The effect of IR compensation on stationary and oscillatory patterns in dual-electrode metal dissolution systems

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A R T I C L E   I N F O
Article history:
Received 30 October 2008
Received in revised form 26 February 2009
Accepted 27 February 2009
Available online 14 March 2009

Keywords:
IR compensation
Electrode arrays
Negative coupling
Amplitude death
Switching entrainment ratios

A B S T R A C T
We report an experimental and model based study on the effect of negative coupling, induced by adding IR compensation, on bistability, and synchronization behavior of a dual-electrode metal dissolution electrochemical system. We show that, unlike the case of a single electrode, IR compensation cannot be used to remove bistability; with a large IR compensation the electrodes do not exhibit uniform steady states and patterned surface develops. In the case of oscillatory system, addition of IR compensation produces aperiodic time series that are characterized by switching between oscillations with 1:1, 1:2, and 2:1 entrainment ratios. For higher negative coupling strengths (i.e., larger magnitude of IR compensation) amplitude death occurs and either coexistence of oscillations with steady state or multiple anti-symmetric steady states are observed.

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1. Introduction

Interplay among electrode kinetics, transport of ions, potential drop in the electrolyte, and external circuitry can lead to a variety of nonlinear phenomena in electrochemical systems including bistability [1], oscillations [2], phase locked entrainment [3–9], standing waves [10,11], rotating waves [12], clusters [5,13,14], accelerating fronts[15], and stationary patterns [16]. In classical electro-kinetic studies such “cell instabilities” are usually avoided by minimizing the potential drop either by placing the reference electrode to the close proximity of the working electrodes, or by electronic means with IR compensation [17]. It has been shown, however, that placing the reference electrode in close proximity to the electrode surface induces negative coupling [18,4] that can cause stationary spatial patterns [19,20], remote triggerings of waves [21], and oscillatory cluster formation [22]. Krischer et al. have shown that external IR compensation can introduce a negative global feedback in the circuit whose effect is equivalent to moving a reference electrode close to the working electrode [6].

The investigation of the effect of negative coupling induced by IR compensation on the behavior of electrochemical cells is complicated because IR compensation not only changes the amount of negative coupling among the reaction sites, but also changes the local dynamics through affecting the overall cell potential drop. For example, in a study with two oscillatory iron electrodes [9] at intermediate reference-to-working electrode distances, a ‘gray’ region was found in which it was difficult to identify in-phase or anti-phase entrainment typically seen with distant and close electrode placements, respectively.

In this paper, we investigate the effect of negative coupling induced by IR compensation on stationary and oscillatory pattern formation. We utilize a dual working electrode setup in which the negative coupling of IR compensation can be studied without changing the local dynamics by carrying out the experiments at fixed total resistance. We carry out a systematic study over a wide, but finely tuned, range of negative coupling strength without changing other conditions such as driving force for the reaction. The stationary and oscillatory patterns are analyzed as a function of the imposed negative coupling with nickel and iron electrodissolution, respectively. Complementary numerical simulations are performed to confirm the experimental findings and to explore the nature of dynamical transitions leading to pattern formation.

2. Experimental

A schematic of the experimental set up as well as a representa-tive equivalent circuit are shown in Fig. 1. The two (nickel or iron) working electrodes are embedded in epoxy. The reference electrode is Hg/H2SO4/K2SO4 and the counter electrode is made of a Pt–Nb mesh. The counter electrode was wrapped around the circumference of the cell. The reference electrode was kept farthest from the electrodes but in the center of the line joining them. A PAR 273A
potentiostat was used to add IR compensation, $R_{\text{comp}} < 0$. In many of the experiments two parallel resistors, $R_{p1} = R_{p2} = R_p$, are also added as shown in Fig. 1. $R_s$ is the collective resistance in series with the electrodes; it models the coupling effect of potential drop in the electrolyte ($R_c > 0$) or negative coupling induced by IR compensation ($R_c < 0$). Because of the presence of parallel and collective resistances in the equivalent circuit (Fig. 1(b)) we can introduce an equivalent resistance, $R_{eq} = R_p + 2R_c$, that characterizes the overall resistance in the cell.

2.1. Experimental methodology in the bistable region; nickel electrodissolution

The electrodes were made of nickel and have a diameter of 1 mm. The electrolyte was 3 M sulfuric acid. The solution was stirred to avoid the formation of a diffusional boundary layer.

2.2. Experiment methodology in the oscillatory region; iron electrodissolution

Iron electrodes of diameter 1 mm were used for the study. The distance between the electrodes was set to 2.8 cm. The electrolyte was 0.5 M sulfuric acid and the series solution resistance between the working and the reference electrodes is 40 $\Omega$, as measured using AC impedance. The experiments were performed by first passivating the iron electrode by scanning the circuit potential at a rate of 5 mV/s) from −934 mV to 150 mV. After passivation, the circuit potential was scanned backwards from 150 mV to −202 mV where the current oscillations were recorded at a given compensated resistance, $R_{\text{comp}}$. To maintain the total resistance of the cell constant during IR compensation, two external parallel resistors $R_p = -2R_{\text{comp}}$ were applied (see Fig. 1).

