



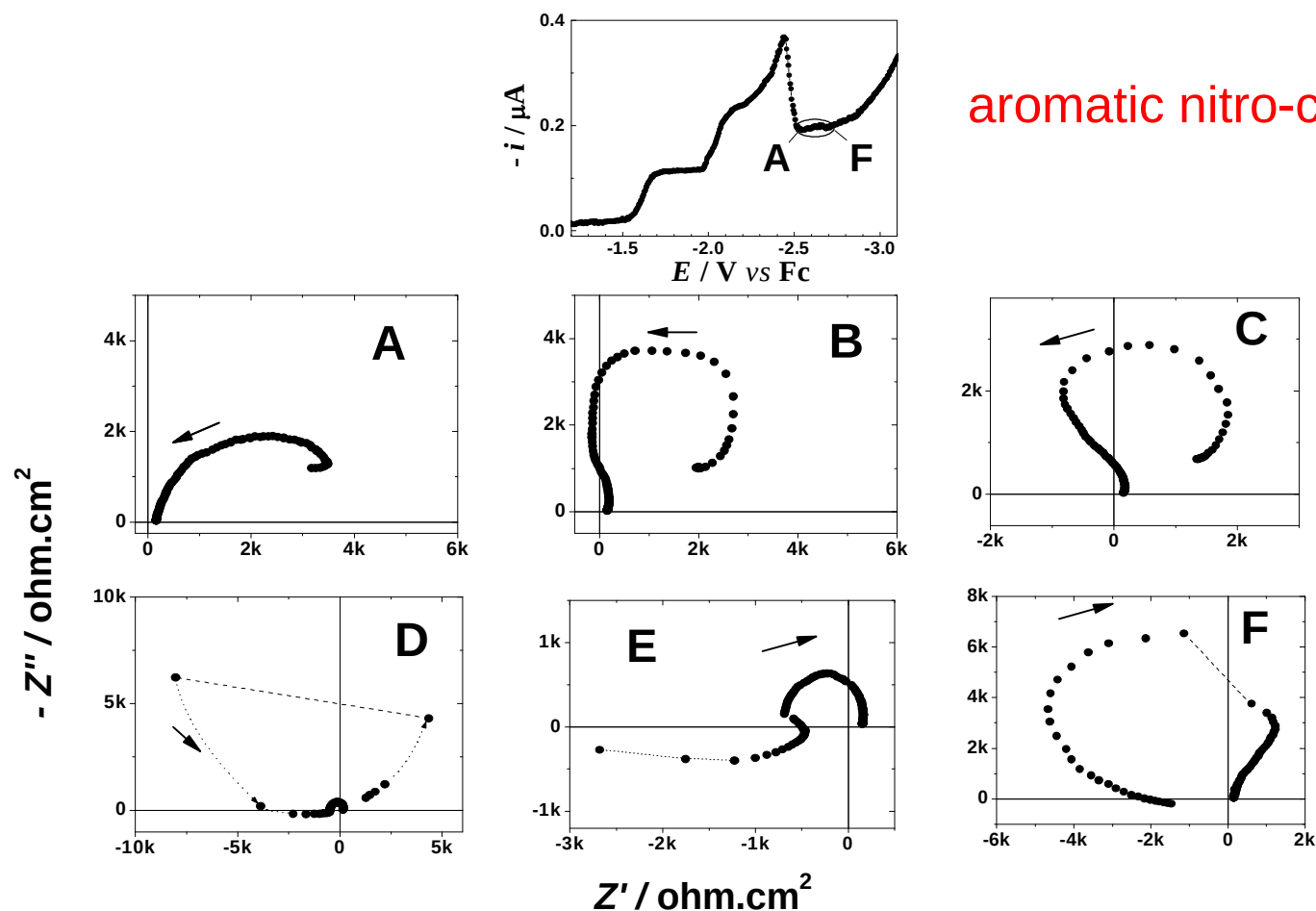
Negative Differential Resistance of Extended Viologen. Oscillations with Odd Harmonic Frequencies. Stochastic Resonance.

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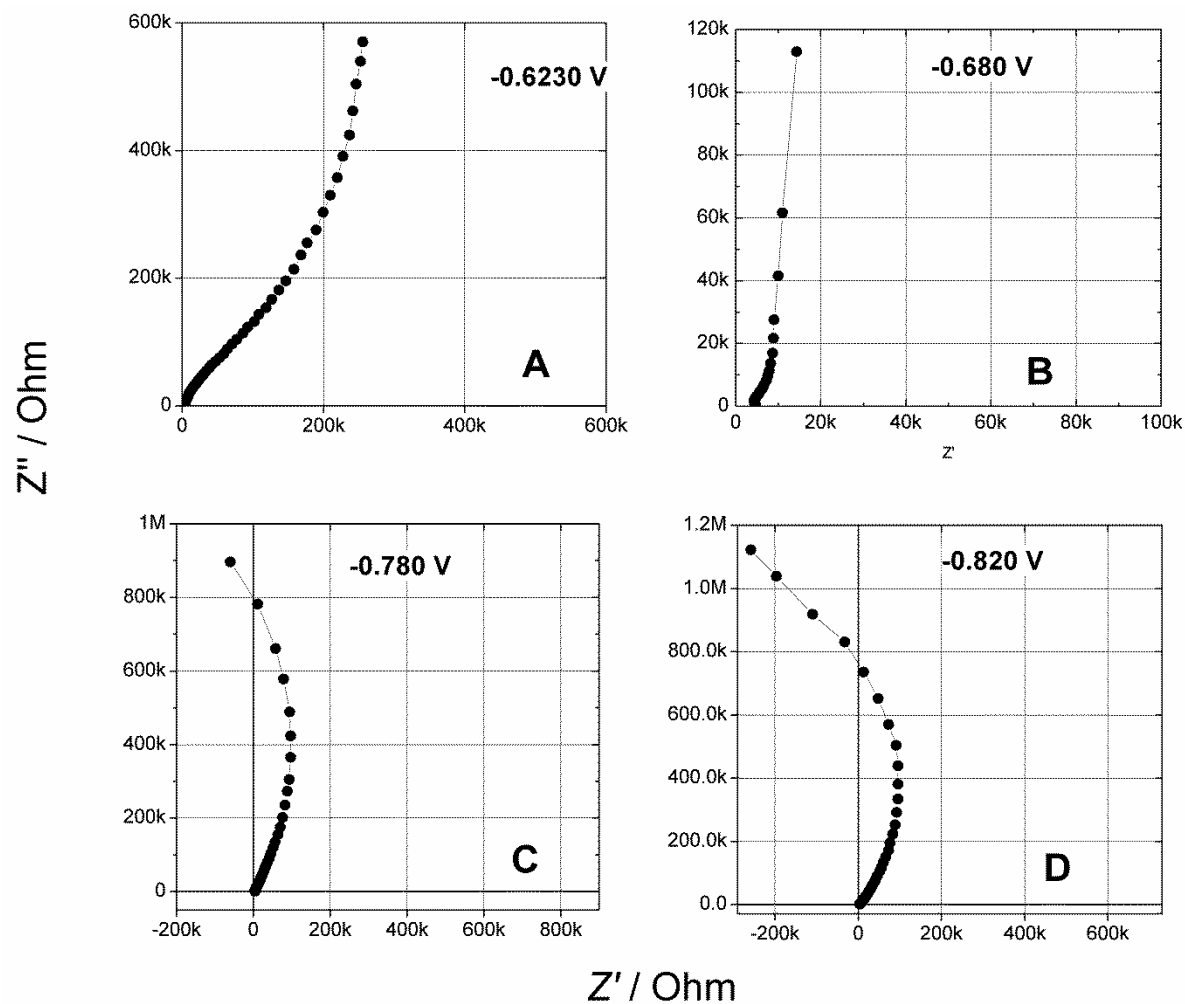
Lubomír Pospíšil, Magdaléna Hromadová

Redox reactions of organic radicals

Example of negative impedance causing oscillations



This presentation: **extended viologen**
Negative differential resistance near E^0





Why to deal with electrochemical oscillators?

Good models for system dynamics

Many controlling parameters

Electrical **current** or **potential** directly monitors the rate of kinetics



Why to model oscillations and chaos?

