

Synthesis of Silicon-Carbon by Polyaniline Coating and Electrochemical Properties of the Si-C|Li Cell

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Si-C composites were prepared by the carbonization of polyaniline (PAn) coated on silicone powder. The physical and electrochemical properties of the Si-C composites were characterized by particle-size analysis, X-ray diffraction, scanning electron microscopy, and battery electrochemical tests. The average particle size of Si was increased by the coating of PAn but somewhat reduced by the carbonization to give silicone-carbon composites. The co-existence of crystalline silicone and amorphous-like carbon was confirmed by XRD analyses. SEM photos showed that the silicone particles were well covered with carbonaceous materials, depending on the PAn content. Si-C|Li cells were fabricated using the Si-C composites and tested using galvanostatic charge-discharge. Si-C|Li cells gave better electrochemical properties than Si|Li cells. Si-C|Li cells using Si-C from HCl-undoped precursor PAn showed better electrochemical properties than precursor PAn doped in HCl. The addition of an electrolyte containing 4-fluoroethylene carbonate (FEC) increased the initial discharge capacity. Also, another electrochemical test, the galvanostatic charge-discharge test with GISOC (gradual increasing of the state of charge) was carried out. Si-C(Si:PAn = 50:50 wt. ratio)|Li cell showed 414 mAh/g of reversible specific capacity, 75.7% of IIE (initial intercalation efficiency), 35.4 mAh/g of IICs (surface irreversible specific capacity).

Key Words : Lithium battery, Anode, Silicon, Carbon

Introduction

Recent technical advances in information electronic devices have made them more portable, compact and lightweight without surrendering performance and multimedia functionality. The power source of these portable devices requires a high-performance secondary battery. In the early 1990s, the Li secondary battery was adopted as a power source for many of these devices. As consumers demand ever higher standards of performance from their personal electronics products, researchers around the world are engaged in a massive effort to increase battery efficiency.¹⁻⁵ One focus of interest is anode materials based on silicone, which has the theoretical specific capacity of 4200 mAh/g with a density of 2.33 g/cm³. In comparison, graphite has a specific capacity of 372 mAh/g. The intercalation potential of silicone is similar to that of graphite. The major disadvantages of silicone, in this case, are low electronic conductivity at the semi-conductor level ($\sim 10^{-4}$ S/cm) and a volume expansion of 297% (Li₂₁Si₅) during Li alloying/dealloying to lead fast capacity fade.⁶⁻¹²

In the present study, carbon coated silicone (Si-C) was prepared by the carbonization of polyaniline (PAn) coated silicone. Carbon in the carbon-coated silicone encapsulates the silicone particles in the sponge-like foam. The carbon foam may mitigate the volume expansion of silicone particles during Li alloying/dealloying, provide an electronic conduction path, and provide an ion conduction path through

the void. The electrochemical properties of Si-C materials were analyzed by the galvanostatic charge-discharge test using a Si-C|Li coin cell with electrolytes, with/without fluoro ethylene carbonate (FEC) additive. Cut-off limits were controlled by the potential range and (GISOC).¹⁰⁻¹² Using GISOC results, we determined IIE (the initial intercalation efficiency) for lithium intercalation reversibility, IIC (the initial irreversible capacity by the surface) for the irreversibility between electrode-electrolyte, and the reversible intercalation range. All were evaluated as the typical electrode performance for the given electrode-electrolyte system.

Experimental Section

Preparation Si-C Composites. Si-C, the anode candidate material, was prepared from Si powder and polyaniline (PAn). Aniline (C₆H₇N), from Aldrich of the U.S.A, in HCl-H₂SO₄ aqueous solution containing 2-5 μ m Si powder (Atlantic Equipment Engineers, U.S.A) was oxidatively polymerized by the slow dropping of an oxidant solution of ammonium persulfate ((NH₄)₂S₂O₈) at a vessel temperature of -5~0 °C. Obtained solid material was washed with water and acetone, dried at 100 °C for 24 hours, and subjected to carbonization (1000 °C, 2 hrs, argon atmosphere) to give Si-C material. Two kinds of Si-C composite materials were prepared based on a 70 : 30 and 50 : 50 weight ratio for Si:PAn. HCl undoped Si-PAn material (70 : 30 weight ratio)

undoped by an ammonia solution (28% NH_4OH) was also carbonized by the identical method.

