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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.

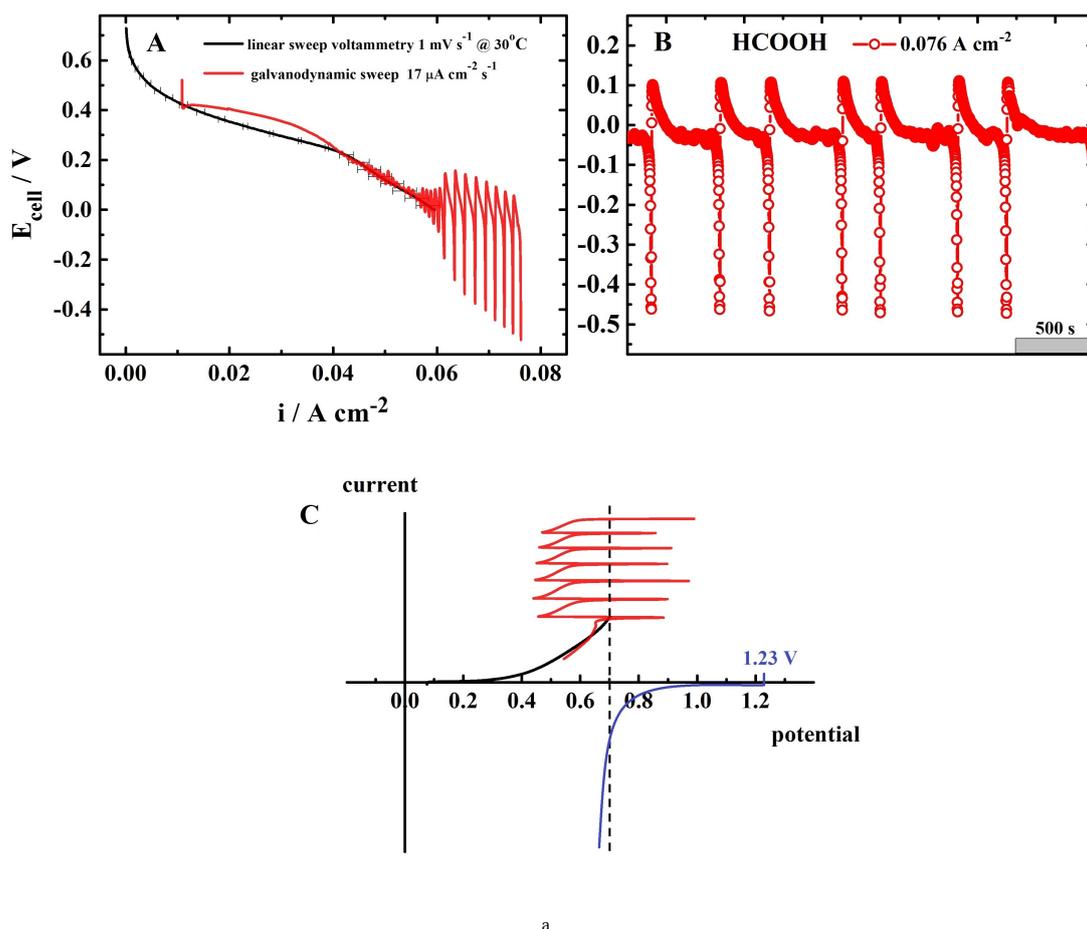


Figure Legend

Figure 1.

(A) Polarization curve of the DFAFC recorded at 1 mV s^{-1} (black curve) and galvanodynamic sweep at $17 \mu\text{A cm}^{-2} \text{ s}^{-1}$ (red curve).

(B) Cell voltage time-series during galvanostatic ($i = 0.076 \text{ A cm}^{-2}$) 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 H_2 in the cathode instead of O_2 , 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 H_2/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_{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_{ad}) which, like CO_{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_{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 *et al.* [15] have showed kinetic instabilities in a DFAFC using H_2 on the cathode instead of O_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 *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_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_{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>.

