Published in final edited form as:

J Electroanal Chem (Lausanne Switz). 2011 August 1; 659(1): 92–100. doi:10.1016/j.jelechem.2011.05.007.

Electrochemical Oscillations of Nickel Electrodeposition in an Epoxy-Based Microchip Flow Cell

Alexander G. Cioffi¹, R. Scott Martin¹, and István Z. Kiss^{1,*}

¹Saint Louis University, Department of Chemistry, 3501 Laclede Ave., St. Louis, MO 63103

Abstract

We investigate the nonlinear dynamics of transpassive electrodeposition of nickel in sulfuric acid in an epoxy-based microchip flow cell. We observed bistability, smooth, relaxation, and period-2 waveform current oscillations with external resistance attached to the electrode in the microfabricated electrochemical cell with 0.05 mm diameter Ni wire under potentiostatic control. Experiments with 1 mm × 0.1 mm Ni electrode show spontaneous oscillations without attached external resistance; similar surface area electrode in macrocell does not exhibit spontaneous oscillations. Combined experimental and numerical studies show that spontaneous oscillation with the on-chip fabricated electrochemical cell occurs because of the unusually large ohmic potential drop due to the constrained current in the narrow flow channel. This large IR potential drop is expected to have an important role in destabilizing negative differential resistance electrochemical (e.g., metal dissolution and electrocatalytic) systems in on-chip integrated microfluidic flow cells. The proposed experimental setup can be extended to multi-electrode configurations; the epoxy-based substrate procedure thus holds promise in electroanalytical applications that require collector-generator multi-electrodes wires with various electrode sizes, compositions, and spacings as well as controlled flow conditions.

Keywords

non-linear dynamics; corrosion; electrochemical oscillation; microfluidics; microfabrication; microelectrode

1. Introduction

Electrochemical systems exhibit a wide spectrum of dynamical behavior including multistability and periodic, quasiperiodic, and chaotic oscillations. [1-4] Two major factors that orchestrate large majority of these phenomena are the negative differential resistance (NDR) of the current-potential characteristics determined by the kinetics of the electrochemical reactions and the ohmic potential drop in the electrochemical cell. [2, 3] Most of the experimental studies are performed in standard three-electrode cell with a standing or rotating disk working electrode, pointwise reference electrode, and a large surface area counter electrode. [1] In such configurations the effects of physical parameters (series resistance, rotation rate and size of the working electrode) on oscillation properties can be quantitatively described with nonlinear analysis of predictive skeleton models for NDR type of electrochemical systems. [5-8] For example, it was shown that appearance of oscillatory instabilities with large rotation rates [7, 9-11] and large electrode sizes [7, 12] can be quantitatively contributed to the presence of a minimal ohmic (IR) drop requirement [7, 13]: large electrodes with ohmic drops that surpassed the critical IR drop

*Corresponding author. Phone: +1-314-977-2139. Fax: +1-314-977-2521. izkiss@slu.edu.

exhibited oscillations while small electrodes with small IR drops retained their stable stationary states. (Note that there could also exist a maximum IR drop above which oscillations cease to exist[2, 3].)

Microchip-based devices have opened new perspectives in electro-analytical applications for fast analysis times (on the order of seconds), the possibility of portability and disposability, small analyte volumes, and full integration with direct on-chip electrode fabrication. [14-16] The sensitivity of electroanalytical analysis is increased due to the increased flux towards the microelectrode surface [17] and the reduced background current of microelectrodes. [18] Increase of surface area of the electrode offers potential for increase of limit of detection, however, for reactions with NDR characteristics oscillatory instabilities may arise because of the presence of IR potential drop. In a previous study, oscillatory electrooxidation of formic acid on Pt [19-21] was investigated in a micro-chip based microfluidic electrode flow cell. [22] The fluidic component of the chip, made of poly(dimethylsiloxane) (PDMS) with soft lithography [23], was reversibly sealed to a glass round with 100 μm wide Pt band electrode. The main dynamical features of current oscillations that had been observed in macro-cells[19-21] were reproduced in the microfabricated electrochemical cell. [22] The previous experimental design enables the investigation of the dynamical behavior of electrochemical reactions on a thin noble metal (Pt, Pd, Au) band electrode with well-defined control of flow of the electrolyte in a manner where the size of the electrode can be easily varied.

In this paper, we propose a microfabricated flow cell design for investigations of dynamic features of metal electrodisolution reactions. In contrast to the previous study[22], we utilize an epoxy-based substrate for embedded metal wires with the PDMS chip. The effects of added external resistance, electrode size, and flow rates are investigated on features of current oscillations of Ni electrodisolution in potentiostatic mode of cell operation. The relative effects of geometric factors on the observed critical phenomena are compared for the traditional macrocells (where the nonlinear dynamics of Ni electrodisolution is very well characterized [24, 25]) and the microfabricated cells. The unexpected strong dependence of oscillatory instabilities on electrode size in microcells is interpreted by numerical simulations of the potential drop in the flow channel in a simplified two dimensional geometry.

