Low cost high performances electrochemical analysis

Project ELABORE (MITI CNRS 2021-2022)

Partners :

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- IRD : Agnès Aubouy, Alexis Chaigneau, Valérie Grefeuille
- LSTE : Martin Aina
- Université Abomey-Calavi : Latifou Lagnika
- Associations : Physique sans frontières (François Piuzzi), Chimistes sans Frontières (Manuel Cervera-Marzal), Puya Raimondi (Raymond Campagnolo)

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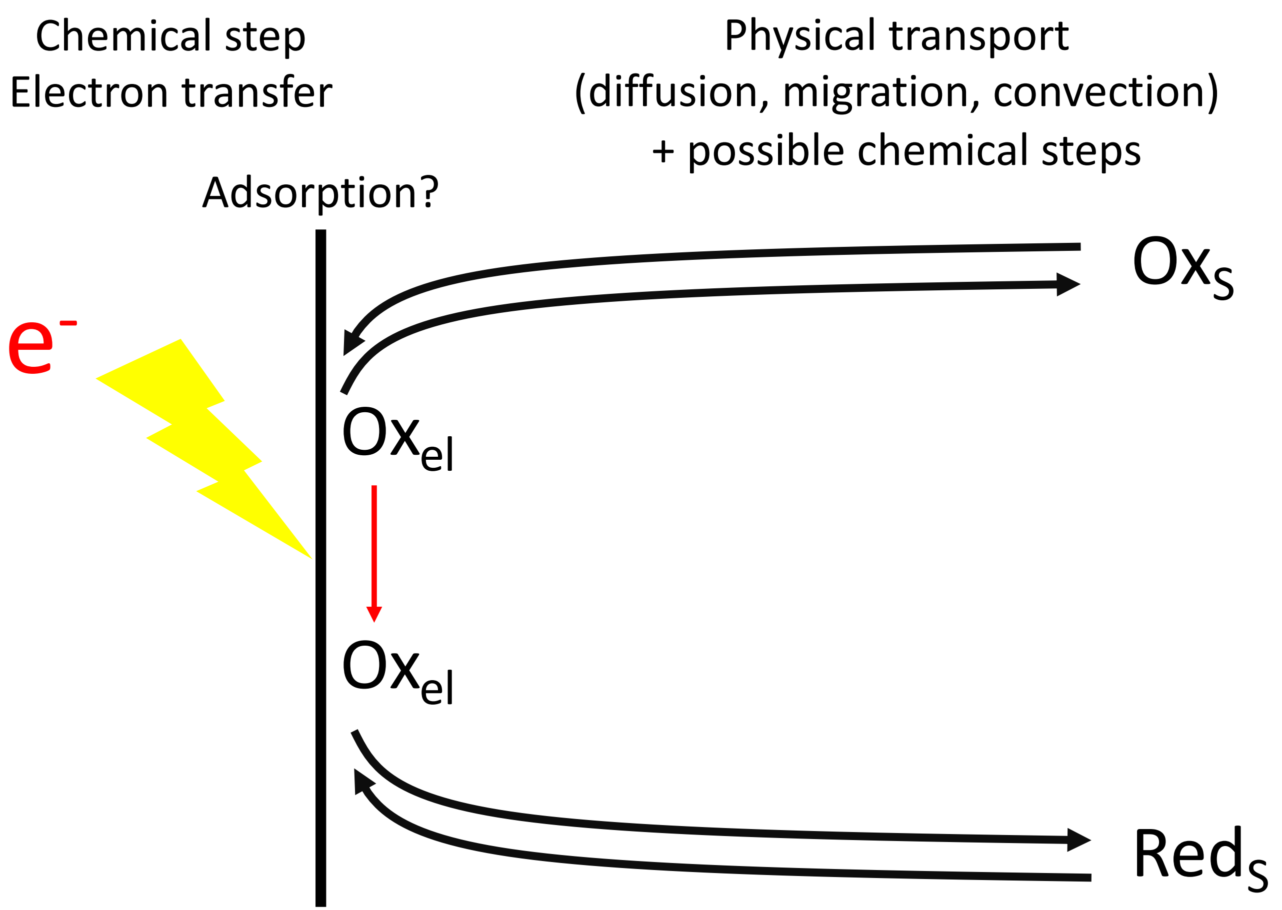
Outline

- Electrochemical analysis and instrumentation
- PassStat 1 : fast and simple
- PassStat 2 : low cost and easy to adapt
- A few applications in Africa
- Some reflexions and perspectives

What is electrochemistry?

Dictionnary :

Science and technique of reciprocal transformation of chemical energy and electrical energy.



Many applications

Energy

Corrosion

Depollution/Envirronnement

Métallurgy

(Bio)sensors

Electronics

Electrochemistry

Photovoltaic

Biology

Fuel cells

Batteries

Electrosynthesis

Nuclear

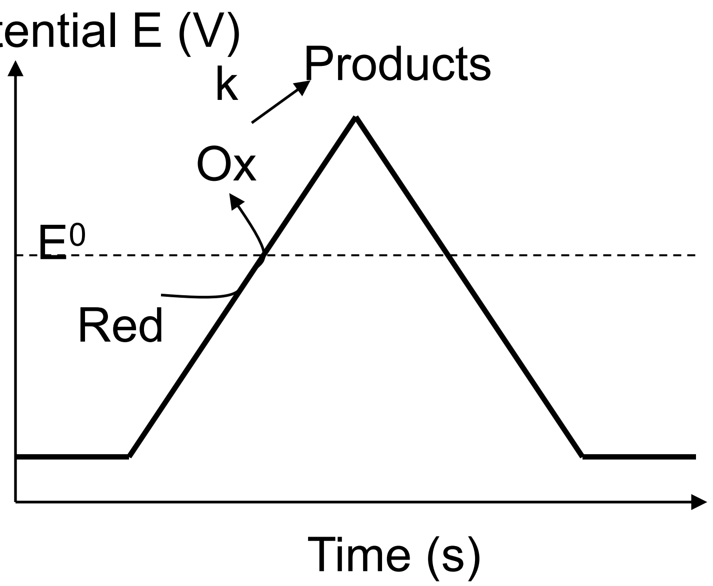
→ Important to train students and implement research in developping countries

Two usual electrochemical techniques

Cyclic voltammetry

Exemple:
Initially on Red in solution

Red → Ox + e^-



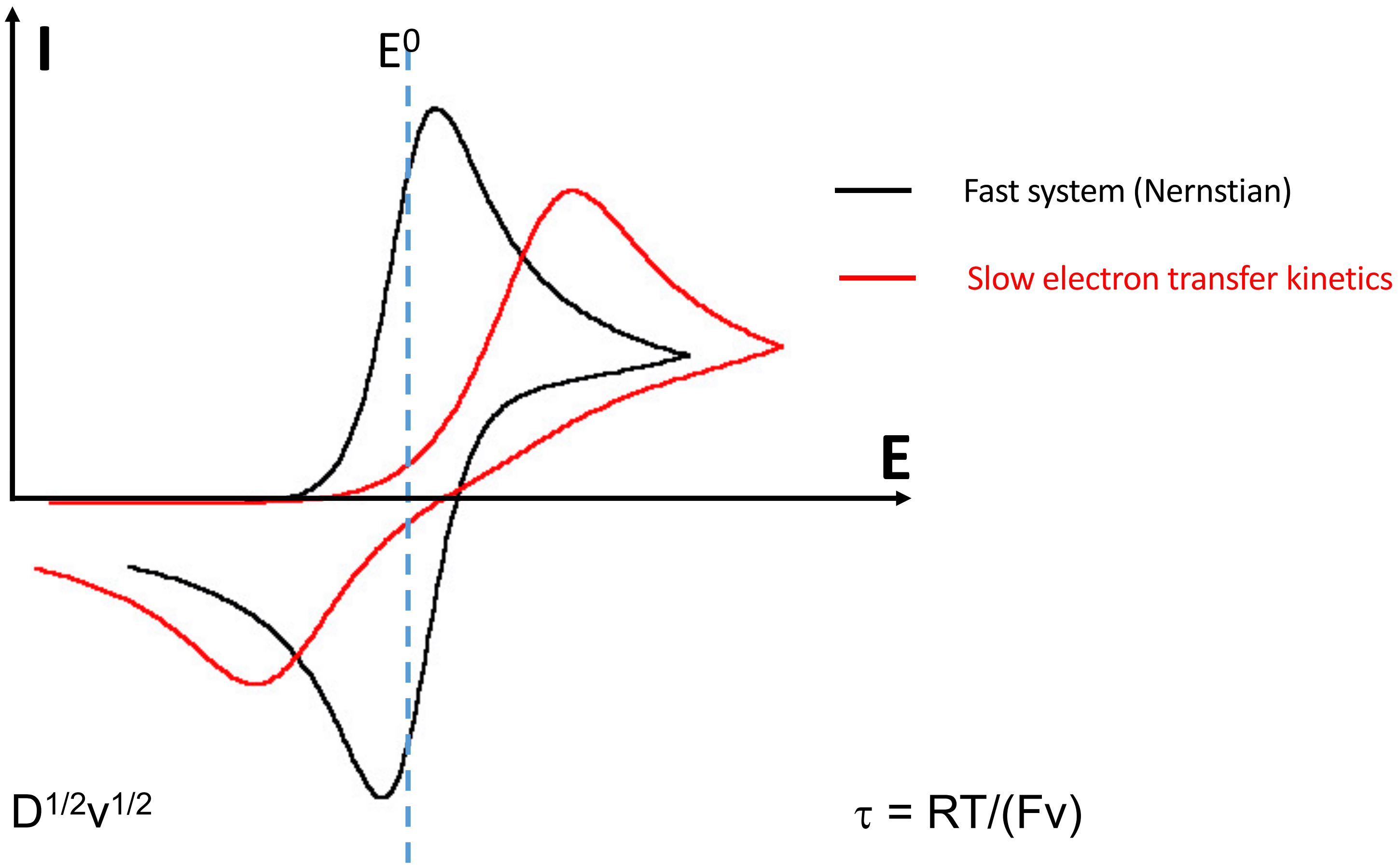
Characteristic timescale: $\tau = RT/(Fv)$

v : scan rate = slope (en V/s)

Two usual electrochemical techniques

Cyclic voltammetry

No chemical reaction



$i \propto D^{1/2}v^{1/2}$

$\tau = RT/(Fv)$

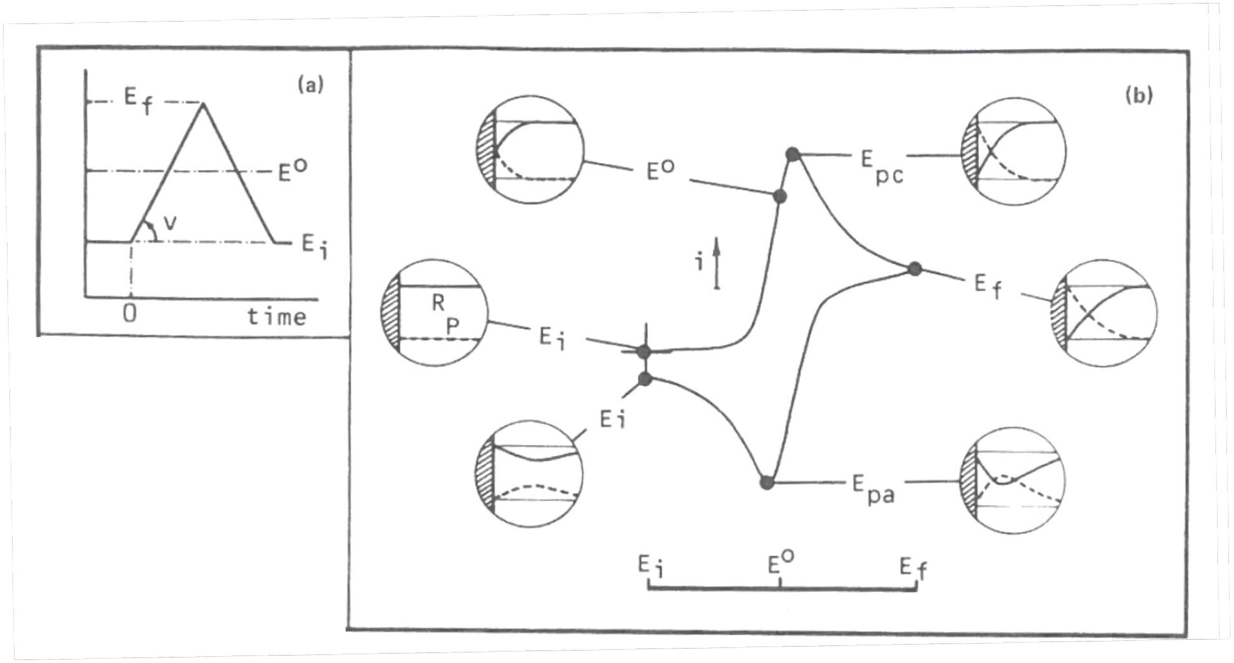
Saveant, JM, Elements of Molecular and Biomolecular Electrochemistry

