

Short communication

Al-laminated film packaged organic radical battery for high-power applications

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Abstract

A 100-mAh class of aluminum-laminated film packaged organic radical battery with a poly(2,2,6,6-tetramethyl-1-piperidinyloxy-4-yl methacrylate) (PTMA) composite cathode and a graphite anode has been fabricated. Its total weight was 22 g and the thickness was 4.3 mm. Because PTMA comprised only 6.2% of the total cell weight, the energy density was considerably less than that of a lithium ion battery. However, the power density per active material weight was found to be better than that of lithium ion battery. The applications which require high-power capability rather than high-energy density, such as the sub-battery in electronic devices and motor drive assistance in electric vehicles, would be appropriate for organic radical batteries in the future.

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1. Introduction

In the field of electronic devices, the demand for low power consumption is growing at a significant rate. On the other hand, in case of rechargeable batteries, high-power capability is becoming more and more important. It is considered that high-power rechargeable batteries make it possible not only to achieve smooth acceleration and efficient regeneration in electric vehicle and hybrid electric vehicle applications, but also to reduce the charging time for all applications. So, high-power capability is now one of the most important topics for the advanced research of rechargeable batteries. So far, many efforts have been carried out to develop high-power lithium ion batteries. Zaghbi et al. reported that smaller particle size is effective for increasing the rate capability, but it also resulted in an increase of irreversible capacity [1]. The use of thinner electrodes is also known to increase rate capability but it causes a decrease of energy density.

There is always conflict between power capability and energy density.

In the previous work, we first reported that a stable radical polymer, poly(2,2,6,6-tetramethyl-1-piperidinyloxy-4-yl methacrylate) (PTMA) can be used as a cathode active material for lithium rechargeable batteries and it showed high-power capability [2–5]. A PTMA is easily converted to a quaternary ammonium cation electrochemically. We called it the organic radical battery. The anion in the electrolyte takes part in the charge–discharge reaction at the PTMA cathode to keep the charge balance, in contrast to ordinary lithium ion/extraction type cathode in lithium ion batteries. PTMA absorbs electrolyte solution in the cell, we think that the lithium ion and its anion would move easily in the PTMA particle, and that is why high-power capability would be achieved.

In the present study, we fabricated a 100-mAh class of aluminum-laminated film packaged organic radical batteries with graphite anodes. By making batteries with a practical capacity, comparison of it with conventional batteries would be possible and their problems for commercialization would be apparent. This paper suggests a process for making organic radical

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batteries, and presents the results of a comparison with lithium ion batteries.

2. Experimental procedures

PTMA was synthesized in our laboratory by a radical polymerization of 2,2,6,6-tetramethylpiperidine-4-yl methacrylate monomer (LA-87, Asahi-denka) using 2'-azobisisobutyronitrile (AIBN) followed by oxidizing it with 3-chloroperoxybenzoic acid (m-CPBA). The synthesis procedure was described somewhere else in detail [2,3]. All electrolytes were obtained from Ube Industries Ltd.

The PTMA cathode was prepared by following procedure. In order to make a viscous solution, we added 5.0 g of carboxy methyl cellulose, CMC (HB9, ZEON Corp.) to 500 g of pure water, and stirred until it was dissolved completely. Then, 1.25 g of PTFE fine powder (60% water dispersion, D-1B, DAIKIN Industries Ltd.) and 56.25 g of vapor grown carbon fibers (VGCFTM, Showa Denko K.K.) were added to the CMC solution, and stirred intensively for 1 h. We completed the preparation of the slurry by adding 62.5 g of PTMA fine powder to the well dispersed carbon ink and mixed it well. The resulting slurry was spread on carbon coated aluminum foil by the doctor blade method on one side. After evaporation of the solvent water by heating (100 °C, 10 min) the other side of the foil was also coated uniformly. This electrode had a thickness of 180 μm on each side and contained PTMA (50 wt.%), VGCF (45 wt.%), CMC (4 wt.%) and PTFE (1 wt.%). A graphite, meso-carbon microbeads (MCMB, Osaka-gas), anode was prepared by the normal process using an NMP slurry and the doctor blade method. This anode contained graphite (90 wt.%), conductive carbon black (1.0 wt.%) and PVdF (9.0 wt.%). The thickness was adjusted to be 20 μm on each side.

