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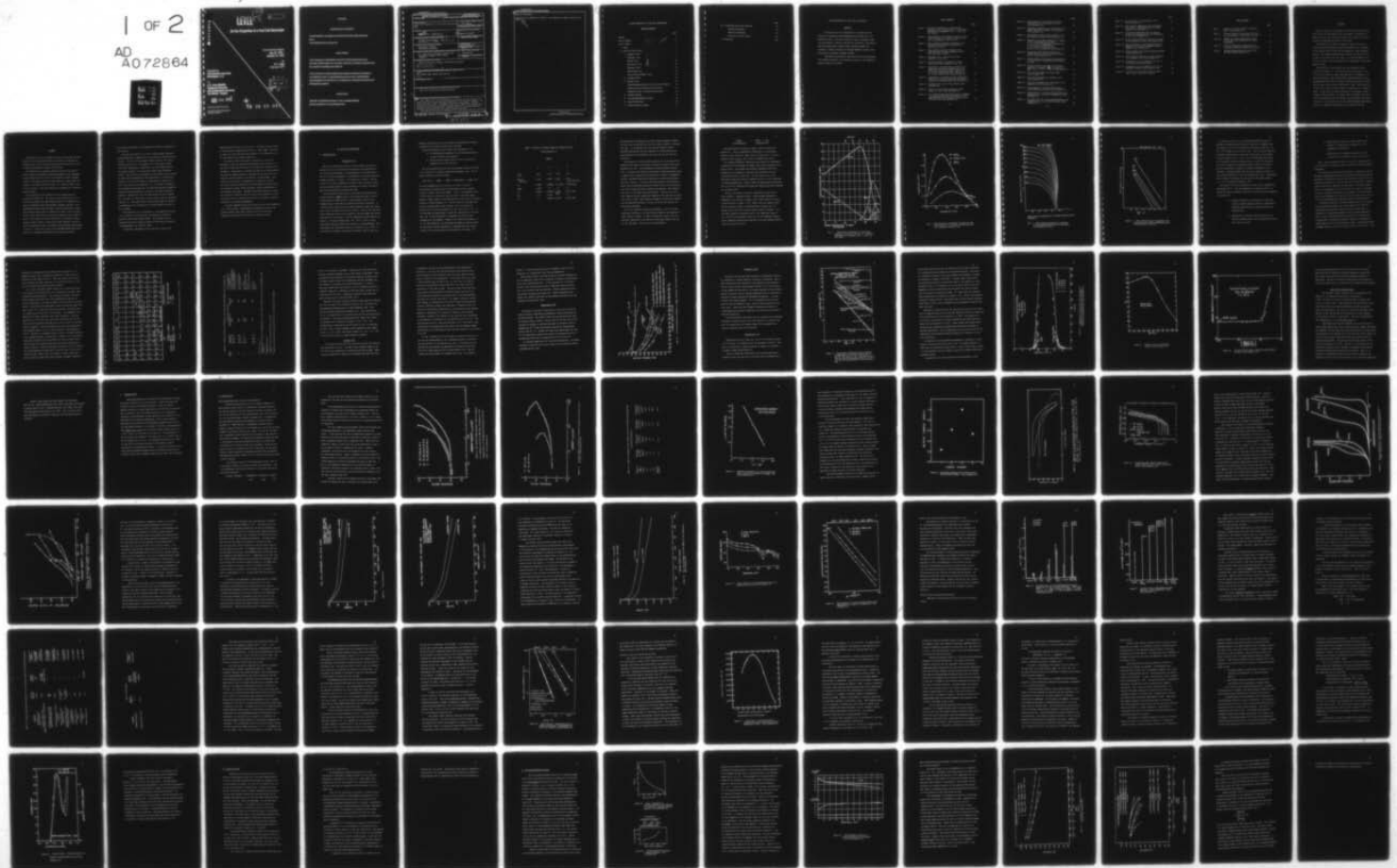
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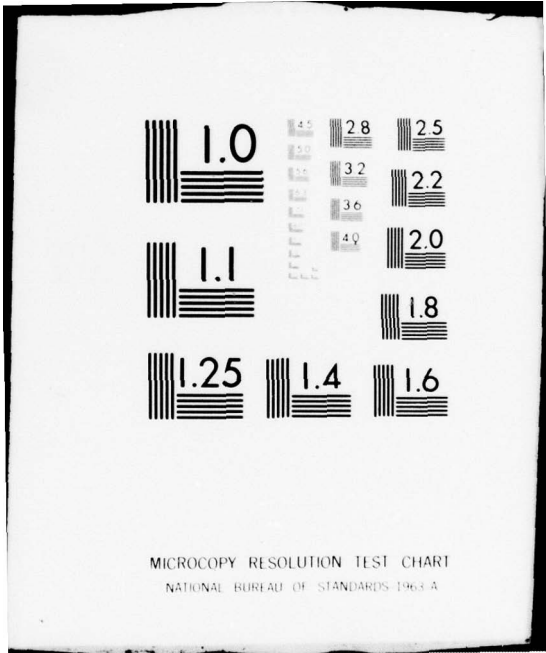
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On the Properties of a Fuel Cell Electrolyte

Final Technical Report
July 10, 1978 -
January 15, 1979

By
R.T. Foley
February 1979

Prepared by
The American University
Washington, D.C.

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

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questions to be answered to develop a low temperature organic sulfonic acid system.



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ON THE PROPERTIES OF A FUEL CELL ELECTROLYTE

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ON THE PROPERTIES OF A FUEL CELL ELECTROLYTE

Abstract

The field of fuel cell electrolytes is surveyed with the objective of learning the deficiencies and good properties of the available systems. The survey included a study of inorganic acids such as phosphoric, sulfuric, hydrochloric, perchloric, hydrofluoric and other strong acids; organic acids including sulfonic and carboxylic; alkaline systems; ion exchange membrane systems; solid electrolytes; and molten carbonate systems.

Some general and specific conclusions are listed indicating the technical questions to be answered to develop a low temperature organic sulfonic acid system.

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I SCOPE

With this survey it is intended to review the work that has been done on fuel cell electrolytes with the objective of defining the present status of the field and indicating those directions in which it would be profitable to proceed in the future.

The evaluation of a specific compound is made in the light of certain physical and chemical properties possessed or not possessed by the compound and this part of the evaluation is fairly straightforward. The complete evaluation must, however, be made within the context of the overall fuel cell field, i.e., where we expect to be in 10 or 20 years. This view requires the consideration of some more general factors.

The objectives of the national fuel cell program have been reviewed by Lawrence (1). He projects future applications of fuel cells such as systems for small municipalities (5-27 megawatts), oil and coal converters, small installations (shopping centers), using air-methane mixtures from coal mines, vehicular applications, conversion of waste, and the use of a multitude of fuels. What this means is that a fuel cell electrolyte should be compatible with a number of fuels. In the future it would be desirable to use methane, ethane, propane, butane, methanol, hydrocarbon liquids (naphtha, heating oil, jet fuel, gasoline), as well as hydrogen, carbon monoxide, and mixtures of the two. It may well be that in the 1990-2000 period this country will be in a hydrogen economy which would certainly alter the

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electrolyte requirements. This possibility should be considered but not relied on.

The fuel cell should fit in with an overall energy conversion program implying its compatibility in such systems as hybrid electric vehicles. The fuel cell development should dove-tail with energy storage objectives (2). For example, 4% of the nation's energy conversion requirement is industrial, e.g., the aluminum and the chlor-alkali industry, that uses direct rather than alternating current. The fuel cell, producing, as it does, direct current, should be particularly advantageous in such applications. On theoretical grounds, a fuel cell can operate on hydrocarbon-air mixtures and this is the trend in the technology. So, in addition to operation with reformates (containing CO), the electrolyte should be capable of sustaining operation directly on naturally occurring hydrocarbon mixtures. Additionally, there are indications that our technology has proceeded to a point where a direct coal-air cell is technically feasible (3). This implies that the electrolyte might be required to scavenge the ash, tolerate CO₂ as the main product, and use air as the oxidant.

Electrocatalysis is, by definition, a low temperature process, i.e., the energy of activation for the process is furnished by electrical rather than thermal energy. This implies that the preferred electrolyte should be capable of operating at relatively low temperatures, e.g., 100°C or lower.

An important requirement for the electrolyte lies in the

expected operating life of the fuel cell. This has now been extended to 40,000 hours at temperatures in the 125 - 150°C range. This must be reflected in the allowable vapor pressure of the compound as well as other physical and chemical properties.

With some of these more general considerations in mind the behaviors of specific compounds were examined, where practical, in fuel cell systems, and the reasons for acceptance or rejection were determined. Specifically, an attempt was made to cite the properties that make the compound useful, the properties that have led to its rejection, and what remains to be done for its improvement. Such items as the fuel used, the temperature of operation, the life, the current density allowable with H₂ and propane, the power density, the voltage at certain current densities, and the availability of the material were sought. Throughout an attempt was made to extract the scientific principles that would lead to the formulation of the specifications for an electrolyte, such as acid strength, adsorption properties, or conduction mechanisms.

The major emphasis during this review has been on low temperature (25 - 175°C) systems. Comprehensive and detailed reviews of the molten carbonate electrolyte field and the solid oxide high temperature electrolyte field have been conducted recently.

II FUEL CELL ELECTROLYTES

A. Inorganic Acids

Phosphoric Acid

Much of the early fuel cell work in acid solution was done with sulfuric acid, but, when attention was drawn to the hydrocarbon-air cell (4) certain advantages to using phosphoric acid became obvious. At 89 °C the electro-oxidation of cyclopropane at a platinum anode was roughly the same in 3 M H₂SO₄ , 6.8 M H₃PO₄ and 4 M HClO₄. However at 150 °C, 14.6 molar phosphoric acid was the most effective electrolyte and propane supported current densities in excess of 100 ma/cm² when platinum-catalyzed electrodes were used.

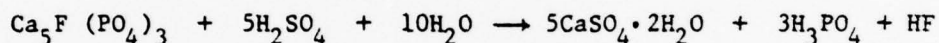
In most practical systems such as the United Technologies Power Systems Division's TARGET project, their Utilities project, and the "first generation" ERDA project (1) 85% phosphoric acid is used. Phosphoric acid is the best air breathing electrolyte available. It is also tolerant toward dilute and impure hydrogen streams which means that it can be matched with many fuel sources. The acid has reasonable ionic conductance almost in its anhydrous form which means that precise H₂O content is not required. Also the temperature control need not be precise. At elevated temperatures, 150 - 200 °C, the Pt or noble metal alloy catalysts exhibit some tolerance to carbon monoxide. Carbon dioxide, N₂, and methane act only as diluents for H₂. Thus, in the search for alternate electrolytes, phosphoric acid is taken as a

reference electrolyte and for this reason the properties and behavior of phosphoric acid should be known quite precisely.

Commercial phosphoric acid is made by two processes (5, 6);

- 1) by burning molten phosphorous in air followed by hydration of P_2O_5 to form an acid solution;
- 2) the wet process wherein sulfuric acid is reacted with phosphate rock to give the acid.

The first process gives pure acid with analyses indicated in Table I (5). Source "C" is listed as Food Grade phosphoric acid. The wet process involves an overall reaction



but other compounds also are present in the rock so that the resulting acid includes certain concentrations of iron, aluminum, fluorine, calcium, sulfur and arsenic. Most of the phosphoric acid in this country is produced by the wet process, exceptions being: Monsanto, Hooker, Mobil Oil and FMC and much of the latter is converted directly to sodium phosphate (7). The fact that so little goes into the pure chemical market would indicate a lack of attention of manufacturers in producing grades with, say, very low Fe, or As. To our knowledge the significance of these low concentrations of arsenic, iron, etc. on electrocatalysis in phosphoric acid has not been systematically investigated. However it was observed by Brummer, et al. (8) that phosphoric acid (ACS grade from Baker or 85% Food Grade from Monsanto) contains impurities or compounds which are rapidly adsorbed on Pt and which inhibit the deposition of H atoms. They

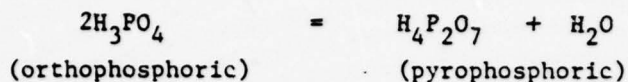
Table I Analyses of Typical Commercial Phosphoric Acids
(from reference 5)

	<u>Source</u>			
	A	B	C	D
H_3PO_4	80 %	75 %	85 %	75 %
Density 20°/20° C	1.628	1.5799	1.6922	1.584 (15.5°/15.5° C)
Fe	0.0010%	0.0010%	5-1.5 ppm	0.5-10.0 ppm
H_3PO_3	0.02%	----	----	----
As	0.0003%	0.0002%	0.2 ppm (max)	0.1-0.5 ppm
SO_4	----	0.01%	----	----
Pb	----	0.0010%	0.5 ppm	0.2-2.0 ppm

speculated that this impurity was a lower valent phosphorus compound and found that the detrimental effect was largely removed by refluxing with H_2O_2 . It is apparent that this question deserves further attention particularly from the standpoint of establishing precise specifications for the phosphoric acid that will go into fuel cell production.

The adsorption of electro-oxidized species on the Pt electrode is apparently the reason for potential cycling with propane cells run in phosphoric acid (9). This phenomenon has been described by Cairns (10). It involves the periodic cycling under constant-resistance load. It appears that, during the electrode process, anions or incompletely oxidized hydrocarbon species are adsorbed on the electrode blocking the flow of current. To provide the needed current, the potential is driven from the operating potential of about 0.5V up to 1.0V at which point the blocking species are oxidized and desorbed. The potential then drops to the normal operating potential. When the cell is not under constant-current loading the potential of the cell may drop from e.g. 0.58V to 0.28V. This cycling is thought to involve anion adsorption and desorption because it is not seen in HF (the fluoride ion being weakly adsorbed).

One of the desirable properties of phosphoric acid is its high temperature stability or at least relative stability in comparison to other "aqueous" systems. It must be recognized, however, that the molecular composition of the solution of 85% H_3PO_4 differs from that of, say, 95% H_3PO_4 . This is due to the equilibrium



This equilibrium is pictured in figure 1 which is taken from reference 11. Thus, at equilibrium, 105% H_3PO_4 is an equilibrium mixture of about 58% ortho, H_3PO_4 , 38% pyro, $\text{H}_4\text{P}_2\text{O}_7$ and 3.5% tripolyphosphoric acid, $\text{H}_5\text{P}_3\text{O}_{10}$, with a trace of higher polymer acids.

This change in molecular composition also affects the conductance-concentration curve although the change in H_2O activity probably has a greater effect. The conductivity reaches a maximum at about 50%, dependent on the temperature, and drops off drastically at those concentrations used in fuel cells. For this reason, one of the undesirable properties cited for phosphoric acid is its low conductance at elevated temperatures. Figure 2 shows the conductance-concentration plot for 40 °C in comparison with H_2SO_4 and $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$, which compounds are discussed below.

Further, the change of molecular composition accounts for the vapor pressure - temperature curve. Vapor pressure isotherms for phosphoric acid are given in figure 3 and a vapor pressure vs inverse temperature plot in figure 4 (15). These curves are working curves for the isopiestic method of measuring vapor pressures and it is against these curves that possible organic acids are compared. The low vapor pressure of phosphoric acid in the temperature range of 150 - 200 °C is one important reason why, of the available inorganic acids, phosphoric acid has been selected as the most suitable electrolyte for the acid fuel cell.

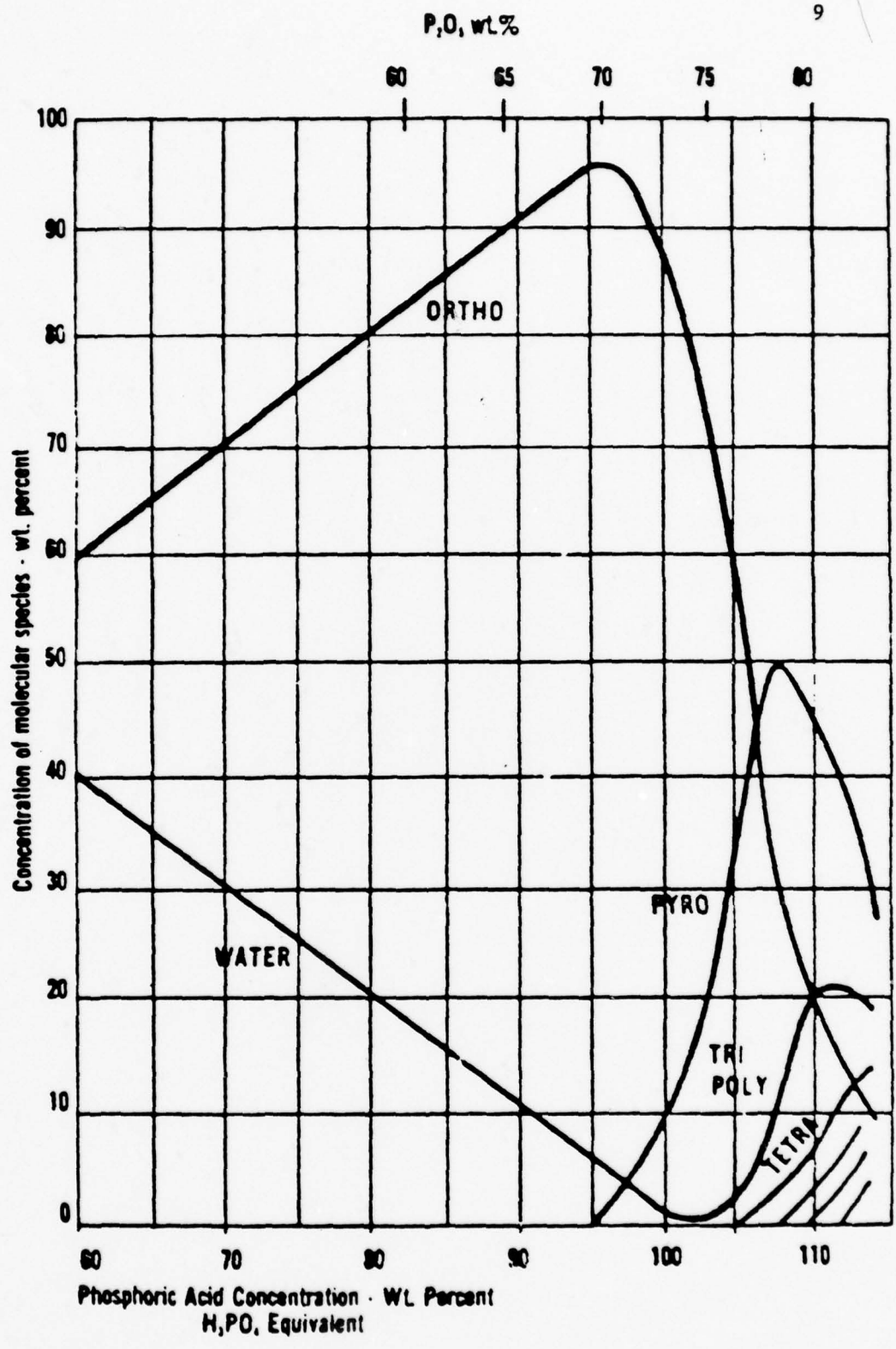


Fig. 1 Equilibrium composition of concentrated phosphoric acid (from reference 11, originally from Huhti and Gartaganis, Can. J. Chem. 34, 785 (1956))

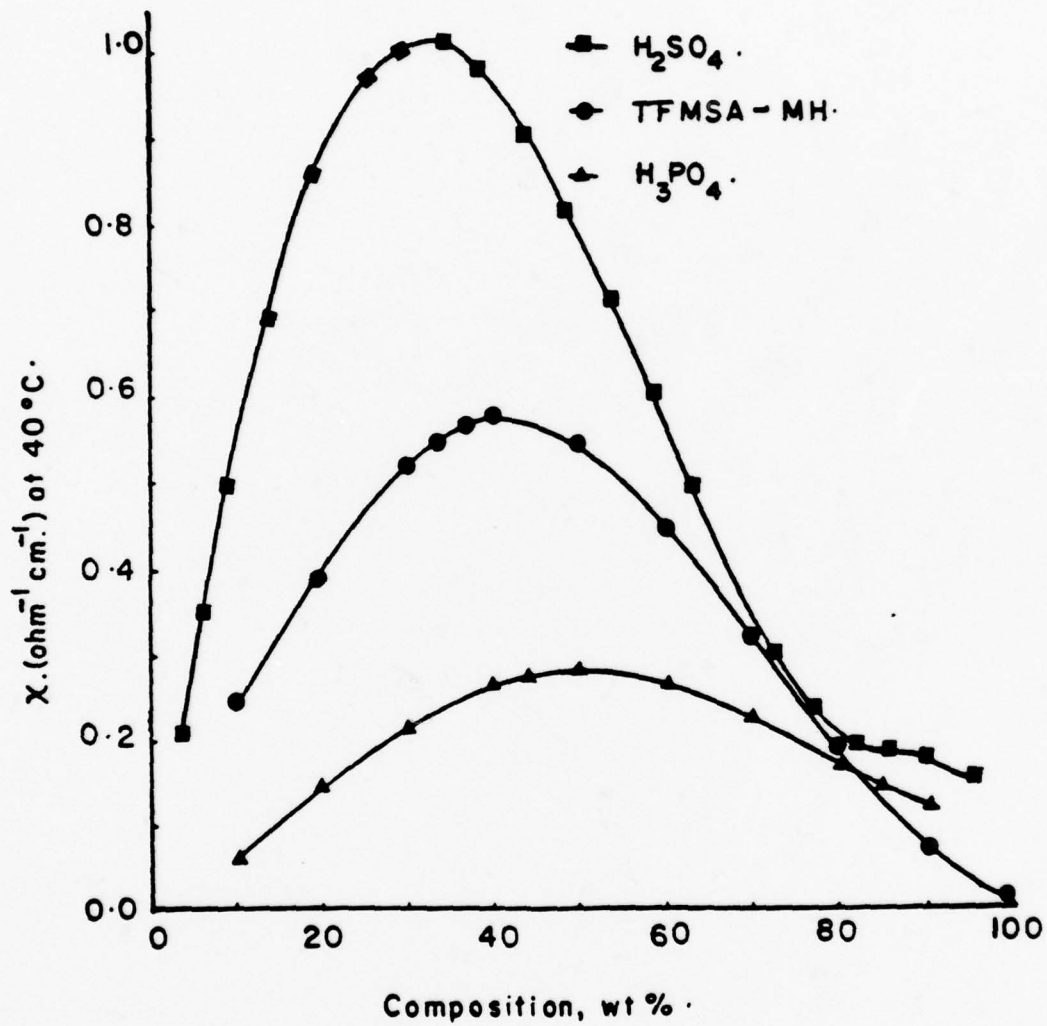
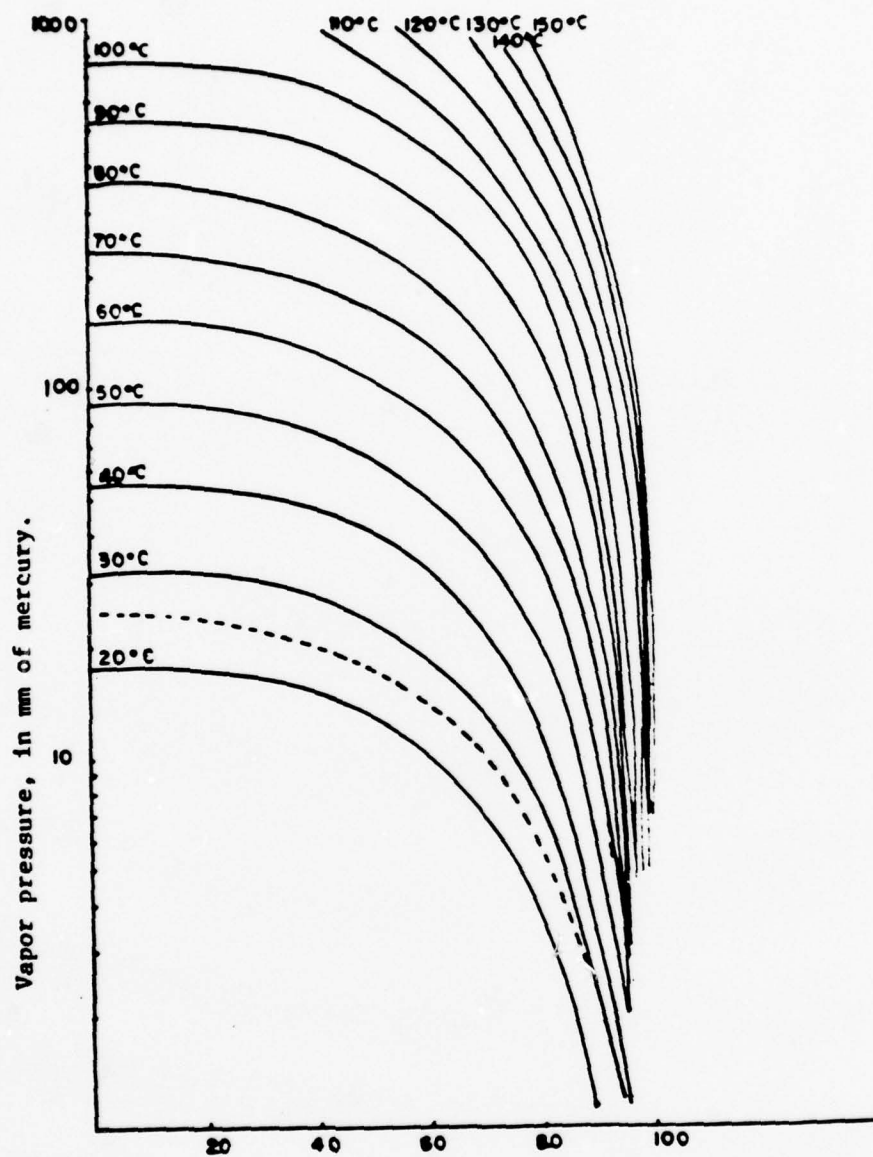


Fig. 2 Conductivities of acid-water solutions at 40°C (from reference 12, sulfuric acid data from ref (13), phosphoric from ref (11)).



