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DEFINITION OF CHEMICAL AND ELECTROCHEMICAL PROPERTIES OF A FUEL--ETC(U)
JAN 80 J AHMAD, R T FOLEY DAAK70-77-C-0080

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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 would be the preferred electrolyte.

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DEFINITION OF CHEMICAL AND ELECTROCHEMICAL PROPERTIES OF A FUEL CELL ELECTROLYTE

Interim Technical Report

J. Ahmad and R. T. Foley

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SUMMARY

The present research is oriented toward the task of developing an improved electrolyte for the direct hydrocarbon-air fuel cell. The electrochemical behavior of methanesulfonic acid, ethanesulfonic acid, and sulfoacetic acid as fuel cell electrolytes was studied in a half cell 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, but, attempts to purify the compound were unsuccessful.

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 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. Scope of the Present Research

The overall objective of this work is to contribute to the increase in fuel cell performance by improvement in the fuel cell electrolyte. This would include identifying new, improved, fuel cell electrolytes.

A review of electrolyte systems has been conducted and a comprehensive report, "On the Properties of a Fuel Cell Electrolyte" has been issued (1). The presently used systems have detrimental properties some of which are inherent in the particular systems 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, suggests further investigation of organic electrolytes, particularly, sulfonic acids.

The physical properties of a number of organic sulfonic acids have been measured or abstracted from the literature and these have been reported in the last progress report on this project (2). A preliminary report (3) on methane sulfonic acid had indicated that this acid possessed outstanding properties as an electrolyte. Based on the physical property data and the literature data an investigation of the electrochemical properties of methane sulfonic acid, ethane sulfonic acid, and sulfoacetic acid was indicated. These electrochemical studies are the subject of this report.

II. Literature Background on Sulfonic Acids as Fuel Cell Electrolytes

It is possible to develop a list of properties by which an "ideal" electrolyte may be characterized (4). This list includes a number of physical, chemical, and electrochemical specifications. All of the inorganic acids, phosphoric, sulfuric, hydrochloric, perchloric and hydrofluoric fall short for one or more reasons. The search for alternate electrolytes was extended to organic acids because it was felt that the ability to alter the structure of organic compounds allowed for a flexibility not available with inorganic systems. The concentration on organic acids arose because protons are needed in the stoichiometry of the fuel cell reaction and the concentration on sulfonic acids because these are the strongest acids available.

The first organic acid studied in any depth was trifluoromethanesulfonic acid and its monohydrate. Trifluoromethanesulfonic acid is one of the strongest acids known. This is due to the strong tendency of the $-SO_3H$ group to dissociate to $-SO_3^-$ and H^+. The charge stability of the sulfonic anion is great because the negative charge of the anion is highly delocalized. The replacement of C-H with C-F bonds increases the acid strength further. TFMSA has a high dielectric constant, 38, and is an excellent ionic conductor (5). Trifluoromethanesulfonic acid forms a stable monohydrate which melts at 33.8°C (6) and boils at 217-218°C at 756.9 mm (7). The acid itself boils at 162°C and does not produce fluoride ions even in the presence of strong nucleophiles. In the light of these promising properties the behavior of $CF_3SO_3H \cdot H_2O$ as an electrolyte with helium, hydrogen, hydrogen--3% CO, propane, "reduced" carbon dioxoide, and methanol have been investigated at various temperatures (4).

Helium was used to provide the background information on the electrolyte. Propane and methanol were used to observe the expected behavior of $CF_3SO_3H \cdot H_2O$ in direct-oxidation fuel cells while hydrogen-carbon monoxide mixtures were used to simulate activity in the "indirect" hydrocarbon-air fuel cells. The results (4) obtained were as follows:

a) Polarization curves with helium suggest that the $CF_3SO_3H \cdot H_2O$ electrolyte does not show any detrimental reaction over the potential range of 0.1 to 1.0 volt.

b) The current carrying capacity goes up with temperature and no breakdown is observed with increasing temperature up to 150°C.

c) The TFMSA monohydrate is superior to phosphoric acid for both the electro-oxidation of hydrogen and the electro-reduction of air.

d) No indication of anion adsorption on the platinum electrocatalyst has been detected during anodic charging curves.

e) The measured open circuit potentials at 55°, 95°, and 115°C were well within the limits of accuracy (8) expected of a clean electrode surface. Apparently there was no anion adsorption on the electrode.

f) The activation energy for the oxidation of propane in $CF_3SO_3H \cdot H_2O$ was found to be 13 Kcal/mole while in other electrolytes, the activation energy was 16 Kcal/mole (9). Evidently, the oxidation process of propane has a lower energy barrier to overcome in $CF_3SO_3H \cdot H_2O$ compared to the other electrolytes.

When TFMSA$\cdot H_2O$ was used in a practical fuel cell, several problems developed (10) related to the vapor pressure of the electrolyte and its tendency to attack most organic substances such as polyethylene, polysulfone and phenol-formaldehyde (Kynol) except the fluorocarbons (11). Unfortunately, the fluorocarbons, generally utilized in conventional porous fuel cell electrodes to form hydrophobic regions within the structure, are readily wetted by the $CF_3SO_3H\cdot H_2O$ which leads to massive flooding within the electrode macropores. This flooding problem was partially overcome by a pressure compensation method in which both the hydrogen and air sides of the fuel cell are equally pressurized to force the electrolyte out of the electrodes.

Another problem noticed during the testing was the evolution of thick white fumes from both gas exit lines of the cell. Improvements in the cell performance were achieved by diluting the monohydrate to 63% acid and reducing the operating temperature of the cell to 23°. In a separate study (12) it was reported that, to alleviate the wetting problem and to increase the conductivity, the acid monohydrate should be diluted with 50% H_2O. But the dilution of the acid increases the vapor pressure of H_2O over the solution and therefore, a lower operating temperature is required.

At this point an attempt is also being made (13) to employ dilute aqueous TFMSA as an electrolyte in the cell instead of TFMSA$\cdot H_2O$ to eliminate the wetting and corrosion problems encountered during the monohydrate testing.

A major problem with the perfluorinated sulfonic acids appeared to be their high volatility. This led to the evaluation of tetrafluoroethane disulfonic acid (14). It was observed that TFEDSA improved the performance of a propane-air fuel cell by 100% over that of phosphoric acid at the same temperatures, although it was noted that some vaporization of the acid did occur during testing. The limiting currents obtained during the polarization study with propane in TFEDSA were found to be 4.20, 10.05 and 22 $\mu a/cm^2$ at 100^o, 120^o and 135^oC respectively. The energy of activation for propane oxidation on platinum as calculated from an Arrhenius plot was 14.5 Kcal/mole whereas in $CF_3SO_3H \cdot H_2O$, the activation energy was only 13 Kcal/mole; also, the limiting current obtainable in $CF_3SO_3H \cdot H_2O$ was consideraly higher than in TFEDSA. The reason why TFEDSA was inferior to $CF_3SO_3H \cdot H_2O$ is not known. Possibly, the higher molecular weight of TFEDSA adversely affects its transport properties.

Unsuccessful attempts were made to evaluate methanedisulfonic, ethanedisulfonic, benzene sulfonic, perfluorobenzenesulfonic, and perfluorobutanedisulfonic acids, in their anhydrous state.

All these acids were discarded because of the chemical instability, apparently desulfonation at $120^o \pm 20^oC$. Sulfur dioxide and sulfur trioxide produced during desulfonation were adsorbed and reduced by fuel cell anodes to give sulfides which poisoned the electrocatalyst.

Recently the feasibility of using a number of methane polysulfonic acids as electrolytes, particularly methanepolysulfonic acids such as $CXX'(SO_3H)_2$ and $CX(SO_3H)_3$, where X or X' can be a halogen or electron withdrawing substituent, for example, -COOH, was evaluated (15). These acids were selected after observing the wetting and volatility problems in CF_3SO_3H. Dichloromethanedisulfonic acid and chloromethanetrisulfonic acid were synthesized and then tested at 80^oC using 1 mg Pt electrodes with H_2, H_2+2%CO, and CH_4. The curve for H_2 in chloromethanetrisulfonic acid showed an ohmic behavior. The limiting current which was achieved in chloromethanetrisulfonic acid with H_2+2%CO was inferior to that in H_3PO_4 but the performance of the cell with CH_4 in chloromethanetrisulfonic acid was superior to H_3PO_4. The currents due to the oxidation of H_2 obtained in 4.2 M dichloromethanedisulfonic acid at 80°C were 30% better than those obtained in 85% H_3PO_4. On the other hand, the O_2 reduction currents in both acids were lower. It was conjectured that the reason for such a result could be due to the hydrophobic characteristic of the electrodes.

Several strong organic acids such as pentafluoropropanoic acid, trichloroacetic acid, chlorodifluoroacetic acid, benzene sulfonic acid hydrate, methane disulfonic acid, benzoic acid, and methane sulfonic acid were recently evaluated as electrolytes for the oxidation of hydrogen (3). Among these electrolytes, only methane sulfonic acid showed any promise as a fuel cell electrolyte for H_2 oxidation and the rest were ruled out as possible candidates due to the lack of better electrochemical performance and chemical stability. Their findings were as follows:

Pentafluoropropanoic acid had an undesirably high vapor pressure and underwent polymerization upon heating at only 50°C. This acid cannot be considered as a potential electrolyte because the 90 wt% aqueous acid solution has a low conductivity and allowed only a very low limiting current.

Chlorodifluoroacetic acid decomposed at 50°C producing chlorine and offered a low limiting current.

Trichloroacetic acid is hygroscopic, has a high vapor pressure and produces chlorine gas upon heating.

Benzenesulfonic acid-hydrate, in the presence of the platinum-black electrode, decomposes and turns from a light brown color into a black color.

The resistivity as well as the vapor pressure are high. The acid yields a lower limiting current than H_3PO_4.

Methane disulfonic acid, in the form of a 50% aqueous solution is commercially available and has a reasonable ionic conductance. At 27° and 54°C, the limiting current densities obtained in methane disulfonic acid are higher than those in H_3PO_4 or H_2SO_4 but when the temperature is increased to about 80°C, irreproducible results are obtained due to the excessive loss of water.

Benzoic acid was discarded since it is insoluble in water and has a very low ionic conductance; that is, 5.0×10^{-8} ohm^{-1} cm^{-1} at 140°C. On the other hand, it has a reasonable vapor pressure.

Methane sulfonic acid, as the 95% practical grade, was selected as an electrolyte to study the electro-oxidation of H_2 and H_2+CO on a platinized-platinum electrode using the rotating disc electrode technique. This acid has a low vapor pressure, 10 mm Hg at 167°C and a reasonable ionic conducance, 1.5×10^{-2} ohm^{-1} cm^{-1} at 135°C. Methane sulfonic acid with H_2 supports currents that are more than an order of magnitude higher than those in phosphoric acid under the same experimental conditions whereas with H_2+CO, continuous decrease in the currents was observed due to the poisoning effect of CO on the electrode surface.

The high current densities achievable with methane sulfonic acid as a fuel cell electrolyte suggested further investigation of this compound. Ethane sulfonic acid was also chosen for evaluation because it has the same characteristics as methane sulfonic acid except for is molecular weight. The higher molecular weight should lead to a lower vapor pressure. Also, sulfoacetic acid is a stable acid with high boiling point, 245°C. This acid is highly soluble in water and would not be expected to adsorb on platinum because of the electron withdrawing substituent (-COOH).

In summary, a review of the literature suggested that methane sulfonic, ethane sulfonic, and sulfoacetic acid be investigated electrochemically as fuel cell electrolytes. The experiments should be conducted at various temperatures with hydrogen and propane as fuel to make the results applicable to the hydrocarbon-air fuel cell.

III. Experimental

Methane sulfonic acid, ethane sulfonic acid and sulfoacetic acid were evaluated as fuel cell electrolytes after considering their promising physical and chemical properties (tabulated in Table 1). Sulfuric acid as well as trifluoromethanesulfonic acid monohydrate were also used in certain experiments because the electrochemical behaviors of these acids are very well know.

Preparation, Purification and Analysis of Electrolytes

Methane Sulfonic Acid

The methane sulfonic 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 or above 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 methane sulfonic acid was slightly yellow in color.

The double-distilled acid was further cleaned in the cell with a cleaning electrode maintained at 0.5 volt overnight with the Beckman

Table I - A SUMMARY OF THE PERTINENT DATA ON THE ELECTROLYTES TO BE EVALUATED

Compound	Melting Point°C	Boiling Point°C	Solubility in Water	Specific Conductance at 40°C		Contact angle on Teflon	
				ohm^{-1} cm^{-1}	concentration wt%	angle	concentration wt%
Methane Sulfonic Acid, CH_3SO_3H	19 - 20°	167°/ 10 mm	Miscible in all proportions	0.019	98	93.59°	100
Sulfoacetic Acid HO_3S-CH_2-COOH	84 - 86°	245 d	Very soluble	0.464	58	90.15°	59
Ethane Sulfonic Acid, $CH_3-CH_2-SO_3H$	-17°	123°/ 1 mm	Very soluble	0.009 at 25°C	98	-	-

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.

The methane sulfonic 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.

Ethane Sulfonic Acid

The ethane sulfonic 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 leaving the electrolyte for 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 having a specific resistance of 415,000 ohms. The homogeneous light reddish brown colored acid was obtained by diluting it to approximately 30% and filtering under vacuum. Sulfoacetic acid also foamed during bubbling of gas through the cell.

All the acid electrolytes mentioned above were pre-electrolyzed overnight before using them. The dilution of the electrolyte, if required, was done by adding conductivity water.

Electrochemical Techniques

The following three types of experiments were performed:

a) polarization studies of argon, hydrogen and propane in the three electrolytes. The apparatus including the pre-treatment of the gases is described in reference 7.

b) cyclic voltammetry experiments with the apparatus and techniques previously described (12).

c) adsorption studies using potential step sequences described in reference 4.

IV. Results and Discussion

Methanesulfonic acid, ethane sulfonic acid, and sulfoacetic acid were evaluated as fuel cell electrolytes with argon, propane, and hydrogen using polarization, cyclic voltammetry, and adsorption techniques in the temperature range of 80° to 135°C. Argon data were used to get the background information on the electrolytes. The investigation of the behavior of hydrogen in different electrolytes is applicable to the H_2-air fuel cell and propane to the direct hydrocarbon oxidation fuel cell.

Sulfuric acid and trifluoromethanesulfonic acid were also used for calibration purposes.

