Supplementary information

A Dimensionally Stable and Fast-Discharging Graphite-Silicon Composite Li-ion Battery Anode Enabled by Electrostatically Self-Assembled Multifunctional Polymer-Blend Coating

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Figure S1. Fundamental chemical unit of (a) polydially dimethylammonium chloride (PDDA) and (b) polysodium 4-styrenesulfonate (PSS).

S2: Experimental:

<u>Preparation of Si@G composite containing Si nanoparticles dispersed on natural</u> <u>graphite:</u>

100 g of Natural graphite (NG, Long Time Technology Corp.) powders were

dispersed in a 130 ml aqueous solution added with 15 g of PDDA solution (Aldrich,

Solid content = 20 wt.%, Mw = 200,000) for 30 min and then dried at 95 °C (PDDA-G). 5 g of Si nanoparticles were dispersed in a 65 ml aqueous solution added with 6.7 g of PSS solution (Aldrich, Solid content = 30 wt.%, Mw = 200,000) for 30 min and then dried at 95 °C (PSS-Si). The PDDA pre-coated graphite and PSS coated Si in a weight ratio of 20:1 were dispersed in aqueous solution for 15 min and finally dried at 100 °C in a vacuum oven at 100 °C to obtain the Si@G powder.

Preparation of polymer and carbon coated Si@G (P&C-Si@G):

100 g of the as-prepared Si@G composite powder was mixed with 10 g of coaltar pitch by solid-mixing and then calcined in a furnace at 1100 °C for 6.5 hours under a N₂ atmosphere with a heating rate of 2 °C min⁻¹ to obtained carbon-coated Si@G (C-Si@G). For the final polymer coating, 100 g of C-Si@G powder was dispersed in a 130 ml aqueous solution added with 4 g of PDDA solution for 30 min and then dried at 95 °C. 100 g of the resulting powder PDDA pre-coated carbon-coated Si@G powder was dispersed in a 130 ml aqueous solution added with 7 g of PSS solution for 15 min and finally dried at in a vacuum oven at 100 °C to achieve P&C- Si@G.

Electrode and cell preparation

Electrodes were prepared from the slurry comprising 93.3 wt.% (on the dry basis) of active materials, 3 wt.% carbon black (Super-P) and 1.2 wt.% carboxymethyl cellulose sodium (CMC) and 2.5 wt.% styrene-butadiene rubber (SBR) as binder dispersed in distilled water. After thoroughly mixed, the slurry was coated onto a copper current collector, and dried under vacuum at 120 °C for 12 hr. The electrode was then pressed and punched to disks of 13 mm in diameter. The active-material loading is ca. 5 mg/cm² with a density of ca. 1.2 g/cm³.The resulting electrodes were assembled into coin cells (CR2032), which contained a metallic Li foil as the counter

electrode and electrolyte solution. The electrolyte was 1 M LiPF₆ in a 1:1:1 (in vol.) mixture of ethylene carbonate/ethyl methyl carbonate/dimethyl carbonate with 1 wt.% vinylene carbonate (VC) and 5 wt.% fluoroethylene carbonate. The cells were assembled in a glove-box filled with argon gas with dew point lower than -40 °C. Charge/discharge cycling tests were carried out on an Arbin Battery Test (BT-2000). For cycling test, discharge (lithiation) was conducted at 0.1C by a constant current-constant voltage (CC-CV) mode and then charged at 0.1 C by a CC mode during the first ten cycles. After ten cycles, the current increased to 0.2 C (0.0 - 1.5 V, versus Li/Li⁺).

Material and electrochemical Characterizations

Microstructural analyses were carried out using scanning electron microscopy (SEM, FEI/Nova230) and EDX analysis was conducted on an EDAX system attached to the Tecnai F20 microscope. XRD measurements were conducted on a Rigaku D/max2500 diffractometer using CuK α radiation. Electrode thickness was determined by Vernier calipers (ABSOLUTE Digimatic Caliper, Series 500/Mitutoyo).



Figure S3: Coulombic efficiency versus cycle number for the C-Si@G and P&C-

Si@G electrodes.



Figure S4. SEM micrographs of (a) C-Si@G and (b) P&S-Si@G after drying mixing in a 3D-mixer. Part of the C layer of C-Si@G shown in (a) breaks after collision during mixing, due to the brittle nature of the C layer. The final polymer coating in the P&C-Si@G shown in (b) protects the C-layer from breaking.



Figure S5: Nyquist plots of P&C-Si@G and C-Si@G measured at the end of 100 cycles. It is shown by the total widths of the arcs along the Z'- axis direction that the C-Si@G electrode has a greater overall (thin-film + charge-transfer) resistance than the P&C-Si@G after the cycling.



Figure S6. Morphologies of the C-Si@G and P&C-Si@G electrodes after 100 cycles. It is shown that the C-Si@G electrode has a thicker SEI than the P&C-Si@G electrode after the cycling.