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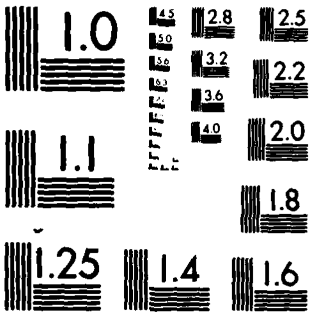

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The research was oriented toward the task of developing an improved electrolyte for the hydrocarbon-air fuel cell. A literature study of the properties of organic acids indicated that the following types of compounds warranted investigation:

1. Aromatic polycarboxylic acids,
2. Perfluoroaliphatic carboxylic acids,
3. Mono, di and poly sulfonic acids, and →

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4. Substituted sulfonic acids.

This was followed by an experimental program wherein the vapor pressure, wetting characteristics, electrical conductivity, chemical stability, and electrochemical stability of specific compounds were measured.

The following compounds (acids) were amoung those evaluated: dichloroacetic, dl-10-camphor sulfonic, heptafluorobutyric, ethanedisulfonic, sulfosalicylic, benzenesulfonic, 1,3,6-naphthalene trisulfonic, sulfosuccinic, sulfopropionic, methanedisulfonic, propanesulfonic, methanesulfonic, ethanesulfonic, and sulfoacetic. Most attention was given to the last three acids.

The electrochemical behavior of methanesulfonic acid, ethanesulfonic acid, and sulfoacetic acid as fuel cell electrolytes was studied in half cells at various temperatures. The rate of the electro-oxidation of hydrogen at 115°C was very high in methanesulfonic acid and sulfoacetic acids. The rate of the electro-oxidation of propane in methanesulfonic acid and ethanesulfonic acid at 80°C and 115°C was low. Further, there is evidence for adsorption of these acids on the platinum electrode. Sulfoacetic acid with H_2 has supported about two times higher current density than trifluoromethanesulfonic acid monohydrate. The compound can be purified by conversion to the Pb salt.

It was concluded that anhydrous sulfonic acids are not good electrolytes; water solutions are required. Sulfonic acids containing unprotected C-H bonds are adsorbed on platinum and probably decompose during electrolysis.. A completely substituted sulfonic acid, preferentially with fluorine, would be the preferred electrolyte.

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DEFINITION OF CHEMICAL AND ELECTROCHEMICAL PROPERTIES OF A FUEL CELL ELECTROLYTE

Final Technical Report

R. T. Foley

June 1980

to

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

Prepared by

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SUMMARY

The research was oriented toward the task of developing an improved electrolyte for the hydrocarbon-air fuel cell. A literature study of the properties of organic acids indicated that the following types of compounds warranted investigation :

1. Aromatic polycarboxylic acids.
2. Perfluoroaliphatic carboxylic acids.
3. Mono, di and poly sulfonic acids.
4. Substituted sulfonic acids.

This was followed by an experimental program wherein the vapor pressure, wetting characteristics, electrical conductivity, chemical stability, and electrochemical stability of specific compounds were measured.

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It was concluded that anhydrous sulfonic acids are not good electrolytes; water solutions are required. Sulfonic acids containing unprotected C-H bonds are adsorbed on platinum and probably decompose during electrolysis. A completely substituted sulfonic acid, preferentially with fluorine, would be the preferred electrolyte.

FOREWORD

This research on the chemical and electrochemical properties of fuel cell electrolytes has been sponsored by the U.S. Army Mobility Equipment Research and Development Command at Fort Belvoir, Virginia, under Contract No. DAAK-70-77-C-0080 with The American University. The work was authorized under DA Project/Task Area/Work Unit No. 1L161102AH51 PA 054 EF.

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DEFINITION OF CHEMICAL AND ELECTROCHEMICAL PROPERTIES OF A FUEL CELL ELECTROLYTE

I. Introduction - Scope of Research

Research and development performed during the last two decades has demonstrated that the fuel cell is indeed a feasible energy conversion device. A recent study (1) has described in detail the impact on the national economy of commercial applications of fuel cell power plants. Some of the same factors that bear on the employment of fuel cells by electric utilities also are pertinent to U.S. Army applications of fuel cells to vehicle propulsion and auxiliary power units. These include fuel conservation leading to energy cost savings, as well as better control of noise and emission levels. Further, fuel cells are more amenable to sizing to meet load requirements. For example, unlike some of the other methods of energy conversion, fuel cell capacity need not be installed at the ultimate required load level but rather, can be added in steps. The employment of modules to meet gradually increased demands is described in the report cited above (1). It is generally accepted now that the fuel cell offers distinct advantages for energy conversion plants of any size.

While the research and development in the fuel cell field has demonstrated the feasibility of the fuel cell as an energy conversion device there are substantial technical problems that remain. These problems are related to cost and endurance. By cost we might take a figure of $160 per kilowatt of installed powerplant manufacturing cost; for endurance, 20 years operation. Improvements must be made with respect to the present materials of construction and electrode materials such as binders and catalysts. It is obvious that directly related to the endurance of the fuel cell are the electrolyte and the corrosion rates and electrode performance that the electrolyte generates.

To improve the relative position of the fuel cell as a power generating device, two main approaches are being taken; one, the improvement of electrode catalysts, the second, the improvement of the electrolyte. These are, of course, interdependent. A specific catalyst must function and endure in a specific electrolyte.

The present research is concerned with the second approach to the problem, electrolyte improvement, and the selection of new electrolytes with better chemical, physical, and electrochemical properties than those presently used.

The evaluation of a new electrolyte is conducted in terms of a list of desired properties of a fuel cell electrolyte, namely,

a) the electrolyte should be a good ionic conductor,
b) the electrolyte should possess proper vapor pressure and viscosity characteristics,
c) the electrolyte should be a good medium for the oxidation of the fuel,
d) the electrolyte should be a good solvent for active materials and for material transport,
e) the electrolyte should be chemically and electrochemically stable over the operating temperature range,
f) the electrolyte should not be corrosive to fuel cell container materials,

g) the electrolyte should possess desirable surface tension characteristics; preferably the solution should not wet Teflon or foam excessively when gases are bubbled through the solution.

A review of electrolyte systems has been conducted and summarized in a comprehensive report, "On the Properties of a Fuel Cell Electrolyte", (21). All of the presently used systems have detrimental properties some of which are inherent in the particular system for chemical or physical reasons. Phosphoric acid, the most commonly used electrolyte for low temperature fuel cells, has several undesirable properties which seriously affects the fuel cell performance. A consideration of all the available systems, weighing advantages and disadvantages, has suggested further investigation of organic electrolytes, particularly, sulfonic acids.

Thus, the scope of the research included identifying potential new fuel cell electrolytes and evaluating them with appropriate chemical or electrochemical tests. The main emphasis has been on organic sulfonic acids.

II. Background on Sulfonic Acids as Fuel Cell Electrolytes

The initial literature search covered all the protonic organic acids. The protonic restriction was based on the desirability of finding an electrolyte suitable for the hydrocarbon-air fuel cell, i.e., a CO_2 rejecting electrolyte. Also H^+ ions are required in the stoichiometry of the electrode reactions as well as providing solutions with high conductivity.

The literature search collected data on four classes of compounds,

1. carboxylic acids--mono, di and poly, both aliphatic and aromatic
2. substituted carboxylic acids, particularly halo substituted aliphatic acids.
3. sulfonic acids--mono, di and poly, aliphatic, aromatic and bicyclic
4. substituted aliphatic sulfonic acids.

The details derived from this literature search are given in reference 3, but some general observations may be made.

In view of their chemical instability aliphatic carboxylic acids, saturated and unsaturated, were not considered as promising electrolytes. This also held for di and poly carboxylic acids.

No chlorine, bromine, or iodine substituted carboxylic acid was considered suitable. However, some fluorine substituted compounds were, based on the following guidelines for carboxylic acids,

1. The maximum number of carbon atoms in the mono or dicarboxylic acid should be 4 or 5 and the minimum number 3.
2. The compound should be completely fluorinated and there should be no unsaturation or aromatic rings.

On the basis of the foregoing perfluorobutyric, C_3F_7COOH, perfluorosuccinic, $(CF_2COOH)_2$ and perfluoroadipic, $(CF_2)_4(COOH)_2$, acids were selected for further study.

From a consideration of the literature bearing on the properties of the sulfonic acids, substituted and unsubstituted, it was decided that sulfoacetic acid, methionic acid, 1,2,3, propane sulfonic acid, and 10-camphor (dl) sulfonic acid should be tested for suitability as fuel cell electrolytes. There was an extensive background on trifluoromethanesulfonic acid and its monohydrate at this point and further examination of this compound was outside the scope of the present research. As a result of the literature search the compounds listed in Table I were considered to merit further investigation. As the investigation proceeded it became evident that more attention should be directed toward methanesulfonic acid, ethanesulfonic acid, and sulfoacetic acid.

III. Chemical and Physical Properties of Potential Electrolytes

Specific Conductance

The specific conductances of a number of these compounds or of their aqueous solutions were measured at temperatures up to 80°C. These data are assembled in Table II. It appears characteristic of the aqueous solutions of these acids to exhibit a maximum in the conductivity-composition curve and this maximum usually falls about 50% (recall similar behavior in the phosphoric acid, sulfuric acid and trifluoromethanesulfonic acid monohydrate systems(2)). In Table II the solutions with the maximum conductances are given for several of the acids. In Table III, the conductances of solutions of trifluoromethane sulfonic acid monohydrate (TFMSA·MH) are given for comparison. It is apparent that, with the exception of the chloroacetic acids, these solutions possess sufficient conductivity to make them interesting electrolytes.

Vapor Pressure

The vapor pressures of selected electrolyte solutions were measured by the isopiestic method (4-6). The method consists of equilibrating solutions of known and unknown vapor pressures in an isolated chamber for an extended period of time, during which period a good thermal contact is established between the pair. After equilibration the vapor pressures

Table I Compounds Selected for Investigation on Basis of Literature Search

Compound	Melting Point °C	Boiling Point °C	Solubility in Water
Sulfoacetic acid HO_3S-CH_2-COOH	84-6°	245d	Very soluble ∿510g/100ml
Methane sulfonic acid CH_3SO_3H (forms a mono or trihydrate)	19-20°	167°/10mm 121°/1mm decomp. over 220°	Miscible in all proportions
5-Sulfosalicylic Acid·$2H_2O$ $C_6H_3(COOH)(OH)(SO_3H)\cdot 2H_2O$	120° 180d	-----	Very soluble 145-150g/100ml at ∿ 25°C
Methane disulfonic	----	> 160 slight decomposition	Very soluble
Benzene sulfonic acid $C_6H_5SO_3H\cdot 1.5H_2O$	65-6 (anhyd.) 45-6	-----	Very soluble
Ethylene disulfonic acid $HO_3S-CH_2-CH_2-SO_3H\cdot 2H_2O$	174 (anhyd.) 111-112°	-----	Very soluble 7.4g/1ml (52°)
Propane sulfonic acid	+7.5°	136/1mm	
Sulfosuccinic acid (meso)	160°	-----	Very soluble
Sulfopropionic acid (α, dl)	100.5	-----	Very soluble
Ethanesulfonic acid	-17°	123°/1mm	Very soluble

Table II Specific Conductances of Organic Acids and Their Aqueous Solutions

Compound	Concentration (Weight Percent)	Temperature (°C)	Specific Conductance ($ohms^{-1}cm^{-1}$)
Sulfoacetic acid	18	40	0.309
	58	40	0.464
	60	80	0.398
	80	80	0.145
Methanesulfonic acid	98	40	0.019
Sulfosalicylic acid	40	80	0.498
	50	80	0.487
Heptafluorobutyric acid	43.59	40	0.2388
10-Camphorsulfonic acid (d l)	50	40	0.292
	60	80	0.266
Benzenesulfonic acid monohydrate	40	80	0.628
	50	80	0.582
Ethylenedisulfonic acid dihydrate	80	80	0.257
1,3,6-Naphthalene trisulfonic acid	40	80	0.197
	50	80	0.185
Sulfosuccinic acid	21	80	0.112
β-Sulfopropionic acid	5	80	0.114
Dichloroacetic acid	80% vol.	40	0.01883
Trichloroacetic acid	80	40	0.01856
H_3PO_4	85	40	0.1381

Table III. Conductivity of Water solutions of Trifluoromethane Sulfonic Acid Monohydrate

Concentration (weight percent)	Specific Conductance ($ohms^{-1}cm^{-1}$) 40°C	80°C
100	0.01122	0.0305
90	0.07109	0.1302
80	0.1847	0.3089
70	0.3232	0.5122
60	0.4309	0.7687
50	0.5500	0.8082
40 (0.062 mole percent)	0.5750	0.8109
30	0.5400	0.7774
20	0.3802	0.5578
10	0.2391	0.3161

of the two solutions are the same and the respective concentrations are measured. A chamber to permit such a thermal contact between two pairs of pyrex containers with a provision to close and open the individual containers without opening the chamber was designed and fabricated. The chamber was set inside a thermostated air oven during the experiment which lasted from 24 hours to a week. One of the drawbacks to the method is that the concentrations of the solutions cannot be prechosen, i.e., at a specific temperature the concentration of the unknown solution is adjusted so that the vapor pressure of this unknown solution is equal to the vapor pressure of the reference solution. Thus, the method required knowing accurately the vapor pressure of a reference solution. In this investigation phosphoric acid solutions were used as references as the vapor pressure data over a wide range of temperatures are available. Table IV presents some electrolytes at concentrations isopiestic with approximately 85% phosphoric acid at room temperature. In figure 1 the data are plotted in the conventional log vapor-pressure vs 1/T plot. The "calculated" values refer to a theoretical method of calculation using heats of vaporizations and critical constants for the compound (9).