Climate & geophysics

(7 years polar motion, El Nino, sea temperature)

Economic & Social

(business cycle, generation gaps, news cycle)

Astronomy

(helioseismology, cosmological cyclic model, neutron stars)



Common chemical reactions:
reactants → **products**

The first electrochemical oscillator:
1828 Fechner
Periodic release of gas bubbles
from iron in HNO_3

G. Th. Fechner: *Schweiger's J. Chem. Phys.* 53 (1828) 129



Important oscillating processes:

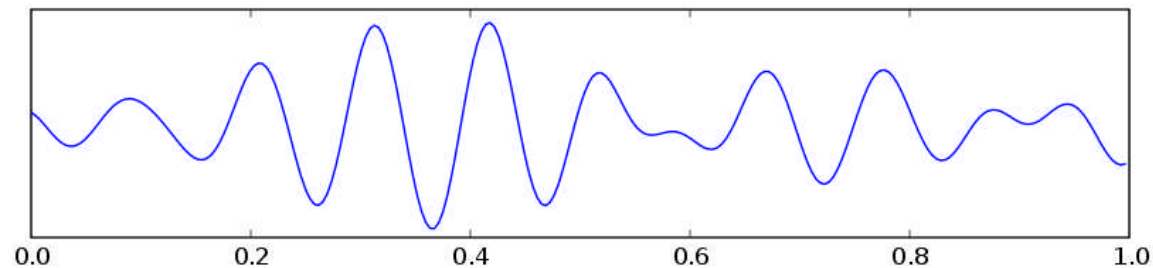
Circadian clock, or **circadian oscillator**
biochemical mechanism
oscillates with a period of 24 hours

Important oscillating processes:

Alpha waves: neural oscillations in brain

frequency 8 – 12 Hz

1931 Berger inventor of electro-encephalography

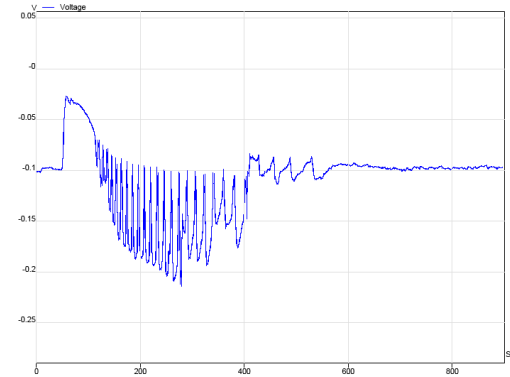


Belousov–Zhabotinsky reaction

1950 Boris Belousov

1961 Anatol Zhabotinsky

1968 congress in Prague and dissemination to the West



Classical example of **non-linear thermodynamics**

mix of potassium bromate, Ce(IV) sulfate, propanedionic acid and citric acid
in dilute H_2SO_4

concentration of the cerium(IV) and cerium(III) ions oscillates

color oscillates: yellow $\leftrightarrow$ colorless

reduction $\text{Ce(IV)} \rightarrow \text{Ce(III)}$ by propanedionic acid

oxidation back to $\text{Ce(IV)} \rightarrow \text{Ce(III)}$ ions by bromate(V) ions.



Damped & driven oscillators

Two driving forces of opposite sense

Mass on a string & gravity

Charging a capacitor in parallel with inductance

Energy dissipation as heat, friction,... damping

External energy source: driven oscillator



Oscillating reactions

- Corrosion of metals in acids
- Oxidation of organic compounds on Cu electrodes
- Electrocatalysis by adsorbed ions
- Oxidation of gaseous CO on Pt
- Bio-processes



Outline of our recent results

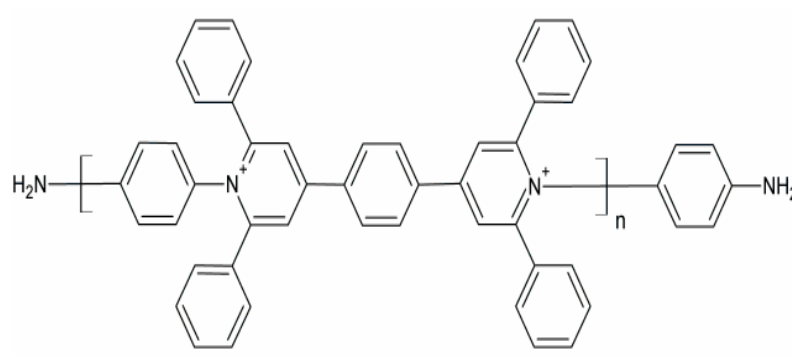
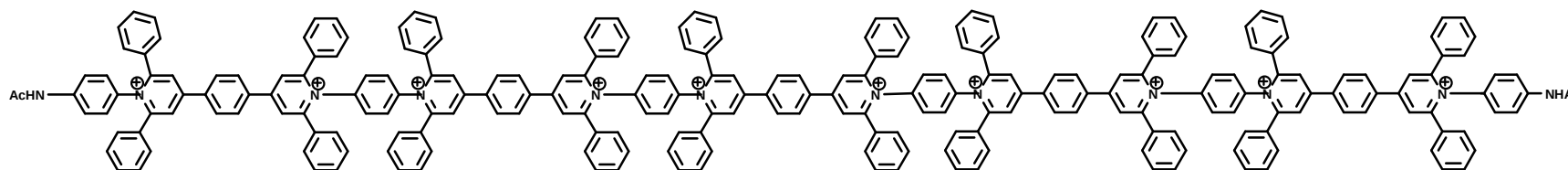
Molecular conductors –
viologen oligomers

Driven **oscillations** yield only **odd harmonics**

Stochastic resonance of a driven system

Molecular conductors

octo- and *deca-*cations of “extended viologens”



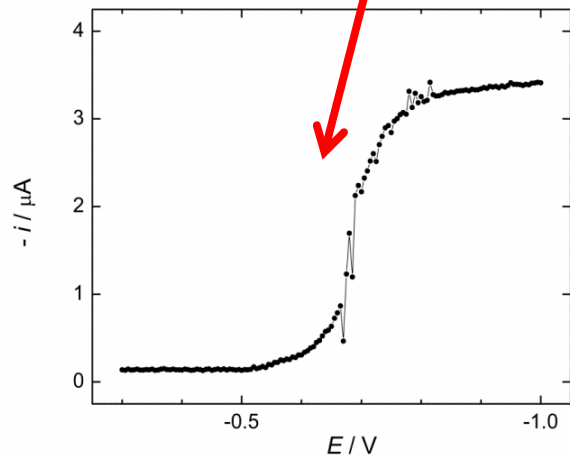
$n = 2, 3, 4, 5, 6$

Two electrons for each viologen unit

DC polarograms (low current damping)

