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Supplementary Information

High-performance nanoporous Si/Al_2O_3 foam lithium-ion battery anode fabricated by selective chemical etching of Al-Si alloy and subsequent thermal oxidation

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Experimental Sections

Preparation of nanostructured micrometer sized Al-Si powder: 13.0 g Al-Si alloy powder (325 mesh, 99%, Al:Si = 88:12 wt.%, Alfa Aesar) was immersed in 400 mL of 3 M hydrochloric acid (HCl) solution (SAMCHUN chemical, Korea) for 30 min with stirring. The chemically etched powder was filtered, washed several times with deionized (DI) water and dried at 70 °C for 12 hr. At this condition, we obtained the production yield of 18%.

Synthesis of Si/Al_2O_3 foam particles: To oxidize residual Al in the chemically etched Al-Si particles, 0.35 g of the etched Al-Si powder was thermally oxidized with water vapor as an oxidant at 600 ^oC for 10, 30 and 60 min. The water vapor was supplied into the tube furnace by bubbling DI water assisted with N_2 gas (5 L min^{-1}).

Characterization: Scanning electron microscopy (SEM, S-4800, Hitachi) at an accelerating voltage of 10kV and high-resolution transmission electron microscopy (HR-TEM, JEOL, JEM-2100F) operating at 200kV were used to characterize morphologies and element mapping of Al-Si and Si/Al_2O_3 samples. To investigate the microstructures of samples, X-ray diffractometer (XRD, D8 Advance, Bruker, Cu Kα radiation) was used between 10 and 90° at a scan rate of 1.4° sec^{-1}.

Electrochemical measurements: To evaluate electrochemical performances of chemically etched and thermally oxidized samples, the electrodes were prepared by mixing 70 wt% active material (etched Al-Si powder, thermally oxidized Si/Al_2O_3 powder), 20 wt% of super P and 10 wt% of binder (poly(acrylic acid)/sodium carboxymethyl cellulose (PAA:CMC = 1:1, w/w)) with a mixer (Thinky mixer, ARE310) at 2200 rpm for 15 min to homogenize slurry. After the slurries were casted on a coper foil, the electrodes were dried at 150 °C for 2 hr in a vacuum oven to solidify electrodes. The mass loading level of active materials in electrodes was around 0.9 mg cm^{-2}. The coin-type half-cell (2016R) was assembled in an Ar-filled glove box with oxygen and water less than 1 ppm. The Li metal foil was used as counter electrode and micro porous polyethylene film (Celgard 2400) was used as a separator. The electrolyte consisted of a solution of 1.3M $LiPF_6$ in a mixture of ethylene carbonate (EC)/diethyl carbonate (DEC) (3:7, v/v) with 10% fluorinated ethylene carbonate (FEC) additive. Galvanostatic charge and discharge cycling (WonATech WBCS 3000 battery measurement system) was performed between 0.005 and 1.2 V (versus Li/Li^+) at 25 °C. For the chemically etched (30 min) Al-Si, 10 min-, 30 min-, and 60 min- oxidized Si/Al_2O_3

electrodes, 1C rate is 2.1, 1.4, 1.0, and 0.8 A/g, respectively. After cycling, the cells were disassembled in a glove box and the electrodes were rinsed with dimethyl carbonate (DMC) for 1 h to remove residual electrolytes and dried at room temperature. The AC impedance analysis was obtained using IVIUM frequency response analyzer ranging from 0.01 Hz to 100 kHz.

Table. S1 EDS data of the amount of elements depending on etching time.

Elements	Before etching	15 min	30 min	45 min	60 min
	Weight%	Weight%	Weight%	Weight%	Weight%
O	4.45	5.88	11.45	12.90	12.56
Al	84.69	60.58	21.10	7.58	4.28
Si	10.87	33.54	67.45	79.53	83.16

