Mesh-structured N-Doped Graphene@Sb₂Se₃ Hybrids as an Anode for Large Capacity Sodium-Ion Batteries

Wenxi Zhao^{a, b}, Chang Ming Li^{a, b, c*}

^a Institute for Clean Energy & Advanced Materials, Southwest University, Chongqing 400715, P.R. China.

^b Chongqing Key Laboratory for Advanced Materials and Technologies of Clean Energies, Chongqing 400715, P.R. China.

^c Institute of Materials Science and Devices, Suzhou University of Science and technology, Suzhou, 215009, China

Corresponding author. E-mail address: ecmli@swu.edu.cn (C.M. Li)

Abstract

A mesh-structured N-doped graphene@Sb₂Se₃ (NGS) hybrid was one-pot prepared to realize N-doping, nanostructuring and hybridization for a sodium-ion battery anode to deliver much larger reversible specific capacity, faster interfacial electron transfer rate, better ionic and electronic transport, higher rate performance and longer cycle life stability in comparison to the plain Sb₂Se₃ one. The better performance is ascribed to the unique intertwined porous mesh-like structure associated with a strong synergistic effect of N-doped graphene for dramatic improvement of electronic and ionic conductivity by the unique porous structure, the specific capacity of graphene from N doping and fast interfacial electron transfer rate by N-doping induced surface effect and the structure-shortening insertion/desertion pathway of Na⁺. The detail electrochemical process on the NGS electrode is proposed and analyzed in terms of the experimental results.

Keywords: mesh structure; N-doped graphene; Sb₂Se₃; sodium-ion batteries; anode

1. Introduction

Sodium-ion batteries as a promising potential substitute of lithium-ion batteries have attract significant attention owing to their abundant resource, low cost and similar chemical properties [1-4]. However, it is very challenging to develop a suitable host material as an anode of sodium-ion battery with high storage capacity and long cycle life for practical applications [5]. Theories and experiments have confirmed that some anodes of sodium-ion batteries that made by materials used for hosting lithium ions possess much lower performance [6]. Therefore, it is important to explore suitable anode materials with high Na⁺ insertion/extraction capability while having high electron conductivity, little volume expansion and change of insertion/extraction potential, excellent chemical stability and good compatibility with electrolyte for long cycle life.

Recently, extensive efforts have been focused on high performance transition-metal selenides materials with analogous structure of graphite, such as MoSe₂ [7, 8], FeSe₂

[9, 10], NiSe₂ [11] and CuSe₂ [12], and results show good sodium storage performance. As one of the important selenides, Sb₂Se₃ with a direct narrow-band gap and highly anisotropic semiconducting nature has been widely explored in various research fields and displayed good chemical stability and excellent photovoltaic properties [13, 14]. In general, 1 mole of Sb₂Se₃ can react with 12 moles Na⁺ to form Na₃Sb in a sodium-ion battery system for a high theoretical capacity of 670 mAh g⁻¹, but it is still far from practical applications because of its low electric conductivity and huge volume expansion to result in structure collapse for a rapid capacity loss [15, 16]. Thus, it is essential to construct an effective structural electrode to overcome these blockages.

Graphene has been known with its superior electron mobility, large surface area and excellent structure flexibility [17-19]. However, graphene directly used as a conductive component of an electrode in a sodium-ion battery cannot maximize capacity, and its low tapping density brings a poor volumetric capacity [20]. Various approaches have been used to modify graphene by heteroatoms such as N, S, and B for modulating its electron donor and acceptor, which could facilitate or improve the electronic conductivity and specific capacity [21, 22].

Herein, a mesh-structured N-doped graphene@Sb₂Se₃ (NGS) composite was one-pot prepared to realize N-doping, nanostructuring and hybridizing as a sodium-ion battery anode material for the first time, displaying high reversible capacity, long cycle-life and superior rate performance while rendering a new universal facile method to fabricate electrode materials for commercial sodium-ion batteries.

