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A study on carbon coating to silicon and electrochemical characteristics of Si-C|Li cells

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Abstract−The aim of this paper is to study the electrochemical behavior of Si-C material synthesized by heating a mixture of silicon and polyvinylidene fluoride (PVDF) in the ratios of 5, 20, and 50 wt%. The particle size of the synthesized material was found to be increased with increase in the PVDF ratio. The coexistence of silicon with carbon was confirmed from the XRD analysis. A field emission scanning electron microscope (FESEM) study performed with the material proved the improvement in coating efficiency with increase in the PVDF ratio. Coin cells of the type 2025 were made by using the synthesized material, and the electrochemical properties were studied. An electrode was prepared by using the developed Si-C material. Si-C|Li cells were made with this electrode. A charge|discharge test was performed for 20 cycles at 0.1C hour rate. Initial charge and discharge capacities of Si-C material derived from 20 wt% of PVDF was found to be 1,830 and 526 mAh|g, respectively. Initial charge/discharge characteristics of the electrode were analyzed. The level of reversible specific capacity was about 216 mAh/g at Si-C material derived from 20 wt% of PVDF, initial intercalation efficiency (IIE), intercalation efficiency at initial charge/discharge, was 68%. Surface irreversible specific capacity was 31 mAh/g, and average specific resistance was 2.6 ohm*g.

Key words: Lithium Battery, Anode, Silicon, Carbon

INTRODUCTION

Thanks to an enormous development in the field of information and technology, the need for a high performance lithium secondary battery has reached its peak. As a result of such a demand, much effort is being devoted to the development of high performance lithium ion secondary battery worldwide. The performance of the lithium battery can be improved by developing the major constituents of the battery, that is, the anode, cathode and the electrolyte [Berthier et al., 1983; Ratner and Shriver, 1988; Ballard et al., 1990; Jin et al., 2004; Poizot et al., 2000; Wang et al., 2002; Doh et al., 2000, 2002, 2004; Park et al., 2004; Choi et al., 2005; Kim et al., 2006]. One such attempt made was the development of a suitable anode material in place of graphite which has a theoretical specific capacity of 372 mAh/g and a density of 2.62 g/ml, respectively. In this regard, silicon-based anode materials are taken for investigation due to their very high theoretical specific capacity, which is in the range of 4,200 mAh/g. Electric potential of lithium intercalation is similar to that of graphite [Dimov et al., 2003] (Fig. 1). In spite of such an excellent feature, silicon-based anode materials undergo a rapid volume change and poor electrical conductivity (~10^{-4} S/cm) during the intercalation/deintercalation reaction with lithium ion [Beauliev et al., 2003].

In order to overcome such a problem with a silicon-based anode, carbon was coated on the surface of the material. This was achieved by heat treating the mixture of PVDF with the silicon powder in an inert atmosphere of argon. Since the carbon coated is in a spongy form with a fine carbon network, the structure caused efficient conduction process that led to the better performance of the battery. Type 2025, coin cells were prepared to examine electrochemical properties with XRD, FESEM, and so on. The measured properties were IIE (Initial Intercalation Efficiency) showing the lithium ion insertion behavior and IIC (Initial Intercalation Capacity), showing the irreversible reaction between the electrode and finally charge discharge were carried out using Gradual Increasing of State of Charge (GISOC) test method [Doh et al., 2001, 2003, 2004].

EXPERIMENTAL

Carbon-coated silicon powder was synthesized by mixing the silicon powder with PVDF-acetone mixture. Initially, PVDF was mixed with acetone and left for agitation for 30 minutes in a mixing unit. Then a fine powder of silicon with a particle size of 2-5 μm, (M/s. Atlantic Equipment Engineers) was mixed with the PVDF solution of acetone and allowed to be dried. Finally, the PVDF-silicon mixture was heat-treated at a temperature of 1,000 °C in an inert gas atmosphere of argon for two hours. The sample was taken out and ground to a finer particle size using the pestle and mortar.

1. Structural and Morphological Characterization

Phase characterization was done by powder X-Ray technique on a Philips 1830 X-Ray diffractometer using Ni filtered Cu Kα radiation (=1.5406) in the 2θ range of 10-120° at a scan rate of 0.04°/sec. Surface morphology of the particles was examined through FESEM images obtained from Hitachi, s-4800 Field Emission Scanning Electron Microscope (FESEM). The actual size of the particles was measured using Malvern easy particle size analyzer (Masterizer, 0.3 m to 300 m, Malvern, UK).

