EIS measurements:
Potentio or Galvano mode ?

I – INTRODUCTION

Electrochemical Impedance Spectroscopy (EIS) measurements are generally performed under potentio control than under galvano control. In most cases, the potentio and galvano modes are equivalent (PEIS or GEIS techniques, in EC-Lab® software). So, performing EIS measurements under potential or current control results in the same impedance diagrams. However, in certain conditions, one does not obtain the same results, typically, when the system evolves during the measurement.

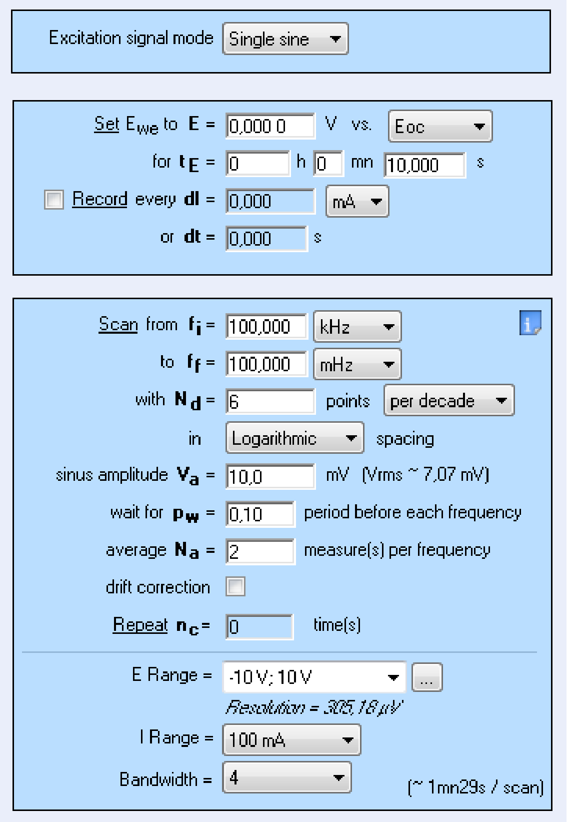
In corrosion applications, *e.g.*, polarization resistance is often determined under potential control around open circuit voltage (OCV). This is an appropriate approach if the corrosion potential does not change during the measurement. If the corrosion potential drifts, the measurements performed at OCV could result in an anodic or cathodic potential respect to the true OCV. Under galvano control, the desired zero-current condition is maintained throughout the recording, ensuring the measurement is performed at the true corrosion potential [1]. In battery applications, it would be interesting to determine the variation of internal resistance during discharge/charge. In this case it could be also appropriate to use the galvano control in EIS measurements [2].

Both type of control, galvano and potentio (GEIS and PEIS techniques, respectively) are available in EC-Lab® software. In this application note, a comparison between the galvano and potentio control in EIS measurements is presented on a commercial Li-ion button battery. Two cases are considered: Firstly, PEIS and GEIS measurements are made around the OCV, and secondly an example, where the use of the galvano control is required, is presented.

II – EIS MEASUREMENTS AROUND THE OCV

EIS measurements were performed in potentio and galvano mode on a commercial Li-ion button cell (nominal capacity 120mAh). After full charge, the battery was discharged under C/10 regime, during 10 min and, after a 40 min rest, the EIS measurements were performed (under potentio or galvano control) around the OCV.

The frequency range for both measurements was between 100 kHz and 100 mHz, with the sine amplitudes of 10mV and 5mA for PEIS and GEIS, respectively. Figs. 1 and 2 show the parameter settings for these measurements.



