

Precision and Accuracy in Coulombic Efficiency Measurements

I – INTRODUCTION

In the last years, several researches were focused on the Coulombic Efficiency (CE) as a tool to study the battery lifetime [1–8]. Quantifying the influence on the battery lifetime by changes in the electrodes or electrolytes, under classical testing conditions (simply charge-discharge conditions), requires extremely long times. Contrarily to a simply cycle cells measurements (until the cells reach the end of life), CE measurements can be improved in short amount of time (3-4 weeks) and also provide a tool to evaluate and compare the stability of different cells.

The CE is defined to be a ratio of the charge delivered during the discharge, Q_{dis} , to that stored during the charge, Q_{ch} ¹:

$$CE = \frac{Q_{dis}}{Q_{ch}} \times 100 \quad (1)$$

I – 1 Precision and accuracy in CE measurements

In this context a high precision² and a good accuracy³ are recommended to determine in a few weeks of measurement, the impact in the lifetime of the change in the electrode material or electrolyte.

The precision in the CE determination is affected by the precision in the Q measurement.

The charge delivered or stored during the discharge/charge, at constant current, is defined as $Q_{dis/ch} = I \times \Delta t$ ⁴ where I is the discharge/charge current and Δt is the time interval during discharge/charge. The variation of voltage during cycling could be affected by different phenomena, *e.g.* temperature. So Q determination is affected by different factors as the precision in current & voltage measurements, time determination, temperature change, etc.

The quality in the CE measurements was quantified in the literature [2, 4] by fitting the CE data (vs cycle number) with a second order polynomial function (least square regression). After fitting, the root-mean-square error (RMSE) can be calculated as:

$$RMSE = \sqrt{\frac{\sum_{i=1}^n (x_{exp_i} - x_{fit_i})^2}{n}} \quad (2)$$

Where x_{exp} is a given data point and x_{fit} is the corresponding point given by the fitting function. The parabolic function is only proposed to accurately fitting the CE vs. number cycles data, and is not intended to provide a predictive model.

A RMSE value at least $\pm 0.01\%$ was recommended to distinguish the impact of changes in the battery components.

II – CE measurement

II-1. Experimental conditions

The tests presented in this application note were performed using commercial batteries:

- $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC) with nominal capacity of 2.6 A h, 18650 format.
- LiCoO_2 (LCO) with nominal capacity of 2.4 A h, 18650 format.
- LiFePO_4 (LFP) with nominal capacity of 2.5 A h, 26650 format.

The discharge/charge measurements were carried out between the 4.2 and 2.75 V for the NMC and LCO technologies and between 3.6 and 2.0 V for the LFP batteries, at C/10 regime. As recommended in the literature, the temperature was controlled accurately at $30.0 \pm 0.1^\circ\text{C}$ (thermostatic chamber Memmert, IPP500).

In order to test the reproducibility of Bio-Logic cyclers, cycling (channel check) were performed on 40 NMC batteries, 20

LCO batteries and 16 LFP batteries, with a VMP3 (16 channels) and a BCS-815 battery cycler (8 channels). Over-crossed measurements were also carried out to validate the obtained results.

II-2. Software tools

These measurements were carried out using the CED technique available in EC-Lab® software (Fig. 1) for the VMP3 and BT-Lab® software for the BCS-815. The CED technique is available in the “Battery testing” section.

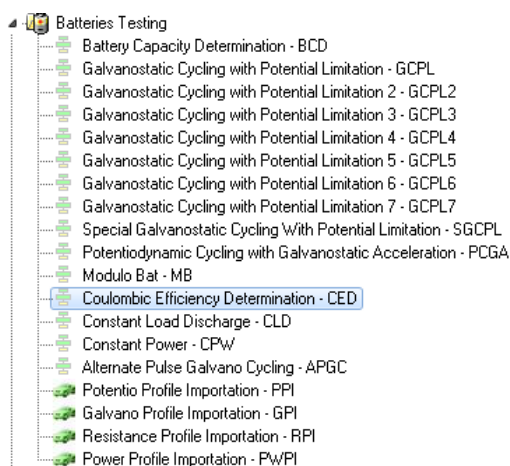


Fig. 1: Parameter setting windows for the CED technique.

Charge and discharge are performed under galvanostatic control, between the limit potentials, E_{M1} and E_{M2} . The charge and discharge periods can be set in current or C-rate. No floating period is available (Fig. 2).

