

Liquid-free rechargeable Li polymer battery

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Abstract

Safety is a key concern for high-power energy storage systems such as will be required for electric vehicles. Present lithium ion batteries, which use a flammable organic liquid electrolyte, lack inherent safety. Our approach in solving this problem is to replace the liquid electrolyte with a liquid-free polymer electrolyte. Data of the composition of the positive electrode, charge–discharge and cycle-life capability are presented. The cell using metallic lithium anode and crosslinked polymer electrolyte P(EO/MEEGE/AGE)-LiTFSI showed a discharge capacity of 134 mAh g⁻¹ of LiCoO₂ at 60°C and 140 mAh g⁻¹ at 140°C. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Battery systems based on solid polymer electrolytes combined with a metallic lithium anode are expected as new generation high-energy storage devices, in particular for electric vehicles and load leveling applications.

Polymer electrolytes have been studied for more than two decades since the first investigation reported by Armand and coworkers in 1979 [1].

Although polyethylene oxide (PEO) which is the most popular material for solid polymer electrolytes and many investigations on the polymer complexed with various lithium salts have been published [2–4], its conductivity is quite insufficient for battery applications.

We have already reported that a high molecular weight comb-shaped polymer, poly[ethylene oxide-co-2-(2-methoxyethoxy)ethyl glycidyl ether], P(EO/MEEGE), which shows a high ionic conductivity, $\sigma = 1 \times 10^{-4}$ S cm⁻¹ at 30°C, and a high electrochemical stability, is one of the best candidates for a dry-type polymer electrolyte [5–7].

We studied the effects of electronic conductive carbon materials in a composite cathode and the electrochemical performances of a liquid-free rechargeable lithium polymer battery comprising of Li/crosslinked P(EO/MEEGE/AGE)/LiCoO₂.

2. Experimental

2.1. Synthesis of polymers

Polymers P(EO/MEEGE) and P(EO/MEEGE/AGE) were prepared by ring-opening copolymerization of ethylene oxide (EO) with 2-(2-methoxyethoxy)ethyl glycidyl ether (MEEGE) and with or without allyl glycidyl ether (AGE) in hexane at 20°C [8].

2.2. Preparation of polymer electrolyte film

Polymer P(EO/MEEGE/AGE) dissolved together with an organic peroxide and lithium bistrifluoromethylsulfonyle imide (LiTFSI) made by 3 M, in dehydrated acetonitrile was cast on a silicone-treated PET film, dried and cross-linked at 100°C for 3 h under an inert atmosphere. The optimum concentration of the lithium salts in the electrolytes was [Li]/[O] = 0.06 as previously reported [6], and the thickness of the film was 50 μm.

2.3. Preparation of cathode film

Composite cathodes consisted of 82 wt.% of LiCoO₂ (Honjo FMC Energy Systems), 5 wt.% of carbon material and 13 wt.% of P(EO/MEEGE = 88/12)-LiBF₄ as an ion-conductive binder. Cathode films, of which thicknesses were in the range of approximately 20 μm, were prepared by a doctor blade casting process on an aluminum foil current collector. After drying, the film was roll-compressed in order

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to increase the packing density which read to improved electrical conductivity.

2.4. Cell assembly

A monolayer coin type cell (CR2032), constructed from Li anode (HONJO METAL CO. LTD.: 0.3 mm thickness), P(EO/MEEGE/AGE) (0.05 mm thickness) and composite cathode, was assembled in a dry argon-filled glove box ($[O_2] < 1$ ppm, $[H_2O] < 1$ ppm).

The apparent surface area of the positive electrode was normalized to 1.327 cm².

2.5. Electrochemical measurement

An interfacial resistance between the electrolyte and electrode and the bulk resistance of the electrolyte were measured at 60°C by the ac impedance method using a impedance analyzer (Solartron SI 1260) over a frequency range from 0.1 Hz to 10 MHz.

2.6. Cell characterization

Battery performances were evaluated by BTS-2004W (Nagano) the charge–discharge controller in the range of 3.0–4.2 V. Charging and discharging were carried out with C.C.C.V. (constant current–constant voltage) and C.C., respectively.

3. Results and discussion

3.1. Optimization of the composite cathode

To obtain a high performance cathode, electronic conductivity and packing density must be suitably high.

In this study, two grades of graphite, 6 μm (LONZA KS6) and 15 μm (LONZA KS15) in diameter, and two types of carbon black, Denka acetylene black (AB) and Ketjenblack (KB) were examined as an electronic conductive additive.

Initial charge–discharge characteristics of the cells using the same cathodes in Table 1 are listed in Table 2.

By the results of the density in Table 1 and discharge capacity in Table 2, it was concluded that cathode adopting AB is the most suitable electronic conductor for the com-

Table 2
Initial charge–discharge characteristics

Conductive additive	Charge capacity (mAh/g)	Discharge capacity (mAh/g)	Efficiency (%)
AB	147.4	137.9	93.6
KB	150.7	121.8	80.8
KS6	120.4	105.1	87.3
KS15	104.6	89.0	85.1

posite cathode from the points of view of conductivity, discharge capacity and coulombic efficiency.

3.2. Study on cell characterization

Every cell hereafter consists of a 20 μm-thick cathode, 82 wt.% of LiCoO₂ + 5 wt.% of AB + 13 wt.% of P(EO/MEEGE)-LiBF₄, 50 μm solid polymer electrolyte P(EO/MEEGE/AGE) complexed with LiTFSI and Li metal anode.

