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Research and Development Technical Report  
ECOM-03743-F

# HYDROCARBON-AIR FUEL CELL

## FINAL REPORT

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HYDROCARBON-AIR  
FUEL CELL

Final Report  
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Report No. 11

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## SUMMARY

This report marks the completion of a three year study aimed at determining the feasibility of a direct hydrocarbon-air fuel cell capable of widespread military application. This program has established that there are no engineering obstacles to the development of high power density direct hydrocarbon-air fuel cell systems. However, the platinum catalyst requirements of the current systems precludes any extensive military application. Consequently, research during this report period has emphasized the search for non-noble metal catalysts and the development of non-corrosive carbon dioxide rejecting intermediate temperature electrolytes. In addition, some noble metal utilization studies were also conducted.

### Task A, Non-Noble Electrocatalysts

The electrochemical activity of the mixed transition-metal-tungsten oxides and bronzes was adequately demonstrated in the previous report, but the observed current capability was quite low due to problems in electrical bonding and catalyst microstructure. Current studies have shown that freeze drying is an effective technique for producing finely divided high surface area conductive metal-tungsten oxides. However, improvements in conductivity and surface area have not resulted in the anticipated performance improvements. Previous data indicated that these metal tungsten oxide catalysts can exist in different ionization states. Work in buffer electrolytes indicates that the state of ionization does not affect catalytic activity.

Tests in the phosphate melt electrolyte have shown that Raney nickel-cobalt catalysts have demonstrable electrochemical activity on butane. This may be the first instance of reported saturated hydrocarbon activity at a non-noble metal anode. This demonstrated activity suggests a potential new area for non-noble catalyst studies.

### Task B, Noble Metal Catalysis

Supported platinum catalysts continue to show promise of significant hydrocarbon and air electrode improvements in both low and intermediate temperature electrolytes. Work with Co-Pt on carbon anode catalysts indicates that increased platinumization is possible but site saturation appears to be a problem. Despite this, the utilization obtained with a 11.6% platinumized carbon was comparable to that obtained with a 5.8% material. However, the response to changes in electrode thickness was significantly different and more work is required to establish the reason for this difference. Work on a modified electrode structure using the Adams catalyst indicates that these systems could hold the key to low loaded cathodes. Dual layer structures gave 140 to 180 mv less polarization than comparable carbon supported systems, but then life in pyrophosphoric acid is limited because of mechanical structure instability.

### Task C, New Electrolytes

Intermediate temperature phosphate melt electrolyte conductivity must be increased in order to facilitate systems design. Unfortunately, attempts to increase melt conductivity have thus far failed to produce the required increase. The use of fluxing agents, increased acidity, chelation agents, etc. resulted in a melt of either unchanged or impaired conductivity. Efforts to improve the conductivity of this electrolyte should continue in view of the potential usefulness of this electrolyte with non-noble metal catalysts. Current conductance levels are just border line, and cell engineering studies could reduce internal resistance losses to tolerable levels.

Direct Hydrocarbon-Air Fuel Cell Feasibility Study -  
General Conclusions

This three year program has examined the feasibility of direct hydrocarbon-air fuel cell system operating with low and intermediate temperature electrolytes. Although significant progress has been made, catalyst activity remains the primary obstacle to practical systems development. Improved electrode structures and electrolytes have been devised. Thus, further research in the areas of low loaded anodes, intermediate temperature electrolytes and non-noble metal catalysts following the leads developed in this program should lead to practical fuel cell systems.

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## SECTION 1

### INTRODUCTION

The objective of these investigations is to determine the feasibility of a direct hydrocarbon-air fuel cell capable of widespread military application. Such fuel cells must use fuels which react to carbon dioxide, must be reasonably available, and pose no unusual corrosion, toxicity, or handling problems. Also, the cell must use a CO<sub>2</sub>-rejecting electrolyte and operate at temperatures consistent with reasonable start-up characteristics. The system should be thermally self-sustaining without excessive loss in efficiency. Other desired requirements include high electrical output per unit volume and weight, high efficiency, long life, high reliability, reasonable cost, particularly, catalyst cost, and ruggedness.

Previous studies have established that a direct liquid hydrocarbon-air fuel cell system is feasible provided that the noble metal catalyst requirement is substantially reduced through improvements in utilization or replacement by non-noble metal systems. Current work is aimed at substantially reducing the platinum requirement through improved electrode and catalyst structures. In addition, non-noble platinum substitutes are being actively sought. Improved catalyst effectiveness could be attained through intermediate (150-300°C) temperature systems. Electrolyte and systems studies aimed at evaluating the overall power density and systems requirements are under way.

The program is thus divided into three parts, referred to as Task A through C in this report. Task A describes studies on non-noble metal catalysts and Task B, research on noble metal catalyst utilization improvement. Task C discusses new electrolyte research.

Section 3 summarizes the results of the overall three year program aimed at establishing the feasibility of the direct hydrocarbon fuel cell.

## SECTION 2

### EXPERIMENTAL STUDIES AND DISCUSSION

#### 2.1 Task A, Non-Noble Metal Catalysts

Development of a practical hydrocarbon-air fuel cell hinges on reducing the cost of expensive components and replacing the platinum group metals with more effective materials. The development of cheap non-noble catalysts provides the best long range solution to this critical problem.

Previous studies (10) have indicated that mixed transition metal-tungsten oxides and tungsten bronzes can yield electrochemically active anode and cathode systems in acidic carbon dioxide rejecting electrolytes. These studies indicated that the low activity levels attained thus far were due to poor electrode structure and low surface area. Consequently, work on the metal tungsten oxide catalysts during this report period has emphasized the development of high surface area bronzes through chemical rather than size reduction procedures. In addition, in view of the wide range of catalytically active compositions found, some additional work on bronzes in aqueous phosphate and carbonate buffers was initiated.

Studies with Raney non-noble alloy catalysts were extended to include the phosphate melt system. Raney nickel-cobalt catalysts were evaluated for butane activity in the phosphate melt since this is the first non-corrosive carbon dioxide rejecting electrolyte with demonstratable saturated hydrocarbon activity. In addition, some carbide, nitride and carbonitride catalysts were also evaluated in sulfuric and aqueous buffer and phosphate melt electrolytes. These latter materials were evaluated at Esso Research under Contract NASW-1525.

#### Phase 1 - Metal-Tungsten-Oxygen System Electrocatalysts

The electrochemical activity of the metal-tungsten-oxygen system has been adequately demonstrated but the current capability remains quite low. This is probably due to problems in catalyst micro-structure since the surface areas of ground materials is quite low, and the ground powders appear to show poor electrical bonding characteristics in the finished electrode. Consequently, current studies are aimed at improving catalyst micro-structure and evaluating if possible the nature of the catalytically active species.

#### Part a - Preparation of High Surface Area Tungsten Bronzes

Previous studies (10) have indicated that rare earth metal tungsten bronzes  $M_xWO_3$ ;  $x \leq 0.2$ ) and ternary tungsten oxide systems containing certain transition metals (e.g., Ti, V, Cr, Mn, Fe, Ni, Zn, Zr) are capable of functioning as electrode catalysts in 30% sulfuric acid at 90°C. However, anodic (current) densities observed (on hydrogen) with electrodes containing these tungsten oxide catalysts were quite low.

Of the several possible factors contributing to the observed poor performance of tungsten oxide systems, the poor electrical conductivities of electrodes used in screening tests (9) was readily identified. These were prepared from mechanically ground catalyst powders (200-325 mesh) that were bonded with Teflon to

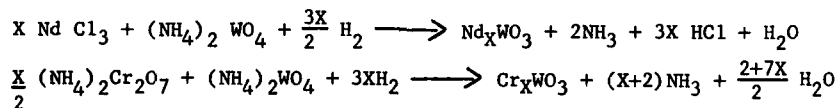
tantalum screen current collectors. Although the catalysts were highly conductive prior to the grinding, the grinding procedure drastically reduced their conductivities (10). Moreover, the low surface area powders, obtainable by grinding (1-5m<sup>2</sup>/gm), suffered a further decrease in conductivity upon being Teflon bonded to current collectors. Typical electrodes had resistances of the order of 1000 ohms between the current collectors and bonded catalysts (10).

Elimination of the mechanical grinding step might result in dramatic increases in anodic current density through improvements in both surface area and conductivity; consequently, recent studies were aimed at synthesizing high surface area tungsten bronzes and ternary tungsten oxides. This approach involves the production of high surface area starting reagents by freeze drying and subsequent reduction of these reagents to bronzes or conductive ternary tungsten oxides under conditions that minimize particle growth.

The use of freeze drying as a technique for producing high surface area tungsten and tungsten-rhenium alloy powders has been recently reported by Landsberg and Campbell (11). Freeze drying involves the removal of water from a frozen solution of a metal compound or compounds by sublimation under reduced pressure. If the solution has been frozen rapidly enough to prevent precipitation of the solute and there is no melting during the sublimation step, the residual solute should retain the state of subdivision and degree of homogeneity that existed in the original solution. In the work reported by Landsberg and Campbell (11), tungsten powders in the 50-200 Å particle size range were obtained by freeze drying aqueous solutions of ammonium tungstate followed by reduction of the high surface area tungstate with hydrogen and hexamine vapors at 400-700°C.

We have attempted the adaptation of this procedure to the more complex problem of preparing high surface area powders of the following compositions: Nd<sub>0.1</sub>WO<sub>3</sub>, Sm<sub>0.1</sub>WO<sub>3</sub>, and Cr<sub>0.5</sub>WO<sub>3</sub>. These materials had been prepared previously (9,10) in pellet form by high temperature solid state reactions of the mixed metal oxides with tungsten, and all three were reported to be active anode catalysts (10).

Homogeneous, submicron particle size, binary mixtures were readily obtained by freeze drying aqueous solutions of the stoichiometrically mixed reagents. Binary mixtures of ammonium tungstate with neodymium chloride, samarium chloride and ammonium dichromate were made by this technique. The high surface area reagents were then reduced with hydrogen at various temperatures and for varying periods, in the hopes of achieving the overall reactions shown below.



Hydrogen reductions of NdCl<sub>3</sub>/(NH<sub>4</sub>)<sub>2</sub>WO<sub>4</sub> and SmCl<sub>3</sub>/(NH<sub>4</sub>)<sub>2</sub>WO<sub>4</sub> mixtures were carried out at 300°C for periods ranging from 2.5 to 12 hours. Dark blue, conductive powders were obtained as products in these runs. X-ray diffraction patterns of the powders showed only broad halos, which in the case of inorganic solids, is indicative of crystallite sizes less than 100 Å. When these hydrogen reduction products were treated with hot sulfuric acid they rapidly underwent a color change from blue to green. This color change was an indication that significant fractions of the hydrogen reduced powders were readily oxidized to yellow tungstic oxide (WO<sub>3</sub>). Since pure tungsten bronzes are stable in hot sulfuric acid, it was apparent that little, if any, interaction had taken place between the rare earth metal and tungsten suboxides produced by the hydrogen treatment at 300°C.

One run with a  $\text{NdCl}_3 \cdot (\text{NH}_4)_2\text{WO}_4$  mix produced drastically different results in that a four hour treatment with hydrogen at  $300^\circ\text{C}$  yielded a very dark blue powder that was stable in sulfuric acid at  $90^\circ\text{C}$ . Moreover, this product gave an X-ray diffraction pattern typical of crystalline solids. Apparently, in this run some sintering occurred, resulting in a solid state reaction between the hydrogen reduced tungsten oxide and the neodymium. The X-ray diffraction pattern was indexed (Appendix A-1) on a hexagonal unit cell,  $a = 7.42\text{\AA}$ ,  $c = 7.61\text{\AA}$ . These unit cell dimensions are virtually identical to those reported (12) for the hexagonal tungsten bronze,  $\text{Rb}_{.27}\text{WO}_3$ . Both the amorphous, unstable hydrogen reduced powders and the acid stable, hexagonal phase were convertible to cubic neodymium and samarium tungsten bronzes (13) by sintering in vacuo at  $800^\circ\text{C}$ . Although there was obviously some particle size growth during this process, the surface areas of the bronzes obtained by this two step reduction process were significantly larger than those obtained previously by mechanical grinding. As evidence of this, Teflon bonded electrodes made from hydrogen reduced-vacuum sintered bronze powders exhibited internal resistances in the 1-30 ohm range.

