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Scientific Program

17th PTASchool of Electrochemistry

Sunday, December 3rd	
09:00 – 09:30 h	Opening Ceremony - *Roberto M. Torresi – IQUSP*
09:30 – 12:00 h	Fundamentals on Electrode Processes - *Gabriel Negrão Meloni – IQUSP*
12:00 – 13:30 h	Lunch
13:30 – 15:00 h	Transport phenomena - *Vitor L. Martins – IQUSP*
15:00 – 15:20 h	Break
15:20 – 16:50 h	Electrochemical kinetics - *Vitor L. Martins – IQUSP*

Monday, December 4th	
08:45 – 10:10 h	Cyclic voltammetry - Guy Denuault – University of Southampton – UK
10:10 – 10:30 h	Break
10:30 – 11:50 h	Reaction Mechanisms - Mauro Bertotti – IQUSP
11:50 – 13:30 h	Lunch
13:30 – 17:30 h	6 Different experiments: 1- Cyclic voltammetry 2- Electrochemical Impedance Spectroscopy 3- Fabrication and application of microelectrodes 4- Disposable Electrochemical Sensors 5- Electrochemical oxidation of dopamine - Determination of the chemical coupled reaction constant 6- Electroanalysis Under Flowing Regime

Tuesday, December 5th	
08:30 – 10:10 h	Electrochemical Impedance Spectroscopy – Germano Tremiliosi Filho - IQSC-USP
10:10 – 10:30 h	Break
10:30 – 11:50 h	Electrochemical Impedance Spectroscopy - Germano Tremiliosi Filho - IQSC-USP
11:50 – 13:30 h	Lunch
13:30 – 17:30 h	6 Different experiments: 1- Cyclic voltammetry 2- Electrochemical Impedance Spectroscopy 3- Fabrication and application of microelectrodes 4- Disposable Electrochemical Sensors 5- Electrochemical oxidation of dopamine - Determination of the chemical coupled reaction constant 6- Electroanalysis Under Flowing Regime

Wednesday, December 6th	
08:45 – 10:10 h	Electrochemical in-situ infrared spectroscopy and its application in Electrocatalysis - Angel Cuesta Ciscar – University of Aberdeen – UK
10:10 – 10:30 h	Break
10:30 – 11:50 h	Energy Storage - Vitor L. Martins – IQUSP
11:50 – 13:30 h	Lunch
13:30 – 17:30 h	6 Different experiments: 1- Cyclic voltammetry 2- Electrochemical Impedance Spectroscopy 3- Fabrication and application of microelectrodes 4- Disposable Electrochemical Sensors 5- Electrochemical oxidation of dopamine - Determination of the chemical coupled reaction constant 6- Electroanalysis Under Flowing Regime

