

Short communication

High-rate capable organic radical cathodes for lithium rechargeable batteries

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Abstract

Poly(2,2,6,6-tetramethyl-1-piperidinyloxy-4-yl methacrylate) (PTMA) is the most common active material with a stable radical molecular structure used for lithium rechargeable cells. Because it is an organic active material, PTMA can be dissolved easily in various solvents. Using a solution of active material in the electrode making process, we formed an extremely large surface area between the active material and the conducting additive. The electrode has excellent power capability and can be charged and discharged in 1 min. We believe that this cell can be used like an electric double layer capacitor. We also believe that the cell, whose cycle life is good, retaining 89% of original capacity after 1000 cycles, can be put into practical use.

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1. Introduction

Polymer materials are one of the most important scientific achievements of modern society. Most personal belongings, including stationary, household goods, and electrical products contain polymer materials. Without these materials, fabrication of rubber tyres, plastic bags, and chemical fibers would be impossible. Polymer materials are widely used because they are good electrical insulators and have good mechanical properties. Electrically conducting polymers were first reported in the 1980s, and their electronic properties began to be studied immediately [1]. Conducting polymers with a π -conjugated electronic structure show over 10^4 S cm⁻¹ of conductivity, and their electronic properties can be controlled by oxidizing or reducing them electrochemically. Because of these capacities they have been used as active materials for rechargeable batteries [2].

In previous papers, we 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 mate-

rial for lithium rechargeable cells [3–6]. This material delivers over 100 mAh g⁻¹ of specific capacity with good cycle life. Its rate capability is much better than that of transition metal oxides used for conventional lithium-ion batteries.

In the present study, we have tried to improve the power capability of the Li/PTMA cell with a new composite cathode-preparation process using a PTMA solution. Since PTMA is an active organic polymer material, a new process, which has never been considered for use with conventional inorganic materials, is possible. In this process, PTMA is first completely dissolved in an organic solvent, then an electrode is prepared from the active material solution. This means a porous electrode can be fabricated from a conducting network coated with an active material film. Scanning electron microscope (SEM) images revealed that a good dispersion of the active materials and a large contact surface area between carbon conducting additives and active materials was formed using this process.

2. Experimental procedures

PTMA was synthesized by radically polymerizing 2,2,6,6-tetramethylpiperidine-4-yl methacrylate monomer (LA-87,

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Asahi-denka) using 2'-azobisisobutyronitrile (AIBN) and then oxidizing it with 3-chloroperoxybenzoic acid (*m*-CPBA). The synthesis procedure was described in detail elsewhere [3,4]. All electrolytes were obtained from Ube Industries Ltd.

The PTMA cathode was prepared using the following procedure. 1.5 g of PTMA and 0.5 g of poly(vinylidene fluoride) (PVdF, KF#1300, Kureha) were dissolved completely in 20 g of *N*-methyl-2-pyrrolidone (NMP) solvent. Then, 3.0 g of vapor grown carbon fiber (VGCF; Showa-denko) was added to the viscous PTMA solution, and stirred intensively. To make a thinner film on the surface of the VGCF conductive fiber, we used additional VGCF. The resulting slurry was spread on aluminum foil using the doctor blade method. After the NMP solvent was evaporated by heating (125 °C, 4 min), the PTMA cathode was complete. This cathode contained PTMA (30 wt.%), VGCF (60 wt.%), and PVdF (10 wt.%). We stamped out some 12-mm diameter circular electrodes. Their thickness and the loading weight were measured using a handy thickness gauge and a precise balance. The thickness was about 50 μm. The electrodes were observed using a scanning electron microscope (S-4100, HITACHI, SEM apparatus).

Coin cells (2320-type) were assembled using Celgard 2400 microporous film separators, and 1.4-mm thick lithium metal disk anodes in a dry room (dew point < −50 °C). As a liquid electrolyte, we used 1.0 M lithium hexafluorophosphate (LiPF₆) in an ethylene carbonate (EC) and diethyl carbonate (DEC) mixed solvent (EC/DEC = 3/7, v/v). Cell charging and discharging was carried out at 20 °C between 3.0 and 4.0 V using a computer-controlled battery measurement system.

