

Low Temperature Discharge Cycle Tests for a Lithium Ion Cell

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Abstract— As all drivers in cold countries know, operating HEV/EV's at cold temperature is rather difficult. Indeed, cold weather increases the internal resistance of the battery system creating a high opposing force while operating the battery: slowdown of Li^+ diffusivity and decrease of ionic conductivity of electrolyte. Thereby, it limits the amount of energy extracted and reduces cell energy and power capability. Therefore, Li-Ion sensitivity to temperature remains one of the major obstacles to HEV/VE's market penetration. In fact, until now, investigations of low-temperature behaviors of Li-ion cells barely provide suitable information because they have only been extended to small battery capacities or non-currently used HEV/VE's batteries. Therefore, a complete thermal characterization of an actual HEV/VE's battery is missing. This characterization is described in this paper. Indeed; a 100 Ah lithium $\text{LiFePO}_4\text{M}_n$ HEV battery was tested under various operating conditions. The experimental process includes charging at ambient temperature, and discharging under extreme cold weather. The experimentations were conducted at four different temperatures to study the effect of seasonal changes in temperature.

Index Terms — *Lithium - ion battery, Hybrid and electric vehicles, Low temperature, thermal management.*

I. INTRODUCTION

As the gasoline price and greenhouse gas emissions have increased, Hybrid electric vehicles (HEVs) and Electric vehicles (EVs) have captivated remarkable attention as a commercially viable substitute to gasoline or diesel powered vehicles because HEVs/EVs are much more environmentally friendly. In the HEV and EV applications, size and weight of the vehicle are the two critical factors that complicate HEV's and EV's efficiency, Lithium-ion (Li-ion), lead-acid and nickel metal hydride (NiMH) secondary batteries are three common energy storage devices being considered in the HEV/EV industry.

Lead-acid battery is the oldest rechargeable batteries with an important Depth of discharge (DOD) (30%) [1], and high power-to-weight ratio (700 W/kg) [1], capable of supplying high pulse currents. However, its energy-to-weight and energy-to-volume ratios are very low (30 Wh/kg and 75 Wh/L, respectively [1]) such that this type of battery cannot provide enough energy and power in a limited space of a HEV/VE.

As for NiMH battery, its success has been driven by its high energy density [1], equivalent to Li-Ion battery, and the

use of environmentally friendly metals [1]. To such an extent that, the firm Toyota® has brought NiMH technology in the forefront for over a decade with efficient and successful HEV's (Prius, Lexus, Honda Civic...) [2]. But nowadays, limitation remains. The significant disadvantage of NiMH batteries is the high rate of self-discharge; NiMH batteries typically lose 20% of their charge on the first day and 4% per day of storage after that. [1]

In addition, although a NiMH battery is capable of delivering high discharge currents; repeated discharges with high load currents reduce the battery's cycle life. In fact, NiMH performances start to deteriorate after 200 to 300 cycles [1] if it's repeatedly deep cycled. Therefore, the NiMH is especially well-adapted to non-plug-in hybrid vehicles, with a low state of charge excursion

Already active on the small appliances market, Lithium ion batteries have gained distinction in the last few years on the market of hybrid electric vehicles (HEV) and pure electric vehicles (EVs). Especially, rechargeable Li-ion batteries are the leading candidates for these vehicles (EVs) due to their high energy-to-weight and power-to-weight ratios (180 Wh/kg and 1500 W/kg respectively) [1, 3]. In addition, the Li-Ion battery has a low self-discharge rate of approximately 2% per month and the battery does not suffer from the memory effect [1]. Despite offering advantage, market penetration of HEVs/EVs is limited by a series of technical barriers of Li-ion batteries such as their safety [4, 5], cost issues [6], recycling issues [7], charging infrastructure [8], charging time [9], etc.

One other issue is the reduced energy and power densities of the cell at low temperatures [10]. As will be detailed in section II, at sub-zero temperature, batteries or others electrochemical systems lose their performances and it has grown to be a major concern in cold climates. Yet, some strategies exist [11-12].

