Electrochemical characteristics of silicon coated graphite prepared by gas suspension spray method for anode material of lithium secondary batteries

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Abstract–Silicon-coated graphite particles were tested as anodes for lithium ion rechargeable batteries. The synthetic graphite particles were first coated with silicon precursor containing solution by gas suspension spray method and then calcined at heat treatment temperature at 500 °C under hydrogen atmosphere. The silicon-coated graphite showed high specific capacity and good cycle performance due to the formation of amorphous silicon-carbon black composite layer on the surface of the graphite particles. It has stable structure under repeated volume expansion and contraction. The silicon-coated graphite still has high irreversible capacity due to the solid electrolyte interface (SEI) formation during the 1st cycle. However, the capacity loss could be lessened to a certain level by controlling the composition of the solvent mixture in the electrolyte.

Key words: Lithium Secondary Batteries, Synthetic Graphite, Gas Suspension Spray Coating, Silicon, Carbon Black

INTRODUCTION

Rechargeable lithium batteries are the common power source for consumer electronics such as Notebook PCs and mobile telephones. Those mobile electronics have now become necessities of human life. Moreover, the excellent performance of lithium batteries may meet the need for high power batteries even in electric vehicles. Thus, the increase of energy density and cyclability for the electrode materials of batteries is very important to meet the future demand [Besenhard et al., 1990].

Commercial carbonaceous materials, synthetic and natural graphite, usually have been employed as the negative electrode because of their better cycling performance and dimensional stability compared to those of lithium alloys. According to the electrochemical reaction between carbon and lithium, however, a lithium ion can react with six carbon atoms. Hence, the theoretical maximum storage capacity of graphite can be limited to 372 mAh/g [Broussely and Archdale, 2004].

In order to increase the specific capacity of the lithium secondary batteries, active nano-coating materials have been investigated. Among them, silicon is considered to be one of the most promising alternative anode materials. According to the electrochemical reactions between silicon and lithium, silicon can alloy with lithium up to 4.4 lithium at high temperature. Therefore, the theoretical capacity of silicon is about 4,200 mAh/g. However, silicon is difficult to apply due to the poor cyclability and the high irreversible capacity at the first cycle [Jung et al., 2003; Nertz et al., 2003].

Another prospective solution for the preparation of anode with high energy density is the nano-composite material. Among the intrinsic properties of the intercalation, the geometric design of the insertion-compound electrode is critically important. The principle of the geometric design is similar for every application. An important strategy in the design and optimization of electrode is the use of smaller intercalation-compound particles. The nano-composite materials may give high electrode-electrolyte interfacial area coupled with short diffusion distance within the electrodes. They also have uniform electric field and smaller change of volume to surface area. On the other hand, with the employment of nano-sized materials, disadvantages also follow. The initial efficiency may decrease due to the increase in SEI (solid electrolyte interface) film surface area. Therefore, optimum design of the active materials is very important to prepare a suitable electrode for high powered batteries.

Here, the purpose of this study is the accomplishment of high capacity of anode material with good cycle performance through the preparation of silicon-carbon black composite on the graphite surface. In the present study, experiments were carried out to obtain the highly dispersed silicon on the graphite anode. In this carbon-silicon composite system, we expect that silicon acts as a lithium alloying reactant during charge-discharge process and also carbon matrix plays a role of the lithium intercalation site and conducting medium between silicon particles as well.

EXPERIMENT

Commercial synthetic graphite, MCMB (meso-phase carbonaceous micro bead), was used as our raw material with an average particle diameter of about 10 μm (MCMB1028, Osaka gas). Silicon-graphite composites were prepared by gas suspension spray coating method.

At the fluidizing point, the frictional force between gas and a particle counterbalances the weight of the particle so that all the particles comprising the bed could be suspended in the upward flowing gas. For spray coating, the atomized liquid droplets from the spray nozzle which is placed at the bottom of the bed contact the suspending particles and spread over on the surface of the particles. The wetted particles are extensively dried through solvent evaporation. The repeated motion of the particles through the spray zone allows the continuous coating of material to build up and finally

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coated particles can be prepared. For particle coating, silicon content can be controlled by adjusting spraying time.

