Microelectrode 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 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 electroanalytical applications for fast analysis times (on the order of seconds), the possibility of portability and disposability, small analytical 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 electrodeoxidation 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 electrodissolution 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 electrodissolution 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 electrodissolution 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 Fig. 1a. The 3 M sulfuric acid/0.01 M NiSO₄ electrolyte is pumped in a 100 µm (width) x 100 µm (height) flow channel at flow rates \( Q = 0.5 \text{ to } 4.5 \text{ mL/min typically used in electroanalytical applications } [26,27] \). For most of the experiments in this study, a flow rate of 1.5 µL/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 Fig. 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 x 100 µm active electrode surface. The working electrode is connected to a potentiostat (Pine AFCB1) through an external resistor. At the end of the flow channel there is an approximately 5 mm diameter channel reservoir: the Hg/Hg₂SO₄/saturated K₂SO₄ reference electrode (exhibiting 655 mV 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 Hg/Hg₂SO₄/saturated K₂SO₄ reference electrode.

2.2. Electrode fabrication and fluids

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 Fig. 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.

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Fig. 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.
The PDMS chip with 100 \( \mu \text{m} \) (width) \( \times \) 100 \( \mu \text{m} \) (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 \( \text{N}_2 \). 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 pumped through the flow channel with \( Q = 1.5 \mu \text{L/min} \) for 30 min after which fluorescent image was taken. (Fluorescent images were obtained by IX71 fluorescence microscope (Olympus America) 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 \( Q = 0.5–4.5 \mu \text{L/min} \). Leak-free seal was also observed with the 1 mm 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 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 Fig. 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 \(-700 \text{ mV} \), 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–1 MHz where the impedance is determined by resistive components of the flow channel [32].

Polarization scan experiments were carried out with the front-panel 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 \( (500 \text{ mV}) \) 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 \((21 \pm 2 ^\circ \text{C})\).

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 \( \text{mm}^2 \)) 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 \(-600 \text{ mV} \) without attached external resistance is shown in Fig. 2a. The voltammogram illustrates the characteristic kinetic features of Ni electrodissolution [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 \(\text{O}_2\) evolution (region E, \(V > 1.22 \, \text{V}\)).

The rich nonlinear dynamical phenomena of Ni electrodissolution [22,24,25,29,34–37] have been observed at large overpotentials where the kinetics of transpassive dissolution is further complicated by secondary passivation and \(\text{O}_2\) 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 Fig. 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** \(R_{\text{ext}} = 175 \, \Omega\). Fig. 2c and d show the effects on the dynamical behavior of adding a resistance of 175 \(\Omega\) in series with the working electrode. The forward polarization voltammogram in the transpassive region (Fig. 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 Fig. 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 Fig. 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 \(\Omega\).

### 3.1.2. Dynamical behavior of 50 \(\mu\)m diameter Ni wire in microcell

To validate the on-chip integrated microfluidic setup, we first investigated the dynamics of Ni electrode dissolution as a function of attached external resistance and flow rate with the 50 \(\mu\)m diameter electrode.

**No added resistance.** The anodic linear polarization scan of the electrode starting from open circuit potential of \(-600 \, \text{mV}\) without attached external resistance at a flow rate of 1.5 \(\mu\)L/min is shown in Fig. 3a. The voltammogram reproduces the characteristic kinetic regions shown for macrocell in Fig. 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 \(\text{O}_2\) evolution (region E, \(V > 1.21 \, \text{V}\)). In the cyclic scan shown in Fig. 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 \(\text{O}_2\) 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.

**Fig. 3.** Experiments: Dynamical behavior of a 50 \(\mu\)m 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: \(\text{O}_2\) 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 \(V = 1.17 \, \text{V}\). \(Q = 1.5 \, \mu\)L/min.
Oscillations with $R_{\text{ext}} = 30 \, k\Omega$. Fig. 3c and d show the effects on the dynamical behavior of adding a resistance of 30 kΩ in series with the electrode. (The behavior below 30 kΩ is qualitatively similar to those shown in Fig. 3b but with wider bistability region.) The polarization scan in the transpassive region (Fig. 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 $V < V < 1.27 \, V$. At potentiostatic conditions the currents exhibit stable oscillatory behavior; for example, weakly anharmonic current waveform (see Fig. 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 ($V = 1.17 \, V$). 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 Fig. 2. Note that the surface area of the microelectrode (1.9635 $\times 10^{-3}$ mm²) 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 $R_{\text{ext}}$ 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 µL/min to 4.5 µL/min on the dynamical behavior with 30 kΩ external resistance attached to the electrode. Potentiostatic measurements ($V = 1.110 \, V$) were carried out at various flow rates (0.5, 1.5, 3.0, and 4.5 µL/min); the oscillation waveforms, frequencies (0.873 Hz ± 15 mHz) and peak-to-peak amplitudes (3.95 µA ± 0.07 µA) were found to be very similar. Linear polarization scans at 1.5 and 3.0 µL/min flow rates produced visually indistinguishable curves and showed that the onset of oscillations through Hopf bifurcation takes place at about $V = 1.085 \, V ± 0.005 \, V$.

