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# Yolk-shell structured silicon/carbonized polyacrylonitrile composites as anode materials for lithium-ion batteries

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Silicon is a potential anode material for high-energy lithium-ion batteries because of its extremely high theoretical capacity. The most critical issue for the application of silicon anodes is the fast capacity fade caused by the large volume variation of silicon during lithiation and delithiation processes. In this study, silicon/carbon composites agglomerated from yolk-shell silicon@void@pyrolysis carbon particles were prepared by coating aluminum-silicon alloy particles with polyacrylonitrile and subsequently dissolving the aluminum from the carbonized composites in a ferric chloride etchant. The use of a proper amount of the hydrolyzed polyacrylonitrile as a binder in the coating process is beneficial to reduce the structural defects of the composites. The void space between the carbon shell and silicon core formed by removing the aluminum can accommodate the expanded silicon and thus stabilize the composite structures. As a result, the silicon/carbon composites exhibit considerably better cell performances, especially charge-discharge cycling stabilities, than the powder mixture of silicon and pyrolytic carbon. The composite with few structural defects maintained a reversible capacity of more than 500 mAh g<sup>-1</sup> after 50 cycles at a current density of 0.1 C, while the silicon component in the powder mixture lost almost all of its capacity after only a few cycles.

Keywords: lithium-ion batteries; silicon/carbon composite; polyacrylonitrile; yolk-shell

# **1. INTRODUCTION**

Lithium-ion batteries (LIBs) have become an indispensable power source for many emerging applications, such as electric vehicles, portable electronic products, and large-scale energy storage systems, because of their high energy density, good rate capability, and long cycle life [1-3]. However, present LIB technology is reaching its theoretical limit in energy density, and thus is not suitable to meet the rapid growth of energy demand for high performance electronic devices. As one of the most important indicators of battery performance, energy density is mainly determined by the specific

capacities and working potentials of electrode materials [4, 5]. In the case of anode materials for LIBs, silicon has a much larger capacity than traditional graphite anodes, and its potential is only slightly higher, hence, silicon-based anodes are considered to be one of the most promising materials for high-energy LIBs [6, 7]. However, silicon suffers from a large volume change of ~300% during lithiation/delithiation, causing pulverization of silicon particles, loss of electrical contact of the anode materials, continuous formation of solid electrolyte interphase (SEI) and consumption of electrolyte, leading to rapid degradation of anode performance [8-11].

Therefore, the microstructure of silicon materials needs to be well designed to address these issues in battery applications resulting from the expansion/contraction of silicon. One common approach to stabilizing the anode performance is to coat a buffer phase onto silicon surfaces. Carbon is an ideal coating material due to its high electronic and ionic conductivities and great mechanical properties, and it can be synthesized from many kinds of precursors. For example, silicon nanoparticles were coated with single [12-14] or multilayer [15, 16] carbon layers, or dispersed in a porous carbon framework [17, 18]. Furthermore, as a special class of core-shell structures, yolk-shell structures are capable of providing Si/C composites with free space for volume expansion during silicon lithiation, thus eliminating the pressure of the lithiated silicon core on the carbon shell and stabilizing the composite structure and battery performance. Template-assisted synthesis is an effective way to create the void space in yolk-shell composites. A frequently reported method [19-21] for the preparation of yolk-shell Si/C composites is to form a silica layer on the surface of silicon particles and then remove the silica after coating the core-shell silica/silicon composite with a carbon shell.

Aluminum-silicon alloy powder is a low-cost raw material widely used in the powder metallurgy industry. Silicon in the alloy can serve as an active material in anodes, whereas aluminum is chemically active and can be easily removed by corrosion, so it is suitable as a template for the cavities in yolk-shell composites. There have been few reports on Si/C anodes from Al-Si alloys, such as carbon-shell-constrained Si clusters [22] and hierarchical microsized porous Si/C composites [23]. In this study, synthetic hydrolyzed polyacrylonitrile was used as a binder to coat polyacrylonitrile onto Al-Si alloy particles, and the aluminum was gently dissolved into an etchant after polymer carbonization, giving silicon@void@carbon composites. Compared with the powder mixture of silicon and carbon, these composites exhibited good cell performances, including especially superior cycling durabilities.

