EIS measurements: Potentio or Galvano mode?

I – INTRODUCTION
Electrochemical Impedance Spectroscopy (EIS) measurements are more often 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 the EIS measurements under potential or current control result 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., the 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 drift, 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.
The battery voltage changes with time, during discharge, rest, PEIS and GEIS measurements, are shown in Fig. 3. During rest, the battery voltage stabilizes before the EIS measurements.

The change of internal resistance with the potential or state of charge (SoC) is studied by EIS measurements during the 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 evolution of the PEIS Nyquist plot during the discharge.
values of the 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 \( R1 \) with the battery potential. We can observe that \( R1 \) value increases during the discharge.

**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 imposed current was \(-12 \text{ mA (C/10 regime)}\) 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.
As we can observe in Fig. 9 the internal resistance behaviors are not the same around the OCV or in operating condition.

**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**

At most cases, performing measurements in potenti 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 for batteries, a current amplitude of about 10% of the discharge/charge current. As it was shown in this note, the galvano control is the most adequate to follow the change of the internal resistance of an operating cell.

**REFERENCES**

3) Application note # 18 “Staircase Potentio Electrochemical Impedance Spectroscopy and automatic succesive Z Fit analysis.”
4) Application note # 45 “Using ZFit for multiple cycles analysis.”

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