Study of lithium-ion battery ageing cycled with current profiles from railway applications

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***Abstract*—Lithium-ion batteries have been attracting significant attention in transport industry and particularly in hybrid railway transport applications. Despite significant progress, their lifespan is still limited. The knowledge of the operations leading to severe degradation is, therefore, crucial to optimize their use. From this perspective, experimental tests were conducted on lithium-ion battery cells. Two cells were cycled with two different real duty cycles from railway applications. This study aims at comparing the impact generated by the two profiles on the cell capacity, internal resistance and open-circuit voltage.**

***Index Terms*—Lithium-ion battery, NMC, Ageing test, Railway, RPT, ICA**

I. Introduction

Lithium-ion batteries have been developing rapidly over the last two decades in the transport industry. Manufacturers and collectivities identify this technology as an opportunity to prevent particulate emissions and decarbonize transport. In the railway industry, this solution is identified as a relevant alternative in catenary-free applications. Indeed, non-electrified lines represent a considerable part of the railway network. In 2018, 40% of the tracks were not electrified in France, 60% in the UK, and 47% in Germany. This corresponds to 45% of the European railway network [1]. On these lines, the density of train traffic is not sufficient to justify the high fixed costs of the overhead-line installation. Trains operating on these tracks are therefore autonomous and most of them are powered by a diesel engine. Several locally low-carbon alternatives are thus considered, such as the hydrogen fuel cell trains.

In these trains, lithium-ion batteries are used to support the proton exchange membrane fuel cell (PEMFC) and to recover braking energy. Such batteries are currently considered as the most suitable storage systems in railway applications thanks to their high energy and power densities and low self-discharge characteristics [2]. In hybrid fuel cell applications, the degradation of each source is closely linked to their electrical and thermal solicitation [3]. The knowledge of the operations leading to severe degradations is therefore crucial to smartly distribute the energy between sources. In this perspective, performing accelerated experimental ageing tests is particularly relevant to understand the ageing mechanisms at stake.

In automotive applications, several studies have reported experimental investigations of battery ageing when solicited with real-life cycles. Han *et al.* [4] compared the impact of a typical electric vehicle profile on five different cell technologies. Baure *et al.* [5] compared the impact of synthetic and real cycles in terms of degradation. Other studies performed experimental ageing tests to develop state of health estimators [6] or predictive models [7]–[9]. However, battery ageing mechanisms in railway applications has been poorly studied. Such specific applications differ from other transport applications in the battery cells considered and the current profiles applied.

In this study, experimental tests were conducted to investigate the ageing of two nickel manganese cobalt (NMC) lithium-ion pouch cells. Each of the two cells is cycled according to a current profile from a real duty cycle of the hydrogen fuel cell train. These experimental tests aim at comparing the impact of two real missions on cell ageing and to understand the underlying phenomena. Such aging tests based on real railway duty cycles have never been presented in the literature, to our knowledge.

At first, this digest introduces the experimental conditions in Section II. The cells, test bench, characterisation protocols and current profiles are described in this section. In Section III, the experimental results are reported. Finally, Section III-D discusses the results obtained.

II. Materials and methods

A. Test bench

To perform ageing tests on lithium-ion cells, the test bench requires a power source that can impose a specific current profile. Thus, the CHROMA 17020 Battery Pack Tester was used [10]. Furthermore, the characterisation phases of the cells must be performed at specific temperatures. During these phases, the cells are put in a thermal chamber ESPEC LU-124 which allows the ambient temperature to be controlled. Figure 1 introduces the test bench. Apart from these characterisation phases, the cells are cycled at room temperature in a ventilated box, to dissipate the thermal power generated.

B. Lithium-ion cells

The choice of the cells is based on the train energy requirements in the different missions it has to perform. To define them, an energetic model of the train was developed to simulate the train missions. This model determines the required electrical traction power, the auxiliary consumption, and the power distribution between sources through an energy management strategy. This model helped investigate the battery and fuel cell power and energy requirements. It will not be detailed in this article.

To meet all the requirements imposed by the railway application, two 26 Ah NMC/graphite cells in pouch format were chosen. Table I presents their characteristics. In the rest of the article, cell 1 and cell 2 will be used to distinguish these two cells.

