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Cycle Life Evaluation for Lithium-Ion Capacitors

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Summary

Lithium-ion capacitor (LiC) is a hybrid energy storage device which compounds the energy storage mechanisms of lithium-ion batteries (LIBs) and electric double-layer capacitors (EDLCs). Its structure is composed of a positive electrode with activated carbon as in double-layer capacitor and a negative electrode based on Li-doped carbon like the Li-ion battery. The advantage of the LiC technology compared to the conventional storage device is because of the power density, the nominal voltage, and the energy density is higher than the EDLCs. Due to their inherent long cycle life, it is indispensable to predict the cycle life of this cell type. The objective of this paper is to investigate the capacitance degradation of LiCs by calendar life test and power-cycling test. In the calendar life test, the degradation is measured at different floating voltages and temperatures. In the power cycling test, the degradation corresponding to the current level and the temperature is evaluated. The resulting capacitance retention trends declare a dependency to temperature, SoC, and current levels.

Keywords: Lithium ion capacitor, cycle life, calendar life, state of charge, battery model

1 Introduction

Nowadays, the application of energy storage systems based on the rechargeable battery is expanding in many areas like portable electronic devices, large-scale systems, transportation systems and grid-connected applications. Lithium-ion batteries (LIBs) are the optimal battery technology for portable electronic devices and electric vehicles because they have higher energy density and higher specific energy among traditional rechargeable battery technologies. However, there are some drawbacks including the risks of fire or even explosion due to overcharging, abuse, or mechanical damage. In contrast, supercapacitors, formally known as electric double-layer capacitors (EDLCs), are a type of energy storage devices that does not rely on chemical reaction for energy storage mechanisms, offering some significant advantages over traditional rechargeable batteries, like extended cycle life, higher power capability, improved safety, and extended allowable operational temperature range. In spite of the fact that their specific energy (< 15 Wh/kg) is rather low compared to rechargeable batteries, EDLCs are mostly used in hybrid power system [1], including regenerative systems and electric vehicles, and they are operated as high-power energy buffers to complement main rechargeable batteries [2]. Dynamic behavior of EDLCs to adapt for such hybrid applications have also been modeled [3]. As a more practical candidate, lithium-ion capacitors (LiCs) have been developed and commercialized by several manufacturers. LiCs are a hybrid energy storage device that combines the energy storage mechanisms of EDLCs and LIBs, perceives the advantages of EDLCs (i.e. the high power capability, long duration life cycle, and extended operational temperature(-40°C to 70°C) at a relatively high specific energy of > 15 Wh/kg [4]. In [5], detailed characterization for LiCs, comparing with traditional EDLCs [6], and modeling [7] have been done, and in [8] the application of LiC for railway has been investigated. LiCs demonstrate a potential to be an alternative to traditional rechargeable batteries in various applications; from memory back-up and portable power supply to spacecraft power systems [9]. Since the lifetime of LiCs may be estimated in the laboratory more than10 years, life testing under real time span and operation conditions is naturally impractical. In addition, systems cannot be optimally designed without properly estimating cycle life performance of LiCs under practical conditions. Therefore, accelerated aging testing is needed to overcome with the sluggish life testing. Moreover, an accurate cycle life prediction model is required for engineers to effectively design energy storage systems using LiCs. Life testing for LiCs has been performed and accelerated aging testing and cycle life prediction model for LICs have been developed [9] but the effect of current profile on cycling aging and the state of charge (SoC) on calendaring aging at different temperatures has not been considered yet. The target of this paper is typically extending the work performed for LiC in [9] and for the LiC cells procured from JM energy. The chief objectives of this study are to evaluate the cycle life of LIC cells for different applications and to investigate the degradation trend of LiCs. Thus, an accelerated aging characterization based on both calendar life tests and power cycling tests have been investigated and the performances degradation of the LiC was quantified using periodic characterization tests based on the capacity check, hybrid pulse power characterization (HPPC) tests and impedance spectroscopy measurements. Hence, the contribution of calendar aging and cycling aging modes in the performances fading of LiC during power cycling is characterized. The rest of this paper is organized as follows. Experimental conditions are explained in Section 2, the experimental results including charge-discharge cycling tests performed under various conditions and the result of calendaring tests at different temperatures and different SoCs are presented in section 3. The conclusion is given in section 4.