Weight percent concentration of aqueous phosphoric acid solutions.

Fig. 3. Vapor pressure isotherms of phosphoric acid solutions plotted from the data given in references 11 and 14.

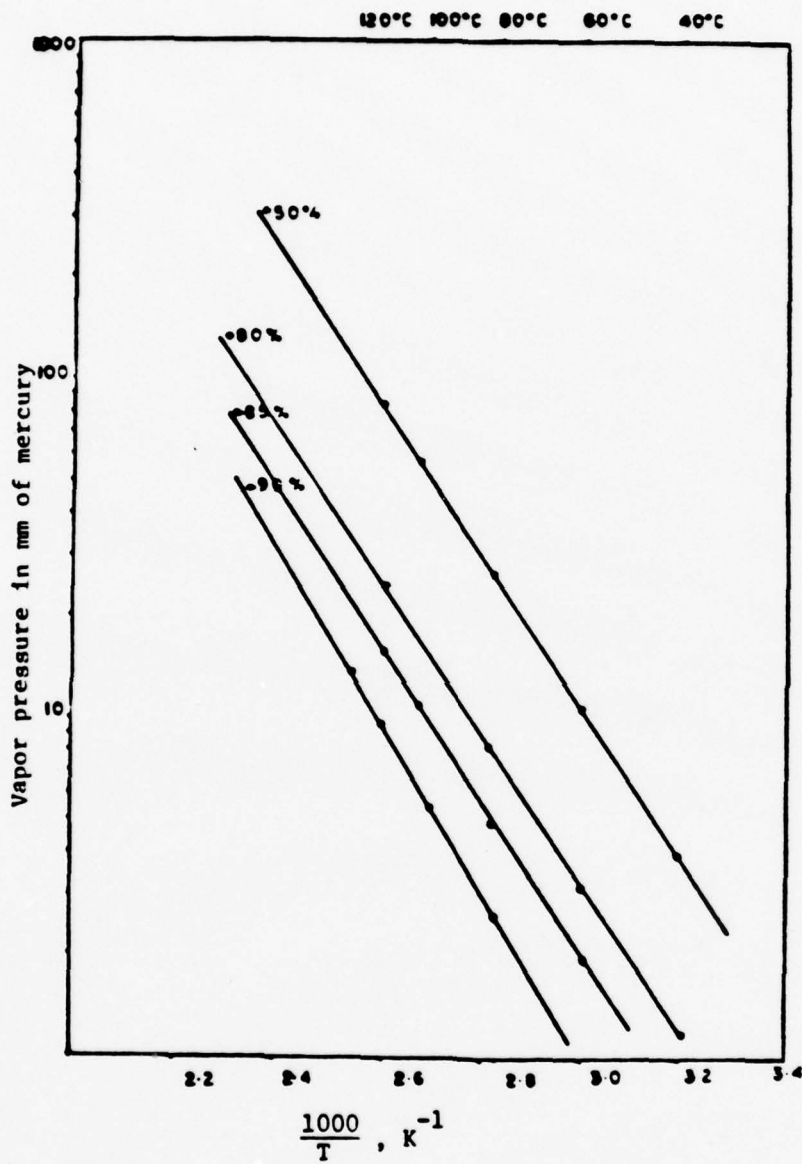


Figure 4. Vapor pressure plots of phosphoric acid solutions versus inverse temperature, data from references 11 and 14.

If the fuel cell is to use a reformed hydrocarbon mixture the question of carbon monoxide tolerance is important. Phosphoric acid can tolerate 2-4% CO in the fuel better than sulfuric acid (16). At 150 - 175 °C H_3PO_4 can use 10-13% CO (16). Thus a fuel cell operating at elevated temperatures can alleviate to some extent the poisoning of the Pt catalyst by CO. At 150 - 170 °C in 85% H_3PO_4 the problem of Pt (catalyst) sintering becomes serious, or, when the temperature is raised to lessen the CO poisoning another problem is introduced. Work is now underway to attempt to clarify the mechanism of this sintering. Tseung speculates that the loss of catalytic activity is due to the dissolution of Pt and its reprecipitation (17). The process may be related to phosphorus in the surface of the carbon support, i.e. -C-O-P bonds that hydrolyze (18).

The trend is to run the phosphoric acid fuel cell at temperatures approaching 200 °C. This high temperature of operation leads to a shorter life and the reasons for the decay have been recently summarized as follows (19):

- 1) "apparent flooding" of the electrode at long term or high potential operation related to carbon-Teflon interface degradation and platinum dissolving and redistribution;
- 2) accumulation of catalyst poisoning from the acid, from the corroding carbon, and from impurities carried in by the air or fuel;

- 3) maldistribution of gases in stacks caused by acid blockage of channels and by blockage due to the degradation of components;
- 4) maldistribution of temperature caused by cooler failure and the non-uniform activity of the cells.

Some of these problems are related to the use of phosphoric acid as an electrolyte but others are simply caused by the high temperature of operation.

The corrosion of various metals and alloys in phosphoric acid has been given considerable attention to allow for the proper selection of materials of construction, matrices, and electrode substrates for the phosphoric acid fuel cell. The corrosion of the materials of construction of fuel cells is important for two reasons. The first obvious reason is the degradation of critical parts of the fuel cell leading to loss of strength or penetration of containers. The second reason lies in the contamination of the electrolyte by metals such as Fe, Cu, or Ni that could destroy the catalytic activity of the electrode.

For metallic materials, including commercial alloys, the subject has been reviewed by Sayano, Seo, and Silverman (20-26) who also investigated and developed certain alloys with a high degree of resistance to concentrated phosphoric acid at elevated temperature. Prior to their investigation Popat and Kuchar (27) had shown that certain metals or alloys were reasonably resistant to corrosion in 87-90% H_3PO_4 at 150 °C in the absence of oxygen. These included gold, platinum, tantalum, and alloys of Ni-Pd, Cr-Pd, Ta-W, and W-Ir. Gold,

platinum, and tantalum were also resistant when polarized at 1.0V. Brummer and Giner (28) investigated the behavior of binary alloys of tantalum in 85-90% H_3PO_4 at 150 °C. They also observed that Ta gave a low corrosion rate when polarized at 1.0V and that alloys of W, Mo, Ni, and Gd with Ta also gave excellent resistance.

Out of their literature search, Sayano, et al constructed figure 5 as a guide to identifying those alloy compositions that might yield corrosion resistant materials. They devised an ingenious "diffusion block" technique with which they could simultaneously measure the corrosion resistance of a number of metals and their binary or tertiary alloys. Their results are summarized in table II which was taken from their report (26). From their study they selected a 35% Mo-Ni alloy for testing at 165 °C and 200 °C in 95% H_3PO_4 . The commercial alloy Hastelloy B is about equivalent under these conditions. They also observed that a 30% Ta-Ni alloy gave better resistance than the 35% Mo-Ni alloy under applied potential such as that to which an electrode would be subjected. This study demonstrated that alloy compositions less expensive than Ta, Au, or Pt were resistant to 85-95% H_3PO_4 at 165 °C. Tantalum is an expensive metal to use as a container material or as a general material of construction. However, in the last decade commercial processes have been developed for coating cheaper metals with tantalum, and tantalum-coated parts have found application in chemical industry. General Technologies Corporation with the "Metalating" electrodeposition process uses a fused salt bath to coat steel, stainless steel, copper, cast iron, graphite, nickel, nickel-base alloys, silver and other alloys with corrosion resistant coatings of

Table II Diffusion Blocks for Phosphoric Acid Fuel Cell Environments (from reference 26)

Block	Components	Diffusion Conditions		Corrosion-Resistant Areas ^{a, b}
		Temperature, °C	Time, hr	
A	Co, Cr, Fe, Mo, Ni, W	1200	300	48 Fe-Mo (intermetallic) 62 Mo-Ni (intermetallic) 4 Cr-80 Co-9 Fe-Ni ^c
B	Cr, Mo, Nb, Ta, V, W	1600	300	1.8 Cr-6 Nb-78 Ta-V 4.6 Cr-60.5 Ta-V
C	Mo, Nb, Ti, V, W	1500 ^d 1200	100 100	67.4 Mo-Ti Nb-V (single phase) 8 Ti-W 6.8 Mo-29.3 Nb-52.3 Ti-V
D	Co, Fe, Mo, Ni, Ta, Ti	900	300	27 Ta-Ti 6-20 Co-Ni Ni-Ta

^a Blocks A and B exposed to 98% phosphoric acid at 200 °C; Blocks C and D to 95% phosphoric acid at 165 °C.

^b Compositions in w/o

^c Elgiloy is 40 Co-16 Fe-20 Cr-15 Ni-7 Mo-2 Mg

^d Temperature lowered after initial 100 hr due to vaporization of titanium

0.003 - 0.005 inches in thickness. Fansteel uses a vapor deposition process to produce coatings of up to 0.015 inches in thickness. These processes have been applied in the chemical industry to produce parts for pumps, valves, heater coils, evaporators and heat exchanges that are resistant to corrosion at elevated temperatures. A coupon of mild steel coated with 0.006 inches of Ta by the Metalating method is completely resistant to 85% H_3PO_4 at 150°C and gives a weight loss of 0.018 $\text{mg cm}^{-2}/\text{hr}$ at 174°C. [Hastelloy C under the same conditions gives a weight loss of 0.042 $\text{mg cm}^{-2}/\text{hr}$ (29).]

Recently, two other corrosion problems in H_3PO_4 have been observed. The first of these is the corrosion of carbon, e.g., Vulcan XC-7-2R and Shawinigan acetylene black, in 200°C phosphoric acid. This reaction has been described by Stonehart (19). The corrosion rate at 1.0 v is proportional to the surface area and the acid concentration is important. The second problem described by Yeager (19) involves the dissolution of platinum at voltages of 0.85 - 0.9 v. The concentration of dissolved Pt was 10^{-4} molar at 0.95 v in 96% H_3PO_4 at 176°C. Both of these problems involve operating at high temperature, i.e., up to 200°C, and higher voltage, i.e., 0.9 - 1.0 v, and at this time no solution to these problems is apparent.

Sulfuric Acid

In the early work on fuel cells, sulfuric acid was the preferred acid electrolyte (16, 30). In terms of acid strength, H_2SO_4 is low (31, 32) but the conductivity of $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ solutions is high. Figure 2, above, compares the conductance of $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ solutions with those

of phosphoric acid and trifluoromethanesulfonic acid monohydrate solutions. To utilize this high conductivity would require working with solutions of 30-40% composition and this would restrict applications to relatively low temperatures. In the early fuel cells, given a choice between H_2SO_4 and KOH for $\text{H}_2 - \text{O}_2$ fuel cells, the alkaline system was chosen because the polarization at the oxygen electrode was about 0.1V less than in H_2SO_4 . The use of other fuels which give a CO_2 product turned attention to acid electrolytes and one of the first employed was sulfuric acid probably due to the long experience with H_2SO_4 as a battery electrolyte. For example, Schlatter, working with 5N H_2SO_4 at temperatures in the 40-80 °C range electro-oxidized ethylene, propylene, propane, and isobutane at "feasible" rates (33). Grubb (34) used 6N H_2SO_4 immobilized by a heterogeneous cation exchange membrane to demonstrate the oxidation of methane, ethane, propane, isobutane, neopentane, and ethylene in the work which was instrumental in establishing the feasibility of the hydrocarbon-air fuel cell. This work was done at 65 °C. When runs were made at 90 °C and higher it was observed that in 4N H_2SO_4 there was a direct reaction between propane and sulfuric acid to give H_2S and other reduction products of the sulfate group (35).

The use of methanol as a fuel has been of interest because of its low cost and transportability, so a considerable amount of attention has been devoted to an air-methanol fuel cell. A prototype cell was developed by Esso Research and Engineering utilizing an electrolyte with 30% by weight H_2SO_4 and 3% by volume methanol (16). The cell voltage and current density is compared with the H_2 - air system in

figure 6. It will be noted that the cell operated at 60 °C but the feasibility of a methanol-air fuel cell was demonstrated.

More recently sulfuric acid and phosphoric acid were compared for the low temperature (about 60 °C) oxidation of methanol in electrolytes of low acid concentration (36). It was concluded that, of the two, sulfuric acid was preferred but also a significant poisoning effect due to the bisulfate anion was observed. Ethanol oxidation has also been studied in H₂SO₄ electrolytes (37). These experiments would suggest that sulfuric acid would be the preferred electrolyte for low temperature methanol fuel cells.

Hydrochloric Acid

Hydrochloric acid has not been used as a fuel cell electrolyte because catalytic electrodes are poisoned by chloride ions which are strongly absorbed. The chloride effect has been observed many times in electrode kinetic studies. Breiter reports (38) that the electro-oxidation of methanol on platinum electrodes in perchloric acid is inhibited by 10⁻⁶ M HCl and prevented entirely at concentrations greater than 10⁻² M. Brummer and Turner have demonstrated (39) that Cl⁻ can successfully compete with propane for adsorption sites on a platinum electrode even at concentrations as low as 0.17 mM.

At elevated temperatures HCl volatilizes excessively. In aqueous solutions at 108.6 °C, HCl and H₂O vaporize as an azeotropic mixture containing 20.2% of HCl.

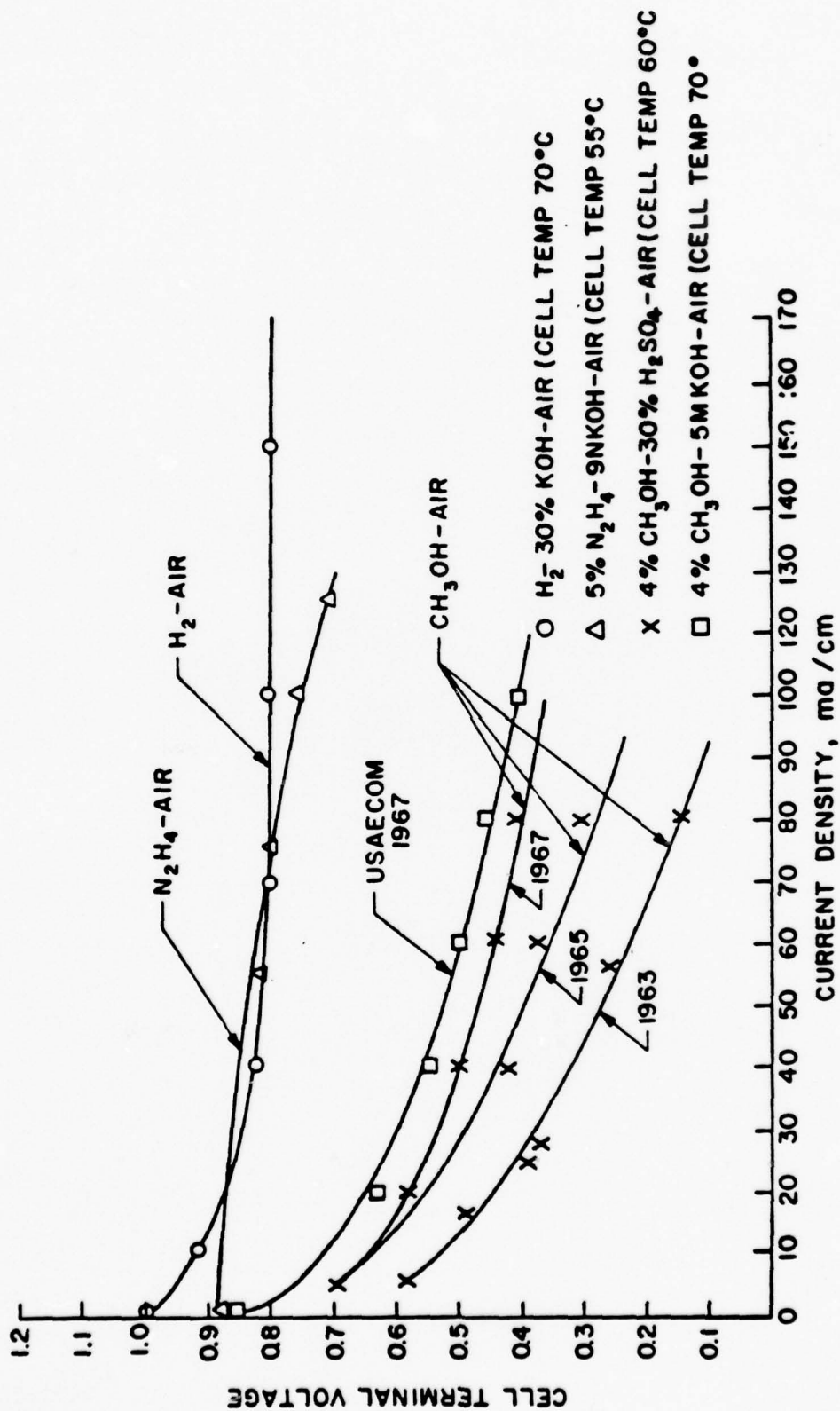


Figure 6. Electro-oxidation of methanol in a H_2SO_4 electrolyte (from reference 16, pg. 36)

Perchloric Acid

Perchloric acid has been used extensively in mechanistic studies, e.g. mechanism of hydrogen kinetics, evaluation of catalysts. Many of these studies have been conducted at room temperature and perchloric acid was chosen because, among inorganic anions, it has less tendency to form complex ions and also is not readily adsorbed on solid surfaces. However, perchloric acid at elevated temperatures and in concentrated solutions is highly unstable and decomposes explosively. It reacts violently with reducing agents. If it is dehydrated the acid loses water to form the anhydride, Cl_2O_7 , which is more unstable than the acid itself. There have been a number of laboratory accidents in lithium battery work caused by explosions that occurred when perchlorates were heated dry.

The electrochemical experiments have not suggested any outstanding advantage to using perchloric acid (over phosphoric or sulfuric) and this fact coupled with the inherent dangers have eliminated this acid as a practical fuel cell electrolyte.

Hydrofluoric Acid

Hydrofluoric acid is a weak acid. HF in a 0.1N aqueous solution at 25 °C ionizes 7.7% compared to 24% for phosphoric acid (40). However, the conductance of $\text{HF}\cdot\text{H}_2\text{O}$ solutions is adequate as indicated in figure 7 taken from reference 41.

The main reason that hydrofluoric acid solutions have been of interest in fuel cell work lies in the fact that the fluoride ion is

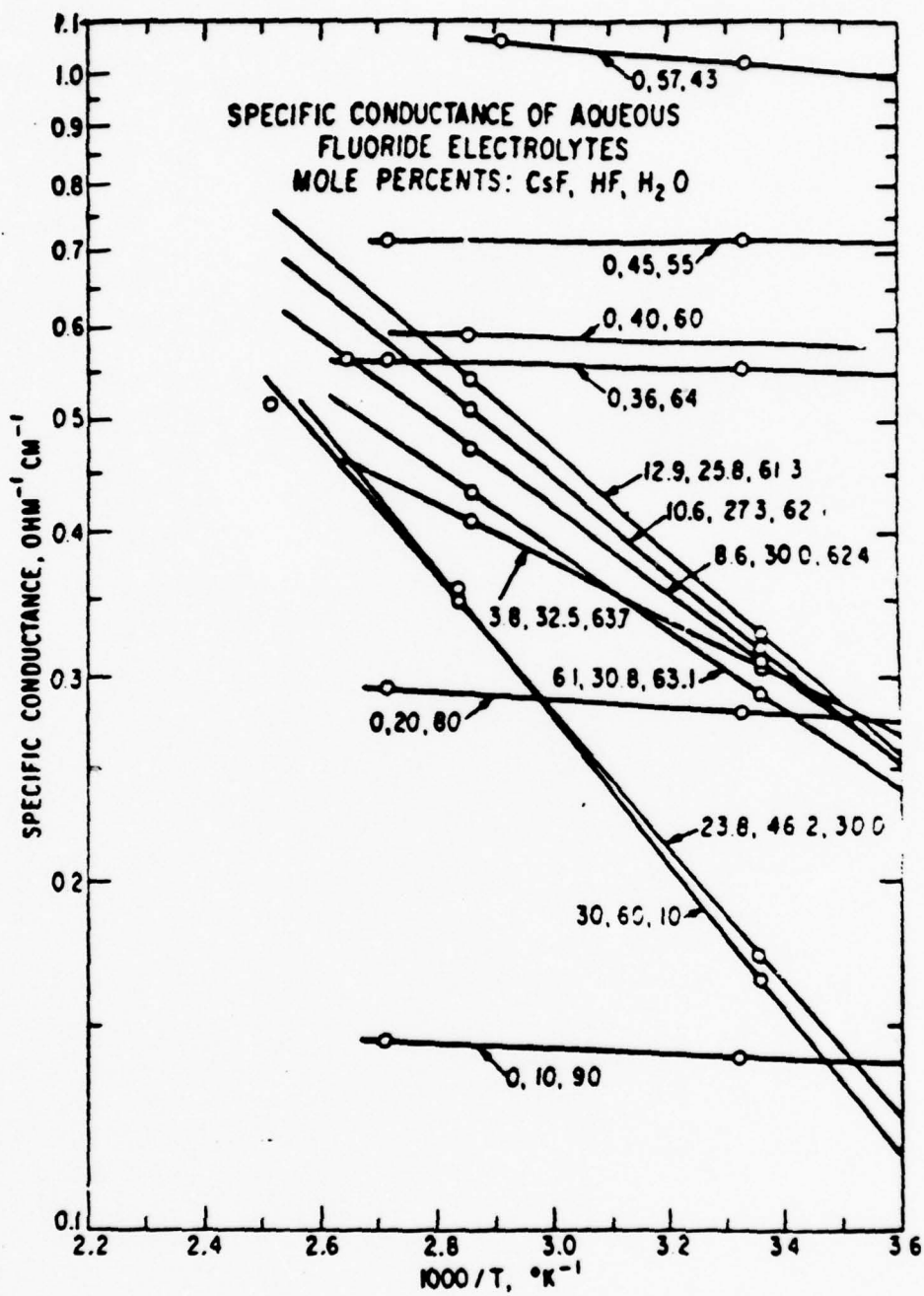


Figure 7. Electrolytic conductivities as a function of temperature for several compositions in the HF - H₂O and CsF - HF - H₂O systems. Numbers on the curves represent mole per cents of CsF, HF, and H₂O respectively (from reference 41).

rather weakly adsorbed and does not interfere with the electro-oxidation of a hydrocarbon such as propane at the platinum electrode. This effect is illustrated in figure 8 (10), which compares the oxidation of propane and reduction of oxygen, at 100-105° C, in H_3PO_4 , H_2SO_4 , $HClO_4$ and HF. The electrode activity is in the reverse order of the tendency for anion adsorption, that is, the fluoride ion is less readily adsorbed than the phosphate, sulfate, or perchlorate and interferes less with the oxidation of propane and reduction of oxygen. HF · H_2O systems are limited by their boiling points as indicated in figure 9 (41). The HF · H_2O system is azeotropic (compare the HCl · H_2O system) and at 37% HF forms an azeotrope which boils at 112° C, thus the maximum operating temperature would be well below this point.

Additions of cesium fluoride to HF · H_2O solutions result in the formation of complexes such as $CsF \cdot HF$ and $CsF \cdot 2HF$ which raise the boiling point of the electrolyte and allow operation up to 150° C. The properties of $CsF \cdot HF \cdot H_2O$ electrolytes of varying compositions have been reported by Cairns (41) and Carreras, et al (42). These include the boiling points, freezing points, densities, viscosities and electrical conductance of selected compositions. The net observation is that there are $CsF \cdot HF \cdot H_2O$ compositions with reasonable physical properties for employment as fuel cell electrolytes.

As expected, the electrochemical performance of electrodes in these mixtures varies with the ratio of HF to CsF, For propane oxidation at 150° C this is illustrated in figure 10(43). Above a F^-/Cs^+ ratio of about 1.2 the pH decreases and the oxidation current at a specific overvoltage increases sharply.

