Synchronization of current oscillations in a dual-anode dissolution reaction in the presence of a common cathode electrode

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ABSTRACT

The formation of synchronization patterns are explored as a result of coupling the dual anode oscillatory nickel electrodissolution and a single cathode hydrogen ion reduction reaction in an electrochemical cell. At the onset of current oscillations, with small surface area cathode in-phase synchronization patterns were recorded, which implies the presence of coupling between the anodic reactions. As the surface area of the cathode was increased, a transition from synchronized to desynchronized behavior was observed. Similarly, the extent of synchronization and thus the coupling can be diminished with increasing the individual resistances attached to the anodes. The effect of coupling induced by the cathode was interpreted with the ratio of charge transfer resistance of the cathode to the total external resistance in the cell. The coupling effects were further demonstrated with anti-phase synchronization of relaxation, and phase and identical synchronization of chaotic current oscillations. The experimental results about the coupling effect of the cathode were also explained with a kinetic model for the reactions. The results show that the nonlinear behavior of a complex cathode-anode cell can be greatly simplified when the majority of the overpotential is due to driving the anodic reactions to a far-from equilibrium state, while the relatively simple cathode (with small overpotential and fast kinetics) acts as a coupling element between the anodes. Such simplification can be a useful tool for interpreting the complex kinetic behaviors of galvanic and electrolytic cells that have time-scale separations between the cathodic and anodic processes.

1. Introduction

Electrochemical systems can exhibit a wide range of self-organized spatiotemporal phenomena., e.g., formation of reaction waves or dynamical clustering [1–3]. These patterns can be interpreted by identification of nonlinear kinetic phenomena (e.g., negative differential resistance with N-shaped current-voltage characteristics) and the type of coupling among the reaction sites (e.g., through mass transport or potential drops in the electrolyte). Traditional 'three-electrode systems' equipped with two working electrodes, a reference, and a counter electrode are particularly useful for such investigations. When oscillatory electrochemical reactions take place in dual working electrode systems, the coupling between the electrodes can generate a variety of synchronization phenomena [4,5], e.g., in-phase [6,7], anti-phase [8–10], out-phase [11–14] synchronization, generation of complex oscillations [6,15], and amplitude death [16,17]. Extent of phase synchronization can indicate the coupling strength between the elements through observation of full synchronization (phase locking), phase-slipping (intermittent locking of the phases), and phase drifting with strong, intermediate, and weak coupling, respectively [18,19]. Such patterns were also identified with chaotic oscillations where coupling caused phase synchronization with weak [20], and identical synchronization [14,21,22] with strong coupling.

In electrochemical cells, the electrolyte acts as a resistive element for passing current; this migration coupling is the dominant form of interactions in the large majority of systems [1,2,7]. The effect of the electrical coupling can be studied directly (through potential drops in the electrolyte [7,11,23]) or with an external resistance interface (through potential drops in the external resistance circuitry) [6]. For example, in microfluidic devices with multiple working electrodes, the potential drop in the flow channel has been shown to couple electrodes depending on the distance between the working and the reference/counter electrodes and in-phase synchronization was observed with oscillatory nickel electrodissolution [24]. External resistances induced in-phase synchronization of smooth, and anti-phase

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synchronization of relaxation oscillations with nickel electro-dissolution [6]. The effect of coupling through capacitance and resistance was demonstrated in the pioneering work of Franck and Meunier [25]. More recently, with the use of theoretical descriptions of the coupling through combination of resistors and capacitors, novel patterns have been confirmed in the form of complex rotating waves and chimera dynamics. (coupling induced co-existing synchronized and desynchronized oscillations) [26,27]. In addition, nonlinear coupling, most likely due to limiting effect of light on current, was also shown to induce a wide range of clustering behavior and chimera patterns with silicon electrodissolution in HF [28–30].

Many of the studies on nonlinear behavior in research setting were performed in the traditional 'three-electrode' configuration with a reference, a counter, and a working electrode system (which can consist of an electrode array) [2,5]. However, nonlinear phenomena can also occur in practical applications, e.g., fuel cells, [31–33], which utilize two electrodes (cathode and anode). In such configurations, interactions between the cathodic and anodic reactions can greatly impact the behavior of the entire cell: In a previous publication [34], we showed that cell instabilities can occur in a cell with single anode nickel electrodissolution and single cathode hydrogen ion reduction under conditions where none of the anode or the cathode could display instabilities.

In this paper, the coupling of nickel electrodissolution reaction in a dual anode system to hydrogen ion reduction reaction on a single cathode is investigated. Synchrony analysis is applied to show the importance of the effect of coupling on the dynamics of the reaction system with smooth oscillations. We explore the variation of synchronization patterns with changing the size ratio between the anode and cathode and interpret the results with the charge transfer resistance variations of the cathode. This coupling mechanism is also confirmed by experiments in which individual resistances are attached to the anode. The coupling effect of the cathode is further demonstrated with anti-phase synchronization of relaxation, and phase and identical synchronization of chaotic oscillations. Finally, a kinetic model is constructed to confirm that the coupling effect of the cathode can synchronize the current oscillations on the anodes and that the coupling strength can be tuned by the size ratio of the cathode and the anode.

