Copper Sulfur Nanowires Coated Silicon as an Anode Material for High Performance Lithium Ion Batteries

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The increasing demand of vehicle electrification as well as renewable energy have stimulated large amount research on high energy density materials for lithium ion batteries (LIB). Among them, silicon is a most promising alternative material due to its remarkably large theoretical charge capacity (4200 mAh). However, there are some critical disadvantages, such as high electrical resistivity and drastic volume change during Li+ insertion and extraction. The high volume change of Si materials disrupted the integrity of the composite electrode, caused rapid capacity fade [1-2]. In this work, conductive fibers were grown on the surface of Si particles to create both electrical connections between the Si particle and additional spaces for the expansion of Si during lithiation process.

CuS nanowire coated silicon particles were prepared by a one step process, template- and surfactant-free method in ethyl glycol (EG)-dimethyl sulfoxide (DMSO) mixture solvent. The as-prepared CuS coated Si particles was studied as anode materials for rechargeable LIBs. The anodes were fabricated by mixing copper sulfur nanowires coated Si, supper C 65, and carboxymethyl cellulose (CMC), Polyvinyl Alcohol (PVA) at a weight ratio of 50:25:20:5 in water. The electrolyte solution was made of 1 M LiPF6 in EC/DEC (1:1 w/w) with 30% FEC. The morphology and structure of the as-prepared products were studied by SEM, TEM and discussed (Fig.1). The results reveal that the Si particles are coved with CuS nanowires uniformly both on the surface and between particles. The CuS nanowires function as a buffer to overcome mechanical breaking of Si during the volume changes



Fig.1 SEM and TEM images of CuS nanowires coated Si.

The CV test (Fig. 2) showed a reduction of CuS materials around 1.5V, followed by SEI formation around 0.8V during the first reduction curve. The peaks at 0.25 and 0 V are lithiation of Si material. The peaks at 0.25 and 0.5V at the oxidation voltage sweep are delithiation of the Si material. The reduction product of the CuS nanowires is Cu, which is an electron conductor in the electrode. Because the anode will only work around 0-1V vs. Li/Li⁺, the Cu will not convert to CuS and remain conductive through out the anode operation. It forms a conductive pathway to increase the electron transfer at the interface of Si particles and the matrix.

The Li⁺ insertion and extraction properties of CuS nanowires coated Si as an anode material was studied by galvanostatic charge-discharge measurements. The electrode of CuS coated Si exhibited a specific capacity of 917 mAh g⁻¹after 100 cycles (Fig.3), and showed coulombic efficiencies up to 98.8% after the fourth cycle and keep constant for more than 100 cycles (Fig.3).

The unique structure of CuS nanowwires coated Si contributed to the high capacity and good cycling stability. The CuS nanowire on Si particles may accommodate the volume change of Si particles and prevent the loss of electric conductivity between Si and the electrode matrix. The engineered conductive pathway between the Si and the matrix enhanced cycle stability.



Fig. 2. CV curves of the CuS coated Si anode during the first two cycles.



Fig. 3. The capacity retaintion and columbic efficiency of the CuS coated Si electrodes at 0.1C charge and discharge rate.

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