Thermal exfoliation of electrochemically synthesized graphite intercalation compound with perrhenic acid

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Received: 9 April 2020 / Revised: 5 May 2020 / Accepted: 7 May 2020 / Published online: 16 May 2020
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Abstract

In present work, we describe the synthesis of graphite intercalation compounds with perrhenic acid (HReO₄-GIC) through the anodic oxidation of graphite in aqueous perrhenic acid solution and their thermal exfoliation. Due to electrochemical treatment of graphite in perrhenic acid solution, ReO₄[−] ions are intercalated into interlayer spaces of graphite. Anodic oxidation of graphite in HReO₄ solution leads to the formation of 3-stage GIC. Simultaneously, some amount of perrhenic acid becomes deposited on the graphite surface and edges. In the next step, thermal treatment of the previously synthesized GIC was performed, causing both the exfoliation of graphitic structure and transformation of perrhenic acid into rhenium oxides on the surface of graphene layers. The yielded product was exfoliated graphite-ReO₂/ReO₃ composite. The obtained composite was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Raman spectroscopy. Additionally, specific surface area of the exfoliated materials was measured.

Keywords Graphite intercalation compound · Perrhenic acid · Electrochemical oxidation · Exfoliation · Rhenium oxide

Introduction

Due to the presence of relatively weak van der Waals forces between the graphene layers in graphite, ions, molecules, or atoms can be inserted into the interlayer spaces of graphite matrix. This process is called intercalation and the yielded product is graphite intercalation compound (GIC) [1, 2]. The direction of electron transfer between the graphite matrix and intercalate defines the type of synthesized GIC. When intercalate accepts electrical charge from the carbon matrix, an acceptor GIC is synthesized. Contrariwise, if the electrical charge is accepted by carbon matrix, the donor-type GIC is obtained [3]. Most of donor-type intercalates are alkali metals, i.e., Li, Na, K, or ammonium quaternary salts [4]. On the other hand, acceptor GICs commonly contain inorganic acids, i.e., H₂SO₄, HNO₃, HClO₄ [5, 6], or metal chlorides [7, 8]. The efficiency of intercalation process is specified by the

intercalation stage. It reveals the number of graphene layers separated by the neighboring layers of intercalate, for example, if every intercalant layer is separated by two graphene layers, the pure 2-stage GIC is synthesized [2, 3].

GIC can be synthesized on the way of chemical [9, 10], electrochemical [11–13], or photochemical reaction [14]. Chemical methods are divided into these carried out in gas or liquid phase. In the first one, the vapors of intercalate are passed through the bed of graphite, i.e., N₂O₅, SO₃, Br₂, or Re₂O₇ [15–18], whereas an intercalation in liquid phase is realized in molten salts, i.e., ZnCl₂, NiCl₂, or FeCl₃, or in the dissolved intercalate [19, 20]. However, the commonly used system comprises of inorganic acids, such as sulfuric or perchloric, dissolved in water [5, 10]. To start the chemical intercalation, the addition of reductant or oxidant, depending on the type of prepared GIC, is needed. Electrochemical intercalation is carried out by polarization of graphite in dissolved intercalate, which plays a role of electrolyte. Depending on the electrons flow direction, the electrochemical processes are performed by anodic oxidation or cathodic reduction. Contrary to chemical methods, the electrochemical ones are more controllable and the product with desired properties is easily obtained. Moreover, they are environmental friendly, because no oxidant/reductant agent is used, and the final product has no impurities caused by the presence of

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oxidation/reduction by-products [21]. On the other hand, chemical methods are cheaper and much more easier to perform. Photochemical methods are relatively rarely used for the GIC preparation. In this case, intercalate is irradiated by UV light generating free radicals, which oxidize graphite matrix thus promoting the intercalation process. The intercalation of graphite by FeCl_3 in chloroform medium can be conducted due to photochemical reactions [14].

