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DISCLAIMER

EVALUATION OF TETRAFLUOROETHANE -1,2- DISULFONIC
ACID AS FUEL CELL ELECTROLYTE

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It has been demonstrated in a number of investigations that the

kinetics of oxygen reduction on Pt are significantly higher in trifluoro-

methane sulfonic acid (TFMSA) solutions than in phosphoric acid (1-3).

These differences appear to be due to the higher oxygen solubility and the

lower specific adsorption of anions in TFMSA (4). However, the further in-

vestigation of TFMSA as a fuel cell electrolyte has revealed the undesirable

physical properties of this material that may limit its usefulness. TFMSA

solutions more concentrated than ca. 7 M have wetting contact angles on

polytetrafluoroethylene (PTFE) surfaces, ionic conductivities lower than

desirable, and high acid vapor pressure (5). The wetting of PTFE

causes loss of the hydrophobic gas-diffusion electrode structure essen-

tial for low transport losses at high current density, and the high vapor

pressure represents a life limitation and/or maintenance problem. Pure

hydrogen-air fuel cells using 6 M TFMSA at 60 C have shown improved per-

formance relative to state-of-the art phosphoric acid fuel cells, but

use with hydrogen containing carbon monoxide at levels above ca. 0.01%

severely poisons the Pt electrode at such a low temperature (6). Use of

less volatile higher homologs of TFMSA was suggested by Baker and co-

workers (7), particularly the dimeric form of TFMSA, tetrafluoroethane

-1,2- disulfonic acid (TFEDSA). The purpose of this communication is

to report some physical properties of TFEDSA relevant to fuel cell use

and preliminary examinations of this electrolyte in fuel cells with hydrogen containing carbon monoxide.

EXPERIMENTAL

Tetrafluoroethane -1,2- disulfonic acid was supplied by KOR (Cambridge, Mass.) as a 50 w/o solution. The acid was purified by repeated vacuum refluxing (200 C) with intermittent peroxide treatment and recrystallization of what was presumed to be the dihydrate, $(CF_2SO_3H \cdot H_2O)_2$; elemental analysis was consistent with this assumption. The purification did not, however, appear to have a significant effect on the physical properties measured here, as equivalent results were obtained with the as- received solutions concentrated by evaporation. Solutions were prepared by weight additions of water to the purified acid hydrate, or by concentration of the as- received solution to a known weight loss. Specific gravity at 25 C was used as an internal standard for concentration measurement. The conductivity of the acid solutions was measured in a thermostatted microconductivity cell (cell constant 0.5 cm^{-1}) using an ac impedance bridge (Wayne-Kerr). The vapor pressure of the acid solutions was measured using the isoteniscope technique (8). The properties of the acid as a fuel cell electrolyte were observed using a small (1 cm^2 active area) free electrolyte cell (1.5 ml) fabricated out of PTFE with phosphoric acid fuel cell standard supported Pt catalyst fabricated into PTFE-bonded fuel cell type electrodes (9). PTFE capillary tubing connected the cell to an external hydrogen electrode in the same electrolyte (all potentials are referenced to this RHE). The Pt loading on both electrodes was 0.25 mg/cm^2. The PTFE content of the hydrogen electrode was fixed at 25 w/o, with a curing temperature 20-30 C below the melting point of

TFE-30B (327 C). Optimum results were obtained for the oxygen electrode using slightly higher PTFE content with a curing temperature of 320 C. A hydrogen - carbon dioxide - carbon monoxide mixture of calibrated composition 80 H_2:19 CO_2:1 CO was purchased from Matheson, and diluted with an 80 H_2:20 CO_2 calibrated mixture (Matheson Ultra-Pure Grade) to produce mixtures containing 0.1 % CO and 0.01% CO. The composition of the dilution gasses was checked on a mass spectrometer using the calibrated mixture as standard. The accuracy of the CO content was estimated to be ±0.05% and ±0.005%, respectively. Fuel cell polarization data were obtained using a PAR 173D Potentiostat, usually in the controlled-current mode, with IR- corrections by current interception using a mercury-wetted relay.

