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A powder particle size effect on ceramic powder based separator for lithium rechargeable battery

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Abstract

To improve the thermal stability of separators for lithium batteries, we have developed heat-resistant separator films based on ceramic powder. These ceramic powder based separators (CPS) consist of ceramic powder with binder resin. We used two different particle size powders of aluminum oxide (0.01 or 0.3 μm). By mixing ceramic powder and resin at an appropriate content ratio, both types of CPS films satisfied needs for the heat-resistance. Furthermore, CPS film using 0.01 μm powder showed excellent charge–discharge cycling properties when applied to lithium rechargeable batteries as a separator.

Keywords: Ceramic powder; Separator; Heat-resisting; Lithium rechargeable batteries

1. Introduction

Lithium rechargeable batteries are used as the power source for a wide variety of such portable electronic equipments as cellular phones and laptop computers. These batteries are also expected to be power storage devices for hybrid electric and fuel cell vehicles. When this battery is applied to these vehicles, it needs a large power storage capacity. Up to now, polyolefin porous films have been used as separators in most commercialized lithium rechargeable batteries. On the other hand, these films indicate a large thermal shrinkage, they may cause a short circuit between electrodes when unusual heat generation occurs. In such cases, it is important to increase the safety of the batteries and improve the thermal stability of battery components [1]. For example, a separator that does not shrink will make a battery secure because it keeps electrical insulation between the positive electrode and the negative electrode in cases of unusual heat generation. We consider that using heat-resistant ceramic powder prevents the separator from shrinking. From these backgrounds, we are developing ceramic powder based separators (CPS) films to improve thermal stability.

In this paper, we describe the thermal properties of CPS films and report on the performance of lithium rechargeable batteries that use CPS films as separators.

2. Experimental

The CPS films were fabricated with ceramic powder and a polymer binder. Two types of aluminum oxide powders of different particle size, 0.01 and 0.3 μm (Nippon Aerosil and Sumitomo Chemical), and poly (vinylidene fluoride) (PVdF) resin (Kureha Chemical) were used as raw materials to make the CPS films. These materials were mixed in *N*-methyl-2-pyrrolidone (NMP) and made into slurries. The CPS films were formed from the slurry by the doctor-blade method and then were dried to evaporate the NMP. The film thicknesses were controlled to about 20 μm after drying. We fabricated several CPS films of different powder content on each powder size. The powder content ratio of the CPS films is shown in Table 1. We defined that powder weight divided by binder weight is P/B ratio in Table 1.

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Table 1
Powder content ratio of CPS films

Particle size (μm)	Powder content	Al_2O_3:PVdF	P/B ratio	Sample ID
0.01	High	3:2	1.5	A
		4:3	1.3	B
		1:1	1	C
	Low	1:2	0.5	D
0.3	High	10:1	10	E
		5:1	5	F
		5:2	2.5	G
	Low	1:1	1	H
–	None	Binder only	0	I

P/B ratio: powder weight/binder weight.

The surface morphology of the CPS films was observed using a scanning electron microscope. The pore size distributions of the CPS films were measured by mercury intrusion porosimeter. The heat shrinkage of the CPS was measured by dimensional change before and after heat treatment at designated temperatures. The relationship between the temperature and dimensional change of the CPS films was evaluated with a thermo mechanical analyzer. This relationship was measured under a constant load (10 kgf cm^{-2}) whose heating rate was 5 °C min^{-1}. Air permeability of the CPS films were measured by an air permeability tester.

$LiCoO_2$ powder was used as a positive electrode material, while mesophase carbon micro beads (MCMB) was used as a negative electrode material. Carbon black was used as a conductive agent in the positive electrode. PVdF resin was used as a binder of these active materials, conductive agent and current collector. The positive electrode was prepared by coating slurry of $LiCoO_2$ mixed with a conductive agent and a binder onto an aluminum foil current collector. The negative electrode was prepared by coating slurry of MCMB and a binder onto a copper foil current collector. To assemble the cells, the positive electrode, the separator films and the negative electrode were laminated and dried under a vacuum at 60 °C. The dried laminates were then packaged in an aluminum-plastic bag injected with electrolyte solution. The electrolyte used was 1 M $LiPF_6$ in a mixture of 50 vol.% ethylene carbonate and 50 vol.% diethyl carbonate. These cells were assembled in a dried condition.

To investigate the effect of different discharge rates, we tested the cells under various discharge rates: 0.25, 1, 2, and 3 C. The cell was charged at the 1 C rate. We tested the performance of the cells at a constant temperature of 20 °C. Other test conditions were as follows. The charge condition was in the constant current–constant voltage (CC–CV) mode and the upper-limit voltage was 4.2 V. The discharge condition was in the constant current (CC) mode and the cut-off voltage was 2.75 V. We also evaluated the charge/discharge cycle life property of the batteries that used the CPS film. The charge condition operated in the CC–CV mode for 2 h and the upper-limit voltage was 4.2 V. The discharge condition was a 1 C discharge rate under the CC mode, and the cut-off voltage was 2.75 V.

