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Hydrogen-Bromine Fuel Cell Advance Component Development

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HYDROGEN-BROMINE FUEL CELL ADVANCE COMPONENT DEVELOPMENT

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SUMMARY

Advanced cell component development is being performed at NASA Lewis to achieve improved performance and longer life for the hydrogen-bromine fuel cells system. The state-of-the-art hydrogen-bromine system utilizes the solid polymer electrolyte (SPE) technology, similar to the SPE technology developed for the hydrogen-oxygen fuel cell system. Our studies were directed at exploring the potential for this system by assessing and evaluating various types of materials for cell parts and electrode materials in a bromine-hydrogen bromide environment and fabricating experimental membrane/electrode-catalysts by chemical deposition.

INTRODUCTION

Future NASA space missions will require long life, high power, and light weight energy storage systems which are beyond the capability of existing systems. The NASA Lewis Research Center is currently involved in assessing and evaluating various types of regenerative energy storage systems for space applications, such as growth space station and unmanned space platforms. The objective of this work is to achieve improved performance, higher energy density, and longer life of electrochemical devices for these space applications. One of the systems being studied is the regenerative hydrogen bromine fuel cell system.

The hydrogen-bromine system is attractive because of the reversibility of the bromine electrode, which allows a single electrochemical unit to be used in both fuel cell and electrolyzer mode.

In the past, others have worked on the hydrogen-bromine system and suggested that one would expect a high round-trip efficiency of greater than 75 percent and an energy density of up to 70 Wh/kg. However, the hydrogen-bromine system currently has some critical technology barriers that must be addressed.

Chemistry and Electrochemistry of Hydrogen-Bromine Fuel Cells

Figure 1 shows a schematic of an aqueous hydrogen-bromine system. During charge (electrolysis), concentrated hydrobromic acid is electrolyzed and bromine is formed at the positive electrode. Hydrated protons are transported across the membrane, and hydrogen gas is formed at the negative electrode. The hydrogen and bromine that are formed during the charge mode are stored external to the cell, and they are fed back to the cell during the discharge (fuel cell) mode to produce electrical energy.

Cell Components

The state-of-the-art hydrogen-bromine system utilizes the solid polymer electrolyte (SPE) technology, similar to the SPE technology developed for the hydrogen-oxygen fuel cell system. Figure 2 illustrates the single cell components which consist of a perfluorosulfonic acid (Nafion) membrane with a fuel cell grade Platinum-black electrocatalyst bonded on the hydrogen side and a Ruthenium electrocatalyst on the bromine side of the membrane. Carbon felt is compressed against both sides of the membrane to allow uniform electrolyte distribution. A thin graphite plate is used as the current collector. All of these components are supported by two Kynar end plates.

Acceptance of the hydrogen-bromine fuel cell as a viable energy storage system for space application depends on its cycle life. An important factor limiting the cycle life of the hydrogen-bromine fuel cell is the degradation of the operating cell materials. These materials are exposed to a highly corrosive bromine electrolyte for long periods of time at elevated temperature.

Bromine diffusion through the Nafion membrane also limits the cycle life. The Nafion membranes would ideally transport only protons or cations and exclude anion provided the solution concentration does not exceed that of the sulfonate in the membrane. Neutral species may diffuse through the membrane depending on their solubility in the membrane. Thus, under ideal conditions in a hydrogen-bromine fuel cell, the hydrogen electro-catalyst will only be exposed to gaseous and ionic hydrogen. In reality, Nafion membranes do not completely prevent bromide ions from migrating across the membrane and adsorbing on the hydrogen electrode. As a result of this, the hydrogen-bromine fuel cell cycle life becomes limited because of the poisoning of the hydrogen electro-catalyst.

Previous electrode and catalyst characterization studies have indicated potential improvements in catalytic activity and stability by using noble metal alloys. Through contractual efforts, alternate Pt alloys which have improved tolerance to bromine/bromide ion adsorption, as compared to Pt-black, have been identified and are being fabricated into an electrode-catalyst structure (ref. 1).

