Performance and Safety of Lithium-ion Capacitors

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Abstract: *Lithium-ion capacitors (LIC) are a recent innovation in the area of supercapacitors and ultracapacitors. With an operating voltage range similar to that of lithium-ion batteries and a very low self-discharge rate, these can be readily used in the place of batteries especially when large currents are required to be stored safely for use at a later time.*

Keywords: lithium-ion capacitors; LIC, LICs, lithium-ion supercapacitor safety; high-voltage range capacitors.

Introduction

Lithium-ion capacitors are a hybrid between lithium-ion batteries and Electric Double Layer Capacitors (EDLC). Not much work has been carried out or published in the area of LICs. The cathode in the LICs is activated carbon and the anode is lithiated or lithium-ion doped carbon. The electrolyte is made up of a combination of organic solvents and a lithiated salt. The charge in the LIC is stored at the surface of the cathode in the electric double layer that develops between the cathode and the electrolyte. Figures 1 and 2 show the difference between the LIC and a lithium-ion battery [1]. The LICs described in this paper were manufactured by JSRMicro LLC. The voltage range provided by these LICs are higher than traditional capacitors, supercapacitors or ultracapacitors. The LICs have an operating voltage range of 3.8 V to 2.2 V. These can be charged to a voltage of up to 4.2 V, if needed, although this may reduce the cycle life of the LICs. The LICs tested under this program were of 1 Ah capacity. This paper will provide the details of the testing carried out on the LICs and will describe the performance and safety under a set of nominal and off-nominal conditions respectively.

Figure 1. Schematic of Lithium-ion Capacitor (LIC). Courtesy: JSR Micro Inc.

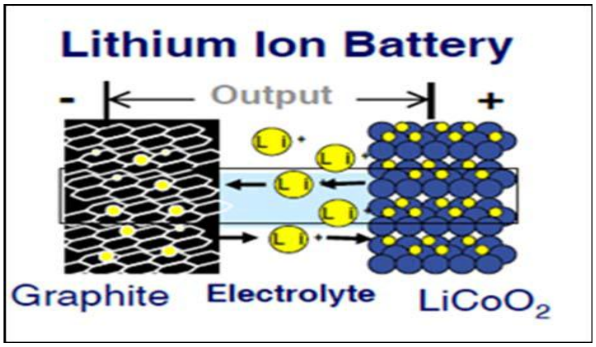

Figure 2. Schematic of a Lithium-ion battery. Courtesy: JSR Micro Inc.

Experimental

The tests carried out on the LICs to determine their performance testing included rate capability tests, performance at different temperatures, self discharge tests at different end-of-charge voltages, and high rate charge to nominal end of charge voltage. The safety tests included overcharge, overdischarge, external short, simulated internal short and heat-to-vent tests. The dimensions of the 1Ah LICs were 93mmX149.5mmX15.5mm and the mass was 370 g.

The rate capability tests included 100 cycles of charge and discharge between 3.8 V to 2.2 V, at various rates with currents of 1.5 A, 5.0 A, 7.5 A and 10 A charge currents and 1.5, 3.0 and 10A discharge currents in various combinations. A typical charge and discharge profile was used for a majority of the tests except the rate capability test which consisted of a charge current of 10 A to 3.8 V limit, hold at 3.8 V for 30 minutes and then discharge using a current of 10 A to 2.2 V. The performance at -30 ºC, -20 ºC, 0 ºC, 40 ºC, 60 ºC and 70 ºC was determined by charging and discharging at the stated temperatures using the typical charge and discharge profile. The self-discharge tests included storing the LICs at different end-of-charge voltages of 2.5 V, 3.0 V, 3.8 V and 4.2 V for more than 60 days. The change in open circuit voltage and the capacity retained were determined. The latter was carried out by discharging the LICs at a current of 1 A to 2.2 V. The high current charge test consisted of charging the LICs to 3.8 V at currents of up to 800 A. When the LIC was subjected to a high rate charge at 100 A, it was stored for seven days at the end of charge voltage and discharged using 10A current to determine the capacity retained under a high rate charge and short storage period.