The output displays show the change of E_{we} vs time and in a second graph the Efficiency vs cycle (Fig. 3).

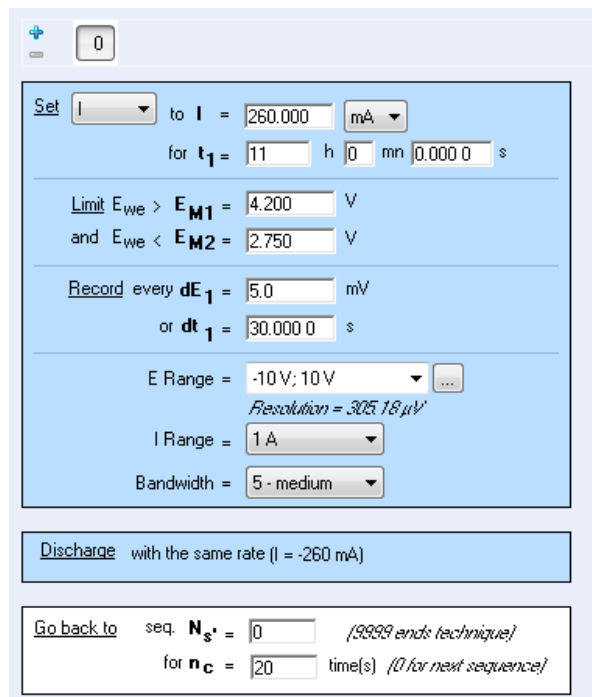


Fig. 2: Parameter setting windows for the CED technique.

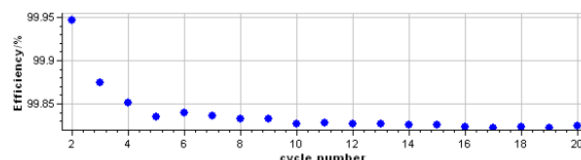
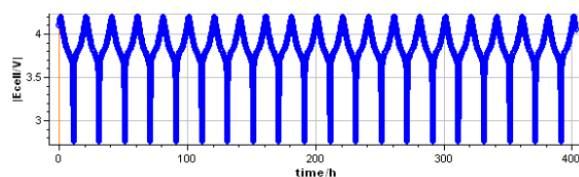


Fig. 3: Potential vs. time during cycling and CE vs. cycle number for a mixed Li-ion battery (LCO-LMO type).

The user can also calculate the RMSE value associated to CE measurements using “CED Fit”, see Fig. 4. The polynomial fit and the corresponding RMSE values are automatically calculated at the end of the measurement. This tool is also available in the “Analysis” → “Battery” menu (or “Supercapacitor” menu). It could be also used “on the fly”.

First points of the cycling may be removed by using the “First Hidden point” option.

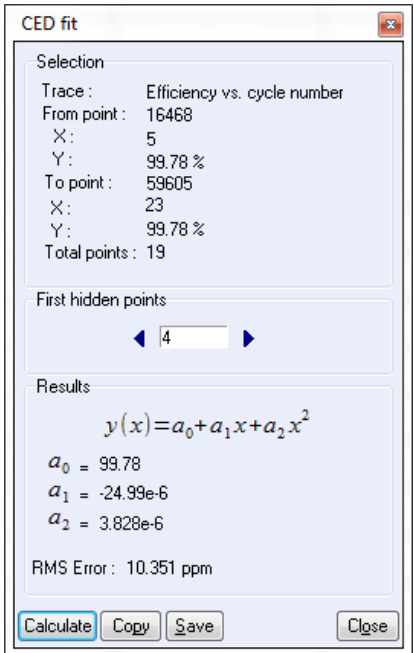


Fig. 4: CED Fit windows.

II-3. Discussion

Fig. 5 shows cell potential vs. time, during the charge and discharge on NMC, LCO and LFP batteries. Typical CE vs. cycle number curve is shown in Fig. 6. The corresponding polynomial fit and the RMSE value obtained are also indicated. Best RMSE result obtained after analysis is also shown in Fig. 6.

Tab. 1 describes the RMSE values obtained after analysis for both Bio-Logic instruments and on different type of batteries. As one can observe, the RMSE value obtained depends on the battery technology. The best results are obtained on LCO batteries for both tested instruments.