It goes without saying that first thermal strategies for HEV systems focused on cooling issues. To compare with, studies on battery heating are in a stalemate. Heating strategies appeared because battery degradation and driving range are of great concern for new launched HEV's/VE's in cold environment. Therefore, new heating strategies have become a pressing necessity. However, a literature survey indicates that the first thermal management studies date back to a decade ago with Pesaran et al. [11]. They studied preheating techniques on a battery pack in cold climates including core heating, casing

heating and fluid heating. Their studies emphasized by a finite element method reveal that core heating was the most effective method. In addition, Ji and Wang [12] presented further strategies namely self-internal heating, convective heating and mutual pulse heating. The study reveals that for battery power heating, convective heating requires the least heating time, while mutual pulse heating consumes the least battery capacity. Mutual pulse heating has the other advantage of uniform internal heating and is free of convective heat transfer system.

As few heating strategies have been proposed, it remains unclear which strategy is suitable for cold environments and HEV systems and how much space there is for further improvement. As a consequence, the actual thermal management battery system in HEVs/VEs has to be reconsidered in order to input low temperature effect.

For instance, PosiPlus®, a Canadian company based in Victoriaville (QC), manufactures Bucket Trucks running with an Internal Combustion Engine (ICE); a Posiplus® Bucket Truck is illustrated in Fig. 1. However, a battery system has been developed to move the bucket in order to avoid the using of the ICE when the vehicle is stopped (causing communication troubles between the workers and used at a bad efficiency point). The truck is now based on hybrid system, lithium-ion batteries and ICE. Although this hybrid system is efficient, battery performances rapidly fall down due to the local winter temperature. An alternative solution has been found (an external heating system) and set up. Nevertheless the batteries performances are not well-known and improvements remain possible. But it requires a thorough knowledge of the batteries thermal behaviors. Therefore, exhaustive thermal characterization tests of the batteries used in the PosiPlus® hybrid system has been carried out at the UQTR.

At the end, operating HEVs/VEs in winter is a major problem and needs a thorough examination of sub-zero behaviors of large capacities lithium-ion cells because to counter low temperature effect, present thermal strategies for HEVs/VEs are not fully developed yet. The objective of this paper is first to study the battery correlation between electricity and thermal behavior by discharging high capacity Li-ion batteries in winter conditions for a stationary application like PosiPlus®,. In a future second phase, more realistic tests for a non-stationary application will be conducted and a new thermal strategy will be proposed.



Fig. 1. Posiplus® hybrid bucket truck. <http://www.posi-plus.com/fr/>

II. ELECTROCHEMICAL PHENOMENA

As a rule, the decreased operating voltage and by extent the power can be ascribed to an increased internal resistance of the cell mainly due to a decline of the ionic conductivity of electrolyte and to a slowdown of the cell electrochemical reactions [10, 13]. In fact, in [14], Gu and Wang defined the ionic conductivity as part of the electronic charge balance governing equation in solution phase:

$$\nabla \cdot \left\{ K^{eff} \left[-\nabla \Phi_2 + K d^{eff} \frac{\nabla c_2}{c_2} \right] \right\} = S_{a,i} j_{loc} \quad (1)$$

With K^{eff} , thermal conductivity ($W (m.K)^{-1}$), Φ_2 , the electric potential (V), c_2 , the lithium ion concentration on active material particles ($mol.m^{-3}$), $S_{a,i}$ the specific surface area (m^{-1}), j_{loc} the local current density ($A m^{-2}$). In which the ionic conductivity, $K d^{eff}$, is:

$$K d^{eff} = \frac{2RT}{F} \left[1 + \frac{\delta \ln f}{\delta \ln c_2} \right] (1 - t_+) \quad (2)$$

