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Polyacene capacitors

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Abstract

We fabricated two types of polyacene capacitor with extremely stable polyacenic semiconductor (PAS) as the positive and negative electrodes. The first one is a coin-type PAS capacitor (six different sizes), which possesses large capacity with high reliability. Its capacity is much larger than that of the conventional electric double-layer capacitor which uses activated carbon as electrode. PAS capacitor can maintain more than 70% of the initial capacity even after 100 000 cycles. Moreover, this capacitor can be charged and discharged in a few minutes as well as at low rate. The second one is a cylinder-type PAS capacitor (diameter: 18 mm, height: 65 mm) which shows high capacity of 100 F and can discharge at the extremely high rate of 80 C. The coin-type PAS capacitor is currently used for memory back-up of electrical and communication equipment, and the cylinder-type is considered to be useful as power back-up for starting drive parts of electric equipment which needs high power density.

Keywords: Polyacene; Semiconductors; Conductive polymers

1. Introduction

Electric double-layer capacitors (EDLCs) using activated carbon as their electrodes are peculiar power sources with a high reliability. Especially, small coin-type EDLCs are widely used as memory back-up devices in many fields of portable electronic and communication equipment. Recently, EDLCs with relatively large capacity, such as the cylindrical and square types, have been developed for power back-up for electric equipment that needs high power density. Furthermore, these EDLCs are being developed for hybrid systems with regular batteries such as lead/acid batteries in electric vehicles.

On the other hand, we have developed polyacenic semiconductor (PAS) material prepared from pyrolytic treatment of phenol-formaldehyde resin [1,2]. PAS is a conductive polymer which can be doped to either p-type or n-type quite successfully and is extremely resistant to oxidation, chemicals and heat treatment [1,2]. Structural and electric transport analyses have shown that this material is essentially amorphous, with a rather loose structure [3,4]. This structure enables PAS to store a large amount of dopant with high stability. We have carried a study on the possibilities to apply this material in non-aqueous secondary batteries [5–8].

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Because PAS can be doped with both electron acceptors and donors, it is possible to design an 'all polymer' battery using PAS as the positive and the negative electrodes. By taking advantage of its stability, PAS batteries can embody greater reliability and longer service life than conventional secondary batteries.

PAS can be stably doped with a great number of lithium atoms, because of the amorphous structure, with much space in its interlayer. The theoretical doping amount of lithium in conventional carbon materials, for example graphite, is well known: LiC_6. We reported also that PAS can be doped up to an LiC_2 stage, which is three times as much as that of graphite, and that PAS has almost the same energy density as lithium metal for volumetric comparison [9,10].

In 1989 we commercialized coin-type PAS batteries, employing the PAS materials as both the positive and the negative electrodes. The charging/discharging curves of these batteries are well fitted by straight lines, as well as that of EDLCs. PAS batteries last for 100 000 charge/discharge cycles or more and show high reliability. The performance of PAS batteries is similar to that of EDLCs except for their capacity, which is twice or three times higher than that of common EDLCs [11]. Since the large capacity for PAS fits with the consumer's demand to have small batteries with high capacity, these types of PAS batteries are currently used for memory back-up in small-size electronic devices, such as pagers, cellular phones, IC memory cards, etc.

In recent years, we developed a cylindrical prototype PAS battery, which has about 10 to 100 times larger volume than the coin-types, and evaluated the capacity for the cylinder-type PAS batteries to be much higher than that of EDLCs in the same volume [12].

In this paper, we review the coin-type PAS battery (PAS capacitor) and report on the fundamental performance of the cylinder-type PAS battery (PAS capacitor).

2. Experimental

2.1. Preparation of PAS

Polyacenic semiconductor (PAS) was prepared by pyrolysis of phenol-formaldehyde resin molded with $ZnCl_2$ in advance [4,6,7]. In this study, the PAS sample with the [H]/[C] molar ratio of 0.22 was used, which was heat-treated at a pyrolytic temperature of 510 °C in a nitrogen atmosphere.

