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ELECTROLYTES FOR HYDROCARBON AIR FUEL CELLS.(U)
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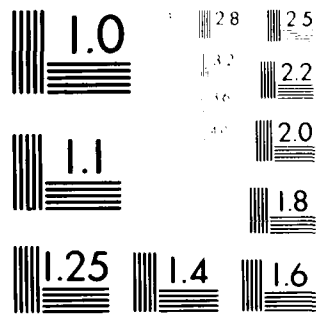
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ELECTROLYTES FOR HYDROCARBON AIR FUEL CELLS

Interim Technical Report

M. Walsh, F. Walsh, D. N. Crouse and R. S. Morris
April 1980

to

U. S. Army Mobility Equipment Research and
Development Command
Fort Belvoir, Virginia

Prepared by

ECO, Incorporated
56 Rogers Street
Cambridge, MA 02142

Contract No. DAAK70-79-C-0165

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1.0 Summary

The present research is directed towards obtaining an improved electrolyte for hydrocarbon-air fuel cells. No commercially available electrolyte appears to demonstrate promise. Two new electrolytes, difluoromethanediphosphonic acid and difluoromethanedisulfonic acid, have been synthesized and are being tested.

The present status of the project and the outstanding problems are reviewed.

1.1 Program Objective

The objective of this effort is to obtain an electrolyte with sufficient electrochemical activity and stability to replace phosphoric acid in direct oxidation fuel cells.

This is a formidable challenge and has been the subject of intensive research¹⁻⁶ by many groups for many years. The eight desired properties³ of the electrolytes are:

- a. Good ionic conductivity.
- b. Thermal stability to 180°C.
- c. Electrochemical stability between 0-1V vs. HRE.
- d. Low vapor pressure and high viscosity.
- e. Non-corrosive to fuel cell components.
- f. Supports high rates of electrooxidation of hydrogen and propane and high rates of electroreduction of air and oxygen.
- g. Sufficient surface tension so as not to wet Teflon.
- h. Good solvent for reactants and products.

1.2 Technical Approach

In this program, fuel cell performance data are the ultimate criteria for evaluating electrolytes. The performance of each candidate electrolyte is compared to phosphoric acid under the same conditions. At least two separate but identical tests are made to ensure reliable data.

Because this is an electrolyte evaluation program, all tests are made with commercially-available fuel-cell electrodes backed by gold-plated titanium screens. No effort is made to optimize electrode structure.

The experimental testing includes IR free polarization curves for short and long term performance testing. Test

apparatus and procedures are summarized in Section 2.

1.3 Commercially Available Electrolytes

Commercially available electrolytes received prime consideration. However, no commercially available electrolyte appears to meet the program objective.

Commercially available electrolytes have been thoroughly⁶ reviewed. Many have been thoroughly studied and found to lack physical and/or chemical stability at 180°C.

ECO's view is that only perfluorocarbon acids promise the necessary thermal, chemical and physical stability at 180°C. This view is based both on the literature³ and on tests performed on four commercially available electrolytes; namely,

- methanedisulfonic acid
- sulfoacetic acid
- 10-dl-camphorsulfonic acid
- and pentadecafluorooctanoic acid.

These four electrolytes were chosen for test as commercially available representatives of:

- aliphatic sulfonic acids
- substituted aliphatic sulfonic acids
- and perfluorinated carboxylic acids.

Specific results of these tests are summarized in Section 3.

1.4 New Electrolytes

Two new electrolytes have been synthesized. Preliminary data on difluoromethanediphosphonic acid are encouraging but as yet, incomplete.

Historically, fuel cell investigations have been limited to materials that can be easily synthesized from a proven preparation scheme. ECO has developed new synthesis routes

and has produced two new electrolytes; namely,

- difluoromethanedisulfonic acid (DFMDSA)
- and difluoromethanediphosphonic acid (DFMDPA).

The details of the syntheses are summarized in Section 4.

DFMDPA was synthesized first. The material is only 70% pure. It contains 30% monofluoroisopropyl methane bisphosphonate. Even with this impurity, DFMDPA appears to have remarkable thermal and electrochemical stability. Preliminary test results are summarized in Section 5.

DFMDSA is an extremely difficult and potentially dangerous synthesis. The large amounts needed for test are presently being carefully synthesized.

1.5 Future Work

The remainder of the contract will be spent testing, in full fuel cells, the purest DFMDSA and DFMDPA that can be achieved. These cells will be run for periods up to 2,000 hours at 150°C at constant voltage (0.6V versus DHRE). Cell performance will be periodically checked over the current density range of 0-120mA/cm². Performance will be measured on propane and air.

2.0 Experimental Procedures and Apparatus

2.1 Fuel Cell Electrodes

Fuel cell performance is measured on commercial electrodes. No attempt is made to optimize electrode structure for a given electrolyte.

The electrode chosen was purchased from Prototech, Inc. (Newton Highlands, MA). This RA-2 electrode is a thin (0.35mm) carbon board which is platinum catalyzed (0.33mgPt/cm²) on one side and Teflon wet-proofed on the other. Circular test electrodes are cut from these 4"X4" RA-2 electrode sheets using a metal punch. The geometric area of the test electrode exposed to the electrolyte is 5.06 cm².

2.2 ECO Half Cell

The first part of this program called for half-cell screening tests of four commercially available electrolytes using oxygen and hydrogen as reactants. These tests were performed on electrodes secured in the electrode holder shown in Figure 1. These holders are milled from blocks of heat-treated Teflon. The holder is plumbed to permit gas flow behind the electrode, and utilizes gold wires for electrical contact to a gold-plated-titanium screen current collector on the back of the test electrode. The half-cell counter electrode consists of a platinum flag (5 cm²) with a platinum wire lead. The dynamic hydrogen reference electrode is composed of two 1cm² platinum flags held in a quartz tube, the end of which is drawn out to a capillary.