2. Experimental

The electrochemical cell in the cathode-anode configuration was constructed with two 1 mm diameter Ni wire (99.98%, Goodfellow) anodes and one Ni plate cathode (99 +% 0.05 mm thick annealed nickel foil, Alfa Aesear). The schematic of the cell is shown in Fig. 1a. The two nickel anodes were embedded in epoxy so that only the cross-section of the wire is exposed to the solution. The surfaces of these electrodes are polished before the experiments with a series of sandpapers (P120 to P4000). (After polishing the metal surfaces were flushed with deionized water for cleaning.) The anodes were connected to the working point of the potentiostat (Pine AFCBP1) through two separate variable resistance boxes. The cathode plate, cut to the given surface area using the foil, was connected to the reference and counter points of the potentiostat. The potentiostat set the constant circuit potential (V) between the dual anode and cathode electrodes; the currents of the anodes were measured independently by zero resistance ammeters (Bank Elektronik) connected to the working electrodes. The experiments were carried out at 10.0 °C in a water-jacketed 250 mL beaker. The electrolyte is 3 M or 4.5 M sulfuric acid (Macron) for periodic or chaotic oscillations, respectively.

For interpretation of the experimental results, the charge transfer resistance of the corresponding cathode plates were also measured. The charge transfer resistance, R_{ct}, is defined as the

inverse of the slope of a quasi-stationary current vs. potential curve at a given current level. [35] R_{ct} was determined using a slow linear polarization scan (scan rate of 1 mV/s) in a traditional three-electrode cell with the Ni plate as working, a Pt rod counter, and a Hg/Hg$_2$SO$_4$/sat. K$_2$SO$_4$ reference electrode. From this voltammogram, R_{ct} was calculated by taking the inverse of the slope of the voltammetric curve at the specified current levels.

The extent of synchronization between the oscillatory currents of the two anodes was performed with a phase analysis. First, the phase of the oscillations ($\phi_1(t)$ and $\phi_2(t)$) was calculated using the Hilbert-transform method described previously [18,20]. Next, the cyclic phase difference (modulus 2π of $\Delta\phi(t) = \phi_2(t) - \phi_1(t)$) was obtained, and a histogram was constructed; in each bin of the histogram, the fraction of data points (p_i) was obtained for the given phase difference. Finally, a synchronization index (σ) was calculated using the Shannon entropy (S) of the cyclic phase difference as a measure of synchronization [20]. The index is calculated by:

$$\sigma = \frac{S_{max} - S}{S_{max}} \tag{1}$$

$$S = -\sum_{i=1}^{M} p_i ln p_i \tag{2}$$

where M is the number of bins in the histogram and $S_{max} = \ln M$. The values of σ range from 0 (no synchrony) to 1 (full synchrony).

The frequency of the oscillations was determined from the slope of a linear least square fit to the phase vs time plots. (The experimental error of the frequency is about 1 mHz for a 200 s data set using 200 Hz data acquisition rate.)

3. Results and Discussion

3.1. Experimental results

Nickel electrodissolution in 3 M sulfuric acid can exhibit current oscillations under potentistatic conditions. [6,36] These current oscillations occur through a Hopf bifurcation with increasing potential [37]; such oscillation have nearly sinusoidal waveform and are called smooth oscillations. At sufficiently large external resistance and far away from the Hopf bifurcation, the oscillations have relaxation character. [6,38] When the concentration of the acid is increased to 4.5 M, chaotic oscillations can be obtained. [21,36] We present the results on the effect of the cathode on synchronization of current oscillations of the two working electrodes for the smooth, relaxation, and chaotic oscillations separately.

3.1.1. Synchronization of smooth oscillations

3.1.1.1. Effect of surface area. Fig. 2 shows the current oscillations (left column) and the phase difference between the oscillations (right column) for three cathode sizes. First, a relatively small cathode surface area $A = 0.135$ cm^2 was chosen. The time series data in Fig. 2a show that the current oscillations are nearly indistinguishable with identical frequencies of 0.247 Hz. The corresponding phase difference graph (Fig. 2d) shows that the phases of the oscillations are locked to a value close to zero (0.16 radian). The results thus indicate that with the given cathode size strongly synchronized behavior occurs. Because without any coupling the oscillations typically have different frequencies due to surface heterogeneities [6], the observed synchronized behavior is the result of a coupling mechanism in the system. We assume that the cathode reaction (hydrogen ion reduction) acts as coupling