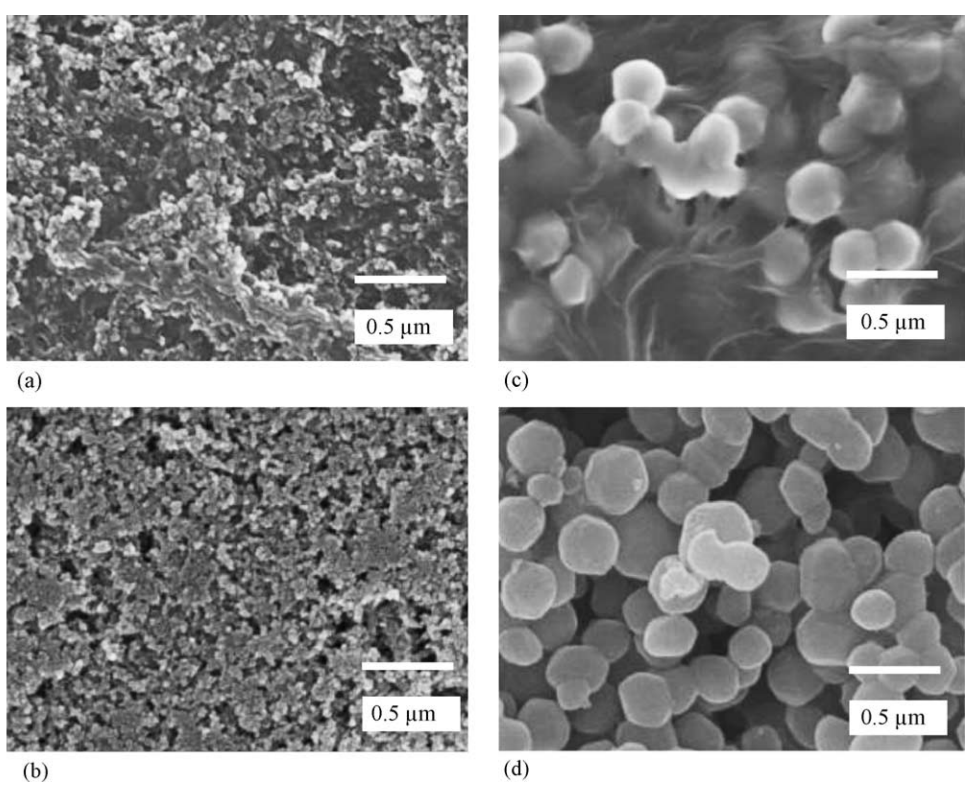

Fig. 1. Surface SEM image of CPS films: (a) 0.01 μm size, low powder content; (b) 0.01 μm size, high powder content; (c) 0.3 μm size, low powder content; (d) 0.3 μm size, high powder content.

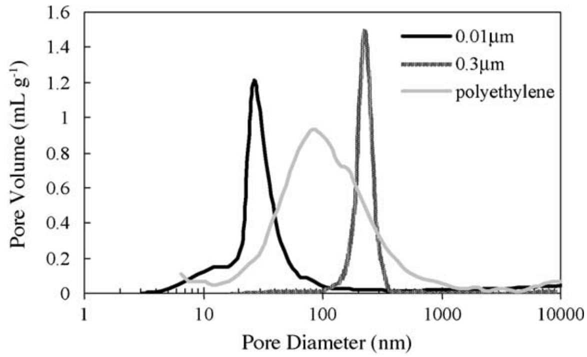

Fig. 2. Pore distribution in the CPS films and PE separator. The CPS films use: (a) 0.01 μm powder; (b) 0.3 μm powder.

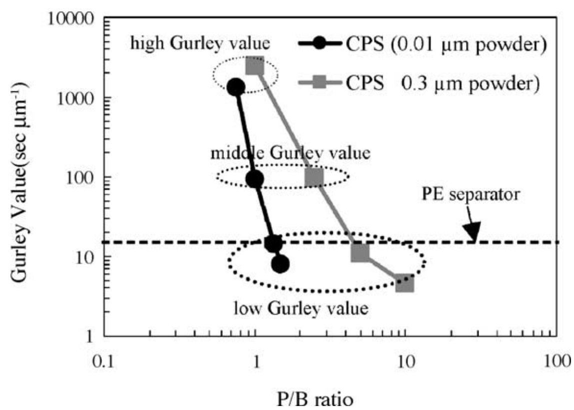

Fig. 3. Relationship between Gurley value and P/B ratio of CPS film on each powder size.