The coating material used was dichlorodimethyl silane which was diluted in n-hexane solvent and the apparatus for coating consists of a spouted bed with a draft tube insert. The draft tube could be easily adjusted up or down relative to the distributor plate and the bed was equipped with a spray nozzle located at the center of the distributor plate. The nozzle was an air atomizing one with an air cap used to spray a coating liquid into the bed. In this gas suspension spray coating process, fluidized graphite powders were coated and dried simultaneously inside the bed. After the particles were coated, they were calcined in a furnace at 500 °C under H_2 atmosphere.

Electrodes for half-cells of lithium ion batteries were manufactured with the coated graphite samples prepared under different conditions and their electrochemical properties were compared. Negative electrodes were fabricated by mixing a slurry containing 6 wt% polyvinylidene fluoride (PVDF) binder, 3 wt% acetylene black as the conductor, and 91 wt% active materials. The metal-coated carbon electrode does not contain acetylene black. The graphite, in the presence of some acetone, was mixed in a vortex mixer at 5,000 rpm. A slurry containing carbonaceous material was spread to form a 100 μm thick sheet on a copper foil by dipping. The sheet was allowed to dry at ambient temperature for a day, followed by drying in an oven at 80 °C. The composite was then pressed at 110-120 °C by a roll press. The pressed composite was cut into 2×2 cm pieces and dried in a vacuum at 110 °C for 24 hours. All cells were assembled in a dry-room (max. moisture content<5%). The counter electrodes were lithium metal foils of 75 μm thickness, while the separator was a polypropylene film. The electrolyte employed in this study was 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC), propylene carbonate (PC) and dimethyl carbonate (DMC).

Silicon-coated graphite samples, prepared by gas suspension coating, were characterized by inductively coupled plasma (ICP; Ash Thermo Jarrel POLYSCAN 61E), X-ray diffractometer (XRD, Rigaku RINT/DMAS-2500) with a CuKα source, scanning electron micrograph (SEM employing a Hitachi S-4200), and BET surface area measurement (ASAP : Micromeritics ASAP-2010).

Typical charge-discharge cycling tests for the silicon-coated graphites were carried out using galvanostatic cycling at various charge-discharge rates between 0 and 1.2 V vs. Li/Li+ and cyclic voltammetry tests were carried out between 0 and 2 V at a scan rate of 0.1 mV (Won A Tech WBC3000). The AC impedance measurements for the metal-coated graphites were carried out under an open-circuit condition in a frequency range from 0.1 to 106 Hz. The perturbation amplitude was ±5 mV. The employed experimental set-up consists of a frequency response analyzer and a potentiostat/galvanostat (ZAHNER IM6).

RESULTS AND DISCUSSION

As explained in the experimental section, the raw graphite was coated by silicon using gas suspension spray coating method. Scanning electron microscopy was employed to investigate the difference in surface morphology between the raw graphite and the silicon-coated one. Fig. 1(a) shows the surface morphology of raw MCMB.
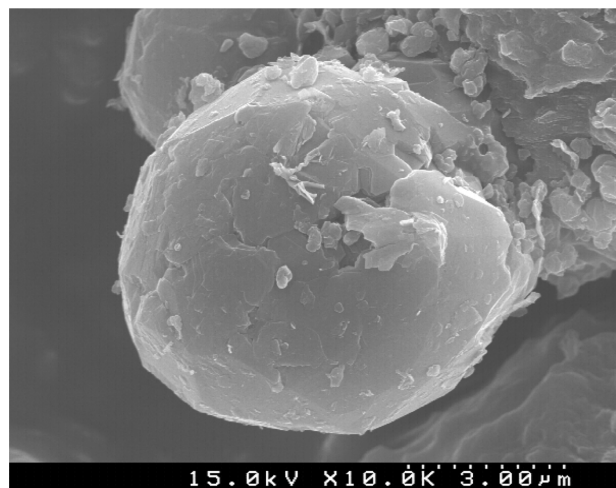
(a)
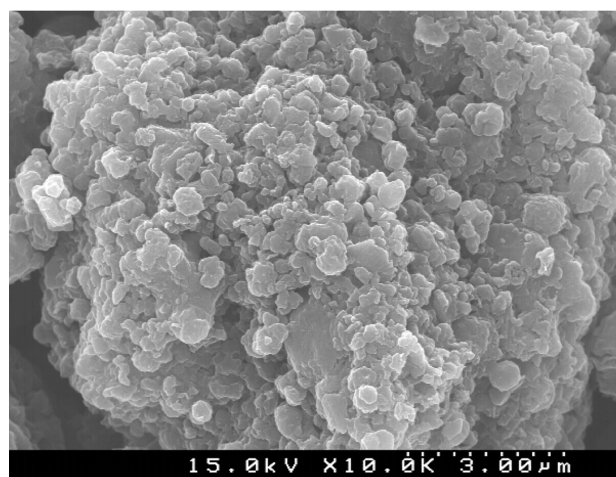
(b)