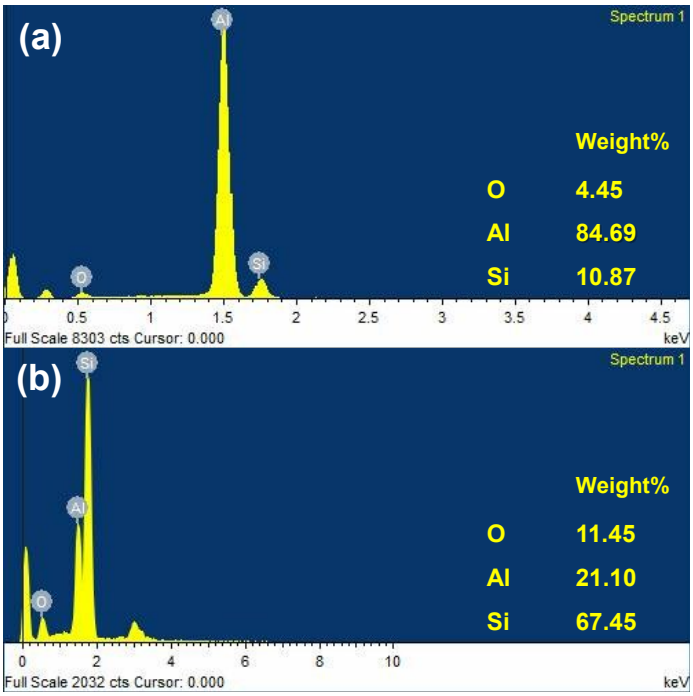

Fig. S1 EDS spectra of (a) Al-Si alloy powder and (b) chemically etched Al-Si powder.

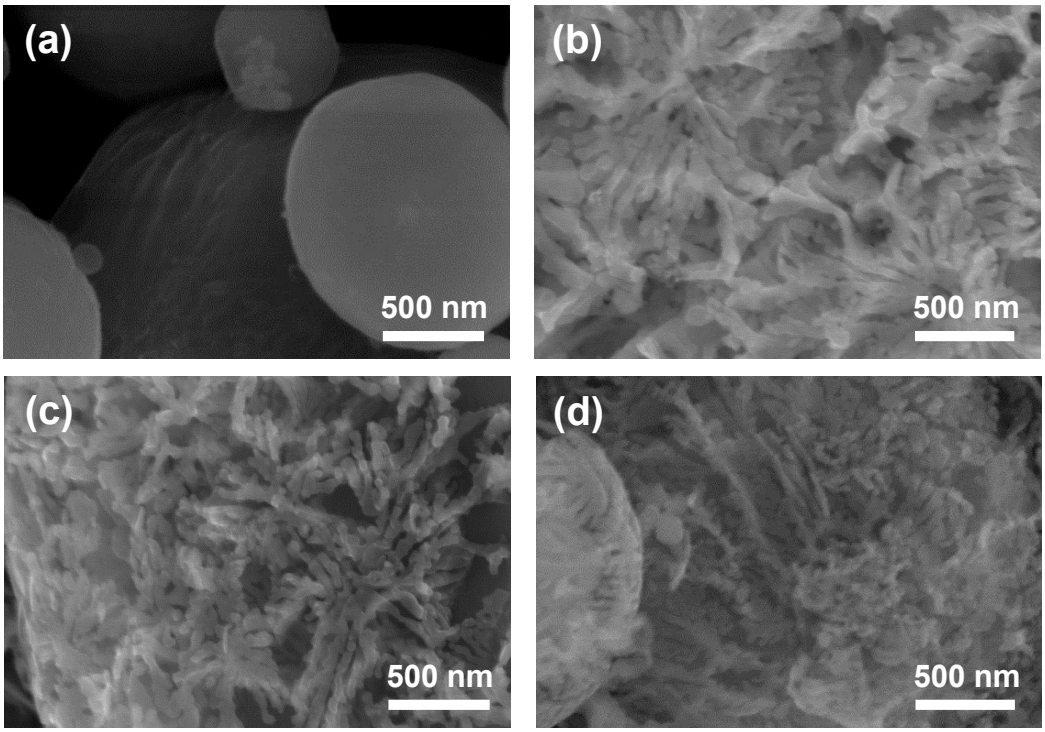

Fig. S2 SEM images of chemically etched Al-Si particles for (a) 10 min, (b) 30 min, (c) 45 min, and (d) 60 min at room temperature.

