



Facile synthesis of titanium nitride-graphene nanocomposite and its improved rate-dependent electroactivity with respect to lithium storage



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ABSTRACT

Titanium nitride/graphene nanocomposite as an anode material of lithium ion batteries has been fabricated through the reaction of TiCl_4 and NaN_3 in supercritical benzene medium followed by ammonia treating at 1000°C for 10 h. The synthesized TiN/G nanocomposite depicts rate-dependent behavior in such a way that it shows specific capacity of 115 mAh g^{-1} when is cycled at higher rate (1.6 C) while it shows 76 mAh g^{-1} when is cycled initially at lower rate (0.2 C) and is subsequently subjected to higher rate (1.6 C). Moreover, TiN/G anode demonstrates capacity retention of 112%, 100%, and 70% after 250 cycles at charge/discharge rates of 1.6, 0.7, and 0.2 C, respectively. This unusual behavior can be due to (i) an affected lithiation/delithiation mechanism and consequently stabilized carbon layered structure, and (ii) less solid electrolyte interface formation. Furthermore, the possible mechanisms of this rate-dependent behavior of TiN/G anode are discussed.

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1. Introduction

Graphene based materials show superior properties as host materials for lithium intercalation, due to their unique two-dimensional structure and great intrinsic physical properties, such as high electrical conductivity and large surface area [1–4]. However, the electrochemical performance of graphene anodes is highly dependent on the orderliness of crystalline structure, porosity, specific surface area, and surface functional groups [5–9]. According to these structural parameters, the specific capacity, columbic efficiency, rate capability, and cycling performance of graphene anode can be determined. Wu et al. correlated the fast capacity fading of carbonous anodes to the change of carbon structure as a result of C—C bondings failure and consequential disappearance of electronic and ionic conductivity and agglomeration of graphene sheets [10]. During charge process, Li ions intercalate between (002) planes of graphite crystallites and form LiC_6 compound. Meanwhile, the further introduced Li ions intercalate into micropore places in form of Li atoms. Consequently, Li ions can react with neighboring defects in micropores and

lead to structural transformation [11–15]. This lithiation/delithiation pathway into/from micropores accompanied with structural alteration is called micropore mechanism [10]. The capability of the electrode can be declined as a result of induced phase instability caused by Li intercalation and consequently poor electronic/ionic conductivity. Recently, there are tremendous efforts to improve graphene performance by doping various elements as conducting agent or decreasing crystallite size and increasing pore structure [16–19]. Using active-inactive composites as a mixed-conductive matrix which electrically isolates the active particles from the current collector is one of the solutions to improve the anode performance. The inactive phase can avoid aggregation of the particles and recover electrical connection between the anode particles and the current collector [20,21]. Titanium nitride (TiN) shows excellent chemical resistance, superior electrical conductivity, and good adhesion with most materials [22–24]. Therefore, there are great interests to upgrading anode performance by doping TiN into anode matrix [25–29]. In this regard, Yue and co-workers doped TiN nanoparticles on graphene sheets to improve its capacity, energy density, power density and capacity retention [22,30]. Anchoring of TiN nanoparticles on graphene not only promotes the electrical conductivity along c-axis, but also suppresses the agglomeration of graphene sheets, resulting in the formation of a flexible porous texture. The fast electron and ion mixed transport capability at high current

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densities caused by enhancing the electrical conductivity, and the pore-transport system in the nanocomposite that would ensure the fast accessibility of the ions, promote the rate performance of TiN/G anode [22,30]. On the other hand, charge/discharge (C/D) rate can also control rate capability and cycling performance because of its effect on crystalline phase transition [31]. Previous electrochemical works have focused only on the high capacity and coulombic efficiency and capacity retention of TiN/G nanocomposite as anode material. The effect of initial galvanostatic charging/discharging rate on the performance of TiN/G nanocomposite, as anode material, has not been reported previously.

In this work, a TiN/G nanocomposite has been prepared by using benzene as carbon source through partial decomposition under supercritical condition to form simultaneously TiN/C nanocomposite in one-step followed by ammonia treatment to form nanocrystalline TiN/G composite for use as an anode for high-performance LIBs. X-ray diffraction (XRD) and Raman spectroscopy are used to characterize the structure of the synthesized TiN/G nanocomposite, while chemical state of carbonaceous phase and respective nitrogen distribution are studied by time of flight secondary ion mass spectrometry (ToF-SIMS) analysis. The morphology of the sample are studied by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). Furthermore, the carbon content and relevant phase fractions are measured by CHN elemental analysis and X-ray photoelectron spectroscopy (XPS). In the active-inactive composite of G and TiN, the G acts as a reactant during the lithiation process to form Li_xC , which is enclosed by the TiN inactive matrix. The TiN in the composite electrode does not alloy with lithium but serves as an inactive matrix to support the intergrain electronic contact in the material. The effect of charge/discharge rate on electrochemical performance of the synthesized TiN/G nanocomposite is studied for the first time and the appropriate mechanisms are discussed.

