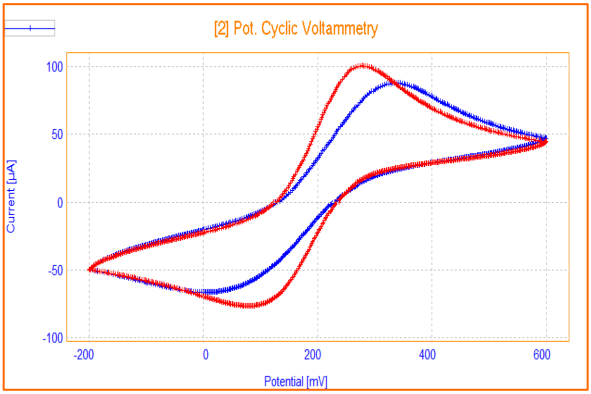
Application Note

General Electrochemistry
AP-GE13

Influence of Ohmic Drop compensation on cyclic voltammetry results



The ohmic drop (OD) is the product of the current which flows through the resistance of the electrolyte between the reference electrode and the electrochemically active interface of the working electrode or the resistance of the cables, which draw the real imposed potential of the system far away from the real value. But how can we compensate these resistances to have more accurate data? This is the issue of this application note.

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INTRODUCTION

A potentiostatic experiment imposes a potential and record a current. This potential is expected to be the potential of the electrochemical active surface. However, because of the ohmic drop phenomenon, the potential at the interface is slightly lower than the potential which is expected to be imposed. In these conditions, when a linear potential sweep versus time, the potential at the interface is not linear.

Example: The applied setpoint potential at the WRK versus the REF is +100 mV. Due to an ohmic drop of 20 mV, the potential really applied at the WRK (versus the REF) by the potentiostat is +120 mV.

Why is it necessary to compensate the iR? Numerous theories, especially in cyclic voltammetry, are valid only if the potential is driven linearly as a time function at the interface itself. The linearity is not respected, because there is an ohmic drop. The theoretical solution is to drive the potential with a compensation of the ohmic drop.

With OrigaMaster software there are 4 ways to perform Ohmic Drop compensation:

- **Feed Back manual**
- **Feed Back Auto**
- **Static Manual**
- **Static Auto**

In manual mode you need to inter the exact value of R in the box, while in Auto mode the software compensate the OD automatically

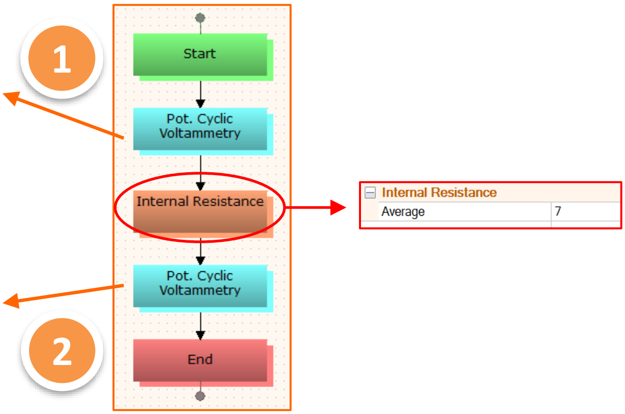
NOTE: Normally "Auto" mode is used when you are not sure about the R value or the R is not stable enough. "Auto" modes are more user friendly as well.

For more information about other methods of OD compensation please contact us: contact@origalys.com

PARAMETERS OF THE TEST

In order to show the influence of Ohmic Drop on the cyclic voltammetry, two CV tests were performed. One without compensation (1) and the other with compensation (2). The parameters of the tests could be found in figure 1.

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)	100
Minimum current (mA)	-100
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



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Scan rate (mV/sec.)	100, 0.018, 1.8
Sampling rate	1:1
Maximum current (mA)	100
Minimum current (mA)	-100
Ohmic Drop Comp.	Static auto
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

Figure 1: In the first CV test, no IR compensation is defined while in the second one it is defiend as « Static Auto ».

