FUEL CELL ELECTROLYTE FOR PORTABLE ELECTRICAL GENERATING EQUIPMENT

Final Technical Report

F. Walsh and K. Ayers
August, 1982

to

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

Prepared by

ECO
228 Main Street
P.O. Box 578
Buzzards Bay, MA 02532

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1.0 Summary

The goal of the Phase I research program was to produce a substitute electrolyte for phosphoric acid in primary fuel cells with the necessary physical, chemical and electrochemical stability to operate from room temperature to 150°C. This goal was successfully met and exceeded with a perfluorinated acid (hexafluorobutane tetrasulfonic) produced which operates over the temperature range of at least 0°C to 150°C in hydrogen-oxygen fuel cells. In addition, ECO prepared a second perfluorinated acid (hexafluoro-2,3-butene disulfonic acid) which appears to have similar properties. The use of these new electrolytes in primary fuel cells is expected to significantly reduce start-up time, extend operational temperature range, and to minimize problems related to CO-poisoned fuels.

During Phase I, hexafluorobutane tetrasulfonic acid (liFBTSA) was shown to have:

1. ionic conductivity equal to phosphoric acid;
2. thermal stability as a liquid between a minimum temperature range of -20°C and 150°C;
3. electrochemical stability between 0 - 1.0 V vs DHE;
4. very low vapor pressure at elevated temperatures;
5. non-corrosive to most fuel cell components;
6. high rates of electrooxidation of hydrogen and high rates of electroreduction of oxygen, especially at low (0° - 65°C) temperatures;
7. a high contact angle on TeflonR (does not wet); and
8. good solvent for reactants and products.

Further work is needed to develop data on the electrochemical performance of fuel cells using this acid in cell start-up and cycling tests, in cell freezing tests, in cell life tests, and in cell tests using hydrocarbon or CO-poisoned fuels for extended
periods of time.

1.1 Program Objective

The objective of the Phase I research effort was to synthesize and generally characterize a new perfluorinated sulfonic acid that would combine the chemical and physical stability of phosphoric acid with the desirable electrochemical properties at low temperatures found in hydrofluoric or sulfuric acids.

This objective has been the goal of a number of researchers\textsuperscript{1-7} and was most nearly achieved in 1980 by ECO under MERADCOM Contract No. DAAK 70-79-C-0165.\textsuperscript{7} The eight desired properties\textsuperscript{3} of the ideal electrolyte are:

1. good ionic conductivity;
2. thermal stability to 180°C;
3. electrochemical stability between 0 - 1.0 V vs RHE;
4. low vapor pressure and high viscosity;
5. non-corrosive to fuel cell components;
6. supports high rates of electrooxidation of hydrogen and propane and high rates of electroreduction of air and oxygen;
7. sufficient surface tension so as not to wet Teflon\textsuperscript{R}; and
8. good solvent for reactants and products.

The perfluorinated sulfonic acid prepared and tested under the Phase I program meets all of these desired properties.

1.2 Technical Approach

The Phase I research program was by necessity (due to its short duration and low funding level) only an initial evaluation program. Tests were carried out which provided the maximum
amount of information with a minimum of expense or effort. In-house fuel cells and commercial electrodes were relied on even though they did not necessarily provide an optimum picture of the performance characteristics of the new electrolytes. No efforts were made to optimize any systems or to completely purify the new electrolyte. Reference data for comparison purposes as well as testing facilities used were available from a previous program (MERADCOM Contract No. DAAK 70-79-C-0165) and only minimum effort was made to expand upon these sources of data and test systems. All the experimental data obtained were based on at least two separate but identical tests to ensure reliable data. The physical and chemical parameters examined included conductivity, melting point, contact angle on Teflon, acid strength, vapor pressure, cyclic voltammetry, and chemical composition by IR, NMR (proton and fluorine), MS and mass composition. Following this physical and chemical evaluation, half-cell tests using the acid as the electrolyte were carried out over the temperature range of 0° - 95°C and IR-free polarization data obtained. Test apparatus and procedures are summarized in Section 2.

