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Hybrid Capacitors Using Organic Electrolytes

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Abstract. Electric double-layer capacitors based on charge storage at the interface between a high surface area activated carbon electrode and an electrolyte solution are characterized by their long cycle-life and high power density in comparison with batteries. However, energy density of electric double-layer capacitors obtained at present is about 6 Wh/kg at a power density of 500 W/kg which is smaller as compared with that of batteries and limits the wide spread use of the capacitors. Therefore, a new capacitor that shows larger energy density than that of electric double-layer capacitors is proposed. The new capacitor is the hybrid capacitor consisting of activated carbon cathode, carbonaceous anode and an organic electrolyte. Maximum voltage applicable to the cell is over 4.2 V that is larger than that of the electric double-layer capacitor. As a result, discharged energy density on the basis of stacked volume of electrode, current collector and separator is more than 18 Wh/l at a power density of 500 W/l.

Key words : Polyurethane acrylate, Lithium ion battery, Gel polymer electrolyte, Curable mixture, Ionic conductivity

1. Introduction

Electric double-layer capacitors based on the charge storage at the interface between a high surface area activated carbon electrode and an organic electrolyte have been developed, and are widely used as maintenance free power source for IC memories and microcomputers[1].

The popularity of electric double-layer capacitors is due to their long cycle life and high power density relative to batteries. Electric double-layer capacitors exhibit, in principle, unlimited cycle life and maintenance free operation as an alternative to batteries in power circuits[2]. One of the new promising applications for electric double-layer capacitor is a pulse power source in electric and hybrid electric vehicle (HEV) applications. The pulse power source provides the peak power during acceleration and recovers energy during braking using a generator.

Ni-hydrogen battery and Li-ion battery are now practically used in HEV as pulse power sources. Furthermore, redox capacitors have been proposed and are being studied[3]. However, batteries and redox capacitors are not so stable in cycle-life performance as the electric double-layer capacitors and some safety device needs to be installed in practical use.

On the other hand, the energy density of electric double-layer capacitors is smaller than that of redox capacitors and batteries because of the small capacity. The energy of electric double-layer capacitor is expressed as $1/4CV_e^2$, where C is the capacitance of an activated carbon electrode and V_e is the cell voltage. Accordingly, large capacitance and high cell voltage are required to obtain high energy. This condition may not be realized in practical application of electric double-layer capacitors because the utilization efficiency of pore surface of activated carbon electrode restricts the capacitance and the decomposition potential of electrolyte limits the cell voltage. To obtain the new device that shows large energy density, high power density and stable performance, a new hybrid capacitor is developed. This new capacitor is comprised of an organic electrolyte containing Li salt, an activated carbon cathode and a carbonaceous anode that can intercalate and de-intercalate Li ion.

In this paper, the construction, the material and the performance of the new hybrid capacitor are described.

1.1. Principle

To obtain pulse power source of excellent performance, various hybrid capacitors such as activated carbon/$Li_4Ti_5O_{12}$[4], PFPT/activated carbon[5] and NiOOH/ carbon nano fiber[6] have been proposed. One of the electrodes in hybrid capacitor has redox capacity that is far larger than the electric-double layer capacitance of activated carbon. In such a case, the energy of hybrid capacitor is expressed as $1/2CV_h^2$, where C is the capacitance of activated carbon electrode and V_h is the cell voltage of the capacitor. In order to obtain large anode capacity and high cell voltage, we studied hybrid capacitor comprised of an activated carbon cathode, a carbonaceous anode and an organic electrolyte containing Li-salt.