Structural and Morphological Characterization. Structural characterization was done by powder X-Ray technique on a Philips 1830 X-Ray diffractometer using Ni filtered Cu K radiation ($\lambda = 1.5406$) in the 2θ range of $5^\circ \sim 120^\circ$ at a scan rate of $0.04^\circ/\text{sec}$. The surface morphology of the particles was examined through FE-SEM images obtained with a Hitachi s-4800 Field Emission Scanning Electron Microscope (FE-SEM). The actual size of the particles was measured using a Malvern easy particle size analyzer (Masterizer, 0.3 μm to 300 μm , Malvern of the UK). The thermal characteristics of the polyaniline were analyzed using a DSC-TGA (SDT Q600 thermal analyzer from TA Instruments of the U.S.A.).

Electrochemical Characterization. Electrochemical properties were evaluated by fabricating 2032-type coin cells. The electrode slurries were made by dispersing 92 wt.% of active material, 4 wt.% of CMC (carboxymethyl cellulose 1.2 wt.% solution in water) binder, and 4 wt.% of SBR (styrene butadiene rubber 40 wt.% solution in water). The resulting slurries were coated on copper foil and dried for 30 minutes at 110°C to remove solvent. (The coated slurries were pressed into a sheets to 70% rate: Editor's note: The preceding is rewritten as follows:) The slurry-coated foil was pressed with a twin roll calender, resulting in sheets that were 70% of their original thickness. The foil was then dried under vacuum at 60°C for 24 hours to give the apparent density of $1.501.6 \text{ g/cm}^3$.

Coin cells were constructed with Li metal as the counter electrode and the coated electrode as the anode (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, Korea) with/without 4-fluoroethylene carbonate (FEC, 5 wt.%; Ulsan Chemical Co., Ltd., Korea). The constructed cells were aged for 24 hours at ambient temperature. The galvanostatic charge-discharge test was carried out at C/10 hour rate. Discharge limits were controlled by the potential of 0 V and by the specific capacity, adopting the gradual increasing of state of charge (GISOC) test method.¹⁰⁻¹² Charge potential limits were 3 V. For comparison, a Si|Li cell was constructed using the Si active material, as in the identical procedure mentioned above, and the cell was subjected to cycle test, using the identical condition as mentioned above.

Results and Discussion

Particle Size Analyses. The average particle size distribution of Si-C material was about 10 μm , an increase from 1.2 μm , the average value of the starting Si powder. HCl undoped and doped Si-PAn material as a precursor of Si-C had an average particle size of 10 μm and 10 μm , respectively.

Figure 1 shows the change in the average particle size during the preparation of Si-C material through the Si:Pan (70 : 30 wt. ratio) precursor. Average particle size was increased by the coating of polyaniline and decreased by the shrinkage during the carbonization.

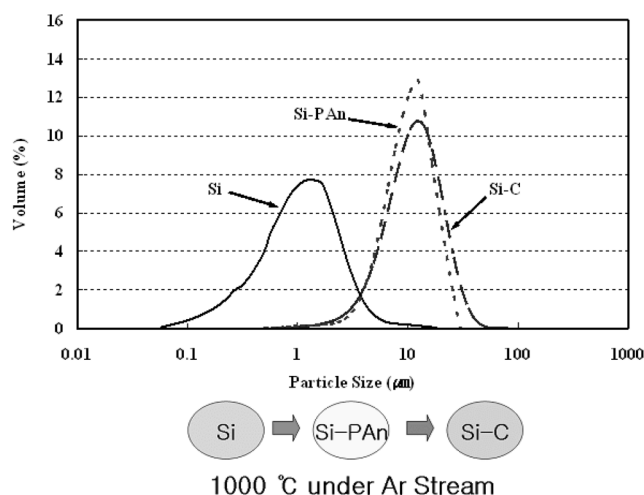


Figure 1. Change of particle size distribution during carbon coating to silicone powder.