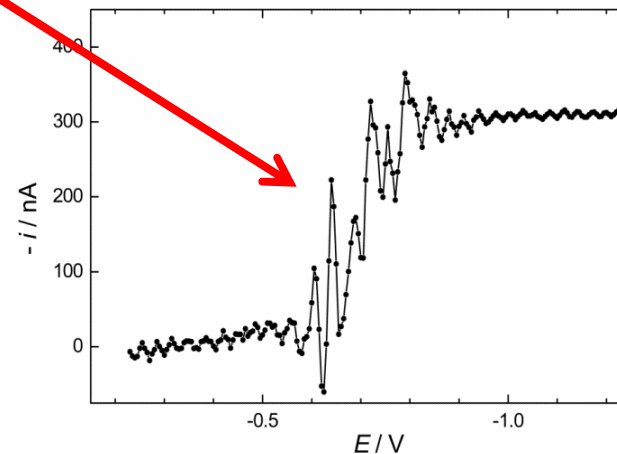
Reversible 3-electron reduction

Current instability near potential E^0



0.7 mM

Concentration
of extended viologen

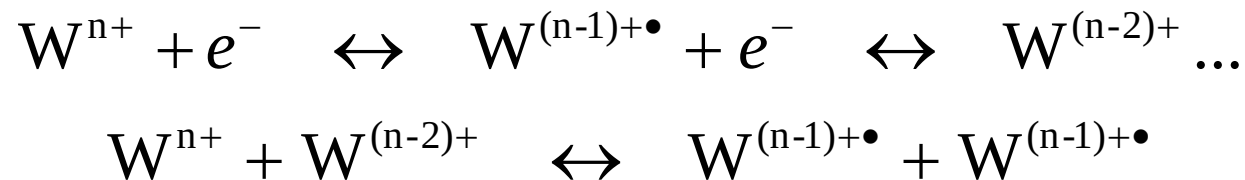


0.07 mM

Mechanism & models

- **Positive feed-back loop:**

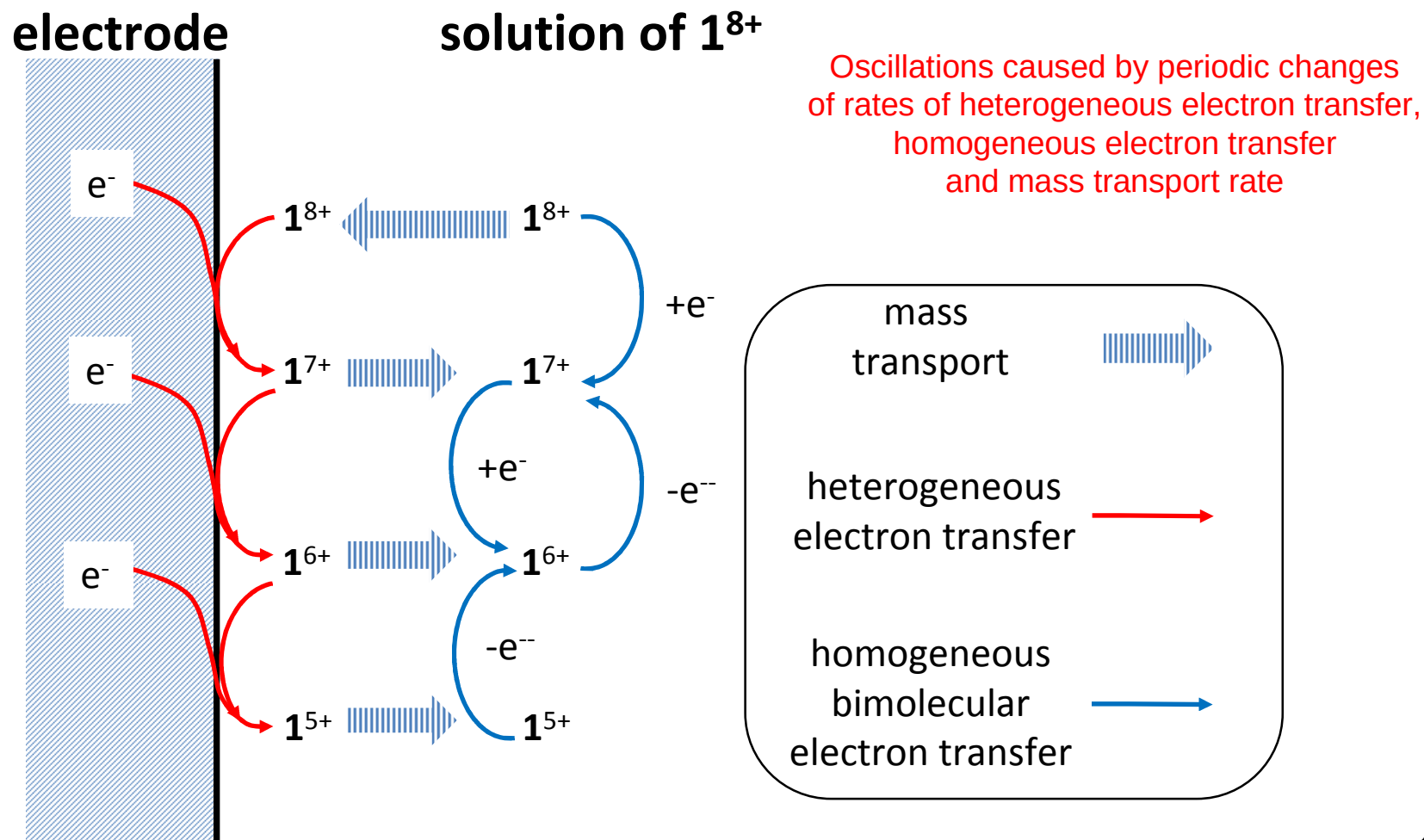
disproportionation re-generates reducible parent form



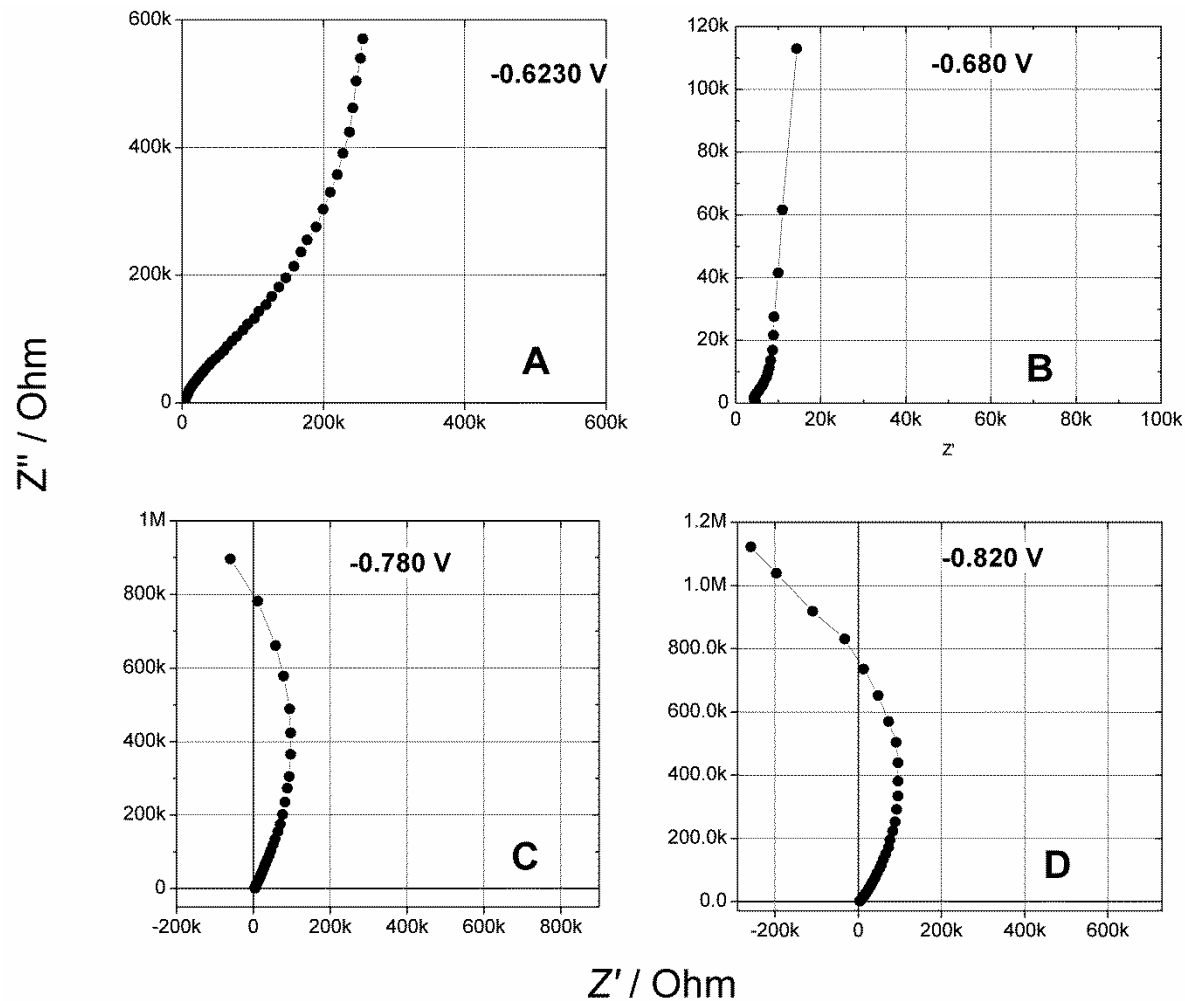
- **Negative feed-back loop:**

change of concentration gradient & mass transport

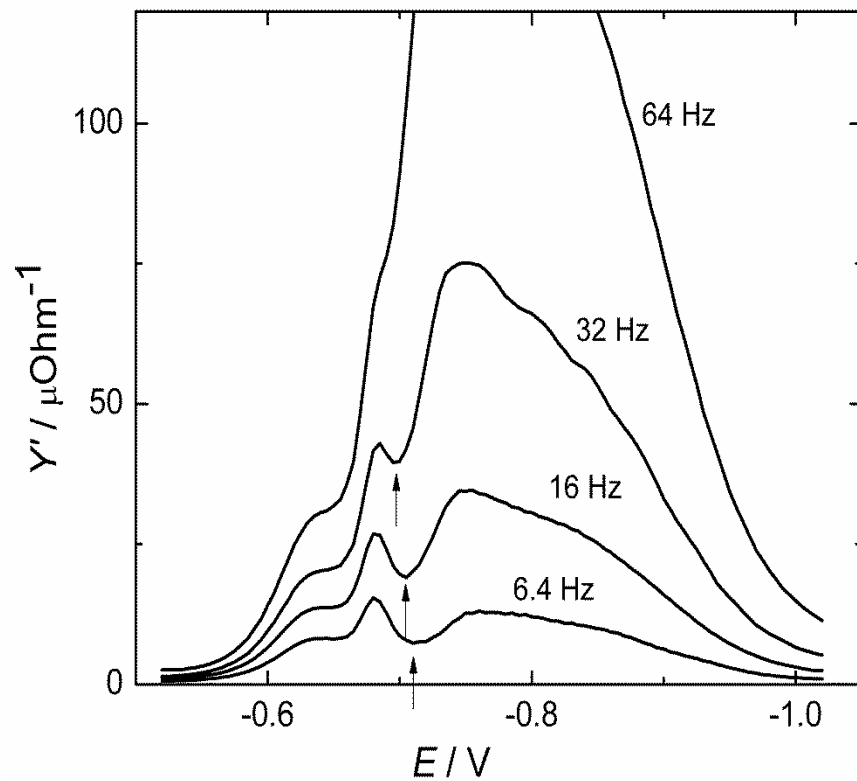
Coupling of heterogeneous and homogeneous electron transfers & mass transport