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Institute of Chemistry

First Floor

Ground Floor

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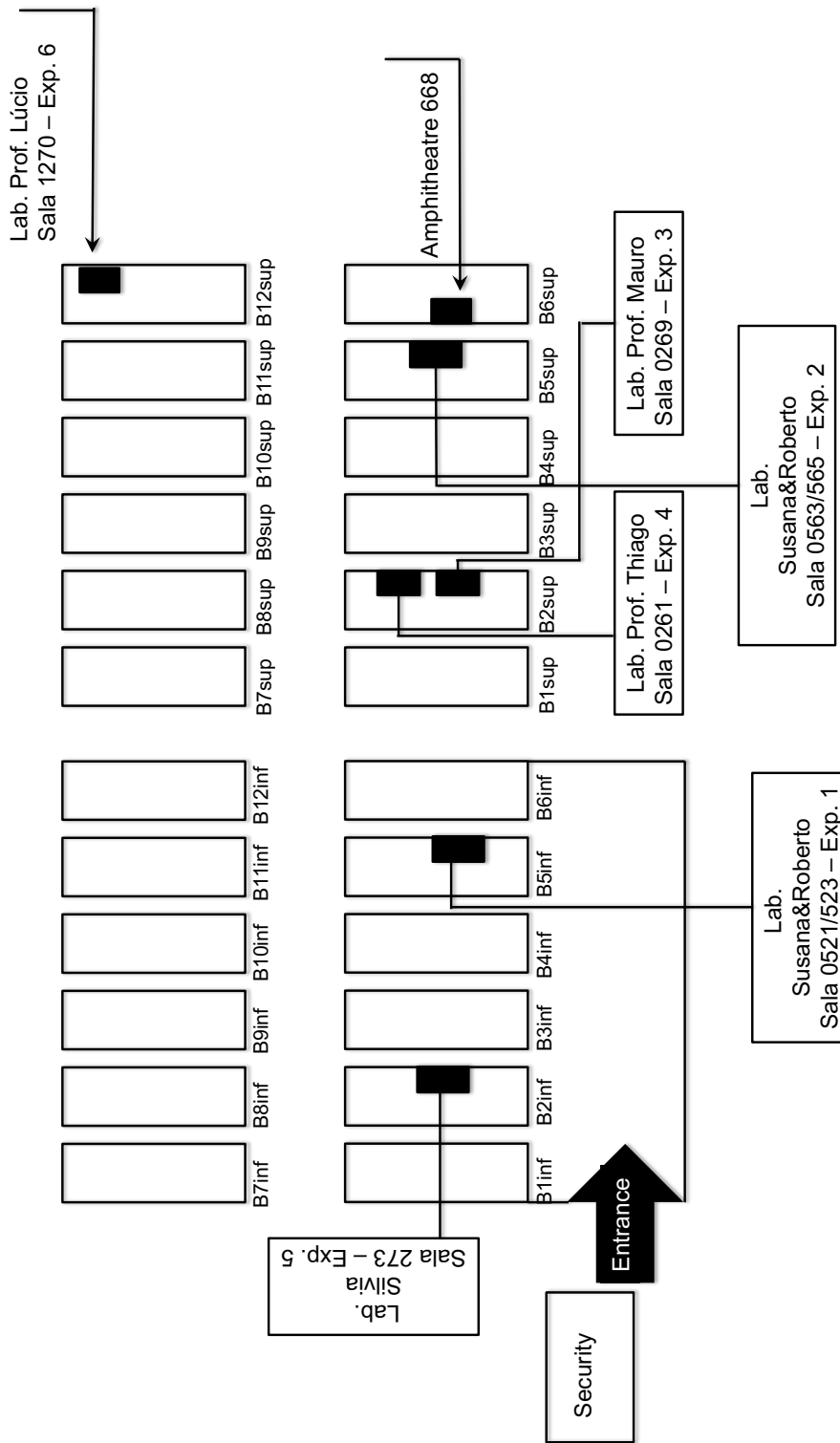
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Experiments

Time	Experiment	Wednesday, December 11th	Thursday, December 12th	Friday, December 13th
13:30-15:30	**1-** Cyclic Voltammetry (Prof. Susana's lab)	G1	G4	G6
15:30-17:30	**1-** Cyclic Voltammetry (Prof. Susana's lab)	G2	G3	G5
13:30-15:30	**2-** Electrochemical Impedance Spectroscopy (Prof. Susana's lab)	G3	G6	G1
15:30-17:30	**2-** Electrochemical Impedance Spectroscopy (Prof. Susana's lab)	G4	G5	G2
13:30-15:30	**3-** Fabrication and application of microelectrodes (Prof. Mauro's lab)	G5	G2	G4
15:30-17:30	**3-** Fabrication and application of microelectrodes (Prof. Mauro's lab)	G6	G1	G3
13:30-15:30	**4-** Disposable Electrochemical Sensors (Prof. Thiago's lab)	G2	G3	G5
15:30-17:30	**4-** Disposable Electrochemical Sensors (Prof. Thiago's lab)	G1	G4	G6
13:30-15:30	**5-** Electrochemical oxidation of dopamine - Determination of the chemical coupled reaction constant (Prof. Silvia's lab)	G4	G5	G2
15:30-17:30	**5-** Electrochemical oxidation of dopamine - Determination of the chemical coupled reaction constant (Prof. Silvia's lab)	G3	G6	G1
13:30-15:30	**6-** Electroanalysis Under Flowing Regime (Prof. Lucio's lab)	G6	G1	G3
15:30-17:30	**6-** Electroanalysis Under Flowing Regime (Prof. Lucio's lab)	G5	G2	G4