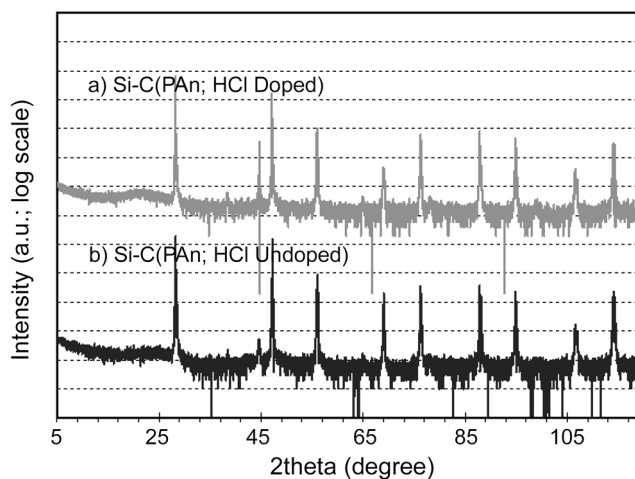


Figure 2. XRD patterns exhibited by Si-C materials from the precursor of Si:Pan (70:30 wt. ratio).

Structural Results-PXRD Studies. Figure 2 shows the XRD patterns of the carbon coated silicon powder in logarithmic scale. The presence of a peak is easily identified due to silicon. The existence of amorphous carbon is recognized at a 2θ value of 23° . Carbon with low crystallinity was found in the form of co-existence with silicon. The average layer spacing for d_{002} was calculated as approximately 3.864 Å. The calculated degree of graphitization was found to be nearly amorphous.¹³ Si-C from HCl doped and undoped PAN precursor showed similar amorphous structure but slightly different distribution of d_{002} bands.

Morphological Results-SEM. Figure 3 shows the SEM image of the carbon-coated silicon material in the increasing order of PAN content. HCl doped and undoped Si-PAn gave similar Si-C materials, as shown in Figure 3b and Figure 3c. The carbon content increased proportional to the total amount of PAN polymerized by comparison in Figure 3.

Electrochemical Characterization Results. Electrochemical characterization of 2032 type coin cells, using the

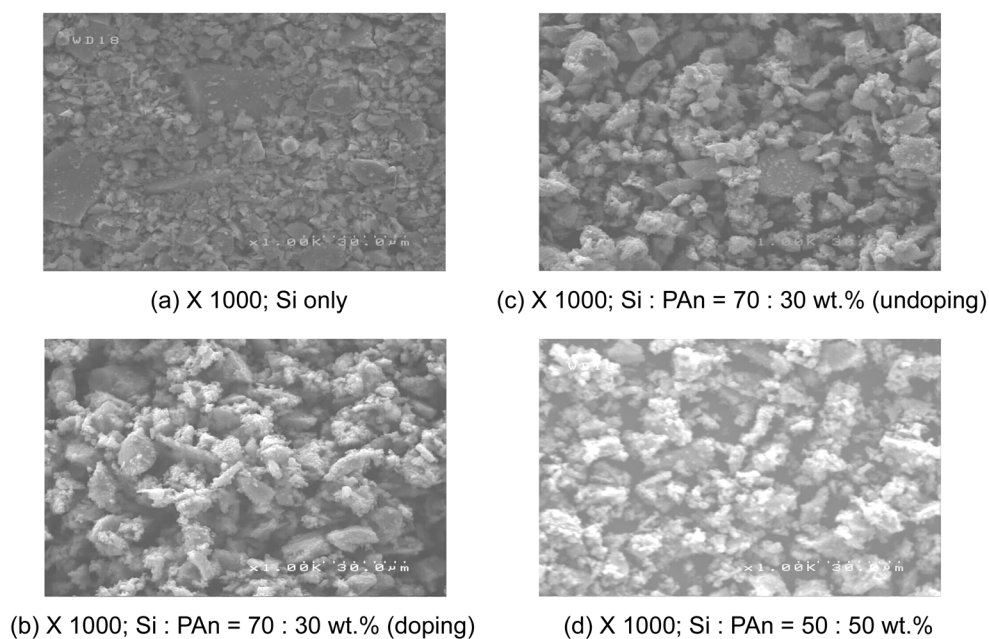


Figure 3. SEM images of Si and Si-C materials.

coated electrode as the working electrode and the lithium metal as the counter electrode, was carried out by the galvanostatic method using a cycle test and GISOC test.

The constructed coin cells were subjected to the charge/discharge test for 20 cycles with a current of $C/10$ hour rate and at a potential range of 0-3 V. The specific capacity and the potential behavior of Si-C|Li cells were plotted as the function of cycle number and specific capacity, as shown in Figure 4.

