EXPERIMENTAL STUDY of the FORCED Ni|H_2SO_4 OSCILLATOR

F. Berthier
LEMHE, UMR 8647, Université Paris XI, 91405 Orsay.
Fabienne.Berthier@lemhe.u-psud.fr

J.-P. Diard, B. Le Gorrec
LEPMI, UMR 5631 CNRS-INPG-UJF, Domaine Universitaire,
BP 75, 38402 Saint Martin d'Hères.
erase@lepmi.inpg.fr

Experimental Study of the Forced Ni|H_2SO_4 oscillator, F. Berthier, J.-P. Diard, B. Le Gorrec, Poster, 203th Meeting of the Electrochemical Society, Paris, 27 Mai-4 Avril 2003.

Abstract

Without any modulation of the current density, the Ni|1 M H_2SO_4 interface oscillates for a current density greater than a critical value, showing a Hopf bifurcation.

Using theoretical results obtained for forced oscillator (Fig. 1) it has been possible to organize the experimental study of the Ni|1 M H_2SO_4 system near this Hopf bifurcation under current control conditions.

The different behaviours expected in forced self-oscillating systems have been experimentally observed for the Ni|1 M H_2SO_4 oscillator:

- bi-periodic behaviour (Fig. 4),
- period-n behaviour (Figs. 5, 6),
- period-1 behaviour (Fig. 8).

Experimental Study of the Forced Ni|H_2SO_4 oscillator, F. Berthier, J.-P. Diard, B. Le Gorrec, Poster, 203th Meeting of the Electrochemical Society, Paris, 27 Mai-4 Avril 2003.

