Measurements and Signal Processing of Li-ion Electrochemical Noise

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Measurements and Signal Processing of Li-ion Electrochemical Noise

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Introduction

Nowadays, an efficient way to store electrical energy is charging electrochemical batteries. Power densitie characterize the ease of transport of these batteries. Among current technologies on the market, technologies based on lithium element, called lithium-ion (Li-ion), are the best. The central interest of this work is the measurement and analysis of Li-ion batteries Electrochemical Noise (Li-ion EN). The objective is to show how we measured it and how we analyzed it. Our new method can lead to a non-intrusive diagnosis of electrochemical systems, and particularly Li-ion batteries. Generally, the components of a Li-ion battery (Fig. 1) are: a graphitic anode LiC_6 ; an electrolyte composed of Li salt $LiPF_6$ mixed with (propylene & ethylene) carbonate ; a cathode among the top five technologies LMO, LCO, LTO, NMC, LFP, NCA. The performance of Li-ion batteries are high, still they remain expensive and they pose three main safety issues. Indeed, there are the Solid Electrolyte Interphase (SEI), dendrites, and thermal runaway. Aging has to be consider too. Aging manifests itself by a capacity fading and a internal resistance rising leading to a decreasing performance. The main source of aging is the thickening of the SEI.

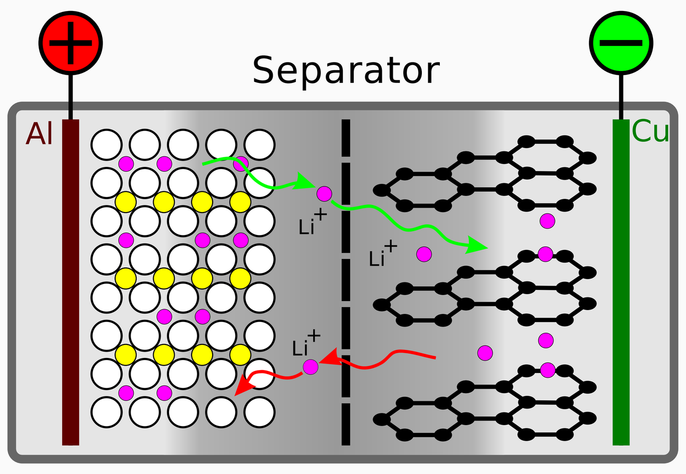

Fig. 1: Li-ion battery schema

DCNS is interested in our work on Li-ion batteries for a defense application, including its embedded power systems. The Li-ion battery is a critical component representing about 30 per cent of the total price of an exercice torpedo and must guarantee faultless safety of this system for defense applications.

Li-ion EN Measurements

It should now be noted that the development of such device was not easy. Li-ion EN is extremely difficult to measure, it require extreme caution. In general, a noise is a signal that disturbs the measurement. Here the desired signal is the electrochemical noise (EN). It is in fact electric voltage fluctuations to very small scales. Electrical noise is due to the discontinuous nature of the charge carriers. The average noise is zero, its energy is equal to its standard deviation (STD): $\sigma_{\text{eff}} = \sqrt{\langle \sigma^2 \rangle}$. There are three basic types of electrical noises:

- Thermal noise, or *Johnson-Nyquist* noise, where voltage noise STD is $\sigma_{\text{th}}^2 = 4k_B T R \Delta f$;
- Shot-noise, or *Poisson* noise, where current noise STD is $\sigma_{\text{ig}}^2 = 2eI_0 \Delta f$;
- and the Flicker noise, or $1/f$ noise, characterized by a pink Power Spectral Density, which is an important component of EN.

Usually the electrochemical noise is studied for small electrodes (a few square centimeters). However, the active surface of the Li-ion battery electrodes is much greater. It was demonstrated that the electrochemical systems noise is inversely proportional to the active surface of the electrode. The Nanovoltmeter Keithley 2182 is the device chosen for our Li-ion Samsung 18650 EN measurements. The acquisition system developed is quite simple. In fact, each additional element adds noise and measurement disturbances. To mitigate electromagnetic interference, the circuit is enclosed in a metal box (Faraday cage) grounded the Keithley (Fig. 2).