2.2. Coin-type capacitor fabrication

Our electrodes were prepared from a mixture of PAS powder, Teflon binder and carbon black conductor. The density and the electric conductivity of the PAS electrode at room temperature were 0.60 g/cm^3 and 5×10^{-2} S/cm, respectively. After drying in vacuum at 250 °C, two PAS electrodes were contacted with the positive and negative cans separately using a conductive adhesive to collect the electric current. The coin-type capacitor was fabricated by inserting a piece of glass felt separator of high purity grade between the positive and the negative electrodes. A solution of 1 M Et_4NBF_4/PC was used as the electrolyte. The positive and the negative cans were made mainly of stainless steel and the gasket was made of polypropylene. We fabricated six coin-type PAS capacitors: 414-type (diameter: 4.8 mm, height: 1.4 mm), 609-type (diameter: 6.8 mm, height: 0.96 mm), 621-type (diameter: 6.8 mm, height: 2.1 mm), 920-type (diameter, 9.5 mm, height: 2.0 mm), 2016-type (diameter 20 mm, height: 1.6 mm) and 2025-type (diameter 20 mm, height: 2.5 mm). The thickness of the PAS electrodes were 200–800 μm, in relation to the size of capacitor.

2.3. Cylinder-type capacitor fabrication

The electrodes were prepared from a mixture of PAS powder, polyvinylydene fluoride binder and carbon black conductor. The mixture was spread on aluminium foil and then dried. The thickness of this electrode was about 200 μm; its density and electric conductivity were 0.65 g/cm^3 and 1.5×10^{-2} S/cm, respectively. A tab was welded to each electrode to collect the electric current. The cylinder-type capacitor was fabricated by rolling spirally a positive electrode and a negative electrode inserted the polypropylene separator, and putting the rolled unit in negative can. A solution of 1 M Et_4NBF_4/PC was used as the electrolyte. The positive and negative tabs were welded to the positive cap and the negative can, respectively. The capacitor was sealed with a polypropylene gasket. This cylindrical capacitor was a 18650-type (diameter: 18 mm, height: 65 mm).

2.4. Performance of PAS capacitors

The charge/discharge characteristics of PAS capacitors were studied using the combination of potentiogalvanostat (Hokuto HA301 or HA 320) and a function generator (Hokuto HB 104). The internal resistance at 1 kHz, 1 mA a.c. was measured with an Ando AJ-2730B instrument.

The following characteristics on all the coin-type PAS capacitors were examined:

1. initial capacity and internal resistance;
2. charge/discharge behaviour at constant current;
3. charge/discharge behaviour at constant load;
4. temperature dependence of the capacity and internal resistance;
5. cycle-life performance, and
6. reliability in floating charge at 70 °C.

The following characteristics on the cylinder-type PAS capacitors were examined:

1. initial capacity and internal resistance;
2. capacity at high rate charge or discharge;
3. temperature dependence of the capacity and internal resistance, and
4. cycle-life performance.

3. Coin-type PAS capacitors

In these days, electronic and communication equipment carry microcomputers and, thus, batteries for memory back-up in microcomputers become essentially important parts. These batteries for memory back-up must demonstrate high reliability and it is desirable that their size be smaller and thinner owing to the miniaturization of the appliance. The coin-type PAS capacitor is an 'all polymer' battery and carries high reliability because of using PAS as electrodes. Furthermore, since the capacity of this capacitor is much larger than that of common EDLCs, which use activated carbon, PAS capacitor can be fabricated in a smaller size than EDLCs with the same capacity. The coin-type PAS capacitors is described in the Sections 3.1 to 3.5.

3.1. Capacity and internal resistance

Fig. 1 shows the charge/discharge curves for a coin-type PAS capacitor (609-type) at a constant current. With increasing doping amount, the cell voltage increases linearly, a similar behaviour to that of EDLCs. After being charged up to

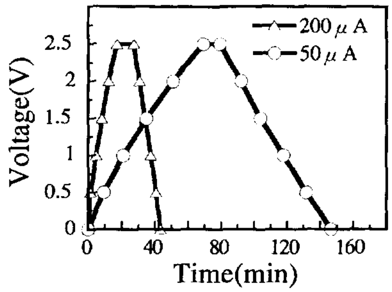

Fig. 1. Charge/discharge curves of the coin-type (609-type) PAS capacitor at constant current.