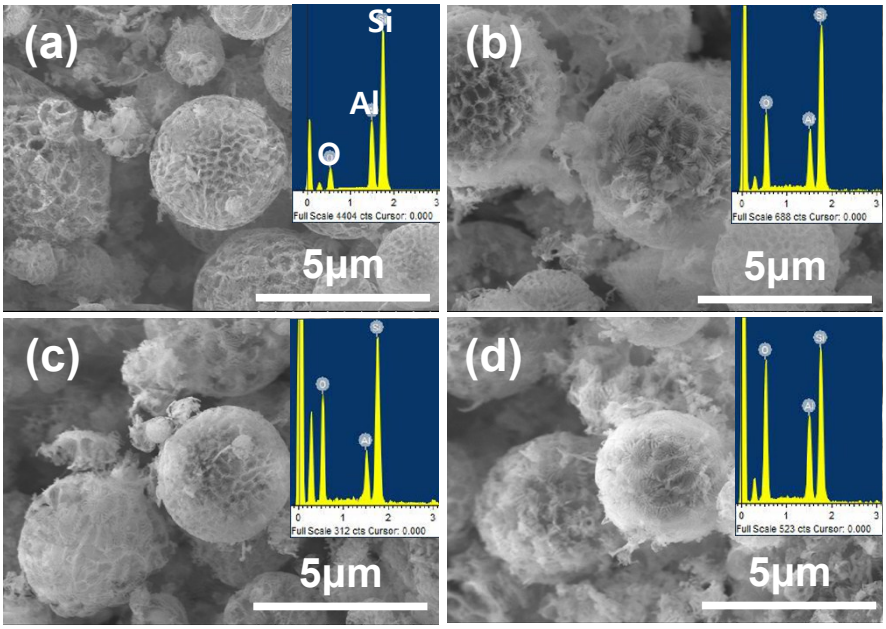

Fig. S3 SEM images and EDS spectra of (a) chemically etched Al-Si powder and Si/Al_2O_3 particles thermally oxidized for (b) 10 min, (c) 30 min, and (d) 60 min.

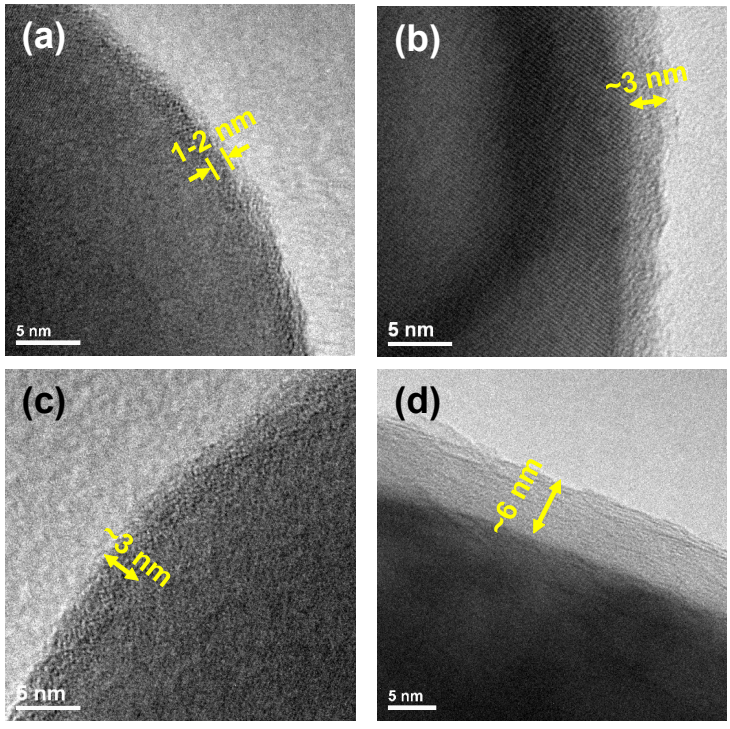

Fig. S4 TEM images of thermally oxidized samples at 600 ºC: Thermally oxidized Si for (a) 10 min, (b) 30 min, (c) 60 min and (d) thermally oxidized Al sample for 10 min. In the case Al particle, we used micrometer-sized Al (an average particle size of 3 μm). After thermal oxidation at 600 ºC for 10 min, a focused-ion beam technique was employed to obtain sectioned sample for TEM measurement.

