EVS24
Stavanger, Norway, May 13-16, 2009

Modelling of On-board Energy Storage System ageing The French SIMSTOCK research network

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Abstract

On board Energy Storage Systems (ESS) remains one of the major issues to be solved in order to succeed in a massive diffusion of electrified, hybrid, then electric, vehicles. The ESS in-use ageing forecasting remains one of the major problems to be solved and involves fundamental research in the field of material together with experimentation, simulation and design by the end users.

This paper describes the 3-year, 4,2 M€ SIMSTOCK program, which has recently been launched, associates research labs, ESS manufacturers, components and vehicle manufacturers, with the support of the French ADEME.

The ageing mechanisms and their precursors for the ESS considered, together with all the testing protocols and procedures are detailed. Unfortunately, these initial phases, together with the specification and acquisition of the 12 tests channels have delayed the recording of the initial results which are now under processing and can't be reported in this paper. However, the SIMSTOCK network now operates 23 tests channels for batteries and supercapacitors and will soon generates interesting results for the purpose of ESS ageing simulation.

Keywords list : lithium battery, nickel metal hydride battery, battery cycle life, battery model, simulation

1 Context

Electricity has become more and more widely used in recent years in light duty vehicles for the purpose of comfort, safety and communication or directly for the purpose of vehicle propulsion in innovative drivetrains. As far as high duty vehicles are concerned, electrification has already been in use for a while in the propulsion of rail vehicles and trolleybuses but new applications have appeared recently with off-catenary operations in city centers or end-of-line cases for instance.

2 Consequences

The constraints of energy consumption and greenhouse gas emission, encountered by the newly developed vehicles leads to very complex drivetrain architectures which will require an optimized energy management. This will necessitate a system approach involving simulation of the vehicle together with its drivetrain components. This simulation will require accurate models of the components, and especially the energy storage system which appears to be the most complex.

Furthermore, energy storage systems used in light duty vehicles (batteries, supercapacitors or a combination of both) appear to be very sensitive to their conditions of use (temperature, depth of discharge, current levels...) and present ageing behavior which has still to be clarified. Such uncertainties will have to be reduced in order to enable a widespread diffusion of innovative drivetrain vehicles in our fleets.

Consequently, industrialists and research labs have joined their efforts to set up a complete research program with the following goals:

- Create a set of validated and up-dated simulation modules for a large number of batteries and supercapacitors representative of the last generation of high power energy storage systems for hybrid light duty vehicles applications
- Take into account the ageing effects in the cell simulation
- Include these modules in a system level simulation model, able to forecast the cell ageing and translate it into a vehicle behavior.

3 Objectives of research program

A cost-shared research program has been set up with the following partners (see fig. 1):

- Research labs involved in ageing mechanism comprehension, simulation and ageing test realization (INRETS LTE Lyon and LTN Paris, LRCS Amiens, CEA Grenoble and Chambéry, EIGSI La Rochelle, LEC Compiègne, IMS Bordeaux)
- Energy storage systems manufacturers SAFT and BATSCAP who provide the cells to be tested together and participate in the interpretation of ageing mechanisms
- LMS, an industrial partner in charge of the realization, the diffusion and the support of energy storage system simulation modules in the automotive industry
- Vehicle manufacturers (PSA Peugeot Citroën and RENAULT), other suppliers (VALEO), energy providers (EDF) and labs (IFP) as end users of the program
- The Mobility and Advanced Transportation (MTA) Competitiveness Cluster for the coordination of this complex project with 16 partners.