The LICs were subjected to an overcharge test using a charge current of 1 A to a voltage limit of 20 V for a period of 6 hours. The overdischarge test consisted of discharging the LIC to 0 V using a current of 1 A. The external short test consisted of shorting the LIC using a load of less than 1 mohm (~0.85 mohm) with data collected at the rate of 1 kHZ for the first three seconds and then at the rate of 1Hz for the rest of the test. The simulated internal short was carried using a blunt rod and causing an indentation that would cause an internal short without penetrating the cell. The heat to vent test was carried out by heating the LIC at full state-of-charge at a rate of 3 ºC per minute until the LICs vented.

Results and Discussion

The Table 1 provides details of the various charge and discharge rates that the LICs were subjected to. It was observed that the capacity obtained under these various rates were greater than 1.4 Ah except for the 5.0 A charge and 10 A discharge protocol where capacities between 1.3 and 1.4 Ah were achieved. The capacity loss in all cases after the 100 cycles was insignificant with a maximum capacity loss recorded of less than 2 %. Figure 3 shows a typical charge and discharge profile for the LIC under the conditions described in the Experimental section.

Table 1. Results of Rate Capability Test on the 1 Ah LICs.

PCTest SAMPLE #	Test Number	Serial #	1st Cycle Capacity (Ah)	100th Cycle Capacity (Ah)	Capacity Change (%)	Capacity Change (Ah)
01	Protocol 1-1 (1.5A/10.0A)	3AL16-54	1.451	1.438	0.9%	0.013
02	Protocol 1-2 (1.5A/10.0A)	3AL16-56	1.469	1.463	0.4%	0.006
03	Protocol 1-3 (1.5A/10.0A)	3AL16-55	1.459	1.433	1.8%	0.026
04	Protocol 2-1 (5.0A/10.0A)	3AL16-57	1.314	1.310	0.3%	0.004
05	Protocol 2-2 (5.0A/10.0A)	3AK16-7	1.396	1.374	1.6%	0.022
06	Protocol 2-3 (5.0A/10.0A)	3AK16-9	1.413	1.399	1.0%	0.014
07	Protocol 3-1 (7.5A/10.0A)	3AK16-6	1.420	1.402	1.3%	0.018
08	Protocol 3-2 (7.5A/10.0A)	3AK16-8	1.424	1.425	-0.1%	-0.001
09	Protocol 3-3 (7.5A/10.0A)	3AK16-3	1.420	1.396	1.7%	0.024
01	Protocol 4-1 (10.0A/1.5A)	3AL16-54	1.491	1.488	0.2%	0.003
02	Protocol 4-2 (10.0A/1.5A)	3AL16-56	1.484	1.482	0.1%	0.002
03	Protocol 4-3 (10.0A/1.5A)	3AL16-55	1.496	1.494	0.1%	0.002
04	Protocol 5-1 (10.0A/3.0A)	3AL16-57	1.443	1.433	0.7%	0.010
05	Protocol 5-2 (10.0A/3.0A)	3AK16-7	1.458	1.456	0.1%	0.002
06	Protocol 5-3 (10.0A/3.0A)	3AK16-9	1.449	1.446	0.2%	0.003
07	Protocol 6-1 (1.5A/1.5A)	3AK16-6	1.456	1.451	0.3%	0.005
08	Protocol 6-2 (1.5A/1.5A)	3AK16-8	1.467	1.464	0.2%	0.003
09	Protocol 6-3 (1.5A/1.5A)	3AK16-3	1.459	1.458	0.1%	0.001

The performance at various temperatures indicated that at -30 ºC 1 Ah capacity was obtained, 1.2 Ah capacity was obtained at -20 ºC, 1.33 Ah capacity was obtained at 0 ºC, and 1.5 Ah capacity was obtained at 40 ºC, 60 ºC and 70 ºC. The maximum temperature increase observed through the discharge was 4 ºC. Figure 4 gives the charge and discharge profile at -30 ºC.

