The effect of chloride on spatiotemporal dynamics in the electro-oxidation of sulfide on platinum

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A B S T R A C T
The adsorption of poisonous species on the catalyst surface impacts electrocatalytic reactions to different extents and by distinct means. The impact of adsorbing anionic species on electrocatalytic reactions has generally been investigated in the non-oscillatory regime or, at most, with temporal oscillations. Here, we report on spatiotemporal pattern formation in the electro-oxidation of sulfide on a platinum disk perturbed with dissolved chloride. The spatiotemporal dynamics was followed simultaneously with an electrochemical workstation and a charge-coupled device (CCD) camera. Perturbing the system with chloride results in (a) enhancement of dynamic instabilities throughout the current-potential curve, including regions of both positive and negative slope; (b) emergence of several spatial patterns; and (c) decreasing the width of pulses with increasing [Cl−]. The results are interpreted in terms of surface poisoning by chloride adsorption.

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1. Introduction

Generally, the primary result of anion adsorption on electrocatalytic reactions is to block surface sites, resulting in inhibition and a consequent decrease in reaction rates. The consequences of halide adsorption on platinum have been extensively studied in a number of electrocatalytic reactions [1–6]. The competition between dissolved species for surface sites may cause quite complex behavior under oscillatory conditions [7]. Examples include the effect exerted by dissolved anions on metal corrosion/dissolution [8,9], on the electro-oxidation of small organic molecules [10,11] or hydrogen [12,13] and on the electro-reduction of hydrogen peroxide [14,15] on platinum. Regarding the study of spatiotemporal patterns in electrochemical systems [16–19], the adsorption of halide (especially chloride) in certain electrochemical systems [19–22] is essential in producing spatiotemporal patterns.

Following previous investigations in the temporal domain [23–25], we recently reported the occurrence of self-organized spatiotemporal patterns in the electrocatalytic oxidation of sulfide on a platinum disk [26]. We explored the effect of sweep rate and of the series resistance connected between the working electrode and the potentiostat, and were able to record patterns comprising fronts, pulses, twinkling eyes, labyrinths and homogeneous oscillations. From the experimental point of view, the rich dynamics and the fact that macroscopic sulfur deposition and dissolution are easily observed with a CCD camera are important advantages. Moreover, in contrast with the situation for metal dissolution and/or deposition systems, the two-dimensional sulfur deposition observed in the electro-oxidation of sulfide on platinum are expected to be confined to the topmost layer of the surface, as observed on Cu (1 1 0) in acidic chloride solution using a high-speed scanning tunneling microscope with atomic resolution [27,28]. Here, we use the sulfide electro-oxidation on a platinum disk system to investigate the effect of chloride perturbation on spatiotemporal pattern formation.

2. Experimental

All experiments were performed in a conventional three-electrode electrochemical cell with a volume of 40 mL. A polycrystalline platinum disk embedded in an insulator with a diameter of 2 mm was used as the working electrode (WE). The counter electrode (CE) was a platinum ring arranged below the WE at a distance of 1.5 cm. The ohmic resistance of our setup was about 11.6 ohms. The reference electrode (RE) was a saturated
calomel electrode (SCE) inserted into a J-shaped glass capillary, whose tip was located between the WE and CE and close to the surface of the WE. All the potential values in this work were measured and are quoted with respect to the SCE. All electrochemical experiments were performed on a CHI-660 electrochemical workstation (CH Instruments Inc., USA). A charge-coupled device (CCD) camera was utilized to investigate pattern formation on the WE.

Before each experiment, the platinum disk was first polished to a mirror-like shine with fine alumina powder (0.05 μm) and then immersed in a 0.5 mol/L HNO₃ solution for 30 min. After that, it was cleaned with ultrapure water (Millipore system, 18.2 MΩ·cm) in an ultrasonic bath for 5 min and then rinsed with ultrapure water. Next, the potential was cycled from −0.25 to 1.30 V vs. SCE at a scan rate of 50 mV/s in 0.5 mol/L H₂SO₄ to further clean the electrode surface. Finally, the electrode was rinsed repeatedly with ultrapure water.

