

Nonlinear phenomena in the electrochemical oxidation of sulfide

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Abstract

The electro-oxidation of sulfide on a Pt electrode is found to exhibit both N-NDR (negative differential resistance) and HN-NDR (hidden negative differential resistance) types of oscillations, making it the first system known to be capable of supporting both types of nonlinear instabilities without changing electrolyte compositions. Six distinct oscillation windows are observed when the external current is adjusted as the control parameter. In addition, temperature also exhibits subtle influences on the observed reaction behavior, where varying the temperature from 30.0 °C results in more complicated oscillatory phenomena.

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1. Introduction

Understanding the onset of non-equilibrium phenomena in electrochemical reactions has far reaching impacts [1–5]. The observation of Turing-type patterns on electrode surfaces [5], for example, points to a prospective exploitation of pattern-forming mechanism to manufacture structured electrodes similar of those being developed for the (bio)sensors, where wavelength of the pattern could be conveniently manipulated by changing reaction conditions such as temperature, concentrations of electrolytes and values of the applied potential/currents. Based on the electrochemical impedance spectra (EIS), Strasser and co-workers [6] and Krischer [7] have classified electrochemical oscillations into four categories. According to their methods, the appearance of an N-shaped potentiostatic curve indicates that the studied system belongs to class-III, N-NDR (negative differential resistance), or class-IV, HN-NDR (hidden negative differential resistance) oscillators.

Due to their importance in both industrial productions and scientific researches, oxidations of sulfur-containing species have garnered a great deal of interests in the last two decades [8–21]. The oxidation could take place by reacting with various oxidants such as chlorite, bromate and hydrogen peroxide or via an electrochemical method. Nonlinear phenomena including both simple and complex oscillations and bistabilities have been seen in the studies of electrochemical oxidations of sulfur compounds [8–10]. For example, Chen and Miller [8] recently reported potential oscillations in the electrocatalytic oxidation of sulfide on a microstructured Ti/Ta₂O₅–IrO₂ electrode. In this study, we report that the electro-oxidation of sodium sulfide on a platinum electrode is capable of exhibiting both N-NDR and HN-NDR types of oscillations. As shown in the following, various new phenomena including six distinct oscillation windows are observed.

2. Experimental procedure

The working electrode is a polycrystalline platinum disk electrode with a diameter of 2.0 mm (CH Instruments INC., USA) and the counter electrode is a Pt wire. A Hg|Hg₂SO₄|K₂SO₄ electrode is used as the reference

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electrode. The working electrode is polished with fine alumina powder ($0.05\ \mu\text{m}$) before its usage and is then activated in $1.0\ \text{M}\ \text{H}_2\text{SO}_4$ solution by cyclically varying the applied potential between -0.2 and $1.2\ \text{V}$ (vs. SCE) at a rate of $1.4\ \text{V/s}$ for $30\ \text{min}$. The Pt electrode is rinsed repeatedly with de-ionized Milli-Q water (Millipore) after the activation process. All experiments are carried out with a CHI-660A Electrochemical Station (CH Instruments), except that the electrochemical impedance spectroscopy (EIS) is measured with a IM6e Electrochemical Workstation (Zahner-elektrik GmbH Co. KG). Reactions take place in a single cell reactor thermostated through a circulating water bath ($\pm 0.1\ ^\circ\text{C}$, Polyscience Instrument). The volume of the reactor is $40.0\ \text{ml}$.

The cylindrical reactor has an internal diameter of $5.5\ \text{cm}$. The three electrodes form an equilateral triangle with a length of $1.8\ \text{cm}$. The resistance of solution in the electrochemical cell is about $25\ \Omega$. Experiments performed with deaerated electrolyte solution produced the same results as reported in this study. All reagents used in this study are analytical grade. Na_2S and H_2SO_4 solutions are prepared with de-ionized water. The concentration of H_2SO_4 solution is determined by titrating against a standard Na_2CO_3 solution.