With T the absolute temperature (K), t_+ the transference number of Li ion species dissolved in liquid. Plus, in their model [11], they considered the cell electrochemical reaction using the Butler- Volmer equation as account for charge transfer kinetics:

$$i = i_0 \left[\exp \left(\frac{\alpha_a F}{RT} \eta \right) - \exp \left(-\frac{\alpha_c F}{RT} \eta \right) \right] \quad (3)$$

Where, i is driven by overpotential, η , defined as the difference between solid and electrolyte phase potentials minus the nominal voltage of the cell, α_a and α_c are transfer coefficient for anodic and cathodic current (respectively). The strong dependence of the thermodynamic, kinetic and conductivity parameters on temperature in (2) and (3), offers feedback to the cell performances while operating at low temperatures. In this way, electrochemical performance and thermal behaviors are deeply coupled.

Hence, operating HEVs/VEs at low temperature is a serious issue in countries such as Canada, Russia or Scandinavian countries where the temperature during winter plummets under $-20^\circ C$ and lasts at least for four to six months. For example, at -20° only 50% of the battery energy is available [15].

On that matter, a number of papers have addressed the problem of the low temperature performance of Li-ion batteries [10, 16–19]. But until now, investigations of low-temperature behaviors of Li-ion cells have been limited to small battery capacities [10, 16–18] and to non-currently used in a HEV batteries [19] and they don't provide noteworthy information for a HEV/VE study case. Indeed, in [19], the initial temperature of cell is upper than $0^\circ C$ so it doesn't fit for a Canadian winter application. Furthermore, it has been reported in [10, 16–18] an association between the quick rise of the cell temperature and the output current. But on account of the cell geometries and the small capacities, these investigations are no longer thermally valuable in a HEV system where a larger

battery scale is preferred. Therefore, a new breach for HEV thermal strategies is open and studying thermal behaviors of large capacities batteries will fill in this breach.

III. EXPERIMENTAL SETUP

A. Battery feature

To explore the strong impact of low temperatures, a lithium-ion battery cell nominally rated at 3.3 volts and 100 Ah is tested, with a working voltage between 2.5V and 3.8V. The lithium battery can charge and discharge -20°C to 60°C temperature range

B. Experimental Test Bench

All the tests were carried out using the test set-up shown in Fig. 2. The cell under test is placed into a climatic chamber. The temperature inside the chamber is regulated by liquid Nitrogen and controlled by a PC interface. A power supply (TSSerieIV 15kW) drives the current flowing in the cell (up to 150 A). As far as the cell discharge is concerned, an electronic load Dynaload XBL 12kW is used. As the electronic load comes with no digital interface, the available analog ports are connected to a National Instruments NI PCIe-6323 DAQ. In this way, the load can be easily controlled from a PC. The same DAQ reads the analog output of the TSSerieIV and also senses the temperature probes of cell through two thermocouples SA1-K-SRTC displayed along the length of the cell. Software developed with LabVIEW2010 controls all the equipment.

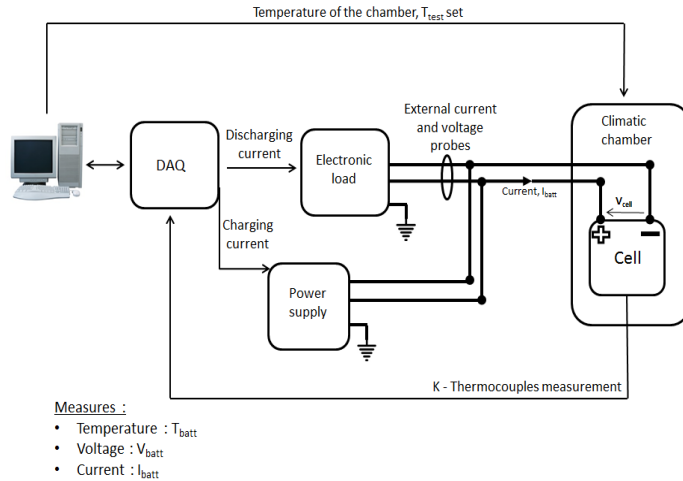


Fig. 2. Experimental test bench.