2 Experimental conditions

2.1 Lithium-Ion Capacitors definition

LiC is a new hybrid energy storage device. Its structure consolidates the EDLCs and lithium-ion technology. Its basic structure includes a positive electrode with activated carbon as in double-layer capacitor and a negative electrode based on Li-doped carbon like the Li-Ion battery. In Fig. 1, the chemical structure of LiBs, LiC s and EDLCs has been compared [10].

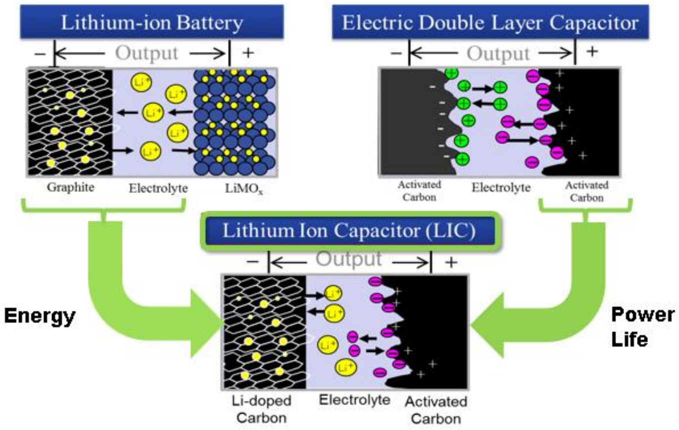

Figure 1. Chemical structure of three different technologies [10]

The advantage of the LiC technology compared to the conventional energy storage systems is the higher power density in comparison with LiBs, the higher nominal voltage and the much higher energy density in comparison with the EDLCs. Some other features of LiC are high peak currents for fast charge and discharge, linear charge and discharge characteristics which allow accurate SoC determination, wide operating temperature range, excellent durability and reliability, low self-discharge, and safe in-use [10]. The LiC cells which were used in this study for the cycle life performance evaluation were procured by JM energy manufacturers. In table 1, some characteristics of the new type of LiC cells (CPQ2300SB) are shown.

Table 1: LiC cells characteristics used for tests [10]

Measurement Items			**ULTIMO 2300F ULR Prismatic**	**Conditions**
Range of Operating Temperatures			-30°C~70°C	
Rated Voltage		Maximum	3.8V	
		Minimum	2.2V	
Initial Characteristics		Capacitance	2300F	Constant Current Discharge, 25°C
		ESR	0.6mΩ	1kHz
		DC-IR	0.7mΩ	Constant Current Discharge, 25°C
		Weight E-density	8Wh/kg	Constant Current Discharge, 25°C
		Volume E-density	14Wh/L	
Temperature Dependence	-20°C	Capacitance ratio (vs 25C)	85%	Constant Current Discharge, 25°C
	70°C		100%	
Self-Discharge Characteristics		Voltage Reduction	< 5%	3 Months,25°C
Cell size			150.0x93.0x15.5mm	Without Terminal
Weight			0.355kg	

2.2 Cycling and calendaring conditions

To investigate the degradation dependence to the temperatures, current level and initial voltage level (SoC), eighteen cells were assigned for life-cycle tests. For cycle aging tests, nine cells as shown in table. 2 were cycled at three different temperatures with different load profiles as shown in Fig. 2. These power profiles are used to evaluate degradation trend for different applications like UPS (uninterrupted power supply), heavy transportation like tramways and stationary application for peak power shaving. As shown in the Fig. 2, the load profiles are different in terms of the durations and the Root Mean Square (RMS) value of power. It means that the exchanged energy in one cycle of different load profiles are completely different. To compare the effect of current level and number of cycles on the capacity degradation, the equivalent number of cycles is considered. The equivalent cycle is the division of accumulative discharged capacity over the initial capacity as a reference which is measured at 25°C. The equivalent cycle is calculated by equation (1) [10]:

$$Number\ of\ equivalent\ cycles = \frac{Accumulative\ discharge\ capacity}{Initial\ capacity} \quad (1)$$

The load profiles used for cycling tests are shown in Fig. 2. The low duty (LD) power profile corresponds to the applications in which LiCs are used as an alternative to rechargeable batteries. The heavy duty (HD) load profile corresponds to a peak power shaving application and the root mean square (RMS) load profile corresponds to a transportation application. After every 10000 cycles of the above-mentioned load profile, the capacity is measured at the ambient temperature (25°C) and is normalized with the initial capacity of the cell at the beginning of life (BOL). As it is seen, these load profiles are power based. The charge and discharge current is limited with the boundaries of tester which is 250A.