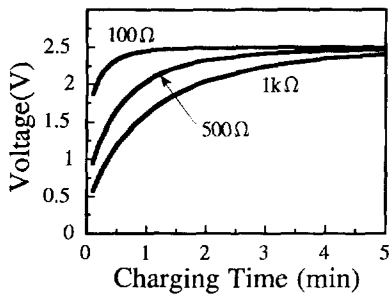

Fig. 2. Charging coin-type (609-type) PAS capacitor at constant load.

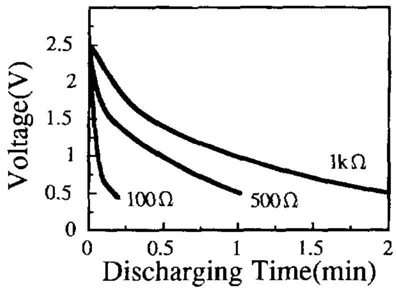

Fig. 3. Discharging coin-type (609-type) PAS capacitor at constant load.

2.5 V, it is discharged at a constant current. In the discharge processes, the cell voltage also decreases linearly. The capacity of the 609-type is 0.08 F from the slope of the discharge curve, in other words, 0.056 mAh (from 2.5 to 0 V), which is a remarkably high value in comparison with that of an EDLC of the same size. The internal resistance for this capacitor showed a value of 30 Ω, which is considered a good value. We also measured the capacity and internal resistance for a 414-type (diameter: 4.8 mm, height: 1.4 mm), 621-type, 920-type, 2016-type and 2025-type. The results are shown in Table 1. We confirmed that all the types of PAS capacitor have the capacity of two to three times higher than that of the corresponding EDLCs [13]. We obtained good interal resistance values.

3.2. Charge/discharge characteristics

In general, a charging system is inevitable for batteries. For example, if a battery can be charged only with a constant current, the battery charger would be complicated. It might be convenient for batteries to be chargeable at high as well as at low rates. We examined the charging capacity of the PAS capacitor (609-type) covering from high to low rate in a constant load. Charging at a constant load should be the simplest and the most convenient method. These results are shown in Fig. 2. It is obvious from the figure that PAS capacitor stores a sufficient quantity of electricity in a few minutes and that it can be almost 90% charge (at 100 Ω) within only 1 min. Furthermore, we tested the discharge-rate dependence of the capacity at various currents. The results are shown in Fig. 3. In a fairly short time (about 1 to 2 min), 90% of the capacity can flow out, this capacitor can thus be discharged in about 10 s. These results indicate that PAS capacitors can be charged and discharged at a very high as well as at a low rate. We consider that these capacitors can be conveniently used in equipment with a variety of applications.

3.3. Temperature versus capacitor performance

Batteries should be operable in a wide temperature range, e.g. in both hot and cool regions. We examined the temperature dependence of the capacity and the internal resistance in the range of −30 to 70 °C for the 609-type PAS capacitor. The results are presented in Figs. 4 and 5, each value of capacity being normalized by the value at 25 °C. As shown, the capacity increases and internal resistance decreases with increasing temperature. At lower temperatures, the capacity slightly decreases, for example, to 85% at −30 °C and the internal resistance inceases to 110 Ω, this value is almost three to four times larger than that at 25 °C. PAS capacitors, however, can operate at such a low temperature.

3.4. Cycle life

Cycle-life tests for a 609-type PAS capacitor were carried out by applying 2.5 V to the cell for 9 min through a 500 Ω

Table 1
Capacity and the internal resistance of coin-type PAS capacitors

Type	Diameter (mm)	Height (mm)	Capacity (mAh)	Capacity (F)	Internal resistance (Ω)
414	4.8	1.4	0.028	0.04	120
609	6.8	0.96	0.056	0.08	30
621	6.8	2.1	0.23	0.33	30
920	9.5	2.0	0.49	0.7	15
2016	20.0	1.6	2.08	3.0	2
2025	20.0	2.5	3.96	5.7	2

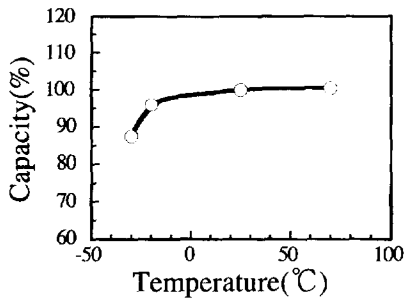

Fig. 4. Temperature vs. capacity for the coin-type (609-type) PAS capacitor in the range from −30 to 70 °C.