Aluminum-laminated film packaged organic radical batteries were fabricated by the following procedures. PTMA cathodes and graphite anodes were cut into 45 mm × 55 mm rectangular pieces with a 10 mm wide margin of current collector. One single-side coated and nine double-side coated cathodes were assembled together with microporous film separators, Celgard 2400, and graphite anodes. As a result, 19 layers of cathodes and the same number of layers of anodes were facing each other through the separators. After all the electrodes were aligned, the margin parts of all aluminum cathode current collectors were connected into an electrode by using a supersonic welder, and we performed the same process for the copper anode current collectors. By attaching electric lead tabs, a complete cell pack was prepared. Then we covered it with formed aluminum-laminated film and sealed three sides of the film by heating. Into the opened pouch of the battery we put a 1.0 M lithium hexafluorophosphate (LiPF₆) in ethylene carbonate (EC) and diethyl carbonate (DEC) mixed solvent (EC/DEC = 3/7, v/v) as a liquid electrolyte. After we held the cell under a weak vacuum for a while, we sealed the last side to complete the fabrication of the cell. The weight of the fabricated cell was 22 g, and the thickness was 4.3 mm. Fig. 1 shows an example of the appearance of a cell. The electrode size was 45 mm × 55 mm and it corresponds to almost half the size of a business card. Its reversible capacity was about 100 mAh.



Fig. 1. An appearance of an Al-laminated film packaged organic radical battery.

3. Results and discussion

Fig. 2 shows the first charge and discharge curves for the cell obtained at 20 °C. The charging and discharging were carried out at a constant current of 80 mA. The upper and lower voltage limits were set at 4.2 and 2.5 V, respectively. When charging, the cell voltage rose gradually and a voltage plateau was observed at around 3.5 V. The capacity of the first charge was 147 mAh. Calculated from the weight of PTMA, the specific capacity of PTMA was found to be 108 mAh g⁻¹. The discharge plateau was observed at 3.4 V. The first discharging capacity was 109 mAh. Therefore, we found that 38 mAh (26%) of the charging capacity was lost during the first cycle. A small MCMB graphite particle (3 μm) shows the relatively large initial capacity loss about 20%. So we considered that this capacity loss would be mainly caused by the irreversible capacity of the MCMB graphite anode. Fig. 3 shows the second charge and discharge curves. The curves were very flat and the charge and discharge capacities were 103 and

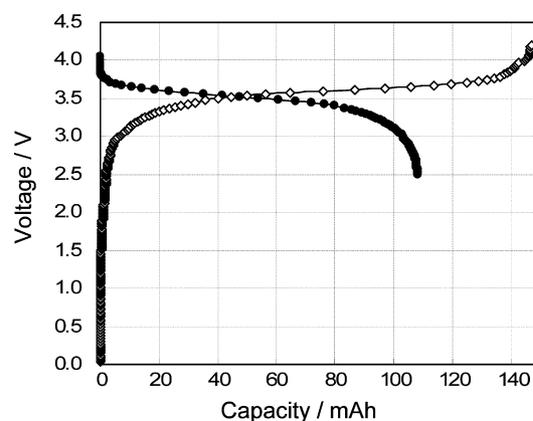


Fig. 2. The first charge and discharge curves of a cell at 20 °C. The charge and discharge were carried out at a constant current of 80 mA.

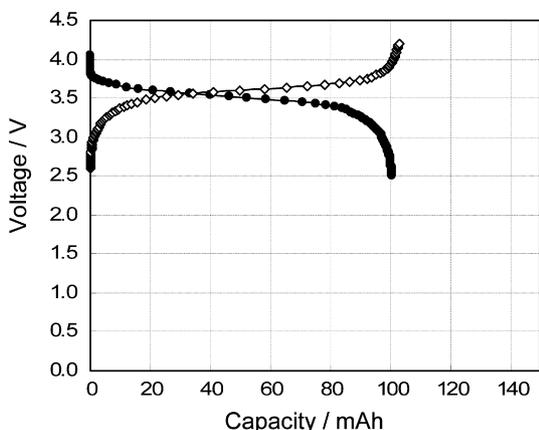


Fig. 3. The second charge and discharge curves of a cell at 20 °C. The charge and discharge were carried out at a constant current of 80 mA.

101 mAh, respectively. The capacity leveled off and there was no significant change in the shape of curves after that until the cell reached 100 cycles.