Electrolyte solutions were prepared by dissolving appropriate amounts of analytical grade sodium sulfide and sodium chloride (Sinopharm Chemical Reagent Co., Ltd., China) in ultrapure water. The Na₂S concentration was 1.00 mol/L in all experiments, whereas different concentrations of chloride were used. Before each electrochemical experiment, the electrolyte was deaerated with purified nitrogen for 20–25 min, and a nitrogen atmosphere was maintained during all experiments. The temperature was held at 20.0 ± 0.1 °C with a circulating water bath (Polyscience Instrument, USA).

3. Results and discussion

3.1. Temporal dynamics

3.1.1. Oscillations and mechanistic analysis in the absence of chloride

Fig. 1 shows a slow linear potential sweep (−0.20 V to 1.80 V at dE/dt = 1 mV/s) for the electro-oxidation of 1.00 mol/L sulfate in the presence of different amounts of dissolved chloride, as well as a cyclic voltammogram (Fig. 1a, dashed curves) in 1.00 mol/L sodium hydrosulfide solution. We observe a linear current increase associated with oxygen evolution of sodium hydrosulfide solution at potentials above about 0.70 V as well as oxide formation and reduction between about −0.5 V and 0.3 V seen in the dashed curves in the lower inset of Fig. 1a. In the absence of chloride (solid curve, Fig. 1a), when the potential is increased from −0.20 V to −0.60 V vs. SCE the current measured remains close to zero and barely fluctuates. Within this region the electrode surface is passivated by a sulfur layer associated with a small peak [24,29] centered at −0.08 V vs. SCE and seen in the solid line in the upper inset in Fig. 1a. This process can be described as

\[
Pt(s, u) + HS^−(aq) + OH^−(aq) → PtS(adss) + H₂O(l) + 2e^− \quad (R1)
\]

Here, s, u and adss represent solid electrode, unoccupied surface sites and adsorbed surface species, respectively. However, the applied potential of sulfur passivation is more positive in acidic solution (e.g. 0.70 V vs. a Ag/AgCl reference in 0.1 mol/L H₂SO₄ [30]). At pH about 14, as in the present case, HS⁻ rather than S²⁻ is the predominant sulfur species. As the potential increases above 0.60 V, the current density increases slightly to about 10 mA/cm², and then it jumps abruptly to ~120 mA/cm². This sudden increase of the current density is due to surface oxide growth and removal of electrodeposited sulfur from the electrode surface, as confirmed by in situ surface-enhanced Raman scattering (SERS) spectroscopic investigation [31] and triangular potential scan experiments [29]. The minimum potential (E_min) of oxide formation [29,32] increases with acidity, the concentration of Na₂S and the potential scan rate. For 1.00 M NaOH solution without sulfide, E_min was determined to be about −0.32 V at a scan rate of 1 mV/s (dashed lines in the lower inset of Fig. 1a). With 1.00 M sulfide solution, whose pH is close to that of the 1.00 M NaOH solution, and the same scan rate, the calculated E_min is about 0.60 V vs. SCE [29], which is consistent with the experimental result in Fig. 1a. Thus, the oxidation of the Pt surface:

\[
PtS(adss) + OH^−(aq) → PtOH(adss) + S(s) + e^− \quad (R2)
\]

\[
Pt(s, u) + OH^−(aq) → PtOH(adss) + e^− \quad (R3)
\]

\[
PtOH(adss) + OH^−(aq) → PtO(adss) + H₂O(l) + e^− \quad (R4)
\]

gives rise to an N-shaped negative differential resistance (N-NDR), inducing positive feedback, i.e., the autocatalytic character of the double layer potential [16,19]. The OH adsorption and oxide formation in the range of the potential scan also can be inferred from an observed anodic current peak during the negative potential scan [24,26,29], which was explained in terms of oxide reduction (reverse reaction of (R4) and (R3)) and a consequent current increase due to the oxidation of sulfide [29].

