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Simulation study on the lifetime of electrochemical capacitors using the accelerated degradation test under temperature and voltage stresses

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ABSTRACT

Several studies on the degradation mechanism of electrochemical capacitors have been conducted, but they have not predicted and analyzed the lifetime of the capacitors. A capacitor's life is normally considered to end when its capacity is reduced to 20% of the initial level or its ac equivalent series resistance (ESR) increases by 200% compared its initial value. Once the ac ESR reaches a failure state, it becomes impractical to use it as a factor to determine the failure of an electrochemical capacitor; hence, only the capacity is considered as a factor when determining a capacitor's failure. This method, which is used for small-scale electrochemical capacitors employed as capacitance backup, cannot be applied to new electrochemical capacitors with high output and low resistance. Therefore, we analyzed a failure mechanism by conducting a load-life test on high-output cylindrical-shaped electrochemical capacitors under different voltages (2.5, 2.7, and 2.9 V) and temperatures (333.15 K, 343.15 K, and 353.15 K) for 1000–1500 h, using the simulation software ALTA 8 PRO and Weibull++8. By proposing an appropriate dc ESR as a life-determining factor for existing capacitors and by analyzing different failure conditions (150%, 180%, and 200%) through comparison, we found that a 180% increase in the dc ESR over its initial level is the most appropriate factor to be used as a failure condition for electrochemical capacitor performance. In addition, in the case of performance degradation due to voltage and temperature changes, an acceleration factor for each condition has been deduced, facilitating a preliminary performance evaluation w an accelerated life test.

1. Introduction

An electrochemical capacitor is an energy storage device used for memory and real-time clock backup because of its low capacity and long lifetime, and it was first commercialized in VCR, audio, and industrial products [1]. After the capacitance of this type of capacitor was increased by increasing its size, it was used in products that require high output performance.

Recently, several applications have required a long life cycle—over 1000,000 cycles—within pulse power applications, such as idle stop and start, voltage stabilizer systems, forklifts, container cranes, subways, and elevators. The general charge and discharge cycle per day ranges from 200 to 500 cycles, and the lifetime is more than 10 years; the life cycle in these applications is therefore more than 1000,000 cycles. With the widespread use of electrochemical capacitors, the demand for performance improvement in these capacitors has increased. Accordingly, because of the changes in the estimation methods of the lifetime of electrochemical capacitors, numerous studies have been conducted on the degradation mechanism and lifetime estimation of electrochemical capacitors [2,3]. Various degradation mechanisms, such as gas generation in high-voltage experiments and impedance analysis in high-speed charging/discharging, have been reported. Nevertheless, some experiments and studies have been conducted on lifetime estimation [1,3].

The lifetime of electrochemical capacitors is known to be 100,000–1000,000 cycles, depending on the charging/discharging conditions; thus, a considerable amount of time is needed to estimate capacitor lifetime. For this reason, accelerated life tests and degradation tests have been performed because they can provide quick results for analysis. The high-temperature tests are conducted to study performance over 1000 h (42 days) or even longer, such as 2000 h or 3000 h. Techniques for reducing the time required for high-temperature tests have recently been reported [1,3]. Kobayashi applied the "10 K law of temperature" for electrolytic capacitors, which states that a 10 K increase in temperature reduces the lifetime of the electrochemical capacitor by half, which is similar to the case of metal-can-enclosed electrical double-layer capacitors. However, this law is not applicable at temperatures greater than 343.15 K [1]. Kotz monitored the capacitance, internal resistance, and leakage current in a reliability test for 1000 h. Aging was significantly accelerated by elevated temperatures and increased voltage. The capacitors failed only under extreme conditions, at voltages of

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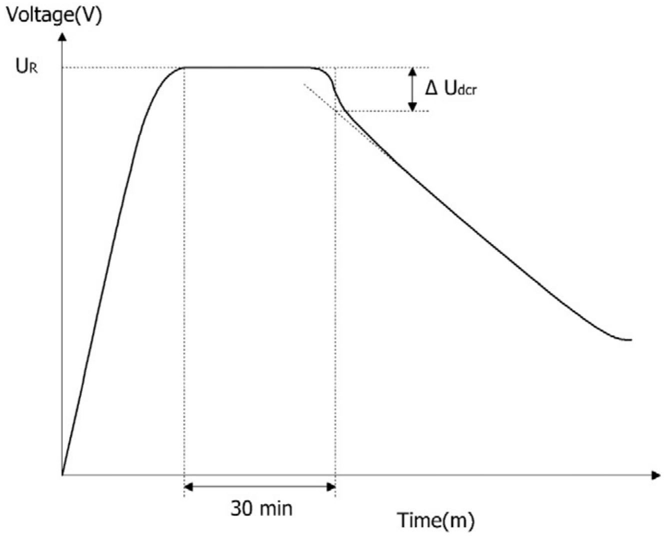

Fig. 1. Voltage across capacitor terminals.

