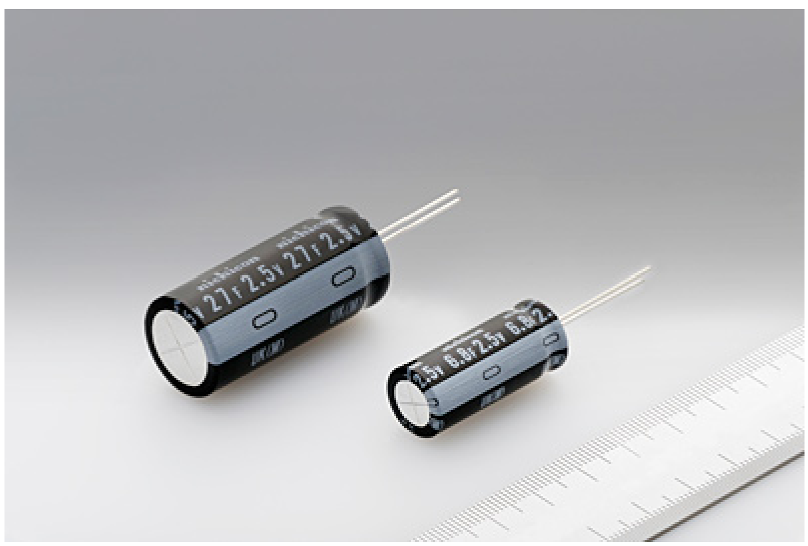
Latest Technologies for Electric Double-layer Capacitors

1. Introduction

The market for electric double-layer capacitors has so far seen them used in compact, backup power sources for equipment and devices. In recent years, however, along with advancements in large-scale and unit technologies, there has been a growing market for their use in large products such as automobiles, cranes, forklifts, and elevators that use regenerative energy. Because these applications electrically charge and discharge with large currents, it is crucial that the internal resistance of the capacitors be made as low as possible.

Relatively compact lead-type electric double-layer capacitors are used in backup power sources for game consoles, as well as in auxiliary power sources for printers and projectors. They are also becoming the capacitor of choice for use in backup power sources for smart meters, which have gained in popularity in recent years around the world. Because smart meters must have instantaneous power output when conducting wireless transmission, they require low-resistance power devices. And since they are generally installed outdoors, their power devices must be able to function within a wide temperature range; particularly pressing has been the need to improve these devices' resistance characteristics to withstand operation in low temperatures.

Nichicon's UK Series was developed to meet the needs of smart meter manufacturers who require capacitors with lower resistance and the ability to operate in a lower temperature range.



UK Series low-resistance electric double-layer capacitors for smart meters

2. Principles of Electric Double-layer Capacitors

Figure 1 shows how electric double-layer capacitors store electricity. When voltage is applied to one of the electrodes, the ions in the electrolyte which is between the two electrodes move to negate the polarity of one of the electrodes. In other words, the negatively charged ions are absorbed to the positive electrode, which has been given a positive charge. Positively charged ions are absorbed to the negative electrode, which has been given a negative charge. When this happens, a positively charged layer and a negatively charged layer line up opposite each other on the boundary between the electrodes and the electrolyte… a phenomenon called electric double-layer. During charging, the ions are absorbed to the electrode surface, and during discharging, the ions separate from the electrode surface when the electric charge of the electrode is discharged. Because a higher capacity results from having a greater number of these absorbing and de-absorbing ions, materials with a high specific surface area are used for the electrodes. Charging and discharging in this type of capacitor is extremely simple: the only thing happening is the absorption and de-absorption of the ions. Because of its simple structure, electric double-layer capacitors give high output (they allow easy charging and discharging in a short time) and long life (they experience minimal deterioration from charging and discharging). These characteristics make electric double-layer capacitors the ideal device for applications requiring high output and many repeated charges and discharges.

