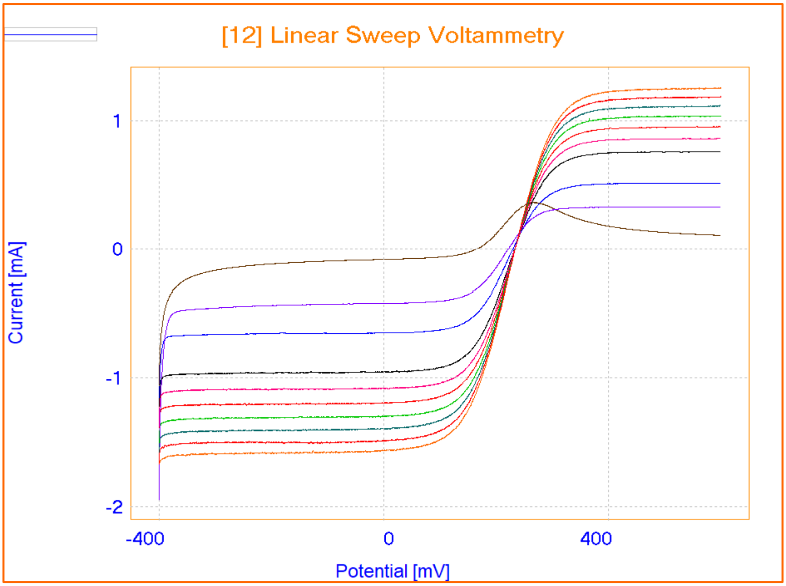
Application Note

General Electrochemistry
AP-GE08

Levich Study (RDE)



This Application Note describes how the rotation speed of the Rotating Disk Electrode (RDE) impacts the current of Voltammetry tests.

Introduction

The electrochemical reaction occurs at the surface of the working electrode. The reactors must go towards the working electrode, whereas the products must go away from the working electrode. This phenomenon is called mass transport towards the surface of the working electrode. In Electrochemistry, the mass transfer can take place in three ways: diffusion, migration and convection.

These are kinetic parameters which influence the rate of reaction. Adding electrolyte or mixing the solution could reduce these effects.

A Rotating Disk Electrode (RDE) allows the precise control of mass transport of reacting species to the electrode surface in an electrochemical setup. It therefore enables us to distinguish between mass transport and reaction kinetics.

The general theory describing mass transport at a rotating disk electrode (RDE) was developed by Veniamin Grigorievich Levich. The Levich equation gives the height of the sigmoidal wave observed in Rotating Disk Voltammetry. The sigmoidal wave height is often called the Levich current. According to Levich plot the current of voltammogram is related to rotation speed of RDE:

$$i_L = 0{,}620 * n * F * S * D^{2/3} * v^{-1/6} * \sqrt{\frac{2\pi}{60}} * \Omega^{1/2} * C_\infty$$

With:
i_L = Levich current (A)
n = number of electrons
F = Faraday (96,500 C/mol)
S = Surface of Working Electrode (m^2)
D = Diffusion coefficient (m^2/s)
v = Kinematic viscosity (10^{-6} m^2/s)
Ω = Speed rotation (rpm)
C_∞ = The analyte concentration (mol/m^3)

PURPOSE: In this application note the influence of rotation speed of RDE on electrochemical behaviour of Ferri/Ferro Cyanide couple is investigated through Linear Sweep Voltammetry method.

Parameters

This experiment was performed by OrigaMaster software. The parameters are shown in figure 1. The Pot. Linear Voltammetry (also called Linear Sweep Voltammetry or LSV) method was run 10 times and each time the rotation speed of RDE was increased from 0 to 2,000 rpm.

Each time the rotation speed increased by 200 rpm. Before sweep the potential, the OCP of working electrode was measured for 4 minutes to have more stable electrode.

Pot. Linear Voltammetry	
Potential 1 (mV)	-400, REF
Potential 2 (mV)	600, REF
Scan rate (mV/sec.)	20, 0.015, 0.3
Sampling rate	1:1
Maximum current (mA)	100
Minimum current (mA)	-100
Ohmic Drop Comp.	No
Maximum range	Auto
Minimum range	Auto
Open circuit at end	Yes
Save points	Yes
Analog Filter	1 msec.
Digital Filter	0
Auxiliary input	No

Figure 1: The parameters of the Pot. Linear Voltammetry

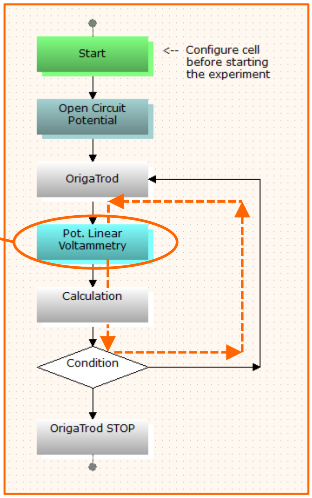


Figure 2: The flowchart of the test

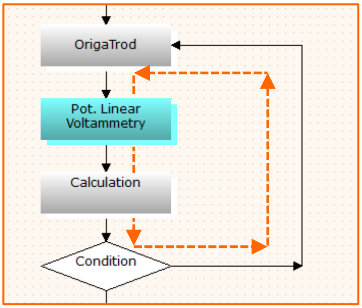


Figure 3: Manual loop

TIPS: By using "Calculation", "Condition" and "Linkable line" tools, we create a manual loop. By this way, the Pot. Linear Voltammetry method can be repeated as many time as needed through a defined cycle. In each cycle the rotation speed of the RDE is different.
See page 3 for more details.

