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Aging evaluation of high power lithium cells subjected to micro-cycles

M. Ceraolo, G. Lutzemberger*, D. Poli

Department of Energy, Systems, Territory and Constructions Engineering, University of Pisa, Largo Lucio Lazzarino n. 1, 56123 Pisa, Italy

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ABSTRACT

A typical operating condition of storage batteries requires to deliver and absorb small currents in large intervals of time, in order of minutes or hours. However, in the last years lithium batteries have been more and more considered in "power oriented" applications, in which they are required to manage large currents in short intervals of time, typically a few seconds or tens of seconds. Unfortunately, very limited information about this kind of usage is available in literature, in terms of battery performance and aging.

Therefore, the paper focuses firstly on the experimental evaluation of performance of high power and super high power lithium batteries also in comparison to other power oriented storage systems adequate for use onboard hybrid vehicles, such as supercapacitors (SCs). The evaluation has been performed through experimental tests. Results have shown that these batteries are able to guarantee significant performance, even higher than data declared by manufacturer, with slight over-temperature.

Then, for high power lithium batteries aging is discussed, when they are subjected to shallow-depth charge/discharge cycles. The aim is to evaluate if the battery life corresponding to such micro-cycles can reach several hundreds of thousands that are required for applications such as hybrid vehicles and hybrid stationary generation systems. Also in this case experimental tests able to prove it have been executed. They have shown a substantially unaltered capacity fade during the execution of hundreds of thousands of micro-cycles, thus confirming the vocation of these devices for power-oriented applications.

1. Introduction

A frequent operating condition for storage batteries requires to deliver and absorb relatively small currents in large intervals of time, typically tens of minutes or hours. However, energy storage systems more and more are required to deliver or absorb very high currents in short intervals of time, typically a few seconds or tens of seconds. This kind of usage is commonly described saying that this energy storage is "power oriented", opposed to the conventional "energy oriented". As example, three main case studies can be cited.

- *Hybrid vehicles*. According to a standard definition (ISO/TR 8713), the power needed from propulsion comes from at least two independent sources at least one of which being reversible. Typically, one path is composed by a "fueled source", here called *primary converter*, the other one by an, electrochemical energy storage system. According to the most common energy management strategy, the primary converter delivers average load powers, while the battery delivers or absorbs the ripple around that average, thus delivering energy during acceleration, or recovering energy during braking. Typically, these acceleration and braking phases involve durations in the order of seconds or tens of seconds, and require relatively high currents. More precisely, considering that currents are usually given as multiple of the nominal capacity, we can estimate values higher than $10C_n$ [1–5].
- *Tramways*. In the most common tramway systems, the feeding points (electrical substations) power flow cannot be reversed. Therefore, the braking energy of a tram can be recovered only in case there are other trains capable of absorbing that energy. In case, however, the feeding network is equipped in one or more points with an energy storage system, it can absorb energy during braking of some trams, and send it back to the traction system, whenever there is request from the load. This solution promises to enlarge the quantity of the recovered energy significantly. Therefore, the energy storage is subjected to high peak currents up to $10C_n$ when the tram is breaking or accelerating, typically for durations of around 10–20 s [6,7].
- *Stationary applications*. In recent years, electricity grids moved towards an increased share of renewable energy sources (RES), which are continuously being connected to the system and have a distributed nature. RES's, however generate energy in an undispatchable way; sending large RES amount of energy into

* Corresponding author.
E-mail address: lutzemberger@dsea.unipi.it (G. Lutzemberger).

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the grid might cause network stability problems as well as reduced efficiency of other power sources on the grid [8], and therefore it is often highly advisable to store this energy locally to deliver to loads at later times, i.e. when the local generation-load balance allows.

In some of the examined cases, the main concern of using lithium batteries at high currents is during charging, since manufacturers impose limits on the charging current that imply much smaller charging powers than discharging ones. An additional concern over the proposed usage of lithium batteries regards the cell life. In fact, manufacturers typically consider full-depth charge-discharge cycles at continuous, low currents (i.e. $0.5 \div 1C_n$) for which a life of few thousands of cycles is expected [9]. On the other hand, no data are often available for shallow-depth cycles at high currents, hereinafter called "micro-cycles", characterised by a SOC fluctuation lower than 5%, and amplitudes at least higher than $5C_n$.

Also scientific literature lacks details on this topic. In fact, identification of the aging mechanism by analysis of equivalent electrical models, typically involve full-depth SOC fluctuation and reduced current rates [10–12]. In some cases, dependence by thermal effects has been considered [13]. Indeed, aging effects have been also evaluated by performing charging and discharging cycles at highest temperature than ambient [14].