2. Material and methods

2.1. Schematic

A schematic of the microfluidic flow cell set-up is shown in Figure 1a. The 3 M sulfuric acid/0.01 M NiSO_4 electrolyte is pumped in a 100 μm (width) $\times$ 100 μm (height) flow channel at flow rates $Q = 0.5\text{--}4.5$ $\mu\text{L}/\text{min}$ typically used in electroanalytical applications. [26, 27] For most of the experiments in this study, a flow rate of 1.5 $\mu\text{L}/\text{min}$ was utilized corresponding to a linear velocity of 0.250 cm/s. The electrolyte flows over the working electrode to the reservoir. Two different types of nickel working electrode is applied. In most of the experiments a 50 μm diameter nickel wire (Puratronic, 99.994%, Alfa Aesar) is placed approximately to the middle of the flow channel (see figure 1b). In another set of experiments a 1 mm diameter Ni wire (Goodfellow Cambridge Ltd, 99.98%) is applied so that the flow channel is placed to the middle of the electrode forming an approximately 1 mm $\times$ 100 μm active electrode surface. The working electrode is connected to a potentiostat (Pine AFCBP1) through an external resistor. At the end of the flow channel there is an approximately 5 mm diameter channel reservoir; the $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{saturated K}_2\text{SO}_4$ reference electrode (exhibiting 655mV electrode potential vs. standard hydrogen electrode) and a 0.5 mm thick Pt wire counter electrode is placed into the center of the reservoir. All the given potentials are with reference to the $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{saturated K}_2\text{SO}_4$ reference electrode.

2.2. Electrode fabrication and fluidics

A four-electrode array of nickel wires (either 1 mm or 50 μm diameter) was made by casting the electrodes with 2 mm spacing in an epoxy (Armstrong C7 with activator A, Ellsworth Adhesives) mold. (Details about construction of epoxy embedded array of nickel electrodes are given in previous publications. [28, 29]) The electrodes were polished so that only the ends are exposed. Only one electrode of the array was connected in the array during the experiments. (The four-electrode array gave flexibility in choosing a properly connected/positioned working electrode.)

When the effect of electrode size on solution series resistance was studied, a Pt thin band electrode was used on glass substrate (see Figure 1d); the preparation and assembly of this electrode have been described previously. [22] This chip had a variety of electrodes using a jagged-edge step to vary the electrode sizes from 100 μm to 5 mm in 100 μm increments.

The PDMS chip with 100 μm (width) $\times$ 100 μm (height) fluidic channel was created by standard soft photolithography using a negative photoresist. [16, 23] To create the fluidic microchip from the silicon master a mixture of 20:1 elastomer base and curing agent was used (Sylgard 184, Ellsworth Adhesives); the detailed procedure is described in a previous work. [22]

2.3. Cell Assembly and Procedures

Before the experiments, the electrode was wet polished with series of sandpapers (P180-P4000) with a Buehler Metaserv 3000 polisher. The electrode and the PDMS chip were then cleaned with isopropanol and dried with N_2 . The PDMS chip was reversibly sealed over the electrode such that the electrode is at a specified distance to the outlet reservoir. Proper placement of the electrode and measurement of the distance to the reservoir were made with an Olympus SZX-12 microscope equipped with Q Imaging QICAM Fast 1394 camera. Unless otherwise noted, the distance to the reservoir was 7 mm. Figure 1b shows the capability of the epoxy resin substrate to reversibly seal to the PDMS flow channel for the 50 μm diameter electrode. For these experiments 0.1 mM fluorescein solution was pumped through the flow channel with $Q = 1.5 \mu\text{L}/\text{min}$ for 30 min after which fluorescent image was taken. (Fluorescent images were obtained by IX71 fluorescence microscope (OlympusAmerica) equipped with a cooled 12-bit monochrome QICAM FAST digital CCD camera (QImaging, Montreal, Canada).) Similar to the standard glass-based substrate [30] the seal is leak-free for the investigated flow rates $Q = 0.5\text{--}4.5 \mu\text{L}/\text{min}$. Leak-free seal was also observed with the 1mm diameter Ni electrode and with other metal electrodes such as copper as well.

A Harvard Apparatus microsyringe pump was used to pump the electrolyte into the system via 0.508 mm i.d. Tygon microbore tubing (New England Small Tube Corp, Litchfield, NH), through a steel pin that is simply inserted into the small hole created by the luer stub adaptor [31]. Fluid introduction is done by way of the steel pin through a hole in the PDMS layer, and the fluid exits into the channel reservoir on the other side of the working electrodes where the reference and counter electrodes both reside. An assembled device is shown in Figure 1c.

Before the start of the experiment the electrolyte was pumped through the flow channel for 15 min and the open circuit potential (OCP) was monitored during this time. When the OCP reached the expected value of -600 to -700 mV, the series resistance of the flow channel was determined with impedance spectroscopy with a Gamry Reference 600 potentiostat; the provided software was used to measure the impedance of the cell at large frequencies in the range 10 kHz – 1Mhz where the impedance is determined by resistive components of the flow channel. [32]

Polarization scan experiments were carried out with the frontpanel control of the Pine AFCBP1 potentiostat and the potential/converted current was digitized with a National Instrument PCI6251 data acquisition card and Labview software. Constant potential experiments were carried out by scanning the circuit potential (V) from passivated electrode (500 mV) to the target potential where the current data was saved at data acquisition rate of 200 Hz after discarding about 5 min of transient response. The experiments were carried out at room temperature (21 ± 2 °C).

3. Results and Discussion

3.1 Experimental results

3.1.1 Dynamical behavior of 1 mm diameter Ni wire in traditional three-electrode macrocell—Before the results with microcell are shown, we briefly present the dynamical behavior of a 1 mm diameter Ni wire (geometrical surface area of 0.7854 mm^2) in traditional three-electrode configuration. These experiments will serve as comparison examples when the results with the microfabricated cell are presented and discussed.