Two usual electrochemical techniques

CV : reversible behaviour

Peak for the maximum gradient: $$i_p = 0.446FSC\sqrt{\frac{DFv}{RT}} \propto \sqrt{v}$$

Peak to peak difference ΔE_p: 59 mV (à 25°C)

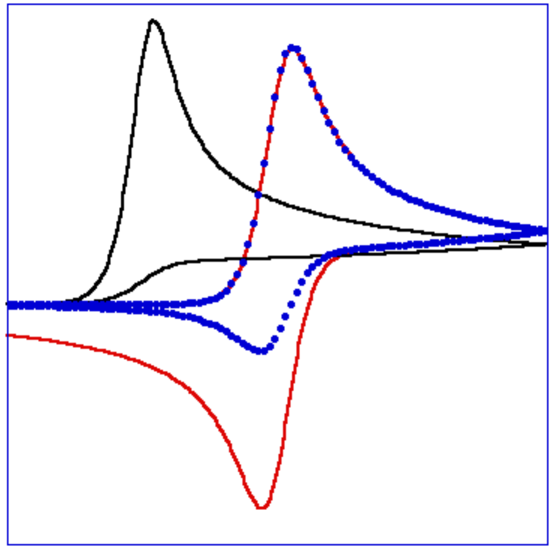


From Amatore, in Organic Electrochemistry, an introduction and a guide

Two usual electrochemical techniques

Influence of a chemical reaction

$$\text{Red} \rightleftharpoons \text{Ox} + e^- \longrightarrow \text{Products}$$



No chemical reaction
Fast reaction
Moderately fast reaction

Slow scan rates

Peak shift
No backward current

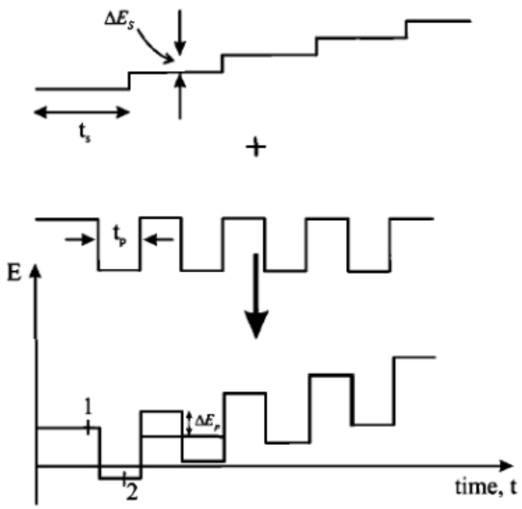
Fast scan rates

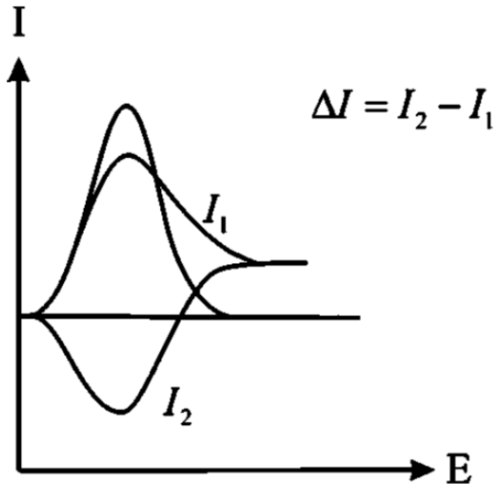
E^0 and k

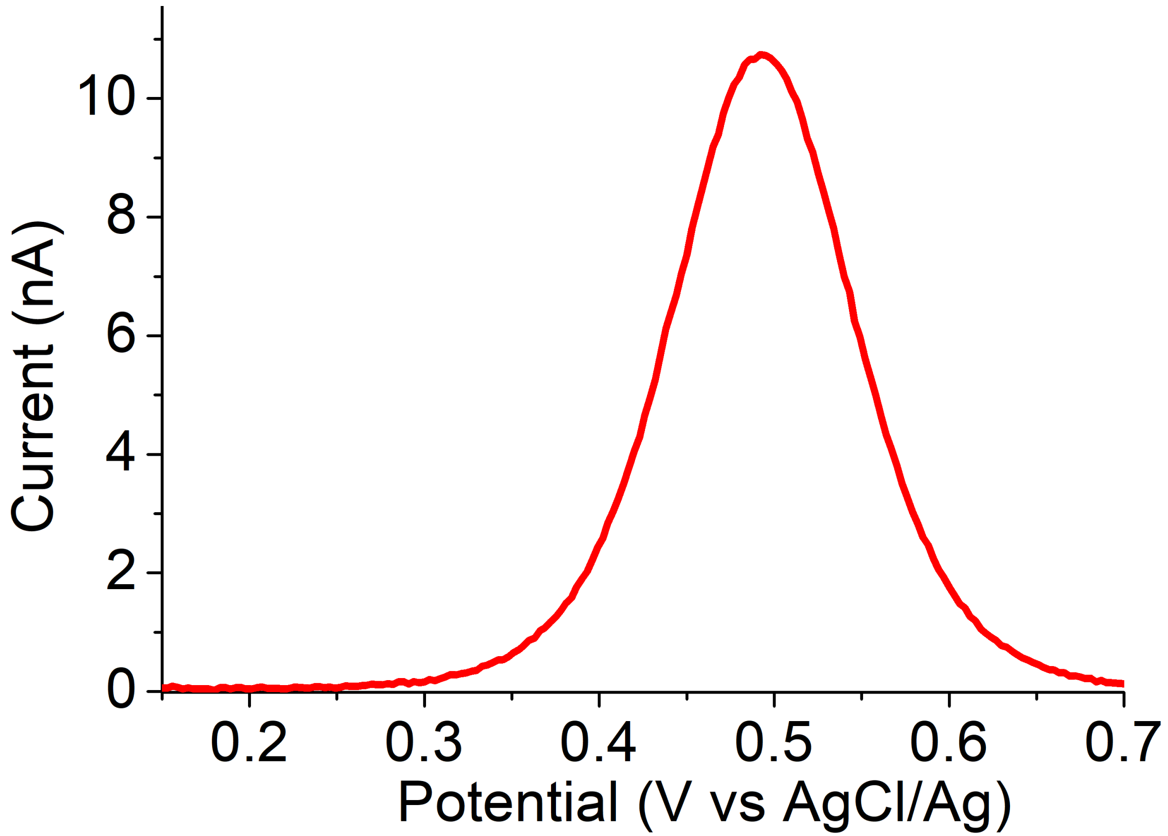
Analysis of current peaks provides information on mechanism

Two usual electrochemical techniques

Square wave voltammetry



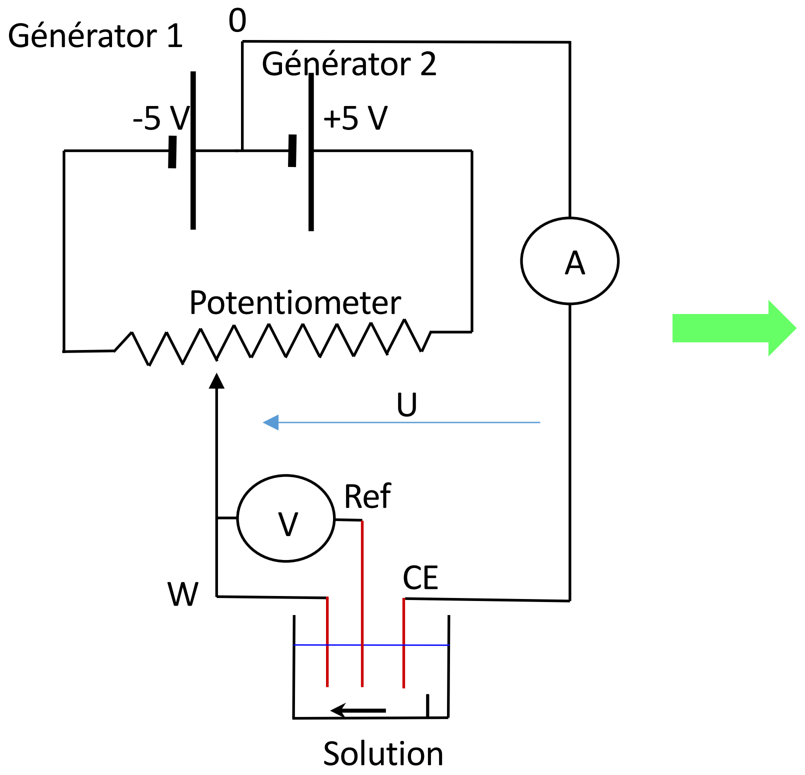




More sensitive !

How to properly perform electrochemical experiments: 3 electrode systems

Concept: add a reference electrode for which $I_{ref} = 0$.



If $I_{ref} = 0$, $E_{ref} = C^{te}$ (Nersnt…)

Control of $E = V_W - V_{ref}$ with a voltmeter

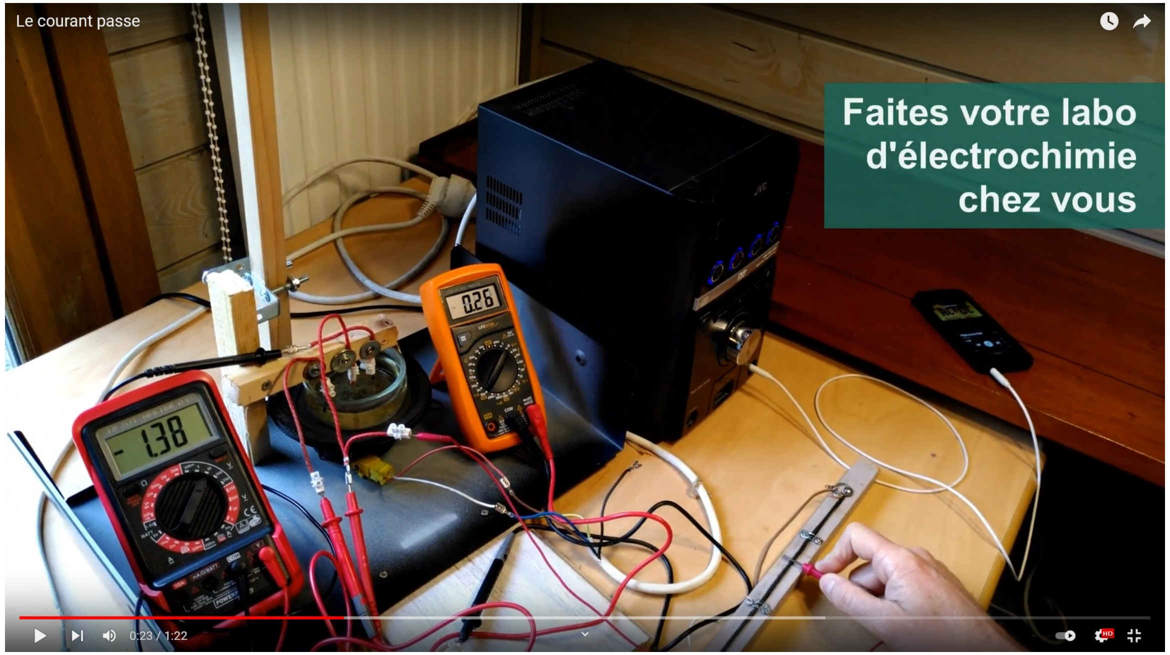
Simply adjust U to get the E you want

Then $V_{CE} - V_{ref}$ is no more important

Possible to do I-E curves!

