AN ABSTRACT OF THE THESIS OF

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Title: SOME ELECTROCHEMICAL PROPERTIES OF THE

VANADIUM PENTOXIDE ELECTRODE

Abstract approved *Redacted for Privacy*

Dr. Allen B. Scott

Vanadium pentoxide single crystals were grown from the melt. These crystals were made the cathode in an electrolytic cell and the polarization and recovery of the electrode were studied under a variety of experimental conditions.

A study of the electrode potential versus that of the standard hydrogen electrode as a function of electrolyte pH was carried out on both pure and discharged samples. It was found in both cases that the cell potential decreased an average of 0.059 ± 0.005 v/pH unit, thereby indicating that an equal number of electrons and protons are involved in the discharge reaction.

The potential difference between the V_2O_5 and the standard hydrogen electrode was plotted as a function of time during polarization and recovery. The resulting curves were compared with those calculated from a theory based on the diffusion of the discharge

product from the surface to the interior of the electrode. This theory successfully predicted the experimental curves between pH 2 and 5.5; outside this range the theory failed due to dissolution at low pH and air oxidation at high pH of the discharge product.

Experiments conducted at pH 4.7 utilizing a tritium tracer showed the presence of hydrogen in the electrode following the polarization and recovery of the electrode.

A study on the degree of polarization as a function of temperature was conducted; the activation energy for the diffusion of the product from the electrode surface was found to be 6.7 kcal/mole. This value indicates that it is probable protons and electrons diffuse rather than the entire reduced compound.

Some Electrochemical Properties of
the Vanadium Pentoxide Electrode

by

Kenneth Russ Newby

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SOME ELECTROCHEMICAL PROPERTIES OF THE
VANADIUM PENTOXIDE ELECTRODE

I. GENERAL INTRODUCTION

Preface

The use and importance of primary electrochemical cells have

been well established. Most of these cells utilize a metallic oxide

for the cathode material. While several oxides are, or could be,

used, only manganese dioxide has been thoroughly studied. Thus,

if new cathode materials for higher quality cells are to be forth-

coming, additional fundamental research is needed on old, as well

as new, materials. This research should be concerned with the

electrochemical properties of these materials including the electrode

mechanisms involved when the materials are used in primary cells

which undergo discharge.

This study was undertaken in an attempt to establish the

mechanism by which single crystal vanadium pentoxide electrodes

are discharged when made the cathode in a primary cell. Although

there has been no previously reported work on this exact subject,

Watson (57) showed that the discharge or polarization mechanism for

a polycrystalline V_2O_5 electrode was qualitatively similar to that of

the manganese dioxide electrode. A subsequent study was made on

pressed pellets of V_2O_5 and graphite by Shuklev and Kuz'min (53)

which stated that the discharge mechanism for the manganese dioxide electrode did not apply to the vanadium pentoxide electrode.

Vanadium pentoxide has several inherent physical advantages which aid a study of its electrode polarization mechanism. It is a fairly good semiconductor and has a high reduction potential. While the melting point of this oxide has been reported at values between 656°C. and 690°C. (35, p. 76), the important feature is the low value, which simplifies the production of electrodes.

Another important advantage found in vanadium pentoxide is that it has only one crystalline modification. This alleviates many of the problems found in the study of manganese dioxide and many other metal oxide electrodes.

The most serious disadvantage in working with vanadium pentoxide in an aqueous medium is the solubility of both the V_2O_5 and many of its possible reduction products. Another minor problem is the toxicity of V_2O_5 which affects the respiratory system in a cumulative manner. Thus care must be taken when handling the oxide in its powdered form.

While vanadium pentoxide is not a well known depolarizer for primary cells, a patent was granted in 1958 to Louzos of Union Carbide Corporation (40) for a cell utilizing this oxide. A longer shelf life and a wider temperature range were claimed as advantages for this cell over the more common cells. A patent was, also,

granted to Zellhoefer of the National Union Electric Co. for a thermal

cell using V_2O_5 as a depolarizer (60).

Vanadium Pentoxide as an Electrode Material

The following section surveys the properties of vanadium

pentoxide which may affect its electrode characteristics. The survey

will include crystal structure of the oxide, reported V(V) ions in

aqueous solutions, pertinent electrical properties of the solid, and

the properties of reported compounds which could possibly be the

reduction product of vanadium pentoxide. General reviews on

vanadium pentoxide are available in texts by Gmelin (35), Mellor

(46, pp. 714-825), Remy (51, pp. 90-104) and Sidgwick (54, pp.

804-834).

Crystal Structure of Vanadium Pentoxide

Historically, crystallographers have been in agreement that

vanadium pentoxide belongs in the orthorhombic crystal system.

However, the structure was in dispute until 1950 when Bystrom,

Wilhelmi and Brotzen (14) proposed the structure now generally

accepted. Prior to that time Ketelaar (31) had reported that V_2O_5

belongs to the point group C_{2v}^7-P mmn with unit cell dimensions of

a = 11.48 ± 0.01 Å, b = 4.36 ± 0.005 Å and c = 3.55 ± 0.005 Å. This

structure leads to a two-dimensional network of tetrahedra with

vanadium atoms in the center and oxygen atoms on the points of each tetrahedron. Later in the same year (1936) Machatschki (43) proposed a structure consisting of double chains with the composition $(V_2O_5)_\infty$.

Bystrom, et al. after a careful x-ray study determined the space group for vanadium pentoxide to be D_{2h}^{13}-P mmn and the unit cell dimensions to be a = 11.519 $\pm$ 0.006 Å, b = 4.373 $\pm$ 0.002 Å and c = 3.564 $\pm$ 0.002 Å. In this structure the vanadium atoms are surrounded by five oxygen atoms which form a distorted trigonal bipyramid. There is a near perfect cleavage along (010). This weak cohesion of the crystals in the b - direction is attributed to the sixth V-O bond which is much weaker than the five V-O bonds forming the trigonal bipyramid. Figure 1 gives a three dimensional drawing of vanadium pentoxide according to the structure given by Bystrom, et al.

Vanadium Pentoxide in Aqueous Solution

Vanadium pentoxide is soluble in both strong acid solutions and in basic solutions. It has a solubility of 0.07 g per 100 ml (47) at 25°C and at pH = 7.0. The solubility decreases to 0.04 g/100 ml at pH = 2.1 and then increases as the pH is lowered further, having a value at 0.285 g/100 ml at pH = 1.0 (13).

The ions formed when vanadium pentoxide dissolves are

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

b

4.373 Å   c   3.564 Å

a

11.519 Å
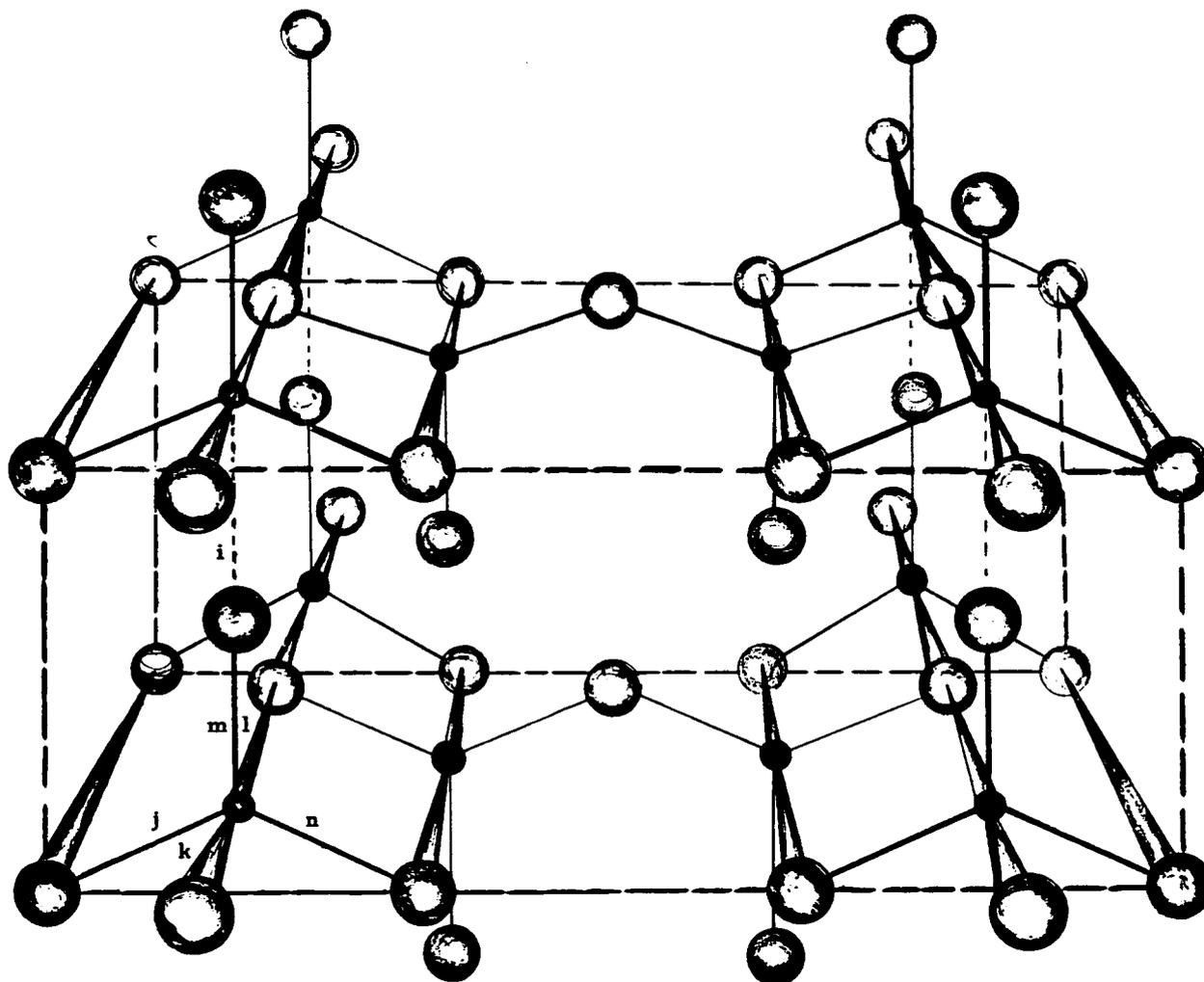
Unit Cell Lengths

Figure 1.   Crystal Structure of Vanadium Pentoxide.   Unit cell
indicated by heavy broken line.   After Bystrom (14).
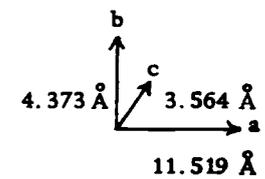
numerous; the varieties formed depend upon pH. Gmelin's Handbuch

der Anorganischen Chemie (35, pp. 132-145) gives a comprehensive

review of these ions. Figure 2 gives the pH range of existence at

various vanadium concentrations for the most important ions. In

this study vanadium pentoxide is present in the electrolyte only in

very small quantities. Therefore, with reference to Figure 2, the

only vanadium (V) species in acidic solution which might be im-

portant are $VO_2^+ \cdot aq$, $HVO_3 \cdot aq$, and $VO_3^- \cdot aq$. The vanadic ion

(VO_2^+) is a clear yellow color, while HVO_3 is a yellow-orange color

and the orthovanadate ion (VO_3^-) is colorless.

Electrical and Electrochemical Properties

Vanadium pentoxide is an n-type semiconductor with non-

isotropic conductivity. However, within the temperature range of

this study the specific conductivity of crystals grown in this labora-

tory is between 10^{-4} and 10^{-3} $ohm^{-1}cm^{-1}$ along all three crystallo-

graphic axes (42).

Vanadium pentoxide can be electrolytically reduced to lower

oxides with vanadium in the +4, +3, or +2 states (54). Deltombe,

Zoubov and Pourbaix (19) give the Nernst equations for the reduction

of vanadium (V) to vanadium (IV) at $25^{\circ}C$.
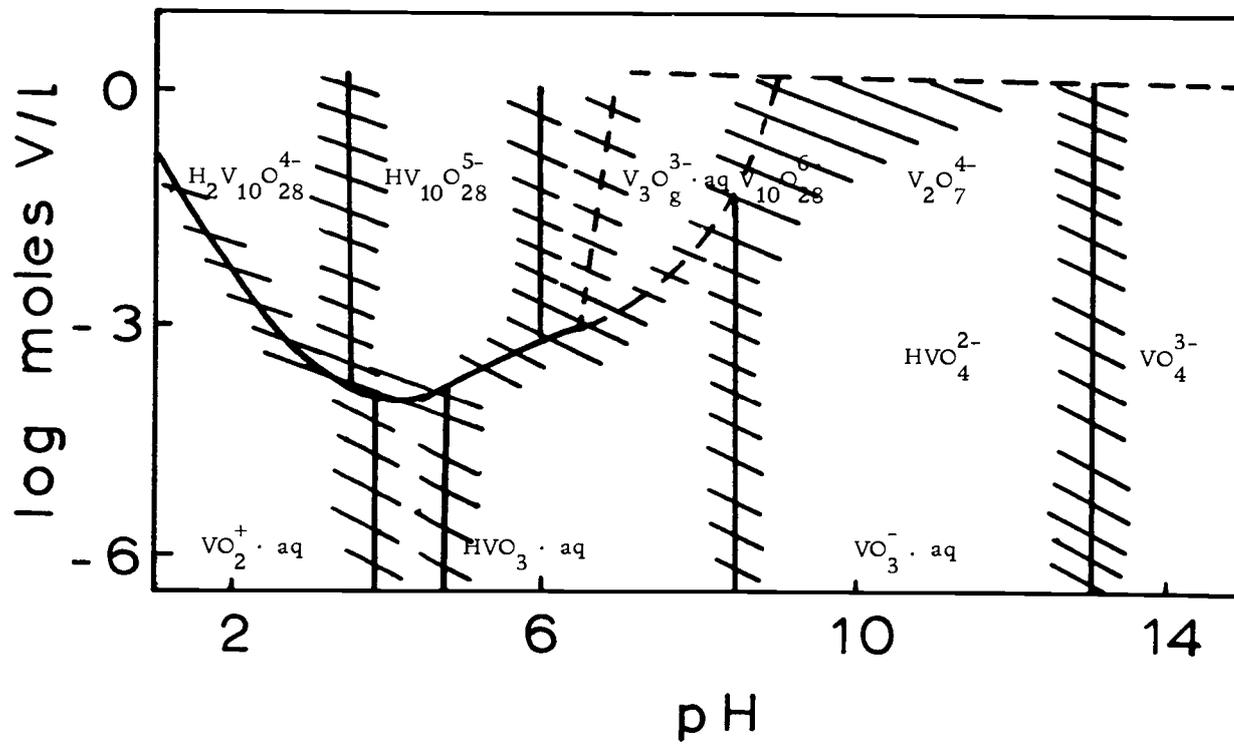
Figure 2. Range of existence for V(V) ions in water solution.

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

$\quad E = 0.958 - 0.1773pH - 0.0591 \log [VO^{++}]$

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

$\quad E = 1.004 - 0.1182pH - 0.0591 \log \frac{[VO^{++}]}{[VO_2^+]}$

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

$\quad E = 1.096 - 0.2068pH - 0.0295 \log \frac{[VO_2^{++}]^2}{[H_3V_2O_7^-]}$

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

$\quad E = 1.314 - 0.2364pH - 0.0591 \log \frac{[VO^{++}]}{[H_2VO_4^-]^2}$

[5] $\quad 2H_2VO_4^- + 3H^+ + 2e^- = HV_2O_5^- + 3H_2O$

$\quad E = 0.719 - 0.0886pH - 0.0591 \log \frac{[HV_2O_5^-]}{[H_2VO_4^-]^2}$

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

$\quad E = 0.501 - 0.0591pH - 0.0295 \log \frac{[HV_2O_5^-]}{[H_3V_2O_7^-]}$

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

$\quad E = 1.281 - 0.1477pH - 0.0295 \log \frac{[HV_2O_5^-]}{[HVO_4^{-2}]^2}$

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

$\quad E = 1.962 - 0.2068pH - 0.0295 \log \frac{[HV_2O_5^-]}{[VO_4^{-3}]^2}$

$$[9] \quad H_3V_2O_7^- + 3H^+ + 2e^- = V_2O_4 + 3H_2O$$
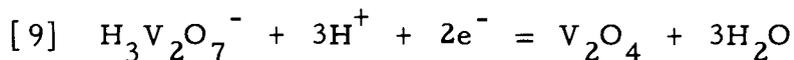
$$E = 0.806 - 0.0886pH + 0.0295 \log [H_3V_2O_7^-]$$

$$[10] \quad 2H_2VO_4^- + 4H^+ + 2e^- = V_2O_4 + 4H_2O$$
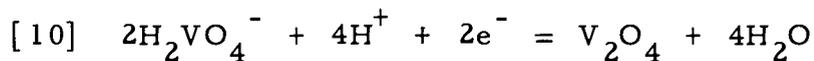
$$E = 1.022 - 0.1182pH + 0.591 \log [H_2VO_4^-]$$

$$[11] \quad 2HVO_4^{-2} + 6H^+ + 2e^- = V_2O_4 + 4H_2O$$
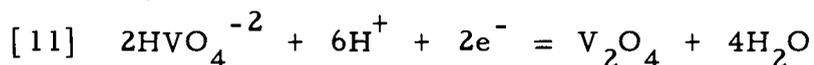
$$E = 1.586 - 0.1773pH + 0.0591 \log [HVO_4^{-2}]$$

Reduction Products of Vanadium Pentoxide

The products which conceivably could be formed by the reduction of a vanadium pentoxide electrode in an aqueous medium would include the oxides and oxy-hydroxides of vanadium and their ions. While there are a minimum of fifteen distinct vanadium oxides with a composition between that of the pure metal and V_2O_5 which have been reported, only those having an oxidation state of three or higher will be considered here. Anderson (4) in 1954 prepared and characterized ten oxides having an oxidation state of three or more. Below is a list of these oxides along with their appearance.