GIC with Re_2O_7 was synthesized for the first time by Fuzellier [22]. For this preparation, the melted oxide and vapors were used. In both cases, the prepared GICs were characterized by low content of intercalate. In 1991, Scharff et al. have successfully synthesized Re_2O_7 -GIC by heating the graphite and dirhenium heptoxide in sealed glass ampoules filled with O_2 , N_2 , or Ar [18]. They obtained Re_2O_7 -GIC with mixed third and fourth stages. Fröba et al. investigated the structure of Re_2O_7 -GIC using X-ray adsorption near-edge structure [23, 24]. They noted that charge transfer from graphite to rhenium occurs and between the graphene layers slightly disordered tetrahedral symmetry of ReO_4^- ion appears. Electrochemical method of HReO_4 -GIC formation was studied also by Scharff [25]. An anodic oxidation of highly oriented pyrolytic graphite (HOPG) in 65–70% HReO_4 by voltammetry technique yielded 3-stage GIC with a ninterlayer distance of 1370 pm.

Due to redox character of rhenium oxides, they can be applied in different types of catalytic reactions. For example, Re_2O_7 -based catalysts reveal high catalytic activity in olefin metathesis with high efficiency at room temperature [26, 27]. Additionally, catalysts containing ReO_x demonstrate high catalytic selectivity and activity for partial oxidation of methanol to methylal [28–30].

Exposition of GIC to a high temperature causes evaporation and thermal decomposition of intercalate occupied the interlayer spaces of graphite matrix. Accumulation of gases and increasing pressure lead to the damage of graphene layers. Due to the rapid removal of intercalate, the graphite structure expands up to hundreds of times along the crystallographic *c* axis yielding exfoliated graphite (EG) [31, 32]. Such a material is characterized by low density, relatively high specific area, hydrophobicity, and high thermal stability [33–35]. Generally, the properties of obtained EG depend on the type of GIC used for synthesis as well as conditions employed during exfoliation process. EG finds application as a precursor for flexible graphite foil preparation, filler in composites, material for oil sorption, or as a matrix for composite preparation [32, 33, 35–38].

The thermal exfoliation of GIC containing intercalates with catalytic activity can lead to transfer of intercalate from GIC matrix to developed surface area of EG yielding EG/catalyst system. Such composites can be used in chemical power sources production as active material for hydrogen storage or methanol electrooxidation.

In this work, we present the preparation of EG-rhenium oxide composites through shock thermal exfoliation of the beforehand synthesized HReO_4 -GIC. GIC with perrhenic acid was prepared by anodic oxidation of natural graphite in 75–80% HReO_4 electrolyte using galvanostatic technique. The synthesized graphitic materials were thermally treated in N_2 atmosphere in 700 °C to conduct exfoliation. Structural changes of the gathered samples were investigated by XRD and Raman spectroscopy, whereas morphology was examined by SEM analysis. Surface composition of the synthesized composites was studied using an energy-dispersive X-ray spectroscopy (EDS). The characterization of as prepared materials was completed by the calculation of the Brunauer-Emmet-Teller (BET) surface area.

Experimental

Sample preparation

Natural graphite flakes (170–283 μm , purity 99.5%, Graphit Kropfmühl) were anodically oxidized using galvanostatic technique and current density equal to 40 mA g^{-1} . Graphite (400 mg) was closed in current collector made of platinum gauze (purity 99.9% 120 mesh, Goodfellow). A counter electrode made of platinum wire (purity 99.9%, 1mm diameter, Goodfellow) was used. Both electrodes were immersed in a three-electrode reactor beforehand filled with HReO_4 solution (75–80%, Sigma-Aldrich). Anodic and cathodic chambers were separated by glass frit. As a reference electrode, the $\text{Hg}/\text{Hg}_2\text{SO}_4/1 \text{ M H}_2\text{SO}_4$ was used, which was connected with working electrode by salt bridge filled with 1 M H_2SO_4 . Different charge densities ranging from 60 to 1800 $^\circ\text{C g}^{-1}$ were passed through the working electrode yielding samples denoted as ReGIC60 , ReGIC120 , ReGIC600 , and ReGIC1800 . After, electrochemical process samples were washed with acetone to prevent the deintercalation of perrhenic acid.

