ELSEVIER

Journal of Power Sources 60 (1996) 213–218

JOURNAL OF POWER SOURCES

Electric double-layer capacitors with sheet-type polarizable electrodes and application of the capacitors

Akihiko Yoshida, Seiji Nonaka, Ichiro Aoki, Atsushi Nishino

Matsushita Electric Industrial Co. Ltd., Moriguchi, Osaka, Japan

Received 5 January 1995

Abstract

Sheet-type polarizable electrodes with low sheet resistances for electric double-layer capacitors were outlined. The sheet-type electrodes consisted of activated carbon layers on aluminium foils. The sheet resistance of the sheet-type electrode mainly correlated with a filling density of activated carbons in the carbon layer. The species of activated carbons and the particle size of activated carbons affected the filling density of activated carbons in the layer. High filling ratio of activated carbons with small particle size resulted in the sheet-type electrodes with very low sheet resistance and high capacitance. Capacitors employing sheet-type electrodes showed very low internal resistance. Some application examples of the capacitor are described.

Keywords: Capacitors; Sheet-type electrodes; Activated carbon

1. Introduction

Electric double-layer capacitors consist of activated carbon polarizable electrodes, collector electrodes, separators, and electrolytic solutions. The electrical characteristics of the capacitors are significantly affected by the chemical and physical interactions between activated carbon and electrolytic solutions. Physical configuration of polarizable electrodes also affects capacitor characteristics such as capacitance and resistance [1–3].

Recently, we have developed capacitors with very low internal resistances and high capacitances [4–6]. A new sheet-type carbon electrode with very low sheet resistance resulted in the high performance capacitor with organic electrolytic solutions. The sheet-type electrode consisted of a mixture layer of activated carbon particles and organic binding material on aluminium foil collector electrodes. The sheet resistance of the sheet-type electrode significantly correlated with the species and particle size of activated carbons. Consequently, we found that high filling ratio of activated carbons with small particle size resulted in sheet-type electrodes with very low sheet resistance and high capacitance.

In this paper we will discuss: (i) relationship of a filling ratio of activated carbon particles versus sheet resistance of the electrodes; (ii) relationship of a filling ratio of activated carbon particles versus particle size; (iii) improved capacitor characteristics with sheet-type carbon electrodes, and (iv) several application examples of the new capacitors.

0378-7753/95/$09.50 © 1995 Elsevier Science S.A. All rights reserved
SSDI 0378-7753(95)02285-1

2. Experimental

2.1. Preparation of sheet-type polarizable electrodes

Fig. 1 shows the preparation procedure of the sheet-type polarizable electrode. In this experiment, several species of activated carbons and binding material were tested. The detailed description of the procedures are given in Section 2.1.1 to 2.1.3, see Fig. 2.

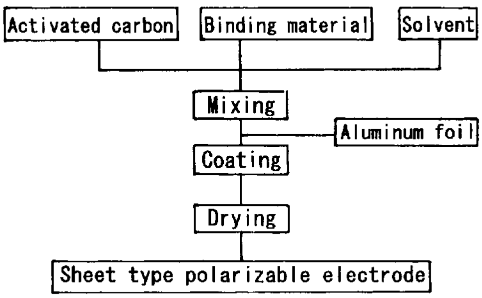

Fig. 1. Preparation procedure of sheet-type polarizable electrodes.

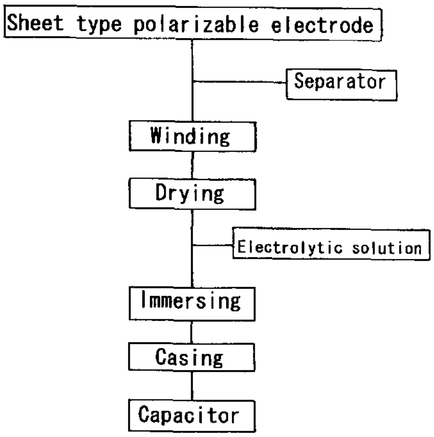

Fig. 2. Preparation process of the electric double-layer capacitors with sheet-type polarizable electrodes.

