Voltage Inversion Caused by Self-organized Oscillations in a Direct Formic Acid Fuel Cell

Jéssica A Nogueira, Hamilton Varela
Department of Physical Chemistry, Institute of Chemistry of São Carlos, University of São Paulo, POBox 780, 13560-970, São Carlos, SP, Brazil

Abstract
Fuel cells are electrochemical devices that convert chemical into electrical energy with comparatively high efficiency. In this report, we present the occurrence of inversion in the cell voltage that accompanies the self-organized voltage oscillations in a fuel cell fed with formic acid and oxygen, the so-called direct Direct Formic Acid Fuel Cell (DFAFC).

Introduction
Oscillations in electrocatalytic reactions have a long history in electrochemistry [1] [2], and example include many oxidation reactions which are relevant in the interconversion between chemical and electrical energies. Beyond half-cell, laboratory experiments, kinetic instabilities have been also found in polymer electrolyte membrane fuel cells (PEMFC) fed with CO contaminated H₂ [3] [4] [5] and, more recently, methanol [6] and formic acid [7]. Under oscillatory regime, most systems are expected to result in higher efficiency [2] [3] [4] [8] [9]. Motivated by the recent reports of oscillatory kinetics in fuel cell fed directly with carbon-containing fuels [6] [7], we have investigated the occurrence of voltage oscillations in a Direct Formic Acid Fuel Cell (DFAFC). Herein we report the inversion of voltage that results of the emergence of self-organized oscillations in a DFAFC.

Objective
The current study aims at explaining the voltage inversion that follows the kinetic instabilities of formic acid electro-oxidation in a Direct Formic Acid Fuel Cell.
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DOI: 10.19185/matters.201705000005

Matters (ISSN: 2297-8240) | 2

Figure Legend

Figure 1.
(A) Polarization curve of the DFAFC recorded at 1 mV s⁻¹ (black curve) and galvanodynamic sweep at 17 µA cm⁻² s⁻¹ (red curve).
(B) Cell voltage time-series during galvanostatic (i = 0.076 A cm⁻²) operation of the DFAFC.
(C) Schematic current-potential curves for formic acid oxidation in DFAFC obtained by either a current (red curve) or potential (black curve) sweep, and for oxygen reduction (blue curve). The curves for formic acid oxidation were obtained using H₂ in the cathode instead of O₂, which allows to read directly the anodic overpotential.

Results & Discussion

The dynamic behavior of the DFAFC was initially studied via slow potential and current sweeps, and characteristic results are presented in figure 1A. When the potential is the control parameter, a typical stationary response is reached, and the cell voltage decreases monotonically with the increase of the current. However, under galvanostatic control, the DFAFC presented voltage oscillations above a certain current threshold, has been already reported for the cell fed with H₂/CO [3] [4] [5] [8] [9] and directly with methanol [6] and formic acid [7]. Additionally, it is observed in figure 1A that the oscillations during the electro-oxidation of formic acid start at approximately 0 V, have an amplitude of about 0.6 V and that an inversion in the cell voltage occurs. To better assess the dynamics of these oscillations, it was selected a current value where the system presents kinetic instability, 0.076 A cm⁻², and a chronopotentiometry was performed to evaluate how the voltage evolves over time, figure 1B. It can be seen that between about 0.13 and ~0.05 V there is a slow poisoning of the anode electrode due to carbon monox-
ide adsorbed (CO\textsubscript{ad}) from the dehydration of weakly adsorbed formic acid [10]. Another stable intermediate that also contributes to the loss of electrode activity is the bridged-bonded formate (HCOO\textsubscript{ad}) which, like CO\textsubscript{ad}, inhibits the direct oxidation pathway of formic acid [10] [11]. Eventually the electrode reaches a critical coverage of catalytic poisons and, in order to keep the current constant, the anode overpotential increases (therefore the cell voltage decreases) leading to the formation of oxygenated species on platinum. These species react with CO\textsubscript{ad} via the Langmuir-Hinshelwood mechanism, releasing free sites which causes the anodic overpotential to decrease and the new cycle begins again [1] [9].

The emergence of oscillatory kinetics during the electro-oxidation of formic acid has been extensively studied with the aid of techniques such as infrared spectroscopy [12] and numerical modeling [13] [14]. Mota \textit{et al.} [15] have showed kinetic instabilities in a DFAFC using H\textsubscript{2} on the cathode instead of O\textsubscript{2}. An intriguing aspect to be understood in this contribution consists of the inversion in the DFAFC voltage observed during oscillations. This fact adds a difficulty in studying this system, since cells operating at negative voltages results in degradation of the carbon support contained in the catalytic layer as well as in the diffusion layer. Lopes \textit{et al.} [8] observed this polarity inversion during the oscillatory dynamics in a PEMFC with PdPt/C anodic catalyst. They assumed that this phenomenon is caused by the abrupt increase of the anodic overpotential due to the dynamic of the oscillations with H\textsubscript{2}/CO. Nevertheless, this voltage inversion may be better understood as follows.

Figure 1C shows a schematic description of the current-potential curves for the electro-oxidation of formic acid (anodic reaction), and for the oxygen reduction (cathodic reaction). The amplitude of the potential oscillations are comparable to that found in half-cell experiments. In the present case, i.e. a DFAFC fed with oxygen in the cathode, the sluggish kinetic of the cathodic reaction [16] and its consequent huge overpotential, contributes to the voltage inversion. In fact, as presented in figure 1C, the overpotential (E\textsubscript{cell} in Fig. 1A) remains positive for lower applied currents and when potential oscillations set in, the higher current required causes a higher overpotential in both electrodes, that is, anode and cathode, and consequently the voltage inversion.

Conclusions
Herein we communicate the occurrence of voltage inversion that follows the oscillatory dynamics in a low temperature fuel cell fed with formic acid (anode) and oxygen (cathode). The voltage inversion was suggested to result of the sluggish kinetics in the oxygen reduction reaction that considerably reduces the potential at the cathode. The present finding adds to the understanding of the individual contributions of anodic and cathodic reactions in a direct liquid fuel cell operating under oscillatory regime. This reasoning is crucial for the exploration of oscillatory instabilities to, for instance, improve the overall performance of PEM reactors and other practical systems.

Additional Information

Methods and Supplementary Material
Please see https://sciencematters.io/articles/201705000005.

Funding Statement
J.A.N. and H.V. acknowledge São Paulo Research Foundation (FAPESP) for the scholarship (grant #2015/09295-9) and financial support (grants #2012/21204-0, and #2013/16930-7). H.V. (#306151/2010-3) acknowledges Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for financial support.

Acknowledgements
We thank Dr. Valdecir Paganin for technical assistance.

Ethics Statement