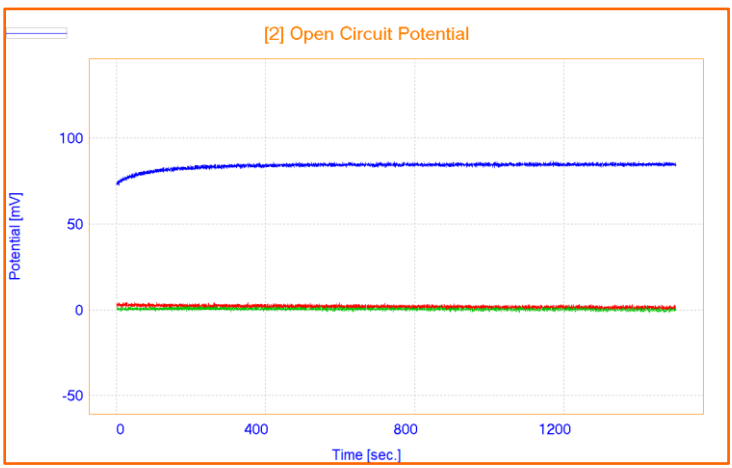
Application Note

General Electrochemistry
AP-GE11

Verification of Reference electrode through OCP method



In electrochemical analysis, reference electrode is used to measure the potential of working electrode. Reference electrode must have stable and well-known potential. These parameters play a significant role on accuracy of results.
In this application note it will be described how to check if a reference electrode works well through OCP determination.

Origalys Electrochem

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INTRODUCTION

In electrochemical cells Reference Electrode is used to measure the potential of working electrode in different configurations (2, 3 or 4 electrodes configurations). Having a stable and well-defined potential is the specification of an ideal reference electrode. There are different kinds of reference electrodes as SHE, Ag/AgCl, Calomel, etc.

Many factors can influence on functionality of reference electrode:

- The filling solution (always needs to be checked to be clear without any crystal or precipitation)
- Bubbles (make sure that there is not any bubble inside the electrode)
- Porous Plug (some times it is contaminated or broken)

While all these parameters have been checked, in order to verify the accuracy of reference electrode and calibrating, it is needed to check its potential with a validated reference electrode.

The best electrode for this reason is Standard Hydrogen Electrode (SHE) which has 0 potential as default. But it is not possible to use this electrode in all laboratory because of its special specifications and condition.

In this order, other verified reference electrodes are recommended like Ag/AgCl or Calomel electrode as well.

In this application note 2 main methods are described to check the accuracy of Ag/AgCl and Calomel reference electrodes.

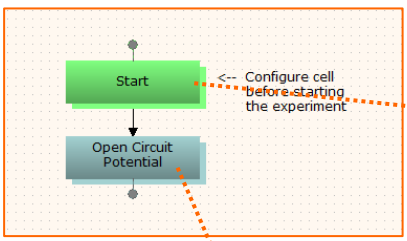
TIPS: The main concept of this evaluation is gaining more accurate and reliable electrochemical curves and results.

TEST IN 2 ELECTRODE MODE

1

Parameters: OCP of 1,500 sec.

Set the START block on 2 electrodes



Properties

Display all | Details | Graph

Initialization - Cell configuration	
Electrodes connected with	OGS/OGF/LDS
Connection cel on	**2 electrodes**
E1 input	No
E2 input	No
Temperature sensor	No
Settings Instruments	
Stopping criteria	
Variables initialization	

Open Circuit Potential	
Duration	1500, sec.
Meas. period (sec.)	0.2
Drift threshold (mV/min.)	0
Analog Filter	Auto
Polarise at end	No
Save points	Yes
Auxiliary input	No

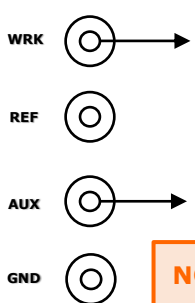
NOTE: We measure the potential between two electrodes.

Figure 1: Parameters of the OCP test with 2 electrodes configuration

2

Connections: It requires two REFERENCE electrodes

One to be checked and the other one should be already checked



Connect here the REF electrode you need to verify

Connect here a "validated" REF electrode

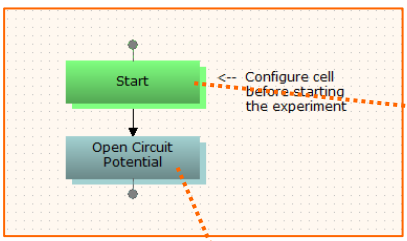
NOTE: This reference electrode must have high accuracy and stable potential.