Table 1
Properties of various kinds of activated carbon

No.	Raw material	Specific surface area (S/(m^2 g))	Average diameter (D/μm)
1	Phenolic resin	2200	5.0
2	Phenolic resin	2000	3.5
3	Coconut shell	1700	5.2
4	Coconut shell	1500	5.3
5	Wood	1000	18.6
6	Petroleum coke	2000	30.0

2.1.1. *Mixing*

Activated carbons, organic binding material and organic solvent were mixed with an electric mixer, at room temperature, to form a carbon slurry. The raw material of the activated carbon powders were phenol resin, coconut shell, wood and petroleum coke. Table 1 shows the specific surface areas, average particle sizes of several types of activated carbon powders. Several types of organic binding materials for the carbon slurry were tested in order to form a uniform and smooth structure of the carbon layer; the final slurry composition was also determined.

2.1.2. *Immersing*

The carbon slurry was applied on the substrates to form carbon films. An aluminium foil with a thickness of 20 μm was dipped into the slurry, withdrawn from the slurry, and dried. Alumina ceramic substrates were used in order to measure the thickness of the carbon layer obtained.

2.1.3. *Drying*

The carbon slurry layer on the substrates (aluminium foils or alumina ceramics) was heated at 150 °C to form an activated carbon layer (thickness: about 60 μm).

2.2. *Properties of the sheet-type polarizable electrodes*

The sheet-type polarizable electrodes of the aluminium foil with activated carbon layers were examined with the following procedures.

2.2.1. *Filling ratio of activated carbons*

The sheet-type polarizable electrodes were buried in epoxy resins. The cross-sectional view of the polarizable electrodes was observed with an optical microscope. The filling ratio of the activated carbons in the carbon layer was calculated from the photomicrographs of the cross-sectional view of the polarizable electrodes; the filling ratio was determined by the occupation ratio of the activated carbon area to the total layer area in the photomicrograph of the cross-sectional view of the layer. Magnification for the microscopic observation was 500 × and the occupied areas were determined by the following procedure with cross-section graph papers; transparent cross-section graph papers were laid on the photomicrograph, and over and under 50% of occupation of each 1 mm^2 section area with carbon particles were accepted as areas of 1 mm^2 and 0 mm^2 for carbon particles, respectively.

2.2.2. *Measurement of the sheet resistance of the electrodes*

Electric sheet resistance was measured by an a.c. four-probe method with an electrometer (Kyowa Riken 705RL) for the activated carbon layer with a thickness of 60 μm on the alumina ceramic substrates.

2.3. *Preparation of electric double-layer capacitors with sheet-type polarizable electrodes*

A pair of the sheet-type polarizable electrodes obtained above, was wound with separators to form a capacitor electrode unit. The unit was dried under vacuum at 150 °C for 12 h to eliminate residual water, and immersed into the electrolytic solution, a mixture of propylene carbonate and 0.6 mol/l tetraethylammonium tetrafluoroborate, followed by casing with a rubber cap and an aluminium case. Fig. 3 shows the structure of the capacitor obtained. The diameter and the height of the capacitors were 10 and 15 mm, respectively.

2.4. *Estimation of the capacitor.*

Electric capacitances and d.c. resistances of the new capacitor were analysed in comparison with the conventional

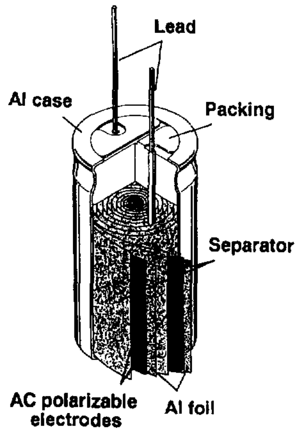

Fig. 3. Setup of the capacitor.

wound-type capacitor with activated carbon electrodes of high resistances.