Hydrogen reduction of homogeneous, high surface area mixtures of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 - (\text{NH}_4)_2\text{WO}_4$ , obtained by freeze drying, yielded dark blue, conductive, amorphous powders. As in the case of the hydrogen reduced rare earth tungsten oxides, these powders were unstable in sulfuric acid at  $90^\circ\text{C}$ . This material could be sintered in much the same way as the rare earth bronzes to produce the ternary oxide system. However, this remains to be established.

#### Part b - Electrode Tests of High Surface Area Bronze

Several Teflon bonded, tantalum screen electrodes were prepared with the hydrogen reduced-vacuum sintered cubic  $\text{Nd}_x\text{WO}_3$  and  $\text{Sm}_x\text{WO}_3$  powders, as well as the low temperature hexagonal neodymium tungsten oxide. In all cases the resistance between bonded powder and tantalum screen was less than 30 ohms. The electrodes were tested for anodic activity with hydrogen fuel in 30% sulfuric acid at  $90^\circ\text{C}$ . The results of the tests were disappointing, since most of the electrodes showed no activity. Those that did show activity produced current densities in the  $.01 \text{ ma/cm}^2$  range. These results indicate that low surface area per se is not the primary source of the low activity observed previously. Rather it appears that the active species is probably present in low concentration. Thus the most important area for future research is the isolation of this active compound.

#### Part c - Tungsten Bronze in Buffer Electrolytes

Voltage scan studies (10) indicated that the anodic and cathodic electrochemical process might be due to a reversible oxidation-reduction process involving a hydrogen bronze intermediate. The existence of hydrogen bronze such as  $\text{H}_{0.1}\text{WO}_3$  and  $\text{H}_{0.33}\text{WO}_3$  are reported in the literature (14). In view of this hypothesis, it is important to determine if the catalytic activity of these systems has any pH dependency. Furthermore, it is possible that operating at higher pH could result in improved activity similar to that observed with platinum on platinum co-catalysts electrode systems (10,12).

Previous studies have shown that most of the bronzes studied could function as reasonably good hydrogen ion indicator electrodes. This is possible only if the bronze systems can enter into redox reactions in which hydrogen or hydroxide ion is

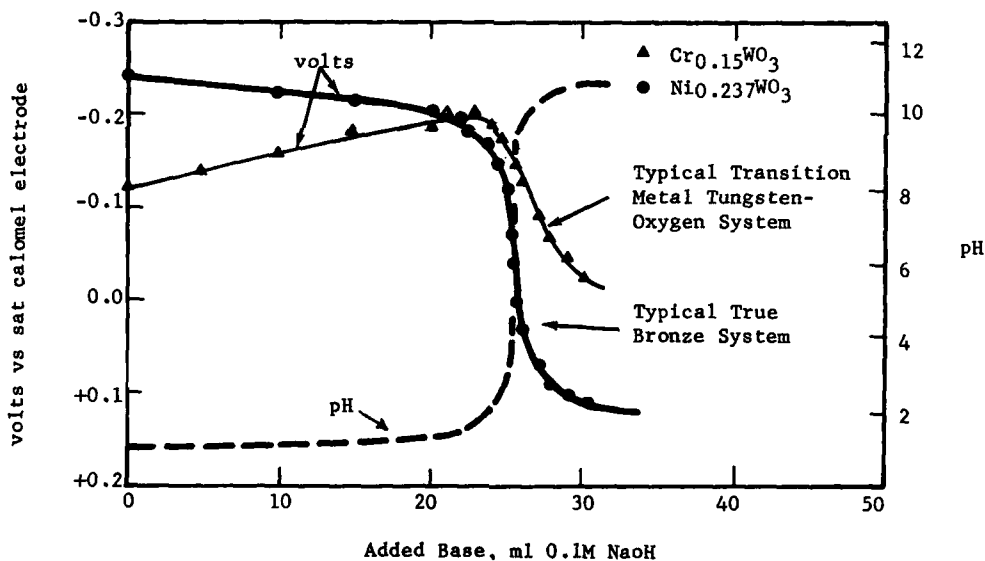
a reactant. That oxides of tungsten and molybdenum have hydrogen ion indicating properties is known (16,17,18).

Solutions of hydrochloric acid were titrated with sodium hydroxide using a measuring system consisting of a  $M_xWO_3$  indicator electrode and a saturated calomel reference electrode.

The bronze electrode was prepared by pressing an 85/15 wt% bronze Teflon mixture into a gold screen at moderate pressures. Simultaneous pH and voltage measurements were made in the course of the titration. Figure A-1 compares the pH response of typical mixed transition metal-tungsten oxide with that of a true bronze system. Notice that the true bronze shows a continuous decrease in potential with increasing pH while the mixed oxide systems generally show an initial increase to a pH of 1.5 to 2. All of the mixed tungsten oxides and tungsten bronzes showed breaks in the voltage-pH response indicative of a system with intermediate acid strength. Consequently, it is possible to examine the catalytic activity of the more basic forms of the tungsten bronzes by using various aqueous buffer electrolytes. Detailed titration results may be found in Appendix A-2.

Figure A-1

Hydrogen Indicator Properties Of The  
Metal-Tungsten-Oxygen System



Finally, a series of tungsten bronzes were tested for catalytic activity on methanol in phosphate and carbonate buffers at 90°C. Catalyst density in all cases was 150 mg/cm<sup>2</sup>. Methanol was chosen as the test reactant because there are no electrode structure problems to contend with and because other catalyst systems have shown higher activity with this fuel at higher pH.

As shown in Figures A-2 and A-3 none of the bronzes exhibited significant activity in the useful voltage range in either the phosphate or carbonate buffer systems.

Figure A-2

Methanol Activity of Various Bronzes in Carbonate Buffer

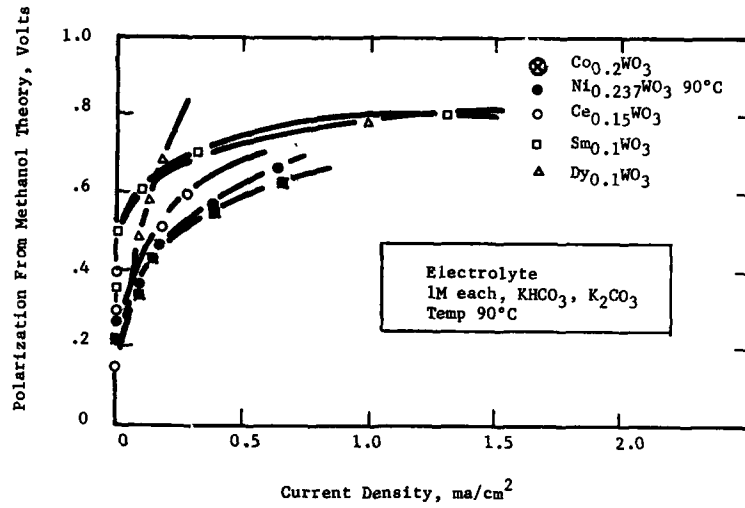
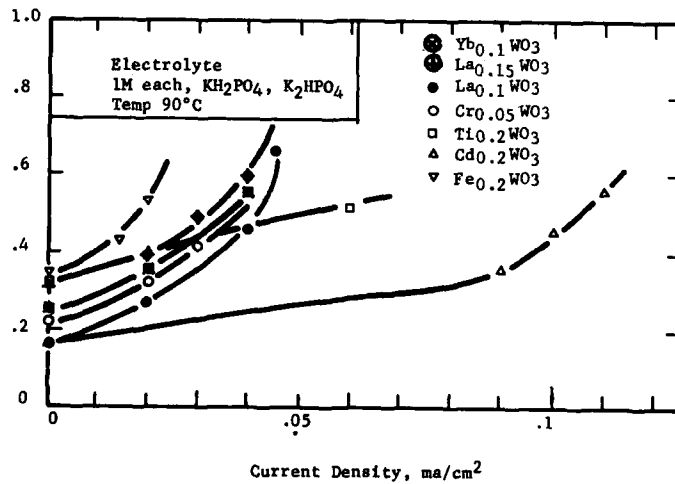


Figure A-3

Methanol Activity On Various Bronzes In Phosphate Buffer





## Phase 2 - Nickel-Cobalt Catalysts in the Phosphate Melt

Previous studies have indicated that a modified Raney alloy technique was effective in producing high surface area metal alloys (9). A number of inter alloys of the first transition period, particularly a 75-25 atom percent Ni-Co alloy had shown significant activity on H<sub>2</sub> in KOH (9). This latter catalyst was an outgrowth of an examination of the effect of d-band occupancy on catalyst performance. The development of a non-corrosive carbon dioxide rejecting electrolyte (phosphate melt) with established saturated hydrocarbon capability (10) allows further extension of this earlier study (9) into the intermediate temperature range where hydrocarbon activity should be more readily detected. If successful this would open a new avenue of catalyst research.

Raney Ni-Co catalyst was incorporated into a modified Teflon bonded (unsintered) electrode. Fabrication was carried out in the dry box under a nitrogen blanket because of the pyrophoric nature of the catalyst. This blanket was maintained until the phosphate melt was charged and the fuel admitted to the electrode chamber gas space.

Several electrodes were prepared in this manner and all exhibited activity on butane. Steady state activity was maintained over eight hour periods without loss of activity as long as the current density did not exceed 5 ma/cm<sup>2</sup>. Table A-1 details a typical electrode performance. Notice that above 1 ma/cm<sup>2</sup>, a voltage oscillation is observed. However, the voltage remained in the indicated range during the entire test period at a given current density level. Introduction of nitrogen in place of the fuel at current densities as low as 1 ma/cm<sup>2</sup> results in an immediate 0.24 volt polarization increase which was still increasing when the fuel was re-admitted, whereupon the electrode recovered its original performance level.

Table A-1

Butane Activity On Unsintered Raney Ni-Co-Teflon  
Electrode In Phosphate Melt At 250 °C(a)

Current Density ma/cm <sup>2</sup>	Polarization From Butane Theory, volts (b)
0	0.08
1	0.14
2	0.22 - 0.29
3	0.30 - 0.47
4	0.47 - 0.60
5	0.59 - 0.74

(a) Butane pre-humidified with H<sub>2</sub>O  
(b) Catalyst density, about 50-80 mg/cm<sup>2</sup>

Tests for Ni<sup>+2</sup> and Co<sup>+2</sup> in the phosphate melt after butane runs on Raney Ni-Co electrodes were negative, indicating negligible electrochemical corrosion currents. Prepared samples of melt containing Ni<sup>+2</sup> and Co<sup>+2</sup> at concentration as low as 0.002 Molar imparted the characteristic colors of these ions to the melt. No colors were observed in the electrolyte which had been run for sufficient time under load with butane to produce solutions more than 0.037 Molar if electrochemical dissolution of the electrode was the only, or major source of the current.

Only when nitrogen is used as the test fuel did corrosion occur, and even then only under severe anodic conditions. A Raney Ni-Co electrode tested in the phosphate melt with nitrogen as the fuel polarized rapidly and severely. After 15 minutes at 1 ma/cm<sup>2</sup> the electrode was polarized 1.2 volts from hydrogen (about 0.1 volt anodic to theoretical oxygen). Polarization was still increasing. Normally the electrodes are run under atmolyzing conditions. In order to observe oxygen evolution atmolysis was prevented. At 2 ma/cm<sup>2</sup> very slight gas evolution could be observed off the back of the electrode which is mounted horizontally. The oxygen polarization was 0.37 volts. After about two hours, a pink color was observed in the electrolyte indicating simultaneous electrochemical dissolution of the electrode. Comparison with the prepared standards showed that the cation concentration is considerably greater than 0.002 Molar probably closer to 0.02 Molar. The total number of coulombs with nitrogen was enough to produce solutions 0.023 Molar in these cations if oxygen evolution is backed out.

