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AQUEOUS TRIFLUOROMETHANE SULFONIC ACID FUEL CELLS.(U)
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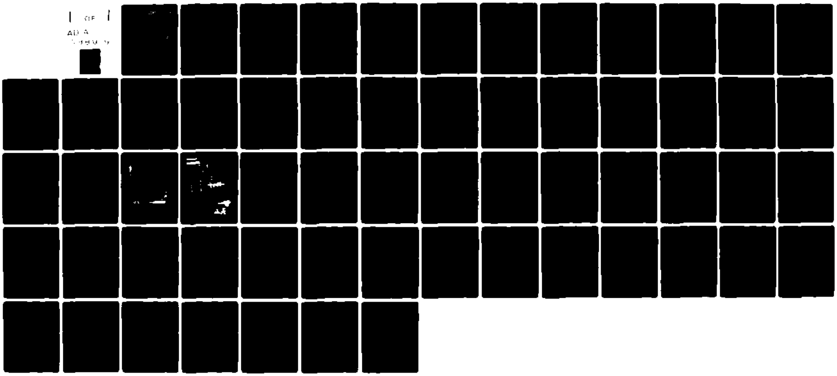

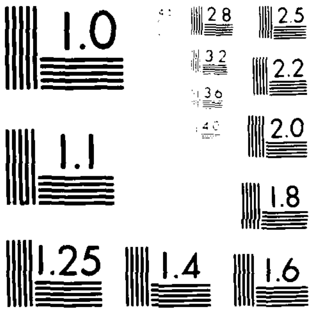

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AQUEOUS TRIFLUOROMETHANESULFONIC ACID FUEL CELLS

FINAL TECHNICAL REPORT

February 1981

Prepared by:

Michael George

Prepared for:

U.S. ARMY MOBILITY EQUIPMENT
RESEARCH AND DEVELOPMENT COMMAND
Fort Belvoir, VA 22060

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Hydrogen-air fuel cells were successfully operated with 6M TFMSA as the electrolyte at temperatures as high as 90°C. The fuel cell performance was enhanced over similarly loaded electrodes in H_3PO_4 due to the apparent improved kinetics for the oxygen reduction reaction. A variety of unsupported and supported Pt electrocatalysts could be effectively utilized. Subscale TFMSA fuel cells could be operated stably for periods as long as 3000 hours. Evaluation of TFMSA electrolytes in stack configurations was encouraging as acceptable initial performance levels were demonstrated.

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1.0 INTRODUCTION

This is the Final Technical Progress Report for Contract No. DAAK70-78-C-0103 entitled "Aqueous Trifluoromethanesulfonic Acid Fuel Cells". The work, performed between June 1978 and October 1980, is summarized within this report.

Phosphoric acid, currently recognized as the most practical acid fuel cell electrolyte, is preferred since it allows fuel cells to operate at moderately high temperatures (in the range of 150 to 200°C). At these temperatures, phosphoric acid resists decomposition and exhibits low volatility characteristics. Although it is an exceptionally stable electrolyte, phosphoric acid possesses other characteristics which hinder its application in an actual fuel cell. It is not a particularly strong acid; therefore it has less ionic conductivity than more fully ionized electrolytes such as sulfuric acid. In addition, the anion of phosphoric acid is believed to readily adsorb on noble metal catalysts which impedes the electrochemical kinetics in the fuel cell. Since the acid fuel cell is nearly always controlled by the rate of oxygen reduction reaction, this suspected poisoning effect associated with phosphoric acid tends to severely limit its efficiency in the fuel cell.

Various solutions (including some common acids such as sulfuric and perchloric) which have less tendency to restrict the kinetics of the electrochemical reactions have been proposed for use in fuel cells. Many of these acids, however, are susceptible to decomposition, even at moderate fuel cell temperatures. In 1973, a promising, new family of potential fuel cell electrolytes was revealed: the perfluoroalkane sulfonic acids.[3] Subsequent studies have suggested that the monohydrate of trifluoromethanesulfonic acid (TFMSA) would be a viable fuel cell electrolyte since its oxygen reduction reaction was considerably more enhanced than phosphoric acid's.[4]

TFMSA, commonly referred to as triflic acid, is sometimes described as one of the strongest known acids. In the pure form, however, it is reported to have an extremely low ionic conductivity.[9] The boiling point of the pure acid is only 162°C which indicates that the pure acid would readily vaporize at moderate fuel cell temperatures. The monohydrate of TFMSA was initially attractive since it appeared to be a constant boiling point mixture with a normal boiling point of 217°C. This would suggest that the monohydrate was a maximum boiling point azeotrope and subsequently the composition with the lowest total vapor pressure.

An extensive evaluation of the merits of TFMSA monohydrate was conducted during Contract No. DAAK02-75-C-0045, entitled "New Materials for Fluorosulfonic Acid Electrolyte Fuel Cells".[8] During initial evaluation of the monohydrate at moderate fuel cell temperatures, acid loss from operating cells was very evident. White fumes, visible in the cell exit gas streams, suggested that the partial pressure of the pure acid was significant with the monohydrate composition. Since the monohydrate was an azeotropic mixture, the vapor phase in equilibrium with the monohydrate solution would also have the monohydrate composition. Thus the partial pressures of the pure acid and water should be in a one-to-one ratio and each equivalent to 50% of the total vapor pressure. Although the monohydrate had the lowest total vapor pressure, it was not the composition with the lowest acid partial pressure.

The monohydrate was also observed to wet PTFE, the common acid fuel cell electrode binder and wetproofing agent. This severely complicated the fabrication of a non-flooding electrode structure. Cells containing the monohydrate also exhibited abnormally high internal resistances which implied the ionic conductivity of the azeotropic composition was relatively poor. Conductivity of the monohydrate was later estimated to be less than 0.03 $(\text{ohm-cm})^{-1}$ at 60°C. This value compares unfavorably with the ionic conductivity of 100% phosphoric acid at 180°C (.60 $(\text{ohm-cm})^{-1}$).

Since the monohydrate of triflic acid was not feasible within a real fuel cell, subsequent emphasis was placed on evaluating aqueous TFMSA solutions. Aqueous solutions in which the mole fraction of TFMSA was less than about 0.20 did not appear to have the same limitations as the monohydrate. The dilute solutions did not have the tendency to wet PTFE, and also possessed ionic conductivities at 60°C, roughly equivalent to concentrated phosphoric acid at 180°C. In addition, the acid partial pressures were inherently reduced with the dilute TFMSA solutions, eliminating any short-term acid loss problems.

During Contract DAAK02-75-C-0045, considerable progress was made in operating Pt black type electrodes in aqueous TFMSA fuel cells at ambient temperatures. It was generally acknowledged that the fuel cell performance was enhanced over similarly loaded electrodes operating in phosphoric acid cells at much higher temperatures. Although the potential for aqueous TFMSA fuel cells was demonstrated, many problem areas also became evident. The TFMSA fuel cell was more difficult to operate than the phosphoric acid fuel cell. There was a general inability to effectively operate cells either at higher than ambient temperature or with supported catalyst type electrodes.

Contract DAAK-70-78-C-0103 represents an effort to overcome some of the difficulties previously identified with aqueous TFMSA fuel cells. The major objectives are:

- Demonstration of stable performance by effective water management within continually operating cells.
- Demonstration of stable performance at higher than ambient temperature.
- Improved performance with supported catalyst type electrodes.
- Identification of optimum electrolyte concentration levels.
- Demonstration of stable performance in large (350 cm^2) multicell configurations.

2.0 TECHNICAL APPROACH

2.1 ANALYTICAL PROCEDURES

2.1.1 Water Management Problem

Although very promising initial performance levels were demonstrated for aqueous triflic acid fuel cells during Contract DAAK02-75-C-0045, difficulties were encountered in maintaining cell stability for long operational periods. Since continually functioning cells produce significant amounts of product water at normal current densities, operation at ambient temperatures necessitated passage of abnormally high air flows. Decay was evident in all cells although, in some cases, initial performance could be restored by changing the cell operating parameters. Much of the cell decay appeared to be related to increased electrode diffusional losses (flooding) as increased oxygen gains generally occurred. The electrode flooding problem probably was created by electrolyte concentration changes. It could be rationalized that electrode flooding would occur if the original acid was either diluted or concentrated to any degree. Acid dilution would greatly increase the volume of electrolyte present in the electrode structure while acid concentration would adversely affect the wetting characteristics of the electrolyte on PTFE. The cell water balance problems at room temperature were compounded by attempts to operate aqueous TFMSA cells at higher temperatures (60 to 70°C). Since the partial pressure of water increased significantly from ambient temperatures to 70°C, the aqueous TFMSA fuel cell was prone to electrolyte dryout. In some cases the acid concentration probably reached to nearly the monohydrate composition level previously shown to be very undesirable.

The water balance factor became more complicated due to the lack of reliable vapor pressure data for TFMSA solutions. The available data showed inconsistencies between different investigators and generally was not at the concentrations of interest. Attempts were unsuccessful to correlate the available information into a meaningful estimation of water partial pressure as a function of acid concentration and temperature.

An analytical technique was finally utilized to predict the vapor pressures of various TFMSA solutions. The technique involves calculation of activity coefficients which essentially measure the deviations from ideal behavior of each component within the binary solution. The van Laar equations were utilized to determine the activity coefficients at various concentrations. Knowledge of the vapor pressure relationships of the two pure components (as well as the boiling point and composition of the azeotropic mixture) was utilized to derive the van Laar equations.

The van Laar equation is an empirical relationship which is thermodynamically consistent with the Gibbs-Duhem equation. It expresses a relationship between the activity coefficient (γ) for a component in a binary solution as a function of only the mole fractions (X_1, X_2) of each component within the solution. The van Laar equation can be written in the following form.

$$\log \gamma_1 = \frac{a}{\left(1 + \frac{X_1}{X_2}\frac{a}{b}\right)^2}$$

The two constants, a and b in the van Laar equation, can be determined if the activity coefficients for both components (γ_1, γ_2) can be estimated at one particular concentration.

Raoult's Law states that the partial pressure of a component in an ideal solution is the product of the vapor pressure of the pure component times the mole fraction of that component in the liquid phase.

$$\bar{P} = P\ X$$

For a non-ideal solution such as TFMSA-water mixtures, the partial pressure deviates from Raoults' Law and is corrected by a factor identified as the activity coefficient.

$$\overline{P} = \gamma P X$$

The partial pressure of a component, according to Dalton's Law, is also equal to the total pressure times the mole fraction of that component in the vapor phase.

$$\overline{P} = P_{total} Y$$

The activity coefficient can therefore be expressed as

$$\gamma = \frac{P_{total}}{P} \frac{Y}{X}$$

The monohydrate of triflic acid is assumed to form a maximum boiling point azeotrope. The liquid and vapor phases for azeotropes have identical compositions, thus:

$$X = Y$$

A simple expression for the activity coefficient at the monohydrate composition is therefore:

$$\gamma = \frac{P_{total}}{P}$$

The total vapor pressure of the monohydrate is known to be 760 mm Hg at its boiling point (217°C).

The vapor pressure of pure water at 217°C is reported to be about 16420 mm Hg.[17] The vapor pressures of pure TFMSA have been reported at the following temperatures.[16]

162°C	760 mm Hg
84°C	43 mm Hg
54°C	8 mm Hg

An extrapolated value for the vapor pressure of pure triflic acid at 217°C could be determined from this data. As shown in Figure 1, this value was approximately 3600 mm Hg. An activity coefficient for both triflic acid and water could be calculated at the monohydrate composition where

$$(X_T = X_W = 0.5)$$

$$\gamma_T = 760/3600 = 0.2111$$

$$\gamma_W = 760/16400 = 0.0463$$

Since a van Laar equation for both TFMSA and water could be written at the monohydrate composition, the two constants within the equations could be determined.

$$a = -5.978$$
$$b = -3.027$$

The following equations were therefore derived for the activity coefficients of both components as a function of only the solution composition.

$$\log \gamma_T = \frac{-5.978}{\left(1 + \frac{X_T}{X_W} \; \frac{-5.978}{-3.027}\right)^2}$$

$$\log \gamma_W = \frac{-3.027}{\left(1 + \frac{X_W}{X_T} \; \frac{-3.027}{-5.978}\right)^2}$$

These equations were utilized to calculate the activity coefficients for TFMSA and water at various solution compositions. These values are summarized in Table 1 over the entire range of possible concentrations. A temperature of 60°C was arbitrarily selected as the elevated temperature of interest to be evaluated under this program. At this temperature:

P_T = vapor pressure of pure TFMSA = 12 mm (Figure 1)

P_W = vapor pressure of pure water = 150 mm

TABLE 1

ACTIVITY COEFFICIENTS AND PARTIAL PRESSURES AT 60°C

Liquid Composition		Activity Coefficient		Partial Pressure, mm		Total Vapor Pressure, mm	Vapor Composition	
X_T	X_W	γ_T	γ_W	$\bar{P}_T$	$\bar{P}_W$		Y_T	Y_W
0	1.000	.000001	1.000	0	150	150	0	1.000
.100	.900	.000095	.798	.00011	107.7	107.7	0	1.000
.109	.891	.000132	.768	.00017	102.6	102.6	0	1.000
.169	.831	.000905	.564	.0018	70.3	70.3	0	1.000
.200	.800	.0021	.467	.0050	56.0	56.0	0	1.000
.300	.700	.0176	.231	.063	24.25	24.31	.002	.998
.400	.600	.0769	.105	.369	9.45	9.82	.038	.962
.500	.500	.2111	.0463	1.27	3.47	4.74	.268	.732
.565	.435	.339	.0271	2.298	1.768	4.066	.565	.435
.600	.400	.416	.0203	3.00	1.218	4.22	.711	.289
.700	.300	.645	.0090	5.42	.405	5.83	.930	.070
.800	.200	.840	.0041	8.06	.12	8.18	.985	.015
.900	.100	.961	.0019	10.38	.03	10.41	.997	.003
1.000	0	1.000	.00094	12	0	12	1.00	0

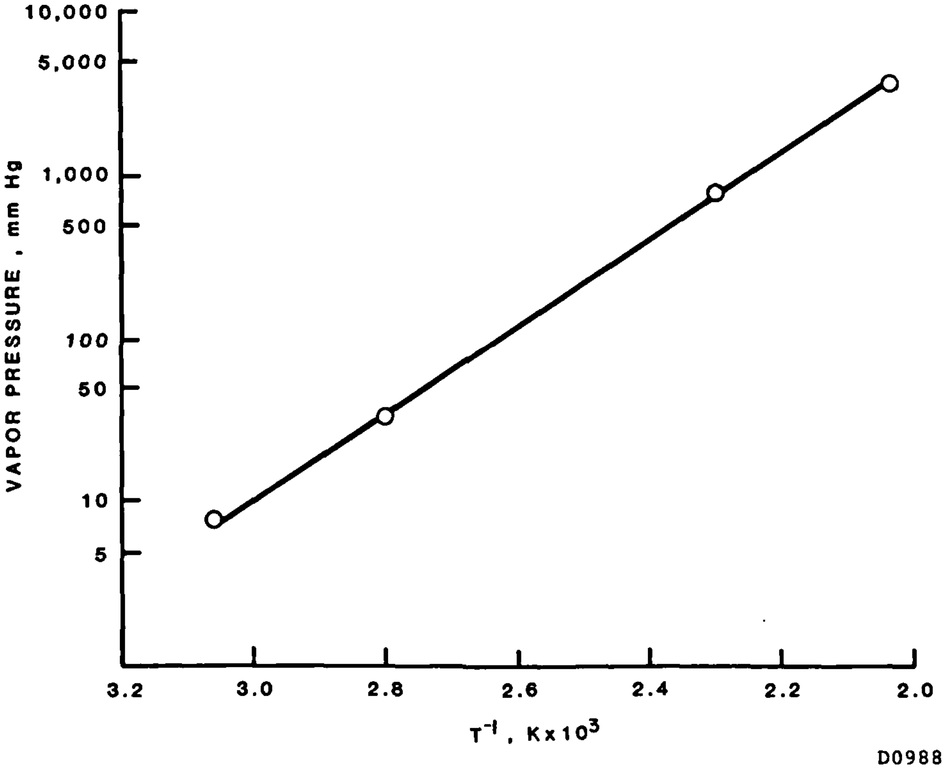


FIGURE 1. VAPOR PRESSURES OF PURE TFMSA

The partial pressures of each component at 60°C could therefore be calculated by the following relationships.

$$\bar{P}_T = \gamma_T P_T X_T$$

$$\bar{P}_W = \gamma_W P_W X_W$$

The total vapor pressure would be the sum of the individual partial pressures.

$$P_{total} = \bar{P}_T + \bar{P}_W$$

The vapor phase compositions could also be determined by:

$$Y_T = \frac{\bar{P}_T}{P_{total}} \qquad Y_W = \frac{\bar{P}_W}{P_{total}}$$

The partial pressures, total vapor pressure, and vapor phase compositions for each solution are also reported in Table 1. It is significant to note from this data that when the mole fraction of TFMSA in the solution is 0.20 or less, the mole fraction of TFMSA in the vapor phase is insignificant compared to water. This would suggest that acid loss using dilute TFMSA solutions at 60°C will not be a severe problem. The low acid partial pressure values, however, cannot be totally ignored during long-term acid loss considerations. Also, by this analysis at 60°C, the apparent azeotropic composition is not exactly at 0.50 mole fraction but rather at 0.565 mole fraction TFMSA. This is the point at which: the total vapor pressure is at a minimum; and the liquid and vapor phases have identical values.