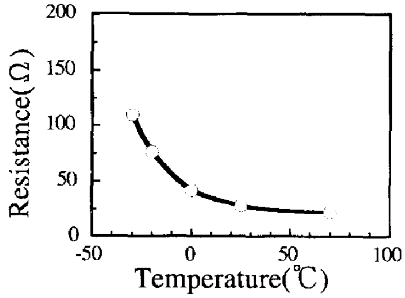

Fig. 5. Temperature vs. internal resistance for the coin-type (609-type) PAS capacitor in the range from −30 to 70 °C.

load and then to 0 V for 1 min at room temperature; this cycle has been repeated many times. The results shown in Fig. 6 demonstrate that the capacity stays at more than 70% of its initial value and the internal resistance increases very slightly after 100 000 cycles. This confirms that the PAS capacitors show excellent reliability with little deterioration even after almost 100 000 fully charge/discharge cycles.

3.5. Floating tests

We measured the capacity and internal resistance for a 609-type PAS capacitor after continuously applying 2.5 V at 70 °C for a certain time. The results are shown in Fig. 7. The capacitor can maintain more than 70% of the initial capacity, and the resistance of capacitor increased less than three times of its initial value, even at the severe condition, floating at 70 °C for 1000 h.

4. Cylinder-type PAS capacitors

The charge/discharge mechanism of the PAS capacitor does not rely on normal chemical reactions but on a doping/undoping process. The capacitor performance obtained for the coin-type PAS capacitors indicates that PAS is an excellent electrode. We supposed that this result can be extended to high power capacitors.

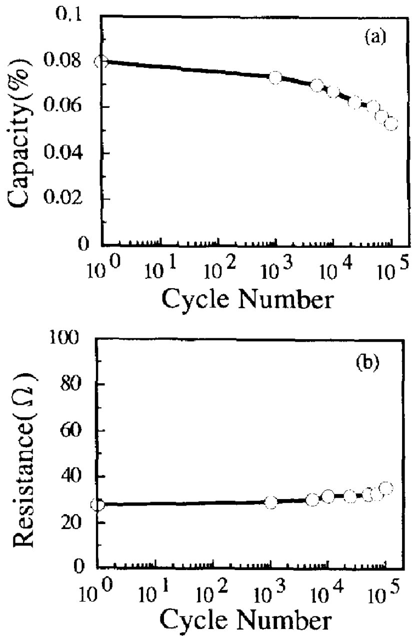

Fig. 6. Cycle-life test for the coin-type (609-type) PAS capacitor at room temperature: (a) change in capacity, and (b) change in internal resistance.

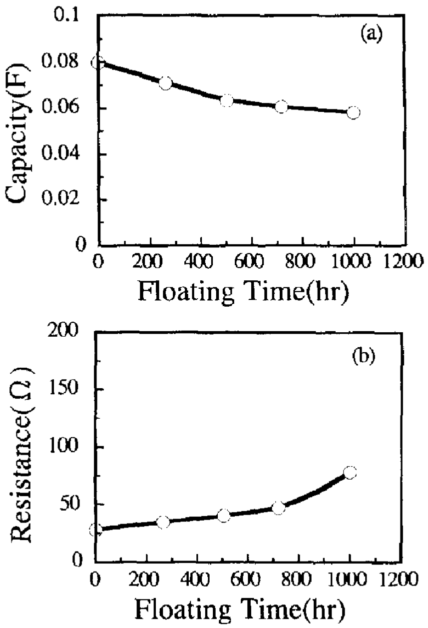

Fig. 7. Change in (a) capacity and (b) internal resistance by floating of 2.5 V at 70 °C for the coin-type (609-type) PAS capacitor.

In order to give high power to batteries, the surface area of electrodes must be more enlarged in comparison with that of the coin-type battery. Accordingly, we made a cylinder-type capacitor using the technique to wind spirally long and thin PAS electrodes.