Behavior without added external resistance: The anodic linear polarization scan of the electrode starting from open circuit potential of -600 mV without attached external resistance is shown in Figure 2a. The voltammogram illustrates the characteristic kinetic features of Ni electrodisolution [2]. At low anodic overpotentials (region A, $-0.60 \text{ V} < V < -0.36 \text{ V}$) the current increases due to active dissolution after which the electrode passivates and the current drops to very low values (region B, $-0.36 \text{ V} < V < 0.80 \text{ V}$). Similar to the previous reports, the appearance of the dissolution peak at around $V = -0.36 \text{ V}$ strongly depends on the pretreatment of the electrode surface and thus was difficult to reproduce[33]; in some experiments two peaks have been observed. At large overpotentials (region C, $0.80 \text{ V} < V < 1.16 \text{ V}$) transpassive dissolution occurs where the Ni ions are capable of penetrating the oxide layer. The transpassive dissolution is limited by secondary passivation (region D, $1.16 \text{ V} < V < 1.22 \text{ V}$) which is followed by O_2 evolution (region E, $V > 1.22 \text{ V}$).

The rich nonlinear dynamical phenomena of Ni electrodisolution [2, 24, 25, 29, 34-37] have been observed at large overpotentials where the kinetics of transpassive dissolution is further complicated by secondary passivation and O_2 evolution (regions C-E). At small ohmic drops (often provided by the cell series resistance) bistability is expected [2, 34, 36, 37]. This bistability can be observed in the cyclic polarization scan shown in Figure 2b: in a potential region of $1.11 \text{ V} < V < 1.16 \text{ V}$ a high- and a low-current steady states coexist on the forward and backward polarization scans, respectively.

Oscillations with $R_{\text{ext}}=175 \text{ }\Omega$: Figures 2c and d show the effects on the dynamical behavior of adding a resistance of $175 \text{ }\Omega$ in series with the working electrode. The forward polarization voltammogram in the transpassive region (Figure 2c) shows that current oscillations appear on the positive slope of the scan in a circuit potential region of $1.09 \text{ V} < V < 1.21 \text{ V}$. The onset and disappearance of oscillations with finite frequency and zero amplitude indicates that with small added resistance the oscillations are obtained through Hopf bifurcations; the nature of these bifurcations have been proved by impedance spectroscopy. [2, 34] At potentiostatic conditions the currents exhibit oscillatory behavior; an example is shown in Figure 2d at $V=1.130 \text{ V}$. During these oscillations the mean current is 0.47 mA from which we can approximate that the approximate IR potential drop that is needed to induce oscillations is about 80 mV . Note that it is possible to obtain bistability between oscillatory and stationary states because of the overlap of the corresponding regions as shown in the reverse scan in Figure 2c for $1.19 \text{ V} < V < 1.21 \text{ V}$. This bistability region can

expand to several hundreds of millivolt with larger external resistance than the applied 175 Ω .

3.1.2. Dynamical behavior of 50 μm diameter Ni wire in microcell—To validate the on-chip integrated microfluidic setup, we first investigated the dynamics of Ni electrodisolution as a function of attached external resistance and flow rate with the 50 μm diameter electrode.

No added resistance: The anodic linear polarization scan of the electrode starting from open circuit potential of -600 mV without attached external resistance at a flow rate of 1.5 $\mu\text{L}/\text{min}$ is shown in Figure 3a. The voltammogram reproduces the characteristic kinetic regions shown for macrocell in Figure 2a: active dissolution (region A, $-0.60\text{ V} < V < -0.31\text{ V}$), passivation (region B, $-0.31\text{ V} < V < 0.80\text{ V}$), transpassive dissolution (region C, $0.80\text{ V} < V < 1.16\text{ V}$), secondary passivation (region D, $1.16\text{ V} < V < 1.21\text{ V}$), and O_2 evolution (region E, $V > 1.21\text{ V}$). In the cyclic scan shown in Figure 3b the small bistability region $1.08\text{ V} < V < 1.16\text{ V}$ can also be identified when a high (SS1) and a low (SS2) current steady states coexist on the forward and backward polarization scans, respectively. Because O_2 evolution blocks the electrical connection of the working electrode to the reference and counter electrodes in the narrow flow channel we investigated the dynamical behavior well before potential region E.

Oscillations with $R_{\text{ext}}=30\text{ k}\Omega$: Figures 3c and d show the effects on the dynamical behavior of adding a resistance of 30 $\text{k}\Omega$ in series with the electrode. (The behavior below 30 $\text{k}\Omega$ is qualitatively similar to those shown in Figure 3b but with wider bistability region.) The polarization scan in the transpassive region (Figure 3c) shows that current oscillations appear with qualitative characteristics of Hopf bifurcations on the positive slope of the scan in a circuit potential region of $1.09\text{ V} < V < 1.27\text{ V}$. At potentiostatic conditions the currents exhibit stable oscillatory behavior; for example, weakly anharmonic current waveform (see figure 3d) with a frequency of 1.07 Hz and peak-to-peak amplitude of 5.6 μA is obtained when the circuit potential is set to approximately to the middle point of the oscillatory region ($V = 1.17\text{ V}$). The mean value of the current oscillation is 3.38 μA that gives an IR potential drop of 101 mV on the external resistor; this IR drop compares well with the 80 mV value obtained in the macrocell. The results are thus consistent with the dynamical behavior shown with the macrocells in Figure 2. Note that the surface area of the microelectrode ($1.9635 \times 10^{-3}\text{ mm}^2$) is 400 times smaller than that of macroelectrode while the applied resistance to induce oscillations is 171 times larger. Previously, it was shown that in cells with similar geometry with the same R_{ext} A quantity same dynamical features are expected. [7] Therefore, the results show that the macrocell experiments can give an order-of-magnitude type of estimate on the external resistance needed to induce oscillations (when the series resistance of the electrolyte can be neglected, see discussions later).

