PHEV battery ageing study using voltage recovery and internal resistance from On-board data

Lluc Canals Casals, *UPC,* Adrían Schiffer González, *UPC,* Dr. Beatriz Amante García, *UPC* and Prof. Dr. Jordi Llorca, *UPC*

***Abstract*—It is well known that batteries do not perform equally the first day of use than some years later. Their properties are in constant degradation, their capacity fades and the maximum power reduces. Batteries ageing has been widely studied under laboratory controlled conditions for different types of cells. In real life, however, every person has its own driving profile, which is almost unique and unpredictable, making the State of Health during real life cycles highly difficult to accurately estimate. This study presents a methodology for ageing estimation based on data extracted from on-board data-loggers installed in an electric vehicle. When a driver turns off the vehicle, the battery voltage slowly increases until it finally reaches the Open Circuit Voltage (OCV). It has been observed that the recovery voltage transition depends on the temperature and ageing, providing new elements to verify the battery State of Health.**

***Keywords*—Ageing, Battery, EV, PHEV, Lithium Ion, On-Board, SOH.**

I. INTRODUCTION

SImilar to mobile phones and laptops, the Lithium-ion batteries of electric vehicles (EV) and plug-in hybrid electric vehicles (PHEV), lose capacity and power along time and usage [1]. In small devices this is not so problematic, because battery replacement is affordable, devices can still work connected to the power plug and, normally, technology evolution is so fast that most people replace the whole device when the battery depletes [2]. On the contrary EV batteries cost thousands of dollars, thus replacement is not foreseen [3]. A battery for traction services is considered inappropriate when it has lost about 20% of its unaltered capacity. This capacity loss has been studied in many laboratories for different types of cells and under different controlled conditions [4]. Repeating specific tests after a number of cycles or months makes parameters tendency relatively simple to identify and, consequently, estimate the State of Health (SOH) [5], [6]. Unfortunately, conditions in a vehicle are not so repetitive and controlled. Not only the way the vehicle is driven or the temperature influence on the SOH, but also in which state the car is getting charged, if it stays parked for long periods of time or where does most of the driving take place (city, landscape, highway). Each of these aspects affect the battery in different ways and may lead to non-desired chemical reactions [7]. Thus, it is very difficult to find a common situation that provides robust and reliable parameters to estimate the SOH. It is important to know the battery SOH in order to calculate, for example, the range with a full charged battery or the necessity to replace the battery at the end of its lifetime. Battery life-length is something that car manufacturers are really concerned about, in order to keep the 8 to 10 year battery warranty. For this reason, many researches and engineers are implementing all sorts of algorithms in their Battery Management System (BMS) [8]. These algorithms go from the simple coulomb counting [9] to more complicated methodologies like support vector machine techniques [10] or statistic tools like particle filter [11] amongst others [12]. In this study, we have analyzed the ageing effects during one year of use on a PHEV in Spain. We focused on two battery characteristics: Internal resistance R_i and the switch off voltage recovery $V_{recovery}$. Although using on-board data, the analysis has been done offline, in contrast to Kalman-filter or black-box, which are online techniques. However, the implementation of the presented methodology can be integrated in online systems.

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II. METHODOLOGY

Temperature, voltage, current and energy exchanges are the parameters mostly used to track the battery behavior. Based on these four parameters, this study focuses on two derived variables to delve into the battery ageing analysis using on-board data: R_i and $V_{recovery}$.

A. R_i calculation

Normally to calculate the R_i of lithium batteries in laboratories, the Ohm's law is applied after a specific current flow during 18 seconds [13]. As these specific conditions are impossible to obtain while driving, the ratio between the delta voltage and current after one second was used in eq. 1 [14].

$$R_i = \frac{V}{I} = \frac{\Delta V}{\Delta I} = \frac{V_t - V_{(t-1)}}{I_t - I_{(t-1)}} \tag{1}$$

In order to reduce the errors resulting from small denominator values ($I_t - I_{(t-1)}$), the only R_i values that have been taken into account, come from current drops of at least 20 A: $\Delta I \geq 20$. With this method, hundreds of R_i values were obtained per trip. In fig. 1 (top) the differences between charge and discharge on internal resistance are appreciable after processing these values using a moving average [15]. Bibliography reported that at higher SOC and temperature, cells have higher potential activity, hence, lower internal resistance [16]. Since fig. 1 (top) shows that R_i reduces along the

