Electronic Supplementary Material (ESI) for Energy & Environmental Science. This journal is © The Royal Society of Chemistry 2020

Supplementary Information

A Gas Phase Synthesis of Amorphous Silicon Nitride Nanoparticle for High-Energy LIBs

Sujong Chae^{1†}, Seungkyu Park^{1†}, Kihong Ahn¹, Gyutae Nam¹, Taeyong Lee¹, Jaekyung Sung¹, Namhyung Kim¹, and Jaephil Cho¹*

¹ Department of Energy Engineering, School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan 689-798, Republic of Korea † These authors contributed equally to this work.

*Corresponding author.

E-mail: jpcho@unist.ac.kr

Experimental

Synthesis of Si-rich silicon nitride (SiN) nanoparticle.

SiN nanoparticle was synthesized by the specialized vertical furnace described in Figure 1. To obtain the homogeneous phases of Si and N, high-purity silane gas (99.9999%) and ammonia gas (99.9995%) streamed at flow rates of 100 sccm and 30-100 sccm through static mixer built in gas line. The pyrolysis was carried out at 700 °C while the reactive gas flowing. Detailed synthesis step with the furnace is presented in Supplementary Figure 1. Likewise, SiNP nanoparticle is synthesized by the same process of SiN nanoparticle except for the flow of ammonia gas. Carbon coating on the surface of SiN nanoparticle and SiN was carried out with high-purity acetylene (C_2H_2) gas in the rotatable furnace with the flow rate of 1.5L min⁻¹ during 10 min at 900°C.

Material characterization.

Structural investigation on SiN nanoparticle and SiNP was carried out using scanning electron microscopy (SEM, Verios 460, FEI) which is equipped with energy-dispersive spectroscopy (EDS, Bruker XFlash 6130), high resolution transmission electron microscopy (HR-TEM, ARM300, JEOL) with energy-dispersive spectroscopy (EDS, Aztec, Oxford) and electron energy loss spectroscopy (EELS, Quantum 965, Gatan), X-ray diffraction (XRD, D/MAZX 2500V/PC, Rigaku), and raman spectroscopy (NRS-5100, JASCO). The cross-sectional samples for TEM and SEM analysis were prepared by dual-beam focused ion beam (FIB, NX2000, Hitachi) and ion milling system (Hitachi IM4000, Hitachi High-technologies). To observe the changes of SiN nanoparticle and SiNP upon cycling, cells were disassembled and the electrodes were rinsed with excess dimethyl carbonate (DMC) in an Ar-filled glove box.

Electrochemical characterization.

The electrodes of SiN nanoparticle and SiNP were fabricated by mixing active material, carbon black (Super P, Imerys), carboxymethyl cellulose (CMC, Nippon paper), and styrene butadiene rubber (SBR, Zeon) in distilled water at the mass ratio of 80:10:5:5. The homogeneous blended slurry was loaded on 18 μ m of Cu current collector at a loading level of ~1.2 mg cm⁻² and dried at 80 °C for 30 min. Then, these electrodes were vacuum-dried at 110 °C for 8 h. 2032R coin-type half-cells were fabricated in a glove box (Koreakiyon, H₂O < 1 ppm, O₂ < 1 ppm) with Li metal (>99%, Honjo metal) as the counter electrode. Microporous

polyethylene (15 μ m, Celgard), 1.3 M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (=3/7, v/v) containing 10% FEC (Enchem) were used as separator and liquid electrolyte, respectively. The electrochemical characterization of half-cells was measured over the voltage range 0.005–1.5 V for the first cycle at 0.1C with constant-voltage mode for lithiation (0.01C cut-off), and 0.005–1.0 V for the cycling test at 0.5C (for both of charging and discharging) with same constant-voltage mode. The electrochemical tests for the half-cell were conducted with TOSCAT-3100 battery cycler (TOYO SYSTEM).