V_2O_3	grayish powder
V_3O_5	dark gray powder or very small crystals
V_4O_7	dark lustrous powder or aggregates of very small crystals

V_5O_9 black lustrous powder or aggregates of small crystals

V_6O_{11} lustrous powder or aggregates of blue-black crystals

V_7O_{13} strongly lustrous blue-black powder or very small crystals

V_4O_{15} see V_7O_{13}

VO_2 (V_2O_4) needle or rod shaped blue-black crsytals

V_6O_{13} black lustrous powder or small crystals

V_2O_5 brownish yellow crystals.

X-ray diffraction powder patterns are available for V_2O_3 (2), V_3O_5 (35), VO_2 (5), V_6O_{13} (1), and V_2O_5 (3). Only V_2O_3, VO_2 or V_2O_4, and V_2O_5 of the above ten oxides have been carefully studied.

Vanadium trioxide, V_2O_3, can be prepared by heating V_2O_5 with carbon monoxide or hydrogen. It can also be prepared by electrolysis of ammonium vanadate solutions. The oxide is gray to black in color and crystallizes in the hexagonal system. It can be air-oxidized to VO_2 at room temperature. In acid solutions its ions which are always green in color can be air-oxidized to the tetra-valent state (35, pp. 32-49; 54, p. 825).

Vanadium dioxide, VO_2, (or the tetroxide, V_2O_4) crystallizes in the monoclinic system as blue-black needles or rod shaped crystals. The dioxide can be prepared by a variety of methods, the simplest of which is to heat the pentoxide with either the trioxide,

oxalic acid or sulphur dioxide. It can be oxidized to the pentoxide

by heating in air or by treatment with concentrated nitric acid. While

insoluble in water it is readily dissolved in either acidic or basic

solutions. In solution vanadium dioxide forms the blue vanadyl ion,

VO^{2+}, at pH values up to 5.3. At higher pH values the hypovanadate

ion, $HV_2O_5^-$, which is a brownish-red color, is present (5; 54, pp.

818-819).

Four oxy-hydroxides of vanadium have been reported in the

literature in recent years. One of these was prepared by Glemser

and Schwarzmann (27) and given the formula $V_3O_5(OH)_4$. This black

oxy-hydroxide was prepared in concentrated NH_4Cl solution by re-

ducing vanadium pentoxide with zinc turnings at $100^{\circ}C$. The initial

green product turns to the black compound desired in approximately

one hour. They claim the oxy-hydroxide is stable for several

weeks in air and that it is soluble in dilute sulfuric acid giving a

green color. An x-ray diffraction pattern is also given.

Bernard and Theobald (10) in a later study found that the com-

pound reported by Glemser and Schwarzmann as $V_3O_5(OH)_4$ was

really $V_6O_{13}(OH)_2 \cdot 5H_2O$.

Vanadyl hydroxide, $VO(OH)_2$, which is also known as the

mineral Duttonite, has been studied to a considerable extent recently.

As the mineral Duttonite, $VO(OH)_2$ occurs as pale-brown transparent

platelets which, while crystallizing in the monoclinic system, are

pseudo-orthorhombic (55). Glemser and Schwarzmann (27) prepared

a rose colored vanadyl hydroxide by reducing vanadium pentoxide

with sulfur dioxide and then heating the product in a nitrogen atmos-

phere. The hydroxide is easily air oxidized in basic solution and

also dissolves in sulfuric acid giving a blue solution. Gmelin (35,

pp. 64-70) gives a further review of this compound.

The remaining two oxy-hydroxides have been studied by Evans

and Mrose (22). The mineral Montroseite, $VO(OH)$, is deposited in

crystalline masses in a sandstone matrix. It is always found associ-

ated with vanadium dioxide and, indeed, is air oxidized to the dioxide

by either the atmosphere or by ground water. It is believed that this

oxidation involves the migration of hydrogen ions through the crystal

and that an intermediate, $V_2O_3(OH)$, is involved in this process.

Theories on the Mechanism of Polarization and Recovery of Certain Metal Oxide Cathodes

The Manganese Dioxide Electrode

The manganese dioxide electrode has received extensive study

due to its use in the commercially successful Leclanché cell.

Vosburgh (56), who along with his many students did much of the

early work on the mechanism of this electrode, published a review

article in 1959 on the manganese dioxide electrode. As summarized

in this review, the earliest theories dealing with the discharge of

MnO_2 involved the evolution of hydrogen which was subsequently oxidized by MnO_2. Thus, according to this theory the MnO_2 acted as a depolarizer. While there has been no experimental evidence to support this theory, the term "depolarizer" is still used with respect to this electrode.

Divers in 1882 explained the polarization (i.e. departure from the equilibrium potential) of the MnO_2 electrode as the result of the accumulation at the electrode surface of the discharge product. He correctly identified this product as MnOOH. Divers's theory received little attention although recent experiments led to a similar conclusion.

Coleman (18) in 1946 advanced the mechanism most widely accepted today for discharges at moderate current densities and at a pH in the middle range. He proposed that the composition of the oxide surface in contact with the electrolyte determines the electrode potential. During discharge the following reaction occurs.

[12] $$MnO_2 + H^+ + e^- = MnOOH$$
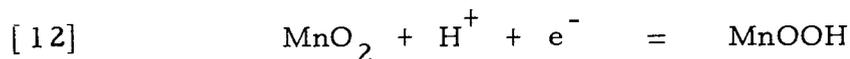
It is believed that this reaction takes place mostly at the electrode-electrolyte interface. As the MnOOH concentration increases on the electrode surface a difference of chemical potential is developed causing the solid-state diffusion of the reaction product from the surface to the interior of the electrode. Coleman further proposed

that this diffusion need only involve protons and electrons. Since

the product removal by the diffusion process is much slower than

the product accumulation during discharge, there is a resulting

large potential drop or polarization during discharge. However,

when the discharge is terminated this polarization decreases due to

the continuing diffusion of the product to the electrode's interior and

the corresponding increase in MnO_2 concentration at the surface.

This latter process is known as recovery.

Scott (52) applied the solution of the diffusion equation for the

diffusion of heat into a semi-infinite solid to Coleman's theory (see

Section VI). In this manner Scott was able to predict the general

shape of the polarization curves obtained by Ferrell and Vosburgh

(25). Scott's equation was subsequently modified by Kornfeil (33)

such that the form of the recovery curve could be predicted from the

slope of the discharge curve.

Working in a pH range of 5.2 - 5.4, Cahoon (15) proposed that

the MnO_2 is reduced directly to Mn^{++} which goes into solution.

The manganese (II) ion is subsequently oxidized by MnO_2 to MnOOH

at the electrode surface.

Era (20) and his co-workers tested the above theories over a

range of electrolyte pH values in an attempt to establish the pH

limits for the two mechanisms. They found that the discharge

product, MnOOH, is formed at the electrode surface and subsequently

is removed by various mechanisms depending on the electrolyte pH as follows:

1. in acidic electrolyte (pH $<$ 6), MnOOH reacts with the electrolyte forming Mn^{++} and MnO_2.

2. in alkaline electrolyte (pH $>$ 8), removal of the MnOOH from the electrode surface is accomplished by the diffusion of protons and electrons to the electrode interior.

3. in neutral electrolyte, both 1 and 2 occur.

Other Oxide Electrodes

A study by Mark and Vosburgh (45) compared the discharges of PbO_2, TiO_2 and Tl_2O_3 electrodes with that of MnO_2. In their study they proposed that the discharge mechanism for the thallium (III) oxide electrode involves an unstable valence state between the initial and final products. This would be similar to the manganese dioxide case in which, if the discharge is allowed to continue, the MnOOH is the intermediate and the final product is $Mn(OH)_2$.

Recent studies by MacArthur (41) indicate that the diffusion of protons from the interior to the surface of the electrode is involved when nickel (II) hydroxide, as found in the nickel-cadmium battery, is used as an anode.

II. PREPARATION AND PROPERTIES OF VANADIUM
PENTOXIDE ELECTRODES

Stockbarger Crystals

The starting material for all the electrodes was Baker's analyzed

reagent, 99.5%, vanadium pentoxide which contained 0.10% chlorine

and 0.30% carbon dioxide.

The Stockbarger technique (37) was attempted as a method of

single crystal growth. In this method the V_2O_5 powder was sealed

under an oxygen atmosphere in a 19 mm Vycor tube which was both

drawn out to a fine point at the lower end and constricted about 5 cm

from the tip. This tube was then lowered at 0.5 cm/hr through a

temperature gradient of about $6^\circ C/cm$ starting at $705^\circ C$. Ideally

the melted vanadium pentoxide commences freezing in the drawn out

portion of the tube. In this way only a small number of seeds will

be formed of which usually only one will predominate and a single

crystal will eventually be produced. The constriction 5 cm from the

tip further insures the formation of only one crystal.

The solid emerging from the furnace appeared as though it had

grown rapidly in a vertical direction and had not had time for a seed

selection to take place. Apparently this rapid solidification was due

to supercooling of the melt. A few small crystals were, however,

obtained, but they were unsuitable for use as electrodes. It should

also be noted that the V_2O_5 attacked the Vycor tubing to a small extent, imparting a light green color to some of the tubes. If the supercooling problem could be overcome, possibly by changing the temperature gradient, this method would provide a way of growing V_2O_5 single crystals under an oxygen atmosphere and, thereby, reduce the nonstoichiometry of the samples.

Crystals Grown from the Melt

Single crystals were grown using a modification of a method originally due to Arsen'eva and Kurchatov (6) and supplied to this laboratory by Boros in a private communication. The method is similar to that reported by several workers (6, 11, 29, 30, 49). Gillis and Boesman (26) have also recently reported growing single crystals by a zone refining technique.

The vanadium pentoxide crystals were grown in an air atmosphere in a platinum crucible which was cemented into an Alumdum crucible. The alundum crucible was in turn placed in a Hevi-Duty type 86 furnace. Temperature within the furnace was monitored by a chromel-alumel thermocouple placed 0.5 cm to 2 cm above the melt. The furnace temperature was controlled and recorded by a Leeds and Northrup Micromax recording potentiometer. In order to decrease the sinusoidal temperature fluctuations due to a time lag between current flowing to the coils of the furnace and heat reaching

the oxide, a small current was constantly bled directly to the furnace.

The powdered reagent grade V_2O_5 was heated to its melting point of $690^\circ C$. When the oxide was completely melted a seed crystal obtained from microtome shavings of previously grown crystals was dropped into the melt and held on the surface by surface tension. The temperature was then very slowly raised until only a single, barely visible crystallite remained. A penlight was used to help determine if the crystallite was single and should be allowed to grow. At this point the melt was cooled at a rate of approximately $1^\circ C$ every three minutes for about $10\text{-}20^\circ C$. If during this cooling the crystallite developed polycrystalline sections then the melt was reheated and the above process repeated; however, if the crystallite remained single then after sufficient growth had taken place a stain-less steel spatula was dipped into the melt alongside of the crystal. The melt between the crystal and the spatula would freeze, thereby, allowing the crystal to be lifted from the furnace.

An alternative to the above method of seeding the melt is a similar process whereby the powder is never allowed to melt com-pletely. In this method the last powder crystallite serves as the seed crystal. This method is advantageous in that it avoids the problem of having the melt supercool before seeding in which case the melt rapidly freezes to a very polycrystalline solid. Also, since vanadium pentoxide dissociates to a small extent giving off oxygen

at elevated temperatures, and since Kennedy, et al. (29) reported

finding 0.02% platinum in their crystals which were held at $800^{\circ}C$

for three hours. This latter method of seeding the melt was generally

used in this work, thus avoiding temperatures much above the melt-

ing point of the oxide.

By the above methods crystals were grown to a diameter of 5

cm (the platinum crucible's diameter) and a thickness in excess of

4 mm. However, for convenience crystals were usually lifted from

the melt with dimensions of about 20 x 10 x 2 mm.

The crystals grow with the ac crystallographic plane parallel

to the surface of the melt. They grow faster in the $\vec{c}$ direction than

in the $\vec{a}$ direction. This is especially true when the rate of cooling

is rapid. The crystals were platelets of a dark red-brown color,

with the top surface being highly reflective.

An x-ray powder pattern of a pulverized single crystal was

compared with the pattern obtained from the powdered oxide before

melting and with the ASTM values. The d-line spacings were found

to be identical within experimental error; however, the intensities

varied due to the effect of crystal orientation which was not totally

destroyed in the grinding of the crystals.

While Laue patterns have not been taken on these crystals, a

preliminary study of their single crystallinity was made in this

laboratory by Charles Bryden using a polarizing microscope.

Vanadium pentoxide crystallizes in the orthohombic system (32).
When an orthorhombic crystal is rotated on the stage of a polarizing
microscope with the polarizer and analyzer crossed, extinction oc-
curs every 90°. This extinction every 90° means that an optic axis
of the crystal is parallel to the axis of the polarizer or the analyzer . An
optic axis is a direction parallel to which there is no double refraction.

For a thinly sliced crystal the single-crystallinity could be
indicated by observing various parts of the sample while not changing
the crystal orientation relative to the polarizer. In each case the
angles of the extinction were the same and were 90° apart. Had the
sample been polycrystalline the angles at which extinction occurred
would have varied from place to place on the sample. This study,
therefore, gives a preliminary indication that the crystals are
single.

Crystal growth is frequently classsed more as an art than as a
science. This statement is applicable to the growth of vanadium
pentoxide; patience and luck are required in order to obtain a good
crystal.

Preparation of Crystals for Electrochemical Experiments

Two types of leads were attached to the vanadium pentoxide
crystals. Unless otherwise specified the lead consisted of a
platinum wire which was fused into one end of the oxide crystal.

This was done by heating the wire with an oxygen torch and allowing

the heat to be conducted down the wire to melt the vanadium pentoxide

around the wire. This method provided a good electrical contact as

well as a strong mechanical contact.

The above method, however, left the vanadium pentoxide in

the region of the platinum wire in a polycrystalline state. In order

to keep this portion and the polycrystalline back side of the electrode

from being exposed to the electrolyte and, thereby, becoming part

of the electrochemical cell, they were covered with a heavy coating

of paraffin. This left only the smooth, shiny front surface of the

crystal exposed to the electrolyte (see Figure 3).

In order to insure that the method by which leads were

attached to the electrodes had no detectable effect on the discharge

experiments to be described, a second method which was a modifi-

cation of that given by McCulloch (42, pp. 9-14) was used. The

crystals were sliced on an American Optical Company Model 860

microtome in order to remove the polycrystalline material from the

back side. After slicing, the crystals were washed first in hot

petroleum ether and then in hot ethanol. Gold was then evaporated

on to the back side. An aluminum mask was placed over the

shiny side of the crystal in order to protect it from the gold.

The gold contact was then cleaned with lactic acid. After the

lactic acid had dried a copper wire, which was "tinned" with indium
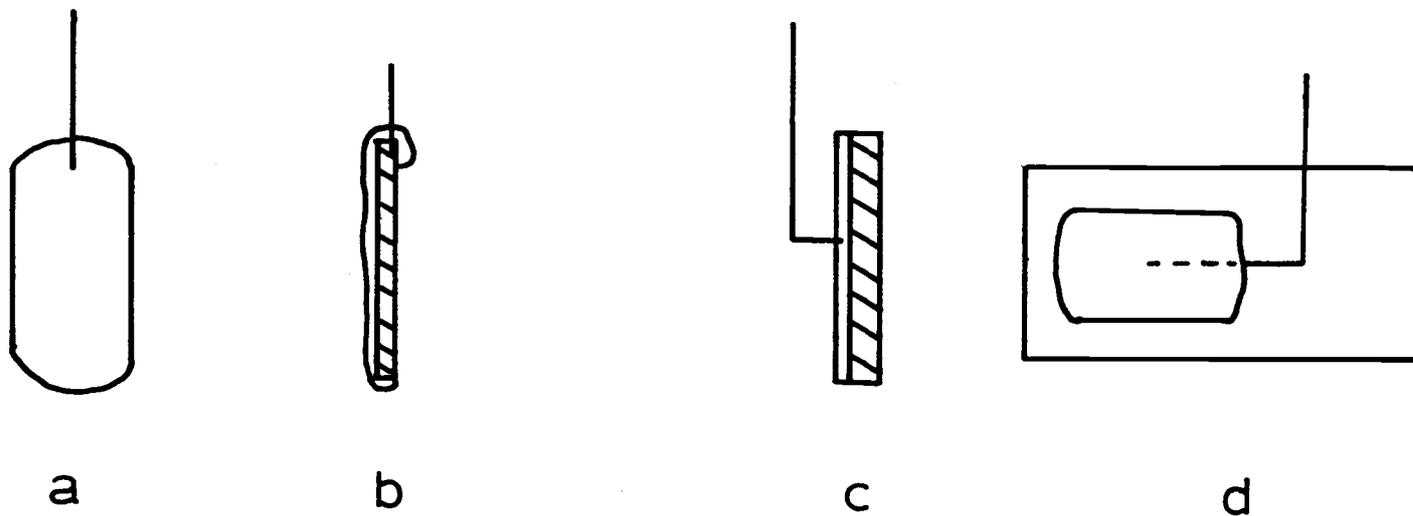
Figure 3. Vanadium pentoxide electrodes. a, b, front and side view of electrode with
Pt lead and paraffin; c, side view of gold plated electrode with Cu lead; d, gold
plated electrode mounted on microscope slide.

solder, and a small amount of indium solder were placed on the gold leaf. These were then heated on a hot plate until the solder melted and a contact was made. In order to avoid oxidation of the indium, the contact was cooled as rapidly as possible after being made.

