Expanded graphite as a support for Ni/carbon composites

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ABSTRACT

Expanded graphite decorated with nickel oxide particles (EGNiO) has been synthesized through electrochemical oxidation of natural graphite in an aqueous nickel nitrate solution followed by a heat treatment. EGNiO was used to prepare nickel/carbon composites using two techniques: (a) hydrogen reduction of nickel oxide particles loaded on the expanded graphite surface and (b) pyrolysis of coal tar pitch-impregnated EGNiO blocks. The EGNiO as well as the nickel/carbon composites have been characterized by X-ray diffraction, scanning and transmission electron microscopy, energy dispersive X-ray spectroscopy and selected area electron diffraction.

1. Introduction

Nickel/carbon composite materials received great attention because of their application in a variety of processes, especially the growth of carbon nanowires and nanotubes [1–3], oxidation of alcohols in methanol and ethanol fuel cells [4,5], hydrogenation of various organic compounds [6,7]. Nanosized Ni/C composites could be attractive for hydrothermal gasification of organic compounds [8,9], application in electrochemical devices as sensors [10] and electrodes [11], or hydrogen storage [12–16].

The main requirements for a carbon support are its high porosity, large surface area, facility in recovery of metals and high density of surface defects. Several types of carbon materials have been used to prepare nickel/carbon composites (activated carbons, graphite, carbon black, etc.) [7–9,13,14]. New carbon forms such as carbon nanotubes and magnetically separable carbon materials have been synthesized [5,6,10,11,15–17]. However, their high cost limits their practical utility in industrial applications.

Graphite materials that are available and low cost could become the perfect candidate as a support for Ni particles if they possess a large surface area and a high Ni load capability. Both the surface area and the density of surface defects responsible for Ni trapping could be developed either by physical methods (mechanical grinding [18], electrical arc discharge [14], plasma treatment [19] or ion irradiation [20,21]), or by chemical methods (synthesis of expanded graphite (EG) via heat treatment of graphite intercalation compounds [22,23]). The advantages of using EG as a support are its light weight and the ability to be compacted without a binder over a wide range of densities.

Traditionally EG is produced by exfoliation of graphite intercalation compounds with Brensted acids or expandable graphite [24]. Recently, expandable graphite was obtained by means of a novel technique including anodic oxidation of graphite in diluted solutions of nickel nitrate [25]. EG formed from this material contains nickel oxide particles (hereafter EGNiO). Its pore structure with pores ranging from 1.5 nm to 100 μm implies several possible applications including catalysis if NiO is converted to Ni.

Conventional way to produce metal catalysts from their oxides is hydrogen reduction of the oxides though it was not still elaborated for EG supports. Another way is carbon
reduction. Graphite reduces nickel oxide above 900 °C [26], whereas more active carbon forms like activated carbons or charcoal reduce NiO at as low temperature as 500 °C [27] or even 450 °C [28]. Although expanded graphite contains a number of defects its reducing ability is expected to be not very remarkable due to graphic nature of the material. Therefore, to provide reduction of nickel oxide at moderate temperatures the EG_{NiO} was modified by coal tar pitch producing coal coke after carbonization. Coal tar pitch was chosen because of its high fluidity, availability, and low cost [29].

Here we report a comparative microstructural study of new nickel/carbon composite materials from EG_{NiO} synthesized by two different techniques: hydrogen treatment of nickel oxide particles loaded on the expanded graphite surface and pyrolysis of coal tar pitch-impregnated EG_{NiO} blocks.

2. Experimental

2.1. Synthesis

Expandable graphite was synthesized by anodic polarization of graphite in 50 wt.% aqueous solution of nickel nitrate at stabilized current of 30 mA with a total electrical charge transfer of 1500 C/g. Details of the preparation method can be found in [25]. EG containing 20 wt.% of NiO (EG_{NiO}) with a bulk density of 1.5 g/l and a specific area of 120 m²/g was obtained by exfoliation of this expandable graphite at 600 °C in air.

