Chaos during H_2/CO electroxidation: trends and usefulness

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Kinetic oscillations are extensively reported in fuel cells fed with CO-containing hydrogen. Relaxation oscillations are fully explained by the electrochemical mechanism, but chaotic oscillations are not. Regardless the exact mechanism description, we are able to analyze the phenomenology of the experimental findings. Herein, chaos is reported to have a special trend, the predictability at short range, i.e. it is possible to predict how long will be the period of the next cycle given the spike (amplitude) of the previous cycle. Furthermore, other useful information could be obtained. Different chaotic states could be compared since the predictability at short range is linked to the CO_2 production, as experiments with on-line mass spectrometry point out.

H_2/CO electroxidation has proved to have a chemical mechanism (or chemical network) represented by a set of differential equations that exhibits instability of the hopf-bifurcation type, which in turn leads to galvanostatic oscillations that were extensively reported in practical fuel cells[1-3] as well as in fundamental systems.[4, 5] Herein, long chaotic time series are observed and captured, in a practical fuel cell, following experimental procedures described elsewhere.[6]

Oscillations are characterized by period (time for one cycle) and amplitude (the range of values in which a variable changes). Period (t_n) and amplitude (A_n) of an experimental time series are shown in figure 1. Chaos is an oscillatory behavior with unpredictable trajectory and, therefore, undefined value of period and amplitude; according to the analyses shown in figure 1, chaos during H_2/CO electroxidation exhibits a correlation between the amplitude of a given cycle (A_n) and the period of the next one (t_{n+1}). This correlation is labeled as being "predictability of short range" because it is possible to predict the behavior at short intervals of time. In other words, if the potential oscillates over time, in the exact moment that the abrupt change of potential occurs (spike) the amplitude A_n is registered and a new cycle is initiated (t_{n+1}), but with a period that is predictable. However, there is no way to predict the amplitude. The predictability at short range is the first remarkable trend found in the electrochemical chaos observed during CO-containing hydrogen oxidation. It attests the presence of deterministic chaos, i.e. that the chaotic behavior derives from a singular solution of a set of differential equations rather than the variation of parameters that is random (fluctuations), which in turn has a complete lack of predictability.

The correlation A_n *vs* t_{n+1} may be exploited with a mechanistic interpretation. In the presence of a spatial variation of parameters such as the conductivity of Nafion membrane and gas composition along the gas channels, the correlation A_n *vs* t_{n+1} would be interpreted as spatial distribution of oscillators. With that, chemical network passing the hopf bifurcation has an attractor peculiar for each location (position on the electrode) because different locations have different values of parameters. On this matter, we are performing experiments which will be delivered in a future contribution.

For low temperature, namely 30°C, the correlation A_n *vs* t_{n+1} is fairly linear. Using linear regression, angular coefficient (α) is estimated and each

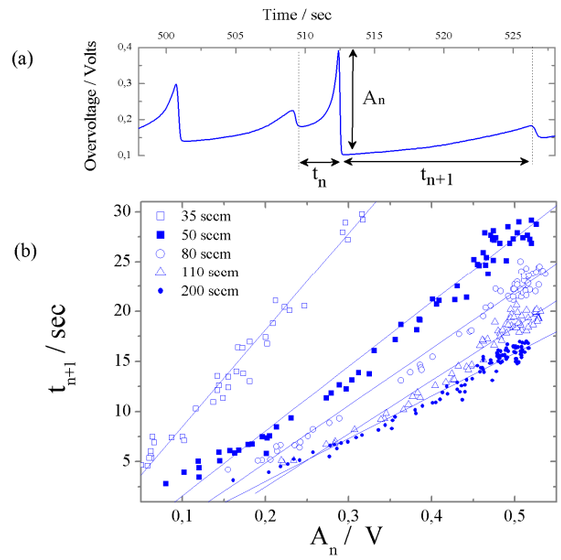

Figure 1: (a) experimental chaotic time series and (b) correlation A_n *vs* t_{n+1}.

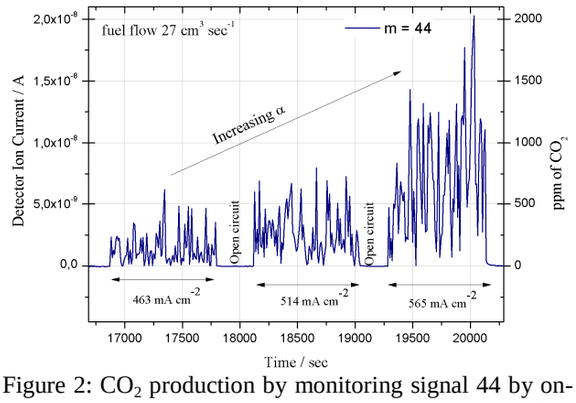

Figure 2: CO_2 production by monitoring signal 44 by on-line mass spectrometry for three chaotic time series (not shown).

experimental time series would be reduced to this unique value. Using online mass spectroscopy, CO_2 production for each time series is estimated. Details about analytical-estimation procedure are delivered in the expanded version. Remarkably, the angular coefficient (α) of the correlation A_n *vs* t_{n+1} encloses information about the CO_2 production. As seen in figure 2, positive increasing α leads to increased spectrometric signal for 44-mass.

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