4.1. Fundamental properties

We made the cylinder-type (18650-type) PAS capacitor, (diameter, 18mm, height: 65 mm). Its setup is shown schematically in Fig. 8. This cylinder-type capacitor was charged at a constant voltage of 2.5 V (maximum current at 100 mA)

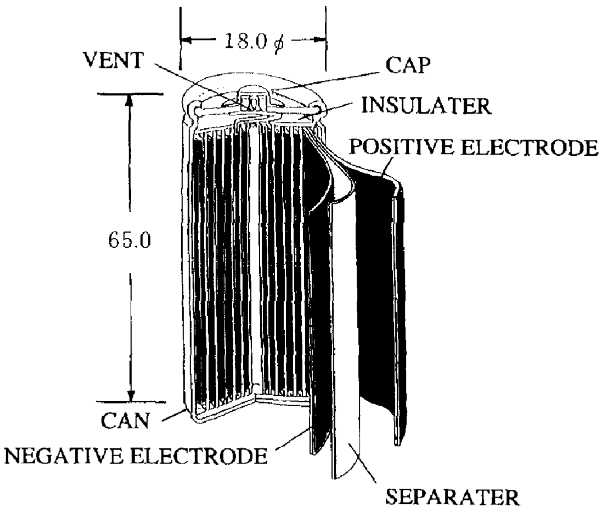

Fig. 8. Setup of the cylinder-type (18650-type) PAS capacitor.

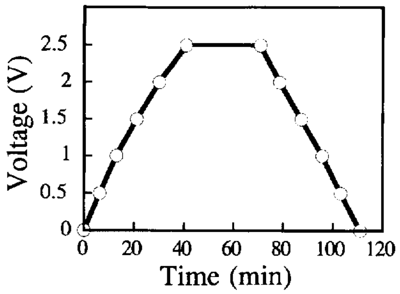

Fig. 9. Charge/discharge curve of the cylinder-type (18650-type) PAS capacitor at a constant current of 100 mA.

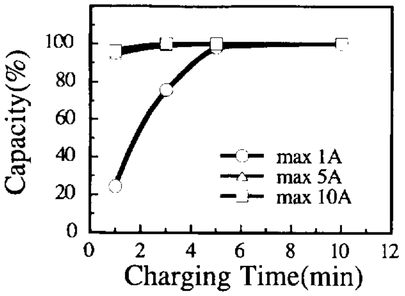

Fig. 10. Rapid charge performance by limiting at the maximum current of 1, 5 and 10 A for the cylinder-type (18650-type) PAS capacitor.

and then discharged at a constant current of 100 mA. We considered these conditions as a standard. A charge/discharge curve measured is presented in Fig. 9. Similarly to a coin-type PAS capacitor, the charge/discharge curve is also on a straight line and we estimated that the capacity is about 100 F from the slope of the discharging line, e.g., 70 mAh from 2.5 to 0 V. This value was much higher than that of an EDLC of the same size. We measured the internal resistance with an alternate current of 1 mA at 1 kHz and obtained the small value of 30 mΩ. This small internal resistance confirms that this capacitor can provide extremely high power density.

4.2. Rapid charge/discharge performance

We measured the capacity by charging in a few minutes. These results are shown in Fig. 10. In this test, we limited at a maximum current (1, 5 or 10 A). It is obvious from these results that this capacitor can be fully charged within a few minutes and even in a short time of 1 min 95% of the capacity in the standard condition can be charged.

Fig. 11 shows discharge current dependence of the capacity. The cylinder-type cell shows the ability of high rate discharging at 5 or 10 A. In 5 A discharge, the operating time is about 45 s, corresponding to a discharge at the rate of 80 C. We confirmed that the cylinder-type PAS capacitor can be a power source with extremely high power density.

