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A new oscillatory mechanism for the electro-oxidation of iodide involving two phase transitions and a disproportional reaction

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Abstract

Oscillations have been first observed during iodide oxidation in alkaline solution on a static platinum electrode, where phase transitions at the interface of electrode/solution are essential. The film formation of solid iodine acts as a negative nonlinear feedback slowing down the iodide oxidation due to its poor conductivity, and oxygen evolution as a positive nonlinear feedback by destroying the iodine film mechanically and by promoting its dissolution through convection mainly via a disproportional reaction. Based on the results of electrochemical experiments and in situ Raman spectroscopy, a tentative mechanism is given concerning the interfacial phase transitions and the disproportional reaction.

1. Introduction

The mechanism and reactive kinetics for the anodic oxidation of iodide have been extensively studied, including the behavior of strong adsorption of iodide and the nature of thick iodine films [1–8]. Oscillations in current were first reported by Gokhshten during iodide oxidation on platinum in acid media [9]. Tributsch et al. studied current oscillations and simultaneous electrode reflectivity during iodide oxidation on illuminated n-type $MoSe_2$ semi-conductor electrodes [10]. Lately, Vitt and Ma investigated the current oscillations in nitric acid at a rotating gold–gold ring–disk electrode, and they attributed the oscillations to the film formation of iodine and its dissolution by forming I_3^- [11,12]. To our knowledge only current oscillations have been observed up to date mostly in acidic solutions and on rotating electrodes.

We found both potential and current oscillations during the oxidation of iodide in alkaline media on a static platinum electrode, in which two kinds of phase transitions at the electrode/solution interface were observed. Solid films of iodine that formed at the surface during the oxidation of iodide were dissolved mainly through a disproportional reaction, which was speeded up by the gas evolution of oxygen. Some key species involved in the oscillatory reactions were characterized by means of Raman spectroscopy.

2. Experimental

Electrochemical experiments were carried out with a CHI 660A electrochemical station (CH Instrument Inc., USA). A platinum disk (2 mm in diameter), a platinum wire and a saturated mercurous sulfate electrode (SMSE) were served as the working, counter and reference electrode, respectively. The working electrode was polished with metallograhic paper and successively finer grades of alumina (1.0 and 0.05 μm), then cleaned with ultrasonic waves in triply-distilled water, and followed by electrochemical cleaning in the background solution of NaOH ($0.5\ \mathrm{mol\ dm^{-3}}$) until repeatable cyclic voltammograms were obtained. Raman spectra were obtained with a Renishaw RM1000 confocal microscope. The exciting wavelength was 632.8 nm. More details on the Raman instrument and the spectroscopic cell can be found elsewhere [13]. All solutions were prepared on daily basis with triply-distilled water and analytical grade chemicals.

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3. Results and discussion

Fig. 1 shows the cyclic voltammograms (CVs) for 1 mol dm^{-3} KI in 0.5 mol dm^{-3} NaOH on the platinum disk with different upper potential limits: 1.7 (a), 1.1 (b), and 0.7 V (c). During the positive potential scan from −1.3 to 1.7 V (the dotted line), a large current peak appears at ca. 0.1 V due to the oxidation of iodide in the solution (sol) near the surface (∗)

$$2I^-(sol^*) = I_2(s) + 2e^- \tag{i}$$

Then the current drops dramatically and a plateau follows because of film formation of solid iodine $I_2(s)$ on the surface, and the current rises rapidly again after 1.5 V for oxygen releases continuously

