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Electrochemical Noise Analysis applied to new generation Li-ion batteries

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Context

This study aims at assessing the feasibility of Electrochemical Noise Analysis (ENA) to be used as a diagnosis method for new generation Li-ion cells (LNMO, LTO, TNO) :

- only based on electrical fluctuations (so called “noise”) generated by the system
- undisputed advantage of being non-invasive, operando and low cost
- Do not require any additional hardware, since cell voltage measurements is mandatory in a battery pack.

Nevertheless, the very low level of voltage fluctuations (<μV) provided by the batteries renders a proper measurement challenging.

In this work, an ultra low noise instrumentation (2 nV/√Hz above 10 Hz) has been purposely designed and realized to extract the voltage noise signature of four Li-ion coin cells with different electrode materials.

Principles and Experimentations

Data acquisition chain

Specific high quality discrete components conditioning circuit

Resistors with 0.25 % precision, and 25 ppm/°C stability/ thermal noise limitation at maximum

A low cut off frequency of 87 mHz is obtained which is necessary to get information about long term processes related to mass transport.

Circuit strong grounding to filter out the interfering 50 Hz AC signal

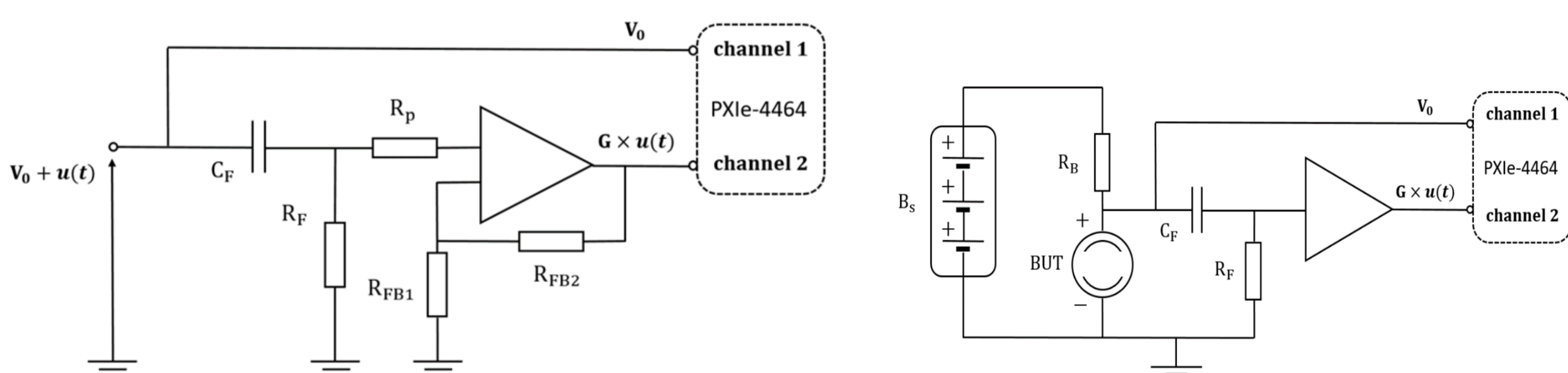


Fig 1. (a) diagram of the acquisition chain – (b) charging setup

Circuit screwed inside an aluminum box to inhibit external electrical interference

OA supplied by two Li-ion 14.8 V 2.6 Ah battery packs : “cleanest” voltage source

Data acquisition conducted with a high precision (24 bits) and high speed (204.8 kHz) NI PXIe-4464 DAQ

Battery cells under test

Negative electrode	Positive electrode	Operating voltage (V)	Estimated capacity (mAh)
Li	LiNi _{0.5} Mn _{1.5} O ₄	3.5-5	1.8
Li ₄ Ti ₅ O ₁₂	LiNi _{0.5} Mn _{1.5} O ₄	2-3.5	1.8
Li	TiNb ₂ O ₇	0.8-3	1
TiNb ₂ O ₇	LiNi _{0.5} Mn _{1.5} O ₄	3.5-5	1

