APPLICATION NOTE

Determination of diffusion coefficient of electroactive elements through Randles-Sevcik equation by Cyclic Voltammetry

General Electrochemistry AP-GE19

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Introduction

In electrochemical systems, mass transport of electroactive species through the electrode surface, plays a key role in the shape and intensity of voltametric signals. Diffusion is one of the kinetic factor in mass transport phenomena.

Among the different methods used to investigate diffusion, the Randles-Sevcik equation offers a straightforward way to determine the diffusion coefficient of a redox species from cyclic voltammetry experiments, under conditions of semi-infinite linear diffusion.

When a redox system is electrochemically reversible, the peak current observed in a cyclic voltammogram is directly proportional to the square root of the scan rate.

This relation is described by the Randles-Sevcik equation:

$$i_p = 0{,}4463 nFAC \sqrt{\frac{nFD}{RT} v_b}$$

With:
ip = Levich current (A)
n = number of electrons
F = Faraday (96,500 C/mol)
A = Surface of Working Electrode (m²)
C = bulk concentration (mol/m3)
D = Ideal gas constant (8,314 J/mol/K)
R = Kinematic viscosity (10-6 m²/s)
T = Temperature (K)
vb = The scan rate (V/s)

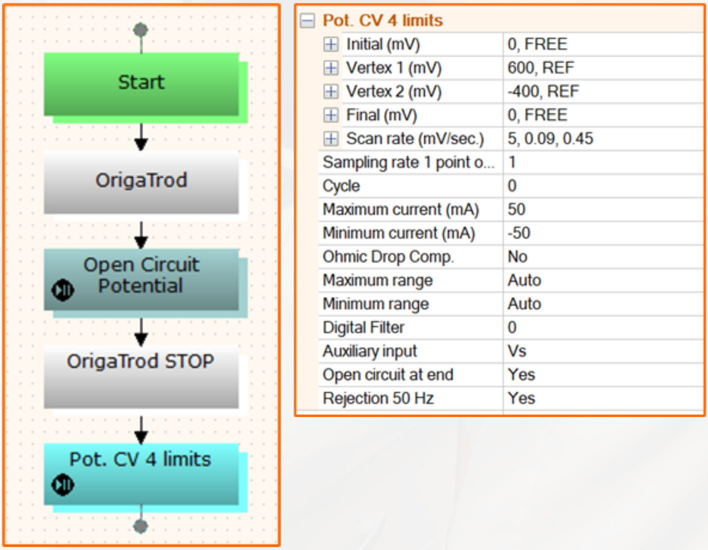
The measurements were carried out in a solution containing 0.01 M potassium ferricyanide ($K_3[Fe(CN)_6]$) and 0.5 M potassium chloride (KCl) as supporting electrolyte. The working electrode was a 5 mm diameter platinum disk, offering a well-defined surface area for accurate current measurements and diffusion coefficient determination.

Parameters

This experiment was performed by OrigaMaster software. The flow chart and parameters are shown in figure 1. The CV4limits were repeated 20 times increasing the scan rate by 5 mV/s each time (from 5 mV/s to 100 mV/s).

Before sweeping the potential, the OCP of the working electrode was measured for 100 seconds to be sure that the cell assembly is well stable.

Figure 1: Parameters of the Pot. CV 4 limits



Pot. CV 4 limits	
Initial (mV)	0, FREE
Vertex 1 (mV)	600, REF
Vertex 2 (mV)	-400, REF
Final (mV)	0, FREE
Scan rate (mV/sec.)	5, 0.09, 0.45
Sampling rate 1 point o...	1
Cycle	0
Maximum current (mA)	50
Minimum current (mA)	-50
Ohmic Drop Comp.	No
Maximum range	Auto
Minimum range	Auto
Digital Filter	0
Auxiliary input	Vs
Open circuit at end	Yes
Rejection 50 Hz	Yes

TIPS: Enabling the “Rejection 50 Hz” option reduces environmental noise, resulting in cleaner and more readable curves. For further details, please refer to the “Rejection Filter” application note.

Results and Discussion

An overlay of the 20 CV curves made from the previous flowchart is shown in figure 2.

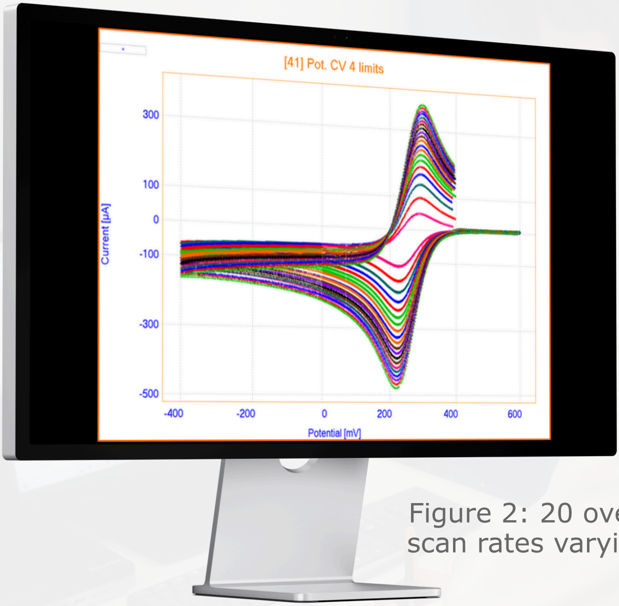


Figure 2: 20 overlayed voltammograms with scan rates varying from 5 mV/s to 100 mV/s

As predicted, it is observed a clear increase in the cathodic peak current with the square root of the scan rate, consistent with diffusion-controlled electron transfer. From the slope of the linear fit, the calculated diffusion coefficient is :

D = 7.04 × 10-10 m²/s, which falls within the expected order of magnitude [1] [2].

These results validate both the experimental setup and the reliability of cyclic voltammetry as a tool for estimating diffusion coefficients. This also reinforces the method’s relevance in preliminary studies of electropolishing conditions, where diffusion processes can influence reaction kinetics and surface behaviour.

References

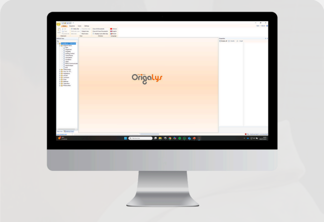
[1] : Klymenko, Oleksiy & Evans, Russell & Hardacre, Christopher & Svir, Irina & Compton, Richard. (2004). Double potential step chronoamperometry at microdisk electrodes: Simulating the case of unequal diffusion coefficients. Journal of electroanalytical chemistry. 571. 211-221. 10.1016/j.jelechem.2004.05.012.

[2] : Nassim Ait Mouheb, Agnès Montillet, Camille Solliec, Jacques Comiti, Patrick Legentilhomme. Caractérisation des écoulements et des transferts de matière dans les micromélangeurs. CFM 2009 - 19ème Congrès Français de Mécanique, Aug 2009, Marseille, France. ffhal-03391323

Necessary instruments and materials

OGS055

Cable and adapter



OrigaMaster 5

REF: Ag/AgCl Electrode

AUX: Platinum Electrode

WRK: OrigaTrod Lt & tip

Glass cell with support

Polishing kit

- Electrolyte: Ferri Cyanide solution 1 x 10^{-2} M in KCl 5 x 10^{-1} M

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