An Electric Double-Layer Capacitor with a 260°C Reflow Compatibility

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Abstract
The electric double-layer capacitor (SuperCapacitor) is an energy storage/supply device that makes use of the electric double-layer phenomenon in which positive and negative charges are accumulated at the interface of a solid and liquid.

NEC TOKIN has already produced the FC Series of SuperCapacitors with a 235°C reflow compatibility for use in surface mounting. Recently, NEC TOKIN has succeeded in the development of a high heat resistance product (FCS type SuperCapacitor) that has compatibility with lead-free solder reflow conditions (260°C reflow temperature). Details of this development are introduced in this paper.

Keywords
surface mounting, lead-free, reflow, electric double-layer capacitor, high heat resistance, 85°C guarantee

1. Introduction

The double-layer capacitor (SuperCapacitor) is an energy storage/supply device that makes use of the electric double-layer phenomenon with which the positive and negative charges are oppositely distributed at extremely short distances at the interface of two different phases that are solid and liquid respectively.

The recent decrease in size and increase in the number of functions of electronic devices is promoting an increase in the density of PC boards. Electronic components are therefore required to be suitable for surface mounting by means of the reflow process. To meet this requirement, NEC TOKIN has been marketing the FC Series of SuperCapacitors that feature a reflow surface mounting compatibility since the year 2000. However, the recent rise in interest in issues of global environment conservation and the trend in adopting measures against it has been increasing the amount of electronic equipment that uses high melting point lead-free solder. This trend has resulted in an increase in the temperature of the soldering used in the packaging.

On the other hand, since the electric double-layer capacitors use an electrolytic solution internally, any increase in the soldering temperature (reflow temperature) during packaging tends to cause degradation of characteristics and shortening of life span, the existing products have had difficulties in achieving compatibility with reflow using lead-free solder.

Under these circumstances, we reviewed the design of the FC Series products from the materials to the structural aspects and developed the “FC Series, FCS type SuperCapacitors” with a heat resistance capability of 260°C reflow and an 85°C maximum operating temperature (Photo). Below, we introduce details of the new product.

2. SuperCapacitor Product Outline

The advantages of electric double-layer capacitors include “large electrostatic capacitance,” “long service life thanks to the number of charging/discharging cycles, which are in principle unlimited” and “absence of environmental load-imposing substances,” that make the device suitable for use in the memory back up of car navigation systems, DVD players, etc.

Fig. 1 shows a schematic of the basic cell structure of the
The basic cells of the SuperCapacitor use active carbon powder (solid) and diluted sulfuric acid (liquid) as the electrode materials and a separator is installed between the +ve and -ve electrodes (active carbon powder).

In addition, conductive rubber is placed on the backs of both electrodes (active carbon powder) so that voltage can be applied to the basic cells. To ensure insulation between the electrolytic solution seal and the conductive material, a sealing rubber is placed on the sides of the electrodes (active carbon powder).

The withstanding voltage of the basic cells is determined by the electrolyzing voltage of the electrolyte solution. The electrolyzing voltage of the SuperCapacitor cell using a water solution type electrolyte (diluted sulfuric acid) is about 1.2V, so a SuperCapacitor device with maximum operating voltage of 5.5V can be designed by layering five or more basic cells in series.

The layered basic cells are pressurized in order to stabilize the electrical connections between the basic cells; between the active carbon powders, and between the active carbon powder and the conductive rubber, before applying the exterior finishing.

### 3. Issues Regarding Lead–Free Reflow Compatibility

With regard to the market requirements for the reflow conditions of the lead-free products, JEDEC (an organization under the Electronic Industries Alliance, USA) and JEITA (Japan Electronics and Information Technology Industries Association) require peak temperatures from 245°C to 260°C and a period of heating at 220°C or more from 30 to 150 seconds.
However, the previous FC Series of SuperCapacitors with a surface mounting capability have been capable of meeting the electrical characteristic requirements only up to a peak temperature of 235°C or for a heating period at 200°C or more up to 30 seconds.

It should be noted that the ESR (Equivalent Series Resistance) characteristic rises and its variance increases after reflow. This trend is more noticeable when the reflow temperature is high (Fig. 4).

The mechanism of the ESR variation before and after reflow is assumed to be as follows (Fig. 5).

