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Review

Liquid electrolyte-free cylindrical Al polymer capacitor review: Materials and characteristics

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HIGHLIGHTS

- Novel materials and the production method for Al polymer capacitors are introduced.
- The benzenesulfonate doped PEDOT contributed to the low ESR and large capacitance.
- Carbon and TiO_2 applied negative current collectors enhanced the capacitance.
- Aramid based separators helped to simplify the manufacturing process.
- The proposed Al polymer capacitor has the excellent reliability.

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ABSTRACT

The manufacturing methods for liquid electrolyte-free Al polymer capacitors are introduced by using new materials like novel oxidants, separators and negative current collectors. The Al polymer capacitor is constructed by an Al foil as an anode, Al_2O_3 as a dielectric, and poly(3, 4-ethylenedioxythiophene) (PEDOT) as a cathode. There are also various synthetic methods of 3, 4-ethylenedioxythiophene (EDOT) and the chemical polymerization of PEDOT from EDOT using iron benzenesulfonate as a new oxidant and dopant. Furthermore, various cathodic current collectors such as conventional Al foils, carbon and titanium dioxide deposited on Al foils or substrates, as well as various separators with manila-esparto paper and synthetic fibers (series of acryl, PET, etc.) are studied. The Al polymer capacitors with the newly introduced oxidant (iron benzenesulfonate), separator (aramid based synthetic fibers) and current collector (TiO_2) exhibit considerably enhanced capacitance values and the extremely low resistance (7 mΩ), so there is low power consumption and high reliability. Additionally, the newly developed Al polymer capacitor is guaranteed for 5,000 h at 125 °C, which means there is a long life time operation over ~ 5×10^6 h at 65 °C.

1. Introduction

Since the ‘Industrial Revolution’, one of the great problems for the human race has been energy. The energy crisis challenges are ‘creating new energy sources and energy diversification’ like alternative energies and the energy harvestings, and ‘efficiently using existing energy’ through smart grids and highly efficient products manufacturing. Efficiently using energy is a quicker process than the former issue. Developing highly efficient electronic devices and installing smart grids at the national level have been considered in order to overcome the energy crisis. Capacitors, key passive components of electronic devices, have high efficiency and a long life time. As industrial systems are digitalized, most industrial equipment are multifunctional and minimized. Consequently, capacitors nave become diversified according to their purposes. To satisfy these requirements, capacitors have to show low equivalent series resistance (ESR) and large capacitance on a small scale. Thus, advanced Al polymer capacitors have been developed, for use as promising alternative candidates for conventional Al electrolytic capacitors containing liquid electrolyte.

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Al polymer capacitors have been commercialized for 20 years and the market has expanded continuously and considerably. The market scale of Al polymer capacitors approached approximately 5.5 billion dollars in 2013 and is projected to increase to 7.6 billion dollars by 2017 [1,2]. Despite the large market volume, Al polymer capacitors have not discussed intensively and faithfully in any academic documents due to limited key materials like EDOT, PEDOT and exclusive applying method protected by a patent.

As he essential patents expired in 2009, the EDOT has been studied again for cost-effective mass production and electrical property enhancement through engineering the functional group of EDOT. In Addition, as current electrical devices need more advanced functions such as longer life time, lower energy consumption, higher operating voltage, high temperature endurance, and high frequency operation-ability, the Al polymer capacitors also need improved characteristics.

Thus, we reviewed the materials and manufacturing method utilized for electrolyte-free Al polymer capacitors and have introduced new materials for high performance and long life time Al polymer capacitors, which are novel oxidant, separators and negative current collectors. Furthermore, the electrolyte-free Al polymer capacitor in this study has several unique advantages like large capacitance to minimize electronic device size and low ESR to reduce power consumption and to guarantee long life time. The proposed Al polymer capacitors will become essential components for high-end electric devices.

Capacitors are energy storage components that consist of two conducting plates separated by an insulating material called the dielectric as described in Fig. 1. Energy is stored in dielectrics electrostatically through charge transfers. The positively charged plate that combines electrochemically with the dielectric is called the anode and the negatively charged plate is called the cathode [3].

