AN ABSTRACT OF THE THESIS OF

Naola VanOrden Watson for the Doctor of Philosophy in Physical
(Name) (Degree) (Major)

Chemistry

Date thesis is presented 6 August 1963

Title The Discharge and Recovery of the Vanadium Pentoxide Electrode

Abstract approved [redacted]
(Major professor)

Vanadium pentoxide electrodes were prepared by melting the powdered oxide around a platinum foil in a pyrex tube. The electrode was discharged, and the discharge product was studied, but not identified, by means of chemical and x-ray diffraction analysis. A study was made of the relationship between the electrode potential and the pH of the electrolyte solution. It was found that the number of electrons per hydrogen ion in the discharge reaction was unity at a pH between two and five.

The electrode potential during discharge was plotted against the time of discharge and the resulting curves were compared with curves calculated upon a theory based upon diffusion of the reduction product into the solid electrode. It was found that the diffusion equation predicted the shape of the experimental curves.

The diffusion coefficient for the discharge product was calculated from experimental discharge curves and the equations

for diffusion. A diffusion coefficient of 3×10^{-18} cm^2 per sec was obtained.

A mechanism for the discharge and recovery of the vanadium pentoxide electrode is proposed. It is suggested that the discharge consists of the reduction of the vanadium pentoxide to a lower oxy-hydroxide accompanied by an effective diffusion of the oxy-hydroxide by the migration of protons and electrons into the body of the electrode. The electrode potential is dependent upon the composition of the solid solution formed between the pentoxide and the oxy-hydroxide on the surface of the electrode. The recovery, after the discharge current is removed, consists of the further diffusion of the oxy-hydroxide away from the surface and the resulting increase in the activity of the pentoxide on the surface, until the composition is uniform throughout the electrode.

THE DISCHARGE AND RECOVERY OF THE VANADIUM PENTOXIDE ELECTRODE

by

NAOLA VANORDEN WATSON

A THESIS

submitted to

OREGON STATE UNIVERSITY

in partial fulfillment of
the requirements for the
degree of

DOCTOR OF PHILOSOPHY

August 1963

APPROVED:

[redacted]

Professor of Chemistry

[redacted]

Head of Department Chemistry

[redacted]

Dean of Graduate School

Date thesis is presented 6 August 196[illegible]

Typed by Penny Self

ACKNOWLEDGEMENT

The author wishes to express her appreciation to Dr. Allen B. Scott whose direction and encouragement made this work possible. The author also wishes to thank Dr. Max B. Williams for his help in interpreting the results of the x-ray diffraction studies.

The author is fortunate to have been the recipient of a National Science Foundation Graduate Cooperative Fellowship which supported the major portion of this work. Support of the last part of this investigation by the Office of Naval Research is also acknowledged.

Finally the author wishes to express her gratitude to her husband, Tom, for his constant encouragement, for the many electrodes which he prepared, and for the long hours which he spent babysitting in order that the author could write this thesis.

TABLE OF CONTENTS

LIST OF FIGURES

THE DISCHARGE AND RECOVERY OF THE VANADIUM PENTOXIDE ELECTRODE

I. GENERAL INTRODUCTION

A. Preface

The importance of primary electric cells in modern technology is well known. Since most of the primary cells used today utilize a solid metal-oxide as a cathode material, basic research on the electrode properties of such oxides is essential for improving the quality and kinds of primary cells.

The present investigation was undertaken with a three-fold purpose in mind: (1) to lay a groundwork for the study of the electrode properties of solid oxides in general, and vanadium pentoxide in particular, (2) to make an extensive study of the electrode behavior of polycrystalline vanadium pentoxide, and (3) to determine optimum conditions for the use of vanadium pentoxide in primary cells.

Vanadium pentoxide was selected as the material for beginning this study for several reasons. One is that a preliminary study indicated that this oxide had good electrode properties, such as being a relatively good semiconductor and having a high reduction potential. Another is that the low melting point of the oxide, about $650^{\circ}C$, makes it possible to prepare the oxide as either a cast electrode or as a single-crystal electrode. Other reasons are that

vanadium pentoxide has only one crystal modification, in contrast to some other oxides, including manganese dioxide; and that the pentoxide can be obtained commercially as a very pure material.

Vanadium pentoxide has one serious drawback in an aqueous system study. The oxide and many of its reduction products are relatively soluble in water, thus making the study of the electrode behavior more difficult because of the increased number of possible reduction products.

Another reason for selecting vanadium pentoxide is that it has already attained some commercial importance as a cathode material, and hence, basic research may have immediate practical value. A patent was granted to Louzos, of the Union Carbide Corporation (31) for a primary cell utilizing vanadium pentoxide. The advantages claimed for this cell over the conventional cells are that the pentoxide cell has a much longer shelf life and that it can be operated over a much broader temperature range. Thus this cell is ideal for many uses in the modern space age.

B. Vanadium Pentoxide as an Electrode Material

The purpose of this section is to present a survey of the properties of vanadium pentoxide which may affect its electrode characteristics. These properties include the composition and behavior of aqueous solutions of the pentoxide, the electrical properties of the solid oxide, the crystal structure of the solid oxide, and

the properties of the possible reduction products of vanadium pentoxide.

1. Chemical and Physical Properties of Vanadium Pentoxide. Vanadium pentoxide has been known for many years and hence its physical and chemical properties have been fairly extensively studied, although there is poor agreement among various workers concerning the values of these properties. Several comprehensive reviews on the chemical and physical properties are available, among which are Kirk and Othner (27, p. 596-598), Mellor (33, p. 714-825), Remy (36, p. 90-104), and Sidgwick (37, p. 904-834).

2. Vanadium Pentoxide in Aqueous Solution. Deltombe, et al. (14) have given a very comprehensive summary of the properties of aqueous solutions of all the vanadium oxides. They state that the principal constituents of an aqueous solution of vanadium pentoxide are the following ions: vanadic (VO_2^+), which is clear yellow in color and present at a pH of less than 2.5; pyrovanadate ($H_3V_2O_7^-$), which is orange in color and present at a pH from about 2.5 to about 9.5; and three colorless orthovanadates: ($H_2VO_4^-$), pH 2.5 to 9.5; (HVO_4^-), pH 9.5 to 11.5; and (VO_4^{---}), pH greater than 11.5.

Vanadium pentoxide has a solubility minimum at a pH of 2.15 with a calculated solubility at that pH of 0.655 g V_2O_5 per liter of water at 25°C (14). This calculated solubility agrees well with

the experimentally determined solubility of 0.7 g V_2O_5 per liter of water at a pH of 2.15 and at 25°C (15). The experimentally determined solubility products of the two most common ionic forms are:

$$[1] \quad \tfrac{1}{2} V_2O_5 + \tfrac{1}{2} H_2O = VO_2^+ + OH^-$$

$$(VO_2^+)(OH^-) = 8 \times 10^{-15}$$

$$[2] \quad V_2O_5 + 2H_2O = H_3V_2O_7^- + H^+$$

$$(H_3V_2O_7^-)(H^+) = 5 \times 10^{-4}$$

3. Electrical and Electrochemical Properties. Esin and Zyazev (16) state that vanadium pentoxide is a hole semiconductor. Kawaguchi (25) found that the conductivity is not isotropic, but varies with the three crystallographic axes, being the greatest in the "c" direction. Klemm and Pircher (28) found that they could not determine the specific conductivity of pure vanadium pentoxide with any measure of exactness since the loss of only a slight amount of oxygen from the oxide increased the conductivity greatly, and stoichiometrically exact vanadium pentoxide was very difficult to obtain. Boros (8) however, found that the heat treatment of vanadium pentoxide did not influence its conductivity, which result is unexpected if the conductivity is greatly influenced by the loss of oxygen atoms. More work is needed on the conductivity of the pure oxide before this problem can be resolved.

The specific conductivity of vanadium pentoxide was given by Klemm and Pircher (28) as about 10^{-4} to 10^{-3} ohm^{-1} cm^{-1} as

compared with the specific conductivity of the dioxide of 5×10^{-2} $ohm^{-1}\ cm^{-1}$, and that of the trioxide of 5×10^{2} $ohm^{-1}\ cm^{-1}$.

Vanadium pentoxide can be electrolytically reduced to the +4, +3 and +2 oxidation states (37). Deltombe, et al. (14, p. 9-10) determined the Nernst equations for the oxidation of the +4 to the +5 oxidation states at 25° C. Below are given the Nernst equations for the reverse reactions, the reduction of the +5 to the +4 state:

[3] $V_2O_5 + 6H^+ + 2e^- = 2VO^{++} + 3H_2O$

$$E = -0.958 + 0.1773\ pH + 0.0591 \log (VO^{++})$$

[4] $VO_2^+ + 2H^+ + e^- = VO^{++} + H_2O$

$$E = -1.004 + 0.1182\ pH + 0.0591 \log \frac{(VO^{++})}{(VO_2^+)}$$

[5] $H_3V_2O_7^- + 7H^+ + 2e^- = 2VO^{++} + 5H_2O$

$$E = -1.096 + 0.2068\ pH + 0.0295 \log \frac{(VO_2^{++})^2}{(H_3V_2O_7^-)}$$

[6] $H_2VO_4^- + 4H^+ + e^- = VO^{++} + 3H_2O$

$$E = -1.314 + 0.2364\ pH + 0.0591 \log \frac{(VO^{++})}{(H_2VO_4^-)}$$

[7] $2H_2VO_4^- + 3H^+ + 2e^- = HV_2O_5^- + 3H_2O$

$$E = -0.719 + 0.0886\ pH + 0.0295 \log \frac{(HV_2O_5^-)}{(H_2VO_4^-)^2}$$

[8] $H_3V_2O_7^- + 2H^+ + 2e = HV_2O_5^- + 2H_2O$

$$E = -0.501 + 0.0591\ pH + 0.0295 \log \frac{(HV_2O_5^-)}{(H_3V_2O_7^-)}$$

$$[9]\quad 2\,HVO_4^{=} + 5\,H^+ + 2e^- = HV_2O_5^- + 3\,H_2O$$

$$E = -1.281 + 0.1477\ pH + 0.0295 \log \frac{(HV_2O_5^-)}{(HVO_4^{=})^2}$$

$$[10]\quad 2\,VO_4^{\equiv} + 7\,H^+ + 2e = HV_2O_5^- + 3\,H_2O$$

$$E = -1.962 + 0.2068\ pH + 0.0295 \log \frac{(HV_2O_5^-)}{(VO_4^{\equiv})^2}$$

$$[11]\quad H_3V_2O_7^- + 3\,H^+ + 2e^- = V_2O_4 + 3\,H_2O$$

$$E = -0.806 + 0.0886\ pH - 0.0295 \log (H_3V_2O_7^-)$$

$$[12]\quad 2\,H_2VO_4^- + 4\,H^+ + 2e^- = V_2O_4 + 4\,H_2O$$

$$E = -1.022 + 0.1182\ pH - 0.0591 \log (H_2VO_4^-)$$

$$[13]\quad 2\,HVO_4^{=} + 6\,H^+ + 2e^- = V_2O_4 + 4\,H_2O$$

$$E = -1.586 + 0.1773\ pH - 0.0591 \log (HVO_4^{=})$$

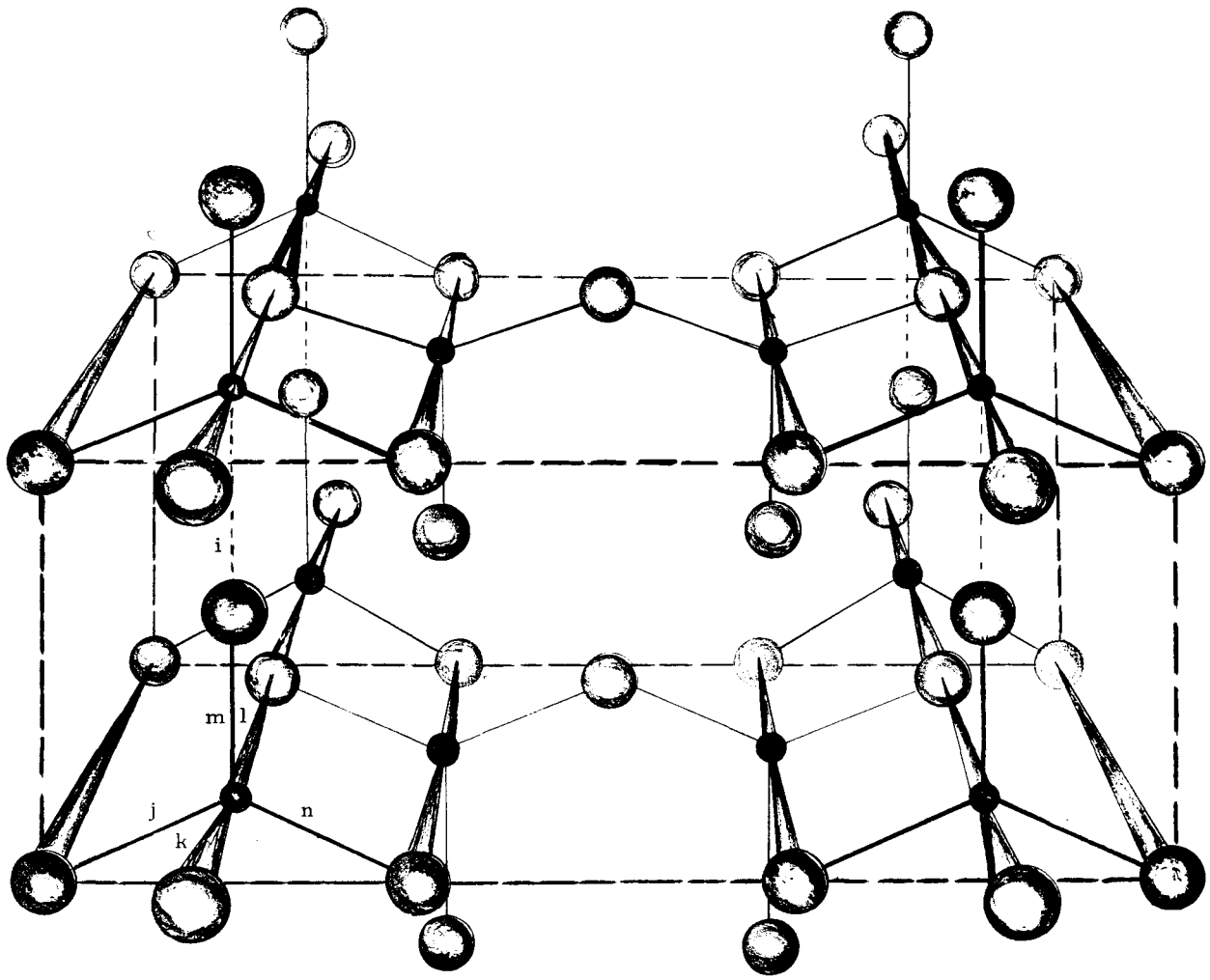
4. Crystal Structure of Vanadium Pentoxide. Although there is general agreement among the workers in the field that vanadium pentoxide belongs to the orthorhombic crystal system, there is considerable disagreement as to the actual structure of the crystal. Ketelaar (26), from an x-ray diffraction study of the oxide concluded that the crystal belongs to the point group C_{2v}^7 Pmmn and consists of a network of tetrahedra of oxygen atoms with a vanadium atom in the center of each tetrahedron. He gives the lattice constants as a = 11.48 Å, b = 4.36 Å, and c = 3.55 Å. Machatschki (30) however, suggests that the structure is composed of double

chains of the composition $(V_2O_5)_\infty$.

Bystrom, et al. (9) have concluded from their x-ray diffraction studies combined with crystal habit and etch figure studies of vanadium pentoxide that the crystal belongs to the D_{2h}^{13} Pmmn point group and consists of distorted trigonal bipyramids of five oxygen atoms surrounding each vanadium atom. The bipyramids are linked together by sharing corners in the x and y directions, with much weaker bonds in the z direction. They give the lattice constants as a = 11.519 Å, b = 4.374 Å, and c = 3.564 Å. Figure I gives a sketch of a three dimensional model of the vanadium pentoxide structure according to the dimensions given by Bystrom, et al. (8).