3. Model

3.1. Bistable region

The electrical coupling between the two electrodes can be modeled by a combination of parallel and collective resistors shown in Fig. 1(b). Thus the double layer potentials of the two electrodes ($e_1$ and $e_2$) in the presence of coupling vary as [23,24,9,25]:

\[
\frac{de_1}{dt} = \frac{v - e_1}{R_{eq}} - i_F(e_1) + K \frac{1}{2}(e_2 - e_1) + A \xi_1 \\
\frac{de_2}{dt} = \frac{v - e_2}{R_{eq}} - i_F(e_2) + K \frac{1}{2}(e_1 - e_2) + A \xi_2
\]

A forward or a backward scan can be made at a rate $s$.

\[
\frac{dv}{dt} = s
\]

The coupling strength $K$ is given by [23]

\[
K = \epsilon \frac{1}{1 - \epsilon} \frac{R_p}{R_{eq}}
\]

where $\epsilon = 2R_c/R_{eq}$ is the collective resistance fraction. Note that $\epsilon/(1 - \epsilon) = 2R_c/R_p$. IR compensation applied to both electrodes introduces negative coupling: $R_c = R_{\text{comp}} < 0$ thus $K < 0$. The term $A \xi_1$ has been added to the system to account for unavoidable small noise that exists in the experimental system. This noise eliminates long, spurious transients that can occur with two coupled identical systems. $A$ is noise amplitude and was set to a low value of 0.05.

\[
\xi(t) = \text{ran}(1) - 0.5
\]

$\text{ran}(1)$ is a uniform random number between 0 and 1.

The reaction current $i_F(e_i)$ is approximated by a cubic equation.

\[
i_F(e_i) = 1.1e_i^3 - 2.3e_i^2 + 1.4e_i + 0.013
\]

The approximation simulates a negative differential resistance of the electrochemical system: an initial increase is followed by a decrease of Faradaic current with electrode potential.

3.2. Oscillatory region

A model that describes the relaxational active–passive oscillations for a single electrode was proposed by Koper and Sluyters [24]; the model incorporates variables for electrode potential ($e$), surface hydrogen ion ($h$) and iron($I$) ion ($u$) concentrations. This model has been modified here to describe an IR compensated system of two relaxational oscillators coupled through the electrolyte with a series (collective) resistance $R_s$ and IR compensation $R_{\text{comp}} < 0$ in series. Therefore, in Fig. 1(b) $R_c = R_s + R_{\text{comp}}$. To maintain the system at constant equivalent resistance, $R_{eq} = R_s$, we introduce parallel resistances $R_{p1} = R_{p2} = R_p = -2R_{\text{comp}}$. In this way, we can investigate the effect of negative coupling exerted by the IR compensation without changing the dynamics through changing $R_{eq}$. The model in dimensionless form:

\[
(1 + \gamma) \frac{de_1}{dt} = \frac{v - e_1}{R_{eq}} - qK_{\gamma}(1 - \theta_1) + \kappa \frac{(e_2 - e_1)}{2} \\
\frac{d\theta_1}{dt} = d(h_2 - h_1) - \frac{h_1 q^{1/2}}{q} \left( \frac{v - e_1}{R_{eq}} + \kappa \frac{(e_2 - e_1)}{2} \right)
\]
\[ \frac{du_1}{dt} = -\alpha du_1 + d^{1/2} k_1 (1 - \theta_1) - \frac{t_{ui} d^{1/2}}{q} \left( \frac{v - e_1}{r_{eq}} + \kappa \left( \frac{e_2 - e_1}{2} \right) \right) \]  
(7)

\[ (1 - \gamma) \frac{d e_2}{dt} = \frac{v - e_2}{r_{eq}} - q k_2^2 (1 - \theta_2) + \kappa \left( \frac{e_1 - e_2}{2} \right) \]  
(8)

\[ \frac{dh_2}{dt} = d (h_b - h_2) - \frac{t_{ui} d^{1/2}}{q} \left( \frac{v - e_2}{r_{eq}} + \kappa \left( \frac{e_1 - e_2}{2} \right) \right) \]  
(9)

\[ \frac{du_2}{dt} = -\alpha du_2 + d^{1/2} k_2 (1 - \theta_2) - \frac{t_{ui} d^{1/2}}{q} \left( \frac{v - e_2}{r_{eq}} + \kappa \left( \frac{e_1 - e_2}{2} \right) \right) \]  
(10)

\( \theta_i \) is the fractional coverage of the ith electrode with a passive oxide layer.

\[ \theta_i = \frac{1}{1 + (k_2/k_{-2}) h_i} \]

\( \kappa \) is the electric coupling strength

\[ \kappa = \frac{R_{comp} + R_i}{R_i R_{comp} (D_{iq})} \]

Note that \( \kappa \) plays the same role as \( K \) in Eqs. (1), (2), and (4) because the \( R_{eq} = 2R_i \) and \( R_e = R_{comp} + R_i \). \( R_{comp} < 0 \) is the external compensation. \( C_q \) is the capacitance, \( D \) is the diffusivity, and the terms \( 1 + \gamma \) and \( 1 - \gamma \) account for the difference in the capacitance of the two electrodes.