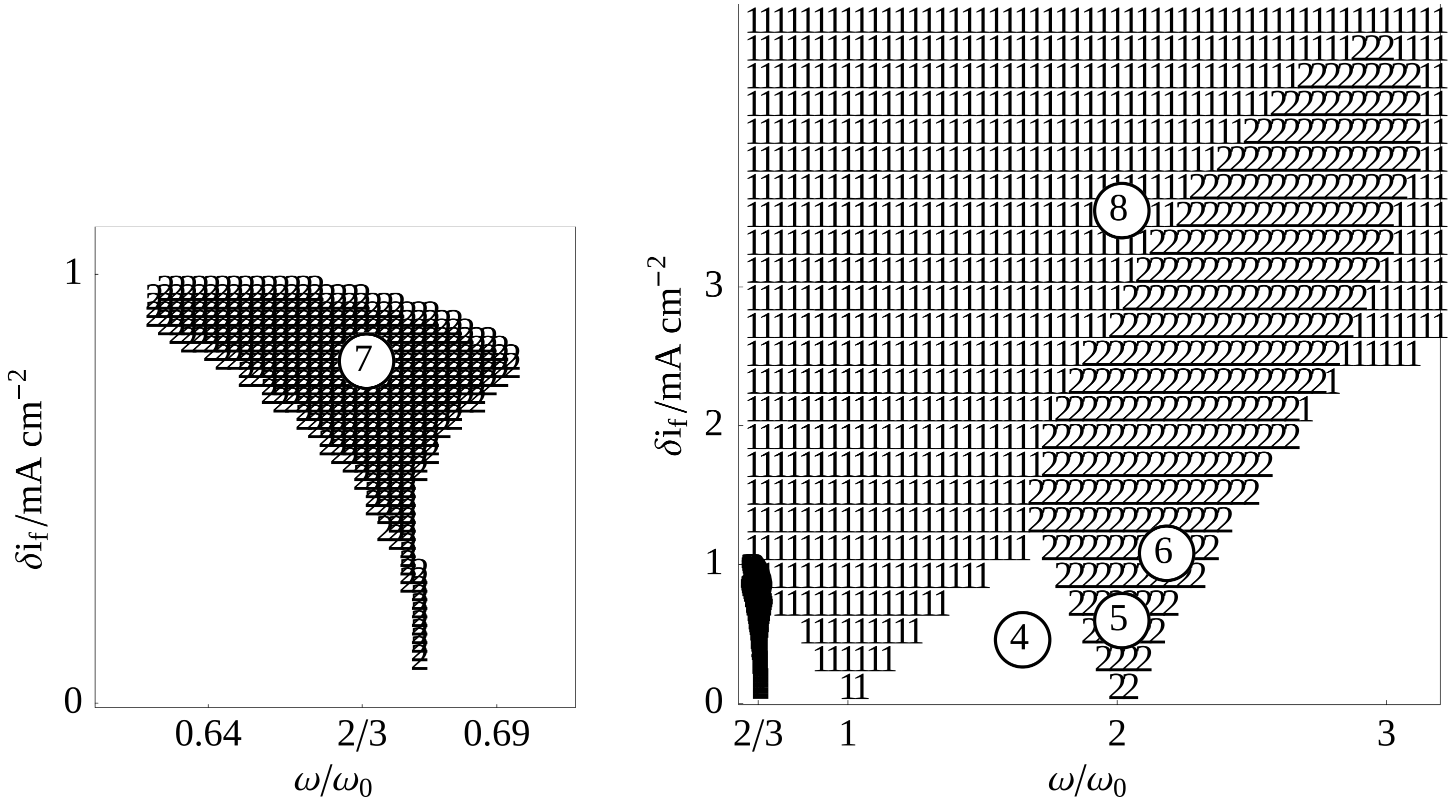
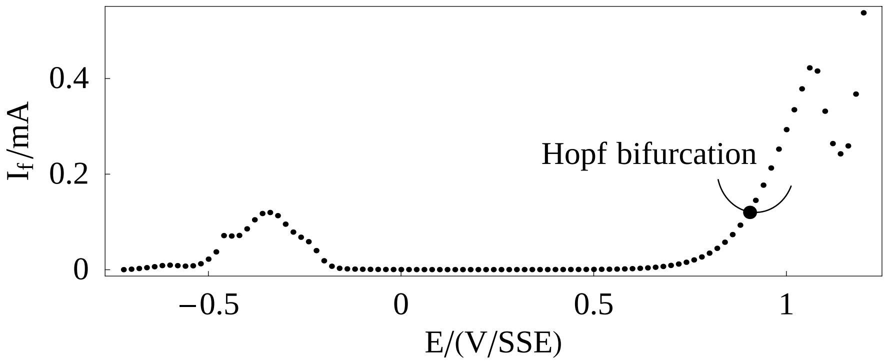
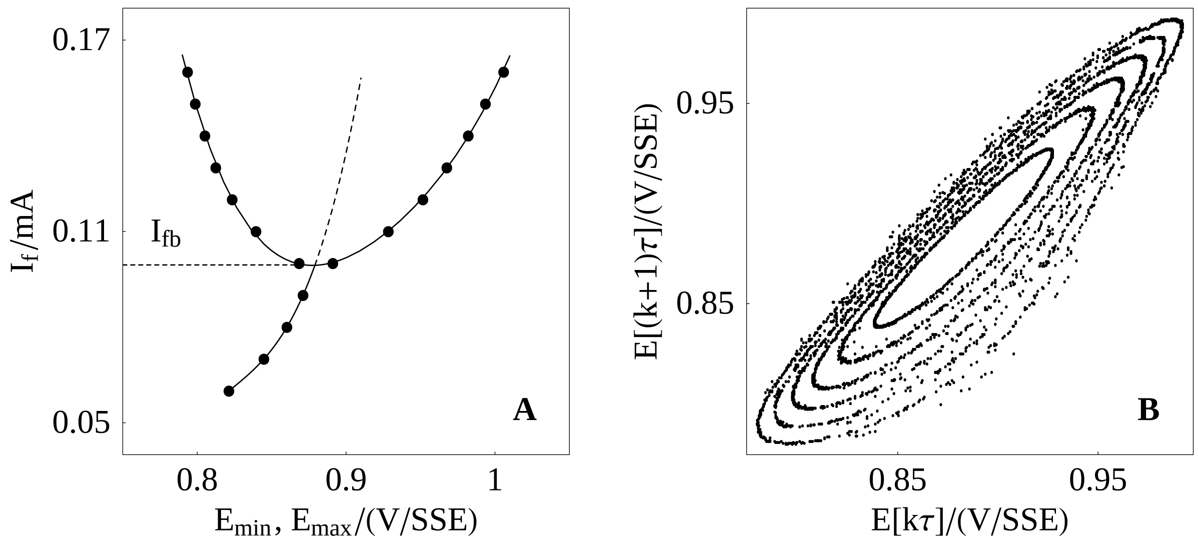


Fig. 1: Arnold tongues plotted for a oxydation-passivation mechanism. n (n = 1, 2) indicates a period-n stable regime. Encircled numbers indicate the corresponding figures. Left is an enlargment of right near $f/f_0=2/3$. (http://preprint.chemweb.com/physchem/0109001)

Experimental Study of the Forced Ni|H_2SO_4 oscillator, F. Berthier, J.-P. Diard, B. Le Gorrec, Poster, 203th Meeting of the Electrochemical Society, Paris, 27 Mai-4 Avril 2003.