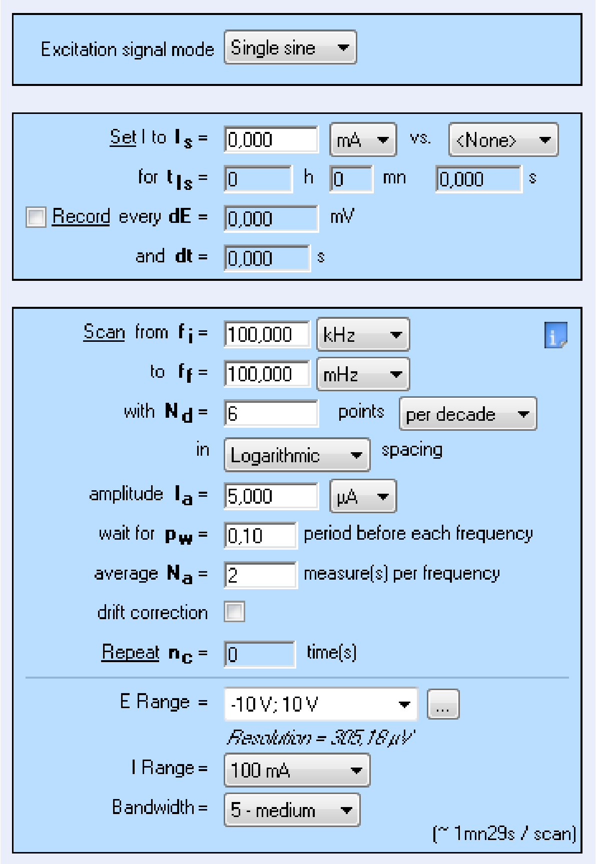
Excitation signal mode: Single sine

Set E_{we} to E = 0,000 0 V vs. Eoc
for t_E = 0 h 0 mn 10,000 s
☐ Record every dI = 0,000 mA
or dt = 0,000 s

Scan from f_i = 100,000 kHz
to f_f = 100,000 mHz
with N_d = 6 points per decade
in Logarithmic spacing
sinus amplitude V_a = 10,0 mV (Vrms ~ 7,07 mV)
wait for p_w = 0,10 period before each frequency
average N_a = 2 measure(s) per frequency
drift correction ☐
Repeat n_c = 0 time(s)

E Range = -10 V; 10 V
Resolution = 305,18 µV
I Range = 100 mA
Bandwidth = 4
(~ 1mn29s / scan)

Figure 1 : Parameter setting windows for the PEIS technique.



Excitation signal mode Single sine

Set I to I_s = 0,000 mA vs. <None>
for t_{Is} = 0 h 0 mn 0,000 s
☐ Record every dE = 0,000 mV
and dt = 0,000 s

Scan from f_i = 100,000 kHz
to f_f = 100,000 mHz
with N_d = 6 points per decade
in Logarithmic spacing
amplitude I_a = 5,000 µA
wait for p_w = 0,10 period before each frequency
average N_a = 2 measure(s) per frequency
drift correction ☐
Repeat n_c = 0 time(s)

E Range = -10 V; 10 V
Resolution = 305,18 µV
I Range = 100 mA
Bandwidth = 5 - medium
(~ 1mn29s / scan)

Figure 2: Parameter setting windows for the GEIS technique.

The battery voltage changes with time, during discharge, rest, PEIS and GEIS measurements, which are shown in Fig. 3. During the rest period, the battery voltage stabilizes before EIS measurements.

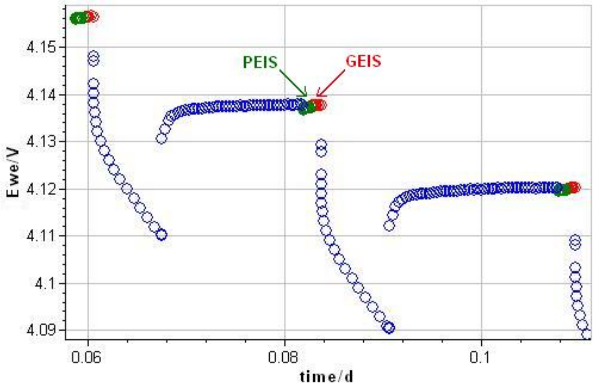


Figure 3 : Voltage *vs.* time during C/10 discharge and rest (blue circles), PEIS (green circles) and GEIS (red circles) techniques.

Figure 4 (Top) shows the first cycle of both PEIS and GEIS and Fig. 4 (Bottom) the evolution of the PEIS Nyquist plot during the discharge.

As shown in Fig. 4 PEIS and GEIS show the same results across the whole range of frequencies, for both experimental conditions. These criteria (same results under potentio and galvano control) could be used empirically to choose the GEIS amplitude.