Surface Properties

There are three surface properties or reactions of importance in the characterization of a fuel cell electrolyte:

a) the tendency of the electrolyte to wet Teflon and lower the efficiency of a Teflon-bonded catalytic electrode,

b) the tendency of the electrolyte to foam when gases are bubbled through, and

c) the tendency of the compound to adsorb on the electrode and

Table IV. Concentrations of Some Electrolytes, Isopiestic With 85% H_3PO_4 at Room Temperature

Electrolyte	Initial Concentration (weight percent)	Final Concentration			
		(1) t=24.5°C ±0.5	(2) 25.5°C ±0.5	(3) 26.5°C ±0.5	(4) 26.5°C ±0.5
Phosphoric acid	85	79.6 (5.5mm)*	82.28 (4.5)	83.10 (4.5)	80.17 (5.35)
TFMSA-Monohydrate	100	---	91.98	95.43	86.71
Perfluoro butyric acid**	100	weight loss 4.44	4.53	4.67	-----
Methane disulfonic acid	50	52.05	51.30	51.10	54.25
10-Camphor (dl) sulfonic acid	50.6	56.62	55.82	54.67	67.26
Ethane 1-2 disulfonic acid	50.85	52.73	---	52.91	58.28
Perfluoro succinic acid	50	50.03	53.64	53.36	62.27
Octafluoro adipic acid	50	57.57	55.31	54.30	63.84***

*values of vapor pressure in mm of Hg given in parenthesis under concentration of H_3PO_4. From references (7,8)

**very volatile liquid

***this may be the limit of solubility at this temperature

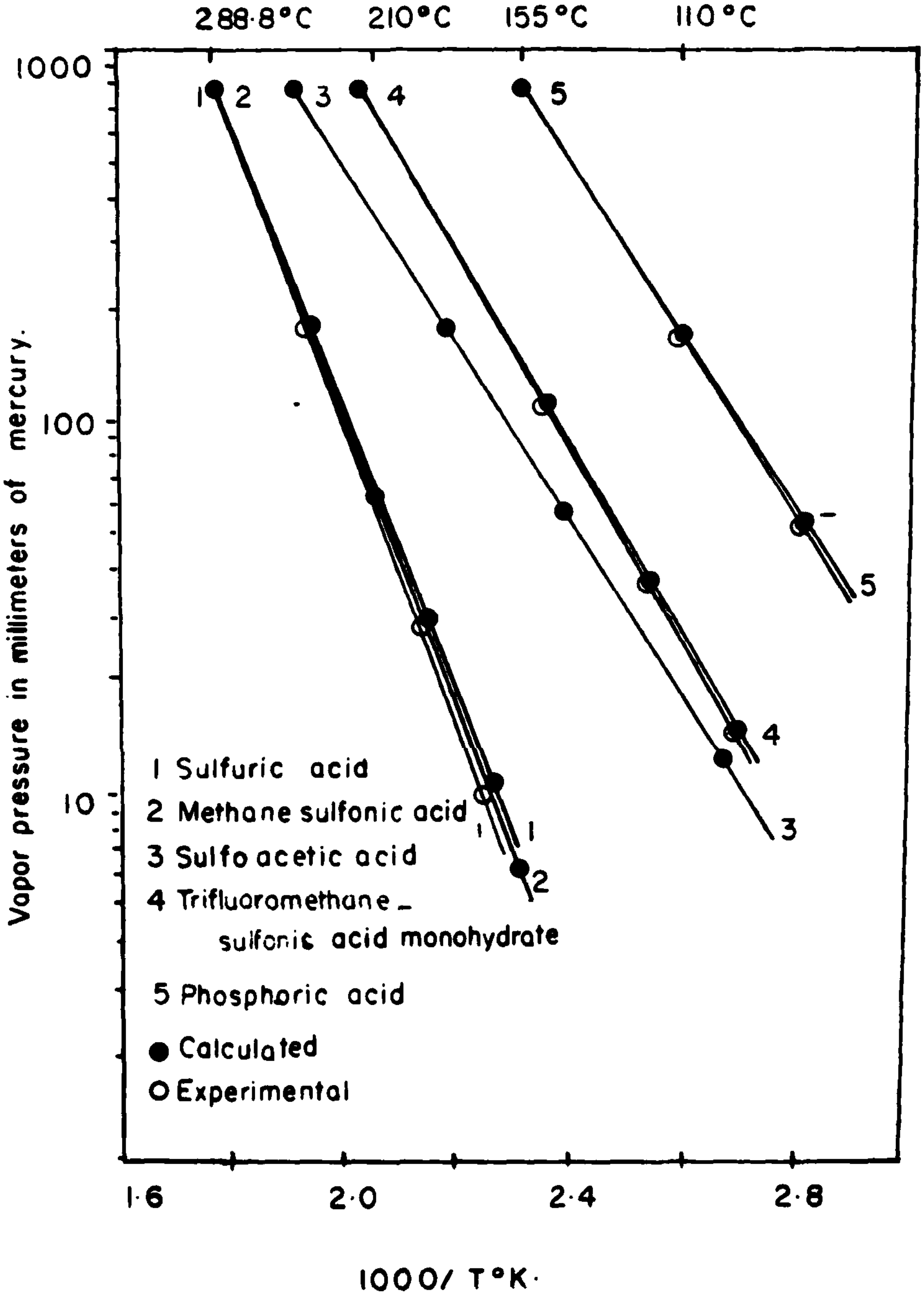

Figure 1 Vapor pressure-temperature plot for several electrolytes. Experimental and calculated compared.

compete with the oxidation or reduction of fuel cell reactants.

The third reaction will be considered below under electrochemical behavior. The second is also observed in the electrochemical experiment but in a qualitative fashion. The first reaction, the wetting of the Teflon by the compound, is amenable to direct measurement. The technique has been described in a previous report (10). In Table V are given some contact angle data for some of the electrolytes under consideration. It is noted that several of the sulfonic acids have fairly high contact angles, i.e., the compounds do not wet Teflon.

Chemical Stability

The aqueous solutions of the acids were tested qualitatively for decomposition products. They were then refluxed and, while refluxing, argon gas was passed through the solution. The argon passed then through a train consisting of silica gel to pick up water and pre-treated barium hydroxide to pick up CO_2, SO_2, or HF. The changes in weight in the absorption tubes were determined. The acidities of the solutions, before and after refluxing, were determined volumetrically. The results of some tests are given the Table VI. Solutions of sulfoacetic acid and dl-10 camphor sulfonic acid appear to be chemically stable to hydrolysis. On the other hand the aromatic sulfonic acids appear to be very susceptible to hydrolysis.

IV. Electrochemical Behavior of Potential Electrolytes

Experimental

The following types of experiments were performed:

polarization studies of argon, hydrogen and propane in the chosen

Table V Contact Angle Data for a Few Sulfonic Acids at Room Temperature on Teflon

Electrolyte	Concentration (Weight Percent)	Contact Angle (Angle in Degrees & 2 Significant Decimal Places)	Temperature (°C)
Benzenesulfonic acid monohydrate	80	72.40	25.5
Benzenesulfonic acid monohydrate	40	90.75	25.5
5-Sulfosalicylic acid	62	93.88	25
Meta-Benzene disulfonic acid	74 g/100 ml	95.21	25.5
Methanesulfonic acid	98	83.05	26
1,2-Ethanedisulfonic acid	70	99.64	25
TFMSA · monohydrate	100	72.83°	26
Trimellitic acid monopotassium salt	10	97.59°	26
dl-10 Camphor sulfonic acid	50	81.06°	26
Sulfoacetic acid	59	90.15°	26

Table VI Summary of Stability Tests on Electrolytes

Acid	Nature of test	Remarks
Dichloroacetic acid	Hydrolysis test	Very unstable in the presence of water.
Trichloroacetic acid	"	"
Dibromosuccinic acid	"	"
Heptafluorobutyric acid	Vapor pressure	Very volatile.
Perfluorooctanoic acid	Solubility	Very soapy solution (froths and foams)
2-3 Naphthalene dicarboxylic acid	Solubility	Very low solubility.
Trimellitic acid	Solubility	Sparingly soluble and hence a mono-potassium acid salt must be used.
5, Sulfosalicylic acid	An aqueous solution was tested with solution $BaCl_2$	All the aromatic sulfonic acids give a precipitate on standing at room temperature and more easily on heating.
1,5 Naphthalene disulfonic acid	"	"
1,3,6 Naphthalene trisulfonic acid	"	"
Benzenesulfonic acid	"	"
Metacarboxylic-benzenesulfonic acid	"	"

electrolytes. The apparatus including the pre-treatment of the gases as described in reference 11 was used.

cyclic voltammetry experiments with the apparatus and techniques previously described (10) and modified as follows :

1) A saturator was introduced into the argon bubbling system to compensate for water loss in aqueous solutions whenever they were used as electrolytes.
2) A lower temperature was used for the preliminary work reported here.
3) Purging with argon was continued for a longer period of time before the start of the scan, but was stopped during the voltage scan to leave the system undisturbed.
4) The rate of sweep was reduced and shorter voltage range was used.

Calibration of System

Electrochemical Behavior of Hydrogen in Trifluoromethanesulfonic Acid Monohydrate

The dynamic hydrogen electrode designed by Giner (12) was used as a reference electrode. The open circuit potential of H_2 against the D.H.E. in monohydrate was measured over a temperature range of 80° and 135°C and found to be -15.0 mV ± 10.0 mV which is considered within the limits of accuracy (12).

The polarization curves in $CF_3SO_3H \cdot H_2O$ with hydrogen and argon (figure 2) were the same as obtained previously in this laboratory (13). A cyclic voltammogram obtained with argon in $CF_3SO_3H \cdot H_2O$ at 80°C is also shown in figure 3. In this cyclic voltammogram, hydrogen desorption,

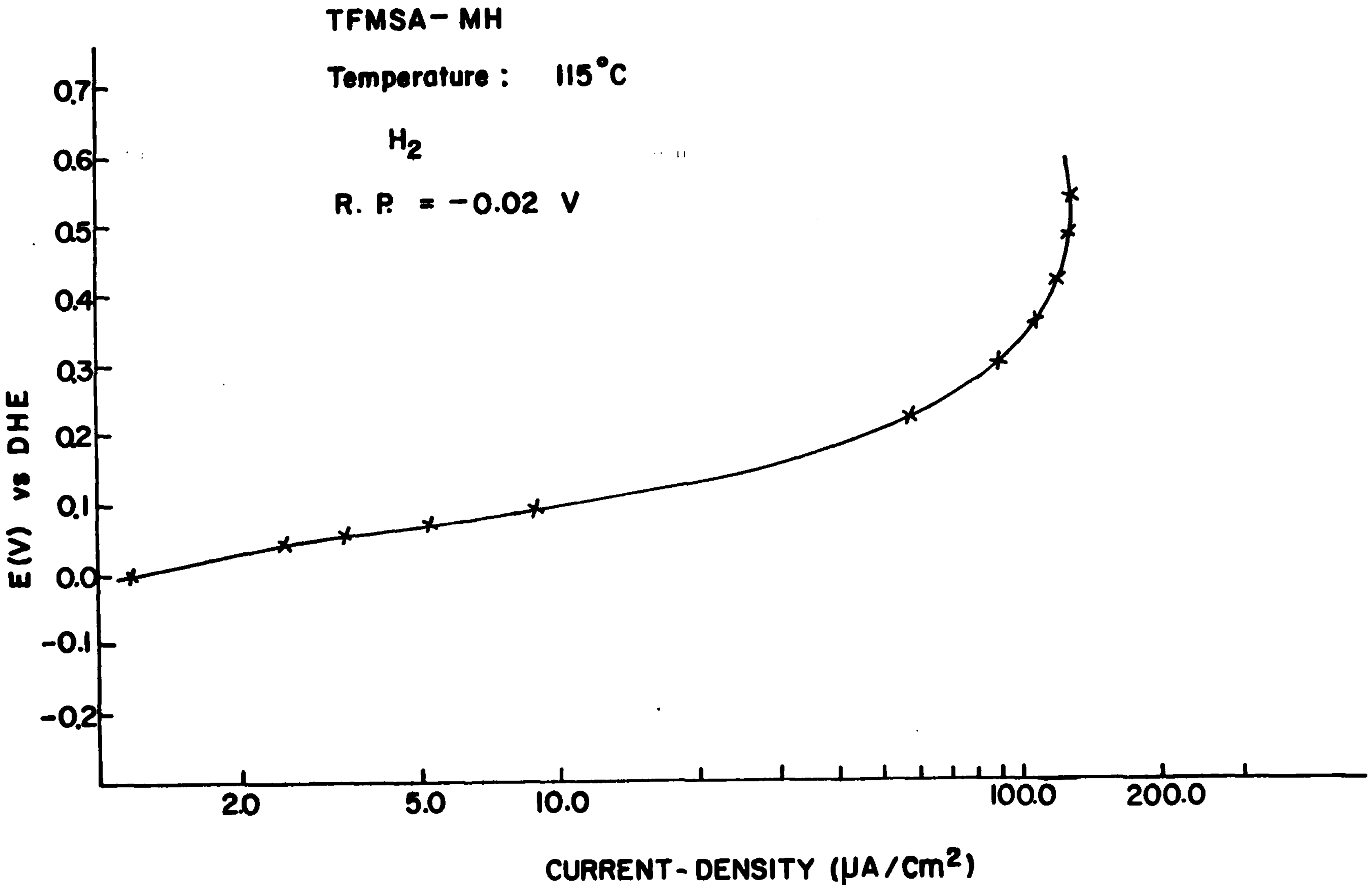

Figure 2 Polarization curve for H_2 in $CF_3SO_3H \cdot H_2O$ at 115°C

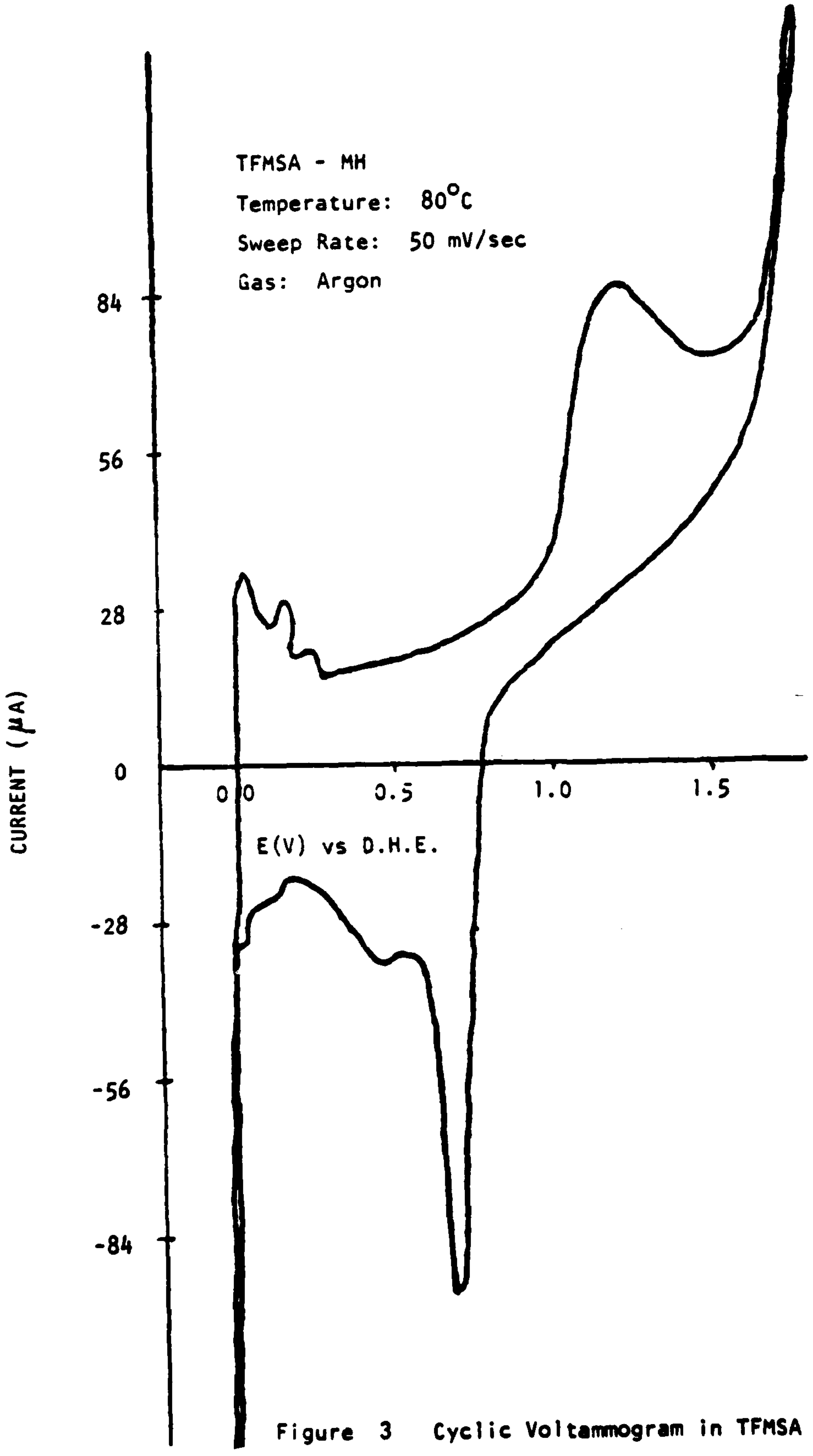

Figure 3 Cyclic Voltammogram in TFMSA - MH

double layer, oxide film formation, and oxygen evolution regions are quite visible in the positive-going portion of the sweep and reduction of oxygen film, hydrogen adsorption, and hydrogen evolution regions are visible in the negative-going portion of the sweep as expected.