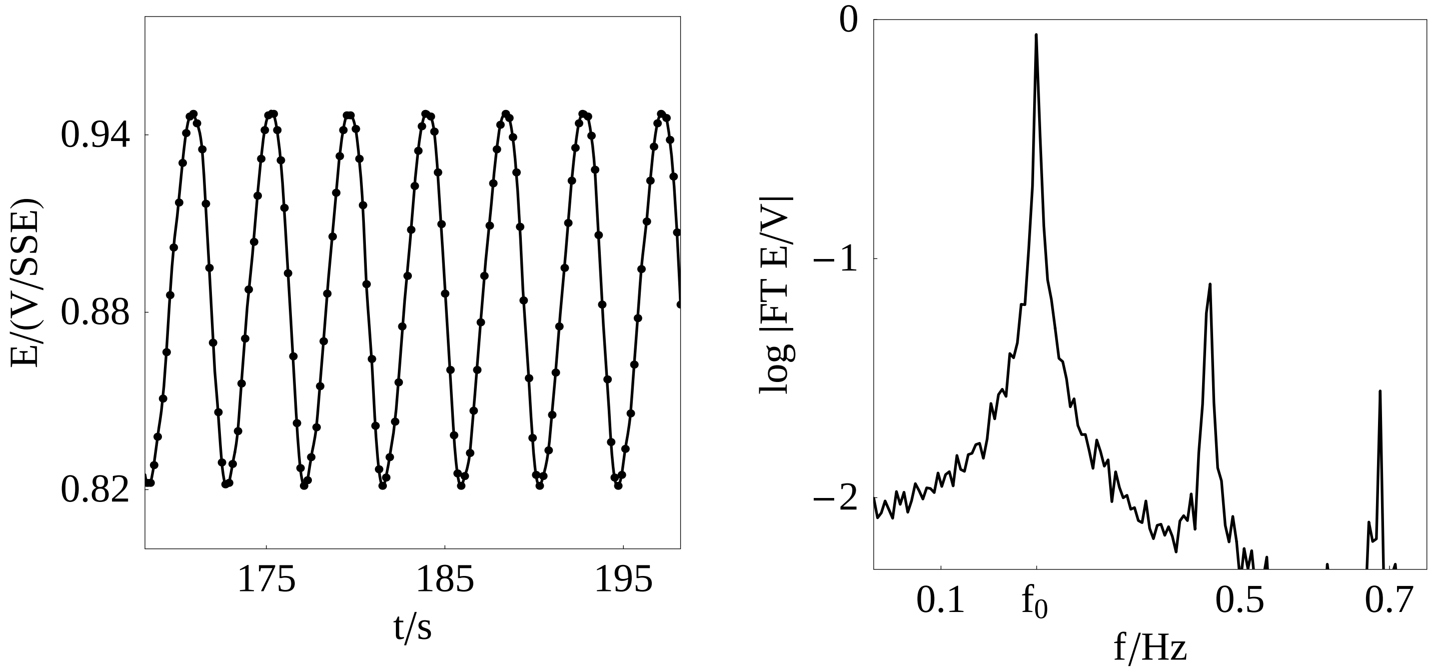




A: Experimental bifurcation diagram showing minima and maxima of electrode potential oscillations. Dots: experimental points, solid lines: stable steady-states and minima and maxima of the oscillations (fit curves), dashed curve : unstable steady-states (extrapolation of the fit curve).