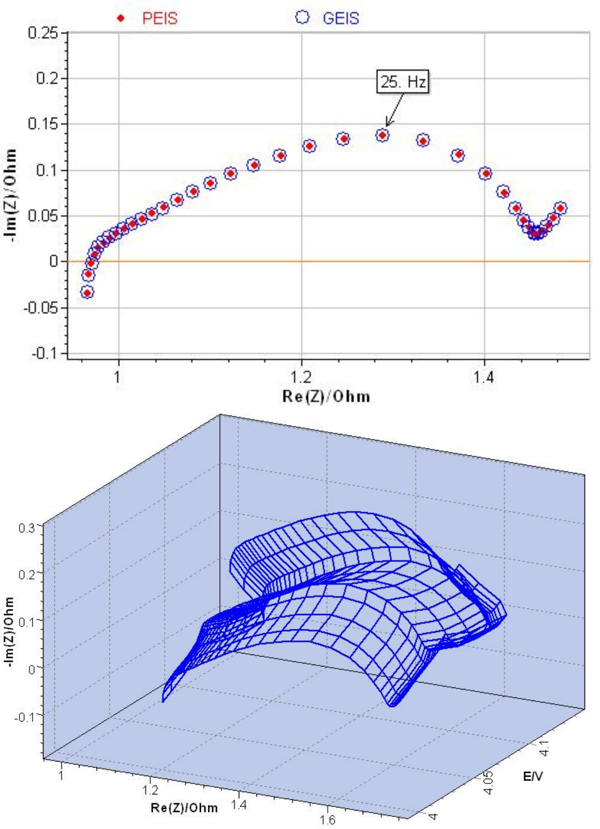


Figure 4 : Top, EIS diagrams under potentio control (PEIS technique, red points) and under galvano control (GEIS technique, blue circles). Bottom, EIS diagram evolution (under potentio control) during the discharge.

The change of internal resistance with the potential or state of charge (SoC) is studied by EIS measurements during discharge (or charge). This resistance is determined fitting the EIS graphs with an Equivalent Electric Circuit. EC-Lab® software provides a powerful user-friendly tool to analyze the successive impedance measurements: Z Fit [3–5]. Z Fit also (automatically) determines and plots the values of electric circuit components for a series of impedance diagrams.

Figure 5 shows the result of the fitting process for the first potentio controlled cycle with the equivalent circuit : L1 +R1 +Q2=R2 +Q3=(R3 +Q4), and the progression of the internal resistance *R*1 with the battery potential. We can observe that the *R*1 value increases during the discharge.

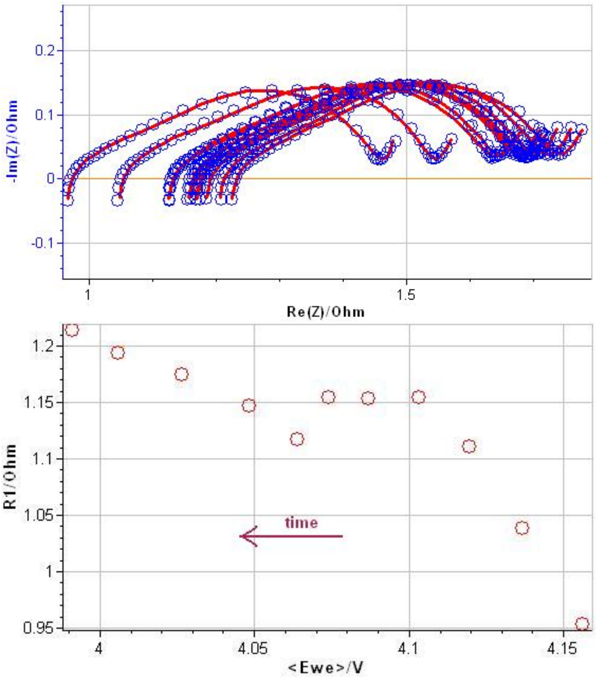


Figure 5 : of the fitting process with Z Fit. Bottom: E change of *R*1 with the battery potential.

III – CONTINUOUS DISCHARGE

In the previous section, we showed that the EIS measurements under potentio or galvano control are equivalent in this context. However, the galvano control is needed if the user is interested in studying the variation of the EIS diagrams during charge or discharge. To illustrate this case, the EIS measurements under discharge in galvano control mode were performed after full charge. The current applied was -12 mA (C/10 regime) and the corresponding sine amplitude was 5 mA. Figure 6 shows the variation of potential as a function of time, during the EIS measurements and Fig. 7 shows the EIS graph during continuous discharge. As one can observe, the low frequency behavior is not the classical restricted diffusion behavior expected on a Li-ion battery.

