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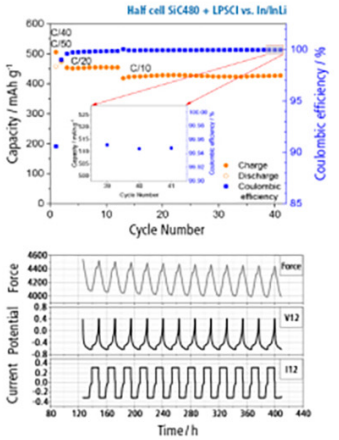
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Development of a Lithium-Type Advanced Energy Storage Device

Akira Yoshino,[a,*] Toshio Tsubata,[a] Michiko Shimoyamada,[a] Hisashi Satake,[b] Yukiko Okano,[b,z] Shiro Mori,[b] and Shizukuni Yata[b]

[a]*Asahi Kasei EMD Corporation, Battery Materials Business Development Department, Shinjuku-ku, Tokyo 160-0023, Japan*
[b]*KRI, Incorporated, Energy Conversion Research Laboratory, Shimogyo-ku, Kyoto 600-8813, Japan*

We have developed a device using a novel composite material as the negative electrode and ordinary activated carbon as the positive electrode. The composite material was obtained by heat-treatment of activated carbon with pitch. The structure of this composite was shown to be amorphous based on the X-ray diffraction pattern, and the surface area decreased from 2200 m^2/g (activated carbon) to 250 m^2/g (composite). This device can discharge at an extremely high current density of 10,000 mA/g based on the composite weight. The power density of around 2.2 kW/L was two times higher than EDLCs, and the energy density of around 20 Wh/L was three times higher. The discharge capacity maintained its initial capacity for at least 100,000 cycles. This device also had excellent storage characteristics at 60°C.
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Recently, hybrid electric vehicles (HEVs) have attracted attention as environment friendly cars. A high power density, high energy density, and extremely high durability are requirements when energy storage devices are applied to HEVs. Promising candidates for application in HEVs are batteries such as the nickel-metal hydride (Ni-MH) battery, lithium ion battery (LIB), and electric double-layer capacitor (EDLC). Batteries have a high energy density but a poor power density and poor durability. EDLC has a high power density and high durability but a poor energy density.

We developed a composite material based on activated carbon for the negative electrode, which could be efficiently doped with lithium and has an excellent rate capability.[1-6] This composite material was obtained by heat-treatment of activated carbon with pitch. The composite exhibited a high efficiency during the first charge-discharge process, which was much greater than that of general activated carbon. In addition, the composite could be doped/undoped with lithium at an extremely high rate over 100 C. These characteristics indicated that this composite has a suitable structure for lithium doping and undoping.

In this paper, we reported the preparation method and the characteristics of a modified activated carbon composite. Furthermore, we investigated the basic performance and durability of a new energy storage device using the above-described composite as the negative electrode.

Experimental

Preparation of the negative electrode active material and negative electrode.—The negative electrode active material was modified an activated carbon composite prepared by the heat-treatment (700°C) of activated carbon [the Brunauer-Emmett-Teller (BET) surface area was 2200 m^2/g] with pitch under an inert atmosphere.[2] An X-ray diffraction (XRD) measurement of the composite was performed using a Rigaku Geigerflex-4036A2 XRD with Ni-filtered Cu Kα radiation. The interlayer spacing was estimated by the Bragg method, and the crystallite size was estimated by a Scherrer-type formula. The BET surface area and pore size distribution of the composite was measured using a Quantachrome Nova 1200.

The composite, acetylene black as the conductive filler, and n-methyl pyrrolidone (NMP) solution of poly(vinylidene fluoride) (PVDF) were mixed and coated on copper foil current collectors. The density of the electrode was 0.8 g/cm^3. The electrochemical properties of the composite were investigated using a three-electrode cell with lithium counter and reference electrodes.

Preparation of the positive electrode.—The positive electrode active material was ordinary activated carbon and its BET surface area was 2200 m^2/g. The activated carbon, acetylene black as the conductive filler and NMP solution of PVDF were mixed and coated on aluminum foil current collectors. The density of the electrode was 0.6 g/cm^3.

Fabrication of the test devices.—Test devices were fabricated by the same method using a nonaqueous electrolyte containing Li ion as previously reported.[2] The positive electrode and the negative electrode were stacked by insertion of a microporous polyethylene membrane, and 1 M $LiPF_6$ in ethylene carbonate/diethyl carbonate (EC/DEC, 3:7 by volume) as the electrolyte. These devices were investigated the evaluations of their electrochemical characteristics under various conditions.