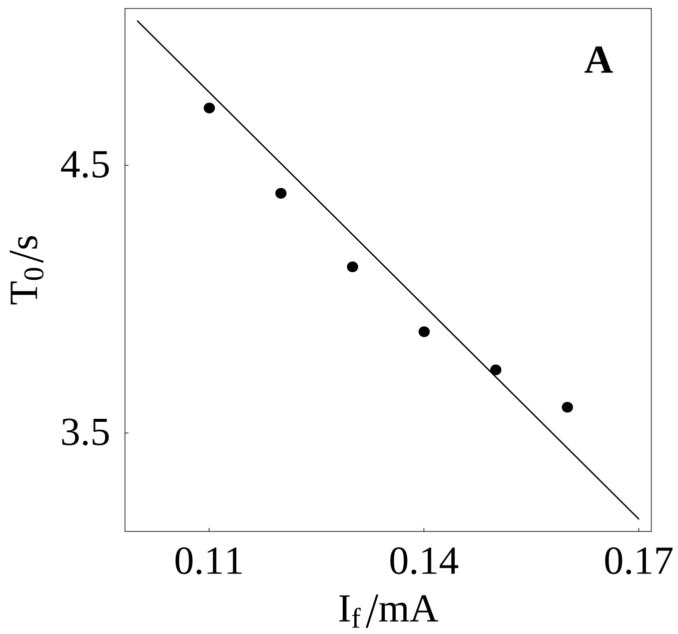
B: Phase portrait for I_f/mA = 0.11, 0.12, 0.13, 0.14, 0.15, 0.16; τ = 0.2 s.

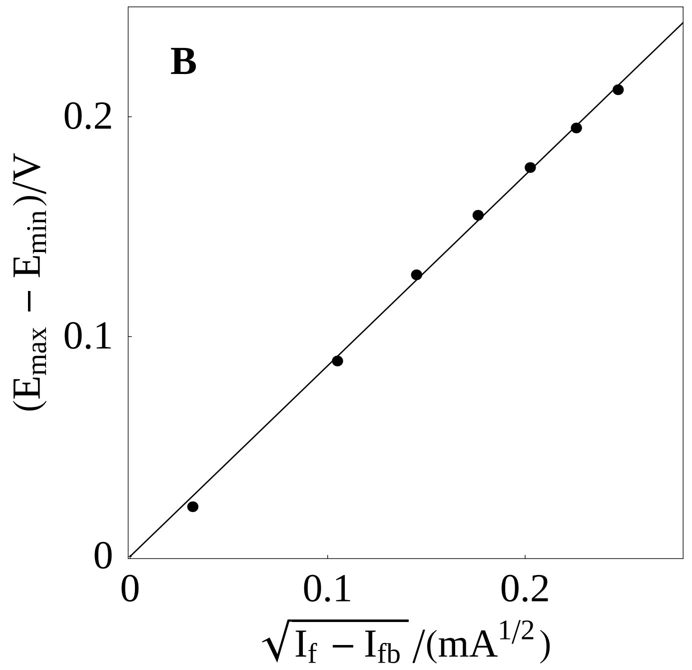
Experimental Study of the Forced Ni|H_2SO_4 oscillator, F. Berthier, J.-P. Diard, B. Le Gorrec, Poster, 203th Meeting of the Electrochemical Society, Paris, 27 Mai-4 Avril 2003.



Electrode potential oscillations (time series, dots : experimental points, solid line: interpolation curve) and Fourier power spectrum of the oscillations measured for I_f = 0.12 mA. f_0 = 0.228 Hz, T_0 = 4.4 s.

Experimental Study of the Forced Ni|H_2SO_4 oscillator, F. Berthier, J.-P. Diard, B. Le Gorrec, Poster, 203th Meeting of the Electrochemical Society, Paris, 27 Mai-4 Avril 2003.





Period of the limit cycle *vs*. I_f (A) and amplitude of the electrode potential oscillations *vs*. square root of the distance from the bifurcation point $(I_f - I_{fb})^{1/2}$ (B).

Experimental Study of the Forced $Ni|H_2SO_4$ oscillator, F. Berthier, J.-P. Diard, B. Le Gorrec, Poster, 203th Meeting of the Electrochemical Society, Paris, 27 Mai-4 Avril 2003.

