The effect of diethylenetriamine on the solvothermal reactions of polyethyleneimine-graphene oxide/lithium titanate nanocomposites for lithium battery anode

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HIGHLIGHTS

- The preparation of NG/LTO-TiN from the reactions of PEI-GO/LTO and DETA.
- The metallic TiN increases the electrical conductivity and ionic transport.
- The NG provided an electrical network and reduce the diffusion length of Li ions.
- The NG/LTO-TiN exhibited an excellent electrochemical performance in Li-battery.

ARTICLE INFO

ABSTRACT

A simple preparation of N-doped graphene/$Li_4Ti_5O_{12}$–TiN (NG/LTO-TiN) from the polyethyleneimine-graphene oxide/$Li_4Ti_5O_{12}$ (PEI-GO/LTO) is achieved through a solvothermal reaction in the presence of diethylenetriamine (DETA). The solvothermal reaction converts PEI-GO/LTO into corresponding NG/LTO-TiO_2, which could be simultaneously converted into NG/LTO-TiN via reacting with DETA as an N source. It is proposed that the electrically conductive titanium nitride (TiN) is formed at the interface between the surfaces of $Li_4Ti_5O_{12}$ (LTO) and nitrogen doped graphene (NG). When used as an anode material for lithium ion battery (LIB), the NG/LTO-TiN exhibited superior rate capability in comparison to LTO, reduced GO/$Li_4Ti_5O_{12}$–TiO_2 (RGO/LTO-TiO_2) and NG/LTO-TiO_2 nanocomposites, with excellent cyclic stability up to 100 cycles. Moreover, the ionic diffusion coefficient is 3.6×10^{-12} cm^2 s^{-1} for NG/LTO-TiN-94.3%, which is a higher value than that of the LTO (8.85×10^{-13} cm^2 s^{-1}), RGO/LTO-TiO_2-93.5% (1.48×10^{-12} cm^2 s^{-1}), and NG/LTO-TiO_2-94.2% (2.51×10^{-12} cm^2 s^{-1}) nanocomposites studied.

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1. Introduction

Recently, lithium ion batteries have attracted much interest in the field of portable electronic devices due to their high energy density, light weight, and long lifetime in comparison to other battery devices [1,2]. However, the current lithium ion batteries use graphite/carbon-related compound as negative electrodes (anode), which produces a growth of lithium dendrites during the overcharge process that is detrimental to the stability of the electrode [3–5]. Recently, spinel LTO has been considered as a better alternative to carbon based anode because it uses a higher operating potential (1.55 V vs. Li), exhibits a negligible volume change, and has no solid electrolyte interface formation [6]. However, the poor electrical

conductivity (10^{-13} S cm^{-1}) and moderate lithium ion diffusion coefficient (10^{-9} to 10^{-13} cm^2 s^{-1}) of LTO limits the practical applications of LIB [1,6,7]. In order to overcome these shortcomings, the doping of metal or non-metal ions in Li, Ti or O sites or surface modification by using conductive materials such as carbon, graphene, carbon nanotube, Ag, TiN, etc. have been considered [8–14].

The surface modification of LTO via anatase TiO_2 could considerably increase the electrochemical performances, due to the high theoretical capacity of TiO_2 (335 mAh g^{-1}) [15]. The dual phase LTO–TiO_2 is obtained via a molten salt precipitation method, one pot hydrothermal process, or by hydrothermal reactions of LTO [5,16–19]. It is well known that both the LTO and TiO_2 are not conductive and require electrical conductivity for the fast charge and ionic transportation. In another approach, the nitridation or deposition of a thin layer of TiN using an atomic vapor deposition method is applied to increase the electrical conductivity of LTO for high rate

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Li-ion batteries [4,14,20–23]. Generally, TiN is obtained by reacting TiO$_2$ and N containing compounds at higher reaction temperatures [24,25]. In our study, we applied a simple and scalable solvothermal reaction to change the LTO to LTO–TiN via the simultaneous formation and modification of dual phase LTO–TiO$_2$. In the meantime, to increase the electrical conductivity and suppress the reduction of electrolyte or gassing behavior of the electrode materials, the use of graphene or carbon coating is more appropriate.

In recent times, graphenes and graphene based materials have been considered as excellent substrates for improving the electrode properties of metal oxides due to their superior electrical conductivity, vast surface area, and structural flexibility [26–30]. To achieve good contact between the graphene and LTO, the in-situ solvothermal method seems appropriate, in which the LTO particles are decorated uniformly on the graphene sheets [31–33]. Another interesting approach is the electrostatic co-assembly of positively charged metal oxide and graphene oxide (GO), which is frequently applied for the preparation of various LTO/RGO and Co$_3$O$_4$/RGO nanocomposites [27,34,35]. Moreover, to increase the electrochemical stability and rate capability of the electrode, the doping of hetero atoms (N, P or B) on the carbon or graphene has been considered, which increases the electrical conductivity and lithium ion diffusion rate of the electrode [36–41]. Therefore, to improve the electrochemical performances of the graphene nanocomposites, the graphene sheets should be in close contact with metal oxides and doping should take place on the 2D graphene.