The data in Table 1 could be plotted to give a complete phase diagram of the TFMSA-water system at 60°C. As shown in Figure 2, the upper curve is a plot of the total vapor pressure as a function of the solution composition while the lower curve shows the total vapor pressure as a function of the vapor phase composition. The figure illustrates that the azeotropic composition is at 0.565 mole fraction and that the vapor pressures of dilute TFMSA solutions are essentially composed of 100% water.

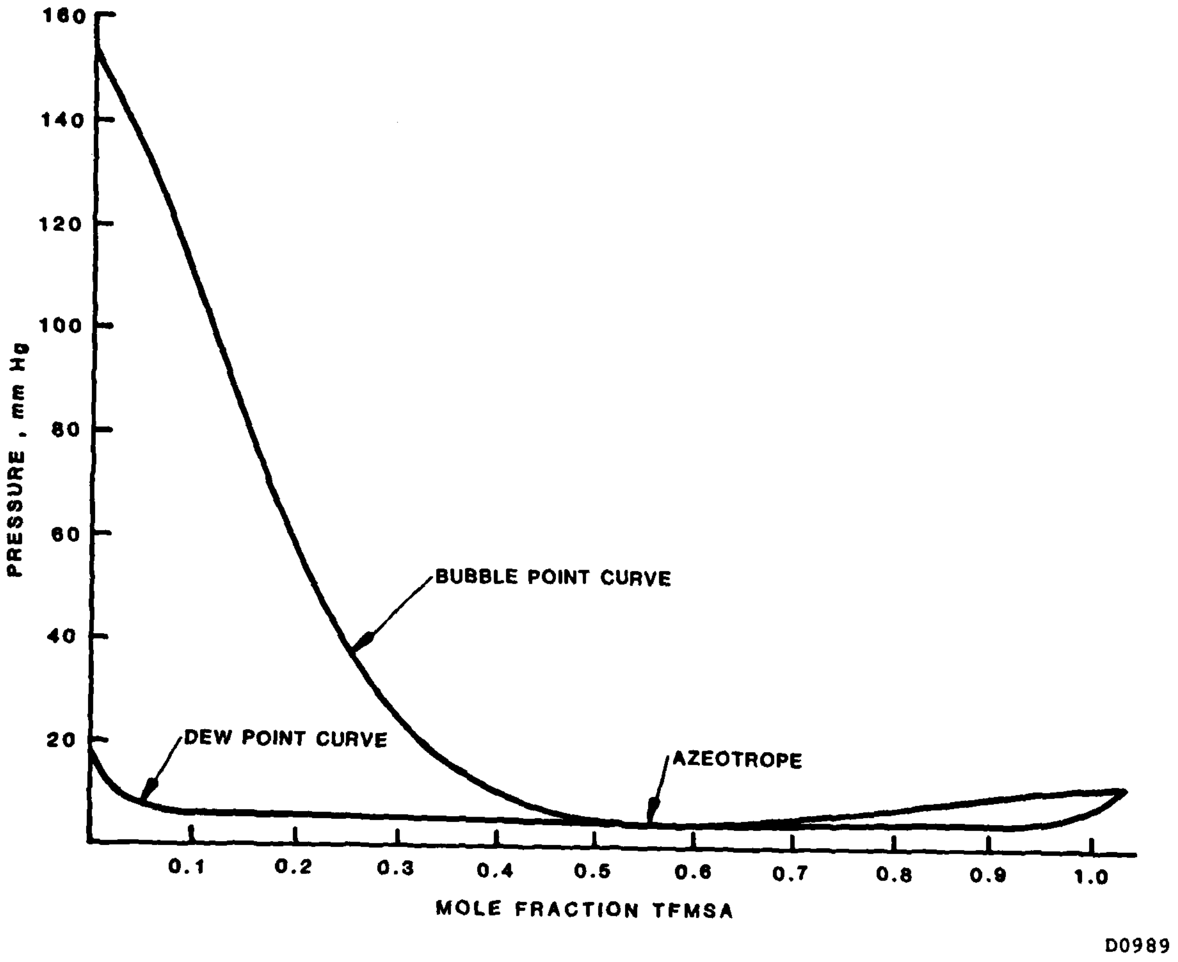


FIGURE 2. PHASE DIAGRAM OF TFMSA-WATER SYSTEM AT 60°C

The use of the van Laar technique in conjunction with aqueous TFMSA solutions may possibly be questioned. The van Laar equations generally are utilized for systems of non-electrolytes. By tradition for electrolyte solutions, activity coefficients for the solute are standardized on an ionic rather than on a molecular basis. This does not necessarily mean that electrolytes cannot be considered as undissociated molecules.[12] Activity coefficients for the solute ions are generally expressed as deviations from ideal dilute solution behavior (Henry's Law) rather than deviations from ideal solution behavior as utilized in this report. In other words, the activity coefficient (mean ionic activity coefficient) is arbitrarily designated equal to one when the mole fraction of the solute is equal to zero. In the Raoult's Law sense, the activity coefficient for a component is equal to one when its mole fraction is also equal to one.

It can be rationalized that at the monohydrate composition (which serves as a basis for the van Laar derivation), complete dissociation of the TFMSA molecule may be difficult. This would require that every single acid molecule must protonate every single water molecule. The relatively poor conductivity of the monohydrate may support this hypothesis. The monohydrate has been shown to have the lowest ionic conductivity for any TFMSA-water mixture in the range of 0.05 to 0.95 mole fraction.[6]

In other respects, the TFMSA-water system does appear to be well suited to the van Laar analysis. The van Laar equations have been described as being reasonably consistent with experimental data for mixtures of organic liquids and water and in cases where the two constants (a and b) within the equations do not differ by more than a factor of two.[13] It has also been stated that the use of azeotropic data to predict activity coefficients is generally meaningful if the azeotropic mole fraction is within the interval 0.3 to 0.7.[14] Since the monohydrate is exactly 0.5 mole fraction, this criteria for validity appears to have been met.

Although reliable experimental vapor pressure data for aqueous TFMSA solutions was lacking at the initiation of this program, some data did become available during the course of this study. American University obtained the vapor pressure data presented in Figure 3 utilizing an isopiestic technique.[7] The experimental data at 60°C, presented as a function of wt% TFMSA, was converted to mole fraction TFMSA. The experimental and analytical values for total vapor pressure are compared in Figure 4. At low concentrations, a reasonable correlation existed between the two techniques. At these concentrations, the partial pressures of TFMSA would be expected to be very low. Therefore the experimental data appears to verify the predicted analytical values for water partial pressures. At higher concentrations, the acid partial pressures are becoming

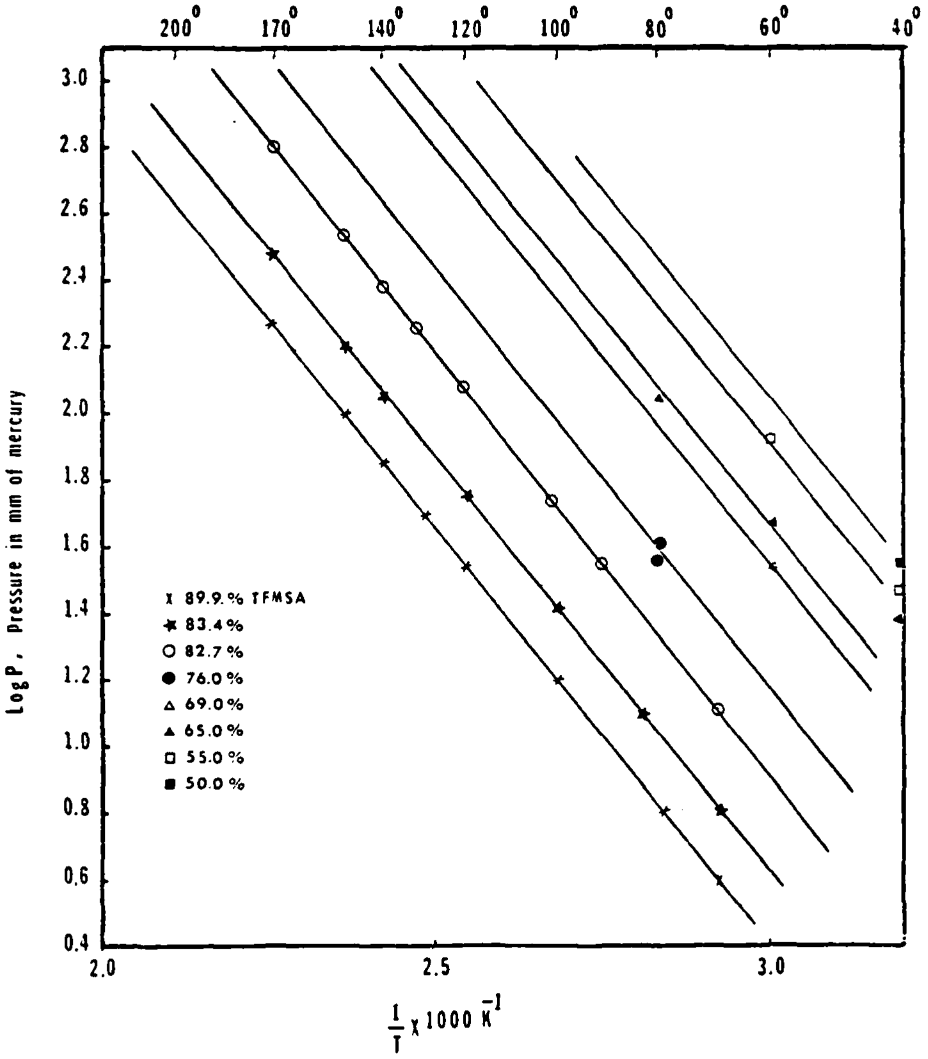


FIGURE 3.
EXPERIMENTALLY OBTAINED VAPOR PRESSURES OF TFMSA SOLUTIONS D0995

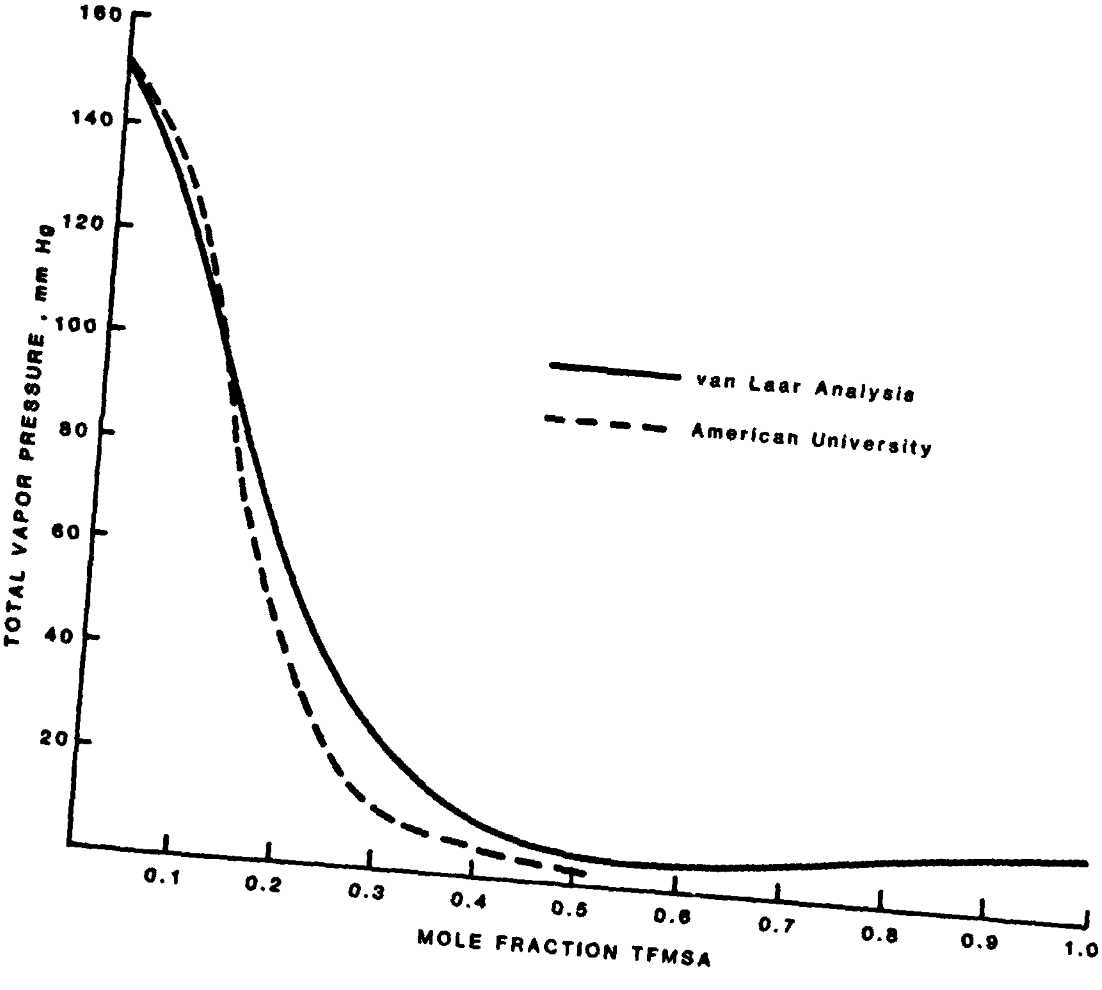


FIGURE 4. VAPOR PRESSURES OF TFMSA-WATER SOLUTIONS AT 60°C

significant and less correlation was observed between the analytical and experimental results. This may suggest a greater degree of certainty for the water partial pressure data than for the acid partial pressure values.

Overall, the van Laar analysis does appear to give a reasonable first approximation of the vapor pressures of aqueous TFMSA solutions. It is only approximate as activity coefficients can be temperature dependent and azeotropic data at 217°C was utilized to predict values at much lower temperatures. This temperature dependency can be calculated if heat of mixing data is available. In the future, more precise data relating to the vapor pressures of aqueous TFMSA solutions will probably be required. Both analytical and experimental techniques should continue to be explored.

2.1.2 Identification of Optimum Concentration

During Contract DAAK02-75-C-0045, four different TFMSA concentrations (25, 37.5, 50, and 60 vol%) were evaluated. These solutions correspond approximately to the 3, 4.5, 6, and 7.1 molar concentrations, respectively. In general, the more dilute electrolytes appeared to give the highest fuel cell performance levels; however the most stable cells contained the 50 and 60 vol% acid. The most important properties of TFMSA solutions relating to actual fuel cell use are believed to be:

- ionic conductivity
- wettability with PTFE
- acid partial pressure
- water partial pressure

All of the above characteristics are very concentration-dependent. The ideal triflic acid solution would possess a maximum ionic conductivity, a minimum acid partial pressure, and have no wetting tendency with PTFE. This might suggest that the very dilute solutions would be preferable. However at low acid concentrations, the high water partial pressures would make fuel cell water management difficult. A trade off between the optimum electrolyte characteristics would probably be necessary.