Temperature dependence of the discharge capacity was measured. The cell was charged at rate of 0.2 C (0.14 mA/cm²) at 60°C and discharged at different temperatures from 40 to 140°C at 0.2 C. The discharge curves at various temperature are illustrated in Fig. 1a. At higher temperatures, 80–140°C, the values of the discharge capacities were >140 mAh g⁻¹. But at lower temperatures, especially below 40°C, a significant decrease in the capacity was observed. The capacity at 40°C went down to 40% in comparison with that of at 80°C.

Though the cell confirmed the advantage at high temperatures, it still needs further improvement for ambient temperature applications.

The cell also left a problem in high-rate discharging performance. As shown in Fig. 1b, discharge capacity at rates above 1 C remarkably were deteriorated, <50 mAh g⁻¹. It appears that the reason of the low capacity at a high rate may be attributed to the low diffusion rate of a lithium ion inside the cathode.

The cycleability of the cell was measured at 0.2 C and 60°C. As clearly explained by the result in Fig. 2a, the discharge capacity gradually decreased at the rate of 0.13% per cycle with the number of charge–discharge cycles, in spite of keeping constant a coulombic efficiency of 98.5%.

At the 200th cycle, the capacity declined to 63% of the initial value of 128 mAh g⁻¹.

Table 1
Packing density, capacity and electric conductivity of cathode films

Conductive additive	Density calculated (g/cc)	Density measured (g/cc)	Capacity ^a (mAh/cc)	Electrical conductivity ^b (S/cm)
AB	3.31	3.30	370	1.06E-04
KB	3.33	2.88	323	1.00E-03
KS6	3.37	2.80	314	4.52E-07
KS15	3.37	2.86	320	1.94E-06

^a Theoretical value calculated from measured density and cathode composition.

^b Measured by dc method.

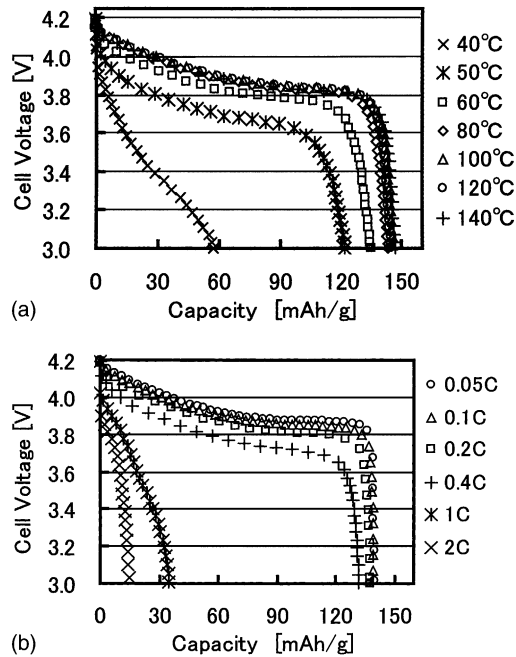


Fig. 1. (a) Temperature dependency on discharge capacity from 40 to 140°C. (b) Rate dependency on discharge capacity from 0.05 to 2 C.

In an impedance measurement of the cell (Fig. 2b), the second semicircle seems to represent the charge transfer impedance. It continuously enlarged with an increase in the cycle number, while the first semicircle caused by the bulk impedance of electrolyte film kept a constant value throughout beyond the 200th cycle.

As the charge transfer resistance of the interface between the electrolyte film and lithium in a symmetrical cell Li/electrolyte/Li was very stable during the cycles [9], it appeared the increase in the impedance was due to the deterioration of cathode/electrolyte interface.

4. Summary

A composite cathode with a high discharge capacity, 370 mAh/cc, was obtained by using acetylene black as an electronic conductor.

A liquid-free rechargeable lithium polymer battery using the cathode showed excellent cell performance at low discharge-rates and high temperatures.

Improvement of the interfacial characteristics between the cathode and electrolyte, and making a thinner electrolyte

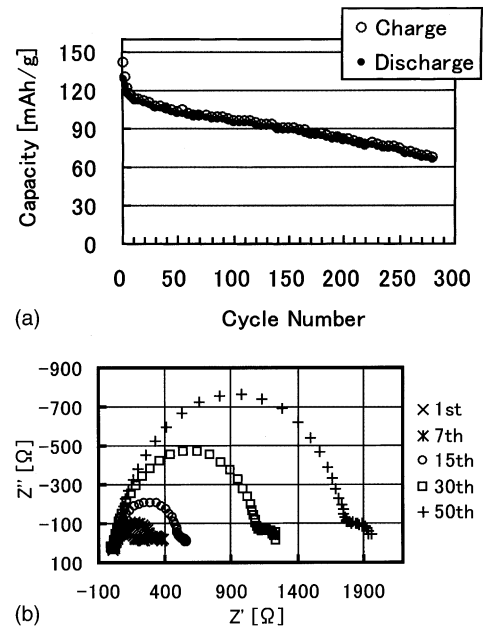


Fig. 2. (a) Cycleability of the cell. (b) Cole-cole plots for ac impedance of cell as a function of cycleability.

film are key factors to solve the problems at high-rate and low temperature applications.

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