From funny unconventional teaching…

Le courant passe: electrochemistry@home



https://www.youtube.com/playlist?list=PL4-5RJd2oIUwrvTe3DuxuikS14xa0iJpy

An electrochemical series:

- To distract students, colleagues and friends
- To suggest students to make experiments at home (in safe conditions)
- To do a maximum with a minimum

… to something almost serious.

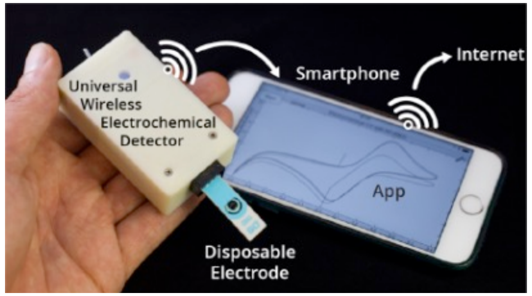
Raymond Campagnolo (Puya Raymondi)
Why not making a real low cost potentiostat?
As simple as possible!

A few low cost potentiostats…

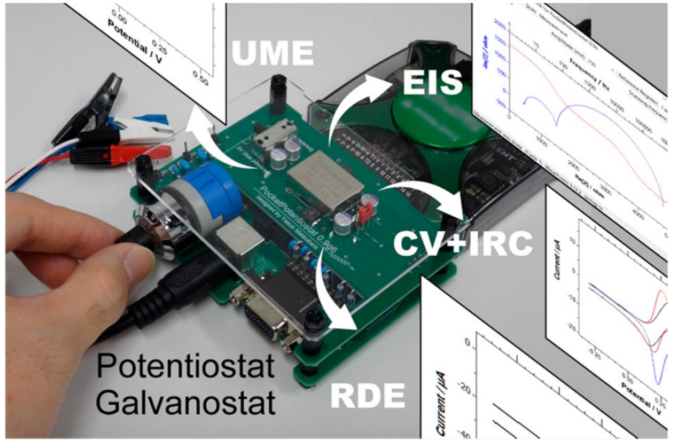
Bibliographie

[2] A. Nemiroski, D.C. Christodouleas, J.W. Hennek, A.A. Kumar, E.J. Maxwell, M.T. Fernández-Abedul, G.M. Whitesides, Universal mobile electrochemical detector designed for use in resource-limited applications, PNAS 111 (33) (2014) 11984–11989,
[3] A. Ainla, M.P.S. Mousavi, M.-N. Tsaloglou, J. Redston, J.G. Bell, M.T. Fernández-Abedul, G.M. Whitesides, Open-source potentiostat for wireless electrochemical detection with smartphones, Anal. Chem. 90 (10) (2018) 6240–6246
[4] Y.C. Li, E.L. Melenbrink, G.J. Cordonier, C. Boggs, A. Khan, M.K. Isaac, L.K. Nkhonjera, D. Bahati, S.J. Billinge, S.M. Haile, R.A. Kreuter, R.M. Crable, T.E. Mallouk, An easily fabricated low-cost potentiostat coupled with user-friendly software for introducing students to electrochemical reactions and electroanalytical techniques, J. Chem. Educ. 95 (9) (2018) 1658–1661,
[5] A.A. Rowe, A.J. Bonham, R.J. White, M.P. Zimmer, R.J. Yadgar, T.M. Hobza, J.W. Honea, I. Ben-Yaacov, K.W. Plaxco, M. Wanunu, CheapStat: An opensource, ‘‘do-it-yourself’’ potentiostat for analytical and educational applications, PLoS ONE 6 (9) (2011) e23783,
[6] P. Irving, R. Cecil, M.Z. Yates, MYSTAT: a compact potentiostat/galvanostat for general electrochemistry measurements, HardwareX. 9 (2021) e00163,
[7] C. Mercer, R. Bennett, P. Conghaile, J. Rusling, D. Leech, Glucose biosensor based on open-source wireless microfluidic potentiostat, Sensors Actuators B Chemical.290 (2019) 616–624
[8] G.N. Meloni, Building a microcontroller based potentiostat: a inexpensive and versatile platform for teaching electrochemistry and instrumentation, J. Chem. Educ. 93 (7) (2016) 1320–1322
[9] S.T. Rajendran, E. Scarano, M.H. Bergkamp, A.M. Capria, C.-H. Cheng, K. Sanger, G. Ferrari, L.H. Nielsen, E.-T. Hwu, K. Zór, A. Boisen, Modular, lightweight, wireless potentiostat-on-a-disc for electrochemical detection in centrifugal microfluidics, Anal. Chem. 91 (18) (2019) 11620–11628
[10] M.D.M. Dryden, A.R. Wheeler, D.T. Eddington, DStat: a versatile, open-source potentiostat for electroanalysis and integration, PLoS ONE 10 (10) (2015) e0140349
[11] Y. Matsubara, A small yet complete framework for a potentiostat, galvanostat, and electrochemical impedance spectrometer, J. Chem. Educ. 98 (10) (2021) 3362–3370
[13] https://iorodeo.com/collections/cheapstat-open-source-potentiostat, (n.d.). https://iorodeo.com/collections/cheapstat-open-source-potentiostat.
[14] M.W. Glasscott, M.D. Verber, J.R. Hall, A.D. Pendergast, C.J. McKinney, J.E. Dick, SweepStat: a build-it-yourself, two-electrode potentiostat for
macroelectrode and ultramicroelectrode studies, J. Chem. Educ. 97 (1) (2020) 265–270, https://doi.org/10.1021/acs.jchemed.9b00893.

Whitesides



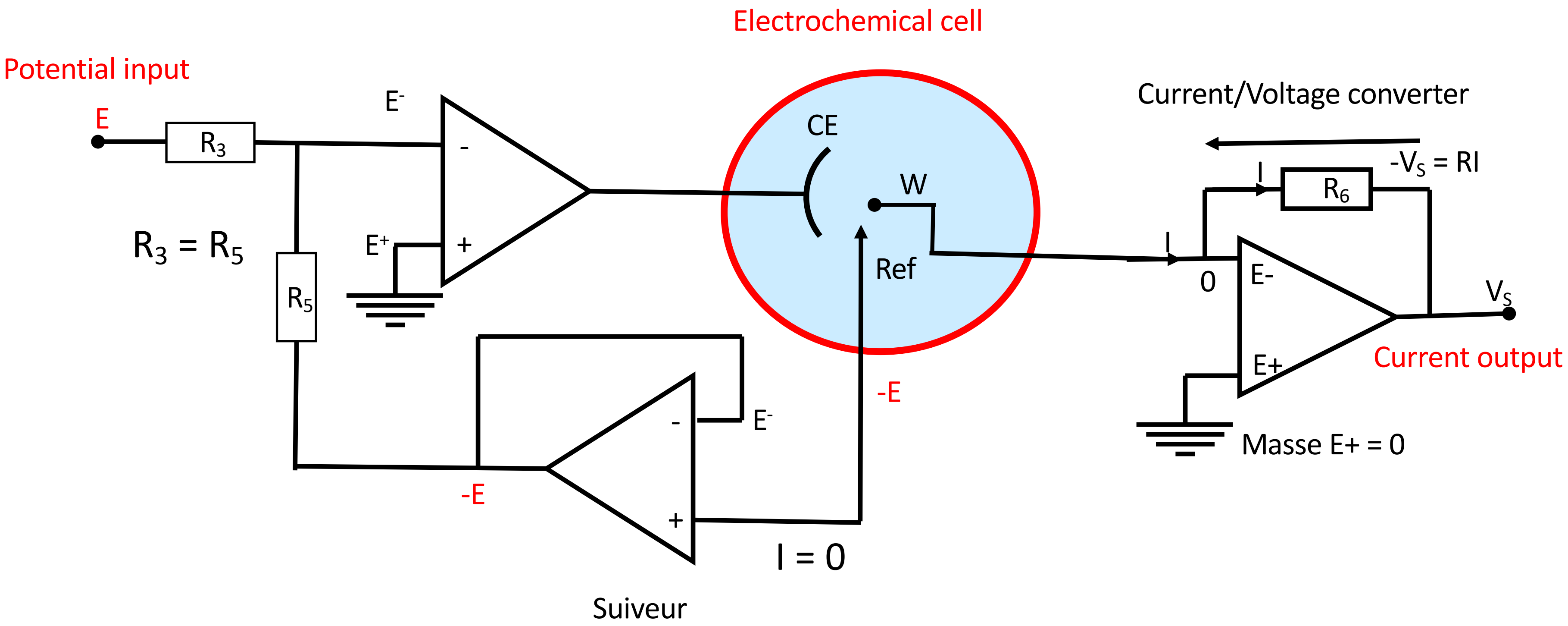
Matsubara



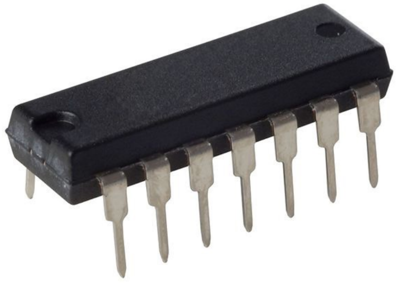
- Few descriptions of the limits
- Hard to repare
- Design complicated

