FINAL REPORT

SPACE POWER SYSTEMS TECHNOLOGY

NASA Grant Number NCC 3-23

Cleveland State University


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George A. Coulman
Principal Investigator

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ABSTRACT

Reported here is a series of studies which examine several potential catalysts and electrodes for some fuel cell systems, some materials for space applications, and mathematical modeling and performance predictions for some solid oxide fuel cells and electrolyzers. The fuel cell systems have a potential for terrestrial applications in addition to solar energy conversion in space applications. Catalysts and electrodes for phosphoric acid fuel cell systems and for polymer electrolyte membrane (PEM) fuel cell and electrolyzer systems were examined.
# Table of Contents

ABSTRACT

INTRODUCTION

RESULTS AND DISCUSSION
  Phosphoric Acid Fuel Cells
  Materials
    Flight Qualified
    Moving Belt Radiator
  Regenerative Fuel Cell Systems
    Dedicated
    Unitized
  Solid Oxide Fuel Cells and Electrolyzers

EXPERIMENTAL

REFERENCES

APPENDIX
Introduction

This report is a summary of studies funded by the National Aeronautics and Space Administration which address some problems inherent in energy conversion. One specific aspect of energy conversion is involved with electrocatalysis, which is one of the processes central to the conversion of solar radiation to forms useful to spacecraft and to planetary settlements. By use of regenerative fuel cells which require reliable and efficient electrocatalysis, solar energy can be stored during dark periods. The fuel cell systems have a potential for terrestrial applications in addition to solar energy conversion in space applications. Catalyst and electrodes for phosphoric acid fuel cells were developed and evaluated. Catalysts and electrodes for polymer electrolyte membrane (PEM) fuel cell and electrolyzer systems are under development and evaluation. Materials for a moving belt radiator in space and the means of qualifying materials for spaceflight missions were examined. Mathematical modeling and performance predictions for some solid oxide fuel cells and electrolyzers were developed.

This report will consist of a general reporting of what has been accomplished in the areas described above. Results which have already been published in the open literature will be summarized and commented on. The actual papers will be included as appendices. Results which have not yet been published will be reported as well.

Results and Discussion

Phosphoric Acid Fuel Cells (Ref. 1, 2, 3, 4, 5)

Research and technical analyses were conducted in the areas of fuel cell catalysts and electrodes for phosphoric acid fuel cells. The purpose was to provide major improvements in electrode performance and life, in addition in
aiding in reducing fuel cell costs. The baseline catalyst is platinum. Binary and ternary alloys of platinum were developed and evaluated. Improved activity and stability were the goals, together with attention being given to understanding the reason(s) for the increased activity. Attention was also given to the problem of the catalyst support and the need for corrosion-resistant materials.

The issue of costs was addressed by seeking organometallic catalysts as enhancers and as replacements for platinum at the cathode. Improved performance with mixed (i.e., Pt plus organometallic) catalysts was observed over that of platinum alone, and also reasonably good performance was found for mixed catalysts that contained no noble metal. A model for the improved performance observed with the mixed catalyst was developed.

Diffusion processes in gas diffusion electrode structures were studied since it was recognized that the preparation of efficient gas diffusion electrodes is to a large extent an art, and the detailed mechanisms of their operation are not understood. Guidelines for making improvements in electrode structures were developed, using both experimental and theoretical approaches. Computer software for a mathematical theory of mass transport of reactants in porous gas diffusion electrodes was developed. In the theory a simplified model for the electrode structure was used and fitted to experimental data. Electro catalysts for phosphoric acid fuel cells typically consist of platinum which is prepared in a finely divided form dispersed uniformly over the surface of a conductive carbon black. Much current research is aimed at enhancing the efficiency as well as extending the lifetime of the fuel cell electrodes, primarily the oxygen electrode. Both catalyst deactivation as well as electrode degradation mechanisms are involved, and simultaneous
achievement of high efficiency and long life is a difficult task. Two major causes of performance decay are support corrosion and catalyst deactivation, mainly through surface area loss due to sintering of metal particles. Several modifications of carbon blacks and substitute conductive materials such as TiC are being investigated to improve the corrosion resistance of supports, and modifications of platinum are being investigated to enhance the efficiency and lifetime of the platinum catalyst. Heat-treatment and alloying of the platinum have been investigated.

Materials

Flight qualified materials for advanced concentrators (Ref. 6)
The purpose of this effort was to aid in assessing the technical base for flight qualified materials for advanced concentrators. No firm technical data base exists for concentrator materials. Thus, no material is commercially available that can be certified for long-term application. Included in the consideration of concentrator materials are materials of construction, optical films, and coatings. The literature survey included laboratory reports and workshops. Applicable materials were identified from shuttle spacecraft and photovoltaic programs carried out by NASA and DOD. And the procedures used for qualifying the materials were identified and evaluated. Identified also were the different environment(s) and subsequent different criteria that needed to be addressed depending on the intended mission(s), e.g., a 30-yr lifetime in Low Earth Orbit or a 5-15 yr. lifetime for missions subject to high energy radiation. Further, the study showed that it was critical that testing of materials be done in a suitable combined simulation of the space environmental conditions, in which simultaneous irradiation could be done.
The means of obtaining a reliable data base for materials for long-term application in space were summarized. They included the ability to develop a reliable prediction model to assess the effects of long-term exposure of materials to the LEO environment, the ability of ground-based facilities to simulate the space environment, and aeronometric determination of low earth orbit environment composition.

Moving Belt Radiator (Ref. 7)
The purpose of this effort was to aid in establishing a data base of candidate materials which can be used in a Moving Belt Radiator system. The database was to include the materials to be used for the heat exchange fluid bath, the fluid bath containment, and the belt to be used in the MBR concept. The hybrid belt and the solid belt were the ones to be considered. The report focuses on belt materials only, since there was nothing obvious to suggest a better bath material than gallium, and containment with certain types of stainless steels has been demonstrated. The focus of this report was the search for belt materials having a heat of fusion of about 300 kj/kg (400-800K) and an emissivity of 0.8.

Regenerative Fuel Cell Systems
Dedicated (Ref. 8, 9)
NASA's planning for the future exploration of the Solar System includes the establishment of manned outposts, as well as central basestations on the Moon and Mars. Supporting human expeditions to, and operations on, the surface of the Moon or Mars represents a substantial technology challenge for current and projected power system capabilities. A solar-based surface power system must
supply usable power continuously, that is during the day as well as the night, and thus, a regenerative system is required. The highest potential for successfully achieving the required surface power storage capabilities was judged to lie in the regenerative fuel cell concept. During the light portion of the orbit, photovoltaic solar arrays generate sufficient power to service the system electrical loads plus a water electrolysis unit. The amount of electrical energy required by the electrolysis unit is determined by the amount of hydrogen and oxygen needed to generate power in a fuel cell, which supplies electrical power during the dark portion of the orbit. Water is produced by the fuel cell as a by-product of the electrochemical reaction. It is collected and stored for use in the electrolyzer in the succeeding orbit.

To meet the mass, energy, and life requirements for operating on the Moon or Mars requires substantial improvements in the technology areas of solar power generation, energy storage, and electrical power management. For energy storage, two candidate fuel cell and electrolyzer technologies were considered, the alkaline and the proton exchange membrane (PEM). The state-of-the-art of alkaline systems had been very much advanced over that of PEM technology because of the use and development of alkaline systems in previous NASA space missions. However, recent technology efforts on fuel cells for transportation applications have advanced the PEM technology. Thus, a technology assessment was undertaken to provide guidelines for selecting the technology to be carried into full development. Given the history of prior development, the technology assessment considered alkaline fuel cells and electrolyzers as baseline. The first activity, thus, was to determine the viability of PEM fuel cells as a competing technology. Despite the lack of background development in PEM fuel cells, it was determined that there was a high probability of
success in attaining the basic technology improvements needed to meet the RFC system requirements within a reasonable time. Further, it was determined that a PEM, metal hardware fuel cell stack appeared to be the only candidate that could meet the performance and life requirements needed for repeated start-up and turn-down cycles necessary to follow the solar cycles on the lunar surface. PEM electrolysis stacks were also selected.

Most of the tests in PEM systems have been made with Nafion 120 and 117 membranes, which are perfluorinated sulfonic acid membranes made by DuPont. These are relatively thick and of higher equivalent weight and thus of higher resistance than found for thinner Nafions and for other newer ion exchange polymeric material. In general, thicker membranes give lower electrical output than thinner membranes and higher equivalent weight material gives lower electrical output than lower equivalent weight material. Under consideration are membranes made by DOW and Asahi, which are of similar composition and structure to Nafion. Some properties of typical membranes are given in TABLE I.

**TABLE I. Physico-chemical Characteristics of Polymer Electrolyte Membranes**

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Equiv. Conductivity, S/cm</th>
<th>Membrane</th>
<th>Equiv. Conductivity, S/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion 1100</td>
<td>7.5</td>
<td>Nafion 1100</td>
<td>5.9</td>
</tr>
<tr>
<td>Nafion 1200</td>
<td>5.0</td>
<td>DOW 800</td>
<td>11.4</td>
</tr>
<tr>
<td>Nafion 1500</td>
<td>3.3</td>
<td>Asahi 1000</td>
<td>10.8</td>
</tr>
</tbody>
</table>

Recently, linear polymeric chain perfluorinated bis-sulfonimides have been synthesized. They are stable strong acids, and like sulfonic acids are hydronium ion conductors which require the presence of water to obtain significant ionic conductivity. They show promise of conductivity better than \(10^{-2}\) S/cm.
Some of the more desirable characteristics for hydrogen-oxygen fuel cell systems, particularly for long-time automated operation, are high energy density, small volume, high efficiency, high reliability, and long life. A recent GEO mission analysis indicated that a significant increase in energy density is possible if a two-unit alkaline fuel cell and electrolyzer system is replaced with a single-unit alkaline fuel cell/electrolyzer system. The efficiencies of fuel cell and electrolyzer systems under load are considerably less than 100 percent due, primarily, to the irreversibility of the oxygen electrode. Therefore, active bifunctional O\textsubscript{2} electrocatalysts are needed to increase the kinetics for both O\textsubscript{2} reduction and evolution to maximize the efficiency of a single-unit alkaline fuel cell/electrolyzer system. Metals and oxides have been investigated for monofunctional O\textsubscript{2} electrocatalysts for alkaline fuel cells and electrolyzers. Studies of bifunctional O\textsubscript{2} electrocatalysts are rare. Long-life candidates must be stable under both reducing and oxidizing conditions. Although Pt and Pt alloys exhibit moderate bifunctional O\textsubscript{2} electrode activity, long-time stability for Pt, particularly during O\textsubscript{2} evolution, is questionable. Pt bronzes, composed of oxides of Pt and an alkali metal, are believed to have greater stability than metallic Pt particularly under oxidizing potentials. Na-Pt bronze powders (i.e., Na\textsubscript{x}Pt\textsubscript{3}O\textsubscript{4}) have been prepared (Giner, Inc.) as a single phase and in moderately high surface area. Porous gas diffusion electrodes using mixtures of Na\textsubscript{x}Pt\textsubscript{3}O\textsubscript{4} powders as the electrocatalyst and polytetrafluoroethylene (PTFE) as the binder were fabricated. O\textsubscript{2} reduction and evolution activities and stabilities of these PTFE-bonded electrodes were determined under both reducing and oxidizing
conditions.

Solid Oxide Fuel Cells and Electrolyzers (Ref. 10, 11, 12)
Development of predictive techniques, with regard to cell behavior, under various operating conditions is needed to improve cell performance, increase energy density, reduce manufacturing cost, and to broaden utilization of various fuels. Such technology would be especially beneficial for the solid oxide fuel cell at its early demonstration stage. Thus, computer models were developed to calculate the temperature, current density, and reactant distributions in tubular and monolithic solid oxide fuel cells. The results indicate that problems of non-uniform heat generation and fuel gas depletion may be encountered in the tubular cell module during fuel cell operation. In the monolithic (MOD9) design, problems of size limitations may be encountered. A computer model was used to estimate the effects that the current-voltage characteristics, the average array temperature, and the inlet reactant gas temperatures have upon the range of feasible fuel utilization ratios and oxidant utilization ratios. The results can be used as constraints for system optimization studies.

Fuel cell operation has been demonstrated with monolithic solid oxide fuel cells. It is also possible to operate the monolithic structure in the reverse, or electrolysis, mode. Performance predictions of monolithic solid oxide electrolyzer arrays were made by revising the computational algorithm previously formulated for the fuel cell arrays. Computer modeling results of this type may be used to aid the design of a monolithic solid oxide electrolysis sub-system and of a regenerative fuel cell system.
Experimental (Ref. 13, 14)

Prior work in developing electrocatalyst systems and electrode structures for single-unit regenerative fuel cells looked at a large number of candidate bifunctional positive electrode catalysts. These catalysts were evaluated for chemical and electrochemical stability and for catalytic activity in 30% KOH at 80°C. As a result, two potentially bifunctional catalyst systems were identified: Na$_x$Pt$_4$ and metal/metal oxide combinations of Rh, Pt and Ir. For the regenerative PEM fuel cell, many of the same catalysts are being considered.

To alternate between oxygen reduction and oxygen evolution on the same electrode, it is necessary to have a structure that can perform in both of these modes. The approach taken was to develop catalyst/binder compositions optimized separately at the particulate level for either oxygen reduction or oxygen evolution and then combine these at an optimal ratio in a single electrode, referred to as an "integrated dual-character" (IDC) electrode. In this approach the catalyst for each function can be the same material if it shows bifunctional activity (e.g., Na$_x$Pt$_4$) or two different monofunctional catalysts (e.g., Pt for O$_2$ reduction and Ir for O$_2$ evolution). For PEM systems a two-layer structure is used to achieve an appropriate interface to the proton exchange membrane.

The electrodes used in this study were prepared by Giner, Inc. The measurements were made in half cells as part of the research program to develop a detailed understanding of how the different components of porous gas-fed oxygen electrodes function. The results are preliminary and presented in the figures.
Figure 1: Schematic of a Bifunctional Hydrogen-Oxygen PEM Cell with Giner, Inc. Composite Electrodes

Figure 2: Giner Dual Function System (Two Electrodes)

Figure 3: Teflon Half Cell for O₂ Reduction & Evolution

Figure 4: O₂ Reduction Potential with O₂ Flow Rate (H₂O) for Giner PEM/IR0₂, PT & PT Free-Standing Electrode (-0.1A, 24°C, 1M H₂SO₄)
Figure 5: O₂ Reduction Potential with O₂ Flow Rate (Dry) for Giner PEM/IRO₂, PT & PT Free-Standing Electrode (-0.1A, 24°C, 1M H₂SO₄)

Figure 6: R with Time during cycling at -0.05A & +0.05A for Giner PEM/IRO₂, PT & PT Free-Standing Electrode (23°C, 1M H₂SO₄)

Figure 7: R Polarization with Time during Cycling for Giner PEM/IRO₂, PT & PT Free-Standing Electrode (-0.05 & +0.05A, RT, 1M H₂SO₄)

Figure 8: R Polarization with Log Time during Cycling for Giner PEM/IRO₂, PT & PT Free-Standing Electrode (-0.05 & +0.05A, RT, 1M H₂SO₄)
Figure 9: R Polarization with Time during Cycling
Giner PEM/IRO₂, PT & PT Free-Standing Electrode (-0.05 & +0.05A, RT, 1M H₂SO₄)

Figure 10: R Polarization with Log Time during Cycling
Giner PEM/IRO₂, PT & PT Free-Standing Electrode (-0.05 & +0.05A, RT, 1M H₂SO₄)

Figure 11: R Polarization with Time during Cycling
Giner PEM/IRO₂, PT & PT Free-Standing Electrode (-0.05 & +0.05A, RT, 1M H₂SO₄)

Figure 12: R Polarization with Log Time during Cycling
Giner PEM/IRO₂, PT & PT Free-Standing Electrode (-0.05 & +0.05A, RT, 1M H₂SO₄)
Figure 13: R Polarization with Log Time (O₂ Reduction)
Giner PEM/IRO₂, PT & PT Free-Standing Electrode
(Cycle at -0.05 & + 0.05A, 23°C, 1M H₂SO₄)

Figure 14: R Polarization with Time during Cycling
Giner PEM/IRO₂, PT & PT Free-Standing Electrode (-0.05 & +0.05A, 23°C, 1M H₂SO₄)

Figure 15: R Polarization with Time during Cycling
Giner PEM/IRO₂, PT & PT Free-Standing Electrode (-0.05 & +0.05A, RT, 1M H₂SO₄)

Figure 16: R Polarization with Time during Cycling
Giner PEM/IRO₂, PT & PT Free-Standing Electrode (-0.05 & +0.05A, RT, 1M H₂SO₄)
Figure 17: R Polarization with Log Time during Cycling
Giner PEM/IRO₂, PT & PT Free-Standing Electrode (-0.05 & +0.05A, RT, 1M H₂SO₄)

Figure 18: R Polarization with Time during Cycling
Giner PEM/IRO₂, PT & PT Free-Standing Electrode (-0.05 & +0.05A, RT, 1M H₂SO₄)

Figure 19: R Polarization with Log Time during Cycling
Giner PEM/IRO₂, PT & PT Free-Standing Electrode (-0.05 & +0.05A, RT, 1M H₂SO₄)

Figure 20: R Polarization with Time (O₂ Evolution)
Giner PEM/IRO₂, PT & PT Free-Standing Electrode
(Cycle at -0.05 & +0.05A, 23°C, 1M H₂SO₄)
Figure 21. R WITH TIME FOR O2 REDUCTION AT -0.15A GINER PEM/IR02,PT & PT FREE STANDING ELECTRODE (H2O, 80.6°C, 1M H2SO4)

200CC/MIN O2(H2O)/O2 SIDE (PREHEAT 80°C FOR 60)

Figure 22. R WITH LOG TIME FOR O2 REDUCTION AT -0.15A GINER PEM/IR02,PT & PT FREE STANDING ELECTRODE (H2O, 80.6°C, 1M H2SO4)