Important factors that establish the capacitor use are operating voltage, capacitance and ESR. The operating voltage depends on the anode, while ESR is affected by material properties and components composition. The capacitance is determined by the permittivity and the dielectric surface area calculated by Equation (1)

$$C = \frac{\varepsilon A}{d} \quad (1)$$

The capacitance (C) increases with the dielectric area (A) and with the permittivity (ε) of the dielectric material. It decreases with distance (d).

Capacitors are classified by energy storage mechanisms, like electrostatic, electrolytic and electrochemical capacitors summarized in Table 1. The electrostatic capacitors are made with ceramic dielectric materials which endure a high voltage condition (~>1 kV). For electrostatic capacitors, energy is stored in dielectrics by electron flows. The electrolytic capacitors consist of the metal-oxide with a high dielectric constant as the dielectric material and the electrolyte with high ionic conductivity. They usually operate at moderate voltage conditions (~<400 V) and display a wide range of capacitance, which can be applied for general electronic circuits. The energy of electrolytic capacitors is stored in dielectrics by ion transport. The electrochemical capacitor, like a supercapacitor, store charges in the electric double layer with or without redox reaction. They could apply for the hybrid energy source or uninterrupted power supply. In general, these capacitors are not used alone, but together in the electric circuit.

Table 1
Capacitor classification.

Type	Name	Dielectric	Capacitance
Electrolytic	Al capacitor	Al_2O_3	uF ~ F
	Ta capacitor	Ta_2O_5	uF ~ mF
	Nb capacitor	Nb_2O_5	uF
Electrostatic	Ceramic capacitor	$MgNb_2O_6$, $ZnNb_2O_6$, $MgTa_2O_6$, $(ZnMg)TiO_3$, $Ba_2Ti_9O_{20}$, etc	pF ~ uF
	Film capacitor	Film (PP, PET, etc.)	pF
Electrochemical	Supercapacitor	Electric double layer	F ~ kF

Among these capacitors, electrolytic capacitors occupy about half of the capacitor market, and of which over 90% is Al electrolytic capacitors. They are widely used because they have shown a very large capacitance-to-volume ratio and the lowest cost-per-capacitance/voltage value. They are used as bypass, coupling, smoothing and buffer applications in power supplies and DC-links. Although they have a large capacitance, Al electrolytic capacitors have a short life time, relatively high ESR values, and a limiting ripple current, which induces difficulties in high-frequency applications, like PCs, LED lights, displays, etc. To overcome these problems, Al polymer capacitors without liquid electrolyte are suggested as advanced electrolytic capacitors.

1.1. Al polymer capacitors

Al polymer capacitor categorized electrolytic capacitor consists of a metal-oxide layer as a dielectric material. The construction is similar to that of Al electrolytic capacitors. Fig. 2(a) shows the structure of conventional Al electrolytic capacitors.

Conventional Al electrolytic capacitors are constructed from two aluminium foils and a spacer called a separator soaked in liquid electrolytes. The positive foil is an anode in the form of highly etched and anodized aluminium foil, and the negative foil is a cathodic current collector, which is bare aluminium foil. When power is loaded, the electrolyte anion is transported to the dielectric layer. The electrolyte is polarized and plays the role of the cathode. The electrolyte is also the contact medium between the dielectric material and the negative current collector. After two aluminium foils and separators are stacked and winded up, the winded cells are impregnated in the electrolyte and sealed. The

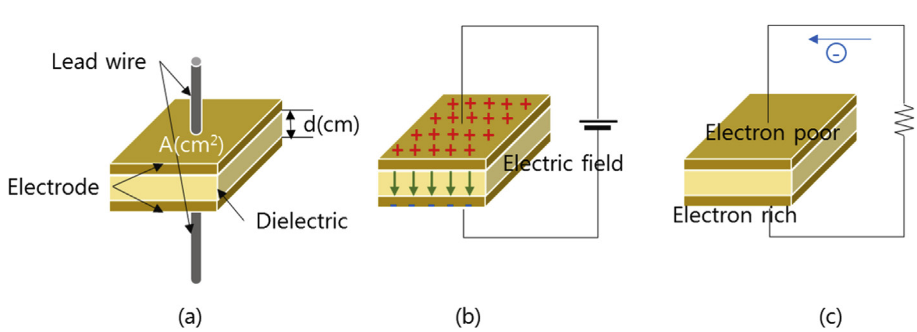

Fig. 1. Theoretical capacitor structures (a) charge storage, (b) discharge, and (c) mechanisms.