Extended viologen: Negative differential resistance near E^0

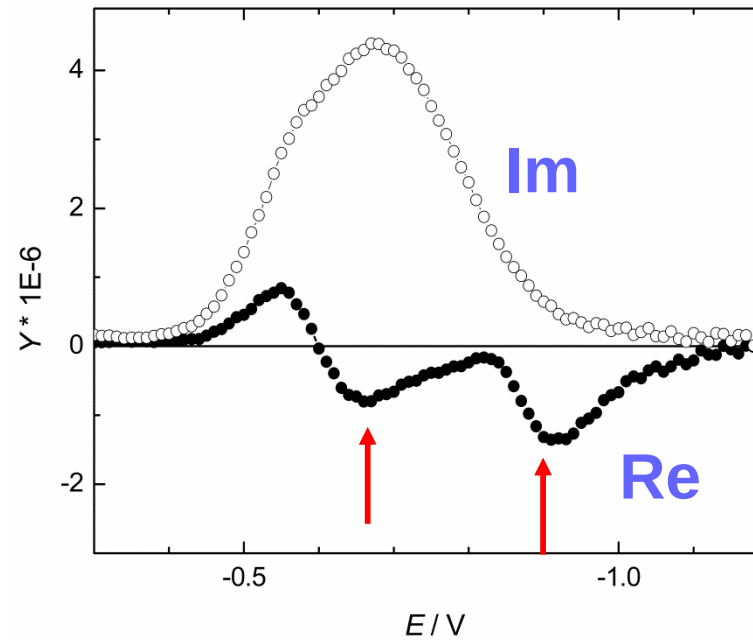


Extended viologen: AC polarograms with admittance < 0

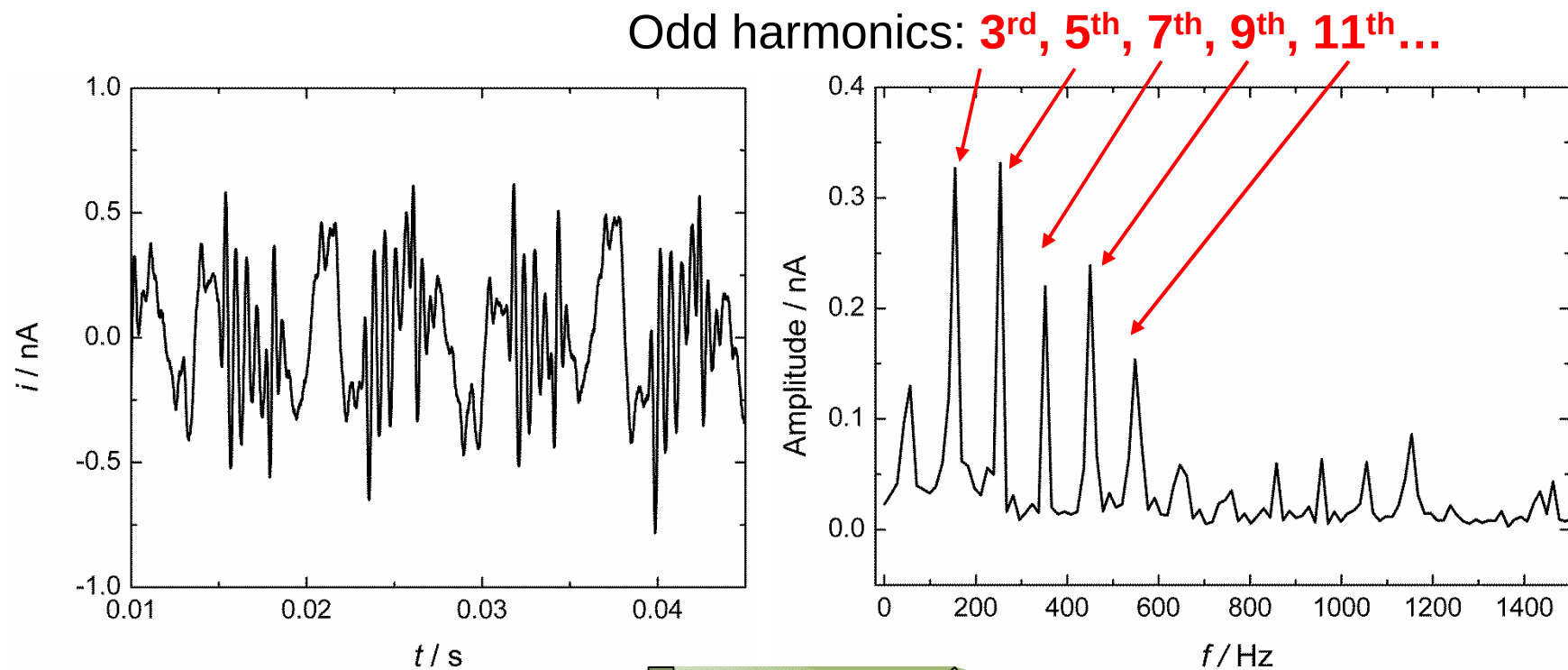


Low frequency AC polarogram

0.32 Hz



Extended viologen: Current—time series & FFT



Fourier transform



Extended viologen:
Odd harmonics due to stochastic resonance

Stochastic resonance (SR)

cooperative action of fluctuation and
periodic driving in bi- & multi-stable systems

SR can trigger the transfer of power
to the periodic signal and enhance it.

Driving by pickup of ~ 1 mV & 50 Hz



Theory of stochastic resonance in non-linear systems

- 1980's: **Bartussek** and co-workers: theory of **higher harmonics** for non-linear systems
- cases with potential-symmetric, potential-asymmetric, and additive or multiplicative fluctuations
- **potential-symmetric systems suppress 2nd harmonics and retain the odd harmonics**
- **Fast and reversible viologens are potential symmetric systems.**



Examples of stochastic resonance from other fields

Geoscience

Laser optics

Acoustics

Enzymatic reactions

M. Hromadová, M. Valášek, N. Fanelli, H. N. Randriamahazaka, L. Pospíšil
Stochastic Resonance in Electron Transfer Oscillations of Extended Viologen.
J. Phys. Chem. C, **2014**, [dx.doi.org/10.1021/jp501608b](https://doi.org/10.1021/jp501608b)

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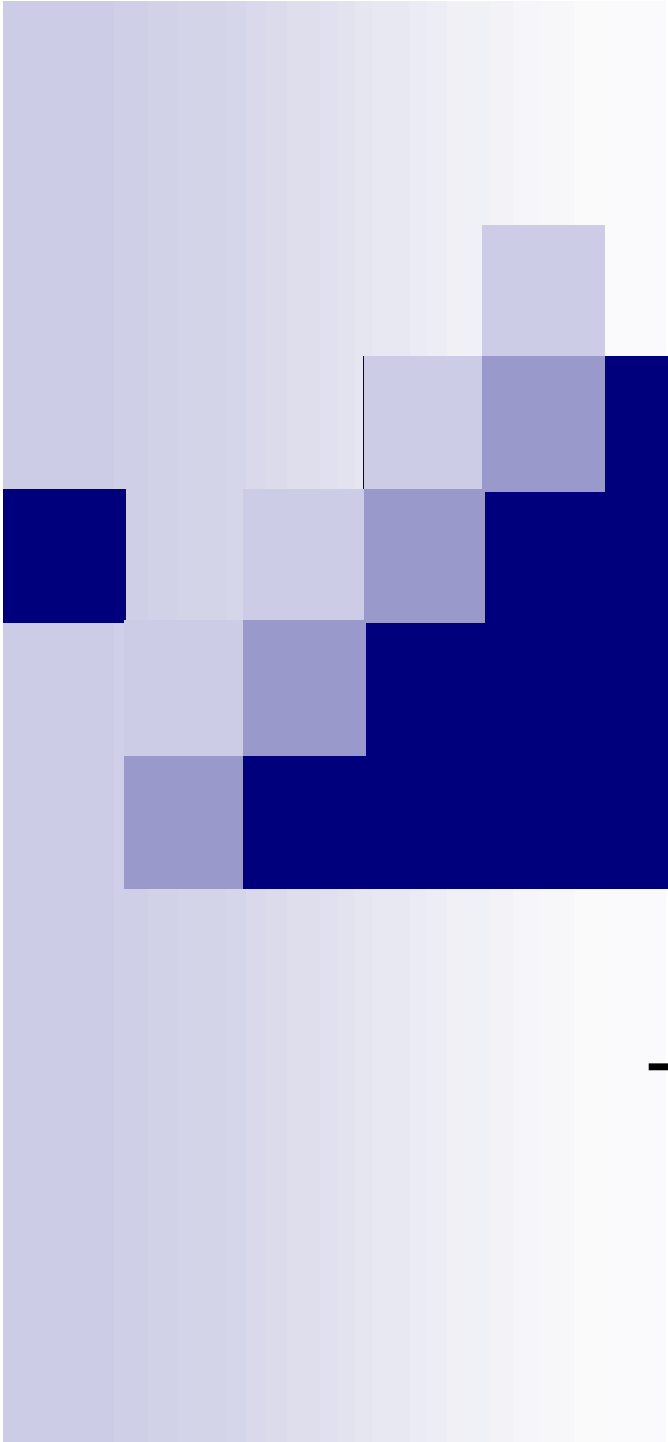
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Joint project C.N.R.S.-AS CR



Thank you for your attention



Chaos is life
Periodicity is boring
Stability is death

Thank you for your attention



Can we predict a change:

stability – periodicity – deterministic chaos

???



