Enhanced lithium ion battery performance of nano/micro-size Si via combination of metal-assisted chemical etching method and ball-milling

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ABSTRACT

Up to now, designing special Si with high coulombic efficiency and cycling stability in a bulk electrode remains a significant challenge. In this work, nano/micro-structured Si was successfully synthesized via a simple and scalable process with combination of the modified Metal-assisted chemical etching (MACE) method and ball-milling. The modified MACE method was used to purify micro-silicon (mSi) and produce porous structure. Moreover, we decrease the size of porous Si (pSi) and introduce the oxidation layer ($\sim 3.8\,nm$) through simple ball-milling to prepare nano/micro-structured Si (M-pSi), which delivers a high initial coulombic efficiency of 85.2%, high capacity and good cycle performance. The initial discharge capacity of M-pSi is $2349\,mA\,h\,g^{-1}$ at a current density of $0.2\,C$ ($1\,C = 4200\,mA\,g^{-1}$) and remains $2231\,mA\,h\,g^{-1}$ after 100 cycles, suggesting an average decrease of 0.05% per cycle. Even at a higher current density of $2\,C$, it delivers a high discharge capacity of $750\,mA\,h\,g^{-1}$.

1. Introduction

To face with the rapid expanding markets of electric vehicles (EVs) and portable electronic devices, stringent requirements for lithium-ion batteries (LIBs) with larger specific capacity and higher power density have to be settled urgently [1,2]. Due to the highest theoretical lithium storage capacity ($4200\,mAhg^{-1}$) and relative low discharge voltage, silicon is regarded as one of the most promising alternative candidates for commercial carbon-based anode materials [3]. Besides, silicon is also one of the most abundant elements in the earth crust, implying its enormous potential of practical use. More importantly, Si can very well pair with sulfur cathode in a full cell configuration [4–7]. However, Si materials undergo a huge volume change (around 300%) during the lithiation/delithiation process, leading to severe pulverization which further results in bad reversibility and poor cycling life in consequence of losing electrical contact between the current collector and Si. Another problem is constant consumption of electrolyte by repeated formation of solid-electrolyte-interface (SEI) films at exposed surface of Si [8–10]. The above-mentioned defects set hindrances for Si anode to be applied in next generation LIBs.

Two main strategies are reported to overcome the above critical defects and improve the electrochemical performance of Si anodes. The first strategy is decreasing the dimension of Si into nanometer scale, since the nanostructure of Si can effectively suppress the strain induced by the volume change upon cycling and decrease the Li$^+$ diffusion path through the high specific surface area and developed porosity [11]. Extensive studies on constructing Si nanoparticles [12,13], nanofilms [14,15], nanowires [16–18], nanotubes [19,20] have been reported. Another effective strategy is combining Si with other conductive matrix, such as carbon [21–24], metal [25–28], and oxide [29,30], which can not only enhance the electrical conductivity of Si based anodes, but also assist the accommodation of Si during lithiation/delithiation.

Recently, porous Si materials have attracted more attention due to their stable cycling performance, which is originated from the large electrolyte-accessible surface area and appropriate space which shorten the lithium ion transmission path and accommodate volume expansion. Various methods have been explored to prepare porous Si. For example, Wei Wang et al. reported a facial way for preparing highly mono-dispersed porous silicon spheres via surface-protected magnesiothermic reduction [31]; Jian Yang synthesized porous amorphous Si particles through a solvothermal reaction combined with a high-temperature annealing [32]. The obtained porous Si particles possess a capacity of $1025\,mAhg^{-1}$ after 700 cycles at $3\,A\,g^{-1}$.

Metal-assisted chemical etching (MACE) is a top-down method to fabricate porous Si on polished silicon wafer [33]. For example, Bin Wang et al. reported silicon@graphitic carbon nanowire array by

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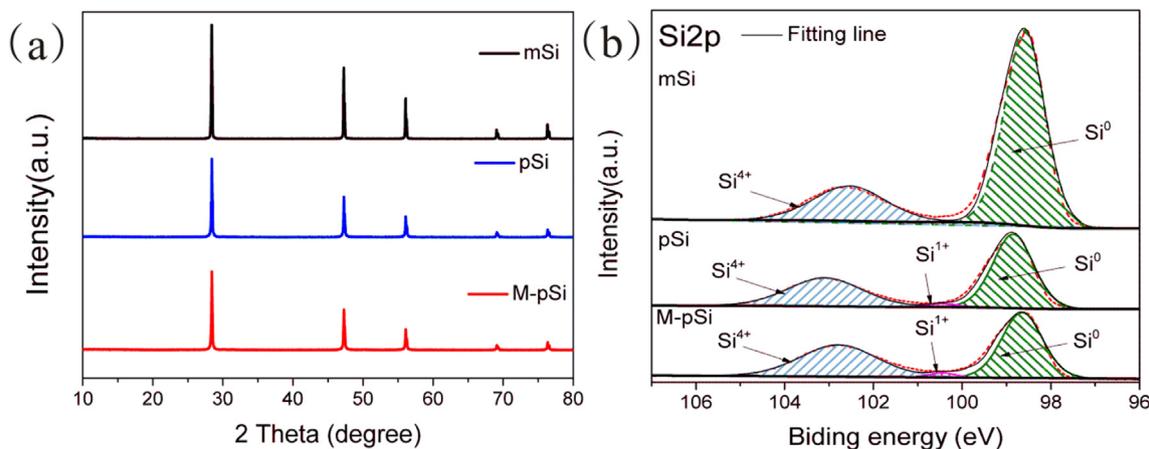
Fig. 2. (a) XRD of mSi, pSi and M-pSi. (b) XPS Si 2p spectra of mSi pSi and M-pSi.