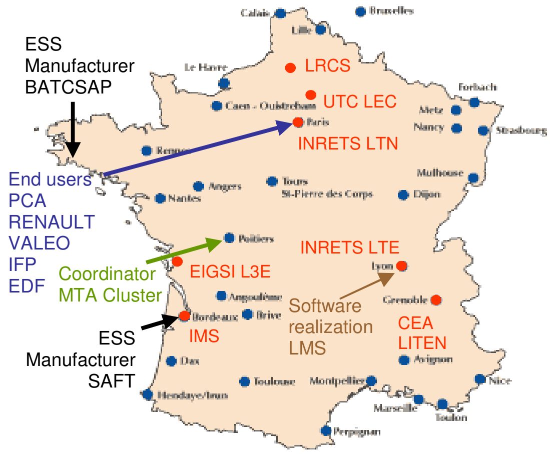

Figure1: Location of the SIMSTOCK project partners

This 4.2 M Euro overall cost program is supported by the French ADEME and was launched in November 2007 for 3 years. As described hereafter, the main task of the program is the testing of energy storage systems for ageing evaluation. 23 battery and supercapacitor testers will be involved in the six research labs, among which 12 have been purchased especially for the SIMSTOCK project. Consequently, more than merely a 3-year research program, the partners and the French ADEME intend to create a network able to operate in the future in the field of energy storage system ageing evaluation and simulation for road vehicle applications.

4 Main tasks of research program

4.1 Reminder about battery and supercapacitor ageing mechanisms

4.1.1 General context

This preliminary task is very important as the ageing mechanisms should be identified, together with the operating parameters to which they are sensitive (SOC, ΔSOC, temperature, current...), with the aim to precisely define the testing protocol and find the correct exploitation of the experimental results recorded.

Following remarks should be made first:

- As the purpose of the program is to simulate the ESS behavior in hybrid vehicle operations, the ageing mechanisms taken into account will only be those encountered during operations within the manufacturer specified operating range. This means that no abuse tests will be conducted in the SIMSTOCK program,

leaving this area to other specific research programs
- As already stated, the calendar ageing processes will be covered in the accompanying SIMCAL program, involving the same partners, now under investigation by the French authorities and which should hopefully be launched in the second part of this year.

4.1.2 NiMH ageing mechanisms

For this electrochemistry, the main ageing mechanisms have been described by the Lab. d'Electromécanique de Compiègne (LEC) in one of the preliminary tasks of the program as followed [1], [2]:

For the anode in nominal working conditions:

- Fragmentation of the metal alloy grains which is due to the electrode volume variation because of the hydrogen intercalation and extraction during the charges and discharges of the cell (see fig. 2). The fragmentation effect may induce a loss of electric contact among the metal alloy particles and between these particles and the current collector. This phenomenon is linked to the battery SOC variations (ΔSOC) and will be responsible for an increase in resistance.

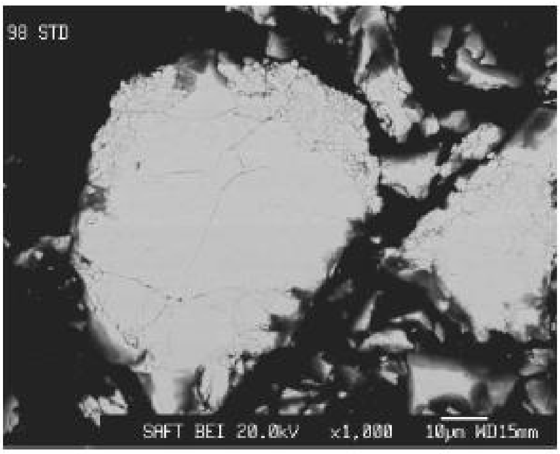

Fig. 2a: SEM analysis of the initial MH electrode [1]

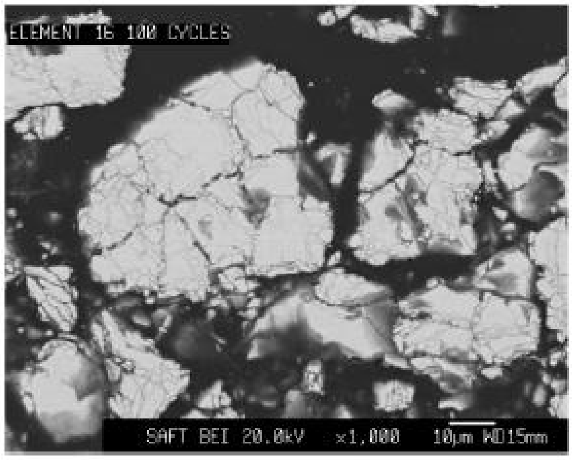

Fig. 2b: SEM analysis of the MH electrode after 100 cycles (96 Ah) [1]

- Corrosion of the metallic alloy by the aqueous electrolyte. This phenomenon is accelerated through continuous fragmentation and increases with the temperature. Corrosion will be responsible for a decrease in the cell capacity because of a loss of electrode active material, together with the electrolyte consumption.

