



Application Note AN-EC-004

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Part 2 – Measurement: Current interrupt and positive feedback

In Application Note [AN-EC-003](#), the concepts of ohmic drop (also called iR drop or uncompensated resistance) and ohmic resistance were explained and some strategies for reducing the errors due to the ohmic drop were discussed. By employing some of these strategies, the ohmic iR drop can be reduced but cannot be totally eliminated. Fortunately, further steps can be taken with a modern potentiostat,

making it possible to measure the remaining iR drop and then compensate for it. However, only up to 90% of the ohmic iR drop can be compensated for.

This Application Note introduces two tools that researchers using Metrohm Autolab products have at their disposal in order to measure and then correct (or compensate) for ohmic iR drop—current interrupt and positive feedback.

ESTIMATING THE OHMIC DROP

In a potentiostat connected to a three-electrode cell setup, the potential between the working electrode (WE) and a reference electrode (RE) is controlled by means of a control loop. The desired potential difference between the RE and WE is maintained by adjusting the current flow between the counter (CE) and the working electrodes. The ohmic resistance R_u , also known

as uncompensated resistance, causes a potential control error called ohmic drop iR_u . This control error can be corrected by adding a correction voltage proportional to the current flow to the input of the potentiostat. Unfortunately, it is not possible to use a correction potential exactly equal to iR_u and fully compensate the ohmic drop, because the system will go into oscillation.

The ohmic drop depends on the ohmic resistance R_u , which is a function of the cell geometry and the conductivity of the electrolyte. For a planar electrode with uniform current density across its surface, the ohmic resistance is given by the equation shown here, where X (cm) is the distance of the RE from the WE, κ (S cm⁻¹) is the solution conductivity, and A (cm²) is the WE surface area.

$$R_u = \frac{X}{\kappa A}$$

For a spherical electrode (e.g., dropping mercury electrode / DME, or hanging dropping mercury electrode / HMDE) of radius r_0 , the ohmic resistance is given by:

$$R_u = \frac{1}{4\pi\kappa r_0} \left(\frac{X}{X + r_0} \right)$$

For a rotating disc electrode (RDE) of radius r , when the RE is placed far from the working electrode (typically for RDE measurements), the ohmic resistance is given by:

$$R_u = \frac{1}{4\kappa r}$$

MEASURING THE OHMIC DROP

In most cases, the geometries are more complicated and consequently the ohmic drop must be measured experimentally. The three most common methods for measuring the ohmic drop are:

1. Current interrupt
2. Positive feedback
3. Electrochemical impedance spectroscopy (EIS, see [AN-EC-034](#))

The electrical equivalent circuit shown in **Figure 1** is used to illustrate the first two methods in the list above. This circuit corresponds to dummy cell circuit (c) of the Autolab dummy cell 2.

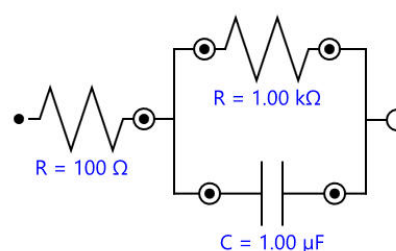


Figure 1. The equivalent circuit used in this study.

CURRENT INTERRUPT

The measurement of ohmic drop using the current interrupt technique is based on the simple application of Ohm's law. When a current i flows through the circuit mentioned in **Figure 1**, the voltage drop across the resistor R_u is equal to iR_u , and the voltage drop across (R_pC) is iR_p . If the

current is interrupted, then i becomes 0 and the voltage across R_u drops almost instantaneously while the voltage across (R_pC) drops with an exponential decay proportional to $\text{EXP}(t/R_pC)$, due to the presence of the capacitor C .

If the voltage is measured just before and immediately after the current has been interrupted, the difference in the measured voltages is the ohmic drop E_{ohmic} . The ratio between the ohmic drop and the current before the interruption is the ohmic resistance R_u . The measurement of the ohmic drop for the dummy cell circuit (c, the equivalent circuit in **Figure 1**) using a PGSTAT302N with an ADC10M fast sampling module is illustrated in **Figure 2**.