The corrosion of the electrode also gives a good indication of the electrode structure problems with this electrolyte. Examination of the electrode showed that the gas side was relatively conductive (20 to 100 ohms between point contacts). This indicates that a considerable portion of the catalyst was not wetted by the electrolyte as electrochemical corrosion could only have occurred where electrode-electrolyte contact occurs.

Most of the catalyst is probably not in contact with the electrolyte thus minimizing the three phase (fuel/catalyst/electrolyte) contact required for electrochemical oxidation of the fuel.

The importance of electrode structure is clearly evident when one compares the activity of a sintered platinum Teflon electrode performance with that of a platinum electrode prepared by the procedure used to make the Ni-Co electrodes. The sintered electrode is capable of 200 ma/cm<sup>2</sup> while the unsintered structure could barely maintain 1 ma/cm<sup>2</sup> a level poorer than the comparable nickel cobalt electrode.

These results are quite promising in that they represent the first demonstrated non-noble metal hydrocarbon catalyst. These results open a new route to developing more effective systems with d-band occupancy optimized for saturated hydrocarbons.

### Phase 3 - Bureau of Mines Catalysts

Part of our initial non-noble metal catalyst program involved the evaluation of eta phase carbides as potential hydrocarbon anode catalysts. These studies were discontinued in favor of the tungsten bronze work. Fortunately, NASA has made available a series of carbide, nitride and carbo-nitride catalysts which were prepared by the U.S. Bureau of Mines. These materials are being evaluated as potential hydrocarbon anode and cathode catalysts under NASA Contract NASW-1525. This evaluation includes a preliminary corrosion screening study in aqueous buffers and the phosphate melt. Chemically stable samples are also evaluated electrochemically in finished electrode structures.

### Part a - Corrosion Testing

The stability of all samples was qualitatively evaluated at room temperature in distilled water, pH 10.2 carbonate-bicarbonate buffer, pH 7 phosphate buffer, and 3.7 M H<sub>2</sub>SO<sub>4</sub>. In addition, corrosion tests at 220°C in the phosphate melt electrolyte were conducted. The tests involved exposing small samples of each material to the electrolyte in question, and visually observing any interaction.

All manipulations were conducted in the dry box under a nitrogen atmosphere, but after the sample was immersed in the electrolyte, the test vessels were removed from the dry box and stored in air. The electrolytes were not pretreated to exclude dissolved oxygen.

All samples reacted with 3.7 M  $H_2SO_4$  at room temperature. In most cases, violent gas evolution was observed, and the overall reaction complete in a few seconds. In two cases, both  $Fe_2C$  samples, gas evolution was noticeable slower, but complete reaction still occurred in a few minutes. These observations are summarized in Appendix A-3. Details of sample preparation and analysis by the Bureau of Mines are described in References (20) and (21). Almost complete dissolution of all the nitrides was observed, with only trace amounts of brown residue remaining in the acid solutions. With the materials containing carbon, black residues were observed which usually had densities less than the solution, and thus were no doubt carbon. This lack of acid stability precluded attempts to test the materials for catalytic activity in acid electrolyte.

In the aqueous neutral and basic media, the stability of many of the materials was satisfactory, although all materials were corroded in the phosphate buffer and several even in water. The results of these studies are outlined in Appendix A-3. Nearly all samples showed trace gas evolution on initial exposure to the solutions, presumably due to surface oxidation. Samples stable in the carbonate buffer were tested for electrochemical activity. These included:  $X-Fe_2C(7C, 11C)$ ,  $C-Fe_3C(15C)$ ,  $C-Fe_2C(23C)$  and  $C-Fe_2 X(C,N)$ ,  $Ag(7CN)$ .

Evaluation of stability in the phosphate melt was made by visual observation after a four day exposure at 220°C. Only four of the samples, two iron carbides (7C and 11C) and two carbonitrides, (7CN and 9CN) showed signs of instability, leaving a fine grey residue. Eight samples remained unchanged. This is a very encouraging finding, suggesting that even at elevated temperature, the non-aqueous melt is less corrosive than aqueous electrolytes at room temperature. Electrochemical testing in this intermediate temperature electrolyte is planned.

#### Part b - Electrode Fabrication and Passivation

Electrodes were prepared in a dry box flushed with nitrogen, because of the pyrophoric nature of the catalysts. About 750 mg of catalyst ( $150 \text{ mg/cm}^2$ ) and 75 mg of Teflon were pressed by hand onto a gold screen. Teflon in emulsion form (Teflon 42 BX) was used except for one electrode in which the powder form (Teflon 7) was evaluated. Anodes were stored in pure methanol before being immersed in the electrolyte containing methanol in the test cell to insure against oxidation of pyrophoric catalysts.

Cathodes require passivation prior to operation on pure oxygen or air. Recent studies at Tyco (16) indicate that induction of the surface by pre-exposure to various solvents (petroleum ether, diethyl ether, acetone, and methanol) leads to increased activity. On the other hand our studies indicate that passivation can be accomplished by programmed exposure to oxygen. While still in the nitrogen flushed dry box the electrode is mounted in the test cell, electrolyte is added and a nitrogen blanket is applied to the air side. The complete assembly is then removed from the dry box and trace amounts of oxygen were added to the nitrogen blanket to passivate the electrode. After about 15 minutes, pure oxygen could be introduced with no adverse effect.

As indicated in Table A-2, the oxygen induction procedure yields somewhat better cathode structures, and this procedure was adapted for cathode testing.

Table A-2

Effect of Passivation Procedure on Oxygen Activity

(1 M KHCO<sub>3</sub>/1 M K<sub>2</sub>CO<sub>3</sub>, 80°C)

	Polarization From Theoretical Oxygen at Indicated ma/cm <sup>2</sup> , Volts					
	0	1	5	10	15	20
Solvent Induction	0.41	0.52	0.70	0.80	0.87	0.90
Programmed O <sub>2</sub> Addition	0.41	0.47	0.59	0.71	0.79	0.84

Part c - Methanol Activity

Tests of electrodes prepared with the catalysts that were stable in carbonate-bicarbonate buffer for methanol oxidation showed that no samples had anodic activity. Initially, whether methanol was present or not, very good open circuit potentials near theoretical hydrogen were observed, and some transient anodic currents could be drawn at low polarizations. However, this activity soon died out, and was not recoverable. It is suspected that this transient performance is due to either oxidation of the catalyst itself, or to hydrogen occluded in some samples during preparation. It is not due to electrocatalytic oxidation of methanol.

Part d - Cathodic Activity

Initial studies showed that electrodes prepared using Teflon emulsion were more active than those prepared from Teflon powder. Current densities of greater than 25 ma/cm<sup>2</sup> were obtained with the Fe<sub>2</sub>C catalyst at polarizations below 0.9 volts as shown by the data in Table A-3.

Table A-3

Effect of Teflon Particle Size  
on Cathode Performance

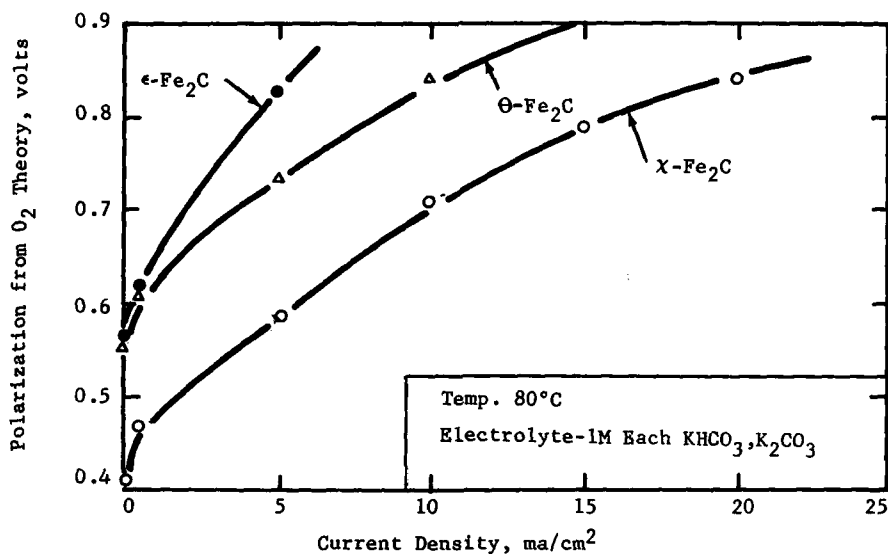
(O<sub>2</sub>, 1 M KHCO<sub>3</sub>/1 M K<sub>2</sub>CO<sub>3</sub>, 80°C)

	Polarization From Theoretical Oxygen at Indicated ma/cm <sup>2</sup> , Volts				
	0	1	5	10	20
Teflon 7 (7M)	0.48	0.56	0.73	0.84	1.01
Teflon 42 BX Emulsion (0.15 M)	0.41	0.47	0.59	0.71	0.84

Consequently, Teflon 42 emulsion was selected for catalyst evaluation studies. Screening studies of the other iron carbides summarized in Figure A-4 indicates that  $\chi$ -Fe<sub>2</sub>C(11C) was the most active. However, two of the carbides 7C and 23C were found to corrode in these tests and gave relatively poorer performance. This is summarized in Appendix A-5.

Figure A-4

Comparison Of Various Iron Carbide Cathode Catalysts



It has been shown that various carbides, nitride and carbonitride catalyst systems do not corrode in carbonate-bicarbonate buffers. Those systems stable in the buffer did not show activity as anode catalysts for the oxidation of methanol. Cathodic activity in carbonate was exhibited by an iron-carbide ( $\chi$ -Fe<sub>2</sub>C). Current densities as high as 25 ma/cm<sup>2</sup> could be obtained at polarizations under 0.9 volts.

Considering the low surface area of these materials these results are quite promising. Although silver is an active cathode catalyst in caustic electrolyte, its activity drops off sharply with decreasing pH. The iron-carbide catalyst has promise as a non-noble metal electrode for oxygen dissolution in an intermediate pH, CO<sub>2</sub> rejecting electrolyte.

#### Phase 4 - Conclusions

Freeze drying has been shown to be an effective technique for producing finely divided, high surface area, conductive metal-tungsten oxygen systems. Unfortunately, improvements in these properties have not resulted in the anticipated performance improvements. Thus it appears that future studies should emphasize work to determine the nature of the anodically active species in the bronzes. Evidence that the metal-tungsten oxygen catalyst can exist in forms containing ionizable hydrogen indicates that these systems could exist in different ionization states. However, those ionized states do not appear to influence catalysis because tests in phosphate and carbonate buffers showed that the catalytic of these systems were independent of pH.

Tests in the phosphate melt electrolytes have shown that Raney nickel-cobalt catalysts have demonstrable electrochemical activity on butane. This may be the first instance of reported saturated hydrocarbon activity at a non-noble metal anode in CO<sub>2</sub> rejecting electrolytes. This demonstrated activity suggests a potential new area for non-noble catalyst studies.

Evaluation of the Bureau of Mines catalysts indicates that the X-Fe<sub>2</sub>C catalyst is a promising cathode catalyst for the carbonate buffer system. Despite its low surface area current densities as high as 25 ma/cm<sup>2</sup> could be obtained at polarizations under 0.9 volts polarized. However, no anodic methanol activity was detected with any of the ion carbide, nitride and carbonitride catalysts, and many were found to be chemically unstable in water and aqueous buffers.