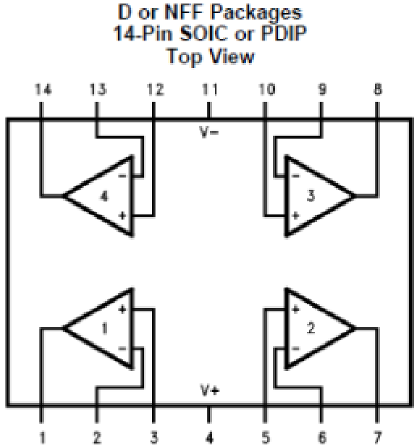
Reminder: basic potentiostat scheme

3 électrodes scheme, only 3 amplifiers



LMC 6484

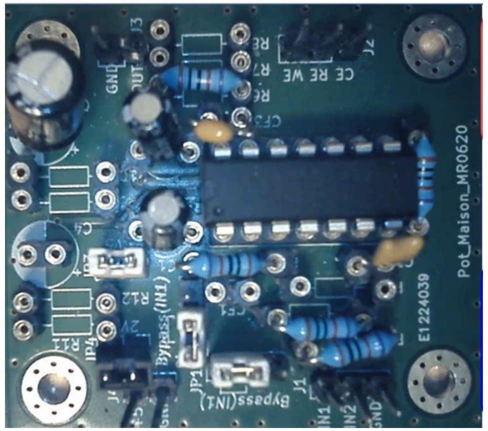




Simple electronic components

PassStat 1 : fast and simple

PassStat 1.0



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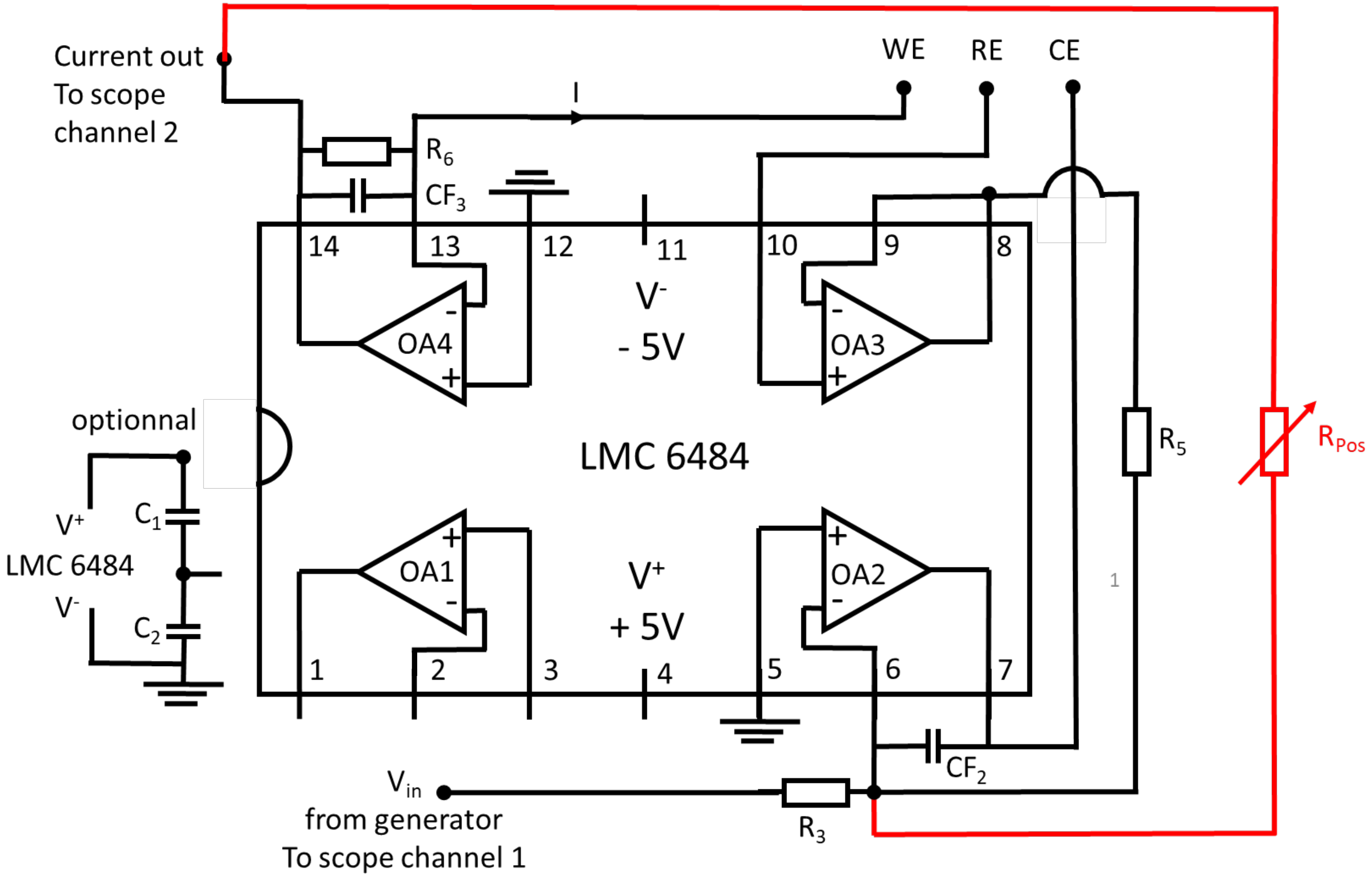


The most simple !

Necessitates power supplies, generator and oscilloscope

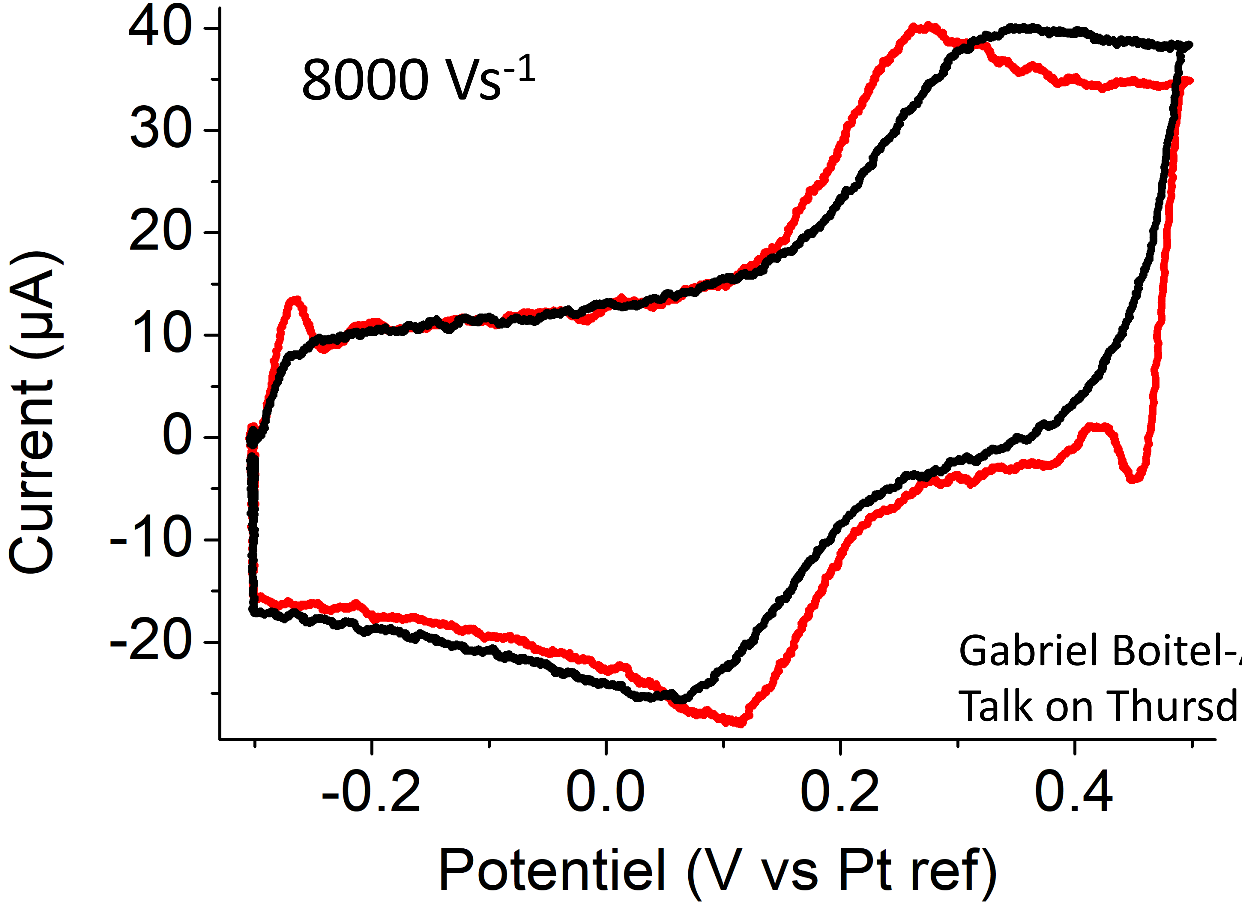
Analog Discovery 2 : 304 €

No dedicated soft for electrochemistry (see however Matsubara)

PassStat 1: fast and simple

Performances: PassStat 1.0

1 mM Ferrocene
In CH_3CN + 0.1 M $TBAPF_6$
Micrometric electrode

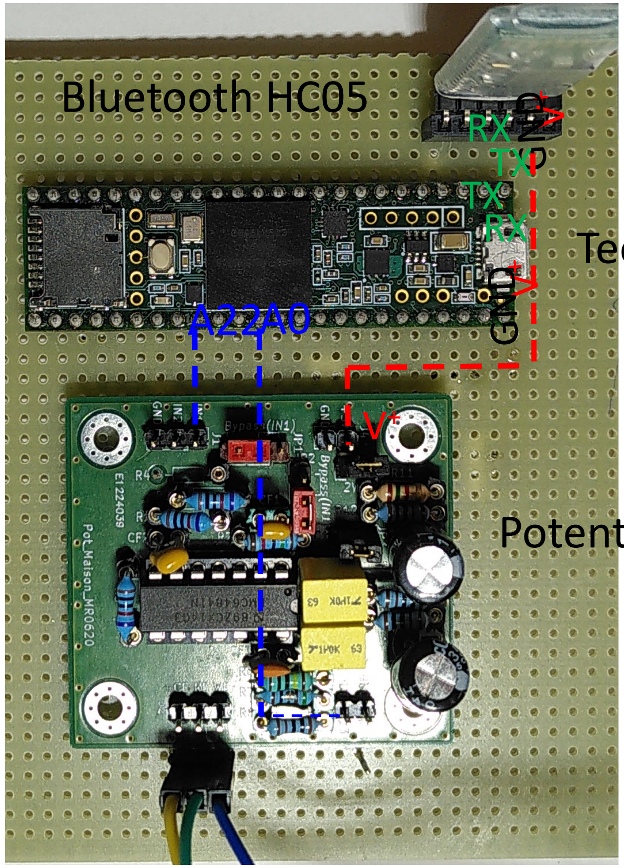


Gabriel Boitel-Aullen
Talk on Thursday !

Rather fast !
Rather for confirmed electrochemists

PassStat 2: low cost and easy to adapt

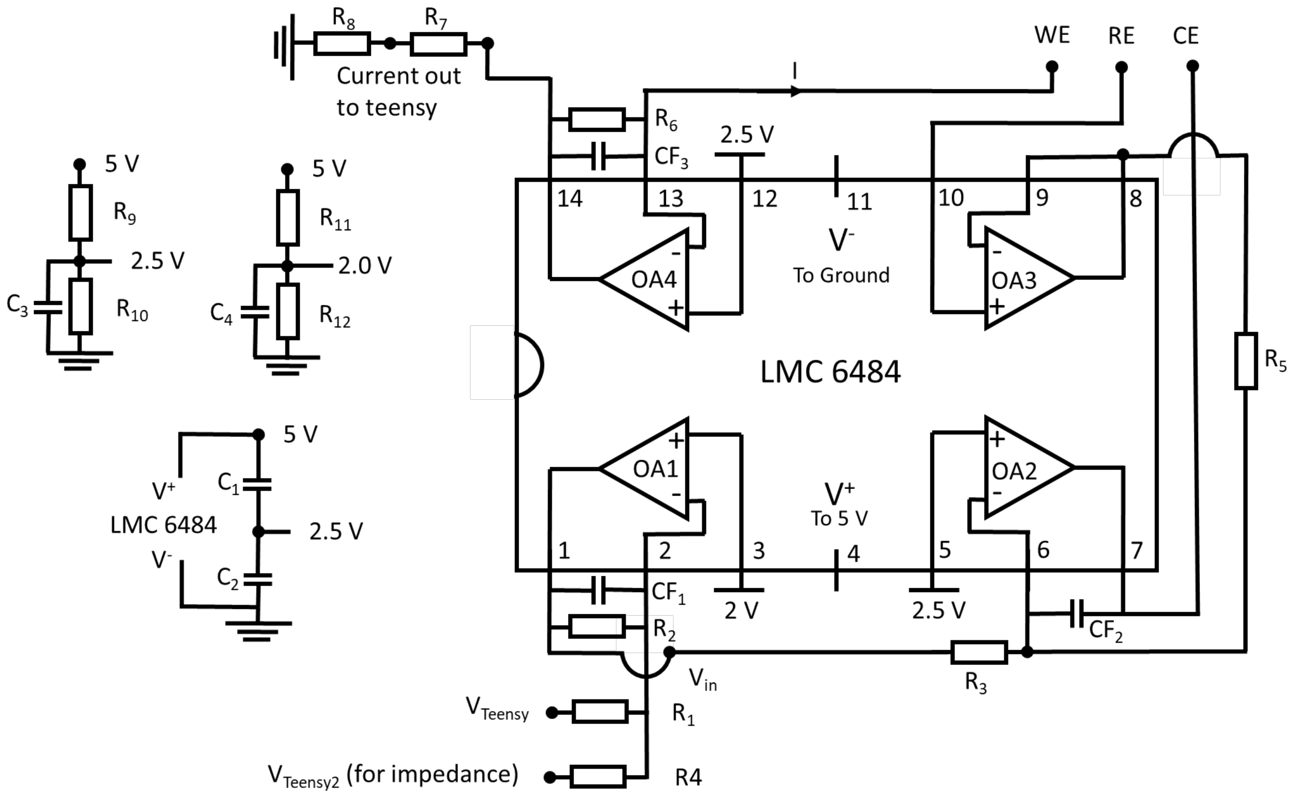
PassStat 2.0, 2.1 et 2.2



Teensy 3.6 card

Potentiostat

Electrodes



Works on computer or through Bluetooth

Price: between 50 and 80 €

Limited scan rate (100 Vs^{-1})

