Z Fit and multiple impedance diagrams fitting

I Introduction

Electrochemical impedance spectroscopy (EIS) measurements are widely implemented in all fields of electrochemistry (*e.g.* energy and corrosion application). The impedance diagrams are usually fitted using equivalent electrical circuits (EC) [1–3]. Often, one can observe a variation of EIS measurements with physical parameters, like the potential or temperature. This behavior results in the variation of the value of the EC parameters. The analysis of EIS measurements at different conditions becomes important to understand the physical behavior of the system of interest [1, 2].

In this context EC-Lab® software provides a powerful and user-friendly tool to fit successive EIS measurements called Z Fit. Z Fit automatically determines (and plots) the successive values of the EC components for a series of impedance diagrams. Its advance features would allow the user to model experimental results [4].

SPEIS and SGEIS techniques allow the user to perform successive impedance measurements. In the Application Note # 17, the use of SPEIS technique is described, as well as the use of Z Fit [5] to fit the presented EIS diagram. In this note, the use of Z Fit to adjust the component values of EC, for several impedance diagrams, is explained. The different options to fit several EIS diagrams are also presented. Examples in batteries, photovoltaic cells and corrosion application are shown to illustrate the functionalities of Z Fit.

II Fitting multiple impedance diagrams

Z Fit permits to choose an EC between a list of predefined circuit or edit and create a new equivalent circuit which is not in this list[1]. Equivalent Circuit edition windows of Z Fit is shown in Fig. 1.
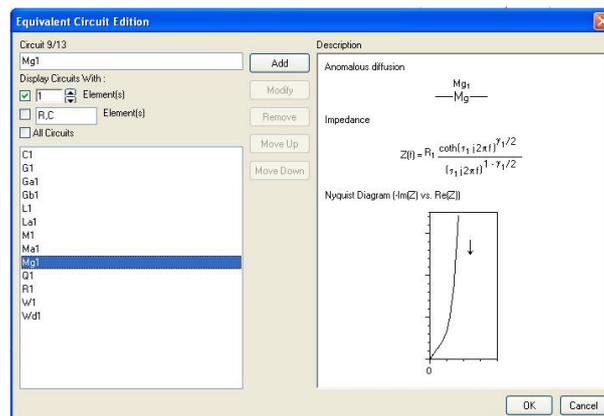

Fig. 1: Equivalent Circuit Edition window.

To fit multiple EIS graphs, after selecting (or creating) the EC in the **Equivalent Circuit** block, the user must choose Select "all" cycles in the Z Fit windows (Fig. 2) in the **Fit** block.

Z Fit provides three minimization algorithms, Randomize, Simplex and Levenberg-Marquardt. The user can combine Randomize with Simplex or Levenberg-Marquardt. Using Randomize option is recommended to provide automatically suitable initial values for a further minimization. If Randomize + Simplex or Randomize + Levenberg-Marquardt option is selected, the Randomize minimization could be performed on the first cycle only or on every cycle. If the parameters are close (between the successive cycles) it is recommended use the Randomize option only in the first cycle. The number of iterations for which the Randomization is stopped can be chosen.

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[1] Z Fit has 13 components to build the equivalents circuits. Among them, there are the specific electrochemical elements, as W_{δ_1} (diffusion-convection) or M_1 (restricted linear diffusion).
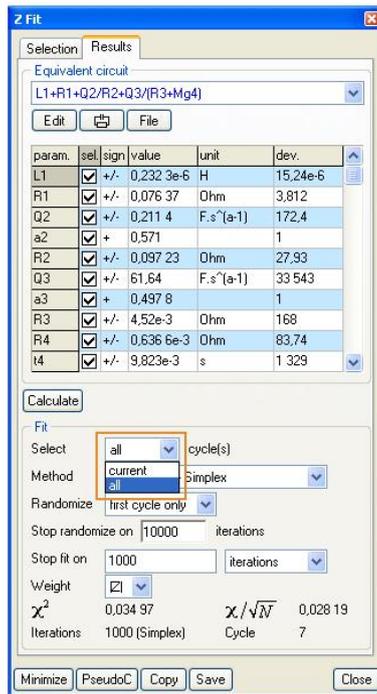
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Fig. 2: Z Fit window.

frequencies (attributed to the solid electrolyte interphase, SEI, and the transfer charge, respectively). At low frequencies one can highlight a diffusion region.
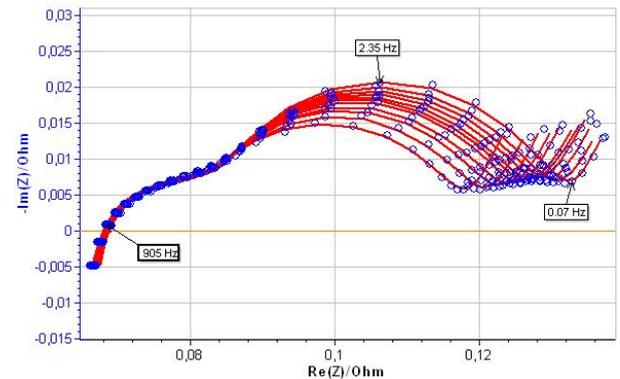

Fig. 3: Results of fitting process with Z Fit.