For the cathode under nominal working conditions: Aluminum deposit inside the electrode material. This phenomenon is due to the migration of an anode metallic alloy which has been removed from the anode, in the case of mishmetal alloy composition. The consequence will be an increase of the electrode impedance.

In case of over-charge or over-discharge: These cases have been considered even though they will probably not be encountered, thanks to the battery management system, especially for charge sustaining hybrid operations. In these cases, the anode corrosion, and accompanying capacity fade can sometimes reduce the gas recombination capabilities of the electrode and consequently lead to a cell pressure increase and finally to an electrolyte drying through the security valve.

4.1.3 Li-Ion ageing mechanisms

Numerous types of Li-ion cells or cell designs are proposed and implemented by battery manufacturers. Referring to the partners and to the project objectives, layered, spinel and olivine oxides are considered as cathode materials, while graphite is used at the anode. Ageing mechanisms and their precursors were highlighted by the LRCS team of Amiens in one of the preliminary program tasks, the main ones are listed below [3], [4], and [5]:

For the anode the following phenomena were considered:

- Solid Electrolyte Interphase (SEI): This layer, which is created during the first cycles of the battery due to partial electrolyte decomposition on the graphite surface, has the effect to limit further electrolyte decomposition. During battery ageing, the SEI may be altered by electrode volume modification due to SOC variations. This leads to microcracks that will promote the SEI growth over the battery life. SEI growth is more pronounced at high SOC and temperature,
- Li plating: in low-temperature conditions, high SOC and high charging current, lithium plating may occur at the anode. This is quite detrimental for the battery longevity since metal lithium promotes uncontrolled electrolyte decomposition reactions that usually alter the good quality of the SEI,
- Active material : Insertion-disinsertion of Li ions in the graphite structure has a limited effect due to low volume variation (typically 10%), the most significant effect is probably the solvent co-intercalation in the graphite layers, resulting in a material exfoliation and cracking encountered at high SOC, (see fig. 3),
- Plating of soluble metallic impurities coming from the cathode (e.g. from spinel oxides),
- Electrode porosity diminution due to solid products accumulation within the electrode (high SOC and temperature),
- Composite electrode: Phenomena such as electronic contact loss in the electrode material or between the electrode material and the collector, due to high ΔSOC and to electrode volume variations. Current collector corrosion at anode may also occur at low SOC. Non-uniformities within the anode yields non-uniformities of the current density, which in turn act toward the promotion of other aging phenomena.

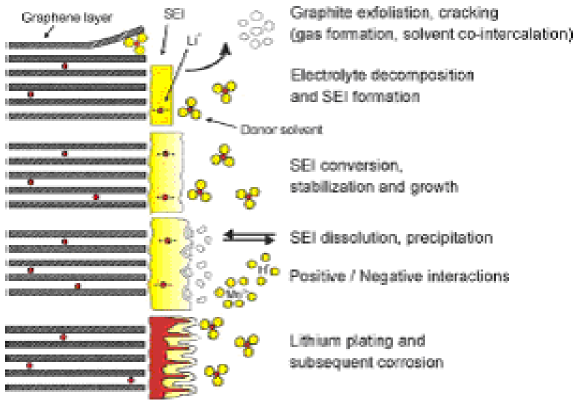

Fig. 3: Anode-electrolyte interface ageing phenomena, from [2]

For the cathode the following phenomena have been considered:

- Irreversible phase transitions leading to inactive phases or to phases with a poor electrochemical activity. (sensitive to ΔSOC, high SOC and low SOC for spinel oxides),
- Structural disordering,
- Electrolyte oxidation on the electrode surface, current collector and conductive particles, occurring at high SOC and temperature, and possibly giving rise to the growth of surface layers,
- Dissolution of the active material (or some impurities in olivine oxide case) with possible re-precipitation of new phases and deposition of metallic impurities on the anode particles. This mainly occurs for spinel electrode at both high and low SOC, and usually at high temperature,
- Phenomena at the composite electrode level, such as electronic contact losses within the electrode itself and between the electrode material and the collector, due to high ΔSOC and due to electrode volume variations. Oxidation of conducting particles in case of high temperature and SOC. Current collector corrosion may also occur at high SOC.

