Electronic Supplementary Material (ESI) for Nanoscale.
This journal is © The Royal Society of Chemistry 2014

Electronic Supplementary Information

Novel design of ultra-fast Si anodes for Li-ion batteries: crystalline Si@amorphous Si encapsulating hard carbon

Chanhoon Kim,[a] Minseong Ko,[a] Seungmin Yoo,[a] Sujong Chae,[a] Sinho Choi,[a] Eun-Ho Lee,[b] Seunghee Ko,[a] Sang-Young Lee,[a] Jaephil Cho*[a] and Soojin Park*[a]

[a] *School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology, Ulsan 689-798, Republic of Korea*

[b] *Department of Chemical Engineering, Kangwon National University, Chuncheon, Kangwondo , 200–701 , South Korea*

* Corresponding authors: jpcho@unist.ac.kr, spark@unist.ac.kr

Experimental details

1) Synthesis of hard carbon: Agarose was purchased from Sigma-Aldrich. 5 wt% of agarose aqueous solution was prepared by stirring at 90 °C for 1 h. The solution became transparent and then it was moved to a petri dish for cooling at room temperature for 1 h. The resultant product was dried at 70 °C in a convection oven for 12 h. Subsequently, carbonization process of the agarose was conducted in a quartz tube furnace and ramping rate is 5 °C min^{-1}. The dried agarose film was heated to 200 °C for 1 h under argon atmosphere for stabilization. After the stabilization, temperature increased to 900 °C for 1h to enhance electrical conductivity and to increase the carbon quality.

2) Synthesis of HC@c-Si@a-Si: Amorphous Si (a-Si) was deposited on the HC through chemical vapour deposition using silane (SiH_4) as Si precursor. The HC particles were placed in a tube furnace and heated to 550 ˚C at a ramping rate of 5 °C min^{-1}. Once the temperature reached to 550 ˚C, SiH_4 (5% diluted in argon) was introduced into a tube furnace for 36 min with feeding rate of 50 sccm. In order to make stable SEI layer and increase electrical conductivity of HC@a-Si, carbon coating was conducted using acetylene gas. As-synthesized HC@a-Si particles were heated to 900 °C at a ramping rate of 10 °C min^{-1} in a quartz tube furnace under argon atmosphere. After temperature reached to 900 °C, we switched the gas in the tube furnace with acetylene gas (10% diluted in argon) and carbon coated on the surface of HC@a-Si for 3 min with 150 sccm.

3) Synthesis of HC/n-Si composite: Si nanopowder (~200 nm particle size, Sigma-Aldrich) was carbon coated in the same way of HC@a-Si and mixed with HC (Si/HC = 20/80, wt/wt).

4) Physical characterization: HC, HC/n-Si, HC@n-Si@a-Si were characterized by a scanning electron microscope (SEM, S4800, Hitachi) operating at 10 kV. The crystalline structure of HC and HC@n-Si@a-Si were analysed with a powder X-ray diffractometer (MPD) using Cu Kα radiation (λ=1.54056 Å) between 10° and 90° at a scan rate of 0.01° s^{-1}. Raman spectra were obtained from a JASCO spectrometer (NRS-3000, WITec) to investigate the characteristics of the HC and HC@n-Si@a-Si using a He-Ne laser operating at λ = 632.8 nm. A dual-beam focused-ion beam (FIB, Helios Nanolab 450HP, FEI) was operated by using Ga ions to observe the cross-section of the HC@n-Si@a-Si samples. To characterize the morphologies of the HC@n-Si@a-Si and carbon coated n-Si, high resolution transmission electron microscope (HR-TEM, JEOL, JEM-2100F) operating at 200 kV. Elemental analysis was conducted on elemental analysis instrument (Thermo Scientific, Netherlands).

5) Electrochemical measurements: Electrochemical test was performed using coin-type half and full cells (2016 R-type) assembled in an argon-filled glove box. The anodes (HC, n-Si/HC, HC@n-Si@a-Si) were composed of active materials, super P carbon black, poly(acrylic acid)/sodium carboxymethyl cellulose (50/50 wt%/wt%, Aldrich) binder at a weight ratio of 80:10:10. The resulting slurry was coated on a Cu current collector and dried in a vacuum at 150 °C for 2 h. The mass loading of active materials were ~5 mg cm^{-2} for HC and ~3 mg cm^{-2} for n-Si/HC and HC@n-Si@a-Si. $LiCoO_2$

