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Effect of the conductive materials and press ratio of an anode electrode on the electrical properties in a lithium-ion battery using SiO_x

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A Lithium-ion battery was prepared by controlling the content of conductive materials and the press ratio of the anode electrode to optimize cell properties. Increasing of the content of conductive material, increased the capacity, and decreased the DC-ESR. The discharge capacity retention as a function of current rates increased with an increasing amount of conductive material. With an increasing press ratio, the active material was evenly distributed on the Cu collector and a dense anode was obtained. The capacity and DC-ESR decreased with an increasing press ratio. The discharge capacity and DC-ESR retention as a function of current rates did not change remarkably with an increasing press ratio. However, the adhesion force between the Cu collector and active materials increased with an increasing press ratio.

Keywords: Li-ion battery, SiO_x, Conductive materials, Press ratio

Introduction

Lithium-ion batteries (LIBs) have been established as one of the most important energy storage technologies and are widely used in importable electronics and electric vehicles (EVs) because of their high energy and power densities as well as long lifespan [1-4]. However, the increasing energy density and cost demands for general public acceptance of EVs have begun to exceed the ultimate capability of current commercial LIB technology [5-8].

Silicon monoxide (SiO) has recently aroused great interest as one of the most promising alternative anode materials for next-generation LIBs due to its appropriate working potential (< 0.5 V vs. Li+/Li), high theoretical specific capacity (-2,400 mAh g^{-1}), and enhanced cycling stability compared to Si [9-13]. Silicon monoxides (SiO or SiO_x) have also received some attention as another type of silicon-based anode because of their based on its ability to offer high energy density while they suffer from poor electronic conductivity [14].

A conductive additive as a necessary ingredient has been widely used in the lithium ion battery system to enhance the conductivity of electrodes [15-18], especially for the Si-based anode [19, 20]. Conductive additive wrapping around the active material grains has greatly reduced the contact resistance between grains, decreased the inner resistance and improved the rate capability [21]. At present, the commonly used conductive additives in commercial lithium ion batteries are acetylene black, Super-P, Ketjen Black, CNTs and vapor-grown carbonfibers (VGCFs).

In this paper, Super-P was chosen as a conductive material for a SiO_x/graphite composite anode. We investigated the effect of the amount of conductive material and the mechanical press ratio of the anode electrode on the electrical properties for lithium ion batteries using a SiO_x

Experimental

To prepare a cathode electrode, as shown in Table 1(a) below, NMC111 ($LiNiMnCoO_2$) and LCO ($LiCoO_2$) as an active material, Super-P (Timcal) as a conductive material, and PVdF (HSV900) as a binder were slurried at a ratio of 86.7:6.93:6.37 (vol%) in an NMP (n-methyl-2-pyrrolidone) solvent; the slurry was coated on

Table 1. Composition of cathode.

	Cathode	
Active materials	NMC111	66.00%
	LCO	20.70%
	Total	86.70%
Conductive materials	Super P	6.93%
	Total	6.93%
Binder	PVdF(HSV900)	6.37%
	Total	6.37%
Total Ratio	100.00%	
Solid content	47.5%	

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Table 2. Composition of the anode as a function of the amount of conductive material.

	Conductive material 2%		Conductive material 6%		Conductive material 10%	
Active materials	A.G	81.90%	A.G	79.20%	A.G	74.70%
	SiOx	9.10%	SiOx	8.80%	SiOx	8.30%
	Total	91.00%	Total	88.00%	Total	83.00%
Conductive materials	Super P	2.00%	Super P	6.00%	Super P	10.00%
	Total	2.00%	Total	6.00%	Total	10.00%
Binder	CMC	3.00%	CMC	3.00%	CMC	3.00%
	SBR	4.00%	SBR	4.00%	SBR	4.00%
	Total	7.00%	Total	7.00%	Total	7.00%
Total Ratio	100.00%					
Solid content	42%		44%		42%	