## 2.2 Task B, Noble Metal Catalysis

Research on supported noble metal electro-catalysts is aimed at improving the overall platinum utilization levels at both the hydrocarbon anode and air cathode. Anode studies have stressed increasing the platinization levels of the carbon supported catalysts to attain enhanced utilization through reduction in electrode thickness. In view of the high butane utilizations obtained with the Co-Pt on carbon system (10) at 200°C work was initiated to increase the platinization level of this system to the 12% target level. This increased platinization can be obtained through a sequential adsorption procedure described previously (10). In addition, other support systems and novel electrode structures were also investigated.

Although carbon supports offer one of the best routes to supported anode catalysts, it does introduce a serious open circuit debit at the cathode. Elimination of this cathodic mixed potential by the use of a more inert support could lead to still further utilization improvements especially since materials work has shown that there may be a minimum platinization level below which the carbon based electrode does not function properly (9,10). This may be due to support conductivity and more conductive substrates may be required.

### Phase 1 - Carbon Supported Anode Catalysts

Previous studies (10) have shown that utilization improvements can best be attained through the alteration in platinum deposition selectivity and increased platinization. Specific attempts to alter platinum deposition selectivity by varying adsorbate composition failed to produce any significant change in crystallite size. However as reported previously this led to the development of a new Co-Pt on FC-30 carbon catalyst system with enhanced hydrocarbon utilizations at 200°C. For example a 1.8 mg Pt/cm<sup>2</sup> electrode sustained 200 ma/cm<sup>2</sup> at 0.45 volts polarized. However, electrode life remains to be established.

In view of these promising results, studies were initiated to increase the platinization level attainable with the Co-Pt system from 5.8% to 12%. This can be accomplished by successive multiple adsorptions as described in the last report. However, site saturation could occur which would result in deposition of cobalt and platinum at widely separate sites. This could result in cobalt losses during the intermediate reduction steps since a 205°C hydrogen treat would not result in cobalt reductions in the absence of co-deposited platinum.

The effect of increased platinization on the butane performance of Co-Pt on FC-30 catalysts is summarized in Table B-1. Notice that increasing platinization from 5.8 to 11.6% at the 4 mg pt/cm<sup>2</sup> level resulted in a slight (but not significant) utilization improvement. However reducing the electrode thickness of the 11.6% platinized catalyst from 13 to 7 mils did not result in any performance improvement. This is contrary to the response observed with the 5.8% platinized Co-Pt catalyst, where a reduction from 31 to 13 mils resulted in almost a three fold improvement.

Table B-1

Effect Of Platinization Level  
on Butane Performance  
(Co-Pt on FC-30 carbon)  
(16.9 M H<sub>3</sub>PO<sub>4</sub>, 200°C)

Platinization, Wt% Platinum	Electrode Thickness, mils	Butane Utilization at 0.45 Volts Polarized ma/mg	Tafel Slope mv/decade
4 mg Pt/cm <sup>2</sup>			
5.8	31	44	200
11.6	13	52	130
2 mg Pt/cm <sup>2</sup>			
5.8	13	110	200
11.6	7	49	160

The reason for this difference in response is not clear. Only limited electrode structure data are available on this catalyst in 14.7 M phosphoric acid. Thus, the unusual thickness response may be related to the fact that we have not optimized these electrodes for operation in 16.9 M H<sub>3</sub>PO<sub>4</sub>. On the other hand, the Tafel slopes obtained are intermediate between that of pure platinum and cobalt platinum systems. Thus the previously discussed saturation effect could be responsible for this difference in response.

Phase 2 - Adams Catalyst Structures

Research to develop a suitable cathode for the Methanol-Air Fuel Cell (22) (Contract DA 36-039-AMC-02387(E)) has led to the development of a new electrode structure which has potential application to the hydrocarbon air system. This structure involves the preparation of an Adams type catalyst for incorporation into a sintered catalyst Teflon structure prior to reduction of the oxide to platinum black. This in effect prevents catalyst surface area loss during the sintering step. Consequently, this new structure was evaluated using both unsupported and supported catalysts.

Part a - Unsupported Adams Electrodes

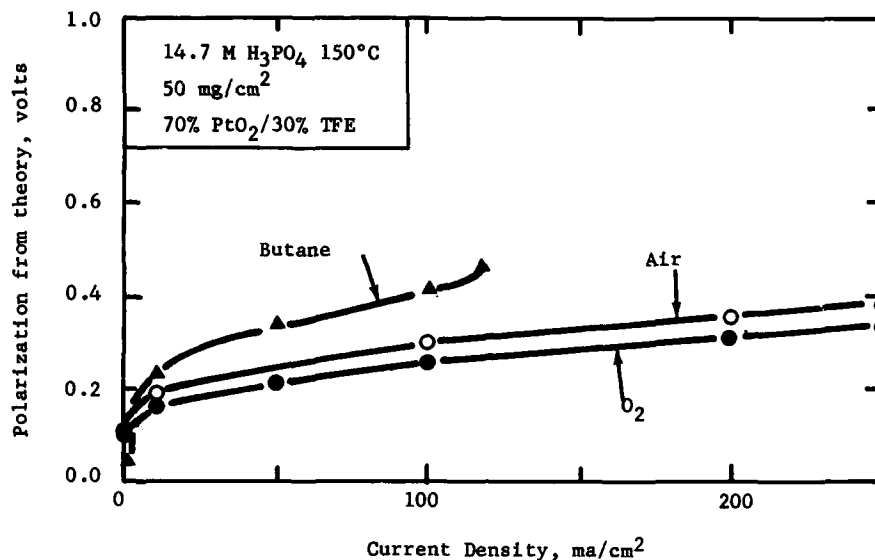
A 50 mg Pt/cm<sup>2</sup> sintered platinum-Teflon electrode (containing 30 wt% Teflon) was prepared from PtO<sub>2</sub> by sintering at 1000 psi for 75 sec at a temperature of 329°C. This electrode was subsequently reduced in potassium borohydride to produce a highly porous electrode structure. These electrodes were evaluated on oxygen and butane in 14.7 M H<sub>3</sub>PO<sub>4</sub> at 150°C.

As indicated in Figure B-1, the oxygen performance was comparable to the best sintered platinum Teflon cathodes. However, the butane performance was significantly poorer than comparable sintered platinum Teflon electrodes. No additional work in this area is planned.



Figure B-1

Performance of Unsupported  
Adams Structure

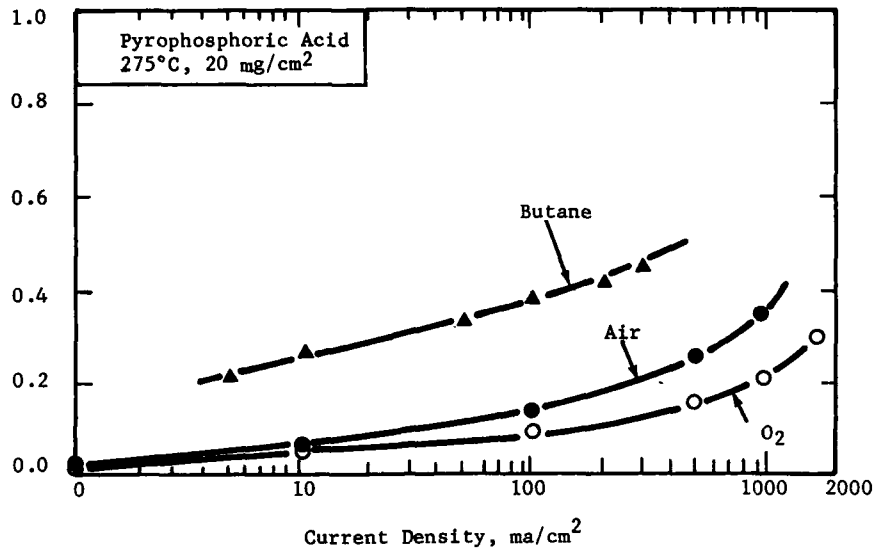


Part b - Dual Layer Platinum  
on Gold

Previous studies with low platinum content electrodes were concerned with carbon supported systems. An alternate approach is the use of a gold substrate to support the catalyst layer. Although this substrate is more costly than carbon, reductions of platinum requirements without the ensuing mixed potential loss at the cathode could result in a less costly electrode.

Electrodes were prepared by the modified Adams Procedure. A test electrode was made by spreading a platinum oxide-Teflon paste onto a screen, and then spreading a gold oxide-Teflon mixture on top of the catalyst layer before hot pressing. The oxides were subsequently reduced in sodium borohydride solution. The performance of a 20 mg Pt/cm<sup>2</sup> electrode prepared by this procedure was evaluated on oxygen, air and butane in pyrophosphoric acid at 275°C. The results are summarized in Figure B-2. Details are summarized in Appendix B-1 and 2.

Figure B-2  
Intermediate Temperature Performance  
Dual Layer Electrode



The oxygen performance illustrated in Figure B-2 indicates that the dual layer structure has some promise since no performance deterioration was noted. Unfortunately, the platinum utilization was somewhat poorer on oxygen than the conventional 50 mg/cm<sup>2</sup> sintered platinum Teflon structure, yielding only 5 ma/mg Pt (at 0.1 volts polarized) compared to the standard value of 8 ma/mg Pt. The butane utilization of this dual layer structure was also poorer than the conventional electrodes.

However, this structure may be useful in preparing low loaded systems since the sintered platinum Teflon structure is not interface maintaining below 20-25 mg/cm<sup>2</sup>. For example a 5 mg Pt/cm<sup>2</sup> platinum on gold electrode compared quite favorably with a carbon electrode at a comparable loading. As indicated in Table B-2, the dual layer cathode was 140-180 mv less polarized across the entire operating range.

Table B-2

Comparison of Low Loaded Electrodes  
(275°C, Pyrophosphoric Acid, 5 mg Pt/cm<sup>2</sup>)

	Polarization from O <sub>2</sub> Theory, Volts	
	100 ma/cm <sup>2</sup>	500 ma/cm <sup>2</sup>
Pt on Carbon	0.28	0.38
Pt on Au	0.14	0.21

This low loaded dual layer electrode ran well for two and one half hours after which a performance loss was noted. This was apparently due to checking and cracking in the Pt-Au layer (resembling a network of canals). It is therefore assumed that improvements in structural stability would prevent the observed performance loss.

Phase 3 - Conclusions

Supported platinum catalysts continue to show promise of significant hydrocarbon anode and air cathode improvements in both low and intermediate temperature electrolytes. Work on the Co-Pt on carbon anode catalysts indicates that increased platinization is possible, but site saturations maybe a problem. Despite this, the utilization obtained with a 11.6% platinized carbon was comparable to that obtained with the 5.8% material. However its response to changes in electrode thickness was significantly different. More work is required to establish whether this is due to site saturation or electrode structure problems.

Work with a modified electrode structure using the Adams catalyst indicates that these systems could hold the key to improved low loaded cathodes. Dual layer structures gave 140-180 mv less polarization than comparable carbon supported electrodes, but their life in pyrophosphoric acid was limited by structural stability problems. However, these mechanical structure problems do appear to be soluble ones.

Unfortunately, both modified structures (unsupported Pt and Pt on Au) failed to demonstrate any performance improvement when operating on butane in either 150°C 14.7 M H<sub>3</sub>PO<sub>4</sub> or 275°C pyrophosphoric acid.

### 2.3 Task C, New Electrolytes

Previous studies have shown that substantial improvements in hydrocarbon anode and cathode activity can be obtained by operating in the intermediate temperature range. This has been demonstrated both with pyrophosphoric acid and alkali metal phosphate melt electrolytes. The former system has the disadvantage of being highly corrosive, while the phosphate melt has a high resistivity.

Work in the electrolyte area centered primarily on the phosphate melts because of the possibility of using non-noble metal catalysts with these systems.