TABLE I: Cells characteristics

Characteristics	**Value**
Technology	NMC/Graphite
Format	pouch
Nominal capacity	26 Ah
Nominal energy	95 Wh
Specific energy	249 Wh/kg
Volume energy density	573 Wh/m^3
Maximal voltage	4.2 V
Minimal voltage	2.7 V
Nominal charge rate	1 C
Nominal discharge rate	2 C
Lifetime *(30 % capacity loss)*	3000 cycles *(1C charge, 1C discharge 90 % DOD at 25 °C)*

C. Cell characterisation protocol

Every month, these cells are submitted to a characterisation procedure to track the evolution of the cell capacity, the internal resistance and its open-circuit voltage characteristics (OCV). This characterisation phase is called RPT (*Reference Performance Test*).

Based on the RPT presented in the literature [11], a characterisation protocol has been defined. This procedure is performed monthly, and allows the properties of the cells to be assessed at the reference temperature of 25 °C. The RPT consists in a capacity test, an internal resistance test and an OCV test. For the capacity test, the cells are discharged three times at C/5 and the last discharge defines the capacity value. For the internal resistance test, the HPPC (*Hybrid Power Pulse Characterisation*) protocol is performed. These pulses are performed at several SOC levels which are reached by discharging the cell: 80 %, 50 %, and 20 %. The pulse series consists in discharge peaks of 10 s at C/2, C, 3C/2 and 2C and charge peaks of 20 s at C/4, C/2, 3C/4 and 1C. These charge and discharge pulses alternate with 30 s of rest between a discharge and a charge, and then 10 min between a charge and a discharge, as proposed in [12].

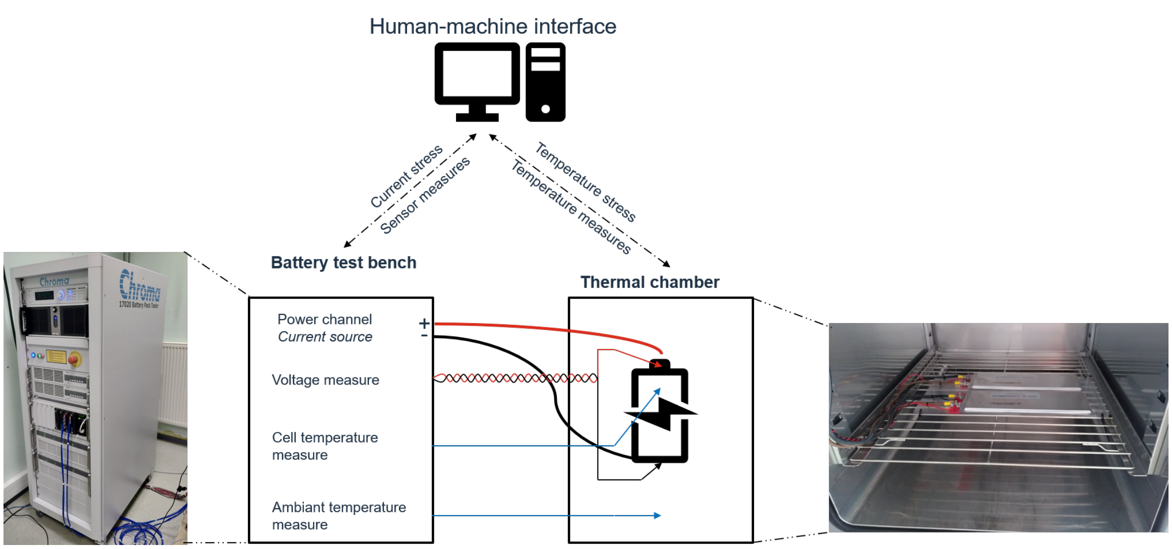

Fig. 1: Experimental design

D. Missions characteristics

Two duty cycles from a real railway project were considered, to determine the current stress to be applied to the cells. The first mission, called mission A, is characterised by an altitude elevation of 400 m over the first 1800 seconds. The power requirement is thus high for both sources. In addition, the train only serves two intermediate stations on this mission. Braking is therefore not frequent, which limits the charging phases of the battery. The energy requirement on this mission is thus very high, which leads to a deep discharge of the battery.

On the second mission, called mission B, the train serves twelve intermediate stations. This leads to frequent acceleration and braking phases. The power requirements of the battery during acceleration phases are almost balanced by the power recovered during braking phases. The battery is therefore subject to numerous charge-discharge cycles of limited depth of discharge. The train speed profiles, altitude variations and train traction power on missions A and B are illustrated in figure 2.

The train route on missions A and B have been then simulated, which allows the sources characteristics to be determined. On this same figure, the power profiles supplied by the battery and the fuel cell are also represented. These profiles were determined from the energy model of the train, using information from the cell suppliers.