Figure 1 and 2 show the principle of the hybrid capacitor[7-9]. The activated carbon cathode in the hybrid capacitor adsorbs anions at the electric double-layer in the same way as the activated carbon cathode in the electric double-layer capacitor during charging and linearly polarizes to positive side. On the other hand, carbonaceous anode in the hybrid capacitor intercalates Li ions into its graphene layer during charging and de-intercalates Li ions during discharging. When the

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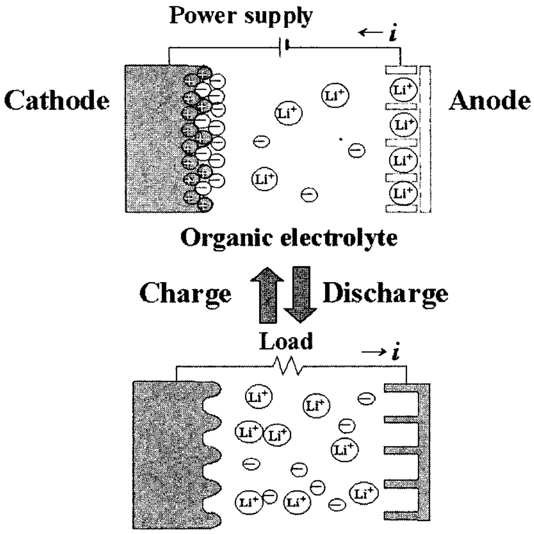

Fig. 1. Principle of the hybrid capacitor.

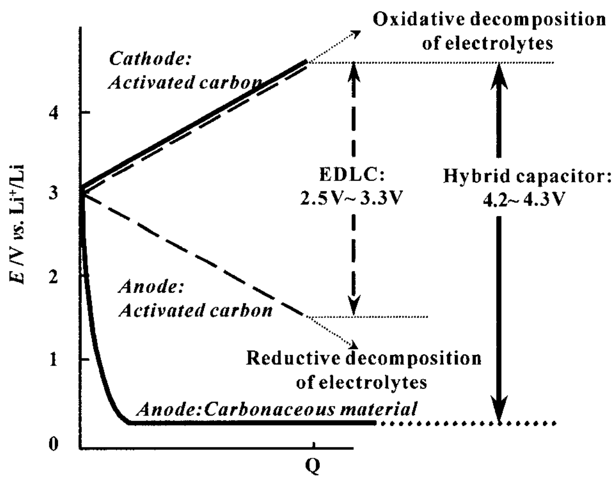

Fig. 2. Schematic polarization curves of capacitors.

anode is charged, potential of the anode becomes very low and approaches to the potential of Li-metal anode. As a result, voltage applicable to the cell is over 4.2 V and larger than that of the electric double-layer capacitor. Moreover, capacity of the carbonaceous anode is about 370 mAh/g and far larger than the electric double-layer capacity of the activated carbon. Therefore, the energy of the hybrid capacitor becomes larger than that of the electric double layer capacitor.

2. Experimental

The anode should show low working potential, quick charge and discharge characteristics and long cycle-life performance. The carbonaceous material that shows low potential during charging is used as an anode.

Electrolyte solution should not only be compatible with the graphitic carbon anode and the activated carbon cathode but also show high conductivity. So, the mixed solution of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) containing 1 M Li-salt is used as the electrolyte.

The hybrid capacitor shown in Fig. 3 is assembled. The assembly consists of a stack of a pair of the activated carbon cathode layer coated on Al-foil and the carbonaceous anode layer coated on Cu-foil and a porous separator. These Al- and Cu-foils act as current collectors.

The anode, the porous separator and the cathode are stacked and housed in prismatic Al-laminated film cell. After the organic electrolyte solution is poured, the cell is sealed taking out the leads. The size and the capacity of the cell are $53^h \times 31^w \times 2^t$ mm and 1.8mAh, respectively.

To compare the performance of the hybrid capacitor with others, Li ion battery and electric double layer capacitor of the same construction and dimension as the hybrid capacitor are also prepared and tested.

3. Results and Discussion

Figure 4 shows the charge characteristics of the hybrid capacitor under constant current of 50, 100 and 300 mA to the cell voltage of 4.2 V. The capacitor can be charged within 44 seconds for 100 mA and 7 seconds for 300 mA.