EG- $\text{ReO}_2/\text{ReO}_3$ composites were synthesized using shock thermal treatment under a constant flow of N_2 . For this purpose, quartz crucible filled with GIC was placed in half of quartz tube which was outside the heating zone of the tube furnace. When the temperature of 700 °C was reached, GIC was rapidly moved to the heating zone causing the simultaneous exfoliation and deposition of rhenium oxides on graphene layers surface. After 4 min, the composite was moved out of the heating zone to cool down until room temperature was reached. Depending on the exfoliated material, obtained materials were named as Ex- ReGIC60 , Ex- ReGIC120 , Ex- ReGIC600 , and Ex- ReGIC1800 .

Fig. 1 Galvanostatic curve recorded during electrochemical oxidation of graphite in 75–80% perrenic acid

Instrumentation

All electrochemical measurements were performed using potentiostat/galvanostat Autolab PGSTAT 302N. Raman spectra were recorded by inVia Renishaw micro-Raman system with Ar laser and wavelength 514.5 nm. XRD diffractograms were obtained using PANalytical diffractometer with Cu K α radiation (0.154 nm) with step size of 0.04° and range from 4 to 60°. Morphology and chemical surface composition of synthesized carbon materials were investigated by SEM equipped with EDS detector using S-3400N Hitachi microscope. Specific surface area of exfoliated samples was gained from N₂ adsorption isotherms measured at 77 K with 3Flex Micromeritics apparatus.

Results and discussion

Electrochemical oxidation of graphite in 75–80% HReO₄

Galvanostatic curve recorded during anodic oxidation of graphite in perrenic acid solution is presented in Fig. 1. The potential jump to 0.9 V is associated with the formation of electrical double layer. Next, the gentle potential increment to around 1.15 V depicts the formation of HReO₄-GIC with higher stages. It cannot be excluded that in parallel the electrochemical deposition of

Fig. 3 Raman spectra recorded for pristine graphite and HReO₄-GICs

perrenic acid in form of H(ReO₄)(H₂O) may also occurs [39]. Potential plateau ranged between the charge densities from 120 to 900 C g⁻¹ is connected to further deposition of HReO₄ on graphite surface as well as filling the interlayer spaces between the graphene layers. The last potential plateau starting at around 1.5 V corresponds to the partial oxidation of graphene layers and water electrolysis leading to deintercalation of HReO₄. Measured weights of ReGIC60, ReGIC120, ReGIC600, and ReGIC1800 were equal to 517, 606, 803, and 659 mg, respectively.

From SEM images (Fig. 2) of graphite electrooxidized in HReO₄ solution, it can be noted that during the anodic treatment the deposition of HReO₄ forming H(ReO₄)(H₂O) on graphite surface and edges occurs [39]. The amount as well as size of the deposited H(ReO₄)(H₂O) increases with the treatment time. For the sample ReGIC1800 (Fig. 2 g, h), the insignificant electrochemical exfoliation of graphite flakes can be observed likely caused by the partial oxidation of graphene layers as well as electrolysis of intercalates closed between the graphene layers.

Fig. 2 SEM images of ReGIC60 (a, b), ReGIC120 (c, d), ReGIC600 (e, f), and ReGIC1800 (g, h)

Fig. 4 XRD patterns recorded for pristine graphite and HReO₄-GICs

Raman spectra recorded for graphite and synthesized GICs are shown in Fig. 3. Typical bands for carbon materials are observed at 1355, 1580, 2725, and 2910 cm⁻¹. The first one, D band, is associated with the presence of sp³ hybridized carbon deriving from defects, edges, or functional groups [40, 41]. It can be noted that elongation of graphite oxidation causes the increase of D band intensity, due to the formation of oxygen functionalities on the surface of graphene layers. The second one, called as G band, is assigned to the first-order scattering of E_{2g} mode arising from the sp² bonded carbon [40, 42]. For graphite, the regarded band has one maximum, whereas Raman spectra for HReO₄-GICs reveal the second maximum of G band, called E'_{2g}. It evidences the presence of intercalated graphite structure. During the anodic treatment of graphite, the intensity of E'_{2g} band increases compared with E_{2g} band thus indicating the enhanced amount of intercalated HReO₄ [43,