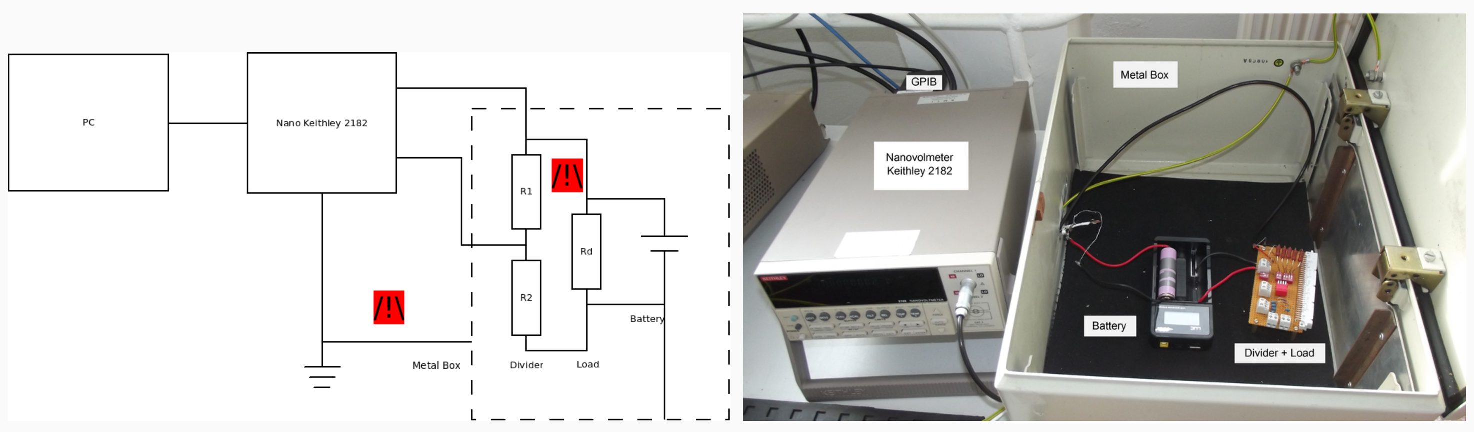

Fig. 2: Schema and photography of our device

Noise are numerically extracted by using a high-degree polynomial fitting. This method is robust and noise show good reproductibility as we can see on the discharge curve and short-time STD of EN during 5 Ω (Fig. 3) [1]. While the overall look remains the same despite the difference in value, a mild form of difference we notice: The V of the strong discharge (3.33 Ω) is sharper, more closed than V of the weak discharge (5 Ω) (Fig. 4 right). Mathematically, this means that the derivative $\left|\frac{\partial \text{STD}(3.33\,\Omega)}{\partial \text{SOC}}\right|$ is greater than $\left|\frac{\partial \text{STD}(5\,\Omega)}{\partial \text{SOC}}\right|$.