3. Results and discussion

Fig. 1(a)–(d) show surface SEM images of the CPS films of different powder particle sizes and compositions to powder and binder. In the film made of 0.01 μm particles, no pores were observed in the film with low powder content (Fig. 1(a)) because the powders were buried in the binder resin. On the other hand, many pores formed in the film with high powder content (Fig. 1(b)). We observed the same results for the film made of 0.3 μm particles (Fig. 1(c) and (d)). Therefore, it was

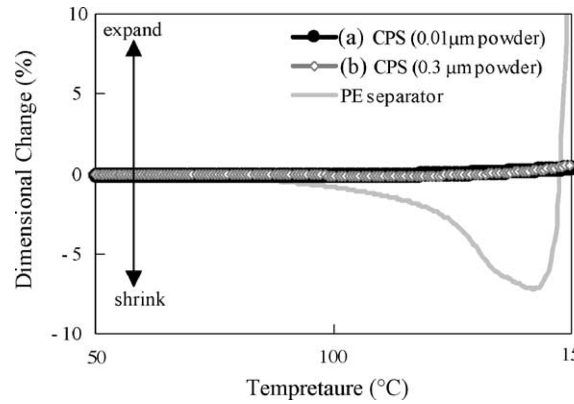

Fig. 5. Relationship between temperature and dimension change of CPS films and polyethylene separator.

found that many pores were formed when the powder content of the CPS film was high.

The CPS films with high powder content featured many pores between the particles. To evaluate the pore size in the films, we measured the pore size distribution of the CPS films. Fig. 2 shows the pore distribution of the CPS films with high powder content (sample A and E) and a polyethylene (PE) porous film used as a conventional separator for lithium rechargeable batteries. The pore size distribution of the film using 0.01 μm particles has a peak between 10 and 30 nm, while the film using 0.3 μm particles peaks between 200 and 300 nm. Furthermore, the pore distribution of the CPS films was narrower than the PE separator film. Therefore, pore size in the CPS films is nearly equal to powder particle size. Thus, we can design the pore size of CPS film by choosing a powder particle size.

Fig. 3 shows the air permeability of the CPS films and the PE separator film. Gurley value is the indicator of air permeability, and low Gurley value means high air permeability. The Gurley value was normalized by film thickness of sample. As the P/B ratio of the CPS films increased, the Gurley value decreased. The Gurley value of the CPS film using 0.01 μm powder was easily controlled by powder weight variation. Therefore, the lower Gurley value of the CPS film is designable. In the view point of the film tear strength, the

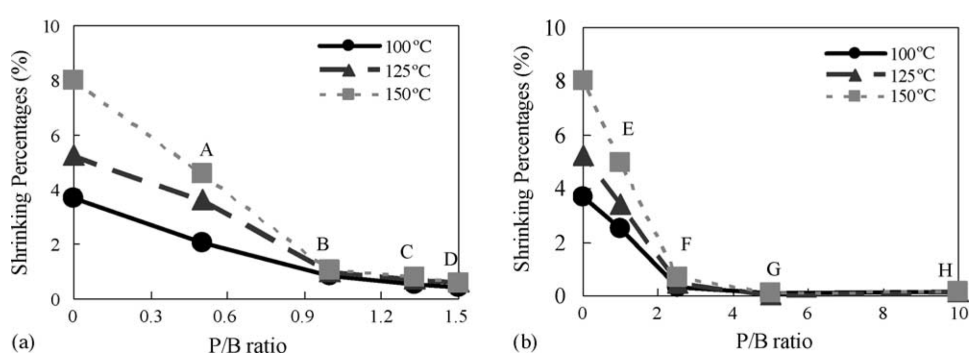

Fig. 4. (a) Relationship between shrinking percentage and P/B ratio of CPS film using 0.01 μm powder; (b) relationship between shrinking percentage and P/B ratio of CPS film using 0.3 μm powder.

