Z FIT
A POWERFUL TOOL FOR MULTIPLE IMPEDANCE DIAGRAM FITTING

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INTRODUCTION

EIS measurements are commonly used in different areas of electrochemical applications, especially for energy and corrosion applications. Most of time the EIS data are analyzed as electrical circuits, the so-called equivalent circuit (EC). Processing tools using algorithm to minimize the EIS diagram are used since years. The physical meaning of the components of the EC can be investigated by studying the change of the parameter value(s) in function of the DC level (current or potential), light intensity, time, temperature…

Bio-Logic has been developing an EIS data fitting tool, Z Fit which is available in the EC-Lab® package. For successive measurements, Z Fit is able to determine automatically the values of the elements of the chosen EC for each EIS diagram. The utilization of this tool is illustrated in different electrochemical applications such as:

- batteries (EIS measurement performed along a continuous or non-continuous discharge),
- photovoltaic cells (EIS measurement at different DC level of potential),
- corrosion (polarization resistance change in function of the time

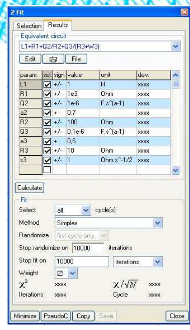


Fig. 1 : Z Fit tool window in EC-Lab®.

I. BATTERY

I.1 During a continuous discharge

The discharge is carried out on a $LiFePO_4$ battery of 2.3 A.h at slow rate (C/20).
EIS measurements are performed every 60 min. During the EIS measurements, the DC level at C/20 is hold.
The EIS data are modeled by R1 + La1 + Q2/(R2+W2).

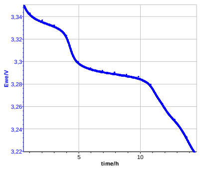


Fig. 2 : Voltage change of the battery during the discharge.

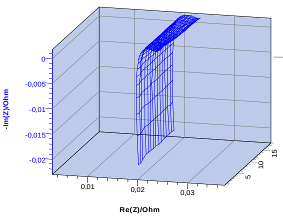
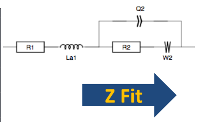


Fig. 3 : 3D EIS diagram along the discharge of the 2.3 Ah battery. Discharge at 120 mA. Frequency range: 20 kHz – 0.5 Hz. Ampl. 50 mA.



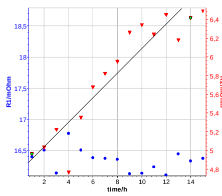


Fig. 4 : R1 (●) and R2 (▲) change during the discharge.

R1 corresponds to the internal resistance of the battery. The R1 values remains stable in the range of 16.1 – 16,7 mΩ.
R2 follows an affine law, such as: R2 = 1.4 10^{-4} Ω/h × time + 4.7 10^{-3} Ω.

The plot of the change of the component values along the discharge is a tool which allows the user to check the SOC of the battery.
Such plot can also be used to determine the kinetic parameters if a theoretical model is available.

I.2 During an intermittent discharge

The discharge is performed on a $LiCoO_2$ battery of 2 Ah at a discharge rate of C/4.
EIS measurements are carried out every 12 min after a rest period of 15 min.
The EIS data are modeled by R1+R2/Q2+ Q3/(R3+W3).

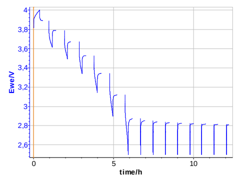
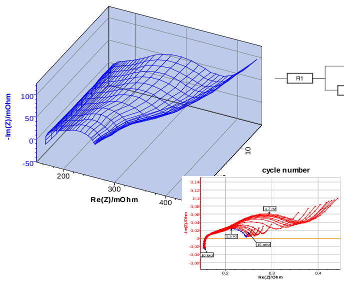


Fig. 5 : Voltage change of the battery along the discharge.



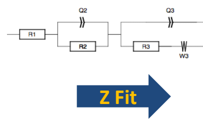


Fig. 6 : 2D/3D EIS diagram along the discharge of the 2 Ah battery. Discharge at 500 mA. Frequency range: 10kHz – 0.01 Hz. Ampl. 2.5 mV.

