



Oscillatory electro-oxidation of thiosulfate on gold



Wenyan Bi^{a,b}, Yuxiu He^a, Murilo F. Cabral^c, Hamilton Varela^{c,d,*},
Jiaping Yang^a, Rongli Jiang^a, Qingyu Gao^{a,*}

^a College of Chemical Engineering, China University of Mining and Technology, Xuzhou 221008, China

^b School of Physics and Chemistry, Henan Polytechnic University, Jiaozuo 454000, China

^c Institute of Chemistry of São Carlos, University of São Paulo, P.O. Box 780, 13560-970, São Carlos, SP, Brazil

^d Fritz Haber Institute of the Max Planck Society, Department of Physical Chemistry, Faradayweg 4-6, D-14195 Berlin, Germany

ARTICLE INFO

Article history:

Received 30 January 2014

Received in revised form 9 April 2014

Accepted 9 April 2014

Available online 18 April 2014

Keywords:

Thiosulfate

Gold

Electro-oxidation

Bifurcation

Mixed mode oscillations.

ABSTRACT

We report experimental results on the oscillatory electro-oxidation of thiosulfate on polycrystalline gold electrode in buffered media of pH 6.0. Importantly, we observed oscillations in the current density (potential) when the system was studied under linear sweep of potential (current density). The system displayed supercritical Hopf, period-doubling, homoclinic and bursting bifurcations at different applied currents and potentials. After presenting the dynamics under both potentiostatic and galvanostatic regimes, we characterized the system in terms of its electrical (ohmic drop compensation and electrochemical impedance spectroscopy) and chemical (Capillary Electrophoresis analysis) aspects. Ohmic resistance compensation and electrochemical impedance spectroscopy confirmed the hidden N-shaped negative differential resistance oscillatory character. Capillary electrophoresis analysis revealed the predominance of different oxidation products as a function of the applied potential. Finally, we suggest a tentative mechanism underlying the kinetic instabilities.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Thiosulfate is a very important chemical substance in fields such as chemical synthesis, biological chemistry, wastewater treatment, mineral separation, paper manufacturing and photographic industry [1–3]. Thiosulfate can be oxidized chemically or electrochemically to sulfate and, as a number of intermediate oxidation states are possible, rather complex reaction mechanisms are commonly observed. The oxidation of thiosulfate is generally associated with rich nonlinear behavior in chemical and electrochemical systems [4–11]. Many homogeneous chemical reactions exhibiting autocatalysis and sustained oscillations have been reported, including the chlorite–thiosulfate [4,5], bromate–thiosulfate [6], hydrogen periodate–thiosulfate [7] and hydrogen peroxide–thiosulfate [8–10] systems. The electrocatalytic oxidation of thiosulfate on platinum surfaces can also result in interesting dynamics, including the emergence of period-doubling, mixed-mode, quasiperiodic oscillations, and chaos [11].

Most studies on the nonlinear phenomena observed during the electro-oxidation reactions at the solid/liquid interfaces are conducted on platinum surfaces. This is due to the high electrocatalytic activity of platinum towards many reactions, including the dehydrogenation and oxidation of small organic molecules and the oxidation of molecular hydrogen [12,13]. Expanding the current knowledge of electrochemical oscillations to reactions on other surfaces is a major step towards the understanding of surface processes underlying complex chemical kinetics at the electrified solid/liquid interface. This is also of importance when considering the possibilities of application and development of other imaging techniques.

Gold, as a noble and relatively inert metal, is a very weak chemisorber, which in the presence of pure electrolytes shows only non-Faradaic processes over a wide potential region, and exhibits a monolayer (or Au₂O₃) oxide at quite positive potentials [14–17]. However, many electrocatalytic reactions on gold surfaces were observed in aqueous media, and were commonly discussed in terms of the active states of gold and explained by the IHOAM (incipient hydrous oxide/adatom mediator) model [17]. The IHOAM model also rationalizes the high catalytic activity of oxide-supported gold microparticles as reported by Haruta and co-workers [18]. The electrocatalytic reduction of periodate [19] and of molecular oxygen and hydrogen peroxide on Au (100) in alkaline media [20] are examples of the rare reports to date on oscillatory kinetics on

* Corresponding authors.

