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A Discussion of Electrolyte and Product Management in Hydrazine-Oxygen Fuel Cells under Cyclic Pressure

a phase report

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NAVAL SHIP RESEARCH AND DEVELOPMENT CENTER

Washington, D.C., 20034

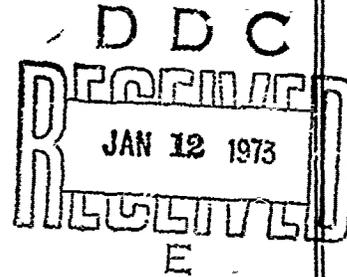


A DISCUSSION OF ELECTROLYTE AND PRODUCT MANAGEMENT IN HYDRAZINE-OXYGEN FUEL CELLS UNDER CYCLIC PRESSURE A PHASE REPORT

by

H. B. Urbach, R. J. Bowen, and D. E. Icenhower

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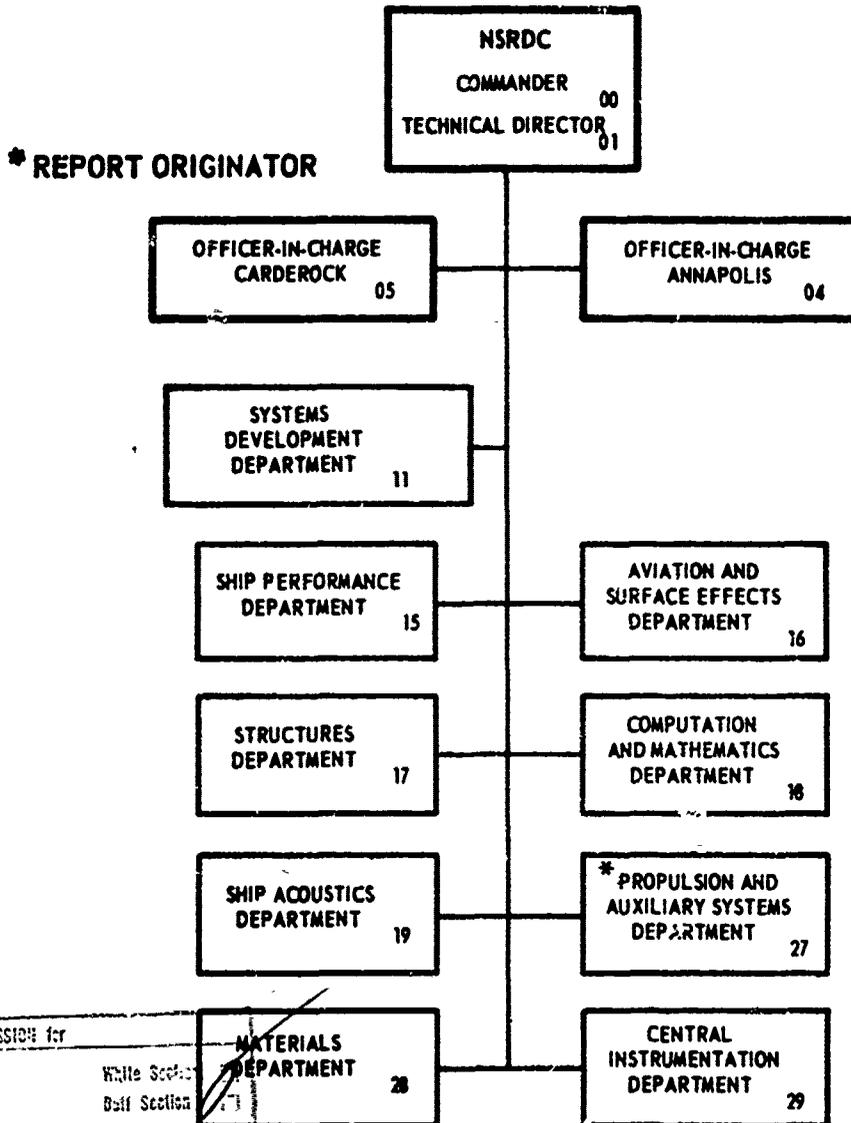
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<p>Fuel cells Hydrazine fuel cells Porous electrodes High-pressure fuel cell Pressure-equilibrated cell</p> <hr/> <p>Abstract (Cont)</p> <p>depressurization without sacrifice of power or efficiency during normal operating regimes. This configuration employs a sintered (no wetproofing) anode, an open-structured cathode (to facilitate nitrogen respiration) and operates at low hydrazine concentration.</p> <p>(Authors)</p>						

ABSTRACT

The performance of hydrazine fuel cells is strongly influenced by management of the gaseous reaction product, particularly in dynamic pressure-equilibrated underwater environments. The nitrogen product of hydrazine oxidation and decomposition dissolves in the electrolyte and separator of the cell under pressure. The classic sandwich fuel-cell structure of hydrogen-oxygen fuel-cell technology, which employs wetproofed electrodes, was designed to stabilize the gas-liquid interface. In hydrazine cells, wetproofing has proved responsible for severe anode polarization arising from nitrogen occlusion. The use of plate or sintered anodes without wetproofing tends to minimize nitrogen-produced anode decay.

In addition, ohmic losses from nitrogen gas in supersaturated electrolytes produce undesirable transient reductions in performance in cells undergoing rapid depressurization. Cells designed for forced or natural convection of the interelectrode fluids (no asbestos separator) exhibit relatively insignificant reduction in performance from nitrogen formation. However, the sandwich design (with separator) yields superior performance over types without separator. One configuration of sandwich cell exhibits a satisfactory performance during depressurization without sacrifice of power or efficiency during normal operating regimes. This configuration employs a sintered (no wetproofing) anode, an open-structured cathode (to facilitate nitrogen respiration) and operates at low hydrazine concentration.