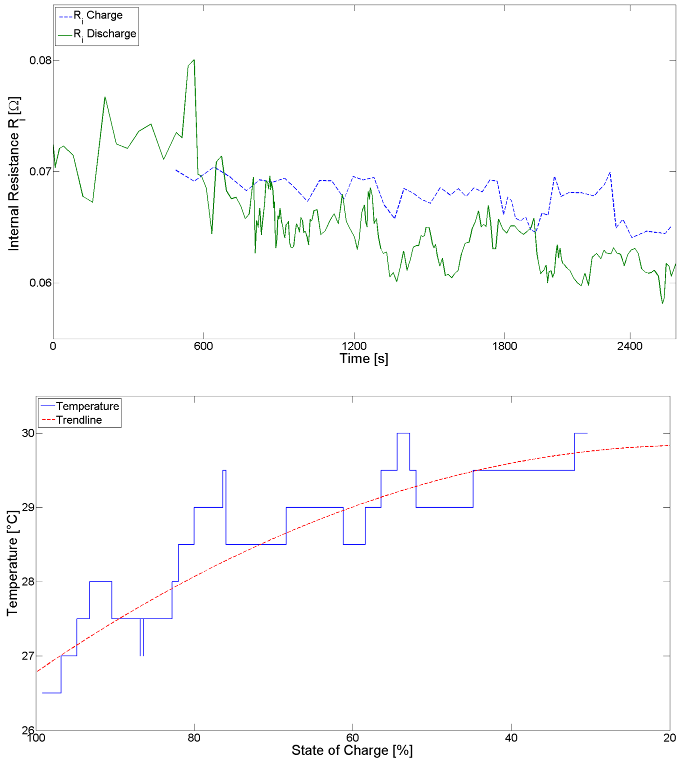


Fig. 1. Top: Evolution of filtered R_i charge and discharge against time during one trip. Bottom: Evolution of the temperature against SOC (the SOC decreases along a trip).

trip and the battery discharge SOC, it means that temperature and SOC should play an important role. The relation between the battery SOC and the temperature (fig. 1, bottom) shows that, effectively, temperature increases during the trip, which means that temperature has a higher influence onto the internal resistance than the SOC. This fact was also observed by Huria et. al. [17] when they defined that the R_i is composed of several resistances: Ohmic, charge-transfer, SEI, etc. and explained that some of them depend more on temperature than SOC.

B. R_i and ageing

To proceed with the EV battery R_i analysis along a year, an average R_i value per trip was used. Then, these R_i values were first correlated with time, observing its particular behaviour as trips were distributed randomly during a year. This same R_i correlation was done against the total capacity exchanged by the battery. As it will be seen in the results, nothing could be extracted from these two comparisons and finally the R_i was related to temperature in order to observe any clear tendency.

C. Voltage recovery

A similar procedure was followed for the study of voltage recovery using EV on-board parameters. Four factors, described by eq. 2, define battery voltage [13]:

$$V_{batt} = V_{equilibrium} + V_{resistance} + V_{reaction} + V_{diffusion} \tag{2}$$

$V_{resistance}$ represents the Ohmic voltage drop visible at the beginning of current flow, being the electrolyte resistance the major contributor. The $V_{reaction}$ is principally caused by electrochemical and chemical reactions at inner surfaces. The $V_{diffusion}$ is caused by a deficit or surplus of reactants. Finally the equilibrium voltage is the measurable battery voltage after a long period without use. As mentioned, the $V_{equilibrium}$ is not reached immediately after disconnection, there is a transition period and a voltage stabilization time, while the effects of reaction and diffusion progressively decrease [18]. From a theoretical point of view, the voltage relaxation could be used as an indirect measure of degree of lithiation in the cathode and anode of a Lithium-ion battery. These state of lithiation, in turn, determine the state of charge of a battery. Therefore, the relaxation trends, over the course of a battery life, keep changing as a consequence of lithiation states in the two electrodes. Additionally, during the battery use, there is a loss of active lithium mostly caused by the Solid Electrolyte Interface (SEI) growth and the side reactions seem to be the major cause during storage periods. [10]. Accordingly, if a battery voltage relaxation is compared under two identical operating conditions, the differences observed should be considered as an indicator of ageing. In fact, this transition period has been widely studied and there are also patents relating it with the ageing [19]. From now on, this effect will be defined as $V_{recovery}$. When analyzing the driving data from the PHEV, the major problem was to find long enough pauses to observe the voltage evolution and having similar operating conditions that would lead to a possible ageing correlation at the same time. In PHEV, this situation was found at the end of long trips, when the battery has been fully discharged. In the specific case of the studied PHEV, after the car was stopped, the battery continued transmitting data during 5 minutes. A $V_{recovery}$ example during these last 5 minutes is shown in fig. 2. It can be observed that it follows a logarithmic curve with different slopes on each measurement, never finishing above 2V.

