

Supporting information for
Silicon Nanotube Battery Anodes

MI-HEE PARK¹, MIN GYU KIM², JAEBUM JOO³, KITAE KIM⁴, JEYOUNG KIM⁴,
SOONHO AHN⁴, YI CUI^{5**}, JAEPHIL CHO^{1*}

¹School of Energy Engineering

Ulsan National Institute of Science & Technology, Ulsan, Korea 689-805

²Beamline Research Division, Pohang Accelerator Laboratory, Pohang, Korea 790-784

³Department of Applied Chemistry, Hanyang University, Ansan, Korea 426-791

⁴Battery R&D, LG Chem, Ltd. 104-1, Moonji-dong, Yuseong-gu, Daejeon, Korea 305-380

⁵Department of Materials Science and Engineering, Stanford University, Stanford, California 94305, USA

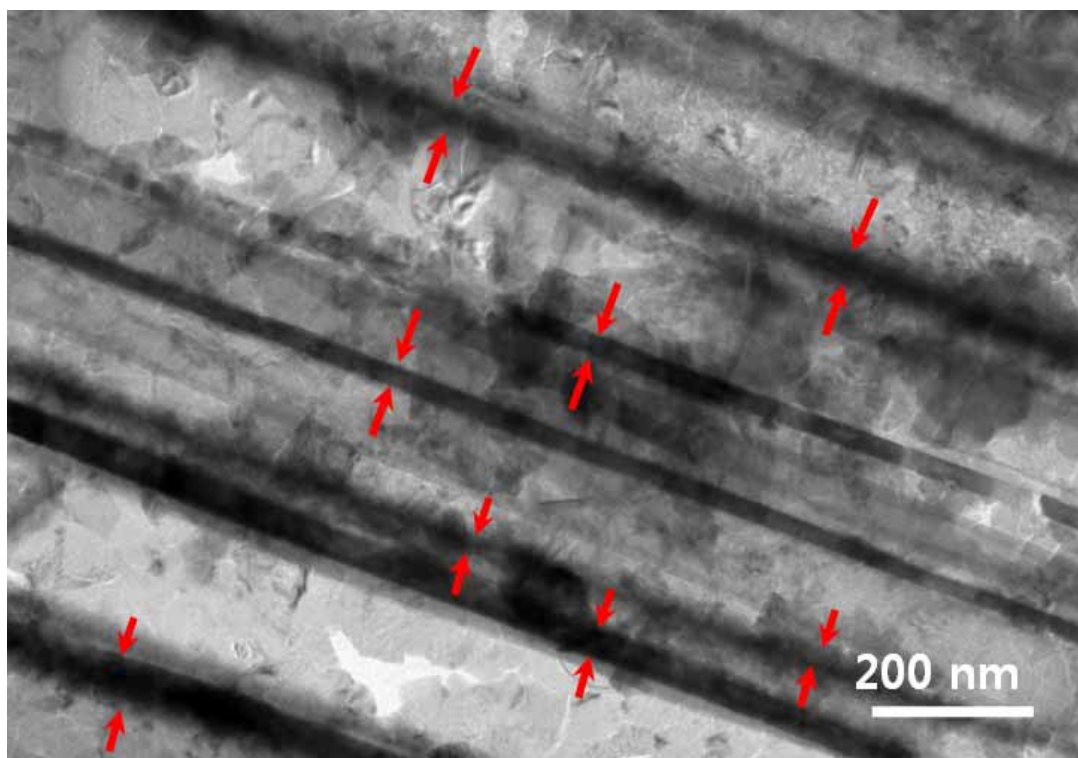
Experimental Methods

Butyl-capped Si solutions were prepared by reduction of SiCl_4 with sodium naphthalide according to a modified published method^{31,32}. SiCl_4 (30 g, 99.999%, Aldrich) and 200 g of Tri (ethylene glycol dimethyl ether) solvent were thoroughly mixed and added into a solution of sodium naphthalide (100 g). The resulting solution was heated at reflux at 400°C for 9 h. This solution was mixed with butyllithium (80 mL, 99%) and stirred overnight. The solvent and naphthalene were removed by using a rotary evaporator and by heating under vacuum at 120°C , respectively, and NaCl and LiCl byproducts were removed by partitioning between excess n-hexane and water. The final product was a pale-yellow viscous gel, which was then combined with n-hexane to decrease the viscosity. A porous anodized alumina membrane (Whatman, Anodisc, $\phi \sim 200\text{-}250\text{ nm}$) was immersed in Butyl-capped Si solution at 25°C for 2 min, and dried and annealed at 200°C for 2h under vacuum. This process (impregnation and drying) was repeated three additional times to obtain the Si-butyl/ Al_2O_3 nanotubes. The composite was further annealed at 1000°C for 3h in a vacuum, and the Al_2O_3 template was removed from the composite by treating with 3M NaOH solution for 3 hours and washing with distilled water and ethanol several times. Finally, the product was vacuum-dried at 120°C overnight.