ADMINISTRATIVE INFORMATION

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INTRODUCTION

Fuel-cell power systems proposed for underwater applications may be categorized according to the method of adaptation to the hydrostatic pressure environment, namely a pressure-equilibrated or an encapsulated concept. The pressure-equilibrated concept is attractive in systems using liquid reactants because it eliminates requirements for any hard containment vessel with its significant weight penalty.¹⁻³ Because hydrazine fuel cells have been operated safely and successfully in the pressure-equilibrated mode,¹⁻³ the hydrazine fuel-cell power system may be considered a candidate power source for deep-sea applications.

In addition to nitrogen produced in direct proportion to the delivered electrical current during normal operation in the cell, the hydrazine reactant also decomposes into hydrogen and nitrogen as a result of heterogeneous reaction with the surface of the device and containment walls. The hydrogen is a reactive fuel that under proper operational control^{4,5} may be consumed without significant loss of efficiency. The nitrogen, however, is a cumulative product that must be transported from the cell stack to prevent occlusion of the electrodes and displacement of the fuel and electrolyte, which together produce cell starvation and increase the internal cell resistance. These effects, associated with nitrogen product formation, were recognized features of hydrazine-cell performance long before pressure-equilibration studies were initiated. The evolution of the commercial hydrazine fuel cell was in fact influenced by problems arising from nitrogen product removal.

Pressure-equilibrated concepts aggravate the problem of nitrogen transport because nitrogen is solubilized in the working fluids and particularly in the interstitial structures of the electrodes and separator in proportion to pressure. During depressurization, nitrogen supersaturation of the fuel-cell system occurs. Resultant nitrogen-phase formulation in the electrodes and interelectrode structures produces a loss in performance.² The effects associated purely with nitrogen-phase formation during pressure falloff have been generally designated "bend" phenomena. Other effects arising from normal thermodynamic and electrokinetic factors color the interpretation of results associated with bend phenomena because the two are complexly interrelated. In this report, an attempt will be made to interpret fuel-cell performance and to resolve fuel-cell problems arising from operation in dynamic pressurized environments as they relate to fuel-cell design. Unfortunately, many gaps in the experimental studies exist with respect to some fuel-cell types, such as those with membrane separators between forced-convection streams of anolyte and

¹Superscripts refer to similarly numbered entries in the Technical References at the end of the text.

catholyte. Extrapolation of performance based on in-house studies and information from published and private sources will be attempted.

In addition to recently acquired experimental data, this phase report also summarizes some previously developed experimental results. These results are repeated here to facilitate the presentation of conclusions relative to preferred design and preferred operational parameters for fuel cells in hydrazine power plants operating in the pressure-equilibrated mode.

FUEL-CELL STRUCTURES

As mentioned above, the mechanical design of hydrazine fuel cells is influenced by nitrogen product removal, as well as reactant feed. At least five distinctive types of experimental structure may be identified and classified with respect to nitrogen transport based largely on diffusion, convection, or hydrostatic bubble displacement. The diffusion type was borrowed (item (a) of figure 1) directly from hydrogen-oxygen fuel-cell technology and features an asbestos separator, which absorbs potassium hydroxide by capillary action, forming an immobile electrolyte layer.

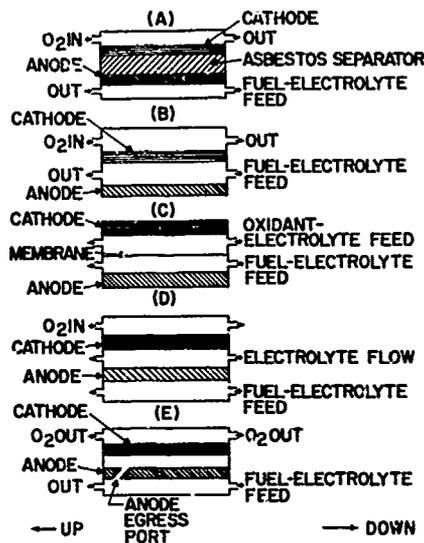


Figure 1
Structural Aspects in the Reactant and Product Management of Hydrazine Fuel Cells

Fuel dissolved in the electrolyte is pumped past the back side of the anode. Nitrogen formed in the interelectrode region is transported from the interelectrode region by diffusion alone.

In the forced-convection concepts, nitrogen is removed by a flowing liquid-gas system. In one convective type (item (b) of figure 1), the fuel-electrolyte mix is pumped through an interelectrode space (which does not contain a separator). Nitrogen product gas is forced from the interelectrode space by the mix and removed in a gas-liquid phase separator.

A second convective type (item (c) of figure 1) uses two forced-convection streams, which pass through the interelectrode space on opposite sides of an ion-conducting membrane. One stream containing fuel and electrolyte sweeps nitrogen from the interelectrode space as soon as it is formed at the anode, while a second electrolyte stream carries the oxidant.

A third convective system (item (d) of figure 1) employs forced feed of a hydrazine-electrolyte mix across the back side of the anode, as well as a separate flowing electrolyte that forces bubbles from the interelectrode space.

Another concept is based upon natural convection arising from hydrostatic displacement of bubbles (item (e) of figure 1). Gas-egress ports permit nitrogen to escape from the interelectrode space.

A new design concept appears superficially identical to the classic design of item (a) of figure 1. The anode is a high-porosity catalyzed sinter, although its blow-through pressure is large because of small pore size. The catalyst is pressed upon a thin screen to form a cathode that is open in the sense that light, as well as gas, passes through the structure quite freely. Such a structure would not impede the escape of nitrogen. The concept is based on the principle of preventing nitrogen and hydrazine transport to the interelectrode space.