Ni dissolution is under kinetic control in macrocells, [2] therefore, we anticipated no dependency of the dynamical behavior on the flow rate of the electrolyte. We investigated the effect of flow rate in the range of 0.5 $\mu\text{L}/\text{min}$ to 4.5 $\mu\text{L}/\text{min}$ on the dynamical behavior with 30 $\text{k}\Omega$ external resistance attached to the electrode. Potentiostatic measurements ($V=1.110\text{ V}$) were carried out at various flow rates (0.5, 1.5, 3.0, and 4.5 $\mu\text{L}/\text{min}$); the oscillation waveforms, frequencies ($0.873\text{ Hz} \pm 15\text{mHz}$) and peak-to-peak amplitudes ($3.95\text{ }\mu\text{A} \pm 0.07\text{ }\mu\text{A}$) were found to be very similar. Linear polarization scans at 1.5 and 3.0 $\mu\text{L}/\text{min}$ flow rates produced visually indistinguishable curves and showed that the onset of oscillations through Hopf bifurcation takes place at about $V=1.085\text{ V} \pm 0.005\text{ V}$.

These experiments thus confirm that the flow rate does not have an important effect on the observed dynamics and a value of 1.5 $\mu\text{L}/\text{min}$ is applied for the rest of the experiments.

Oscillations with $R_{\text{ext}}=60 \text{ k}\Omega$: The dynamical behavior with 60 k Ω external resistance attached to the electrode is shown in Figure 4. The polarization scan (figure 4a) in the forward direction indicates that the region of current oscillations ($1.14 \text{ V} < V < 1.37 \text{ V}$) is shifted to the more anodic potentials compared to the region observed with 30 k Ω external resistance, partly because of the increased level of ohmic IR drops. The onset of oscillations at 1.14 V occurs through a Hopf bifurcation, however, the cessation of the oscillations at 1.37 V exhibits distinctly different features than those seen with 30 k Ω resistance in figure 3c: the oscillations have finite amplitude and the period lengthens very quickly just before the bifurcation point. These features in macrocells were associated with the appearance of homoclinic (saddle-loop) bifurcation. [2, 29, 36-38] On the reverse scan bistability is observed between a lower steady state and oscillatory region in potential region $1.27 \text{ V} < V < 1.37 \text{ V}$. The structure of the polarization scans at the increased level ohmic drop reproduces the dynamical features of the macrocell behavior. [2, 29, 36-38] The oscillatory waveform just above the onset of oscillations with Hopf bifurcation ($V=1.15 \text{ V}$, see Figure 4b) is relatively smooth with a frequency of 0.89 Hz. As the potential is increased to $V=1.330 \text{ V}$ (Figure 4c) the waveform becomes moderately relaxational and the frequency decreases to 0.59 Hz. At potential very close to the homoclinic bifurcation point ($V=1.373 \text{ V}$, figure 4d) very slow (frequency=0.32 Hz), strongly relaxational oscillations occur where quick current spikes alternate with low-current 'silent' states in accordance with the presence of a saddle point in the neighborhood of the limit cycle for the homoclinic bifurcation scenario. [2, 29, 36-38]

Oscillations with $R_{\text{ext}}=100 \text{ k}\Omega$: The general dynamical features of the polarization scan with 100 k Ω shown figure 5a are similar to those observed with 60 k Ω except that the oscillatory region is shifted to more anodic potential region of $1.20 \text{ V} < V < 1.49 \text{ V}$. Above the Hopf bifurcation point the oscillation waveform is smooth (see Figure 5b) and close to the homoclinic bifurcation point the oscillations are slow and strongly relaxational (see Figure 5d). However, careful inspection of the potentiostatic experiments revealed that in small potential region close to the Hopf bifurcation point complex, period-2 oscillations occur when the waveform of every other cycle repeats itself (see Figure 5c). (Complex oscillations, e.g., chaos through period-doubling bifurcation sequence, have been previously observed in macrocells under both galvanostatic [24, 25] and potentiostatic [35] conditions.)

3.1.3 Dynamical behavior of $1 \text{ mm} \times 100 \text{ }\mu\text{m}$ Ni electrode in microcell—The results with increased surface area $1 \text{ mm} \times 100 \text{ }\mu\text{m}$ electrode obtained by positioning 100 μm flow channel through the center of a 1 mm diameter electrode are shown in Figure 6. The linear polarization scan without any external resistance ($R_{\text{ext}}=0 \text{ k}\Omega$, Figures 6ab) reveals onset of oscillations at very large anodic potential ($V = 1.54 \text{ V}$) through a Hopf bifurcation. Zoom to the polarization scan (Figure 6b) reveals that period-two oscillations occur very close the onset of oscillations; these period-two oscillations are confirmed in potentiostatic measurements at $V = 1.543 \text{ V}$ shown in figure 6c. At potentials above the period-two region simple periodic oscillations are observed; an example is shown in figure 6d at $V = 1.685 \text{ V}$. The results with the large surface area $1 \text{ mm} \times 100 \text{ }\mu\text{m}$ electrode are thus similar to those with the 50 μm diameter with large external resistance of $R_{\text{ext}}=100 \text{ k}\Omega$ shown in Figure 5: the oscillatory region shifts to large anodic overpotentials and there exists a region of period-two oscillatory region close to the onset of oscillations. These results indicate the presence of very large ohmic drop in the microcell with the $1 \text{ mm} \times 100 \text{ }\mu\text{m}$ electrode that can induce oscillations without any added external resistance. We note that the presence of spontaneous oscillations are quite surprising. For example, in macrocell an electrode with a 7.85 times larger surface area electrode (see Figure 2) exhibited only bistability without added resistance and oscillations were observed with attached external resistance of 175 Ω . The results thus indicate that in the microfabricated cell very large ohmic drops can be

induced in the flow channel that can make the cell unstable even without any added external resistance. Next we quantitatively characterize the effects of cell geometry on the series resistance in the microcell and explain the difference between the macrocell and microcell experiments.

