



Gallium oxide nanorods as novel, safe and durable anode material for Li- and Na-ion batteries



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ARTICLE INFO

Article history:

Received 14 October 2016

Received in revised form 24 February 2017

Accepted 6 March 2017

Available online 9 March 2017

Keywords:

gallium oxide

nanorod

anode

lithium battery

sodium battery

ABSTRACT

Gallium oxide nanorods prepared by template-free synthesis are reported for the first time as safe and durable anode material for lithium- and sodium-ion batteries. The ambient temperature electrochemical response of the nanorods, tested by cyclic voltammetry and constant-current reversible cycling, is highly satisfying in terms of remarkable stability and capacity retention upon long-term operation (400 cycles), even at high current densities. The newly proposed application of gallium oxide nanorods as electrode material is notable also because this material can preserve the electrical pathway without the need of any “buffer matrix” to compensate for the expansion upon lithium or sodium reversible storage. The highly promising electrochemical performance is attributed to the high aspect ratio and high surface area that stem from the nanorod morphology and which can lead to short diffusion path and fast kinetics of both cations (Li⁺ or Na⁺) and electrons.

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1. Introduction

Affordable, safe and environmentally friendly energy conversion and storage are crucial targets for enabling the World to thrive. Electricity generated from renewable sources represents a prime choice to meet the demand for low-emission energy supply systems. The growing use of intermittent energy sources to generate electricity, such as solar and wind power, necessitates the development of reliable, affordable and efficient electric energy storage systems [1]. In this context, the development of high performing, safe and cost-effective batteries will play a fundamental role [2–4]. Li-ion batteries (LiB) have emerged as the power source of choice thanks to their superior characteristics, such as high capacity, long life and fast rate capability [5]. However, LiB suffer from limited energy density of individual cells, lack of fast recharge cycles and improvable durability and safety [6]. When the

focus is on large-scale and high-volume applications as EV or smart grids, it is also important to take into account the eco-friendliness, recyclability and costs associated with the fabrication of energy conversion and storage devices [7,8].

Over the years, innovation in materials chemistry has been the key to a number of advancements in LiB technology [9]. Regarding the negative electrode, the slow diffusivity of lithium ions within the stacked layers that constitute graphite is a major issue for the typical intercalation/de-intercalation (sodium ion intercalation is even forbidden), which restricts its use to low-medium power devices. Moreover, the practical specific capacity vs. lithium of graphite is limited to about 350 mAh g⁻¹. As a result, particularly when application in large-scale storage systems is envisaged, carbonaceous structures must be replaced with new materials, which should ensure enhanced performances. For this purpose, considerable research efforts have been devoted to develop viable lithium alloys and/or lithium intermetallic compounds [10,11]. Moreover, various transition metal oxides (TMO, where M = Co, Ni, Cu, Fe) have been intensively studied, because of their practical reversible specific capacity up to 700 mAh g⁻¹, safety, environmental benignity and low cost [3,12]. Unlike carbon-based anodes,

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the mechanism of alkali metal ion storage in TMO is a conversion process and the capacity of the final device is determined by the accessibility of the active sites of the active material particles in the electrode. Thus, decreasing the scale of the materials constituting the electrode to the nanoscale can result in enhanced reversible charge storage, as a consequence of reduced volume and structural changes upon cycling [9,13]. Unravelling the huge potentialities of nanomaterials and learning how to exploit them in practical devices can lead to remarkable advances [14,15].

In this work, we report for the first time the use of gallium oxide nanorods, obtained by a template-free synthesis method, as a novel and promising anode material for Li-ion batteries. Gallium (III) oxides (Ga_2O_3) are important functional materials with very diverse applications [16,17]: they are employed in vacuum deposition and as part of the manufacturing of semiconductor devices, in lasers and luminescent phosphors [18], in gas sensors and dielectric coatings for solar cells, in tight junctions [19], as heterogeneous catalysts [20–22]. Like other post-transition metal oxides, gallium oxide reversibly reacts with lithium ions [23], which suggests its applicability as active electrode material in LiB. On the other hand, Li-Ga is a largely unstudied binary system for application as LiB anode, due to the relatively complicated synthesis and low melting point of metallic gallium. In 2005, Tarascon and co-workers [24] unravelled the electrochemical behaviour of some Li_xGa_y alloys, which provided a rather stable specific capacity approaching 250 mA h g^{-1} after 20 charge/discharge cycles. Meng et al. [25] synthesised a core-shell SWCNT- GaS_x nanostructured composite yielding a stable capacity approaching 575 mA h g^{-1} at high current. Gallium selenide (GaSe) with a layered structure was synthesised through chemical reduction by Jeong et al. [26] and showed a discharge capacity as high as 760 mA h g^{-1} at the 50th cycle, almost doubling the values for the corresponding Ga_2O_3 -based electrode. Very recently, Patil et al. [27] reported the hybridisation of gallium oxide with reduced graphene oxide to optimise the electrode performance and charge transport of the nanocomposites, approaching the calculated theoretical reversible capacity of 769 mA h g^{-1} for few initial cycles.

