WATER RESEARCH PROGRAM

BIENNIAL PROGRESS REPORT
FOR THE PERIOD
MARCH 15, 1966 TO MARCH 15, 1968

REACTIONS AND TRANSPORT PHENOMENA
AT SURFACES

MASTER

for the
OFFICE OF SALINE WATER
U.S. Department of the Interior

OAK RIDGE NATIONAL LABORATORY

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WATER RESEARCH PROGRAM BIENNIAL PROGRESS REPORT

For the Period March 15, 1966, to March 15, 1968

REACTIONS AND TRANSPORT PHENOMENA AT SURFACES

Compiled by Franz A. Posey and George E. Moore

K. A. Kraus, Program Director

For the
OFFICE OF SALINE WATER
U.S. DEPARTMENT OF THE INTERIOR
OSW-AEC INTERAGENCY AGREEMENT 14-01-0001-937

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MARCH 1973

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CONTENTS

PREFACE	3
SUMMARY	5
1. KINETICS OF PITTING ATTACK OF TITANIUM IN CHLORIDE SOLUTIONS; F. A. Posey, E. G. Bohlmann, S. S. Misra, and D. V. Subrahmanyam. . .	9
2. PITTING OF TITANIUM ALLOYS IN SALINE WATERS;* F. A. Posey and E. G. Bohlmann.	26
3. KINETICS OF INITIATION OF CREVICE CORROSION OF TITANIUM; F. A. Posey and D. V. Subrahmanyam.	37
3.1 Oxygen Reduction in a Crevice.	38
3.2 Buildup of Acid Within a Crevice	39
3.3 Effect of Migration of Reactants and Products.	45
4. EFFECT OF FLOW RATE ON EFFICIENCY OF OXIDATION-REDUCTION REACTIONS IN POROUS AND TUBULAR ELECTRODES; F. A. Posey and F. Nelson	50
5. RECTIFYING PROPERTIES OF VALVE METALS IN A ONE-COMPARTMENT ELECTROLYSIS CELL; P. M. Lantz and K. A. Kraus.	54
6. CHRONOPOTENTIOMETRY OF THE Ag-AgCl SYSTEM AND ANALYSIS FOR THE CHLORIDE ION;* R. E. Meyer, F. A. Posey, and P. M. Lantz.	56
7. INFLUENCE OF INERT ELECTROLYTES ON CHRONOPOTENTIOMETRIC CONSTANTS; F. A. Posey and R. E. Meyer	67

* Paper published in open literature.

PREFACE

The Water Research Program at the Oak Ridge National Laboratory, sponsored by the Office of Saline Water, U.S. Department of the Interior, was authorized in March 1962 under an interagency agreement (14-01-0001-937) between the Department of the Interior and the U.S. Atomic Energy Commission. Results of the work carried out under this program have been reported on a regular basis to the Office of Saline Water, and completed portions of the work were published in the open literature. A biennial report covering the activities under the program for the period March 15, 1962 to March 15, 1964, was issued in a single volume as U.S. Office of Saline Water Research and Development Progress Report 302 (ORNL-CF-67-8-55). For the second biennium, March 15, 1964 to March 15, 1966, work was divided into three categories, "Properties of Solutions," "Reactions and Transport Phenomena at Surfaces. Corrosion Studies," and "Separations Processes." The report for "Separations Processes" was issued as U.S. Office of Saline Water Research and Development Progress Report 508 (February 1970) and also issued as ORNL-CF-69-5-41 (September 1969). The report for "Properties of Solutions" for this period was issued as U.S. Office of Saline Water Research and Development Progress Report 685 (July 1971) and was previously issued as ORNL-CF-70-6-30 (October 1970). The 1964-1966 biennial reports for "Reactions and Transport Phenomena at Surfaces" and for "Corrosion Studies" were combined into a single document because the work in these fields was so closely related; a joint report (ORNL-TM-4097) is planned. The present report covers work on "Reactions and Transport Phenomena at Surfaces" during the third biennium, the period March 15, 1966 to March 15, 1968.

In order to retain maximum coherence in subject matter, a sharp time distinction has not been drawn. That is, in some cases articles which appeared in the open literature after March 1968 but which cover work that was done mainly in the third biennium have been included in this volume, and, conversely, some work started during this period but developed mainly in the fourth biennium is only briefly mentioned in this report.

In the interest of economy and completeness of presentation, work that was reported in the open literature is given as a direct reproduction of the corresponding journal articles. We are grateful to the publisher (Elsevier Publishing Company) for permission to reprint the complete texts of these articles. A notation of the source appears at the head of each reprinted article. Part of the work reported here was cosponsored by the U.S. Atomic Energy Commission; such support is acknowledged in the individual articles.

The desalination program at the Oak Ridge National Laboratory has two branches: the Water Research Program directed by K. A. Kraus during the period of this report, and the Nuclear Desalination Program directed by R. P. Hammond. This report is concerned with the Water Research Program, Reactions and Transport Phenomena at Surfaces, coordinated by Franz A. Posey.

SUMMARY

Numerous technologies, including water desalination, depend on favorable kinetic properties of various reactions and transport phenomena at phase boundaries. For example, corrosion in its various manifestations is frequently one of the most important factors to be considered in the selection of materials of construction for desalting plants. A continuing need exists for extension of our knowledge of the corrosion behavior of metals, particularly with respect to factors which influence the susceptibility of metals and alloys to pitting attack and crevice corrosion. During this biennium we have studied both theoretical and experimental aspects of the interaction between interfacial and mass-transport reactions during pitting and crevice corrosion of titanium. Other studies of reactions and transport phenomena at phase boundaries have been concerned with fundamental investigations of the properties of electrode configurations, such as porous electrodes, which are designed for optimum interaction of hydrodynamic and electrochemical parameters. Such electrode systems have potential applicability for treatment of flowing streams with high efficiency and modest power requirements. And finally, other studies have dealt with the problem of rapid, precise electroanalysis of the chloride content of saline waters.

In continuing studies of the initiation of pitting corrosion of titanium and its alloys in chloride solutions, a number of observations were made on relationships among electrode potential, applied current, and time. Application of a constant anodic current to a titanium electrode causes the electrode potential to increase with time as a consequence of formation of a protective oxide layer (anodization) at essentially constant field strength. In the presence of a sufficient concentration of chloride ions, the anodization process is abruptly terminated when chloride ions penetrate the passive film and form a pit on the electrode surface. A relatively simple model was developed to account for the observed regularities in this process. The model assumes that chloride ions adsorbed in sufficient concentration at the oxide-solution interface can migrate through the passive oxide layer under the influence of the anodization

field. Solution of the appropriate form of the transport equation leads to a relation which accounts for the observation that an increase in the anodic current causes both a decrease in the initiation time for pit formation and an increase in the value of the breakdown potential. Other experiments were carried out in which estimates of the thickness of the passive oxide layer were obtained at various points along the anodization transients by use of capacity measurements. The observations suggest that pit initiation actually occurs much earlier during anodization of titanium in chloride solutions than had been generally realized on the basis of conventional anodization transients. The qualitative significance of these and other findings is discussed (Section 1).

In other studies of electrochemical aspects of the corrosion of titanium and some of its alloys in flowing, high-temperature salt solutions at temperatures up to 220°C, it was found that a pitting potential exists at sufficiently high potentials for all the alloys. Increase of temperature greatly affects the pitting potentials of titanium alloys. Plots of pitting potential as a function of temperature are reproducible and quite characteristic of each grade of titanium alloy and show clearly which alloys are superior in tendency towards pitting attack. The results suggest an upper temperature limit of usefulness for many titanium alloys without risk of severe localized attack. Alloys of titanium which contain molybdenum show promise for application in high-temperature saline waters (Section 2).

A theoretical model for the early stages of the initiation of crevice corrosion was developed for the case of metals (especially titanium) having corrosion products which undergo appreciable hydrolysis. A simple mechanism accounts for the existence of an induction period for initiation of severe crevice corrosion. Experimental studies showed that over the greater part of the pH range, from weakly alkaline and neutral solutions down to pH about 1, the rate of the anodic reaction of titanium in the passive region (formation of a TiO_2 layer) is essentially independent of pH. However, in more acidic solutions the rate of the anodic reaction depends directly on the hydrogen-ion concentration. Solution of the transport equations for this case shows that if sufficient acidity is developed in a crevice due to hydrolysis of corrosion products the anodic process can become autocatalytic. Whether or not this will happen depends

on the initial acidity, on the rate constant for the corrosion process in acid solutions, and on the ratio of crevice length to thickness, among other factors. If the corrosion reaction does become autocatalytic, the anodic current which passes through the solution within the crevice can easily become large enough to develop an appreciable potential gradient in solution, forcing the potential at the closed end of the crevice down into the region of active corrosion and resulting ultimately in very severe crevice corrosion. Additional studies involved computer simulation of the initiation process by numerical integration of appropriate field-dependent mass-transport equations which define particle fluxes due to diffusion, migration, and reaction, together with use of theoretical or empirical statements of the rate laws of pertinent interfacial reactions. These calculations have been valuable in identifying the important factors which control the complex sequence of events which takes place on initiation of crevice corrosion (Section 3).

Experiments on hydrodynamic and electrochemical aspects of oxidation-reduction reactions in porous, tubular, and other "flow-through" electrodes were carried out in order to increase our understanding of factors which contribute to lowered efficiencies at high flow rates. The efficiency of redox reactions decreased for flow rates in excess of an optimum value which was determined by the length of the capillary or porous electrode or the diameter of the wires of screen electrodes. In the region of lowered efficiency, the limiting current was controlled by convective diffusion to the electrode surface and at sufficiently high flow rates in the laminar regime could be expressed by the well-known Levich equation. A generalized expression was derived for the limiting current obtainable from redox reactions in porous and tubular electrodes as a function of solution flow rate which is valid for both low and high flow rates. These results allow one in principle to calculate optimum operating points and other parameters of interest in the use of porous electrodes for efficient electrolysis of saline waters (Section 4).

In the previous biennium,¹ a number of one-compartment electrolysis

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1. P. M. Lantz and K. A. Kraus, "Electrochemical Reactions in Flowing Streams Using Porous Electrodes," Section 1.5 in Water Research Program Biennial Progress Report for Period March 15, 1964 to March 15, 1966, Reactions and Transport Phenomena at Surfaces. Corrosion Studies, ORNL-TM-4097 (in preparation).

cells were designed and tested by which various electrochemical reactions could be carried out in flowing streams. These cells have a narrow gap between the two electrodes and thus can be used at high current densities with modest voltage drops. In the electrolysis of water to produce acid or base, it was found that high current efficiencies could be obtained through proper control of the hydrodynamics of the system and of solution withdrawal rates. Additional experiments have been carried out in preliminary evaluation of the feasibility of using valve metals (Al, Zr, Ta, Nb, Ti, Ti-Mo alloys) as rectifying electrodes for AC electrolysis of solutions in a one-compartment cell (Section 5).

Research has been carried out on the feasibility of using silver electrodes in a rapid electroanalytical method for determining the chloride content of saline waters. After examination and rejection of several alternative methods, a chronopotentiometric technique was found to satisfy a number of criteria and detailed studies were carried out on the rapidity, reproducibility, and precision of the method (Sections 6 and 7).

1. KINETICS OF PITTING ATTACK OF TITANIUM IN CHLORIDE SOLUTIONS

F. A. Posey, E. G. Bohlmann, S. S. Misra, and D. V. Subrahmanyam

In continuing studies of electrochemical aspects of the initiation of pitting corrosion of titanium and its alloys in chloride solutions, a number of observations were made on relationships among electrode potential, applied current, alloy and solution composition, temperature, and time. Titanium is one of the modern materials of construction which is being considered for use in large desalination plants. Years of accumulated experience at low temperatures had disclosed no tendency of titanium to undergo catastrophic forms of corrosion, such as pitting and crevice attack. However, a number of long-term experiments in dynamic loops on corrosion of titanium in high-temperature chloride solutions, which were carried out at ORNL,¹ have demonstrated severe, but sometimes erratic, pitting attack at temperatures from 100° to 200°C.

Typically, the rate of the anodic or corrosion reaction of titanium is essentially independent of the electrode potential up to very high potentials in such media as sulfate and nitrate solutions. However, in the presence of a sufficient concentration of chloride ions, titanium and its alloys exhibit a pitting potential which in some cases is low enough to allow pitting attack to proceed spontaneously (i.e., in the absence of externally applied anodic polarization). Pits can form on the electrode surface at and above the pitting potential and exist simultaneously with passive areas. Experience with this and other systems shows that pitting potentials are independent of the pH of the external solution but depend significantly on temperature.

Application of a constant anodic current to a titanium electrode causes the electrode potential to increase with time as a consequence of formation of a protective oxide layer (anodization) at essentially constant field strength. In the presence of a sufficient concentration of chloride ions, the anodization process is abruptly terminated when chloride ions penetrate the passive film and form a pit on the electrode surface,

1. See Section 2, this report.

whereupon the electrode potential suddenly plunges from a high value (breakdown potential) down to a value (pitting potential) which depends on the composition of the alloy and on the temperature. The final pitting potential is essentially independent of the anodic current over wide limits. It was found earlier² that the value of the breakdown potential depends to some extent on the initial thickness of the passive layer as well as on other factors: fresh electrodes with thin films exhibit lower breakdown potentials than aged electrodes having thicker films, although the final pitting potential is about the same in either case. The studies described below were carried out to extend our knowledge of various aspects of the process of initiation of pits on titanium in chloride solutions.

