Spatio-temporal pattern formation
by non-linear electrochemical reactions

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1   Introduction

Spatio-temporal pattern formation in electrochemical systems can take place on the reaction surface (electrode/electrolyte interface), the electrolyte solution or both. Electrochemical systems can be considered as a special case of non-homogeneous physicochemical systems where four main processes take place: (a) Movement of ions towards or from the reaction surface via diffusion, migration and convection, (b) electrochemical reaction on the electrode surface, (c) movement of products via diffusion, migration and convection and, (d) homogeneous chemical reaction in the solution. The presence of externally applied electric potential complicates the understanding of electrochemical dynamical behavior due to two principal factors. The coupling between local active elements can be non-local and the resulting modeling equations constitute a boundary value problem with strongly non linear boundary conditions. Additionally, the microscopic processes taking place during the dynamical behavior are often unknown. In the following report three different examples of electrochemical systems giving rise to coupling and spatio-temporal pattern formation are presented as well as an attempt of mathematical modeling.

2   Electrochemical Dynamical Behavior

2.1   Coupling

In order to investigate the possible coherent and synchronized behavior during electrochemical oscillations the following experiment was set up. A rather long (3 cm) iron wire embedded in an insulating plane was immersed in 1M H_2SO_4 solution. The electrode surface was divided in two equal regions either by an insulating film of variable length or by a physical partition. The length of the insulating film was assumed to affect the strength of coupling between the two identical electrochemical oscillators whereas the physical partition can be considered as a limiting case of very small coupling. The behavior of the surface was monitored by a logic analyzer and the potential on the electrode was controlled by a potentiostat.

When the length of the insulating film is small (strong coupling between the two oscillatory regions) the response of the system is always simply periodic (Fig. 1a). The two regions tend to oscillate exactly with the same frequency and phase. On the other hand, the electrode surface does not behave in a homogeneous manner. As it can be seen in Fig.1b during the periodic oscillations of the current the surface tends from the passive to the active state via a potential front starting from one edge of the electrode surface and traveling towards the other edge.

By decreasing the coupling strength the resulting response remains periodic but the two oscillatory regions oscillate with different frequency and phase. As a result, the total current time series consists of a series of small and large peaks following the relation k/n where k is the number of peaks of region A and n the number of peaks of region B within a repeating pattern in the time series. A big variety of temporal patterns can be observed during intermediate and small coupling like 2/1, 4/3, 6/5 in phase and out of phase response. Some examples of this kind of response are presented in Fig. 2.

As the coupling becomes very small (partitioning with an acrylic plate) the response is not-periodic any more. The two regions tend to oscillate somehow independently and the resulting pattern is very complex. In order to understand the temporal patterns observed during the coupling of the two identical oscillators the following simplified model was introduced [1],

$$\epsilon \dot{u}_i = (v - u_i)/R_i - k_1(1 - \theta) + (u_j - u_i)/R_{coup}, \tag{1}$$

$$\dot{c}_{1,i} = (1 - c_{1,i}) - t_1(v - u_i)/R_i, \tag{2}$$

$$\dot{c}_{2,i} = -ac_{2,i} - t_2(v - u_i)/R_i + k_1(1 - \theta), \tag{3}$$

where $i = 1$ when $j = 2$ and vice versa, u is the dimensionless electrode potential, c_1 and c_2 the surface concentrations of hydrogen and metal ions, respectively and the rest of the symbols have a meaning according to [1]. In Eq.(1) the far right term represents the coupling between the two regions due to the difference of their surface potential. By integrating Eqs.(1-3) it is shown that while the coupling is not infinitesimal, the response is always k/n. For strong coupling $k/n = 1/1$ as in Fig.1 where as for very small coupling the response is complex.
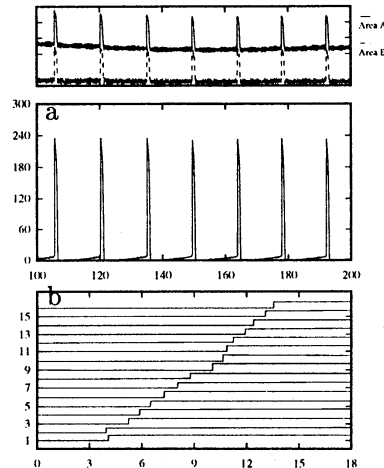

