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Highly stable carbon coated Mg_2Si intermetallic nanoparticles for lithium-ion battery anode

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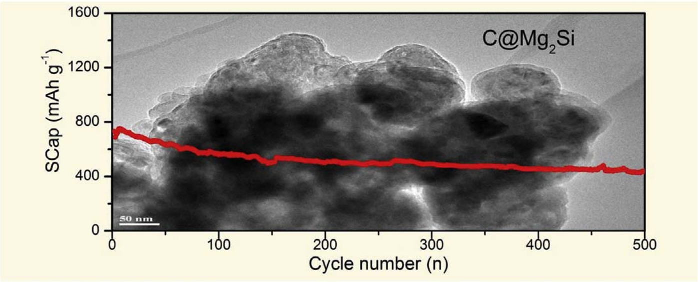
HIGHLIGHTS

- Carbon coated Mg_2Si nanoparticles have been synthesized for LIB anode material.
- The electrode exhibits first reversible capacity of 726 mAh g^{-1} at 100 mA g^{-1}.
- The electrode shows high rate capability (380 mAh g^{-1} at high rate of 2 A g^{-1}).
- High cycle stability with capacity retention of 65% after 500 cycles has been attained.

GRAPHICAL ABSTRACT



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ABSTRACT

Silicon is an ideal candidate anode material for Li-ion batteries (LIBs). However, it suffers from rapid capacity fading due to large volume expansion upon lithium insertion. Herein, we design and fabricate highly stable carbon coated porous Mg_2Si intermetallic anode material using facile mechano-thermal technique followed by carbon coating using thermal vapour deposition (TVD), toluene as carbon source. The electrode exhibits an excellent first reversible capacity of 726 mAh g^{-1} at a rate of 100 mA g^{-1}. More importantly, the electrode demonstrates high rate capability (380 mAh g^{-1} at high rate of 2 A g^{-1}) as well as high cycle stability, with capacity retentions of 65% over 500 cycles. These improvements are attributable to both Mg supporting medium and the uniform carbon coating, which can effectively increase the conductivity and electronic contact of the active material and protects large volume alterations during the electrochemical cycling process.

1. Introduction

The development of high power and energy Li-ion batteries has gained much attention as a source of power in portable electronic devices, hybrid and all-electric vehicles, and other renewable energy storage devices. To realize Li-ion batteries for such demanding applications, electrode materials with high specific energy and long cycle life are needed [1]. High specific energy can be attained by exploiting materials that have higher specific capacity than the conventional graphite electrodes [2]. To this end, silicon (Si) has drawn much attention as an ideal anode material candidate for Li-ion batteries. This interest is primarily due to: (i) its high theoretical gravimetric capacity of ~4200 mAh g^{-1} which is ten times more than the theoretical capacity of conventional graphite anodes, (ii) its moderately low discharge potential (~0.5 V *vs.* Li/Li^+), (iii) its high natural abundance, and (iv) its non-toxicity and environmental benignity [3–6]. Nevertheless, Si-based anodes materials face critical problem of large volume expansion (~400%) upon lithium ion insertion/desertion [5–7]. These

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huge volumetric alterations can cause breakdown and pulverization of the electrode material, which lead to electrical contact loss and growth of too much solid–electrolyte interphase (SEI) [3]. For the past few years, with tremendous efforts, exciting progresses have been achieved through various techniques such as nanostructuring [8–10], carbon-based composites [10–13], using protective coatings [12,14,15], using porous nanostructures [16–18] etc. So far, exciting results have been achieved in terms of specific capacity, rate capability and cycling life using Si-based electrodes. However, no information was disclosed about across-the-aboard performances such as high energy and power density, superior battery stability, and sustaining safety in a single Si-based storage unit. Only in this unit we can principally substitute the current commercial graphite anodes with improved performance Si-based materials.

Among Silicon-based anode materials, intermetallic compounds (silicides) have gained a considerable interest, because they can, not only act as a stress-buffer to relieve the large volume change during lithiation/delithiation processes, but also have enhanced electronic conductivity [19–21]. In addition, intermetallic silicide compounds have low working voltages, higher volumetric and gravimetric capacities than the conventional carbon materials [22]. Some of these compounds include Mg_2Si [22–28], $CaSi_2$ [29], NiSi [30,31], FeSi [32], $TiSi_2$ [33], $FeSi_2$ [32], $NiSi_2$ [34] etc. Among these intermetallic silicides, Mg_2Si, the only intermetallic Mg-Si system, has numerous useful features [23]. First, Li can be inserted into Mg, Si, and their alloy electrochemically at room temperature [23]. Second, both Mg and Si are naturally copious and cheap. Third, since both elements are lightweight, huge specific capacities can be attained. In addition to these, Mg_2Si has a considerable theoretical specific capacity of 1370 mAh g^{-1} and a favorable voltage profile [25]. Unfortunately, the fast capacity fading of Mg_2Si upon cycling prevents its practical application as an anode material.