These experiments thus confirm that the flow rate does not have an important effect on the observed dynamics and a value of 1.5 µL/min is applied for the rest of the experiments.

Oscillations with $R_{\text{ext}} = 60 \, k\Omega$. The dynamical behavior with 60 kΩ external resistance attached to the electrode is shown in Fig. 4. The polarization scan (Fig. 4a) in the forward direction indicates that the region of current oscillations (1.14 $V < V < 1.37 \, V$) is shifted to the more anodic potentials compared to the region observed with 30 kΩ 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 kΩ resistance in Fig. 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 $V < V < 1.37 \, V$. 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 ($V = 1.15 \, V$, see Fig. 4b) is relatively smooth with a frequency of 0.89 Hz. As the potential is increased to $V = 1.330 \, V$ (Fig. 4c) the waveform becomes moderately relaxational and the frequency decreases to 0.59 Hz. At potential very close to the homoclinic bifurcation point ($V = 1.373 \, V$, Fig. 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 $R_{\text{ext}} = 100 \, k\Omega$. The general dynamical features of the polarization scan with 100 kΩ shown Fig. 5a are similar to
3.1.3. Dynamical behavior of 1mm Ni electrode in microcell

The results with in increased surface area 1 mm × 100 μm electrode obtained by positioning 100 μm flow channel through the center of a 1 mm diameter electrode are shown in Fig. 6. The linear polarization scan without any external resistance (Rs = 0 kΩ, Fig. 6a and b) reveals onset of oscillations at very large anodic potential (V = 1.54 V) through a Hopf bifurcation. Zoom to the polarization scan (Fig. 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 V shown in Fig. 6c. At potentials above the period-two region simple periodic oscillations are observed; an example is shown in Fig. 6d at V = 1.685 V. The results with the large surface area 1 mm × 100 μm electrode are thus similar to those with the 50 μm diameter with large external resistance of Rs = 100 kΩ shown in Fig. 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 1 mm × 100 μm 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 Fig. 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 Faraday current density at the given potential. The series resistance of the 50 μm diameter Ni wire, the 1 mm × 0.1 mm Ni electrode, and a 0.1 mm × 0.1 mm Pt band electrode all had very similar series resistances of Rs = 7.6 kΩ, 7.4 kΩ, and 7.6 kΩ 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 Rs value with impedance spectroscopy for six thin-band Pt electrodes with widths of 0.1–3.2 mm in a 100 μm × 100 μm flow channel using the glass round shown in Fig. 1d. The dependence of Rs on width is shown in Fig. 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 Rs value of 6.6 ± 1 kΩ. Because the Rs value does not change with the width the electrode, the potential drop IR = jARs 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 Rs 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 Rs value increases linearly with increase of the length.

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**Fig. 5.** Experiments: Dynamical behavior of a 50 μm diameter nickel wire with Rs = 100 kΩ added resistance in microfluidic setup. (a) Cyclic polarization curve with scan rate = 5 mV/s. (b) Smooth periodic current oscillations at V = 1.194 V. (c) Period-two current oscillations at V = 1.205 V. (d) Strongly relaxational current oscillations at V = 1.527 V. Q = 1.5 μL/min.
(see Fig. 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\( \Omega \)), 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 Fig. 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 the 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 simulations confirm that the series resistance has a slightly elevated value around 130. Nonetheless, the reservoir (on the series resistance) is shown in Figs. 9c and d. For electrode sizes in the range 0.5 < W < 5, the resistance value does not change and has a value of 115 ± 1. For the smaller size electrodes 0.01 < W < 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 channel width on the series resistance in the range 0.01 < W < 5 is shown in Figs. 9a and b. For electrode sizes in the range 0.5 < W < 5 the resistance value does not change and has a value of 115 ± 1. For the smaller size electrodes 0.01 < W < 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 channel height with very little dependence on the electrode width, i.e., r ∝ l/H.

4. Conclusions

The dynamical features of nickel electrodissolution 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 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 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 mm × 100 μm 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 (IRs ∝ A) vs. the weak, square root dependence in macrocell (IRr ∝ √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 experi-
ments by disassembling the device, polishing the electrode, and re-sealing the PDMS channel. Although the method was tested with electrodissolution 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 and metastable pitting corrosion 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. 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 and peristaltic pump. 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.

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