Calibration of the System

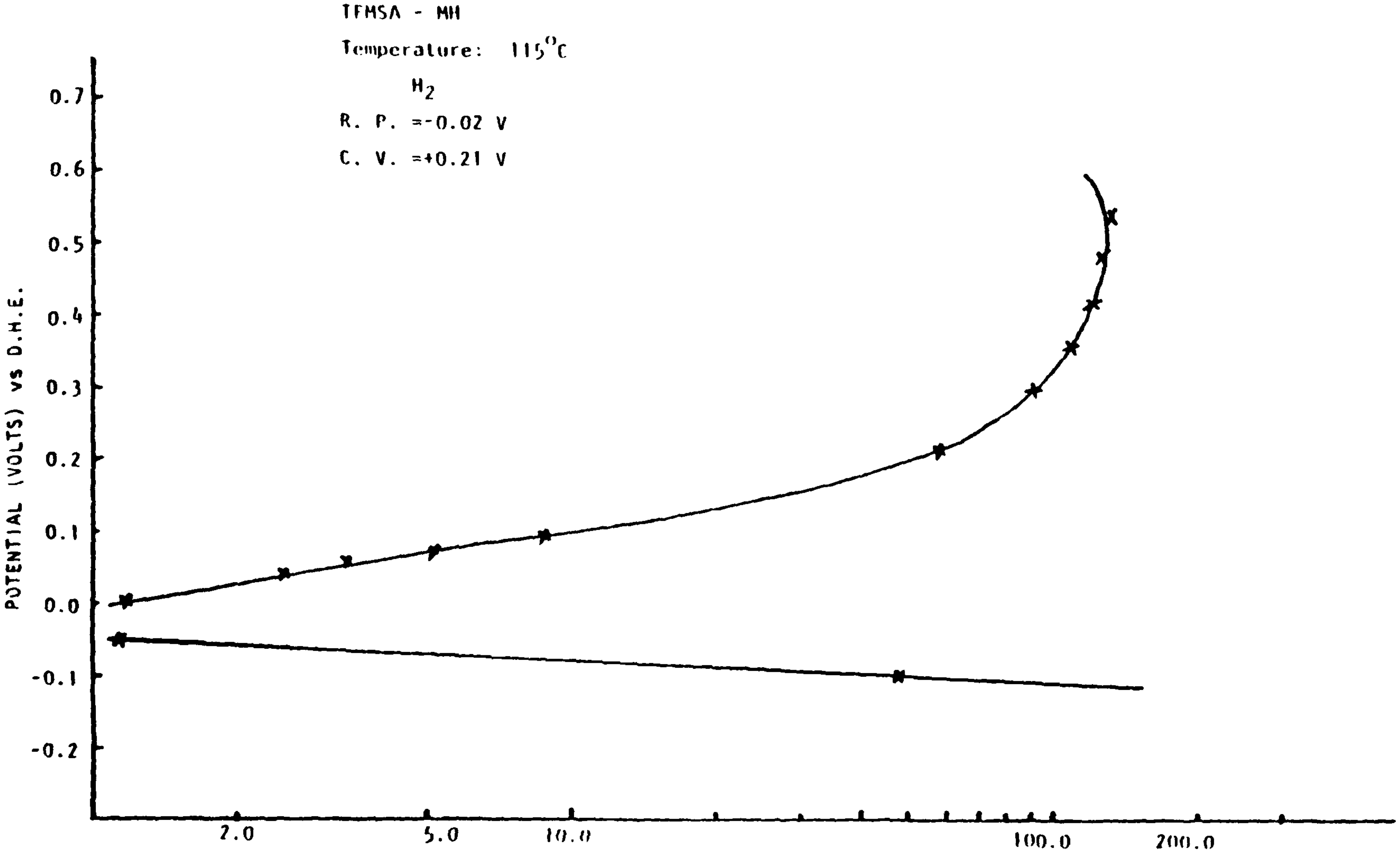
Electrochemical Behavior of Hydrogen in Trifluoromethanesulfonic Acid Monohydrate

The dynamic hydrogen electrode designed by Giner (8) was used as a reference electrode. The reliability of the dynamic hydrogen electrode reference system in $CF_3SO_3H \cdot H_2O$ depends on the open circuit potential of H_2 on a smooth platinum electrode. This open circuit should ideally be zero. The open circuit potential of H_2 against the D.H.E. in monohydrate was measured over a temperature range of 80° to 135°C and found to be -15.0 mV ± 10.0 mV which is considered within the limits of accuracy (8).

The polarization curves in $CF_3SO_3H \cdot H_2O$ with hydrogen and argon (figure 1) were the same as obtained previously in this laboratory (4). A cyclic voltammogram obtained with argon in $CF_3SO_3H \cdot H_2O$ at 80°C is also shown in figure 2. In this cyclic voltammogram, hydrogen desorption, 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 3. This voltammogram is identical with that reported by Bold and Breiter (16).



CURRENT DENSITY ($\mu a/cm^2$)

Figure 1 - Polarization Curve for H_2 in $CF_3SO_3H \cdot H_2O$ at 115°C

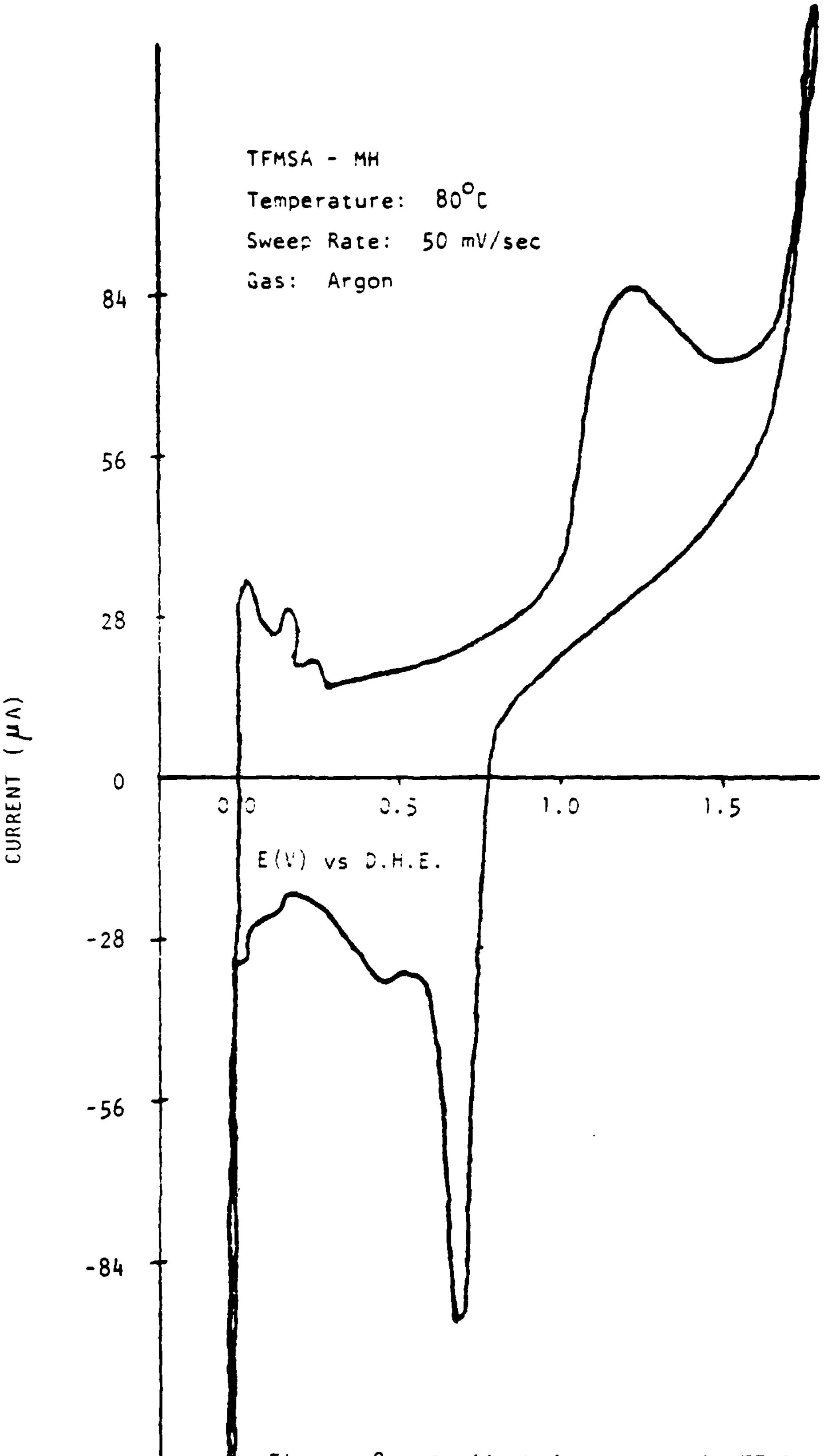


Figure 2 - Cyclic Voltammogram in TFMSA - MH

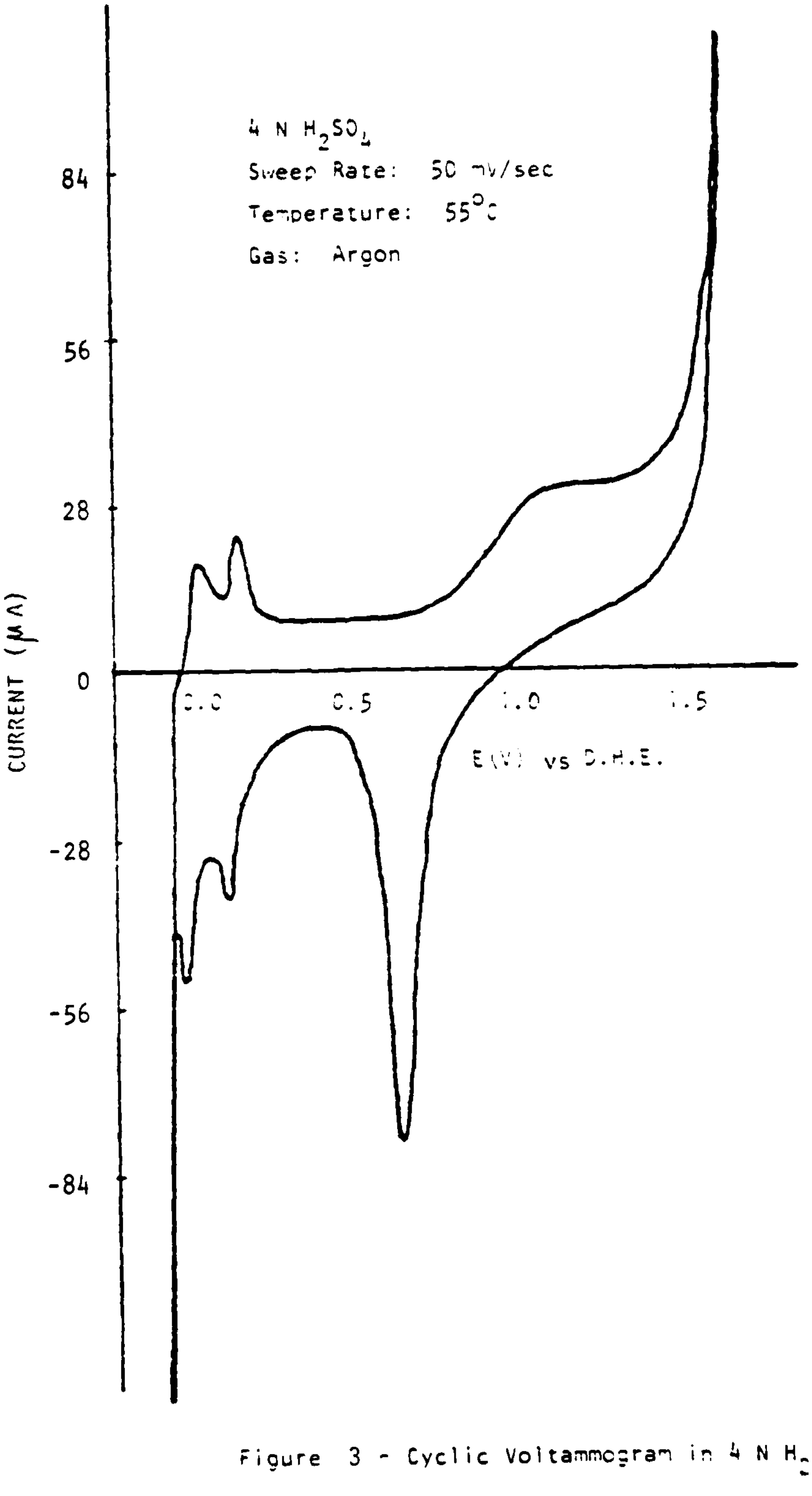


Figure 3 - Cyclic Voltammogram in 4 N H_2SO_4

In this way, 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 systems' reliability and freedom from impurities.

Electrochemical Behavior of Hydrogen in 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 4. 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 4 are the current density-potential plots for the oxidation of hydrogen in $CF_3SO_3H{\cdot}H_2O$ as reported by Adams (4). 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 (7).

Electrochemical Behavior of Propane in Methanesulfonic Acid

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 5. The limiting current density at 80°C was 1.7 $\mu a/cm^2$ while at 115°C 2.3 $\mu a/cm^2$. The maximum cell voltage values were 0.4 to 1.0 volt at different temperatures. The open

