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Qualitative dependence of the electro-oxidation behavior of sulfite on solution pH

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ABSTRACT

Electrochemical oxidation of sulfite at a platinum electrode was investigated, in which changing the pH of supporting electrolytes caused qualitative changes in the oxidation behavior. In an acidic environment, oscillations in current were found to occur; however, only transient behavior was observed without the incorporation of an external resistor. Electrochemical impedance spectroscopic measurements indicate that the system possesses a region of negative differential resistance (NDR) at acidic conditions. To gain insights into the influence of pH, electrochemical oxidation of bisulfite was also studied, in which NDR was found, suggesting that changes in the dominant species induced by pH is responsible for the observed phenomena. Perturbation experiments illustrate the presence of bistability under galvanostatic conditions, lending support that the observed instabilities belong to the N-NDR class of electrochemical oscillators. Mass spectroscopic analysis and precipitation with barium ion suggest that SO_4^{2-} is a major product of the electro-oxidation of sulfite.

1. Introduction

Sulfite (SO_3^{2-}) has been significantly used in industrial settings as well as the food industry [1–3]. Its main benefit in the food industry is its ability to act as a food preservative, dramatically increasing the shelf life of both foods and beverages [4–6]. However, it has been found that increased amounts of sulfite can be harmful and can in fact lead to asthma, gastrointestinal disease, and skin allergy [7,8]. Research has been conducted toward understanding the oxidation kinetics of sulfite under various conditions and using methods such as electrochemical [9–12]. Interestingly, sulfite anions have also been found to play an important role in many nonlinear chemical oscillators and reaction diffusion systems such as the thiourea-iodate-sulfite system, the bromate-sulfite-ferrocyanide reaction, the iodate-thiosulfate-sulfite reaction, and the hydrogen peroxide-sulfite-ferrocyanide reaction [13–17]. Of the various electrochemical oscillators in literature, sulfur-containing systems have also been a topic of great interest since their multiple oxidation states offer tremendous potential of seeing exotic reaction behaviors. In fact, sulfur compounds such as sulfide, aqueous sulfur dioxide, and thiosulfate have been found to support various modes of oscillations during electrochemical studies [18–25].

In the last two decades significant advances have been made in the study of electrochemical oscillating systems, stemming from the ability to characterize the mechanism driving the inherent nonlinear behavior through the use of electrochemical impedance spectroscopy (EIS). EIS measurements are often conducted in regions that may possess negative differential resistance (NDR) (where increasing potential during slow scan linear voltammetry experiments leads to a decrease in current). Measuring the impedance of the electrochemical system at different potentials gives insight into the underlying mechanism, and the presence of NDR has been found to be a prerequisite for an electrochemical oscillator [26,27]. The presence of NDR in systems that possess an n-shaped linear voltammogram is classified as either an N-NDR or HN-NDR oscillator, depending whether the negative resistance is located on the negative slope or is hidden on the positive slope in the voltammogram. The oscillations in these types of systems arise through the presence of a positive feedback loop (supplied through the NDR, where the double layer potential plays the role of an essential variable) and a negative feedback loop (surface concentration of an electro-active species or the surface coverage of an adsorbed species) [26,28].

Nonlinear instabilities have also recently been uncovered in systems which do not possess NDR, and have been determined to be caused by capacitance mediated positive differential resistance (CMPD) or through convection driven instabilities (where bubble formation and detachment are responsible for replenishing the diffusion layer with the electro-active species) [29–32]. Systematic exploration of the studied system found that oscillations in current could be seen during the electrochemical oxidation of sulfite when the supporting electrolyte solution was acidic. Through EIS measurements it was determined that the sustained oscillations occurred in an area of NDR, implying that the

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system belongs to the NDR type of oscillators. Parallel experiments with bisulfite suggest that the qualitative change in oxidation behavior arises from the influence of pH on the major electro-active species in the solution.

2. Experimental

All the electrochemical experiments were performed on a CHI660D Instrument (CHI Instruments, US). Polycrystalline platinum with a diameter of 2.0 mm (CHI Instruments) was applied as working electrodes. The counter electrode was a platinum wire and a saturated calomel electrode (SCE) was applied as the reference electrode. All the potential values reported in this study are versus SCE. 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 min, 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 ± 1 °C). Stock solutions of sulfuric acid (Aldrich, 95–98%), 6.0 M, were prepared with double-distilled water and the sodium sulfite (Na_2SO_3, Aldrich, 98 + %), sodium bisulfite ($NaHSO_3$, Aldrich, 98 + %) and potassium sulfate (K_2SO_4, ACP Chemicals) were directly dissolved in the reaction mixture. Reaction solution volumes were held constant at 60.0 mL. Electrochemical impedance spectroscopy (EIS) experiments were measured in the frequency range of 100 kHz to 0.001 Hz with an amplitude of 5.0 mV and 12 points per frequency decade.