Herein, we report on the preparation of NG/LTO-TiN by changing the LTO of dual phase LTO–TiO$_2$ and then LTO–TiN in the presence of graphene using the solvothermal method, with DETA as a phase modifier, which had a large number of N atoms. The polyethyleneimine (PEI) is applied to wrap the GO on LTO aggregates via the electrostatic interaction between the PEI and GO intercalated-LTO aggregates and the N-dopant for graphene sheets. In this approach, firstly the solvothermal reactions of PEI-GO/LTO converts the PEI-GO and LTO into their corresponding N-doped graphene (NG) and LTO–TiO$_2$. Secondly, reactions in the presence of DETA serve as an excess N source to promote the surface TiO$_2$ into electrically conductive TiN. The partially converted TiN offers an electronic conducting network on pristine LTO, which can be expected to induce the fast electron transfer in LIB. Furthermore, the N-doped graphene on LTO acts as a conducting network to increase the electronic transport and shorten the length of time of ionic diffusion. The synthesized NG/LTO-TiN via the formation and simultaneous modification of LTO–TiO$_2$ using solvothermal reaction is new and is reported here for the first time.

2. Experimental

2.1. Materials and methods

Expandable graphite (Grade 1721) was purchased from Asbury Carbon (USA). Concentrated sulfuric acid (H$_2$SO$_4$), potassium permanganate (KMnO$_4$), hydrochloric acid (HCl), and hydrogen peroxide (H$_2$O$_2$) were purchased from Samchun Chemical (Korea). Hydrazine monohydrate, DETA and PEI were purchased from Sigma Aldrich (USA). The commercial grade of LTO (PAAM-T30-Dx) was provided by POSCO ESM (Korea). All chemicals were used as received without further purification.

2.2. Preparation of GO

The expanded graphite was obtained from expandable graphite by heating in microwave oven (Panasonic, NN-5653A) for 10s. The GO was prepared from expanded graphite [30]. Typically, 1000 ml of concentrated H$_2$SO$_4$ was charged into a 2 L beaker, equipped with a mechanical stirrer. The beaker was cooled to 0 °C into an ice bath. About 7 g of the expanded graphite was gradually loaded on to the beaker and stirring to make a suspension. Then, 42 g of KMnO$_4$ was gradually added, and keep the temperature at 20 °C. Then, the temperature was increased to 30 °C, and stirring for additional 2 h. The temperature of the beaker was cooled again in ice bath, and 1 L of deionized water was slowly added and maintain the temperature below 70 °C. The suspension was stirred for 1 h and diluted with 5 L of deionized water. About 50 ml of H$_2$O$_2$ was slowly added, the color of the suspension was changed from dark brown to yellow. The suspension was centrifuged at 3 wt% HCl solution for four times, and deionized water for several times to completely remove the acid until the pH of the GO suspension reached at 6.

2.3. Preparation of PEI-GO/LTO

A predetermined amount of GO (0.075 g, 0.1 g, 0.15 g, and 0.2 g with a concentration of 10 mg/mL) was dispersed in a mixed solution of ethanol/water (1:1) and ultra sonicated for 15 min. A desired quantity of LTO dispersed in a mixed solvent was added to the GO suspension and ultra sonicated for another 15 min. About 5% solution of PEI in ethanol was prepared separately. For wrapping the GO on LTO aggregates, the PEI solution was gradually added while stirring at about 200 rpm until complete precipitation occurred. The precipitated PEI-GO/LTO was filtered and washed with ethanol/water for further use.

2.4. Preparation of RGO/LTO-TiO$_2$, NG/LTO-TiO$_2$, and NG/LTO-TiN nanocomposites

The PEI-GO/LTO dispersed in 200 ml of DI water was loaded onto a 350 mL Teflon lined stainless steel autoclave; DETA was added (GO/DETA; mass ratio of 1:30) and thermally treated at 180 °C for 4 h. The final precipitate was washed with DI water and ethanol, then ground into a fine powder after drying at 80 °C for 12 h, and was named NG/LTO-TiN. The NG/LTO-TiO$_2$ was prepared in a similar way, but without using DETA. The control sample of LTO and RGO/LTO-TiO$_2$ was obtained by following the same
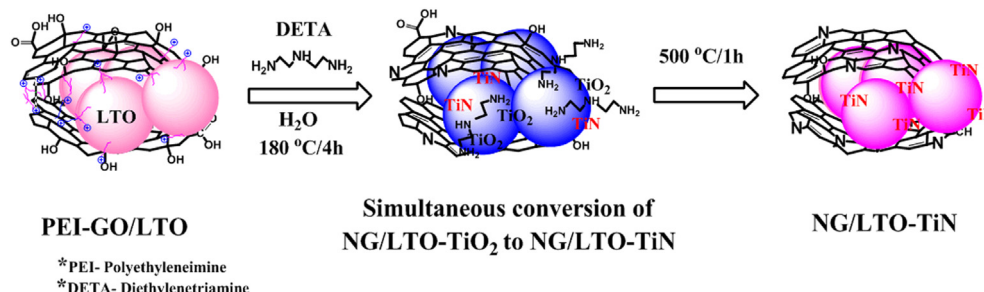

Fig. 1. Schematic illustration for the preparation of NG/LTO-TiO$_2$ and NG/LTO–TiN nanocomposites.