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Impact of periodic current pulses on Li-ion battery performance

François Savoye, Pascal Venet, Michael Millet, Jens Groot

Abstract-- Pulse charging and pulse discharging have been reported by many authors in the literature to improve the performance of various secondary electrochemical cells. Only a few authors mentioned the effects of such charge and discharge method on Lithium-ion batteries. The overall objective of this work is to experimentally investigate the impact of certain current pulse profiles on the electrical performance of Li-ion batteries. The results highlight a detrimental impact of periodic pulses on the cell performance compared to profiles with constant current.

Index Terms-- Concentration gradients - Current pulses - Energy Storage System- Electrical performance- Lithium-ion batteries

I. NOMENCLATURE

Lithium-ion battery (Li-ion) is considered to be one of the most promising battery chemistry for numerous applications. Especially in the field of transportation, where high power and energy density are needed for electric vehicles (EV) and hybrid electric vehicles (HEV). Hence, significant scientific efforts have been made to overcome the disadvantages linked to the relative lack of maturity of this battery chemistry. This work, which deals with an experimental investigation of the impact of specific load profiles on battery performance is a part of this context. The objective is to increase Li-ion batteries performance in its widest sense by a better understanding of their internal mechanisms. In particular, this work aims to experimentally investigate the effect of particular discharge or charge profiles on the electrical behaviour of Li-ion batteries.

II. BACKGROUND ON LI-ION BATTERIES

A Li-ion cell is constituted from the association of two

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electrodes. When a discharge current flows through the cell the negative active material is oxidized. Thus electrons are extracted from it and Li^+ ions are released into the electrolyte where they slowly diffuse. On the other side of the cell, electrons are supplied to the positive active material where the Li^+ ions are reduced and intercalated into the host insertion sites. The charging and discharging of a Li-ion battery thus involves material transportation since chemical species are released from active material in one electrode and accumulated in the other. Several mechanisms are known to be a part of the process: diffusion, which is inherent to the existence of concentration gradients, migration which is linked to potential gradients, and convection which appears in case of temperature and/or density gradients. The transportation mechanisms are clearly identified to be the kinetically limiting processes for Li-ion batteries, especially at high charge or discharge rates. In addition, the transport mechanisms involving ionic species not only appear when the battery is in use. Indeed, a charge or discharge current affects the internal state of the battery, and it may take several hours for the battery to reach its equilibrium, depending on the electrical stress level. This process, called relaxation [1], impacts the electrical behaviour of the cell, especially the difference between terminal voltage and rest (equilibrium) potential called overpotential. Thus, we can identify three types of overpotential:

- The activation or kinetic overpotential is linked to the thermodynamic irreversibility of some chemical processes
- The concentration overpotential is linked to the transient non-homogeneity in the spatial repartition of the electroactive species.
- The ohmic overpotential is linked to the finite conductivity of the non-electroactive cell constituents.

The potential interest for pulse charge/discharge current strategies on batteries with porous electrodes, and in particular, Li-ion batteries, is related to overpotential and is the main topic for the work presented in this paper.

III. BACKGROUND ON PULSE CHARGE/DISCHARGE OF BATTERIES

A. Pulse charge/discharge principle

The concept of pulse charging is based on successive changes in current rate and/or direction rather than using a constant charging current. Basically, the current can either be interrupted, introducing a shorter rest period, or replaced by a

short discharge pulse. Here, short rest periods may increase the speed of relaxation, and short current inversions may enable both accelerated relaxation and reverse the electrochemical processes direction within the battery. The notation “pulse profile” generally refers to a periodic current/power pattern consisting of a repetition of a reference profile constituted of at least two steps.

Application of such current patterns can have miscellaneous effects on a battery cell. Firstly, pulsating current has been known in the field of electrochemistry to have widely varying effects at the electrode-electrolyte interface. In electrodeposition, U. Landau [2] demonstrated the effect of periodic current inversions in the control of the deposit thickness and uniformity. Literature also suggests that pulsed current or voltage can affect the transport mechanisms of secondary batteries. The use of « depolarizing » pulses can enable a reduction of concentration gradients [3][4], thus enabling a considerable enhancement of the battery charge/discharge performance [5][6]. Chiasserini and Roa [7] claimed that the use of a pulse discharge profile with carefully selected amplitudes and rest periods can increase both specific energy and specific power of the cell. Furthermore, other studies [8][9] indicated that pulsing the potential of the electrode enables a control of the thickness of the equivalent diffusion layer and hence limit the concentration overpotentials. Pulse charge/discharge can thus be considered as an interesting candidate for battery performance optimization. Therefore, improving the speed of relaxation seems to be a possible method for performance optimization since overpotentials have been identified as a large contributor to cell losses at high current rates. The mechanisms involved in the relaxation, namely the spatial redistribution of electroactive species within time also determines the maximum instantaneous battery power. Physically linked to the immediate availability of electroactive species within the close vicinity of the electrodes, maximum instantaneous battery power is more generally linked both to the battery state i.e. temperature, SoH, SoC, and to its recent past which determines the internal spatial repartition of electroactive species. In fact, high charge/discharge rates tend to first and foremost utilize active material in the superficial regions of the electrodes rather than in the bulk mass. This principle may decrease the observed capacity for all battery chemistries at high discharge rates since, due to high concentration overpotential, the electrode voltage limit can be reached before the active bulk material have been accessed. This principle also explains the strong time dependence of the instantaneous power ability of the batteries. Indeed, at high rates, the easily accessible regions of the electrodes are preferably used in the beginning of the pulse. It involves high power ability due to the immediate availability of reactants. When the process proceeds longer, all the easily accessible reactants are consumed and the system has to use less accessible regions of the electrodes for the reaction. This weak accessibility engenders high concentration gradients which lead to high concentration overpotential that is the direct cause