$$2OH^-(sol^*) = H_2O(l) + (1/2)O_2(g) + 2e^- \tag{ii}$$

which should occur much earlier positive to 0.2 V in the absence of the iodine film in the background solution (d). While the potential scan is reversed to the negative direction, a sharp upswing in current appears as oxygen bubbles burst out of the iodine film. The eruption of oxygen gas not only breaks the solid film mechanically, but also imposes a strong convection mass transfer. The latter is the main reason for the fact that the peak current at ca. 1 V in the reversing scan is even larger than that at ca. 0.1 V in the forward scan since convection can speed up the electro-oxidation of iodide before the film formation again. Note that the position and the height of this larger peak in the reversing scan vary with the upper limit potentials (comparing curves a and b in Fig. 1). Both of them mainly depend on the film thickness. On one hand, the peak potential shifts negatively with a thinner iodine film in (b) due to reversing the scan earlier with a shorter deposition time for iodine. The peak disappears at an even lower reversing potential of 0.7 V in (c) without the gas eruption. On the other hand, the peak is higher in (a) than in (b) because the gas pressure in (a) is larger enwrapped under a thicker iodine film, which will result in a stronger convection mass transfer during the gas eruption. The current then declines rapidly after oxygen eruption for iodine deposit covers the electrode surface again. The peak height for the reduction of iodine at ca. −0.2 V is much smaller than that at ca. 0.1 V for the oxidation of iodide, indicating that most of the iodine deposited is dissolved again before the potential returns to −0.2 V more through a disproportional reaction

$$3I_2(s) + 6OH^-(sol^*) \rightarrow IO_3^-(sol) + 5I^-(sol) + 2H_2O(l) \tag{iii}$$

than through a coordinative reaction [14]

$$I_2(s) + I^-(sol^*) = I_3^-(sol) \tag{iv}$$

The disproportional reaction (iii) in an alkaline medium might undergo two steps like

$$I_2(s) + 2OH^-(sol^*) \rightarrow IO^-(sol) + I^-(sol) + H_2O(l) \tag{v}$$

$$3IO^-(sol) \rightarrow IO_3^-(sol) + 2I^-(sol) \tag{vi}$$

The small wave at ca. −1 V is for the reduction of IO_3^- (sol) [6] from the disproportional reaction (iii).

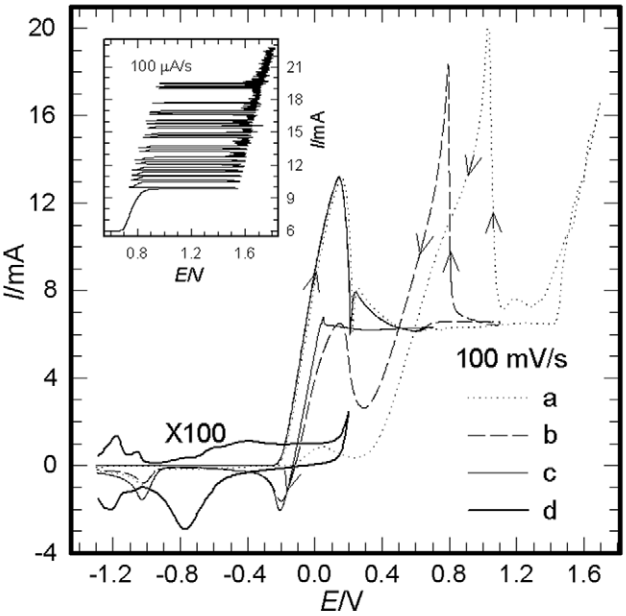


Fig. 1. Cyclic voltammograms with different upper potential limits: (a) 1.7 V, (b) 1.1 V, (c) 0.7 V, and (d) 0.2 V on the platinum electrode in 0.5 mol dm^{-3} NaOH solution containing 1 mol dm^{-3} KI, except for (d) with 0.5 mol dm^{-3} NaOH only and with a 100-fold enlargement in current. The inset shows the typical potential oscillations obtained by current scan.

The curves in the CVs (Fig. 1a,b) cross while the current for the backward scan is larger than that for the forward scan, and crossing cycles form during the potential cycling in the plateau range. Clearly, such a crossed CV generates from two opposite kinetic processes, i.e. formation and dissolution of iodine films. We found that crossed CVs are common phenomena in oscillatory electrochemical systems, and oscillations generally appear in the area of the crossing cycles [15]. To oscillate in two states, both negative and positive nonlinear feedback steps should co-exist between the two states and predominate alternately, so that the system is able to move to and fro between the two states. Such ‘two-way’ information of nonlinear feedbacks for oscillations can be easily obtained by potential cycling in the CV. The crossing cycle can serve as a practical criterion for electrochemical oscillations [15]. So oscillations can be expected to occur from the crossing cycle both in potential within the plateau range and in current between those of the plateau (forward scan) and of the peak (backward scan).