200CC/MIN O2(H2O)/O2 SIDE (PREHEAT 80°C FOR 60)
Figure 23. R FOR O₂ REDUCTION WITH TIME AT -0.15A
GINER PEM/IR0₂,PT & PT FREE STANDING ELECTRODE
(DRY, 23.8°C, 1M H₂SO₄)

Figure 24. R FOR O₂ REDUCTION WITH LOG TIME AT -0.15A
GINER PEM/IR0₂,PT & PT FREE STANDING ELECTRODE
(DRY, 23.8°C, 1M H₂SO₄)
Figure 25. R FOR O₂ REDUCTION WITH TIME AT -0.015A GINER PT FREE STANDING ELECTRODE ONLY (H₂O, 22.2°C, 1M H₂SO₄)

200CC/MIN O₂(H₂O)/O₂ SIDE

Figure 26. POTENTIAL WITH TIME DURING CYCLING GINER PEM/IR02, PT & PT FREE STANDING ELECTRODE (-0.05A & +0.05A, 23°C, 1M H₂SO₄)

1, 3, 5 CYCLE (-0.05A FOR 2 HR)
2, 4, 6 CYCLE (+0.05A FOR 1 HR)
Figure 27. Potential with time during cycling
Giner PEM/IRO2, Pt & Pt Free Standing Electrode
(-0.05A & +0.05A, 23°C, 1M H2SO4)

1st cycle (-0.05A for 2 hr)

Figure 28. Potential with time during cycling
Giner PEM/IRO2, Pt & Pt Free Standing Electrode
(-0.05A & +0.05A, Pt, 1M H2SO4)

O2 reduction

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Figure 29. O2 REDUCTION POTENTIAL WITH LOG TIME
GINER PEM/IR02,PT & PT FREE STANDING ELECTRODE
(CYCLE -0.05A & +0.05A, 23°C, 1M H2SO4)

1ST CYCLE
3RD CYCLE
5TH CYCLE

POTENTIAL, V (IR CORR)

LOG TIME, SEC

1.3.5 CYCLE (-0.05A FOR 2 HR)

Figure 30. POTENTIAL WITH TIME DURING CYCLING
GINER PEM/IR02,PT & PT FREE STANDING ELECTRODE
(-0.05A & +0.05A, 23°C, 1M H2SO4)

2ND CYCLE (+0.05A FOR 1 HR)
Figure 31. O2 Evolution Potential with Time during Cycling (GINER PEM/IRO2, Pt & Pt Free Standing Electrode (-0.05 & +0.05A, RT, 1M H2SO4))

Figure 32. O2 Evolution Potential with Log Time (GINER PEM/IRO2, Pt & Pt Free Standing Electrode (Cycle -0.05A & +0.05A, 23oC, 1M H2SO4))

2, 4, 6 Cycle (+0.05A for 1 HR)

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Figure 33. O2 REDUCTION POTENTIAL WITH TIME AT -0.15A
GINER PEM/1RO2,PT & PT FREE STANDING ELECTRODE
(H2O, 80.6oC, 1M H2SO4)

Figure 34. O2 REDUCTION POTENTIAL WITH LOG TIME AT -0.15A
GINER PEM/1RO2,PT & PT FREE STANDING ELECTRODE
(H2O, 80.6oC, 1M H2SO4)
Figure 35. O2 Reduction Potential with time at -0.06A
Giner PEM/IRO2, Pt & Pt Free Standing Electrode
(DRY, 27.2°C, 1M H2SO4)

Figure 36. O2 Reduction Potential with log time at -0.06A
Giner PEM/IRO2, Pt & Pt Free Standing Electrode
(DRY, 27.2°C, 1M H2SO4)
Figure 37. O2 REDUCTION POTENTIAL WITH TIME AT -0.015A
GINER PT FREE STANDING ELECTRODE ONLY
(H2O, 22.2°C, 1M H2SO4)

Figure 38. O2 REDUCTION POTENTIAL WITH LOG TIME AT -0.015A
GINER PT FREE STANDING ELECTRODE ONLY
(H2O, 22.2°C, 1M H2SO4)

200CC/MIN O2(H2O)/O2 SIDE

GPT465

GPT466

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Figure 39. TWO HOUR CYCLING OF O2 REDUCTION & EVOLUTION
GINER PEM/IR02, PT & PT FREE STANDING ELECTRODE
AT -0.05 A/CM² (21.7°C, 1M H2SO4)
FROM OCV, START AT -0.05 A/CM², THEN AT +0.05 A
GFT251
500CC/MIN 02/H201/O2 SIDE

Figure 40. POTENTIAL VS TIME WITH 2 HOUR CYCLING
GINER PEM/IR02, PT & PT FREE STANDING ELECTRODE
AT -0.05 A/CM² (21.7°C, 1M H2SO4)
FROM OCV, START AT -0.05 A/CM², THEN +0.05 A
GFT501
500CC/MIN 02/H201/O2 SIDE

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Figure 41. POTENTIAL VS LOG TIME WITH 2 HOUR CYCLING GINER PEM/IP02, PT & FT FREE STANDING ELECTRODE AT -0.05 A/cm2 (21.7°C, 1M H2SO4)

FROM OCV, START AT -0.05 A/cm2, THEN +0.05 A FOR -0.05 DATA

Figure 42. POTENTIAL VS TIME WITH 2 HOUR CYCLING GINER PEM/IP02, PT & FT FREE STANDING ELECTRODE AT +0.05 A/cm2 (21.7°C, 1M H2SO4)

FROM OCV, START AT -0.05A/cm2, THEN AT +0.05 A FOR +0.05 DATA
Figure 43: Potential vs Log Time with 2-Hour Cycling
Giner PEM/IR02/FT & FT Free Standing Electrode
At +0.05 A/cm² (23.3°C, 1 M H2SO4)

Figure 44: Potential vs Time with Cycling
Giner PEM/PT/IR02 & PT Free Standing Electrode
(23.3°C, 1 M H2SO4, O2/0.0001 M HCl)

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Figure 45. Anodic Potential vs Time at 0.1A
Giner PEM/PT/IR02 & Pt Free Standing Electrode
(23.3°C, 1M H2SO4, Cycle)

After -0.1A for 2.5 HR
(FROM 0.79 V)(BUBBLES?)

500CC/Min O2(H2O)/O2 Side

Figure 46. Anodic Potential vs (Time)1/2 at 0.1A
Giner PEM/PT/IR02 & Pt Free Standing Electrode
(23.3°C, 1M H2SO4, Cycle)

After -0.1A for 2.5 HR
(FROM 0.79 V)(BUBBLES?)

500CC/Min O2(H2O)/O2 Side
Figure 47. ANODIC POTENTIAL VS (TIME)\(^{1/2}\) AT 0.1A
GINER PEM/PT/IR02 & PT FREE STANDING ELECTRODE
(23.3°C, 1M H\(_2\)SO\(_4\), CYCLE)

AFTER \(-0.1A\) FOR 2.5 HR
(FROM 0.79 V)(BUBBLES?)

GPT329
500CC/MIN O\(_2\)(H\(_2\)O)/O\(_2\) SIDE

Figure 48. ANODIC POTENTIAL VS LOG TIME AT 0.1A
GINER PEM/PT/IR02 & PT FREE STANDING ELECTRODE
(23.3°C, 1M H\(_2\)SO\(_4\), CYCLE)

AFTER \(-0.1A\) FOR 2.5 HR
(FROM 0.79V)(BUBBLES?)

GPT117
500CC/MIN O\(_2\)(H\(_2\)O)/O\(_2\) SIDE

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Figure 49. ANODIC POTENTIAL VS LOG TIME AT 0.1A
GINER PEM/PT/IRO2 & PT FREE STANDING ELECTRODE
(23.3°C, 1M H2SO4, CYCLE)

AFTER -0.1A FOR 2.5 HR
(FROM 0.79V)(BUBBLES?)
500CC/MIN O2(H2O)/O2 SIDE

Figure 50. CATHODIC POTENTIAL VS TIME/START & AFTER ANODIC
GINER PEM/PT/IRO2 & PT FREE STANDING ELECTRODE
ALTERNATE 1 HR CATHODIC & ANODIC AT 0.01A

(22.2°C, 1M H2SO4)
500CC/MIN O2(H2O)/O2 SIDE
Figure S1. CATHODIC POTENTIAL VS LOG TIME/START & AFTER
GINER PEM/PT/IRO2 & PT FREE STANDING ELECTRODE
ALTERNATE 1 HR CATHODIC & ANODIC AT 0.01A

POTENTIAL, V (IR CORR)

LOG TIME, SEC

(22.2°C, 1M H2SO4)
500CC/MIN O2(H2O)/O2 SIDE

Figure S2. CATHODIC POTENTIAL VS LOG TIME AFTER 1 ANODIC
GINER PEM/PT/IRO2 & PT FREE STANDING ELECTRODE
ALTERNATE 1 HR CATHODIC & ANODIC AT 0.01A

POTENTIAL, V (IR CORR)

LOG TIME, SEC

(22.2°C, 1M H2SO4)
500CC/MIN O2(H2O)/O2 SIDE
Figure 53. Cathodic potential vs log time with cycling
Giner PEM/PT/IrO2 & Pt free standing electrode
(22.2°C, 1M H2SO4, 500cc/min)

Figure 54. Potential vs time with cycling
Giner PEM/PT/IrO2 & Pt free standing electrode
Alternate 1 hr cathodic & anodic at 0.01A

(22.2°C, 1M H2SO4)
500cc/min O2(H2O)/O2 side
Figure 55. Anodic Potential vs Time after Cathodic Giner PEM/PT/IRO2 & PT Free Standing Electrode Alternate 1 hr Cathodic & Anodic at 0.01A.

(22.2oC, 1M H2SO4)
500CC/MIN O2(H2O)/O2 SIDE

Figure 56. Anodic Potential vs Log Time after Cathodic Giner PEM/PT/IRO2 & PT Free Standing Electrode Alternate 1 hr Cathodic & Anodic at 0.01A

(22.2oC, 1M H2SO4)
500CC/MIN O2(H2O)/O2 SIDE

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Figure 57. Anodic Potential vs Time at 0.01A
Giner PEM/PT/IRO2 & PT Free Standing Electrode
(22.2°C, 1M H2SO4)

After -0.01A for 1 HR
500CC/MIN O2(H2O)/O2 SIDE

Figure 58. Anodic Potential vs Time at 0.01A
Giner PEM/PT/IRO2 & PT Free Standing Electrode
(22.2°C, 1M H2SO4)

After -0.01A for 1 HR
500CC/MIN O2(H2O)/O2 SIDE

GPT326
Figure 59. ANODIC POTENTIAL VS (TIME)1/2 AT 0.01A
GINER PEM/PT/IR02 & PT FREE STANDING ELECTRODE
(22.2oC, 1M H2SO4)

AFTER -0.01A FOR 1 HR
500CC/MIN O2(H2O)/O2 SIDE

Figure 60. ANODIC POTENTIAL VS (TIME)1/2 AT 0.01A
GINER PEM/PT/IR02 & PT FREE STANDING ELECTRODE
(22.2oC, 1M H2SO4)

AFTER -0.01A FOR 1 HR
500CC/MIN O2(H2O)/O2 SIDE
Figure 61. ANODIC POTENTIAL VS LOG TIME AT 0.01A  
GINER PEM/PT/IR02 & PT FREE STANDING ELECTRODE  
(22.2°C, 1M H2SO4) 

AFTER -0.01A FOR 1 HR  
500CC/MIN O2(H2O)/O2 SIDE  

Figure 62. ANODIC POTENTIAL VS LOG TIME AT 0.01A  
GINER PEM/PT/IR02 & PT FREE STANDING ELECTRODE  
(22.2°C, 1M H2SO4) 

AFTER -0.01A FOR 1 HR  
500CC/MIN O2(H2O)/O2 SIDE  

GPT242
Figure S6. Giner Data for O₂ Reduction at 80 C
Giner: NAFION, 3 ATM
PEM/IR0₂, PT & PT Free Standing Electrode
Single Cell (3 ATM)

Figure S6. Giner Data for O₂ Reduction at 80 C
Giner: NAFION, 3 ATM
PEM/IR0₂, PT & PT Free Standing Electrode
Single Cell (3 ATM)

Figure 65. Giner and Laer Data for O₂ Reduction at 80 C
Giner: NAFION, 3 ATM
Laer: DOW, 5 ATM

Figure 65. Giner and Laer Data for O₂ Reduction at 80 C
Giner: NAFION, 3 ATM
Laer: DOW, 5 ATM

Figure 66. Giner Tafel Data for O₂ Reduction Giner
PEM/IR0₂, PT & PT Free Standing Electrode
Single Cell (3 ATM)

Figure 66. Giner Tafel Data for O₂ Reduction Giner
PEM/IR0₂, PT & PT Free Standing Electrode
Single Cell (3 ATM)
Figure 69: Compare O₂ Reduction of LeRC & Giner Data

Figure 67. PEM/IRO₂, PT & PT Free Standing Electrode (80°C, 1 ATM O₂ for LeRC, 3 ATM for Giner)

Figure 68. Potential-Current Plots for O₂ Reduction Giner PEM/IRO₂, PT & PT Free Standing Electrode Comparison Giner (3 ATM) with CALC LeRC (3 ATM)
Figure 7a: Cathodic R Polarization for Giner Electrode PT Free Standing Only (39.4°C, 1M H₂SO₄, 0.09MA DHE)

Figure 7b: Tafel Plot for O₂ Reduction Giner PT Free Standing Electrode Only (81.0°C, 1M H₂SO₄)

Figure 7c: Cathodic R Polarization for Giner Electrode PT Free Standing Only (26.1°C, 1M H₂SO₄, 0.09MA DHE)

Figure 7d: Tafel Plot for O₂ Reduction Giner PT Free Standing Electrode Only (60.0°C, 1M H₂SO₄)
Figure 7A: Tafel Plot for O₂ Reduction Giner PT Free Standing Electrode Only (39.4°C, 1M H₂SO₄)

Figure 7B: Activation Energy for O₂ Reduction Giner PT Free Standing Electrode Only for 0.06 Region (1M H₂SO₄)

Figure 7C: Tafel Plot for O₂ Reduction Giner PT Free Standing Electrode Only (26.1°C, 1M H₂SO₄)
Figure 84: Activation Energy for O$_2$ Reduction Giner PT
Free Standing Electrode Only for 0.12 Region (1M H$_2$SO$_4$)

Figure 85: Tafel Plot of O$_2$ Reduction Giner PEM/IRO$_2$ PT Electrode Only (78.9°C, 1.5M H$_2$SO$_4$)

Figure 86: R Polarization vs. Current for O$_2$ Reduction Giner PEM/PT/IRO$_2$ Electrode (No Free Standing) (80.6°C, 3N H$_2$SO$_4$, After 1-2 Min)

Figure 87: Compare Tafel Plots for O$_2$ Reduction at 80°C Giner Electrodes (1M H$_2$SO$_4$)
Figure 83. R FOR O2 REDUCTION AT 80.0°C (GALVANOSTATIC)
Giner PEM/IRO₂, Pt & Pt Free Standing Electrode
(1M H₂SO₄)

(PREHEAT 80°C FOR 30)
EACH DATA POINT TAKEN AFTER ABOUT 2 MIN
R = 2.835 OHM (1.89 OHM/CM²)

Figure 84. R POLARIZATION FOR O2 REDUCTION
Giner PEM/PT/IRO₂ & Pt Free Standing Electrode
(60.6°C, 1M H₂SO₄)

80°C FOR 30, 60°C FOR 30
200CC/MIN O₂/H₂O/O₂ SIDE
0-100(R = 2.9367) 120(2.9370) 150(2.9335)
Figure 85.  
R POLARIZATION FOR O2 REDUCTION
GINER PEM/PT/IR02 & PT FREE STANDING ELECTRODE
(40.6°C, 1M H2SO4)

\[
\begin{align*}
\text{CURRENT, MA} & \quad 0 & \quad 50 & \quad 100 & \quad 150 \\
\text{POLARIZATION, MV} & \quad 0 & \quad 100 & \quad 200 & \quad 300 & \quad 400 & \quad 500 \\
\end{align*}
\]

80°C FOR 30, 40°C FOR 30
200CC/MIN O2(H2O)/O2 SIDE
R = 3.4826 (S = 3.4835, I = -0.1310)
GPEMFS38-49
GPT371

Figure 86.  
R POLARIZATION FOR O2 REDUCTION
GINER PEM/PT/IR02 & PT FREE STANDING ELECTRODE
(28.3°C, 1M H2SO4)

\[
\begin{align*}
\text{CURRENT, MA} & \quad 0 & \quad 50 & \quad 100 & \quad 150 \\
\text{POLARIZATION, MV} & \quad 0 & \quad 100 & \quad 200 & \quad 300 & \quad 400 & \quad 500 & \quad 600 \\
\end{align*}
\]

80°C, 60°C, 40°C, 28°C FOR 30
200CC/MIN O2(H2O)/O2 SIDE
R = 3.4826 (S = 3.4835, I = -0.1310)
GPEMFS38-49
GPT371
Figure 87. TAFEL PLOT FOR O₂ REDUCTION
GINE PEM/IR0₂,PT & PT FREE STANDING ELECTRODE
(80.0°C, 1M H₂SO₄)

LOG CURRENT DENSITY, A/CM²(GEOMETRIC)

Polarization, V (IR CORR)

(1) (2) (3)

(PREHEAT 80°C FOR 30)
200CC/MIN O₂(H₂O)/O₂ SIDE
S = 0.0715(1=0.4128), 0.12(0.4978)

GLEMPS1-12
GPT366

Figure 88. TAFEL PLOT FOR O₂ REDUCTION
GINE PEM/IR0₂,PT & PT FREE STANDING ELECTRODE
(80.0°C, 1M H₂SO₄)

LOG CURRENT DENSITY, A/CM²(GEOMETRIC)

Polarization, V

(1) (2) (3)

(PREHEAT 80°C FOR 30)
200CC/MIN O₂(H₂O)/O₂ SIDE
S = 0.0715(1=0.4128), 0.12(0.4978)

GLEMPS1-34
GPT368
**Figure 89. Tafel Plot for O₂ Reduction**
Giner PEM/IRO₂, Pt & Pt Free Standing Electrode
(40°C, 1 M H₂SO₄)

