

TECHNOLOGICAL ASPECTS OF RELIABILITY OF ELECTROCHEMICAL CAPACITORS BEING USED AT HEAVY- DUTY OPERATING CONDITIONS

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Abstract:

Introduction:

Reliability as a subject of present talk means safe use of the capacitors at user and retaining of technical properties within a certain period of use.

Heavy-duty conditions of use for electrochemical capacitors (EC) with aqueous electrolytes mean first - increasing of temperature and constant cycling (charge-discharge) or constant being under nominal operating voltage.

Issue of reliability of smaller EC designed for electrical and electronic application is studied sufficiently within last years they being made and used (1). A number of papers evidences stability of single EC of high capacity, nevertheless the reliability of systems with a single store of tens kilojoules and operating voltage to 500 volts and higher is not described, yet.

There exist great differences in constructions and technologies of small and large EC. It is impossible to use the ratio of active and passive components of small capacitors to larger ones, because specific performances will decrease unavoidably. From the point of view of safe the explosion of small EC will not cause serious outcome, as explosion of larger devices.

This paper observes some of aspects of safe and reliable operation of EC at temperature from plus 55°C (131°F) to plus 70°C (158°F).

1. Processes And Their Outcome

Looking at dynamics of electrochemical processes at non-polar EC we can single out only one dynamic part – electrolyte solution. The rest of EC, such as collectors, carbon electrodes, separators are static. Electrolyte provides EC with conductivity of the second type (i.e. moving of charge) and either creating or destruction of double electric layer on electrode surface. We have already shown in our previous papers the influence of type of electrolyte, its concentration and quantity (2) on electrical properties. In the further we shall show reliability of EC at higher temperature depends on electrolyte.

Some words about physical and chemical processes within a cell at increased temperature.

First of all, increasing of temperature causes mobility of ions and their penetration into micro- and mezopores which were not wetted with electrolyte before. That some enlarge capacity of DLC. In the same time it increases leakage current due to thermal destruction of DLC.

I want to remind that conductivity and quantity of electrolyte within EC both create its power. That's the reason the developers want to hold technologically maximum of electrolyte up to maximum sorption capacity of carbon. When temperature gets higher then sorption capacity of carbon get lower sufficiently and there appears "not-planned" surplus of electrolyte. If we go on with heating then there appears the thermal expand of the surplus of electrolyte and pressure of its saturated vapors. This is that moment when there can appear mechanical destruction of sealant and leakage current due to electrolyte short circuiting between separate cells.

It's important to point out that polymers of sealant are under intensive influence of hostile electrolyte at higher temperature and that leads to accelerated aging. Increased temperature causes oxidizing of surface of carbon of positive electrode, and forming of complex compounds of oxides on the surface, and polar groups. All that can reduce potential of water decomposition and slight gassing in a real system.

Now some words about high-voltage circuit consisting of bipolar cells of high power and small thickness. We can see the electrolyte space of a cell is separated of electrolyte containing in other cell by collector only. Thickness of the collector is just 15 – 60 microns. Thus egress of electrolyte from several cells will cause short circuiting immediately. I've talked that heating increases leakage current. That means that fast and uneven heating of EC as a real system will lead to disbalance of leakage currents and internal resistance of single cells of the circuit. In one ore some of the cells voltage can reach value of voltage of electrolyte decomposition, and unsealing followed by electrolyte short circuiting. Gassing in this confined space can provoke rupture of the capacitor battery.

On the other hand the design of cell allows gas to pass away freely from the cell and thus discharge power goes down.

So, at increasing of temperature within EC with aqueous electrolyte the following processes take place:

- Increasing of wetting ability of electrolyte and capacity;
- Increasing of leakage current;
- Decreasing of sorption ability of carbon and appearing of "surplus" of electrolyte;
- Increasing oxidizing of active surface of carbon electrode, decomposition of water;
- Increasing of pressure in cell;
- Disbalance of performance in series connected circuit at uneven heating.

We can see all the processes, but the first one, can cause either gradual or sharp failure of EC.

Tests And Results

To estimate changing of properties at heavy-duty operating conditions we used standard EC with performances as following:

Electrical capacity	14 – 20 F
Internal resistance (at 1 kHz)	8 – 20 mOhm
Operating voltage (nominal)	12.5 V

This block was constructed as bipolar device, pressed by covers to operating pressure. Each cell of circuit had its outlined sealant which did not prevent gassing out at in case of internal pressure get higher. For safe the block was covered with a special harder compound used as gas exit through terminals. For the testing we assembled groups of EC (blocks) with differ dose of electrolyte: minimum and maximum. It was done by special technological expedient within applying of thin layers of activated carbon mixed with electrolyte.

General view of depending of ESR on pressure value in single cells is shown in Figure 1. Advantages of surplus of dosing is visible.

3.1. Exposition At Increased Temperature And Nominal Voltage

The first group of the blocks was made with no special control over electrolyte in electrode mass. The tests were led at ambient temperature plus 61°C (142°F) and operating voltage 12.6 V. Initial performances of the blocks were measured after 379 hours exposition by impedance spectroscopy methods. We noticed that after 24 hours all the blocks were leaking with electrolyte to outer space through terminals. Data measured before and after the exposition are given in Figure 2. – Bode plot, Figure 3. –Phase angle VS Frequency, Figure 4. –Nyquest plot.

Analyses of the graphs shows 2 blocks of 3 increased their impedance and lost power properties (158, 159). Nyquest plot shows ionic contribution and polar groups on electrode surface. This is evidence of increased oxidation of positive electrode at higher temperature.

Figure 5 shows frequency dependence of capacity before and after exposition.

Figure 6 shows changing of Magnitude of the real part of impedance. Here is visible some lost of capacity, it is approximately 20 per cent in the worst-case scenario.

The tests shown us technological instability at EC blocks assembling. This instability showed itself electrolyte leakage and lessening of performances at 2 blocks of 3.

The other group of blocks was divided to two subgroups differ by technological dosing of electrolyte. The tests were led at temperature plus 70 °C (158°F). Picture of changing of ESR of blocks with smaller and larger dosing of electrolyte is given in Figure 7. The blocks containing more electrolyte have obvious advantages, i.e. 1.4 – 1.9 times lower resistance. At the same time the ESR of the blocks with lower quantity of electrolyte trends positively to increasing and thus remains meeting customers' requirements.

Nevertheless we saw insufficient leakage of electrolyte through negative terminal of the block containing more electrolyte. Later tests showed its commercial properties did not get worse.

Capacity changes of block are shown at Figure 8. We can see great difference in the trends to changing, but deviation of capacity was in admissible window (<5%) within more than 500 hours. It happened to the blocks of lower as well as the blocks of higher dosing of electrolyte.

3.2. Fast Cycling Test

Testing of EC blocks at accelerated cycling was led by cyclogram which is closest to real use condition (Figure 9):

- Charge by pulsing current (100 Hz) ~45 A to maximum operating voltage ~14.4 V during 428 msec;
- Pause 10 – 12 msec;
- Discharge by current 120 A during 0.5 msec, by current 80 – 85 A during 51 msec.