Materials Letters 228 (2018) 297–300

Contents lists available at ScienceDirect

Materials Letters

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

Liquid gallium encapsulated in carbon nanofibers for high performance lithium storage

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ARTICLE INFO

Article history:
Received 23 April 2018
Received in revised form 8 June 2018
Accepted 12 June 2018
Available online 13 June 2018

Keywords:
Liquid gallium
Electrospinning
Lithium storage
Electronic materials
Material structure

ABSTRACT

Freestanding membrane built from interwoven carbon fibers with encapsulated liquid gallium (Ga) nanodroplets has been demonstrated via the ultrasonic cell disrupting and electrospinning approaches along with a subsequent annealing process. Employing this membrane as a freestanding anode for lithium storage, the severe volume changes of Ga can be effectively accommodated due to the unique encapsulated 3D network structure. As a result, the membrane exhibits superior electrochemical performance, including high reversible capacity (450 mAh g^{-1}), enhanced cycling stability (247 mAh g^{-1} at 0.65 A g^{-1} over 250 cycles), as well as good rate performance (200 mAh g^{-1} at 2 A g^{-1}).

1. Introduction

Lithium-ion batteries (LIBs) have been widely used as energy storage in the field of electric vehicles, owing to their high energy density, long lifespan and environmental friendliness [1]. New anode materials with improved performance are urgently required for the development of next generation LIBs. Gallium (Ga) is a promising anode material for LIBs with a high theoretical gravimetric capacity of 769 mAh g^{-1}, in which each Ga atom could host two Li atoms on full lithiation [2]. Specially, Ga exists in liquid phase at room temperature with a relatively low melting point (30 °C) [3]. Liquid Ga experiences a unique liquid-to-solid phase transition when lithiation and forms crystalline Li_2Ga with over 160% volume change, while during delithiation process, reverse phase transition happens, and the cracks formed in solid lithiated state will be healed partially by the final liquid state Ga [4].

However, during delithiation of bulk Ga, electrically connected solid state Li_xGa tends to break down and turns to smaller Ga droplets with some electrically isolated Li_xGa particles remained. It is difficult for them to convert to an integrated liquid-phase Ga. With the accumulation of isolated Li_xGa particles and solid electrolyte interface (SEI), there are decreased available Li^+ storage sites, inducing massive capacity fading for long time cycling. Besides, long diffusion length of Li^+ in bulk Ga results in poor rate performance. Building nanostructures is a common method to address the above-mentioned problems of bulk materials [5,6]. However, the nanonization of liquid metals remains a big challenge and special current collectors are required when used as active materials [3], increasing the difficulty of their practical application.

Herein, we developed an approach to prepare the Ga nanodroplets (GaNDs) encapsulated in carbon nanofiber (GaNDs/CF) for lithium storage. With this structure, nano-sized Ga was confined in continuous, highly conductive carbon fibers, offering enough space for volume expansion, preventing the agglomeration of GaNDs and enhancing charge transfer kinetics of electrode. Through this method, high reversible capacity (450 mAh g^{-1}), enhanced cycling stability (247 mAh g^{-1} at 0.65 A g^{-1} over 250 cycles) and excellent rate performance (200 mAh g^{-1} at 2 A g^{-1}) have been achieved.

2. Experimental

Typically, 2.0 g liquid Ga was dispersed in 10 mL N, N-Dimethylformamide (DMF) by ultrasonication for 5 h, and then 1.0 g polyacrylonitrile (PAN) was dissolved in the dispersant with vigorous stirring for 24 h. The resultant liquid was loaded into a syringe with a 22-gauge needle for eletrospinning. Flow rate was set at 1.0 mL h^{-1}, and a voltage of 7 kV was applied between needle and Cu foil collector with a distance of 10 cm. The as-spun membrane was annealed at 280 °C for 2 h in argon environment with a heating rate of 1 °C min^{-1} and a successive heat treatment was

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https://doi.org/10.1016/j.matlet.2018.06.043
0167-577X/

applied at 700 °C for 2 h with a heating rate of 5 °C min^{-1}, generating the GaNDs/CF membrane.

3. Results and discussion

The synthesis process of GaNDs/CF membrane involves three steps as shown in Fig. 1. Firstly, homogeneous GaNDs-DMF emulsion is obtained via ultrasonic cell disrupting of bulk liquid Ga, where the dispersant DMF efficiently prevents the agglomeration of nano-sized Ga (Fig. 1a). Then, during the following electrospinning process in Fig. 1b, GaNDs are separately encapsulated in PAN fibers and the composite fibers are weaved into an interconnected network, generating a flexible GaNDs/PAN membrane. Finally, after stabilization and carbonization in argon condition, flexible GaNDs/CF membrane was attained and can be used as electrode directly (Fig. 1c).