In general the use of HF systems has been discouraged, in part

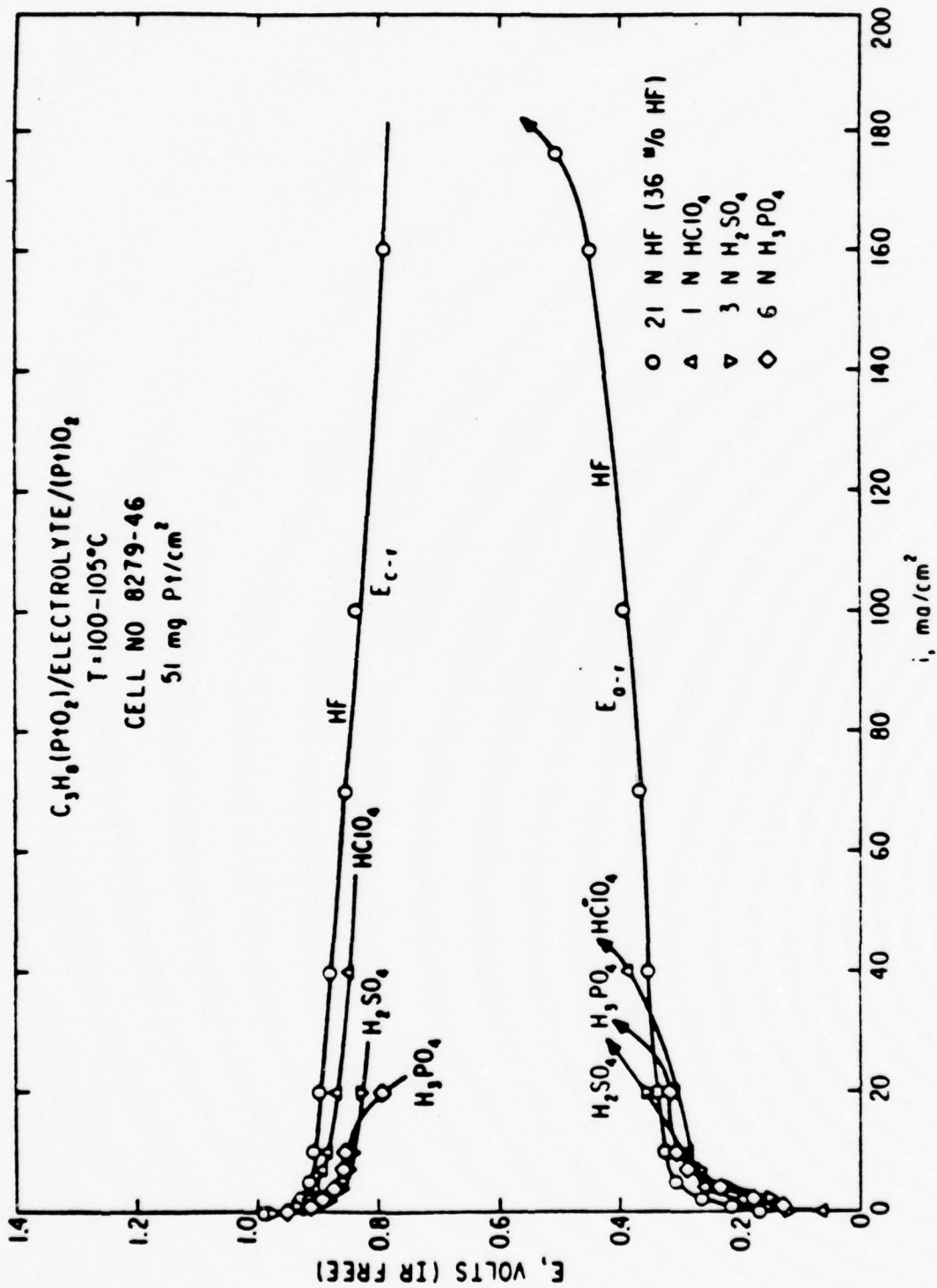


Figure 8. Comparison of the effects of four strong acid electrolytes on propane oxidation and oxygen reduction on platinum black (from reference 10).

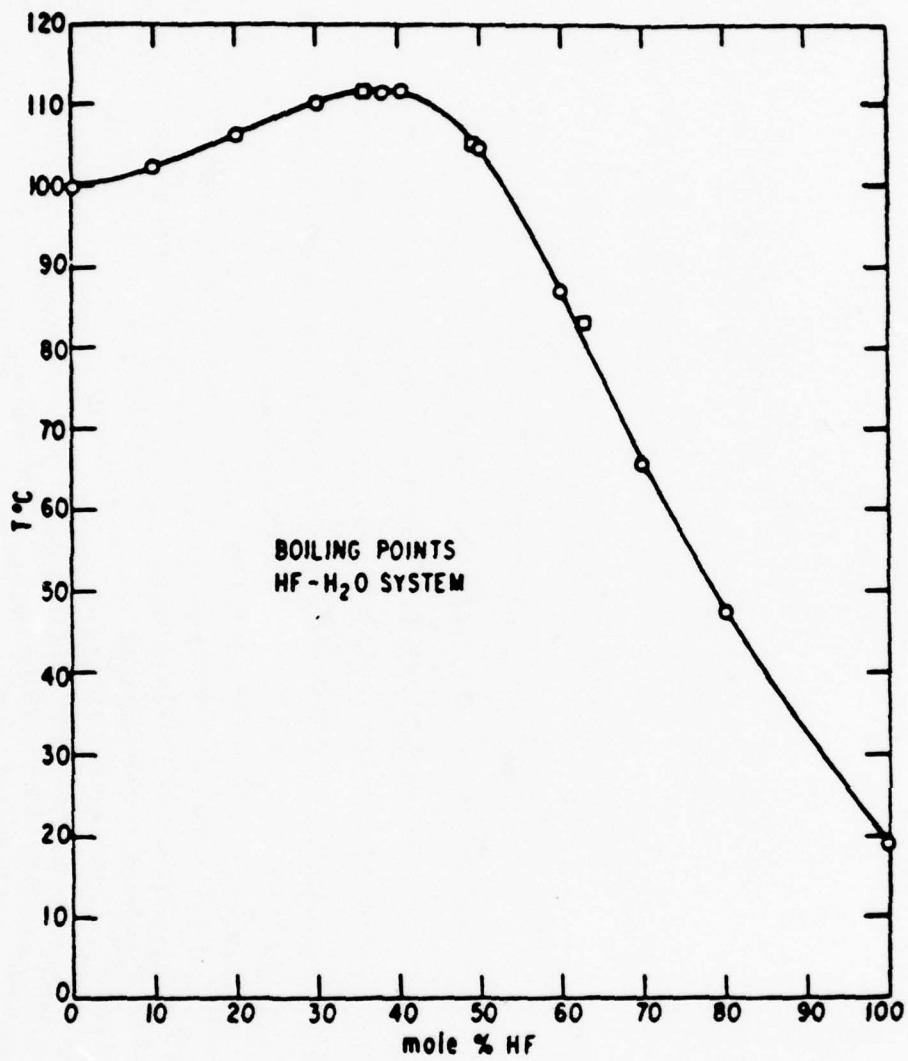


Figure 9. Boiling points for the HF-H₂O system (from reference 41)²

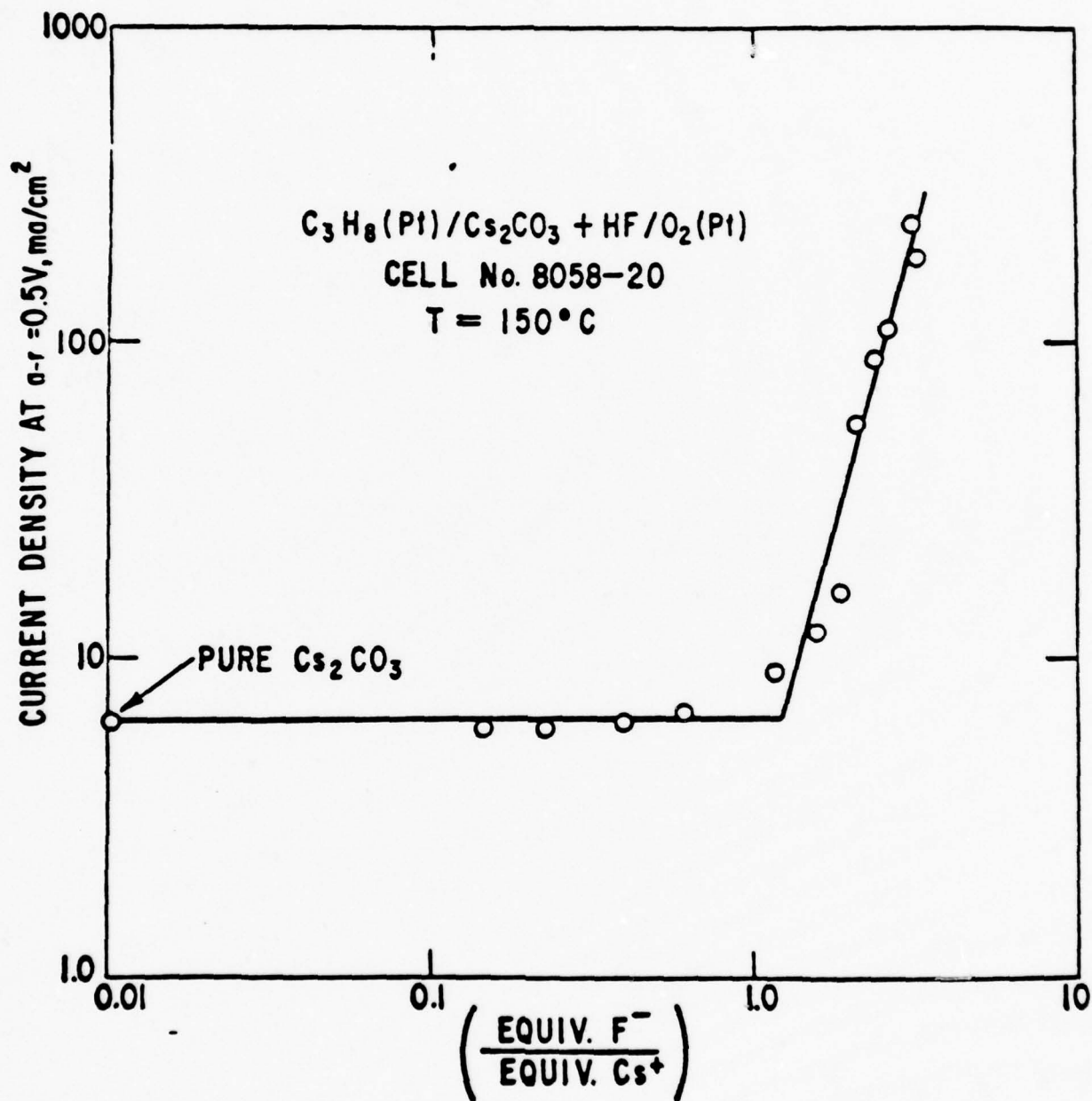


Figure 10. Effect of F^-/Cs^+ ratio on propane current density at $150^\circ C$ (from reference 43).

by the corrosion problem, and in part by the fact that the vapor distilling from the solution at elevated temperature contains HF as well as H_2O , thus making the electrolyte management problem very complicated. However, the corrosion problem would not be expected to be any more severe than it is with many other concentrated acid systems.

Other Strong Inorganic Acids

The strongest, simple, protonic acid is fluorosulfuric acid, FSO_3H (44). The electrical conductivity of the acid is $1.085 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ which is lower than that of sulfuric acid ($1.043 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$). The boiling point is 162.7°C which is also lower than sulfuric acid and fluorosulfuric acid distills directly from a reaction mixture. The acidity of the acid is increased by the addition of SbF_5 and SbF_5-SO_3 but the stability of these compounds in the presence of water is questionable. The acids, $H[SbF_5(SO_3F)]$ and $H[SbF_2(SO_3F)_4]$, are termed super acids (44).

These super acids have been proposed (45) as electrolytes for direct hydrocarbon-air fuel cells utilizing methane, propane, and octane. The compounds cited are those formed from fluorosulfonic, chlorosulfonic, and hydrofluoric acid combined with Lewis acids such as SbF_5 , $SbCl_5$, and AsF_5 , with the preferred combination being fluorosulfonic acid and antimony pentafluoride. Such electrolytes have been claimed (45) for fuel cells operating up to 150°C . However, it is mentioned that the super acid electrolytes have a tendency to decompose in the presence of water and non-aqueous electrolytes are preferred. Thus, it is difficult to understand how this electrolyte will be stable in the presence of the fuel cell reaction product, H_2O , at elevated temperatures.

Several other strong acids were examined in the Argonne work (31,32). Hexafluorophosphoric acid, HPF_6 , fumed badly and appeared to distill from the cell. Hexafluorostibonic acid, HSbF_6 , also fumed badly and gave up HF when held at 85 - 90°C. This, of course, would pose the problem of electrolyte invariance over prolonged periods of operation.

B. Inorganic Salts

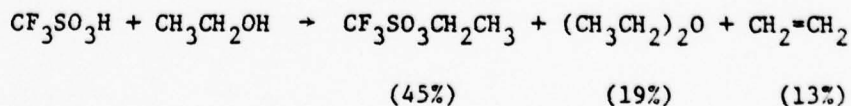
Some investigations have been made with the objective of employing neutral inorganic salts as electrolytes. Cairns (46) found that solutions of cesium and rubidium carbonates, which are alkaline, remained invariant at certain temperatures, even when CO_2 was generated. This is apparently due to the high solubilities of the hydroxides, carbonates, and bicarbonates of these metals and the instability of the bicarbonate ion at elevated temperatures. With a cesium carbonate electrolyte current densities for hydrocarbon oxidation were very low. For hydrocarbon oxidation it is necessary to add HF, as discussed above under Hydrofluoric Acid, and the improved current density occurs at a F^-/Cs^+ ratio of 1.0 and above (see figure 10). The performance of the O_2 electrode was compared in 2 N H_2SO_4 (pH, 0.3), 2 M KHCO_3 (pH, 8), and 2 M NaH_2PO_4 (pH, 3.5) (47). The electrode polarization was severe for the last two offering no promise of establishing a neutral electrolyte for hydrocarbon-air systems. It should be noted that mixed alkali metal dihydrogen phosphate melts are good CO_2 rejecting electrolytes (48) but their employment moves one into fused salt technology.

C. Organic Acids

Trifluoromethanesulfonic Acid and Its Monohydrate

Trifluoromethanesulfonic acid, as a chemical compound, has been studied in great detail; its preparation, physical properties and chemical reactions have been reviewed by Howells and McCown (49) who cite 302 references of the literature after 1965. The literature up to that point had been reviewed by Senning (50). The properties and some important reactions are described in condensed form in reference 51. TFMSA has been of considerable interest from the chemical viewpoint because it is the strongest, or one of the strongest (compare fluorosulfuric above) acids, known. The acid and the anion have considerable thermal stability and resistance to both reductive and oxidative cleavage. The acid does not produce fluoride ions even in the presence of strong nucleophiles so there is no possibility of fluoride ion adsorption on fuel cell electrodes. There are well-known reactions for preparing the acid in high purity and the monohydrate is easily prepared by refluxing and distilling the compound. The monohydrate distills sharply at 217 - 219°C; the acid itself boils at 162°C (760 mm).

One chemical reaction of trifluoromethane sulfonic acid is of particular interest in its use as a fuel cell electrolyte. This is the exothermic reaction with alcohols to form esters with ether and olefin byproducts



This reaction would complicate the usage of the acid in the methanol-air fuel cell and this particular application is discussed below.

Trifluoromethanesulfonic acid has a relatively high dielectric constant, 38, and has been investigated as a nonaqueous solvent for electrochemical reactions such as organic synthesis (52). The acid has a "domaine d'electroactivite" from +0.5 v cathodic to 2.4 v anodic when polished platinum electrodes are used with a supporting electrolyte of $(\text{CH}_3)_4\text{N PF}_6$.

The first promising electrochemical results were achieved with trifluoromethanesulfonic acid monohydrate rather than the acid itself. It was observed (29) that the monohydrate supported a current density for the electrooxidation of hydrogen on platinum of about an order of magnitude higher than in phosphoric acid. These rates are compared in figure 11 wherein the rate in the monohydrate is seen to be six times as rapid at a temperature 20° lower. A similar enhancement of electroactivity over phosphoric acid was observed for the propane reaction. Figure 12 compares the electrooxidation of propane at 135°C on platinum electrodes in the two electrolytes. The current densities at several overvoltages are given in table III. A plot of the temperature dependence for the reaction (figure 13) indicated an activation energy of 12.2 kcal/mole which is about 5 kcal less than the value reported for the same reaction in phosphoric acid and other inorganic acids (10).

The exact reason for this enhanced activity is not known. More recently an attempt was made to interpret the improved rate of the

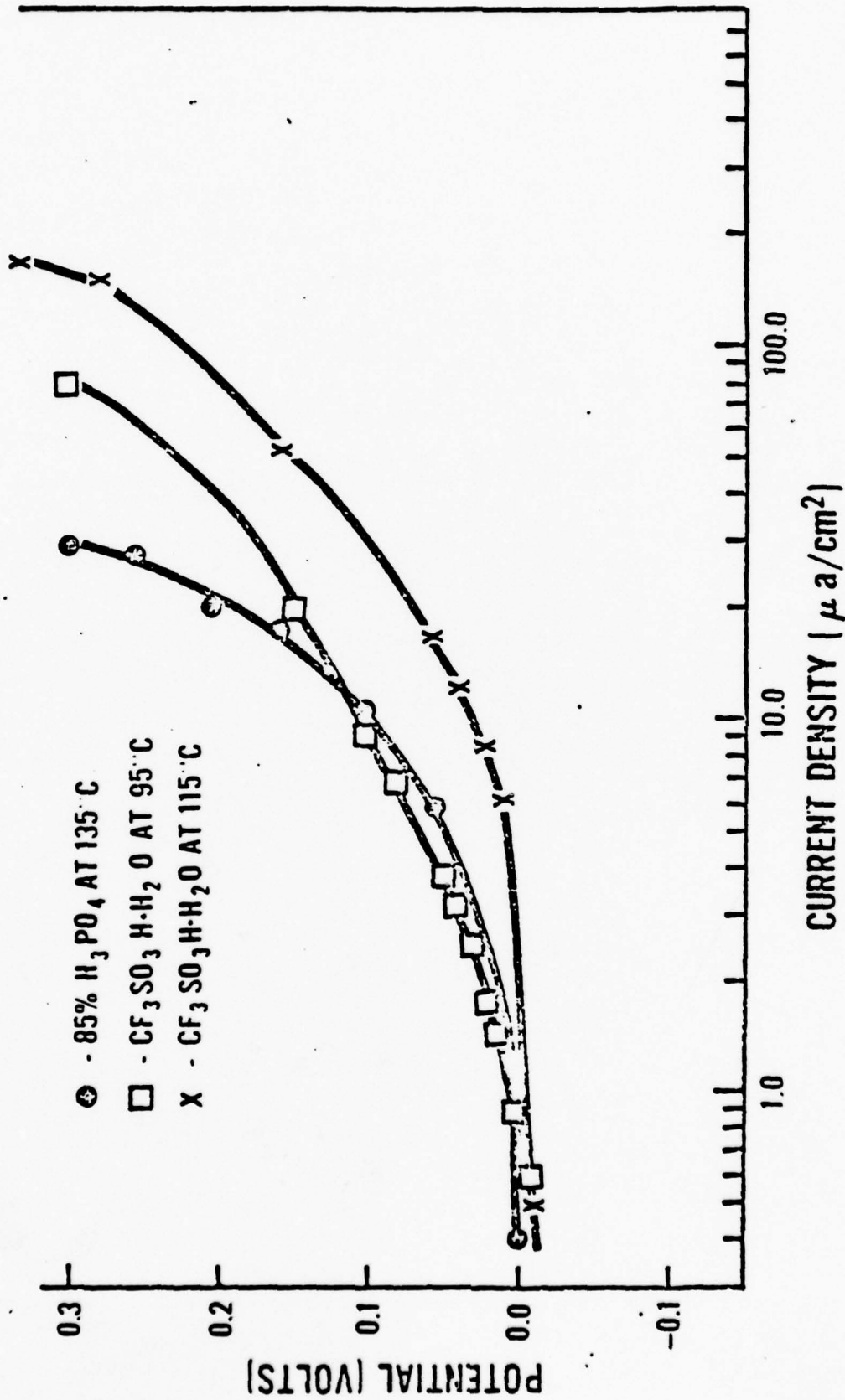


Figure 11. The current density-potential curve for hydrogen at a platinum electrode in 85% H₃PO₄ electrolyte at 135°C compared with H₂ in CF₃SO₃H·H₂O electrolyte at 95°C and 115°C. (from reference 29)

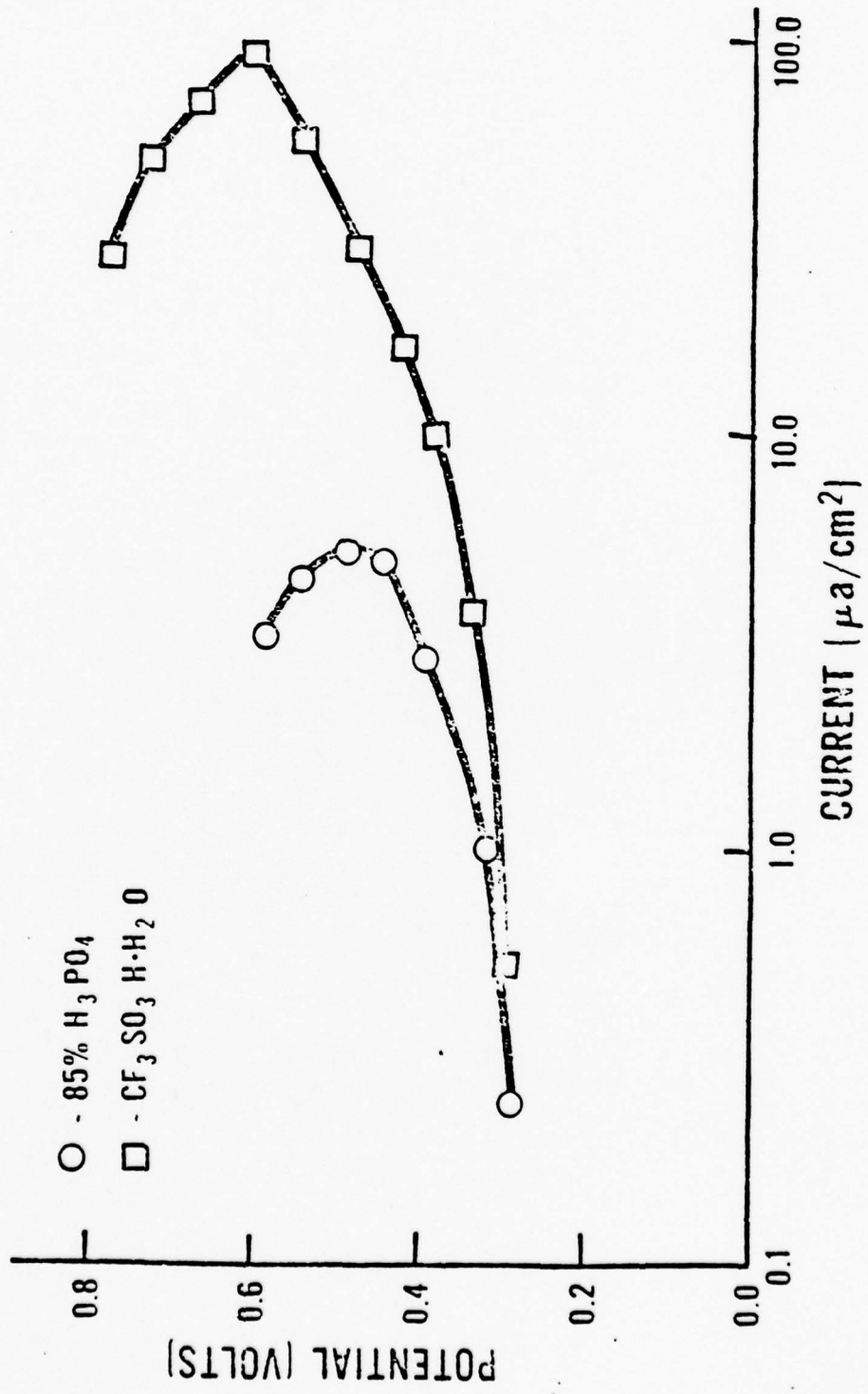


Figure 12. Electro-oxidation of propane on platinum electrodes in two electrolytes at 135° C (from reference 29)

Table III Summary of Propane Current Density Data for 85% H₃PO₅ and CF₃SO₃H·H₂O
at Several Potentials

Potential vs DHE	85% H ₃ PO ₄ at 135°C	CF ₃ SO ₃ H·H ₂ O at 95°C	CF ₃ SO ₃ H·H ₂ O at 115°C	CF ₃ SO ₃ H·H ₂ O at 135°C
	μA/cm ²	μA/cm ²	μA/cm ²	μA/cm ²
Volts				
0.4	1.4	0.68	1.3	25.0
0.5	5.3	2.8	4.5	53.0
0.6	4.7	7.2	9.4	66.0
Limiting Current	5.5	24.0	16.0	82.0

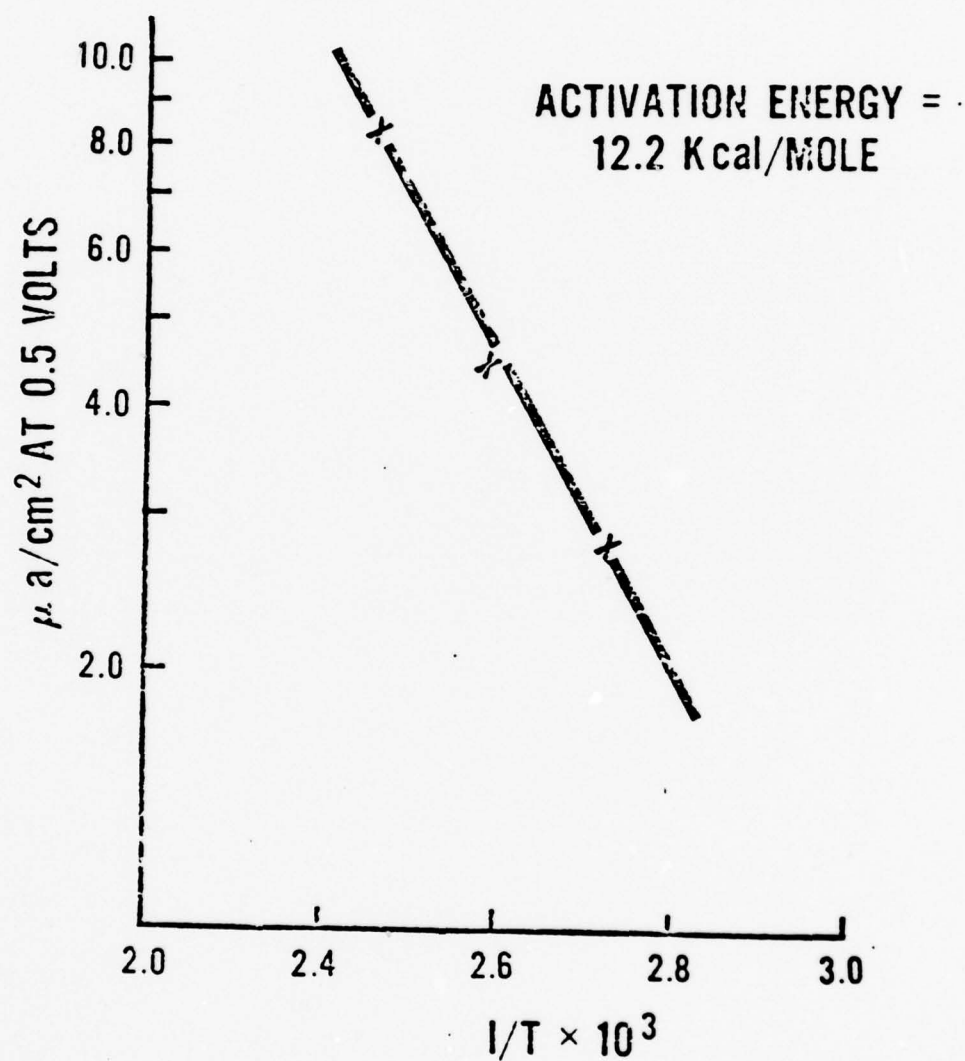


Figure 13. Temperature dependence of current density for anodic oxidation of propane in $CF_3SO_3H \cdot H_2O$ (from reference 29)

electrooxidation of hydrogen and propane in trifluoromethanesulfonic acid monohydrate by Riedhammer and Bruckenstein (53) using a rotating platinum disk electrode. It was found that the rate of oxidation of methane and propane was controlled by a kinetic process occurring at the electrode surface rather than a convective diffusion process. On the other hand, hydrogen electrooxidation and oxygen electroreduction were found to be convective-diffusion controlled at the rotating electrode.

