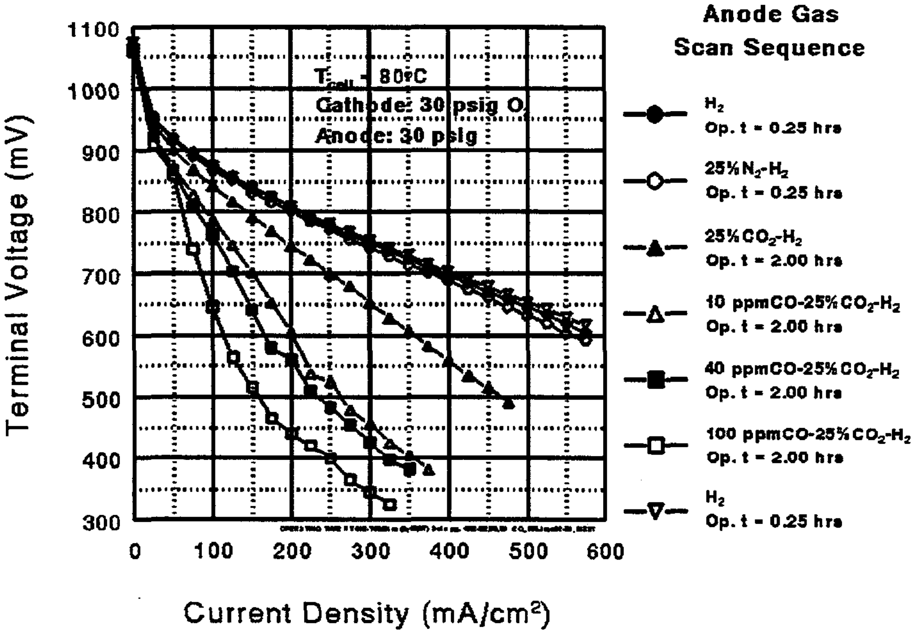

Figure 9. PEMFC Performance on Simulated Reformate Gases

Addition of ppm-levels of CO to the simulated reformate caused a much larger decrease in fuel cell performance, ranging from approximately 300 mV at 300 mA/cm^2 for 10 ppm CO to approximately

410 mV at the same current density for 100 ppm CO. The performance loss due to operation on simulated reformate containing 100 ppm CO is somewhat higher than the approximately 300-mV loss obtained in a previous program. This may be due to electrode-to-electrode variations, or perhaps to the effect of 7500 hours to 9600 hours of operation on the present electrode.

Although CO poisoning does occur on the Pt-RuPc/Vulcan catalyst, the extent of poisoning on this catalyst appears to be significantly lower than that of other anode catalysts on a noble metal loading basis. (It should be mentioned that the term "poison" may not be the most appropriate in the case of the metal macrocyclic catalysts since it implies that the catalyst is irreversibly damaged. In the case of the metal macrocycle, full catalytic activity is recovered shortly after removal of the CO from the process stream, as will be discussed.) A loss of 390-400 mV at 400 mA/cm^2 for operation on 20 ppm CO in H_2 (no CO_2) has been reported by Los Alamos National Laboratory (Wilson et al., 1993) for a thin-film anode structure containing four times the noble metal loading of the Pt-RuPc/Vulcan catalyst. This loss with 20 ppm CO in H_2 is comparable to the loss obtained on the Pt-RuPc catalyst with 100 ppm CO and 25% CO_2 in H_2. Also, testing at Giner, Inc. has shown that the loss due to 40 ppm CO in simulated reformate is only slightly higher for the Pt-RuPc/Vulcan anode than for a 20% Pt/Vulcan anode having a Pt loading of 1 mg/cm^2.