2. Electrochemical Characterization

Electrochemical properties were evaluated by fabricating 2025 type coin cells. The electrodes were made by dispersing 92 wt% of active material, 2 wt% of the conducting carbon and 6 wt% of PVDF

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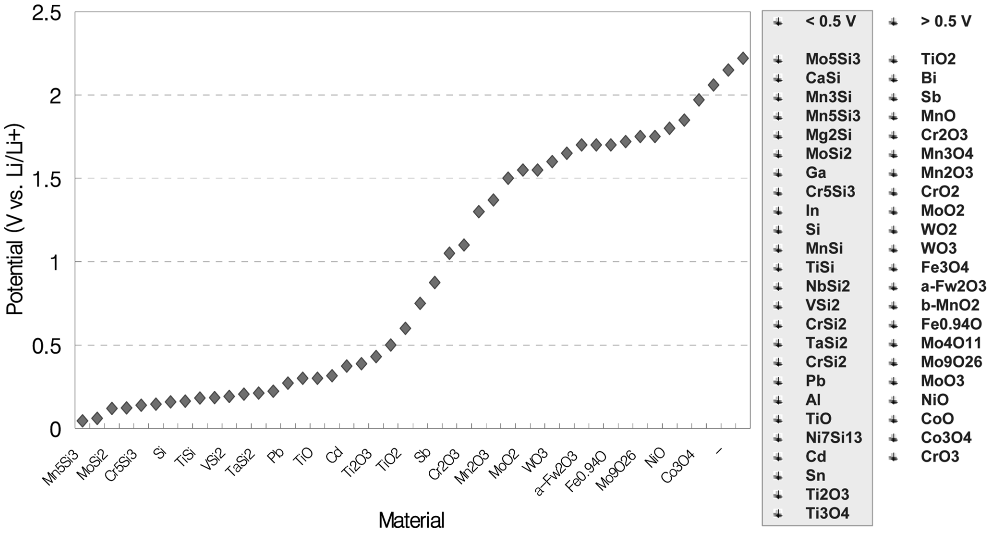


Fig. 1. Potential properties of various materials.

binder in N-methyl-2-pyrrolidone (NMP) solvent. The resulting slurries were spread on a copper foil, dried for 2 hours at 110 °C to remove NMP solvent. The coated slurries were pressed into sheets to 70% rate using a twin roll calender, and dried under vacuum at 60 °C for 24 hours. Coin cells were constructed with Li metal as the counter electrode and the coated electrode as the anode or working electrode. The electrolyte solution for the cell was 1.0 M $LiPF_6$ in EC/DMC/EMC/PC in the ratio of 4 : 3 : 3 : 1 vol% (Cheil Industries Ltd, South Korea). The constructed cells were aged for 24 hours at ambient temperature. Charge discharge performance was carried out at C/10 hour rate and in the voltage range of 0-3 V using Gradual Increasing of State of Charge (GISOC) test method [Kim et al., 2006; Dimov et al., 2003; Beauliev et al., 2003]. For the sake of comparison, a Si|Li cell was constructed by using the Si active material, in the same procedure mentioned above, and was subjected to cycle test using the same condition as mentioned above.

RESULT AND DISCUSSION

1. Structural Results-PXRD Studies

Fig. 2 (normal scale) and Fig. 3 (logarithmic scale) shows the XRD pattern of the carbon-coated silicon powder obtained by the heat treatment of the mixture of Si and PVDF at a temperature of 1,000 °C in an inert atmosphere of argon for 2 hours. One can easily identify the presence of a peak due to silicon from Fig. 2. However, there is no evidence of carbon or the co-existence of carbon in the XRD pattern, because of the poor crystalline nature of carbon. In Fig. 3, the same XRD pattern in logarithmic scale, the existence of carbon can be easily recognized at a 2θ value of 22°. Carbon with low crystallinity was found as a form of co-existence with silicon. Average layer spacing for d_{002} was calculated as around 4.037 Å using λ value of 1.54056 Å. The calculated degree of graphitization was found to be nearly amorphous [Kihoshita, 1988].

2. Particle Size Analyses

The average particle size distribution was directly proportional to the total amount of PVDF added, and Fig. 4. shows the trend. The average particle size increased with increase in PVDF. The particle size increased from 12 μm to 22 μm as the PVDF ratio increases from 95 : 5% ratio to 50 : 50 % ratio.

3. Morphological Results-FESEM

Fig. 5 shows the FESEM image of the carbon-coated silicon material in the increasing order of PVDF content. In the early stage of

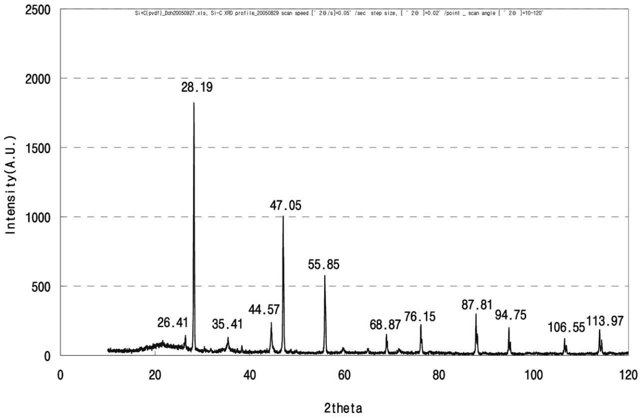


Fig. 2. XRD pattern exhibited by Si-C (normal intensity scale).