The electrooxidation of other low molecular weight hydrocarbons in this electrolyte has also been measured. The order of reduction, figure 14, is similar to that observed in other electrolytes, i.e., propane and butane are oxidized easier than methane and ethane (54). The electroreduction of air on a platinum electrode was also investigated in trifluoromethane sulfonic acid monohydrate (55). At 135°C the open-circuit potential of the air electrode was 1.135 v (vs. the dynamic hydrogen electrode) and the limiting current was higher than that observed in phosphoric acid. Figure 15 makes this comparison with some results obtained in another laboratory (56). Figure 16, taken from reference 56, illustrates the substantial electrolyte effect on oxygen reduction of Pt. The open circuit potential for the electroreduction of oxygen is about 150 mv higher in the monohydrate than in 85% phosphoric acid. The significance of this result, however, has been ignored by those working on the mechanism of oxygen reduction on platinum electrodes.

The carbon monoxide tolerance of the TFMSA·H₂O electrolyte is better than that of 85% H₃PO₄ in the sense that a higher current

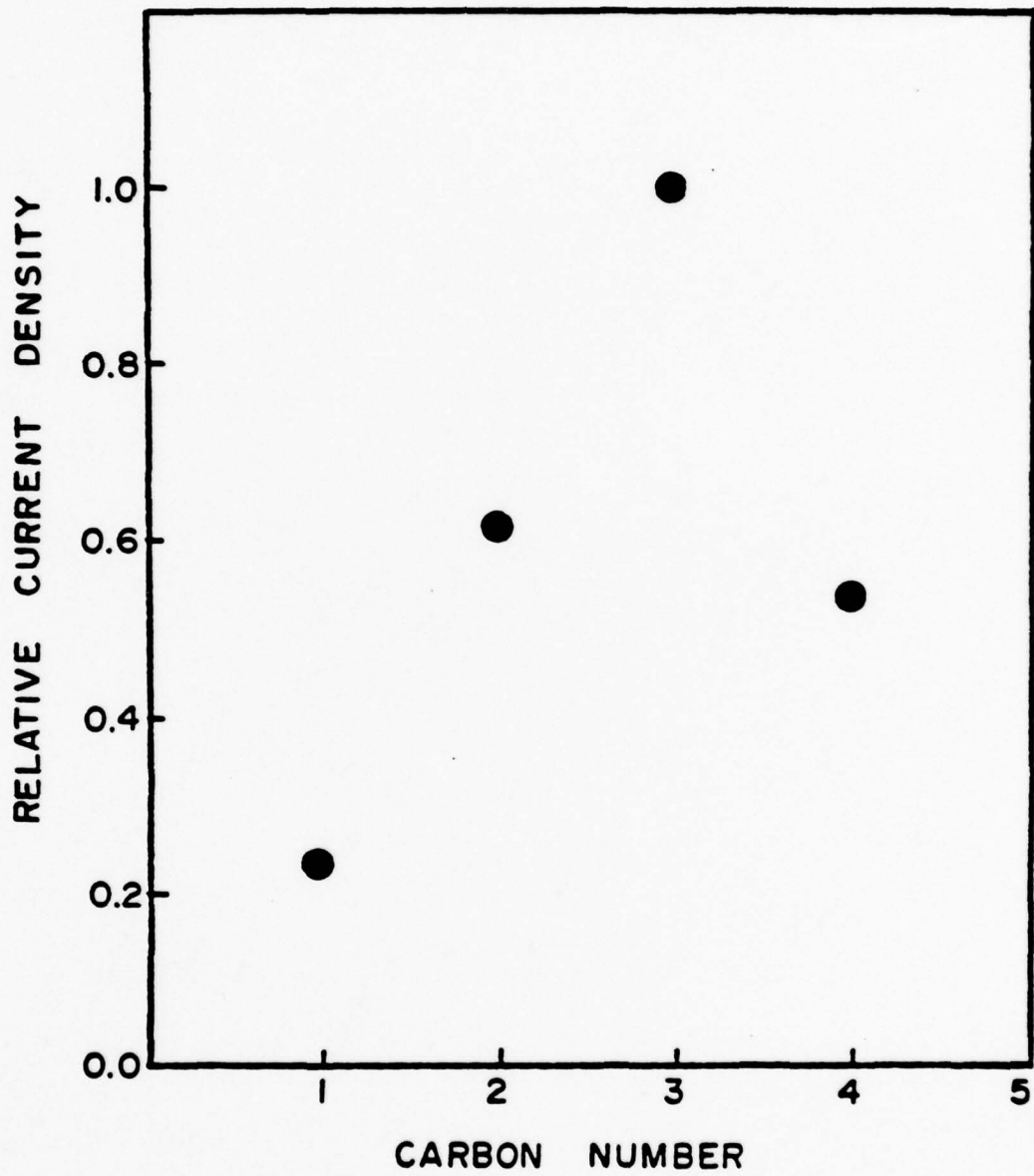


Figure 14. Relationship Between Electrooxidation Rate and Hydrocarbon Number. (from reference 54).

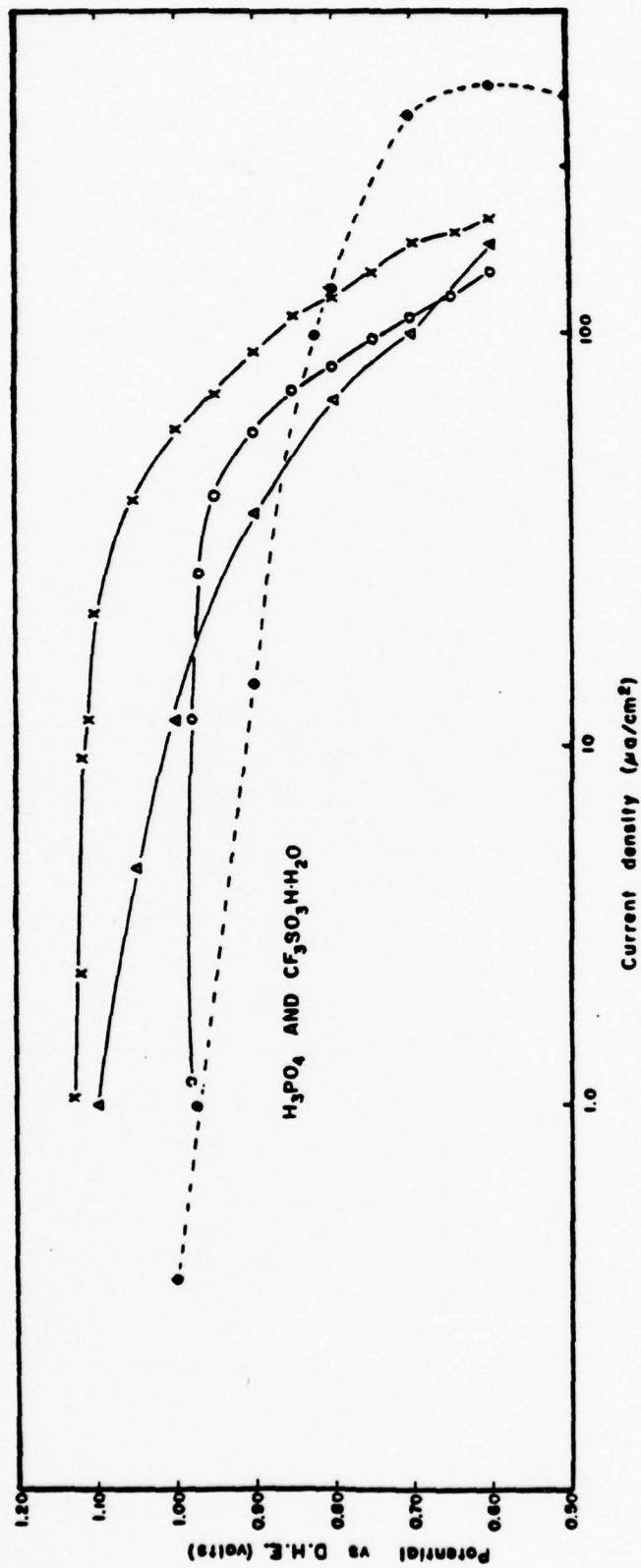


Figure 15. Comparison of the electroreduction of oxygen and air in $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ and H_3PO_4 . Δ , O_2 at 80°C in $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ (reference 56); X, air at 135°C in $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$; O, O_2 at 80°C in H_3PO_4 (ref. 56); ●, air at 135°C in H_3PO_4 (from reference 55)

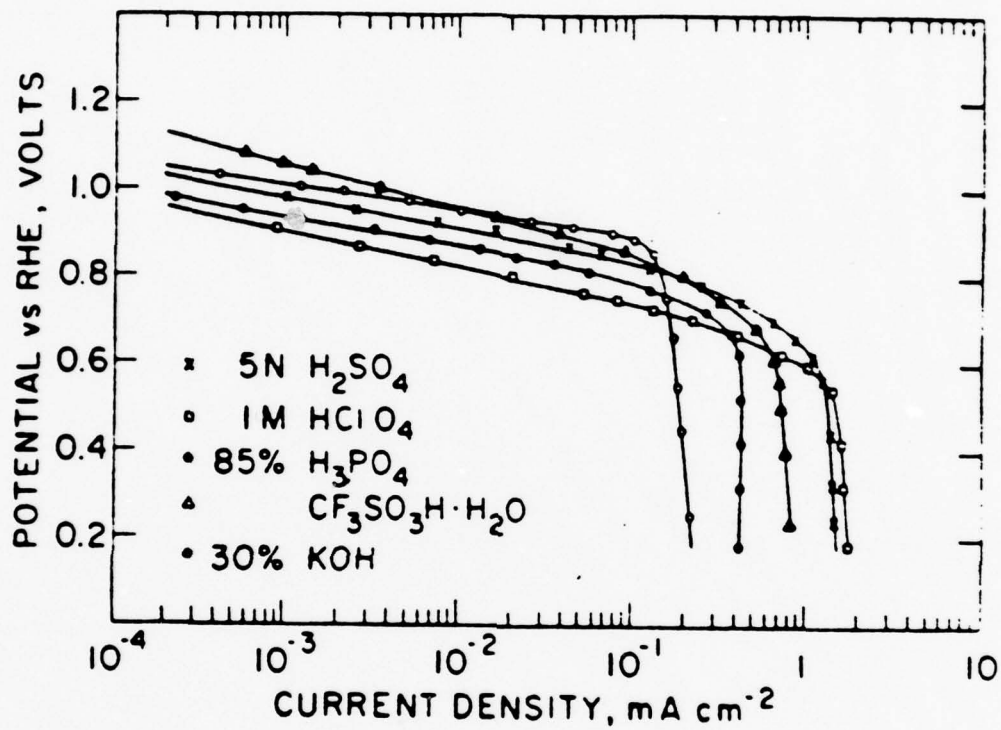


Figure 16. Potential-current density relations for oxygen reduction at Pt in some electrolytes at 80°C (from reference 56)

density can be maintained for a given CO-H₂ mixture (57). Figure 17 compares the rates for 3% CO-H₂ and 10% CO-H₂ mixtures. There is a definite poisoning effect with CO but the net current density supported is about an order of magnitude higher than that in 85% H₃PO₄. Recently these results were confirmed by Walker (58) who not only tested H₂ mixtures with 3%, 6%, and 10% CO but also reformat mixtures composed of 3% CO, 12% CH₄, and 85% H₂ and 2.0% CO, 26 % CO₂ and 72% H₂. In the TFMSA·H₂O electrolyte the CO is rapidly desorbed when the CO mixture, say 10% CO-H₂, is changed to undiluted H₂.

The situation with respect to the electrooxidation of methanol in TFMSA·H₂O is not as clear-cut as hydrocarbon oxidation. Figure 18 (29) shows the potential-current density plots for the electrooxidation of methanol (concentration one molar) at 23°, 80°, 115°, and 135°C. Also shown in this figure are the results reported by Bagotzky and Vassiliev (59) for one molar CH₃OH in 1 N H₂SO₄ at 80°C. At 80°C the open circuit potential is 0.375 v and the limiting current density is about 4.0 μamp cm⁻². At 80°C the system was quite stable over a number of days indicating little loss of methanol due to vaporization from the cell containing a solution that was originally one molar in methanol. Further experiments indicated, however, that the vaporization of methanol became excessive above 100°C and nmr examination of solutions taken from cells that were held at 115° and 135°C suggested that an esterification reaction was occurring. These results do not agree with a recent report by Hughes, et al. (60), who evaluated TFMSA·H₂O as an electrolyte for methanol oxidation. They report that the performances of conventional noble metal catalysts

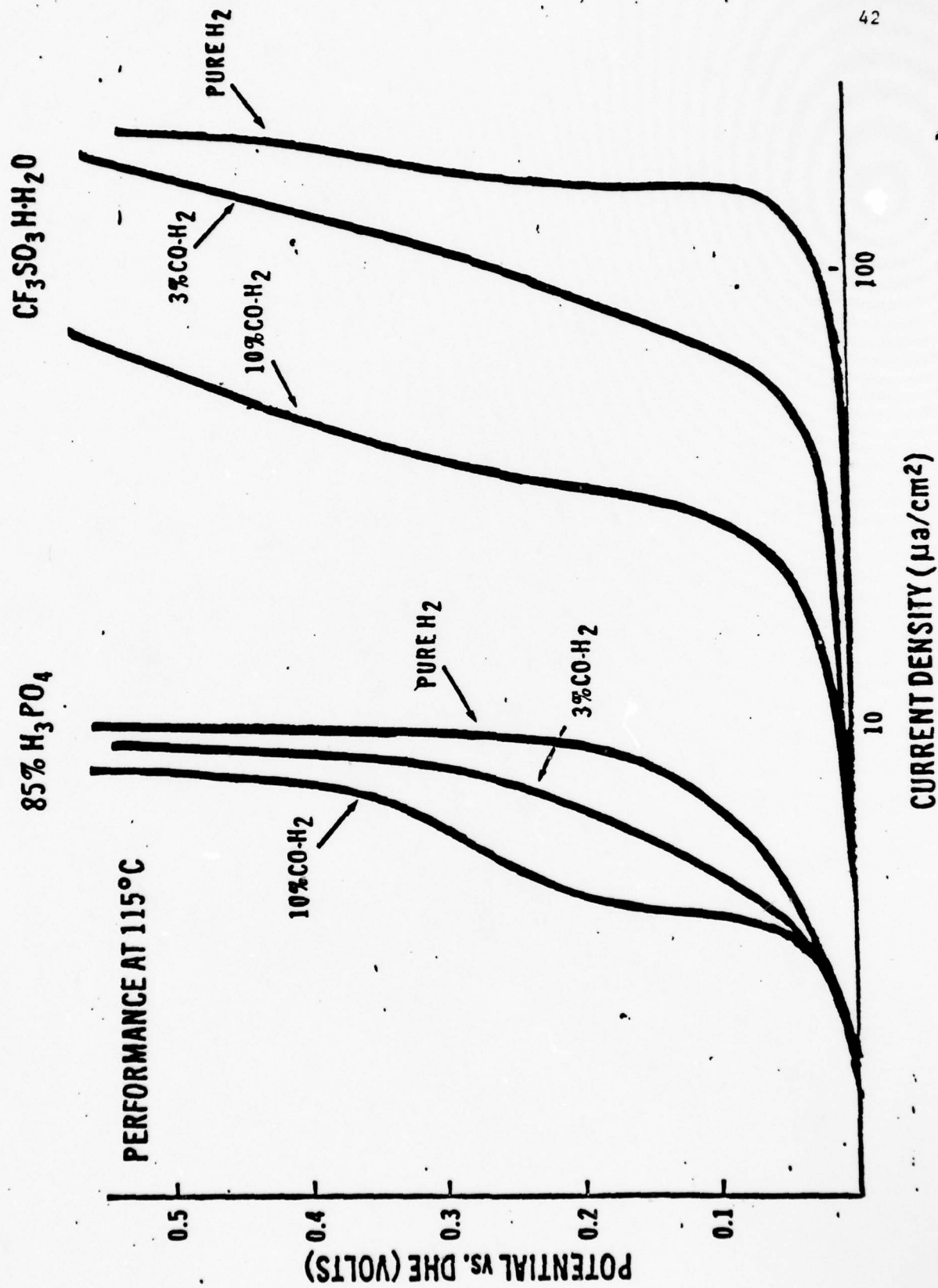


Figure 17. Electro-oxidation of H₂ and CO-H₂ mixtures on a Pt electrode in CF₃SO₃H · H₂O and 85% H₃PO₄ at 115°C (from reference 57)

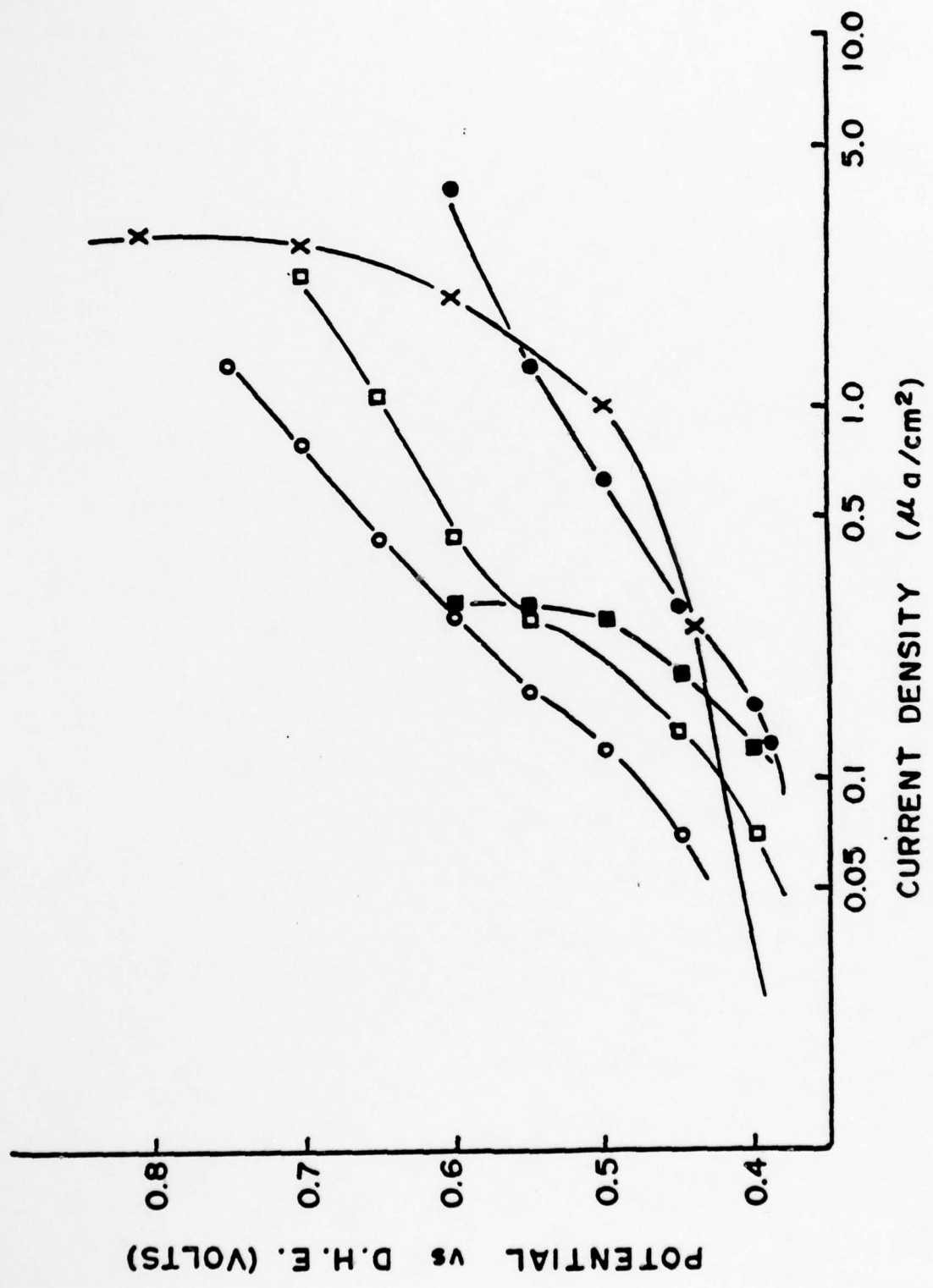


Figure 18. Current-potential diagrams for the electrooxidation of methanol. ■, 23°C; ●, 80°C; □, 115°C; ○, 135°C; X data from reference 59.

were poor in the monohydrate as compared to results in 3 M sulfuric acid. On the other hand, improved performance was observed in 10 - 50% aqueous solutions at 60°C. Apparently, the poisoning effect of acid radicals was considerably less than in H₂SO₄ solutions. These investigators reported that the monohydrate was unstable above 60°C and listed sulfur and carbon monoxide as decomposition products. This instability has not been observed in other laboratories in experiments that were run at 135°C over a period of weeks. It is now apparent that the Shell results were due to the use of an impure grade of trifluoromethanesulfonic acid (97%) which included some SO₃ which would be electroactive. The use of an impure electrolyte makes it very difficult to evaluate the significance of these results.

Qualitatively, a number of laboratories have reached the same conclusion with respect to improved electrochemical performance of the hydrogen, propane, and oxygen electrodes in TFMSA·H₂O over that in phosphoric acid. A number of the "deficiencies," reported for phosphoric acid above, appear to disappear in TFMSA, its water solutions, or its monohydrate.

When an effort was made to use trifluoromethanesulfonic acid monohydrate in a practical fuel cell, several problems developed related to the vapor pressure of the compound and the tendency of the compound to wet Teflon (bonded electrodes). Work at Argonne Laboratories (31, 32) disclosed that Teflon was wet by the acid, and, gas electrodes that were leakfree and reliable with other electrolytes passed large amounts of electrolyte into the gas chambers even at 25°C. This flooding made the electrode, and the fuel cell, inoperative.

To a certain degree the flooding of gas electrodes may be remedied by a pressure compensation method (61, 62). A practical fuel cell using a pressure compensation method was run with the monohydrate. Graphite test plates were free of corrosion and a number of matrices were used with good results, e.g., 75% Ta₂O₅ - 25% tetrafluoroethylene, 50% boron nitride - 50% polytetrafluoroethylene. A second problem that arose was the fuming of the vapors in the gas exit lines, both H₂ and O₂ lines, and the depletion of the electrolyte when the cell was operated over 90°C. To circumvent some of these problems, the electrolyte was diluted, a 63% TFMSA-H₂O solution was used, and the temperature was reduced to 23°C. A comparison of two fuel cells, one with the TFMSA-H₂O solution and the second with 85% H₃PO₄, taken from reference 62, is shown in figures 19 and 20. The higher open circuit potential is obvious. At 0.6 v the TFMSA cell gave a current density of 156 mA/cm², the 85% H₃PO₄ cell, 65 mA/cm², a factor of improvement of 2.4. In more recent work the cells are run at 60°C.