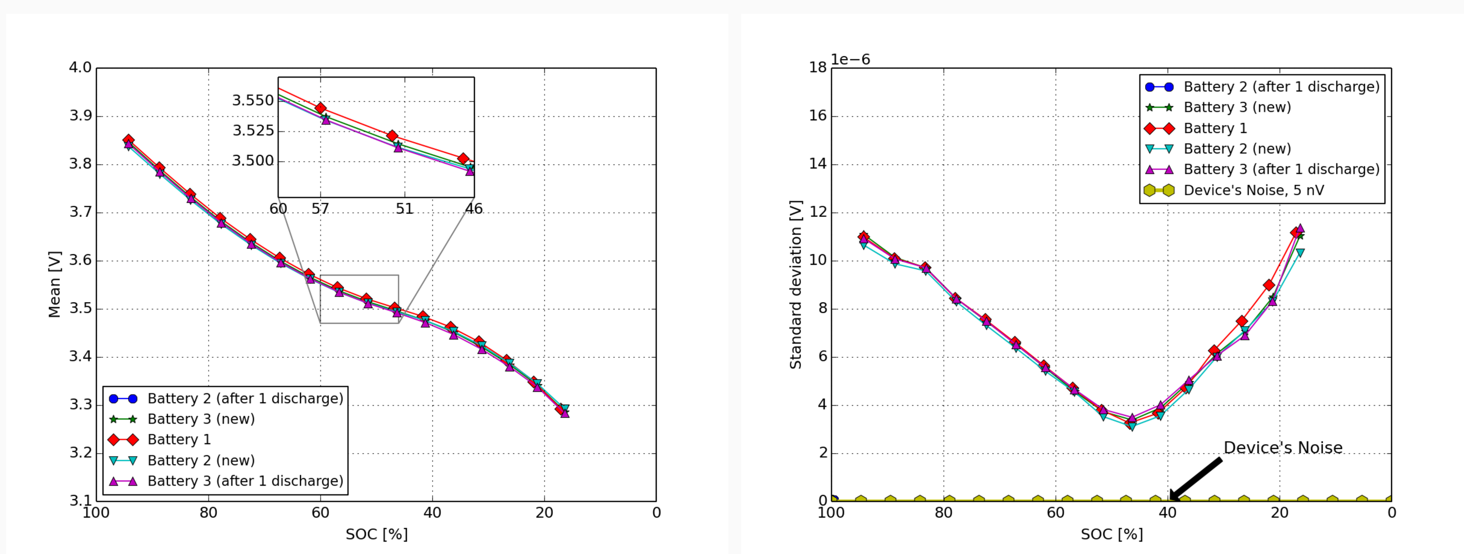

Fig. 3: Reproductibility on 5 Ω discharge curve (left) ; reproductibility on Short-time STD of 5 Ω discharge EN (right)

Effect of Ageing on Li-ion EN

We made a preliminar accelerated aging test on the batteries, and the protocol is: we did undergo a series of short circuits to the battery for a few minutes before recharging completely. In the first experiment, we carried out a single short circuit and in the second we added nine shorts (for a total of ten). Landfills voltage curves are similar. The V curve changes with aging (Fig. 4 left) [1]. It tends to decrease for a SOC between 100% to 55% and grow to a SOC ranging from 55% to 0%. The maximum values range from 15 µV to 18 µV and minimum values 7 µV to 5 µV. The noise of beginning of the discharge decreases with aging, the hollow of the V increases with age and the end of the discharge also increases as a function of aging. In addition, two SOC is observed for which the curves intersect to reverse (60% & 27%).

