



WHITE PAPER

ULTRACAPACITOR VOLTAGE, TEMPERATURE, AND LIFETIME

Capacitance and resistance change in time during the continuous cycling

An ultracapacitor is an energy storage device, in which the energy is stored on porous carbon electrodes by physical adsorption. Therefore, they are free of chemical reactions, unlike batteries, and can survive hundreds of thousands of charge-discharge cycles. This means that when using ultracapacitors between rated voltage U_R and $\sim 1/2$ of U_R , theoretically, the resistance and capacitance should be very stable over long period. In reality, however, the capacitance and resistance change during cycling. When cells are used at room temperature, these parameters change almost constantly. Generally, end of life criteria are either reaching 80% of the ultracapacitor's original capacitance, or 200% of its original internal resistance R . Fig.1 shows typical C and R degradations at different operative U_R voltages. It is clear that when capacitors are used below U_R , the lifetime can be significantly longer than 1 million of cycles at room temperature.

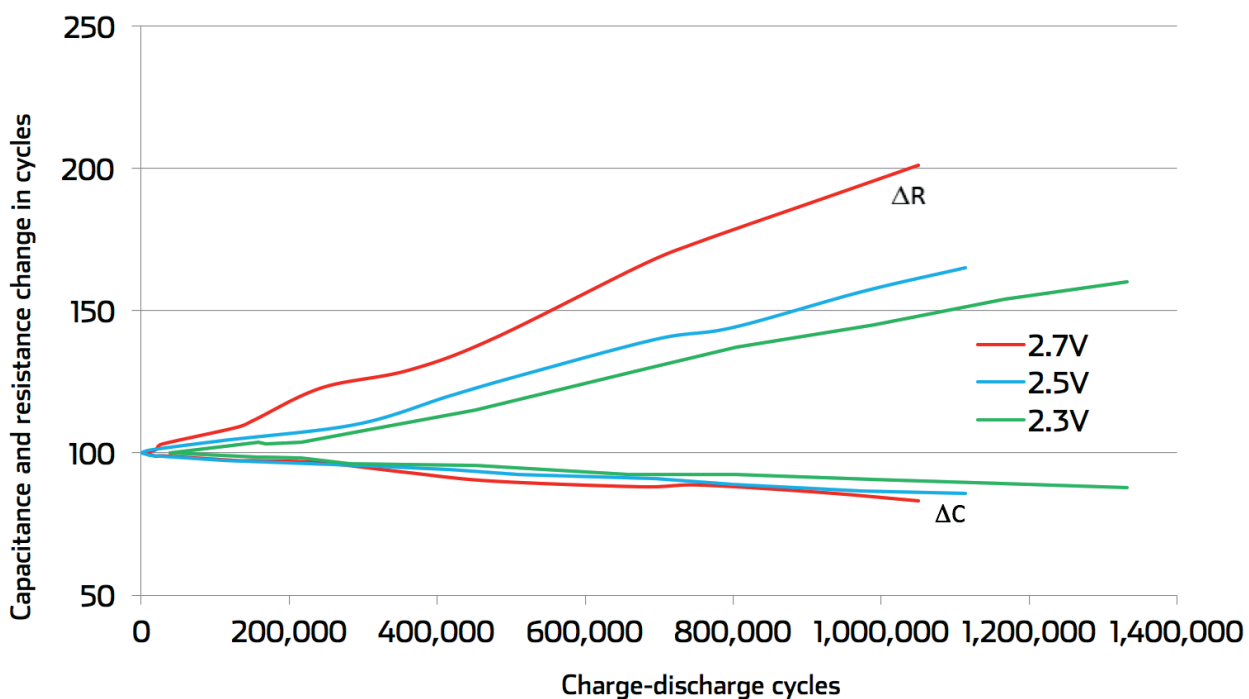


Fig. 1. Capacitance and resistance degradation of ultracapacitors by the cycling at different voltages.

Influence of temperature

The working temperature of an ultracapacitor has a direct influence on its lifetime. By increasing the capacitors application temperature, the lifetime shortens, i.e. capacitance decreases and resistance increases. In accordance with Arrhenius law, increasing the cell temperature by 10°C decreases the lifetime twice over. For establishing the lifetime dependency on working temperature, the capacitors are kept at elevated temperature at constant voltage U_R . During capacitor ageing, C and R are measured regularly as shown on Fig. 2. The changes in C and R values are mostly caused by the side-reactions in the electrochemical system.

