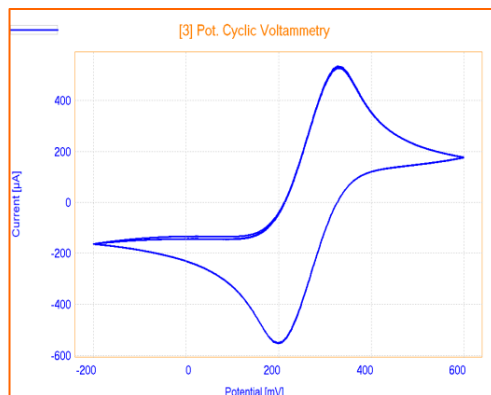
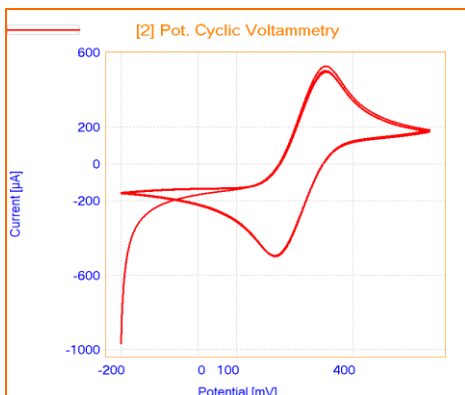




General Electrochemistry AP-ORI06

Stabilization of Working Electrode in Electrochemical Analysis



In Potentiostatic mode, before starting imposing potential, it is very important to stabilize the working electrode to have more accurate results. This application note describes how important methods of stabilizing the working electrode in voltametric and Impedance analysis.



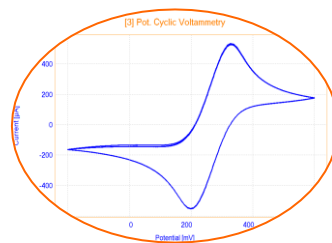
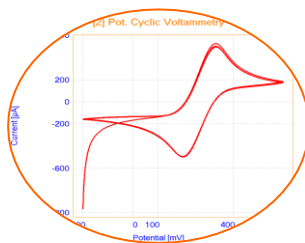
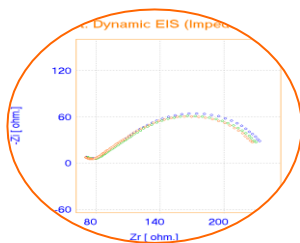
INTRODUCTION

Working electrode is the electrode on which the electrochemical reaction of interest is taking place. In potentiostatic methods (like CV, DPV or EIS) the potential is sweeping or imposing on working electrode.

In microscopic world, potential of working electrode is influenced from its interaction with environment (like electrolyte). The potential stability of working electrode playing a significant role on gaining accurate results.

In order to improve the stability of this electrode, different technics are being used before run potentiostatic tests. Generally, two different electrochemical approaches are more common, the first relying on single chronoamperometry (in many cases it is called stabilization step) and the second on measuring the Open Circuit Potential (OCP) to have a stable OCP value.

In this text the parameters and results of these two approaches will be explained.



TIPS: Although there are many other process to have stable potential on working electrode, like polishing the surfaces, electrochemical cleaning or electrodeposition. In this application note Chronoamperometry and OCP are more focused.



STABILIZATION BY MEASURING OCP

Reach to a stable OCP value is highly recommended before starting electrochemical tests, but this measurement plays more significant role in corrosion studies or in any analyze in which the working electrode react directly with the electrolyte and participate in redox reaction.

When the start potential is defined as "FREE" or versus "FREE" (FREE means OCP potential), the stability of OCP is very important. In these tests the potentials are not defined versus Reference electrode potential but versus OCP potential.

Figure 3 shows a flowchart about corrosion study. In this flow chart the OCP duration is defined as 120 minutes to have a stable OCP value.