Interestingly, the anticipation from the crossing cycle proves to be true. The range of oscillatory potential in the inset of Fig. 1 agrees well with that where the crossing cycle occurs. Three typical waveforms of potential oscillations are also shown in Fig. 2. The system stays at the lower potential state during the film formation of iodine, and shifts to the higher potential state rapidly soon after the film covers the electrode surface completely (negative nonlinear feedback). Oxygen eruption occurs at the higher

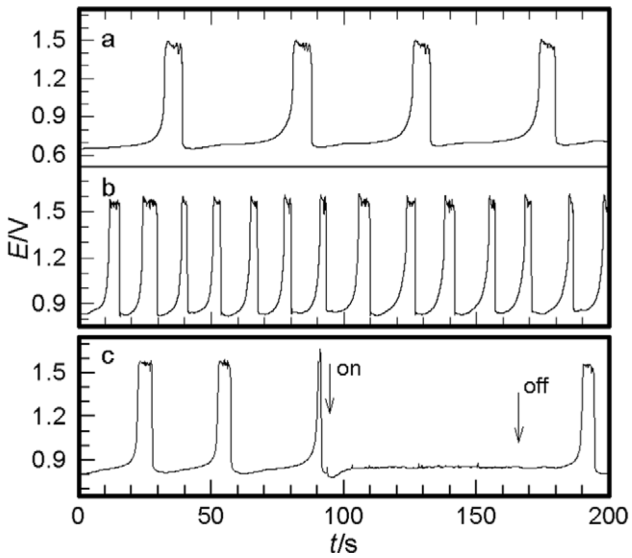


Fig. 2. Potential–time curves at different currents: (a) 8.5 mA, (b) 12 mA, and (c) 9 mA, on the platinum electrode. 'On' and 'off' in curve (c) indicates the strong agitation begins and stops.

potential state during the oscillations. The gas bubbles destroy the iodine film mechanically and enforce convection mass transfer to promote the film dissolution chemically via the disproportional reaction (iii) as well as the coordination reaction (iv) (positive nonlinear feedback). Some noise can be observed at the higher potential state because of the gas evolution. Then new cycles repeat. Increasing the applied current the oscillatory period gets shorter, mainly for the film formation of iodine is accelerated. It can be clearly seen in Fig. 2 that the system stays much shorter at the lower potential state during oscillations under 12 mA in (b) than under 8.5 mA in (a). The role that the periodic convection mass transfer from oxygen evolution plays in the oscillations can be simply testified by imposing a constant strong agitation. The oscillation stops while keeping on the strong agitation between 'on' and 'off' and the system stays at the lower potential state as shown in Fig. 2c. This fact implies that convection accelerates not only the oxidation of iodide but also the film dissolution. The oscillation restores right after ceasing the agitation.

Typical current oscillations are presented in Fig. 3 with (c,d) or without (a,b) an external resistance (R_e) in series. Oscillations can be easily got with the R_e of 100 Ω in a much wider potential range and their waveforms behave more regularly. The introduction of an R_e can intensify the unstable nature of oscillatory systems to our understanding [15]. The mechanism of the current oscillations is similar to that of the potential oscillations. During the current oscillations, the system stays at the higher current state at the beginning of the film formation, and then moves to the lower current state after completion of the film formation. Oxygen releases at the lower current state, which breaks the iodine film mechanically and accelerates its dissolution mainly through the disproportional reaction (iii). In this way the cycles proceed continuously. While imposing a strong agitation between 'on' and 'off' as shown in Fig. 3b, current oscillations stop, too, and the system stabilizes at the higher current state because the enforced convection promotes the film dissolution, as well as the oxidation of iodide.

