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Report No. 1

Research on Electrochemical Energy Conversion Systems

Interim Technical Report

By

R.T. Foley and A.A. Adams

JULY 1972

To

U.S. Army Mobility

Equipment and Development Center

Fort Belvoir, Virginia

Prepared by

The American University
Washington, D.C.

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The utilization of organic electrolytes such as γ-butyrolactone solutions of lithium perchlorate appears feasible on a qualitative basis from some preliminary experiments on the anodic oxidation of propane. This phase of the project is being suspended in favor of other more promising approaches.

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SUMMARY

The research on electrochemical energy conversion systems has involved work on two tasks: the corrosion characteristics of electrolytes for intermediate-temperature hydrocarbon-air fuel cells, and the feasibility of using organic electrolytes in fuel cells.

The investigation of the corrosion characteristics of fuel-cell electrolytes has considered materials of construction for use in phosphoric acid electrolytes as well as electrolytes alternative to phosphoric acid. Tantalum coatings are being studied for use in phosphoric acid and polyphosphates are being considered as suitable electrolytes without the corrosivity of phosphoric acid.

The utilization of organic electrolytes such as γ-butyrolactone solutions of lithium perchlorate appears feasible on a qualitative basis from some preliminary experiments on the anodic oxidation of propane. This phase of the project is being suspended in favor of other more promising approaches.

FOREWORD

This research on electrochemical energy conversion systems has been sponsored by the U.S. Army Mobility Equipment Research and Development Center at Fort Belvoir, Virginia under Contract No. DAAK02-72-C-0084 with the American University. The work was authorized under DA Project/Task area/Work Unit No. 1T061102A34A 03 100 EF.

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I. Introduction

This is the first semi-annual report on Contract No. DAAK02-72-C-0084 sponsored by the U.S. Army Mobility Equipment Research and Development Center at Ft. Belvoir, Virginia. The project entitled "Research on Electrochemical Energy Conversion Systems" consists of two technical tasks both of which are directed toward improvement of the hydrocarbon-air fuel cell for ground power systems and vehicular propulsion.

Task I. Corrosion characteristics of electrolytes for intermediate-temperature hydrocarbon-air fuel cells.

Task II. Feasibility of utilization of organic electrolytes in fuel cells. The work done on these two tasks is reported in detail in the following two sections.

II. Task I Corrosion Characteristics of Electrolytes for Intermediate-Temperature Hydrocarbon-Air Fuel Cells

A. Introductory

The scope of this task includes the consideration of new electrolytes as well as the investigation of corrosion in the presently used 35% H_3PO_4 electrolyte.

The number of electrolytes used in the hydrocarbon air fuel-cell has been rather restricted, probably owing to the relative success of phosphoric acid as an electrolyte. Aqueous solutions of KOH were used in some of the early work (1) and Schlatter (2) reported on the oxidation of propane, ethylene, and acetylene in 35% aqueous KOH at 100° C. However, difficulties occur in the employment of KOH in hydrocarbon-air fuel cells mainly because one of the products of hydrocarbon oxidation is CO_2. Carbon dioxide reacts with KOH to form carbonate and bicarbonate ions resulting in a lower limiting current due to the lower diffusion coefficient of potassium carbonate, decreased conductivity in the electrolyte, and lower solubility and precipitation of the bicarbonate. An improvement was offered by solutions of cesium and rubidium carbonates as reported by Cairns and Macdonald (3). Aqueous cesium carbonates, while alkaline, reject CO_2 formed by the oxidation of hydrocarbons and also can be operated in the range of 100-200° C. A further improvement in performance was shown by the use of acid electrolytes which reject the CO_2 produced in oxidation. Of the strong acids used, orthophosphoric acid appears to possess the best physical and chemical properties. The report of Grubb and Niedrach (4) is representative of some of the behavior exhibited in the better acid electrolytes. They successfully operated a propane-air cell at 150° C in 85% phosphoric acid with special catalytic electrodes. At a current density of 20 ma/cm^2 the oxidation was about 98% efficient. Recent studies (5) with improved electrodes make possible higher current densities without greater polarization but generally the acid is used at a concentration of 85-95% and a temperature of 130-150° C. These operating conditions favor corrosion of the fuel cell structural materials which include the substrates for the catalytic electrodes. In the latter case the metal or alloy when exposed to the corrosive solutions is maintained at a potential which will be either positive or negative depending on whether the electrode is the fuel or air electrode in the cell. At this point the corrosion of structural materials (apart from electrode materials) appears to be less of a problem than originally anticipated, as some relatively inexpensive materials such as carbon have been found suitable for some components (6).