There is considerable advantage to the fabrication of a solid polymer electrolyte in which the electro-catalyst is bonded directly to the surface of the membrane (ref. 2). There are two approaches which have been used. In one case the electro-catalyst material is physically applied to the surface of the membrane in the form of a slurry followed by treatment at elevated temperatures and pressures. The other involves the chemical deposition of the electro-catalyst into and onto the membrane surface. The latter method has been investigated in several laboratories, and our interest has been to study the effect of several variables on the chemical deposition of a platinum black electro-catalyst onto a Nafion type membrane.

In this paper, experimental results of the materials compatibility studies of cell parts and electrode materials and membrane fabrication by chemical deposition will be presented and discussed.

EXPERIMENTAL

Materials Compatibility

The hydrogen-bromine system corrodes most materials. A material compatibility study was carried out to help select adequately resistant materials for electrodes and cell construction.

These materials were assessed and evaluated by visual observations, percent weight loss or gain, and scanning electron microscopy. Two series of tests were conducted, the first series of materials were weighed and immersed into a highly concentrated bromine-hydrogen bromide solution for 30 days and the second series of materials were weighed and immersed into a highly concentrated bromine-hydrogen bromide solution for 6 months.

Static corrosion test. - The first series of sample materials were weighed and placed into a Teflon bottle filled with 10 mL of a 4.4M Br_2/6.0M HBr solution. Each bottle was then closed securely and sealed with Teflon tape to reduced the amount of bromine gas leakage.

Each Teflon bottle was placed into a 1-1/2 inch Teflon coated stainless steel pipe half-filled with water as shown in figure 3. The pipe was then sealed with a stainless steel cap and tightened with a pipe wrench.

The samples were placed into an oven at 80 °C for 30 days. After the 30-day soak test, the samples were then rinsed several times in distilled water to remove the excess bromine. The samples were air dried and reweighed.

The Series 2 static corrosion test followed the same procedure as Series 1, with the exception that the sample materials remained in the bromine solution for 6 months.

Scanning electron microscopy. - The scanning electron microscopy technique was used to investigate the detailed structure of each material before and after being exposed in a bromine environment. This technique provided information on the degree of surface corrosion of each material, which may not be readily noticeable from a visual observation.

Photomicrographs were taken with an Amray 1200B Scanning Electron Microscope (SEM). Samples were coated with platinum using a Polaron E5100 "Cool" Sputter Coater. After the samples were coated they were placed into the vacuum chamber of the scanning electron microscope. Photomicrographs were taken before and after the static corrosion test, with magnifications ranging from 25X to 500X.

ELECTRO-CATALYST-MEMBRANE ASSEMBLY

Materials

Chlorplatinic acid hexahydrate. - $H_2PtCl_6*6H_2O$ was obtained from the Fisher Scientific Company and used without further purification.

Potassium hexachloroplatinate (IV). - K_2PtCl_6, was prepared by dissolving 1.37 g (2.64 mmol) of chloroplatininc acid hexahydrate in 4 mL of water. To this was added 0.546 g (7.32 mmol) of potassium chloride. This mixture was boiled for 15 min, then cooled in ice. The product was filtered, washed with acetone, and air dried. Yield 1.51 g, 89.9 percent based on the manufacturer's platinum assay of the chloroplatinic acid.

Potassium tetrachloroplatinate (II). - K_2PtCl_4 was prepared by dissolving 0.202 g (1.55 mmol) hydrazine sulfate and 1.49 g (3.06 mmol) potassium hexachloroplatinate (IV) in 7 mL of water. This was placed in a water bath at room temperature, and then brought to a boil. Heating was continued for 40 min. The hot solution was filtered and the volume of the filtrate reduced to 5 mL. This was cooled in ice and the product filtered. An additional crop of crystals may be obtained by further reduction of the filtrate, chilling, and filtering. Yield 0.963 g, 75.8 percent based on potassium hexachloroplatinate.