Fig. 1. Scanning electron micrographs of surface morphology of raw MCMB and Si coated MCMB.
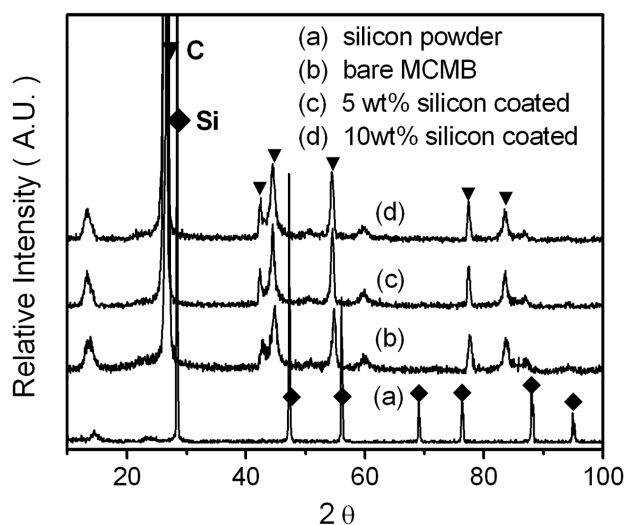

Fig. 2. X-ray diffraction patterns of the crystalline silicon powder, raw graphite and the silicon coated graphite.

Rather smooth surface with very few pores can be observed. Fig. 1(b) shows that silicon particles with spherical shape of about 50 nm thoroughly cover the specimen. The SEM shows that surface coating morphology appears to be agglomerate or cluster form instead of entirely uniform coating.

Fig. 2 shows the X-ray diffraction patterns of raw graphite and the silicon-coated graphite. Comparing the X-ray diffraction patterns,
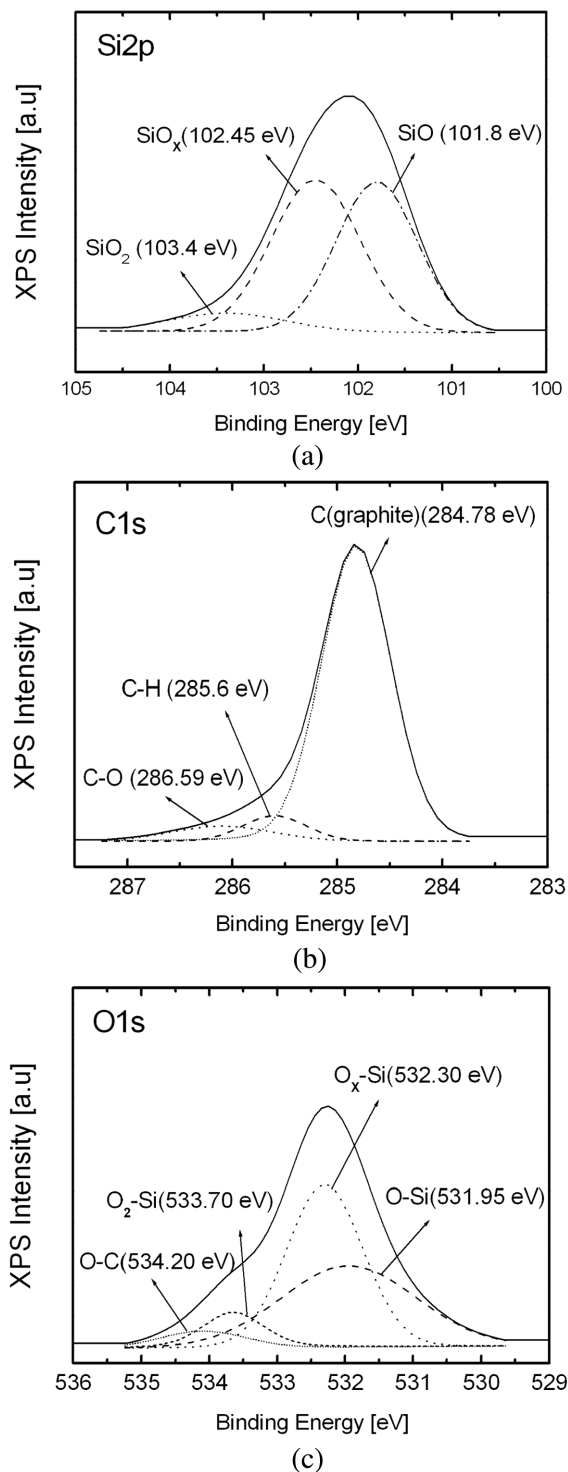
we note that the characteristic peak positions of MCMB phase remain unchanged after silicon coating. In other words, these two samples completely maintained their hexagonal structure even after the silicon coating. The results suggest that silicon film on the graphite surface has very thin layer of crystal which cannot be revealed by X-ray diffraction or amorphous structure.