2. Experimental and characterization

2.1. Preparation of N-doped graphene@ Sb₂Se₃ hybrids (NGS)

N-doped graphene @ Sb₂Se₃ hybrids was prepared by one-pot hydrothermal reaction. In a typical process, 3 mmol selenium (Se) powder was dissolved into 25 ml deionized water under stirring for 15 mins, followed by slowly adding 6ml hydrazine hydrate (N₂H₄·H₂O) under continuous stirring for 30mins. Then 2 mmol antimony

triacetate ($\text{Sb}(\text{CH}_3\text{COO})_3$) and 5 g urea ($\text{CO}(\text{NH}_2)_2$) were added in to form a suspension solution, followed by adding 60 mg graphene oxide under stirred for 30 mins. The resulted precursor suspension was then transferred to a 50 ml autoclave and was heated at 180 °C for 24 h. Finally, the produced product was cleaned using deionized water for several times by filtration and drying by freezing method. In addition, control experiments were also performed to prepare graphene@ Sb_2Se_3 (GS) and plain Sb_2Se_3 using the same method but without adding urea or graphene.

2. 2. Materials characterization

The as-prepared product was examined with X-ray diffraction (XRD, Shimadzu XRD-7000 X-ray diffractometer) with Cu $K\alpha$ radiation at a scanning rate of 2° min^{-1} . Scanning electron microscopy (SEM, JSM-6510) and transmission electron microscopy (TEM, JEM-2100) were used to characterize the morphology of the product. XPS data were collected by using X-ray photoelectron spectroscopy (XPS-ESCALAB250). Raman spectra were measured using a confocal Raman microscope (DXR, Thermo-Fisher Scientific) with a 532 nm argon-ion laser. The Brunauere Emmette Teller (BET) surfaces areas and porosity of the samples were evaluated using an automatic adsorption instrument NOVA1200e (Quantachrome, Boynton Beach, Florida).

2.3. Electrochemical measurements

Two electrode coin cells were assembled to measure electrochemical performance of NGS, of which metal sodium and polypropylene microporous films (Celgard 2300) used as the counter electrode and separator, respectively. The electrolyte was 1M NaPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DEC) (1:1 in volume) with 5 vol% addition of fluoroethylene carbonate (FEC). The working electrode was made from a slurry prepare by the active electrode material, super P and carboxymethyl cellulose (CMC) at a weight ratio of 7:2:1, which was coated directly on Cu foil and dried at 120 °C under vacuum overnight. The typical loading of the prepared sample was approximately 0.7~1 mg per electrode. The 2032 coin cells were assembled in an Ar-filled glove box. Galvanostatic charge–discharge tests were performed at a potential range of 0.01 ~ 3 V vs. Na/Na^+ using Land testing system (Wuhan, China) at

room temperature (26 °C). Cyclic voltammetry (CV) was measured at a scan rate of 0.5 mV s⁻¹ between 0 and 3 V using a CHI-660D electrochemistry workstation.

3. Results and discussion

The XRD patterns of NGS, GS and Sb₂Se₃ in Fig.1a show that a same crystalline structure assigned to an orthorhombic Sb₂Se₃ phase with space group *Pbnm* (JCPDS#15-0086), which is in agreement with the previous reported literature [14]. It is noted that the peak intensities of NGS and GS are obviously stronger than that of Sb₂Se₃, indicating their better crystallinity. No obvious diffraction peak relating to carbon is observed in XRD patterns of NGS and GS, revealing the amorphous phase of the reduced graphene oxide (rGO). Raman spectra of NGS and GS in Fig.1b show that two strong peaks around 1338.5 and 1578.1 cm⁻¹, respectively, which correspond to the defect-induced D band and graphite-induced G band. The peak intensity ratio of D and G band ($I_D / I_G = 1.31$) for NGS is larger than that of GS ($I_D / I_G = 1.15$) showing more distorted crystal structure of graphene by N-doping [23], which not only benefits to Na⁺ diffusion, but also offers more active sites of Na-storage. Since surface area and pore structure of an electrode material can greatly affect its performance, the specific surface area of NGS, GS and Sb₂Se₃ are measured by nitrogen adsorption–desorption isotherm method (Fig.1c), displaying a type-IV behavior with a calculated specific surface area of 56 m²/g for NGS, which are larger than that of GS (51 m²/g) and Sb₂Se₃ (28 m²/g), while the plots of pore size distributions in Fig.1d show that NGS, GS and Sb₂Se₃ all have mesopores with an average pore size of ~17 nm.

