



# One novel and universal method to prepare transition metal nitrides doped graphene anodes for Li-ion battery



Linfei Lai<sup>a,b,c</sup>, Jixin Zhu<sup>d</sup>, Baosheng Li<sup>c</sup>, Yongda Zhen<sup>b</sup>, Zexiang Shen<sup>a</sup>,  
Qingyu Yan<sup>d</sup>, Jianyi Lin<sup>c,\*</sup>

<sup>a</sup> Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore, 637371, Singapore

<sup>b</sup> Institute of Chemical and Engineering Sciences, A\*STAR, 1 Pesek Road, Jurong Island, Singapore, 627833, Singapore

<sup>c</sup> Energy Research Institute @ NTU (ERI@N), Singapore, 637141, Singapore

<sup>d</sup> School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore, 639798, Singapore

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## ABSTRACT

Transition metal nitrides (TMN)/N modified graphene (N-rG-O) composites are prepared by annealing of Metal<sup>n+</sup>-EN (EN: ethylene diamine) chelate and G-O composite. Li-storage and cycling behavior of TMN/N-rG-O composite have been evaluated by galvanostatic discharge-charge and cyclic voltammetry in coin cells with Li-metal as counter electrode. FeN/N-rG-O, CoN/N-rG-O, FeCoN/N-rG-O, NiN/N-rG-O are prepared using this method, and all have shown pronounced cyclability and considerable high capacity value. Even a low loading of TMN (12.5% ± 2.0%) on graphene can significantly improve the Li-ion storage capacity of graphene. For example, FeN/N-rG-O with FeN weight ratio of only 12.5% has an initial reversible capacity of 665 ± 10 mAhg<sup>-1</sup> at a current density of 50 mA g<sup>-1</sup>, and the capacity value further increase consistently to 698 ± 10 mAhg<sup>-1</sup> after 50 cycles. The excellent cyclability, low charge/discharge potentials (<1.5 V), high reversible capacity values of TMN/N-RG-O indicate they are prospective anodes for Li-ion batteries.

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## 1. Introduction

Among various energy conversion/storage systems proposed over the two last centuries, electrochemical storage and more specifically battery exhibiting improved energy densities and life-times is promising, [1,2] but research aiming at meet commercial application requirements is still in imperious need. Graphite is conventional anode material for lithium-ion batteries (LIBs) with high columbic efficiency (> 85%) and excellent cycle performance. However, the theoretical lithium storage capacity of graphite is only 372 mAh g<sup>-1</sup> by forming intercalation compounds (LiC<sub>6</sub>). [3] Metals and semimetals can electrochemically form alloys with lithium with large capacity achieved from alloying reactions (Sn + 4.4 Li ↔ Li<sub>4.4</sub>Sn). However the huge volume change associate to the de-alloying process introduces large strain in metals/semimetals, which subsequently cause their structural deformation, and irreversible capacity loss of the electrodes. Metal oxides, such as Co<sub>3</sub>O<sub>4</sub>, [4,5] SnO<sub>2</sub>, [6,7] Fe<sub>x</sub>O<sub>y</sub>, [8,9] which have been extensively studied as anode for Li-ion batteries, can reversibly

react with Li through conversion reaction (eg., Fe<sub>2</sub>O<sub>3</sub> + 6Li ↔ 2Fe + 3Li<sub>2</sub>O). These metal oxides could deliver capacity values two or three times larger than that of graphite. However, the practical utilization of these materials needs to apply carbon coating, carbon additives or reduce the size of metal oxides to nano scale in order to reduce the capacity loss from structural deformation during cycling. [10] The structural and component control of metal oxides composite [11] would somewhat alleviate their capacity loss during cycling, but their performance is still far from satisfying.

Due to the low conversion reaction potentials of transition metal nitrides (TMNs) with Li, [3] there has been surge of interest in developing advanced materials of twofold metal nitrides as LIBs negative electrodes, such as SnN, [12] CrN, VN, [13] Mn<sub>3</sub>N<sub>2</sub>, [14] and NiN, [15] etc. The electrochemical behavior of these metal nitrides (such as CoN, [16] FeN, [17] CrN, [18,19] VN [13]) with lithium as anode materials have been widely investigated, which can be indexed to conversion reaction mechanism. Lithiated transition metal nitrides (LiTMNs), such as Li<sub>3</sub>FeN<sub>2</sub> and Li<sub>3-x</sub>Co<sub>x</sub>N, which are byproducts of TMN after Li-ion insertion, can store Li ions by intercalation and de-intercalation mechanism in early studies. [14,20,21] These LiTMNs, such as LiMnN<sub>2</sub>, [22] Li<sub>3-x</sub>TM<sub>x</sub>N (M = Co, Ni), [23] Li<sub>2.6</sub>Co<sub>0.4</sub>N [24] have been identified to be the most promising negative electrodes, with reversible capacity between 400 and 760 mAhg<sup>-1</sup>.