The $V_{recovery}$ is calculated by subtracting the instantaneous positive voltage step V_{stop} at the current-cut and the battery voltage V_{5min} after 5 minutes from it:

$$V_{recovery} = V_{5min} - V_{stop} \tag{3}$$

The $V_{recovery}$ evolution has fast, medium and long time memory relations with current, SOC and voltage conditions previous to this transitory state. In this study, it is assumed that the $V_{recovery}$ starting conditions are similar. The V_{stop} and SOC are almost the same in all cases, due to the fact that the battery was discharged. Additionally the current flows before switch off are also similar in all cases. In fact, whenever a driver finishes a trip the car demands low current intensities during 15 to 100 seconds prior to the complete stop of the car. We observed that these currents were around 2 and 4 A.

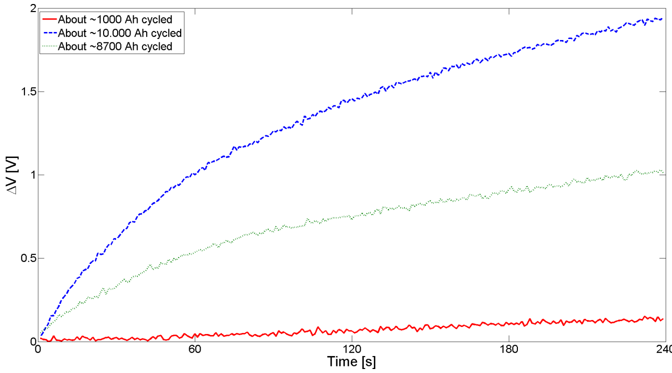


Fig. 2. $V_{recovery}$ during 5 minutes after the EV stops for different trips. $V_{recovery}$ behaves different at different ageing states during its life-time.

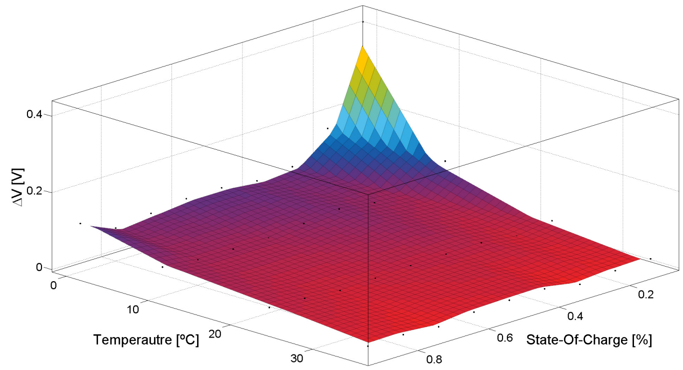


Fig. 3. $V_{recovery}$ of a single cell 5 minutes after the discharge pulse at different temperatures and SOC points applying a pulse test at different SOCs in a climate chamber.