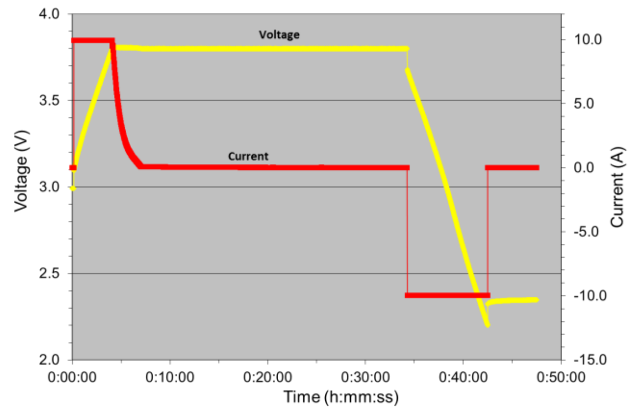

Figure 3. Typical charge and discharge profile for the Lithium-ion Capacitor (LIC).

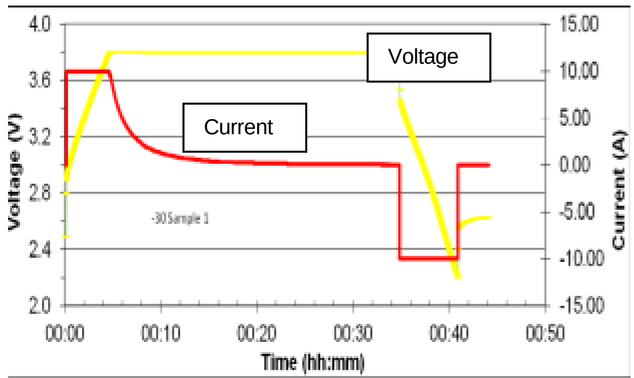

Figure 4. Performance of the LIC at -30 ºC.

The self-discharge test indicated that the maximum discharge occurred when the LICs were stored at 4.2 V displaying a loss in voltage of 7.4 % over the storage period where no change in voltage was observed when the LICs were stored at 2.5 V and 3.0 V. Table 2 provides the data on the voltage change and the capacity retained by the LICs after the storage period. Figure 5 provides the open circuit voltages (OCV) recorded once a day during the storage period.

Table 2. Results of the Self-Discharge Test on the 1 Ah LICs.

Sample #	Sample ID	Initial OCV (V)	Final OCV (V)	Capacity Retained (Ah)
1	16	4.183	3.868	1.724
2	17	3.784	3.698	1.425
3	18	2.996	2.984	0.675
4	19	2.524	2.540	0.306

The high-rate charge test with a charge current of 100 A and a storage period of even days after the charge provided up to 1.5 Ah capacity when discharged using a current of 10 A, after the storage period. Charging at currents of up to 800 A indicated that the maximum charge current accepted by the LIC was 140 A which is 140C rate for the 1 Ah LIC.

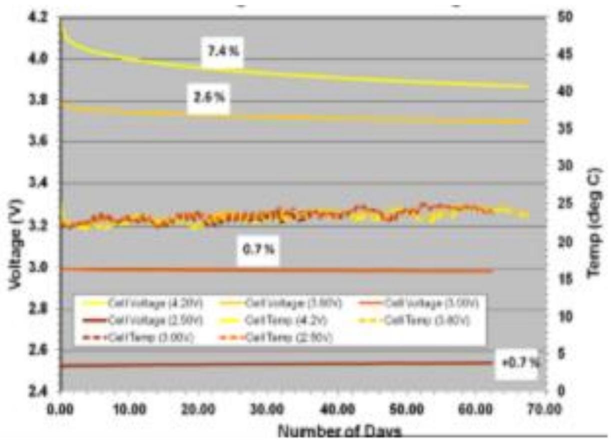

Figure 5. Self-Discharge tests showing OCV recorded each day for the Lithium-ion Capacitor (LIC) during the storage period.