Cyclic Voltammetry in Sulfuric Acid

The cyclic voltammogram obtained in sulfuric acid with argon at 55°C is shown in figure 4. This voltammogram is identical with that reported by Bold and Breiter (14).

The polarization curves and the cyclic voltammograms obtained in $CF_3SO_3H \cdot H_2O$ and H_2SO_4 with hydrogen and argon are consistent with previous work and therefore provide an indication of the system's reliability.

Dichloroacetic acid

The cyclic scan for dichloroacetic acid is given in figure 5. The solution was a 50% by volume solution with H_2O. The rest potential was 310 mV (versus DHE) and the scan rate was 50mV/sec.

Sweeping in the anodic direction a very low current was observed until about 600 mV, then the current began to increase in the positive direction. The current changed from 0 μA to 20 μA between the anodic potentials 600 mV and 1200 mV. The scan direction was reversed at 1500 mV. Then the current decreased steadily from 40 μA to 6 μA as the potential decreased by 500 mV. A slight increase in current occurred and a cathodic reduction peak was found at 375 mV with a maximum current of 8 μA. This peak is likely due to platinum oxide reduction. The dichloroacetic acid used in this experiment was vacuum distilled at 6mm from Fisher Scientific so it could be considered as a reasonably pure sample. This electrolyte and other halogenated acids were found to be easily hydrolyzed in aqueous

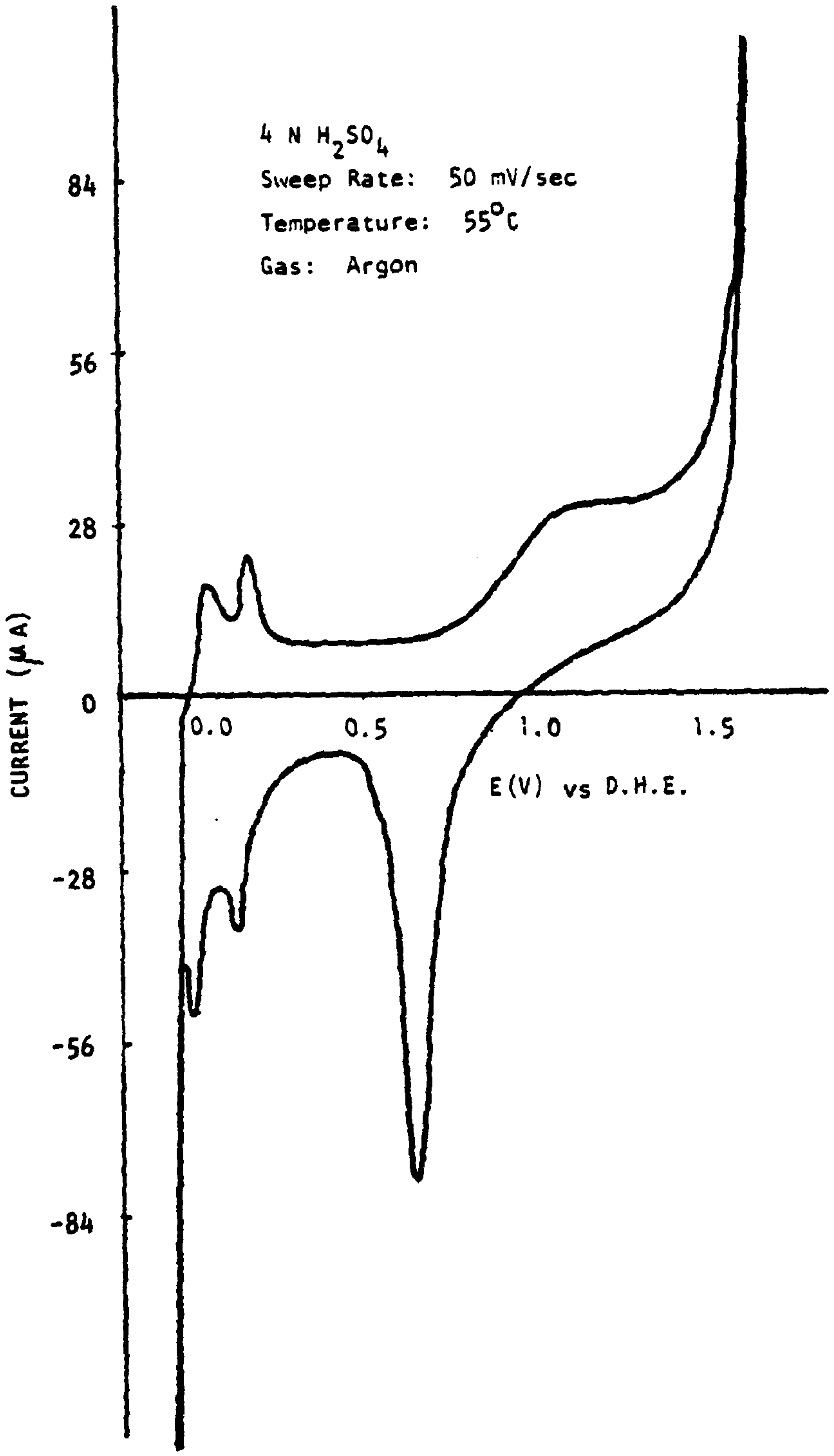

Figure 4 Cyclic Voltammogram in 4 N H_2SO_4

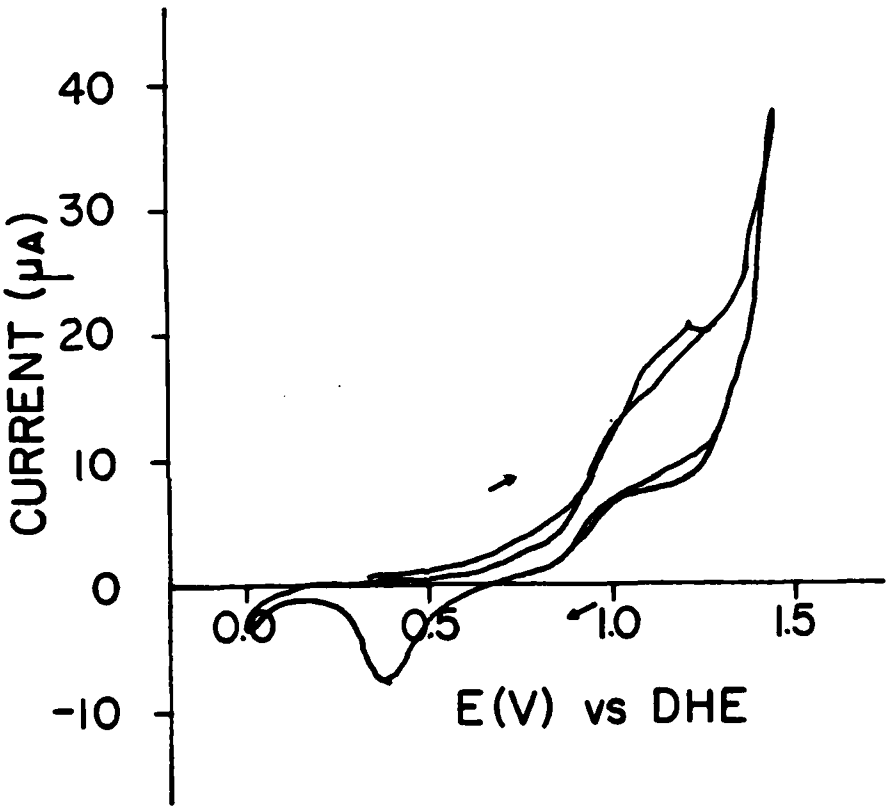

Figure 5 Cyclic voltammogram in dichloroacetic acid. Solution 50% by volume. 80°C. Scan rate, 50 mV/sec, Rest potential, 310 mv.

solution so they were not investigated further.

Camphor Sulfonic Acid

The voltage scan obtained with a solution 31% by weight of dl-10 camphor sulfonic acid is given in figure 6. This run was made at 80°C at a scan rate of 10 mV/sec. The rest potential was 360 mV. Preliminary to these experiments the system was purged for two hours with argon. Hydrogen was then used to purge the system for twenty minutes because of an unusually high rest potential (due to the presence of oxygen). Argon was used a second time to purge the system of hydrogen. Scanning in the positive direction the current increased steadily from 0 μA to 22 μA at which point the anodic potential was 1200 mV. The current then decreased slightly to 18 μA and the scan was reversed at 1500 mV. (The first scan gave a slightly higher current, 27 μA at 1300 mV.) The current increased to 1 μA where a cathodic reduction peak was observed at a potential of 725 mV. The current then dropped off to 2 μA and was nearly steady until zero potential was reached, where the current increase was due to hydrogen reduction. The reduction of current with successive sweeps indicated that some electroactive species were being removed. The reactivity of this compound does indicate its unsuitability as an electrolyte.

Heptafluorobutyric Acid

The scan obtained with a 50% solution of heptafluorobutyric acid is given in figure 7. Scanning in the positive direction the current increased slightly from 0 μA at a rest potential of 300 mV to about 5 μA at 1000 mV; at this point the current increase was much sharper to a maximum of 11 μA at 1075 mV. The scan was reversed at this point. The current decreased in a regular fashion until a maximum of 5 μA was reached

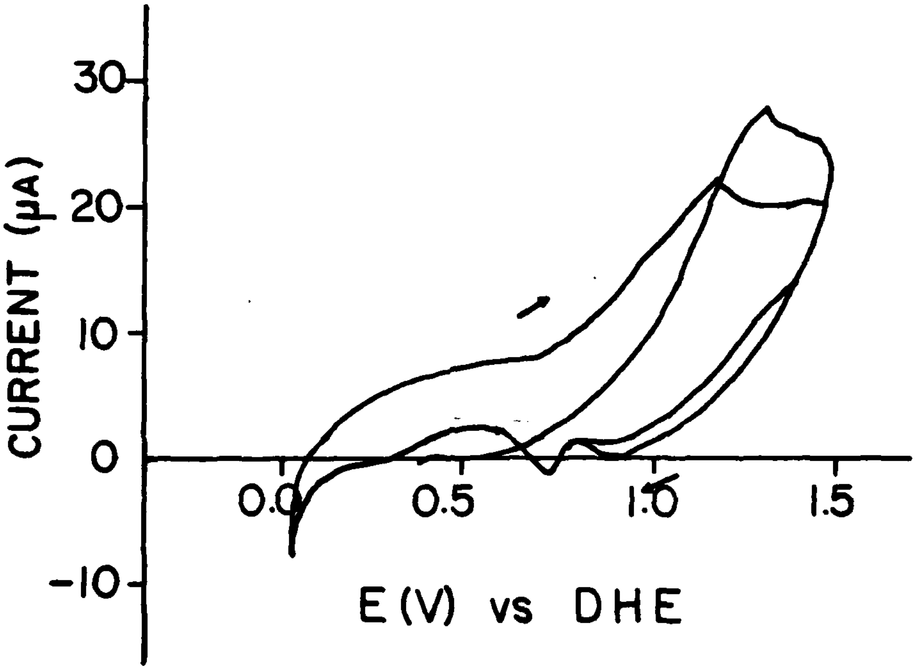

Figure 6 Cyclic voltammogram in dl-10 camphorsulfonic acid. Solution 31% by weight. 80°C. Scan rate, 10 mV/sec. Rest potential, 360 mV.

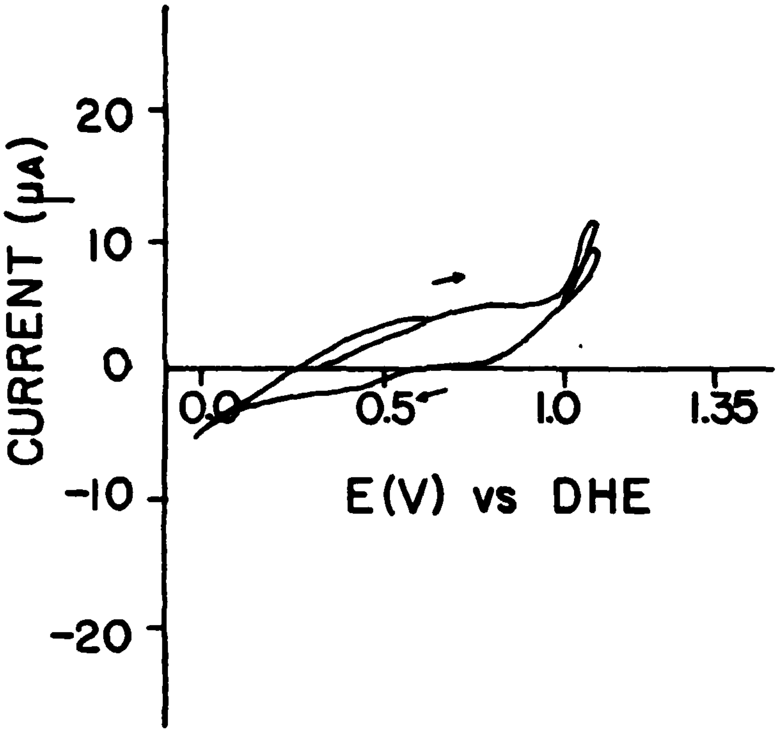

Figure 7 Cyclic voltammogram in heptafluorobutyric acid. Solution 50% by weight. 80°C. Scan rate, 50 mV/sec. Rest potential, 300 mV.

at approximate zero potential. This electrolyte appears to be reasonably stable electrochemically but its vapor pressure appears to be too high.

