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New methodology of electrochemical noise analysis and applications for commercial Li-ion batteries

S. Martemianov[1] · N. Adiutantov[1,2] · Yu. K. Evdokimov[2] ·
L. Madier[3] · F. Maillard[1] · A. Thomas[1]

Abstract Electrochemical noise analysis (ENA) is performed on ICR 18650 commercial lithium-ion batteries. The interest of ENA relates with the possibility of in-situ diagnostics during charging or discharging of the battery. Thus, the extraction of small voltage fluctuations should take into account the time evolution of the mean signal. The non-stationary character of the phenomenon (charging and discharging battery) limits the use of traditional methods of signal filtering and attenuation, so a special methodology has been developed to calculate the noise standard deviation (STD). A good reproducibility of the results has been demonstrated, and V-shape form curves have been obtained with a minimum STD value at about 55 % of state of charge (SOC). It can be noted also that fast discharge provided with 3.3 Ω load is noisier than the slow one with 5 Ω load. Some promising results have been obtained regarding the possibility of battery state of health determination.

✉ S. Martemianov
serguei.martemianov@univ-poitiers.fr

1   Institut Pprime, Université de Poitiers-CNRS-ENSMA, UPR 3346, 2
     Rue Pierre Brousse, Bâtiment B25, TSA 41105, 86073 Poitiers
     Cedex 9, France

2   Kazan National State Research University, 10 K. Marx street,
     Kazan, Russia

3   DCNS/DGD/ASM/DI/ING/EN, St-Tropez, France

Introduction

In recent decades, much attention has been devoted to the development of electrochemical sources of energy, in particular, rechargeable lithium-ion (Li-ion) batteries [1–4]. These batteries are key components of the portable, computing, telecommunication equipment required today by the information-oriented society. Moreover, gaseous emissions from the burning of fossil fuels are polluting the air of large cities and creating global warming with dangerous consequences. These concerns initiate utilization of alternative sources of energy (solar radiation, wind, waves) that are variable in time and diffuse in space. All these sources require energy storage, and batteries provide a promising way in this direction.

Certainly, the progress in energy storage is much slower when compared with electronic industry where a doubling of memory capacity every 2 years follows well Moores' law prediction. Nevertheless, spectacular advances in electrochemical storage of energy via the emerging technologies of Ni-MeH, Li-ion batteries and fuel cells stimulate further R&D studies in physico-chemistry and engineering of electrochemical systems.

Economic impact of battery failures can be important when they are used in critical applications, and much attention has been devoted to the determination of state of health (SOH) of these systems. Existing diagnostic technologies such as conductance and impedance testing [5, 6] give only a partial answer on this question, and using alternative approaches seems to be very interesting. The present paper deals with electrochemical noise analysis (ENA) and its possible applications to studding rechargeable Li-ion batteries.

Noise measurements have been widely used not only in the 1960s in relation to communication systems [7] and

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semiconductors [8] but also from time to time in electrochemical studies [9–12]. Electrochemical noise can be caused by different phenomena such as turbulent mass transfer [13–17], gas evolution [18–20], electrode corrosion [21–24] and passivation [25], or water transfer in fuel cells [26]. Usually ENA concerns small-size electrodes up to a few square centimetres. But for the practical applications related with commercial batteries, the active surface of the electrodes is much more important. The works of Professor M.A. Vorotyntsev and co-authors [13, 14], related to turbulent noise in electrochemical systems, have been demonstrated that relative intensity of the electrochemical noise is inverse to the electrode surface. For this reason, the ENA of commercial batteries is a delicate problem related with the extraction of very small voltage fluctuations, and very few measurements have been provided with real industrial systems [27, 28]. The interest of ENA relates with a possibility of in-situ diagnostics during charging or discharging of the battery. Thus, the extraction of small voltage fluctuations should take into account the time evolution of the mean signal. The non-stationary character of the phenomenon (charging and discharging battery) limits using of traditional methods of signal filtering and attenuation.

The main goal of the paper concerns the methodology of ENA with its application to monitoring of commercial Li-ion batteries. Special attention is given to the difficulties related with the extraction of very small voltage fluctuations during a battery's discharge. Some promising results related with the application of ENA for in-situ diagnostics of commercial batteries are presented as well.