1.3 Reported Electrolyte Characteristics

In 1974, Adams and Barger identified the perfluoroalkane sulfonic acids as superior fuel cell electrolytes; these acids have theoretically high acid strength and ionic conductivity. Until 1981, the only commercially available member of this family was the simplest member, trifluoromethane sulfonic acid (TFMSA; CF₃SO₃H⋅H₂O). Tests on this acid demonstrated relatively rapid electrochemical oxidation of fuels at modest temperatures (135°C). Unfortunately, in this case, the simplest acid is not optimum for primary fuel cell application, TFMSA has a high vapor pressure (the monohydrate has a vapor pressure of 25 mm Hg/125°C) and wets Teflon R.
MERADCOM has sponsored an extensive screening program of organic acids for their potential use as fuel cell electrolytes. These screening programs included commercially available aromatic polycarboxylic acids, perfluoroaliphatic carboxylic acids, sulfonic acids, and substituted aliphatic sulfonic acids. However, all of these potential electrolytes have some physical or chemical property (vapor pressure, thermal stability, contact angle on Teflon\textsuperscript{R}) which restricts their use as fuel cell electrolytes. Only tetrafluoroethane disulfonic acid (TFEDSA), sold commercially by ECO, meets all the desired electrochemical and physical properties, including vapor pressure (0.05 mm Hg/125\textdegree C) but it suffers from a melting point of 65\textdegree C which restricts low temperature fuel cell operation.

1.4 New Electrolytes

A substitute electrolyte for phosphoric acid with the necessary physical, thermal, chemical and electrochemical stability to operate from room temperature (or lower) to 150\textdegree C would significantly expand the potential number of useful applications of the primary fuel cell. The theoretically most interesting acids, the perfluoroalkane sulfonic acids, are extremely difficult to synthesize and have been, with the exceptions of TFMSA and TFEDSA, not commercially available. A longer chain perfluorosulfonic acid would be the preferred electrolyte because it would have all the desirable electrochemical characteristics of TFMSA and TFEDSA, along with the required lower vapor pressure. Under this Phase I research program, ECO has prepared such an acid with the synthetic protocol presented in Section 3.

2.0 Experimental Procedures and Apparatus

2.1 Fuel Cell Electrodes

Fuel cell performance was measured on commercial electrodes. No attempt was made to optimize electrode structure for
the physical properties of a given electrolyte.

The electrode chosen was purchased from Prototech, Inc. (Newton Highlands, MA); this electrode (RA-2) is a thin (0.35 mm) carbon board which is platinum catalyzed (0.33 mg Pt/cm$^2$) on one side and Teflon wet-proofed on the other. Circular test electrodes were cut from 4" x 4" RA-2 electrode sheets using a metal punch. The geometric area of the test electrode exposed to the electrolyte was 5.06 cm$^2$.

2.2 **ECO Half-Cell**

The electrochemical properties of the perfluorinated organic acids were obtained using electrodes secured in the electrode holder shown in Figure 1. These holders are milled from blocks of heat-treated Teflon$^R$. The holder is plumbed to permit gas flow behind the electrode, and utilizes gold wires for electrical contact on the back of the test electrode. The half-cell counter electrode consists of a platinum flag (5 cm$^2$) with a platinum wire lead. The dynamic hydrogen reference electrode$^8$ is composed of two 1 cm$^2$ platinum flags held in a quartz tube, the end of which is drawn out to a capillary.

Figure 2 is a diagram of the half-cell in the working mode. The half-cell rested on a hot plate and the temperature was monitored by a Teflon$^R$-tipped thermometer immersed directly in the electrolyte.