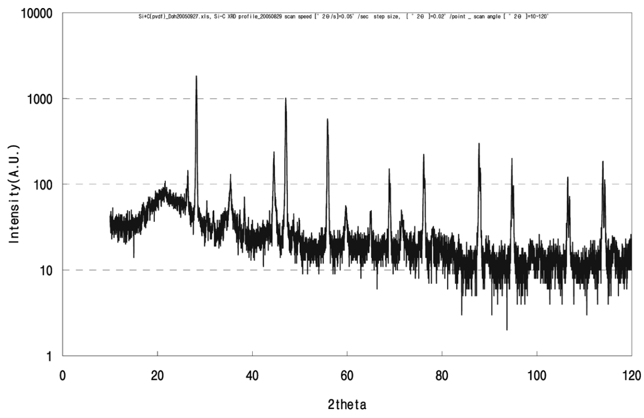
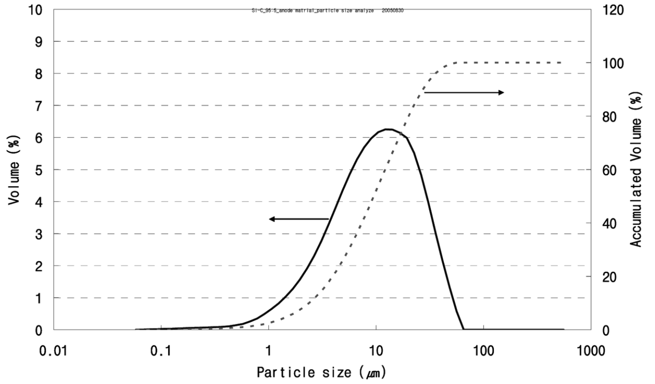
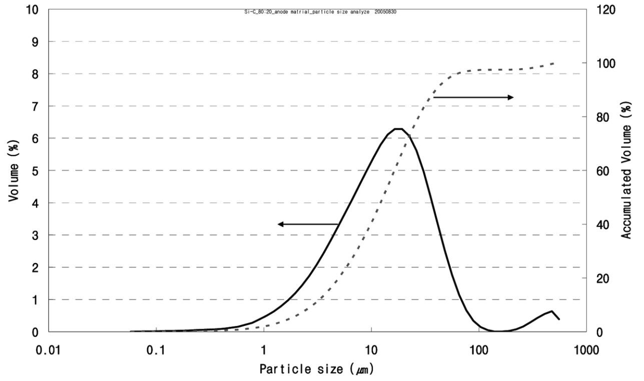


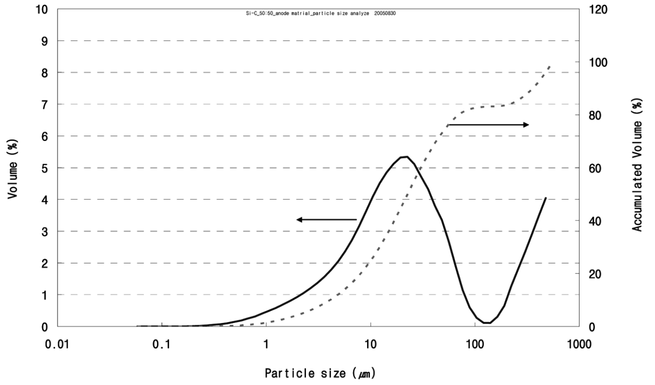
Fig. 3. XRD pattern exhibited by Si-C (log intensity scale).



(a) Si : PVDF = 95 : 5 wt.%



(b) Si : PVDF = 80 : 20 wt.%



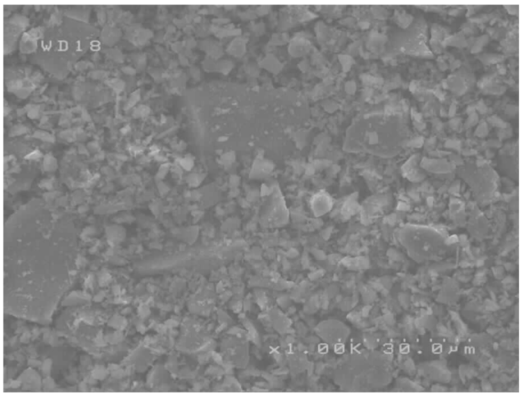
(c) Si : PVDF = 50 : 50 wt.%

Fig. 4. Particle size distribution of Si-C materials.

