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Free-standing $Ca_2Ge_7O_{16}$ nanorod arrays anode with long-term stability and superior rate capability in lithium ion batteries

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ABSTRACT

We report a facile one-step route to synthesize a free-standing $Ca_2Ge_7O_{16}$ nanorod anode for the first time. The $Ca_2Ge_7O_{16}$ nanorod arrays are uniformly grown on the surface of three-dimensional copper foam used as the conductive current collector. The $Ca_2Ge_7O_{16}$ nanorod is used as a binder-free anode for lithium-ion batteries, which exhibits excellent cycle performance (134.6% retention of its 1st cycle reversible capacity after 450 cycles) and superior rate capability (350 mA h g^{-1} at 5 A g^{-1}, the good cycling stability at 20 A g^{-1}). Even at higher current density of 0.5 A g^{-1} after 10 cycles activation at 0.2 A g^{-1}, the nanorod electrodes can deliver a reversibility capacity as high as 1001.2 mA h g^{-1}. Furthermore, a binder free full cell is fabricated, which shows excellent cycle performance with 91% retention of its 1st cycle capacity after 200 cycles. The superior cycling performance is attributed to shortened Li^+ transport length, enough buffering space, electrical conductivity of the Cu foam and the unique 1 D nanorod arrays structure.

1. Introduction

Recently, lithium batteries (LIBs) have been widely developed to meet the demands of a variety of energy applications, such as grid storage, hybrid electric vehicles (HEV), and portable electronic devices because of their high energy density and long lifespan [1–5]. However, broader applications of LIBs are still hampered by limited capacity and insufficient cycling lifetime of traditional graphite-based anodes [6–8]. Compared with graphite with a relatively low theoretical capacity of 372 mA h g^{-1}, group IV elements with higher theoretical specific capacity have attracted increasing attention [9]. Although Ge has a relative lower capacity (1600 mA h g^{-1}) than that of Si (4200 mA h g^{-1}), it has a higher diffusivity of lithium (400 times faster than in Si), a lower specific volume change and high intrinsic electrical conductivity (100 times higher than in silicon) during the Li insertion/extraction process, thus making Ge an attractive electrode material for high-rate LIBs [10–11]. However, bulk-phase Ge suffers from a serious problem of quick capacity fading triggered by large volume change (370%) of Ge during lithiation and delithiation [12–13]. Since Ge is neither abundant nor inexpensive, it may be prohibitive for use on a realistic scale. One of the promising ways to solve this problem is to form composite compounds in which the oxide may buffer the volume change and lower the material cost [14]. In 2009, the electrochemical behavior of $MGeO_3$ (M = Cu, Fe and Co) in the potential range of 0.01–3 V was investigated by Kim et al. [15]. M metal nanoparticles in situ generated by $MGeO_3$ can not only serve as electronic conductive network and electrocatalyst for Li_2O decomposition but also minimize the volume change of $MGeO_3$. Ternary metal germanate nanomaterials containing metal elements (Zn [16–17], Cu [19], Ba [20], Sr [20], Cd [21], Fe [22], Ca [18,20,23,24]) have attract considerable interest as a new class of high capacity due to their superiority. Among them, $Ca_2Ge_7O_{16}$ has been shown to improve the performance of Ge-based materials for low-cost, environmentally benign, and good stabilized matrix formed during cycling [18,20, 23,24]. The CaO and Li_2O formed in situ after the initial lithiation process ($Ca_2Ge_7O_{16} + 28e^- + 28Li^+ \rightarrow 2CaO + 7Ge + 14Li_2O$) provide buffer matrix to accommodate the volume changes as well as effectively catalyze GeO_2 decomposition ($Ge + Li_2O \leftrightarrow GeO_2 + 4Li^+ + 4e^-$) to improve capacity. For example, Guo et al. [20] showed the better cycling performance of $Ca_2Ge_7O_{16}$ nanowires (NWs) with a specific capacity of 601 mA h g^{-1} after 100 cycles under a current density of 100 mA g^{-1} than $BaGe_4O_9$NWs and GeO_2. The rate performance is significantly improved (about 374.8 mA h g^{-1} at 800 mA g^{-1}). The urchin-like hollow structured $Ca_2Ge_7O_{16}$ microspheres synthesized by Guo et al. [24] showed high reversible specific capacity of up to 804.6 mA h g^{-1} at 100 mA g^{-1} after 100 cycles and remarkable rate capability of 341.3 mA h g^{-1} at a current density of 4 A g^{-1}. Shen et al. [23] showed improved cycling performance of the $Ca_2Ge_7O_{16}$ nanowires/