1) The reflow applies high heat to the product.
2) The application of high heat vaporizes the electrolyte solution in the basic cells and causes thermal expansion.
3) The thermal expansion of the gas increases the internal pressure of the product.
4) The rise in the internal pressure curves the exterior component and causes plastic deformation.
5) The product cools down after completion of reflow.
6) The cooling liquefies the vaporized electrolyte solution and returns it to the original liquid phase.
7) Liquefaction of the electrolyte solution decreases the internal pressure of the product.
8) Meanwhile, the exterior component retains a plastic-deformed shape even after cooling, so the contact pressure between the basic cells and the exterior component is reduced.
9) The reduction of the contact pressure increases the ESR.

4. Improvement of Reflow Heat Resistance

In order to improve the reflow heat resistance of the SuperCapacitor, it is necessary to reduce the rise in ESR after reflow. The key to this lies in controlling the rise of the product internal pressure due to heat and to reduce the amount of plastic deformation of the exterior component even when the internal pressure is increased.

4.1 Reduction of Rise in Product Internal Pressure

Because the SuperCapacitor uses dilute sulfuric acid as the electrolyte solution, the electrolyte solution is vaporized and the pressure inside the basic cells is increased when a thermal load higher than the boiling point of diluted sulfuric acid is applied to the basic cells.

To reduce the rise in internal pressure of the SuperCapacitor, it is therefore important to reduce the vaporization of diluted sulfuric acid due to reflow heat.

So we reviewed first the characteristics related to the diluted sulfuric acid solution. Fig. 6 shows the vapor pressure data of sulfuric acid. The boiling point of diluted sulfuric acid is dependent on the sulfuric acid concentration under constant pressure; it rises as the concentration increases. When the concentration is constant the boiling point rises as the pressure increases.

This means in other words that the boiling point of the electrolyte solution can be increased either by increasing the sulfuric acid concentration or the pressure applied to the diluted sulfuric acid. However, the electrical conductivity decreases if the diluted sulfuric acid concentration is increased.

Fig. 7 shows the electric conductivity values of various water solutions. The electric conductivity of a sulfuric acid solution reaches the maximum when the concentration is around...
30%. In other words, the internal resistance would be increased if a sulfuric acid solution with high concentration is used in the electric double-layer capacitor. We therefore decided to improve the heat resistance of the basic cells by increasing the pressure applied to the dilute sulfuric acid solution. Consequently, by increasing the pressure applied to the basic cells by 50% compared to before it becomes possible to rise the vaporization temperature of diluted sulfuric acid and to reduce the increase in the internal pressure of the basic cells, even at a temperature of 260°C.

### 4.2 Increase in Strengths of External Components

In order to increase the pressure applied to the basic cells by 50% and retain the pressure, it is necessary to improve the strength of the exterior component.

Since the ESR characteristic does not change provided that the exterior component is not deformed even when the internal pressure of the basic cells are increased, we also tried to increase the strength of the exterior component.

In general, an increase in the strength is accompanied by an increase in the number of components as well as in the product dimensions due to increased thickness. But, in the recent development, we set the target to improve the heat resistance while maintaining similar dimensions to those of the previous products. Therefore, we improved the exterior component strength by 50% by adopting the measures described below.

First, we increased the thickness of the exterior case by 50%, from 0.2mm to 0.3mm. On the other hand, we reduced the thickness of the insulating case from 0.5mm to 0.3mm and filled the decreased thickness by adding a reinforcing plate made of SUS that is stronger than the resin. In order to compensate for the increase in the exterior case thickness and to prevent the product dimensions from being increased due to the increase, we installed a groove for relieving the height of the outer case of the curved section on the bottom plate. **Fig. 8** shows the comparison of structure between the new FCS0H104ZF and previous FC0H104ZF products.

### 5. Reflow Heat Resistance Evaluation

The developed product features high exterior component strength that has been increased by pressurizing the basic cells at 150% of the previous pressure. This section deals with the comparison of the reflow heat resistance achieved with the developed product and that of the previous product.

**Fig. 9** shows the changes in ESR characteristics of the FCS0H104ZF (developed product) and the FC0H104ZF (previous product) after twice applying thermal load by means of 260°C reflow.

The figure shows that, with the FCS0H104ZF, the rise in ESR is reduced even after the thermal load of 260°C reflow and that its variation is also small. We also made a high temperature load evaluation in order to identify the maximum operating temperature, and found that the FCS type has the structure and strength sufficient for an 85°C guarantee while the guaranteed temperature for the previous FC Series was only 70°C.
6. Conclusion

The newly developed FCS0H04ZF (5.5V/0.1F) is a high resistance double-layer electric capacitor that is compatible with lead-free reflow conditions. In the future, we will expand the product line to offer a range of products that will meet the needs of every customer.

References


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