ELECTRODE POLARIZATION STUDIES
IN HOT CORROSION SYSTEMS

Progress Report
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ABSTRACT

Work on the following discrete tasks is reported:

Thermodynamic analysis of gasifier models (task complete). Equilibrium calculations have been performed on two and three phase equilibrium involving components of coal gas, sodium salts, and carbon. Electrode polarization studies in molten sodium carbonate. Polarization tests have been performed on iron, steel, nickel, and on 304 and 316 stainless steel in molten sodium carbonate under a variety of exploratory environments. Gas/metal reaction studies. Initial evaluation studies, iron in hydrogen/hydrogen sulfide mixtures, pertaining to a new gravimetric facility are presented. Evaluation of reaction kinetics from polarization (task complete). A visual regression procedure utilizing interactive computer graphics is described for the fitting of multiparameter, nonlinear equations to experimental curves.

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SUMMARY OF RESEARCH

The work reported herein is in compliance with the proposed technical scope of this project, which stated:

"The scope of the work under this contract will be unclassified and will consist of polarization experiments on metals and alloys in sulfur-bearing molten salts under reducing atmospheres. Parallel metallographic analyses and gas/metal reaction studies will be performed. As per agreement, principal investigator effort has constituted approximately 9 academic months at 10% of full time plus 2 1/2 summer months at full time.

PROGRESS REPORT

A. Overall Project

1. Personnel

a. Principal Investigator

Owen F. Devereux, Professor of Metallurgy

b. Graduate Assistants

Richard Cooke - MS completed; employed by Gillette Co., Boston, Mass.

Kyooyoung Kim - PhD expected January, 1980.

Dane Wilson - PhD expected May, 1980.

Also: Ross Boland - inactive during 1978-9, MS thesis re gas phase reactions in preparation.

Venkat Iyer - MS expected January, 1980, initiating study of liquid line corrosion.

2. Publications

a. R. A. Cooke, "Coal Gas/Sodium Salt Equilibria", MS Thesis, University of Connecticut, 1978.

b. K. Y. Kim and O. F. Devereux, "Use of Alumina as a Sheath for the Pt, $\text{CO}/\text{CO}_2|\text{Na}_2\text{CO}_3$ Reference Electrode", J. Electrochem. Soc. **125**, 1796 (1978).

c. O. F. Devereux, "Polarization Curve-Fitting by Computer Modelling", Corrosion, accepted for publication.

3. Result of Major Significance - Evaluation of Electrode Polarization Curves For Fundamental Kinetic Parameters.

a. Scientific Importance

Electrode polarization studies are of scientific interest only to the extent that the data thus obtained can be interpreted in terms of parameters of fundamental scientific meaning. Due to the complex shape of most polarization curves and the multiplicity of parameters involved, such analysis is very difficult in all but the simplest of cases. The technique developed in

this laboratory permits a rapid, inexpensive and accurate determination of these parameters using a visual regression procedure employing interactive computer graphics via the Conversational Monitor System component of the IBM Virtual Machine Facility/370.

b. Relevance to Energy Technology

This technique is of value to energy technology in permitting greatly enhanced facility in scientific interpretation of corrosion test data, thus permitting engineering predictions of materials lifetimes with increased accuracy.

B. Task Summaries

1. Thermodynamic Analysis of Gasifier Models (Cooke)

This task has been completed as per objective. The results of extensive computer calculations and graphical representation are published in thesis form (Ref. 1); one manuscript stemming from this work has been submitted for publication and another manuscript is planned. This work lends numerical understanding to our knowledge of chemical equilibria in coal conversion systems and serves to map composition regions of particular significance, for example, the gas phase compositions that dictate dominance of various anions in the liquid phase. No further work on this task, per se, is planned, although detailed computations regarding specific system compositions are routinely performed as needed.

2. Electrode Polarization Studies in Molten Sodium Carbonate (Kim)

As of the last reporting period the molten salt polarization cell had not achieved a status whereby electrode polarization tests were being performed on a routine basis. The primary goal for this task during the present fiscal period was the achievement of this status, and the use of the facility in the routine generation of significant experimental data for evaluation.

The facility is now in routine use, incorporating the new reference electrode described in the previous report which, at that time, was subject to final testing. We have completed a series of exploratory studies involving various electrode materials and various environments, and are routinely collecting morphological data pertaining to the electrode/electrolyte interface in conjunction with polarization data. We are, at this point, just commencing a restricted methodical study of particular electrode/environment systems for the purpose of identifying specific electrode reactions and evaluating the kinetic parameters thereto.

Our survey indicated experimental restrictions in the use of hydrogen sulfide environments, as described in the next section, and an incomplete understanding of electrode reactions in a simple carbon monoxide/carbon dioxide environment. We have also seen, especially in nickel-bearing materials, an apparent passivity, but

without the dramatic reduction in anodic current associated with passivity in aqueous systems.