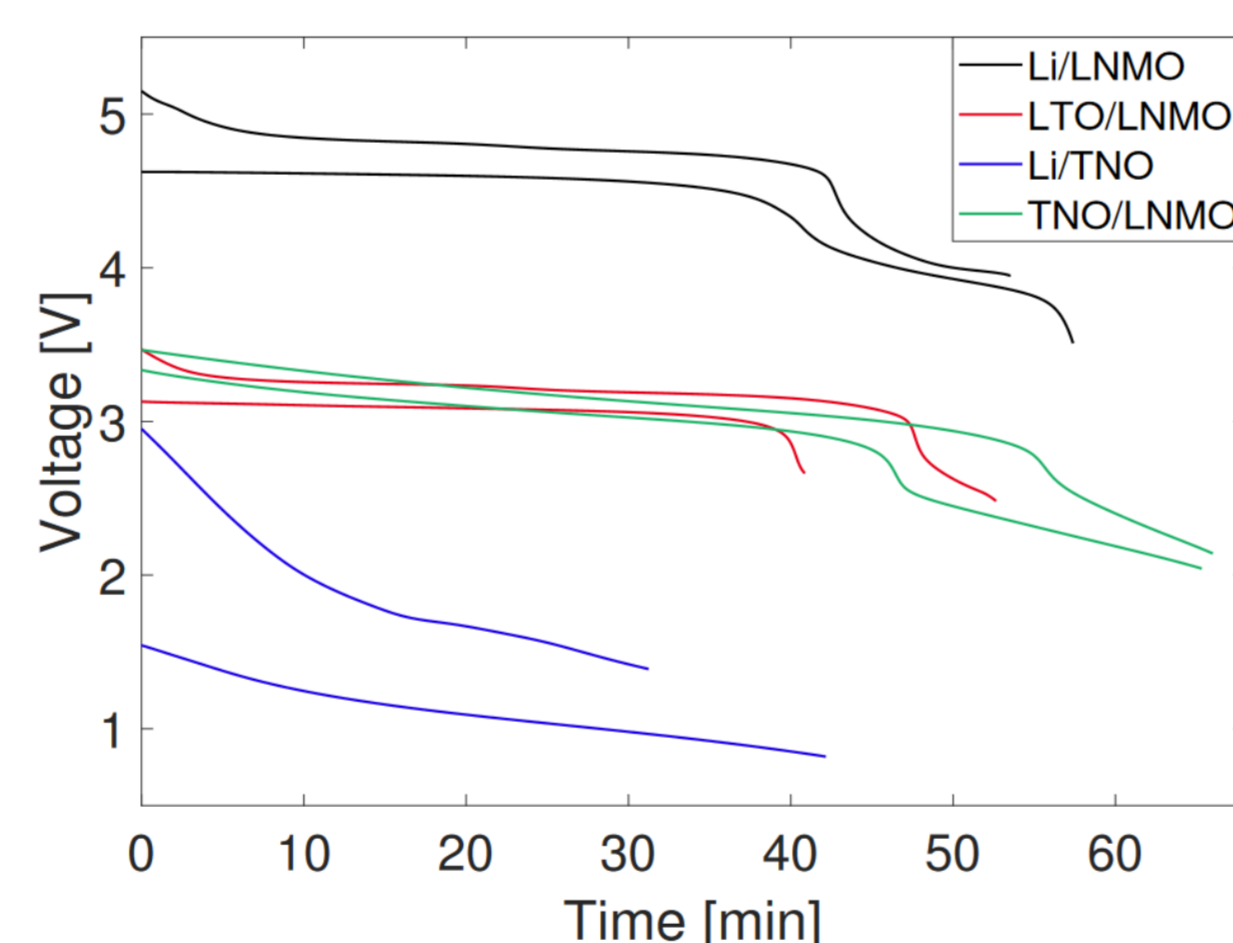


Fig 2. characteristics and charge/discharge curves of the coin cells under test

Analysis Method

- Power Spectral Density (PSD) based on FFT to describe the voltage noise
- Linear detrending applied on each sample before applying the Hann window, then FFT
- Low frequency PSD estimated over 104 seconds samples (2^{21} data points)
- Upper frequency PSD calculated over 3 seconds samples (2^{16} data points → Precision is improved for the high frequency part of the PSD)
- Noise analysis down to 10 mHz
- Sensitivity of the instrument limited by a flicker noise in the low frequency (1 μV/√Hz at 10 mHz) / the upper frequency region is mostly governed by the thermal noise from the protection resistor R_p , (2 nV/√Hz).

