



Nonlinear Instabilities during the Electrochemical Oxidation of Hydroxymethanesulfinate

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ABSTRACT

Electrochemical oxidation of hydroxymethanesulfinate on platinum and gold electrodes was investigated in this study. Scanning electron microscopy measurements show that the electro-oxidation process caused significant pitting of Au electrodes. The continuous dissolution of the Au surface is likely to have played an important role in the sustained simple and complex oscillatory behaviors in both current density and potential observed on Au surface. On a Pt surface, only transient oscillations were observed under potentiostatic conditions, whereas sustained potential oscillations were seen under galvanostatic conditions. Electrochemical impedance spectroscopy (EIS) results indicate that the oxidation of hydroxymethanesulfinate possesses a hidden negative differential resistance, suggesting that this electrochemical oscillator belongs to the HN-NDR class. Mass spectroscopy analysis of the reaction solution suggests the formation of thiosulfate ($S_2O_3^{2-}$), bisulfate (HSO_4^-) as well as sulfite (SO_3^{2-}).

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1. Introduction

Dynamic instabilities in electrochemical reactions have been a topic of great interest ever since the first report of oscillating current in an electrochemical cell in 1828 [1–4]. Oscillations in electrochemical systems have been uncovered during the oxidation or reduction of various organic and inorganic substances as well as during the corrosion of various metals [5–14]. For example, the dissolution of vanadium, iron, copper, nickel, and cobalt (amongst others) has been found to lead to oscillatory behavior [15–21]. In the dissolution or corrosion driven oscillatory systems the decrease in active surface area caused by transitions between passivation and activation of the electrode surface are suggested to be responsible for the nonlinear characteristics.

An important mechanistic tool in the characterization of electrochemical oscillators is electrochemical impedance spectroscopy (EIS), which measures the systems impedance at a specific potential over a range of frequencies. The resulting information, when plotted as a Nyquist diagram, can easily give important information regarding the type of electrochemical oscillator [22,23]. The common aspect of these oscillators is the presence of a negative differential resistance (NDR). In terms of the

shape of their linear voltammogram, the three most frequently occurring types of electrochemical oscillators are S-Shaped with a negative differential resistance (S-NDR), N-Shaped with a negative differential resistance (N-NDR) and hidden N-Shaped with negative differential resistance (HN-NDR) [22]. In systems that contain NDR the double layer potential (φ_{dl}) acts as an essential variable (autocatalytic in the case of N-Shaped plots or acting as the slow variable in S-Shaped plots) occurring at regions of negative Faradic resistance [24]. The oscillations in these types of systems arise through the presence of a positive feedback loop (supplied through the NDR) and a negative feedback loop (surface coverage of a potential dependent adsorbed species or surface concentration of an electroactive species) [22,24]. Less commonly, oscillations in electrochemical systems can also occur through other mechanisms such as convection induced or capacitance mediated positive differential resistance, neither of which relies on the presence of NDR [25,26].

In this study, dynamical behavior in the electro-oxidation of hydroxymethanesulfinate (HMS) was investigated. HMS is an important sulfur based reducing agent and has been used in the reduction of vat dyes, in anticancer formulations as an antioxidant stabilizer, and in emulsion polymerization experiments as a redox initiator [27–29]. Earlier studies have shown that the decomposition of HMS may occur in parallel with main reactions, resulting in the conspicuous consumption of the reagent in the industrial process. Polenov and coworkers have developed a kinetic model

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for the decomposition of HMS in aqueous solution [30]. The investigation of its electrochemical reaction behavior shall provide useful insights into the chemical stabilities. The fact that HMS contains a hydroxyl group as well as a sulfur atom also makes this kinetic study particularly interesting due to the fact that (1) very rich nonlinear phenomena have recently been observed during the oxidation and bromination of aromatic compounds containing hydroxyl functional groups [31–33], and (2) many sulfur-containing compounds have been found to be ideal candidates for the study of macroscopic reaction dynamics due to the fact that sulfur contains multiple oxidation states. Temporal oscillations have been reported in systems utilizing sulfur compounds, and various interesting spatial patterns have been observed in reaction diffusion experiments [34–37]. Sulfur containing compounds such as thiosulfate, thiourea, and hydrogen sulfide have also been found to support electrochemical oscillations [38–43]. As shown in the following, oscillations in both potential and current density are observed at Pt and Au electrodes. Notably, the oxidation products of HMS show strong interactions with Au, leading to severe pitting of the Au surface.

2. Experimental

The electrochemical experiments were performed on a Voltalab PGZ100 system (Radiometer Analytical, USA) and CHI 660D/760E (CHI Instruments, Texas, US). Polycrystalline platinum and gold electrodes with diameters of 2.0 mm (CHI Instruments) were applied as working electrodes. The counter electrode was a platinum film (Shanghai Ruosull Technology Co., LTD) and a saturated calomel electrode (SCE) was applied as the reference electrode. Before each experiment the working electrode was polished with fine alumina powder (0.05 μm), rinsed with double distilled water, cleaned by an ultrasonic cleaner (Branson 1510, USA) for 10 minutes, and again rinsed with double distilled water. The three electrodes were placed in the traditional triangle configuration and all electrochemical experiments were performed at room temperature ($22 \pm 2^\circ\text{C}$).