HOW TO INCREMENTE ROTATION SPEED

1

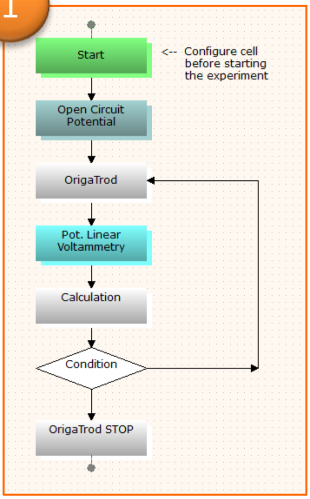


Figure 4: Flowchart with loop

CREATE THE FLOWCHART

Insert all the methods and tools in the right place:

1. Start
2. 1st method (Open Circuit Potential in our case, not included in the loop)
3. OrigaTrod
4. 2nd method (Pot. Linear Voltammetry in this case)
5. Calculation
6. Condition
7. OrigaTrod

Then, with “Linkable line” tool, create a line between the beginning of the loop and the condition.
Finally, link this line with “Condition” and the first method of the loop.

2

ialization - Cell configuration	
Electrodes connected with	OGS/OGF/LDS
Connection cell on	3 electrodes
E1 input	No
E2 input	No
Temperature sensor	No
Settings Instruments	
Delay before disjunction (msec.)	20
Auto ranging delay (msec.)	5
Bandwidth limit	No
Stopping criteria	
Use the potential limits	
Maximum potential (mV)	15000
Minimum potential (mV)	-15000
Use the current limits	
Maximum current (mA)	100
Minimum current (mA)	-100
Variables initialization	
A	0
B	0
C	0
D	0
LoopX	0
LoopY	0
Cycle	0

Figure 5: Start block

CHECK THE VARIABLE

In the START, we define a variable which will be used for the manual loop:
A, B, C, D, LoopX, LoopY and Cycle.

Indeed, this variable can be used as: Rotation speed, Cycle, Potential or Other as you need.

In our example, we took “A” and we define as Speed of the RDE, by putting A as value for the Speed in OrigaTrod block.

OrigaTrod	
Speed (rpm)	A

Figure 6: OrigaTrod block

3

Calculation	
Equation	A, A+200

CREATING THE EQUATION OF THE LOOP

The calculation is the incrementation, so the concept to create an equation.
In this example, we want to increase the rotation speed by 200 rpm per loop.
If the variable "A" is the rotation speed, so the equation is:

$$A = A + 200$$

4

Condition	
Condition	A>2000

CREATING THE CONDITION OF THE LOOP

We have defined the equation behind the loop, now we need to define when the loop ends.
In this example, we want to stop the rotation speed of the RDE when it reaches 2,000 rpm, so when A is strictly upper than 2,000.

We put A > 2000.

Results

An overlay of the 10 Linear Voltammetry curves made from the loop and by different rotation speeds of the RDE are shown in figure 7.

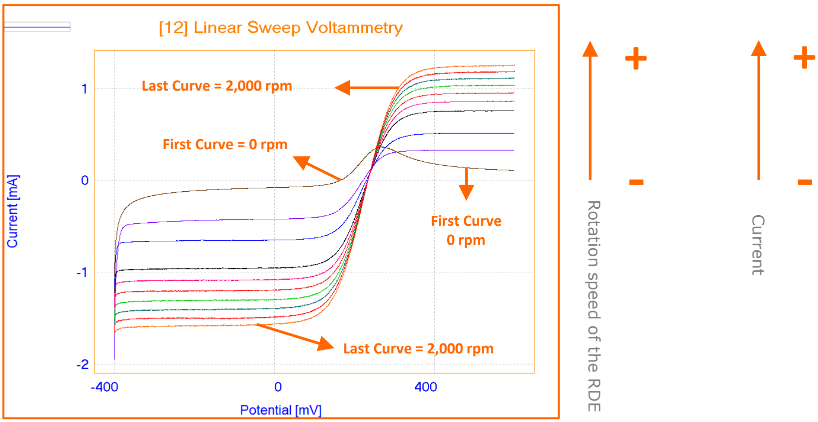


Figure 7: The LSV curves

CONCLUSION: From the loop, we got 10 curves of Pot. Linear Voltammetry. The first curve was made with 0 rpm as RDE speed rotation, the 2nd one with 200 rpm, 3rd one with 400 rpm… up to last one with 2,000 rpm. By overlaying the 10 curves, we notice that, higher the rotation is, higher the current is. So, the rate of mass transport of Ferri/Ferro ions increases per rpm.

Instrument and Electrodes

Figure 8: OrigaStat OGS100

Electrode setup	
Reference Electrode (REF)	Calomel Type: OGR003
Counter Electrode (AUX)	Platinum wire Ø1mm Type: OGV005
Working Electrode (WRK)	Platinum Ø5mm Type: EMEDTPTD5 + OrigaTrod
Electrolyte	Ferri/Ferrate solution 5 x 10^{-2} M in KCl
Instrument	OrigaStat OGS100
Software	OrigaMaster

Figure 9: Electrochemical cell

REF
Calomel

AUX
Platinum wire Ø1 mm

WRK
OrigaTrod
+ Platinum Ø5 mm

OrigaLys ElectroChem SAS

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