for large voltage drops, what inherently limits the cell’s power ability. In this context, Venkat Srinivasan and John Newmann [10] showed the existence of “path dependence” for a specific Li-ion chemistry, that could be extended to other chemistries also limited by transportation mechanisms. They concluded that the discharge performance was better if the discharge followed after a charge path, and vice versa. In this case, concept of pulse profile seems promising because it inherently involves regular inversion of the current direction. In other words, during a discharge process, the insertion of a charge pulse enables the cell to offer good discharge performance as it comes from a charging process. Reciprocally during a charging process, the application of a discharge pulse increases the future charge performance of the cell since it will come from a discharge process. This reasoning can also be extended to rest pulses which also constitute periods enabling relaxation.

However, pulse profiles still inherently hold paradoxes. In fact, we can find in the literature ageing models of batteries based on counting of cumulative effects of individual electrical stress occurrences [11][12]. These investigations indicate that comparing a constant current charge/discharge profile and the associated pulse profile on the basis of an identical mean current will not lead to identical root-mean-square (RMS) values for the two profiles. Obviously, the RMS value associated to the pulse profile will be higher. This principle is against the principle of minimizing the energy throughput that has been implemented in many control strategies for hybrid ESS (Energy Storage System) involving batteries and supercapacitors [13][15]. Furthermore, the increase in RMS current might yield increased heating in the cell. The temperature being identified as a first order parameter regarding battery ageing, it seems in first approach very difficult to achieve longer lifetime with increased cell temperature. In addition, other works showed that pulse discharge was detrimental to battery performance mainly due to the fact that the peak currents cause transients on the cell’s voltage that may be interpreted by the voltage cut-off circuit as an end-of-charge/discharge voltage [16]. This would stop prematurely the charge/discharge and hence decrease the apparent available energy.

B. Background of pulse charge/discharge in the field of Lead-Acid batteries

Application of pulse currents has been thoroughly investigated for Lead-acid batteries. Since charge ability is very poor compared to the discharge ability for this chemistry, the research efforts have been focused on the effects of pulse charge, without considering the potential benefits on discharge. Many authors linked several effects of pulse current strategies to the double-layer capacity’s contribution in the charging process [17] [20]. These studies aimed to understand the effects of “depolarizing” pulses on Lead-acid batteries for frequencies between 25mHz and 50Hz. Pulse charge strategy was also shown to bring benefits mainly at the end of charge. In other words, and more generally, the effect of pulse charge was identified to be widely varying with SoC.

Doering and Svaboda [21], who also studied pulse charge as a method for reducing the charge time of Lead-acid cells, concluded that at equal mean current, pulse charge leads to higher losses and do not enable to reduce charge time since no effect on diffusion processes were highlighted. These results were opposed to those of Sung Chul kim and al., who showed by mathematical modelling of Lead-acid cells that those pulses effectively reduce concentration gradients within the electrolyte [4] and thus affect the transportation mechanisms. Lam and al. [22] also found that pulse current charge delays the occurrence of the crystallization process of the active material and thus contributes to the enhanced cycle life of Pb-Sn and Pb-Sn-Ca secondary batteries under rapid charging utilization. As a conclusion, pulse profiles have been studied through various approaches and all authors agreed on the fact that pulse profiles had an impact on Lead acid batteries electrochemical processes; i.e. Lead-acid batteries do not behave like basic non-linear resistive loads regarding pulse profiles.