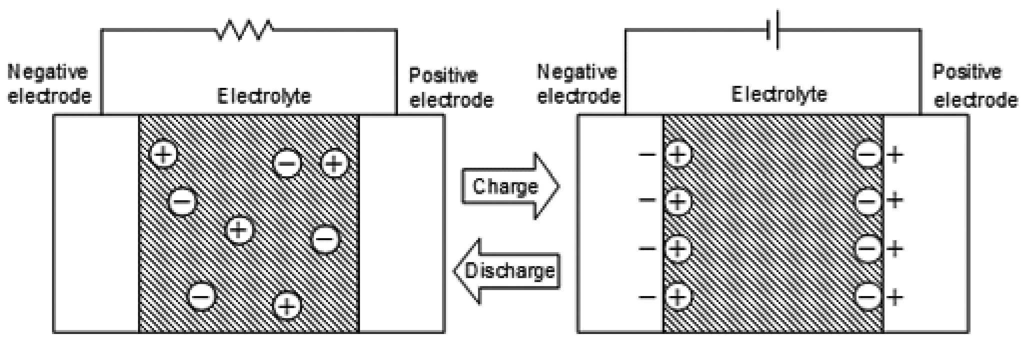


Figure 1 How electric double-layer capacitors store electricity

3. Structure

There are two main kinds of structure for electric double-layer capacitors: stacked type and wound type. In the stacked-type electric double-layer capacitor, there are alternate layers of electrode foil and separator, with lead tabs coming off each electrode foil to increase the current path and thus decrease internal resistance. In the wound-type electric double-layer capacitor, layers of electrode foils and separators are rolled up together (a roll-to-roll structure), effectively creating negative and positive electrodes in a short time. It also offers stable structure and high reliability. Because of their high productivity and reliability, Nichicon uses wound-type electric double-layer capacitors, with a range of products from compact lead types (φ6.3 x 9L to φ18 x 40L) to large screw-terminal types (φ35 x 85L to φ63.5 x 150L). The larger the capacitor, the greater the surface area of the electrode foil, and the greater the current that flows; therefore, multiple lead tabs are used to prevent internal resistance from rising.

Small lead-type electric double-layer capacitors have an extremely simple structure in which the lead wire functions directly as the external terminal. This makes it difficult to attach multiple lead wires (figure 2). This is why in developing the aforementioned UK Series, Nichicon concentrated on making improvements through changes in the material.

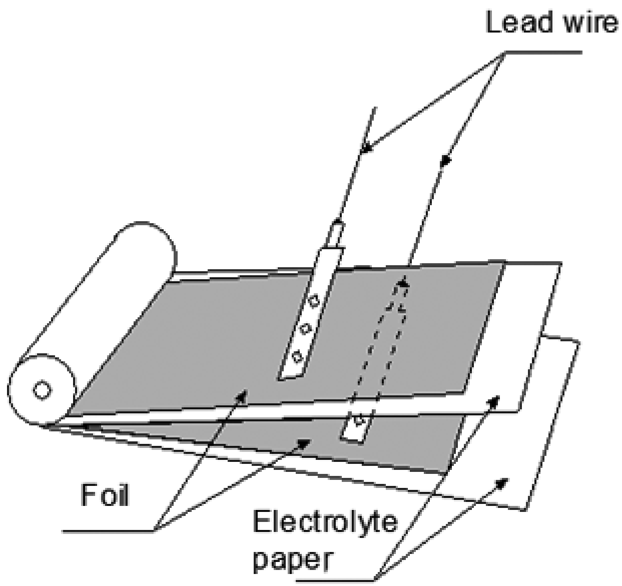


Figure 2 Structure of lead-type electric double-layer capacitor

4. Electrodes

Activated charcoal is used for the electrodes of electric double-layer capacitors. Activated charcoal comes from numerous sources, such as coconut shells, petroleum pitch, phenol resin, and polyvinylidene chloride. The main activation methods are gas and alkali activation. Although alkali activation is a more expensive process than gas activation, it yields fine, consistently sized pores, and thus gives greater capacity. However, the smaller the pore diameter, the more limited the path for the ions that are either trapped or pass through, so smaller pores means greater resistance. For resistance characteristics and cost effectiveness, Nichicon uses activated charcoal from coconut shells activated by gas for the electrode active material.