A Si|Li cell in Fig. 4a showed only 0.5 mAh/g for the first specific charge capacity. Si-C(Si: PAN = 70:30 wt.%)|Li cells showed 1410 mAh/g for the first discharge capacity and 124 mAh/g for the first charge capacity for HCl-doped PAN precursor, as seen in Figure 4b, and 1337 mAh/g for the first discharge capacity and 371 mAh/g for the first charge capacity for HCl undoped PAN precursor as seen in Figure 4c. Different electrochemical characteristics were found in two Si-C(Si: PAN = 70:30 wt.%)|Li cells, varying from the HCl-doped and undoped PAN precursors. The difference might have originated with the formation of carbon material between the amine type and ammonium-salt type precursors of polyaniline. DSC-TGA analyses of HCl-doped and undoped PAN were performed, as shown in Figure 5, and compared. The endothermic DSC peaks of HCl-doped PAN appear at 98 °C and 246 °C, with the full width of half maximum (FWHM) at 64 °C and 70 °C, respectively. The endothermic heat values were 569 J/g and 50 J/g for the peaks of 98 °C and 246 °C, respectively. The weight was based on the loaded polyaniline. Another endothermic peak appeared at 958 °C with a FWHM of 176 °C and an endothermic heat value of 1039 J/g. Total endothermic heat in the range of 25-1200 °C was 1089 J/g. TGA analysis showed a weight loss of 49% through 200 °C, corresponding to the first endothermic route, followed by an additional 11% loss

from 200 °C to 400 °C. Further weight loss of 16% was observed at 700 °C without endothermic peaks. Total weight loss was 81% through 1200 °C. The endothermic DSC peaks of HCl-undoped PAN appeared at 63 °C, with an endothermic heat of 52 J/g, which was smaller than that of HCl-doped PAN. These DSC-TGA results show that the first endothermic peak of HCl-doped PAN resulted from the desorption of HCl. Another endothermic peak appeared at 1031 °C with a FWHM of 64 °C and an endothermic heat value of 113 J/g. Total endothermic heat in the range of 25-1200 °C was found to be 472 J/g. TGA analysis showed a small weight loss of 2.5% through 400 °C. Additional weight loss of 35.5% was observed through 700 °C without endothermic peaks. Total weight loss was 53% through 1200 °C. The formula weight of PAN·HCl and PAN are 127.5 g and 91 g/formula, respectively. In case of PAN·HCl, the initial weight loss of 49% seems due to the desorption of HCl and H₂O. The water content of PAN·HCl was calculated as three molecules per PAN unit from the weight loss value.

The charge-discharge characteristics of Si-C|Li cell, Si-C material from the HCl doped PAN precursor and Si powder (50 : 50 weight ratio), as shown in Figure 4d showed high capacity compared with that of Si-C material from PAN and Si (30 : 70 weight ratio). The first discharge and charge capacities were 1950 mAh/g and 205 mAh/g, respectively.

Using the electrolyte containing FEC additives, charge-discharge characteristics are presented in Figure 6. Si-C(Si: PAN = 70:30 wt.%)|Li cells showed 1759 mAh/g of the first discharge capacity and 127 mAh/g of the first charge capacity for HCl-doped PAN precursor, as shown Figure 6a, and 2057 mAh/g of the first discharge capacity and 224 mAh/g of the first charge capacity for HCl-undoped PAN precursor, as shown Figure 6b. The adoption of FEC to electrolyte increased the initial discharge capacity, compared