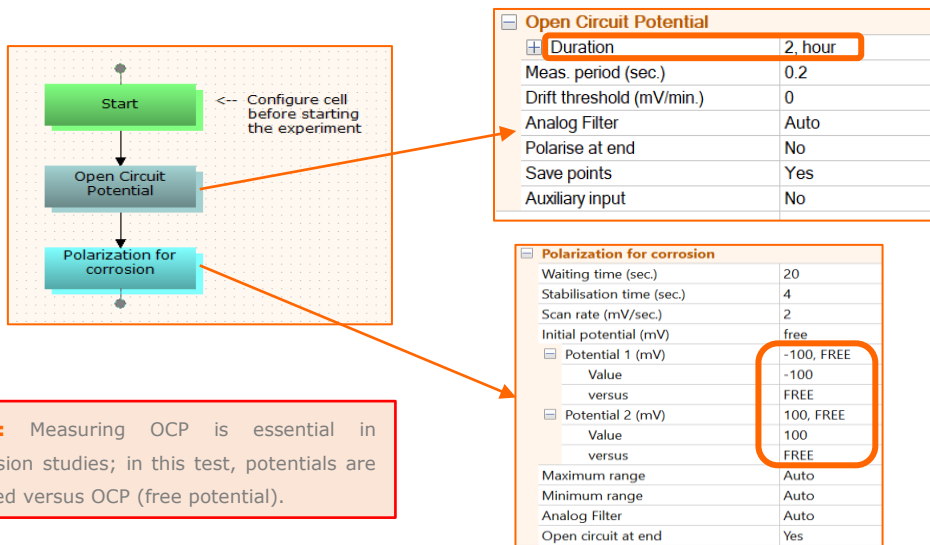


Figure 3: Measuring OCP before corrosion studies

NOTE: Duration of OCP measurement depends on sample and method. For example, some metals need few days to reach to stable OCP.



STABILIZATION BY MEASURING OCP

Figure 4 shows the result of OCP measurement of the mentioned flow chart. The sample is steel in NaCl 2 gr/L. It could be clearly seen from the OCP curve that it took about 70 minutes to reach to stable OCP value.

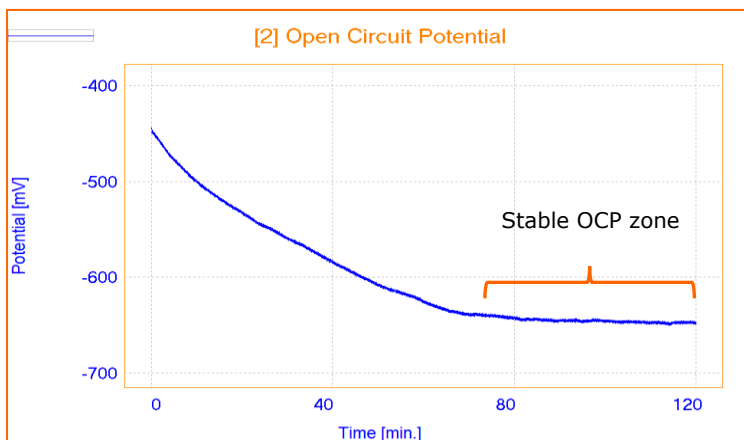


Figure 4: OCP curve of steel in NaCl 2 gr/L; after 70 minute the OCP value is stable.

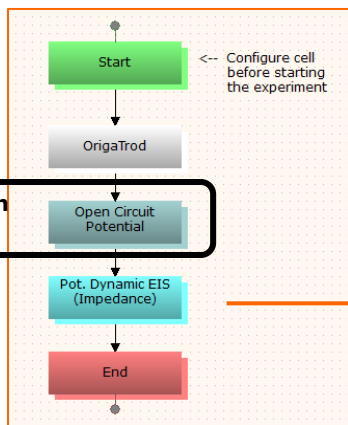
In this test, Steel is consider as working electrode which reacts with electrolyte (NaCl solution) directly and its corrosion behavior was studied.

In Impedance tests, if the DC potential is defined as "FREE", then stable OCP value will highly increase the data accuracy as it is shown in figure 5.