\* Corresponding author.

E-mail address: [lin.jianyi@ices.a-star.edu.sg](mailto:lin.jianyi@ices.a-star.edu.sg) (J. Lin).

TMN also exhibit excellent properties of high melting point and chemically inert behavior, therefore, advantageous for electrode materials to be protected from moist or erosive environments. [17] There have been several reports concerning the preparation and application of TMNs in the past few years, in which magnetron sputtering is commonly used method, [25–27] and nitrogen gas is the metal nitridation source. However, as the inert nature of N<sub>2</sub>, the reaction is costly and not suitable for large-scale preparation.

Graphene, a monolayer of carbon has attract numerous interest from fundamental research to practical applications due to its interesting electrical properties, such as high surface area, chemical tolerance and broad electrochemical window. [28,29] It is found that the theoretical specific Li storage capacity for graphene is 744 mAhg<sup>-1</sup>, corresponding to the formation of LiC<sub>3</sub>. [30] However, graphene-based all-carbon electrodes are reported to suffer from a low initial coulombic efficiency, and large capacity fade during cycles. Graphene combined with transition metal oxides are reported to exhibit high capacity value, long cycle life, and good rate performance, however, these materials, like graphene/Co<sub>3</sub>O<sub>4</sub> [31], and graphene/Fe<sub>2</sub>O<sub>3</sub> [32] etc., still have high discharge profile. The high discharge voltage of these transition metal oxides/graphene composites will cause the full cell voltage reduction after matched with suitable cathode materials, and further cause decrease of energy density. Therefore, the combination of graphene with TMNs which has low conversion reaction potentials towards Li would have practical application as Li-ion battery anodes.

In this paper, we report the synthesis of TMNs (FeN, FeCoN, NiN, and CoN)/N-rG-O composite by a simple and universal chemical method. The transition metal chelates (TMN<sup>n+</sup>-EN) which has -NH<sub>2</sub> functional groups could be easily attached onto O-containing functional groups on G-O surface. The G-O was reduced and doped with N after refluxing with TMN<sup>n+</sup>-EN/G-O composite and further annealing, while TMN nanoparticles were formed on graphene surface meanwhile. Electrochemical measurements demonstrated that TMN/N-rG-O presented a higher relative specific capacity and excellent cycling stability, compared with rG-O, N-rG-O sheets, indicating its great potential as an anode material for Li-ion batteries.

## 2. Experimental Section

GO were prepared from natural graphite powder by chemical exfoliation using modified Hummers method. The GO solution with concentration of 2 mg/mL was freeze dried for further use.

Preparation of FeN/N-rG-O: 200 mg of iron acetate was fully dissolved in 125 mL of ethanol before adding 1 mL of ethylenediamine (EN). The solution was stirred for half an hour, creating a Fe-EN complex. 100 mL of 2 mg/mL G-O solution was separately dispersed in 125 mL of ethanol and then added to the Fe-EN complex solution. The combined solution was then refluxed at 100 °C for an hour under ambient pressure and further dried. The remaining dried precipitate was pyrolyzed at 550 and 850 °C for 1 h under 5% NH<sub>3</sub>/Ar (120 sccm) protection. The as-obtained powder was then grounded with mortar for 20 mins and treated with 1 M H<sub>2</sub>SO<sub>4</sub> at 80 °C for 12 h before being filtered, washed with large amount of DI water and vacuum-dried at 80 °C. The CoN/N-rG-O, NiN/N-rG-O and FeCoN/N-rG-O were prepared in the same procedure but replacing iron acetate with cobalt nitrate, nickel nitrate, or iron acetate and cobalt nitrate mixture (molar ratio of Fe:Co = 1:1), respectively.