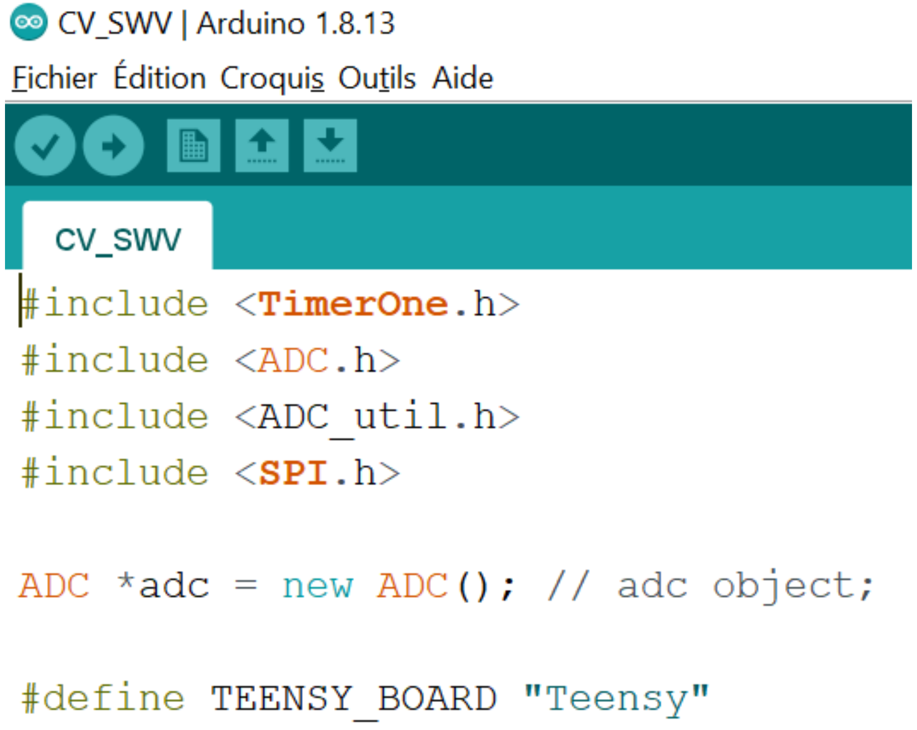
Limited compliance (± 2.4 V)

Take care of calibration!

PassStat 2: low cost and easy to adapt

Open source considerations

Arduino core



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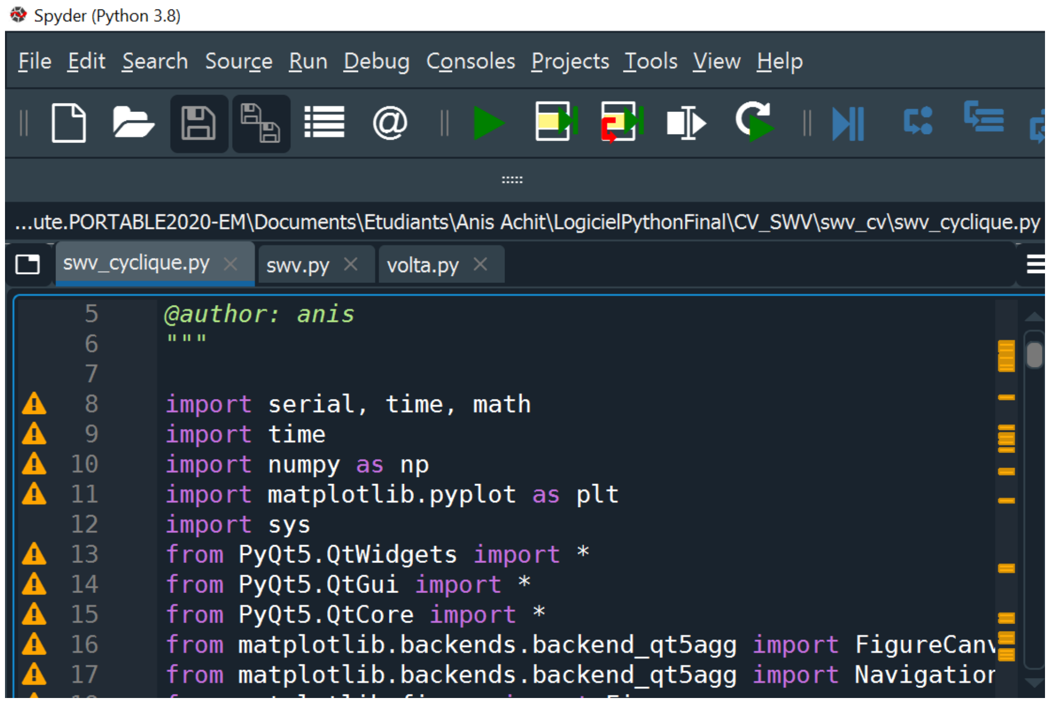
Python interface

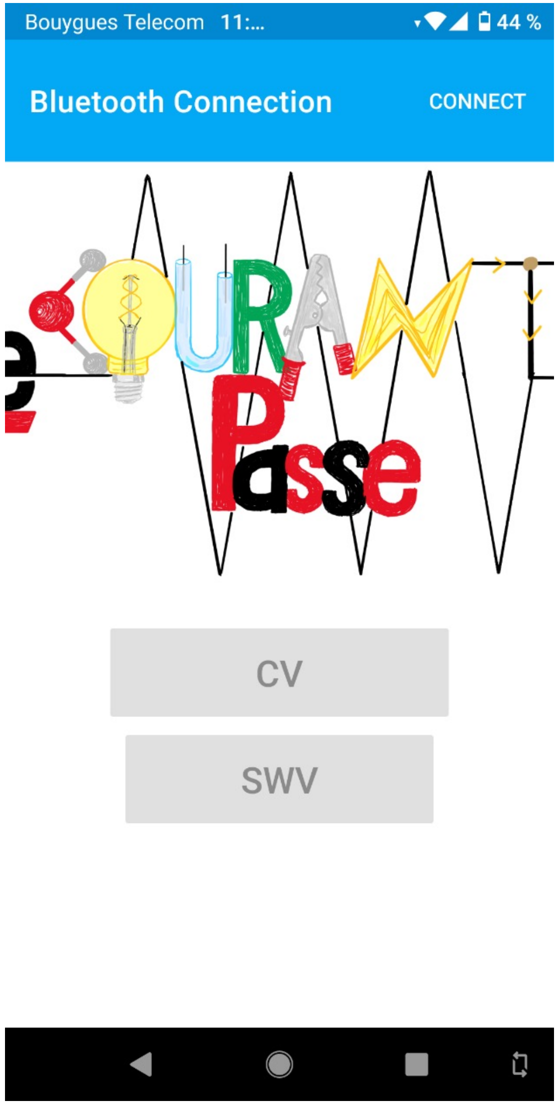


PassStat 2: low cost and easy to adapt

Open source considerations

Application Android conçue avec Android Studio

Stage Anis Achit, 3 mois, étudiant M1 ingénierie



Paper in Hardware X (Caux et al., 2022)
Dépôt sur Zenono
Wiki sur https://ohwr.org/project/passstat/wikis/home
Projet GitHub
Certifié par l'Open Source Hardware Association
A diffuser sans restrictions !

Open Source Licenses	
Hardware	CERN-OHL-S-2.0
Software	GPL-3.0-or-later
Documentation	CC-BY-4.0