#### 2. EXPERIMENTAL

#### 2.1. Preparation

Hydrolyzed polyacrylonitrile (HPAN): polyacrylonitrile (PAN, MW = 250 000) powder, hydrochloric acid ( $36 \sim 38 \text{ wt.\%}$ ) and water were mixed in a mass ratio of 6:20:3 and heated at 80 °C for 72 h with stirring. A creamy paste was precipitated by adding an equal volume of water to the mixture. To purify the product, the solid was redissolved in boiling water and then reprecipitated after cooling. This procedure was repeated until the pH of the washing water was above 3. The product was dried under vacuum at 80 °C to give a yellowish transparent solid.

Silicon/pyrolytic carbon composites: Al-Si alloy powder  $(1 \sim 2 \mu m, 21 \text{ wt.}\% \text{ Si})$  was mixed with an ethanol solution of HPAN (40 wt.%) by ball-milling in a polytetrafluoroethylene (PTFE) container with zirconia balls at a rotation speed of 200 rpm for 6 h and then partially dried under vacuum at 40 °C to remove part of the ethanol, resulting in a viscous slurry without lumps. Then PAN was added, and the mixture was ball-milled for 12 h. After removing all of the ethanol under vacuum at 40 °C, the dried mixture was ball-milled for another 12 h. The composite particles were sieved out and calcined at 550 °C for 5 h in a nitrogen atmosphere. The obtained solid was gently ground into powder, and then added to a 1 mol L<sup>-1</sup> aqueous solution of ferric chloride. The solution gradually became lighter in color under continuous stirring. Aqueous hydrogen peroxide (30 wt.%) and hydrochloric acid were added dropwise to restore the color and pH of the solution. When the color of the solution no longer became lighter, the suspended solid was collected by filtration though a PTFE membrane (0.45 µm pore size), washed successively with dilute hydrochloric acid and water, dried under vacuum at 80 °C, and further calcined at 900 °C for 8 h in a nitrogen atmosphere to give a black powder as the final product. Three composites were prepared with mass ratios of Al-Si alloy, HPAN and PAN of 1:0:1.4, 1:0.05:1.35 and 1:0.1:1.3, and named H0P28, H1P27 and H2P26, respectively, according to their ratios of HPAN to PAN. Using similar preparation procedures, pure PAN was pyrolyzed to carbon at 900 °C, and the Al-Si alloy was corroded by ferric chloride solution to give pure silicon powder. The pyrolytic carbon and silicon powders were mixed in a mass ratio of 11:36 (named S+C) to be used as a reference sample for the subsequent electrochemical measurements.

#### 2.2. Characterization

The morphologies of the samples were examined by scanning electron microscopy (SEM, Quanta FEG 250 FEI, USA). An ESCALAB 250Xi instrument (Thermo Fisher Scientific) was used to determine the surface chemical composition of the composites. X-ray powder diffraction measurements were performed on a Bruker AXS D8 Advance diffractometer with Cu Kα radiation.

#### 2.3 Electrochemical measurements

The Si/C materials were mixed with super P and polyvinylidene fluoride (PVDF) binder with a mass ratio of 8:1:1 in N-methyl pyrrolidone (NMP) to form a homogeneous slurry. The slurry was cast onto a copper foil and dried at 110 °C for 50 min in air (environmental relative humidity  $\leq 10\%$  at 25 °C). The as-prepared electrode sheet was punched into circular discs with a loading of approximately 1.5 mg cm<sup>-2</sup>, and some discs were pressed by a roller. CR2032 coin cells were assembled in an Ar-filled glove box. Each cell contained a Si/C electrode, a polyethylene separator (16 µm) made by a wet process, and a lithium foil counter electrode. The electrolyte was 1 mol L<sup>-1</sup> LiPF<sub>6</sub> in ethylene carbonate/dimethyl carbonate (EC/DMC/DEC, 1:1:1 by volume) without any additives.