![Image](image_url)

Log Current Density, A/cm² (Geometric)

(Freeheat 80°C, 60°C, 40°C Pt: 30)

2000 CC/min O₂(H₂O)/O₂ Side

S=0.0706(1=0.4554).0.12(0.5526)

GPEMFS38–49

---

**Figure 90. Tafel Plot for O₂ Reduction**

Giner PEM/IRO₂, Pt & Pt Free Standing Electrode

![Image](image_url)

Log Current Density, A/cm² (Geometric)

Preheat 80°C, 60°C, 40°C, 28°C for 30

2000 CC/min O₂(H₂O)/O₂ Side

S=0.0706(1=0.4554).0.12(0.5526)

GPEMFS38–49

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Figure 91. TAFEL PLOTS FOR O2 REDUCTION
GINER PEM/IR02, PT & PT FREE STANDING ELECTRODE
(1M H2SO4)

Figure 92. R VS POLARIZATION FOR O2 REDUCTION FOR GINER
PEM/PT/IR02 & FREE STANDING ELECTRODE
(25 60C, 1M HC104, 10mA DHE)

R = 6.336 (S = 6.3455, t = -0.5402)
GPT443

FROM HIGH CURRENT
5000/60 MIN O2/PLATE - 0.95/SEC

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Figure 93. TAFEL PLOT FOR O₂ REDUCTION
GINER PEM/IRO₂, PT & PT FREE STANDING ELECTRODE
(25.6°C, 1M HC10₄)

\[ S = 0.0694(I = 0.4647)(-2.47) \]
\[ S = 0.127(I = 0.6066) \]

500CC/MIN O₂(H₂O)/O₂ SIDE
GPT488

Figure 94. COMPARISON OF TAFEL PLOTS FOR O₂ REDUCTION
GINER PEM/IRO₂, PT & PT FREE STANDING ELECTRODE
1M H₂SO₄ VS 1M HC1₀₄ (ABOUT 27°C)

1M H₂SO₄(28.3°C) 1M HC1₀₄(25.6°C)
GPT490
Figure 95. TAFEL PLOT FOR O2 REDUCTION
GINER PEM/IR02,PT & PT FREE STANDING ELECTRODE
(80.6, 1M HC1O4)

Polarization, V (IR CORR)

S = 0.0694(I = 0.4647)(-2.47)
S = 0.127(I = 0.6066) 500CC/MIN O2(H2O)/O2 SIDE

Figure 96. COMPARISON OF TAFEL PLOTS FOR O2 REDUCTION
GINER PEM/IR02,PT & PT FREE STANDING ELECTRODE
1M H2SO4 VS 1M HC1O4

Polarization, V (IR CORR)

1M H2SO4(80.0oC) 1M HC1O4(80.6oC)
Figure 97. Tafel plots for O2 reduction
Giner PEM/IR02, Pt vs Pt free standing electrode
& 2 electrodes (about 800°C, H2SO4)

0.5

0.4

0.3

0.2

0.1

Potential, V (IR corrd.)

Log current density, A/cm² (geometric)

(1) PEM only

(2) PEM & FS

(3) FS only

Pem, S=0.12 (I=0.6371)

GPT454B

Figure 98. O2 reduction slopes with temperature
Giner PEM/IR02, Pt & Pt free standing electrode
For 0.06 region

Slope, V/decade

In H2SO4

2.3RT/F

Srinivasan (micro)

Average S=0.0708

GPT373
Figure 99. SLOPES FOR O2 REDUCTION AT ABOUT 800°C
0.06 REGION

(GINER & MICRO AT 800°C, UNSUPPORTED AT 850°C)

Figure 100. O2 SLOPE V THERmPERATURE
GINER PERCENTAGE Pt FREE STANDING ELECTRODE
0.12 REGION

2.3RT aF

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Figure 101.

ACTIVATION ENERGY FOR O2 REDUCTION
GINER PEM/IR02, PT & PT FREE STANDING ELECTRODE
0.06 REGION (1M H2SO4)

\[ E_a = 6.5 \text{KCAL/M (S=-1423.5, I=-1.703)} \]

EXCHANGE CURRENT DENSITY IS GEOMETRIC

200CC/MIN O2(H2O)/O2 SIDE

Figure 102.

ACTIVATION ENERGIES FOR O2 REDUCTION
GINER VS SRINIVASAN MICROELECTRODE
0.06 REGION

GINER \( E_a = 6.5 \text{KCAL/M (TRUE CM2, 1 ATM)} \)
ASSUME: SRINIVASAN FOR 80oC
SRINIVASAN \( E_a = 17.8 \text{(5 ATM, MICRO)} \)

FACTOR OF 470CM2/CM2

GPT374C
Figure 102. Activation Energy for O2 Reduction
Giner PEM/IrO2, Pt & Pt Free Standing Electrode
0.12 Region (1M H2SO4)

\[ E_a = 1.8 \text{ Kcal/M}(S = -390.59, l = -3.056) \]

Figure 104. Srinivasan Activation Energy for 0.12 Region
Microelectrode/Nafion
(5 ATM O2)

\[ E_a = 7.1 \text{ Kcal/M}(S = -1537.1, l = -1.4848) \]
Figure 105.

**ACTIVATION ENERGY FOR O2 REDUCTION**

GINER PEM/IR02, PT & PT FREE STANDING ELECTRODE

0.12 REGION (1M H2SO4)

**LOG EXCHANGE CURRENT DENSITY, A/FM2**

**RECIPIROCAL TEMPERATURE, (K-1)**

GINER \( E_0 = 1.9 \text{KCAL/M} \)

SRINIVASAN \( E_0 = 7.4 \text{KCAL/M} \)

\( (S = -1615, \mu = -1.232) \)

GPT3740:

2000CC/MIN 02(H20) O2 SIDE

Figure 106.

**R WITH TIME FOR O2 EVOLUTION AT +0.1A**

GINER PT FREE STANDING ELECTRODE ONLY

(H20, 84.4°C, 1.5M H2SO4)

2000CC/MIN 02(H20) O2 SIDE

GPT/IR02/41

PREHEAT 90, 80°C FOR 30

GPT255

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Figure 107. R with time for O2 evolution at +0.06A
GINER PEM/IR02,PT & PT FREE STANDING ELECTRODE
(H2O, 23.9oC, 1M H2SO4)

100CC/MIN O2(H2O)/O2 SIDE
PREHEAT 80oC

Figure 108. R with log time for O2 evolution at +0.06A
GINER PEM/IR02,PT & PT FREE STANDING ELECTRODE
(H2O, 23.9oC, 1M H2SO4)
Figure 109. R POLARIZATION FOR O2 EVOLUTION
GINER PEM/IR02, PT & PT FREE STANDING ELECTRODE
(77.2°C, 1M H2SO4)

R = 2.603 (1.735 OHM/CM2)
500CC/MIN O2(H2O)/O2 SIDE
90, 80°C FOR 60

DATA AFTER 2-3 MIN
GPT1
GPT224

Figure 110. R VS POLARIZATION FOR O2 EVOLUTION FOR GINER ELECTRODE (PEM/PT/IR02 & FREE STANDING )
(40.0°C, 1M H2SO4, 0.09MA DHE)

R = 2.937 (S = 2.9363, I = 0.09540)
500CC/MIN O2(H2O)/O2 SIDE

GPT228

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**Figure III.**  R VS POLARIZATION FOR O2 EVOLUTION FOR GINER ELECTRODE (PEM/PT/IR02 & FREE STANDING)  
(60.0oC, 1M H2SO4, 0.09MA DHE)

![Graph showing polarization vs current](image)

\[ R = 2.693 (S = 2.6897, I = 0.6000) \]

500CC/MIN O2(H2O)/O2 SIDE

---

**Figure II.**  TAFEL PLOT OF O2 EVOLUTION  
GINER PEM/IR02, PT & PT FREE STANDING ELECTRODE  
(77.2oC, 1M H2SO4)

![Graph showing polarization vs current](image)

\[ S = 0.0475 (I = 0.3482) (-2.555) \]

\[ S = 0.0379 (I = 0.3237) \]

500CC/MIN O2(H2O)/O2 SIDE

---

90, 80oC FOR 60
Figure 113. TAFEL PLOT OF O2 EVOLUTION
GINER PEM/IR02, PT & PT FREE STANDING ELECTRODE
(60.0oC, 1M H2SO4)

S=0.0479 \times (1=0.3586)(-2.8) GPT2
S=0.0373 \times (1=0.3291) 500CC/MIN O2(H2O)/O2 SIDE
AFTER 2-3 MIN 90,80,60oC FOR 60

Figure 114. TAFEL PLOT OF O2 EVOLUTION
GINER PEM/IR02, PT & PT FREE STANDING ELECTRODE
(40.0oC, 1M H2SO4)

S=0.0477 \times (1=0.3689)(-2.875) GPT3
S=0.0379 \times (1=0.3406) 500CC/MIN O2(H2O)/O2 SIDE
AFTER 2-3 MIN 90,80,60,40oC FOR 60
Figure 115. TAFEL PLOT OF O\textsubscript{2} EVOLUTION
GINER PEM/IR\textsubscript{02},PT & PT FREE STANDING ELECTRODE
(81.7°C, 1M HClO\textsubscript{4})

S=0.037 (I=0.3043)
90,80°C for 60
500CC/MIN O\textsubscript{2}/H\textsubscript{2}O/02 SIDE

Figure 116. TAFEL PLOT OF O\textsubscript{2} EVOLUTION
GINER PEM/IR\textsubscript{02},PT & PT FREE STANDING ELECTRODE
(61.2°C, 1M HClO\textsubscript{4})

0.037/I=0.31071
90,80°C FOR O2
500CC/MIN O\textsubscript{2}/H\textsubscript{2}O/02 SIDE
Figure 117: Tafel Plot of O2 Evolution
Giner PEM/iRO2, Pt & Pt Free Standing Electrode
(40.0°C, 1M HClO4)

Figure 118: Tafel Plot of O2 Evolution
Giner PEM/iRO2, Pt & Pt Free Standing Electrode
(26.1°C, 1M HClO4)
Figure 119. Tafel plots with temperature for O₂ evolution
Giner PEM/IR02, Pt & Pt free standing electrode
(1 M HClO₄)

Figure 120. Activation energy for O₂ evolution
Giner PEM/IR02, Pt & Pt free standing electrode
(1 M HClO₄)
Figure 121. COMPARISON OF TAFEL PLOTS FOR O2 EVOLUTION
GINER PEM/IR02, PT & PT FREE STANDING ELECTRODE
ABOUT 80°C (1M H2SO4 VS 1M HClO4)

H2SO4(77.2°C), HClO4(81.7°C)
500CC/MIN O2(H2O)/O2 SIDE.

Figure 122. ANODIC R POLARIZATION FOR GINER ELECTRODE
PEM/IR02, PT ELECTRODE ONLY
(H2O, 27.2°C, 1M H2SO4)

200CC/MIN O2(H2O)/O2 SIDE
80°C, 60°C, 40°C, RT FOR 30
R=7.384(S=7.4101,l=-1.5597)
Figure 123. Anodic R polarization for Giner electrode
PEM/IRO2, Pt electrode only
(H2O, 40.0°C, 1M H2SO4)

200 CC/Min O2(H2O)/O2 side
80°C, 60°C, 40°C for 30
R = 7.065 (S = 7.092, I = -1.631)

GPT469

Figure 124. Anodic R polarization for Giner electrode
PEM/IRO2, Pt electrode only
(H2O, 59.4°C, 1M H2SO4)

200 CC/Min O2(H2O)/O2 side
80°C, 60°C for 30
R = 6.460 (S = 6.475, I = -0.9552)

GPT468
Figure 125. ANODIC POLARIZATION FOR GINER ELECTRODE PEM/IR02.PT ELECTRODE ONLY
(H2O, 80.0°C, 1 M H2SO4)

200CC/MIN O2(H2O)/O2 SIDE
80°C FOR 30
R = 6.233(S = 6.2603, l = -1.6496)

Figure 126. R POLARIZATION VS CURRENT FOR O2 EVOLUTION GINER FREE STANDING ELECTRODE ONLY (NO PEM)
(85.0°C, 3 M H2SO4, 0.09MA DWE)

R = 1.897(S = 1.9102, l = -1.8545)
200CC/MIN O2(H2O)/O2 SIDE
**Figure 127. Tafel Plot for O2 Evolution**
GINER PEM/IR02, Pt Electrode Only
(80.0°C, 1M H2SO4)

![Graph showing Tafel plot for O2 evolution](image)

- $S = 0.0475 (I = 0.3377) (-2.765)$
- $S = 0.039 (I = 0.3142)$
- 200cc/min O2(H2O)/O2 side
- 80 FOR 60 BEFORE

**Figure 128. Tafel Plot for O2 Evolution**
GINER PEM/IR02, Pt Electrode Only
(40.0°C, 1M H2SO4)

![Graph showing Tafel plot for O2 evolution](image)

- $S = 0.347 (I = 0.3412)$
- 200cc/min O2(H2O)/O2 side
- 80, 60, 40°C FOR 30 BEFORE
Figure 129. TAFEL PLOT FOR O$_2$ EVOLUTION
GINER PEM/IR02, PT ELECTRODE ONLY
(59.4°C, 1M H$_2$SO$_4$)

![Graph showing Tafel plot for O$_2$ evolution.]

- Polarization voltage (V) vs. Log current density (A/cm$^2$) (geometric).
- Region 1: 0.039 region (I = 0.3285) after 2 min.
- 200cc/min O$_2$(H$_2$O) / O$_2$ side.
- 80-60°C for 30 before.

GPT472
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2
Last decade advances in the phosphoric acid fuel cell technology brought it to "almost commercial" status. Today's acid fuel cells are intended to use oxygen from ambient air and relatively expensive fuel (light distillates, methanol, natural gas, etc.) or gaseous fuel from a gasifier. Two applications are envisioned for commercialization: as a dispersed power plant for electric utility cogeneration plants of 40-200 kilowatt size for buildings utilizing waste heat, operating at ambient pressure. Both types of power plants use concentrated phosphoric acid in an immobilized matrix with Teflon bonded gas diffusion coating containing 0.25 and 0.5 mg Pt/sq.cm at the anode and cathode, respectively. Typical goals for cell voltage at ambient pressure and 70-120 psig and 210-340 psig are 0.7 and 1.2 volts for air and fuel, respectively. About five years of operating life with decay (less than 3 mV/1000 hrs) is targeted.

Catalysts for phosphoric acid fuel cells typically consist of a finely divided form dispersed uniformly on the face of a conductive carbon black. Much current research is enhancing the efficiency as well as extending the lifetime of electrodes, specifically the oxygen electrode. Both catalysis as well as electrode degradation mechanisms are involved in the simultaneous achievement of high efficiency and long life in a fuel cell. Major causes of performance decay are support corrosion and activation, mainly through surface area loss due to sintering of catalyst particles. Several modifications of carbon blacks and substitutive materials such as TiC are being investigated to improve the resistance of supports. Many modifications of platinum are attempted to enhance the efficiency and lifetime of the platinum during the operation of a fuel cell. Electrochemical sintering of the platinum catalyst takes place. The associated decrease in surface area extent increases its "activity" for oxygen reduction but increased Tafel slope; the net result is a significant loss in activity. Some advances were made in reducing the sintering of platinum catalysts, mainly by alloying the platinum catalysts. It is possible to substantially reduce the sintering of the platinum catalysts by alloying the free energy, reaction, mixed between activity and lifetime. Among many alloy catalysts, one that stands out is the platinum-palladium alloy while the platinum-tungsten alloy catalyst. By using the concept of using environmental science of the fuel cell, some promising results were obtained. A heat-treatment for one hour was mostly with high surface times more is not performance structure. In the platinum-tungsten alloy catalysts
ADVANCED ELECTROCATALYSTS
FOR
PHOSPHORIC ACID FUEL CELLS

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OBJECTIVES AND SCOPE

* DEVELOP CATALYSTS WITH APPROXIMATELY FIVE YEARS LIFE
* IMPROVE PERFORMANCE USING PLATINUM ALLOY CATALYSTS
* IMPROVE STABILITY USING PLATINUM ALLOY CATALYSTS
GENERAL ALLOYING TECHNIQUE

Pt / C + MO\textsubscript{x} \rightarrow Pt - M / C + CO\textsubscript{2}
PERFORMANCE OF Pt AND Pt ALLOY CATALYSTS

200°C
100% H₃PO₄

CURRENT DENSITY (mA/cm²)

VOLTAGE (iR Corrected, V)
SPECIFIC O$_2$ REDUCTION ACTIVITY

190°C
100% H$_3$PO$_4$

SPECIFIC ACTIVITY AT 900 mV, $\mu$A/cm$^2$

NEAREST NEIGHBOR DISTANCE, Å
CHARACTERIZATION TECHNIQUES

* X-RAY DIFFRACTION
* TEM
* EDAX
XRD OF Pt/VULCAN XC-72 AND Pt-Cr/VULCAN XC-72

Pt-Cr/VULCAN XC-72
\( a_0 = 3.861 \)

Pt/VULCAN XC-72
\( a_0 = 3.918 \)

2.224 Å (111)
1.931 Å (200)
1.365 Å (220)

2.262 Å (111)
1.983 Å (200)
1.388 Å (220)
STANDARD 10% Pt/C

PL TERNARY ALLOY/C
EDAX OF SINGLE Pt-Cr/VULCAN XC-72 PARTICLE

INTENSITY

ENERGY (kev)

Pt

Cr

5.41

9.44
OPTIMIZATION OF G82-5-19

* EFFECT OF HEAT-TREATMENT TEMPERATURE

* EFFECT OF PLATINUM CONTENT
EFFECT OF HEAT-TREATMENT TEMPERATURE ON $O_2$ PERFORMANCE AND LATTICE PARAMETER

- $O_2$
- $a_0$
- $200 \text{ mA/cm}^2$
- $200 \degree C$
- $100\% \text{ H}_3\text{PO}_4$
- G82-5-19
EFFECT OF HEAT-TREATMENT TEMPERATURE ON
O₂ REDUCTION PERFORMANCE

TEST CONDITIONS:
- 200°C
- 100% H₃PO₄
- FLOATING HALF-CELL

CELL VOLTAGE (iR-Corrected mV)

HEAT-TREATMENT TEMPERATURE (°C)
EFFECT OF INCREASING Pt CONTENT ON HALF-CELL PERFORMANCE

- Δ = O₂
- O = AIR
- 200 mA/cm²
- 200°C
- 100% H₃PO₄

VOLTAGE (iR-Corrected, mV)

INCREASING Pt CONTENT (%)
STABILITY
LIFE PERFORMANCE OF A FULL CELL CONTAINING THE G82-5-34 ELECTROCATALYST AT ATMOSPHERE PRESSURE (BUILD 40)

DECAY RATES FROM PEAK

<table>
<thead>
<tr>
<th>Condition</th>
<th>DECAY RATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>-4.7 mV/1000 Hr</td>
</tr>
<tr>
<td>AIR</td>
<td>-4.2 mV/1000 Hr</td>
</tr>
</tbody>
</table>

200 mA/cm²

190 °C

100% H₃PO₄

ATMOSPHERIC PRESSURE
CORROSION CURRENTS OF GRAPHITIZED AND NON-GRAPHITIZED SUPPORTS

TEST CONDITIONS:
800 mV vs. RHE
70 psig
200°C
100% H₃PO₄

○ HT BLACK PEARL 2000
○ VULCAN XC-72
△ HT VULCAN XC-72

CORROSION CURRENT (µA/mg) vs. TIME (Minutes)
EFFECT OF CATALYST SUPPORT ON PERFORMANCE

200 °C
100% H₃PO₄

- VULCAN XC-72
- HT VULCAN
- HT BLACK PEARLS
- G-82-5-19 TYPE

VOLTAGE (IR Corrected, V)

CURRENT DENSITY (mA/cm²)
CATALYST AND ELECTRODE RESEARCH FOR PHOSPHORIC ACID FUEL CELLS

By A. C. Antolne and R. B. King*

The U. S. Department of Energy (DOE) is funding phosphoric acid fuel cell commercialization programs at Westinghouse, Engelhard, and UTC. In support of these commercialization efforts, DOE Morgantown Energy & Technology Center, Morgantown, WV, is also funding research under an advanced research and technology development (AR&TD) program. These programs are managed by NASA Lewis Research Center, Cleveland, OH, and include, in addition to catalyst and electrode research, carbon component technology development at Great Lakes Research Corp. and fuel cell modelling and analysis support work at Cleveland State University.