AC impedance measurements were carried out using Swagelok cells. First, the voltage of the cell was set to 3.0 V and swept up to 3.4 V at a rate of 0.5 mV s^{−1} controlled by a VMP Multi-channel potentiostat from Science Instruments. Then the cell was removed and its AC impedance was measured at room temperature using an SI-1260 Impedance/Gain Analyzer, Solartron. Frequency range was 10⁶ to 10^{−2} Hz, with an AC amplitude of 10 mV. After impedance was measured, the cell was reconnected to the potentiostat, and the voltage was swept up to 3.6 V. We repeated the voltage sweeps and impedance measurements in this manner, obtaining AC impedance results at 3.4, 3.6, 3.8, and 4.0 V.

3. Results and discussions

The left image in Fig. 1 is a scanning electron microscope image of a PTMA–carbon composite electrode surface. Since the active material PTMA was first completely dissolved before the electrode was fabricated, it coated the carbon fiber conductor uniformly. The carbon fibers were about 150 nm in diameter and 10–20 μm in length. Compared with conventional powder mixed PTMA electrodes [5], right side of Fig. 1, it was clear that a good dispersion of the active materials and a large contact surface area between carbon conducting additives and active materials had been achieved using this process. The loading and specific density of the electrode were 0.9–1.1 mg cm^{−2} and 0.4–0.5 cm^{−3}, respectively.

A Li/PTMA half cell was fabricated using this PTMA–carbon composite cathode. Fig. 2 shows the rate dependence of the discharge curves at constant discharge rates of 1, 5, 10, 20, and 50C, wherein *C* corresponds to the capacity of the cell, which was 0.04 mAh. The charging and discharging was carried out at 20 °C within a voltage range of 3.0–4.0 V. All charging was carried out at the 1C rate. We found that the discharge rate capability of the cell was significantly better than previously reported [3,4].

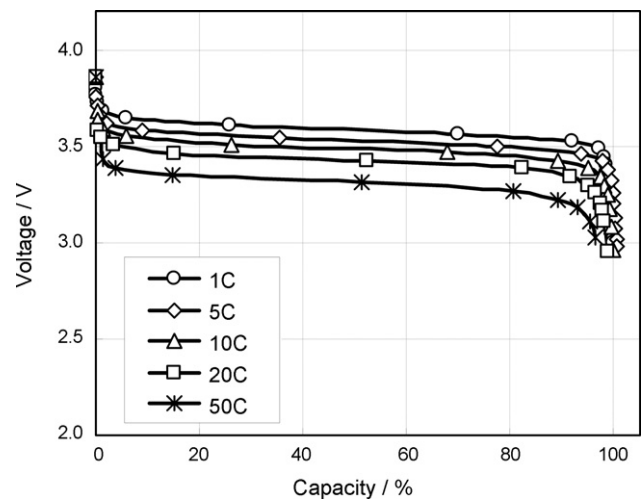


Fig. 2. Discharge rate capabilities of a Li/PTMA half cell at 20 °C. Charging process was carried out in 1C rate.

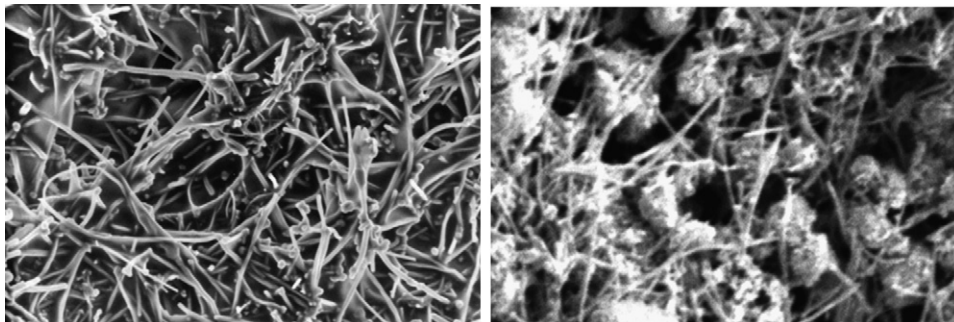


Fig. 1. Scanning electron microscope (SEM) images of a PTMA–carbon composite electrode made by solution (left) and powder-mix methods (right) [5].