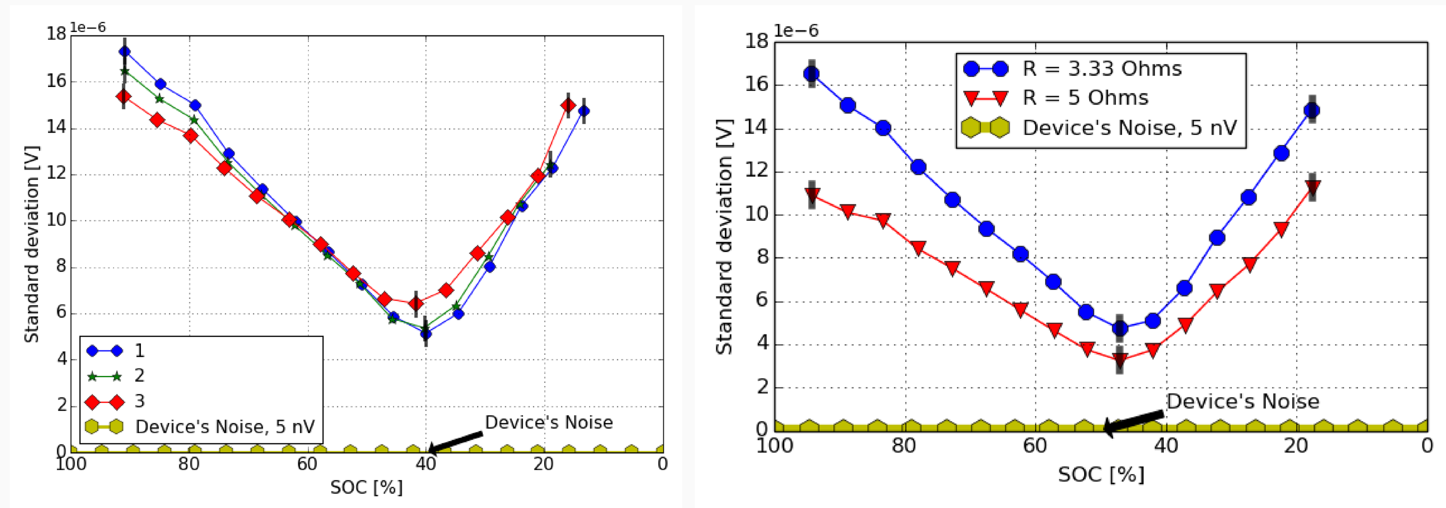

Fig. 4: Effect of Ageing on Short-time STD (left) and comparison of 5 Ω and 3 Ω discharge Short-time STD EN (right)

Signal Processing of Li-ion EN

We saw before that noise is extracted numerically. There is three areas inside this signal where noise is completly different: Beginning (SOC from 100% to 96%), Middle (SOC from 96% to 12%) & End (SOC from 12% to 3%). The Short-time STD was calculated on each pieces and show good reproductivity on 5 Ω discharge (Fig. 5).

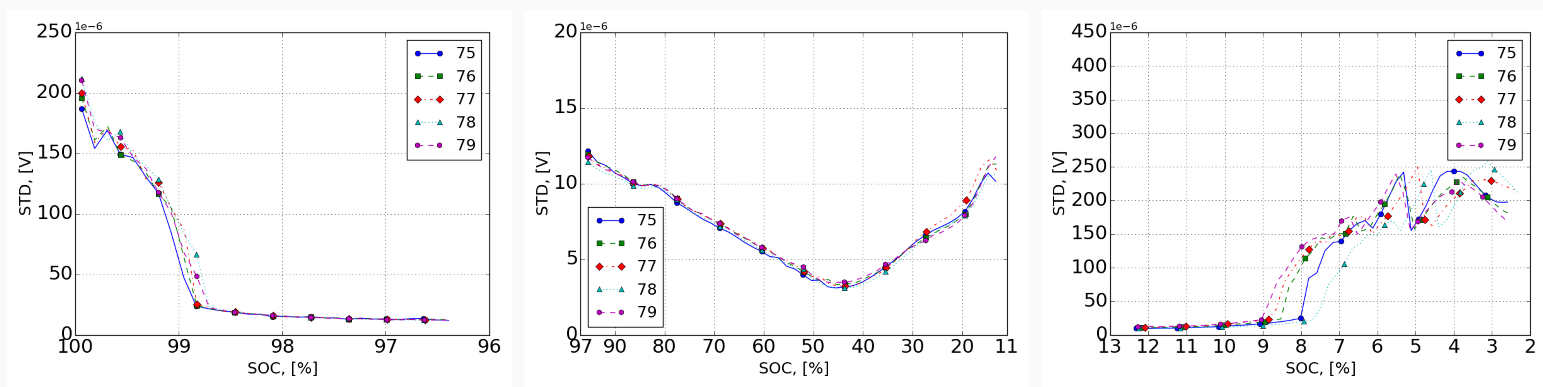

Fig. 5: Short time STD on each part : Beginning, Middle and End

If ψ is a wavelet and x the analyzed signal, then continous wavelet analysis is defined by :

$$\forall (u,s) \in \mathbb{R}^2 \quad \mathcal{W}x(u,s) = \langle x|\psi_{u,s}\rangle = \int_{\mathbb{R}} x(t) \frac{1}{\sqrt{s}} \psi^*\left(\frac{t-u}{s}\right) \mathrm{d}t, \qquad (1)$$

where s is the scale. Continous wavelet analysis of the edges (Begin and End) show good results with Morlet wavelet (Scalograms on Fig. 6).