The chemical compositions of the silicon coated samples were examined using PHI5800 surface analysis system with mono-chromatic AlKα radiation. Binding energies were referenced to the C1s carbon peak at 284.7 eV. Fig. 3 shows (a) Si2p, (b) C1s, and (c) O1s spectra on the natural surface of silicon coated MCMB. Si2p spectrum can be resolved into three components. The first one located at 101.8 eV is due to Si-O (http://www.lasurface.com/). The second one at 102.45 eV seems to be due to SiO$_x$ [Yang et al., 2002]. The x range from 1 to 2. And the third one at 103.0 eV is due to SiO$_2$. Surface elemental mole ratios of the three main peaks with Si-O, SiO$_x$ and SiO$_2$ bond determined from peak area ratios are present in a 37.0 : 56.1 : 6.9 ratio. The curve fit for the C1s spectrum suggests the presence of C (graphite) at 284.7 eV, C-H at 285.6 eV and C-O at 286.59 eV because of thermal surface oxidation. And O1s peak components at 531.95 eV for the O-Si, 532.3 eV for the Ox-Si, 533.7 eV for the O$_2$-Si and 534.2 eV for the O-C exactly correspond to (a) and (b). These results suggest that silicon atoms react with contaminated oxygen during the process.

Fig. 4 shows a CV diagram for the cells from bare MCMB, 5 wt% and 10 wt% silicon-coated MCMB. The evidence of alloy formation could be found in the figures. For bare MCMB, little peak was observed at the potential range of 0.15-0.18 V vs Li/Li$^+$. However, in case of the silicon-coated graphite, alloying peaks due to electrochemical reaction between the silicon and the lithium clearly exist at the same potential range. Much stronger peak was observed with increase of silicon coating amount. As to silicon-coated MCMBs, Li ions deintercalation peak got higher with increase of silicon coating amount. These results can be explained as that discharge rate and capacity increased with the silicon coating amount.

Fig. 5 shows the specific charge capacities and discharge capacities of bare synthetic graphite and silicon-coated graphite. For revers-
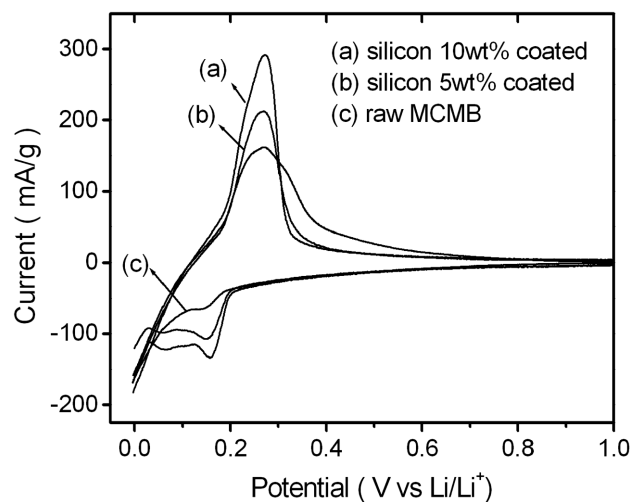

Fig. 3. XPS Si2p, C1s and O1s spectra of the silicon-coated graphite.