THE ECO HALF CELL
ELECTRODE HOLDER

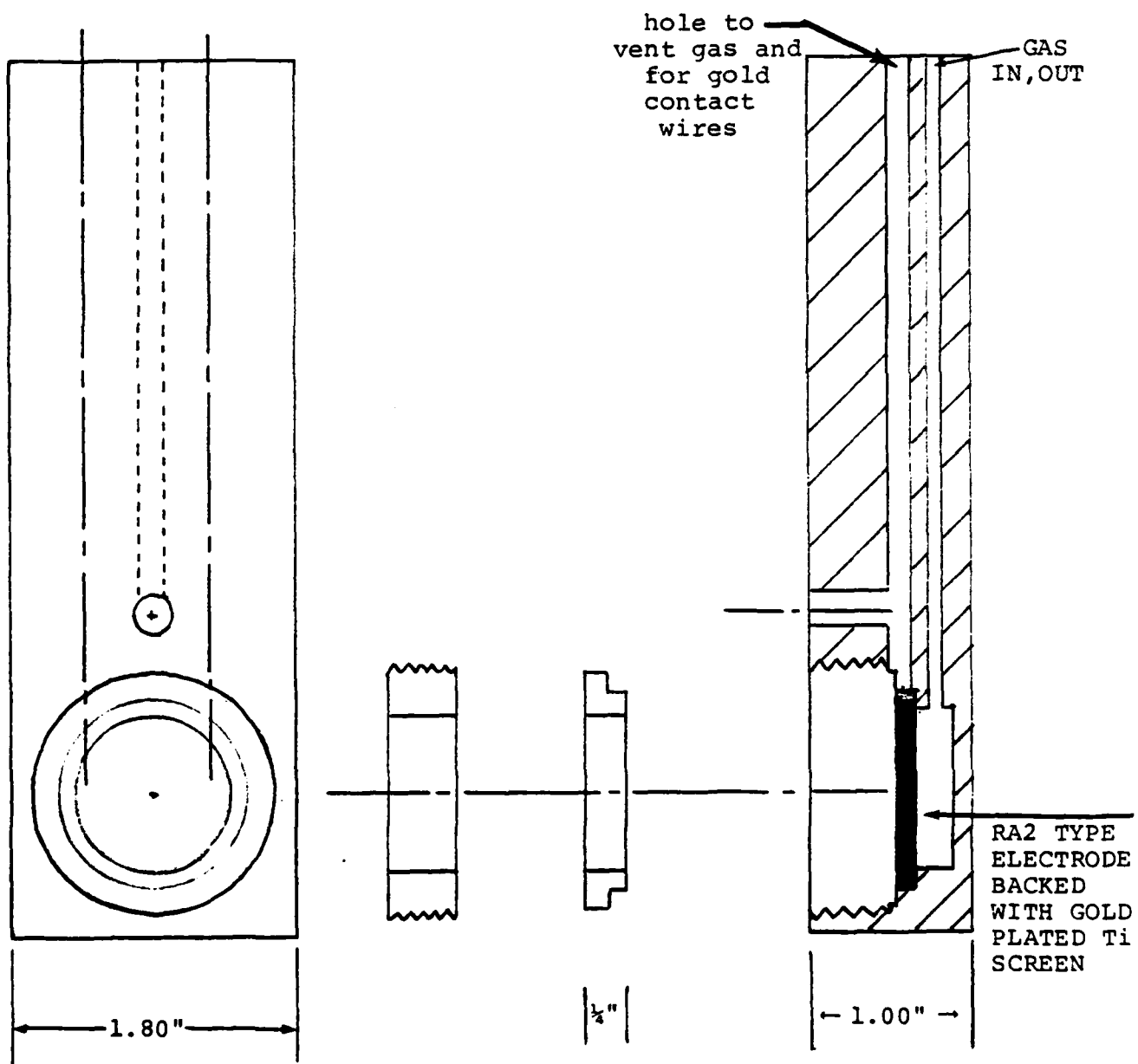


FIGURE 1

The cell case is a rectangular quartz vessel which is placed into a Glas-Col Model TM-614 heat mantle. The temperature is regulated by an Electro-Flex Model 5000R heat controller.

Half-cell tests were run using oxygen and hydrogen as reactants for up to 100 hours each at 100°C. The entire assembly is shown in Figure 2.

2.3 ECO Small Volume Fuel Cell (SVFC)

Early in this contract it was realized that the efforts to synthesize novel organic compounds would probably yield small quantities (< 100 grams) of material. The half-cell apparatus for testing commercially available electrolytes requires 150 grams of material for each half-cell test.

Faced with this dilemma, ECO designed, fabricated, and successfully tested a Teflon fuel cell which requires only 10 grams of electrolyte. Figures 3 and 4 illustrate the ECO small volume fuel cell (SVFC). This cell is, in fact, two ECO half-cells facing one another with cell gases plumbed in from the sides of the cell rather than from the top.

The small volume fuel cell is designed to accommodate two Prototech RA-2 type electrodes backed with gold plated titanium screens. Gold wires connect the electrodes to the outside world. The reference electrode permits the sequential gathering of voltage and current data from either of the two in-situ electrodes. Consequently, half-cell data can be gathered while running the electrolyte in the fuel