The evolution of the EC parameters obtained by the fit are automatically displayed in a new graph.

III Experimental Results

III.1 Li-ion batteries application: SOC and SOH

EIS technique was used to study the state of charge or the state of health (SOC or SOH) of batteries. EIS appears as a non-destructive, fast and easy-to-use technique. The variation of EIS diagrams (EC parameters) would permit to determine the SOC and SOH [2]. In the present note, the EIS measurements on a commercial Li-ion battery are presented (nominal capacity 2.4 Ah). The EIS diagrams were analyzed using Z Fit.

The Nyquist diagrams were obtained using PEIS protocol (Fig. 3). Each diagram was measured after a discharge at C/10 rate for 30 min, followed by 10 min at open circuit potential, OCP (GCPL technique). One can observe the two typical capacitive arcs at high and middle

The EIS graphs have been fitted with the EC: $L_1+R_1+Q_2/(R_2+Q_3/R_3)+Q_4$ (Fig. 4). The results of the fitting process are also shown in Fig. 3.
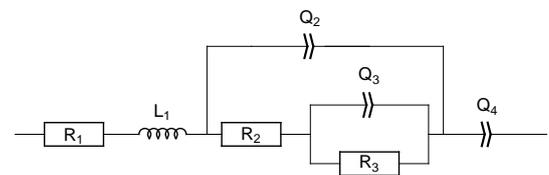

Fig. 4: Equivalent circuit use to fit the experimental result from Fig. 3.

As was mentioned above, one can use Z Fit to study the evolution of EC parameters. Fig. 5 shows the evolution of internal resistance (R_1), and the SEI and transfer charge associated resistances (R_2 and R_3, respectively) with the potential.
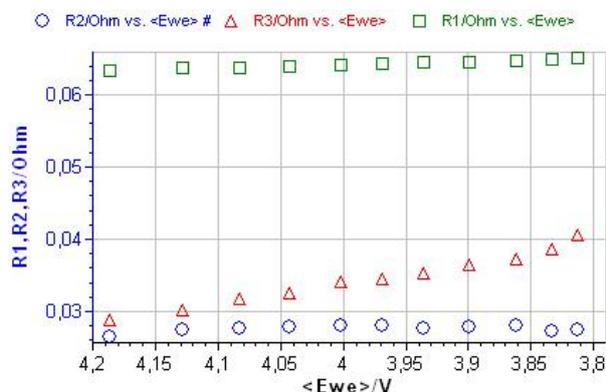

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Fig. 5: Evolution of R_1 (□), R_2 (○) and R_3 (△) with the potential.

In the battery domain, these values are interesting to characterize and further to determine the state of charge, SOC, or the state of health, SOH, of batteries [1–3, 6].

III.2 Photovoltaic cells application

Silicon solar cells can be characterized by plotting polarization curves and measuring their impedance at several points on the curve [7,8]. The photovoltaic cell (PV) was characterized under white-LED constant illumination. The EIS measurements have been performed under potential control (SPEIS technique) between 0 and 3.8 V with steps of 200 mV. The results of these measurements are shown in Fig. 6.
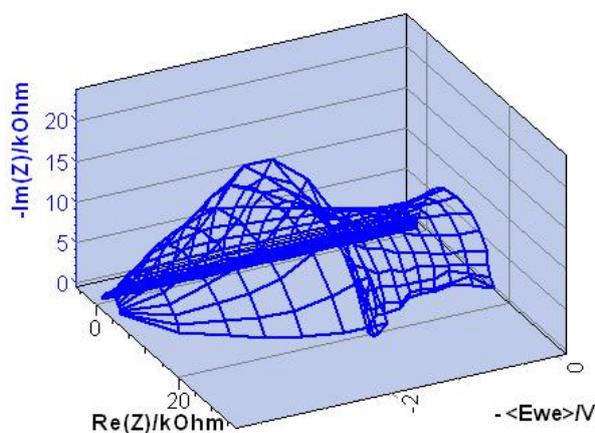

Fig. 6: Results of SPEIS measurements on a PV cell.

