Application of the bipotentiostat
to an experiment with a Rotating Ring-Disk Electrode (RRDE)

I - INTRODUCTION
The aim of this document is to show the capability offered by a multichannel potentiostat (VSP-300, BP-300, VMP-3, VMP-300) to run experiments with a rotating Ring-Disk electrode system.

The SP-300 and BP-300 are two channel potentiostats/ galvanostats especially designed to work as a bipotentiostats. The bipotentiostat is mainly used in electrochemical experiments with two working electrodes in a hydrodynamic regime. The hydrodynamic regime is ensured with a rotating electrode led by a rotating power unit. The working electrode in the electrochemical cell is typically made either of a single disk or with a rotating ring-disk electrode. The rotating ring-disk electrode was developed by Frumkin and Nekrasov in 1959. The theoretical part was definitely achieved in 1971 [1]. The applications are numerous in the fields of electrochemical analysis, especially in reaction mechanism study. The rotating electrode is often used for the detection of short life intermediate species.

II - DESCRIPTION AND PRINCIPLE
The ring-disk electrode is made of two electrically isolated electrode surfaces. The ring and the disk electrodes are made of conducting material such as platinum, gold, silver, copper, glassy carbon. The material of each electrode can be different and are separated by an isolating material such as PTFE or PEEK.

The electrochemical solution flow near the electrode surface describes a spiral that is growing from the middle to the periphery of the surface. The electroactives species are moving from the disk to the ring electrode. When used in the ring-disk configuration, the ring and the disk electrodes are usually polarized with different potentials, $E_R$ and $E_D$, using both channels of the bipotentiostat. For example $E_D$ could be an oxidation potential and $E_R$ a reduction potential. The electrochemical reactions that can take place on the electrode surface according to the applied potential can be defined as follow:

Disk: \[ X \leftrightarrow Y + n \text{e}^- \]

if $E_D$ enough positive

Ring: \[ Y + n \text{e}^- \leftrightarrow X \]

if $E_R$ smaller than $E_D$ (enough for the reduction).

The Y compound made on the disk electrode is moved by diffusion and convection to the ring electrode where it can be electrochemically detected and studied. A possible experiment is to sweep the potential on the disk electrode from a reduction potential to an oxidation potential and to fix a reduction potential on the ring electrode to detect by amperometry the species made on the disk.

For this kind of experiment, the electrochemical cell also contains a reference electrode and a counter electrode that are common for both working electrodes. The characteristic value that must be considered is the collection efficiency of the ring electrode: \[ N = - \ln I_0 \]

This coefficient is characteristic of the RRDE.

III - EXPERIMENTAL PART
The electrochemical cell contains a four electrode system with two working electrodes (rotating ring-disk electrode), one Pt counter electrode and one silver/silver chloride electrode as reference. The solution used in the experiment is made with Fe(CN)$_6^{4-}$ $(5.10^{-3} \text{ mol.L}^{-1})$ with KCl $(0.5 \text{ mol.L}^{-1})$ as support electrolyte. The instrument used is a VMP-3 with EC-Lab software version 11.21. The connection used is in the
“CE to Ground” mode with one common reference and one common counter electrode.

There is three bipotentiostat techniques presented on the following figure:

![Figure 1: Bipotentiostat techniques (window “Insert Techniques”).](image)

In this experiment, Cyclic Voltammetry & Chronoamperometry technique (CV-CA) has been used. Bipotentiostat techniques require two channels: one for each working electrode, the disk and the ring. We can choose which channel is linked to which electrode by going to “Edit” -> “Group / Synch / Stack / Bipot” (Fig. 2)

![Figure 2: Window “Group / Synch / Stack / Bipot”](image)

The parameters of the experiment are shown on the following figure (Fig. 3).

![Figure 3: Parameters of the experiment.](image)

### IV – RESULTS

The VMP-3 is used as a bipotentiostat. On the disk electrode surface a potentiodynamic mode is applied (2000 rpm) from 0 V/OCV to 1 V/OCV in order to oxidise the Fe(II) species into Fe(III) species. In the same time on the other channel connected to the ring electrode, a potentiostatic mode with 0V/OCV is applied in order to reduce the Fe(III) species previously formed on the disk electrode. The curves are shown in the following figure.
Both experiments were synchronized to apply the constant potential on the ring electrode when the potential sweep on the disk electrode started. The curves show clearly that the Fe(III) formed species during the oxidation step are partly reduced on the ring electrode. The quantity of reduced iron is growing with the quantity of Fe(III) formed.

The diffusion limit currents on the disk and on the ring electrodes have been obtained thanks to the previous curves (Fig. 4). We can obtain the collection efficiency:

\[ N = - \frac{I_{\text{Ring}}}{I_{\text{Disk}}} = 0.405 \]

The calculated collection efficiency according to the previous curves is 40.5%. The theoretical collection efficiency has been calculated using an expression given in [2] and gives a value of 42.5%, which is a little higher than the calculated one, but similar.

\[ \text{REFERENCES} \]

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