3.1.4 Effect of electrode width and distance to reservoir on IR drop—To

interpret the strong effect of electrode width on the oscillations we shall analyze the IR potential drop in the flow channel. Under kinetic control the current is expected to depend linearly on the surface area with $I=jA$, where j is the Faradayic current density at the given potential. The series resistance of the 50 μm diameter Ni wire, the 1mm $\times$ 0.1 mm Ni electrode, and a 0.1mm $\times$ 0.1mm Pt band electrode all had very similar series resistances of $R_s = 7.6 \text{ k}\Omega$, $7.4 \text{ k}\Omega$, and $7.6 \text{ k}\Omega$ with approximately 7 mm distance to the reservoir. To test the hypothesis that the electrode width in the geometrical arrangement typically used in this study (and other electroanalytical applications [15]) does not affect the series resistance, we have measured the R_s value with impedance spectroscopy for six thin-band Pt electrodes with widths of 0.1 mm–3.2mm in a 100 $\mu\text{m} \times 100 \mu\text{m}$ flow channel using the glass round shown in Figure 1d. The dependence of R_s on width is shown in Figure 7a. The results show that, in accordance with the preliminary observation with Ni electrodes, the Pt electrodes of various widths (and surface areas) have approximately the same R_s value of $6.6 \pm 1 \text{ k}\Omega$. Because the R_s value does not change with the width the electrode, the potential drop $IR=jAR_s$ is expected to increase linearly with the surface area.

For completeness and comparison with numerical simulations below, we have also measured the dependence of the R_s value on the length from the downstream edge of the electrode to the outlet point to the reservoir with the 50 μm diameter Ni wire. As expected the R_s value increases linearly with increase of the length (see figure 7b); the non-zero intercept in the limit of zero length can be associated with the resistance of the electrolyte in the reservoir between the flow channel outlet point and the reference/counter electrodes.

3.1.5. Comparison of IR potential drops in macro and microcells—

In macrocell the solution resistance provides small series resistance ($R_s = 2.5 \Omega$) therefore the IR potential drop is small. In small flow channels the resistance can be quite large (in our setup, about 7 k Ω), therefore the IR potential drop can be sufficient alone to induce oscillations in the negative differential resistance electrochemical system. The difference between the traditional, and flow channel geometry, however, is not simply a result of former having low, and the latter having large R_s . In macrocell with disk working electrode, the current increases linearly with surface area ($I \propto A$) while the resistance decreases with the radius of the electrode [7, 39], i.e., $R_s \propto 1/\sqrt{A}$; therefore the IR potential drop increases with the square root of the surface area ($IR_s \propto \sqrt{A}$). In the flow channel geometry the current is expected to increase with the surface area ($I \propto A$), however, the series resistance is nearly constant ($R_s \approx \text{const}$); thus the IR potential drop increases with the surface area of the electrode ($IR_s \propto A$). The strong, linear dependence of the IR drop on surface area in the flow channel vs. the weak, square root dependence in macrocell implies that very large ohmic drops can be obtained in the flow channel geometry even with relatively small electrodes sizes.

3.2 Modeling results

For interpretation of the unusually strong, linear dependence of IR potential drop on surface area we have carried out modeling simulations of the potential distribution in a two-dimensional flow channel shown in top panel of Figure 8. The flow channel was simulated with an open ending to the reservoir at right side (at the Counter Electrode). The working electrode (WE) with a width of W is placed at the left side of the flow channel with a

distance of L to the outlet point. The flow channel has a height of H . In this simulations it is assumed that along the depth of the flow channel the potential drop will be approximately uniform and thus a two-dimensional simulation can provide insight in the geometrical effects (channel width, length, and height) on the extent of potential drop.

For description of spatiotemporal electrochemical phenomena we follow modeling approach of Birzu and Krischer [40] who described the dynamics of the electrochemical reactions in terms of dimensionless variables as boundary condition to the Laplace equation to model the potential drop in a cell

$$\Delta\varphi=0$$

where $\varphi(x,y)$ is the dimensionless potential in the flow channel. (See original paper for the full model equations.) At the working electrode the potential is set to zero, while at the counter electrode the potential is set to 1; everywhere else at the insulating sides of the flow-channel zero-flux boundary condition is applied (see Figure 8, bottom panel). The overall length of the flow channel is set to $D=1.5+W+L$. (The origin of the co-ordinate system is the left edge of the working electrode.) The dimensionless total current is obtained as [40]

$$\tilde{i} = -\sigma \int_0^W \frac{\partial \phi(x, 0)}{\partial y} dx$$

where $\sigma=1$ is the dimensionless conductivity. The dimensionless series resistance (r) is thus obtained as

$$r = \frac{\phi(WE) - \phi(CE)}{\tilde{i}} = \frac{1}{\int_0^W \frac{\partial \phi(x, 0)}{\partial y} dx}$$

The Laplace equation with boundary conditions shown in bottom panel of equation 8 were solved with finite element method implemented in Matlab PDEToolbox. (Four consecutive mesh refinements were used that typically gave 5825 nodes and 11264 triangles).