The electrode structure plays a significant role in fuel-cell performance as indicated above. Anodes employed in early hydrazine fuel cells were often hydrogen anodes prepared from powdered metal catalysts and a "glue" of polytetrafluoroethylene (TFE), which, by virtue of its wetproofing properties, was deliberately designed to stabilize a gas-liquid interface inside the electrode pores.

Electrodes constructed of powdered catalyst and TFE (pressed onto a substrate of metal screen or metal sinter) will be called "composite" types. Those constructed from catalyzed sintered metal powders without TFE will be referred to simply as "sintered" types. Some cells (item (c) of figure 1) employ catalyzed non-porous plate anodes.

EXPERIMENTAL RESULTS AND DISCUSSION

POTENTIAL RESPONSE OF CELLS UNDER PRESSURE

The enhanced potential of hydrazine-oxygen fuel cells under pressurized conditions has been described previously.^{1,6-8} The major results, restated here to clarify the interpretation of data, were that each 10-fold increase of pressure produces approximately a 40- to 60-millivolt (mv) increase in output potential at a given current density. The 40- to 60-mv response was identified with the cathode alone and was shown to be caused by kinetic and mass transport factors, as well as thermodynamic response to oxygen pressure.⁶⁻⁸ Also, it was shown that above the reversible hydrogen potential, hydrazine anodes exhibit a negligible response to pressure, because the hydrazine electrode is irreversible.²

STATIC PRESSURE EFFECTS; TEMPORAL RESPONSE

Figure 2 represents the behavior of a single hydrazine cell constructed with a composite anode of platinum (9 mg/cm²)* and TFE pressed upon a gold-plated nickel screen (see figure legend for other details).

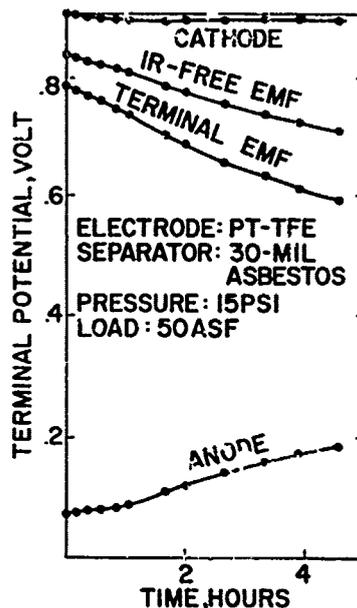


Figure 2
Components of Potential Decay in a Cell with
Composite Anode at Atmospheric Pressure

*Abbreviations used in this text are from the GPO Style Manual, 1967, unless otherwise noted.

The terminal potential, the cell potential corrected for ohmic losses, and the anode and cathode potentials (the last three were obtained by using the interruptor technique with a Kordes-Marko bridge and dynamic reference electrode systems) were obtained as a function of time over 5 hours. The decay of the terminal potential (well known to hydrazine-cell researchers) cannot be attributed to the cathode. The oxygen electrode shows only a slight falloff with time over the first 30 minutes, a decay that is caused by transport of nitrogen or hydrazine to the oxygen side. The deleterious effect of nitrogen transport on the oxygen cathode can be decreased by increasing the oxygen purge rate from the cathode manifold² (turbulent or pulsed purge is effective) or by decreasing the nitrogen transport rate.

The anode potential decreases by approximately 25 mv/hr. The ohmic potential drop (which is the difference between the cell potential and IR-free cell potential) increases by 11 mv/hr. Thus, by far the largest components of the deterioration under static conditions are the anode activity and an ohmic loss generally considered characteristic of the interelectrode space.

Figure 3 permits an evaluation of hydrazine cells using composite anodes under static high pressure after a period of steady pressurization to 1400 psi.

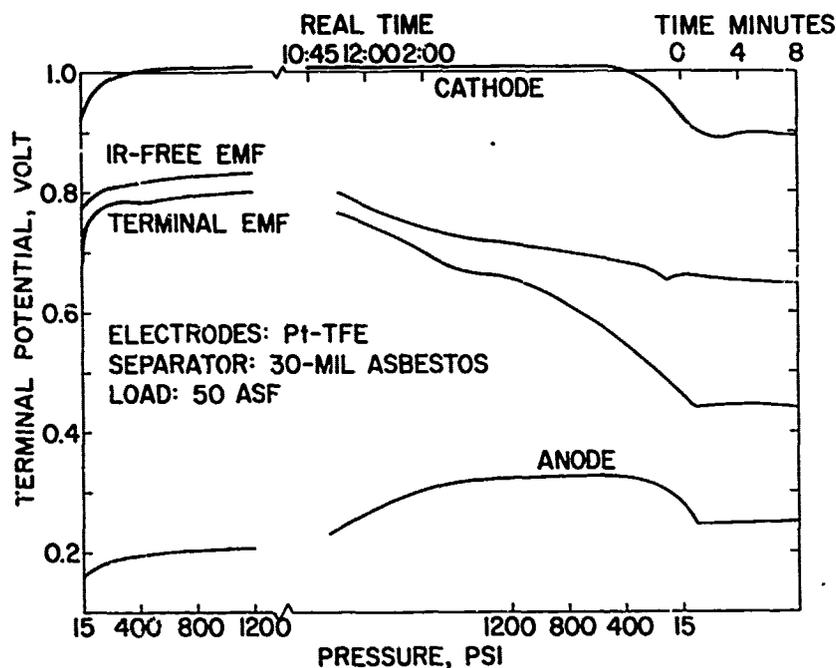


Figure 3
Components of Potential Decay in a Cell with
Composite Anode Under Cyclic Pressurization

The data in figures 2 and 3 were obtained from identical cells and conditions except that the temperatures were 28° and 50° C, respectively. The reader's attention is directed to that data point where static pressure (1400 psi) is maintained and the real-time axis begins. Three results can be identified starting at 10:45 on the real-time axis. The cathode remains stable. In contrast, as at atmospheric pressure, the anode polarizes, this time only 20 versus 25 mv/hr (figure 2); the ohmic loss increases 4 versus 11 mv/hr at atmospheric pressure. The difference may be attributed to pressure, which increases the relative nitrogen solubility and, in any given accumulation rate, compresses the relative volume fraction of the nitrogen phase.