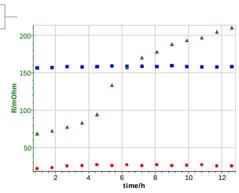
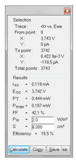


Fig. 7 : R1 (■), R2 (●) and R3 (▲) change during the discharge.

It is noteworthy that the R3 value increases along the discharge whereas the other values remain stable.

II. PV CELL

The current *vs.* time characterization of a silicon PV cell was carried out at 20 mV/s.
EIS measurements are performed on the PV cell at different location (step of 200 mV) of the I-V curve under the constant light of a white LED .
A R/C EC is used to fit the EIS data.



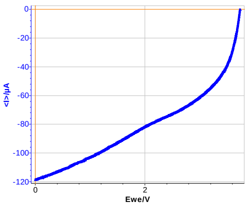


Fig. 8 : Current-Potential curve of the PV cell. PV analysis data is given on the left.

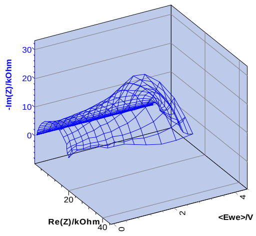
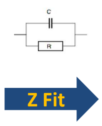


Fig. 9 : 3D EIS diagram of the PV cell *vs.* potential. Frequency range: 100 kHz – 5 Hz. Ampl.: 50 mV.



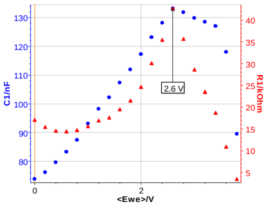


Fig. 10 : R (●) and C (▲) change *vs.* potential.

Both R and C values increase from the open circuit potential to 2.6 V and then decrease up to the short-cut potential.
The change in R value *vs.* potential is in agreement with the I-V curve (Fig. 8). The slope is less and less important and becomes stable around 0.9 V.

III. CORROSION

A sample of AISI 108 (mild steel) in sulfuric acid (0.5 M) solution is studied as a function of time.
In a first step, the sample is slightly passivated (1 V/ECS applied during 10 s). Then, the open circuit voltage of the sample is monitored for 2 h 15 min. An EIS measurement is performed every 5 min.
The data are modeled by R1 + La1 + C2/R2

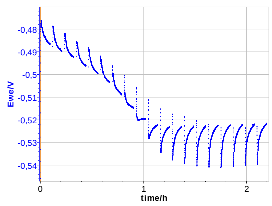


Fig. 11 : Voltage of the mild steel AISI 108 in H_2SO_4 (0.5 M).

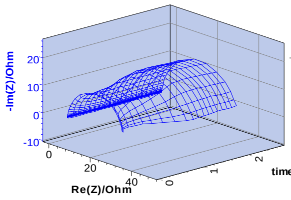
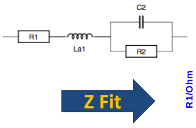


Fig. 12 : 3D EIS diagram of the mild Steel AISI 108 *vs.* time. Frequency range: 20 kHz – 0.1 Hz. Ampl: 20 mV.



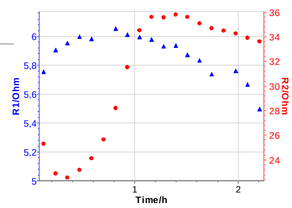


Fig. 13 : R1 (▲) and R2 (●) changes *vs.* time.

La remains stable with time. The value of R2, corresponding to the polarization resistance is stable for the three first cycles and then increases until the cycle 10. After 10 cycles (1h15min), the R2 value becomes stable. In the early stages of exposure, the metal oxide layer is dissolved and, after one hour, a protective stable layer appears that limits the corrosion of the sample.

CONCLUSION

The successive EIS measurements have been carried out in different domains of electrochemical applications. After the appropriate EC selection, Z Fit plots automatically the changes of parameter values. These plots allow the users to draw an empirical law. This model may be validated latter by a theoretical law.

More information can be found in the application notes available: http://www.bio-logic.info/potentiostat/notesan.html

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