The cycling characteristics at 20 and 45 °C are shown in Fig. 4. The capacity of the cell decreased gradually during cycling, and after 100 cycles, 82% of the initial capacity remained (20 °C). In the case of elevated temperature operation (45 °C), the capacity decreased more rapidly. We confirmed that the cell expanded at 45 °C; slight expansion was detected at 20 °C. Gas generation might occur during cycling. We suspected the existence of residual water in the PTMA electrode, because we employed a water dispersion slurry for preparing the electrodes.

The rate capability of the cell was investigated. Fig. 5 shows the discharge curves at constant currents of 0.1–5.0 A. The upper and lower limit voltages were set to be 4.2 and 2.4 V, respectively. This experiment was carried out at 20 °C, and the same cell was used for all of these measurements. As the current was increased, the average discharge voltage decreased, and the capacity decreased. However, even at 5.0 A (50 C), 71% of the 0.1 A (1 C) capacity was obtained. And the beginning of the discharging process at high rate, we observed a slight rise of the voltage. A temperature rise might occur because of the high current. Next, we fabricated a battery pack consisting of four series

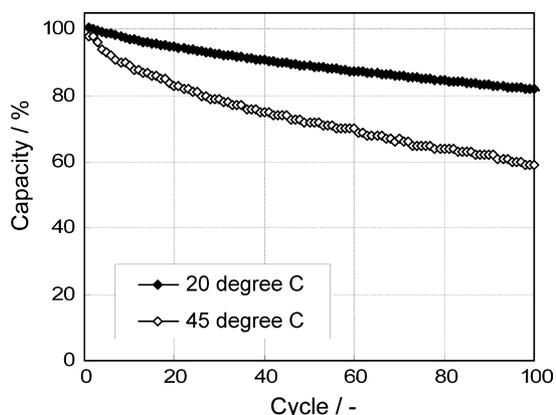


Fig. 4. The cycling characteristics of a cell at 20 and 45 °C. The charge and discharge were carried out at 80 mA between 2.5 and 4.2 V.

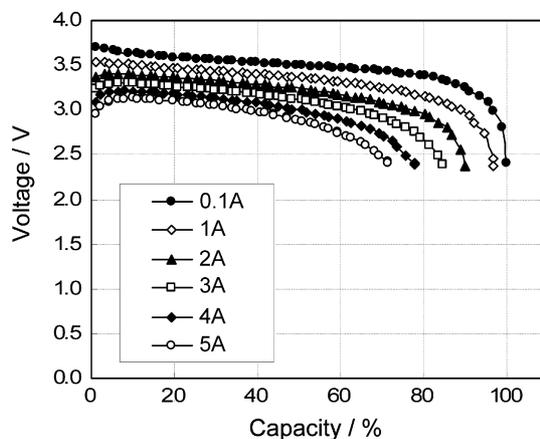


Fig. 5. The discharge rate capabilities of a cell at 20 °C. The charge was carried out at 100 mA.

connected cells in order to get sufficient power for electronic devices, and measured the rate capability. The upper and lower limit voltages were set to be 16.8 and 8.0 V, respectively, or 4.2 and 2.0 V per cell. All charging was carried out at 0.2 A. Fig. 6 shows the discharge curves at constant currents of 1–13 A. As shown here, although the capacity decreased to half of the low-rate value and the voltage dropped significantly, a 13 A (130 C) discharge was achieved. The voltage rise was also apparent here at the beginning of discharge. The rate capability of the battery pack was better than that calculated from the single cell experiments. When we made a battery pack, we pressed the cells and packed it in a case in order to secure it. The pressure would suppress lowering the volume change of the cell during the charge–discharge reaction. That would result in lowering the cell impedance and prevent the generated gas from affecting on the cell performance.

