

Ohmic Drop

I- Effect on measurements

I-Introduction

The ohmic drop (IR drop) describes the over-potential due to the electron flow through a material. In electrochemistry, it often refers to the potential induced by the resistance of the electrolyte or any other interface (Fig. 1) such as surface films or connectors [1].

For a voltammetry on a given system, the applied potential, in presence of an ohmic drop, should abide by the following equation:

$$E(t) = E_i + v_b t - R_{\Omega} I(t)$$

where E_i is the polarization potential, v_b is the scan rate and t is the time.

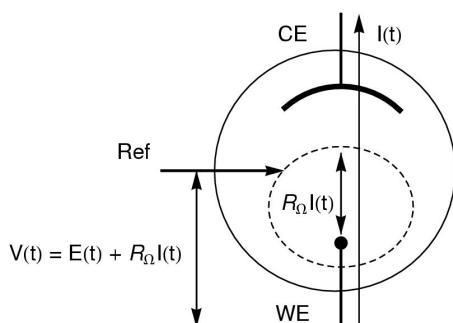


Fig. 1: Scheme of ohmic drop in the standard three-electrode set-up (V: potential applied by the potentiostat; E: potential at the electrode and R_{Ω} : ohmic drop).

As it will be shown in this note, ohmic drop can have an influence on the shape of the curves measured and be a source of error during the analysis of the results obtained. In this context, the effect of the IR drop on several electrochemical techniques are highlighted.

N.B.: All settings and raw data files presented hereafter are available in the Data Sample folder of EC-Lab® Software with the name as follows: techniquesXOhm_ODI.mpr.

II-Steady-state condition

The ohmic drop has an effect on the shape of voltammetry measurements.

N.B.: It is important to note that ohmic drop effect is a critical parameter for ultra fast scan rate investigation [2].

II.1 Voltammetry

In this context, steady-state voltammetry is performed according to settings described in Fig. 2.

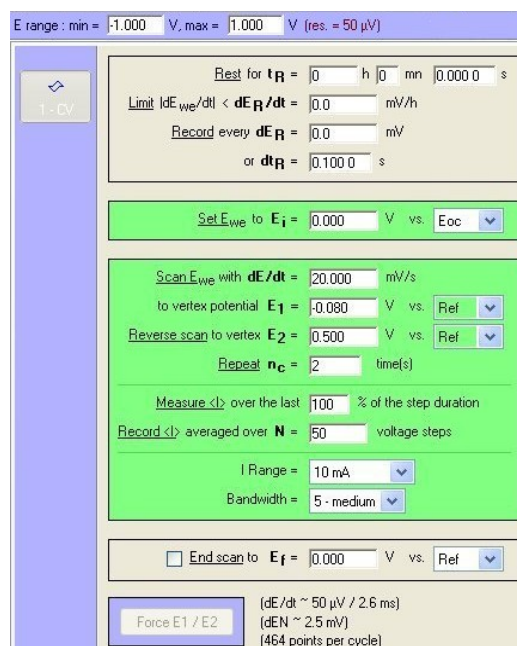


Fig. 2: Voltammetry settings window.

Investigations are carried out with a solution of $[\text{Fe}(\text{CN})_6]^{3-}$ (0.6 mM) with KCl as supporting salt (0.5 M). Three-electrode set-up is used and constituted as follows:

- platinum electrode (surface electrode $A = 3.14 \text{ mm}^2$) as working electrode (WE),
- Standard Calomel Electrode (SCE) as reference electrode,
- platinum wire as counter electrode.

Scan rate and rotating rate are of $20 \text{ mV}\cdot\text{s}^{-1}$ and 2 000 rpm, respectively.

Resulting curves are presented in Fig. 3.

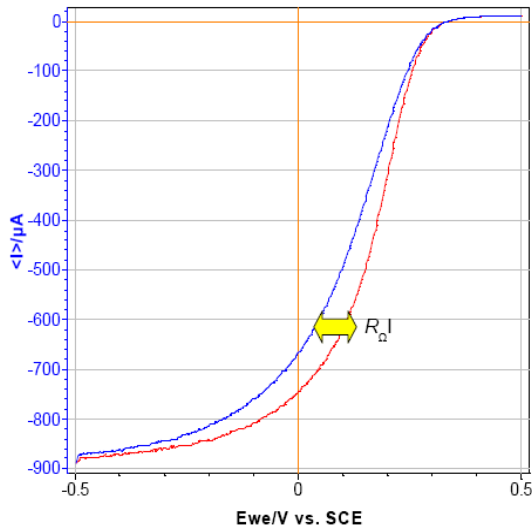


Fig. 3: Steady-state curves of $[(Fe(CN)_6)^{3-}]$ (0.6 mM) + KCl (0.1 M). No resistance and resistance of 100 Ω added in series with the WE.