Figure 1: (a) In-phase 1/1 current response during strong coupling (Film length 3 mm, $V = 275$ mV) and (b) spatio-temporal response.
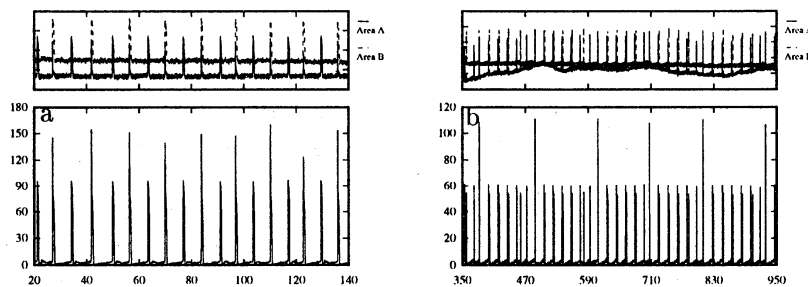

Figure 2: (a)In-phase 2/1 response (Film length 15 mm, $V = 274$ mV) and (b) in-phase 6/5 response (Film length 22 mm, $V = 280$ mV).

2.2 Bifurcations and Spatio-temporal response on the electrode/electrolyte interface

Spatial perturbations on the electrode surface can be used for the elucidation of the bifurcation structure of the electrochemical dynamical system. Specially, in the case of Fe/H_2SO_4 system, the system can be spatially perturbed with the use of a laser beam while the system is on its passive state. The perturbation experiments can offer direct information like excitability, coexistence of stable steady states as well as indirect information about the existence of unstable steady states or limit cycles. A detailed experimental investigation of the above system under spatial perturbations suggests the bifurcation curve presented in Fig. 3, by considering V as a bifurcation parameter.

Most of the spatio-temporal dynamical response observed experimentally (oscillations, excitability, bistability, bifurcations and front propagation) is reproduced by considering the following model [2],

$$\beta^2 \frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial z^2} = 0, \tag{4}$$

with boundary conditions,

$$\Phi(x, z = 1, t) = 0, \tag{5}$$

$$\Phi(x, z, t) = \Phi(x + 2\pi, z, t), \tag{6}$$

$$\epsilon \frac{\partial \Delta \Phi_{DL}}{\partial t} = -i_F - \frac{\sigma}{\beta} \frac{\partial \Phi}{\partial z}\bigg|_{z=0}, \tag{7}$$

$$\frac{\partial c}{\partial t}\bigg|_{z=0} = i_{F,2} + 1 - c(x, z = 0, t) + \frac{\sigma}{\beta} \frac{\partial \Phi}{\partial z}\bigg|_{z=0}, \tag{8}$$

$$V = \Delta V_{ex}(t) + \Delta \Phi_{DL}(x, t) + \Phi(x, z = 0, t), \tag{9}$$

where $\Phi \to RT\Phi/F$, $x \to lx/2\pi$, $z \to dz$, $\beta = 2\pi d/l$ and i_F is the Faradaic current due to the dissolution and passivation reactions, and $i_{F,2}$ is the Faradaic current due to the passivation reaction. An example of the spatio-temporal response during bistability is shown in Fig. 3b. The above formulation was originally applied for a ring electrode geometry. It can be shown rather easily that the model can be expanded in different geometries, like the "hallow cylinder" configuration. The spatio-temporal response in this case can be very rich varying from homogeneous to non-homogeneous, as it is shown in Fig.4.
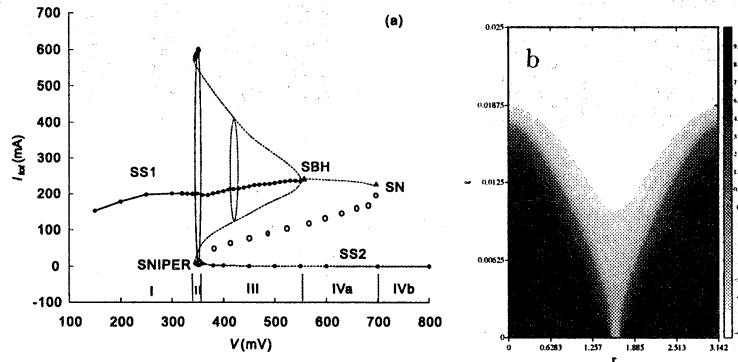