This method, while giving good electrical contact, provides relatively poor mechanical strength. For this reason and also to keep the gold from direct contact with the electrolyte the soldered contact and the gold were entirely covered with paraffin. In order to add still further mechanical support and to protect the copper wire from the electrolyte the crystal was mounted by means of paraffin to a microscope slide. The copper wire was paraffined to the slide, thereby leaving only the desired vanadium pentoxide exposed to the electrolyte (see Figure 3).

<div align="center">

Solubility of the Vanadium Pentoxide Electrodes
in 1. 0 N NH$_4$Cl Solution

</div>

According to the literature, vanadium pentoxide dissolves to the extent of 0. 07 grams per 100 ml water at 25°C. Watson (57) found that it was necessary with polycrystalline electrodes to saturate the electrolyte with vanadium pentoxide in order to prevent the electrode from dissolving. However, in early experiments with the single crystal electrodes grown from the melt the vanadium pentoxide did not appear to dissolve to an appreciable extent. Therefore, in

order to determine whether it was necessary to saturate the electrolyte with vanadium pentoxide a preliminary solubility study was undertaken.

A single crystal, which after being paraffined on the back side had a surface area of 2.1 cm^2, was placed in 20 ml of 1 N NH_4Cl solution which was contained in a stoppered 25 ml Erlenmeyer flask. This flask was then mounted in an American Instrument Company shaker bath. The water in the bath was thermostated at $25^O \pm 2^OC$.

The concentration of dissolved vanadium pentoxide was determined by optical means using a Perkin-Elmer Model 450 Spectrophotometer. Calibration curves were prepared by dissolving powdered V_2O_5 in 1 N NH_4Cl and then measuring the absorbance at 260 mμ and at 215 mμ against an NH_4Cl blank. This method was able to detect concentrations as low as a 1.0 μg of V_2O_5/ml solution.

Figure 4 shows the results of this experiment. The first point at 3.5 hours was taken when the solution first became visibly colored by the dissolved oxide.

The relatively small amount of solution used should not have affected the rate of dissolving as long as equilibrium was not approached. This is borne out by the roughly linear relationship between the amount of oxide dissolved and the time up to about eight
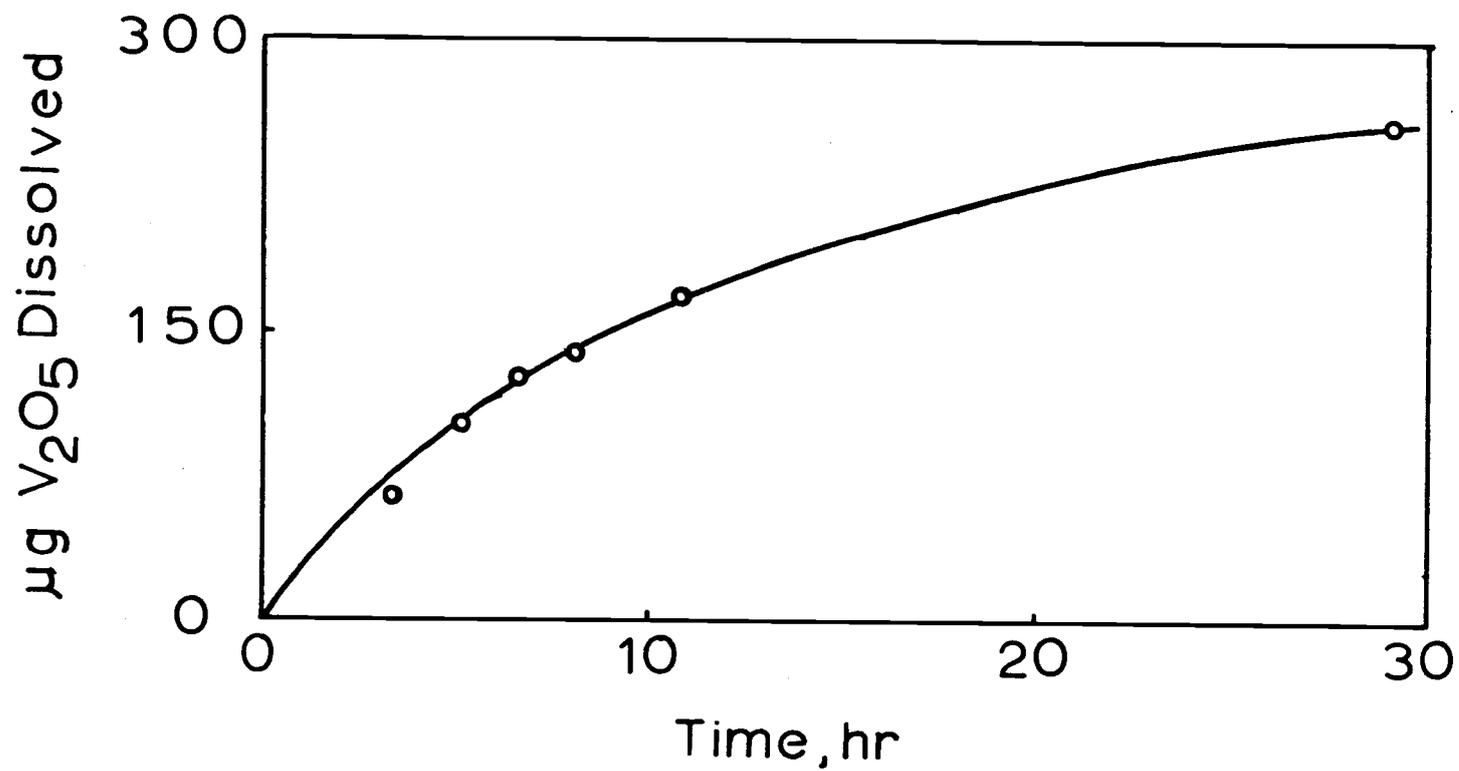
Figure 4. Amount of V_2O_5 dissolving in 20 ml of 1 N NH_4Cl at 25 °C as a function of time.

hours.

Since in this study the solution and crystal were agitated much more vigorously than in most of the experiments to be described in later sections of this paper, it was concluded that in the time span (usually 1-2 minutes) used in these later experiments the effect of the electrode dissolving into the electrolyte could be neglected. Therefore, it was unnecessary to saturate the electrolyte with V_2O_5 as was done by Watson. Being thus able to use a colorless electrolyte, it was possible visually to observe the electrode surface and watch for changes both there and in the electrolyte during experiments.

III. APPARATUS

Electrolytic Cell

Discharge experiments can be conducted in a variety of ways, two of which are described below. The vanadium pentoxide electrode can be made the cathode, i.e., the electrode where reduction occurs, in a galvanic cell and a constant current drawn from the cell by means of a variable resistance placed across the electrodes. The second method is that of applying a constant current to the vanadium pentoxide electrode and measuring the change in potential difference between the V_2O_5 electrode and some non-current carrying reference electrode as a function of time.

Due to the relatively small V_2O_5 electrodes used and their rapid polarization it would be difficult to draw a constant current from a galvanic cell using this electrode; therefore, the second method was used in this study. Current was supplied by means of an external source which maintained electronically a constant current at any chosen value.

The cell used in all of the electrochemical experiments is shown in Figure 5.

The experimental cell consisted of a 150 ml beaker containing between 100 and 125 ml of electrolyte. The anode or working electrode was a 1/4 inch spectroscopic grade carbon rod immersed in
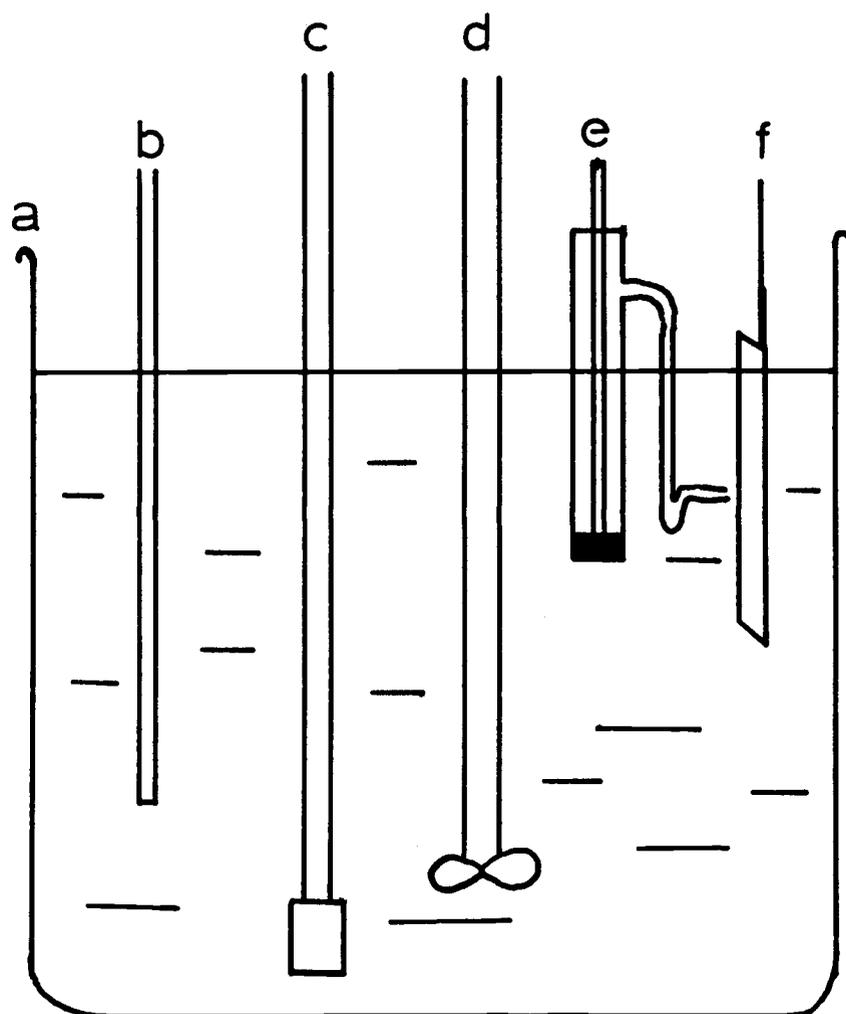
Figure 5. Discharge cell. a, 150 ml beaker; b, carbon rod;
c, gas dispersion tube; d, stirrer; e, saturated
calomel electrode; f, V_2O_5 electrode.

the electrolyte from 1.5 to 2 inches. The vandium pentoxide cathode

was placed as far as possible from the carbon rod and directed such

that the side which had not been paraffined faced toward the carbon

rod. The oxide electrode was never immersed in the electrolyte to

a depth such that the platinum lead which was not covered by

paraffin would be in direct contact with the electrolyte. In order to

follow the potential change of the V_2O_5 electrode a calomel elec-

trode, saturated with KCl, having a constant potential of -0.242

volt with respect to the standard hydrogen electrode[1] at 25°C was

used as a reference electrode. The calomel electrode was equipped

with a Luggin capillary tip (see Figure 6) having a radius of less

than 0.5 mm. This tip in accordance with a study by Barnartt (8)

was always placed a minimum distance of four times the capillary

radius or 2 mm away from the vanadium pentoxide electrode surface.

A glass stirring rod attached to a variable-speed electric

stirring motor was inserted into the discharge cell when stirring of

the electrolyte was desired. The stirring rod was placed as near as

possible to the vanadium pentoxide and calomel electrodes.

For the experiments which involved saturating the electrolyte

with a given gas a coarse, fritted glass gas dispersion tube having

an outside diameter of 12 mm was placed near the bottom of the cell.

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[1] All potentials in this paper are given with respect to the standard
hydrogen electrode.

To reference electrode
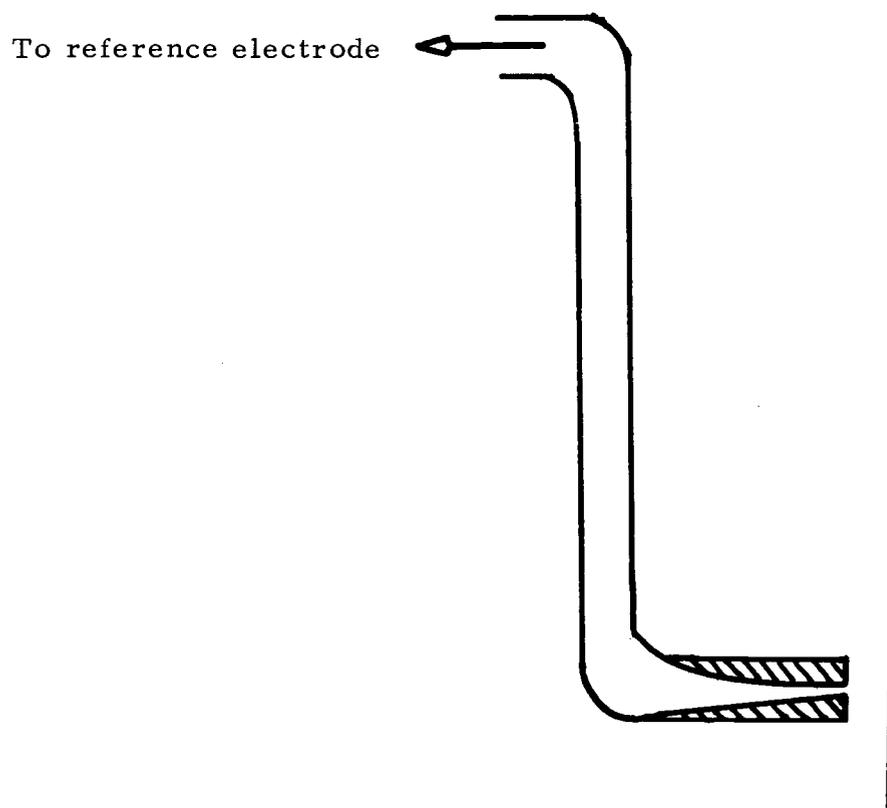
Figure 6. Luggin capillary in vicinity of the electrode.

High purity, 99.98% nitrogen gas containing 0.02% oxygen was used to sweep the electrolyte solution free of dissolved oxygen and 99.8% oxygen gas was used for saturating the electrolyte with oxygen.

The cell was placed in a thermostated 20 l water bath. Unless otherwise noted the temperature of the bath was $25^{\circ} \pm 0.2^{\circ}C$.

<div align="center">Discharge Circuit</div>

The carbon rod anode and V_2O_5 cathode were connected in series with a constant current source and a Simpson microammeter. The constant current source (44, p. 368) was constructed utilizing a Heathkit Model EUW-194 operational amplifier, four 1-1/2 v dry cell batteries connected in series, and a Heathkit Model IN-11 decade resistance box. For the range of current desired in these experiments, this circuit was capable of maintaining within the detectability of the microammeter a constant current flow between the carbon and vanadium pentoxide electrodes regardless of the potential change occurring at the vanadium pentoxide electrode.

To measure and record the emf change at the oxide electrode a Hewlett-Packard strip chart recorder, Model 7100 BM, was placed across the saturated calomel electrode and the vanadium pentoxide electrode. This recorder had a 0.5 sec. full scale response time, and for electrode discharges of a few minutes or less it was usually operated at 0.5 volts full scale and chart speed of 15 cm per min.

A Heathkit voltage source Model EUW-16 was included in the measuring circuit as a bucking potential in order to neutralize the ohmic overpotential drop. The bucking potential was connected by means of a double pole switch such that it was turned on and off at the same instant as the current in the discharge circuit was turned on and off. This bucking potential allowed a smaller full scale voltage range to be employed on the recording potentiometer, thus increasing the experimental sensitivity. This circuit is illustrated in Figure 7.

Except in experiments where pH was a variable, 1 N NH_4Cl having a pH of 4.7 was used as an electrolyte. When other pH values were desired dilute HCl or NH_4OH was added to the NH_4Cl solution. For pH values below 5.5 this system gave a stable electrolyte pH. At higher values of pH the electrolyte slowly became more acid.
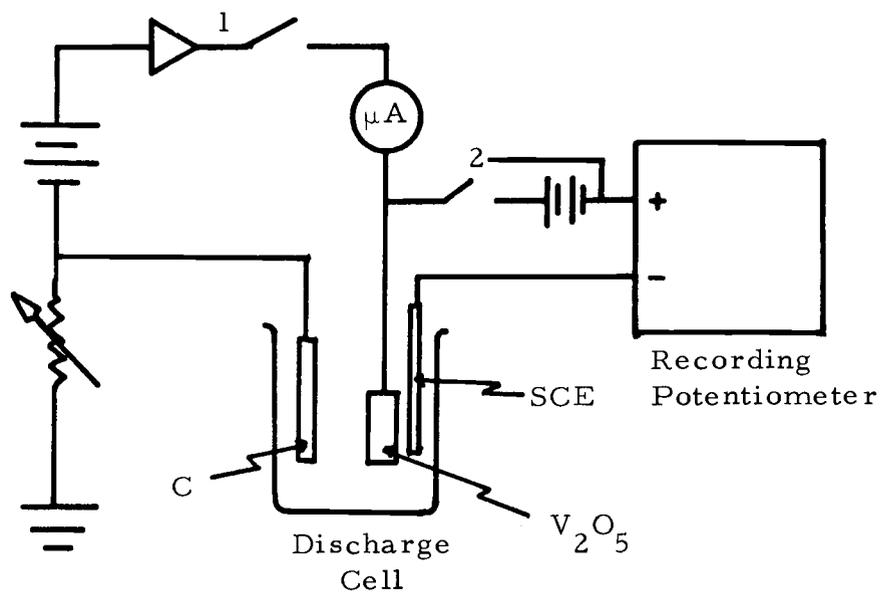
Figure 7. Discharge circuit. Switches 1 and 2 open and close simultaneously.