The effect of the ohmic drop appears clearly in Fig. 2 and the difference of potential between both curves for each current value is equal to $R_{\Omega}I$. For example, at -500 μA, potentials are 150 and 98 mV without and with additional resistance, respectively. This yield to a resistance of about 100 Ω.

II.2 Tafel plot

The user must be careful when trying to determine the corrosion current, for example, with Tafel plot analysis from LP curves of circuit #2 of TestBox-3 according to settings presented in Fig. 4 [3].

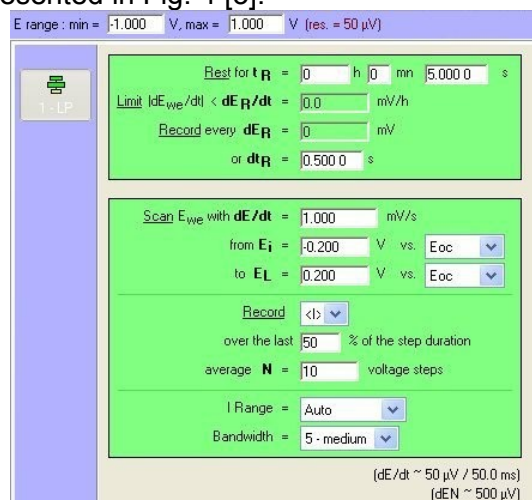


Fig. 4: LP Settings window.

As Fig. 5 shown the ohmic drop has an influence on the curves plotted in $\log |i|$ vs. E_{we} .

In the cathodic and the anodic areas (red arrow in Fig. 5), the curve with the additional resistance of 1 kΩ doesn't exhibit linear behavior but a curved one due to the ohmic drop. That's why, Tafel Fit of each curve give different results. In this case, the current corrosion of the curve obtained without additional resistance ($I_{corr} = 23$ nA) is twice than those obtained with the additional resistance ($I_{corr} = 44$ nA).

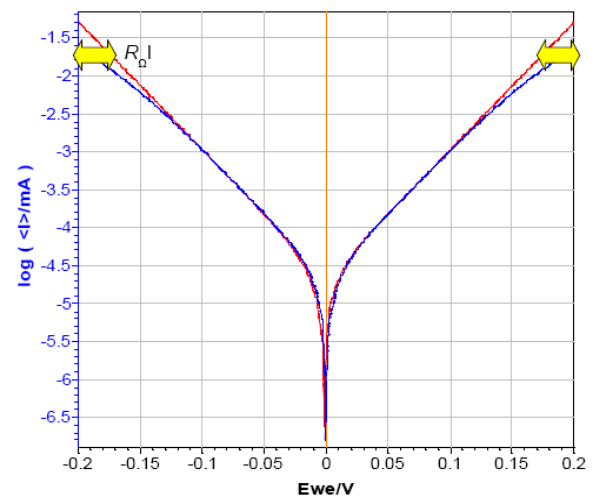


Fig. 5: Steady-state curves of circuit #2 of TestBox-3. No resistance and additional resistance of 1 kΩ in series with the WE.

II.3 Other example

Addition of resistant can also induce some tricky behavior. For example, the circuit #3 of TestBox-3, its steady-state curve with the settings of Fig. 6 gives typical peak for a Z-shaped curve. But if a resistance (for instance: 1 kΩ) is added in series with the WE in order to simulate the ohmic drop, the shape of the resulting curve is totally modified *i. e.* shift of the potential maximum and appearance of a hysteresis phenomenon between forward and reverse scan (Fig. 7). This phenomenon is due to the specific behavior of this circuitry.

From the shift potential, it is possible to calculate the resistance of the ohmic drop. For example, in this experiment the potential shift is 1.7 V and the current at the maximum is 1.7 mA which corresponds to a resistance of 1 kΩ.

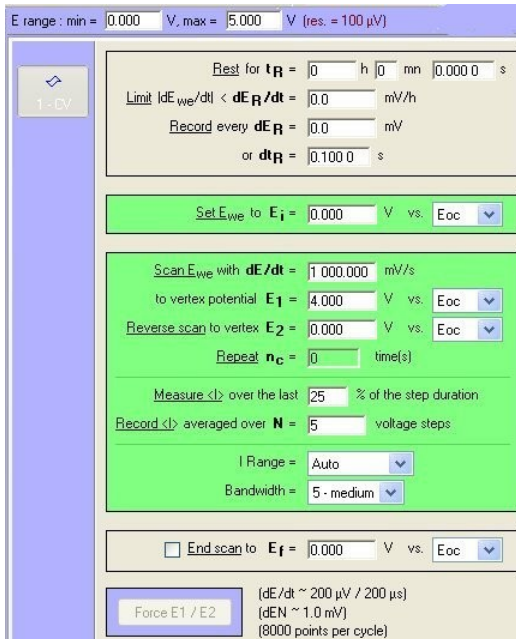


Fig. 6: CV setting window.

