

## Application of the bipotentiostat to an experiment with a rotating ring-disk electrode.

### Available instruments for the rotating electrode control

Instrument	MPG	VMP	VMP2	BiStat
Used				×
Alternative			×	

### OVERVIEW

The aim of this document is to show the capability offered by a BiStat or a VMP2 to run experiments with a rotating Ring-Disk electrode system.

### INTRODUCTION

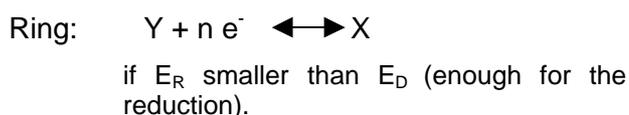
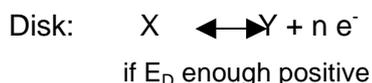
The BiStat is a two channel potentiostat/galvanostat especially designed to work as a bipotentiostat. The bipotentiostat is mainly used in electrochemical experiments with two working electrodes in a hydrodynamic regime. The hydrodynamic regime is ensured with a rotating electrode laid by a rotating power unit. The working electrode in the electrochemical cell is typically made either with 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.

### DESCRIPTION AND PRINCIPLE

The ring-disk electrode is made with two electrically isolated electrode surfaces. The ring

and the disk electrodes are made with 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 teflon or polyethylene.

The electrochemical solution flow near the electrode surface describes a spiral that is growing from the middle to the periphery of the surface. The electroactive 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 BiStat. 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:



Y compound made on the disk electrode is laid by diffusion and convection to the ring electrode where it can be electrochemically detected and studied. A possible experiment is to apply an oxidation potential on the disk electrode and a potential sweep on the ring electrode to detect the species made on the disk. We can do the same experiment with a potentiodynamic mode on the disk and a potentiostatic one on the ring.

For this kind of experiment, the electrochemical cell also contains a reference electrode and a counter electrode that are common for both working electrodes.

Two characteristic values must be considered:

- The collection efficiency of the ring electrode  $N = -I_R/I_D$
- The screen coefficient of the disk electrode:

## EXPERIMENTAL PART

The electrochemical cell contains a four electrode system with two working electrodes (rotating ring-disk electrode), one steel counter electrode and one Saturated Calomel electrode as reference.

The solution used in the experiment is made with  $\text{Fe}(\text{CN})_6^{4-}$  ( $5 \cdot 10^{-3} \text{ mol.L}^{-1}$ ) with KCl ( $0.5 \text{ mol.L}^{-1}$ ) as support electrolyte. The instrument used is a BiStat with EC-Lab software version 8.50. The connection used is in the "CE to Ground" mode with one common reference and one common counter electrode.

The rotating speed is controlled by EC-Lab software through the DB9 auxiliary cable (Analog Output BNC).

Note that a triggering signal can be used to start the rotation at the beginning of the experiment and (or) to stop the rotation at the end of the experiment.

## RESULTS

### Rotating speed effect of a single disk electrode

In a first time, the instrument is used as a single potentiostat (one channel). An experiment has been built in order to show the rotating speed effect of the disk electrode on the current values. The experiment is made with the protocol linker available in EC-Lab software. Three protocols were linked, a "modular potentiodynamic" followed by a "wait" and finally a "loop" experiment. The wait protocol is specific because it is dedicated to the rotating electrode control when the channel has this ability. The Wait protocol for the rotating electrode control is as follow:

The Wait protocol has been especially designed for linked experiments. It is possible either to choose the wait duration ( $t_d$ ) or to define the time of the end of the wait protocol. This protocol's table is made of sequences. Each sequence is taken into account successively for each loop. Only one sequence of the wait is executed at each protocol loop. It is a very interesting tool to study the rotating speed effect on the measured current. The following figure shows the curve obtained with this protocol.

