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Development of coin-type lithium-ion rechargeable batteries

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Abstract

We developed coin-type lithium-ion rechargeable batteries made of crystalline V_2O_5 for the cathode and pitch-based carbon for the anode. We optimized the capacity balance of cathode and anode materials. The batteries have a high operating voltage of about 2.7 V and excellent charge/discharge cycle characteristics. We also designed the batteries whose cathode potential is over 3 V versus lithium when the batteries are overdischarged to 0 V. Therefore, the batteries have excellent recovery characteristics even after overdischarge. The batteries have high energy density (about 100 Wh/l) which is about two times that of the coin-type Ni–Cd batteries. It can serve as a memory backup power source with a single battery.

Keywords: Rechargeable lithium batteries; Vanadium pentoxide

1. Introduction

Much effort in recent years has yielded remarkable progress in the development of lithium rechargeable batteries. A new type of these batteries, using vanadium pentoxide [1], lithium cobalt oxide [2], and lithium manganese oxide [3] for the positive material, and lithium aluminum metal alloy [4] and carbon [5] for the negative material, are now distributed commercially. These batteries mainly have a cyclindrical or coin shape. Cylindrical batteries are used for camcorders and portable telephones, while coin batteries are used as backup power sources for CMOS S-RAM memories, real-time clocks, and various other uses.

Required characteristics of coin-type batteries are different from those of cylindrical batteries. Required characteristics of coin-type rechargeable batteries are:

(i) a high operating voltage of more than 2 V;

(ii) excellent recovery characteristics even after overdischarge and overcharge;

(iii) a high energy density, and

(iv) excellent characteristics of the charge/discharge cycles.

Until now, button-type Ni–Cd batteries, capacitors and primary lithium batteries were used as a memory backup power source. They almost satisfy these criteria, but they have some problems. If the Ni–Cd batteries are stored at high temperatures, their capacity will decrease over time. The capacitors will not be able to supply power for long periods of time because they have low capacity density. Primary lithium batteries which are not rechargeable, but which are most popular for memory backup have excellent characteristics as a memory backup power source because of low self-discharge, but it is necessary to change them periodically.

Because of these limitations, we have developed and manufactured coin-type lithium-ion rechargeable batteries, VG2025 and VG2430, with excellent charge/discharge cycle characteristics and long-term reliability.

2. Experimental

2.1. Positive materials

There are many positive materials for lithium-ion rechargeable batteries. We investigated V_2O_5 with a high operating voltage and high energy density, and fabricated coin-type batteries that use crystalline vanadium pentoxide (c-V_2O_5) and amorphous vanadium pentoxide–phosphorus pentoxide (a-V_2O_5) as cathode and lithium metal as anode and measured them under nearly conditions as those used for coin-type batteries.

The a-V_2O_5 was prepared from 95 m/o a-V_2O_5 and from 5 m/o P_2O_5. These raw materials were mixed and melted thoroughly in a platinum crucible for 1 h at 750 °C in air, and were subsequently quenched on a cooled iron roll. We identified the amorphous stable by X-ray diffraction.

To make the positive electrode mixture, we mixed either a-V_2O_5 or c-V_2O_5 powder, graphite powder as a conductor, and polytetrafluoroethylene as a binder

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and pressed the mixed powder into pellets and dried them at 120 °C in a vacuum. To make coin-type cells, we punched out a lithium disk from lithium metal foil and pressed it into the prepared cap with a net as a current collector and a gasket as a sealant. We poured the electrolyte on the pressed lithium metal and we punched out a separator disk made of non-woven polypropylene film, and placed it on a lithium disk. We placed the positive electrode pellet on a separator disk and we poured electrolyte on the electrode. The can with the net as a current collector was on the positive electrode pellet. We crimped the parts closed. The electrolyte was a solution of one molar lithium perchlorate in propylene carbonate. The cells were cycled at a constant current of 150 $\mu A/cm^2$ between the voltage limits of 2.5 and 3.4 V.