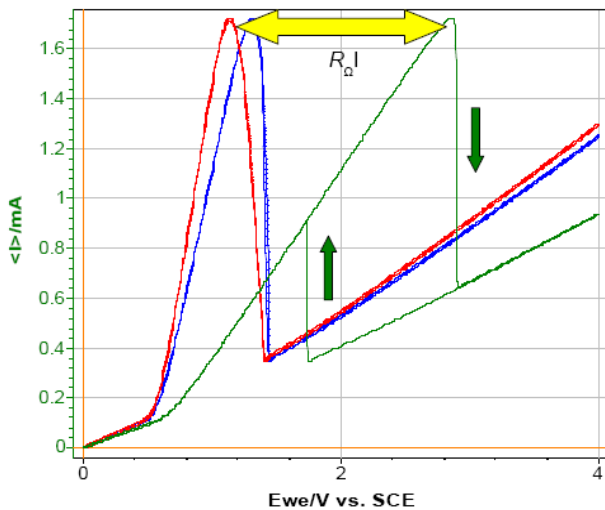


Fig. 7: Steady-state curves of circuit #3 of TestBox-3. **No resistance, resistance of 100 Ω and 1 kΩ** added in series with the WE.

III-Impedance measurements

The ohmic drop is very easy to determine from impedance measurements in the Nyquist plot. It is often associated with the ohmic resistance R_{Ω} which can be identified looking at the real part of impedance for high frequencies [4]. Indeed, the ohmic drop can be modeled in an electrical circuit by adding a resistance in series between the working electrode and the reference electrode [1].

Nyquist plots were obtained by performing Potentiostatic Electrochemical Impedance

Spectroscopy (PEIS) investigations on circuit #3 of TestBox-3 according to settings of Fig. 8, resistance of 100 Ω or 1 kΩ is added to the circuit to simulate the ohmic drop. By looking at the diagram (Fig. 9), the ohmic drop effect is obvious. Indeed, the shift at high frequency is due to the presence of the additional resistances.

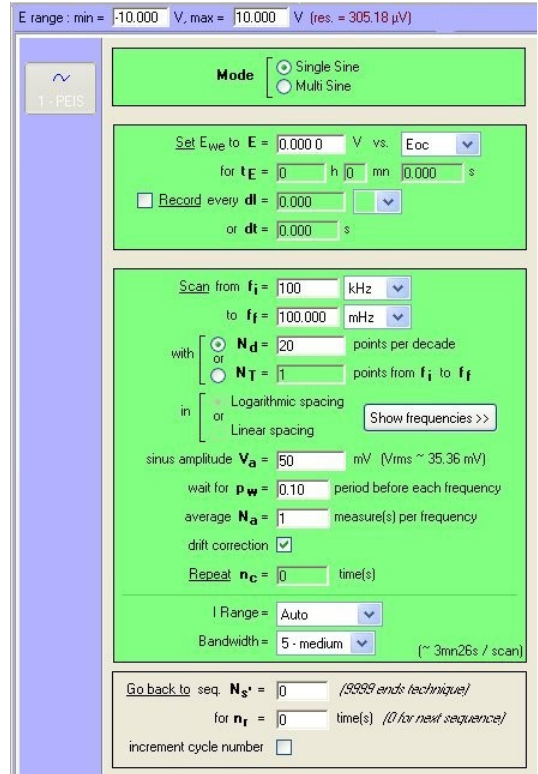


Fig. 8: PEIS Settings.

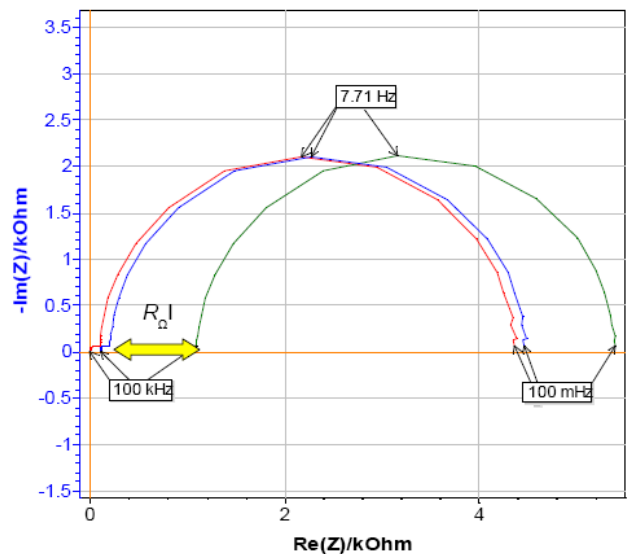


Fig. 9: Nyquist plot of circuit #3 of TestBox-3 in the. **No resistance, resistance of 100Ω and 1 kΩ** added in series with the WE.