5. Reduction Products of Vanadium Pentoxide. The products which might be formed during the discharge of a vanadium pentoxide electrode include a series of solid oxides and oxy-hydroxides, and several different ionic species.

Only two of the possible solid reduction products have been studied extensively, the dioxide and trioxide. The dioxide, VO_2 (or the tetroxide, V_2O_4) is a blue-black solid which is prepared by the partial reduction of the pentoxide with the hydrogen halides, sulfur dioxide, oxalic acid or any of several other fairly mild reducing agents. The dioxide is amphoteric, dissolving easily in both acids and bases. It forms a great number of complex salts, especially with organic acid radicals. The dioxide is oxidized to the pentoxide

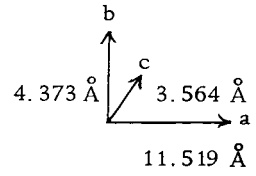


Nearest Neighbor Distances

i = 2.81 Å
j = 1.77 Å
k, l = 1.88 Å
m = 1.54 Å
n = 2.02 Å

Vanadium atoms

Oxygen atoms



Unit Cell Lengths

Figure I. Crystal Structure of Vanadium Pentoxide.
(Unit cell indicated by heavy broken line)

by concentrated nitric acid or by heating in air (37, p. 817-818). The dioxide crystallizes in the monoclinic system with a deformed rutile type structure (5).

Vanadium trioxide, V_2O_3, is a very high melting black powder which is prepared by heating the pentoxide in the presence of carbon or hydrogen. It has also been prepared by the electrolytic reduction of the dioxide (37, p. 825). It is insoluble in water and does not react rapidly with alkalies (27, p. 598). It absorbs oxygen from the air slowly to transform to the blue dioxide (14). The trioxide crystallizes in the hexagonal system (2).

In a phase analysis of mixtures of vanadium pentoxide and vanadium trioxide which were heated together, Andersson (4) identified 11 distinct oxides with compositions between VO and $VO_{2.5}$. These oxides, with their description, are given below:

VO	---	gray powder
V_2O_3	---	grayish powder
V_3O_5	---	dark gray powder
$VO_{1.75}$	---	dark lustrous powder
$VO_{1.80}$	---	nearly-black lustrous powder
$VO_{1.84}$	---	lustrous powder, blue-black
$VO_{1.86}$	---	strongly lustrous blue black powder
$VO_{1.87}$	---	aggregates of blue black crystals
VO_2	---	needle or rod-shaped blue black crystals
V_6O_{13}	---	black lustrous powder
V_2O_5	---	brownish yellow crystals

Of the above oxides, x-ray diffraction patterns are available for

V_2O_3 (2), V_3O_5 (4), VO_2 (5), V_6O_{13} (1), and V_2O_5 (3).

Several oxy-hydroxides have also been studied in recent years. One, which was given the formula $V_3O_5(OH)_4$, was prepared by Glemser and Schwarzmann (21) by reducing vanadium pentoxide in a concentrated ammonium chloride solution with zinc metal. They described this hydroxide as a black powder which is stable in air for weeks, and which dissolves in dilute sulfuric acid to produce a green solution. They also give the powder x-ray diffraction pattern for the oxy-hydroxide.

Two oxy-hydroxides in the +4 oxidation state, both with the formula $VO(OH)_2$ are described in the literature. One occurs in nature as the mineral Duttonite in the form of brown plate-like crystals. The crystals, although in the monoclinic system, are pseudo-orthorhombic (40). The other $VO(OH)_2$ was prepared by Glemser and Schwarzmann (21) by reducing vanadium pentoxide with sulfur dioxide and then heating the product. The oxy-hydroxide is described as a rose colored orthorhombic crystal which is oxidized readily in air, especially in the presence of water, to give a deep blue product. This oxy-hydroxide also dissolves in dilute sulfuric acid to give a blue solution.

Two other oxy-hydroxides have been studied by workers at the U.S. Bureau of Mines in Colorado (17; 40). Both of these oxy-hydroxides are found in nature associated with vanadium dioxide. One is the mineral montroseite, with the formula VO(OH); the other

is a "diffuse phase" and may have the formula $V_2O_3(OH)$. Both of these oxy-hydroxides belong to the orthorhombic crystal system.

There are many ionic species which might possibly be formed during the discharge of the vanadium pentoxide electrode. Vanadium dioxide forms the following ions in aqueous solution (14): Vanadyl (VO^{++}) which is blue in color and is present in the pH range up to 5.3; hypovanadate ($HV_2O_5^-$) which is brownish red in color and is present in the pH range above 5.3. When the vanadium is present in very low concentrations, the ion (HVO_2^+) is present in the pH range of 5.3 to 7.3.

In solution the trioxide forms three ions, all of which are green in color (14). They are(V^{+++}) which is present in the pH range up to about 2.8;(VOH^{++}) which is present in the range 2.8 to 3.4; and (VO^{+})which is present in the pH range above 3.4.

C. Theories of the Discharging and Recovery Mechanism of Oxide Electrodes

Since manganese dioxide is the only oxide electrode for which a mechanism has been proposed, this survey will be limited to theories involving that oxide. W. C. Vosburgh (41) gives a recent review of the earlier theories of the discharge and recovery mechanism and a discussion of the theories most widely accepted today. The theory which presently has the most support was first proposed by Coleman (12). This theory assumes that the composition of the oxide surface in contact with the solution determines the electrode

potential. During the discharge, the electrons from the inert electrode reduce the manganese dioxide from the +4 to the +3 oxidation state, while at the same time protons from the solution diffuse into the oxide to form the oxy-hydroxide, MnOOH. The reduction is believed to occur mainly at the solution-oxide interface, although some reduction may also occur within the body of the oxide. As the hydroxide concentration builds up on the surface there is a chemical potential developed which causes the hydroxide to diffuse into the body of the oxide. This diffusion is believed to be actually accomplished by the diffusion of electrons from manganese atoms of different oxidation states and protons from the hydroxide to the underlying oxide ions. Since this diffusion is much slower than the electrical reduction, the electrode potential drops considerably due to the dilution of the manganese dioxide on the surface with the oxy-hydroxide. When the circuit is broken, the diffusion continues until the oxide and the oxy-hydroxide are uniformly distributed throughout the electrode. This latter process is known as the recovery of the electrode, since the concentration of the dioxide on the surface builds up and approaches its original value.

Scott (38) found that a solution of the diffusion equation applied to a semi infinite solid (11, p. 75-76) satisfactorily predicted the general form of the discharge and recovery curves obtained by Ferrell and Vosburgh (18). Kornfeil (29) modified Scott's equation such that the recovery curve could be predicted by the shape of the

discharging curve. He then found close agreement between his calculated and experimental recovery curves.

Cahoon (10) proposed a somewhat different theory in that the manganese dioxide is supposed to be reduced electrochemically directly to Mn^{++}, which passes into solution. The manganous ion then reacts with the dioxide on the surface of the electrode to give the hydroxide, MnOOH, or with the dioxide and zinc to give hetaerolite.

Brenet and Ghosh (20) proposed a slightly modified mechanism which they limited only to the gamma form of manganese dioxide, since they assert that the mechanism depends upon the crystal modification. They postulate that there is a dilation of the lattice of the gamma dioxide during the first part of the discharge and then afterwards there is a reduction to alpha or gamma Mn_2O_3, and finally a transformation to the MnOOH.

Daniel-Bek (13) has proposed an entirely different theory. He states that the graphite is an active component of the graphite-manganese dioxide system, rather than just an inert electrode. When the cell is discharged, the surface of this combination electrode is partially discharged. When the external circuit is broken, the combination electrode is recharged by the local cell current.

Much of the disagreement concerning the mechanism of discharge and recovery is due to the assumption that the same mechanism applies to any and all experimental conditions. For example

the pH of the solution undoubtedly plays a large part in establishing the type of mechanism. Still much work remains to be done before a unified theory can be proposed.

II. PREPARATION AND PROPERTIES OF VANADIUM PENTOXIDE ELECTRODES

A. Introduction

In the discussion of the electrodes that follows, and in this entire work, the European sign convention is followed with regard to the electrode potential. That is, the sign of the electrode potential is taken as the sign of the given electrode measured relative to the standard hydrogen electrode, which means that substances which have a greater tendency than hydrogen to give up electrons are given a negative sign.

All of the potentials are measured on the hydrogen scale, on which the zero of electrode potential at any temperature is defined as the potential corresponding to the reversible equilibrium between hydrogen gas at one standard atmosphere pressure and hydrogen ions at unit activity. However, since the hydrogen electrode is inconvenient to use, the saturated calomel electrode (SCE) was used as the reference electrode in all experiments in this investigation. The saturated calomel electrode has a potential with respect to the standard hydrogen electrode of +0.2420 volts at 25°C. To convert the potentials given in this work to potentials with respect to hydrogen, it is necessary to add +0.2420 volts to the value given (30, p. 254-255; 35, p. 110-113).

In order to study the discharge and recovery of the vanadium pentoxide electrode, it was first necessary to construct an electrode

system in which the oxide was in intimate contact with an inert electrode. Several problems were encountered in constructing the electrodes, and of the several methods tried, no method was completely satisfactory in all respects.

B. Vanadium Pentoxide Powder Electrodes

The starting material in the preparation of most of the electrodes was Baker's analyzed reagent grade, 99.5 percent vanadium pentoxide, which contained 0.1 percent chlorides and 0.3 percent carbon dioxide. The simplest way to make the electrodes was to place the oxide powder, either alone or mixed with graphite powder, on a depression in a graphite block. A carbon rod was connected to the block and the entire assembly was placed in the electrolyte solution. This electrode was difficult to handle since the powder did not remain on the graphite. The electrode could not be transferred easily from one solution to another. However, this electrode did have a relatively low resistance, which would be advantageous in some experiments.

The initial electrode potential (emf) of these electrodes varied from +0.4 to +0.5 with respect to the reference electrode in a saturated vanadium pentoxide solution with a pH of about 2.4. The emf decreased 0.1 volt the first day and about 0.02 volt per day thereafter for five days.

In order to obtain better contact between the vanadium

pentoxide powder and the graphite, and to obtain an electrode which was easier to handle, electrodes were made by compressing the oxide into a small hole in a graphite cylinder. The performance of these electrodes was similar to that of the loose powder electrodes.

A bobbin electrode was constructed by mixing the oxide with graphite, placing the mixture on a piece of cotton cloth and fastening the cloth to a carbon rod with a rubber band. These electrodes were easy to handle and could be transferred readily from one solution to another. However, the emf decreased very rapidly and also a fungus began growing on the cotton after a few days, so these electrodes were abandoned.

C. Electrolytically Deposited Electrodes

The most convenient type of electrode, which also had a low resistance, was one wherein the vanadium pentoxide was electrolytically deposited on a carbon rod. Several attempts of varying success were made to construct this type of electrode. A vanadyl solution was prepared by reducing vanadium pentoxide with concentrated hydrochloric acid by a method similar to that of Gooch and Curtis (23). The mixture of oxide and acid was heated to about 200^{o}C for from three to six hours. During this time a dark opaque solution was formed which, when diluted with about five times as much water, produced a deep blue solution.

The deposition of vanadium pentoxide from this solution

was found to be quite difficult and very capricious. Electrolyses were attempted over a pH range from very acid to about pH = 12. At values above a pH of 1, a grey precipitate formed which remained in suspension during the electrolysis. A red-brown deposit on the anode was obtained---sometimes--within the pH range of 0 to 8. Several different values of current density were also tried. Although a pH of about 7 and a current of about 100 ma were most effective in producing the deposit, really satisfactory conditions were not found.

The initial emf of these electrodes, in a saturated vanadium pentoxide solution of pH 5 varied from +0.40 to +1.10 volts vs SCE. In all cases the emf decreased very rapidly when the electrodes were allowed to stand in the solution. The electrodes could be charged and discharged immediately after they were prepared. However, if an electrode was discharged and then allowed to stand in the solution it could not be recharged. Also, if the charged electrode were allowed to stand for very long in the solution, the emf dropped to a great extent and the electrode could not be recharged. Upon close examination of the electrodes which had been standing in solution, it was found that the oxide had apparently dissolved off the carbon. An x-ray diffraction pattern taken of the electrolytic vanadium pentoxide which had been plated on platinum foil, showed only very diffuse lines. A similar pattern was obtained with chemically pure vanadium pentoxide which had been ground to a very fine

powder in a ball mill. This indicated that the vanadium pentoxide was being plated out on the carbon in the form of very small crystals. This perhaps explains the increased solubility of the electrolytic vanadium pentoxide.

D. Pressed Pellet Electrodes

These electrodes were first made from technical grade vanadium pentoxide which was placed around a zig-zag piece of platinum wire in a stainless steel die 2.54 cm high, 1.41 cm inside diameter and 1.27 cm outside diameter. The pellets were pressed on a hydraulic press with a force of 12,000 pounds. These pellets, as taken from the die, disintegrated immediately when placed in a water solution. However a heat treatment in a furnace at 200 to 250^{o}C for six to 12 hours made the pellets stable in a water solution for a few days.

When the reagent grade vanadium pentoxide was used, the pellets under the same conditions of pressing would not hold together. The few that could be made were found to disintegrate rapidly in solution, even though they had been previously heat treated. Hence, although this method had appeared to be very satisfactory when the technical grade vanadium pentoxide was used, it could not be utilized with the reagent grade vanadium pentoxide.

E. Electrodes Cast from Molten Oxide

Since vanadium pentoxide melts at a relatively low temperature (650°C) a logical way of preparing the electrodes was to cast the melt into forms. However several problems were involved in obtaining good contact with the inert electrode. It was found that dipping a carbon rod or platinum wire into the melt was not satisfactory because the melt very quickly dropped off the inert electrode when the electrode was placed in an aqueous solution. Also, it was found that the resistance of such electrodes was very high indicating that the contact between the melt and the rod was not good.

A more successful method consisted of melting the oxide in a pyrex tube around a platinum wire spiral or a strip of platinum foil. The electrodes prepared this way remained intact in a water solution for several weeks.

The melt electrodes consisted of a cylinder of many needle-like crystals which in the aggregate appeared to be purple in color. An x-ray diffraction study was made of these electrodes to compare them with the original vanadium pentoxide powder. The patterns were found to be identical, within experimental error, except that the intensities of the lines were different. This change in intensity showed the effect of the orientation of the crystals which had been formed from the melt. Table II, page 31 compares the line spacing for the two patterns.

The emf of these electrodes became more positive upon

standing in solution. The change was very gradual, the emf increased only 100 mv in 30 days. It was found that the emf of the electrode also increased when it was transferred from a saturated vanadium pentoxide solution to a solution which contained a salt, such as potassium or ammonium chloride, as well as the vanadium pentoxide. It was also found that the resistance drop of the electrodes decreased when the electrodes were allowed to stand in the vanadium pentoxide solution for several days.

The resistance of the melt electrode was estimated in the following manner. The electrode was discharged in a cell (described in Figure III, p. 51) in which the entire resistance of the cell was considered to be due to the resistance of the vanadium pentoxide electrode. The electrode was considered to consist of a flat piece of platinum foil in the center of a cylinder of vanadium pentoxide with a 0.05 cm thickness of oxide between the foil and the solution. The following calculations were made from the measured resistance drop and the current flowing through the cell. This is just a sample calculation to illustrate the method.

$$IR = 24 \text{ mv}$$

$$I = 0.38 \text{ ma}$$

$$R = 63.3 \text{ ohm}$$

$$\rho = \frac{RA}{l} = \frac{63.3 \text{ ohm} \times 1 \text{ cm}^2}{0.05 \text{ cm}} = 1.26 \times 10^3 \text{ ohm cm}$$

$$K = 1/\rho = 7.94 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$$

where ρ is the resistivity, A is the cross-sectional area, l the

length and K is the specific conductivity of the electrode. This conductivity was compared with the specific conductivity measured by Klemm and Pircher (28) of 10^{-4} to 10^{-3} ohm^{-1} cm^{-1} and found to be in good agreement.