The current is calculated as

\[ I_1 = \frac{(v - e_1)}{r_{eq}} + \kappa \left( \frac{e_2 - e_1}{2} \right) \]

\[ I_2 = \frac{(v - e_2)}{r_{eq}} + \kappa \left( \frac{e_1 - e_2}{2} \right) \]

Other parameters and variables in the model are described below.

\( v, e_i, r, q \) are the dimensionless quantities given by

\[ v = \frac{V_{app} F}{RT} \]

\[ r_{eq} = 2DC_{iq} (R_i) \] and

\[ e_i = \frac{E_i F}{RT} \]

\[ q = \frac{F^2 A^{1/2}}{2RTC_d} \]

\[ d = \frac{A}{\delta} \]

\( V_{app} \) is the applied potential, \( E_i \) is the potential drop across the double layer of the i-th electrode, \( h_i \) is the local concentration of the hydrogen ions near the surface and \( u_i \) is the local concentration of metal ions near the surface.

\( R \) is the universal gas constant, \( T \) is the temperature, \( F \) is Faraday constant. \( \theta \) is the fractional coverage of the surface by the oxide. \( \delta \) is the thickness of boundary layer.

\( \alpha \) is the ratio of diffusivities of Red and \( H^+ \),

\[ t_{ui} = \frac{c_{ui}}{h_i (1 + \alpha) + 2\alpha u_i} \]

\[ t_{ui} = \frac{h_i}{h_i (1 + \alpha) + 2\alpha u_i} \] transference numbers for the metal ions and the hydrogen ions.

\[ k_i^* = k_i \left( 1 - \frac{u_i}{\alpha c_i} \right) \]

\[ k_i = k_0 \exp \left( \frac{e_i - e_{eq}}{2} \right) \]

\[ \frac{k_2}{k_{-2}} = \frac{k_0}{k_0} \left( \exp (e_i - e_{eq}) \right) \]

\[ u_e = -\frac{1}{2} h_i + \left( \frac{1}{4} h_i^2 + K_{sol} \right)^{(1/2)} \]

Eqs. (5) and (8) are the result of application of the Ohms law and Kirchoff law to the electrochemical circuit. Eq. (6), (7), (9), and (10) are the equations describing the local kinetics and molar diffusion in the system. Note that although the coupling between the electrodes is electric, the coupling strength \( \kappa \) also appears for the mass balance of hydrogen and iron(ii) ions because they transfer a portion of the current, and, as shown in Eqs. (11) and (12), the currents of the electrodes depend on \( \kappa \).

3.3. Data analysis: reconstruction of phase

To interpret the synchronization behavior of the two oscillators in the presence of coupling we will use a phase difference measure for m:n entrainment [26]. An approach based on Hilbert transform [27] is used to assign a phase to every point on the limit cycle. The Hilbert transform shifts the time series signal by an angle of \( \pi/2 \) and the phase can be calculated with respect to the shifted signal. The instantaneous phase \( p_i(t) \) for a current signal \( i(t) \) can be obtained as the arc tangent of a complex function \( \xi(t) \); where,

\[ \xi(t) = \tilde{i}(t) + jH(\tilde{i}(t)) \]

\[ \tilde{i}(t) = I - \text{mean}(l) \]

\( H(\tilde{i}(t)) \) is the Hilbert Transform of \( \tilde{i}(t) \).

The frequency \( f_i \) (i.e.,1,2) of the signal from the i-th electrode is given by

\[ f_i = \frac{1}{2\pi} \left| \frac{d\phi_i}{dt} \right| \]

If the oscillators are m:n entrained, the phase difference, \( \Delta \phi_{mn} = np_1 - mp_2 \), should be a constant. This is equivalent to the frequency difference \( (nf_1 - mp_2 = (d\Delta \phi_{mn}/dt)) \) being zero.

4. Results and discussion

4.1. Experiments

4.1.1. Bistable region

Fig. 2(a) shows the forward and backward polarization curves for the two nickel electrodes in 3 M sulfuric acid with no added external resistance. The electrodes are monostable at these conditions but exhibit negative differential resistance for 1.06 V < V < 1.14V. Fig. 2(b) shows the result of adding an external resistance, \( R_p = 602\Omega, \) to each electrode. As a result of the presence of the resistors, bistability can be observed for 1.16 V < V < 1.22 V. This bistability develops because of the negative slope on the polarization curve in Fig. 2(a).