Figure 9 summarizes how the series resistance depends on the width of the electrode, the channel length and height. A typical flow channel with $W=0.1$, $L=10$, and $H=0.1$ had a resistance of $r=131$. (Note that this geometry simulates well a typical flow channel used in electroanalytical chemistry with $0.1 \text{ mm} \times 0.1 \text{ mm}$ band electrode with a channel height of 0.1 mm and distance to the reservoir of 10 mm .)

The effect of channel width on the series resistance in the range $0.01 \leq W \leq 5$ is shown in Figures 9 ab. For electrode sizes in the range $0.5 \leq W \leq 5$ the resistance value does not change and has a value of 115 ± 1 . For the smaller size electrodes $0.01 \leq W \leq 0.5$ the resistance has a slightly elevated value around 130. Nonetheless, the simulations confirm that the series resistance has only very weak dependence on the electrode width in the investigated realistic ranges.

The effect of L (distance of downstream edge of the electrode to the reservoir) on the series resistance is shown in Figures 9 cd. Because the potential drop is linear for most part of the flow channel, the simulations confirm the linear dependence of resistance on the length in the range of $0.5 \leq L \leq 100$. (In the log-log plot, Figure 9d, a linear least square fit to $\log_{10}(r)$ vs. $\log_{10}(L)$ data gives a slope of 0.99 indicating linear dependence).

The simulations also allow the investigation of the effect of channel height ($0.01 \leq H \leq 5$) on the solution resistance. Figures 9e,f show that the solution resistance increases linearly with the inverse of the channel height, i.e., $r \propto 1/H$; the linear least square fit to $\log_{10}(r)$ vs. $\log_{10}(H)$ data in Figure 9f gives a slope of -0.99.

The numerical simulations thus indicate that the solution resistance is proportional to the channel length and inversely proportional to the channel height with very little dependence on the electrode width, i.e., $r \propto L/H$.

4. Conclusions

The dynamical features of nickel electrodisolution were characterized in an on-chip integrated microfluidic flow cell. The results show that as experimental parameters such as circuit potential and external resistance were varied, bistability, simple periodic smooth and relaxation oscillations that develop through Hopf and homoclinic bifurcations, respectively, and period-2 oscillations occurred with a small, 50 μm diameter electrode in the flow channel. The overall dynamical features are thus consistent with those observed with large (e.g., 1 and 2 mm diameter) electrodes in traditional macrocells. [2, 6, 24, 25, 34-36]

It was also shown that oscillations in a flow channel with $1\text{ mm} \times 100\text{ }\mu\text{m}$ electrode occurred spontaneously, i.e., without the need for an external resistance. This finding is in contrast with experiments in traditional macrocells with similarly sized (e.g., 1 mm diameter) electrodes where oscillations were observed only with external resistance. These observations were interpreted by the strong, linear dependence of the IR potential drop on electrode surface area in the microcell ($IR_s \propto A$) vs. the weak, square root dependence in macrocell ($IR_s \propto \sqrt{A}$). Consequently, on-chip integrated electrode assemblies with microfluidic flow channel provide excellent opportunities for investigations of IR drop induced temporal and spatial phenomena with negative differential resistance electrochemical systems. [3]

The proposed experimental procedure utilized an epoxy-based substrate for the embedded Ni electrode with a PDMS flow channel reversibly sealed over the electrode. The epoxy-based approach is advantageous as the same epoxy can be used for multiple experiments by disassembling the device, polishing the electrode, and re-sealing the PDMS channel. Although the method was tested with electrodisolution of a single Ni electrode, the procedure for fabricating and integrating epoxy-embedded electrodes with microchip-based analysis system holds promise in analytical applications. The multi-electrode arrays can be fabricated with the epoxy-embedding of metal wires as demonstrated for uniform [28, 29, 41] and metastable pitting corrosion [42, 43] studies. Electrodes of various compositions, sizes, and spacing could be integrated with which the limit of detection could be increased in optimized multi-electrode collector/generator modes. [44] The microfluidic flow control provides a unique advantage in providing fast laminar flow to an electrode array over previous attempts that utilized impinging jet system [45] and peristaltic pump [46]. The controlled cell geometry (with the use of carefully designed electrode arrays and flow channels) and flow conditions (with microfluidics) could allow exploration of complex dynamical responses in electrocatalytic, corrosion, and battery/fuel cell applications.

Acknowledgments

This material is based upon work supported by the National Science Foundation under CHE-0955555. IZK acknowledges support from Research Corporation Cottrell College Science Award and President's Research Fund of Saint Louis University. Support for RSM came from the National Institutes of Health (9R15GM084470-02). We express our gratitude to Timea Nagy and Asmira Selimovic for help with the experiments.