an etched Al foil, and then pressed. The thickness of the coated cathode electrode was adjusted to 130 μm after it was pressed, and the electrode density was 29 mg/cm^2. To prepare an anode electrode, as shown in Table 1(b), artificial graphite (Sigma Aldrich, 10 μm) and SiO_x were used as anode active materials, Super-P was used as a conductive material, and a mixed aqueous binder of CMC (carboxylmethyl cellulose) and PAA (polyacrylic acid) was used as a binder. Artificial graphite and SiO_x (x=1; a product manufactured by OTC company; average particle diameter: 5 μm) were set at 9:1, and slurries were prepared in a DI water solvent while the content of the conductive material super-p was changed to 2%, 6% and 10%, and then it was coated on Cu foils and pressed, thereby preparing anode electrodes. The thickness of the coated anode electrode according to the content of the conductive material was set at 100 μm after pressing, and then the electrode density was adjusted to 9.8 to 11.0 mg/cm^2 depending on the press ratio. To fabricate a lithium secondary battery unit cell, we used the same cathode as described above, and prepared a jelly-roll by winding using a cellulose-based separator, and finally we immersed it in a 1.5 M $LiPF_4$/acetonitrile electrolyte for 24 hours, and then sealed using a curing method in a cylindrical can with a 2245 size. The fabricated lithium secondary battery unit cell was measured for its charge/discharge and rate characteristics (C-rate) using an Arbin cycler. To confirm the crystallinity of powdery SiO_x samples, X-ray diffraction analysis (XRD, D/MAX 2000 by Rigaku Corp.) was performed using Cu Kα1 rays (1.5406 Å). Each sample was measured at 20° to 80° with a scan speed of 5° min^{-1} (40 kV, 100 mA).

Results and Discussion

Fig. 1 shows the results of the XRD analysis of the SiO_x used in this experiment. The diffraction of the

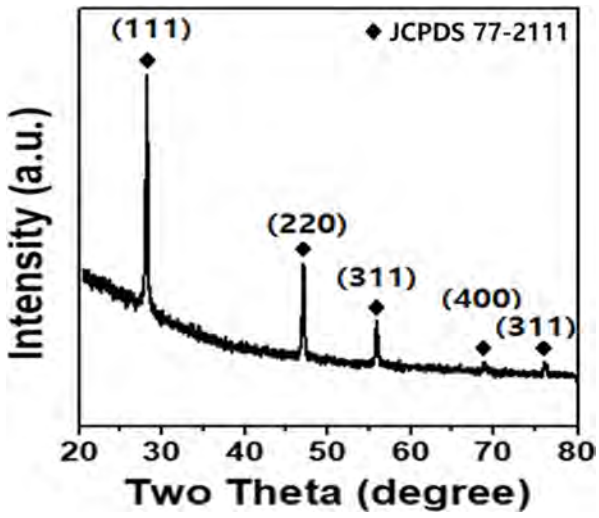

Fig. 1. Results of the XRD measurement of SiO_x

(111), (220), (311), (400) and (331) planes appeared at 28.4°, 47.3°, 56.1°, 69.1° and 76.3°, and these results are identical to those of JDPDS Card JCPDS No. 77-2111.

Characteristics as a function of the amount of conductive material of in the anode electrode

Fig. 2 depicts FE-SEM images of the anode electrodes as a function of the amount of conductive material, The conductive material is uniformly distributed in the space between the artificial graphite and the SiO_x particles and around the particles as the content of the conductive material which has a structure in which 20 to 30 nm particles are connected to one another like chains is increased. Fig. 3 shows the results of measuring electrical characteristics as a function of the conductive material content by performing charge/discharge at 1C. The charge capacity and the discharge capacity show a tendency to increase as the amount of conductive