III-Non steady-state condition

Non-stationary curves were also plotted for the system described in II.1 according to the settings of Fig. 10. Results (Fig. 11) show an influence of the ohmic drop on the potential peak AND also on the current.

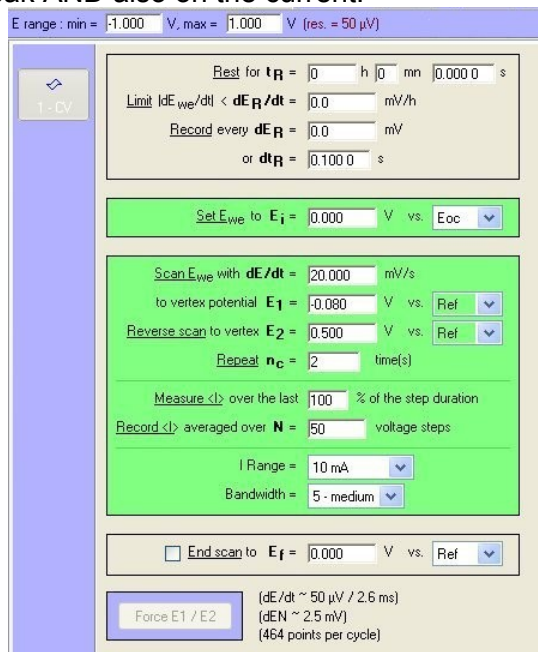


Fig. 10: CV setting window.

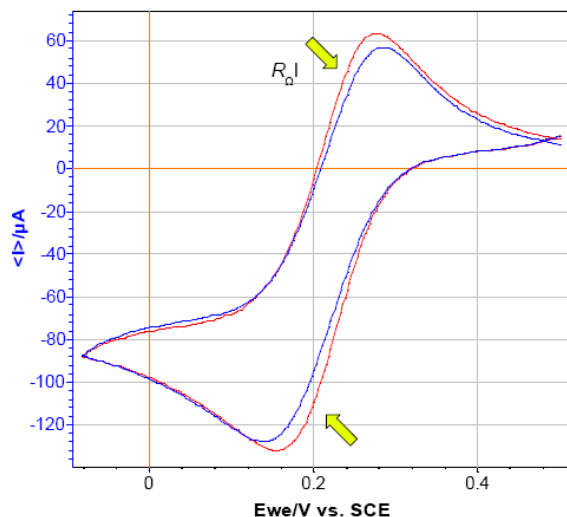


Fig. 11: CV curves of $[(\text{Fe}(\text{CN})_6)^{3-}]$ (0.6 mM) + KCl (0.1 M). **No resistance** and **resistance of 100 Ω** added in series with the WE.

Indeed, on one hand, potential peaks are shifted towards cathodic values for the reduction peak and towards anodic values for the oxidation peak. On the other hand, maximum current values are under-estimated. These two changes could mislead the user to

think the electrochemical system is slower than what it actually is.

IV-Conclusion

The ohmic drop can have a relevant influence on the different types of measures in electrochemistry. That's why, users should pay attention to its set-up (connection, electrode geometry, ...) in order to minimize the ohmic drop effect.

However, it can be determined quite easily (directly with EIS measurement or by simulation with polarization). This determination can be performed by several techniques in EC-Lab® *i. e.* Current interrupt vs. EIS methods will be discussed in another application note [5].

Moreover, beyond the determination of the ohmic drop, EC-Lab® and EC-Lab® Express software make that it is possible to compensate its influence by manual IR compensation (MIR) or IR compensation by EIS (ZIR).

References

- [1] Cinétique électrochimique, J.P. Diard, B. Le Gorrec, C. Montella, ed., Hermann, 1996, p. 17.
- [2] Ultrafast cyclic voltammetry: performing in the few megavolts per second range without ohmic drop, C. Amatore, E. Maisonhaute, G. Simonneau, Electrochem. Comm., 2000 (2), 81–84.
- [3] Traité des Matériaux, 12, Corrosion et Chimie de Surfaces des Métaux, D. Landolt, ed., Presses Polytechniques et Universitaires Romandes, 2003, p. 184.
- [4] EIS measurements on Li-ion batteries - EC-Lab software parameters adjustment, Application note 23, <http://www.bio-logic.info/potentiostat/notes.html>
- [5] Ohmic Drop. II – Introduction to Ohmic Drop measurement techniques. Application note 28, <http://www.bio-logic.info/potentiostat/notes.html>