Recently American University completed an extensive study of the properties of TFMSA relating to fuel cell use.[15] This proved useful in selecting triflic acid concentrations to be evaluated under this program. In Figure 5, ionic conductivities of various TFMSA solutions are shown as a function of temperature and concentration. Since the American University data at 40°C gave the same profile as the ERC data at 25°C, conductivity values were also estimated at higher temperatures. Estimation of the profile at 80°C was aided by the fact that the maximum conductivity has been reported to be 0.81 $(\text{ohm-cm})^{-1}$.[15]

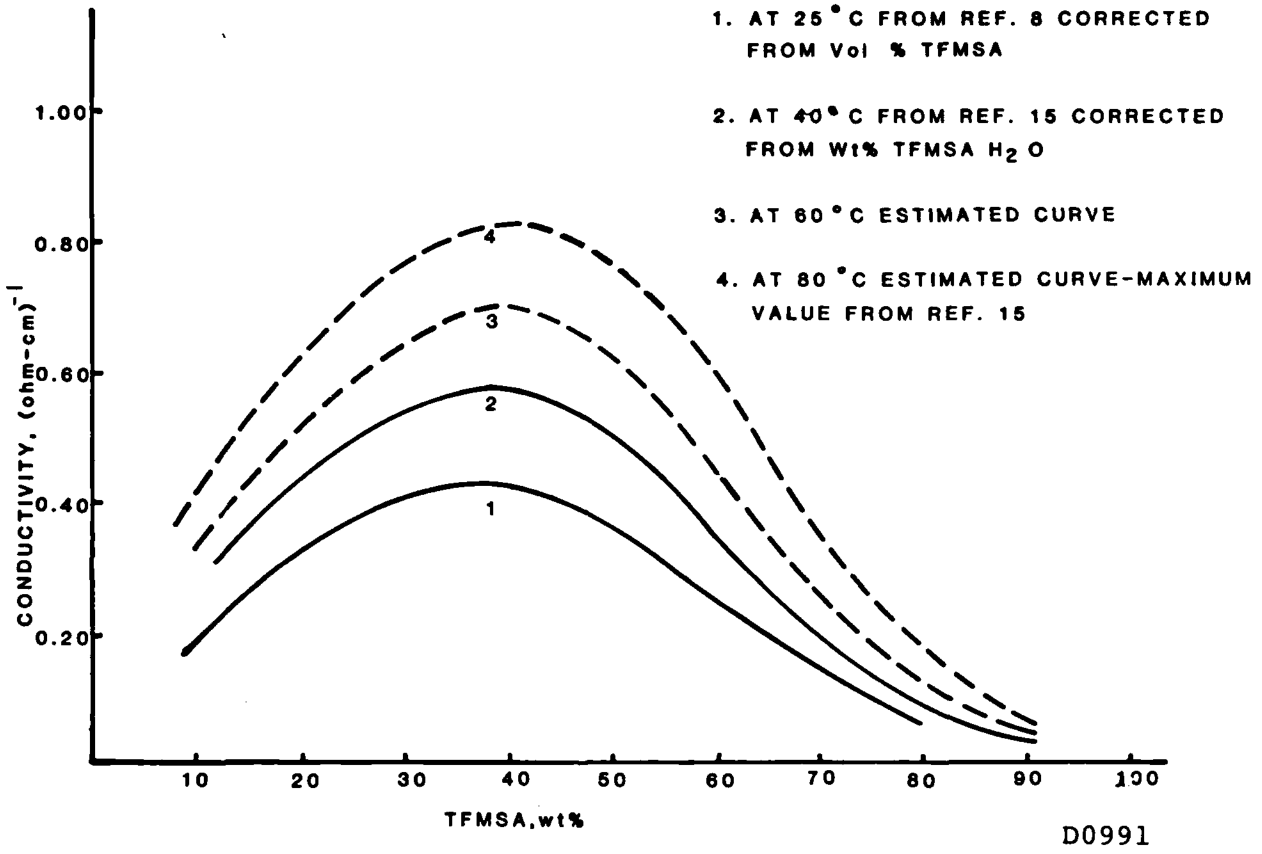


FIGURE 5. CONDUCTIVITIES OF TFMSA-WATER SOLUTIONS

American University also conducted a study to quantitatively determine the wetting tendencies of TFMSA solutions with PTFE. The extent of wetting is measured by the contact angle between the liquid and solid: a contact angle of 90°C is considered to be nonwetting while 0° indicates total wetting. In Figure 6, the contact angles of various TFMSA solutions with PTFE are shown as a function of electrolyte concentration. The tendency for a fuel cell electrode to flood is generally enhanced with the more concentrated TFMSA solutions. This observation correlates well with the contact angle measurements.

Partial vapor pressures for both acid and water could be calculated utilizing the activity coefficients determined by the van Laar method. The acid partial pressure would be important as it relates to the amount of acid loss experienced by a cell during continual operation. Acid loss would increase as the acid concentration increases. Table 2 summarizes the partial pressures of each component as well as the ionic conductivities and contact angles for each of the TFMSA solutions under consideration. The properties are presented at 60°C, an operational goal selected for this program. Undoubtedly the optimum electrolyte concentration will be influenced to some degree by cell temperature. Concentration of the acid would naturally occur as the cell temperature is increased. A temperature of 60°C was selected because some investigators have indicated that acid decomposition begins to occur at this point.[10]

The stoichiometric air flow rate necessary to maintain a constant acid concentration within an operating fuel cell is presented in Table 2 for each of the proposed TFMSA solutions. These values were calculated by making an appropriate material balance of the cell products and reactants during operation. It was assumed that a constant acid concentration would be maintained if all water produced within the cell was removed by the air stream through the cell. This would require that the average of the water partial pressures within the inlet and outlet air streams equal the water partial pressure of the original electrolyte. Since the inlet water partial pressure is generally known (≃20 mm Hg for saturated air at ambient temperature), the outlet water partial pressure can be determined. Thus at the cell outlet, the following relationship is valid.

$$\frac{\bar{P}_{H_2O}}{760-\bar{P}_{H_2O}} = \frac{\text{moles } H_2O \text{ (enter)} + \text{moles } H_2O \text{ (produced)}}{\text{moles air (enter)} - \text{moles } O_2 \text{ (consumed)}}$$

The required air flow rate could therefore be calculated.

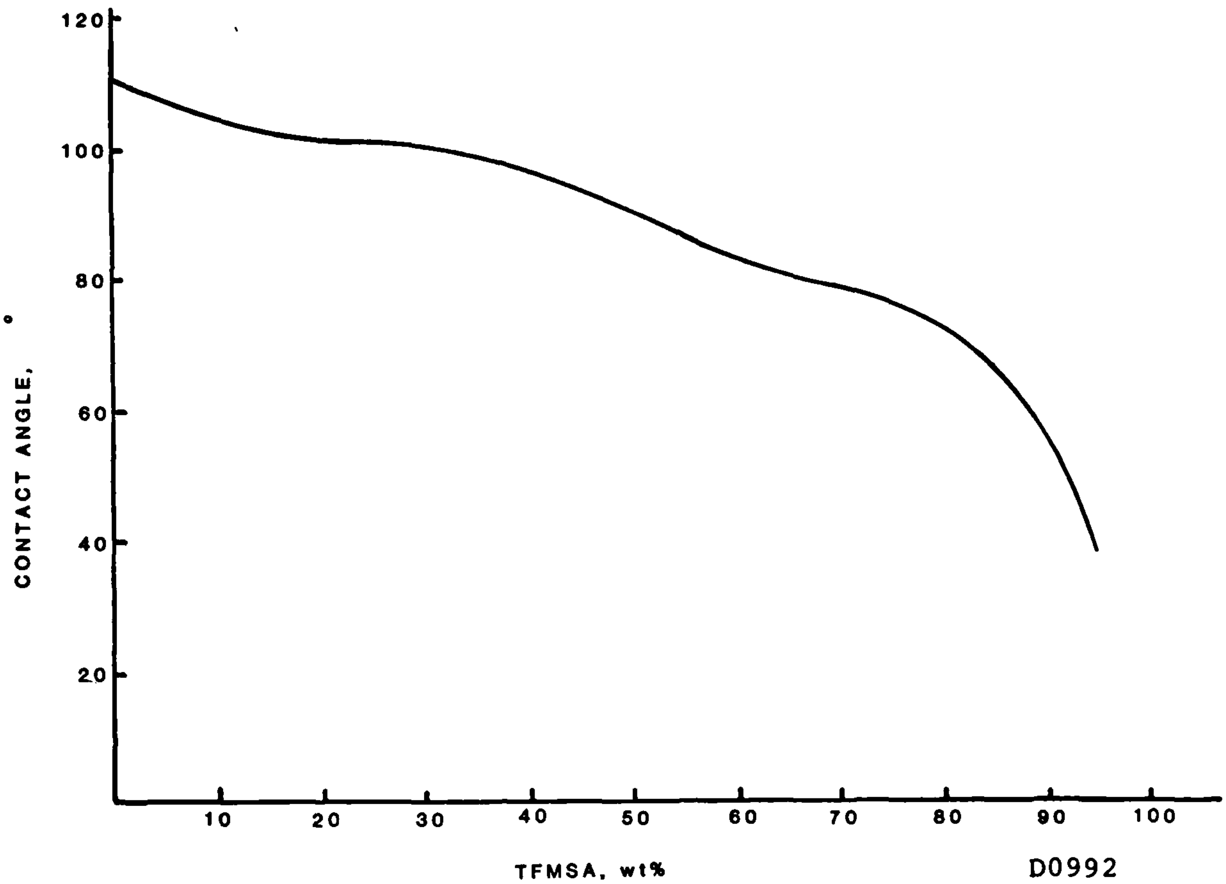


FIGURE 6. CONTACT ANGLES OF TFMSA-WATER SOLUTIONS ON PTFE

TABLE 2

PROPERTIES OF TFMSA-WATER SOLUTIONS AT 60°C

PROPERTIES	MOLAR CONCENTRATIONS			
	3	4.5	6	7.1
Solution, vol%	25	37.5	50	60
TFMSA, wt%	36.1	50.4	62.9	71.8
TFMSA, Mole Fraction	0.063	0.109	0.169	0.234
Conductivity $(\text{ohm-cm})^{-1}$	0.70	0.63	0.40	0.23
Contact Angle on PTFE,°	98	91	83	78
Partial Pressure TFMSA, mm Hg	0.000016	0.00017	0.0018	0.0132
Partial Pressure Water, mm Hg	127	102.6	70.3	42.8
Stoichiometric Air Flow Rate Required	1.2	1.5	2.5	4.6

As shown in Table 2, the 3 M and 4.5 M triflic acid solutions did offer some attractive advantages: high conductivites, high contact angles with PTFE, and low acid partial pressures. The 3 M solution is, in fact, the composition with the maximum ionic conductivity.[6] The low air flow rates required to maintain water balance, however, would tend to make fuel cell operation problematic. The fuel cell would become air starved and severe polarization losses would occur due to low average oxygen partial pressures. The 6 M TFMSA electrolyte, therefore, appears to be the approximate optimum concentration for use at 60°C. (The dilute concentrations would be attractive at lower temperatures.)

2.2 EXPERIMENTAL PROCEDURES

2.2.1 Electrode Fabrication

The fuel cell electrodes prepared for this program consist of a catalyst layer mounted on an electrode substrate. Fabrication techniques have generally been identical to those previously developed for phosphoric acid fuel cell electrodes. The catalyst layer, consisting of the electrocatalyst and a binder, could be prepared utilizing two completely different techniques. One method involves use of a machine calendering mill in which a thin, discrete catalyst layer with excellent structural integrity is formed by essentially a rolling operation. The second method, described as a sheet mold process, involves depositing the electrocatalyst-binder mixture directly on the electrode substrate. Differences in performance of electrodes prepared by the two techniques have previously been shown to be insignificant when tested in phosphoric acid fuel cells. During this program, the method of preparation did have some bearing on the subsequent electrode performance.

Electrodes produced by either the rolling or sheet mold process are then subsequently sintered at 350°C. The sintering operation gives a hydrophobic nature to the catalyst layer to prevent flooding and to insure ready gaseous reactant access to the electrocatalyst.

Three different electrocatalysts were selected for evaluation during this study: Pt black, Pt on carbon black, and Pt on Kocite. Emphasis was initially placed on Pt black type electrodes since the supported catalyst type had previously proven to be difficult to operate. These difficulties were attributed to an inability to effectively wet the electrocatalyst with the TFMSA electrolyte. All Pt black electrodes were prepared by the rolling process and contained 2 to 4 mg/cm^2 of Pt. Later in the program, Pt on Kocite and Pt on carbon electrodes were effectively utilized. These electrodes generally contained 0.50 to 0.60 mg/cm^2 Pt.

2.2.2 Small Single Cell Assembly and Testing

A systematic determination of the kinetic parameters affecting TFMSA fuel cells was not conducted during this program. Therefore no attempt was made to evaluate electrodes in half cell test apparatus. All efforts were directed at developing a practical triflic acid fuel cell using real fuel cell components at conditions which simulate a real fuel cell environment. All testing was performed within model subscale size full cells utilizing pure hydrogen as the fuel and either air or oxygen as the oxidant. Test electrode size was standardized at 25 cm^2 throughout this phase of the program.

Cell assembly techniques and test procedures were similar to those currently utilized for phosphoric acid fuel cells. Cell components (such as matrices and test plates) were also identical to those optimized for use with phosphoric acid with one major exception. At the low temperatures of interest under this program, a glass fiber matrix could be effectively utilized.

All cells were constructed within molded graphite hardware. The graphite plates were a composite structure of a commercially available graphite and a phenolic type resin. The anode plate also contained a reservoir for periodic electrolyte addition. The reservoir was in intimate contact with the cell matrix which extended beyond the periphery of the cell electrodes. During previous aqueous TFMSA programs, some difficulties were experienced in adequately sealing the reservoir area, as the electrolyte tended to readily leak from the cell. An O-ring sealing technique was successfully employed to overcome this problem. During this problem adequate sealing was provided through use of PTFE gaskets.

Glass fiber and silicon carbide were extensively utilized as cell matrix materials during this study. The glass fiber matrix is a commercially available filter paper (Reeve Angel 934AH). Although its bubble pressure is relatively low, gas reactant crossover was generally not a major problem and thus consistent cell builds could be made. The glass fiber paper was highly porous and was readily compressed during cell assembly. The silicon carbide matrix was a composite structure consisting of a particulate SiC and PTFE binder.

The cell assembly procedure consisted of initially saturating the cell matrix with electrolyte and compressing it between the two dry electrode structures. Partial filling of the electrodes occurred during the assembly process and further wetting also occurred during cell operation. Some electrodes proved to be difficult to wet. At times, electrode wetting could be enhanced by electrode pre-polarization and cell reversal procedures. Operation at 60°C also appeared to aid the wetting characteristics of the electrocatalysts contained within the electrode structures. All cells constructed during this program have contained identical electrodes, tested as both anode and cathode. As in the case of most acid fuel cells, cell performance was normally cathode limited. An abnormally dry anode could at times influence overall cell performance. This generally occurred shortly after cell assembly and could be alleviated by switching the reactant gas flows to the individual electrodes.

FC-24 produced by the 3M Company was utilized exclusively as the triflic acid evaluated for fuel cell use. No attempt was made to purify the as-received acid; it was simply added to water to produce the desired final concentration. Considerable heat was evolved during the mixing process and a volume loss of about 5% was generally observed. Periodically the resulting solution had a slight yellowish tint but it could not be determined whether this discoloration had any detrimental effect on subsequent fuel cell performance.

Actual fuel cell testing normally consisted of passing pure hydrogen to the anode and air to the cathode. Performance data on oxygen was also obtained to serve as a diagnostic aid. The difference between air and oxygen performance (O_2 gain) is a measure of the diffusional losses existing within a fuel cell electrode. The air flow rate to operating cells was generally controlled to maintain a constant acid concentration. The hydrogen flow was held at a minimum purge rate to eliminate the possibility of significant water rejection occurring at the anode.