To improve this situation it is reasonable to consider a) other electrolytes with the same electrochemical properties as phosphoric acid but not its severity as a corrosion medium, and b) materials of construction suitable for use in phosphoric acid under the operating conditions of the hydrocarbon-air fuel cell. These approaches are discussed in the following two sections.

B. Polyphosphates - as Electrolytes

1. Application to Fuel Cell

Before discussing the properties of polyelectrolytes, it is in order to mention how these compounds would be used in fuel cells. It would appear desirable to use, with the polyelectrolyte, a simple electrolyte at such concentration as to obtain a reasonable specific conductivity. The degree of polymerization would be such that the solution would be stable but not of such high viscosity as to render transport difficult. It would appear reasonable to incorporate the electrolyte in a stable matrix. Whereas, the polyelectrolyte is more stable at a neutral pH it would appear feasible to work at a pH such as 5-6 accepting a steady state degradation in the degree of polymerization to achieve an acid rejecting composition.

2. Preparation and Properties

In the following is given the preparations of the three main sodium polyphosphate salts, Madrell's salt, Graham's salt, and Kurrol's salt. Other metallic polyphosphates are normally prepared by the use of ion exchange techniques followed by freeze-drying to remove the solvent (7-9). The degree of polymerization of the sodium polyphosphates may be determined by an end group titration method (10). The degree of polymerization has also been determined by the viscosity of the sodium salt solution (7).

Madrell's Salt $(NaPO_3)_x$

Madrell's Salt may be obtained by heating the residue from evaporation of a solution of $NaNO_3$ and H_3PO_4 (11). 20 grams of $NaNO_3$ are dissolved in 25 ml of H_2O, mixed with 42 ml H_3PO_4 (density

1.3, approximately 45% H_3PO_4) and evaporated on a water bath. The residue is heated for four hours at 330° C and the melt extracted with water. Madrell's salt is practically insoluble in water, but is moderately soluble in salt solutions containing ammonium ions or alkali metal ions (12). The salt is not soluble in acetic acid but is readily soluble in cold dilute HNO_3, cold dilute H_2SO_4, and hot dilute HCl. Structurally, the salt is a chainlike, polymerized polymetaphosphate, which exists in two modifications differing in chain lengths.

Graham's Salt $(NaPO_3)_y$

Graham's salt may be prepared by the quenching of any melt having a $NaO:P_4O_{10}$ ratio between 2:1 and 10:3 (11). The degree of polymerization appears to depend on the heating temperature with the maximum polymerization at 1100° C. A quantity of $NaH_2PO_4 \cdot 2H_2O$ is placed in a platinum dish and dehydrated for 2 hours above 200° C. The material is placed in an electric furnace for 4 hours at the desired temperature and the melt quenched as quickly as possible by pouring into an iron dish containing dry ice and CCl_4. The vitreous product can be filtered off and the glassy material should be stored immediately in an air-tight container.

Graham's salt is extremely hygroscopic becoming moist and sticky with short exposure to air (11). The salt dissolves slowly in cold water and is quite soluble in water over 30° C (solubility at 20°, 973.2 g/liter; at 80° C, 1744 g/liter) (11). Graham salt is a glassy chain polymer containing a small percentage of cyclic rings; the glass is considered to be of a metaphosphate composition, $Na_2O \cdot P_2O_5$ (13).