The melt electrodes were used in all of the following experiments, except where otherwise noted.

III. PREPARATION, PROPERTIES AND ANALYSIS OF DISCHARGE PRODUCT

A. Preparation

Since a knowledge of the identity and characteristics of the discharge product would be helpful in understanding the mechanism of the discharge and recovery of the electrode, many attempts were made to prepare the pure discharge product. It was found in early experiments that during a discharge of a few hours the surface of the electrode changed in color from purple or brown to jet black; upon further discharge the black color appeared to have penetrated the entire electrode. However, it was impossible to separate the black discharge product from the vanadium pentoxide either by scraping the black coating from the electrode or by crushing the electrode and mechanically picking out the black particles. No matter how carefully the separation attempt was made, vanadium pentoxide was always found, by x-ray diffraction analysis, with the discharge product. It appeared that the two substances were intimately mixed as would be the case in a solid solution.

Discharges were performed in which the current density, the time of discharge, and the pH of the solution were varied, in an attempt to discharge the entire electrode. However it was found under all conditions tried that the discharge reaction proceeded to a certain extent and then other electrode reactions, such as the reduction of the vanadium to a soluble form or the decomposition of

water, took place. A method was not found for the preparation of the pure discharge product by the electrolytic reduction of the vanadium pentoxide. Table I gives the conditions used in several attempts to prepare the pure discharge product.

Table I. Preparation of the Discharge Product

Current (ma)	Discharge Time (hrs)	Solution pH	Appearance Electrode	Solution
1.5	72	1	black	green
1.5	72	2.9	black	green
1.5	72	8.2	black	colorless
10	24	2.5	black	green
15	6	2.5	black	green
30	24	4.5	brown	blue
30	72	4.5	dissolved completely	blue

B. X-ray Diffraction Analysis

1. Method. The x-ray diffraction analysis was made with a North American Phillips Co. diffraction spectrometer equipped with a Geiger-Muller tube and a Brown recorder. The radiation was Cu K_{α} and the scanning speed was one degree 2θ per minute for all samples. The one degree divergence and scatter slits combined with the 0.006 inch receiving slits were found to be advantageous for optimum height of the recorded spectra. The rate meter was set at a scale factor of 16, a multiplier of 0.8 and a time constant of 2 for all analyses. The data were interpreted with the aid

of the ASTM x-ray powder data cards by the Hanawalt method (6).

In the Hanawalt method the interplanar spacings, d, of the unknown material are determined from the wavelength of the x-radiation, λ, and the angle, 2θ, which is obtained from the geometry of the detector, with the use of the Bragg relation where n

$$n\lambda = 2 d \sin\theta$$

is the order of the reflection. (In practice tables of d values tabulated against the angle 2θ for the particular radiation are used to obtain the interplanar distances.) The relative intensities of the diffraction line, I/I_1, are obtained from the height of the diffraction peak on the recorder divided by the height of the tallest peak, which is given the value of 100.

A table is then prepared listing all the observed reflections in the unknown, arranged in order of decreasing d values. By trial and error, the three most intense lines are matched with lines listed in the ASTM index. Then an attempt is made to match all the d values and relative intensities of the lines of the unknown with that of a known compound. This procedure is aided greatly if the possible composition of the unknown can be determined by some other means.

There are several sources of error inherent in the Hanawalt method. If a constituent is present in the unknown in small amounts only it may be missed entirely. (Most substances must comprise at

least 5 percent by weight of the sample in order to be detected.) Also the presence of impurities which partially replace the atoms of the major component may cause the interplanar distances to be shifted slightly from that of the pure material. The relative intensities of the lines may also be altered by several things. One is that the intensity is dependent upon the type of radiation used for the diffraction. Another is by the presence of needle shaped or plate-like particles in the sample since these tend to become aligned during the preparation of the sample, and hence cause an intensification of some of the lines and a weakening of others. If two components contain certain lines in common, the intensity of the particular lines will be much greater than the corresponding intensity reported for one component (6, p. 190-258).

If a solid solution is present in small amounts (usually less than 30 percent by weight) the resulting x-ray pattern will be the pattern of the major component, slightly distorted. The pattern of the minor component will not appear unless it is also mixed in the sample in pure crystalline form. When both components are present in roughly equal amounts, the atoms of one usually begin to distribute themselves regularly through the lattice of the other. A new x-ray pattern different from that of either component will result due to the presence of what is known as a "geometrical compound". The presence of this "compound" is revealed by the appearance of numerous new lines in the x-ray pattern, interspersed

between the original lines due to the solid solution (39, p. 435).

Although it was believed that the product of the discharge of the vanadium pentoxide electrode was a solid solution, attempts were made to obtain an x-ray diffraction pattern of this product.

2. Standards. Several materials which were used as standards of comparison were analyzed under the same conditions as were the discharge products. This was done so that any instrumental errors would affect both the standards and the unknowns. The standards used were the following: Baker's analyzed vanadium pentoxide; this same vanadium pentoxide after it had been melted in pyrex tubes, cooled and then ground in a mortar; the technical grade vanadium pentoxide used in preparing the pressed pellet electrodes; and $V_3O_5(OH)_4$ which was prepared according to the directions given by Glemser and Schwarzmann (21). The line spacings and relative intensities of the x-ray diffraction patterns taken of the standard vanadium pentoxides and also the values given in the ASTM data file (3) are shown in Table II. The values for $V_3O_5(OH)_4$ are shown in Table III.

The precision to be expected in comparing unknowns with the values given in the ASTM file is $\pm$ 0.1 Angstrom for low d values and 0.02 Angstrom for high d values. It will be seen that the pattern for the Baker's analyzed vanadium pentoxide obtained in this laboratory agrees within the experimental error with the pattern given on the ASTM data card. It will also be noted from

Table II that the intensities of the lines for the vanadium pentoxide which had been melted are quite different from the intensities of the same lines for the Baker's vanadium pentoxide which had not been melted. This difference is due to the preferred orientation of the crystals which were cooled from the melt. (The melted vanadium pentoxide crystallized in the form of long needles; even though these crystals were ground in an agate mortar, their form was not completely distroyed.)

It will also be seen from Table II that the pattern of the technical grade vanadium pentoxide does not resemble very closely the pattern of either the Baker's vanadium pentoxide or the pattern given on the ASTM card. No attempt was made to determine further the components present in the technical grade pentoxide.

The agreement between the patterns for the $V_3O_5(OH)_4$ which was prepared in this laboratory and that prepared by Glemser and Schwarzmann is not very good, as can be seen in Table III. However the patterns do indicate that the samples are probably the same material. It is quite possible that both the sample prepared here and that prepared by Glemser and Schwarzmann contain impurities.

3. Discharge Products. The discharged electrodes were washed with distilled water, dried in a desiccator and then ground in an agate mortar. Since it was found that the powdered electrodes were oxidized upon standing a few days, as indicated by a change in

color from greenish black to greenish yellow, the x-ray diffraction analyses were performed as soon as possible after the electrode was discharged. However, there was still the possibility that the discharged products were at least partially oxidized during the sample preparation and the process of the analysis.

The discharged technical grade pellets were first to be analyzed. Table III gives the pattern for one of the samples, comparing it with the pattern for $V_3O_5(OH)_4$. It will be seen that the agreement between the pattern for this discharge product and for $V_3O_5(OH)_4$ is very good. (This is the reason that $V_3O_5(OH)_4$ was selected as a standard for comparison.) Although it would appear that success had been obtained in the identification of the discharge product, the pattern for $V_3O_5(OH)_4$ was obtained only when technical grade vanadium pentoxide was discharged. And since the technical grade vanadium pentoxide obviously contains impurities (as shown in Table II) the $V_3O_5(OH)_4$ may be produced from a reaction other than the one being studied in this work.

Several x-ray diffraction patterns were taken of the reduced reagent grade melt electrodes; in all cases the pattern resembled that of pure vanadium pentoxide. Table IV gives the patterns for two samples of the discharge product compared with the pattern for the vanadium pentoxide which had been cooled from the melt. It will be noted that the patterns for the discharge products resemble very closely the pattern for the vanadium pentoxide, with the exception

that some of the intensities are markedly different. In comparing the patterns No. 1 and No. 2 in Table IV, it is interesting to note that the relative intensities of the lines at 5.79, 4.10, and 2.189 Ångstroms are very different; in all cases the intensities of the lines for the discharge product are greater than the intensities for the corresponding lines of the vanadium pentoxide. Since these are some of the most important lines in the pattern, the difference in the intensities are significant.

Since both the vanadium pentoxide and the reduced vanadium pentoxide electrodes consisted of needle-like crystals, it is not likely that the difference in intensities is due to a preferred orientation of the crystals. The other two possibilities are that the lines of the reduced product consist of a superposition of lines of two components, or that the reduced product pattern is that of a solid solution of vanadium pentoxide and another minor component.

4. Conclusions. Definite conclusions cannot be drawn from the results of the x-ray diffraction analyses. However, these results, combined with the results of the chemical analysis and the discharge experiments (to be discussed in later sections), do indicate that it is likely that a solid solution is formed during the discharge of the vanadium pentoxide electrode.

If a solid solution is formed during the discharge it will not be possible to obtain an x-ray diffraction pattern for the discharge product unless the electrode can be reduced to the extent

Table II. Comparison of X-ray Powder Diffraction Patterns for Vanadium Pentoxides.

V_2O_5 ASTM (3)		V_2O_5 No 1		V_2O_5 No 2		V_2O_5 No 3	
d	I/I_1	d	I/I_1	d	I/I_1	d	I/I_1
---	---	---	---	---	---	9.63	11
---	---	---	---	---	---	7.32	28
---	---	---	---	---	---	6.94	100
5.76	40	5.82	38	5.79	17	---	---
---	---	---	---	---	---	4.79	9
4.38	100	4.40	100	4.39	100	---	---
4.09	35	4.12	33	4.11	59	---	---
---	---	---	---	---	---	3.89	16
3.48	7	3.48	7	3.50	6	3.50	20
3.40	90	3.43	68	3.42	24	3.40	16
---	---	---	---	---	---	3.21	41
---	---	---	---	---	---	3.09	22
---	---	---	---	---	---	3.02	30
2.88	65	2.89	56	2.89	39	2.93	14
2.76	35	2.77	27	2.77	15	2.74	9
2.687	15	2.697	9	2.699	5	2.66	7
2.610	40	2.623	29	2.623	10	2.64	7
---	---	---	---	---	---	2.32	9
---	---	---	---	---	---	2.29	11
---	---	---	---	---	---	2.28	12
2.185	17	2.194	17	2.191	49	2.19	7
2.147	11	2.154	10	2.154	20	---	---
1.992	17	1.999	14	1.997	5	1.96	8
1.919	25	1.934	17	1.925	11	---	---
1.900	17	1.905	10	1.905	20	---	---
1.864	13	1.870	10	1.868	8	---	---

No 1: Baker's analyzed vanadium pentoxide

No 2: Baker's analyzed vanadium pentoxide cooled from melt

No 3: Technical grade vanadium pentoxide

Table III. Comparison of X-Ray Powder Diffraction Patterns for Reduced Vanadium Oxy-hydroxides

$V_3O_5(OH)_4$ No 1		$V_3O_5(OH)_4$ No 2		Discharge Product No 3	
d	I/I_1	d	I/I_1	d	I/I_1
5.54	100	5.29	100	5.64	100
4.46	50	4.20	14	4.48	7
3.97	100	4.00	80	4.01	52
3.46	80	3.49	24	3.50	13
3.23	100	3.26	100	3.25	80
3.14	40	3.16	14	3.16	60
2.79	80	2.82	46	2.82	33
---	---	2.80	24	2.80	22
---	---	2.75	6	2.74	6
2.50	70	2.52	25	2.52	22
---	---	2.47	5	2.47	6
---	---	2.29	6	2.29	6
2.25	40	2.26	7	---	---
---	---	2.23	4	2.23	7
2.09	40	2.10	2	---	---
---	---	2.07	2	---	---
1.98	70	1.99	13	1.99	13
1.86	60	1.88	9	1.86	6
1.74	50	---	---	1.74	10
1.68	60	---	---	---	---
1.66	40	---	---	---	---
1.62	40	---	---	1.58	10

No 1: Prepared by Glemser and Schwarzmann (19)

No 2: Prepared in this laboratory by method of Glemser and Schwarzmann

No 3: Prepared by discharge of technical grade V_2O_5 pellet

Table IV. Comparison of X-Ray Powder Diffraction Patterns for the Discharge Products

V_2O_5 No 1		Discharge Prod. No 2		Discharge Prod. No 3	
d	I/I_1	d	I/I_1	d	I/I_1
---	---	7.43	11	7.37	12
5.79	17	5.79	36*	5.76	36
---	---	4.87	16	4.84	6
4.39	100	4.39	100	4.39	100
4.11	59	4.10	85*	4.18 4.10	12 70
3.50	6	3.49	9	---	---
3.42	24	3.42	13	3.41	10
---	---	3.13	9	---	---
---	---	3.08	4	---	---
2.89	39	2.89	40	2.89	28
---	---	---	---	2.88	24
2.77	15	2.77	10	2.76	6
2.699	5	2.691	4	---	---
2.623	10	2.620	5	---	---
---	---	2.415	4		
---	---	2.220	8		
2.191	49	2.189	95*		
---	---	2.047	3		
1.997	5	1.994	4		
1.925	11	1.922	10		
1.905	20	1.902	22		
1.868	8	1.831	6		

No 1 Chemically pure V_2O_5 cooled from melt

No 2 V_2O_5 discharged at 15 ma for five hours

No 3 Vanadium pentoxide discharged at 1.5 ma for 72 hours

* Lines which may be due to $VO_x(OH)_y$ and V_2O_5

that the discharge product is the major component in the sample. This might be possible if a thin layer of vanadium pentoxide could be reduced.

C. Chemical Analysis

In this work an analysis was made only for the amount of reduced vanadium in the samples. This was done primarily to determine if the vanadium had actually been reduced during the discharge. It was also important for other studies, which will be described later, to ascertain the relative solubility of the discharge product in acid and in basic solutions. This was determined by an analysis of the amount of reduced vanadium in the electrode compared with the amount in the electrolytic solution, after the electrode was discharged.

1. Method. At first the analysis was made by the method suggested by Furman (19, p. 195) in which the discharge product was titrated with potassium permanganate and the endpoint was determined visually. However, when the discharge products were analyzed by this method, the precision on duplicate samples was very poor since the end point was difficult to detect.

It was found more satisfactory to use a potentiometric method which utilized a platinum wire and a saturated calomel cell as detecting electrodes and a Varian recording potentiometer, with a chart speed of two inches per minute, to record the change in

potential. The procedure used was as follows: The sample to be analyzed was dissolved in 100 ml of 2 N sulfuric acid and then heated to 90°C. The sample was stirred vigorously with a magnetic stirrer and titrated with standard ceric ammonium sulfate which was added from a micro buret at a rate of about 15 drops / minute (.04 ml/drop). After each addition of oxidant, the recorder jumped to a higher positive value. The endpoint was taken when the greatest change in emf per volume of titrant was obtained.

The ceric ammonium sulfate was standardized by the method given above against reagent grade sodium oxalate which had been dried overnight at 110°C. The average precision on triplicate samples was $\pm$ 1 percent.

A blank was analyzed using reagent grade vanadium pentoxide. It was found that the end point was reached very quickly, although the precision was poor in these titrations where such a small amount of the titrant was used. To reach the endpoint required from 0.04 to 0.10 ml of the ceric ammonium sulfate, a constant blank of .07 ml was subtracted from the volumes of the oxidant used in the titrations of the discharge products.

