Synchronization properties of coupled electrochemical bursters

D. Koutsaftis, A. Karantonis, N. Kouloumbi, [1]M. Pagitsas
National Technical University of Athens, School of Chemical Engineering, Dept. of Materials Science and Engineering, 9 Iroon Polytechneiou Steet, Zografou, 15780 Athens, Greece; tel. +302107724067, e-mail: dkoutsaftis@yahoo.gr; [1]Aristotle University of Thessaloniki, 54006 Thessaloniki, Greece.

1. Introduction

During the electrodissolution of Fe in sulfuric acid apart from active electrodissolution and passivation, periodic current oscillations take place. More specifically within a certain potential region the current does not rest at steady state but oscillates with a certain amplitude and frequency which depend on the value of the applied potential. Various models have been constructed to explain the existence of these oscillations such as the one proposed by Kado et al. [1] which is as follows:

$$\begin{aligned}
&Fe + H_2O && \rightarrow (FeOH)_{ads} + H^+ + e^-\\
&(FeOH)_{ads} + H_2O && \rightarrow [Fe(OH)_2]_{ads} + H^+ + e^-\\
&Fe + [Fe(OH)_2]_{ads} && \rightarrow Fe[Fe(OH)_2]_{ads}\\
&Fe[Fe(OH)_2]_{ads} && \rightarrow FeOH^+ + (FeOH)_{ads} + e^-\\
&FeOH^+ + H^+ && \rightarrow Fe^{++}_{aq} + H_2O
\end{aligned}$$

The addition of a small quantity of halide ions changes the dynamic response drastically. The periodic oscillations cease to exist giving their place to new phenomena such as aperiodic oscillations, bursting etc. The exact mechanism leading to these phenomena has not been made clear yet, although it is a common belief that the halide ions participate in the whole mechanism during both the active electrodissolution and passivation [2].

In the present work emphasis is given only on bursting oscillations. More specifically synchronization properties of coupled electrochemical bursters are examined. In order to interpret and explain the observed dynamic response of the system mathematical tools from the theory of non linear dynamical systems are employed.

2. Experimental

Potential control measurements were performed using an EG&G PAR 263A potentiostat - galvanostat and the PowerSuite software. A three - electrode electrochemical cell was employed for the experimental procedures. The working electrode consisted of a pair of Fe wires (Sigma - Aldrich, 99.9%) of 1.0 mm diameter which were embedded together in acrylic resin (Acryfix kit) in such a way so that only their tips were exposed to the electrolytic solution, having a fixed distance D. Before the onset of each experiment, the electrodes were polished using a series of wet sandings which was followed by an electrochemical pretreatment using a potential scan from open circuit conditions to 1.5 V with scan rate of 20 $mV\cdot s^{-1}$. The electrodes were connected to the potentiostat through two small resistors of 1Ω in order to measure the current flowing through each of the Fe wires. Current recordings were performed by means of a Yokogawa DL 708E digital oscilloscope equipped with a 701853-HR module. The reference electrode was a silver/silver chloride electrode combined with a Haber - Luggin capillary. The tip of the capillary was placed at a distance L below the level of the two Fe disks exactly in the middle between them. The counter electrode was a carbon rod ($\Phi = 1.0$ mm). The electrolytic solutions that were used in experiments contained 0.75 mM H_2SO_4 and 15 mM Cl^-. The experimental setup is presented in Fig 1.