Working Groups

G1	Tuani Carla Gentil Murilo Machado Amaral Mariel Andrea Godoy Pérez Agnes Nascimento Simões Rafael Silva Santos Bárbara Scola Rodrigues	**G2**	Maria Zilda Oliveira Nicolas de Andrade Ishiki Marcos Eduardo Gomes do Carmo Bruna Rafaela Silva Ibiapina Ana Paula Loperena Andrea Paola Gualdron Plata
G3	Rainy Alves de Sousa Pepe Jordá-Faus Luiz Otávio Orzari Caio César Gonçalves Silva Pedro Henrique Alves Damasceno Ana Clara Maia	**G4**	Rafael GalizaYoshimura Sofía Tsunoda Luan Pereira Camargo Higor de Oliveira Alves Ketley Caroline Rocha Pereira
G5	Oscar Eduardo Churio Silvera Mariana Bianchini Silva Luan Gabriel Baumgarten Jéssica Nogueira da Cunha Felipe Machado	**G6**	Naiza Vilas Bôas Larissa Magalhães de Almeida Melo Leandro Vitor da Silva José Guilherme Aquino Rodrigues Andy Alfredo Cardenas Riojas

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1. Cyclic Voltammetry

Goals

➤ To familiarize the researcher with the parameters of a cyclic voltammetry (CV) experiments.

➤ To illustrate the difference in response for electrode reactions involving surface changes and redox couples in solution.

➤ To understand ohmic compensation.

➤ To define the electrochemistry of ferricyanide in aqueous solution.

Experiments will be done with KCl 1 mol L^{-1} + K$_3$Fe(CN)$_6$ 0,01 mol L^{-1} + K$_4$Fe(CN)$_6$ 0,01 mol L^{-1} aqueous solution as electrolyte
Part 1: Effect of electrolyte ohmic resistance
Observe and discuss the change in the voltammogram profile with increasing the electrolyte ohmic resistance:
Experiment conditions:

Scan rate:	50mV s^{-1}
Resistors:	0 Ω, 10 Ω, 100 Ω, 300 Ω, 500 Ω and 1000 Ω

Part 2: Calculation of diffusion coefficient

✓ Cyclic voltammetry at different scan rates (*v*= 5, 10, 25, 50, 100, 150, 200 mV s^{-1}) to plot the peak current as a function of *v*$^{1/2}$

✓ *Randles-Sevcik* equation for calculation of diffusion coefficient

$$I_p = -0.4463nF \left(\frac{nF}{RT}\right)^{\frac{1}{2}} C^\infty D^{1/2} v^{1/2}$$

I$_p$ = peak current density (A cm^{-2})
n = number of transferred electrons
F = 96485.3 C mol^{-1}
R = 8,31447 J K^{-1} mol^{-1}
T = temperature (K)
C = bulk concentration (mol cm^{-3})
D = diffusion coefficient (cm^2 s^{-1})
v = scan rate (V s^{-1})

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2. Electrochemical Impedance Spectroscopy

Goals

➢ To illustrate the principles of electrochemical impedance with a simple reversible redox system.

➢ To become familiar with Bode and Nyquist representations of complex impedance data.

➢ To practice the use of equivalent circuits in the analysis of the AC response of an electrochemical system.

Part 1: Measurements with electronic elements and circuits
Before the measurements with an electrochemical system, let´s study the EIS response of some electronic elements and circuits that are disclosed below:

Resistor (R)	Capacitor (C)	R-C in series	R-C in parallel	R(R-C)

The conditions for these measurements are:

Applied potential	0V
Frequency range	10kHz - 100mHz
Number f points	26
Amplitude	0.01rms

Discussion about the obtained diagrams and the relationship with real systems.

Part 2: Measurements with the system [Fe(CN)$_6$]$^{3-}$/[Fe(CN)$_6$]$^{4-}$ - diffusion coefficient
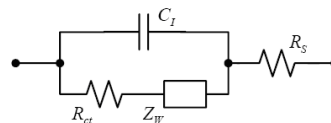Conditions:
✓ Electrolyte solution: KCl 1mol L^{-1} + K$_3$Fe(CN)$_6$ 0.01mol L^{-1} + K$_4$Fe(CN)$_6$ 0.01 mol L^{-1}
✓ Applied potential: determined by polarization curves
✓ Frequency range: 10kHz - 100mHz
✓ Number of points: 26
✓ Amplitude: 0.01 rms

Simulation using equivalent circuit:
Calculation of diffusion coefficient:

R	8.314 J (K^{-1} mol^{-1})
T	298 (K)
n	number of transferred electrons
F	96485.3 (C mol^{-1})
A	Electrode area (cm^2)
D	Diffusion coefficient (cm^2 s^{-1})
C$_0$	Bulk concentration of oxidized species (mol cm^{-3})
C$_R$	Bulk concentration of reduced species (mol cm^{-3})

$$\sigma = \frac{RT}{2^{1/2} n\ F^2 AD^{1/2}} \left(\frac{1}{C_0^\infty} + \frac{1}{C_R^\infty} \right)$$

σ = slope of plot R$_s$ vs. $1/\omega^{0.5}$

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3.   Fabrication and application of microelectrodes

Section I: Fabrication methods, surface inspection, and polishing procedures

a) You will be shown how microelectrodes can be fabricated in our laboratory using different procedures.

Section II: Comparative study: electrochemical behavior of ferricyanide by using a conventionally-sized electrode and a microelectrode

a) Record CVs in a 5 mM ferricyanide + 0.1 M KCl solution with a Pt disc electrode (r = 1 mm) and a Pt microelectrode (r = 12.5 µm) at 10 mV/s. The radius of the microelectrode (r) can be calculated by taking into account the limiting current I_L ($I_L = 4nFDCr$).

b) Using the same solution, examine the effect of the scan rate (10, 100, 500 mV/s) on the shape of the voltammograms recorded with both electrodes.

Section III: Electroanalysis with a microelectrode

a) Using the Pt microelectrode and a reference electrode, try to get a CV by inserting both electrodes directly into an orange.

b) Idealize an experiment to confirm that the response obtained in the previous experiment refers only to the anodic oxidation of ascorbate.

Section IV: Scanning Electrochemical Microscopy

a) Move a Pt microelectrode towards insulating and conductive surfaces in a 5 mM ferricyanide + 0.1 M KCl solution and record the current during this procedure.

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4. Low-cost Electrochemical Sensors

Part 1 – Electrochemical test with redox probe by CV

Goal: Compare the electrochemical behavior of the redox probe using a Laser-scribed paper-based electrode and a 3D-printed electrode.

● Add 360 µL of a 1 mol L^{-1} KCl solution to the electrochemical cell. Record cyclic voltammetry (CV) from -0.3 to +0.8 V with a scan rate of 20 mV s^{-1}.

● Add 40 µL of a 50 mmol L^{-1} $K_3Fe(CN)_6$ solution to result in a 5 mmol L^{-1} solution (homogenizing the solution with the pipette). Perform the voltammetric measurement from -0.3 to +0.8 V with a scan rate of 20 mV s^{-1}.

Part 2 – Non-enzymatic determination of glucose by LSV

Goal: Glucose determination in isotonic drinks using a 3D-printed sensor-modified AuNPs.

3D-printed electrode modification: Add the $HAuCl_4$ solution to the working electrode, and the CO_2 laser was applied to reduce the solution to metallic gold.

1) Characterization of gold surfaces

● Perform the CV using the 3D-printed and commercial gold electrodes in 0.5 mol L^{-1} KOH from +1.2 to -1.0 V with a scan rate of 50 mV s^{-1} and compare the voltammograms.

2) Calibration curve (standard addition)

Before each measure, apply +0.4 V for 10 seconds (anodic polarization)

● Add 5 mL of a 0.5 mol L^{-1} KOH solution to the electrochemical cell (10 mL beaker). Perform the linear sweep voltammetry (LSV) from +0.4 to -0.6 V with a 100 mV s^{-1} scan rate.

● Add 100 µL of a 100 mmol L^{-1} glucose stock solution prepared in 0.5 mol L^{-1} KOH. Perform the LSV measurements in the same conditions. Repeat the additions more three times to obtain a calibration curve ranging from 2 to 10 mmol L^{-1}.

3) Sample: Isotonic drinks

● Dissolve the 33 mg of the powdered isotonic drink in 5 mL of 0.5 mol L^{-1} KOH and perform the LSV measurements in the same conditions as the item above.

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5. Electrochemical Oxidation of Dopamine - Determination of the coupled chemical reaction rate constant.

The electrochemical oxidation of dopamine involves the molecule's loss of 4 electrons and 4 protons[1]. After the remotion of the second electron, the primary amine group present in the molecule attacks the *o*-benzoquinone ring, forming a bicyclic compound. This intramolecular chemical reaction is known as the cyclisation of dopamine. The formal oxidation potential of the cyclised product is lower than dopamine's formal potential so that once the cyclisation occurs, the product is easily oxidised on the electrode's surface. This process involves 2 electrons, adding up to 4 electrons in the total process. This mechanism can be considered as an analogous of a simple ECE (electrochemical-chemical-electrochemical).

