

TITANIUM AND ZIRCONIUM AS ELECTRODES  
FOR PRIMARY CELLS

by

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A THESIS

submitted to

OREGON STATE COLLEGE

in partial fulfillment of  
the requirements for the  
degree of

DOCTOR OF PHILOSOPHY

June 1958

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Date thesis is presented June 28, 1957

Typed by Clara Homyer

## ACKNOWLEDGMENT

I wish to express my appreciation to Dr. Allen B. Scott for his helpful suggestions and constant inspiration throughout this project. My association with Dr. Scott has been a worth-while and valuable experience.

I would like to thank Dr. W. J. Kroll for his financial assistance and valuable suggestions in behalf of this project.

I would also like to acknowledge the following companies for generously supplying materials necessary for the completion of the project: Titanium Metals Corporation of America for titanium samples; the National Carbon Company of the Union Carbide Corporation for the depolarized carbon electrodes; the Burgess Battery Company for carbon electrodes; the Foote Mineral Company for the Iodide process zirconium, and the Carborundum Metals Company for the Kroll process zirconium samples.

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TITANIUM AND ZIRCONIUM AS ELECTRODES  
FOR PRIMARY CELLS

I. INTRODUCTION

Titanium and Zirconium were both discovered well over 100 years ago, but their usefulness and potential has only begun to be fully realized within the past 30 years. The discovery of titanium is credited to W. Gregor (19), a priest in Cornwall, England, who in 1791 found a black sand in a valley of his parish which he described as being much like gunpowder in appearance. He concluded from his examination that the sand was composed of oxides of iron and a new metal. The discovery went almost unnoticed until 1797 when M. H. Klaproth (24) identified the oxide of this unknown metal with that which he had extracted from rutile of Boinik, Hungary. Klaproth applied the name "titanic earth" with reference to the Titans, the fabled giants of ancient mythology, and hence the name titanium.

Klaproth (25) also played a role in the discovery of zirconium. In 1795 he reported that in analyzing the zircon of Ceylon he found that it contained 68% of a mineral differing from any known to him. He called this zirkonerde. In 1797, Guyton (20) published his analyses of zircons from various localities, confirming the work

of Klaproth.

Titanium, although relatively unfamiliar until recently, is actually one of the more abundant elements, comprising approximately 0.63% of the earth's crust. It is the ninth most plentiful element and the fourth most plentiful metal, aluminum, iron, and magnesium being more common (10, p. 20). Although 0.63% may seem insignificant, when compared with percentages of other common metals such as copper - 0.01%, nickel - 0.02%, zinc - 0.004%, and lead - 0.002%, it is seen that it is indeed plentiful. Titanium occurs mainly as ilmenite ( $TiO_2 \cdot FeO$ ) and rutile ( $TiO_2$ ) in either sand or rock deposits. Large deposits are found in India and Canada, but it has an extremely widespread distribution, being found in varying amounts in such places as deep sea dredgings, coals, volcanic dust, meteorites, the atmosphere of the sun and some stars, the water from the Danube River, in organic matter such as oak wood, cotton seeds, and the bones and flesh of men and lower animals.

Zirconium is somewhat less abundant than titanium, but is still more plentiful than copper, lead, nickel, and zinc. The zirconium content of the earth's crust is estimated to be 0.026% (10, p. 20) which places it eleventh among the elements and seventh among the metals. The most common mineral containing zirconium is the silicate,

known as zircon ( $ZrSiO_4$ ). The main zircon deposits, which are usually found as or with black sands, are found in the United States and Australia. Zirconium also occurs as the oxide ( $ZrO_2$ ), known as baddeleyite. The main deposits of this mineral are found in Brazil. Zirconium, as titanium, has been found in certain waters, meteorites, and the solar spectrum.

Both titanium and zirconium metals are produced by chlorinating the oxide ore, and then reducing the tetrachloride with sodium or magnesium. Somewhat purer metal can be produced by introducing crude titanium or zirconium and iodine into an evacuated bulb and heating to form a volatile titanium tetraiodide, which is decomposed to titanium and free iodine by a hot filament. The metal deposits on the filament and the free iodine reacts with more crude titanium. The main impurities occurring in titanium are iron, carbon, oxygen and nitrogen (1, p.1-12) while those in zirconium are aluminum, titanium, iron, nitrogen, oxygen and hafnium (34, p. 15-85). Titanium, zirconium and their compounds find many and varied uses, particularly as structural materials and in high temperature alloy systems. Properties which make them useful in these fields are their densities which are 4.5g/cc and 6.5g/cc, respectively, as compared with that of iron, 7.8g/cc and their melting points of 1800° and

1845° as compared with that of iron, 1530°. Both metals are quite strong and corrosion resistant. Titanium compounds are used for paint pigments, dyes, refractory materials, smoke screens, incandescent filaments, abrasives, gem stones, additives for quick drying cement, catalysts, and nitrogen fixation. Zirconium compounds find application in incandescent filaments, gas mantles, reduction of metals, electric furnace electrodes, refractory materials, glass, abrasives, dyes, and gem stones.

It has been suggested that titanium or zirconium might find additional application as an electrode in a battery (28). The purpose of this research was to explore this possibility. In order to make the research somewhat better defined, it was agreed that the primary goal should be to explore the possibility of using either of these metals as the anode in a primary battery; however, other possibilities were not ignored if they appeared to hold some promise. In this discussion, "anode" will refer to the electrode where oxidation occurs, and "cathode" to the electrode where reduction occurs. The project is an exploratory one and is the first investigation of this type to be conducted in this laboratory.

A literature search revealed that very little work of this type has been conducted on these metals, and only

a limited amount of related work has been done. Schlain (37), in connection with corrosion studies, determined steady state values of single electrode potentials for titanium in sodium chloride, hydrochloric acid, sulfur dioxide, and sulfuric acid electrolytes. He also determined the potential of various galvanic couples in 3% sodium chloride, and the effect of dissolved metal on the titanium potential in 1 N hydrochloric acid. He found that it required from 25 to 309 hours to reach a steady state potential and that, of the electrolytes studied, 7.5 N hydrochloric acid gave the best anodic potential,  $-0.37$  V, as compared with a standard hydrogen electrode. The best galvanic couple was obtained with magnesium in which about eleven miliamps were obtained and the titanium was cathodic. He also found that 2 mg per liter of cuprous ion will passivate titanium in hydrochloric acid up to a concentration of 5 N, and that more noble metal ions in 1 N hydrochloric acid cause larger increases in titanium electrode potentials. Straumanis and Chen (40) found that the potential of titanium in hydrofluoric acid is approximately  $-0.77$  V and in the presence of ammonium fluoride, it is about  $0.95$  V. A United States patent (31) has been issued for a highly porous titanium, coated with manganese dioxide or some other depolarizing or conducting substance, for

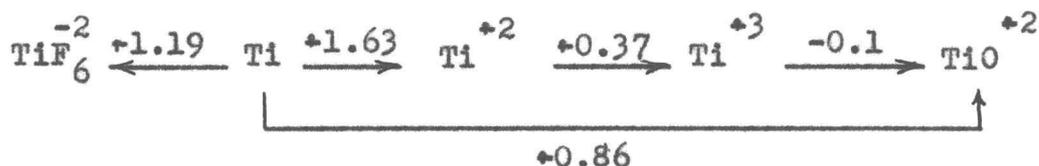
use as an electrode in a primary cell. The electromotive force measured against zinc in the usual LeClanché electrolyte is 2.1 V. By coating the titanium mass with silver, it can be made the cathode in a cell with a 70% potassium hydroxide electrolyte and an amalgamated zinc anode. The potential of this cell is 1.95 V, and heavy currents can be drawn without depolarization.

Straumanis and Chen (41), in connection with their investigation on the rate and mechanism at which titanium dissolves in hydrofluoric acid solutions, have also reported that the open circuit potential of titanium in hydrofluoric acid became more anodic (negative) as the concentration of the acid increased from 0.0125 N to 0.2 N. Above 0.2 N the potential became nearly constant at -0.768 V as compared with a standard hydrogen electrode.

Several attempts have been made to determine the standard oxidation potential of titanium. The first was by Botts and Krauskopf (6) who measured potentials of titanium in 0.25 M titanous sulfate and 0.25 M titanous chloride solutions. They obtained values of +0.13 V and +0.23 V, respectively. Since activity coefficients of the solutions are not known, the standard potentials of titanium in both solutions were calculated by means of change in concentration. The results they obtained were

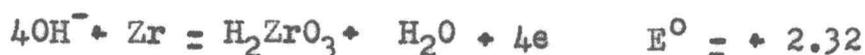
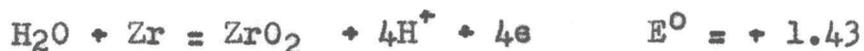
+0.168 V and +0.218 V, respectively. These values are considerably smaller than expected. Satoh and Yamane (36) repeated the experiment in 0.0215 M titanous sulfate and obtained a value for the standard electrode potential of +0.355 V. This is larger than the earlier value but still smaller than expected. These authors have also calculated a value for the titanium-titanous couple using thermodynamic data for titanous chloride and have obtained a value of +1.30 V. Using this value, they then obtain a value of +0.99 V for the titanium-titanic couple. As a result they place titanium between aluminum and manganese in the electrode potential series.

Latimer (29, p. 269) has made some calculations of standard oxidation potentials of titanium and zirconium in various solutions based on the thermodynamic data, much of which has been estimated, of Bichowsky and Rossini (3, p. 101-102). A summary of some of the more pertinent values is given below:



The large discrepancy between the theoretical and actual values of the titanium couples is attributed to the irreversible nature of titanium. Latimer has also calculated values for various zirconium couples with the

following results:



Of considerable interest in the investigation of electrode phenomena is polarization. This is defined as the difference between the reversible potential of an electrode and the potential actually measured. Polarization is generally divided into two main types, concentration polarization and overvoltage. Concentration polarization is caused by a concentration change of the electrolyte at the two electrodes. As current is drawn, the cell will essentially produce a concentration cell and the direction of the potential will be opposite to the electromotive force normally produced; and, therefore, the working voltage of the cell will be reduced. This effect can be eliminated by stirring the electrolyte to maintain a uniform concentration at both electrodes. Overvoltage, sometimes simply called polarization, is a resistance or back electromotive force set up at the electrode due to the formation of some insoluble product when current is drawn.

Several workers have investigated the polarization

of titanium and zirconium in various solutions. Hall and Hackerman (22) investigated the charging process on anodic polarization of titanium in 0.05 M sodium chloride. They reported that the increase in polarization is proportional to the quantity of electricity passed and, therefore, to the amount of oxygen deposited on the surface; but that the decay and repolarization are not simply a function of the amount of oxygen deposited. They conclude that two processes are involved: (1) the anodic deposition of oxygen on the titanium surface, and (2) the charging of an electrical double layer. The original polarization requires a charge 360 times the charge for repolarization. This is attributed to a change produced on the surface which is not reversed by standing on open circuit. This irreversible change can best be explained as a layer of chemisorbed oxygen. It is calculated that there are three oxygen atoms for each titanium atom, corresponding to a monolayer of oxygen the same size as covalently bonded oxygen. At higher current densities, more  $\text{TiO}_2$  is formed. When oxygen evolution stops, all current is available to make  $\text{TiO}_2$ . Titanium migrates to the surface and the  $\text{TiO}_2$  layer thickens. The anodic potential versus current density of titanium in the cell  $\text{Ti}/\text{HF}, \text{NH}_4\text{F}/\text{Pt}$  has been measured for high concentrations of the acid (39). For solutions of 4 N acid with

various amounts of  $\text{NH}_4\text{F}$  added, it was found that the empirical equation  $\eta = -(a + b \log i)$ , first proposed by Tafel (42), was followed where " $\eta$ " is the overvoltage, "a" and "b" are constants, and "i" is the current density. The increase in overvoltage is attributed to an increase in the "a" term. The same author reports that titanium becomes less positive with time in hydrochloric acid, sulfuric acid, and hydrofluoric acid solutions with ammonium fluoride added. This is different from many other metals. Straumanis and Chen (41) also reported that the potential of titanium in hydrofluoric acid became less positive with time.

Less work has been done on the polarization of zirconium although at least two investigations have been made. Maragluni (32) studied the anodic polarization of zirconium and zirconium alloys over a range of current densities between 0.5 and 2000  $\mu\text{a}/\text{cm}^2$  in hydrochloric acid, potassium chloride, sodium carbonate, and sodium sulfate. Potential-time measurements were made in the absence of an external current. He observed two types of curves depending on whether or not chloride ion was present. Hackerman and Cecil (21) studied the cathodic polarization of zirconium in neutral salt solutions over a range of current densities from .0035 to 3500  $\mu\text{a}/\text{cm}^2$ . In plotting the polarization versus the log of the

current density, two waves were found. The lower one was attributed to oxygen going to a hydroxide ion and the upper one, which was above  $200 \mu\text{a}/\text{cm}^2$ , was attributed to hydrogen ions forming hydrogen gas.

A considerable amount of work has been done on the general measurement and interpretation of polarization (4, 5, 7, 8, 9, 14, 15, 17, 27, 30, 38, 42, 43). To summarize briefly, there are two separate methods by which polarization can be measured (11, p. 481-484). In both a direct current is passed through the electrode in such a way that the titanium is oxidized or reduced depending on whether anodic or cathodic polarization is being investigated. In this study anodic polarization was of interest, so the current was passed in such a way that the titanium or zirconium was oxidized. In the direct method of investigating polarization, the potential of the electrode is measured with respect to a calomel half-cell while the direct current is flowing. In the commutator method, the potential of the electrode is measured with respect to a calomel half-cell a short time after the direct current has stopped. It has been shown that both methods give the same result if careful measurements are made. Polarization is caused by two or possibly three separate resistances: an IR drop through the solution, the resistance caused by the formation of some polarization

product on the electrode; and it has also been suggested that there might be a resistance at the electrode-electrolyte interface in the nature of a "transfer resistance." This "transfer resistance" was supposedly of an IR nature, and the commutator method was developed to investigate this cause of polarization. Since the current is not flowing when the potential is measured, there can be no IR included in the measured value. However, it has been shown that the true polarization drops very rapidly when the current stops. Those that support the direct method maintain that a portion of the true polarization has disappeared before the measuring instruments used in the commutator method can detect it. A continuing controversy has taken place over the existence and nature of this "transfer resistance", and the major effort for the last 50 years has been to develop and perfect equipment and methods that would decide which of the two methods gives the true value for polarization. Oscillographic methods were developed which would trace the polarization decay curve after the current was stopped. If part of the polarization were a "transfer resistance" or IR drop there should be a vertical drop in the polarization curve immediately when the current is stopped. No such drop was found. Further, instruments were developed which would separately measure the IR drop

across the solution, the decay potential of the electrode, and both simultaneously. It was found that the only vertical drop in the decay curve corresponded to the IR drop across the solution and that there was no IR drop corresponding to a "transfer resistance." It has also been shown that the overvoltage apparently consists of two parts; when the circuit is first opened there is a part that drops very rapidly and the remainder then drops more slowly. This second part, i.e. the part which drops slowly, is independent of the current density for any metal (13). The following points can be established concerning overvoltage measurements: (1) The commutator method, using brushes, contains inherent errors; (2) the commutator method gives identical values with the direct method if sufficient time is allowed for the charging potential to reach a maximum stable value; (3) the overvoltage decay curves are different for different metals; (4) there is no "transfer resistance" polarization in oxygen or hydrogen overvoltage on any ordinary metals up to  $30 \text{ ma/cm}^2$ , and (5) decay curves depend only upon current density and not on the quantity of electricity passed after the maximum potential has been reached.

