Reaction Propagation over a Ring Electrode during Self-Sustained Current Oscillations in the Fe/H_2SO_4 System

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Spatio-temporal propagation of a reaction front along a ring electrode was observed during self-sustained iron dissolution current oscillations. The propagation was strongly related to the periodicity of the system, which depended on the cell geometry.

Non-linear electrochemical oscillations have been investigated since the beginning of 20th century.[1] Among the non-linear electrochemical reactions,[2,3] iron electrodissolution in sulfuric acid has been most extensively studied. In this system, current oscillations are induced by the formation and reduction of a surface oxide, and the periodicity of the system seems to be caused by the dynamical behavior of ionic species near the surface of the electrode. During periodic current oscillations on a straight iron wire electrode, propagation of a reaction front along the iron electrode was observed.[4,5] The oxide formation seems to proceed randomly along the iron wire whereas the propagation of the oxide reduction is accelerating along the electrode. This kind of pattern formation during electrochemical oscillations has been widely reported; for example, cobalt dissolution in phosphoric acid on a straight wire or a ring electrode,[6–8] iron dissolution on a continuous or discrete ring electrode,[9,10] the reduction of peroxodisulfate on a Ag ring electrode.[11,12] In this article, the non-linear electrochemical oscillations of the iron dissolution current on a ring shaped electrode was studied. The periodicity of the current oscillations was strongly affected by the geometric configuration of working and reference electrode.

A schematic representation of the cell is shown in Figure 1. Electrochemical conditions of the working electrode were adjusted by a potentiostat, Hokuto-Denko HA-320. The working electrode was an iron ring electrode (99.9% purity) with outer diameter 19 mm and inner diameter 17 mm, embedded in an acrylic plate. The electrode was immersed in 1 mol dm^{-3} sulfuric acid solution in a horizontal position. The reference electrode was a saturated calomel electrode (Toa-Denpa HC205C) and the counter electrode was a ring shaped platinum wire, the ring diameter was 80 mm and the wire diameter was 0.8 mm. The propagation of the reaction front along the electrode surface during oscillations was measured by the time course of the potential difference between the iron electrode and each of 16-channel platinum potential probes. Every platinum probe was covered with nail enamel except for its tip and it was arranged about 1 mm above the iron electrode surface. The potential signal was recorded by a 16-channel logic analyzer, HP-54645D, which was electrically isolated by a transformer, Denken-Seiki, NCT-F1. The internal impedance of the logic analyzer was high enough (100 kΩ, 8 pF) to avoid current flow through the platinum probes. The time evolution of the 16-channel signal could form a two-state (low and high) spatio-temporal map, representing the propagation of the reaction front along the electrode. The observed potential difference (a low or high signal) was related to the ohmic potential drop between the probe and the iron electrode.

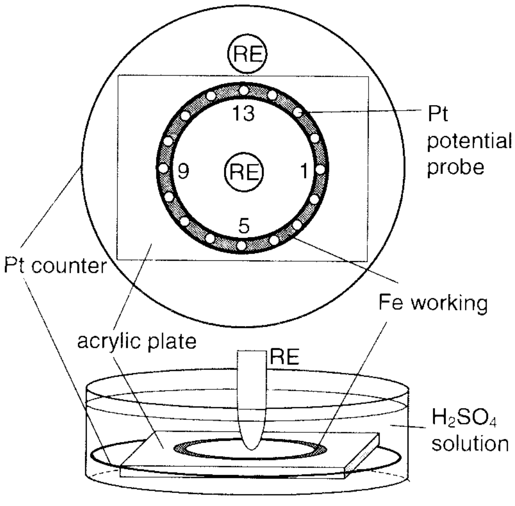

Figure 1. Schematic representation of the electrochemical cell.

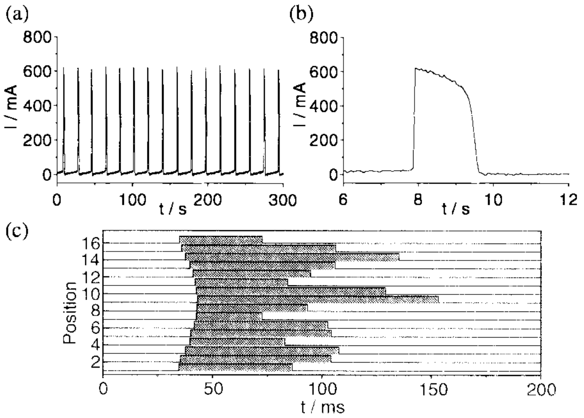

Figure 2. Temporal current response when the reference electrode was placed beside the working ring electrode, (a); a single current oscillation, (b); spatio-temporal response during one oscillatory peak (threshold potential = 0.05 V), (c).