Using cyclic voltammetry and varying the potential scan rate, one can obtain the rate constant of the coupled chemical reaction. If the scan rate is too low, the chemical reaction occurs extensively, and the reversibility of the dopamine oxidation is not observed. If the scan rate is too high, there is not enough time for the chemical reaction to take place significantly, and the reduction of the oxidised form of dopamine is observed in the voltammogram. The kinetic studies[2] lie on the "intermediate" scan rate, in which the chemical reaction occurs at some extension, but the voltammogram's reverse peak remains.

Under adequate conditions, it is possible to use working curves to determine this rate constant of an ECE mechanism's chemical step, as Savéant[3] described. Another approach is the kinetic convolution. Convolution is a mathematical operation that gives access to the analyte's concentration on the electrode's surface when applied to a cyclic voltammogram. By inserting a rate constant into the convolution model, it is possible to use this technique to determine the rate constant of a chemical couple's reaction on an "ECE-like" mechanism.

References

(1) BACIL, R. P. et al. Dopamine oxidation at gold electrodes: Mechanism and kinetics near neutral pH. Physical Chemistry Chemical Physics, v. 22, n. 2, p. 607–614, 2020.

(2) WOODARD, F. E.; GOODIN, R. D.; KINLEN, P. J. Kinetic Convolution Analysis of Cyclic Voltammetric Data. Analytical Chemistry, v. 56, n. 11, p. 1920–1923, 1984.

(3)SAVÉANT, J.; COSTENTIN, C. Elements of Molecular and Biomolecular Electrochemistry. [s.l: s.n.]

(4) WOODARD, F. E.; GOODIN, R. D.; KINLEN, P. J. Kinetic Convolution Analysis of Cyclic Voltammetric Data. Analytical Chemistry, v. 56, n. 11, p. 1920–1923, 1984.

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6. <u>Electroanalysis Under Flowing Regime</u>

Electroanalysis under flowing regime can be very advantageous. Flow regime contributes to enhance the speed of analysis, increases the sensitivity, enlarges the dynamic working region and lowers the detection limit. Furthermore, is propitious for automation of routine analysis. In our laboratory, experiments involving flow injection analysis (FIA) and batch injection analysis (BIA) will be presented. FIA utilize a peristaltic pump (concepts of gravitational propelling or pressurized propulsion will be also discussed) a modular injector and a thin layer cell (containing the three electrodes). This simple arrange allows to perform 120 to 180 measurements per hour. BIA is centered in a motorized pipette, which can be programmed to dispense precise volumes in a reproducible flow rate. The BIA cell is constructed in way that the working electrode is positioned perpendicularly from the bottom, exactly in front of the point where the pipette tip will be positioned, from the cover of the cell. The other two electrodes are also positioned in this cover. During the injection of the analyte, the mass transport to the electrode is elevated and generates a current proportional to its concentration. The solution attains the electrode and disperses in the solution. Few seconds after the end of each injection, the mechanical transport ends and all the predominant transport process is the diffusive. So, for each injection the time required is very short and a measurement requires 15-20 seconds. Details about construction of alternative electrodes and electroanalytical cells for FIA and BIA will be discussed and practical demonstrations will be presented. Participants will be stimulated to make the injections and experience the simplicity of the system.

<u>Experiments</u>:

a)Batch Injection Analysis (BIA) utilizing modified electrodes: In this experiment, the potentiality of BIA will be demonstrated, and the students will be stimulated to perform a series of injection. Supramolecular porphyrins modified electrodes will be utilized in experiments where sulfite will be quantified and strategies for its quantification in real samples will be discussed.

b)Flow injection analysis (FIA) associated with microchannels: In this practical experiment the advantages of FIA will be presented. Experiments utilizing microchannels containing immobilized glucose oxidase in their walls will be explored and application for the quantification of glucose in soft drink will be demonstrated. In addition, we will present different electrochemical cells developed in the lab and also show how we construct microchannels utilizing laser ablation. Having time, we will also "pass through" the different forms of construction of electrodes, flow systems and instruments developed in the lab.