

A TRANSITION METAL NITRIDE/CARBON COMPOSITE AND A METHOD FOR PRODUCING SAID COMPOSITE

FIELD OF INVENTION

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The present invention relates to a transition metal nitride/carbon composite and a method for producing the aforementioned composite.

BACKGROUND

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An increasing amount of emphasis and attention is placed on clean energy and renewable energy sources in this age of enhanced environmental awareness. Batteries are viewed as an important component of clean energy, particularly when used to power vehicles which typically rely on the burning of polluting fossil fuels. Existing electric vehicles generally face
15 issues relating to the batteries used to power the vehicles, and resolving these issues will lead to better reliability and more widespread acceptance of electric vehicles.

Improvements are continually sought to enhance the energy densities and usage life of batteries. Extensive research has been carried out in these areas for lithium-ion (Li-ion)
20 batteries, particularly in relation to improving the volumetric and gravimetric capacity of the anode of the batteries.

The anode of batteries is typically made from graphite, which has a gravimetric capacity of 372 mAh/g. Lithinated transition metal nitrides have been found to provide high gravimetric
25 capacities, such as, for example, 900 mAh/g for $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$. As such, lithinated transition metal nitrides are suitable for use as anodes of batteries.

Even though the preparation and application of transition metal nitrides using magnetron sputtering is commonly employed with nitrogen gas being the metal nitridation source, the
30 inert nature of N_2 leads to high costs and as such, the use of magnetron sputtering is not suitable for large-scale applications.

As such, the cost to produce lithinated transition metal nitrides using conventional methods is high, and the batteries which utilize pure lithinated transition metal nitrides as anodes
35 suffer from issues like, for example, low reversible capacity and poor cycling behavior.

SUMMARY

There is provided a method for producing a transition metal nitride/carbon composite. The method includes heating at least one transition metal ion precursor and at least one organic amine under reflux in an alcohol solvent, the heating being for obtaining at least one transition metal chelate; and loading the at least one transition metal chelate onto a graphene oxide layer to form the transition metal nitride/carbon composite.

The method may further include annealing the transition metal nitride/carbon composite at a predetermined temperature under inert gas conditions, the predetermined temperature being between 550°C and 1050°C. The method may also further include reduction of graphene oxide via chemical exfoliation of graphite. The method may also further include washing the transition metal nitride/carbon composite in diluted acid, de-ionised water and ethanol to remove excessive iron oxide, the diluted acid being 1M of sulphuric acid. The transition metal nitride may be a salt of, for example, iron (Fe), cobalt (Co), zinc (Zn), nickel (Ni) and the like. The at least one organic amine may be ethylene di-amine, and the alcohol solvent is either ethanol or methanol.

Preferably, the graphene oxide is decorated with oxygen containing functional groups, the oxygen containing groups being, for example, carboxylic acids, phenols, lactones, carboxylic anhydrides, ketones, ethers, pyrones, quinines and so forth.

There is also provided a transition metal nitride/carbon composite as produced using the aforementioned method. The transition metal nitride/carbon composite can be used in applications such as, for example, an anode in a Li-ion battery, a fuel cell catalyst, and a lithium-air battery cathode. A gravimetric capacity of the composite is advantageously higher than a gravimetric capacity of graphite when the composite is used as the anode. In addition, the gravimetric capacity of the composite advantageously increases during repeated charging cycles when the composite is used as the anode.

There is provided a Li-ion battery using the aforementioned transition metal nitride/carbon composite as an anode in the battery. There is also provided a lithium-air battery using the aforementioned transition metal nitride/carbon composite as a cathode in the battery. Finally, there is provided a fuel cell using the aforementioned transition metal nitride/carbon composite as a cathode in the fuel cell.

DESCRIPTION OF FIGURES

In order that the present invention may be fully understood and readily put into practical effect, there shall now be described by way of non-limitative example only preferred
5 embodiments of the present invention, the description being with reference to the accompanying illustrative figures.