It should be noted that oxygen release, which is of concern mainly for layered materials when overcharged (high SOC) and at high temperature, leads to exothermic side reactions, self-heating, and eventually to possible burst and cell explosion. They have not been taken into account here, as being far away from normal operation on a charge sustaining hybrid.

4.1.4 Supercapacitor ageing mechanisms

Very few publications have been released in the field of supercapacitor ageing in cycling. The main ageing factors for supercapacitors have been identified by INRETS LTN and IMS Labs. They are the following:

- First order factors :
  - Temperature
  - Maximum voltage on cycle
- Second order factors :
  - Maximum current
  - RMS current (relative to heat release in the component)
  - Depth of discharge (relative to minimum voltage)

It should be noted that rest period is also recognized as having an influence on supercapacitor ageing.

4.2 Energy storage simulation modules

The simulation modules of the various considered cells will be carried out and validated by LMS partner using the AMESim environment.

The battery simulation module has already been done, it will exchange information with the other components of the vehicle system, as illustrated in fig. 4a.

The model will take into account open circuit voltage with hysteresis (when relevant), internal resistance, charge transfer and double layer capacitance, together with diffusion phenomenon and temperature, as illustrated in fig. 4b.

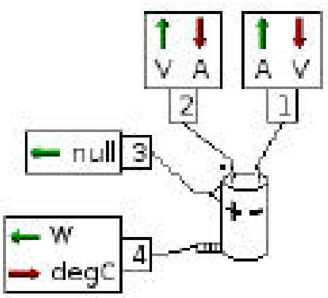

Fig. 4a: Battery simulation sketch

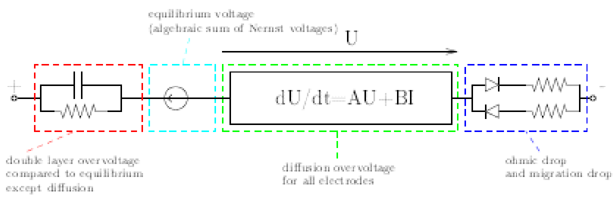

Fig. 4b: Battery simulation principles

The data for the simulation, together with the recorded values for the validation process, will be deduced from the experiments carried out in the different labs involved (see Chap. 4.3.3).

4.3 Ageing tests

The testing protocols will have to consider the parameters which will be influent on the ESS ageing phenomenon, according to what has been presented in chapter 4.1 above, it appears that SOC, ΔSOC, current and temperature will have to be considered.

The following chapters will only consider the battery case. Tests for supercapacitors are described in Chap. 4.3.4.

4.3.1 Cycling experimental protocols

Considering the ESS behavior in a HEV highlights the fact that the power, and consequently the current and voltage, follow very complex patterns that will have to be simplified in order to appropriately discriminate between the current and SOC variables. Previous research programs indicate that elementary current profiles have been used, as illustrated in fig. 5.

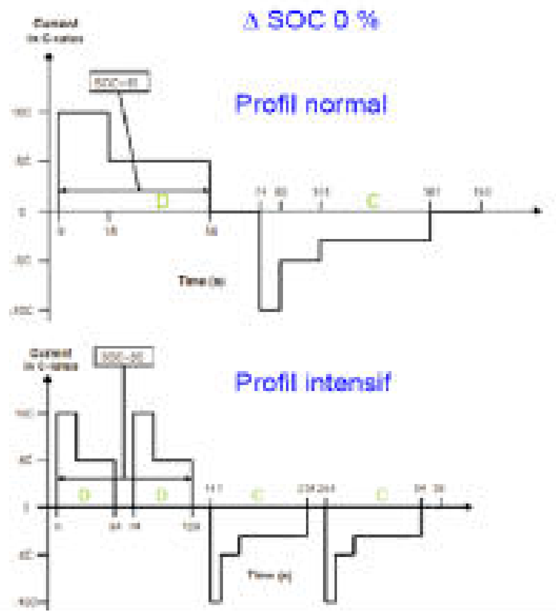

Fig. 5a: Ageing cycles used in LIBERAL program [6]