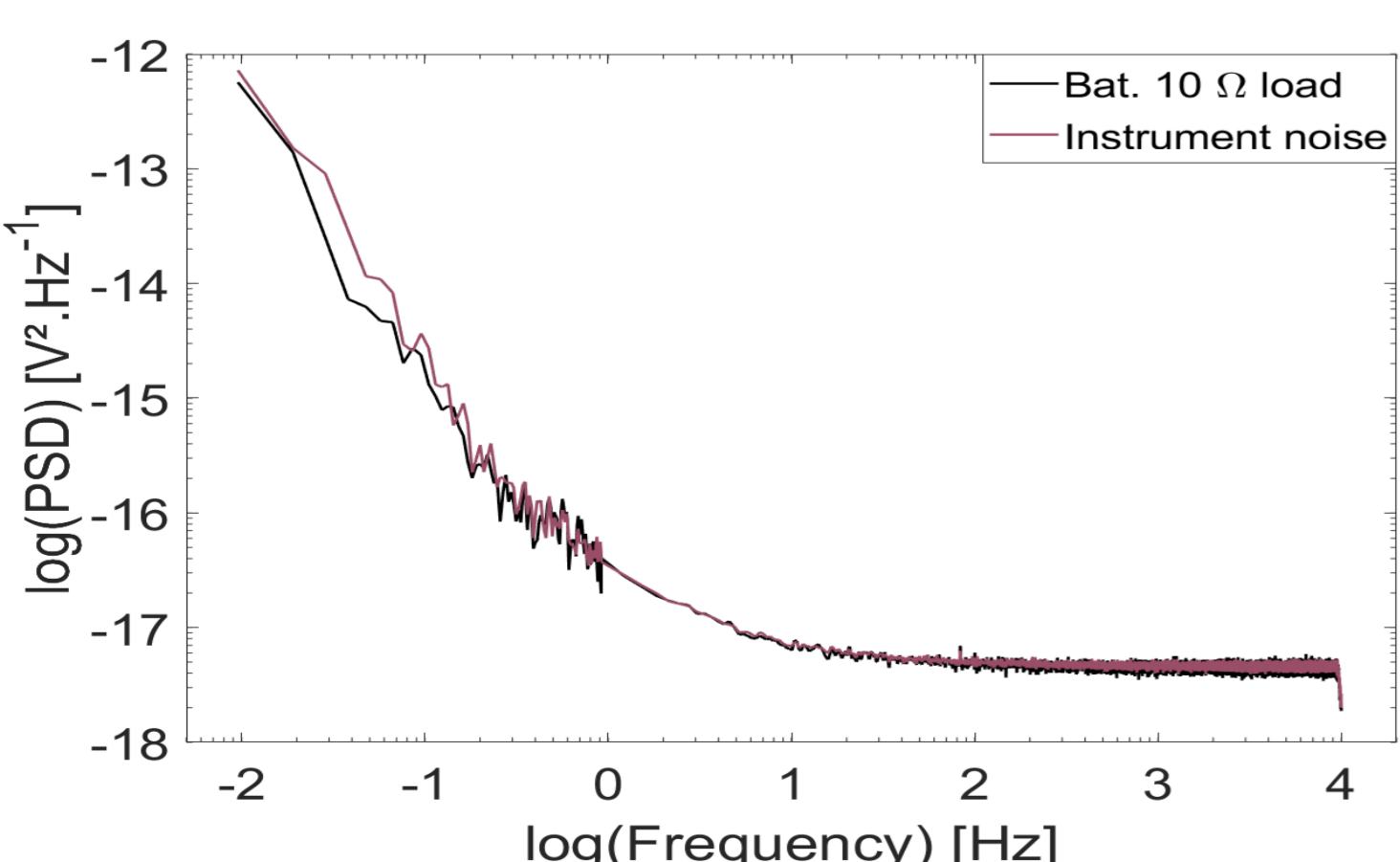


Fig 3. Noise of the conditioning circuit (black) vs noise of the charging setup with a 10 Ω load (brown)

Results

Battery cells Noise Analysis - Correlations

We have highlighted that **Electrochemical noise clearly depends on the current level, the SOC level and the chemistry type of the cell.**

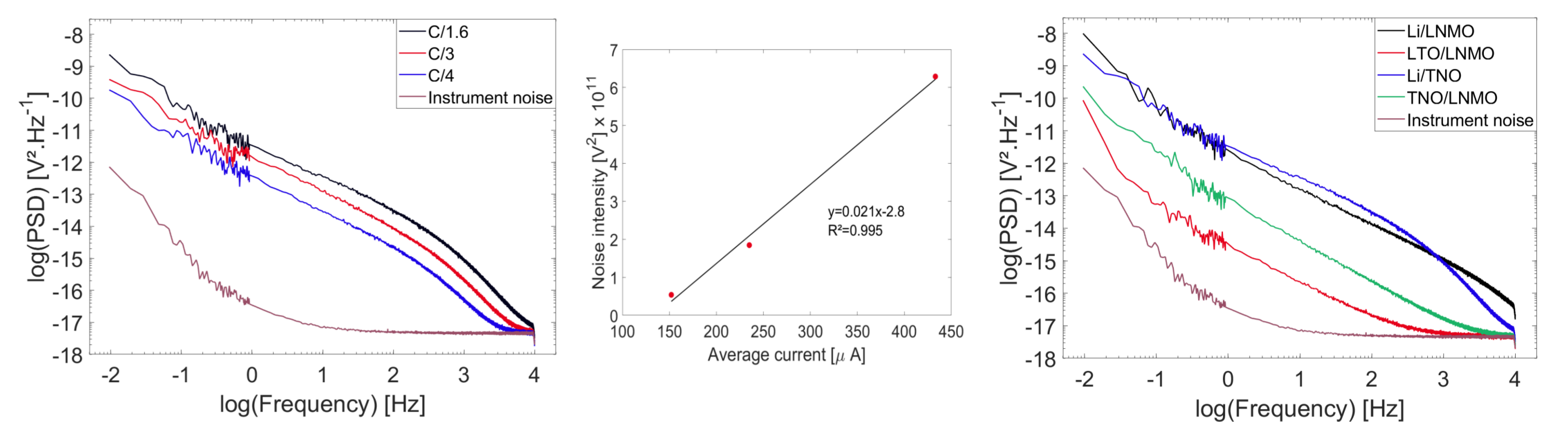


Fig 4. (a) PSD of Li/TNO voltage fluctuations when discharging at different DC current load – (b) Model fitting of Noise intensity regarding the DC current load – (c) PSD of the voltage fluctuations after conditioning for each cell type during discharge at C/5

Overcharge detection

Noise level clearly increases with SOC

Low frequency plateau before a 1/f4 decrease after 1 Hz. Sharp transients after 118 % SOC

Before 75 % SOC, STD # to the low frequency noise of the NI PXIe 4464 DAQ (about 20 μVrms).