Figure 1 shows a schematic diagram for the production of transition metal nitride/carbon composite.

10 Figure 2 shows a process flow for the production of transition metal nitride/carbon composite.

Figure 3 shows cyclic voltammetry curves of a FeN-graphene composite electrode (90% graphene) for three cycles at a scan rate of 0.1 mV/s.

Figure 4 shows charge/discharge profiles of a FeN-graphene composite electrode (90% graphene) between 0.02V and 1.5V at a current density of 0.05 A/g.

15 Figure 5 shows charge/discharge profiles of a FeN-graphene composite electrode (90% graphene) between 0.02V and 1.5V at a current density of 0.1 A/g.

Figure 6 shows charge/discharge profiles of a FeCoN-graphene composite electrode (90% graphene) between 0.02V and 1.5V at a current density of 0.05 A/g.

20 Figure 7 shows charge/discharge profiles of a FeCoN-graphene composite electrode (90% graphene) between 0.02V and 1.5V at a current density of 0.1 A/g.

Figure 8 shows field-emission scanning electron microscopy (FESEM) images of a FeN-graphene composite.

Figure 9 shows transmission electron microscopy (TEM) of FeN-graphene composite post-annealing.

25 Figure 10 shows a N1s x-ray photoelectron spectroscopy (XPS) spectrum of FeN-graphene composite.

Figure 11 shows the first three charge/discharge profiles of a FeN-graphene composite electrode (90% graphene) at a current density of 100 mA/g.

30 Figure 12 shows capacity retention and coulombic efficiency profiles of a FeN-graphene composite electrode (90% graphene) at a current density of 50 mA/g for 50 cycles.

Figure 13 shows electrochemical capacity comparison curves of reduced graphene oxide (rG-O), N modified rG-O (N-rG-O) and FeN-graphene at a current density of 100 mA/g.

Figure 14 shows capacity retention profiles of CoN-graphene and NiN-graphene at a current density of 50 mA/g for 80 cycles

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DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention relates to a transition metal nitride/carbon composite which demonstrates favourable characteristics for use as an anode in Li-ion batteries, amongst other applications. The favourable characteristics include low cost of production, ease of scalability for the production process, high reversible capacity, and desirable cycle behavior. In addition, a method to produce the composite is also provided. Details relating to how the aforementioned advantages are brought about will be provided in the following description.

Referring to Figures 1 and 2, there is provided a schematic diagram and a process flow respectively for a method 20 for the production of a transition metal nitride/carbon composite. Graphene and some functionalized carbons can be effectively loaded with transition metal nitrides in order to form a transition metal nitride/carbon composite.

Figure 1 shows the functionalization of carboxyl groups 18, adsorption of transition metal chelates 16, and annealing 14 after the adsorption stage 16. Greater detail of the method 20 is provided in Figure 2.

Graphene can be obtained from treating graphene oxide (22) using the reduction of graphene oxide via chemical exfoliation of graphite (24). The graphene oxide itself is decorated with oxygen containing functional groups, such as, carboxylic acids, phenols, lactones, carboxylic anhydrides, ketones, ethers, pyrones, or quinines. The functional groups provide abundant adsorption sites for transition metal chelates. The transition metal nitride is a salt of, for example, iron (Fe), cobalt (Co), zinc (Zn), nickel (Ni) and the like.

Subsequently, at least one transition metal nitride is heated together with at least one organic amine (for example, ethylene di-amine) under reflux in an alcohol solvent (for example, ethanol, methanol and the like) (26), the heating being to obtain at least one transition metal chelate, and the at least one transition metal chelate is then loaded onto the graphene oxide layer (28). It should be appreciated that transition metal ions coordinate with organic amine and forms transition metal chelate. Next, the transition metal chelate/graphene oxide composite is then annealed under inert gas conditions (30) at a temperature range of 550°C to 1050°C. After annealing, the composite may be washed in diluted acid like for example, 1M of sulphuric acid (H_2SO_4), de-ionised water and ethanol to remove excessive iron oxide.