The added external resistance can be compensated by adding IR compensation. The polarization curves for a fully compensated external resistance \( R_{comp} = -R_p/2 = -301\Omega \) are plotted in Fig. 2(c). Now the total added resistance is zero, however, instead of obtaining the polarization curve in Fig. 2(a) we observed a symmetry broken state in a potential range where the negative slope of the polarization curve starts to develop: one electrode exhibits larger, the other electrode lower current than it would be expected from the polarization curve without added resistance.
Fig. 2. Polarization scan curves of nickel electrodes at different values of added external resistance, $R_p$ and IR compensation $R_c$; forward scan rate: $= 1 \text{ mV/s}$ and backward scan rate: $= -1 \text{ mV/s}$. (a) $R_p = 0$, $R_c = 0$. (b) $R_p = 602\Omega$, $R_c = 0$. (c) $R_p = 602\Omega$, $R_c = -301\Omega$.

Apparently, because of the global nature of the IR compensation symmetry broken patterns develop in the two-electrode system.

4.1.2. Oscillatory region

The effect of IR compensation in an oscillatory system is investigated with the oscillatory iron electrodissolution.

The conditions of the experiments were chosen such that the current signal from the two electrodes without adding IR compensation exhibits relaxational active–passive oscillations ($V_{app} = -202\text{ mV}$, $R_{comp} = 0$, and $R_p = 0$).

The current oscillations for single electrodes of the two-electrode setup are shown in Fig. 3(a). (The currents from these two separate experiments are overlaid for better comparison of the amplitudes and frequencies.) The two electrodes exhibit a large frequency (28%) and small peak-current (3%) difference. Fig. 3(b) shows the phase difference, $\Delta\phi_{11}$, between the uncoupled oscillators (time series in Fig. 3(a)). Since the oscillators are not entrained, the phase difference changes almost linearly with time.

Fig. 3(c) shows the time series for the two oscillators that are connected simultaneously to the circuit with no IR compensation or an external resistor. The oscillators are 1:1 in-phase synchronized.

The current for uncoupled electrodes $f_1 = 0.192\text{ Hz}$ and $f_2 = 0.24642\text{ Hz}$. (b) Phase difference ($\Delta\phi_{11} = \phi_1 - \phi_2$) as a function of time for current in (a). (c) Current for the simultaneously connected electrodes. (d) Phase difference for 1:1 entrainment for current in (c).
because the electrodes are coupled through the potential drop in the electrolyte. The phase difference, $\Delta \phi_{11}$, Fig. 3(d)) is nearly a constant with time with a mean value close to zero.

### 4.1.2.1. Effect of adding negative coupling between the oscillators.

Negative coupling was now added by applying IR compensation, $R_{\text{comp}}$. The coupling strength was increased by increasing the magnitude of $R_{\text{comp}}$ and the time series of the current were recorded at each $R_{\text{comp}}$. Because IR compensation adds a negative resistor in series with the electrodes, we add $R_p = -2 \times R_{\text{comp}}$, parallel resistors to each electrode. Thus the total resistance of the cell is not changed and the negative coupling induced by IR compensation can be studied without changing the local dynamics of the oscillators.

Fig. 4(a) shows the current time series for very weak added negative coupling, $R_{\text{comp}} = -2.5\Omega$. The oscillators are not synchronized. The phase difference plot in Fig. 4(b) indicates a drifting behavior with a frequency difference (28%) that corresponds to that of the individual (uncoupled) oscillators.

For weak negative coupling strengths, i.e., $5\Omega \leq |R_{\text{comp}}| \leq 15\Omega$, the oscillators were out of phase 1:1 synchronized with some intermittent phase slips. The current time series and the phase difference at $R_{\text{comp}} = -10\Omega$ are shown in Fig. 4(c) and (d), respectively.

At moderate added negative coupling strength, $20\Omega \leq |R_{\text{comp}}| \leq 55\Omega$, the time series were aperiodic; snapshots of the time series for $R_{\text{comp}} = -30\Omega$ and $R_{\text{comp}} = -40\Omega$ are shown in Fig. 5(a) and (c), respectively. In each time series there are long time intervals for which the oscillators are either entrained with a ratio of 1:1, 1:2, or 2:1. For example, see the phase difference plots for 1:1 entrainment ($\Delta \phi_{11}$), 1:2 entrainment ($\Delta \phi_{12}$), and 2:1 entrainment ($\Delta \phi_{21}$) are shown in Fig. 5(c) and (d) for $R_{\text{comp}} = -30\Omega$ and $R_{\text{comp}} = -40\Omega$, respectively. Repeated switching between these entrainment states was seen, however, there was no obvious trend in switching times or length of the time interval of a particular type of entrainment in a time series.