2. Results. Vanadium pentoxide electrodes which had been discharged at several different current densities for several different times were analyzed for reduced vanadium. In all cases some of the original pentoxide had been reduced to a lower oxidation state during the discharge. Table V shows the results of the analysis of

two typical electrodes which had been discharged at about 0.3 ma/cm^2 in a solution of pH 8.8. The results are given in weight percent of three assumed possible products. Although it is quite possible that none of the three assumed products is the one which is actually formed, it is likely that the pentoxide is reduced to some compound in which the vanadium is within the oxidation state range of +4.67 in $V_3O_5(OH)_4$ to +4.0 in $VO(OH)_2$.

Table V. Analysis of the Discharge Product

Discharge Time	ml 0.0975 N oxidant	Wt. % $VO(OH)_2$	Wt. % $V_2O_2(OH)_5$	Wt. % $V_3O_5(OH)_4$
36 hours	0.34	2.7	6.9	7.9
69 hours	0.55	5.1	13.1	14.9

A calculation of current efficiency can be made using the discharge at 69 hours. The equivalents of reduced vanadium found in both the discharge solution and in the solid electrode was $(0.72 \times 10^{-3})(0.0975) = 7.02 \times 10^{-5}$. The number of equivalents of electricity used was $\frac{(3.0 \times 10^{-4}\ \text{amp})(2.47 \times 10^{5}\ \text{sec})}{96500\ \text{coul/sec}} = 7.7 \times 10^{-4}$ equivalents. The efficiency was then $\frac{(7.02 \times 10^{-5})(100)}{(7.7 \times 10^{-4})} = 9.1\%$. This current efficiency is very low, but it is in agreement with the observation that the pure discharge product was not formed with more than twice the number of coulombs calculated for a complete discharge for any of the three possible products given above. There are several possible reasons for the low current efficiency. One is

that the ammeter used to measure the current was found to be reading high. But even if the current were 2 ma, the current efficiency would be only 16 percent. Another reason is that competing reactions were taking place during the discharge. The most probable reaction would be the liberation of hydrogen from the water. This is in agreement with the observation of bubbles rising within the solution during long discharges.

Table VI shows the results of solubility measurements as a function of pH and of discharge current density. After the discharge was completed, the electrolytic solution was analyzed for reduced vanadium. Then the electrode was washed, dried, weighed and analyzed. The solubility in this Table is reported as the amount of reduced vanadium found in the electrolytic solution divided by the total amount of reduced vanadium found in both the solution and in the electrode.

Table VI. Solubility of Discharge Product as a Function of pH and of Current Density

Discharge C.D.	Discharge Time	Wt. % of Product in Solution	
		pH 1	pH 8
0.3 ma/cm^2	48 hours	31%	5%
3.0 ma/cm^2	24 hours	60%	

3. Conclusions. From the chemical analysis performed on the discharge product it is evident that the vanadium pentoxide is

reduced during the discharge, although the oxidation state of the reduction product is not known. The analyses also indicate that the discharge product produced at low current densities is considerably more soluble in acid solutions than in basic solutions.

IV. DEPENDENCE OF ELECTRODE POTENTIAL ON pH OF SOLUTION

A. Introduction

During the discharge of the vanadium pentoxide electrode the vanadium in the +5 state is reduced to some ion of lower oxidation state. Since the identity of the discharge product was not determined, the product was given the general formula $VO_x(OH)_y$ in which x and y can be any numbers, including zero, with the only restriction being that 2x + y must be less than 5. Hence the reaction taking place during the discharge can be written as:

$$[14] \quad V_2O_5 + ne^- + nH^+ + m\,H_2O = VO_x(OH)_y$$

where $y = n + 2m$ and $x + y = m + 5$. The electrode potential, according to the above reaction, is given by the Nernst equation as:

$$[15] \quad E = E^o - \frac{RT}{n\mathcal{F}} \ln \frac{[VO_x(OH)_y]}{[V_2O_5][H_2O]^m[H^+]^n}$$

where the brackets refer to the activities of the corresponding species. The activity of pure water is taken as unity, and since the water is in great excess in the electrolytic solution, it is reasonable to assume that its activity will not change appreciably as the pH of the solution is changed. If it can be assumed that the activity ratio of the two solids remains constant as the pH changed, then at 25°C

$$[16] \quad E = E^{o} - \frac{0.0591}{n} \log \frac{1}{[H^{+}]^{n}}$$

which can be rewritten as

$$[17] \quad E = E^{o} + 0.0591 \text{ pH}$$

The activity ratio of the two solids will be constant if the two are pure solids or if they form a solid solution, the composition of which does not change as the pH is changed. The discharge experiments, which will be discussed later, indicate that a solid solution is formed during the discharge. The reasons for believing that the composition of the solid solution does not change with changing pH are given in the Discussion at the end of this section on p.45 .

B. Temperature Control

In order for the Nernst equation to be applied to the experimental values of emf and pH, it is necessary that the temperature be accurately known and that it remain constant for the duration of the experiment. Also, since a reference electrode must be used in making any emf measurements, it is necessary to keep the temperature constant in order that the reference potential be constant. The potential of the saturated calomel electrode, which was used as a reference electrode in all the experiments, is relatively sensitive to temperature, changing about 0.6 mv/degree centigrade.

All of the measurements of emf and pH were made with the cells partially immersed in a large (100 liter) water bath. The

temperature of the bath was controlled by a mercury regulator and an electronic relay which actuated a 250 watt heating coil. The temperature of the bath was controlled within 0.2 degree during the experiments. A Beckmann thermometer, which had been calibrated with a Leeds and Northrup standard platinum resistance thermometer, was used to measure the temperature of the bath.

C. Measuring Instruments

The pH of all solutions was measured with a Beckman Model G pH-meter used with a Beckman saturated calomel electrode and a Beckman glass electrode. The pH meter was calibrated at frequent intervals with a series of standard buffer solutions. The electrode potentials were measured with a Varian Model G-14 Graphic Recording potentiometer. The pH meter could be read to 0.02 pH unit and the potentiometer to 2 mv on the one-volt scale.

D. Experimental Conditions

1. Buffer Solutions. In order to maintain the various solutions in which the experiments were being carried out at a constant pH, it was necessary to use buffer solutions. The McIlvaine's Standard Buffer solutions (24, p. 1715) were used for all of these experiments.

2. Electrodes. Two types of electrodes were used in these experiments. The first type consisted of freshly prepared melt

vanadium pentoxide electrodes which had been allowed to stand in a saturated vanadium pentoxide solution until all the electrodes had attained the same electrode potential. The other type consisted of melt electrodes which were discharged for several hours. These electrodes were then allowed to stand in the discharge solution for two to three hours until they attained the same potential.

E. Determination of Relationship Between Emf and pH

1. Measurement with Vanadium Pentoxide Electrodes. It was found during the course of these experiments that the emf of electrodes placed in high pH solutions decreased almost exponentially with time, even though the pH remained constant. Since the emf in high pH solutions was so variable the measurements were confined to the pH range between two and five. The vanadium pentoxide electrodes were placed in the respective buffer solutions and left there for 30 minutes. At the end of this time, the emf and pH of each solution was measured, beginning with the electrodes in the solution of highest pH. The results are shown in Figure II, curve e.

2. Measurement with Partially Reduced Electrodes. The vanadium pentoxide electrodes were discharged in a parallel arrangement at a total current of 1.5 ma for 12 hours; after which the electrodes were allowed to stand for two hours in the discharge solution until the electrode potentials were the same, within five

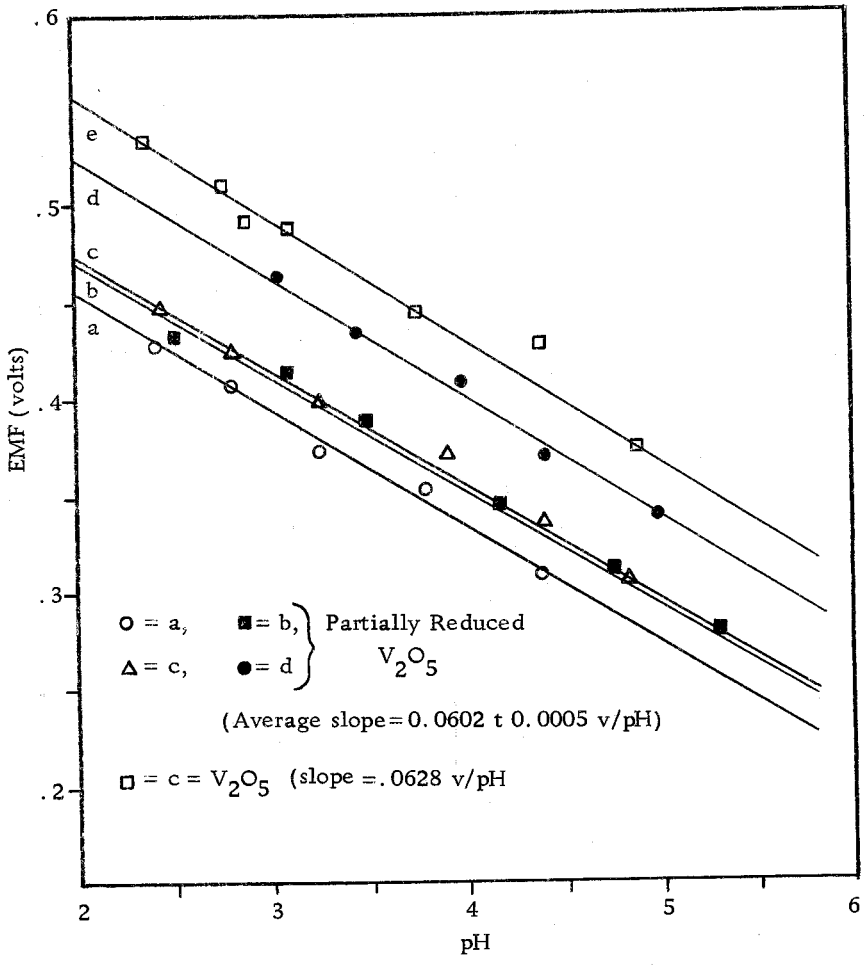


Figure II. Dependence of EMF Upon pH.

millivolts. The electrodes were then placed in the respective buffer solutions and left for 30 minutes. At the end of this time the electrode potentials and pH values were determined. The results are shown in Figure II, curve a. These electrodes were returned to the pH solutions and left for another 30 minutes, after which the emf and pH values were again determined. The results are shown in Figure II, curve c.

The above experiment was repeated with new electrodes and new buffer solutions. These results are also shown in Figure II, curve d.

3. Measurement in Buffer Solutions Saturated with Vanadium Pentoxide and the Discharge Product. Since both V_2O_5 and the $VO_x(OH)_y$ were found to be quite soluble in aqueous solutions, an attempt was made to saturate the buffer solutions with both of these solids before making the measurements. To obtain solid $VO_x(OH)_y$, several vanadium pentoxide electrodes were reduced at about one milliamp current for seven days. The electrodes were ground in a mortar and, along with powdered vanadium pentoxide, were added to each of the buffer solutions. The solutions were stirred vigorously and then allowed to stand in contact with the two solids for two days before any measurements were made.

The partially reduced electrodes were placed in these buffer solutions and left there for 15 minutes. At the end of this time the emf of each electrode and pH of each solution were

determined. The results are shown in Figure II, curve b.

4. Results. The emf of each electrode was plotted against the corresponding solution pH for each of the above experiments. The best straight line was drawn between the points for each experiment, and the slope of each line was determined. The slope of the line representing the relationship between emf and pH for the pure vanadium pentoxide electrodes was found to be 0.0628 volts per pH unit. The slopes of the lines for the partially reduced electrodes were: A = 0.0605 v/pH, B = 0.0595 v/pH, C = 0.0600 v/pH, D = 0.0609 v/pH; with an average slope of 0.0602 $\pm$ 0.005 volts/pH unit.

F. Discussion

The fact that a plot of the electrode potential vs the solution pH gave a slope which was very near the theoretical 0.0591 volt/pH-unit indicates that the number of electrons per hydrogen ion in the discharge reaction is unity, provided that the activity ratio of the two solids remains constant as the pH is changed.

Since the vanadium pentoxide in the electrodes was, in all cases, in great excess, it is reasonable to assume that its activity in the solid solution does not change appreciably even though some of the pentoxide dissolves in the higher pH solutions.

Although the $VO_x(OH)_y$ was present in the electrode in only small quantities, it is also reasonable to assume that its activity

remained constant as the pH was increased. The reason for this assumption is that the electrodes were allowed to come to an equilibrium in a solution of low pH and then placed in solution of higher pH, in which the $VO_x(OH)_y$ is less soluble. Thus it would be expected that a negligible quantity of the $VO_x(OH)_y$ would dissolve during the measurement of emf and pH, and hence, the concentration in the electrode would remain constant.

The dependence of the electrode potential upon solution pH indicates that the ratio of electrons to hydrogen ions consumed in the discharge reaction is unity. This means that only those reactions in which both the V(V) and the discharge product are solids, or in which the V(V) and the discharge product are both ions with the same charge, can be considered as possible discharge reactions. Of all the known reactions in solution (see p. 5) only the one shown below has a (e^-/H^+) ratio of unity.

$$[18] \quad H_3V_2O_7^- + 2H^+ + 2e^- = HV_2O_5^- + 2H_2O$$

However, since the $HV_2O_5^-$ is present only in solutions with a pH greater than 5.3, this reaction is not important in the discharge of the electrode in the pH range considered.

Hence, these results provide evidence that both the V(V) and the discharge product are solids. Below are given the reactions involving all of the known oxides and oxy-hydroxides with an oxidation state between three and five. Any of these reactions

would fit the data found in the above experiments.

$$[19]\quad 3\,V_2O_5 + 2\,H^+ + 2\,e^- + 3\,H_2O = 2\left[V_3O_5(OH)_4\right]$$

$$[20]\quad 3\left[V_2O_5\right] + 4\,H^+ + 4\,e^- = V_6O_{13} + 2\,H_2O$$

$$[21]\quad V_2O_5 + 2\,H^+ + 2\,e^- + H_2O = 2\left[VO(OH)_2\right]$$

$$[22]\quad V_2O_5 + 2\,H^+ + 2\,e^- = V_2O_4 + H_2O$$

$$[23]\quad V_2O_5 + 3\,H^+ + 3\,e^- = V_2O_3OH + H_2O$$

$$[24]\quad V_2O_5 + 4\,H^+ + 4\,e^- = 2\,VOOH + H_2O$$

$$[25]\quad V_2O_5 + 4\,H^+ + 4\,e^- = V_2O_3 + 2\,H_2O$$

G. Conclusions

It is proposed that the discharge of the vanadium pentoxide electrode in the pH range from two to five consists of a reduction of the solid vanadium pentoxide, utilizing one hydrogen ion per electron to produce a solid oxide or oxy-hydroxide. This proposal is verified by the foregoing experiments showing the dependence of the electrode potential upon the solution pH. Since both the vanadium pentoxide and the discharge product are solids, the discharge and recovery mechanism can be treated as a solid state diffusion problem. This will be done in the sections which follow.

V. DISCHARGE AND RECOVERY OF THE VANADIUM PENTOXIDE ELECTRODE

A. Introduction

An electrode immersed in a solution develops a potential with respect to a reference electrode. The passage of current through the electrode alters its potential from the calculated reversible potential. The difference between the reversible potential and the actual potential is defined as the overpotential or overvoltage. When an electrode exhibits overpotential it is said to be "polarized".

There are various types of overpotential which are encountered in the discharge of an electrode. The first type, known as ohmic or resistance overpotential, is due to the resistance which the electrode itself provides. The ohmic overpotential of a certain electrode is measured as the fraction of the IR drop through the cell which is due to the resistance of the electrode in question.

Another type of overpotential, called a pseudo-ohmic overpotential, is due to the resistance to the passage of current through the section of electrolyte between the reference electrode tube tip and the working electrode surface. This pseudo-ohmic overpotential is observed only when the distance between the reference electrode tube and the working electrode is appreciable, and then only at high current densities or low electrolyte concentrations.