Two different mechanisms have been proposed to explain the observed cathodic overvoltage curves. The first suggests that a double layer is built up at the

electrode-electrolyte interface. Investigators differ as to the exact mechanism for the double layer, but it is supposed to be in the nature of a condenser. This theory is based on the assumption that cathode potential-time curves are linear. The second mechanism, proposed to explain non-linear curves, suggests that hydrogen ions are discharged and the hydrogen atoms formed reionize immediately building up a back potential that eventually becomes equal to the applied potential and passivation occurs. The theories agree in postulating a slow step in the electrode reaction, which requires the surmounting of a considerable potential energy barrier. For a charged particle the applied electromotive force serves to lower the energy barrier.

A considerable amount of work is presently being carried out to explain the exact nature of polarization. The problem is complicated by such side effects as a corroding electrode, local action currents, concentration polarization, and by possible changes in the predominant electrode reaction.

Other factors that effect overvoltage and which are at least partially controllable include electrode material, purity of electrode, the electrolyte, condition of electrode surface, and the current density. An increase in temperature may raise, lower, or not effect

the overvoltage. An increase in acid strength usually decreases the overvoltage because of a breakdown in the polarization product. In general, overvoltage increases with time while the current is flowing. Depolarizers, which are materials that will remove the polarization product, have a marked effect on the overvoltage. Small amounts of poisons and colloidal material may markedly increase the overvoltage. A superimposed alternating current and ultra violet light will decrease the overvoltage.

In the investigation of electrode-electrolyte relations, corrosion plays an extremely useful and important role. Corrosion is, itself, an electrochemical phenomenon and furnishes a great deal of information on possible electrode-electrolyte combinations. Because of their importance as structural materials, many investigations have been conducted on the corrosive properties of titanium and zirconium (1, 18, 34, 37, 39, 41). Both metals are extremely corrosion resistant. Titanium, for instance, is resistant to nitric acid, sulfurous acid, and solutions of inorganic chlorides. It is corroded by sulfuric acid above 5%, mixtures of sulfuric acid and nitric acid (although the addition of the nitric acid slows the corrosion rate), hydrochloric acid above 5%,

phosphoric acid above 30%, all concentrations of hydrofluoric acid, hot concentrated ammonium chloride, and certain organic acids.

Titanium is similar to stainless steel in that when other metals are in contact with titanium, the other metal will corrode; or, in other words, the titanium becomes cathodic. A notable exception is a titanium-aluminum couple in sulfuric acid. In this case, the titanium is anodic and corrodes. Various additives will effect the rate of corrosion of titanium in various solutions. Cupric ions will passivate titanium in hydrochloric acid. The following metal ions will increase the rate of corrosion of titanium in hydrofluoric acid and the rate of increase becomes larger in the order listed; ferrous, nickel, silver, cupric, gold, and platinum. Magnesium has no effect on the rate, and lead and ammonium fluoride slow the rate of dissolving. Ammonium fluoride, on the other hand, increases the rate of dissolution in hydrochloric and sulfuric acid probably because of the formation of hydrofluoric acid. After a large amount of ammonium fluoride has been added to sulfuric acid, the rate suddenly decreases very rapidly indicating passivation of the titanium. The passivation is reportedly due first to the formation of a yellow film of  $\text{[TiF}_6\text{]}^-$  and then at constant potential to a colorless

$\text{TiF}_6^{=}$  film. Various stresses placed on the metal will cause an increase in corrosion.

The corrosion properties of zirconium are quite similar to those of titanium. Like titanium, it is resistant to nitric acid, sulfurous acid, and most inorganic chlorides. In addition, it is resistant to phosphoric acid, hydrochloric acid, organic acids and strong bases. It is attacked by sulfuric acid above 80%, hydrofluoric acid, slowly by aqua regia, chlorine in water, ferric chloride, and cupric chloride. No report was found on corrosion inhibitors for zirconium.

Based on the previous information, a project was undertaken to determine the suitability of titanium and zirconium as anodes in a primary battery. The properties of a good electrode are based, to a large extent, on the electrolyte in which it is used. Therefore, various electrolytes were investigated to determine their suitability (1) to give a satisfactory voltage with the titanium or zirconium, (2) to cause corrosion of the electrodes only when current is drawn, (3) to cause the electrode to follow Faraday's Law when current is drawn, (4) to cause the voltage to remain high when current is drawn, and (5) not to cause an appreciable change in the voltage characteristics when the electrode is inoperative for some time.

Various possible improvements over existing systems were sought during the investigation. These included any improvements in the characteristics of the electrode in the electrolyte just mentioned as well as possible improvements in high or low temperature coefficient of the voltage or in the size limitations of the system. It is realized that the economics of a battery are quite important in the acceptance of a system for general use and that the system must either be less expensive or include some desirable characteristic that would justify an additional cost over existing systems. The present cost of titanium and zirconium is about \$20 to \$25 a pound and not competitive with zinc at about \$1.50 a pound, even if consideration is taken of the fact that for an equivalent amount of electricity, the weight of zinc required is about one and a half that of zirconium and nearly two and a half times the weight of titanium. However, as titanium and zirconium come into more general use, and as production methods are improved, the cost will certainly be reduced. If the titanium or zirconium system has certain improved characteristics over the zinc system, there is certainly a good possibility that it can become a competitive system in the future.

The method by which this problem was approached is as follows: Commercially available sheets of titanium

were obtained from Titanium Metals Corporation, and of zirconium from the Carborundum Company. Using small pieces of these as the electrodes, an investigation was made of various possible electrolytes in which the metals might behave ideally as anodes with a good voltage. Based on corrosion data from the literature and some additional data from the laboratory, the potentials of the metals in various electrolytes opposite several cathodes were obtained on open circuit and with various loads.

Investigations were made to determine if the metals followed Faraday's Law in the electrolytes which showed some promise. Information was then obtained on the polarization of the metals in the various electrolytes by measuring the single electrode potentials at various current densities of the metals using a 1 N calomel half-cell as a reference electrode.

Information was also obtained as to the nature of the polarization by making X-ray diffraction measurements of the polarization products obtained in the Faraday Law measurements and also the products obtained by drawing current from a cell using the metals as an anode. Investigations were also conducted on possible cathodes that would be satisfactory opposite the metals and in the electrolyte which appeared most satisfactory. Finally, actual cells were made using titanium tubing as the anode,

and the characteristics of these cells were examined.

The order in which these investigations are discussed is not necessarily the order in which they were conducted because as new information was obtained many experiments were repeated with slight modifications. The investigations of the two metals were conducted on a roughly parallel basis, although titanium has shown more promise and more emphasis was placed on it near the conclusion of the study.

## II. EXPERIMENTAL RESULTS

The investigations of the two metals were conducted using identical methods; however, the results are essentially independent and thus will be reported independently.

### Titanium

#### A. Corrosion

The corrosion properties of titanium as found in the literature have been discussed in the introduction. Based on this information, the following were given considerable attention as possible electrolytes; phosphoric acid, hydrofluoric acid, oxalic acid, ammonium fluoride, trichloroacetic acid, and sodium hydroxide. An electrolyte was wanted which would corrode the metal when current is drawn, but would not corrode it when the metal was simply standing in the electrolyte. For the ones that do not corrode the metal, it was thought that corrosion might be induced by making a galvanic couple and drawing current. For those substances that do cause corrosion, it was thought that they might make a satisfactory electrolyte if they were used at concentrations slightly lower than that which would cause corrosion. It was thought that in the case of electrolytes, such as

hydrofluoric acid, that will corrode titanium at all concentrations, the addition of certain additives might eliminate corrosion when no current was drawn.

The most significant fact noted was that ammonium fluoride appreciably slows the corrosion rate of titanium in hydrofluoric acid. This has been noted in the literature and was reconfirmed in the laboratory.

Two pieces of titanium of approximately equal weight and surface area were placed in solutions of 0.2 N hydrofluoric acid, and 0.2 N hydrofluoric acid with 4% ammonium fluoride added. The titanium lost 10.3% of its weight in the hydrofluoric acid, but only 0.55% in the acid with the ammonium fluoride added in an equal time. In both cases a black coating was formed on the surface of the titanium; but in the solution containing the ammonium fluoride, the coating appeared to be more dense. In both cases a gas was given off when the metal was placed in the acid, but it appeared to stop after a short while in the solution containing ammonium fluoride.

When titanium was placed in 0.2 N hydrofluoric acid and allowed to completely dissolve, an oily yellow material was formed. Titanium tetrafluoride has been reported as both an oily yellow (33, p. 66) and as a white powder (23, p. 538). There was some doubt as to the actual identification of the oily yellow material

reported, but it is probably a hydrated titanium tetrafluoride.

In studying rates at which titanium will dissolve in hydrofluoric acid, it was found that titanium went to the trifluoride (41). This was determined by titration of the product with potassium permanganate and by measuring the volume of hydrogen evolved. Titanium trifluoride is a water soluble violet or red compound. There is apparently a contradiction as to what occurs when titanium dissolves in hydrofluoric acid. Additional information concerning the corrosive properties of titanium was obtained in connection with Faraday's Law measurements and will be reported in that section.

#### B. Galvanic Cell Potentials

In order to obtain considerable information rapidly on the behavior of titanium-metal couples in various electrolytes, a series of galvanic cells were set up in open beakers and their characteristics noted. The electrolytes used were those indicated above. The measurements were made at room temperature, approximately 25°, using a student potentiometer. Both titanium and the other electrode were rubbed with emery paper to remove possible surface contamination before immersing in the electrolytes. The electrolytes were stirred to

prevent any concentration polarization.

The size of both the titanium and the other electrode was approximately 1 cm. by 3 cm. and about 100 ml. of electrolyte were used. Resistances of one and 12 ohms were placed across the electrodes and the circuit was closed. The voltage changes were noted. The 12 ohm resistance was subsequently replaced by a 10 ohm resistance.

In all cases, the cells were allowed to stand for at least several hours or until the open circuit voltage became constant. In some cases, various substances were added to the electrolyte; and their effects on the cell potential were noted. The results are shown in Table I. The additives indicate materials added in an attempt to improve the voltage characteristics.  $V_0$  is the initial open circuit voltage,  $V_c$  is the constant open circuit voltage which was attained in time T.  $V_1$  and  $V_{12}$  are the initial voltages with a one ohm and 12 ohm load across the cell, respectively. In all cases the titanium assumed a negative polarity except with aluminum in  $H_3PO_4$ , copper in 85%  $H_3PO_4$  when the load was across the cell and initially with lead in 75%  $H_3PO_4$ .

TABLE I

GALVANIC CELL POTENTIALS FOR TITANIUM AND ANOTHER  
ELECTRODE IN VARIOUS ELECTROLYTES

<u>Electrolyte</u>	<u>Additives</u>	<u>Electrode</u>	<u>V<sub>o</sub>,</u> <u>Volts</u>	<u>V<sub>c</sub>,</u> <u>Volts</u>	<u>T,</u> <u>Hours</u>	<u>V<sub>1</sub>,</u> <u>Volts</u>	<u>V<sub>12</sub>,</u> <u>Volts</u>
85% H <sub>3</sub> PO <sub>4</sub>		Al	0.4526	0.0530	25		0.005
"	CrO <sub>3</sub>	Al					0.010
"	"	C					0.001
"	"	Pb					0.00
"	"	Cu					0.00
"	"	Zn					0.395
75% H <sub>3</sub> PO <sub>4</sub>		Stainless Steel	0.5175	0.3770	1/3	0.001	0.003
"		Cu	0.2465	0.6120	4	0.0008	0.005
"		C	0.4825	0.8475	36	0.0002	0.002
"		Al	0.3595	0.1075	6	0.0002	0.011
"		Pb	0.2210	0.0979	3 1/2	0.0005	0.003

TABLE I - Continued

<u>Electrolyte</u>	<u>Additives</u>	<u>Electrode</u>	<u>V<sub>0</sub>, Volts</u>	<u>V<sub>c</sub>, Volts</u>	<u>T, Hours</u>	<u>V<sub>1</sub>, Volts</u>	<u>V<sub>12</sub>, Volts</u> <u>10 ohms</u>
8% NH <sub>4</sub> F		C:MnO <sub>2</sub>	0.7900	0.8200	1/4	0.003	0.020
"	CrO <sub>3</sub>	"	0.7800			0.010	0.100
3.5% HCl		"	0.97	1.01	1/6	0.010	0.110
5% HCl		"	0.74	1.06	1/6	0.005	0.025
(Sat) Oxalic Acid		"	0.65	0.60	1/6	0.005	0.080
10% Trichlor- acetic Acid		"	0.59	0.40	1/6	0.005	0.025
20% NaOH		"	1.28	0.93	1/6	0.003	0.035
3% N <sub>4</sub> Cl		"	0.79	0.65	1/6	0.003	0.003
0.2 N HF*		"	0.59	1.05	1/4	0.013	0.120
" *	1% NH <sub>4</sub> F	"	1.14	1.06	1/6	0.045	0.310
" *	"	"	1.43	1.43	-	0.010	0.490
0.1 N HF*		"	0.86	1.43	1/12	0.002	0.030 <sub>Ω</sub>

TABLE I - Continued

<u>Electrolyte</u>	<u>Additives</u>	<u>Electrode</u>	<u>V<sub>o</sub>,</u> <u>Volts</u>	<u>V<sub>c</sub>,</u> <u>Volts</u>	<u>T,</u> <u>Hours</u>	<u>V<sub>1</sub>,</u> <u>Volts</u>	<u>V<sub>12</sub>,</u> <u>Volts</u>
0.1 N HF*	1% NH <sub>4</sub> F	C:MnO <sub>2</sub>	1.43	1.45	1/12		0.025
" **		"	1.19	1.13	1/12	0.037	0.280
1 N HF		"	1.37	1.04	1/4	0.12	0.600
0.5 N HF		"	1.15			0.065	0.400
0.1 N HF		"	1.05			0.035	0.250
0.05 N HF		"	1.02			0.020	0.200
0.01 N HF		"	0.47			0.003	0.015

\* From NaF + HCl

\*\* This and subsequent HF from KF + HCl

### C. Faraday's Law Measurements

When an electric current passes through a solution, certain chemical processes take place at the electrodes, such as the liberation of a gas, the deposition of an element, the formation of a product such as an oxide or a salt, or the dissolution of the electrode. The same is true for a cell from which current is drawn. Faraday was the first to measure these chemical effects of the electric current quantitatively and, in so doing, discovered the laws which govern these processes (12, p. 156). These laws now bear his name and can be given in the single statement that the number of equivalents of any substance liberated or deposited at an electrode is exactly proportional to the quantity of electricity which passes across the metal - solution junction. This law was found to be true, irrespective of the shape of the electrode, the temperature, the rate at which the electricity is passed, or the electrolyte.