Our present level of knowledge concerning the metal/carbonate system suggests delineating specific goals as follows:

- a. Evaluation of the behavior of candidate materials (nickel, iron, steel, stainless steel) in sodium carbonate under simple CO/CO_2 mixtures to identify electrode reactions and evaluate the pertinent kinetic parameters.
- b. In conjunction with item a. it is of particular interest to understand the appearance of current 'blips' and apparent passive behavior during anodic polarization.
- c. Subsequent to work with the CO/CO_2 environment, it is appropriate to add hydrogen and, therefore, water to the gas phase. At this point, a significant alteration in behavior due to the presence of hydrogen is not expected.
- d. On determining the effect, if any, of hydrogen additions to the environment, low levels of hydrogen sulfide will be added.
- e. Study of electrode polarization in systems with a high sulfide content will be identified as a separate task inasmuch as it will be pragmatic to start with a sodium sulfide electrolyte rather than the carbonate electrolyte employed thus far.

Accelerated corrosion at the interline common to metal, salt, and gas phases was seen in some cases. It is convenient to isolate further study of this phenomenon, well-known in aqueous systems, as a distinct task.

3. Gas/Metal Reaction Studies (Wilson)

Following a period of somewhat exploratory work on this task, we now have a fully operational recording gravimetric balance facility for studying the reactions of metals in gases at atmospheric pressure with controlled oxygen and

sulfur activities at temperatures to 1000°C. Familiarity runs have been made, using iron in H_2/H_2S mixtures and achieving results comparable to those reported in the literature. Objectives as presently delineated are:

- a. Complete calibration, etc., of gas flow system,
- b. Determine kinetics and mechanisms of reaction of iron and iron alloys with $CO/CO_2/H_2/H_2S$ mixtures as functions of P_{O_2} , P_{S_2} , and temperature.

This task bears an important relation to the overall program emphasis on reactions in molten salts in that certain parallels in behavior are to be expected. In the gas phase we can duplicate the thermodynamic, but not the kinetic, environment occasioned by the salt, lending additional data to the interpretation of the more complex hot corrosion phenomena.

4. Evaluation of Reaction Kinetics from Polarization Data (Devereux)

This task arose from the simple problem of relating experimental data to complex, non-linear, multiparametric kinetic models. It is essentially complete as per objective. An interactive computer graphics technique has been developed to permit the operator to optimize a kinetic model through visually regressing upon the experimental polarization curve. This is performed rapidly, accurately, and unambiguously. The technique has been reported (Ref. 16 and 17). The method will require sporadic updating as various kinetic models evolve.

C. Extended Discussion of Progress

1. Thermodynamic Analysis of Gasifier Models (Cooke)

Two models of coal gasifier systems were established with the intent of determining the range of system compositions that might be encountered in laboratory environments containing the prime ingredients of the gasifier atmosphere. Model I consisted to two phases, a gas phase containing CO , CO_2 , H_2 , H_2O , H_2S , S_2 , SO_2 , and SO_3 , and a liquid phase consisting of the sodium salts of $\text{CO}_3^{=}$, $\text{O}^{=}$, $\text{S}^{=}$, $\text{SO}_4^{=}$, and OH^- . Eight independent chemical equilibria were assumed to exist between these thirteen species; application of Gibbs' Phase Rule thus indicates five degrees of freedom for the model, logically chosen as total pressure, temperature, and three compositional parameters. The latter were chosen to be P_{CO} , P_{H_2} , and $P_{\text{H}_2\text{S}}$, parameters that could be feasibly controlled in bench-scale apparatus. Numerical solutions were determined and plotted in $P_{\text{CO}} - P_{\text{H}_2} - P_{\text{H}_2\text{S}}$ space for the remaining gas partial pressures and for anion activity ratios for one temperature (1300 K) and two total pressures (1 atm and 10 atm).

Model II consists of Model I with the addition of CH_4 , COS , and O_2 to the gas phase, and a third phase, solid carbon. Twelve independent chemical equilibria exist between these seventeen species, leading to four degrees of freedom for the three phase system, total pressure, temperature, and two compositional parameters, P_{CO} and $P_{\text{H}_2\text{S}}$. This model inherently restricts the carbon activity to $a_{\text{C}} \equiv 1$; solutions for the dependent gas partial pressures and for anion activity ratios were determined through numerical solution of the equilibrium equations and represented graphically for a range of P_{CO} and $P_{\text{H}_2\text{S}}$ values, three temperatures (1100, 1200, and 1300 K) and four total pressures (1, 20, 50, and 100 atm).

The equations resulting from thermodynamic analysis of these models are non-linear, and in the case of Model II yielded multiple solutions in the compositional region of interest. This arises not as a violation of the phase rule; the corresponding equations in chemical potential are linear and have a unique solution, but inasmuch as the overall system composition is not specified the system is

treated mathematically as an open system and, therefore, the standard chemical potentials, inherently unknown, do not drop out of the computation. The pragmatic result of this circumstance is that in regions of multiple solutions one of the 'dependent' compositional parameters, e.g., P_{H_2} , must be arbitrarily assigned one of the two or three unique values that it can possess. This, in essence, constitutes an additional partial degree of freedom.

