

Comprehensive cell impedance measurements using the Interface™ 5000E potentiostat's dual electrometer

Introduction

We often hear positive feedback from our users on the Reference™ 3000 potentiostat with Auxiliary Electrometer (AE). The AE option was designed for users who want to monitor multiple voltage signals synchronized to electrochemical measurements. Four extra cables extended from the front panel of the original Reference 3000 potentiostat, making the AE option a readily identifiable feature. Our Framework Software was also designed to recognize the AE option with our standard scripting. Therefore, from the perspective of the user, the AE option is well known.

In this technical note, we look at the less well-known dual-electrometer feature in our Interface 5000E potentiostat. The dual electrometer allows the user to make a second voltage measurement in addition to the one made by the potentiostat. This is very similar to the AE option of the Reference 3000 potentiostat, with the exception that it uses the pre-existing counter sense (orange) lead to make the second voltage measurement. With no added cables, this feature can be easily overlooked. Effectively, the dual-electrometer feature allows users to make five-electrode measurements.

See our Application Note at Gamry.com:

[Two, Three and Four Electrode Experiments](#)

Setup

Schematically, the dual electrometer is shown in Figure 1. The working electrode (WE) and counter electrode (CE) are the current-carrying electrodes. This is always true in all cell setups with our potentiostats. The working sense (WS), reference electrode (RE), and counter sense (CS) are voltage-sensing electrodes. Using the five-electrode setup, we can measure three independent parameters:

1. The cell current, i_{cell}
2. The cell voltage V_{cell} , which is equivalent to $V_{\text{WS}} - V_{\text{CS}}$

3. The half-cell voltages, V_{pos} and V_{neg}
 - a. V_{pos} is equivalent to $V_{\text{WS}} - V_{\text{CS}}$
 - b. V_{neg} is equivalent to $V_{\text{CS}} - V_{\text{WS}}$

i_{cell} , V_{cell} , and V_{pos} (or V_{neg}) are the parameters that allow us to measure the whole cell impedance and each individual half-cell impedance simultaneously using only a single potentiostat!

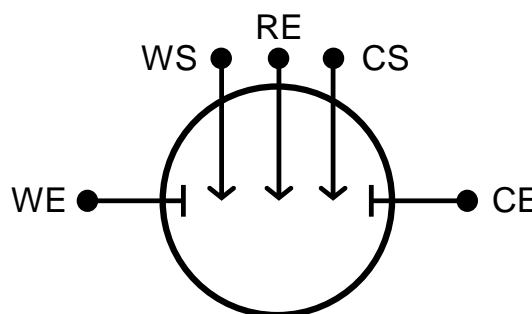


Figure 1. Electrochemical cell setup for a five-electrode measurement. WE: working electrode; WS: working sense; RE: reference electrode; CS: counter sense; CE: counter electrode.

To demonstrate this capability, we connected our Interface 5000 potentiostat to our AC Dummy Cell (part no. 990-00419), which is shown in Figure 2. The front has a pair of five banana jacks (2 mm and 5 mm) to which you connect the potentiostat cell-cable leads. The back shows the RC-R-RC electrical circuit with the traces also visible. This simple circuit approximates the impedance behavior assuming linearity of two electrochemical interfaces separated by an internal resistance.



Figure 2. Front and back of the AC Dummy Cell (part no. 990-00419).

Schematically, the front and back can be overlaid to show where each individual connection is made to the AC Dummy Cell. This is shown in Figure 3. On the AC Dummy Cell, the CS and CE are—ignoring trace resistance—connected to the same node. Similarly, the WS and WE share the same node. Thus, the AC Dummy Cell is not a true four-terminal measurement. In true four-terminal probes such as our battery holders, WS and WE make independent contact with the cell. Using the dual-electrometer mode, we can measure the voltage across the AC Dummy Cell as well as between the CS-RE and WS-RE.