2.3 **Cyclic Voltammetry**

The cell used for this experiment was a quartz container with an approximate electrolyte volume of 10 ml. The working and counter electrodes were smooth platinum flags, each with an area of 0.5 cm$^2$. The reference electrode followed the dynamic hydrogen electrode design of Giner$^8$. The cell was allowed sufficient time to
FIGURE 1. Electrode Holder
achieve thermal equilibrium and to be purged of dissolved oxygen by bubbling nitrogen into the electrolyte before cyclic voltammetry was carried out.

2.4 Physical Characterization

The specific conductance of the acid was measured using a YSI Model 31 conductivity bridge at temperatures ranging from 20°C to 120°C.

Contact angle measurements were performed at room temperature and atmospheric pressure, with no provisions made for humidifying the electrolyte, using a Gaertner M101 telescope with a M205 protractor eyepiece. The acid was placed on a flat piece of Teflon® and contact angle measured; the goniometer apparatus was precalibrated using a variety of organic solvents and by comparing contact angle results with those of Fox and Zisman⁹.

Acid strength determinations were made by titrating a 0.1 M solution of the acid with 0.1 M NaOH at room temperature.

Vapor pressure determinations were obtained using a Welch vacuum pump, Model 1400, and a Lab Glass, Inc. (Vineland, NJ) No. 8731 McLeod Gauge. Temperature was maintained by using a Glas-Col Apparatus Company (Terre Haute, IN) heating mantle controlled by a variable autotransformer.

2.5 Electronic Apparatus and Gas Systems

An ECO Model 552 potentiostat was employed to obtain the IR-free Tafel slope data. This potentiostat has a built-in IR-compensation circuit to overcome ohmic drop across the cell. During steady state periods, the cell voltages were maintained to ± 0.001 V by a Heathkit Model IP-18 power supply.
Cyclic voltammogram results were obtained with an ECO Model 552 potentiostat and an ECO Model 567 function generator. Chart recordings were acquired on a Hewlett Packard Model 704A X-7 recorder.

The hydrogen, oxygen and nitrogen used were 99.995% purity and were obtained from Taunton Oxygen Supply Co. (Taunton, MA). All plumbing was either copper, brass or Teflon®. Unless otherwise noted, gases were used without humidification.

3.0 Chemical Preparation Techniques

3.1 Reference Electrolytes

The three reference acids used were phosphoric acid (H₃PO₄), trifluoromethane sulfonic acid (TFMSA; CF₃SO₃H•H₂O) and tetrafluoroethane disulfonic acid [TFEDSA; C₂F₄(SO₃H•H₂O)₂]. Prior to testing, the phosphoric acid and the TFEDSA were treated with hydrogen peroxide at 110°C for twelve hours and then held for eight hours at -2.0 V vs DHE. Data on TFMSA was taken from the literature¹-³.

3.2 Preparation of Hexafluorobutane Tetrasulfonic Acid

The synthesis route for hexafluorobutane tetrasulfonic acid [HFBTSA; C₄F₆(SO₃H•H₂O)₄] used by ECO followed the route previously used by ECO to produce TFEDSA. The starting material, hexafluoro-1,3-butadiene (C₄F₆), obtained from PCR Research Chemicals, was reacted with eight molar equivalents of dimethyl sulfide [(CH₃S)₂; Aldrich Chemical Co.] in the presence of a catalytic amount of iodine. The reaction was carried out in a pressurized steel bomb; the bomb was heated for 48 hours at 250°C with maximum pressure of 700 psi observed. The bomb was cooled and vented; the liquid remaining was distilled under nitrogen. Two high boiling fractions (125°C ± 5°C and 135°C ± 5°C)
were obtained and characterized by IR, MS, proton-NMR and F-NMR. The higher boiling fraction was characterized as being the fully-substituted tetramethyl sulfide $\left[ C_4F_6(CH_3S)_4 \right]$. 

