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Mixed-Mode and Chaotic Oscillations in a Simple Model of an Electrochemical Oscillator

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We present some preliminary results obtained with a simple three-variable model that should adequately describe the mixed-mode and chaotic oscillations observed during the reduction of indium(III) at mercury in the presence of thiocyanate. This model is the first to satisfactorily reproduce such complex dynamic behavior in an electrochemical system.

In the past couple of years, electrochemical reactions have proven to be excellent paradigms in the study of nonlinear dynamics in chemical kinetics. Such diverse systems as the electrolysis of copper in an acidic environment, oxidation of formaldehyde or formic acid at platinum, the reduction of hydrogen peroxide at platinum, and the reduction of indium(III) at mercury in the presence of thiocyanate have been shown to exhibit typical far-from-equilibrium behavior like multistability, oscillations (periodic, quasiperiodic, multiperiodic, often of the mixed-mode type), and chaos. So far, however, there does not exist, for any one of these systems, a complete and reliable theory or model that helps us in understanding why electrochemical reactions are so easily persuaded to display a dynamic behavior whose embedding phase space should at least be three-dimensional.

Of concern in this Letter are some preliminary results obtained with a three-variable model that seems to be, to the best of our knowledge, the first physically reasonable model that is able to explain mixed-mode and chaotic oscillations in an electrochemical system. Our model is in principle concerned with describing the spontaneous current oscillations observed during the reduction of indium(III) catalyzed by thiocyanate at a hanging mercury drop electrode, but we believe that the model possesses some general features that could make it promising in the interpretation of complex oscillations in other, more intricate systems as well.

The system is described by diffusion of In(III) in an electrolyte solution containing a large excess of sodium thiocyanate, coupled with a heterogeneous reaction at the hanging mercury drop. The general equations of the system are the following:

Equation 1 describes the electric charge conservation at the electrode. V is the adjustable potential difference acting on the entire circuit, E is the electrode potential, C_E is the capacity of the electrical double layer, R_s is the external series resistance, A is the available drop area, n is the number of electrons involved in the charge-transfer reaction, F is the Faraday constant, and k(E) is the overall rate constant for the indium(III) reduction in the presence of thiocyanate. We shall define here below this rate as a function of the electrode potential E. Equation 2 is the diffusion equation for the indium(III) concentration C in the spherical geometry of the drop. Equations 3 give the boundary conditions for (2) at the surface of the drop of radius a and at a large distance in the bulk.

To capture the essence of the phenomenon of mixed-mode oscillations, we shall simplify (1)–(3) in the following way. The electrolyte around the drop of radius a is divided in two fictive spherical diffusion layers which are both of thickness a/2. We use here an extension of the well-known Cottrell result that the diffusion layer thickness can be estimated by the drop radius. Furthermore, we assume that the indium concentration is uniform at the value C_{bulk} in the layer neighboring the electrode while the concentration has the uniform value C_{bulk} in the next-neighboring layer. Outside these two layers, i.e., outside a fictive sphere of radius 2a, we assume that the concentration has reached the bulk value, C_{bulk}. These assumptions allow us to reduce eqs 1–3 to the following three-dimensional vector field

In eqs 4 e is the dimensionless electrode potential, v is the circuit potential, r is the adjustable series resistance (Ohmic solution resistance included), m is some dimensionless parameter proportional to the bulk concentration of the indium(III), d is a parameter proportional to its diffusion coefficient, u and w are its normalized concentrations, and k(e) is the dimensionless heterogeneous rate constant. The electric current i flowing through the circuit is equal to (v - e)/r.

While the first equation in (4) is an expression of the conservation of current, the second equation is a mass balance equation for the surface concentration u, taking into account the chemical conversion at the interface and the diffusion toward it from the next-neighboring layer. The coefficients in the evolution equation for w stem from the spherical geometry and from our assumption about the thickness of the different diffusion layers. The choice of this geometry is to some extent arbitrary but does not change qualitatively the following results. In particular, we observed the same behaviors replacing these coefficients by those of second spatial difference.

The dimensionless rate constant k(e) for the reduction of In(III) in the presence of thiocyanate can be written as:

(5)

The first term is the translation of the catalyzing action of the thiocyanate ions.