The galvanostatic charge/discharge behavior of the Si/C||Li cells was investigated by a Land CT2001A battery testing system (Wuhan Jinnuo Electronics Co. Ltd., China) within a voltage window of  $0.01 \sim 1.5$  V. The as-assembled cells were first activated at a current density of 0.1 C (1 C = 800 mAh

g<sup>-1</sup>) for 2 cycles before measuring their rate capacities, and they were cycled once at 0.1 C between two adjacent high-rate charge or discharge measurements to eliminate interference (see the Supporting Information for details). The cells were cycled at 0.1 C for 50 cycles to evaluate the cycling stability of the Si/C electrodes. Electrochemical impedance spectroscopy (EIS) measurements were performed on an impedance meter (HIOKI 3522-50 LCR HiTESTER) over the frequency range from 10 mHz to 100 kHz with 10 mV amplitude and a DC bias of 1.5 V.

#### **3. RESULTS AND DISCUSSION**

#### 3.1. Preparation and structure

Since silicon expands by as much as three times in volume during lithiation, the volume ratio of aluminum to silicon in the alloy used as the starting material should not be lower than three, that is, the mass fraction of silicon cannot be higher than 22%. Hence, an alloy containing 21 wt.% silicon was used in this study. To bind PAN firmly to the surfaces of the alloy particles to form a uniform and dense coating, partially hydrolyzed polyacrylonitrile (HPAN) was synthesized by acidolysis to convert some of the cyano groups into carboxyl groups. The resulting acrylonitrile-acrylic acid copolymer was incorporated into the PAN powder and acted as a binder in the subsequent ball-milling process. Then, the PAN coating was carbonized at a temperature below the melting point of the alloy to stabilize the composite structure and prevent HPAN from dissolving into the aqueous solution involved in the subsequent corrosion process. A ferric chloride solution, rather than a protic acid, was used to gently core inside the composite particles that may damage the carbon shell. Fe (III) was regenerated by slowly adding hydrochloric acid and hydrogen peroxide according to the pH and color of the solution. Finally, the organic matter in the coating was further carbonized at a higher temperature.

As shown in Figure 1, three Si/C composites were prepared in this study. In the case of the raw materials, the mass ratio of the Al-Si alloy to the total amount of PAN and HPAN was 1:1.4, and the ratios of HPAN to PAN were 0:28, 1:27 and 2:26, respectively, so the as-prepared composites were named H0P28, H1P27 and H2P26. The silicon contents of the composites were determined by treating the composites with a mixed aqueous solution of hydrofluoric acid and hydrogen peroxide and then calculating the weight loss rates. In addition, a powder mixture of silicon and pyrolytic carbon with a mass ratio of 11:36 was prepared as a reference sample and named S+C.



**Figure 1.** Composition of the raw materials (left one of a bin pair) and products (right one of a bin pair) of the three Si/C composites, and composition of the powder mixture of silicon and pyrolytic carbon.