C. Discharging protocol

In order to observe the cell behavior at low temperature during a discharge cycle, a protocol is proposed in this paper with the primary objective of assessing the energy delivered by the cell at different temperature.

Nonetheless, an important fact to take into consideration in the usability of these batteries is the distinct difference between the discharge and charge cycle. On one hand, the discharging test cycle is an important evaluation tool in the electric vehicle because this will restrict the maximum energy available at low temperature.

On the other hand, the charge process regenerates the discharged battery power. So in order to evaluate experimentally this energy, a protocol is realized and takes into account both discharge and charge cycle. However, with the aim of comparing the tests results, the charge cycle is always executed in the same conditions. Fig.3 shows the protocol established.

- Step 1: the cooling chamber temperature T_{amb} is lowered to the temperature, T_{test} .
- Step 2: meanwhile, cells are kept in the chamber until the temperature of the battery, T_{batt} reaches thermal equilibrium, i.e. the temperature test, T_{test} .
- Step 3: is the core of the discharging protocol. All the tests discharge the cell from maximum state of charge (SOC) to beyond the minimum voltage discharge limit of 2V. Even though it accelerates battery's deterioration and goes against the manufacturer recommendation of 2.5V, the aim of this test is to fully investigate the discharge behavior of the cell, so battery's degradation it is not crucial as regards [20]. Also, during the discharge tests, T_{batt} is rising up because of a heat generation happening from the electrochemical reaction inside the cell which shows what occurs truthfully in a realistic HEV driving cycle.
- Step 4: once the discharge cycle is done, the cooling chamber is set off, and T_{test} is warming slowly to T_{amb} .
- Step 5: before each charge process, the cell is maintained at the same temperature, 25°C , to ensure an identical SOC of the battery at the beginning of the protocol and also in order to compare the tests results. Because of the heat generation happening at step 3, one night rest is used for T_{batt} to reach 25°C .
- Step 6: the charge process is performed with a protocol presented in Fig.4 [21]. At room temperature, the cell is firstly charged by a constant current, 20A (0.2C) until V_{max} value reaches 3.8V, Then, following, a constant voltage phase (3.8V) with 1/20 C cutoff current.

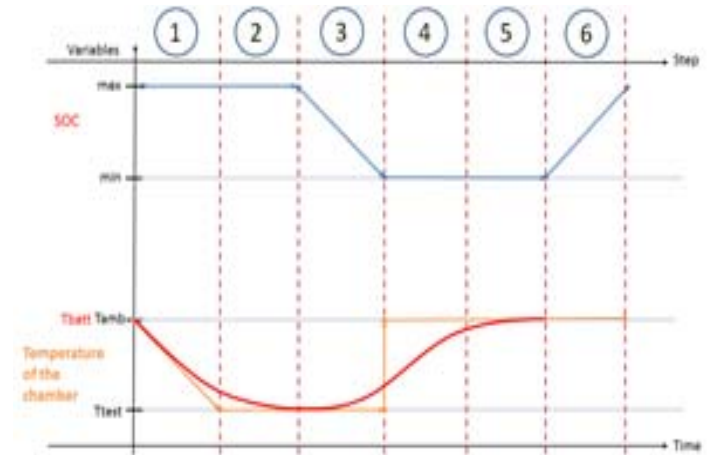


Fig. 3. Schematic of the discharging protocole.

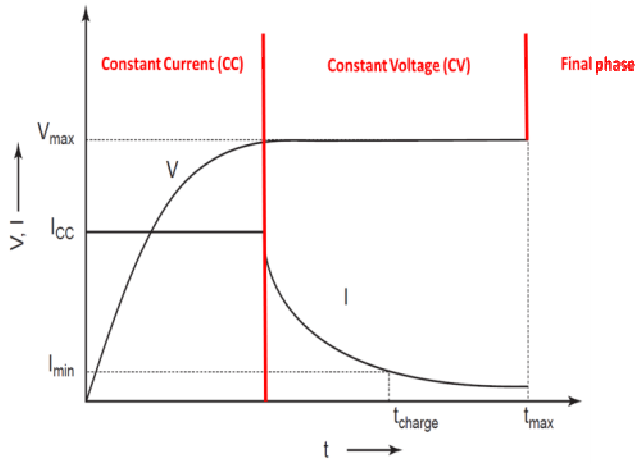


Fig. 4. Charge protocol for the charge cycle performed under the same conditions[21].