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Referring to Figure 8(a), field-emission scanning electron microscopy (FESEM) shows graphene oxide with platelets in crumpled conformations. Figure 8(b) shows FeN-graphene composite at 850°C, where FeN with size of approximately 10 to 20 nm is uniformly distributed onto graphene layers of G-O. Figure 9(a) shows transmission electron microscopy (TEM) images of FeN-graphene with FeN nanoparticles intercalated between the graphene layers. Figure 9(b) shows uniform size distribution. Figure 9(c) shows an enlarged view of a portion of Figure 9(b). Figure 9(c) shows FeN with lattice spacing of 0.21 ± 0.05 nm coated with graphitic shells with 5 to 7 layers of carbon. Referring to Figure 10, a survey scan of the FeN-graphene composite using x-ray photoemission spectroscopy (XPS) also confirms the presence of Fe-N bond with binding energy of approximately 398.4 eV.

In order to demonstrate the properties of the FeN-graphene composite, the FeN-graphene composite was assembled into a model cell as the anode and LiClO_4 solution was used as the electrolyte in the model cell. The properties being demonstrated include capacity and cyclic behavior.

Referring to Figure 3, there is shown cyclic voltammetry curves (CV) of the FeN-graphene composite for three cycles at a scan rate (current density) of 0.1 mV/s. It should be appreciated that the 2nd and 3rd cycle curves of the FeN₂-graphene composite are consistently shaped, indicating predictable cycle behavior and that reversible electrochemical reactions between lithium ions and the FeN-graphene composite occurred after the 1st cycle.

Referring to Figures 4 and 5, there is shown charge/discharge profiles of a FeN-graphene composite electrode (90% graphene) between 0.02V and 1.5V at a current density of 0.05 A/g and 0.1 A/g respectively. Referring to Figure 4, it can be observed that reversible charging/discharging capacity of 630 (± 10) mAh/g is maintained for about 25 cycles at a current density of 0.05 A/g. Referring to Figure 5, it can be observed that reversible charging/discharging capacity of around 500 (± 20) mAh/g is maintained for about 120 cycles at a current density of 0.1 A/g. Thus, it is clearly demonstrated that the FeN-graphene composite electrode (90% graphene) has very high reversible capacity.

Referring to Figures 6 and 7, there is shown charge/discharge profiles of a FeCoN-graphene composite electrode (90% graphene) between 0.02V and 1.5V at a current density of 0.05 A/g and 0.1 A/g respectively. Firstly, the charge/discharge profiles of both FeN-graphene composite electrode (90% graphene) and FeCoN-graphene composite electrode (90%

graphene) are similar. Furthermore, it should be appreciated that a reversible charging capacity of 500 – 600 mAh/g is demonstrated by the FeCoN-graphene composite electrode (90% graphene) for both current densities of 0.05 A/g and 0.1 A/g. In addition, it should be noted that the capacity does not decrease with an increase in the number of cycles and the capacity actually increases with the number of cycles.

Figures 11 to 13 show electrochemical characterisations of a half cell composed of FeN-graphene and Li. The specific capacities are calculated based on the mass of FeN-graphene composite including binder and carbon black.

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Referring to Figure 11, there is shown charge/discharge profiles of a FeN-graphene composite electrode (90% graphene) between 0.02V and 3V at a current density of 0.1 A/g. The third cycle curve shows slight differences compared with the second cycle curve, indicating the electrochemical reversibility of FeN-graphene occurs after the first cycle.

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Referring to Figure 12, it can be observed that reversible charging/discharging capacity of approximately 650 (± 20) mAh/g is maintained for about 25 cycles at a current density of 0.05 A/g.