The motivation for studying gallium oxide nanorods as electrode material in lithium-based batteries stems from the recently reported template-free synthesis method that allows producing these nanostructures with very small dimensions (20–80 nm length and 3–5 nm width, thus large aspect ratio) and high specific surface area [28]. In addition, based on recent concerns on the reduced availability of global lithium resources along with their restricted geographical localisation that are leading to a rapid increase of the request for Li metal [29], the electrochemical behaviour of the gallium oxide nanorods was also evaluated in lab-scale sodium cells, which to our knowledge represents the first literature report in this respect. The high abundance of Na, its suitable redox potential of -2.71 V vs. SHE (i.e. only 0.3 V above that of lithium, meaning that there is only a small energy penalty to pay compared to common LiB) and the active support of the well-established and consolidated know-how on LiB technology imply that Na-based secondary electrochemical cells hold much more promise than Li-based for the near future practical implementation in large-scale grid energy storage, where safety and cycling stability are fundamental requirements.

2. Experimental

2.1. Materials

GaCl_3 (anhydrous, granular, 99.999%, ABCR), 2-butanol (Sigma-Aldrich), sodium carboxymethylcellulose (NaCMC, average

M_w : 250,000, Sigma-Aldrich), carbon black (Super P, MMM Carbon, Belgium) were used as received, without further purification.

2.2. Synthesis

Gallium oxide nanorods (Ga_2O_3 -NR) were prepared using a precipitation method involving solvolysis of GaCl_3 with 2-butanol, followed by hydrolysis and condensation of the formed species, as reported in detail elsewhere [28]. Briefly, 15 mmol of GaCl_3 were weighed under inert atmosphere and then dissolved by slow addition of 2-butanol: first, 4.80 g were added dropwise within 15 min, followed by addition of the remaining 2-butanol (25.23 g) within 30 min. The solution was stirred for 1 h, after which deionised water (2.94 g) was added dropwise under continuous stirring. The solution was stirred at room temperature for 3 h and then heated to 70°C for 23 h. The obtained sample was aged for 3 days at room temperature, after which the resulting white precipitate was separated by centrifugation, thoroughly washed with ethanol and dried overnight in air at 100°C .

2.3. Structural analysis and characterisation

Powder X-ray diffraction (XRD) patterns were recorded on a STOE Stadi MP diffractometer with a linear position sensitive detector (PSD) in the region of $2\theta=5$ to 82° , with internal resolution of 0.03° . The measurements were performed in Debye-Scherrer mode at ambient temperature using $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$) selected by means of a Ge (111) monochromator. N_2 -physisorption measurements were performed using Micromeritics Tristar 3000 equipment. Prior to analysis, the samples were outgassed under reduced pressure during 12 h at 120°C (rate: 5°C min^{-1}). The specific surface area was calculated using the Brunauer-Emmet-Teller (BET) method [30]. Bright field transmission electron microscopy (TEM) images were collected on a Philips FEG CM-200 operated at 200 kV. The samples were prepared by dispersing oxide powders in few drops of absolute ethanol in an agate mortar followed by deposition on 300 mesh carbon-coated copper grids.

2.4. Electrode preparation, cell assembly and electrochemical testing

The electrodes for the evaluation of the electrochemical properties were prepared by a water-based, spray-assisted procedure. In a typical procedure, NaCMC was used as binder. The solid was dissolved in doubly deionised water followed by the addition of Super P as electrical conductor and the gallium oxide nanorods under continuous stirring ($\sim 3 \text{ h}$) [31]. The obtained slurry was then spray-coated on a copper or aluminium current collector film for assembly of lithium or sodium cells, respectively. After the evaporation of the solvent under a fume hood at ambient conditions, discs of 2.54 cm^2 were punched out of the foil and vacuum-dried overnight at 130°C . After their transfer in an Ar-filled dry glove box, the discs were weighed before their assembly in test cells and, by subtraction of the average mass of the Cu (or Al) discs, the mass of the coating mixture was calculated. The exact composition of the electrodes was 82:13:5 wt. % in Ga_2O_3 -NR, Super P and NaCMC. These composite electrodes were used in three electrode electrochemical test cells with reference electrode (model ECC-Ref test cells, EL-CELL GmbH, <http://el-cell.com/products/test-cells/ecc-ref>), with lithium (or sodium) metal as the counter electrode (also as the reference electrode in the case of cyclic voltammetry) and a glass wool (Whatman GF/A) disc as the separator. Lithium metal foils ($120 \mu\text{m}$ thick) were purchased from Chemetall. Sodium metal was cut from sodium pieces (Sigma Aldrich), roll-pressed and punched on the current collector. The surface of Na metal was refreshed using a scalpel before test cell

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