A third type of overpotential, known as concentration

overpotential, is due to a difference in concentration of the ions between the electrode-solution interface and in the bulk of the solution. This concentration difference is caused by ions being removed or added at the electrode surface at a higher rate than they are replenished or taken away by ionic migration and mechanical agitation. This type of overpotential can be greatly diminished by stirring the electrolyte, by rotating the electrode, by raising the temperature and by increasing the bulk concentration of the electrolyte.

A fourth kind of overpotential, which is also a type of concentration overpotential,and will be called solid-concentration overpotential, is encountered only when the electrode is not a pure material. It is due to changes in concentration of solid solution components within the electrode itself. This type of overpotential is the chief concern of the study described herein; hereafter when the word "overpotential" is used without qualification it refers to the solid-concentration overpotential.

A fifth type of overpotential, known as activation overpotential, is concerned with the reaction occurring at the electrode itself. This overpotential is connected with the energy of activation of the rate controlling process in the electrode reaction (30, p. 394-399; 35, p. 141-148).

B. Experimental Methods

Discharge experiments can be conducted in several ways. In one method a galvanic cell can be set up with the vanadium pentoxide as the cathode, i.e., the electrode at which reduction takes place, and a current can be drawn from the cell by placing a resistance across the electrodes. In another method an external source is used and a measured current passed through the electrode in such a way as to cause reduction to take place at the vanadium pentoxide electrode.

The latter method has several advantages over the former. In the former method, with the small electrodes used in the cell in this study, the decrease in emf due to polarization is too great and too rapid for the current drawn from the cell to be kept at a constant value. In the latter method the current is supplied from a high capacity external source and can be kept at a constant and a convenient value.

1. Discharge Cell. The experimental cell is shown in Figure III. The cell consisted of a 250 ml beaker containing about 100 ml of electrolyte; the beaker was immersed in the constant temperature bath described on page 62. The anode, which was used for the discharge, was made from a semicircular strip, 10 cm long by 4 cm wide, of platinum foil connected by pressure to a platinum wire. (It was found that platinum was the only metal which

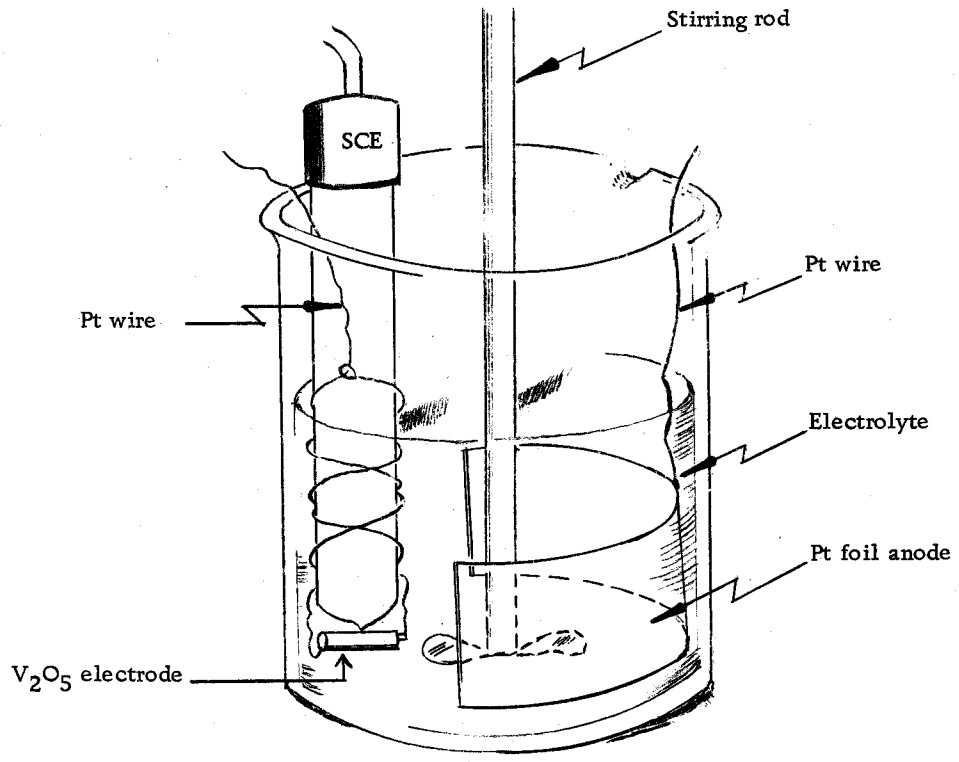


Figure III. Discharge Cell.

could be used as an anode, since all others that were tried corroded after a very short time.) The vanadium pentoxide-platinum foil cathode was connected to a platinum wire which was wrapped around the calomel reference electrode in such a way as to keep the vanadium pentoxide in the same position with reference to the calomel electrode throughout all of the experiments. A stirring rod from a motor-driven stirrer was inserted in the beaker as close to the reference electrode as possible. The anode and cathode were connected in series with a high capacity storage battery, an ammeter and a variable resistance box. The cathode and the reference electrode were connected in parallel with a Varian Model G-14 Graphic recording potentiometer.

2. Ohmic Overpotential. An attempt was made to eliminate the pseudo-ohmic overpotential by placing the vanadium pentoxide electrode in contact with the reference electrode tube tip, by keeping the current density low and by using fairly concentrated solutions of electrolyte.

The ohmic overpotential was quite large and could not be eliminated because vanadium pentoxide is a relatively poor semiconductor. However, since the ohmic overpotential sets up and decays instantaneously, it could be distinguished from the solid-concentration overpotential by the use of the oscilloscope.

The overpotential which was recorded as a vertical drop on the recorder was calibrated with the instantaneous potential drop

shown by the oscilloscope trace. The circuit is shown in Figure IV. A Tektronix type 502 oscilloscope was used with controls set at a sensitivity of 20 mv/cm and a probe attenuation of 10, such that the scope trace registered 200 mv/cm. The sweep speed was set at 0.5 sec/cm, which was slow enough to follow visually. The current controlling switch was turned on or off just as the oscilloscope trace reached the vertical calibration lines on the scope face. The voltage drop was estimated visually and then compared with the vertical voltage drop of the recording potentiometer.

When the chart speed of the recorder was set at two inches per minute, the recorder pen could follow, within the accuracy of the experiment, the actual IR drop as traced by the oscilloscope. Hence, when the recorder was used at this speed, the experimental IR drop could be determined directly from the vertical drop of the recorder. However, when the chart speed was set at 0.1 inch per minute, the recorder pen traced an apparently vertical voltage drop which was about three times as great as the voltage drop traced by the oscilloscope. Since the initial solid-concentration polarization of the electrode was steep, it was not possible to determine the amount of the vertical drop on the recorder which was due to ohmic overpotential and the amount due to the solid concentration overpotential. Thus, when this chart speed was used, the oscilloscope had to be used in each experiment to determine the IR drop.

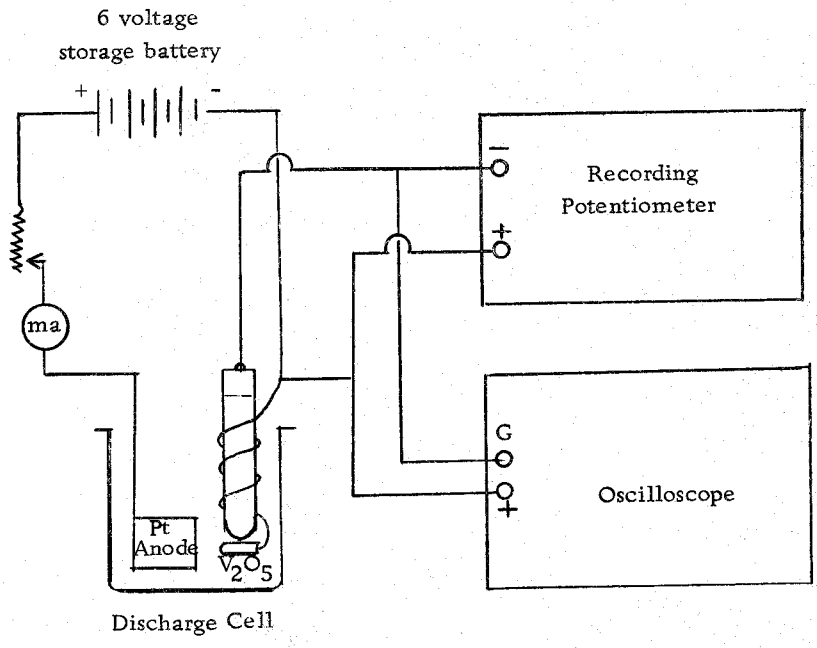


Figure IV. Discharge Circuit.

3. Other Types of Overpotential. The difference between the total overpotential and the ohmic overpotential was taken to be the value of the solid-concentration overpotential. This was based on the assumptions that the solution-concentration overpotential and the activation overpotential were negligible. The assumption that the solution concentration overpotential was negligible was reasonable since the solutions were stirred vigorously and since a relatively concentrated electrolyte was used for most of the discharges. The only way known to determine if the activation potential were actually negligible was to see if the diffusion equation would predict the shape of the discharge curve. This test was made and it was found that the diffusion equation, which took into account only the solid-concentration polarization, predicted the shape of the experimental discharge curve. Hence the assumption that the activation potential was negligible was considered good.

4. Determination of Current Density. The electrode current density is defined as the current flowing through an electrode of unit surface area. In practice, the surface area is considered to be equal to the measured geometrical surface area. However, since no electrode is perfectly smooth, the actual surface area may be several times as great as the apparent or geometrical surface area. However, for most of the experiments in which the behavior of different electrodes of the same material was compared, it was assumed that the actual surface area was directly

proportional to the geometrical surface area.

The electrodes as formed from the melt were somewhat irregular in shape, especially at the top where a rough cone had formed. In order to calculate the geometrical surface area with some accuracy, the top of each electrode was coated with paraffin. In this way the exposed geometrical surface area could be made reasonably constant from one electrode to another.

C. Effect of Factors Other Than Diffusion Upon the Discharge and Recovery of the Vanadium Pentoxide Electrode

One of the purposes of the discharge experiments was to determine whether or not the discharge and recovery of the vanadium pentoxide electrode were diffusion-controlled processes. It was found early in the work that although the solid state diffusion played an important part in the mechanism, many other factors were involved in the discharge and recovery of the electrodes. An attempt was made to determine the effect of these other variables, and where possible, to eliminate them.

1. Effect of Electrical Contact Between the Vanadium Pentoxide and the Platinum.

One of the most important factors which affected the discharge and recovery curves (curves made by plotting the electrode potential against the time) was the degree of electrical contact between the platinum foil and the vanadium pentoxide. If the contact was not excellent, the hydrogen overpotential

on the platinum was superimposed on the vanadium pentoxide electrode overpotential and the discharge and recovery were due to a combination of the behavior of the two kinds of polarization.

A study was made of the discharge and recovery curves of a bare platinum foil of approximately the same surface area as the vanadium pentoxide electrodes. Figure V shows the type of polarization curves obtained at two different current densities. This polarization was recorded as instantaneous on the Varian Graphic recorder at either chart speed. After the saturation value of potential was reached, the potential remained constant as long as the current was on. When the current was stopped the recovery was almost instantaneous.

Vanadium pentoxide electrodes which had poor electrical contact with the platinum foil, showed an instantaneous voltage drop on the recorder which is much greater than the IR drop displayed on the oscilloscope. The discharge and recovery were more rapid than normal due to the rapid recovery of the polarized platinum electrode. Figure VI gives some examples of discharge and recovery curves obtained with electrodes which did not have good electrical contact with the platinum.

A method was not found for separating the platinum overpotential from the vanadium pentoxide overpotential, hence electrodes which had an appreciable platinum overpotential were of little use in these experiments. Also, it was not possible to tell by looking

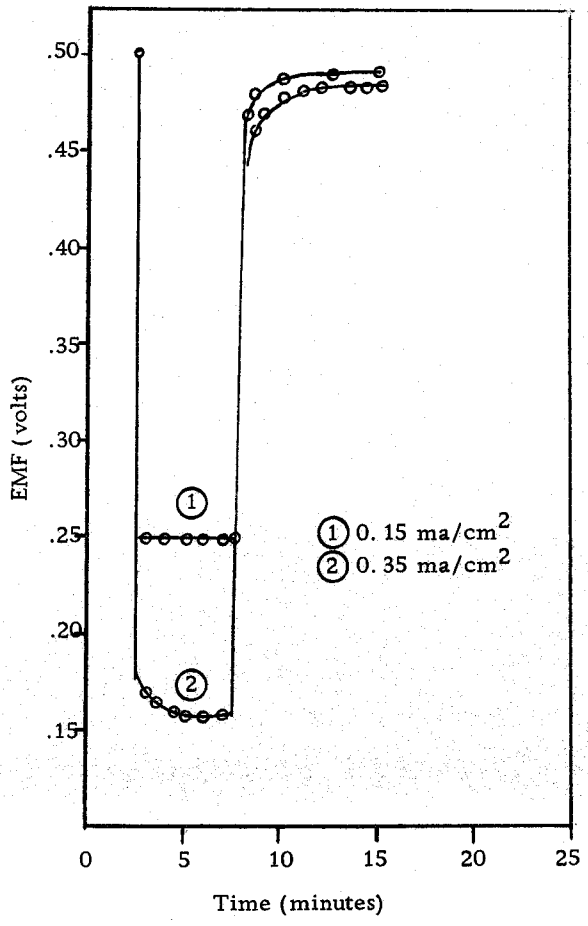


Figure V. Discharge and and Recovery of the Platinum Electrode.

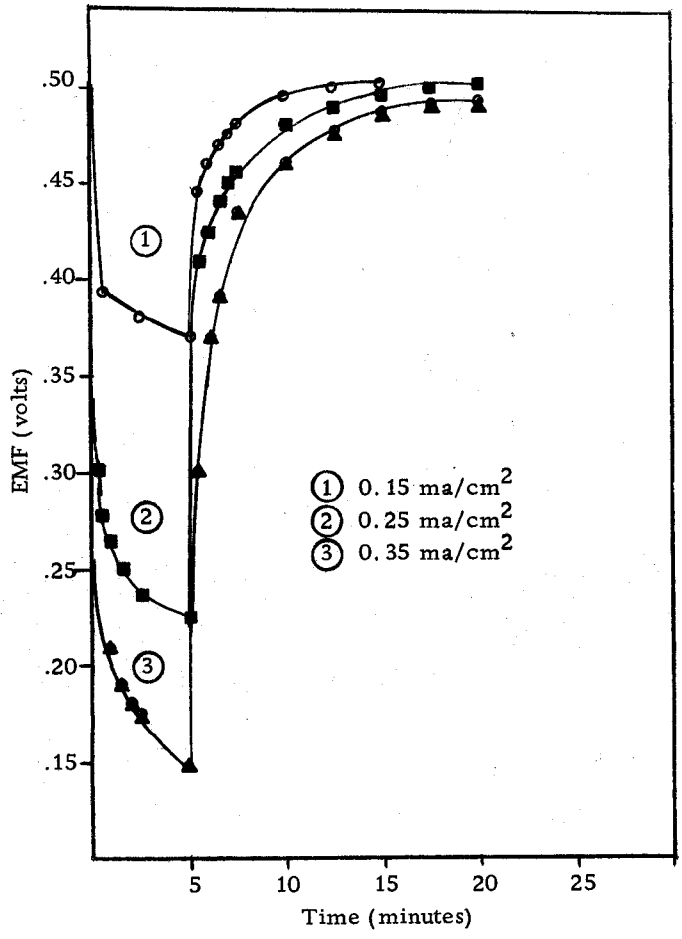


Figure VI. Discharge and Recovery of Vanadium Pentoxide-Platinum Electrodes Having Poor Contact.

at a melt electrode whether or not the electrical contact with the platinum was good; only during the discharge could that be determined. Thus the selection of suitable electrodes was a matter of trial and error and many electrodes had to be discarded.