2.2.3 Stack Assembly and Testing

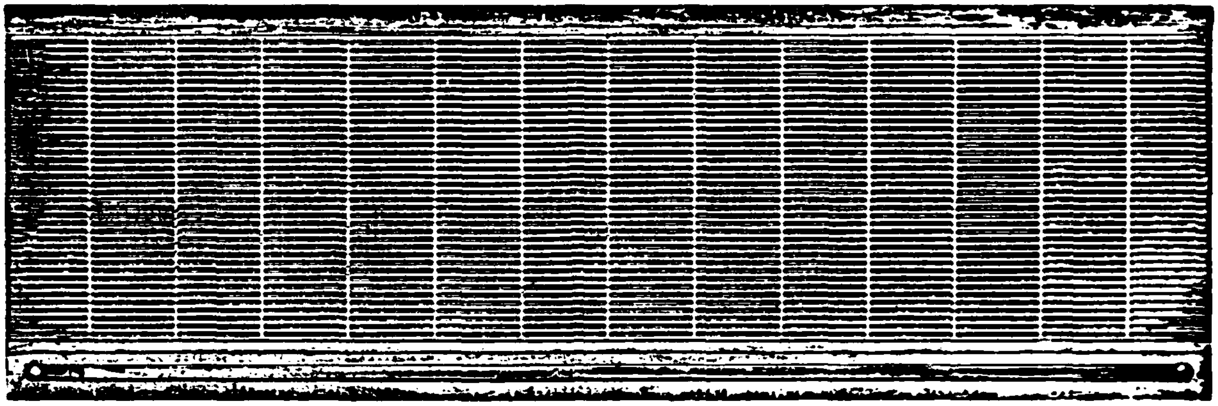
The assembly techniques and operational procedures for use with TFMSA stacks were similar to those developed for phosphoric acid stacks.[1,2] Under these ERC programs improved assembly procedures have been implemented into large stack configurations. Fortunately all of the major fuel cell components developed for phosphoric acid stacks appear to be compatible with TFMSA electrolytes. Some of the components evaluated during the small, single cell phase of this program were not considered for use within the larger multicell units. For instance Pt black electrodes were not considered as they are no longer mass-produced at ERC. In addition the glass fiber matrix was judged to have poor structural integrity, possibly making it susceptible to damage during the assembly procedure. Throughout this phase, an attempt was made to be consistent with components currently employed with similar phosphoric acid stacks.

The bipolar plate is a key component in any acid fuel cell stack. It serves several functions: current collection, gas distribution, and gaseous reactant separation from one cell to another. The bipolar plates for TFMSA stacks were compression molded. Several gas distribution configurations for bipolar plates have been tested at ERC. The AB design was selected for evaluation under this program. A Type A design plate contains straight line grooves perpendicular to the direction of gas flow and an enclosed electrolyte reservoir groove (anode side only). A Type B plate is marked by the presence of staggered grooves perpendicular to the direction of gas flow. An AB plate is therefore a hybrid design consisting of an A side for the flow of hydrogen and a B side for the flow of air. This configuration is shown in Figure 7.

All electrodes tested within these stack configurations were prepared from supported type catalysts. Both Pt on carbon black and Pt on Kocite were evaluated. The nominal loading for both anodes and cathodes was 0.50 mg/cm^2 of Pt. The SiC matrix was normally supported on the cell cathodes. A proprietary matrix, designated Mat-1, was utilized in several of the experimental stacks.

The stack assembly procedures initially consisted of positioning each electrode within the plate recess. Small amounts of Viton cement were utilized to hold the electrodes in place. Since electrode and matrix thickness did vary to some degree, PTFE shims, attached to the plates, were utilized to standardize electrode compression. Wet assembly techniques were utilized exclusively for all TFMSA stacks. Thus no attempt was made to wick fill the various cell components after a dry assembly. Between 12 and 25 ml of 6 M TFMSA, depending on the cell matrix, was added to the components of each cell. Additional electrolyte could also be supplied through the electrode reservoir within the anode plate.

Gold-plated copper sheets served as stack current collectors. These were placed between the end graphite plates and the outside support plates. The support plates were 1 in. thick aluminum with an attached 0.25 in. thick fiberglass-epoxy composite material which served as an insulator. Stack compression was maintained by hardened steel compression bars. A phenolic material and Viton rubber gaskets were utilized as the gas manifolds. A photograph of a TFMSA stack appears as Figure 8. Both 2 and 3-cell stacks were assembled and tested. The active area of each cell was ∿350 cm^2. Stacks were normally endurance tested at 100 mA/cm^2 on pure hydrogen and air at 60°C. The inlet air was normally saturated at ambient temperature.



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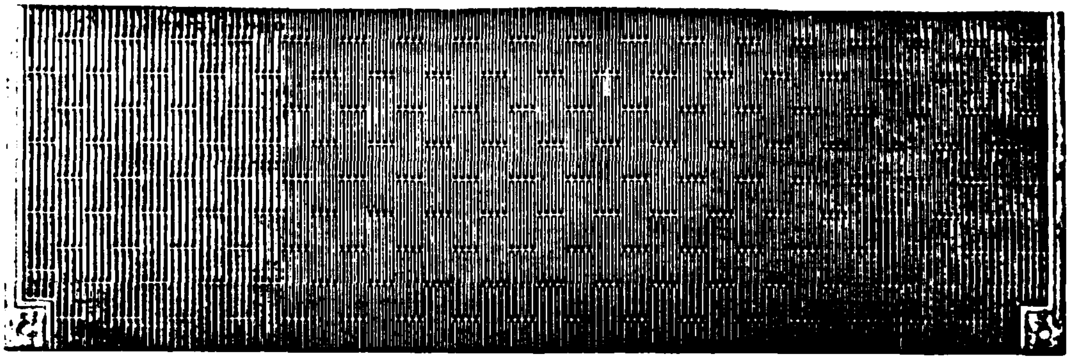
HYDROGEN SIDE -- "A" DESIGN



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AIR SIDE - "B" DESIGN

FIGURE 7

TYPE AB BIPOLAR PLATE DESIGN

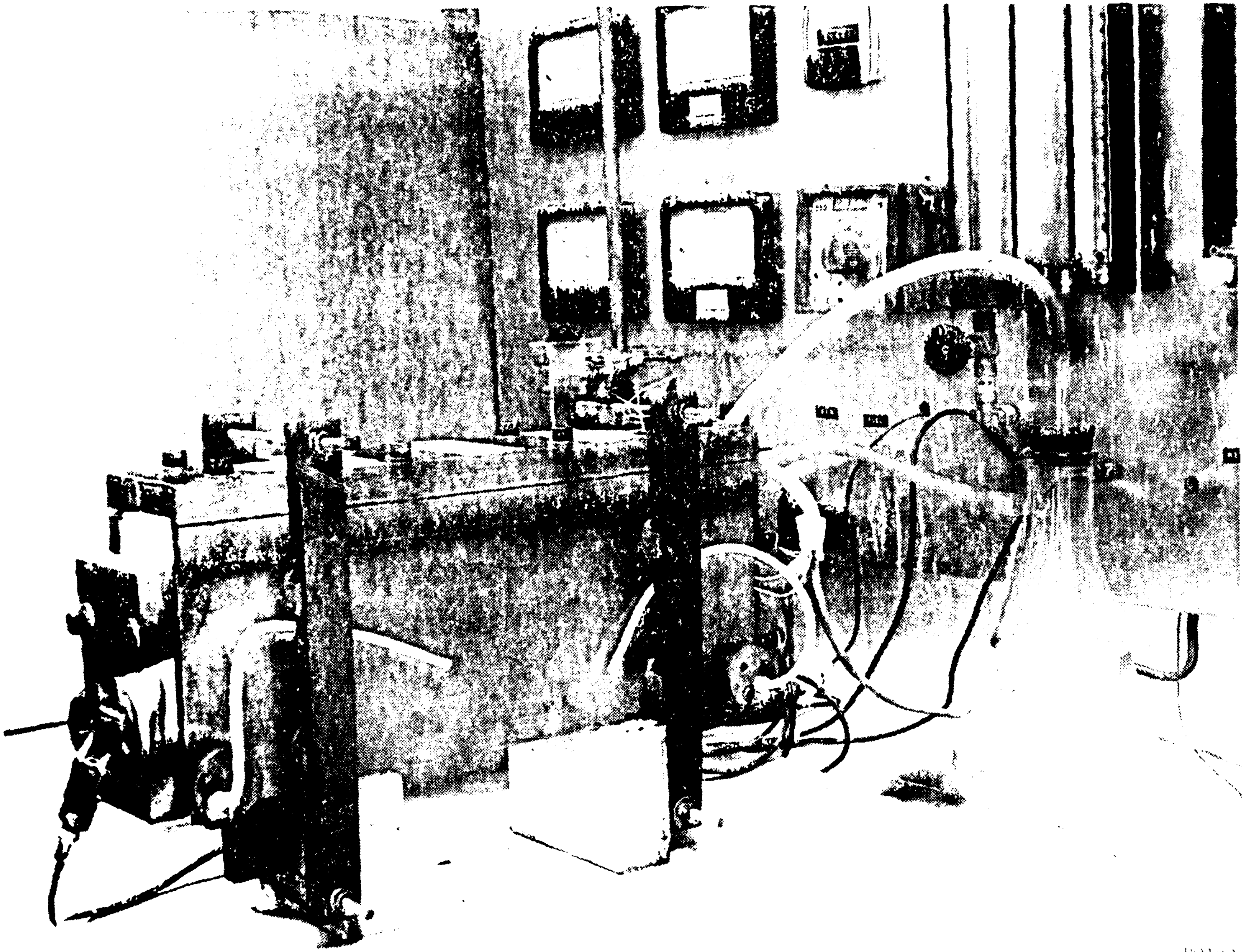

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FIGURE 8. TFMSA 3-CELL STACK (350 cm^2 Cell Size)

2.3 RESULTS AND DISCUSSION

2.3.1 Small, Single Cell Evaluation

The major objective of this program has been to demonstrate that aqueous TFMSA fuel cells can be operated stably for long periods both at ambient and elevated temperatures. The demonstration of high cell performance with low loaded supported catalyst type electrodes was also given priority. The specific goals have included a minimum hydrogen-air performance level of 650 mV at 100 mA/cm^2 and a cell endurance capability of at least 2500 hours. Generally the minimum performance goal posed no major difficulties even during the initial contract stages. Many cells, especially those with high loaded Pt black electrodes, easily surpassed the contract requirements. However the endurance goal presented a more formidable challenge.

Approximately 100 subscale TFMSA fuel cells were assembled and tested. Initial emphasis was placed on obtaining maximum performance levels. Although many of the initial cells exhibited high potentials, a few cells had extremely low load carrying capabilities. These cells were marked by the presence of low open circuit voltages which implied that little electrolyte had penetrated into the electrode structures.

The most reproducible test results were obtained with Pt black electrodes. Acceptable performance levels generally could be attained within 24 hours after initial startup even at ambient temperature. A typical performance curve for 2 mg/cm^2 loaded Pt black electrodes with 6M TFMSA as the electrolyte at room temperature is shown in Figure 9. Although the performance was acceptable by acid fuel cell standards, the cells generally showed very erratic behavior. Cell instability was accentuated when attempts were made to continually operate cells at current densities as high as 200 mA/cm^2. Also evident was the fact that for many cells, the oxygen gain increased significantly as a function of current density. This suggested that electrode flooding was prevalent. When flooding became apparent, the cells were air sensitive and at times could be unflooded by merely increasing the air flow rate. The air flow was generally maintained at about the 7 to 10 stoichiometric rate (or 7 to 10 stoich) although periodically it was adjusted in an attempt to stabilize cell performance. It became obvious after operating a number of similar type cells that water production within the cell was creating significant electrolyte changes; these, in turn, probably caused the apparent electrode flooding tendency.

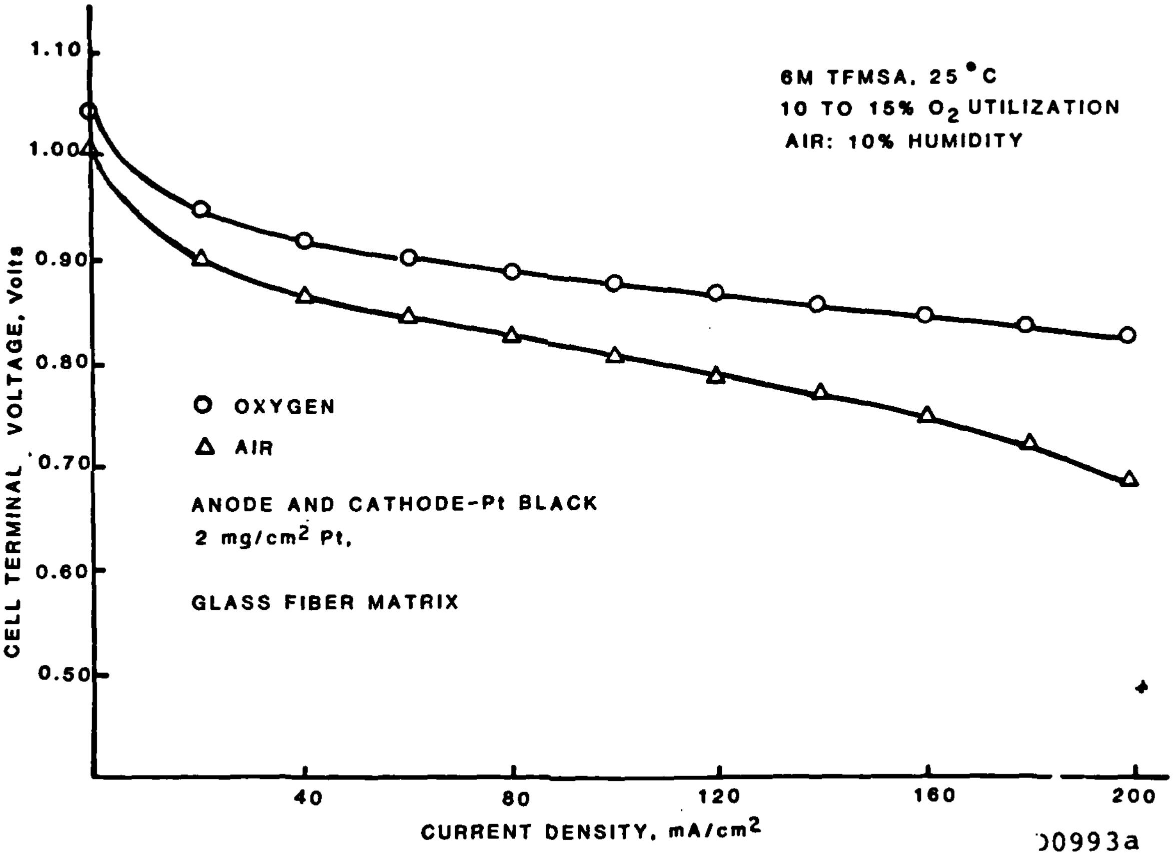

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FIGURE 9. PERFORMANCE OF Pt BLACK ELECTRODES WITH 2 mg/cm^2 Pt LOADING

A large batch of identical Pt black type electrodes was prepared in order to conduct a systematic evaluation of the water balance problems within TFMSA cells. Since Pt black electrodes are no longer utilized in phosphoric acid fuel cells at ERC, the electrodes were prepared with twice the normal Pt loading. However these electrodes did result in consistent initial performance levels in aqueous TFMSA fuel cells. Two of every three TFMSA cells assembled gave cell terminal voltages estimated to be at least 50 mV higher than for similarly loaded electrodes operating with ≈100% H_3PO_4 at 180°C. These 4 mg/cm^2 loaded Pt black electrodes were also selected for evaluation at elevated temperature. As shown in Figure 10, a cell terminal voltage of 760 mV at 200 mA/cm^2 was obtained on pure hydrogen and air at 60°C. A typical internal resistance for these cells was 6 mΩ which resulted in an IR loss of only 15 mV per 100 mA/cm^2. At 200 mA/cm^2 the cathode potential was therefore at least 790 mV. The internal resistance of the triflic acid cells at 60°C was generally lower than that experienced with phosphoric acid cells. A typical value of 10 to 12 mΩ is normally obtained for cells with ≈100% H_3PO_4 at 180°C. The lower resistance of the triflic acid cells (compared to phosphoric acid cells) was probably due to the thin and porous nature of the glass fiber matrix utilized rather than to any improved electrolyte conductivity.

In Figure 11, the IR-free data for the 4 mg/cm^2 Pt black electrodes is plotted on semilog graph paper. As shown, the Tafel slope for the oxygen performance was approximately 70 mV per decade. This experimentally obtained Tafel slope approximates the 66 mV per decade value predicted by theory if the Tafel slope is equivalent to 2.303 RT/F. A 70 mV Tafel slope on oxygen was not obtained for every cell. A slope between 80 and 90 mV per decade appeared to be more typical. In some cases, two distinct slopes were observable. This generally occurred when severe electrode flooding due to inadequate cell water balance was suspected.

