Porous silicon derived from waste solid of organosilane industry as anode materials for lithium-ion batteries
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Among the various anode materials, silicon has attracted considerable attentions due to its much higher theoretical specific capacity (about 4200 mAh g⁻¹) than graphite (about 372 mAh g⁻¹) and satisfactory potentials for lithium insertion and extraction (≤ 0.5 V vs. Li/Li⁺) [1]. Nevertheless, the practical use of Si has been hindered by its poor performance due to its low intrinsic electric conductivity and the significant volume change during the alloying/dealloying processes of Si with lithium, which can result in pulverization of the initial particle morphology and causes the loss of electrical contact between active materials and the electrode framework [2-3]. A lot of efforts have been made thus far to overcome these problems, such as preparation of Si/C composites, fabrication of some types of nanostructured silicon materials including silicon nanowires [4], silicon nanotubes [5], silicon hollow nanospheres [6] and dispersion silicon in an active/inactive matrix [7]. In addition, more attention has also been paid to the porous Si-based anode materials. Its internal porosity would supply sufficient inner free space to absorb the large volume expansions and ease the internal strain to prevent the particle pulverization and thereby enhance the cycling stability. However, the synthetic methods of the porous Si-based anode materials which have been reported are complicated, costly and difficult to scale up. Herein, we report the porous silicon materials which are obtained from the waste solid of organosilane industry. Methylchlorosilanes are synthesized by the reaction of Si powder with chloromethane via copper or copper compounds as catalysts. During this process, a large amount of waste solid composed of 75-90 wt% of porous Si is inevitably produced due to the limitation of reaction kinetics and thermodynamics. The waste solid contaminates the environment and is not easy to store. The residual porous Si particles have not been utilized valuably. In this work, we use the residuals as raw materials to make porous silicon particles as anode materials for lithium-ion batteries by simple and low cost method.

The waste solid is firstly washed with sulfuric acid solution to remove the metal impurities and then is milled with planetary ball mill to obtain purified Si particles. Electrochemical measurements were carried out with 2025 coin cells assembled in an argon-filled glove box with lithium metal as the counter electrode. Charge-discharge performances were tested between 1.5 V-0.01 V at a current density of 100 mAg⁻¹. The working electrode was prepared by mixing porous silicon material, carbon black and sodium alginate in a weight ratio of 6:2:2. The electrolyte was 1M LiPF₆ in the mixture of ethylene carbonate(EC) and dimethyl carbonate(DMC) (1:1 in volume ratio).

The waste solid has a high content of Si, about 82.3 wt%. After the acid-washing treatment, the Si content can reach 98 wt%. Fig. 1 shows the XRD pattern of the waste solid after acid washing, all peaks are solely assigned to Si, further indicating its high purity. After the acid-washing treatment, the specific surface area of the sample, as determined by using BET measurements, is 20.2 m²g⁻¹, indicating it has a porous structure. Its HRTEM image in Fig. 6 reveals the well-resolved lattice planes with a distance of about 0.313 nm, corresponding to the (111) planes of the Si crystal. Fig. 7 shows the cycling performance of the porous silicon derived from the solid waste. It exhibits the higher initial discharge and charge specific capacity of 2746 mAhg⁻¹ and 2025 mAhg⁻¹ respectively. Although further work is still necessary to improve the capacity retention of the sample, these results demonstrate that using the porous silicon derived from the waste solid as a promising anode material for lithium-ion batteries is feasible.

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