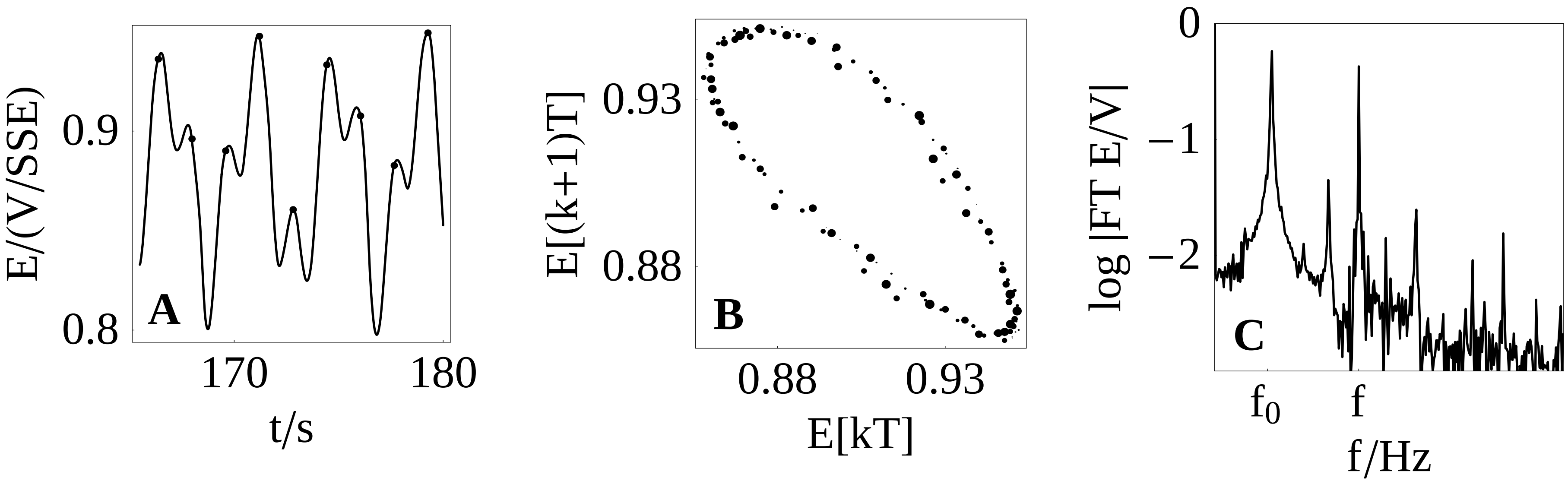


Fig. 4: Electrode potential response to a current modulation. A: electrode potential oscillation, B: Poincaré section in the E((k+1)T) vs. E(kT) plane, C: potential oscillation Fourier power spectrum. Bi-périodic behaviour. I_f = 0.12 mA, δI_f = 20 µA, f = 0.62 Hz.

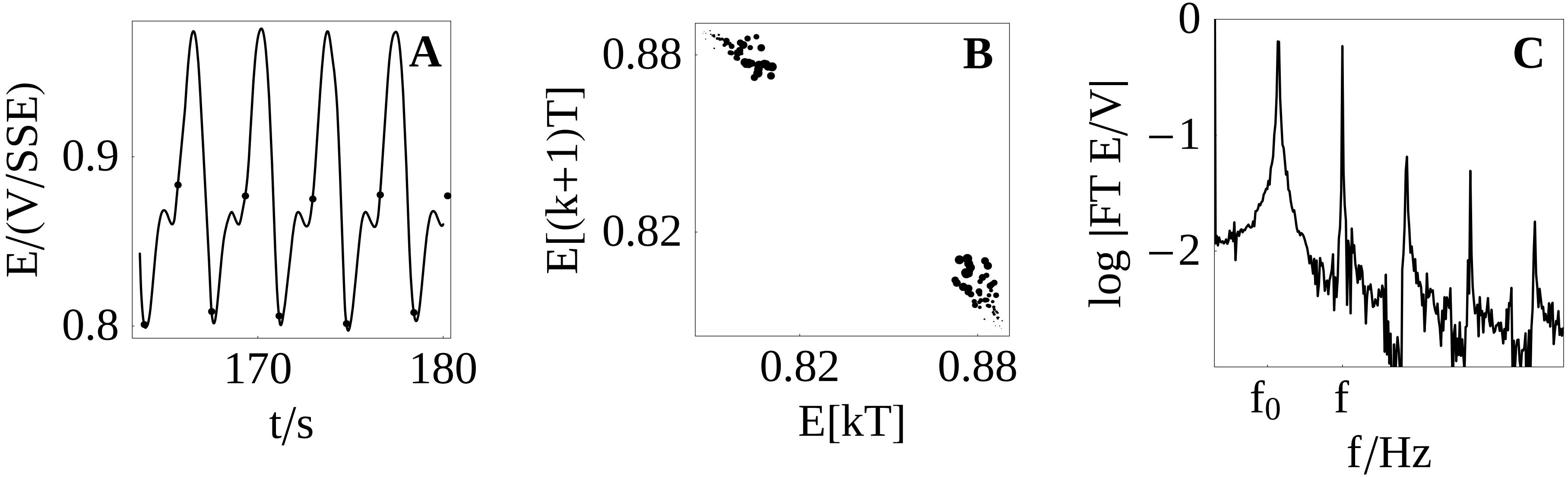


Fig. 5: Period-2 behaviour. I_f = 0.12 mA, δI_f = 20 µA, f = 0.55 Hz. Other captions as in Fig 4.

