Improvement of cycling properties for porous Si powder prepared by acid etching Al-Si alloy powder

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As a promising anodic material, Si presents high theoretical capacity (4200mAh·g⁻¹), but the problems of severe volume expansion (>300%) during charge process and low electrical conductivity restrain its further development. In our previous paper we developed a novel, simple and low cost method for preparing porous Si powder [1]. The porous silicon powder was prepared by acid etching Al-Si alloy powder (consisted of 80% Al : 20% Si, for metallurgy use, Jieweixin Co., China). The as-prepared porous silicon particle composed of silicon nano-bars with diameter about 50nm, length of 1.5µm, and intertwined. It was measured that the porous silicon powder was well crystalline, with specific surface area 102.8m²/g, and two kinds of nano porous. The charge – discharge properties of porous Si electrode was tested in coin cell (Model CR2016) with a metal lithium foil as counter electrode, in the voltage region of 0.01-1.5V.

The charge/discharge cycling properties of pure porous silicon powder is not satisfied yet, but it can be improved by following methods:

1. Use of additive FEC (fluoroethylene carbonate): For as-prepared porous Si electrode in 1M LiPF₆/EC:DMC = 1:1 (V/V) + 15% FEC electrolyte, with current density of 100 mAh/g, at 258th cycle it discharge capacity was 1368mAh/g, (Ref. 1).

2. Use of additive VC (vinylene carbonate): In electrolyte 1M LiPF₆/EC:DMC (1:1) + 2% VC, porous Si electrodes, which consisted of porous-Si : carbon black: binder = 7:2:2, presented more stable behavior, than that of in additive-free electrolyte, as shown in Fig.1. In the solution containing 2% VC, at 117th charge-discharge cycle its discharge capacity was 807 mAh/g, while in additive-free electrolyte the discharge capacity decreased rapidly to 364 mAh/g after 35 cycles, at current 100mA/g.

3. Surface modified by nano-Cu particles: At first, the surface of porous-Si powder was sensitized by Sn²⁺, and then activated by Ag⁺, finally nano-Cu particles coated on the surface of porous nano-Si fibers (see Fig.2) by chemical deposition method. The nano-Cu particles could increase the conductivity of electrode and inhibit the combination process between nano Si fibers during charge process. Therefore improve its high rate discharge ability. In the case of Cu-coated porous-Si : carbon black: binder = 7:1.5:1.5, in 1M LiPF₆/EC:DMC (1:1) + 1.5% VC solution, the Cu-coated porous Si electrode presented a discharge capacity about 1100 mAh/g in 35cycles, at current 1A/g, as shown in Fig.3.

4. Use of graphene as conduction material instead of conducting carbon: Fig.4 shows the cycling behavior of porous-Si electrode, which consisted of porous Si : graphene : binder = 7:1.5:1.5, in 1M LiPF₆/EC:DMC (1:1) + 1.5% VC electrolyte, at current 200 mA/g. At first cycle the discharge capacity was 1580 mAh/g, and then it increased to 2000 mAh/g gradually. This phenomenon may attribute to the structure rearrange of porous nano-Si powder during charge/discharge process.

References:
1. ZY Jiang, CL Li, SJ Hao, K Zhu, P Zhang, Electrochimica Acta, 115 (2014) 393-398