RESULTS

The vapor pressure data are shown in Fig. 1. For intermediate temperatures of 80-160 C, the vapor over the acids was water with no detectable acid content. Vapor pressure data for pure H_2O (10), and 85 and 98 w/o H_3PO_4 solutions (11) are added for references purposes. Practical fuel cell experience indicates that H_2O vapor pressures greater than ca. 200 torr create a problem in water balance in the cell. Most of the water in an acid fuel cell is carried out by the air stream, and the cathode polarization is reduced by use of more than stoichiometric air flow (12). Simple material balances indicate vapor pressures more than ca. 200 torr require air flows close to stoichiometric resulting in a polarization penalty. TFEDSA solutions of 60-70 w/o have water vapor pressures comparable to 85 w/o H_3PO_4, which is ca. 200 torr at 100-110 C. For use at higher temperature, both TFEDSA and H_3PO_4 must become

considerably more concentrated to be in equilibrium with H_2O vapor at 200 torr. At 170 C, for example, the H_3PO_4 concentration would be about 98 w/o, while for TFEDSA the concentration would be about 88-90 w/o, which is nominally the composition of the hydrate of the acid.

Quantitative measurements of contact angle have not yet been made. However, less precise observations of the wetting of cleaved PTFE surfaces were made for 70-85 w/o TFEDSA electrolyte at 100 C. The contact angles appeared to be greater than 90°, indicative that a hydrophobic structure would be obtained with these electrolytes in a PTFE-bonded electrode.

The conductivity data is shown in Fig. 2. As expected, solutions more concentrated that 40 w/o are on the descending side of the conductivity - concentration curve. At an equivalent normality of 6 N and at 80 C, TFEDSA appears to have about the same conductivity (ca. 0.4 $\Omega^{-1}cm^{-1}$) as TFMSA (5). The conductivity of these acids at 6 N is significantly higher than that for 6 M H_3PO_4 (11), which might be expected from the stronger acidity. However, H_3PO_4 exhibits the unusual and desirable property that the conductivity remains high even in extremely concentrated form, e.g. the conductivity of 98 w/o H_3PO_4 at 170 C is 0.6 $\Omega^{-1}cm^{-1}$. That is not the case with either TFMSA or TFEDSA solutions, as the data in Fig. 2 shows clearly. The tie-line drawn in Fig. 2 represents (approximately) the concentration and conductivity of acid in equilibrium with H_2O vapor at 200 torr in the temperature range of 90-170 C. In comparison to H_3PO_4 solutions, comparable or superior conductivity is observed only for 60-70 w/o at 100-110 C. At 170 C, the conductivity of TFEDSA in equilibrium with 200 torr H_2O vapor is only 0.12 $\Omega^{-1}cm^{-1}$, a factor

of <u>five</u> lower than in 98 w/o H_3PO_4 at this temperature. The technological consequences of this lower conductivity are severe. In a full-scale H_3PO_4 fuel cell, the internal resistance losses due to resistance in the electrolyte matrix are ca. 40 mV at rated load (13); increasing this by a factor of five by substitution of TFEDSA would mean the non-Ohmic polarization would have to be reduced by about 200 mV just to break even (!). Laboratory fuel cell tests have confirmed that optimum results were obtained when this electrolyte was used at the lower temperatures of 100-110 C.

Fuel cell cathode polarization in 70 w/o TFEDSA is shown in Fig. 3, relative to the polarization observed with similar cathodes in TFMSA and H_3PO_4 electrolyte. The curves are on an IR-free basis, but all three electrolytes have about the same conductivity at the conditions shown (ca. 0.3 $\Omega^{-1}cm^{-1}$). The polarization behavior in TFEDSA was intermediate between that for 85 w/o H_3PO_4 and that for 60 w/o TFMSA. Anode polarization in the simulated reformed hydrocarbon fuels are summarized in Table 1. CO poisoning of 0.25 mg Pt/cm^2 anodes is severe at 70 C in TFMSA even with CO levels as low as 0.01%. Raising the temperature 40 C had an enormous effect on polarization, as would be expected from the CO adsorption isotherms reported by Stonehart and Ross (14). The polarization of 20 mV in TFEDSA at 110 C on 0.1% CO is about the same as in 98 w/o H_3PO_4 at 170 C on 2% CO with the same electrode. In the case of methanol as fuel, CO levels as low as 0.1% can be achieved using a combination of thermal cracking and low temperature shift conversion (15). These results indicate that it should be possible to operate a reformed methanol fuel cell with 70% TFEDSA at 110 C and

achieve 0.63-0.64 V per cell at 200 mA/cm^2 with 0.75 mg Pt/cm^2 of catalyst. This performance level is ca. 30 mV better than what is observed with H_3PO_4 at the same temperature, but is about the same as what is observed with H_3PO_4 at 170-180 C.

There has been some controversy in the literature (16) over the stability of TFMSA and its possible reduction at Pt electrodes at the reversible hydrogen potential. We have examined this problem ourselves both for TFEMSA and TFEDSA, and our findings are in agreement with the comments of Adams and Foley (16). An impurity in TFMSA appears to be the source of sulfur produced at a hydrogen electrode in unpurified acid; the impurity is probably SO_3. Early samples of TFEDSA from KOR were badly contaminated with sulfur oxides (and possibly CS_2); but improvements in the synthesis eliminated these impurities for the most part. Purified forms of either TFMSA or TFEDSA showed no chemical instability in the fuel cell tests in this laboratory.