2. Effect of Solution pH. Another factor which was found to affect the shape of the discharge and recovery curves was the pH of the discharge solution. Figure VII shows this affect. It will be noted that in acid solutions of pH = 1.5 there is very little polarization during discharge and an almost immediate recovery. It is supposed that the discharge product at this pH is soluble in the solution and hence the V(V) surface is constantly being renewed and thus the electrode potential remains high. It will also be noted that the amount of polarization increases with increasing pH, although the shapes of the discharge curves are similar at all pH values shown. The amount of recovery in solutions of high pH is poor, as will be seen in the pH 7.7 discharge curve in Figure VII. The reason for this poor recovery was not established, but it is possible, because of the low solubility of the discharge product in solutions of high pH, that a layer of the $VO_x(OH)_y$ is formed on the surface and is mechanically separated from the rest of the electrode, and hence presents a barrier to the recovery.

To eliminate the problems encountered in solutions of high pH, the discharge experiments were conducted in the pH range of 2-5. This is the range in which previous experiments (see p. 45)

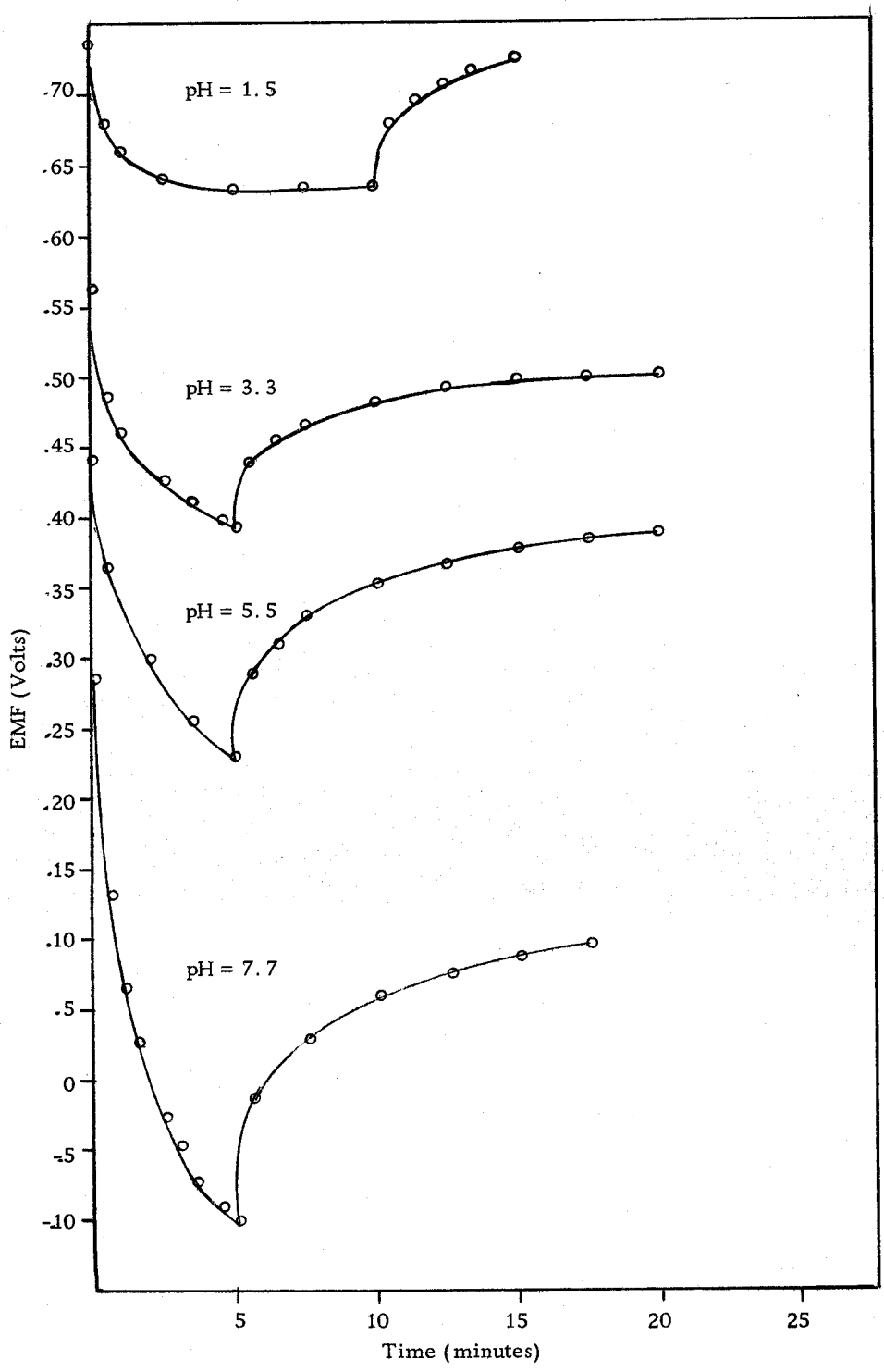


Figure VII. Effect of pH Upon the Discharge and Recovery of the Vanadium Pentoxide Electrode.

had indicated that there was a linear relationship between the Emf of the electrode and the pH of the solution.

3. Effect of Temperature. A few preliminary experiments were carried out to determine the effect of temperature upon the discharge and recovery curves. It was found that the amount of polarization increased with decreasing temperature. Figure VIII shows the difference in discharge and recovery curves run at temperatures of 40°C and 14°C. To eliminate the temperature variable the discharge and recovery experiments were all carried out at 25 $\pm$ 0.2°C.

D. Results of Discharge Experiments

1. Discharge and Recovery as a Diffusion-controlled Process. It was assumed that the discharge and recovery of the vanadium pentoxide electrode was a diffusion-controlled process. If this were so, then a diffusion equation should satisfactorily account for the experimental curves, provided that the assumptions used in solving the diffusion equations are correct.

Figure IX shows a typical discharge and recovery curve for the vanadium pentoxide electrode, plotted from the data in Table VII. The data was obtained with a vanadium pentoxide electrode 4 mm in diameter and 15 mm high which was discharged for ten minutes in a 0.25 M KCl solution saturated with vanadium pentoxide. The electrode was discharged at a total current of 0.5 ma,

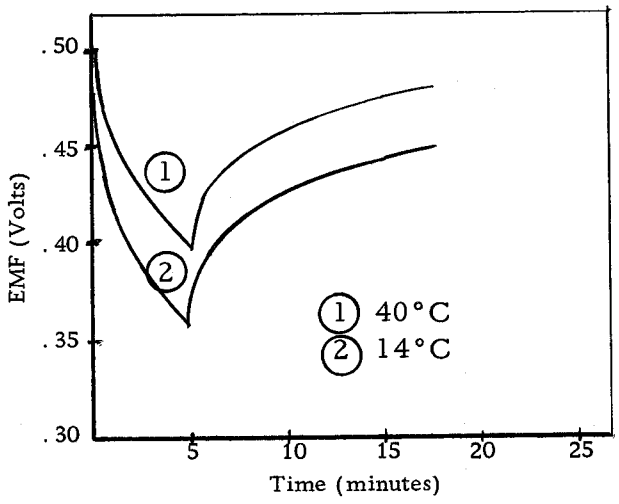


Figure VIII. Effect of Temperature on the Discharge and Recovery of the Vanadium Pentoxide Electrode.

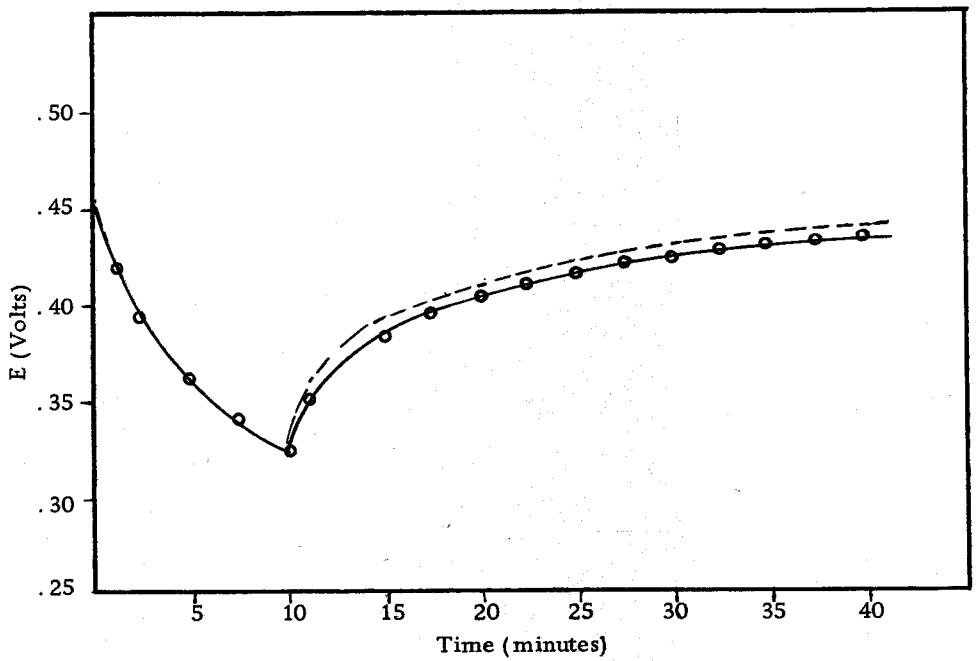


Figure IX. Discharge and Recovery of the Vanadium Pentoxide Electrode. (For $i = .25\ ma/cm^2$, solid line observed, dashed line calculated)

which corresponds to a current density of about 0.25 ma/cm^2. The corrected emf in Table VII was obtained after taking into account the IR drop of 0.01 v obtained with the oscilloscope.

The diffusion equations developed by Scott (38), and modified by Kornfeil (29), can be applied to the discharge and recovery curves with the assumption that the discharge consists of the formation of a reduced vanadium compound, $VO_x(OH)_y$, on the surface of the electrode and its subsequent diffusion into the solid, and that the recovery consists of the continued diffusion of the $VO_x(OH)_y$ throughout the solid until the equilibrium is reached. (The actual diffusing species were assumed to be protons accompanied by electrons.) By the use of the Scott-Kornfeil equations the experimental discharge curve was used to calculate the theoretical recovery curve, which is shown as a dotted line in Figure IX. The development of the equations and the calculations are shown below:

Rewriting the equation for the case of linear heat flow in a semi-infinite solid, initially at zero temperature, with a constant flux of heat across the boundary surface which is then shut off at time t, the form appropriate for diffusion (38) becomes

$$[26] \quad C_{(x,t)} = \frac{2F_o}{D^{\frac{1}{2}}} \left[t^{\frac{1}{2}} \left(\text{ierfc} \frac{x}{2(Dt)^{\frac{1}{2}}} \right) - (t-T)^{\frac{1}{2}} \left(\text{ierfc} \frac{x}{2D^{\frac{1}{2}}(t-T)^{\frac{1}{2}}} \right) \right]$$

where C is the concentration of the reduced form at time t and distance x from the surface, F_o is the number of moles of the

reduced form produced per unit area per unit time, $\underline{T}$ is the discharge time, $\underline{D}$ is the diffusion coefficient for protons, accompanied by electrons, in the solid, and ierfc(y) is defined by

$$\text{ierfc}(y) = \pi^{\frac{1}{2}} \exp(-y^2) - 2y\pi^{-\frac{1}{2}} \int_y^{\infty} \exp(-z^2)\, dz$$

It can be seen that at the surface of the electrode, equation [26] reduces to

$$[27] \quad C_{(o,t)} = \frac{2 F_{o_1}}{(\pi D)^{\frac{1}{2}}} \left[\left(t^{\frac{1}{2}} - (t-T)^{\frac{1}{2}} \right) \right]$$

When volume changes in the solid phase of the electrode are neglected, the sum of the concentrations of the reduced and the oxidized form is constant, the potential-time relation is of the general form

$$[28] \quad E = E_o + k \log \left[\frac{A}{t^{\frac{1}{2}} - (t-T)^{\frac{1}{2}}} - 1 \right]$$

Differentiation of equation [28] with respect to time gives the slope $\underline{S}$.

$$[29] \quad S = \frac{dE}{dt} = -0.434\, k \, \frac{A}{2t(A-t^{\frac{1}{2}})}$$

Having two corresponding values of $\underline{S}$ and $\underline{t}$ one may obtain the constant A.

$$[30] \quad A = \frac{\Delta \left[St(t^{\frac{1}{2}}) \right]}{\Delta (St)}$$

For the electrode described above, $\underline{A} = 4.98\ \text{min}^{\frac{1}{2}}$, which value was obtained from the slope of the curve at five minutes and at 2.5 minutes. $\underline{E}_o$ and $\underline{k}$ were then obtained by solving equation [28] at two values of $\underline{E}$ and $\underline{t}$. $\underline{E}_o$ was found to be 0.342 v and $\underline{k} = 0.128$. Then, with these constants, equation [28] was used to calculate the emf at any given time. These calculated values of emf are given in the fourth column of Table VII.

From the curves in Figure IX it will be seen that the theory predicts the experimental recovery curve with a high degree of accuracy.

Another electrode was discharged in a similar solution at approximately the same current density for 20 minutes, and then allowed to recover. The solid line in Figure X depicts the discharge and recovery for this electrode. The theoretical recovery curve was calculated for this electrode in the same manner as discussed above; this is shown by the dotted lines in Figure X. It will be seen that the theoretical curve deviates more from the experimental curve than was found for the ten minute discharge.

One experiment was performed to illustrate the effect of a repeated discharge of an electrode. The results of this experiment are shown in Figure XI. It will be noted that each time the electrode was discharged, the recovery reached almost the value of the original electrode potential.

Experiments were performed to show the effect of current

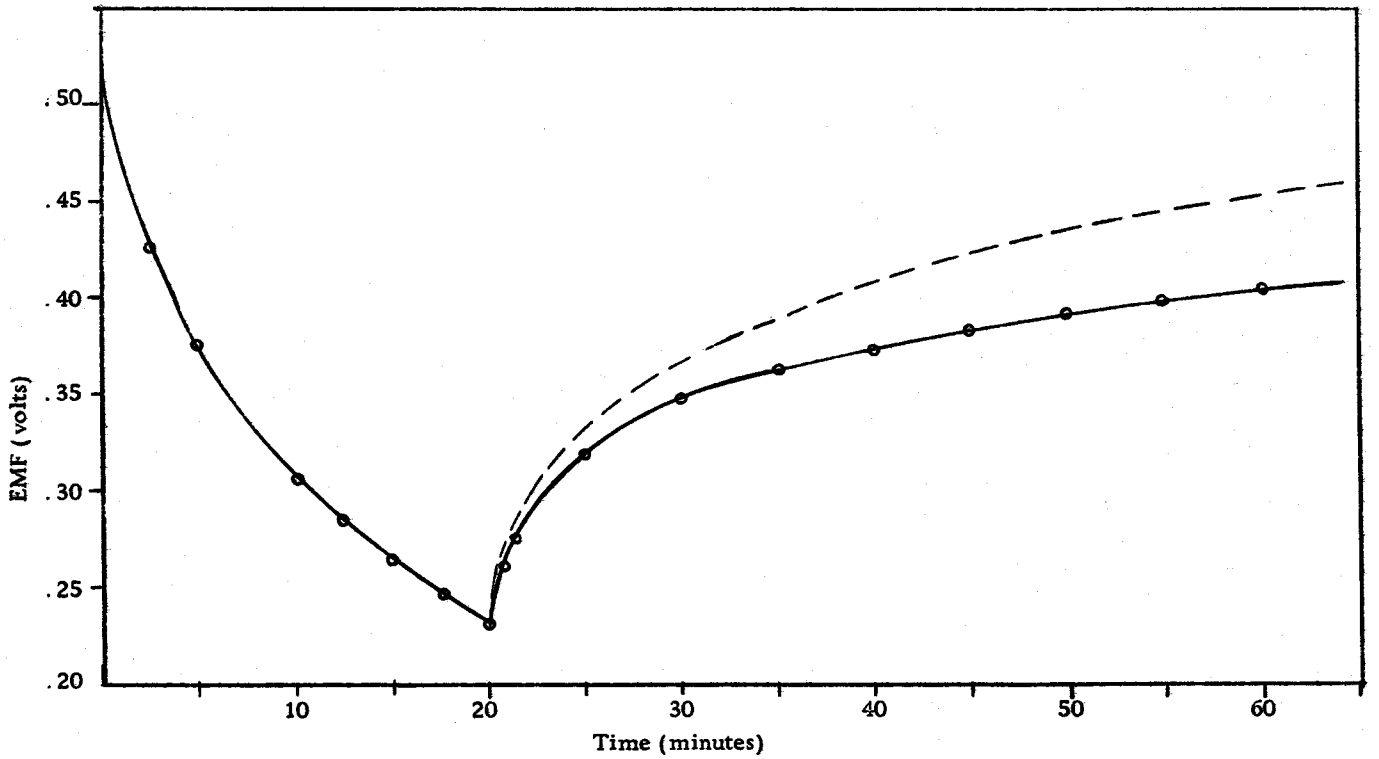


Figure X. Twenty Minute Discharge and Recovery of the Vanadium Pentoxide Electrode. (For $i = .25$ ma/cm^2, solid line observed, dashed line calculated)