E-mail addresses: varela@iqsc.usp.br (H. Varela), gaoqy@cumt.edu.cn (Q. Gao).

¹ ISE Member

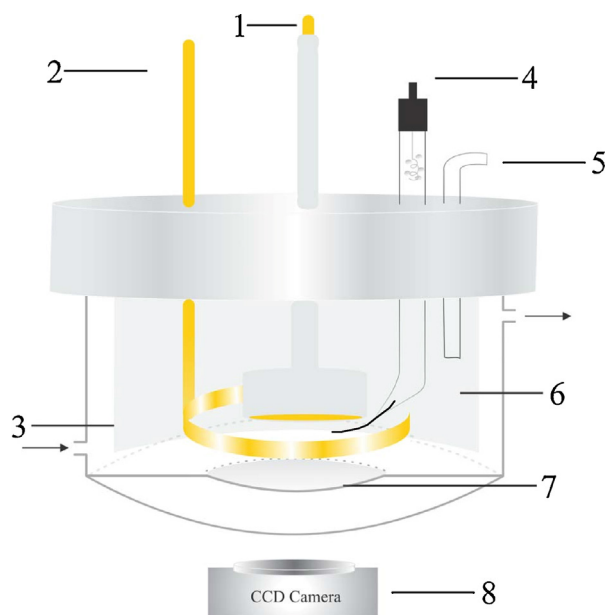


Fig. 1. Schematic diagram of the electrochemical apparatus: (1) WE; (2) CE; (3) cycling water; (4) RE; (5) gas tube; (6) reactor; (7) quartz window; (8) CCD camera.

gold surfaces. There are apparently no reports of instabilities in electro-oxidation reactions, in spite of the considerably high electrochemical activity towards the oxidation of carbon monoxide and small alcohols in alkaline media [21–24].

We report in this paper a comprehensive experimental investigation of the electro-oxidation of sodium thiosulfate on polycrystalline gold, with emphasis on the self-organized potential and current density oscillations. The study was performed in phosphate buffer (pH 6.0) and the system was investigated using cyclic voltammetry (CV), chronoamperometry, chronopotentiometry, and electrochemical impedance spectroscopy (EIS). Furthermore, Capillary Electrophoresis (CE) analysis was also employed to infer on the chemical identity of soluble oxidation products.

2. Experimental Section

All electrochemical experiments were performed by a computer controlled Autolab PGSTAT 302N electrochemical workstation (Metrohm Ltd., Switzerland) at 20.0 °C. The electrochemical set-up is depicted in Fig. 1. A conventional three-electrode electrochemical cell with a volume of 100 mL was used. A gold disk with a diameter of 20.0 mm, embedded in an insulating Teflon cylinder, was served as the working electrode (WE). The counter electrode (CE) was a gold thin foil with the dimension of 10.0 cm long, 1.0 cm wide and 0.02 cm thick, bended into a circular shape. The top edge of the CE and the bottom plane of the WE were arranged in the same plane, c.f. Fig. 1. As the reference electrode (RE), a reversible hydrogen electrode (RHE), made with a “J” glass tube in which 0.50 mol dm⁻³ H₂SO₄ was used as the electrolyte, was placed between WE and CE. The distance between RHE and WE is 5 mm. A charge-coupled-device (CCD) camera under the quartz window was adopted to observe the WE surface. Both working electrode and the electrolyte solution were kept stationary in all experiments. Potentials measured (or controlled) in all experiments are referred to the RHE scale. Electrolyte solutions were prepared by dissolving appropriate amounts of analytical grade sodium thiosulfate (Johnson Matthey Company) in ultrapure water (Millipore system, 18.2 MΩ·cm). Buffer solutions of NaH₂PO₄–Na₂HPO₄ were used to maintain the electrolyte pH 6.0. The capillary