Table 1
ICP results of mSi and pSi (ug g^{-1}).

Sample	Ag	Cr	Fe	Mn	Ni	Zr	Ca	Al
mSi	–	101.9	496.7	42.6	49	193.9	52.1	366.8
pSi	85.7	2.7	10.7	0.5	0.3	0.3	36.1	10.8

etching of silicon wafer and coated with the graphitic carbon sheets, demonstrating an enhanced electrochemical performance compared with bulk Si [34]. Comparing with the general preparation methods of porous silicon, the significant advantage of MACE is to fabricate micro-sized porous silicon which have great potentialities on industrialized application.

Yu Chen et al. developed a MACE followed with post annealing to prepare Si/SiOx nanowires from metallurgical micro-silicon [35]. The Si/SiOx nanowires show a stable cycle performance. Nevertheless, the initial coulombic efficiency of Si/SiOx is extremely low due to the oxide surface. Park and co-workers have also done a great quantity of work in this field [36–38]. They synthesized three-dimensional macroporous silicon particles (7 μm) via a developed two-step etching method. These materials exhibited remarkable coulombic efficiency after adding a carbon-coated layer via chemical vapor deposition (CVD) method [36]. However, the CVD process which involves the use of flammable precursors and complicated instruments is complicated for mass production. In addition, a large amount addition of carbon composition will also reduce the proportion of silicon on the electrode, leading to a decreased specific capacity. Therefore, it is still challenging for this method to synthesize porous Si with excellent performance and cost-effective process.

Herein, we propose a scalable synthesis of highly purified silicon modified with a thin SiOx layer to be used as an anode material for LIBs. Cheap micro-silicon (5–10 μm, 99.9%) powder is treated by a two-step MACE method and the obtained pSi demonstrate superior initial coulombic efficiency of 87.6% without any further treatment or carbon-coated layers. In order to further improve its electrochemical performance against long term cycling and high current density, we decrease the pSi size through a simple ball-milling process. The obtained M-pSi after ball-milling process exhibits better capacity than pSi of around 2212 mA h g^{-1} at a rate of 0.2C after 100 cycles and a capacity around 750 mA h g^{-1} at a rate of 2 C.

2. Materials and methods

2.1. Synthesis of pSi

Micro-silicon (2 g, RuiTeng, average diameter 5–10 μm, 99.9%) was dispersed in 50 ml ethanol solution of 5 ml absolute ethanol by ultra-sonicaton for 30 min. At the same time, the etching solution which is consists of 22 ml hydrofluoric acid, 0.17 g AgNO$_3$ and 28 ml deionized (DI) water was added into above solution and stirred for 5 min. After vacuum filtration, the micro-silicon coated with Ag nanoparticles was dispersed into 50 ml alcohol solution of 5 ml absolute ethanol again. Then, the etching solution consists of 22 ml hydrofluoric acid, 6 ml H$_2$O$_2$ and 22 ml DI water was added into the above solution very slowly and then stirred at 50 °C for 2 h to synthesize 3D porous silicon particles. Especially, we sprayed ethanol into the etching solution several times in above process in order to facilitate Si powder sink into etchant. After the etching process, the Ag particles was removed by 20% HNO$_3$ at 50 °C for 1 h. Finally, the pSi particles were dried in vacuum oven at 60 °C for 12 h.

2.2. Synthesis of M-pSi

The as-synthesized pSi then ball-milled by planetary ball-milling for 5 h at a speed of 500 r min^{-1}, with a ball-to-powder mass ratio of 20:1.

2.3. Characterization

The crystalline structures of pSi and M-pSi were measured by X-ray diffraction (XRD, Rigaku-TTRIII) with Cu Kα radiation at a scanning rate of 10°/min. The surface element analyses of samples were recorded by X-ray photoelectron spectroscopy (XPS, ThermoFisher-VG Scienfic) with a monochromatic Al Kα X-ray source. The ICP analyses were measured on a SPECTRO BLUE SOP spectrometer. The microscopic features and internal structures of the samples were observed by field emission scanning electron microscopy (FESEM, Nova NanoSEM230) energy dispersive X-ray (EDX) spectroscopy and transmission electron microscopy (TEM, JIOL JEM-2100F) respectively. Brunauer-Emmett-