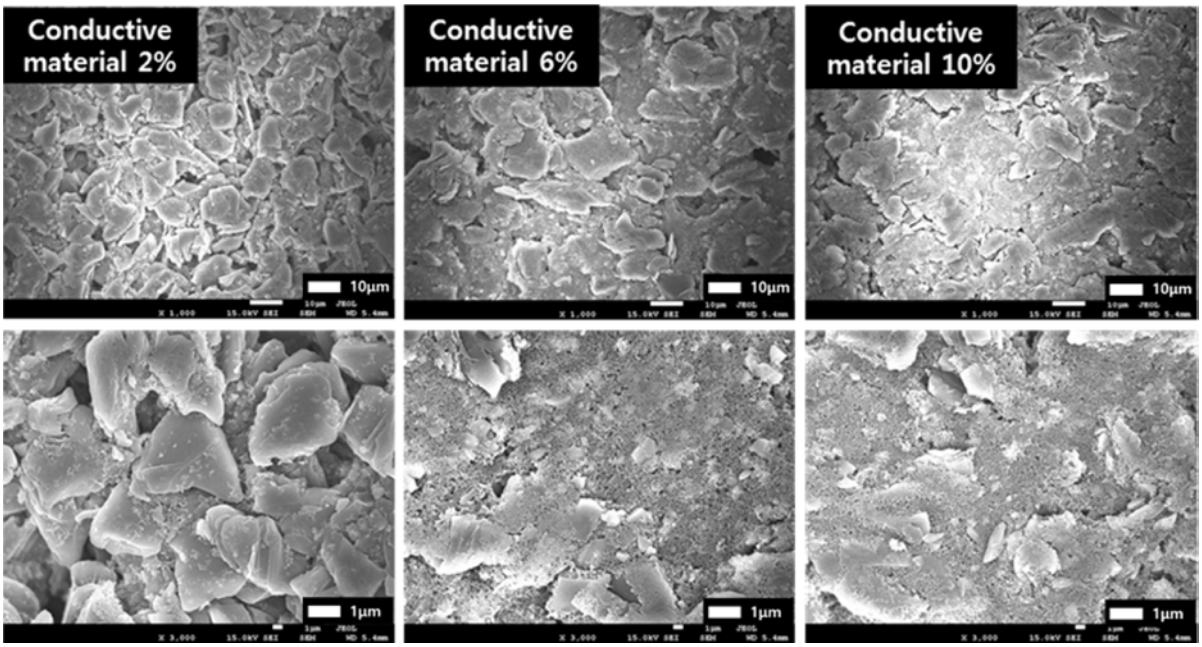

Fig. 2. FE-SEM images of anode electrodes as a function of the amount of conductive material.

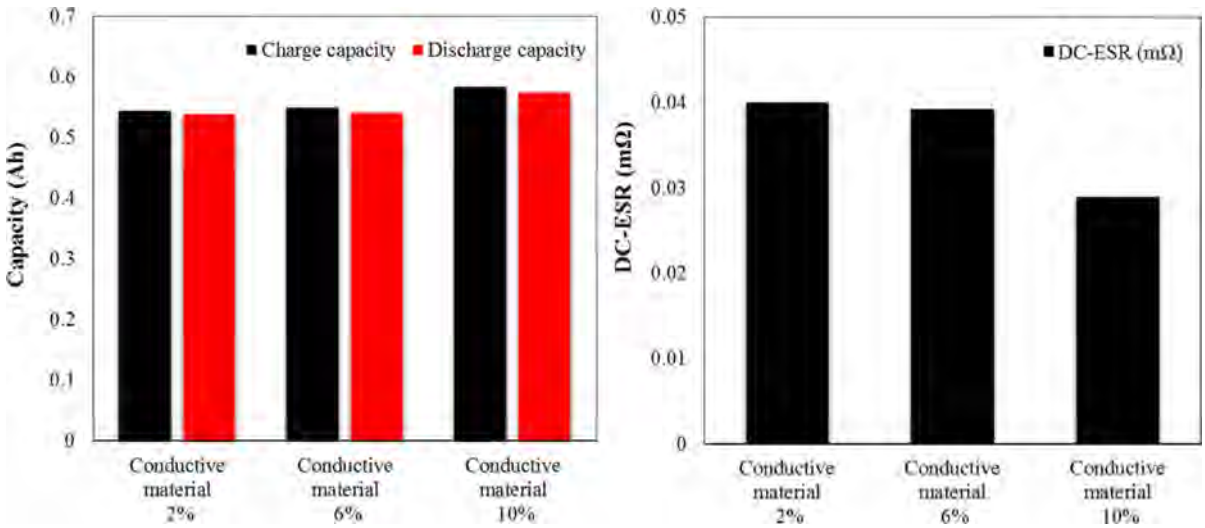

Fig. 3. Capacity and DC-ESR as a function of the amount of conductive material.