Ethanedisulfonic Acid

The voltage sweep with smooth platinum electrodes at a sweep rate of 25 mV/sec at 80°C in ethanedisulfonic acid is shown in Figure 8. The clear cut oxidation of hydrogen near 0 V and the oxidation maximum near 0.8 V appear to be obscured although there is an inflection at about +0.8 V (oxidation). The cathodic curve resembles what would be expected from a stable electrolyte.

Methanesulfonic Acid

The polarization curves for H_2 in CH_3SO_3H were obtained at 80° and 115°C. The run at 115°C is shown in Figure 9. There was a significant difference in the limiting current values at 80° and 115°C being approximately 5.0 $\mu a/cm^2$ and 225 $\mu a/cm^2$ respectively. The current density increases at each potential with increasing temperature. The open circuit potential was -30 mV with respect to the dynamic hydrogen electrode at 115°C. The cell voltage was also measured during the polarization to gain information regarding the resistance build-up in the system. The average of the maximum cell voltages was found to be 1.0 volt.

Also shown in Figure 9 are the current density-potential plots for the oxidation of hydrogen in $CF_3SO_3H \cdot H_2O$ as reported by Adams (13). The limiting current density was higher in CH_3SO_3H than in $CF_3SO_3H \cdot H_2O$ as well as the limiting current density was achieved in CH_3SO_3H at a slightly higher potential than in $CF_3SO_3H \cdot H_2O$. The limiting current density value in 80% CH_3SO_3H was approximately 90 $\mu a/cm^2$ higher than in $CF_3SO_3H \cdot H_2O$ at 115°C and about eleven times more than in 85% H_3PO_4 (11).

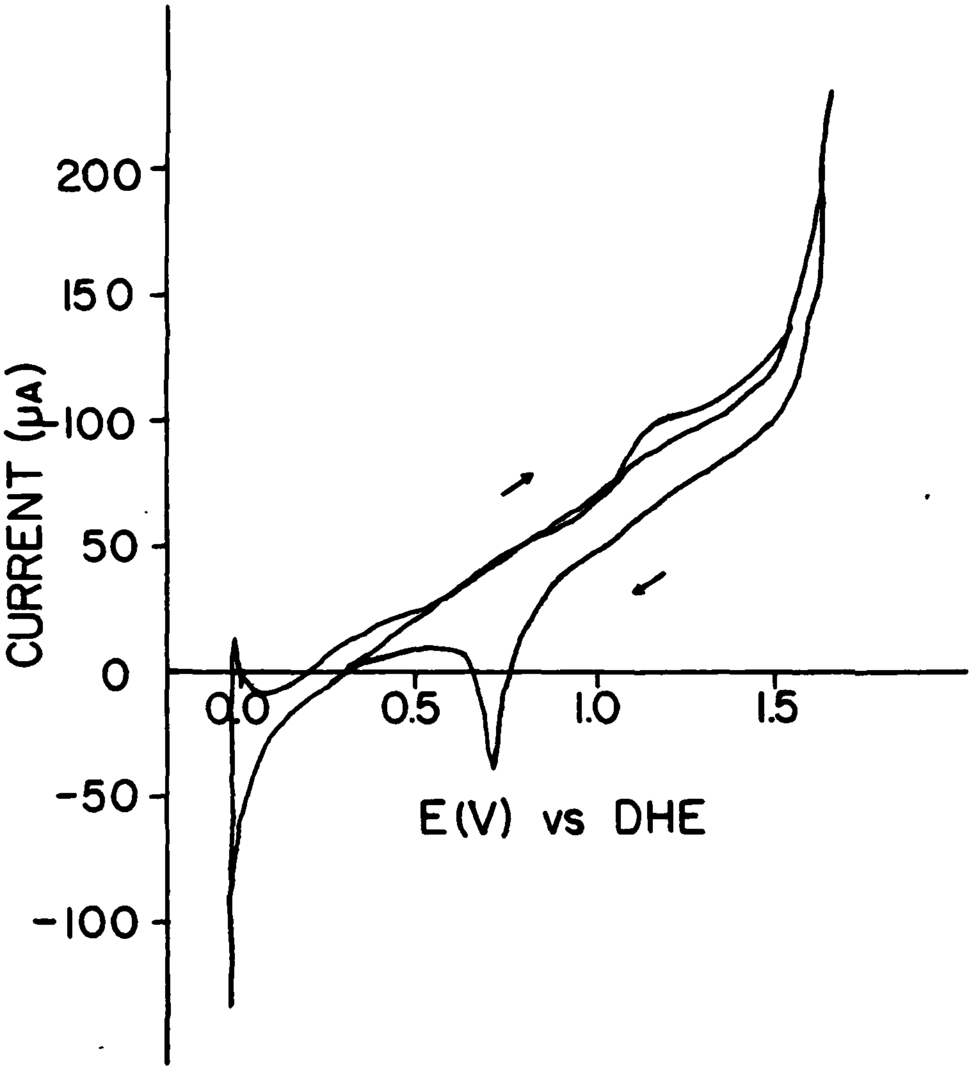

Figure 8 Cyclic voltammogram for Pt electrode in ethanedisulfonic acid. Solution 42% by weight. 98°C. Sweep rate, 25 mV/sec.

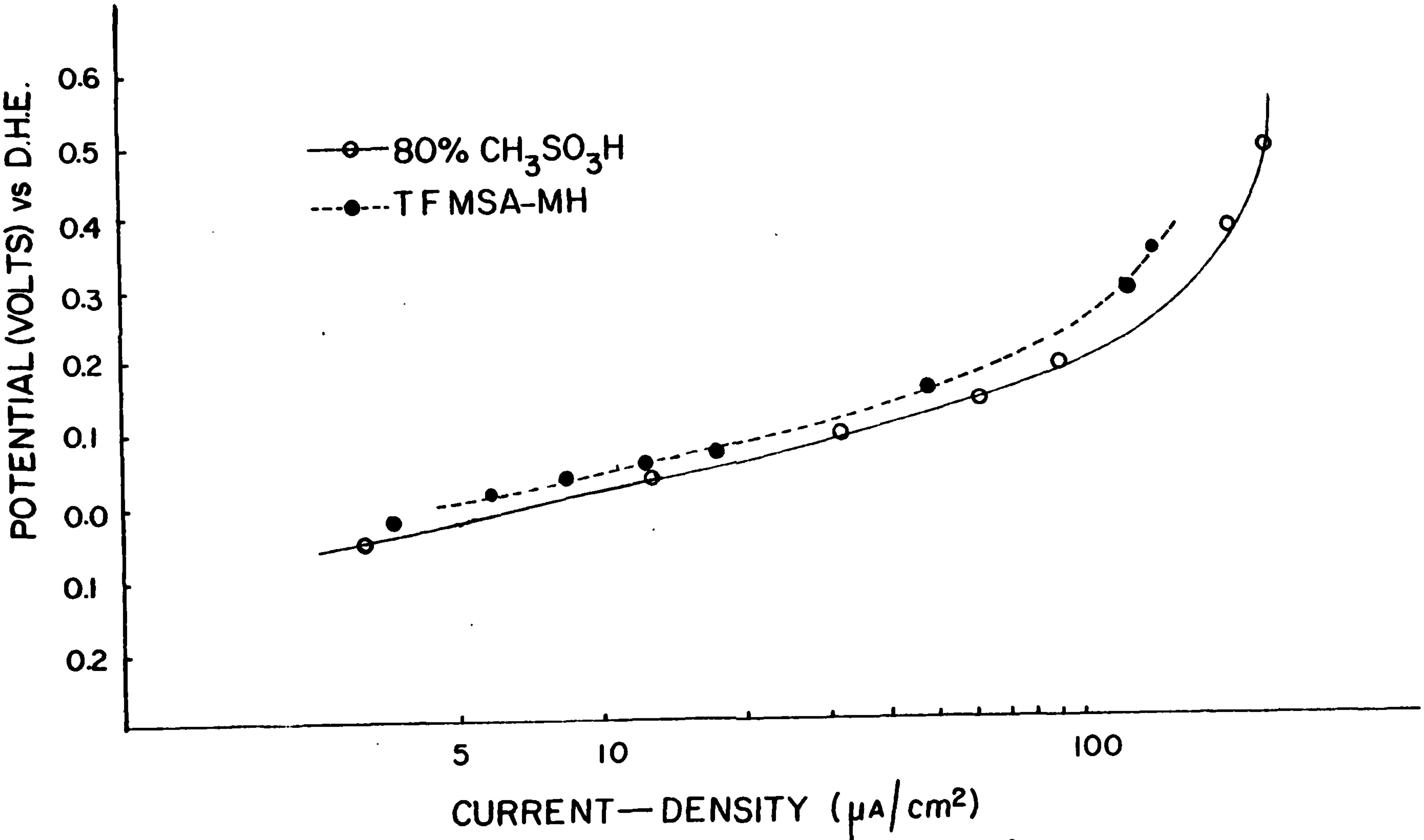

Figure 9 Polarization curves for H_2 in 80% CH_3SO_3H and TFMSA-MH at 115°C.

The polarization curves for propane in CH_3SO_3H were also run at 80° and 115°C. The 115°C experiment is shown in Figure 10. The limiting current density at 80°C was 1.7 μa/cm^2 while at 115°C 2.3 μa/cm^2. The maximum cell voltage values were 0.4 to 1.0 volt at different temperatures. The open circuit potentials with respect to the dynamic hydrogen electrode were 0.35 volt and 0.30 volt at 80°C and 115°C respectively. The limiting current density achieved in CH_3SO_3H with propane (2.3 μa/cm^2) was much less than that in $CF_3SO_3H \cdot H_2O$ (18 μa/cm^2).

The typical voltammogram obtained with argon, in methanesulfonic acid at 115°C are shown in Figure 11. Upon examining this voltammogram (in 80% CH_3SO_3H) it was apparent that the hydrogen adsorption and desorption peaks were absent. The voltammogram was highly reproducible even for a large number of cycles. The absence of hydrogen adsorption and desorption peaks in 80% CH_3SO_3H might be the effect of the following :

a) CO_2 or/and adsorption as impurities due to the decomposition of the electrolyte.

b) Other organic impurities adsorption on the electrode surface.

c) An adsorption of the electrolyte itself.

To investigate this adsorption phenomenon, the following experiment was performed.

A typical cyclic voltammogram was obtained in 4N H_2SO_4 with argon at 55°C as shown in Figure 12. This voltammogram was consistent with the previous one obtained by Bold and Breiter (14). In this current-potential curve, hydrogen, double-layer, and oxygen film regions were well-separated in the positive-goingportion of the sweep, that is, the anodic portion. The voltammogram was highly reproducible for the large number of cycles.

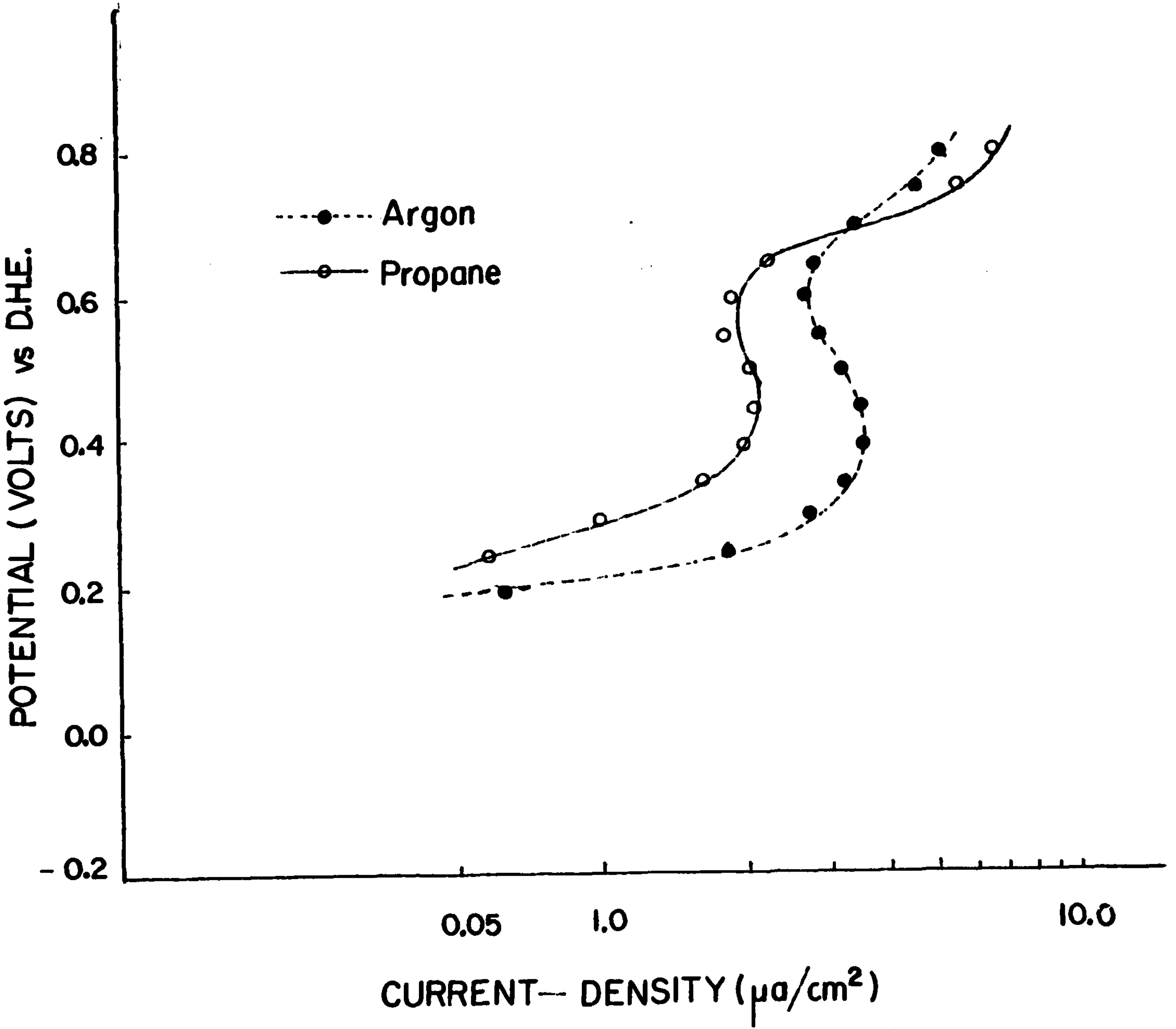

Figure 10 Polarization curve for propane in 80% CH_3SO_3H at 115°C.