2.4.1. Capacitance

The new capacitors were charged at a current of 10 mA for 12 h at 2.5 V and the conventional type at 2.3 V, followed by a discharge at a constant current of 10 mA to 0 V. The capacitance was calculated as follows:

$$C = 0.01t \quad (1)$$

where C is the capacitance in F, t the discharge time for the cell voltage from 1.5 to 0.5 V in s.

2.4.2. Internal resistance

The internal resistance was obtained from the initial voltage drop during the discharge of the capacitor at a constant-current discharge of 100 mA. Eq. (2) was used to calculate the internal resistance of the capacitor:

$$R = E/0.1 \quad (2)$$

where R is the internal resistance in Ω, E the initial voltage drop down of the cell voltage in V during discharge.

3. Results and discussion

3.1. Characteristics of sheet-type electrodes

3.1.1. Activated carbons

Fig. 4 shows the relationship between the sheet resistances of polarizable electrodes and the filling ratios of activated carbons, in which polarizable electrodes were formed with six species of activated carbons (see Table 1) and organic binding materials of a given composition. As shown in Fig. 4, the sheet resistance of the sheet-type polarizable electrodes depends only on the filling ratio of activated carbons in polarizable electrodes and not on the species of activated carbons. Although the weight ratio of binding materials and activated carbons in the slurry was set at a constant value, the filling ratio of activated carbons in the carbon layer ranged considerably from 35 to 75%. We are now studying the results in relation to particle size, specific surface area, surface structure, etc., that will be published elsewhere.

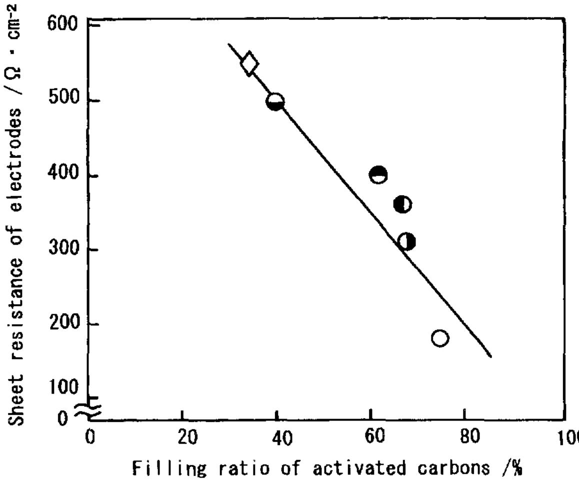

Fig. 4. Relationship between sheet resistance of polarizable electrodes and filling ratio of activated carbons. Numerals below coincide with those in Table 1: (○) no. 1; (◑) no. 2; (◐) no. 3; (◒) no. 4; (◒) no. 5, and (◇) no. 6.

3.1.2. Particle size of activated carbons

Fig. 5 shows the relationship between sheet resistances of the sheet-type electrodes and filling ratios of activated carbons with particle size from 18.1 to 3.5 μm. In the experiment, phenolic resin-based activated carbons were used with the binding material in Fig. 4, to form sheet-type electrodes. From Fig. 5, one may observe that the sheet resistance decreased with an increase in the filling ratio of activated carbons.

Fig. 6 shows a photomicrograph of the cross-sectional view of polarizable electrodes with activated carbons with particle sizes of 18.1 to 3.5 μm. Fig. 7 shows the relationship between the filling ratio of activated carbons in the carbon layer and particle sizes of activated carbons in the polarizable electrodes. Smaller particle size of activated carbons resulted in a higher filling ratio of activated carbons in the carbon layer. Short separation between activated carbon particles decreased the sheet resistance of the electrodes as shown in Fig. 5.

3.2. Characteristics of electric double-layer capacitors

3.2.1. Internal resistance

Fig. 8 shows the relationship between the internal resistance of the capacitors and the particle size of activated carbons. As seen from the figure, the internal resistance of the capacitors decreased with a decrease in particle size of the activated carbons. The low sheet resistance of the sheet-type electrodes resulted in a low internal resistance of the capacitor.