This project is now complete and has been documented.^{1,2}

2. Electrode Polarization Studies in Molten Sodium Carbonate (Kim)

An electrochemical cell has been developed in which metal electrodes may be anodically or cathodically polarized under molten sodium salts in a controlled gaseous environment at pressures equal to or less than one atmosphere. The practical temperature limit of the cell is presently 1100 C. A standard three electrode configuration is employed, using a platinum counter electrode and a reference electrode developed as part of this program.³ The reference electrode employs a preset CO/CO₂ mixture bubbled over a platinum electrode immersed in molten sodium carbonate; the reference electrolyte is separated from the test cell electrolyte by a recrystallized alumina tube which serves as a membrane permeable to Na⁺. The reference environment is 0.382 atm CO, 0.618 atm CO₂ for convenience; Borucka has noted that the Nernstian correction for this mixture is zero.⁴ The cell is presently in routine use to determine the anodic and cathodic behavior of nickel, iron, and steel in molten sodium carbonate equilibrated with simulated coal gasifier atmosphere. A schematic diagram of the cell and associated peripheral equipment is shown in Figure 1.

Aside from the expected problems of salt/container compatibility, vacuum sealing, pressure regulation, etc., two specific idiosyncrasies of this system have led to delays in the experimental program. First, the significant deliquescence of the sodium carbonate and consequent off-gassing during initial heat-up led to gas lift of sodium carbonate under vacuum, leading to considerable electrolyte

loss and to corrosion of exterior support components of the electrolyte container. This was eliminated via two procedures: 1) Employing only coarse chips of sodium carbonate derived by melting, casting, and crushing the as-received reagent, and 2) Following a carefully programmed out-gassing/drying procedure in which, following a slow temperature increase under vacuum, the reaction vessel was back-filled with the test environment at one atmosphere below the melting point of the salt. The second problem deals with a serious splashback of molten salt into the immersed gas delivery tube when gas mixtures containing hydrogen sulfide are introduced. This is manifested in back pressure in the gas delivery system, occasional cessation of gas flow due to blockage of the delivery tube by solidified salt, and occasional perforation of the Tygon tube bringing gas to the cell. The phenomenon is attributed to a high localized pressure occasioned by rapid reaction of hydrogen sulfide in the feed gas with the molten sodium carbonate although during operation the cell is essentially open to the ambient atmosphere via an unimpeded gas outlet tube. The previously cited thermodynamic analysis of the system indicated that for $P_{H_2S} \gtrsim 10^{-4}$ atm the equilibrium value of the ratio $a_{S^{2-}}/a_{CO_3^{2-}}$ is greater than unity, i.e., the system has a strong propensity to be a sulfide rather than a carbonate. The problem is handled in one of two ways. First, the measurements may be restricted to low values of P_{H_2S} . Despite the higher levels found in typical coal gases, measurements at low values will still permit kinetic determination of the involvement of hydrogen sulfide in electrode reactions. While our present method of flow rate monitoring will not permit accurate setting of levels of $P_{H_2S} < 10^{-2}$ atm, a controlled leak source is being installed to permit P_{H_2S} values as low as 10^{-6} atm to be established. To permit polarization measurements at higher hydrogen sulfide concentrations, the electrolyte can be adjusted to near the equilibrium S^{2-} activity through addition of sodium sulfide. This does pose two problems: 1) Sodium sulfide is very deliquescent; such additions increase the possibility of significant unknown water levels in the electrolyte, and 2) The electrolyte will become essentially a sulfide melt, rather than a car-

bonate melt. While the molten sulfide environment represents a viable area for study, it is a distinctly different program from the study of reactions in a carbonate environment and will be treated as such.

As originally stated in the proposed program, it was intended to control the gaseous and liquid environments of the polarization cell through control of five degrees of freedom, total pressure, temperature, and the partial pressures of hydrogen, carbon monoxide, and hydrogen sulfide. While feasible in principle, this has become difficult in practice because through monitoring gas flow rates we are establishing only pressure ratios, not absolute partial pressures. Hence an additional element of control on the gas feed has been added, P_{H_2O} , and the three compositional variables that are now controlled are P_{CO}/P_{H_2} , P_{H_2S}/P_{H_2} , and P_{H_2O}/P_{H_2} . This has required some modification of the procedure for determining equilibrium activities in the system; however, the previously described thermodynamic analyses remain valid. It is worth noting that the input pressure ratios of four gases are being controlled; equilibrium is presumed to occur via reactions of these gases. Thus it is necessary to control the inlet pressures of those gases that are present in the equilibrium mixture in largest quantity so that the inlet concentrations may be presumed to approximate the equilibrium concentrations.

For the polarization studies described in the following paragraphs, sodium carbonate was prepared as described above and baked in the cell at 250°C overnight at 10^{-4} torr. The system was heated on the following day under vacuum, with the desired gas mixture being introduced into the cell when the temperature reached 800°C (m.p. 858°C). The system was allowed to equilibrate at operating temperature, typically 1000°C, until a stable rest potential obtained, typically five to seven hours. Polarization curves were then obtained at a stepping rate of 3 mv/30 sec. Following polarization, the system was cooled to room temperature and the test specimen was removed for morphological study.

