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Micro-sized Silicon-carbon composite composed of carbon-coated sub-10 nm Si primary particles as high-performance anode materials for lithium-ion batteries

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1. Experimental

1.1 Synthesis of silsesquioxane

In a typical procedure, 25 ml triethoxysilane (96%, Aldrich) was added dropwise in 120 ml of HCl aqueous (0.1 M) with mechanical stirring at room temperature. After two hours continuous stirring, a large amount of white precipitate was observed and followed by filtration and then dried under vacuum at 60 ^{o}C overnight, obtaining white powder of silsesquioxane.

1.2 Preparation of micro-sized carbon coated silicon (Si-C) composite

The as-synthesized silsesquioxane precursor was placed in a quartz reaction boat and transferred to a high temperature tube furnace. Calcination was carried out at defined peak processing temperatures of 1200 ^{o}C with heating rate of 5 ^{o}C/min in a reducing atmosphere (5% H_2/95% Ar). After cooling to room temperature, the Si/SiO_2 solids ranging in color from white to dark amber were obtained. The resulting Si/SiO_2 powder was grounded and then suspended in the mixture of hydrogen fluoride acid/hydrogen chloride (6:1, v/v) to remove SiO_2 to get silicon particles. Bare silicon particles were coated with a carbon layer though thermal decomposition of acetylene gas at 600 ^{o}C for 20 min and further carbonization at 800 ^{o}C for 30 min. The carbon content is about 3.8 wt% in the micro-sized Si-C composites, which is based on the mass changes of the silicon before and after coating.

2. Materials Characterization

The structure of the as-prepared composite was characterized by X-ray diffraction on a Rigaku Miniflex II analyzer using Cu Kα radiation. XPS measurements were carried out with a Kratos XSAM800 Ultra spectrometer. The surface morphologies of the composite particles were investigated with a JEOL JSM-2010 TEM microscope. Raman spectroscopy was conducted with a WITec CMR200 confocal Raman instrument.

3. Electrochemical Measurement

Electrochemical tests were performed by using 2016 coin-type half cells assembled with lithium metal as the counter in Argon filled glove box. The composite cathodes were prepared by coating slurries containing active materials (60 wt.%), Super P acetylene black (20 wt.%), and polyacrylic acid binder (20 wt.%) on copper foil. The typical loading of the electrode is 1 mg/cm^2. The electrolyte consisted of 1 mol/L $LiPF_6$ in a mixture of ethylene carbonate, diethyl carbonate and dimethyl carbonate (EC: DEC: DMC, 1 : 1 : 1 by volume) and fluoroethylene carbonate (FEC,

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10 vol.%). The FEC additive can increase the cycling efficiency of silicon anodes, due to the formation of a more stable SEI layer. Galvanostatic cycling test was carried out at different constant current densities between 0.01 and 1.5V vs Li/Li^+ on a BT2000 battery testing system (Arbin Instruments, USA). The specific capacity was calculated on the basis of the weight of the active materials.

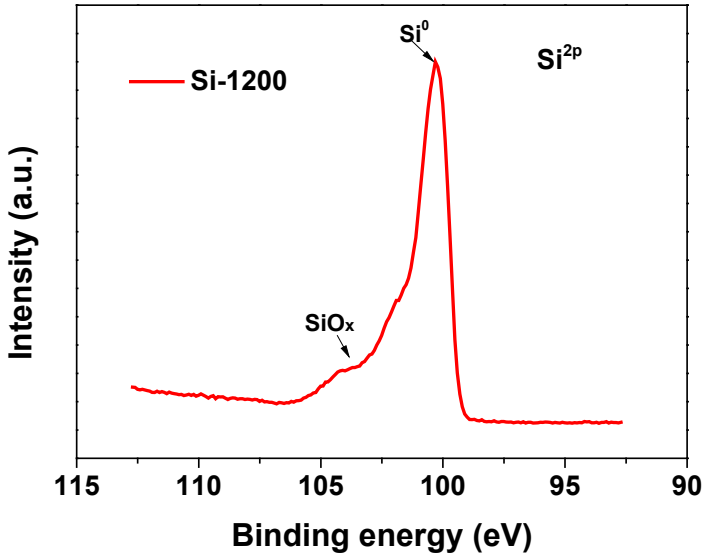

Fig. S1. X-ray photoelectron spectroscopy (XPS) of Si_{2p} peak for the Si-1200. This spectrum is divided into two main regions. The principal peak, located at ~100 eV, is assigned to bulk silicon, while the other peak (~102-105 eV) is ascribed to SiO_x ($x \leq 2$).[S1-S3]

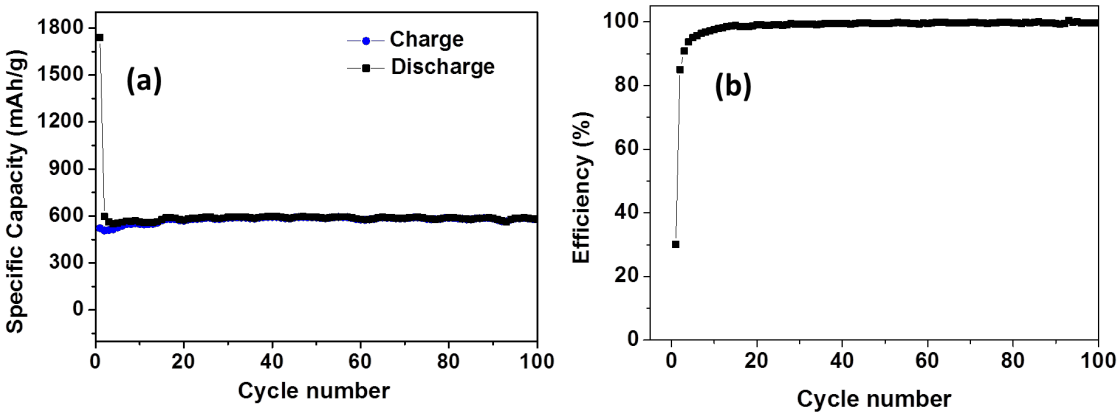

Fig. S2. (a) The cycling stability and (b) Coloumbic efficiency of Si/SiO_2-C composite anode at 400 mA/g in the potential window of 0.01V-1.5V vs. Li^+/Li.

Reference

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