

Kinetics of Iron Dissolution: A New Approach for Modeling the Anodic Potentiodynamics Based on Transient Analysis

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ABSTRACT

In this work, a new approach is introduced to determine the kinetic constants of the elementary steps involved in the overall reaction of iron anodic dissolution. A procedure based on transient analysis is established, for the first time, that enables the estimation of a series of kinetic parameters that can be used for modeling the anodic potentiodynamics over a wide range of environmental conditions. The findings of the present research enhance the ability of explaining how different environmental factors (CO₂ presence, pH, temperature, steel type, etc.) mechanistically affect the kinetics of iron dissolution.

INTRODUCTION

Although extensive research has been carried out on modeling the cathodic potentiodynamic sweep during the corrosion of iron/steel, previous studies have not been able to layout a systematic approach to mechanistically describe the kinetics and model anodic dissolution. This study offers some insights into the mechanistic modeling of electrochemical anodic reactions at different experimental conditions. For iron dissolution, there are two well-known mechanisms valid for strong acid solutions (pH ≤ 4) in the literature; namely, the “catalytic mechanism” proposed by Heusler et al.,¹ and the “consecutive mechanism” proposed by Bockris et al.² In 1981 and 1986, Keddam, et al.,⁴⁻⁷ reported that multiple dissolution paths exist as several time constants were observed during EIS measurements under well controlled experimental conditions. They claimed that more than one single intermediate and three dissolution paths can be occurring in parallel during iron dissolution under certain experimental

conditions. Hence, Keddam, et al., combined both consecutive and catalytic mechanisms into a single multipath scheme (Figure 1) to define a plausible explanation for such observations.⁴

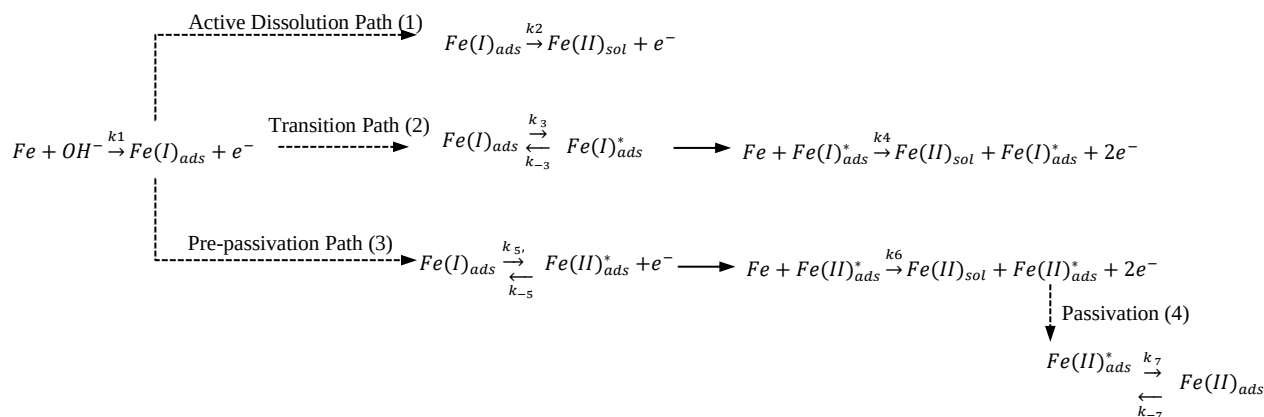


Figure 1. The multipath iron dissolution mechanism, adapted from Keddam et al.⁴

In this scheme (Figure 1), the first and the second elementary steps (Path (1)) approximate the Bockris' mechanism (non-catalytic path).² In our previous research,⁸ thirty-eight different pathways were investigated for the mechanism of iron dissolution in strong acid and it was found that the experimental observations in the active range of dissolution were explainable only by relying on Bockris' mechanism.²