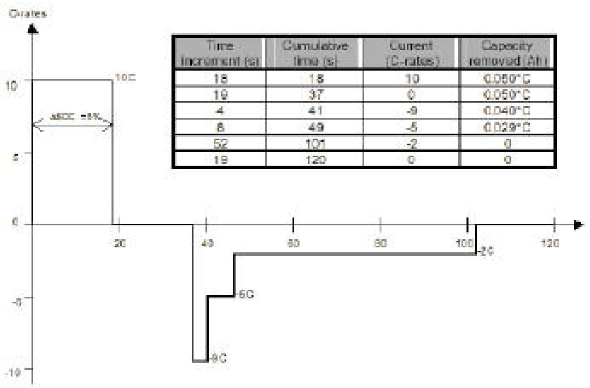

Fig. 5b: Ageing cycles used in EUCAR program [7]

The design rules for the experiments are:

- A cycling day, which consists of 22 h of cycling and 2h of rest. This rest period is necessary in order to preserve an electrode charge homogenization time, as is the case in vehicle type use
- The cycling consists of a succession of microcycles (i.e. charging/discharging pulses)
- The cycling period is divided into macrocycles: some are globally charging and others are globally discharging, in order to cover a SOC variation twice a day
- A daily SOC adjustment with an average value of 60% is performed during the rest period
- The 4 studied parameters are the temperature of the cell (T), the amplitude of SOC variation (ΔSOC), the amplitude of the charging pulse current (I) and the charge throughput of a microcycle (CT in Ah).

The daily voltage profile of a single cell is shown in Fig. 6. The cell, initially at an average SOC, is first discharged, then charged, etc… The detail of the microcycle is also shown in the same figure. The duration of the discharging pulse is set to 5s. The charging or discharging nature of the macrocycle is tuned by the value of the ratio between the charges of the charging and the discharging pulses. The current between two pulses is set to zero.

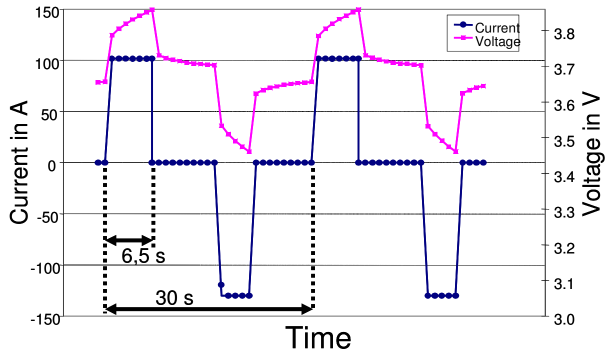

Fig.6a: Micro cycles defined in the SIMSTOCK program

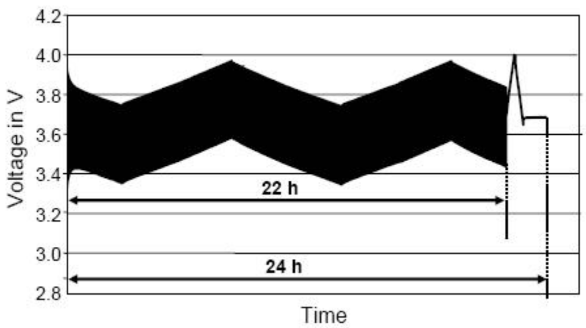

Fig.6b: Macro cycles defined in the SIMSTOCK program

4.3.2 Parameter variations and control

Parameter variations

The number of tests for the study of the influence of the parameters on the ageing process needs to be optimized. It was decided that each of the 4 parameters can have 2 values (a min and a max). The design of an optimal planned experiment showed that 11 different tests are the minimum number. An additional test using median values will be carried out as a validation of the result. Table 1 gives the values of the parameter for each test.

Table 1: Values of the studied parameters for the different tests of the planned experiment on the batteries

Test No.	1	2	3	4	5	6	7	8	9	10	11	12
T	Max	Max	Max	Max	Max	Max	Max	min	min	min	min	med
ΔSOC	Max	Max	Max	Max	min	min	min	Max	Max	min	min	med
I	Max	min	min	Max	min	Max	Max	min	Max	Max	min	med
CT	Max	Max	min	min	Max	Max	min	Max	min	Max	min	med

The SOC variation is obtained using an unbalanced ratio of the quantity of electricity attached to the charging and discharging pulses. In our case, the ratio is adjusted with the values of the current, as the pulse duration is kept constant.