Figure 1.1 shows some quasi-steady-state anodic polarization curves, with breakdown potentials and pitting potentials, for titanium 150A (2.8% Cr, 0.3% Fe) in 1 M NaCl as a function of temperature. Experimental points shown in Fig. 1.1 are not true steady states because of the anodization process referred to above; each point shown represents the potential exhibited at the current in question after a few minutes. These results (and other obtained previously) show that both the pitting potential and the breakdown potential drop sharply in a rather narrow temperature range near 70°C. Furthermore, much less current is required to initiate pitting attack above that temperature. These observations suggest that perhaps some property of the passive oxide layer undergoes a relatively sudden change in the critical temperature range. This property may be concerned with the ability of chloride ions to exchange with lattice oxide ions at the oxide-solution interface (probably the first step in pit initiation) or may be concerned with transport of chloride ions through the passive layer.

Addition of sulfate ions to the system markedly increases the value of the breakdown potential at any temperature. Sulfate ions probably compete with chloride ions for adsorption at the oxide-solution interface and thereby affect the kinetics of pit initiation. Especially noteworthy

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2. F. A. Posey and S. S. Misra, "Kinetics of Pitting Attack of Titanium in Chloride Solutions," Section 2.4 in Water Research Program Biennial Progress Report March 15, 1964 to March 15, 1966, Reactions and Transport Phenomena at Surfaces. Corrosion Studies, ORNL TM 4097 (in preparation).

FIG. 1.1 EFFECT OF TEMPERATURE ON GALVANOSTATIC POLARIZATION CURVES, BREAKDOWN POTENTIALS, AND PITTING POTENTIALS OF TITANIUM 150A IN 1 M NaCl.

is the observation that in the presence of sulfate ions a sharp drop in the value of the pitting potential is no longer obtained in the vicinity of 70°C, and the pitting potential varies smoothly with temperature from 23° up to 80°C, the highest temperature of these measurements.

The influence of alloy composition on pitting of titanium and its alloys is shown in Fig. 1.2, containing a comparison of polarization curves, breakdown potentials, and pitting potentials of a number of titanium alloys in 1 M NaCl at 23°C. Pure titanium exhibits the highest breakdown and pitting potentials and is least susceptible to pitting attack. Titanium of commercial purity (type 55A) has a much lower breakdown potential, a somewhat lower pitting potential, and requires much less current for initiation of pitting attack. Although titanium 150A pits at a lower potential than Ti-55A, it requires more current for pit initiation, comparable to that needed for pure titanium. Titanium 110AT is highly susceptible to pitting attack (especially at higher temperatures) and breakdown and pitting potentials are both correspondingly low. Polarization curves of this type evidently can serve to assess the relative sensitivity of various alloys to pitting attack.

In further studies on phenomenological aspects of the initiation of pitting corrosion, a number of observations have been made on relationships among electrode potential, applied current, and initiation time. These measurements were carried out on titanium 55A electrodes in a high-temperature, all-titanium loop assembly.³ As stated earlier, application of a constant anodic current to a titanium electrode causes the electrode potential to increase essentially linearly with time as a consequence of a constant rate of formation of a protective oxide layer (anodization). In the presence of a sufficient concentration of chloride ions, the anodization process is abruptly terminated when chloride ions penetrate the passive film and form a pit on the electrode surface. We have observed certain regularities in this process, and some preliminary results and a provisional analysis are presented below.

An increase in the anodic current causes a decrease in the time required for breakdown of the oxide layer and initiation of a pit. This

3. See Section 2, this report.

FIG. 1.2 EFFECT OF TITANIUM ALLOY COMPOSITION ON ANODIC POLARIZATION CURVES, BREAKDOWN POTENTIALS, AND PITTING POTENTIALS IN 1 M NaCl AT 23°C.

effect is shown in the logarithmic plot of Fig. 1.3. Correspondingly, the potential at which breakdown occurs is increased by an increase in current, as shown in Fig. 1.4. We find that a relatively simple model can account for the observed results.

To a first approximation, film formation on titanium may be described by the conventional anodization relation given by

$$j_a = j_a^0 \exp \left[\frac{q_+ a_+}{kT} \cdot \frac{\Delta\phi(t)}{\ell(t)} \right], \quad (1)$$

where j_a is the anodic current density (amp/cm²), j_a^0 is a measure of the mobility of charge carriers in the oxide film in the absence of the field (amp/cm²), q_+ is the charge on the mobile species (coulombs), a_+ is the "half-jump" distance (cm), kT is the thermal energy (electron volts), $\Delta\phi(t)$ is the average potential difference across the oxide layer (volts), and $\ell(t)$ is film thickness (cm). We suggest that chloride ions adsorbed from solution at the oxide-solution interface probably exist in equilibrium with chloride ions in lattice or interstitial sites at the outer edge of the film. These ions can then migrate through the lattice under the influence of the anodization field. We may postulate that the flux equation for migration of chloride ions is of the same form as Eq. (1); this is shown in Eq. (2).

$$j_{Cl-}(x,t) = - Fk_- C_{Cl-}(x,t) \exp \left[\frac{q_- a_-}{kT} \cdot \frac{\Delta\phi(t)}{\ell(t)} \right], \quad (2)$$

where $j_{Cl-}(x,t)$ is the component of the (anodic) current density due to chloride-ion migration in the direction normal to the surface, F is Faraday's constant (coulombs/equivalent), k_- is a specific rate constant (cm/sec) which is proportional to the mobility of chloride ions in the lattice in the absence of the field, $C_{Cl-}(x,t)$ is chloride-ion concentration (moles/cm³) in the lattice at any point (x) and time (t), and q_- and a_- are the ion charge (coulombs) and "half-jump" distance (cm), respectively, for the migration process. At constant current (j_a) the film thickness increases with time according to

$$\frac{d\ell(t)}{dt} = Q (j_a - j_{dis}), \quad (3)$$

where j_{dis} is the rate of dissolution of the film in the electrolyte (amp/cm²),

FIG. 1.3 RELATIONSHIP BETWEEN APPLIED CURRENT DENSITY AND TIME FOR INITIATION OF PITS ON TITANIUM 55A IN 1 M NaCl.

FIG. 1.4 RELATION BETWEEN BREAKDOWN POTENTIAL AND APPLIED CURRENT DENSITY FOR INITIATION OF PITS ON TITANIUM 55A IN 1 M NaCl.

and Q is a proportionality constant ($\text{cm}^3/\text{coulomb}$) which depends on the molecular weight and density of the film.

Differentiation of Eq. (2) and substitution from Eq. (1) lead to

$$\frac{\partial C_{\text{Cl}^-}(x,t)}{\partial t} = k_- \left(\frac{j_a}{j_a^\circ} \right)^{\frac{q_- a_-}{q_+ a_+}} \frac{\partial C_{\text{Cl}^-}(x,t)}{\partial x}, \quad (4)$$

which may be integrated subject to the initial condition $C_{\text{Cl}^-}(x,0) = 0$ and the boundary condition $C_{\text{Cl}^-}(\ell,t) = C_{\text{Cl}^-}^\circ$ (assumed constant). The result of the integration is given by

$$C_{\text{Cl}^-}(x,t) = C_{\text{Cl}^-}^\circ \cdot \mathcal{U} \left[t - \left(\frac{j_a^\circ}{j_a} \right)^{\frac{q_- a_-}{q_+ a_+}} \frac{\{\ell(t) - x\}}{k_-} \right], \quad (5)$$

where $\mathcal{U}$ is the Heaviside unit step function. Since diffusion has been assumed to be negligible compared to migration, this solution represents the motion of a sharp concentration "front" from $x = \ell$ to $x = 0$. Integration of Eq. (3) leads to Eq. (6) for film thickness as a function of time:

$$\ell(t) = \ell_o + Q (j_a - j_{\text{dis}}) t, \quad (6)$$

where ℓ_o is the initial film thickness. Solution of Eqs. (5) and (6) for the time required for migration of the chloride ions through the layer leads to Eq. (7) for the initiation time as a function of the anodic current density:

$$\tau = \frac{\ell_o}{k_-} \left(\frac{j_a^\circ}{j_a} \right)^{\frac{q_- a_-}{q_+ a_+}} \quad (7)$$

Certain approximations made in the derivation of Eq. (7) imply that the velocity of the migration reaction is considerably larger than the linear rate of increase of film thickness; this condition is fulfilled in the present experiments. The form of Eq. (7) accounts for the linearity of the logarithmic plot of Fig. 1.3.

Solution of Eq. (1) for $\Delta\phi(\tau)$ and substitution of expressions for $\ell(\tau)$ and τ lead to Eq. (8) for the relation between breakdown potential

and anodic current density, provided approximations similar to those used in deriving Eq. (7) are made:

$$\Delta\phi(\tau) = \ell_o \frac{kT}{q_+ a_+} \ln \left(\frac{j_a}{j_a^o} \right) . \quad (8)$$

Equation (8) is of the same form as the results shown in Fig. 1.4. Furthermore, Eqs. (7) and (8) suggest that the breakdown potential and initiation time are a function of initial film thickness, in agreement with previous experience.

In other studies, galvanostatic (constant current) anodization transients were measured on titanium 55A in 1 M NaCl + 10⁻⁴ M HCl and in 1 M NaCl + 10⁻² M HCl solutions at 25°C as a function of anodic current density for various pretreatments of the electrode surface. Simultaneously, estimates of the thickness of the passive oxide layer were obtained at various points along the anodization transients by use of capacity measurements. Capacities were measured by application of a square wave of current to the electrode and observation of the resulting potential "sawtooth" on an oscilloscope. Sawtooth potential amplitudes were not allowed to exceed a few millivolts in magnitude. Square-wave frequencies in the range 10³ - 10⁴ Hz were used; no significant effect of frequency on capacity could be detected. Film thicknesses were calculated from values of differential capacity by use of the conventional parallel-plate capacitor formula. A relative dielectric constant of 100 was assumed for the TiO₂ layer; this is the mean value of the normal dielectric constant of rutile.

A typical anodization transient and corresponding measurements of the film thickness during the transient are shown in Fig. 1.5. It can be seen that film thickness varies linearly with electrode potential during the anodization transient; this behavior is typical of metals on which film growth takes place at constant field strength. For the transient shown in Fig. 1.5, field strength was close to 10⁶ V/cm, and in all cases studied the field had the same order of magnitude. After a certain time the electrode potential more or less suddenly drops to a potential which is called the pitting potential. Stable pit growth seems not to be possible at potentials below the pitting potential, and the pitting potential is essentially independent of the current passed through the electrode

FIG. 1.5 VARIATION OF ELECTRODE POTENTIAL AND FILM THICKNESS WITH TIME DURING ANODIZATION OF TITANIUM 55A.

surface. Pitting potentials are to be understood as average potential values exhibited by an electrode undergoing pitting corrosion. In many cases, large fluctuations of potential are detectable on devices, such as a strip-chart recorder, which normally possess restricted bandwidths and are insensitive to rapid phenomena. Oscilloscopic observations show that there are additional potential fluctuations which occur in the millisecond range. The origin of such rapid potential fluctuations is not known with certainty; possibly the influence of natural convection and of formation of gaseous reaction products on potential and concentration distributions inside the pits must be considered.

The pit-propagation potential shown in Fig. 1.5 is a new name for what, in the studies described above, we referred to as the breakdown potential. Correspondingly, the time required to reach the pit-propagation potential is now called the pit-propagation time instead of the initiation time or some similar term. The change in nomenclature seems desirable because of the following rather unexpected observations made during the course of the capacity measurements. If anodization transients are observed on a recorder, as usual, the potential transients seem to be free of potential fluctuations up to the pit-propagation potential. The fall of potential which occurs after the pit-propagation potential has been reached can be very rapid for high values of applied current, and significant potential fluctuations generally appear only as the final pitting potential is approached. Therefore it has been the practice to associate the sharp fall of potential with initial breakdown of the passive layer and the development of the first pit, so that use of the terms breakdown potential and initiation time is natural. However, we found during the oscilloscopic capacity measurements that rapid potential fluctuations, which consist individually of a very fast drop followed by a somewhat slower return, take place even at potentials which are several volts below the final pitting potential. The first few events are small in amplitude (only a few millivolts) and may be spaced many seconds apart, depending on applied current, initial film thickness, etc. As the film thickness and electrode potential increase, the frequency and amplitude of these rapid potential fluctuations increase considerably. There seems to be no significant change in the rate of increase of fluctuation amplitude and frequency as the pit-propagation potential is reached

and the system approaches the final pitting potential--the fluctuations merely become larger and more numerous with time until the final pitting potential is attained.

These observations suggest that pit initiation actually occurs much earlier during anodization of titanium in chloride solutions than had been supposed. Pits formed at low potentials and relatively small oxide layer thicknesses appear not to be stable, however, and repassivation takes place very quickly. The reason for repassivation of pits is not known. Our measurements of film thickness show that oxide layers of the order of $1000 \text{ \AA}$ in thickness are formed before stable pit formation becomes possible. Perhaps such film thicknesses are needed to provide a sufficiently confined "column" of electrolyte at sites of incipient pit formation so that the interacting forces of diffusion and migration can lead to formation of both an acid electrolyte in the pit and a sufficient IR drop in the electrolyte phase so that the metal at the base of the pit can remain in the active region of corrosion. During the ascending branch of the anodization transient, the potential is determined almost exclusively by the film-formation reaction and by oxidation reactions (production of O_2 and/or Cl_2) at the oxide-solution interface. However, as the film thickness increases, repassivation of incipient pits becomes more difficult, and an appreciable fraction of the applied anodic current begins to be involved in the pit-growth process so that finally the electrode potential is no longer determined by the film-formation process but by the pit-growth process. The pit-propagation potential and the pit-propagation time therefore signal this change in potential control.