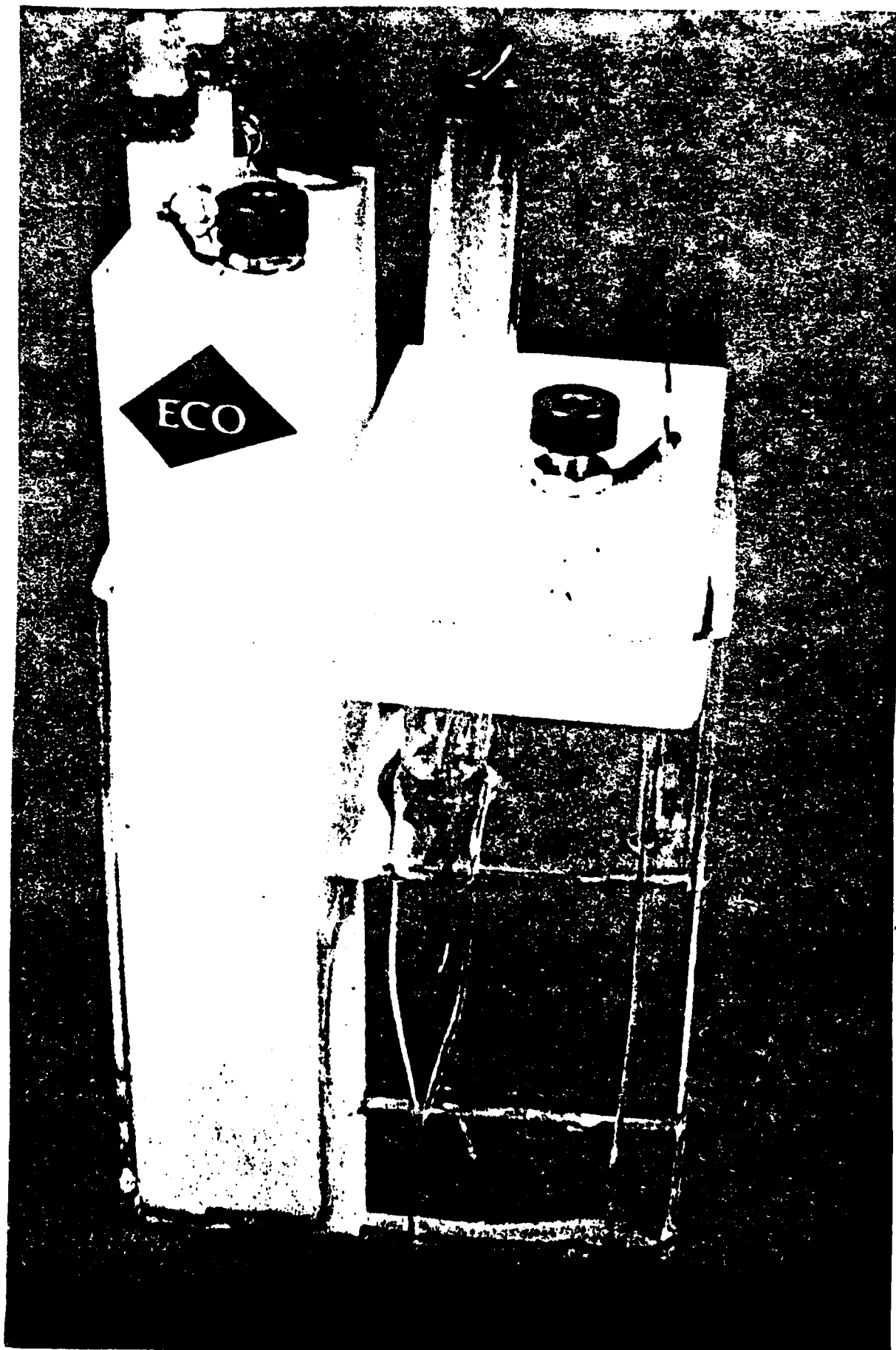
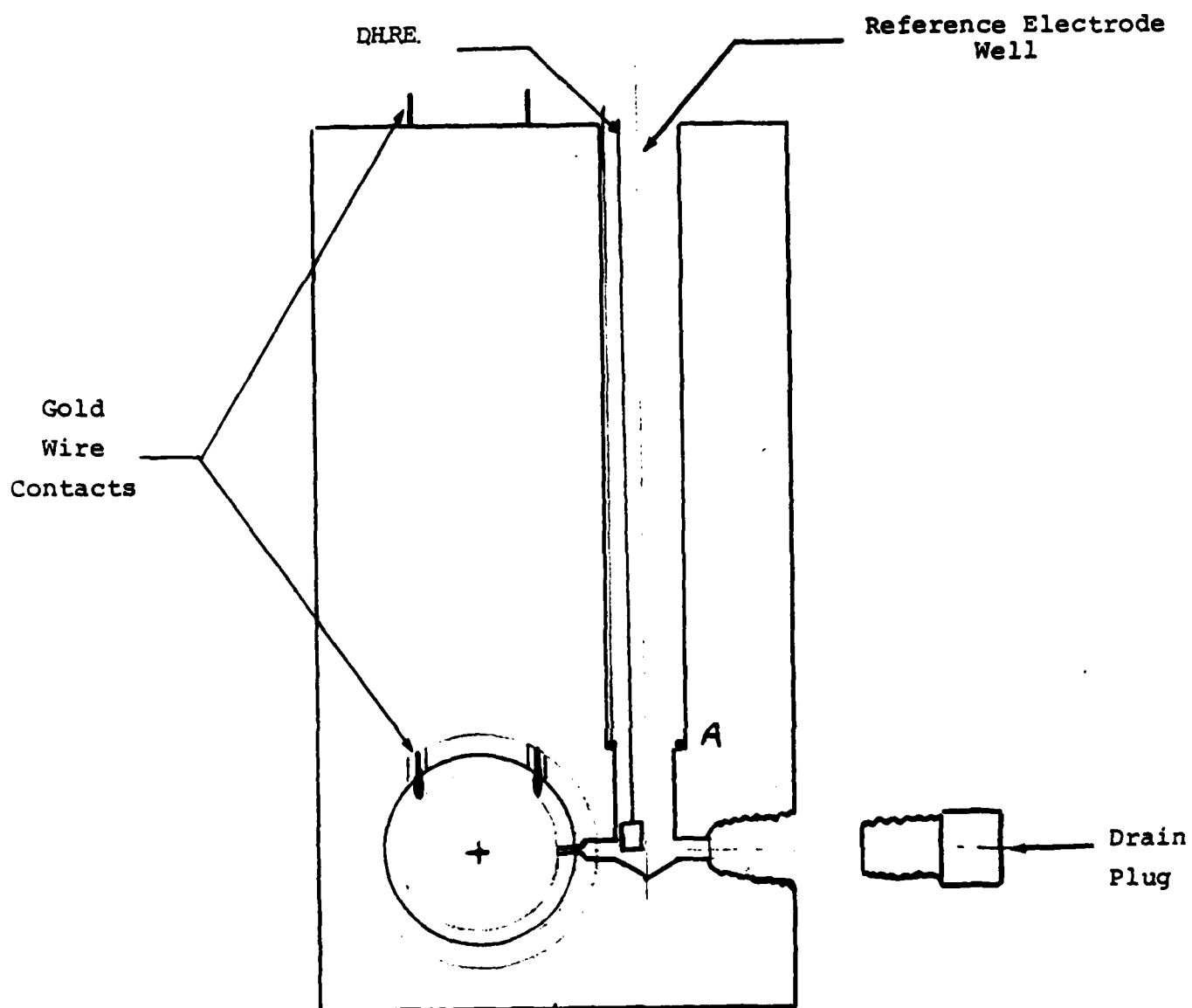