Therefore, we assumed that the fast and part of the medium memory dependency were alike for all trips. As it happened with R_i, the $V_{recovery}$ strongly depends on temperature. In fact, temperature is another factor to be taken into account when searching for the similar conditions needed to evaluate the $V_{recovery}$. In order to determine the exact temperature effect on $V_{recovery}$, pulse tests at different temperatures and SOC using a single cell were executed under laboratory conditions. In our laboratory, the precise and fast measurement devices needed for this accurate test have a limited working voltage range from 0 to 18V. Therefore, we could not put the whole battery (280 – 370V) under test to evaluate the temperature effects. However, the results from the PHEV battery capacity test, done at the beginning and at the end of the project, showed that the different cells inside the battery had a similar SOH (with a difference lower than a 2% SOH. Additionally it has been checked that the cells response is similar by taking a look to the voltage evolution during the relaxation periods. These two facts allowed us to conclude that the study of a single cell to extract the temperature effect on the $V_{recovery}$ was robust enough. The tested cell is the same as the ones mounted in the PHEV battery, which are prismatic NMC cells with a nominal capacity of 40Ah. The $V_{recovery}$ response is presented on fig. 3 for temperatures of -18, 0, 10, 25 and 35°C and in steps of 10% SOC.

There are two details to highlight from these responses:

- The first one is that cold temperatures cause higher $V_{recovery}$, thus, lower responses and slower voltage stabilization.
- The second one is the fact that around 70% SOC and 30% SOC, the $V_{recovery}$ is lower (either way, the voltage stabilization is faster), while in the edges, at 10 and 90% SOC, we find the worst responses. These results are directly related to the li-ion cell characteristic dSOC/dOCV peaks [20].

The usual lower discharge capacity limit for PHEV batteries is around 25%-30% SOC [21]. That is nearby the point where we took the voltage recovery data from the electric vehicle. Therefore, this is the SOC in which the cell thermal analysis was done. The equation related to the $V_{recovery}$ and the temperature is presented in part III.

D. Voltage recovery and ageing

To start with the analysis of the relations between the $V_{recovery}$ and ageing, the first thing to do was to calculate the $V_{recovery}$ for each trip by eq. 3. This showed a dispersed cloud of points that should be arranged. As it has been already mentioned in section C, it is necessary to have similar conditions to evaluate the ageing effects through $V_{recovery}$. Two methods were used to find these similar conditions: The first one was grouping the $V_{recovery}$ values from trips ending at similar temperatures. This showed a clear picture of the responses, but without much data per temperature range. The second method was the subtraction of the temperature correction using the equation found with the single cell characterization multiplied by the number of cells from the PHEV battery:

$$V_{recovery(corrected)} = V_{recovery} - n_{cell} \cdot V_{recovery(T)} \quad (4)$$

Where $V_{recovery}$ is the value obtained directly for each trip, n_{cell} is the number of cells in the battery, (84 in this case) and $V_{recovery}(T)$ is the voltage recovery correction factor at the temperature when the car stopped. This process allowed the evaluation of the impact of normal use on ageing and a possible way to implement new data to the algorithms that evaluate the SOH with on-board data.

III. Results

A. Internal resistance study

Literature reports that R_i increases with cell and battery ageing [22]. To analyze if this parameter is useful for SOH determination with on-board data, a first comparison was done relating the R_i average per trip and the SOH of the battery. Instead of observing an ascending slope as the SOH decreased, it could be observed that this relation goes up and down independently; therefore, it showed that there was something more relevant than ageing forcing this behavior (fig. 4, top).

Knowing that temperature is a key factor for internal resistance calculation, we took special attention on battery temperature and climate conditions over the year. Thus it was observed that the internal resistance values increased during winter and