Preferred position of Fig. 1

XPS spectra in Fig.2 show that all the expected elements of NGS are recorded including Sb, Se, C and N (Fig.2a). The high-resolution XPS of Sb 3d in Fig.2b is divided into three peaks, of which the peaks at 530.4 and 539.7 eV are related to Sb 3d_{3/2} and Sb 3d_{5/2} of Sb³⁺, respectively for NGS. The separated XPS spectra of N 1s such as 398.4, 399.6 and 400.6 eV in Fig.2c are attributed to pyridinic-N, pyrrolic-N and quaternary-N [24], respectively; meanwhile, a high N content of 6.7% is

calculated by XPS element analysis. There are four peaks located at 284.2, 285, 288.0 and 289.1 eV from the high resolution XPS spectrum of C1s, corresponding to SP^2 C (C-C), SP^3 C (C=C), C=O and O=C-OH, respectively [19]. It is noted specifically that two additional peaks at 285.9 and 286.7 eV are observed in the C1s spectrum, which are associated with C=N and C-N, revealing the successful doping of N element into graphene sheets.

Preferred position of Fig. 2

The SEM image in Fig.3a shows that a large quantity of N-doped graphene and Sb_2Se_3 nanorods are intertwined together to form a spider mesh-like porous structure for effective transport of Na^+ and electrolyte diffusion, while the corresponding TEM image of NGS in Fig.3d clearly displays that graphene sheets are coated on the Sb_2Se_3 nanorods, which is in agreement with the SEM image. The selected area electron diffraction (SAED) pattern in the inset of Fig.3d illustrates a single phase of Sb_2Se_3 with [001] growth direction. As a control, the SEM and TEM images of GS in Fig.3b and 3e show that it has identical physical structure without N-doping. It can be seen that the Sb_2Se_3 nanorods are randomly distributed on the surface of graphene sheets, however, SEM and TEM images of Sb_2Se_3 in Fig 3c and 3f display that the irregularly shaped nanorods were scattered over whole surface. It is noted that the morphology of Sb_2Se_3 is changed by adding nitrogen source or graphene. In addition, there are two lattice fringes with the d-spacing of 0.379 and 0.828 nm observed in Fig. 3g, matching with the (101) and (110) planes of orthorhombic Sb_2Se_3 , respectively. The electron diffraction X-ray spectroscopy (EDS) spectrum of NGS in Fig.3h shows that all elements are uniformly distributed in the product and no any obvious impurity is detected, indicating the well-defined compositional profile of NGS. Furthermore, the EDS result of GS and Sb_2Se_3 is also examined as in Fig.S1 and S2, which also shows the uniform distribution of Sb and Se.

Preferred position of Fig. 3

The discharge-charge curves of the NGS electrode in a potential window of 0.01 to 3 V for the initial 3 cycles were measured at 100 mA g^{-1} as in Fig.4a. During the first sodiation/desodiation process, the NGS electrode has a high discharge capacity of

1023.4 mAh g⁻¹, which is the largest in comparison to GS electrode (796 mAh g⁻¹ in Fig.4(c)) and plain Sb₂Se₃ electrode (625.3 mAh g⁻¹ in Fig.4(e)). The initial Coulombic efficiency (CE) of 68.2% of NGS electrode also is the highest among all three electrodes; however, CEs for three electrodes all achieve 100% at the 2nd cycle. The low initial CEs associated with the initial irreversible Coulombic losses should be caused by formation of a solid electrolyte interphase (SEI) layer and decomposition of electrolyte [25, 26]. Meanwhile, two redox plateaus are located in ~ 1 / 1.5 V and 0.5 / 0.75 V, respectively, revealing the insertion/extraction of Na⁺. The cyclic voltammograms (CVs) measured in a voltage window of 0 to 3 V at a scan speed of 0.5 mV s⁻¹ show that all three electrodes exhibit similar redox peaks (Fig.4b, d and f). In the first cathodic scan, three reduction peaks at about 0.98, 0.76 and 0.23 V should be resulted from the formation of SEI layer, the decomposition of Sb₂Se₃ to form Sb/Na₂Se and the generation of Na-Sb alloy phase, respectively as the previous report [27]. Furthermore, the oxidation peaks at around 0.88, 1.45 and 1.88 V can be ascribed to the dealloying and conversion reactions of Sb₂Se₃. The conversion and alloying reactions of Sb₂Se₃ during the discharge-charge process are schematically shown in Scheme 1(a). It is worthy of a note that the CV of the first scan is obviously different from that of the 2nd and 3rd scans, indicating the presence of irreversible capacity for the first scan. It is also observed that the CV curves of NGS start to better overlap their previous scan from the 2nd scan than GS (Fig. 4d) and Sb₂Se₃ (Fig. 4f) electrode, revealing better cycle stability of NGS even from the 1st cycle. EIS spectra of NGS electrode measured during the 4th scans in Fig.S3 clearly show that the charge transfer resistance of NGS electrode gradually increase along with the Na⁺ insertion but it reduces with the Na⁺ extraction. The relationships between Z' and ω^{-1/2} at different discharged and charged states in Fig.S3b and Fig.S3d show that the smallest slopes occurs at 0.23 V for the sodiation process and 0.86 V for charge profiles, respectively, both of which show the highest Na⁺ diffusivity.