The major purpose of the AR&TD program is to conduct research on fuel cell catalysts and electrodes, the results of which will provide major improvements in electrode performance and life, and also will aid in reducing fuel cell costs. The research is being carried out at Giner, Inc., under contract DEN3-294; ECO under contract DEN3-206; and Stonehart Associates, Inc., under contract DEN 3-350. Correlated research is being carried out at Lawrence Berkeley Laboratory and Los Alamos National Laboratory.

At Giner, the original objective was the development of electrocatalysts, particularly ternary alloys of platinum which will exhibit improved activity and stability as cathodes in hot, concentrated phosphoric acid. Binary alloys were identified which exhibited increased activity over the baseline platinum catalyst. Also, using the results from X-ray diffraction measurements on binary alloys, a correlation between the electrocatalyst activity and the crystallographic nearest-neighbor distance was found. This is illustrated in Fig. 1 (1). This correlation was significant in that it provided a guideline for the selection of additional candidates.

In recent years it has become apparent that to reach the efficiency required, phosphoric acid fuel cells will have to be operated under pressure. This requirement places some additional constraints on fuel cell component parts, including the

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catalyst support. Although the usual support, Vulcan XC-72, shows good stability in long-time testing, it lacks the corrosion resistance needed for pressurized operation. Therefore, another objective of the Glner program is to prepare the high activity ternary alloy catalysts on more corrosion-resistant materials. The materials selected are graphitized carbon blacks, and several promising candidates have been identified which have shown good corrosion resistance under pressurized conditions. At present, heat-treated (2700°C) Black Pearls 2000 is the material of choice and the major emphasis is being put on developing efficient electrodes with this carbon support.

In developing efficient electrodes with the new supports, particular attention will be paid to the preparation of oxide-free ternary alloys. Recent tests have shown that standard methods of preparing ternary alloys in some cases leads to a resultant mixture of alloys and oxides. Further, in addition to oxide-free alloys, known mixtures of alloy-free mixed oxides will be prepared and studied. The purpose is to obtain a better understanding of the chemical and physical states of the catalysts and their effects on the catalytic activity.

Throughout this research, attention has been given to understanding the reason for the increased activity of alloy catalysts. This effort will be aided by some analyses using advanced techniques that have been brought into the electrocatalyst development program. These analyses will be performed by the DOE National Laboratories. They will be using an ion beam equipped with a nuclear microprobe with PDCE and RBS analyses. TDS, XRF, XPS, and EXAFS will also be used. These analytical tools will be used to characterize the electrode preparation before as well as after use in a fuel cell - for example, after 1,000 hours. An important part of this effort is the monitoring of changes in catalyst and electrode form, composition, and structure during use, and effects on activity and stability.

At ECO, efforts to improve cell performance and reduce catalyst costs were attempted by the investigation of a class of organometallic cathode catalysts primarily represented by the tetraazaannulenes (TTAs). Under the program, a new mixed catalyst was developed. This catalyst is a mixture of carbons catalysed with an organometallic and a noble metal. The stability and performance of the mixed catalyst was verified in 1,000-hour tests in half-cells and in full cells using oxygen or air and hydrogen as reactants. Test conditions included constant current loads in 85 percent H₃PO₄ in the temperature range of 160°-200°C. At a load of 100 mA/cm² with platinum as the noble metal and CoTAA as the organometallic, the performance achieved was in the range of 720-750 mV versus the DHE. This cathode performance is 15-25mV higher than that obtained by using platinum alone.

A model for the improved performance observed with the mixed catalyst was developed: these catalysts act to reduce oxygen on the organometallic and to further reduce the hydrogen peroxide formed on the noble metal. This model was verified based on cathode performance response to hydrogen peroxide addition, on the effect of the use of non-noble metal peroxide reducing agents, on rotating ring-disk evaluation, and on observed increases in open-circuit potential.

With continued emphasis on seeking ways to reduce costs, additional work was done to develop non-noble metal alternatives for the noble metal in the mixed catalyst. Among the best identified was a mixed catalyst of Mn and CoTAA. Testing in a complete cell was done for 1,000 hours with hydrogen and oxygen as reactants. During this test period, the cathode performance decayed by 19 mV (from 676 to 657 versus DHE) and the anode performance by 15 mV (74 mV to 89 mV versus DHE). (This test demonstrates that the TAA-based mixed catalyst is stable in the 200°C, H₃PO₄ environment, and that whatever degradation products are produced at the
The cathode do not significantly affect anode performance. A patent application on "Mixed Catalyst for Primary Acid Fuel Cell" has been filed.

The purpose of the work at Stonehart Associates, Inc., is to study diffusion processes in gas diffusion electrode structures. The reason for this approach is the premise that the preparation of efficient gas diffusion electrodes is recognized to be, to a large extent, an art and that the detailed mechanisms of their operation are not understood. Using the results of the study, and considering models that have been presented in the literature (2, 3), the contractor was required to formulate a series of guidelines for making improvements in electrode structures.

The work under this program has been both experimental, trying different approaches, and theoretical, developing a mathematical model that fits the experimental data. One of the experimental approaches tried involved the flocking of the electrode materials using various quantities of benzyl alcohol to reduce the agglomerate size in the finished electrode.

In another experimental approach, a dry blending of three carbon components (one catalyzed, two uncatalyzed) was chosen to improve ionic conduction and to provide gas channels that are not filled with electrolyte.

Other attempts are being made using a water-floc fabrication technique for ultrasonic dispersion. Also, surfactants with different physical and chemical properties are being screened for their carbon dispersing ability in the formation of electrode structures. Experimental investigations will also be carried out in other areas. The effect of the thickness of the electrocatalyst backing layer on gas diffusion through the backing layer will be determined. Other electrodes of constant thickness, but with different platinum loadings will be investigated. Finally, the pore volume within the electrode structure will be progressively modified with the use of selected pore formers.

Parallel to, and in conjunction with, the experimental work, using the models of Ref. 2 and Ref. 3, Stonehart Associates, Inc., has developed computer software for a mathematical theory of mass transport of reactants in porous gas diffusion electrodes. In the theory, a simplified model for the electrode structure was used and fitted to experimental data. Various numerical parameters contributing to the electrode structure were examined. Comparisons of the model to experimental performance data were carried out using diagnostic gas mixtures of oxygen, air, one percent oxygen in helium, and one percent oxygen in nitrogen. Fig. 2 shows the results using a standard electrode. The fit is especially good for the low concentrations.

Additional work has been done, and more is in progress, to develop a detailed model of the electrode structure. This model will encompass numerical values for all of the physical parameters operating within the electrode structure and will hold for all four gas compositions. Using the model, it will be possible to show to what extent the various resistances that influence electrode performance are operative at various potentials and corresponding current densities. This use of the model can give valuable information in a convenient form to aid in selecting the parameters for the electrode formulation process, where the goal is the development of more effective electrode structures.
Fig. 1. Specific activity for oxygen reduction versus electrocatalyst nearest-neighbor distance.

Fig. 2. Cathode performance curves.

References
The purpose of this effort was to aid in assessing the technical base for flight qualified materials for advanced concentrators. At present, no firm technical data base exists for concentrator materials. Thus, no material is commercially available that can be certified for long-term application. Included in the consideration of concentrator materials are materials of construction, optical films, and coatings.

Some general 'reference' books are available such as the "Space Materials Handbook (3rd ed.) 1969." (Ref. 1) In it are new materials knowledge and data obtained from the design and successful launching of a wide variety of space systems. Selections and recommendations for a variety of materials are made, based on space experience and ground-based simulation. Further, materials are recommended for the performance of several hypothetical space missions, with the space environments varying depending on the specific mission parameters. Selections are made for thermal control materials, optical materials, lubricants for several systems, polymeric materials for adhesives, seals, and structural applications, spacecraft antennas, electronic and miscellaneous components and materials. In addition to organic structural materials, inorganic structural materials are also considered, though their selection is not usually determined by the effects of the space environment on them.

Another 'reference' book is the "Engineered Materials Handbook, Vol. 1, Composites, 1987," (Ref. 2) which contains in-depth engineering information on composite materials. Contents include information on the properties and forms of the basic fibers and matrix materials, as well as of the composite materials themselves. Included, also, are analysis and design of composite materials and of the structures made from them; testing of composites, manufacturing and fabrication processes, quality control, failure analysis, applications and experience are also included. For space structures, trusses, platforms, pressure vessels and tanks, and shells are considered. A chapter on long-term environmental effects is included, but these were primarily related to ground and flight environments on composites used in aircraft.

In 1986, Marshall Space Flight Center published the "Materials Selection List for Space Hardware"
Systems" (Revisions of MSFC Hdbk - 527 and Johnson Space Center 09604). (Ref. 3). Ratings for metallic materials are based on corrosion resistance, stress corrosion cracking susceptibility, $N_2O_4$ and $N_2H_4$ fluid system compatibility, compatibility with liquid and gaseous oxygen, mechanical impact with liquid and gaseous oxygen, gaseous oxygen pneumatic impact, and fluid system compatibility with low and high pressure gaseous hydrogen. For nonmetallic materials, ratings are based on flammability, toxicity/offgassing, odor, thermal vacuum stability, static age life, and fluid system compatibility (nitrogen tetroxide, hydrazine, hydraulic fluid, liquid oxygen, and gaseous oxygen).

Standard/Commercial parts are also rated for flammability, toxicity, thermal vacuum stability, static age life (for nonmetallics) fluid systems compatibility, stress corrosion cracking, and corrosion.

Mention is made of atomic oxygen effects, but no ratings are given. Mention is also made of the fact that long term effects on metals are unknown, but that some protective coatings which show promise include silicone based coatings, fluorinated overcoats, thin metal overcoats and metal oxide overcoats.

More specific information can be found in reports such as NASA Technical Paper 1220, Evaluation of Materials for High Performance Solar Arrays (Status Report No. 1), (1978), Ref. 4).

About 50 materials were identified as candidates from the following functional categories: (1) solar cell covers, (2) adhesives, (3) substrate paddings, (4) harness materials, (5) substrate strength materials, (6) mast materials, and (7) thermal control treatments. About 25 materials were tested and evaluated. The UV/vacuum test series consisted of exposures of 500 Equivalent Sun Hours (ESH) at 1 sun, 1500 ESH at 3 suns, 1500 ESH at 6 suns, and 500 ESH at 10 suns at $10^{-4}$ pascal. Particle irradiation/vacuum test series consisted of electron flux densities of $10^{12}$ particles/cm$^2$ to $10^{16}$ particles/cm$^2$ at $10^{-4}$ pascal. The portion of the tests covered included out-gassing exposures, UV/vacuum exposure through 1500 ESH at 3 suns, and proton exposures in vacuum to $10^{16}$ particles/cm$^2$. Property determinations considered were absorptivity, emissivity, spectral reflectance, breaking strength, elongation, and flexure for appropriate materials. Some of the results are given in Tables 1, 2, 3, and 4. It was concluded from this work that all non-metallic materials selected for long duration mission spacecraft must be evaluated. Further, that deleterious effects of synergistic interactions of different particulate and solar radiation must also be determined for otherwise acceptable materials. A next phase in the test program was
planned with exposures at higher levels of particulate and solar radiations, and an assessment made of the damage mechanisms. No further report, though, has been made.

Another report with more specific information is NASA TM-78306, Space Environmental Effects on Materials, 1980. (Ref. 5) This report describes research oriented toward the acquisition of long-term environmental effects data needed to support the design and development of large Low Earth Orbit (LEO) and Geosynchronous Earth Orbit (GEO) space platforms and systems for the decade of the eighties. The space vacuum, electromagnetic radiation, particulate radiation, and space debris were considered. Charged particle radiation on silicon solar cells was studied. Results are shown in Figure 1. It was noted that the combined electron and proton effects were not known. Another report was referred to (Ref. 6) in which it was noted that a major portion of that study effort was directed toward developing a laboratory facility that would provide a suitable combined simulation of the critical space environmental conditions, and in which simultaneous irradiation could be done. The results from testing 23 different flexible film materials exposed to a simulated 5-year GEO equatorial environment showed the initial analytical unpredictability of the synergistic effects of electrons, protons, and UV encountered in the GEO environment. Teflon materials (FEP and PFA) undergo substantial changes in optical, thermophysical, and mechanical properties. For example, Teflon specimens subjected to combined near UV and high energy electron radiation became brittle after 17 to 30 months of exposure, while specimens exposed to 5-year equivalent electron radiation, only, retained a percentage of their original ultimate elongation. The spectral reflectance of aluminized Kapton holds up well in LEO, where UV only need be considered, but is seriously affected by a combined UV, electron, and proton environment. The results for a 5-year exposure are shown in Figure 2. Among the conclusions from this NASA TM is that the acquisition of additional data from long duration exposure in the combined environment is mandatory.

Other evidence for the need for combined radiation testing is given in Reference 7. The purpose of that investigation was to compare the effects of UV-only radiation on the solar absorptance of contaminated second surface thermal control mirrors. Optical solar reflectors were contaminated with volatile condensible material outgassed from inertial upper stage solid propellant. The combined radiation simulation consisted of 40 keV electrons and 30 keV protons at a flux of $5 \times 10^9$ particles/cm$^2$-sec each and a one sun level of UV. Total fluence of each type of particle, by the end of 245 hrs of testing, was estimated at $5 \times 10^{15}$ particles/cm$^2$. The radiation environment of the second test used the same one-
sun level of UV, but had no charged particles. The results from the two tests showed a larger increase in solar absorptance with combined radiation (protons, electrons, and UV) than with UV radiation alone. The degrading effect of combined radiation was more than twice that of UV alone.

For making selections of materials from the data available to date, some guidelines are becoming available. One such, in a preliminary (not yet published) version, has been prepared by Johnson Space Center. The title is “Material Selection Guidelines to Limit Atomic Oxygen Effects on Spacecraft Surfaces” (Ref 8). The purpose is to provide guidelines in selecting materials for satellites and space platforms, designed to operate within the LEO environment, which limit the effects of atomic oxygen interactions with spacecraft surfaces. The guidelines apply to spacecraft which require extensive use of organic films, polymeric materials, and composite structures. Included in the specification is a nomograph for estimating atomic oxygen fluence and, consequently, the degree of surface erosion the spacecraft will experience over its lifetime. Use of the nomograph is included in this report as Appendix 1. A summary of data obtained from spaceflight experiments are shown in Tables 5, 6, and 7. The reaction rate data can be used for general assessment of the effects of atomic oxygen on spacecraft surfaces. The authors claim that, "sufficient data exists at this time to permit generalizations which can be used to provide a gross assessment of surface effects. These generalizations are...

1. Unfilled organic materials containing only C, H, O, N, and S react with approximately the same reaction efficiency, \(2-4 \times 10^{-24} \text{ cm}^3/\text{atom}\).

2. Perfluorinated carbon-based polymers and silicones have lower reaction efficiencies by a factor of ten or more than organics.

3. Filled or composite materials have reaction efficiencies that are strongly dependent upon the characteristics of the fillers.

4. Metals, except for silver and osmium, do not show macroscopic changes. Microscopic changes have, however, been observed and should be investigated for systems very sensitive to surface properties. Silver and osmium react rapidly and are generally considered unacceptable for use in uncoated applications.
5. Magnesium fluoride and oxides in various forms show good stability.*

A complete list of "basically everything that is known from the actual flight experiments," on the effects of atomic oxygen on materials, is given in Table 8. This table was obtained from JPL in January 1988.

Selections of best candidate materials (when considering atomic oxygen effects) to date (as of May 1988) were made after consideration of advantages and disadvantages of the materials use in the space environment. These results are shown in Tables 9 and 10. The material was presented at a workshop in June 1988. (Ref. 9).

