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Molten salt electrolytic synthesis of silicon-copper composite nanowires with enhanced performances as lithium ion battery anode

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ABSTRACT

A facile metallurgical method named molten salt electrolysis was introduced to prepare silicon nanowires (Si NWs) and Cu_9Si/Si composite nanowires that were used as the anode materials for lithium-ion batteries (LIBs). Simply utilizing SiO_2 and Cu/SiO_2 mixture as the raw materials, by tailoring voltage into the molten salt chamber, SiO_2 was constantly deoxidized to form Si flexible nanowires with 1–3 μm in length and 100–200 nm in width. Cu ingredient further catalyzed the growth of silicon nuclei to generate straight wires with longer 10 μm and narrower 60–100 nm. Benefiting from the compositional and structural advantages, the Cu_9Si/Si nanocomposite anode exhibited a better capacity retention that delivered a specific capacity of 601.3 $mAh \cdot g^{-1}$ at 200 mA g^{-1} after 200 cycles and 398.8 $mAh \cdot g^{-1}$ at 500 mA g^{-1} after 500 cycles. Notably Cu_9Si/Si NWs anode with enhanced rate capability was also obtained, with a specific capacity of 747.6 $mAh \cdot g^{-1}$, 550.6 $mAh \cdot g^{-1}$ and 412.2 $mAh \cdot g^{-1}$ at the current density of 200 mA g^{-1}, 500 mA g^{-1} and 1000 mA g^{-1}, respectively.

1. Introduction

Lithium-ion batteries have become the key-enabling commodity in energy storage fields due to their high energy and long-term cycles. Presently, the anode material served in commercial LIBs is made of graphite, but the practical low capacity (less than 372 $mAh \cdot g^{-1}$) limits its marketing demands [1–3]. Plenty of researches are needed to replace the traditional graphite with new anode materials that contain a relatively higher capacity, energy and power density. Nowadays, there has existed considerable alternative anode materials, including Sn with the theoretical gravimetric specific capacities of 994 $mAh \cdot g^{-1}$ [4], Si with 4200 $mAh \cdot g^{-1}$ [5–7], transition oxides such as Co_3O_4 [8–10], CuO [11], Fe_2O_3 [12], TiO_2 with much higher gravimetric specific capacities [13] and spinel $Li_4Ti_5O_{12}$ [14–17], $Na_2Li_2Ti_6O_{14}$ [18] and $LiNbO_3$ [19]. Amongst them, silicon is deemed to be one of the most promising anode materials for LIBs because of the almost tenfold theoretical capacity higher than that of graphite, and exhibits low discharge voltage (vs. Li^+/Li) during the lithiation/delithiation process. Moreover, the rich abundance of silicon presents itself as an ideal alternative candidate for use [20]. However, constant lithium ion insertion/extraction from silicon is unavoidable accompanied by the huge volumetric change of silicon anode (>300%), leading to the formation of unstable solid electrolyte interphase (SEI), structure disintegration, particle pulverization, poor electrical contact among electrode, and finally resulting in the fast capacity fading and unsatisfactory rate performance [21]. In order to overcome the above issues, many works have been attempted based on the nanocrystallization and recombination solution. First, minimizing the particle size to nanoscale such as nanowires, nanocomposites, thin films, nanobelts and nanotubes; these types of nanosized structures provides individual geometries to help accommodate the large volumetric expansion, alleviate

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pulverization of electrode and promote the lithium ions transmission into and out of the anode matrix [22,23]. Second, manufacturing silicon and carbonaceous agent or Si-Metal binary composite to increase the conductivity of materials [24]. Third, covering silicon nanoparticles by metal oxide layer [25]. Mostly, the Si-Metal binary composite, such as silicon-copper nanocomposite, is suggested to be an efficient way by forming an electrochemically inactive matrix, with the advantages of increasing the total conductivity of anode and mitigating the mechanical stress. For instance, using chemical vapor deposition (CVD) method, Chen et al. fabricated copper coated Si nanowire with a capacity retention of 2216 mAh·g^{-1} at 3.1 A g^{-1} over 30 cycles [26]. With the thermal reduction method, Zhou et al. synthesized Cu_3Si@Si core-shell nanoparticles showed a capacity of 903.6 mAh·g^{-1} at 2 A g^{-1} over 400 cycles [27]. Jae-Young Woo et al. synthesized Cu_3Si/Si nanoparticles showed the discharge capacity of 3036.4 mAh·g^{-1} with a coulombic efficiency of 90.49% at the first cycle [28]. By the high-energy ball milling method, Yoon et al. prepared Cu_3Si doped layers with a stable capacity of 850 mAh·g^{-1} for 30 cycles at 100 mA g^{-1} [29]. However, there might still exist difficulties for preparing industrially viable copper-silicon nanoparticles when considering the cost and technique. For example, the CVD method probably seems to be complicated because this technique presents pricy reactant dependence, low productivity and the limitation of complex equipment [30]. The ball milling process could unavoidable give rise to a highly metastable state and crystal defects [31]. Therefore, developing a facile strategy for fabricating Si-based nanomaterial continues to be a hot spot.