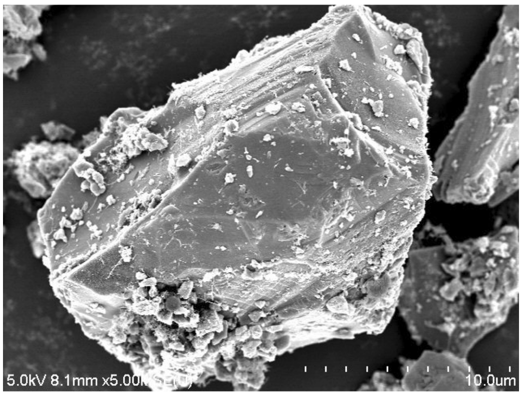
coating, the ratio of silicon and PVDF was equal to 95 : 5 wt%. The coating of carbon was poor at this stage on the surface of the silicon particle (Fig. 5b). There was a slight improvement with the coating when the PVDF content increased to 80 : 20 wt% ratio (Fig. 5c) and finally this was increased considerably and the carbon was found to enfold the silicon particle when the ratio of PVDF increased to 50 : 50 wt% ratio (Fig. 5d).

4. Electrochemical Characterization Results

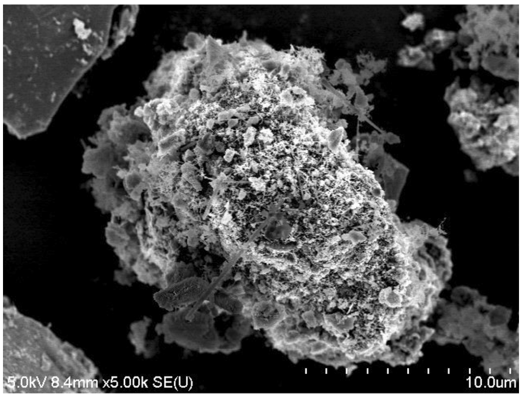
Electrochemical characterization was performed by constructing 2025 type coin cells, by using the coated electrode as the working electrode and the lithium metal as the counter electrode. The tests were carried out using cycle test and GISOC test by constant current method.



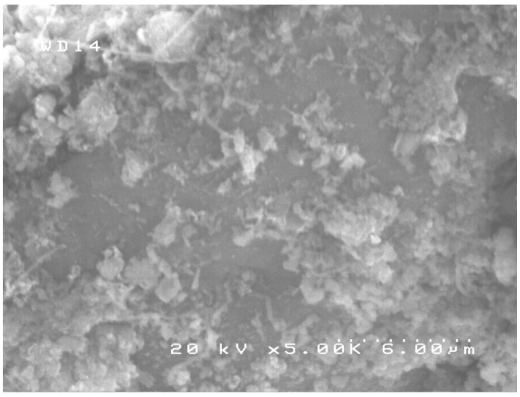
(a) x 1000 ; Si only



(b) x 5000 ; Si : PVDF = 95 : 5 wt.%

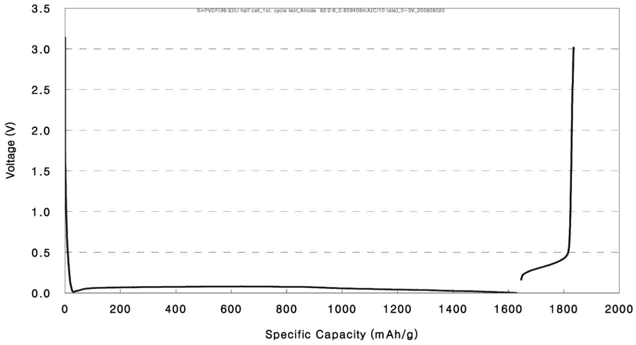


(c) x 5000 ; Si : PVDF = 80 : 20 wt.%

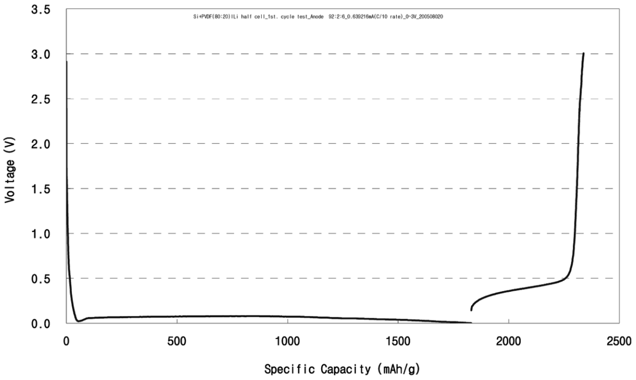


(d) x 5000 ; Si : PVDF = 50 : 50 wt.%

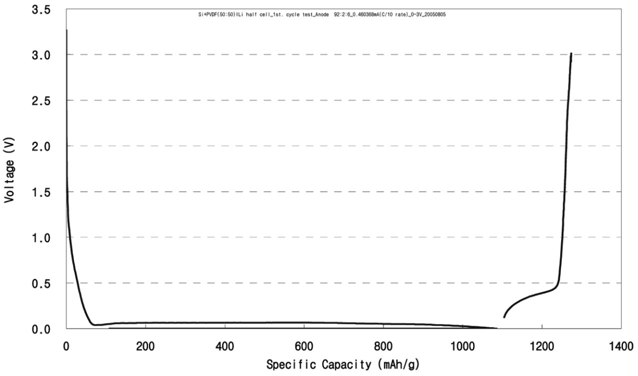
Fig. 5. FESEM images of Si-C materials.