Our experimental observations (Fig. 1a) suggest that for the positive slope region of the j-E curve between 0.60 V and 1.00 V, pale elemental sulfur (S) is produced by (R2) and also mainly by (R5), resulting in a much larger area of the j-E curve for OH adsorption and oxide formation through reaction cycling of (R3) and (R5) than for S-layer formation (R1). The elemental sulfur then gradually changes to soluble yellow polysulfide S²⁻ in the region of rising current density through the dissolution reactions (R6) and (R7) [29,33,34].

\[
PtOH(adss) + HS^−(aq) → Pt(s, u) + S(s) + H₂O(l) + e^− \quad (R5)
\]

\[
S(s) + HS^−(aq) + OH^−(aq) → S²⁻(aq) + H₂O(l) \quad (R6)
\]

\[
S(s) + S²⁻(aq) → S²⁻(aq) \quad (R7)
\]

Reaction (R5) is accelerated by increasing the applied potential. The availability of more Pt sites causes a current increase, which thus hides the NDR of OH adsorption and oxide formation, thereby introducing a negative feedback and possibly producing a hidden N-NDR (HN-NDR) region [16,19]. If the concentration of Na₂S is increased further, from 1.00 mol/L to 2.00 mol/L, the rates of (R5), (R6) and (R7) increase, enhancing the negative feedback and inducing HN-NDR oscillations, as found by Miller and Chen [24].

Along the negative slope of the j-E curve, the limited diffusion of HS⁻ in the electric double layer for oxide (passive film) reduction (R8) and the dissolution reactions [(R6) and (R7)], which cause a current increase, constitutes a slow negative

\[
PtO(s) + HS^−(aq) → Pt(s, u) + S(s) + OH^−(aq) \quad (R8)
\]

feedback, resulting in N-NDR oscillations [16,19] as shown in Fig. 1a. Both the HN-NDR and N-NDR oscillations correspond to the alternate deposition and dissolution of sulfur on the WE surface.

3.1.2. Effect of chloride on temporal dynamics

The addition of chloride causes pronounced changes in the j-E curves, as can be seen in Fig. 1b–f. First, as [Cl⁻] is increased, the potential at which current starts to increase is shifted to more positive values. In Fig. 1a the onset potential is ~0.60 V vs. SCE. This value gradually shifts, and reaches as high as −0.80 V vs. SCE when the chloride concentration is 500 mmol/L (Fig. 1f). As anticipated above, dissolved chloride ions can compete for platinum sites in the whole potential region via R9.

\[
Pt(s, u) + Cl^−(aq) → Pt − Cl(adss) + e^− \quad (R9)
\]
Fig. 1. Current response during a linear sweep for the electro-oxidation of 1.00 mol/L of Na₂S, at 1 mV/s in the presence of dissolved chloride [Cl⁻]=[a] 0 mmol/L, (b) 30 mmol/L, (c) 50 mmol/L, (d) 70 mmol/L, (e) 90 mmol/L, and (f) 500 mmol/L. Dashed line in Fig. 1a denotes the cyclic voltammetry curve in 1.00 mol/L NaOH solution. j–E curves of upper and lower sets in Fig. 1a illustrate S-layer formation and oxide formation in the presence and absence of sulfide, respectively.

3.2. Spatiotemporal patterns

3.2.1. Synchronization of sulfur deposition and dissolution

We have previously reported the occurrence of synchronized sulfur deposition and dissolution in the NDR oscillation regions [26]. When the slope of the j–E curve is positive, there is no synchronization, but fronts are observed in the absence of chloride. Fig. 3i and ii show the evolution of fronts corresponding to Fig. 1a. We see from Fig. 1a that the current density in the positive slope region of the j–E curve increases monotonically with potential, which indicates that (R4) occurs on the electrode surface and sulfur deposits from the rim of electrode. As a result, the waves observed in this potential region are mainly fronts. However, when 500 mmol/L of chloride is added, HN-NDR oscillations occur in the positive slope
Fig. 2. Current time series obtained at 0.90 V for the electro-oxidation of sulfide perturbed with different amounts of dissolved chloride: (a) 0 mol/L, (b) 70 mmol/L, and (c) 500 mmol/L.