cathodes were fabricated by coating an N-methyl-2-pyrrolidone (NMP, Aldirch)-based slurry comprising 95 wt% of $LiCoO_2$, 3 wt% of PVDF binder, and 2 wt% of super P carbon black on an aluminium current collector and the mass loading of $LiCoO_2$ was ~9 mg cm^{-2}. The coin-type half cells consisted of lithium metal as a counter electrode, a polyethylene separator, and 1.3 M $LiPF_6$ in ethylene carbonate/diethyl carbonate (EC/ DEC, 3/7 v/v) with 10 wt% fluoroethylene carbonate (FEC) as the electrolytes. The coin-type full cells consisted of synthesized anodes, LCO cathodes, and the same electrolytes and separator with half cells. The cell performance was examined using a cycle tester (Wonatech). The coin-type half cells were cycled at a rate of 0.2–20 C between 0.01 and 2 V, whereas coin-type full cells were cycled at a rate of 0.5–5 C between 2.3 and 4.1 V. The loading levels of active materials were 1.8 mAh cm^{-2} (anodes) and 1.5 mAh cm^{-2} (cathodes). The AC impedance (frequency range = 10 mHz to 1 MHz at an amplitude of 10 mV) and cyclic voltammetry (scan rate = 0.1 mV s^{-1} under 0–2 V) of cells were obtained using a potentiostat/galvanostat (VSP classic, Bio-Logic).

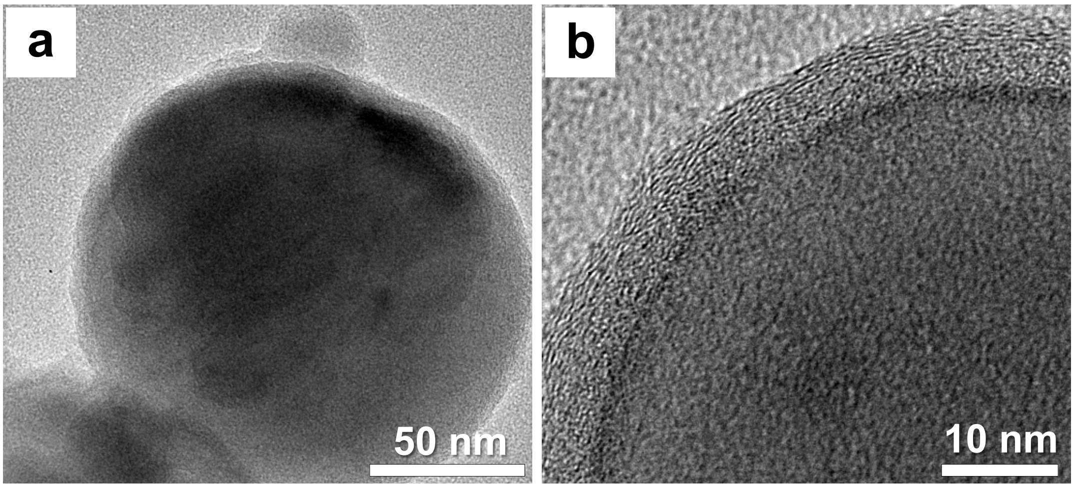

Fig. S1 The HRTEM images of a) the carbon coated nano-sized crystalline Silicon (n-Si, ~200 nm), b) the magnified n-Si with carbon coating layer of about 5 nm)