Kurrol's Salt $(NaPO_3)_x$

Kurrol's salt may be prepared by tempering a super cooled melt of Na_2HPO_4 and $NH_4H_2PO_4$ at 550° C (11). The potassium form of Kurrol's salt may be prepared by heating monopotassium orthophosphate above 150° C (12). A mixture of 85 grams of Na_2HPO_4 and 15 g $NH_4H_2PO_4$ are heated to 800° to 900° to remove all water and NH_3 (11). The mixture is cooled to 550 to 650° and held at temperature for a few hours. The melt solidifies to form a fibrous product which is washed with H_2O to remove excess H_3PO_4.

Kurrol's salt is partially soluble in water; after a few hours in warm water the crystals become gummy and swell. If enough water is present a cloudy viscous solution forms. As in the case of Madrell's salt, solutions containing alkali metal ions accelerate the dissolution of the Kurrol's salt. Structurally, the salt is in long fibrous crystal which exists in two forms, showing two different X-ray powder patterns (11).

3. The stability and degradation of metallic polyphosphates

Linear polyphosphates degrade in aqueous solution by several paths dependent very much on the chain length of the polymer. Polyphosphates degrade through hydrolytic chain splitting and through random scission in the interior of the chains, although the rate constants for the two differ considerably. Hydrolytic chain splitting results in the formation of orthophosphate and, in the case of short chains, where the degree of polymerization is less than 4, trimetaphosphate. Rings are formed when the degree of polymerization is large, >30; in addition to orthophosphate, trimeta- and tetrameta- phosphates are formed.

In a study (14) of the catalytic effects of divalent metal ions on the degradation of polyphosphates in acid aqueous solutions, trimetaphosphates and orthophosphates were formed. Results indicated that the divalent metal ions, Mg, Ca, and Ni were bound more strongly to interior groups in the chain than is hydrogen ion. The divalent metal ions catalyze the reaction occuring at the chain end only splitting off trimetaphosphate from the end of the chain. The catalytic effect of the divalent metal is decreased in acidic solutions and the metal ion catalysis is very large on unprotonated end groups, but small for the protonated end groups (14).

Graham salts with a degree of polymerization varying from 30 to 170 and degraded at pH 5 and 65.5° C, were used to investigate the hydrolysis of long chain sodium polyphosphates (15). It was determined that the formation of orthophosphate and trimetaphosphate from end groups was independent of the degree of polymerization. The formation of orthophosphate and trimetaphosphate from middle or interior phosphate groups scission was dependent on the chain length of the polymer. The degradation of the polymer by reaction of the endgroup was confirmed by the fact that the rate constant for end group-splitting over interior scission was 50 and 10 times for orthophosphate and trimetaphosphate respectively.

Strauss and Day (8) studied the degradation of short chain sodium polyphosphates in the study of the degradation of sodium hexaphosphate at pH 5 and 65.5° C. The predominate pathway for the hydrolysis was

$$P_x + H_2O \rightarrow P_1 + P_{x-1}$$

In this equation, x is the degree of polymerization, for the hexaphosphate, 6. Thus, for the hexaphosphate the major product was

P_1, the orthophosphate, that accounted for 80% of the hydrolysis product. The other product, P_{X-1}, or P_5, can degrade in turn. The kinetics can be expressed in terms of the relative concentrations of the various degrees of polymerization. Thus, after 1260 minutes the concentrations for the different polymers were as follows (concentrations in terms of moles of species P_X per 100 g atoms of phosphorus)

P_6	2.77
P_5	4.26
P_4	3.40
P_3	3.23
P_2	2.82
P_1	-

Over a long period to time the concentration of trimetaphosphate appears to reach an approximately steady state.

In the work of Ise and Okubo (9) the degradation of sodium polyphosphate, with an average degree of polymerization of 600, was found to be negligible, i.e. constant concentration over several weeks within 3%, if the solutions were neutral. The activity coefficients for the alkali metal polyphosphates are smaller than for the organic polyphosphates such as tertiary butyl amine hydroxide polyphosphate. The alkali metal ions are considered to be structure formers, in that they immobilize water molecules due to the electric field surrounding the charged site. Polyphosphate ions also form an ordered structure and in aqueous solutions are considered to be structure formers. The extent of ion association of the alkali metal polyphosphates decreases in the order

$$Li > Na > K > Cs.$$

The solvent-solute interactions in the alkali metal polyphosphates must be considered as important as the metal ion association with the polyphosphate.