E. Current profiles

From the simulations performed, it is possible to determine the current profiles to be applied to cell 1 and cell 2. These profiles are introduced in figure 3. On this figure, several indicators are plotted: the values of the average current, the RMS current and the charge and discharge average currents. It is interesting to note that the values of the mean and RMS currents are close for both missions, slightly higher for mission A, while the current profiles are very different. Indeed, the distribution of these high charge and discharge rates within the cycles differs greatly. On mission B, the main DOD is therefore much lower and reaches 39.6 % compared to 75 % for mission A. At the end of each cycle, the cells are charged at C to the initial SOC of 85 %. Once reached, a 30 min relaxation time is imposed and then the next cycle can begin. Considering the mission phase and the following charging phase, the profile applied on mission A exchanges 31 % more charges.

III. Results and discussion

The two lithium-ion cells were stressed according to the current profiles associated with missions A and B. These tests lasted only two months, as cell 1 was no longer able to

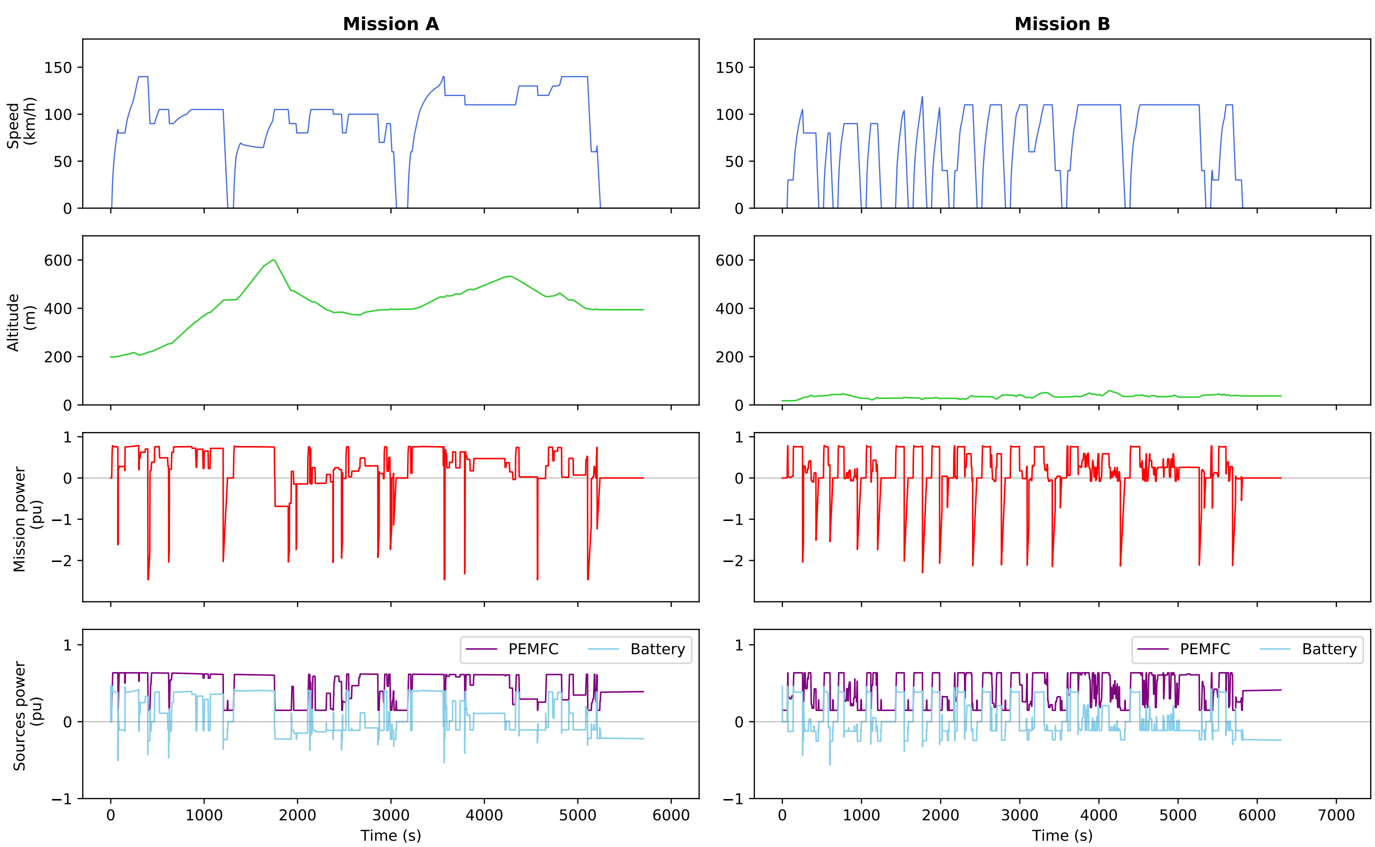

Fig. 2: Missions A and B characteristics. From top to bottom : speed, altitude, normalized mission power, sources power profile