The batteries were tested at four different ambient temperatures, namely -20°C , -10°C , 0.0°C , and $+25^{\circ}\text{C}$. The discharging tests subject the battery to the same operating currents as those in the actual hydraulic pump system. Thereby, testing was initiated with a series of three constant discharging currents, namely 300A (3C), 100 (1C) and 50A (0.5C). (The charge and discharge current of a battery is measured in C-rate. This means that a 100 Ah battery would provide 100 A for one hour if discharged at 1C rate.). The amount of energy extracted during tests is calculated with [1]:

$$W = \int V_{batt}(t) \cdot I_{batt}(t) dt \quad (4)$$

Where, W is the energy delivered (Wh), V_{batt} and I_{batt} are the measured cell voltage (V) and the discharging current (A) respectively.

Plots of the experimental discharging test data with evolution of T_{batt} are presented in Fig. 6 through Fig. 8. Also from the same data tests, to illustrate the dynamic evolution of the temperature details of the evolution of the temperature of cell versus the discharging current applied are plotted in Fig. 9 to Fig. 11. Tests results and Wh characteristics at four different ambient temperatures are shown in TABLE I. To be noted that for T_{test} of -20°C and constant current of 300A; the test didn't start because the voltage, V_{batt} , drop was so elevated due to the current and the temperature, the electronic load limitation wouldn't initiate the test. Therefore, the test result will not be shown here.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

Fig. 5 to 7 compare discharge curves of a Li-ion cell at various temperatures, T_{test} , and show T_{batt} evolution for all currents during discharge. It is shown that with low temperatures, both the operating voltage and energy delivered are reduced. Moreover, for some discharging currents (Fig. 6 to 7), the voltage goes under the BMS limit, generally of 2V.

Furthermore, from these experimental analyses, one can accentuate the impact of the test temperature on the cell performances. At subzero temperatures the dependence of cell resistance is strong due to kinetic and conductivity parameters,

see equation (1). In [10], the authors show that the cell resistance is mainly credited to the cell's electrolyte resistance.

However, Fig. 8 to Fig. 10 show that heat generation from the cell is significant and non-negligible. This is potentially due to electrochemical processes inside the cell and the electrons density passing through the circuit, which causes higher heat generation rate when the discharging current (C-rate) value is important. Indeed, according to [10], heat generation rates from various sources, but only joule heating (ohmic) prevails at this current rate over the others resistances:

$$Q_{ohm}(W) = R_{batt}(\Omega) \cdot I_{batt}^2(A) \quad (5)$$

It follows a capacity benefit attributed to the suppression of the electrolyte resistance due to higher ionic conductivity and salt diffusivity resulting from temperature rise leading to a voltage rise.

This phenomenon means that at low temperature by applying a high constant discharging current, the cell heats itself and restores its performances to a point where unexpectedly the energy delivered appears to be the same for the three discharging currents (TABLE I).

As a result, this self-heating process can replace or assist an existing heating source in a HEV thermal management system when the temperature of the cell is low. But, the battery management system (BMS) voltage limit has to be altered; if not the discharging cycle is blocked and cannot start.