The tetramethyl sulfide (10 g) was heated to 100°C and two molar equivalents of 40% peracetic acid (43 g) were added dropwise; the reaction mixture was then held at reflux (105°C) for twelve hours. Following cooling, the aqueous liquid was extracted three times with ether and the ether fractions pooled. The ether was removed under vacuum and the resulting brown liquid was characterized by proton-NMR, IR and MS. IR spectroscopy showed removal of the methyl sulfide absorbance peak (1510 cm\(^{-1}\)) and the presence of sulphone absorbance peaks (1120 and 1320 cm\(^{-1}\)).

The tetrasulphone was then further oxidized with aqueous potassium permanganate (KMnO\(_4\); 18% sol.) under pressure (40 psi) at 150°C for 6 hours. The resulting potassium salt of the tetrasulfonic acid was acidified using an ion exchange resin (Dowex 50) and the aqueous acid concentrated under vacuum. The acid was heated at 150°C for 12 hours, refluxed at 105°C with a three-fold weight equivalent of 30% hydrogen peroxide for 12 hours, treated with activated carbon (Norite) and barium hydroxide, held for eight hours at -2 V vs DHE, treated again with barium hydroxide, Dowex 50 resin and Norite, and finally concentrated under vacuum to remove water. The resulting acid was characterized by IR, MS, proton-NMR, F-NMR and mass composition analysis (as the sodium salt) to be the desired hexafluorobutane tetrasulfonic acid (HFBTSA).

3.3 Preparation of Hexafluoro-2,3-butene Disulfonic Acid

The lower boiling $(125^\circ \pm 5^\circ C)$ product of the reaction between hexafluoro-1,3-butadiene and dimethyl sulfide was also oxidized to the disulfonic acid using first peracetic acid and then
potassium permanganate as described in Section 3.2. Purification of this disulfonic acid was carried out following the procedure previously described and the resulting acid was characterized by IR, MS, and proton-NMR. The results obtained were not inconsistent with characterization of the product as a mixture of HFBTSA and hexafluoro-1,3-butene disulfonic acid (HFBDSA).

3.4 Characterization of HFBTSA

Characterization of HFBTSA was carried out based on IR, MS, H-NMR, F-NMR and mass composition analysis. IR showed two broad bands (2000 to 1500 cm\(^{-1}\) and 1400 to 1200 cm\(^{-1}\)); H-NMR showed a broad singlet at 3.8 ppm. F-NMR showed two singlets spaced approximately the same distance as for the tetramethyl sulfide. Conventional MS did not show any peaks at a mass greater than 110. Mass composition analysis provided the most positive chemical characterization results with observed percentage composition ratios of the sodium salt close to predicted values (Table 1).

4.0 Electrolyte Evaluation

4.1 \(\text{H}_3\text{PO}_4\) Performance

Phosphoric acid fuel cells operate best at temperatures above 150\(^{\circ}\)C. This makes rapid start-up from cold conditions difficult to achieve. Phosphoric acid fuel cells also require a synthetic source of hydrogen. The reformer to make hydrogen constitutes a large percentage of total fuel cell cost and weight. The more pure the hydrogen required by the fuel cell, the more complex the system becomes.

4.2 TFMSA and TFEDSA

Adams and Barger\(^3\) identified the perfluoroalkane sulfonic
Table 1
Elemental Composition Analysis of HFBTSA

Compound: C$_4$F$_6$Na$_4$O$_{12}$S$_4$
MW: 574.032

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<tr>
<th></th>
<th>Predicted*</th>
<th>Observed</th>
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<tr>
<td>% C</td>
<td>8.37</td>
<td>10.14</td>
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<tr>
<td>% Na</td>
<td>16.02</td>
<td>18.28</td>
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<tr>
<td>% S</td>
<td>22.30</td>
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<tr>
<td>C/Na</td>
<td>1/1.91</td>
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<td>Na/S</td>
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* Based on ratio of atomic weights
acids as a promising family of compounds. The simplest acid, trifluoromethane sulfonic acid (TFMSA) has since been studied in great depth, primarily because it is commercially available. The positive results are as follows:

a) TFMSA monohydrate\(^6\) is superior to phosphoric acid for both the electrooxidation of hydrogen and the electro-reduction of air.