It is apparent from the curvature of the anodization transient in Fig. 1.5 that the film-formation process is not 100% efficient. The capacity measurements have allowed us to study this matter in more detail, and a typical set of results is shown in Fig. 1.6. The anodization efficiency was computed by dividing the film thickness as determined by capacity measurements (assumed to be the "true" thickness) by the film thickness which would have been obtained if the film-formation reaction proceeded with 100% efficiency. A density of 4.26 g/cm^3 was assumed for TiO_2 in the calculation. One sees in Fig. 1.6 that efficiency of the film-

ORNL-DWG. 68-13742

FIG. 1.6 EFFECT OF ANODIC CURRENT DENSITY AND ELECTRODE POTENTIAL ON EFFICIENCY OF FILM FORMATION ON TITANIUM IN CHLORIDE SOLUTION.

formation process varies both with electrode potential and with applied current density. Other experiments have shown that the pH of the solution is an additional variable. Anodization efficiency is quite low at current densities below about 1 mA/cm^2 . Use of larger current densities leads to increased efficiency of the film-formation process. The factors which affect anodization efficiency are not yet known with certainty. The minimum in the efficiency - potential curves which appears at 9 to 11 V is characteristic of all systems studied. It corresponds to a maximum in the current due to the oxidation reactions which lead to formation of gaseous O_2 and/or Cl_2 . Such a maximum in the oxidation current may be a result of two opposing tendencies: (a) the rate of an anodic process tends to increase with increasing electrode potential; (b) the film thickness also increases with increasing potential and thus may affect transport and/or surface concentrations of electrons and/or holes which are involved in the oxidation processes which lead to formation of gaseous O_2 and/or Cl_2 at the oxide-solution interface. At potentials of 12 V or higher, a further drop in anodization efficiency always takes place as the pit-propagation potential is approached. This final drop in efficiency is probably associated with the increased fraction of the anodic current which is devoted to the pit-growth process in this region of the transient. As the potential of the system approaches the final pitting potential, most of the current is then involved in the growth and maintenance of stable pits.

A correlation exists to some extent between applied anodic current density and pit-propagation time. Results from a number of experiments are shown plotted in Fig. 1.7. A single straight line of slope = -0.5 has been drawn through the points corresponding to experiments run in $1 \text{ M NaCl} + 10^{-4} \text{ M HCl}$. A different line of somewhat smaller (more positive) slope may be drawn through the few data obtained in $1 \text{ M NaCl} + 10^{-2} \text{ M HCl}$. Film-formation efficiencies are much lower in the more acid medium and therefore longer times are necessary to grow oxide layers of comparable thickness at the same current density. We find that film thicknesses ranging from 800 - 1500 Å are attained at the pit-propagation potential for all specimens which exhibit low anodization efficiency. However, film thicknesses

FIG. 1.7 DEPENDENCE OF PIT-PROPAGATION TIME ON ANODIC CURRENT DENSITY FOR TITANIUM 55A IN CHLORIDE SOLUTIONS AT 25°C.

of only about 200 - 300 Å are needed at current densities where the film-formation reaction takes place with essentially 100% efficiency. Thus it appears that conditions required for stabilization of pit growth are less stringent at high currents.

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2. PITTING OF TITANIUM ALLOYS IN SALINE WATERS*

F. A. Posey** and E. G. Bohlmann***

SUMMARY

Electrochemical aspects of the corrosion of titanium and a number of its alloys were studied in flowing, high-temperature salt solutions at temperatures up to 220° in a titanium loop facility. Measured polarization curves show that a pitting potential exists at sufficiently high potentials for all the alloys. Increase of temperature greatly affects the pitting potentials of titanium alloys. Plots of pitting potential as a function of temperature are reproducible and quite characteristic of each grade of titanium alloy and show clearly which alloys are superior in tendency towards pitting attack. The results suggest an upper temperature limit of usefulness for many titanium alloys without risk of severe localized attack. Alloys of titanium which contain molybdenum show promise for application in high-temperature saline waters.

Titanium is an attractive material of construction which is being considered for use in large desalination plants (1). A number of investigators have established its immunity to all forms of corrosive attack in sea water and chloride solutions at ambient temperatures (2-5). Others have shown it to be resistant to attack in most chloride media at elevated temperatures (4-6). However, under certain conditions in concentrated aqueous chloride solutions at elevated temperatures (100°-200°C), catastrophic attack of titanium and its alloys in the form of pitting and crevice corrosion has been observed (7).

Pitting corrosion of titanium occurs rarely at temperatures below about 100°C, except in unusually aggressive media, and the metal is normally passive. In order for pitting attack to be initiated, the electrode potential of titanium must exceed a certain critical value, known as the pitting potential (8). Pitting potentials of titanium alloys in chloride solutions at room temperature are usually several volts more positive (noble) than the spontaneous corrosion potentials, and pitting occurs only if the metal is polarized up to the pitting potential by passage of anodic current. Certain aspects of the pitting corrosion of titanium in various media have been investigated previously (9-24). We have studied the effect of temperature on the polarization behavior of titanium and a number of its alloys in chloride solution, and find that increase of temperature profoundly affects the value of the pitting

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potential. The results suggest that the pitting potential may impose an upper temperature limit of usefulness for some titanium alloys beyond which there is risk of localized attack.

EXPERIMENTAL

In order to investigate more closely the nature of the localized attack, a corrosion loop facility was developed for electrochemical studies of the behavior of material; in flowing, high-temperature salt solutions. The loop, shown schematically in Fig. 1, is constructed entirely of titanium. It is equipped with a heater and a pump capable

Fig. 1. High-temperature titanium loop for electrochemical studies of corrosion.

of circulating the 650 cm³ volume of solution past the electrode surfaces at various linear velocities (typically 8 to 24 ft/sec), depending on electrode diameter and the pump speed, which may be varied during operation. Provisions are available for continuous addition and withdrawal of fresh solution. Other features include a sampling valve, a metering pump for injection of various reagents or of acid or base for control of pH, and provisions for deaerating, aerating, or oxygenating solutions to be circulated in the loop. Corrosion and polarization studies can be conducted over the temperature range 25–225°C.

Details of the electrode assembly are shown in Fig. 2. The specimens are used as hollow cylindrical electrodes through which the solution flows. The assembly contains two specimen electrodes in tandem separated by the polarizing electrode. Each electrode is insulated from the loop and from the other electrodes by use of silicone rubber gaskets. Electrolyte circulates past the interior surfaces of the electrodes which were used in the "as-machined" state following standardized cleaning procedures. The polarizing electrode, constructed of titanium, is in the center of the elec-

Fig. 2. Test assembly for electrochemical studies of dynamic corrosion.

trode assembly; titanium rods welded to this central electrode extend axially through the electrolyte inside the other two electrodes. This arrangement minimized IR drops in solution between the test specimens and the polarizing electrode and promoted uniformity of current density. Electrode potentials were measured by use of a high-impedance electrometer-recorder combination with respect to externally situated (room temperature) saturated-calomel reference electrodes which were bridged into the loop solution by use of an asbestos wick assembly (25). The titanium electrodes (cf. Fig. 2, specimen nos. 1 and 3) were polarized by use of a constant current source consisting of high voltage batteries (135 V) of large capacity in series with high resistances or by use of a potentiostat (ORNL Model Q-2003 or Anotrol Model 4700).

RESULTS AND DISCUSSION

Titanium, in common with many other metallic materials of construction, owes its immunity to corrosion to the existence of a passive oxide layer at the metal-solution interface (26). Except in strongly acidic solutions, titanium normally corrodes spontaneously at a very low rate in the passive region and the current density of the anodic process (formation of a TiO_2 layer) is independent of the value of the electrode potential over a wide potential range. However, in solutions containing a sufficient concentration of chloride ions (also bromide or iodide ions), titanium exhibits a pitting potential similar to that observed for aluminum, iron, stainless steel, and other metals and alloys which are capable of existing in both active and passive states. Fig. 3 shows a typical anodic polarization curve measured for type 110-AT titanium (5.5% Al, 2.5% Sn) in 1 M NaCl at 190°C. The rate of the anodic process is shown to be independent of electrode potential up to about + 0.4 V vs. S.C.E.,

Fig. 3. Anodic polarization curve of titanium (Type 110-AT) in 1 M NaCl at 190°C.

at which point pitting attack can be initiated. In this case the pitting potential is quite low compared to that found for commercial titanium at the same temperature (about + 1.0 V). As for other systems where pits can exist simultaneously with unattacked, passive areas, the potential exhibited by a titanium electrode which has been forced up to the pitting potential by passage of sufficient anodic current is essentially independent of the value of the current over wide limits. Pitting potentials of titanium, although dependent on alloy composition, appear to be independent of the pH of the external solution. Fig. 4 shows the typical appearance of a titanium

Fig. 4. Pitting corrosion of titanium electrode.

electrode after undergoing pitting corrosion by passage of anodic current.

The primary cathodic reaction in the titanium-saline water system in neutral, weakly alkaline, or weakly acidic solutions is the reduction of dissolved molecular oxygen at the oxide-solution interface. Fig. 5 shows cathodic polarization curves

Fig. 5. Effect of acidity and temperature on polarization curves for the reduction of molecular O_2 on titanium (110-AT Alloy) in O_2 -saturated 1 M NaCl.

for oxygen reduction on type 110-AT titanium as a function of pH and temperature. At high current densities a limiting current for convective diffusion of dissolved O_2 to the electrode surface is observed. At lower current densities the reduction rate depends exponentially on electrode potential in the usual manner; in this region the rate-determining step is thought to be the interfacial charge-transfer process. Increase of temperature accelerates the rate of the reduction process. Computations based on these data show that the oxygen reduction reaction is first order with respect to hydrogen ion concentration over the pH range studied.

Schematic polarization curves which summarize the electrochemical behavior of titanium in chloride solutions are shown in Fig. 6. Regions of active corrosion, passive corrosion, and pitting corrosion may be distinguished; which type of attack will occur in practice depends on experimental conditions. In strongly acid solutions the rate of the anodic process in the active region increases with increasing hydrogen ion concentration (11, 13, 16, 23, 27-31). A number of workers have presented evidence showing that trivalent titanium ions are formed as the initial product of the anodic process for active corrosion in acid solutions (19, 29, 32-37). The primary cathodic process which occurs during spontaneous corrosion in the active region in

Fig. 6. Schematic diagram of polarization curves for corrosion of titanium in chloride solutions.

Fig. 7. Effect of temperature on pitting potentials of titanium alloys in 1 M NaCl.

acid solutions is the reduction of hydrogen ions (not shown in Fig. 6). With increase of pH the rates of anodic and cathodic processes in the active state decrease considerably until a stable corrosion state can be attained only in the passive region. The corrosion potential in the passive region is determined by the pH, the dissolved oxygen concentration, and the rate of the anodic process (cf. points A and B in Fig. 6). Under these conditions the metal maintains its passivity and corrodes at a very low rate. However, at sufficiently high temperatures, certain titanium alloys may exhibit pitting potentials which are low enough so that the metal can corrode at the pitting potential (cf. point C in Fig. 6).

The effect of temperature on the pitting potentials of a number of titanium alloys is shown in Fig. 7. These data were obtained by variation of the temperature of the loop solution while titanium electrodes were polarized to their pitting potentials by passage of a constant anodic current. Commercial tubing, type 55A, and alloys with small amounts of added elements (e.g., the 0.15% Pd alloy) show high pitting potentials (9–11 V) in the vicinity of room temperature. With increasing temperature the pitting potentials of these materials decrease more or less uniformly to values of the order of + 1.0 V at 175°–200°C. A relatively sudden change in the

Fig. 8. Effect of small percentages of alloying elements on the pitting potential of titanium in 1 M NaCl.

pitting potential of the 0.15% Pd alloy occurs in the vicinity of 125°C. The type 150A alloy (2.8% Cr, 0.3% Fe) shows a very sharp drop in the value of its pitting potential in the vicinity of 76°C: the pitting potential changes about 2.5 V over a temperature range of only a few degrees. Pitting potentials of the type 110-AT alloy (5.5% Al, 2.5% Sn) are quite low, attaining values of only about + 0.4 V at 190°C.

Effects of relatively small percentages of alloying elements on the pitting potential of titanium are shown in Fig. 8. Additions of Al, Sn, and Ni increase the value of the pitting potential significantly at temperatures below about 100°C. In the region from 100° to 150°C, the pitting potentials of these alloys drop sharply to values somewhat less than that of commercial titanium (55A), and at temperatures above 175°C the pitting potentials of these alloys are more noble than that of 55A titanium. Above 125°C the pitting potential of the 1% Mo alloy is significantly more positive than those of the other alloys; this material should be quite resistant to pitting corrosion under most circumstances (cf. Fig. 10). The addition of 0.15% Pd to titanium does not greatly affect the pitting potential (cf. Fig. 7). At a temperature of 220°C the pitting potential of 55A titanium is quite low, and the possibility exists that pitting corrosion could be initiated spontaneously at this and higher temperatures,

Fig. 9. Pitting potentials of titanium-aluminum alloys in 1 M NaCl.

depending on solution composition and acidity. It can be seen from these results that even small percentages of alloying elements can exert important effects on the tendency of titanium to undergo pitting corrosion at elevated temperatures.

Pitting potentials of a number of titanium-aluminum alloys are shown in Fig. 9. Addition of 1% Al has a generally beneficial effect on the pitting potential of titanium at both low and high temperatures, but further increase in aluminum content causes the pitting potential to drop to low values. These results suggest caution in the use of materials with high aluminum contents in solutions having high chloride and hydrogen ion concentrations. Solutions of low pH could cause these materials to corrode spontaneously at the pitting potential (cf. point C in Fig. 6).