Effects other than atomic oxygen and for materials other than for surfaces have also been considered. A bibliography entitled, "Durability of Materials for Precision Space Structural Applications" was compiled at Langley in late 1987. The papers included relate to moisture effects, thermal expansion, impact penetration, microcracking, thermal cycling effects, and space radiation, primarily on composites. The bibliography is included as Appendix II in this report.

Specific attention is being paid to solar dynamic concentrator materials at LeRC. The Electro-Physics Branch of the Power Technology Division has prepared a list of candidate materials (substrates, optical coatings, protective coatings), (Table 11) together with some results of optical performance and atomic oxygen durability (Table 12). The laboratory tests used an RF plasma asher. In other work with Kapton solar array blankets, protective coatings of silicon dioxide or a mixture of silicon dioxide and polytetrafluoroethylene are projected to be durable for more than 27 years in a 500 km Space Station orbit (Ref. 10). With expected use of adhesives in solar dynamic concentrator, durability tests must be conducted. One recent study (Ref. 11) evaluated selected adhesive/adherend bonded joints after a simulated, ten-year thermal-vacuum cycling, (±250°F, 10^-15 torr 3650 cycles) space environment exposure. The adhesives (all epoxies) were used to bond titanium, aluminum, and magnesium to various composite adherends.

In the preparation of concentrators in the past a recurring problem has been that of differing (unmatched) coefficients of thermal expansion of materials being bonded together. In Figure 3 some thermal expansion
coefficients of various material are shown (Ref. 12). It can be seen that the metals have smaller coefficients than the usual epoxy resin or silicone rubber. Recently, though, low thermal expansion polyimides have become available, and a desired CTE can be obtained by blending of low and high CTE material, or by copolymerization. In Figure 4 the extent of warping in polyimide coated silicon wafers is shown. PIQ (Hitachi Chemical Co., LTD) is a conventional polyimide; PIQ 100 is a modified low thermal expansion polyimide. Figure 5 shows the relation between the thermal expansion coefficient of polyimide films and the radius of curvature of stainless steel foil. A flat shape results when the CTEs (about 1.8 x 10⁻⁵ K⁻¹) are close.

Polyimides are also being developed as adhesives for high temperature use with Kapton film. At M&T Chemicals Inc., a siloxane modified flexible thermoplastic polyimide (called M&T 4605-40 adhesive) has been developed which behaves excellently as a high temperature adhesive for Kapton film. Kapton to copper adhesion for flexible circuit applications has been accomplished, and aluminum to aluminum bonding is being evaluated. Epoxy coatings that do not shrink on curing are being prepared at Epolin. These are based on a ring-opening, expansion polymerization technology during which monomers expand in volume on polymerization. Enhanced adhesion can occur also, since expanding resins can penetrate microcracks in substrates, rather than shrink away from substrates on curing, as conventional coating resins do.

Aromatic polyimides are being considered for use on large space structures where the need exists for high temperature (200° - 300°C) stable, flexible polymeric film and coating materials, that have high optical transparency in the 300 - 600 nm range. Currently available polymers which are transparent/colorless (polyesters, aliphatic polyimides) have limited long-term thermal stability. Thermally stable aromatic polyimides generally have poor transparency in the visible range. A recent research effort was made to synthesize and characterize linear aromatic polyimide film having maximum optical transparency (Ref. 13). Some of the more optically transparent were evaluated for potential use in a space environment. The results are shown in Figures 6 and 7. The UV transmission cut-offs ranged from 310 to 388 nm compared to 450 nm for commercial polyimide film of the same thickness. Following electron irradiation, the films were 2 to 2.5 times more transparent at 500 nm than commercial polyimide film (Kapton). Further, the films are all relatively thermally stable in air at 300°C. In addition, some of these new polymers are soluble in common organic solvents, such as chloroform, and can then be spray-coated for space applications where the substrate cannot endure the traditional 300°C polyimide cure temperature.
Radiation effects, electrons and protons, on four polysulfone films were studied (Ref. 14). These materials are prime candidates for graphite fiber/polymeric matrix composites for use in structural application in large space systems. The preliminary results show that both chain scission and crosslinking occur as a result of irradiation, and that a threshold for major property changes occurs at approximately $10^9$ rads total dose. In GEO, it is estimated that the interior dose of a 4-ply composite would be about $10^9$ rads during a 30-year use life. Some of the results are shown in Figure 8, and the conclusion is reached that the polysulfones studied (3 commercial, 1 experimental) seem to be relatively stable to both electron and proton radiation. Recent work on the combined effects of UV and charged particle radiation on aluminized Kapton was reported at the Workshop on Solar Concentrators for Space Solar Dynamic Power Systems (LeRC, June 7, 1988). Samples of direct manufactured Kapton polyimide film were exposed on the aluminized side to continuum ultraviolet radiation and monoenergetic electrons and protons nearly continuously for 1363 hours. Irradiation rates were set to provide exposure at real-time intensities, and the exposure was in "ultra-high" ($10^{-8}$ torr) vacuum. In past tests, polyimides exposed at rates greater than one sun have shown questionable stability. These tests show that the tensile, dimensional, and reflective properties of these Kapton samples were much more stable and a conclusion was reached that a threshold for damage was found to be above one sun. Therefore, these Kapton polyimide films may be usable in long-term space applications where they are deployed in tension and unsupported or without thermal contact. Some of the results of the tests are shown in Table 13 and Figure 9.

Some thermal cycling durability tests of coated Kapton were also recently reported (private communication, Electro-Physics Branch). The results are shown in Figure 10. HMDS/TFE 8/5 and 8% PTFE-92% SiO$_2$ coated Kapton were thermal cycled from +80 to -80°C for 10,000 cycles (each cycle lasted approximately one minute). Following thermal cycling, these samples and similarly coated but not thermal cycled samples were fully dehydrated under vacuum and ashed for 66.58 hours. Thermal cycling appears to have little or no effect on the atomic oxygen durability of the plasma polymerized coatings evaluated.

An example of ground-based simulation facilities to provide meaningful data was given at Space Environmental Effects on Materials Workshop (SEEM), June 1988. This was testing the effects of
thermal cycling on composite materials for space structures. Some of the results are shown in Figures 11, 12, and 13. Testing to date showed little difference in the crack density.

Closing Remarks

The means of obtaining a reliable data base for materials for long-term application in space can be summarized by the key issues described in the NASA Workshop on AO effects, November 1986:

“1) The ability to develop a reliable prediction model to assess the effects of long-term exposure of materials to the LEO environment,

2) The ability of ground-based simulation facilities to provide meaningful data in the development of LEO durable materials; and

3) Aeronometric determination of the compositional details of the low earth orbital environment.”

Thus, despite the amount of information available regarding the reactivity of spacecraft materials to atomic oxygen, it was recognized that the existing data base was limited in its application, and not adequate for long-lived (30-year) missions. Therefore, ground-based simulation must be accomplished. For atomic oxygen, simulation facilities are being developed that will accurately simulate the LEO environment. The goal is a beam of neutral atomic oxygen at an energy level of 5eV, with a flux in the range of $10^{16} - 10^{17}$ atoms/cm$^2$-sec. An exposure of 50 hours would give the needed fluence of $10^{22} - 10^{23}$ atoms/cm$^2$. With simulations characteristic of the natural environment, basic interaction mechanisms can be studied. With a reliable materials interaction data base and an understanding of the surface chemistry which gives rise to the interactions, development of new materials or coatings that do not degrade in the LEO environment can be accomplished. This approach must of course be taken with regard to other environmental factors.

One of the outputs of the SEEM Workshop was an evaluation of the current status of various environmental effects, and the needs and recommendations for future work. In this report, only the material related to solar (UV) radiation will be addressed. The current status includes the recognition that most materials degrade as result of solar radiation. It is also recognized that the information
available on UV effects on materials is almost entirely short-term, and thus provides a limited data base. Flight data on coating degradation is confused by contamination. In ground testing, there is little correlation between testing laboratories in regard to UV exposure conditions, calibration techniques, and detectors. Further, there are few facilities with EUV exposure capability. Lastly, there is limited data on thermal cycling effects from laboratories and from space.

Needed information would include material behavior for a 30-year lifetime under UV + AO + thermal cycling, and for 5 to 15-year lifetime (SDI missions) UV + high energy radiation and UV + AO + thermal cycling. To obtain the information, UV testing methodology with standardized test procedures for accelerated UV testing has to be developed. This would be complemented by a data base of flight data from long-term missions. Also needed would be a flight data base on UV flux/distribution. Finally, long-term thermal cycling data is needed. The composites on board the LDEF could provide 5-year flight data, for example.
REFERENCES


13. Ibid, pg. 16.

14. Ref. 11, pg. 256.
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<td>Substrate Padding</td>
</tr>
<tr>
<td>White Paint S13GLO</td>
<td>T-3</td>
<td>DTI</td>
<td>Silicone Paint/Low Outgassing</td>
<td>Thermal Control</td>
</tr>
<tr>
<td>Aluminumized Teflon - Acrylic PSA</td>
<td>T-4</td>
<td>Sheldahl</td>
<td>Aluminum/Teflon Acrylic</td>
<td>Thermal Control</td>
</tr>
<tr>
<td>Graphite Epoxy</td>
<td>M-3</td>
<td>Fiberite Corporation</td>
<td>High Modulus Graphite/934 Epoxy</td>
<td>Panel Skin Containment Box Cover and Bottom</td>
</tr>
<tr>
<td>Scotchcast Epoxy 250</td>
<td>P-3</td>
<td>3M</td>
<td>Epoxy</td>
<td>On Array Padding</td>
</tr>
<tr>
<td>Kapton - Silicone PSA</td>
<td>A-4</td>
<td>Sheldahl</td>
<td>Polyimide/Silicone</td>
<td>Adhesive System</td>
</tr>
<tr>
<td>Silvered (3 mil) Mylar</td>
<td>T-5</td>
<td>Sheldahl</td>
<td>Silver/Polyester</td>
<td>Thermal Control</td>
</tr>
<tr>
<td>Aluminum (1 mil) Mylar</td>
<td>T-6</td>
<td>Sheldahl</td>
<td>Aluminum/Polyester</td>
<td>Thermal Control</td>
</tr>
<tr>
<td>Aluminum - (2 mil) Mylar - (2 mil) Teflon Coating</td>
<td>T-7</td>
<td>Sheldahl</td>
<td>Aluminum/Polyester Teflon</td>
<td>Thermal Control</td>
</tr>
<tr>
<td>Silvered (1 mil) Polyester with 4 mil Acrylic Coating</td>
<td>T-8</td>
<td>Sheldahl</td>
<td>Silver/Polyester/Acrylic</td>
<td>Thermal Control</td>
</tr>
<tr>
<td>Material</td>
<td>Mechanical Property</td>
<td>Breaking Strength</td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>---------------------</td>
<td>-------------------</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>S-1</td>
<td></td>
<td>10^{13}</td>
<td>10^{14}</td>
<td>10^{15}</td>
</tr>
<tr>
<td>M-1</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>M-2</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>M-3</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>A-2</td>
<td>NC</td>
<td>-5</td>
<td>+15</td>
<td>+11</td>
</tr>
<tr>
<td>P-2</td>
<td>-42</td>
<td>-36</td>
<td>-50</td>
<td>-65</td>
</tr>
<tr>
<td>M-5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P-3</td>
<td>-</td>
<td>-</td>
<td>NC</td>
<td>-1</td>
</tr>
<tr>
<td>A-4</td>
<td>-</td>
<td>NC</td>
<td>-19</td>
<td>-</td>
</tr>
<tr>
<td>T-6</td>
<td>*</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

NA = Data not applicable to sample.
NC = No significant change, within 2σ statistics.
- = Data not available for this report.
* = Vacuum produced severe warpage and degradation.
**Table 3. Percentage Change in Mechanical Properties of UV Irradiated Materials**
(Data Generated Using 2σ Statistics) (Ref. 4)

<table>
<thead>
<tr>
<th>Material</th>
<th>Mechanical Property</th>
<th>Breaking Strength</th>
<th>Elongation</th>
<th>Maximum Fiber Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>500 ESH at 1 sun</td>
<td>1500 ESH at 3 suns</td>
<td>500 ESH at 1 sun</td>
</tr>
<tr>
<td>S-1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-3*</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

NA = Data not applicable to sample.
NC = No significant change, data within 2σ limits.
— = Data not available.
* = Data obtained after only 4 h/12 ESH exposure due to excessive outgassing.
### Table 4. Percentage Change in Optical Properties of UV Irradiated Materials
(Data Generated Using 2σ Statistics) (Ref. 4)

<table>
<thead>
<tr>
<th>Optical Property</th>
<th>Absorptivity</th>
<th>Emissivity</th>
<th>Spectral Reflectance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>500 ESH at 1 sun</td>
<td>1500 ESH at 3 sun</td>
<td>500 ESH at 1 sun</td>
</tr>
<tr>
<td>Material</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T-2a</td>
<td>NC</td>
<td>NC</td>
<td>NC</td>
</tr>
<tr>
<td>T-4</td>
<td>-</td>
<td>NC</td>
<td>-</td>
</tr>
<tr>
<td>T-3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>NC, NC</td>
<td>-</td>
<td>NC, NC</td>
</tr>
<tr>
<td>T-8&lt;sup&gt;b&lt;/sup&gt;</td>
<td>NA</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. Data generated for 1000 ESH and 3000 ESH at 1 sun

b. Severe degradation during weight loss test.

NA = Data not applicable to sample.

NC = No significant change, data within 2σ limits.

- = Data not available.
<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>REACTION EFFICIENCY CM$^3$/ATOM</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAPTON</td>
<td>3 x 10$^{-24}$</td>
</tr>
<tr>
<td>MYLAR</td>
<td>3.4</td>
</tr>
<tr>
<td>TEDLAR</td>
<td>3.2</td>
</tr>
<tr>
<td>POLYETHYLENE</td>
<td>3.7</td>
</tr>
<tr>
<td>POLYSULFONE</td>
<td>2.4</td>
</tr>
<tr>
<td>GRAPHITE/EPOXY</td>
<td>2.1</td>
</tr>
<tr>
<td>1034C</td>
<td></td>
</tr>
<tr>
<td>5208/T300</td>
<td></td>
</tr>
<tr>
<td>EPOXY</td>
<td>2.6</td>
</tr>
<tr>
<td>POLYSTYRENE</td>
<td>1.7</td>
</tr>
<tr>
<td>POLYREZINIMIDAZOLE</td>
<td>1.5</td>
</tr>
<tr>
<td>25% POLYSILXOKANE/45% POLYIMIDE</td>
<td>0.3</td>
</tr>
<tr>
<td>POLYESTER 7% POLYSILXOKE/93% POLYIMIDE</td>
<td>0.6</td>
</tr>
<tr>
<td>POLYESTER</td>
<td>HEAVILY ATTACKED</td>
</tr>
<tr>
<td>POLYESTER WITH ANTIOXIDANT</td>
<td>HEAVILY ATTACKED</td>
</tr>
<tr>
<td>SILICONESE</td>
<td></td>
</tr>
<tr>
<td>RTV-560</td>
<td>0.2*</td>
</tr>
<tr>
<td>DC6-2204</td>
<td>0.2*</td>
</tr>
<tr>
<td>T-650</td>
<td>0.2*</td>
</tr>
<tr>
<td>DC1-2577</td>
<td>0.2*</td>
</tr>
<tr>
<td>BLACK PAINT 2306</td>
<td>0.3-0.4*</td>
</tr>
<tr>
<td>WHITE PAINT A276</td>
<td>0.3-0.4*</td>
</tr>
<tr>
<td>BLACK PAINT 2302</td>
<td>2.03*</td>
</tr>
<tr>
<td>PERFLUORONATED POLYMERS</td>
<td></td>
</tr>
<tr>
<td>TFE</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>FEP</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>CARBON (VARIOUS FORMS)</td>
<td>0.9-1.7</td>
</tr>
<tr>
<td>SILVER (VARIOUS FORMS)</td>
<td>HEAVILY ATTACKED</td>
</tr>
<tr>
<td>OSMIUM</td>
<td>0.026</td>
</tr>
</tbody>
</table>

* UNITS OF MG/CM$^2$ FOR STS-8 MISSION. LOSS IS ASSUMED TO OCCUR IN EARLY PART OF EXPOSURE; THEREFORE, NO ASSESSMENT OF EFFICIENCY CAN BE MADE.
### TABLE 6. Some Effects Observed on Thin Films Exposed to $3.5 \times 10^{20}$ Oxygen Atoms cm$^{-2}$ In Low Earth Orbits (Ref. 8)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Optical Density</th>
<th>Metal Thickness (nm)</th>
<th>Estimated Thickness Changes (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unexposed</td>
<td>Exposed</td>
<td>Unexposed</td>
</tr>
<tr>
<td>Indium film</td>
<td>1.76</td>
<td>1.98</td>
<td>32.3</td>
</tr>
<tr>
<td>Au/Al film</td>
<td>1.79</td>
<td>1.91</td>
<td>15.6</td>
</tr>
<tr>
<td>Au/Ag film</td>
<td>0.35</td>
<td>0.31</td>
<td>4.8</td>
</tr>
<tr>
<td>Nb film</td>
<td>0.70</td>
<td>0.54</td>
<td>16.9</td>
</tr>
<tr>
<td>Hf film</td>
<td>1.0</td>
<td>1.65</td>
<td>47.3</td>
</tr>
<tr>
<td>Hf film</td>
<td>1.0</td>
<td>1.65</td>
<td>47.3</td>
</tr>
</tbody>
</table>

*Results were obtained for both contamination and temperature as described in the text; results shown are for ambient temperatures believed to be between 271 and 300 K.

* Films were deposited on fused silica flats described in text unless noted otherwise.