TEST IN 3 ELECTRODE MODE

1

Parameters: OCP of 1,500 sec.

Set the START block on 3 electrodes



Properties

Display all | Details | Graph

Initialization - Cell configuration

Electrodes connected with	OGS/OGE/LDS
Connection cell on	3 electrodes
E1 input	No
E2 input	No
Temperature sensor	No

Settings Instruments

Stopping criteria

Variables initialization

Open Circuit Potential

Duration	1500, sec.
Meas. period (sec.)	0.2
Drift threshold (mV/min.)	0
Analog Filter	Auto
Polarise at end	No
Save points	Yes
Auxiliary input	No

WARNING: Perform only OCP measurement. Electrodes may be dammaged by any method applying a potential or a current to the electrodes.

Figure 2: Parametres of the OCP test with 3 electrode configuration

2

Connections: It requires two REFERENCE electrodes and ONE AUXILIARY electrode

WRK → Connect here the REF electrode you need to verify

REF → Connect here a "validated" REF electrode

AUX → Connect here the AUX electrode: Platinum counter-electrode

GND

NOTE: This validated reference electrode must have high accuracy and stable potential.

RESULT AND DISCUSSION

Figure 3 shows the OCP measurement of 3 Ag/AgCl reference electrodes. The validated reference electrode which used for this experiment was Ag/AgCl electrode.

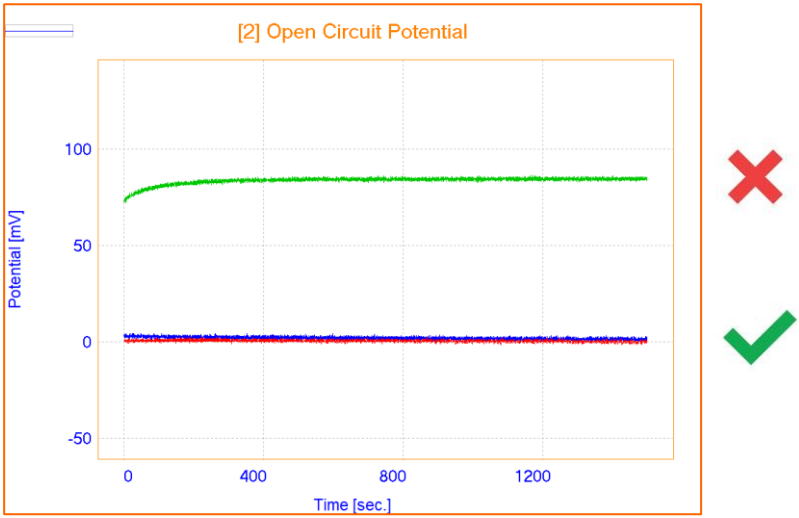


Figure 3: OCP curve of 3 reference electrodes

The red and blue curves correspond to the reference electrodes which works well, because they show few mV of difference in potential, whereas the green curve is related to a defective electrode.

The results of both configurations (2 or 3 electrode) are the same.

NOTE: The potential of Ag/AgCl reference electrode versus SHE is 199 mV. It should be considered that here the 0 mV is the difference of potential between two Ag/AgCl electrodes.

TEST IF WE DO NOT HAVE A VALIDATED REF

1 Measuring the OCP potential of a copper rod.
In a Cu2+ solution.

If no validated reference electrode is available, then there is a second solution. In this method, a copper rod or pellet (which is well polished) will be immersed in a Cu2+ solution (with well-know concentration). As the standard potential of copper reaction is 337 mV versus, SHE:

$Cu^{2+} + 2e \Longrightarrow Cu \qquad E_0 = 337$ mV (vs SHE in 25°C)

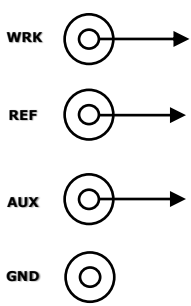
Then the OCP value will show this potential but versus the reference electrode that is used according to Nernst equation.