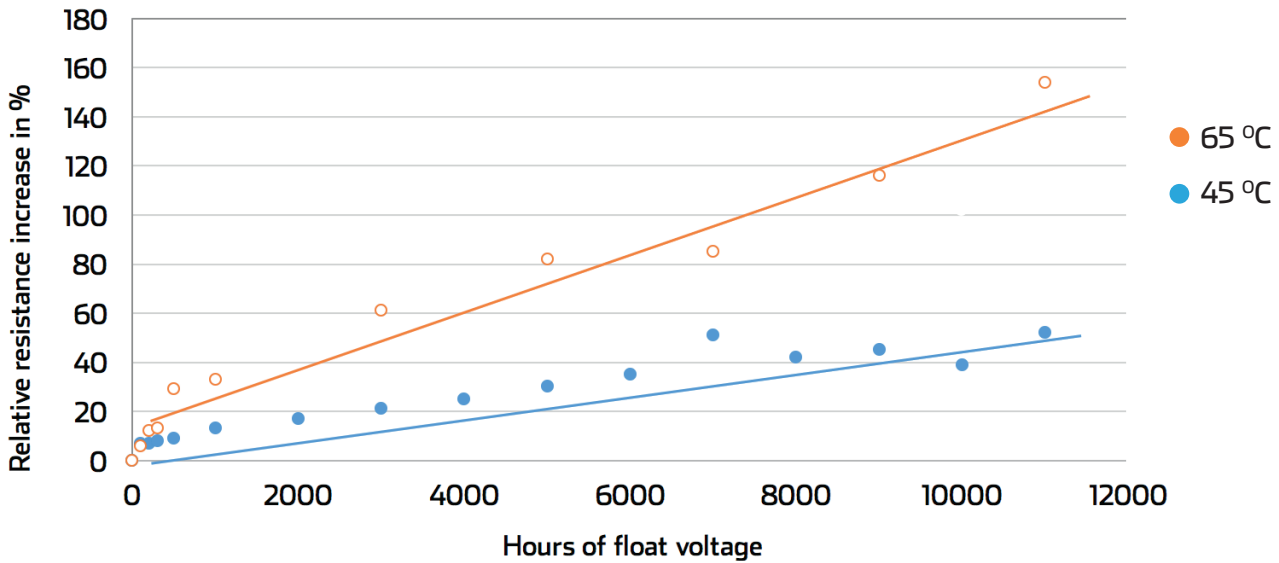


Fig. 2. Resistance change of ultracapacitors at different temperatures from lifetime tests.

Fig. 3 shows the lifetime dependency of ultracapacitors at different rated voltages and temperatures. The generalized ultracapacitor lifetime model shows temperature and voltage combinations expected to yield a similar lifetime in hours. For example 2.5 V @ 40°C and 2.7 V @ 30°C are both very close to the 40 000 hours of lifetime (slightly above for the higher voltage). Also very nearly equivalent are 65°C at 2.7 V and 50°C at 2.85 volts, both yielding around 4000 hours of lifetime.

