

Enhanced efficiency with autonomous oscillations: challenges for DAFC

Andressa Mota and Ernesto R. Gonzalez

Instituto de Química de São Carlos, Av. Trab. Sancarlene 400,13560-970. São Carlos-SP, Brazil

In previous work in our group¹ CO-containing hydrogen exhibited enhanced efficiency with autonomous oscillations compared to the usual steady stationary state. As CO-containing H₂ mimics the oscillating mechanism for alcohols electrooxidation, this contribution is dedicated to formally extend the analyses over the electrooxidation of small molecules.

Current oscillations on Direct Alcohol Fuel Cells (DAFC) emerge² depending on parameters such as the alcohol flow rate and the potential. Another possibility for oscillations in the practical DAFC operation was reported by Du et al.³ as a result of the methanol crossover; in the latter case, the presence of methanol at the cathode led to superposition of the anodic MOR on the cathodic ORR. In the first case, oscillations are said to be Autonomous since they arise from a chemical instability and would represent a benefit for enhancing the rate of energy conversion which is the point to be proven here. For that, we performed electrooxidation of small molecules on a conventional-three-electrode cell and practical fuel cells which reinforces the parallel rationalization between them. For the calculation, we employ energy balance for a conventional electrochemical device as recommended in references^{1,4}.

$$I\varphi_{cell} = I\varphi_{rev}^{\circ} - I(\eta_c + \eta_a) - I^2 R_{electrolyte} \quad (1)$$

being φ_{cell} the potential between working and counter electrodes; φ_{rev}° is the standard reversible potential for the global reaction; η_c and η_a are the overpotentials for the respective faradaic anodic and cathodic processes; $R_{electrolyte}$ is the resistance of the electrolyte (support solution or Nafion membrane) and I is the nominal current. Moreover, according to the energetic balance, efficiency (E) is defined as follows

$$E = 1 - \frac{\{I(\eta_c + \eta_a) + I^2 R_{electrolyte}\}}{I\varphi_{rev}^{\circ}} \quad (2)$$

According to equation (2), increasing efficiency would be attained by reducing the overpotential (η). That possibility is entirely confirmed by experimental findings in oscillating electrochemical reactions, as shown in two examples below.

Current vs potential profiles for methanol electrooxidation with a three-electrode electrochemical cell, seen in figure 1, display oscillatory region (between 2,2 and 4,5 mA cm⁻²) under current control. Oscillations lead to a smaller overvoltage, in average, compared to the stationary branch observed under potential control.

On the basis of our experience, the feasibility of using the benefits from oscillations will run a searching for catalysts that promote the oscillation onset at lower overpotential. To elucidate that, figure 2 shows results on a Direct Formic Acid Fuel Cell (DFAFC) with a special set up (hydrogen on the cathode) that allows reading anodic overvoltage directly. It is possible to have the oscillation onset with lower (~ 850 mV) and higher overpotential (~ 1500 mV), a fact named by non-linear specialists as bi-rhythmicity. In the experimental

conditions in figure 2, only oscillations with higher onset overvoltage seem to be stable over time.

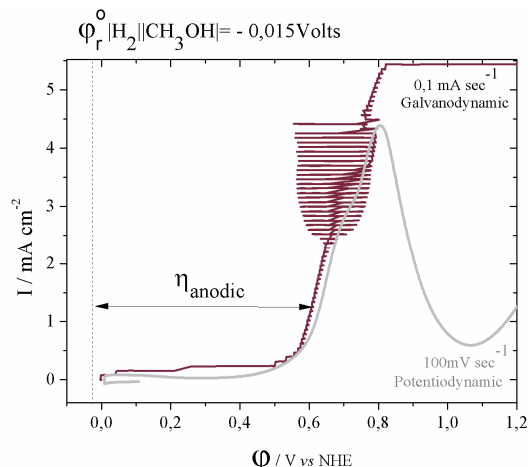


Figure 1. Methanol oxidation on a three-electrode electrochemical cell under potential and current control. Others: 0.1M CH₃OH and 0.1M H₂SO₄.

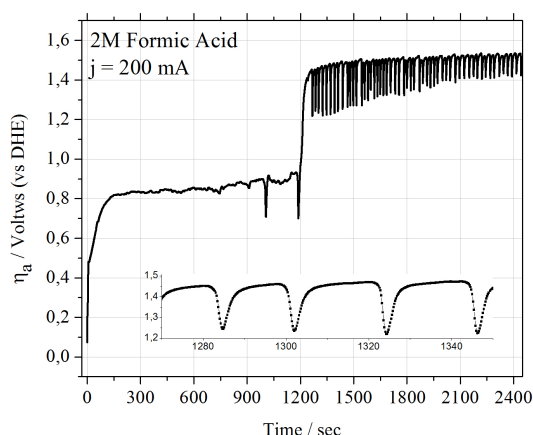


Figure 2. Galvanostatic oscillations in a Fuel cell operating with 2M formic acid flowing on the anode, and hydrogen on the cathode. Others: Nafion 115, I = 40 mA cm⁻², Pt/C (cathode), Pd/C (anode), 50°C.

Finally, we recall the understanding gained with the electrooxidation of CO-containing hydrogen¹ which works as mimetic for the methanol electrooxidation mechanism. Kadyk et al.⁵ reported 600mV anodic overpotential for the oscillation onset on Pt/C which is around 300mV larger than for the oscillation onset on PtRu/C⁶. According to the energy balance, this 300 mV higher overvoltage represents dissipation of energy.

References

- Lima, A. B. d. M. Kinetic instabilities in the electro-oxidation of CO-containing hydrogen. Phd Thesis, USP-IQSC, São Carlos, 2012.
- Hacquard, A. Improving and understanding direct methanol fuel cell (DMFC) performance. Worcester Polytechnic Institute, 2005.
- Du, C. Y.; Zhao, T. S.; Yang, W. W. Effect of methanol crossover on the cathode behavior of a DMFC: A half-cell investigation. *Electrochim. Acta* **2007**, 52 (16), 5266-5271.
- Mota, A.; Gonzalez, E. R.; Eiswirth, M. Enhanced efficiency of CO-containing hydrogen electrooxidation with autonomous oscillations. *submitted to J. Phys. Chem. A* **2013**.
- Kadyk, T.; Kirsch, S.; Hanke-Rauschenbach, R.; Sundmacher, K. Autonomous potential oscillations at the Pt anode of a polymer electrolyte membrane fuel cell under CO poisoning. *Electrochim. Acta* **2011**, 56 (28), 10593-10602.
- Mota, A.; Gonzalez, E. R.; Eiswirth, M. Kinetic insights over a PEMFC operating on stationary and oscillatory states. *J. Phys. Chem. A* **2011**, 115 (47), 13773-13782.