With the use of light scattering and viscosity measurements with sodium and lithium polyphosphates in aqueous sodium and lithium bromide solutions, it was shown that sodium polyphosphate has much less solvent affinity than lithium polyphosphate. The degree of ionization for lithium polyphosphate was found to be 0.13 and for sodium polyphosphate a value of 0.10 was calculated (16).

4. Binding of metal ions to polyphosphate ion

The degree of association of counter ions with polyphosphate ions determines roughly the mobility of the polyphosphates in an electric field and the electrical conductance of the solution (19). The apparent binding constant, K_m', is defined by

$$K_m' = \frac{(MPO_3)}{(M^+)_{eff}\ (PO_3^-)}$$

$(M^+)_{eff}$ is the effective concentration of the alkali ion, M^+, near the polymer chain and is given by

$$(M^+)_{eff} = (M^+)\ \exp\frac{(-e\psi)}{kT}$$

where e is the charge on the cation, k is the Boltzmann constant and T is the absolute temperature. The quantity, ψ, theoretically is the electrostatic potential at the surface of the polymer chain and the zeta potential is used for the numerical value. The zeta potential is calculated from the experimentally determined electrophoretic mobility from

$$Z = \frac{6\ \pi\ \eta\ u}{D}$$

η and D are the viscosity and dielectric constant of the solvent respectively.

From zeta potential measurements, Strauss (17) concluded that the model of a polyelectrolyte in solution as proposed by Overbeck and Stigte was realistic, that is, the polyelectrolyte in a solution containing a high concentration of simple electrolyte could be considered to be a loosely coiled chain, with each section enveloped by a double layer of cylindrical symmetry.

Viscosity and electrophoretic measurements were used to study the site-binding characteristics of lithium, potassium and sodium ions to polyphosphate ions. It was found that sodium and lithium polyphosphates "salted-out" as gels during phase separation from their corresponding bromide solutions while potassium polyphosphate salted-out as a semi-crystalline material. The metallic ions were considered to be found at specific ionic sites of the polyion, with the sitebound groups having specific and characteristic solvent affinities which affect the overall solubility of the polymer (7).

Similar methods were used to study the binding of magnesium ions by polyphosphates in aqueous electrolyte solutions. It was noted that the chain length had no effect on the binding of magnesium ions but a salt effect was observed. More magnesium ion was necessary for phase separation in tetramethylamine bromide than in sodium bromide solutions. The binding by magnesium ion could be, therefore, considered as being stronger in a tetramethylamine environment than in a sodium environment. The ratio of the fraction of phosphate groups which are neutralized by bound magnesium ions to the normality of free magnesium ions, $(Mg^{+2})_f$, was calculated to be 4×10^3 in 0.2 N NaBr for binding of magnesium ions in sodium environments (18).

In an earlier work Strauss and Ross (19) determined the binding constants of counterion with polyphosphate to decrease in the order

$$Li^+ > Na^+ > K^+ > Cs^+ \quad (CH_3)_4\,N^+$$

The binding constant was observed to increase with the diminishing size of the anhydrous cation, indicating the polyphosphate could penetrate the hydration layer of the cation.

5. Conductivity data for polyphosphates

In a study of binding of univalent cations by polyphosphates, Strauss and Bluestone (20), constructed the following table of electrical transport data of polyphosphates (Graham salt preparations) in 0.2 M electrolyte solution.