The crystalline structure was inspected by X-ray diffraction (XRD) measurement. As shown in Fig. 2a, three broad peaks are shown to exist in the XRD pattern, one of which at 20° can be

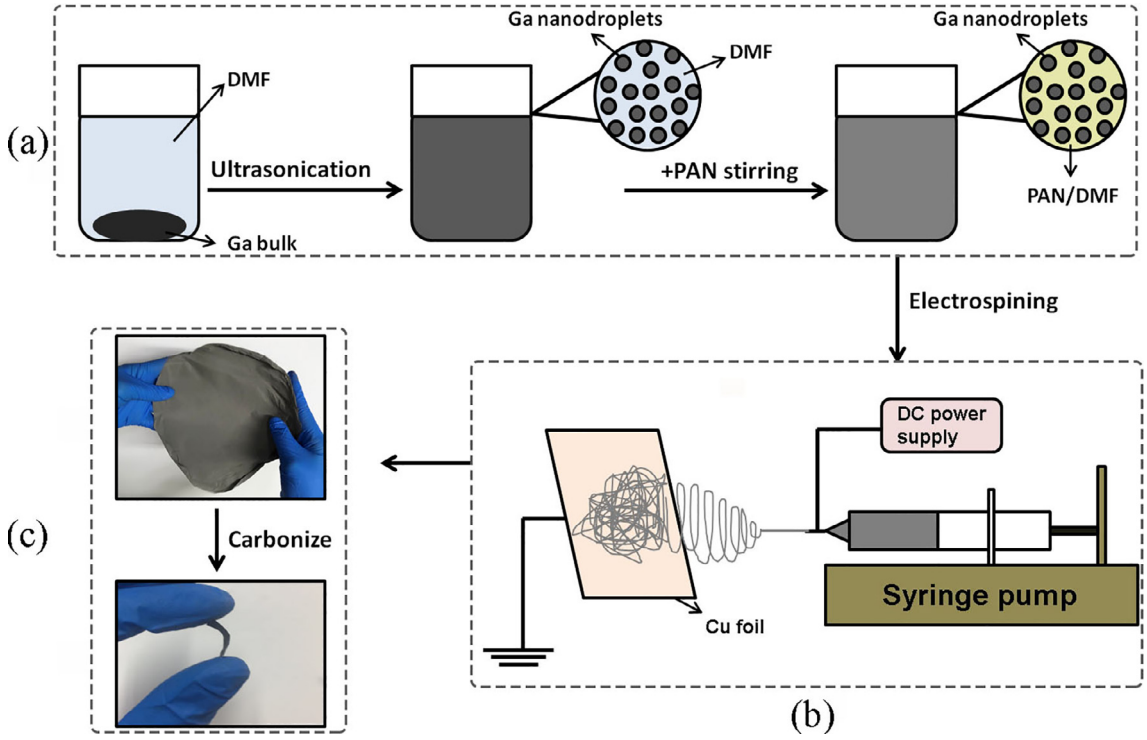

Fig. 1. Synthesis of GaNDs/CF membrane: (a) GaNDs/PAN dispersion used as the electrospinning solution via ultrasonication; (b) electrospinning process to get the GaNDs/PAN membrane; (c) optical photographs of flexible GaNDs/PAN and carbonated GaNDs/CF membranes.

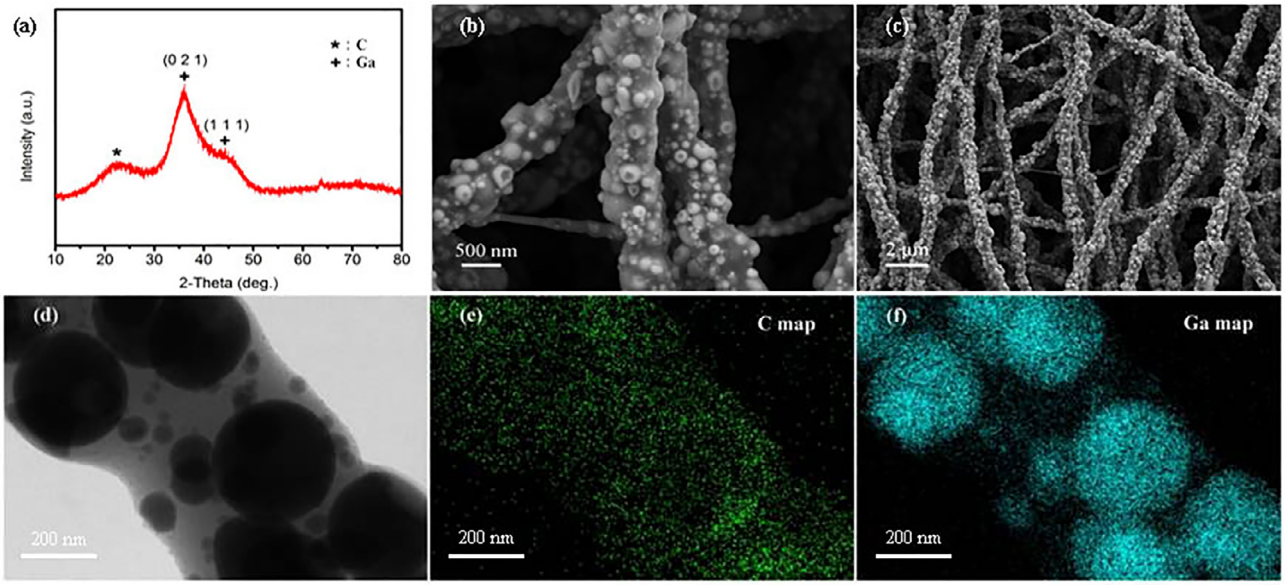

Fig. 2. (a) XRD pattern of GaNDs/CF. (b-c) SEM images of GaNDs/CF with different magnifications. (d) STEM BF image of GaNDs/CF and corresponding elemental mapping images of (e) C and (f) Ga.