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Current and potential oscillations during the electro-oxidation of bromide ions

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ABSTRACT

Electrochemical oxidation of bromide ions was investigated in aqueous solution, in which sustained oscillations in both current and potential were observed. Under galvanostatic conditions the electrode potential only oscillates within two narrow regions around 0.9 V and 1.6 V, respectively. Sustained current oscillations at the high potentials applied were accompanied with bubble formation and are often irregular, implicating that their development may be attributed with convection-driven processes. At the low potentials, the current oscillations exhibit several features associated with a capacitance mediated electrochemical oscillator, such as (1) taking place around a current plateau in a cyclic voltammogram, (2) occurring without the need of an external resistor, (3) showing a decreasing amplitude with the increase of external resistance, and (4) emerging on a positive differential resistance branch. Admittance spectra at a potential close to the bifurcation point also exhibit resonance behavior. The reversible formation and dissolution of tribromide complexes (Br_3^-) from the reaction between bromide (Br^-) and its electro-oxidation product bromine (Br_2) play a key role in this system.

1. Introduction

Electrochemical oxidation of bromide ions on platinum electrodes has recently been thoroughly researched due to their importance in the construction of a new class of energy storage devices [1–3]. Recent reports, for example, have indicated that the recombination of hydrogen, H_2, and bromine, in a fuel cell allows for up to 90% of the chemical energy stored in the reactants to be converted to electricity, which is much higher than that associated with the state of the art H_2/air fuel cells, for which the conversion can only reach about 50% [3,4]. Investigation undertaken by Conway and co-workers has led to the suggestion that the recombination of bromine radicals is the rate determining step in the formation of bromine ($2Br^* \rightarrow Br_2$) [1]. Other possible reaction steps from the most recent report on bromide electro-oxidation include [3]:

1) $Br^- \rightarrow Br^* + e^-$
2) $Br^- \rightarrow Br^{(1-\delta)} + \delta e^-$
3) $Br^* + Br^- \rightarrow Br_2 + e^-$
4) $Br^- + Br_2 \leftrightarrow Br_3^-$

Despite the earlier investigation on its electrode kinetics, there is no report on nonlinear instability during the oxidation of bromide ions at polycrystalline Pt electrodes. On the other hand, the importance of bromide ions in chemical and electrochemical oscillations is well documented [5–10]. For example, oscillations have been observed during the electro-dissolution of gold in an electrolyte solution containing bromide ions [9]. The introduction of bromide ions to a solution of hydrogen peroxide and sulfuric acid has also been found to induce chaotic behavior when being studied with a platinum electrode [10]. Overall, nonlinear behavior in electrochemical systems has been a subject which constantly attracts intense attention [11–19]. The first reported instance of nonlinear dynamics in electrochemistry can be dated back to 1828 [20], and since then electrochemical oscillations have been found during the dissolution of certain metals such as iron, copper, and nickel, the oxidation of H_2 on platinum, the oxidation of sulfur containing compounds such as thiosulfate, and the oxidation of small organic molecules such as methanol [21–29].

Thorough investigation of electrochemical oscillations has led to the classification of four types of oscillators based on the system's Electrochemical Impedance Spectroscopic (EIS) results [30]. Of the four categories the three most prevalent classes of electrochemical oscillators are N-Shaped Negative Differential Resistance (N-NDR), S-Shaped Negative Differential Resistance (S-NDR), and Hidden N-Shaped Differential Resistance (HN-NDR). An important feature of the NDR systems is that there exists a negative Faradic resistance where the double layer potential becomes an essential variable in the mechanism describing the oscillations [31]. Oscillatory phenomena can also occur when convection assumes the role of the essential parameter through the process of replenishing the diffusion layer with the electroactive species [32]. Very recently, Zensen and co-workers demonstrated with two and three-variable models the possibility of capacitance mediated positive differential resistance oscillators, in which the formation and dissolution of inhibiting surface layers played a key role [33]. Through

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systematic exploration, this study uncovered that the electro-oxidation of bromide ions could undergo both potential and current oscillations under a positive differential resistance and without external resistor, pointing to the possibility of being a capacitance mediated electrochemical oscillator. Under high applied potentials (>1.5 V), the current oscillates above the limiting current and is accompanied with vigorous bubble formation, suggesting that the observed oscillations are likely driven by convection processes [32].

2. Experimental

All the electrochemical experiments were performed on a CHI660D Instrument (CHI Instruments, US). Polycrystalline platinum electrodes with a diameter of 2.0 mm (CHI Instruments) were applied as working electrodes. The counter electrode was a platinum film (3 mm × 5 mm, Shanghai Ruosull Technology Co., LTD) 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.

All reactions were carried out in a custom built thermal-jacketed electrochemical cell with 5 multi purpose ports. 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 bromide (NaBr, Aldrich, 98 + %) and potassium sulfate (K_2SO_4, ACP Chemicals) was 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.