The results of the first charge/discharge cycle of these cells are shown in Fig. 1. The a-V_2O_5 Fig. 1(b) shows a slope of the charge/discharge curve with about a 95 mAh/g reversible capacity between the voltage limits of 2.5 and 3.4 V. The a-V_2O_5 had good characteristics in long-term charge/discharge cycle tests.

The cell with c-V_2O_5 Fig. 1(a) shows a flat charge/discharge curve with about 140 mAh/g reversible capacity between the voltage limits 2.5 and 3.4 V. The c-V_2O_5 also had good characteristics in long-term charge/discharge cycle tests.

Because the c-V_2O_5 showed that it has higher capacity and operating voltage, we chose to use it as the positive material of coin-type lithium-ion rechargeable batteries.

2.1. Negative materials

A variety of carbon materials, such as thermally decomposed carbon [6], cokes [7], carbon fiber [8], and graphite [9] have been examined by many researchers. We investigated four types of carbons under conditions nearly the same as those used for coin-type cells. The characteristics of four types of carbons are shown in Table 1.

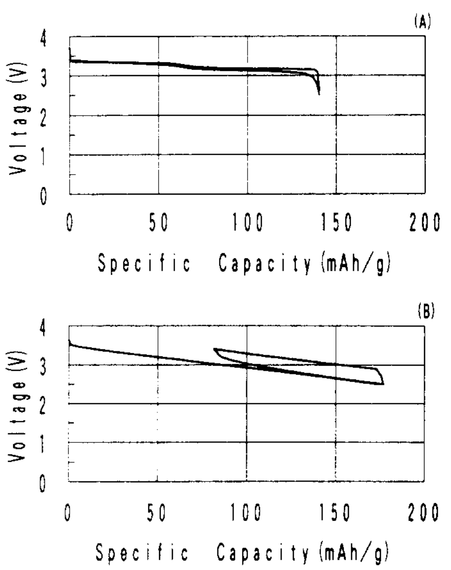

Fig. 1. First charge/discharge curves of (a) c-V_2O_5 and (b) a-V_2O_5 batteries at a constant current (150 $\mu A/cm^2$) between voltage limits of 2.5 and 3.4 V.

Table 1
Crystal parameters and specific surface area evaluated by the BET method for various carbon materials

Carbon material	$d(002)$ (nm)	L_c (nm)	Surface area (m^2/g)
Thermally decomposed carbon	0.346	5.82	1.63
Pitch-based carbon	0.354	1.72	3.55
Meso-phase pitch-carbon (sphere)	0.346	5.16	0.84
Meso-phase pitch-carbon (fiber)	0.347	4.82	1.84

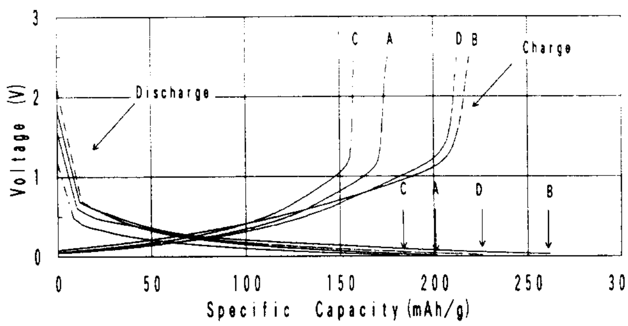

Fig. 2. First charge/discharge curves of various carbons at a constant resistant discharge (200 Ω, 96 h) and constant-current charge (150 $\mu A/cm^2$, cutoff voltage 2.5 V): (A) thermally decomposed carbon; (B) pitch-based carbon; (C) meso-phase pitch-carbon (sphere), and (D) meso-phase pitch-carbon (fiber).

To make the negative electrode mixture, we mixed carbon powders with polyethylene powder as a binder and pressed the mixed powder into a pellet and dried it at 110 °C in a vacuum.

We made coin-type cells of carbon/lithium system to evaluate the characteristics of these carbons. The cells were cycled at a constant resistant discharge of 200 Ω for 96 h and a constant-current charge of 150 $\mu A/cm^2$ to a cutoff voltage of 2.5 V.