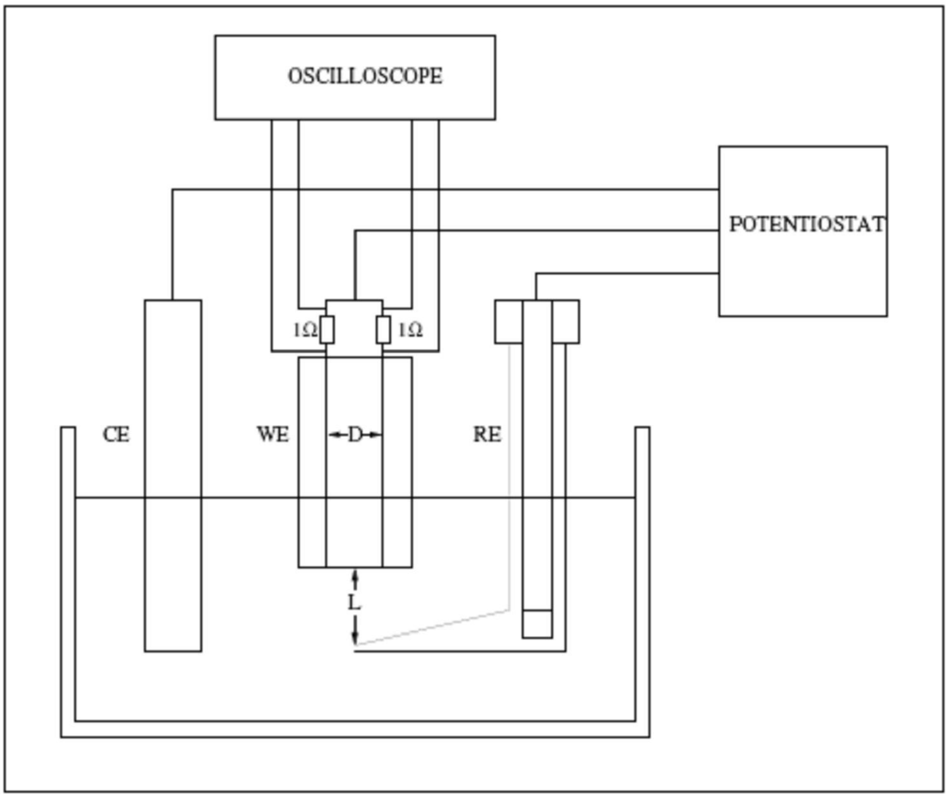

Figure 1: Experimental setup

3. Experimental Results

3.1 Coupling of Elliptic Bursters

Bursting oscillations have been found to take place during the electrodissolution of iron in sulfuric acid in the presence of halide ions at relatively low potential values and more specifically at the beginning of the oscillatory window. This type of bursting activity is called elliptic [3]. It's name originates from the mechanisms that give birth and terminate a single burst. The type of bursting activity is of great importance when studying the response of a network of such coupled bursters. Thus a potential step was applied to the coupled system within the elliptic bursting potential region and the current flowing through each of the iron electrodes has been recorded.

In the present work two parameters besides the applied potential have also been examined; the type and the strength of the connection. The type of the connection (excitatory or inhibitory) has been found in previous works to depend on the distance L between the level of the two iron electrodes and the tip of the Haber - Luggin capillary. In excitatory connections one oscillator activates the other while in inhibitory connections it impedes the other. Thus for small distances the connection is inhibitory while over a critical value the connection becomes excitatory [4]. On the other hand the coupling strength depends on the distance D between the two iron electrodes and has been found to be inversely proportional to it [4].

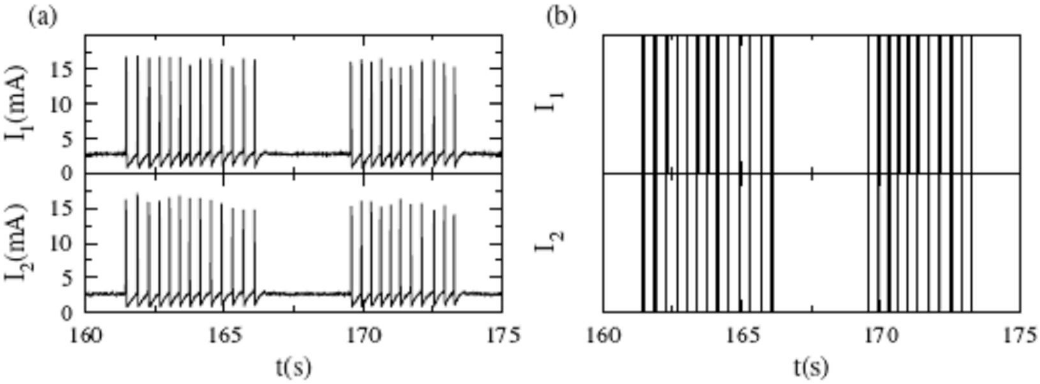

Figure 2: (a) Excitatory coupling of two elliptic electrochemical bursters at 340 mV. (b) The same result in binary form.