Parameter I is the value of the discharging pulse current of the microcycle. The value of the charging pulse current is linked to that parameter as the ratio Icharging/Idischarging is imposed as a constant for a given type of cell. The ratio is in fact fine-tuned to adjust the SOC variation and its eventual drift which results in a shift of the cell voltage.
Parameter CT is the quantity of charge exchanged during a discharging or a charging pulse of a microcycle. Great care was taken in order to ensure that only one parameter at a time will be varied during the protocol, this means that when the current maximum amplitude varies (from Imin to Imax) the number of pulses varies in order to maintain CT constant together with the duration of a pulse [8]. When parameter CT is modified, the number of pulses in one microcycle is doubled, with the aim of keeping the maximum current and pulse duration constant.

Microcycle shapes
Figure 7 illustrate the microcycles used for the different values (maximun and minimum) of the couple of parameters I and CT.

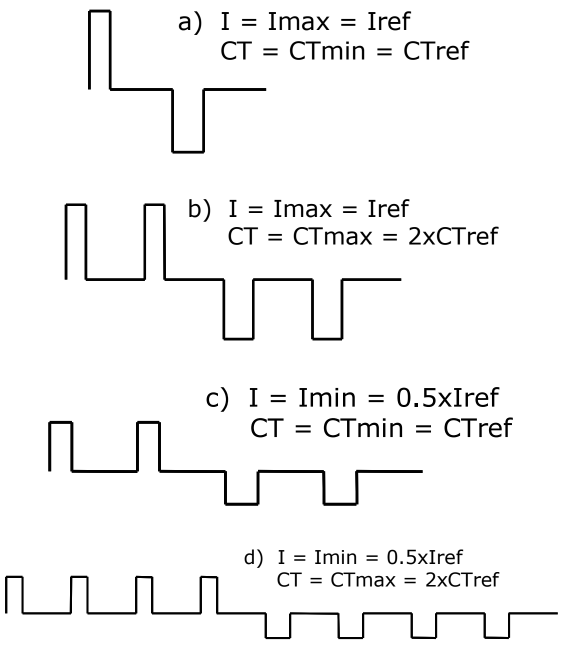

Fig. 7: Microcycle shapes (I vs. time) for the different values of I and CT in the planned experiment

SOC adjustment
The adjustment of the SOC at the end of each cycling day is necessary to compensate the drift due to the inevitable small inaccuracy of the power test equipment in Ah counting during pulse operation. In the case of Lithium-ion cells this adjustment consists in a CC-CV charge to reach 100% SOC and then a CC discharge to reach the desired SOC window for the next test to be carried out.

Cell temperature control
The temperature is measured at the surface of the cell. This implies periodically adjusting the ambient temperature in the climatic chamber according to the type of cell, the characteristics of the test and ageing of the cell. An example of the measured temperature during a complete cycling day is given in figure 8. It appears that the variation of the cell temperature is less than 2°C during the cycling operation. When the cycling stops, the cell temperature decreases to the value of the climatic chamber in less than 2 hours.

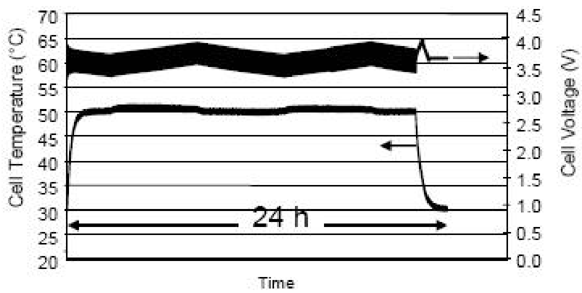

Fig. 8: Temperature of the cell during a cycling day

4.3.3 Characterization protocols

The tested cells are characterized at different phases of the program, i.e.:

- Initially to establish the reference values of the parameters
- Periodically during the cycling in order to record all the changes in their performances during their ageing.

The characterization protocol principle is described in figure 9. It consists of a capacity measurement of each cell, an Electrochemical Impedance Spectroscopy (EIS) of each cell and a time response to a pulse profile. This pulse profile is applied to the full pack and each cell voltage is recorded. The profile contains low current – long time pulse (typically 1C-5min) and high current – short time pulse (typically 7C-10s).