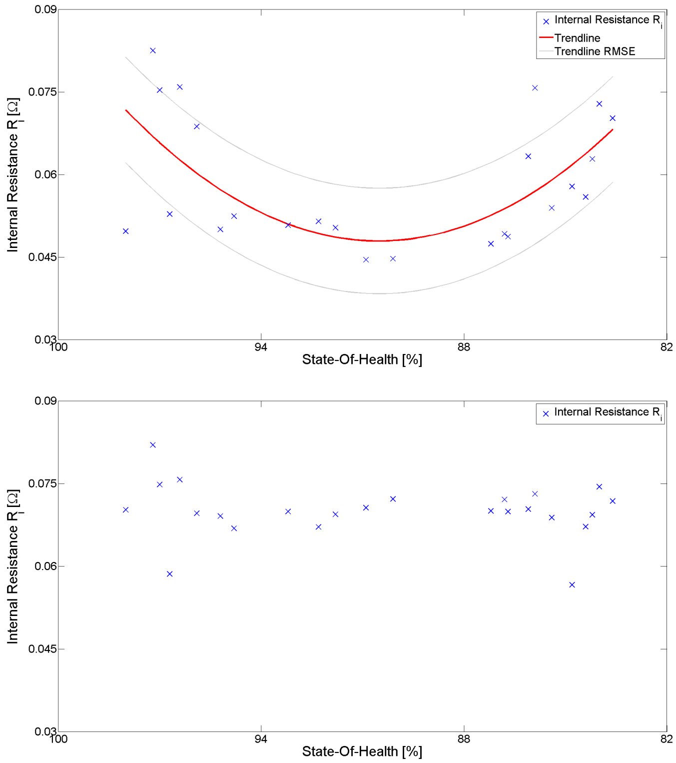


Fig. 4. Top: Average R_i evolution against State-of-Health; Bottom: Average R_i evolution after temperature correction against SOH.

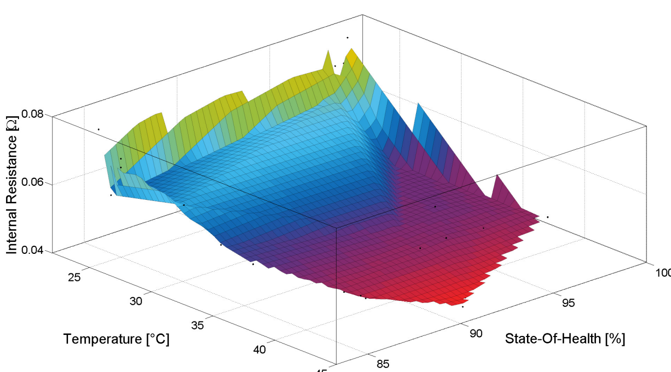


Fig. 5. Temperature and State-of-Health against average internal resistance.

got much lower on summer. As it can be seen in figure 4, the internal resistance apparently has no correlation to the SOH. It was observed that the ambient temperature changed along time, being lower at the beginning and end of the tests and higher in the middle. To evaluate the Arrhenius-like temperature effect on R_i, in figure 4-bottom, the temperature effect has been removed. As it can be seen the internal resistance stays almost constant against SOH until the end of life in the vehicle. The 3D representation of both temperature and SOH (fig. 5) shows the effect of temperature as a major cause of battery R_i change, but it does not bring much information about ageing tendency on R_i.

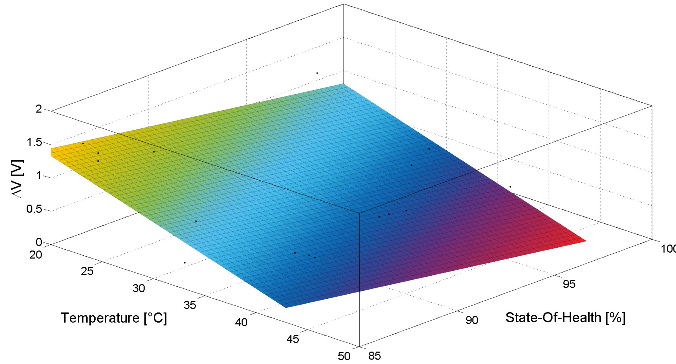


Fig. 6. Linear tendency of temperature and SOH over voltage recovery.

B. Voltage recovery

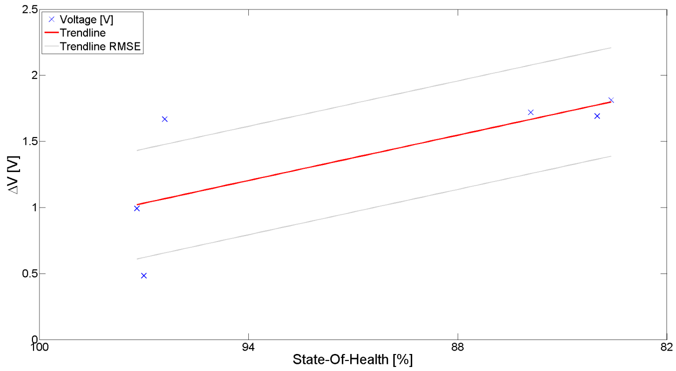
This second part of the article focuses on the $V_{recovery}$ during the last 5 minutes of the trips.