It must be noticed that regarding Nernst equation, the Temperature and concentration of solution must be considered as well:

$E = E_0 + RT/nF \ Ln \ [Ox]/[Red]$

$E = E_0 + 0.059/n \ Log \ [Ox]/[Red]$ (in 25 °C)

2 Connections: It requires one REFERENCE electrode, ONE AUXILIARY electrode and one Copper Rod as WORKING electrode.



WRK → Connect here the COPPER ROD

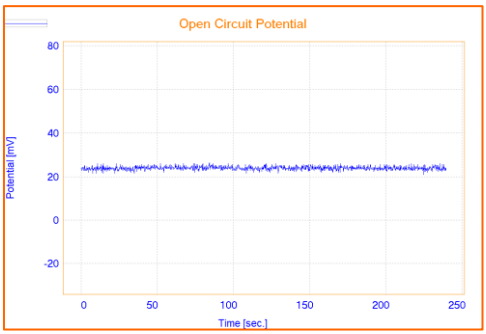
REF → Connect here the REF electrode you need to verify

AUX → Connect here the AUX electrode: Platinum counter-electrode

TIPS: The parameters of the test were the same as Figure 2 in duration of 4 minutes.

RESULT FOR CALOMEL REF ELECTRODE

Figure 4 shows the OCP value of the Copper rod immersed in Cu2+ 0.004 M versus **Calomel** reference electrode.



Between 20 and 30 mV versus Calomel electrode

=>

The REF electrode is fine

Figure 4: OCP curve of copper rod in Cu^{2+} 0.004 M versus Calomel electrode

In this curve the average value of OCP is 25 mV versus Calomel electrode.
The Potential of Calomel electrode versus SHE is 244 mV. Therefore, the average value of OCP is 269 mV versus SHE.
According to the Nernst equation, now we can verify if the reference electrode works well or not:

$E = E_0 + 0.059/n \text{ Log } [Ox]/[Red]$ (in 25 °C), Where:

E= 269 mV

[Ox] = 0.004 M

n=2

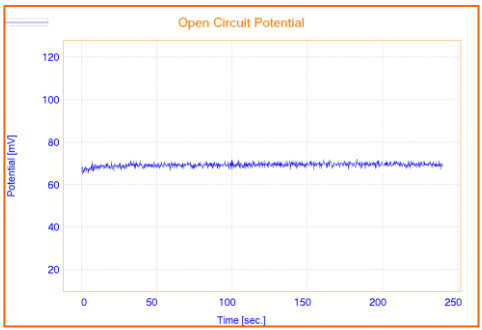
=➔ $269 = E_0 + (0.03) \times \log (0.004)$

=➔ E_0 = 341 mV (Value which is gained in laboratory)

To compare this value with the standard E_0 value, (341 mV ….. 337 mV), there is around 4 mV difference.

RESULT FOR Ag/AgCl REF ELECTRODE

Figure 5 shows the OCP value of the Copper rod immersed in Cu2+ 0.004 M versus **Ag/AgCl** reference electrode.



Between 60 and 70 mV versus Ag/AgCl electrode

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The REF electrode is fine

Figure 5: OCP curve of copper rod in Cu^{2+} 0.004 M versus Ag/AgCl electrode

Here the average value of OCP is about 69 mV versus Ag/AgCl electrode.

The Potential of Ag/AgCl electrode versus SHE is 199 mV. Therefore, the average value of OCP is 268 mV versus SHE.

Again, thanks to the Nernst equation, verification of the reference electrode will be possible:

$E = E_0 + 0.059/n \text{ Log } [Ox]/[Red]$ (in 25 °C), Where:

E= 268 mV

[Ox] = 0.004 M

n=2

=➔ $268 = E_0 + (0.03) \times \log (0.004)$

=➔ E_0 = 340 mV (Value which is gained in laboratory)

There is 3 mV of difference from standard value (340 mV ….. 337 mV).

Note: Considering that the temperature of laboratory was not 25 °C and all situation were not completely standard, ±5 mV of difference is acceptable.

INSTRUMENT AND ELECTRODES

Figure 5: OrigaStat OGS100

Electrode setup	
Reference Electrode (REF)	Ag/AgCl Type: OGR007 Calomel Type: OGR003
Counter Electrode (AUX)	Platinum wire Ø1mm Type: OGV005
Electrolyte	KCl 0.1 M Standard Copper Solution 1000 ppm
Instrument	OrigaStat OGS100
Software	OrigaMaster

Figure 6: Standard Copper solution 1000 ppm (0.004 M)

REF
Ag/AgCl

Calomel

AUX
Platinum wire Ø1 mm

WRK
Copper Rod

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