Polarization of Various Materials in CO/CO₂

Figure 2 displays typical anodic polarization curves for platinum, nickel-200 (commercially pure), Armco iron (commercially pure), and 316 stainless steel in sodium carbonate at 1000°C under an atmosphere of 95% CO, 5% CO₂. Several points are notable. The 316 stainless steel shows a rest potential distinctly more active than the other three materials. The rest potential and initial polarization behavior of nickel is indistinguishable from that of platinum. The iron curve is essentially simple, displaying initial mixed potential behavior which becomes increasingly influenced by resistance polarization. The stainless steel is qualitatively similar, but shows a suggestion of passive behavior in the 'blip' appearing at -100 mv. This feature has been seen frequently on different metals and in different environments; it is reproducible and clearly represents an initial electrode reaction being terminated and succeeded by another electrode reaction. The platinum polarization curve displays, in essence, active, passive, and transpassive regions, although the passive current is only a slight decrease from the maximum active current seen. It is possible that two distinct electrode reactions are contributing to the active region. The transpassive region is at this time presumed to represent the anodic half-cell:

The nickel behaves qualitatively in a similar fashion to the platinum; however, a naive interpretation would suggest two distinct regions of passivity. This would have to be interpreted as successive formation of two distinctly different types of passive film, perhaps representing different valence states of nickel. The transpassive reaction is apparently the same that occurs on platinum. It should be noted that, while the traditional onset of passivity in room temperature systems is marked by a large decrease in anodic current density, both the electronic and ionic conductivity of the room temperature oxide that presumably con-

stitutes the passive film are many orders of magnitude lower than those of the same oxide at 1000°C. Hence, the apparent difference between the behavior of iron in an aqueous system and platinum in molten sodium carbonate may be regarded as one of degree and not of kind.

Photomicrographs of sections through the surfaces of the nickel, iron, and stainless steel specimens are shown in Figures 3, 4, and 5, respectively. A thin, uniform, adherent oxide has formed on the nickel, with no noticeable subsurface attack. In contrast, the oxide formed on the iron specimen is thick, granular, and porous, with a thin adherent oxide layer adjacent to the metal underlying the bulk of the film. A subsurface attack predominantly along grain boundaries has preceded actual oxide formation. A substantial portion of the scale spalled off during immersion in the salt. Energy dispersive spectrometry (EDS) did not reveal sodium within the corrosion product. The stainless steel specimen shows two distinct oxide layers, the outer layer being the coarser of the two. Furthermore, there is formation of a second phase in the subsurface region, both along grain boundaries and as a crystallographically oriented precipitate within grains. This is largely restricted to the near surface region. Available analytical techniques have not established whether this phase is an oxide or carbide.

Morphology of Corrosive Attack on Nickel

Sections through the near-surface region of nickel electrodes that have undergone exposure to a number of different cell conditions are shown in Figures 6 through 9. The specimen shown in Figure 6 was simply immersed in quiescent sodium carbonate at 1000°C exposed to ambient air. This exposure has produced a subsurface precipitate, with sporadic precipitation further from the surface. The surface region does not appear to be a discrete film of oxide by virtue of the continuous nature of the grain boundaries in this region. Figure 7 is typical of specimens that were polarized in both anodic and cathodic directions, in sodium carbonate at 1000°C with air, oxygen, or argon passing through the melt.

These specimens are qualitatively similar to that shown in Figure 6 save for the appearance of the dark grain boundary precipitate in the near-surface region. This precipitate has not as yet been identified and, as the specimen underwent polarization in both directions, it is not apparent whether it is associated with an oxidation or a reduction process. Figure 8 depicts an electrode that has been polarized anodically and cathodically at 1000°C under a strictly controlled atmosphere of 95% CO, 5% CO₂. The near-surface precipitation seen is qualitatively similar to that resulting from simple immersion in the air-saturated carbonate. Specimens shown in Figures 6 and 8 are distinguished from that in Figure 7 in that the environment to which the Figure 7 specimen was exposed was continuously depleted of CO₂. Figure 9 illustrates a specimen that was polarized sequentially to environments first containing carbon monoxide and hydrogen sulfide, and subsequently carbon monoxide and hydrogen. The formation of a sulfide scale is clearly evident; an EDS spectrum in Figure 10 documents the presence of NiS in this region.

Morphological analysis of these materials is very incomplete, but the results shown document the dramatically increased attack in the presence of hydrogen sulfide.