This flowchart was performed on Pt working electrode immersed in Ferri-Ferro Cyanide 0.5 M. The Pt pallet was screwed to RDE and rotated by 500 rpm.



STABILIZATION BY MEASURING OCP



Pot. Dynamic EIS (Impedance)	
DC signal : Stabilisation phase	
DC Potential (mV)	free
Stability max duration (sec.)	60
Stability criterium (µA/min.)	0
Analog Filter	Auto
AC Signal : Frequency scan definition	
Initial frequency	1, kHz
Final frequency	100, mHz
Freq. per decade	20
Frequency distribution	Log
AC sine wave amplitude zero to p...	5
Delay before integration (sec.)	0.1
Average Measurement	
Number of zones	1
Average zone 1	5, 1, kHz
Global parameters	
AC current range	20 mA
Real time plot	Nyquist
Open circuit at end	Yes

TIPS: Before impedance test, OCP must be stable.

Figure 5: The DC potential is defined as OCP value

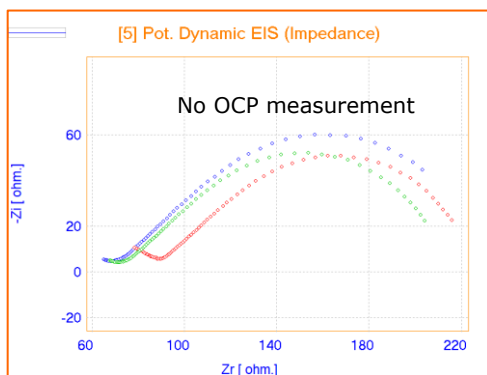
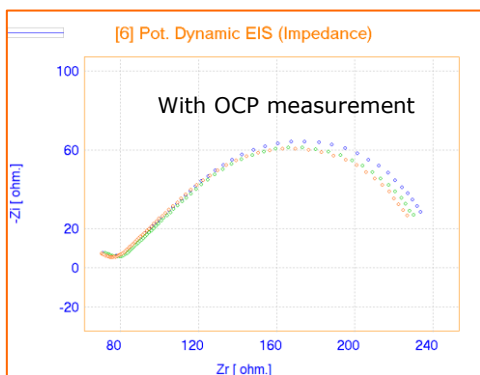


Figure 6: Nyquist plot of Pt electrode in Ferri-Ferro Cyanide 0.5 M

TIPS: In the left curves the working electrode is stabilized. In the right curves, no stabilization was performed so the results are not repeatable.

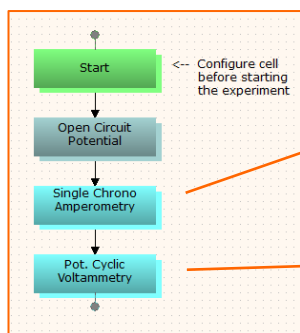


STABILIZATION BY CHRONO AMPEROMETRY

In voltametric methods like CV, LSV, DPV or SWV the electrochemical reaction will be analyzed through changing the potential of working electrode. The potential will be scanned from the defined start potential "Potential 0" (in cyclic methods) or "Potential 1" (in Linear or Pulse methods).

Before starting to scan the potential, it is recommended to impose fixed potential (the same value as start potential) between 5 to 10 seconds through "Single chrono amperometry" on working electrode.

For example, in figure 7, the main test is Cyclic Voltammetry, but as it could be seen in the flow chart, for 10 seconds -200 mV will be imposed on working electrode, because in CV method the start potential "Potential 0" is defined as -200 mV. **The "Open circuit at end" in the "Single Chrono Amperometry" method must be defined "No" enabling the system to consider this voltage.**



Single Chrono Amperometry	
Potential (mV)	-200
Duration	10, sec.
Value	10
Unit	sec.
Open circuit at end	No
Save points	Yes
Auxiliary input	No

Pot. Cyclic Voltammetry	
Potential 0 (mV)	-200
Potential 1 (mV)	600
Potential 2 (mV)	200
Scan rate (mV/sec.)	100, 0.018, 1.8
Sampling rate	1:1
Maximum current (mA)	500
Minimum current (mA)	-500
Ohmic Drop Comp.	No
Maximum range	Auto
Minimum range	Auto
Analog Filter	Auto
Digital Filter	0
Cycle	10
Open circuit at end	Yes
Save points	Yes
Auxiliary input	No

TIPS: In order to get a stabilized working electrode for the CV method, we perform a Chrono Amperometry, at the same Start potential as the CV, for only few seconds.

