

Electronic Supplementary Information

Extreme-rate capable and highly stable SiCO-TiO₂ hybrids for Li on battery anodes

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1 Materials Processing

The composition was designed so as to have 75% (by volume) of the pyrolyzed SiCO phase and 25% of TiO₂. The density of SiCO and TiO₂ was taken as 2 and 4.23 gm cc⁻¹, and batch calculations was carried out from precursor materials 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (TTCS, Gelest, NJ, USA) and TiO₂ nanopowders (Sigma-Aldrich). The TiO₂ was of 100% anatase phase of 25 nm average particle size. The required amount of TTCS was taken in a test tube to which 1% dicumyl peroxide, radical initiator, was added for crosslinking of the oligomer. TiO₂ nanoparticles were slowly dropped into the TTCS solution with mechanical agitation, and followed by ultrasonic agitation for homogeneous dispersion of the slurry. To adjust the consistency of the slurry, some amount of acetonitrile was used. Subsequently the slurry was polymerized in a furnace (Thermolyne, IA, USA) at 380 °C in flowing Ar environment. The polymer cake was pulverized using ZrO₂ media in a jar mill, and the powders were calcined between 800 °C in flowing Ar. The resulting black powder was used for battery testing.

2 Materials Characterization

N₂ adsorption-desorption experiments were carried out to study the porosity and pore size distribution of the bulk SiCO powders as well as the TiO₂-SiCO hybrids. The isotherms were collected at 77 K with relative pressure [$\frac{p}{p_0}$] between 0.05 to 0.99 (Micromeritics ASAP 2010, Norcross, GA, USA). Samples were degassed at 220 °C overnight before analysis. Specific surface area was computed by the Brunauer-Emmet-Teller (BET) model. X-ray diffractograms of the powders was recorded in transmission mode (Anton Parr) and the data over 5-40° 2 θ were analyzed. Barrett-Joyner-Halenda (BJH) model was applied for calculating the pore size, pore volume distribution and average pore diameter. To study

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the morphology of the powder composites and the anode, scanning electron microscopy (SEM, JEM 7100, JEOL, Japan) of the powders and the calendared anode was performed in secondary electron mode. Additionally, the cell was opened after severe cycling (3000 cycles), and the anode foil washed with dimethyl carbonate (DMC) for microscopy of the cycled anode.

3 Electrochemical Testing

The electrochemical response was measured with CR-2032 type coin cell assemblies in half cell configuration. First the SiCO-TiO₂ composite powders, acetylene black, and polyvinylidene fluoride (PVdF) were mixed in a ratio of 60:20:20 with the help of 1-methyl-2-pyrrolidinone in an acid washed agate mortar. The slurry was cast onto a Cu foil (Goodfellow) by doctor-blade process, dried in an oven, and circular electrodes were punched out. The electrodes were further dried on a hot plate overnight in neutral atmosphere for degassing. The half cells were assembled inside a glove box with <1 ppm of moisture and oxygen levels. LiPF₆ (1 M) dissolved in a solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) in 1:1 ratio (Novolyte, USA) was used as the battery electrolyte. Trilayered polymeric microporous membranes (Celgard, USA) soaked in the electrolyte was used as the separator between the working electrode, and Li foil (Alfa Aesar) was used as the counter electrode. Galvanostatic charge-discharge cycles were recorded in a battery tester (BT 2000 Arbin Instruments, USA). Throughout this paper we have reported electrochemical data from symmetric current cycling; the current in the insertion cycle was unchanged in the extraction cycle. It may be noted that during high current cycling, capacities obtained in symmetric cycling are underestimated due to kinetic effects.

4 C-Rate

The nomenclature of C-rate followed in this paper is slightly different than what is generally followed in the literature. Since polysiloxane derived SiCO ceramics are amorphous in nature it is difficult to assign the number of lithium ions intercalated for every molecular unit of the anode (SiCO). Additionally, it also changes with pyrolysis temperature, type of preceramic polymer, and composition. Instead, we have followed a simple definition for C-rate: the ration of current density to the specific capacity of the materials at the said current density. The C-rate (nC) can be written as per the following equation:

$$n = \frac{i_a}{q_a}$$

where n is in hr^{-1} , and i_a is the current density in mA g^{-1} and q_a is the specific capacity in mAh g^{-1} .