Polarization of Nickel in Sulfur-Bearing Environments

Problems concerning the introduction of hydrogen sulfide into the polarization cell were described above. Sporadic success with this procedure did occur, however. An anodic polarization curve for nickel at 1000°C in an atmosphere containing hydrogen sulfide is shown in Figure 11 along with a curve for nickel in a simple carbon monoxide - carbon dioxide environment for comparison. The sulfide-bearing atmosphere was established by mixing carbon monoxide, hydrogen, and hydrogen sulfide in the ratio 47.0 : 52.7 : 0.3 at one atmosphere and passing the mixture through water ($P_{H_2O} = 0.03$ atm) prior to introduction into the cell. Assumption of subsequent equilibrium yields the values shown in Table I. The corrosion rate

Table I

Equilibrium Pressures and Activities Corresponding to Figure 11

<u>Species</u>	<u>Pressure (atm)</u>	<u>Species</u>	<u>Activity</u>
H ₂	0.504	CO ₃ ⁼	1.000*
H ₂ S	2.87 x 10 ⁻³	O ⁼	9.87 x 10 ⁻⁵
H ₂ O	2.87 x 10 ⁻²	S ⁼	1.53 x 10 ³
CO	0.450	SO ₄ ⁼	6.53 x 10 ⁻⁸
SO ₂	6.28 x 10 ⁻¹⁰	OH ⁻	6.23 x 10 ^{-3**}
SO ₃	4.22 x 10 ⁻¹⁹	C	7.01 x 10 ⁻²
S ₂	2.14 x 10 ⁻⁷		
O ₂	3.00 x 10 ⁻¹⁷		
CH ₄	1.41 x 10 ⁻⁴	* defined	
COS	7.93 x 10 ⁻⁵	** activity squared	
CO ₂	1.43 x 10 ⁻²		

is approximately one order of magnitude higher in the presence of sulfide. There is a suggestion of three anodic processes, although this result is not definitive. The high over-potential anodic process seen in the carbon monoxide - carbon dioxide environment, if present, is masked by the high overall corrosion rate. Figure 12 shows a section through this specimen following anodic polarization. The virtual lack of corrosion product in comparison to Figure 9 is suggestive of a high rate of dissolution at large overpotentials.

One experiment was prepared in which the electrolyte was brought to 2.3% sulfur via admixing of sodium sulfide. In this environment, the nickel specimen completely reacted to liquid Ni₂S₃ (established via X-ray diffraction from the recovered solid pellet) in ten hours, without stabilizing electrochemically.

Polarization of Various Materials under H₂/H₂S

Figure 13 shows polarization curves obtained for nickel 200, Armco iron, 1018 steel, 304 stainless steel, and 316 stainless steel at 1000°C under an atmosphere of 95% H₂, 5% H₂S. Due to the aforementioned problem with hydrogen sulfide introduction, each of these experiments had to be interrupted in progress for replacement of the gas inlet tube, resulting in some admission of air. Furthermore, in the absence of control on two other gas species (e.g., CO and H₂O) the thermodynamic state of the system was not established. Nonetheless, these results were recorded for the purpose of documenting the relative anodic behavior of these materials in sulfide-bearing carbonate. Some generalizations are possible. First, nickel is clearly noble, by 300 mv, relative to the other materials tested, while 316 stainless steel is relatively active, by 600 mv. Nickel is the only one of these materials to suggest significant 'passive' behavior and even nickel does not display a significant reduction in anodic current in this region. The Armco iron, 1018 steel, and 304 stainless steel are qualitatively and quantitatively similar, save for the slight 'blip' on the curve for 304 stainless steel, mimicking similar, but more noticeable behavior on nickel and 316 stainless steel and suggestive of a second anodic process. Each of the materials shows two cathodic processes. These are presumed to be

Cathodic polarization curves obtained under a carefully controlled carbon monoxide - carbon dioxide environment showed a single cathodic process.

Effect of CO/CO₂ Ratio on Polarization of Nickel

Polarization curves for nickel 200 at 1000°C are shown in Figure 14 for two different carbon monoxide - carbon dioxide ratios (no hydrogen or hydrogen sulfide) along with the nickel curve obtained in hydrogen - hydrogen sulfide from Figure 13. It is seen that an increase in carbon dioxide content of the environment decreases the cathodic current and increases the anodic current. This is in opposition to the result expected by application of the principle of Le Chatelier to the half cell

This result suggests an inadvertent confusion of anodic and cathodic in the instrumentation; this does not appear to be the case. Alternative possibilities have not been evaluated as of this writing.

Liquid-Line Corrosion

Figure 15 illustrates a partial section through a nickel specimen that partially immersed in sodium carbonate under vacuum at 1000°C; a severe corrosion at the liquid line is evident. In a similar experiment under the 95% H₂, 5% H₂S environment comparable liquid line corrosion was not observed. This phenomenon is well-known in aqueous systems and is related to the diffusion of oxidizing species from the atmosphere through the liquid film comprising the meniscus at the specimen surface. This suggests that a simple diffusion model may be suitable to predict the geometry and rate of this mode of attack in molten systems.

3. Gas/Metal Reaction Studies (Wilson)

Following initial exploratory manometric studies and pursuant to the objectives outlined in the previous progress report, i.e., to study the simultaneous formation of oxide and sulfide on iron and its alloys, a continuous recording gravimetric facility has been designed and constructed; its performance is currently being evaluated.

