Experimental demonstration of delay and memory effects in the bifurcations of nickel electrodissolution

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It is shown experimentally that the rate of change v of the applied potential affects the delay associated with the Hopf and saddle-node bifurcations in the anodic nickel dissolution in aqueous sulfuric acid solutions. The magnitude of the delay is proportional to v^p where $p \approx 1$ for the Hopf and $p \approx 2/3$ for the saddle-node bifurcation. A memory effect, i.e., the onset of oscillation exhibiting dependence on the starting potential, is observed during a fast scan through the Hopf bifurcation point. [S1063-651X(96)03607-0]

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Many experimental and theoretical bifurcation problems involve slowly varying control parameters. This variation may be due to a natural transient of the system such as slow irreversible degradation of a catalyst, or is imposed deliberately by the experimenter. Knowledge about the influence of a time-dependent control parameter is useful in predicting undesirable jump transitions, and in the construction of a system's bifurcation diagram.

Theoretically, the problem has been studied in the limit of small rates of change of the bifurcation parameter [1,2]. In general, it is found that the parameter value μ_v where the transition due to the bifurcation occurs is delayed with respect to the critical parameter value μ_s of the static problem; the delay $\mu_v - \mu_s$ follows a power-law dependence on the rate of change v of the parameter:

$$\mu_v - \mu_s = c v^p, \tag{1}$$

where c is a constant and p is an exponent characteristic of the type of bifurcation. For a saddle-node bifurcation, $p = 2/3$ [1,3]; for a Hopf bifurcation, $p = 0$ [2] (i.e., the delay in the Hopf bifurcation is predicted to be independent of v). For the reverse Hopf bifurcation, namely, that from the oscillatory to the stationary solution, Holden and Erneux [4] have shown that the amplitude of oscillations at the Hopf bifurcation is expected to decrease with decreasing v, and, in the limit of small v, is proportional to an $O(v^{1/4})$ quantity. Another interesting prediction from these asymptotic theories is the existence of a memory effect [2], which stipulates that the delay $(\mu_v - \mu_s)$ for the Hopf bifurcation depends on the initial value μ_i of the control parameter according to $\mu_v - \mu_s = \mu_s - \mu_i$. These predictions follow from a deterministic treatment of the mathematical problem and do not include the role of internal or external noise. However, since we are dealing with potentially unstable systems, we may expect an increasingly important role of noise as v decreases [2,5].

On the experimental side, there are several papers studying the role of a slowly varying control parameter on bifurcation phenomena including electrophysiology [6], optics [7], electrical circuits [8], and chemical reactions [3,9–11]. However, to our knowledge, there is as yet no quantitative study on all of the above-mentioned effects in a single system.

In this paper, we describe the effect of a slowly varying parameter on the Hopf and saddle-node bifurcations in the anodic dissolution of nickel in sulfuric acid (for a comprehensive bifurcation study of this system, see Lev *et al.* [12]). The advantage of using an electrochemical oscillator lies in the ease of its experimental control and in the fact that the oscillations are usually much faster (0.1−10 Hz) than in other chemical systems. Also, Ni dissolution is a remarkably robust system that exhibits a clear supercritical (nonsingular) Hopf bifurcation and a saddle-node bifurcation, both of which are quite reproducible.

The electrochemical cell in our experiments consists of a nickel wire as working electrode (99.994%, Alfa) with an exposed area of ca. 1 mm^2, a nickel foil as counterelectrode, and a saturated calomel reference electrode. The electrolyte solution is 1.0N H_2SO_4 in doubly distilled water. Before transferring to the cell, the nickel wire was rinsed in ethanol and water. The cell was connected to a PAR 173 potentiostat-galvanostat, which was connected to a PAR 175 Universal Programmer generating the potential sweeps. In contrast to earlier studies, which reported potential oscillations under a fixed applied current (galvanostatic conditions) [12], we choose to employ a potentiostatic control with an Ohmic resistor connected in series with the working electrode. This gives rise to current oscillations that are of the same mechanistic origin as the galvanostatic potential oscillations [13], and, in addition, it allows a convenient exploration of a two-parameter bifurcation diagram involving the applied potential and the series resistance. Scan rates rarely went below 1–2 mV/s to avoid undesirable changes in the electrode surface area due to continuous dissolution of the electrode. Experiments were carried out at room temperature.

To investigate the effect of the scan rate on the onset of oscillations, the following procedure was followed for each run: the potential was scanned at a fixed rate starting at 1300 mV and ending at 2100 mV at which point the scan was reversed. Prior to each scan in the forward direction, the system was allowed to relax to the steady state at 1300 mV.