FIGURE 2

ECO Small Volume Fuel Cell

Figure 3



ECO Small Volume Fuel Cell

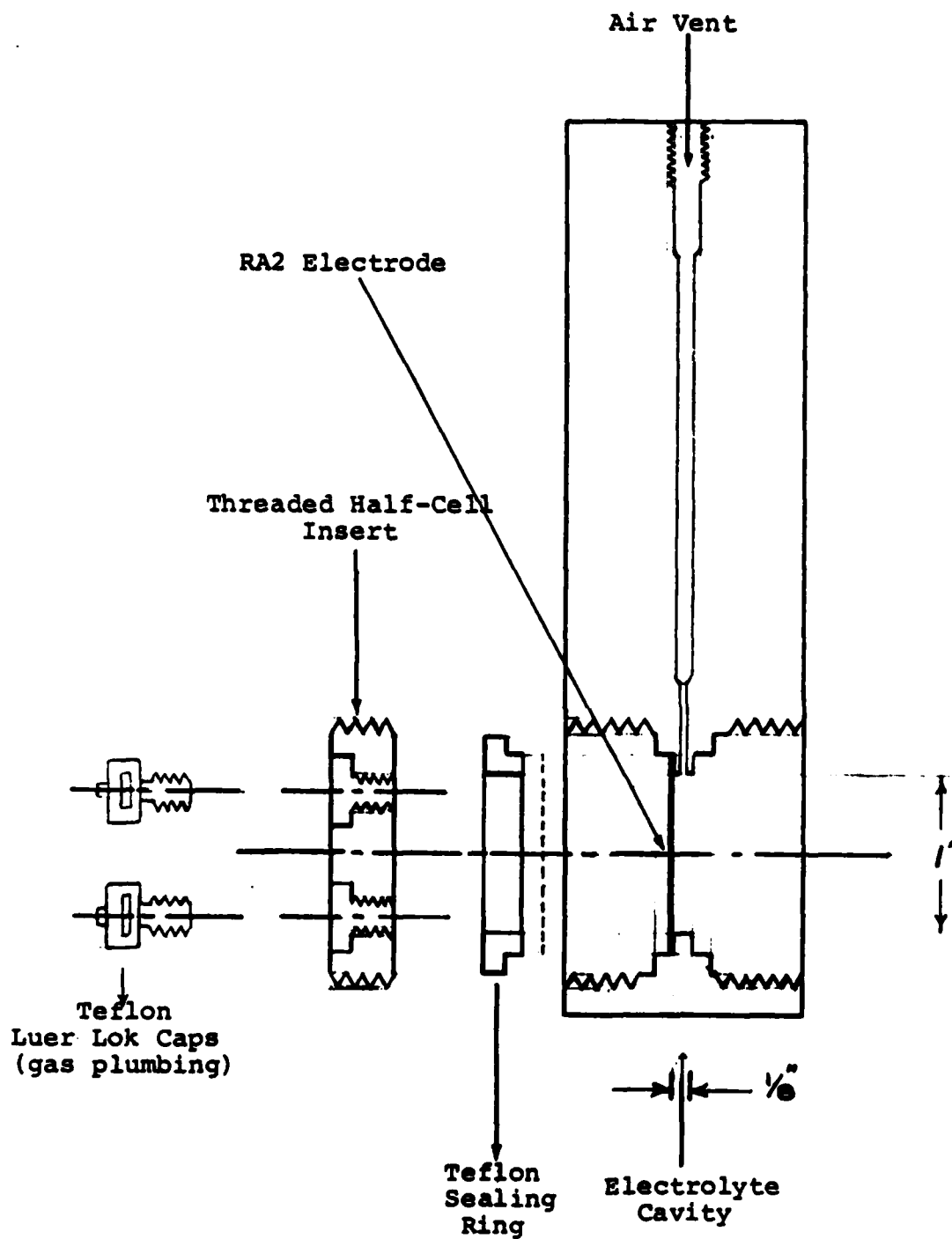


Figure 4

cell mode.

The reference electrode used in the SVFC is a dynamic hydrogen electrode and consisted of a 0.02" thick platinum wire ring anode (located at position A in the reference electrode well), and a 1 cm² platinum cathode (the DHE) suspended in the electrolyte at the bottom of the cell.

As in the case of the ECO half-cell apparatus, temperature regulation is accomplished by placing the entire SVFC into the Glas-Col heat mantle, and maintaining the desired temperature using an Electro-Flex Model 5000R heat controller.

2.4 Electronic Apparatus and Gas Systems

An ECO Model 552 potentiostat is employed to obtain the IR free Tafel slope data. This potentiostat has a built-in IR compensation circuit, which enables the experimenter to overcome ohmic drop across the cell. During steady state periods, the cell voltages are maintained to $\pm 0.001V$ by a Heathkit Model 1P-18 power supply.

The hydrogen, oxygen and nitrogen used are 99.995% purity and are obtained from Med-Tech Gases (Medford, MA). All plumbing is either copper, brass, or Teflon. Gases are normally used without humidification.

3.0 Commercially Available Electrolytes

The data and recommendations found in the work of ERC⁴, Argonne National Laboratory⁵, and the American University⁶ and EIC⁷ were carefully reviewed. This work spans more than eight years and appears to cover every important commercially available electrolyte. All appear to lack at least one critical property.

ECO selected and tested four commercially available electrolytes to learn first-hand the problems associated with sulfonic acids and perfluorinated carboxylic acids. These acids do not have sufficient physical and/or chemical stability at 180°C to merit further study.

3.1 Phosphoric Acid

The performance of each candidate electrolyte is compared with phosphoric acid under the same conditions. Figure 5 illustrates the IR free performance of Mallinckrodt 85% phosphoric acid at various temperatures in the ECO small volume fuel cell. The reversibility of the hydrogen electrode and the oxygen Tafel slope of about 120mV/decade together demonstrate that the ECO fuel cell is working properly. Dry gases are used throughout the tests.

At higher temperatures, the phosphoric acid "dries out" and cell decay is quite rapid. Figure 6 illustrates this effect. This limits phosphoric acid to lower temperatures or to pressurized humidified gases.

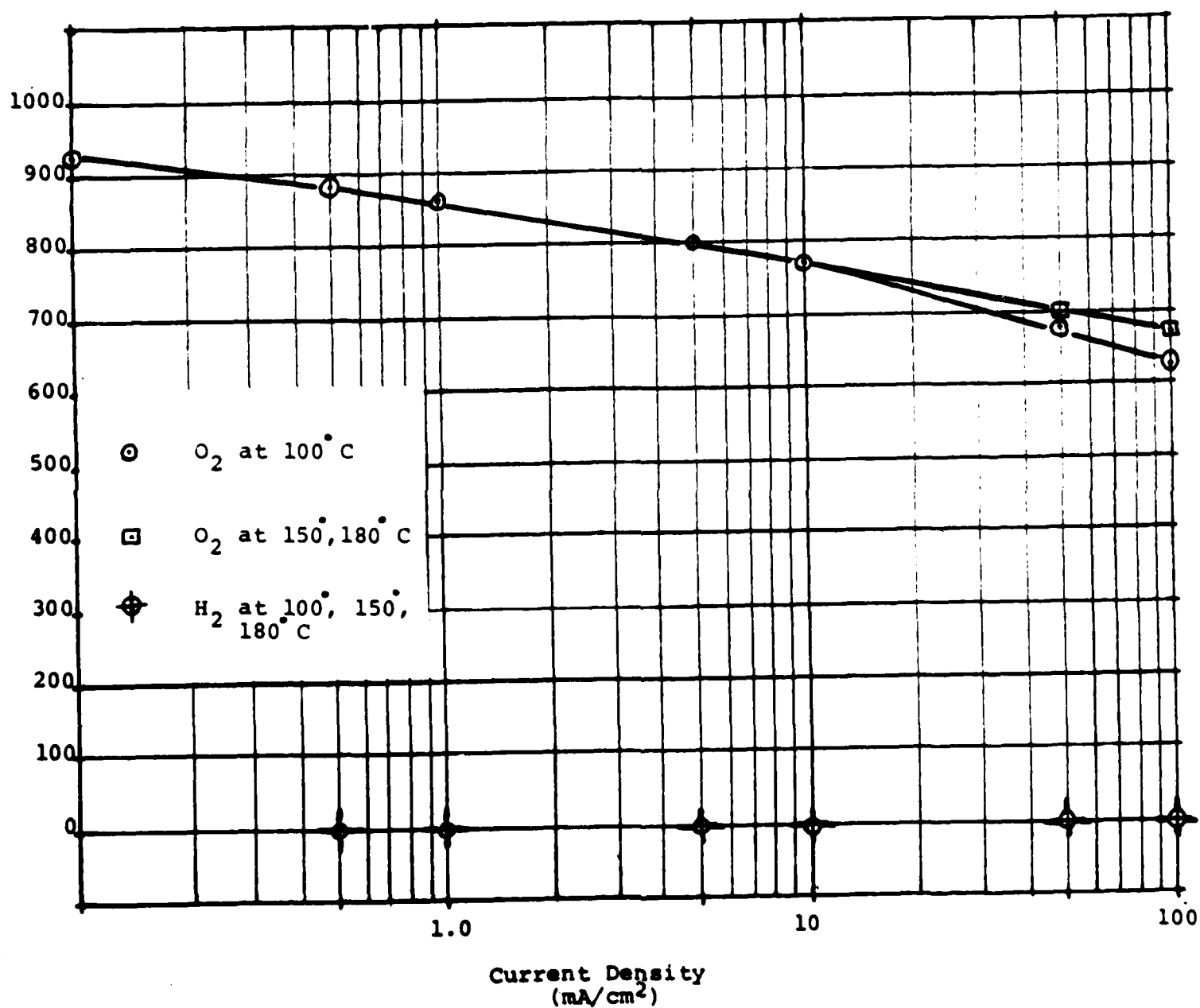
Potential (mV)
vs. HREFuel Cell Performance of
Mallinckrodt 85% H_3PO_4 