Specimens are suspended from a Cahn RG recording electrobalance within a vertical, 1.6 cm ID quartz reaction tube, in turn passing through a Nichrome resistance furnace, 1 in. ID, with proportioning control. This balance has a load capacity of 1 g., and can record a weight change of 200 mg. Sensitivity is cited as 0.2 μ g. The furnace is hinged to facilitate removal of the reaction tube and specimen and is fitted with a platinum/platinum-rhodium control thermocouple exterior to the winding, and a chromel/alumel measurement thermocouple exterior to the reaction tube at specimen height. The reactant gas mixture, which is set via a series of needle valves and rotameter gauges, passes into the reaction tube above the furnace and exits below. A stream of argon is simultaneously passed directly into the balance housing and exits with the reactant gas to provide protection of the balance from the sulfide environment. The exit gas is bubbled through a basic solution to absorb the hydrogen sulfide and subsequently flared in a fume hood. Schematic diagrams of this apparatus are shown in Figures 16 and 17. To date there has been some difficulty with back pressure in the gas flow system due to the liquid absorbent downstream from the reaction tube. This in turn causes instability in the gas flow rate, which is manifested in a variation in the drag force seen by the balance. This problem has been controlled by the insertion of a positive displacement gas pump in the line downstream from the reaction tube.

Work to date has been performed on Armco iron, cold-rolled from 1/4 in. dia. round stock into strip, and thence formed into 1.9x0.8x0.04 cm coupons. These are polished through 600 grit paper, degreased, and suspended from the balance on a platinum chain. The reaction chamber and balance vessel are then evacuated to forepump pressure to reduce oxygen content of the system and to seat joints, then flushed with argon. The argon is then displaced with hydrogen and the furnace is brought to reaction temperature. The specimen is held at temperature in hydrogen for annealing and reduction of residual oxide prior to introduction

of the reactant gas. Following reaction the reactant gas is flushed from the system with argon and the specimen is furnace-cooled in the argon environment.

Two typical reaction curves are shown in Figure 18, obtained at 900°C with a constant volumetric flow rate of 210 cm³/min at a nominal one atmosphere pressure. In one experiment the reactant gas was hydrogen sulfide and hydrogen in the ratio 1:10; the other employed the same mixture diluted with argon in the ratio of 1 part argon to 2 parts of reactive gas mixture. The curves are typically S-shaped, with an initial region controlled by linear kinetics, a middle region that is parabolic, and a terminal region presumed to still be diffusion-controlled, but with an increasing time dependence of the geometry due to near-consumption of the specimen. Specimens were completely reacted by the termination of the experiment and were mounted for examination. The parabolic rate constants are of the order of $3 \times 10^{-5} \text{ gm}^2 \text{ cm}^{-4} \text{ min}^{-1}$, of the same order observed by Worrell and Turkdogan.⁵ Although the sulfur activity of the gas in these two experiments is constant, the reaction rate increases with $P_{\text{H}_2\text{S}}$ suggesting that the exterior surface of the reaction film is not at local equilibrium with the environment as is usually assumed. This was noted and treated quantitatively.^{5,6} Inasmuch as there was no remaining metal substrate, the spalling noted by other investigators^{7,8} did not occur. The scale was two-layered, however, with the outer scale being the coarser. The final weight gain is consistent with FeS formation, also reported by many others;^{9,10,11} this has not yet been verified by x-ray diffraction.

4. Evaluation of Reaction Kinetics from Polarization Data (Devereux)

Introduction

The interpretation of semilogarithmic electrode polarization curves is especially difficult when there are competing electrode reactions or when there is no clear-cut region of Tafel behavior.¹²⁻¹⁴ Under these circumstances graphical analysis of polarization curves may be impossible, and statistical analysis difficult due to the nonlinearity of the current-voltage relationship and the

number of empirical parameters needed for a system involving several reactions. To avoid the pitfalls, complexity, and expense of developing and operating the nonlinear regression procedure necessary to a statistical analysis, we have devised a computer-graphics interactive program which enables the operator to make intelligent guesses for the values of the various parameters of a model equation and subsequently test their validity by plotting the equation and the experimental data on a graphics terminal. Subsequent guesses may then be made, tested, etc., until a reasonable fit of equation to data is obtained. This procedure is relatively fast and inexpensive, and efficient in its use of computer time.