The quantity of electricity found necessary to deposit or liberate one equivalent is 96,494 coulombs. Usually, more than one reaction is possible at a single electrode; and, occasionally, more than one process will occur. In this case, one of the reactions usually takes place to a lesser extent. If this secondary reaction is

unknown or uncompensated for in the measured reaction, it will appear that Faraday's Law is not exactly followed.

In a galvanic cell, the normal reaction of the anode is to oxidize and form a salt which is soluble in the electrolyte. Other possible anode reactions might be the formation of a gas such as oxygen, or the formation of an insoluble salt or oxide. If an insoluble salt or oxide is formed, it may coat the electrode causing a change in the electrode process that originally occurred. This insoluble coating is likely to cause a high resistance at the electrode surface or, perhaps, set up a back electromotive force, either of which would appreciably reduce the voltage of the cell. The electrode is then said to be "polarized." If the anode forms a single product upon oxidation, and if the measured effect follows Faraday's Law, it is said to be ideal. By the use of Faraday's Law, the actual anode process may be determined, or at least the oxidation state to which the metal goes. The actual oxidation process is dependent upon the current density, which is defined as the current per unit area of electrode surface, rather than the total current, and the process may be different at high and low current densities. Therefore Faraday's Law measurements were made at various current densities in order to determine something of the electrode process throughout a

range of current densities. Various solutions were used to determine something of the behavior of titanium in different electrolytes.

Experimentally, the measurements can be conducted in two ways. An electrolysis cell can be set up and measured current passed through the electrode in such a way that the desired electrode reaction is induced. That is, since titanium is being considered as an anode, the current is passed in such a direction as to cause oxidation to occur at that electrode. The second way these measurements can be made is to set up a galvanic cell and draw current from it by placing a resistance across the electrodes. By knowing the cell voltage and the load resistance, the current can be determined from Ohm's Law. The difficulty with the second method is that as current is drawn, the cell voltage usually drops due to polarization; and, consequently, for a constant resistance, the current also decreases. This is particularly a problem when small electrodes are used.

The measurements made by passing current through the cell seem to offer more advantages than the other method. The experimental arrangement is quite simple, and the data can be taken quickly and accurately. The experimental apparatus consists of two electrolysis cells in series with a variable resistance and a

milliammeter. A direct current source, which in this case was a 6 V battery charger, was included with the current flowing in such a direction as to cause oxidation of the titanium. One cell contained the titanium anode and the other was a copper coulometer. Both consisted of 250 ml. beakers.

The titanium was rubbed with emery paper to remove any surface contamination and placed in the cell connected to the positive side of the battery charger. In early experiments, the titanium was simply placed in the cell; but in later experiments, it was coated with paraffin except for a definite area on one side. This allowed the current to pass through only a known area of the electrode and thus the current density could be more closely known and controlled. The cathode was lead or carbon. About 100 ml. of the electrolyte being studied was placed in the cell.

The copper coulometer was used to measure the quantity of electricity passed and consisted of two copper electrodes in a copper sulfate - sulfuric acid solution. As the current is passed, one electrode dissolves; and copper is plated on the other electrode. By weighing the electrode on which the copper deposits before the current is on and after completion of the experiment, and by applying Faraday's Law to the gain in weight, the quantity of electricity passed can be determined.

The milliammeter is placed in series to determine the current or current density which is passing. The current was regulated by a variable resistance. At low current densities less than  $3 \text{ ma/cm}^2$ , the copper coulometer was not satisfactory as the copper ions will not deposit on the copper cathode in accordance with Faraday's law. This is possibly because at lower current densities, larger crystals are formed and the deposit becomes soft. If the current density becomes too low, the large copper crystals will not adhere to the cathode. Therefore, at low current densities, the quantity of current was determined from the reading on the milliammeter and the time the current was allowed to flow. As the experiment progressed, the current usually dropped slightly; so a range of current densities and an average number of coulombs is indicated. This decreased current effect is very small at low current densities, but increases with increasing current density. Between 300 and 600 coulombs were passed in most experiments. The experiments were conducted at room temperature, about  $25^\circ$ , and neither the cell electrolyte nor the coulometer solution was stirred. More elaborate experimental apparatus is described in the literature (11, p. 32). The results from this series of experiments are tabulated in Table II.

TABLE II  
 FARADAY'S LAW MEASUREMENTS ON TITANIUM  
 IN VARIOUS ELECTROLYTES

<u>Electrolyte</u>	<u>Size</u> <u>cm<sup>2</sup></u>	<u>I,</u> <u>ma</u>	<u>i,</u> <u>ma/cm<sup>2</sup></u>	<u>C</u>	<u>Ti,</u> <u>grams</u> <sup>***</sup>	<u>Ti,</u> <u>grams</u> <sup>****</sup>	<u>Weight</u> <u>Loss,</u> <u>grams</u>	<u>Ti<sup>x</sup></u>
0.1 N HF 4% NH <sub>4</sub> F 0.1 N KCl	-	100	-	348	0.0575	0.0432	0.521	3.31
"	-	50	-	300	0.497	0.0372	0.1265	1.17
"	-	100	-	417	0.0690	0.0518	0.0882	2.34
0.075 N HF 4% NH <sub>4</sub> F 0.1 N KCl	-	100	-	374		0.0463	0.0464	4.00
"	-	100	-	333	0.0550	0.413	0.0422	3.96
"	-	75	-	344.5		0.0427	0.0426	4.00
0.075 N HF 5% NH <sub>4</sub> F 0.1 N KCl	-	100	-	318		0.0396	0.0398	3.96
"	-	100	-	303		0.0363	0.0359	4.18
"	-	130	-	236		0.0293	0.0285	4.11

TABLE II - Continued

<u>Electrolyte</u>	<u>Size</u> <u>cm<sup>2</sup></u>	<u>I,</u> <u>ma</u>	<u>i,</u> <u>ma/cm<sup>2</sup></u>	<u>C</u>	<u>Ti<sup>+++</sup></u> <u>grams</u>	<u>Ti<sup>++++</sup></u> <u>grams</u>	<u>Weight</u> <u>Loss,</u> <u>grams</u>	<u>Ti<sup>x</sup></u>
0.075 N HF 6% NH <sub>4</sub> F 0.1 N KCl	-	100	-	323		0.0400	0.0401	4.00
0.075 N HF 6% NH <sub>4</sub> F 0.1 N KCl	-	130	-	374		0.0464	0.0465	4.00
"	-	100	-	266		0.0331	0.0318	4.15
"	-	2.5-3	-	302	0.0500		0.0528	2.83
"	-	6-10	-	336	0.0555	0.0417	0.0424	3.93
"	6.6	6-8	0.9-1.2	493	0.8150		0.1000	2.45
"	6	11-15	3.7-5	1009	0.1660	0.1245	0.0933	5.47
"	2.76	5	1.8	1045	0.1725	0.1290	0.1514	3.42
"	2.25	7-10	3.1-4.4	955	0.1580	0.1185	0.1344	3.52
"	3.04	15-20	4.9-6.6	1110	0.1832	0.1375	0.1588	3.47
"	2.75	20-30	8.9-13.3	705	0.1165	0.0875	0.0883	3.96
"	2.42	5-15	2.1-6.2	620	0.1025	0.0770	0.0714	4.31

TABLE II - Continued

<u>Electrolyte</u>	<u>Size</u> <u>cm<sup>2</sup></u>	<u>I,</u> <u>mA</u>	<u>i</u> <u>mA/cm<sup>2</sup></u>	<u>C</u>	<u>Ti<sup>+++</sup></u> <u>grams</u>	<u>Ti<sup>++++</sup></u> <u>grams</u>	<u>Weight</u> <u>Loss,</u> <u>grams</u>	<u>Ti<sup>X</sup></u>
0.075 N HF 6% NH <sub>4</sub> F	2.41	8-15	3.3-6.2	495	0.0820	0.0615	0.0842	2.91
0.1 N KCl								
"	3.19	8-15	2.5-4.7	702	0.1160	0.0870	0.0818	4.26
0.075 N HF 6% NH <sub>4</sub> F	2.88	6-10	2.1-3.5	832	0.1375	0.1032	0.0894	4.62
0.1 H KCl								
"	2.31	10	4.3	800	0.1320	0.0990	0.0971	4.08
"	2.2	5	2.3	563	0.0931	0.0700	0.0844	3.31
"	2.2	3	1.4	503	0.0833	0.0624	0.0627	3.98
"	2.2	2	1.1	551	0.0912	0.0684	0.0597	4.58
0.075 N HF 8% NH <sub>4</sub> F	-	100	-	260		0.0322	0.0320	4.00
0.1 N KCl								
"	-	100	-	286		0.0355	0.0354	4.00
"	-	100	-	311	0.0514	0.0386	0.0457	3.37

TABLE II - Continued

<u>Electrolyte</u>	<u>Size</u> <u>cm<sup>2</sup></u>	<u>I,</u> <u>mA</u>	<u>i,</u> <u>mA/cm<sup>2</sup></u>	<u>C</u>	<u>Ti<sup>+++</sup></u> <u>grams</u>	<u>Ti<sup>++++</sup></u> <u>grams</u>	<u>Weight</u> <u>Loss,</u> <u>grams</u>	<u>Ti<sup>X</sup></u>
0.05 N HF 4% NH <sub>4</sub> F	-	100	-	297		0.0368	0.0368	4.00
0.1 N KCl	-	100	-	195		0.0242	0.0234	4.14
"	-	100	-	195		0.0242	0.0234	4.14
0.5 N HF 6% NH <sub>4</sub> F	-	100	-	348	0.0577	0.0432	0.0426	4.06
0.1 N KCl	-	120	-	318	0.0526	0.0395	0.0473	3.34
"	-	50	-	312		0.0387	0.0375	4.13
"	-	70	-	108		0.0134	0.0116	4.62

The columns titled  $Ti^{+++}$  and  $Ti^{++++}$  are the weights of titanium that would have been lost if the electrode were ideal and the electrode reaction were  $Ti \longrightarrow Ti^{+++} + 3e$  or  $Ti \longrightarrow Ti^{++++} + 4e$ . The actual weight of titanium used was determined by weighing the titanium electrode before and after the current was passed and is given in the column titled "Weight Loss."

" $Ti^X$ " is the average number of electrons involved in the oxidation process of the titanium, if it is assumed that no chemical corrosion is occurring at the same time. This assumption is approximately correct for the electrolytes having hydrofluoric acid concentration of 0.10 N or less, as corrosion studies have shown that with the acid concentration this low, and with the addition of ammonium fluoride, titanium corrodes very slowly or not at all. In the cases where chemical corrosion is occurring, it is taking place slowly enough so that it is negligible in the times required to conduct the experiment. Since the average number of electrons is not a whole number, it is likely that more than one reaction was occurring. This possibility will be discussed further when additional evidence is presented. " $Ti^X$ " is determined by using the actual weight loss and applying Faraday's Law. The calculation is illustrated below.

Number of coulombs passed . . . . . 348

Actual weight of Titanium used . . . . 0.0521 gm.

$$\frac{348}{96,494} = 0.00361 \text{ equivalents of titanium dissolved}$$

$$(0.00361) \frac{\text{Atomic weight}}{\text{Valence state}} = 0.0521$$

$$(0.00361) \frac{47.9}{x} = 0.521$$

$$x = 3.31$$

In the first series of experiments, the current was maintained at a high value of around 100 milliamps. At these values of the current, the electrodes were of such a size that the current density was 20 ma/cm<sup>2</sup> or greater. At and above this value of the current density, the electrode reactions are apparently the same. The electrode size and current densities are, therefore, not noted; but it should be remembered that the current densities are high. In the first few experiments at lower current densities, the electrodes were not paraffin-coated; and the electrode size was determined from the area of one side of the electrode.

It can be seen from the table that the major emphasis has been placed on certain electrolytes. This is because these particular electrolytes were shown to be the most satisfactory with titanium in voltage and polarization characteristics.

#### D. Polarization

Polarization is probably the most important and least understood of all electrode phenomena. It is particularly important in the construction of current-producing cells as any polarization will cause a decrease in the efficiency and capacity of the battery. It is the cause of decreased voltage when current is drawn from a cell. The most satisfactory cell is one in which there is a minimum voltage change under operating conditions. It is, therefore, important that the polarization process be understood, and then, if possible, eliminated. The possible causes have previously been discussed and will not be repeated here. The polarization effects of titanium in various electrolytes were studied by making a series of current density - voltage measurements and by trying to identify the polarization products. The current density - voltage measurements were made by the direct method as the commutator method has little or no advantage and requires much more cumbersome experimental apparatus.

The purposes of polarization measurements are twofold. First, information can be obtained concerning the chemical reaction that occurs at the electrode; and, second, the behavior of the electrode in the electrolyte during the passage of current can be established without

having actually to construct a cell and draw current from it.

The apparatus for making polarization measurements consisted of the following: A cell containing the titanium and a second electrode was set up in a 250 ml. beaker. Electrical connections were made to a 6 V battery charger in such a way that the direct current causes oxidation at the titanium electrode. The second electrode was used simply to pass the current, and was made from a lead sheet or a carbon rod. A variable resistor and a milliammeter were placed in series with the source and cell. The resistor was used to regulate the current. The back and part of the front of the titanium electrode were coated with paraffin so that a known area was exposed to the electrolyte. A 1 N potassium chloride salt bridge with a capillary opening at one end was placed so that the capillary end was very close to the exposed titanium surface and the other end was in a beaker containing a 1 N potassium chloride solution. A 1 N calomel half-cell was connected to the beaker containing the potassium chloride. The potential was then read between the titanium electrode and the calomel half-cell on a Leeds and Northrup type "K" potentiometer. A series of readings were taken of the voltage as a function of the current. This was then converted to the single electrode potential of the

titanium as a function of the current density. The value of the 1 N calomel half-cell was taken as +0.2825 V at 25° (35, p. 464). The cell containing the titanium was placed in a water bath at 25° and the temperature maintained at this value  $\pm$  0.5 degrees.

Several current density - voltage measurements were made by setting up a cell and drawing current from it through an external resistance while measuring the single electrode potential of the titanium. The results agreed, within the experimental error, with those obtained by the other method.