b) No indication of anion adsorption on a platinum electro-catalyst has been detected during anodic charging currents.

c) The measured open circuit voltage at 55\(^\circ\), 95\(^\circ\) and 115\(^\circ\)C are well within\(^8\) the limits of accuracy expected for a clean electrode surface. Apparently there is no anion adsorption on the electrode.

d) With 10\% CO, a concentration far greater than produced in a modern reformer, anode performance in the monohydrate\(^10\) is four times greater than pure hydrogen performance in phosphoric acid.

These very positive results are unfortunately balanced by two properties that make TFMSA not very useful in practical fuel cells: TFMSA has relatively high vapor pressure and wets\(^5\) Teflon\(^R\).

In 1981, ECO synthesized\(^11\), in quantity, tetrafluoromethane disulfonic acid (TFEDSA). This strong acid is very similar to TFMSA except that it has 1/500 the vapor pressure and the dihydrate does not wet Teflon\(^R\). Unfortunately, while the vapor pressure is a significant improvement over TFMSA (0.05 mm Hg @ 125\(^\circ\)C vs 25 mm Hg @ 125\(^\circ\)C for TFMSA), it is still too high for use in fuel cells for high temperature applications. The freezing point of TFEDSA is 65\(^\circ\)C which limits low temperature fuel cell
operation. The fuel cell performance of TFEDSA at 95°C is shown with that of phosphoric acid in Figure 3. On the basis of this superior performance, ECO proposed the Phase I research program: HFBTSA, as a larger organic molecule, was suspected as having a wider liquid temperature range and a lower vapor pressure.

4.3 Characteristics of Hexafluorobutane Tetrasulfonic Acid

4.3.1 Physical Properties

The physical properties of HFBTSA were measured and compared with those of TFMSA and TFEDSA (Table 2). These results show HFBTSA to have the desired wide temperature range as a liquid without significant sacrifices in specific conductance.

4.3.2 Conductivity Tests

HFBTSA is as conductive as 85% phosphoric acid. The actual conductivity measurements are shown in Table 3. The HFBTSA used had a low water content (less than 2% w/w). It did not fume at 150°C and the conductivity measured on cooling reproduced the conductivity measured on heating.

4.3.3 Contact Angle Measurements

HFBTSA does not wet Teflon®. The contact angle for HFBTSA is 98.75°. The contact angle for Malinckrodt 85% orthophosphoric acid under identical conditions is 114.0°. This large difference in contact angles suggests that electrodes optimized for use in phosphoric acid should not be optimum with HFBTSA; the importance of this difference was not investigated in the Phase I program.

4.3.4 Acid Strength of HFBTSA

Monoprotic strong acids, such as HCl, HNO₃ and HClO₄, all
FIGURE 3. Comparison of the Performance of TFEDSA with Phosphoric Acid
### Table 2

**Physical Properties**

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<th>TFMSA</th>
<th>TFEDSA</th>
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<tr>
<td><strong>Melting Point</strong></td>
<td>34°</td>
<td>65°</td>
<td>liquid to -20°C (probably supercooled)</td>
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<tr>
<td><strong>Contact Angle on Teflon @ 20°C</strong></td>
<td>73°</td>
<td>95°</td>
<td>99°</td>
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<td><strong>Vapor Pressure 125°C, mm Hg</strong></td>
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<td>Temperature °C</td>
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<td>.195</td>
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appear equally strong when dissolved in water because they react quantitatively with water to yield $\text{H}_3\text{O}^+$ in each case. HFBTSA is also a very strong acid but it appears to be quite unusual because, unlike many polyprotic acids, electrostatic effects do not appear to dominate its successive dissociations. The preliminary evidence, shown in Figure 4, suggests that all four sulfonic acid groups react almost quantitatively with water to yield $\text{H}_3\text{O}^+$, at least in 0.1 M HFBTSA at room temperature.

