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Preliminary analysis of the chaotic behavior in hydrogen electrochemical devices

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Abstract: The chaotic analysis is often used to investigate electrochemical signals. The proposed work applies it to understand the behavior of hydrogen electrochemical devices, with particular attention to electrochemical hydrogen compressors (EHC). Measurements, carried out at the C.N.R – Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano" of Messina, show a current fluctuation with a fixed voltage. The oscillating phenomenon is not justifiable by the Nernst equation and the possible chaotic behavior of the EHC has been investigated. The system is highly sensitive to the initial conditions and presents a density of periodic orbits, shown in the reconstructed phase plane through the time delay embedding technique.

Keywords: Chaotic behavior; Lyapunov exponents; phase space; dynamics analisys; Nernst equation; hydrogen electrochemical devices.

1. INTRODUCTION

Chaotic systems are dynamical systems whose apparently random states of disorder and irregularities are often governed by deterministic laws, highly sensitive to initial conditions. This behavior exists in many natural systems (fluid flow, climate changes) and also in systems with artificial components, such as road traffic. It can be modeled mathematically or through analytical techniques.

The chaotic analysis is a powerful tool used in electrochemistry to investigate electrochemical signals. Bahena et al. (2011) analyzed the electrochemical noise measured on a NiCoAg alloy immersed in Hank solution. The time series, observed during the corrosion process, were characterized by non-linear fractal analyses and showed irregularity, correlated to deterministic chaos rather than random noise. Trzaska and Trzaska (2011) studied the chaotic phenomena on an electrochemical reactor using a fractional-order non-linear circuit. Guderian et al. (1998) control chaos in the experimental Belousov-Zhabotinsky (BZ) reaction. They stabilized several unstable periodic orbits, sinusoidally modulating the electric current on a Pt-working electrode. Others studied synchronization phenomena in electrochemical oscillators. Cruz et al. (2007) immersed two anodes in an electrolytic solution and, decreasing the distance between the two anodes, identified different domains of chaotic synchronization, experimentally proving the existence of a synchronization sequence.

Today an important topic in research is constituted by studying renewable energy as alternative forms of energy to traditional fossil sources. Some forms of renewable energy, like wind or sunlight, fluctuate over time and geography (Ley et al. (2014)), so it is difficult to realize efficient long-term storage (Mackay (2009)). Hydrogen does not have these problems; for this reason, it holds a key role in the so-called green revolution as a possible energy carrier for the storage of renewable energy (Ritter et al. (2003), Züttel (2003)). A particular application is represented by fuel cells (FC), which produce energy from hydrogen and oxygen. The same cell in a different configuration can be used as an electrochemical hydrogen compressor (EHC) in which hydrogen is supplied to the anode and compressed hydrogen is collected at the cathode. This system can be

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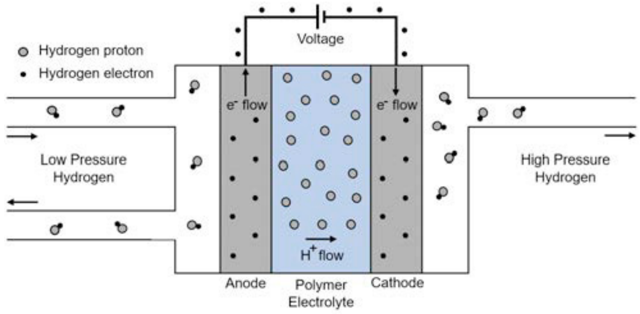

Fig. 1. Working process of an EHC: anode, polymer electrolyte and cathode, with a power supply to increase the hydrogen pressure from anode to cathode.

used for hydrogen storage, heat pump, thermal compression, gas separation, etc.

This study proposes the result of a chaotic test on an EHC unstable measurement. The measure, carried out at the C.N.R – Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano" of Messina, is performed with a fixed voltage, but the current shows an oscillating phenomenon in the time domain. This behavior, not justifiable by the Nernst equation, motivates the reason for performing the chaotic analysis.

The work is organized as follows: Section 2 presents background on Electrochemical Hydrogen Compressors and chaotic systems; Section 3 describes the experimental setup; in Section 4 the measurements are presented; Section 5 illustrates and discusses the results; in Section 6 conclusions and future research activities are reported.

2. BACKGROUND ON EHC

An Electrochemical Hydrogen Compressor can be used for several applications, the most important are: hydrogen purification, recirculation of hydrogen in a fuel cell stack or compression for storage.