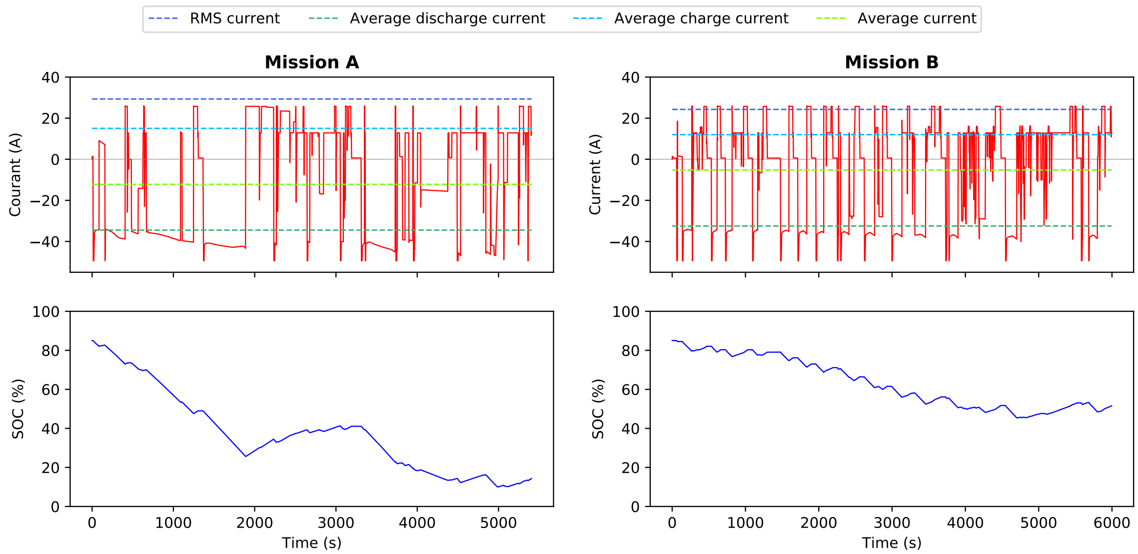

Fig. 3: At the top : Current profiles applied to cells 1 (mission A) and 2 (mission B). At the bottom : SOC estimation

meet the requirement of the profile associated with mission A. The monthly RPT tracked the evolution of the three battery characteristics: internal resistance, capacity and OCV.

A. *Evolution of cells capacity*

Figure 4 introduces the cells capacity evolution according to the charges exchanged during the tests.

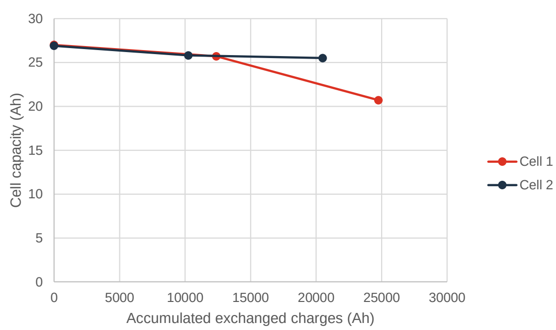

Fig. 4: Measurement of both cells capacity

The capacity measured at the beginning of the tests was almost identical for both cells: 27 Ah for cell 1 and 26,9 Ah for cell 2. After one month of tests, a capacity loss of 4.8 % was measured for cell 1 and 4 % for cell 2. However, at the end of the second month of tests, it can be observed that the ageing process has been greatly accelerated on cell 1. Indeed, it lost 23 % of its capacity, while a loss of only 5.2 % have been measured on cell 2.

B. *Evolution of the internal resistance*

The internal resistance value was measured monthly at different current rates, SOC levels, in charge and discharge. The current pulses cause a rapid variation in cell voltage, which evolves over the 10 seconds of the pulses. Figure 5 introduces the evolution of the resistance measured in discharge, at 2C and 0.1 s, and the resistance measured in load at 1C and 10 s.