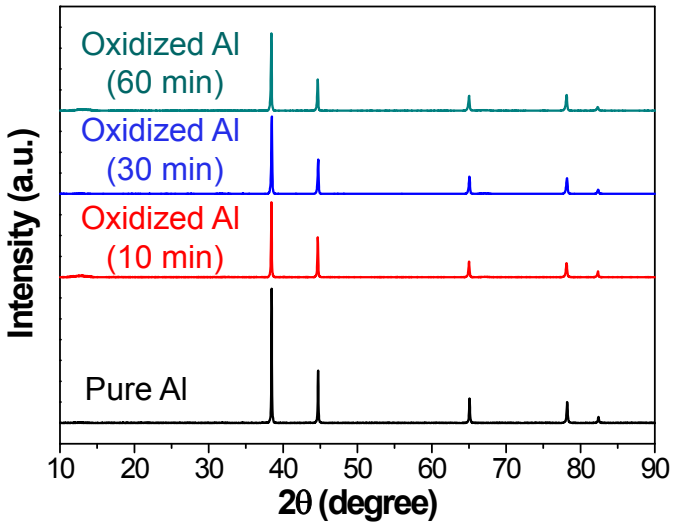

Fig. S5 XRD patterns of pure Al and samples thermally oxidized at 600 °C for 10 min (red), 30 min (blue), and 60 min (cyan). As the oxidation time increased, the Al peak was gradually decreased. From the first order scattering peak of each sample, we estimated the Al_2O_3 contents from the Al contents remained after the thermal oxidation. When the pure Al was thermally oxidized for 10 min, 30 min, and 60 min, the Al_2O_3 layers of 20%, 25%, and 35% were formed on the Al surface, respectively. It should be noted that the Al of 65% was still left, even though the pure micrometer-sized Al particles was oxidized at 600 °C for 60 min.

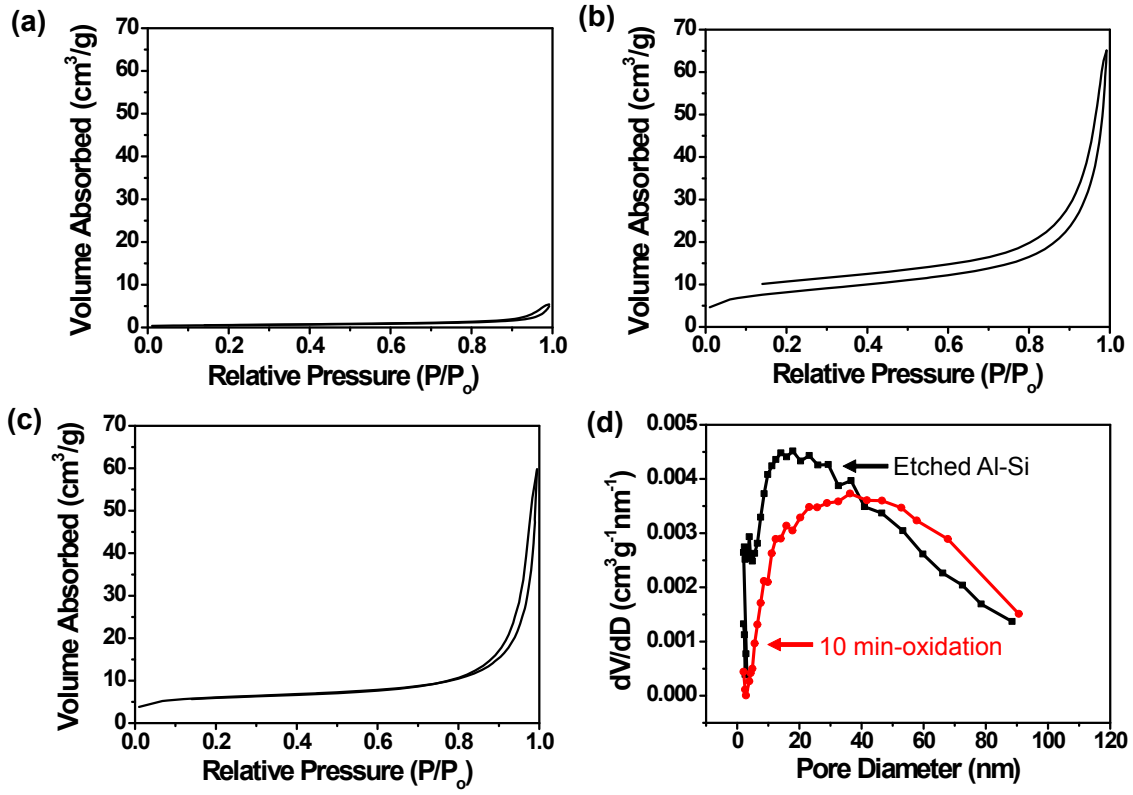

Fig. S6 BET surface area of (a) pristine Al-Si alloy, (b) 30 min-etched Al-Si, and (c) 10 min-thermally oxidized Si/Al_2O_3. (d) Pore size distribution of the chemically etched and 10 min-oxidized particles.