Fig. 4. Cyclic voltammograms with scan rate of 0.1 mV/s in the potential range from 0.0 to 1.2 V.
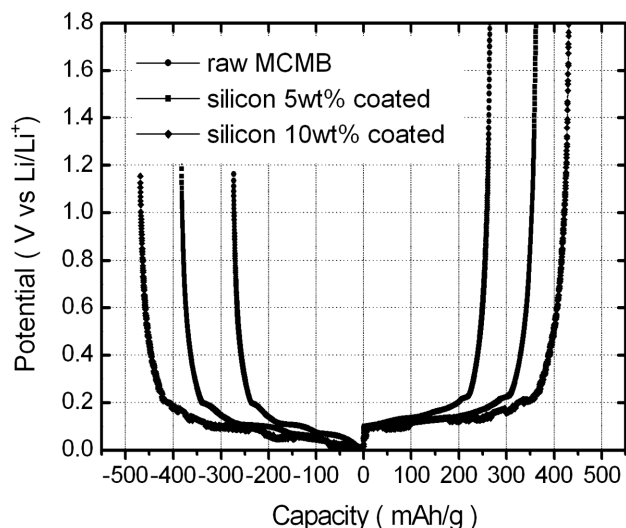
Fig. 5. Charge-discharge curve of raw MCMB and silicon coated MCMB at 10th cycle with 0.2 mA/cm² current density.

ible capacity of bare MCMB showed about 280 mAh/g, but the reversible capacity of the silicon-coated graphite increased with increase of coating amount and then reached up to 430 mAh/g for 10 weight % silicon-coated graphite. The enhancement of specific

capacity was attributed by alloying formation between silicon and lithium during cycles.

Fig. 6 shows the charge and discharge capacities and irreversible capacity of silicon coated graphite within 5 cycles for the different species and compositions of solvents. The electrode was prepared by the 10 wt% silicon coated MCMB and salt used in the electrolytes was 1 M LiPF₆. As is well known, EC helps enhance ionic conductivity, while EMC, DMC and DEC favor lowering viscosity [Yamaka et al., 2002]. As shown in those figures, the composition of electrolyte strongly affects the electrochemical performance of silicon-coated graphite. The figure shows the rate capability of the silicon-coated graphite under various kinds of electrolyte. The discharge capacity of the silicon-coated graphite decreased with C-rate. As shown in the figure, the composition of the electrolytes affects the rate capabilities of the silicon-coated graphite. The difference in discharge capacity may come from lithium ion transfer during the charge and discharge cycles.

Table 1 summarizes the specific charge capacities, Coulombic efficiency and irreversible capacity of silicon-coated graphite for four different kinds of electrolytes. It is observed from the table that the values of electrochemical performance are dependent on the species and composition of the solvents in the electrolyte. In the case of EC : EMC : DMC 1 : 1 : 1, obtained were the highest charge capacity and irreversible capacity. On the other hand, EC : DEC 1 : 2 showed the lowest charge capacity and irreversible capacity.
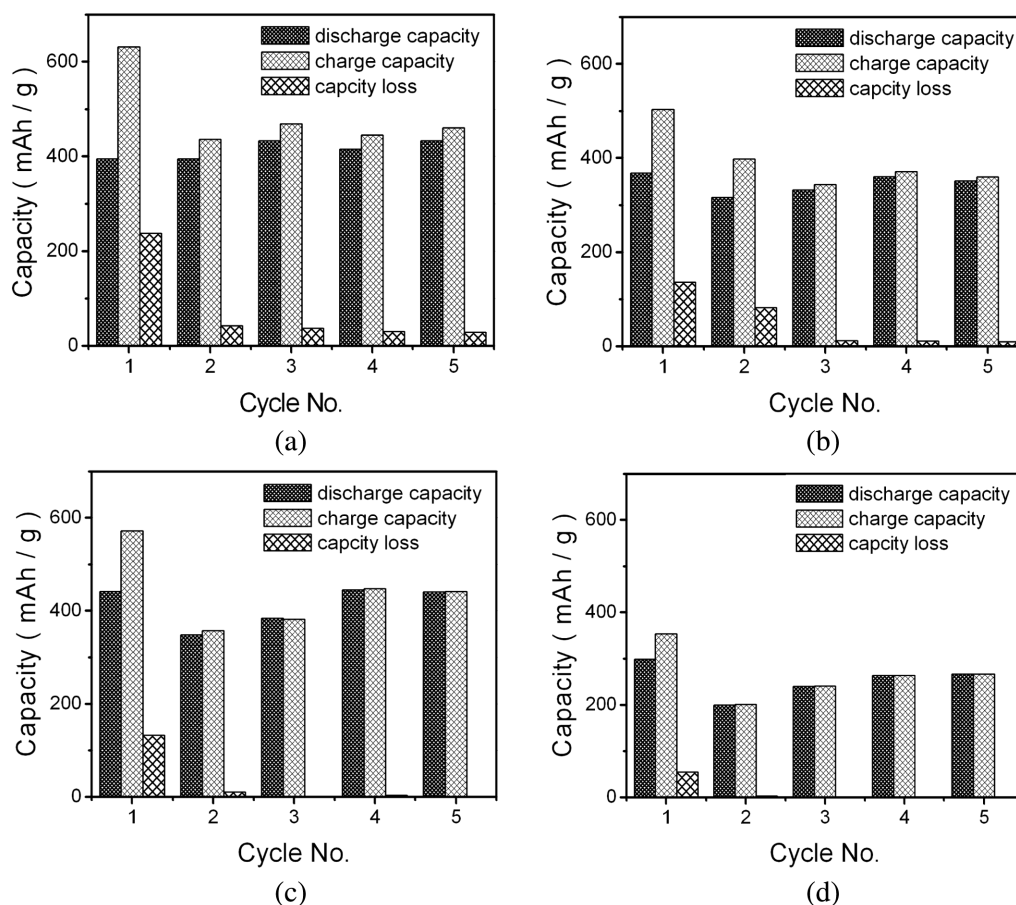