Besides the activated charcoal manufacturing method, another crucial factor that influences the performance of the electric double-layer capacitor is the manufacturing technology for the electrode foil. Electrode foil is made in two ways: (1) the electrode material is made thin, and is applied to the collector foil; and (2) the activated charcoal is made into a sheet to which a conductive additive and binder are added, and is then attached to the collector foil using an adhesive. In general, when the goal is higher capacity, the latter method of making a sheet (sheet-type electrode) is used since it allows a thicker film. When the goal is lower resistance, the former method of applying the thin electrode material to the collector foil (coated electrode) is used since it allows a thin film to be made. A thinner electrode foil allows use of a greater surface area and thus gives less resistance. However, from the point of durability, the sheet-type electrode maintains its shape, and retains its resistance characteristics over long periods. As well, in sheet-type electrodes, the gaps between charcoal particles are larger, making it easier for the electrolyte to penetrate; this gives them superior resistance characteristics to the coated electrodes at low temperatures. As well, in recent years there have been advances in thin film technologies for sheet-type electrodes, and sheets can now be made that are comparable in thickness to coated electrodes. Against this background, Nichicon has used ultra-thin sheet electrodes to reduce resistance over conventional electrodes by approximately 50% by optimizing parameters such as the pore size of the activated charcoal and the thickness of the electrodes.

5. Electrolyte

For the organic solvent-based electrolyte used in electric double-layer capacitors, generally either quaternary ammonium chloride or amidine chloride is used as the solute. As well, propylene carbonate (PC) is used as the solvent. Increasing the concentration of either quaternary ammonium chloride or amidine chloride reduces the resistance of the electrolyte, which in turn contributes to a low-resistance capacitor. However, there is a major difference in the solubility of the chloride component in each at low temperatures. For example, with triethylmethylaminium tetrafluoroborate (TEMA-BF4), used widely as a quaternary ammonium chloride, the solute precipitates at -30℃ at a concentration of 1.8 mol/L. However, with 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF4), a typical amidine chloride, the solute does not precipitate even at -40℃ at a concentration of 2.0 mol/L.

For this reason, Nichicon uses amidine chloride for the electrolyte since it maintains low resistance even at -40℃.

For the solvent, besides using propylene carbonate as the base, we tried mixing in a low-viscosity auxiliary solvent to increase the mobility of the ions and thus lower the resistance. Acetonitrile is commonly used as a low-viscosity solvent in other countries, but acetonitrile can emit a poisonous gas under combustion. Therefore, for reasons of safety and environmental protection, Nichicon does not use acetonitrile. One auxiliary solvent used is dimethyl carbonate (DMC), and the proportion at which it is mixed in affects the internal resistance of the capacitor (figure 3). Considering a range of other factors, including temperature characteristics, durability, and cost, Nichicon uses the optimal types and proportions of auxiliary solvents, and in doing so has developed electrolytes that give approximately double the conductivity of conventional electrolytes and can be used at temperatures as low as -40℃.

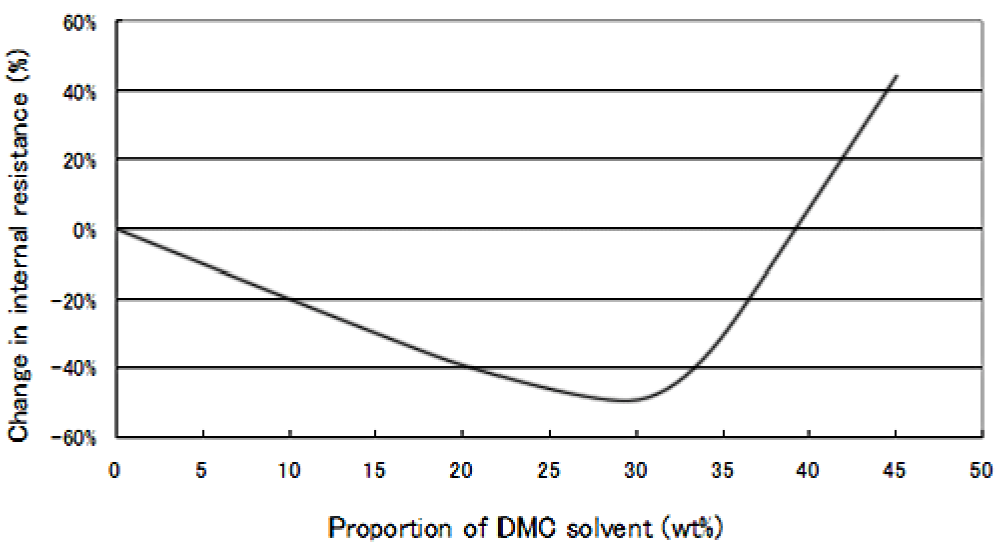


Figure 3 Effect on internal resistance of varying proportions of dimethyl carbonate solvent (-40℃)