References

1. Hudson JL, Tsotsis TT. Chem Eng Sci. 1994; 49:1493–1572.
2. Koper MTM. Adv Chem Phys. 1996; 92:161–298.
3. Krischer, K. Principles of temporal and spatial pattern formation in electrochemical systems. In: Conway, BE.; Bockris, OM.; White, RE., editors. Modern Aspects of Electrochemistry. Kluwer Academic; New York: 1999. p. 1
4. Krischer, K.; Varela, H. Oscillations and other dynamic instabilities. In: Vielstich, W.; Lamm, A.; Gasteiger, HA., editors. Handbook of Fuel Cells - Fundamentals, Technology and Applications. John Wiley & Sons; Chichester: 2003. p. 679-701.
5. Kiss IZ, Gáspár V, Nyikos L. J Phys Chem A. 1998; 102:909–914.
6. Kiss IZ, Kazsu Z, Gáspár V. J Phys Chem A. 2005; 109:9521–9527. [PubMed: 16866403]
7. Kiss IZ, Kazsu Z, Gáspár V. Phys Chem Chem Phys. 2009; 11:7669–7677. [PubMed: 19950506]
8. Kiss IZ, Pelster LN, Wickramasinghe M, Yablonsky GS. Phys Chem Chem Phys. 2009; 11:5720–5728. [PubMed: 19842490]
9. Albahadily FN, Ringland J, Schell M. J Chem Phys. 1989; 90:813–821.
10. Albahadily FN, Schell M. J Chem Phys. 1988; 88:4312–4319.
11. Schell M, Albahadily FN. J Chem Phys. 1989; 90:822–828.
12. Glarum S, Marshall JH. J Electrochem Soc. 1985; 132:2872–2878.
13. Sazou D, Pagitsas M. Electrochim Acta. 2006; 51:6281–6296.
14. Mecker LC, Martin RS. Electrophoresis. 2006; 27:5032–5042. [PubMed: 17096314]
15. Martin RS, Root PD, Spence DM. Analyst. 2006; 131:1197–1206. [PubMed: 17066186]
16. Martin RS, Gawron AJ, Lunte SM, Henry CS. Anal Chem. 2000; 72:3196–3202. [PubMed: 10939387]
17. Wang J, Tian BM, Nascimento VB, Angnes L. Electrochim Acta. 1998; 43:3459–3465.
18. Wightman RM. Anal Chem. 1981; 53:1125 A.
19. Albahadily FN, Schell M, Electroanal J. Chem. 1991; 308:151–173.
20. Schell M, Albahadily FN, Safar J, Xu Y. J Phys Chem. 1989; 93:4806–4810.
21. Strasser P, Lubke M, Rasper F, Eiswirth M, Ertl G. J Chem Phys. 1997; 107:979–990.
22. Kiss IZ, Munjal N, Martin RS. Electrochim Acta. 2009; 55:395–403. [PubMed: 20160883]
23. Duffy DC, McDonald JC, Schueller OJA, Whitesides GM. Anal Chem. 1998; 70:4974–4984. [PubMed: 21644679]
24. Lev O, Wolffberg A, Pismen LM, Sheintuch M. J Phys Chem. 1989; 93:1661–1666.
25. Lev O, Wolffberg A, Sheintuch M, Pismen LM. Chem Eng Sci. 1988; 43:1339–1353.
26. Moehlenbrock MJ, Martin RS. Lab Chip. 2007; 7:1589–1596. [PubMed: 17960290]
27. Daridon A, Sequeira M, Pennarun-Thomas G, Dirac H, Krog JP, Gravesen P, Lichtenberg J, Diamond D, Verpoorte E, de Rooij NF. Sensor Actuators B Chem. 2001; 76:235–243.
28. Kiss IZ, Zhai YM, Hudson JL. Science. 2002; 296:1676–1678. [PubMed: 12040190]
29. Kiss IZ, Wang W, Hudson JL. J Phys Chem B. 1999; 103:11433–11444.
30. McDonald JC, Whitesides GM. Accounts Chem Res. 2002; 35:491–499.
31. Li MW, Martin RS. Electrophoresis. 2007; 28:2478–2488. [PubMed: 17577199]
32. Bard, AJ.; Faulkner, LR. Electrochemical Methods. Wiley; New York: 1980.
33. Shein AB, Ivanova OS, Minkh RN. Prot Met. 2008; 44:32–38.
34. Kiss IZ, Kazsu Z, Gáspár V. Chaos. 2006; 16:033109. [PubMed: 17014214]
35. Wang W, Kiss IZ, Hudson JL. Chaos. 2000; 10:248–256. [PubMed: 12779380]
36. Pyragas K, Pyragas V, Kiss IZ, Hudson JL. Phys Rev Lett. 2002; 89:0244103.
37. Pyragas K, Pyragas V, Kiss IZ, Hudson JL. Phys Rev E. 2004; 70:026215.
38. Koper MTM. J Chem Soc Farad Trans. 1998; 94:1369–1378.
39. Newman, J.; Thomas-Alyea, KE. Electrochemical Systems. Wiley; 2004.
40. Birzu A, Krischer K. Phys Chem Chem Phys. 2006; 8:3659–3668. [PubMed: 16883395]

41. Sadeghi S, Thompson M. *Phys Chem Chem Phys*. 2010; 12:6795–6809. [PubMed: 20448882]
42. Lunt TT, Scully JR, Brusamarello V, Mikhailov AS, Hudson JL. *J Electrochem Soc*. 2002; 149:B163–B173.
43. Budiansky ND, Bocher F, Cong H, Hurley MF, Scully JR. *Corrosion*. 2007; 63:537–554.
44. Amatore C, Da Mota N, Lemmer C, Pebay C, Sella C, Thouin L. *Anal Chem*. 2008; 80:9483–9490. [PubMed: 19007242]
45. Fei Z, Kelly R, Hudson JL. *J Phys Chem*. 1996; 100:18986–18991.
46. Karantonis A, Koutsaftis D, Bredaki M, Kouloumbi N. *Chem Phys Lett*. 2008; 460:182–186.

Biographies

Alex G. Cioffi

B. Sc. Chemistry, Saint Louis University (USA), 2007-present

István Z. Kiss

Diploma (MS) in Chemistry - University of Debrecen (Hungary), 1995

Ph.D. Chemistry, University of Debrecen (Hungary), 2000

Research Associate, University of Virginia (USA), 2000-2003

Research Scientist, University of Virginia (USA), 2003-2007

Assistant Professor, Saint Louis University (USA), 2007-present

R. Scott Martin

B.S. in Chemistry, Southwest Missouri State University, cum laude, 1994

M.S. in Chemistry, Southwest Missouri State University, 1996

Ph.D. in Analytical Chemistry, The University of Missouri, Columbia, 1999

NIH Post-doctoral Fellow, Department of Pharmaceutical Chemistry, University of Kansas (1999-2002)

Assistant Professor of Chemistry, University of Iowa (2002-2003)

Assistant Professor of Chemistry, Saint Louis University, (2003-2008)

Associate Professor of Chemistry, Saint Louis University, (2008-Present)

Figure 1.