The data presented in Figures 10 and 11 is considered to be equilibrium cell performance in which the potentials were maintained at least for a period of 24 hours. In many cases, the performance could be temporarily increased by prepolarizing the cell cathode. This treatment has been described previously in conjunction with phosphoric acid cathodes.[11] Performance gains by prepolarization were significantly greater in TFMSA cells than are normally obtained with phosphoric acid fuel cells. At times

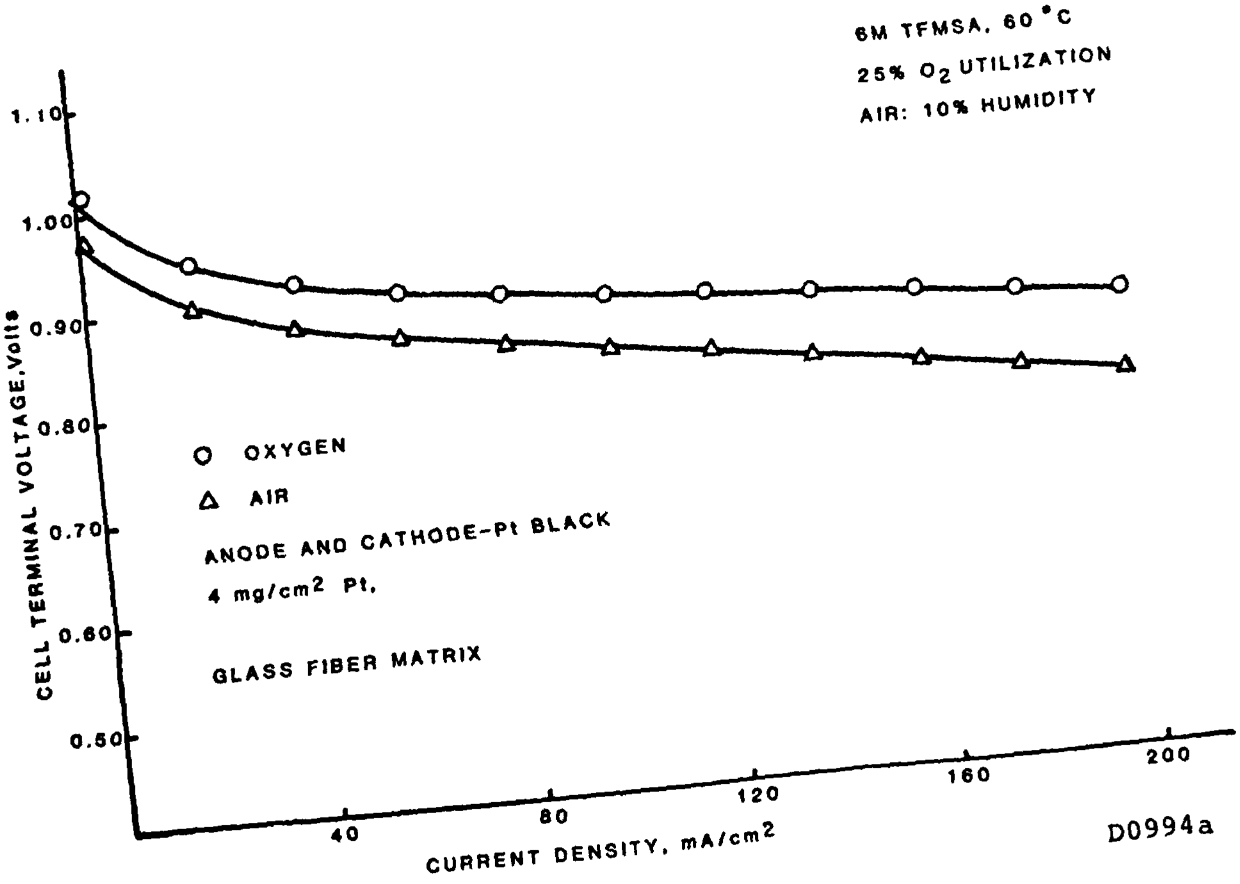

FIGURE 10. PERFORMANCE OF Pt BLACK ELECTRODES WITH 4 mg/cm² Pt LOADING

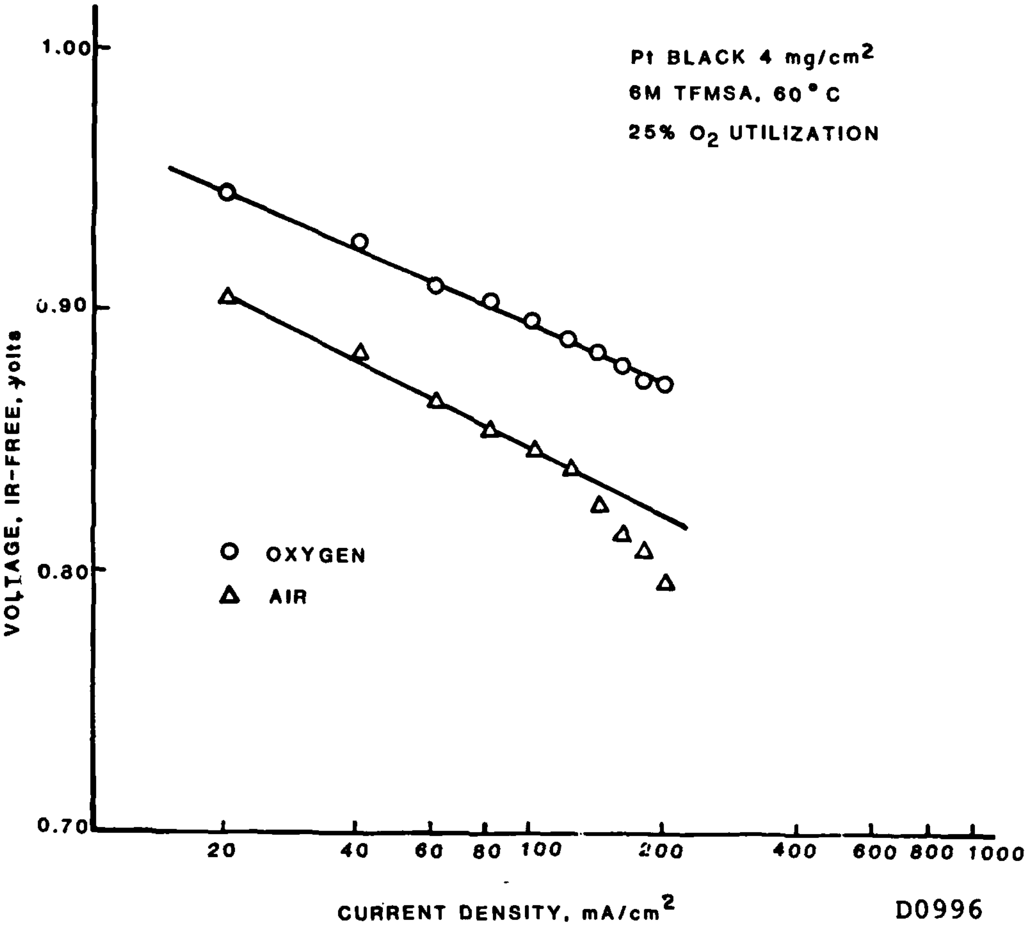

FIGURE 11. TAFEL PLOT OF 4 mg/cm^2 Pt BLACK ELECTRODE

it was possible to momentarily increase TFMSA cell performance by 50 to 70 mV following a cathode prepolarization treatment. TFMSA cells with 4 mg/cm^2 loaded Pt black electrodes were actually observed to operate in excess of 800 mV (cell terminal at 200 mA/cm^2 on hydrogen and air) for short durations. The cathode prepolarization treatment was simply performed by shutdown of the air supply to an operating cell under load. This would exhaust the oxygen within the cell and drive the cathode potential toward the anode potential.

Initial endurance testing of triflic acid fuel cells at 60°C did involve a trial and error approach to the water balance problem existing within continually operating cells. Water balance control was emphasized at the elevated temperature rather than at ambient temperature. It was rationalized that 60°C would more closely simulate actual operating conditions existing within any projected TFMSA fuel cell system. Any practical system involving multi-cell units would produce significant heat, automatically setting higher cell operating temperatures. One cell at 60°C did show reasonable stability for a period of several weeks with an air flow equivalent to about 4 stoich. As shown in Figure 12, eventual cell decay occurred which appeared to be mainly related to electrode flooding. The flooding was evident by the large increase in oxygen gains with time. It was not then clear whether the flooding tendency was created by electrolyte dilution or electrolyte concentration. During operation, electrolyte was replenished to the cell on a regular basis since acid loss was suspected to be a major problem at 60°C.

It became obvious after operating numerous, unstable 6 M TFMSA cells at 60°C that additional data pertaining to the partial pressures of TFMSA-water solutions would be required to make significant advances in TFMSA fuel cell technology. At this time, the van Laar analysis, as presented previously, was conducted. The initial van Laar calculations predicted that the partial pressures for water and TFMSA would be 67 mm Hg and 0.0014 mm Hg, respectively, for the 6M TFMSA solution at 60°C. This value for the partial pressure of water allowed calculation of an air flow rate to operating cells which would maintain the average acid concentration within the cell at 6M. If the entering air was at ambient temperature and had a relative humidity of 10%, a flow equivalent to 2.2 stoich would be necessary. If the inlet ambient temperature air was saturated, the air flow could be increased to about 3 stoich. Attempts to operate cells for extended periods with the dry inlet air were unsuccessful. As shown in Figure 13, significant cell decay occurred after 300 hours of operation presumably due to electrode flooding. Later it was concluded that the dry air would have a tendency to remove water from the electrolyte near the inlet air portion of the cell.

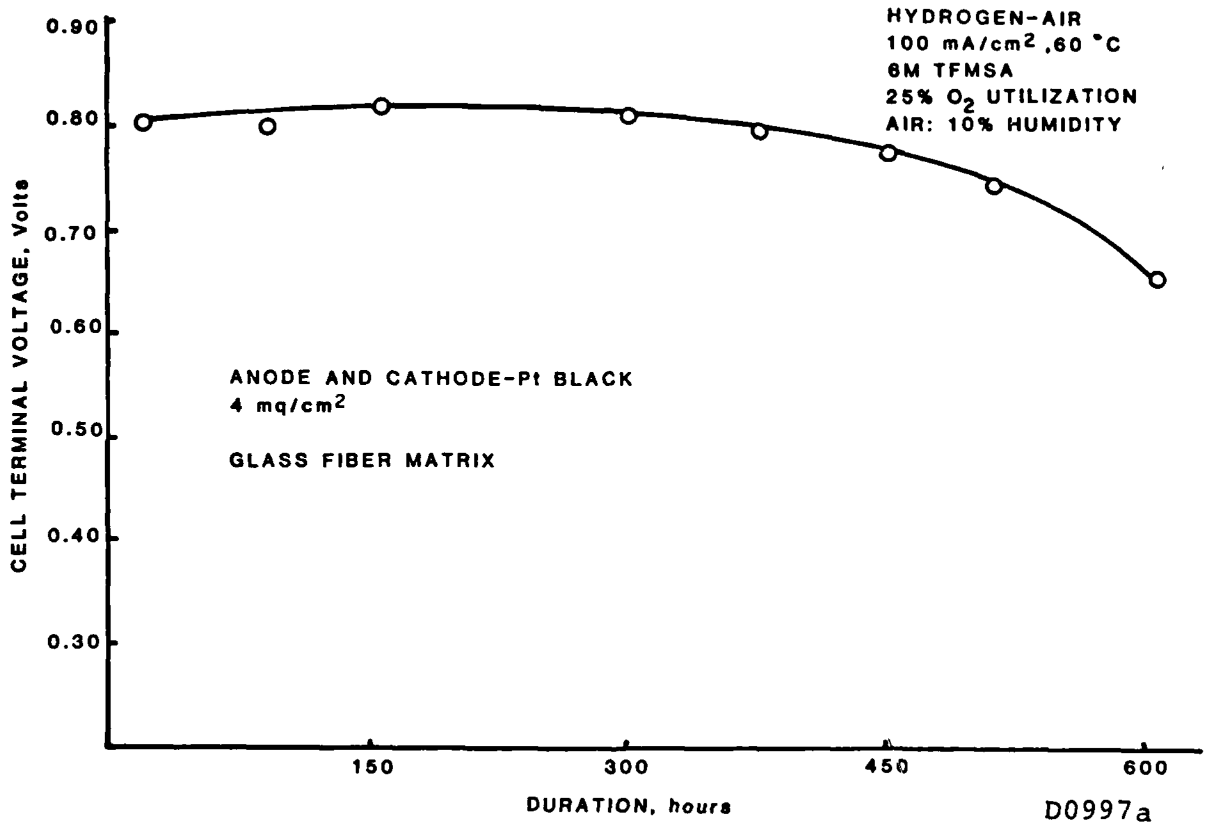

FIGURE 12. ENDURANCE OF Pt BLACK ELECTRODES

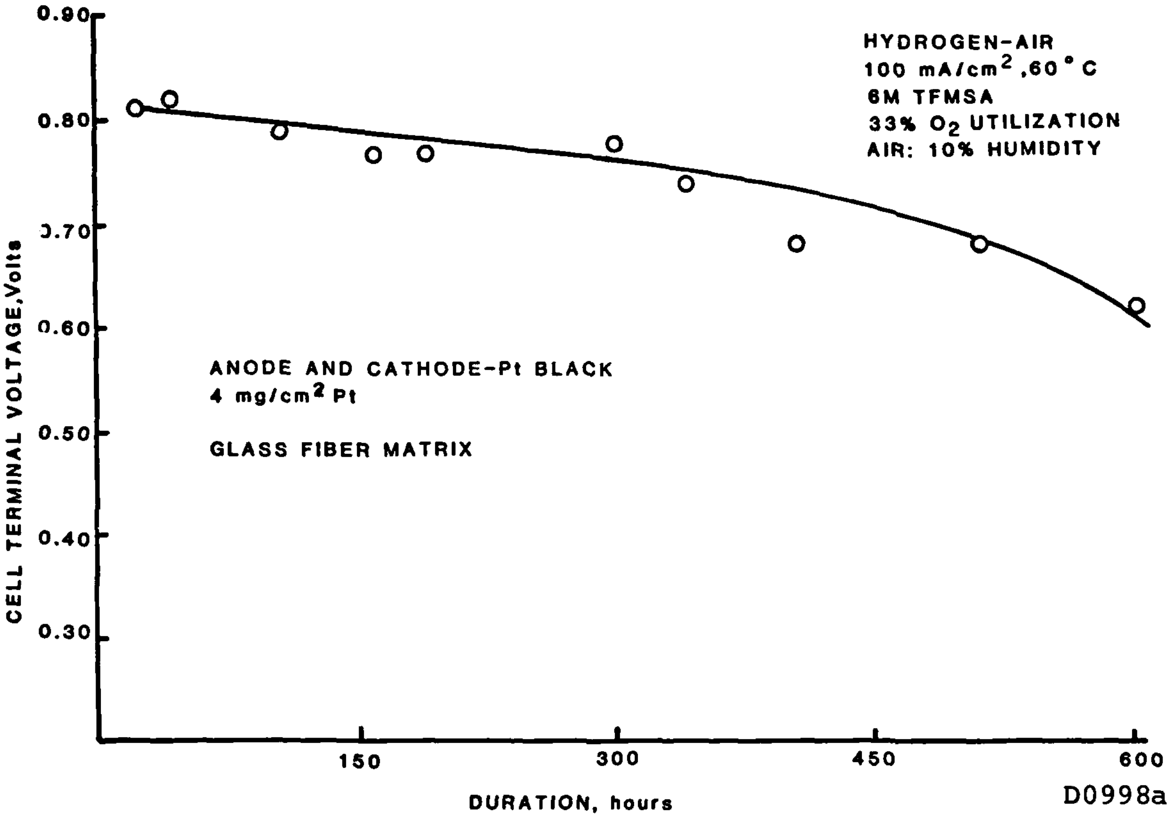

FIGURE 13. ENDURANCE OF Pt BLACK ELECTRODES WITH DRY AIR

This localized concentration of the acid would have an adverse effect on the wetting of PTFE by the electrolyte.

Use of humidified entering air appeared to improve the subsequent stability of 6M TFMSA cells operating at 60°C. A 2100 hour endurance plot for Pt black electrodes is presented in Figure 14. As shown, reasonable stability was maintained for a period of 1600 hours when operating continually at 200 mA/cm^2 on hydrogen and air. After that time, significant decay was evident due to both crossover and electrode flooding. The electrode flooding was probably caused by loss of water balance within the cell. The loss of water balance may have been due to improper control of cell operational parameters.