Figure 2 shows an anodic sweep for a pure iron rotating disk electrode (RDE) sample in 0.5 M Na₂SO₄ electrolyte at pH 5 (25 °C). In Figure 2, at low anodic overpotentials, active dissolution takes place, while a decrease in current density can be observed at more positive overpotentials in the transition range. This behavior is described as the “S-shape” segment of the anodic sweep. At more positive overpotentials beyond the transition region, there is an increase in current which is defined as the pre-passivation dissolution range, followed by the passive state and a marked drop in the current density. These transformations in the anodic sweep cannot be explained by assuming only a single dissolution path (or a single adsorbed intermediate) as hypothesized by Bockris.²

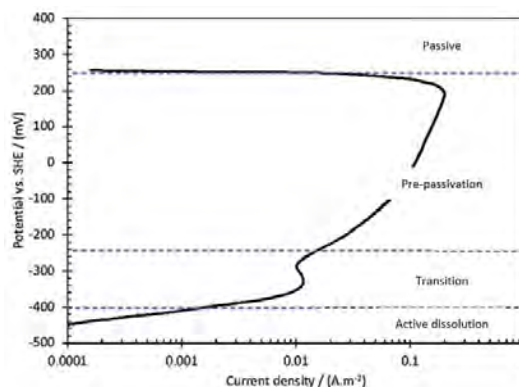


Figure 2. Anodic sweep for pure iron RDE sample in 0.5M Na₂SO₄ at pH 5 (25 °C), scan rate: 6.6 mV/s, rotation rate: 4140 rpm.³

At more positive overpotentials, paths (2) and (3) are written following Heusler's catalytic iron dissolution mechanism.¹ The reason they are called catalytic is because of the formation of an intermediate (those compounds marked by a star) that can react more readily with another reactant to proceed with the dissolution reaction much faster. These intermediates are neither consumed nor produced.

Although it seems comprehensive, Keddam's multipath scheme⁴ is very complex. Seven elementary steps with 20 kinetic constants make it almost impossible to determine independent values

for each of them using a methodical approach. Keddam et al.⁴ used trial and error to determine the various kinetic constants in order to model the entire potentiodynamic sweep range as well as EIS data. In contrast, a different approach is developed in the present study to estimate the kinetic parameters using a simplified theory. In order to do that, the scheme developed by Keddam et al.⁴ needed to be abridged to have fewer degrees of freedom, enabling the introduction of a deterministic method for estimating the parameters and subsequently modeling the anodic sweeps.

A two-path scheme, shown in Figure 3, is proposed in this study. In this scheme, the non-catalytic path is in parallel with only one catalytic path. Indeed, this idea combines two fundamental theories into a single one without any further complications. In this work, it has been proposed that using this scheme can reasonably model the anodic potentiodynamic and capture the nonlinearity of the anodic sweep over the potential ranges slightly above the transition region as shown in Figure 4. This simplified scheme is more pragmatic since it provides a platform based on which one can more easily model the steady-state kinetics. In addition, this platform enhances the capability of describing the influence of different environmental/metallurgical factors on anodic dissolution.

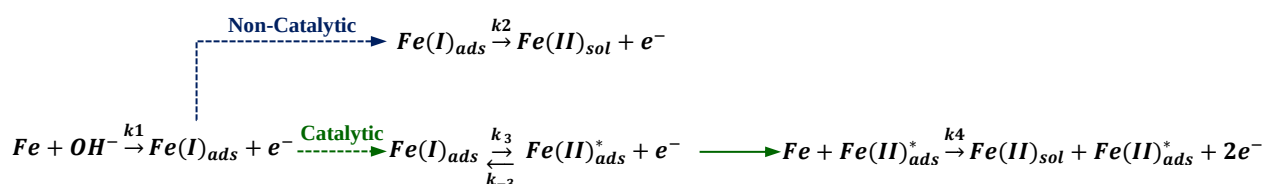


Figure 3. The theoretical scheme introduced in this study.