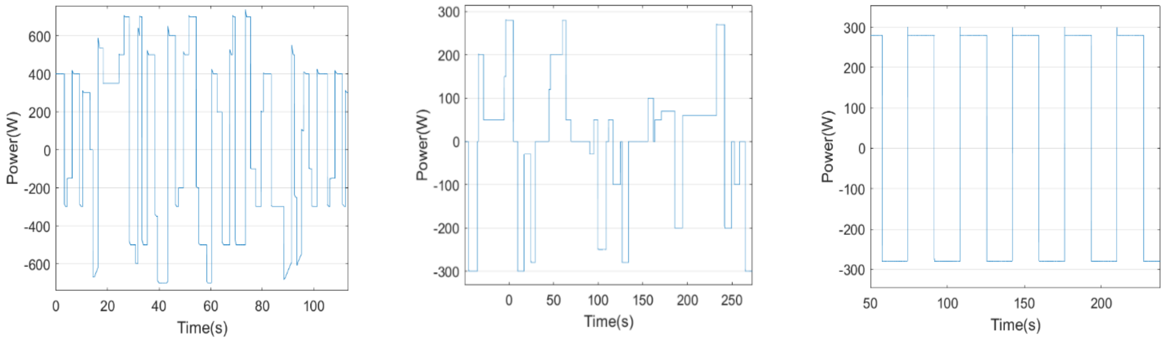

Figure 2: HD profile (left), LD profile (center), and HD RMS (right)

Table 2: Cycling conditions and test profiles

Cell number	Cycling profile	RMS value (W)	Temperature (°C)
1	HD	479	0
2	HD RMS	280	
3	LD	148.15	
4	HD	479	25
5	HD RMS	280	
6	LD	148.15	
7	HD	479	45
8	HD RMS	280	
9	LD	148.15	

For the calendar aging test, nine cells are placed at three different temperatures with different SoCs, as shown in table 3. Every month, the capacity and internal resistance is measured at the ambient temperature and is normalized with the initial characteristic at BoL.

Table 3: calendaring conditions

Cell number	SOC (%)	Temperature (°C)
10	0	0
11	50	
12	100	
13	0	25
14	50	
15	100	
16	0	45
17	50	
18	100	

3 Experimental results for cycling and calendaring tests

3.1 Cycling tests

The capacity degradation trend during the cycle aging tests for different load profiles are shown in fig.3. For the HD load profile, the cell in 45°C has the highest capacity degradation. However, because of the cycling in this temperature, the internal resistance and as a result the heat generated in the cell has increased. Finally, the cell temperature reached to 70°C and the test was stopped for safety. For the cell cycled at 25°C with HD load profile, the capacity degradation is less than the others which means cycling at 25°C has less aging effect. For cells cycled with LD profile, the capacity degradation trend is to some extent similar. The degradation deference for this load profile at different temperature and after 60000 equivalent cycles is less than 0.5%. It means that for the LD load profile, the temperature does not have a big impact on the cells degradation. For HD (RMS), the cell cycled at 0 degrees has less degradation in comparison with others. the impact is significantly less than others. For a certain number of equivalent cycles and at a certain temperature, HD load profile has the most impact on the cells in comparison with the other load profiles. However, for a better understanding, we still need to go further and investigate more results.

