



Short communication

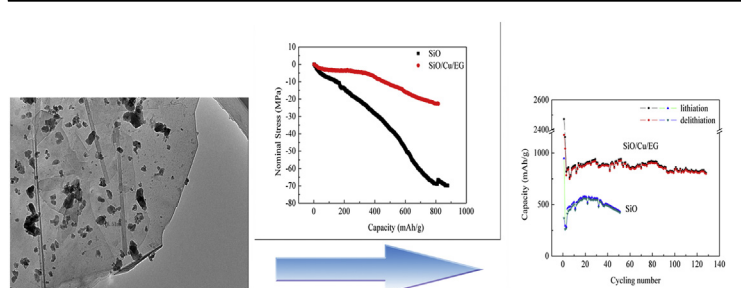
Electrochemical and stress characteristics of SiO/Cu/expanded graphite composite as anodes for lithium ion batteries

Jingze Zhang ^{a,b}, Jian Zhang ^a, Tianzeng Bao ^c, Xiaohua Xie ^{a,*}, Baojia Xia ^a^a Shanghai Institute of Microsystem and Information Technology, Shanghai, 201800, China^b University of Chinese Academy of Sciences, Beijing, 100049, China^c Pylon Technologies Co., Ltd., Yizheng, 211400, China

HIGHLIGHTS

- SiO/Cu/EG composite was prepared by electroless plating followed by ultrasonication.
- Stress behaviors of SiO/Cu/EG electrodes were quantitatively studied.
- The electrodes showed good electrochemical performance due to stress mitigation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 5 November 2016

Received in revised form

14 February 2017

Accepted 21 February 2017

Keywords:

Lithium ion batteries

Silicon monoxide

Electroless copper plating

Expanded graphite

Stress

Performance

ABSTRACT

To enhance the electrochemical performance of SiO, a simple electroless plating and ultrasonication method is used to prepare SiO/Cu/expanded graphite(EG) composite. Electrochemical results show that the electrode has a reversible specific capacity of 836 mAh/g and the capacity retention ratio is 90.2% in the 100th cycle at 200 mA/g current density (25 °C). Moreover, real time stress measurements quantitatively show that EG effectively suppresses stress development in the electrodes, which results in good cycling performance.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Graphite is the most successfully applied anode material for lithium ion batteries, and its available specific capacity has nearly reached its theoretical value (372 mAh/g). However, there is an

urgent need for higher energy density lithium ion batteries used in cell phones (a higher volumetric energy density is required) and electric vehicles (higher volumetric and gravimetric energy densities are required). Among various anode materials, silicon is the most intensively studied because of its high theoretical specific capacity (3579 mAh/g for $\text{Li}_{15}\text{Si}_4$). Unfortunately, large volume change (volumetric strain of 2.7 for $\text{Li}_{15}\text{Si}_4$, compared to 0.1 for LiC_6) [1] during (de)lithiation leads to rapid capacity fade, slowing down its commercialization.

* Corresponding author.

E-mail address: xiexiaohua@mail.sim.ac.cn (X. Xie).

SiO has a smaller volume effect (volumetric strain <2) [2,3] during (de)lithiation than Si, which results in better integrity of the electrodes. Besides, irreversible products like Li_2O and Li_4SiO_4 are formed during first lithiation [4], which buffer the volume change during the following Li^+ (de)intercalation. Consequently, the cycling performance of SiO is superior to Si, but poorer than graphite. Moreover, its electronic conductivity is 16 orders of magnitudes lower than graphite (10^{-12} vs. 10^4 S cm^{-1} [5]). Many solutions have been proposed to overcome the above mentioned problems, such as decreasing the SiO particle size by high energy ball milling [6] to lower intra-particle stress during (de)lithiation; composite formation with other carbon materials, like graphite [7] and graphene [8] to enhance the electronic conductivity of SiO electrodes and buffer the volume change.

Here we chose two materials to form composite with SiO. The one is copper, which has high conductivity of $5.8 \times 10^7 \text{ S cm}^{-1}$ and good ductility to maintain short range electric network. The other is expanded graphite (EG), which has similar properties to graphene, such as large sheets and good flexibility to maintain long range electric network, good liquid absorption ability [9,10] to maintain ionic pathways, plus, it is much cheaper than graphene. Although the electronic conductivity of EG is not very high (e.g. $10^{-1} \text{ S cm}^{-1}$ [11]), it is still much higher than that of SiO. The SiO/Cu/EG composite electrode was tested in Li-ion batteries as anode materials. In addition to normal characterization methods, real time stress measurements were also adopted to further explore the effects of EG on the electrode for the first time.

2. Experimental section

Commercial bulk SiO (Guangde Tewang Photoelectric Material Co., China) was smashed and ball milled at a speed of 3000 r/min for 2 h in deionized water, during which process the particle size (d50) decreased from 8.326 μm to 253 nm. The electroless plating solution was prepared by dissolving 11.7 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (AR), 23.4 g of $\text{EDTA} \cdot 2\text{Na}$ (AR), and 16.4 g of NaOH (AR) in 300 mL distilled water. Then 5.9 g 37% HCHO solution (AR) as the reducing agent and 15 g as-prepared SiO were simultaneously added into the solution with vigorous magnetic stirring at $25 \pm 1 \text{ }^\circ\text{C}$ for 2 h. The SiO/Cu composite was filtered and washed with distilled water until no SO_4^{2-} ions in the filtrate could be detected by 0.1 M BaCl_2 solution. Afterwards, the composite was dried to a constant weight in vacuum at $80 \text{ }^\circ\text{C}$. EG was prepared by heating expandable graphite to $900 \text{ }^\circ\text{C}$ for 2 h in Ar atmosphere. Then 1.4 g SiO/Cu and 0.6 g EG were added to 50 mL ethanol and the mixture was ultrasonicated for 2 h, and finally it was dried to a constant weight in vacuum at $80 \text{ }^\circ\text{C}$.