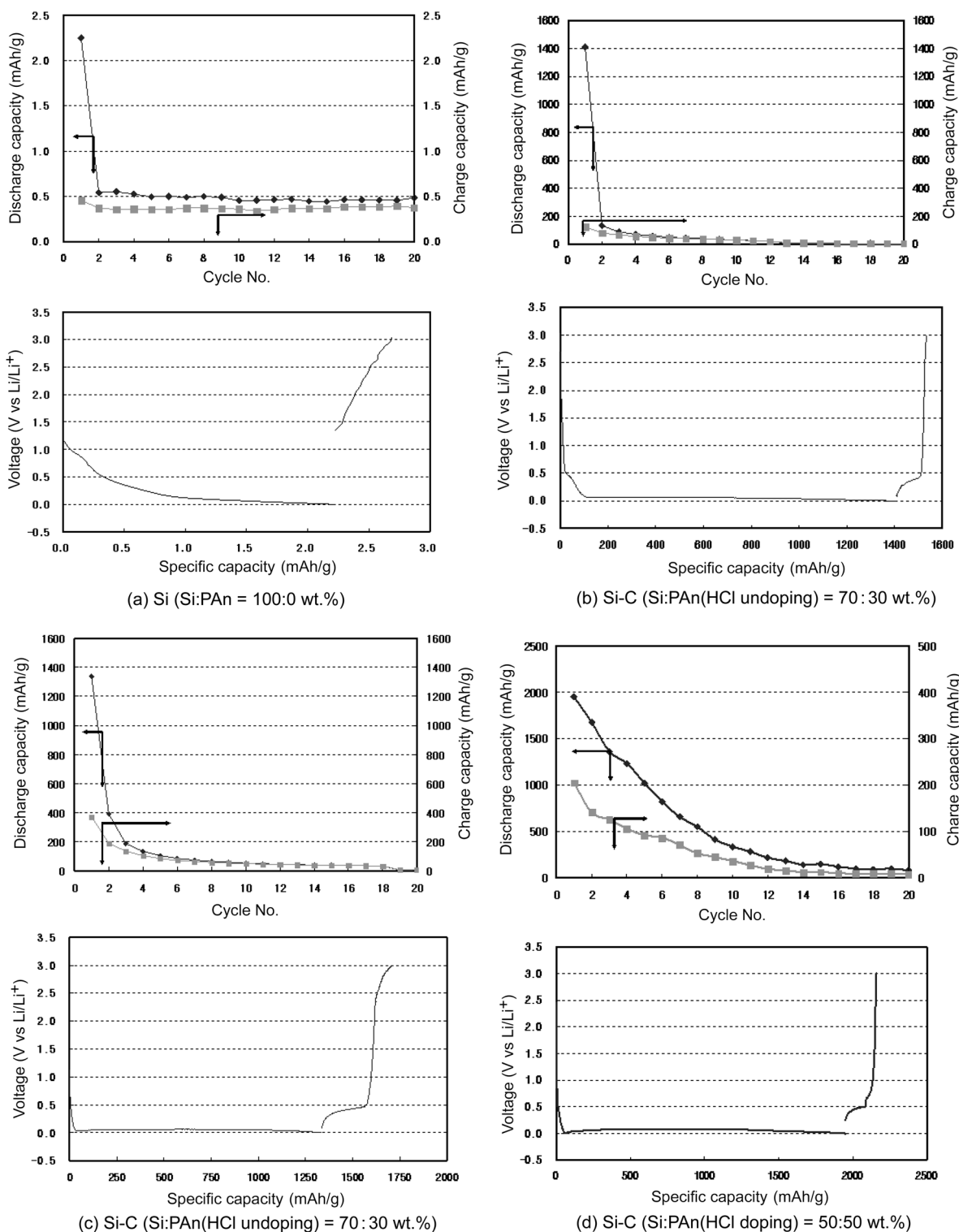


Figure 4. Specific capacity and cycleability behavior of Si|Li and Si-C|1M LiPF₆/EC+EMC+DMC+PC=4:3:3:1|Li cells.

with the case of electrolyte without FEC, as shown Figure 4b and Figure 4c.

The irreversible capacity of Si-C(Si:PAAn = 50:50 wt. ratio)|Li cell has been plotted against the specific discharge capacity as the results of the GISOC test in Figure 7. Analytical results of the GISOC test for various cells are summarized in Table 1. The reversible range of the specific

capacity of Si|Li, Si-C(Si:PAAn = 70:30 wt. ratio)|Li, and Si-C(Si:PAAn = 50:50 wt. ratio)|Li cells with the electrolyte without FEC additive were *ca.* 49, *ca.* 150, and *ca.* 414 mAh/g, respectively. For these reversible ranges, the initial intercalation efficiencies, IIE, were 27.8, 55.1 and 75.7%, and the surface irreversible capacities were 49.3, 46.6 and 35.4 mAh/g, respectively.