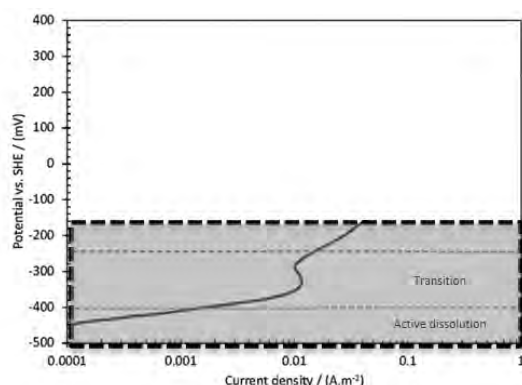


Figure 4. The range of interest for the current corrosion studies.

A few assumptions have been made in this study. First, it has been assumed that no corrosion product is produced. Although the applicability of the present work for corrosion modeling is promising, the formation of corrosion film adds further complexities beyond the scope of the present work. It is also assumed that the reaction rate for each elementary step (i) follows an exponential function of potential as described by Eq. 1 (Tafel law):

$$k_i = k_{i,0} \exp\left(\frac{2.3E}{b_i}\right) \quad (1)$$

where $k_{0,i}$ is k_i at the reference potential of zero vs. SHE reference electrode. b_i is the Tafel value or the magnitude of the polarization that is needed to initiate that specific elementary step. k_i is a function

of potential. The kinetic parameters $k_{0,i}$ and b_i are independent of potential but are influenced by environmental parameters such as pH, temperature, electrolyte, etc. b_i is different from the conventional known Tafel slope, as the latter one is defined for only the overall reaction containing a single rate-determining step (rds). Considering the new scheme shown in Figure 3, there are five potential-dependant k_i and each one contains two potential-independent variables ($k_{0,i}$ and b_i). Therefore, ten kinetic parameters need to be estimated in this study for every experimental condition ($k_{0,1}$, $k_{0,2}$, $k_{0,3}$, $k_{0,-3}$, $k_{0,4}$, b_1 , b_2 , b_3 , b_{-3} , b_4 ; where b_i is in V/dec. and $k_{0,i}$ is in $\text{mol.m}^{-2}.\text{s}^{-1}$).

EXPERIMENTAL METHOD

A 2-liter glass cell with a rotating cylinder electrode (RCE) as a working electrode (WE) was used. A ring-shaped platinum-coated titanium mesh counter electrode (CE) was used for completing the circuit to allow the charge to flow, and an Ag/AgCl reference electrode (RE) was used with respect to which all potentials were measured. The ring-shaped counter electrode was used to provide a more symmetric current distribution around the rotating WE. An overview of the experimental setup and test matrix are shown in Figure 5.



Parameter	Conditions
pH (± 0.02)	4 - 6
Environment	Strong acid: 0.97 bar N_2 sparged
	Weak acid: 0.97 bar CO_2 sparged
Electrolyte	2.5 – 2.9 wt.% NaCl ($R_s \sim 0.78 \pm 0.08 \Omega$ for all measurements)
rpm	100, 1000
Temp. (± 0.5) $^{\circ}\text{C}$	25 - 45
Test set-up	2L glass cell, RCE
Motor rotation speed	2000 rpm
Materials	Pure Fe, X65, 2% Cr steel

Figure 5. Overview of the RCE experimental setup and test matrix.

Potentiodynamic and potentiostatic transient measurements with a high sampling rate (~ 3 microseconds per data point) were conducted using a Gamry potentiostat Reference 600. Each test was repeated at least four times to reduce the statistical uncertainty. Uncertainty for all measurements is reported in this study. All RCE specimens were polished up to 1200-grit, rinsed with DI water and isopropanol alcohol, and dried with nitrogen gas before every experiment. High-purity N_2 or CO_2 gas was sparged continuously through the test solution to de-oxygenate the electrolyte during all measurements. Diluted NaOH and HCl were used to adjust the pH. It was important to make sure that the solution resistance for all measurements was the same. Before each measurement, EIS was recorded to assure that the solution resistance was consistent for all measurements and always within the range of $0.78 \pm 0.08 \Omega$.