Deterministic chaos × random fluctuations

Observation at time t_n depends on values at t_{n-1} , t_{n-2} , ...

Functional dependence exists - may not be known

Random events do not correlate with previous events

No functional law



The proof of a hidden functional dependence:

Do the observation in time
form an attractor ?



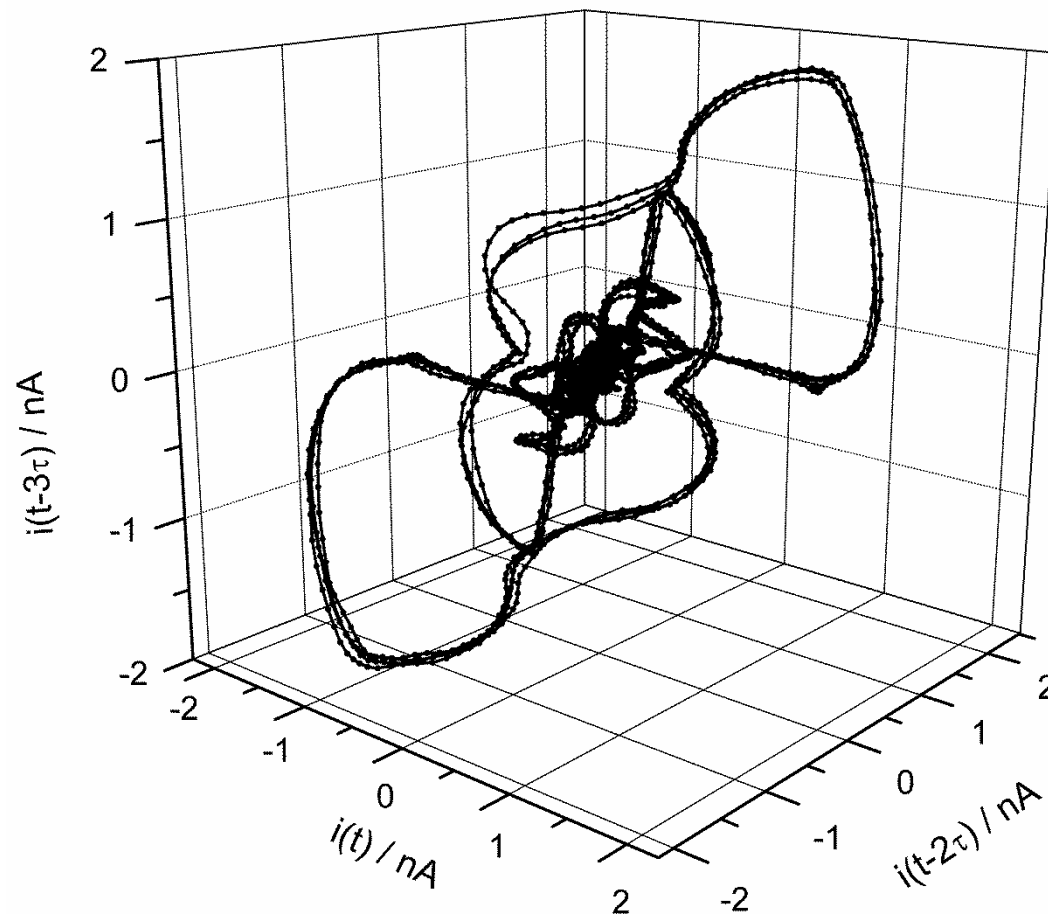
Attractor

An attractor can be a **point**, a finite **set of points**, a **curve**, a **surface**,
or even a complicated set with a fractal
structure known as a ***strange attractor***.

Observed time series: $i(t_1), i(t_2), \dots, i(t_{n-1}), i(t_n)$

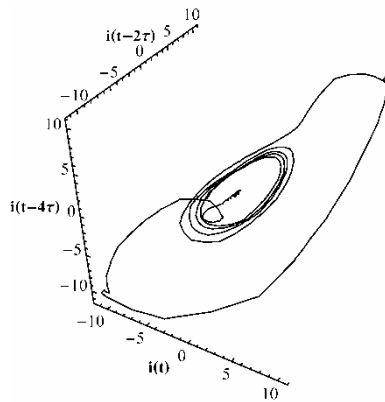
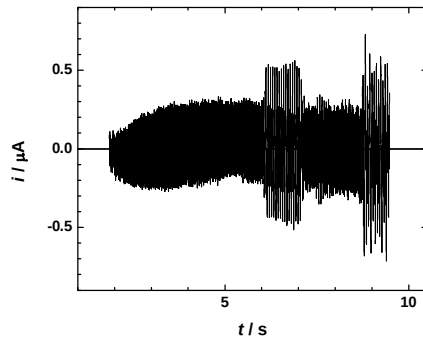
Plotting $i(t)$ vs $i(t - 2\tau)$ vs $i(t - 4\tau)$

Extended viologen: Time delay analysis of experimental series

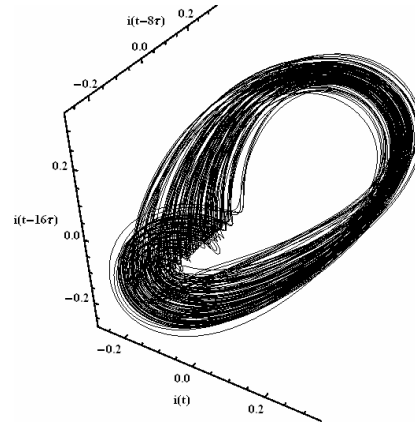


Deterministic chaos × random fluctuations

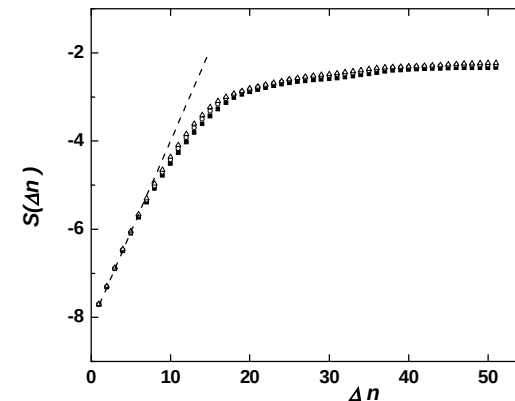
Diagnostic criteria



Reconstructed attractor



Current-time series → Time-delayed plot →
→ Phase space diagram → **Attractor orbit** →
→ Exponential evolution → **Ljapunov exponent λ**



exponential divergence of nearby trajectories for three embedded space dimensions → **$\lambda=0.41 > 0$!!!**



Ljapunov exponent :

quantifies the strength of chaos

Adjacent trajectories diverge in time

Chaos: exponentially fast rate of separation

δ_0 distance between two points

$$\delta_{\Delta t} = \delta_0 e^{\lambda \Delta t}$$

Ljapunov exponent : averaged exponent λ

Type of motion: $\lambda < 0$... fixed point

$\lambda = 0$... stable orbit **periodicity**

$\lambda > 0$... **deterministic chaos**

$\lambda = \infty$... noise



Universal theory of deterministic chaos

Mitchell Feigenbaum (*1944)