A slight modification was made within the original van Laar analysis during the course of this study. An extrapolated value of 19000 mm Hg had been utilized initially for the vapor pressure of water at 217°C. This was corrected to 16420 mm Hg when a literature value was found. Recalculation of the partial pressures at 60°C indicated that values of 70.3 mm Hg and 0.0018 mm Hg would be more accurate for water and TFMSA, respectively. This modification essentially lowered the predicted optimum air flow from about 3 to 2.5 stoich. Since the van Laar analysis is probably not absolutely precise, changes were not performed in the air flow rates of existing cells on endurance test.

After improvements were made regarding the water management problem, subsequent emphasis was placed on the evaluation of supported catalyst type electrodes in triflic acid fuel cells. The Pt on carbon black type electrodes currently utilized in phosphoric acid fuel cells continued to pose difficulties in TFMSA fuel cells. Very inconsistent test results were generally obtained with the Pt on carbon black catalyst especially during the first half of this contract. Since alternate supported catalysts (such as Pt on Kocite) were made available for this program, a significant influence of catalyst on cell performance was observed. Pt on Kocite is a proprietary electrocatalyst of UOP Inc. and its optimization for use in phosphoric acid fuel cells was performed during Contract No. DAAG53-76-C-0014, a joint UOP-ERC effort. One batch of Pt on Kocite, designated 3648-115, gave reasonably reproducible performance levels in TFMSA fuel cells. A polarization curve for an electrode structure prepared from 3648-115 Kocite electrocatalyst containing 0.64 mg/cm^2 Pt is presented in Figure 15. This identical electrode had been evaluated with phosphoric acid electrolytes during Contract No. DAAG53-76-C-0014.[18] In Figure 16, a comparison is made between the hydrogen-air performance of the same electrode in 6M TFMSA and 101.6% H_3PO_4. The cells differed only with respect to operating temperature and the cell matrix. (A Kynol matrix was uti-

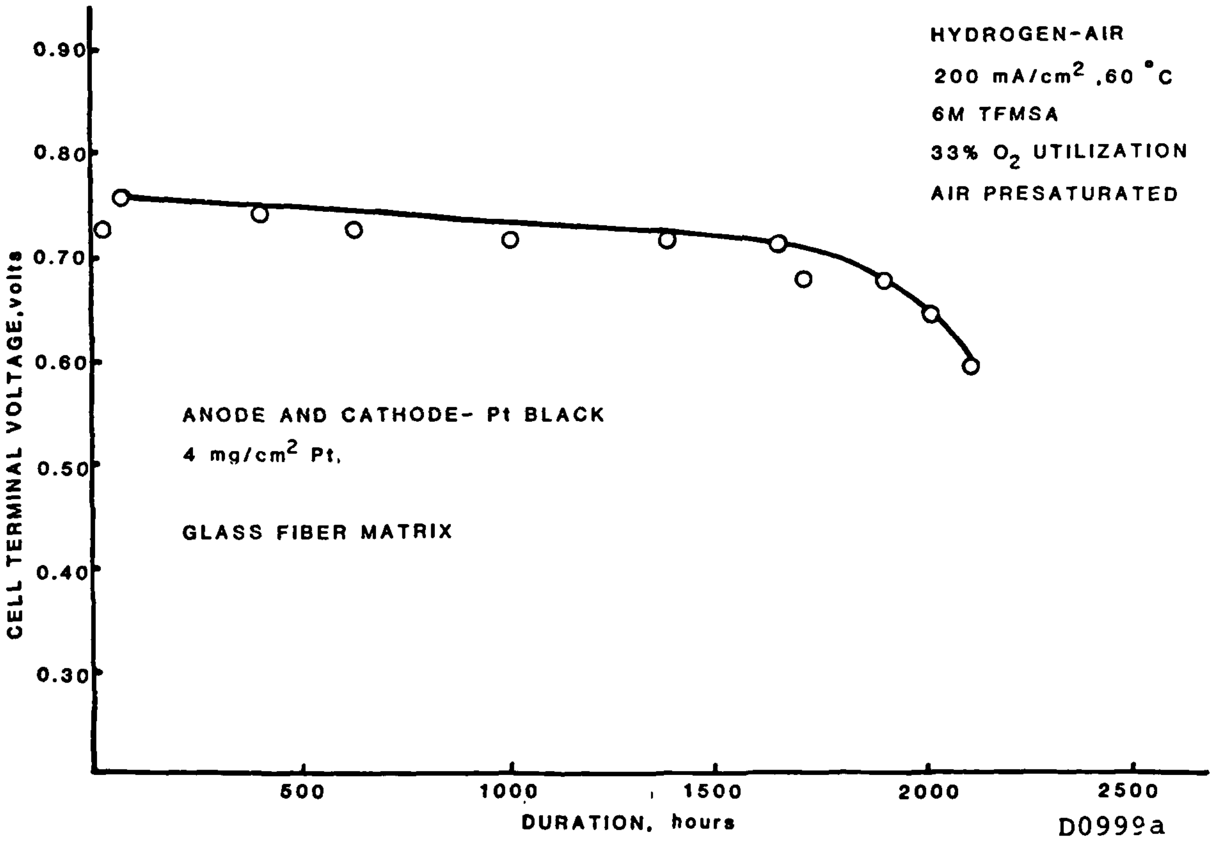

FIGURE 14. ENDURANCE OF Pt BLACK ELECTRODES WITH PRESATURATED AIR

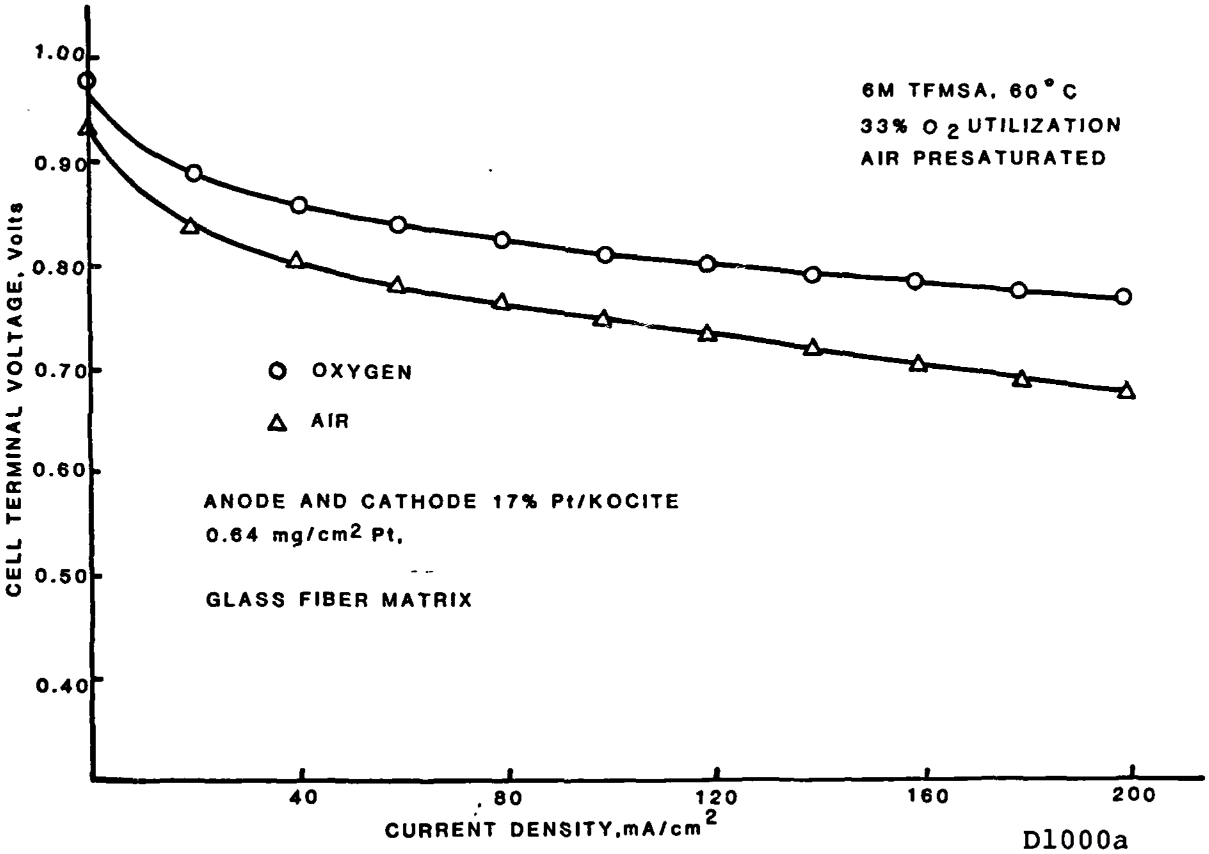

FIGURE 15. PERFORMANCE OF Pt ON KOCITE ELECTRODES

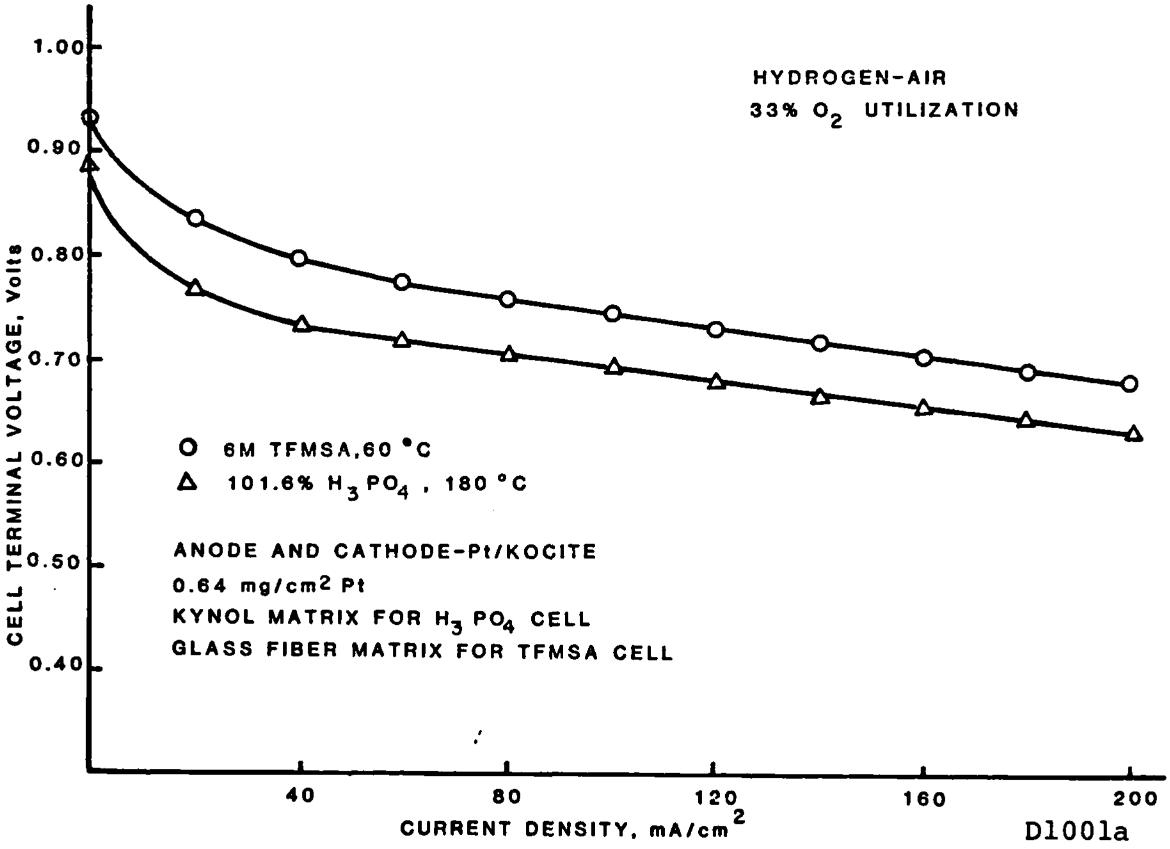

FIGURE 16. COMPARISON OF ELECTRODE PERFORMANCE IN TFMSA AND H_3PO_4

lized within the phosphoric acid cell.) As shown, the air performance of the triflic acid cell at 200 mA/cm^2 was 50 mV higher than for the phosphoric acid cell. Twenty mV of this difference was attributed to a lower cell resistance. The lower cell resistance was probably due to the thin nature of the glass fiber matrix utilized in the triflic acid cell. In Figure 17, a 2300 hour endurance history of Pt on Kocite electrodes with 6M TFMSA electrolyte is presented. Reasonable cell stability was maintained for a period in excess of 2000 hours. Eventual cell failure appeared to be related to electrode flooding.

Pt on carbon black catalysts were successfully employed in TFMSA fuel cells when the sheet mold electrode fabrication technique was substituted in place of the calendering process. As shown in Figure 18, performance levels equivalent to similarly loaded Pt on Kocite electrodes could be obtained. The reason for the improved results with the sheet molded electrodes over the rolled electrodes with the Pt on carbon black catalyst is not precisely known. A cell with the Pt on carbon black type electrodes was successfully operated for approximately 3900 hours. The endurance plot (Figure 19) indicates that acceptable stability was maintained for at least 3000 hours. Significant performance loss was related to matrix degradation, as evidence by severe gas crossover and some electrode flooding.

Although the glass fiber matrix had been successfully operated for long periods in TFMSA cells, it was recognized that its reliability was in question. Silicon carbide, because of its inertness in acid solutions did appear to be a more promising matrix material. Initial attempts to duplicate the high performance levels of the glass fiber matrix cells generally were unsuccessful with the SiC cells. Cell resistances appeared to be about double that for similar cells with the glass fiber. Later in the program, the high resistance problems were eliminated. In addition, improved cell assembly procedures were utilized in which more compression was applied to the cell components. As shown in Figure 20, acceptable cells could be assembled with the SiC matrix.

A systematic study of the effects of temperature on cell performance was not performed. However some testing was conducted at temperatures in excess of 60°C. The primary purpose of the higher temperature operation was to determine whether acid decomposition could occur. Also it would probably be necessary to raise cell temperatures in the future to impart carbon monoxide tolerance to low loaded anodes in TFMSA cells. Operation at temperatures higher than 60°C would have a natural tendency to further concentrate the 6M solution. To prevent this occurrence, more water was initially added to the inlet air stream of the fuel cell. For instance at 90°C, an appropriate water balance indicated that a 3 stoich air flow rate could be supplied to the