Experimental setup

In the frame of the present work, electrical noise analysis (ENA) was applied to ICR 18650 commercial lithium-ion batteries; 18650-type is a cylindrical cell with a 3.7-V nominal voltage and 2.6-Ah rated capacity. To measure the low voltage fluctuations of lithium-ion batteries, experiments are performed in an appropriated experimental setup shown in Fig. 1. Battery voltage is measured by a 2182-Nanovoltmeter (Keithley) allowing, in the 10-mV range, to perform measurements with a nanovolt resolution. Nanovoltmeter is directly connected to a resistor divider that allows dividing by 500 the battery voltage and working in the 10-mV nanovoltmeter range (Fig. 2). Voltage is measured during battery discharges with two different loads, 3.3 and 5 Ω. To avoid, as much as possible, the electromagnetic interferences, the lithium battery, the divider and the load are placed into a metal box connected to the ground.

For discharge, the battery is maintained under a constant load until 5 % of state of charge (SOC) that takes approximately 2.5 h for 3.3 Ω and 4 h for 5 Ω. After each discharge, the battery is charged with a constant current of 0.5 A until the charging voltage of 4.2 V and kept at this constant voltage to the end of a current drop around 0.1 A. All measurements are performed with a frequency of 10 Hz using LabVIEW for data acquisition and Python for signal processing.

To validate and quantify the intrinsic noise of our experimental setup, voltage measurements have been performed without the battery. The battery has been replaced by a wire, and measurements of the voltage have been done for two circuits, one with nanovoltmeter plus wires and another with nanovoltmeter plus wires and divider.
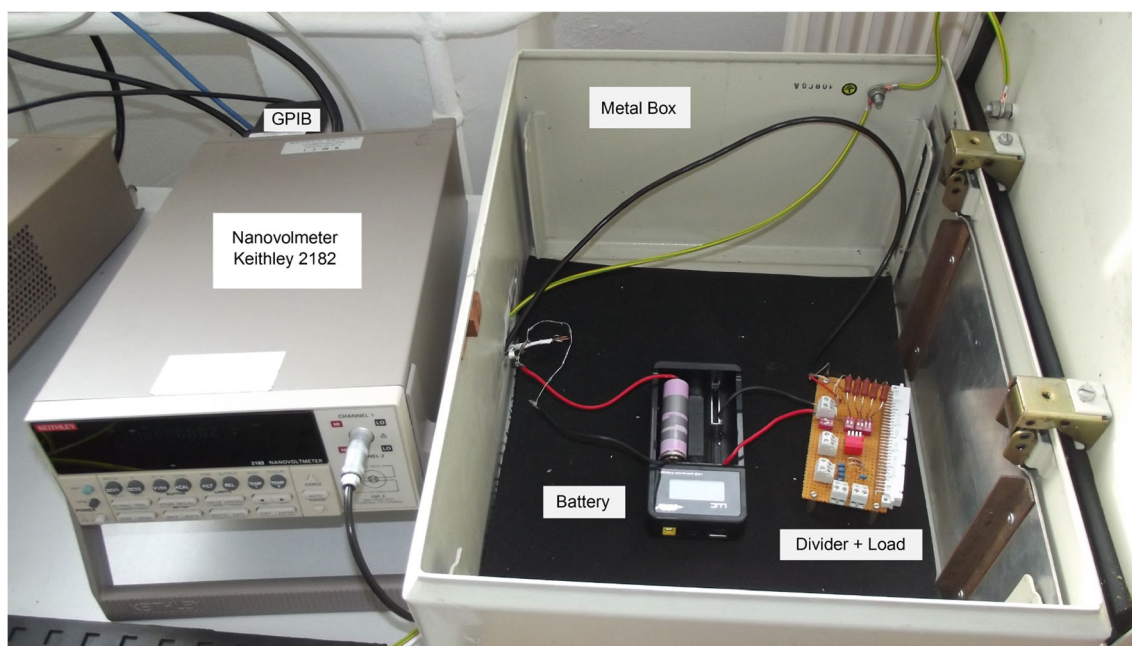

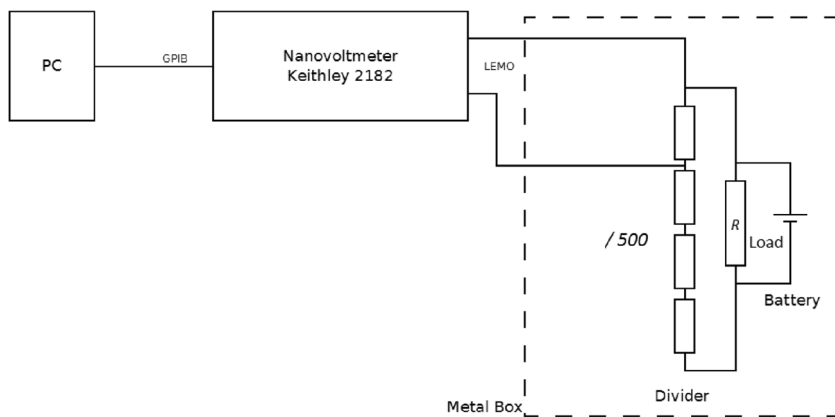Fig. 1 Experimental setup for lithium-ion battery noise measurements