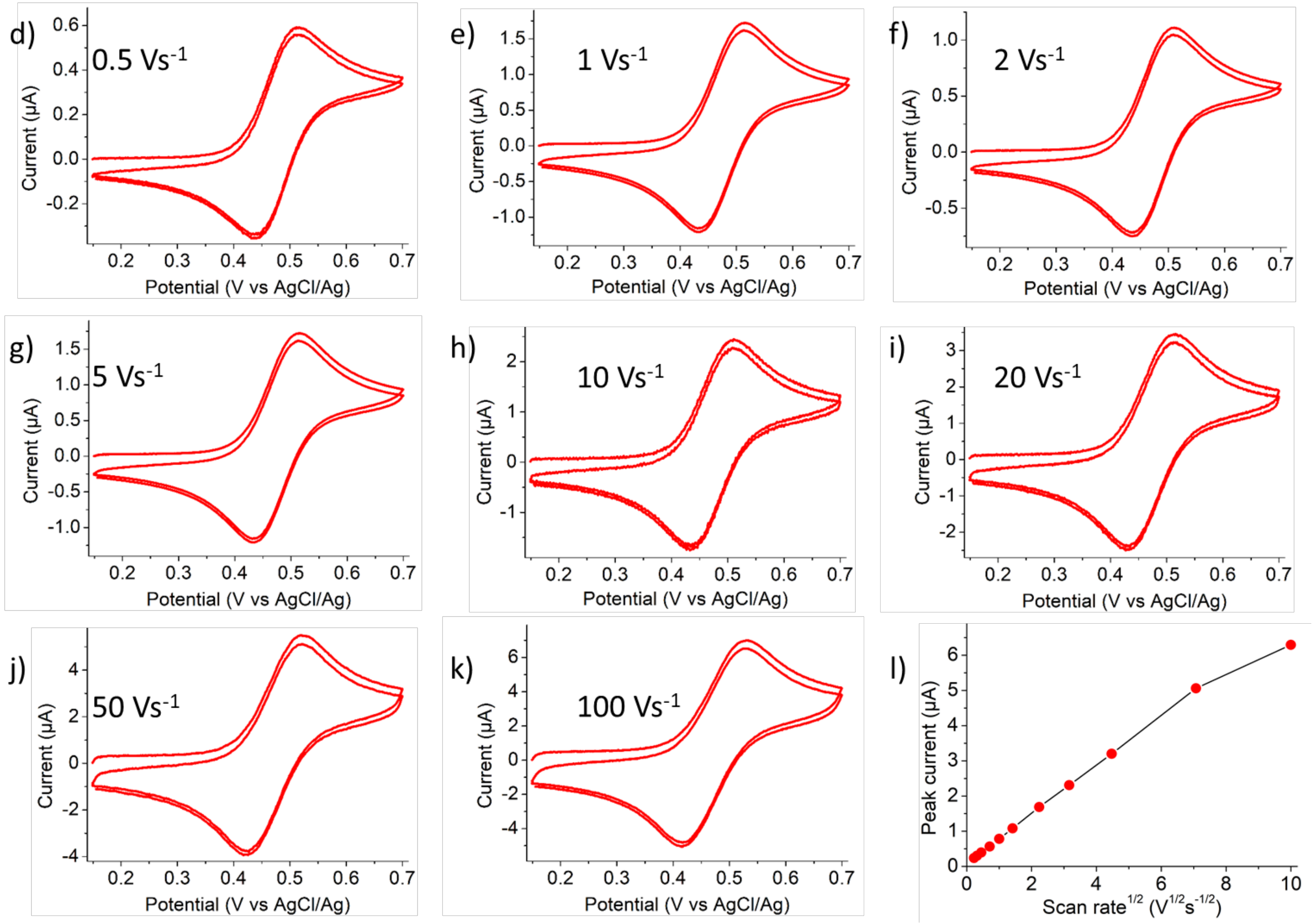
OSHW FR000017

PassStat 2: low cost and easy to adapt

Validation

$$Fc \rightleftharpoons Fc^{+} + 1e^{-}$$

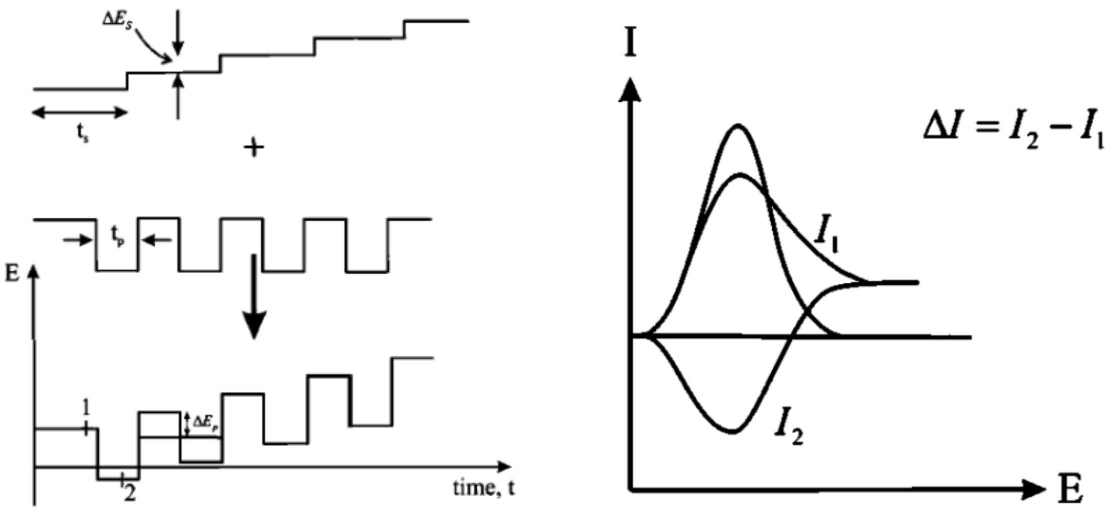
Standard conditions:
1 mM Ferrocene
inCH_3CN + 0.1 M $TBAPF_6$
Pt ∅ 0.5 mm



OK!!!

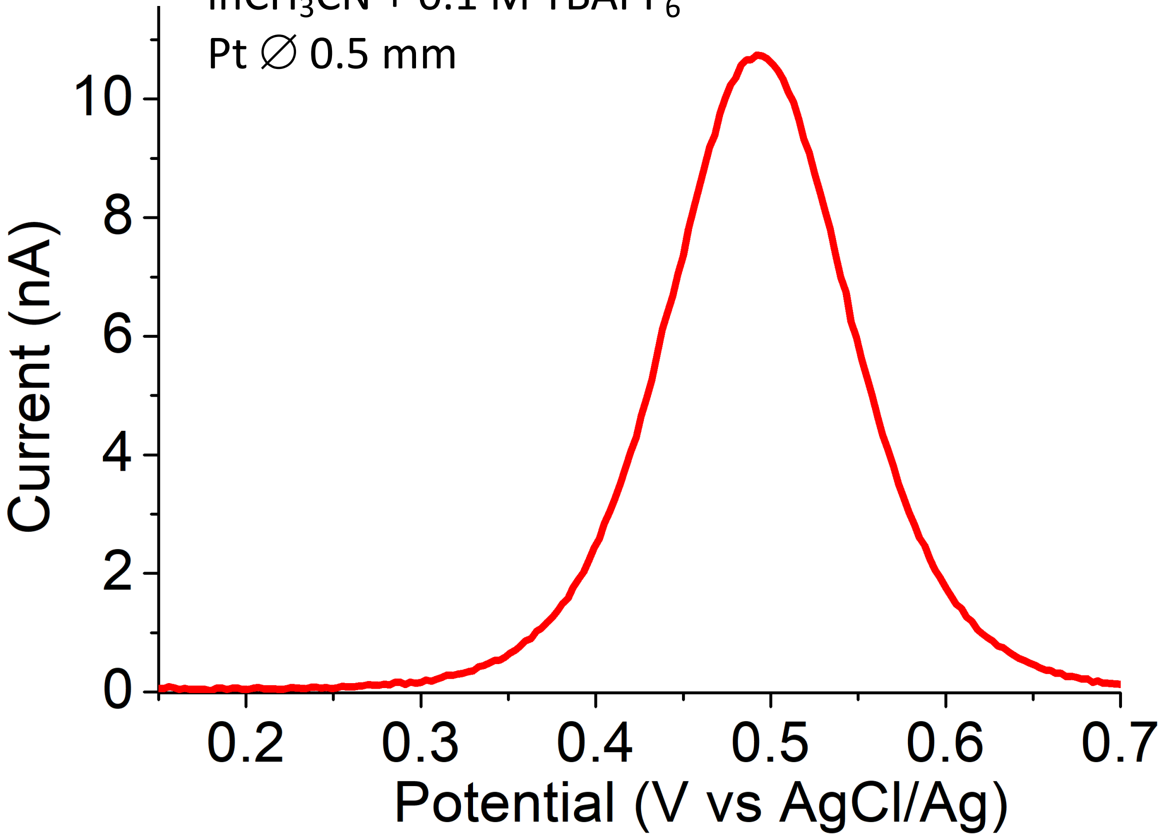
PassStat 2: low cost and esy to adapt

Validation: Square Wave Voltammetry



From Compton, understanding electrochemistry

Standard conditions:
1 mM Ferrocene
inCH_3CN + 0.1 M $TBAPF_6$
Pt ∅ 0.5 mm



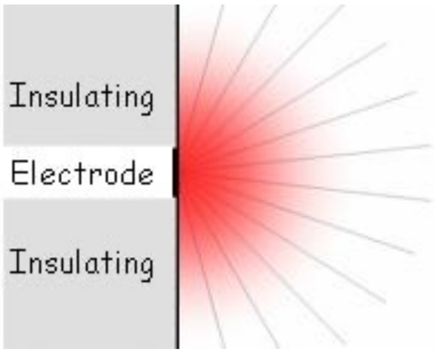
OK!!!

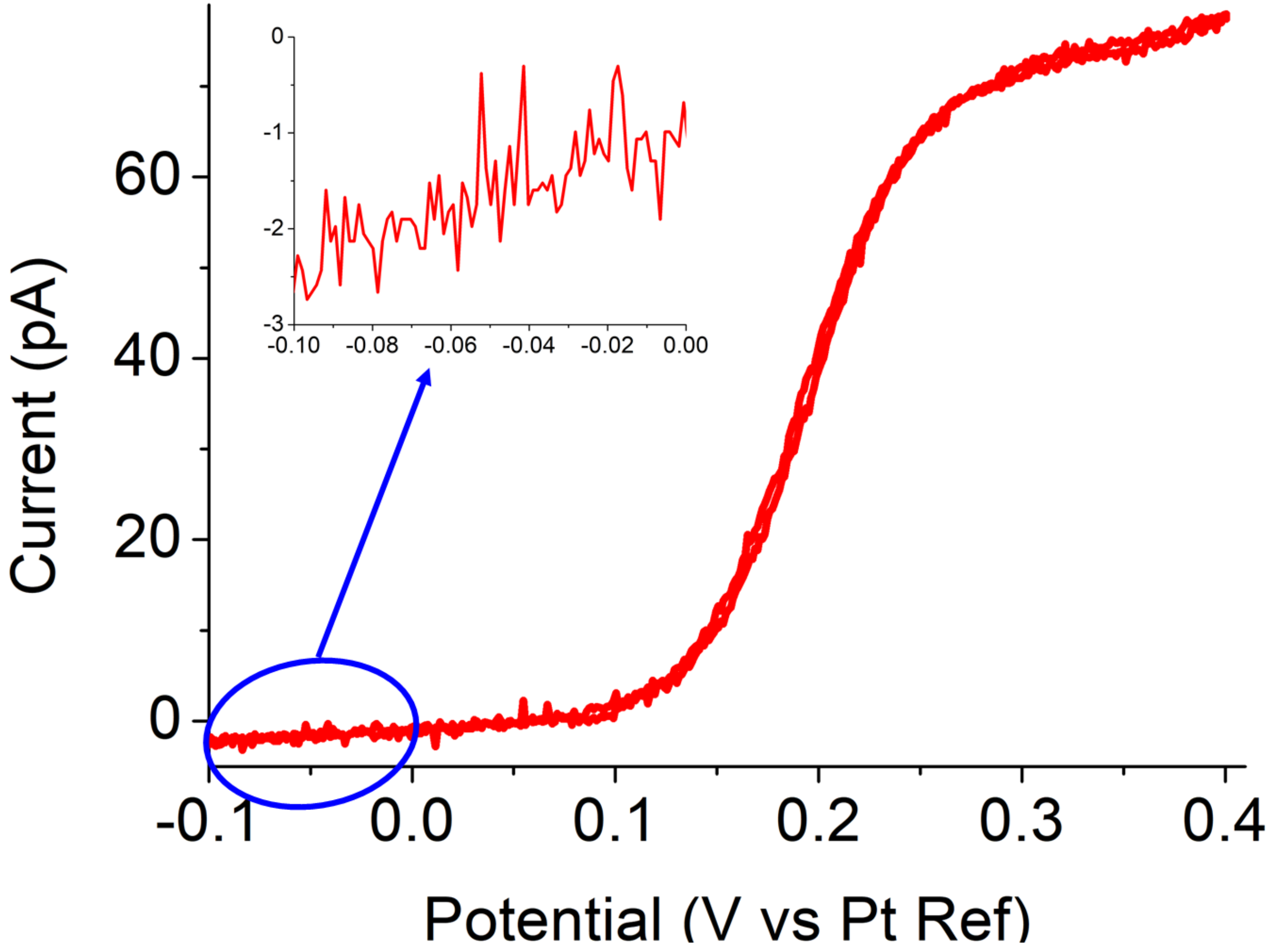
PassStat 2: low cost and easy to adapt

Validation: low currents

Extreme conditions :
Ferrocene 25 µM
in CH_3CN + 1 mM $TBAPF_6$
UME Pt ∅ 4 µm
Scan rate 20 mVs^{-1}