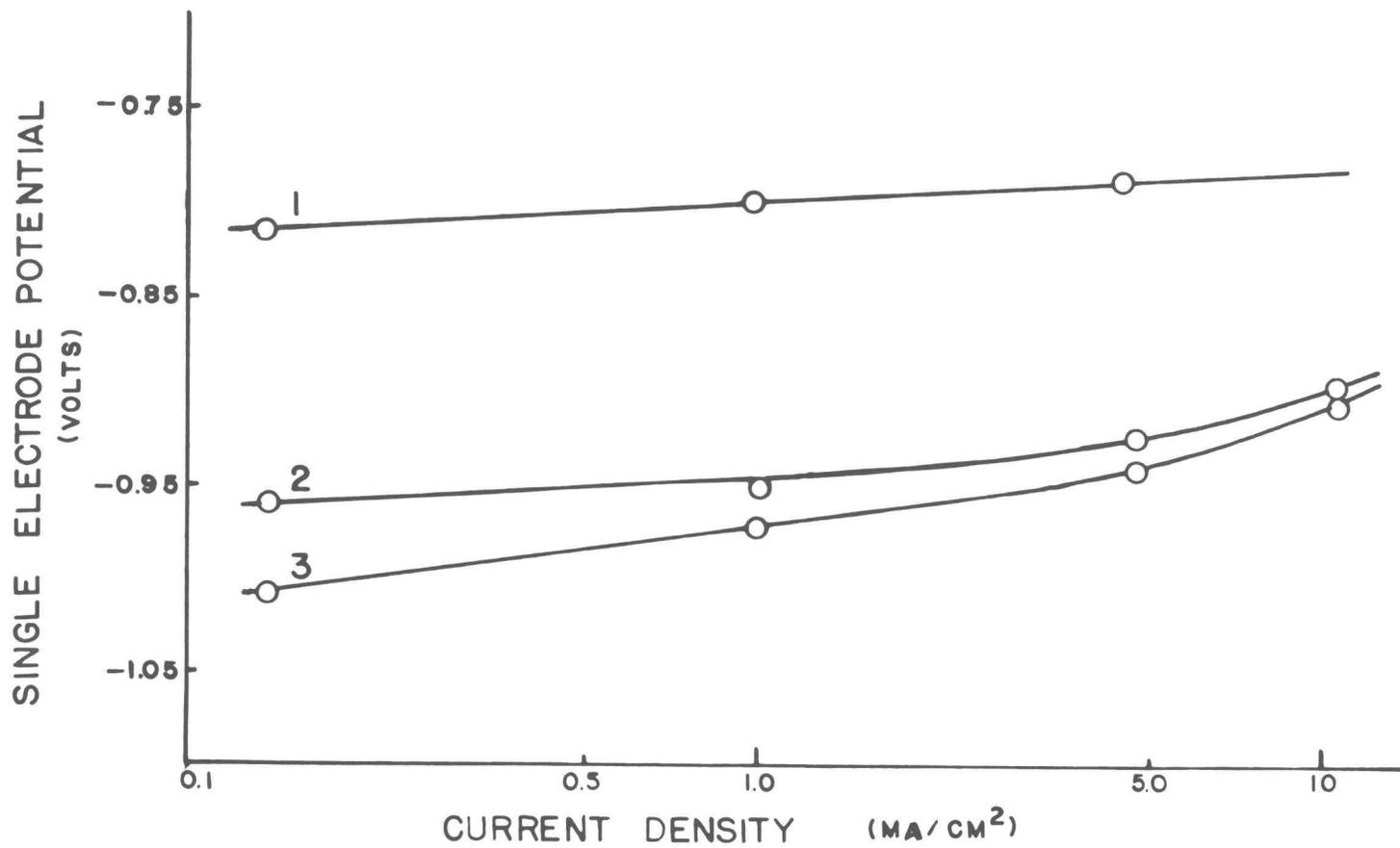
Passivation is a phenomenon associated with polarization that occurs when a very large resistance or back electromotive force is formed across the electrode, the current falls nearly to zero, and the single electrode potential changes radically from its normal value. This is not an unusual occurrence. However, it is important that it does not occur until the current density is higher than the normally useful range. For a flashlight type dry cell to draw one ampere, a current density of about 20 ma/cm<sup>2</sup> is required. One ampere for this size battery is considered to be a much heavier load than it is normally required to deliver. Therefore, any electrolyte in which passivation of the titanium occurred below 20 ma/cm<sup>2</sup> was not considered further.

On the following electrolytes current density-voltage measurements were made, but in each case the titanium became passive below a current density of  $5 \text{ ma/cm}^2$ : 8 and 9%  $\text{NH}_4\text{F}$ , 0.1N hydrofluoric acid, 9% ammonium fluoride - 1.0 N potassium chloride, 7% ammonium fluoride - 1.0 N potassium chloride, 7% ammonium fluoride - 1.0 N potassium fluoride, 8% ammonium fluoride - 0.1 N hydrofluoric acid and 7% ammonium fluoride - 0.1 N hydrofluoric acid. These electrolytes were therefore eliminated as possibilities.

Typical current density - voltage curves are shown in Figure I. Curve 2 is for titanium in a 0.2 N hydrofluoric acid, 0.05 N potassium chloride, 4% ammonium fluoride electrolyte. Curve 3 is for titanium in a 0.075 N hydrofluoric acid, 0.1 N potassium chloride, 6% ammonium fluoride electrolyte. The curves are plotted using the voltage of the titanium electrode rather than the true polarization, because it gives a better picture of what would actually occur at the titanium electrode if it were in a cell and current was being drawn at the indicated current density. For comparison with the behavior of the zinc anode in a dry cell electrolyte, the current density-voltage curve for it is included as curve 1. It is seen that there is a possibility of developing a titanium anode with an open circuit voltage of about 0.2 V better

## FIGURE 1

CURRENT DENSITY VS. SINGLE ELECTRODE POTENTIAL



than the present zinc anode. The usual procedure is to plot the log of the current density versus the voltage, but there is no particular significance to this.

A summary of current density-voltage measurements is tabulated in Table III. The column marked "Maximum Current Density" is an approximate value at which the electrode becomes passive. This point is dependent not only on the current density, but also upon the rate at which the current density is increased. This value can therefore vary by a considerable amount, particularly with the electrolytes that cause passivation at  $40 \text{ ma/cm}^2$  or less. The values indicated are, therefore, an average of the values found. The most satisfactory electrolytes with regard to passivation are those having the highest values.

The values of the single electrode potentials are an average of two and in most cases three determinations for the particular electrolyte. At low current densities, that is below  $1.0 \text{ ma/cm}^2$ , the separate determinations agreed in most cases to 1% or less. The agreement became less at higher current densities and in some cases was as high as 5% although, for the most part, it did not exceed 3%. It should be noted that the values have been multiplied by -1, and that the electrolytes that maintained the greatest negative value throughout the range of current

TABLE III  
 SINGLE ELECTRODE POTENTIALS  
 OF TITANIUM AT VARIOUS CURRENT DENSITIES  
 (Volts)

Electrolyte	Current Density ma/cm <sup>2</sup>					Maximum Current Density ma/cm <sup>2</sup>
	<u>0.2</u>	<u>0.5</u>	<u>1.0</u>	<u>5.0</u>	<u>10</u>	
(Electrode potentials are all negative)						
0.2 N HF 4% NH <sub>4</sub> F 0.2 N KCl	.951	.945	.941	.927	.909	70
0.2 N HF 4% NH <sub>4</sub> F 0.1 N KCl	.949	.943	.938	.910	.877	65
0.2 N HF 4% NH <sub>4</sub> F 0.05 N KCl	.958	.948	.941	.916	.888	60
0.15 N HF 4% NH <sub>4</sub> F 0.1 N KCl	.969	.956	.953	.915	.888	55
0.15 N HF 4% NH <sub>4</sub> F 0.05 N KCl	.964	.955	.947	.917	.885	55
0.1 N HF 4% NH <sub>4</sub> F 0.5 N KCl	.883	.970	.957	.903	.753	20
0.1 N HF 4% NH <sub>4</sub> F 0.2 N KCl	.979	.967	.956	.904	.867	40
0.1 N HF 4% NH <sub>4</sub> F 0.1 N KCl	.975	.962	.953	.905	.866	40

TABLE III - Continued  
(Volts)

Electrolyte	Current Density ma/cm <sup>2</sup>					Maximum Current Density ma/cm <sup>2</sup>
	<u>0.2</u>	<u>0.5</u>	<u>1.0</u>	<u>5.0</u>	<u>10</u>	
(Electrode potentials are all negative)						
0.1 N HF 4% NH <sub>4</sub> F 0.05 N KCl	.974	.965	.954	.898	.849	45
0.075 N HF 2% NH <sub>4</sub> F 0.1 N KCl	.974	.957	.943	.871	.785	30
0.075 N HF 3% NH <sub>4</sub> F 0.1 N KCl	.991	.971	.957	.905	.847	35
0.075 N HF 4% NH <sub>4</sub> F 0.1 N KCl	.989	.969	.954	.919	.883	45
0.075 N HF 5% NH <sub>4</sub> F 0.1 N KCl	1.005	.973	.967	.931	.885	40
0.075 N HF 6% NH <sub>4</sub> F 0.1 N KCl	1.009	.988	.971	.933	.875	40
0.075 N HF 8% NH <sub>4</sub> F 0.1 N KCl	1.025	1.015	1.001	.925	.815	25
0.075 N HF 10% NH <sub>4</sub> F 0.1 N KCl	1.023	1.005	.983	.935	.875	25

TABLE III - Continued

(Volts)

<u>Electrolyte</u>	Current Density ma/cm <sup>2</sup>					Maximum Current Density ma/cm <sup>2</sup>
	<u>0.2</u>	<u>0.5</u>	<u>1.0</u>	<u>5.0</u>	<u>10</u>	
<u>Electrolyte</u> (Electrode potentials are all negative)						
0.05 N HF 4% NH <sub>4</sub> F	1.001	0.986	.974	.915	.835	30
0.1 N KCl						
0.05 N HF 6% NH <sub>4</sub> F	1.025	1.004	.989	.923	.799	20
0.1 N KCl						

densities are the most satisfactory.

The electrolytes are those that were considered as having good possibilities of being satisfactory for titanium anodes. The first few investigated were essentially trial and error, but certain patterns were established as the investigation progressed.

The electrolytes which appear to be the most satisfactory from the standpoint of a good negative open circuit voltage, a fairly linear current density-voltage curve with not too large a slope, and a high value of the current density before passivation occurs, and the least corrosive effects are 0.075 N hydrofluoric acid, 0.1 N potassium chloride, and 6% ammonium fluoride; and 0.1 ammonium fluoride, 4% ammonium fluoride, 0.1 N potassium chloride. Major emphasis has been placed on developing and improving these electrolytes.

Additional current density-voltage curves were run to determine the effect of small amounts of additives on the polarization curves. The materials added were zinc chloride, ammonium chloride, mercuric chloride, and manganese dioxide which are all found in a LeClanche type dry cell. It was thought that a carbon-manganese dioxide type anode might be used with the titanium cathode and if any of these substances had an adverse effect on the single electrode potential of the titanium, it would be well

to consider eliminating them from the system. Results indicated that small amounts, less than 1%, of any of these materials caused no greater variation in the single electrode potential than is expected from the normal experimental variation. However, when 1% zinc chloride was added to the electrolyte, the titanium potential became about 0.35 V more positive than is normally found. Further, the current dropped to nearly zero at a current density of about 20 ma/cm<sup>2</sup>, but the potential of the titanium remained negative at the value it had at around 15 ma/cm<sup>2</sup>.

Various other factors relating to polarization have been considered. It is known that polarization generally increases with time as the current is drawn. Several investigations were made using both a 0.1 N hydrofluoric acid, 4% ammonium fluoride, 0.1 N potassium chloride and a 0.075 N hydrofluoric acid, 6% ammonium fluoride, 0.1 N potassium chloride electrolyte. In general, for fairly low current densities the single electrode potential becomes slightly more positive when the current is passed and then recovers somewhat, where it remains fairly constant for some time. It then becomes more positive at an increasing rate until it becomes passive and has a very positive value. The lower the current density, the longer the time required for the electrode to become passive. The results are indicated in Table IV.

TABLE IV

Electrolyte: 0.1 hydrofluoric acid,  
4% ammonium fluoride,  
0.1 N potassium chloride

Current Density  $\text{ma/cm}^2$

Time (hours)	Single Electrode Potential (volts)		
	<u>1.325</u>	<u>1.665</u>	<u>2.96</u>
0	-0.719	-0.917	-0.924
$\frac{1}{2}$	-0.847	-0.940	-0.737
1	-0.910	-0.938	-0.937
2	-0.914	-0.935	-0.931
5	-0.905	-0.902	-0.899
10	-0.857	-0.730	+1.862
20	-0.783	-0.617	

Electrolyte: 0.075 N hydrofluoric acid,  
6% ammonium fluoride,  
0.1 N potassium chloride

Current Density  $\text{ma/cm}^2$

Time (hours)	Single Electrode Potential (volts)		
	<u>2.07</u>	<u>0.957</u>	<u>0.685</u>
0	-.968	-.970	-.967
$\frac{1}{2}$	-.655	-.587	-.714
1	-.664	-.580	-.627
2	-.618	-.652	-.610
5	-.550	-.858	-.661
10	-.560	-.435	

The pattern by which the single electrode potential changes with time at a given current density is actually quite erratic. The tables indicated the general trend, but there is considerable unpredictable variation in the behavior. This illustrates the type of behavior that could be expected from a titanium anode in a cell from which current is continuously being drawn at the indicated current density.

The final way in which polarization was studied was to investigate the polarization products. When current is drawn from a cell containing a titanium anode and a hydrofluoric acid, ammonium fluoride, potassium chloride electrolyte, or when current is passed through a titanium electrode in this electrolyte in such a way as to cause oxidation, a blue or black insoluble polarization product is formed. If it were possible to identify this compound, it might then be possible to alter the electrolyte in some way to either prevent its formation or to dissolve it as it is formed. Two methods were used to investigate these products. X-ray diffraction measurements were taken in an attempt to identify it from its characteristic X-ray pattern. In addition, stoichiometric amounts of component parts of the suspected compound were added together in an attempt to make and isolate the compound, and compare it with the one obtained by oxidizing the titanium.