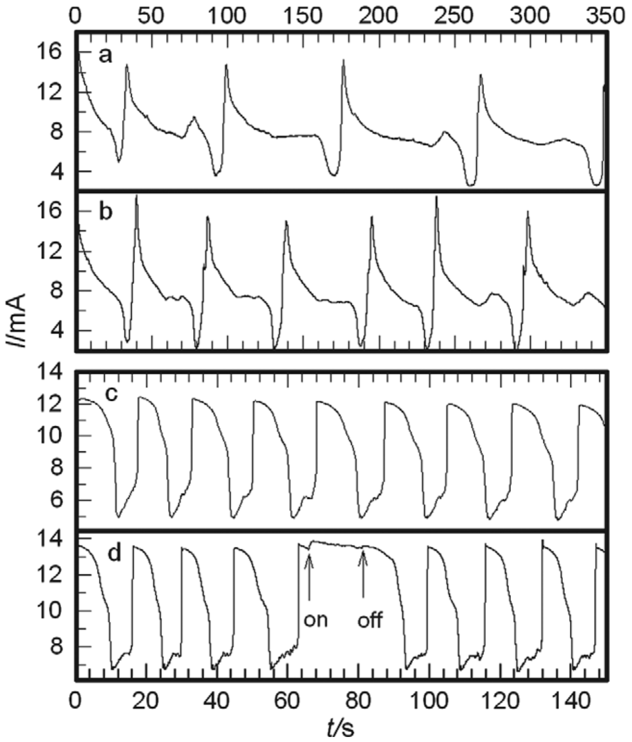


Fig. 3. Current–time curves at different applied potentials: (a) 1.17 V, and (b) 1.2 V without the external resistance (R_e); (c) 2 V, and (d) 2.2 V with an R_e of 100 Ω in series. 'On' and 'off' have the same meaning as in Fig. 2.

Fig. 4 shows the in situ images from a microscope for the film formation (a) and destruction/dissolution (b) of iodine at the electrode surface during the oscillations. Gas bubbles of oxygen that grow under the film (b) destroy the solid film of iodine in return. The enforced convection mass transfer of I^- and OH^- induced by oxygen evolution speeds up, respectively, the iodide oxidation and the film dissolution of iodine, especially the latter since the agitation excludes the film formation. We found that the solid film of iodine on the static platinum electrode is too difficult to be removed in acidic media and no oscillations can be observed. That might be the reason why rotating the electrode is necessary for current oscillations in acidic solutions as reported [11,12], where the film dissolved only through the coordinative reaction (iv). Apparently, convection from periodic gas evolution of oxygen and film dissolution of iodine by disproportional reaction are the remarkably distinctive factors that make the oscillations possible on a static electrode here.

I_2(s), IO_3^-(sol) and I_3^-(sol) in reactions (i), (iii) and (iv), respectively, are the key species involved in the oscillatory electro-oxidation of iodide, for I_2(s) denotes the film formation, and IO_3^-(sol) with I_3^-(sol) the film dissolution.

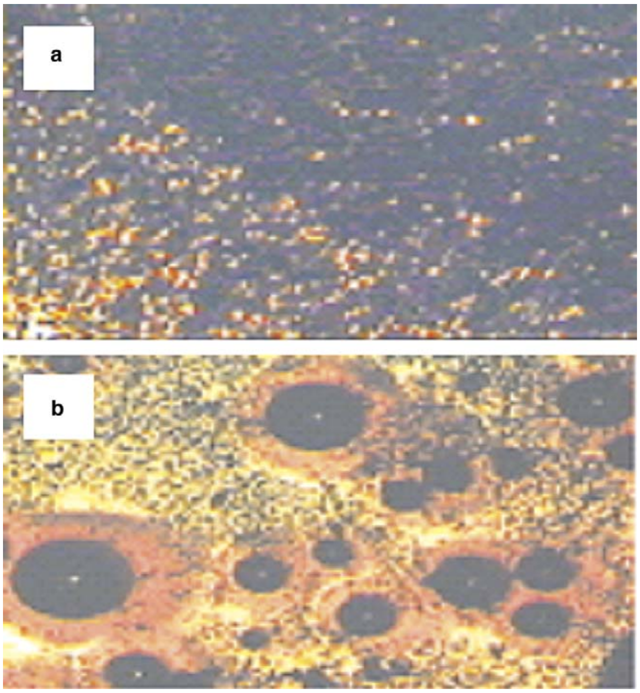


Fig. 4. In situ microscopic images during oscillations: (a) film formation of iodine and (b) film destruction/dissolution of iodine facilitated by the gas bubbles of oxygen.

These three species produced in the reactions have been detected in situ by the potential-dependent Raman spectroscopy, and typical illustrative data are given in Fig. 5.