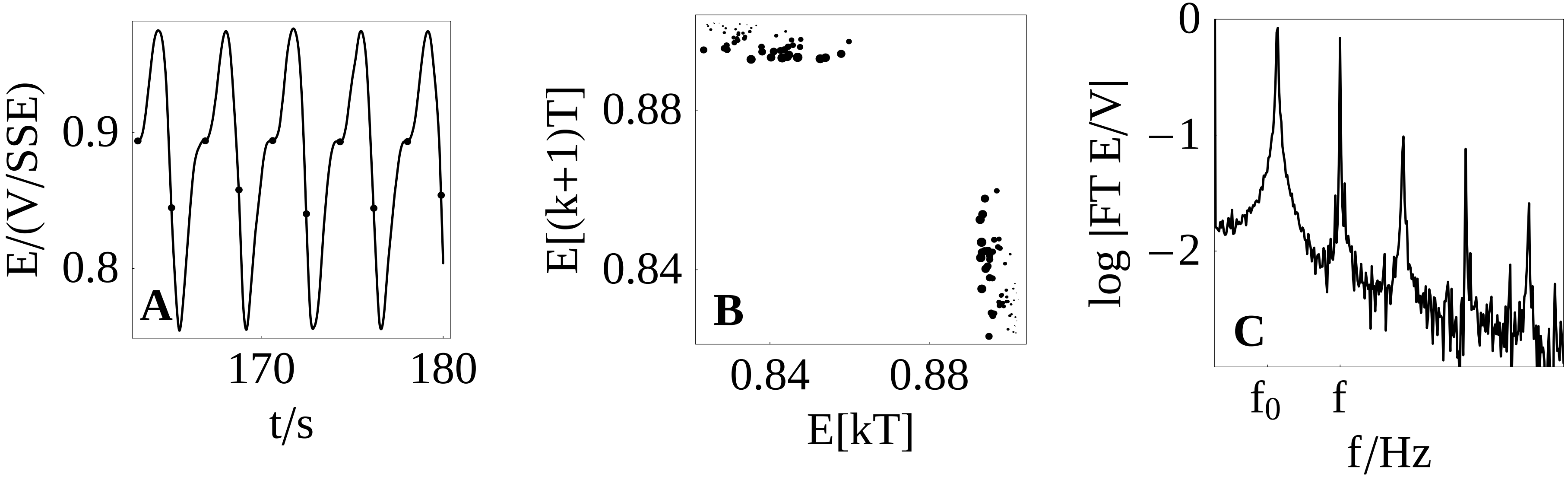
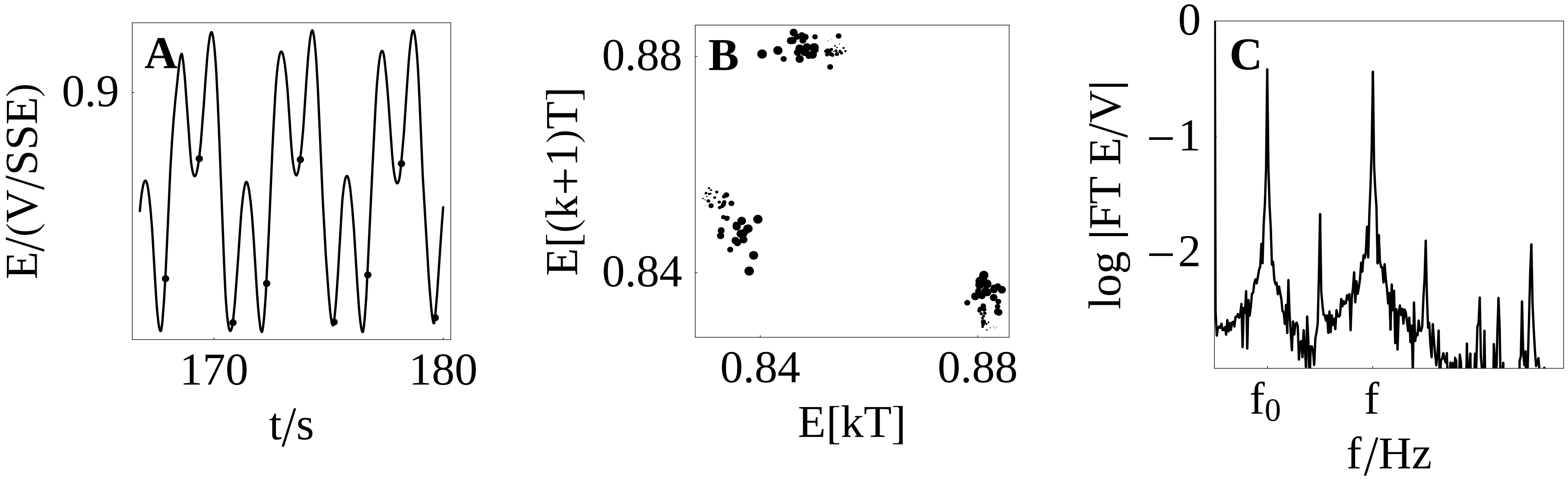