Analysis

The current due to a single cathodic reaction experiencing activation, concentration, and resistance polarization may be written¹²

$$i_c = \left[1 - \frac{i_c}{i_{sc}}\right]^{RT/nFb_c} \exp\left[-\frac{v-v_c^0}{b_c}\right] \exp\left[-\frac{i_c R_c}{b_c}\right] \quad (1)$$

where v is the potential of the electrode (relative to a suitable reference electrode); i_c is the current due to this electrode process; R , T , and F are the usual constants; n is the number of charges on the ion whose limiting diffusion rate is responsible for the concentration polarization; i_{sc} is the limiting diffusion current; $2.303b_c$ is the Tafel slope; R_c is the applicable cell resistance; and $\exp\left[\frac{v_c^0}{b_c}\right]$ may be written

$$\exp\left[\frac{v_c^0}{b_c}\right] \equiv i^0 \exp\left[\frac{v^0}{b_c}\right]$$

where i^0 is the 'exchange current' and v^0 , the 'rest potential'. A single empirical constant is chosen to represent the exchange current and rest potential because those parameters have significance only if the reverse electrode reaction makes a significant contribution to the total cell current, and because their arbitrary retention in the model makes intelligent guessing of suitable values somewhat more difficult. Similarly, the current due to a single anodic reaction experiencing

activation, concentration, and resistance polarization may be written.

$$i_a = \left[1 - \frac{i_a}{i_{sa}}\right]^{RT/nFb_a} \exp\left[\frac{v-v_a^0}{b_a}\right] \exp\left[-\frac{i_a R_a}{b_a}\right] \quad (2)$$

Although the choice is completely flexible, our program was written to incorporate one or two anodic reactions, and one or two cathodic reactions. For cases in which there are two cathodic reactions, the reaction possessing the smaller saturation current is presumed not to display resistance polarization; this is both likely and pragmatic inasmuch as the limited data available for that portion of a polarization curve usually precludes accurate determination of a resistance. A similar presumption is made in the case of two anodic reactions. To a first approximation these four current components can be treated as independent and, therefore, additive. In fact, a subtle interaction of these components must exist; however, discussion of this is beyond the scope of this paper. Consequently, the net current passed by the electrode is calculated as

$$i = i_{a1} + i_{a2} - i_{c1} - i_{c2} \quad (3)$$

where i_{a1} , i_{a2} , i_{c1} and i_{c2} are determined from appropriate expressions of equations (1) and (2). At a given electrode potential, v , the following fourteen parameters must be input to the calculation: i_{sa1} , i_{sa2} , i_{sc1} , i_{sc2} , b_{a1} , b_{a2} , b_{c1} , b_{c2} , v_a^0 , v_a^0 , v_c^0 , v_c^0 , R_a , and R_c . The resistances R_a and R_c apply to the second anodic and cathodic components only, the values applicable to the first components being defined as zero. Furthermore, R_a and R_c may well possess the same value; however, there is no particular advantage in so stipulating. In addition, it may be noted that one of the cathodic reactions may be the reverse of one of the anodic reactions; this point is not and need not be specifically addressed. Were this the case and were the energy barrier to that reaction symmetrical, the corresponding values of b_a and b_c would have the same value. Concentration polarization is usually addressed in the context of a cathodic reaction wherein a species in a higher oxidation state in the electrolyte must diffuse to the electrode for reduction.^{12,15} Clearly this can occur with an anodic re-

action also if the reaction involves diffusion of a species in a lower oxidation state in the electrolyte to the electrode for oxidation, or an impeded diffusion of a oxidation product from the electrode as in the formation of an oxide film on the electrode surface. The latter case would not necessarily be described by equation (2), but would, at least, exhibit similar dependencies.

Equipment and Procedure

Although fitting of equation (3) to a set of experimental data involves selection of values for up to fourteen empirical constants, the task is made possible by the fact that each of these constants has a unique, discernible effect on the shape of the curve plotted from the equation. Values for the saturation currents are readily guessed from the data and accurately established by subsequent readjustment. Tafel slopes, even in the case of curves which do not develop a significant straight portion on semilogarithmic plotting, clearly effect the slope of the activation-limited portions of the plot, with a slight effect on vertical or horizontal curve displacement. The values of v_{a1}^0 , etc., affect the displacement of the curve components relative to the axes, while the values of R_a and R_c affect the curve shape only in the high current regions.

Curve fitting is accomplished through a series of programs written in Fortran and PL/I, run via the Conversational Monitor System (CMS) component of an IBM Virtual Machine Facility/370. Input and output, including graphical output, is accomplished with a Tektronix 4006-1 graphics terminal which, in our case, operates as a remote terminal, communicating with the University of Connecticut Computer Center via the telephone line and an acoustic coupler. All programs necessary to the process are stored on disk and are readily accessed through simple commands. To determine the values of the empirical constants corresponding to a given polarization curve, the experimental points to which the fit is to be accomplished are first read onto disk. Subsequently, initial guesses as to the values of the constants are read in, along with the number, 1 or 2, of anodic components and the number, 1 or 2, of cathodic components, and

the experimental and calculated curves are plotted. Based on a visual comparison, new estimates are made and the process is repeated until a satisfactory fit is evidenced. Using the facility described above, a single iteration, from input of trial values to completion of the corresponding plot, occurs in approximately 3 minutes, using about 24 seconds of CPU time for a cost of about \$1.75. It should be noted that use of the telephone line for communication with the central computer facility entails a considerable reduction in transmission rate, and that the iteration time is significantly shorter for direct-wired terminals.