IV. DEPENDENCE OF V_2O_5 ELECTRODE POTENTIAL
UPON pH

Introduction

During cathodic discharge of a vanadium pentoxide electrode

the +5 vanadium in the V_2O_5 is reduced to some lower oxidation

state. In an acid medium this reaction can be written

[13] $V_2O_5 + ne^- + n'H^+ + mH_2O = PRODUCT + pH_2O$
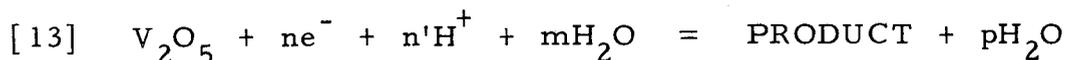
where "product" represents the reduced form of the vanadium

pentoxide and n, n', m, and p may individually have any value

including zero.

At $25^\circ C$ the Nernst equation for this reaction is

[14] $E = E_o - \dfrac{.0591}{n} \log \dfrac{[product][H_2O]^p}{[V_2O_5][H^+]^{n'}[H_2O]^m}$

where [   ] represents the activity of the enclosed species. Pure

water is commonly chosen as the standard state and its activity

assigned a value of one. Since water is in great excess in the elec-

trolytic solution it is a reasonable assumption that its activity will

remain near unity as the pH is varied. If it is also assumed that the

ratio of activities of the product and solid vanadium pentoxide remains

constant as only the pH is altered, then at $25^\circ C$ equation [14] can be

reduced to

[15]
$$E = E_o{}' - \frac{.0591}{n} \log \frac{1}{[H^+]^{n'}}$$

where $E_o{}' = E_o - \frac{.0591}{n} \log \frac{[\text{product}][H_2O]^P}{[V_2O_5][H_2O]^m}$ and is a con-

stant. Equation [15] can then be rewritten as

[16]
$$E = E_o{}' - .0591 \frac{n'}{n} pH$$

Thus the slope of the electrode potential versus pH is simply $-.0591$ n'/n.

The assumption involving the activities of the V_2O_5 and of the "product" will be valid provided both the V_2O_5 and the product are solids. The activity of a solid is independent of pH since it is in a second phase.

Experimental

The measurements of the potential of the V_2O_5 electrode as a function of pH were performed at $25^o \pm 0.2^oC$ in the constant temperature bath previously described. The electrolyte was one normal ammonium chloride to which either ammonium hydroxide or hydrochloric acid was added as necessary in order to obtain the desired pH. In making the measurements on any given electrode,

the pH was varied in a random manner in order to avoid any systematic emf change due to crystal handling.

A Beckman Zeromatic pH Meter having an accuracy of 0.05 pH units and a reproducibility of 0.015 pH units was used for all pH measurements. Standard McIlvain buffer solutions (28, p. 1715) and saturated potassium hydrogen tartrate solution (pH = 3.555 at $25^{o}C$) were used to standardize the pH meter before and after each pH measurement on the electrolyte. Also, before and after each emf reading at a given pH, the pH of the electrolyte was measured. To be considered an acceptable value, the pH had to remain constant within the reproducibility of the meter.

EMF measurements, accurate to ± 1 mv, were made utilizing either a Systems Research Corporation differential voltmeter Model 5501 or a Hewlett-Packard strip chart recorder, Model 7100 BM. To be acceptable the emf reading was required to remain constant to within a millivolt for ten minutes.

Some exceptions to the requirements set forth above were made at pH values above 5.5. At these higher values the electrolyte pH failed to maintain the constancy desired. The electrolyte slowly became more acid, probably due to a slight evolution of ammonia to the atmosphere. To alleviate this problem the emf was only required to come to a constant value within a mv for 5 min.

Results

Figure 8 gives the emf dependence on pH for an undischarged vanadium pentoxide electrode (A) as well as three electrodes which had been previously discharged. The electrode represented by B was discharged at 100 μamps per electrode for a total of ten minutes and then allowed to recover for several days before the emf versus pH measurements were performed. Electrodes C and D were both discharged at 500 μamps per electrode for a total of ten minutes. Two days were allowed for these two samples to recover before the measurements were taken.

A least-squares analysis was made to determine the best slope for each electrode. For electrode A, the undischarged electrode, the slope was -0.064 ± 0.012 volts per pH unit. For the discharged samples the slopes were: $B = -0.054 \pm 0.004$ volts per pH unit; $C = -0.058 \pm 0.003$ volts per pH unit; $D = -0.060 \pm 0.002$ volts per pH unit. The average of these four slopes is -0.059 ± 0.005 volts per pH unit.

Discussion

The above data on single crystals confirms the previous work of Watson and Scott (58) on polycrystalline vanadium pentoxide electrodes and also that reported by Shukler and Kuz'min (53) on pressed
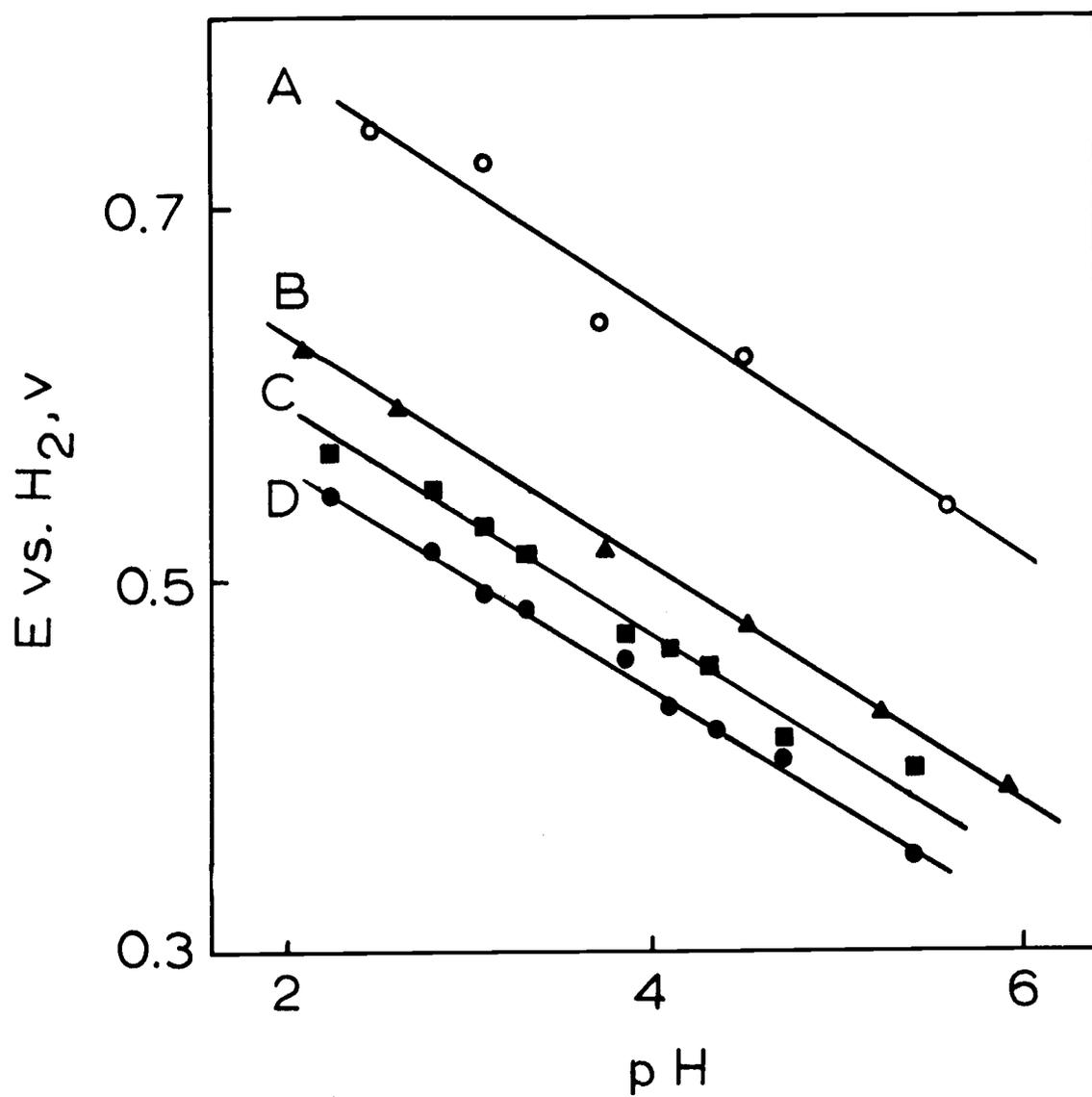
Figure 8. Dependence of electrode EMF vs. standard H_2 electrode on pH at 25°C. Curve A is for unreduced V_2O_5; B, C, and D are for partially reduced V_2O_5.

pellet electrodes made of 80% vanadium pentoxide and 20% graphite.

Provided the assumption involving the constancy of the activities of

the product and vanadium pentoxide while only the pH is varied is

valid, then the fact that a plot of electrode potential versus pH yields

a slope very nearly equal to -0.0591 volts per pH unit indicates that

in equation [16] $n = n'$. This would mean that in the discharge re-

action, equation [13], the number of electrons involved is equal to

the number of protons involved.

The fact that steady potentials were unattainable outside of this

pH range is probably due to several factors including: at pH $<$ 2 the

"product" begins to dissolve to a significant extent; at pH $>$ 5.5 the

"product", as will be described later, is air oxidized.

The conclusion that the number of electrons and protons is

identical in the discharge reaction means that, in order to maintain

electroneutrality within the system, either the V(V) reactant and the

discharge product are both solids or else they are both incorporated

in aqueous ions having identical charges. Of the known reactions in

solution (see p. 8) only the one below has an electron-to-proton ratio

of unity.

[17] $H_3V_2O_7^- + 2H^+ + 2e^- = HV_2O_5^-$ $2H_2O$
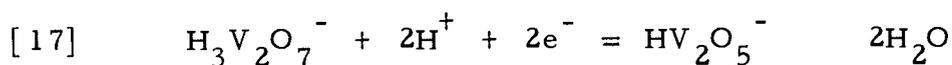
This reaction cannot, however, be of major importance since the

$HV_2O_5^-$ only exists in solutions of pH greater than 5.3. Also, no vanadium pentoxide was initially dissolved in the electrolyte and since the amount which dissolved during this experiment (also, during the discharge experiments described in Section VI) was insufficient to detect visually, the results of these experiments indicate that both the reactant and product must be solids.

The known reactions involving vanadium pentoxide as a reactant and vanadium oxides or oxy-hydroxides having an oxidation state between three and five as a product are given below. They all have an electron-to-proton ratio of unity and would each, therefore, fit the experimental results described above.

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

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

[20] $\quad V_2O_5 + 2H^+ + 2e^- + H_2O = 2VO(OH)_2$

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

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

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

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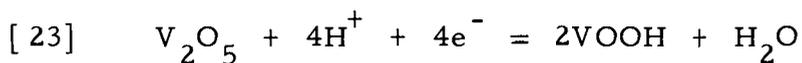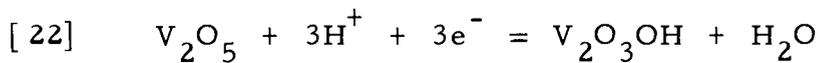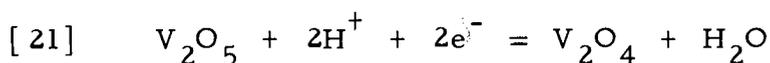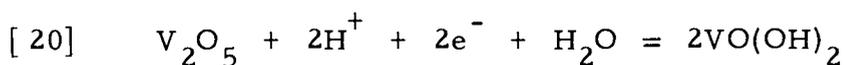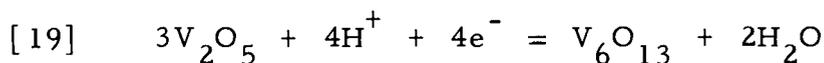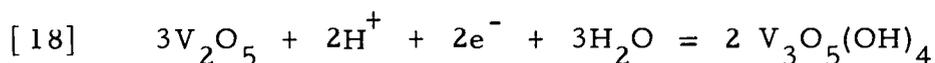
Conclusions

It is proposed that within a pH range of 2 to 5.5 the discharge of a vanadium pentoxide electrode consists of the reduction of solid vanadium pentoxide to a solid oxide or oxy-hydroxide having an oxidation state of less than five. The reduced product must also be in a solid solution in the V_2O_5 since the electrode potential changes with the amount of charge which has passed during the discharge. As shown by the experiments described in this section, this reduction involves the same number of hydrogen ions as it does electrons. Since both reactant and product exist in a solid solution, the discharge and recovery mechanism should and will be in the following sections treated as a solid state diffusion problem.

V. DISCHARGE EXPERIMENTS USING
TRITIATED ELECTROLYTE

Introduction

If, as has been proposed, protons diffuse into the interior of a
vanadium pentoxide electrode during discharge and recovery, then
its presence should be detectable by either x-ray studies or by the
use of deuterium or tritium tracers. Bell and Huber (9) showed
by means of x-ray powder photographs that when a manganese dio-
xide electrode is discharged the lattice undergoes a dilation. They
attributed this to the penetration of cations into the lattice. In
another study on the manganese dioxide electrode, Kozawa and
Powers (36) compared discharge curves made at the same current
in KOH and KOD electrolytes. They found that in the deuterated
electrolyte the polarization was 1.35 - 1.55 times greater than in
the non-deuterated electrolyte. This range brackets the 1.41 value
derived for the case where the simple inward diffusion of protons or
deuterons controls the degree of polarization.

Feitknecht, Wyttenbach and Buser (24) in following up previous
work in which Feitknecht had reported that the first step of the oxi-
dation of the hydroxides $Mn(OH)_2$, $Fe(OH)_2$ and $Ni(OH)_2$ leads to
compounds $MeO_x(OH)_{2-x}$ with the $Me(OH)_2$ structure, used a
tritium tracer to show that the mechanism for the oxidation of at

least the nickel (II) hydroxide and iron (II) hydroxide electrodes in-
volved the diffusion of hydrogen ions through the crystal to the sur-
face of the electrode.

In the case of the vanadium pentoxide electrode x-ray powder
photographs failed to show any new lines after the crystal was dis-
charged. This was attributed to the low concentration of the reduced
product in the lattice. Therefore, in an attempt to prove the presence
of hydrogen ions in the interior of the electrode after discharge,
experiments involving a tritiated electrolyte were conducted.

Experimental

Preliminary experiments with vanadium pentoxide showed that,
similar to the nickel (II) hydroxide and iron (II) hydroxide cases (24),
a considerable amount of tritium was adsorbed on the surface of the
electrodes when they were immersed in the electrolyte. In order to
standardize this adsorption and thus obtain a valid blank for the en-
suing discharge experiment the following procedure was adopted.
Each electrode was allowed to stand for a minimum of one hour in
1 N NH_4Cl solution which contained 25 $\mu c/ml$ of tritium.
The electrode was then rinsed for one minute with manual agitation
successively in each of three 10 ml distilled water baths. These
three rinses were followed by one three hour rinse in a fourth 10 ml
distilled water bath. One milliliter samples of each of these four

rinses were then counted in a manner to be explained below. The fourth rinse served as the pre-discharge blank for the given electrode.

It was found that in the above procedure the first three rinses succeeded in removing almost all of the tritium adsorbed on the electrode surface. The fourth rinse removed any tritium which may have been absorbed by the electrode or which had been entrapped in cracks or defects on the surface or which might have gotten between the back of the electrode and its protective paraffin coating.

Following the predischarge blank the electrode was returned to the tritiated electrolyte and discharged at a measured current for three hours. The potential of the vanadium pentoxide electrode versus saturated calomel electrode was followed potentiometrically in order to insure that reduction to V_2O_4 or $VO(OH)_2$ (see Figure 10) did not occur. At the completion of the three hour discharge the electrode, while remaining in the tritiated electrolyte, was allowed to recover for a minimum of 1.5 hours.

After the electrode had recovered it was rinsed for one minute in each of three 10 ml distilled water baths as was done for the blank. In a fourth 10 ml distilled water bath the electrode was made the anode and oxidized at a current equal to or slightly less than the discharge current. This charging procedure was undertaken in order

to reverse the discharge reaction and thereby aid in the release of $^3H^+$ incorporated in the electrode. One milliliter samples of each of these four rinses were then counted.

After the discharge and charging operations, a post-discharge blank was made. The procedure for this was identical to that of the predischarge blank.

From each of the 10 ml water baths 1 ml was pipetted into 10 ml of Bray's (12) solution. Bray's solution is a liquid scintillator used for counting aqueous radioactive samples.

If the sample to be counted was color quenched due to the presence of vanadium pentoxide dissolved in the solution, as was frequently the case after charging the electrode, then two samples were made. One of these was internally spiked with fifty lambda of tritiated toulene which was known to give 116,000 counts per minute (CPM). By using this spike the counting efficiency and, therefore, the degree of quenching could be determined. All samples were counted on a Packard Tri-Carb Liquid Scintillation Counting System, Model 314EX, at least three times with each counting lasting a minimum of five minutes.

Blanks, consisting of 1.0 ml of distilled water and 10 ml of Bray's solution, and tritium standards consisting of 0.10 ml of tritiated electrolyte, 0.90 ml distilled water and 10 ml of Bray's solution were also counted.

The activity of the electrolyte during these experiments was such that 28.0 CPM corresponds to one micro equivalent of hydrogen.

Results

The results of the experiments conducted with tritiated electrolyte are reported as counts per minute for the activity counted in the 1 ml sample which was taken from the 10 ml baths. All data were corrected for the background count and for color quenching.

Typical counts per minute for all of the rinses on a given electrode are given in Table I.

Table I. Counts per Minute for a Typical V_2O_5 Discharge Experiment Using Tritiated Electrolyte.