Preferred position of Fig. 4

Preferred position of Scheme 1

The phase evolution mechanism of NGS during the first insertion/extraction

process was further explored by using XRD, XPS and HR-TEM. In Fig.5a, when the battery discharged to 0.72 V, the diffraction peaks of Sb_2Se_3 were detected along with the formation of metallic Sb (Fig.5a (A1)), indicating that Sb_2Se_3 reacts with Na to form Sb for the conversion process. During the discharging process from 0.72 to 0.01 V, the diffraction peaks of Sb_2Se_3 gradually disappeared (Fig.5a (A2)). After fully discharging to 0.01 V (Fig.5a (A3)), a phase of NaSb(OH)_6 was detected, which can be attributed to the reaction between Na-Sb alloy phase with water and oxygen because the disassembled electrode was exposed in the air for a long time in our experiment [28, 29]. During the desodiation process, metallic Sb was detected at the charged state of 0.86 V (Fig.5a (A4)), revealing the dealloying reaction of Na-Sb phase. XRD pattern further shows the formation of Sb_2Se_3 phase along with the absence of metallic Sb when fully charging to 3 V (Fig.5a (A6)), indicating a reversible conversion reaction of Sb_2Se_3 . Moreover, no diffraction peak of Na_2Se was detected during the first sodiation and desodiation process, demonstrating its amorphous structure. The morphology changes of Sb_2Se_3 nanorod at different charge/discharge states were measured using TEM as shown in Fig.S4, revealing that the surfaces of Sb_2Se_3 nanorods become rough along with the formation of thick SEI layer owing to the presence of fluoroethylene carbonate (FEC) additive in the electrolyte.

Fig.5b displays the valence state conversion of Sb element at different sodiation and desodiation state. After discharging to 0.72 V (Fig. 5b (B1)), the peak intensities of Sb^{3+} become weaker along with the formation of Sb^0 at 537.5 and 532.8 eV, corresponding to the interlayer distance of 0.312 nm for metallic Sb in Fig.5c (C1). When the battery is further discharged to 0.01 V (Fig.5b (B2)), metallic Sb^0 disappeared and the peak area of Sb^{3+} at 530.6 eV increases, indicating generation of Na-Sb alloy phase of NaSb(OH)_6 with a d-spacing of 0.211 nm, which is in agreement with the (213) plane of NaSb(OH)_6 (Fig.5c (C2)). However, after fully charging to 3 V, Sb_2Se_3 phase is recovered to the pristine state because of the dealloying and conversion reaction from Na-Sb alloy phase to Sb_2Se_3 (Fig.5b (B4)), which is in line with two lattice fringes of (110) and (001) of Sb_2Se_3 , matching with the d-spacing of

0.828 and 0.398 nm (Fig.5c (C4)), respectively. Thus the detail electrochemical reaction mechanism can be schematically expressed as in Scheme 1(b). According to the result discussed above, the electrochemical reactions of Sb₂Se₃ with Na⁺ during the first discharging and charging are as follows [27]:

Discharging process:

Charging process:

Preferred position of Fig. 5

EIS spectra of NGS, GS and Sb₂Se₃ electrode measured at the oxidation state of 1.42 V for the 4th scans over a frequency range from 100 kHz to 0.01 Hz in Fig. 6a show that NGS electrode has a charge transfer resistance of 197.1 Ω over the high frequency range, which is much smaller than that of GS (285.3 Ω) and Sb₂Se₃ (354.5 Ω) electrode. The corresponding parameters calculated from the equivalent circuit (the inset of Fig.6a) are shown in Table S1. Moreover, the diffusion coefficients of Na⁺ in all electrodes can be calculated in terms of Nyquist plot over the low frequency region from the following equation [30]:

$$D_{\text{Na}^+} = \left(\frac{2RT}{\sqrt{2}n^2F^2\sigma_wAC} \right)^2 = \frac{2R^2T^2}{n^4F^4A^2C^2\sigma_w^2} \quad (5)$$

where R, T, A, F, n, C and σ_w are the gas constant, the absolute temperature, the surface area of the electrode, the Faraday's constant, the number of electrons per molecule during oxidation, the insertion/extraction Na⁺ concentration in the anode material and the Warburg factor, respectively. Fig. 6b shows the relationship of the real impedance Z' and ω^{-1/2} (ω=2πf) over the low frequency region. It is known that the slope of fitting line (Z' vs ω^{-1/2}) represents the sodium ion kinetics in the electrode materials [31]. The diffusion coefficient of NGS is larger than that of GS and plain Sb₂Se₃ by 3 and 8.8 times, respectively. This strongly indicates that the mesh-like NGS structure can facilitate a fast sodium ion transport.

Preferred position of Fig. 6

The cycling performance of NGS, GS and Sb_2Se_3 electrode measured at a current density of 100 mA g^{-1} in Fig.7a clearly shows that NGS electrode has the best cycling stability, which can deliver a discharge capacity of 548.6 mAh g^{-1} with a CE over 100% after 50 cycles. In contrast, the GS and Sb_2Se_3 electrode exhibit obvious capacity fading with a reversible discharge capacity of 350 and 200 mAh g^{-1} , respectively after 50 cycles. After 50 cycles, the capacity retention of NGS electrode (72.1%) is much larger than that of GS (58%) and Sb_2Se_3 (43%) electrode, indicating that N doping can effectively improve the electron conductivity and reversible capacity. At the same time, the cycling performance of the NGS electrode at high rate of 1 A g^{-1} was also measured and delivered a discharge capacity of 177.3 mAh g^{-1} with a CE of about 100% after 70 cycles (Fig. S5). The capacity loss of NGS electrode could be attribute to the volume expansion resulting in aggregation and collapse of Sb_2Se_3 structure during the discharging-charging process. SEM images of NGS electrode at different cycles in Fig.S6 show slight aggression of Sb_2Se_3 nanorods along with the formation of thick SEI layer after 5 cycles but still maintaining the electrode structure after 5 to 50 cycles, indicating good cycle stability. Fig.7b shows a superior rate performance of NGS electrode, in which the discharge capacities at current densities of 0.05, 0.1, 0.2, 0.4, 0.8 and 1.5 A g^{-1} are about 957, 705, 557, 474, 396 and 337 mAh g^{-1} , respectively. Even if the current density returns from discharge status of 1.5 to 0.05 A g^{-1} , NGS can still have a reversible capacity of 783 mAh g^{-1} with a retain rate of 81.2%, while GS and Sb_2Se_3 only have reversible capacities of 112 and 27 mAh g^{-1} with retaining rates of 76.2% and 96.3%, respectively, indicating that NGS has much better rate capability than GS and Sb_2Se_3 (Fig.S7). In addition, the EIS spectra of NGS at different cycles were measured, showing an enhanced charge transfer resistance with the cycle increasing (Fig.S8).

Preferred position of Fig. 7

The results and analysis above clearly show that the sodium storage performance enhancement for the NGS electrode superior to the GS and plain Sb_2Se_3 can be attributed to the highly interknitted porous structure of NGS and a synergistic

electrocatalytic effect of Sb_2Se_3 and N-doped graphene. The electron and ion conductivity is also dramatically improved in comparison to that of GS and plain Sb_2Se_3 by the intertwined and mesh-like structure, respectively, of which the former offers more electron transport paths between Sb_2Se_3 nanorods and conductive graphene, and the latter enables good electrolyte penetration and short insertion pathway of Na^+ . The N-doped graphene favors a larger reversible capacity by the pyridinic N resulting in surface defects to provide more active sites for Na^+ insertion [32, 33] and the intertwined mesh-like structure renders more continuous short Na^+ transport paths to Sb_2Se_3 nanorods for Na^+ insertion/desertion process. These apparently can make much faster interfacial electron transfer rate [34]. In addition, a flexible mesh-like grapheme covering the Sb_2Se_3 nanorods provides an elastic buffer spacing to accommodate the volume expansion/reduction, thus efficiently retaining the structural integrity during the sodiation and desodiation process for good cycle life stability.

