

# PREPARATION AND CHARACTERIZATION OF Si/CARBON COMPLEX AS ANODE MATERIALS FOR LITHIUM HYBRID BATTERY

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## Introduction

Recently, a high-powered electric energy storage device requires high energy density, high charging rate, and long life. Rechargeable batteries, such as lithium ion (LIB) and nickel hydride batteries (NHB) have problems with the power density, charging rate, life, and costs [1]. It is well known that electric double layer capacitors (EDLC) have the advantages of high charging rates and good durability. These advantages of EDLC are superior to those of any other rechargeable batteries presently available, but EDLC has drawbacks in energy density and costs. In particular, activated carbon for EDLC are reaching their limits in improvements in volumetric energy density even with its high specific surface areas [2]. Therefore, a new concept of electric energy storage device is needed.

The lithium hybrid battery (LHB) is a hybrid device of a carbon negative electrode and an activated carbon positive electrode, making it a device which is half LIB and half EDLC. With LHB, it would be possible to aim at much larger energy densities than that of EDLC without diminishing the advantages of capacitors over batteries.

Silicon (Si) has been considered as ideal anode material for high capacity of LIB, because it has the highest known theoretical capacity of about 4200 mAh/g [3]. However, Si has not been commercially applied yet due to its low cycle-ability in the charge/discharge processes. For broad application of lithium hybrid battery, the improvement of cycle-ability should be necessary. Therefore, Si/carbon complex is expected to be used as an anode material of Lithium hybrid battery. Si/carbon complex can improve mechanical stability and electronic conductivity of Si. It is also helpful to conserve stable capacity and cycle-ability.

In this study, Si/carbon complexes were prepared by electrospinning for anode materials of lithium hybrid battery.

## Experimental

Polyacrylonitrile (PAN, Aldrich) was dissolved in *N,N*-Dimethylformamide (DMF, Acros) to make 10 wt% solution at 80 °C. 1.46 g of silicon dioxide (SiO<sub>2</sub>, Degussa, Germany) was mixed with 30 g of PAN solution as silicon source. The prepared solution was spun out of fibers by electrospinning.

16 kV was applied for electrospinning at room temperature and in air. The feed rate of the solution was kept at 1 mL/h. Then, electrospun PAN/SiO<sub>2</sub> fibers were stabilized at a temperature of 260 °C for 5 h in air. After Stabilization, heat-treatment of electrospun PAN/SiO<sub>2</sub> fibers was carried out at 1300, 1400, 1500, and 1600 °C for 1 h in argon atmosphere with heating rate of 3 °C/min. The prepared samples were named as follows; SC13, SC14, SC15 and SC16, respectively. In order to study the surface morphology of the prepared samples, specimens for microscopic analysis were sputter coated with platinum-palladium and analyzed using scanning electron microscope (SEM, JEOL, JSM-7000F, Japan). The samples were examined by X-ray diffraction (XRD, Rigaku International Corporation, D/MAX-2200 Ultima/PC, Japan) and X-ray photoelectron spectroscopy (XPS, XPS, MultiLab 2000, Thermo) to investigate crystalline and surface chemical structures.

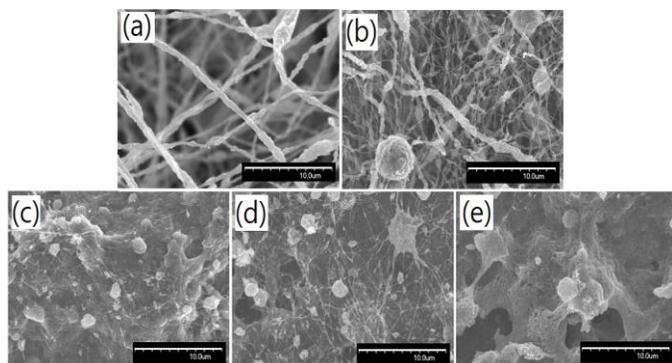
## Results and Discussion

Fig. 1 showed the morphologies of as-spun SiO<sub>2</sub>/PAN complex fiber and Si/carbon complexes prepared different carbothermal temperature. As-spun SiO<sub>2</sub>/PAN complex was produced as ununiform fibers, due to decrease of spinnability by the addition of SiO<sub>2</sub> powder to PAN solution. At Fig. 1 (b), morphology of SC13 was maintained fibril structure after heat-treatment like as-spun SiO<sub>2</sub>/PAN complex fiber. And the fiber diameter was reduced due to the heat-treatment. However, at Fig. 1 (c-e), Si/carbon complexes were not observed as fibril structure. This result might be caused that electrospun fibers were fused during heat-treatment above 1400 °C.