Fig. 3. Fronts (i and ii) and synchronization (iii–viii) corresponding to Fig. 1a and f, respectively.

The patterns observed evidence the transition from fronts to synchronization of sulfur deposition and dissolution, shown in Fig. 3iii and iv. In the N-NDR region, synchronized patterns of sulfur deposition and dissolution, like those in Fig. 3v–viii, are generally observed. An increase in surface-deposited sulfur typically accompanies the current increase.

3.2.2. Effect of chloride concentration on pattern formation

Fig. 4 shows time series of the current density with snapshots of the corresponding yellow pulses on the electrode surface under potentiostatic control at 1.30 V during the electro-oxidation of sulfide in the presence of various amounts of chloride. The sulfur deposition patterns observed at this potential are mainly pulses, including spirals and targets. With increasing chloride concentration the morphology of the pulses changes significantly. In the absence of dissolved chloride, regular, smooth wave fronts are

Fig. 4. Potentiostatic time series of current density at 1.30 V and the corresponding evolution of pulses for the electro-oxidation of sulfide in the presence of (a) 0 mmol/L, (b) 50 mmol/L, (c) 70 mmol/L, and (d) 90 mmol/L of dissolved chloride. Red circles show snapshots of pulses at different moments. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
observed. At $[\text{Cl}^-] = 50$ mmol/L, both the wave front and tail become irregular. Only some fragments of pulses can be seen in Fig. 4b. More regular but rough pulses are found in the presence of 70 mmol/L chloride, and, as the current density increases, the wave fronts display a smooth, serrated structure (Fig. 4c). When the concentration of chloride rises to 90 mmol/L, regular, smooth pulses are again observed in Fig. 4d. Now, however, the current fluctuates with time. These pulses are mostly triggered from the edge of the electrode and propagate toward the center. This behavior results from the fact that the current density of a disk electrode embedded in an insulator is not uniform, but is higher at the rim of the electrode than at the center [35, 36]. These pulses disappear through collision either with each other or with the edge of the disk electrode.

Perhaps the most remarkable effect of added chloride anions is the resulting change of the pulse width. Fig. 5 shows the width of typical pulses registered at 1.30 V, cf. Fig. 4, as a function of the

![Fig. 5. The width of typical pulses displayed in Fig. 4 as a function of chloride concentration.](image)

Fig. 6. Spatiotemporal patterns at different potentials for the electro-oxidation of sulfide in the presence of 70 mmol/L of chloride. (a) Current time series at different potentials. (b) Respective snapshots of the electrode surface at selected times illustrated in (a).
chloride concentration. Increasing chloride concentration clearly results in a decrease of the pulse width. In terms of mechanism, activity pulses reflect local rates of (R5)–(R7). Chloride adsorption via (R9), which competes with OH adsorption on Pt, decreases the rate of (R5), and therefore the pulse width as well. Sufficiently high chloride concentrations can even suppress the formation of activity structures completely.