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graphene anodes with a specific capacity of 950 mA h g^{-1} at a current density of 100 mA g^{-1} after 100 cycles and better rate capability (400 mA h g^{-1} at 3.2 A g^{-1}). However, these $Ca_2Ge_7O_{16}$ electrodes had short cycling life (<300) under a lower current density and low rate capability cannot meet the requirements of the electrical grid and EV applications. To overcome these issues, the synthesis of $Ca_2Ge_7O_{16}$ with desired nanostructures and excellent lithium storage capacity remains full of challenges owing to the volume expansion of $Ca_2Ge_7O_{16}$.

Organizing one dimensional integrated arrays on conducting substrates is helpful to solve these issues because of their sufficient buffering space which can accommodate the strain caused by volumetric variation during the cycling [25]. Cu substrates with foam structure not only offer pores that can accommodate the volumetric expansion of active materials but also enable fast electrochemical reactions due to its high surface area. Recently, C. Li and co-workers have designed Si nanowire arrays on Cu foam for lithium-ion batteries, exhibiting an improved cycling stability and an excellent rate capacity [26]. Therefore, fabricating 1 D nanostructure arrays on Cu foam will be great benefit for lithium batteries.

In this study the $Ca_2Ge_7O_{16}$ nanorod (NR) arrays have been fabricated on the Cu foam by employing a simple, fast and high yield hydrothermal method for the first time. These $Ca_2Ge_7O_{16}$ NR electrodes exhibit excellent cycle performance (134.6% retention of its 1st cycle capacity after 450 cycles), an outstanding initial discharge capacity of 1811.3 mA h g^{-1} at current density of 200 mA g^{-1}. Even at higher current density of 0.5 A g^{-1} after 10 cycles activation at 0.2 A g^{-1}, the NR electrodes can deliver a capacity as high as 1001.2 mA h g^{-1} after 1000 cycles. To our knowledge, there are no reports on $Ca_2Ge_7O_{16}$-based anodes capable of cycling up to 1000 cycles until now. Moreover, the $Ca_2Ge_7O_{16}$ NR anodes display superior rate performance (the cycling stability is quite excellent, although the current density increases to 20 A g^{-1}). We use the $Ca_2Ge_7O_{16}$ NRs as the anode and the commercial $LiCoO_2$ (LCO) material as the cathode to assemble a $Ca_2Ge_7O_{16}$ NR/LCO full cell. The binder free full cell exhibits excellent cycle performance with 91% retention of its 1st cycle capacity after 200 cycles.

2. Experimental section

2.1. Chemicals

High purity reagent GeO_2 powders (purity ≥99.99%) and $Ca(CH_3COO)_2\cdot H_2O$ (AR grade, purity ≥98.0%) were purchased from Shanghai Longjin Metallic Material Co., Ltd. and Sinopharm Chemical Reagent Co., Ltd. of China, respectively. Cu foam and commercial $LiCoO_2$ were purchased From Shenzhen Biyuan Electronic Co., Ltd.

2.2. Synthesis of $Ca_2Ge_7O_{16}$ NRs

In a typical procedure, 176 mg GeO_2 and 366.1 mg $Ca(CH_3COO)_2\cdot H_2O$ were added into resultant solution, respectively. The $Ca(CH_3COO)_2\cdot H_2O$ solution was added dropwise to resultant solution under vigorous stirring. The mixture was stirred for 60 min and then transferred to a Teflon-lined auto-clave with a 100 mL inner volume. Then a piece of cleaned Cu foam was placed into the solution. The hydrothermal synthesis was performed at 180 °C for 30 min, followed by natural cooling to room temperature. The product was collected by centrifugation, washed thoroughly with water and alcohol for several times and then dried at 60 °C in air for 12 h. Finally, the $Ca_2Ge_7O_{16}$ NR arrays were obtained.

2.3. Synthesis of $Ca_2Ge_7O_{16}$ NWs

In a typical procedure, 176 mg GeO_2 and 366.1 mg $Ca(CH_3COO)_2\cdot H_2O$ were dissolved in 30 mL deionized water, respectively. The mixture was stirred for 60 min and then transferred to a Teflon-lined auto-clave with a 100 mL inner volume. Then a piece of cleaned Cu foam was placed into the solution. The mixture was performed at 180 °C for 25 h followed by natural cooling to room temperature. The product was collected by washed thoroughly with water and alcohol for several times and then dried at 60 °C in air for 12 h. Finally, the $Ca_2Ge_7O_{16}$ NWs were obtained.