These EIS graphs can be, in a first approximation, fitted by a R/C circuit. The evolution of the resistance with the potential is shown in Fig. 8. R_1 value reaches a maximum at 2.6 V.
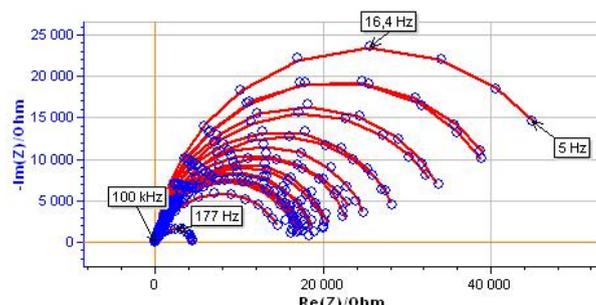

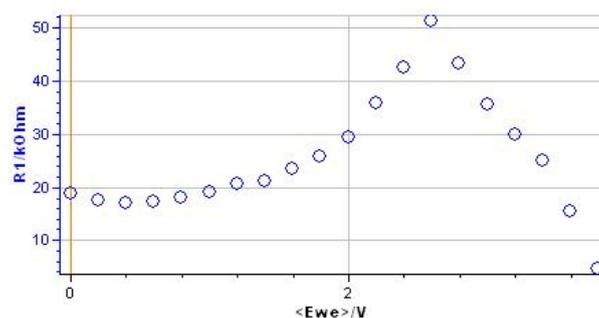**Fig. 7: Results of fitting process with Z Fit.**

Fig. 8: Evolution of resistance R_1 with the potential.

III.3 Corrosion: polarization resistance evolution as a function of time

The corrosion current can be determined by measuring the polarization resistance, (R_p), at the corrosion potential and using the Stern-Geary relationship [9, 10]. Stationary (voltammetry at low scan rate) or dynamic measurements (as the EIS) can be performed to determine the R_p value.

The corrosion rate variations, as a function of time, are particularly useful in the chemical industry, to evaluate, for instance the possible damages due to experimental conditions changes in a reactor (addition of a reagent, changes in temperature, etc.).

In this note, we present the EIS measurements performed (under control of potential) on AISI

108 steel sample in 0.5 M H_2SO_4. The electrode surface was slightly passivated applying 1 V/SCE until 1 s. The EIS measurements were performed at the corrosion potential. The EIS diagrams obtained are shown in Fig. 9. The EC: $L_{a1}+R_1+C_2/R_2$ was used to fit the experimental results (where R_2 corresponds to R_p) (Fig. 10).
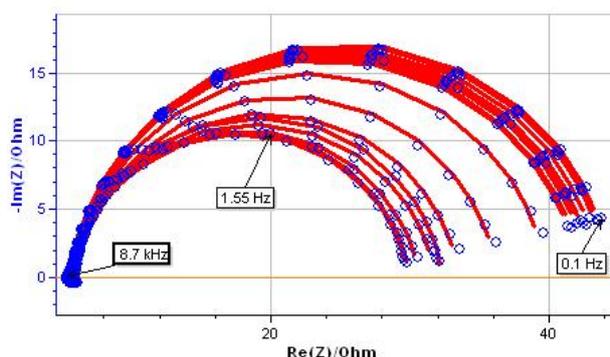

Fig. 9: EIS measurements on AISI 108 steel sample (blue points) and results of fitting process with Z Fit (dashed red line).

Fig. 11 shows the evolution of R_p during the passivation process. One can observe the non-monotonic variation of R_p with the cycle number (equivalent to time). Between the first and third cycle the R_p value decreases, then the value increases up to the twelfth cycle. After that, the R_p value slightly decreases.
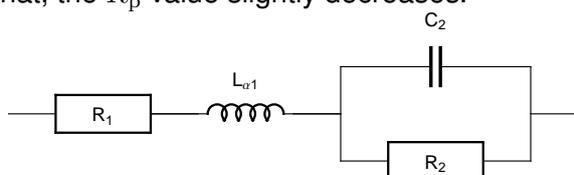

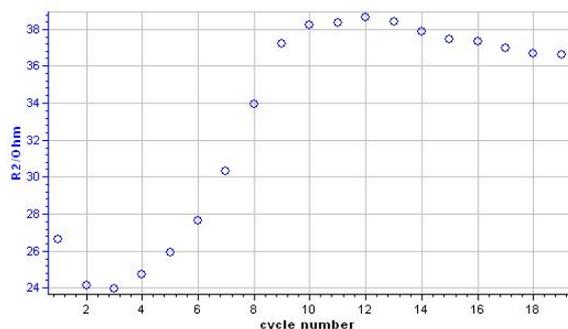**Fig. 10: Equivalent circuit use to fit the experimental result from Fig. 9.**

Fig. 11: Evolution of the polarization resistance with the number of cycles (time).

IV Conclusion

Successive EIS measurements were performed in different application areas. Z Fit permits in these cases, after choosing an EC, to study the value variations of the EC components. These changes in the EC component values facilitate the identification of empirical laws of evolution. These empirical laws could be compared later with theoretical laws.

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