Figure 3 shows intrinsic noise of the experimental setup during 400 s for the two abovementioned configurations. Measurements indicate that the apparatus noises are in the nanovolts order. The calculated standard deviation (STD) of the apparatus noise is equal to 2.74 nV for nanovoltmeter plus wire configurations (1) and 3.74 nV when divider is added (2). STD values are near the manufacturer values for the dc noise of the nanovoltmeter, which in the range of 10 mV, equals to 5 nV. So, the experimental setup was validated, and a STD of 5 nV has been accepted for the device noise.
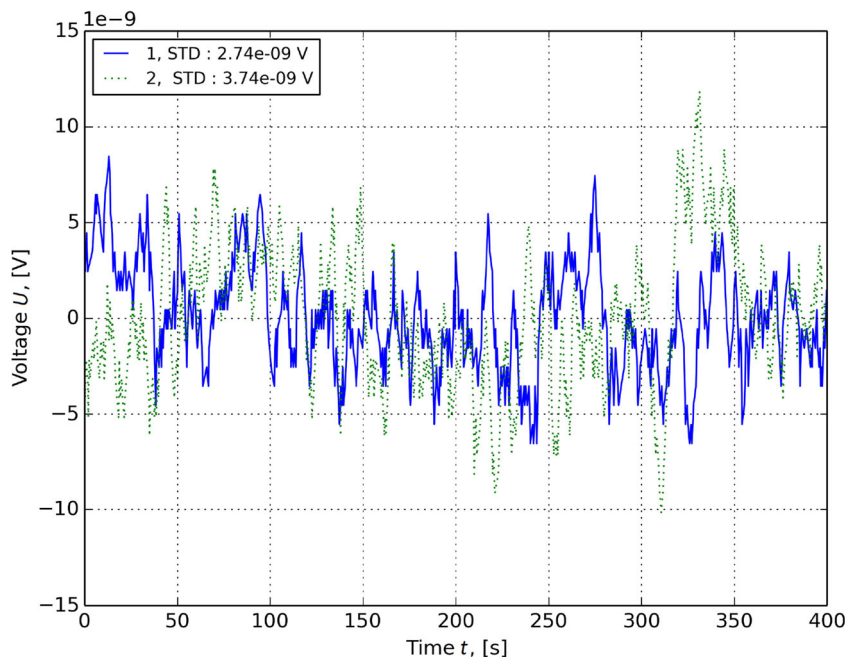
Signal processing

Figure 4a shows a quasi-full discharge of the battery during 14,000 s (around 4 h). The discharge starts at the open-circuit voltage (OCV) of 3.98 V (charging voltage equals to 4.2 V) and run until 1.2 V. For signal processing, the total time domain have been divided into 20 pieces and the special procedure for the extraction of the noise fluctuations have been performed. Figure 4b shows the extracted voltage fluctuations for the tenth piece. The amplitude of the battery noise is in the microvolt order, 1000 times higher than the device noise (5 nV).

The procedure for the extraction of the noise fluctuations is the following: each of the 20 pieces contains approximately $n=7000$ experimental points (instantaneous voltage magnitudes); each of these 20 pieces is separated on time subintervals containing m points ($m=50$, 75 or 150). The signal in each sub-interval containing m experimental points is approximated by a n-order polynomial, and the signal fluctuations are calculated with respect to the mean value determined by this polynomial.