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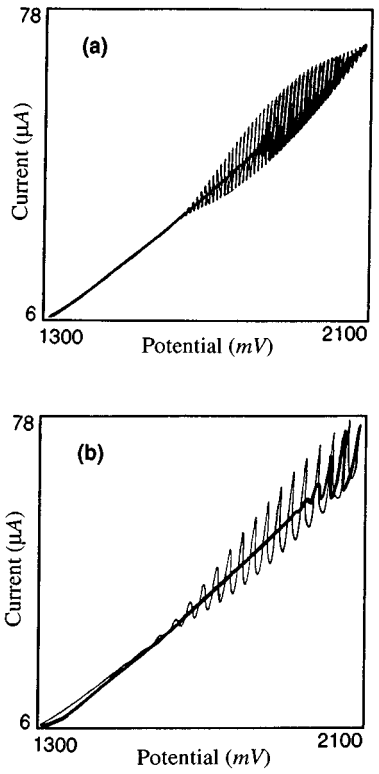

FIG. 1. Current-voltage scans for Ni dissolution in $1N$ H_2SO_4 illustrating the effect of varying scan rate on the oscillatory behavior: (a) scan rate = 3 mV/s, (b) 10 mV/s. The Hopf bifurcation under consideration is at 1750 mV. Note the presence of a second Hopf bifurcation near the upper potential limit of the scan. External resistance is 10 kΩ.

The onset of oscillations is defined to be at the potential for which the envelope of the oscillations reaches a small predefined threshold value. Figure 1 shows two current-voltage scans for the scan rates of 3 and 10 mV/s; for each scan, the thick curve indicates the forward direction and the thin curve indicates the reverse. Note that the oscillations are significantly delayed at the higher scan rate. Figure 2 gives a log-log plot of the delay versus the scan rate (here, the Hopf bifurcation point was extrapolated from the lowest scan rates); the slope of the straight line is 0.94, which is indicative of a linear dependence ($p=1$). This contradicts the result of Baer, Erneux, and Rinzel [2]. However, these authors noted that, for the lower scan rates, their result is masked by the influence of noise and even round-off errors in their numerical calculations. In fact, if we replot their numerical calculations in single precision [using the curve labeled ''SP'' in Fig. 4(a) of Ref. [2]] as delay versus scan rate, an approximately linear curve is obtained. We conclude that the internal noise is responsible for the roughly linear dependence of the delay in the Hopf bifurcation on the scan rate. We note that a similar result was obtained by Fronzoni, Moss, and McClintock [8], in their study of the Hopf bifurcation in an electronic model of the Brusselator, although their plot is slightly curved instead of linear.

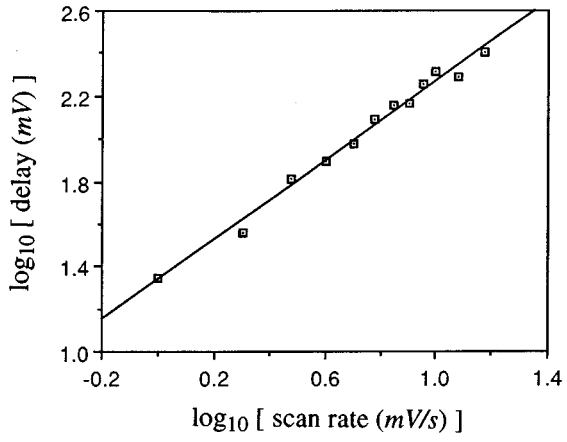

FIG. 2. Log-log plot of the delay in the Hopf bifurcation at 1750 mV versus the scan rate. Linear regression gives a slope $p=0.94$. Experimental conditions as in Fig. 1.

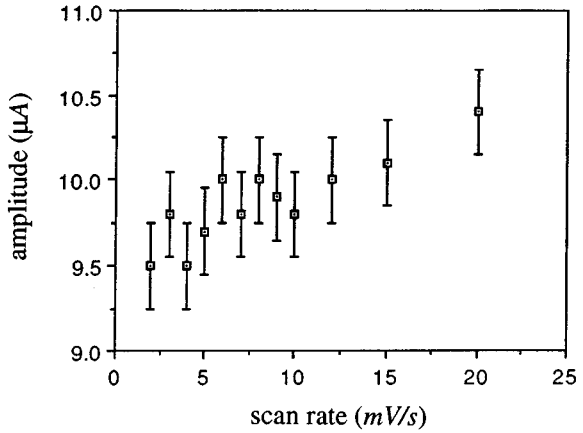

FIG. 3. The amplitude of oscillation during the return scan at the Hopf bifurcation point (1750 mV) as a function of the scan rate. Experimental conditions as in Fig. 1.