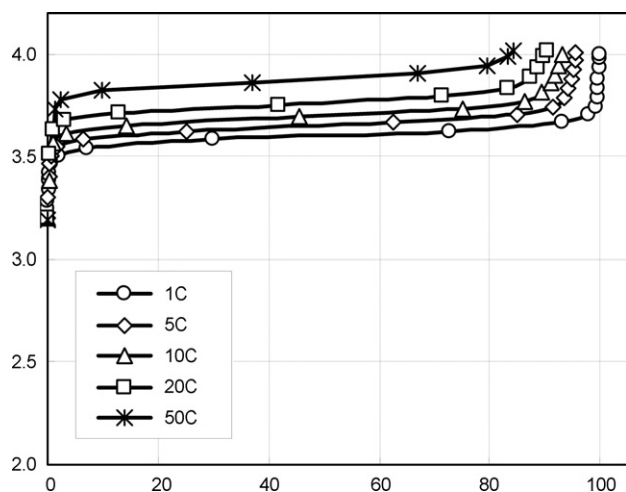


Fig. 3. Charge rate capabilities of a Li/PTMA half cell at 20°C.

Even at a high discharge rate of 50C, almost the same capacity as that for 1C was obtained. Since we always used a standard electrolyte solution for Li-ion battery (1.0 M in ED/DEC = 3/7, v/v), the voltage drop did not change much as current increased. We believe that the good dispersion of the active materials and the large contact surface area, which was measured by SEM observation, improved the efficiency and the high-rate capability of this electrode.

Fig. 3 shows charging curves measured at constant rates of 1, 5, 10, 20, and 50C. Although the upper voltage limit of 4.0 V was relatively low, the charging process was carried out successfully. Even when it is charged at the 50C rate, 84% of the capacity at 1C was charged. That means charging takes about 1 min. Fig. 4 shows the discharge curves at 1C after rapid charging. It was confirmed that charging energy was stored successfully.

We also found that the charging rate capability was slightly lower than the discharging rate capability. For cells using PTMA electrodes, it was already reported that the electrolyte salt concentration changes continuously while charging and discharging. We already knew that salt concentration was at a

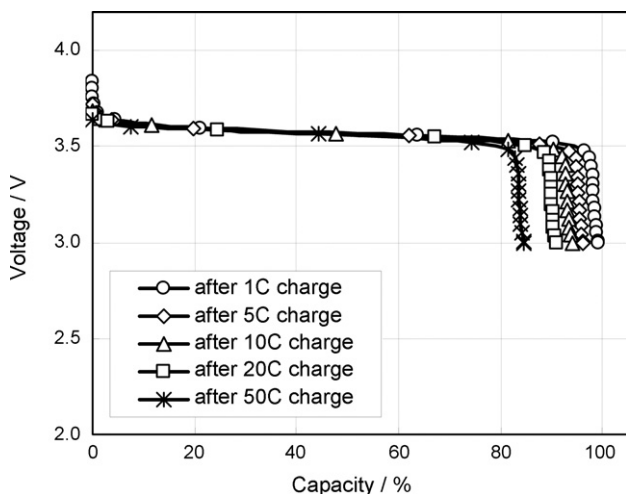


Fig. 4. Discharge curves of a Li/PTMA half cell at 1C (20°C) after rapid charging at 1, 5, 10, 20, and 50C rates.

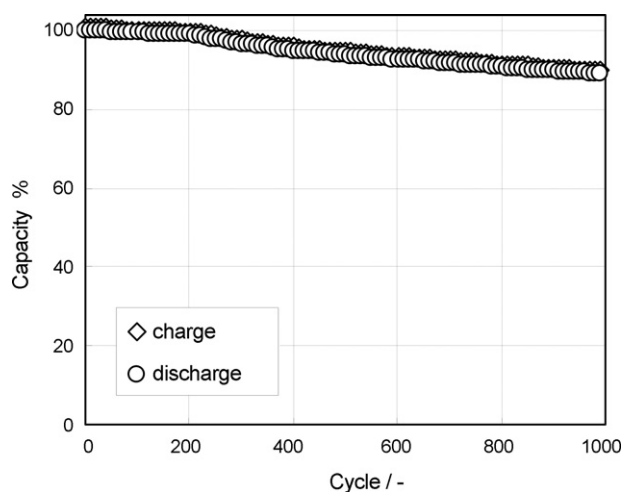


Fig. 5. Cycling behavior of a Li/PTMA half cell at 1C (20°C).

maximum in the discharged state and decreased gradually as charging proceeded.