3.5 V or temperatures above 343.15 K, due to internal pressure build-up. No other failure events, such as an open circuit or a short circuit, were observed [2].

The lifetime of lithium secondary cells have been reported by analyzing the failures during the charging/discharging cycle tests [4–8]. Eom reported a lifetime prediction and reliability assessment for lithium secondary batteries. The applied software tool was the min-tab, and the test method was the cycle life of the charge and discharge at room temperature [4]. Belt investigated the effect of temperature on the capacity and power of rechargeable lithium batteries. Temperature had a very small effect on the capacity and power [5]. A lifetime prediction and analysis of lithium secondary cells in accelerated degradation tests was reported by Thomas [6,7]. Gualous studied the lifetime of electrochemical capacitors and their degradation due to the charging/discharging cycles [3]. Bohlen reported an aging model for electrochemical capacitor cells and a lifetime simulation model for modules using impedance analysis and Mat-lab software [12,13]. Oukaour investigated the diagnosis method using an aging test at a constant voltage and temperature of 2.9 V and 338.15 K, respectively [14]. Alam studied the two stress conditions, at 378.15 K and 398.15 K and at 250 V and 285 V, for the Multi Layers Ceramic Capacitor [15].

There is no adequate international standard to estimate the capacity of electrochemical capacitors for use in pulse power applications. Moreover, there is a lack of evaluation methods in the literature. In the present study, we report dc equivalent series resistance (ESR) as the new evaluation factor for electrochemical capacitors used in pulse power applications with more than 1000,000 cycles. The capacitance, ac ESR, and dc ESR are the criteria used to determine the failure and degradation of electromechanical capacitors. Stress factors related to the lifetime (voltage and temperature) and performance factors (dc ESR, ac ESR, and capacitance) are used as the basis for the lifetime degradation test, and a lifetime model is proposed based on the corresponding analysis. An accelerated model, which explains the relationship between the accelerated and average lifetime, is developed and is aimed at reducing the lifetime prediction time by applying an acceleration factor (AF).

Table 1
Number of samples for each stress factor (temperature and voltage).

Voltage	Constant load			Total number
Temperature	2.5 V	2.7 V	2.9 V	
333.15 K	16	16	16	48
343.15 K	16	16	16	48
353.15 K	16	16	16	48
Total	48	48	48	144

Table 2
Experimental conditions.

Test temperature	Test time (h)	Measurement time (h)
333.15 K and 343.15 K	1,500	0, 100, 200, 500, 880, 1,000, and 1,500
353.15 K	1,000	0, 100, 200, 500, 880, and 1,000

2. Experiment

2.1. Capacitor cell preparation

In this study, a high power-structured cylinder-shaped (diameter = 10 mm and length = 20 mm) 1020-size 2.5 V and 2.5 F capacitor cell sample that exhibits high instant-output performance was manufactured. YP-50 (active carbon with high-voltage and high-output performance, produced by activating a palm family tree using a vapor deposition method) from Kuraray Chemical was used as the active material for the electrodes. A slurry was prepared by coating (through dry and wet mixing processes) with a conductive agent (SUPER-P®, TIMCAL) and a rubber binder (SBR, Zeon). An aluminum etching foil (CB-20, Korea JCC) was used for the bipolar plate, and 130 μm electrodes were prepared after coating the two sides. The prepared electrodes were installed on the cylindrical structure and vacuum dried in an oven at 423.15 K for 24 h, impregnated with a 1.0 M $TEABF_4$/propylene carbonate electrolyte (C1110, SK Chemical), sealed with a rubber closure, and assembled after curing within an aluminum case. From the manufactured capacitor cells, 144 cells were selected by measuring the capacitance and the dc and ac ESRs without aging.

2.2. Performance test method

The performance test method was based on International Standard IEC 62391-1 and the ac and dc ESR measurement methods established in 2006. The performance of the prepared samples was tested using the capacitance and conformed to the corresponding IEC 62391-1 Class 2 standard as a small-output device [9].

2.2.1. Capacitance

A constant charging current of 1 mA/F was passed for 30 min, and the time was measured for discharging from 2.0 V dc to 1.0 V dc. The capacitance was calculated using the following formula:

$$C = \frac{(i \times T)}{V_c}$$

where C is the capacitance (F), i is the discharge current (mA), T is the discharge time (s), and V_c is the voltage (V) [9].

2.2.2. AC ESR

The voltage readings in the range of 0.2–0.5 V measured at 1 kHz ± 200 Hz were recorded. The internal resistance ac ESR of a capacitor was calculated as follows, after measuring the voltage within the 1-kHz frequency, for a current between 1 mA and 10 mA:

$$R = \frac{V}{I}$$

where R is the ac internal resistance (Ω), V is the effective ac voltage (V), and I is the effective ac current (A) [9].

2.2.3. DC ESR

An auxiliary line that extends the straight part of the time-varying voltages between the capacitor terminals obtained from the voltage