Equations (1) and (2) cannot be solved in closed form for i as a function of v and of the empirical constants; thus it is necessary, for each point on the calculated curve, to determine the values of i for each of the two, three, or four components of the curve by a numerical procedure. In the programs described above this was accomplished by establishing reasonable upper and lower limits of a current range of interest. (The maximum possible value for a given current component is the limiting diffusion current, while very small values are simply negligible.) The initial guess as to the current consisted of the geometric mean of these values. Depending upon the relative magnitudes of the right and left-hand sides of equation (1) or (2), either the lower limit or the upper limit of the current range was reset as this initial guess and the process was repeated. A total of twenty such iterations were performed for each point, accomplishing an increase in resolution for the current value by a factor of $2^{20} \approx 10^6$. For polarization plots covering $-2000 < v < 2000$ mv and $10^{-2} < i < 10^4$ ma/cm² points were determined at 50 mv intervals. This resulted in some loss of resolution in the vicinity of the rest potential for the electrode, where the v vs. $\log i$ curve is nearly horizontal, but the effect is primarily aesthetic and does not interfere with curve fitting.

Typical Results

As an illustration of this procedure, a complete polarization curve was fit to equation (3). The curve represents data obtained by potentiostatic polarization of nickel in molten oxygen-saturated sodium carbonate at 1000°C. Potentials were measured relative to the previously-described reference electrode. This curve had one anodic component and two cathodic components. The value of n was chosen as 2 for all reactions. The most appropriate values found for the empirical constants are listed in Table II.

Table II

Values of Empirical Constants

i_{sa2}	=	360 ma/cm ²
i_{sc1}	=	7 ma/cm ²
i_{sc2}	=	105 ma/cm ²
b_{a2}	=	100 mv
b_{c1}	=	140 mv
b_{c2}	=	20 mv
v_{a2}^0	=	-210 mv
v_{c1}^0	=	50 mv
v_{c2}^0	=	-500 mv
R_a	=	1.5 ohm
R_c	=	1.5 ohm

Points from the experimental polarization curve together with the curve calculated using these parameters are shown in Figure 19.

This visual regression procedure for polarization curve analysis and the corresponding program and its use have been documented.^{16,17}

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FIGURE CAPTIONS

1. Schematic diagram of molten salt polarization cell.
2. Anodic polarization curves for various materials in sodium carbonate at 1000°C under an environment of 95% CO, 5% CO₂. Corresponding electrode morphologies after polarization are shown in Figure 3, 4, and 5.
3. Nickel 200 after polarization under 95% CO, 5% CO₂. 400X.
4. Armco iron after polarization under 95% CO, 5% CO₂. 400X.
5. 316 stainless steel after polarization under 95% CO, 5% CO₂. Top, 80X. Bottom, 400X.
6. Nickel 200 following immersion in quiescent sodium carbonate under air at 1000°C. 400X.
7. Nickel 200 following polarization in sodium carbonate at 1000°C under argon. 300X.
8. Nickel 200 following polarization in sodium carbonate at 1000°C under 50% CO, 5% CO₂. 400X.
9. Nickel 200 following polarization in sodium carbonate at 1000°C first under 50% CO, 50% H₂S and subsequently under 50% CO, 50% H₂S. 300X.
10. EDS spectrum for the sample shown in Figure 9.
11. Anodic polarization curves for nickel 200 in sodium carbonate at 1000°C under 50% CO, 50% CO₂ and under the sulfur-bearing simulated environment described in Table I.
12. Nickel 200 following polarization in sodium carbonate at 1000°C under the simulated environment described in Table I.
13. Anodic and cathodic polarization curves for various materials in sodium carbonate at 1000°C under an environment of 95% H₂, 5% H₂S.
14. Anodic and cathodic polarization curves for nickel 200 in sodium carbonate at 1000°C under 50% CO, 50% CO₂, under 95% CO, 5% CO₂, and under 95% H₂, 5% H₂S.

15. Liquid line region of nickel 200 specimen partially immersed in sodium carbonate at 1000°C under vacuum. 500X.
16. Schematic diagram of gas/metal reaction chamber.
17. Schematic diagram of gas flow through balance chamber.
18. Parabolic plots for reaction of Armco iron in H_2S/H_2 mixtures at 900°C.
19. Experimental polarization curve (dotted line) with curve calculated according to equation (3) using the constants listed in Table II.

Figure 1

Figure 2

Figure 3 400X

Figure 4 400X

80X

400X

Figure 5

Figure 6. 400X

Figure 7. 300X

Figure 8 400X

Figure 9 300X

Figure 10

Figure 11

100X

Figure 12

Figure 13

Figure 14

50X

Figure 15

FIGURE 16
FURNACE AND REACTION CHAMBER

FIGURE 17
BALANCE ASSEMBLY

FIGURE 18

$(\text{WEIGHT GAIN/AREA})^2$ VERSUS
TIME FOR THE SULPHIDATION OF
ARMCO IRON IN H_2S , H_2 AND Ar
GAS MIXTURES, $\text{H}_2\text{S}/\text{H}_2 = 0.1$ AT 900°C .