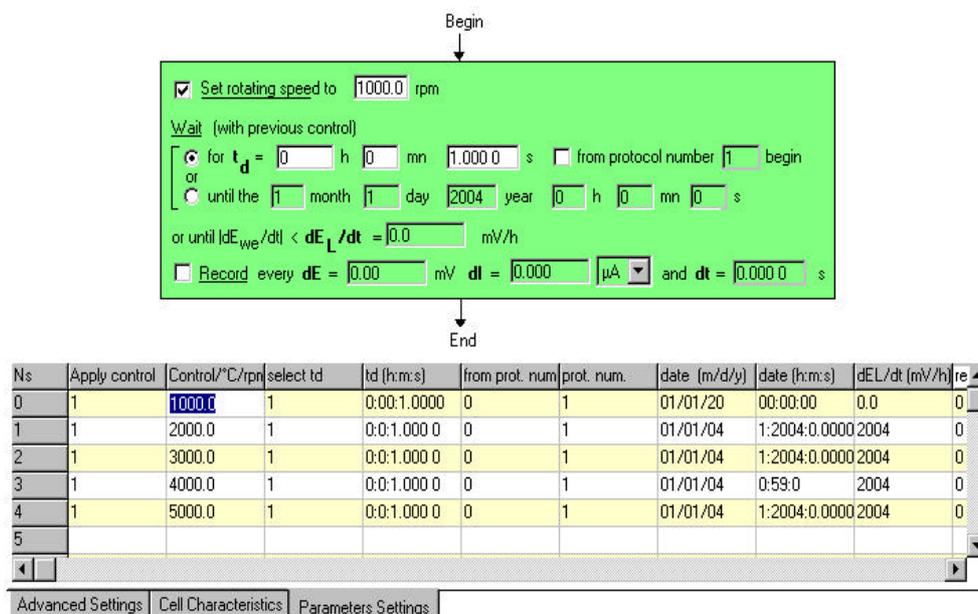
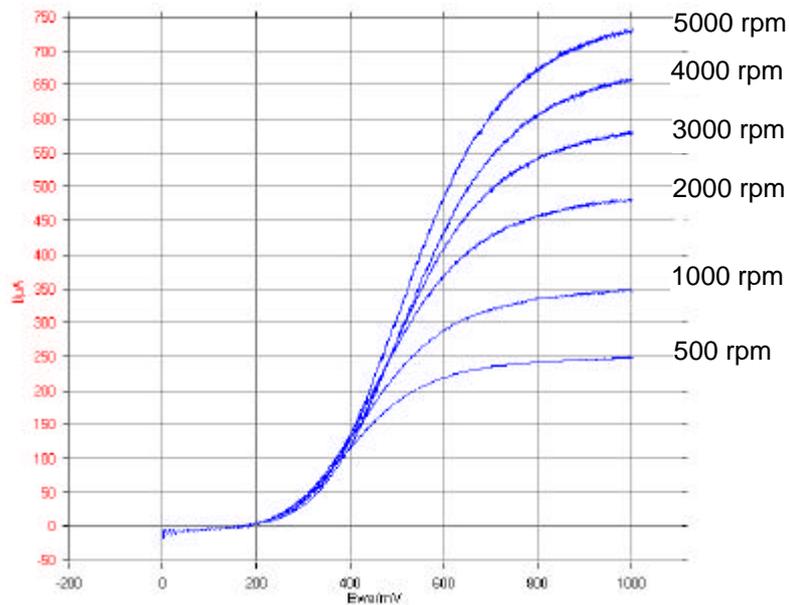
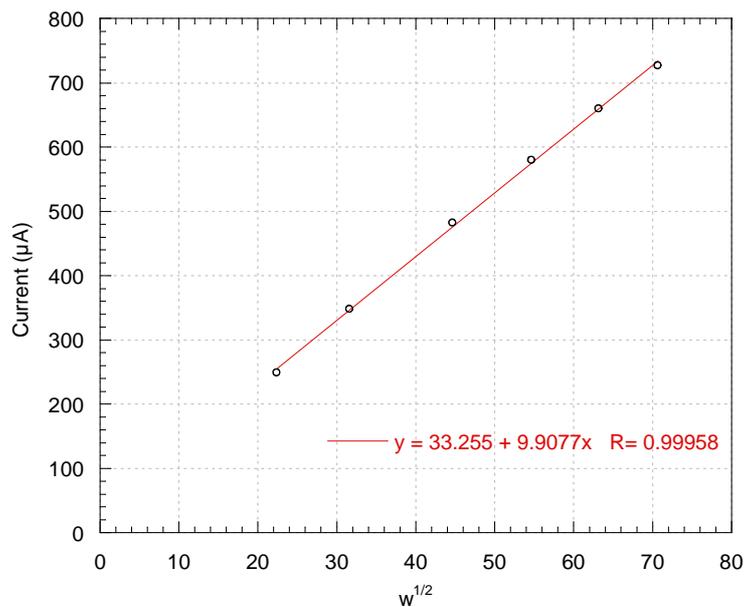