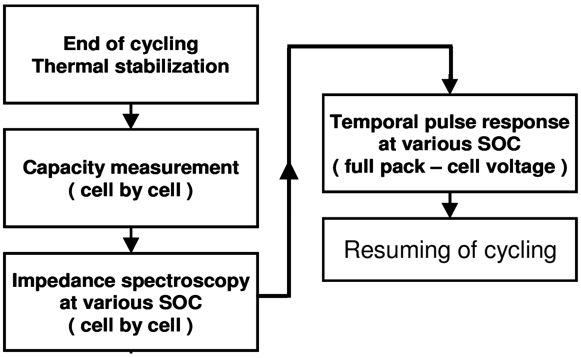

Fig. 9: Description of the characterization sequence

The initial characterization is performed at different temperatures (minimum 2) whereas the periodical characterization is performed at only one temperature in order to save time. The complete protocol at one temperature lasts a minimum of 4 days for the whole 3-cell pack.

4.3.4 Case of supercapacitors

A specific cycle describing supercapacitor use in a vehicle has been defined by the 2 labs INRETS LTN and IMS in charge of the cycling experiments (see fig. 10). The cycle takes into account the following events:

- I.C. Engine cranking with an extremely short, very high discharge current (1)
- Boost operation during vehicle acceleration with a moderate discharge down to the minimum voltage (2)
- Vehicle steady speed operation with no use of the supercapacitor (3)
- Regenerative braking of the vehicle with SC charging up to the maximum voltage (4)
- Vehicle standstill with no current (5).

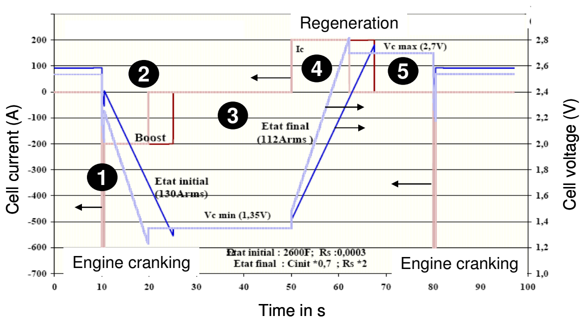

Fig. 10: Supercapacitor specific ageing cycle

It should be noted that the initial cycle will be adapted to the supercapacitor ageing with a shortening of the discharge (2) and charge (4) periods, according to the cell capacity fade during the cycling process.

5 ESS considered in the program

ESS manufacturers SAFT and BATSCAP being active partners of the project, the ageing experiment started using their technology. (SAFT will deliver JCS (Johnson Controls - Saft) cells in the frame of the program). Table 2 hereafter illustrates the different technologies that will be considered in the program.

New technologies for batteries and supercapacitors from other manufacturers may be considered within the 3-year program itself or during phases which may be carried out later.

Table 2: ESS specifications

Manufacturer	Type	Performances
JCS	Li BAT	3,6 V, 7 Ah
JCS	NiMH BAT	3,6 V*, 5,5 Ah
BATSCAP	AN SC	2,5 V, 2000F
BATSCAP	PC SC	2,5 V, 2600 F
LG Chem	Spinel BAT	4 V, 4 Ah
A123	FePO4 BAT	3,4 V, 2,3 Ah
Maxwell	AN SC	tbd
LSMtron	PC SC	tbd

*: 3 modules connected in series

Manufacturer	Chemistry / Reference	Status
JCS	NCA / VL6P	On test
JCS	NR6*	On test
BATSCAP	AN	On test
BATSCAP	PC	On test
LG Chem	LMO	Under discussion
A123	LFP	Considered
Maxwell	AN	Under discussion
LSMtron	SC	Considered

*: 3 modules connected in series

6 Experimental facilities

The realization of such a number of tests needs to gather the experimental facilities of the different partners of the project. The minimum equipment each partner made available to the project consists of a power-testing system (typically 50V 150A for the batteries tests), an EIS-meter and a climatic chamber. Table 3 summarizes the available equipment.