Establishment of a gas barrier to effective hydrazine fuel feed, as a result of nitrogen phase formation, is believed to be the probable cause of the depression in anode performance in the data of figures 2 and 3. However, a more serious factor is that the most efficient and reactive anode sites are most occluded by bubble formation. Thus, the apparent current density is increased. Ionic paths around bubbles are elongated. As a consequence, a complex mix of nonseparable (by the method of interruptor techniques⁹) activation and ohmic polarization is produced.

A comparison of anodic decay versus the ohmic decay (82 versus 17 mv) shows that the problem is more serious in the anode than in the more diffuse interelectrode regions where purely ohmic loss occurs. The mechanistic interpretation is that, under static pressure conditions, nitrogen formation and nitrogen supersaturation are greater at the anode where reaction takes place than in the interelectrode space.

Figure 3 reveals that deterioration of the anode potential and the ohmic loss begins abruptly when pressurization ceases on the real-time axis. In any case potential losses, and particularly ohmic losses, are recovered largely by compression sufficiently rapid to collapse all nitrogen bubbles. In fact three methods can be employed to get rid of the nitrogen phase: (1) evacuation of liquid and gas under vacuum followed by refill;¹⁰ (2) prolonged flushing of the cell with hydrazine- and nitrogen-free electrolyte; and (3) pressurization. Recovery of potential losses caused by nitrogen bubbles appears equally effective by the three techniques.

Ohmic losses (as measured in porous systems by the interruptor technique⁹) build up with time in hydrazine fuel cells constructed with composite anodes according to figure 4. The results for the ohmic loss at high and low static pressures parallel results for the anode polarization. Ohmic loss builds up more rapidly at low pressure than at high pressure, probably because the relative volume of the nitrogen phase is greater at low pressure. However, the rate of increase in the ohmic resistance is not inversely proportional to pressure (slope ratio is about 2 in figure 4), possibly because bubble nucleation and displacement are more rapid at low pressure.

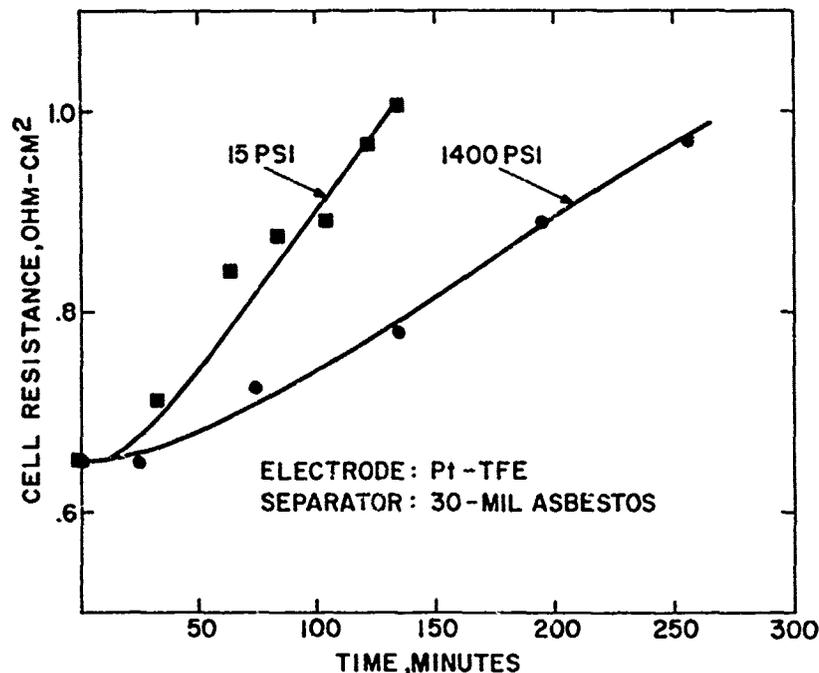


Figure 4
Effect of Pressure on the Temporal Behavior of the Internal Resistance in a Cell with Composite Anode

Ohmic loss and anode polarization do not increase indefinitely, as might be suggested by figure 4. During normal operation of hydrazine cells with composite electrodes, a steady state of terminal potential is reached in about 8 hours in which partial recovery of some potential is observed (as much as 50 mv) in abrupt (1- to 2-second) reductions of ohmic potential loss. It is possible to interpret these abrupt reductions as arising from the extrusion of gas. Experimental observations suggest that such sudden extrusions of gas, if they are indeed fact, may occur when the volume of the phase exceeds the physical volume of the space in which the nitrogen has become immobilized. It is plausible that excess capillary pressure in the liquid phase tends to make large bubbles metastable near the interface of gas and liquid.

Metastability in the gas phase is useful because it simplifies removal and elimination of nitrogen. As suggested above, metastability may be induced by structural considerations such as elimination of TFE from the anode, which is equivalent to the elimination of the composite anode structure. Another significant structural factor that appears to foster metastability is the use of thin separators in the interelectrode space. For a given bubble size, metastability might be expected to increase with decrease in the thickness of the asbestos separator. Such conclusions may be supported by the data of figure 5, which illustrate the effect of separator thickness. Both sets of data represent the same cell, with an uncompressed separator thickness

of 0.030 inch, under different torque conditions as specified. The actual changes in the dimensions of the separator resulting from the torque increase were unknown.