2. Experimental

2.1. TiN/G nanocomposite synthesis

TiN/G nanocomposite was synthesized by a supercritical process using benzene (C_6H_6 , Merck, 99.96%) as solvent and carbon source, and titanium tetrachloride (TiCl_4 , Merck, >99%) and sodium azide (NaN_3 , Merck, >99%) as reactants. In this regard, 1.95 g NaN_3 , 0.8 cm^3 TiCl_4 and 10 cm^3 of benzene were put into a stainless steel batch reactor (with capacity of 30 cm^3) in an ultra high purity (UHP) N_2 filled glove box. The temperature was set at 380°C with holding time of 1 h. Afterwards, the reactor was removed from a furnace and quenched, and the obtained nanoparticles were collected, filtered, and washed with 0.1 M hydrochloric acid solution and distilled water. The prepared powder was further dried under vacuum at 80°C for 10 h. Subsequently, the as-prepared sample was further heat-treated at 1000°C for 10 h using anhydrous ammonia followed by a constant cooling to room temperature with gas flow rate of $100 \text{ cm}^3 \text{ min}^{-1}$.

2.2. Characterization

In order to examine the phase evolution and crystallization behavior, a STOE D-64295 diffractometer (Cu-K α radiation, $\lambda = 1.54056 \text{ \AA}$) was used employing a step size of 0.015. The nature of the crystalline structure of carbon inclusion was further studied by Raman spectrum taken on an ALMEGA XR Raman spectrometer at 532 nm. Field emission scanning electron microscopy (JSM-7001F) equipped with an energy dispersive spectroscopy (EDS) probe and transmission electron microscopy (JEM-2100) were used to observe the morphology of the synthesized powder.

Moreover, ToF-SIMS analysis was carried out to investigate the carbonaceous species and distribution of N in carbon structure, with a TRIFT V, ULVAC-PHI Inc. time of flight secondary ion mass spectrometer equipped with a Bi liquid-metal cluster ion source. Negative ion spectra was acquired with a pulsed, electro-dynamically compressed 30 keV primary ion beam by riling the ion beam over a $16.4 \mu\text{m} \times 16.4 \mu\text{m}$ sample area. The results were analyzed with "WinCadence N" software. The prepared nanocomposite was also analyzed chemically using a Yanaco CHN CORDER MT-6 carbon, hydrogen, and nitrogen analyzer to determine the amount of carbon in the sample. To calculate phase fractions, XPS analyses were performed by using a ULVAC-PHI 5600 spectrometer with an Al K α exciting X-ray source.

2.3. Electrochemical measurements

The electrochemical properties of the synthesized sample were examined using a two-electrode electrochemical cell at room temperature. The working electrodes were prepared by mixing active material, conductive agent, and poly(vinylidene difluoride) (PVDF) binder in a weight ratio of 85:10:5 in NMP solvent to form a homogeneous slurry and pasted on a copper foil, then dried in vacuum oven at 80°C for 12 h. It should be noted that in spite of using conductive material in these experiments, the TiN/G anode can be used without adding any conductive material [22]. Lithium foil was used as the counter electrode and was separated from the anode by a Celgard[®] 2400 membrane. The electrolyte was 1.0 M LiPF_6 in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) with a volumetric ratio of 1:1:1. The cells were charged and discharged over a voltage range of 0.005–3.0 V (vs Li/Li^+) at different rates and the tests were performed with a charge-discharge unit (Hokuto Denko, HJ-1010 M) in a galvanostatic mode. In this regard, the C-rates were calculated based on the required time in hour for charge/discharge process in a specific C/D current density. Electrochemical impedance spectroscopy (EIS) measurement was performed using a potentio-stat Ivium CompactStat by applying an AC voltage of 10 mV amplitude in the frequency range of 10 mHz–100 kHz at room temperature.

3. Results and discussion

3.1. Characterization

The X-ray diffraction profile of the TiN/G sample is shown in Fig. 1(a). There are peaks at around 36.8° , 42.6° , 62.0° , and 74.2° , which can be indexed to (111), (200), (220), and (311) reflections of TiN with face-centered-cubic (fcc) phase, respectively. In addition, the wide peak between 12 – 32° , and diffraction lines located at 44.8° , and 54.2° suggest the presence of the crystalline carbon nanostructures. For better understanding of the carbon state, the wide peak between 12 and 32° was analyzed separately by fitting deconvoluted bands after background subtracting into two bands located at about 17.6° and 24.2° (the inset graph of Fig. 1(a)). The peak at 24.2° corresponds to graphene structure while the peak at 17.4° suggests aliphatic bands appear in the carbon structure.

The Raman spectrum of the TiN/G sample, as indicated in Fig. 1(b), demonstrates the presence of D, G, 2D peaks at 1350 , 1593 , and 2686 cm^{-1} , respectively, that reveals the presence of graphene structure. The presence of G peak demonstrates the E_{2g} mode of graphite, which is related to the vibration of sp^2 -bonded carbon atoms in a 2-dimensional hexagonal lattice. Meanwhile, the presence of D peak is an indication of defects and disorder associated with vacancies and grain boundaries. The presence of 2D peak is evidence of bi-layer graphene structure and good indication of c axis ordering [32–34]. Fig. 1(c & d) represents the

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