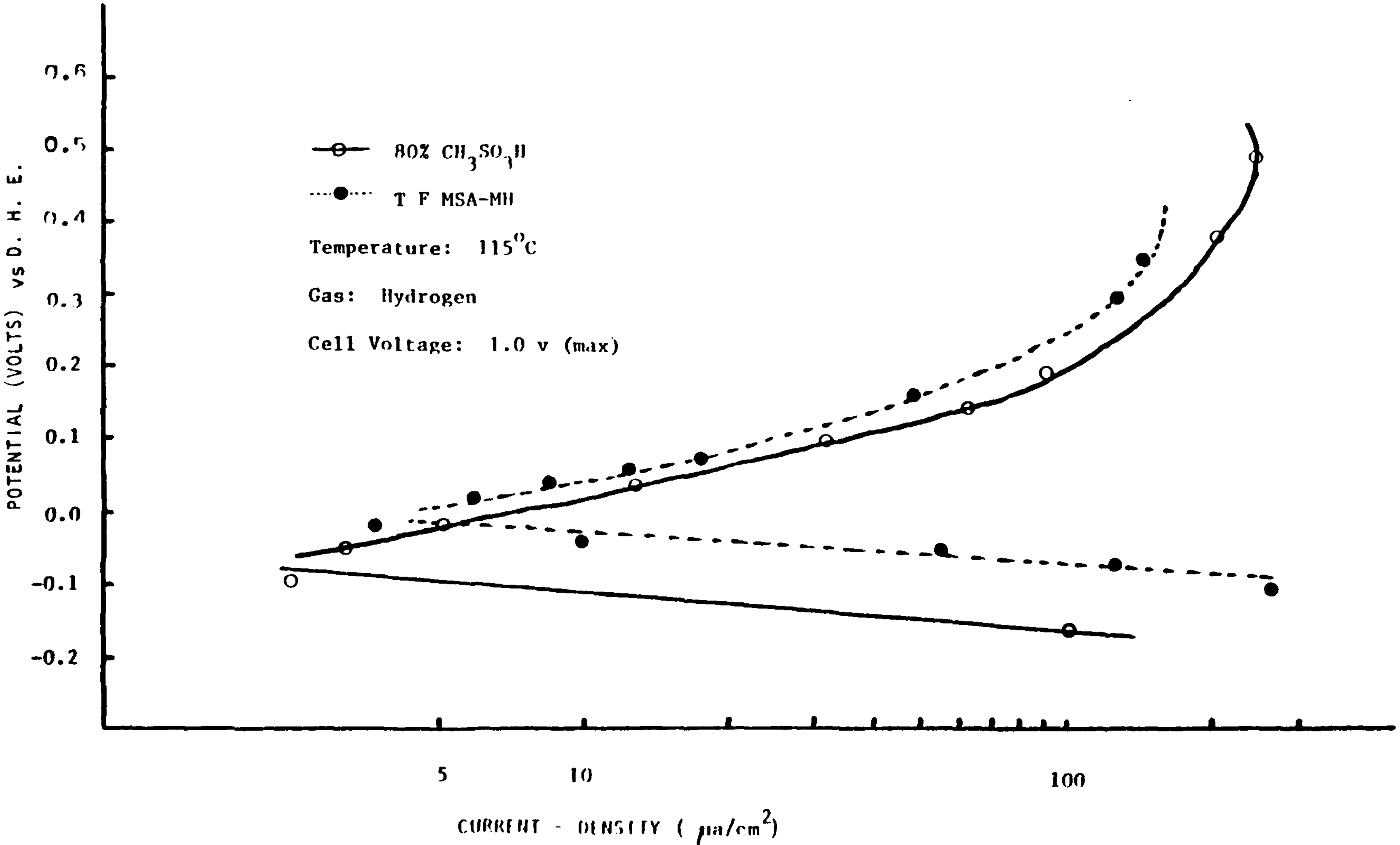


Figure 4 - Polarization Curves in 80% CH_3SO_3H and TFMSA.MH at 115°C

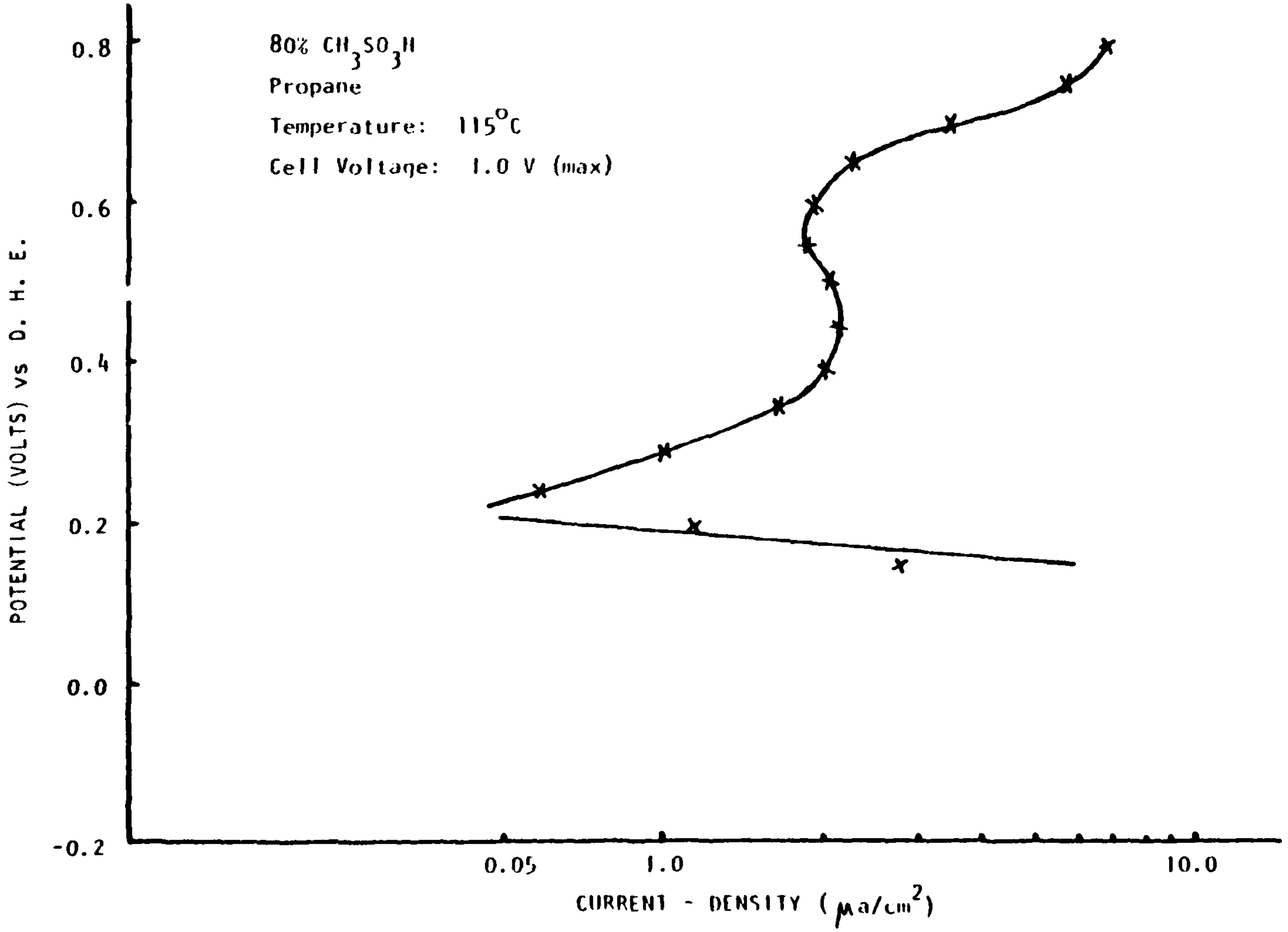


Figure 5 - Polarization Curve for Propane in 80% CH_3SO_3H at 115°C

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 current density-potential data were also obtained in CH_3SO_3H with argon at 80° and 115°C to get background information. The open-circuit potentials with respect to the D.H.E. were found to be 0.32 volt and 0.22 volt at 80°C and 115°C respectively while the cell voltage was a maximum of 0.8 volt. It was observed that the limiting current density was increased with rising temperature. But the limiting current density in CH_3SO_3H with argon appeared to be high, that is, 1.8 μa/cm^2 at 80°C and 3.8 μa/cm^2 at 115°C indicating some sort of adsorption at the electrode surface. The adsorption phenomenon at the electrode surface became more obvious when the low limiting current densities in CH_3SO_3H with propane were compared to argon both at 80° and 115°C. The comparison in the limiting current densities at 115°C is shown in figure 6. This could be due to the adsorption of the electrolyte, impurities, or both. To understand this reaction, cyclic voltammetry and charge balance (galvanostatic) techniques were used.

The typical voltammograms obtained with argon, propane, and hydrogen in methanesulfonic acid at 115°C are shown in figures 7-9. Upon examining the voltammograms obtained with argon and propane in 80% CH_3SO_3H, it was apparent that the hydrogen adsorption and desorption peaks were absent. The voltammograms were highly reproducible even for the large number of cycles. The absence of hydrogen adsorption and desorption peaks in 80% CH_3SO_3H might be the effect of the following:

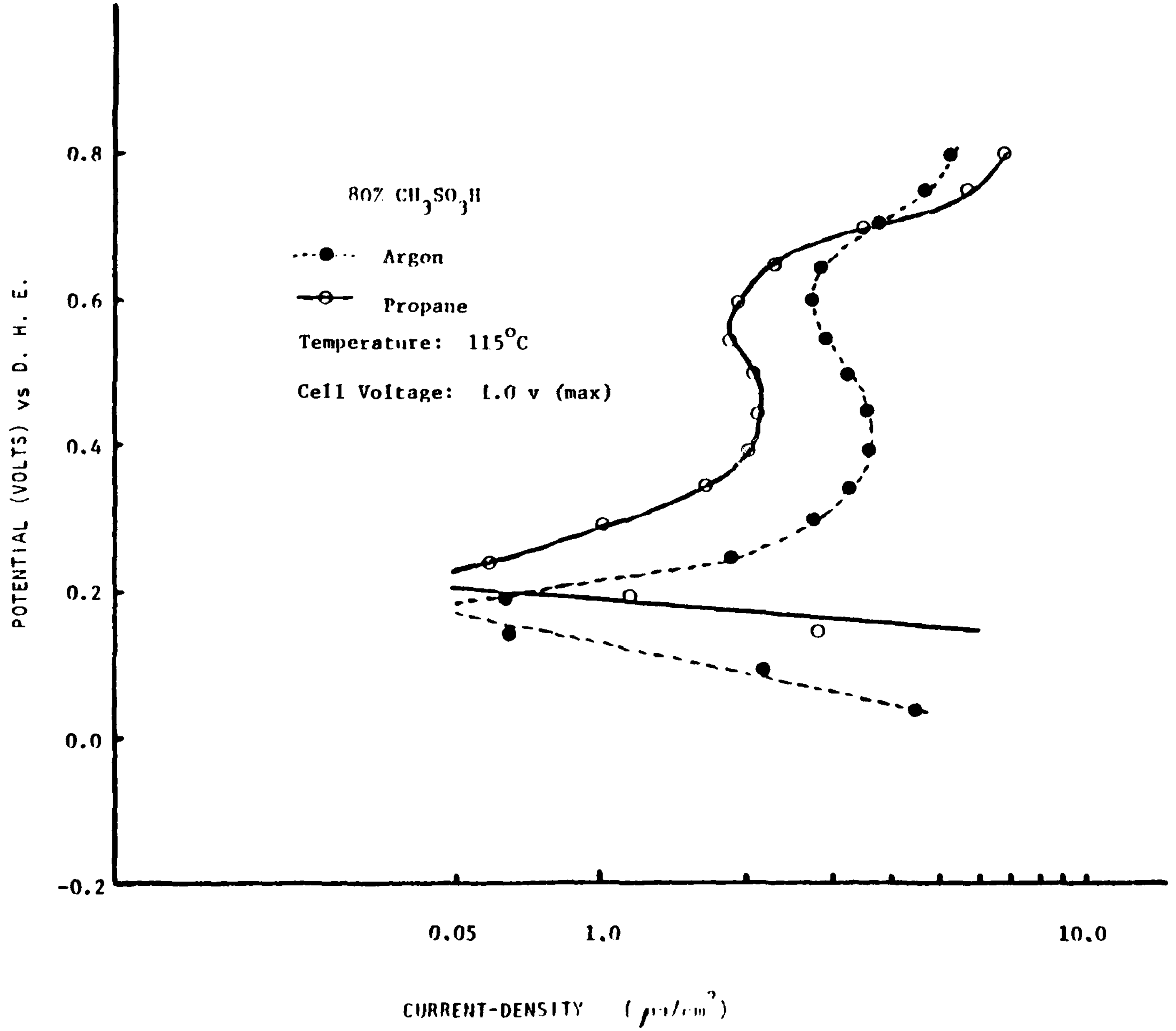


Figure 6 - Polarization Curves for Argon and Propane in 80% CH_3SO_3H at 115°C

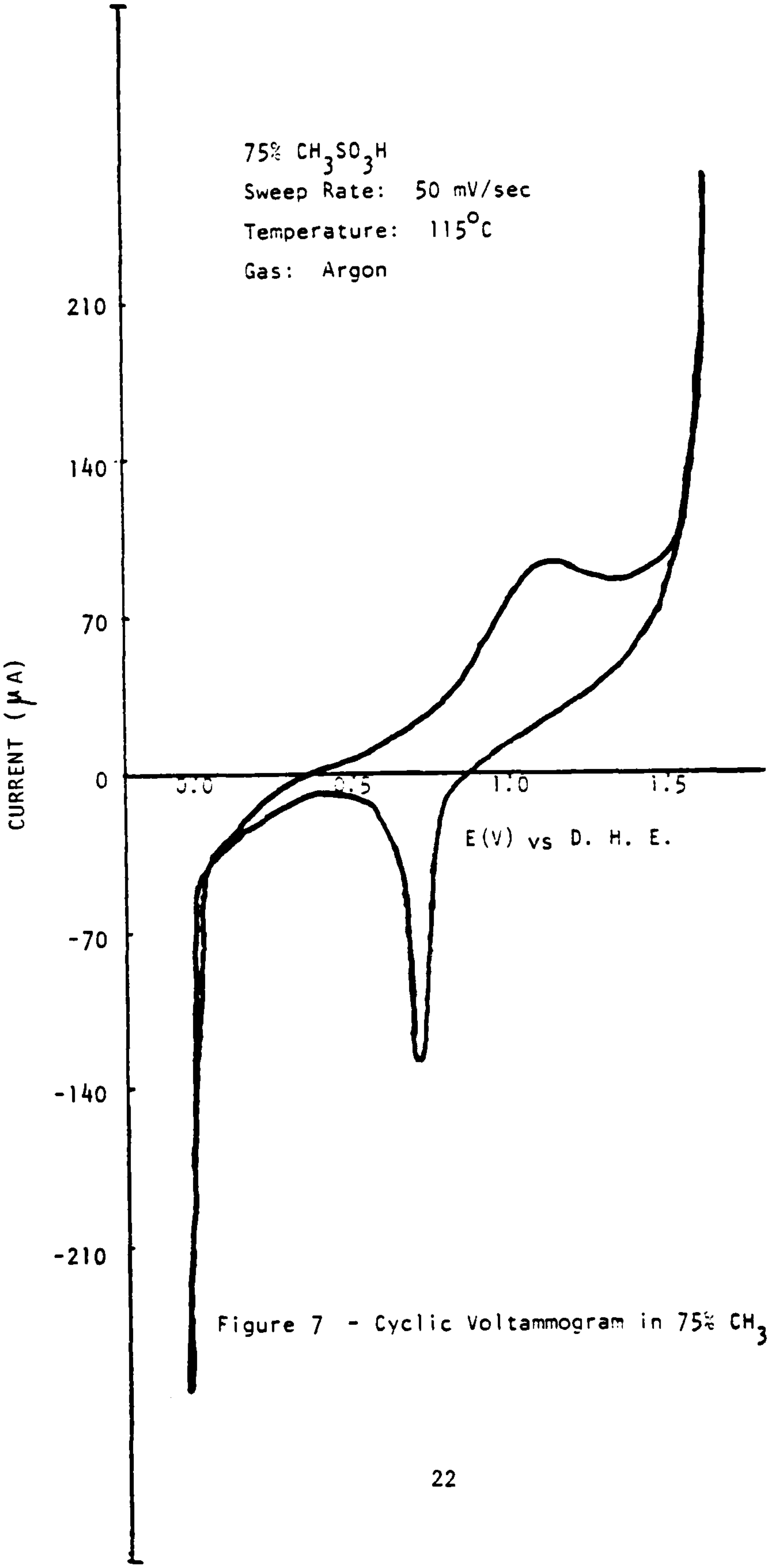


Figure 7 - Cyclic Voltammogram in 75% CH_3SO_3H with Argon

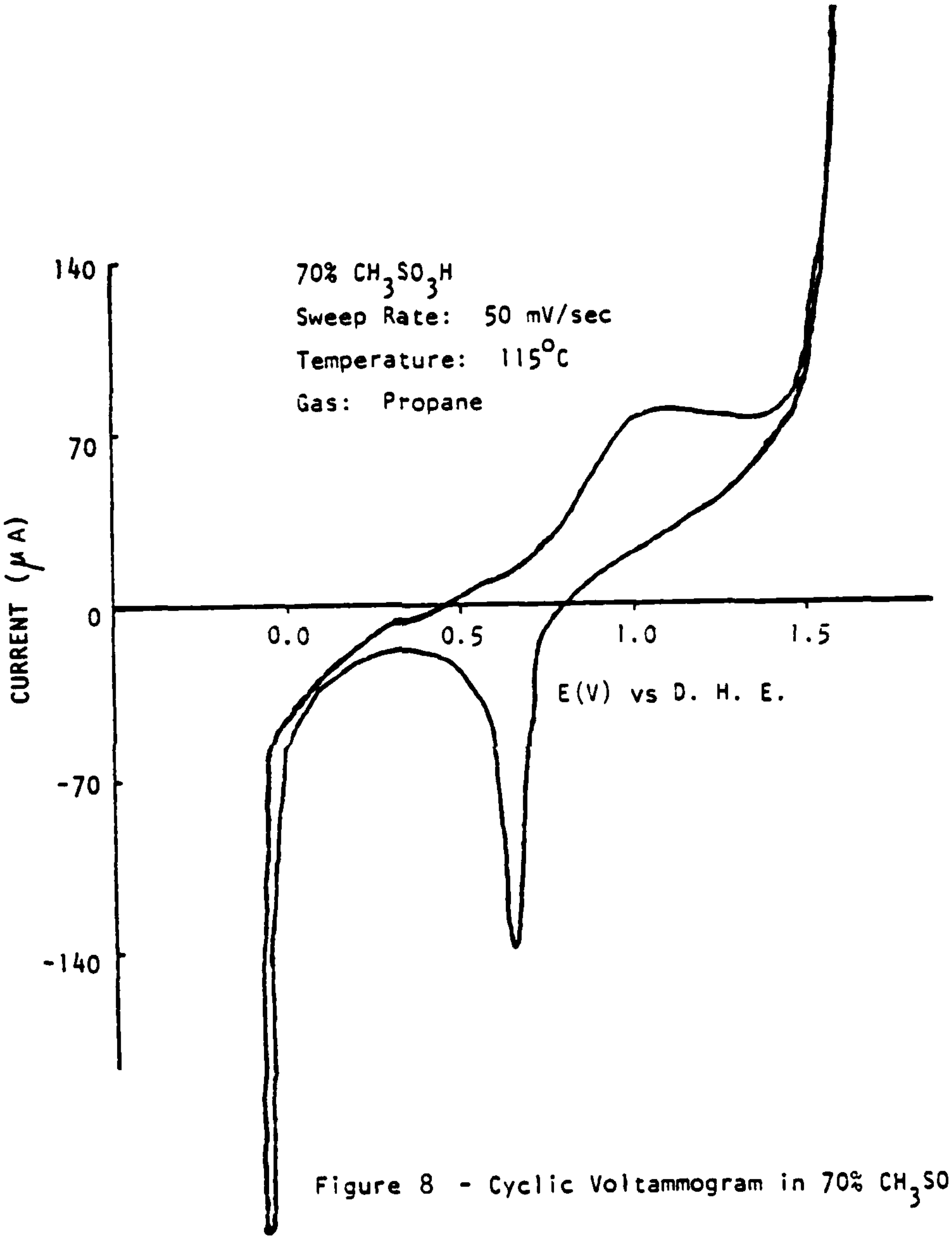


Figure 8 - Cyclic Voltammogram in 70% CH_3SO_3H with propane

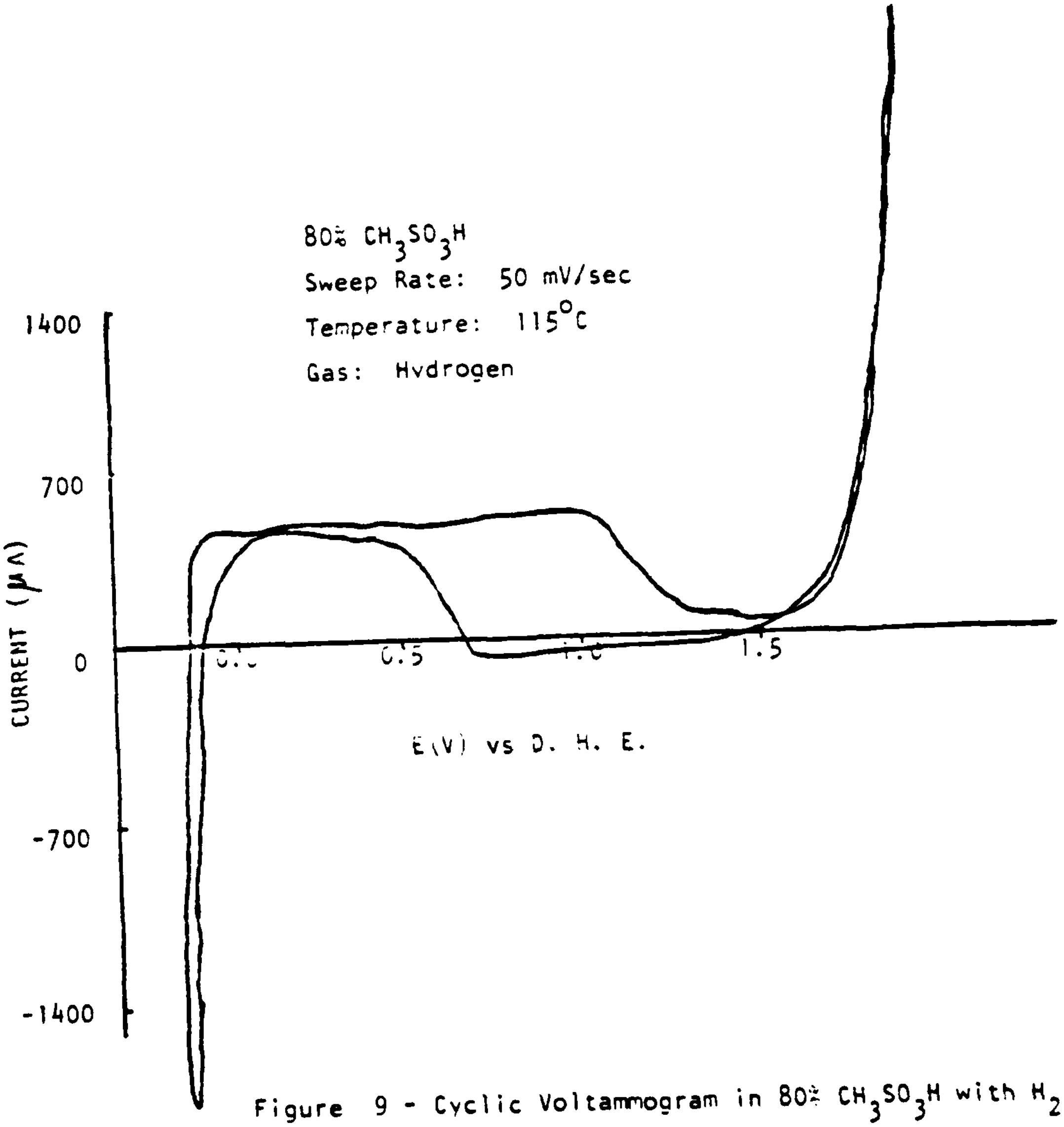


Figure 9 - Cyclic Voltammogram in 80% CH_3SO_3H with H_2

a) CO_2 or/and H_2S 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 10. This voltammogram was consistent with the previous one obtained by Bold and Breiter (16). In this current-potential curve, hydrogen, double layer, and oxygen film regions were well-separated in the positive-going portion of the sweep, that is, the anodic portion. The voltammogram was highly reproducible for the large number of cycles. 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_4 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 10). 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. It should be noted that this technique has been used before to study adsorption; adsorption of benzene on a platinum electrode in 1N H_2SO_4 at 25°C by Gileadi, Duic, and Bockris (17) using the cyclic voltammetry technique;

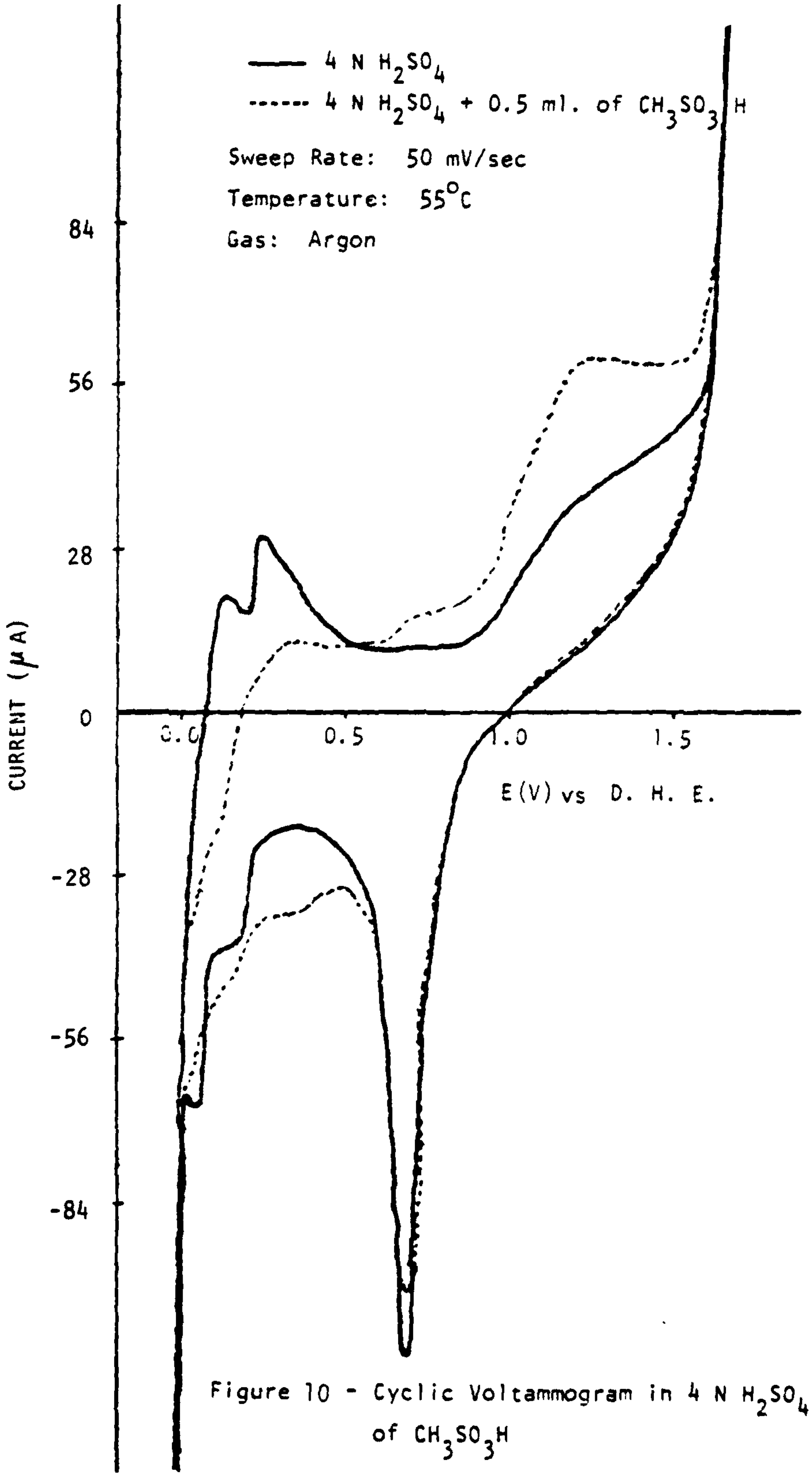


Figure 10 - Cyclic Voltammogram in 4 N H_2SO_4 during the addition of CH_3SO_3H

adsorption of methanol and its intermediates formed during its oxidation, with the cyclic voltammetry technique by others (18-20); adsorption of methanedisulfonic acid (MDSA) and dichloromethanedisulfonic acid (DCMDSA) on platinum by Brummer, et al. (21). The above measurements were checked over a range of sweep rates. A voltammogram obtained without hydrogen and oxygen evolution also showed the disappearance of the hydrogen peaks upon the addition of CH_3SO_3H in 4N H_2SO_4. This voltammogram was obtained without going to the potential higher than 1.35 volt and lower than 0.05 volt. The sweep rate was selected to be 100 mV/sec. At low sweep rates, readsorption from solution could occur whereas at high sweep rates, the oxidation process could be incomplete.

In a separate experiment during the sweeping voltammogram with argon in 4N H_2SO_4, a few drops of TFMSA-MH were added through a syringe into the experimental cell. The resultant voltammogram (figure 11) 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 or other impurities taking place.

The above discussion and the experimental results show that methanesulfonic acid as an electrolyte does support the high current density with hydrogen as previously reported 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 hydrocarbon-air fuel cell.

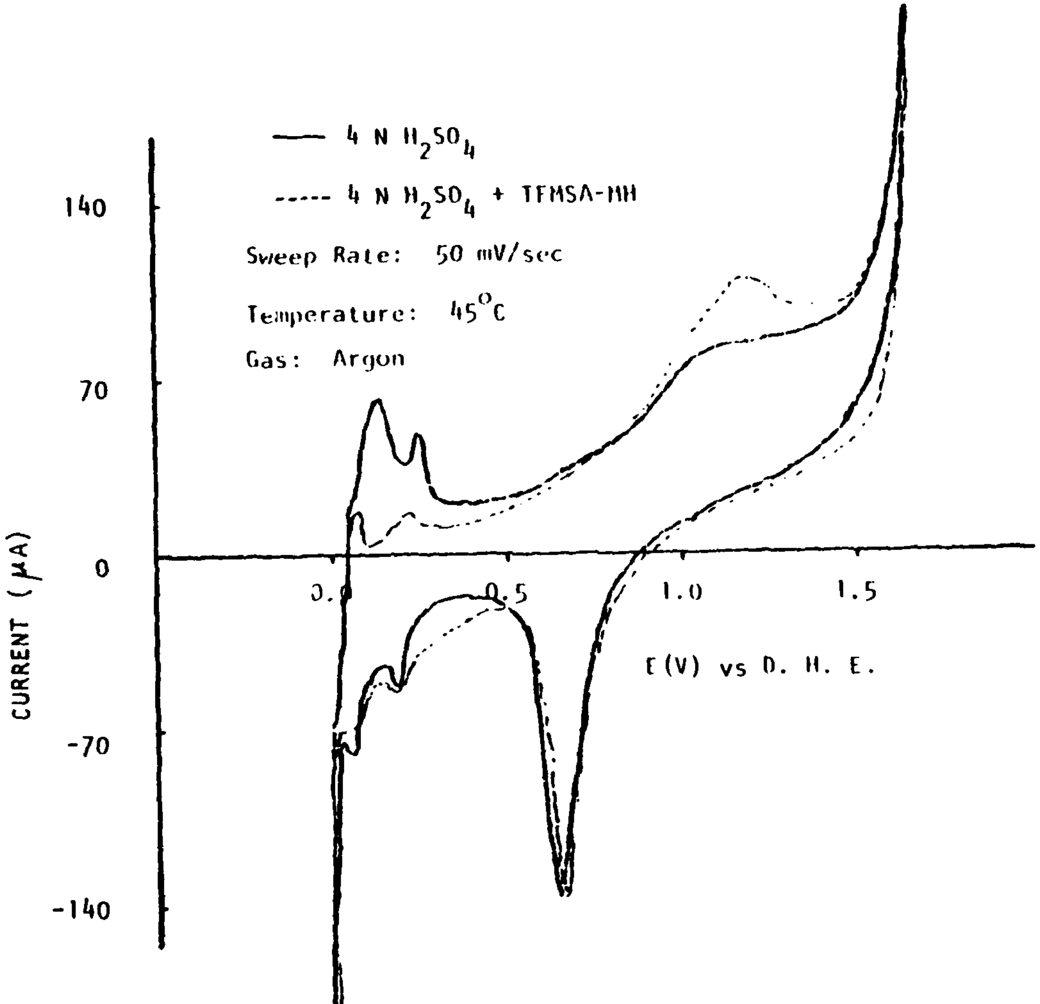


Figure 11 - Cyclic Voltammogram in 4 N H_2SO_4 + few drops of TFMSA-MH

Nuclear Magnetic Resonance and Gas Chromatography Studies of Methanesulfonic Acid

To attempt to explain some of these electrochemical results the methanesulfonic acid was analyzed using ^{1}H nmr, ^{13}C nmr, and gas chromatography techniques. The ^{1}H nmr spectra were recorded employing as-supplied, electrolyzed, and double distilled methanesulfonic acid samples. With all three samples, deuterium oxide (D_2O) was used as a solvent and tetramethylsilane (TMS) as an external standard. The obtained ^{1}H nmr spectra (A, B, and C) over a 1000-HZ range using a 250-sec sweep time at room temperature are shown in figure 12. The peaks' position are recorded in Table II. Peak 1, of course, corresponds to the $-CH_3$ group while Peak II corresponds to the combined effect of the sulfonic group and solvent. Figure 13 shows that when the samples were run after heating them to 60°C, Peak II of spectrum C had shifted to 5.2 ppm. Originally, in figure 12, Peak II of spectrum C was found at 4.2 ppm. The peaks' positions of the spectra A and B in figure 13 remained the same as in figure 12. These positions can be seen in Table III. 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. These spectra are shown in figures 14-16. Not much information was obtained on examining these spectra except for the following two indications:

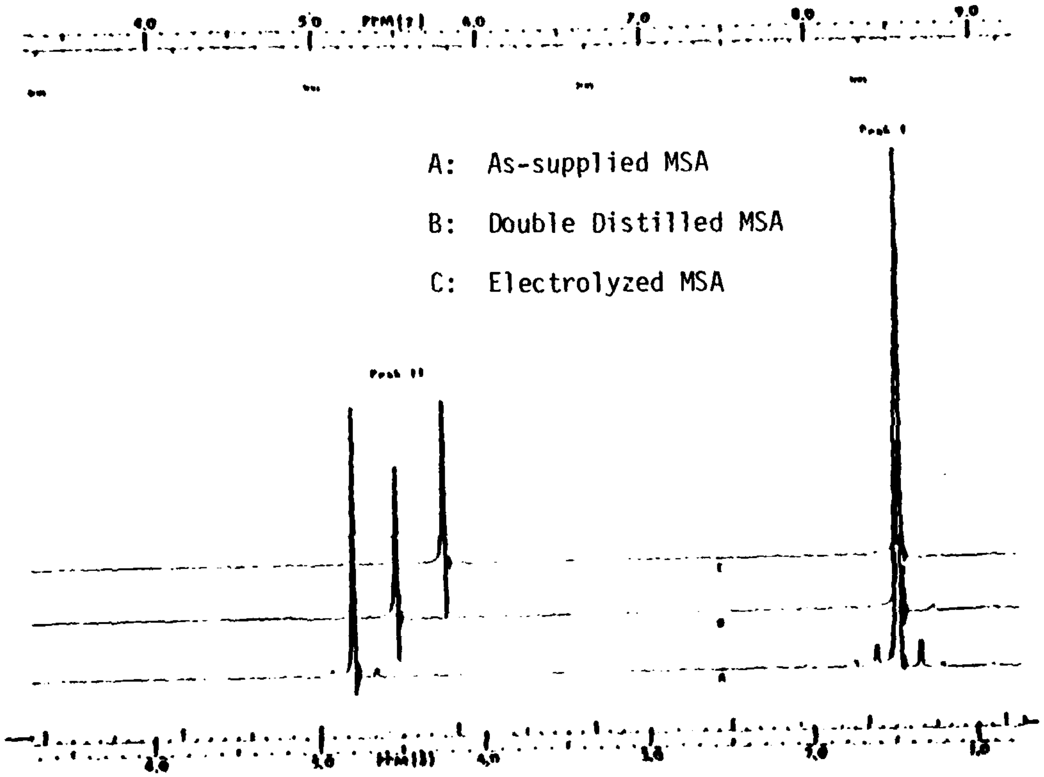


Figure 12 - ^{1}H NMR Spectra Obtained with As-Supplied, Double Distilled and Electrolyzed Methanesulfonic Acid Samples at Room Temperature. Solvent, D_2O; Temp. 25°C; Filter Bandwidth, 4 Hz; R. F. Field, 0.05 mG; Sweep Time, 250 sec.; Sweep Width, 1000 Hz.

TABLE II - THE PEAK POSITIONS OF THE OBTAINED SPECTRA AT ROOM TEMPERATURE

Spectrum #	*Position of Peak I (ppm)	*Position of Peak II (ppm)
A	1.5	4.8
B	1.5	4.55
C	1.5	4.2

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

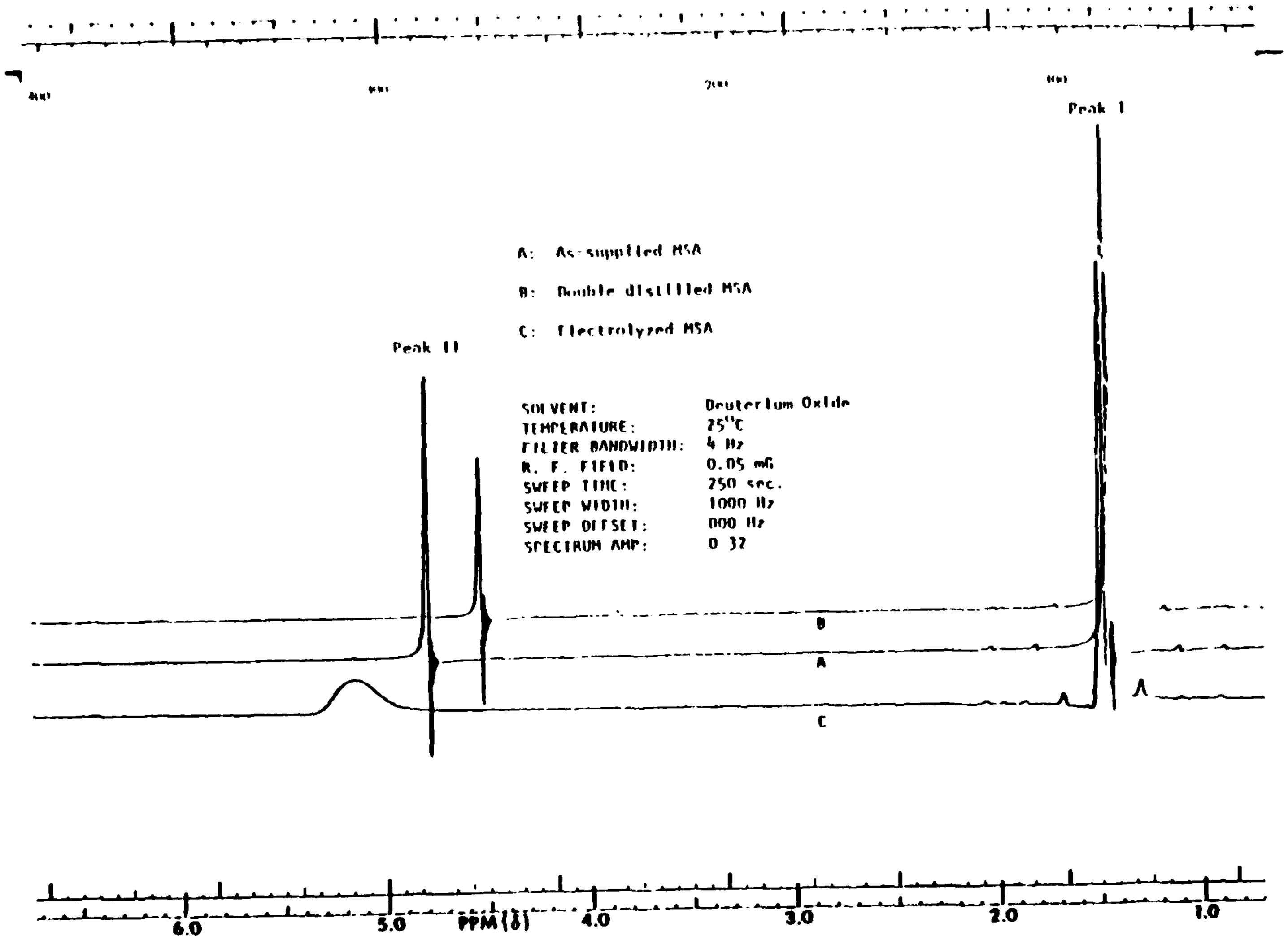
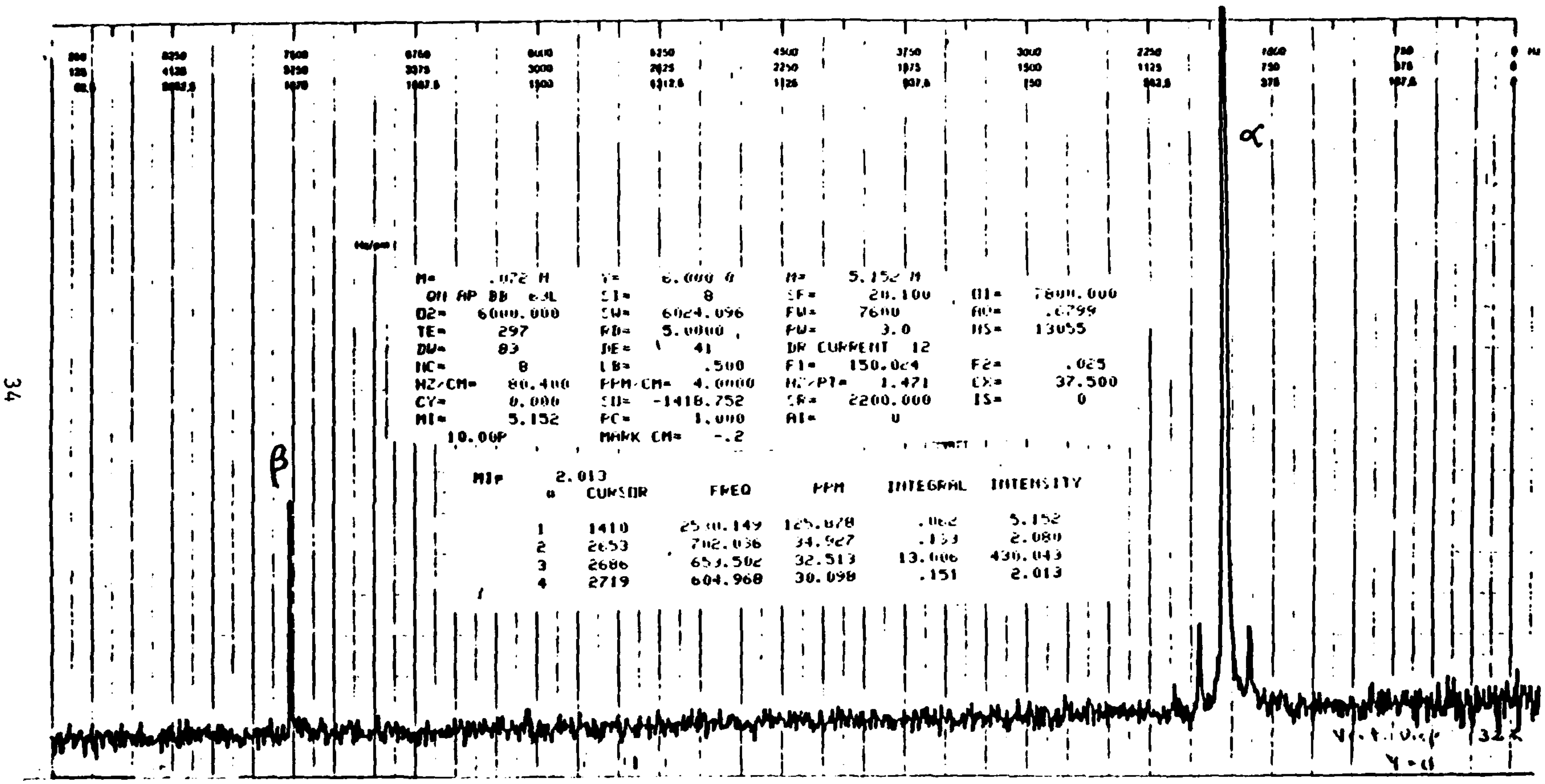


Figure 13 - ^{1}H NMR Spectra Obtained with As-Supplied, Double Distilled and Electrolyzed Methane Sulfonic Acid Samples after heating them to 60°C

TABLE III - THE PEAK POSITIONS OF THE OBTAINED SPECTRA AT 60°C

Spectrum #	*Position of Peak I (ppm)	*Position of Peak II (ppm)
A	1.5	4.8
B	1.5	4.55
C	1.5	5.2

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



```
M=      .072 M      Y=      6.000 6       M=    5.152 M
 ON AP BB  e.JL     SI=         8         SF=      20.100   O1=    7600.000
D2=   6000.000      SW=    6024.096       FW=    7600       AQ=     .6799
TE=     297         RD=    5.0000 ,       PW=       3.0     NS=    13055
DW=     83          DE=   \  41           DR CURRENT  12
NC=      8          LB=        .500       F1=   150.024     F2=       .025
HZ/CM=   80.400     PPM/CM=  4.0000       HZ/PT=    1.471   CX=     37.500
CY=      0.000      SD=   -1418.752       SR=   2200.000    IS=        0
MI=      5.152      PC=       1.000       AI=        0
   10.00P           MARK CM=    -.2

      MI=     2.013
            #  CURSOR       FREQ      PPM     INTEGRAL  INTENSITY

            1   1410     2530.149  125.878      .062      5.152
            2   2653      702.036   34.927      .133      2.080
            3   2686      653.502   32.513    13.006    430.043
            4   2719      604.968   30.098      .151      2.013
```