Table VII. Discharge and Recovery of the Vanadium Pentoxide Electrode

Time (min)	EMF (volts)	EMF(Corr) (volts)	EMF(Calc.) (volts)
Discharge	Discharge	Discharge	Discharge
0	0.483	0.483	
1.25	0.412	0.422	0.421
2.50	0.385	0.395	
5.00	0.353	0.363	
7.50	0.332	0.342	0.341
10.00	0.313	0.323	
Recovery	Recovery	Recovery	Recovery
11.25	0.364	0.354	0.362
12.50	0.377	0.367	0.377
15.00	0.394	0.384	0.392
17.50	0.405	0.395	
20.00	0.413	0.403	0.409
22.50	0.420	0.410	
25.00	0.425	0.415	
27.50	0.430	0.420	
30.00	0.433	0.423	0.428
32.50	0.437	0.427	
35.00	0.440	0.430	
37.50	0.442	0.432	
40.00	0.445	0.435	0.439

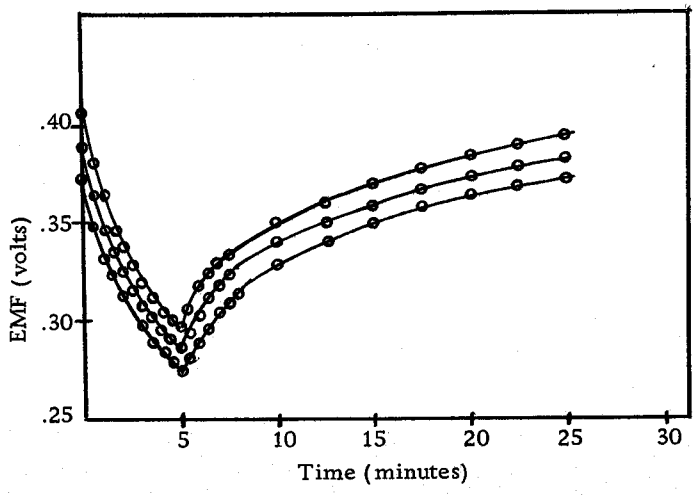


Figure XI. Repeated Discharge and Recovery of the Vanadium Pentoxide Electrode.

density upon the discharge and recovery of the electrode. Figure XII shows the results of one of these experiments in which an electrode was discharged at different current densities in the same solution. (The electrode was permitted to recover almost completely between discharges.) The dotted lines shown in the figure give the theoretical curves calculated from the Scott-Kornfeil equation. It will be noted that for current densities within the range 0.15 to 0.35 ma/cm^2, for ten minute discharges, the theory predicts the experimental curve very well. In the case of the discharge at 0.15 ma/cm^2 the experimental and theoretical recovery curves coincide.

E. Discussion

A theory for the discharge and recovery mechanism of the vanadium pentoxide electrode was formulated on the basis of the results described in this work. The discharge experiments described in this section led to the proposal of a theory analogous to that proposed for the manganese dioxide electrode (see p. 11). The fact that a diffusion equation successfully predicted the shape of the discharge and recovery curves indicated that a diffusion-controlled process is involved. This is in agreement with the proposed theory that the discharge consists of the reduction of the vanadium pentoxide at the surface according to the equation

$$[31] \quad V_2O_5 + n\,e^- + n\,H^+ + m\,H_2O = VO_x(OH)_y$$

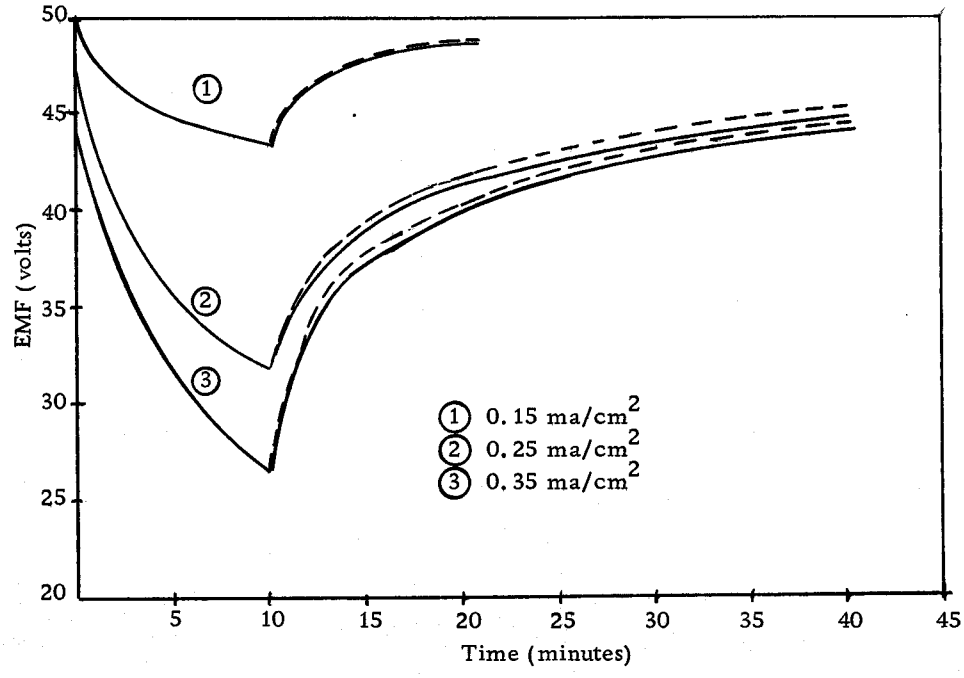


Figure XII. Discharge of the Vanadium Pentoxide Electrode at Different Current Densities (solid lines observed, dashed lines calculated)

where $y = n + 2m$ and $x + y = m + 5$, and where both the V_2O_5 and the $VO_x(OH)_y$ are compounds in solid solution with each other. The reduction is accompanied by a diffusion of the $VO_x(OH)_y$ into the solid. The recovery consists of the continued diffusion of the $VO_x(OH)_y$, until its concentration is uniform throughout the solid. The effect of diffusion of the $VO_x(OH)_y$ during recovery is to increase the concentration of the vanadium pentoxide on the surface, and hence to increase the electrode potential.

The discharge experiments verify the proposal that a solid solution is formed between the two oxides by showing that a very small quantity of current, and hence a slight change in oxide composition, caused the electrode potential to be lowered greatly. If the two oxides were not in solution, this change in composition would not affect the electrode potential. The proposal of the solid solution is also indirectly supported by the x-ray diffraction studies in which the only substance found was vanadium pentoxide, even though the discharge product was present in fairly significant amounts. This behavior would be expected if a solid solution was formed in which the vanadium pentoxide was the major component.

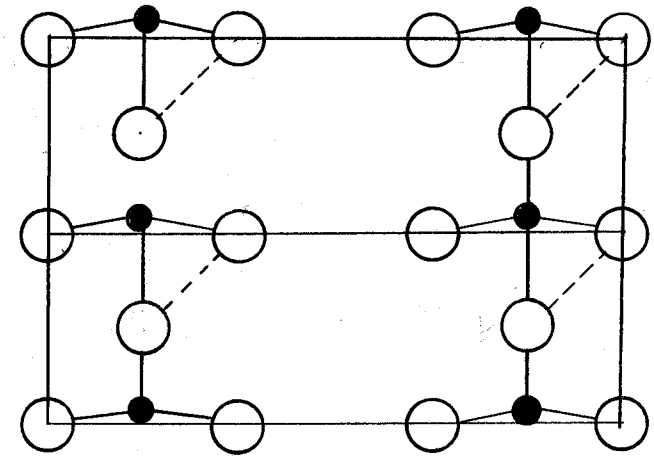
There was no question as to the site of the reduction. In all the discharge experiments it was noted that the color change began at the solution surface and proceeded inward toward the platinum as the discharge continued.

In the theory as described above, it is not necessary to

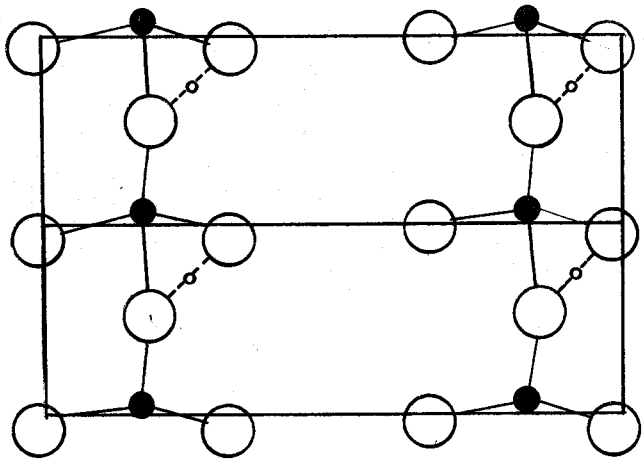
assume that the $VO_x(OH)_y$ actually diffuses through the solid; it is much more likely that protons, in the case of an oxy-hydroxide, or vanadium ions, in the case of an oxide, is the diffusing species. It is more reasonable to assume that the discharge product is an oxy-hydroxide rather than an oxide, since the very rapid recovery of the electrodes indicated that the diffusion was very rapid. It is reasonable to assume that protons could diffuse through the lattice more rapidly than could vanadium ions. Also, the rate of recovery was comparable to that found for manganese dioxide electrodes for which it has been shown that the discharge product is an oxy-hydroxide.

It is possible that the protons upon entering the vanadium pentoxide crystal during the reduction form hydrogen bonds with neighboring oxide ions and that these protons can migrate through the crystal under the influence of the chemical potential. The formation of hydrogen bonds would distort the crystal somewhat, but the basic orthorhombic structure of the vanadium pentoxide (see Figure I, p. 8) would be maintained, thus making the formation of a solid solution very probable. Figure XIII (a) shows the ab plane of the vanadium pentoxide crystal. Figure XIII (b) shows how the crystal might be distorted to form hydrogen bonds in the $VO_x(OH)_y$.

Although no experimental evidence was obtained for the formation of the hydrogen bonds, there is a precedence for the idea. Evans and Mrose (17) found that the mineral montroseite, VO(OH)



(a)



(b)

Figure XIII. View of the Crystal Structure showing the ab plane of (a) vanadium pentoxide, and (b) $VO_x(OH)_y$, showing hydrogen bonds

contained hydrogen bonds between neighboring oxide atoms. They also found that this mineral is converted in nature to paramontroseite, VO_2, by an oxidation process which is accomplished by a migration of the protons through the VO(OH) crystal structure to the crystal surface where they combine with oxygen. The VO(OH) has the same basic crystal structure as does VO_2, with the exception that the VO(OH) is slightly distorted by the presence of the hydrogen bonds.

VI. DETERMINATION OF THE DIFFUSION COEFFICIENT FOR THE DISCHARGE PRODUCT

A. Introduction

Scott (38) was able to determine experimentally the electrochemical surface area of the manganese dioxide electrode and from it the diffusion constant for the (effective) diffusion of the discharge product (MnOOH) through the body of the solid. According to Scott, if the discharge is rapid enough that the loss of MnOOH by diffusion is negligible compared with that produced by the reduction reaction, the number of equivalents of MnOOH produced per unit area per unit time, F_o, can be calculated from the equation

$$[32] \quad C_s = \frac{F_o}{\underline{l}} t_s$$

where t_s is the time necessary to saturate the surface with MnOOH, C_s is the concentration of MnOOH when the surface is saturated and $\underline{l}$ is the thickness of the surface layer. C_s and $\underline{l}$ can be obtained from the crystal structure of the manganese dioxide and t_s is obtained experimentally. If the electrode potential is plotted against the time during a rapid discharge, an "S" shaped curve is obtained. From equation [15] it may be deduced that the time at which the surface becomes saturated corresponds to the point marked $\underline{t_s}$ in Figure XIV.

Having $\underline{F_o}$, one may calculate the surface area. It should

be remarked that the area observed may be different from that observed by other methods; for this reason it will be called the electrochemical surface area. Once the surface area has been obtained, one may discharge the oxide at a lower rate and determine the diffusion coefficient from the equation

$$[33] \quad C_s = \frac{2 F_{o_1}}{(D\pi)^{\frac{1}{2}}} \; t_s^{\frac{1}{2}}$$

Scott calculated the electrochemical surface area of a sample of β-MnO_2 and found this area to be only about 12 percent of the surface area as measured by the BET method. He also calculated the diffusion coefficient to be 2.7×10^{-17} cm^2/sec.

B. Determination of the Diffusion Coefficient

1. Method. An electrode composed of vanadium pentoxide powder on a graphic block was discharged at a current of about 100 ma in a solution of pH = 1.5. An "S" shaped curve, indicating the saturation of the surface with the discharge product, was not obtained. The experiment was repeated at 75 and 50 ma with the same results. The experiment was repeated using melt electrodes at current densities from 0.2 ma to 2.0 ma in solutions with a pH from 2-5, and the same results were obtained. Finally it was concluded that the solubility of the reduced product in the acid solutions prevented the surface of the electrode from being saturated with the reduced product. Hence an attempt was made to

obtain saturation by a rapid discharge in basic solutions.

Although it was found that the emf of the electrodes decreased with time in solutions of high pH, it was decided that in the saturation experiments described above that the discharge was too rapid for the emf to be substantially affected by the slow drift in basic solutions. While the results of Figure VII indicate a difference in the recovery characteristics at high pH compared to those found in the lower pH range, the discharge portions of the curves are sufficiently similar to permit use of the higher pH's for saturation experiments.