The nickel/carbon composites were prepared by means of both hydrogen and carbon reduction techniques. The former one was carried out as follows: EG_{NiO} compressed to a density of 0.2 g/cm³ was subjected to a hydrogen flow of 10 ml/min at 350 °C for 4 h in a quartz tube. This composite is denoted hereafter as Ni/C. The latter one was performed by heat treatment of EG_{NiO} blocks impregnated with a coal tar pitch supplied by GU «Altay-Koks» (Table 1). EG_{NiO} was slightly compressed to a density of 0.02 g/cm³ and impregnated with 10 wt.% pitch solution in toluene. The sample was dried in air at 130 °C to obtain a EG_{NiO}/pitch block containing 18 wt.% EG_{NiO}. The blocks were pyrolysed under a nitrogen flow of 10 ml/min at a constant heating rate of 1 °C/min to a temperature of 550 °C followed by 1 h dwell resulting in a composite containing 36 wt.% EG (hereafter Ni/CC).

2.2. Characterization and measurements

The phase composition of expanded graphite decorated with NiO particles and the both Ni/carbon composites were determined by X-ray diffraction on an ARL X'TRA diffractometer (CuKα radiation, λ = 1.5418 Å) in the angular range of 2θ = 10–60° at a continuous scan rate of 2°/min. Morphologies of the EG_{NiO}, Ni/C and Ni/CC composites as well as dispersion of the NiO and Ni particles were characterized by scanning electron microscopy (SEM) performed at 20 kV accelerating voltage on a JEM-5510 instrument coupled with an EDX spectrometer (INCA Energy+, energy resolution below 1 eV). Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) (Philips CM-20, 200 kV, point resolution 2.5) and high resolution transmission electron microscopy (HRTEM) (Jeol 4000EX, 400 kV, point resolution 1.7) were performed for Ni/C and Ni/CC composites. Specimens for TEM and HRTEM were prepared by mechanical grinding in methanol and depositing the suspension on a carbon grid.

3. Results and discussion

The XRD patterns of EG_{NiO}, Ni/C and Ni/CC composites are shown in Fig. 1. In each XRD pattern the peaks located at ca. 26.2°, 42.2° and 54° (2θ) correspond to (002), (100) and (004) planes of the graphite support respectively (JCPDS, Card No. 75-1621). The other two peaks in the XRD pattern of EG_{NiO} (Fig. 1a) at the 2θ values of 37.3° and 43.3° are characteristic of the fcc structure of crystalline NiO and are indexed as (111) and (200) correspondingly (JCPDS, Card No. 78-0643).

Besides graphite reflections, the XRD patterns of the Ni/C (Fig. 1b) and Ni/CC (Fig. 1c) composites exhibit only characteristic peaks of fcc Ni at 44.3° and 51.7° (2θ) which are attributed to the (111) and (200) planes (JCPDS, Card No. 65-0380). There are no reflections from NiO in the Ni/CC composite convincing a carbon reduction process of NiO is completed. For the Ni/C

| Table 1 – Coal tar pitch characteristics. |
|-----------------|-----------------|--|--|------|
| SP a            | QI b            | TI c | CY d | Ash  |
| 63              | 5               | 19   | 46   | 0.1  |

a Softening point (°C).
b Quinoline insoluble content (wt.%).
c Toluene insoluble content (wt.%).
d Carbon yield (wt.%).
composite the Ni peaks appear stronger and sharper than those in the Ni/CC composite indicating the better crystallinity of Ni particles.

The average size of the NiO and Ni crystallites in the species estimated using the Scherrer formula appears to be about 10 nm for NiO, 13 nm and 9 nm for Ni in Ni/C and Ni/CC composites, respectively. The similar crystallite size of nickel oxide and nickel can probably be explained by the fact that this size is already assigned in the process of expandable graphite synthesis or exfoliation. Hence the reduction technique does not influence the size of the crystallites.