Fig. 6. Capacity loss with cycles of the silicon-coated graphite under various electrolytes: (a) EC : EMC : DMC (1 : 1 : 1), (b) EC : EMC (1 : 2), (c) EC : DMC (1 : 2) and (d) EC : DEC (1 : 2).

Table 1. First charge-discharge cycle capacities and initial efficiencies of the silicon coated graphite under various electrolytes

	EC : EMC : DMC=1 : 1 : 1	EC : EMC=1 : 2	EC : DMC=1 : 2	EC : DEC=1 : 2
Charge capacity (mAh/g)	630.9	502.7	571.9	352.6
Coulombic efficiency (%)	62	73	77	85
Irreversible capacity (mAh/g)	237.2	135.8	131.5	53.7
Discharge capacity at 10th cycle (mAh/g)	433.5	382.4	479.3	257.1
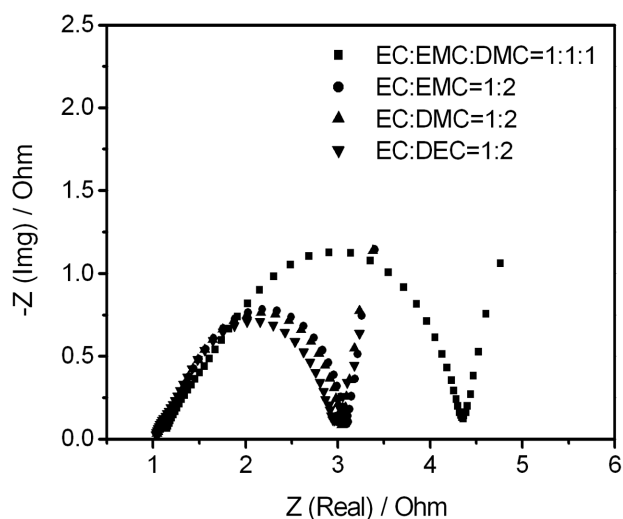
Fig. 7. Nyquist plots measured at the 1st cycle of the silicon-coated graphite under various electrolytes.

Fig. 8. Cycle performance of full cell with the law MCMB and silicon anode material; EC : EMC : DMC (1 : 1 : 1).

Those results seem to be closely related to the SEI film characteristics, which are formed by interfacial reaction between lithium and electrolyte on the surface of silicon coated graphite. The change in SEI film characteristics caused by different species and composition of electrolyte possibly leads to the difference in electrochemical performance such as specific capacity and irreversible capacities.

Fig. 7 compares Nyquist plots measured at first cycle under four different kinds of the electrolytes aforementioned. The AC impedance was measured at 0.158 V. The diameter of the semicircle equivalent to Faradic impedance of electrode changed with the electrolytes. Comparing the diameter of the semicircles, that of solvent composition at EC : EMC : DMC=1 : 1 : 1 is larger than those of other electrolytes. Those results indicated that larger semicircle diameter was caused by more active reaction between lithium and electrolytes on the surface of silicon-coated graphite. Hence, the larger impedance possibly leads to the higher irreversible capacity.