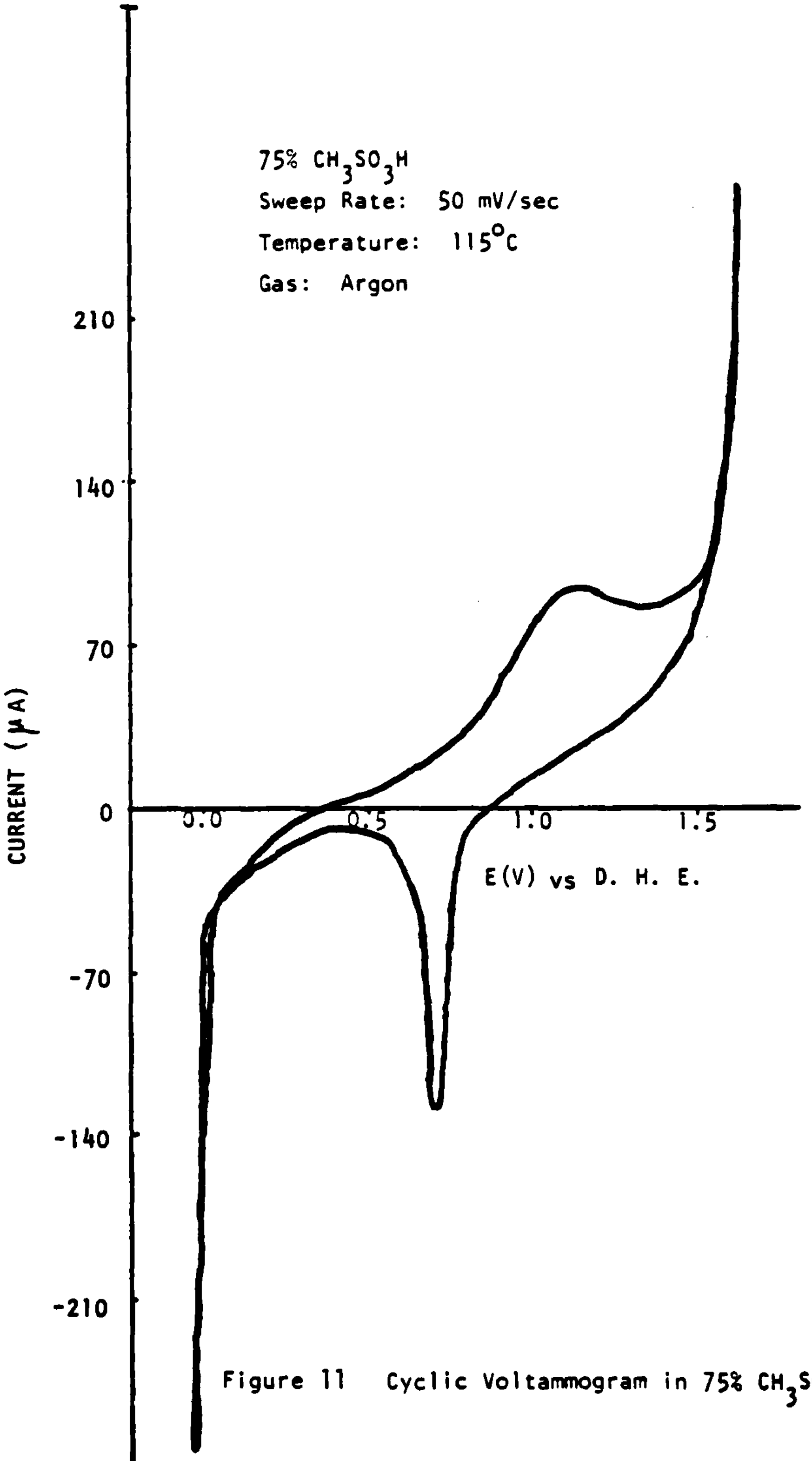

Figure 11 Cyclic Voltammogram in 75% CH_3SO_3H with Argon

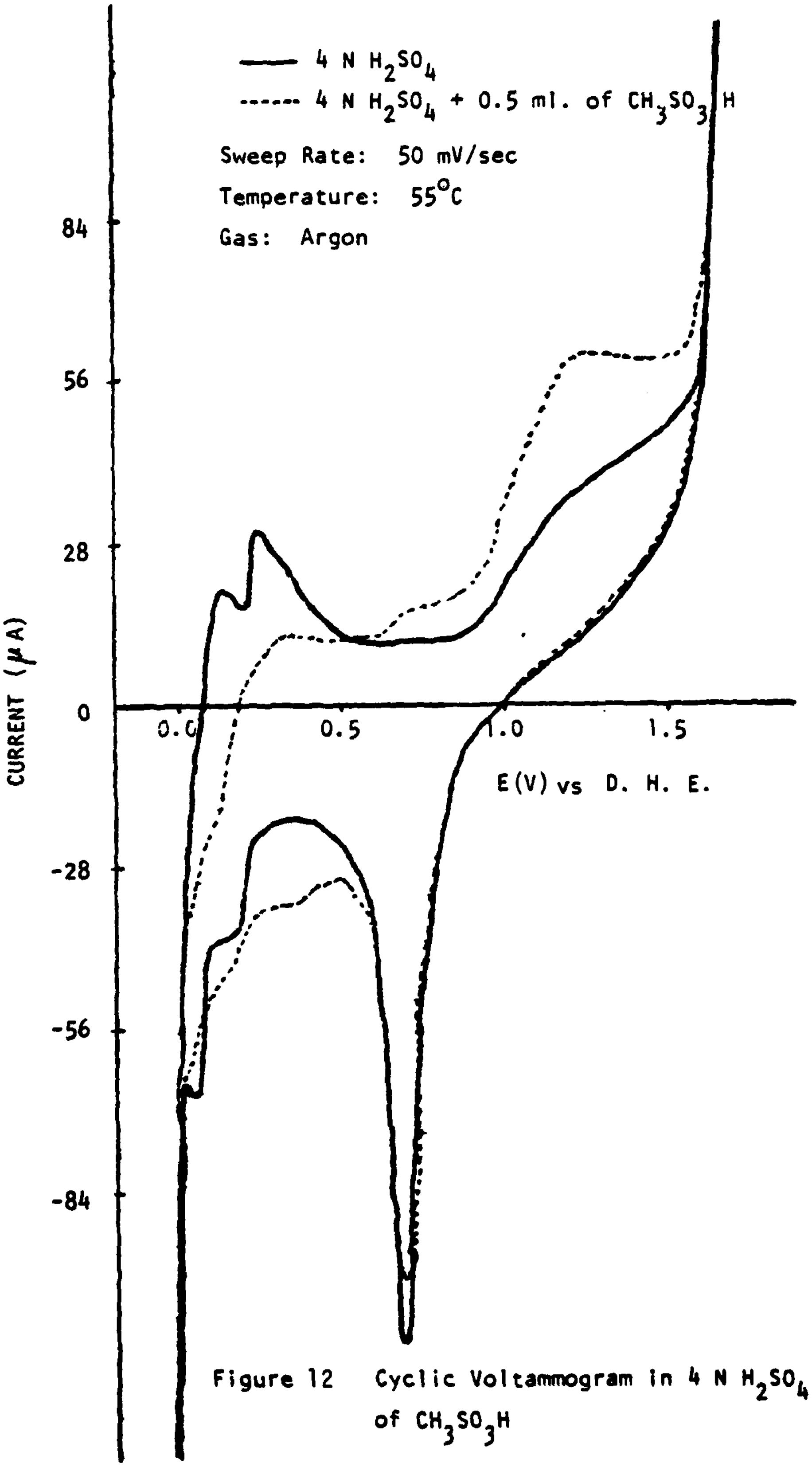

Figure 12 Cyclic Voltammogram in 4 N H_2SO_4 during the addition of CH_3SO_3H

The sweep rate was 50 mV/sec. During the scan, a few drops of highly pure double-distilled CH_3SO_3H was added through a glass syringe into the experimental cell containing 4N H_2SO_4H at 55°C. Immediately after the addition of methanesulfonic acid, the hydrogen adsorption and desorption peaks, which were very pronounced in the beginning, disappeared (Figure 12). The scanning was continued for five more cycles but the peaks were gone and the resulting voltammogram was reproducible although the anodic current for the hydrogen dissolution region was decreased and for the oxygen film region was increased compared to the original voltammogram in 4N H_2SO_4. In the cathodic portion of the display, the oxygen film reduction current was decreased and the hydrogen adsorption region current was increased.

In a separate experiment during the sweeping voltammogram with argon in 4N H_2SO_4, a few drops of trifluoromethanesulfonic acid monohydrate were added through a syringe into the experimental cell. The resultant voltammogram (Figure 13) still showed the hydrogen adsorption and desorption peaks but the peaks were not as pronounced as in the sulfuric acid solution. Even with a change of sweep rates from 50 mV/sec to 100 mV/sec, the hydrogen peaks were quite evident. In the aqueous system, there should be pronounced hydrogen adsorption and desorption peaks provided that there is no adsorption of the electrolyte itself of other impurities taking place.

The above discussion and the experimental results show that methanesulfonic acid as an electrolyte does support a high current density with hydrogen but with the probable adsorption of the acid itself on the electrode surface. A very low limiting current density obtained utilizing propane as a fuel discourages the use of methanesulfonic acid as an electrolyte in a direct hydrocarbon-air fuel cell.

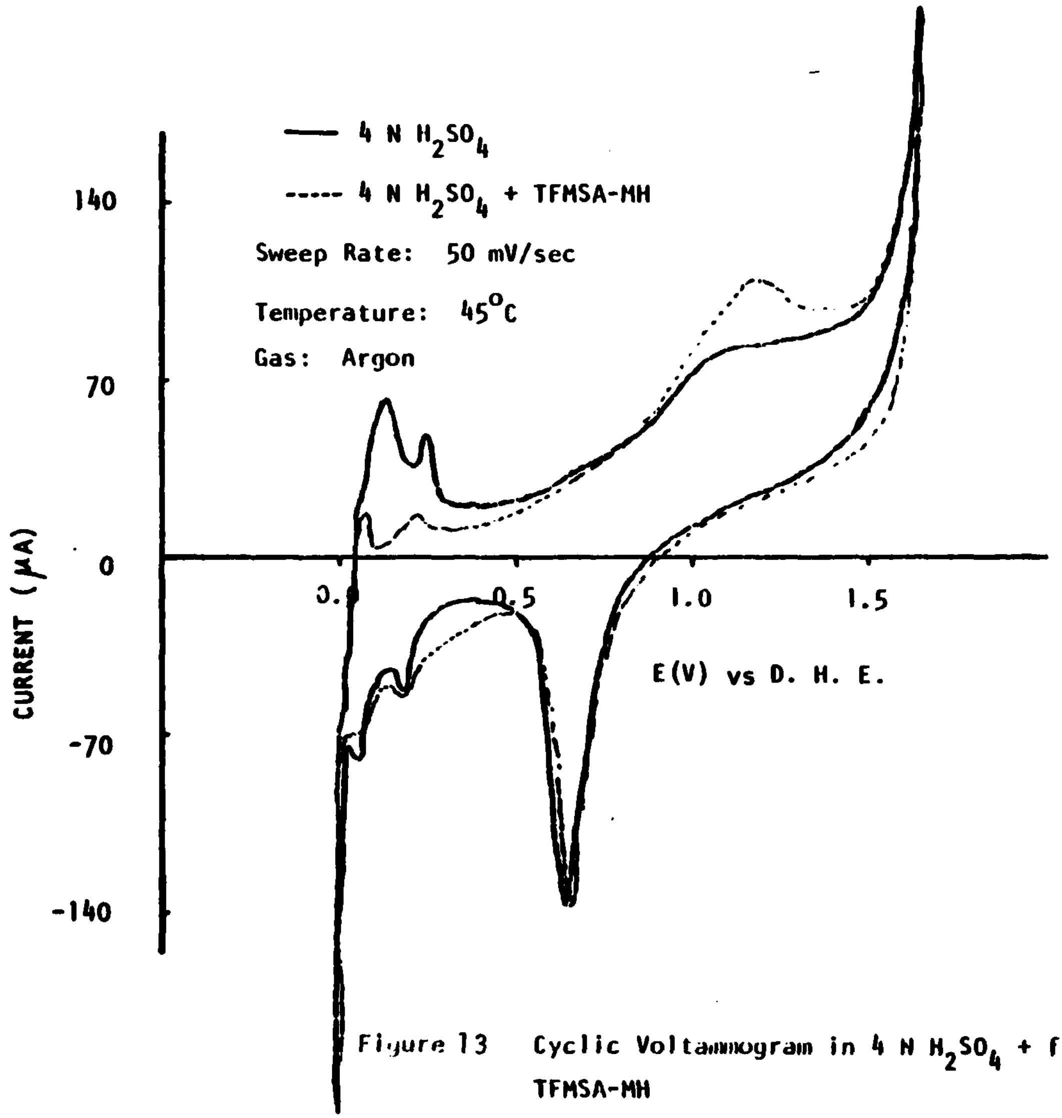

Figure 13 Cyclic Voltammogram in 4 N H_2SO_4 + few drops of TFMSA-MH

Ethanesulfonic Acid

Ethanesulfonic acid, as received, was diluted to 70% with conductivity water. Polarization curves were obtained with hydrogen, propane, and argon at 80°, 115°, and 135°C. The 115°C curves for argon and propane are shown in Figure 14. Upon examining the polarization curves, it was seen that the maximum limiting current density achieved was 9.0 $\mu a/cm^2$ using different temperatures, concentrations and fuels. The maximum limiting current density utilizing hydrogen as a fuel was 9.0 $\mu a/cm^2$ at 135°C while, with propane, 3.0 $\mu a/cm^2$ at 80°C. Thus, ethanesulfonic acid did not support high current densities either with hydrogen or with propane. Upon considering the limiting current density achieved with argon in ESA and the rest potential in the presence of hydrogen, it was obvious that some sort of adsorption was taking place on the electrode surface. The rest potential measured when hydrogen was bubbled over the platinum electrode was found to be 0.2 volt ± 30mV in ESA. Actually, it should be close to zero. Even after the pretreatment of the electrode (that is, anodically increasing and bringing the potential to 1.35 volt and cathodically going down to 0.05 volt and staying at both stages for about five minutes) and gaining the equilibrium, the rest potential was still quite high (about 0.2 volt). The limiting current was found to be about 3.5 $\mu a/cm^2$ when argon was bubbled over the platinum electrode.