At a stronger added negative coupling, $R_{\text{comp}} = -75\Omega$, the oscillators are 1:1 entrained and are anti-phase with respect to each other (see Fig. 6(a) and (b)). To check the robustness of the oscillations and possible existence of other dynamic states a perturbation was applied to the system by quickly turning the potentiostat off and on. On applying the perturbation at high added negative coupling strengths, the oscillations were replaced by steady states that are anti-symmetric with respect to each other, i.e., one electrode was active and the second electrode was passive; as an example current time series for $R_{\text{comp}} = -75\Omega$ is shown in Fig. 7(a) and (b). This phenomenon of disappearance of oscillations is referred to as amplitude death.

No oscillations were seen at IR compensation larger than $75\Omega$. Anti-symmetric steady states are seen at $R_{\text{comp}} = -100\Omega$ (Fig. 7(c)). If a perturbation was applied to this state the electrode that was active before applying the perturbation became passive and the passive electrode was now active; the time series after perturbation is shown in Fig. 7(d).

### 4.1.2.2. Characterization of the trend of appearance of different entrainment ratios as a function of coupling strength.

The phase difference, $\Delta \phi_{\text{ms}}$, is constant with respect to time when the oscillators are m:n synchronized. This property of the phase difference is used here to estimate the length of the time for which the oscillators are m:n entrained in a time series at a fixed coupling strength. Fig. 8 shows the proportion of the time for which the oscillators are entrained with a particular entrainment (1:1, 1:2, or 2:1) ratio in a time series, as a function of $R_{\text{comp}}$.

The percentage of 1:1 entrained oscillations in a time series decreased from 100% at $R_{\text{comp}} = 0\Omega$ to a minimum at $R_{\text{comp}} = -5\Omega$, the point where the oscillators are drifting with respect to each other and there is no synchronization (time series in Fig. 4(a)). The proportion of 1:1 entrained oscillations rises again to a value near one at weak added coupling strengths (time series in Fig. 4(c)).
For $R_{\text{comp}}$ less than $R_{\text{comp}} = -20\Omega$ no 2:1 or 1:2 entrainments are seen; therefore, the proportion for these in the current time series is 0.

At higher coupling strength $20\Omega \leq |R_{\text{comp}}| \leq 65\Omega$ all three forms of entrainment are seen. The percentage of 1:1 entrainment falls to a minimum at $R_{\text{comp}} = -40\Omega$ and then rises again to a value of 1 at $R_{\text{comp}} = -75\Omega$, where we see anti-phase oscillations (Fig. 6). However, the decrease is not monotonous and there is a local maxima at $R_{\text{comp}} = -25\Omega$.

Only two instances of 1:2 entrainment were seen, at $R_{\text{comp}} = -20\Omega$ and $R_{\text{comp}} = -40\Omega$. The percentage of number of 2:1 entrained oscillations in a time series rise from zero at $R_{\text{comp}} = -25\Omega$ to a maxima and then drops back to zero at $R_{\text{comp}} = -75\Omega$.

The quantitative analysis of the entrainment regions confirmed the qualitative observation that at intermediate negative coupling strengths 1:1, 1:2, and 2:1 entrainment coexist. In particular, at about $R_{\text{comp}} = 40\Omega$ the three entrainment regions exist for about the same overall time intervals.

4.2. Simulations

4.2.1. Bistable region

The existence of stationary patterns due to IR compensation is modeled with numerical integration of a general electrochemical model with negative differential resistance described with Eqs. (1–4). The system is monostable for small added external resis-

![Fig. 5](image1)

**Fig. 5.** Current time series (electrode 1: solid line and electrode 2: broken line) and phase difference for two iron electrodes at intermediate added negative coupling strengths at $V_{\text{app}} = -202\text{ mV}$. (a) Current for $R_{\text{comp}} = -30\Omega$ and $R_p = 2R_{\text{comp}} = 60\Omega$; regions of different entrainment are also marked. (b) Phase difference $\Delta\phi_{11}$ (top panel), $\Delta\phi_{12}$ (middle panel), and $\Delta\phi_{21}$ (bottom panel) as a function of time for current in (a). (c) Current for $R_{\text{comp}} = -40\Omega$ and $R_p = 2R_{\text{comp}} = 80\Omega$; (d) Phase difference $\Delta\phi_{11}$ (top panel), $\Delta\phi_{12}$ (middle panel), and $\Delta\phi_{21}$ (bottom panel) as a function of time for current in (c).

![Fig. 6](image2)

**Fig. 6.** (a) Current time series (electrode 1: solid line and electrode 2: broken line) for a strong added negative coupling strength: $V_{\text{app}} = -202\text{ mV}$ and $R_{\text{comp}} = -75\Omega$, $R_p = 2R_{\text{comp}} = 150\Omega$. (b) Phase difference, $\Delta\phi_{11}$, as a function of time for current in (a).
Fig. 7. Amplitude death in the experiments. Current (electrode 1: solid line and electrode 2: broken line) as a function of time at $V_{app} = -202 \text{ mV}$. (a) Oscillations at $R_{comp} = -75 \Omega, R_p = -2R_{comp} = 150 \Omega$ (same as Fig. 6(a)). (b) Coexisting anti-symmetric steady state with oscillations in (a). (c) Anti-symmetric steady states at higher coupling strength: $R_{comp} = -200 \Omega, R_p = -2R_{comp} = 400 \Omega$. (d) Anti-symmetric steady states after applying the perturbation to time series in (c).