The conclusions of our study of TFEDSA as a fuel cell electrolyte is that it offers no advantage over H_3PO_4 in applications where systems considerations favor higher (>150 C) temperature operation, but it does have an advantage over H_3PO_4 in a lower temperature system.

ACKNOWLEDGMENT

FIGURE CAPTIONS

1. Vapor pressure of water over TFEDSA solutions.

2. Conductivity of TFEDSA solutions as a function of concentration and temperature. Tie represents the acid in equilibrium with 200 torr H_2O vapor over the range 90-170 C.

3. Oxygen electrode polarization curves (IR corrected) in H_3PO_4, TFMSA and TFEDSA.

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Table 1. Polarization[†] Relative to Pure Hydrogen for 80 H_2: 20 CO_2
          Mixtures Containing Various Levels of CO.

	CO Level (vol. %)			
	1%	0.1%	0.01%	No CO
TFMSA (70 C)	>300	>300	345	5
TFEDSA (110 C)	60	20	10	5

[†] in mV at 200 mA/cm^2 and low utilization of hydrogen

Fig. 1

XBL 927-7109
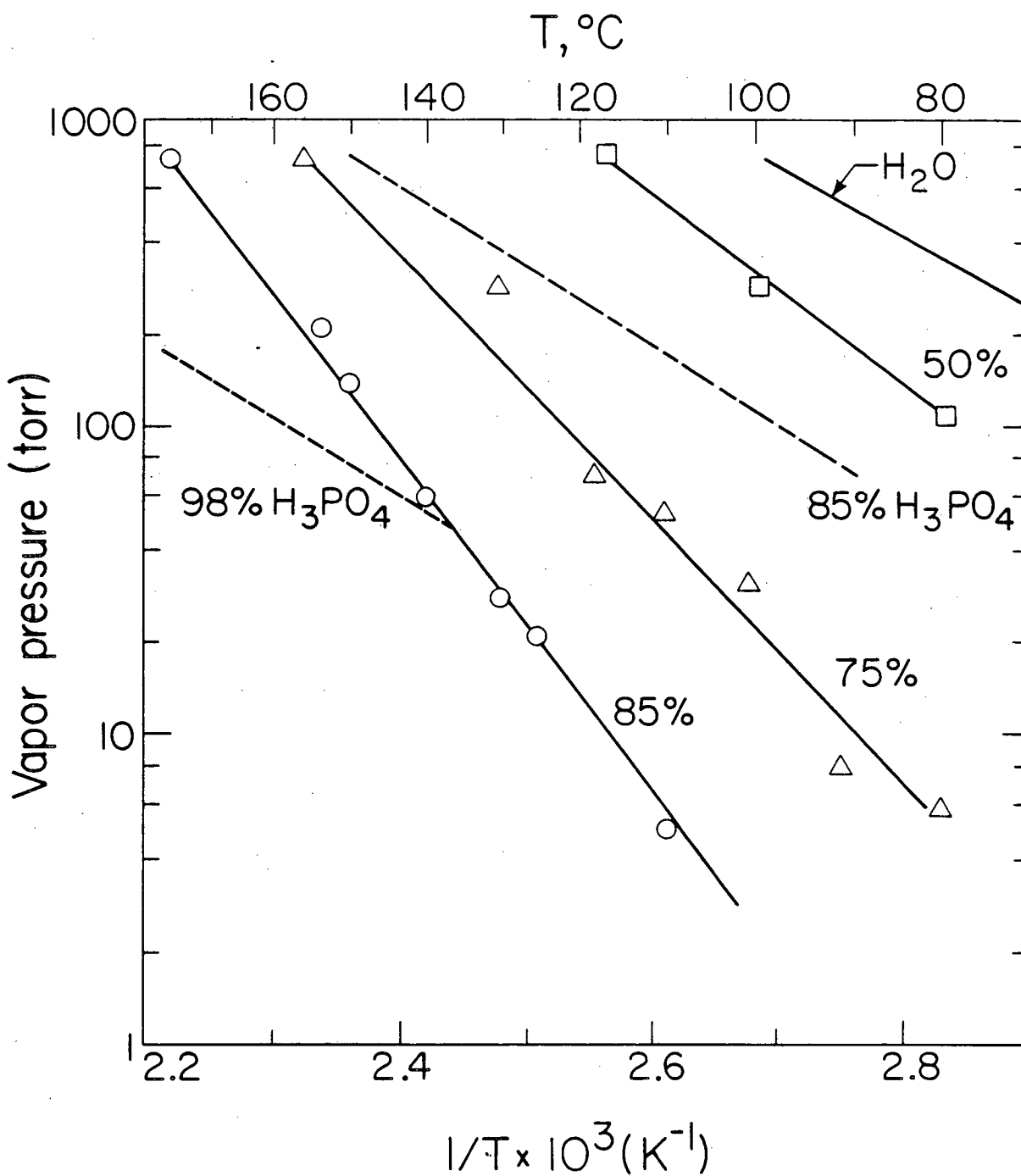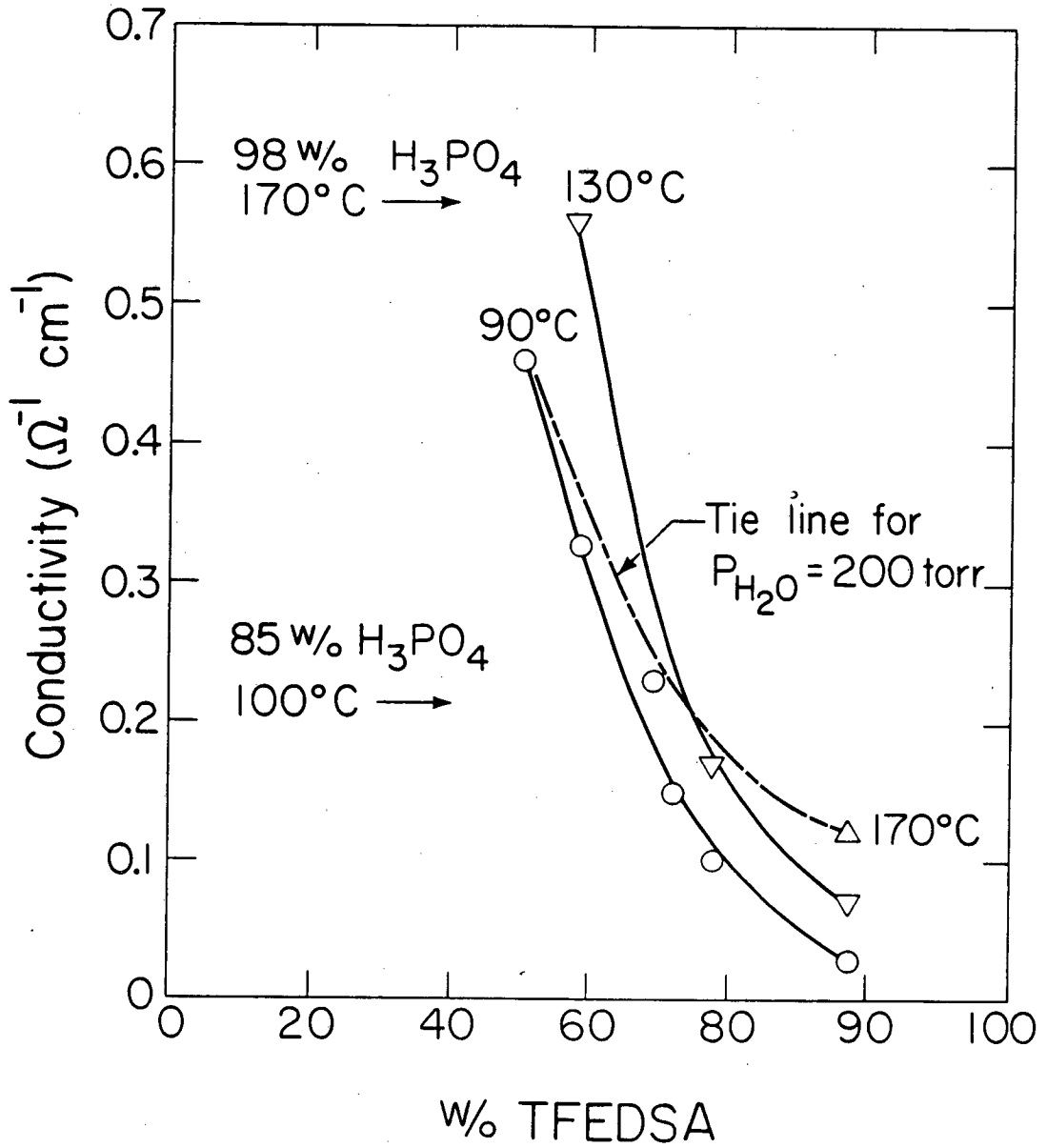
Fig. 2

XBL 827-7108

Fig. 3

XBL 827-7110