X-ray patterns were made on a General Electric XRD unit using the powder method. The sample to be studied was ground to a fine powder, glued to a small glass rod and mounted in the camera. The X-rays were produced using a copper target, and the film was exposed for one hour. X-ray diffraction patterns were obtained for compounds obtained as follows: (1) The polarization product obtained when current is drawn from a cell using titanium anode, carbon-manganese dioxide cathode, and 0.075 N hydrofluoric acid, 6% ammonium fluoride, 0.1 N potassium chloride electrolyte; (2) the polarization product obtained by drawing current from a cell using a titanium anode in a 0.075 N hydrofluoric acid, 6% ammonium fluoride, 0.1 N potassium chloride electrolyte and a lead oxide cathode in a sulfuric acid electrolyte of density 1.1 g/cc; (3) the blue polarization products obtained from Faraday's Law measurements at a current density of 2.46 ma/cm<sup>2</sup>, 2.06 ma/cm<sup>2</sup>, and 2.27 ma/cm<sup>2</sup>; (4) a black chemical corrosion product formed on the surface of a piece of titanium which sat in a solution of 0.075 N hydrofluoric acid, 6% ammonium fluoride, and 0.1 N potassium chloride for about two weeks; (5) a white polarization product found adhering to the titanium anode at the completion of Faraday's Law measurements at 4.33 ma/cm<sup>2</sup>; (6) a white

material formed on the carbon cathode during Faraday's Law measurements at 2.06 ma/cm<sup>2</sup>.

The distance between planes of atoms in a crystal which give rise to a given diffraction line is determined by Bragg's equation

$$\lambda = 2d \sin \Theta$$

where  $\lambda$  is the X-ray wave length being diffracted expressed in angstrom units,  $\Theta$  is the angle of diffraction, and "d" is the interplanar spacing in angstrom units. The wave length of the X-ray is known from the target metal of the X-ray tube. Knowing this, it is only necessary to evaluate the diffraction angle to be able to calculate the interplanar spacing. This is accomplished as follows:

$$4 \Theta_{\text{rad}} = \frac{S}{R}$$

$$\text{or } \Theta_{\text{deg}} = \frac{S}{4R} \times 57.297$$

S = distance between corresponding arcs of the same cone of diffracted rays

or S = 2 x distance of the arc from the center

R = radius of the camera = 7 cm.

$$\Theta_{\text{deg}} = 2.043 S \quad (16, \text{ p. } 31)$$

The distance from the center of the arcs and the interplanar spacing (d) are given below for the various compounds investigated. The lines are given in order of

decreasing intensity as nearly as could be determined.

- 1.) The polarization product obtained by drawing current from a cell using a titanium anode and carbon-manganese dioxide cathode.

<u>Distance from center (cm)</u>	<u>d (angstroms)</u>
4.310	2.594
3.250	3.417
5.885	1.926
5.765	1.963
6.795	1.683
7.075	1.621

- 2.) The polarization product obtained by drawing current from a cell using a titanium anode and a lead dioxide cathode.

<u>Distance from center (cm)</u>	<u>d (angstroms)</u>
4.57	2.450
2.90	3.823
5.90	1.920
6.78	1.686

- 3.) The blue polarization product obtained from Faraday's Law measurements.

<u>Distance from center (cm)</u>	<u>d (angstroms)</u>
3.42	3.250
1.81	6.099
4.71	2.380
5.71	1.980
6.58	1.734
3.74	2.978
10.23	1.173 (?)
30.50	2.742 (?)
30.67	2.858 (?)

The question marks following the lines indicate that the lines were extremely faint, and it is not certain whether they were actually lines or some imperfection in the film.

- 4.) Black chemical corrosion product formed on the titanium surface by the electrolyte.

<u>Distance from center (cm)</u>	<u>d (angstroms)</u>
1.83	6.033
5.90	1.920
4.67	2.400
3.43	3.241
3.64	3.958
3.80	2.932
4.11	2.716
7.46	1.545

It can be seen that samples numbered "3" and "4" give nearly identical lines although the order of intensity is not the same. This might be expected as the lines were quite faint, and it was difficult to determine just which line was the darkest. It is therefore shown that the polarization product obtained by inducing oxidation with an electric current contains some of the same material as the chemical corrosion product in the same solution of 0.075 N hydrofluoric acid, 6% ammonium fluoride, and 0.1 N potassium chloride. The colors of the two materials were not the same. The product from Faraday's Law measurements was deep blue while the chemical corrosion product was black. After the materials were

ground to a powder for X-ray studies, they both appeared to be black.

It is also seen that samples "1" and "2" have some nearly identical lines and others that are very close. In this case, both materials appeared to be the same when formed; however, when the samples were ground to a powder, sample "1" was much darker than sample "2". This may indicate that these two substances consisted of more than one compound, but that they both contained some of the same constituents.

Additional evidence that the polarization product contains more than one compound is found by examining the patterns from samples "3" and "5". Sample "3", the blue material, was found either loosely adhering to the titanium electrode or at the bottom of the cell directly under the titanium. Sample "5" was found adhering rather tightly to the titanium electrode and beneath a layer of the blue material at the completion of a Faraday's Law measurement which was run at  $4.33 \text{ ma/cm}^2$ . An X-ray pattern of the blue material from this measurement was not made because of its similar appearance to the blue material from Faraday Law measurements. It is evident that these two materials are not the same as they do not have any similar lines.

Attempts to identify these compounds were made by

matching the diffraction lines with those found in the ASTM Handbook (2). In no case was a compound found with matching lines.

Further information was obtained on the blue polarization product by conducting a series of solubility tests. It was found that it is insoluble in 0.2 N hydrofluoric acid, acetone, ether, acetic acid, 1 N potassium chloride, benzene, alcohol, and ammonium fluoride. It slowly dissolved in concentrated hydrochloric acid after first changing to a white or pink color. It dissolved fairly rapidly in 6 N sulfuric acid with the evolution of a gas. Before completely dissolving, it had changed to a brown color. It dissolved in hot water, giving a pale yellow milky solution. Upon evaporation, a white powder resulted. In boric acid, it appeared to partially dissolve; however, a small amount of pink residue remained. This would give further evidence that there is more than one compound present.

Based on these observations, the titanium compounds most likely to be present in the blue polarization product are  $Ti_3O_5$ ,  $TiF_3$ ,  $(NH_4)_2TiF_6$ , or  $Ti(OH)_3$ . An attempt was made to make and isolate  $(NH_4)_2TiF_6$  by adding stoichiometric amounts of titanium to hydrofluoric acid to produce  $TiF_4$  and then ammonium fluoride to produce the complex salt. The compounds were added to a water solution and

allowed to evaporate in air. The resulting compound was white and did not resemble any of the polarization products. It was insoluble in water, ammonium fluoride, concentrated hydrochloric acid, and 6 N sulfuric acid, and slowly dissolved in 0.2 N hydrofluoric acid.

The results seem to strongly indicate that the polarization product is more than a single compound. It is further possible that it is hydrated.

#### E. Investigation of Cathodes

In order to obtain a satisfactory dry cell, it is important that a usable cathode be found that will have the properties of a good electrode as noted in the introduction. It is also desirable to find a cathode that can be used in the same electrolyte as the titanium anode; however, it might be possible to develop a cell having two electrolytes and a diaphragm separating them. Various cathodes were considered when the original galvanic cells were made and the voltages measured as a function of load. In addition, lead dioxide was given considerable attention as a possible cathode and showed the most promise.

The lead dioxide electrodes were made according to the instructions by Vinal (45, p. 27-46). A mixture was made consisting of 20%  $Pb_3O_4$ , 80%  $PbO_2$ , a small amount of graphite, and enough sulfuric acid of specific gravity

1.1 to make a paste-like consistency. The paste was smeared on lead grids from a lead storage battery and electrolyzed in sulfuric acid of the same specific gravity at a current density of 0.2 to 0.5 amps/dm<sup>2</sup>. The electrode was made the positive side in the electrolysis cell so that the lead oxides would be oxidized to lead dioxide. The electrolysis was continued for approximately 40 to 48 hours or until the electrode appeared completely black. The electrodes were made as flat plates, approximately five cm. by eight cm., and also as cylinders approximately 1.5 cm. in diameter and 8 cm. high. The cylinders would be useful as the center cathode in a dry cell.

Current density-voltage measurements were made on a lead dioxide electrode in sulfuric acid of specific gravity 1.1 in order to become familiar with its behavior in its normal electrolyte. The experimental method used was identical to that used on the titanium except that the lead dioxide was reduced at various current densities instead of oxidized as in the case of titanium. The measurement was made several times on different electrodes, and the figures represent a typical result. The measurements were made using the cylindrical electrodes which were quite rough. The current density is, therefore, an approximation based on the estimated total surface area immersed in the electrolyte. The figures represent an

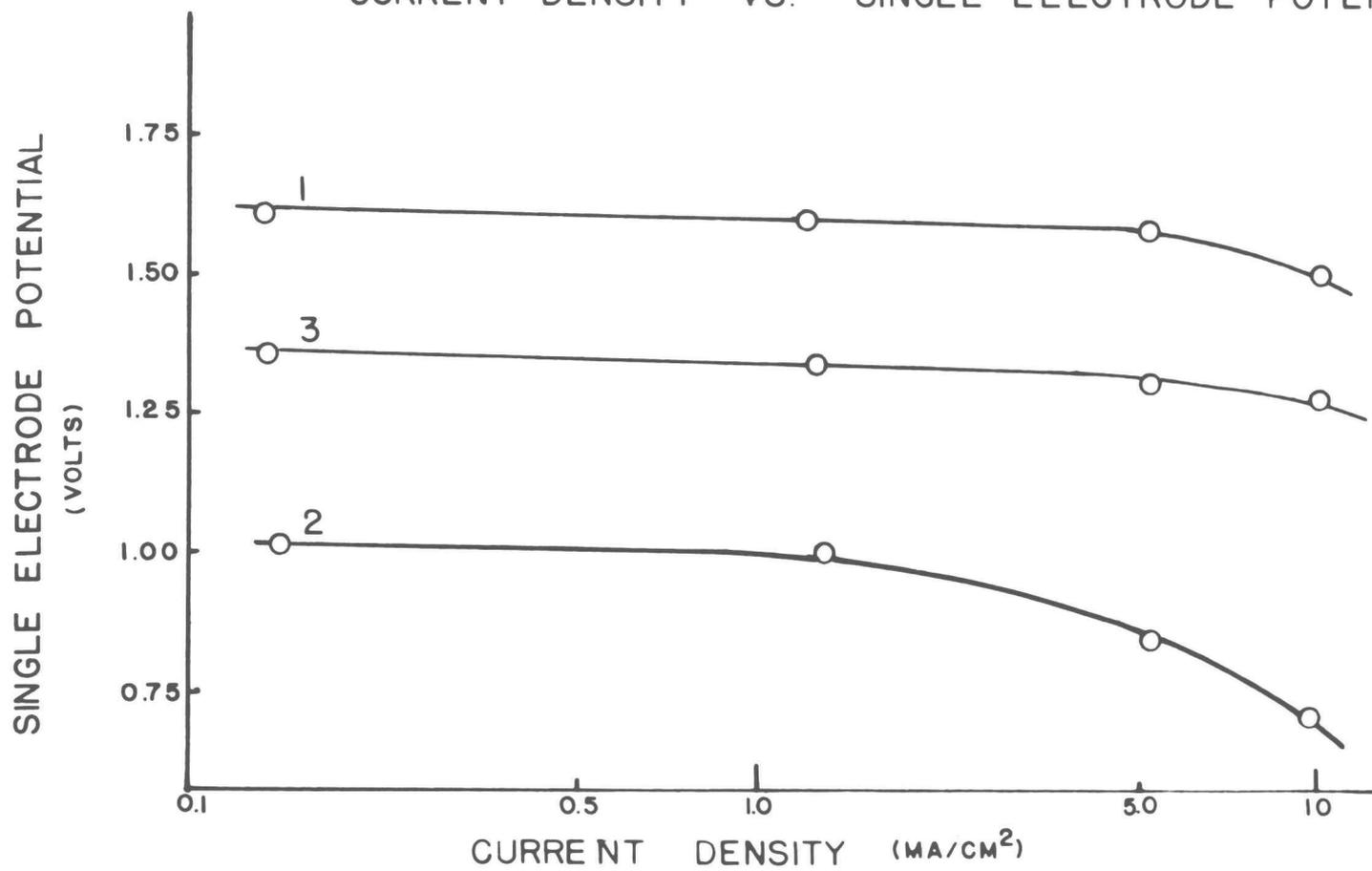
indication of the behavior of the electrode in the electrolyte rather than absolute values. Curve 1 of Figure II shows this behavior.

Polarization studies of the lead dioxide cathode were also made in various other electrolytes. The electrolyte of composition 0.075 N hydrofluoric acid, 6% ammonium fluoride, and 0.1 N potassium chloride, which will henceforth be called electrolyte A, showed the most promise as an electrolyte for the titanium, so the single electrode potential of the lead dioxide was determined in this electrolyte. The potential of the lead dioxide at zero time was +1.531 V, but after 6 hours in the electrolyte with no current passing, the voltage had dropped to +1.06 V. When current was passed through a lead dioxide electrode in such a direction to cause reduction in this electrolyte, the single electrode potential dropped quite rapidly. The results are shown as curve 2 of Figure II. It is apparent that the lead dioxide is not as satisfactory in this electrolyte as in sulfuric acid.

It was thought that some combination of the electrolyte A and sulfuric acid might make a satisfactory electrolyte for both the titanium and the lead dioxide electrodes. In order to study such a possibility, current density-voltage measurements were made with lead dioxide in sulfuric acid with increasing amounts of

FIGURE 2

CURRENT DENSITY VS. SINGLE ELECTRODE POTENTIAL



sulfuric acid added and with titanium in the hydrofluoric acid electrolyte with varying amounts of sulfuric acid added. Curve 3 of Figure II represents the results of the lead dioxide in a mixture of 75% electrolyte A and 25% sulfuric acid. The results are summarized in Table V and Table VI. The values in the tables were obtained from only a single determination, so may not represent the best values; however, they do indicate the approximate values and the general trend of the voltage at various current densities. In no case did either electrode become passive below a current density of 30 ma/cm<sup>2</sup>.

It can be seen that by using any of the combination electrolytes studied, an appreciable voltage should be obtainable even at current densities of 20 ma/cm<sup>2</sup>. The lead dioxide electrode voltage was more stable when just standing in the combination electrolytes than in electrolyte A alone. A lead dioxide electrode which had been used for current density-voltage measurements, and, therefore partially reduced in electrolyte A, maintained an essentially constant voltage of +1.36 V while standing in the combination electrolyte for 24 hours.

