

## EIS measurements with multisine

### I- Introduction

EIS measurements sometimes take a very long time, especially at low frequencies. It can be an important issue for systems varying with time.

To overcome this problem, it would be useful to work in the multisine impedance measurement mode. This measurement mode consists of exciting and measuring various frequencies in the same time contrary to the single sine measurement mode.

The multisine measurement is defined as the sum  $u(t)$  of the sinusoids at different frequencies with the same amplitude  $A$  and different phases  $\Phi$  [1,2]:

$$u(t) = A \sum_{k=1}^N \cos(2\pi f_k t + \Phi_k) \quad \text{with the phase}$$

$\Phi_k = \Phi_1 - 2\pi \sum_{n=1}^{k-1} \frac{(k-n)}{N}$  and  $N$  the number of frequencies.

The EIS multisine measurement developed in EC-Lab<sup>®</sup> software is defined in order to reduce the crest factor defined by:

$$Cr(u) = \frac{u_M - u_m}{2u_{\text{eff}}} \quad \text{with } u_{\text{eff}} = A \sqrt{\frac{N}{2}} \quad [3,4]$$

The aim of this application note is to compare EIS measurements with and without multisine mode.

### II- Experimental part

Electrochemical Impedance Spectroscopy measurements in single sine or multisine were done on a lithium-ion battery (ANR26650, A123 System). This 2.3 Ah battery, with nanophosphate as the positive electrode, was studied using the PEIS technique.

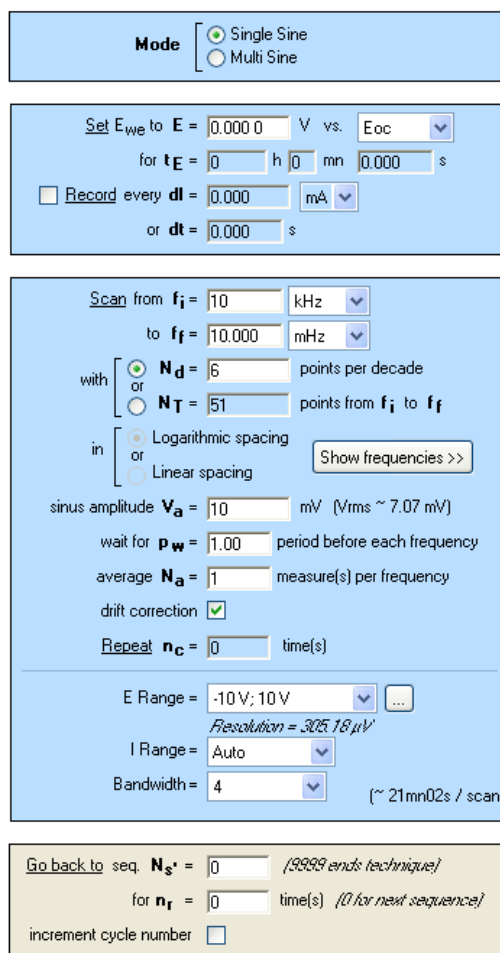
All the measurements were done at 0 V vs. the Open Circuit Potential, *i.e.* ~ 3.31 V.

Impedance scans were done from 200 kHz down to 10 mHz.

Note that measurements were done with EC-Lab<sup>®</sup> software and an 8 A booster kit. The multisine measurements are effective only below 1 Hz.

The other parameters are set to be equal to 10, 5, and 0.5 for the sinus amplitude ( $V_a$ ), the  $p_w$  value, and the average  $N_a$ , respectively. The drift correction option was on.

The settings for the single and multisine measurements on a lithium-ion battery are identical, and multisine settings are reported in Fig. 1.



**Mode**  Single Sine  Multi Sine

Set  $E_{we}$  to  $E = 0.0000$  V vs.  $E_{oc}$   
 for  $t_E = 0$  h  $0$  mn  $0.000$  s  
 Record every  $dI = 0.000$  mA  
 or  $dt = 0.000$  s

Scan from  $f_i = 10$  kHz  
 to  $f_f = 10.000$  mHz  
 with   $N_d = 6$  points per decade  
 or   $N_T = 51$  points from  $f_i$  to  $f_f$   
 in  Logarithmic spacing  Linear spacing Show frequencies >>

sinus amplitude  $V_a = 10$  mV ( $V_{rms} \sim 7.07$  mV)  
 wait for  $p_w = 1.00$  period before each frequency  
 average  $N_a = 1$  measure(s) per frequency  
 drift correction   
 Repeat  $n_c = 0$  time(s)

E Range = -10V; 10V ...  
*Resolution = 305.18  $\mu$ V*  
 I Range = Auto  
 Bandwidth = 4 [~ 21mn02s / scan]

Go back to seq.  $N_s = 0$  *(9999 ends technique)*  
 for  $n_r = 0$  time(s) *(0 for next sequence)*  
 increment cycle number

Fig. 1: EIS multisine measurement settings.