As described here, Nichicon’s UK Series uses newly developed electrodes and electrolyte to achieve lower resistance. This series achieves the industry’s best resistance characteristics for lead-type electric double-layer capacitors using non-acetonitrile solvent; as low as one-third the resistance of the same sized capacitor in Nichicon’s UM Series (figure 4). Nichicon has also dramatically improved the low-temperature characteristics of the capacitor: while the company's current products offer low temperature stability down to -25℃, the UK Series is guaranteed to -40℃.

Lead-type electric double-layer capacitors are seeing increasingly wider use in backup power applications, and Nichicon is expanding its lineup with this new low-resistance series. Mass-production began in April 2012.

In addition to smart meters, electric double-layer capacitors are also becoming the choice for backup power sources in products like drive recorders and storage servers, and as a replacements for secondary batteries since they require no maintenance and have minimal environmental impact.

With the goal of increasing the number of applications, Nichicon is working to develop capacitors that can operate at higher temperature ranges and withstand higher voltages.

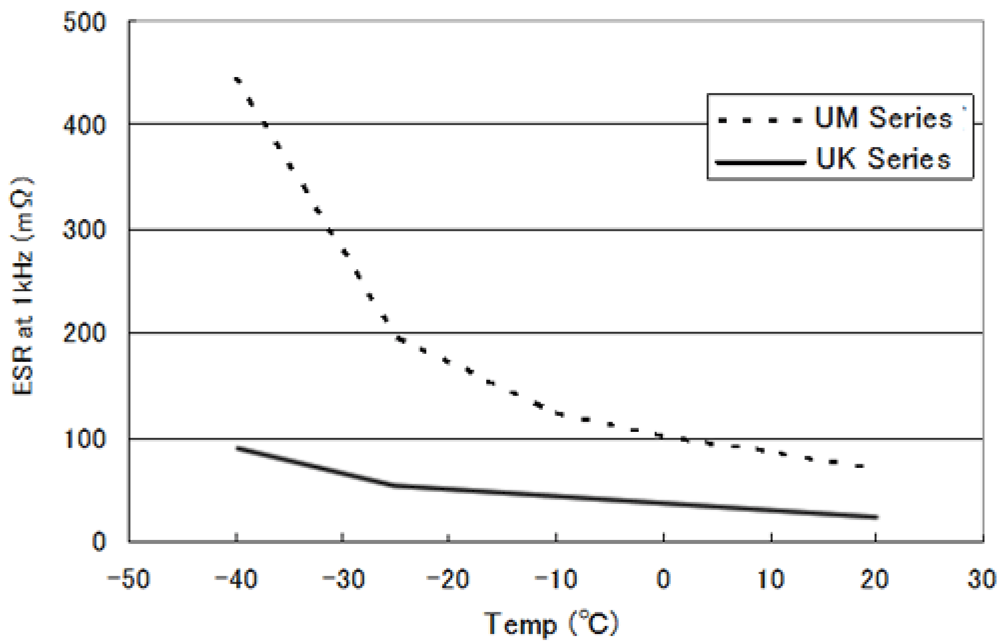


Figure 4 Relation between temperature and internal resistance
Comparison of the UM Series (current series) and UK Series

(Table) UK Series products

Rated Voltage	**Rated Capacitance (F)**	**ESR (at 1kHz) (mΩ)**	**DCR Actual Value (mΩ)**	**Case size Φ D x L (mm)**
2.5V	6.8	75	85	12.5 × 31.5
	12	60	65	16 × 31.5
	18	55	55	18 × 31.5
	27	40	35	18 × 40

Nichicon Corporation
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