Results and Discussion

Structural characteristics of the modified activated carbon composite.—The modified activated carbon composite was prepared by the heat-treatment of activated carbon with pitch. The rate of increase after heat-treatment was about 55% by measurement of its weight. We consider that some carbonaceous material attaches during the heat-treatment. The XRD patterns of the composite and activated carbon are shown in Fig. 1.

Although the peak of the activated carbon is unclear, we can find a broad peak in the pattern of the composite. We consider that the appearance of the new peak is caused by attached carbonaceous material. The crystallite size (in the *c* axis direction for graphite) and space distance ($d002$) of the composite is 12.1 and 3.66 Å, respectively. This pattern shows that the attached carbonaceous material has an amorphous structure.

As shown in Fig. 2, the pore size distribution of activated carbon is drastically changed by the heat-treatment. Both the mesopores (between 20 and 500 Å) and micropores (under 20 Å) significantly decrease in all ranges of the diameters; the BET surface area also decreases from 2200 to 250 m^2/g. The particle size does not change.

These results indicate that by the heat-treatment the vapor generated from the pitch became attached to the inner surface and pyrolyzed into an amorphous carbonaceous material. We conclude that this amorphous carbonaceous material covering the original surface of activated carbon causes the change in the pore structure.

Electrochemical characteristics of the modified activated carbon composite.—We evaluated the coulombic efficiency of the composite and base activated carbon as a reference by using a three-

* Electrochemical Society Active Member.
z E-mail: yukiko_o@kri-inc.jp

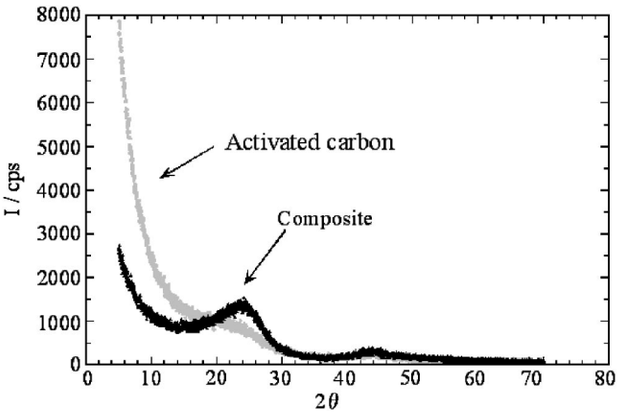


Figure 1. The XRD patterns of the composite and base-activated carbon.

electrode cell with lithium counter and reference electrodes. The efficiency of the composite for the first lithium doping/undoping process is 53.3%. This is much higher than 27.1% for activated carbon.

As a preliminary study, we assembled the test cells with the composite electrode being made up of a negative electrode and the activated carbon electrode as a positive electrode and evaluated the rate capability. The cell can discharge at an extremely high current density of 10,000 mA/g based on the composite weight.

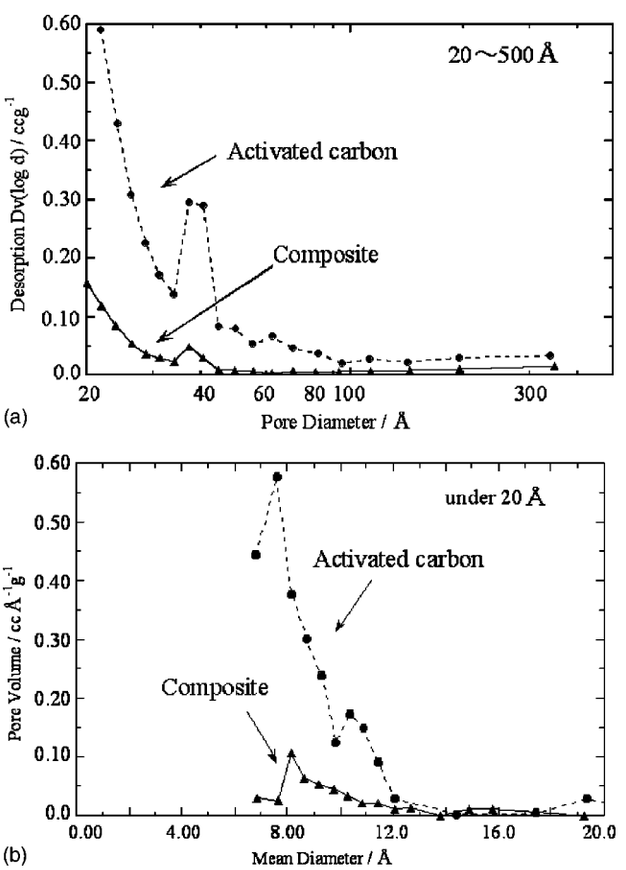


Figure 2. The pore size distribution of activated carbon and composite. (a) The distribution of the mesopores (between 20 and 500 Å), and (b) distribution of micropores (under 20 Å).