Electrolyte	M_s	Λ_p	$u \times 10_4$ cm^2/volt-sec	Λ_s	t_c	λ_c
LiBr	0.203	6.51	1.23	51.1	0.313	16.0
NaBr	0.199	7.35	1.14	57.2	0.384	22.0
KBr	0.216	12.8	1.41	70.8	0.488	34.6
tetramethyl-amine bromide	0.209	14.7	2.07	48.3	0.362	17.5

where M_s is the actual stoichiometric molarity of the simple electrolyte

Λ_p is the equivalent conductance of the polyphosphate salt

u is the electrophoretic mobility of the polyphosphate salt,

Λ_s is the equivalent conductance of the simple electrolyte

t_c is the transference number of the cation

λ_c is the equivalent conductance of the counterion in the solution of simple electrolyte as a solvent.

The degree of polymerization by other measurements was found to be 102 for lithium polyphosphate, 130 for sodium polyphosphate, 8000 for potassium polyphosphate, and 7800 for tetramethylamine polyphosphate.

In salt free sodium polyphosphate solutions, the equivalent conductance increases with the degree of polymerization up to a chain length of 10 and then has a constant value of 65 ohm^{-1} cm^2 $equiv.^{-1}$. (21).

C. Corrosion in Phosphoric Acid

1. Background

Several reviews of the corrosion of metals and alloys in phosphoric acid over a complete concentration range have been made (22,23). These studies indicate that only highly alloyed steels or alloys of Ta, Mo, or Cr are suitable for service in 85-95% H_3PO_4 at temperatures 125-170° C. Examples of commercial alloys which might be employed include Incoloy 825, Hastelloy G, and Ta, either unalloyed or alloyed with Ni or Ti. It appears that resistance to phosphoric acid is achieved by two mechanisms; the first, characteristic of stainless steel type 316, in which resistance is accomplished with a passive film and the second, represented by Ta, Au, or Pt, wherein the metal itself is noble with respect to the corrosive environment. Whereas, the first type might be quite suitable as normal materials of construction for fuel cell components they often exhibit higher rates under potential. The implication is that the more desirable materials would be Ta-based alloys or Ta itself.

2. Experimental

Several of the alloys with improved corrosion resistance as indicated by these studies in phosphoric acid have been obtained for tests in polyphosphate solutions and other alternate electrodes.

Alloy	Approximate Composition	Sources
Inconel alloy 625	76Ni-16Cr-7Fe	International Nickel Co. (D.L. Graver)
Incoloy alloy 825	42Ni-21Cr-3.0Mo--33 Fe	" "
Hastelloy C	56Ni-15Cr-3.7W-16Mo	Stellite Division, Cabot Corp. (R.B. Leonard)
Hastelloy G	44Ni-22Cr-20Fe-6.5Mo	" "
Carpenter 20 Cb-3	34Ni-39Fe-20Cr-2.5Mo-3.3Cu	Carpenter Technology Corp (M. Henthorne)

The use of tantalum as a material of construction is restricted by expense, the difficulty of fabricating structures, and oxygen embrittlement in certain environments. Recently, at least two industrial companies have developed processes on a commercial basis for coating steel with tantalum. Fansteel applies the "Fan Clad" process (24) to produce coatings up to 15 mils thick for service in concentrated acids at elevated temperatures. General Metals Technologies Corporation (25) has developed the fused salt "metalating" process for tantalum plating. Samples have been prepared by the latter process, tantalum coatings on steel in the range of 6-8 mils, which will be subjected to testing in various electrolytes.

The apparatus to conduct the corrosion testing at elevated temperature has been assembled. The testing unit consists of a number of three-necked flasks immersed in a constant temperature oil bath. The sample to be tested is held in one neck of a flask with provisions for potentiostating the metal strip. A second neck is fitted with a water cooled condenser and the third with a thermometer. It is also possible to run a gas dispersion tube into this third neck. The flask is immersed in a constant temperature oil bath, a "Magni Whirl" model MW - 1145 - 1 unit manufactured by the Blue M Co. which is capable of operating to 260° C.

D. Conclusions and Future Work

On the basis of the physical and chemical data reported in the literature it appears reasonable to consider polyelectrolytes as fuel cell electrolytes. It is planned to prepare solutions of the Graham's salt type for measurement of conductance, and corrosion characteristics. Assuming reasonable properties in this respect, the solutions will be tested in a hydrocarbon-air fuel cell.