SEM images of EG containing NiO (a), Ni/C (b) and Ni/CC composites (c) are represented in Fig. 2. Almost similar morphology of the composites is observed. Slight difference in the morphology of carbonized coal tar pitch-impregnated EG sample can be seen (Fig. 2c) due to formation of coke particles that cover the EG surface forming 1–2 μm islands. Each composite contains bright contrast particles of various size randomly distributed on the surface but concentrated preferentially at the graphite grain boundaries of the EG support. The SEM–EDX line scan technique was used to detect the distribution of the elements shown in the insets of Fig. 2. The particles in the composites comprise Ni. Surprisingly, carbon was also detected in each particle. The registration of carbon in the particles placed on the graphite support was possible because of a very low bulk density of the support consisting of thin laminar crystals of expanded graphite separated by macropores. The thickness of the lamina (around 10 nm as shown in Fig. 4) is lower than the electron penetration depth approaching dozens of nanometers for graphite at an accelerating voltage of 20 kV, so the electron beam is only partially consumed to excite carbon in the laminae and partially penetrates them; therefore the enhancement in the EDX signal is produced by extra carbon in the particles. We suggest that the origin of carbon in the samples is different: in the Ni/CC sample it comes mostly from the carbonized pitch, whereas in the NiO and Ni/C samples carbon appears from the exfoliation process accompanied by its redox amorphization. Oxygen is also detected in the particle of the EGNiO composite in addition to Ni and C. A concord of the EDX intensities for Ni and O is indicative for the presence of NiO.

TEM, HRTEM, and SAED analyses were undertaken to elucidate a microstructural arrangement of Ni and C.

Fig. 3 is a TEM image of the Ni/C composite in which inhomogeneous distribution of small dark dots is clearly discernible. Two areas were selected for SAED: area A, which is almost entirely occupied by a big dark-contrast particle including a number of small dark dots, and area B, which is almost free of the dots. The dots are identified as the Ni nanocrystals. The spotty ring pattern of the SAED A is indexed as fcc Ni. The SAED pattern B contains a dot ring assigned to (002) reflection from the graphite support and the Ni reflections as well. Thus, the nanocrystals are distributed over the whole observed area although their concentration varies remarkably. The size of the individual metallic nickel nanocrystals mostly ranges from 10 to 30 nm correlating with the data calculated from the XRD.

Highly inhomogeneous dispersion of Ni in the Ni/C composite can be attributed to following reasons: inhomogeneous precipitation of Ni(NO₃)₂ converting to NiO upon heating and further to Ni upon hydrogen reduction, and redistribution of NiO nanoparticles caused by their migration and gathering effect. Distribution of Ni(NO₃)₂ can be improved either by optimization of electrochemical oxidation parameters such as concentration of the nitrate, temperature and current density or by addition of Ni-sequestering agents to the electrolyte. An increase of density of expandable graphite surface defects where nucleation appears gives an additional room for the improvement. This can be achieved by plasma oxidation pretreatment, for example. Migration is a thermo-activated process and it will slow down along with reduction of exfoliation temperature which also promotes the enhancement of expanded graphite carbon yield thus reducing agglomeration via gathering effect.

HRTEM analysis of the Ni/C composite reveals that the graphitic-like disposition in EG is preserved after the decoration.

Fig. 2 – SEM images of the EGNiO (a), Ni/C composite (b) and Ni/CC composite (c). The inset shows an EDX line scan along the directions indicated by the white arrows in the image.
with NiO and reduction by H₂ (Fig. 4). The interplanar distance of 0.336 nm corresponds to that of graphite. The dark grey contrasts pointed with arrows in Fig. 4 are attributed to Ni. The lower arrow indicates a big Ni cluster of irregular shape precipitated on the edge of the graphite lamina. The upper arrow shows an unusual agglomeration of Ni nanobubbles with an average inner diameter of approximately 2 nm. Such metal nanobubbles should have an enormous excess of surface energy, which would cause their collapse or, in fact, would prevent their formation. Therefore, we speculate that they might be rather metallic covers on fullerenes than hollow spheres. Their formation is possible through a migration process of Ni atoms from Ni–carbon precursor [30] during its densification while fullerene formation. The detailed investigation of these Ni nanoparticles remains the subject for further studies.