The difficulty encountered in using the mixed electrolyte is that the addition of even a small amount of sulfuric acid to electrolyte A increases the chemical corrosion appreciably. Titanium in the 10% sulfuric acid

TABLE V

Single Electrode Potentials for  $\text{PbO}_2$  in  $\text{H}_2\text{SO}_4$   
 (Sp.G. = 1.1) with Increasing Amounts of  
 0.075 N HF, 6%  $\text{NH}_4\text{F}$ , 0.1 N KCl Electrolyte Added  
 (Volts)

Electrolyte % by volume	Current Density $\text{ma/cm}^2$					
	<u>0.1</u>	<u>0.5</u>	<u>1.0</u>	<u>5.0</u>	<u>10</u>	<u>20</u>
	(Electrode potentials are all positive)					
100% $\text{H}_2\text{SO}_4$ (Sp.G. = 1.1)	1.595	1.592	1.584	1.540	1.512	1.435
99% $\text{H}_2\text{SO}_4$ 1% HF*	1.595	1.592	1.590	1.575	1.565	1.543
90% $\text{H}_2\text{SO}_4$ 10% HF*	1.595	1.592	1.590	1.575	1.565	1.535
75% $\text{H}_2\text{SO}_4$ 25% HF*	1.587	1.574	1.572	1.504	1.545	1.521
50% $\text{H}_2\text{SO}_4$ 50% HF*	1.566	1.506	1.503	1.518	1.492	1.405
25% $\text{H}_2\text{SO}_4$ 75% HF*	1.413	1.407	1.405	1.362	1.331	1.268

\*HF represents the whole electrolyte indicated above.

TABLE VI

Single Electrode Potentials for Titanium  
 in 0.075 N HF, 6% NH<sub>4</sub>F, 0.1 N KCl Electrolyte  
 With Increasing Amounts of H<sub>2</sub>SO<sub>4</sub> (Sp.G. = 1.1) Added  
 (Volts)

<u>Electrolyte</u> <u>% by volume</u>	Current Density ma/cm <sup>2</sup>					
	<u>0.1</u>	<u>0.5</u>	<u>1.0</u>	<u>5.0</u>	<u>10</u>	<u>20</u>
	(Electrode potentials are all negative)					
100% HF*	1.010	.987	.971	.923	.881	.819
99% HF* 1% H <sub>2</sub> SO <sub>4</sub>	.975	.973	.967	.934	.875	.770
95% HF* 5% H <sub>2</sub> SO <sub>4</sub>	.961	.960	.955	.920	.846	.725
90% HF* 10% H <sub>2</sub> SO <sub>4</sub>	.945	.941	.937	.923	.895	.843
75% HF* 25% H <sub>2</sub> SO <sub>4</sub>	.886	.887	.887	.883	.866	.846
50% HF* 50% H <sub>2</sub> SO <sub>4</sub>	.773	.773	.773	.773	.767	.750
25% HF* 75% H <sub>2</sub> SO <sub>4</sub>	.728	.728	.728	.726	.720	.705

\* HF represents the whole electrolyte indicated above.

and 90% electrolyte A corroded quite visibly with the evolution of a gas. It is thought that this increase in corrosion is caused by an increase in the hydrofluoric acid concentration when the sulfuric acid is added to a solution containing ammonium fluoride. It was noted that when additional ammonium fluoride was added to the combined electrolyte, the corrosion appreciably slowed and in some cases apparently stopped. Approximately a 10% addition of ammonium fluoride to the 75% electrolyte A - 25% sulfuric acid combination slowed the titanium corrosion appreciably, but did not stop it entirely. Approximately a 4% addition to the 90%-10% combined electrolyte stopped any visible corrosion. The effects of the combined electrolytes and in particular the combined electrolytes with additional ammonium fluoride on the voltage-time relation of the single electrode potentials has not been thoroughly investigated. By adding the proper amount of additional ammonium fluoride to the combined electrolytes, a single electrolyte can be found for both the titanium and the lead dioxide electrodes which has satisfactory voltage-current density and voltage-time characteristics and will not cause excessive corrosion.

## F. Construction of Cells

Based on the information obtained in the first five sections, several primary cells were set up to determine their characteristics under actual operating conditions. The cells were first made in open beakers using the two electrodes and a liquid electrolyte. If the system appeared satisfactory and it was believed that it could be used with a paste electrolyte, an actual dry cell was constructed.

The results of the initial studies made in open beakers are summarized in Table VII.  $R$  is the load across the cell;  $V_C$  is the total cell voltage;  $V_A$  is the single anode potential,  $V_B$  is the single cathode potential;  $I$  is the current drawn from the cell, and  $i_a$  is the current density at the anode.

For all the studies involving the carbon-manganese dioxide, the electrode was made by placing the bobbin obtained from the Union Carbide Corporation in an alundum thimble, and then placing this in the electrolyte. This was done to prevent the electrode from becoming excessively wet and falling apart. In all cases, the titanium electrode was from 2 cm.<sup>2</sup> to 3 cm.<sup>2</sup> The cathode was the larger electrode. Therefore, the current density was higher on the anode than the cathode.

TABLE VII

## GALVANIC CELLS USING A TITANIUM ANODE

<u>Cathode</u>	<u>Electrolyte</u>	<u>R,</u> <u>Ohms</u>	<u>V<sub>C</sub></u> <u>Volts</u>	<u>V<sub>A</sub></u> <u>Volts</u>	<u>I,</u> <u>ma</u>	<u>i<sub>a</sub>,</u> <u>ma/cm<sup>2</sup></u>
#1	0.1 N HF 4% NH <sub>4</sub> F	0	1.740	-0.972	0	0
C:MnO <sub>2</sub>	0.1 KCl	5000	1.734	-0.962	0.348	0.126
		2000	1.731	-0.962	0.865	0.314
		1000	1.726	-0.955	1.726	0.627
		500	1.721	-0.951	3.45	1.25
		200	1.709	-0.958	8.55	3.10
		100	1.660	-0.918	16.6	6.05
		75	1.577	-0.906	21.0	7.65
		50	1.507	-0.890	30.0	10.9
		25	1.332	-0.840	53.4	19.4
		20	1.260	-0.829	62.9	22.8
		10	1.057	-0.759	106	38.4
		5	1.065	-0.738	213	77.5

TABLE VII - Continued

<u>Cathode</u>	<u>Electrolyte</u>	<u>R, Ohms</u>	<u>V<sub>C</sub> Volts</u>	<u>V<sub>A</sub> Volts</u>	<u>I, ma</u>	<u>i<sub>a</sub>, ma/cm<sup>2</sup></u>
#2	0.075 N HF 4% NH <sub>4</sub> F	0	>1.6	-0.998	0	0
C:MnO <sub>2</sub>	0.1 N KCl	5000	"	-0.988		
		2000	"	-0.981		
		1000	"	-0.975		
		500	"	-0.967		
		250	"	-0.958		
		100	"	-0.940		
		90	1.604	-0.928	17.8	6.54
		75	1.578	-0.924	21.0	7.70
		50	1.509	-0.902	30.2	11.0
		35	1.433	-0.881	41.0	15.0
		25	1.335	-0.858	53.5	19.5
		15	1.155	-0.811	77.1	26.7
		10	0.993	-0.759	99.3	36.4

TABLE VII - Continued

<u>Cathode</u>	<u>Electrolyte</u>	<u>R, Ohms</u>	<u>V<sub>C</sub> Volts</u>	<u>V<sub>A</sub> Volts</u>	<u>I, ma</u>	<u>i<sub>a</sub>, ma/cm<sup>2</sup></u>
#3	0.075 N HF 6% NH <sub>4</sub> F	0	>1.6	-0.977	0	0
C:MnO <sub>2</sub>	0.1 N KCl	5000	"	-0.961		
		2000	"	-0.955		
		1000	"	-0.946		
		750	"	-0.944		
		500	"	-0.931		
		250	"	-0.903		
		200	"	-0.886		
		100	1.556	-0.857	15.5	5.4
		75	1.497	-0.818	19.9	6.9
		50	1.422	-0.785	28.4	9.87
		25	1.237	-0.737	52.1	20.8
10	0.9035	-0.547	90.3	31.3		

TABLE VII - Continued

<u>Cathode</u>	<u>Electrolyte</u>	<u>R, Ohms</u>	<u>V<sub>C</sub> Volts</u>	<u>V<sub>A</sub> Volts</u>	<u>I, ma</u>	<u>i<sub>a</sub>, ma/cm<sup>2</sup></u>
#4	0.075 N HF 6% NH <sub>4</sub> F	0	1.097	-1.009		
Cu	0.1 N KCl	5000	0.9636	-0.997		
		2500	0.8431	-0.982		
		1500	0.6400	-0.979		
		500	0.3731	-0.972		
		200	0.2823	-0.967		
		50	0.2066	-0.965		
#5	0.075 N HF 6% NH <sub>4</sub> F			<u>V<sub>B</sub> Volts</u>		
PbO <sub>2</sub>	0.1 N KCl	0	2.56	1.483	0	
		5000	2.48	1.470	0.497	
		2000	2.46	1.395	1.23	
		1000	2.40	1.385	2.40	
		500	2.37	1.286	4.75	
		300	2.30	1.267	7.66	

TABLE VII - Continued

<u>Cathode</u>	<u>Electrolyte</u>	<u>R, Ohms</u>	<u>V<sub>C</sub>, Volts</u>	<u>V<sub>A</sub>, Volts</u>	<u>V<sub>B</sub>, Volts</u>	<u>I ma</u>	<u>i<sub>a</sub>, ma/cm<sup>2</sup></u>
		200	2.28		1.229	11.4	
		100	2.21		1.216	22.1	
		50	2.13		1.176	42.5	
		25	1.90		1.152	76.2	
		10	1.48		1.058	14.8	
#6	Anode in 0.075 N HF 6% NH <sub>4</sub> F	0 1000	2.60 2.60	-1.020 -1.009		0 2.60	
	0.1 N KCl	750	2.60	-1.018		3.46	
PbO <sub>2</sub>	Cathode in H <sub>2</sub> SO <sub>4</sub> (Sp.G. = 1.1)	500 300	2.60 2.58	-1.007 -0.993		5.20 8.60	
	with 1 N KCl salt bridge	250 200	2.52 2.31	-0.935 -0.635		10.1 11.5	

TABLE VII - Continued

<u>Cathode</u>	<u>Electrolyte</u>	<u>R,</u> <u>Ohms</u>	<u>V<sub>C</sub>,</u> <u>Volts</u>	<u>V<sub>A</sub>,</u> <u>Volts</u>	<u>I,</u> <u>ma</u>	<u>i<sub>a</sub>,</u> <u>ma/cm<sup>2</sup></u>
		100	2.30	-0.420	23.0	
		75	2.30	-0.608	30.7	
		50	2.31	-0.421	46.1	
		25	2.32	-0.422	92.8	
#7	Anode in 0.075 N HF	0	2.45		0	
	6% NH <sub>4</sub> F	1000	2.58		2.58	
	0.1 N KCl	750	2.26		3.02	
PbO <sub>2</sub>	Cathode in H <sub>2</sub> SO <sub>4</sub>	500	2.22		4.43	
	(Sp.G = 1.1)	250	2.16		8.65	
	with Alundum	200	2.11		10.5	
	diaphragm	150	2.03		13.5	
		100	1.95		19.5	
		75	2.20		27.2	

TABLE VII - Continued

<u>Cathode</u>	<u>Electrolyte</u>	<u>R,</u> <u>Ohms</u>	<u>V<sub>C</sub>,</u> <u>Volts</u>	<u>V<sub>A</sub>,</u> <u>Volts</u>	<u>V<sub>B</sub>,</u> <u>Volts</u>	<u>I,</u> <u>ma</u>	<u>i<sub>a</sub>,</u> <u>ma/cm<sup>2</sup></u>
		50	1.12			22.4	
		25	0.790			31.5	
#8	10% H <sub>2</sub> SO <sub>4</sub>	0	2.26			0	
	(Sp.G. = 1.1)	1000	2.24			2.24	
	90%	750	2.24			2.98	
PbO <sub>2</sub>	0.075 N HF	500	2.23			4.46	
	6% NH <sub>4</sub> F	250	2.21			8.83	
	0.1 N KCl	150	2.18			14.5	
		100	2.14			21.4	
		75	2.10			28.0	
		25	1.84			73.7	
		10	1.45			145	

Cell number "6" was made up using two separate electrolytes and a 1 N potassium chloride salt bridge. This type of cell has a large internal resistance which possibly could be eliminated. Therefore, the cell voltage for a given load was read immediately after the load was removed. It is assumed that the recovery time of the electrodes is sufficiently slow that the voltage read immediately upon removing the external resistance will be the same as the voltage of the polarized cell without the internal resistance. Studies have shown that the polarization decreases very rapidly when the current is stopped; so this is actually not a true value. However, it is a closer approximation to the true value than when the internal resistance of the cell is included.

Cell number "7" is the same as cell "6", only a different mechanical arrangement is used in an attempt to reduce the internal resistance. The sulfuric acid with the lead dioxide electrode was put in an alundum thimble, and this was placed in a beaker containing the hydrofluoric acid electrolyte and titanium anode. In this way, the alundum thimble served as a diaphragm to separate the two electrolytes. This greatly reduced the internal resistance and the data obtained were probably more accurate indication of the true behavior of the cell than that for number "6".

In all cases only the single electrode potential of one electrode was determined. The other was then determined from this value and the total cell potential. The current and current densities were determined from the total cell potential and the external resistance using Ohm's Law, assuming zero internal resistance.

Some additional information was obtained on these cells by determining the stability of the voltage with time while a constant resistance is applied across the cell. For titanium and lead dioxide electrodes in electrolyte A, the initial open voltage was 2.10 V. When 250 ohms were applied across the cell, the voltage dropped to 2.02 V and then decreased to 1.08 V in 7 hours. Assuming zero internal resistance, this represents an anodic current density decrease from 2.24 to 1.19 ma/cm<sup>2</sup>. The voltage fluctuated somewhat over the given time period. Occasionally it would increase by as much as 0.1 V but the general trend was a very definite decrease in voltage with time.

On the basis of the information obtained from the galvanic cells set up in open beakers, an attempt was made to construct usable dry cells similar to commercial dry cells (44, p. 49-52). The electrolyte was made by adding about 20% of a mixture of 2 parts cornstarch to 1 part flour to the electrolyte and heating between 60° and 90°

until the electrolyte had the consistency of a thick paste. The titanium anodes were made from a piece of titanium pipe, 3 cm in diameter and 7 cm to 8 cm long. A circular piece of titanium was attached to one end of the pipe with a high melting wax to serve as the bottom of the cell. The cells were roughly the size of a standard flashlight battery. The cathode to be used was placed inside the titanium; and the starch, flour, electrolyte mixture was poured between the cathode and the titanium pipe. The cell was placed in a beaker of water at the required temperature until the electrolyte solidified. The voltage characteristics were then measured.