Like with the R_i, the first step we did was to find visible relations between the $V_{recovery}$, the temperature and the SOH with the data obtained from the vehicle. In fig.6 its relation is presented in a 3D overview that demonstrates a weak but existent interaction between them.

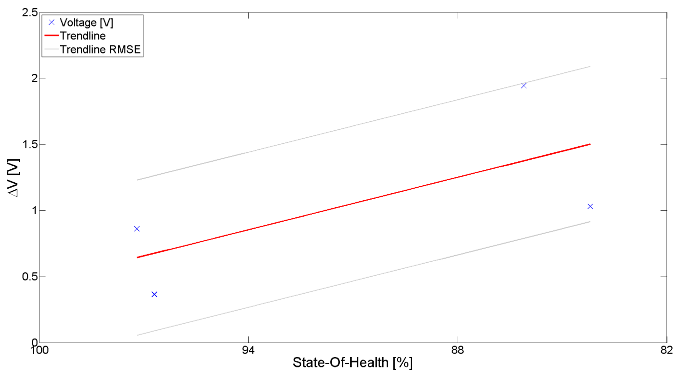
An effective way to isolate the temperature effects on ageing was achieved by grouping the $V_{recovery}$ values in 3 group of temperatures: 25, 30 and 40 ± 2ºC. The results are shown in fig. 7, where the ageing effect is observable by the positive slope of the tendency curve. The temperature effect is also appreciable by the lower $V_{recovery}$ values at higher temperatures. It is also visible that at higher temperatures the dispersion is also lower and the correlation is stronger. The few datapoints available for these specific temperature ranges and the dispersion derived from the one second data acquisition in the vehicle originate a severe variability at lower temperatures. However, the tendencies are noticeable.

The same relation is visible in the battery $V_{recovery}$ evolution during the 5 minutes when the car is harvesting data from the battery before completely switching off. The lighter-colored curves in fig. 8-top, which are the ones with lower State-of-Health, demonstrate the above mentioned tendency and have higher voltage values than the ones that made less charge and discharge cycles. In order to offer a useful algorithm for SOH calculation using $V_{recovery}$ with on-board data, it was needed to go deeper into the temperature analysis. It started with the laboratory tests using a new single battery cell. After the characterization of the $V_{recovery}$ at different temperatures and SOC states presented in the methodology, the study was centered at the 30% SOC. This is the SOC where the $V_{recovery}$ is calculated using on-board data.

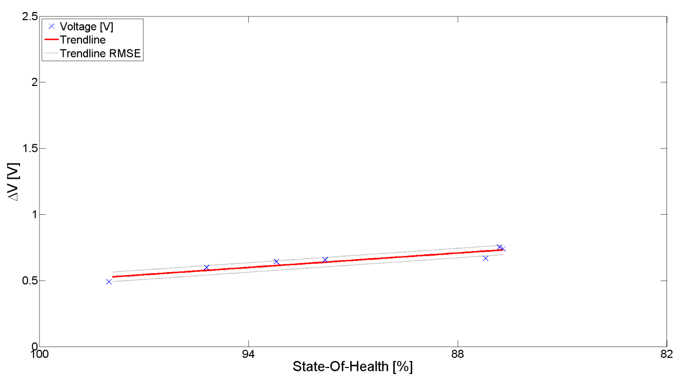
The laboratory equipment offers higher resolution and shorter time steps (in the PHEV the data was saved every second). This fact allowed a more accurate observation of the $V_{recovery}$ evolution during the first seconds and minutes after cell disconnection. The $V_{recovery}$ evolution observable in fig. 8-middle confirms that at lower temperatures we obtain higher transition times to achieve the voltage stabilization, which



(a) 25 °C



(b) 30 °C



(c) 40 °C

Fig. 7. Voltage recovery against State-of-Health with linear interpolated trend line for determined temperatures at 25, 30 and 40 °C.