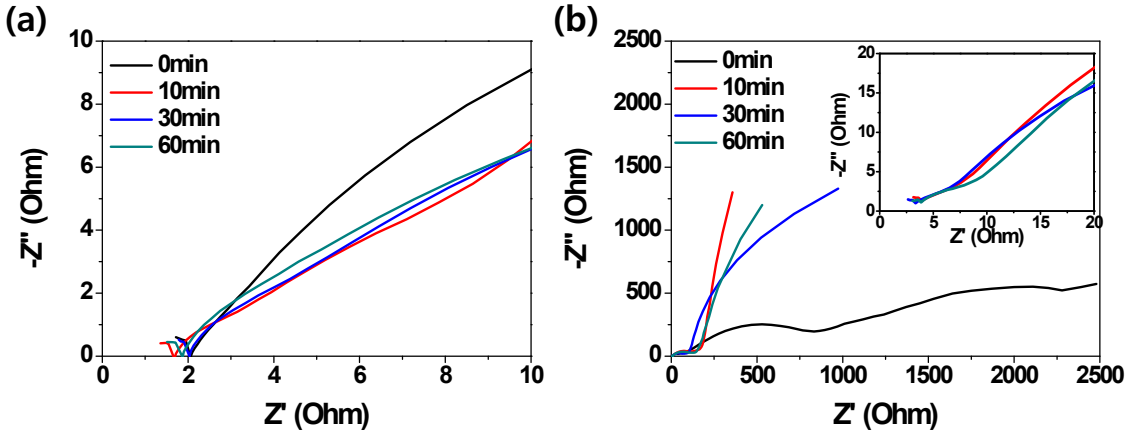

Fig. S7 Electrochemical impedance spectra of chemically etched Al-Si and Si/Al_2O_3 electrodes thermally oxidized for 10, 30 and 60 min (a) after 1st cycle (b) after 120th cycle.

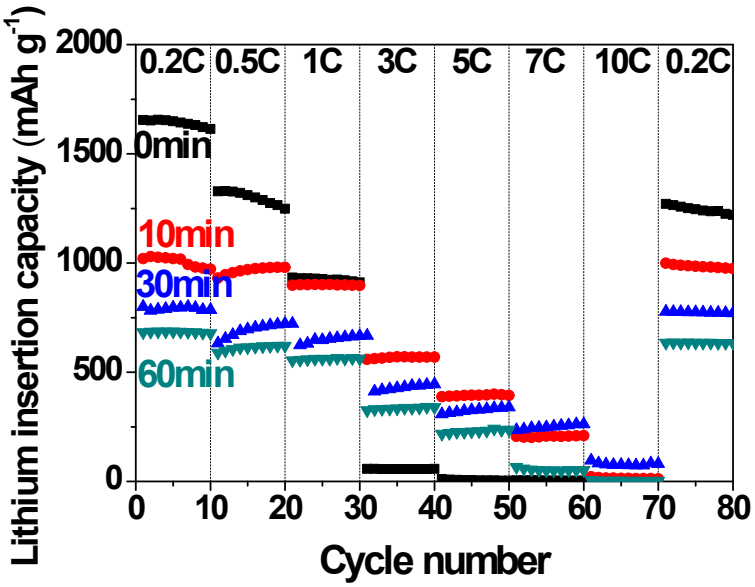

Fig. S8 Rate capabilities of chemically etched Al-Si and Si/Al_2O_3 electrodes thermally oxidized for 10, 30, and 60 min. The Li extraction rate was fixed at C/5 and Li insertion rate was varied from C/5 to 10C.