Figure 14 - ^{13}C nmr spectrum of as-supplied methane sulfonic acid sample

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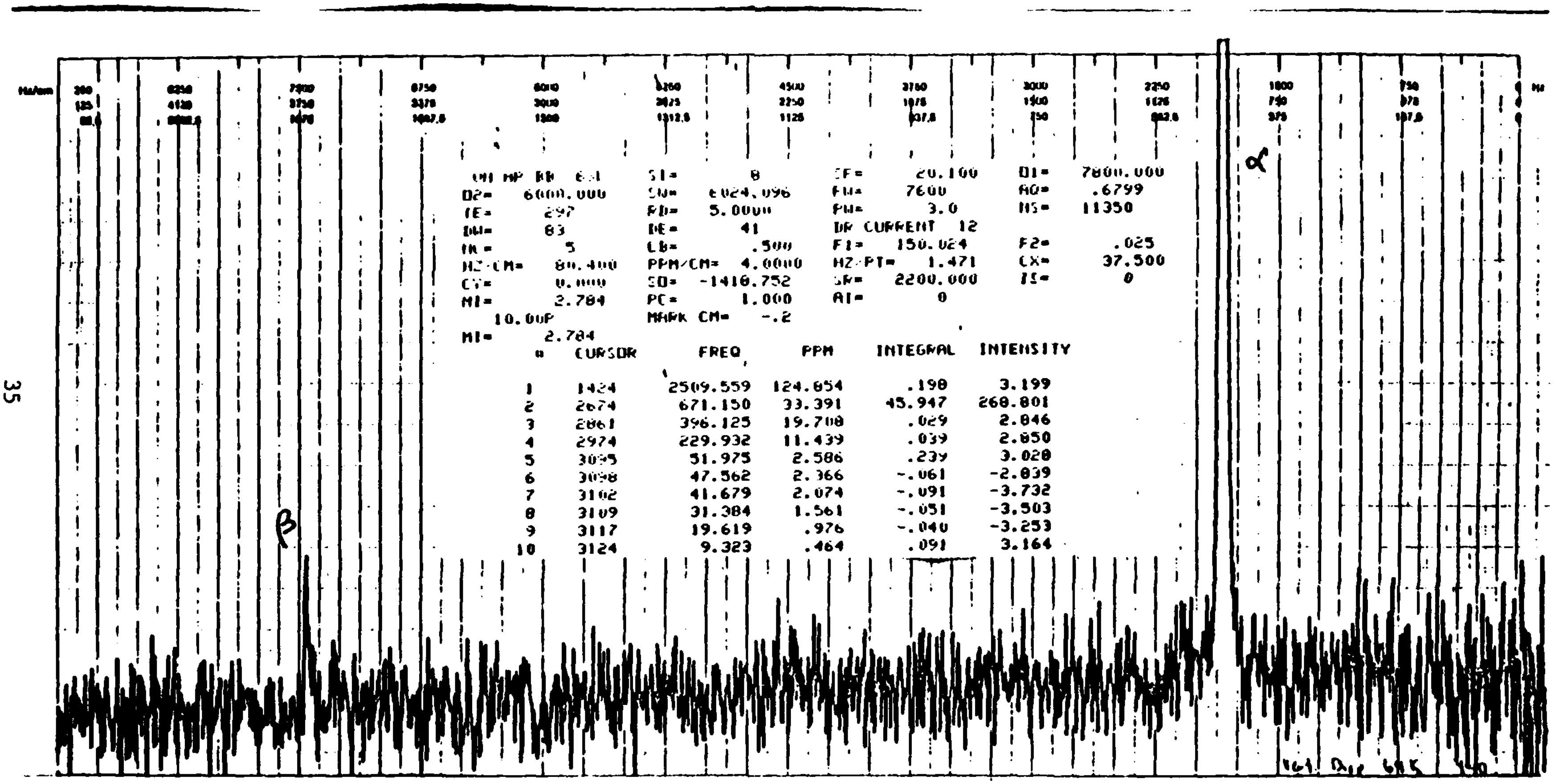
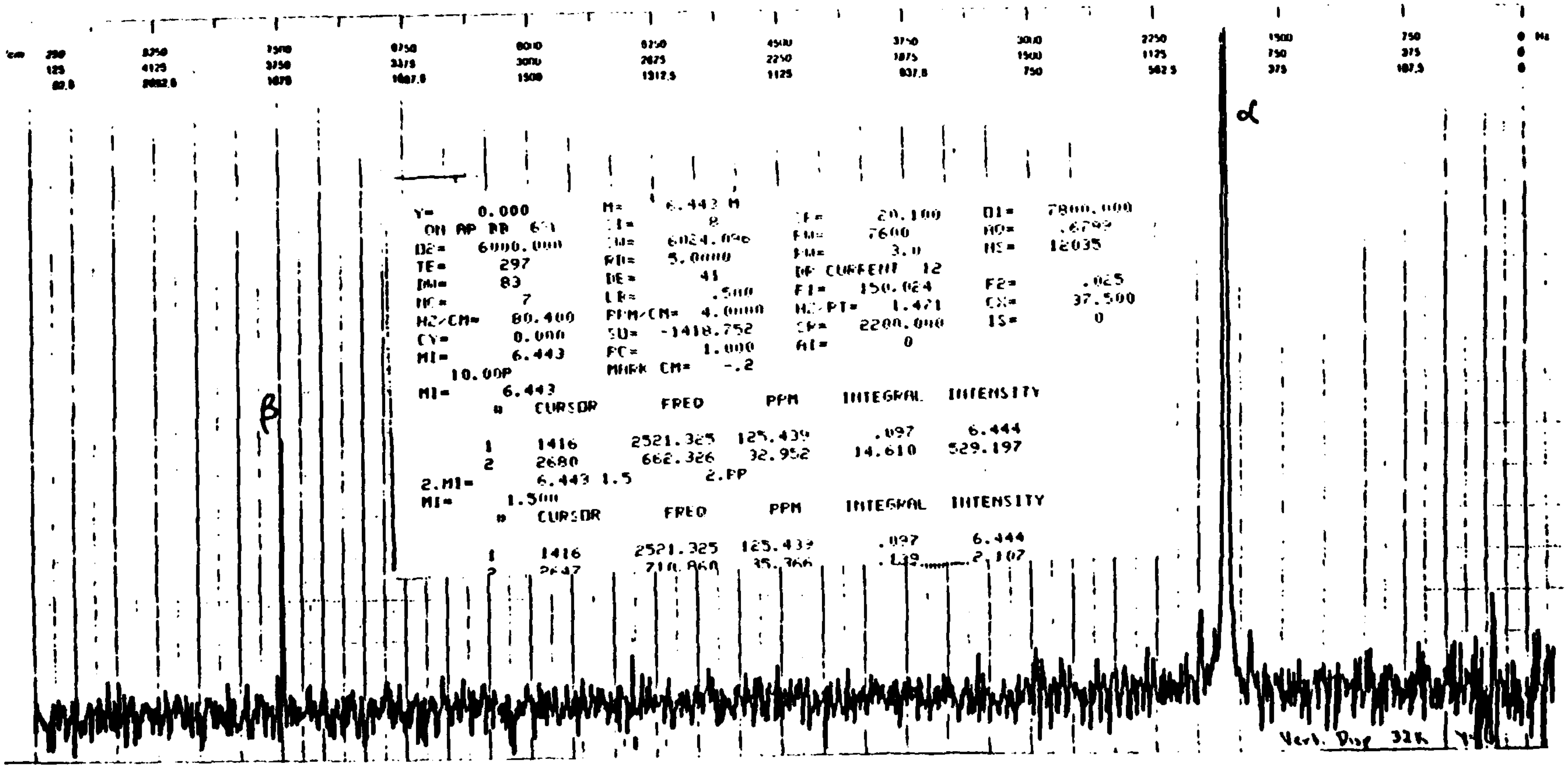


```
 UHI MP RR  6.1    SI=         8       SF=     20.100   O1=   7800.000
O2=   6000.000     SW=   6024.096      FW=    7600      AQ=     .6799
TE=      297       RD=   5.0000        PW=       3.0    NS=   11350
DW=       83       DE=       41        DR CURRENT  12
TN =       5       LB=         .500    F1=   150.024    F2=        .025
HZ/CM=    80.400   PPM/CM=  4.0000     HZ/PT=    1.471  CX=     37.500
CY=        0.000   SD=  -1416.752      SR=   2200.000   IS=         0
MI=        2.784   PC=       1.000     AI=        0
   10.00P          MARK CM=    -.2
MI=       2.784
      #   CURSOR       FREQ       PPM     INTEGRAL  INTENSITY

      1   1424     2509.559   124.654       .198      3.199
      2   2674      671.150    33.391     45.947    268.801
      3   2861      396.125    19.708       .029      2.846
      4   2974      229.932    11.439       .039      2.850
      5   3095       51.975     2.586       .239      3.020
      6   3098       47.562     2.366      -.061     -2.839
      7   3102       41.679     2.074      -.091     -3.732
      8   3109       31.384     1.561      -.051     -3.503
      9   3117       19.619      .976      -.040     -3.253
     10   3124        9.323      .464       .091      3.164
```

Figure 15 - ^{13}C nmr spectrum of the electrolyzed methane sulfonic acid sample



```
Y=     0.000          M=     6.443 M      IF=      20.100     DI=    7800.000
 ON AP RR  6?1        II=       8          FW=     7600        MO=     .6792
DZ=   6000.000        IW=    6024.096      FW=        3.0      NS=    12035
TE=     297           RD=    5.0000       DF CURRENT  12
DM=     83            DE=       41        F1=   150.024       F2=      .025
NC=       7           LB=        .500     HZ/PT=    1.471     CX=    37.500
HZ/CM=   80.400       PPM/CM=  4.0000     SP=   2200.000     IS=       0
CY=       0.000       SU=   -1418.752     AI=        0
MI=       6.443       FC=       1.000
   10.00P             MARK CM=    -.2
MI=      6.443
       #   CURSOR        FREQ       PPM     INTEGRAL   INTENSITY

       1    1416      2521.325  125.439      .097       6.444
       2    2680       662.326   32.952    14.610     529.197
2.MI=       6.443 1.5             2.PP
MI=       1.500
       #   CURSOR        FREQ       PPM     INTEGRAL   INTENSITY

       1    1416      2521.325  125.439      .097       6.444
       2    2647       710.860   35.366      .139       2.107
```

13 of double distilled methane sulfonic acid sample

1. The presence of an impurity (peak β in all three spectra) in the samples,
2. The distance between peak α and peak β differs by 22 ppm in the electrolyzed and as-supplied methanesulfonic acid samples.

In ^{13}C nmr, the spectrum was run at room temperature. It was decided to analyze the electrolyte samples 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 17, 18, and 19 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 17 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 19. The second peak in the double 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

```
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
```

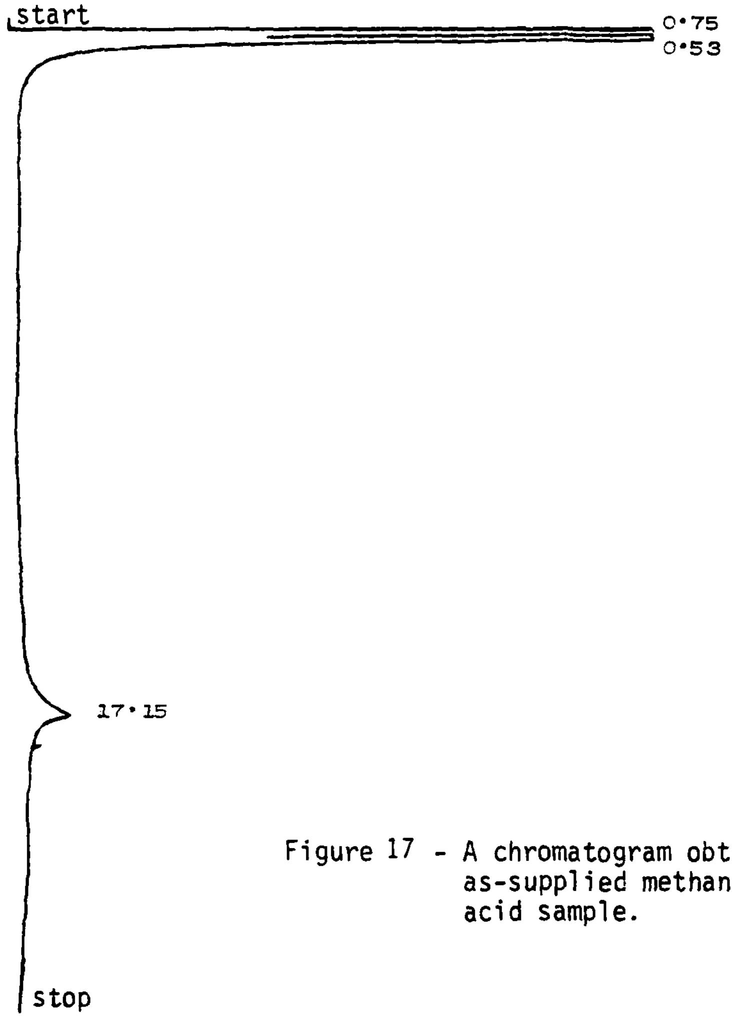
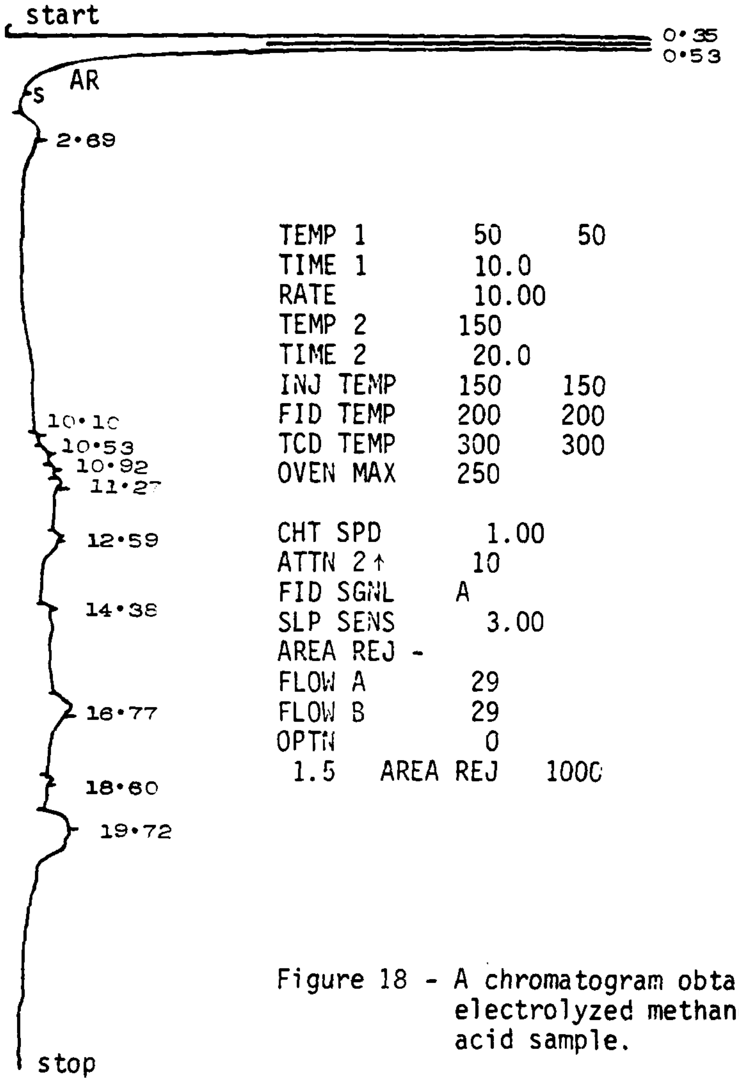


Figure 17 - A chromatogram obtained with as-supplied methane sulfonic acid sample.

```
h  5830A
 F
AREA %

 RT        AREA      AREA %

17.15     101100    100.000
```



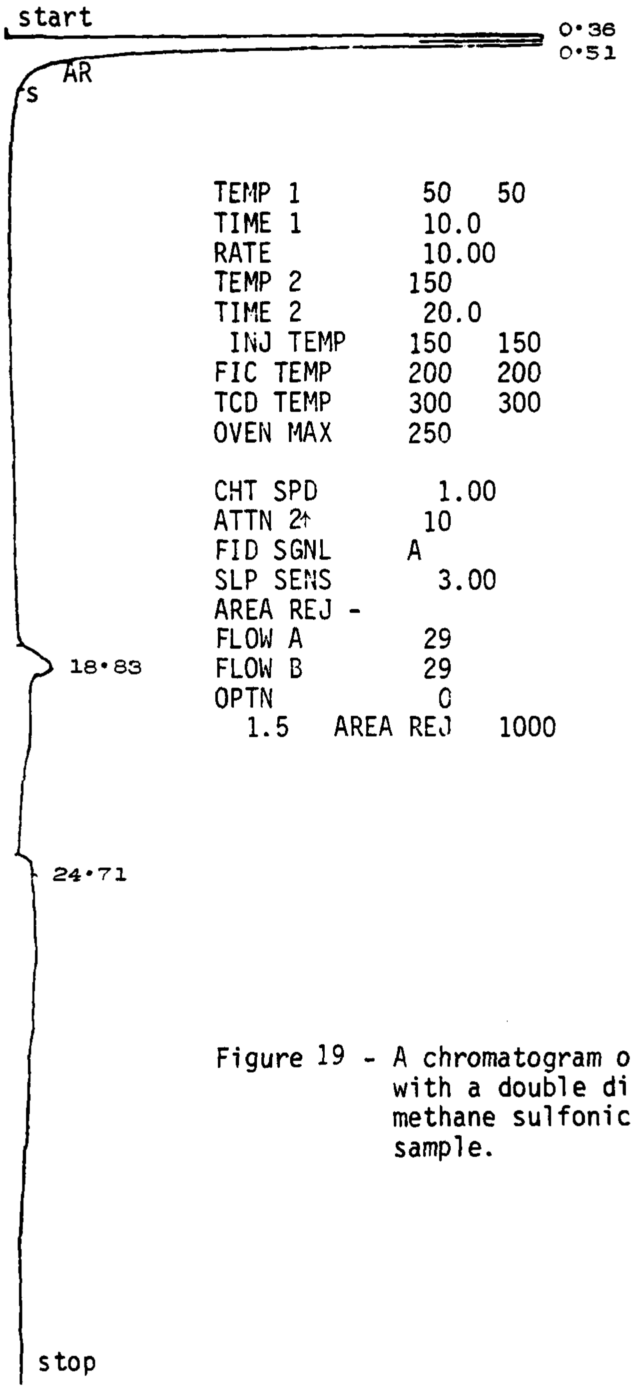
```
TEMP 1         50      50
TIME 1          10.0
RATE            10.00
TEMP 2         150
TIME 2          20.0
INJ TEMP       150     150
FID TEMP       200     200
TCD TEMP       300     300
OVEN MAX       250

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 18 - 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 19 - 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
```

different peaks recorded in figures 17, 18, and 19 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.