FIGURE 5

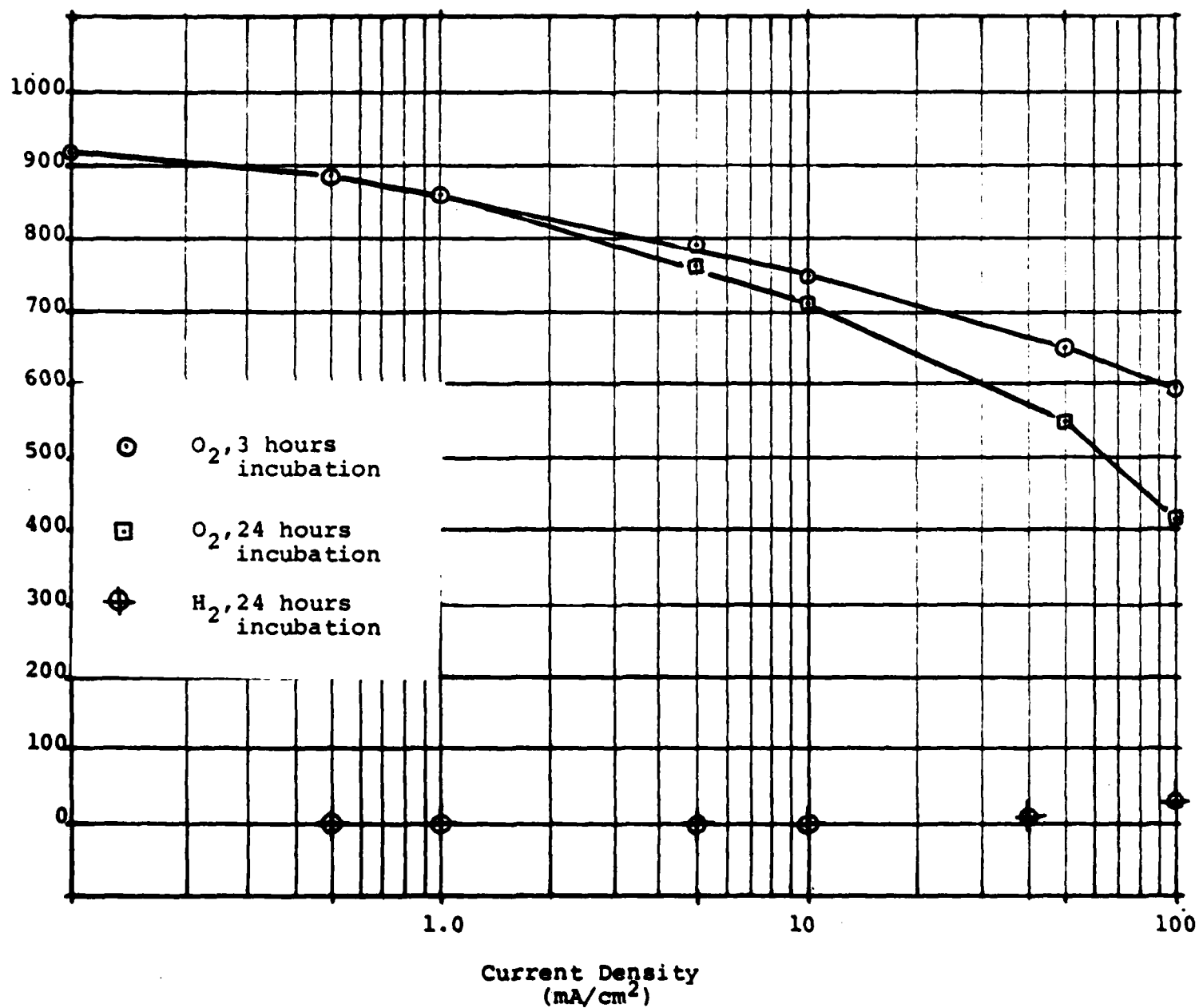
Potential (mV)
vs. HREFuel Cell Performance of
Mallinckrodt 85% H_3PO_4 at 200°C 

