Electrochimica Acta 223 (2017) 39–46

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Bacteria-inspired Fabrication of Fe_3O_4-Carbon/Graphene Foam for Lithium-Ion Battery Anodes

Ning Zhang[a], Chong Chen[a], Xiaohui Yan[a], Yuan Huang[a], Jia Li[a], Jianmin Ma[b,*], Dickon H.L. Ng[a,*]

[a] Department of Physics, The Chinese University of Hong Kong, Hong Kong, China
[b] Key Laboratory for Micro-/Nano-Optoelectronic Devices, School of Physics and Electronics, Hunan University, Changsha 410082, China

ARTICLE INFO

Article history:
Received 1 September 2016
Received in revised form 30 November 2016
Accepted 2 December 2016
Available online 3 December 2016

Keywords:
Bacteria
Fe_3O_4
Graphene foam
Lithium-ion battery
Electrochemical properties

ABSTRACT

Although lithium-ion batteries are commonly used to our daily life, achieving superior properties in low-cost is still our current challenge. Here we report the fabrication of a bacteria-inspired, micro-/nanostructured Fe_3O_4-carbon/graphene foam hybrid material for lithium-ion battery anodes. The process employing biological adsorption is featured with low-cost and can have mass-production. Attributed to the graphene foam substrate, the fabricated micro-/nanostructure can be directly employed as a binder-free LIB anode without the need of complex treatments. The product used as an anode delivers a high reversible capacity of 1112 mAh g^{-1} at the current density of 100 mA g^{-1} even after 200 cycles, and exhibits good rate performance. These results demonstrate fabrication and electrochemical properties of a bacteria-inspired Fe_3O_4-carbon/graphene foam, suggesting a facile method for making anodes to be used in high-performance lithium-ion batteries.

1. Introduction

Rechargeable lithium-ion batteries (LIBs) are considered as a promising power source for the portable electronic devices in our daily life [1–5]. Energy stored in LIBs is basically by the shuttle of lithium ions (Li^+) between cathode and anode. Some practical applications have been achieved, but critical issues such as cost, stability, energy capacity and rate performances for electrode materials are still needed to be addressed [6–8]. Many interests are drawn to the development of anode materials based on transition metal oxides: MO_x, where M can be Fe, Co, Ni, *etc* [5–10]. Their discharge/charge in LIBs is actually a reversible conversion reaction with Li^+, including formation and decomposition of lithium oxide, accompany with the reduction and oxidation of MO_x [6–8]. This mechanism endows them with high theoretical capacity reaching to 500–1000 mAh g^{-1}, much higher than ~372 mAh g^{-1} of conventional graphite anode material [9–12].

Magnetite (Fe_3O_4), an MO_x, possessing relatively high theoretical capacity (~926 mAh g^{-1}), low-cytotoxicity nature and low-cost for large-scale production, is extensively studied as an anode for LIBs [12–15]. However, the large volume variation, particle agglomeration, and intrinsic kinetic limitations exist of Fe_3O_4 during discharge/charge processes, have been reported resulting in its irreversible capacity loss and poor stability [17–22]. Hybridization with carbon-based materials *e.g.*, activated carbon, carbon nanotube, and graphene at nanoscale offers one promising strategy to overcome these challenges of Fe_3O_4 [22–26]. Due to small dimensions and relatively high specific surface area, nanoscale Fe_3O_4 can shorten effective diffusion length of ions and electrons, thus provides abundant active sites for Li^+ storage, and accommodates volume variation caused by Li^+ insertion/extraction [23–30]. Meanwhile, the carbon-based component can act as a buffer to reduce or even remove the aggregation and volume effects, as well as a conductive media to improve electron transport of Fe_3O_4 [31–35]. Of various carbon-based materials, three-dimensional (3-D) graphene foam (GF) constituting sheets of graphene is of excellent electron transport and many other superior properties *e.g.*, light weight and chemical resistance, representing one of powerful substrate candidates for LIBs [36–40]. So far, several works have reported hybrid Fe_3O_4/carbon-based LIB anodes, Li et al., had successfully fabricated a bio-inspired hierarchical nanofibrous Fe_3O_4-TiO_2-carbon composite by employing the natural cellulose. Such composite showed a significant improvement in stability and rate capability while using as the anode for LIBs [33]; Luo et al., used atomic layer deposition (ALD) to synthesize hierarchical

---

* Corresponding authors.
E-mail addresses: nanoelechem@hnu.edu.cn (J. Ma), dng@phy.cuhk.edu.hk (D.H.L. Ng).

http://dx.doi.org/10.1016/j.electacta.2016.12.006

porous Fe_3O_4/VO_x/graphene nanowires. The product exhibited high Coulombic efficiency and outstanding reversible specific capacity [34]; Hu et al., had developed a supercritical carbon dioxide ($scCO_2$) method to anchor Fe_3O_4 nanoparticles onto the graphene foam, and the composite could be able to deliver excellent capacity [35].

Bacteria, micro-organism widely distributed in nature, exhibit unique structures and functionalities [41–49]. To our interest, they provide abundant biomass for the batch fabrication of micro-/nanostructures with controlled size, structure, and functionality in a low-cost manner. In this study, we developed a route utilizing biological adsorption to synthesize bacteria-inspired Fe_3O_4-carbon/GF for LIB anodes. The *Escherichia coli* (*E. coli*)-based fabrication is demonstrated as an example. The fabricated Fe_3O_4-carbon/GF being of hierarchical structures can be directly employed as a binder-free LIB anode without any complex treatments. Results from electrochemical measurements reveal that this kind of anode with a high reversible capacity, long cycle stability and good rate performance. The fabrication of this bacteria-inspired LIB anode takes advantage of biological adsorption, suggesting a versatile and facile method for the low-cost production of high-performance LIBs.