44]. Surprisingly, in the case of sample ReGIC1800, the intensity of E'_{2g} band in turn decreases. Such a behavior is caused by the partial degradation of graphitic structure due to oxidation of graphene layers accompanied by the partial deintercalation of ReO₄⁻ ions from graphite matrix. 2D band comes from the splitting of π electron dispersion energies and consists of two peaks [40–42]. The last band seen in Fig. 3, called as D + G band, is characteristic for oxidized graphene layers [45, 46]. For graphite and ReGIC60, the above-mentioned band is absent. It appears only on Raman spectra for samples ReGIC120, ReGIC600, and ReGIC1800. Its intensity increases with time of electrochemical oxidation. Such a behavior coincides with electrochemical results revealing that prolongation of anodic treatment of graphite leads to the partial oxidation of graphite matrix. Raman bands recorded under 1000 cm⁻¹ can be assigned to the appearance of tetrahedral ReO₄⁻ groups [47–50]. The low-frequency modes at 245 and 341 cm⁻¹ correspond to the bending motion of Re–O bonds [50, 51], whereas modes with higher frequencies at 889, 914, 965, and 988 cm⁻¹ arise from the stretching vibration of Re–O bonds in ReO₄⁻ tetrahedra [48, 50, 51]. The most pronounced effect of ReO₄⁻ bands is present for sample ReGIC120. Further, electrooxidation causes the diminution in their intensities, which indicate that deintercalation of perhenic ions as well as deposition of H(ReO₄)(H₂O) on graphite surface takes place.

XRD measurements for graphite and oxidized samples provided information on changes in structure caused by electrochemical treatment of a graphite in perhenic acid (Fig. 4). XRD pattern of graphite shows two main diffraction peaks at 26.6 and 54.4° revealing that the interlayer distance between the graphene layers is equal to 3.35 Å [52]. For sample ReGIC60, a new diffraction peak at 25.7° corresponding to stage-3 HReO₄-GIC with average interlayer distance of 13.8 Å can be observed. This result is in agreement with the results presented by Scharff [18, 25]. XRD spectrum of graphite being oxidized using charge density of 120 °C g⁻¹ involves two

Fig. 5 SEM images of Ex-ReGIC60 (a, b), Ex-ReGIC120 (c, d), Ex-ReGIC600 (e, f) and Ex-ReGIC1800 (g, h)

Fig. 6 SEM and EDS maps of exfoliated graphite-rhenium oxide composites

sharp diffraction peaks at 26.9 and 55.0° . Those peaks confirm the formation of $\text{H}(\text{ReO}_4)(\text{H}_2\text{O})$ particles on the graphite surface. Further oxidation of graphite in HReO_4 solution leads to the degradation of stage-3 GIC and partial oxidation of graphite matrix. For ReGIC1800 , an insignificant peak at 10.2° can be observed. It likely means the existence of graphite oxide structure within the deeply oxidized sample [53, 54].

Thermal exfoliation of the previously synthesized HReO_4 -GIC

The morphological changes in GIC structure caused by thermal treatment under ambient atmosphere were investigated using SEM (Fig. 5). As one can see, the shock treatment of GICs performed in N_2 atmosphere contributed to the deformation and separation of graphene layers. With increasing intercalation duration, an exfoliation process becomes more efficient. This correlation is clearly connected with the increasing amount of perrhenic acid ions between the graphene layers of exfoliated GIC. Partial transformation of graphite to graphite oxide during the electrochemical overoxidation may be also responsible for the above-mentioned tendency. From the presented SEM images, it can be also noted that all exfoliated materials are covered by rhenium oxides particles. BET measurements reveal that samples Ex-ReGIC60, Ex-ReGIC120, Ex-ReGIC600, and Ex-ReGIC1800 have the surface areas equal to 3.5 , 6.2 , 18.5 , and $19.6 \text{ m}^2 \text{ g}^{-1}$, respectively. EDS mapping shows homogeneous distribution of rhenium

oxides over the exfoliated materials (Fig. 6). The highest atomic percent concentration of rhenium in reached for sample Ex-GIC600 (Table 1). Decrease in Re amount in sample Ex-GIC1800 is likely caused by the partial deintercalation during overoxidation of GIC.