The experiment performed was to titrate a 0.1 M solution of HFBTSA with 0.1 M NaOH. Assuming that the HFBTSA reacts quantitatively with water, it can be shown for pH less than 4,

$$[\text{H}^+] = \frac{(4 - x)}{10(x + 1)} \left(\text{moles} \frac{\text{moles}}{1}\right)$$

where $x =$ number of equivalents of 0.1 M NaOH added to the solution. Figure 4 compares the pH of the solution (measured with a Corning pH meter) with that theoretically obtained for a completely dissociated acid. The data obtained agree well with the theoretical curve.

Future studies using solvents less basic than water (and in which incomplete reaction occurs) are needed to study the dissociation process.

4.3.5 Temperature Range

HFBTSA was observed to remain a liquid over the temperature range -20° to 150°C. At -20°C, HFBTSA probably acts as a super cooled liquid; a second possibility is that the presence of trace amounts of hexafluoro-2,3-butene disulfonic acid (the reaction by-product) may act to lower the freezing point by imposing dissymmetry on the liquid. Because this second acid is an equally strong and chemically stable acid, its presence does not affect electrochemical suitability.
FIGURE 4. Titration of HFBTSA: Complete Dissociation
HFBTSA was shown to be chemically stable at temperatures at least as high as 150°C. Samples of the acid were stressed for extended periods of time in the presence of oxygen with no decomposition observed. Only at cathode potentials not observed in a primary fuel cell (i.e.: over +1.4 V vs DHE) was chemical degradation observed.

4.3.6 Electrochemical Characterization

Cyclic voltammetry on smooth platinum showed voltammograms similar to those found with TFMSA\(^7\). HFBTSA does not show any detrimental reaction over the potential range of +0.1 to +1.5 volts vs DHE (Figure 5). An anodic peak observed at approximately +0.8 V could be the result of an impurity or the formation of platinum oxide; the absence of any additional peaks indicates a relatively high degree of chemical purity of the HFBTSA.

4.3.7 Anode Performance

IR-free anode performance data in HFBTSA were taken using the ECO small volume fuel cell at 65°C. The anode was a Prototech RA-2 electrode; dry hydrogen was the fuel. No significant anode polarization vs DHE was observed in the test range of 0 - 50 mA/cm\(^2\).

4.3.8 Fuel Cell Performance Tests

Half-cell cathode data were taken using a counter electrode evolving oxygen. HFBTSA has outstanding performance, especially from room temperature to 95°C with a slope of about 80 mV/decade. The data provided on cathode performance at temperatures over 65°C are not considered accurate because of the effect of anodic poisons (obtained from operating the half-cell counter electrode at potentials over 1.4 V) on the reference electrode.
HFBTSA
TEMPERATURE: 20°C
SWEEP RATE: 50 mV/sec
GAS: NITROGEN

FIGURE 5. Cyclic Voltamgram in HFBTSA
Shown in Figure 6 is the performance of a commercial cathode in HFBTSA over the electrolyte temperature range of 00 to 95°C. Cathode performance at 00 is significantly (100 mV) better than that with phosphoric acid at 65°C.

ECO half-cell IR-free cathode performance of HFBTSA, compared with TFEDSA and 85% phosphoric acid under similar conditions, are provided in Figure 7. At 65°C, cathodes in HFBTSA operate at over 800 mV (vs DHE) for a load of 100 mA/cm²; use of this electrolyte in primary fuel cells will significantly reduce cell start-up times.

The second acid, a mixture of HFBTSA and hexafluoro-2,3-butene disulfonic acid (HFBDSA) demonstrated performance data equal to or better than those of HFBTSA (Figure 8).