* See text for details. 6 nm Pt/0.4 nm Os was poorly protected, we were unable to make measurements of the 6 nm Pt/0.4 nm Os because the back of the substrate was rough ground.
The Materials were exposed to the RAM direction to obtain a total atomic oxygen fluence of $2.45 \times 10^{10}$ atoms/cm$^2$
### TABLE 7.A
**STS - 41G PROPERTY DATA ON OVERCOATED PAINTS**

<table>
<thead>
<tr>
<th>Evaluations</th>
<th>2302 Glossy Black with OI 651 Overcoat</th>
<th>2302 Glossy Black with RTV-602 Overcoat</th>
<th>2302 Glossy Black with MN-1-1104-0 Overcoat</th>
<th>2853 Glossy Yellow with MN-1-1104-0 Overcoat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exposed Flight Specimens</td>
<td>.972</td>
<td>.969</td>
<td>.970</td>
<td>.469</td>
</tr>
<tr>
<td>Optical Property, Absorptivity (a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nominal Control Values of Absorptivity (a)</td>
<td>.972</td>
<td>.973</td>
<td>.972</td>
<td>.458</td>
</tr>
<tr>
<td>Mass Loss of Flight Specimen due to Atomic Oxygen Exposure</td>
<td>None</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Negligible</td>
</tr>
<tr>
<td>Comments on Exposure Effects</td>
<td>Maintains specular character of 2302</td>
<td>Loss of 2302 specular character</td>
<td>Loss of 2302 specular character</td>
<td>Loss of 2853 specular character, slight increase partially due to UV darkening</td>
</tr>
</tbody>
</table>

**NOTE:** The effect of applying an overcoat to these paints is to increase the initial absorptivity by 1 to 2%.
TABLE 7.B
STS - 41G RESULTS ON PROTECTIVE OVERCOATS FOR SILVER

<table>
<thead>
<tr>
<th>Overcoat Material/ Nominal Thickness</th>
<th>Preparation Technique</th>
<th>Comments on Protection Effectiveness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum 500 Å</td>
<td>Vapor deposition</td>
<td>Aluminum generally protective, but spots and streaks indicate some silver oxidation. Film thickness considered insufficient for good protection.</td>
</tr>
<tr>
<td>Gold 500 Å</td>
<td>Vapor deposition</td>
<td>No evidence of silver oxidation (scaling) and very few surface imperfections. Film thickness insufficient based on discoloration for long term protection.</td>
</tr>
<tr>
<td>Gold 5000 Å</td>
<td>Vapor deposition</td>
<td>Significant amount of spots and scaling which tend to indicate contamination of the interconnect before and during plating yielding a porous, non-uniform coating. Analyses complicated by contamination effects.</td>
</tr>
<tr>
<td>Gold 2500 Å</td>
<td>Electroplated</td>
<td>Significant scaling on surface.</td>
</tr>
<tr>
<td>Gold 5000 Å</td>
<td>Electroplated</td>
<td>Generally provided good protection. Film thickness insufficient based on discoloration for long term exposure.</td>
</tr>
<tr>
<td>Palladium 500 Å</td>
<td>Vapor deposition</td>
<td>Poor protection, extensive discoloration and spots. Oxygen in palladium.</td>
</tr>
<tr>
<td>Palladium 5000 Å</td>
<td>Vapor deposition</td>
<td>Slightly better protection than 500 Å. Oxygen in palladium. Poor adhesion.</td>
</tr>
<tr>
<td>DC-1104 ~ (0.5 mil)</td>
<td>Brushed</td>
<td>No silver oxidation. Good adhesion. Thick coating.</td>
</tr>
<tr>
<td>DC-1200 Primer ~ (0.1 to 0.5 mil)</td>
<td>Brushed</td>
<td>Inadequate protection.</td>
</tr>
</tbody>
</table>
### TABLE 8. EFFECTS OF ATOMIC OXYGEN ON MATERIALS

<table>
<thead>
<tr>
<th>Reaction Efficiency</th>
<th>Range of Reaction Efficiency</th>
<th>No. of Samples (Est.)</th>
<th>Optical Property Changes</th>
<th>Comments</th>
<th>Data Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teflon</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FEP &amp; TFE</td>
<td>0.2</td>
<td>0.03</td>
<td>0.1</td>
<td>0-0.2</td>
<td>&gt;22</td>
</tr>
<tr>
<td>75% Polysiloxane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyimide</td>
<td>0.3</td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Teclor, White</td>
<td>0.4</td>
<td>0.6</td>
<td>0.6</td>
<td>0.4-0.6</td>
<td>&gt;11</td>
</tr>
<tr>
<td>75% Polysiloxane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyimide</td>
<td>0.6</td>
<td>0.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>1.2</td>
<td>1.2</td>
<td>0.9-1.7</td>
<td>≥ 4</td>
<td></td>
</tr>
<tr>
<td>Polybenzenimidazole (PBI)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Epoxy</td>
<td>1.7</td>
<td>1.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polystyrene</td>
<td>1.7</td>
<td>1.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kapton, black</td>
<td>1.4</td>
<td>2.2</td>
<td>1.8</td>
<td>1.4-2.2</td>
<td>&gt;13</td>
</tr>
<tr>
<td>Teclor, clear</td>
<td>1.3</td>
<td>2.3</td>
<td>2.3</td>
<td>1.3-3.2</td>
<td>16</td>
</tr>
<tr>
<td>Polysulfone</td>
<td>2.4</td>
<td>2.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kapton</td>
<td>2.5</td>
<td>3.0</td>
<td>2.6</td>
<td>2.2-3.1</td>
<td>&gt;81</td>
</tr>
<tr>
<td>Mylar</td>
<td>2.3</td>
<td>2.9</td>
<td>2.8</td>
<td>1.8-4.5</td>
<td>&gt;46</td>
</tr>
<tr>
<td>Phra</td>
<td>3.1</td>
<td>3.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyimide</td>
<td>3.3</td>
<td>3.3</td>
<td>2.3-4.7</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Polyethylene</td>
<td>3.7</td>
<td>3.7</td>
<td>3.3-4.3</td>
<td>&gt; 2</td>
<td></td>
</tr>
</tbody>
</table>

Reaction Efficiencies Not Determined:
- Polyester
- Polyester with antioxidant
- Mylar with antioxidant

Heavily Attached

For most materials without an estimate of the number of samples tested, the efficiency OR mass loss data is based on only one (1) sample.
### TABLE 9. MATERIALS APPLICATIONS IN SPACE ENVIRONMENT

**SILICONES/FLUOROSILICONES:**

**ADVANTAGES**
- FORM TOUGH, FLEXIBLE COATINGS
- CURED CONTROLLED VOLATILITY VERSIONS EXHIBIT LOW OUTGASING
- FLEXIBLE AT LOW TEMPERATURES (DIMETHYLSILICONE: Tg ~-60°C)
- SILICONES AVAILABLE IN MANY COMMERCIAL FORMULATIONS
- EASILY APPLIED (SPRAY, DIP, BRUSH)
- SPACE USE/QUALIFICATION DATABASE AVAILABLE
- RELATIVELY CHEMICALLY INERT

**DISADVANTAGES**
- STRIPPED, SPACE GRADE CONTROLLED VOLATILITY FLUOROSILICONES WILL BE SIGNIFICANTLY MORE EXPENSIVE THAN SILICONES
- FLUOROSILICONES MAY BE DIFFICULT TO BOND
- LONG TERM SOLAR UV EFFECTS ARE UNKNOWN
- LONG TERM CONVERSION OF SILICONE TO SILICA UNDER ATOMIC OXYGEN EXPOSURE, CAUSING LOSS OF FLEXIBILITY
- FLUOROSILICONES LESS DEVELOPED THAN SILICONES
### TABLE 9. (cont'd) MATERIALS APPLICATIONS IN SPACE ENVIRONMENT

**FLUOROCARBONS:**

**ADVANTAGES**

- **COMMERCIALY AVAILABLE:**
  - AS COATING ON KAPTON
  - AS FREE STANDING FILM

- **SPACE USE/QUALIFICATION DATABASE AVAILABLE**

- **RELATIVELY CHEMICALLY INERT**

- **FORMS FLEXIBLE COATINGS**

- **LOW OUTGASSING**

**METALS:**

**ADVANTAGES**

- **THIN (< 0.1 MIL) COATINGS READILY FORMED**

- **LARGE AREA SUBSTRATES CAN BE COATED BY CONTINUOUS ROLL-TO-ROLL COMMERCIAL PROCESSES**

- **LOW OUTGASSING**

- **SPACE USE/QUALIFICATION DATABASE AVAILABLE**

- **INERT TO ELECTROMAGNETIC RADIATION IN SOLAR UV REGION**

- **MANY RELATIVELY INERT/SELF PASSIVATING**

**DISADVANTAGES**

- **EMBRITTLED BY SOLAR UV/AO COMBINATION**

- **DIFFICULT TO BOND**

- **LIMITED FLEXIBILITY**

- **DIFFICULT TO PRODUCE DEFECT-FREE COATINGS**

- **OPAQUE—REQUIRES COATING FOR ACCEPTABLE**
<table>
<thead>
<tr>
<th>MATERIALS</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>SILICONES</td>
<td></td>
</tr>
<tr>
<td>PLASMA DEPOSITED HMDS HMDS/TFE</td>
<td>AO RESISTANT, TACK-FREE, LOW OUTGASSING</td>
</tr>
<tr>
<td>CVI-1144-0</td>
<td>AO RESISTANT, LOW OUTGASSING, FLEXIBLE, ROLL-TO-ROLL PROCESS</td>
</tr>
<tr>
<td>S13G-LO</td>
<td>WIDE RANGE APPLICATION, LOW OUTGASSING, TACK FREE</td>
</tr>
<tr>
<td>FLUOROSILICONES</td>
<td></td>
</tr>
<tr>
<td>CV-3530</td>
<td>AO RESISTANT, LOW OUTGASSING, FLEXIBLE, ROLL-TO-ROLL PROCESS</td>
</tr>
<tr>
<td>FLUOROCARBONS</td>
<td></td>
</tr>
<tr>
<td>TFE</td>
<td>AO RESISTANT, LOW OUTGASSING, TACK FREE</td>
</tr>
<tr>
<td>FEP</td>
<td></td>
</tr>
<tr>
<td>HYBRID</td>
<td></td>
</tr>
<tr>
<td>S10/AI</td>
<td>AO RESISTANT, TAILORED, LIMITED FLEX. OPTICAL PROPERTIES, TACK FREE, LOW OUTGASSING</td>
</tr>
</tbody>
</table>

TABLE 10. BEST CANDIDATE MATERIALS AS OF MAY 1988
### Table 11. Solar Dynamic Concentrator Materials

<table>
<thead>
<tr>
<th>Candidate Substrate Materials:</th>
<th>Graphite/epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Titanium honeycomb sandwich</td>
</tr>
<tr>
<td></td>
<td>Aluminum honeycomb sandwich</td>
</tr>
<tr>
<td></td>
<td>Aluminum honeycomb</td>
</tr>
<tr>
<td></td>
<td>Aluminum foam</td>
</tr>
<tr>
<td></td>
<td>Vitreous carbon foam</td>
</tr>
<tr>
<td></td>
<td>Stainless steel with Sol-Gel</td>
</tr>
<tr>
<td></td>
<td>Boron carbide</td>
</tr>
<tr>
<td></td>
<td>Boron carbide foam</td>
</tr>
<tr>
<td></td>
<td>Kevlar</td>
</tr>
<tr>
<td></td>
<td>Ultralow expansion glass</td>
</tr>
<tr>
<td></td>
<td>Silicon carbide foam</td>
</tr>
<tr>
<td></td>
<td>Zerodur</td>
</tr>
<tr>
<td></td>
<td>Silicon dioxide</td>
</tr>
<tr>
<td></td>
<td>Beryllium</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Candidate Optical Coatings:</th>
<th>Aluminum</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Silver</td>
</tr>
<tr>
<td></td>
<td>Platinum</td>
</tr>
<tr>
<td></td>
<td>Beryllium</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Candidate Protective Coatings:</th>
<th>Silicon dioxide</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aluminum oxide</td>
</tr>
<tr>
<td></td>
<td>Silicon nitride</td>
</tr>
<tr>
<td></td>
<td>Aluminum nitride</td>
</tr>
<tr>
<td></td>
<td>Magnesium oxide</td>
</tr>
<tr>
<td></td>
<td>Magnesium fluoride</td>
</tr>
<tr>
<td></td>
<td>Beryllium oxide</td>
</tr>
<tr>
<td></td>
<td>Beryllium nitride</td>
</tr>
</tbody>
</table>
## TABLE 12. SDFS CONCENTRATOR MATERIALS OPTICAL PERFORMANCE AND ATOMIC OXYGEN DURABILITY

<table>
<thead>
<tr>
<th>A. SUBSTRATE</th>
<th>INITIAL SOLAR SPEC. REFLECTANCE</th>
<th>FINAL SOLAR SPEC. REFLECTANCE</th>
<th>HOURS ASHED</th>
<th>EQUIVALENT KAPTON A/O FLUENCE ATOMS/CM²SEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. ALUMINUM</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Platinum</td>
<td>0.698</td>
<td>0.691</td>
<td>39.3</td>
<td>4.6 x 10²⁰</td>
</tr>
<tr>
<td>a. None</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Rhodium</td>
<td>0.656</td>
<td>0.631</td>
<td>54.3</td>
<td>6.4 x 10²⁰</td>
</tr>
<tr>
<td>a. None</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Silver</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. Al₂O₃ (350 Å)</td>
<td>0.850</td>
<td>0.823</td>
<td>62.0</td>
<td>7.3 x 10²⁰</td>
</tr>
<tr>
<td>b. MgF₂ (920 Å)</td>
<td>0.892</td>
<td>0.879</td>
<td>88.5</td>
<td>1.0 x 10²¹</td>
</tr>
<tr>
<td>c. SiO₂ (400 Å)</td>
<td>0.886</td>
<td>0.762</td>
<td>62.0</td>
<td>7.3 x 10²⁰</td>
</tr>
<tr>
<td>d. Si₃N₄ (820 Å)</td>
<td>0.907</td>
<td>0.518</td>
<td>48.5</td>
<td>5.7 x 10²⁰</td>
</tr>
<tr>
<td>e. Si₃N₄ (2,000 Å)</td>
<td>0.789</td>
<td>0.725</td>
<td>400.5</td>
<td>4.7 x 10²¹</td>
</tr>
<tr>
<td>f. Si₃N₄ (2,500 Å)</td>
<td>0.545</td>
<td>0.482</td>
<td>271.5</td>
<td>3.2 x 10²¹</td>
</tr>
<tr>
<td>B. BERYLLIUM</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Platinum</td>
<td>0.697</td>
<td>0.685</td>
<td>39.3</td>
<td>4.6 x 10²⁰</td>
</tr>
<tr>
<td>a. None</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Rhodium</td>
<td>0.634</td>
<td>0.418</td>
<td>54.3</td>
<td>6.4 x 10²⁰</td>
</tr>
<tr>
<td>a. None</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Silver</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. Al₂O₃ (350 Å)</td>
<td>0.866</td>
<td>0.779</td>
<td>62.0</td>
<td>7.3 x 10²⁰</td>
</tr>
<tr>
<td>b. SiO₂ (400 Å)</td>
<td>0.914</td>
<td>0.859</td>
<td>62.0</td>
<td>7.3 x 10²⁰</td>
</tr>
<tr>
<td>c. Si₃N₄ (820 Å)</td>
<td>0.914</td>
<td>0.634</td>
<td>48.5</td>
<td>5.7 x 10²⁰</td>
</tr>
<tr>
<td>C. BERYLLIUM/COPPER</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Silver</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. Si₃N₄ (2,000 Å)</td>
<td>0.886</td>
<td>0.854</td>
<td>400.5</td>
<td>4.7 x 10²¹</td>
</tr>
</tbody>
</table>
### TABLE 13. TENSILE PROPERTIES

<table>
<thead>
<tr>
<th>KAPTON SAMPLE</th>
<th>BREAKING STRENGTH</th>
<th>ELONGATION AT BREAKING</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unirradiated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.70 lb, 2.4 x 10^4 psi</td>
<td>15%</td>
</tr>
<tr>
<td>2</td>
<td>0.68</td>
<td>16</td>
</tr>
<tr>
<td>3</td>
<td>0.64</td>
<td>12.5**</td>
</tr>
<tr>
<td>4</td>
<td>0.66</td>
<td>13</td>
</tr>
<tr>
<td>5</td>
<td>0.64</td>
<td>12</td>
</tr>
<tr>
<td>Irradiated*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.60 lb, 2.1 x 10^4 psi</td>
<td>5.7%</td>
</tr>
<tr>
<td>2</td>
<td>0.45</td>
<td>2.2</td>
</tr>
<tr>
<td>3</td>
<td>0.60</td>
<td>5.0</td>
</tr>
</tbody>
</table>

*After 1363 equivalent solar UV hours, 1.5 x 10^{16} electrons/cm² (50-keV), and 1.5 x 10^{16} protons/cm² (50-keV), as described in detail on page 5.

**The third digit is not "significant". It is shown since it is the value read out by the equipment operator, and to indicate a trend.
Figure 1. Electron and proton degradation of silicon solar cells. (Ref. 5)
Figure 2. Directional spectral reflectance of 2-mil second surface aluminized kapton. (Ref. 5)
Figure 3. Thermal expansion coefficients of various materials. (Ref. 12)
Figure 4. Extent of warping in polyimide coated silicon wafer. (Ref. 12)
Figure 5. Relation between thermal expansion coefficient of polyimide film and radius of curvature of stainless steel foil. (Ref. 12)
Figure 6a. UV-visible spectra of 0.5 mil 6F-containing polyimide films

Figure 6b. UV-visible spectra of UV-irradiated 6F-containing polyimide films before irradiation. (Ref. 13)
Figure 7. UV-visible spectra of e-irradiated 6F-containing polyimide films (Ref. 13)
Figure 8. Radiation effects on four polysulfone films. (Ref. 14)

\[ (10^8 - 10^{10} \text{ rads} @ 2(10)^6 \text{ rad/hr}) \] (1 Mev protons or electrons)

\[
\begin{align*}
&\left( 0 - \bigcirc - \text{SO}_2 - \bigcirc - 0 - \bigcirc - \bigcirc \right)_{n} \\
&\left( 0 - \bigcirc - \text{SO}_2 - \bigcirc \right)_{n} \\
&\left( 0 - \bigcirc - \text{SO}_2 - \bigcirc - 0 \bigcirc \right)_{n}
\end{align*}
\]

RaDEL 5000 (COMMERCIAL)

Polyether sulfone

P 1700

Disphenol A HQ (EXPERIMENTAL)

A. The Chemical Structures of Four Polysulfones.
B. The Effect of Electron Radiation on Modulus.

C. The Effect of Proton Radiation on Modulus.
FIGURE 9. REFLECTANCE OF 0.1-MIL ALUMINIZED KAPTON BEFORE AND AFTER UV, PROTON, AND ELECTRON IRRADIATION FOR 1363 HOURS

<table>
<thead>
<tr>
<th>CURVE</th>
<th>MEASUREMENT CONDITIONS</th>
<th>S_A</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Before Exposure</td>
<td>0.101</td>
</tr>
<tr>
<td>2</td>
<td>After 1363 UV ESH., $1.5 \times 10^{16}$ e/cm$^2$ (50-keV),</td>
<td>0.110</td>
</tr>
<tr>
<td></td>
<td>$1.5 \times 10^{16}$ p/cm$^2$ (50-keV)</td>
<td>0.107</td>
</tr>
<tr>
<td></td>
<td>(3 samples)</td>
<td></td>
</tr>
</tbody>
</table>
Figure 10. Mass loss vs. ashing time for uncoated Kapton, coated Kapton, and coated and thermal cycled Kapton.