Procedures

In situ platinum (II). - Platinum (II) was generated in situ by pipetting 1 mL of 0.047 M chloroplatinic acid hexahydrate and 0.40 mL of 0.449 M hydrazine sulfate into a 5 mL volumetric flask and diluting to the mark with water. This was heated for 15 min in a boiling water bath to effect the reduction.

Membrane preparation. - The solid polymer electrolyte, Nafion 117 (lot number 5577) was obtained from the Dow Chemical Company. All membranes were pretreated with water at 100 °C for 1 hr, then converted to the H^+-form by treatment with 1 N hydrochloric acid for 1 hr. They were then washed in deionized water until the washings were neutral. When membranes in the K^+- or NH_4^+-forms were required, the membranes in the hydrogen form were treated with 0.1 N potassium hydroxide or 1.0 N ammonium hydroxide, respectively, for 1 hr. They were then washed with deionized water until the washings were neutral.

Fabrication of membrane-electrode assembly. - Membrane-electrode assemblies were prepared using a U-shaped cell as shown in figure 4, in which the membrane could be clamped between the two compartments of the cell. Each compartment of the cell was equipped with a stirrer in order to maintain homogeneous solutions. The platinum containing solution was placed in one compartment and the reducing solution in the other. The deposition time started when the last reagent was added to the cell and was considered complete when all of the platinum was consumed. The reducing agent was always in excess. The platinum was considered consumed when the addition of a drop of a sodium borohydride solution was added to an aliquot of the platinum solution and did not produce a black precipitate or a grey cloudiness.

The membrane-electrode assembly was removed from the cell, rinsed thoroughly with water, and converted to the H^+-form. Loadings were calculated based on the assumption that all of the platinum in the original solution was deposited on the membrane. Typical loadings were 0.6 mg/cm^2.

RESULTS AND DISCUSSION

Materials Compatibility Studies

Table I shows the results of the visual observations of the Series 1 static corrosion test. All materials from Series 1 were exposed to the bromine-hydrogen bromide environment for 30 days. Figure 5 shows the percent weight loss and gain of the materials in Series 1. Polyethylene showed a 68 percent weight gain and Viton rubber showed a 16 percent weight loss. Graphite plate, titanium and tantalum showed less than a 1 percent weight loss. Since these materials along with carbon plate and the coated and uncoated vitreous carbon indicated a very low corrosion rate for the 30 day static corrosion test, they were included in the 6 month static corrosion test. Other materials that were included in the 6 month static corrosion test were reticulated vitreous carbon (RVC), thornel, and carbon felt. Table II shows the results of the visual observations of the Series 2 static corrosion test. Figure 6 showed that all of the materials tested in Series 2 had an increase in weight, with the exception of tantalum and carbon felt.

All materials were examined with an Amray 1200B Scanning Electron Microscope (SEM). Although visual observations indicated that there was no change in the physical structure of some of the materials, it was evident from the photomicrographs that there was corrosion within the surface of some of the materials. Figure 7 shows photomicrographs of reticulated vitreous carbon (RVC) before and after the 6-month static corrosion test. The after RVC sample shows a loss in the surface roughness due to corrosion. Figure 8 shows excessive pitting on the titanium metal sample after 6 months exposure of bromine. Complete removal of the coating of the vitreous carbon can be shown in figure 9.

Electro-Catalyst-Membrane Assemblies

Nafion 117 is a perflourinated polyethylene resin containing pendant sulfonate groups. The pendant sulfonates are bound to the polymer backbone via perfloro-oxyethyl linkages. In the H^+ form after pretreatment with water at 100 °C, the membranes have absorbed 0.28 g of water per gram of dry resin, and the ion exchange capacity of the resin is 0.895 milli-equivalents per gram of dry resin. This corresponds to about seventeen water molecules per sulfonate group which exceeds that needed to solvate the individual cations and anions. Thus in the fully hydrated form the resin contains the very hydrophobic flouromethylene groups and the hydrophillic water and solvated ions. Hsu and coworkers (ref. 3) have shown that the membrane exists as two distinct phases. The hydrophillic phase consists of spherical regions of about 46.5 Å in diameter connected by channels 50 Å long and 10 Å in diameter. The average concentration of sulfonate groups in this phase is approximately 3 molar. It is in this phase and on the surface, that electro-catalyst deposition is likely to occur.