(a) Si : PVDF = 95 : 5 wt.%

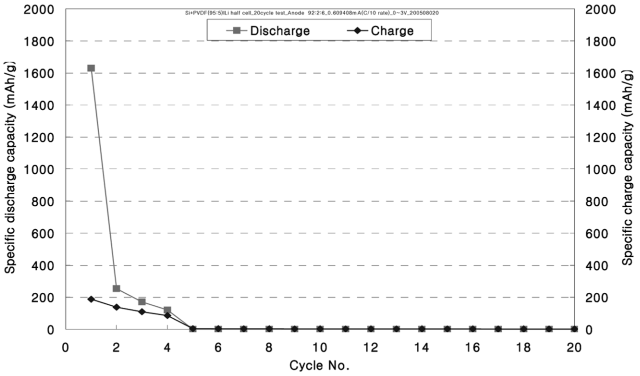


(b) Si : PVDF = 80 : 20 wt.%

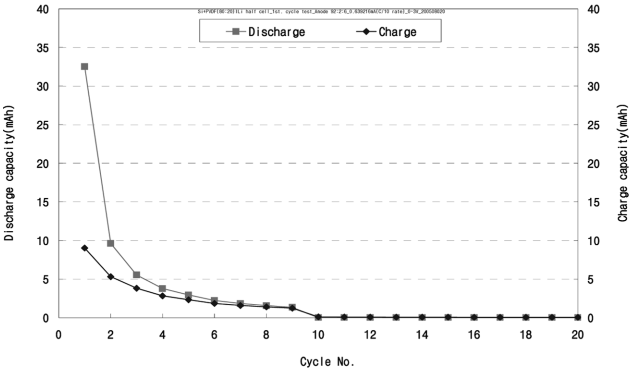


(c) Si : PVDF = 50 : 50 wt.%

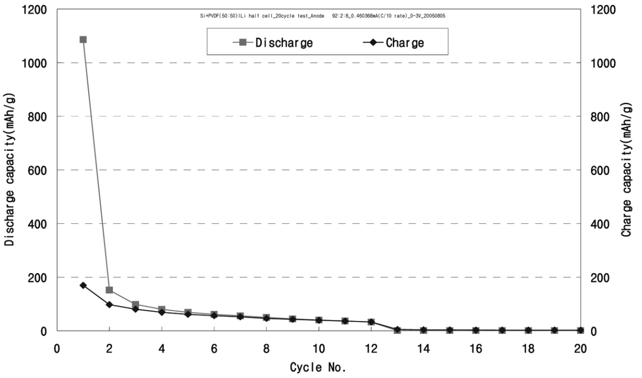
Fig. 6. The first charge-discharge behavior of Si-C|Li cells.



(a) Si : PVDF = 95 : 5 wt.%



(b) Si : PVDF = 80 : 20 wt.%

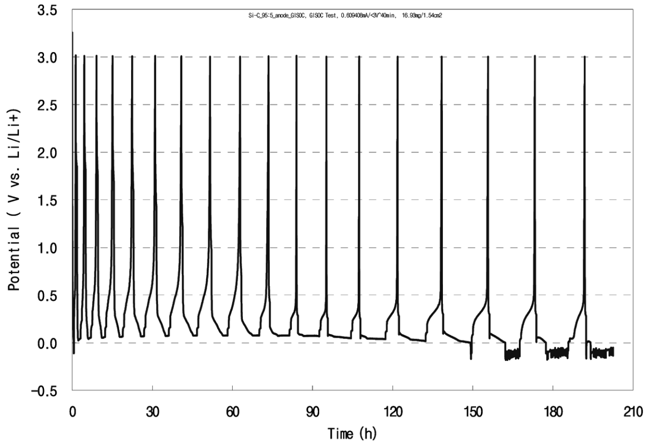


(c) Si : PVDF = 50 : 50 wt.%

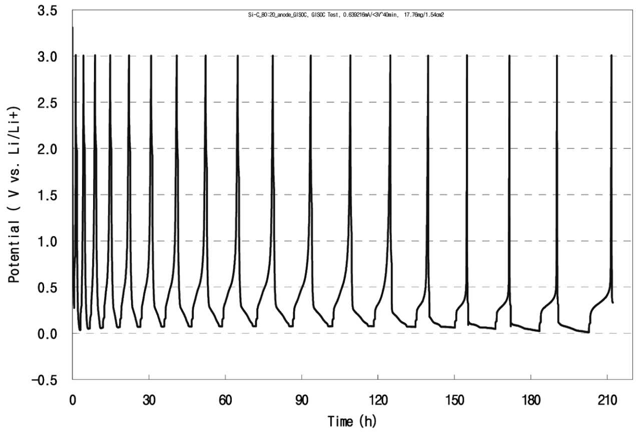
Fig. 7. Specific capacity and cycle behavior of Si-C|Li cells.