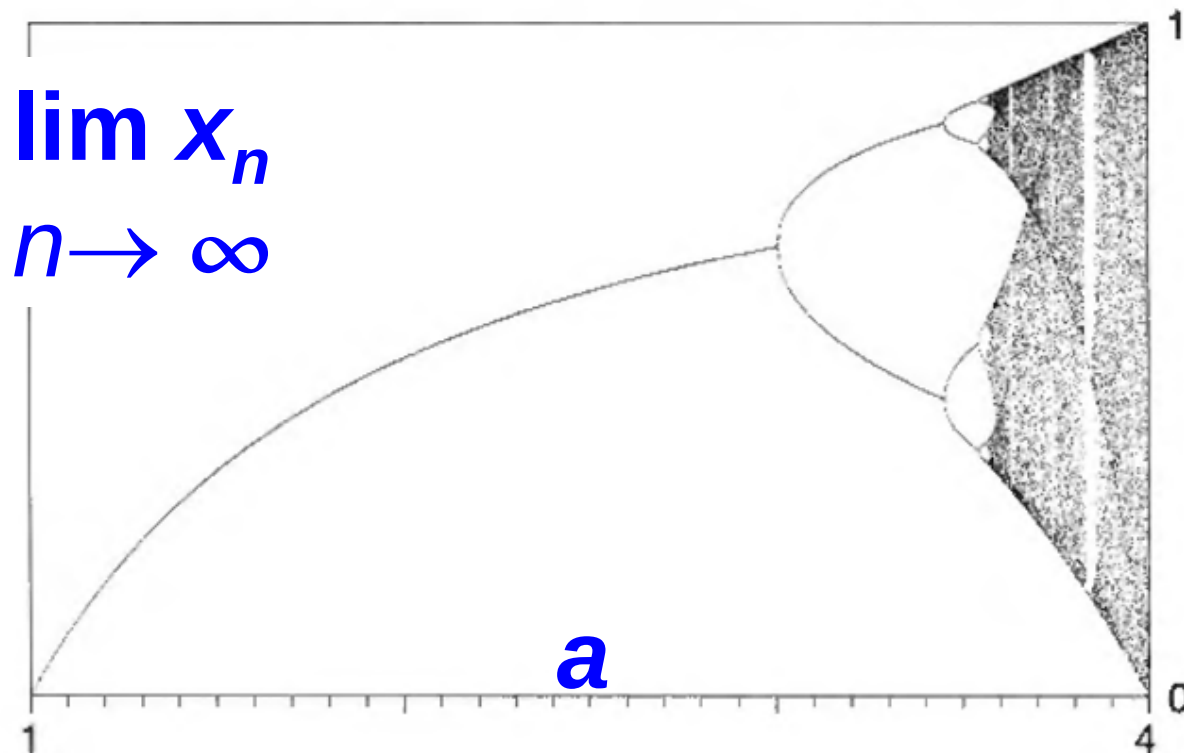
Properties of iterating equations

Feigenbaum universality constant δ

Stability depends on parameter a

Quadratic iterator: $x_{n+1} = a x_n(1-x_n)$

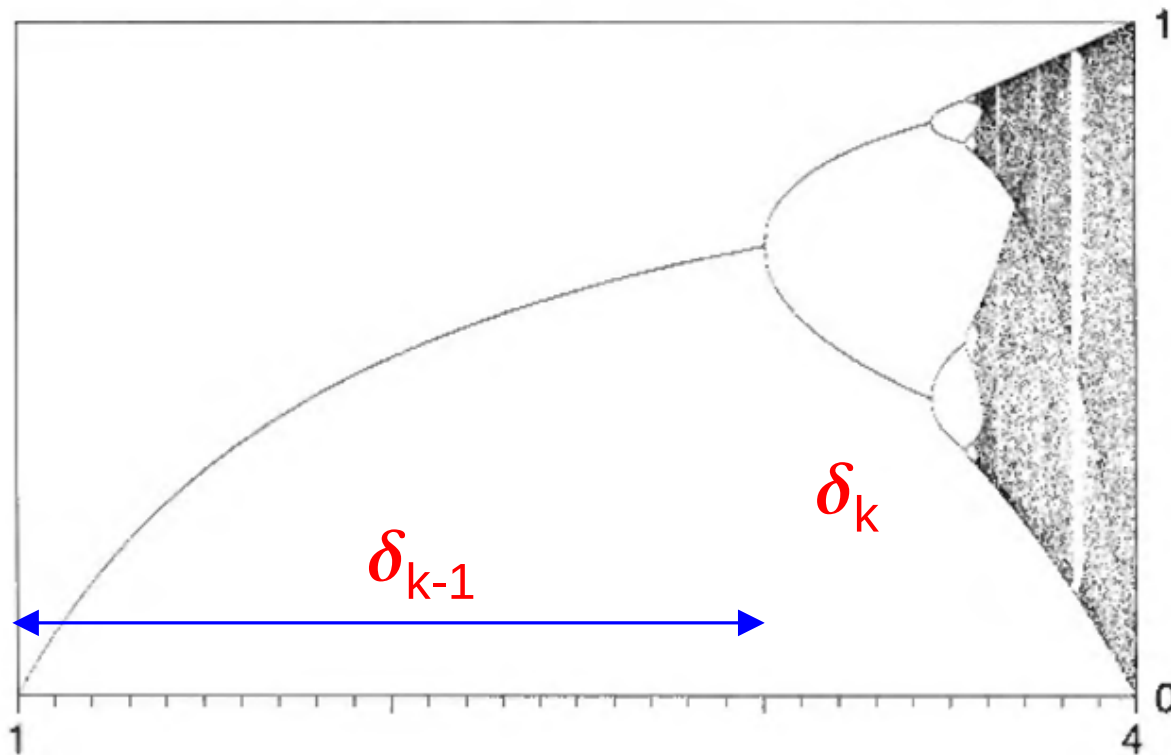
(Peitgen, Juergens, Saupe: Chaos and Fractals)



Final-State Diagram

Final-state diagram for the quadratic iterator (11.1) and parameter a between 1 and 4.

Feigenbaum constant δ



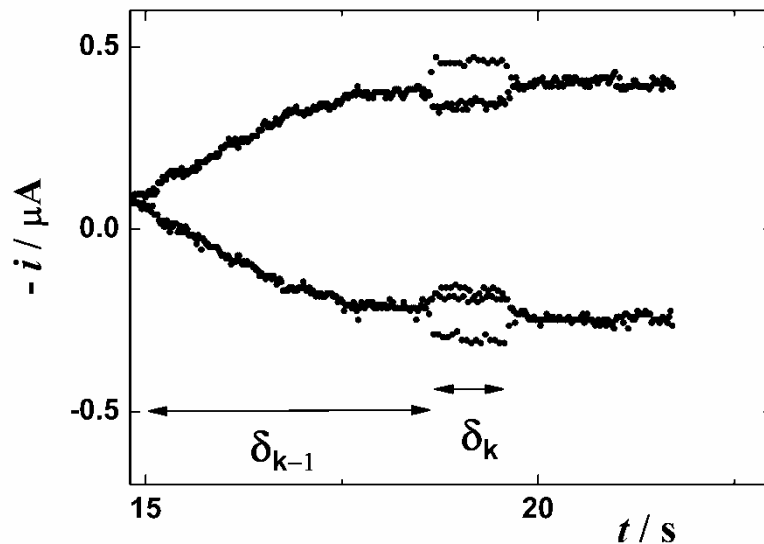
Final-State Diagram

Final-state diagram for the quadratic iterator (11.1) and parameter a between 1 and 4.

$$\lim_{k \rightarrow \infty} \delta = \delta_{k-1} / \delta_k$$

Feigenbaum constant δ

stability – oscillation – deterministic chaos



$$\lim_{k \rightarrow \infty} \delta = \delta_{k-1} / \delta_k$$

Experiment: $\delta = 4.68$

Theory: $\delta = 4.6692\dots$

Universal constant δ : similar to universality of π

Experimental verification of δ only in few cases

Feigenbaum constant for prediction of chaos



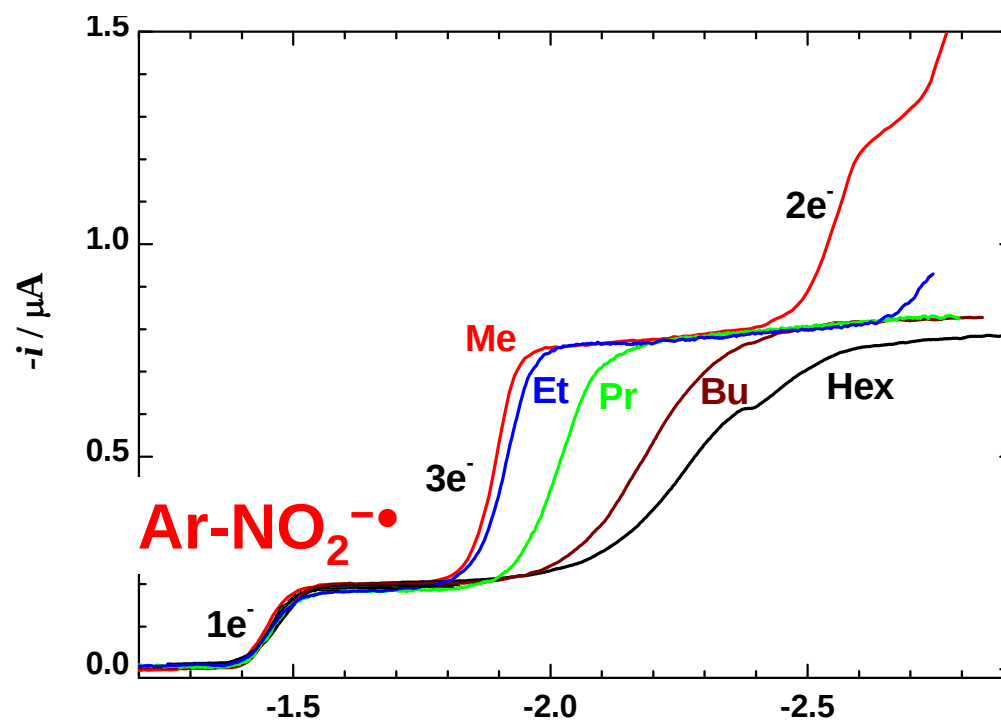
Other examples of
electrochemical oscillators:

Cationic electrocatalysis
Anionic electrocatalysis

Reduction of aromatic radical anion

Repulsion is size-dependent

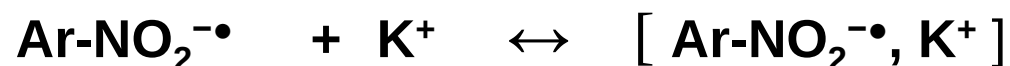
Different tetra-alkyl ammonium salts as electrolytes
DC polarograms:





Acceleration effect : Cationic catalysis

Ion- pair formation eliminates electrostatic repulsion



Ion pairs are reduced at **less negative potentials by 800 mV**:

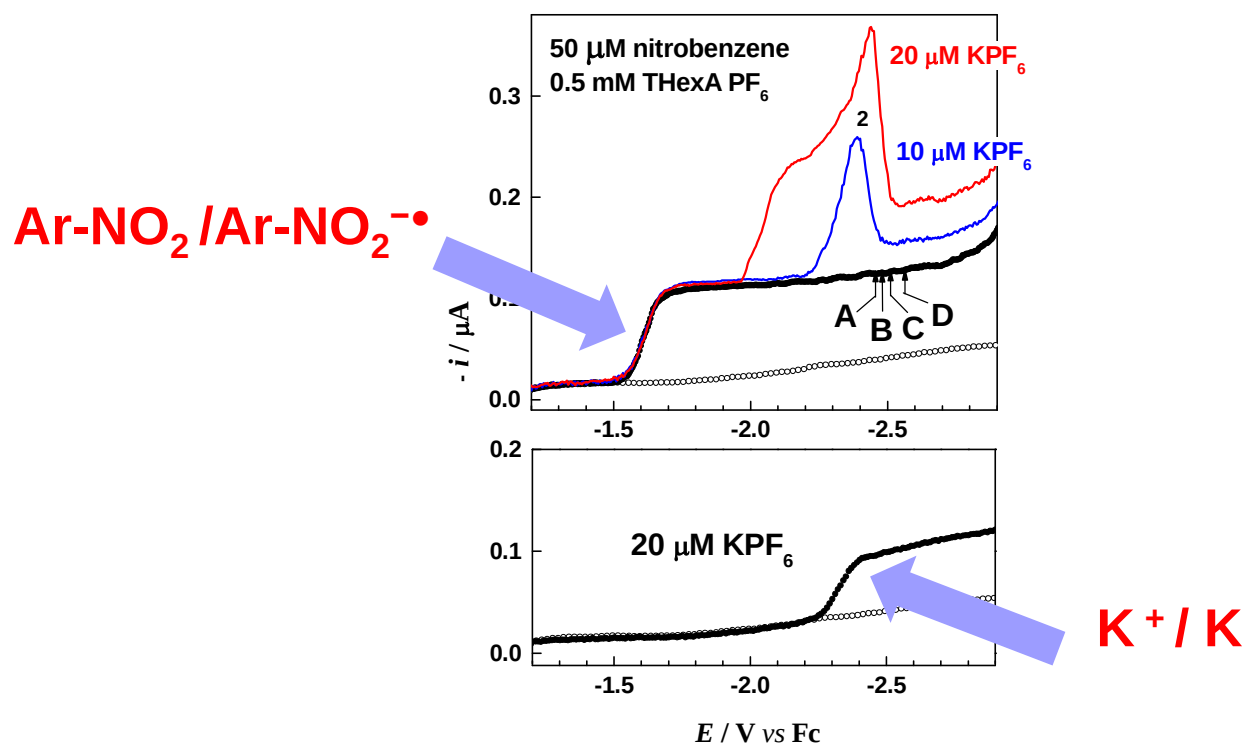


" cationic catalysis "