The curves of the first cycle of these cells are shown in Fig. 2, and capacities of these carbons are shown in Table 2. These carbons show good characteristics for long-term charge/discharge cycle tests. From these results, we selected carbon B with the highest capacity.

3. Capacity balance of lithium rechargeable batteries

The characteristics of coin-type lithium-ion rechargeable batteries are changed by the capacity balance of c-V_2O_5, pitch-based carbon, and lithium. When we designed it, we considered the following:

Table 2
Lithium-doped and lithium-undoped specific capacity for various carbon materials

Carbon material	Dope capacity (mAh/g)	Undope capacity to 1 V (mAh/g)	Undope capacity to 2.5 V (mAh/g)
Thermally decomposed carbon	201.5	163.5	175.8
Pitch-based carbon	262.0	189.8	219.3
Meso-phase pitch-carbon (sphere)	181.1	147.8	157.9
Meso-phase pitch-carbon (fiber)	226.3	183.1	212.8

(i) large capacity;
(ii) capacity of lithium that does not decrease the reversibility of positive and negative materials, and
(iii) capacity of lithium that does not exceed the limit of the reversibility of positive materials when batteries are overdischarged.

4. Characteristics of the coin-type lithium-ion rechargeable batteries

The structure of the coin-type lithium-ion rechargeable battery is shown in Fig. 3. It has the same shape as the coin-type primary lithium battery. The battery has a current collector for both the positive and negative electrodes to maintain electrical connection, even if the electrode expands and contracts because of charging and discharging.

The discharging curves of the VG2430 at various constant currents are shown in Fig. 4. The VG2430 is a coin-type lithium rechargeable battery with a diameter of 24 mm and an overall height of 3 mm; its capacity is about 54 mAh at 250 μA, and 43 mAh at 1 mA. Its operating voltage is high and about 44 mAh can be obtained at 250 μA to the cutoff voltage of 2.5 V.

The discharge curves of the VG2430 battery at various temperatures are shown in Fig. 5. At 20 °C, it takes 300 h to discharge to 2.0 V, and at −20 °C, it takes 235 h.

The charge characteristics of the VG2430 battery is shown in Fig. 6. Constant-voltage charging method is used for charging this battery. The charging current is

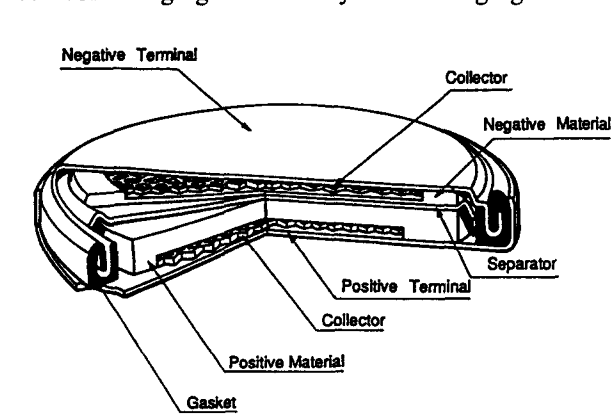

Fig. 3. The structure of the VG2025 battery.

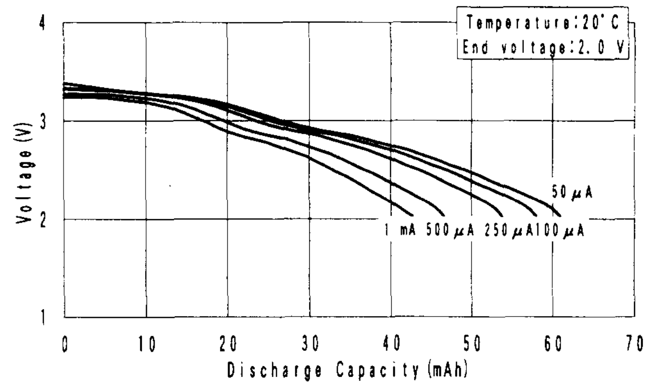

Fig. 4. Discharge curves at various constant currents.