Reagents sodium hydroxymethanesulfinate ($\text{CH}_3\text{NaO}_3\text{S} \cdot 2\text{H}_2\text{O}$, 98+%), potassium ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6$, 99%) and potassium chloride (KCl, 99+%) were purchased from Sigma Aldrich. All reactions contained 0.2 M sodium hydroxymethanesulfinate (with no additional supporting electrolyte), unless otherwise stated. Reaction volumes were held constant at 60.0 mL, and all experiments were performed under ambient conditions (no purging with inert gases). Electrochemical impedance spectroscopy experiments were measured in the frequency range of 100 kHz to 34 mHz (unless otherwise stated) with an amplitude of 5 mV and 12 points per frequency decade were collected. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were performed with a Quanta 200 FEG microscope (FEI, Inc.). Mass Spectroscopy measurements were taken on a Micromass LCT – electrospray ionization time-of-flight mass spectrometer. Images were also taken with a charge coupled device (CCD) camera equipped with a zoom lens.

3. Results and Discussion

3.1. Oxidation Behavior on a Gold Surface

Fig. 1a shows a linear sweep voltammogram at a scan rate of 0.5 mV/s. Using such a low scan rate allows one to mimic potentiostatic conditions where the applied potential can be considered a control parameter, gaining information on the various dynamic regimes of the system. Here, oscillations with a high frequency emerged at around 0.8 V (vs. SCE electrode) and existed over a large potential range (0.8–2.0 V). At even higher potentials,

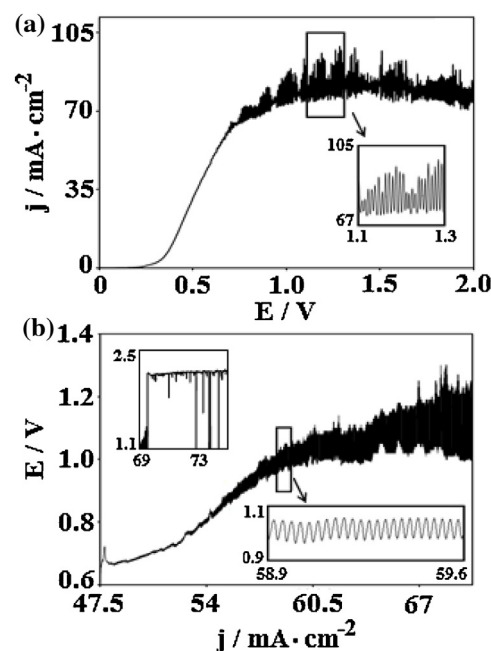


Fig. 1. (a) Linear sweep voltammogram performed with a scan rate of (i) 0.5 mV/s. (b) A current ramp experiment performed between 47 mA/cm² and 70 mA/cm² mA at a scan rate of 1.0×10^{-4} mA/s. Experiments were performed on a gold working electrode.

vigorous bubble formation was seen, indicating that the oxidation of hydroxide ions became significant under those conditions. Fig. 1b shows a current ramp experiment performed between 47 and 70 mA/cm² at a scan rate of 3.2×10^{-3} mA/cm² s. As can be seen here, high frequency potential oscillations occur, which grow in amplitude as the current is increased. Past 70 mA/cm² large bubbles may form on the working electrode which cause an immediate jump in the potential to approximately 2.2 V, which returns to the low potential once the bubble bursts, as shown in the inset in Fig. 1b.

The effect of altering the applied potential on the electrochemical oscillations is shown in Fig. 2. At a constant external potential of 0.9 V (Fig. 2a) the current density can be seen to decrease while oscillations of a moderate frequency persist for approximately 10 minutes before low frequency, low amplitude oscillations emerge. When the potential was increased to 1.0 V in Fig. 2b the current density again decreased at the onset of the reaction, reaching a stable current density after approximately 5 minutes. The amplitude and frequency of the oscillations had increased in comparison to the results of Fig. 2a. Complex behavior in the form of quasi-periodic oscillations was found to emerge when the applied potential was between 1.2 V and 1.3 V (Fig. 2d and e). At these potentials there was no decrease in current density at the onset of the reaction, and increasing the external potential caused an increase in the mean current density around which the system oscillated. A further increase in the potential to 1.5 V caused the current density to again decrease where low frequency, small amplitude simple oscillations were observed. The above observed oscillations are not transitory and could last for several hours, but become irregular as the time period increased. The frequency of the oscillations seen under potentiostatic conditions on gold were seen to range from 43 mHz at an applied potential of 1.0 V, which increased to 95 mHz at applied potentials of 1.2 and 1.3 V, before decreasing to 25 mHz at 1.5 V. According to literature, nonlinear behavior of sulfur compounds electrochemically oxidized on a gold surface has only been conducted once [39], for the oxidation of thiosulfate. Bi et al. found that the frequency of oscillations under

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