Electrochemical Behavior of Hydrogen and Propane in Ethane Sulfonic Acid

The ethane sulfonic acid, as received, was diluted to 70% with conductivity water. Polarization curves were obtained with hydrogen, propane, and argon at 80°, 115°, and $135^{\circ}C$. The $115^{\circ}C$ curves are shown in figure 20. 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 $135^{\circ}C$ while, with propane, 3.0 $\mu a/cm^2$ at $80^{\circ}C$. Ethane sulfonic 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

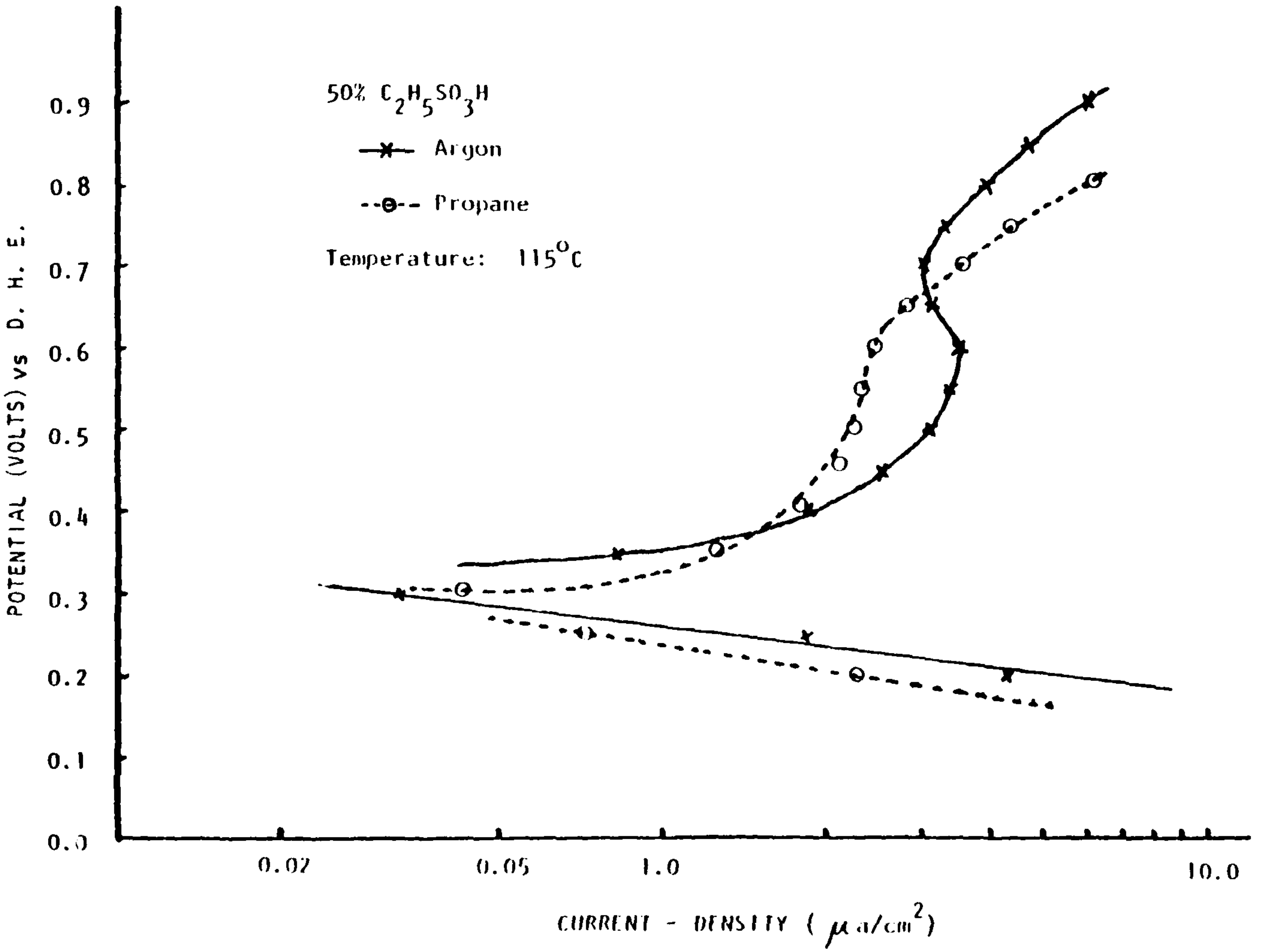


Figure 20 - Polarization Curves for Argon and Propane in 50% $C_2H_5SO_3H$ at 115°C

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 μa/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 ethane sulfonic acid on the platinum electrode surface. The voltammograms obtained in 50% ESA with hydrogen, propane and argon at 115°C are shown in figures 21-23. The voltammogram with argon 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 ethane sulfonic acid were added to the sulfuric acid solution during the scanning. The sweep rate was 50 mV/sec. The resultant voltammogram after the addition of ethane sulfonic acid is shown in figure 24. In this voltammogram, the disappearance of hydrogen peaks and the increase in the anodic charge indicated that ethane sulfonic acid has 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.