4.3. Temperature dependence

We examined the temperature dependence of the capacity and the internal resistance in the range from −25 to 70 °C. Fig. 12 shows the results measured at a discharge current of

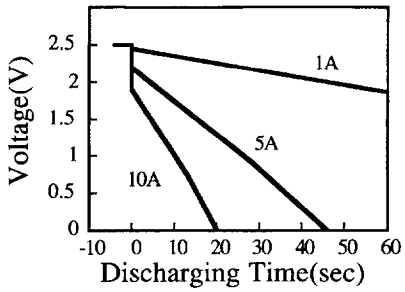

Fig. 11. Rapid discharge performance at constant current of 1, 5 and 10 A for the cylinder-type (18650-type) PAS capacitor

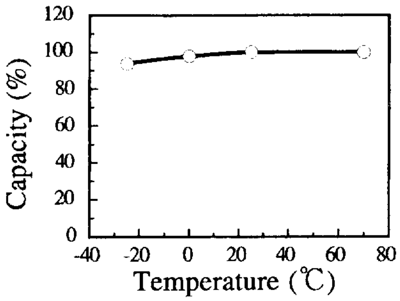

Fig. 12. Temperature vs. capacity for the cylinder-type (18650-type) PAS capacitor in the range from −25 to 70 °C.

100 mA at certain temperatures after the standard charging. The results show that the capacity decreases with decreasing temperature, but the capacity, even at −25 °C, is maintained at more than 95% of the value at room temperature. On the other hand, at 70 °C this capacitor can drain almost the same quantity of electricity as at room temperature. Fig. 13 shows the temperature dependence of the resistance. Even at low temperature of −25 °C, the 18650-type PAS capacitor has the internal resistance of 80 mΩ. This value can be affordable in practical use. The cylinder-type PAS capacitor has a good performance of the temperature dependence similar to the coin-type one.

4.4. Cycle-life performances

Cycle-life tests of a cylinder-type PAS capacitor were carried out by charging at 2.5 V for 10 min and discharging at 0 V for 2 min, repeatedly. The results are shown in Fig. 14. It is found that this capacitor can maintain a capacity of more

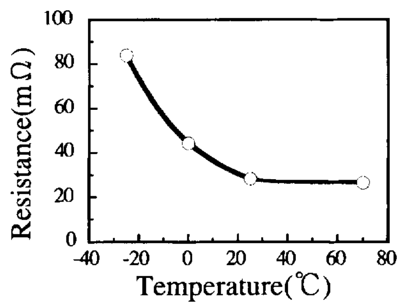

Fig. 13. Temperature vs. internal resistance for the cylinder-type (18650-type) PAS capacitor in the range from −25 to 70 °C.

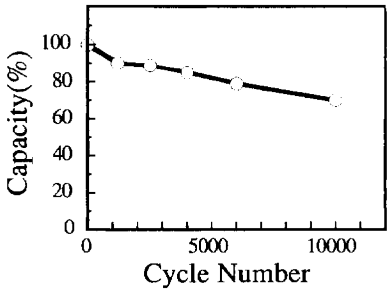

Fig. 14. Change in capacity by cycle-life tests for the cylinder-type (18650-type) PAS capacitor at room temperature.

than 70% of its initial value after 10 000 cycles and that it can be considered as a power source with high reliability.

4.5. Applications

This cylinder-type PAS capacitor is a power source with the excellent characteristics such as high reliability, high capacity and remarkable charge/discharge performance similar to the coin-type one. We, therefore, believe that this capacitor can be used as power back-up for starting drive parts of electric equipment, such as solenoids, motors, etc.

5. Conclusions

In the present paper, we investigated the performance of PAS capacitors with the peculiar polyacenic structure as the electrodes. We summarize the features of PAS capacitors as follows:

1. High capacity: with greater capacity than the conventional electric double-layer capacitor, PAS capacitors provide excellent back-up performance.
2. Small size: high capacity and excellent processibility of PAS electrodes permit battery miniaturization.
3. Long life: capacitors last for 100 000 charge/discharge cycles or more.
4. Rapid charge/discharge. Less than a few minutes are needed for charging or discharging.
5. High reliability: always reliable since they are better at withstanding overcharging for extended periods of time, and operable in environments of −30 to 70 °C.
6. Safe and environment/friendly: does not contain inflammable materials such as lithium, or heavy metals such as cadmium or mercury.

The coin-type PAS capacitors may be used in memory back-up and the cylinder-type PAS capacitors are considered to be useful as power back-up for starting of electric and electronic equipment.

We are in the middle of investigation of the PAS capacitor and are planning to apply it to electric vehicles.

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