This battery consists of PTMA (6.2 wt.%), graphite (1.4 wt.%), conducting additives (6.3 wt.%), electrolyte (28.4 wt.%), current collectors/tab leads (40.2 wt.%), packing film (14.8 wt.%) and porous separator (2.7 wt.%). As described here, the main components of this battery were current collectors, tab leads, electrolyte and packaging film. They occupied over 80% of the battery total weight. The active material PTMA

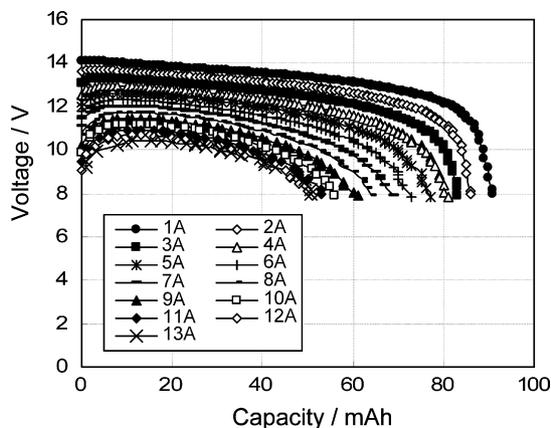


Fig. 6. The discharge rate capabilities of a battery pack (four cells connected in series) at 20 °C. The charge was carried out at 100 mA between 8.0 and 14.8 V.

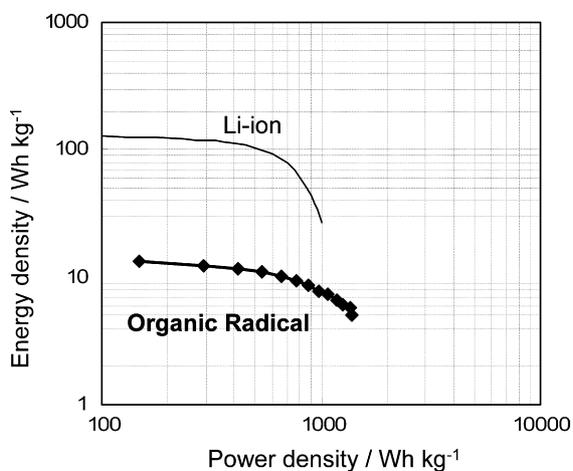


Fig. 7. A Ragone-plot of an organic radical battery pack compared it with a conventional lithium ion battery. The energy density and the power density were calculated from the total weight of the battery pack.

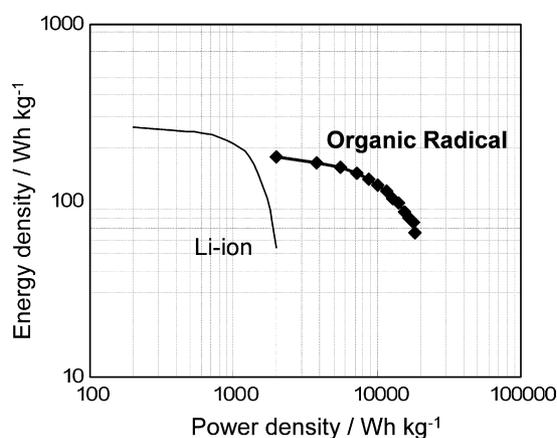


Fig. 8. A Ragone-plot of an organic radical battery pack compared it with a conventional lithium ion battery. The energy density and the power density were calculated from the weight of active material inside of the battery pack.

occupied only 6.2% of the cell weight. In order to make a practical battery, PTMA will have to be packed more densely. Fig. 7 shows a Ragone-plot of the battery pack comparing it with the conventional lithium ion battery [6]. We found that the energy density of the organic radical battery was significantly inferior to that of lithium ion battery. However, if we compare the Ragone-plot normalized to the active materials weight inside of the battery, the result is different. Fig. 8 is a result of recalculation of the energy and power density based on the weight of active materials. In that case, we found that although the energy density of organic radical battery was smaller, the

power density was quite superior to that of the lithium ion battery.

4. Conclusions

A 100-mAh class of organic radical cell with a graphite anode has been fabricated, and investigation for practical applications has just begun. This battery has satisfactory rate properties and its cycling performance is adequate for practical use. Although practical development is in the early stages, it is expected that the performance of the battery will be improved by optimizing the capacity balance and improvements in the fabrication process. The energy density of an organic radical battery is considerably less than that of a lithium ion battery with a transition metal oxide cathode. However, the specific power per active material weight was found to be better than that of a lithium ion battery. That is why we think one of its possible applications is a high specific power energy source, such as a sub-battery in electronic devices and motor drive assistance in electric vehicles, replacing electric double-layer capacitors and nickel metal hydride batteries. These applications require high-power capability rather than high-energy density, so the organic radical battery would be suitable. Rapid charging would also be an advantage in practical applications.

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