2. Experimental methods

2.1. Pure GF preparation.

The pure GF was prepared *via* chemical etching process of nickel foam supported graphene sheets, which was purchased from *Shenzhen 6 carbon technology Co., Ltd* (China). We utilized the $FeCl_3$ purchased from *Sigma-Aldrich* (USA) to remove the nickel backbone and get the pure GF as follows. The nickel foam supported graphene sheets was firstly cut into small pieces of $80 \times 80\,mm^2$, and then immersed into the 80 °C 2 M $FeCl_3$ solution for 1 h. The nickel was etched away while the foam-like graphene sheets remained. After several times of washing with deionized (DI) water and ethanol, the as-obtained GF was stored in the DI water for further using.

2.2. Cultivation of E. coli onto the GF.

We selected *E. coli* (strain HCB1737-a derivative of wild-type *E. coli* AW405 from Howard C. Berg Lab, Harvard University, USA) as our biomass. The *E. coli* was cultivated overnight in a 3 ml LB (Luria-Bertani) medium containing 1% Bactotryptone, 0.5% yeast extract, and 0.5% NaCl at 30 °C. During cultivation, they were reproduced from single-colony isolates under soft shaking reached to a stationary phase. 0.5 ml of the *E. coli* solution was injected into a vented tube containing 3 ml of LB solution and the as-obtained pure GF. After incubation at 30 °C over 16 h, the *E. coli* cells were attached to the surface of the GF.

2.3. Fabrication of the Fe_3O_4-carbon/GF.

The *E. coli* attached GF (*i.e.*, *E. coli*/GF) was firstly washed for several times with DI water to exclude the residual cultivating solution. Then, the as-obtained *E. coli*/GF was treated with ethanol for improving cells' permeability, retaining cell morphology, and dissolving lipid layer on *E. coli* membrane [46–49]. The *E. coli*/GF was then placed into a 0.1 M $FeCl_3$ solution for 3 h to allow *E. coli* adsorb Fe^{3+} ions (*i.e.*, Fe^{3+}-*E. coli*/GF) at room temperature. Followed by vacuum-drying at 60 °C, the Fe^{3+}-*E. coli*/GF was subject to annealing at argon for 1 h at 550 °C, generating Fe_3O_4-carbon/GF hybrid sample, and its thickness was measured to be ~1.25 mm. We have also prepared some control samples: (1) pure GF; (2) carbon/GF: using *E. coli*/GF without Fe^{3+} ion adsorption but subject to the same annealing condition (550 °C for 1 h in argon) to obtain carbon/GF; (3) Fe_3O_4/GF: pure GF subject to the 0.1 M $FeCl_3$ solution adsorbing for 3 h and post annealing at same condition; (4) Fe_3O_4 NPs: commercial Fe_3O_4 nanoparticles purchased from *Sigma-Aldrich* (USA).

2.4. Structural characterizations.

The structural and composition of the Fe_3O_4-carbon/GF hybrid sample were carried out by various techniques. The X-ray diffraction (XRD) was performed with RU300 (*SmartLab*, *Rigaku*) using Cu K_α radiation ($\lambda = 0.1540598$ nm) to identify crystalline phases in the samples. Raman scattering spectrum was performed using a Micro-Raman spectrometer (*RM- 1000*, *Renishaw Co.*, *Ltd*), equipped with a 10 mW, 514 nm helium-neon laser to identify radical groups in the samples. X-ray photoelectron spectroscopy (XPS) was collected with Al Kα radiation on a PHI Model 5802 (calibrated with C1s at 284.8 eV) to perform an elemental analysis. The Brunauer–Emmmett–Teller (BET) test and Barrett-Joyner-Halenda (BJH) analyses were conducted by the ASAP 2000 to obtain the surface area of the samples. Thermogravimetric analysis (TGA) was performed from ambient to 930 °C with a TGA Q600 at a heating rate of 10 °C min^{-1} to study the weight ratio of the components in the sample. Field-emission scanning electron microscope (FE-SEM) imaging and element analysis were carried out using FEI Quanta 200 equipped with an energy-dispersive X-ray spectrometer (EDX). Transmission electron microscopy (TEM) images were captured with a Tecnai F20 microscopy operating at 200 kV.

2.5. Electrochemical characterizations.

The working electrode of the LIBs in this work used as-prepared Fe_3O_4-carbon/GF without any binder or conductive agents. Same procedures were also applied to the control samples (1) pure GF, (2) carbon/GF, and (3) Fe_3O_4/GF mentioned in Section 2.3. In preparing working electrode of control sample (4) Fe_3O_4 NPs, its needs a combination of Fe_3O_4 NPs, conductive carbon black, and the PVDF (polyvinylidene fluoride) in the weight ratio of 80:10:10. The as-prepared mixture was placed onto a copper foil and went

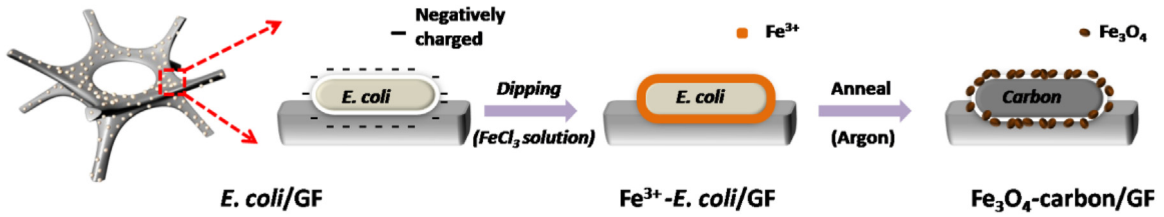

Fig. 1. Schematic illustration of the fabracation approach of Fe_3O_4-carbon/GF sample.