TABLE I. OUTPUTS CHARACTERISTICS OF THE LOW TEMPERATURE TESTS

Test temperature	Test characteristics			
	Max Temperature of the cell ($^{\circ}\text{C}$)	Discharging time (s)	Energy delivered (Wh)	Discharging current (A)
25°C	31.63	7022	302	50
	38.25	3541	293	100
	52.20	1213	276	300
0°C	9.62	6206	238	50
	11.45	3132	233	100
	24.74	1096	231	300
-10°C	-0.62	6264	225	50
	8.75	3217	226	100
	18.89	1084	212	300
-20°C	-13.75	5491	183	50
	-7.78	3198	215	100

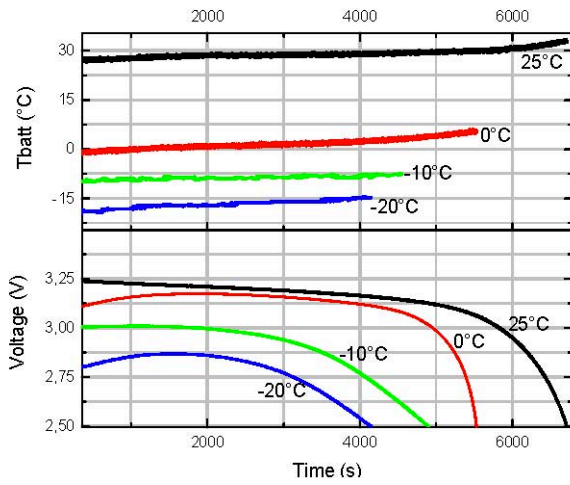


Fig. 5. Battery discharging cycles and battery temperature evolutions at four temperatures tests for a constant discharging current of 50A.

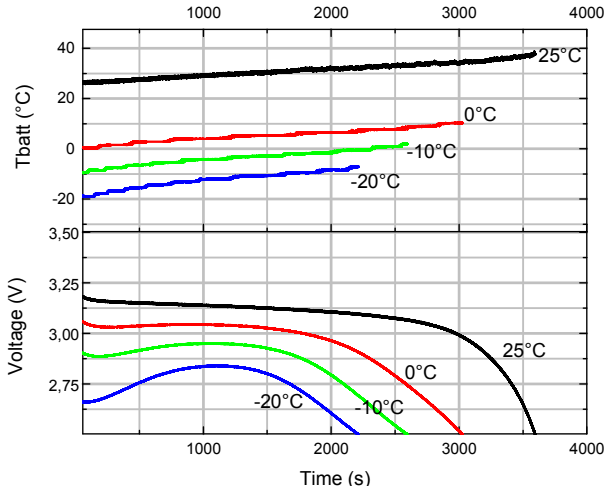


Fig. 6. Battery discharging cycles and battery temperature evolutions at four temperatures tests for a constant discharging current of 100A.

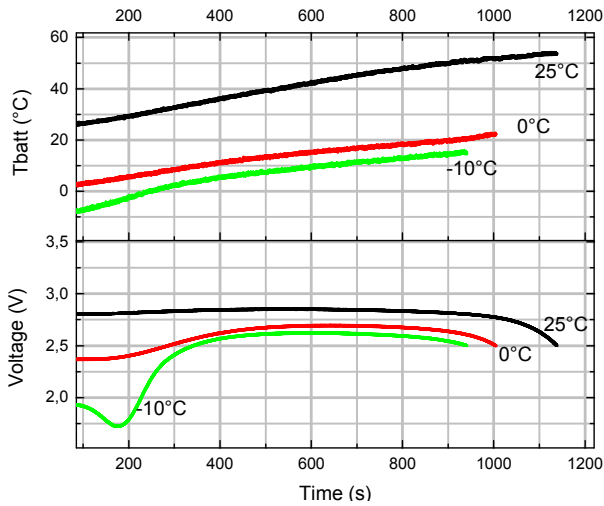


Fig. 7. Battery discharging cycles and battery temperature at four temperatures tests for a constant discharging current of 300A.