The acid was then distilled under vacuum to purify. The 70% solution of distilled ESA was used for further polarization studies. The limiting current values obtained at 115°C and 135°C were almost the same as those measured prior to distilling. The cyclic voltammetric technique was used to study the adsorption of ethansulfonic acid on the platinum electrode

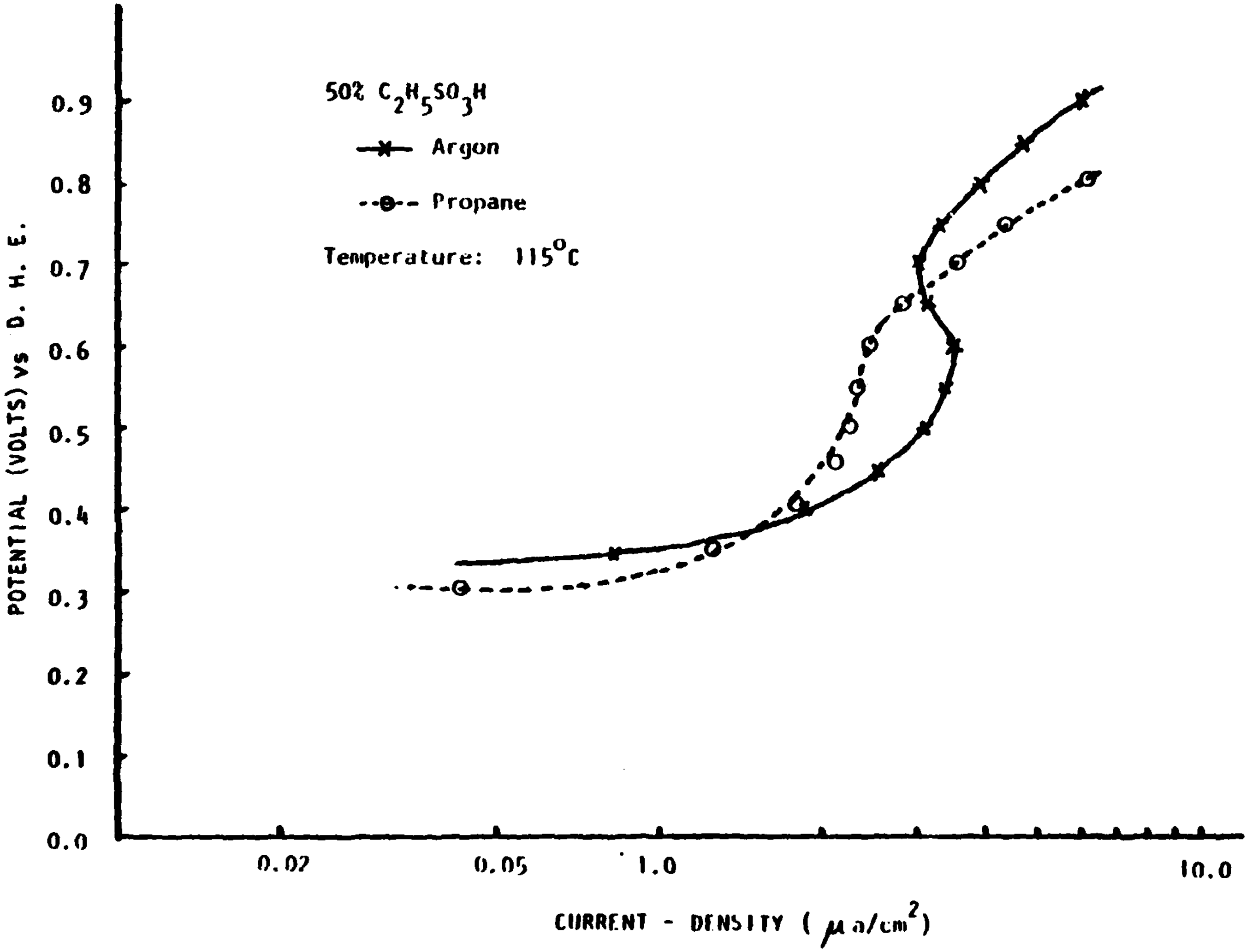

Figure 14 Polarization Curves for Argon and Propane in 50% $C_2H_5SO_3H$ at 115°C

surface. The voltammograms obtained in 50% ESA with argon at 115°C are shown in Figure 15. The voltammogram showed the following three features very clearly :

a) the irreversible process taking place on the electrode surface,
b) the absence of hydrogen adsorption and desorption peaks,
c) an indefinite double layer region.

A voltammogram with the well-separated hydrogen, double layer and oxygen film regions was obtained in 4N H_2SO_4 with argon and then a few drops of distilled ethanesulfonic acid were added to the sulfuric acid solution during the scanning. The sweep rate was 50 mV/sec. In the resulting voltammogram, the disappearance of hydrogen peaks and the increase in the anodic charge indicated that ethanesulfonic acid had been adsorbed on the electrode surface. An attempt was made without any success to observe the hydrogen peaks by increasing the sweep rates. Increasing the sweep rate definitely changed the anodic and cathodic charge values, as expected.

From measurements of the electro-oxidation of hydrogen and porpane in ethanesulfonic acid, it is obvious that this acid as an electrolyte does not support satisfactory limiting currents in the temperature range of 80° to 135°C either in the presence of hydrogen or propane. Moreover, it is adsorbed on the platinum electrode surface. Therefore, this electrolyte does not show promise either for H_2-air fuel cell or for the hydrocarbon-air fuel cell.

Sulfoacetic Acid

The polarization curves for argon, propane, and hydrogen in sulfoacetic acid at 110°C are given in Figure 16. It has been customary in these polarization plots for the current to achieve a limiting value at an overpotential

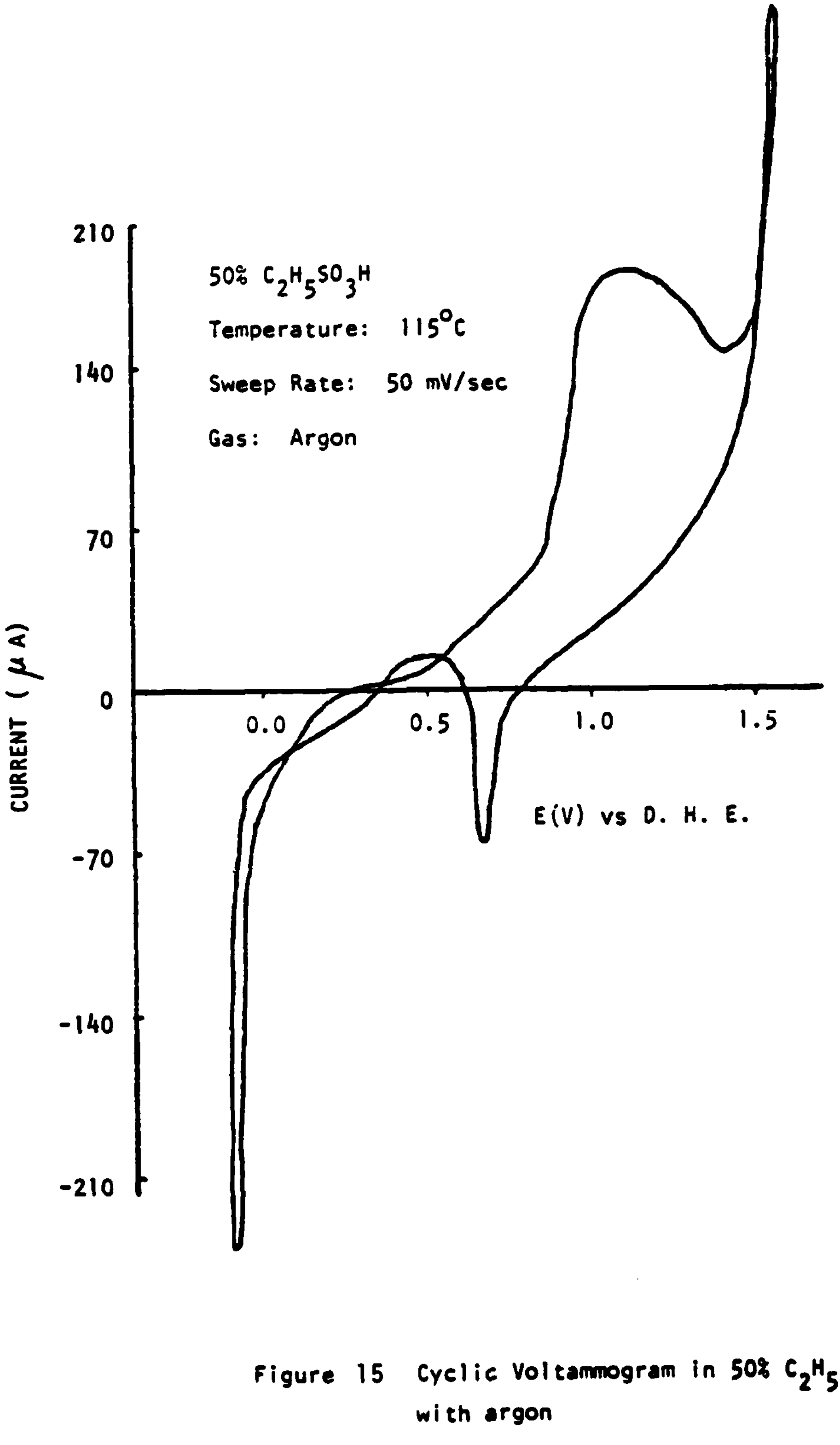

Figure 15 Cyclic Voltammogram in 50% $C_2H_5SO_3H$ with argon

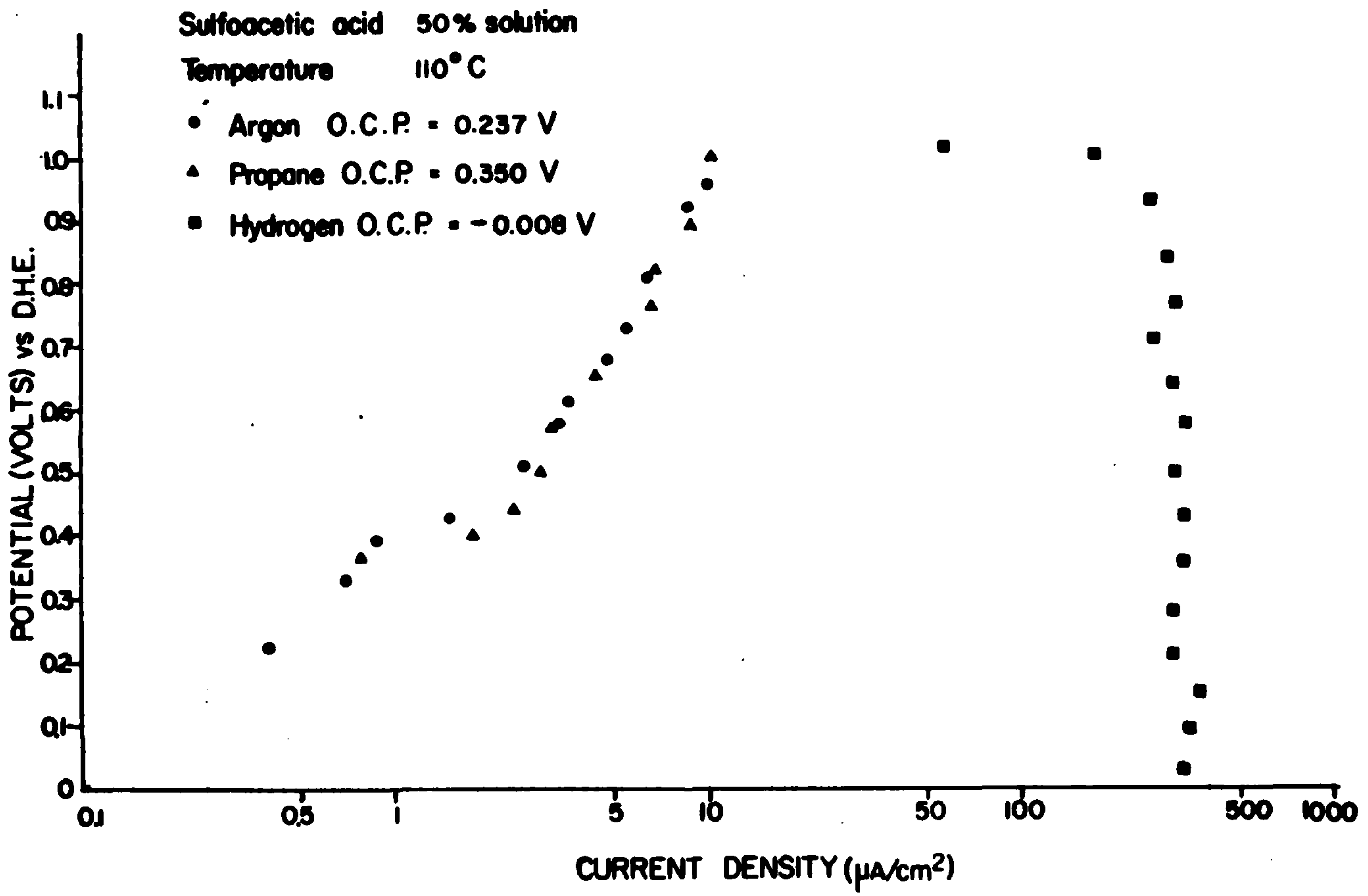

Figure 16 Polarization curves for argon, propane, and H_2 in 50% HSO_3–CH_2–COOH at 110°C

of approximately 0.5 v. However, as is obvious from Figure 16, with argon and propane a limiting current was not achieved so, for the sake of comparison, the current at 0.6 v was selected. This was 0.3 v above the open circuit potential of approximately 0.3 v. The current for hydrogen oxidation at 80°C and 110°C was approximately the same, 377 and 351 $\mu a/cm^2$ respectively. This is considerably greater than that supported by methanesulfonic acid or $TFMSA \cdot H_2O$.

The attempts to purify the acid are described in Appendix I. A reasonably successful procedure involves the formation of the Pb salt which is removed by precipitation as PbS. Unfortunately sufficient sulfide remained with the acid to poison the platinum electrode during the polarization run. The experiments reported here were performed with the 98% pure material.

A voltammogram with argon in sulfoacetic acid at 90°C is shown in Figure 17. The voltammogram was obtained to study the adsorption of the acid on the platinum surface using the cyclic voltammetric technique with a sweep rate of 50 mV/sec. From the voltammogram obtained with argon in 30% sulfoacetic acid at 90°C, the following features could be noticed:

a) the irreversibility of the process,

b) the hydrogen adsorption and desorption, double layer and oxygen film formation regions were not well-separated or perceived,

c) an absence of the hydrogen peaks.