FIGURE 6

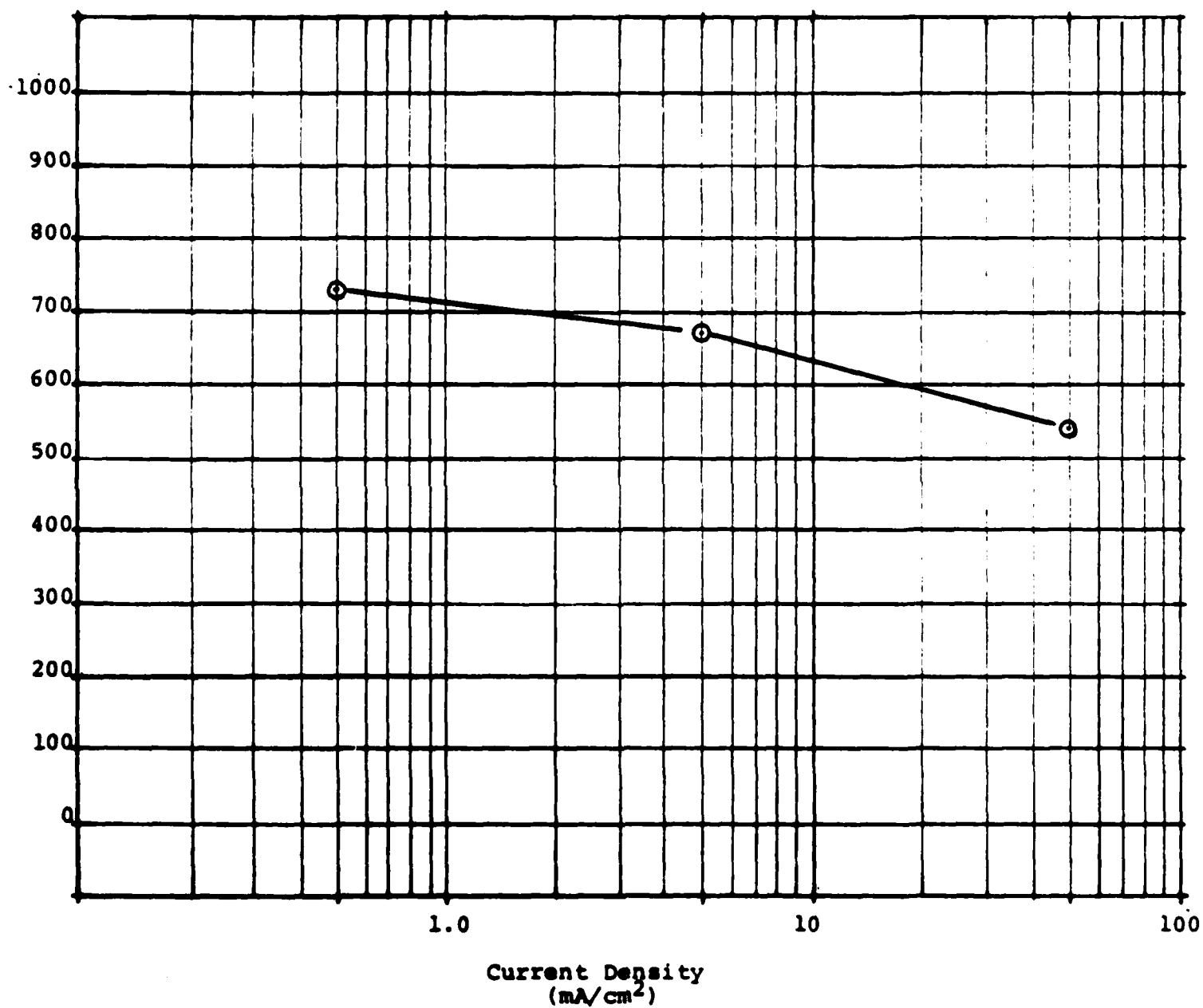
3.2 Aliphatic Sulfonic Acids

Aliphatic sulfonic acids are, in general, inert towards strong oxidizing agents. They are very stable to heat, acid, and alkali. Yet, methionic acid, (or methane-disulfonic acid $\text{CH}_2(\text{SO}_3\text{H})_2$) was investigated by ERC⁴ in fuel cells and was a terrible electrolyte. ERC observed "desulfonation" at 130°C.

Since ECO is synthesizing $\text{CF}_2(\text{SO}_3\text{H})_2$, and since "desulfonation" is apparently⁸ not a problem¹ with $\text{CF}_3(\text{SO}_3\text{H})$, ECO investigated the behavior of $\text{CH}_2(\text{SO}_3\text{H})_2$ in half cells.

The oxygen half-cell performance of methanedisulfonic acid at 100°C is shown in Figure 7. The electrolyte in the oxygen half-cell appeared unchanged. The performance was steady and there were no indications of chemical decomposition except at the dynamic hydrogen reference electrode.

This experiment was repeated with a hydrogen half-cell. No meaningful performance curve resulted. The electrolyte rapidly darkened and there was a noticeable odor of H_2S . A yellow colored crystalline material formed around the cooler edges of the quartz test cell. This material was collected and found to be insoluble in methanol, to be quite soluble in CS_2 , and to contain no acidic protons. This suggests that methanedisulfonic acid at 100°C is easily reduced at a platinum/hydrogen anode.

Potential (mV)
vs. HREOxygen Half Cell Performance of
Methanedisulfonic Acid at 100° CFIGURE 7

Unsubstituted aliphatic sulfonic acids are, therefore, unsuitable as fuel cell electrolytes. Presumably, substitution of fluorine protects the SO_3H group in $\text{CF}_3(\text{SO}_3\text{H})$. Future work will determine the degree of protection in $\text{CF}_2(\text{SO}_3\text{H})$ at the platinum/hydrogen anode.

3.3 Substituted Aliphatic Sulfonic Acids

Substitutions in the hydrocarbon chain can increase the stability of aliphatic sulfonic acids. Sulfoacetic and dl-10-camphorsulfonic acids were tested and found to decompose thermally.

Sulfoacetic acid thermally decomposes at 180°C apparently due to decarboxylation. This is substantially below the 245°C reported by previous workers.⁶

dl-10-camphorsulfonic acid decomposes at its melting point of 193°C .

With the possible exception of fluorinated substituted aliphatic sulfonic acids, substituted aliphatic sulfonic acids are unsuitable as fuel cell electrolytes. The promise of the perfluoroalkane sulfonic acids was recognized³ in 1974.

3.4 Perfluorinated Carboxylic Acids

Perfluorinated carboxylic acids have been suggested⁵ as interesting electrolytes. A typical member of this family, pentadecafluorooctanoic acid, boils at $187\text{--}189^\circ\text{C}$ and melts at 53°C .

However, after incubating pentadecafluorooctanoic acid at 55°C for 16 hours, roughly one quarter of the acid had evaporated. This reflects a very high vapor pressure at the melting point.

It is likely that high vapor pressure will make perfluorinated carboxylic acids unacceptable long before thermal decarboxylation takes place.

4.0 Syntheses of New Electrolytes

The program objective requires an electrolyte with eight very specific properties. ECO's approach is to synthesize compounds which can have these properties, rather than to select compounds primarily because they are commercially available.

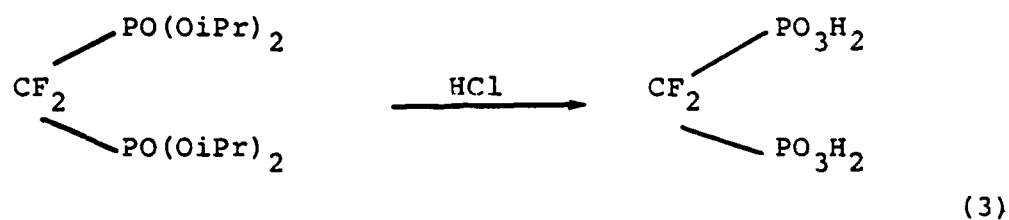
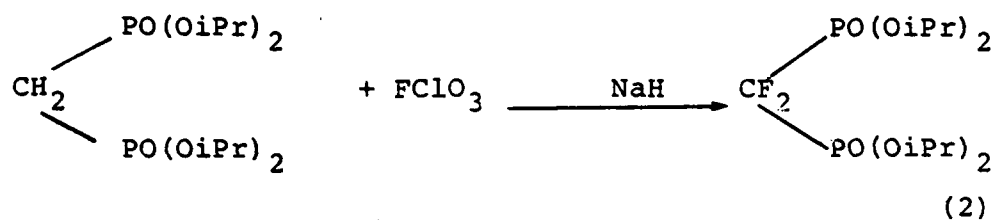
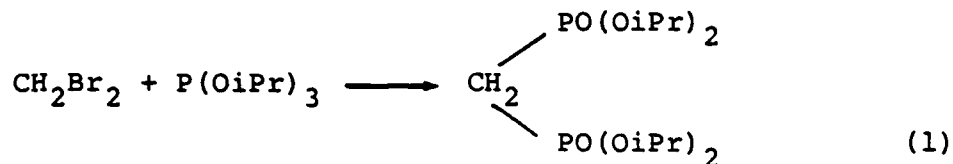
For chemical stability and electrochemical activity⁹, the electrolyte must have no carbon-hydrogen bonds. So as not to wet Teflon, the oxygen to fluorine ratio should be greater than one. The electrolyte must have a very low vapor pressure at 200°C and should be made by a short high-yield synthesis from inexpensive starting materials.

These conditions can all be met with perfluorocarbon bis-acids. Since the thermal stability of fluorosulfonic and fluorophosphonic acids are known to be high and usually exceeds 200°C, these are good groups to consider.

There are numerous possible acids. However, dissymmetry always means extra synthetic steps and the greater the number of fluorine atoms per molecule, the higher the cost. Hence, difluoromethane disulfonic acid (DFMDSA) and difluoromethane diphosphonic acid (DFMDPA) were selected for synthesis.

4.1 Synthesis of Difluoromethane diphosphonic Acid

Difluoromethane diphosphonic acid (DFMDPA) was synthesized by a route developed for the Energy Power Research Institute (EPRI) under contract RP 1676-1-1. This three step route can be represented as :



The second step, the fluorination of tetraisopropylmethylene diphosphonate, can be hazardous and should be approached with caution.