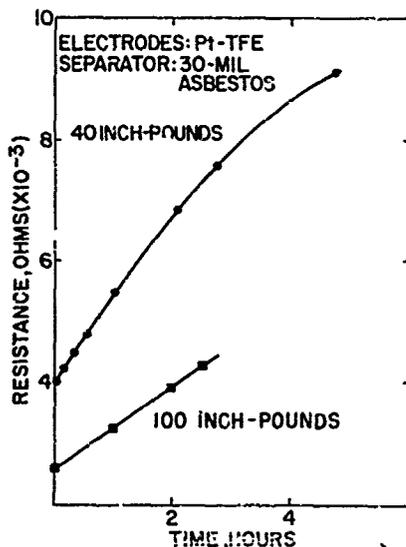


Figure 5
Effect of Torque (Thickness of the Cell) on the Internal Cell Resistance

The initial value of the cell resistance is smaller for the thinner structures, as expected. However, the relative rate of increase of cell resistance appears to be less (0.24 versus 0.33 per hour) for the thin structure, in conformity with expectation. At long-time values, the upper curve indicates a leveling out in the cell resistance.

It is emphasized that these results are characteristic of cells constructed with composite anodes. Hydrazine cells constructed with sintered anodes or simply solid plate anodes (item (c) of figure 1) do not exhibit any extensive anode decay. Ohmic losses in cells with sintered anodes have risen less than 13 mv over a period of 500 hours (see discussion of figure 12), whereas ohmic losses in the composite cells have been observed to rise over 100 mv in the space of hours (see figure 2) at the 100 ampere per square foot (ASF) level. This generalization applies to hydrazine cells using sintered anodes with or without asbestos separators, provided that in the former case, the cathodes are open structured.

STATIC PRESSURE; POTENTIAL RESPONSE TO CONCENTRATION

All hydrazine fuel cells show increases in output potential within limits imposed by cross-diffusion factors and other effects.^{1,2,4,5,10-18} Cells with asbestos separators and back-of-

the-anode feed (items (a), (d), and (e) of figure 1) exhibit near-logarithmic potential rise with concentration (again within limits as indicated above). The upper plot of figure 6 illustrates such behavior (which is well known at atmospheric pressure) at 9000 psi in a cell employing a composite type of nickel boride-TFE anode.

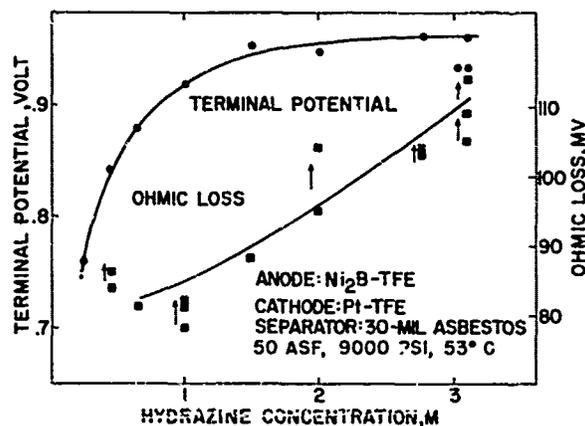


Figure 6
The Influence of Hydrazine Concentration on the Terminal Potential and the Ohmic Potential Loss

The unusually high pressure-induced potential has been discussed elsewhere.^{2,6,7} The lower curve represents the rise over a 10-minute time period of the ohmic potential loss as hydrazine concentration moves from 0.3 to 3.1 molar (M). The arrows are associated with the ohmic potential curve and depict the temporal shifts of measured points during the short fuel-injection periods (10 to 30 seconds). At low hydrazine concentrations, nitrogen is diffusing out of the cell as indicated by falling ohmic loss. Ohmic loss measurements show a slight decrease between fuel additions because the concentration of hydrazine is reduced slightly. However, the clear trend is that the ohmic loss increases approximately in proportion to the hydrazine level, which is, of course, the progenitor of nitrogen in the interelectrode space.

Figure 7 indicates why a point is reached where hydrazine concentration depresses the cell potential. Increase of hydrazine concentration from 0.7 to 1.1 M improves the anode performance (reducing the net anode polarization). However, the improvement at the anode is only about 5 mv compared with the loss of about 25 mv at the cathode. In addition, the cell potential is depressed by an additional few millivolts of ohmic loss because of the rise in the nitrogen level in the interelectrode space.

The results plotted in figure 7 are representative of cell structures of the type shown in item (a) of figure 1.

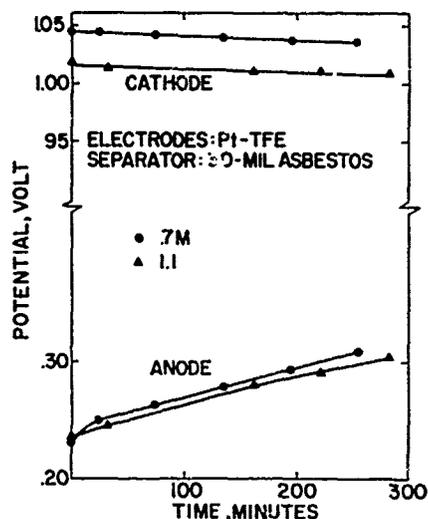


Figure 7
Effect of Hydrazine Concentration on the Temporal Response of the Electrode Potentials in a Cell with Composite Electrodes

Cell structures with anode egress ports (item (e) of figure 1) and cell structures with interelectrode feed (items (b) and (c) of figure 1) show depression of the cathode potential at lower levels of hydrazine concentration than those indicated in figure 7. Thus, concentration levels become more critical particularly in cell types with interelectrode feed where direct contact of feed and cathode is tolerated.¹⁴

STATIC PRESSURE; COULOMBIC EFFICIENCY AND CONCENTRATION

Whereas the effect of hydrazine concentration on the fuel-cell potential is beneficial (within limits), increasing hydrazine concentration depresses coulombic efficiency. This result was previously reported for a seven-cell stack.⁴ Figure 8 shows the depression in a single cell at various current densities. The falloff in coulombic efficiency is fastest at low current densities.