Spherical diffusion





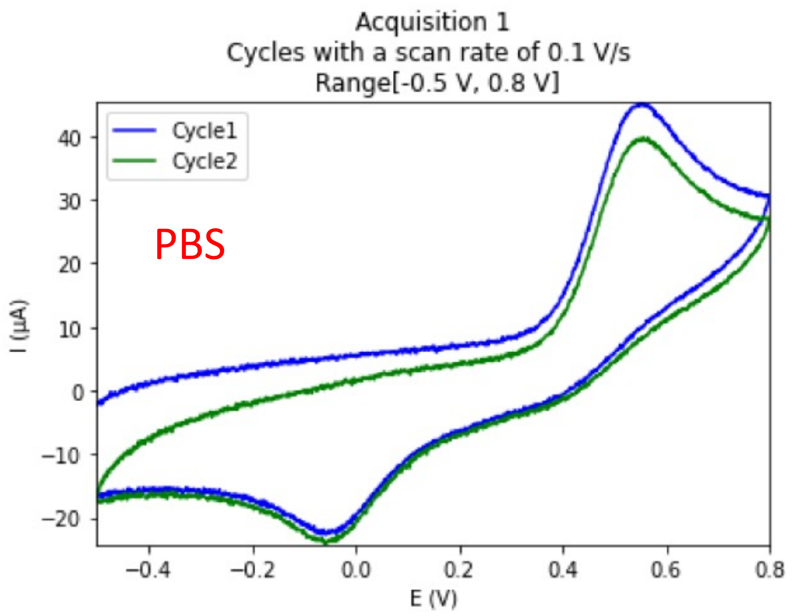
Very good S/N!
No stray capacitance

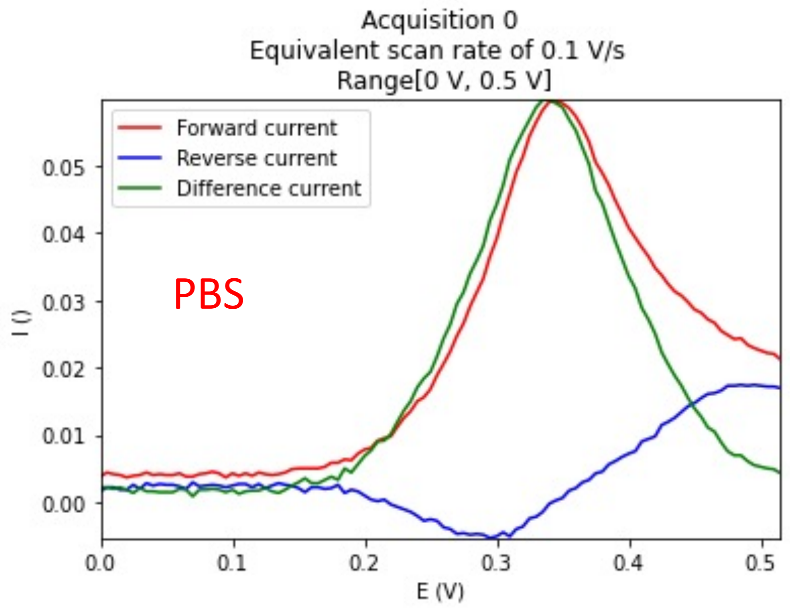
A few examples

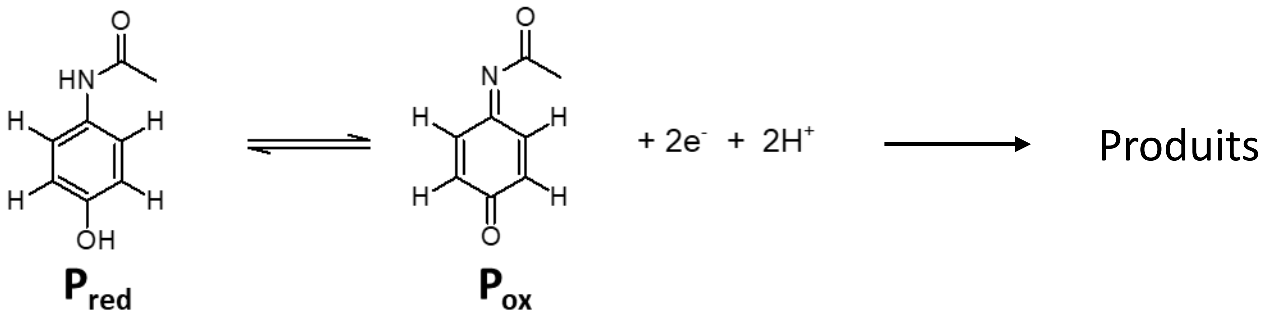
A few examples

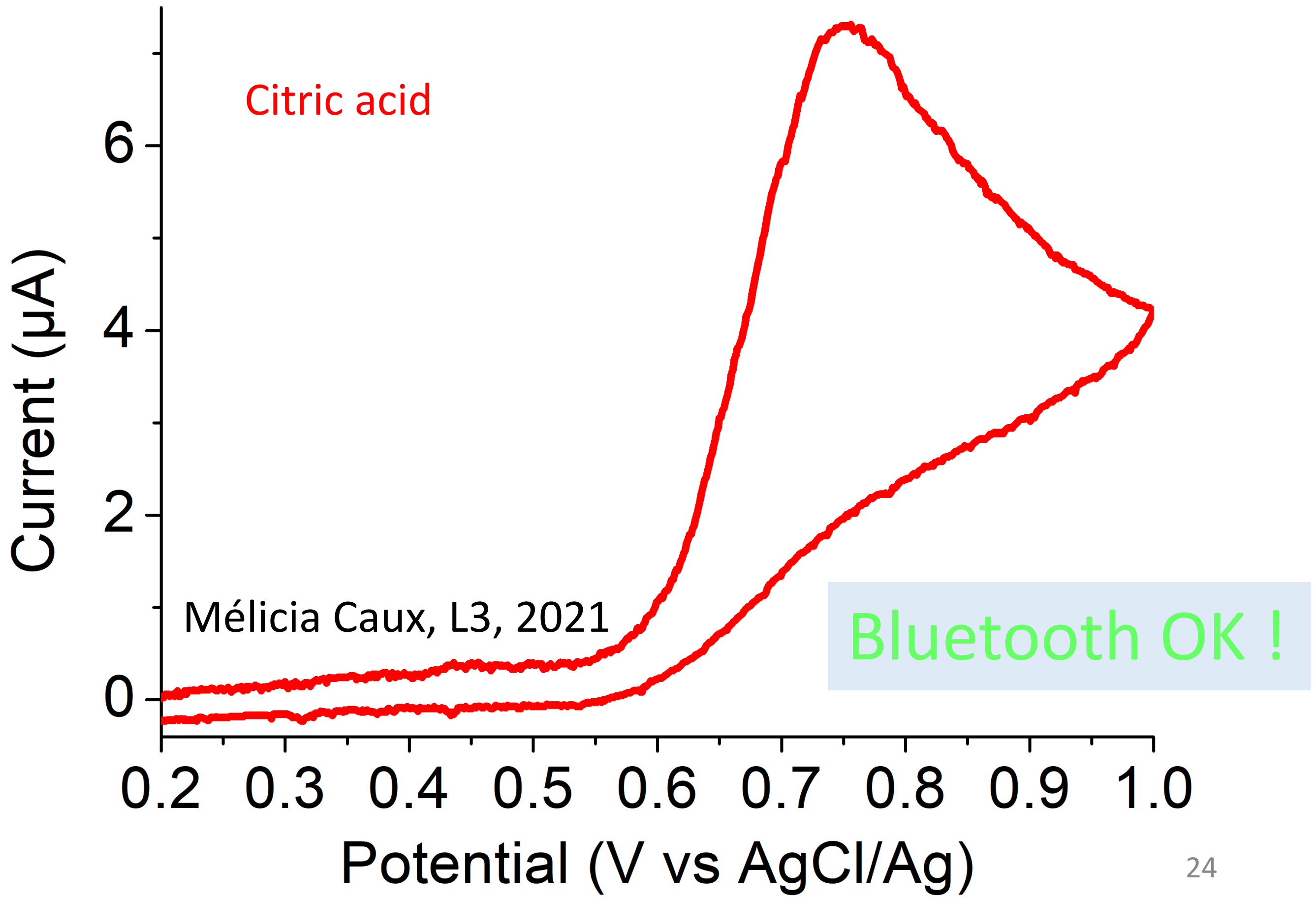
A few examples: paracetamol

Drugs: paracetamol



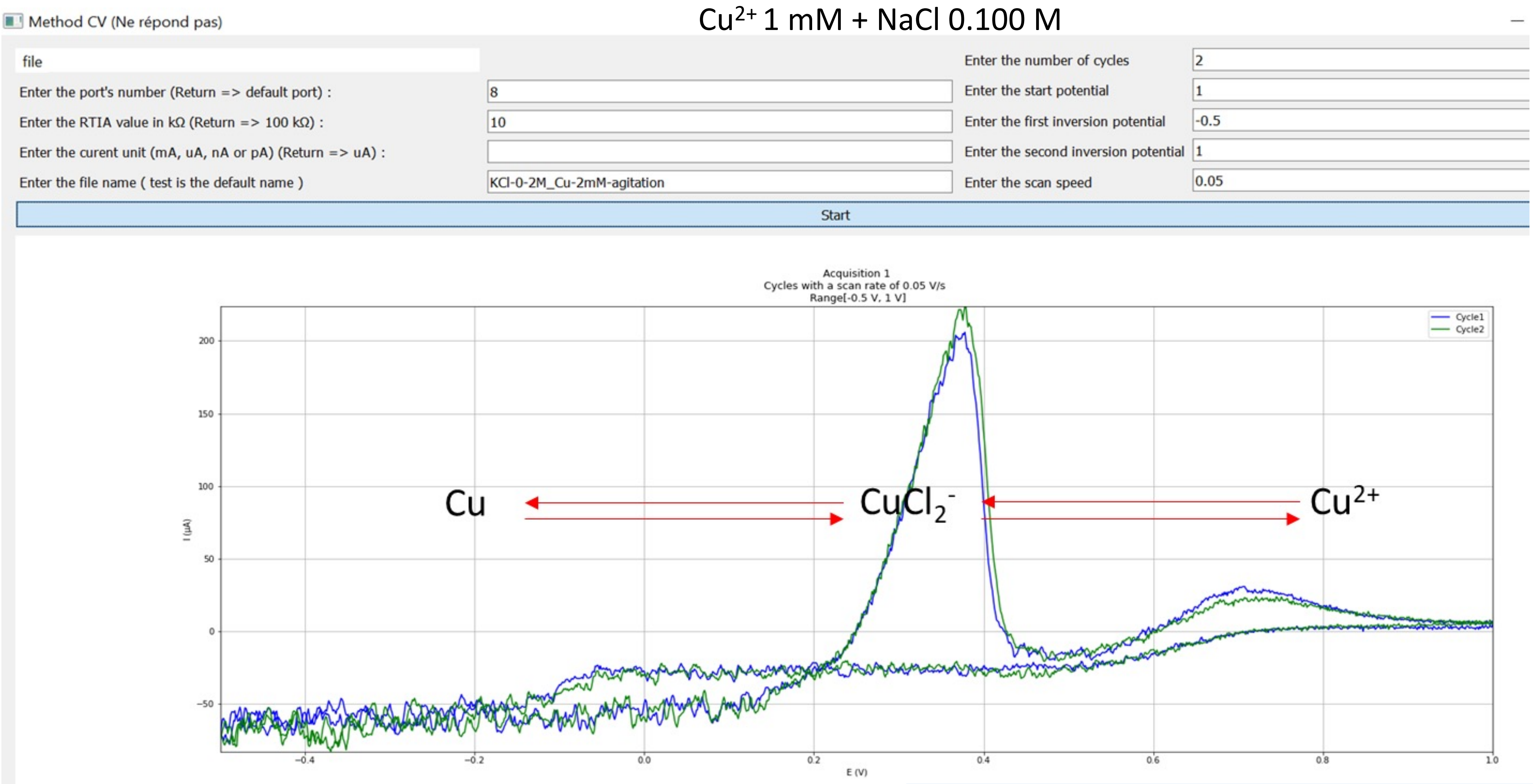






A few examples: copper analysis

Anodic stripping of Cu



Results Université d'Abomey-Calavi, october 2021
Internship M1 Florença Wassolua, 2022