Rinse	Predischarge blank (CPM)	Discharge-charge (CPM)	Postdischarge blank (CPM)
1	1154	156	3220
2	444	93	67
3	18	47	42
4	126	1397	493

The activity or counts per minute recorded for the first rinse should be totally disregarded since the electrode was taken directly from the tritiated electrolyte to the rinsing bath and any amount of

electrolyte could be physically transferred in this process. The low number of counts for the third rinse shows that most of the adsorbed tritium was removed from the crystal. The higher activity obtained from the fourth (that is, the three hour) rinse indicates that some tritium was absorbed or trapped in cracks or defects on the electrode surface or possibly between the electrode and the protective paraffin on the back side of the electrode as was previously suggested. In each of these instances all of the adsorbed tritium was evidently not removed by the end of the third rinse.

As is seen in Table II which gives the counts per minute obtained during the three-hour rinse for the pre- and post-discharge blanks as well as the sample obtained during the three-hour charging period, there was significantly more tritium incorporated when current was passed than when current was not passed.

The number of Faradays passed can be related to the number of CPM which would be obtained in the charging sample if the reaction had been 100% efficient and if all of the tritium had been recovered. This theoretical yield (CPM) when divided into the difference between the actual counts obtained during the charging period and the counts of the blank gives a percentage yield value for the experiment. These values, after being multiplied by $\sqrt{3}$ to take into account the diffusion rate ratio for the difference in isotopic

Table II. Comparison of Three-Hour Rinses Corrected for Background and Color Quenching.

Sample	Pre-discharge Blank	Discharge-charge	Post-discharge Blank	% yield using	
				Pre-discharge Blank	Post-discharge Blank
1	216	526	97	40	54
2	101	750	268	81	61
3	64	715	258	64	45
4	70	374	487	29	-
5	48	720	98	95	88
6	26	1397	493	100	66
7	26	242	210	36	5
8	26	708	429	90	36
9	32	640	255	95	61

mass between tritium and hydrogen[2], are given in the fifth and sixth
columns of Table II. It should be noted that when samples 4 and 7
were discharged, a gas (probably hydrogen) was visibly evolved at
the cathode. This side reaction, which was probably always in-
volved to a small extent, could explain why the low yields were ob-
tained for these samples.

During the charging process, in which the vanadium pentoxide
electrode was the anode, a colorless gas was evolved in nearly
every case. The electrolyte at the conclusion of the charging period
was colored a light yellow indicating the presence of dissolved
vanadium pentoxide. The electrode was also visibly roughened as
compared to the electrode at the end of the discharge period. While
these phenomena do not affect the amount of tritium in the fourth
rinse at the end of the charging period, the roughening of the elec-
trode helps to explain why the post-discharge blanks were generally
much higher then the pre-discharge blanks. Thus, since at the end
of the discharge period, during which the tritium was both adsorbed
and electrochemically incorporated into the electrode, the electrode
had not been visibly roughened, the predischarge blank should be
considered as a more accurate measure of the amount of tritium

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[2]The use of isotopic mass ratios is well known in diffusion work.
This ratio, also, has been previously used in similar electrochemi-
cal discharge experiments on MnO_2 performed by Kozawa and
Powers (36).

adsorbed during the discharge process than the postdischarge blank.

A brief study was made to insure that tritium was not being carried over from the predischarge blank and subsequently counted in the discharge-charge cycle. An electrode with an unusually high blank (699 CPM) was discharged and recharged in 10 ml of non-tritiated distilled water. During this process the sample was immersed in the distilled water for a total of six hours. The water gave only 39 CPM indicating that very little tritium was carried over from the predischarge blank.

It might also be expected that there would be some cumulative effect between the discharge-charge cycle and the post-discharge blank since all the incorporated tritium may not have been removed. To check this possibility a crystal was rinsed in distilled water for one and a half hours after the discharge-charge cycle and before the post-discharge blank. This sample yielded a counting rate 10% as high as the charge sample. This experiment showed that not all of the tritium was necessarily removed from the electrode during the charging process. This cumulative effect would also serve to explain the high postdischarge blank. It would have helped if this type of wash could have been employed on all samples, however, dissolution of the electrode was too extensive.

Conclusion

The use of tritium as a tracer proves that hydrogen ions are incorporated into the vanadium pentoxide electrode when as a cathode it is reduced in 1 N NH_4Cl. This tritium can be recovered from the electrode by a combination of hydrogen-ion exchange with the electrolyte and of making the vanadium pentoxide electrode the anode in an electrolytic cell and reoxidizing the discharged electrode.

VI. DISCHARGE AND RECOVERY AT THE
VANADIUM PENTOXIDE ELECTRODE

Introduction

When current exists between an otherwise reversible electrode and a solution, the electrode potential departs from its reversible value. The difference between the potential during current flow and the reversible potential is called polarization or overpotential.

There are several distinguishable types of polarization which may be encountered in discharging an electrode. Ohmic or resistance polarization is caused by the resistance to current flow in an electrode or on its surface. Pseudo-ohmic polarization is caused by the resistance to current flow within the electrolyte between the electrode and the Luggin capillary tip. It arises when a high current density and electrolyte of low conductivity are involved.

Another type of polarization, known as concentration polarization, is caused by a difference in the concentration of ions at the electrode-electrolyte interface and the bulk electrolyte. This difference is due to electrolysis and can be greatly diminished by a variety of methods which increase the rate of diffusion and convection of the ions from the interface. These methods include mechanically stirring the electrolyte, rotating the electrode, increasing the bulk concentration of the electrolyte and raising the electrolyte

temperature.

Another type of concentration polarization is involved when the composition of the electrode itself varies with time. This can occur when an electrode incorporates or releases a component of a solid solution. It is this type of so-called solid-concentration polarization which is of primary interest in this study. Hereafter when the term "polarization" is used without qualification in this paper, it refers to solid-concentration polarization.

A third type of polarization known as activation polarization is connected with the energy of activation for the rate controlling step in the electrode reaction.

The total polarization of an electrode is the sum of the ohmic, concentration, and activation polarizations. Experimentally these can be distinguished by examining their rates of decay with time after the polarizing current ceases. Ohmic polarization decays instantaneously while concentration polarization decays slowly obeying no simple time relationship and activation polarization decays exponentially with respect to time (34, pp. 394-399; 50, p. 124, 141-148).

Figure 9 shows a typical discharge and recovery curve for V_2O_5. The initial instantaneous (less than 0.2 sec) fall in potential at the start of the discharge and instantaneous rise at that end of the discharge is due to the ohmic and activation polarizations. (The
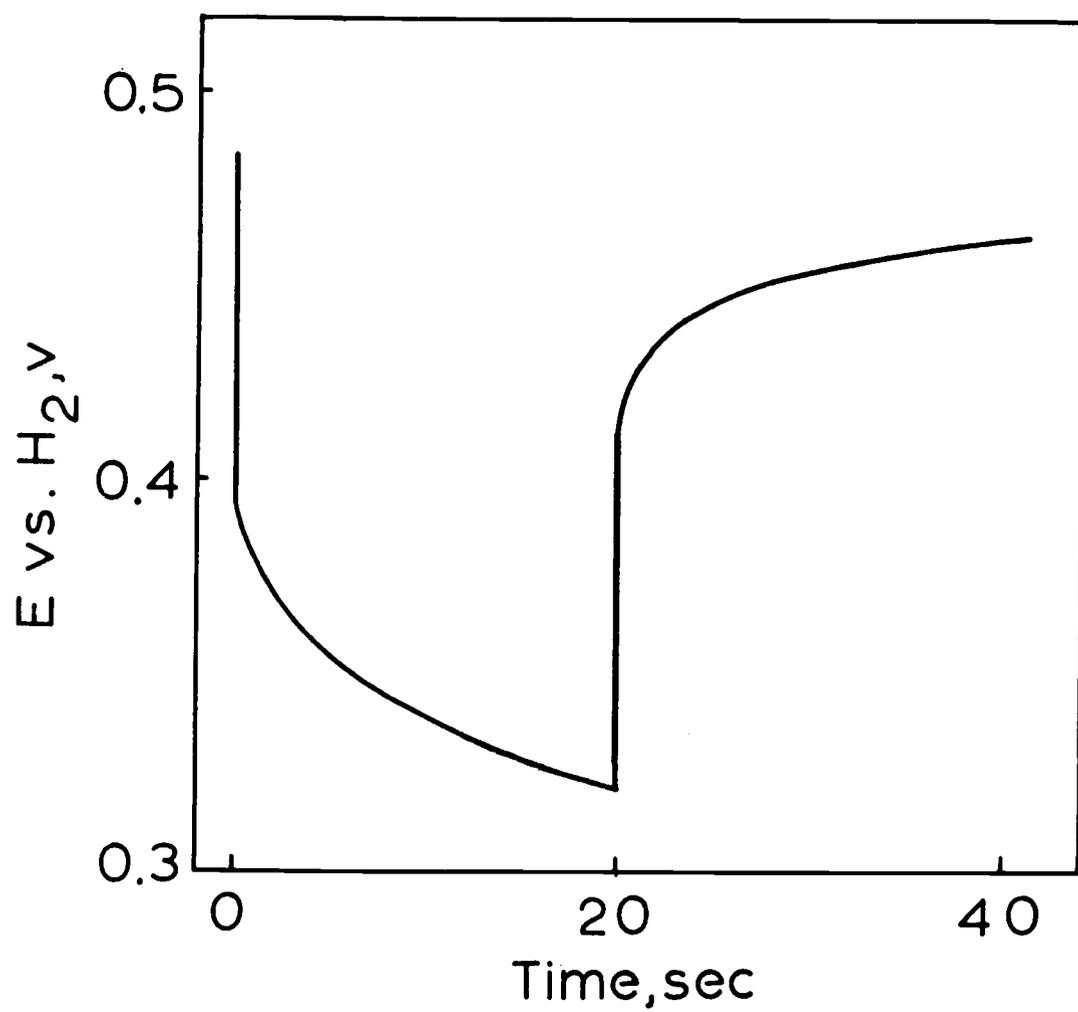
Figure 9. Discharge and recovery of V_2O_5 electrode at pH 4. 7
and current density 48 μa/cm^2.

activation polarization forms and decays with a time constant of

10^{-2} sec or less (50). This time is much smaller than the 0.2 sec

recorder response time.) The ohmic polarization results primarily

from the passage of current through the semiconducting vanadium

pentoxide electrode. The pseudo-ohmic polarization was eliminated

as far as possible by placing the Luggin capillary tip close to the

V_2O_5 electrode and by using an electrolyte of high conductivity.

This initial instantaneous polarization or IR drop was pro-

portional to the current, and for short discharges, where the overall

composition of the electrode was changed only to a slight degree,

it was the same at the start and end of the discharge. However, for

long discharges where the electrode composition does significantly

change, the IR drop at the end of the discharge was less than the

initial value, which indicates an increase in the electronic conducti-

vity of the electrode.

The difference between the total polarization and the initial

instantaneous polarization was taken to be the value of the solid-

concentration polarization. Support for the polarization being due

to the solid-concentration type is given by the following experimen-

tal observations which have been reported earlier in this paper: 1.

the cell potential dependence on pH showed that the discharge pro-

duct was a solid; 2. the experiments with a tritium tracer showed

the presence of hydrogen in the electrode after discharge. This

would not be possible without the product having first formed on the electrode surface; 3. the fact that the slope of the discharge curve in Figure 9 is non-zero implies that no phase change is taking place on the electrode surface and, therefore, that a solid solution is being formed there.

This initial IR drop, while always present in the primary data, is subtracted out of all of the polarization curves and calculations presented in the remainder of this paper. The initial IR drop in no way affects the shape of the solid-concentration polarization curve and it does not enter into the calculations.

Proposed Mechanism for the Discharge and Recovery of the V_2O_5 Electrode

It is proposed that the mechanism for the discharge and recovery of the V_2O_5 cathode at low current densities in 1 N NH_4Cl is the same as the Coleman diffusion mechanism for MnO_2 which was previously described. If this theory is correct, then the diffusion equation derived by Scott (52) and modified by Kornfeil (33) for the manganese dioxide electrode should be applicable in this instance. The development of the Scott-Kornfeil equation is given below. The electrode reaction may be written

[25] $$V_2O_5 + ne^- + n'H^+ = \text{(product)}.$$
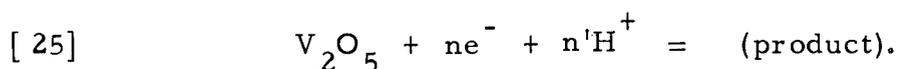
Scott (52) used the solution to the problem for the conduction

of heat into a semi-infinite solid of constant thermal conductivity,

heated by a constant flux of heat to the surface for a specified length

of time and then allowed to cool, as the solution to the diffusion

problem. The solution of this heat conduction problem is available

in the literature (16).

The vanadium pentoxide electrode, which is discharged at a

constant current density, is considered to consist of a semi-infinite

solid bounded by the plane x = 0 such that the region x < 0 is occu-

pied by the electrolyte. Also, at t = 0 there is no current flowing

and the concentration of the product is zero both on the surface and

in the interior of the electrode. Then, assuming the diffusion co-

efficient is a constant, the concentration of the reduced species is

$$[26] \quad C_{(x,t)} = \frac{2\phi}{\sqrt{D}} \left[\sqrt{t} \ \text{ierfc} \ \frac{x}{2\sqrt{Dt}} - \sqrt{t-\tau} \ \text{ierfc} \ \frac{x}{2\sqrt{D(t-\tau)}} \right]$$

where ϕ is the number of equivalents of product formed at the sur-

face per unit area per unit time, and D is the diffusion coefficient

for the removal of product by diffusion inward from the electrode

surface, t is the time following the start of the discharge, τ

represents the time at which the discharge ceases and recovery

begins, and ierfc(y) is defined by

$$\text{ierfc}(y) = \pi^{-1/2}[\exp(-y^2) - 2y\int_y^\infty \exp(-z^2)dz].$$

At the surface of the electrode, equation [26] reduces to

$$[27] \qquad C_{(o,t)} = \frac{2\phi}{\sqrt{\pi D}} [\sqrt{t} - \sqrt{t-\tau}]$$

If the activity of the V_2O_5 and the reduced product is expressed on the mole fraction scale, i.e. $a_{V_2O_5} = \gamma \times_{V_2O_5}$, with $\gamma = 1.00$, then $a = \times$ and $\times_{V_2O_5} + \times_{prod} = 1.00$ by definition. Thus by substituting $C_{(o,t)}$ and $1 - C_{(o,t)}$ for the activities of the product and V_2O_5 respectively into equation [14] and simplifying, the potential-time relationship for the discharge and recovery process becomes

$$[28] \qquad E = E_o'' + \frac{RT}{nF} \ln\left[\frac{A}{\sqrt{t} - \sqrt{t-\tau}} - 1\right]$$

which is known as the Scott-Kornfeil equation.

In equation [28] E_o'' which includes E_o along with other constants varies with pH, has little significance other than to establish the initial ordinate of the polarization curve. A is defined by

$$[29] \qquad A = \frac{\sqrt{\pi D}}{2\phi} .$$

Since $\sqrt{t-\tau}$ is taken as zero for $t < \tau$, equation [28] becomes, for

the discharge period,

$$[30] \qquad E = E_o{}'' + \frac{RT}{nF}\left[\ln \frac{A}{\sqrt{t}} - 1\right]$$

The remainder of this section involves application and limits

of the above theory to polarization of the V_2O_5 electrode.

Results

Discharge and Recovery at 25°C in 1 N NH_4Cl

The polarization curve for a 20 sec discharge at 48 $\mu a/cm^2$

in 1 N NH_4Cl at 25°C, followed by recovery, is illustrated in Figure

9. This figure is typical of 50 polarization curves involving 12

individual electrodes which were made at currents up to 500 μa for

short discharges, i.e. usually less than 1 minute.

Figure 10 shows that at pH 4.7 and 25°C and a current density

of 1 ma/cm^2, if the discharge is allowed to continue for a long time,

the discharge curve bends downward after about 5 sec. Still later

the electrode potential becomes relatively constant, and finally falls

again after two hours.