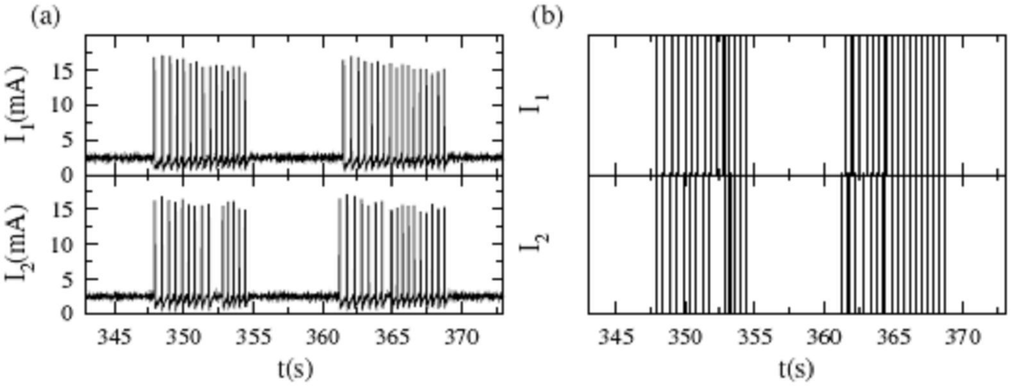

Figure 3: (a) Inhibitory coupling of two elliptic electrochemical bursters at 280 mV. (b) The same result in binary form.

For large values of the distance L while keeping D fixed the two bursters are completely synchronized in phase. Both spike and burst in phase synchronization are observed in the system's dynamic response. Results are presented in Fig. 2 for excitatory coupling and in Fig. 3 for inhibitory coupling. In binary forms black lines correspond to the system being at the oscillatory state while white regions idicate that the system rests at a steady state. By gradually decreasing the distance L, after a critical value only burst synchronization seems to be present. More specifically bursts tend to synchronize in phase or one burster to fire a pair of bursts while the second fires only one. On the other hand there is no sign of any kind of spike synchronization and the two oscillators seem to act as if they were uncoupled in the oscillatory regime.

3.2 Coupling of Square Wave Bursters

Another type of bursting is also present at relatively high potential values during the electrodissolution of iron in sulfuric acid in the presence of halide ions. This type of bursting activity is called square wave and has completely different properties compared to elliptic bursting and so is the response of a coupled network of square wave bursters [3]. The same method of potential step is also applied in this case and the current owing through the the two Fe electrodes is recorded. Experimental results for excitatory and inhibitory coupling between two such square wave bursters are presented in Figs. 4 and 5 respectively.

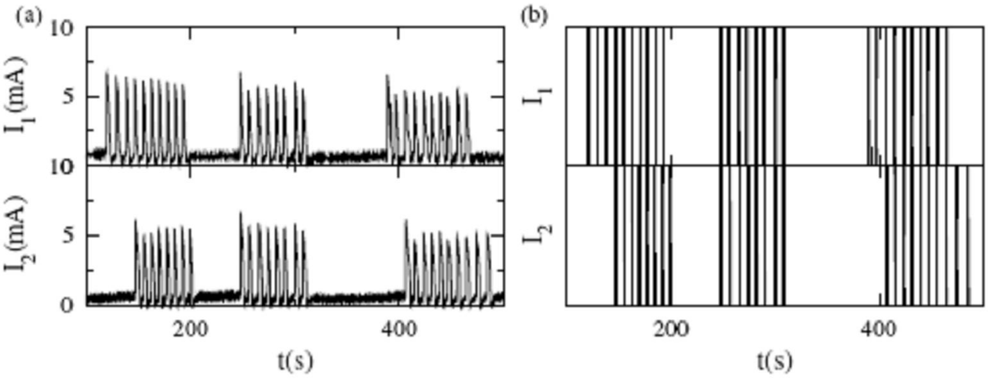

Figure 4: (a) Excitatory coupling of two square wave electrochemical bursters at 440 mV. (b) The same result in binary form.