5 Supplementary Figures

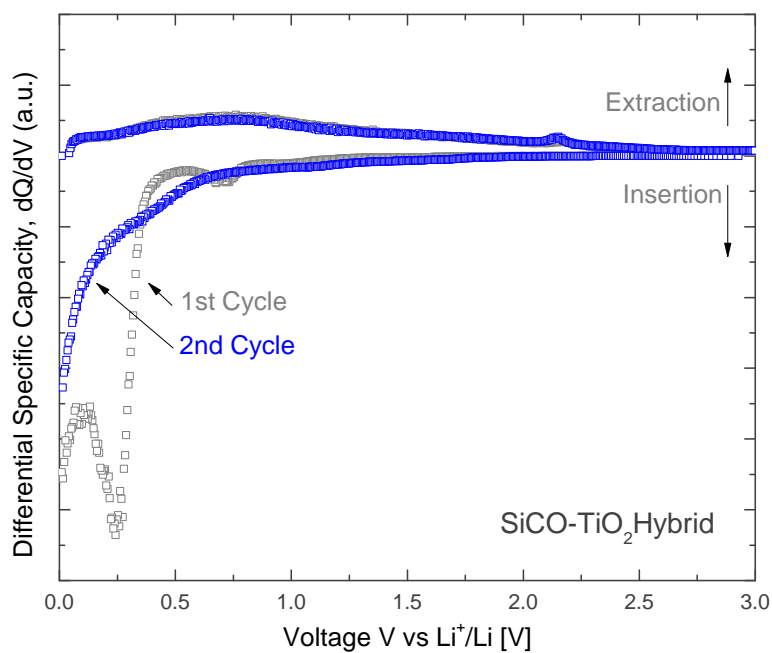


Figure 1: Differential specific capacity of SiCO-TiO₂ powders

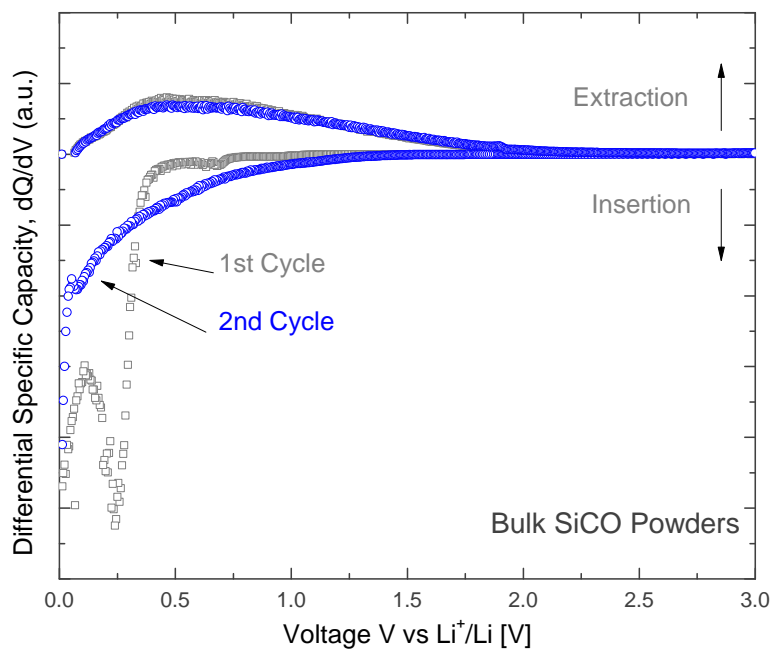


Figure 2: Differential specific capacity of bulk SiCO powders

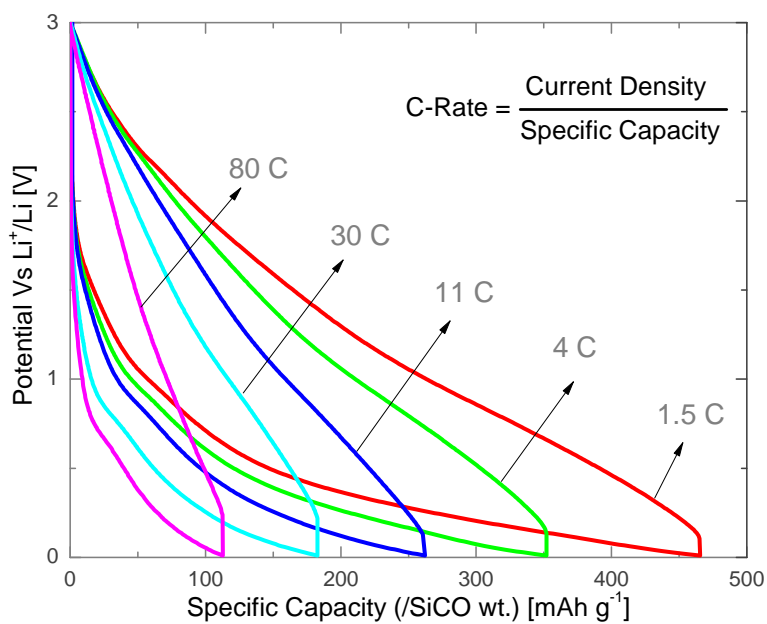


Figure 3: Capacity-voltage profiles of the cell under galvanostatic cycling at the said current rates.