From the same scans as depicted in Fig. 1, the amplitude of oscillations at the Hopf bifurcation during the return scan can be determined. The results are collected in Fig. 3 which confirm the expected decrease in amplitude for the lower scan rates. Unfortunately, no reliable power law can be extracted from these data.

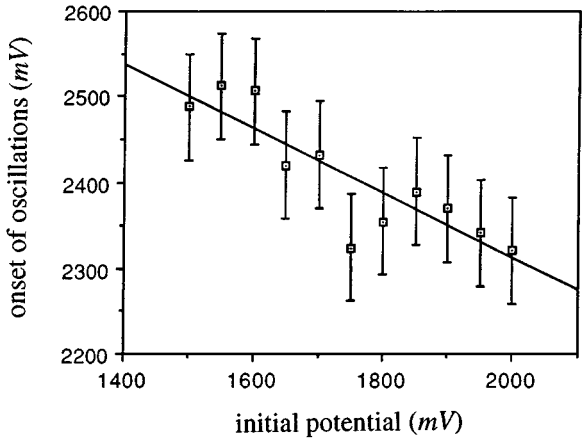

FIG. 4. Illustration of the memory effect for Ni dissolution in $1N$ H_2SO_4. Plotted is the onset of oscillation as a function of the initial potential of the scan. Scan rate = 40 mV/s. External resistance = 40 kΩ.

Next, the influence of the initial potential on the onset of oscillations was studied. The procedure used was similar to that given above except that we only considered forward scans (all conducted at the same rate); on every scan the initial potential was increased by 50 mV (a procedure in which the initial potential was stepped down on every scan yielded similar results). For the low scan rates ($\leqslant 10$ mV/s), there is no detectable influence of the initial potential on the transition to oscillations. For the higher scan rates ($\geqslant 20$ mV/s), a plot of the onset of oscillations versus initial potential always showed a significant negative slope (in spite of a large scatter of data points). Figure 4 gives a typical example for 40 mV/s. The slope of the best-line fit is -0.37, which is still far from the theoretical (and noise-free) slope of -1. Nevertheless, this result seems to be a reliable demonstration that the memory effect is a real phenomenon. The role of the scan rate is easy to understand: since noise erases memory effects [2], high scan rates are needed to minimize the integrated influence of noise. We want to emphasize that, in the experimental procedure, it is important that the system be allowed to equilibrate (i.e., given enough time) to its stationary current value at the initial potential. Due to critical slowing down, equilibration time becomes longer as the Hopf bifurcation point is approached. We always took care that any residual damped oscillations had fully died out before a scan is started.

When the limit potential in the scan is chosen more positive than that in Fig. 1, two new jump transitions are observed in the scan due to saddle-node bifurcations [see Fig. 5(a)]. Since the jump transition in the return scan is sharper, we choose this transition to test the 2/3 power law. On the fast time scale of a sharp transition, a relatively high scan rate might still be considered as small, rendering a confirmation of the asymptotic result of Eq. 1 more likely. Figure 5(b) shows the jump transition as a function of the scan rate. As the exact value of the saddle-node bifurcation could only be determined inaccurately, the jump transition is plotted versus the 2/3 power of the scan rate in Fig. 5(b). A reasonably straight line is obtained. If the parameter value for the saddle node is extrapolated from this figure, a log-log plot of the delay versus the scan rate gives a slope of 0.78 (if the two points that are farthest from the straight line are not considered, a slope of 0.61 is obtained). A similar result was obtained for another set of parameters (i.e., a different value of external resistance). These numbers are not too far from the theoretical exponent of $p = 2/3$. An earlier experimental confirmation of this law was obtained by Erneux and Laplante [3] for the bistable iodate-arsenous acid reaction (these authors found a value of $p \approx 0.63$).

In conclusion, we have shown that varying the scan rate has a considerable effect on the delay associated with Hopf and saddle-node bifurcations in the electrochemical dissolution of nickel in sulfuric acid solution. The effect of the scan rate is succinctly expressed by Eq. (1) with $p \approx 1$ for Hopf bifurcation and $p \approx 2/3$ for saddle-node bifurcation. Our result for the characteristic exponent for the Hopf bifurcation differs with the theoretical prediction, but this deviation may be understood by considering the role of noise. As far as we know, our work provides the first evidence for a memory effect in the delay associated with a Hopf bifurcation, which was first predicted theoretically by Baer, Erneux, and Rinzel [2]. Here, also, the role of noise is important.