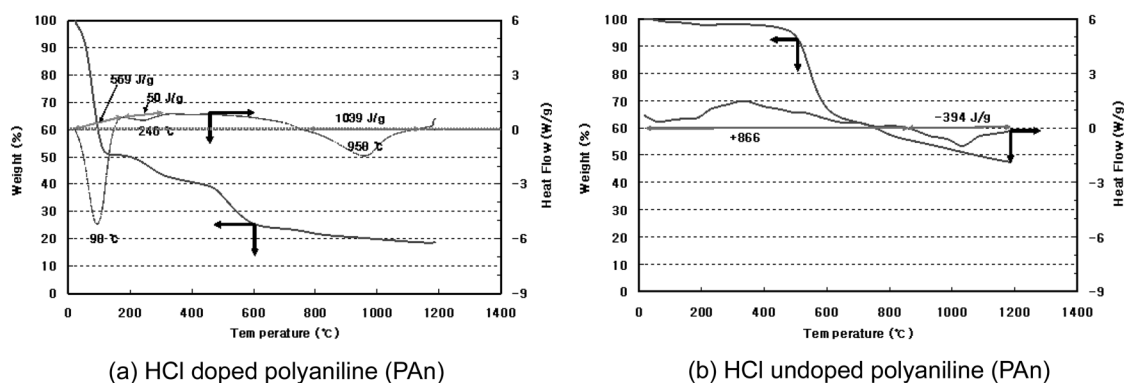


Figure 5. TGA-DSC analyses of HCl doped/undoped polyaniline (PAN).

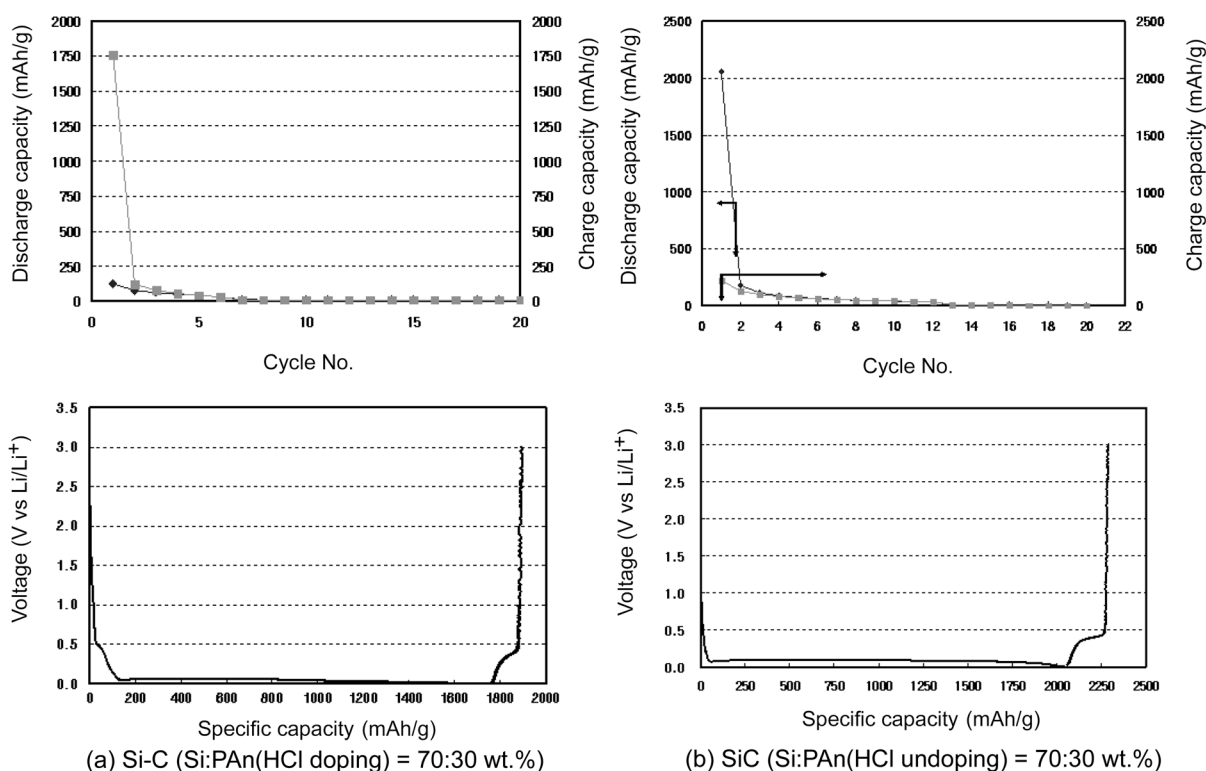


Figure 6. Specific capacity and cycleability of Si-C|1M LiPF₆/EC+EMC+DMC+PC=4:3:3:1 with FEC|Li cell.