The SEM images in Figure 2 ( $a \sim c, e \sim g$ ) show that the particles of the Si/C composites are irregular in shape and  $10 \sim 20 \,\mu\text{m}$  in size with many protrusions and dimples on the surfaces. The sizes of these protrusions and dimples are approximately 1 µm, similar to those of the alloy particles in Figure 2 (d, h). Furthermore, the insides of some dimples are regular and spherical. Careful observation of the broken protrusions reveals that the protrusions are hollow with smaller particles inside. Therefore, it can be inferred that these particles are agglomerates of small yolk-shell particles formed from the alloy particles as a template, and some of the carbon shells near the surfaces were broken during the preparation, producing visible dimples and cavities. By comparing the morphologies of the three composites, it can be seen that the carbon shell of HOP28 is relatively thin, and there are large gaps among the small protrusions. Obviously, a thick and dense coating was difficult to form without the use of HPAN binder, resulting in the fragile carbon shells of H0P28. In the case of H2P26, a large amount of HPAN was used in the synthesis; consequently, the powder of the PAN-coated alloy was calcined into a hard mass due to the softening and fusion of HPAN during heating (in fact, if the amount of HPAN was further increased, the calcined product would be as hard as cement and thus difficult to use). Many yolk-shell particle units were crushed in the subsequent grinding process, resulting in a large number of bowl-shaped dimples on the surfaces of H2P26. Due to the moderate amount of HPAN, the particles of the H1P27 precursor had a thick PAN coating and they did not fuse into hard lumps after calcination, so there were relatively few structural defects in H1P27. The formation mechanism of the Si/C composite particles is schematized according to these inferences (Figure 3). Transmission electron microscopy (TEM) was also used in an attempt to further examine the particle structure, but these aggregates are too large in size to be effectively observed.



Figure 2. SEM images of the Si/C composites and Al-Si alloy.



Figure 3. Formation mechanism of the three Si/C composites during preparation.

The XPS survey spectra in Figure 4 (a) show that the main elements at the surfaces of the Si/C composites are C, O, N and Si, and their percentages are listed in Table 1. The silicon contents at the surfaces are lower than the overall silicon contents shown in Figure 1, suggesting that most of the silicon particles are covered by thick carbon shells and cannot be detected by XPS. It is well-known that silicon surfaces are easily oxidized in a humid, oxidizing environment [24]; therefore, there are not only peaks of pure silicon at approximately 98 eV in the Si2p spectra in Figure 4 (b), but also peaks of silica at approximately 102 eV. There is oxygen at the surfaces due to the presence of silica. The high N contents

indicate that the PAN coatings were not completely carbonized. In fact, a high temperature of 1900 °C [25] is required to carbonize PAN completely, which far exceeds the upper limit of our equipment.

On the other hand, the XRD patterns in Figure 4 (c) show that the composites are mainly composed of silicon and pyrolytic carbon, and there is no diffraction peak of aluminum or silica, indicating that aluminum metal in the alloy was completely removed during the corrosion process; silica is low in content, and is concentrated on the surfaces of the exposed silicon particles.



**Figure 4.** XPS (a) survey and (b) high-resolution Si2p spectra of the Si/C composites, and (c) XRD patterns of the composites, Al-Si alloy and pyrolytic carbon.

Table 1. Weight percentages (%) of the near-surface elements determined from the XPS survey spectra.

Si/C composite	С	0	Ν	Si
H0P28	62.09	14.25	9.93	13.73
H1P27	66.79	13.72	9.24	10.25
H2P26	61.34	15.35	9.54	13.77

## 3.2. Electrochemical performance

Si/C||Li cells based on Si/C composites and a powder mixture of silicon and pyrolytic carbon were assembled to investigate the effects of the structure and composition of the active materials on the electrochemical performance.

Fresh cells were first cycled at a current density of 0.1 C to measure the initial capacities and coulombic efficiencies. From the results summarized in Figure 5 (a) (see Figure S1 for details), it can be seen that the capacity of the powder mixture is much lower than the theoretical value, and the coulombic efficiency is also very low, only approximately 50%, suggesting a serious structural failure of the bare silicon in S+C during the first cycle. By contrast, the capacities of the Si/C composites are close to the theoretical values, and the coulombic efficiencies are approximately 70% ~ 75%. Moreover, H1P27, with fewer structural defects (as shown in Figure 2), has the highest coulombic efficiency. This is because the formation of the SEI is the major contribution to the irreversible capacity loss [26, 27], and a large number of broken carbon shells in H0P28 and H2P26 provided more interfaces for SEI

deposition. In addition, the roller-pressing process crushed some of the carbon shells in the Si/C composites but improved the electrical contact of the electrode particles. Therefore, pressing is beneficial to improve the initial performance of H0P28 with a loose structure but has a negative effect on H2P26 with a compact structure.