In going to the employment of the dilute solution of TFMSA, as opposed to the monohydrate, the conductivity of the cell electrolyte was improved and the wetting problem with regard to Teflon-bonded electrodes partially alleviated. The aqueous solution of TFMSA was evaluated in a fuel cell using fuel cell components that had been developed for phosphoric acid fuel cells (63, 64). In this design, the high ohmic and diffusional losses previously encountered were reduced and tungsten carbide could be used as an anode catalyst. These cells were operated at temperatures 25 - 70°C

FUEL CELL PERFORMANCE FOR DILUTE TFMSA

ELECTROLYTE 63% TFMSA
ELECTRODES 2mg/cm² Pt
MATRIX - QUARTZ
TEMPERATURE - 23°C

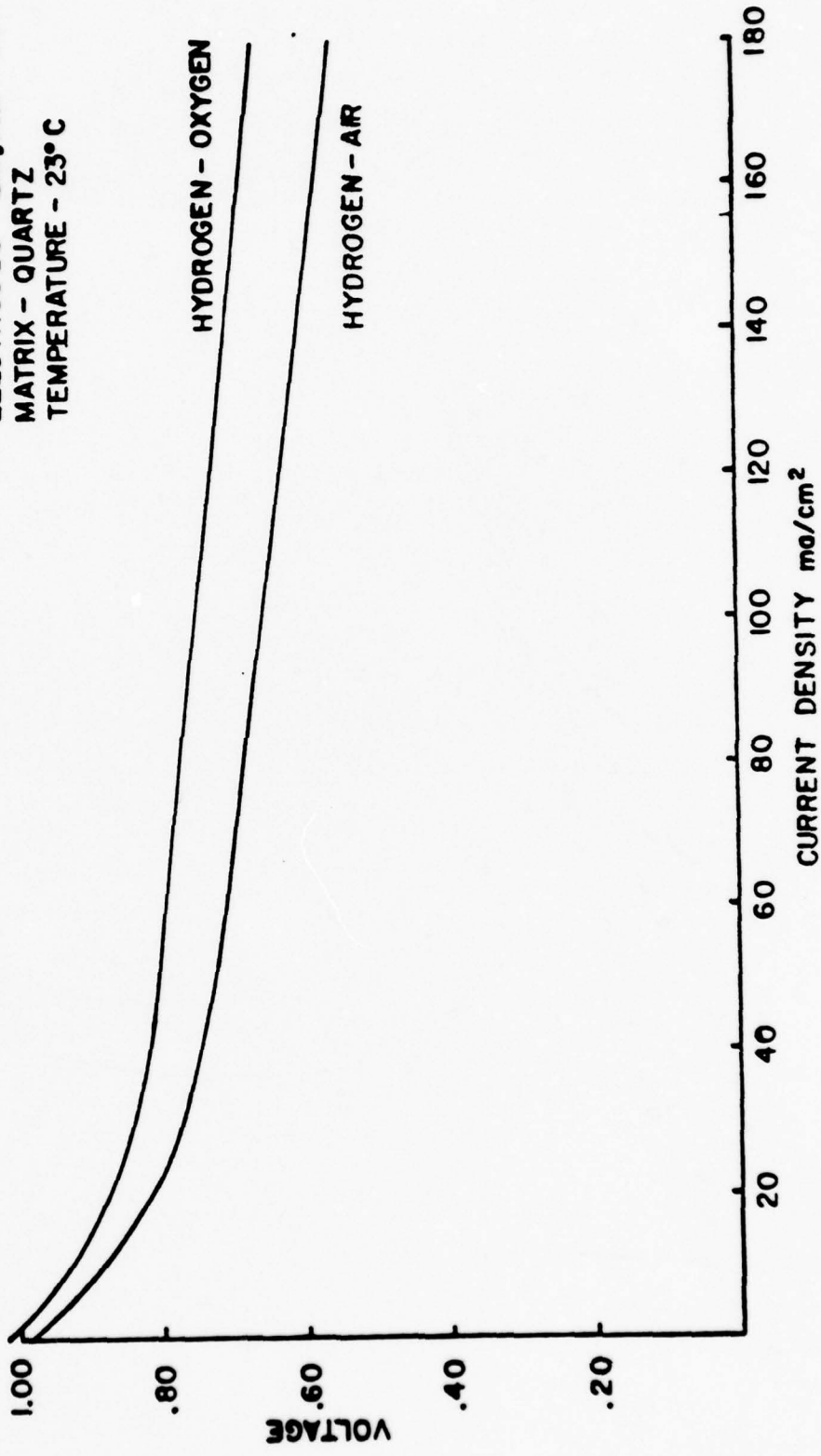


Figure 19. (from reference 62)

FUEL CELL PERFORMANCE FOR PHOSPHORIC ACID

ELECTROLYTE 85% H_3PO_4
ELECTRODES $2\text{mg}/\text{cm}^2$ Pt
MATRIX - QUARTZ
TEMPERATURE - 23°C

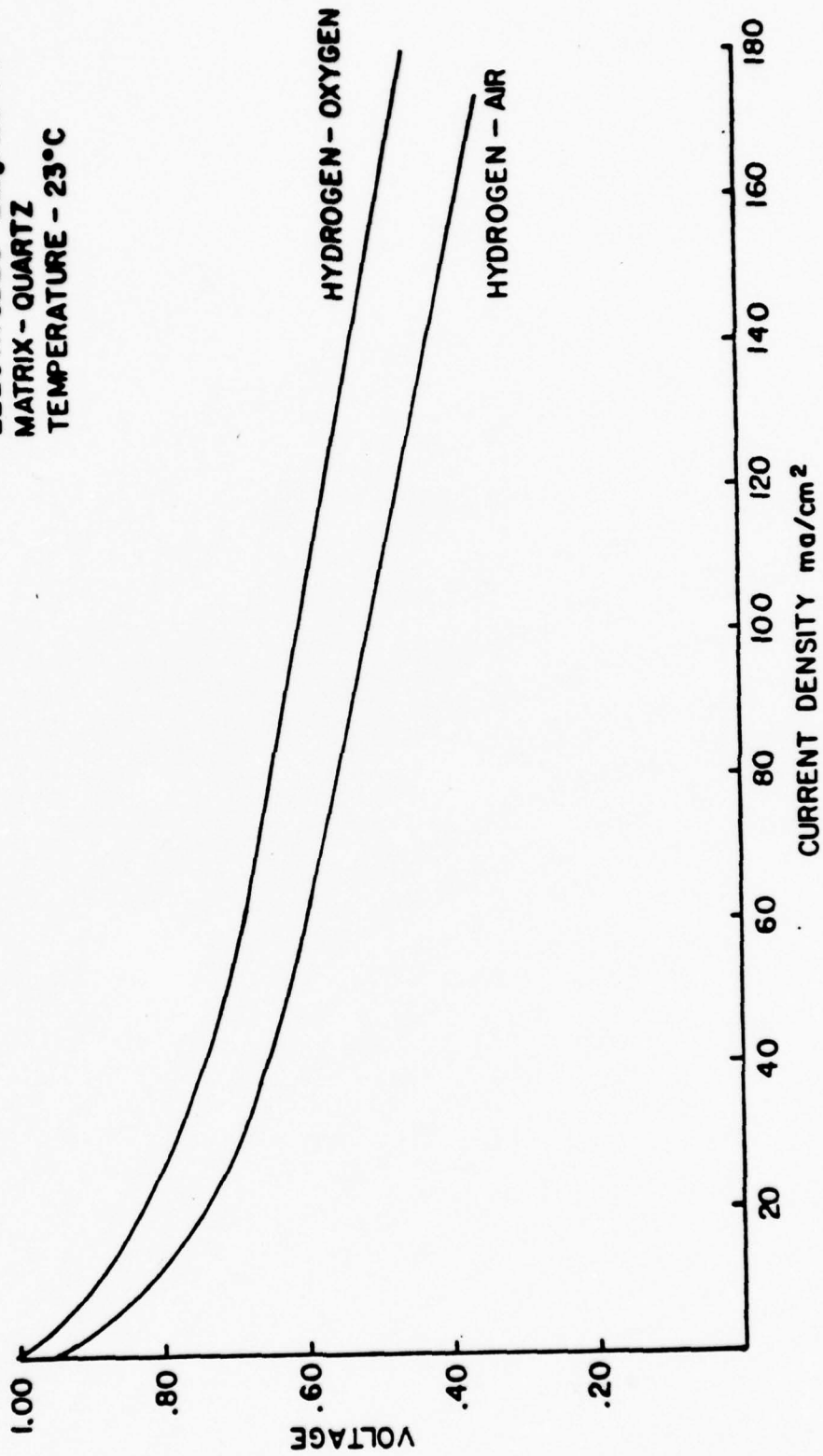


Figure 20. (from reference 62)

up to 1000 hrs. The performance of the cell run for 600 hrs at room temperature is represented in figure 21. The particular electrolyte concentration was 60% TFMSA which was close to the composition of maximum conductance. The catalyst loading was 2 mg Pt/cm². The current density at 0.6 v was about 400 mA/cm². Such experiments constitute a successful reduction to practice of organic acid fuel cells.

The problems that arose when attempts were made to use TFMSA·H₂O in practical fuel cells dictated further investigation of the properties of the monohydrate and water solutions of the acid. This extensive investigation is reported by Sarada et al. (12). In this study the electrical conductivities of the monohydrate and water solutions were measured and compared with phosphoric and sulfuric acids (see figure 2). All three systems show a maximum in the conductivity-composition curve with that of the monohydrate system falling at 40 - 45% of the monohydrate. Whereas the conductances of H₂SO₄ solutions are better than those of TFMSA·H₂O, those of H₃PO₄ are poorer, but with all three systems, other properties such as vapor pressure discourage working at the composition of maximum conductance. The measurement of the contact angle of TFMSA·H₂O and water solutions indicate (figure 22) that solutions containing about 50% H₂O should greatly reduce the tendency of Teflon-bonded electrodes to flood. The vapor pressure of the monohydrate was measured by an isopiestic method (figure 23). A solution of 99.99% of the monohydrate is isopiestic with a solution of 96.83% H₃PO₄. The vapor pressure data available on TFMSA·H₂O do not indicate a problem

ANODE AND CATHODE - 2 mg PT/CM²
GLASS FIBER MATRIX - 600 HOURS

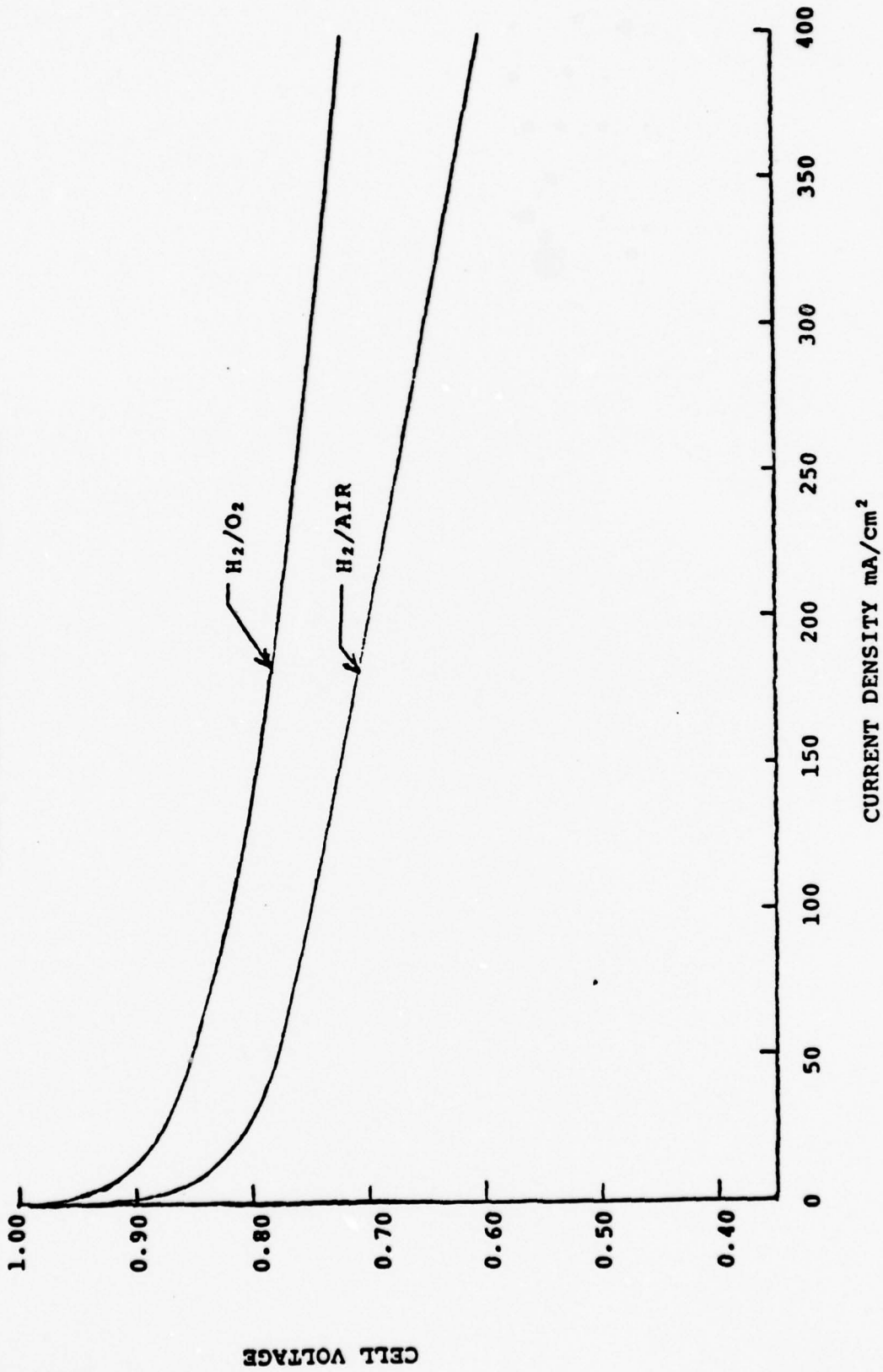


Figure 21. Fuel cell performance with 60% TPMSA at room temperature (from reference 64)

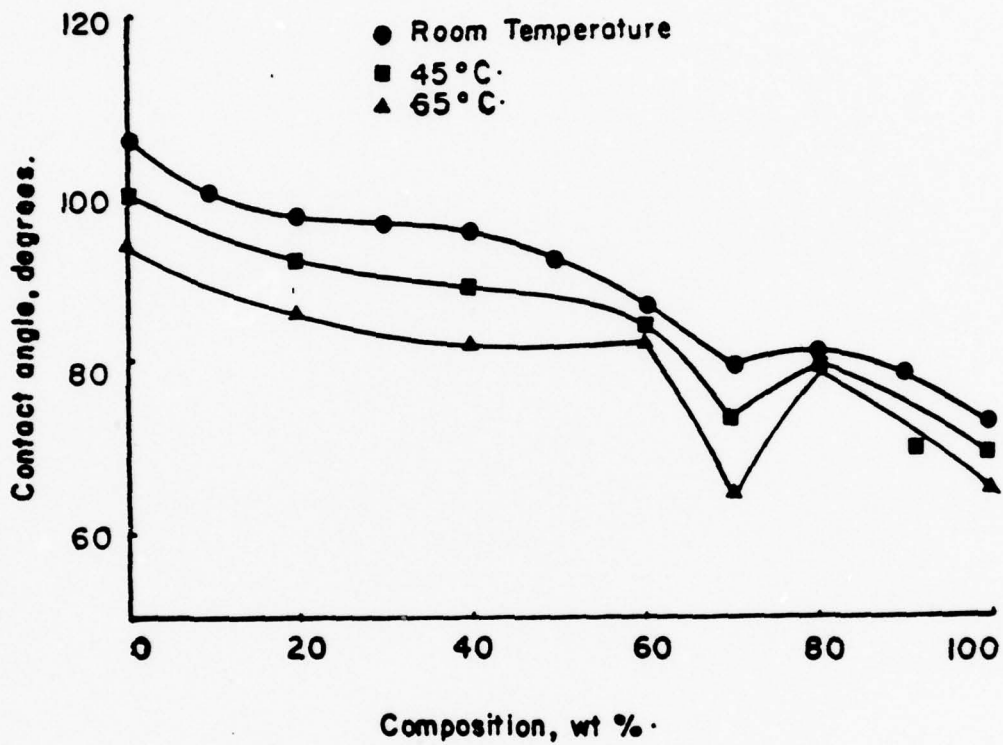


Figure 22. Contact angles of trifluoromethanesulfonic acid monohydrate solutions (from reference 12)

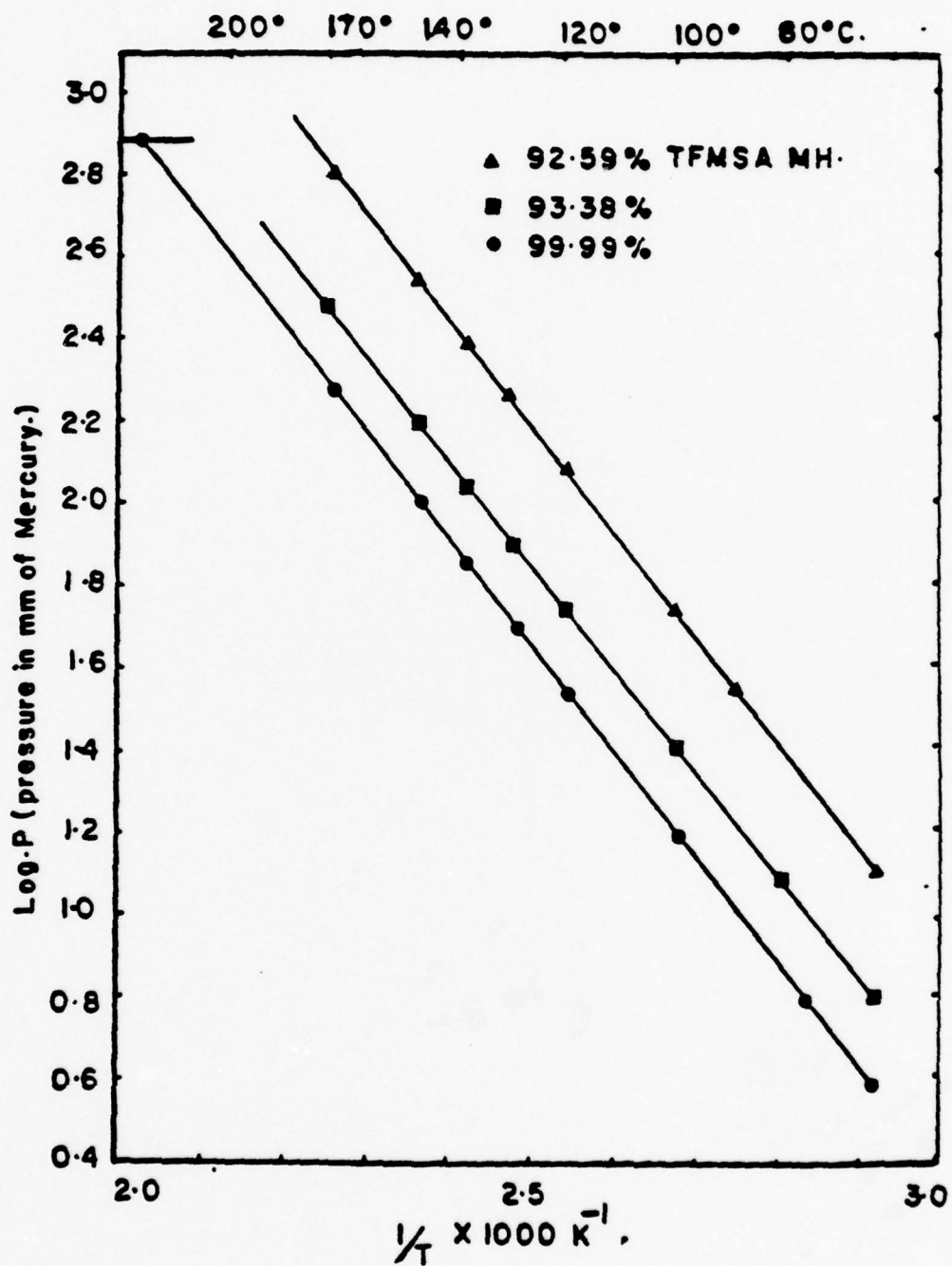


Figure 23. Vapor pressure of trifluoromethanesulfonic acid monohydrate as a function of temperature (from reference 12)

greater than that encountered with 85% phosphoric acid.

The selection of potential materials of construction for use in trifluoromethanesulfonic acid monohydrate and its water solutions was investigated. Corrosion tests, both stationary and under potential, showed that alloys such as ingot iron, chrome steel, Incoloy 825, tantalum coated steel, and niobium offer considerable resistance to corrosion in the electrolyte. Figure 24 gives some quantitative results of 8 week tests at 125°C of some of the more resistant alloys. Figure 25 compares the corrosion at 125°C for one week duration in 85% phosphoric acid.

The interrelationship of these properties should be emphasized. The TFMSA·H₂O gives excellent electrochemical behavior and allows operation at 135°C. To improve the conductivity, it would be desirable to dilute the monohydrate or the acid with 50% H₂O. Dilution of the monohydrate increases the vapor pressure of H₂O over the solution and requires a lower operating temperature. Also, dilution with H₂O will alleviate the Teflon wetting problem. But dilution with H₂O will increase the corrosion rate of most of the commercially available alloys. Dilution with H₂O will not, however, change the stability of certain materials such as pyrolytic graphite, silicon carbide or boron carbide that are considered as matrix materials.

Sulfonic Acids as Potential Electrolytes

Some general observations may be drawn from the literature (65,66).

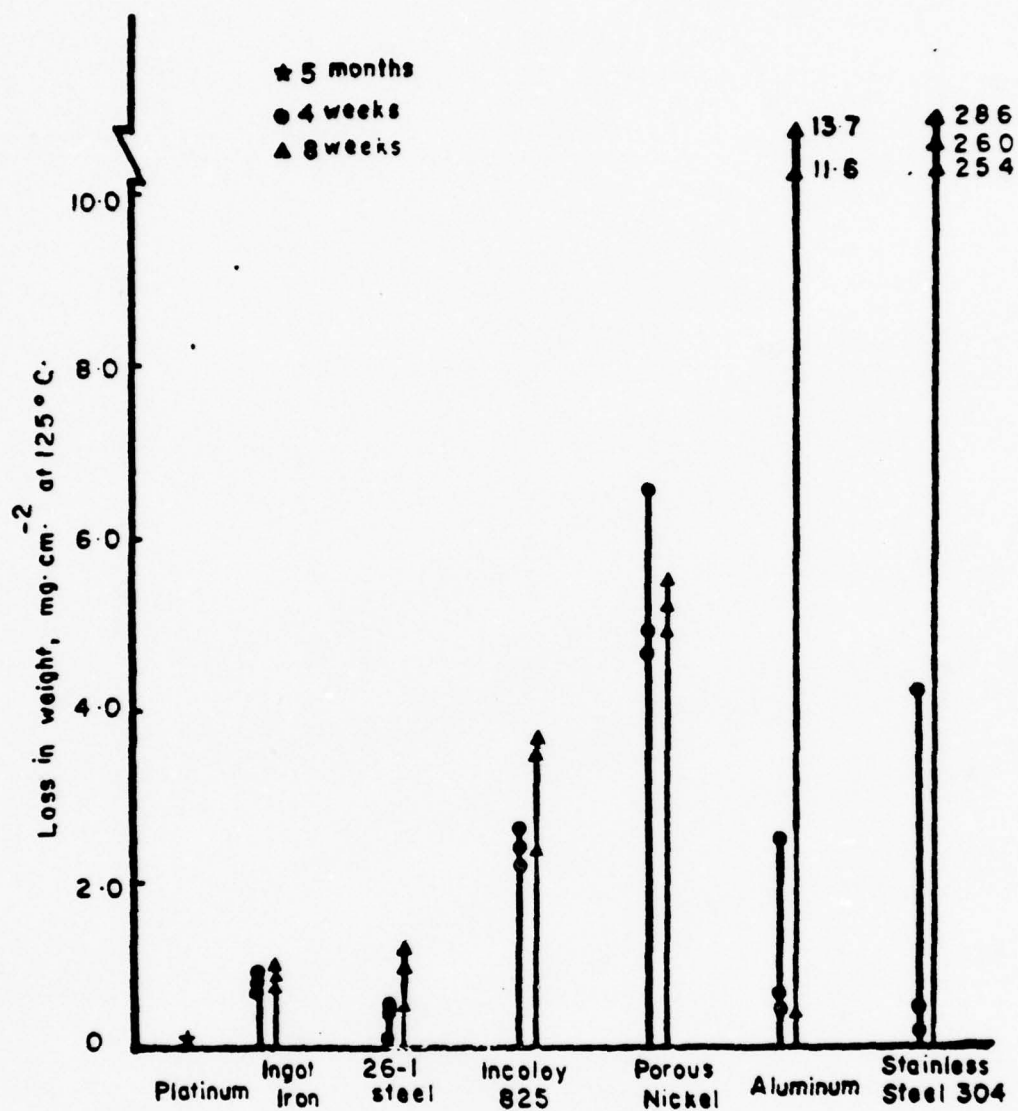


Figure 24. Corrosion tests in trifluoromethanesulfonic acid monohydrate of some resistant materials. Temperature, 125°C ●, loss in weight in 4 weeks; ▲, loss in weight in 8 weeks; ★, loss in weight in 5 months. (from reference 12)

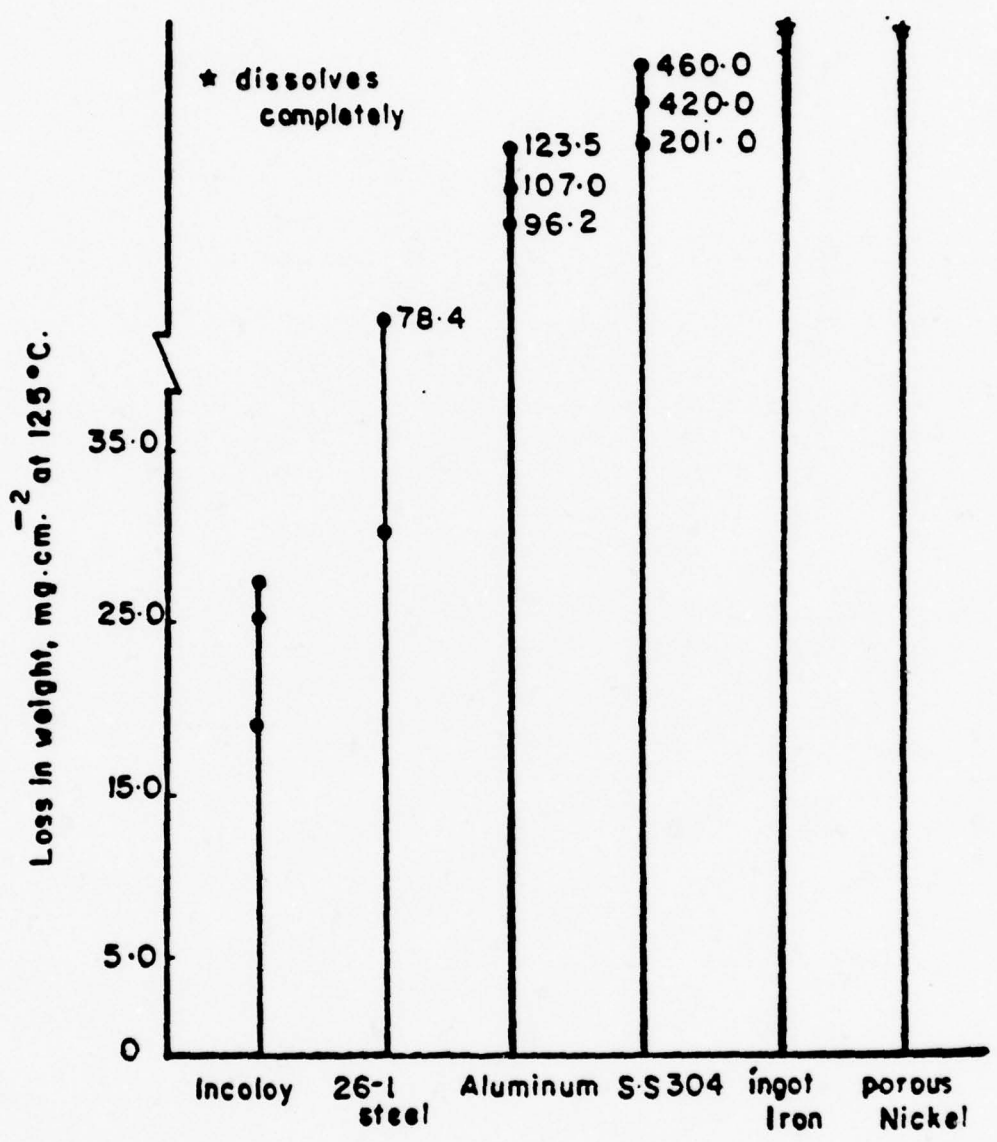


Figure 25. Corrosion tests in 85% phosphoric acid. Duration, 1 week. Temperature, 125°C. (from reference 12)

With respect to unsubstituted aliphatic sulfonic acids, the lower members are strong electrolytes, but from heptane upwards show a behavior similar to that observed with solutions of higher soaps, i.e., they form colloidal solutions.