The effect of varying the current was studied as shown in Fig-

ure 11. In this experiment the same electrode and, therefore, the

same electrode area, was discharged at a series of different cur-

rents.
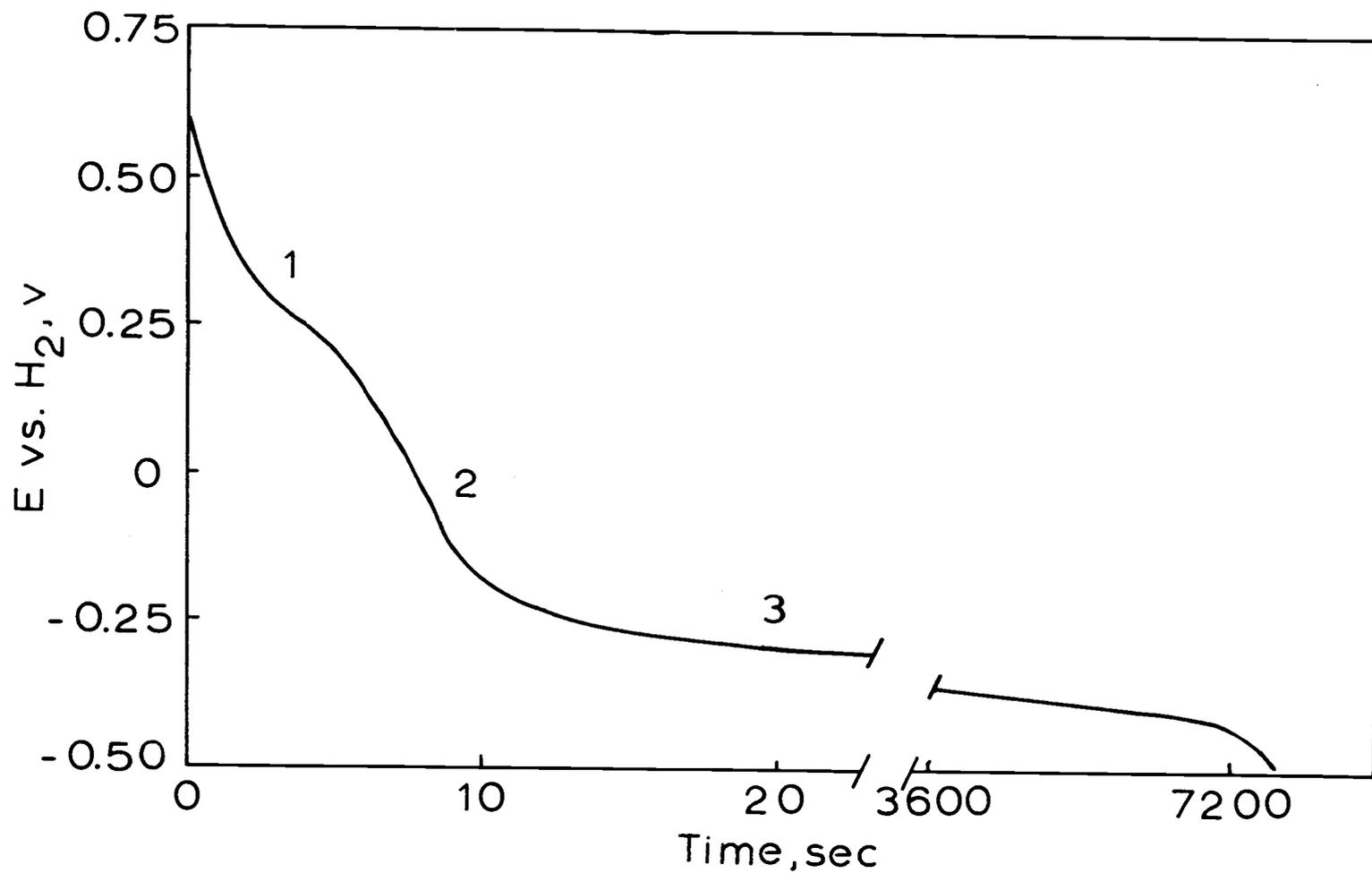
Figure 10. Long discharge of vanadium pentoxide at 1 ma/cm^2. 1, addition of first electron; 2, addition of second electron; 3, phase change to $VO(OH)_2$ or V_2O_4.
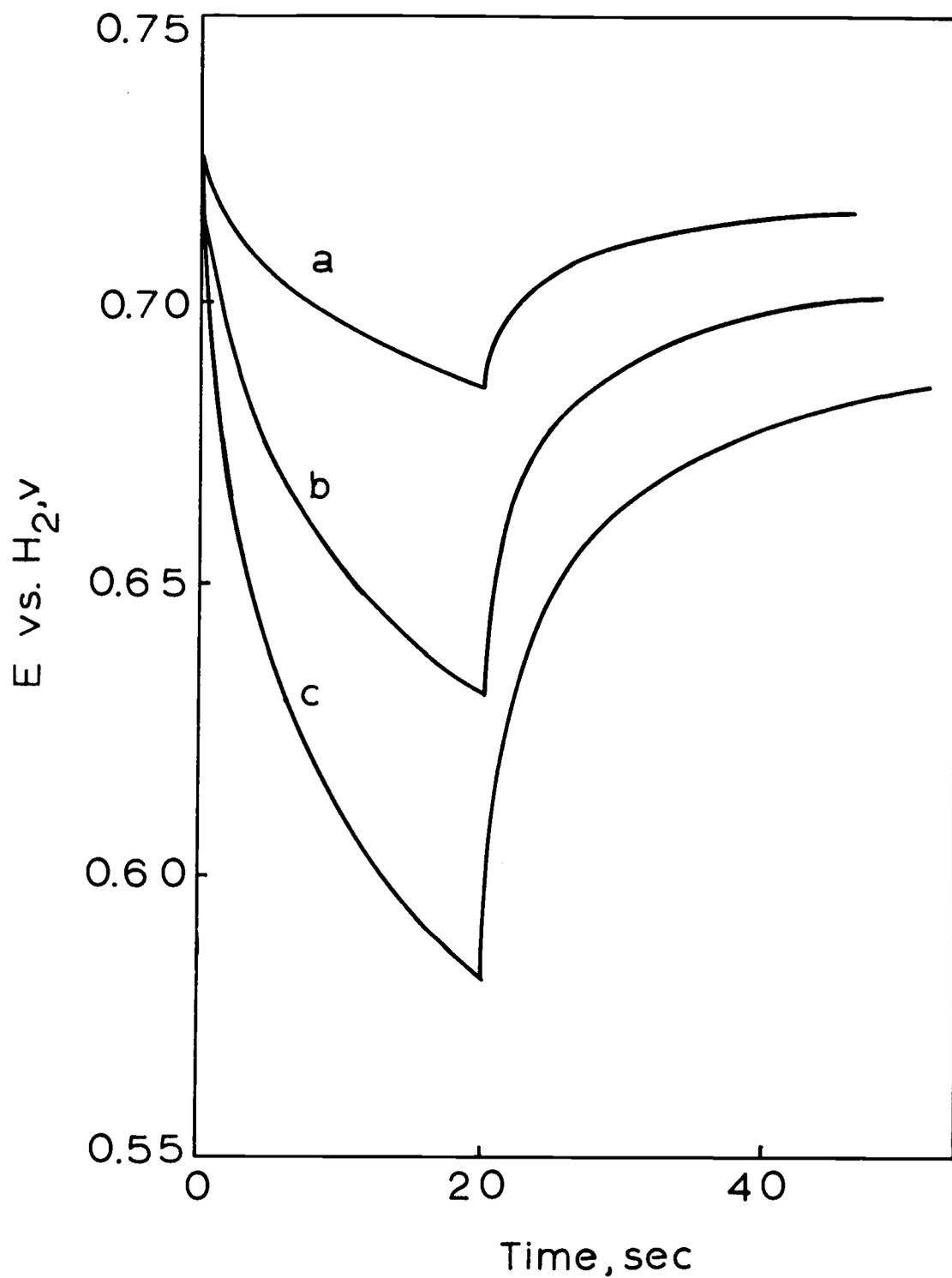
Figure 11. Discharge and recovery of a V_2O_5 electrode at pH 3.1.
Current, μa: a, 36; b, 80; c, 123.

Effect of Stirring the Electrolyte

In order to determine the effect of stirring the electrolyte on
potential-time curves, experiments were conducted at several pH
values with and without the electrolyte being stirred. Stirring was
found to have no effect at pH between 0.7 and 5.0; however, there
was an effect at pH = 7.0. As illustrated in Figure 12, at pH =
7.0 and a current of 61 μa there was less polarization when the
electrolyte was stirred. This is due to a more rapid removal of
the product from the surface when the electrolyte is stirred. It
should be noted that V^{+4} readily air-oxidizes in basic solutions.
Also, the electrolyte was colored by dissolved vanadium pentoxide
at the conclusion of the experiments at this pH.

Effect of Oxygen Dissolved in the Electrolyte

A possible means of removing the discharge product from the
electrode surface is by oxidation of the product to V_2O_5 by oxygen
dissolved in the electrolyte. In order to determine if oxidation did
indeed occur, a series of electrode polarization curves were made
at various electrolyte pH values in solutions in which the concentra-
tion of oxygen dissolved in the electrolyte was varied. The dissolved
oxygen concentration was controlled by bubbling either N_2 or O_2
into the electrolyte for a minimum of 1/2 hour before the discharge
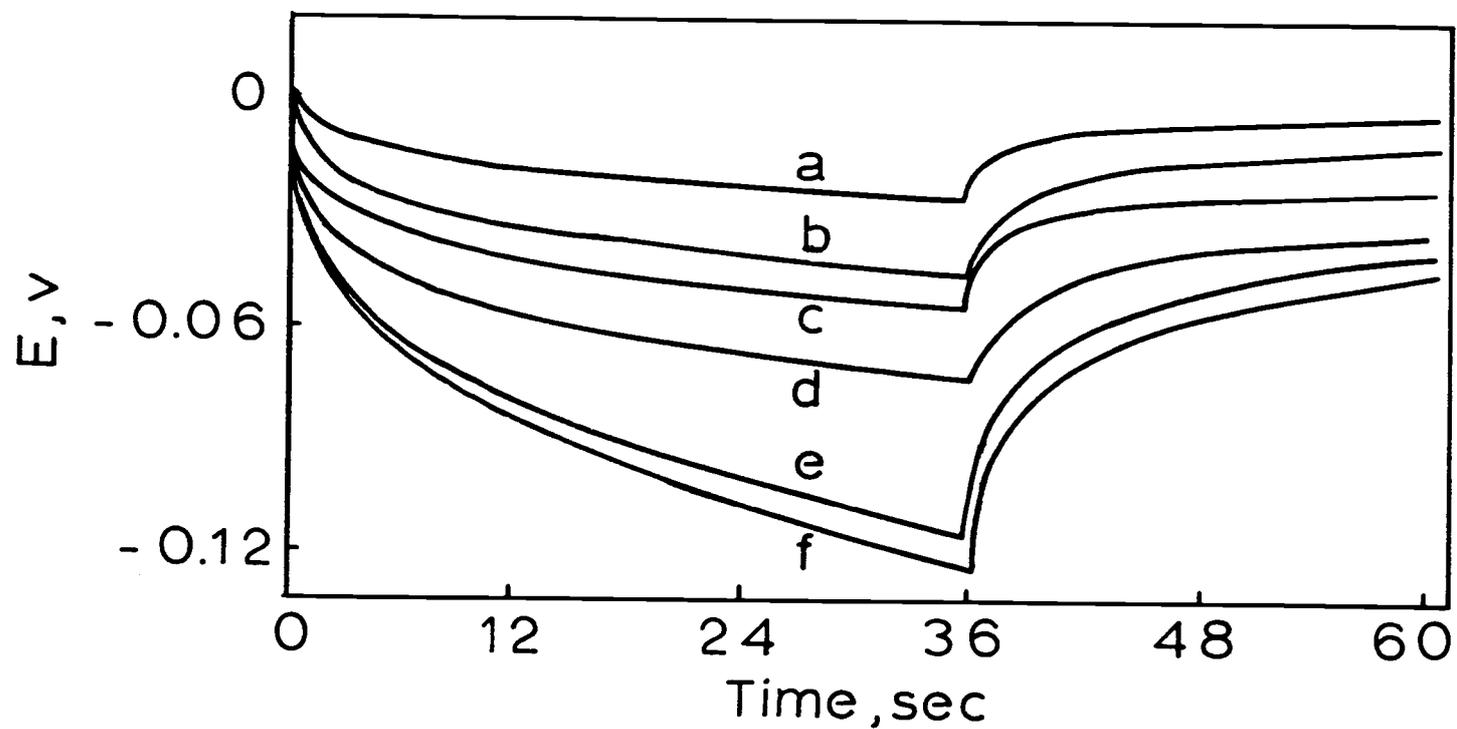
Figure 12. Effect of pH and stirring on the polarization of a V_2O_5 electrode at 61 μa. (The initial potential has been arbitrarily set at zero.) pH: a 0.7; b, 1.7; c, 3.0; d, 4.5; e, 7.0 stirred; f, 7.0 not stirred. Curves a-d represent both stirred and unstirred discharges.

experiment began.

It was found that at pH less than six, the variations of concentration of dissolved oxygen had no detectable effect on the polarization curves. However, at pH 8.3 recovery was more rapid and occurred to a greater extent when oxygen was passed into the electrolyte, as shown in Figure 13. This indicated that the reduced product was being oxidized back to the plus five state and, thereby, reducing its concentration on the surface more rapidly than when dissolved oxygen was not present. That this oxidation seems to occur is in accordance with the known fact that V(IV) is air oxidized to V(V) in basic solutions.

Effect of the Method by which the Contact to the Electrode is Made

Polarization experiments were conducted in which contact to the vanadium pentoxide electrode was accomplished by two different methods as described in the section dealing with electrode preparation. There was no difference detected in the discharge and recovery curves between the two types of contacts.

Effect of Electrolyte Temperature

Most experiments in this study were conducted at $25^{\circ}C$. However, the shape of the polarization curves is altered, as would be
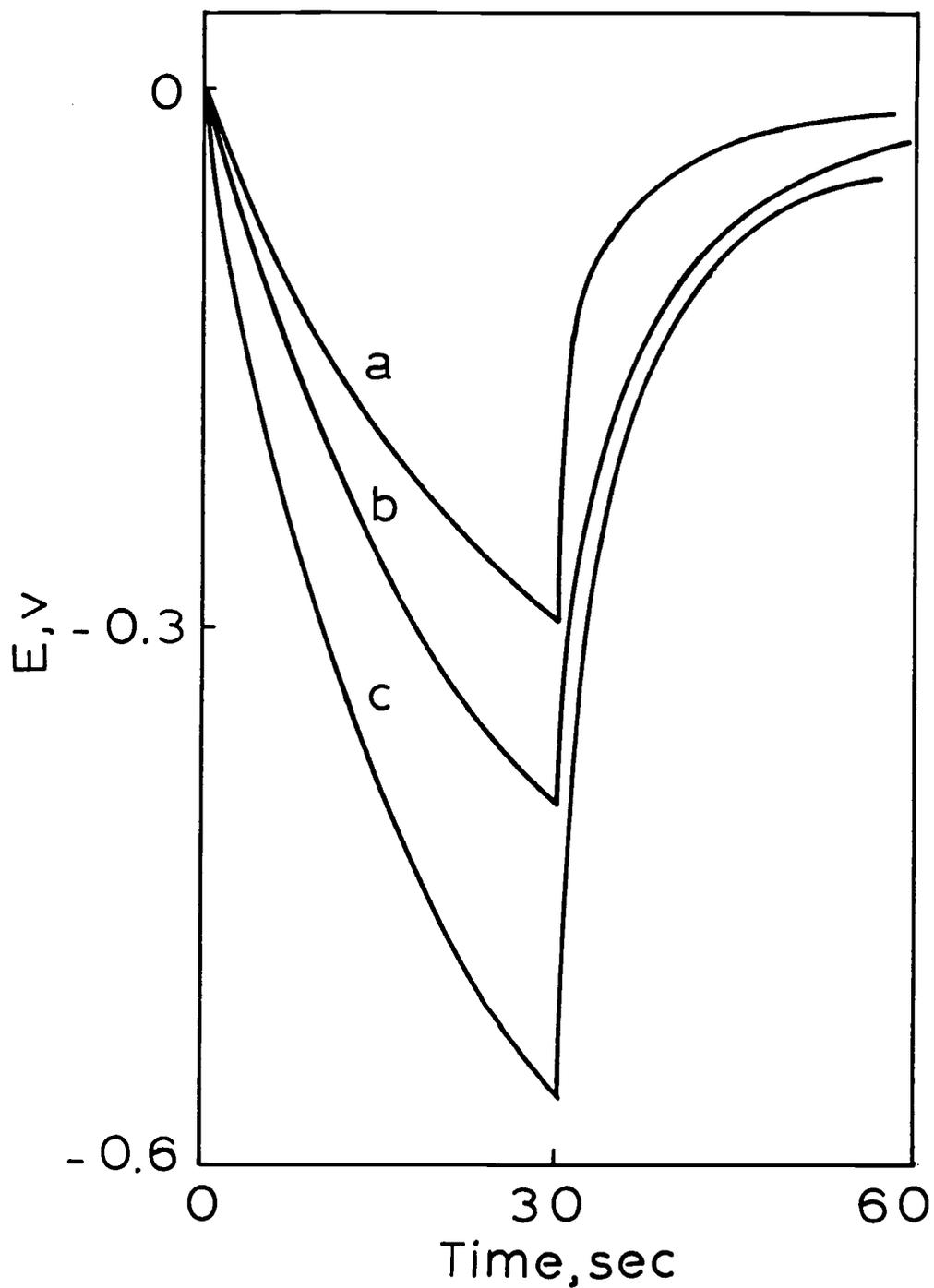
Figure 13. Effect of dissolved oxygen on the V_2O_5 electrode at
pH 8. 3 and current density 0. 15 ma/cm^2. Curve a is
saturated with O_2; b contains dissolved air; c is
purged with N_2.

predicted by equation [30], by a change in the electrolyte temperature. The effect of temperature is illustrated in Figure 16 and will be more fully discussed in a following section (see p. 75).

Discussion

Adherence to Scott-Kornfeil Equation

Kornfeil (33) differentiated both sides of equation [30] with respect to time, and found A from the slope of the discharge curve at two values of time. E_o'' and n could then be calculated from equation [30]. While this method of calculating the various parameters is sound theoretically, it was found to be impractical experimentally since the slope of the potential-time curve could not be determined with sufficient accuracy.

A successive-approximation computer program was attempted in order to determine the parameters in equations [28] and [30] but it failed since relatively accurate initial values were not available.