Similarly, Figure 5 (b, c) (see Figure S2 for details) shows that, the rate capacities of the composites are significantly larger than that of the powder mixture, and the roller-pressing process is more detrimental to the reversible capacity of a composite based on a larger amount of HPAN binder. Since the particle structure of S+C is not hollow and thus remains stable during the roller-pressing process, the pressed electrode has a better rate performance than the unpressed electrode.



**Figure 5.** (a) Discharge (lithiation, the total height of the stacked pink and green bins), charge (delithiation), irreversible capacities and coulombic efficiency (the percentages on the green bins) of the Si/C||Li cells in the first cycle at a current density of 0.1 C. (b) Charge and (c) discharge capacities of the cells at 0.1 C, 0.25 C, 1 C and 3 C. The hollow five-pointed stars on the left vertical axes are the theoretical specific capacities calculated according to the composition of each material in Figure 1 (silicon 3580 mAh g<sup>-1</sup>; pyrolytic carbon 372 mAh g<sup>-1</sup>, with an assumption that the polymers have been fully graphitized). The names of the roller-pressed electrodes are suffixed with "\_r".

The Si/C electrodes were cycled 50 times at a current density of 0.1 C in the electrolyte without any additives to investigate the effect of the special yolk-shell aggregation structure of the composites on the cycling stability. As shown in Figure 6, H1P27 with fewer structural defects had the best cycle stability. After 50 cycles, it still maintained a specific capacity of 513 mAh g<sup>-1</sup>, whereas the other two composites only had a capacity of approximately 350 mAh g<sup>-1</sup> remaining, which results are similar to those reported [28] for the yolk-shell Si@void@carbonized PAN nanofibers. All three composites were significantly more stable than the powder mixture of silicon and pyrolytic carbon during cycling. The cells based on the composites showed a rapid decline in capacity during the first 6 cycles, probably due to the degradation of the exposed silicon cores in the defective yolk-shell particle units. Similar to the results from the rate performance data plotted in Figure 5, some carbon shells of the hollow composites were crushed during the roller-pressing process, resulting in the exposure of silicon cores and thus causing the cycling instability of the electrodes. Moreover, roller pressing had a greater negative effect

on H2P26 than on H0P28. The capacities of S+C also declined rapidly in the first 10 cycles and dropped to as low as approximately 1/4 of the theoretical capacity but changed little during subsequent cycling; this finding means that the silicon in the S+C electrodes had completely failed to contribute to the capacities after the first few cycles, and only the pyrolytic carbon played a role as an active material due to its high electrochemical stability. Roller pressing is beneficial to the cycling stability of S+C because it increased the probability of contact between the electrode particles and, as a result, slowed the electrical contact failure process.



Figure 6. Cycling performance of the Si/C||Li cells cycled at a current density of 0.1 C.

The mechanism of capacity fading of these Si/C electrodes was further investigated by EIS measurements. The Nyquist plots of the Si/C||Li cells during cycling are shown in Figure 7. There is a high-frequency arc in each curve, corresponding to the charge transfer resistance ( $R_{CT}$ ) of a cell (since the SEI layers on the Si/C electrodes grew very slowly due to the small number of cycles and the small current rate of the cycling test, their impedances were very small and thus had no obvious manifestation in the EIS, so their influence is ignored here). By comparing the fitted resistance values in the inset tables, it can be seen that the cells based on the Si/C composites had similar initial  $R_{CT}$  values; however, the  $R_{CT}$  values of the pressed electrodes increased faster than those of the unpressed electrodes with cycling, indicating that the crushed carbon shells of the yolk-shell particle units failed to provide buffer spaces for the lithiated silicon cores, resulting in the more rapid deterioration of the microstructures of the pressed electrodes. In addition, the unpressed H1P27 electrode with better cell performance had a relatively small growth rate of the  $R_{CT}$ . H0P28 had a larger initial  $R_{CT}$  of H0P28 than on those of the other two composites during cycling, which is consistent with the cycling stability results obtained from Figure 6. The  $R_{CT}$  of S+C and its growth rate were reduced due to the dense electrode structure

formed during roller pressing. As expected, the unpressed S+C electrode with the shortest cycle life has the largest  $R_{CT}$ .