material increases. The DC-equivalent series resistance is as low as 0.028 Ω when the content of the conductive material is 10%. We obtained the result for the charge/discharge capacity and DC-equivalent series resistance characteristics because the conductive material, Which had high conductivity was uniformly distributed in the space between the active materials as confirmed by the FE-SEM image of the anode electrode in Fig. 2, thereby facilitating the migration of lithium ions to the artificial graphite and the SiO_x active material.

Fig. 4 shows the results obtained by charging the cell at 1C to 5C-rate, and then maintaining for 10 seconds in the CV region, and then discharging at the same current as the charge current and measuring the C-rate for each three cycles. The results of the C-rate measurement indicated that the capacity retention increased as the content of the conductive material content increased and that the lithium ion battery fabricated using the electrode with a conductive material of 10% had a discharge capacity retention of 78% at 5C compared to 100% at 1C. The DC-equivalent series resistance did not significantly change according to the change in the conductive material content, while the discharge capacity did.

Characteristics as a function of the anode electrode

The delamination between the Cu foil (current collector) and the coating layer when a cell is fabricated using lithium secondary battery electrodes influences the fabrication process and reliability characteristics. In

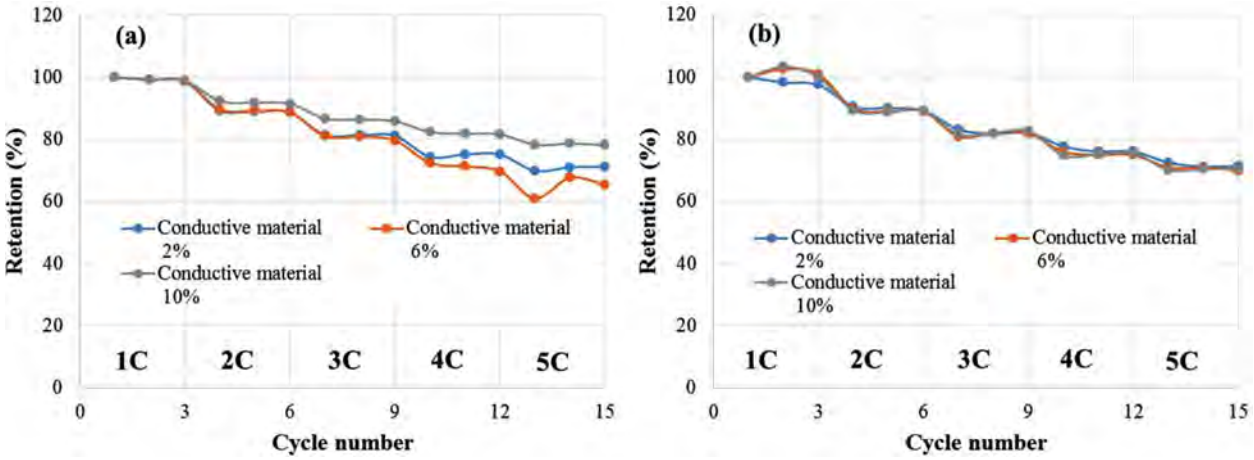

Fig. 4. C-rate as a function of the amount of conductive material: (a) capacity retention. (b) DC-ESR retention.