Fig. 3 Internal noise of
experimental setup of **1**
nanovoltmeter and wires and **2**
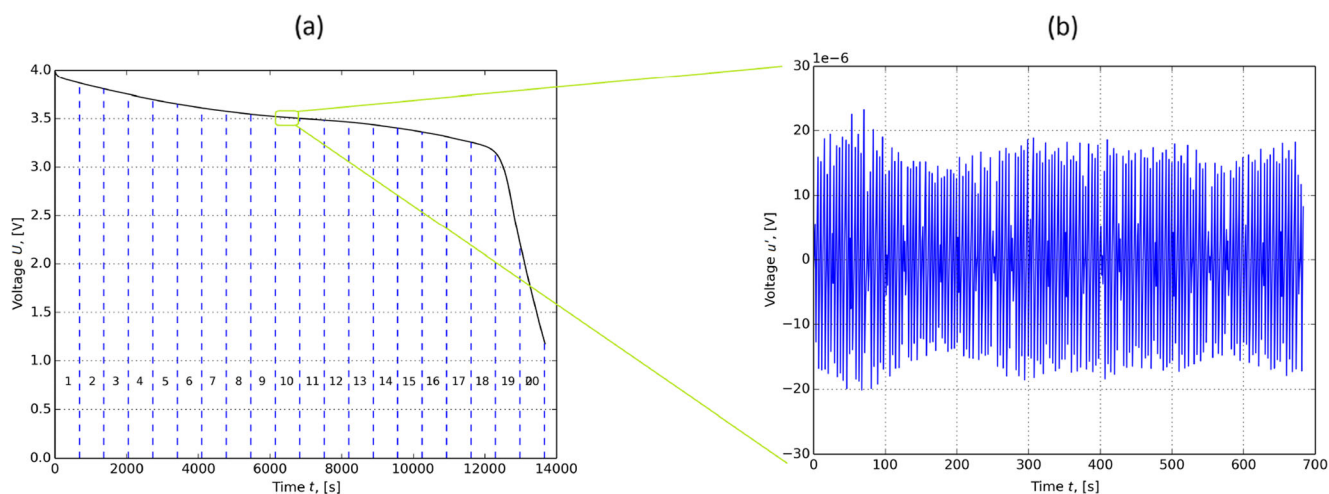nanovoltmeter, wires and divider

Fig. 4 **a** Discharge of Li-ion battery and **b** associated voltage fluctuations

Figure 5 illustrates the results of the signal processing when the steady-state and the linear approximation are used for determining the mean signal value. It is clear that the results (STD of voltage fluctuations) are very sensitive to data processing parameter, namely the value m, which characterises the time-span of the sub-interval where the signal fitting is provided. For this reason, the high-order polynomials have been used for the fitting of the mean signal value, as shown in Fig. 6. It can be seen that for high-order polynomials ($n=5, 7, 9$), the results are not sensitive to the data processing parameters (n and m). For the following, the data processing has been performed using $n=7$ and $m=75$ for extraction of the voltage fluctuations.

Experimental results and discussion

All obtained results are given in terms of state of charge (SOC) to permit the comparison for each discharge The

noise (voltage fluctuations) of the lithium-ion battery is characterised by STD of the processing signal, and this STD is multiplied by 500 because the nanovoltmeter measures the voltage of the divider and not directly of the battery. The device noise of 5 nV is plotted for the comparison.

Influence of the discharge load

Voltage measurements have been performed for two different discharge loads of 3.3 Ω and 5 Ω for characterising the influence of a low (5 Ω) and fast discharge (3.3 Ω) on voltage drop and noise.