Under study is the chemical deposition of the electro-catalyst, platinum black, into and onto the surface of a Nafion 117 membrane. In the process a solution of a salt of the metal to be deposited, in this case platinum, is place on one side of the membrane and a solution capable of reducing the metal to its zero valent state is placed on the other. The solution component is then allowed to diffuse through the membrane.

In all of our studies hydrazine sulfate at elevated temperatures or sodium borohydride at room temperature was used as a reducing agent. Both of these reagents have been used successfully by other investigators. A series of electro-catalyst depositions were carried out using 0.00095 M chloroplatinic acid as the platinum source. When the membranes were in the H^+-form and 0.2 M sodium borohydride was used, large amounts of hydrogen were evolved. In addition to the deposition of platinum on the surface of the membrane, there was extensive formation of platinum black in the platinum solution, but no platinum black formation in the borohydride solution. When membranes in the K^+-form were used, and the pH of both solutions adjusted to eight with potassium hydroxide, the results were the same as described above except that the hydrogen evolution was diminished. In both cases poorly adhering platinum black films were deposited on the membrane and these could be easily removed. There was no evidence of significant deposition within the membrane.

For cases in which 0.0040 M hydrazine sulfate was used depositions were carried out at 95 to 100 °C, and solutions were at their natural pH's. As in the case of sodium borohydride the platinum deposited on the membrane adhered poorly and could be easily removed, and there was no evidence of deposition within the membrane. The same results were obtained for membranes in the H^+-form and the K^+-form. When hydrazine was used, there was no platinum black formation in either solution.

The presence of platinum black in the platinum solution is evidence that a borohydride derived species capable of reducing the hexachloroplatinate ion passed through the membrane. The absence of a similar precipitate when hydrazine sulfate was used, suggests that hydrazine did not pass into the platinum solution. The deposition of platinum on the platinum solution side of the membrane requires that hydrazine did transverse the membrane, however. The absence of platinum black in the reductant solutions indicates that the hexachloroplatinate ion did not tranverse the membrane, and the absence of platinum black within the membrane itself and its facile removal from the surface of the membrane supports the proposal that the hexachloroplatinate ion did not enter the membrane.

Given these results K_2PtCl_4 0.00076 M in 1 M ammonia was used in the platinum containing cell. This solution was warmed in a boiling water bath for 15 min. The reductant was 0.079 M sodium borohydride and the membrane was initially in the H^+-form. There was no platinum black formation in either solution and a robust electro-catalyst formed on the platinum solution side of the membrane. Next K_2PtCl_4 was used as the platinum source and sodium borohydride as the reductant. The membrane was in the K^+-form and the pH was adjusted to 9. No ammonia was added nor were the solutions heated. Under these conditions extensive platinum black formation occurred in the platinum solution, and there was no deposition on the surface of the membrane. It was not necessary to use platinum (II) salts as the platinum source. Excellent depositions could be obtained using hexachloroplatinic acid, if it was first reduced in situ with a stoichiometric amount of hydrazine sulfate at 55 to 65 °C.