In this flow chart, between two CVs, there is another measurement: « Internal Resistance » which permits user to know the average value of the electrochemical cell's resistance. In the related box the average time measurement is defiend.

In this test, the internal resistance of Ferri-Ferro Cyanide 0.5 M without any salt in electrolyte is about 257 Ω and with KCl is about 25 Ω (figure 2).

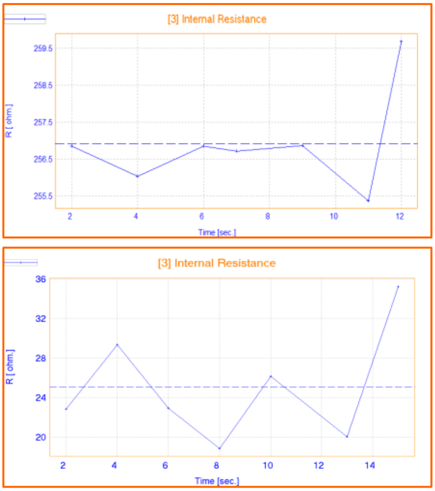
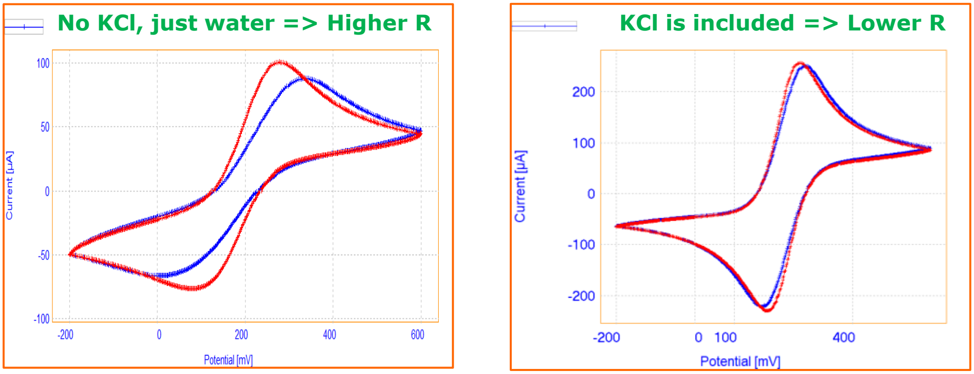


Figure 2: Internal resistance of electrochemical cells

RESULTS AND DISCUSSION

Figure 3 shows the two different CVs. One of them was performed on Ferri/Ferro cyanide 0.5 M with KCl and the other one was performed in the same sample but without KCl. It is obvious that the resistance of the electrochemical cell with KCl is much lower than the other one (figure 2). It could be understood from the curves that the red graph is more closed to a reversible electrochemical redox reaction with higher peak current. The IR compensation is more sensible in the electrochemical cell with higher resistance.



Red: with IR compensation
Blue: without IR compensation

Figure 3: Cyclic Voltammetries of Ferri/ferro cyanid solution 0.5 M in different electrolytes

The principle is that an impedance measurement is performed on a preset current range before measurements start. 90% of the iR compensation found is added by the potentiostat to the potential to be applied, it is a "hardware" type compensation, nearly instantaneous. The scan rate and current range are two parameters needs to be considered if you use “manual” mode.

NOTE: In OrigaFlex series of potentiostats only “Static” mode of OD compensation is available. The “Feed back” mode is only active for OrigaStat series.

INSTRUMENT AND ELECTRODES

Figure 4: OGF500 potentiostat

Electrode setup

Reference Electrode (REF)	Calomel Type: OGR003
Counter Electrode (AUX)	Platinum wire Ø1mm Type: OGV005
Working Electrode (WRK)	Platinum Ø5mm Type: EMEDTPTD5
Sample	Ferri-Ferro Cyanide solution 0.5 M
Instrument	OrigaFlex OGF500
Software	OrigaMaster

Figure 5: Electrochemical cell

REF
Calomel

AUX
Platinum wire Ø1 mm

WRK
Platinum Ø5 mm

OrigaLys ElectroChem SAS

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