Experimental study of the forced Ni-H_2SO_4 oscillator

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Many electrochemical system oscillating under potentiostatic or galvanostatic conditions are known [1] Surprisingly few studies of forced oscillator with a time-periodically signal have been reported even if impedance spectroscopy is widely used in electrochemistry. The Co-H_3PO_4 and the Fe-H_2SO_4 electrochemical oscillators [2-5] under potentiostic condition have been experimentally studied under sinusoidal perturbation of the potential applied in the active-passive transition region. These two oscillators are of relaxation types, the oscillations are large amplitude oscillations. Anodic dissolution-passivation of Ni has been widely studied [6-10] and potential oscillations of the Ni- H_2SO_4 under galvanostatic are of a different type, the oscillations are small amplitude harmonic oscillations due to a Hopf bifurcation. A systematic approach of the singularities observed in anodic Ni dissolution in sulfuric acid, including bistability, periodic oscillations bounded by Hopf and saddle node bifurcation have been presented [11-12]. At high sulfuric acid concentrations (6-8 M), the galvanostatic dissolution of nickel shows an transition to chaos via quasiperiodic oscillations.

The aim of this communication is to present experimental observations for the Ni-H_2SO_4 time-periodically forced electrochemical oscillator near the Hopf bifurcation in a manner analogous to the experimental study of hydration of 2,3 epoxy-1-propanol carried out in a continuous stirred tank reactor [13] or the theoretical study of the forced Van der Pol oscillator [14]. The measurement setup is composed of a Hewlett-Packard Vectra computer, driving a Schlumberger 1286 electrochemical interfaced configured for galvanostatic control and a Schlumberger 1250 Frequency Response Analyser. The working electrode were 2 mm diameter nickel rotating disc electrode, polished with an abrasive disk and rinsed carefully with distilled water. The auxiliary electrode was made of a platinium wire. The measurements have been made under galvanostatic conditions in the transpassive branch of the anodic oxidation of nickel. To access the transpassive branch in a galvanostatic manner, the system is stabilized in that branch under potentiostatic condition before switching to the galvanostatic condition.

It is shown that periodic and quasi-periodic behaviours (Fig. 1). can be observed for the forced Ni-H_2SO_4 oscillator, according to the classical behaviour or forced self-oscillating systems.

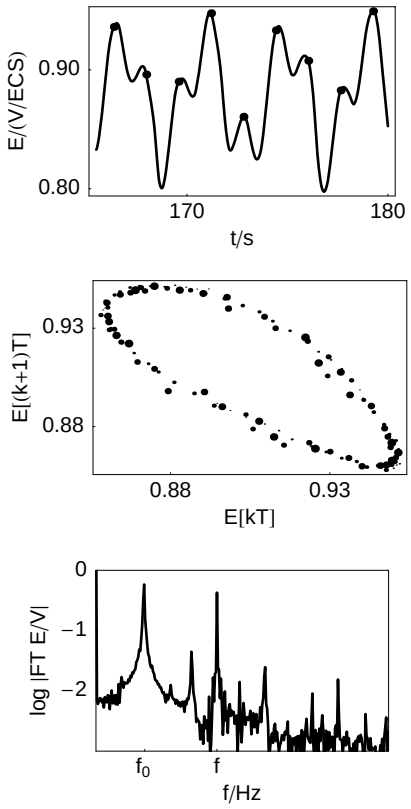

Fig. 1: Electrode potential quasi-periodic response to a current density modulation. Electrode potential oscillation, Poincaré section and potential oscillation Fourier power spectrum. f_0 (free frequency) and f (modulation frequency) are incommensurable.

REFERENCES

[1] Koper, M. T. M. Advances in Chemical Physics, vol XCII 1996 161.
[2] Pagitsas, M.; Sazou, D. J. Electroanal. Chem., 386 1995 88.
[3] Pagitsas, M.; Sazou, D. Electrochim. Acta, 40 1995 755.
[4] Sazou, D.; Karantonis, A.; Pagitsas, M. Int. J. of Bifurcations and Chaos, 3 1993 981.
[5] Karantonis, A.; Pagitsas, M.; Sazou, D. Chaos, 3 1993 243.
[6] Epelboin, I.; Keddam, M. Electrochim. Acta, 17 1972 177.
[7] Jouanneau, A.; Keddam M.; Petit, M. C. Electrochim. Acta, 21 1976 287.
[8] Keddam, M.; Takenouti H.; Yu, N. J. Electrochem. Soc., 132 1985 2561.
[9] Hoar, T. P.; Mowat, J. A. S. Nature (London), 165 1950 64.
[10] Osterwald J.; Feller, H. G. J. Electrochem. Soc., 107 1960 473.
[11] Lev, O.; Wolffberg, A.; Pismen L. M.; M. Sheintuch, L. M. J. Phys. Chem., 93 1989 1661.
[12] Haim, D.; Lev, O.; Pismen L. M.; Sheintuch, M. J. Phys. Chem. 96 1992 2676.
[13] Vance, W.; Ross, J. J. Chem. Phys. 88 1988 5536.
[14] Mettin, R.; Parlitz, U.; Lauterborn, W. Int. J. Bifurcation and Chaos, 3 1993 1529.