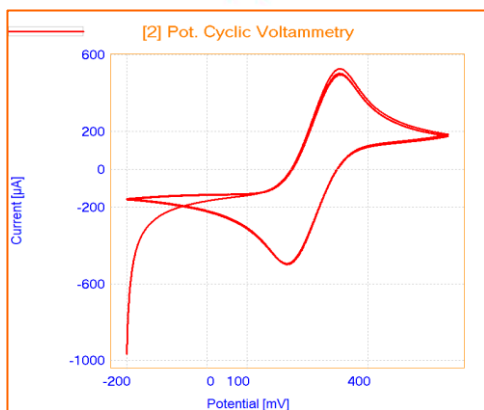
Figure 7: Using a Chrono Amperometry method as stabilization



STABILIZATION BY CHRONO AMPEROMETRY

Figure 8 shows two cyclic voltammograms in Ferri-Ferro Cyanide solution. In the red curve the working electrode (WRK) is not stabilized while in blue curve, before starting the CV, -200 mV was imposed for 10 seconds on working electrode.

No stabilization



Stabilization

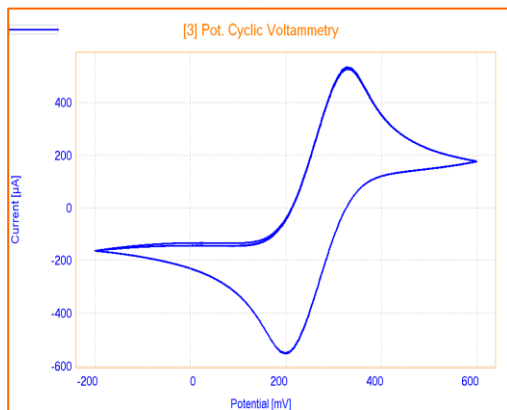


Figure 8: Cyclic voltammograms of Ferri-Ferro cyanide in KCl.

NOTE: In the cyclic voltammetry methods, the "Potential 0" is considered as start potential while in other voltammetry methods like LSW, DPV, SWV, the "Potential 1" is the start potential. It must be noticed that for stabilizing the working electrode, the start potential, is the potential that will be defined in chrono amperometry.



INSTRUMENT AND ELECTRODES



Figure 9: OrigaStat OGS100

Electrode setup

Reference Electrode (REF)	Calomel Type: OGR003
Counter Electrode (AUX)	Platinum wire \varnothing 1mm Type: OGV005
Working Electrode (WRK)	Platinum and steel \varnothing 5mm connected to RDE
Electrolyte	Ferri/Ferrate solution 0.5 M in KCl, NaCl solution
Instrument	OrigaStat OGS100
Software	OrigaMaster

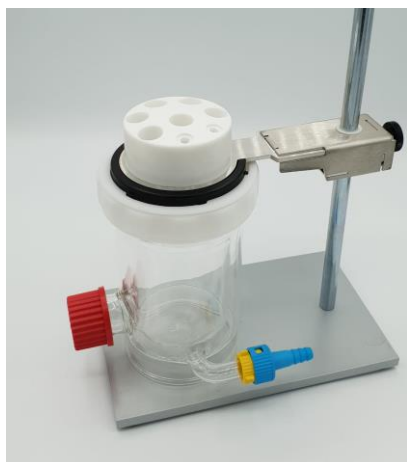


Figure 10: Electrochemical cell

REF

Calomel



AUX

Platinum wire \varnothing 1 mm



WRK

*Platinum and steel
tips \varnothing 5 mm*



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