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The pattern formation under a condition of low conductivity of electrolyte

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Abstract

Decreasing the electrolytic conductivity leads to the formation of more plentiful patterns, in comparison to normal electrochemical system. In this experiment local standing wave, cluster pattern, modulated pulse, pulse failure, pulse reflection, standing wave and pulse have been observed during the electrocatalytic oxidation of formic acid on a platinum ring electrode in a system with a very low conductivity of electrolyte and discussed. The resistivity of electrolyte used in this article is 526 Ω cm. The potential ranges of existence of different types of patterns were analysed with the help of theoretical researches and it was found that the potential ranges where different types of patterns exist can superpose each other to some extent.

Keywords: Nonlinear electrochemistry; Electro-oxidation; Pattern formation; Spatiotemporal structure; Formic acid

1. Introduction

Except for traditional electrochemistry (metal electrodeposition, metal dissolution, chemical power sources, corrosion science, etc. [1–8]), nonlinear electrochemistry has attracted more attention of researchers. As a fascinating phenomenon, the spontaneous pattern formation in time and space is displayed in many systems. The motivation includes several key observations in the last century, such as in fluid dynamics, chemistry, laser physics and biology [9–13]. In electrochemical system, the necessary conditions for pattern formation are easier to be realized, i.e., the far state from thermodynamic equilibrium and positive feedback mechanism. Based on the nature of nonlinear dynamics combined with the characters of electrochemical system, there are mainly two kinds of electrochemical oscillators: S-shape current-potential (S-NDR) and N-shape current-potential (N-NDR) characteristics. In S-NDR system, an electrochemical Turing structure is observed in experimental and theoretical researches [14]. Most of the electrochemical oscillators (for example, metal electro-dissolution, electro-catalytic oxidation of small organic molecules and hydrogen oxidation) belong to N-NDR system [15–41]. In S-NDR system the double layer potential acts as an inhibitor, but in N-NDR system the situation is opposite.

Under the existence of electric field in electrochemical system's solution, the main way of mass transportation is electric migration caused by the potential gradient. When one fluctuation occurs at one position, the mass migration took place along with the working electrode in parallel to the working electrode. In this way, the different locations feel each other, and this phenomenon is named as migration coupling and it physically stems from the tendency of the electrolyte to maintain electro-neutrality. The rate ratio of migration and diffusion in typical electrochemical system can be calculated to be 10^3–10^4 by using the dimensionless equation $d = (L\sigma)/(2\pi DC)$, where L denotes the electrode length, D is the diffusion coefficient, C represents the double-layer capacitance and σ is the ionic conductivity in electrolyte [14]. There are two approaches to calculate the potential distribution (i.e., pattern formation) at the

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electrode surface: the first one is to directly solve the Laplace equation in the entire electrolyte in every step of time and this is quite time consuming. Krischer's group often employed this approach [14,35]; the second one is to use Green's function, which assumed that the electrolyte maintains electro-neutrality at any time and there is no net charge and the potential distribution in electrolyte is determined by the boundary conditions, i.e., charge distribution at the electrode surface. Eiswirth's group's theoretical researches were based on it [26,39]. Of all the three kinds of couplings, the migration coupling is non-local. Diffusion coupling is infinity only in very narrow neighbor domains; the global coupling is equal to every location. The migration coupling intensity decreases with the distance.

The reported electrochemical systems displaying oscillation phenomenon mainly include metal electro-dissolution and electro-oxidation of organics. In electrolytes with medium ion intensity (for example, 1.0 M phosphorous species of pH 1.1 [26,27] or 0.1 M $HCOONa + 10^{-6}Bi^{3+} + 0.033$ M H_2SO_4 [39]), the migration coupling is relatively strong and there are mainly three kinds of patterns that have been formed: pulse, standing wave and anti-phase oscillation. For the latter, the electrolytic resistivity is 114 Ω cm. We expected the formation of plentiful patterns when the conductivity of the electrolyte is very low, as shown in this article, the used electrolyte has a resistivity of 526 Ω cm.