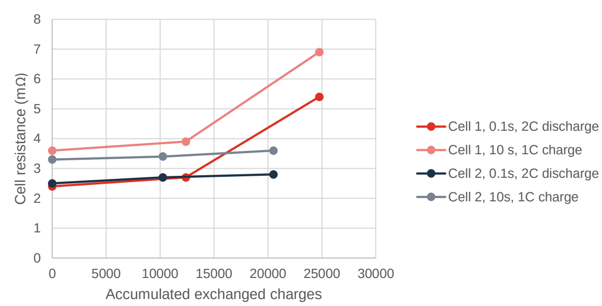

Fig. 5: Evolution of the internal resistance of cell 1 and 2, at two different conditions

These two conditions are chosen arbitrarily, the conclusions are similar for the other resistances. These values lead to several remarks:

- The internal resistance of cell 1 has significantly increased between the initial characterisations and the second month. Its value has increased by 75 %. Over the same period, the internal resistance of cell 2 has increased by 10 %.
- The gap between the first and second months was particularly wide for cell 1.
- For cell 2, the evolution of the internal resistance is constant over the two months.

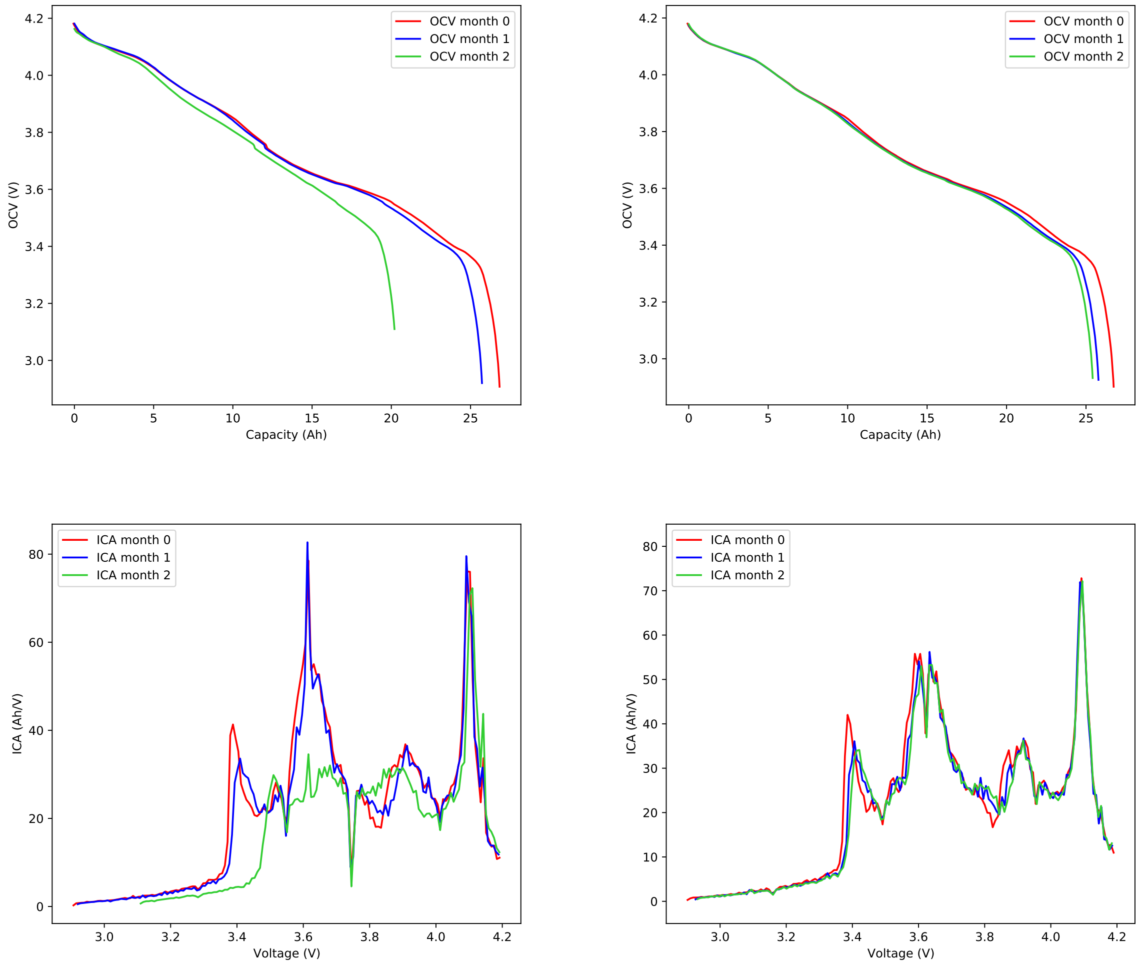

Fig. 6: Evolution of the OCV at the top, and ICA at the bottom of cells 1, left, and 2, right