3. Results and Discussion

Fig. 1(i) is a linear sweep voltammogram (LSV) of 0.075 M bromide in a 0.75 M H_2SO_4 solution conducted at a scan rate of 1.0 mV/s. It shows that following the onset of bromide oxidation at around 0.8 V, oscillations in the current take place on an otherwise rather flat branch. When the potential is increased to above 1.5 V, the current density resumes its increase, but in an oscillatory fashion. Meanwhile, small bubbles begin to form at the working electrode, suggesting that this second positive branch is increasingly dominated by the oxidation of hydroxide ions. To examine the relative influence that oxygen formation would have on the oxidation of bromide ions, Fig. 1(ii) shows the LSV of 0.75 M sulfuric acid without the presence of bromide ions, where the current density begins to increase sharply, accompanied with bubble formation, once the potential reaches approximately 1.5 V.

Results in Fig. 1 suggest that convection processes are negligible at low potentials, but may have played a very important role in the reaction kinetics at the potential above 1.5 V. At a high potential of 1.75 V, irregular oscillations are observed which begin at a current value that is above the limiting current. The presence of visible bubbles on the working electrode is supportive that convection induced by bubble formation and detachment plays an important role in those current oscillations, where the irregularity is due to the non-uniform formation of bubbles. As suggested in an earlier report [32], at the minimum peak current of the oscillations, oxygen gas evolution becomes prominent, while at the maximum peak currents of the oscillations, gas evolution is repressed by the oxidation of Br^- ions that are replenished through the convection induced by the gas evolution. If the system is exposed to a constant agitation with a strength that is equal or larger than that induced by the oxygen evolution, the oscillations shall stop and the current stabilizes at a state where only the bromide ions are oxidized (i.e., the oxidation of OH^- is negligible) [32]. Our experiments conducted with a rotating disk electrode confirm the above scenario.

Fig. 2 presents a series of potentiostatic experiments conducted at the low potential range where convection effect is considered negligible. At the applied potential of 0.75 V no oscillations take place and the current density remains near 0. When the applied potential is increased to 0.85 V in time series (b), oscillations emerge after a brief induction period. A further increase to 0.95 V shows oscillations occurring without an induction time, where the oscillation frequency is 0.042 Hz. The time series (d) shows current oscillations at the applied potential of 1.15 V, where the oscillation frequency increases slightly to 0.05 Hz. Notably, for the applied potential between 1.0 V and 1.5 V, the current was found to oscillate around a plateau in a CV (see Fig. 1(i)). This is one of the features associated with a capacitance mediated electrochemical oscillation [33]. No external resistor is required in the above current oscillations, which is another property associated with the capacitance mediated electrochemical oscillator [33].

EIS measurements have been found very useful in the classification of the type of electrochemical oscillators [30]. Here, the electro-oxidation of bromide ions exhibits oscillations even without the presence of external resistance, which restricts us to conduct impedance spectroscopy measurement at low potentials (see Fig. 1(i)). Fig. 3a shows EIS obtained at an applied potential of 0.84 V with the applied perturbation of 0.0008 sin(ωt) V. There is a semicircle, reflecting the charge transfer resistance, and a Warburg diffusion impedance. Notably, at the low frequency range, while remaining in the positive range, the impedance showed some fluctuation. Admittance spectrum in Fig. 3b shows a small resonance peak at a frequency of 0.014 Hz, which is close to the frequency of current oscillations seen at 0.85 V (i.e. 0.025 Hz). It is useful to point out that time series in Fig. 2 indicate that the frequency of oscillation decreases as the applied potential moves closer to the bifurcation point. The resonance behavior is also affected by its distance from the bifurcation point, which is consistent with the simulations performed by Zensen et al. [33]. This admittance spectrum, together with the two features mentioned above, suggests that at the low potential range (0.85 to 1.4 V) this system is likely a

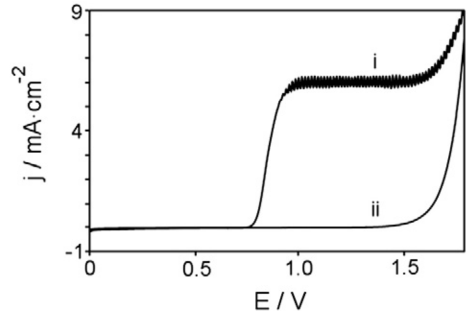

Fig. 1. Linear sweep voltammogram of the solution consisting of (i) 0.075 M NaBr and 0.75 M H_2SO_4 and (ii) 0.75 M H_2SO_4.

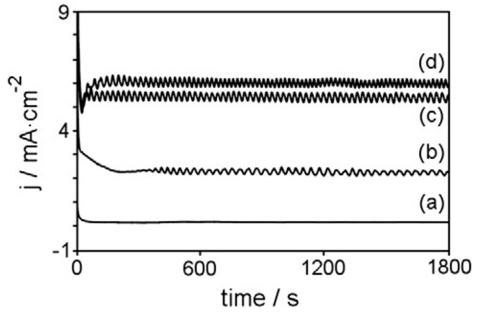

Fig. 2. Potentiostatic experiments performed with applied potentials of (a) 0.84 V, (b) 0.85 V, (c) 0.95 V, and (d) 1.15 V (vs. SCE). Other reaction conditions were: [NaBr] = 0.075 M and [H_2SO_4] = 0.75 M.