The influence of molybdenum additions on the pitting potential of titanium is shown in Fig. 10. The addition of as little as 1% Mo has a significant effect on the pitting potential at temperatures above 125°C (cf. Fig. 8). Further increase in molybdenum content lowers the pitting potential at temperatures below about 150°C, with little improvement at more elevated temperatures.

Qualitatively, the curves of Figs. 7-10 suggest that in general the presence of small percentages of an alloying element causes a significant increase in the pitting potential of titanium at low temperatures and a smaller but important increase at high temperatures. Larger percentages of Al, Mo, and Cr decrease the pitting potential of titanium; this is consistent with observations of Fischer (18) on effects of various surface treatments and of intentionally added impurities on the initiation of titanium

Fig. 10. Effect of molybdenum on pitting potentials of titanium alloys in 1 M NaCl.

pitting corrosion. The pitting potentials of titanium alloys with small percentages of alloying elements are probably high enough so that pitting attack may never be a serious problem under conditions of spontaneous corrosion up to about 200°C in concentrated chloride solutions. However, it seems clear that pitting can be expected to occur at high temperatures on alloys which have high percentages of added elements (except Mo) under certain conditions of pH and oxygen concentration or in the presence of oxidizing agents.

Differences in the pitting potentials of various alloys of titanium probably originate from specific effects of additives on the ionic conductivity of the passive layer (rutile, presumably). The total applied anodic current is the sum of the current due to growth of pits and the current due to the ionic transport processes in the unattacked portion of the passive oxide layer. The pitting potential should therefore reflect the impedance properties of both the transport processes inside the pits (interfacial reactions at the pit wall and transport processes in solution inside the pit) and the transport processes in the film. Conductivity properties of rutile are believed to be determined in large part by oxygen vacancies which exhibit large values of diffusivity and are influenced significantly by the presence of impurities; large effects of ionic drift are observed in rutile under applied fields (38, 39). The influence of small amounts of added elements and the general trend of pitting potentials with temperature are probably associated with corresponding changes in the ionic transport properties of the passive layer. Impurity concentrations in rutile tend to saturate at a few mole per cent (40). Possibly the small changes in the value of the pitting potential observed on increasing the Al or Mo content of titanium alloys above a few per cent can be attributed to this factor.

Other experiments have shown that crevice corrosion of titanium can be initiated at temperatures much lower than those at which pitting is an important mode of catastrophic attack (7). Several alloying elements seem to be effective in preventing the initiation of crevice corrosion without at the same time shifting the pitting potential to very low values. Fractional percentages of Pd or Ni or somewhat larger percentages of Mo seem to be effective in this respect. The results of Fig. 8 show that the presence of these same elements confers increased protection against pitting corrosion, so that it seems possible to develop titanium alloys which are resistant to both pitting and crevice corrosion attack up to at least 200°C.

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REFERENCES

1. F. W. FINK, *Advances in Chemistry Series*, No. 27, American Chemical Society, Washington, D.C. (1960) p. 27.
2. H. B. BOMBERGER, P. J. CAMBOURALIS AND G. E. HUTCHINSON, *J. Electrochem Soc.*, **101** (1954) 442.
3. F. R. LAQUE AND H. L. COPSON, *Corrosion Resistance of Metals and Alloys*, 2nd ed., Reinhold, N.Y. (1963) p. 654.
4. L. B. GOLDEN, I. R. LANE AND W. L. ACHERMAN, *Ind. Eng. Chem.*, **44** (1952) 1930.
5. D. SCHLAIN, *Corrosion Properties of Titanium and Its Alloys*, U.S. Bureau of Mines Bulletin No. 619 (1964).
6. P. J. GEGNER AND W. L. WILSON, *Corrosion*, **15** (1959) 341t.
7. E. G. BOHLMAN AND F. A. POSEY, *Proceedings First International Symposium on Water Desalination*, Washington, D.C., October 3-9, 1965, U.S. Government Printing Office, Washington, D.C., (1967), **1**, 306.
8. H. KAESCHE, *Die Korrosion der Metalle*, Springer-Verlag, Berlin, (1966) p. 251.
9. C. D. HALL, JR. AND N. HACKERMAN, *J. Phys. Chem.*, **57** (1953) 262.
10. H. BÖHM, *Metalloberfläche*, **11** (1957) 197.
11. O. RÜDIGER AND R. W. FISCHER, *Techn. Mitt. Krupp*, **15** (1957) 194.
12. W. R. FISCHER, *Korrosion* **12**, II Kongress der Europäischen Föderation Korrosion, Frankfurt/Main, 1958, Verlag Chemie GmbH (1960) p. 98.
13. O. RÜDIGER AND W. R. FISCHER, *Z. Elektrochem.*, **62** (1958) 803.
14. S. MORIOKA AND A. UMEZONO, *J. Japan Inst. Metals*, **23** (1959) 185.
15. W. R. FISCHER, *Werkstoffe Korr.*, **10** (1959) 243.
16. R. OTSUKA, *Sci. Papers Inst. Phys. Chem. Res. (Tokyo)*, **54** (1960) 97.
17. W. R. FISCHER, *Techn. Mitt. Krupp*, **19** (1961) 61.
18. W. R. FISCHER, *Techn. Mitt. Krupp, Forsch. Ber.*, **22** (1964) 65.
19. I. DUGDALE AND J. B. COTTON, *Corrosion Sci.*, **4** (1964) 397.
20. W. R. FISCHER, *Techn. Mitt. Krupp, Forsch. Ber.*, **22** (1964) 125.
21. S. MORIOKA AND A. UMEZONO, *Trans. Japan Inst. Metals*, **5** (1964) 198.
22. A. R. PIGGOTT, H. LECKIE AND L. L. SCHREIR, *Corrosion Sci.*, **5** (1965) 165.
23. T. SHIMOSE AND A. TAKAMURA, *J. Japan Inst. Metals*, **29** (1965) 416.
24. H. ZITTER, F. MATZER AND G. KRAXNER, *Werkstoffe Korr.*, **16** (1965) 741.
25. A. L. BACARELLA AND A. L. SUTTON, *J. Electrochem. Soc.*, **112** (1965) 546.
26. E. E. MILLAWAY, *Mater. Protect.*, **4** (1965) 16, 21.
27. R. OTSUKA, *J. Electrochem. Soc. Japan*, **27** (1959) E41.
28. R. OTSUKA, *Sci. Papers Inst. Phys. Chem. Res. (Tokyo)*, **53** (1959) 9.
29. M. STERN AND H. WISSENBERG, *J. Electrochem. Soc.*, **106** (1959) 755.
30. N. D. TOMASHOV, G. P. CHERNOVA AND R. M. ALTOV'SKII, *Russ. J. Phys. Chem.*, **35** (1961) 523.
31. N. D. TOMASHOV, G. P. CHERNOVA AND R. M. ALTOV'SKII, *Z. physik. Chem. (Leipzig)*, **214** (1961) 523.
32. M. E. STRAUMANIS AND P. C. CHEN, *Corrosion*, **7** (1951) 229.
33. M. E. STRAUMANIS AND P. C. CHEN, *Metall*, **7** (1953) 85.
34. M. E. STRAUMANIS AND J. I. BALLASS, *Z. anorg. allgem. Chem.*, **278** (1955) 33.
35. D. FRANZ AND H. GÖHR, *Ber. Bunsenges. physik. Chem.*, **67** (1963) 680.
36. A. J. JOHNSON AND L. L. SCHREIR, *Corrosion Sci.*, **5** (1965) 269.
37. M. POURBAIX, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Pergamon, Oxford, (1966) p. 213.
38. J. MASERJIAN, *Conduction Through Thin Titanium Dioxide Films*, J. P. L. Techn. Rept. No. 32-976, Pasadena, Calif. Oct. 1, 1966.
39. F. A. GRANT, *Rev. Mod. Phys.* **31** (1959) 646.
40. P. EHRLICH, *Z. Elektrochem.*, **43** (1939) 362.

3. KINETICS OF INITIATION OF CREVICE CORROSION OF TITANIUM

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Crevice corrosion is one of several manifestations of localized attack of metals and alloys by electrolytic solutions. Other modes of localized attack include pitting, stress-corrosion cracking, attack at points of contact of metals with dielectrics, and attack in three-phase regions such as at menisci (water-line attack). The possibility of crevice corrosion exists in a solution when contact between metals, or between metal and insulator or dielectric, creates adjacent to the metal a more or less stagnant region of the electrolyte in which molecular and ionic transport are hindered. Common sites for this type of attack are small holes, crevices associated with gaskets, lap joints, bolts and nuts, and in some cases surface deposits such as scales or corrosion products. Many metals, particularly those which can exist in both active and passive states, are subject to crevice corrosion; these include iron and stainless steels, aluminum, copper, titanium, and other pure and alloyed metals.

During this biennium we have analyzed an idealized model of the early stages of initiation of crevice corrosion, with special reference to the case of titanium, on the basis of macroscopic mass-transport theory. Interest in this approach arose as a consequence of some high-temperature measurements carried out previously and subsequent detailed investigation by Griess¹ on crevice corrosion of titanium and some of its alloys. Certain predictions of the model are in substantial agreement with many qualitative observations on the early stages of initiation of crevice corrosion of titanium and may also be useful in understanding the sequence of events which takes place during crevice corrosion of other metals and alloys.

Because of the complexity of the series of events which lead to severe crevice corrosion of titanium in chloride solutions, it was necessary to restrict a kinetic analysis to the very early stages of the process and to make a number of approximations and assumptions. The processes of oxygen

1. J. C. Griess, Jr., Corrosion 24, 96 (1968).

reduction and buildup of acidity within a crevice were treated on the basis of a simplified one-dimensional model. Thus, a liquid-filled crevice of length ℓ and thickness δ ($\delta \ll \ell$) is considered to contain dissolved oxygen at an initial concentration C_O^0 and dilute hydrochloric acid, the only electrolyte present, at an initial concentration C_{HCl}^0 . As time proceeds, oxygen diffuses into the crevice and reacts at the metal surface, and hydrogen ions are produced (100% efficiency for hydrogen-ion production is assumed) as a result of the anodic process on titanium in the passive state. Concentrations of ionic and molecular species are assumed to be constant at the mouth of a crevice ($x = 0$) and equal to bulk concentrations. The current densities, the concentrations, and the potential of the solution phase within the crevice [$\phi(x, t)$] are in general functions of both position and time. The appropriate mass-transport relations (Nernst-Planck equations) were solved explicitly for several interesting cases; both transient and steady-state behavior were examined. The relations presented and discussed below contain the following symbols:

C_H^0, C_{HCl}^0, C_O^0	initial concentrations of H^+ , HCl , and O_2 (moles/cm ³)
$C_H(x, t), C_{Cl}(x, t)$	ion concentrations at position x and time t
D_H, D_{Cl}, D_O	diffusion coefficients of H^+ , Cl^- , and O_2 (cm ² /sec)
F	Faraday's constant (coulombs/equivalent)
j_o	initial current density of the corrosion reaction, pH-independent rate (amp/cm ²)
$j_a(x, t)$	total anodic current density
$j(x, t)$	net current density (difference between anodic and cathodic current densities)
$\bar{k}_a$	formal heterogeneous specific rate constant of the pH-dependent anodic reaction (cm/sec)
n	number of electrons

3.1 Oxygen Reduction in a Crevice

The ultimate distribution of dissolved oxygen within a crevice, due to the competing influences of diffusion from the bulk solution into the mouth of the crevice, diffusion through the electrolyte within the crevice,

and reaction at the metal surface, is given approximately by:

$$\frac{C_0(x)}{C_0^{\circ}} = \frac{\cosh [\sqrt{\gamma} (1 - \frac{x}{\ell})]}{\cosh(\sqrt{\gamma})} \quad (1)$$

with

$$\gamma = j_o \ell^2 / (\delta n F D_0 C_0^{\circ}) \quad (2)$$

The dimensionless parameter γ may be regarded as a measure of the relative rate of removal of oxygen by reaction at the surface compared to the rate of diffusion of oxygen within the crevice. For large values of γ (greater than about 10) the effective depth of penetration of oxygen into the crevice in the steady state is given approximately by $\ell/\sqrt{\gamma}$. Also, the final oxygen concentration at the base of the crevice $[C_0^{\circ}/\cosh(\sqrt{\gamma})]$ is proportional to crevice thickness and bulk oxygen concentration and inversely dependent upon corrosion rate and on the square of the crevice length. Thus Eq. (1) may be useful in predicting semi-quantitatively the oxygen level to be expected within a crevice during the important early stages of the initiation process, since in general the distribution of oxygen within a crevice approaches a steady state well before the acidity within the crevice changes substantially.

3.2 Buildup of Acid Within a Crevice

Figure 3.1 shows experimental data on the corrosion rate of passive, zone-refined titanium, held potentiostatically at an electrode potential of +0.5 V vs S.C.E., as a function of hydrogen-ion concentration and temperature (10^{-6} amp/cm² equals approximately 0.34 mils/year for Ti). In spite of considerable scatter of the data, our expectations were confirmed that the corrosion rate is practically independent of acidity up to about 0.1 M HCl, beyond which the rate increases proportional to the hydrogen-ion concentration. Lines of unit slope were drawn through the data at high acidity in Fig. 3.1. Measurements of this type are quite difficult to make because of problems of reproducibility and of the time required to establish steady states. A minimum of 24 hours was allowed for the attainment of a steady state for each point in Fig. 3.1. As noted

FIG. 3.1 INFLUENCE OF HYDROGEN-ION CONCENTRATION AND TEMPERATURE ON THE PASSIVE CORROSION RATE OF ZONE-REFINED TITANIUM IN 1 M NaCl.

above, the corrosion rate begins to depend directly on hydrogen-ion concentration at about 0.1 M HCl. In a confined area, this is the acidity which would have to be attained in order for the corrosion reaction to become autocatalytic, as discussed below. There seems to be no clearly defined variation of this transition region with temperature. Such data are in qualitative agreement with observations made previously in high-temperature autoclave experiments¹ that solutions contained in highly corroded crevice regions attain acidities as high as 1 M HCl.