The constructed coin cells were subjected to the charge/discharge test for 20 cycles with C/10 hour rate and at a potential range of 0-3 V. The potential behavior of Si-C|Li cells were plotted as a function of specific capacity as shown in Fig. 6. The capacity was found to increase with increase in the ratio of PVDF. Initial specific charge capacity was 1,085-1,830 mAh/g and the discharge capacity was 188-526 mAh/g. The low capacity behavior of the material at the ratio of 50 : 50 wt% can be explained, such that capacity was by the coated carbon instead of silicon, since because the carbon particles fully wrap the silicon particle. So, a better performance can be produced by mixing the silicon and PVDF in the ratio of 20 : 80 wt%. Fig. 7 shows the cycle behavior of Si-C|Li coin cells in the increasing order of PVDF ratio. The cycling behavior was shown with increase in the PVDF content, i.e., with increase in the carbon coating of the material.

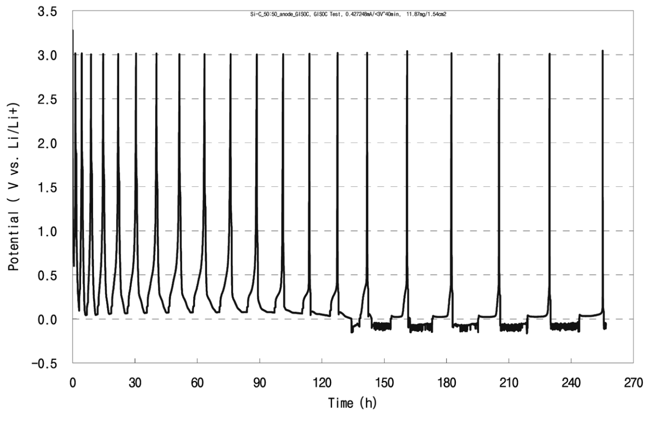
The initial charge discharge results with varying content of PVDF, obtained from the GISOC test are shown in the Figs. 8, 9 and 10. There was a reversible specific capacity of 130 mAh/g at 5 wt% of PVDF, 216 mAh/g at 20 wt% of PVDF and 168 mAh/g at 50 wt% of PVDF, respectively (Fig. 9). The IIE, the intercalation efficiency, was 65% at 5 wt% of PVDF, 68% at 20 wt% of PVDF and 58% at 50 wt% of PVDF for the range of reversible specific capacity. Surface irreversible specific capacities are 16, 31 and 17 mAh/g for the Si-C materials produced from PVDF content of 5, 20 and 50 wt%, respectively. Fig. 10 shows the specific resistance at the end of charge at each step obtained from GISOC test. The specific resistance was found to be larger at the initial charging stage and was reduced rapidly proceeding of lithium insertion. After that, it is converged. Average



(a) Si : PVDF = 95 : 5 wt.%



(b) Si : PVDF = 80 : 20 wt.%

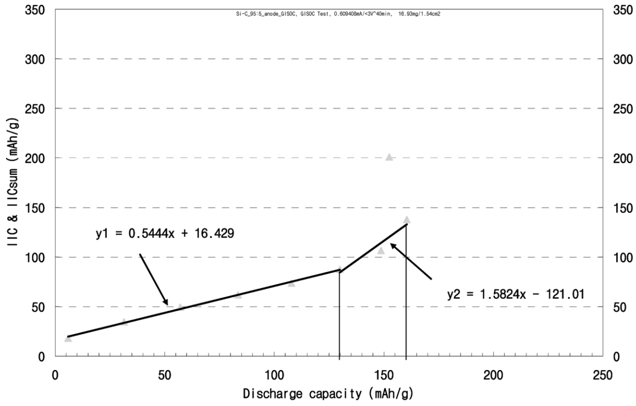


(c) Si : PVDF = 50 : 50 wt.%

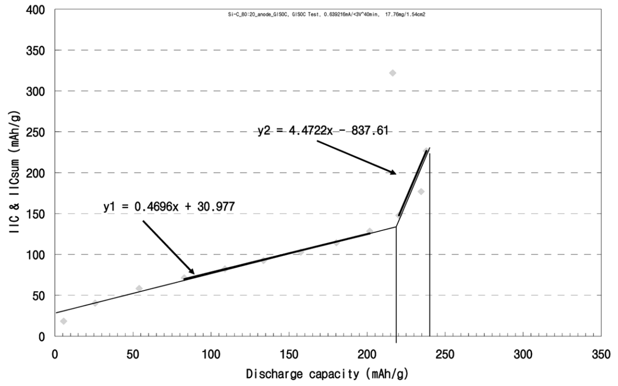
Fig. 8. Potential profiles of Si-C|Li cells by GISOC charge-discharge test.

specific resistances of Si-C|Li cells produced from PVDF content of 5, 20 and 50 wt% show 2.5, 2.6, and 2.4 ohm*g, respectively. GISOC characteristics are summarized on Table 1.