Conclusions

In summary, a unique N-doped graphene@ Sb_2Se_3 hybrid is prepared by one-step hydrothermal reaction. As a sodium-ion battery anode, NGS electrode delivers a high discharge capacity of 548.6 mAh g^{-1} at 100 mA g^{-1} after 50 cycles, which is 1.6 and 2.8 times larger than that of GS and plain Sb_2Se_3 , respectively, thus delivering a much better rate capability at 1.5 A g^{-1} by 3 and 12.5 times, respectively. In addition, the NGS electrode has much better cycle life performance. Those results are ascribed to the unique intertwined mesh-like porous structure synergistically associated with the effect of N-doped graphene for dramatic improvement of electronic and ionic conductivity by the novel structure, the specific capacity of graphene from N doping and fast interfacial electron transfer rate by N-doping induced surface effects and the structure-shortening insertion/desertion pathway of Na^+ . The detail electrochemical process on the NGS electrode is proposed and analysed in terms of the experimental results.

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Figure Captions:

Fig. 1 (a) The XRD patterns of NGS, GS and Sb_2Se_3 . (b) Raman spectrum of NGS and GS. (c, d) The N_2 adsorption-desorption isotherms and BJH pore size distribution of NGS, GS and Sb_2Se_3 .

Fig. 2 XPS spectrum of the as-prepared NGS: (a) survey spectrum; (b) Sb 3d; (c) N 1s; (d) C 1s.

Fig. 3 SEM images: (a) NGS, (b) GS, (c) Sb_2Se_3 ; The TEM image (d) NGS, the inset is SAED pattern of NGS; (e) GS; (f) Sb_2Se_3 . (g) The high resolution TEM image of NGS. (h) The EDS spectra of NGS.

Fig. 4 Discharge-charge profiles of the electrode during first 3 cycles in a potential window of 0.01 ~ 3 V at a current density of 100 mA g^{-1} : (a) NGS; (c) GS; (e) plain Sb_2Se_3 ; Cyclic voltammograms of the electrode at a scan rate of 0.5 mV s^{-1} at 100 mA g^{-1} : (b) NGS; (d) GS; (f) plain Sb_2Se_3 .

Fig. 5 (a) XRD patterns of NGS electrode at different charge/discharge states during the first discharge-charge profiles. (A1) discharged to 0.72 V. (A2) discharged to 0.23 V. (A3) discharged to 0.01 V. (A4) charged to 0.86 V. (A5) charged to 1.42 V. (A6) charged to 3 V. (b) XPS spectrums of NGS electrode at different charge/discharge states. (B1) discharged to 0.72 V. (B2) discharged to 0.01 V. (B3) charged to 1.42 V. (B4) charged to 3 V. (c) HR-TEM images of NGS electrode at different chemical state at the first discharge-charge profiles. (C1) discharged to 0.72 V. (C2) discharged to 0.01 V. (C3) charged to 1.42 V. (C4) charged to 3 V

Fig. 6 (a) EIS spectra of NGS, GS and Sb_2Se_3 electrode at the oxidation state of 1.42 V during the 4th cycle. (Inset shows the equivalent circuit corresponding to the Nyquist plots.). (b) Relation of Z' vs. $\omega^{-1/2}$ in the low frequency region at the oxidation state of 1.42 V during the 4th cycle.

Fig. 7 (a) Cycling performance of NGS, GS and Sb_2Se_3 electrode. (d) Rate capability of NGS,

GS and Sb_2Se_3 electrode at various current densities.

Scheme 1. (a) Schematic illustration of transport of sodium ions and electrons. (b) Conversion and alloying reaction mechanism of NGS electrode during the cycling profiles.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Scheme 1