Fig. 5 shows a typical TEM image of the Ni/CC composite. A homogeneous dispersion of tiny dark particles is observed. The inset shows the corresponding ED pattern. The spotty ring pattern was indexed as fcc Ni and the blurry inner ring was assigned as (002) reflection of imperfect graphitic carbon being apparently a carbonization product of the coal tar pitch. The particle diameter is in a good agreement with the data calculated from the XRD. Thus, in the Ni/CC composite the remarkably narrow dispersion of Ni nanoparticles largely spherical in shape and approximately 10 nm in size is observed.

It should be pointed out that no Ni conglomerations are observed in the Ni/CC composite. We assume that impregnation of the EGNiO sample with the pitch/toluene solution leads to pitch penetration through the NiO grain boundaries, thus forming carbon layers encapsulating the NiO particles during the heat treatment which is accompanied by their reduction to Ni. Thus, amorphous carbon is effective in preventing the agglomeration of the nanoparticles and contributes to their dispersion implying application of the composite in catalysis after proper activation. Investigation of catalytic properties of the composite is in progress.

The HRTEM indicates that the Ni nanoparticles are spherical in shape without any well-developed facets (Fig. 6). The HRTEM confirms that particle agglomeration does not occur. It can be seen in Fig. 6 that carbon shells (area A) have started to develop around the Ni nanoparticle. The core–shell structure is not so well pronounced as for graphitic onions [30–33]. The fringes are of wavy appearance and the carbon shells are poorly ordered that was also observed in [34]. The carbon network exhibits numerous defects like dangling or incomplete shells. Despite the poor crystallinity of the shells they possess some degree of ordering if compared with completely...
New nickel nanoparticle/carbon composites have been prepared on the base of expanded graphite decorated with NiO particles as an example to show the superior characteristics of expanded graphite as a novel carbon support material. The incontestable preferences of the composites are their light weight, the high shaping ability, and the high capacity for Ni nanoparticles loading and controlling their dispersion.

Well crystallized multi-shell carbon onion particles especially having no inner hollow and free of metal by-product would find applications as nano-additives for lubricants, polymers or carbon composite materials when produced in commercial quantities at low cost. It has been pointed out that to synthesize dense hollow-free carbon onions the starting carbon phase should have a density nearly related to graphite [33]. Albeit semi-coke produced by pyrolysis of coal tar pitch at moderate temperatures has a low volume density below 1.0 g/cm³ its microstructure shown in Fig. 6 indicates that local density is significantly higher. Indeed, an amorphous carbonaceous material between the particles (the area B) is designated as hydrogenated amorphous carbon either α-C:H or α-C:H [35] (because of lack of sp²-bonded carbon). Density of these carbon materials ranges from 1.6 up to 2.4 g/cm³ depending on hydrogen content [36]. We suppose that Ni-catalyzed ordering of such hydrogenated amorphous carbon towards the onion-shells marked as A will proceed further after removal of the Ni nanoparticle. We believe that a commercial method for production of onion-like carbon nanoparticles could be developed based on catalytic carbonization of coal tar pitch. Further studies will be dedicated to removal of the metal from the particles and improvement of the onion-graphite walls crystallinity.

Fig. 6 – HRTEM image of the Ni/C composite. Carbon shells and disordered carbon areas are marked by A and B, respectively.

4. Conclusion

It has been shown that the conventional hydrogen reduction of NiO at 350 °C leads to inhomogeneous dispersion of uncovered Ni nanoparticles on EG support. Ni comprising hollow nanobeads with an inner diameter of ~2 nm are observed in this composite as well.

Carbon reduction of NiO at 550 °C during pyrolysis of coal tar pitch impregnating the EG allows obtaining of well-dispersed Ni nanoparticles with a narrow size distribution of ~10 nm imbedded in amorphous carbon matrix. Beginning of formation of Ni-filled carbon onion particles by catalytic graphitization of the amorphous carbon is detected.

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