Figure 5 shows the discharge characteristics of the hybrid

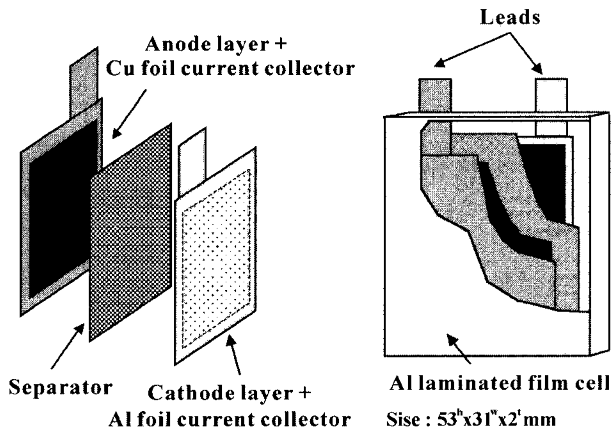

Fig. 3. Cell construction.

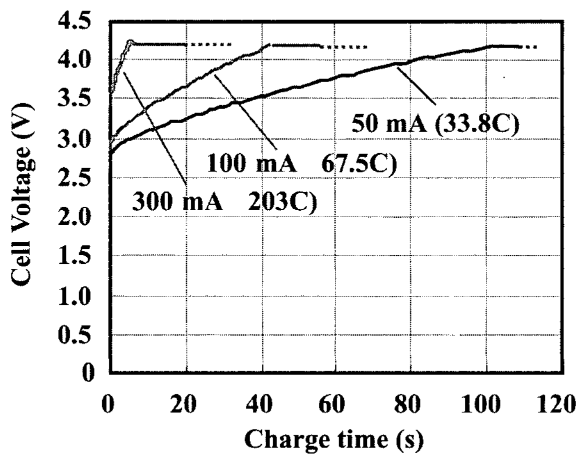

Fig. 4. Charge characteristics of the hybrid capacitor.

capacitor under various constant discharge currents. The cell voltage of the capacitor decreases almost linearly under constant discharge current from 4.2 V to 2.75 V in 46 seconds for discharge current of 100 mA and in 8 seconds for discharge current of 300 mA. Constant charge and discharge current of 100 mA and 300 mA correspond to the charge and discharge rate of 67.5C and 203C, respectively. It is seen that the hybrid capacitor shows excellent charge and discharge rate capability.

Figure 6 compares rate capability of capacitors and Li ion battery. As shown in the figure, capacity percentage of the Li-ion battery decreases drastically as the discharge rate becomes large. While, decrease in capacity percentage of capacitors with the increase in discharge rate is not so large as that of Li-ion battery. This is probably because the rate of intercalation of Li ions at the oxide cathode is slower than the rate of de-intercalation of Li ions at the carbonaceous anode in Li-ion battery. In other words, the rate of de-intercalation of Li ions at the carbonaceous anode in the hybrid capacitor is considerably fast and comparable with the rate of the desorption reaction at the activated carbon anode in the electric double layer capacitor.

The temperature dependence of the capacity of the hybrid capacitor using carbonaceous anode is shown in Fig. 7. The capacity of the hybrid capacitor decreases with the lowering of temperature and the increase in discharge rate. The hybrid capacitor at -25°C maintains 50% of the capacity at 25°C at the discharge rate less than 6.8C.

Figure 8 compares the energy density and power density of the hybrid capacitors, the Li-ion battery and the electric double-layer capacitor on the basis of the stacked volume of electrodes, current collectors and separator of each cell. Energy density of the hybrid capacitor using carbonaceous anode discharged from the cell voltage of 4.0 to 1.5 V is 18 Wh/l at a power density of 500 W/l and becomes small as the power density increases. Although, the energy density of the hybrid capacitor is smaller than that of Li-ion battery discharged from the cell voltage of 4.0 V to 1.5 V at the power density of less than 1500 W/l, it becomes higher than that of Li-ion battery at the power density of more than 1500 W/l. This is probably because the rate of de-intercalation of Li ions out of carbonaceous anode is fast. The energy density of the hybrid capacitor is 2 or 3 times larger than that of electric