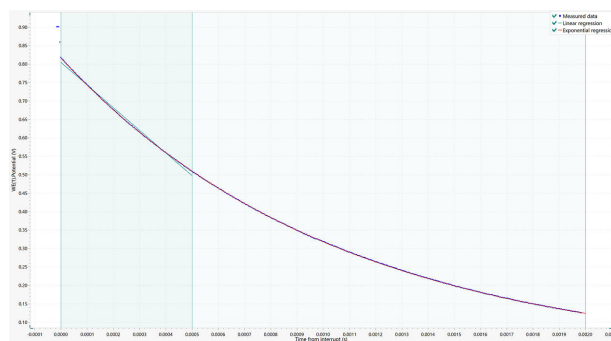


Figure 2. Measurement of ohmic resistance with current interrupt using a PGSTAT302N with the ADC10M.

If an ADC10M module is not available, the method can still be used. However, fewer data points will be recorded, resulting in a less accurate measurement (**Figure 3**).

The measured values are fitted using a linear and an exponential regression, and the calculated R_u values are displayed in the Results tab of the software (**Figure 4**).

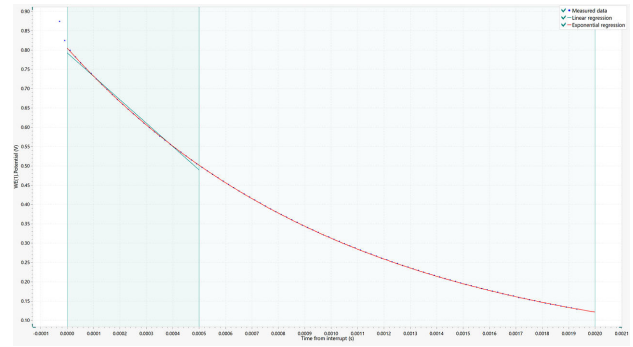


Figure 3. Measurement of the ohmic resistance with current interrupt using the PGSTAT302N. Fewer data points are recorded compared to Figure 2.

The calculated values strongly depend on the specified start and stop positions for the linear and exponential regression. If these positions are not adjusted properly, the calculated values can be significantly different from the real uncompensated resistance. Note that there is no linear part in either **Figure 2** or **Figure 3**, so the value fitted from the exponential regression should be taken as the more accurate value.

POSITIVE FEEDBACK

Another way to measure the ohmic drop is the so-called positive feedback. Since the ohmic drop iR_u is proportional to the ohmic resistance R_u , it might be possible to compensate for the ohmic drop by measuring the current i , multiplying it by the ohmic resistance R_u , and feeding back the resulting ohmic

Results

Ru linear 129.2 Ω

Ru exponential 114.1 Ω

Figure 4. The resistance values obtained from the linear and exponential fitting of the data.

drop to the control loop. In this case, the following points need to be considered: the ohmic resistance is unknown at this stage, and a complete compensation of the ohmic drop would leave the system in oscillation – losing control of the potentiostat.

In the positive feedback measurement, a voltage iR_x is fed back into the control loop during a short potential step measurement. The goal is to find the value of R_x (the iR compensation value) close enough to the ohmic resistance R_u . This is accomplished by trial and error, i.e., repeating the procedure with different values of the iR compensation resistance and checking the resulting plot. An acceptable iR compensation results in damped oscillations of the signal, like the example shown in **Figure 5**.

This method should be used with care. A system that oscillates is a system with more potential, and thus more energy, than necessary. Therefore, undesired side reactions could be triggered, affecting the

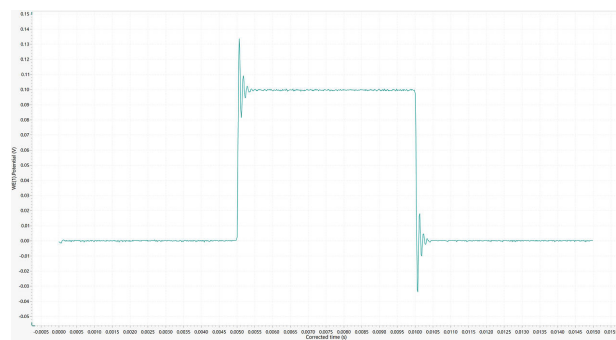


Figure 5. A positive feedback measurement of the circuit from Figure 1, dummy cell (c), with an acceptable iR compensation value of $95\ \Omega$.

electrolyte or damaging the working electrode. The positive feedback can be directly measured in the NOVA software.