C. Extension of pulse charge/discharge concept to Li-ion batteries

The literature concerning impact of pulse profiles is more common for Lead-acid cells than for Li-ion. However these strategies have also been studied for Li-ion chemistry, with diverse conclusions. We know today that cell kinetics are mostly limited by insertion mechanisms and by diffusion both in the solid and in the liquid phase, especially at high current rates. Taking into account the occurrence of parasitic reactions, low transportation capability can significantly impact charge and discharge maximum rate. As an example, during charge, the Lithium ions migrate through the electrolyte to be reduced at the anode. Then they diffuse through the graphite to reach the host sites where they are inserted. If the charge strategy involves too high current rates, Lithium reduction imposes kinetics higher than that of the intercalation process. The potential of the anode can hence reach 0V vs. Li/Li⁺, which causes Lithium metal plating at the solid electrolyte interface [23]. The occurrence of this parasitic reaction called Lithium plating, which has been identified as one of the major ageing mechanisms of graphite anode [24], can be limited by increasing the anode charge ability, and thus the ability of the materials to propagate the Li-ions to the insertion sites. According to Jun Li and al. [3], pulse charge is a promising candidate for reduction of concentration polarizations. In this study, they reported both a better utilisation of active material of cells charged with pulse charge and a shorter charging-time. Furthermore, the implemented pulse strategy resulted in an increased cell lifetime. Micrographs of electrode surfaces showed that the pulse charge had reduced the effects of two major ageing mechanisms, namely the SEI (Solid Electrolyte Interface) build-up and the surface cracking. Additional XRD (X-ray diffraction) analysis also showed that both electrodes of the cells that were cycled with pulse charge had kept a better structural integrity. Other research investigated how pulse charge and/or discharge could be implemented in practical

applications such as telecommunication devices [7]. Puroshothaman and al. proposed in recent publications 1D semi-infinite and restricted diffusion models in order to describe the impact of specific current patterns on the concentration profiles shapes inside the cell [25][26]. These models provide a good view of how electroactive species can migrate and how the concentration perturbation inherent to a specific electric stress can propagate inside the host material. This study concluded that the interfacial concentration of the electrode as a function of time, duty ratio and amplitude of profiles, could be lowered compared to that of a continuous current condition. Basically, they showed that current pulses were strongly affecting the superficial regions of the electrode material, but had only little consequences on the mean concentration profile that was set by the global mean material flux and thus by the mean current. The depth of the region of the electrode affected by the pulses generally depends on the period and on the amplitude of pulses. Purushothaman and al. concluded thus that the use of pulsed current profiles does not bring any potential benefit regarding inherent material transportation limitations in Li-ion batteries.

D. Conclusion

Miscellaneous results can be found in the literature concerning the impact of pulse profiles on accumulators. The answer to this question is made complex by the diversity of battery chemistries, as well as by the diversity of ways to consider this impact, at the material scale or at the cell scale. Some authors claim that current pulses can bring benefit to electrochemical cells when others claim that impact of pulse profile can be detrimental. The aim of the work is to experimentally investigate the impact of current pulse profiles on Lithium-ion batteries performance.

IV. IMPACT OF CURRENT PULSES ON LI-ION BATTERY PERFORMANCE

This part of the paper will deal with the impact of pulse profiles on Li-ion batteries performance in the time frame of milliseconds to minutes. The effects considered in this section were observed on dynamic cell voltage, and on charge/discharge capacities. The following paragraphs detail the main steps that lead to the results and the main points that emerged from this study.

A. Experimental assessment on 100% DoD synthetic profiles - Protocol

A specific measurement protocol was developed to achieve this work, the aim being to correlate the impacting parameters of the pulse profiles to the impacted parameters of the cell performance. The most delicate task in this case was to reduce the impact of the drift of the cell parameters. Indeed, in order to compare the impact of varying profiles on the cell behaviour, the profiles needed to be successively applied to the same cell to be compared. However, the cell parameters highlight an inherent drift, linked to the continuous acting aging mechanisms. In this context, it is clear that an experimental method had to be developed in order to

overcome this major practical issue. The method that was developed consisted in applying alternatively the constant current profiles that were considered as the reference profiles and the profiles to be investigated. Fig.1 presents the algorithm that was applied. To extract the impact of the pulse profile indexed i on the battery performance, we compared the measures related to the pulse profile indexed i to the measures related to the reference profiles indexed $i-1$ and i . Hence, the results take into account the slow drift in parameters of the cells due to aging like capacity fade or impedance increase. Furthermore, we ensured that the cells parameters like temperature or state of charge were always set in the same condition in the “Initialization of cell state” phase preceding the test sequence for of each profile.