Figure 3: (a) Experimental bifurcation curve for $R_{ex} = 0.5 \, \Omega$ and (b) Theoretical front propagation during bistability.
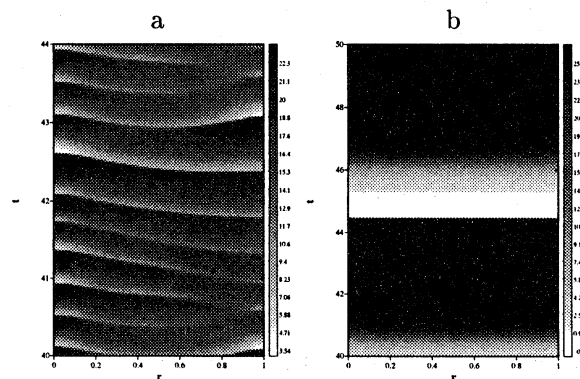

Figure 4: Spatio-temporal evolution of the potential for the hallow cylinder configuration, (a) $V = 26.55$ and (b) $V = 27.76$.

2.3 Patterns in the electrolytic solution

A different class of spatio-temporal patterns are the ones observed within the electrolytic solution. An example of cellular pattern formation between two parallel Cu wire electrodes in $CuSO_4$ solution is presented in Fig. 5a. It can be seen that due to the interplay of the electrochemical reactions (electrodissolution

and electrodepossition) a convective flow is generated leading to patterns similar to the case of thermal convection. Due to the fact that the above patterns are observed within the limiting current plateau in the presence of a binary electrolyte, the problem can be formulated as follows,

$$\nabla \cdot \mathbf{u} = 0, \tag{10}$$

$$\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla p + \nabla^2 \mathbf{u} - \frac{R_{el}}{P_{el}} c \mathbf{e}, \tag{11}$$

$$\frac{\partial c}{\partial t} + \mathbf{u} \cdot \nabla c = -\mathbf{u} - P_{el}^{-1} \nabla^2 c. \tag{12}$$

The above simple formulation, which has a one-to-one similarity with the thermal case can predict the transition from steady state to cellular convection, as it is shown in Fig. 5b. Additionally, the movement of the cells under the effect of the magnetic field is predicted by the mathematical formulation [3].
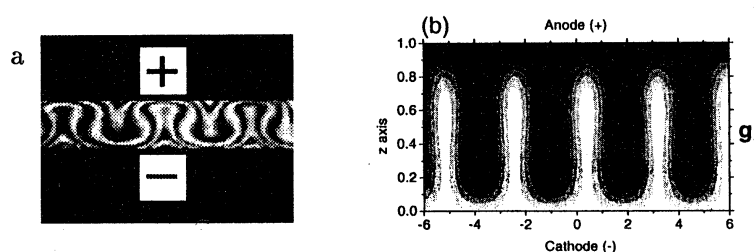

Figure 5: (a) Experimental cellular convection for $V = 0.4$ V and (b) model calculations.

3 Conclusions

Electrochemical oscillators can be considered to consist of an infinite number of identical elementary oscillatory elements. The principal cause of coupling is migration currents flowing along the electrode surface. Even though the reaction surface does not behave in a pure coherent manner during oscillations, strong coupling forces the system to oscillate macroscopically in a periodic manner - simple or more complex. Oscillatory and excitable behavior as well as potential front propagation during bistability can be reproduced by formulating a boundary value problem based on Laplace equation and simplifications of the mass balance equation and the equation of conservation of charge. The formulation can be applied to different system geometries and predict many of the spatio-temporal features. Special classes of spatio-temporal patterns in electrochemical systems have the same hydrodynamic origin with systems of during thermal convection.

References

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