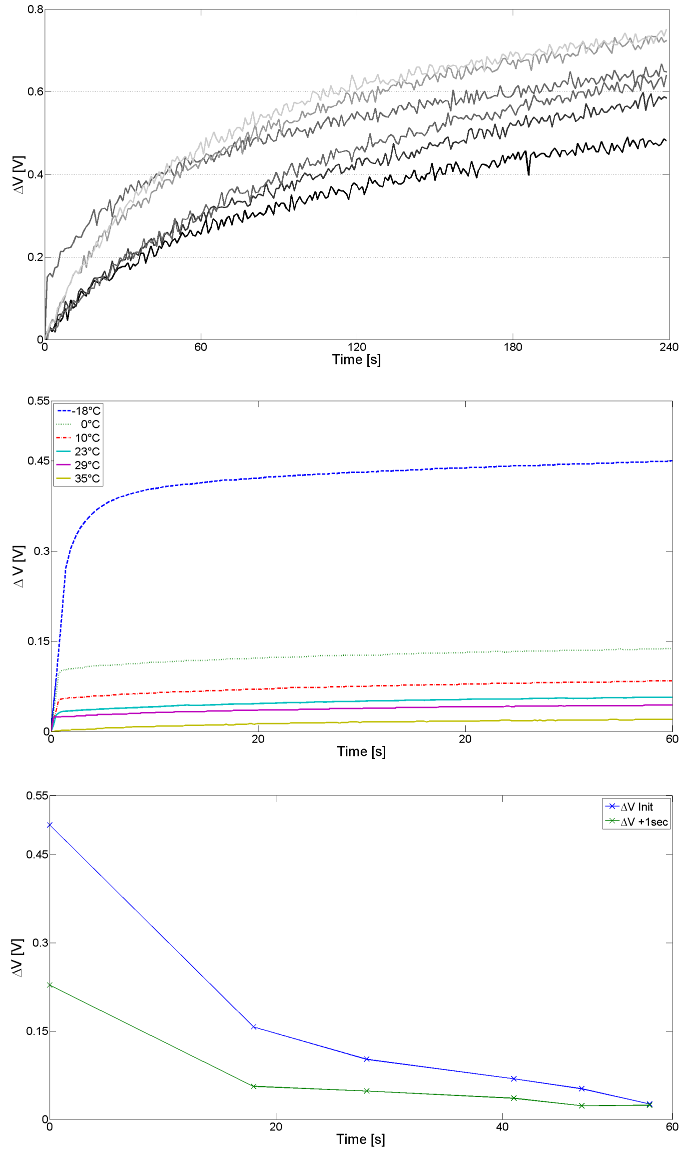


Fig. 8. Top: $V_{recovery}$ evolution for 7 trips during the first 5 minutes after the car stops ending at 40°C and different States-of-Health. The lighter the color of the lines, the more energy was conducted though the cells. Middle: Voltage recovery behavior at different temperatures, showing the bigger variances during the first seconds. Bottom: 30 % SOC $V_{recovery}$ comparison starting one second after current cut.

means higher internal resistance and capacitance. Additionally, it can be noticed that it was during the first two seconds after cell disconnection, when there are the higher voltage differences. This means that, if the voltage recovery starts counting 1 or 2 seconds after the current cut, the differences encountered in the final value might differ up to a 50%, as it is shown in fig. 8-bottom. Hence, the growing variability of the $V_{recovery}$ values obtained at lower temperatures with on-board data can be explained by the fact that the data harvesting in the car is done every second. In any case, from fig. 8-middle, it was observed that the $V_{recovery}$ against temperature follows an exponential behaviour described by eq. 5.

$$V_{recovery}(T) = a \cdot e^{b \cdot T} \tag{5}$$

Where a = 147.95 and b = -0.0286 at 30% SOC for the analyzed cell. When exporting this analysis to other SOC or cell type, the parameters should be recalculated.