Si-C materials from Si:Pan (70:30 w/w) had low carbon content compared with that of Si:Pan (50:50 w/w). The degradation of the electronic conduction pathway of Si-C electrode with low carbon content might be easier than the case with high carbon content. The electronic conduction pathway of Si-C electrode will be degraded, caused by the volume expansion of silicon during the long lasting charge-discharge. An increase of the IIE value with an increase of PAN precursor contents in Si-C materials was achieved by an improvement of the electronic conduction pathway. Si-C(Si:Pan = 70:30 wt. ratio)|Li cells with PAN precursor, excluding HCl dopant and the electrolyte without FEC additive, showed the range of reversible capacity of 169 mAh/g, the IIE of 70.9%, and IICs of 11.3 mAh/g. And the cell with FEC additive showed the range of reversible

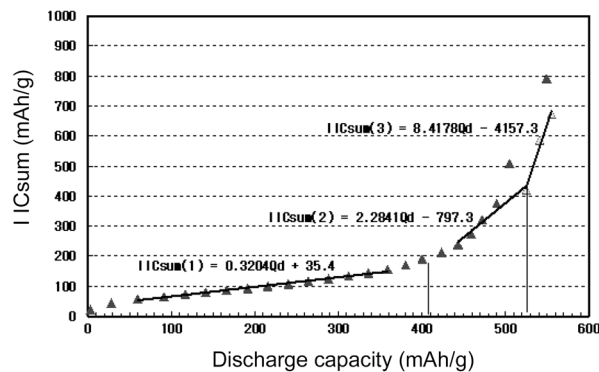


Figure 7. The accumulated irreversible capacity of Si-C(Si:Pan (50:50 wt.ratio))Li cell against discharge capacity.

Table 1. GISOC Characteristics of Si-C|Li Cells

PAn content in Si-PAn composite for Si-C (wt.%)	Electrolyte	HCl Doped & Undoped	The 1st reversible specific capacity range (mAh/g)	The 1st initial intercalation efficiency (IIE, %)	The 1st initial irreversible specific capacity (IICs, mAh/g)	The 2nd reversible specific capacity range (mAh/g)	The 2nd initial intercalation efficiency (IIE, %)
0	[E]	–	49	27.8	49.3	50	0.71
30	[E]	Doped	150	55.1	46.6	160	–
30	[E]	Undoped	168	70.9	11.3	189	4.58
50	[E]	Doped	414	75.7	35.4	527	30.4
0	[E] with FEC	–	50	25.5	276.2	–	–
30	[E] with FEC	Doped	194	71.4	30.2	200	–
30	[E] with FEC	Undoped	187	66.7	3.8	–	–
50	[E] with FEC	Doped	330	73.8	38.2	394	9.8

[E]: 1 M LiPF₆/EC:EMC:DMC:PC (4:3:3:1)

capacity of 195 mAh/g and the IIE of 71.4%, and IICs of 30.2 mAh/g.

Conclusion

Modified Si-C materials were prepared by Si powder and polyaniline (PAn), and their physical and electrochemical properties were characterized. Si-C materials from the carbonization of Si-PAn, which was obtained by the oxidative polymerization of aniline to coat Si particles, showed the co-existence of low crystalline carbon. Carbon covering of Si particle was efficient for high PAn content. The better electrochemical performances were confirmed for Si-C materials compared with that of Si materials by cycling and GISOC tests.

Some differences in electrochemical performance was observed between doped and undoped PAn. PAn precursors not doped with HCl showed better results than HCl-doped PAn precursors. TGA-DSC analyses showed the initial evaporation of one HCl and three H₂O per PAn unit formula. The cell with the electrolyte-including FEC additive showed a high initial discharge capacity compared with that without the FEC additive. The Si-C(Si:PAn = 50:50 wt. ratio)|Li cell showed a range of reversible capacity of ca. 414 mAh/g, the IIE of 75.7% and the IICs of 35 mAh/g.

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