The temperature coefficient of the corrosion rate was measured at various acidities in a separate series of experiments. These results are shown in Fig. 3.2. Although considerable scatter of data is evident, it appears that the corrosion process at the potential +0.5 V vs S.C.E. requires an overall activation energy of about 20 kcal/mole. This value is in line with activation energies of other solid-state transport processes of a similar nature. At high acidity, the corrosion rates are shifted to larger values, but the slope of the line, and thus the overall activation energy, seems to be about the same as at low acidities.

These results support a rather simple mechanism which accounts for the existence of an induction period for the initiation of severe crevice corrosion. As noted above, over the greater part of the pH range, from weakly alkaline and neutral solutions down to pH about 1, the rate of the anodic reaction of titanium in the passive region (formation of a TiO₂ layer) is essentially independent of pH. However, in solutions of stronger acidity, the rate of the anodic reaction depends directly on the hydrogen-ion concentration. The current density of the anodic reaction in the interior of a crevice is therefore given by

$$j_a(x,t) = j_o + n F \bar{k}_a C_H(x,t) . \quad (3)$$

Potential gradients, migration, and natural convection may be neglected to a first approximation compared to diffusion and reaction in the early stages of initiation of crevice corrosion. At constant potential the buildup of acidity in a crevice is described approximately by

$$\frac{\partial C_H(x,t)}{\partial t} = D_H \frac{\partial^2 C_H(x,t)}{\partial x^2} + \frac{1}{\delta F} j_a(x,t) . \quad (4)$$

FIG. 3.2 EFFECT OF TEMPERATURE ON PASSIVE CORROSION RATE OF ZONE-REFINED TITANIUM IN 1 M NaCl AS A FUNCTION OF HYDROGEN-ION CONCENTRATION.

Assuming that the initial hydrogen-ion concentration is C_H^0 and that this concentration is maintained constant at the mouth of the crevice ($x = 0$), Eq. (4) may be integrated with use of the dimensionless distance variable, $\zeta = x/\ell$, and the dimensionless time variable, $T = D_H t/\ell^2$, to give the solution

$$\frac{C_H(x,t)}{C_H^0} = 1 + (\Phi_1 + \Psi) \frac{2}{\pi} \sum_{k=0}^{\infty} \frac{(-1)^k \cos[\pi(k+\frac{1}{2})(1-\zeta)]}{(k+\frac{1}{2})[\Psi - \pi^2(k+\frac{1}{2})^2]} \{e^{[\Psi - \pi^2(k+\frac{1}{2})^2]T} - 1\}. \quad (5)$$

In Eq. (5) the dimensionless parameters Φ_1 and Ψ are given by:

$$\Phi_1 = \frac{j_o}{[FD_H C_H^0/\ell]} \left(\frac{\ell}{\delta}\right); \quad \Psi = \frac{n F \bar{k}_a C_H^0}{[FD_H C_H^0/\ell]} \left(\frac{\ell}{\delta}\right).$$

If enough acid is developed in the crevice due to hydrolysis of corrosion products, the anodic process will become autocatalytic. Whether or not this will happen is determined by the magnitude of the Ψ parameter. If the reaction does become autocatalytic, the current can easily become large enough so that, in later stages, a substantial IR drop will develop in the solution phase and force the potential at the closed end of the crevice down into the region of active corrosion; the result is very severe crevice corrosion.

Figure 3.3 shows solutions of Eq. (5) for various values of the Ψ parameter. It plots the relative increase in acidity at the closed end of a crevice as a function of time. For small values of the catalysis parameter Ψ , the ultimate acidity is determined largely by the rate of the anodic reaction in the pH-independent region, as expressed by the Φ_1 parameter. Thus, for $\Psi = 0$, we have $C_H(1,\infty)/C_H^0 = 1 + \Phi_1/2$. For $\Psi \neq 0$, the ultimate acidity is given by

$$\frac{C_H(1,\infty)}{C_H^0} = 1 + (1 + \Phi_1/\Psi)[\sec(\sqrt{\Psi}) - 1]. \quad (6)$$

Solutions of Eq. (6) exist for $\Psi < \pi^2/4$; for $\Psi \geq \pi^2/4$, diffusion of hydrogen ions out of the crevice is insufficient to permit attainment of a steady state and the buildup of acidity and corrosion current would inevitably lead to severe crevice attack. The time required for a significant increase

FIG. 3.3 BUILDUP OF ACIDITY IN CREVICES AS A FUNCTION OF THE CATALYSIS PARAMETER Ψ .

of the acidity in the crevice is of the order of $\delta/\bar{k}_a$; the thinner the crevice and the larger the rate constant of the anodic reaction, the shorter will be the time required for initiation of crevice corrosion.

3.3 Effect of Migration of Reactants and Products

Here we present results of integration of the transport relations for the case where reduction of dissolved oxygen and accumulation of hydrogen ions in a crevice due to diffusion and reaction are considered simultaneously. In addition, the effect of migration of reactants and products on the initiation process is included. Consequently it is possible in this case to estimate both the distributions of hydrogen ions and dissolved oxygen in a crevice and the distribution of potential in the aqueous phase as a function of various kinetic and geometric parameters. However it should be noted that the effect of autocatalysis of the anodic reaction, treated in Section 3.2, is not included in the present case.

In the early stages of the initiation of crevice corrosion, the net current density at any point (x, cm) in the crevice and time (t, sec) is given to a first approximation by

$$\frac{j(x,t)}{j_0} = 1 - \frac{C_0(x,t)}{C_0^0} \quad (7)$$

In the case of titanium the anodic process consists of the formation of a TiO_2 passive layer with simultaneous production of hydrogen ions according to the appropriate stoichiometry, while the cathodic process is reduction of molecular oxygen to form hydroxide ions which can neutralize hydrogen ions formed as one of the products of the anodic process. In crevices of the proper dimensions, diffusion of O_2 from the external solution into the crevice is insufficient to maintain the supply of cathodic reactant. With time hydrogen ions accumulate and chloride ions are transported into the crevice to preserve electroneutrality, the net anodic current density becomes appreciable, and a significant potential drop develops in the solution phase. If the acid concentration and potential drop are large enough, it is then possible for the system to transform to the mode of active corrosion (not treated here), in which the metal corrodes with hydrogen evolution in the absence of the protective oxide layer.

The rate of accumulation of hydrogen ions in the crevice is given approximately by

$$\frac{\partial C_H(x,t)}{\partial t} = D_H \left[\frac{\partial^2 C_H(x,t)}{\partial x^2} + \frac{\partial}{\partial x} \left\{ C_H(x,t) \frac{\partial \Phi(x,t)}{\partial x} \right\} \right] + \frac{j(x,t)}{F \delta} \quad (8)$$

The dimensionless potential variable $\Phi(x,t)$ is equal to $\phi_s(x,t) F/RT$ where RT/F is the thermal volt equivalent (volts) and $\phi_s(x,t)$ is the Galvani or inner potential of the solution phase (volts). The rate of accumulation of oxygen in the crevice is given by

$$\frac{\partial C_O(x,t)}{\partial t} = D_O \frac{\partial^2 C_O(x,t)}{\partial x^2} - \frac{j_O}{n F \delta} \cdot \frac{C_O(x,t)}{C_O^0} \quad (9)$$

where n is the number of electrons involved in the reduction reaction.

The rate of accumulation of chloride ions is given by

$$\frac{\partial C_{Cl}(x,t)}{\partial t} = D_{Cl} \left[\frac{\partial^2 C_{Cl}(x,t)}{\partial x^2} - \frac{\partial}{\partial x} \left\{ C_{Cl}(x,t) \frac{\partial \Phi(x,t)}{\partial x} \right\} \right] \quad (10)$$

Equations (8), (9), and (10) must be solved simultaneously with the electroneutrality restriction, $C_H(x,t) = C_{Cl}(x,t) = C_{HCl}(x,t)$, and the following initial and boundary conditions:

$$\begin{aligned} C_H(x,0) &= C_H(0,t) = C_{HCl}^0 \\ C_{Cl}(x,0) &= C_{Cl}(0,t) = C_{HCl}^0 \\ C_O(x,0) &= C_O(0,t) = C_O^0 \end{aligned} \quad (11)$$

$$\left. \frac{\partial C_H(x,t)}{\partial x} \right|_{x=l} = \left. \frac{\partial C_{Cl}(x,t)}{\partial x} \right|_{x=l} = \left. \frac{\partial C_O(x,t)}{\partial x} \right|_{x=l} = 0$$

In these boundary conditions, the length of the crevice is denoted by $l(\text{cm})$, and concentrations of hydrogen ions, chloride ions, and oxygen are maintained constant at their initial values ($C_H^0 = C_{Cl}^0 = C_{HCl}^0$ and C_O^0) at the mouth of the crevice.

The general solutions of Eqs. (8), (9), and (10) with the boundary conditions of Eq. (11) give the transient behavior of the system in terms of relations involving Jacobian theta functions. The behavior of these general solutions is somewhat difficult to visualize without resort to

numerical methods, and the distributions of concentration and potential attained in the ultimate steady state are of more direct interest. Equations (12) and (13) give the steady-state distributions of HCl and O₂ in the crevice as a function of the various parameters.

$$\frac{C_{\text{HCl}}(x)}{C_{\text{HCl}}^{\circ}} = 1 + \frac{j_o}{2 \delta F D_H C_{\text{HCl}}^{\circ}} x \left(\ell - \frac{x}{2} \right) - \frac{n D_O C_O^{\circ}}{2 D_H C_{\text{HCl}}^{\circ}} \left\{ 1 - \frac{\cosh [\sqrt{P} (\ell - x)]}{\cosh [\sqrt{P} \ell]} \right\}, \quad (12)$$

$$\text{and} \quad \frac{C_O(x)}{C_O^{\circ}} = \frac{\cosh [\sqrt{P} (\ell - x)]}{\cosh [\sqrt{P} \ell]} \quad (13)$$

The parameter P in Eqs. (12) and (13) is given by $j_o / (\delta n F D_O C_O^{\circ})$; the quantity $1/(P)^{1/2}$ is a measure of the depth of penetration of oxygen into the crevice in the steady state.

The distribution of potential in the aqueous phase inside the crevice is given by

$$\Phi(x) - \Phi(0) = \ln \left[C_{\text{HCl}}(x) / C_{\text{HCl}}^{\circ} \right], \quad (14)$$

where the ratio $C_{\text{HCl}}(x)/C_{\text{HCl}}^{\circ}$ is given explicitly by Eq. (12). In a manner common to other problems of this type, the potential drop in the crevice is composed of two components. One of these is an ohmic potential drop, the magnitude of which may be obtained by multiplying Eq. (12) by the ratio $2 D_H / (D_H + D_{\text{Cl}})$. The other component is a junction potential due to differences in mobilities of the hydrogen and chloride ions; this component may be calculated by multiplying Eq. (12) by the ratio $(D_{\text{Cl}} - D_H) / (D_H + D_{\text{Cl}})$.

The importance of the present derivation lies principally in the use of Eq. (14) to estimate the potential drop developed in a crevice. It follows from Eq. (14) that the difference in interfacial potential difference $[\Delta\phi(x)]$ between the mouth and the base of a crevice is given by

$$\Delta\phi(0) - \Delta\phi(\ell) = \frac{R T}{F} \ln \left[1 + \frac{j_o \ell^2}{4 \delta F D_H C_{\text{HCl}}^{\circ}} - \frac{n D_O C_O^{\circ}}{2 D_H C_{\text{HCl}}^{\circ}} \{1 - \text{sech} [\sqrt{P} \ell]\} \right]. \quad (15)$$

The interfacial potential difference at the base of the crevice is polarized negatively by the passage of anodic current due to the corrosion reaction

through the solution phase. If the potential is low enough and if the hydrogen-ion concentration attains a sufficiently high value, then active corrosion of the metal can commence.

The relations presented above may be used to estimate the ultimate acid concentration and potential drop developed in a crevice. Table 3.1 contains results of such a calculation using Eqs. (12) and (15) which were

TABLE 3.1

ESTIMATES OF ACID CONCENTRATION AND POTENTIAL DROP
DEVELOPED IN A TITANIUM CREVICE AS A FUNCTION OF TEMPERATURE*

T(°C)	j_o (amp/cm ²)	D_H (cm ² /sec)	C_{HCl} (ℓ) (M)	$\Delta\phi(0) - \Delta\phi(\ell)$ (volts)
25	2×10^{-8}	9.3×10^{-5}	5.57×10^{-2}	0.221
50	4×10^{-8}	1.35×10^{-4}	7.68×10^{-2}	0.244
100	2×10^{-7}	2.1×10^{-4}	2.47×10^{-1}	0.325
150	7×10^{-7}	2.7×10^{-4}	6.72×10^{-1}	0.405
200	2×10^{-6}	3.5×10^{-4}	1.48×10^0	0.485

*Assumed values of parameters: $\delta = 10^{-5}$ cm; $\ell = 1$ cm; $C_{HCl}^o = 10^{-5}$ M.

based on certain assumed values of parameters thought to be typical of the titanium system. Values of corrosion rate (j_o) as a function of temperature were estimated from available experimental data. Estimates of the diffusion coefficient of the hydrogen ion were obtained from values of the limiting equivalent conductance reported by Quist and Marshall² with use of the Einstein relation between ionic mobility and diffusion coefficient. Crevice thickness was assumed to be approximately equal to the mean surface roughness of polished metal surfaces.³ Other measurements on the influence of hydrogen-ion concentration on polarization curves of titanium, and numerous observations on crevice specimens in autoclave and loop experiments, show that the hydrogen-ion concentration must be of the

2. A. S. Quist and W. L. Marshall, J. Phys. Chem. **69**, 2984 (1965).
3. American Society of Tool Engineers, Tool Engineers Handbook, McGraw-Hill, New York, 1949, p. 1330.

order of magnitude of 1 M and the potential drop in the crevice must be of the order of 0.5 V before severe crevice attack in the active mode of corrosion can be initiated.^{1,4} The results of Table 3.1 show that temperatures of 150°C and above are required to fulfill these conditions for crevices of the assumed dimensions. This conclusion is in good agreement with accumulated experience in corrosion testing of titanium crevice specimens. The increase of corrosion rate with temperature determines principally whether or not sufficient acidity and potential drop can be developed in a crevice to allow initiation of active corrosion of pure titanium.