Fig. 7 shows the comparison of RMSE values obtained on different batteries technologies carried out with the Bio-Logic instruments. One can highlight that the LCO results are close of the RMSE value reported in the literature [4].

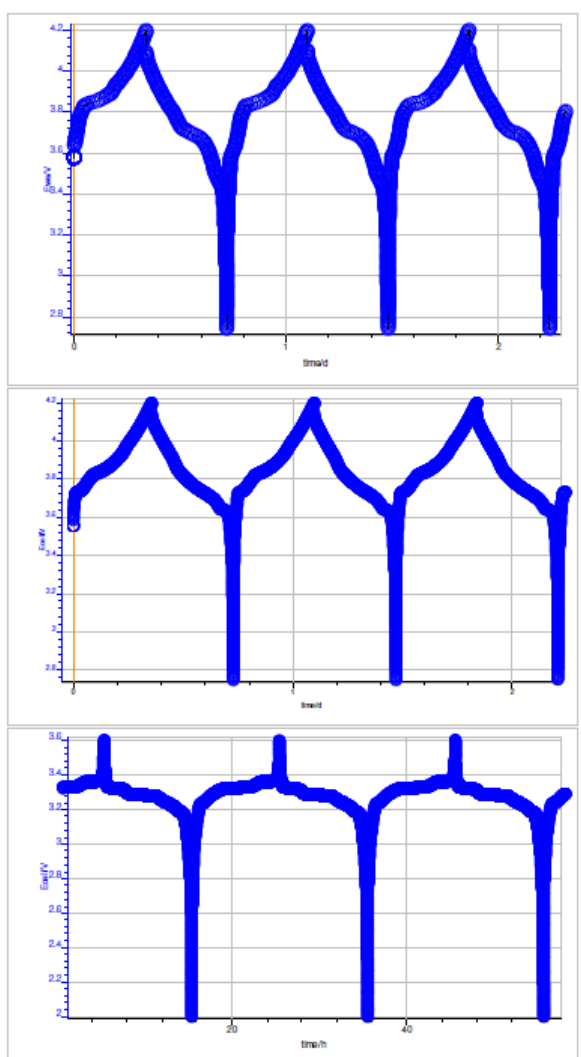


Fig. 5: Potential vs. time during the charge and discharge at C/10 for: top: a NMC battery, middle: LCO battery and bottom: LFP battery.

Tab. 1: RMSE typical and best values obtained after analysis on different batteries technologies with Bio-Logic instruments.

Battery type	VMP3	BCS
NMC	Typical	32±8 ppm
	Best	11.5 ppm
LCO	Typical	11±3 ppm
	Best	6.4 ppm
LFP	Typical	21±5 ppm
	Best	15 ppm

Note: 1 ppm = 0.0001%

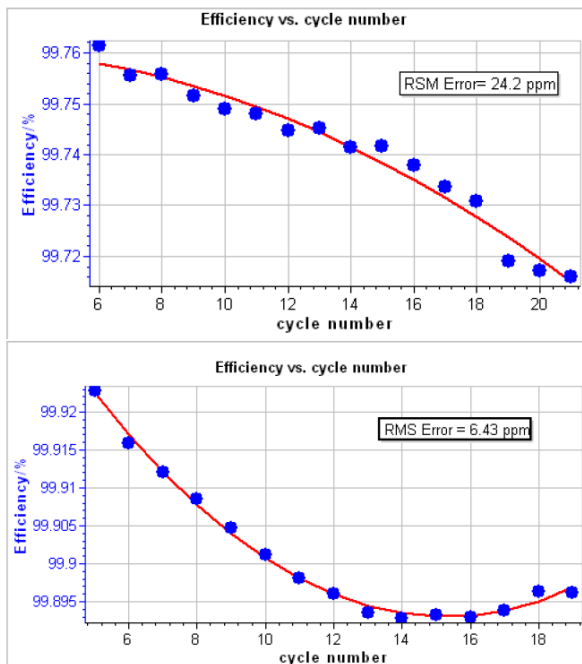


Fig. 6: CE vs. cycle number, the corresponding polynomial fit. Inset: RMSE value. Top: typical result on a 18650 - NMC battery. Bottom: best result obtained on LCO battery.