The geometric configuration, i.e. the position of the reference electrode, strongly affected the behavior of the system. Periodic oscillations were observed when the reference electrode was placed beside the ring working electrode as shown in Figure 2 (a), where the electrode potential was fixed at 300 mV. One of the current peaks is shown in Figure 2 (b), where a quick rise, saturation and slow decay is observed. During the transition from a low current to the maximum of the oscillatory peak the electrode surface changes rapidly from the passive to

Table 1. The maximum current I_p and the charge Q during one oscillatory peak

	RE is placed beside the ring WE	RE is placed in the center of the ring WE
I_p / A	0.62	0.97
Q / C	0.89	0.55

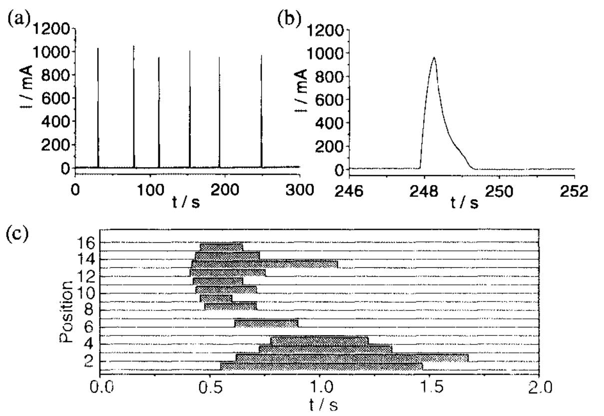

Figure 3. Temporal current response when the reference electrode was placed in the center of the working ring electrode, (a), a single current oscillation, (b), spatio-temporal response during one oscillatory peak (threshold potential=0 V), (c).

the active state. This fast transition is followed by a slower decrease of the current to an almost zero value, during which the electrode surface changes from the active to the passive state. In this case, the propagation of the reaction front of the activation and/or passivation along the ring electrode was observed through the 16-channel signals of the logic analyzer, as shown in Figure 2 (c). During one oscillatory peak, the electrode area was not homogeneous. The transition from the passive to the active state started at some point of the ring (around ch1 and 16) and propagated along the ring in both directions. The initial activation point varied from peak to peak during the time series. During activation the propagation speed was not constant but the potential front was accelerated as it traveled from the initial point along the two pathways. The situation was more complicated during passivation; as the current decreased from the active to the passive state, the electrode surface was passivated somehow randomly and finally the whole electrode surface was covered by the oxide film.

This kind of propagation during the passive-to-active and active-to-passive transitions of a periodic oscillation has been observed on the straight wire electrode also.[4,5] The active-to-passive transition takes place in a random way and still remains an open topic, whereas the passive-to-active transition, which takes place through the propagation of an accelerating potential front on the electrode surface, has been studied not only in this system but also in other electrochemical reactions.[6,11] The origin of the propagation has been widely considered as the coupling caused by the migration currents flowing along the electrode surface through the electrolytic solution.[11]

When the reference electrode was placed in the center of the ring electrode, the current response was not periodic, as shown in Figure 3 (a). The shape of the current peak was different from the previous one. Rapid but rather slower rise and slow decay without saturation was observed in Figure 3 (b) in comparison with Figure 2 (b). The amplitude was 1.5 times larger than the previous case and the charge of the peak was about 60% smaller, as shown in Table1. Figure 3 (c) shows the propagation of the reaction fronts during passive-to-active and active-to-passive transitions. In this case, the propagation was not accelerated, the speed was decreased as the reaction front propagated along the electrode. This propagation started at some point of the ring (around ch12) and propagated to two opposite directions. However the propagation was not complete because some regions remained passive during propagation. As in the previous case, the initial activation point as well as the regions which remained passive changed from peak to peak. In this case, the repassivation process was also somehow random, but it took place before the whole electrode was activated, i.e. some parts of the electrode turned to the passive state while others were still activating.

The effect of the relative position of working, reference and counter electrodes on the spatio-temporal response was studied recently for a general electrodissolution model.[13] From the present experimental results it is evident that the periodicity of the oscillations depends strongly on the coherence of the reaction on the electrode, which changes for different geometries of the electrochemical cell. The coupling strength depends on the ohmic potential drop or migration currents in the solution.[11] When the reference electrode is placed in the center of the iron working ring electrode, the coupling which is induced though the solution changes and periodic oscillations are not observed. The origin of propagation failure and its relation to the periodicity of the system is not clear yet, and a more detailed analysis is being performed in our laboratory.

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