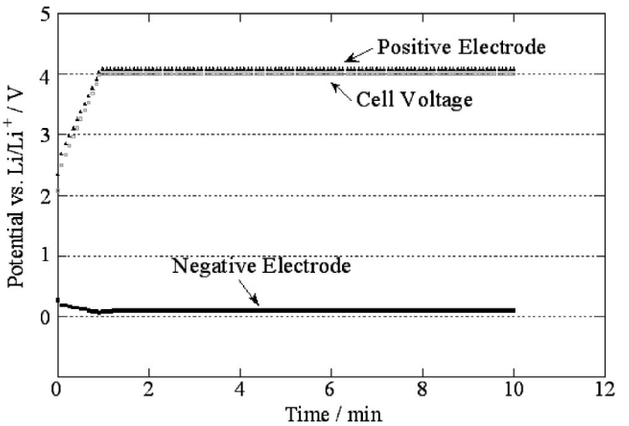


Figure 3. Potential profiles during charging at a constant current/constant voltage (4.0 V max).

Electrochemical system of the lithium-type advanced energy storage device.—We evaluated the potential profile of the positive and negative electrodes using a test device with a Li reference electrode. Figure 3 shows the potential profile of this device during constant current/constant voltage charging. The cell was charged to 4.0 V under constant current and then maintained at 4.0 V for 10 min. The potential of the positive electrode changes from 2.4 to 4.1 V *vs.* Li/Li^+. Double-layer formation by charge separation at the interface between the activated carbon and electrolyte occurred during charging, that is the same phenomena as that in a positive electrode of a conventional double-layer capacitor. The potential of the negative electrode changed from 0.3 to 0.1 V *vs.* Li/Li^+. During charging the potential of the negative electrode was maintained above that of Li metal. The detailed mechanism of these phenomena within the negative electrode is still under investigation, but it seems that both the double-layer formation and faradaic reactions simultaneously occurred.

After discharging, the potential of the positive electrode and negative electrode return to the same values as those before charging. This new device can reversibly work between 4.0 and 2.0 V, and the working voltage is about two times higher than that of conventional EDLCs.

High charge rate capability of the lithium-type advanced energy storage device.—Figure 4 shows the discharge curves for the above-

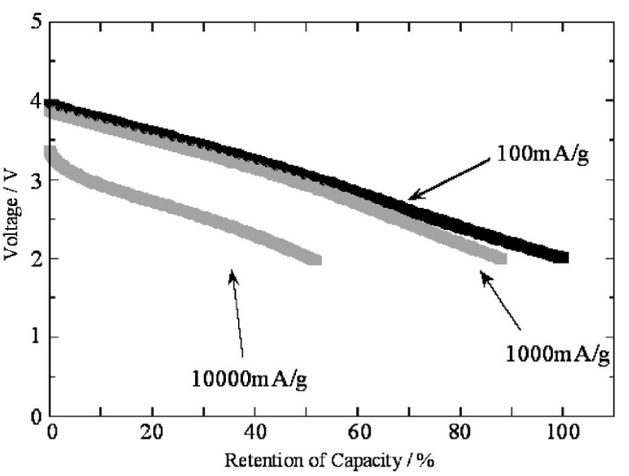


Figure 4. Rate capability of the test device using the composite as negative electrode.

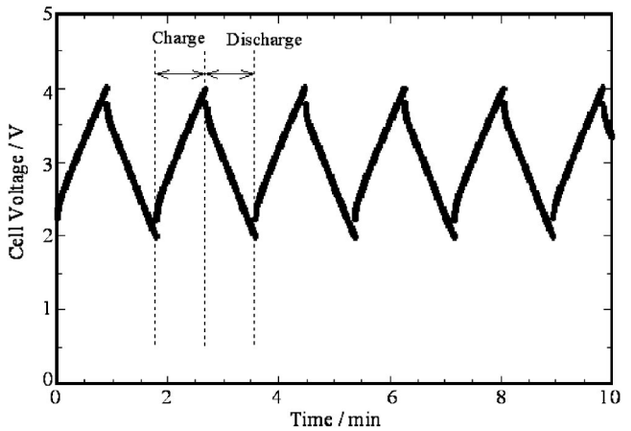


Figure 5. High rate charge and discharge profiles.