C. Evolution of OCV characteristics

To determine the quasi-OCV, a conventional method is to perform a charge-discharge cycle at a very low current and to average the two characteristics. This method minimises the error related to the voltage losses. Figure 6 presents the OCV obtained for cells 1 and 2 during the periodic RPT. For cell 2, it can be observed that the OCV was hardly affected. The difference is observed at low voltages, below 3.4 V. For cell 1, it can be noted that the month 1 characteristic is very close to the initial one. However, the OCV has been much more impacted during the second month. On the curves for cell 1, a slight voltage jump can be identified around 3.75 V. After investigation, it was concluded that the test bench was the cause of this sudden variation. These curves also provide the capacity loss, at C/25. This value corresponds to the gap between the maximum capacity reached by the monthly characteristic and the initial one.

D. Discussion

The evolution of the capacity, the internal resistance and the OCV revealed more accelerated degradations on cell 1 than on cell 2. These degradations cannot be justified by the average current values or by the amount of exchanged charges. Indeed, these values are quite close between the two profiles.

In addition, the OCV characteristics can be rich in information about the ageing mechanisms that have taken place within the cells. The incremental capacity analysis (ICA) method is particularly suitable [13]. This method analyses the voltage variations to make conclusions on the chemical reactions that occurred and that led to the ageing of the cell. Figure 6 shows the evolution of the ICA over the two months of testing.

Several observations can be made on cell 1:

- The first peak at 3.4 V has shifted to the right especially in the last month. This peak is mainly influenced by the reactions occurring at the anode [14]. The observed shift shows the increase of the internal resistance of the cell.

- The area under this same peak decreased from the first month. This indicates that the degradations took place rapidly at the anode, limiting ions insertion during deep discharges.
- During the second month, the peak at 3.6 V has almost disappeared. Several studies have shown that the reduction of the area under this peak is proportional to the loss of active lithium ions from the cell [15], [16].

Finally, a post-mortem analysis of these cells has been realised. Figure 7 shows a scan of the two anodes, taken during this analysis. This investigation revealed the presence of lithium plating on cell 1: lithium ions are reduced in metallic lithium on the electrodes. In the literature, this phenomenon is generally related to extreme SOC cycling and to high current charges [17]. It is therefore likely that the low SOC cycling has considerably accelerated the degradations on cell 1.

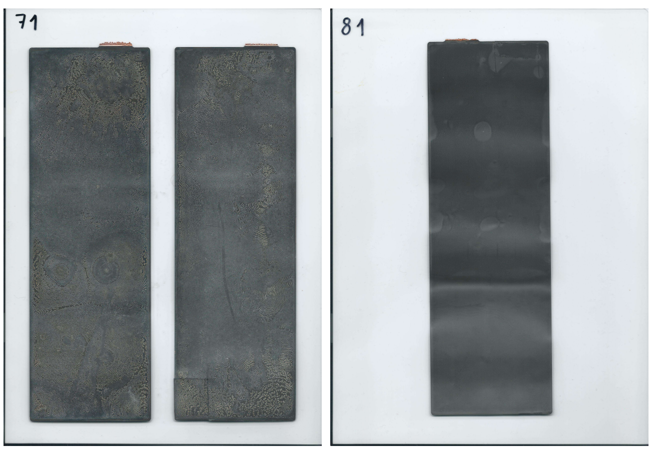

Fig. 7: Scan of the anodes of cell 1 (left) and cell 2 (right)

IV. Conclusion

In this study, experimental tests were conducted to study the ageing of two identical lithium-ion cells. These cells were stressed according to two different current profiles, from real hydrogen hybrid train duty cycles. The current profile applied to cell 1 results in a deep discharge leading to a rise in temperature. On cell 2, the profile is much more dynamic. Charging phases alternate with discharging phases with much shorter durations. The characteristics from the RPT, in terms of capacity, internal resistance and OCV were compared. It has been observed that cell 1 shows considerable ageing as early as the second month of testing. The ICA study has shown a reduction in the amount of lithium that can be intercalated in the electrodes. The post-mortem analysis attributed this reduction to the lithium-plating phenomenon, which probably results from the low SOC cycling and to the charge up to the initial SOC. It would thus be interesting to perform additional tests by reducing the depth of discharge.

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