The capacity as a function of the cycle number for operation at 20°C is shown in Fig. 5. Cycling was carried out at a constant rate of 1C within a voltage range of 3.0–4.0 V. We found that 89% of the initial capacity remained after 1000 cycles, which is a significant improvement over a previous report [7]. In previous study, a water dispersion slurry was used in the electrode-preparation process, whereas in the current one an NMP solution of PTMA was used. We think that the lower water content in the current electrode improved the cycle life of the cell.

Cole–Cole plots of the cell at various voltages are shown in Fig. 6. The x -axis and y -axis represent the real part (Z') and the imaginary part (Z'') of the impedance, respectively. The high frequency range (10^1 to 10^6 Hz) of all plots showed semicircles with diameters of 300–400 Ω , and no significant difference among these semicircles was obtained at the various voltages. These are considered to products of the Faraday process of lithium metal anode fabrication. However, the low frequency range of the plots significantly varies with cell potential. In the discharged state (3.4 V, SOC = 0%), the impedance rose dramatically as frequency decreased and showed only the early portions of very large semicircles, because of the high impedance. On the other hand, the spectra obtained at 3.6 V (SOC = 8%) and 3.8 V (SOC = 71%) did not increase as the frequency decreased. In the charged state (4.0 V, SOC = 100%), the impedance was rising again as frequency decreased. This behavior indicates that although the impedance of the cell is higher in completely charged and discharged states, it decreases significantly in an operating voltage range of 3.4–3.6 V. That is why, the charging and discharging curves of the cell are very flat and the cell has extremely good rate capability. On the other hand, the solution resistance had not changed so much, nevertheless the salt concentration changes during the charging and discharging process. We consider that the amount of electrolyte is excess for the capacity of the cell. That would be another reason, why the cell showed good rate capability.

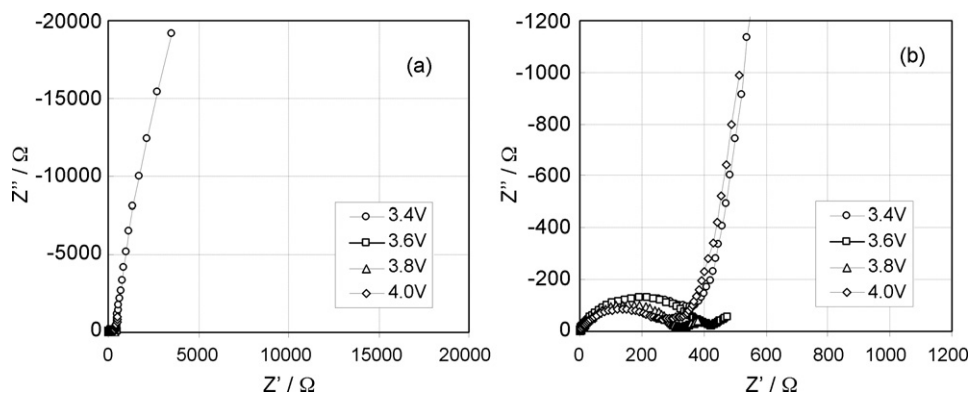


Fig. 6. Cole–Cole plots of a Li/PTMA half cell at 20 °C (a). The frequency range was 10^{-2} to 10^6 Hz. (b) Magnification of the low impedance region of (a).

4. Conclusion

An active material, PTMA, was first completely dissolved in a solvent and then electrodes were fabricated from the PTMA solution and conductive carbon fibers. In this new process, we were able to form a very large surface area between the active material and the conducting carbon. As a result, the power capability of the electrode improved significantly. These cells can be charged and discharged in 1 min and can be used like an electric double layer capacitor. It was also found that the cycling capability is good and that 89% of the initial capacity remained after 1000 cycles.

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