The major impurity generated during the synthesis of DFMDPA is formed during the fluorination, by isopropylation of the methylene backbone, via $\text{S}_\text{N}2$ substitution. This route normally produces 70% DFMDPA and 30% monofluoroisopropylmethane bisphosphonate.

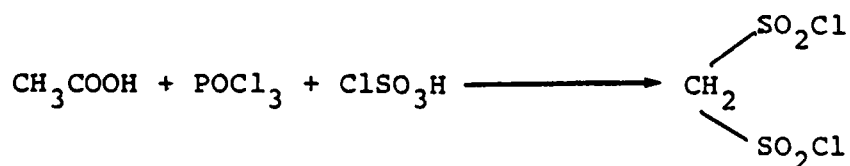
A portion of the tetrasodium salt of the impure DFMDPA has been sent out for toxicological testing. DFMDPA is a potentially toxic material due to its similarity to pyrophosphate.

To improve the purity of the DFMDPA, ECO has taken two approaches. Forming a trimethyl silyl tetraester instead of the isopropyl tetraester fails because the trimethyl silyl tetraester is unstable. Replacing sodium hydride with potassium hydride in the fluorination reaction raises the purity to 90% DFMDPA. However, while the potassium hydride is a strong reducing agent for the perchloryl fluoride, it is pyrophoric in the presence of FClO_3 and several explosions have recently resulted.

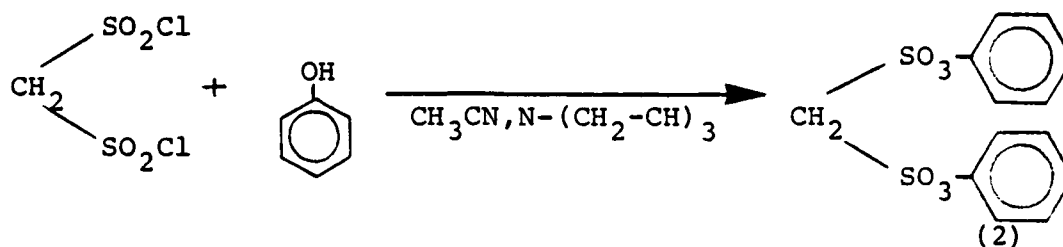
The present plan is to use sodium hydride which will be surface activated by running the reaction in an ultrasonic bath. Sodium hydride, stirred with tetraisopropyl ester of DFMDPA, at room temperature, gives 1 equivalent of H_2 gas. If ECO could run the fluorination at low temperature (0°C), isopropylation could possibly be eliminated. However, sodium hydride does not metallate well at low temperature; therefore, surface activation is required.

4.2 Synthesis of Difluoromethane disulfonic Acid

The synthesis route for difluoromethane disulfonic acid is:



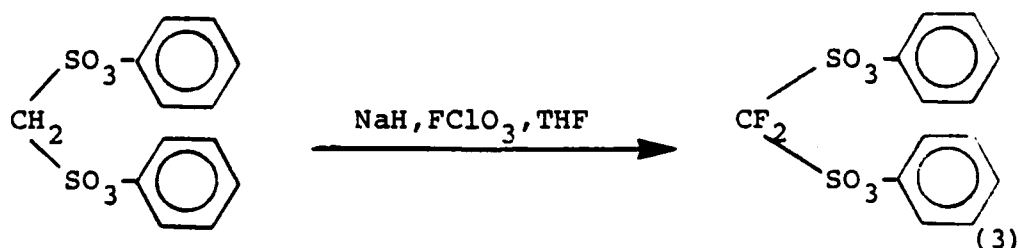
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ECO has developed this route which prepares diphenylmethane disulfonate. This differs from EIC's route⁷ by the utilization of acetic acid, instead of methylene bromide, as a starting material.

ECO's route permits the production of the bis sulfonyl chloride in one step (as opposed to the two steps required by the EIC route). ECO's preparation of crystalline methane bis sulfonyl bis phenol ester from bis sulfonyl chloride is also a unique procedure which requires inexpensive triethylamine as an organic soluble base.

The next step, the fluorination step, can be hazardous. ECO experienced a severe detonation when using potassium hydride instead of sodium hydride. The hydrogen-fluorine exchange is achieved in one step:



This ester strongly resists hydrolysis. Attempts to convert the ester to the free acid with acetic, hydrochloric, and nitric acids have failed. Our current procedure involves the ozonization of the two aromatic rings, followed by the hydrolysis of the resulting mixed anhydride in HCl/ethanol/H₂O mixtures.

5.0 Preliminary Test Results on DFMDPA

The following measurements were made on 70% DFMDPA, 30% monofluoroisopropyl bisphosphonate.

5.1 Contact Angle Measurements

DFMDPA does not wet Teflon.

The contact angle for the untreated 70% DFMDPA was determined to be 96.0° . The contact angle for Mallinckrodt 85% orthophosphoric acid was determined under identical conditions to be 114.0° .

Contact angle measurements were performed on 70% pure DFMDPA at room temperature, atmospheric pressure, with no provisions made for humidifying the electrolyte. A Gaertner M101 telescope with an M205 protractor eyepiece was used to make the contact angle measurements. The DFMDPA was placed on a flat piece of 0.02" thick PTFE for the measurement. The goniometer apparatus was pre-calibrated using a variety of organic solvents, and comparing contact angle results with those of Fox and Zisman.¹⁰

5.2 Physical Stability

DFMDPA does not evaporate at 220°C . It does, however, dry out.

A small quantity of 90% pure DFMDPA was heated to 220°C in air. After 6 hours the material was cooled to room temperature. The material had changed from an amber liquid to a glass. Addition of water regenerated the original liquid.

5.3 Electrochemical Behavior

Impure DFMDPA performs poorly at the anode and well at the cathode. It is likely⁹ that organic fragments from the thermal decomposition of impurities influence anode performance.

Figure 8 compares IR free cathode performance on oxygen of DFMDPA with the performance of phosphoric acid under similar conditions.

Figure 9 compares the IR free anode performance on hydrogen of DFMDPA with the performance of phosphoric acid under similar conditions.

Tafel slopes at 150°C and 236°C appear, within experimental accuracy, to be between 95 and 110mV/decade. When one corrects for the effect of temperature, these slopes appear to be the same.