An EHC has the same structure as a fuel cell, but the working process is different. Fig. 1 shows that the structure behaves as a load, therefore it is necessary a power source in the external circuit. The applied voltage allows the transport of electrons from anode to cathode upon the dissociation of hydrogen molecules at the anode (Rico-Zavala et al. (2019)). At the anode occurs a hydrogen oxidation reaction (HOR) with hydrogen at low pressure (LP):

$$H_2(LowPressure) \rightarrow 2H^+ + 2e^- \tag{1}$$

The hydrogen ions, similar to fuel cell system, flow to the cathode through the polymer electrolyte. Here, with the electrons coming from the external circuit, the hydrogen evolution reaction (HER) take place (Hao et al. (2016)):

$$2H^+ + 2e^- \rightarrow H_2(HighPressure) \tag{2}$$

Considering the overall of the two reactions, an EHC takes into input low-pressure hydrogen and gives in output high-pressure hydrogen (Nordio et al. (2019)).

The required potential for hydrogen pumping across the membrane in an EHC is given by the Nernst equation (Dale et al. (2008)):

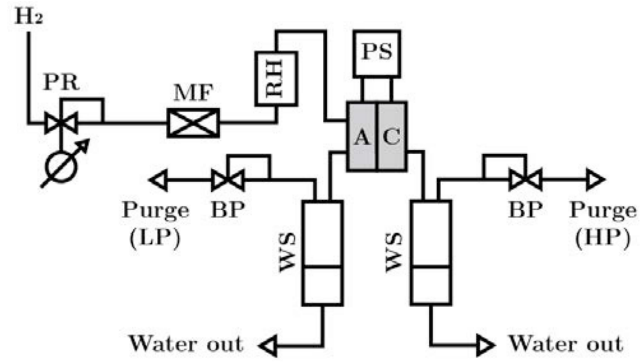

Fig. 2. EHC setup: anode (A), cathode (C), pressure regulator (PR), mass-flow controller (MF), bubble humidifier (RH), power supply (PS), liquid water separator (WS), back-pressure (BP), low pressure (LP), high pressure (HP).

$$V_{th} = E_0 + \frac{RT}{nF} \ln \frac{p_2}{p_1} \tag{3}$$

where R is the universal gas constant, T the absolute temperature, E_0 the standard potential, n the number of electrons, F the Faraday constant, $\frac{p_2}{p_1}$ the ratio between the hydrogen pressure at the cathode and the anode. In the Nernst equation, there are no terms that justify a possible chaotic behavior of EHC.

3. EXPERIMENTAL SETUP

The experimental EHC measurements were carried out at the C.N.R – Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano" (CNR-ITAE) of Messina. Fig. 2 and 3 represent the experimental setup: hydrogen feeds the anode through a pressure regulator, a mass-flow controller (used to measure and control the flow) and at the end a bubble humidifier; two back-pressure regulators are used to maintain the desired pressure. The cell was connected to a power supply. The CNR lab is provided with two specific devices: Autolab PGSTAT302N and Keysight Technology N6973A power supply. The first one is a high current potentiostat/galvanostat and the maximum current is 2A, which can be extended to 20A with the BOOSTER20A module. The Nova software is compatible with Autolab and it is also intuitive. Instead, the N6973A power supply (Fig. 4) is less precise, but it works at more than 2 A currents, that is the reason for which it was used in the experiments. It was not equipped with software to perform polarization curves or time tests on the EHC. This represented a big limit for the dynamic analysis of the system, therefore a part of the research activity was based on the realization of dedicated software.

Preliminary measurements were performed on FC modality, in which the cell is fed by hydrogen and oxygen. The CNR lab is provided of a specific station called Fuel Cell Technologies Testing Station (FCT-TS). It monitors the flow, temperature, humidity and pressure for anode and cathode gases, and includes an electronic DC load from Agilent Technologies. The experimental setup is represented in Fig. 5.

Fig. 3. EHC experimental setup.

Fig. 4. N6973A power supply.

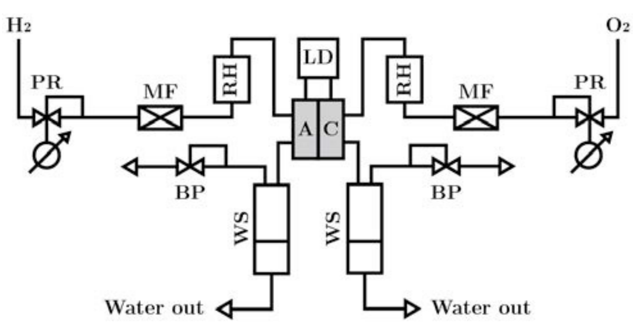

Fig. 5. FC setup: anode (A), cathode (C), pressure regulator (PR), mass-flow controller (MF), bubble humidifier (RH), electronic load (LD), liquid water separator (WS), back-pressure (BP).