In order to determine if the technique for making the dry cells was satisfactory, a standard zinc and carbon-manganese dioxide dry cell was made, and its voltage measured over a period of time. The zinc and cathode bobbin, for this and other experiments using a carbon-manganese dioxide cathode, was furnished by the Union Carbide Corporation. The electrolyte consisted of 26% ammonium chloride, 8.8% zinc chloride, 65.2% water and a trace of mercuric chloride and was made into a paste in the manner described above. The initial open circuit voltage of the cell was greater than 1.6 V. After 5½ months, the open voltage had dropped to 1.56 V. Initially, the voltage with a 50 ohm load across the cell was also

greater than 1.6 V. After standing  $5\frac{1}{2}$  months with no load the voltage with a 50 ohm load was 1.52 V. The indication is that the technique used to make the dry cells is satisfactory, at least for a normal LeClanche cell.

A cell was made using a titanium anode, a carbon-manganese dioxide cathode, and a 0.1 N hydrofluoric acid, 4% ammonium fluoride, 0.1 N potassium chloride electrolyte. The initial open circuit voltage was about 1.72 V, but slowly dropped to 1.1 V in 24 hours and 0.84 V in 48 hours. When 12 ohms were placed across the cell the voltage quickly dropped to zero. When 50 ohms were placed across the cell, the voltage initially dropped by only a small amount but continued to decrease at an excessive rate.

The second attempt was made using the same type of electrodes in electrolyte A. The initial open voltage was again greater than 1.6 V; however, this dropped to 1.1 V in 24 hours and to 0.76 V after 5 days. When a 50 ohm load was applied across the cell when its voltage had dropped to 0.76 V, it further decreased to 0.23 V. The cell was sealed at both ends, so the drop in open voltage is not due to the evaporation of the electrolyte.

As long as the electrolyte was kept quite wet the open voltage remained high. The rapid drop in voltage that occurs when a load is placed across the cell might

be due to a polarization product that could drop off of the electrode when the cell was in a beaker, but which was held against the electrode by the solid electrolyte of a dry cell.

One further attempt was made to construct a dry cell using titanium and lead dioxide electrodes with the combination sulfuric acid, electrolyte A and a paper extraction thimble for a diaphragm. The sulfuric acid in contact with the starch-flour mixture caused the evolution of a gas and a frothing of the electrolyte; so this system has not successfully been made into a dry cell.

A great deal of art as well as science is involved in the construction of dry cells, and further research upon the constructional details is warranted.

From the measurements obtained in this investigation it is concluded that titanium possesses the characteristics of a useful anode material for primary cell use in either wet or dry cells, although additional development of electrolytes and dry cell construction technique is required.

### Zirconium

The investigation of zirconium as a possible anode in a primary cell was conducted along the same line as the titanium investigation. The entire study can be divided

into the same 6 main divisions. The experimental methods used with the zirconium were identical to those used for titanium and a detailed description of the methods will not be repeated. In the original experiments two types of zirconium were used; the type made by the Kroll process and the type made by the Iodide process.

#### A. Corrosion

The corrosive properties of zirconium have been discussed in the introduction. Based on this information, the following substances were considered likely electrolytes for zirconium:  $H_2SO_4$ ,  $H_3PO_4$ ,  $FeCl_3$ ,  $CuCl_2$ ,  $NaOH$ ,  $NH_4Cl$ , and  $HF$ . It was thought that a satisfactory concentration of one of these might be found that would cause no chemical corrosion, but in which the electrode would corrode when current was drawn. If none of these electrolytes would produce the desired effects, certain additives might improve the electrolyte enough to make it useful.

It was determined that the addition of ammonium fluoride to hydrofluoric acid solutions at the same concentrations as were used for titanium will not prevent corrosion. The addition of  $NH_4F$  actually increases the corrosion in  $HF$ . Two pieces of zirconium of nearly equal size and weight were placed in 0.001 N hydrofluoric acid, and in 0.001 N hydrofluoric acid with 8% ammonium fluoride

added. The zirconium in the HF lost less than 1% of its weight while the second piece lost 50% of its original weight in an equal time. It was also found that corrosion in HF continued to a concentration of 0.0005 N although it was extremely slow. Tetraethylammonium bromide was considered as a possible electrolyte. A 0.1 M solution corroded the zirconium to the extent of about 0.5% of its original weight in five and a half days. Additional corrosion data has been obtained in connection with the galvanic cell potentials.

#### B. Galvanic Cell Potentials

Galvanic couples were made in a series of electrolytes and their voltage noted on open circuit and with a 12 ohm load across the electrodes. The cells were allowed to stand for some time, and it was noticed that the cell potential varied sometimes by as much as 0.1 V. The voltages indicated are the maximum noted in the time the cell was allowed to stand. In connection with this study, additional corrosion information was obtained in the various electrolytes by weighing the zirconium before and after the cell was made. The electrodes from the Kroll process zirconium weighed about 0.2 gm. while those from the iodide process weighed 0.5 gm. Only the loss in weight will be indicated. A summary of these galvanic

couples is given in Table VIII. The type indicates the method of production of the zirconium. "K" designates that made by the Kroll process, and "I" that made by the Iodide process. The polarity is that for the zirconium when coupled with the other electrode and in the electrolyte indicated. " $V_0$ " is the maximum open circuit voltage obtained within the designated time, "T". " $V_{12}$ " is the maximum voltage found for the couple with the 12 ohm load across the cell.

On the basis of these galvanic couples, it appeared as if the carbon-manganese dioxide cathode was the most satisfactory cathode. Therefore, an additional number of galvanic couples were made using zirconium and carbon-manganese dioxide electrodes in various electrolytes. These couples are summarized in Table VIIIa. The symbols have the same meaning as previously. The zirconium electrodes weighed from 0.3 to 0.4 gm. The additives were in amounts of 1% or less. The carbon-manganese dioxide cathode was made in an alundum thimble using commercial materials. The internal resistance of the electrode made in this manner is undoubtedly higher than one without the diaphragm and therefore the voltage with the 10 ohm load is somewhat reduced.

TABLE VIII

GALVANIC CELL POTENTIALS FOR ZIRCONIUM AND  
ANOTHER ELECTRODE IN VARIOUS ELECTROLYTES

<u>Type</u>	<u>Polar- ity</u>	<u>Other Elec- trode</u>	<u>Electrolyte</u>	<u>V<sub>0</sub>, Volts</u>	<u>V<sub>12</sub>, Volts</u>	<u>Weight Loss, Grams</u>	<u>T, Hours</u>
K	-	Cu	96% H <sub>2</sub> SO <sub>4</sub>	0.6815	0.2865	0.065	3
I	-	"	"	0.6678	0.2450	0.084	3
K	-	C	80% H <sub>2</sub> SO <sub>4</sub>	0.8738	0.0590	0.028	½
I	-	"	"	0.8731	0.0361	0.043	½
K	-	"	40% H <sub>2</sub> SO <sub>4</sub>	0.6910	0.0026	0	4½
I	-	"	"	0.0401	0.0006	0	4½
K	-	"	60% H <sub>2</sub> SO <sub>4</sub>	0.7593	0.0122	0	3½
I	-	"	"	0.6796	0.0168	0	3½
K	-	"	20% FeCl <sub>3</sub>	0.4730	0.2251	0	1
I	-	"	"	0.4380	0.2270	0.007	1
K	+	Al	"	0.9137	0.2696	0	½
I	+	"	"	0.9150	0.2890	0	½
K	+	Pb	"	0.4870	0.0100	0	2
I	+	"	"	0.5023	0.0035	0	2
K	-	C	12% CuCl <sub>2</sub> ·2H <sub>2</sub> O	0.3317	0.0761	0	1½
I	-	"	"	0.2650	0.0650	0	1½

TABLE VIII - Continued

<u>Type</u>	<u>Polar-ity</u>	<u>Other Elec-trode</u>	<u>Electrolyte</u>	<u>V<sub>0</sub>, Volts</u>	<u>V<sub>12</sub>, Volts</u>	<u>Weight Loss Grams</u>	<u>T, Hours</u>
K	-	C;MnO <sub>2</sub>	40% H <sub>2</sub> SO <sub>4</sub>	1.1249	0	0	1
K	-	"	20% FeCl <sub>3</sub>	0.7785	0.0970	0.002	2
K	-	"	12% CuCl <sub>2</sub> · 2H <sub>2</sub> O	1.0281	0.1260	0	4½
K	-	"	10% NAOH	+1.60	0.0178	0	3
I	"	"	"	1.595	0.0425	0	5
K	"	"	Sat. NH <sub>4</sub> Cl	+1.60	0.2790	0.039	21
I	"	"	"	+1.60	0.2340	0.0004	21
K	"	"	10% HCl	1.00	0.4762	0.053	26½
I	"	"	"	1.480	0.2332	0.001	26½
K	"	"	0.1 N HF	+1.60	0.885	0.011	6½
I	"	"	"	1.52	0.2055	0.235	8½

TABLE VIIIa

GALVANIC CELL POTENTIALS FOR ZIRCONIUM AND  
CARBON-MANGANESE DIOXIDE IN VARIOUS ELECTROLYTES

<u>Electrolyte</u>	<u>Additive</u>	<u>V<sub>0</sub>, Volts</u>	<u>V<sub>10</sub>, Volts</u>	<u>Weight Loss, Grams</u>	<u>T, Hours</u>
10% NH <sub>4</sub> F		+1.60	0.704	0.006	1/3
"	Cu <sup>++</sup>	+1.60	0.652	0.005	1/3
"	Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	+1.60	0.612	0.015	1/3
"	ZrCl <sub>4</sub>	1.46	0.074	0.002	1/2
5% NH <sub>4</sub> F		+1.60	0.043	0.001	1/3
"	HgCl <sub>2</sub>	1.55	0.079	0.001	1/4
0.2 N HF		1.58	0.380	0.046	2/3
"	Cu <sup>++</sup>	1.26	0.360	0.005	1/2
"	ZrCl <sub>4</sub>	1.35	0.340	0.012	1/2
0.1 N HF		1.39	0.300	0.009	2/3
"	Cu <sup>++</sup>	1.35	0.230	0.006	1/2
"	ZrCl <sub>4</sub>	1.34	0.118	0.003	2/3
0.05 N HF		1.40	0.220	0.004	3/4
"	Cu <sup>++</sup>	1.34	0.150	0.002	1/2
"	ZrCl <sub>4</sub>	1.34	0.118	0.002	2/3
8% HCl		1.11	0.130	0	1/2
"	Cu <sup>++</sup>	0.95	0.036	0.001	1/2
"	ZrCl <sub>4</sub>	0.94	0.120	0.001	1/2
"	HgCl	1.15	0.050	0.002	1/2

TABLE VIIIa - Continued

<u>Electrolyte</u>	<u>Additive</u>	<u>V<sub>0</sub>, Volts</u>	<u>V<sub>10</sub>, Volts</u>	<u>Weight Loss, Grams</u>	<u>T, Hours</u>
8% HCl	Sn <sup>++</sup>	0.95	0.056	0.001	1/3
0.1 N HF	Pb <sup>++</sup>	1.57	0.110	0.006	1/2
"	Cd <sup>++</sup>	1.58	0.350	0.006	1/2
"	Pb <sup>++</sup>	1.39	0.270	0.004	1/3
7% NH <sub>4</sub> F		1.60	0.581	0.011	1 1/2
"	Sn <sup>++</sup>	+1.60	0.394	0.007	1/2
8% NH <sub>4</sub> F		+1.60	0.581	0.011	1
"	ZnCl <sub>4</sub>	+1.60	0.400	0.004	1 1/3
"	HgCl <sub>2</sub>	+1.60	0.360	0.008	1/3
"	SnCl <sub>2</sub>	1.57	0.310	0.003	1/3
"	Pb <sup>++</sup>	+1.60	0.360	0.009	1/2
"	Cd <sup>++</sup>	1.60	0.390	0.003	1/3

In most cases where corrosion occurs, it takes place to a larger extent with the zirconium made by the Kroll process than with that from the Iodide process. The addition of 2 mg/l of  $\text{Cu}^{++}$  will appreciably decrease the corrosion in 0.1 N hydrofluoric acid for both types of zirconium. In most cases using the same electrolyte, the Kroll process zirconium gave the higher voltage on both open circuit and with the 12 ohm load.

### C. Faraday's Law Measurements

The significance and utility as well as the experimental methods for Faraday's Law Measurements have been discussed in relation to titanium. This discussion applies equally well to zirconium. Based on the corrosion information, a series of measurements were made using zirconium in an identical manner to that used for titanium. Currents of the order of 0.1 to 0.2 amperes were used initially, but were decreased to a few milliamps in later experiments. The areas of the zirconium electrodes were very close to the same size which was about 2 cm<sup>2</sup>. Therefore, a current of 0.1 amperes gave a current density of 50 ma/cm<sup>2</sup> and a 5 ma current gave a current density of about 2.5 ma/cm<sup>2</sup>. The original weights of all the electrodes were approximately 0.4 gm. All of the zirconium used in this and subsequent experiments

was made by the Iodide process.

A summary of the results is given in Table IX; "I" is the current, "C" is the total coulombs, " $Zr^{++++}$ " is the theoretical weight that would be lost if the all zirconium went into solution in the +4 oxidation state, and " $Zr^+$ " indicates the average number of electrons involved in the electrode process assuming no chemical corrosion occurs. It is seen from the Faraday's Law measurements and corrosion studies that nearly all these electrolytes cause appreciable chemical corrosion; so the significance of the average number of electrons is questionable.

#### D. Polarization

Polarization measurements on zirconium were made in an identical manner to those for titanium. The polarization curves appeared quite comparable to those in Figure I. A summary of the current density-voltage measurements is given in Table X. If the chemical corrosion could be prevented, it should then be possible to form a zirconium anode in a hydrofluoric acid, ammonium fluoride electrolyte whose voltage is approximately 0.2 V greater than the zinc anode in the normal dry cell electrolyte. Corrosion, however, has proved a more difficult problem with zirconium than with titanium.