The causes contributing to low coulombic efficiency include diffusion of oxygen to the anode, diffusion of hydrazine to the cathode, and decomposition of hydrazine.^{2,4,5,12,14} The relative contributions of these are, again, functions of fuel-cell design.^{2,4,5,12,14} For example, losses caused by cross diffusion increase rapidly when the barriers to diffusion are reduced. Openstructured anodes and cathodes permit cross diffusion of hydrazine and oxygen, respectively. Removal of the asbestos, or other, separator increases diffusion. When anodes are provided with egress ports of the type described in item (e) of figure 1, convection and diffusion increase. Cells with interelectrode feed (items (b) and (c) of figure 1) may be subject to reduced

coulombic efficiency (<80%) because of direct convection of hydrazine to the cathode.¹⁴ The most significant information of figure 8 is that control of the concentration permits containment of these losses to within 10% with coulombic efficiencies exceeding 90%.

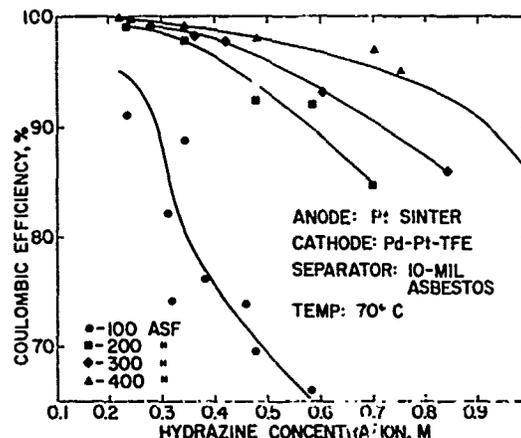


Figure 8
Effect of Current Density on the Concentration Response of Coulombic Efficiency in a Platinum-Catalyzed Hydrazine Cell

It is clear from these results that the asbestos separator contributes beneficially to a high coulombic efficiency and detrimentally to ohmic loss factors. Proper analysis of the trade-offs permits optimum choice of separator thickness.^{2,4,5,12}

STATIC PRESSURE; POWER EFFICIENCY AND CONCENTRATION

The voltage efficiency (the observed cell potential divided by 1.562 volts, the theoretical reversible potential of the hydrazine-oxygen cell) increases with concentration (within limits as determined by crossover of hydrazine), whereas the coulombic efficiency decreases with concentration. The power efficiency, which is the product of the coulombic and voltage efficiency, is the preferred measure of the overall efficiency. (The thermal efficiency is 96.8% of the power efficiency.) Figure 9 shows how the concentration modifies the power efficiency, which exhibits a peak of about 45.5% at approximately 0.45 M hydrazine for the given cell. The particular concentration required to produce the peak value of efficiency again strongly depends on cell structures, temperature, and current density. The concentration for peak efficiency must be relatively low when the anode structure is open and porous. Anodes with high bubble pressure or small porosity (tight), such as were employed to obtain the data of figure 9, permit a relatively wide choice of concentrations under static pressure conditions.

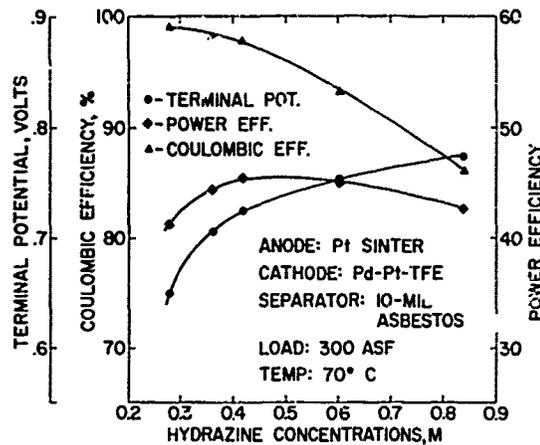


Figure 9
The Response of Terminal Potential, Coulombic Efficiency,
and Power Efficiency to Hydrazine Concentration

Operation of hydrazine cells on the lean side of the efficiency peak is desirable to minimize diffusion of hydrazine and nitrogen into the interelectrode space.

DYNAMIC PRESSURE EFFECTS ON THE POTENTIAL AND OHMIC LOSS

Figure 3 illustrates the effect of dynamic pressure on the components of fuel-cell potential. The left side of the figure shows the measured data during pressurization to 1400 psi. The cathode potential has increased 85 mv; the ohmic loss has decreased 44 mv with an apparent stabilization in value, but the anode potential has decayed 47 mv. The 85-mv cathode potential rise is in conformity with the 40- to 60-mv pressure coefficient for the oxygen cathode mentioned above.^{1,6-8}

The decrease in ohmic loss is attributed to the collapse of nitrogen bubbles in the interelectrode space during pressurization. The anode potential did not stabilize. However, the normal static rate of decay in the anode appears to decrease with pressure in part because the relative volume fraction of nitrogen produced at the active anodic sites at steady current decreases as the nitrogen solubility increases in direct proportion to pressure. Thus, the greater fraction of gas may be dissolved in the electrolyte at sufficiently high pressures.

After depressurization starts (figure 3) at 3:00 on the real-time axis, the cathode remains nearly stable down to 500 psi. Cathode potential decay during depressurization is greater than the potential gain during pressurization (115 versus 85 mv) resulting largely from nitrogen and some hydrogen transfer to the cathode. The anode potential continues to decay slowly at first,

but below 300 psi the anode recovers 80 mv of potential, which may be explained by blowout of metastable nitrogen bubbles from the composite-type electrode. Nevertheless, anode potential decay resumes at atmospheric pressure.