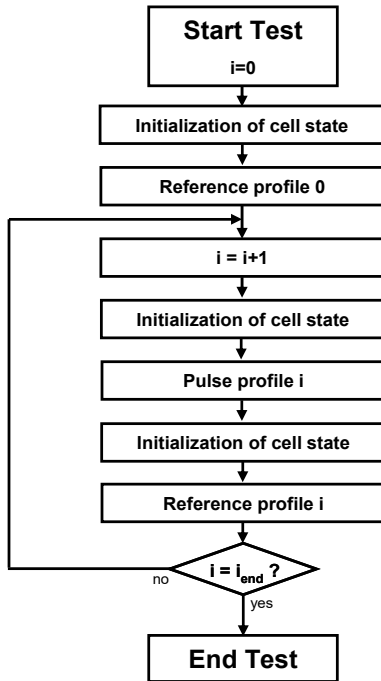


Fig. 1. Experimental algorithm applied to compare the impact on cell performance of profile i and the reference profile. In this case, the relative result for the profile i is elaborated by comparison with the results obtained with the reference profile $i-1$ and i .

For both charge and discharge profiles, both reference profiles and pulse profiles are applied in the voltage range between the upper and lower voltage limits stated in the components datasheet. Thus, the discharge results are obtained by discharging a completely charged cell to the lower voltage limit, i.e. 2.0V, and reciprocally, the charge results are obtained by charging a completely discharged cell to the upper voltage limit, i.e. 3.6V (see fig.2.a and 2.b). When the limit voltage is hit, the test ends and the system initializes the cell state over again. This instant is designated t_{end} on fig. 2.a and 2.b. In the charge case, the cell charge is ended by a CV process @3,6V until current reaches 23mA.

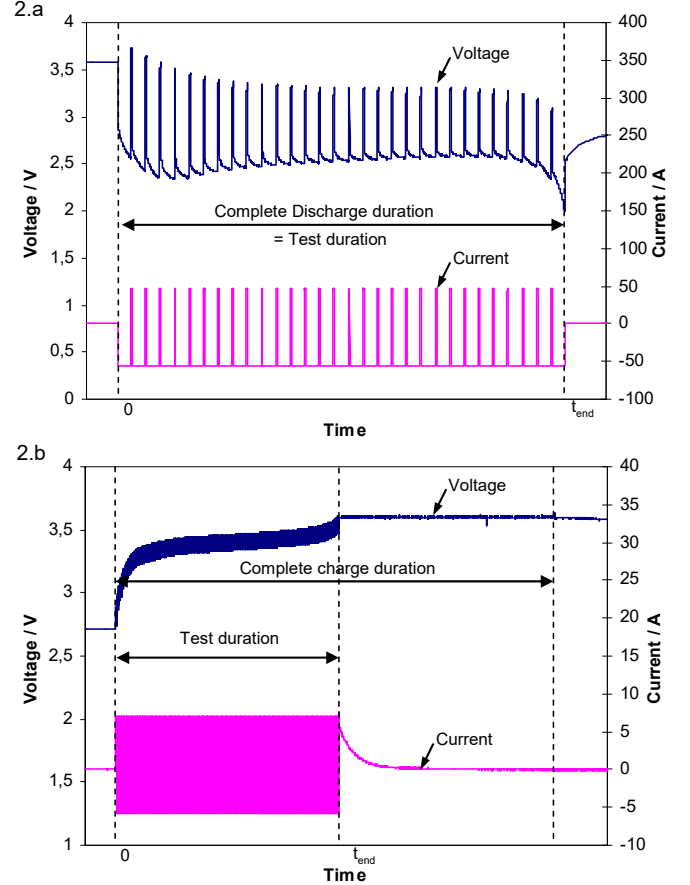


Fig. 2.a and 2b. Current profiles and associated voltage response of a lithium-ion cell under discharge (2.a) and charge (2.b) pulse profile test. Test results are measured during profile, from the initial SOC to the target voltage value.

Usual charge of Li-ion batteries uses CCCV protocols. In this study, we want to retrieve information regarding impact of pulse profiles on charge performance. Thus, on the basis of identical-mean current, we think that the charge potential, as well as the time needed to reach the upper voltage, directly related to the charge capacity during the CC phase, are the right indicators of the cell charge ability.

B. Experimental assessment on 100% DoD synthetic profiles – Cycle selection

A pulse profile can be considered in widely varying ways. In this study, a pulse current profile was defined as a periodic signal described by four parameters. Thus, according to Fig.3, we can define:

- I_{mean} : a mean-current value
- I_{pulse} : a pulse amplitude related to the current value during the pulses
- T : a period related to the duration of a repeating current pattern

- α : a duty ratio defined by the relation $\alpha = \frac{T_{pulse}}{T}$ (1)

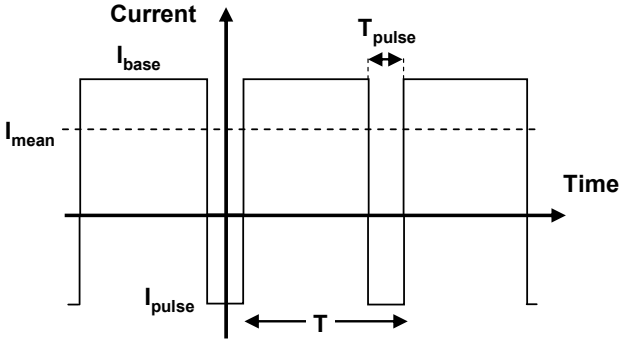


Fig. 3. Schematic representation of a current pulse profile and definition of related parameters. The continuous line represents the current pulse profile and the dotted line represents the associated reference current profile.