Boiling with dilute NaOH solution is without effect but heating in 5% NaOH solution above 300° under pressure results in slow decomposition. The aliphatic sulfonic acids are, in general, inert towards the action of Cl₂ under ordinary circumstances. Ethane sulfonic acid is stable towards chlorine but with solid alkalis reacts to give ethylene. The higher members, invariably, exhibit the properties of colloidal electrolytes.

Methionic acid or methanedisulfonic acid, CH₂(SO₃H)₂, is a hygroscopic material which is strongly acidic in aqueous solutions. It forms a solid hydrate which separates from a concentrated solution of water. It is very stable to heat, acid, and alkali. No reaction takes place when heated with strong oxidizing agents such as nitric acid or chlorine. In considering aromatic sulfonic acids it must be recognized that a basic characteristic of this class is ease of hydrolysis. Complete removal of water is essential for stabilization. Even the carboxyl substituted acids share this property. This applies to both compounds with the benzene ring as well as the naphthalene ring. The rate of hydrolysis for many of the common aromatic sulfonic compounds has not been measured.

As a class, substituted aliphatic sulfonic acids offer a number of possibilities for fuel cell electrolytes. Trifluoromethanesulfonic acid is discussed above. The α-hydroxy acids undergo a variety of

reactions. They decompose both in acid and alkali solutions giving the original carbonyl compounds.

A carboxyl substitution in the hydrocarbon chain increases the stability of the aliphatic sulfonic acid, e.g., sulfoacetic acid. This is a hygroscopic solid which crystallizes as a monohydrate. It is very stable, unlike malonic acid, undergoing no decomposition when boiled with dilute acid or in alkaline solution. By heating to 190°C with conc. H₂SO₄, CO₂ is evolved. With heat alone decomposition sets in at 245°C. Electrolytic oxidation gives CO₂ and H₂SO₄ but the potentials have not been reported.

A bicyclic sulfonic acid 10-camphor (dl) acid is very soluble in water, stable, and does not decompose readily according to the literature.

Strictly from the examination of the literature and exclusive of any electrochemical testing, certain compounds appeared to offer promise as alternate fuel cell electrolytes. These are listed in table IV.

With the exception of trifluoromethanesulfonic acid, only a limited amount of electrochemical experimentation has been done on these sulfonic acids and less under fuel cell conditions.

Some of the first attempts to use sulfonic acids that were not halogenated were unsuccessful (67). This was attributed to desulfonation at elevated temperatures, i.e.,

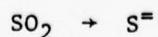
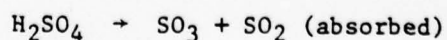


Table IV Sulfonic Acids Which, According to the Literature, Would be Potential Electrolytes

Compound	Melting Point °C	Boiling Point °C	Solubility in Water
Sulfoacetic acid HO ₃ S-CH ₂ -COOH	84-6°	245d	Very soluble ~ 510g/100ml
Methane sulfonic acid CH ₃ SO ₃ H (forms a mono or trihydrate)	19-20°	167°/10mm 121°/1mm decomp. over 220°	Miscible in all proportions
5-Sulfosalicylic Acid·2H ₂ O C ₆ H ₃ (COOH)(OH)(SO ₃ H)·2H ₂ O	120° 180d	---	Very soluble 145-150g/100ml at ~ 25°C
10-Camphorsulfonic Acid-d1 C ₁₀ H ₁₆ O ₄ S	202°d	---	250g/100ml(50°) 340g/100ml(60°)
Benzene sulfonic acid C ₆ H ₅ SO ₃ H·1.5H ₂ O	65-6 (anhyd.) 45-6	---	Very soluble
Ethylene disulfonic acid HO ₃ S-CH ₂ -CH ₂ -SO ₃ H·2H ₂ O	174 (anhyd.) 111-112°	---	Very soluble 7.4g/1ml (52°)
1,3,6-Naphthalene Trisulfonic acid	---	---	Very soluble
Sulfosuccinic acid (<i>meso</i>)	160°	---	Very soluble
Sulfopropionic acid (<i>d,l</i>)	100.5	---	Very soluble
Ethane sulfonic acid	-17°	123°/1mm	Very soluble

Table IV (Continued)

<u>Compound</u>	<u>Melting Point °C</u>	<u>Boiling Point °C</u>	<u>Solubility in Water</u>
Methane disulfonic	---	> 160 slight decomposition	Very soluble
Propane sulfonic acid	+7.5°	116/1mm	

Cells were run with sulfonic acid electrolytes with H_2 and propane, over the temperature range of $80^\circ C$ to $151^\circ C$. The sulfonic acids included methanedisulfonic, ethanedisulfonic, methane sulfonic, and ethanesulfonic. In each case desulfonation was reported as evidenced by an odor of H_2S in the fuel or O_2 exit lines. The cells with propane gave essentially zero performance and it was difficult to measure a stable open circuit value.

An effort was made to eliminate this reaction by working with the dimer of CF_3SO_3H , $SO_3H-CH_2-CF_2-SO_3H$ (68). Cyclic voltametry indicated that propane adsorbed at lower overpotentials in tetrafluoroethanedisulfonic acid than in phosphoric acid and propane oxidation went to completion without side reactions. The polarization curves for propane indicated better performance than H_3PO_4 but, in comparison, $TFMSA \cdot H_2O$ was better by a factor of 3.5 (68). The electrolyte was evaluated in fuel cells using high surface area polytetrafluoroethylene-bonded platinum black electrodes with a variety of low molecular weight paraffinic type fuels. Whereas previous tests had indicated reasonable rates for propane oxidation in these tests, the current-voltage tests fell below those of phosphoric acid (69). It appears that, with this higher molecular weight compound, whereas some of the vaporization difficulties experienced with trifluoromethanesulfonic acid monohydrate may be alleviated, the electrolyte did not exhibit the capability of supporting higher current densities for hydrocarbon oxidation than did H_3PO_4 . It is interesting to note that the open circuit voltage for the cell with the $TFEDSA$ electrolyte is 1.1 v as compared with 0.9 v for H_3PO_4 . This is a pattern consistently followed. The open

circuit voltage of a sulfonic acid electrolyte cell is 0.1 to 0.2 v higher than the corresponding cell with a phosphoric acid electrolyte.

The di- and tribasic methane sulfonic acids, with formulas such as $CX_2(SO_3H)_2$ and $CX(SO_3H)_3$, where "X" is H, F, or Cl are being investigated (70) as electrolytes, specifically for methane fuel cells. The preliminary work focussed on methanedisulfonic acid and methane-trisulfonic acid. From half-cell tests at 130°C, both acids appeared to be susceptible to oxidation and reduction at Pt electrodes. The trisulfonic acid appeared to be stable at about 80°C and supported a current density of about twice that in H_3PO_4 .

Chloromethanetrifluorosulfonic acid and dichloromethanedisulfonic acid were synthesized and the former was tested in half cells with H_2 , $H_2 + 2\% CO$, and CH_4 (71). The electrooxidation of CH_4 at 80°C was improved considerably over that in H_3PO_4 and did not show a "limiting" current at 0.6 v as is characteristic of phosphoric acid. However, the oxidation of a $H_2 + 2\% CO$ mixture proceeded at a lower rate than in H_3PO_4 . H_2 half cell currents were substantially higher (about 30%) in dichloromethanedisulfonic acid than in 85% H_3PO_4 , however, oxygen reduction currents were lower.

The electrochemical behavior of methanesulfonic acid as an electrolyte for the electrooxidation of H_2 on a platinized-platinum electrode has been studied in some depth with the rotating disk electrode technique (72). The compound was chosen because of its low vapor pressure, 10 mm Hg at 167°C, and its resistivity of 66 ohm cm at 135°C. Current-potential curves for H_2 oxidation at 135°C and at various rotation speeds were developed in methane

sulfonic acid in comparison with 85% H_3PO_4 . At the same potential and the same rotation speed, methanesulfonic acid supported oxidation currents an order of magnitude higher than those in phosphoric acid. It was possible to obtain currents at 35°C in methanesulfonic acid comparable to those obtained at 135°C in 85% H_3PO_4 . From the rotating disk electrode experiments it was concluded that the limiting currents are a combination of mass transfer and activation limiting processes. These last results do not agree with some experimental data referred to above. The reason for the discrepancy is not obvious. An important factor in these experiments is the purity of the compound employed. A second factor is the presence or absence of water. The sulfonic acid could desulfonate in the anhydrous state and be stable in aqueous solution at elevated temperature.

A number of sulfonic acids have been synthesized in an effort to improve on the physical properties of trifluoromethanesulfonic acid (73). These include methanedisulfonic, ethanesulfonic, ethane-1,2-disulfonic, propane-1,3-disulfonic, propane-1,2,3-trisulfonic, chlorotrifluoroethanesulfonic, and 1,2,2-trifluoroethane-1,1,2-trisulfonic acid. As yet, not all of these compounds have been tested for electrochemical characteristics.

The sulfonic acids, generally speaking, have desirable physical properties. The vapor pressures of three sulfonic acids are compared with sulfuric and phosphoric in figure 26 (74). The "calculated" refers to a theoretical method developed (74) to construct a vaporization curve from critical parameters. The conductivities of

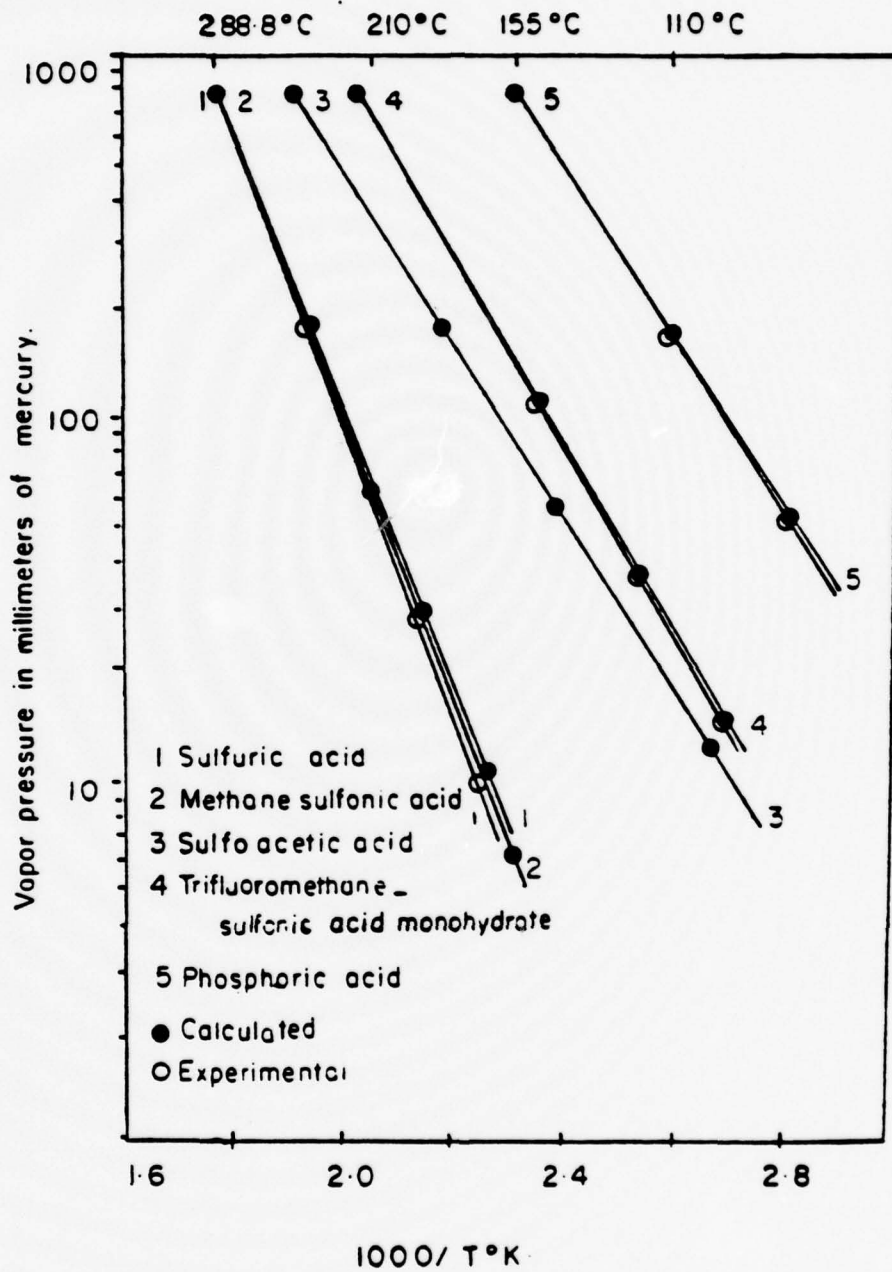


Figure 26. Vapor pressure - temperature plot for several electrolytes. Experimental and calculated compared (from reference 74)

the sulfonic acids are represented in a typical curve as figure 27. The conductivity of the pure compound is low (compare figure 2) but aqueous solutions around 50% give maximum conductances.

Carboxylic Acids as Potential Electrolytes

With respect to the evaluation of carboxylic acids as fuel cell electrolytes, certain of their properties and reactions are pertinent, particularly where they refer to the stability of the compounds at elevated temperatures or under oxidizing or reducing conditions. Some general observations may be drawn from the literature, first considering aliphatic carboxylic acids (75 - 77).

In the saturated monocarboxylic acid the $-COOH$ group is resistant to reduction; and the β -position of a fatty acid is the primary point of attack in a reaction. The acid is not oxidized by air at ordinary temperatures but is by oxygen at elevated temperatures, especially in the presence of catalysts. $KMnO_4$ can degrade the carboxylic acid to give quite heterogeneous products. H_2O_2 attacks the acid, e.g., a 3% H_2O_2 solution oxidizes butyric acid to β -hydroxy butyric acid and then to acetoacetic acid and finally to acetone. The $-COOH$ group is relatively unstable at high temperatures and decarboxylation is a predominant reaction in the higher temperature range, in the presence of catalysts, yielding ketones. Lower acids yield ketones, olefins and cyclic hydrocarbons at $600^\circ C$; the presence of catalysts greatly lowering the temperature at which the fatty acid undergoes decomposition. The carboxylate ion of the aliphatic acid is anodically oxidized at the Pt electrode at a

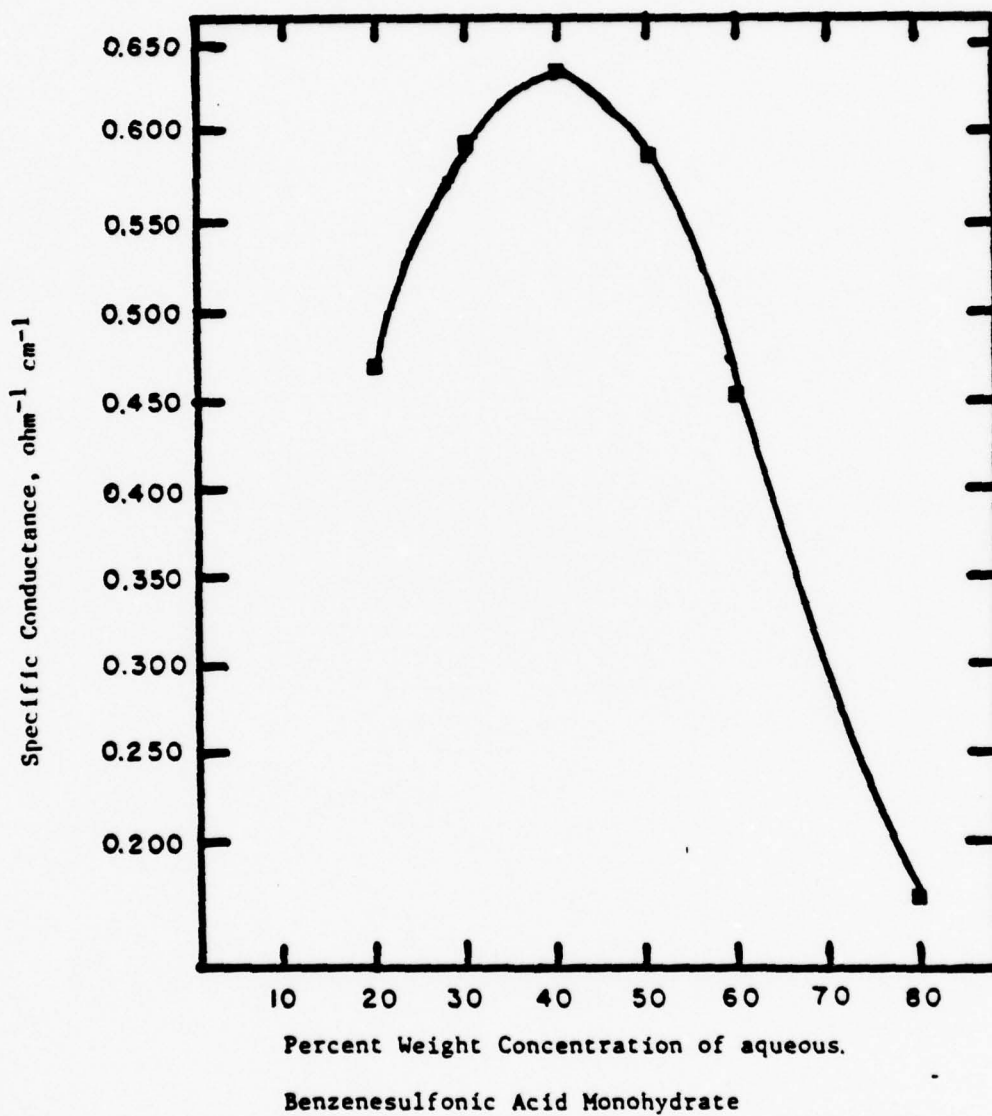


Figure 27. Conductance - composition plot for aqueous solutions of benzenesulfonic acid monohydrate at 80°C (from reference 14)

very high positive potential, i.e., at +2.3 volts. The monocarboxylic acid has a very low solubility, low conductivity and high pK_a value. The unsaturated monocarboxylic acid is a reducing agent and is generally not stable.

In view of this instability, aliphatic monocarboxylic acids, saturated and unsaturated, do not appear to be promising fuel cell electrolytes.

The first effect of introducing a second carboxyl group is to decrease the stability of the dicarboxylate anion. Formation of anhydride by loss of water, and decarboxylation usually result. The lower carbon members decarboxylate quickly and the higher members form lactones, or anhydrides. pK_a values are low enough but supporting electrolytes would probably be required. Under a variety of pyrolytic conditions, fatty acids and their derivatives may suffer simultaneous or successive decarboxylation and dehydrogenation to unsaturated hydrocarbons. In a number of instances aromatic hydrocarbons or ketones are formed. Except in the presence of catalysts these acids are relatively resistant to the action of H_2O_2 . When oxidation occurs, it is not specific or directed and a wide variety of products from partial oxidation have been identified, such as, aldehydes, hydroxy acids, ketones, hydrocarbons, as well as CO_2 . In a buffered oxidation system the acid is always oxidized to CO_2 .

In view of their instability, di- or polycarboxylic acids also are not considered to be promising electrolytes.

Aromatic carboxylic acids (75 - 78) are not strong acids (pK_a values are typically in the range of 4 to 5 at $25^\circ C$). The

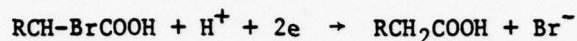
dicarboxylic acids are sparingly soluble in water. The tricarboxylic, the asymmetric ones, like trimellitic acid have reasonably high acid strengths although the solubility is rather low, i.e., less than 10 g in 100 ml. With neutralization of one or two of the carboxyl groups a good protonic solvent may result.

Substituted carboxylic acids (75 - 80) offer diverse properties dependent on the substituting group. The halogen substituted carboxylic acids fall into two subclasses: those with chlorine, bromine, and iodine substitution and those with fluorine substitution. Those with chlorine, bromine, and iodine substitution are stronger acids than the corresponding unsubstituted acids, but the kind and position of the halogen atom in the alkyl chain affects the strength of the acid. A halogen in the α position increases the acidity far more than in the other positions. The effect seems to be electrostatic; the ionizable proton is in a region of relatively high positive charge because it is closer to the positive than the negative end of the larger C-X dipole. The ease of fission of the carbon-bromine bond in the 2-bromo alkanolic acids appears to be related to the length of alkyl chain.

All of these halogen substituted acids are unstable to hydrolysis. For example, monochloroacetic acid when refluxed for 6 hrs at 105°C (in a 50% aqueous solution) hydrolyzes about 5% (74). With α -halo acids, substitution reactions predominate during hydrolysis; with β -halo acids, unsaturated acids are formed; and with γ -acids lactones are formed. These reactions are accelerated by the presence of alkalis. The product, irrespective of the position of

the halogen, is formed either by dehydrogenation or by substitution of new groups. This applies to di and poly halogen substitution as well.

In polarographic reduction according to the equation



the ease of reduction increases progressively as the homologous series is ascended from acetic to decanoic acid.

The ease of replacement of the halogen in fatty acids is in the same order as in alkyl halides, namely $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$. The bromo and chloro acids can be selectively reduced electrolytically under controlled conditions.

In view of these reactions, no compound from the chlorine, bromine, or iodine substituted carboxylic acid subclass is considered to be a suitable electrolyte.

Fluoro-containing carboxylic acids respond normally in many chemical reactions although the reaction rates are determined by the contribution of fluorine to the overall polarity in reactions involving ionic mechanisms. The CF_3 group, for example, is strongly electronegative and exerts a pronounced effect when it is not too remote from the carboxyl group. Two illustrations are included here to show the unique characteristic bestowed on the carboxyl group by fluoro substitution. Alpha-trifluoromethyl- α -hydroxy propionic acid (trifluorolactic acid) shows an unusual reluctance to form a lactide whereas the unsubstituted acid dehydrates very easily. Removal of F from C-F to form an olefin is much more difficult energetically than to remove H_2 from C-H. With partial fluorination, the compounds

become unstable.

β -Fluoro acids resemble β -hydroxy acids in the ease in which unsaturates are formed. In β -difluoro acids this activity should be increase because of the additional inductive effect of the $-\text{CF}_2-$ which makes the α -H more mobile. Difluorosuccinic acid $(\text{CHF}-\text{COOH})_2$ is extremely reactive even with water and immediately forms acetylinic dicarboxylic acids.

Some observations on specific members are pertinent in evaluating this subclass of compounds. Trifluoroacetic acid hydrolyzes rather easily; also it decomposes thermally, very likely, to give a difluorocarbene and CO_2 . Perfluoropropionic acid shows a tendency for hydrolysis. In water, perfluorobutyric acid, $\text{C}_3\text{F}_7\text{COOH}$, slowly decarboxylates at 150°C . The aqueous solution of $\text{C}_3\text{F}_7\text{COOH}$ has essentially the same pH as would be calculated for complete dissociation. The F atoms are stable toward hydrolysis. The compound withstands refluxing with dilute base for hours with negligible formation of fluoride ions. Decarboxylation reactions are difficult with fluorinated monocarboxylic acids. Unsaturated and aromatic perfluoro acids and derivatives are less stable. Free perfluorocarboxylic acids lose HF and CO_2 and form a perfluoroolefin when heated to a higher temperature. Electrolysis of fluorinated alkyl acids in the presence of sodium methoxide gives fluorinated paraffins by coupling.