For pouch-type 1Ah cell test, the slurry for the cathode and the graphite-blended anode was prepared by planetary-despa mixer. The detailed electrode formula and cell design is described in Supplementary table 1. The pouch-type full-cells were assembled in a dry room with a humidity of less than 1%. The electrolyte formula for pouch-type 1Ah cell was 1.3 M LiPF₆ in ethylene carbonate (EC)/ethyl methyl carbonate (EMC)/diethyl carbonate (DEC) (=3/5/2, v/v/v) containing 0.2% LiBF₄, 10% FEC, 0.5% VC, and 1% PS (Enchem). The full-cell tests were run at 2.5–4.2 V for the formation cycles at 0.1C with constant-voltage mode for charging (0.05C cut-off). Cycle life was characterized at 1C (for both of charging and discharging) in the voltage window between 2.75 and 4.2 V. with WBCS3000 Battery Cycler (WonATech)

In situ dilatometry

The electrode swelling during cycling was measured by customized in-situ dilatometry system with digimatic indicator (Mitutoyo). To avoid additional degradation from mechanical stress, the small constant pressure of 2.23 kPa was applied on the top of the cell by 1kg load. A relatively small electrode swelling of cathode is ignored.

Category			G/SiN	G/SiNP	Unit
Material information					
Cathode	Li(Ni _{0.6} Co _{0.2} Mn _{0.2})O ₂	Charge	202.2	202.2	mAh g ⁻¹
		Discharge	185.3	185.3	mAh g ⁻¹
Anode	Graphite-blended SiN	Charge	488.0	482.5	mAh g ⁻¹
	nanoparticle (or SiNP)		450.0	450.0	mAh g ⁻¹
	Si content		4.7	3.1	%
	Graphite content		95.3	96.9	%
Electrode formula					
Cathode	Active material		94.00	94.00	%
	Carbon black		3	3	%
	PVDF		3.00	3.00	%
Anode	Active material		96.00	96.00	%
	Carbon black		1.00	1.00	%
	СМС		1.00	1.00	%
	SBR		2.00	2.00	%
Cell information					
N/P ratio			1.300	1.300	
Cathode	Loading level		26.44	26.44	mg cm ⁻²
	Electrode density		3.12	3.12	g cc ⁻¹
	Electrode thickness		100	100	μm
	Al foil thickness		15	15	μm
	Width		55	55	mm
	Length		73	73	mm
Anode	Loading level		12.49	12.67	mg cm ⁻²
	Electrode density		1.60	1.60	g cc ⁻¹
	Electrode thickness		89	90	μm
	Cu foil thickness		10	10	μm
	Width		58	58	mm
	Length		76	76	mm
Separator			16.0	16.0	μm
Number of stacking			8.0	8.0	
Cell thickness			2.445	2.457	mm

 Table S1 Electrochemical cell design of pouch-type 1Ah cell



Fig. S1 Synthesis process algorithm for SiN nanoparticle in the customized vertical furnace. The synthesis and collection can be continuously operated with maintaining the pyrolysis temperature by the gate valve as a safeguard. This synthetic process can be automated by the installed digital program.

In order to collect the product in safety, the atmosphere in the reaction chamber, which is composed of residual SiH₄, NH₃, Ar, and produced H₂, is exchanged with pure Ar gas immediately after vacuuming the chamber. Then, as opening the gate valves located at the top and bottom of the reaction chamber, the scraper moves down from the top of the reaction chamber with radial motion to brush off SiN powders at the wall effectively, and the powders are accumulated in the bottom collecting chamber. In particular, the tungsten wire brushes are attached at the edge of the scraper for improving the yield and securing the thermal stability at the pyrolysis temperature. This synthetic process is automated with digital program in the system controller. For securing the safety of the process, the interlock system is also set up for shutdown of the process when sensing the abnormal status of cooling water pressure, gas pressure of each chamber, and gas leakage.



Fig. S2 Photograph of collected SiN nanoparticles for 8 hours.



Fig. S3 HR-TEM image of SiN nanoparticle after heat treatment at 1000 °C. Scale bar indicates 10 nm.



Fig. S4 Distribution of Li element from EELS mapping. **a**, lithiated SiN nanoparticle, **b**, delithiated SiN nanoparticle



Fig. S5 Si 2p and N 1s XPS spectra of SiN electrode at the pristine (a, d), lithiated (b, e), and delithiated (c,f) state

It is assumed that the displacement of the binding energy is determined based on the chemical coordination. At the pristine state of SiN electrode, Si 2p and N 1s spectra show the strong peak of Si-N₄ (102.0 eV) and N-Si₃ (398.1 eV), respectively, which is originated from the solid solution phase of Si and N in the SiN nanoparticle.