4. F. A. Posey and E. C. Bohlmann, unpublished observations.

4. EFFECT OF FLOW RATE ON EFFICIENCY OF OXIDATION-REDUCTION REACTIONS IN POROUS AND TUBULAR ELECTRODES

F. A. Posey and F. Nelson

As a result of interest in the possibility of development of new, economical methods for treatment of saline waters, some experiments were carried out on hydrodynamic and electrochemical aspects of oxidation-reduction reaction in porous, screen, and tubular electrodes in order to increase our understanding of factors which contribute to lowered reaction efficiencies at high flow rates. Measurements of polarization curves as a function of solution flow rate through the electrode were made on several types of porous (National Carbon Company, grades 25, 45, and 60) and capillary electrodes operating with equimolar potassium ferricyanide-ferrocyanide (10^{-5} to 10^{-3} M) in 2 M KCl supporting electrolyte.

Deoxygenated solutions were pumped through two porous carbon electrodes of equal length (0.25 to 1.0 cm) and diameter (0.5 cm). The electrodes were held firmly in a section of Tygon plastic tubing and separated by use of a 1-mm glass-wool spacer. Solution entering the back side of one electrode was oxidized or reduced depending upon the polarity of the applied current while the reverse process occurred in the other porous electrode. The current through the cell corresponding to each precisely controlled flow rate was measured with a galvanometer, and the electrical potential difference was determined by use of a potentiometer, in a manner similar to that used in conventional two-electrode polarography.

The current due to the oxidation-reduction reaction was observed to increase with increase in cell potential until it attained a limiting value which depended on the flow rate of the solution. The limiting current per capillary could be computed from Faraday's law for flow rates less than 5×10^{-3} cm³/min (per capillary) in capillaries having diameters in the range 3.3×10^{-3} to 6.4×10^{-2} cm. The efficiency of the redox reaction decreased for flow rates in excess of an optimum value which was determined by the length of the capillary or porous electrode or the diameter of the screen wire. In the region of lowered efficiency, the limiting current was controlled by convective diffusion to the internal surfaces of the electrode and at sufficiently high flow rates could be expressed by a

modification of an equation derived by Levich.¹⁻³ This relation is given by

$$i_L = 5.3 \times 10^5 n C D^{2/3} \ell^{2/3} V_f^{1/3}, \quad (1)$$

where i_L is the limiting current due to convective diffusion of the reacting ions (amp), n is the number of electrons involved in the redox reaction, C is reactant concentration (moles/cm³), D is the diffusion coefficient (cm²/sec), ℓ is capillary length (cm), and V_f is volume flow rate (cm³/sec). It is noteworthy that capillary diameter has no effect on the limiting current.

The results of Fig. 4.1 show how the current (per capillary) varies with solution flow rate for both porous electrodes and a single capillary. The number of capillaries effectively equivalent to a porous electrode was computed from data supplied by the manufacturer. At low flow rates the current efficiency is 100% and the current is given by the expression $i = n F C V_f$, where i is the current per capillary (amp) and F is Faraday's constant (coulombs/equivalent). At higher flow rates the efficiency decreases with increasing flow rate and the current varies with the cube root of the volume flow rate in the laminar flow regime [cf. Eq. (1)]. The Levich equation describes the data well in the region of high flow rates where the rate of the redox reaction is controlled by convective diffusion. Currents (per capillary) calculated for the grade 25 carbon lie below the Levich line because the value of the average pore cross section supplied by the manufacturer was too high.

We have derived a generalized expression for the limiting current, obtainable from redox reactions in porous and tubular electrodes as a function of the solution flow rate, which is valid for both low and high

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1. V. G. Levich, Physicochemical Hydrodynamics, Prentice-Hall, Englewood Cliffs, N. J., 1962, p. 112.
 2. W. J. Blaedel, C. L. Olson, and L. R. Sharma, Anal. Chem. **35**, 2100 (1963).
 3. W. J. Blaedel and L. N. Klatt, Anal. Chem. **38**, 879 (1966).

FIG. 4.1 LIMITING CURRENT FOR 10^{-4} FERRICYANIDE-FERROCYANIDE AS A FUNCTION OF VOLUME FLOW RATE IN POROUS CARBON ELECTRODES.

flow rates. This relation is given by

$$i = n F C V_f \left[1 - e^{-\frac{5.3 \times 10^5}{F} \left(\frac{Dl}{V_f} \right)^{2/3}} \right]. \quad (2)$$

Points calculated by use of Eq. (2) are shown in Fig. 4.1 for the case of electrodes of 0.25-cm length. Good agreement between theory and experiment is evident over the entire range of flow rates, including the transition region between rate control by surface reaction and by convective diffusion. The theory of a number of other cases in the operation of porous electrodes with flowing solutions has also been developed. These results allow one in principle to calculate optimum operating points and other parameters of interest in the use of porous electrodes for electrolysis of saline waters.

5. RECTIFYING PROPERTIES OF VALVE METALS IN A ONE-COMPARTMENT ELECTROLYSIS CELL

P. M. Lantz and K. A. Kraus

A preliminary study was made to determine the feasibility of using valve metals (Al, Zr, Ta, Ti, Nb, Mo-Ti alloys) as rectifying electrodes for electrolysis of 0.25 M Na₂SO₄ at high current density in the one-compartment electrolysis cell described previously.¹ Platinum or lead counter electrodes were positioned opposite the valve metals in the electrolysis cell. The effective area of the electrodes used was 3.2 cm². Voltage was supplied to the electrodes by a Variac operating with 110 volt, 60 Hz AC. Voltage and current were monitored on the screen of a dual-beam oscilloscope and recorded on film with a Polaroid camera.

Visible oxide was formed on the electrode surfaces within a fraction of a second after application of power, and steady states were evidently attained in a short time. However, the 20% and 30% Mo-Ti alloys required much longer to attain a steady state. Possibly this was due to dissolution with time of the Mo in the oxide layer, leaving a more uniform titanium oxide surface.

At an effective voltage of 28 V the ratio of the current flowing in the positive half-cycle to that in the negative half-cycle varied from 6.1 for Zr to 1.1 for Ti. Accordingly, the metals examined may be arranged in the following order of decreasing rectification efficiency: Zr, Ta, Nb, Al, Ti. An applied voltage of 28 V on Zr produced a rectified current of 0.8 amp/cm². The performance of the 30% Mo-Ti alloy was very good for the first 10 minutes at the same voltage, delivering 2.0 amp/cm², but the efficiency decreased after extended use. Tantalum and zirconium were equally good initially, but after use for 30 minutes, zirconium rectified better than tantalum.

In fact, rectification efficiency of all these materials decreased after extended use. It might have been anticipated that the reduction

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1. P. M. Lantz and K. A. Kraus, "Electrochemical Reactors in Flowing Streams Using Porous Electrodes," Section 1.5 in Water Research Program Biennial Progress Report for Period March 15, 1964 to March 15, 1966, Reactions and Transport Phenomena at Surfaces. Corrosion Studies, ORNL-TM-4097 (in preparation).

half-cycle would help to preserve the electrodes, but little evidence is available to support this view. The high resistance of the superficial oxide layer evidently affects adversely the conductance properties in the cathodic half-cycle, thus decreasing rectification efficiency. For these reasons, the utility of valve metals as self-rectifying electrodes in the mode of operation studied appears to be limited.

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6. CHRONOPOTENTIOMETRY OF THE Ag-AgCl SYSTEM AND ANALYSIS FOR THE CHLORIDE ION

Robert E. Meyer, Franz A. Posey, and Paul M. Lantz

Although the theoretical basis of chronopotentiometry is well established for many types of reactions, relatively few analytical applications have been described. Further, little attention has been paid to the case of quasi-reversibility, and there is a tendency to report results as either reversible or irreversible. We present here a discussion of quasi-reversibility of reactions of the type illustrated by the formation of AgCl upon silver, and in addition we show that this system can be used for a simple and accurate analysis for the chloride ion.

DELAHAY, MATTAX AND DERZINS¹ investigated theoretically the case of anodic oxidation of a metal with formation of an insoluble substance and gave the equation for the chronopotentiometric wave assuming that the Nernst equation applies to the reaction. In addition, they showed that reproducible transition times can be obtained for the Ag-AgCl system at a chloride concentration of 5 mM. They reported, however, that the slope which they obtained from the conventional plot of $\log [1 - (t/\tau)^{1/2}]$ vs. potential was 67 mV rather than the theoretical value of 59 mV, at 25°. Furthermore, the value of the solubility product which they calculated from their results is somewhat higher than the generally accepted value, a result which they attributed to the small diameter of the particles of AgCl. They also suggested that reactions of this type might be useful for analytical purposes.

THEORY

The shape of chronopotentiometric waves has been the subject of many treatments and excellent reviews are available²⁻⁴. However, little consideration has been given to the general case of quasi-reversible kinetics. Recently, ANDERSON AND MACERO⁵ have treated the quasi-reversible case for forward and reverse waves. Their treatment covers the case of the reaction, $Ox + e^- = Red$, where both species are under diffusion control. For the case considered here (*i.e.*, the case of a single diffusing reactant ion and an insoluble reaction product) the equations are somewhat different and a graphical method can be used to determine the kinetic constants of the reaction. These equations are given below because our results show that under the conditions investigated here, the formation of AgCl proceeds quasi-reversibly; *i.e.*, the exchange current and the polarizing current are of the same general order of magnitude.

We assume, as did DELAHAY *et al.*¹, that the presence of AgCl on the electrode

surface does not significantly affect the general rate expressions*. JAENICKE, TISCHER AND GERISCHER⁶ have shown that compact highly resistive films are not formed at the current densities used in our work, and therefore no significant resistance is to be expected.

The overall expression for the current density is given by the following equation:

$$[i = i_0(C_1/C_0) \exp [\alpha z(E - E_0)F/RT] - i_0 \exp [-(1-\alpha)z(E - E_0)F/RT] \quad (1)$$

where

$$[i_0 = zFk_a C_0 \exp [+ \alpha z E_0 F/RT] = zFk_c \exp [-(1-\alpha)z E_0 F/RT] \quad (2)$$

In these equations, k_a and k_c are heterogeneous rate constants for the anodic and cathodic reactions, respectively. C_1 is the concentration of the diffusing ion at the interface, C_0 the initial concentration throughout the solution, α the transfer coefficient for the anodic reaction, and the rest of the terms have their usual significance. The equilibrium potential, E_0 , is the potential that a Ag-AgCl electrode system will attain at the concentration, C_0 ; at this potential $C_1 = C_0$. Implicit in these equations is the assumption that the activity of AgCl remains constant during polarization.

The standard boundary conditions for chronopotentiometry are satisfied for this case and therefore²⁻⁴,

$$C_1/C_0 = [1 - (t/\tau)^{1/2}] \quad (3)$$

where

$$\tau^{1/2} = \pi^{1/2} z F \mathcal{D}^{1/2} C_0 / 2i \quad (4)$$

and where $\mathcal{D}$ is the diffusion coefficient of the diffusing ion and τ , the transition time, is the time at which C_1 theoretically decreases to zero.

Setting $\exp [z(E - E_0)F/RT] = \theta$, we have from eqns. (1) and (3),

$$i/i_0 = (C_1/C_0) \theta^\alpha - \theta^{-(1-\alpha)} \quad (5)$$

or

$$[1 - (t/\tau)^{1/2}] = (i/i_0) \theta^{-\alpha} + \theta^{-1} \quad (6)$$

If $(E - E_0)$ and τ are known, then the unknown parameters, αz and i_0 , may be obtained from the chronopotentiometric waves by plotting the data according to the following equation, which is derived from eqn. (6).

$$\log \{ [1 - (t/\tau)^{1/2}] - \theta^{-1} \} = \log (i/i_0) - (\alpha z/2.3) (E - E_0)F/RT \quad (7)$$

The quantity on the left is plotted vs. $(E - E_0)F/RT$, and the slope and intercept yield αz and i_0 , respectively.