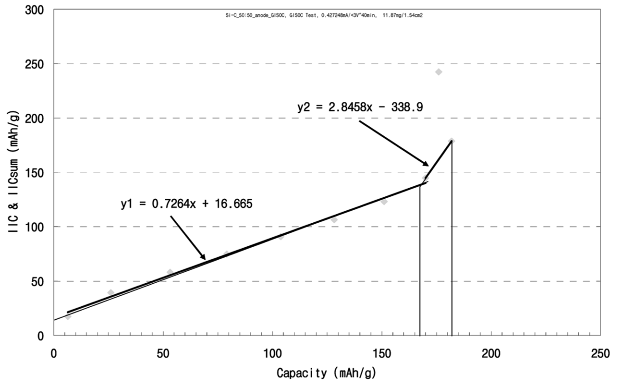
In order to compare the results obtained from the Si-C|Li cells, Si|Li using the silicon powder only was constructed in the same manner of Si-C|Li cells. The results obtained from these cells are presented in Fig. 11. When silicon active material is used alone, charge/discharge could not proceed well. In GISOC test, specific capacity range was about 49 mAh/g only and IIE was 28%. Surface irreversible specific capacity was 1.4 mAh/g. Average specific resistance was 3.0 ohm*g and it was larger than that of Si-C material. From this comparison, electrochemical properties of carbon coated silicon materials was found to be much improved than silicon materials itself.



(a) Si : PVDF = 95 : 5 wt.%



(b) Si : PVDF = 80 : 20 wt.%

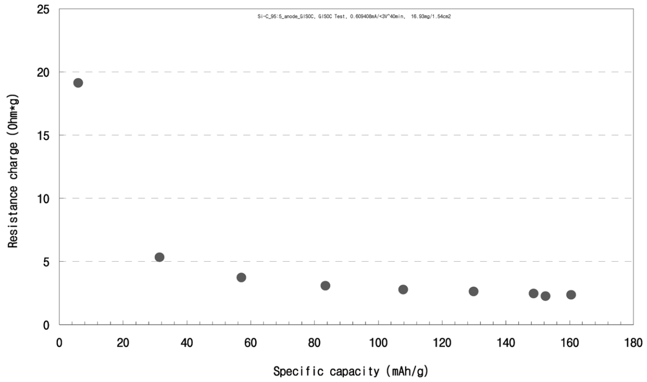


(c) Si : PVDF = 50 : 50 wt.%

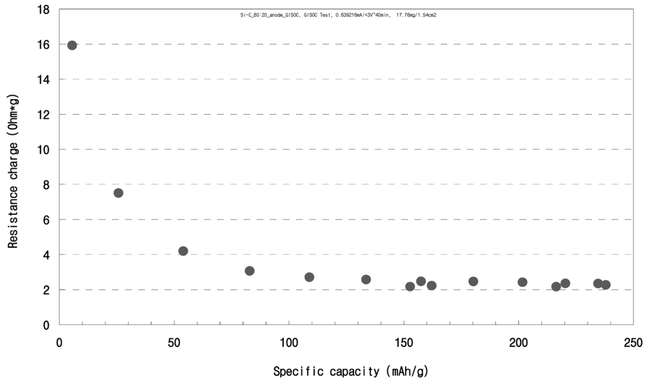
Fig. 9. The accumulated irreversible capacity of Si-C|Li cells against discharge capacity.

CONCLUSION

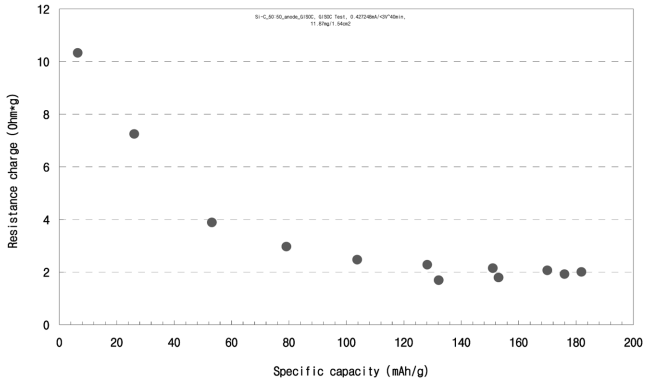
Si-C electrode active material is developed by using silicon and polyvinylidenefluoride (PVDF). Physical and electrochemical char-