These results are consistent with the proposed model in which the membrane behaves as a cationic exchanger and anions are excluded from the membrane. Therefore, whenever the hexachloroplatinate (IV) anion is the species being reduced, it is excluded from the interior of the membrane and from the surface of the membrane, because of its negative charge. As a result reduction occurs in the bulk solution or near but not on the surface of the membrane. When the tetrachloroplatinate (II) ion is used, similar results are obtained. Spectroscopic examination of aqueous tetrachloroplatinate (II) shows that hydrolysis is slow and would not occur to any appreciable extent during the time of deposition. If, however, tetrachloroplatinate (II) is treated with ammonia at elevated temperatures platinum (II) ammines form which are cationic species. Use of these solutions yielded excellent depositions. If hydrolysis is attempted in the absence of ammonia, the insoluble $PtCl_2$ is formed. Because the hexachloroplatinate (IV) ion is kinetically inert, ammine formation is very slow, therefore, reduction to platinum (II) is required in order to effect suitable depositions. This reduction may also be carried out in situ prior to carrying out deposition on the membrane.

The hydrazinium ion is a dipositive ion and is strongly absorbed by the membrane, as a result there is no platinum deposition in either solution. The tetrahydroborate anion is unstable in all but very basic aqueous solutions. In all probability the actual reductant is a neutral derivative of the borohydride ion.

CONCLUSIONS

Materials compatibility studies have been completed and potentially stable materials have been identified for components fabrication. The acceptable metals thus included titanium for short term usage and tantalum can be used during long term operations. Various types of carbon such as thin carbon plate, carbon felt, and thornel were found to be adequately bromine resistant.

Scanning electron microscopy is a good diagnostic tool that can be used to determine the extent of corrosion.

The chemical deposition of an electro-catalyst onto and into the surface of a solid polymer electrolyte has been carried out with varying degrees of success in these and other laboratories (refs. 4 to 6). The platinum source of choice has been the hexachloroplatinate (IV) ion. The hexachloroplatinate (IV) ion is unlikely to yield acceptable depositions unless it is first reduced to a neutral or cationic platinum (II) species. This need not be a separate operation as described here, but conditions may be such that this process occurs in a single operation. The most common reductants have been sodium borohydride and hydrazinium salts. Our studies have explored several factors which determine the quality of the electro-catalyst deposited. The borohydride ion is not the actual reductant, but rather a derivative which readily passes through the membrane. On the other hand the hydrazinium ion does not pass through the membrane, but is absorbed by it.

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TABLE I. - MATERIALS TESTING SERIES 1

[30 days in 4.0 m Br_2/6.0 m HBr at 80 °C.]

Materials	Observations
Polyethylene	Soft, orange color
Vitreous carbon	Cracked on the surface
Coated vitreous carbon	Cracked on the surface
Viton rubber	Gray color
Carbon	No change
Graphite	No change
Titanium	No change
Tantalum	No change
Polysulfone	Decomposed
Karbated graphite	Brittle

TABLE II. - MATERIALS TESTING SERIES 2

[6 months in 4.0 m Br_2/6.0 m HBr at 80 °C.]

Materials	Observations
RVC	No change
Titanium	Black color
Graphite	No change
Thornel	Brittle
Carbon	No change
Vitreous carbon	Swollen, brittle
Coated vitreous carbon	Swollen, brittle
Tantalum	No change
Carbon felt	No change