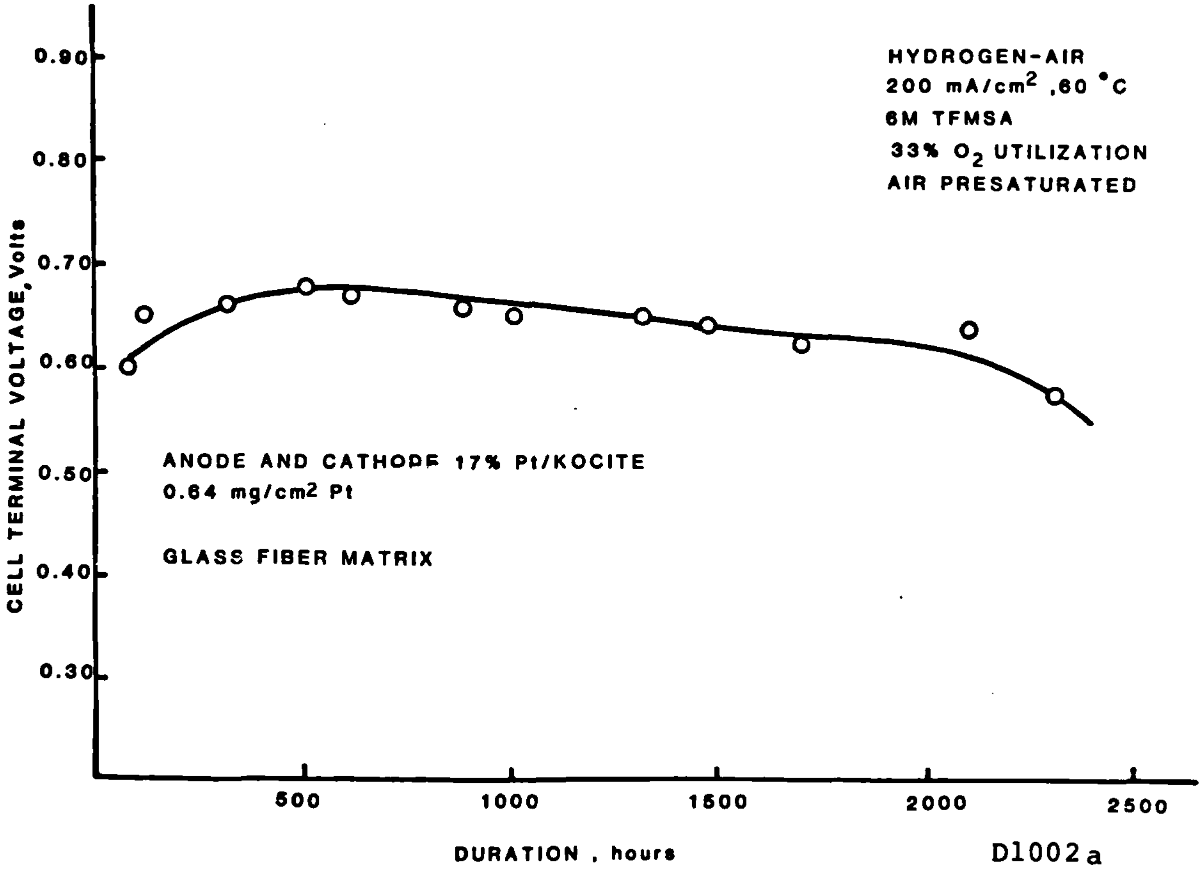

FIGURE 17. ENDURANCE OF Pt ON KOCITE ELECTRODES

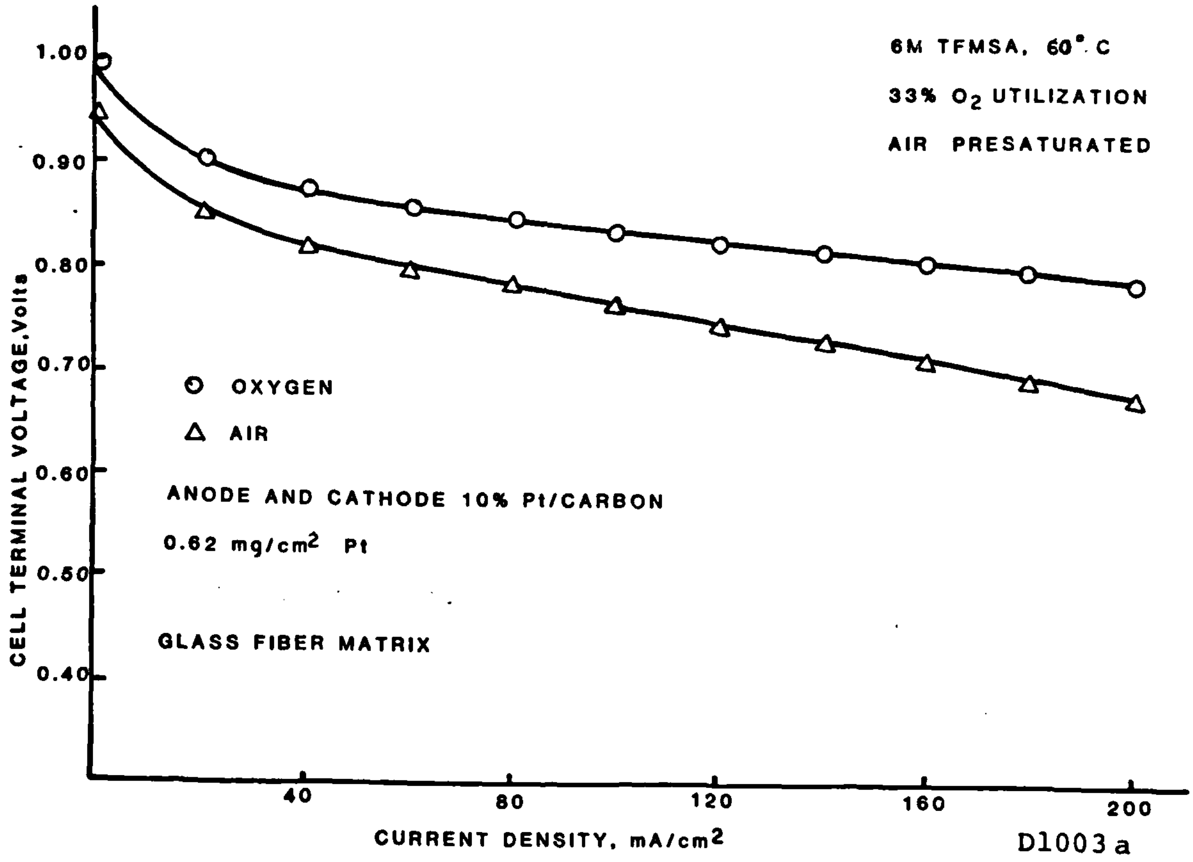

FIGURE 18. PERFORMANCE OF Pt ON CARBON ELECTRODES

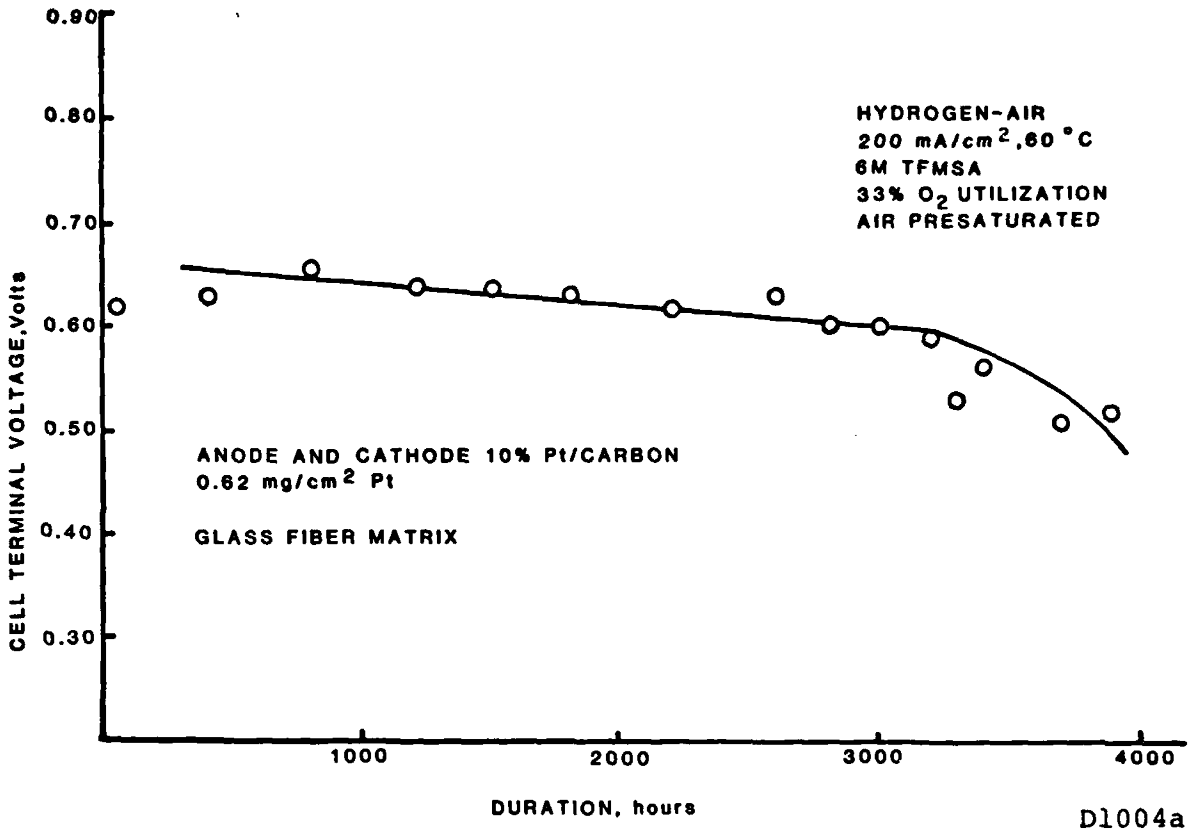

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FIGURE 19. ENDURANCE OF Pt ON CARBON BLACK ELECTRODES

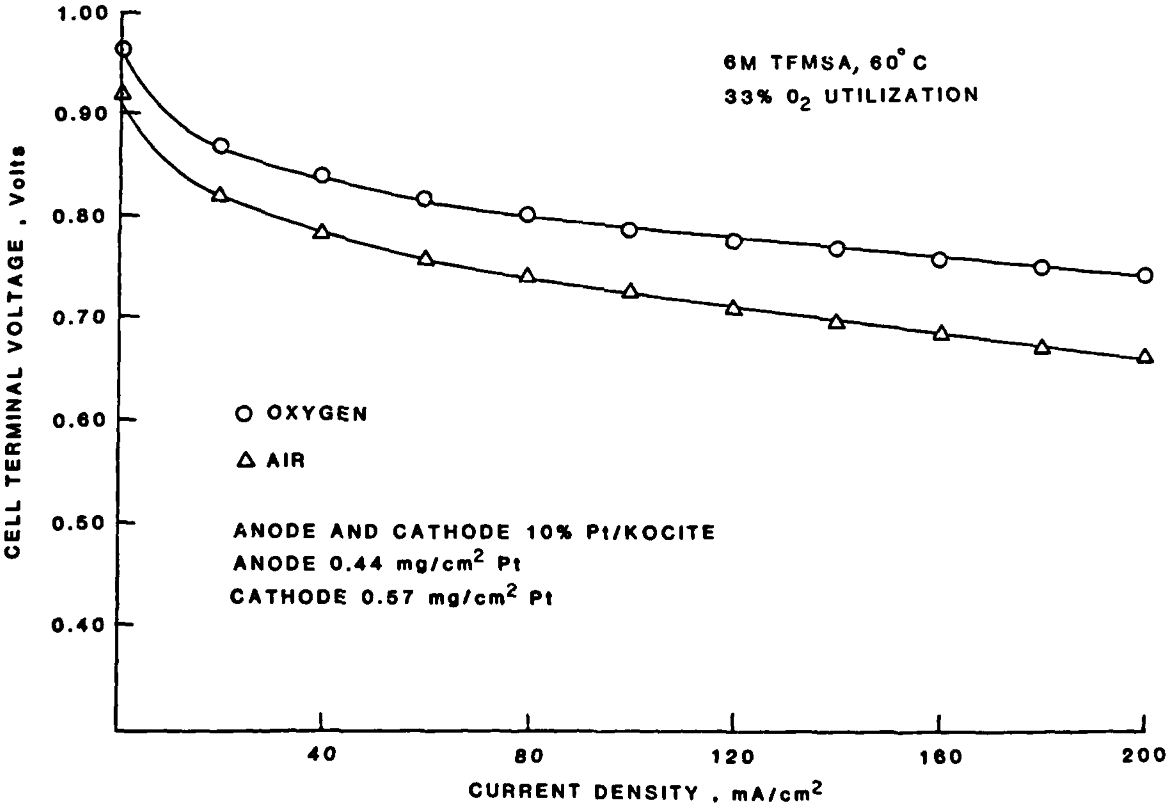

FIGURE 20. SiC MATRIX CELL

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cell if the inlet air was presaturated at a temperature of 68°C. The performance characteristics of a 6M TFMSA cell operating at 90°C is presented in Figure 21. As shown, only slight performance increases were evident over similar cells operating at 60°C. This is consistent with the observations of others, that the activation energy for the air reduction reaction in triflic acid is relatively low and only small gains are incurred by increasing cell temperature.[5] At 90°C, cell stability was acceptable and there was no evidence of any acid decomposition. There was also no indication of the presence of H_2S which is a decomposition product of sulfuric acid electrolytes at this temperature.

It must be pointed out that during endurance testing of TFMSA cells, cell performance fluctuated to a greater degree than is normally experienced with phosphoric acid fuel cells. These fluctuations were probably caused by some temperature cycling during operation, as the cells were not thermostated. Slight acid loss during operation may also have been a factor. Electrolyte replenishment was generally performed at least on a twice a week basis. During this program, all cells appeared to be cathode limited, as is the case with most acid fuel cells. Severe anode polarization effects could be induced if the entering hydrogen contained significant amounts of carbon monoxide. Attempts to operate cells with a fuel containing 1% CO resulted in immediate and severe losses of about 250 mV in the cell terminal voltage. Initial cell performance could be restored when pure hydrogen was again supplied.

2.3.2 Stack Evaluation

A total of seven experimental stacks with 6M TFMSA as the electrolyte were assembled and tested. Both two and three cell stacks were evaluated. A summary of the fuel cell components utilized in each of the multicell units is presented in Table 3.

The initial stack assembled consisted of sheet molded Pt on carbon black electrodes with nominal loadings of about 0.50 mg/cm^2 of Pt. A 0.008 in. silicon carbide layer was utilized as the matrix. Each cell was assembled wet (approximately 12 ml of 6M triflic acid was added). Preliminary calculations suggested that this amount of electrolyte should be sufficient to fill the matrix and electrode structures. In rough terms, the acid was expected to equally distribute between the anode, cathode, and matrix. Initial attempts to operate this three-cell stack were unsuccessful as the stack had little load carrying capabilities. In addition, the open circuit voltages for each cell were less than 0.70V which suggested that crossover was prevalent. Additional electrolyte was added to the cell reservoir to fill the apparently dry cell components. This was also unsuccessful as the electrolyte readily leaked from the reservoir. No meaningful data was obtained from this stack.

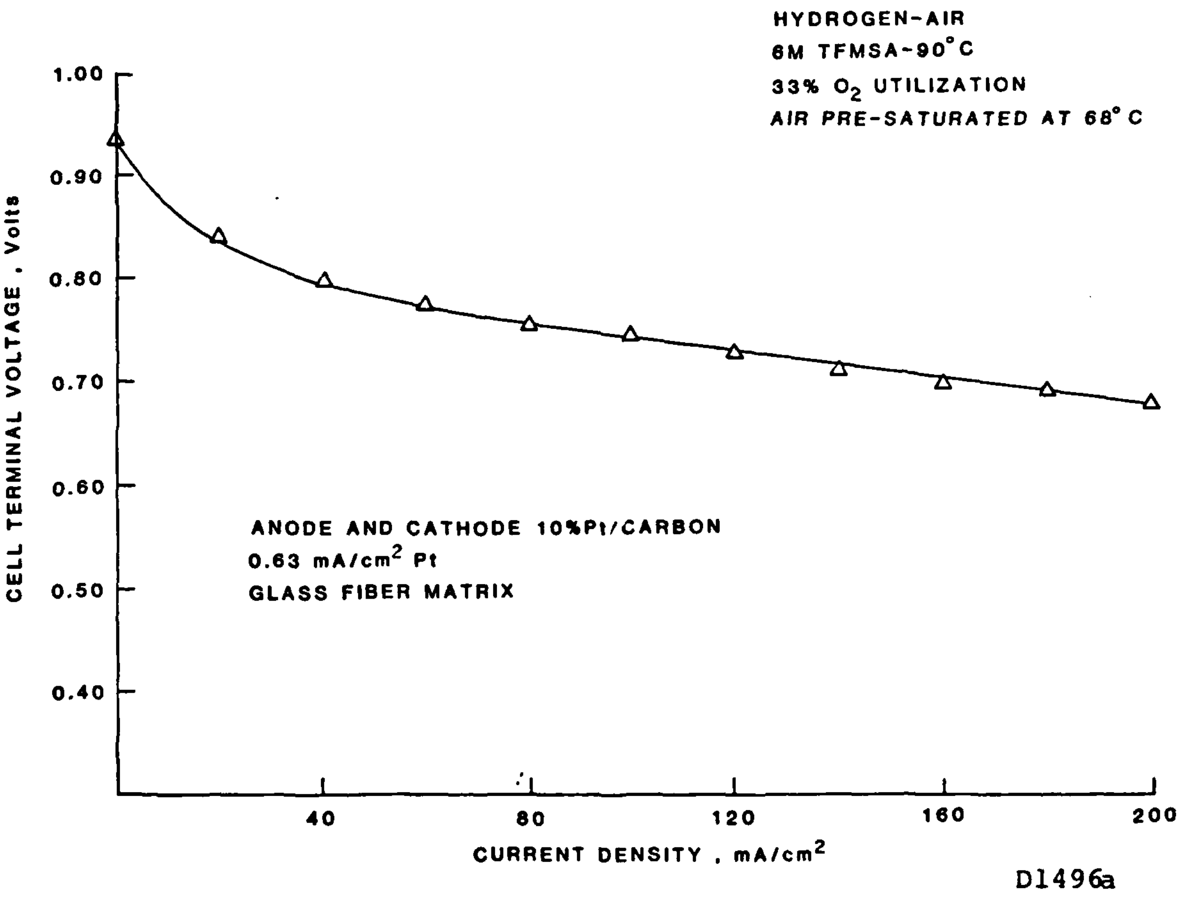

FIGURE 21. CELL PERFORMANCE AT 90°C

TABLE 3

TFMSA STACK COMPONENTS

STACK NUMBER	NUMBER OF CELLS	ELECTRODES		MATRIX
		ANODES	CATHODES	
1	3	10% Pt/Carbon Sheet Mold 0.40 mg/cm^2 Pt	10% Pt/Carbon Sheet Mold 0.50 mg/cm^2 Pt	SiC
2	2	10% Pt/Carbon Sheet Mold 0.25 mg/cm^2 Pt	10% Pt/Carbon Sheet Mold 0.50 mg/cm^2 Pt	SiC
3	2	15% Pt/Kocite Rolled 0.55 mg/cm^2 Pt	15% Pt/Kocite Rolled 0.55 mg/cm^2 Pt	Mat-1
4	2	5% Pt/Kocite Rolled 0.25 mg/cm^2 Pt	5% Pt/Kocite Rolled 0.25 mg/cm^2 Pt	Mat-1
5	2	10% Pt/Carbon Sheet Mold 0.50 mg/cm^2 Pt	10% Pt/Carbon Sheet Mold 0.55 mg/cm^2 Pt	Mat-1
6	2	10% Pt/Carbon Rolled 0.55 mg/cm^2 Pt	10% Pt/Carbon Rolled 0.55 mg/cm^2 Pt	Mat-1
7	2	10% Pt/Kocite Rolled 0.45 mg/cm^2 Pt	10% Pt/Kocite Rolled 0.55 mg/cm^2 Pt	Mat-1