Characterization: The morphology and structure of samples were characterized by field-emission scanning electron microscope (FESEM, JEOL JSM-6700F, 15 kV) and high-resolution analytical transmission electron microscopy (TEM) (Model JEM-2010F, JEOL, Tokyo, Japan, 200 kV). The crystal structure of the samples was examined by a Bruker D/MAX 2500 X-ray diffractometer (XRD)

with Cu K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). The XPS was characterized on Kratos Axis Ultra DLD (delay line detector) spectrometer using monochromatic Al K $\alpha$  ( $h\nu = 1486.6 \text{ eV}$ ) X-ray source with resolution of 0.1 eV. The elemental compositions of the TMN/N-rG-O were analyzed on an inductively coupled plasma-optical emission spectrometer (ICP-OES, Varian Vista-MPX CCD Simultaneous ICP-OES). The individual TMN/N-rG-O sample for the analysis was digested using aqua regia and kept in 2% HNO<sub>3</sub>.

Electrochemical measurements: For electrochemical measurements, the cells were constructed by using as-prepared metal nitrides as a working electrode and lithium metal at a counter electrode. The working electrodes were prepared by mixing 80 wt % active material (TMN/N-rG-O, N-rG-O or rG-O), 10 wt % acetylene black (Super-P), and 10 wt % polyvinylidene fluoride (PVDF, 5 wt %) binder dissolved in N-methyl-2-pyrrolidinone. After coating the above slurries on Cu foils, the electrodes were dried at 110 °C in vacuum for 2 h to remove the solvent before pressing. Then the electrodes were cut into disks (16 mm in diameter) and dried at 100 °C for 24 h in vacuum. The CR2032 (3 V) coin-type cell were assembled in an Ar-filled glove-box with lithium metal as the counter/reference electrode, Celgard 2400 membrane as separator, and 1 M LiPF<sub>6</sub> electrolyte. The electrolyte solution was prepared by dissolving 1 M LiPF<sub>6</sub> in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC/DMC, 1:1 v/v). The CV measurements were carried out using a Solartron 1287 electrochemical workstation at a scanning rate of 1 mV s<sup>-1</sup>. Galvanostatic discharge/charge cycles were tested by LAND CT2001A electrochemical workstation at various current densities of 50~100 mA g<sup>-1</sup> between 0.01 and 3 V (vs Li<sup>+</sup>/Li) at room temperature.

## 3. Results and Discussion

### 3.1. Synthesis and Characterization

The growth of TMN requires the presence of active N atoms and metal ions. Ethylene diamine (EN) is a well-known chelating ligand for coordination compound which forms derivatives with carboxylic acid, carbon disulfide, and ketones etc. EN can be easily coordinated with transition metal ions (TMN<sup>n+</sup>) to form a TMN<sup>n+</sup>-EN complex. G-O has abundant O-containing functional groups, which is capable of adsorbing TMN<sup>n+</sup>-EN chelates through electrostatic interaction. After refluxing TMN<sup>n+</sup>-EN complex and G-O under 110 °C, some of the O-containing functional groups in G-O could be replaced by -NH<sub>2</sub> groups from TMN<sup>n+</sup>-EN complex with covalent C-N bonds formed between TMN<sup>n+</sup>-EN and graphene network. As shown in Fig. 1, the TMN<sup>n+</sup>-EN chelates could be anchored at graphene edges or on the basal plane of graphene layers where located abundant O-containing functional groups. The TMN nanoparticles were formed after TMN<sup>n+</sup>-EN/G-O composite annealed, while G-O was reduced and doped with N meanwhile. The final product was then soaked by 1 M of H<sub>2</sub>SO<sub>4</sub> under 80 °C for 12 h, and then washed by large quantity of water until the pH value of supernatant is around 7.

The composition of the TMN/N-rG-O was confirmed by X-ray diffraction (XRD) pattern as shown in Fig. 2. The FeN/N-rG-O samples prepared in different annealing temperatures (550 and 850 °C) were selected for characterization. Both FeN/N-rG-O 550 and 850 °C show broad peak at 27° suggesting increased interlamellar spacing of N-rG-O compared with that of G-O as reported. [33] For the FeN/N-rG-O annealed under 550 °C, has several sharp peaks correspond to the 104, 110, 024 and 116 faces of Fe<sub>2</sub>O<sub>3</sub> (JCPDS: 01-1053), with peak positions well fitted. XRD pattern of FeN/N-rG-O 550 °C indicate the presence of Fe<sub>2</sub>O<sub>3</sub> which was coated or wrapped by graphene layers, and was not completely removed by acid bleaching. According to phase diagrams of Fe-N and

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