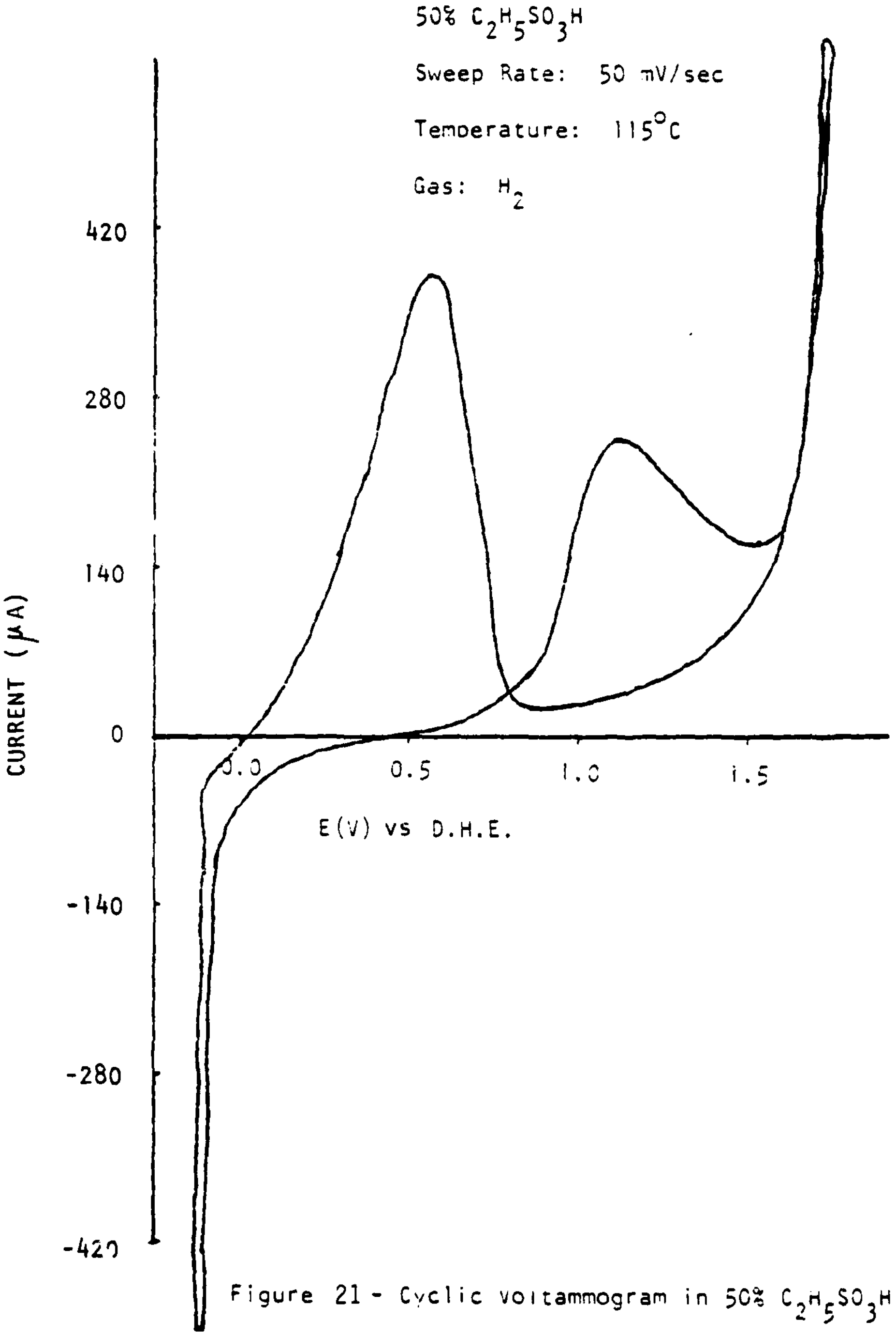


Figure 21 - Cyclic voltammogram in 50% $C_2H_5SO_3H$ with H_2

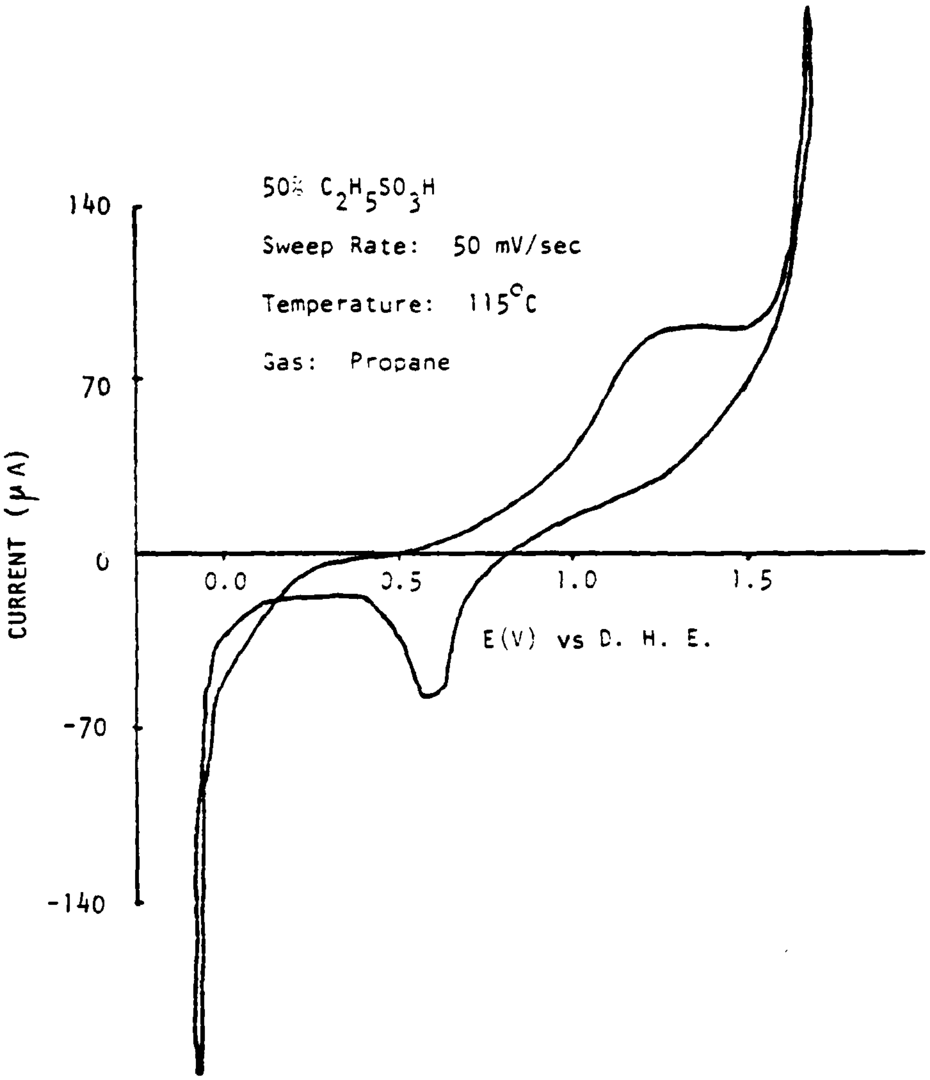


Figure 22 - Cyclic Voltammogram in 50% $C_2H_5SO_3H$ with Propane

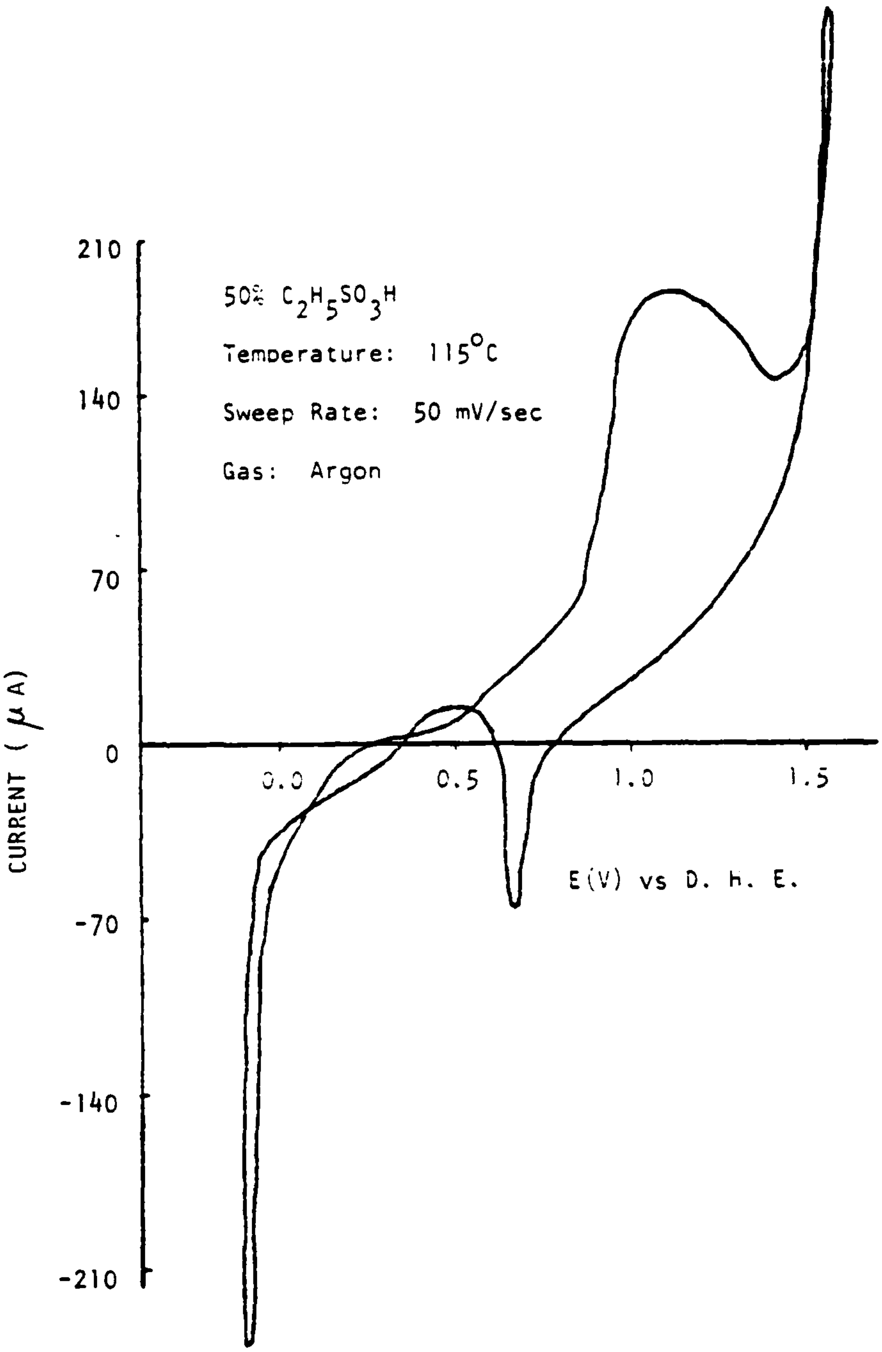


Figure 23 — Cyclic Voltammogram in 50% $C_2H_5SO_3H$ with argon

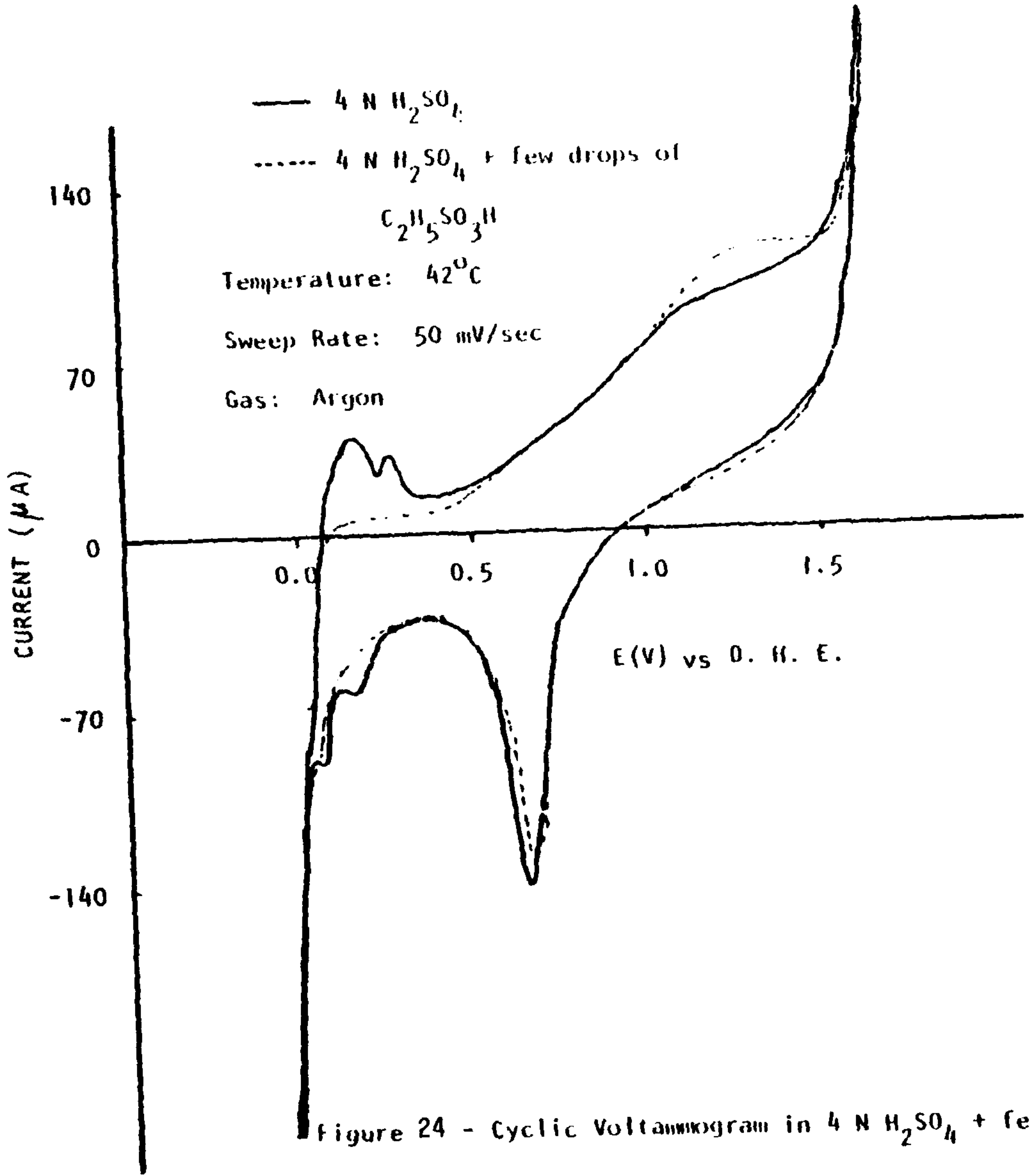


Figure 24 - Cyclic Voltammogram in 4 N H_2SO_4 + few drops of $C_2H_5SO_3H$

The measured conductance of the 80% ethane sulfonic acid -H_2O solution at 25°C was measured as 5.14×10^{-3} ohm^{-1} cm^{-1} which is also not promising.

From measurements of the electro-oxidation of hydrogen and propane in ethane sulfonic 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 the H_2-air fuel cell or for the hydrocarbon-air fuel cell.

Electrochemical Behavior of Hydrogen in Sulfoacetic Acid

During the polarization studies, it was observed that sulfoacetic acid supported a higher current than that supported by MSA or TFMSA-MH; that is, 246 $\mu a/cm^2$ with hydrogen at 90°C. But the impure acid received from the supplier does not seem to be useable as an electrolyte in the fuel cell. An attempt was made to purify this acid without any success. The open circuit potential and the cell voltage values were -0.015 volt and 0.8 volt (maximum) respectively. The concentration of the acid used was approximately 30% having a light reddish brown color.

The limiting current density with argon in sulfoacetic acid was found to be 4.4 $\mu a/cm^2$ at 90°C and the open circuit potential and the cell voltage values were 0.3 volt and 0.9 volt (maximum) respectively. The polarization curve is shown in figure 25 while figure 26 shows the voltammogram with argon in sulfoacetic acid at 90°C. 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 50mV/sec. From the voltammogram obtained with argon in 30% sulfoacetic acid at 90°C, the following features could be noticed:

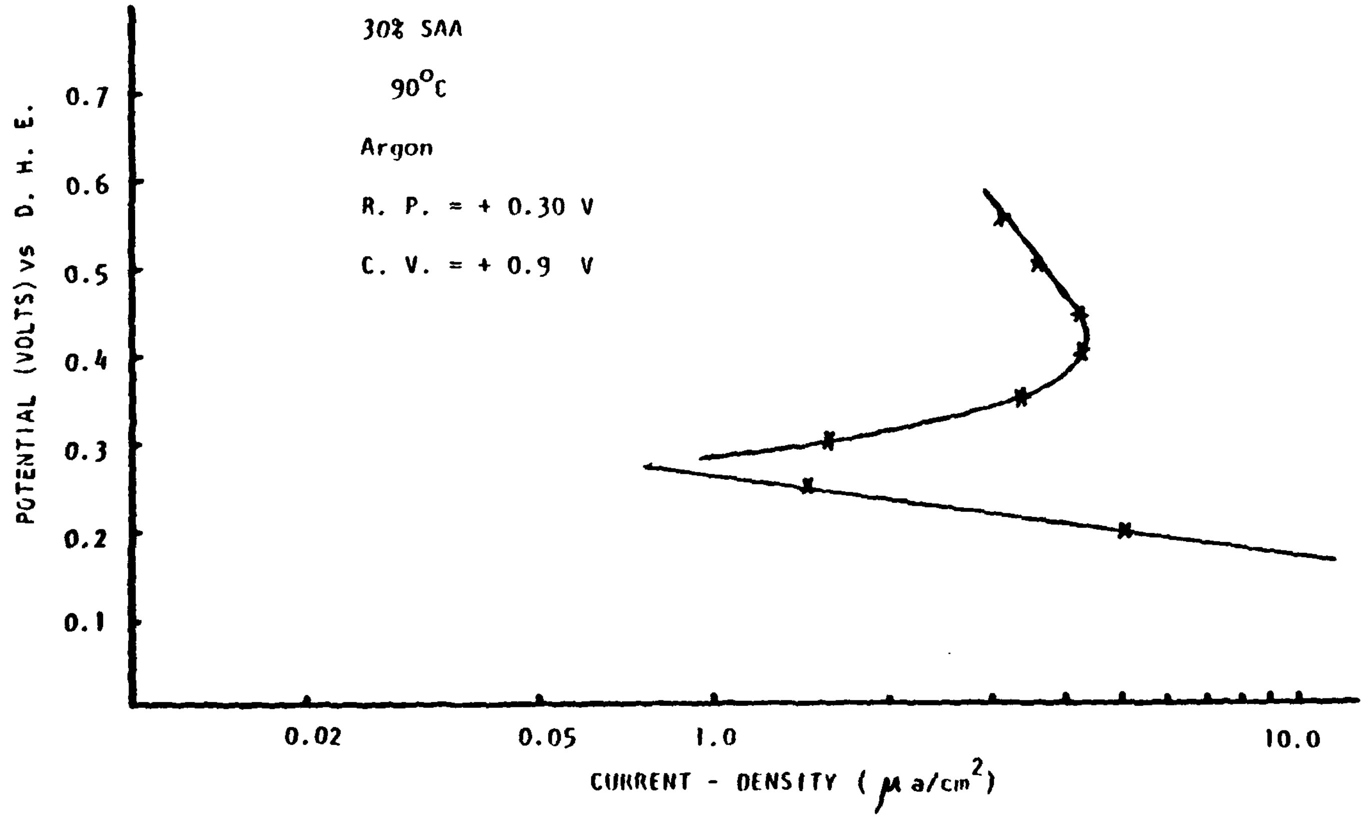
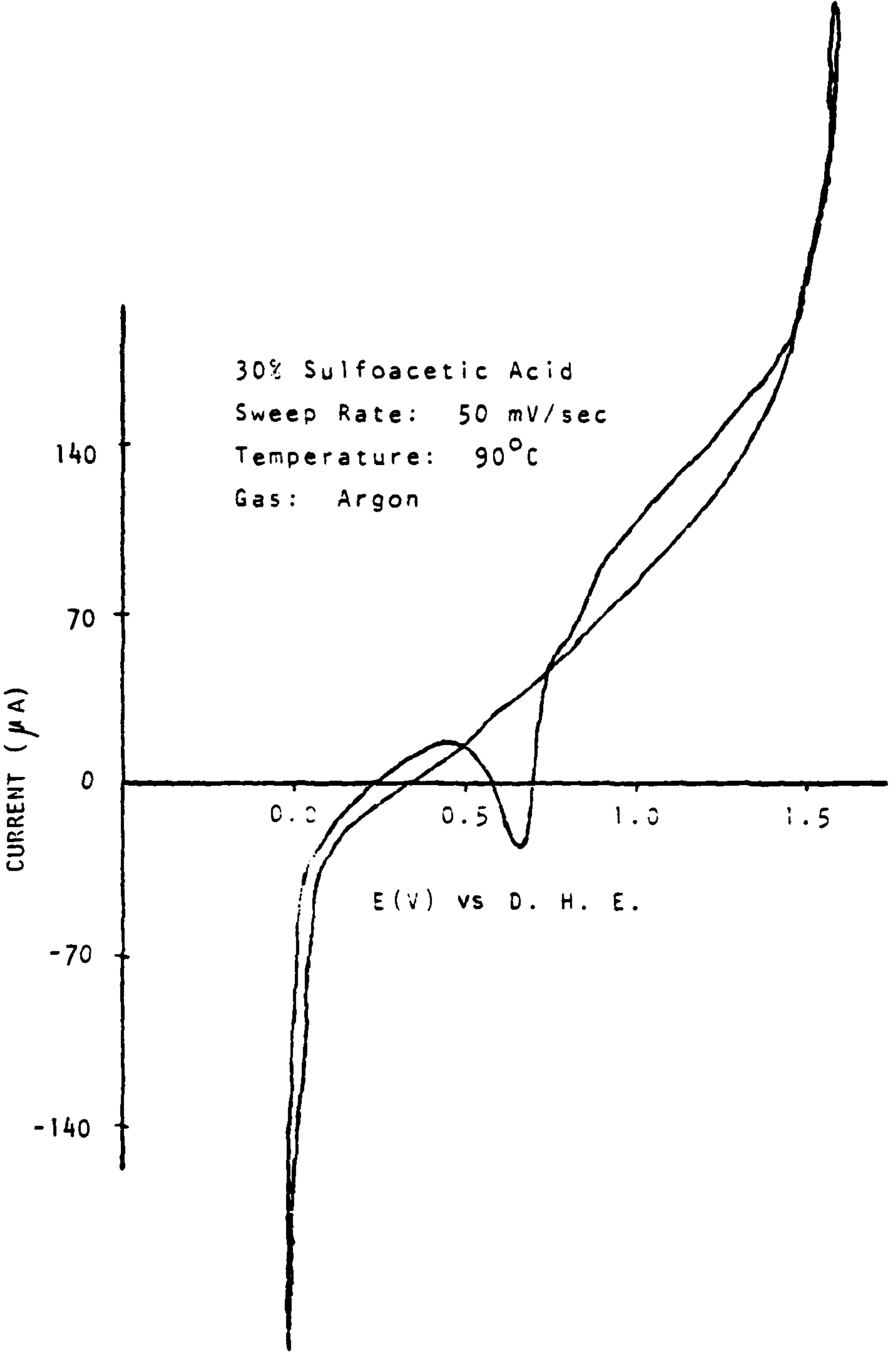


Figure 25 - Polarization Curve for Argon in 30% HSO_3CH_2COOH at 90°C



30% Sulfoacetic Acid
Sweep Rate: 50 mV/sec
Temperature: 90°C
Gas: Argon

Figure 26 - Cyclic Voltammogram in
30% Sulfoacetic Acid with Argon

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 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.

One thing which is obvious from the polarization study is 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 $90^{o}C$ is striking.

The limiting current density obtained in sulfoacetic acid with argon at 90°C was 4.4 $\mu a/cm^2$ whereas with hydrogen, it was 246 $\mu a/cm^2$. 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 4.4 $\mu a/cm^2$. Although the 4.4 $\mu a/cm^2$ current density with argon is usually considered high, it might be due to the presence of the impurities in the acid.

V. Conclusions

The three electrolytes are compared by tabulating the limiting current densities achieved with hydrogen, argon and propane. This comparison is made in table IV for 80° and 115°C

The conclusions with respect to the individual electrolytes are as follows.

Methanesulfonic 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 practical grade (95%) methanesulfonic acid darkens during electrolysis probably due to further decomposition.

The cyclic voltammetry studies indicate that methanesulfonic acid is strongly adsorbed on the platinum electrode surface.

Analysis of this 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.

TABLE IV - SUMMARY OF THE LIMITING CURRENT DENSITY VALUES OBTAINED IN DIFFERENT ELECTROLYTES

Electrolyte	The Limiting Current Densities ($\mu a/cm^2$)					
	Hydrogen		Propane		Argon	
	80°C	115°C	80°C	115°C	80°C	115°C
Methane Sulfonic Acid CH_3SO_3H	5.0	225.0	1.7	2.3	1.9	3.8
Ethane Sulfonic Acid $C_2H_5SO_3H$	7.0	9.0	3.0	2.8	3.5	4.0
Sulfoacetic Acid HO_3SCH_2COOH	-	246.0*	-	-	-	4.4*

*At 90°C

The polarization studies with ethane sulfonic acid indicate that this acid as an electrolyte does not support high current densities either with H_2 or propane. It has shown no promise with either of the fuels.

Ethane sulfonic acid is also adsorbed on the platinum electrode surface.

It is, therefore, concluded that the sulfonic acids such as CH_3SO_3H or CH_3-CH_2-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.

Sulfoacetic Acid

The as-supplied sulfoacetic acid is dark black and in semi-solid form. 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 trifluoromethane sulfonic acid monohydrate. However, the presently available acid which is apparently highly contaminated does not appear to be useable as an electrolyte in a fuel cell. This acid cannot be purified by conventional techniques; therefore, some other method (unknown to us) must be adopted.

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Buffalo, NY 14214

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