The largest change, however, occurs in the interelectrode space where the ohmic loss climbs over 0.2 volt. Most of the ohmic increase is caused by the formation of nitrogen bubbles as a result of supersaturation. After the cell was taken down, the asbestos was observed to have expanded like a bellows in some cases. Thus, for cells similar to that in item (a) of figure 1 with composite anode, the ohmic loss during decompression is the major loss, whereas under static conditions the anode loss predominates.

Figure 10 shows how the measured cell resistance behaves during the course of a pressurization cycle at 100 psi/min followed by 4 hours at 1400 psi and depressurization at 100 psi/min.

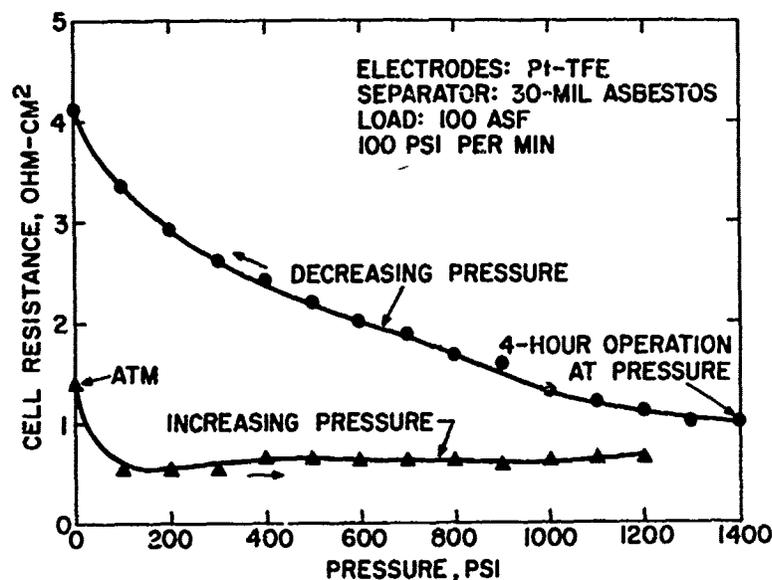


Figure 10
Behavior of the Cell Resistance Under Cyclic Pressurization

The anode of this cell was of the composite type. A minimum cell resistance was reached at about 200 psi in this case. The minimum value of the cell resistance appears to be stable. During the decompression, cell resistance increases sharply according to figure 10.

Figure 11 illustrates the ohmic potential loss in a cell with tight composite electrodes (anode and cathode) over 6 cycles of pressurization. The progressive buildup of ohmic potential

loss indicates that bubble stabilization sites, once developed in a previous depressurization, are reoccupied in successive cycles.

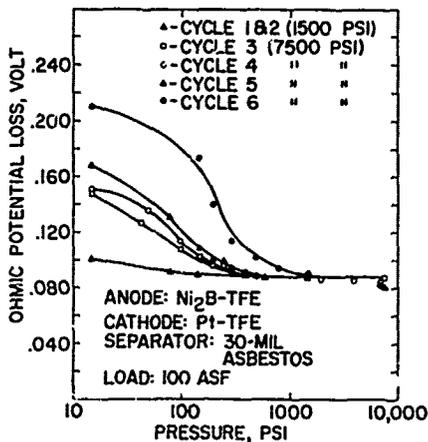


Figure 11
 Effect of Multiple Cyclic Depressurization on the Ohmic Potential Loss in a Cell with Composite Anode

As shown in figure 11, the ohmic loss at high pressure is always the same, indicating again that pressure minimizes the effect of nitrogen bubbles by reducing their size. In addition, the relative rate of depressurization at high pressures is small.

In contrast to the sandwich cell (item (a) of figure 1) with composite electrodes, cells of the type illustrated by item (e) of figure 1 with sintered anode and egress port show little or no buildup in ohmic potential loss over several cycles. In figure 12, the data from a cell such as that in item (e) of figure 1 illustrate this fact. The scatter of the data is in part a result of lack of good hydrazine concentration control during the test. However, the data in figure 12 show, in contrast to the results in figure 11, a relatively flat response of the ohmic potential during the pressure cycle. Thus, cells of the type shown in item (e) of figure 1, with gas egress ports in the anode, exhibit only minor, if any, falloff in performance as a result of bend phenomena. Another type (item (c) of figure 1) of hydrazine fuel cell that is reported to show only minor susceptibility to bend phenomena is based on the use of interelectrode reactant feed employing a separator membrane.¹⁹

Another cell concept is superficially similar to item (a) of figure 1 and utilizes the sintered catalyzed anode and an open-structure cathode (large pores facilitate nitrogen respiration). With control of the hydrazine concentration on the lean side of

the power peak (see discussion of figure 9), very little hydrazine or nitrogen is transported to the interelectrode space. Behavior of such a cell under pressure cycling conditions has demonstrated satisfactory performance similar to that in figure 12.