Table 3: Experimental equipment made available by the partners of the project

Partners	Available channels for battery	Available channels for supercapacitors
IMS - Bordeaux	1	1
LEC Compiègne	1	
LRCS - Amiens	4	
CEA Chambéry	6	
EIGSILa Rochelle	4	
INRETS – Paris - Lyon	2	2
Total number	**18**	**3**

In parallel great care was taken in the way the 3 cells which will be tested together will be assembled and connected in series in their climatic chamber. Such a connection will enable us to have the 3 cells tested with the same current and to collect information on the dispersion, as the individual voltage on each of the 3 cells will be monitored. A specific connection will enable us to perform both the cycling tests and the periodic impedance measurements without dismounting the electrical connections, thus ensuring a better reproducibility for a more accurate results analysis (see fig. 11).

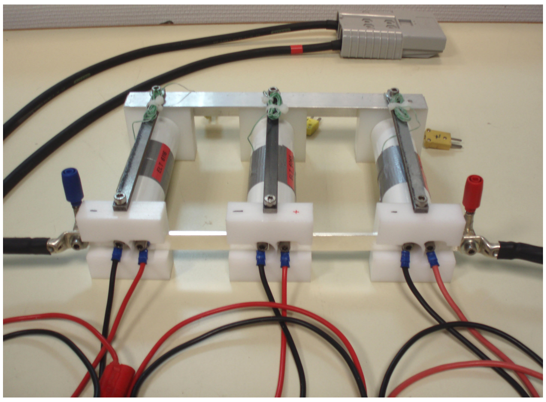

Fig. 11a: Illustration of battery cells connection ready for ageing test

Fig. 11b: Illustration of SC cells connection ready for ageing test

7 Program development

The initial phases of protocol determination and test bench specification and acquisition have now been performed and the ageing experiments on the different test benches started at the end of 2008. One of the major benefits of the program is the setting up of a common testing and evaluation procedure among all the labs involved. Indeed, crossing the methods in the fields of ageing test controls or protocol realization among the different labs involved, from the overall program to the details, was very fruitful. It did delay the project at the beginning but it has enabled the partners to work very closely together, adopting methods that will with no doubt be useful in the future.

The first results recorded after a few months of cycling are now being processed by the partners and will be presented during the conference.

8 Conclusion

The 3-year, 4,2 M€ SIMSTOCK program, which has recently been launched, associates research labs, ESS manufacturers, components and vehicle manufacturers, with the support of the French ADEME.

Partners invested a considerable amount of time at the beginning to establish common testing and evaluation procedures, prior to starting the ageing tests. The research network operates at the present time 23 cycling channels in parallel to perform battery and supercapacitor ageing tests.

SIMSTOCK intends to be more a research network dedicated to ESS ageing than a limited time research program. To that purpose, specific agreements have been made between the French ADEME and the associated research labs in order to be able to continue the ageing research on new ESS types in the coming years, within the framework of possible extended SIMSTOCK research phases.

SIMSTOCK intends to evaluate ESS ageing only during cycling but the network partners have already proposed to the French authorities the SIMCAL program, dedicated to battery calendar life, and which is now in the evaluation process. For the specific case of supercapacitors, an equivalent program SUPERCAL has also been recently proposed by the partners.

Acknowledgments

From the corresponding author to all the SIMSTOCK network partners who have participated: BATSCAP F. Tertrais, CEA Y. Reynier, EIGSI F. Duclaud, EDF L. Jamy, IFP F. Badin, INRETS LTE S. Pélissier, INRETS LTN J. Kauv, IMS J.M. Vinassa, LEC C. Forgez, LMS-Imagine J. Scordia, LRCS C. Delacourt, MTA Cluster C. Adès, PCA D. Porcellato, RENAULT P. Gyan, SAFT S. Bourlot, VALEO B. Soucaze-Guillous, ADEME S. Biscaglia.

The authors wish also to thank the French ADEME for their active support in these researches.

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F. Badin, aged 52, has joined IFP in the beginning of 2008, he is now Director Expert in the field of hybrid vehicles researches. F. Badin has been researcher at the Transports and Environment Lab. (LTE) of the INRETS for more than 20 years. F. Badin was senior researcher, in charge of electric and hybrid vehicles activities at the INRETS.

F. Badin has got a Scientific Doctorate in Environmental Engineering from the University of Chambéry, France and a five years Engineering Degree in thermo-dynamic process at the National Institute of Applied Sciences in Lyon France.

F. Badin is member of the SIA, SAE and IEEE.