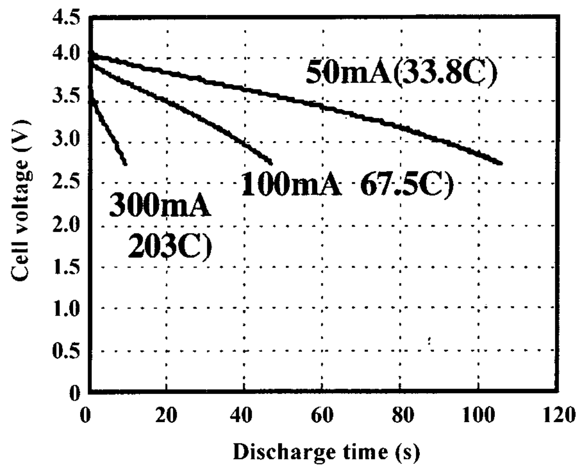

Fig. 5. Discharge characteristics of the hybrid capacitor.

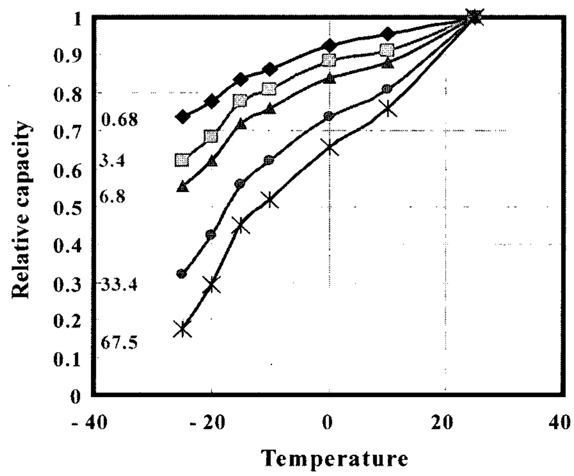

Fig. 7. Temperature dependence of the capacity of the hybrid capacitor.

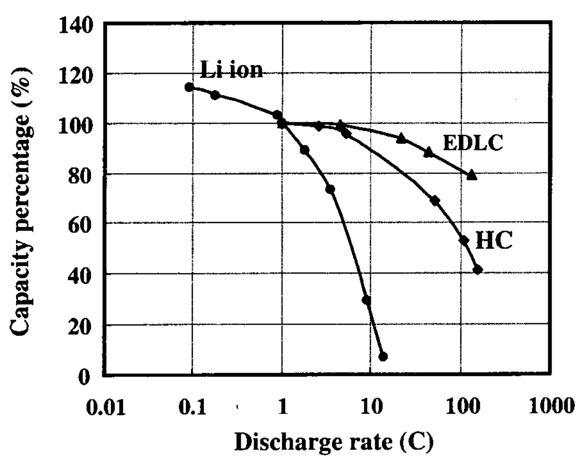

Fig. 6. Dependence of the capacity on the discharge rate.

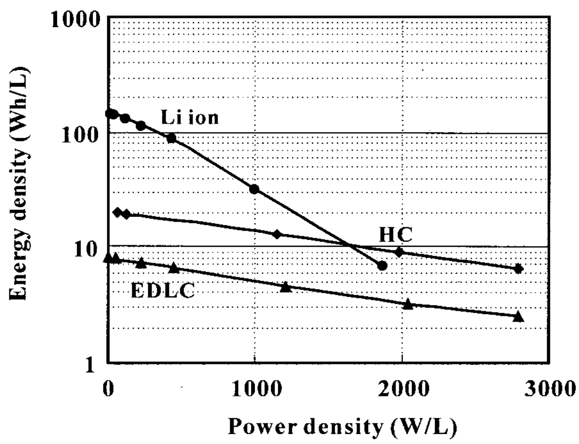

Fig. 8. Energy density and power density of capacitors and Li ion battery.