After that, excess noise is clearly measurable and the STD increases piecewise linearly with SOC

Remarkable slope break around 105 % SOC, i.e. at the beginning of the overcharge

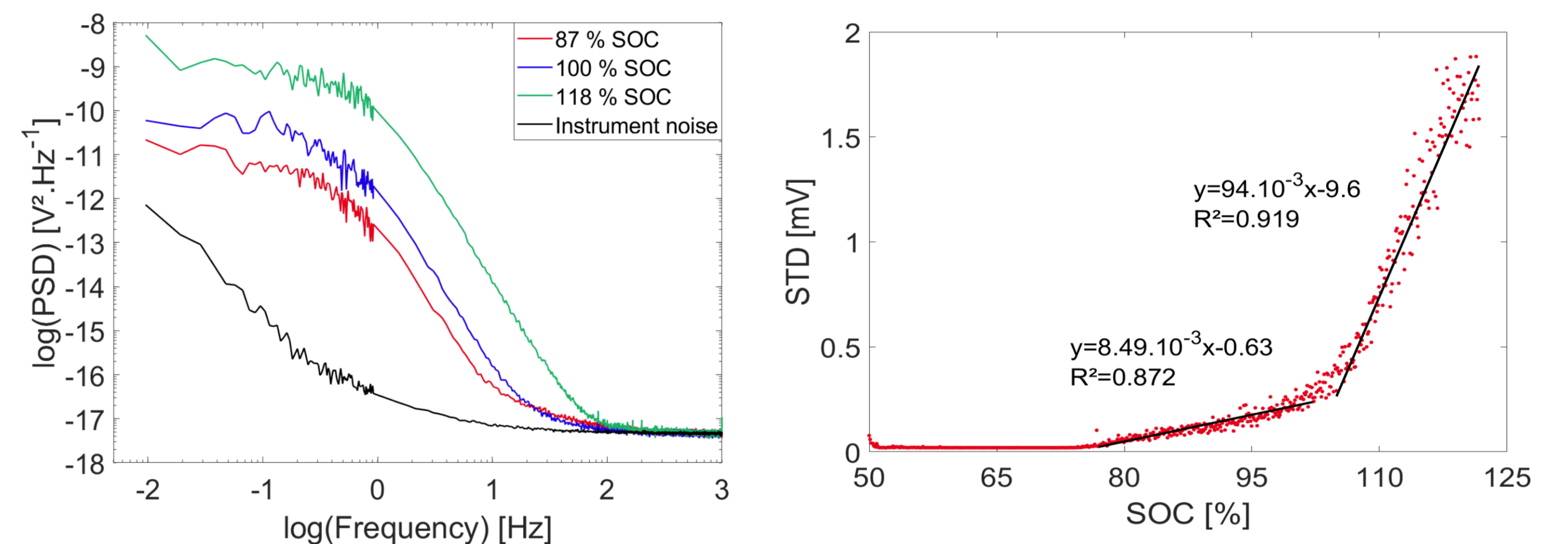


Fig 5. PSD of the voltage noise of the NiMH during charging at C/5, and model fitting of the Noise STD versus SOC

Overcharge detection of the Li/LNMO cell when charging at C/6 between 4.7 V and 5.5 V

Overcharge begins around 5 V. After 20 % overcharging, sharp transients exhibits overcharging

Preliminary explanations : Electrolyte decomposition, releasing gas bubbles that locally and temporary block the active surface, which lead to voltage fluctuations)