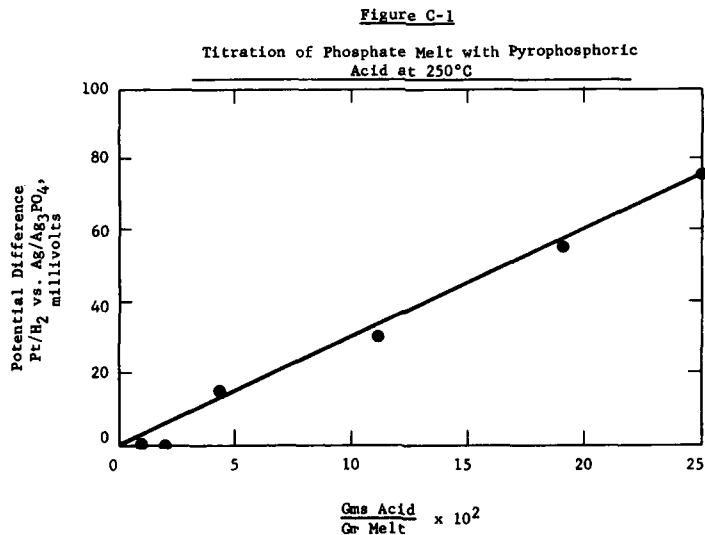
#### Phase 1 - Phosphate Melt Electrolyte Studies

The program to lower the electrolytic resistivity of the phosphate melts was resumed. Previous attempts to improve ionic conductivity using basic fluxing agents such as fluorides, carbonates, and oxides were not successful (9). The new approach which is broader in scope included (a) increasing the melt acidity, (b) fluxing with borate, (c) combined chelation and fluxing, (d) dissolving the phosphate melt in a more conductive molten salt and (e) the addition of lithium ion to utilize its water retention properties to operate the melt above 250°C.

#### Part a - Increasing the Melt Acidity

Pyrophosphoric acid was added in varying amounts to the phosphate melt to determine if increased melt acidity can improve the conductance. The effect of the added acid on electrolyte buffering capability and corrosivity was examined since improvement in conductance at the expense of increased concentration polarization and corrosion could not be tolerated.

The buffering capacity was determined by measuring the potential changes between a bubbling Hildebrand hydrogen electrode and a reference electrode consisting of a silver wire immersed in a melt solution containing three weight percent  $\text{Ag}_3\text{PO}_4$ . This reference electrode was described previously (9). The direct titration results are shown in Figure C-1; detailed data is given in Appendix C-1



The essentially linear titration curve shows that the resultant melt is still a buffer system.

An acid containing melt, consisting of 0.1 gm acid/gm melt was tested for its ability to function as a buffer at platinum electrodes polarized anodically and cathodically in the presence of hydrogen. The results shown in Table C-1 show that the composite melt is a good buffer system, indicating effective coupling of mass transfer with inherent buffer capacity.

Table C-1

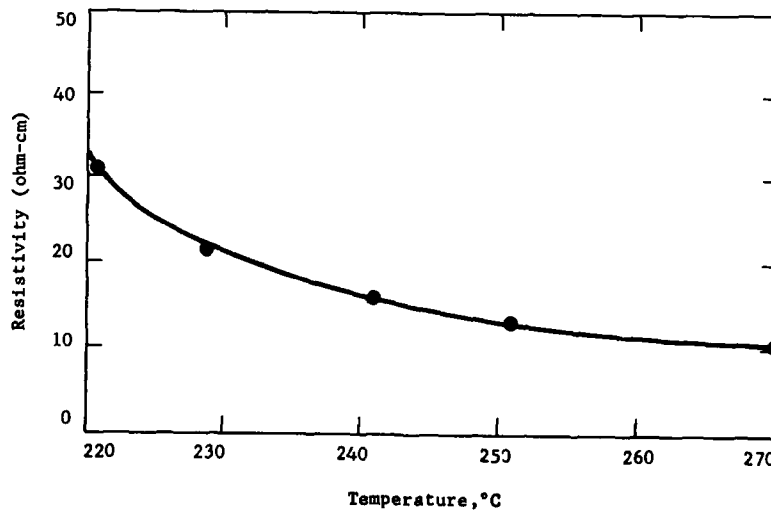
Phosphate Melt Containing 0.1 gm Acid/gm  
Melt Has Adequate Buffer Capacity

Current Density, ma/cm <sup>2</sup>	Volts Polarized on Hydrogen at 250°C on Sintered Pt-Teflon Electrodes	
	Anodically	Cathodically
25	0.00	0.00
50	0.01	0.00
100	0.02	0.03

Conductance measurements shown in Figure C-2 indicate that this property is somewhat improved, although not as much as desired. The conductance of the resultant melt at 250°C (13.5 ohm - cm), was significantly higher than the value of 10 ohm-cm set as the upper resistivity limit.

Figure C-2

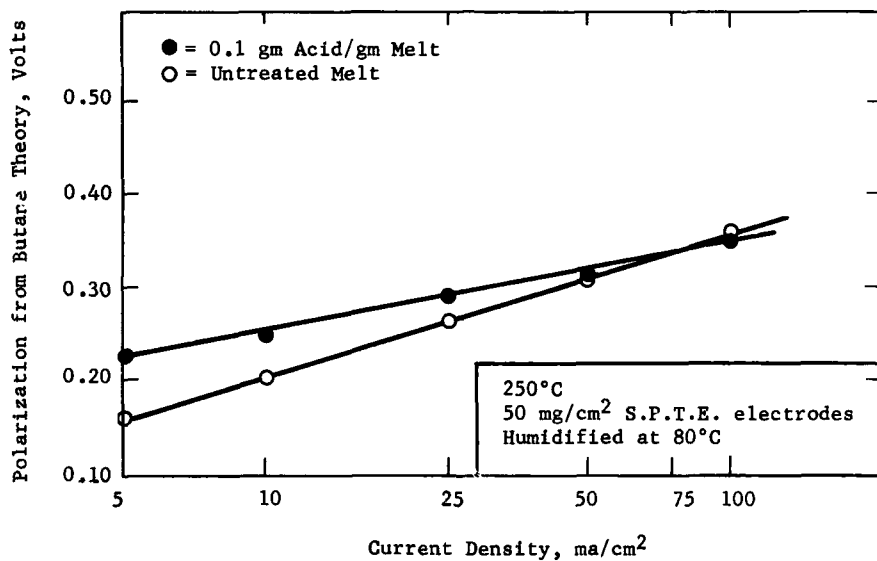
Resistivity of Phosphate Melt Containing  
0.1 gm Acid/gm Melt



The effect of melt acidity on butane and oxygen performance was also determined at 250°C using sintered platinum-Teflon structures containing 50 mg/cm<sup>2</sup> of catalyst. The results on oxygen and butane are shown in Figures C-3 and C-4. The detailed data is given in Appendix C-2. As indicated in Figure C-3 increasing melt acidity results in a lower Tafel slope. However, this is offset by higher polarization at the low current densities, at 25-100 ma/cm<sup>2</sup>, differences in activity become smaller. Consequently, there is no appreciable change in butane performance (at 100 ma/cm<sup>2</sup>) as a result of increased melt acidity. No tests were conducted above 100 ma/cm<sup>2</sup>.

Figure C-3

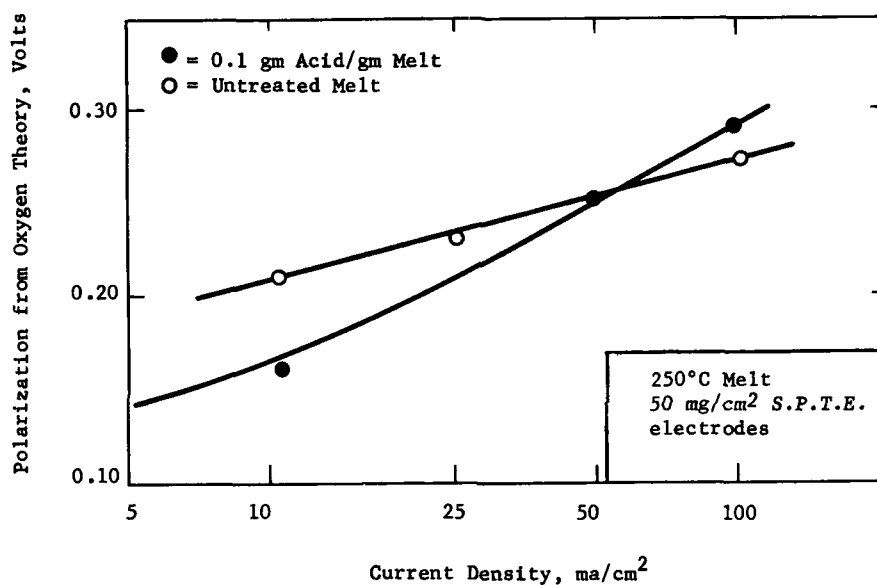
Comparative Butane Activity In  
Untreated And Acidified Phosphate Melts



The effect of melt acidity on oxygen performance is the reverse of that observed with butane. Oxygen exhibits a steeper ( $\eta$ -I) slope (Figure C-4), and a lower polarization at low current density, in the acidified melt. Again the net effect at 100  $\text{ma}/\text{cm}^2$  is not substantially different from that in the untreated melt. Thus, it appears that no appreciable activity benefits or deficits would be incurred using acidified phosphate melt.

Figure C-4

Comparative Oxygen Activity In  
Untreated and Acidified Phosphate Melts



The corrosivity of the acidified melt was examined using tantalum, nickel and silver screens. The screens were immersed in the acidified melt for 72 hours at 250°C. Silver was not attacked. The nickel screen was physically intact, but after a few hours, a green color was imparted to the melt indicating nickel corrosion. The tantalum screen had undergone a 3% weight loss after 72 hours at 250°C, although the screen did not look as if it had undergone attack. The corrosion rate is considerably less than that in pyrophosphoric acid where a tantalum screen disintegrated in five minutes. Phosphate melts of lower pyrophosphoric acid contents were also investigated for corrosiveness toward tantalum, nickel and silver. These tests indicated that both tantalum and nickel were slowly corroded in

melts containing as little as 0.02 gms pyrophosphoric per gram of phosphate melt, while conductivity was not significantly increased. Thus, noble metals would still be required with the composite melts. Consequently, no further work was done with these systems.

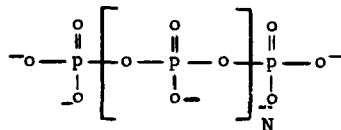
Part b - Fluxing with Borate and Fluoride

Fluxing was attempted with borates, and with borates plus fluorides. In a number of cases, clear melts were obtained, but the melting points exceeded 400°C. Since this is considerably above the desired operation temperatures, this work was terminated. The results are shown in Appendix C-3.

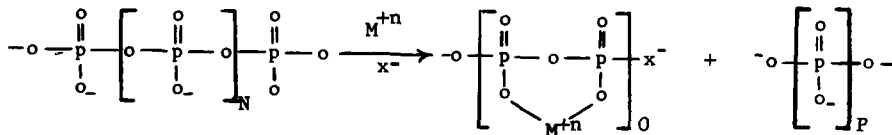
Part c - Chelation plus Fluxing

As mentioned previously, attempts to increase the conductance of the phosphate melt by anionic fluxing were unsuccessful. Chelation was attempted in conjunction with fluxing as a means of decreasing melt viscosity by depolymerization.

Since the inorganic polyphosphates are condensation polymers prepared by controlled dehydration of  $\text{NaH}_2\text{PO}_4$ , the polymeric melt can be represented schematically as



Thus, the melt contains a distribution of anionic polymers of varying molecular weight. A cation ( $\text{M}^{+n}$ ) which would be chelated by the polyphosphate could increase the extent of depolymerization by the fluxing agent  $\text{X}^-$  as shown below.



(Where  $N = 0 + P$ )

Coordination with the cation draws electrons away from the phosphorus atom making it more positive. The increased positive charge of the phosphorus atom should facilitate cleavage by an electron donor such as the anionic fluxing agent ( $\text{X}^-$ ). This approach has its basis in the hydrolysis kinetics of polyphosphates in aqueous medium (18).