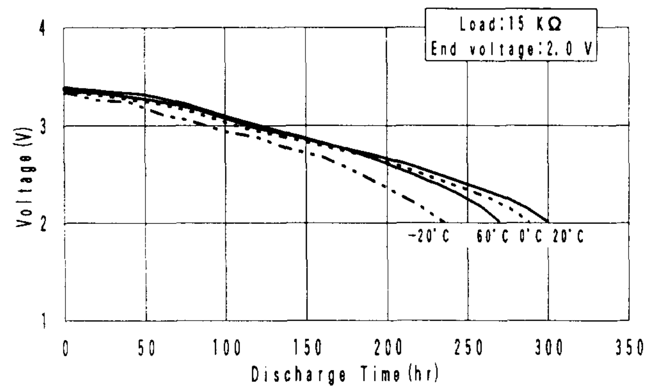

Fig. 5. Discharge curves at various temperatures.

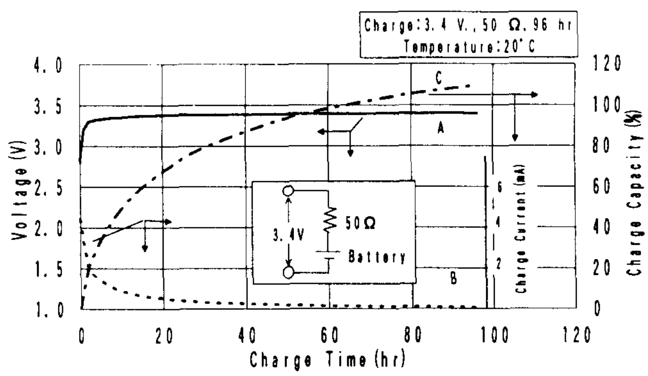

Fig. 6. Charge characteristics of the VG2430 battery: (A) cell voltage; (B) charging current, and (C) charge capacity.

controlled by the resister as shown in Fig. 6. In this case, the constant voltage was 3.4 V, resistance was 50 Ω and the charge time was 96 h. An 80% capacity

Table 3
Specifications of VG2025 and VG2430 batteries

Items	VG2025	VG2430
Nominal voltage (V)	3.0	3.0
Rated capacity (mAh)	25	50
Standard discharge (μA)	250	250
Discharge end voltage (V)	2.0	2.0
Working temperature range (°C)	−20 to +60	−20 to +60
Standard charge (constant voltage) (V)	3.30 to 3.40	3.30 to 3.40
Dimensions		
Diameter (mm)	20.0	24.5
Height (mm)	2.5	3.0
Weight (g)	2.5	4.0

was charged for 30 h, and a 100% capacity was charged for about 64 h under these conditions.

The characteristics of depth-of-discharge and cycle life are shown in Fig. 7. It is possible to have a cycle life of 2000 cycles at a depth-of-discharge of 10% and 1000 cycles at depth-of-discharge of 20%.

The self-discharge characteristics compared with Ni–Cd batteries at various temperatures are shown in Fig. 8. The x-axis is the store period at various temperatures and the y-axis is the residual capacity ratio after storage. Residual capacities of the VG2430 are excellent compared with those of the Ni–Cd batteries at particularly high temperatures.

The overdischarge characteristics are shown in Fig. 9. The overdischarge condition is nearly 0 V when a 15 kΩ resistance is connected to the battery for 20 days at 60 °C. After overdischarge, the battery is charged to 3.4 V, with a 50 Ω resistance for 96 h. The capacity loss is about 15% even after overdischarge.

The continuous charge characteristics are shown in Fig. 10. The continuous charge condition was 3.4 V,

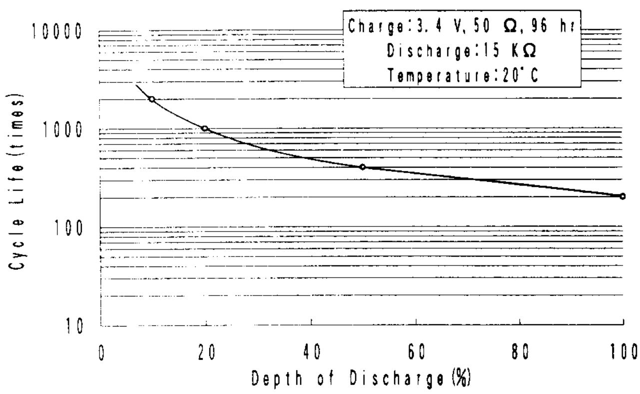

Fig. 7. Depth-of-discharge vs. cycle life.