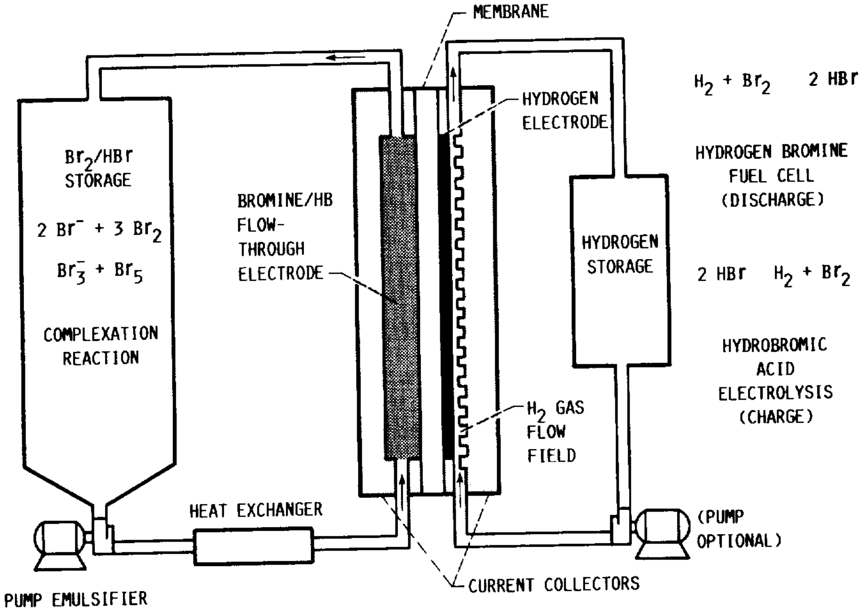


FIGURE 1. - SCHEMATIC OF HYDROGEN BROMINE ENERGY STORAGE SYSTEM.

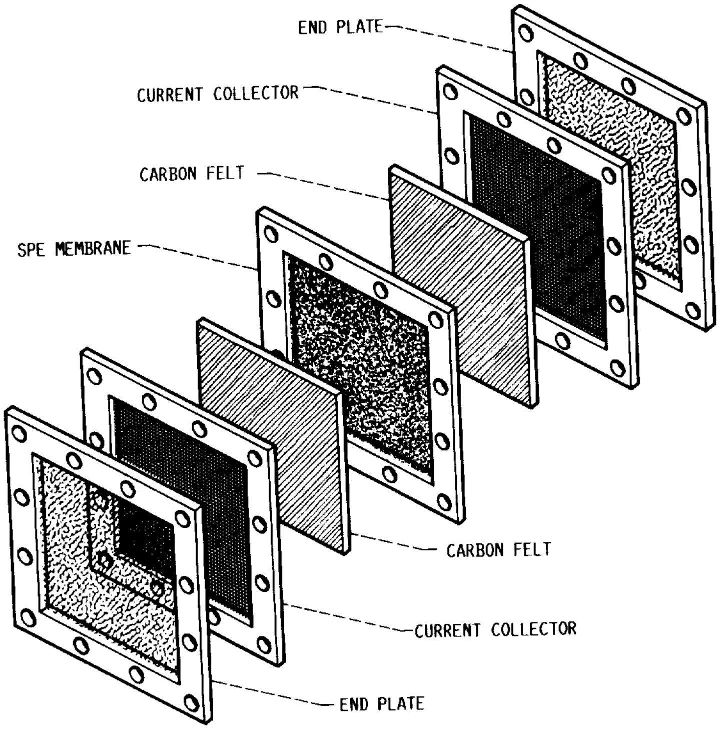


FIGURE 2. - HYDROGEN BROMINE SINGLE CELL COMPONENTS.