3. Results and discussion

The importance of supporting electrolyte in the oxidation behavior of Na_2SO_3 is illustrated in Fig. 1, in which linear sweep voltammetry (LSV) has been conducted at a scan rate of 1.0 mV/s in solutions that all contained 0.5 M Na_2SO_3, but differed in their supporting electrolytes. Fig. 1i contains 0.35 M H_2SO_4 as the supporting electrolyte, where a classic N-shape voltammogram which possesses a NDR branch is seen. When the H_2SO_4 is substituted for K_2SO_4 (Fig. 1ii), there is no evidence of a NDR branch. In Fig. 1iii, when there is no supporting electrolyte, a NDR branch is again absent. LSV experiments were also performed with nitric acid (a different source of H^+), it was found that NDR was present. When sodium hydroxide was employed as the supporting electrolyte, NDR was absent in such a basic solution. Based on the above observation, the presence of an acidic environment seems to be critical for the emergence of a NDR, which is essential for the development electrochemical instability [26–28]. Results in Fig. 1 illustrate that the oxidation of sulfite compounds starts at about 0.3 V (vs. SCE). The activity increases with respect to the external potential. In cases (ii) and (iii), a plateau is reached at a potential of around 0.8 V. As the applied potential is increased further, hydroxide ions begin to get oxidized, leading to the production of oxygen. Hydrodynamic convection induced by oxygen bubble formation also enhanced the local transportation of sulfite, resulting in a rapid increase in the current density. In case (i), however, the dominant forms of electro-active species are HSO_3^- and SO_2(aq). Their diffusion is less dependent on the electrical field than the diffusion of SO_4^{2-}., which is the oxidation product. Stronger adsorption of the oxidation product SO_4^{2-} at a high potential lead to the observed decrease of the current density, until the external potential becomes high enough that the oxidation of hydroxide ions starts. Together with the convection enhanced transportation of HSO_3^- and SO_2(aq), the oxidation current increases again as the external potential becomes higher than 1.3 V (vs. SCE), resulting in the occurrence of a NDR and a kink in the voltammogram.

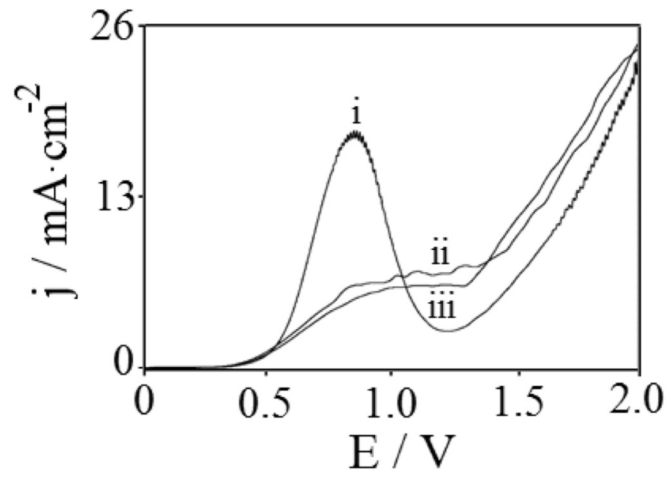

Fig. 1. Linear Sweep Voltammograms obtained at a scan rate of 1.0 mV/s in solutions consisting of (i) 0.5 M Na_2SO_3 and 0.35 M H_2SO_4 (ii) 0.5 M Na_2SO_3 and 0.2 M K_2SO_4 and (iii) 0.5 M Na_2SO_3 with no additional supporting electrolyte

To confirm that the negative differential branch in Fig. 1i is not due to the fast scan rate, in relative to the diffusion mass transportation of these electroactive species, a linear sweep voltammetry was conducted at a 10 times slower scan rate (i.e., 0.1 mV/s). Such a slow scan rate mimics a potentiostatic situation, allowing the applied potential to be explored as a control parameter in a similar way that the flow rate is studied as a bifurcation parameter for reactions conducted in a continuously flow stirred tank reactor. In Fig. 2a, as the applied potential is linearly increased, an oxidation peak can be seen to occur at approximately 0.8 V. The N-shape voltammogram is the same as that seen in

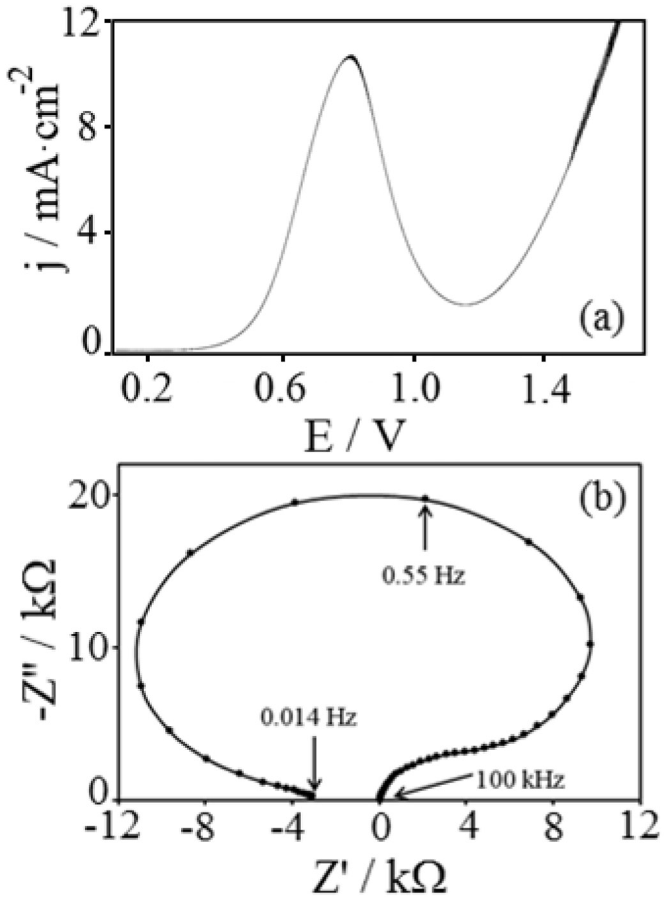

Fig. 2. (a) Linear Sweep Voltammogram obtained at a scan rate of 0.1 mV/s and (b) Electrochemical Impedance Spectrum (EIS) performed at 1.0 V in a solution that consists of 0.50 M Na_2SO_3 and 0.35 M H_2SO_4.