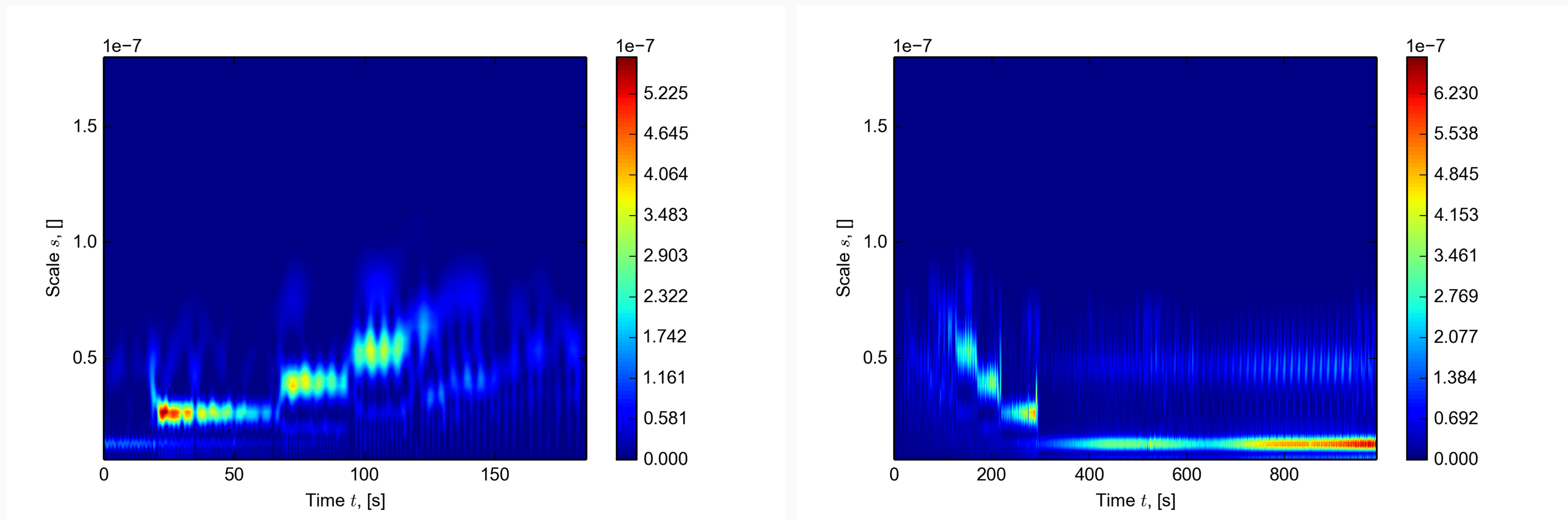

Fig. 6: Scalograms : Beginning (left) and End (Right) of the 3 Ω discharge

Conclusion and Perspectives

The protocol was as follows: we have chosen two resistors discharge and measured five voltages reproducibly for each resistance. Then we extracted the noise through our robust numerical method. This method is based on the use of high-degree polynomial (5, 7 and 9) which accurately interpolate the discharge voltage batteries. The calculation of short time STD showed good reproductibility of the experiment. We discovered three zones (beginning, middle and end) of SOC where the Li-ion EN changes completely. We noted that the noise located in the middle strongly look likes a uniform noise characterized by its short time STD V-shaped. Also, the edges of discharge show good time-scale signatures revealed by wavelet analysis. We conducted a preliminary campaign aging and we have seen that the noise changes with aging. Our database is thin, but the subject of this work is to develop a detection method from the signal processing tools. In future, the database should be enlarged.

References

[1] S. Martemianov, N. Adiutantov, Yu. K. Evdokimov, L. Madier, F. Maillard, A. Thomas. "New methodology of electrochemical noise analysis and applications for commercial Li-ion batteries". *J. Solid State Electrochem.* **19**(9) : 2803-2810, 2015.