With the failure of the above methods for determining the parameters in equation [30], it became necessary to assign a value to n. Shukler and Kuz'min (53) have shown that the third section of Figure 10 corresponds to the formation of either $VO(OH)_2$ or V_2O_4 by the reaction

[31] $V_2O_5 + 2e^- + 2H^+ + H_2O = 2VO(OH)_2$

or

[32] $V_2O_5 + 2e^- + 2H^+ = V_2O_4 + H_2O$
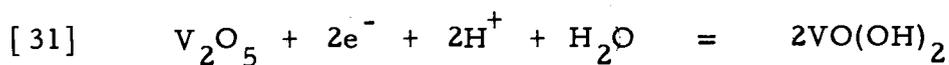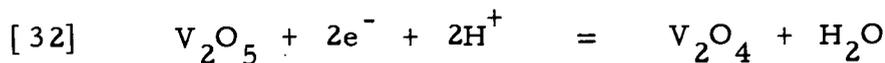
While these authors used too high a current density in their work to observe the first section of Figure 10 and, therefore, said that it did not exist, it is reasonable to assume that in the two electron change between time zero and the 3rd section in Figure 10 that section 1 corresponds to a one electron process and section 2 corresponds to a second one electron process. Therefore, since the experiments dealt with here involve only the first portion of Figure 10, the value $n = 1$ was assigned to n in equations [28] and [30].

Support for the choice of $n = 1$ is also given by the manganese dioxide electrode. The discharge curve for this electrode is similar to Figure 10. However, since the discharge products are known to be MnOOH for section one and $Mn(OH)_2$ for section three, it becomes obvious that the first section corresponds to a one electron process.

With $n = 1$, equation [30] can be solved for A, provided the potential at two separate times are known, giving

[33] $$A = \frac{\sqrt{t_1 t_2}\left[\exp \frac{F}{RT}(E_1 - E_2) - 1\right]}{\sqrt{t_1}\ \exp F/RT\ (E_1 - E_2) - \sqrt{t_2}}$$

where E_1 and E_2 are the potentials at times t_1 and t_2 respective-
ly, E_o'' can then be found by substituting A, E_1, and t_1 into
equation [30].

Using the above method, values of $A = 8.2 \sec^{1/2}$ and
$E_o'' = 0.431$ volt were obtained for the polarization curve illustrated
in Figure 9. Table III gives both the experimental and the calcu-
lated emf at various times for discharge and recovery given in
Figure 9. The agreement is good, thereby showing that the diffu-
sion of the reduced product from the surface quantitatively explains
the polarization observed in Figure 9.

Table III is typical of the results and agreement obtained from
the application of equation [30] to the over 50 discharge and recovery
curves obtained at low currents using 12 different electrodes. The
maximum deviation between the calculated and experimental emf
was 0.006 volts, while the mean deviation was 0.001 v. This latter
deviation represents roughly 2% of the maximum polarization, and
is of the same magnitude as the experimental error in measuring the
emf.

Equation [29] predicts that A should vary inversely with the
flux, ϕ, thus also inversely with the current density. To confirm
this relationship A was calculated, by the method previously de-
scribed for the polarization curves shown in Figure 11, along with
curves obtained from the same electrode at other currents, and

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Table III. Discharge and Recovery of the Vanadium Pentoxide
Electrode in 1 N NH_4Cl at 25°C.

Time (sec)	Experimental EMF (volts)/H_2	Calculated EMF (volts)/H_2	Difference, $E_c - E_e$ (volts)
Discharge			
2	0.458	0.458	0.000
4	0.448	0.447	-0.001
6	0.441	0.440	-0.001
8	0.436	0.434	-0.002
12	0.427	0.426	-0.001
16	0.419	0.419	0.000
20	0.412	0.413	0.001
Recovery			
21	0.433	0.437	0.004
22	0.439	0.441	0.002
24	0.446	0.446	0.000
26	0.450	0.450	0.000
28	0.454	0.453	-0.001
32	0.458	0.456	-0.002
36	0.460	0.460	0.000
40	0.464	0.463	-0.001

plotted against the inverse of the current as shown in Figure 14.

A straight line passing through the origin was obtained, as predicted

by equation [29]. This dependence of A upon (current)$^{-1}$ was

examined in the case of ten different electrodes, and in all cases

agreement equivalent to that typified by Figure 14 was found.

A Failure of the Scott-Kornfeil Equation

As can be seen by examining equation [30] there should be an

inflection in the discharge curve when $A/\sqrt{t} = 2$, i.e., at the time when half

of the surface is reduced. This inflection and the subsequent down

curvature were illustrated by Figure 10. However, the inflection

and downcurve were never observed at the proper time.

The solid line in Figure 15 shows a typical experimental dis-

charge of 40 seconds duration at 210 $\mu a/cm^2$, pH 4.7 and the en-

suing recovery. (IR drop has been subtracted out.) The dashed line

on Figure 15 represents the curve calculated by equations [28] and

[30] where $A = 6.0$. The experimental and calculated curves are

in excellent agreement up to $t = 20$ sec. and after $t = 45$ sec.

Although the discharge curve does not follow the predicted

path after $t = 20$ sec., there is a time relationship between the dis-

charge and recovery curves which has been found to hold at all

times. As can be observed from Figure 15 the potential of the

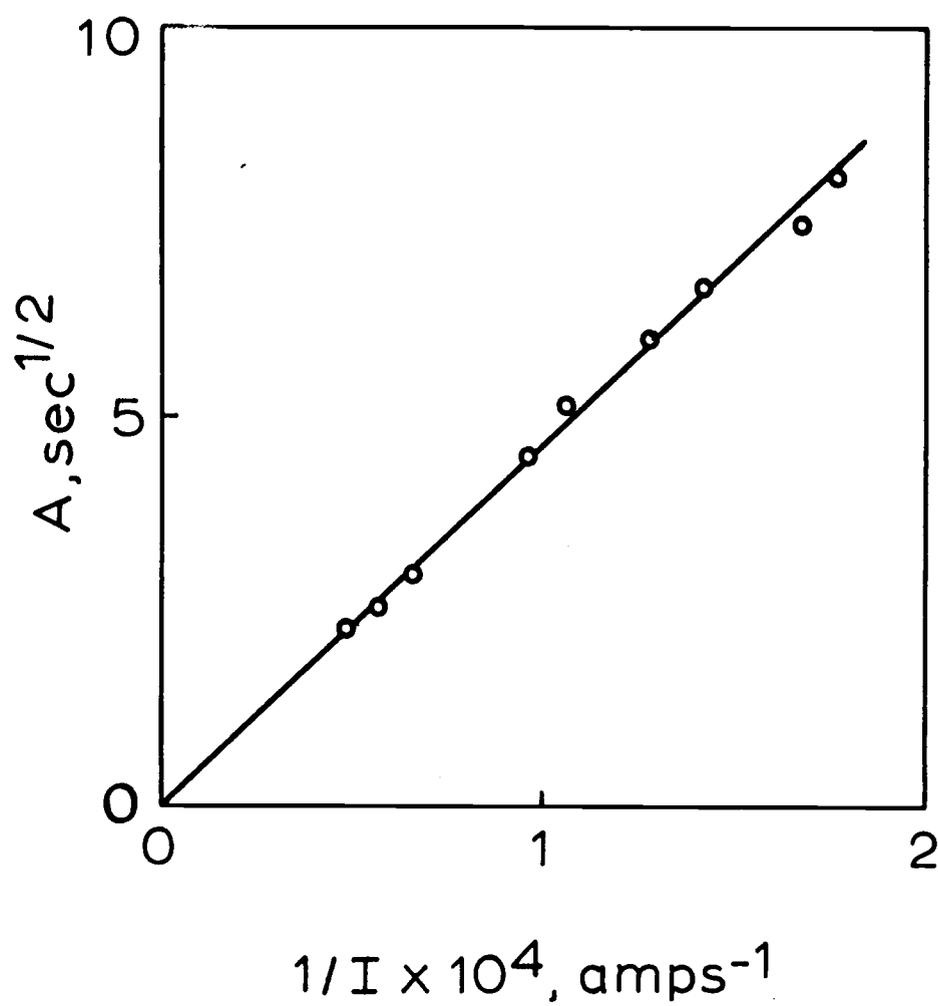vanadium pentoxide electrode is identical at two separate times, t_1

Figure 14. Dependence of A on current for discharge of the
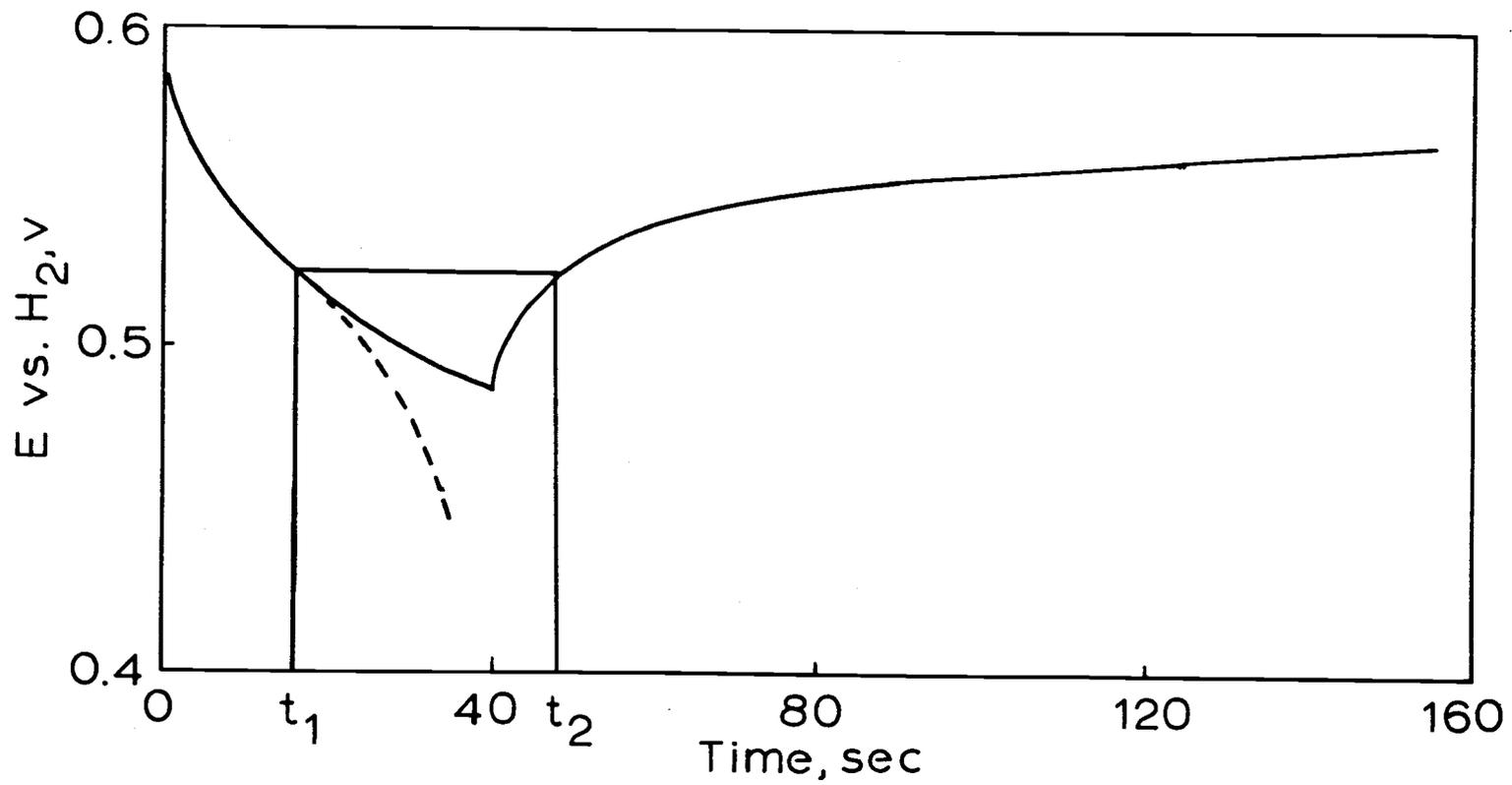vanadium pentoxide electrode.

Figure 15. Calculated versus observed polarization curve at 213 μa. ——————— observed.
----------- calculated.

during discharge and t_2 during recovery. Utilizing this observation, E at t_1 can be set equal to E at t_2 as shown below.

$$[34] \quad E_o'' + \frac{RT}{nF} \ln \left[\frac{A}{\sqrt{t_1}} - 1 \right] =$$

$$E_o'' + \frac{RT}{nF} \ln \left[\frac{A}{\sqrt{t_2} - \sqrt{t_2 - \intercal}} - 1 \right]$$

From equation [34] it may be seen that

$$[35] \qquad t_2 = \frac{(t_1 + \intercal)^2}{4t_1}$$

Thus, knowing only $\intercal$, the time at which the discharge ends, equation [35] allows one to predict the time during recovery at which the vanadium pentoxide electrode will have a potential identical to the potential at some time, t_1, during discharge. Table IV illustrates how well equation [35] applies to Figure 15 even after equation [30] has failed. Equation [35] was tested on more than twenty five polarization curves taken at current densities up to 2 ma/electrode and was always found to be applicable.

The fact that the above time relationship does hold means that, if the general form of equations [28] and [30] is to be retained, then no other term involving time can be included to explain the failure of the experimental and calculated curves to coincide after

Table IV. Comparison at 25°C and pH 4.7 of the V_2O_5 Potential at Discharge Time and Predicted Recovery Time.

Discharge Time t_1 (sec)	Predicted Recovery Time t_2 (sec)	E at t_1 E_1 (volts)	E at t_2 E_2 (volts)	Difference $E_2 - E_1$
0	∞	0.634	-	-
3	154	0.608	0.606	-0.002
4	121	0.602	0.602	0.000
6	88.2	0.694	0.694	0.000
8	72.0	0.687	0.687	0.000
12	51.3	0.675	0.678	0.002
20	45.0	0.657	0.659	0.002
22	43.7	0.653	0.654	0.001
26	41.9	0.646	0.645	-0.001
28	41.3	0.643	0.640	-0.003
30	40.8	0.639	0.636	-0.004
32	40.5	0.636	0.632	-0.004

the time at which $A/\sqrt{t} = 2$. This failure, however, is undoubtedly

due to considering the potential as a function of concentration

(activity) of the product and the vanadium pentoxide at the boundary

$x = 0$, rather than allowing the electrode's potential to be governed

by the concentrations at the boundary $x = 0$ and, also, a finite depth

into the electrode. The qualitative effect of making this change

would be to postpone the theoretical time at which the inflection and

downcurve should occur, since a longer time would be required to

reduce one-half of the vanadium pentoxide in the volume governing

the potential of the electrode than in a surface of infinitesimal thick-

ness.

Measurement of the Activation Energy and Diffusion Coefficient for the Discharge Process

Introduction

In a diffusion process an atom in changing position surmounts

a potential energy barrier. The height of this barrier is known as

the activation energy. To determine activation energy, the

temperature dependence of the diffusion coefficient is measured.

If an Arrhenius type equation

$$[40] \qquad D = D_o e^{-\Delta E/kT}$$

where D_o is the coefficient at $1/T \rightarrow 0$, is followed, then the activation energy, ΔE, can be found by taking the slope of a log D versus $1/T$ plot.

It was shown on p. 67 how the constant A defined by Equation [29] can be calculated from the discharge curve. Equation [29] when solved for D yields

$$[41] \qquad D = \frac{4\phi^2 A^2}{\pi}$$

which can then be substituted into Equation [40] and rearranged to give

$$[42] \qquad A^2 = \frac{\pi}{4\phi^2} D_o \, e^{-\Delta E/kT}$$

or

$$[43] \qquad \log A^2 = \log \frac{\pi}{4\phi^2} D_o - \frac{\Delta E}{2.3 \, kT}$$

Thus, for electrode discharges at constant current density and pH, if log A^2 is plotted versus $1/T$, the activation energy for the removal of discharge product from the electrode surface can be found from the slope of the curve. Also, if ϕ^2 is known, then D_o can be calculated.

Determination of the Activation Energy

A vanadium pentoxide electrode was discharged at pH 4.7 over a range of current densities at each of several different temperatures. The range in temperature was 1° to $44.5^{\circ}C$. This process was carried out on three different electrodes.

Typical electrode potential versus time curves for 20-second discharges are shown in Figure 16. The polarization curves shown are all on the same electrode and all of the discharges were at a current of 120 μa.

Values of the constant A in the diffusion equation were calculated for each polarization curve in the manner described previously. These A values were then plotted versus the reciprocal of the current for each temperature as illustrated in Figure 17. Values of A at a constant current were then taken for each temperature. The logarithm of A^2 was then plotted versus $1/T$ as shown in Figure 18.