Raman spectra of exfoliated samples are depicted in Fig. 7. As one can see, due to thermal treatment, the intensity of D band decreased noticeably as compared with HReO_4 -GIC samples (Fig. 3). It means that thermal treatment under nitrogen atmosphere contributes to the structure ordering. The only sample that exhibits the significant amount of surface defect is Ex-ReGIC1800. In this case, lack of structural ordering likely results the partial electrochemical exfoliation that probably occurs during the overoxidation of graphite in perrhenic acid over potential 1.5 V . It cannot be also excluded that violent removal of oxygen functionalities which formed during overoxidation of graphite generated higher amounts of defects as compared with other exfoliated samples. The presence of oxygen functionalities on the surface of graphene layer of Ex-ReGIC1800 is also confirmed by weak D + G band at 2910 cm^{-1} (Fig. 7). After the thermal treatment of HReO_4 -GICs, Raman spectra do not involve bands corresponding to tetrahedral ReO_4^- . On the other hand, new bands at 141 , 166 , 198 , and 370 cm^{-1} appeared on the regarded spectra. Bands with maximum at 198 and 370 cm^{-1} are attributed to ReO_3 structure [48, 55]. Other two bands at 141 and 166 cm^{-1} can be assigned to $\text{O} = \text{Re} = \text{O}$ bonds deriving from ReO_2 .

Table 1 Atomic % content of exfoliated graphite-rhenium oxide composites

Sample	Ex-ReGIC60	Ex-ReGIC120	Ex-ReGIC600	Ex-ReGIC1800
C atom %:	96.31	94.92	85.59	89.96
O atom %:	3.47	4.75	12.14	8.95
Re atom %:	0.22	0.33	2.27	1.09

Fig. 7 Raman spectra recorded for exfoliated graphite-rhenium oxide composites

XRD patterns of thermally EG-rhenium oxide composites are presented in Fig. 8. Due to insignificant amount of intercalate within the ReGIC60 sample, most of graphitic structure is preserved after the thermal treatment process. It is manifested by the presence of sharp peak at 26.6° . On the other hand, relatively weak peaks arising with the appearance cubic ReO_3 and rhombohedral ReO_2 are also present [56, 57]. Diffraction patterns of Ex-ReGIC120, Ex-ReGIC600, and Ex-ReGIC1800 show that with increasing charge density consumed to anodic oxidation of graphite, the intensity of peaks deriving from the rhenium oxides also increases. It is worth

Fig. 8 XRD patterns recorded for exfoliated graphite-rhenium oxide composites

to note that Ex-ReGIC600 sample is composed mostly of EG and ReO_3 , whereas the graphene layers in the case of sample Ex-ReGIC1800 are covered by ReO_3 and ReO_2 . It means that thermal exfoliation of sample ReGIC1800 with lower concentration of perhenic acid promotes the ReO_2 formation, whereas thermal treatment of ReGIC600 with higher amount of HReO_4 leads to the formation of ReO_3 .

Conclusions

In our work, we describe the two-step process of EG-rhenium oxide composite preparation. Electrochemical oxidation of graphite in aqueous solution of HReO_4 leads to intercalation of ReO_4^- ion between the interlayer spaces thus yielding of stage-3 GIC. Simultaneously, perhenic acid is electrodeposited on graphite surface and edges forming $\text{H}(\text{ReO}_4)(\text{H}_2\text{O})$. Due to long-term oxidation, graphite is partially exfoliated and deintercalation of ReO_4^- occurs. Thermal treatment in nitrogen atmosphere of oxidized graphite in perhenic acid causes the separation of graphene layers and simultaneous deposition of rhenium oxides of its surface. The synthesized EGs are characterized by developed specific surface area up to $19 \text{ m}^2 \text{ g}^{-1}$. Taking into account the rhenium oxides on the surface of EG compounds, it should be emphasized that to their formation the deposition of perhenic acid during electrochemical oxidation is desired. XRD patterns of the synthesized composites reveal that thermal treatment of HReO_4 -GICs leads to the formation of cubic ReO_3 and rhombohedral ReO_2 . The synthesized EG-rhenium oxide composites can be potentially used as catalysts for methanol oxidation to methylal.

Funding information This research was financially supported by the National Science Centre, Poland (2018/02/X/ST5/02765). This research was financially supported by the Ministry of Science and Higher Education.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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