Fig. 1: Wait protocol for the rotating electrode control.



**Fig.2: I versus Ewe curves obtained with the linked protocol and showing the rotating speed effect.**



**Fig.3: Effect of the electrode rotating speed on the limit current.**

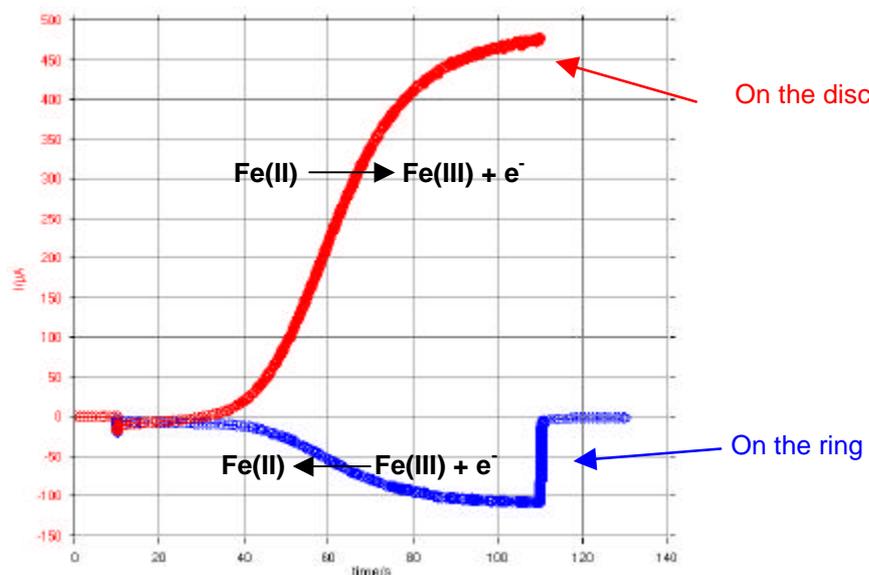
The limit current is growing with the rotating electrode speed. For the first experiment (modular potential), this speed is 500 rpm. It is the reason why the first speed of the wait protocol is 1000 rpm.

As theoretically defined the limit current in the hydrodynamic regime is directly proportional to the rotation speed square root. The linear regression curve is shown in red color with its equation.

### **Electrochemical study on a ring-disk electrode with both BiStat's channels**

In that case the BiStat is used as a bipotentiostat. This experiment has been made with the modular potentiostat protocol on both channels. On the disk electrode surface a potentiodynamic mode is

applied from 0 V/SCE to 1 V/SCE 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/SCE is applied in order to reduce the Fe(III) species previously formed on the disk electrode. The curves are shown on the following figure



**Fig.4: Overlaid chronoamperometric curves obtained simultaneously on the disk and on the ring electrodes.**

Both channel experiments were synchronized in order to start in order 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 rotating electrode supplier defines a theoretical collection efficiency of 22%. The calculated collection efficiency according to the previous curves is 22.6%. The calculated screen coefficient of the disk is near 0.56.

#### **Reference:**

[1] Albery W.J. and Hitchman M.L., Ring-disk electrodes, Clarendon press Oxford, 1971.

### **CONCLUSION**

Coupled with a bipotentiostat, the rotating ring-disk electrode is a powerful tool to study electrochemical mechanisms in solution. In a simple case we have shown that the limit current in hydrodynamic regime is directly proportional to the rotating speed square root. The faisability of linked experiments with rotating electrode control has been demonstrated. Moreover in the case of both working electrodes (ring + disk), the experiment has shown a similar collection efficiency as defined by the supplier.