The fact that a given current density will give rise to the same A value for all electrodes provides a means by which data from more than one electrode can be utilized in this study without specific knowledge as to the electrode area. Namely by consistently using the reciprocal current which gives $A = 7.90$ at $25^{\circ}C$ (this is a convenient but arbitrary choice) in Figure 17 as the value from which
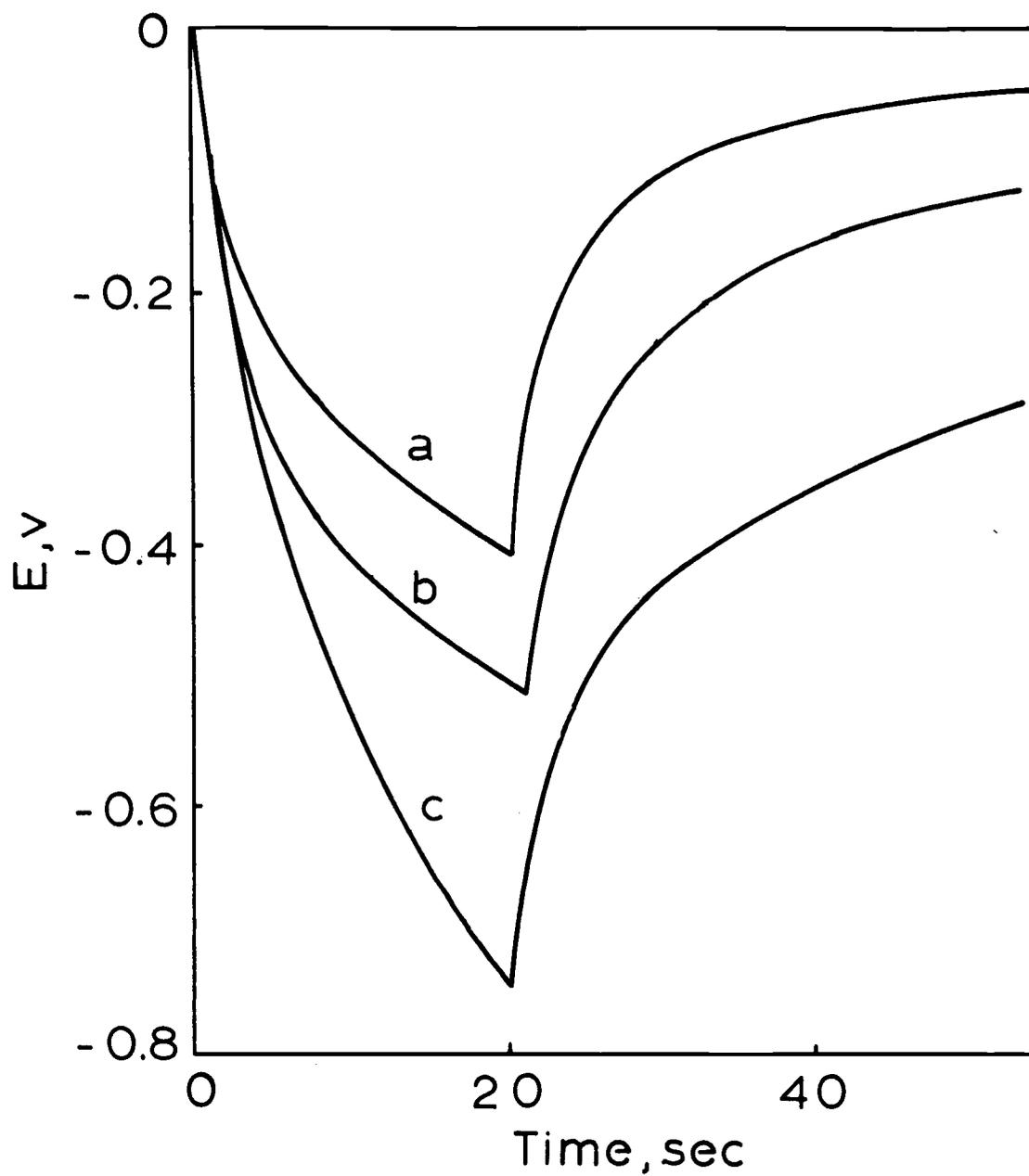
Figure 16. Effect of temperature on the discharge of a V_2O_5 electrode. Temperature: a, $33^{\circ}C$; b, $16^{\circ}C$; c, $4.5^{\circ}C$. Current: $120\mu a$.
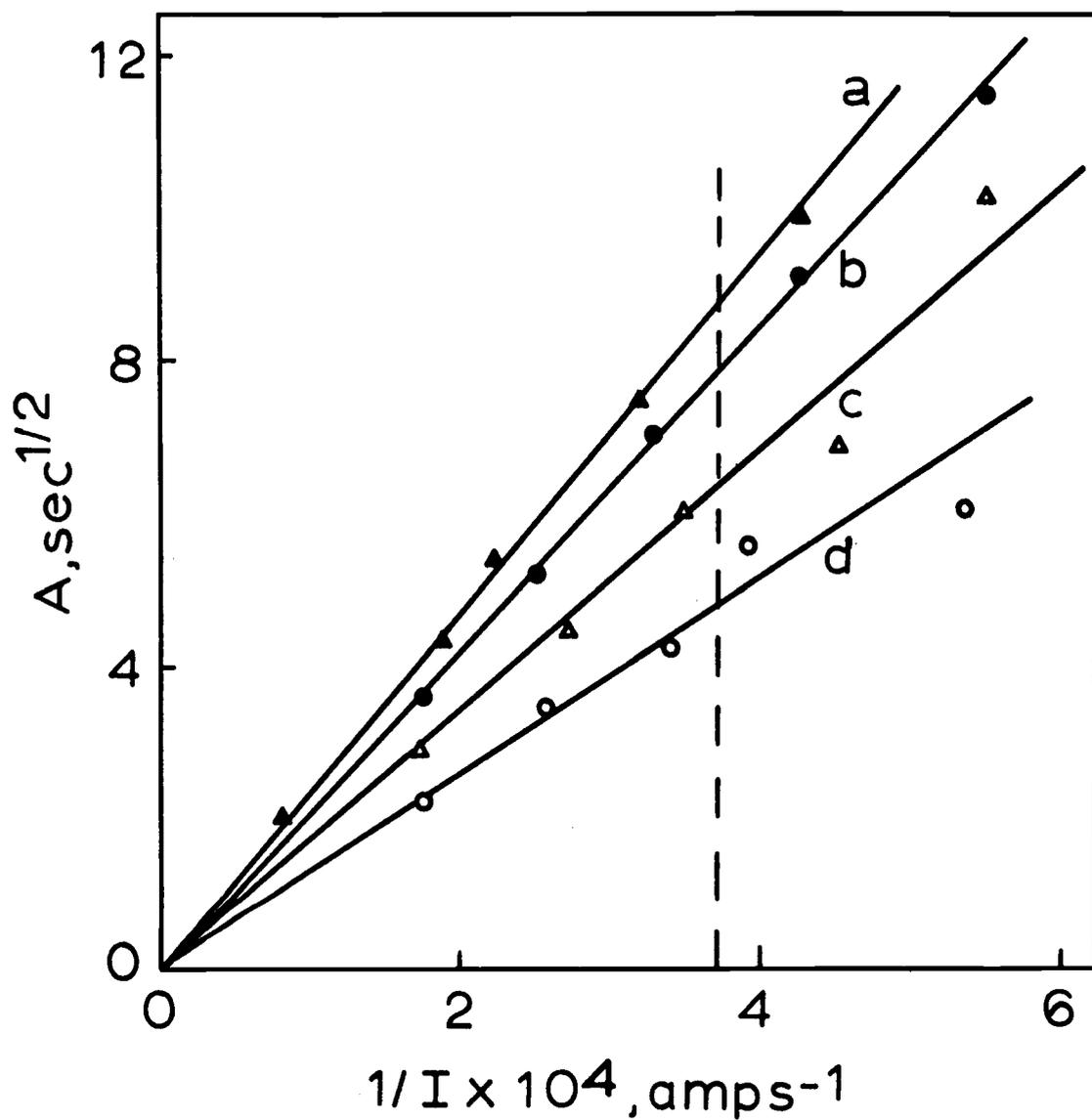
Figure 17. Relationship between A and the current for the discharge of a vanadium pentoxide electrode at several temperatures. Temperature: a, $33^\circ C$; b, $25^\circ C$; c, $16^\circ C$; d, $4.5^\circ C$.

data is compiled for Figure 18, one is in effect using a constant

current density for all electrodes. This was done using measure-

ments from three different electrodes and it is a combination of this

data which is given in Figure 18.

A least-squares analysis was made on the data shown in Fig-

ure 18 in order to obtain the slope. The slope obtained when multiplied

by Boltzmann's constant, gave an activation energy of 0.029 ± 0.01

ev/molecule or 6.7 ± 0.2 kcal/mole.

Cora, Takehara and Yoshizawa (21) reported the activation

energy for proton diffusion in MnO_2 to be 3.6 kcal/mole while

McArthur (41) gives 2.2 kcal/mole for a similar process for the

$Ni(OH)_2$ electrode. Wei and Bernstein (59) give 12.9 ± 0.8 kcal/

mole as the activation energy for the exchange of deuterons in

Boehmite ($\alpha-Al_2O_3 \cdot H_2O$). These workers also found that ^{18}O ex-

changed very slowly relative to the protons. Wei and Bernstein also

calculated from Spernol's work on conductivity and proton mobility

in polycrystalline ice below $-15^\circ C$ an activation energy of 4.5 kcal/

mole for proton diffusion in ice.

While there are no activation energies given in the literature

for the diffusion of vanadium or oxygen atoms or ions in any vanadium

oxides, values for M^{+x} and O^{-2} have been determined for other

oxides. Some of these activation energies are 43.5 kcal/mole for

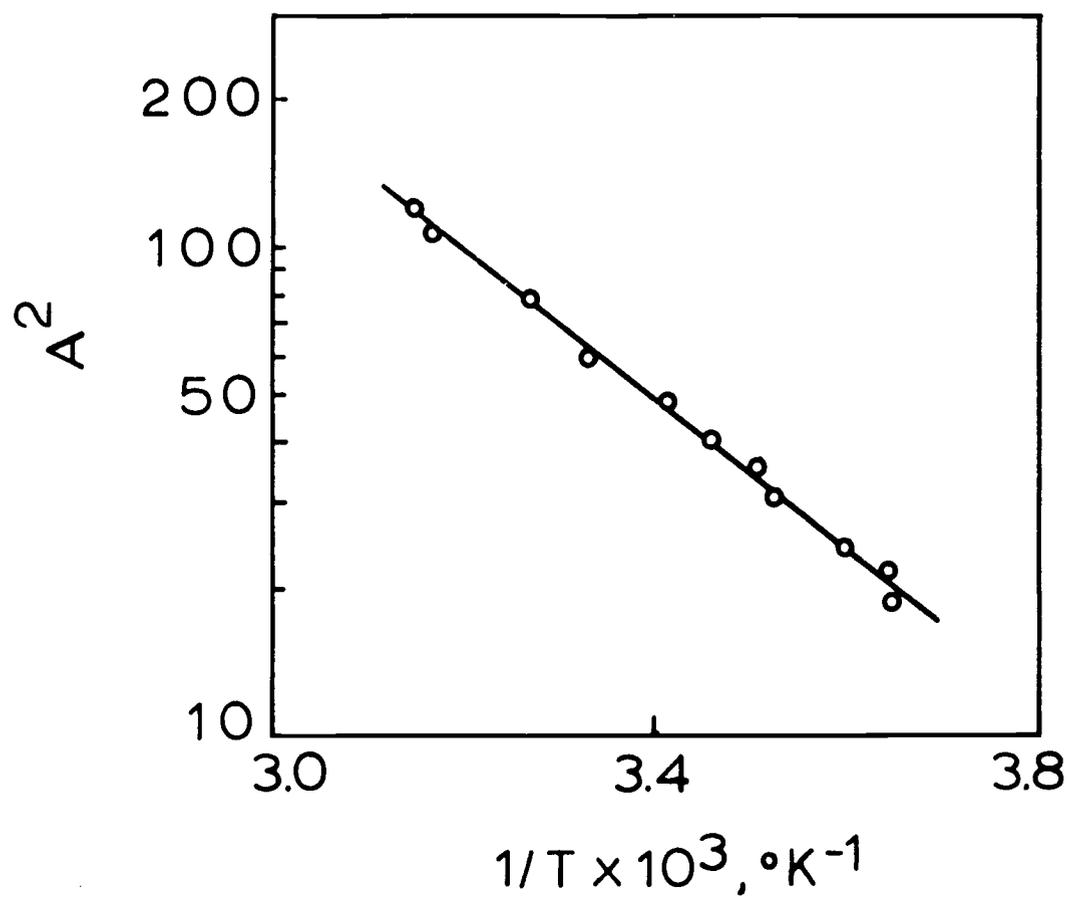Zn^{+2} and 165 kcal/mole for O^{-2} in ZnO (48), 66 kcal/mole for Pb^{+2}

Figure 18. Relationship between log A^2 and 1/T. The slope corresponds to an activation energy of 0.29 ev/molecule.

in PbO (39), 112 kcal/mole for Fe^{+3} in Fe_2O_3 (38), and 89 kcal/mole

for Cr^{+3} in Cr_2O_3 (23). By comparing the value obtained in this

study with these other published values, it seems probable that this

is the activation energy for the movement of protons and not vana-

dium or oxygen ions.

Determination of the Diffusion Coefficient

The least-squares fit to Figure 18 gives an intercept value on

the log A^2 axis of 6.84. Substituting this value into equation [43]

gives

$$[44] \qquad \log \frac{D_o}{4\phi^2} = 6.84$$

Since the electrode surface is quite smooth, the geometric area was

used to calculate a current density of 3.44×10^{-5} amps/cm^2 for the

three samples used in this study as corresponding to $A = 7.90$ at

$25^\circ C$. When this current density is used in equation [44] it is found

that $D_o = 1.0 \times 10^{-12}$ cm^2/sec.

Substitution of the experimental ΔE and D_o values in Equation

[40] gives a diffusion coefficient at $25^\circ C$ of $D = 7.6 \times 10^{-18}$

cm^2/sec.

An alternative method for obtaining the diffusion coefficient is

through substitution $\phi = 3.44 \times 10^{-10}$ eq./cm^2 sec and $A = 7.90$

$cm^3 sec^{1/2}$/equivalent into Equation [41] which gives D = 9.4 x 10^{-18} cm^2/sec.

The diffusion coefficient was also calculated by a different scheme for the two crystals which had leads attached by means of a gold plate. To calculate a diffusion coefficient for these electrodes the slope of an A versus I^{-1} plot was calculated and then using Equation [41] the values D = 1.8 x 10^{-18} cm^2/sec and D = 1.5 x 10^{-18} cm^2/sec were obtained. While these values for the diffusion coefficient are smaller than those given above, they should be considered to be in fair agreement since the error in measuring the geometrical surface area of the electrode is considerable, and during the calculations the area is squared.

The diffusion coefficient of 10^{-17} - 10^{-18} cm^2/sec at pH 4.7 found in this study for the diffusion of the discharged product from the electrode surface at a pH of 4.7 agrees well with Watson's (57) reported value of 4.12 x 10^{-18} cm^2/sec obtained by a different experimental method utilizing polycrystalline electrodes at pH 9. However this value is smaller than might be expected for proton diffusion.

Effect of Electrolyte pH

In order to determine the pH range over which the diffusion theory was valid a series of electrode discharges on the same electrode were conducted at a constant current of 61μa at various electrolyte pH values. The results of these experiments are given

in Figure 12, p. 63. (In order to facilitate comparison of these curves the initial potential for each curve has been moved to an arbitrary zero value.)

These curves can all be fitted by the Scott-Kornfeil equation if the parameter A is allowed to vary with pH. As shown in this figure the degree of polarization decreased as the electrolyte was made more acid. This implies that either less reduced product was formed on the V_2O_5 electrode surface or that the product formed was removed from the surface more rapidly as the electrolyte pH was decreased.

Since it is well known the V^{+4} compounds increase in solubility as the solution pH is decreased, it was initially felt that the decrease in the magnitude of the polarization with the lowering pH was due to the discharge product partially dissolving into the electrolyte. To test this theory the following experiments were conducted.

Electrodes were discharged in 10 ml of electrolyte at 1 ma until (about 10 hours) a blue color was imparted to the electrolyte indicating the presence of V^{+4} in the solution. The concentration of V(IV) in the electrolyte was then determined on a Perkin Elmer Model 450 Spectrophotometer by comparing the absorbance at 750 mμ with standards obtained from solutions of vanadyl sulfate of known concentrations. Since from Faraday's Law the total

equivalents of reduced product was known, the percentage of product

dissolving could be calculated. These values are given in Table V.

Table V. Percentage of Discharge Product Which Dissolves at
          Various pH.

pH	% Dissolving
2.2	18
3.0	15
4.7	8

The values given in Table V appear to support the theory that

the product is dissolving. However, due to the high current and the

long discharge necessary to obtain a sufficient V^{+4} concentration

for measurement, the values in Table V probably correspond to the

percentage of product dissolving in the reaction represented by the

third section of Figure 10 rather than the first section. (The V_2O_5

electrode potential was not recorded since the need for small

electrolyte volumes in this experiment precluded the use of a

reference electrode.)

The above experiments seem to indicate that at least a small

percentage of the discharge product does dissolve. However, the

fact that the Scott-Kornfeil equation, without any terms involving

dissolving, does fit the polarization curves implies that this is

probably not the chief reason for lesser degree of polarization as the electrolyte pH is lowered.

If dissolving of product was not the chief cause of the polarization decrease observed in Figure 12, then it must be due to a decreased reduction of the V_2O_5 surface. However, the same current was passed for all of the discharges. Therefore, a lesser reduction of the V_2O_5 would only be possible if a competing reaction, favored by lowering the pH, and not contributing to the polarization, was involved. A reaction such as

$$2H^+ + 2e^- = H_2$$
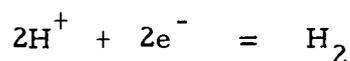
would meet the above criterion. In fact the evolution of H_2 gas was actually observed during the high current density discharges used in tritiated electrolytes. Smaller rates of H_2 evolution would readily escape detection due to the dissolution of H_2.

The evolution of H_2 would have the effect of lowering the value of ϕ, the number of equivalents of reduced V_2O_5 formed per cm^2 sec, and, therefore, as the pH is lowered the value of A in the Scott-Kornfeil equation would increase as predicted, without, however, leading to failure of the equation.

Conclusion

The experiments described here show that:

1. The electrolytic reduction of V_2O_5 results in the incorporation from the elctrolyte of hydrogen within the solid electrode.

2. The discharge and recovery curves at low current and within a pH range of 2-5.5 can be calculated to within experimental error by the Scott-Kornfeil equation.

3. The activation energy of 6.7 ± 0.2 kcal/mole for the discharge process is much lower than that generally characteristic for the diffusion of O^{-2} or M^{+x} in oxides. It is, however, consistent with values for the diffusion of H^{+} in oxides.

4. The effect on the polarization curves of lowering the electrolyte pH may be accounted for by a competing side reaction, the evolution of H_2, which is favored as the pH is lowered.

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