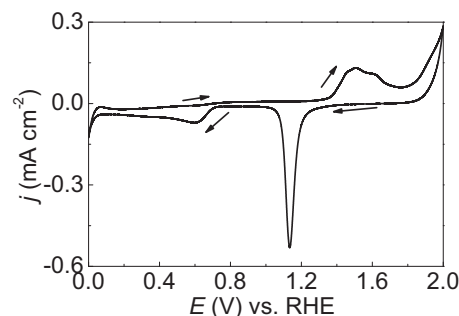


Fig. 2. Cyclic voltammogram of 1.00 mol dm⁻³ phosphate buffer (pH 6.0) with gold electrode at a scan rate of 0.01 V s⁻¹. The scan range is between 0 V and 2.000 V.

electrophoresis (CE) analysis was performed on a CE-based analytical system P/ACE MDQ (Beckman) equipped with a diode array detector (DAD). A fused-silica capillary of 57.0 cm (50.0 cm to the detector) × 75 μm i.d. × 375 μm o.d. was used. The sample was injected into the capillary by overpressure. A negative voltage of 30 kV was applied for separation, and 195.0 nm was selected for the spectrophotometric detection.

Before each experiment, the gold disk was firstly polished to a mirror-like shine with diamond suspension (1 μm) on a Buehler polishing microcloth of a polishing machine (MetaServ 250, Buehler, USA), and then was immersed into a mixture of 1% KMnO₄ and 30% H₂O₂ at room temperature for 12 hours. After that it was cleaned with ultrapure water. The electrolyte was deaerated with purified nitrogen for 20–25 min at room temperature. All experiments started with a series of cycling voltammograms between -0.65 and 0.80 V at a scan rate of 0.1 V s⁻¹ in 0.50 mol dm⁻³ H₂SO₄, until a constant current density vs potential profile was attained.

3. Results and Discussion

3.1. Potentiodynamic and galvanodynamic profiles

Fig. 2 shows the cyclic voltammogram between 0 V and 2.000 V in 1.00 mol dm⁻³ phosphate buffer (pH 6.0) at a scan rate of 0.01 V s⁻¹. It can be seen clearly that the formation of gold oxide occurred around 1.500 V, where two peaks suggest that the different states of gold oxide may be generated [17]. When the electrode potential is higher than about 1.800 V, the current density increases abruptly due to the oxygen evolution as evidenced by gas bubbles on the surface of the WE, as observed by CCD camera. The reduction peak at around 0.600 V results from β gold oxide (hydrrous oxide) yielded by oxidation of metastable metal surface (MMS) gold-atoms [17].

Fig. 3 shows both the potential and current linear sweeps curves in 0.40 mol dm⁻³ Na₂S₂O₃ with buffer (pH 6.0) on gold electrode. The open circuit potential is 0.130 V under these experimental conditions. In the potentiodynamic sweep experiment from 0 V to 2.000 V shown in Fig. 3a, multiple negative differential resistances (NDRs) are discernible. Three main regions marked with A, B and C can be seen. In region A, it is indicated that the NDR is induced by the formation of gold sulfide layer, which blocks surface sites. As a consequence, the current density decreases with increasing potential at around 0.750 V and then it reaches a current plateau around zero, as the electrode is in a passivated state. As the potential increases, the current density gradually increases. Between 1.000 V and 1.600 V, two distinct current density oscillations are clearly observed along the positive slope branch of the current density-potential curve. The first region is in the range of 1.070 V–1.280 V and the second lasts from 1.360 V to 1.400 V. It is speculated that the first oscillatory region is related to the formation of gold oxide

Download English Version:

<https://daneshyari.com/en/article/185491>

Download Persian Version:

<https://daneshyari.com/article/185491>

[Daneshyari.com](https://daneshyari.com)