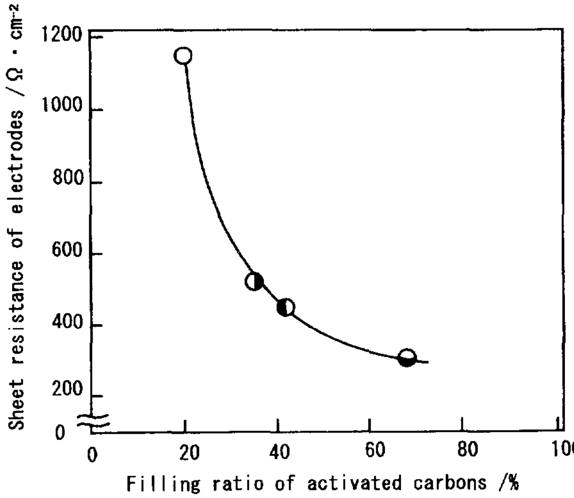

Fig. 5. Relationship between sheet resistance of electrodes and filling ratio of activated carbons: (○) diameter = 18.1 μm; (◑) diameter = 9.5 μm; (◐) diameter = 6.0 μm, and (◒) diameter = 3.5 μm.

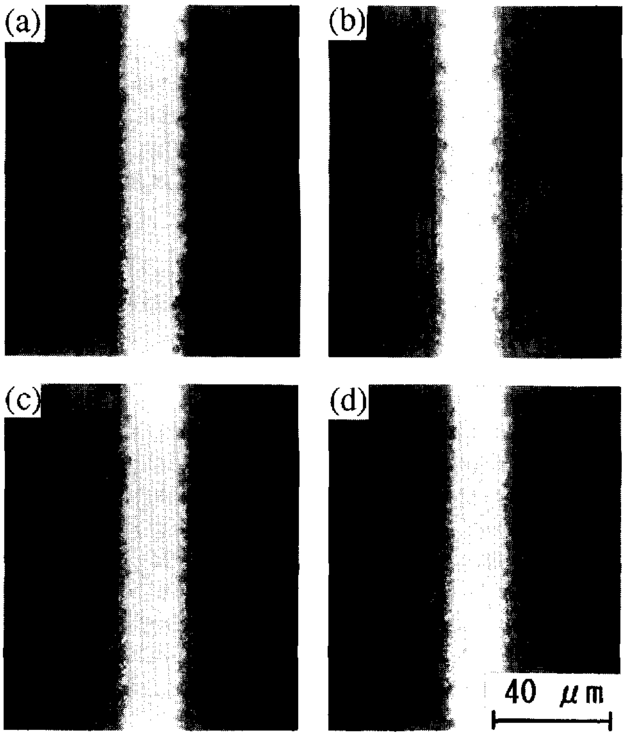

Fig. 6. Microscopic appearance of sheet-type polarizable electrodes: (a) diameter = 18.1 μm; (b) diameter = 9.5 μm; (c) diameter = 6.0 μm, and (d) diameter = 3.5 μm.

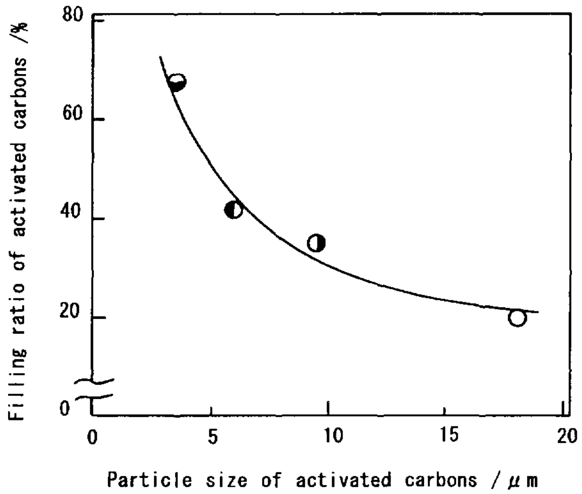

Fig. 7. Relationship between filling ratio of activated carbons and particle size of activated carbons.