Fig. 8. Percentage of different entrainment ratios in the time series (○ 1:1 entrainment, △ 2:1, ■ 1:2) as a function of $R_{comp}$.

Fig. 9. Polarization scan curves (forward scan rate: $s = 0.001$ and backward scan rate: $s = -0.001$) obtained through numerical simulations of the model (Eqs. (1)–(4)). $A = 0.05$. Results are shown for different values of added parallel resistances $R_p$ and IR compensations $R_c$. (a) Very small added external resistance: $R_p = 0.01, R_c = 0$. (b) Large added external resistance with no compensation; $R_p = 10, R_c = 0$. (c) Large added external resistance with almost full compensation. $R_p = 10, R_c = -4.95$. 

The disappearance of the uniform steady states can be explained through the linear stability analysis of the model. (See Appendix for a detailed analysis of the results concerning this section.) For a single electrode, without any external compensation, steady states are stable if the condition $-1/R_{eq} - d\delta e/d\theta < 0$ holds [28]. For the two-electrode model the uniform steady states will be stable when $-1/R_{eq} - d\delta e/d\theta - K < 0$, where $K$ is the strength of electric coupling between the electrodes. This implies that IR compensation contributes to the stability of the cell by reducing the total cell resistance from the original $R_0 = R_{eq}$ to $R_{eq} = R_0 + 2R_{comp}$ but causes cell instability by introducing negative coupling $K < 0$. In the simple configuration used in the experiment we can evaluate the overall effect of the IR compensation: $-1/R_{eq} - K = -1/(R_0)$, where $R_0$ is the equivalent resistance where bistability can be observed without IR compensation. Apparently, the stabilizing and destabilizing effects of IR compensation cancel each other;
the stability does not depend on the extent of IR compensation, $R_{\text{comp}}$.

4.2.2. Oscillatory region

We investigate the effect IR compensation in a two-electrode model for active–passive oscillations. During the experiments the total cell resistance was kept constant. Increasing the IR compensation makes the coupling strength more negative as seen in Eqs. (5)–(12).

Without IR compensation there is positive coupling due to the potential drop in the electrolyte. This coupling can be simulated with a small positive value for $\kappa$. At $\kappa = 0.04$ the oscillators are in-phase synchronized (Fig. 10(a)). As the coupling strength was decreased to $\kappa = 0$ the oscillators are uncoupled (Fig. 10(b)). At a

![Figure 10](image1.png)

**Fig. 10.** Numerical simulations of the model (Eqs. (5)–(10)). Current (electrode 1: solid line and electrode 2: broken line) at different coupling strengths. Other parameters are $r_{aq} = 0.085$, $\gamma = 0.7$, $v = 30$, $K_{\text{sol}} = 16$, $\alpha = 0.2$, $q = 100$, $h_0 = 1$, $k_0 = 0.01$, $k^+_{1}/k^+_{2} = 0.1$, $\epsilon^+_{1} = 20$, and $\epsilon^+_{2} = 20$. (a) Positive coupling: $\kappa = 0.25$. (b) Uncoupled electrodes: $\kappa = 0$ (frequency difference = 28%). (c) Weak negative coupling: $\kappa = -0.14$. (d) Strong negative coupling: $\kappa = -1$.

![Figure 11](image2.png)

**Fig. 11.** Amplitude death in the model. Current (electrode 1: solid line and electrode 2: broken line) as a function of time. (a) Oscillations at $\kappa = -4.85$. (b) Coexisting anti-symmetric steady states with the time series in (a). (c) Steady state at $\kappa = -7$. (d) Second anti-symmetric steady state at $\kappa = -7$. 
small negative coupling strength, $\kappa = -0.14$, the oscillators are 3:4 entrained as shown in Fig. 10(c). As the coupling strength was made more negative from this point various entrainment ratios close to 1:1 were observed, e.g., 4:5, 9:11, 10:12. Eventually, 1:1 entrained, anti-phase oscillations were obtained at large negative coupling strengths; an example at $\kappa = -1$ is shown in (Fig. 10(d)).

The oscillator were 1:1 synchronized at more negative coupling strengths until the point of amplitude death, $\kappa \approx -4.8$. Coexistence of anti-phase oscillations (Fig. 11(a)) and anti-symmetric steady states (Fig. 11(b)) was seen at $\kappa = -4.85$. At higher coupling strengths multiple anti-symmetric steady states similar to the experiments were observed; for example, the anti-symmetric stationary states at $\kappa = -7$ are shown in Fig. 11(c) and (d).