TABLE IX

 FARADAY'S LAW MEASUREMENTS ON ZIRCONIUM  
 IN VARIOUS ELECTROLYTES

<u>Electrolyte</u>	<u>I,</u> <u>ma</u>	<u>C</u>	<u>Weight</u> <u>Loss,</u> <u>Grams</u>	<u>ZR<sup>++++</sup></u> <u>Grams</u>	<u>ZR<sup>+</sup></u>
15% CuCl <sub>2</sub>	200	720	0.2094	0.1700	3.25
30% FeCl <sub>3</sub> .6H <sub>2</sub> O	100	321	0.0784	0.0758	3.86
20% FeCl <sub>3</sub> .6H <sub>2</sub> O	200	480	0.1336	0.1135	3.39
1% FeCl <sub>3</sub> .6H <sub>2</sub> O	100	228	0.0548	0.0539	3.93
20% NH <sub>4</sub> Cl	100	474	0.1188	0.1118	3.77
10% HCl	100	360	0.0765	0.0850	4.44
20% HCl	100	386	0.0948	0.0910	3.85
Sat. NH <sub>4</sub> Cl	100	360	0.0792	0.0852	4.30
5% NH <sub>4</sub> F	200	432	0.0974	0.1018	4.20
10% NH <sub>4</sub> F	280	581	0.1380	0.1369	3.98
0.2 N HF	100	344	0.788	0.0810	4.13
0.1 N HF	100	537	0.1246	0.1264	4.06
0.05N HF	100	394	0.0916	0.0927	4.07
0.1 N HF	100	365	0.1518	0.0862	2.18
0.075 N HF 8% NH <sub>4</sub> F	100	385	0.1317	0.0910	2.76
0.05 N HF 8% NH <sub>4</sub> F	100	327	0.0905	0.0774	3.42

TABLE X  
 SINGLE ELECTRODE POTENTIALS  
 OF ZIRCONIUM AT VARIOUS CURRENT DENSITIES  
 (Volts)

Electrolyte	Current Density ma/cm <sup>2</sup>					Maximum Current Density ma/cm <sup>2</sup>
	<u>0.2</u>	<u>0.5</u>	<u>1.0</u>	<u>5.0</u>	<u>10</u>	
(Electrode potentials are all negative)						
8% NH <sub>4</sub> F	1.047	1.023	1.003	0.960	0.925	+20
8% NH <sub>4</sub> F 1 N KCl	.967	.863	+.374			1
7.8% NH <sub>4</sub> F 1.95% ZrCl <sub>4</sub>	.951	.803				1
0.1 N HF	.695	.631	.582			8
0.1 N HF 1 N KCl	.699	.621	.547			5
0.1 N HF 1% NH <sub>4</sub> F	1.059	1.035	1.010	.931	.585	10
0.1 N HF 2% NH <sub>4</sub> F	1.081	1.059	1.045	1.011	.955	+80
0.1 N HF 4% NH <sub>4</sub> F	1.115	1.073	1.075	1.055	1.035	+75
0.1 N HF 6% NH <sub>4</sub> F	1.087	1.077	1.071	1.055	1.035	+75
0.1 N HF 8% NH <sub>4</sub> F	1.068	1.061	1.055	1.038	1.005	+60
0.1 N HF 10% NH <sub>4</sub> F	1.079	1.071	1.059	.973	.863	+60

TABLE X - Continued

(Volts)

<u>Electrolyte</u>	Current Density $\text{ma/cm}^2$					Maximum Current Density $\text{ma/cm}^2$
	<u>0.2</u>	<u>0.5</u>	<u>1.0</u>	<u>5.0</u>	<u>10</u>	
(Electrode potentials are all negative)						
0.075 N HF 4% $\text{NH}_4\text{F}$	1.092	1.083	1.059	1.030	+45	
0.075 N HF 6% $\text{NH}_4\text{F}$	1.053	1.058	1.031	1.019	+ 40	
0.075 N HF 8% $\text{NH}_4\text{F}$	1.095	1.087	1.059	1.039	+100	
0.05 N HF 4% $\text{NH}_4\text{F}$	1.069	1.059	1.010	.979	+80	
0.05 N HF 8% $\text{NH}_4\text{F}$	1.091	1.081	1.040	1.035	+100	

Several runs were made for each electrolyte, and the values in the table represent typical values. The variation for a given electrolyte was rarely greater than 3%. The column titled "Maximum Current Density" is again an approximation of the current density at which the zirconium became passive. The "+" in this column indicates "greater than". It was noticed that when the zirconium became passive, the value of its single electrode potential did not become as positive as in the case of titanium. Apparently the amount of polarization of zirconium is not significantly different from that of titanium in the same electrolyte at current densities below 20 ma/cm. The mechanism of the polarization might be quite different, however; since chemical corrosion is more pronounced in the electrolytes studied for zirconium than those for titanium.

#### E. Investigation of Cathodes

The methods and results of the investigation of cathodes were covered under titanium. Some additional anodes were investigated during the construction of cells and will be considered in the next section.

## F. Construction of Cells

The construction of the actual cells was conducted in a slightly different manner with zirconium than with titanium. Zirconium pipe was not available for use as an anode for the dry cells; so a series of cells was made up using a cardboard casing with the electrodes at each end and the electrolyte and depolarizer between them. The cells were approximately one inch in diameter and  $\frac{1}{2}$  inch high. The cells were paraffin coated. About 20% mixture of 2 parts cornstarch and 1 part flour was added to the electrolyte, and the combination was poured into the cell. The entire cell was then placed in a water bath between  $40^{\circ}$  and  $90^{\circ}$  and heated until the electrolyte attained a paste-like consistency. Most of the cells were made using a carbon-manganese dioxide cathode. The early cells were made before the commercial cathodes were available. It was found that the type of manganese dioxide made considerable difference in the voltage. Therefore, the characteristics of these cells are probably not as good as could be attained. The voltages are not the optimum, also, because such variables as the degree of solidity of the electrolyte, the pressure used in packing the manganese dioxide, and other factors involved in the technique of constructing the cell determine to a large

degree the maximum voltage that can be obtained. The values do, however, give an indication of the order of magnitude that can be expected. They also indicate what to expect from the voltage over a period of time and with a load across the electrodes.

A summary of these cells is given in Table XI.

" $V_0$ " is the initial open circuit voltage, " $V_T$ " and " $V_{12}$ " are the open circuit voltage and voltage with a 12 ohm load, respectively, at time, "T". Hydrofluoric acid and ammonium fluoride are the best electrolytes and depolarized carbon is the best cathode investigated. Aluminum appears to be a possibility for a cathode, but probably not in a ferric chloride electrolyte. Lead dioxide is another possible cathode but as yet no attempts have been made to construct a cell using it. The results obtained from the dry cell construction are not too conclusive, and additional work is required before an electrolyte for zirconium is found which is as satisfactory as that found for titanium.

TABLE XI

POTENTIALS OF SMALL DRY CELLS USING  
A ZIRCONIUM ANODE

<u>Cathode</u>	<u>Electrolyte</u>	<u>V<sub>0</sub>, Volts</u>	<u>T, Hours</u>	<u>V<sub>T</sub>, Volts</u>	<u>V<sub>12</sub>, Volts</u>
C:MmO	25% FeCl <sub>3</sub>	0.40	24	0.53	0.20
"	10% HCl	0.17	44	0.68	0.01
"	0.5% N HF 6% NH <sub>4</sub> Cl	0.10	136	1.01	0.16
"	28% FeCl <sub>3</sub>	0.43	16	0.83	0.05
"	10% NH <sub>4</sub> Cl	1.05	15	0.62	0.22
"	10% NH <sub>4</sub> F	+1.60	69	1.10	0.36
Al	28% FeCl <sub>3</sub>	0.97	17	1.05	0.04
Pb	10% HCl	0.28	16	0.26	0.0
Cu	30% H <sub>2</sub> SO <sub>4</sub>	0.43	16	0.03	0.0

### III. COMPARISON OF TITANIUM CELLS WITH COMMERCIAL CELLS

On the basis of this study, the possibility of developing a commercially valuable primary battery using titanium or zirconium as an anode appears to be very promising; but additional work will certainly be necessary to fully develop the battery to its greatest capacity.

It is of interest to compare the best cell obtained using a titanium anode and a flashlight size LeClanché cell. The best titanium cell consisted of a 0.075 N hydrofluoric acid, 6% ammonium fluoride, 0.1 N potassium chloride electrolyte for the titanium anode and sulfuric acid of specific gravity 1.1 for a lead dioxide cathode. The electrolytes were fluid, and were separated by an alundum diaphragm. The initial open circuit voltage of the cell was 2.46 V. A 500 ohm load was placed across the cell, and the voltage change with time was noted. In 21 hours the voltage had dropped to 1.48 V, or slightly less than two-thirds of its original value. The titanium anode was relatively small and this represented a current density change from an original 2.24 ma/cm<sup>2</sup> to a final 1.34 ma/cm<sup>2</sup>, assuming zero internal resistance.

By comparison, the voltage of a flashlight battery with a 500 ohm load will drop from its rated 1.5 V to 1 V in something over 2000 hours; however, this represents

current densities on the zinc anode of an original 0.05 ma/cm<sup>2</sup> to a final 0.033 ma/cm<sup>2</sup>. A better comparison can be made by indicating the time for a comparable voltage drop at approximately the same current densities. In order to obtain an initial 2 ma/cm<sup>2</sup> from the LeClanché cell, a 12.5 ohm load should be placed across the cell. With this load the cell voltage will drop to about two-thirds of its rated 1.5 V in only 15 hours. This is then compared with the 21 hours required by the best cell using a titanium anode to drop to two-thirds of its original voltage. At an anodic current density of approximately 30 ma/cm<sup>2</sup>, which is extremely high for a small battery, the titanium cell maintained a voltage greater than two-thirds of its original value for more than 2½ hours. A LeClanché flashlight battery would maintain a voltage two-thirds or greater of its original value for only a few minutes at this current density.

It is realized that the comparison of these two types of cells is not completely valid as the LeClanché cell was actually a dry cell while the titanium cell was made using liquid electrolytes. The comparison does serve, however, to illustrate the possibility that titanium and, by analogy, zirconium have as anodes in primary batteries.

When a cell was made using a mixture of various

proportions of the two electrolytes, without a diaphragm, a good voltage was still obtained; however, the corrosion of titanium increased appreciably. Additional ammonium fluoride added to the combined electrolyte will reduce the corrosion and still maintain a high voltage. The results are not as impressive, however, using the combined electrolyte. With a 25% sulfuric acid, 75% electrolyte A and an additional 10% ammonium fluoride the voltage dropped from an original 2.2 V to nearly two-thirds of this value in three hours with a 100 ohm load. This represented an original current density of about  $0.9 \text{ ma/cm}^2$  at the titanium anode. Corrosion was still taking place at the titanium; however, it was appreciably slowed by the additional ammonium fluoride. A flashlight size LeClanché cell will drop to two-thirds of its rated voltage at this current density in about 50 hours.

A second factor is the decrease in the single electrode potential of the lead dioxide in fluoride solutions. It was noted that the electrode potential of a lead dioxide electrode which was partially reduced in a fluoride solution will not decrease when placed in the mixed electrolyte. Therefore, by making this partial reduction, a satisfactory lead dioxide cathode might

be made for the single mixed electrolyte. A further addition of ammonium fluoride to the mixed electrolyte should essentially stop the chemical corrosion of the titanium.

#### IV. CONCLUSIONS

It has been shown that a useful voltage can be obtained from a primary cell using a titanium anode. However, polarization of the titanium is still an important factor in the maximum performance of the cell, particularly when it is in the form of a dry cell. Polarization studies have indicated that at low current densities, more than one polarization product is formed. A white substance is formed in a layer next to the anode and a blue material forms as a second layer. White titanium compounds indicate that the titanium is in the +4 oxidation state while a blue compound indicates a +3 state. Faraday's Law studies have indicated that at low current densities the average number of electrons involved in the electrode reaction is between 3 and 4.

Based on this evidence, possible electrode reactions are:



The electrode reactions are undoubtedly more complex than this and certainly change with increasing current density. This has been shown by Faraday's Law measurements and by polarization studies. Faraday's Law measurements indicate that at higher current densities, that is, usually above  $10 \text{ ma/cm}^2$  but dependent on the electrolyte, the number of electrons involved in the electrode process is fairly consistently four, indicating that the titanium is probably in the +4 oxidation state. The electrode process is visibly different at different current densities in polarization studies. At low current densities, the electrode forms a black film on the surface, but as the current density is increased, the film becomes lighter and finally turns white or silver usually when the current density is about  $20 \text{ ma/cm}^2$ , or at least at passivation. There is no sharp point at which the process changes; so it is possible that two processes are occurring simultaneously.

This interpretation of polarization is based entirely on the findings from Faraday's Law and polarization studies. It is realized that the polarization products might be different in passing current through a cell and drawing current from a cell. This has been shown by the X-ray patterns of the polarization products obtained by the two different methods. However, it is felt that

because of the similarity of the polarization curves (single electrode potential versus log of the current density), there is an equal amount of polarization at the same current densities in the two methods, and that although the products might be different, the basic oxidation changes are the same.

Polarization of titanium in fluoride solutions is certainly not completely understood. Several statements that can be made with regard to the polarization are:

- (1) At low current densities more than one polarization product is formed when current exists across the electrode-electrolyte interface;
- (2) at low current densities the titanium oxidizes to more than one valence state including the +3 and +4 oxidation states;
- (3) the titanium in the +3 oxidation state is probably in the form of a fluoride or hydroxide and, as indicated by its insolubility, is either a complex ion or a hydrolysed species;
- (4) at high current densities, the titanium is completely oxidized to the +4 oxidation state.

Since polarization is extremely important to the operating characteristics of the electrode it is important that the polarization process be completely understood. A more fundamental approach should be taken to the entire polarization problem. This could be accomplished by positively identifying the polarization

product and by investigating the chemical and physical properties of the polarization products. Various substances which give soluble titanium complexes in fluoride solutions should also be investigated. It might be possible to find a substance that will complex the oxidized titanium and make the product of the electrode reaction soluble. This would then decrease the polarization and make a more satisfactory cell. A decreased polarization is especially important if a successful dry cell is to be built.

Possible substances that might be used as complexing agents are tartrate, oxalate, and citrate ions, all of which strongly complex titanium. Further studies should be made on the sulfuric acid, hydrofluoric acid combined electrolyte. An optimum concentration should be found that will give a satisfactory voltage with a minimum of polarization and corrosion.

The electrolytes studied to date for zirconium are less satisfactory than those for titanium. Fluoride electrolytes give a fairly good voltage with no greater polarization than found with titanium in the same solution, however, excessive corrosion resulted when the electrodes were standing in the electrolyte. Lead ions will decrease the corrosion of titanium in hydrofluoric acid and, therefore, should be investigated as a possible additive

to decrease the corrosion of zirconium.

Other electrolytes should also be investigated as to their suitability with zirconium. These might include organic acids, inorganic salts, tetraalkylammonium halides, and other organic electrolytes. Zirconium should make a satisfactory anode, but the electrolytes investigated thus far have not proved adequate in all aspects.

When a completely satisfactory electrolyte is developed for either titanium or zirconium, its high and low temperature characteristics should be noted. Any size limitations on the cell should also be investigated.

Other possible uses for these metals which should be investigated are as an electrolytic rectifier and as a condenser plate. It was noted that if a direct current was across the electrode electrolyte interface for a certain period in such a way that the titanium was oxidized, a current in the reverse direction would not pass. This was particularly apparent in solutions of strong bases. If this rectifier action is due to a build-up of charge, which has been indicated in polarization studies, the metal might find application as a plate in an electrolytic condenser.

Another possible use for these metals might be their use as electrodes in secondary cells.

The actual values of titanium and zirconium have not

been fully realized as yet, and a great deal more research should be carried out on cheaper production processes as well as on new uses for the metals. The common metal deposits of the country are being rapidly depleted and so new materials will be required to replace them. Titanium and zirconium are two "new" metals that will certainly be useful to this end.

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