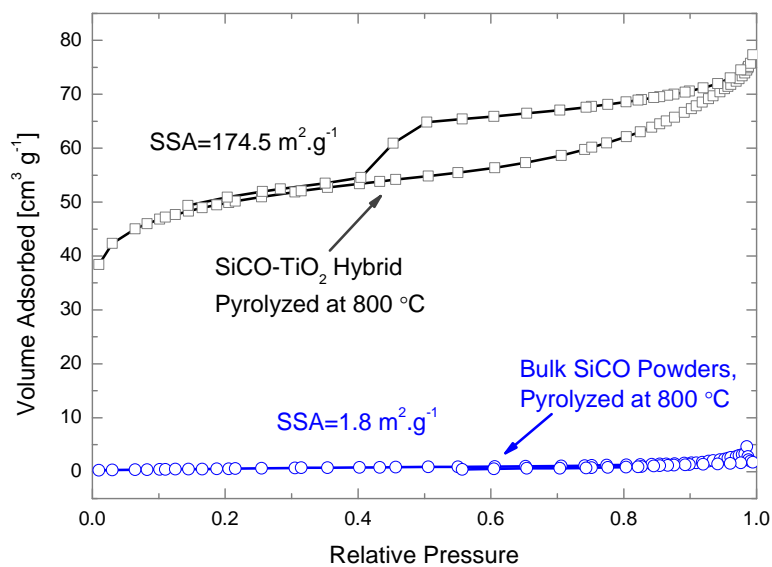


Figure 4: N₂ adsorption-desorption isotherms of bulk SiCO powders and SiCO-TiO₂ hybrids (both pyrolyzed at 800 °C)

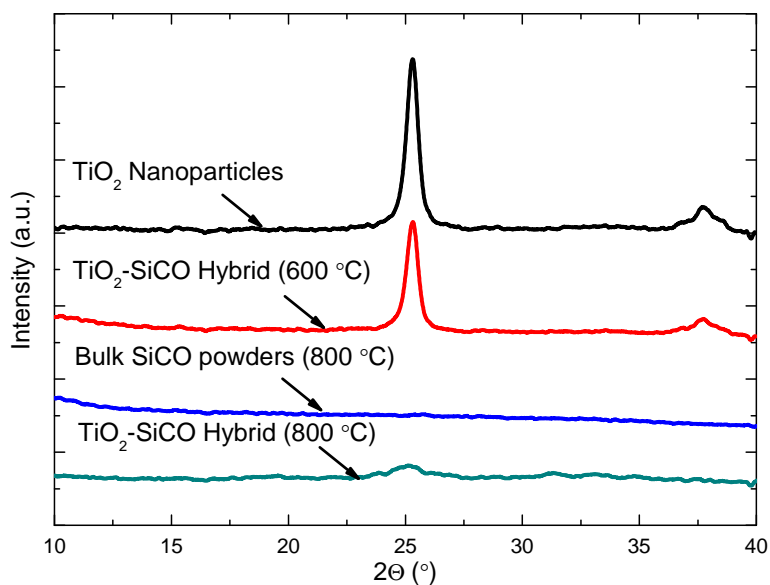


Figure 5: X-ray diffractograms of SiCO (800 °C pyrolyzed), SiCO-TiO₂ (pyrolyzed at 600 °C), SiCO-TiO₂ (pyrolyzed at 800 °C), and TiO₂ nanoparticles.