Figure 7 reflects the reproducibility of voltage drop during several discharges (mean) for each load. For three different batteries, five discharges are compared. After each discharge, the battery is charged until the charging voltage of 4.2 V. In overall, for each load, voltage drop is about 0.6 V until a SOC around 20 %. Figure 7 shows a good reproducibility for all discharges in each case; the voltage difference is 0.25 V (less
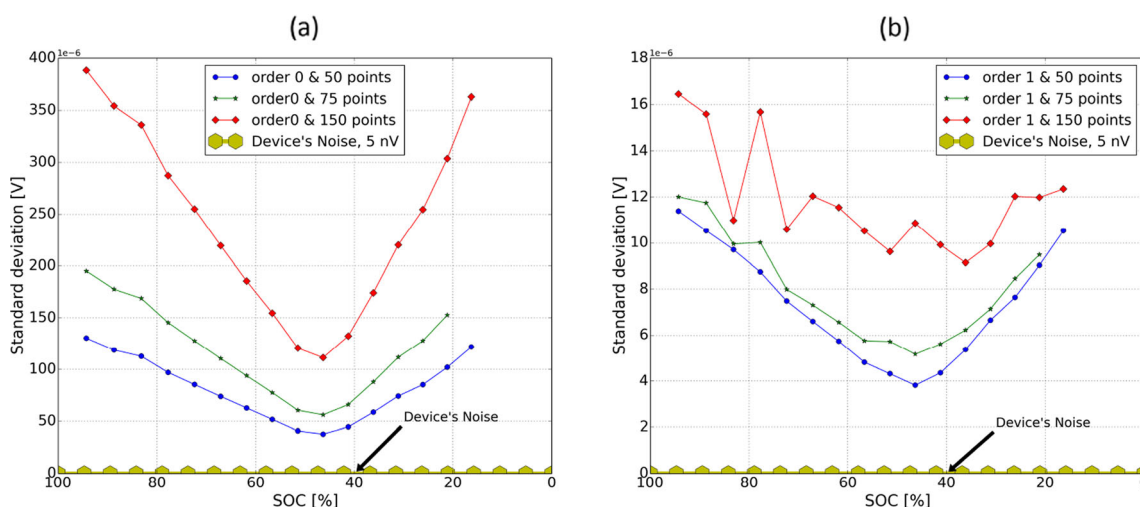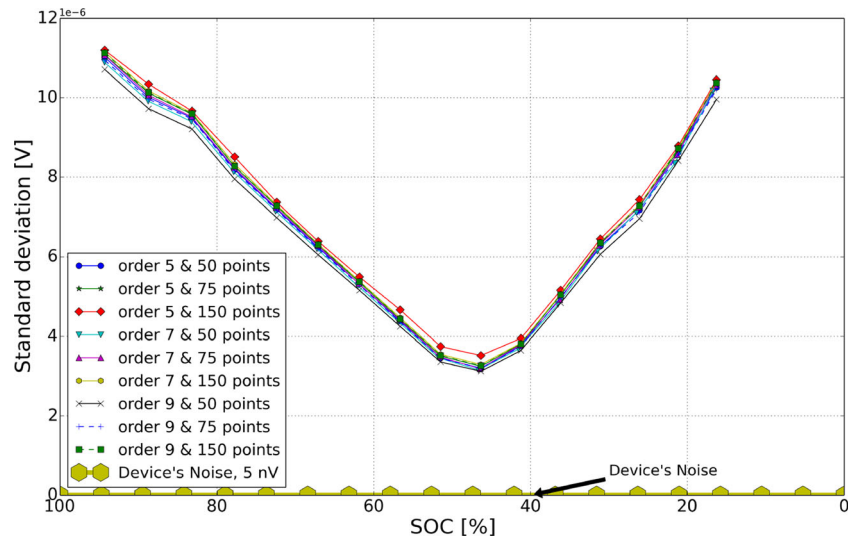

Fig. 5 Signal processing: STD of voltage fluctuations obtained using **a** steady-state and **b** linear approximations for determining the mean value

Fig. 6 Noise standard deviation of voltage fluctuations obtained using polynomial of order n: 5, 7 and 9 for determining the mean value

than 1 %) for all batteries and ten times lower (0.025 V) for the same battery after one discharge. A difference is noted for the started voltage between discharges with 5.5 Ω and 3.3 Ω load, but discharge curves are the same. Namely, started voltage is equal to 3.85 V for R=5.5 Ω (Fig. 7a) and to 3.75 V for R= 3.3 Ω (Fig. 7b).

Figure 8 shows a good reproducibility for the STD recording for each load. A maximal difference of 1 μV is measured for all batteries. The incertitude of 1 μV is reported on Fig. 9 where the comparison of the discharge for two loads is presented.