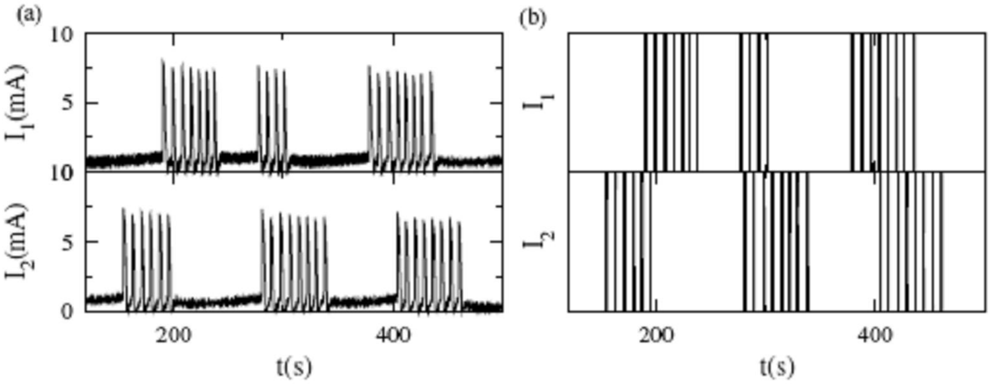

Figure 5: (a) Inhibitory coupling of two square wave electrochemical bursters at 470 mV. (b) The same result in binary form.

As one can notice in Figs 4 and 5 spike and burst synchronization occur only for excitatory coupled square wave busters although it is not so persistent as in the case of coupled elliptic busters. In the case of inhibitory connections the oscillators behave as if they were uncoupled.

4. Discussion

Synchronization of coupled bursters implies two different regimes

- Burst synchronization
- Spike synchronization

In order to study burst synchronization between two coupled bursters one needs to consider the mechanism leading to the generation and termination of a burst, that is to consider the type of a burster. More specifically stable burst synchronization depends crucially on the type of the quiescent steady state [5], which in the present system is the limiting current or the passive state.

In the case of the coupling of two elliptic bursters the quiescent steady state corresponds to the limiting current and from the point of view of non linear dynamics can be classified as a stable focus. Therefore when the system lies on this quiescent state under the influence of external noise small amplitude oscillations appear. Supposing that at a certain time one of the two bursters is at the oscillatory state and the other is at the quiescent state, then burst synchronization requires that the frequency of the spikes of the active burster is resonant with the frequency of the small amplitude oscillations of the silent burster. Furthermore the type of the coupling (excitatory or inhibitory) is of no importance when studying burst synchronization of elliptic bursters [5]. In the present work such resonance between the interspike frequency of the active burster and the frequency of the small amplitude oscillations does exist leading to stable burst synchronization. On the other hand in the case of square wave bursting the quiescent state corresponds to the passive state and from the non linear dynamics point of view is classified as a stable node and there are no small amplitude oscillations. Premature activation of the silent burster requires a high interspike frequency of the active burster. Therefore a tendency towards burst synchronization between coupled square wave bursters may occur only for excitatory connections [5]. Thus as one can notice in Figs. 4 and 5 burst synchronization takes place only for excitatory coupling.

Spike synchronization requires the existence of equal or low order resonant interspike frequencies of the two bursters. Interspike frequency remains relatively constant within a burst of elliptic type but varies significantly during a burst of square wave type especially during it's end. The type of the connection defines whether there will be in phase, out of phase, anti phase synchronization or even no synchronization at all [5]. Therefore stable spike synchronization occurs easily in the case of excitatory coupled elliptic bursters but for inhibitory coupling there is no sign of spike synchrony. On the other hand in the case of square wave bursting spike synchronization occurs for excitatory coupling not so easily though as in elliptic bursters.

As a conclusion it can be stated that the synchronization properties of a network of coupled bursters depends crucially on the type of the bursters that comprise it and on the type of the connections. Even though the electrochemistry of the system remains vague synchronization phenomena can be explained by employing tools from the theory of non lineal dynamical systems.

References

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