3.2.3. Effect of the applied potential

As discussed above, no waves (fronts and/or pulses) are observed in the presence of 500 mmol/L of chloride. If [Cl−] is too low, oscillations cannot occur on the positive slope branch of the j-E curve. We therefore investigate the effect of electrode potential in a system containing an intermediate level of 70 mmol/L of chloride. Fig. 6 shows a time series of current density and typical patterns at several potentials in the presence of 70 mmol/L chloride. Below the onset potential, 0.75 V, the current density is close to zero, which indicates that (R2)–(R4) do not occur on the electrode, and therefore no patterns are observed on the electrode surface. When the potential is controlled at 0.80 V, the current density goes through an abrupt increase, during which fronts are observed, (see Movie 1 in Supplemental Data) and is finally maintained as high as ~100 mA/cm². Thus electrochemical reactions take place, giving rise to the pattern presented in Fig. 6b–i. If the potential is held at 0.90 V, small current density oscillations appear (see also Fig. 2b), and the pattern is similar to the pattern in Fig. 6b–i. Large amplitude oscillations in current density are found under potentiostatic control at 1.00 V. These oscillations have a period as long as 57 s with synchronization of sulfur deposition and dissolution (Fig. 6b–ii and Movie 2 in the Supplemental Data). When the potential is held at 1.05 V, mixed-mode current oscillations are obtained. Compared to the oscillations shown at 1.00 V, the maximum current density of oscillations is much lower, just over 30 mA/cm², and the period is only about half as long, but it is sufficient to generate pattern propagation. Synchronization of sulfur deposition and dissolution is found again, but only local deposition patterns emerge on the electrode during the experiment, suggesting that adsorption of chloride acts as another positive feedback (NDR) on the surface of the electrode, in addition to the positive feedback (NDR) from OH adsorption and oxide formation, producing the mixed-mode oscillations. As the potential changes from 1.10 V to 1.30 V, we observe a series of fluctuations and deposition patterns, shown in Fig. 6b–iv–viii, changing from combined evolution of synchronization and pulses (Movie 3, Supplemental Data) to pulses (Movie 4, Supplemental Data). In this potential range, more regular pulses are observed at the higher potentials, and the sulfur deposition rate is smaller than at 0.80–1.05 V. When the potential is increased as high as 1.50 V no significant deposition patterns are present (Fig. 6b–ix). The current density is nearly steady at ~40 mA/cm². Further increasing the potential will cause the current to rise again, and new feedback loops resulting from other processes, such as further surface oxidation to higher platinum oxides, may result in new complex oscillations and spatiotemporal patterns [24–26].

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2013.03.042.

4. Conclusions

We report in this work the impact of adsorbed chloride on the spatiotemporal electro-oxidation of sulfide on a polycrystalline Pt electrode. The spatiotemporal dynamics was followed by means of a CCD camera, and different chloride concentrations were used to perturb the base system. Chloride induces another positive feedback in addition to oxide formation, and it was found to strongly affect the system's dynamics. In summary, the presence of dissolved chloride enhances potential instabilities throughout the current-potential curve, including regions with positive and negative slopes, and also shifts the entire curve toward more positive potentials. In terms of spatiotemporal structures, adding chloride results in the emergence of several spatial patterns and in a decreased width of pulses with increasing chloride concentration. The structure of the pulses is also affected by chloride. We attribute these effects of enhancement in instability to NDR, i.e., positive feedback, from chloride adsorption.

We suggested in an earlier study of sulfide electro-oxidation on platinum [26] that “…further study and understanding of the detailed mechanism for oscillations and spatiotemporal patterns in this deceptively simple system may promote its application to such challenges as making depositionional materials, controlling sulfur deposition and poisoning in fuel cells, and controlling ordered micro- and nano-structures...”. We believe the present contribution represents an important step in this direction. In particular, our observation of the effect of chloride on the spatiotemporal patterns points to the importance of chemical perturbation, in addition to electrical and transport properties. Moreover, the addition of strongly adsorbing species such as chloride adds a feedback loop and causes a shift in the position of the negative differential resistance region, thus changing the parameter region in which the positive feedback loop occurs. Experimental studies of spatiotemporal patterns on a single chemical system with multi-feedback loops [37] are still rare [38,39], and results in this direction pose interesting fundamental questions for future investigations.

Besides deepening our understanding of the rich spatiotemporal dynamics of sulfur deposition and dissolution on platinum, the findings presented here reveal the impact exerted by surface adsorbed species on surface activity waves. This is an important consideration for engineering spatial patterns on surfaces.

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