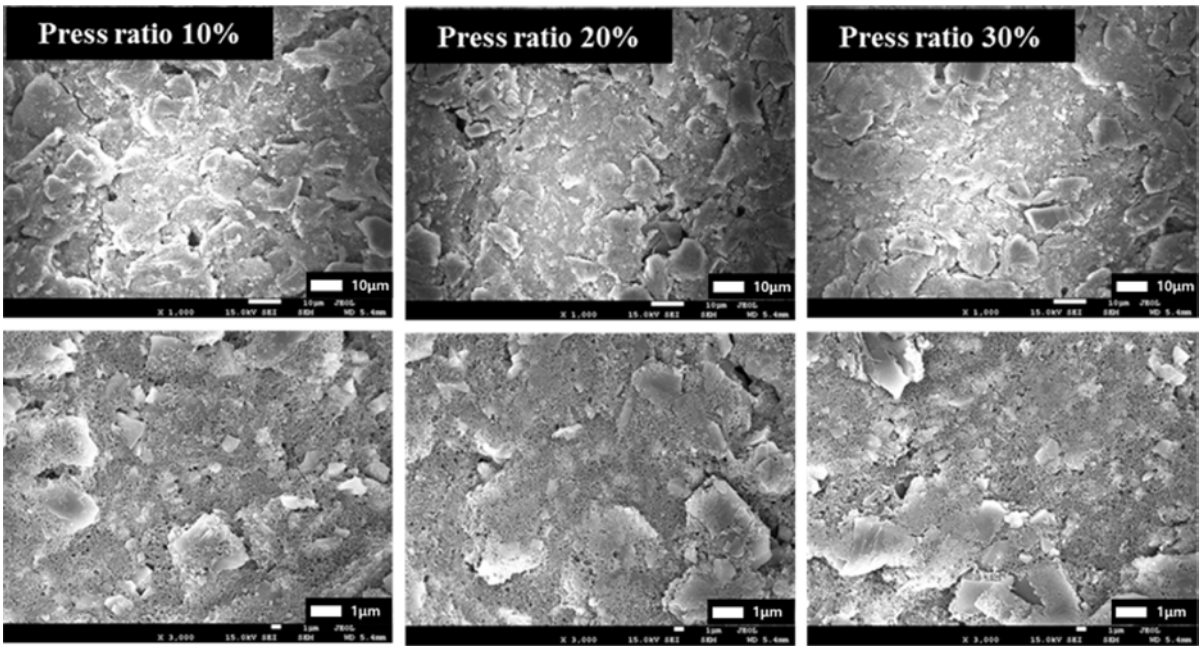

Fig. 5. FE-SEM images of anode electrodes as a function of the pressure ratio.

the anode electrode experiment we performed as a function of the conductive material content, the press ratio was set at 10% and the delamination between the Cu foil (current collector) and the coating layer was measured as a function of the conductive material content. In the result, average adhesion forces of 0.0627, 0.0128 and 0.01 kgf appeared at conductive material contents of 2, 6 and 10%. The results of the experiment performed as a function of the conductive material content indicated that with an electrode with a conductive material content of 10%, which showed the best charge/discharge characteristics and C-rate characteristics, a problem arose: The adhesion force between the current collector and the coating layer decreased.

This was because the amount of the conductive material with a nano-scale size and a large specific surface area increased, and thus the area caught by the binder increased. In order to increase the adhesion force between the current collector and the coating layer, we set the composition as shown in Table 1 and performed pressing using a press at press ratios of 10, 20 and 30%, and then we examined the adhesion force and electrical characteristics. Fig. 5 depicts FE-SEM images as a function of the pressure ratio: As the press ratio increases, particles are pushed and pores decrease. We thought that the distance between the current collector and the coating layer decreased because of the increase in the press rate, and the active material and the conductive material were closely connected to each other.

We fabricated lithium ion battery unit cells and compared the amount of impregnated electrolyte with press ratios. The amount of impregnated electrolyte

decreased to 6.63, 6.23 and 5.77 g at press ratios of 10, 20 and 30%, respectively. From the FE-SEM images and the experiment on the amount of impregnated electrolyte, we confirmed that the pores in the electrolyte decreases as the press ratio increased.

Fig. 6 shows the results for the measurement of the adhesion force between the Cu current collector and the coating layer as a function of the press ratio. The average adhesion forces are 0.01, 0.117 and 0.095 kgf at press ratios of 10, 20 and 30%, indicating that the highest occurs at a press ratio of 20%.