Figure 9 shows the comparison between noise measurements during discharges at different loads (5 Ω and 3.3 Ω) for the same battery. In both cases, a V-shape curve is founded with a minimum of 3.5 μV for 5.5 Ω load and 5 μV for 3.3 Ω load respectively at around 55 % of SOC. For each SOC, the STD for 3.3 Ω load is higher than the one for 5 Ω load. The difference around 6 μV at 95 % of SOC, 2 μV at 55 % of SOC and 4 μV at 18 % of SOC can be noted for STD with respect to a discharge at different loads. The test with 3.3 Ω load implies a faster discharge and a noisier drop voltage.
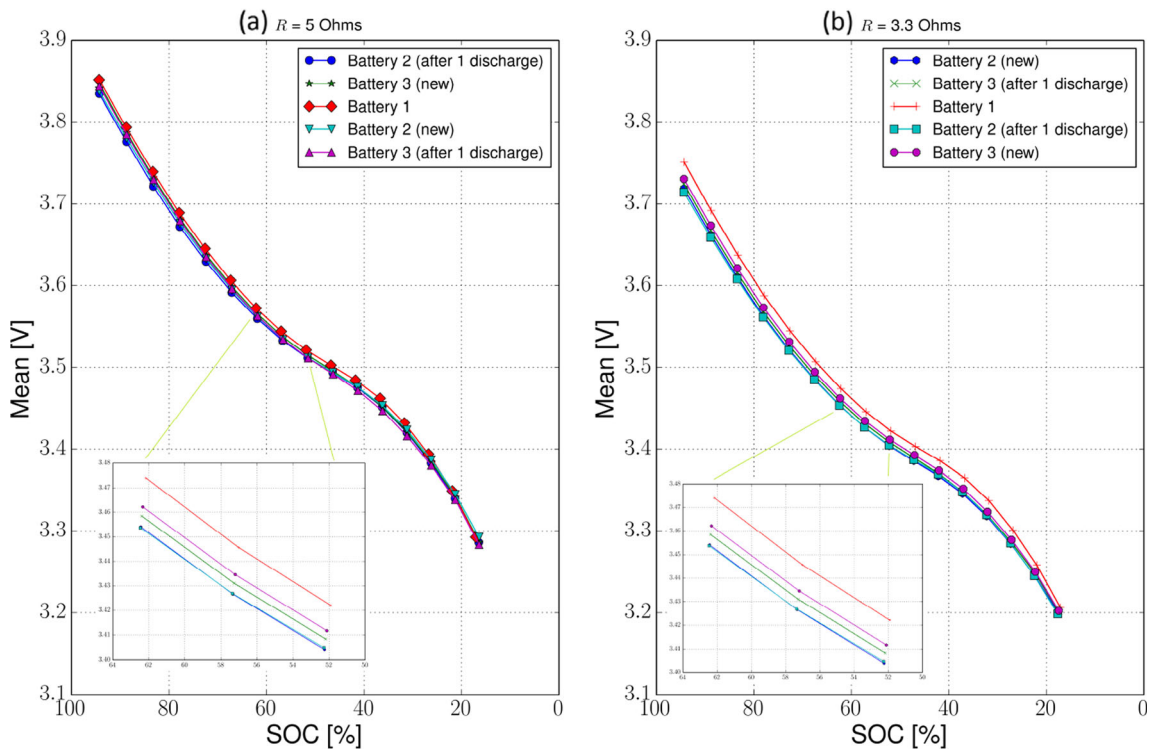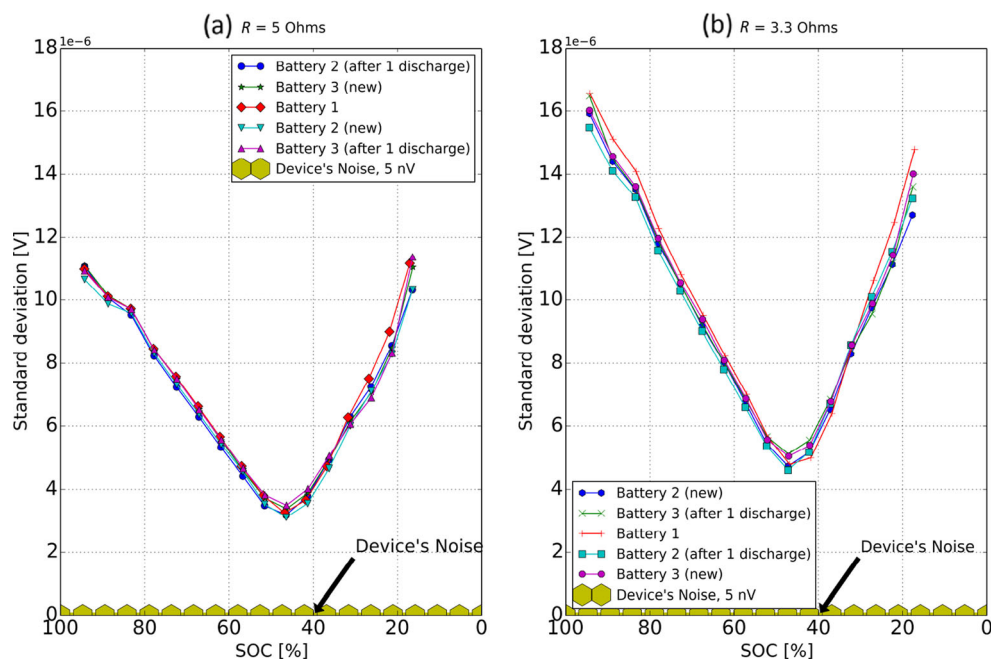

Fig. 7 Discharge of Li-ion battery with different load R **a** 3.3 Ω and **b** 5 Ω. Reproducibility of the mean measurements

Fig. 8 Discharge of Li-ion battery with different load *R* **a** 3.3 Ω and **b** 5 Ω. Reproducibility of the noise measurements

Results show that voltage fluctuations and noise are more important near the OCV, decrease until a minimum at 55 % of SOC, that correspond to the inflexion point of the discharge (Fig. 7), and increases until 20 % of SOC. This V-shape curve can be related to the physical and electrochemical behaviour of the battery. Indeed, it can be supposed that for important SOC values (between 100 and 50 %), the battery discharge is governed mainly by the kinetics of electrochemical reactions (see the voltage drop curve in Fig. 7). Near the inflexion point which is situated around 50 % of SOC, the transport limitations begin to influence on the battery behaviour and become the governing factor for low SOC values. Thus, the decreasing

part of the noise curve can be attributed to the noise of electrochemical reactions and the increasing part to the noise of transport phenomena.