From eqn. (6) we note that if $i \ll i_0$, then

$$E = E_0 - (2.3RT/zF) \log [1 - (t/\tau)^{1/2}] \quad (8)$$

and if $i \gg i_0$, we have

$$E = E_0 + (2.3RT/\alpha zF) \log (i/i_0) - (2.3RT/\alpha zF) \log [1 - (t/\tau)^{1/2}] \quad (9)$$

Equations (8) and (9) are, respectively, the equations for reversible and irreversible

* By making this assumption, we do not consider the complexities that could arise due to crystal growth and related phenomena. Our justification for this assumption is that the equations so derived adequately describe the chronopotentiometric waves. A study of the mechanism of formation of AgCl would be interesting but beyond the scope of this work.

waves. If the reaction is completely irreversible, then the term θ^{-1} in eqn. (7) is negligible, and a plot according to eqn. (7) is essentially identical with the standard treatment of irreversible waves. As the reaction approaches reversibility, this method of determining the kinetic constants becomes less accurate, for the expression $(1 - (t/\tau)^{\frac{1}{2}} - \theta^{-1})$ approaches zero (*cf.* eqn. (8)).

If $\alpha z = \frac{1}{2}$, then eqn. (6) may be solved explicitly for E . For positive values of i , we have after setting $s = \theta^{\frac{1}{2}}$

$$i/i_0 = (C_1/C_0)s - 1/s \quad (10)$$

This is a quadratic equation in s which can be solved to give:

$$s = [i/i_0 + \{(i/i_0)^2 + 4C_1/C_0\}^{1/2}] / (2C_1/C_0) \quad (11)$$

or

$$E = E_0 + 4.6(RT/F) \log \{ [i/i_0 + \{(i/i_0)^2 + 4[1 - (t/\tau)^{\frac{1}{2}}]] / 2[1 - (t/\tau)^{\frac{1}{2}}] \} \} \quad (12)$$

Chronopotentiometric waves of the three types are plotted in Fig. 1. For the reversible case (*cf.* eqn. (8)) the potential begins to depart from the equilibrium poten-

Fig. 1. Theoretical chronopotentiometric waves for the process, $M + X^- - e^- = MX$ (insoluble). $\tau = 10$ sec, $z = 1$, $\alpha = \frac{1}{2}$; quasi-reversible case, $i/i_0 = 1$; irreversible case, $i/i_0 = 10$.

tial smoothly and slowly, and the rise in potential at the transition time is quite distinct. For the other two cases (*cf.* eqns. (9) and (12)) there is a marked jump in potential initially and a less distinct rise in potential at the transition time. However, with the use of appropriate techniques, the transition time may be determined without difficulty in all cases.

In practice, the potential does not increase indefinitely to infinity as indicated in Fig. 1. Rather, the potential tends to level off at the next electrode reaction, and a

2

point of inflection is observed very near the transition time. For many cases, it is preferable to determine the transition time by observing this point of inflection through electronic differentiation. At the point of inflection, a peak in the derivative curve is observed, and the transition time can be determined with much more precision. This differentiation technique is especially useful if the reaction is irreversible or quasi-reversible, for in these cases the potential will shift much more than in the reversible case and the potential may then move into the region of the next half before a well-defined rise is observed.

The use of the derivative to determine the transition time by this method has been reported by IWAMOTO⁷. More recently^{8,9}, derivative chronopotentiometry has been used to determine the transition time by a different technique.

EXPERIMENTAL

Apparatus

The design of the cell was based on that of MORRIS AND LINGANE¹⁰ and is shown in Fig. 2. The electrode was cut from silver sheet and held firmly in place by the large stainless-steel bolt. The working area of the electrode was defined by the cut-out

Fig. 2. Cell for chronopotentiometric waves and their derivatives. See text for details.

Fig. 3. Schematic diagram of apparatus for recording chronopotentiometric waves and their derivatives. See text for details.

in the nylon bottom of the cell, and had an area of 1.13 cm^2 . The counter-electrode was a platinum disk placed symmetrically above the silver disk, and the reference electrode was a silver-silver chloride electrode placed directly into the solution. Care was taken to place the electrode near, but just to the side of, the silver disk. All but a few millimeters of the top of the silver reference electrode were insulated with epoxy resin. Measurements with a calomel reference electrode showed that during polarization the

potential of the Ag-AgCl reference electrode stayed constant to within one or two millivolts.

Care had to be taken to keep the electrode clean. Before use, the electrodes were inspected for visual imperfections, polished with a very fine abrasive (*e.g.*, silver polish) and thoroughly degreased and rinsed with alcohol and distilled water. Periodically, the electrode was removed and treatment was repeated. Poorly defined chronopotentiometric waves and irreproducible transition times were generally the signal for recleaning. Care was also taken to prevent gas formation due to excessive polarization. Finally, it was found necessary to reduce the AgCl on the surface after each oxidation cycle with the relay system described below.

The measurement circuit is shown in Fig. 3. Constant current was supplied by a John Fluke Model 407 regulated power supply (John Fluke Manufacturing Co., Seattle, Washington) feeding through an adjustable bank of resistors (R_1). The voltage and resistance were always great enough to insure constant current. The polarity of the current was reversed for the oxidation and reduction cycles by means of a switch operated by a timer relay. The potential of the silver electrode was monitored with a Keithley model 610 electrometer (A_1) (Keithley Instruments, Inc., Cleveland, Ohio) coupled to one channel of a Hewlett-Packard model 7100B dual-channel recorder (Hewlett Packard-Moseley Div., Pasadena, Calif.) The derivative of the $E-t$ curve was also monitored and recorded on the other channel of the recorder. The derivative was supplied by a derivative unit which made use of a Philbrick P65AU operational amplifier (A_2) (Philbrick Researches, Inc., Boston, Mass.) The differentiating capacitor had a value of 20 μ F and the resistor (R_2) was varied to give gain sufficient to drive the recorder. The current was monitored either with ammeters or by measuring the voltage drop across precision resistors. When ammeters were used, they were always calibrated by the ORNL Standards Laboratory. The sequence of operations (explained below) was controlled by adjustable timer relays (Cycl-Flex HP5 series) (Eagle-Signal Co., Moline, Ill.).

Reagents

No special reagents are required for the analyses. One series of test solutions was made up from Long Island Sound sea water. Sulfuric acid, sodium nitrate, or sodium sulfate were used as inert electrolyte, generally at 0.5 *M*.

Analytical procedure

Solutions containing inert electrolyte and known amounts of sodium chloride were used to determine the chronopotentiometric constant, $K = \tau^{1/2}/C_0$ (*cf.* eqn. (4)), over the concentration range of interest. The unknown solutions were made up to approximately ($\pm 25\%$) the same concentration of inert electrolyte, and the current was adjusted until the observed transition time was about equal (generally $\pm 10\%$) to that used for the standard solutions. The concentration was then calculated from the relation, $C_0 = \tau^{1/2}/K$. For maximum accuracy, the electrode was calibrated immediately before use. Analyses with an accuracy of $\pm 3\%$ can be obtained with only occasional calibration (*e.g.*, daily) if care is taken not to damage the electrode surface by abrasion or allowing it to dry out. Electrodes were pre-aged as discussed below by running them through a cycle of at least ten formations and reductions of the AgCl film at the highest concentration of Cl^- in the concentration range of interest.

The transition time was determined by the following sequence of operations: initially, a reduction current was applied to reduce any AgCl formed on the surface. Stirring was also applied during and for a short time after the reduction cycle. A delay of usually about 30 sec was followed by the actual oxidation cycle. The recorder drive was turned on a few seconds before the initiation of the oxidation cycle, and, after the wave was recorded, the reduction cycle was begun again. Thus, the total cycle was repeated in about one minute for the shorter transition times. The reduction was always carried out with the same value of current as the oxidation cycle but extending over a slightly longer time to insure complete reduction of the AgCl. After a few complete cycles, the transition times in an individual series were generally reproducible to within 1%.

RESULTS AND DISCUSSION

Typical chronopotentiograms are shown in Figs. 4 and 5. The derivative of each $E-t$ curve is shown on the same time axis but with an arbitrary vertical axis. The transition time so measured corresponded closely to transition times measured by conventional techniques applied to the $E-t$ curves^{2,3}. However, for unfavorable conditions, the graphical techniques were quite arbitrary, and the use of the derivative was essential to the accurate determination of the transition time.

Figs. 4-5. Chronopotentiometric waves and their derivatives for formation of AgCl on Ag. (4) $C_0 = 4.86 \cdot 10^{-3} M$ NaCl, $i = 3.26 \cdot 10^{-4} A/cm^2$, $\tau = 35.6$ sec, $0.5 M$ Na₂SO₄. (5) $C_0 = 4.95 \cdot 10^{-2} M$ NaCl, $i = 3.35 \cdot 10^{-3} A/cm^2$, $\tau = 29.7$ sec, $0.5 M$ Na₂SO₄.

A small amount of overshoot is observed in Figs. 4 and 5 at the initial section of the $E-t$ curve. This overshoot was observed also when an oscilloscope was used to monitor the potential. However, if the AgCl was formed on a previously formed AgCl layer, the overshoot was not observed. We conclude that a slight amount of crystallization overvoltage may be involved. The overshoot did not interfere with the analysis.

Figure 6 is a plot of $\log (1 - (t/\tau)^{1/2})$ vs. E for the case shown in Fig. 4. Examination of eqns. (8) and (9) show that such a plot should be linear if this $E-t$ curve represents either the reversible or the irreversible case. Except for the initial section, the plot is linear and has a slope of 91 mV/decade. If the reaction were reversible, the slope would be about 59 mV/decade. The deviation from 59 mV/decade is too large

to be explained by a small perturbation from reversibility. Examination of the potential scale of Figs. 4 and 5 shows that the potential has not departed far enough from the equilibrium potential for the reverse reaction (cathodic) in this case to be neglected. Generally, the reverse reaction cannot be neglected unless there is at least a 120-mV difference from the equilibrium potential. For these reasons we have analyzed the reaction as a case of quasi-reversibility, and eqn. (7) may be used.

Fig. 6. Plot of $\log [1 - (t/\tau)^{1/2}]$ vs. E ; test for reversibility. $C_0 = 4.86 \cdot 10^{-3} M$ NaCl, $i = 3.26 \cdot 10^{-4} A/cm^2$, $\tau = 35.6$ sec. $0.5 M Na_2SO_4$.

Figs. 7-8. Determination of i_0 and αz from chronopotentiometric waves. (7) $C_0 = 4.86 \cdot 10^{-3} M$ NaCl, $i = 3.26 \cdot 10^{-4} A/cm^2$, $\tau = 35.6$ sec, $0.5 M Na_2SO_4$. (8) $C_0 = 4.95 \cdot 10^{-2} M$ NaCl, $i = 3.35 \cdot 10^{-3} A/cm^2$, $\tau = 29.7$ sec, $0.5 M Na_2SO_4$.

Figures 7 and 8 show plots according to eqn. (7). The plots are linear except for the initial sections of the curve and the kinetic constants are reasonable. Values of α ranging from about 0.5 to 0.8 have been found and generally the exchange current is about the same order of magnitude as the polarizing current. Table 1 shows some of the results. Since the formation of the AgCl on a solid silver electrode is not a well-defined, reproducible process, variability in the kinetic constants is to be expected. It should be emphasized that these constants refer to the formation of thin, porous films of AgCl on silver. Deviation of the initial section of the curves of Figs. 7 and 8 results from the fact that overshoot is observed on the initial section of the $E-t$ curve.

Table 2 shows the variation of the chronopotentiometric constant with transition time at $0.01 M$. Here it is shown that this constant varies only slightly from transi-

tion times of about 60 sec to about 3 sec. Below 10 sec the constant rises, and below about 0.5 sec it is difficult to obtain a reproducible time. Analyses at transition times of 1-10 sec can be performed by carrying out calibration and determinations at approximately the same transition times. The amount of variation in transition time that can be tolerated depends on the precision required. According to Table 2, a variation of about -1 and +5 sec must not be exceeded at a transition time of 5 sec, in order to keep the permissible error within 1%. For the same precision, a much larger variation can be tolerated at transition times greater than 10 sec. At lower concentrations, the

TABLE 1

KINETIC CONSTANTS DERIVED FROM CHRONOPOTENTIOMETRIC WAVES

C_0, NaCl ($M \cdot 10^{-3}$)	i ($A/cm^2 \cdot 10^{-4}$)	τ (sec)	α	i_0 ($A/cm^2 \cdot 10^{-4}$)
4.9	2.56	56.7	0.63	3.32
4.9	4.42	20.6	0.52	4.07
4.9	6.63	9.7	0.56	6.19
4.9	8.85	5.8	0.56	5.92
4.86	3.26	35.6	0.61	3.17
9.93	8.40	19.75	0.79	6.10
49.5	33.5	29.7	0.71	22.8

TABLE 2

VARIATION OF CHRONOPOTENTIOMETRIC CONSTANT WITH TRANSITION TIME
0.01 M Cl^- , 0.5 M Na_2SO_4

Current density (mA/cm^2)	Transition time (sec)	$K(=\tau i/C_0) \cdot 10^{-2}$
0.460	56.1	3.45
0.535	45.0	3.60
0.663	30.0	3.64
0.918	20.0	3.63
1.154	10.0	3.65
1.657	5.0	3.71
1.88	4.0	3.76
2.21	2.96	3.81
2.77	1.98	3.90
4.09	1.03	4.16
5.66	0.50	4.0

TABLE 3

COMPARISON OF CHRONOPOTENTIOMETRIC AND CHLORIDOMETRIC METHODS FOR
CHLORIDE ANALYSIS OF LONG ISLAND SOUND WATER

Chloridometric (M)	Chronopotentiometric (M)	% Difference
0.2171	0.2123	-2.2
0.1094	0.1098	0.4
0.05537	0.05570	0.6
0.02749	0.02769	0.7
0.01388	0.01398	0.7
0.006961	0.006933	-0.4
0.001865	0.001866	0.05

variation in the chronopotentiometric constant with transition time becomes somewhat greater. We therefore always reproduce the transition time to $\pm 10\%$ at concentrations below $0.005 M Cl^-$.