To study the adsorption of sulfoacetic acid on the platinum surface, the voltammogram was first obtained only in 4N H_2SO_4 and then a few drops of sulfoacetic acid were added to the cell to observe the change in the voltammogram. The resulting voltammogram was quite different than the

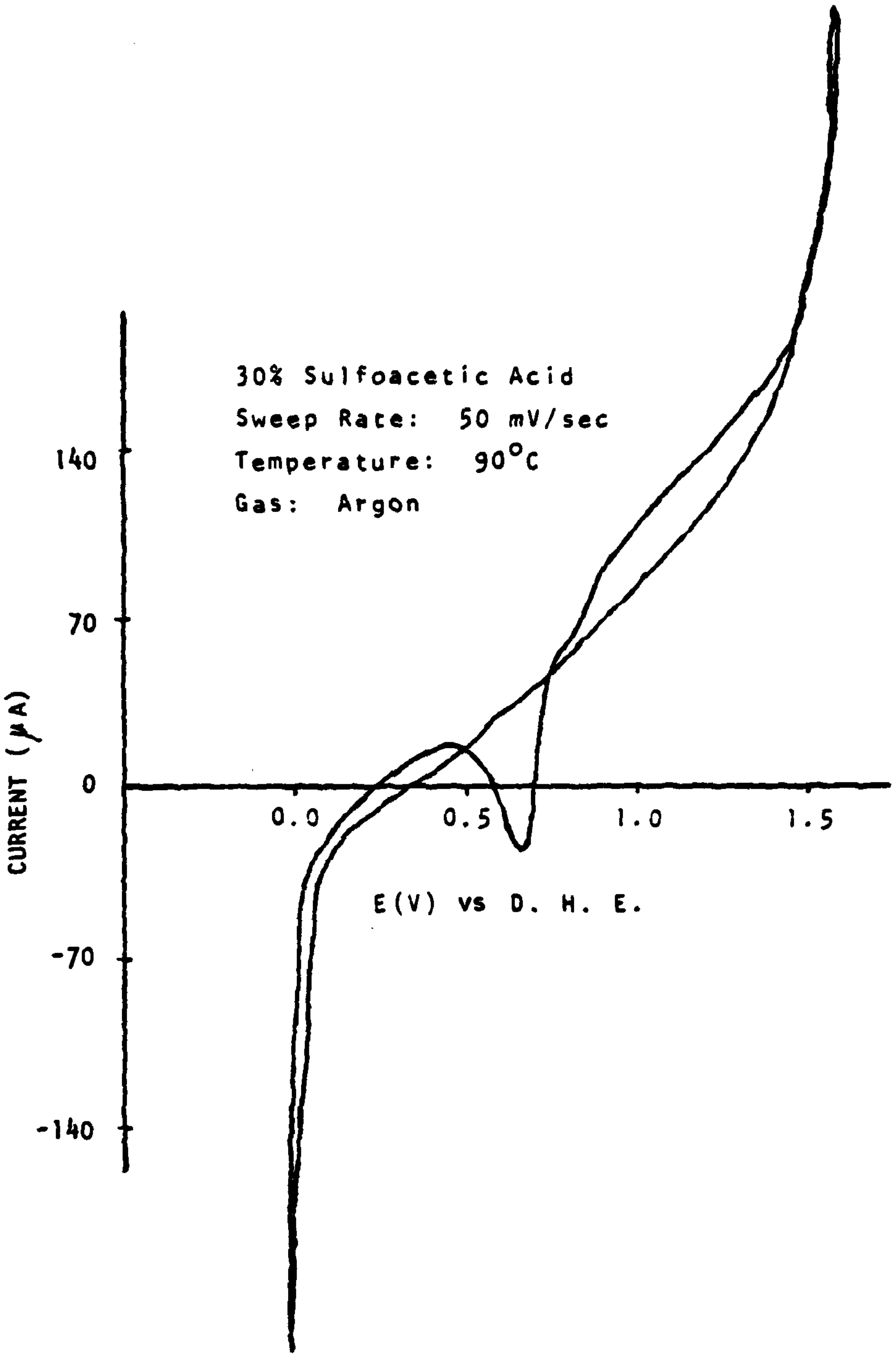

Figure 17 Cyclic Voltammogram in 30% Sulfoacetic Acid with Argon

original one. In the resulting voltammogram, one can see the increase in the anodic charge and the disappearance of the hydrogen peaks. A tiny peak in the hydrogen desorption region was observed that might result from the partial dissolution of hydrogen or adsorption of an unknown impurity on the electrode surface but the overall loss of the hydrogen peaks and the increase in the anodic charge indicate the adsorption of sulfoacetic acid on the platinum surface. The measurements were checked using a different sweep rate in order to observe any noticeable change in the voltammogram. But the resulting voltammogram still did not show the hydrogen peaks. At this stage, nothing can be said with certainty about the adsorption of this acid on the platinum surface as the disappearance of the hydrogen peaks in the 4N H_2SO_4 voltammograms might result from the adsorption of impurities present in the acid.

It is obvious from the polarization study that this acid does support a high current density in the presence of hydrogen. On the other hand, the presence of the impurities in the acid creates some doubts. Nevertheless, the difference in the limiting current densities obtained in sulfoacetic acid with argon and hydrogen at 110°C is striking. The limiting current density obtained in sulfoacetic acid with argon at 110°C was 3.7 $\mu a/cm^2$ whereas with hydrogen, it was 351 $\mu a/cm^2$. In other words, the higher current achievement in sulfoacetic acid with hydrogen is basically the response of the oxidation of hydrogen and not the impurities as the limiting current obtained with argon was only 3.7 $\mu a/cm^2$. Although the 3.7 $\mu a/cm^2$ current density with argon is usually considered high, it might be due to the presence of the impurities in the acid.

The electrochemical behaviors of methanesulfonic, ethanesulfonic, and sulfoacetic acids are compared in Table VII in terms of the limiting currents achieved with hydrogen, argon, and propane

Table VII Summary of the Limiting Current Density Values Obtained in Different Electrolytes

	The Limiting Current Densities ($\mu a/cm^2$)					
	Hydrogen		Propane		Argon	
Electrolyte	80°C	115°C	80°C	115°C	80°C	115°C
Methanesulfonic Acid CH_3SO_3H	5.0	225.0	1.7	2.3	1.9	3.8
Ethanesulfonic Acid $C_2H_5SO_3H$	7.0	9.0	3.0	2.8	3.5	4.0
Sulfoacetic Acid HO_3SCH_2COOH	377*	351* (110°C)	1.1*	3.7* (110°C)	0.12*	3.7* (110°C)

*Current at 0.6v

V. Conclusions

The literature study and the preliminary experiments, both those in which the physical properties of the compounds were measured, and the electrochemical tests, made it possible to eliminate certain classes of compounds, as well as specific compounds, that initially appeared to be potential electrolytes. Unsubstituted aliphatic carboxylic acids and those carboxylic acids that are substituted with iodine, chlorine, and bromine are not sufficiently stable, chemically or electrochemically. Aromatic sulfonic acids hydrolyze in aqueous solution. Some fluorinated aliphatic acids such as heptafluorinated butyric acid have several very desirable physical properties such as high specific conductance but their vapor pressures appear to be too high, or at least the vapor pressure of perfluorinated butyric acid is too high, making it necessary to go to a C5 or C6 acid. The electrochemical stability of 10-dl camphor sulfonic acid is questionable. The tricarboxy acid, trimellitic, would have to be used as the mono or di potassium salt to possess sufficient solubility and conductivity.

From many measurements on many compounds, it is possible to make some general comments regarding the qualifications of organic compounds to replace phosphoric acid as a fuel cell electrolyte.

The ionic conductances of aqueous solutions of these organic compounds appear to be adequate. Most of the aqueous solutions of the compounds give conductance-composition curves with maxima at about 50-60 weight percent of the acid following the behavior of sulfuric and phosphoric acid. These solutions give high conductivities but pose a problem with their high vapor pressures.

The vapor pressures of many of these pure compounds by themselves are low enough to be useful fuel cell electrolytes. However, if it is necessary to work with aqueous solutions then, obviously, the vapor pressure of the solution will be higher. At any rate, the vapor pressures can be measured by the isopiestic method. Further, from theoretical relationships, the heat of vaporization can be estimated and, from a single vapor pressure measurement at a specific temperature, the vapor pressure-temperature curve can be constructed.

With respect to chemical stability, experiments show that certain sulfonic acids do not hydrolyze appreciably in the test used.

The sweep voltammetry experiments demonstrate that some acids such as ethanedisulfonic are stable over potentials in the fuel cell operating range. With other compounds such as camphor sulfonic acid there appears to be excessive adsorption in the double layer region.

The experimental work described above led to the focussing on three compounds, methanesulfonic acid, ethanesulfonic acid , and sulfoacetic acid.

The polarization studies indicate that an electrolytic solution, 80% in methanesulfonic acid and 20% in H_2O, supports high current densities with H_2 but shows no promise with propane. The use of the anhydrous acid does not appear to be feasible because of decomposition.

The cyclic voltammetry studies indicate that methanesulfonic acid is strongly adsorbed on the platinum electrode surface, however, at this point, it is not clear what the adsorption characteristics of a fuel cell electrolyte should be. Analysis of methanesulfonic acid by nmr and gas chromatography indicates that either this acid decomposes into different fragments or forms new compounds during electrolysis, particularly at temperatures

100°C or above.

The polarization studies with ethanesulfonic acid indicate that this acid as an electrolyte does not support high current densities either with H_2 or propane. Thus, it has shown no promise with either of the fuels. Ethanesulfonic acid is also adsorbed on the platinum electrode surface.

The commercially available sulfoacetic acid is black, in semi-solid form, and about 98% pure. It can be purified by conversion to the Pb salt. This acid is a hydroscopic solid, has a reasonable ionic conductance, is highly soluble in water, and according to the literature thermally decomposes at 245°C. A platinum electrode in sulfoacetic acid will oxidize H_2 with about two times higher current density than in trifluoromethanesulfonic acid monohydrate.

It was concluded from this investigation that the sulfonic acids such as CH_3SO_3H or $CH_3\text{-}CH_2\text{-}SO_3H$ containing terminal methyl groups unprotected by fluorination are strongly adsorbed on the platinum surface and decompose easily during electrolysis. It now appears necessary that the sulfonic acid electrolytes to be evaluated in future studies should be properly substituted to protect the molecule against electrolytic oxidation or reduction. Thus, this evaluation of the lower-carbon sulfonic acids, rather than identifying new electrolytes, suggests the direction that must be taken to the development of new electrolytes. The molecule must be so constructed as to eliminate the possibility of dissociative adsorption, eg.

$$RCH_3 \rightarrow R\text{-}CH_2\ (ads) + H\ (ads)$$

It should not be concluded from this investigation that the development of alternate electrolytes to phosphoric acid or the finding of organic sulfonic acids as alternate electrolytes is a less attractive approach to the improvement of the hydrogen-oxygen fuel cell.

Upon completion of this investigation the status of alternate electrolytes can be described as follows:

1. The employment of an electrolyte alternative to phosphoric acid is a highly feasible approach to the improvement of fuel cell performance.
2. This improvement takes place at both the H_2 electrode and the air electrode.
3. The alternative electrolyte appears to be the only promising approach to the direct hydrocarbon-air fuel cell.
4. All the evidence to this point indicates that trifluoromethanesulfonic acid or its monohydrate is the best and probably will be the only suitable alternate electrolyte.
5. The problems associated with the employment of trifluoromethanesulfonic acid are engineering (operational) rather than scientific, e.g. H_2O balance, etc.
6. There is no generally accepted explanation for the improved electrochemical performance for the electrode in the sulfonic acid (versus phosphoric acid).
7. The elucidation of the mechanism will represent a tremendous advance in knowledge in the fuel cell field.
8. It appears now that this mechanism involves the interaction of adsorption processes and chemical reactions.
9. This investigation furnishes some of the guide-lines to future investigations in this area.

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Appendix I Preparation and Purification of Electrolytes

Methanesulfonic Acid

The methanesulfonic acid used was Eastman 95% practical grade. This 95% practical grade MSA is a clear, colorless acid but turns dark black upon heating for a couple of hours at 90°C apparently because of the presence of a significant amount of impurity in the acid. In order to remove this impurity, the acid was distilled and then redistilled under vacuum. The double distilled methanesulfonic acid was slightly yellow in color.

The double-distilled acid was further cleaned in the cell with a cleaning electrode meaintained at 0.5 volt overnight with the Beckman Electroscan. The cleaning electrode was a fuel cell electrode replacing the working electrode assembly in the cell. The pre-electrolysis of the acid was done for about 15 hours at 0.5 volt. The electrolysis was turned off just after taking the cleaning electrode carefully out of the working compartment electrolyte to prevent the mixing of the impurities adsorbed on the cleaning electrode with the cleaned electrolyte left in the cell.

Ethanesulfonic Acid

The ethanesulfonic acid used was supplied by Aldrich and Company. The acid was vacuum distilled in order to remove impurities and then it was further cleaned by overnight electrolysis at 0.5 volt using a cleaning electrode in place of the working electrode. The acid foamed upon bubbling gas through the cell but by increasing the temperature, and reducing the surface tension the foaming was reduced.

Sulfoacetic Acid

The sulfoacetic acid supplied by Eastman was dark black and in semisolid form. This acid, which is highly soluble in water, was dissolved in conductivity water to prepare the electrolyte. The homogeneous light reddish brown colored acid was obtained by diluting it to approximatley 30% and filtering under vacuum.

The sulfoacetic acid available commercially is about 98% pure and for this reason a considerable effort was expended to purify the compound. Sulfoacetic acid is completely soluble in polar solvents such as H_2O, acetone, alcohols, acetic acid, dioxane and mixtures of these solvents. It is completely insoluble in benzene, ether, toluene, petroleum ether, and other non-polar solvents. All attempts to recrystallize from these solvents or mixtures of these solvents were unsuccessful due mainly to the lack of a difference in solubility over the temperature range of 25° to 100°C.

The attempts to purify the acid by conversion to the barium salt and the silver salt (15) were also unsuccessful.

An adequate method was developed through the Pb salt. About 42.3 g. of the 98% material was dissolved in 450 ml. acetone and filtered. To the filtrate was added 73.6 g. Pb CO_3 to bring the solution to a neutral pH. The Pb salt was filtered off and suspended in about 500 ml. of H_2O. The suspension was bubbled with H_2S for 10 hours to precipitate PbS and free the acid. The solution was filtered. The filtrate contains the acid with a yield of 42%.

Appendix II Analysis of Electrolysis

The methanesulfonic acid was analyzed in order to follow the possible oxidation and reduction of this compound during electrolysis. For this purpose, nuclear magnetic resonance spectra and gas chromatograms were obtained. The equipment used for the analysis of the compound was as follows:

a) Varian-Associates A60 analytical NMR spectrometer,

b) Bruker WP-80, ^{13}C NMR spectrometer,

c) Hewlett-Packard 5830 A Gas Chromatograph with 18850 A recorder.

The sample used to obtain an nmr spectrum was prepared by adding equal parts of deuterium oxide (D_2O) and the acid electrolyte to an nmr glass tube of 0.5 cm diameter and 20.32 cm length. The deuterium oxide was used as a solvent and tetramethylsilane (TMS) as an external standard. The tetramethylsilane peak was set at 0.0 ppm after properly phasing and maximizing the resolution. The spectrum was run over a 1000 - HZ range using a 250 - sec sweep time.

The following three mixtures (samples) were run for both ^{1}H and ^{13}C nmr spectra at room temperature:

a) 0.3 ml D_2O + 0.3 ml unelectrolyzed, as-supplied, methanesulfonic acid,

b) 0.3 ml D_2O + 0.3 ml unelectrolyzed, double distilled, methanesulfonic acid,

c) 0.3 ml D_2O + 0.3 ml electrolyzed methanesulfonic acid.