Various bifunctional reagents such as  $\text{CdCl}_2$ ,  $\text{MnCl}_2$  and  $\text{MgCl}_2$  were added to the phosphate melt, but their solubility was limited. Although it was possible to dissolve 4 gms of  $\text{CdCl}_2 \cdot 12\text{H}_2\text{O}$  per 100 gms of melt, alternate solidification and remelting cycles resulted in a solid that had a melting point above  $250^\circ\text{C}$ . No clear melt resulted when the same reagents were combined with the original components of the melt prior to the initial melting preparation step.

Part d - Dissolving the Melt in a  
More Conductive Molten Salt

Another approach to increasing electrolyte conductivity was to dissolve the phosphate melt in a more conductive molten salt. In this manner, the conductance of the molten salt coupled with the buffering capacity of the phosphate component could result in a suitable composite electrolyte. This molten salt system need not be a buffer itself, but it must meet fuel cell electrolyte requirements in every other respect.

The phosphate melt was added to a  $\text{ZnCl}_2$ -KCl eutectic (melting point about  $230^\circ\text{C}$ ). The resistivity of the eutectic itself was about 15 ohm cm at  $250^\circ\text{C}$ . It was possible to add 1/4 gm of the phosphate melt to 1 gm of the  $\text{ZnCl}_2$ -KCl eutectic. The resistivity of the composite melt was about 18 ohm cm, slightly higher than the  $\text{ZnCl}_2$ -KCl eutectic itself. It is probable that the effect of the phosphate melt was to raise the viscosity, thereby increasing the resistance. HCl slowly evolved from the composite melt, thus it is doubtful that the system is stable. However, the stability is adequate to demonstrate the applicability of this concept. Consequently, the buffering properties of this system was tested by anodic and cathodic hydrogen performances. As shown in Table C-2, the buffering properties of this system are quite poor.

Table C-2

Hydrogen Performance of Sintered Pt-Teflon Electrodes  
in Phosphate- $\text{ZnCl}_2$ -KCl Composite Melt at  $250^\circ\text{C}$

Current Density, $\text{ma/cm}^2$	Volts Polarized			
	Anodically		Cathodically	
	Dry $\text{H}_2$	$\text{H}_2$ Pre-humidified with $\text{H}_2\text{O}$ @ $60^\circ\text{C}$	Dry $\text{H}_2$	$\text{H}_2$ Pre-humidified with $\text{H}_2\text{O}$ @ $60^\circ\text{C}$
1	0.08	0.2	0.34	0.21
2	0.22	--	0.36	--

Evolution of HCl may be the reason that the cathodic performance is considerably poorer than the anodic hydrogen performance since this means that the phosphate melt has lost ionizable hydrogen.

Molten KSCN (melting point  $172^\circ\text{C}$ ) was also used as a dispersion medium for the melt. Adding the phosphate melt (0.2 gms phosphate/gm KSCN) resulted in a dark blue but very fluid solution. This color is probably due to the presence of impurities as none of the major components in the melt are colored. Side reactions ensued, however, accompanied by the formation of small amounts of a white precipitate and  $\text{H}_2\text{S}$  evolution. Therefore this study was abandoned.

Part e - Addition of Lithium Ion to the Melt

Lithium dihydrogen phosphate was added to the phosphate melt. As lithium ion is unique in its tenaciousness in holding on to water in molten salts, it was hoped that this would reduce melt dehydration at temperatures higher than 250°C. Higher operating temperatures offered the possibility of bringing the resistance down into the acceptable range, provided the melt was stabilized by lithium ion.

Two lithium ion containing samples of melt were made. Both melts appeared to have higher viscosities than the untreated phosphate melt. The composite melt resistivities, Table C-3, were considerably higher than that of the plain melt.

Table C-3

Addition of  $\text{LiH}_2\text{PO}_4$  Increases Phosphate Melt Resistivity

Resistivity in ohm cm @ 250°C	
<u>0.1 gm <math>\text{LiH}_2\text{PO}_4</math>/gm</u>	<u>0.2 gm <math>\text{LiH}_2\text{PO}_4</math>/gm</u>
45	39

Consequently, there is nothing to be gained by higher operating temperatures since this composite system yields a higher resistance electrolyte than the unmodified phosphate melt.

Phase 2 - Conclusions

Attempts to increase the conductivity of the phosphate melt have not been successful to date. The melt properties were either unchanged or adversely affected. Efforts to improve melt conductance should continue in view of the potential usefulness of this electrolyte with non-noble metal catalysts. This is especially important since the current conductance levels are just border line, and cell engineering studies could reduce IR loss to a tolerable level.

### SECTION 3

#### DIRECT HYDROCARBON-AIR FUEL CELL FEASIBILITY STUDY GENERAL CONCLUSIONS

In 1964 Esso Research and Engineering Company initiated a three year study aimed at establishing the feasibility of a direct hydrocarbon-air fuel cell power package capable of wide spread military application. At the onset of this effort there appeared to be a number of potential problem areas which could prevent the ultimate development of an efficient, reliable, high power density system with a reasonable cost. Critical problems were identified in the areas of electrocatalysis, electrode structure, cell engineering and systems. Research was conducted to establish the technology required to attain a useable solution or determine that a solution either existed or could be found.

This report marks the completion of this three year program. Consequently, the following sections will summarize the significant results of this research effort and suggest areas where additional research is required to produce a direct hydrocarbon air fuel cell battery for military use.

##### Task A - Low Temperature Systems

Low temperature (100-150°C) direct hydrocarbon fuel cells have been shown to be catalyst limited. Practical systems require acidic carbon dioxide rejecting electrolytes, thus limiting available catalysts to acid resistant systems. This latter requirement has restricted the choice of potential systems to platinum or platinum group alloys. However, mechanism studies have identified hydrocarbon adsorption rate as the current limiting step in platinum catalyzed electrodes. Thus improved performance (utilization) can only be achieved by either altering the inherent activity or increasing the operating temperatures. Alloying with other platinum group metals failed to improve the inherent activity of platinum. However, a newly developed cobalt-platinum alloy catalyst has shown some promise.

Thus it appears that significant improvements in performance and utilization can only be achieved by alterations in catalyst micro structure rather than through electronic or chemical effects. Significant improvements in catalyst utilization were obtained with improved platinum on carbon catalysts. At 150°C utilizations as high as 45 ma/mg Pt were readily attained, but this is still well below practical levels of 200 ma/mg.

Development of a non-noble acid stable hydrocarbon electrocatalyst provides the best long term solution to the catalyst cost and availability problem. This approach, if successful, would ensure the widest possible fuel cell application. During this program a number of families of compounds and alloys have been investigated and many have been prepared for the first time. In general, one or more of the essential fuel cell requirements (catalytic activity, conductivity, corrosion stability) were missing. However, one class of compounds, the mixed transition metal tungsten oxides and tungsten bronzes, have been found which meet all of the essential fuel cell requirements. Both hydrogen and oxygen activity was detected in 3.7 M sulfuric acid. Oxygen activity was also detected in the intermediate temperature pyrophosphoric acid electrolyte. This work promises to be a major development in fuel cell research.

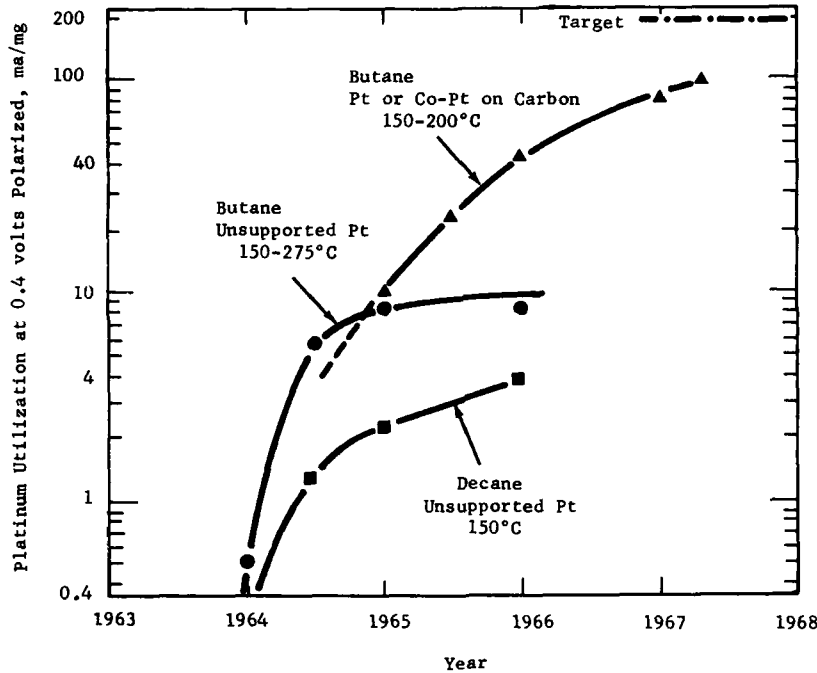
Non-corrosive buffer electrolytes offer additional promise. Suitable electrode structures were developed and catalyst studies were broadened to include non-noble metal alloys. Studies were conducted to establish the catalyst electronic configuration required for optimum hydrogen dissolution. A 75Ni-25 cobalt alloy (1 d-band vacancy) was found to be optimum. No hydrocarbon activity was detected in

aqueous buffers. However, as will be discussed later, this same material did demonstrate hydrocarbon activity in the phosphate melt. Furthermore, application of this data led to the development of a more effective noble metal catalyst for use in intermediate temperature electrolytes (Co-Pt on carbon).

Operation on wide boiling range logistic fuels introduced very severe electrode structure requirements since the resultant electrode must function equally well on liquid or gaseous fuels. Preferential wetting of the catalyst indicated that interface control might not be maintained within the electrode structure and that total electrolyte displacement might occur. The development of the sintered platinum and sintered carbon Teflon emulsion electrode structures has shown that this problem can be circumvented. Highly effective structures have been developed which yield equivalent power densities with both gaseous and liquid fuels. Progress in electrode structure development is illustrated in Figure D-1.

Figure D-1

Progress in Hydrocarbon Anode Development



A liquid hydrocarbon-air multicell unit and operating system was developed and delivered to Fort Monmouth. This system demonstrated the general operability of liquid hydrocarbon air systems and provided insight into problems of operation on a wide boiling range hydrocarbon (JP-4). Although the power density was low, it did show that a total cell system could be engineered to allow safe operation with significant fuel transport through the anode. Additional research in this area is also required.

### Task B - Intermediate Temperature Cells

The activity of hydrocarbon anodes has been shown to be limited by adsorption rather than reactant transport. Operation at elevated temperatures consistent with engineering requirements, should result in substantial increases in anode and cathode performance. Thus, direct oxidation of hydrocarbons proceeds at high rates and the problems of catalysis are reduced in intermediate temperature electrolytes (200-275°C). Based upon demonstrated half cell data, power levels of over 100 mw/cm<sup>2</sup> (including cell IR) were obtained with butane and octane air systems operating in pyrophosphoric acid electrolyte, a performance level seen only with hydrogen up to now. Particularly significant, was the discovery that near theoretical oxygen voltages could be obtained at the cathode. Even at 300 ma/cm<sup>2</sup> the electrode was only 90 mv polarized. Furthermore, this electrolyte was shown to be effective for the electrochemical oxidation of C<sub>3</sub> to C<sub>10</sub> hydrocarbons and "dirty" reformer gas cells and no carbon monoxide poisoning is noted, at 250 to 275°C, even with 10% CO.

Unfortunately, pyrophosphoric acid is quite corrosive and special cell construction materials had to be developed. One such material, a tungsten bronze filled Teflon has shown remarkable resistance to this electrolyte.