Table 3 shows a series of actual determinations which were done under conditions designed to obtain maximum precision. The electrode was calibrated with solutions of known concentration at transition times of close to 5 sec (these analyses have been carried out at transition times of 5 sec rather than the more usual 20-40 sec because of our interest in applying this method to flow cells, as described below). With the same electrode surface and interspersed between the calibration runs, the unknowns were run also at transition times of 5 sec. These unknowns were prepared by dilution with distilled water of a sample of the Long Island Sound sea water as shown in Table 3. Analyses of the unknowns were carried out by a Buchler-Cotlove Chloridometer (Buchler Instruments, Inc., Ft. Lee, N. J.) an instrument which makes use of coulometric titration and which we have found to be accurate to 1%. The agreement between the two methods of analyses is within the sum of the precisions expected for the two methods.

Table 4 shows a test of reproducibility and stability of an electrode that was prepared as described above and cycled through a series of oxidations and reductions

TABLE 4
TEST OF REPRODUCIBILITY OF ELECTRODE

Order of determination	Concn. Cl^- (M)	$K (= \tau^{1/2}/C_0)$ $\cdot 10^{-2}$	Mean K $\cdot 10^{-2}$	Rel. Std. Dev. (%)
1	0.0005	3.74	3.98	3.8
7		3.91		
13		4.10		
19		4.08		
25		4.06		
2	0.00075	3.95	3.94	1.3
9		3.87		
15		3.92		
18		3.97		
23		4.01		
3	0.001	4.07	3.98	2.5
6		3.84		
16		4.08		
20		3.94		
22		3.96		
4	0.005	3.72	3.75	0.8
10		3.73		
11*		3.79		
14		3.75		
24		3.78		
5	0.01	3.72	3.74	1.5
8		3.70		
12		3.76		
17		3.83		
21		3.70		

* Run No. 11 begun after leaving cell standing overnight containing $0.005 M Cl^-$.

at a concentration of $0.01\text{ }M\text{ Cl}^-$ before use. The entire series was run over a period of two days. Examination of this table shows that analyses in this range of concentrations should be accurate to within a few per cent without frequent calibration. We have not been able to obtain reproducible transition times at concentrations below $0.0003\text{ }M$ because the derivative peak broadens. In addition, we have found that extensive use of the electrode at concentrations above $0.1\text{ }M$ changes the electrode surface so that it is advisable to recalibrate the electrode if it is to be used again in the concentration range of Table 4. This is not a serious disadvantage, however, since calibration is a very simple procedure.

The substances used as inert electrolyte (Na_2SO_4 , H_2SO_4 , NaNO_3 , all at $0.5\text{ }M$) were interchanged without changing the value of the chronopotentiometric constant. In so doing, the pH was also changed significantly without effect. Other experiments using HCl as the unknown and Na_2SO_4 as the inert electrolyte also confirmed this result. Reducing the concentration of inert electrolyte from $0.5\text{ }M$ to $0.1\text{ }M$ increased the transition time by a few per cent. In general, we tried to maintain its concentration at $0.5\text{ }M \pm 25\%$, but satisfactory analyses could easily be accomplished at $0.1\text{ }M$. De-aeration was found to be unnecessary even at the lowest concentrations. Operation of a second cell with diffusion upward rather than downward also did not affect the results under the conditions of this work.

Aging of the electrode had a beneficial effect at the lower concentrations (below $0.002\text{ }M$). Silver which was freshly prepared generally showed high transition times at concentrations of $0.002\text{ }M$ or below. After an electrode had been aged and used for several determinations, only slight increases in transition times were noted. For this reason, we generally preaged electrodes by running through a series of at least ten oxidations and reductions at the highest concentration of Cl^- .

Finally, we have found that well-defined chronopotentiometric waves can be produced on silver already covered with a thin layer of AgCl . However, this type of surface was much more difficult to reproduce over a wide range of concentrations and currents than the surface formed by complete reduction of the silver chloride.

DISCUSSION

The transition time was easily and precisely determined by the derivative method described above. Whether the transition time so determined corresponds accurately to that defined by the condition, $C_1 = 0$, is not certain, however. For cases where the potential changes sharply enough so that the transition time can be determined directly from the $E-t$ curve, the two methods give closely corresponding results. For use in analysis, accurate determinations of τ are not necessary, however; only precision and reproducibility are required.

More serious is the validity of the assumption that the chloride ion is depleted uniformly across the electrode surface with 100% current efficiency. A small rise in transition time at low concentrations is frequently observed (*cf.* Table 4), and this may indicate that all of the silver ion does not form AgCl at the surface. Either another compound, perhaps the oxide, is formed, or the silver ion leaves the surface without forming insoluble AgCl in a distance short compared to the thickness of the diffusion layer. The fact that aging lowers the transition time at low concentrations suggests that freshly cleaned silver surfaces may not offer many nucleation sites for formation

of AgCl. Alternatively, at freshly prepared silver surfaces there may be an excess of active sites so that Ag⁺ may diffuse from the electrode surface before it can form AgCl.

From the practical standpoint, it is only necessary to reproduce the current efficiency in each run in order to use this technique for analysis. The most important factors for doing this are first, to remove completely the AgCl formed before repeating a run; second, to run the calibration curves and the unknown curves with a carefully reproduced cycle of operations, and finally, to pre-age the electrode as described above.

Use of this techniques offers certain advantages compared to other methods of analysis for the chloride ion. It should be noted that a much simpler apparatus than that shown in Fig. 2 can be used and that, although a Ag-AgCl reference electrode is used, it is only necessary that the potential of this electrode remain approximately constant or drift uniformly during the measurement. Highly accurate measurement of potential therefore is not required as in potentiometric methods of analysis. In fact, it is not even necessary to measure the potential, for only the derivative of the *E-t* curve is required for analysis.

The rapidity and simplicity of this method suggests its use in a flow cell; use of this method is projected in desalination research for routine monitoring of certain process streams. The useful concentration range of the method ($0.5 - 5 \cdot 10^{-4} M$) is ideal for this application, for this is just the concentration range of interest in desalination.

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SUMMARY

Chronopotentiometry of the formation of AgCl upon silver electrodes is described. The kinetic constants for this reaction are derived from the chronopotentiometric waves, which are interpreted to be quasi-reversible. A method of analysis for the chloride ion based upon this system is described.

REFERENCES

- 1 P. DELAHAY, C. C. MATTAX, T. BERZINS, *J. Am. Chem. Soc.*, 76 (1954) 5319.
- 2 P. DELAHAY, *New Instrumental Methods in Electrochemistry*, Interscience, New York, 1954.
- 3 M. PAUNOVIC, *J. Electroanal. Chem.*, 14 (1967) 117.
- 4 D. G. DAVIS, *Applications of Chronopotentiometry to Problems in Analytical Chemistry*, in *Electroanalytical Chemistry, Vol. I*, edited by A. J. BARD, Marcel Dekker, New York, 1966, p. 157.
- 5 L. B. ANDERSON, D. J. MACERO, *Anal. Chem.*, 37 (1965) 321.
- 6 W. JANNICKÉ, R. P. TISCHER and H. GERISCHER, *Z. Elektrochem.*, 59 (1955) 448.
- 7 R. T. IWAMOTO, *Anal. Chem.*, 31 (1959) 1062.
- 8 D. G. PETERS and S. L. BURDEN, *Anal. Chem.*, 38 (1966) 530.
- 9 P. E. STURROCK, G. PRIVETT and A. R. TAPLEY, *J. Electroanal. Chem.*, 14 (1967) 303.
- 10 M. D. MORRIS and J. J. LINGANE, *J. Electroanal. Chem.*, 6 (1963) 300.

7. INFLUENCE OF INERT ELECTROLYTES ON CHRONO-POTENTIOMETRIC CONSTANTS

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Measurements of transition times in chronopotentiometry are influenced by the presence of inert electrolytes. In studies on the Ag-AgCl system,¹ a large number of measurements of the "chronopotentiometric constant" have allowed us to assess in some detail effects of ionic strength and of the presence of inert electrolytes on the determination of chloride ion concentration by this method. Longer transition times are observed as the relative concentration of inert electrolyte decreases, because the transference number of the reacting ion, Cl^- in this case, becomes appreciable compared with the transference numbers of the other current-carrying ions.

Some insight into the influence of inert electrolyte on the chronopotentiometric constant was obtained by solution of a special case of the general transport equations which apply to the motion of ions in the chronopotentiometric situation. Equation (1) is the conventional one-dimensional description of the flux of an ion due to diffusion and migration:

$$v(x,t) = -D \left[\frac{\partial C(x,t)}{\partial x} + z C(x,t) \frac{\partial \Phi(x,t)}{\partial x} \right] . \quad (1)$$

In this equation $v(x,t)$ is the flux (moles/cm²·sec), D is the diffusion coefficient (cm²/sec), $C(x,t)$ is concentration (moles/cm³), z is ion charge with sign, $\Phi(x,t) = F \phi(x,t)/RT$ is a dimensionless potential variable [RT/F is the thermal volt equivalent (V) and $\phi(x,t)$ is potential in the solution phase (V)], x is the distance variable (cm), and t is time (sec). Change of ionic concentration with time is given by

$$\frac{\partial C(x,t)}{\partial t} = D \left[\frac{\partial^2 C(x,t)}{\partial x^2} + z \frac{\partial}{\partial x} \left[C(x,t) \frac{\partial \Phi(x,t)}{\partial x} \right] \right] , \quad (2)$$

which is analogous to Fick's second law for pure diffusion. We treat the case where three ions are present in the system: Na^+ , Cl^- , and X^- ,

1. See Section 6, this report.

where X^- is an inert anion. Then three expressions of the form of Eq. (2) must be considered together with the electroneutrality restriction:

$C_{Na}(x,t) = C_{Cl}(x,t) + C_X(x,t)$. Initial and boundary conditions are:

$$C_{Na}(x,0) = C_{Na}(0,t) = C_{NaCl}^0 + C_{NaX}^0 = C_o + C_1$$

$$C_{Cl}(x,0) = C_{Cl}(0,t) = C_{NaCl}^0 = C_o$$

$$C_X(x,0) = C_X(0,t) = C_{NaX}^0 = C_1$$

$$v_{Na}(x=0) = v_X(x=0) = 0; v_{Cl}(x=0) = -j/F$$

These conditions correspond to anodic chronopotentiometry with the silver electrode of NaCl of initial concentration C_o in the presence of added inert electrolyte, NaX, of concentration C_1 . Note that j is applied anodic current density (amp/cm²) and F is Faraday's constant (coulombs/equivalent).

The foregoing system of equations can be solved explicitly only for the special case where all diffusion coefficients are equal, so that $D_{Na} = D_{Cl} = D_X = D$. Here we present only final results and do not consider details of concentration and potential profiles during the course of the chronopotentiometric transient. Ion concentrations at the electrode surface are given as a function of time by

$$C_{Na}(0,t) = (C_o + C_1) - \frac{j}{F} \left[\frac{t}{\pi D} \right]^{1/2} \quad (3)$$

$$C_X(0,t) = \frac{C_1(C_o + C_1)}{(C_o + C_1) - \frac{j}{F} \left[\frac{t}{\pi D} \right]^{1/2}} \quad (4)$$

$$C_{Cl}(0,t) = \left[(C_o + C_1) - \frac{j}{F} \left[\frac{t}{\pi D} \right]^{1/2} \right] - \frac{C_1(C_o + C_1)}{\left[(C_o + C_1) - \frac{j}{F} \left[\frac{t}{\pi D} \right]^{1/2} \right]} \quad (5)$$

The time required for the chloride-ion concentration at the electrode surface to reach zero is the transition time (τ). With $C_{Cl}(0,\tau) = 0$ in Eq. (5), one obtains

$$\tau^{1/2} = \frac{F(\pi D)^{1/2}}{j} \left[(C_o + C_1) - \sqrt{C_1(C_o + C_1)} \right] \quad (6)$$

for the transition time as a function of the initial concentrations of NaCl (C_o) and of inert electrolyte, NaX (C_1). The chronopotentiometric constant is given by $\gamma = j\sqrt{\tau}/C_o$, and if one recalls that $\gamma_o = F\sqrt{\pi D}$ is the value of this constant in the absence of inert electrolyte, one obtains

$$\frac{\gamma}{\gamma_o} = 1 + \frac{C_1}{C_o} - \sqrt{\frac{C_1}{C_o} \left[1 + \frac{C_1}{C_o} \right]} \quad (7)$$

for the relative value of the chronopotentiometric constant as a function of the ratio of inert electrolyte (NaX) to NaCl, C_1/C_o . The behavior of this function is shown in Fig. 7.1.

The noteworthy feature of the result shown in Fig. 7.1 is that whereas the chronopotentiometric constant observed in nearly pure NaCl solutions is very sensitive to small amounts of inert electrolyte, the constant observed in excess of inert electrolyte is remarkably insensitive to the ratio, C_1/C_o . For example, the chronopotentiometric constant for $C_1/C_o = 10^{-3}$ is about 3% different from that in the absence of inert electrolyte. However, for $C_1 = C_o$ the constant differs from that for the limiting case of large excess of inert electrolyte by only about 17%. This result suggests the possibility of using intentional additions of inert electrolyte to suppress effects of low levels of inert salts on the chronopotentiometric constant.

The effect of inert electrolyte on chronopotentiometric constants in other cases is not as amenable to complete analysis as the case treated here. However, we expect the behavior to be similar to that noted above.

FIG. 7.1 VARIATION OF CHRONOPOTENTIOMETRIC CONSTANT WITH CONCENTRATION OF INERT ELECTROLYTE ($D_{Na} = D_{Cl} = D_X = D$).