The eq.4 is used to eliminate the temperature effect on the $V_{recovery}$ calculation with the PHEV on-board data. The resulting $V_{recovery}$ values are denominated in this study as

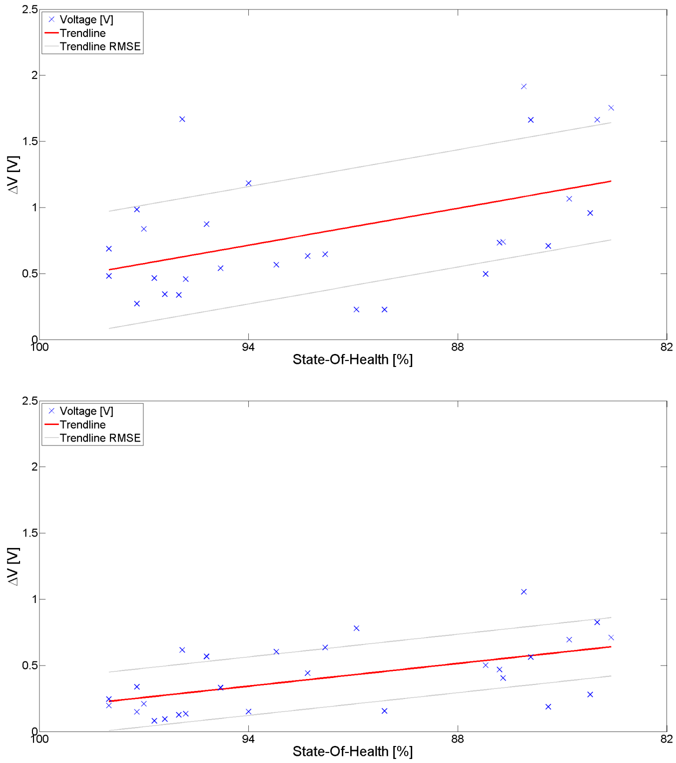


Fig. 9. Top: Bare $V_{recovery}$ values before temperature correction with on-board data. Bottom: Temperature corrected voltage recovery values using on-board data.

temperature corrected recovery voltage. The temperature corrected recovery voltage is presented in fig.9-bottom, where, effectively, the dispersion is reduced compared to the bare $V_{recovery}$ values from fig.9-top. Moreover, it can be appreciated a light but linear increasing tendency that confirms the applicability of this tool for ageing monitoring. Therefore, enclosing the temperature correction, the $V_{recovery}$ strategy can be included in SOH algorithms by integrating eq. 6 from the trendline in figure 9-bottom.

$$V_{recovery} = -0.28581 \cdot SOH + 3.0307 \tag{6}$$

It should be taken into account that EV batteries are expected to last 8 years or more, which means that even if the results of one year seem to provide some evidences of ageing, it should be confirmed with the acquisition of real driving data during a longer period of time. An additional way to improve the results would be the introduction of shorter time intervals for on-board data harvesting, as it has been proved that most of the variability of the obtained results come from the first second after the current-cut. Finally, one last option to offer more robust results could be achieved by giving more weight to the values obtained at higher temperatures (which offer more correlated results) and less weight to the values at lower temperature.

IV. Conclusion

Although under laboratory conditions the internal resistance is an ageing monitoring parameter, the difficulties to obtain robust and accurate values from on-board data calculations, makes it not so interesting to follow in real-life EV algorithms. In fact, when the battery reached the 82% SOH, the internal resistance was mostly affected by temperature changes rather than by ageing. On the contrary, at the end of the trips, the recovery voltage is foreseen as a key parameter for SOH assessments. Anyhow, if the recovery voltage wants to be implemented in SOH algorithms, it should always consider, at least, temperature corrections in order to calculate the useful life prognosis of batteries. Even though the results are encouraging, more data is needed to confirm and validate this preliminary approach. Indeed many alternatives to provide better results have been already proposed.

In this work it has been shown that it is possible to estimate the SOH of the vehicle battery systems with rough on-board data. To implement precise and detailed SOH algorithms using the $V_{recovery}$ methodology, multiple cell tests under laboratory accelerated ageing conditions should be launched or more data from monitored cars has to be available.

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Jordi Llorca graduated and earned his PhD in Chemistry at the University of Barcelona, where he was later appointed Associate Professor and Ramón y Cajal Fellow. In 2005 he joined the Technical University of Catalonia (UPC) as Full Professor. He has received several awards including the Distinction of Generalitat de Catalunya to the promotion of the University Research in 2003, the Humbert Torres Prize in 2003 and the ICREA Academia Award in 2009. From 2011 to 2014 he has been the Director of the Institute of Energy Technologies at UPC. He has written over 10 books, authored 7 patents and has published over 200 scholarly articles.