Major military application of the fuel cell awaits the development of a non-noble metal catalyst. However, if platinum catalyzed electrodes can be developed with utilizations of 200 ma/mg noble metal costs could be brought to a level which would allow special uses. Considerable progress has been made in reducing catalyst loadings. For example, a new cobalt-platinum on carbon catalyst system has been found which yields platinum utilizations of 110 ma/mg on butane at 200°C and 75 ma/mg at 275°C. However, increasing catalyst utilization another two-fold may prove more difficult even though one electrode did give a utilization of 187 ma/mg in pyrophosphoric acid.

Preliminary systems analysis indicates that an octane air fuel cell could be devised with a significant reduction in catalyst loading (1400 vs 61 gm/kw). This reduction was accomplished with only a 14 lbs/kw weight increase. Similar reductions in reformer fuel cell catalyst requirements were also possible, but only at a significant weight increase.

Thus, the results obtained in this study demonstrate the advantage of intermediate temperature operation. The potential development of a non-corrosive CO<sub>2</sub> rejecting electrolyte for this operating temperature range would make further investigation of this area quite promising.

A non-corrosive, CO<sub>2</sub> rejecting electrolyte has been found. Mixed sodium and potassium phosphates yield excellent performance and do not corrode nickel cobalt, tantalum, etc. In exploratory tests, with platinum electrodes (250°C), butane was polarized 0.3 volts at 400 ma/cm<sup>2</sup> and oxygen yielded 300 ma/cm<sup>2</sup> at 0.2 volts polarized. Thus, even with non-optimized electrode structures, the phosphate melt cell should yield power densities (ex-IR) over 100 mw/cm<sup>2</sup> on butane and oxygen. With additional structural improvements, power densities should exceed those obtained with internal reforming or direct phosphoric acid cells without the materials and systems problems currently prevalent with these cells. Also, since the electrolyte rejects carbon dioxide, silver-palladium diffusers and alkali air scrubbers now needed for alkaline electrolyte systems will be unnecessary. Thus, cost and weight would be reduced.

The intermediate temperature buffer electrolyte fuel cell thus promises to overcome many of the difficulties now posed by hydrocarbon fuel cell systems. Operating temperatures will be high enough to obtain significant activity, but low enough to be relatively easily started in the field. (Coupling with a secondary battery would provide instant power where necessary.) The non-corrosive nature of these electrolytes will provide a suitable media for developing non-noble metal catalysts and using low cost materials. Indeed, the electrolyte has been used to successfully demonstrate the electrochemical oxidation of butane on a non-noble 75 Ni-25 Co Raney alloy catalyst. This appears to be the first time that such activity has been observed.

These systems are new and research and development will be required. For example, the conductivity is less than strong electrolytes ( $IR = 0.1$  volt at  $100 \text{ ma/cm}^2$ ) closer cell spacing may be needed. Some work using depolymerization agents to improve conductivity has already been carried out. The behavior under prolonged operation is not known although ten day tests indicate no changes in properties. Systems must be analyzed and engineered. Nevertheless, the system has the potential for significant advance, particularly for application as 300/500 watt and larger field generators.

#### Task C - Mixed Metal Tungsten Oxide and Tungsten Bronze Anode Catalyst Development

The oxide bronzes (no relation to copper alloys) are relatively good electronic conductors and many are exceptionally resistant to acid attack. They are, therefore, of prime interest as potential electrocatalysts. Following the approach taken in our perovskite program, catalytic metals such as the first row transition elements have been introduced into the bronze structure without impairing conductivity and corrosion resistance. Many of these materials have shown catalytic activity as anodes and all are active cathodes.

A modified mixed transition metal tungsten oxide,  $\text{Ni}_{0.237}\text{WO}_3$ , has demonstrated catalytic activity on hydrogen and methanol at low temperatures ( $90^\circ\text{C}$ ). However, performance was limited by low surface area and electrical bonding problems. Hydrocarbons are inactive at these temperatures.

Tests in pyrophosphoric acid indicate that these materials are stable to  $275^\circ\text{C}$ . Cathode performance is significant ( $100 \text{ ma/cm}^2$ ) with reasonably flat Tafel slopes, but open circuit polarizations were quite high.

The discovery that mixed transition metal tungsten oxides and bronzes have electrocatalytic activity opens a large new area for exploitation since the performances obtained thus far are only suggestive of the activity possible. No longer need we be limited to noble metals for acid electrolyte catalysts. A wide variety of non-noble transition elements can be introduced into the structure, oxygen deficient lattices may be investigated and alternate bronze forming materials may be found to be active. These possibilities increase the probability for developing a successful non-noble catalyst system.

#### Conclusions and Recommendations

This three year study has established that there do not appear to be any engineering obstacles to the development of high power density direct hydrocarbon-air fuel cell power systems. Unfortunately, thus far only platinum or its alloys have shown suitable electrochemical activity, but the quantities required preclude any extensive military application. However, the results discussed indicate that

further research and development in the areas of low loaded anodes, intermediate temperature electrolytes and non-noble metal catalysts following the leads developed in this feasibility study should lead to practical fuel cell systems.

#### SECTION 4

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APPENDIX A-1

HEXAGONAL NEODYMIUM TUNGSTEN OXIDE

<u>I/I<sub>0</sub> (rel.)</u>	<u>d<sub>obs.</sub> (Å)</u>	<u>d<sub>calc.</sub> (a = 7.42 Å c = 7.61 Å)</u>	<u>hkl</u>
20	6.45	6.45	100
90	3.79	3.80	002
100	3.21	3.21	200
2	2.66	2.62	112
50	2.45	2.45	202
2	2.14	2.14	300
15	1.90	1.90	004
20	1.86	1.86	220
2	1.78	1.78	310
1	1.73	1.73	311
20	1.66	1.66	222
23	1.63	1.64	204
15	1.60	1.61	400
12	1.48	1.48	402
10	1.33	1.33	224
10	1.22	1.23	404
8	1.21	1.22	331
5	1.17	1.18	206
8	1.15	1.15	422

APPENDIX A-2

pH FUNCTIONALITY OF THE BRONZES  
AS SHOWN BY ACID BASE TITRATION

<u>0.1N NaOH (Total cc)</u>	<u>Ce<sub>0.15</sub>WO<sub>3</sub></u>	<u>pH</u>
	<u>Volts vs. SCE</u>	
0	-0.24	0.85
5	-0.24	0.93
10	-0.225	1.02
15	-0.220	1.16
20	-0.205	1.43
22	-0.195	1.60
23	-0.185	1.75
24	-0.170	2.02
24.5	-0.150	2.35
24.75	-0.140	2.51
25.0	-0.120	2.90
25.25	-0.075	6.90
25.5	-0.045	9.40
25.75	0.00	10.19
26.0	+0.03	10.35
27.0	+0.065	10.80
28.0	+0.09	11.00
29.0	+0.10	11.15
30.0	+0.105	11.20

<u>0.1N NaOH (Total cc)</u>	<u>Ni<sub>0.237</sub>WO<sub>3</sub></u>	<u>pH</u>
	<u>Volts vs. SCE</u>	
0	-0.12	0.80
5	-0.14	0.85
10	-0.16	0.98
15	-0.18	1.10
20	-0.19	1.31
22	-0.20	1.50
23	-0.20	1.65
24	-0.195	1.97
24.5	-0.185	2.15
24.75	-0.180	2.31
25.00	-0.175	2.66
25.20	-0.165	3.00
25.50	-0.155	4.17
25.75	-0.140	8.20
26.00	-0.135	9.55
26.50	-0.120	10.25
27.00	-0.095	10.35
28.00	-0.065	10.62
29.00	-0.050	10.78
30.00	-0.030	10.85

APPENDIX A-2 (Cont'd)

pH FUNCTIONALITY OF THE BRONZES  
AS SHOWN BY ACID BASE TITRATION

Cr<sub>0.5</sub>WO<sub>3</sub>

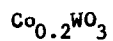
<u>0.1N NaOH (Total cc)</u>	<u>Volts vs. SCE</u>	<u>pH</u>
0	-0.380	0.78
5	-0.365	0.86
10	-0.350	0.97
15	-0.335	1.12
20	-0.315	1.41
22	-0.295	1.64
23	-0.280	1.72
24	-0.255	2.03
24.5	-0.240	2.16
25.0	-0.205	2.60
25.25	-0.170	3.07
25.50	-0.105	8.52
25.75	-0.050	9.65
26.0	-0.005	10.08
27	+0.060	10.63
28	+0.075	10.80
29	+0.084	10.95
30	+0.090	11.03

La<sub>0.15</sub>WO<sub>3</sub>

<u>0.1N NaOH (Total cc)</u>	<u>Volts vs. SCE</u>	<u>pH</u>
0	-0.243	1.00
5	-0.229	1.10
10	-0.220	1.17
15	-0.192	1.28
20	-0.174	1.52
22	-0.157	1.69
23	-0.146	1.86
24	-0.125	2.24
24.5	-0.105	2.49
25.0	-0.045	5.80
25.25	+0.005	9.40
25.50	+0.027	9.89
25.75	+0.056	10.24
26.0	+0.073	10.42
27.0	+0.10	10.86
28.0	+0.11	11.01
29.0	+0.115	11.13
30.0	+0.120	11.21

APPENDIX A-2 (Cont'd)

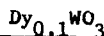
pH FUNCTIONALITY OF THE BRONZES  
AS SHOWN BY ACID BASE TITRATION



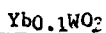
<u>0.1N NaOH</u> <u>(Total cc)</u>	<u>Volts vs.</u> <u>SCE</u>	<u>pH</u>
0	-.322	0.8
5	-.325	0.88
10	-.320	0.98
15	-.320	1.12
20	-.335	1.38
22	-.335	1.57
23	-.335	1.71
24	-.320	1.96
24.5	-.315	2.20
24.7	-.320	2.34
25.0	-.300	2.70
25.2	-.280	3.43
25.5	-.230	9.50
25.75	-.220	10.08
26.0	-.200	10.30
26.5	-.175	10.65
27.0	-.160	10.82
28.0	-.145	11.05
29.0	-.130	11.20
30.0	-.110	11.28

APPENDIX A-2 (Cont'd)

pH FUNCTIONALITY OF THE BRONZES  
AS SHOWN BY ACID BASE TITRATION



<u>0.1N NaOH (Total cc)</u>	<u>Volts vs. SCE</u>	<u>pH</u>
0	-0.185	0.92
5	-0.230	0.90
10	-0.250	1.00
15	-0.275	1.15
20	-0.295	1.41
22	-0.310	1.57
23	-0.335	1.69
24	-0.355	1.84
24.5	-0.390	2.10
25.0	-0.400	2.51
25.25	-0.400	2.75
25.50	-0.360	3.81
25.75	-0.275	9.49
26.00	-0.190	10.01
27.00	-0.090	10.67
28.00	0.00	10.89
29.00	+0.055	11.02
30.00	+0.080	11.13
31.00	+0.095	11.20



<u>0.1N NaOH (Total cc)</u>	<u>Volts vs. SCE</u>	<u>pH</u>
0	-0.215	1.10
5	-0.210	1.12
10	-0.205	1.21
15	-0.205	1.32
20	-0.195	1.59
22	-0.185	1.79
23	-0.185	1.92
24	-0.185	2.23
24.5	-0.185	2.49
25.0	-0.155	3.41
25.25	-0.110	8.17
25.50	-0.065	9.96
25.75	-0.025	10.22
26.0	+0.025	10.45
27.0	+0.075	10.89
28.0	+0.095	11.09
29.0	+0.100	11.21
30.0	+0.100	11.32