The profiles that were considered as reference profiles were constant current profiles. Our main hypothesis was that all the profiles should be compared on the basis of a constant mean current. Then, if we consider the triplet (Reference profile $i-1$; Pulse profile i ; Reference profile i), I_{mean} for the pulse profile indexed i and the current of the reference profiles indexed $i-1$ and i must be equal. This hypothesis was taken as a fundamental for several reasons. Firstly, we had to compare different profiles involving the same total reactant flux between the electrodes, in order to study the impact of pulse profiles on material transportation, and thus, on cell charge/discharge ability. Furthermore, the target application is the HEV or EV application. Even if the sizing in power of the system is also driven by peak power requirements, the sizing in energy in the vehicle is mainly driven by the average power, thus we wanted to compare profiles that would lead to identical practical systems in real applications. The studied profiles involve various behaviour of the cell regarding voltage response. This difference leads the cell to take more or less time to reach the end of charge/discharge voltage, and thus, leads to various charge/discharge times.

A large amount of different combinations of pulse parameters was investigated, as described in Table I. Hence, we studied profiles ranging from very low currents, where the reaction rate is mainly limited by electrochemical kinetics, to high currents, where limitations are strictly inherent to mass transport. A large number of signal periods and thus frequencies were also investigated between 200mHz and 100Hz. For these frequencies, we also investigated the impact of the duty ratio, which, at constant mean current, strongly impacts the RMS current by increasing the harmonic content in the signal spectrum. In addition, we also verified the impact of varying pulse amplitudes. To this end, we implemented profiles involving pulses ranging from rest periods to current inversions. In order also to verify the impact of such profiles on various types of cell, we also implemented tests on different cell designs. The tests were performed on both power optimized and energy optimized cells coming from the same manufacturer and using identical chemistry, namely Graphite//LiFePO₄. Finally, the tests were implemented at -10°C and at 25°C ambient temperature.

C. Experimental assessment on 100% DoD synthetic profiles – Results

All the test results were placed into result matrixes in order to evaluate which of the pulse parameters have the largest impact. Once all of the results were collected, we had two main observations. The first one was that the most impacting parameter of the pulse profile on the battery performance was the form factor F , which is defined as the ratio between the RMS current and the mean current for a given profile (2).

$$F = \frac{I_{\text{RMS}}}{I_{\text{mean}}} \quad (2)$$

Numeric calculation of this expression clearly shows that in the parameter range defined by Table I, by increasing both the duty ratio α and the pulse amplitude difference ($I_{\text{pulse}} - I_{\text{mean}}$), we increase the form factor F . In the case of a reference profile, namely a constant current profile, the profile does not contain any harmonic, and the form factor F is equal to 1. By keeping the preceding hypothesis, if we add harmonics to the signal, even if the signal mean value is kept constant, the form factor F will increase due to the increase in the RMS current. Thus, the form factor appears to be a very good indicator for the pulse content of such a profile.

TABLE I
OVERVIEW OF THE ESTIMATED PARAMETERS RANGE

Parameter	Range of investigation
I_{mean}	0,5C → 20C
T	10ms → 5s
α	1% → 10%
I_{pulse}	0 → - I_{mean}

For the energy optimized cell tested at 25°C, the form factor was correlated to the relative discharged energy W_R (Fig.4). This relative energy, defined by relation (3), is calculated for several pulse profiles and related to the energy drawn from the cell with the reference profiles. It can be concluded that there is a notably strong correlation between the current profile's form factor and W_R .

$$W_R = \frac{2 \cdot W_{\text{pulse}_i}}{W_{\text{ref}_{i-1}} + W_{\text{ref}_i}} = \frac{2 \cdot \int_0^{t_{\text{end_pulse}_i}} u(t)_{\text{pulse}_i} \cdot i(t)_{\text{pulse}_i} dt}{\left(\int_0^{t_{\text{end_ref}_{i-1}}} u(t)_{\text{ref}_{i-1}} \cdot i(t)_{\text{ref}_{i-1}} dt + \int_0^{t_{\text{end_ref}_i}} u(t)_{\text{ref}_i} \cdot i(t)_{\text{ref}_i} dt \right)} \quad (3)$$

$$C_R = \frac{2 \cdot C_{\text{pulse}_i}}{C_{\text{ref}_{i-1}} + C_{\text{ref}_i}} = \frac{2 \cdot \int_0^{t_{\text{end_pulse}_i}} i(t)_{\text{pulse}_i} dt}{\left(\int_0^{t_{\text{end_ref}_{i-1}}} i(t)_{\text{ref}_{i-1}} dt + \int_0^{t_{\text{end_ref}_i}} i(t)_{\text{ref}_i} dt \right)} \quad (4)$$