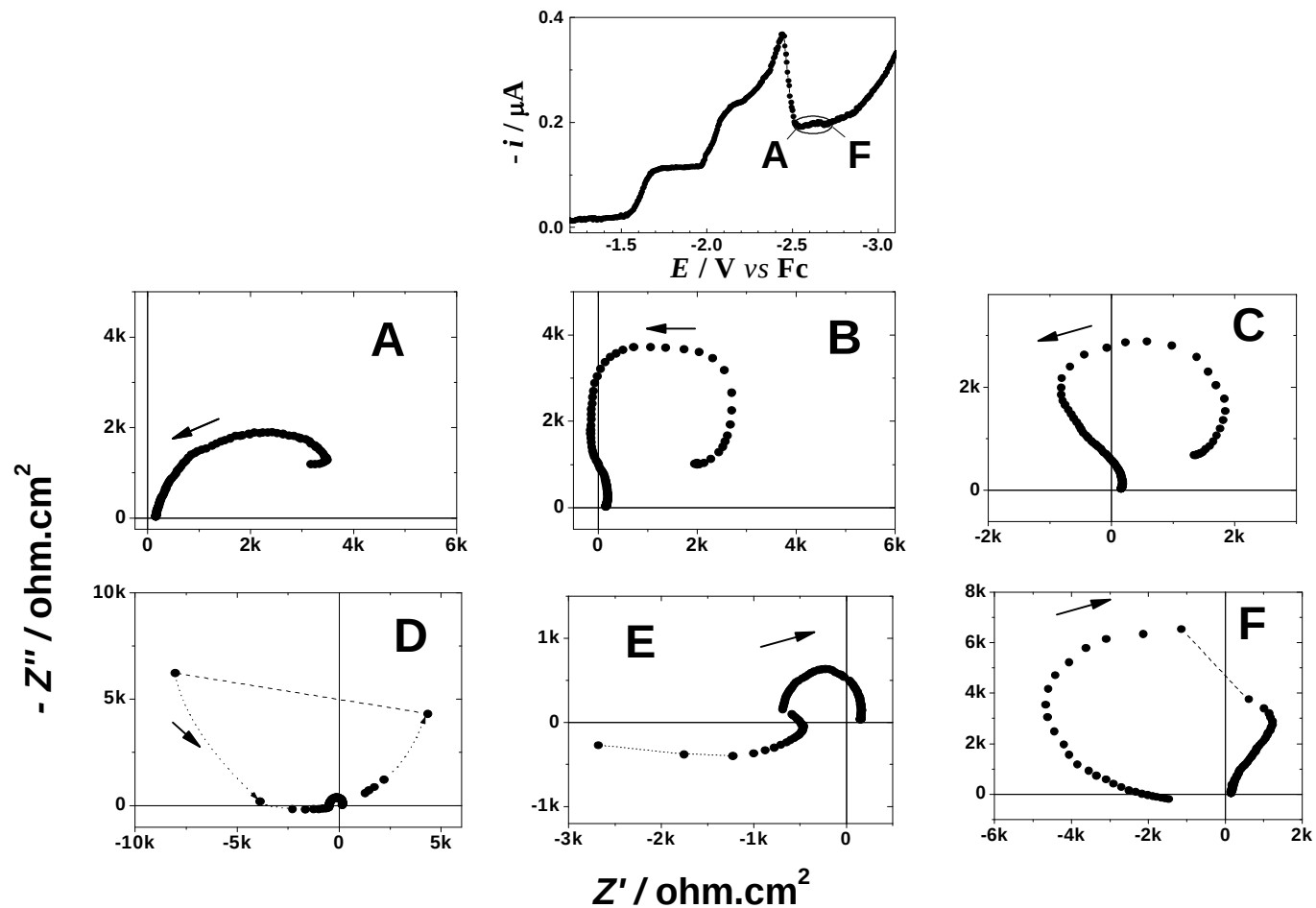


Termination of cationic catalysis

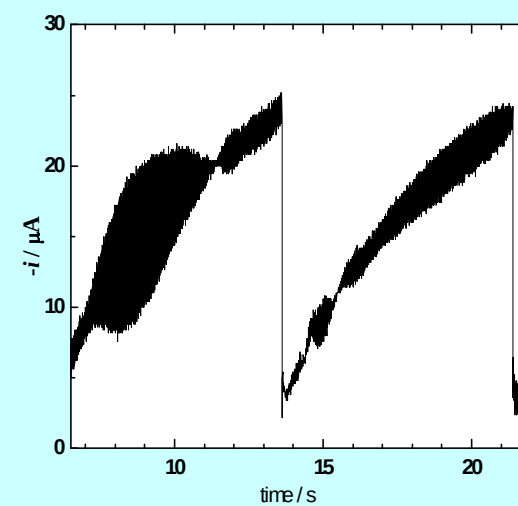
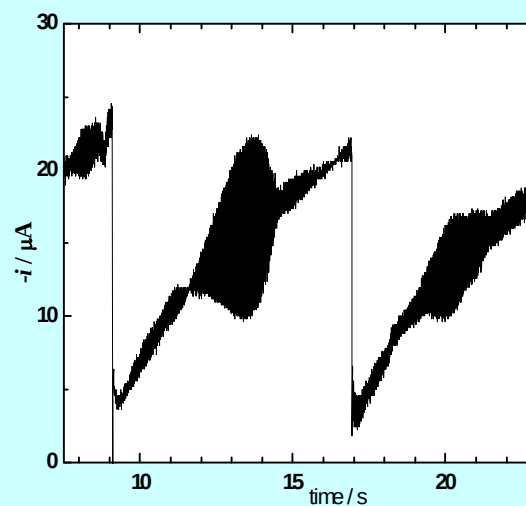
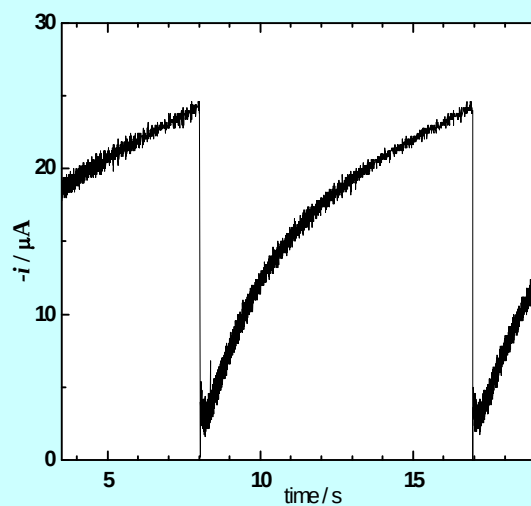
Acceleration effect is terminated at potentials of **K⁺ reduction**



Negative impedance & Impedance discontinuity



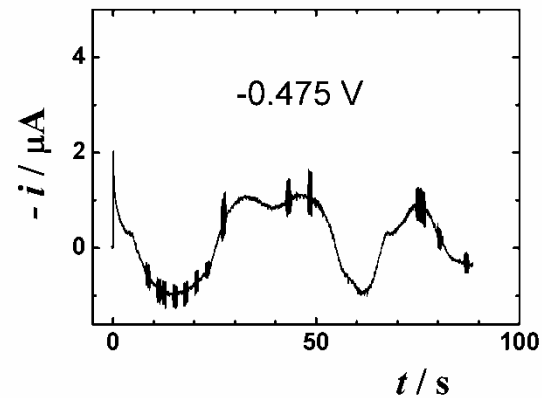
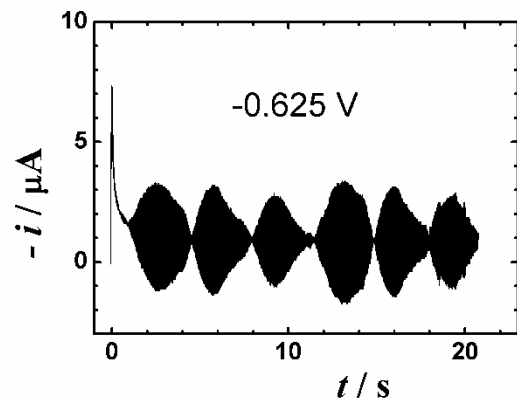
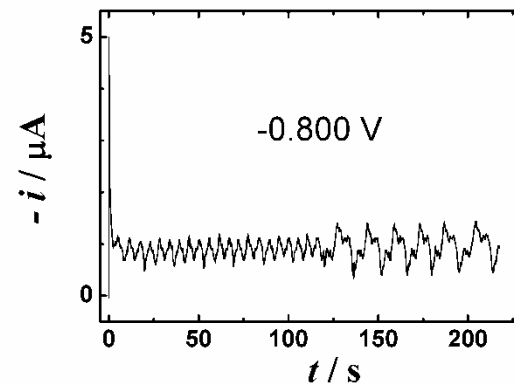
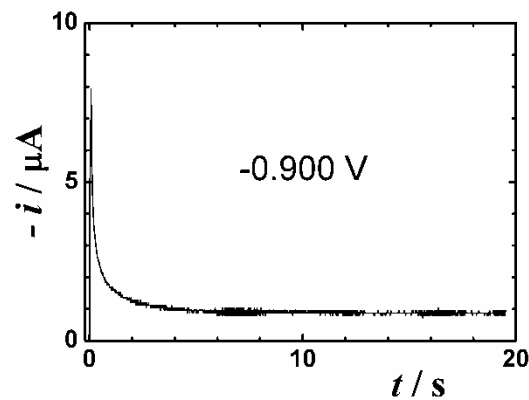
Bursting oscillations at Hg dropping electrode



Chrono-amperometry

(reduction current – time, $E=\text{const.}$)

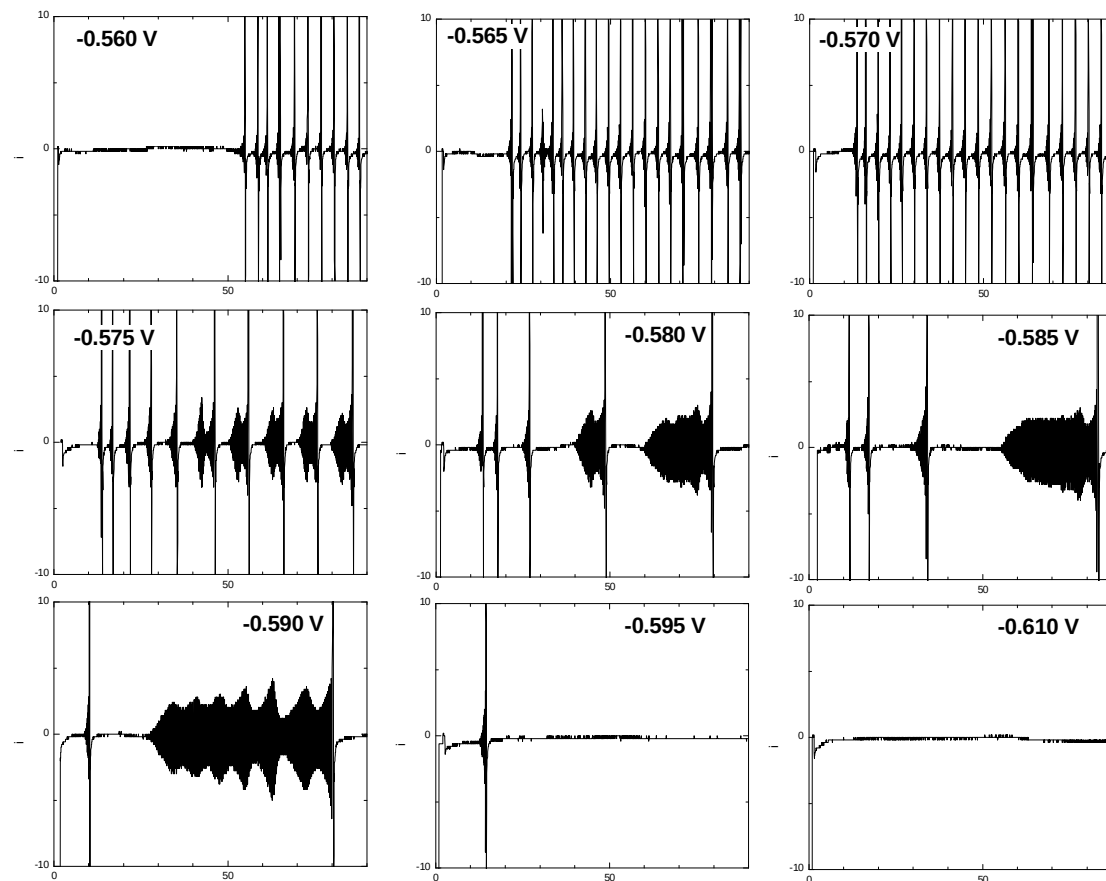
octo-cation



Small changes of potential: large effect on current oscillations

deca-cation

current



time (0 – 100 sec)⁴⁴