(a) Si : PVDF = 95 : 5 wt.%



(b) Si : PVDF = 80 : 20 wt.%

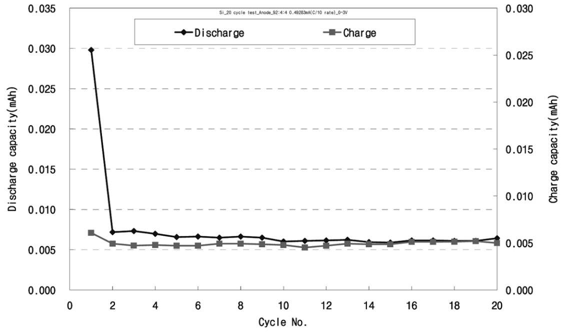


(c) Si : PVDF = 50 : 50 wt.%

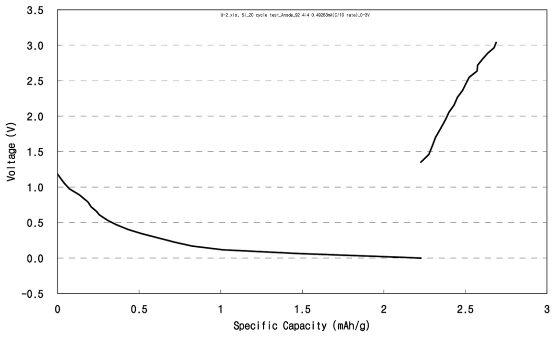
Fig. 10. Specific resistance of Si-C|Li cells against specific charge capacity.

acteristics were analyzed. Coexistence of silicon and carbon material can be confirmed through XRD diffraction analysis on carbonized Si-C generated after coating PVDF to silicon material. It can be observed through FESEM analysis that carbon material is coated on the surface of silicon well as the content of PVDF is increased. From electrochemical analysis by using cycle test and GISOC test, high capacity can be obtained at 20 wt% of PVDF. Average specific resistances obtained through GISOC test are similar over all PVDF content. Electrochemical property of developed Si-C material is much improved if it is compared with Si material case.

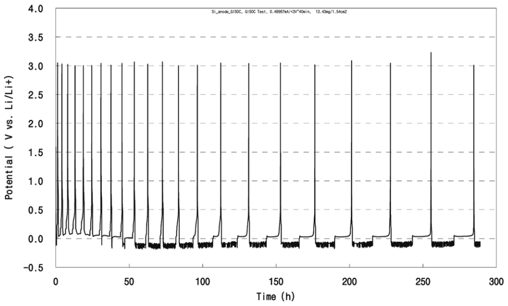
Carbon-coated silicon material was synthesized by mixing the silicon powder with PVDF. Physical and electrochemical character-



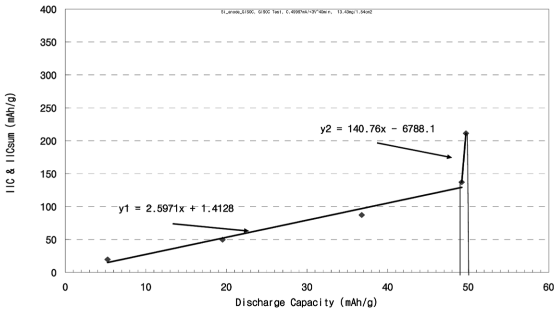
(a) Capacity plot against cycle number



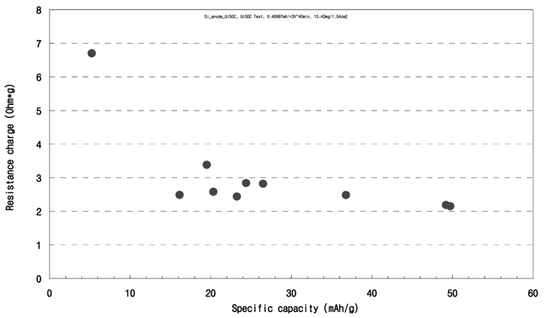
(b) Voltage plot against specific capacity



(c) Potential profile of GISOC test



(d) Accumulated irreversible capacity plot against discharge capacity



(e) Specific resistance plot

Fig. 11. Electrochemical properties of Si|Li cells.

Table 1. GISOC characteristics of Si-C|Li cell

PVDF content in Si-PVDF composite for Si-C wt%	Reversible specific capacity range mAh/g	Initial intercalation efficiency (IIE) %	Initial irreversible specific capacity (IICs) mAh/g	Specific resistance ohm*g
5	130	65	16	2.5
20	216	68	31	2.6
50	168	58	17	2.4

izations were performed. The XRD pattern of the material confirmed the coexistence of carbon and silicon. And surface morphology analysis performed by using the FESEM also confirmed the increase in the coating efficiency as the content of PVDF was increased. From the electrochemical analysis and the GISOC test, it was concluded that, the high capacity performance can be obtained from Si-C material synthesized using 20 wt% of PVDF. The specific resistance obtained through GISOC test was found similar for all the ratios of Si : PVDF. Finally, a comparison of the obtained results with the Si|Li cells also proved that the efficiency of the material was improved after carbon coating.

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