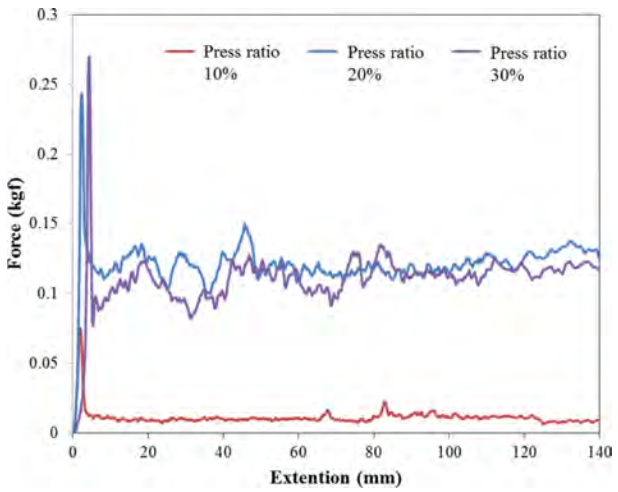

Fig. 6. Adhesion force of anode electrodes as a function of the press ratio.

Fig. 7 shows the measurement results for the electrical characteristics as a function of the press ratio with the performance of charge/discharge at 1C. The charge/discharge capacities and the DC-equivalent series resistance show a tendency to decrease. We believe considered that the decrease in the charge/discharge capacities was due to the decrease in the amount of impregnated electrolyte and that the decrease in the DC-equivalent series resistance was because of the decrease in the distance between the current collector and the coating layer due to the increase in the press ratio rather than the influence of the amount of impregnated electrolyte and because of the compact connection between the active material and the conductive material.

Fig. 8 shows the results obtained for charging the cell at 1C to 10C-rate, and then maintaining it for 10 seconds in the CV region, and then discharging it at the same current as the charge current and measuring the C-rate for each three cycles. The results of the C-rate measurement indicated that the discharge capacity

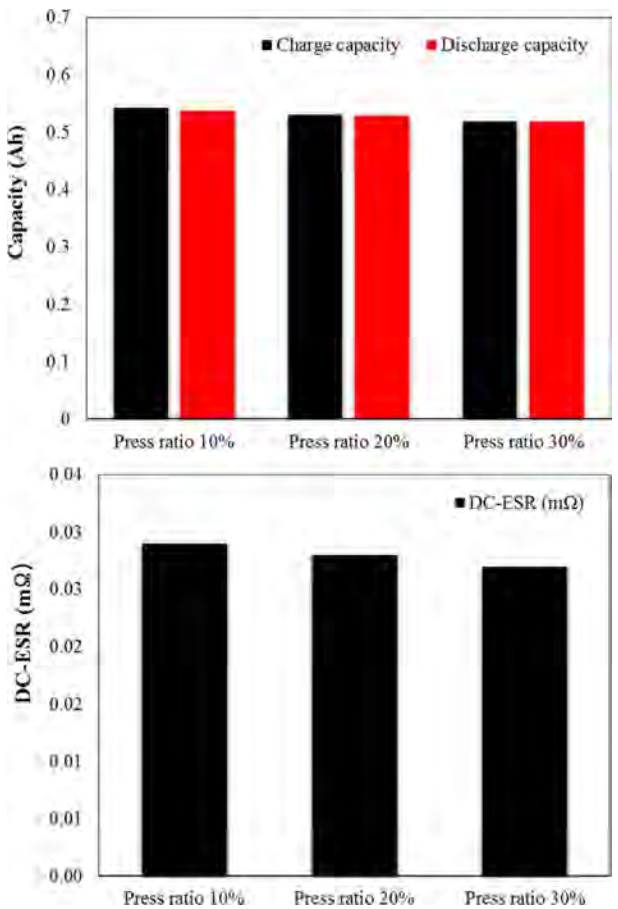

Fig. 7. Capacities and DC-ESR as a function of the press ratio of the anode electrode.