APPENDIX A-2 (Cont'd)

pH FUNCTIONALITY OF THE BRONZES  
AS SHOWN BY ACID BASE TITRATION

Lu<sub>0.1</sub>WO<sub>3</sub>

<u>0.1N NaOH</u> <u>(Total cc)</u>	<u>Volts vs.</u> <u>SCE</u>	<u>pH</u>
0	-0.253	1.03
5	-0.242	1.03
10	-0.224	1.11
15	-0.215	1.19
20	-0.202	1.50
22	-0.191	1.68
23	-0.181	1.81
24	-0.166	2.09
24.5	-0.155	2.31
25.0	-0.124	2.92
25.25	-0.086	4.81
25.50	-0.029	8.99
25.75	+0.005	9.91
26.00	+0.045	10.11
27	+0.091	10.68
28	+0.110	10.90
29	+0.116	11.02
30	+0.120	11.12

Sm<sub>0.1</sub>WO<sub>3</sub>

<u>0.1N NaOH</u> <u>(Total cc)</u>	<u>Volts vs.</u> <u>SCE</u>	<u>pH</u>
0	-0.205	0.98
5	-0.200	1.00
10	-0.200	1.10
15	-0.185	1.21
20	-0.175	1.55
22	-0.165	1.72
23	-0.155	1.85
24	-0.140	2.08
24.5	-0.125	2.25
24.75	-0.115	2.40
25.00	-0.105	2.55
25.25	-0.090	2.95
25.50	-0.075	3.58
25.75	-0.050	9.27
26.00	-0.040	10.00
27.0	+0.015	10.69
28.0	+0.045	10.93
29.0	+0.075	11.06
30.0	+0.095	11.16
31.0	+0.115	11.25
32.0	+0.130	11.30

APPENDIX A-2 (Cont'd)

pH FUNCTIONALITY OF THE BRONZES  
AS SHOWN BY ACID BASE TITRATION

MnO<sub>2</sub>WO<sub>3</sub>

<u>0.1N NaOH (Total cc)</u>	<u>Volts vs. SCE</u>	<u>pH</u>
0	-0.370	1.00
5	-0.360	1.06
10	-0.340	1.14
15	-0.305	1.26
20	-0.275	1.49
22	-0.245	1.69
23	-0.235	1.83
24	-0.215	2.12
24.5	-0.205	2.32
25.0	-0.190	3.04
25.25	-0.175	6.47
25.50	-0.100	9.00
25.75	-0.065	9.79
26.0	-0.020	10.08
27.0	-0.005	10.71
28	0	10.90
29	+0.005	11.04
30	+0.015	11.15

FeO<sub>2</sub>WO<sub>3</sub>

<u>0.1N NaOH (Total cc)</u>	<u>Volts vs. SCE</u>	<u>pH</u>
0	-0.342	1.07
5	-0.337	1.15
10	-0.330	1.26
15	-0.320	1.40
20	-0.310	1.64
22	-0.300	1.82
23	-0.294	2.00
24	-0.280	2.30
24.5	-0.265	2.60
25.0	-0.246	3.14
25.25	-0.223	8.35
25.50	-0.206	9.70
25.75	-0.186	10.36
26.00	-0.166	10.53
27.0	-0.110	10.99
28	-0.072	11.17
29	-0.040	11.30
30	-0.010	11.39
31	+0.012	11.45
32	+0.038	11.50
33	+0.046	11.55



APPENDIX A-2 (Cont'd)

pH FUNCTIONALITY OF THE BRONZES  
AS SHOWN BY ACID BASE TITRATION

Cd<sub>0.2</sub>WO<sub>3</sub>

<u>0.1N NaOH</u> <u>(Total cc)</u>	<u>Volts vs.</u> <u>SCE</u>	<u>pH</u>
0	-0.220	1.02
5	-0.218	1.08
10	-0.216	1.15
15	-0.219	1.27
20	-0.217	1.47
22	-0.215	1.61
23	-0.213	1.71
24	-0.212	1.89
24.5	-0.211	2.00
25.0	-0.210	2.15
25.25	-0.206	2.26
25.50	-0.204	2.39
25.75	-0.200	2.61
26.00	-0.195	2.87
26.25	-0.182	5.50
26.50	-0.167	9.16
26.75	-0.151	9.95
27.0	-0.134	10.19
28	-0.051	10.72
29	-0.010	10.87
30	+0.034	11.08
31	+0.055	11.18
32	+0.067	11.27
33	+0.075	11.32

Ti<sub>0.2</sub>WO<sub>3</sub>

<u>0.1N NaOH</u> <u>(Total cc)</u>	<u>Volts vs.</u> <u>SCE</u>	<u>pH</u>
0	-0.225	0.99
5	-0.216	1.00
10	-0.210	1.08
15	-0.205	1.19
20	-0.198	1.42
22	-0.191	1.60
23	-0.185	1.74
24	-0.176	2.04
24.5	-0.170	2.26
25.0	-0.154	2.74
25.25	-0.137	3.65
25.50	-0.116	9.25
25.75	-0.093	9.92
26.0	-0.060	10.22
27	-0.005	10.68
28	+0.035	10.90
29	+0.071	11.02
30	+0.100	11.12

APPENDIX A-3

CORROSION TESTS IN 3.7 M H<sub>2</sub>SO<sub>4</sub> AT ROOM TEMPERATURE

(Approx. 50 mg of sample in 10 cc 3.7 M H<sub>2</sub>SO<sub>4</sub>)

<u>Sample No. (1)</u>	<u>Composition</u>	<u>Initial Reaction</u>
1N	ε-Fe <sub>3</sub> N, γ'-Fe <sub>4</sub> N	Rapid gas evolution.
9N	ζ-Fe <sub>2</sub> N	" "
10N	ε-Fe <sub>3</sub> N	" "
20N	ε-Fe <sub>3</sub> N	" "
4CN	ε-Fe <sub>2</sub> X(C,N)	" "
7CN	ε-Fe <sub>2</sub> X(C,N) Ag(1Fe/1Ag)	" "
9CN	γ'-Fe <sub>2</sub> X(C,N)	Very rapid gas evolution.
2NC	χ-Fe <sub>2</sub> X(C,N) ε-Fe X(C,N)	Rapid gas evolution.
7C	λ-Fe <sub>2</sub> C	Slow gas evolution.
11C	λ-Fe <sub>2</sub> C	" "
15C	θ-Fe <sub>3</sub> C	Rapid gas evolution.
23C	ε-Fe <sub>2</sub> C, α-Fe(trace)	" "

(1) Bureau of Mines designation.

APPENDIX A-4

STABILITY IN AQUEOUS NEUTRAL AND BASIC MEDIA

Results of Three-Day Exposure

<u>Compound</u>	<u>H<sub>2</sub>O</u>	<u>Phosphate pH 7</u>	<u>Carbonate pH 10.2</u>
$\epsilon$ -Fe <sub>3</sub> N, $\gamma'$ -Fe <sub>4</sub> N	No change	Yellow precipitate	Dark red solution
$\zeta$ -Fe <sub>2</sub> N	"	"	"
$\epsilon$ -Fe <sub>3</sub> N	"	"	Slight reddish solution
$\epsilon$ -Fe <sub>3</sub> N	"	"	"
$\epsilon$ -Fe <sub>2</sub> X(C,N)	Some gas evolution	"	Red solution
$\epsilon$ -Fe <sub>2</sub> X(C,N), Ag	No change	"	No change
$\gamma'$ -Fe <sub>4</sub> X(C,N)	"	"	Red solution
$\chi$ -Fe <sub>2</sub> X(C,N),	"	"	Slight reddish solution
$\epsilon$ -Fe <sub>2</sub> X(C,N)	"	"	"
$\lambda$ -Fe <sub>2</sub> C	Rusty color	"	No change
$\chi$ -Fe <sub>2</sub> C	"	"	"
$\theta$ -Fe <sub>3</sub> C	"	"	"
$\epsilon$ -Fe <sub>2</sub> C, $\alpha$ -Fe	"	"	"

APPENDIX A-5

COMPARISON OF THE PERFORMANCE OF IRON  
CARBIDES AS CATHODE CATALYSTS

(O<sub>2</sub>, 1 M KHCO<sub>3</sub>/1 M K<sub>2</sub>CO<sub>3</sub>, 80°C)

Current Density, ma/cm <sup>2</sup>	Polarization from Theoretical O <sub>2</sub> volts			
	$\chi$ -Fe <sub>2</sub> C <sup>(a)</sup>	$\theta$ -Fe <sub>2</sub> C	$\chi$ -Fe <sub>2</sub> C <sup>(b)</sup>	$\epsilon$ -Fe <sub>2</sub> C, $\alpha$ Fe
	No. 11	No. 15	No. 7	No. 23
0	0.41	0.55	0.50	0.56
1	0.47	0.61	0.52	0.62
5	0.59	0.74	0.69	0.83
10	0.71	0.84	(c)	(c)
15	0.79	0.91	--	--
20	0.84	0.93	--	--
30	1.00	--	--	--

- (a) Sample prepared from alkali promoted magnetite reduced with hydrogen.  
 (b) Sample prepared from leached Raney iron.  
 (c) Corrosion observed.

APPENDIX B-1

CATHODIC PERFORMANCE OF O<sub>2</sub> AND AIR  
DUAL LAYER AU-PT ELECTRODE

Current Density, ma/cm <sup>2</sup>	Volts Polarized on O <sub>2</sub> and Air (IR included) at 275°C	
	O <sub>2</sub>	Air
	<hr/>	
0	0.02	0.03
10	0.06	0.07
100	0.11	0.16
500	0.17	0.26
1000	0.21	0.36
1500	0.29	(Not Attempted)

APPENDIX B-2

BUTANE PERFORMANCE ON DUAL LAYER AU-PT  
ELECTRODE AT 275°C (FUEL PRE-HUMIDIFIED WITH 80°C H<sub>2</sub>O)

<u>Current Density, ma/cm<sup>2</sup></u>	<u>Volts Polarized (Incl. IR)</u>
5	0.21
10	0.27
50	0.35
100	0.38
200	0.41
300	0.43

APPENDIX C-1

COMPARATIVE BUTANE ACTIVITY AT 250°C

Fuel Pre-humidified with water at 80°C  
Sintered Pt-teflon electrodes, 50 mg Pt/cm<sup>2</sup>

Polarization From Butane Theory, Volts

<u>Current Density</u> <u>ma/cm<sup>2</sup></u>	<u>Phosphate</u> <u>Melt</u>	<u>Phosphate Melt Containing</u> <u>0.1 gm Pyro. Acid/gm Melt</u>
0	--	0.14
1	--	0.14
5	0.22	0.16
10	0.23	0.20
25	0.29	0.26
50	0.31	0.31
100	0.37	0.36

Security Classification

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13. ABSTRACT The three year program to determine the feasibility of a direct hydrocarbon-air fuel cell capable of widespread military application has been completed. This program has established that there are no engineering obstacles to the development of high power density direct hydrocarbon-air fuel cell systems. However, the noble metal catalyst requirements precludes any extensive military applications. Consequently, research during this period has emphasized (1) the search for non-noble catalysts, (2) the development of non-corrosive intermediate temperature electrolytes and (3) studies to improve noble metal utilization. Work on metal tungsten oxide catalysts has shown that freeze drying can be an effective method for producing conductive high surface area metal tungsten oxides but these materials did not show any increased activity. On the other hand, Raney nickel-cobalt alloy catalysts have demonstrated electrochemical activity on butane in the 250°C phosphate melt electrolyte. This appears to be the first case of saturated hydrocarbon activity with a non-noble catalyst system in a CO <sub>2</sub> -rejecting electrolyte. However, attempts to increase the ionic conductance of this phosphate melt electrolyte through fluxing and chelation were unsuccessful even though the present conductance is borderline. Supported platinum catalysts continue to show promise of significant activity improvement in both low and intermediate temperature cells. Dual layer (Pt-Au) structures have been developed for cathodes to eliminate the open circuit debit encountered with carbon supported electrodes. These electrodes are more active than carbon supported systems but mechanical instability in phosphoric acid is a problem.		

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14. KEY WORDS	LINK A		LINK B		LINK C	
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