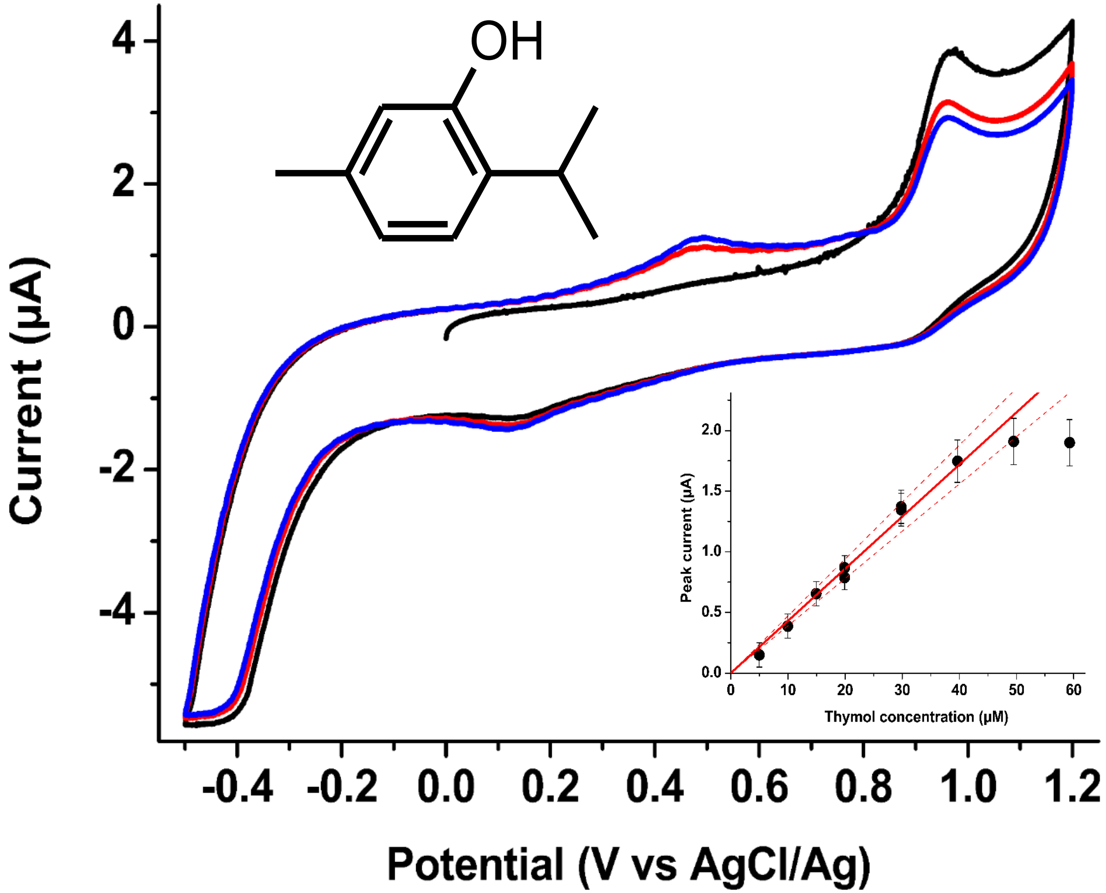
Titration in tap or sea water

A few examples: plant extract

Essential oil: Occimum gratissimum (faux basilic, Bénin)
Collaboration Pr. Latifou Lagnika, UAC and Agnès Aubouy, IRD

A priori contains thymol

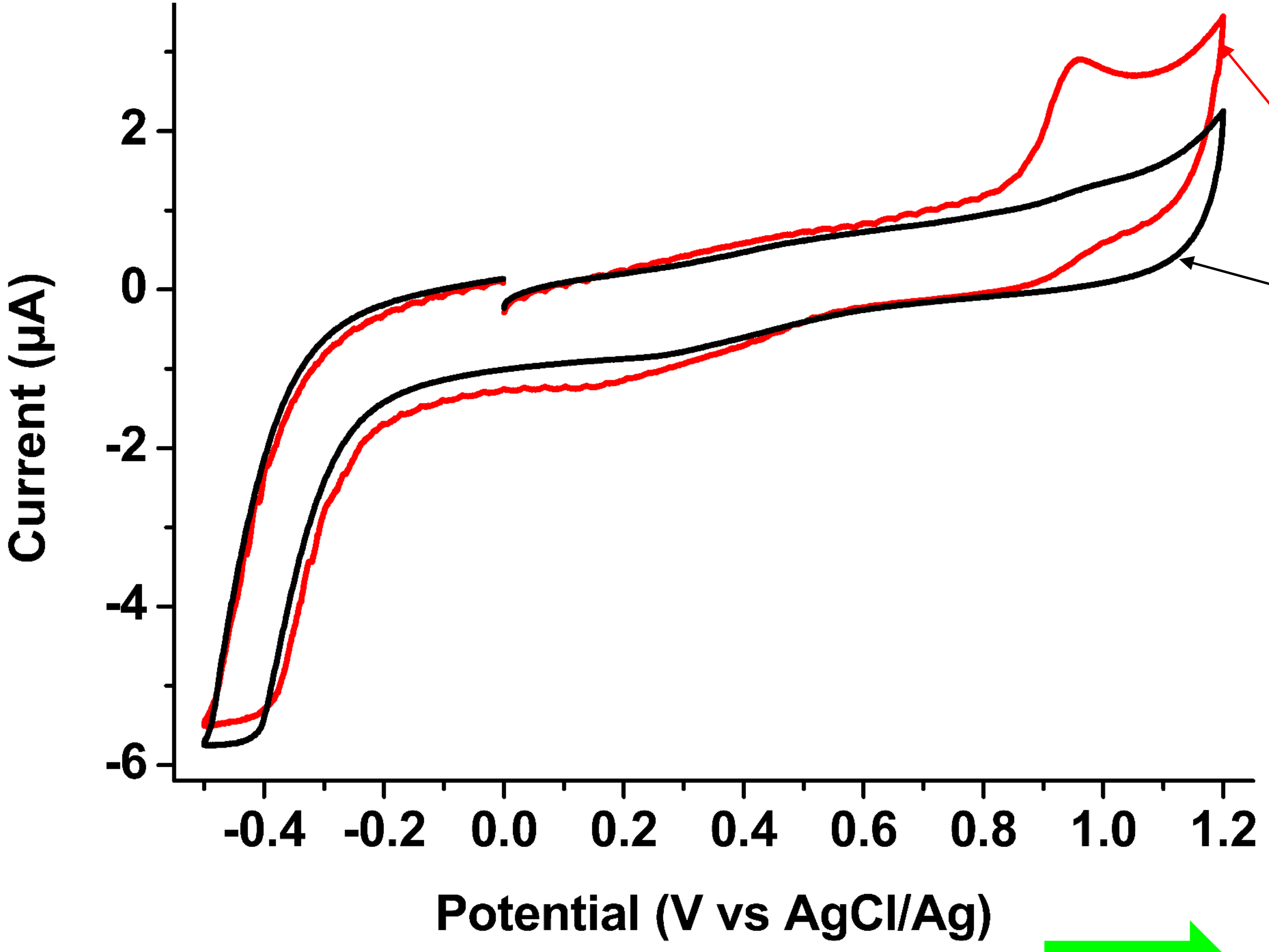
Calibration with pure thymol

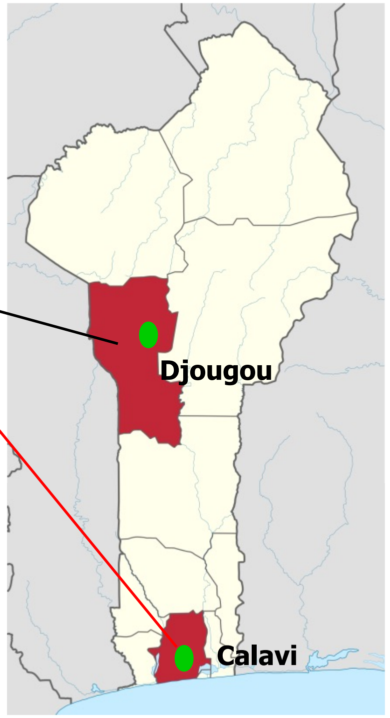


→ Quantification of a complex electrochemical system in a complex matrix

A few examples: plant extract, essential oil

Different thymol composition depending on the area of collection



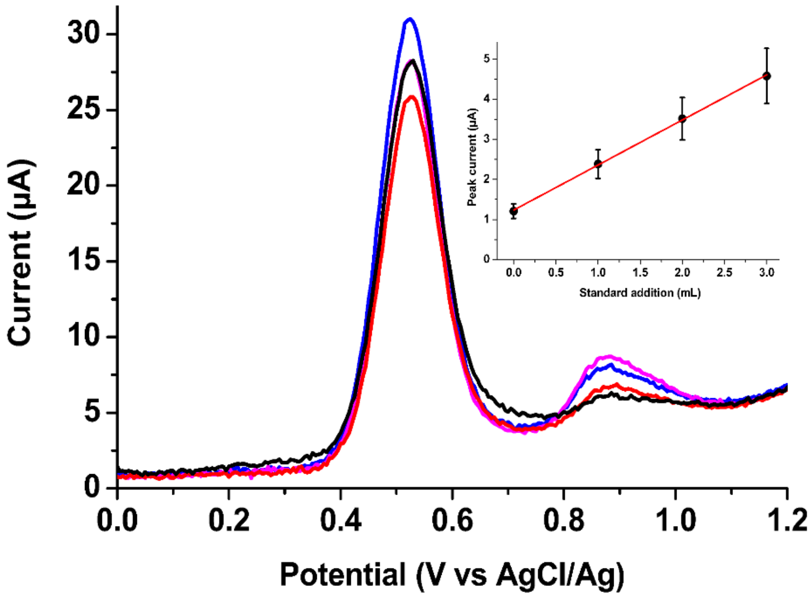


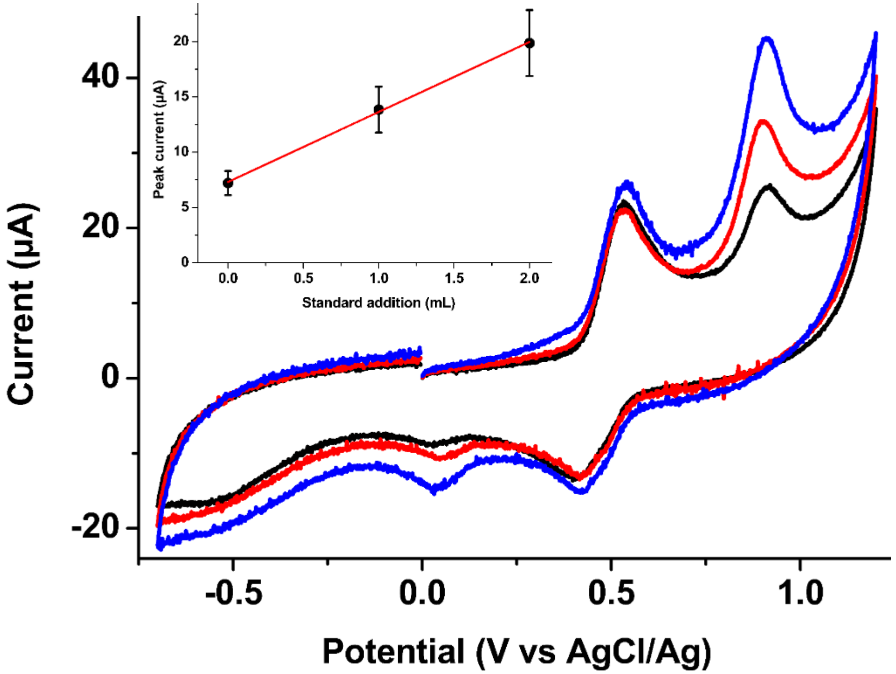
Very different compositions

A few examples: plant extract, infusion

Glassy carbon

Pencil lead





Some reflexions…

Commercial systems

- Plug and play
- Wide range of techniques
- Soft
- Excellent resolution
- Modulables (filters)
- Black boxes
- Sometimes bulky
- Expensive
- Not possible to repair yourself

PassStat and other open hardwares

- To mount yourself (1h)
- Limited functions and soft (to be improved…)
- Correct resolution
- Low compliance (can be solved)
- Easily adaptable at low cost (T, pH, conductivity…)
- Totally open source and easy to repair
- Light, works on battery (low noise)
- Cost-effective for development and participative science
- Perfect to learn instrumentation !

Some perspectives

Electrode material

- Commercial electrodes
- Screen printed electrodes
- Pencil lead (Activation ?)
- UMEs
- Carbon paste
- Modified electrodes

Systems

- Plants ???
- Essential oils
- Infusions
- Metals

Hard and soft improvements

Integration within other techniques (e.g. spectroscopy)

Spread the approach to other users

Autonomous underwater measurements

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- Université de Poitiers : Teko Napporn, Dodzi Zigah
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- Associations : Physique sans frontières, Chimistes sans Frontières, Puya Raimondi (Raymond Campagnolo)