The overcharge test resulted in the LICs swelling but no venting, fire or thermal runaway was observed. The maximum temperature observed was 40.7 ºC and the voltage plateaued at 4.77 V during the overcharge period. Figures 6 and 7 show the pictures of a typical LIC and one that was subjected to the overcharge test. The overdischarge test did not cause any venting or fire of the LICs but swelling of the LICs was observed and the maximum temperature recorded was 47 ºC. The external short test resulted in a maximum temperature rise of 29 ºC and currents of up to ~1900 A was recorded within the first few milliseconds after the short was applied. Figures 8 and 9 provide details of the external short test with data recorded at slow (1Hz) and fast (1kHz) data collection rates respectively. Under the simulated internal short test conditions, a maximum temperature of 97 ºC was recorded and the LICs exhibited venting and smoke but no fire. Similarly, when the LICs were subjected to the heat-to-vent test, the LICs vented at temperatures greater than 175 ºC and exhibited smoke but no fire.

Figure 6. Photo of typical LIC.

Figure 7. Photo of LIC after the overcharge test showing swelling.

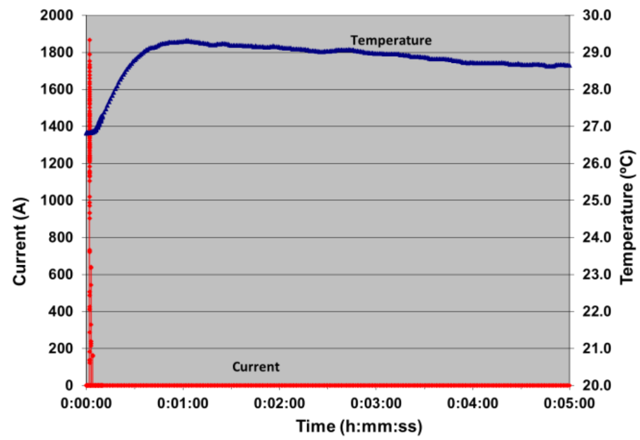

Figure 8. External Short Test on the LIC showing current and temperature recorded at 1Hz rate.

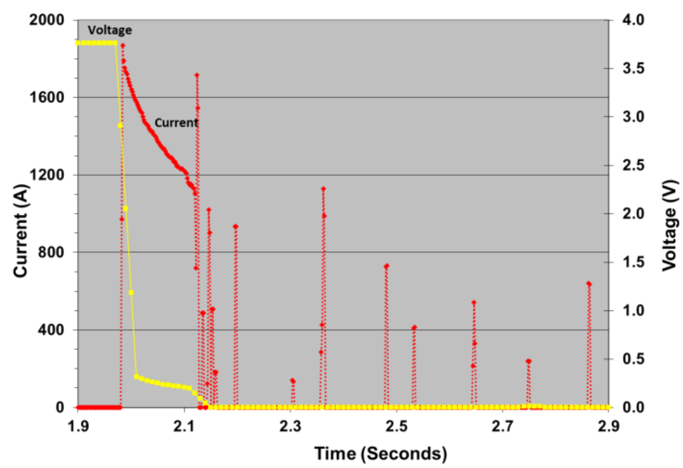

Figure 9. External Short Test on the LIC showing current and voltage recorded at 1kHz rate.

Summary

The performance of the LICs exceeded that stated in the specification sheet. At nominal discharge rates of 10 A, the capacity of the LICs was almost 50% more than the rated capacity. The LICs performed well at temperatures as low as -30 ºC providing the nameplate capacity of 1 Ah. No change in capacity was observed at 70 ºC compared to room temperature capacity. The LICs accepted charge of up to 140 A and although currents as high as 200A were accepted, the upper voltage limit of 3.8 V was reached instantaneously preventing nominal charge. The LICs did not show any fire or venting under conditions of overcharge and overdischarge as well as external shorts. The LICs showed venting and smoke under conditions of simulated internal short as well as high temperatures of greater than 175 ºC. The off-nominal tests indicate that the LICs have a higher tolerance to abuse than lithium-ion batteries.

Acknowledgements

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References

1. Technical Bulletin and communication, JSR Micro Inc.