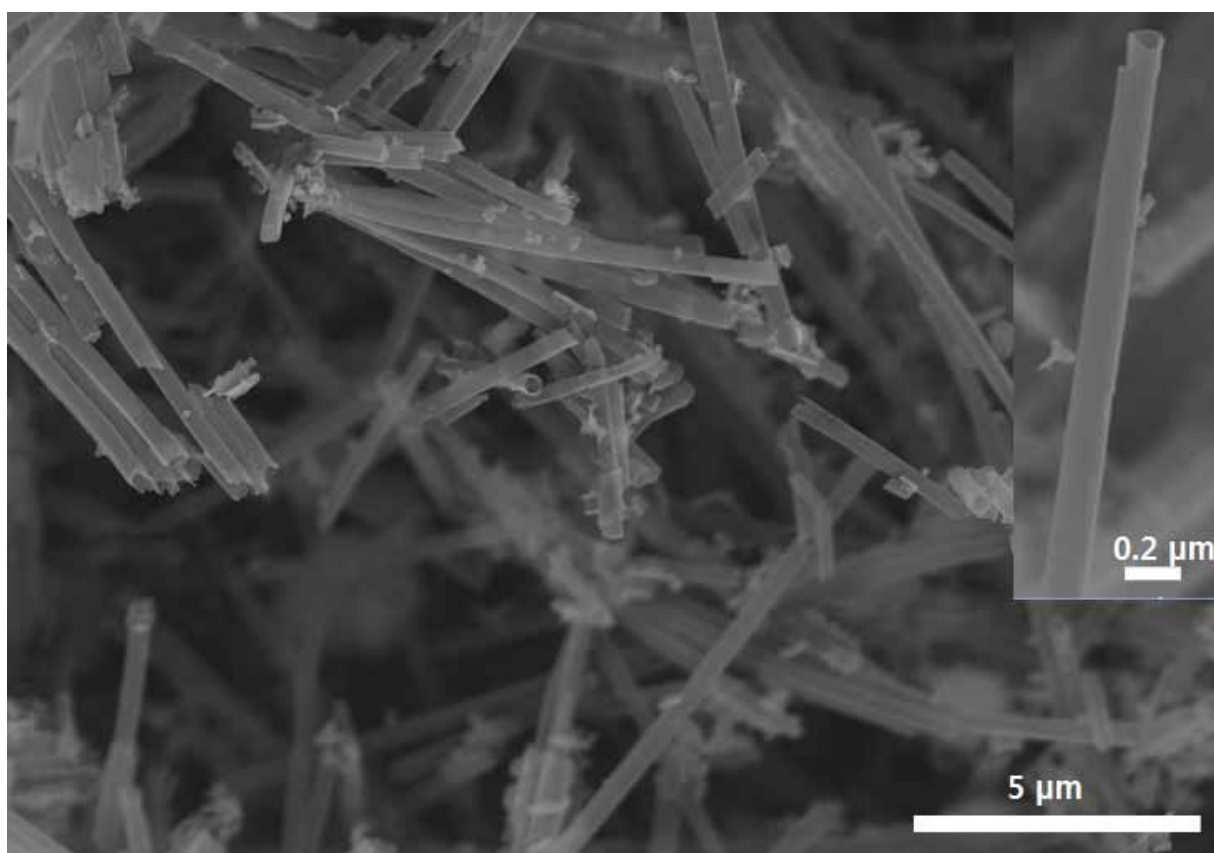
For the electrochemical tests, the electrode for the battery test cells were made of the active material, super P carbon black, and polyvinylidene fluoride (PVDF) binder in a weight ratio of 75 : 12 : 13. The slurry, prepared by thoroughly mixing a *N*-methyl-2-pyrrolidone (NMP) solution of polyvinylidene fluoride (PVDF), carbon black, and the active material, was coated onto Cu foil with a thickness of 30 μm . The coated electrode was dried at 130°C for 20 min and was roll-pressed. For half-cell testing, each anode with area of 1 cm^2 contained $\sim 10\text{ mg}$ of the nanotubes. The coin-type half cells (2016 R-type) prepared in a helium-filled glove box contained an electrode, a Li metal anode, a microporous polyethylene separator, and an electrolyte solution of 1 M LiPF_6 in ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1