Herein, a novel synthetic route is proposed for the production of silicon and copper-silicon composite in nanoscale with molten salt electrolysis. This method is well known as the Fray-Farthing-Chen (FFC) Cambridge electro-deoxidization process [32], and has been operating at the Metalysis company (http://www.metalysis.com/). Generally, this method applies to the direct conversion of metallic oxides into metals and alloys in solid state, such as Cr [33], Ge [34], FeTi [35], Ti_5Si_3 [36,37]. This method provides an effective metallurgical process that the porous mineral precursor is simply 'metallized' in solid state and bulk quantities of meals are obtained by simply increasing the number of oxide once used, offering a potential benefit in both case of mass production and economics. Moreover, silicon nanowires have been prepared successfully with the aid of molten salt [38–40]. These investigations induce a fine way to produce silicon-based alloys in controllable nanosized architectures.

Herein, we proposed a novel safe synthetic process for silicon and copper-silicon composite nanowires applied as the anode materials for LIBs through the direct electrolysis of silica and copper mixture (Cu/SiO_2) in molten salt. The conversion of nascent bulk oxide precursor into silicon and silicide compound nanoparticles was investigated. During the reduction, when the injected cell voltage was much higher than the decomposition voltages thermodynamically, oxygen from SiO_2 could be constantly removed via reaction (1). After Si was produced, it could spontaneously react with Cu to form Cu-Si composite at given working temperature.

$$SiO_2 = Si + O_2(g) E^{\theta}(700^{\circ}C) = 1.90V \qquad (1)$$

2. Experimental

2.1. Electrochemical synthesis of Si and Cu-Si nanocomposite

High purity SiO_2 powders (particle size: ~1 μm, Aladdin, S104600) and Cu powders (particle size: ~0.5 μm, Aladdin, C103843) were blended by molar ratio of 1:1 to serve as the Cu/SiO_2 precursor and SiO_2 powders were solely served as the SiO_2 precursor. The mass of the two samples was kept the same. NH_4HCO_3 (Aladdin, A110536) of 40% by mass was served as the pore-forming agent and added into the mixed powders. After that, the powders were pressed into pellets (diameter: 14 mm; thickness: ~4 mm), and sintered at 500 °C in argon atmosphere for 3 h. The precursor was further sandwiched between two porous molybdenum foils and served as the cathode, and a graphite rod (diameter: 6 mm; length: 80 mm, Aladdin, G103921) was used as the anode. Molten salt consisting equimolar $CaCl_2$ (Aladdin, C110766)-NaCl (Aladdin, C111549) in total 210 g was served as the electrolyte and packed in an Al_2O_3 crucible (inner diameter: 57 mm; external diameter: 63 mm; depth: 75 mm, Aladdin, A2590) chamber. The schematic of experimental apparatus was shown in Fig. 1. To obtain silicon and copper-silicon composite, electrolysis of SiO_2 and Cu/SiO_2 pellets was conducted under a constant cell voltage of 2.4 V for 10 h at 700 °C. In all electrolytic occasions, the chamber was sealed in a vertical quartz tube closed at one end and continuously purged with an argon flow. After electrolytic terminals, the cathode was cooled down with the cell to room temperature under a flow of argon. The products were removed from the chamber, washed in 0.5% HCl solution, deionized water and alcohol, and dried under vacuum at 80 °C for 1 h.

2.2. Material characterization

Rigaku MiniFlex II X-ray diffractometer was used to collect X-ray powder diffraction pattern of the sample in the 2θ range of 10–90° at a rate of 4°/min with a Cu Kα radiation source (λ = 0.154178 nm) operating at 40 kV, 30 mA. The samples were analyzed by X-ray photoelectron spectroscopy (XPS) for the measurement of the binding energy by the use of a PHI Quantum 2000 scanning ESCA Microprobe equipped with an Al $K_{\alpha1,2}$ X-ray radiation source. The survey scans were used a source with power and voltage of 50 W and 15 kV, respectively. Survey scans and high-resolution scans of the Si 2p, Cu 2p, O 1s, C 1s, energy spectra were taken from samples to identify the compounds present on the surface. The spectra were calibrated to the carbon peak at 284.8 eV. The morphology and microstructure of samples were detected by scanning electron microscope equipped a FEI Nova NanoSEM 450 field emission scanning electron microscope (FESEM) at 15 kV and transmission electron microscopy (TEM, JEM2010-HT). The specific surface area and the pore structure of samples were examined by nitrogen sorption measurements at 77 K (Micromeritics ASAP2020).

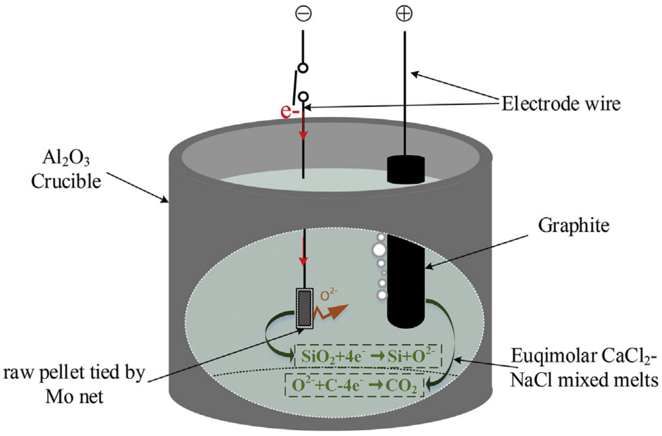

Fig. 1. Schematic diagram of electrolysis apparatus.