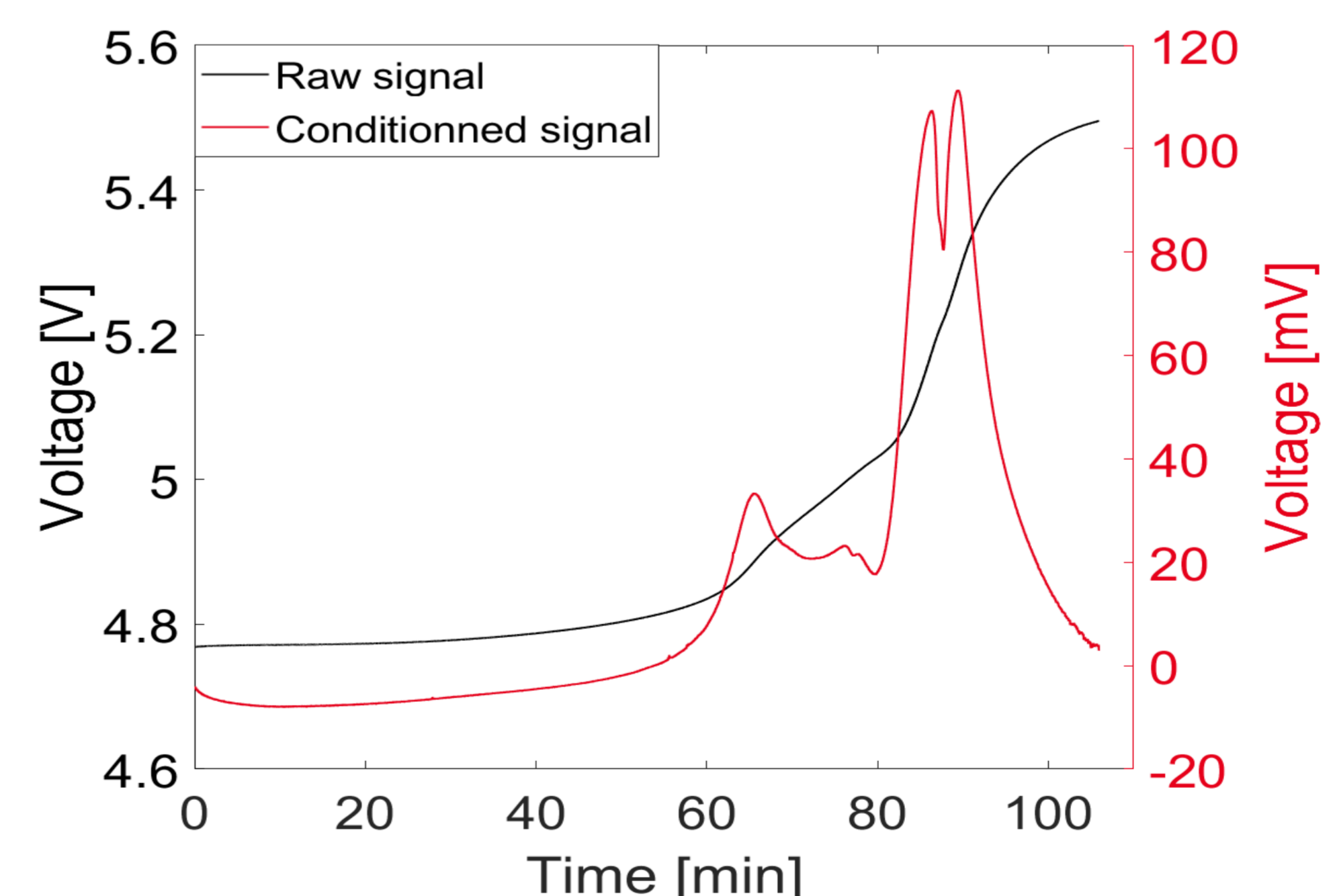


Fig 6. Voltage fluctuations of the Li/LNMO cell before (black) and after conditioning (red) during charging at C/6 rate

Discussion and perspectives

Achievements :

Based on theoretical and experimental developments, ElectroChemical Noise (ECN) fluctuations PSD of a NiMH and four Li-ion coin cells based on newly developed electrode materials performed:

- Exhibition of a significant dependence of ECN on SOC, current, type of cell
- Linear dependency on current, piecewise linearity on SOC
- Electrochemical Noise Analysis based overcharge detection feasibility has been demonstrated

Perspectives :

More sophisticated methods to be addressed for non-stationary signal analysis (ie wavelet transform)

Theoretical interpretation of the results to be performed together with thorough tests campaign validation