Much more sophisticated techniques are currently in use. As example, a new model for expressing the differential capacity characteristics for SOH estimation, directly associated with the transition behavior of active materials is proposed in [15]. Additionally, also EIS (Electrochemical Impedance Spectroscopy) can be often considered [16]. The changing of the impedance spectra of the lithium ion cells can be analysed starting from the new cell, and evaluating the cycle or calendar life of the aged cell. Then, once disassembled, a post mortem analysis can be also performed [17–19]. However, also in this case the cell is aged through full depth charging-discharging cycles, executed at reduced current rates, far from the real cell usage in power oriented applications.

Only in a reduced number of cases, aging effects have been analysed considering high charging or discharging rates. Unfortunately, only full depth cycles have been considered [20], or asymmetric testing conditions have been selected, i.e. maintaining low charging currents in combination with high discharging current rates [21]. In some other few cases, shallow cycles have been directly investigated. However, DOD does not reach lower values than 20% [22], although sometimes currents higher than $5C_n$ are considered. In other cases, current rates remain significant lower [23].

Aging can be also analysed in reference with lithium cells engaged in electric vehicular applications. In this regard, plug-in hybrid and electric vehicles are mainly considered. However, they typically make use of expressively energy oriented battery pack, normally subjected to full charging-discharging profiles, executed at reduced current rates [24–27]. It must finally be said that standard regulations [28,29] used for laboratory testing activities are typically able to reproduce only in an idealized way the effective stress which the cell is effectively subjected. In fact they typically consider constant charging or discharging current phases. On the contrary much more realistic profiles, according to real stress which the battery is subjected, should be carefully considered, as will be discussed later.

In conclusion, all the presented capacity fade technique analysis are typically made in relation to full-depth SOC fluctuation and reduced current rates, indeed referring to unrealistic stress conditions for power oriented applications. Starting from that, the paper focuses on the experimental evaluation of the aging process for high power lithium batteries subjected to high-current shallow cycles. A briefly evaluation of preliminary results on analogue stress characteristics was also shown in [30]. The aim is to evaluate whether the battery life corresponding to such micro-cycles can reach several hundreds of thousands that are required for applications such as hybrid vehicles and hybrid stationary generation systems.

In terms of the considered methodology, according to the theory that aging is thermally induced, it must be carefully assessed if shallow charging-discharging cycles, i.e. micro-cycles in which high current rates are maintained for a short time, may be responsible of slight over-temperature for the battery. If so, it can be assumed after experimental verification that under these stress conditions aging can effectively occur after several hundreds of thousands of micro-cycles.

A similar approach was followed also in [31] and verified on analogue testing conditions, reproducing the behaviour of hybrid vehicles. Some of the aging results achieved for the cell used in [31] have been here briefly recalled, with the main aim to give much more strength in terms of statistical validity to the obtained results.

Table 1
Cell performance under constant discharging current, high power cell.

Discharge regime I/C_n (A/Ah)	0.5	1	2	5	8
Delivered charge (%)	102	98	97	96	96
Average voltage (V)	3.85	3.80	3.70	3.60	3.50

2. Cell performance

To verify the performance of power oriented lithium batteries, two devices have been selected from the market. The first one, for *high power* applications, the second one, for *super-high power* applications, in which higher limits for discharging pulse currents were indicated. The relative characteristics are described below. Firstly, *super high power* cells were compared with supercapacitors, another energy storage system typology expressively power oriented. After that, much more representative tests of effective usage in high power applications were performed also in case of *high power* cells, reducing durations for charging and discharging, and increasing currents. In particular they started from general stylized shapes, such as rectangular and linear shapes, coming up to representation for real existing stresses, such as current profiles derived from simulation of existing hybrid powertrains.

2.1. Devices under test and laboratory setup

The first device under test is one lithium cell capable of high power,[1] having a nominal, two-hour declared capacity of 13.0 Ah.

Performance data for this cell are available for full discharges to up to $8C_n$, while pulse discharges may be performed up to $15C_n$, where C_n represents the nominal battery capacity, reported in manufacture's datasheet, expressed in Ah.

From manufacturer's graphical documentation reported in [9] the numerical data of Table 1 can be inferred, (where the discharge regime, as already mentioned, is reported in ampere per nominal Ah of battery capacity) that confirms the definite vocation of this battery for high powers, since very little charge penalty occurs.

According to this Table therefore a single cell, whose mass is 332 g, should be able to deliver, at $8C_n$ regime, around 1096 W/kg. However it is not clear how long this discharge regime can be maintained without battery damage, nor what are the current limits during charge, since indication on pulse charging is missing

[1] NMC Lithium cell of the "High Power" family, 13.0 Ah, from [9].