3.2.2. Capacitance

Fig. 9 shows the relationship between the capacitances of the capacitors and the particle sizes of activated carbons in the carbon layer. Small particle size of the activated carbons resulted in high capacitance of the capacitor. An increase in filling ratio of activated carbons derived from the smaller particle size of activated carbons, gave a higher surface area of activated carbons in a unit volume of the capacitor.

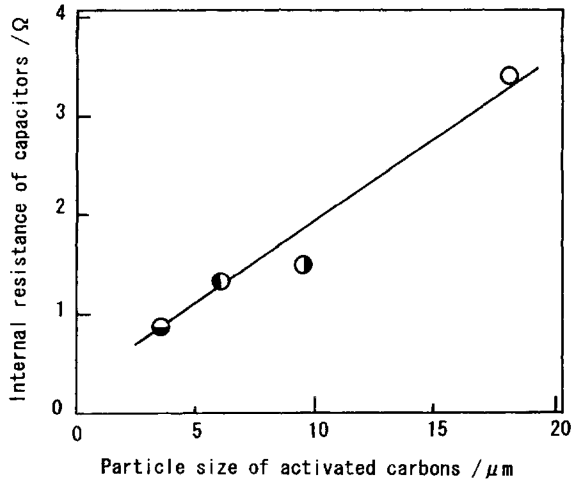

Fig. 8. Relationship between internal resistance of capacitors and particle size of activated carbons.

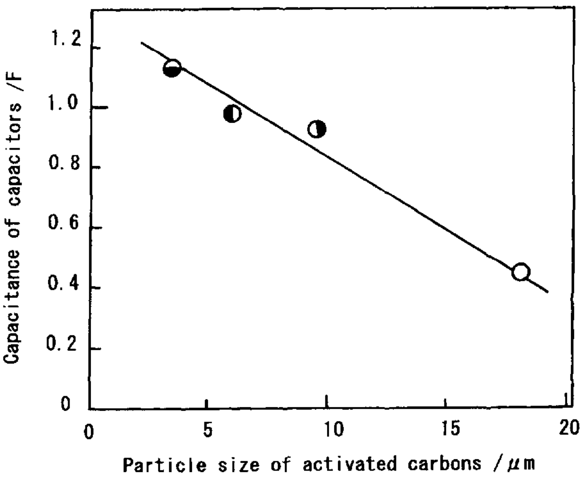

Fig. 9. Relationship between capacitance of capacitors and particle size of activated carbons.

3.2.3. Charge/discharge characteristics of the capacitor with sheet-type polarizable electrodes

Fig. 10 shows discharge characteristics of the 10 F capacitors with sheet-type polarizable electrodes at a constant current of 100, 500 and 1000 mA. In this figure, the discharge

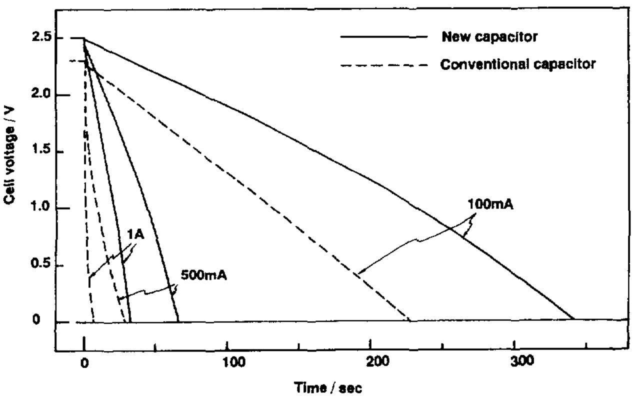

Fig. 10. Discharge characteristics of 10 F capacitors.