5.0 Conclusions

ECO synthesized HFBTSA and an additional acid as a by-product of the HFBTSA synthesis route. HFBTSA was shown to have all the characteristics of an idealized electrolyte suitable to replace phosphoric acid in direct oxidation fuel cells. Excellent half-cell performance was obtained over a wide range of temperatures, especially temperatures in the range of 0°C to 65°C. HFBTSA exhibits a low vapor pressure and does not wet TeflonR; it is an excellent candidate electrolyte to replace phosphoric acid in fuel cells designed for applications which require short start-up times. Based on results obtained with TFMSA10, use of HFBTSA as the electrolyte may also permit cell operation with hydrogen containing high CO levels. This improvement would permit reduced complexity of the fuel cell system by simplifying reformer requirements.

6.0 Recommendations

ECO recommends that future work be focused on five areas;
FIGURE 6. Effect of Temperature on Cathode Performance in HFPTS-A
FIGURE 7. Cathode Performance in Three Acids at 65°C
FIGURE 8. Cathode Performance in Two Acids at 65°C
namely, synthesis improvements, matrix and electrode development, fuel cell system testing, electrolyte production for Army programs and further electrolyte R & D. These areas will form the basis for a Phase II proposal and are briefly summarized below.

6.1 **Synthesis Improvements**

Under the Phase I program, ECO made no attempt to optimize production yields or chemical purity of HFBTSA. Methods to reduce production costs or estimates of production costs on any scale were not considered. For an electrolyte to be useful, it must be readily produced from commercially available starting materials. While HFBTSA meets these two criteria, further work is required to provide accurate cost data on commercial scale. Safety studies, including bio-hazard evaluation, must also be carried out.

6.2 **Matrix and Electrode Development**

A thin, wetable matrix capable of withstanding high bubble pressures is a key element in any successful fuel cell program. Compatibility with the electrolyte is of critical importance. Research is needed to adapt matrix structures already used in phosphoric acid stacks to perfluorosulfonic acids. While the present matrix structures already show HFBTSA to be superior to phosphoric acid, even better cathode performance may be obtained with electrodes designed for use specifically with HFBTSA.

The Teflon® content and platinum loading of fuel cell electrodes have been optimized for phosphoric acid. Similar studies are needed for HFBTSA. It is highly likely that performance improvements will result from a different Teflon® level, due to the difference in contact angle.

6.3 **Fuel Cell Testing**

Cathodes tested in perfluorosulfonic acids have outstanding
low temperature performance and anodes have demonstrated better tolerance to CO than in phosphoric acid. Research is needed to quantify these benefits for HFBTSA and relate them to Army mission requirements. Effects of duty cycle (repeated start-stop cycles, freezing-thawing cycles, long-term tests) on fuel cell performance must also be evaluated.

6.4 Electrolyte Production

In order to supply the immediate needs of the research community and the eventual needs of hardware programs, the production of HFBTSA must be scaled up from gram to kilogram scale. Research is needed into the means of doing this cheaply and safely. HFBTSA will also be required for direct testing in cells at MERADCOM.

6.5 Electrolyte R & D

All the evidence to this point indicates that perfluorinated organic acids are very useful in improving fuel cell performance. ECO recommends that four novel acids be synthesized and their properties evaluated. These acids are:

1) difluoromethane disulfonic acid
2) octafluorobutane 2,3-disulfonic acid
3) hexafluorobutane 2,2,3,3-tetrasulfonic acid
4) octafluorobutane 1,4-disulfonic acid.

These four acids are chosen to permit evaluation of factors affecting cathode or anode performance, due to the physical or chemical properties of the electrolyte. Each acid proposed should have unique properties due to its chemical structure (molecular weight, C/F ratio, and C/\(\text{SO}_3\text{H}\) ratio) which will affect freezing point, boiling point, vapor pressure and chemical stability. Mixtures of these acids may result in even further improved
electrode performance, provided the mixtures remain chemically constant over the cell life time. The general approach to development of alternative fuel cell electrolytes is provided in Figure 9.

ACKNOWLEDGEMENT

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7.0 References

Fig. 9

General Technical Approach to the Development of an Alternative Fuel Cell Electrolyte