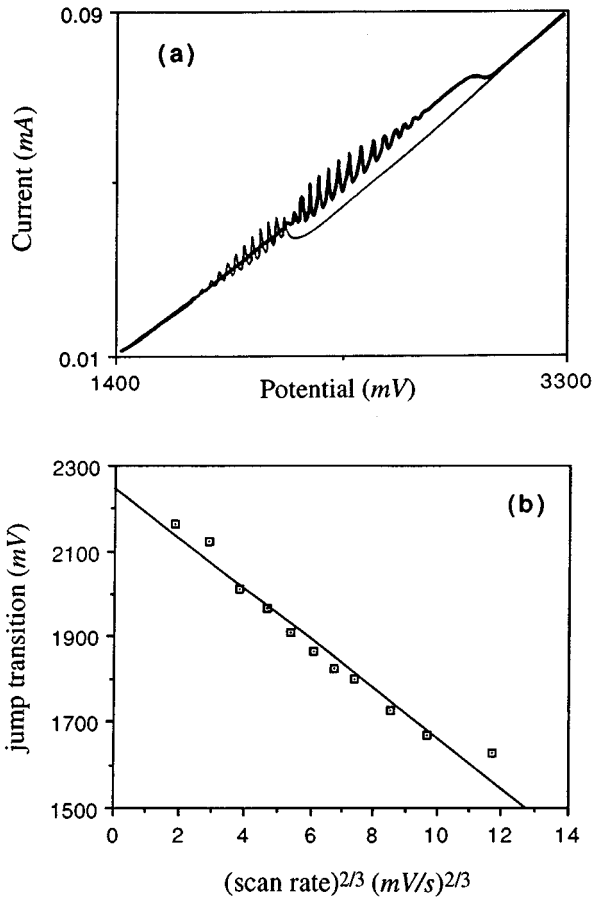

FIG. 5. (a) Current-voltage scan for Ni dissolution in 1N H_2SO_4 in the presence of a 20-kΩ external resistance and scan rate of 10 mV/s. Note the presence of two Hopf bifurcations on the forward scan (thick curve) and two jump transitions due to saddle-node bifurcations, one on the forward and one on the reverse scan (thin line). (b) The potential of the jump transition during the reverse scan as a function of (scan rate)$^{2/3}$. Theoretically, this plot should give a straight line in the limit of small scan rates [3].

Finally, we wish to comment on an alternative explanation that may be given for the observed experimental trends, namely, the internal drift of the system. Although there certainly is some influence of the drift in our experiments, we believe it to be negligible on account of two considerations. First, if there were an appreciable role of the internal drift, then on the time scale of our experiments, one would also expect a noticeable difference between the first and last scans of a set of experimenal runs, e.g., in the total current at the maximum in the voltammogram. No such significant differences were found if the scan rate was kept above 2 mV/s. Second, all observed trends agree within experimental error with theoretical predictions, and were reproducible. We find it difficult to believe that the internal drift might lead to the same situation.

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[1] R. Habermann, SIAM J. Appl. Math. **37**, 69 (1979).
[2] S. M. Baer, T. Erneux, and J. Rinzel, SIAM J. Appl. Math. **49**, 55 (1989).
[3] T. Erneux and J. P. Laplante, J. Chem. Phys. **90**, 6129 (1989).
[4] L. Holden and T. Erneux, SIAM J. Appl. Math. **53**, 1045 (1993).
[5] J. Rinzel and S. M. Baer, Biophys. J. **54**, 551 (1988).
[6] E. Jakobsson and R. Guttman, Biophys. J. **31**, 293 (1980).
[7] W. Scharpf, M. Squicciarini, D. Bromley, C. Green, J. R. Tredicce, and L. M. Narducci, Opt. Commun. **63**, 344 (1987).
[8] L. Fronzoni, F. Moss, and P. V. E. McClintock, Phys. Rev. A **36**, 1492 (1987).
[9] C. L. Creel and J. Ross, J. Chem. Phys. **65**, 3779 (1976).
[10] T. T. Tsotsis, R. C. Sane, and T. H. Lindstrom, AICh J. **34**, 383 (1988).
[11] J. P. Laplante, T. Erneux, and M. Georgiou, J. Chem. Phys. **94**, 371 (1991).
[12] O. Lev, A. Wolffberg, M. Sheintuch, and L. M. Pismen, Chem. Eng. Sci. **43**, 1339 (1988); O. Lev, A. Wolffberg, L. M. Pismen, and M. Sheintuch, J. Phys. Chem. **93**, 1661 (1989).
[13] M. T. M. Koper, Adv. Chem. Phys. **92**, 161 (1996).