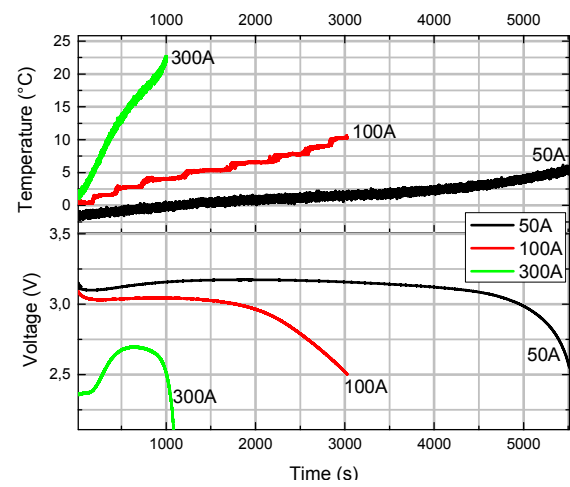


Fig. 8. Battery discharging cycles at three discharging currents for a temperature test of 0°C.

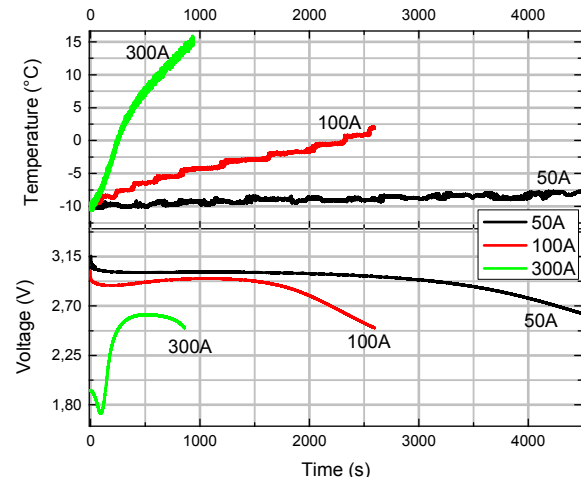


Fig. 9. Battery discharging cycles at three discharging currents for a temperature test of -10°C.

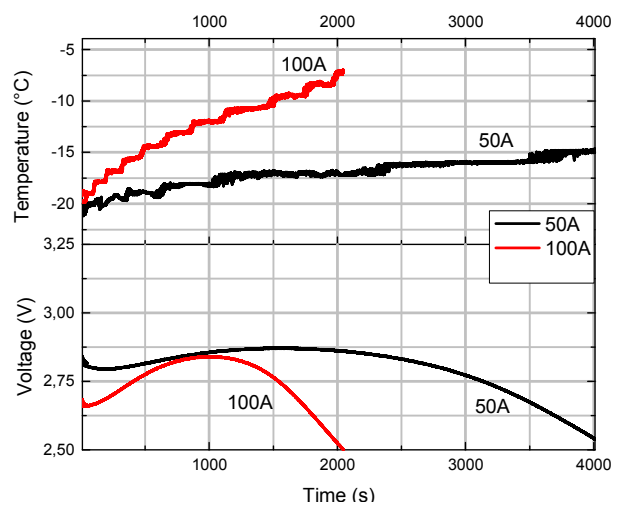


Fig. 10. Battery discharging cycles at three discharging currents for a temperature test of -20°C.

V. CONCLUSION

The lithium batteries performed well when the ambient temperature is above 10°C. However, when the environment temperature is below 0°C the energy stocked is lower and the voltage moves over a wider range than at higher temperatures because voltage drops increased due to increased internal impedance.

Moreover, as the discharging current is high, the cell temperature is rising due to the strong interaction between electrochemical and thermal processes of the cell. As a result, the generated heat can lead to a significant temperature rise of the cell and then restore cell performance. In fact, this self-heating can be used to improve the existing heating strategies [11-12] by replacing or supporting an external heating source but the BMS voltage limit has to be reformed. , it induces a remarkable temperature rise of cell, implying a decreased internal resistance [13] and consist of warming up the cell before use with an external heating system powered either by an external source or mostly by the battery itself. However, to applied a high discharging current value to heat the cell also as a downside effect. It accelerates rapidly cell's deterioration and shortens the life of the cell [22, 23].

As a consequence, an entire innovative heating strategy is workable, but batteries lifetime also has to be considered. Future work will investigate battery degradations and thermal management of a HEV.

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