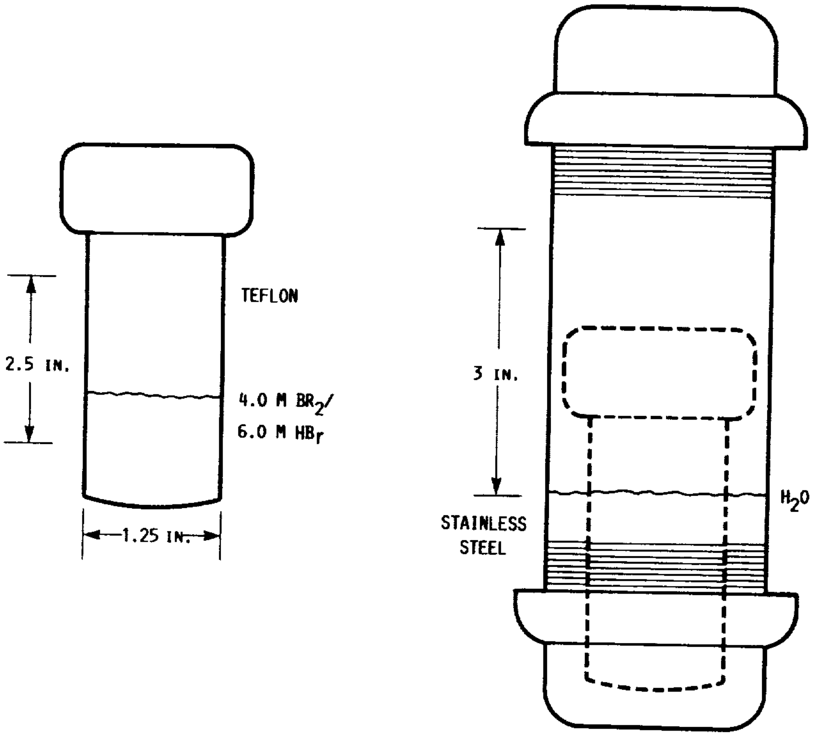


FIGURE 3. - STATIC CORROSION APPARATUS.

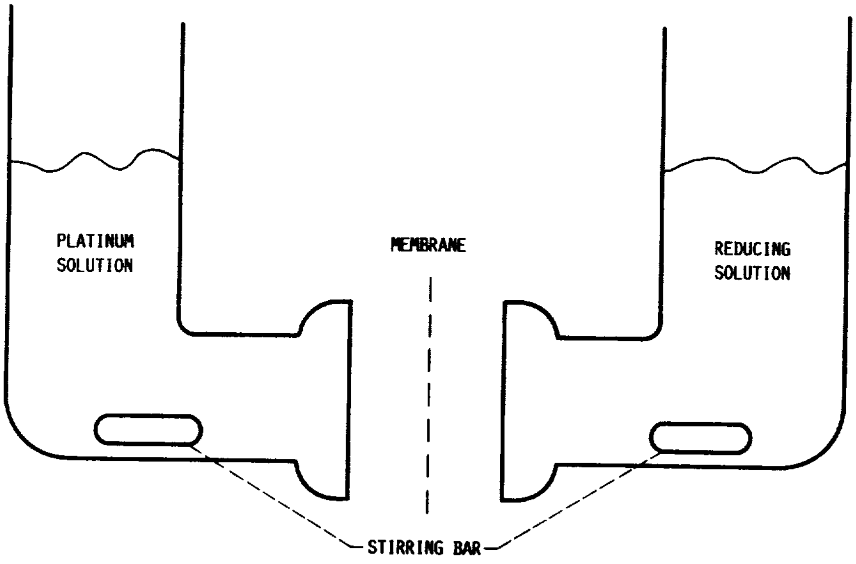


FIGURE 4. - ELECTRO-CATALYST DEPOSITION CELL.

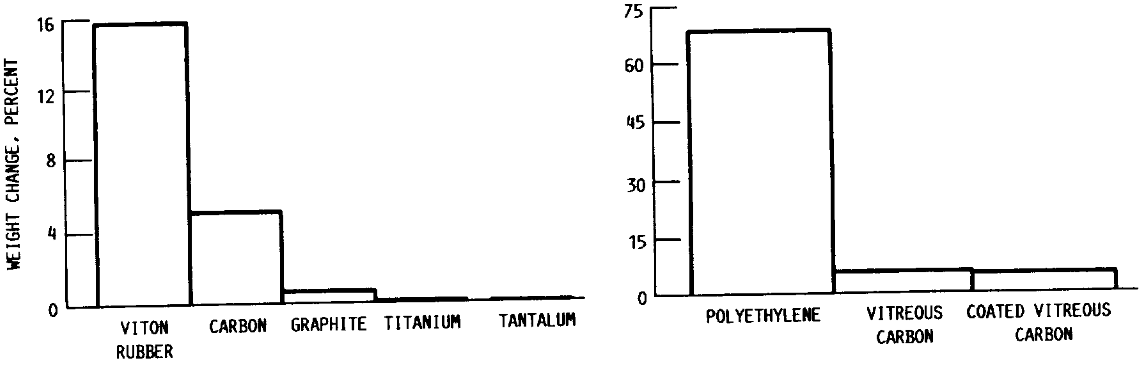


FIGURE 5. - SERIES 1 PERCENT WEIGHT LOSS/GAIN.