With respect to physical properties the effect of fluorine atoms on the acids is to increase the density, to decrease the refractive index, to lower the surface tension, and to increase the

absolute viscosity. Most of these fluoro acids form hydrates or compounds containing some definite hydrate or water-containing azeotropic mixture. The higher perfluoro acids in aqueous solutions are found to lower the surface tension of water to a larger extent than any other type of compound. The solubilities go down as we ascend the series; there is foaming and gel formation in aqueous solutions. From these observations it may be concluded that if any compound is to be chosen from this subclass the following guidelines should be used:

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

On the basis of the foregoing perfluorobutyric, C_3F_7COOH , perfluorosuccinic, $(CF_2COOH)_2$, and perfluoroadipic, $COOH-(CF_2)_4-COOH$ acids should be given consideration as potential electrolytes.

A limited amount of electrochemical work has been done in evaluating these carboxylic acids as electrolytes. Trifluoroacetic acid was used by Pilla et al. (81) to compare adsorption kinetics of propane with that occurring in H_3PO_4 and H_2SO_4 . Solutions 2 F in concentration were used at $65^\circ C$. A multipulse potentiodynamic technique indicated that propane was adsorbed at the highest rate in CF_3COOH . Further measurements with a multi-step potentiostatic relaxation method indicated that, of the three electrolytes, CF_3COOH had the least interaction with the electrode as measured by the

capacitance in the three electrolytes . There was an inverse correlation between interaction and propane adsorption rate. It was also observed that the point at which the platinum electrode oxidation occurs is more anodic for the electrolyte in which propane adsorption is highest. This effect was not too pronounced but the adsorption data indicate considerable differences of adsorption in the sequence, CF₃COOH > H₂SO₄ > H₃PO₄.

Two of the deterrents to using the fluorinated carboxylic acids as fuel cell electrolytes are their low boiling points and their tendencies to decarboxylate. The boiling points of three of the common acids are as follow (82):

Trifluoroacetic (CF ₃ COOH)	71.1°C at 734 mm
Perfluoropropionic (C ₂ F ₅ COOH)	96°C at 740 mm
Perfluorobutyric (CF ₃ CF ₂ CF ₂ COOH)	120°C at 735 mm 107.4° at 455 mm

In an attempt to circumvent the vapor pressure problem, perfluorobutyric acid was chosen for electrochemical study. Heptafluorobutyric acid forms a hydrate (83) and it was expected that the monohydrate would have a better high temperature stability than the acid. The literature (82) reported that the acid decarboxylated at a slow rate at 150°C. The current density-potential behavior of propane in perfluorobutyric acid is given in figure 28 (29). At temperatures over 100° there was excessive vaporization of the acid from the cell.

Dichloroacetic acid was also examined electrochemically as an electrolyte for propane oxidation (29). It was observed that

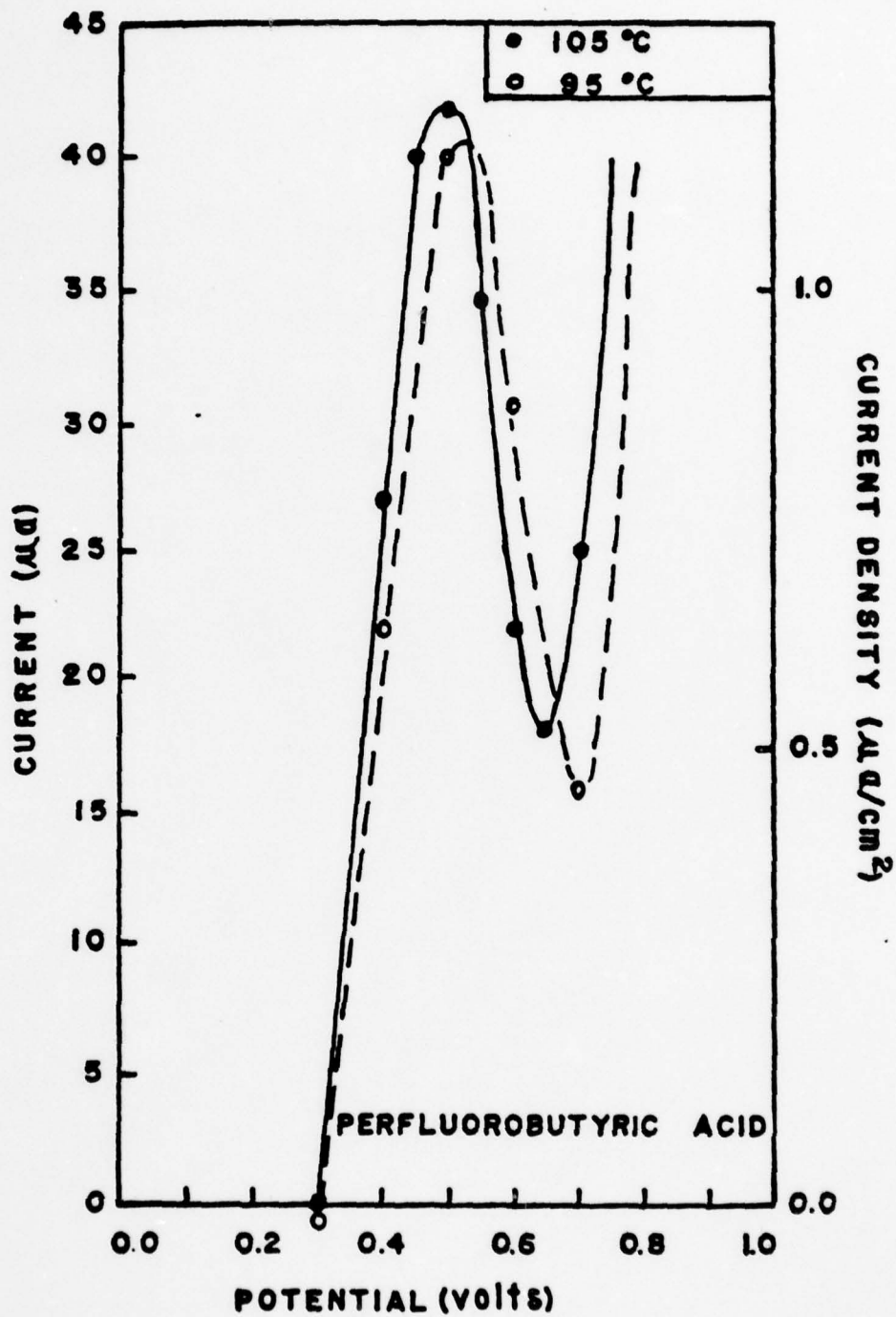


Figure 28. Current density - potential behavior of propane in perfluorobutyric acid (from reference 29)

the polarization maximum shifted from 0.55 v (in phosphoric acid) to 1.0 v. The reason for this odd behavior was not established.

Several carboxylic acids were recently evaluated by Rebert et al. (72) as fuel cell electrolytes. The experimental tests included conductivity measurements, vapor pressure determinations and the ability of the electrolyte to support the electrooxidation of hydrogen on a platinized-platinum rotating disk electrode. The compounds investigated were trichloroacetic, chlorodifluoroacetic and pentafluoropropanoic acids. Trichloroacetic acid was rejected because of its high vapor pressure and the fact that chlorine gas was evolved on heating. The resistance of the pure compound was quite high, requiring dilution with water. Chlorodifluoroacetic acid also decomposed to give chlorine gas. Pentafluoropropanoic acid used as a 90% aqueous solution had an undesirably high vapor pressure and was reported to undergo polymerization upon heating to 50°C.

D. Alkaline Systems

Alkaline fuel cells were the first systems subjected to extensive investigation, mainly due to the Space Program wherein cost was of secondary importance and systems were designed to run on pure hydrogen and oxygen. The case for the alkaline fuel cell has been well presented by Kordesch (84). Alkaline fuel cells exhibit a high power output at ambient temperatures and pressures; the cell uses available catalysts such as noble metals (at low loadings) and Raney metals; the cell uses easily oxidizable fuels, such as H_2 and N_2H_4 . These are advantages. On the other hand there are disadvantages. The alkaline fuel cell cannot use hydrocarbons, directly or indirectly, without a CO_2 scrubber. Further, the cell cannot use air directly; again, a CO_2 scrubber is required. The major factor in the furthering of alkaline cells came about with the development of carbon-air electrodes that could operate at reasonable current densities without platinum catalysts (85). Also carbon-hydrogen electrodes were found to operate at low catalyst loading, e.g., 0.1 mg/cm^2 .

As mentioned above, the major problem in the alkaline fuel cell is carbonation; the electrolyte for many alkaline fuel cells is about 6 N or about 35% KOH. Carbon dioxide enters into the cell electrolyte when air is the oxidant (400 ppm). Also, CO_2 enters with the H_2 when a hydrocarbon reforming process is used (0.33 mole of CO_2 per mole of H_2).

The corrosion of polymeric materials used in the fabrication

of the cell is a third source.

An electrochemical regeneration process for the KOH electrolyte is described by Handley and Meyer (86) but they used hydrogen and unscrubbed air in their cell. Their method would eliminate the need for air scrubbers for a hydrocarbon-air fuel cell but would assume a hydrogen purification process on the fuel supply side.

Giner (87) has approached the problem in a broader fashion. On the air side a scrubber or electrochemical regeneration of the carbonated hydroxide solution can be used. On the fuel side an electrochemical hydrogen separation step is included. Additionally, a regeneration process involving adsorption and thermal regeneration would be required. If carbonation is produced by the corrosion (dissolution) of plastic materials within the fuel cell, some electrolyte regeneration as opposed to pretreatment of the reactants would be necessary.

Assuming that it is possible to remove all CO_2 from the air and fuel stream, a source of carbonation in the KOH cell is the corrosion of plastic materials in the cell construction. This problem is discussed by Getlow et al. (88) in their report on the development of an advanced fuel cell system in a NASA program. In one test over a period of 5000 hrs they report a conversion of 30% KOH to K_2CO_3 in a single cell employing a polysulfone/epoxy-glass frame material. In another test, they observed a conversion of 42.5% KOH to K_2CO_3 due mainly to a silicone rubber gasket material.

It appears that the carbonation problem is inherent in the

alkaline fuel cell system. The solution would require a regeneration system which in all likelihood would involve setting up a parasitic electrochemical cell to regenerate the entire fuel cell electrolyte.

E. Ion Exchange Membrane Systems

The ion exchange membranes should not be considered solid electrolytes even though the fuel cell systems are often referred to as solid polymer electrolyte fuel cells. The ionic conduction mechanism is similar to that in aqueous systems, that is, the movement of hydrated protons in the acid sulfonated polystyrene polymer and hydroxyl ion movement in the quaternary ammonium type polymer. The scientific principles related to the application of ion exchange membranes to fuel cells have been discussed by Gregor (89). A great deal of work has been done employing the acid sulfonated polystyrene polymer in which protons conduct and the polystyrene functions as the backbone or matrix material. One important consideration involves the equilibrium of the membrane with water. As the membrane dries out or as the ambient relative humidity decreases, the resistance of the membrane increases sharply as indicated in figure 29. The fact that only one species moves, cations in the sulfonated polystyrene type, means that solvent water will move only with the proton, i.e., the electro-osmosis effect seen in figure 30. This could lead to drying out of one side of a membrane and flooding of the other. Another important property is the solubility of organic compounds such as hydrocarbon fuels in the membrane. This leads to a lowering of the dielectric constant and a corresponding increase in resistance.

Whereas a large number of possibilities exist for cation and anion exchange membranes, including polyvinyl sulfonic acid, phenol

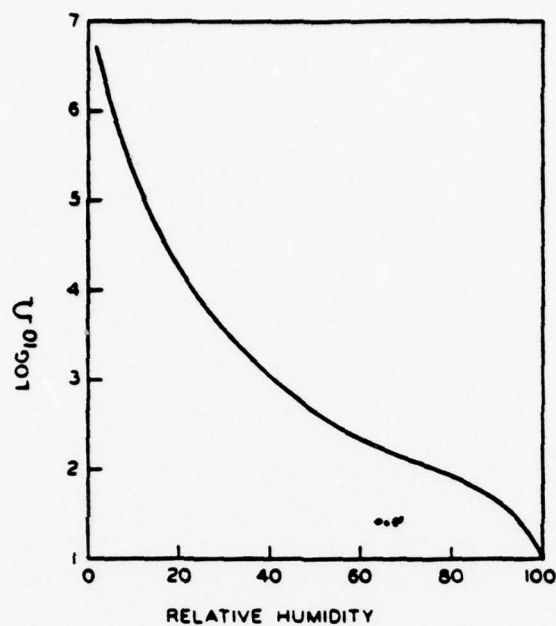


Figure 29. Ohmic resistance of polystyrenesulfonic acid membrane as a function of ambient relative humidity (from reference 89)

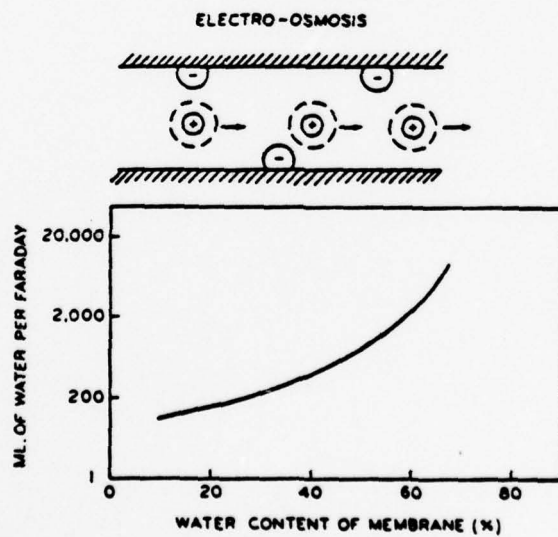


Figure 30. Electro-osmosis with cation exchange membranes (from reference 89)

sulfonic acid, polyacrylic acid, and quaternary ammonium base materials, sulfonated polystyrene appears to have the most suitable properties. Such a membrane has been used in the General Electric ion exchange membrane fuel cell (90). The development of the General Electric system and its application to the Gemini flight are reviewed in a number of reports given at the Annual Power Sources Conference (91 - 96). In these reports a number of the problems associated with the ion exchange membrane were identified. These include the need for structural integrity; in the Gemini cell the polystyrene sulfonic acid was mixed with a Kel-F spine. Control of the membrane water content was important for the reasons given above. The performance decay rate, which amounted to 1 - 5 mv/hr, was due mainly to the degradation of the membrane e.g., by oxidation. The reason for certain periods of poor performance was attributed to flooding of the cells. It appeared that the major life limiting factor was the slow degradation of the polymer, which, in turn, was a function of the temperature. One very early problem was related to the development of pin holes in the membrane. If pin holing occurred during the operation of the cell by drying out a specific site, the hydrogen fuel and oxygen could mix and react chemically. This was remedied by proper fabrication techniques. The early development of the General Electric ion membrane cell was directed toward a power source for the space program, thus the high cost of the platinum catalyst loading was not of great concern. Figure 31 is of interest in identifying the source of polarization in the ion membrane cell. A main source, as expected, is ohmic. There is virtually no

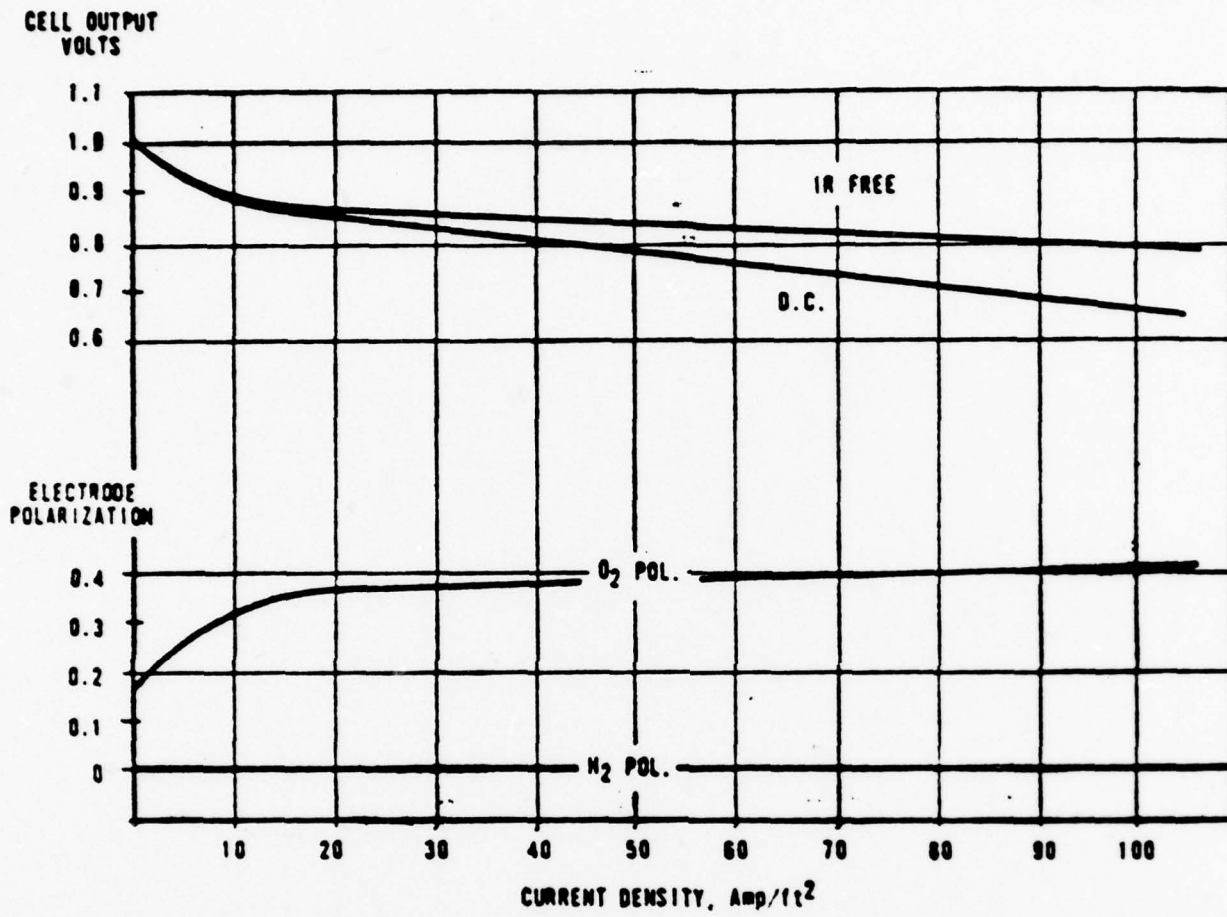


Figure 31. Electrochemical analysis of losses occurring in ion exchange cell (from reference 92)

anode polarization and surprisingly the oxygen polarization levels off at about 20 amp/ft².

The present status of the ion membrane cell is reviewed by McElroy (97 - 99). According to the latest reports, the life of the cell has been extended from 1000 hrs at 25°C (experience with the Gemini flight) to over 40,000 hrs at 82°C and allowable current densities from 42 amp/ft² to 1500 amp/ft². This implies that the problem of the chemical stability of the polymer has been solved, and, indeed, a performance decay rate of one microvolt per cell hour for over 40,000 hrs at 82°C and 100 ASF is cited.

This improvement in performance has been due to electrolyte modification (the Nafion type membrane is used), temperature and pressure increases, and optimized heat and mass transfer characteristics. The initial high cost of the cell has been reduced by the development of low cost solid polymer electrolytes, reduced noble catalyst loadings, and conductive cathode wet proofing. As mentioned above, the first application of the ion membrane cell was in space applications and the cost of a high Pt catalyst loading was not disproportionate. Recent work has indicated that this may be greatly reduced. The early ion membrane cell could only be operated on pure H₂ and O₂, one of the limitations of the cell being a poor CO tolerance. This situation has been improved in recent work (100). Figure 32 gives the current cell performance of an ion exchange membrane cell on H₂ and O₂; figure 33 on a methanol reformat (75% H₂, 24.6% CO₂, 0.3% CO, 0.1% CH₄) and air. Note that the operating temperature is now 104°C.

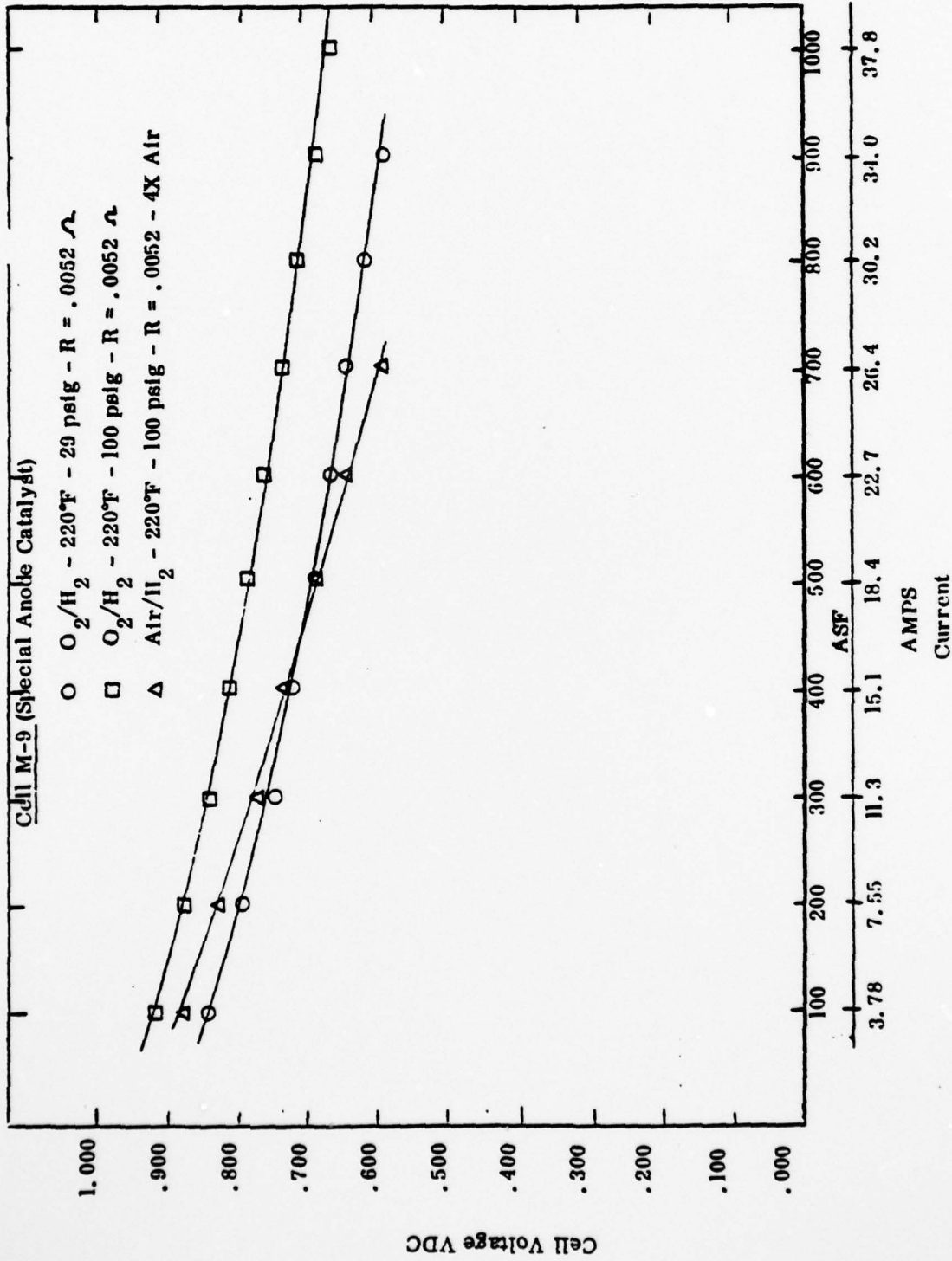


Figure 32. Performance of an ion membrane fuel cell on H₂ and O₂ (from reference 100)

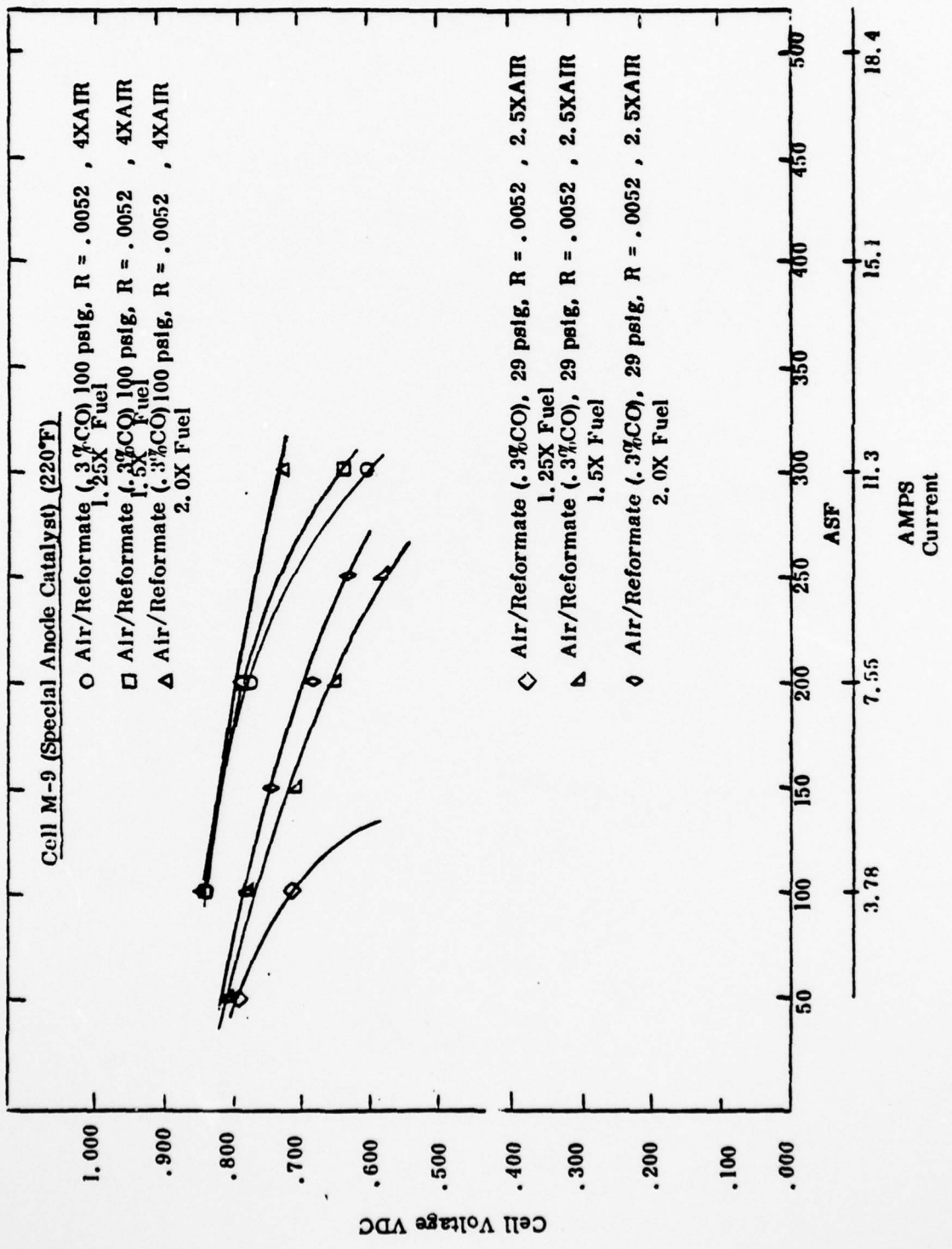
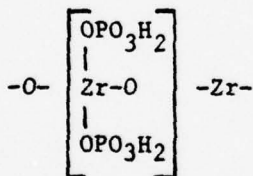


Figure 33. Performance of an ion membrane fuel cell on methanol reformate (from reference 100)

By analogy with aqueous sulfonic acid systems it would be expected that further improvement in the high temperature stability of the membranes might be achieved with fluorinated sulfonic acid membranes.