To investigate cycle performance of silicon-coated MCMB for longer cycle test, we fabricated 45 mAh-class full cell. Here, full cell means the employed cathode material was lithium cobalt oxide instead of lithium metal which was used for half cell. The charging and discharging rates of the cell were performed at 1C. 1C means that the cell is charged up to full capacity in 1.1 hr and discharged all capacity in 1 hour. The cut-off voltage at charging was 4.2 V and cut-off voltage at discharging was 3.0 V. As shown in Fig. 8, the discharge capacity of bare MCMB was reduced by 33% of the first capacity after 500 cycles. The discharge capacity of lithiated MCMB sharply decreased and then the electrode was broken after 200 cycles possibly due to dendrite formation. The capacity loss of silicon-coated MCMB was higher than that of bare MCMB because
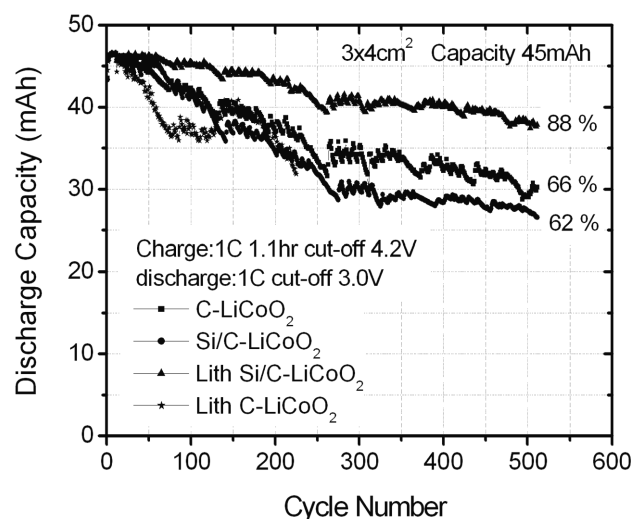
the silicon is consuming more lithium than carbon during the formation of SEI film. However, for the lithiated silicon-coated MCMB, the capacity fading was suppressed to less than 12% of the first capacity. Those results indicate that silicon-coated graphite has more stable electrochemical behavior under pre-lithiated condition, which reduces the SEI film formation reaction and irreversible capacity.

CONCLUSION

Synthetic graphite, MCMB coated with silicon by gas suspension spray coating, exhibited silicon of about 50 nm diameter on the graphite surface after coating and heat treatment. Consequently, gas suspension spray coating is an effective way to modify the active electrode materials for lithium secondary batteries. Electrodes prepared with silicon-coated graphite had higher capacities than that of raw graphite. As the coated amount of silicon increased, the discharge capacity increased due to the presence of a lithium alloy. The irreversible capacity was still higher even after the silicon coating; however, the capacity loss could be lessened to a certain level by controlling the component of the solvent in the electrolyte. The longer cycle tests of silicon-coated and raw graphites were carried out by using 45 mAh class full cell. The experimental result indicated that the capacity fading for silicon-coated graphite could be suppressed under pre-lithiated condition.

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REFERENCES

Besenhard, J. O., Hess, M. and Komenda, P., "Dimensionally stable Li-alloy electrodes for secondary batteries," *Solid State Ionics*, **40**, 525 (1990).

Broussely, M. and Archdale, G., "Li-ion batteries and portable power source prospects for the next 5-10 years," *Journal of Power Sources*, **386**, 136 (2004).

http://www.lasurface.com/

Jung, H., Park, M., Yoon, Y. G., Kim, G. B. and Joo, S. K., "Amorphous silicon anode for lithium-ion rechargeable batteries," *Journal of Power Sources*, **346**, 115 (2003).

Nertz, A., Huggins, R. A. and Weppner, W., "The formation and properties of amorphous silicon as negative electrode reactant in lithium systems," *Journal of Power Sources*, **95**, 119 (2003).

Yamaki, J. I., in Van Schlkwijk, W. A. and Scorosati, B. (Ed.), Liquid Electrolytes: *Advances in lithium-ion batteries*, Kluwer Academic/Plenum Publishers, New York, pp. 155-172 (2002).

Yang, J., Takeda, Y., Imanish, N., Capiglia, C., Xie, J. Y. and Yamamoto, O., "SiO_x-based anodes for secondary lithium batteries," *Solid State Ionics*, **152-153**, 125 (2002).