PRACTICAL COMPENSATION OF THE OHMIC DROP

Once the value of the ohmic resistance has been measured, it can be used in any desired NOVA procedure. In the properties of the Autolab control command, it is possible to toggle the « iR compensation» switch and insert the ohmic resistance value, as shown in **Figure 6**.

The system will apply the iR compensation value similarly to the positive feedback method described earlier. Therefore, it is strongly recommended to use 80–90% of the ohmic resistance to avoid oscillations and damage to the WE and electrolyte.

Another way to use the ohmic drop is to perform one of the three discussed measurements, and then to use the value of the ohmic resistance to correct the experimental data mathematically.

The current i from the electrochemical experiment is multiplied by the ohmic resistance R_u in order to

Figure 6. The properties of the Autolab control command in NOVA, with the iR compensation switch enabled.

determine the ohmic drop $V_{drop} = iR_u$. Then, V_{drop} is subtracted from the experimentally measured potential V_{exp} , resulting in the corrected potential $V_{corr} = V_{exp} - V_{drop}$. Finally, V_{corr} can be used in the plots and in further post-data treatments.

This Application Note describes two different methods of measuring the ohmic drop and the ohmic resistance. The ohmic drop can be compensated by the potentiostat during the measurement, or a mathematical correction can be applied to the data during post-processing.

Current interrupt and positive feedback are fast

methods, but care is required for their use in order to avoid data misinterpretation or damage to the setup. On the other hand, EIS is a more reliable method to determine the ohmic resistance but requires the FRA32M optional module or VIONIC powered by INTELLO. The EIS method is explained separately in [AN-EC-034](#).

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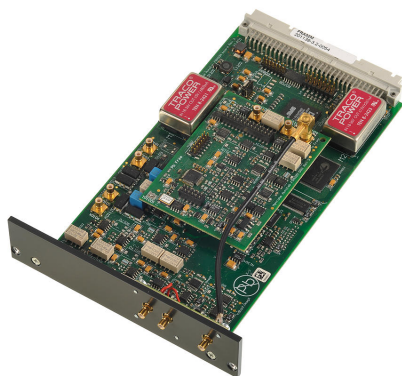
CONFIGURATION



Autolab PGSTAT302N

该恒电位仪/恒电流仪,具有 30 V 顺从电压,带宽为 1 MHz,可与我们的 FRA32M 模块联用,专门针对电化学阻抗谱而设计。

PGSTAT302N 是流行的 PGSTAT30 的后继款型。最大电流为 2 A,借助 BOOSTER20A 电流范围可扩展至 20 A,当电流范围为 10 nA 时电流分辨率为 30 fA。



ADC10M 模块是一个超高速采样模块,可将 Autolab 的采样频率从 50 k样品/s 提高到 10 M样品/s,使您可以拥有间隔为 100 ns 的快速瞬变能力。

如果与 SCAN250 模块联用,您可实现扫描速率高至 250 kV/s 的超高速循环伏安法测量,使其成为研究快速动力学过程的强大工具。



NOVA 是设计为通过 USB 接口控制所有 Autolab 仪器的软件包。

由电化学家针对电化学而设计,集成了超过二十余年的用户体验和最新的 .NET 软件技术,NOVA 使您的 Autolab 恒电位仪/恒电流仪拥有更强性能和灵活性。

NOVA 提供了以下的独特功能:

- 功能强大且灵活的程序编辑器
- 重要实时数据一目了然
- 强大的数据分析和绘图工具
- 集成化控制外围仪器,诸如万通 LQH 液体处理设备

[下载最新版本的 NOVA](#)