Fig. 6: Period-2 behaviour. I_f = 0.12 mA, δI_f = 20 µA, f = 0.54 Hz. Other captions as Fig 4.



Period-3 behaviour. I_f = 0.12 mA, δI_f = 20 µA, f = 0.68 Hz. Other captions as Fig 4

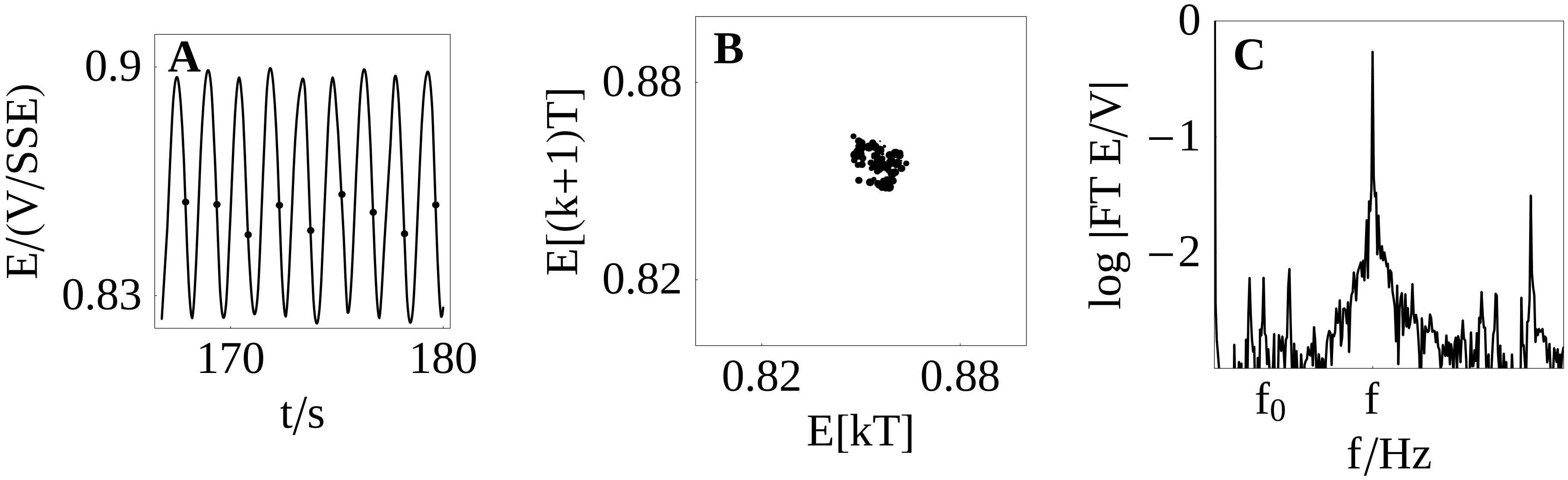


Fig. 8: Period-1 behaviour. I_f = 0.12 mA, δI_f = 30 µA, f = 0.68 Hz. Other captions as Fig 4.

Experimental Study of the Forced Ni|H_2SO_4 oscillator, F. Berthier, J.-P. Diard, B. Le Gorrec, Poster, 203th Meeting of the Electrochemical Society, Paris, 27 Mai-4 Avril 2003.