4. MEASUREMENTS

The measurements were realized on the cell of $25\,\text{cm}^2$ active area. First, it was necessary a running-in phase to bring the cell into the correct working conditions. In particular, the break-in was performed in fuel cell modality, using the experimental setup reported in Fig. 5. The CNR lab uses a common standard for all the cells about the running-in phase, these guidelines foresee 10 polarization curves. A polarization curve represents the voltage output of the fuel cell for a given current density loading and it is the most common electrochemical technique in order to characterize single or stacked fuel cells because it leads information about the performance under operating state. The tenth polarization curve is shown in Fig. 6.

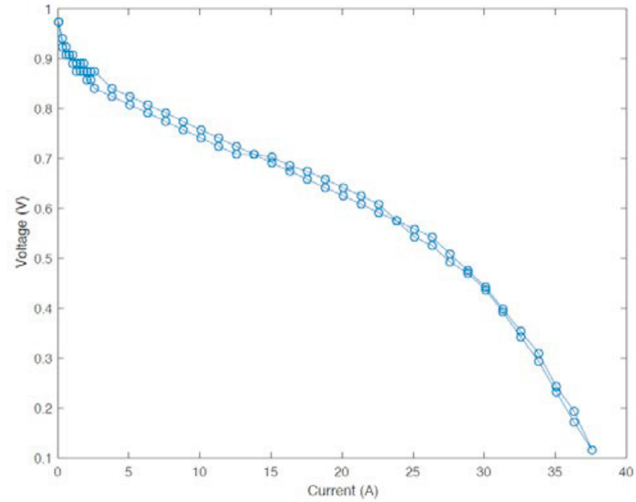

Fig. 6. Polarization curve n. 10.

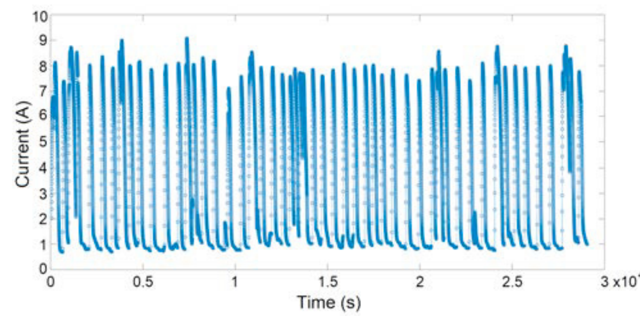

Fig. 7. EHC time test: V = 0,25 V, β = 1, 29000 s.

After the break-in phase, the experimental setup is changed because the cell must work as EHC. The measure is a time test where a voltage of $0.25\,\text{V}$ is imposed for $29\,000\,\text{s}$ to have a more reliable result. The temperature of the cell, humidifier and tape is set to 60° and it is maintained constant for all the measurements phase. Moreover, β, defined as ratio between the pressure at the cathode and at the anode, is 1.

As shown in Fig. 7, the behavior of the EHC is very different from what was expected studying the physical model. The system seems to have a spiking dynamic, therefore the impedance of the EHC will change in time.

5. CHAOTIC ANALYSIS: RESULTS AND DISCUSSION

5.1 Chaotic systems

Chaotic systems are dynamical systems whose apparently random states of disorder and irregularities are often governed by deterministic laws, highly sensitive to initial conditions. Indicators of the high sensitivity of chaotic systems to initial conditions are the Lyapunov exponents

(Buscarino et al. (2017)). They are the first parameters to be calculated.

In order to be able to analyze the dynamic of the system starting from a signal in the time domain, the so-called time delay technique was used (Giannerini and Rosa (2007)). The basic idea is to make copies of the signal with fixed time delays and consider these delayed values as coordinates of a phase space retrieved from data. This technique, therefore, associates to each measure $s(n)$ the m-dimensional vector $y(n)$ as follows:

$$y(n) = [s(n), s(n+\tau), \ldots, s(n+(m-1)\tau)] \tag{4}$$

where τ represents the delay and m is the embedding dimension.

Assuring the equivalence between the original trajectory and the reconstructed one, thanks to Mañé's theorem (Mañé (1981)), Takens' theorem (Takens (1981)) and Eckmann-Ruelle's conjecture (Eckmann and Ruelle (2004)), the dynamics analysis can be performed. To calculate properly the Lyapunov exponents of a system, Mohammadi (2009) realized a Matlab code to perform this kind of analysis. It is characterized by the function lyaprosen, which arguments are the signal y, the delay τ and embedding dimension m. If τ or m are set to zero, the algorithm will calculate the best values using different optimization criteria.

To chose m, the False Nearest Neighbors (FNN) algorithm realized by Hegger and Kantz is used: the idea is to analyze how the number of neighbors of a point along a signal trajectory change with increasing embedding dimension (Hegger and Kantz (1999)). In too low an embedding dimension, many of the neighbors will be false, but in an appropriate embedding dimension or higher, the neighbors are real. With increasing dimension, the false neighbors will no longer be neighbors. Therefore, by examining how the number of neighbors change as a function of dimension, an appropriate embedding can be determined. Alternatively, the symplectic geometry method will be used.

