Electronic Supplementary Information

Electrodeposited 3D Porous Silicon/Copper Film with Excellent Stability and High Rate Performance for Lithium-Ion Batteries

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1. Experimental details

Preparation of 3D porous Cu foam film

Copper foil (Alfa Aesar, 99.8%) was cleaned successively with a diluted HCl aqueous solution, with acetone and with distilled water for 10 minutes each under ultrasonication. Copper foils were placed in an electrolytic cell and set as the counter electrode and the working electrode. The distance between the counter and the working electrodes was kept at 1 cm. A silver/silver chloride (Ag/AgCl) electrode was used as the reference electrode. The electrolyte was an aqueous solution containing 0.1 M $CuSO_4$ and 1.5M H_2SO_4. For the copper deposition process, a constant current (1.5A/cm^2) was applied to the cell using a potentiostat (CompactStat, Ivium Technologies, Netherlands) for 30s to 60s. Electrochemical deposition was performed in a stationary electrolyte solution (without stirring or bubbling). After the deposition process, the surfaces were cleaned with water and acetone, dried in a 60 ^oC oven for 1h, and kept in an Ar-filled glove box.

Fabrication of porous Si/Copper film

All experiments were carried out in an Ar-filled glove box with less than 1 ppm of both water and oxygen. A VMP potentiostat/galvanostat (Biologic, France) was used for the electrochemical experiments. For silicon electrodeposition, a porous Cu foil, Pt mesh and Pt or Ag wire were used as the working, counter and quasi-reference electrode. Silicon was electrodeposited from a bath with 0.1 M $SiCl_4$ and 0.1M tetrabutylammonium chloride (TBACl) in propylene carbonate (PC). The electrodeposition process was carried out in a controlled

potential mode (deposition potential:-2 V vs. Ag QRE).

Film characterization

The morphologies of the film were observed by field emission scanning electron microscopy (FE-SEM, Tescan Mira 3 LMU FEG, Czech Republic). Transmission electron microscopy (TEM) was performed with a FEI Tecnai G2 (Eindhoven, Netherlands) at an accelerating voltage of 10 kV. The TEM samples were prepared by dropping dispersed in ethanol solution after scratching from the Cu substrate onto a carbon-coated, 200 mesh copper grid.

Coin cell assembly and electrochemical measurements

The electrochemical performance of the porous silicon electrodes was tested in a coin cell (2032) using lithium metal foil as the counter electrode and polypropylene film (Celgard 2400) as the separator. The coin cells were assembled in an Ar-filled glove box. The electrolyte consisted of a solution of 1M $LiPF_6$ in ethylene carbonate (EC)/dimethylene carbonate (DMC) (1:1 vol%). The cells were charged (delithiation) and discharged (lithiation) using a BioLogic system in galvanostatic mode operating between 0.01 V and 1.6 V vs. Li/Li^+.

2. SEM Images

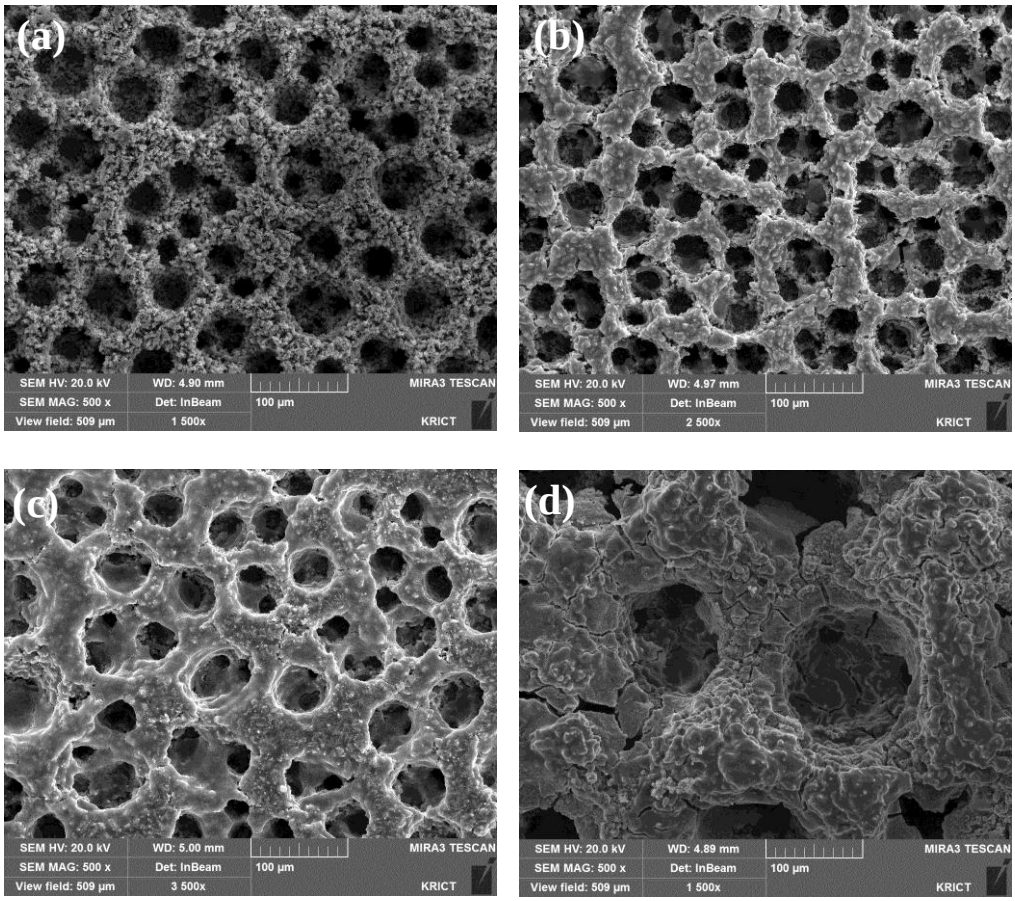

Figure S1. Scanning electron microscopy (SEM) images of various thickness of silicon layers on porous copper films created by constant voltage (-2V). (a) 4 C, (b) 10 C, (c) 20 C and (d) 46 C