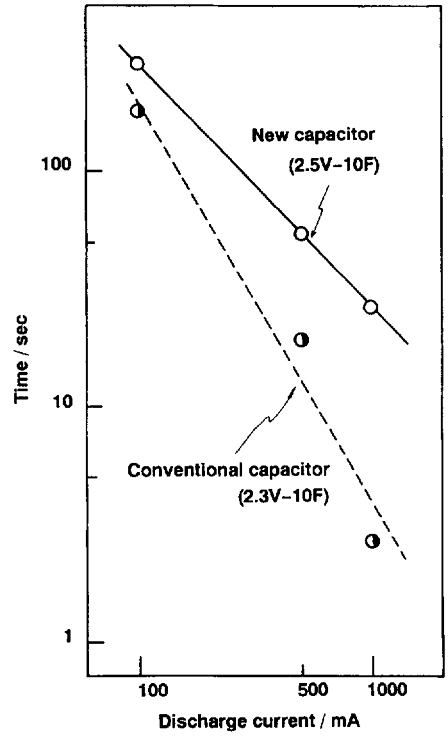

Fig. 11. Relationship between the back-up time and the current loaded to discharge the capacitors.

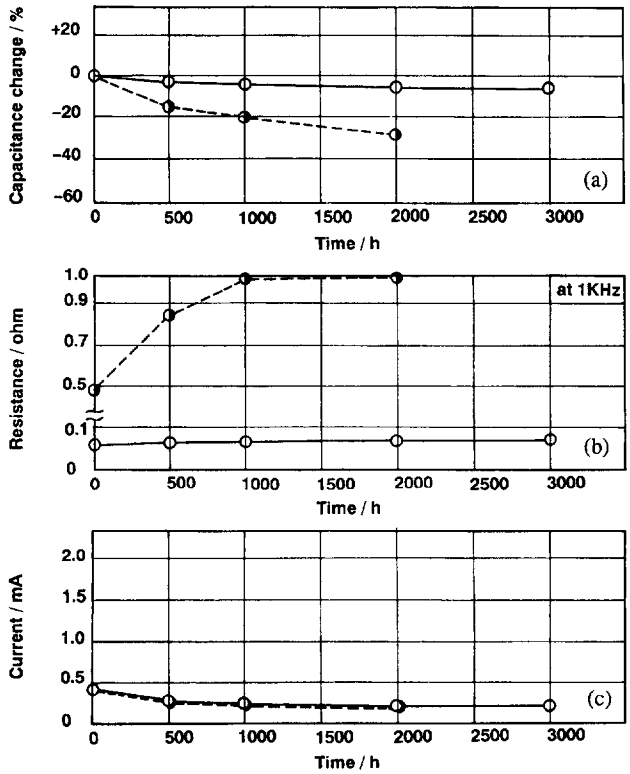

Fig. 12. Electrical performances of 10 F capacitors during cycle-life tests.

characteristics of the conventional capacitor are also given. The new capacitor shows a considerable small initial decrease in voltage compared with that of the conventional capacitor. From the results of 100 mA discharge characteristics, 0.1 and 1.5 Ω of the d.c. resistance were calculated for the new and the conventional capacitor, respectively. Fig. 11 summarizes the relationship between the back-up time and the current loaded to discharge the capacitors; the cutoff voltage was 0.5 V for the back-up time calculation. The conventional capacitor consists of electrodes with low-density carbon layers on aluminium substrates. As seen in these figures, the d.c. resistance of the new capacitors decreased dramatically to less than one tenth of that of the conventional capacitors, resulting in a considerable improvement of the back-up characteristics of capacitors.

Fig. 12 shows the electrical performance of 10 F capacitors during a life test at a maximum rated voltage, i.e. 2.5 V for the new and 2.3 V for the conventional capacitor, at 70 °C. As seen from the results, the changes in capacitance and resistance of the new capacitors are much smaller than those of the conventional capacitors.

Fig. 13 shows temperature characteristics of the new 2.5 V 10 F capacitor (solid lines) and the conventional 2.3 V 10 F capacitor (broken lines). The new capacitor shows excellent temperature characteristics.

3.3. Applications of the capacitors

The new capacitors with high density capacitance, low internal resistance, and small size, can be applied in many electrical appliances in which high current loads are required. Recently, several unique applications of the capacitors have started in the market of toys, home appliances, computer system back-ups, etc. Fig. 14 shows toys with the new capacitors.