4.2.2.1. Stability analysis. The appearance of anti-symmetric steady states, as the parameter K is decreased, can be described with a numerical linear stability analysis of the ordinary differential Eqs. (5)–(10). (The numerical analysis was done using the program AUTO in software XPP.) The obtained bifurcation diagrams showing the steady states and their stability as a function of coupling strength are shown in Fig. 12(a) and (b) for electrode 1 and electrode 2, respectively.

For each electrode, the unstable and symmetric fixed point close to the center of the limit cycle (at around $e = 20$) goes through a pitchfork bifurcation after which unstable, symmetry broken steady states are created. After a saddle-node bifurcation these symmetry broken states become stable for $\kappa < -4.8$ through a Hopf bifurcation. The three regions marked as OSC, CE, MS correspond to the values of the parameter K for which oscillations, coexistence of oscillations and steady state, and multiple steady states are seen. A 3D plot of the limit cycle and fixed points of the oscillators just below and just above the Hopf bifurcation points are shown in Fig. 12(c) and (d), respectively. The fixed points (marked with +) for the two electrodes are created on the opposite sides of the limit cycles.

These numerical simulations and linear stability analysis clarify the experimentally observed transition from in-phase entrainment through anti-phase entrainment to amplitude death with increasing the (negative) coupling strength between the oscillators. The model does show higher mode entrainment between the in-phase and anti-phase behavior, however, transitions among different entrainment regions similar to the experiments were not observed in the simulations.

5. Conclusions

Stationary and oscillatory patterns were observed due to negative coupling induced by IR compensation in dual-electrode electrochemical systems exhibiting negative differential resistance (nickel and iron electrodissolution).

Traditionally, IR compensation has been used to remove the bistability in single electrode systems [1]. Our results show that when IR compensation is applied (globally) to two nickel electrodes, the uniform state corresponding to the negative slope on the polarization curve cannot be stabilized. The stabilizing effect of IR compensation on bistability is counteracted by the destabilizing effect due to negative coupling. The negative coupling induced a symmetry breaking bifurcation resulting in new active (high current) and passive (low current) states that are not seen in the dynamics of the single electrode without interactions. When interactions are considered (e.g., reference electrode placed close the electrode surface), even a single electrode can concurrently exhibit these active and passive states [19,29]. The formation of these patterns cannot be neglected in traditional electrochemical investigations; for example, the patterns strongly affect the impedance spectrum of the system [30].

IR compensation also affected the oscillatory electrodissolution. Without negative coupling in-phase, with strong negative coupling anti-phase synchronization was observed. These results are the same as those found by inducing negative coupling through refer-
ence electrode placement [31] very close to the working electrode. However, with IR compensation used in our study a fine tuning of negative coupling was possible with which the transition from in-phase to anti-phase synchrony could be investigated without changing the inherent dynamics of the oscillators. We found that at negative coupling strengths in between those corresponding to in- and anti-phase synchrony, phase-drift, out-of-phase synchrony, and alternating 1:1, 1:2, and 2:1 synchrony patterns can be observed. Although 1:2 phase locking had been reported for an iron disk electrode, [25], the switching among entrainment states indicates the existence of complicated phase dynamics. There have been reports of similar behavior in the cardio-respiratory system [32]. The signals from the cardiac system and the respiratory system stay synchronized with a certain entrainment ratio for some time and then change the entrainment ratio. Such continuous transitional dynamics in cardiorespiratory system was attributed to the presence of long-term correlated noise, superimposed by the activity of lower frequency oscillatory component [33]. The relationship between the dynamics of electrochemical and the cardiorespiratory system is not clear, however, the large frequency difference among the oscillators probably plays an important role. This observation is also supported by the fact that with oscillatory nickel electrodissolution, where the frequency difference between the oscillators is small (<10%), such switching entrainment ratios were not observed with negative coupling [5].

With IR compensation it was possible to investigate the effect of extremely strong negative coupling; such very strong negative coupling could be imposed with reference electrode placements very close to the working electrode. We observed amplitude death: because of the strong negative coupling the two oscillators repel each other to such an extent that the oscillations cease to exist. Amplitude death has been reported in chemical (BZ reactions), biological and electrochemical systems [34–41]. The amplitude death reported in this work is different than those observed with positively coupled oscillations close to Hopf bifurcation in nickel electrodissolution [41]. In contrast to the symmetric steady states arising close to Hopf bifurcations with the nickel electrodes, the steady states were strongly asymmetric. The amplitude death similar to the results in this work was reported in BZ reactions [35]. In this mechanism, the steady states are created on the opposite sides of the limit cycles of the oscillators.