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oscillation, a state eqs 4-6. Pospisil and de Le~ie. The second term (with the interplay of the specific adsorption and Coulombic repulsion expresses the much slower, uncatalyzed indium reduction. Owing to the electron-transfer coefficient and the diffusion from the bulk toward the electrode/electrolyte interface. Instead of supposing that the flux at the interface is proportional to the concentration, we have introduced here a third variable, the transfer coefficient and that in turn undergoes a Hopf bifurcation at $r = 0.017155$.

**Mixed-Mode Oscillations (MMO).** Shortly hereafter, still raising $r$, the small-amplitude oscillation is destroyed when a sudden relaxation spike appears on the scene, creating the first of a sequence of mixed-mode oscillatory (MMO) states. Some of these states are depicted in Figure 1, and we shall indicate them with a symbolic notation $L^5$, $L$ giving the number of large and $S$ the number of small oscillations in one period. Similar states are also observed at the low-resistance boundary of the oscillatory region in the potential-resistance parameter plane of the In/SCN oscillator. With increasing $r$, we observe the sequence $1^21$, $1^20$, $1^29$, ..., $1^21(13)^n$, $1^2$, $1^2(1)^n$, $1^2$, $1^2(10)^n$, $1^2$ (7) with $n$ going from 1 to 8 or 10 in our numerical computation. In the right-hand part of the sequence, two neighboring states show interjacent periodic states that are concatenations of the two principal states. In the left-hand part, the windows of stability of these interjacent periodic states are so small that we do not observe them. The bifurcation sequence (7) thus presents two complementary regimes whenever $r$ is low or higher.

**Incomplete Homoclinic Scenario.** At low $r$ in the sequence, the stability eigenvalues ($\rho \pm i\omega, \lambda$) of the saddle focus satisfy $|\rho/\lambda| < 1$, which is one of Shil'nikov's necessary conditions to have dynamical chaos. However, the reinjection flow is so contractive that the chaos is squeezed away and there remains only the typical bifurcation sequence of MMO. The role of the saddle focus is demonstrated by the fact that the diagram of the period of MMO versus the control parameter $r$ is reproduced by the formula

$$T(r) = T_0 + \rho(r)^{-1} \ln (1 - r_0^2 + c^2)^{1/2}$$

(8)

where $\rho(r)$ is the real part of the unstable eigenvalue of the saddle focus which is changing with $r$ while $r_0$ is the critical parameter value for the end of the sequence (see Figure 2). The incompleteness of the homoclinic scenario appears in the constant $c$, which expresses the fact that exact reinjection on the saddle focus creating a complete homoclinic connection does not occur on account of the strong contractivity of the flow.

**Incomplete Farey Sequence.** The sequence (7) is very reminiscent of the incomplete Farey sequence observed by Schell and co-workers in the electrode dissolution of copper in phosphoric acid. An incomplete Farey sequence like the one described here should not be confused with the complete, unpruned one that is known to be created at the critical surface of mappings of the circle onto itself. Rather, they are associated with two extremum maps modeling reinjecting phase space flows, like they are known to typically occur near homoclinic tangencies.

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of a phase space flow that can be modeled with an iterative map that possesses two extrema. At states, however, we observed that both a tangent bifurcation and through subsequent subharmonic bifurcations, but for the chaotic behavior during the reinjection is weaker here than in the MMO periodic states between two neighboring states, because con-traction during the reinjection is weaker here than in the MMO sequence at low r. The fixed point becomes a Shil'nikov saddle focus here as well, but again the complete homoclinic connection of mass transport that is frequently encountered in electrochemistry: the coupling between diffusion and hydrodynamic convection may have wider applications, albeit perhaps in a little different argument that led us to introduce a third variable in our description of the diffusion are easily generalized to another kind of mass transport that is frequently encountered in electrochemistry: the coupling between diffusion and hydrodynamic convection at a rotating disk electrode. It is for this reason that our model may have wider applications, albeit perhaps in a little different appearance. In forthcoming work, we hope to elaborate in more detail on both the dynamical as well as the physicochemical properties of our model.

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