Moreover, the considered decrease in discharged energy increases with the form factor. This observation has been verified both for low and high currents. Furthermore, the impact of high current profiles appears to be higher than the impact of low current profiles. According to these observations, the implemented pulse profiles do not bring any benefit to the discharge energy when compared to constant

current discharge profiles on the basis of an identical mean discharge current. For all tests, the impact on the discharge capacity was negligible. Indeed, the relative discharge capacity C_R , defined by the relation (4) for all the pulse profiles, was comprised in the window [99.9%, 100.1%]. Since no specific correlation was found with any of the parameters, the gaps were attributed to measurement accuracy. Hence, if we consider that the parameters of the discharge pulse profile do not impact the relative discharge capacity, the effect observed on the discharge energy is totally attributable to a decrease in discharge potential and thus, an increase in overpotential. Taking this result as main principle, we can basically conclude that the pulse discharge do not seem to affect the battery discharge performance in a beneficial way.

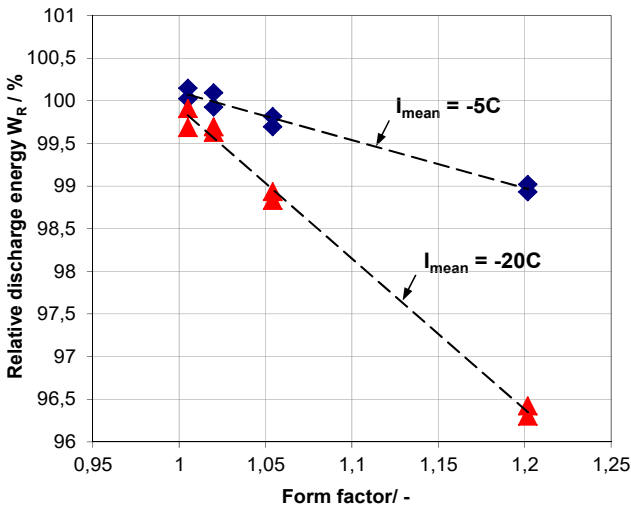


Fig. 4. Relative discharge energy W_R of various current pulse profiles as a function of the form factor for an energy-optimized cell at 25°C ambient temperature. The reference profiles are related to the coordinates (1; 100%).

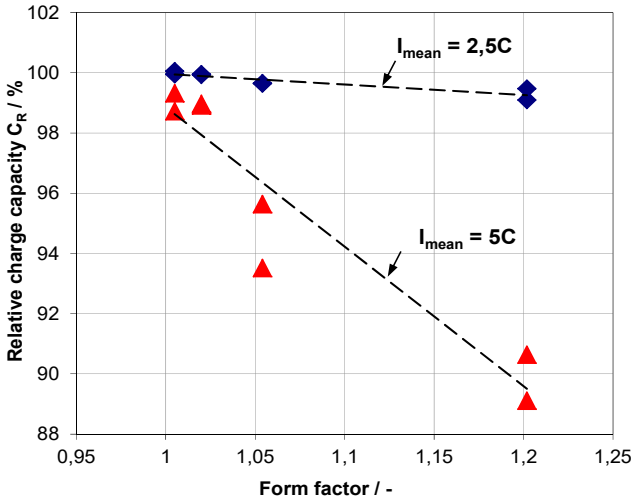


Fig.5. Relative charge capacity C_R of various current pulse profiles as a function of the form factor for an energy-optimized cell at 25°C ambient temperature. The reference profiles are related to the coordinates (1; 100%).

The impact on charge profiles was also investigated. Fig.5 presents the relative charged capacity C_R associated to various pulse profiles as a function of the form factor for an energy