3. Results and discussion

Fig. 1(a) presents the linear galvanic voltammogram of $1.0\ \text{M}\ \text{Na}_2\text{S}$ solution, in which the scanning rate equals $0.01\ \mu\text{A/s}$. The slow variation in current functions as a bifurcation control parameter, leading the system through an oscillatory window. This voltammogram illustrates that as the applied current is increased from 0, the measured potential increases almost linearly until the current density reaches $2.1\ \text{mA/cm}^2$, where large magnitude fluctuations in the potential are detected. When the applied current density is increased to above $4.7\ \text{mA/cm}^2$, oscillations in the potential disappear. Notably, potential of the sulfide system stays constant at about $-0.4\ \text{V}$ after moving out of the oscillatory region, despite the current is continuously increased. The second oscillation window appears when the applied current density becomes larger than $7.0\ \text{mA/cm}^2$ and ends at $8.0\ \text{mA/cm}^2$. From there, further increasing the current density does not induce visible fluctuations in the potential.

Fig. 1(b) presents the linear galvanic voltammogram in an extended current range. In addition to the regions I and II seen in Fig. 1(a), four more isolated windows with distinct dynamic properties are observed. For example, although there is no potential fluctuations seen in region III, transient oscillations could still be observed under galvanostatic conditions (see Fig. 2(c)). There is an abrupt jump in the potential when the current density is increased to $60\ \text{mA/cm}^2$. Beyond that, the sulfide system stays at the high potential state as the current is increased still. There are three distinct oscillatory regions within this current

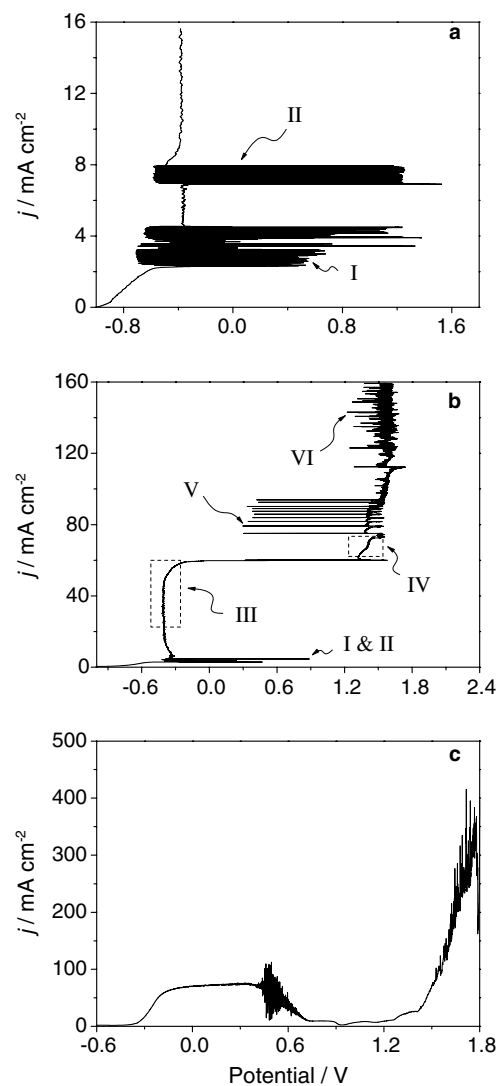


Fig. 1. (a) Linear galvanic voltammogram collected at a scan rate of $0.01\ \mu\text{A/s}$; (b) linear galvanic voltammogram collected at a scan rate of $0.02\ \mu\text{A/s}$; and (c) linear voltammogram obtained under the scan rate of $0.05\ \text{mV/s}$. Temperature is maintained at $20.0 \pm 0.1\ ^\circ\text{C}$.

range. It is noteworthy that properties of the galvanostatic oscillations in these six regions are significantly different from each other. Examples of these oscillations are presented in Fig. 2.

In Fig. 1(c) the potential is scanned linearly from $-0.6\ \text{V}$ at a rate equal to $0.05\ \text{mV/s}$. There is no reaction activity until the potential is larger than $-0.4\ \text{V}$. The current is then found to increase linearly until a plateau is reached. The increase in the anodic current results from the oxidation of sulfide ions. Remarkably, oscillations in current appear when the applied voltage becomes larger than $0.4\ \text{V}$. The result that oscillations take place around a plateau suggests that mass transportation near the Pt electrode is a limiting factor [7]. The oscillatory phenomenon disappears as the potential is increased to $0.7\ \text{V}$. However, as the potential reaches $1.5\ \text{V}$, oscillatory behavior appears again, exhibiting

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