After the lithiation, the peak (99.8 eV) in Si 2p spectrum indicating Si-Si₄ at the pristine state shifts to 100.5 eV, which can be considered as lithium silicide, and becomes stronger with the localization of Si and N. For N 1s spectrum at the lithiated state, the intensity of N-Si₃ peak at 398.2 eV is decreased. The peak at 399 eV can be regarded as N-Li_xSi_y because there is negligible Si-O₄ peak in Si 2p spectrum.

Si 2p spectrum at the delithiated state shows the decrease of the peak intensities for Si-Si₄ and Si-N₄, but the peak at 103.4 eV corresponding to Si-O₄ appears caused by the surface oxidation including the formation of SEI layer. The N 2p spectrum can show the existence of N-Li_xSi_y and N-Si₂O with two peaks at 398.5 eV and 399.8 eV. Particularly, N-Si₃ peak (398.2 eV) at the lithiated state shift to 398.5 eV with a tiny amount of remaining N-Si_x-N_y.



Fig. S6 Electrochemical performances of SiN according to the state including the pristine, heat treated, and the carbon coated.



Fig. S7 Electrochemical performances of SiNP according to the state including the heat treated and the carbon coated.

SiN nanoparticle grows as an amorphous solid solution phase comprising of Si and N that there are five atomic coordinates of Si-4Si, Si-(3Si, N), Si-(2Si, 2N), Si-(Si, 3N), and Si-4N. Because of its highly disordered structure, the (de)lithiation kinetic of Si in SiN nanoparticle is limited by the coordinating N element. Besides, silicon nitride is well known as electrical insulator with high electrical resistance. Thus, SiN nanoparticle without carbon coating at high temperature (900 °C) shows low specific capacity and Coulombic efficiency at the first cycle (748 mAh/g, 1654 mAh/g, and 45.2% for lithiation capacity, delithiation capacity, and Coulombic efficiency). The low Coulombic efficiency can be mainly attributed to irreversible reaction between Li and N.

After only heat treatment at 900 °C without carbon coating, the silicon crystallite grows and Si_3N_4 is formed as a result of diffusion. Thus, the ratio of Si-Si bond becomes large, which leads to high reversible capacity and coulombic efficiency with enhanced reversibility. The SiN nanoparticle after 900 °C heat treatment exhibits 1054 mAh/g and 1583 mAh/g for delithiation and lithiation capacity, respectively, and 66.6% of Coulombic efficiency. It is noted that the first cycle Coulombic efficiency is increased by 21.4% compared to the pristine SiN nanoparticle. Besides, in spite of the crystallite growth of Si upon heat treatment, heat treated SiN nanoparticle shows stable cycling behavior during 50 cycles higher capacity retention than that of pristine as shown in Fig. R3, which in turn demonstrates that Si_3N_4 improves the cycling stability.



Fig. S8 Electrochemical characterization of SiN nanoparticle with various N contents. **a**, Voltage profiles of different SiN nanoparticle at the formation cycle. **b**, Cycle life of various SiN nanoparticles for 200 cycles. The different N contents are controlled by adjusting the flow rate of NH₃ gas for the pyrolysis. The specific reversible capacities of different SiN nanoparticles are 2519, 2327, 1852, and 1404 mAh g⁻¹ for Si_{0.9}N_{0.1}, Si_{0.8}N_{0.2}, Si_{0.75}N_{0.25}, and Si_{0.7}N_{0.3}, respectively. Initial Coulombic efficiencies are 86.8, 87.7, 83.3, and 78.6% in the same order.

Obviously, high N content in SiN nanoparticle gives rise to the enhancement of cycle life by mitigating the mechanical degradation. However, increased N content restricts the lithiation of Si and takes Li ion by forming a lithium silicon nitride phases (Li_xSiN_y), leading to low specific capacity with poor Coulombic efficiency. Thus, when it comes to determining the content of N, there is a trade-off between stable cycle life and high specific capacity with high Coulombic efficiency.