IR Free Cathode Performance on
Oxygen of Impure DFMDPA and 85% H_3PO_4

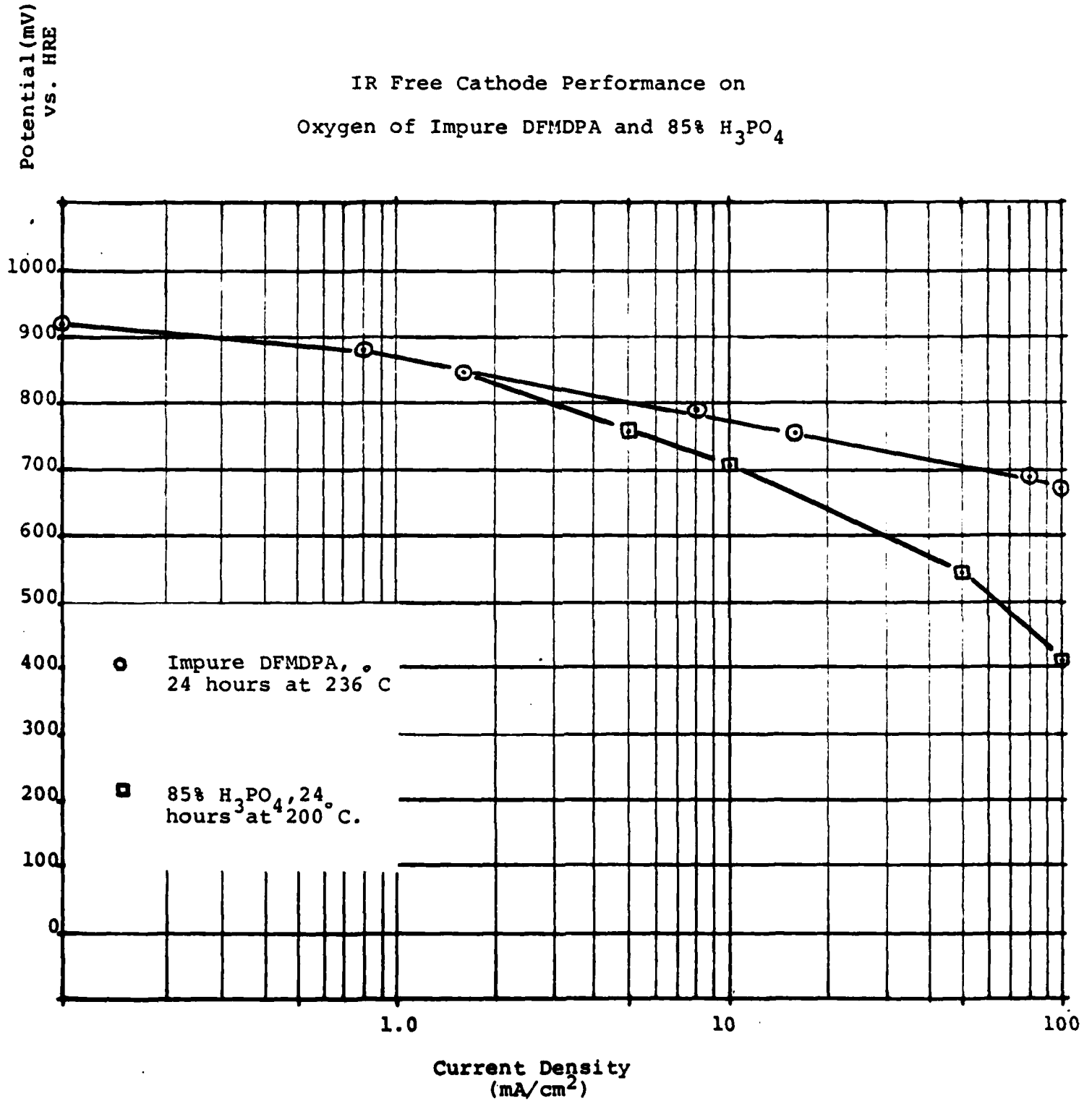
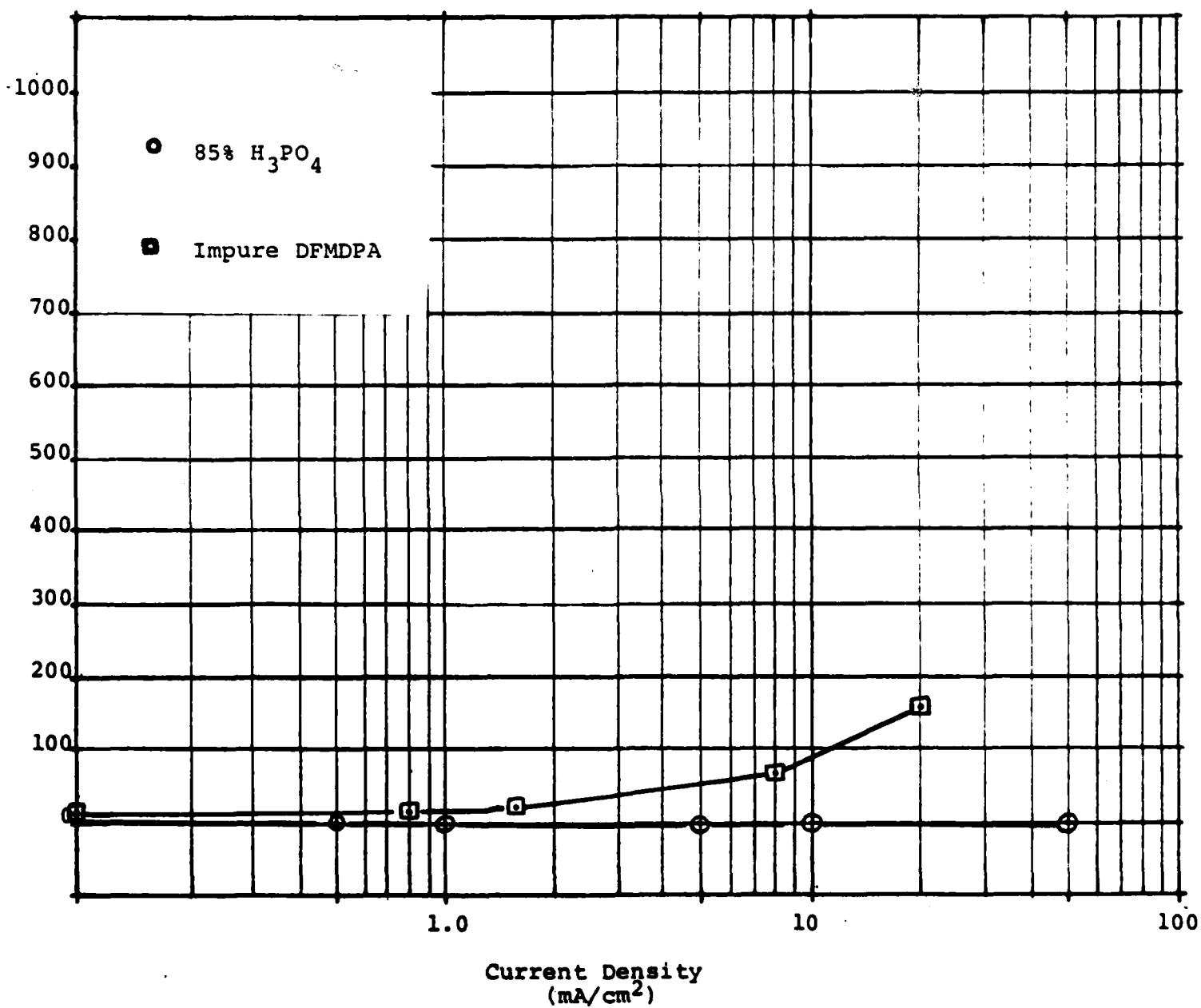


FIGURE 8

Potential (mV)
vs. HREIR Free Anode Performance on
Hydrogen of Impure DFMDPA and 85% H_3PO_4 FIGURE 9

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