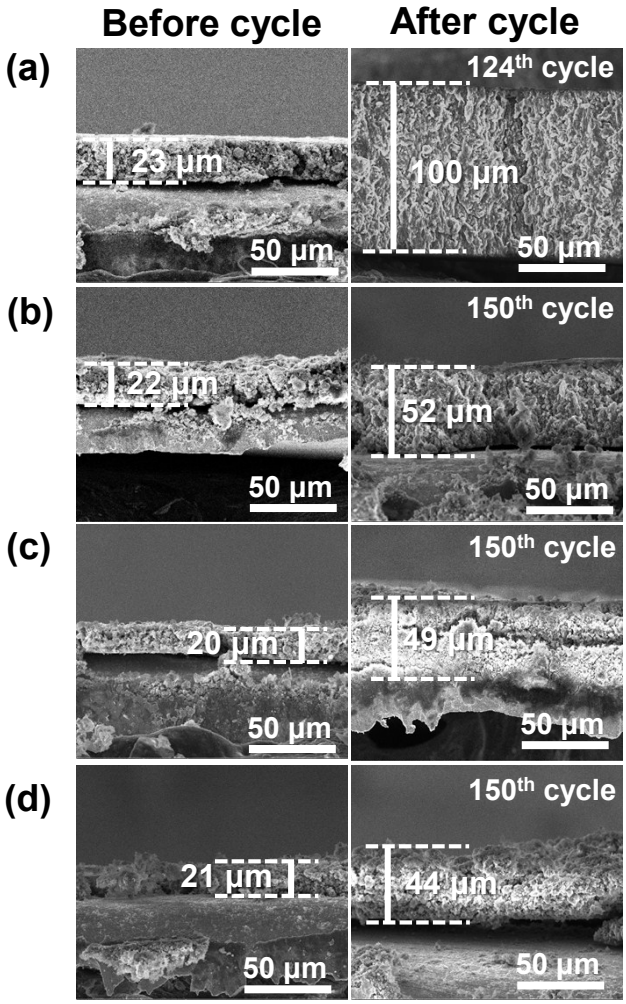

Fig. S9 Cross-sectional SEM images of electrode before and after cycle. (a) Chemically etched Al-Si electrode after 124th cycle and Si/Al_2O_3 electrodes thermally oxidized for (b) 10 min, (c) 30 min, and (d) 60 min after 150th cycle.

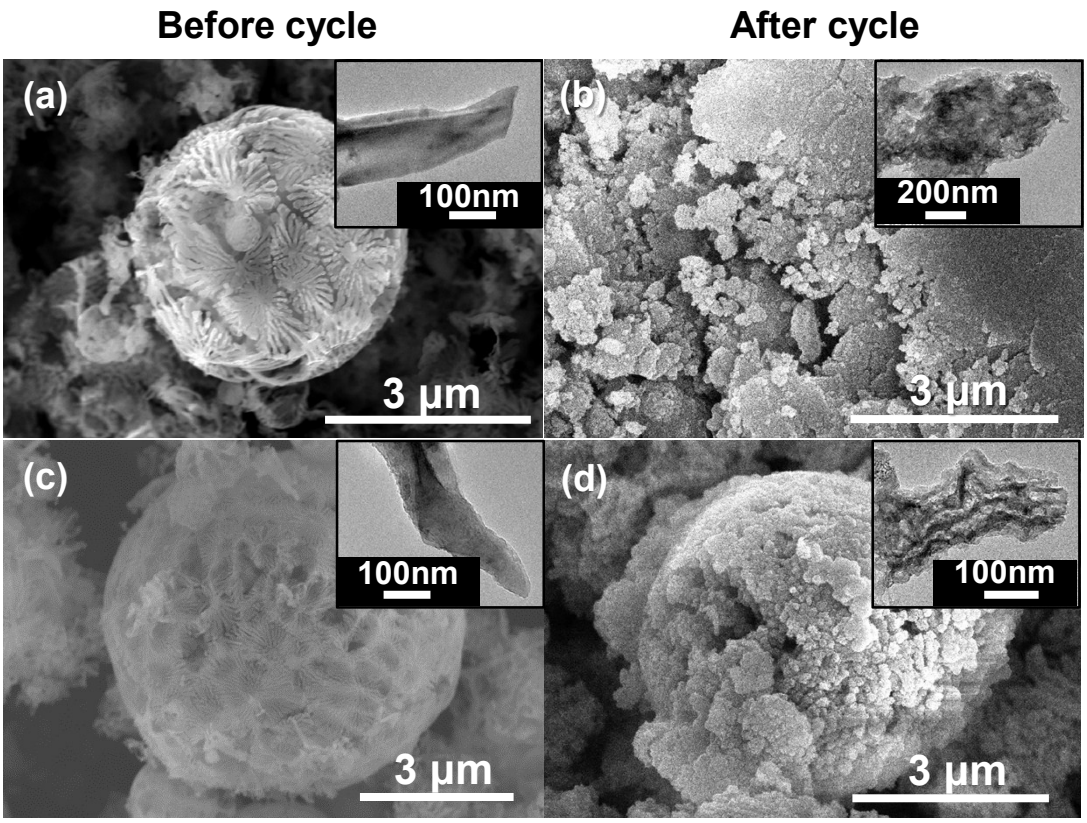

Fig. S10 SEM images of (a) 30 min-chemically etched Al-Si powder before and (b) after 120 cycles. Inset shows the corresponding TEM image of Al-Si frame before and after cycle. SEM images of 10 min-oxidized Si/Al_2O_3 particles (c) before and (b) after 120 cycles. The corresponding TEM image of Si/Al_2O_3 frame was seen in the inset before and after cycle.