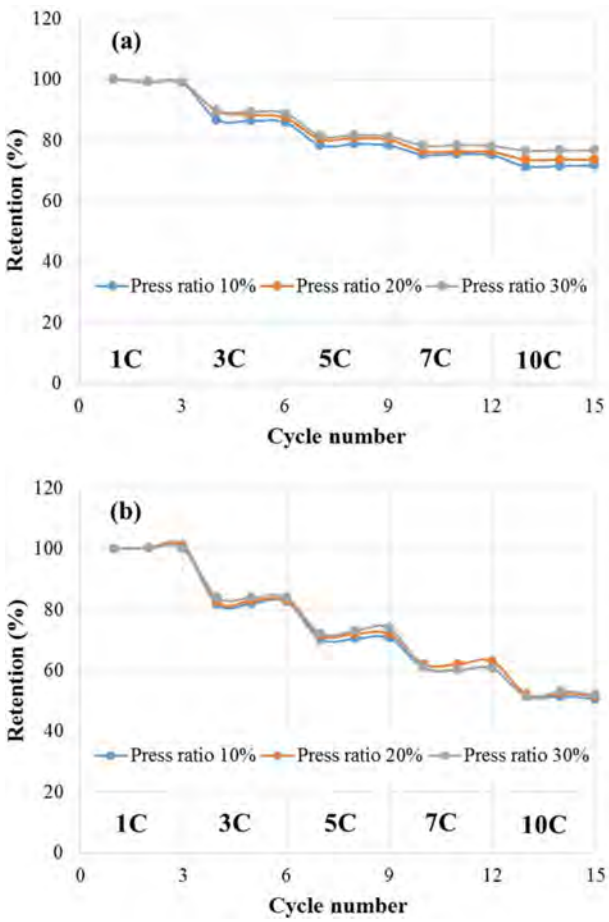

Fig. 8. C-rate as a function of press ratio: (a) capacity retention, (b) DC-ESR retention.

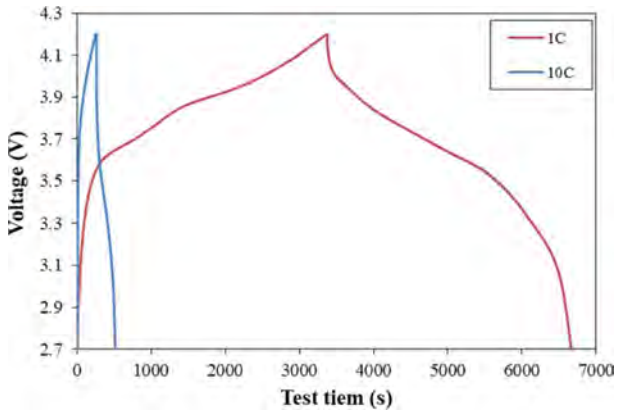

Fig. 9. The charge/discharge curve of cell with press ratio 30% as a function of current rate.

retention at a press ratio of 30% was 76.6% at 10C compared to 100% at 1C. Unlike the discharge capacity, the DC-equivalent series resistance did not significantly change according to the change in the amount of conductive material.

The charge/discharge curve of the cell at a press ratio of 30% as a function of current rate is shown Fig. 9. The charging and discharging time at 1C was 6664 seconds, and the charging and discharging time at 10C was 513 seconds. The discharge capacity at 10C was 76.6% while it was 100% at 1C.

Conclusions

In this study, in order to develop a lithium secondary battery, that is capable of charging/discharging even at high current rates, using SiO_x as an anode active material, we evaluated the electrical characteristics as a function of the amount of conductive material and the press ratio. We adjusted the content of the conductive material to 2, 6 and 10 wt% and evaluated the electrical characteristics were evaluated. We found that as the content of the conductive material increased, the capacity increased and the resistance decreased. The c-rate was measured at 1 to 5C, and the cell with a conductive material content of 10 wt% showed the best capacity retention according to the change in charge current.

We performed the evaluation while changing the press ratio of the electrode with a conductive material content of 10 wt%, and as a result, the capacity and resistance decreased as the press ratio increased. The C-rate was measured at 1 to 10C, and the cell with the highest press ratio (30%) showed the best capacity retention (76.6%) at 10C compared to that of 1C, and the adhesion force of the anode electrode was also excellent.

Our study confirmed that the lithium secondary battery fabricated using SiO_x achieved a capacity retention of 70% or higher in rapid charge/discharge at 10C and had the potential as a lithium secondary battery that is capable of rapid charging/discharging.

Acknowledgements

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