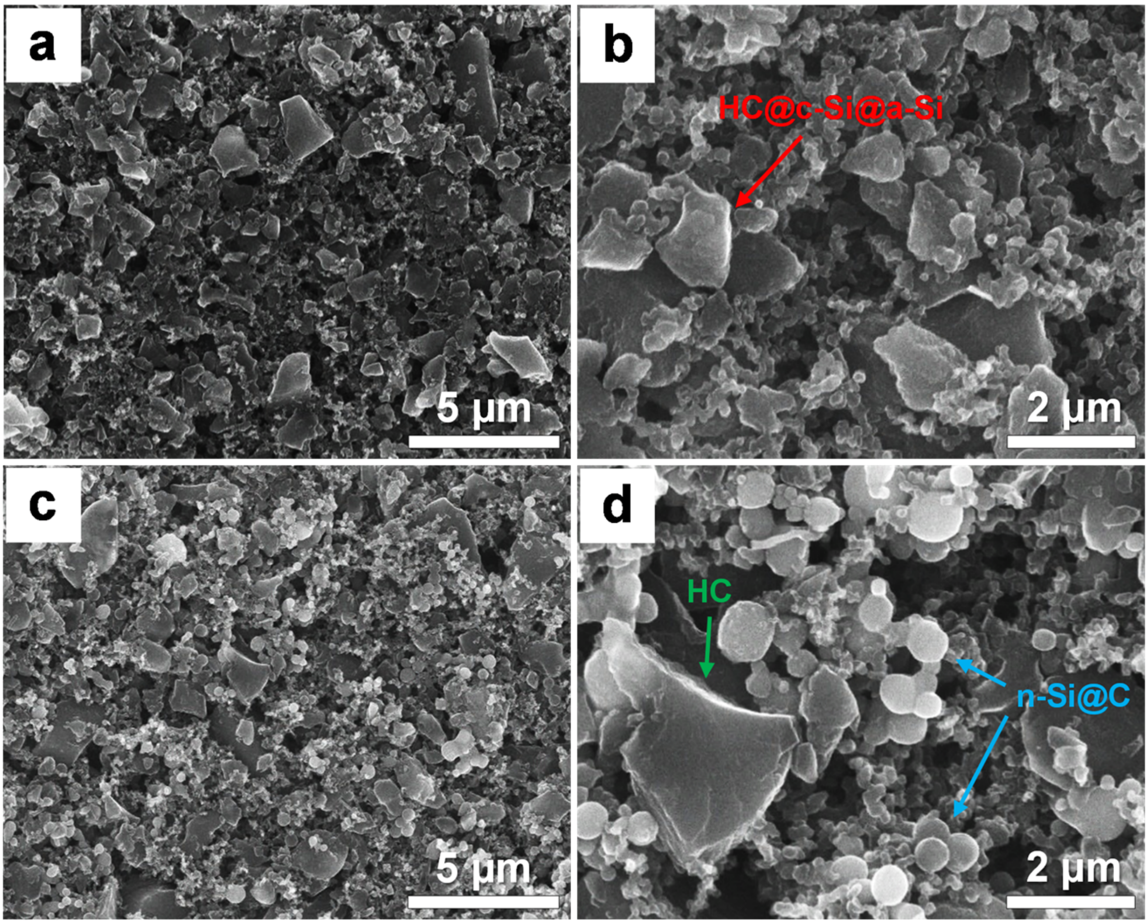

Fig. S2 The SEM image of pristine electrodes of a) the HC@c-Si@a-Si electrodes and b) the magnified HC@c-Si@a-Si electrodes; The SEM image of pristine electrodes of a) the HC/n-Si electrodes and b) the magnified HC/n-Si electrodes.

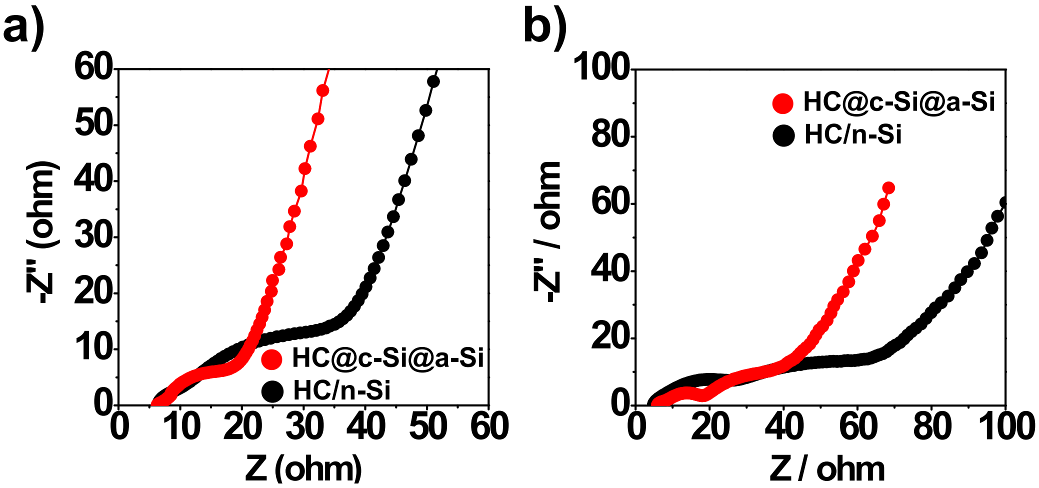

Fig. S3 Nyquist plots of the electrochemical impedance spectra of HC@c-Si@a-Si and HC/n-Si. a) after 1st cycle, and b) after 200th cycles at a rate of 1C.