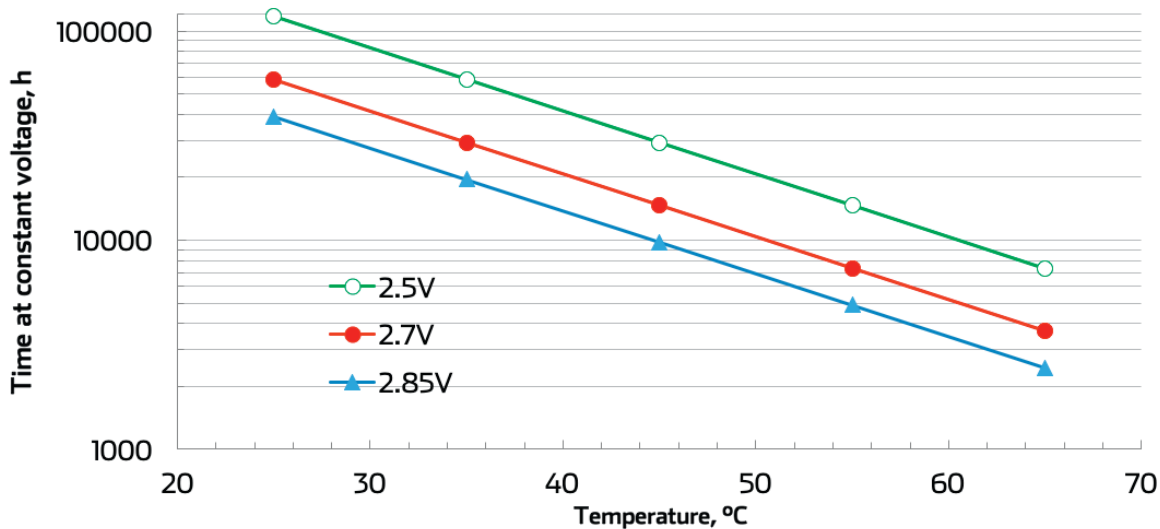


Fig. 3. Lifetime dependency on temperature and rated voltage.

Using ultracapacitors in demanding conditions, e.g., cycling continuously at high current ranges, leads to the cells heating up, and the actual cycling-life will therefore be shorter. If the ambient temperature is higher, then it must be considered when making predictions about the actual cycling-life.

The working temperature in a specific application can be calculated based on average current I , internal resistance R_i ¹ and thermal resistance R_{th} . The following formula will yield the temperature change resulting from these parameters. For actual working temperature, the change in temperature needs to be added to ambient temperature or coolant temperature.

$$\Delta T_f = I^2 \cdot R_i \cdot R_{th}$$

I – average current, [A]

R_i – internal resistance, [Ohm]

R_{th} – thermal resistance, [°C/W]

The table below shows the effect of current on cell temperature for a Skeleton cell and a typical commercial cell with twice the Resistance. Working temperatures above 82 °C are marked in red, since acetonitrile-based electrolytes used in both capacitors starts boiling, destroying the capacitor.

Skeleton SCA 3200, R=0.12 mOhm				Typical 3000 F, R=0.24 mOhm			
Average Current [A]	ΔT_f [°C]	Cell working temp [°C]	Cycles, thousands	ΔT_f [°C]	Cell working temp [°C]	Cycles, thousands	Difference in lifetime
100	3.6	28.6	905	7.2	32.2	819	5%
150	8.1	33.1	799	16.2	41.2	638	25%
200	14.4	39.4	671	28.8	53.8	450	49%
250	22.5	47.5	536	45	70	287	87%
300	32.4	57.4	407	64.8	89.8	166	146%
350	44.1	69.1	294	88.2	113.2	86,7	240%

It is important to keep in mind that these simulation results are performed at nominal working voltage, which at 2.7 V is lower for a typical capacitor, with nominal voltage for SkelCap rated at 2.85 V. When corrected for the voltage difference – both running at 2.7 V – the SkelCap gains another 68% of lifetime.

To avoid a temperature rise in cells in modules, an additional cooling system (liquid or air) is needed. The technical case study shows results from an ageing test that has been found to “fit” specific functions, which can be used as predictive models. Strictly speaking this model is good for only one task: predicting the test results of the same type of a capacitor in the same test without having to run the whole length of the test. The model can not be used to predict the lifetime of the cell in different conditions or different cell models in exactly the same conditions.

¹ Total resistance values are to be used, obtained either from 5 second voltage drop test in constant current conditions, or 0.1 Hz AC test. 10 millisecond test, the result of which is often quoted as nominal internal resistance, denominates contact resistance. Please see Skeleton Whitepaper on ESR for further details.

In reality there are a number of application-specific variables influencing the result:

- + Cell resistance drops at higher temperatures: In the examples shown within this whitepaper the internal resistance of the capacitors is taken as a constant. In reality, cell resistance drops with elevating temperature. While a useful initial guide, it must be said that the temperature related variation in R depends on a particular electrode (please see ESR whitepaper for further details).
- + Rest period between charge cycles: everything else being equal, giving the ultracapacitor some rest between charge/discharge cycles will allow the capacitor to recover, therefore improving the life-time. However, this effect is not linear.
- + Cell size and level of current: cell size influences the temperature difference between the cell core and the cell casing. This difference becomes more apparent when high currents and liquid cooling are used as the outside of the cell receives more cooling than the inside, and as a result, the difference between the temperature measured inside and on the casing surface can be significant. Nevertheless, those differences can be reduced by passing lower current through the cells, or using larger modules with higher total capacitance and applying a proper cooling method.