### III-Results

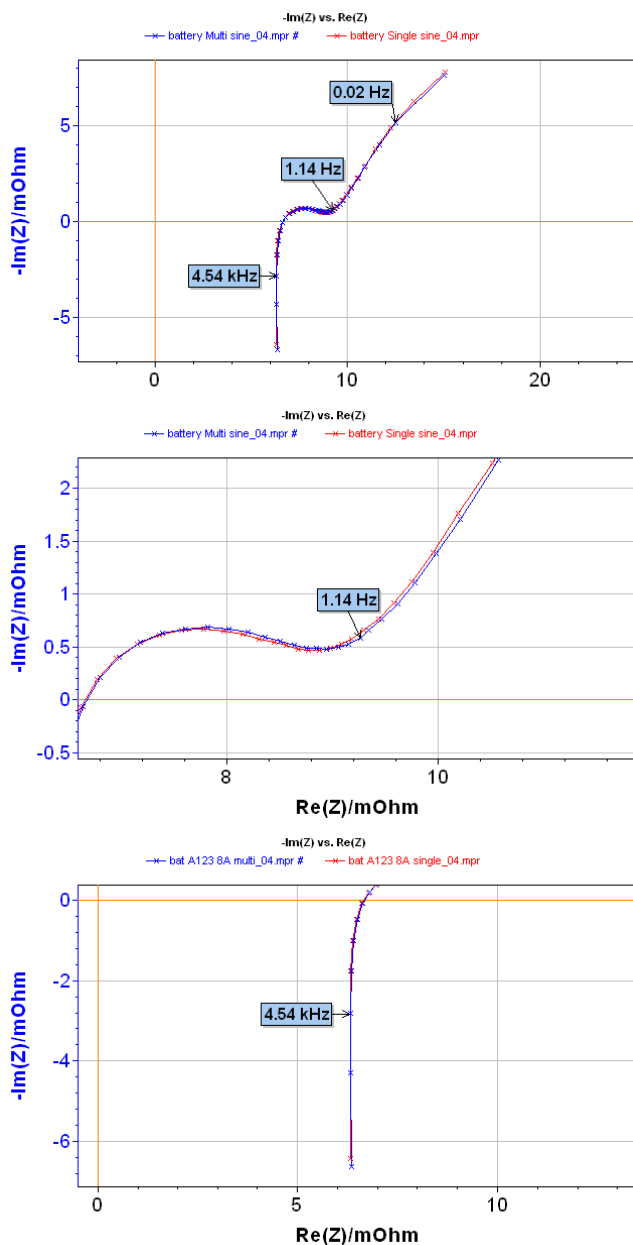
Impedance diagrams obtained are shown in Fig. 2. The whole diagram is given in the top. As expected, the impedance diagrams are superimposed, whatever the frequency. The right overlapping of single sine and multisine impedance diagrams is displayed in the zooms in low and high frequencies in Fig. 2 (middle and bottom).

Fig. 3 gives the time comparison for doing both of the EIS experiments. A single sine measurement needs 20 min 38 s, whereas a multisine measurement takes 5 min 22 s. It is then obvious that multisine measurements are faster by a factor close to four times the measurements in single sine mode. This saving of time and thus a faster measurement is a good way to avoid the drift of some electrochemical systems.

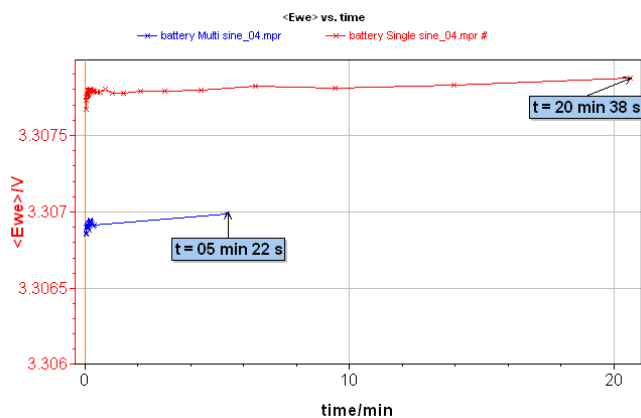
### IV- Conclusion

EIS measurement in multisine mode is a good way to save time and therefore avoid changes or drift of the electrochemical system with time. Depending on the system, EIS measurements allow the user to do experiment 3 to 4 times faster than in single sine mode with the same accuracy.

Nevertheless, user must be careful of the definition of experimental conditions. Indeed, considering the principle of the multisine measurement, the excitation is defined for all the frequencies; consequently each frequency is less excited than in single sine mode. This can imply noisy measurements. However, increasing the level of excitation can cause non-linear conditions for EIS measurement and disturb impedance results [5].



**Fig. 2: Electrochemical Impedance Spectroscopy measurement on a lithium-ion battery done with single sine (red line) and multisine (blue line) mode: total diagram in the top, zoom in the low frequencies range in the middle, and zoom on the high frequencies range in the bottom.**



**Fig. 3: Comparison of the  $E_{we}$  vs. time for EIS measurement on lithium-ion battery using single sine (red line) or multisine (blue line) mode.**

## References:

- [1] Van Gheem E., Vereecken J., Schoukens J., Pintelon R., Guillaume P., Verboven P. and Pauwels L., *Electrochim. Acta* 49 (2004) 2919-2925.
- [2] Van der Ouderaa E., Schoukens J., Renneboog J., *IEEE Trans. Instrum. Meas.* 37(1) (1988) 145-147.
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- [4] Schroeder M. R., Pintelon R., Rolain Y., *IEEE Trans. Instrum. Meas.* IM-49 (2000) 275.
- [5] Bio-Logic AN#9, [www.bio-logic.info/potentiostat/notes.html](http://www.bio-logic.info/potentiostat/notes.html)