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Ethics Statement

Citations

- [1] M. Hachkar, B. Beden, and C. Lamy. "Oscillating electrocatalytic systems: Part I. Survey of systems involving the oxidation of organics and detailed electrochemical investigation of formaldehyde oxidation on rhodium electrodes". In: *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* 287.1 (1990), pp. 81–98. DOI: 10.1016/0022-0728(90)87161-c. URL: [https://doi.org/10.1016/0022-0728\(90\)87161-c](https://doi.org/10.1016/0022-0728(90)87161-c).
- [2] Krewer Ulrike, Vidakovic-Koch Tanja, and Rihko-Struckmann Liisa. "Electrochemical Oxidation of Carbon-Containing Fuels and Their Dynamics in Low-Temperature Fuel Cells". In: *ChemPhysChem* 12.14 (2011), pp. 2518–2544. DOI: 10.1002/cphc.201100095. URL: <https://doi.org/10.1002/cphc.201100095>.
- [3] Mota Andressa, Eiswirth Markus, and Gonzalez Ernesto R. "Enhanced Efficiency of CO-Containing Hydrogen Electrooxidation with Autonomous Oscillations". In: *The Journal of Physical Chemistry C* 117.24 (2013), pp. 12495–12501. DOI: 10.1021/jp311185c. URL: <https://doi.org/10.1021/jp311185c>.
- [4] Richard Hanke-Rauschenbach, Michael Mangold, and Kai Sundmacher. "Nonlinear dynamics of fuel cells: a review". In: *Reviews in Chemical Engineering* 27.1-2 (2011), pp. 23–52. DOI: 10.1515/revce.2011.001. URL: <https://doi.org/10.1515/revce.2011.001>.
- [5] Kirsch S. et al. "The Electro-Oxidation of H₂, CO in a Model PEM Fuel Cell: Oscillations, Chaos, Pulses". In: *Journal of the Electrochemical Society* 160.4 (2013), F436–F446. DOI: 10.1149/2.002306jes. URL: <https://doi.org/10.1149/2.002306jes>.
- [6] Jéssica A. Nogueira et al. "Autonomous Voltage Oscillations in a Direct Methanol Fuel Cell". In: *Electrochimica Acta* 212 (2016), pp. 545–552. DOI: 10.1016/j.electacta.2016.07.050. URL: <https://doi.org/10.1016/j.electacta.2016.07.050>.
- [7] Andressa Mota-Lima et al. "Stationary and Damped Oscillations in a Direct Formic Acid Fuel Cell (DFAFC) using Pt/C". In: *Electrochimica Acta* 235 (2017), pp. 135–142. DOI: 10.1016/j.electacta.2017.03.056. URL: <https://doi.org/10.1016/j.electacta.2017.03.056>.
- [8] Lopes Pietro P., Ticianelli Edson A., and Varela Hamilton. "Potential oscillations in a proton exchange membrane fuel cell with a Pd–Pt/C anode". In: *Journal of Power Sources* 196.1 (2011), pp. 84–89. DOI: 10.1016/j.jpowsour.2010.07.034. URL: <https://doi.org/10.1016/j.jpowsour.2010.07.034>.
- [9] Zhang Jingxin, Fehribach Joseph D., and Datta Ravindra. "Mechanistic and Bifurcation Analysis of Anode Potential Oscillations in PEMFCs with CO in Anode Feed". In: *Journal of The Electrochemical Society* 151.5 (2004), A689. DOI: 10.1149/1.1688795. URL: <https://doi.org/10.1149/1.1688795>.
- [10] Chen Yan Xia et al. "Kinetics and Mechanism of the Electrooxidation of Formic Acid-Spectroelectrochemical Studies in a Flow Cell". In: *Angewandte Chemie International Edition* 45.6 (2006), pp. 981–985. DOI: 10.1002/anie.200502172. URL: <https://doi.org/10.1002/anie.200502172>.
- [11] Samjeské Gabor and Osawa Masatoshi. "Current Oscillations during Formic Acid Oxidation on a Pt Electrode: Insight into the Mechanism by Time-Resolved IR Spectroscopy". In: *Angewandte Chemie International Edition* 44.35 (2005), pp. 5694–5698. DOI: 10.1002/anie.200501009. URL: <https://doi.org/10.1002/anie.200501009>.
- [12] Samjeské Gabor et al. "Potential Oscillations in Galvanostatic Electrooxidation of Formic Acid on Platinum: A Time-Resolved Surface-Enhanced Infrared Study". In: *The Journal of Physical Chemistry B* 109.49 (2005), pp. 23509–23516. DOI: 10.1021/jp055220j. URL: <https://doi.org/10.1021/jp055220j>.
- [13] Mukouyama Yoshiharu et al. "Potential Oscillations in Galvanostatic Electrooxidation of Formic Acid on Platinum: A Mathematical Modeling and Simulation". In: *The Journal of Physical Chemistry B* 110.24 (2006), pp. 11912–11917. DOI: 10.1021/jp061129j. URL: <https://doi.org/10.1021/jp061129j>.
- [14] Perini Nickson et al. "Long-Lasting Oscillations in the Electro-Oxidation of Formic Acid on PtSn Intermetallic Surfaces". In: *ChemPhysChem* 15.9 (2014), pp. 1753–1760. DOI: 10.1002/cphc.201301186. URL: <https://doi.org/10.1002/cphc.201301186>.
- [15] Andressa Motaa and Ernesto Rafael Gonzalez. "Enhanced Efficiency with Autonomous Oscillations: Challenges for DAFC". In: *ECS Transactions* 58.1 (2013), pp. 1879–1884. DOI: 10.1149/05801.1879ecst. URL: <https://doi.org/10.1149/05801.1879ecst>.
- [16] Shao Minhua et al. "Recent Advances in Electrocatalysts for Oxygen Reduction Reaction". In: *Chemical Reviews* 116.6 (2016), pp. 3594–3657. DOI: 10.1021/acs.chemrev.5b00462. URL: <https://doi.org/10.1021/acs.chemrev.5b00462>.
- [17] V. A. Paganin, E. A. Ticianelli, and E. R. Gonzalez. "Development and electrochemical studies of gas diffusion electrodes for polymer electrolyte fuel cells". In: *Journal of Applied Electrochemistry* 26.3 (Mar. 1996), pp. 297–304. DOI: 10.1007/bf00242099. URL: <https://doi.org/10.1007/bf00242099>.