To chose τ, instead, the algorithm will use autocorrelation up to orders 10 to select proper embedding lag, which is the lag before of first decline of autocorrelation value below e^{-1}. If this method does not give any result, the mutual information criteria will be used. Using the signal in Fig. 7, the optimal value of m calculated by the algorithm is 2; instead an optimal value of τ was not found. For this reason, the largest Lyapunov exponent is calculated for three different τ: 10, 100, 1000.

In Table 1 are summarized the largest Lyapunov exponents calculated by the algorithm and they are all positive, so the system is sensitive to the initial conditions for different τ and m.

Table 1. Lyapunov exponents.

	$m=1$	$m=2$	$m=3$
$\tau=10$	0,0594	0,0668	0,0600
$\tau=100$	0,0594	0,0607	0,0507
$\tau=1000$	0,0594	0,0607	0,0507

Continuing with the embedding technique, it is possible to reconstruct the phase plane through the algorithm realized by Leontitsis (2001).

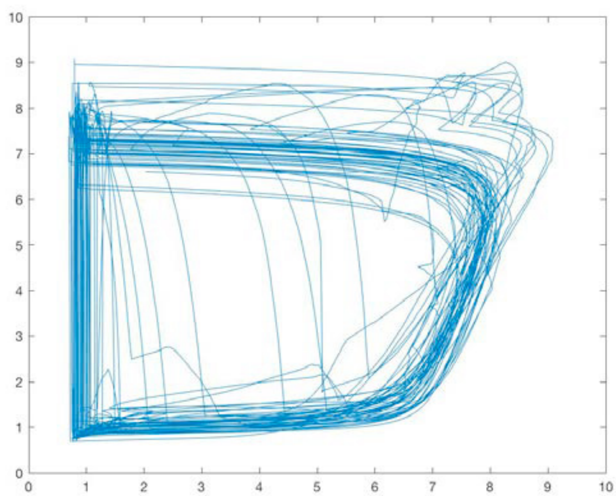

Fig. 8. Phase space reconstruction - 2D.

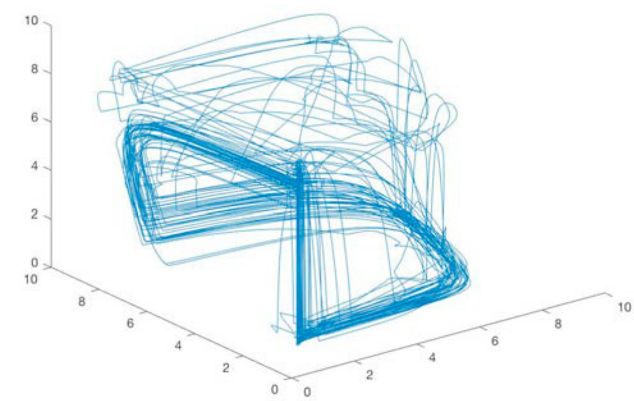

Fig. 9. Phase space reconstruction - 3D.

Imposing $\tau = 100$ and $m = 2$, the reconstructed phase space (both 2D and 3D) are shown in Fig. 8 and 9. From the results it is visible how the reconstructed phase space is characterized by a density of periodic orbit; this feature is common in chaotic systems. Consequently, the dynamic analysis carried out has found evident characteristics of chaotic systems. It is not possible to say with certainty that the system expresses a chaotic dynamic but this research work represents an initial analysis on a unknown phenomenon. At the same time, fractional calculus (Podluby (1998)), is used to model e control PEM fuel cell (Bankupalli et al. (2018) and Lü et al. (2017)). So, starting from (Caponetto et al. (2021),Caponetto and Dongola (2013),Caponetto et al. (2002)) a similar approach could be applied to model and control the described hydrogen electrochemical devices.

6. CONCLUSION AND FUTURE DEVELOPMENTS

In this research activity a dynamic measurement was performed on the electrochemical compressor system. Unlike what was expected from mathematical equations, spiking behavior emerged and it was completely unexpected. The work regards the dynamical behavior analysis, in particular about how the behavior could be associated with that of a chaotic system. From the analysis carried out, the system was highly sensitive to the initial conditions and presented a density of periodic orbits, which were shown in the reconstructed phase plane through the time delay embedding technique. Hence it is conceivable that the system is chaotic.

The analysis, especially the chaotic ones, are the first approach to an unknown and non-predictable phenomenon. Therefore, the obtained results must be confirmed through more detailed analysis, in particular measuring the voltage at a fixed current and extending the time windows.

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