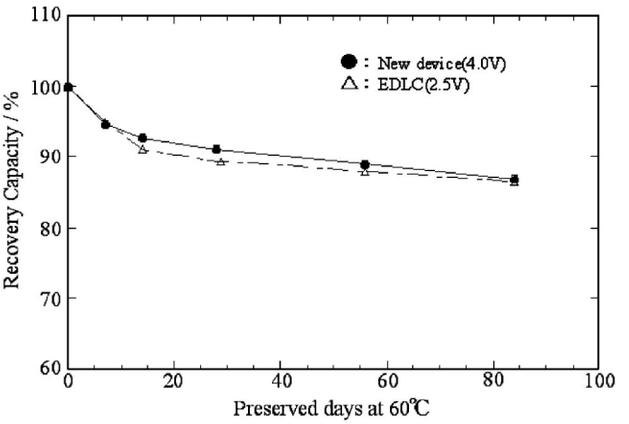


Figure 7. Storage characteristics at 60°C.

mentioned test device at various current densities. At the rate of 100 mA/g based on the composite weight, the cell can discharge for 49 min. The capability based on the 100 mA/g discharge is 88.5% at 1000 mA/g and 52.3% at 10,000 mA/g. The power density and energy density of this device are around 2.2 kW/L and 20 Wh/L, respectively. This power density is two times higher than that of a conventional EDLC, and the energy density is three times higher. As compared with the ultracapacitors with transition metal oxide materials,[7] the RuO_2 capacitor indicated 1.4–5.4 kW/L and 1.6 Wh/L by being converted into the volume. The new device has an equivalent power density and superior energy density.

Durability of the lithium-type advanced energy storage device.—Figure 5 shows the high rate charging and discharging profiles. This testing was performed with a 1 min constant current charging and 1 min discharging. The charging cutoff voltage was 4.0 V, and the discharging cutoff voltage was 2.0 V. The energy density of around 20 Wh/L is obtained during cycling.

Figure 6 shows the result of the cycling test at 25°C. Although there is some dispersion in the capacity during cycling, the discharge capacity of the device maintains its initial capacity for at least 100,000 cycles.

Figure 7 shows the measurement results of the recovery capacity of the device (4.0 V) and EDLC (2.5 V), which were preserved at 60°C. Both cells were recharged to 4.0 or 2.5 V after the measurement of the recovery capacities at each measuring point. The measurement conditions for the recovery capacities were as follows: These cells were charged to 4.0 V for the device and 2.5 V for the EDLC at constant current and maintained at each voltage for 2 h.

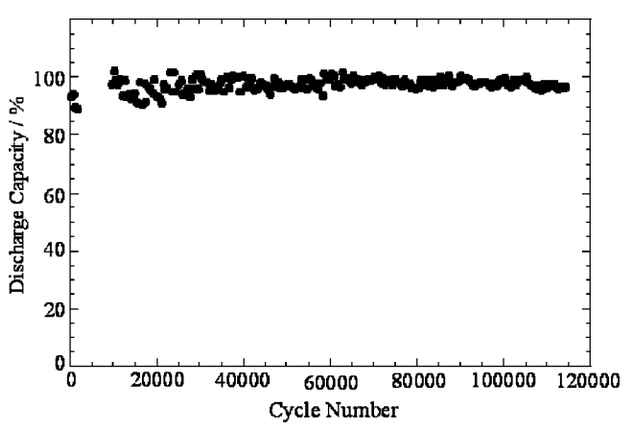


Figure 6. Cycle life at 100% depth of discharge.

Finally, they were discharged to 2.0 V for the device and 0.0 V for the EDLC under constant current. The recovery capacity of the device is 86.9% after 84 days. Although this device was preserved at 4.0 V, it is the same as that obtained for the EDLC preserved at 2.5 V. It is clear that this device has excellent storage characteristics.

Conclusions

1. We developed a novel composite material based on activated carbon for the negative electrode. This composite material was obtained by the heat-treatment (700°C) of activated carbon with pitch under an inert atmosphere. The rate of increase after heat-treatment was about 55% based on a weight measurement. The structure of the composite was amorphous based on the XRD measurements. The BET surface area decreased from 2200 to 250 m^2/g. The efficiency of the composite during the first lithium doping/undoping process was 53.3% using a three-electrode system equipped with a lithium counter electrode and reference electrode. It was much higher than that of activated carbon.

2. We also evaluated a device using this composite as the negative electrode and ordinary activated carbon as the positive electrode. This device can discharge at the extremely high current density of 10,000 mA/g based on the composite weight. The capability based on the 100 mA/g discharge is 88.5% at 1000 mA/g and 52.3% at 10,000 mA/g, respectively. The power density and energy density of this device are around 2.2 kW/L and 20 Wh/L, respectively. This power density is two times higher, and the energy density is three times higher than the conventional EDLC.

3. The discharging capacity of the device maintains its initial capacity for over 100,000 cycles. We preserved this device (4.0 V) and the EDLC (2.5 V) at 60°C. The recovery capacity of the device is 86.7% after 84 days. It is the same as that obtained for the EDLC preserved at 2.5 V. It is clear that this device has excellent storage characteristics.

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