We developed a model for a dual-electrode iron electrodissolution to investigate the effects of IR compensation. The model showed that when negative coupling was added to 1:1 in-phase synchronized oscillators the behavior changed to the anti-phase amplitude oscillations, similar to what is seen in the experiments. It also explained the transition to a region of coexistence of oscillations and anti-symmetric steady states and finally a multiple anti-symmetric steady states as the coupling strength was made more negative. This transition occurs through a series of pitchfork, saddle-node, and supercritical Hopf bifurcations of the individual steady states. However, the model fails to describe the switching between several entrainment ratios. There are (at least) two possible qualitative explanations for the switching behavior: either the oscillators itinerate among the basin of attractions of the stable entrainment states due to noise, or the oscillators travel along heteroclinic orbits of the unstable entrainment states. Either way, noise effects are likely to play a major role. Further development of the model is required to consider external noise (e.g., lack of perfect potential control) or internal noise due to corrosion that can explain the switching behavior.

The results presented in this study show that when IR compensation is applied to a multi-electrode system stationary and oscillatory patterns can develop; in these cases electrochemical methods with spatial and temporal resolution should be applied to ensure that proper kinetic information is extracted from the experiments.

Acknowledgements

We thank the National Science Foundation for financial support under grant CBET-0730597. We also thank Ms. Carolyn Vallas and NSF REU program for their support.

Appendix A

A.1. Model on bistability

A simple model for a bistable electrochemical system consists of a single equation for the charge balance:

\[ C \frac{de}{dt} = \frac{V - e}{R_{eq} A} - j_F(e) \]  

(15)

where \( C \) is double layer capacitance, \( V \) is circuit potential, \( e \) is the electrode potential, \( R \) is the series resistance for a single electrode system, \( A \) is the surface area of the electrode, and \( j_F(e) \) is the Faradic current density. For simplicity \( A = 1 \), \( C = 1 \). The steady states of Eq. (15) are stable [27] if \(-1/R_{eq} - dj_F(e)/de < 0 \). For a system of two electrodes [23,24,9]:

\[ \begin{align*}
\frac{de_1}{dt} &= \frac{V - e_1}{R_{eq}} - j_F(e_1) + \frac{K}{2} (e_2 - e_1) \\
\frac{de_2}{dt} &= \frac{V - e_2}{R_{eq}} - j_F(e_2) + \frac{K}{2} (e_1 - e_2)
\end{align*} \]

(16)  

(17)

In these equations the electrical coupling strength is defined the same manner as in Eq. (4). Around a uniform steady state \( e_2 = e_1 \) where the right hand side of Eqs. (16) and (17) vanish

\[ \frac{d(e_1 - e_2)}{dt} = -\frac{1}{R_{eq}} (e_1 - e_2) - \frac{dj_F(e_1)/de}{e_1 - e_2} + \frac{K}{2} (e_2 - e_1) \]

(18)  

\[ \frac{d(e_2 - e_1)}{dt} = -\frac{1}{R_{eq}} (e_2 - e_1) - \frac{dj_F(e_2)/de}{e_2 - e_1} + \frac{K}{2} (e_1 - e_2) \]

(19)

For \( \Delta e = e_2 - e_1 \),

\[ \frac{d\Delta e}{dt} = -\frac{dj_F(e_1)/de}{R_{eq}} \Delta e - K \Delta e \]

thus we get the stability condition \(-1/R_{eq} - dj_F(e)/de - K < 0 \). Apparently, large negative coupling can destabilize any uniform steady state as long as \(-1/R_{eq} - dj_F(e)/de < K \).

A.2. IR compensation: theory

Assume we apply a parallel resistance \( R_{eq} = R_0 \) in Eq. (15) with which bistability is obtained with a single electrode. Therefore, \(-1/R_0 - dj_F(e)/de < 0 \). In the two electrode setup without IR compensation \( K = 0 \) with the same \( R_0 = R_0 \) we again obtain unstable uniform steady state since the \(-1/R_{eq} - dj_F(e)/de < K \) condition is satisfied.

During IR compensation, a negative resistance is connected in series with cell, \( (R_c = R_{coll} < 0) \). Thus, by IR compensation the original cell resistance \( R_0 \) is decreased to \( R_0 + 2R_c \). This makes the uniform steady state of the cell more stable. However, at the same time, negative coupling is introduced. In Eq. (16)

\[ K = \frac{2R_c}{R_p} \frac{1}{R_{eq}} = \frac{2R_c}{R_p} \frac{1}{R_0} + 2R_c \]

We can see, that from the stability condition \(-1/R_{eq} - K \) is an important quantity that will eventually determine the effect of IR
compensation ($\frac{djF(e)}{de}$ is IR compensation independent). However, this quantity is constant:

$$\frac{1}{R_{eq}} - K = \frac{1}{R_0 + 2R_c} - \frac{2R_c}{R_0 + 2R_c} = -\frac{1}{R_0} = \text{const}$$

The result implies that in the considered situation IR compensation, in contrast to expectation, does not change the stability condition of the steady state.

References