Rated conditions

In an ultracapacitor datasheet, the following rated values play an important role while predicting operational lifetime:

1. Rated voltage U_R .

The manufacturer's specified voltage, which guarantees stable characteristics over the rated period of lifetime. Usually in the range of 2.5-3.0 V.

2. Rated cyclic lifetime n_R at reference temperature T_R , while cycling between U_R and $0.5 U_R$.

Changing the operational voltage and temperature values affect the anticipated lifetime of a cell. It is possible to run an ultracapacitor at higher voltage than rated with tradeoffs in lifetime. This is profitable in programmed obsolescence applications, where the lifetime of the whole supported system is not an issue, e.g. racing cars, guided missiles, electronic warfare (EW), and elsewhere. On the other hand, operating ultracapacitors at lower voltage than rated contributes to additional lifetime, advantageous for example in the UPS systems, or the systems where few extra ultracapacitors in the module do not play a role.

The rule of thumb for operational lifetime forecast

There exists an empiric relationship, which allows to estimate lifetime from actual voltage and temperature conditions. The limitations for a 2.85 V cell usable in empiric formula are:

1. Minimal operational voltage $U \geq 2.5V$;
1. Max operational voltage $U \leq 3.2 V$;
2. Temperature window $T = 0^\circ C \dots 65^\circ C$.

The empiric relationship itself is
$$n_{est} = \frac{n_R}{2 \left(\frac{U-U_R}{0,20} + \frac{T-T_R}{10} \right)}$$

Example

We have a cell with $U_{R^*} = 2.85 \text{ V}$; $n_R = 1\,000\,000$; $T_R = 25^\circ\text{C}$.
What is the lifetime estimation for $U = 2.8 \text{ V}$, $T = 40^\circ\text{C}$?

Solution

$$n_{\text{est}} = \frac{10^6}{2^{\left(\frac{2.8-2.85}{0.20} + \frac{40-25}{10}\right)}} = 420\,448 \text{ cycles}$$

How does the ESR influence lifetime?

From the equation $\Delta T_f = I^2 \cdot R_i \cdot R_{th}$ it can be seen that the final temperature rise at constant current operation is proportional to the ESR. Let us take for example two 2.85 V cells with equal capacitance, but with different ESR:

1. $R_{i1} = 0.22 \text{ m}\Omega$;
2. $R_{i2} = 0.13 \text{ m}\Omega$.

The thermal resistance for both is the same, $R_{th} = 3.2 \text{ }^\circ\text{C/W}$.

Whilst running at rated voltage and cycling with $I = 150 \text{ A}$, with starting temperature $T_0 = 25^\circ\text{C}$, the final temperatures are:

1. $T_{f1} = T_0 + 150^2 \cdot 0.22 \cdot 10^{-3} \cdot 3.2 = 40.8^\circ\text{C}$
2. $T_{f2} = T_0 + 150^2 \cdot 0.13 \cdot 10^{-3} \cdot 3.2 = 34.3^\circ\text{C}$

The lifetime anticipations are accordingly:

1. $n_{\text{est}1} = \frac{10^6}{2^{\left(\frac{40.8-25}{10}\right)}} = 333'555 \text{ cycles}$
2. $n_{\text{est}2} = \frac{10^6}{2^{\left(\frac{34.3-25}{10}\right)}} = 522'680 \text{ cycles}$

Thus, the cell with less ESR can provide 1.65 times more lifetime than the cell with higher ESR value. This fact is important for applying the ultracapacitors in hot climates, where the higher operational temperature must be compensated by using a lower voltage to reach a reasonable lifetime.

The experimental data in this white paper is to be taken as exemplary and it serves mainly educational purposes regarding the relation of lifetime, resistance, and thermal behavior. Final lifetime and behavior of Skeleton Ultracapacitors may vary depending on circumstances of the application.