2. Results. Figure XIV shows the results of the discharge of melt electrodes of similar dimensions in solutions of pH = 9 at different current densities. The following saturation times were found: 0.72 ma = 3.5 min, 0.44 ma = 7.5 min, and 0.22 ma = 23 min. The diffusion coefficient was calculated from Scott's equation as follows: In order to make the calculations a definite oxidation state for the discharge product had to be assumed. Since it was believed that the actual oxidation state was between +4 and +5, +4.5 was selected. From the crystal structure given by Bystrom (9) (see Figure I, p. 8) and the assumed oxidation state change, the saturation concentration was calculated as

$$C_s = \frac{2 \text{ ions}}{\frac{1}{2} \text{ unit cell}} \times \frac{1 \text{ equiv.}}{12 \times 10^{23} \text{ ions}} \times \frac{\frac{1}{2} \text{ unit cell}}{8.9 \times 10^{-23} \text{cm}^3} =$$

$$1.86 \times 10^{-2} \text{ equiv/cm}^3 .$$

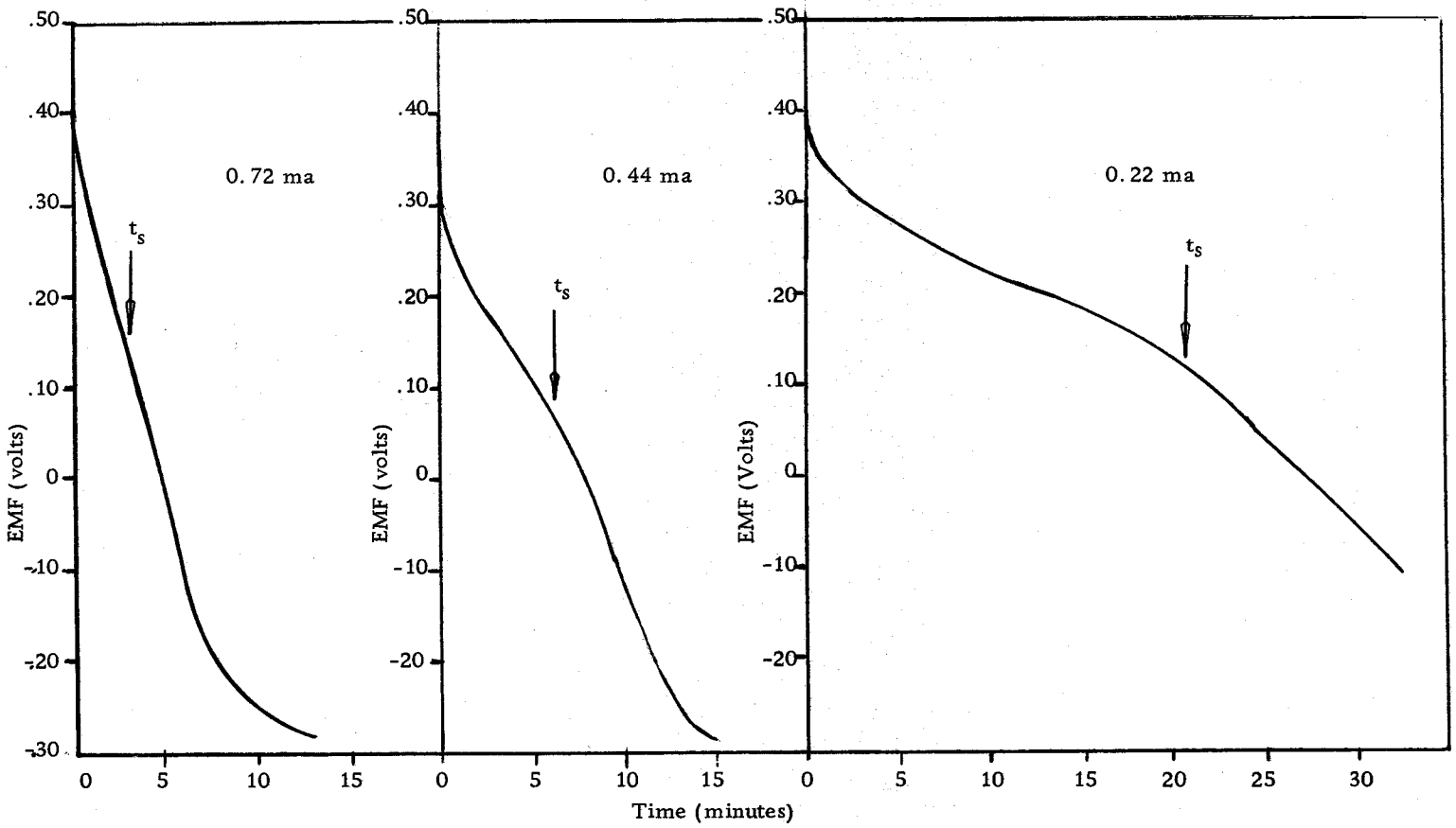


Figure XIV. Discharge Curves Used to Determine the Diffusion Coefficient of the Reduction Product.

The flux, F_o, was then calculated from equation [32]

$$F_o = \frac{(1.86 \times 10^{-2}\ \text{equiv/cm}^3)(4.0 \times 10^{-8}\ \text{cm})(96500\ \text{coul/equiv})}{210\ \text{sec}}$$

$$= 3.42 \times 10^{-7}\ \text{amp/cm}^2 .$$

From the current of 7.2×10^{-4} amp, the area was calculated

$$A = \frac{7.2 \times 10^{-4}\ \text{amp}}{3.42 \times 10^{-7}\ \text{amp/cm}^2} = 2.11 \times 10^{3}\ \text{cm}^2/\text{electrode} =$$

$$2.93 \times 10^{3}\ \text{cm}^2/\text{g} .$$

No we consider the discharge at 0.22 ma to be slow enough for the diffusion to be important, and assume that this electrode had the same surface area as the one discharged at 0.72 ma,

$$F_o = \frac{(2.2 \times 10^{-4}\ \text{amp})}{(2.93 \times 10^{-3}\ \text{cm}^2)(96500\ \text{coul/equiv})} =$$

$$7.8 \times 10^{-13}\ \text{equiv/cm}^2\text{sec} ,$$

and from equation [33] for a slow discharge

$$(DT)^{1/2} = \frac{(2F_o)(t_s)}{(C_s)} = \frac{(2)(7.8 \times 10^{-13}\ \text{equiv/cm}^2\text{sec})(37.1\ \text{sec}^{1/2})}{(1.86 \times 10^{-2}\ \text{equiv/cm}^3)}$$

and

$$D = 3.09 \times 10^{-18}\ \text{cm}^2/\text{sec}$$

The diffusion coefficient was then calculated by the same method using the discharge at 0.72 ma as the rapid discharge and the one at 0.44 ma as the slow discharge. The value of the diffusion

coefficient was found to be 4.12×10^{-18} cm^2/sec.

3. Discussion. It must be emphasized that the diffusion coefficients calculated above are approximate only, based on a few preliminary experiments. It is also an approximation to use the discharge at 0.72 ma to obtain $\underline{F}_o$; the approximation would be better if an even faster discharge were used. The fact that similar diffusion coefficients were obtained by using the discharge at 0.44 and at 0.22 ma as the slow discharge indicates that diffusion played an important part in the discharging at both of these currents.

VII. SUGGESTIONS FOR FURTHER WORK

After the course of this investigation was reviewed, several further experiments could be suggested:

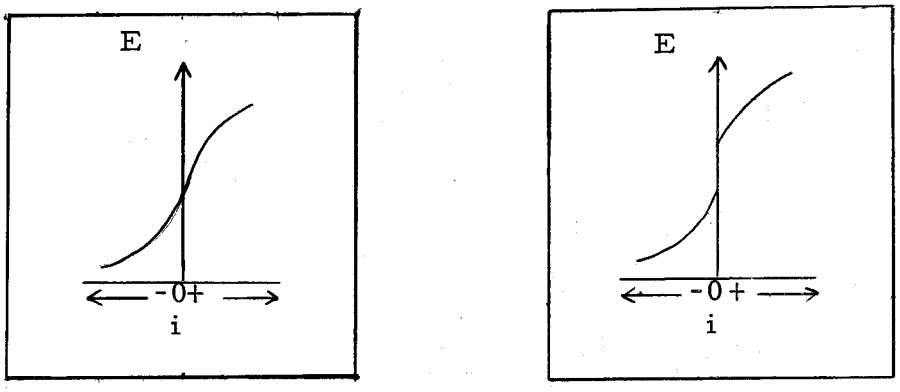
1. In order to identify the discharge product by x-ray diffraction studies it is necessary to reduce the vanadium pentoxide to such an extent that the discharge product will be the major component of the solid solution. To carry out such a reduction it is suggested that an electrode be prepared which consists of a very thin layer of vanadium pentoxide melted on a piece of platinum foil. It is suggested that the way to obtain such an electrode is to melt the pentoxide in a platinum cup and then place the entire cup in the discharge solution. The presence of the cup will prevent the oxide from falling off the platinum, a problem often encountered in very long discharges. It is also suggested that a study of reduction conditions, such as the composition and pH of the electrolyte, be made to determine if the competing processes in the long discharges can be minimized or eliminated, and thus aid the discharge reaction to go to completion.

2. If the reduction of the electrode can be carried to completion, the discharging product should be analyzed chemically for vanadium, oxygen, and if possible, for hydrogen. From this the chemical formula can be determined. Then, if the x-ray diffraction pattern is different from any compound previously studied, a new compound and its diffraction pattern, can be reported.

3. The experiments for the determination of the diffusion coefficient should be repeated at higher current densities better to ensure that the use of equation [32], p. 77, which assumes that the diffusion process is negligible, is valid.

4. One purpose of this study was to determine the conditions under which the polarization of the vanadium pentoxide was a minimum. This minimum was found to occur in acid solutions. It is suggested that an attempt be made to construct a useful primary cell using vanadium pentoxide as a cathode and utilizing an acid electrolyte.

5. It would be of theoretical interest to know whether or not the vanadium pentoxide electrode is thermodynamically reversible. This can be determined experimentally by measuring the emf at different charging and discharging currents. If the electrode is reversible, a plot of emf (E) against current (i) will give a continuous curve as the current goes from negative to positive values. [See Figure XV (a)]. If the electrode is irreversible, there will be a discontinuity as the current approaches and passes zero current. [See Figure XV (b)]. The magnitude of the discontinuity is a measure of the irreversibility of the electrode.



(a) (b)

Figure XV. Determination of the Reversibility of an Electrode

6. It is suggested that the studies reported in this work be repeated using a single-crystal electrode of vanadium pentoxide.

BIBLIOGRAPHY

1. Aebi, Franz. Phasenuntersuchungen im System Vanadin-Sauerstoff und die Krystallstruktur von $V_{12}O_{26}$. Helvatica Chimica Acta 31:8-21. 1948.

2. American Society for Testing Materials. X-ray powder data file. Inorganic. Sets 1-5. Philadelphia, 1960. 685p. (Card no. 1-1293).

3. American Society for Testing Materials. X-ray powder data file. Inorganic. Sets 6-10. Philadelphia, 1960. 775p. (Card no. 9-387).

4. Andersson, Georg. Studies on vanadium oxides. I. Phase Analysis. Acta Chimica Scandinavica 8:1599-1606. 1954.

5. _____. Studies on vanadium oxides. II. The crystal structure of vanadium dioxide. Acta Chimica Scandinavica 10:623-628. 1956.

6. Azároff, Leonid V. and Martin J. Buerger. The powder method in x-ray crystallography. New York, McGraw-Hill, 1958. 342p.

7. Bates, Roger B. Electrometric pH determinations. New York, John Wiley and Sons, 1954. 331p.

8. Boros, J. Elektrische und optische Eigenschaften von Vanadium pentoxyd-Kristallen. Zeitschrift für Physik 126:721-724. 1949.

9. Bystrom, A., K.A. Wilhelmi and O. Brotzen. Vanadium pentoxide-- a compound with five-coordinated vanadium atoms. Acta Chimica Scandinavica 4:1119-1130. 1950.

10. Cahoon, N.C., R. S. Johnson and M.P. Korver. Cathode reactions in the Leclanche dry cells. Journal of the Electrochemical Society 105:296-298. 1958.

11. Carslaw, H.S. and J.C. Jaeger. Conduction of heat in solids. 2d ed. Oxford, Clarendon Press, 1959. 510p.

12. Coleman, J.J. Dry cell dynamics. Transactions of the Electrochemical Society 90:545-583. 1946.

13. Daniel-Bek, V.S. Theory of metal-oxide graphite electrodes. Trudy Soveschaniya po Elektrokhimii, Akademiya Nauk S.S.S.R., Otdelenie Khimicheskikh Nauk 1950:513-522. 1953. (Abstracted in Chemical Abstracts 49:12160a. 1955)

14. Deltombe, E., N. de Zoubov, and M. Pourbaix. Comportment electrochimique du vanadium. Brussels, Centre Belge D'Etude de la Corrosion, January 1956. 25p. (E.D. 39. NZ 24)

15. Ducret, L.P. Contribution a'l' etude des ions des valences quatre et cinq du vanadium. Annales de Chimie 6:705-775. 1951.

16. Esin, O.A., and V.L. Zyazev. Electroconductivity of the oxides of vanadium, lead and copper. Journal of Inorganic Chemistry, U.S.S.R. 2(9):22-30. 1957. (Translated from Zhurnal Neorganicheskoi Khimii 2:1998-2002. 1957).

17. Evans, H.T. Jr., and Mary E. Mrose. A crystal chemical study of montroseite and paramontroseite. American Mineralogist 40:861-875. 1955.

18. Ferrell, D.T. and W.C. Vosburgh. A proposed mechanism for the discharge and recovery of the manganese dioxide electrode. Journal of the Electrochemical Society 98:334-341. 1951.

19. Furman, N. Howell, ed. Standard methods of chemical analysis. 6th ed. vol 1. Princton, N.J., Van Nostrand, 1962. 1252p.

20. Ghosh, Siddhartha and J.P. Brenet. "Study of the mechanism of cathodic reduction of gamma manganese dioxide in the Leclauche cell system." Electrochimica Acta 7:449-455. 1962.

21. Glemser, Oskar and Einhard Schwarzmann, Über niedere Vanadinhydroxyde. I. Zeitschrift für Anorganische und Allgemeine Chemie 278:249-254. 1955.

22. Goncharenko, A.S., and O.A. Suvorova. Cathodic liberation of vanadium compounds. Journal of Applied Chemistry, U.S.S.R. 33:847-850. 1960. (Translated from Zhurnal Prikladnoi Khimii 33:846-850. 1960.)

23. Gooch, F.A. and R.W. Curtis. The action of the halogen acids upon vanadic acid. American Journal of Science, Ser. 4, 17: 41-48. 1904.

24. Hodgman, Charles D. ed. Handbook of chemistry and physics. 41st ed. Cleveland, Chemical Rubber Publishing Co., 1959-1960. 3472p.

25. Kawaguchi, Takeo. Anisotropy of the electrical conductivity of vanadium pentoxide. Kagaku 23:534-535. 1953. (Abstracted in Chemical Abstracts 47:11843f. 1953.)

26. Ketelaar, J.A.A. Die Kristallstruktur des Vanadinpentoxyds. Zeitschrift für Kristallographie 95:9-27. 1936.

27. Kirk, Raymond E. and Donald F. Othner. Vanadium oxides. Encyclopedia of chemical technology. Vol 14. New York, Interscience, 1955. 597p.

28. Klemm W. and P. Pircher. Das Leitvermögen der Vanadinoxyde. Optik 3:75-80. 1948.

29. Kornfeil, F. On the polarization of the manganese dioxide electrode. Journal of the Electrochemical Society 109:343-351. 1962.

30. Kortum, G. and J.O'M. Bockris. Textbook of electrochemistry. Amsterdam, Elsevier, 1951. 882p.

31. Louzos, Demetrios V. Primary electric cell. British Patent 795,910, June 4, 1958.

32. Machatschki, F., Über einer kunstlichen anorganischen Faserstoff. Naturwissenschaften 24:742-743. 1936.

33. Mellor, J.W. Comprehensive treatise on inorganic and theoretical chemistry. vol 9. New York, Longmans, Green and Co., 1929. 967p.

34. Meyer J. und M. Aulich. Zur Kenntnis der Vanadosalze. Zeitschrift für Anorganische und Allgemeine Chemie 194:278-92. 1930.

35. Potter, Edmund C. Electrochemistry. London, Cleaver-Hume, 1956. 418p.

36. Remy, H. Treatise on inorganic chemistry. vol 2. Amsterdam, Elsevier, 1956. 800p.

37. Sidgwick, N.V. Chemical elements and their compounds. vol 1. Oxford, Clarendon Press, 1950. 853p.

38. Scott, Allen B. Diffusion theory of polarization and recuperation applied to the manganese dioxide electrode. Journal of the Electrochemical Society 107:941-944. 1960.

39. Sproull, Wayne T. X-rays in practice. New York, McGraw-Hill, 1948. 615p.

40. Thompson, N.E., Carl H. Roach and Robert Meyrowitz. Duttonite, a new quadrivalent vanadium oxide from the Peanut mine, Montrose County, Colorado. American Mineralogist 42:455-560. 1957.

41. Vosburgh, W.C. The manganese dioxide electrode---a review. Journal of the Electrochemical Society 106:839-845. 1959.

42. Weeks, Alice D., Evelyn A. Cisner and M. Sherwood. Montroseite, a new vanadium oxide from the Colorado plateau. American Mineralogist 38:1235-1238. 1953.