A second stack was assembled with similar components. However the number of cells was reduced from three to two. It was rationalized that if heat buildup problems did occur during continual operation, the middle cell of a three cell stack could be at higher temperatures than the two end cells. Stack No. 2 was assembled with about 16 ml of acid/cell. With the additional acid, the open circuit voltages of the cells (0.85V) approached acceptable values. In addition, cell terminal voltages of about 0.50V/cell at 100 mA/cm^2 and ∿60°C could be sustained for about 90 minutes. During operation, the air flow was maintained at about the three stoichiometric rate. This relatively low flow was insufficient to maintain a constant temperature and the cells gradually got hotter. Efforts to improve performance by adding additional acid were not successful. Upon cell teardown the cell components appeared to be relatively dry.

Several major changes were incorporated in Stack No. 3. Pt on Kocite electrodes with 0.55 mg/cm^2 Pt loadings were utilized. In addition, a proprietary matrix designated Mat-1 was used for the first time. The Mat-1 matrix has a higher bubble pressure than the SiC matrix and also exhibits better acid retention characteristics. Since the Mat-1 matrix is relatively porous, additional electrolyte was initially supplied to this stack. A polarization curve for this stack shortly after startup at 60°C is presented in Figure 22. The cell terminal voltages for each cell averaged 675 mV and 580 mV at 100 mA/cm^2 and 200 mA/cm^2, respectively, on hydrogen and air. At the time, these performance levels were higher than for similarly loaded phosphoric acid stacks operating at 180°C at ERC. This stack was endurance tested at 100 mA/cm^2 for durations of about 3 hours daily over a period of several days. The stack was shut down when the average cell temperature reached ∿65°C. Some portions of the stack reached temperatures as high as 75°C. After several days in this testing mode, significant cell decay was evident. The cells became air sensitive which suggested that electrode flooding was prevalent. The loss of cell water balance (concentration of the electrolyte) was the suspected decay mechanism. Attempts to restore initial performance levels by electolyte addition were unsuccessful. The use of the Mat-1 matrix in this stack did result in some net improvements. High initial performance levels were demonstrated and electrolyte leakage from the reservoir area (prevalent with the SiC cells) was considerably reduced.

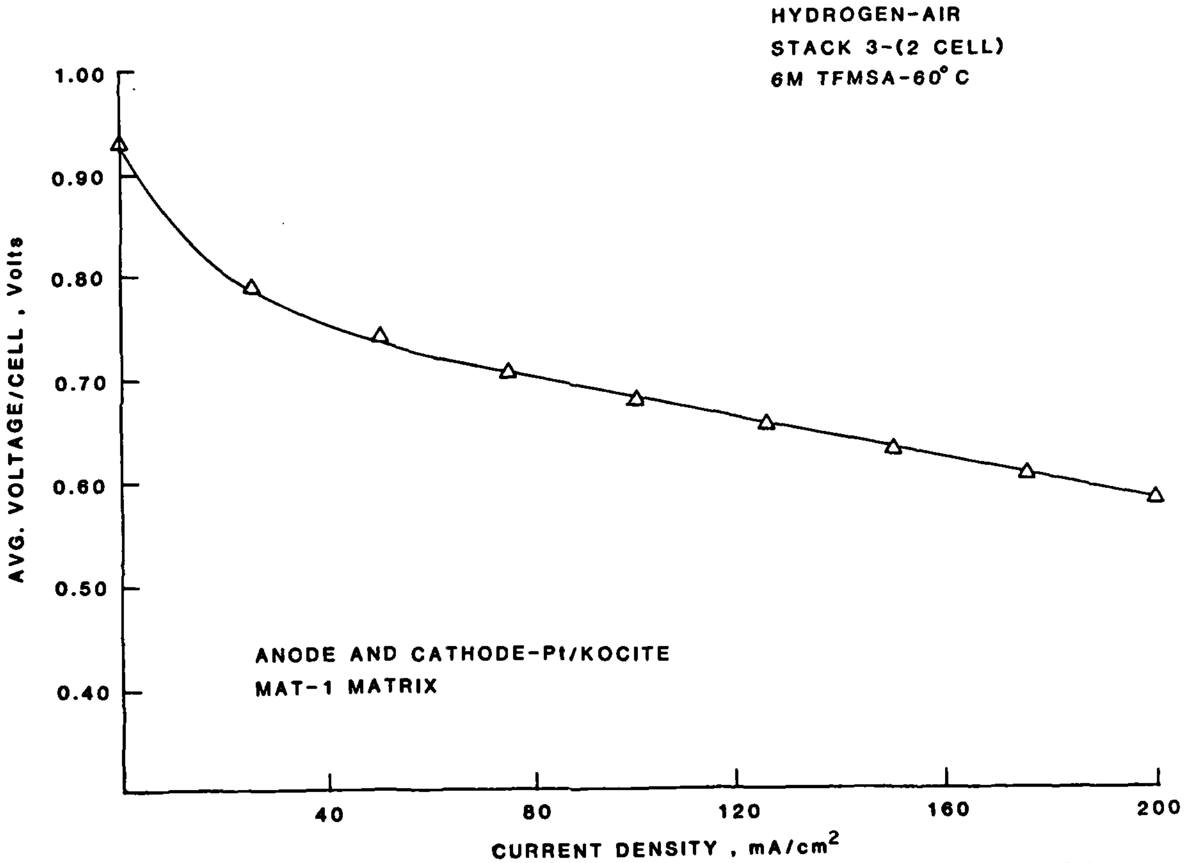

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FIGURE 22. PERFORMANCE OF TFMSA STACK NO. 3

Stack No. 4 was assembled with components similar to Stack No. 3. Due to a lack of sufficient 15% Pt on Kocite electrocatalysts, a 5% Pt on Kocite batch was utilized in fabricating the electrodes. There was a corresponding decrease in nominal electrode loading from 0.50 to 0.25 mg/cm^2 of Pt. Initial performance levels at 60°C were acceptable for this stack, as cell terminal voltages at 100 mA/cm^2 were 640 mV/cell. Correcting for the effect of Pt loading, the performance is equivalent to that of Stack No. 3. An attempt was made to operate this stack at 72°C. The inlet air was pre-saturated at about 40°C to prevent acid concentration. Severe decay occurred at 72°C but the cells did not appear to be air flow sensitive which is indicative of electrode flooding.

Sheet molded Pt on carbon black electrodes were utilized in Stack No. 5. The maximum performance level demonstrated for this stack was only 590 mV/cell at 100 mA/cm^2. Although sufficient acid was initially added to the cells during assembly, the electrodes proved difficult to wet. Apparently much of the electrolyte was squeezed during compression of the stack. In addition, the sheet mold electrodes were not as uniform in thickness as the rolled electrodes. This made it difficult to replenish electrolyte, as the acid readily leaked from the reservoir.

Electrodes for Stack No. 6 were prepared from a modified catalyst formulation. In this case, the carbon black support was initially impregnated with a platinum diammino dinitrite salt. Subsequently the catalyst was thermally decomposed in air at 230°C to convert the salt to noble metal. This catalyst, when prepared into rolled electrode structures, had given satisfactory performance levels in small 25 cm^2 cells with 6M TFMSA. It was speculated that these experimental electrodes would be more easily wetted with the triflic acid electrolyte when assembled into stack configurations. Peak performance levels for electrodes of this type were about 600 mV/cell at 100 mA/cm^2 on air. This technical approach was subsequently terminated.

Stack No. 7, containing heat-treated plates, was also assembled with Pt on Kocite type electrodes and Mat-1 type matrices. Initial performance levels for both cells within the stack were acceptable. As shown in Figure 23, average cell voltages of 670 and 590 mV were obtained at 100 and 200 mA/cm^2, respectively. Endurance testing of this stack was not possible as the performance of one cell became very erratic. Crushing of the electrode backing paper due to overcompression was diagnosed to be the cause of cell decay.

3.0 CONCLUSIONS

Aqueous solutions in which the mole fraction of TFMSA is less than ∿0.20 have been shown to be effective electrolytes for use in low temperature fuel cells. Use of dilute solutions of triflic acid results in improved kinetics for the air reduction reaction when compared with more conventional electrolytes such as concentrated phosphoric acid. When tested in actual subscale size TFMSA fuel cells, various electrode structures exhibited performance increases at least 50 mV higher than similarly loaded electrodes operating in phosphoric acid at much higher temperatures. A variety of electrocatalysts (such as unsupported Pt and Pt supported on carbon and Kocite) were successfully employed in aqueous TFMSA fuel cells.

Aqueous TFMSA cells could be operated stably at temperatures up to 60°C if the initial acid concentration was maintained. Effective water management during long-term testing was the most important factor relating to cell stability. Cells were tested for up to 3900 hours and a moderate stability was sustained for 3000 hours. The van Laar equations appeared to give a reasonable approximation of the activity coefficients of both TFMSA and water as a function of the solution composition.

The partial pressures of water calculated by the van Laar analysis were utilized to maintain cell water balance. The analyses also predicted that acid loss from operating cells at 60°C with dilute triflic acid electrolyte would not be a major problem. The 6M TFMSA solution appears to be roughly an optimum concentration at 60°C if the entering air to the fuel cell is at ambient temperature. Cell stability was improved when the entering air was humidified. Cell operation with the 6M electrolyte was also possible at 90°C if the inlet air was pre-saturated at elevated temperatures. At the temperatures evaluated during this program, there was no evidence of any acid decomposition. The cells were cathode controlled, as no major anode decay mechanisms could be identified when operating with pure hydrogen.

Initial evaluation of TFMSA electrolytes within stack configurations was encouraging as acceptable initial performance levels were achieved. Demonstration of long-term stability in stacks was hampered by the necessity of maintaining both cell water balance and temperature control by means of the process air alone.

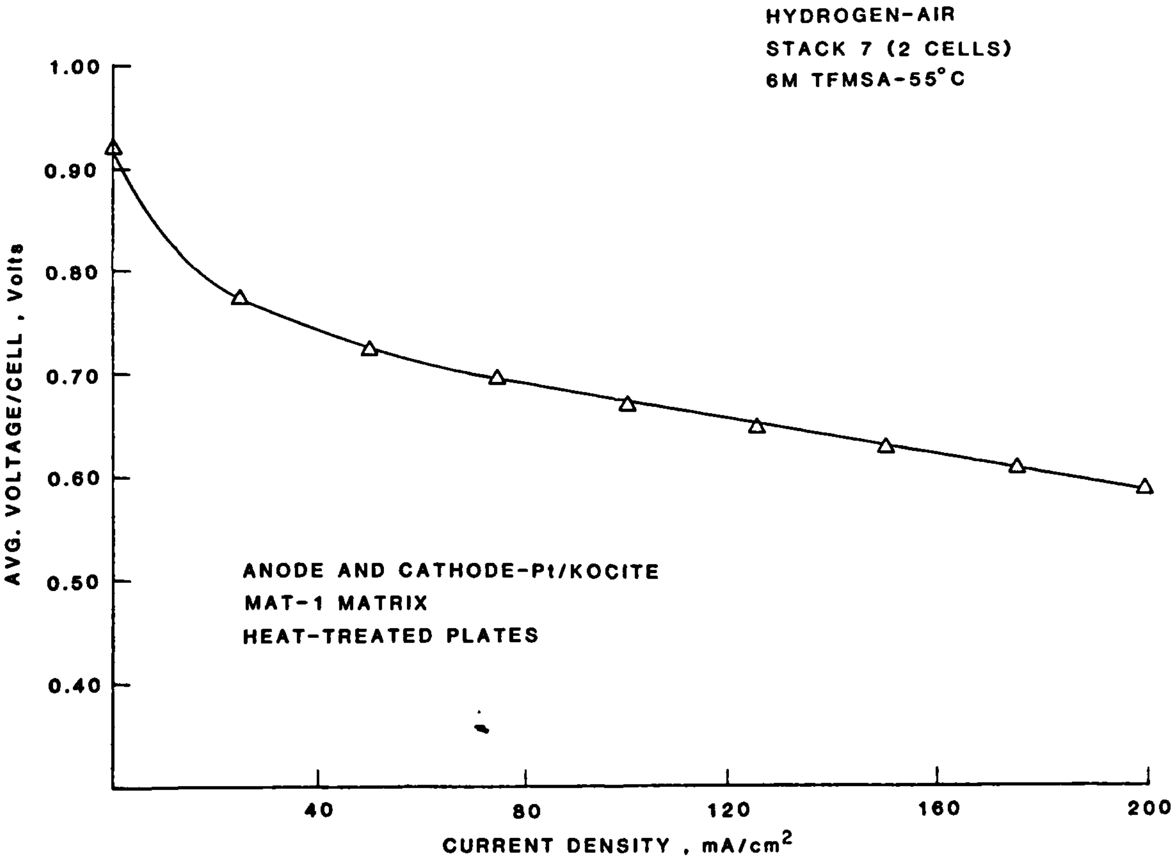

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FIGURE 23. PERFORMANCE OF TFMSA STACK NO. 7

4.0 RECOMMENDATIONS FOR FUTURE WORK

In the future, four main areas involving TFMSA fuel cells should be emphasized:

- liquid-vapor equilibria of TFMSA-water solutions
- improved cathode catalysts and electrodes
- effects of carbon monoxide concentration
- TFMSA stack development

More precise data relating to the partial pressures of water and TFMSA as a function of composition and temperature should be sought. Both analytical and experimental techniques should continue to be evaluated. Knowledge of these properties of aqueous TFMSA solutions will be necessary for stable fuel cell operation, especially at temperatures in excess of 60°C.

Although high cathode potentials have been demonstrated in aqueous TFMSA cells, the electrode structures are probably not totally optimized in TFMSA electrolyte. Cathodes do exhibit higher than normal diffusional losses even during periods of apparent stable operation. This would suggest that alternate degrees of electrode wetproofing should be attempted. Use of graphitized support materials and alloy type electrocatalysts currently being evaluated in phosphoric acid cells may also enhance long-term stability.

It will be necessary to determine quantitatively the relationship between fuel CO content and anode polarization as a function of temperature. Alternate anode catalysts may be required in order to tolerate significant amounts of CO. Noble metal alloys of Pt and either Ru or Rh may be less susceptible to poisoning and should be tested.

TFMSA stack development is complicated by the necessity of maintaining both cell water and heat balance. The use of process air alone to remove excess water and heat is probably impractical within stack configurations. The DIGAS concept, in which a portion of the cell cooling air does not contact the electrolyte, may be a solution to this problem.

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