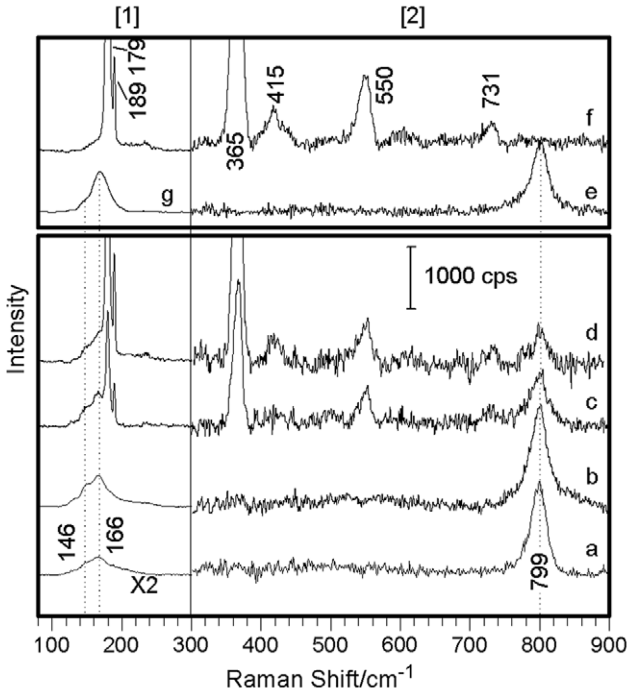
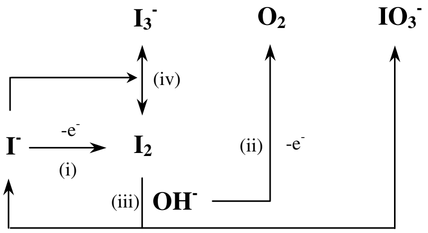


Fig. 5. In situ Raman spectra during the oxidation of iodide on the platinum electrode at different potentials: (a) −0.1 V, (b) −0.05 V, (c) 0.1 V, and (d) 0.8 V. Raman spectra of known samples are also given for comparison: (e) solution of potassium iodate (IO_3^-), (g) solution of I_3^- from iodine plus excess potassium iodide, and (f) solid iodine in water. The exposure time for CCD is 10 and 400 s for sections [1] and [2], respectively.

The Raman spectra (e), (g), (f) in Fig. 5 are from the given samples of IO_3^-(sol), I_3^-(sol), I_2(s), respectively, for direct comparison with those resulting from the reactions. Comparing with spectrum (f), the bands in spectrum (c) at 179, 189, 365, 415, 550, 731 cm^{-1} appearing at around 0.1 V can be assigned to the iodine deposit on the surface. This potential is located in the latter part of the ascending branch in the CV (Fig. 1a). However, in spectrum (a) of −0.1 V only peaks appear for IO_3^- (sol) at 799 cm^{-1} and for I_3^- (sol) at 166 cm^{-1} with a shoulder of 146 cm^{-1}, corresponding to the spectra (e) and (g), respectively. This fact confirms that the iodine deposit in reaction (i) is dissolved completely via reactions (iii) as well as (iv) in the lower potential range, where the oxidation of iodide just begins (Fig. 1a). The intensity decrease of band 799 cm^{-1} in (c) and (d) of Fig. 5 should be due to the influence of the growing iodine film on the confocal Raman measurement.

4. Summary

Phase transitions at the interface of electrode/electrolyte coupled with electrochemical reactions and mass transfer account for the oscillations during the oxidation of iodide in alkaline solution on the static platinum electrode. The oscillatory oxidation mechanism of iodide in alkaline solution can be summarized as follows:



Two electrochemical reactions, i.e. iodide oxidation (i) and oxygen evolution (ii), involve formation of solid and gas phases, initiating at lower and higher potentials, respectively. The solid film of iodine slows down the iodide oxidation due to its poor conductivity, and then the gas evolution of oxygen speeds up the iodide oxidation by means of the film destruction and the film dissolution via reactions (iii) as well as (iv) with enhanced mass transfer of I^- and OH^-. This mechanism is much different from that for iodide oxidation in acid media [12,13], where no disproportional reaction and oxygen evolution were involved in the dissolving process.

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