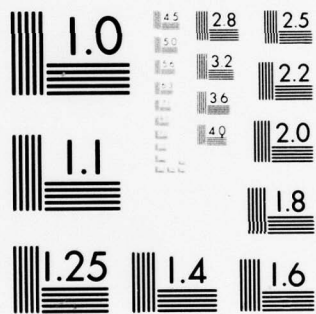
With this type of system one of the parameters requiring close control will always be the moisture content of the membrane. This, however, is a problem inherent with most fuel cell electrolytes and in most recent work (100) the problem has received attention through humidification techniques.

Whereas the major effort on ion exchange membranes has been on organic based polymers of the polystyrene or polyvinyl type, it should be mentioned that inorganic polymers have also been investigated. Dravnieks et al. (101) investigated and constructed an ion membrane cell with a zirconyl phosphate electrolyte. The monomer structure proposed for this polymer unit is



and, in the cell studies, Teflon was used as a binder. The resistance of a typical membrane was of the order of 100 - 200 ohm-cm, about two orders of magnitude higher than a good organic membrane. However, there appears to be no theoretical reason why high conductivity inorganic membranes suitable for fuel cells cannot be developed. It must be kept in mind, however, that the conductance mechanism would be the same, movement of the hydrated proton, so an inorganic membrane would require the same type of moisture control as does the organic.

One would not expect, on the other hand, difficulties with lowering of dielectric constant by the solution of hydrocarbons.



MICROCOPY RESOLUTION TEST CHART
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F. Solid Electrolytes

The field of solid electrolytes, both the theoretical principles of solid oxide electrolytes and their application to high temperature fuel cells, has been critically reviewed by Takahashi (102). His paper covers the field up to 1971. In this context, the solid electrolytes refer to those used in the high temperature fuel cell, e.g., zirconia stabilized with CaO or Y_2O_3 , as opposed to those used in elevated temperature batteries, e.g., β -alumina or modified silver iodide compositions.

The investigation and development of solid electrolyte conductors involve principles and disciplines different from those involved in, say, acid electrolyte development. The mechanism of current conduction is principally oxide ion conduction rather than conduction with protons and hydroxyl ions. Operation at $1000^\circ C$ minimizes activation polarization and the losses in the cell are essentially ohmic and concentration. Thus, the problems shift from those treated by electrochemistry to those treated by solid state chemistry, such as conduction and diffusion of ionic species in crystals, the stability of solid phases at high temperature and order-disorder reactions. Further, operation at $1000^\circ C$ presents substantial materials problems.

The applicable theory related to high temperature solid electrolytes differs in concept from the aqueous cell. Theoretically, the cell is treated as an oxygen concentration cell, the high concentration being the oxygen concentration at the cathode, the air supply, and the low concentration that existing at the anode,

as determined by the fuel reaction. The efficiency of a fuel cell is defined as the ratio of the free energy of the cell reaction to the enthalpy of reaction. The maximum thermal efficiency of fuel cells based on several reactions is given in table V. It is apparent that, for the solid electrolyte cell, operating at 1000°C, the oxidation of methane and carbon is to be preferred over the oxidation of hydrogen.

The oxides found suitable for high temperature fuel cells have been stabilized compositions of zirconia, thoria or ceria, the most important being ZrO_2 stabilized in the fluorite (cubic) structure by CaO , Y_2O_3 or Yb_2O_3 . These structures are oxide ion conductors by an oxide ion vacancy mechanism. In stabilized zirconias the oxide ion transference number is close to unity at 1000°C, that is, the electronic conduction is negligible. In the CaO and Y_2O_3 solid solutions the conductance is a maximum at some specific composition, in the case of the Y_2O_3 stabilized zirconia this maximum occurs at 9 mole percent (see figure 34). The stabilized thorias and cerias are not as satisfactory electrolytes as the stabilized zirconias. With CeO_2 stabilized by La_2O_3 , the oxide ion transference number decreases at low oxygen partial pressure with an increase in undesirable electronic conduction. The conductivity of CaO stabilized ThO_2 is relatively low at 1000°C (compare $9 \times 10^{-4} \text{ ohm}^{-1}\text{cm}^{-1}$ for $(ThO_2)_{0.95}(CaO)_{0.05}$ with $1.6 \times 10^{-1} \text{ ohm}^{-1}\text{cm}^{-1}$ for $(ZrO_2)_{0.91}(Y_2O_3)_{0.09}$).

The high temperature fuel cell including the most satisfactory electrolyte compositions has evolved over the last two decades to a

Table V Maximum Thermal Efficiency of Fuel Cells
at 1250°K (from ref. 102)

<u>Reaction</u>	<u>ΔG° (kcal)</u>	<u>ΔH° (kcal)</u>	<u>E°</u>	<u>$\epsilon^{\circ*}$</u>
$H_2 + 1/2 O_2 = H_2O (g)$	-42.6	-59.7	0.924	0.71
$CO + 1/2 O_2 = CO_2$	-41.4	-67.4	0.898	0.61
$CH_4 + 2 O_2 = CO_2 + H_2O$	-191.9	-191.5	1.039	1.00
$C + O_2 = CO_2$	-94.8	-94.8	1.027	1.00

*efficiency

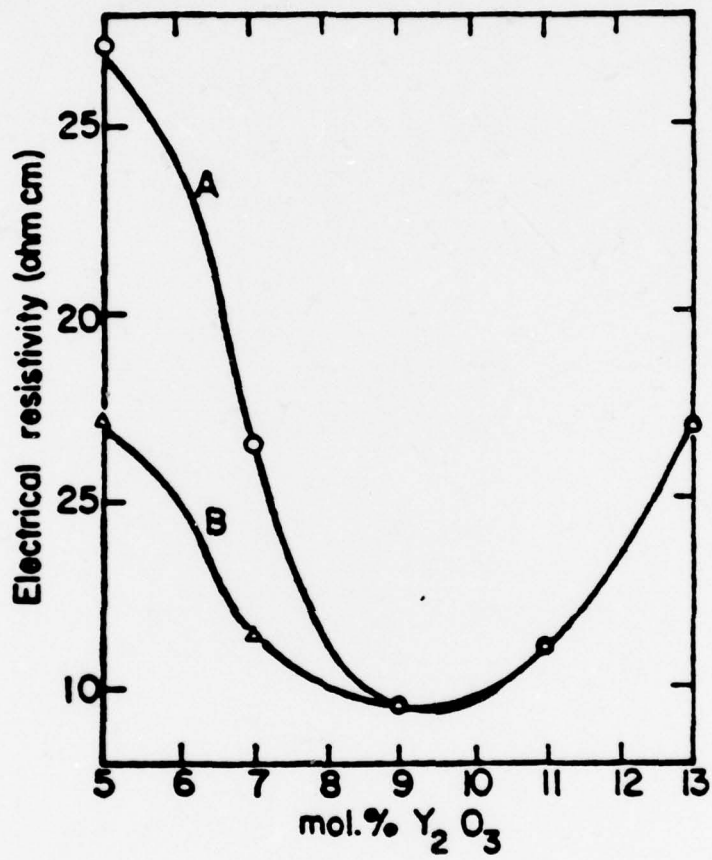


Figure 34. Resistivity of $ZrO_2 - Y_2O_3$ system at $1000^\circ C$,
 $p(\infty)$ - curve A, $p(1hr)$ - curve B

construction represented by the Westinghouse design (103), similar development by General Electric and Brown-Boveri being dropped for economic reasons. The present design uses a yttria-stabilized zirconia $(\text{ZrO}_2)_{0.9}(\text{Y}_2\text{O}_3)_{0.1}$, an air electrode of an electronically conducting oxide, $(\text{In}_2\text{O}_3)_{0.98}(\text{SnO}_2)_{0.02}$ with a praeosodymium oxide (PrO_2) catalyst, and a fuel electrode, a nickel-zirconia cermet, approximately 40% Ni and 60% zirconia (yttria stabilized). The zirconia solid electrolyte was arrived at after consideration of ceria and thoria systems as well as zirconia. As mentioned above, ceria compositons exhibited higher electronic conductivity and lower mechanical strength. Thoria compositions possessed lower (ionic) conductivity and natural thorias presented radiation problems.

The solid electrolyte cells operating at 1000°C are the most efficient fuel cells with efficiencies of 80% claimed for cells operating near 300 mA/cm^2 in the voltage range of 0.95 and 0.65 v. Individual cells have been run for extended periods, e.g., 50 days, but batteries have shown a limited life due to the failure of the cell interconnections. The interconnection material must possess high electronic conductivity, stability in contact with air and fuel gases, and thermal expansion characteristics matched to other cell components, e.g., stabilized zirconia. On the basis of these properties, doped-lanthanum chromites, e.g., $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$ are being tested and methods of fabrication of cell interconnections are being developed.

The solid state problems associated with the high temperature

fuel cell have been described (104). It is recognized that the doped zirconia, or ceria, whichever base oxide is chosen, has a rather narrow composition limit in which it achieves its high ionic conductivity. For example, the high conductance cubic phase of ZrO_2 must be stabilized with 7 - 10 mole % of CaO or $YO_{1.5}$ as indicated in figure 34. Departure from that structure or composition through destabilizing and aging will alter the desirable properties of the oxide as an electrolyte (105). Operation at about $1000^\circ C$ under a potential gradient can lead to electrolyte degradation from, a) ordering of dopant ions, Ca^{++} or Y^{+++} , and a resultant increase in resistivity, and b) migration of dopant or impurity ions leading to the formation of high resistivity layers next to the anode.

These long term solid state reactions are superimposed upon the customary materials problems associated with operating any chemical reactor at elevated temperatures. As pointed out by Tannenberger (106) the major problems associated with the high temperature ZrO_2 fuel cell at present are engineering rather than electrochemical.

G. Molten Carbonate Systems

A comprehensive review of the literature on all phases of the molten carbonate fuel cell has been made by the Institute of Gas Technology (107). The development of the molten carbonate cell from the pioneering work of Baur (1921), Davtyan (1946), and the systematic study of Broers (1958), is traced up to the present state in great detail. The molten carbonates are mixtures, often eutectic mixtures, of the alkali carbonates. The preferred mixtures are the binaries, $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$, and $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ and the ternary $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ systems. Li_2CO_3 serves to lower the melting point of the mixture and increase the conductivity so that the fuel cell is actually run in the range of 600 - 700°C.

As a result of the IGT survey the following mixtures were recommended for further evaluation:

- 62 Li_2CO_3 - 38 K_2CO_3 (488°C)
- 43.5 Li_2CO_3 - 31.5 Na_2CO_3 - 25 K_2CO_3 (397°C)
- 60 Li_2CO_3 - 30 Na_2CO_3 - 10 K_2CO_3 (~ 527°C)
- 52 Li_2CO_3 - 48 Na_2CO_3 (501°C)
- 20 Li_2CO_3 - 45 Na_2CO_3 - 35 K_2CO_3 (~ 577°C)
- 20 Li_2CO_3 - 25 Na_2CO_3 - 55 K_2CO_3 (~ 600°C)

The compositions are given in mole percent and the figure in the parenthesis following is the melting point of the carbonate mixture.

These compositions were selected after a consideration of a number of physical and chemical properties. The consideration started

with the phase diagrams indicating the stability of the mixture and included equilibria such as the decomposition reaction, hydroxide formation, and vapor pressure characteristics. Such physical properties as electrical conductivity, thermal conductivity, viscosity, dielectric constant, density, surface activity and specific heat were evaluated. A great deal of the physical property data were already available in the literature and the data required to make the complete analyses were indicated.

The problems associated with the molten carbonate systems are due mainly to the high temperature of operation. One of the major problems is related to the loss of the electrolyte through vaporization, corrosion reactions, creepage, and entrainment in the gas streams. Further, at high temperature the corrosion of the cell hardware and interaction with support or matrix materials is enhanced. On the other hand, the high temperature of operation of the cell lowers the activation polarization so that the formidable electrocatalysis problem inherent in low temperature acid systems is minimized or nonexistent. The polarization losses in the molten carbonate systems are largely concentration and ohmic.

In most aqueous systems and in high temperature oxidizing conditions the stainless steels depend on an oxide film for passivation. However, several of the oxides interact with molten carbonate melts and corrosion of normally corrosion resistant alloys is accelerated. As reaction products build up in the melt or on the metal surface, corrosion does slow down but the reaction products in the melt represents an undesirable situation.

The many experiments done with a large number of carbonate compositions makes it possible to indicate certain compositions that should be most effective as fuel cell electrolytes. It now remains to optimize the composition of the $\text{Li}_2\text{CO}_3 - \text{Na}_2\text{CO}_3 - \text{K}_2\text{CO}_3$ ternary.

One of the problems that the molten carbonate fuel cell shares with other electrolyte systems even in the advanced designs is a lack of tolerance to the sulfur in the fuel gas (108). Sulfur compounds form in the electrolyte and some sort of sulfur removal process is required.

The high temperature of operation causes sintering in a high surface area electrode. This is seen at about 700°C in nickel electrodes (109) and an attempt is being made to understand the mechanism and control the reaction.

A problem, also common with other fuel cell systems, is the stability and the performance of the matrix holding the fuel cell electrolyte. In the molten carbonate cell the matrix material is lithium aluminate (110). Methods of preparing the LiAlO_2 are being worked out and the long term stability in the presence of molten carbonate is being established.

It is noted that the majority of the problems encountered in the molten carbonate electrolyte fuel cell fall in the materials field or the field of inorganic chemistry rather than electrochemistry.

III CONCLUSIONS AND FUTURE DIRECTION

General Conclusions

The manner in which the fuel cell field has developed in the last few decades explains the trend toward high temperature electrolytes such as molten carbonates and solid oxide electrolytes. From a theoretical viewpoint this trend is paradoxical. The fuel cell is by definition an electrochemical device which converts chemical to electrical energy directly, and, as such, should operate at ambient temperatures with efficiencies approaching 100%. However, to circumvent difficult electrocatalytic problems that could not be solved at low temperature, the reaction temperature was increased. At sufficiently high temperatures the electrocatalytic problem disappears and the electrode now serves as a catalytic surface rather than an electrocatalytic surface. Or, the electrochemical device has now become a chemical-electrochemical hybrid cell with all the restrictions and limitations of a chemical reactor.

To increase the rate of a chemical reaction it is logical to increase the temperature, i.e., to supply the required thermal activation energy. Now, in going to the higher temperature, new problems of a mechanical engineering or materials engineering type are introduced, such as heat transfer, seals, connections, and corrosion problems. In most cases, these problems cannot be solved by electrochemical means, as by altering the electrolyte or the electrodes. For example, at high temperatures, all elements and compounds exert appreciable vapor pressures; even in solids, atoms

tend to diffuse under a concentration gradient to achieve an ordered, thermodynamically stable structure. This suggests that, to minimize operational problems, a low temperature fuel cell (a low temperature electrolyte) is to be preferred. The electrochemical problems, electrocatalysis, conductivity, proton transfer, concentration and ohmic polarizations need to be solved without resorting to high temperatures.

With respect to the alternative of a direct hydrocarbon-air fuel cell and an indirect, chronologically, the fuel cell development field has gone through a cycle. The early investigators envisaged a direct coal burning fuel cell. When electrochemical problems seemed to be insurmountable the "fuel" became hydrogen and hydrazine, mainly because of the space program's ability to absorb the increased cost. Having successfully developed a hydrogen-oxygen fuel cell, the next step was to use diluted hydrogen mixture--reformates from hydrocarbons or methanol. More recently the field is moving back to such fuels as methane and coal. Considering recent advances in technology it is apparent that a direct hydrocarbon-air fuel cell is feasible. Thus, any fuel cell electrolyte should be compatible with such naturally occurring fuels.

However, it is also recognized that more than one fuel cell system, utilizing more than one fuel, might be warranted from economic and technological grounds as well as theoretical. For example, the theoretical efficiency for the reaction, $C + O_2 \rightarrow CO_2$, is 1.0 at 1000°C, whereas for the reaction, $H_2 + O_2 \rightarrow H_2O$, the efficiency is 0.71, suggesting a high temperature coal burning fuel

cell. On the other hand, in the foreseeable future relatively cheap hydrogen will probably become available suggesting a low temperature hydrogen burning fuel cell. It is obvious that the same electrolyte would not serve in both fuel cells.

It is concluded from this survey that some of the concepts that have influenced and guided fuel cell research in the past are of questionable authenticity. For example, one of the precepts in classical fuel cell science regarding the nature of the electrolyte was that it should be invariant. That is, the electrolyte should not change in chemical composition or chemical structure as the fuel cell reaction proceeded. We can no longer regard this concept as generally valid. The most suitable electrolyte for the low temperature cell is now phosphoric acid. The reason that phosphoric acid is successfully used up to 200°C is due to the fact that it varies in structure as the temperature increases and the solution becomes more concentrated. The cell operating at 100°C at a concentration of 85% is essentially orthophosphoric acid, while a concentration of 105% (the concentration stable at 200°C and 20 mm pressure) contains orthophosphoric, pyrophosphoric, and tripolyphosphoric acid. The variation, and subsequent stability, of the phosphoric acid system at elevated temperature furnishes the basis for its employment as a fuel cell electrolyte. A second case in point deals with the involvement of the electrolyte in electro-catalytic reactions. There has been some consideration of anion adsorption but the significant differences in rates of electro-

catalysis in different electrolytes and the involvement of the electrolyte in homogeneous as well as heterogeneous reactions has been ignored.

Specific Conclusions

Viewing the area of low temperature electrolytes broadly, it is necessary to consider alkaline, neutral, and acidic systems. Protons, hydroxyl ions, or oxide ions are required in the stoichiometry of the fuel cell reaction so neutral electrolytes are not suitable. Further, their ionic conductances are too low. From an electrochemical standpoint, alkaline systems are adequate but carbonation presents formidable engineering and design problems. For these reasons, an acid low temperature fuel cell electrolyte system is indicated.

The required strength of the acid has not been specified in a quantitative way except from the property of yielding a sufficiently conducting solution. Hydrofluoric acid is a weak acid and appears to be adequate. The very strong acids, so-called super acids, are not stable in the presence of water. It is evident that a number of inorganic and organic acids have sufficient acid strength. It would appear that the most useful acid concept is the Arrhenius acid concept. Or, the acid is required to be essentially a supplier of protons to provide ionic conduction and prevent concentration polarization.

In acid electrolyte systems corrosion can be quite severe at elevated temperatures. From the results of past investigations it appears that there are suitable materials such as graphite, tantalum coated metals, special alloys, silicon carbide or other refractories that are quite resistant and can provide construction materials for containers, matrices, and electrode supports. One question that has not been answered satisfactorily deals with the influence of trace quantities of corrosion products containing Fe, Ni, and Cu on the electrocatalytic surfaces.

Having elected for an acid system in preference to an alkaline or neutral salt aqueous system the choice must be made between an inorganic or organic system. The inorganic acid electrolytes have been thoroughly tested during the last two decades. With the exception of low temperature methanol cells, with which sulfuric acid is the preferred electrolyte, of the inorganic acids, phosphoric acid has exhibited the most suitable properties. The latter are due mainly to the high temperature stability of the phosphoric acid systems as explained by the equilibrium diagram cited above. The limitations of phosphoric acid are electrochemical in nature and are made evident in its inability to support reasonable current densities for hydrocarbon oxidation. The basis for this inability is not known but it may be due to unfavorable adsorption characteristics of the electrode in phosphoric acid. It was because of the deficiencies in the performance of phosphoric acid fuel cells

that attention turned to organic acid electrolytes.

It has been definitely established that the current density supported by a platinum electrode during the electrooxidation of hydrogen or propane is influenced by the electrolyte among acid electrolytes. This effect is not a marginal one but the observed current densities may vary by one or two orders of magnitude. Appreciably higher current densities have been observed for the electrooxidation of hydrogen and low molecular weight hydrocarbons in organic sulfonic acids. This result has been reported by several laboratories working at different temperatures and different electrode systems. The result has been reported for sulfonic acids and fluorinated sulfonic acids. It has also been established that the open circuit potential for the electroreduction of oxygen is higher in the fluorinated sulfonic acid by 100 - 200 mv over that in phosphoric acid. This result has been seen in several laboratories and when fuel cells were assembled with the fluorosulfonic acid electrolyte the open circuit voltage was 0.1 - 0.2 v higher than a comparable cell assembled with phosphoric acid (same hardware, same matrices, etc.). Or whenever a direct comparison was made between the organic fluorosulfonic acid system and the phosphoric acid system the organic fluorosulfonic acid system offered a substantial improvement. The improvement was such that a cell operating in the organic fluorosulfonic acid at 60°C would give an improved performance over a phosphoric acid cell at 150°C. This is especially important because the high temperature platinum sintering problem becomes critical above 150°C.

Thus, there are strong arguments for turning to organic sulfonic acids as alternate electrolytes. It is not clear at this point which organic sulfonic acid should be selected as an alternate low temperature acid fuel cell electrolyte. Most of the promising electrochemical results have been obtained with trifluoromethanesulfonic acid and its monohydrate. The shortcomings of this compound are not electrochemical but in terms of physical properties such as vapor pressure and surface tension. Conflicting results have been reported with methane sulfonic acid. This might stem from samples of different purity used by different investigators. This is a recurring problem in fuel cell electrolyte work. It was cited in connection with phosphoric acid above and it is now known that the only negative electrochemical results obtained with trifluoromethanesulfonic acid monohydrate were caused by an impure material. It would be, of course, desirable to work with a simple compound such as methane sulfonic acid if the compound possessed suitable physical properties. Alternatively, disulfonic and trisulfonic acids are under investigation with the thought that the higher molecular weight would provide greater chemical stability and improved physical properties. Therefore, the main objective of future work in this field is to provide the scientific basis for the selection of the most suitable organic sulfonic acid as an electrolyte alternative to the inorganic acids: sulfuric, phosphoric and hydrofluoric.

Direction of Future Effort

The development of the scientific basis on which the proper selection of an improved organic sulfonic acid electrolyte can be made, involves providing answers to questions, in the following specific categories:

1. Electrochemical behavior

- the investigation of methane sulfonic acid and its water solutions with respect to the electrooxidation of hydrogen and propane
- the investigation of partially fluorinated sulfonic acids to learn of the possibility of improved electrochemical properties from substitution
- the investigation of higher homologs of the sulfonic acids to learn if the improved electrochemical properties can be maintained with higher molecular weight
- the investigation of the oxygen electrode to learn specifically the reason for the 150 mv gain in open circuit potential in trifluoromethanesulfonic acid monohydrate.

2. Conductance mechanism

to learn if, in the organic sulfonic acid system, RSO_3^-H^+ , sufficient H^+ mobility is provided in the anhydrous compound to support reasonable current densities or is the hydrated proton required.

3. Adsorption mechanisms

the investigation of the manner in which the RSO_3^- anion is adsorbed in comparison to the $\text{PO}_4^{=}$ anion. Is this adsorption displaced to a higher potential or is there less gross adsorption?

the investigation of the effect of trace quantities of corrosion products on the electrocatalytic reaction to establish the tolerable corrosion rate of materials of construction.

4. Chemical stability

the investigation of the desulfonation of organic sulfonic acids and learning the upper temperature and potential limit for stability

the investigation of the homogeneous reaction of the sulfonic acid group with propane at elevated temperature

the investigation of the upper potential at which the $-\text{COOH}$ group is stable in the presence or absence of an $-\text{SO}_3\text{H}$ group in the molecule.

5. Vapor pressure

the analysis of the vapor distilling from trifluoromethanesulfonic monohydrate solutions in the temperature range of $100 - 200^\circ\text{C}$ to learn if free acid is present in the vapor.

6. Surface activity

to measure contact angles of organic sulfonic acids, fluorinated and unfluorinated, on Teflon to establish the wetting behavior of electrolytes on Teflon-bonded fuel cell electrodes.

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