optimized cell at 25°C ambient temperature. In this case, and contrary to discharge, we clearly observe a large influence of the form factor on the charge capacity. We observe a higher effect for both higher current profiles and higher form factor profiles, as we did with discharge profiles. However, this interpretation has to be more thoroughly investigated since the difference between the charge and the discharge is also intrinsically linked to the way they are measured (cf. § IV.A). Since the nominal cell open circuit voltage is around 3.3V, the maximum voltage drop is significantly higher in the discharge direction (1.3V) than in the charge direction (0.3V). In addition, the derivative of the voltage curve at the end of discharge is significantly higher than at the end of charge. Since the pulse profile induces a small increase in overpotential, the voltage limits are reached earlier with pulse profiles than with reference profiles. Also, the time evolution of the voltage being much faster at the end of discharge than at the end of charge, the observed effect of pulse profiles on discharged capacity is negligible. On the opposite, at the end of charge, the cell voltage slowly reaches the upper limit. In this case, the small voltage increase due to the harmonics in the signal induces large time shifts between the several profile's end of charge. Thus, the so-called impact of pulse profiles on the relative charge capacity showed in Fig.5 has mainly to be related to increased charge overpotential. For all the profiles highlighting a pseudo capacity fade, the missing Ah were charged during the constant voltage phase that followed the studied current pattern. Thus, this observation shall not be understood as a real capacity fade. Nevertheless, it provides valuable information concerning the impact of pulse profiles on the charge-ability of the cell. Similar to the cases with discharge profiles, the effect of pulses increases monotonously with the signal form factor. This result can also be represented in another way; we have defined the Profile Performance Index Ipp_i by relation (5) for a given pulse profile.

$$Ipp_i = \frac{W_i}{C_i} \quad (5)$$

$$Ipp_{r,i} = Ipp_i - \frac{1}{2}(Ipp_{ref,i-1} + Ipp_{ref,i}) \quad (6)$$

The profile's performance index Ipp_i is the ratio between an energy, in Watthour and a capacity, in Amphour. Note that it does not represent a measurable physical parameter although its unit is Volt. From an application point of view, it can represent the "quality" of a current profile. For charge profiles, it is desirable to charge maximum capacity with minimum energy, thus minimizing Ipp . In contrast, it is desirable to discharge the maximum energy from a cell while keeping the discharged capacity to a minimum; thus maximizing Ipp .

This index can be related to the results associated to the reference profiles by the relative index Ipp_r , defined by the relation (6), in a similar way as for relative energies and capacities with W_R and C_R .

Fig.6 shows Ipp_r , for the charge, associated to the investigated pulse profiles as a function of the form factor. In

this case, it can be concluded that regardless of the pulse parameter combination, all tested pulse profiles shows a positive $I_{pp,r}$, which basically means that applying pulses during charging leads to a decrease in cell performance. Furthermore, the gap observed with reference profiles increases monotonously with the form factor. This result basically confirms the preceding assumptions and leads to the conclusion that increasing the profile's form factor at constant mean value, both for the charge and the discharge, increases the overpotential build-up, thus reducing both charge and discharge ability and efficiency.

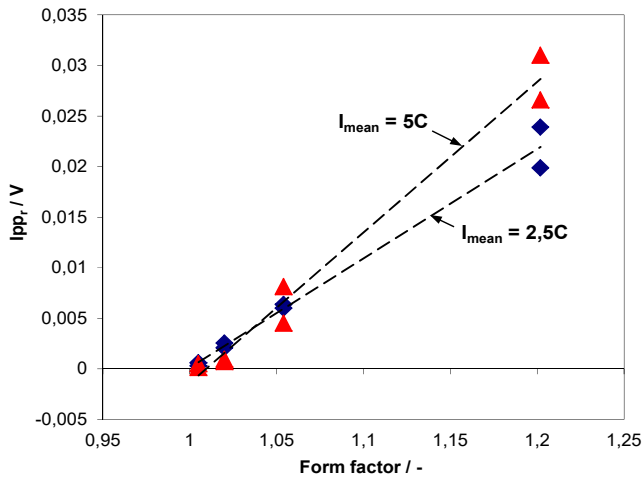


Fig.6. Relative charge profile performance index associated to various pulse profiles as a function of the form factor for an energy-optimized cell at 25°C ambient temperature. The reference profiles are related to the coordinates (1; 100%).

We did not include temperature results in this paper. Actually, we also found an excellent correlation between the heating inherent to losses and the profile's form factor. Increased temperature of the cell involves lower cell impedance. However, in spite of higher cell temperature for pulse profiles and thus lower impedance, the results showed that pulse profiles were associated to lower charge/discharge performance. This result confirms that pulse profiles induce both enhanced losses and lower performances in the cell, if profiles are compared on the basis of an identical mean current.

The second main observation was related to the effect of the signal period. Indeed, other important parameters than the form factor was observed during several tests. This can for example be seen in the Fig.4, Fig.5 and Fig.6 where the several points associated to a given form factor are rarely superposed for both low and high mean currents. Thus, those points seem to be also under the influence of another parameter. This parameter was identified to be the signal period. Fig.7 presents the relative profile performance index $I_{pp,r}$ associated to various pulse profiles at constant form factor and as a function of the signal period.