**Figure 7.** Nyquist plots of the Si/C||Li cells after different numbers of cycles, and the charge transfer resistances ( $R_{CT}$ ) listed in the tables were estimated by fitting the experimental data according to the equivalent circuit inset in (h). In the circuit,  $R_S$  is the ohmic series resistance;  $Q_{DL}$  are constant phase elements, representing the capacitances of the double layer; W is the Warburg impedance.

### 4. CONCLUSION

Moderately hydrolyzed PAN was used as a binder to coat PAN onto the particle surfaces of the low-cost Al-Si alloy, and the aluminum was subsequently removed from the carbonized composite particles through a mild etching process, leaving a cavity that could accommodate the expanded volume of lithiated silicon. The products were agglomerates of yolk-shell silicon@void@pyrolysis carbon particles.

The amount of HPAN in the coating is the key factor influencing the structures and electrochemical performances of the Si/C composites. The absence of HPAN resulted in thin and defective carbon shells, which were nondurable during charge-discharge cycling and thus almost incapable of buffering the volume change of the silicon cores; whereas the carbonized polymer coatings stuck together when a large amount of HPAN was used, some of the yolk-shell particle units were crushed in the grinding process, leading to the formation of structural defects. The cell performances of all the Si/C composites were far superior to those of the powder mixture of silicon and pyrolytic carbon. Among these composites, H1P27 had the highest specific capacity and the best cycling stability due to its relatively perfect structure, and it maintained a capacity of more than 500 mAh g<sup>-1</sup> after 50 cycles.

## SUPPORTING INFORMATION

The rate capacities of the Si/C electrodes were measured as follows:

(1) Activated cells  $\rightarrow$  Discharge @ 0.1 C  $\rightarrow$  Charge @ 0.1 C (Charge capacity at 0.1 C)  $\rightarrow$ Discharge-charge cycle @ 0.1 C  $\rightarrow$  Discharge @ 0.1 C  $\rightarrow$  Charge @ 0.25 C (Charge capacity at 0.25 C)  $\rightarrow$  Discharge-charge cycle @ 0.1 C  $\rightarrow$  Discharge @ 0.1 C  $\rightarrow$  Charge @ 1 C (Charge capacity at 1 C)  $\rightarrow$  Discharge-charge cycle @ 0.1 C  $\rightarrow$  Discharge @ 0.1 C  $\rightarrow$  Charge @ 3 C (Charge capacity at 3 C);

(2) Activated cells  $\rightarrow$  Discharge @ 0.1 C (Discharge capacity at 0.1 C)  $\rightarrow$  Charge @ 0.1 C  $\rightarrow$  Discharge-charge cycle @ 0.1 C  $\rightarrow$  Discharge @ 0.25 C (Discharge capacity at 0.25 C)  $\rightarrow$  Charge @ 0.1 C  $\rightarrow$  Discharge-charge cycle @ 0.1 C  $\rightarrow$  Discharge @ 1 C (Discharge capacity at 1 C)  $\rightarrow$  Charge @ 0.1 C  $\rightarrow$  Discharge-charge cycle @ 0.1 C  $\rightarrow$  Discharge @ 3 C (Discharge capacity at 3 C).



**Figure S1.** Galvanostatic charge-discharge curves of the Si/C||Li cells in the first cycle at a current density of 0.1 C.



**Figure S2.** (a) Galvanostatic charge-discharge curves of the Si/C||Li cells at current rates of (a) 0.1 C; (b) 0.25 C; (c) 1 C and (d) 3 C after being fully discharged/charged at 0.1 C.

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