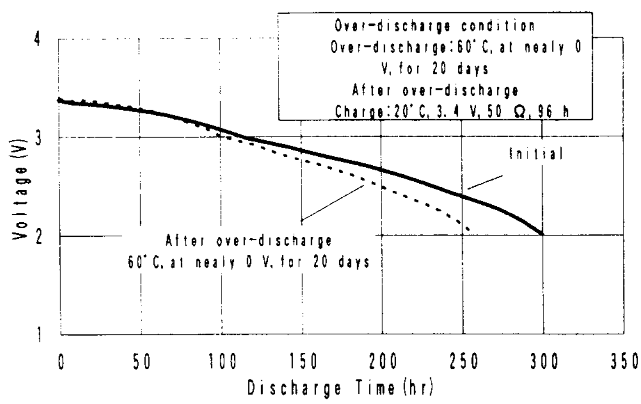

Fig. 9. Overdischarge characteristics at nearly 0 V for 20 days at 60 °C.

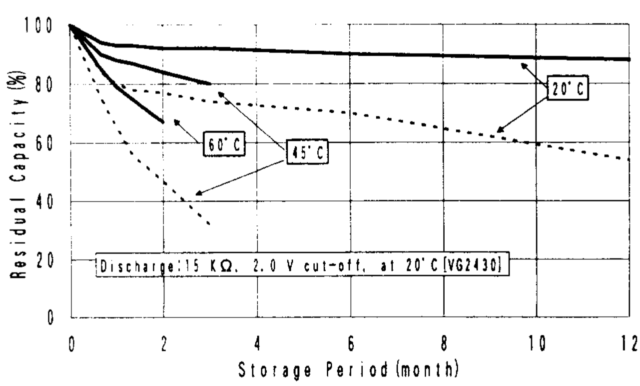

Fig. 8. Self-discharge characteristics at various temperatures: (——) VG 2430 battery, and (– – –) Ni–Cd button-type battery.

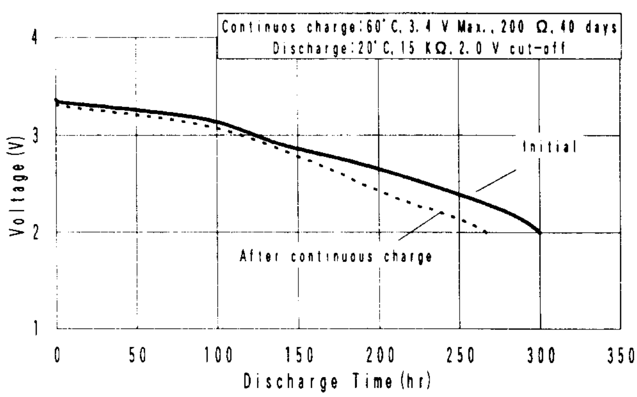

Fig. 10. Continuous charge characteristics at 3.4 V for 40 days at 60 °C.

with a 200 Ω resistance at 60 °C for 40 days. The capacity loss was about 10% even after a continuous charge.

The specifications of the VG2025 and VG2430 batteries are shown in Table 3. The capacity of VG2430 is 50 mAh and the capacity of VG2025 is 25 mAh.

5. Conclusions

We developed the batteries VG2430 and VG2025 of a c-V_2O_5/pitch-based carbon system with excellent charge/discharge cycle characteristics and long-term reliability. We also designed the batteries whose cathode potential is over 3 V versus lithium when the batteries are overdischarged to 0 V. Therefore, the batteries have excellent recovery characteristics even after overdischarge. The batteries are used as a backup power source for such applications as personal computers and facsimiles, and we expect that the demand for those batteries will increase in the future.

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