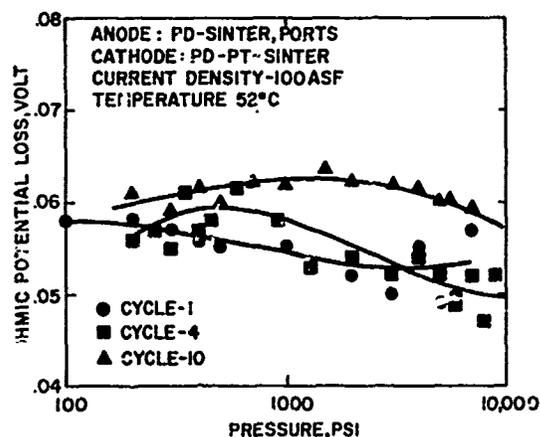


Figure 12
 Ohmic Potential Loss Behavior During Depressurization
 Cycles in a Cell with Sintered Anode

EFFICIENCY AND POWER VERSUS FUEL-CELL STRUCTURE

Only experimental generalities will be presented here in the form of an inequality. The order of power efficiencies and power densities (two-dimensional) observed in these studies is $a > e > b$ (c,d), where the letters refer to the cell types depicted in figure 1. Cells of the type shown in items (c) and (d) of figure 1 were not studied here, but their relative grouping based on efficiency¹⁹ appears to be with cells of the type illustrated in item (b) of figure 1. Tight electrodes exhibit high potential drop between the front and back faces because of ohmic losses.¹⁹

CONCLUSIONS

Design aspects of nitrogen-product management in hydrazine fuel cells are of great importance in their power efficiency, power density, and cyclic pressure behavior. Cells employing wetproofed anodes (composites of metal catalyst and TFE) exhibit anode decay greater than 25mv/hr, a loss that arises from nitrogen stabilization on the TFE. Cells employing anodes constructed from catalyzed plates and sinters show little or no anode decay.

Asbestos separators cause buildup in ohmic loss because of nitrogen gas-phase separation. Although the static pressure loss is small compared to the anode decay, the ohmic loss during

decompression is excessive. Cell designs based on the elimination of the asbestos separator exhibit little or no ohmic loss buildup during decompression. However, such cells normally require tight cathodes (for prevention of oxygen crossover), which cause reduced power efficiency and reduced power density.

A promising design that retains the asbestos separator uses a sintered anode and an open-structured cathode. Achieving attractive performance with this type cell depends upon minimizing nitrogen transport in the form of hydrazine to the interelectrode separator space by operating the cell at lower hydrazine concentrations. The tight anode hinders hydrazine transport. The open-structured cathode permits continuous egress of trapped nitrogen during decompression. Power efficiency and power density are high at atmospheric pressure. Cyclic pressure studies on this cell yield good performance simultaneously with excellent power efficiency and power density.

TECHNICAL REFERENCES

- 1 - Bowen, R. J., et al, "The Hydrazine-Oxygen Fuel Cell at Ambient Deep Sea Pressures," Conference Proceedings of the Intersociety Energy Conversion Engineering Conference, IECEC Record, pp. 845-851 (1968)
- 2 - Urbach, H. B., and R. J. Bowen, "The Efficiency of Hydrazine-Peroxide Fuel Cells," J. Electrochem. Soc., Vol. 117, p. 1594 (1970)
- 3 - Gormley, D. R., and J. H. Harrison, "A Liquid Reactant Fuel-Cell Power System Design for Underwater Applications," Conference Proceedings of the Intersociety Energy Conversion Engineering Conference (Aug 1971)
- 4 - Urbach, H. B., et al, "The Dependence of Hydrazine Fuel-Cell Stack Efficiency on Hydrazine Concentration," Conference Proceedings of the Intersociety Energy Conversion Engineering Conference, IECEC Record, pp. 5-101 (1970)
- 5 - Urbach, H. B., et al, "Optimizing Power Efficiency of Hydrazine-Oxygen Fuel Cells," Proceedings, 25th Power Sources Conference (1972)
- 6 - Bowen, R. J., and H. B. Urbach, "Dynamic Behavior of the Oxygen-Peroxide Couple on Platinum," J. Chem. Phys., Vol. 49, p. 1206 (1968)
- 7 - Urbach, H. B., and R. J. Bowen, "Behavior of the Oxygen-Peroxide Couple on Platinum," Electrochem. Acta., Vol. 14, p. 927 (1969)
- 8 - Bowen, R. J., et al, "Oxygen-Peroxide Couple on Platinum," Nature, Vol. 213, p. 592 (1967)
- 9 - Urbach, H. B., "Theory of Polarization of Porous Gaseous Diffusion Electrodes," Fuel Cells, Chapter 7, Vol. 2, edited by G. J. Young, New York, Reinhold Publishing Corp. (1962)
- 10 - Reiser, Carl, et al, Pratt & Whitney Corp., South Windsor Engineering Facility, private communication (1969)
- 11 - Tompter, S., Allis Chalmers Corp., Milwaukee, Wis., private communication.

- 12 - Kohlmüller, H., "Optimizing Hydrazine-Oxygen Fuel Cells," Energy Conversion, Vol. 10, p. 201 (1970)
- 13 - Daniel-Bek, V. S., and G. V. Vivitskaya, Elektrokimiya, Vol. 3, p. 973 (1967)
- 14 - Kordes, K. V., and M. B. Clark, "Optimization of Hydrazine-Air Cells," Proceedings, 24th Power Sources Symposium, p. 207 (1970)
- 15 - Salathe, R. E., "Evaluation of Replacable Hydrazine Module as a Basic Building Block," Proceedings, 24th Power Sources Symposium, p. 204 (1970)
- 16 - Hymes, L. C., et al, "Hydrazine Fuel Cells," Proceedings, 24th Power Sources Symposium, p. 210 (1970)
- 17 - Gillis, E. A., "Hydrazine-Air Fuel Cell Power Sources," Proceedings, 20th Annual Power Sources Conference, p. 41 (1966)
- 18 - Perry, John, Jr., "Hydrazine-Air Fuel Cell," Proceedings, 22nd Power Sources Conference, p. 10 (1968)
- 19 - Kober, Frederick P., "Hydrazine-Hydrogen Peroxide Fuel Cell for Underwater Application," Proceedings, 25th Power Sources Conference (1972)