This graph (Fig.7) highlights the fact that pulse profiles both increase charge and discharge performance since $I_{pp,r}$ is negative for discharge profiles and positive for charge

profiles. This result shows that when compared to constant current profiles, and for an identical exchanged capacity, pulse profiles induce higher energy for charge and lower energy for discharge. Consequently, pulse profiles seem to reduce both charge and discharge performance when compared to constant current profiles on the basis of an identical mean current. Moreover, this graph also shows an important aspect related to the impact of the signal period. Indeed, all the profiles compared on this graph have identical form factors. Then, it is now clear that both in the charge and in the discharge direction, the signal period seems to have an impact on the performance. Furthermore, this statement can be completed by the fact that the higher the signal period, the more detrimental the effect of the profile on the performance. However, this increasing effect of the signal period on the overpotential seems to stabilize above ~10Hz, which is the frequency approximately corresponding to the beginning of the diffusive tail of the cell EIS spectrum. This result has been understood by the non-linearity of the cell impedance. Indeed, if the battery had followed the laws of a perfect (E; R) model, using the association between a serial resistance and an electromotive force, this impact would not have been observed. However, the cell impedance is not only path dependant, but is also time and current dependant. This induces a strongly non-linear behaviour of the cell that explains the dependency of the cell overvoltage with the period of the pulse signal.

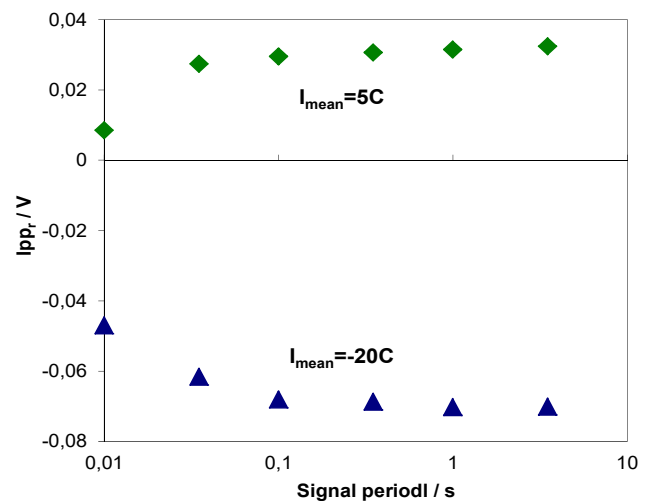


Fig.7. $I_{pp,r}$ associated to various pulse profiles at constant form factor and as a function of the signal period for an energy-optimized cell at 25°C ambient temperature. The reference profiles are related to the coordinates (1; 100%).

As a conclusion, the current pulse profiles, in comparison to constant current profiles on the basis of identical mean current did not show any benefit in cell performance. Profile performance index $I_{pp,r}$ are affected in a detrimental way both in the charge and in the discharge direction. Furthermore, the parameter of a pulse profile that appeared to be the most impacting on the cell performance was the form factor. High form factor signals strongly affect the discharged energy by decreasing the discharge efficiency; they also reduce the cell chargeability by increasing the total cell overpotential. These

effects were observed for both energy and optimized cells, at both low and high temperatures. The main trend was that the observed detrimental effect was more pronounced for cells with high impedance and for lower ambient temperatures. In addition, energy-optimized cells offer higher impedance than power-optimized cells and thus generate more losses when the current signal has a strong harmonic content. The effects were hence not attributed to specific electrochemical behaviour but mainly to the well-known effect of Ohm's law. However, and in order to support this interpretation, further investigation are needed in order to be able to discriminate the possible effects of concentration overvoltage, activation overvoltage, ohmic overvoltage and possible parasitic reactions, especially at end of charge. Nevertheless, and according to the hypothesis of this work, pulse profiles do not seem to induce any positive effect on the cell materials or on electrochemical processes that could be related to cell performance.

V. CONCLUSION AND FURTHER INVESTIGATION

The effect of a large variety of current/power pulse profiles has been experimentally investigated on Lithium Iron phosphate // Graphite cell performance. The effect of periodic pulse profiles was found to be detrimental to Li-ion battery performance when compared to constant current profiles on a basis of an identical mean current. These effects were hence not attributed to specific electrochemical behaviour but mainly to the well-known effect of Ohm's law on non-linear impedance. It is now of interest to develop models enabling to discriminate the contribution of overpotential and of parasitic reactions. Moreover, and contrary to other battery chemistries, pulse profile do not seem to induce any positive effect on the cell materials or on electrochemical processes that could reversibly impact the Li-ion battery performance. However, and relating to the main focus of our research, the long-term ageing impact of such profiles shall be investigated. The reversible effects of the pulse profiles have been up to now observed on the time scale of several milliseconds to few minutes. It is now of interest to quantify the impact that such profiles could have on the cell parameters on the lifetime time-scale.

VI. REFERENCES

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