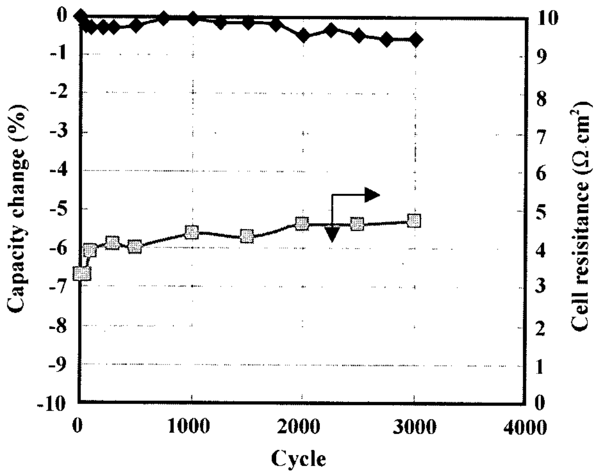

Fig. 9. Charge-discharge cycle life performance of the hybrid capacitor.

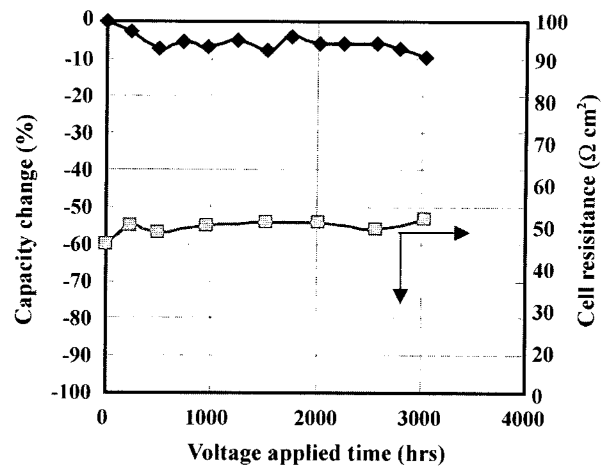

Fig. 10. Stability of the hybrid capacitor against voltage application.

double layer capacitor discharged from the cell voltage of 2.7 V to 1.0V.

It is necessary for pulse power sources to have long-term stability as well as high energy density and power density. Figure 9 shows the cycle-life performance of the hybrid capacitor at 45°C at a constant charge and discharge current of 100 mA cycled between the cell voltage of 4.0 V and 1.5 V. The cell cycled between 4.0 V and 1.5 V shows the capacity loss of less than 6% and internal resistance increase of less than 45% after 30,000 times charge and discharge cycles. Capacity loss and internal resistance increase of the cell become small with the progress of charge and discharge cycles. Although, the deterioration in capacity and energy density of the cell is a little larger than that of electric double-layer capacitor, the deterioration after 10 thousands times fast and deep charge and discharge cycles is expected to be small.

To the contrary, it is said that the batteries such as Li-ion battery deteriorate considerably after thousand times charge and discharge cycles. So, the hybrid capacitor using carbonaceous anode is superior to Li-ion batteries in cycle life performance and suitable for power sources that need to be charged and discharged many times without deterioration.

Stability against voltage application of 4.0 V to the cell at 60°C is shown in Fig. 10. Capacity loss and internal resistance increase of the hybrid capacitor using carbonaceous anode after the voltage application of 3000 hours are less than 10% and 20% respectively, and almost the same with those of the electric double layer capacitor. Therefore, the hybrid capacitor is suitable for power sources that are kept charged for a long time.

4. Conclusions

In conclusion, although, the electric double-layer capacitors show high power density as well as extremely long cycle-life, their energy density is small as compared with that of the battery. To overcome this problem, the hybrid capacitor comprised of activated carbon cathode, carbonaceous anode and mixed solvent of EC and EMC containing 1 M lithium salts was studied.

Maximum voltage applicable to the hybrid capacitor is more than 4.2 V. The energy density of the hybrid capacitor discharged from the cell voltage of 4.0 V to 1.5 V is 18 Wh/l at a power density of 500 W/l, which is higher than that of the electric double-layer capacitor. The hybrid capacitor shows good cycle-life performance and stability against the voltage application.

Therefore, the hybrid capacitor is expected to be suitable for pulse power sources in hybrid electric vehicle and so on.

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