- O Uncoated Kapton
- △ 8% PTFE-92% SiO₂ coated Kapton (Lot 52386A)
- □ 8% PTFE-92% SiO₂ coated Kapton, thermal cycled (Lot 52386A)
- • HMDS/TFE 8/6 coated Kapton, thermal cycled (Batelle)
- ⬤ HMDS/TFE 8/6
**FIGURE 11. MISSION LIFE VS. THERMAL CYCLES**

<table>
<thead>
<tr>
<th>Mission life</th>
<th>No. of 90-min cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 yr.</td>
<td>5840</td>
</tr>
<tr>
<td>5 yrs.</td>
<td>29200</td>
</tr>
<tr>
<td>10 yrs.</td>
<td>58400</td>
</tr>
<tr>
<td>20 yrs.</td>
<td>116800</td>
</tr>
<tr>
<td>30 yrs.</td>
<td>175200</td>
</tr>
</tbody>
</table>
FIGURE 12. COMPARISON OF ACCELERATED AND REAL TIME THERMAL CYCLE IN SPACE

Temperature, °F

Time, min

Real time orbital thermal cycle

Accelerated thermal cycle
FIGURE 13. EFFECTS OF THERMAL CYCLE RATE AND ATMOSPHERE ON MICROCRACKING IN [0/90/0/90]s 075/934 LAMINATE

Crack density, cracks/in.

Number of thermal cycles between ±150° F

5 min cycle, N₂

90 min cycle, vacuum
SURFACE RECESSION PREDICTIONS

As discussed earlier, the amount of surface recession for a material of known reactivity is directly proportional to atomic oxygen fluence, or the total number of atoms impinging on each square centimeter or surface area during the duration of the intended mission. Fluence, in turn, is dependent on such parameters as spacecraft altitude, surface altitude relative to the spacecraft velocity vector, orbit inclination, duration of exposure, and solar activity conditions during the lifetime of the spacecraft.

To aid the spacecraft developer in estimating the fluence on specific surfaces under question and, consequently, the amount of surface erosion for given solar activity conditions, a nomograph (see Figure 1) has been developed which depicts atomic oxygen fluence as functions of altitude, surface altitude and solar activity conditions. To use this nomograph, one should proceed as follows:

1. Using Figure 2, which shows solar activity predictions for solar cycle 22, our next cycle beginning in 1988, estimate the solar flux index \( F_{10.7} \) number for each year the spacecraft is exposed to the LEO environment.

2. Select spacecraft altitude and orbital attitude of the surface in question.

3. Using the above information, read from the lower nomograph scale the amount of fluence per year the spacecraft is in operation. To obtain an estimate of the amount of surface recession on a per year basis for the material in question, multiply these fluence values by the material reactivity shown in Table 5 (in the text). These calculations yield the amount of surface recession (in centimeters) for each year the spacecraft is exposed to orbital conditions. NOTE: If the material is highly reactive such as Kapton \((Re = 3.0 \times 10^{-24} \text{ cm}^3/\text{atom})\), an estimate of surface erosion on a per year basis may be obtained directly from the upper horizontal scale of the nomograph.

4. Sum the values of (1) fluence per year and (2) surface recession per year calculated in Step 3 over the lifetime of the spacecraft. These quantities represent a good estimate for the total fluence and total surface recession that each surface in question will experience during the lifetime of the mission. For example, assume a spacecraft is designed to operate at an altitude of 500 km and is launched in to an orbit with an inclination of 28.5°. Also assume the spacecraft is gravity-gradient stabilized, it is delivered to orbit during 1993 and has an intended operational lifetime of one year. The amount of
surface recession on ram-oriented Kapton surface is determined from the nomograph as follows:

1. From Figure 2, a launch date of 1993 represents maximum solar activity conditions ($F_{10.7}=230$).

2. From the nomograph, curve "1EMAX" represents ram exposure for these attitude conditions. Reading across the altitude scale of 500 km, the fluence and surface recession are $2 \times 10^{21}$ atoms/cm$^2$ year and 60 m/year, respectively. Thus, a highly reactive material such as Kapton which is 127 m (5.0 mil) in thickness will lose 60$\mu$m, or 47% of its thickness during the time the spacecraft is in operation. Using the data in Table 7 in the text, if the material is a fluoropolymer such as Teflon, the thickness loss will be 1.2$\mu$m (.05 mil), or 1/50th the amount predicted for Kapton.

3. If the surface in question is solar inertial, such as solar array panel, curve "1IMAX" on the nomograph represents one side exposure for solar inertial surfaces during the time this spacecraft is intended to operate. Under these conditions, the fluence and surface erosion would be $3 \times 10^{20}$ atoms/cm$^2$ year and 10$\mu$m/year, respectively. For two-sided exposure, this would represent a thickness loss of 20$\mu$m and if the solar array substrate is 127 $\mu$m in thickness, 16% of the Kapton material would be eroded away during the operational period of the spacecraft. Coating the Kapton with Teflon would reduce this erosion rate by a factor of 50 (see Table 5 in the text) and would result in a thickness loss of only 0.4 $\mu$m. Thus, materials unsuited for these applications can be protected from the LEO environment by coating them with materials having low reactivity rates.
FIGURE 2. SOLAR ACTIVITY PREDICTIONS FOR CYCLE 22

LEGEND
1 = SOLAR FLUX F10.7 + 2 SIGMA, (10^4 JANSKY)
2 = SOLAR FLUX F10.7 MEAN, (10^4 JANSKY)
3 = GEOMAGNETIC INDEX MEAN

SOLAR ACTIVITY PREDICTIONS

GEOMAGNETIC INDICES

SOLAR FLUX AND

250.0
200.0
150.0
100.0
50.0
0.0

82.0 84.0 86.0 88.0 90.0 92.0 94.0 96.0 98.0 100.0

YR
APPENDIX II
DURABILITY OF MATERIALS FOR PRECISION SPACE STRUCTURAL APPLICATIONS
LANGLEY RESEARCH CENTER


TO: 5400/Deputy Chief, Power Technology Division
FROM: Research Associate, Cleveland State University
SUBJECT: Characterization of MBR Radiator Materials

The objective of this task was to aid in establishing a data base of candidate materials which can be used in a MBR system. The database was to include the materials to be used for the heat exchange fluid bath, the fluid bath containment, and the belt to be used in the MBR concept. The hybrid belt and the solid belt were the ones to be considered.

This report focuses on belt materials only, since at present there was nothing obvious to suggest a better bath material than gallium, and containment with certain types of stainless steels has been demonstrated. In a report by A. D. Little, an example is given of the substantial heat rejection levels possible with a belt consisting of a hypothetical material having half the heat of fusion of Lithium (~300 kj/kg) and an emissivity of 0.8. A search for such materials was the focus of this report. The temperature range was restricted to about 400-800K. A further (self-imposed) requirement was some demonstration of use of the materials, rather than a listed handbook or theoretical value with no demonstration of use. The materials selected are given in the Table.

Albert C. Antoine
Enclosures
cc: 5440/C. Coles-Hamilton
5490/K. Alan White
## TABLE

**Selected Phase Change Materials**

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting or Transition Temperature</th>
<th>Heat of Fusion or Transition</th>
<th>Density</th>
<th>Thermal Conductivity</th>
<th>Volume Change in Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K</td>
<td>kj/kg</td>
<td>g/cm³</td>
<td>w/mK</td>
<td>%</td>
</tr>
<tr>
<td>LiOH</td>
<td>744</td>
<td>930</td>
<td>1.46</td>
<td>0.85</td>
<td>2.6</td>
</tr>
<tr>
<td>Penta-erythritol</td>
<td>457-461</td>
<td>303</td>
<td>1.34</td>
<td>1.88(443K)</td>
<td>9.0</td>
</tr>
<tr>
<td>NaOH-NaNO₃ (81.5-18.5 mol%)</td>
<td>529</td>
<td>292</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Li₂SO₄-LiCl(2% by Wt.) &lt;851</td>
<td>197 ± 8</td>
<td>(2.2)*</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>HDPE</td>
<td>402-407</td>
<td>167-201</td>
<td>0.96</td>
<td>0.25***</td>
<td>10</td>
</tr>
<tr>
<td>NaNO₃-NaOH(1% by Wt.)</td>
<td>576</td>
<td>168</td>
<td>(2.26)**</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Al-Si</td>
<td>839</td>
<td>489</td>
<td>2.7</td>
<td>180</td>
<td>-7</td>
</tr>
</tbody>
</table>

* Density of Li₂SO₄

** Density of NaNO₃

*** A factor of four increase in conductivity has been noted in paraffins using a metal matrix (1.6%)
Notes

**LiOH**

Solid Liquid Transition

Thermal cycling of LiOH has been done in canisters of low-carbon, pure nickel (Ni-201). Two (2) canisters were cycled between 683 and 803K (58 minutes heating, 36 minutes cooling), one for 12,504 cycles (19,504 hrs.), the other for 10,512 cycles (16,469 hrs.). Very little LiOH decomposition was found, and the rate of gravimetric corrosion of the container was measured as .01±.002 mm/year. In other tests, improved heat transfer (by an average of 15%) was accomplished by adding a rolled metal (copper) screen to the LiOH in the canister.

**Pentaerythritol**

SOLID-SOLID Transition

The transition given in the table is that of solid-solid transition, from a hard brittle wax-like material to a soft, pliable, wax-like material. The melting temperature is about 531-533K. Fibers or felts of metal or carbon have been suggested as conductivity enhancers.

**NaOH-NaNO₃ (81.5-18.5 mol%)**

SOLID-LIQUID Transition

Compatibility tests have been conducted, and carbon steels showed corrosion rates less than 5 μm/year (stainless steels >100 μm/year). A 6700-hr., 1000 melting-freezing cycles, test was performed. The results of the investigation on the materials after the test were essentially the same as those obtained in the compatibility test.
**Li₂SO₄-LiCl (2% by Wt.)**

SOLID-SOLID Transition

Pure Li₂SO₄ has a transition with a latent heat of 214 kJ/kg at 851K. Thermal cycling tests (up to 3 months duration) of Li₂SO₄ and binary and ternary mixtures of Li₂SO₄ and other sulfates showed that all samples containing Li₂SO₄ were gradually deformed, and this deformation resulted in the breaking of sample containers (Vycor, fused quartz, stainless steel). The deformation was completely eliminated by transforming parts of the sample into a two-phase region by adding small amounts of LiCl (2% and 4%). Temperature cycling between 793 and 923K was done, and no attack on the sample containers could be detected even after prolonged thermal cycling. No sample deformation occurred in the 4% samples and only very small traces of deformation in the 2% samples (the Vycor containers were intact).

**High Density Polyethylene**

SOLID-SOLID Transition

High density (HDPE) or "linear" polyethylene can be crosslinked, chemically or by ionizing radiation, such that the heat of melting is preserved, but liquefaction of the polymer is prevented. The polymer is thus form stable. This material has been used as beads encapsulated in rubbers and elastomeric materials, as well as 'encapsulating' some fibrous materials.

**NaNO₃-NaOH (1% by Wt.)**

SLURRY-LIQUID Transition

Off-eutectic compositions in the NaNO₃-containing systems were examined because of the hard freeze experienced with eutectics. It was found that NaNO₃ containing 1% (by wt) of NaOH forms a slurry. The mixture is thermally stable, and when kept free from moisture has an acceptable corrosion rate (with mild steel).
This aluminum-silicon alloy was included because of potential use in the future. The material is prepared in a ceramic shell (alumina-silicon carbide). The usual size is about 1-2 inches, but shells of about 1/4 inch have been made. In addition to fabrication problems with smaller sizes, the heat change in the alloy may not be the same because some of the shell may be consumed.

Environmental Compatibility

It has been recently determined that in low earth orbit the susceptibility to attack by atomic oxygen may be the limiting factor for long-lived spacecraft. In general, metals have little reactivity. Organic materials, however, are highly reactive. If high density polyethylene or pentaerythritol are to be used, they will have to be protected. Perfluorinated polymers, such as Teflon, are considerably less reactive than the carbon-hydrogen compounds, and can be considered for use as protective coatings. (It should be noted that chemical etching of Teflon can be done, leaving the surface variously described as dark discolored, purple, even near black. The effect of atomic oxygen on a modified surface would have to be determined.)

Metal surfaces can be treated in various ways to increase their emittance, reaching 0.8 and better. In some tests, exposure to atomic oxygen in an RF plasma asher did not significantly change the emittance of those samples that had been heat treated as part of their texturing process.
References

LiOH


PE


NaOH-NaNO3


Li2SO4-LiCl


HDPE


NaNO3-NaOH


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ABSTRACT

NASA's planning for the future exploration of the Solar System includes the establishment of manned outposts, as well as central base stations on the Moon and Mars. Supporting human expeditions to and operations on, the surface of the Moon or Mars represents a substantial technology challenge for current and projected power system capabilities. The high levels of power associated with an operational base, somewhere in the 100's to 1000's of kilowatts, will require nuclear power systems. During the installation of these permanent nuclear systems, power systems based on solar energy hold the greatest promise for supplying needed power. These systems will also be required to augment and serve as back-up power sources for the permanent nuclear-powered bases.

Because the solar-based surface power system must supply usable power continuously, that is during the day as well as the night, a regenerative system is required. During the daylight hours the power generation subsystem will recharge the energy storage subsystem and also supply power directly to the system's electrical loads. Thus, continuous power is supplied to the load: it is provided by the power generation subsystem during sun periods and from the energy storage subsystem during periods of darkness.

In a Lunar application, the period of darkness extends for two weeks, while a Mars application presents a more manageable 12-hour night. Both applications require very high energy density and reliable energy storage systems. The highest potential for successfully achieving surface power storage capabilities for these applications lies in the regenerative fuel cell (RFC) concept. The regenerative fuel cell system is depicted in Figure 1. During the light portion of the orbit the photovoltaic solar arrays generate sufficient power to service the system electrical loads plus a water electrolysis unit. The amount of electrical energy required by the electrolysis unit is dictated by the amount of hydrogen and oxygen needed to generate power in a fuel cell, which supplies the electrical loads during the dark portion of the orbit. In generating this power, water is produced by the fuel cell as a by-product of the electrochemical reaction. To complete the cycle, the by-product water is collected and stored for use in the electrolyzer during the succeeding orbit.

The mass and specific energy benefits to be realized by employing a regenerative fuel cell system are displayed in Figure 2. Low system mass for a given power level is a central requirement for achieving acceptance of transportation costs.
to the Moon or Mars. Another requirement, even more challenging, is appreciable system lifetime without sacrificing performance even after an extended period of dormancy. Also a relatively high power level requirement of 25 kW is projected to support an initial surface outpost of four to six astronauts. To develop the technology base for a system which will meet these requirements, a program has been initiated as one of the elements of NASA's Project Pathfinder. This program was developed and is being managed by NASA's Lewis Research Center. It focuses on the technology areas of solar power generation, energy storage and electrical power management. Advancing these technologies and coupling their performance potentials with an advanced low mass, reliable electrical power management subsystem can lead to surface power systems having a reliable life in excess of 20,000 hours with system specific powers of 3 W/kg for Lunar application and 8 W/kg for Martian applications. These projected specific powers represent substantial improvements over the state-of-the-art, up to a factor of 30. System mass reductions of this magnitude, coupled to the expected factor of 10 increase in life, should enable extra-terrestrial surface missions where life and mass are the driving forces for success.

The Energy Storage element of the Pathfinder Surface Power Program is a 6-year effort culminating in the verification of a regenerative fuel cell system operating in a relevant environment. The near-term, 3-year, Phase I effort, will provide the development and verification of the system critical components, those being the fuel cell and electrolyzer stacks. The second 3-year phase will focus on the development and verification of the complete RFC breadboard system.

The two candidate fuel cell and electrolyzer technologies for the Pathfinder system are the alkaline and proton exchange membrane (PEM). Because alkaline was the system of choice for both Apollo and the Space Shuttle, the state-of-the-art of alkaline systems had been advanced considerably over that of the PEM technology. However, the major deficiency facing the alkaline technology in the Pathfinder application is the lack of long term catalyst layer stability, which translates into performance degradation with time. Unlike with PEM and other acid-type fuel cells, a stabilizing catalyst support has not been developed for the alkaline system. PEM, on the other hand, offers a stable, long life system but one whose efficiency has, until recently, been significantly lower than alkaline. Recent improvements in the conductivity of PEM membranes increase the probability that this technology could replace alkaline as the Pathfinder RFC baseline. At present, the weakness in the PEM technology stems from the fact that the membrane technology improvements are very recent and, therefore, the data base needed to justify commitment to this technology does not exist. Accordingly, a technology assessment and trade-off analysis has been undertaken to provide guidelines for selecting the technology to be carried into full development in the Pathfinder Program.
SPECIFIC ENERGY OF 25 kWe ENERGY STORAGE SYSTEM

TECHNOLOGY IMPACTS 25kW SURFACE POWER SYSTEM

FIGURE 2: ADVANTAGES OF REGENERATIVE FUEL CELL ENERGY STORAGE VERSUS BATTERY SYSTEMS FOR LONG DISCHARGE APPLICATIONS
Mathematical Modeling of Solid Oxide Fuel Cells

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Development of predictive techniques, with regard to cell behavior, under various operating conditions is needed to improve cell performance, increase energy density, reduce manufacturing cost, and to broaden utilization of various fuels. Such technology would be especially beneficial for the solid oxide fuel cell (SOFC) at its early demonstration stage.