Despite Mg_2Si has high theoretical specific capacity and other promising properties only few efforts have been focused to enhance its cyclic stability which is the main performance bottleneck. G. A. Roberts et al. have reported Mg_2Si anode material which was prepared by mechanically activated annealing [23]. They have found a maximum first discharge capacity of 830 mAh g^{-1} which was immediately faded up. Similarly, J. M. Yan and co-workers reported mechanical mixtures of Mg_2Si/carbon nanotube and Mg_2Si/carbonaceous mesophase sphere materials [25]. They have indicated that the first discharge capacity of pristine Mg_2Si was 580 mAh g^{-1}, but only 50 mAh g^{-1} capacity was left after 5 cycles. The Mg_2Si/carbon nanotube mixture delivered about 800 mAh g^{-1} initial capacity in the first cycle, but the capacity decreased to 480 mAh g^{-1} after 5 cycles that corresponds to 40% loss of its initial capacity. For the Mg_2Si/carbonaceous mesophase sphere mixture materials, the first cycle discharge capacity of 800 m mAh g^{-1} was achieved but the capacity decrease to 500 mAh g^{-1} with in the first five cycles.

In this study, we have designed and synthesized Mg_2Si nanoparticles which are conformally coated with carbon employed as anode material for Li-ion batteries. First, Mg_2Si nanoparticles were synthesized by mechanically activated annealing technique. Then, carbon coating was made by thermal vapour deposition (TVD). The electrochemical performance of the resulting electrode was assessed as anode material for LIBs, for example, the charge/discharge profile, cycling stability and rate capability. Also the mechanism responsible for the improved performance was discussed.

2. Experimental

2.1. Preparation of carbon coated Mg_2Si nanoparticles

Mg_2Si nanoparticles were synthesized *via* facile mechano-thermal (mechanically activation followed by thermal annealing) technique. Typically, 2.066 g magnesium powder and 1.123 g of silicon powder were mixed in mortar and pestle transferred and sealed in ball milling jar inside glove box. The mixture of Mg and Si powder was then mechanically activated using a high energy Fritsch (FRI_Z0004) ball mill with an 80 ml zirconium oxide grounding bowl at ball to powder mass ratio of 25:1 and rotation speed of 250 rpm for 1 h. The activated mixture was then transferred to a 20 ml alumina crucible and transferred to tube furnace. The mixture was then heated at 600 °C for 3 h with a ramping rate of 10 °C min^{-1} under Ar atmosphere. After the as-prepared product was cooled to room temperature naturally, it was immersed into 200 ml of 95% ethanol solution which comprises 2 g of PVP k29 ~ 32. After that, it was treated by ultrasonication for 2 h to hydrate impure MgO sufficiently. The insoluble $Mg(OH)_2$ was removed by mild centrifugation of the subsequent suspension at 5000 rmp for 10 min. Then, the dispersed solution was further centrifuged at 10,000 rpm for 25 min and the Mg_2Si were collected and washed with ethanol three times. For the preparation of carbon coated Mg_2Si (C@Mg_2Si) samples, TVD has been applied using toluene as a carbon source. First, the Mg_2Si samples were loaded on alumina boat and introduced to a tube furnace. Then, the furnace was purged with Ar gas and heated to 700 °C at a heating rate of 10 °C min^{-1}. After that, the precursor toluene vapour was introduced into the furnace (Ar was allowed bubbled through a toluene reservoir) and the temperature was kept at 700 °C for 4 h. Then, the carbon source was closed and the temperature was raised to 800 °C and held at 800 °C for 2 h while the Ar was kept flowing. Finally, the furnace was cooled down naturally to room temperature, and the resulting carbon coated samples (C@Mg_2Si) were obtained.

2.2. Characterization

The morphology and structures of the samples were investigated by Scanning Electron Microscope (SEM) (JSM-6390, microscope JEOL). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images of the samples were obtained using a Tecnai G2 F20 S-Twin (America FEI) microscopy operating at 200 kV. X-ray diffraction (XRD) measurements were carried out using a Bruker D8 Focus power X-ray diffractometer with *Cu Kα* radiation ($\lambda = 0.1506\ nm$) generated at 40 kV and 40 mA. Scans for 2θ values were recorded with a step size of 0.02° and exposition time of 0.5 s per step. The carbon loading of the C@Mg_2Si composite samples was studied using Energy Dispersive Spectroscopy (EDS). The surface of as-prepared sample was characterized by Raman spectroscopy (LABRAM-1B).

2.3. Electrode fabrication and electrochemical measurements

Electrochemical properties were examined by using a CR2016 coin cell. The electrode material was prepared from slurry made by mixing 80 wt% active material, 10 wt% carbon black and 10 wt% sodium alginate (NaAlg) binder in DI water. Then, the slurry was pasted onto Cu foil using doctor blade technique to obtain the electrode film. After that, the film was dried at 80 °C for 2 h in air to eliminate the solvent. The film was further dried in a vacuum oven at 80 °C for overnight. Electrochemical cells (CR2016 coin type) were assembled using Mg_2Si or carbon coated Mg_2Si active materials as the working electrode, Li foil as the reference and counter electrode, a Celgard 2300 film as the separator. The electrolyte solution consisted of 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate(DC) (1:1 by volume) plus 2 wt% vinylene carbonate(VC) and 10 wt% fluoroethylene carbonate (FEC) to improve the electrochemical stability. The cells were galvanostatically discharged (lithiated) and charged (delithiated) over a voltage range of 0.02–2 V versus Li/Li^+ at a current density of 100 mA g^{-1}. The total weight of active materials was used to calculate the specific capacity values. Lithium insertion into the working electrode was referred to as discharge, and the extraction was referred to as charge. The cyclic voltammograms (CV) and Electrical impedance spectroscopy (EIS) were performed on the work station (Princeton Applied Research, AMTECT