20 With reference to Figure 13, for rG-O material, the capacity retention after 100 cycles was only about 278 mAh/g and the irreversible capacity loss for rG-O during cycling was 959 mAh/g. Reduced graphene (rG-O) by thermal annealing of graphite oxide (850°C in Ar gas environment) has large amount of defects at edge sites and internal/basal plane (vacancies etc.) which can react with electrolyte irreversibly and further induce capacity loss and cycle degradation. Heteroatoms doping, especially N, is effective for Li-ion battery capacity and cycling improvement. However, the reversible capacity of N doped graphene (5% NH₃ in Ar at 850°C for 1h) is larger than that of reduced graphene, but still lower than that of FeN-graphene. The elemental composition of the catalysts was analyzed on an inductively coupled plasma-optical emission spectrometer (ICP-OES). The weight ratio of FeN is found to be 10 $\pm$ 2% in FeN-graphene composite. Therefore, the addition of FeN with weight ratio of only 10% could increase the capacity of graphene by at least 200 mAh/g or 50%. Thus, it is clearly demonstrated that the FeN-graphene composite electrode (90% graphene) has very high reversible capacity.

35 With reference to Figure 14, there is shown cycling stability of NiN-graphene, and CoN-graphene. At current density of 50 mA/g, the capacity retention of NiN/N-rG-O, and CoN/N-

rG-O are 710 and 600 mAh/g respectively. Furthermore, it should be appreciated that a reversible charging capacity of 500 – 700 mAh/g is demonstrated by the MeN-graphene composite electrode (90% graphene) for both current densities of 0.05 A/g and 0.1 A/g. In addition, it should be noted that the capacity does not decrease with an increase in the number of cycles and the capacity actually increases with the number of cycles.

It should be appreciated that the method 20 is a process which is easily scalable, and as such, large scale production of the transition metal nitride/carbon composite is possible. Compared with magnetron sputtering as mentioned in the background, chemical methods are much cheaper and easily up-scaled.

The transition metal nitride/carbon composite which results from the method 20 can be used to replace graphite as the anode material in a Li-ion battery, whereby there is no necessity to modify existing battery production processes. Moreover, the higher gravimetric capacity of the transition metal nitride/carbon composite and the no-degradation behavior over repeated charging cycles of the transition metal nitride/carbon composite anode clearly brings about several advantages compared to use of graphite anodes. In addition, the transition metal nitride/carbon composite also has advantageous properties which enables it to be used as, for example, a fuel cell catalyst, and a lithium-air battery cathode.

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Whilst there has been described in the foregoing description preferred embodiments of the present invention, it will be understood by those skilled in the technology concerned that many variations or modifications in details of design or construction may be made without departing from the present invention.

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CLAIMS

1. A method for producing a transition metal nitride/graphene composite, the method including:

5 heating at least one transition metal ion precursor and at least one organic amine under reflux in an alcohol solvent, the heating being for obtaining at least one transition metal chelate; and

loading the at least one transition metal chelate onto a graphene oxide layer to form the transition metal nitride/graphene composite;

10 wherein the graphene oxide is decorated with oxygen containing functional groups, the oxygen containing groups being selecting from a group consisting of: carboxylic acids, phenols, lactones, carboxylic anhydrides, ketones, ethers, pyrones, and quinines.

2. The method as claimed in claim 1, further including annealing the transition metal nitride/graphene composite at a predetermined temperature under inert gas conditions, the
15 predetermined temperature being between 550°C and 1050°C.

3. The method as claimed in either claim 1 or 2, wherein the transition metal nitride is selected from a salt of a group consisting of: iron (Fe), cobalt (Co), zinc (Zn), and nickel (Ni).
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4. The method as claimed in any one of claims 1 to 3, further including reduction of graphene oxide via chemical exfoliation of graphite.

5. The method as claimed in any one of claims 1 to 4, further including washing the
25 transition metal nitride/graphene composite in diluted acid, de-ionised water and ethanol to remove excessive iron oxide, the diluted acid being 1M of sulphuric acid.

6. The method as claimed in any one of claims 1 to 5, wherein the at least one organic amine is ethylene di-amine, and wherein the alcohol solvent is either ethanol or methanol.
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