A survey of the existing corrosion data with respect to phosphoric acid at concentrations and temperatures of fuel cell interest suggest that tantalum or tantalum alloys are the most reliable materials of construction. The application of tantalum by means of coatings would appear to circumvent to some extent problems of cost and fabrication. The coated steel specimens prepared by the fused salt process will be tested in phosphoric acid and other electrolytes.

In addition to the polyphosphates salts mentioned above, it is intended to investigate organic based electrolytes as alternative electrolytes. These would be such compounds as halogen substituted aliphatic carboxylic acids (26), i.e. strong acids, as contrasted to the cyclic esters discussed in the following section.

III. Task II. Feasibility of Utilization of Organic Electrolytes in Fuel Cells.

A. Introductory

In this section, reference to organic electrolytes means such solutions as lithium perchlorate in gamma-butyrolactone or propylene carbonate as contrasted to strong organic acids mentioned above as alternate electrolytes. Such systems were considered as they offer the possibility of providing solutions to some of the problems encountered in aqueous systems. It would be expected that solubility of the fuel would be increased with an accompanying increase in anode limiting current density. It would be expected that the rate of adsorption of the hydrocarbon would be altered and consequently the efficiency of electrocatalysis. The degree of side reactions and polymerization would also be affected - whether favorably or unfavorably - would be difficult to predict.

The work done with organic electrolytes in fuel cells has been limited, excluding, of course, work done with the ion-exchange membrane type which might be thought of as an organic electrolyte. A study was performed by Smith (27) using hydrazine and N_2O_4 as fuels. N_2O_4 reacted with some of the organic solvents and in solvents such as propylene carbonate, acetonitrile, and dimethyl formamide, the cell voltages were low suggesting slow diffusion processes, slow adsorption, or other slow reactions. On the other hand in the last 10 years a considerable amount of knowledge has been accumulated in the field of non-aqueous batteries from which to draw in constructing an organic based fuel cell. In the following some preliminary experiments on the oxidation of propane in an organic solvent are described.

B. Experimental

A two-compartment electrolysis cell with the two compartments separated with a glass frit was set up in the dry box in an argon atmosphere. The working electrode was a platinized Pt electrode, the counter-electrode was a platinum gauze and the reference electrode was a silver wire. The electrolyte was redistilled γ-butyrolactone, 1M in anhydrous $LiClO_4$. Propane (Air Products Research Grade) was bubbled over the working electrode (anode) at the rate of 10 ml/minute. The working electrode was held at 1.68 V. versus the Ag reference and the electrolysis was allowed to proceed for 630 minutes at a current density of about 0.1 ma/cm.^{2} The solution was analyzed with an Anakro-I Gas Chromatograph with a Poropak Q column. The relative peak height for H_2O, CO_2, and propane were compared from the start of electrolysis and after the run completion. The relative peak heights increased by factors of 8 and 7 for H_2O and CO_2 respectively. On the basis of such qualitative experiments it was concluded that propane is oxidized in γ-butyrolactone electrolytes but nothing can be said about the efficiency in a quantitative sense.

C. Conclusions and Future Work

These preliminary experiments are only sufficient to indicate that propane is oxidized in this organic system. If work on this phase of the project were to continue it would be desirable to make quantitative studies with respect to the production of CO_2 to achieve some knowledge of the efficiency of oxidation and then to proceed to more sophisticated studies of hydrocarbon adsorption, etc.

On the basis that other electrolytes e.g. polyphosphates, halogenated organic acids, appear more promising approaches to the alternative electrolyte problem, this phase of the project was suspended. Previous studies in this Laboratory (28) and at Globe Union (29) have indicated that the air electrode is only capable of sustaining a low and limited current density in these organic electrolytes. The implication is that even if a fuel electrode were to be feasible then a major problem would still exist with respect to the air side of the fuel cell. For this reason this work was put aside in favor of other approaches.

IV REFERENCES

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