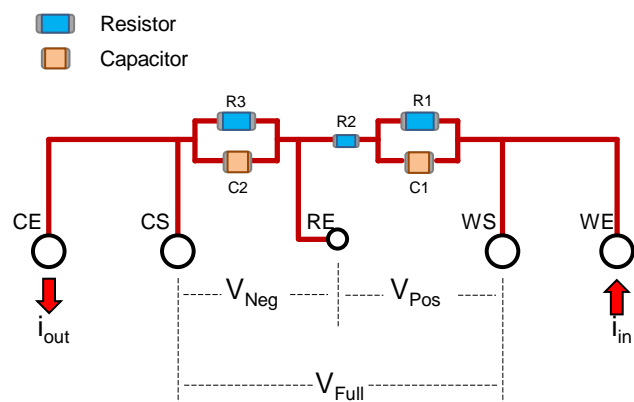
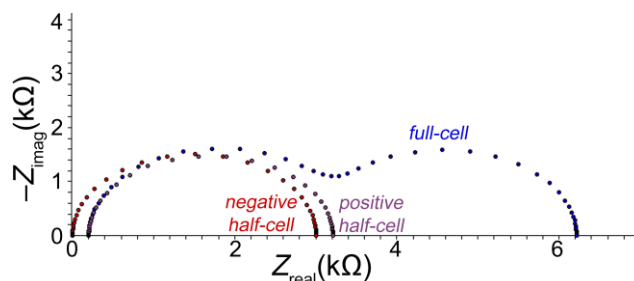


Figure 3. Diagram of the AC Dummy Cell from Gamry Instruments.

Operation

With the cables attached as in the upper photo of Figure 2, we measured the impedance of the AC dummy cell in dual-electrometer mode. The data are plotted as a Nyquist plot and tabulated in Figure 4. Three spectra are shown corresponding to the full-cell impedance (R1C1-R2-R3C2), the positive half-cell (R1C1-R2), and the negative half-cell (R3C2). As expected, the full-cell impedance response is two partially overlapping arcs shifted to the right of the y-axis. This is consistent with two RC pairs in series with a single resistor. The positive half-cell impedance is a single arc shifted to the right of the y-axis. This is consistent with one RC pair in series with a single resistor. Finally, the negative half-cell impedance is a single arc starting at the origin. This is consistent with a single RC pair.



	Full-cell		Positive		Negative	
$R_1(\Omega)$	3000	46.76	3000	13.76		
$C_1(F)$	9.36×10^{-7}	4.15×10^{-8}	9.32×10^{-7}	7.16×10^{-9}		
$R_2(\Omega)$	200.9	1.514	200.2	0.901		
$R_3(\Omega)$	3010	36.74			3010	9.269
$C_2(F)$	3.32×10^{-8}	3.21×10^{-10}			3.33×10^{-8}	1.34×10^{-10}
χ^2	7.78×10^{-6}		1.96×10^{-5}		2.19×10^{-4}	

Figure 4. Nyquist plots of the AC dummy cell. Table shows the fitting results of the impedance data.

The importance of this measurement is as follows: In dual-electrometer mode, we can separate, identify, and model the impedance elements in each half-cell. The important factor is the position of the reference electrode relative to both the working sense and counter sense leads.

Right away, we can identify some advantages for using the dual-electrometer mode.

- Consistency: The full-cell impedance is always a sum of the half-cell impedance unlike with two or

three sequential impedance scans. Drift over time is minimized.

- Time-savings: One impedance scan can yield three sets of impedance data.
- Control: With smart placement of leads, it is possible to isolate and control the impedance elements present in each half-cell impedance spectrum.

As a final sanity check, we should compare the fitted values to the specified values and tolerances of each resistor and capacitor. A quick comparison of the fitted values (Fig. 4) against the nominal values (Table 1) shows that we were successful in measuring the impedance of the AC Dummy Cell.

Table 1. Resistor and capacitor values for the AC Dummy Cell.

	Value	Form-factor	Tolerance
R ₁	3.01 kΩ	SM2010	1% (±30 Ω)
R ₂	200 Ω	SM1206	1% (±2 Ω)
R ₃	3.01 kΩ	SM2010	1% (±30 Ω)
C ₁	1 μF	SM1812	5% (±50 nF)
C ₂	33 nF	SM1206	5% (±1.7 nF)

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