2. Experimental

The traditional one-compartment, three-electrode electrochemical system is employed, as shown in Fig. 1. The working electrode of polycrystalline platinum (WE) has ring-shaped geometry with the inner and outer diameters being 34 and 40 mm, respectively, and with a thickness of 0.1 mm. Although individual crystallites exhibit different catalytic and adsorption properties [42], the difference in the activity caused by the crystallographic orientation could be neglected because of large scale of the working electrode and because the dynamics and pattern considered here do not concern to the microscopic scale. A concentric Pt wire ring of 1 mm thickness and 70 mm diameter served as a counter electrode that is located at a 5 mm plane above the working electrode. A Luggin–Haber capillary that contains an Hg/Hg_2SO_4 reference electrode was placed in the centre of the working electrode and the tip of the capillary is in the plane similar to the working electrode. The potential microprobes are located at the electrode surface along the WE to measure the spatial potential profile across electric double layer.

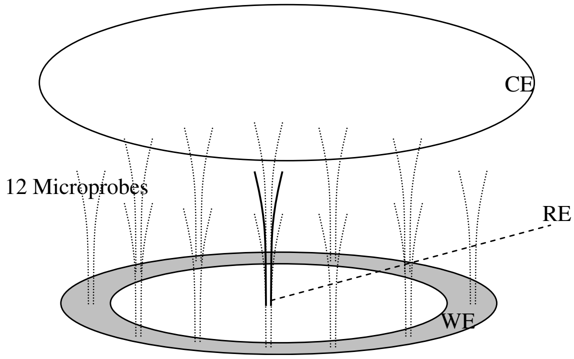

Fig. 1. The schematic diagram of the experimental three-electrode setup. The inner and outer diameters of the working electrode (WE) are 34 and 40 mm, respectively, and its thickness is 0.1 mm. Twelve microprobes, the end of which is Luggin–Haber capillary, stand on the WE with an interval of 30°. The counter electrode is located at 5 cm above the WE. The reference electrode is in the same plane with the WE for all the measurements in this article.

The used electrolyte is 0.1 M $HCOOH + 10^{-6}$ M $Bi^{3+} + 0.001$ M Na_2SO_4 (HCOOH p.a., Na_2SO_4 p.a.), of which the measured resistivity is 526 Ω cm.

WE pre-treatment procedures include chemical cleaning in concentrated H_2SO_4/H_2O_2 solution and voltammetric cycling between −650 mV and 800 mV in 0.5 M H_2SO_4 solution with a scan rate of 100 mV/s until a stable cyclic voltamagram was obtained. A home-built potentiostat was used throughout that can be connected with at best 16 tenfold potential amplifiers amplifying the instantaneous local electrode potential, which are sampled by an A/D multiplexer at approximately 1 kHz. The final potential corresponded to the local potential drop between WE and the individual microprobes, i.e., the qualitative instantaneous local double layer potential drop. Limited by the measurement system, for an oscillatory test with a longer duration than 1 h (in the case of low ionic conductivity, the oscillatory state can sustain for more than 12 h), the acquisition of the data has been manually interrupted for a while (about 5 min) and then restarted after the stored data have been transmitted to the PC hard disk.

The conductivity of the electrolyte was measured with a Conductivity Pocket Meter (Handylab pH/LF 12, Schott Instruments) under room temperature.

In this paper, the measured parameter is the local potential on the electrode surface. In the spatio-temporal figures, the hot color represents the high potential state (passive state) and cold color represents the low potential state (active state). As a result, the color represents the local potential.

3. Results

In an electrolyte of relatively high conductivity ($12.6 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$ or more), in oscillatory potential region three main types of patterns could be found: in the relatively low potential region we can find a standing wave. When the potential increases further the pulse occurs. Further increasing the potential leads to the formation of anti-phase oscillation. Under a high conductivity the identification of the measured pattern is easier and the possible reason is that the measured pattern is relatively simple. In addition, these patterns are easier to be captured because the transient duration should be shorter even when there is no transient state between different types of