The "electrolyzed" methanesulfonic acid was a sample which was taken out of the experimental cell after electrolyzing it at 0.9 volt and 100°C temperature for 20 hours.

Similarly, the electrolyzed, as-supplied, and double distilled methanesulfonic acid samples were analyzed by gas chromatography. These three samples were injected into a gas chromatography column using ether as a solvent, methanesulfonic acid being highly soluble in ether. The 1% solution of the acid electrolyte was prepared by mixing 1 ml of methanesulfonic acid and 99 ml of ether. One microliter of this 1% solution was injected by a syringe into a 3% OV-225 gas chromatography column (183 cm x 0.32 cm). This column is made of cyanopropylmethylphenylmethyl silicone and has an intermediate polarity. A flame ionization detector (FID) was used to obtain a chromatogram of the acid. The programmed temperature range was 50° to 150°C with a 10°C/minute rate. The injection and FID temperatures were 150° and 200°C respectively. The other experimental and controlled conditions are shown on the chromatograms. Three different chromatograms were recorded for electrolyzed, as-supplied, and double distilled methanesulfonic acid.

The results of the nuclear magnetic resonance spectra studies were not particularly informative. The ^{1}H nmr spectra were recorded employing as-supplied (A), double-distilled (B), and electrolyzed (C) methanesulfonic acid samples.

The ^{1}H nmr spectra over a 1000-HZ range using a 250-sec sweep time were obtained at room temperature. The peaks' position are recorded in Table VIII. Peak 1 corresponds to the $-CH_3$ group while Peak II corresponds to the combined effect of the sulfonic group and solvent. When the samples were run after heating them to 60°C Peak II of spectrum C had shifted to 5.2 ppm; originally, this peak had been found at 4.2 ppm. The peaks' positions of the spectra A and B remained the same. The 1 ppm chemical shift to the left, that is, to a higher ppm value in the electrolyzed sample cannot be due to the presence of water as the presence of the water will shift the peak to the right or to a lower ppm value. This chemical shift created some doubts regarding the stability and reliability of methanesulfonic acid as an electrolyte.

To establish the presence of the impurities and/or new compound (produced during electrolysis) in the electrolyzed electrolyte, ^{13}C nmr spectra were recorded at room temperature for all three samples. The information

Table VIII - The Peak Positions in the ^{1}H nmr Spectra

Spectrum #	*Position of Peak 1 (ppm)		*Position of Peak 11 (ppm)	
	∿ 25°C	60°C	∿ 25°C	60°C
A	1,5	1.5	4.8	4.8
B	1,5	1,5	4,55	4.55
C	1,5	1.5	4,2	5.2

* These positions are over a 1000 - HZ range using a 250 - sec sweep time.

obtained on examining these spectra was limited to the following two indications:

1. The presence of an impurity (labelled peak "B" in all three spectra) in the samples,
2. The distance between peak "A" (the methyl group) and peak "B" differs by 22 ppm in the electrolyzed and as-supplied methanesulfonic acid samples.

In ^{13}C nmr, the spectrum was run at room temperature. To further study the possible instability the electrolyte samples were analyzed at higher temperature using gas chromatography.

The electrolyzed, as-supplied, and double distilled methanesulfonic acid samples were run over a programmed temperature range of 50° to 150°C. All other experimental and control conditions are recorded on the chromatograms. Because of the fact that the acid to be run was a strong acid, a 1% solution was prepared using ether as a solvent. The employment of the neat acid (or even highly concentrated) could create two major problems; one, the acid could destroy the column, the other, overloading of the detector and column could result.

The chromatograms obtained by injecting one microliter of as-supplied, electrolyzed, and double distilled methanesulfonic acid solutions (1%) are shown in figures 18, 19, and 20 respectively. On examining these chromatograms, it is obvious that the chromatogram recorded using the electrolyzed methanesulfonic acid contains several peaks at various times. These peaks could be due to different compounds produced during electrolysis or fragments of the decomposed acid electrolytes. Figure 18 shows only one peak at 17.15 minute and about 120°C (ignoring the ether peak) which corresponds to the acid while two peaks can be seen in figure 20. The second peak in the double

```
CHT SPD        1.00             TEMP 1       50     50
ATTN 2↑                         TIME 1       10.0
FID SIGNL    A                  RATE         10.00
SLP SENS       3.00             TEMP 2      150
AREA REJ -                      TIME 2       20.0
FLOW A       29                 INJ TEMP    150    150
FLOW B       29                 FID TEMP    200    200
OPTN         0                  TCD TEMP    300    300
  1.5    AREA REJ   1000        OVEN MAX    250
TEMP 1       50     50
```

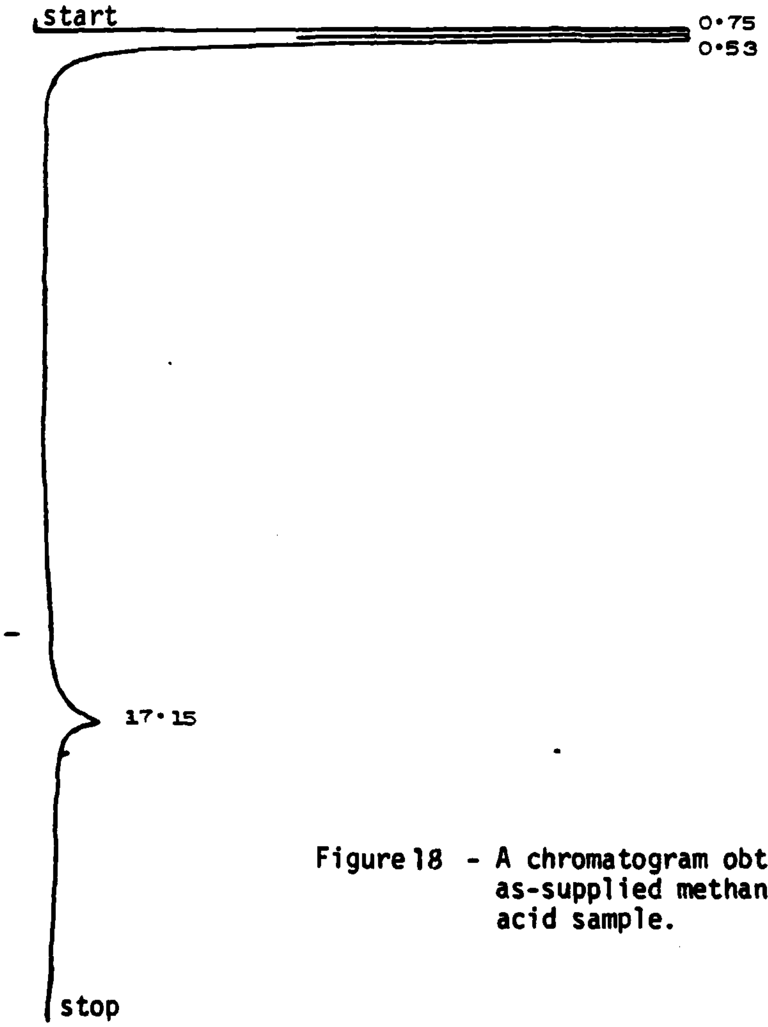


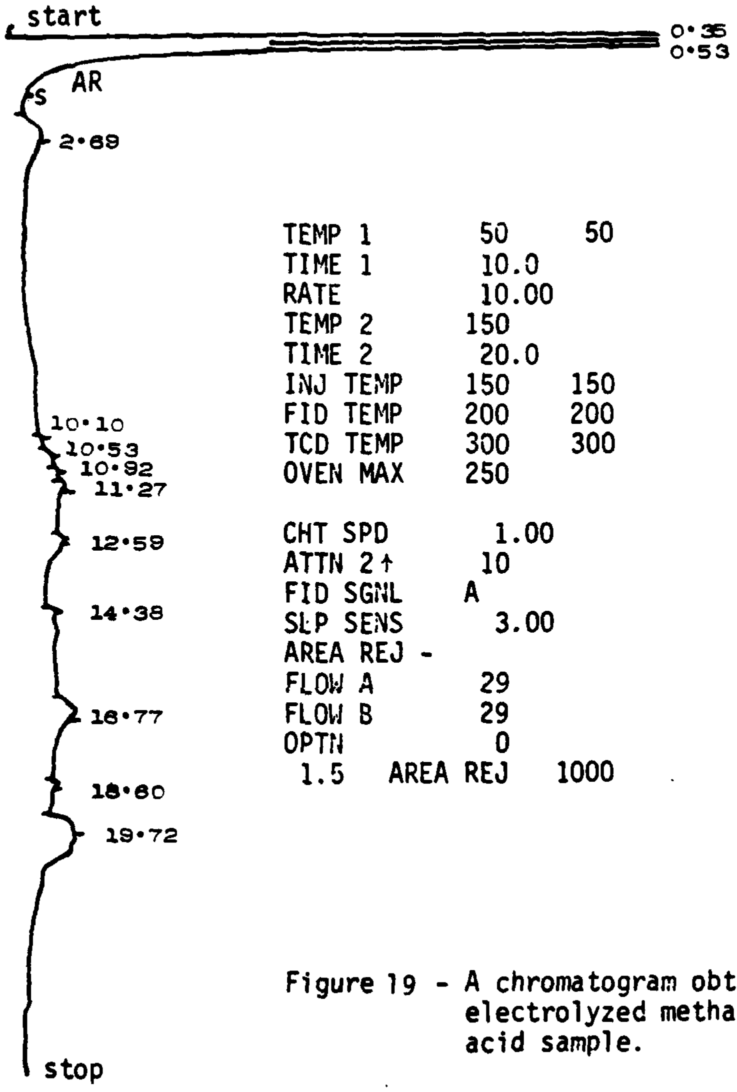
Figure 18 - A chromatogram obtained with as-supplied methane sulfonic acid sample.

```
hF 5830A

AREA %

  RT        AREA        AREA %

17.15      101100      100.000
```



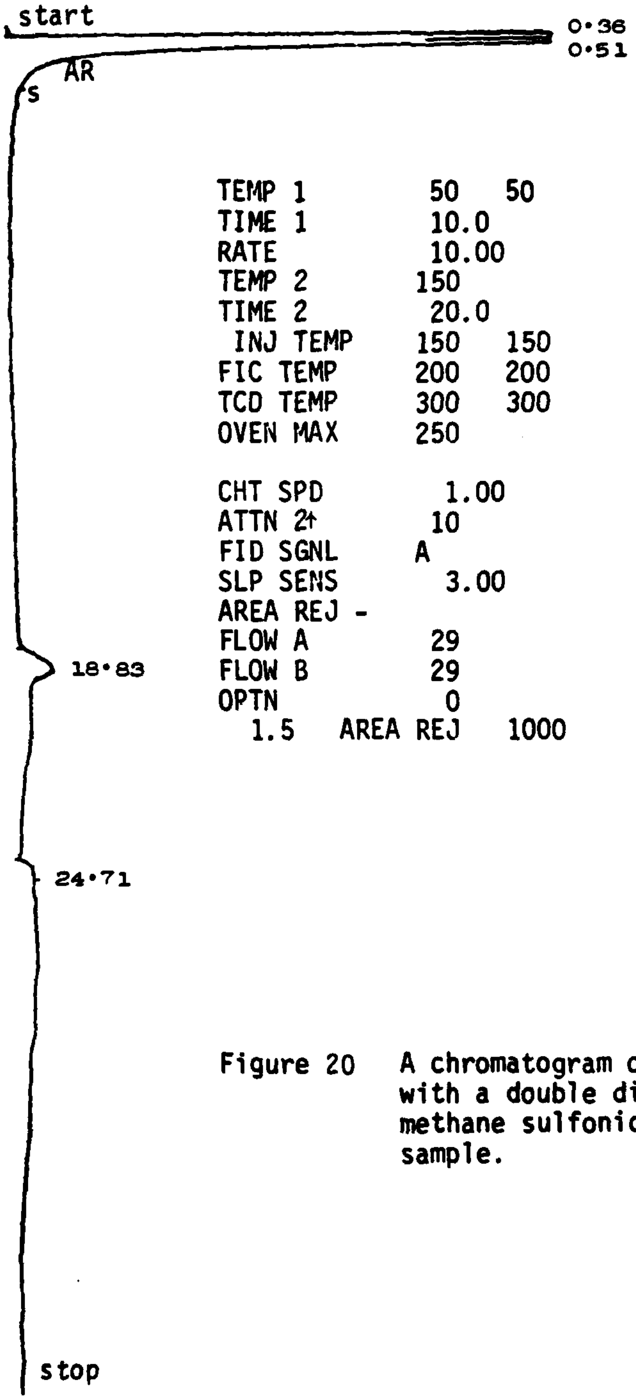
```
TEMP 1         50      50
TIME 1         10.0
RATE           10.00
TEMP 2        150
TIME 2         20.0
INJ TEMP      150     150
FID TEMP      200     200
TCD TEMP      300     300
OVEN MAX      250

CHT SPD         1.00
ATTN 2↑        10
FID SGNL      A
SLP SENS        3.00
AREA REJ -
FLOW A         29
FLOW B         29
OPTN            0
 1.5    AREA REJ    1000
```

Figure 19 - A chromatogram obtained with the electrolyzed methane sulfonic acid sample.

```
hF 5830A
AREA %
  RT        AREA      AREA %
  2.69     124000     34.236
 10.53       5731      1.582
 10.92       1821      0.503
 11.27       8558      2.363
 12.59      11700      2.230
 14.38      18750      5.177
 16.77      48740     13.457
 18.60      12090      3.338
 19.72     130800     36.114

           XF:  1.0000 E+ 0
```



```
TEMP 1        50   50
TIME 1         10.0
RATE           10.00
TEMP 2        150
TIME 2         20.0
 INJ TEMP     150   150
FIC TEMP      200   200
TCD TEMP      300   300
OVEN MAX      250

CHT SPD         1.00
ATTN 2↑        10
FID SGNL      A
SLP SENS        3.00
AREA REJ -
FLOW A         29
FLOW B         29
OPTN            0
  1.5   AREA REJ   1000
```

Figure 20 A chromatogram obtained with a double distilled methane sulfonic acid sample.

```
hF 5830A
AREA %

RT         AREA      AREA %
18.83     263500     74.815
24.71      88700     25.185
```

distilled chromatogram at 24.71 minute and 150°C could be the result of a shift in the base line during the run. The % area of the different peaks recorded in figures 18, 19, and 20 are shown on the corresponding chromatograms after rejecting the % area under the ether peak.

Hence, it is now obvious from the recorded chromatograms that during electrolysis, methanesulfonic acid either decomposes into different fragments or forms new compounds. The characteristics and chemical nature of these fragments or compounds remain unknown. At any rate, these analyses indicate that the stability and dependability of methanesulfonic acid as an electrolyte in a fuel cell is highly doubtful.

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