From the practical point of view, we put top priority on the first cycle Coulombic efficiency. In contrast with the half-cell, cyclable Li ion is limited by the cathode in the full-cell if there is no additional Li source from the prelithiation. Thus, the first cycle Coulombic efficiency plays a critical role in determining the energy density of battery. Based on the practical cell design, we carefully controlled the adequate ratio of Si to N. However, we would like to note that the adequate ratio of Si to N for the best performance is adjustable depending on the material design.



Fig. S9 Differential discharge capacity versus voltage plot for SiNP and SiN nanoparticle. SiN nanoparticle shows clear one phase reaction between amorphous Li silicides, whereas SiNP suffers hysteric crystallization of Li silicide at the lithiation.



Fig. S10 Structural and electrochemical characterization of nitridated SiNP. **a**, Cross-sectional HAADF images of nitridated SiNP nanoparticles in pristine state with EELS mapping. **b**, Voltage profile of nitridated SiNP compared with SiN nanoparticle. **c**, Cycle life of nitridated SiNP compared with SiN nanoparticle. The nitridation of SiNP is carried out by the heat treatment at 700 °C in the tube furnace which is fully filled with NH₃.



Fig. S11 Voltage profiles depending on various C-rates. **a**, Voltage profiles of SiN nanoparticle with different C-rates from 0.2C to 7C. **b**, Voltage profiles of SiNP with different C-rates from 0.2C to 7C.



Fig. S12 Differential capacity versus voltage plots during cycling. **a**, Differential capacity versus voltage plots of SiN nanoparticle at 1st, 20th, 50th, and 100th cycle. **b**, Differential capacity versus voltage plots of SiNP at 1st, 20th, 50th, and 100th cycle. These differential capacity versus voltage plots demonstrates the different phase transformation of Si during repeated delithiation in SiN nanoparticle and SiNP. SiN nanoparticle exhibits constant one phase reaction during cycling, whereas SiNP drastically lose its capacity from c-Li_{3.75(-δ)}Si during 20 cycles.



Fig. S13 Modified linear sweep voltammetry (LSV) of SiN nanoparticle and SiNP. The modified LSV is comprised of typical constant current-constant voltage for reaching fully lithiated satate and with various sweep rates for delithiation. The sweep rates for SiNP and SiN nanoparticles are 0.04, 0.09, 0.16, 0.25, 0.36, 0.49, 0.64, 0.81, and 1 mV s⁻¹.



Fig. S14 Diffusivity as a function of depth of discharge at the formation cycle.

In order to prove the faster Li ion diffusion behavior of SiN electrode compared with SiNP, we estimated diffusion coefficient from GITT using following representative equation:

$$D = \frac{4}{\pi} \left(\frac{iV_m}{Z_A FS} \right) \left[\frac{dE(\delta)}{d\delta} / \frac{dE(t)}{d\sqrt{t}} \right]^2 \text{ where } t << L^2/D$$

i: Applied constant current

 $V_{\mbox{\scriptsize m}}$: Molar volume of the electrode material, assumed to be constant during the electrochemical process

Z_A: Charge number of electroactive species A

F: Faraday constant

S: Electrochemical active area between electrode material and electrolyte

 $E(\delta)$: Steady-state equilibrium voltage of the working electrode at the composition of $A_{\delta}B$,

E(t): Transient voltage response of the working electrode during the constant current interval

L: Characteristic length of the electrode material



Fig. S15 Cross-sectional SEM images of SiN (a) and SiNP (b) electrodes after 100 cycles



Fig. S16 Discharge voltage profiles of 1Ah pouch-type cells with different C-rates. **a**, Voltage profiles of SiNP during discharging process from 0.5C to 5C. **b**, Voltage profiles of SiN nanoparticle during discharging process from 0.5C to 5C.



Fig. S17 | Voltage profiles and differential capacity versus voltage plots during cycling. **a**, **b**, Voltage profiles of SiNP (**a**) and SiN nanoparticle (**b**) at the 1st, 20th, 50th, and 100th cycle. **c**, **d**, Differential capacity versus voltage plots of SiNP (**c**) and SiN nanoparticle (**d**) at the 1st, 20th, 50th, and 100th cycle. The capacity contribution from Si is distinguished by the voltage (\leq 3.4V).