Table I. Effect of Reformate Gases on PEMFC Performance*

Anode Feed	7500 Hours		9600 Hours	
	Terminal Voltage (mV, @ 300 mA/cm^2)	ΔV (mV,@ 300 mA/cm^2 vs. H_2 Performance)	Terminal Voltage (mV, @ 300 mA/cm^2)	ΔV (mV,@ 300 mA/cm^2 vs. H_2 Performance)
H_2	751	0	764	0
25%N_2 - Balance H_2	743	8	729	35
25%CO_2 - Balance H_2	653	98	635	129
10 ppm CO - 25%CO_2 - Balance H_2	457	294	455	309
40 ppm CO - 25%CO_2 - Balance H_2	426	325	430	334
100 ppm CO - 25%CO_2 - Balance H_2	346	405	348	416

* 80°C, 30 psig both sides, O_2 on cathode

Poisoning of the Pt-RuPc/Vulcan catalyst by 100 ppm CO in simulated reformate occurs quickly. Figure 10 shows polarization scans taken approximately every 15 minutes during two hours of testing. Most of the performance loss occurred during the initial 15 minutes of exposure. After 30 minutes of exposure, performance was quite stable.

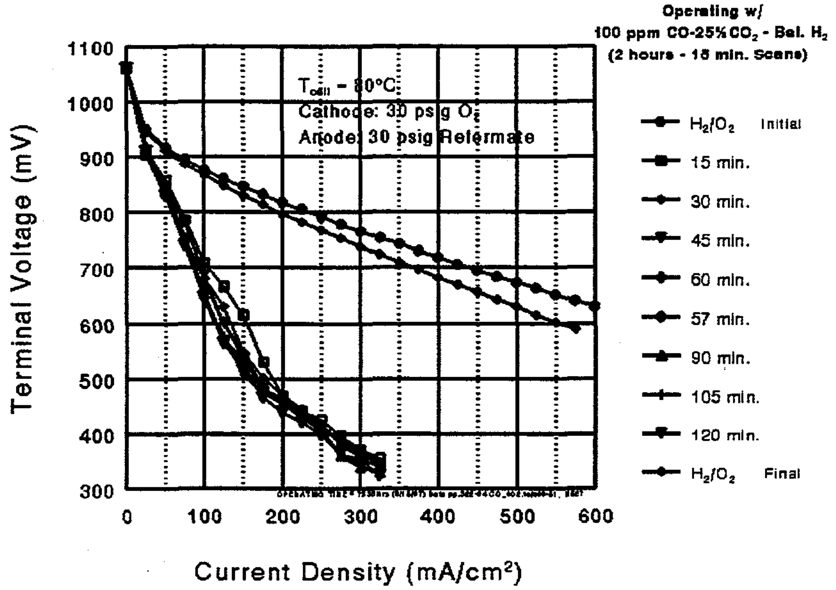

Figure 10. Effect of Time of CO Exposure on PEMFC Performance

Carbon monoxide poisoning is very reversible upon removal of the CO. As shown in Figures 4 and 5, after 15 minutes of operation on pure H_2 following the CO testing, fuel cell performance was equivalent to the performance obtained prior to CO testing.

CONCLUSIONS AND RECOMMENDATIONS

Metal phthalocycanine complexes have been evaluated as alternate catalysts for Pt in H_2/O_2 PEM fuel cells. Preliminary results with $(Pt\text{-}RuPc)_n$ and $(CoPc)_n$ show very promising catalytic activity for H_2 oxidation. PEM fuel cells with unoptimized MEAs using these catalysts performed as well as MEAs containing Pt catalyst. The Pt-RuPc/Vulcan catalyst has demonstrated fuel cell performance stability over a 9600-hour life test comparable to that obtained with PEMFCs having two orders of magnitude higher anode catalyst loadings. This material has also demonstrated excellent chemical stability, with no detectable quantities of Pt and Ru found in the anode effluent water. This clearly demonstrates the stability of the metal macrocyclic complex in the operating environment of the fuel cell. To further verify performance and chemical stability, duplicate testing of this catalyst is recommended using an improved cathode structure to minimize flooding.

The effect of CO and CO_2 on PEMFC performance of the SNL Pt-RuPc/Vulcan catalyst was similar to that obtained in a previous NSF program, although the effect of 100 ppm CO was somewhat larger than previously noted. Continuous operation for 9600 hours has not significantly affected the CO tolerance of the catalyst. Carbon monoxide poisoning causes a rapid decrease in fuel cell performance, but upon further exposure, a steady-state performance is reached. Carbon monoxide poisoning is rapidly reversible upon elimination of CO in the fuel.

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