vol. %). Pouch type Li-ion batteries with LiCoO_2 cathodes and Si nanotube anodes were assembled, and the nominal capacity was 20 mAh. The test cathode consisted of 92 wt % cathode material, 4 wt % polyvinylidene fluoride, and 4 wt % carbon black. Each cell was aged for 24 h at room temperature before commencing the electrochemical tests, and the internal resistance of as-prepared Li ion cells was 60 m Ω . The cycling tests of the coin-type Li ion cells were performed using a charge cutoff voltage of 4.3 V at various charge and discharge rates of constant current.

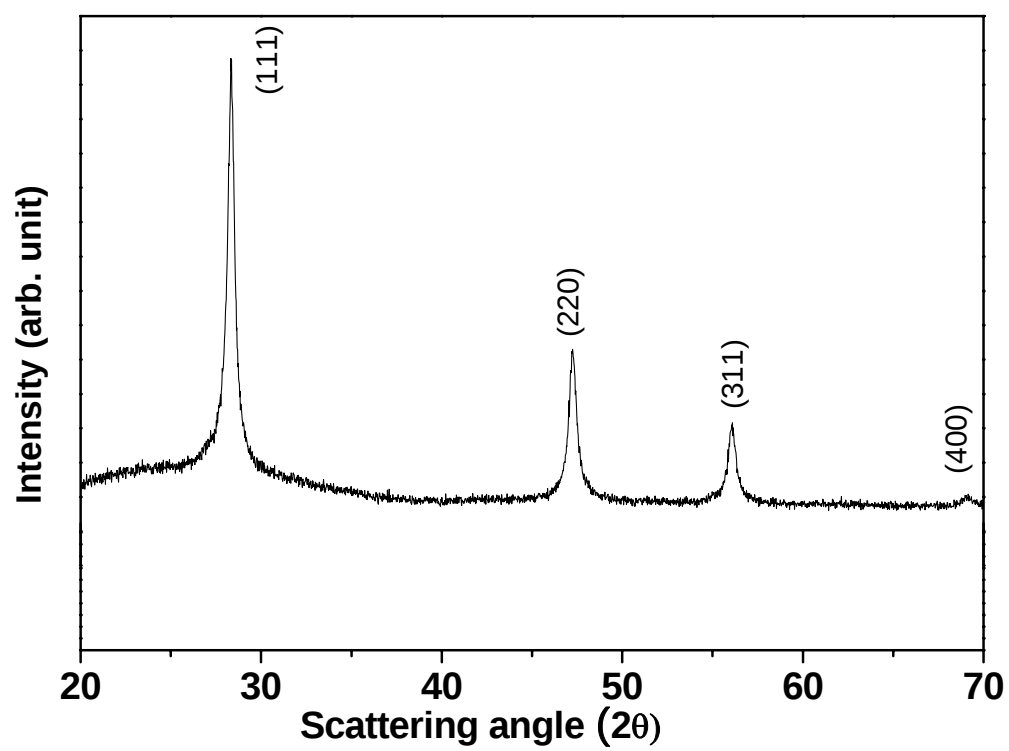
HRTEM samples were prepared by the evaporation of the dispersed nanotubes in acetone or hexane on carbon-coated copper grids. The field-emission electron microscope was a JEOL 2010F operating at 200 kV. The carbon concentrations were measured using a CHNS analyzer (Flash EA 1112, Thermo Electron Corp.) and was 10 wt % in the sample. Raman spectroscopy (JASCO, NRS-3000) was used to obtain the degree of graphitization of an amorphous carbon phase in the sample (ratio of D- and G-band of the carbon), using 633 nm laser excitation. In order to avoid laser heating effects, it was necessary to use low laser power density with a 20x microscope objective and an exposure time of 30 seconds. The laser spot diameter reaching the sample was about 2 μm . The laser power at the sample used in this study was 1 mW. The spectra were recorded at 2 cm^{-1} resolution between 3000 and 50 cm^{-1} .



S1. TEM images of the bundle of Si nanotubes. Arrows indicate the tubewalls.



S2. SEM image of Si nanotubes after ultrasonic treatment. An inset is expanded image of the single nanotube.



S3. X-ray diffraction pattern of Si nanotubes.