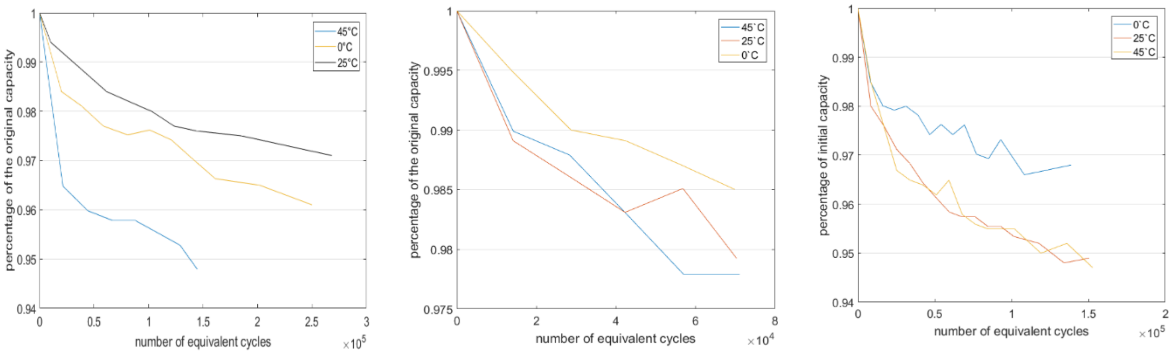

Figure 3: The capacity degradation trend for HD (left), LD (center), HD average (right) load profiles and at different temperatures

3.2 Calendaring tests

The capacity degradation trend for cells placed at different temperatures with different SOCs is shown in fig.4. It is observed that the cells with 100% SOC have the capacity increment for the first 3 months and later the capacity fluctuation can be seen. At this SoC, less capacity degradation is related to the higher temperature which means at higher temperature, materials stay active and the degradation speed is lower. For 50% SoC the impact of temperature is quite significant so that after 8 months, the cell stored in the 45°C climate chamber has lost 4 percent of the initial capacity while for the cell at 0°C it is only 2 percent. In comparison with 100% SoC, it is concluded that the initial SoC has a big effect on the cell. For cells with 0% SoC, the impact of temperature is even worse than cells at 50% SoC. Since this test has not been performed previously, it is needed to investigate this test for a longer period to see the effect of SoC on this trend.

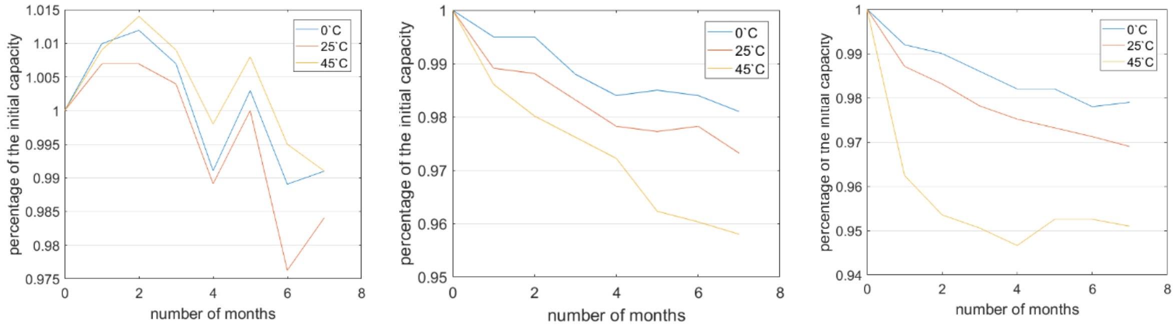

Figure 4: the capacity degradation trend for 100% SOC (right), 50% SOC (centre) 0% SOC (right) and at different temperature

4 Conclusion

Cycle life performances of LiC cells were evaluated in this study. LiC cells were procured from JM energy manufacturer were cycled at various temperatures and with a different load. The capacitance retention trend of LiC cells were briefly investigated and the dependency on the temperatures and load profile has been proven. The higher the temperature is, the more the LiCs deteriorated, implying that aging can be accelerated by elevated temperatures. The impact of load profile on the degradation trend is also confirmed. For the HD load profile, 25°C has less effect while for LD and HD(RMS) the 0°C has less effect. For calendaring tests, it is seen that the SoC and temperature affect the degradation trend. The higher SoC is, the lower degradation will be. Moreover, for 0%SoC and 50%SoC, keeping the cells at 45°C has the biggest effect on aging while for 100%SoC, keeping the cell at 45°C has the lowest effect. According to the test results a combination of temperature, load profile, and the initial SoC should be considered in the lifetime modeling. Moreover, in a real application, a combination of these parameters will affect the lifetime which is necessary to find a way to translate these parameters to a normalized value for a quick state of health (SoH) estimation and lifetime prediction.

5 Acknowledgments

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7 Authors

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