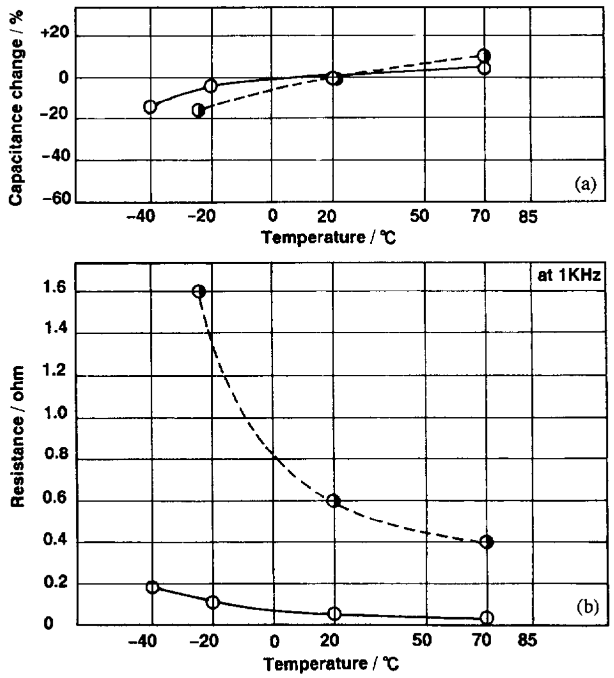

Fig. 13. Temperature characteristics of the capacitors.

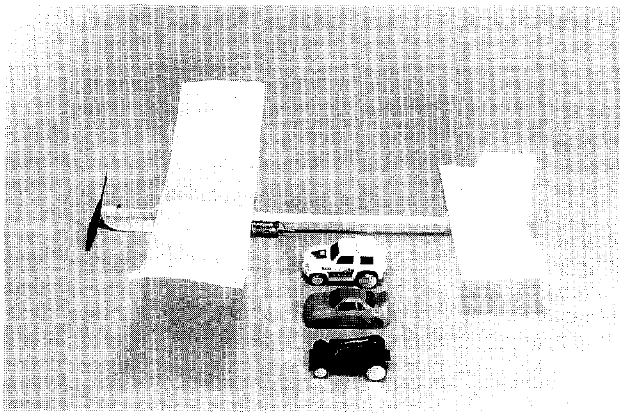

Fig. 14. Toys driving with the new capacitors.

4. Summary

Sheet-type polarizable electrodes with low-sheet resistance for electric double-layer capacitors were outlined. The sheet-type electrodes consisted of activated carbon layers on aluminium foils. The sheet resistance of the sheet-type electrode is mainly related to the filling density of activated carbons in the carbon layer. The species of activated carbons and the particle size of activated carbons affected the filling density of activated carbons in the layer. We have found that a high filling ratio of activated carbons with small particle size resulted in sheet-type electrodes with a very low sheet resistance and a high capacitance. The capacitors with sheet-type electrodes showed a very low-internal resistance and recently the capacitors are being used in many appliances.

References

[1] A. Yoshida, I. Tanahashi, Y. Yakeuchi and A. Nishino, *IEEE Trans. Comput., Hybrids Manuf. Technol., CHMT-11* (10) (1987) 100.
[2] A. Yoshida, I. Tanahashi and A. Nishino, *Carbon, 28* (1990) 611.
[3] A. Nishino, *Proc. Elecrochemical Society Meet., Hawaii, HI, USA, 1993.*
[4] A. Yoshida and K. Imoto, *US Patent No. 5 150 283* (1992).
[5] A. Yoshida, K. Imoto, H. Yoneda and A. Nishino, *IEEE Trans. Comp. Hybrids Manuf. Technol., CHMT-15* (1) (1992) 133.
[6] A. Yoshida, A. Nishino and K. Ohara, *Proc. 2nd Seminar Electric Double Layer Capacitors and Similar Energy Storage Devices, FL, USA, 1992.*