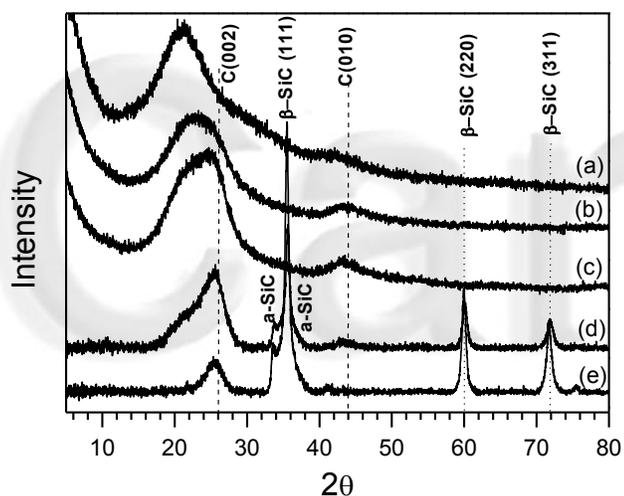
Fig. 2 showed the XRD patterns of SiO<sub>2</sub> and Si/carbon complexes prepared at different carbothermal temperature. In Fig. 2, it was shown that SC13 and SC14 were mixtures of SiO<sub>2</sub> and PAN-based carbon without reaction between carbon and SiO<sub>2</sub>. And it was also observed that SiC was formed from SiO<sub>2</sub>/PAN complex during heat-treatment above 1500 °C (SC15 and SC16). The peaks at 35.6, 59.9 of 2θ corresponded to (111) and (220) peaks of β-SiC, respectively [4]. In case of SC15, it was observed as a mixture of SiO<sub>2</sub>, PAN-based carbon and SiC. The SiO<sub>2</sub> was not completely separated as Si and O<sub>2</sub> in SiO<sub>2</sub>/PAN complex. The heat-treatment at 1500 °C was low temperature for complete separation of Si and O<sub>2</sub> from SiO<sub>2</sub>, because the Si was attributed to the decomposition of SiO<sub>2</sub> at about 1550 °C [4]. However, XRD pattern of SC16 did not have SiO<sub>2</sub> peak at 21.1 of 2θ. The SC16 was expected to be a mixture of SiC and carbon.

The broad scan XPS spectra of SC14, SC15, and SC16 and their analytical results were shown in Table 1 and Fig. 3, respectively. The survey spectra in the 0-1300 eV of binding energy range were investigated to identify the elements on the surface of the prepared samples and perform a quantitative analysis. All of the survey spectra show distinct C1s, O1s and Si2p peaks at around 284.1, 532.4 and 101.2 eV, respectively. The rate of elemental Si on the surface of Si/carbon composites increased with increased heat-treatment

temperature. Especially, the surface Si content of SC16 was the most of all the samples prepared in this study. This result might be caused by SiC formation and surface pyrolysis of SiO<sub>2</sub>/PAN complex during higher temperatures treatment.



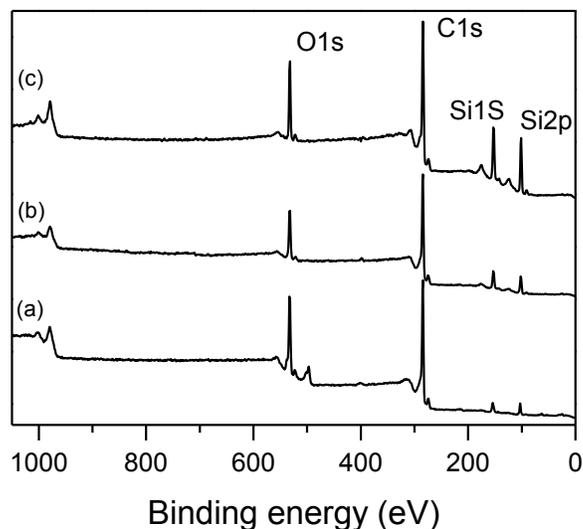
**Fig. 1** SEM images of (a) as-spun SiO<sub>2</sub>/PAN complex fiber, (b) SC13, (c) SC14, (d) SC15 and (e) SC16.



**Fig. 2** XRD patterns of (a) SiO<sub>2</sub>, (b) SC13, (c) SC14, (d) SC15 and (e) SC16.

**Table 1.** XPS surface element analysis parameters.

	Elemental content (at %)		
	C	O	Si
SC14	70.90	21.13	7.97
SC15	72.15	13.32	14.53
SC16	62.16	10.76	27.08



**Fig. 3** XPS survey peaks of (a) SC14, (b) SC15 and (c) SC16.

### Conclusions

In this study, Si/Carbon complexes were prepared by electrospinning for anode materials of lithium hybrid battery. After heat-treatment above 1400 °C, morphology of Si/carbon complexes was not observed as fibril structure. It could be explained that electrospun fibers were fused, due to high temperature. The SC13 and SC14 were mixtures of SiO<sub>2</sub> and PAN-based carbon. The SC15 was mixture of SiO<sub>2</sub>, PAN-based carbon, and SiC. And the SC16 was expected to consist of SiC and carbon mixture. SiC was formed from SiO<sub>2</sub>/PAN complex during heat-treatment above 1500 °C, because the Si was attributed to the decomposition of SiO<sub>2</sub> at about 1550 °C. From the XPS results, the rate of elemental Si on the surface of Si/carbon composites was increased with increased heat-treatment temperature. This result might be due to SiC formation and surface pyrolysis reaction in SiO<sub>2</sub>/PAN complex during higher temperatures treatment. Therefore, Si/carbon complexes were expected to exhibit different electrochemical properties with crystal structure and chemical bond state of Si and carbon.

### References

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