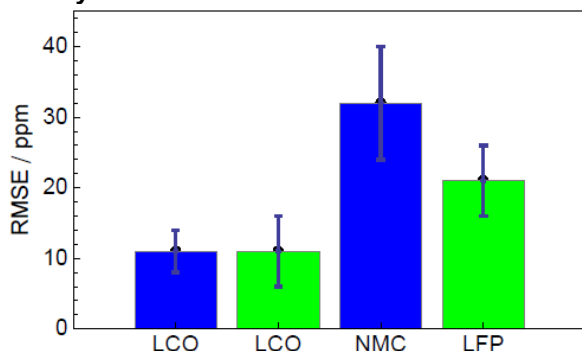


Fig. 7: Comparison of RMSE values yielded on different batteries technologies with Bio-Logic instruments: VMP3, BCS-815.

III – CONCLUSION

The CE measurements performed with a high precision can be used to evaluate the impact of electrolyte additives, impurities, electrodes material, temperature, in the lifetime of the Li- ion batteries. The VMP3 and BCS-815 instruments allow performing CE measurements with a high precision, typical RMSE value of about 11 ppm, compared with the value reported in the literature.

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NOTES

- ¹ The CE is noted ϕ_Q in IUPAC nomenclature.
- ² The precision here is defined as the closeness of agreement between indications or measured quantity values obtained by replicate measurements on the same or similar objects under specified conditions according with [10].

³ The accuracy here is defined as the closeness of agreement between a measured quantity value and a true quantity value of a measurand according with [10].

⁴ The charge is calculated in general by integrating the current that is transferred during the time it takes to carry out a given discharge or charge: $Q = \int I(t)dt$. The error calculation in the Q determination is shown in the Appendix.

Appendix: Error calculation

I-1. dQ error calculation

Under constant current charge/discharge, the charge is defined as:

$$Q = It_e \quad (3)$$

where I is the applied current and t_e the elapsed time during the charge/discharge. If dI and dt are the uncertainties, or error, on I and t determination, the error associated with the Q determination could be expressed as:

$$dQ = \left| \frac{\partial Q}{\partial t} \right| dt + \left| \frac{\partial Q}{\partial I} \right| dI \quad (4)$$

Where $\partial Q/\partial t$ is the discharge/charge current and $\partial Q/\partial I$ is the discharge/charge time.

dI corresponds to precision in the current measurement and, the time precision, dt , is a function of battery potential and temperature ($t_e = f(V, T)$) and it has a dependence with the detection of limit potentials. So, dt can be expressed as:

$$dt = \left| \frac{\partial t}{\partial V} \right| dV + \left| \frac{\partial t}{\partial T} \right| dT \quad (5)$$

By combining (4) and (5), we obtain:

$$dQ = \left| \frac{\partial Q}{\partial I} \right| dI + \left| \frac{\partial Q}{\partial t} \right| \left| \frac{\partial t}{\partial V} \right| dV + \left| \frac{\partial Q}{\partial t} \right| \left| \frac{\partial t}{\partial T} \right| dT \quad (6)$$

Where $\partial t/\partial V$ is the reciprocal slope of potential as a function of time curve, at end of charge/discharge, dV is the error associated with the potential measurement, dT is the error of temperature measurement, and $\partial t/\partial T$ is the variation of charge/discharge time with the temperature. We can estimate this value as follow:

$$\frac{\partial t}{\partial T} = \frac{\partial t}{\partial V} \frac{\partial V}{\partial T} \quad (7)$$

Where $\partial V/\partial T$ is the thermal drift of potential. We can consider that this contribution is dominated by the battery. So, we can write dQ as:

$$dQ = \left| \frac{\partial Q}{\partial I} \right| dI + \left| \frac{\partial Q}{\partial t} \right| \left| \frac{\partial t}{\partial V} \right| dV + \left| \frac{\partial Q}{\partial t} \right| \left| \frac{\partial t}{\partial V} \right| \left| \frac{\partial V}{\partial T} \right| dT \quad (8)$$

I-2. dΦ_Q error calculation

As mentioned above the Coulombic Efficiency (Φ_Q or CE) is defined as:

$$\phi_Q = \frac{Q_{dis}}{Q_{ch}} \quad (9)$$

So the associated error in the ϕ_Q determination is therefore:

$$d\phi_Q = \frac{dQ_{dis}}{Q_{ch}} + \frac{Q_{dis}}{Q_{ch}^2} dQ_{ch} \quad (10)$$