Three designs of SOFC cell/stack configurations are now available and they are Westinghouse tubular, Argonne National Laboratory (ANL) monolithic, and Ztek planar FC models. A comparison among these designs in the previously stated areas is needed. Basically, the differences among these configurations are shape of cell, channel geometry for reactant flow, and size/thickness of cell components. These designs were compromised with manufacturability, which is still the most difficult task aspect of the SOFC development. Due to this difficulty, there are limitations on the size of monolithic and planar cells and on the weight (and cost) of tubular cell. But the manufacturability is not the only factor that limits the size of SOFC. As soon as the cell is put on operation, the temperature and the current density (CD) distributions on the plate will determine the success of the performance in the following ways: (1) hot spot temperatures exceeding the sintering, coating, or E(C)VD temperature will cause material problems, (2) severe non-uniform temperature distributions will result in cracking due to thermal stresses, and (3) non-uniform CD distribution will increase the possibility of reactant depletion at exit, especially at high utilization ratios. This paper describes the development of computer models to calculate the temperature, CD, and reactant distributions in the tubular and monolithic SOFCs. Results indicate that problems of non-uniform heat generation and fuel gas depletion in the tubular cell module, and of size limitations in the monolithic (MOD 0) design may be encountered during FC operation.

V-I Characteristics  
The SOFC semi-empirical V-I characteristics was modeled with respect to cell components (thickness) and operating conditions (temperature, pressure, inlet fuel gas...
compositions, and fuel and oxidant utilization ratios).

Tubular Cell

For the Westinghouse tubular SOFC, a two-dimensional CD profile (circumferential and axial) was generated by assuming an isothermal condition (1000 °C). Recently reported performances of tubular SOFC using DOE specified fuel (67% H2, 22% CO, 11% H2O at 85% fuel utilization) and air [1] were applied in this study. First, an analytic model (Figure 1) was solved and the solutions were used to calculate the circumferential CD distribution around the tubular SOFC using specific fuel and oxidant gas flow rates. Because of symmetry, only one half of a cell was modeled. Secondly, a finite difference model was used to calculate the fuel and oxidant gas flow rates along the axis of the tubular SOFC. Reforming and water shift reactions were considered at equilibrium at the operating temperature of 1000 °C. Rated operating conditions and cell dimensions of the Westinghouse 5 kW module were applied. Figure 2 shows the circumferential and axial CD profiles. It is noted that there is non-uniformity of CD along the axis and around the circumference of the tubular cell. For a 0.275 A·cm² (average) operation, the CD ranges from 0.632 to 0.154 A·cm². The peak CD occurs at circumference equal to 1.85 cm in Figure 1, where the current flows radially out of the cell, and where the fuel and oxidant gases enter the cell axially. The lowest CD occurs at the opposite end of the cell. Figure 2 also shows that in an operating cell, the peak CD, as well as the largest heat generation, is near the interconnection. This will worsen the critical stress problem since the thermal expansion will not be compatible between the interconnection and other cell components.

Another important issue pertains to the probability of fuel gas depletion in the Westinghouse 5 kW module. The non-uniform fuel gas flow distribution in the passages (main, side, and corner) caused by the equal pressure gradient of the flow, is compared with the amount of fuel needed to achieve a parallel connection (e.g., the current for three cells in parallel is equal to 80 A). Documented performances from specimen testing [1] were adapted as the basis. Among these reported data, the performance is a function of the cell itself and the testing time. The probabilities of total fuel gas depletion (at operating time equal to 200 hours) around the edge cells for two types of flow passages and two to six cells in parallel are shown in Figure 3. It shows that in a design with three cells in parallel there is a 7% probability that fuel gas will be depleted at the exit of edge cells (corner cells and side cells in Type I & II flow distributions, respectively). In addition, a shorted cell (by assuming voltage of
arbitrarily chosen cell equal to 0) in the operation will always result in fuel gas starvation for the remaining, i.e., unshorted cells.

These results strongly imply that the design of more uniform fuel gas passages is necessary, which can be achieved by increasing the thickness of Ni felt or by redesigning the fuel gas intake plenum.

**Monolithic Cell**

Monolithic solid oxide fuel cells are currently being developed at Argonne National Laboratory. For many applications, operating conditions such as total pressure, average cell temperature and current density, as well as inlet reactant gas temperatures and compositions are fixed or are predetermined. A two dimensional computer model has been implemented to predict the effects of fuel utilization ratios (FUR), oxidant utilization ratios (OUR), and cell dimensions upon the temperature and current density distributions within cross-flow arrays of the MOD 0 design, subject to a specific set of the above mentioned operating conditions. Results from the model were used to determine limits on cell sizes and on reactant gas utilizations by evaluating the three performance indicators outlined earlier. In the subsequent analyses, the following operational parameters were maintained: pressure = 1 atm; average array temperature = 1000 °C; average current density = 500 mA/cm²; inlet molar fuel gas composition: 97% H₂, 3% H₂O; inlet molar oxidant gas composition: 21% O₂, 79% N₂; and each inlet gas temperature = 800 °C.

All V-I relationships for the monolithic fuel cells were assumed to behave linearly within the range of interest. Some representative V-I curves are displayed in Figure 4, where the best case accounts only for ohmic resistance and the estimated case includes slow polarization effects. Both the best case and the estimated case are more favorable than the experimental V-I curve, however, it is reasonable to expect that the experimental relationship has been improved since the December 1985 status [2].

Figure 5 shows the relationship between FUR and OUR that must exist in order to satisfy the specified operating conditions. While Figure 5 represents the case for a 10 cm x 10 cm array, the shape of the curve is similar for other cell dimensions as well. It is evident from the figure that lower limits on both FUR and OUR will be encountered. The effect of FUR on overall operating efficiency is also depicted in Figure 5 and it is seen that the maximum efficiency is obtained at a relatively small FUR value, near FUR = 0.2.
A typical temperature distribution is shown in Figure 6 where the peak temperature is reached at the extreme corner of the array, since reactant gas depletion is at the maximum there. The minimum array temperature occurs at the opposite corner. In all cases, the maximum temperature is located along the edge of the array where oxidant gas departs, however, as FUR is increased, the hot spot location moves closer to the fuel gas inlet. One of the performance criteria requires that the peak cell temperature be lower than the sintering temperature used in the manufacturing process, which is approximately 1600 °K. Results obtained using the best possible V-I curve indicate that the array sizes could exceed 20 cm x 20 cm and still satisfy the hot spot requirement. For cases where the estimated V-I curve was applied, however, the peak temperature rose above 1600 °K for cell dimensions as small as 5 cm x 5 cm, as seen in the diagram.

Since the location of the minimum array temperature is invariant, both the magnitude and the relative location of the maximum temperature must be considered when assessing thermal stresses. At large FUR values, the peak temperature is in close proximity to the minimum temperature and large thermal gradients will be developed, the severity of which depends on the materials used.

Results from the computer model show that array dimensions for a cross-flow monolithic fuel cell can be restricted as a result of non-uniform temperature distributions. Improvements in the V-I curve will alleviate much of this problem. Also, a range of allowable reactant utilization ratios will be established when a set of operational parameters are specified.

References


Acknowledgment

This study was supported by U.S. Department of Energy, Morgantown Energy Technology Center through the NASA Lewis Research Center Fuel Cell Project Office.
Figure 1. Model Used to Analyze Circumferential Current Density Distributions for Tubular SOFC

Figure 2. Tubular SOFC Current Density Profile (Isothermal)

Figure 3. Probability of Fuel Depletion (of the Edge Cells) vs. Cell Configuration
Figure 4. Monolithic SOFC V-I Curves

Figure 5. OUR and Efficiency vs. FUR

Figure 6. Monolithic SOFC Temperature Distribution for Example Case
PREDICTED RESTRICTIONS ON REACTANT GAS UTILIZATIONS IN MONOLITHIC SOLID OXIDE FUEL CELL OPERATION

By T.M. Maloney*, C.-Y. Lu**, and G.A. Coulman*

Abstract

For power system designs that include monolithic solid oxide fuel cell (MSOFC) arrays, it is desirable to identify a fixed set of operating parameters and to maintain a certain performance level. The interrelationships among the various operating parameters impose restrictions upon the range of feasible choices of those parameters. A computer model was used to estimate the effects that the I-V characteristics, the average array temperature, and the inlet reactant gas temperatures have upon the range of feasible fuel utilization ratios (FUR) and oxidant utilization ratios (OUR). The results can be used as constraints for system optimization studies.

Introduction

Monolithic solid oxide fuel cells (MSOFC) are being developed at the Argonne National Laboratory. McPheeters et al. explained that the most important task at the present time is perfecting the fabrication procedures. While it is generally desirable to manufacture large monolithic arrays in order to achieve high power output, some restrictions on the feasible ranges

Left to Right:
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of operating parameters will be encountered. Lu et al. have recently reported on the effects that the I-V characteristics and the array dimensions have upon hot spot temperatures and upon reactant gas depletion in the MSOFC design. A range of choices for the fuel utilization ratio (FUR), the oxidant utilization ratio (OUR), and the array dimensions were approximated for a fixed set of operating conditions. Feasible FUR and OUR ranges and feasible array sizes were defined as those values which prevented maximum array temperatures to be greater than 1600° K and also prevented reactant gas depletion. The present work investigates the effects that the average array temperature, the I-V characteristics, and the inlet reactant gas temperatures each have upon the ranges of feasible FUR and OUR values. The material problems associated with hot spots in the arrays are disregarded.

Operating Conditions and Computer Algorithm

The fuel cell simulation algorithm developed by Lu et al. has been modified to estimate MSOFC array behavior. The following operating parameters were specified and are assumed to prevail for all subsequent analyses unless otherwise noted: operating pressure = 1 atm; average current density = 500 mA/cm²; molar fuel gas composition: 97% H/3% H₂; oxidant gas: air; array dimensions: 10 cm x 10 cm. The I-V curve, the average array temperature and the inlet reactant gas temperatures were varied, then the FUR-OUR relationships were examined. If the computer algorithm did not converge to a reasonable solution, then the set of input parameters that were used were considered to be infeasible.

Results

Figure 1 represents two sample I-V curves that were used in the analyses. The Best Case accounts only for material resistances while the Estimated Case includes various polarization sources. Figure 2 summarizes the effects that the I-V curves have upon the range of feasible FUR and OUR values, in this case for a 5 cm x 5 cm MSOFC MOD 0 array. As the I-V characteristics are improved, the feasible FUR and OUR ranges both widen. For the Best Case, the minimum and maximum FUR values are approximately 0.15 and 0.88, respectively, while the corresponding OUR values that are required to satisfy the specified operating conditions are roughly 0.99 and 0.34, respectively. But for the Estimated Case, feasible FUR values are between 0.18 and 0.75 with corresponding OUR values between 0.84 and 0.33. In general, the range of allowable FUR values increases as the I-V curve improves and the upper OUR limit is extended.

Effect of Average Array Temperature

One means of increasing the average MSOFC array temperature is to increase the FUR and/or the OUR. Observe in Figure 3 that the range of feasible FUR values becomes smaller as the average array temperature increases while the feasible OUR range is shifted upward. The computer model predicts FUR limits between 0.10 and 0.80 with corresponding OUR limits between 0.60 and 0.18 for an average array temperature of 1173° K. As the average array temperature increases to 1323° K, the feasible FUR values are between 0.20 and 0.47 with OUR values between 0.98 and 0.52.

Effect of Inlet Reactant Gas Temperatures

299
Some system designs allow flexibility for choosing the inlet reactant gas temperatures while other systems have these temperatures defined. Figure 4 shows the effects that the inlet temperatures have upon the feasible FUR and OUR ranges for an average array temperature of 1273° K. As the inlet reactant gas temperatures increase for a fixed FUR, then the corresponding OUR must obviously decrease since more inert gas is required to remove heat. The present model predicts lower limits for feasible inlet gas temperatures, which are approximately 1050° K for a FUR of 0.20 and 985° K for a FUR of 0.50.

Considerable interest has been focused towards operating tubular solid oxide fuel cells at fuel utilization ratios up to 85% (4). Figure 5 shows the behavior of a MSOFC array operating at a FUR of 85%. As expected, the average array temperature increases as OUR increases, but note the nearly linear relationship for this case. Convergence was not achieved for OUR less than 5% and for OUR greater than 31%.

Concluding Remarks

The practical values of computer modeling are usually realized by recognizing trends in the predicted results, rather than by accepting the results as being completely accurate and precise. While it is known that all of the operating parameters cannot be arbitrarily chosen for MSOFC operation, computer modeling results can be used for sensitivity analyses, thereby approximating the interrelationships among the operating parameters.

References


Acknowledgement

This study was supported by the US Department of Energy, Morgantown Energy Technology Center, through the NASA Lewis Research Center Fuel Cell Project Office.
Figure 1. SOFC I-V Curves

Figure 2. Effect of I-V Curve on Feasible FUR-OUR Ranges

Figure 3. Effect of Avg. Array Temperature on Feasible FUR-OUR Ranges

Figure 4. OUR vs. Inlet Reactant Gas Temperatures at Constant FUR

Figure 5. Feasible OUR Range for FUR = 85%
Monolithic solid oxide fuel cells (MSOFC) were devised at the Argonne National Laboratory in the early 1980's (1) and are presently in the fabrication development stage at Allied Signal Aerospace (2) for various applications. The monolithic fuel cell is an all-ceramic structure which is assembled in a 'honeycomb' shape similar to that of corrugated cardboard. While fuel cell operation has been demonstrated (3), it is also possible to operate the monolithic structure in the reverse, or electrolysis, mode. Performance characteristics of monolithic solid oxide electrolyzer (MSOZE) arrays were estimated in order to determine the effects that inlet gas temperatures, i-V relationship, and the average current density, have upon the average cell temperature and upon the applied voltage requirements.

Performance predictions of MSOFC arrays have been previously reported (4,5) and the computational algorithm formulated by Lu and Maloney (4) was revised to predict performance characteristics of MSOE2 arrays for the Mod 0 design. The algorithm consisted of a finite difference scheme to solve the mass and energy balance equations which pertain to the electrolyte and to the anode and cathode gas channels. The inlet reactant gas stream is a hydrogen-steam mixture and the water in that stream is electrolyzed to produce hydrogen (in the \( \text{H}_2-\text{H}_2\text{O} \) channel) and oxygen (in the pure \( \text{O}_2 \), or air channel). The solid electrolyte mass and energy balance equations were derived elsewhere (6) and Table I lists the operating conditions which were maintained constant unless otherwise noted.

### Table I

**Electrolyzer Array Operating Conditions**

- Operating Pressure = 1 atm
- Average Current Density : 500 mA/sq.cm.
- Water Utilization Ratio (WUR) : 86.6 %
- Array Dimensions : 10 cm x 10 cm
- Inlet Gas Temperatures : 1423 K

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'The solid electrolyte mass and energy balance equations were derived elsewhere (6)'
i-V Relationship

Current-voltage characteristics for single solid oxide fuel cells were predicted by Maloney (6) and simplified for implementation to both fuel cell and electrolyzer array analyses. For MSOEZ arrays, two i-V relationships were used: A Best Case i-V relationship which included only material resistance; and an Estimated Case i-V relationship which encompassed all overpotential sources. Figure 1 represents typical Best Case and Estimated Case i-V curves for electrolysis operation while Figures 2 and 3 represent calculated Temperature Distributions and Current Density Distributions, respectively, for the solid electrolyte.

Effect of Inlet Reactant Gas Temperature

MSOEZ array performance is affected by the inlet gas temperatures. As the inlet gas temperatures increased, the average MSOEZ array temperature increased for both the Best Case and Estimated Case i-V relationship, as expected. Furthermore, average array temperatures for the Estimated Case were higher than those for the Best Case since more resistive heat is generated using the former case. The required applied voltages varied with the inlet gas temperatures in the manner shown in Figure 4.

Effect of Average Electrolyzer Array Current Density

The average current density of the MSOEZ array influenced both the average array temperature and the applied voltage requirements. Array voltage increased with average current density in the manner shown in Figure 5. The effect of current density on the average MSOEZ array temperature is shown in Figure 6.

![Figure 1. i-V Relationships used for Moe 3 Electrolyzer Array Analyses](image-url)
MALoney AND COULMAN

SOLID STATE ELECTROLYTE TEMPERATURE DIST.

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**Figure 3:** Temperature Distribution in 10 cm x 10 cm
Non-d Electrolyte Array Electrolyte with Best Case I-V Curve

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**Solid Oxide Electrolyte Corr. Zone Data:**

- Avg. Temp. = 1275 K
- Avg. C.P. = 520 kJ/kg K
- I = V = Best Zone
- W = 4.44; V = 1.35

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**Figure 4:** Current Density Distribution in
10 cm x 10 cm Non-d Electrolyte Array Electrolyte with Best Case I-V Curve

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Conclusion

Performance estimations for Mod 0 MSOEII arrays were completed and some of the results were provided. Computer modeling results of this type may be used to aid the design of a monolithic solid oxide electrolysis sub-system and of a regenerative fuel cell system with various applications. An assessment of thermal stresses should also be undertaken as part of the design study.

REFERENCES


Acknowledgement

This study was supported by the U.S. Department of Energy, Morgantown Energy Technology Center, through the NASA Lewis Research Center Fuel Cell Project Office.
Figure 4. Effect of inlet Electrolyzer Gas Temperature on Applied Electrolyzer Voltage

Figure 5. Relationship between the Average Electrolyzer Array Current Density and the Applied Voltage

Figure 6. Effect of Electrolyzer Array Current Density on the Average Electrolyzer Array Operating Temperature