It is interesting to note that both types of STD versus SOC behaviour have been noted in the literature. Thus, Baert and Vervaet [27] note the increasing of the noise voltage during discharge of Hoppecke batteries. Contrary, Martinet et al. [28] have presented the results concerning with Ni-MH batteries which indicate the decreasing of the noise power with SOC. The possible explanation relates with the influence of different phenomena (electrochemical and transport limitations) on the noise behaviour of different batteries.

Fig. 9 Comparison of noise characteristics (STD) during discharge at different load *R* **a** 3.3 Ω and **b** 5 Ω for the same battery
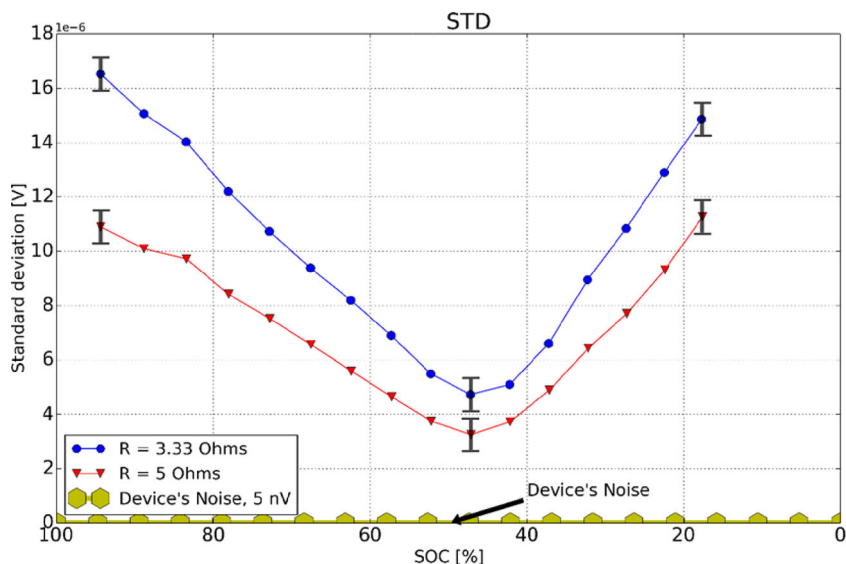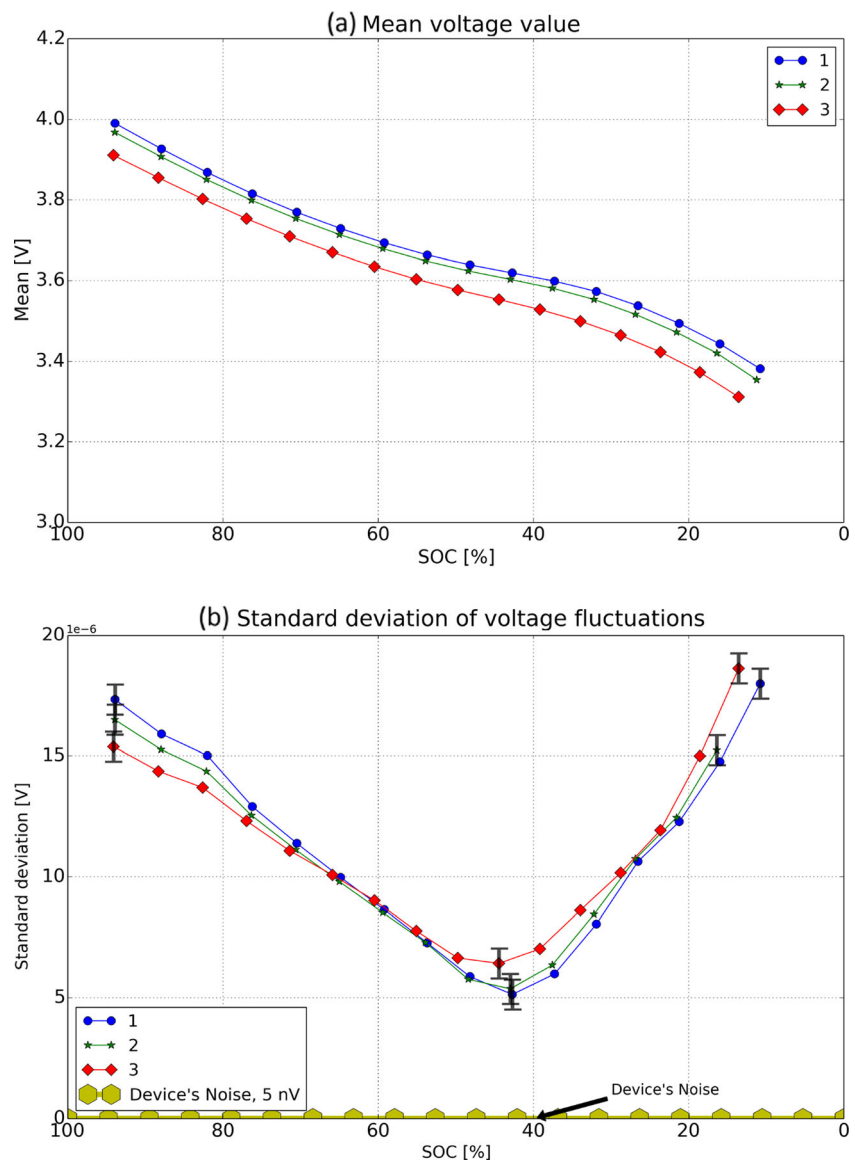
Fig. 10 Aging effect on **a** mean and **b** noise characteristics of the battery. **1** New battery, **2** after one short-circuit and **3** after ten short-circuits