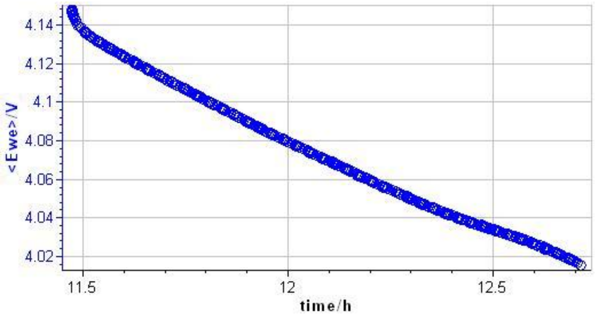


Figure 6 : Battery potential during the discharge

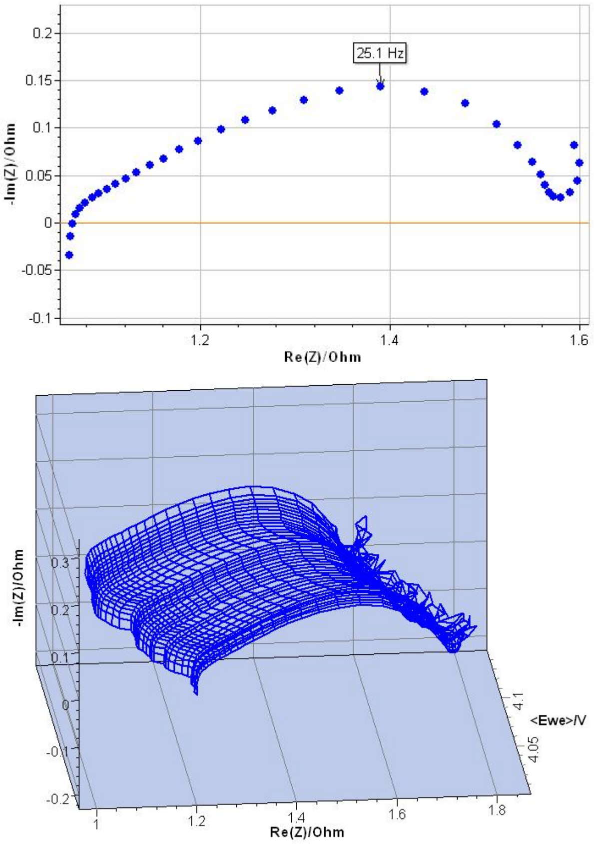


Figure 7 : EIS measurements under galvano control with I_a = - 12 mA.

Under continuous discharge, the system changes during the measurement, so only the high and middle frequencies (between 100 kHz and 5 Hz) were considered in the fitting procedure. Therefore, the EIS measurements were fitted using ZFit using the equivalent circuit L1 + R1 + Q2=R2 + Q3=R3.

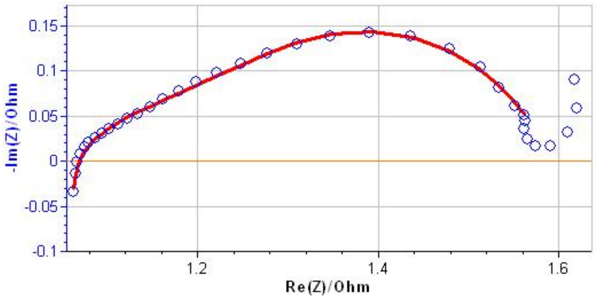


Figure 8 : Result of the fitting process with Z Fit.

As we can observe in Fig. 9 the internal resistance behaviors are not the same around the OCV or in operating conditions.

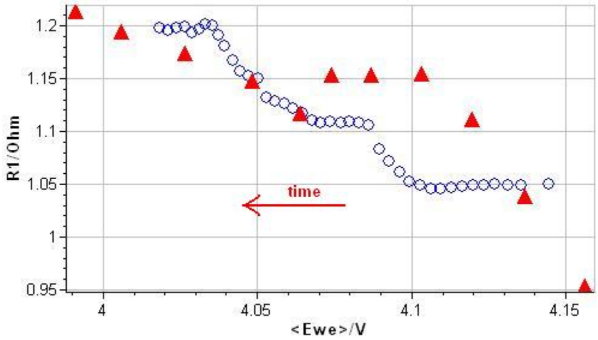


Figure 9 : Variation of the internal resistance *R*1 as a function of the battery potential: around the OCV (red triangles) and under continuous discharge (blue circles).

IV – CONCLUSION

In most cases, performing measurements in potentio or galvano control are equivalent. Usually the difficulty is to find the sine current amplitude equivalent to the voltage sinus amplitude. As a rule of thumb, we recommend a current amplitude of about 10% of the discharge/charge current for batteries. As shown in this note, the galvano control is the most adequate means of following the change of the internal resistance of an operating cell.

REFERENCES

1) A. Guyader, F. Huet, and R. P. Nogueira. *Corrosion*, 65(2) (2009) 136.
2) J.-P. Diard, B. Le Gorrec, and C. Montella. *J. Power Sources*, 70 (1998) 78.
3) Application note # 18 “Staircase Potentio Electrochemical Impedance Spectroscopy and automatic succesive Z Fit analysis.“
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5) A. Pellissier, N. Portail, N. Murer, B. Molina-Concha, S. Benoit, and J.-P. Diard. *Z Fit a powerful tool for multiple impedance diagram fitting*. EIS2013-9th International Symposium on Electrochemical Impedance Spectroscopy, poster, Okinawa, Japan (2013).

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