The dc electrical conductivity was measured in a pressed pellet configuration by a direct volt-ampere method [12]. The diameter of the pressed disk samples were 17.0 mm. Electrical conductivity measurements were conducted on an Autolab electrochemical workstation (Metrohm) by linear sweep voltammetry after the obtained powders were pressed into disks under a pressure of 20 MPa for 5 min.

The crystalline structure of the samples was determined by XRD (Rigaku D/max 2200/PC, Japan). The morphology of the samples was characterized by SEM (Hitachi S4700, Japan) and TEM (FEI Tecnai, USA). The Cu content was analyzed by ICP-AES (IRIS Advantage1000, Thermo Jarrell Ash Co., USA) after dissolution of the sample in nitric acid.

The composite electrodes were prepared by mixing 80 wt% as-prepared powder, 10 wt% Super P (TIMCAL) as a conductive agent, 5 wt% CMC (QUANTUM HI-TECH GROUP LIMITED) and 5wt% SBR (BASF SE) as binders in deionized water. The slurry was uniformly coated on a copper foil current collector by doctor blade method,

and dried at $80 \text{ }^\circ\text{C}$ in vacuum to a constant weight. The total material loading of an electrode was around 1.6 mg cm^{-2} . A 2025 type coin cell with lithium metal as counter electrode was used to perform electrochemical tests. The organic electrolyte was 1M LiPF_6 in EC/DMC/EMC (1:1:1, vol) + 4% VC, and the separator was Celgard 2320 (Celgard Inc., USA). Galvanostatic cycling was carried out using Neware battery testing system at $25 \pm 1 \text{ }^\circ\text{C}$ with potential limits of 0.01 and 1.5 V (vs. Li/Li^+ , the same below).

The stress and electrochemical behaviors of as-prepared electrodes were investigated simultaneously during galvanostatic cycling in a custom made cell with a glass window. A lithium foil was placed at the bottom of the cell, acting as both counter and reference electrodes. A separator (Freudenberg FV1E) was placed on top of the lithium foil, followed by the electrode. The Cu foil of the electrode was epoxy bonded to a Si (100) wafer (400 μm in thickness, 50.8 mm in diameter). Both the separator and the electrode were completely soaked in the electrolyte before the cell was sealed. The Si wafer was not submerged in the electrolyte. The stress evolution of the electrodes was measured by monitoring the curvature change of the Si wafer with a multi-beam optical sensor (MOS, k-Space Associates, Dexter, Michigan). The calculation of stress was similar to that given earlier by Sethuraman [13] and the stress obtained was average in-plane equi-biaxial stress.

3. Results and discussion

XRD patterns of SiO, SiO/Cu and SiO/Cu/EG powder are shown in Fig. 1a. A broad peak in the range of $20\text{--}30^\circ$ in SiO XRD pattern indicates its amorphous nature [14]. In SiO/Cu XRD pattern, the peaks at $43, 50$ and 74° are assigned to Cu (111), (200) and (220) plane, respectively. A strong peak at 26° in SiO/Cu/EG XRD pattern is attributed to (002) plane of graphite, indicating the layered structure of EG.

The thin-layer structure of EG is clearly shown in Fig. 1b. In SiO/Cu/EG composite, SiO/Cu particles are distributed evenly on EG (Fig. 1c and d), so EG can effectively buffer the expansion of SiO during lithiation and provides a conductive network. The conductivity of SiO/Cu/EG is $7.91 \times 10^{-2} \text{ S cm}^{-1}$, which is eight orders of magnitude higher than that of SiO ($1.77 \times 10^{-10} \text{ S cm}^{-1}$).

The lithiation and delithiation curves and cycling performance of SiO, SiO/Cu, SiO/EG and SiO/Cu/EG are shown in Fig. 2, note that the specific capacity is calculated based on the weight of SiO in every case. Cu content was 13.3% in SiO/Cu according to the ICP analysis. The current density of the initial cycle was 50 mA/g, which was increased to 200 mA/g in the following cycles. The lithiation capacities during the initial cycle of the above four samples are 1264, 1090, 1414 and 2471 mAh/g, with coulombic efficiencies of 34.3, 41.6, 43.3 and 47.6%, respectively. If the capacities of EG and SP (Fig. 2e) are taken into account, the initial lithiation capacities of SiO, SiO/Cu, SiO/EG and SiO/Cu/EG are 1210, 1028, 1259 and 2293 mAh/g, with coulombic efficiencies of 34.1, 41.8, 42.7 and 47.6%, respectively. The theoretical capacity of SiO is unclear at the moment, since there are various reactions consuming Li^+ , such as the formation of Li_4SiO_4 and Li_2O . The main reactions are as follows:



If only reactions (1) and (3) are taken into account, the reversible and irreversible capacities are 2278 and 1215 mAh/g, respectively, and those calculated from reactions (2) and (3) are 1709 and 608 mAh/g, respectively. Thus, the theoretical value of the reversible

Download English Version:

<https://daneshyari.com/en/article/5149486>

Download Persian Version:

<https://daneshyari.com/article/5149486>

[Daneshyari.com](https://daneshyari.com)