Aging effect on the noise measurements

In this part, aging tests are performed via short-circuit cycling at ambient temperature. This aging test consists to short-circuit the battery during 2 h and to wait temperature equilibrium before start of another short-circuit. Figure 10 shows the drop of mean voltage (Fig. 10a) and noise characteristics (Fig. 10b) for a fresh battery, after one short-circuit and after a cycle of ten short-circuits. Figure 10a reflects that the voltage are decreased about 0.04 V after one short-circuit and about 0.1 V after ten short-circuits for all SOC. Voltage decrease is higher after ten short-circuit cycles, due to higher degradation processes in Li-ion battery. Figure 10b reflects the V-shape curve for the three state of health (SOH) with a variation of STD between 17 and 6 μV. For a SOC between 95 and 60 %, the STD of the fresh battery is higher than the battery after ten short-circuits. Around 55 % of SOC, a reverse occurs; STD

(noise) of the aged battery, after ten short-circuit cycle, becomes higher than the fresh battery with a maximal difference at 45 % of SOC. At this SOC, STD after ten short-circuits is 6.5 μV against 5 μV for the fresh battery. The difference in the aging effect for low and high SOC can be related with the difference in preponderant effects (electrochemical or transport phenomena) which is governing the noise behaviour of the battery, but this issue needs more careful studies.

Conclusions

In this work, a methodology allowing to apply ENA for studying commercial batteries is presented. The commercial batteries have very important active surface of the electrodes and consequently very small voltage noise. The small voltage fluctuations have been extracted during

discharge of commercial Li-ion batteries using appropriated instrumentation (Nanovoltmeter) and a special data treatment procedure. This procedure is based on using high-order polynomials for fitting the mean signal value in small time windows. It is worth to note that the steady-state or the linear approximations for the fitting of the mean signal value do not allow correct extraction of the voltage noise during battery discharge because the noise characteristics depend dramatically in this case on data treatment parameters.

The noise standard deviation (STD) versus state of charge (SOC) has been measured for commercial Li-ion batteries, and good reproducibility of the results has been demonstrated. The obtained curves have a V-shape form with the minimum value at about 55 % of SOC. At our knowledge, this type of noise behaviour has never been published previously. Thus, the noise of the commercial Li-ion batteries is different on well-known noise sources. A possible explanation of a V-shape noise behaviour deals with superposition of different phenomena which governing the battery behaviour. For high SOC values, the electrochemical kinetics of the electrode's processes plays a dominant role while at small SOC values, the transport phenomena become more important.

It can be noted also that fast discharge provided with 3.3 Ω load is noisier than the slow one with 5 Ω load. Some promising results have been obtained with respect to possible monitoring of the battery's SOH by means of ENA. Indeed, at the minima of a V-shape curve, STD after ten short-circuits, is 6.5 μV against 5 μV for the fresh battery. This difference is much more important in comparison to the reached accuracy of ENA.

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