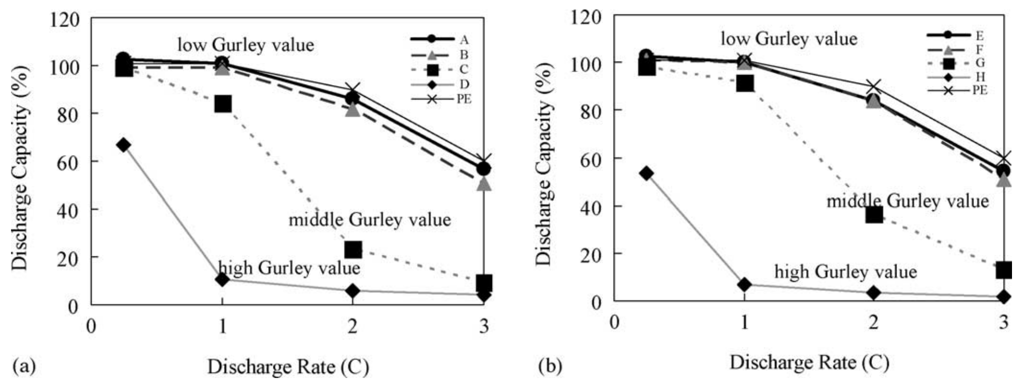

Fig. 6. (a) Dependence of discharge capacity on discharge C-rate of CPS film using 0.01 μm size powder; (b) dependence of discharge capacity on discharge C-rate of CPS film using 0.3 μm size powder.

lower P/B ratio is preferable. In the case of using 0.01 μm powder, we could fabricate the CPS film with the low Gurley value under small P/B ratio compared with the CPS using 0.3 μm powder. From these reason, it is expected that the CPS film using 0.01 μm powder is more suitable than using 0.3 μm powder.

To evaluate the CPS film's heat-resisting properties, we measured the film shrinkage after heat treatment of 100, 125, and 150 °C. Fig. 4(a) and (b) show the relationship between powder weight ratio and the shrinkage of the CPS films. As the powder weight ratio increased, the shrinkage of the film using 0.01 μm particles decreased. The CPS films of low powder content shrank by crystallization of binder resin. It is considered that the high powder content of the CPS film prevents damage to the film by deformation because of the frame structure with the ceramic powder. Therefore, low shrinkage can be obtained with high powder content films. The shrinkage tends to be low in the CPS film using 0.3 μm particles, because of the low ratio of binder weight.

To evaluate thermal stress changes of CPS film, we measured its thermal analysis. Fig. 5 shows the relationship between the temperature and dimensional change of the CPS films with high powder content (sample A and E) and a PE separator film. Neither CPS films shrank at any range. On the other hand, the PE separator film shrank over 90 °C and expanded over 140 °C. Since the manufacturing process of porous PE film includes a drawing step, this film shrinks easily by the heat treatment due to internal stress [2]. Melting explains the expansion over 140 °C on the PE separator film. On the other hand, since the CPS film is formed by a casting method, it is difficult to induce internal stress.

Fig. 6 shows the relationship between the discharge rate and discharge capacity ratio of the battery using CPS film. For each particle size, the discharge rate properties of the batteries that used low Gurley value of the CPS films was almost equal to a conventional PE separator. However, discharge capacity fell steeply at higher discharge rates when high Gurley value of the CPS films were used. Gurley value is related to the specific ionic resistance of a separator, and the internal resistance of a cell increases when the Gurley value is high [3]. Therefore, the CPS film with high Gurley values made a low discharge capacity of the cell at a higher rate of discharge.

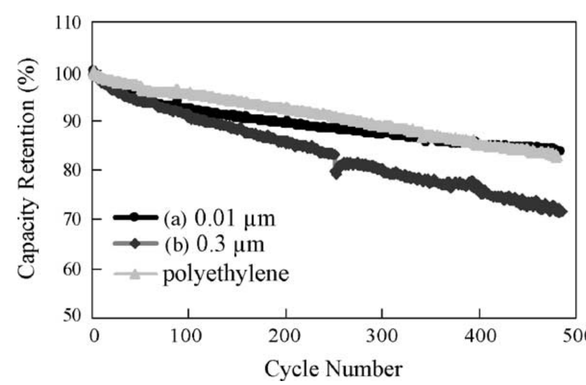

Fig. 7. Cycle properties of sample cells using CPS films and PE separator.

Fig. 7 shows the charge–discharge cycling properties of the test cells using the CPS films (sample A and E) and a PE separator. After 500 cycles, the capacity retention of the cell using 0.01 μm powder almost equals the cell using the PE separator. On the other hand, the capacity retention of the cell using 0.3 μm powders was lower than the one using 0.01 μm. Since the pore size of the CPS film using 0.01 μm powders is smaller than using 0.3 μm, the ability to keep electrolytes in the pores using 0.01 μm powders might be higher than that using 0.3 μm powders because of the difference of capillary action. This capillary action helps avoid a lack of electrolytes.

4. Conclusion

We evaluated the pore structure, air permeability, heat-resisting properties, and battery properties of CPS films made of either 0.01 or 0.3 μm aluminum oxide powders and PVdF resin. The experimental and analysis results showed that the CPS films of high powder content possessed good thermal stability and battery performance. The CPS film using 0.01 μm powders showed especially excellent cycling properties. These results suggest that these CPS films can be used as separators for lithium rechargeable batteries that satisfy the required thermal stability and cell performance.

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