Experimental set-up. (a) Schematic of nickel wire embedded in epoxy with PDMS sealed over electrodes in microfluidic setup. Arrow indicates flow of electrolyte. (b) Fluorescence microscope image of PDMS flow channel sealed over 50 μm diameter nickel wire. No fluorescein leak is observed. (c) Photo of assembled cell. (d) Glass round containing Pt electrodes of varying sizes and distances.

Figure 2.

Experiments: Dynamical behavior of a 1 mm diameter nickel wire without (top row) and with small (bottom row, $R_{\text{ext}} = 175 \Omega$) added resistance in traditional threeelectrode macrocell setup. (a) Linear sweep polarization curve at $R_{\text{ext}} = 0 \Omega$ and scan rate = 5 mV/s. (b) Cyclic polarization curve showing bistability. $R_{\text{ext}} = 0 \Omega$ and scan rate = 5 mV/s. (c) Cyclic polarization curve at $R_{\text{ext}} = 175 \Omega$ and scan rate = 5 mV/s showing bistability and oscillations. (d) Smooth periodic current oscillations at $V = 1.130 \text{ V}$.

Figure 3.

Experiments: Dynamical behavior of a 50 μm diameter nickel wire without (top row) and with small (bottom row, $R_{\text{ext}} = 30 \text{ k}\Omega$) added resistance in microfluidic setup. (a) Linear sweep polarization curve without added resistance. $R_{\text{ext}} = 0 \Omega$, scan rate = 15 mV/s. A: active dissolution. B: passivation. C: transpassive dissolution. D: secondary passivation. E: O_2 evolution (b) Cyclic polarization curve without added resistance showing bistability. $R_{\text{ext}} = 0 \Omega$, scan rate = 15 mV/s. (c) Linear sweep polarization curve showing oscillation with small added resistance. $R_{\text{ext}} = 30 \text{ k}\Omega$, scan rate = 5 mV/s. (d) Potentiostatic current oscillations with small added resistance ($R_{\text{ext}} = 30 \text{ k}\Omega$) at $V = 1.17 \text{ V}$. $Q = 1.5 \mu\text{L/m}$

Figure 4.

Experiments: Dynamical behavior of a 50 μm diameter nickel wire with $R_{\text{ext}} = 60 \text{ k}\Omega$ added resistance in microfluidic setup. (a) Cyclic polarization curve with scan rate = 5 mV/s showing onset of oscillations through Hopf bifurcation and cessation of oscillations through homoclinic bifurcation. (b) Smooth current oscillations above Hopf bifurcation at $V = 1.150 \text{ V}$. (c) Moderately relaxational oscillations at $V = 1.330 \text{ V}$. (d) Strongly relaxational current oscillations close to the homoclinic bifurcation at $V = 1.373 \text{ V}$. $Q = 1.5 \text{ }\mu\text{L/min}$.

Figure 5.

Experiments: Dynamical behavior of a 50 μm diameter nickel wire with $R_{\text{ext}} = 100 \text{ k}\Omega$ added resistance in microfluidic setup. (a) Cyclic polarization curve with scan rate = 5 mV/s. (b) Smooth periodic current oscillations at $V = 1.194 \text{ V}$. (c) Period-two current oscillations at $V = 1.205 \text{ V}$. (d) Strongly relaxational current oscillations at $V = 1.527 \text{ V}$. $Q = 1.5 \text{ }\mu\text{L}/\text{min}$.

Figure 6.

Experiments: Dynamical behavior of a 1 mm × 100 μm nickel electrode without added external resistance ($R_{\text{ext}} = 0 \text{ k}\Omega$) in microfluidic setup. (a) Linear polarization curve with scan rate = 5 mV/s. (b) Zoom to the onset of the oscillatory region of panel a. (c) Period-two current oscillations at $V = 1.543 \text{ V}$. (d) Smooth periodic current oscillations at $V = 1.685 \text{ V}$. $Q = 1.5 \text{ }\mu\text{L/min}$.

Figure 7.

Experiments: The effect cell geometry on series resistance of the $100\ \mu\text{m} \times 100\ \mu\text{m}$ flow channel. (a) The effect of electrode width on series resistance. The experiments were performed with $100\ \mu\text{m}$ depth platinum electrodes etched on glass with a distance to the reservoir of about 7 mm. (b) The effect of distance to the reservoir on series resistance. Experiments were performed with $50\ \mu\text{m}$ nickel wire. Error bars indicate 95% confidence intervals.

Figure 8.

Numerical simulations: two-dimensional flow channel for calculations of channel resistance. Top: Schematic of flow channel. WE: working electrode. CE: counter electrode. L , H , and D are the length, the height, and the overall length of the flow channel, respectively. W : width of the electrode. Bottom: Boundary conditions used for calculation of potential drop in the flow channel.

Figure 9.

Numerical simulations: Effects of cell geometry on series resistance (r) of the cell. Left column: resistance vs. characteristic parameters. Right column: log-log plots. (a-b): r vs. electrode width (W). $L=10$, $H=0.1$. (c-d): r vs. channel length (L). $W=0.1$, $H=0.1$ (e-f) r vs. channel height (H). $W=0.1$, $L=10$.