2.4. Characterization

The morphology and element distribution of the electrodes were investigated by field emission-scanning electron microscopy (FE-SEM; Hitachi S-4800) operating at 20 kV. Transmission electron microscopy (TEM) was performed using an FEI Tecnai G2F30 operated at 300 kV. X-Ray diffraction (XRD) measurements were performed at a Rigaku D/max-rB X-ray diffractometer with Cu Kα ($\lambda = 0.1548$ nm) incident radiation. The diffraction patterns were collected at room temperature in the 2θ ranges of 10 to 90°.

Electrochemical charge-discharge behaviors were investigated in stimulant cells (2032 coin-type half-cells) assembled with $Ca_2Ge_7O_{16}$ NRs as the positive electrode (cathode), a Li metal foil as the negative electrode (anode), a separator film (Celgard 2400), and a liquid electrolyte (ethylene carbonate and dimethyl carbonate (1:1 by volume)) with 1.0-M LiPF6 in an Ar filled glove box. The loading density of the $Ca_2Ge_7O_{16}$ NRs active materials was calculated to be 0.5–1.5 mg cm^{-2}. Each cell was aged for 24 h at room temperature before commencing the electrochemical tests. The galvanostatic charge-discharge measurements were conducted in a battery test system (NEWARE BTS-610, Newware Technology Co., Ltd., China) at room temperature. The cut-off voltage for all tests was 0.01–3.0 V. A full cell was assembled by using the as-fabricated $Ca_2Ge_7O_{16}$ NRs as the anode, commercial $LiCoO_2$ as the cathode, $LiPF_6$ as the electrolyte, and a polymer separator. The electrochemical tests were cycled between 2.0 and 4.2 V for the complete anode-limited full cells at a constant current density of 200 mA g^{-1} with respect to the mass of the anode. Cyclic voltammograms (CV) were measured at a scan rate of 0.1 mV s^{-1} for 5 cycles on an electrochemical work station (CHI660E). AC impedance of the half-cells was also performed on an electrochemical work station (CHI660E) at a frequency range of 100 mHz–100 kHz. All testing was performed at room temperature.

3. Results and discussion

3.1. Microstructure characterization

The synthetic process of the $Ca_2Ge_7O_{16}$ NRAs is schematically illustrated in Fig. 1. Firstly, $HGeO^{3-}$ was formed from the reaction of GeO_2 and OH^- which came from CH_3COO^-. Then free Ca^{2+} ions which derived from $Ca(CH_3COO)_2\cdot H_2O$ reacted with $HGeO^{3-}$, and finally the $Ca_2Ge_7O_{16}$ nanoparticles generated on Cu foam. The $Ca_2Ge_7O_{16}$ nanoparticles serve as the crystalline nuclei for the anisotropic growth of $Ca_2Ge_7O_{16}$ (Fig. 1 a). As the reaction time prolonged, the smaller nanoparticles vanish at the site of the longer nanorods through an Ostwald ripening process [27–28] due to their higher surface free energy compared to the longer NRs. The linear growth is attributed to the preferential adsorption of nanoparticles to special crystal facets, which direct the growth of the nanoparticles to NRs (Fig. 1b).

The crystal structure and phase purity of the free-standing $Ca_2Ge_7O_{16}$ NR arrays and the $Ca_2Ge_7O_{16}$ NWs were analyzed by using X-ray diffraction (XRD) and the corresponding XRD patterns are shown in Fig. 2. All of the peaks can be readily indexed to pure $Ca_2Ge_7O_{16}$ with an orthorhombic phase (JCPDS Card No. 34-0286).

Fig. 3 shows the morphology the free-standing $Ca_2Ge_7O_{16}$ NR arrays supported on the Cu foam. It reveals that a large number of $Ca_2Ge_7O_{16}$ NRs with the diameter ranging from 50 to 100 nm grow vertically and uniformly on the Cu foam, as shown in Fig. 3 (a–c). Fig. 3 d shows the lengths of $Ca_2Ge_7O_{16}$ NRs are about 2 μm. The $Ca_2Ge_7O_{16}$ NWs with the diameter about 100 nm can be observed clearly from Fig. 3 (e-f).