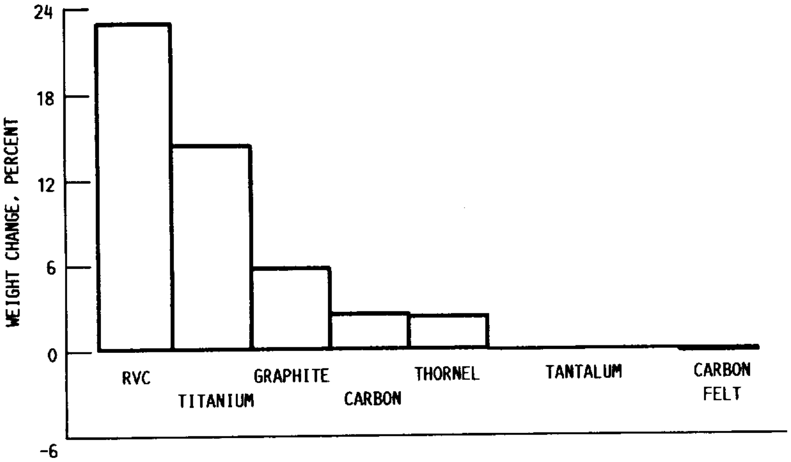


FIGURE 6. - SERIES 2 PERCENT WEIGHT LOSS/GAIN.

BEFORE

AFTER

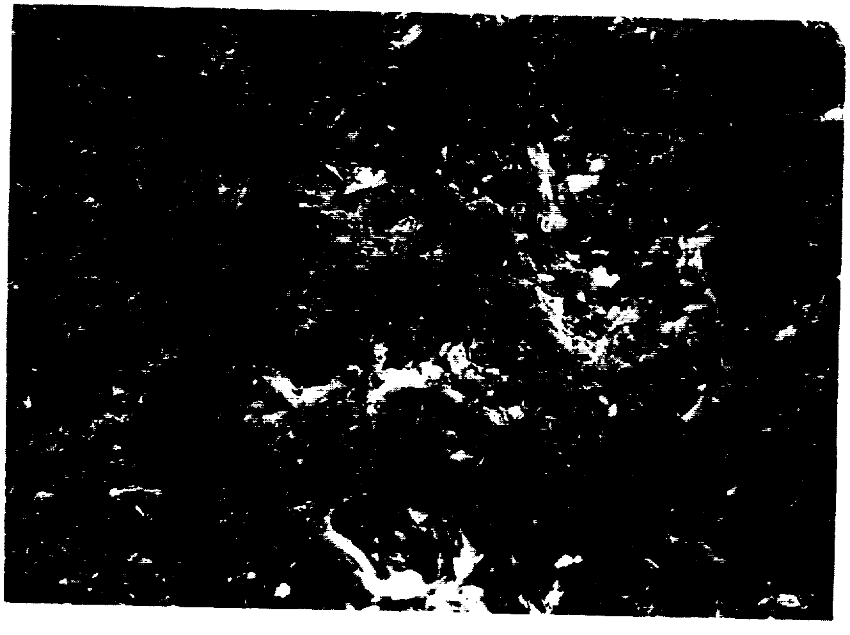
FIGURE 7. - SEM PHOTOMICROGRAPHS OF RETICULATED VITREOUS CARBON (RVC) BEFORE AND AFTER 6 MONTH STATIC CORROSION TEST.

BEFORE

AFTER

FIGURE 8. - SEM PHOTOMICROGRAPHS OF TITANIUM BEFORE AND AFTER 6 MONTH STATIC CORROSION TEST.

BEFORE



AFTER

FIGURE 9. - SEM PHOTOMICROGRAPHS OF COATED VITREOUS CARBON BEFORE AND AFTER 6 MONTH STATIC CORROSION TEST.

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16. Abstract

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