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Improved hydrogen sorption/desorption capacity of exfoliated $NiCl_2$-graphite intercalation compound effected by thermal treatment

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ABSTRACT

In the present work an advantageous effect of thermal exfoliation of graphite intercalation compound with nickel chloride ($NiCl_2$-GIC) on the kinetics of the reaction of hydrogen sorption/desorption occurring in alkaline solution in electrodes made of exfoliated material is proven. The electrochemical investigations were carried out using the cyclic voltammetry method. It was shown that the changes occurred in the crystalline and chemical structure and morphology due to the subsequent thermal exfoliation of $NiCl_2$-GIC primarily exfoliated by chemical method give rise to the increase of the anodic charge associated with both the recovery reaction of hydrogen stored in the electrode material during the precedent process of hydrogen adsorption/absorption and the oxidation reactions of metallic nickel. The improvement of the reversible hydrogen storage capacity is attributed to both the porous structure of graphite and the presence of nickel oxide highly dispersed in the exfoliated graphite matrix. The anodic charge corresponding to the recovery reaction of hydrogen stored in the electrode material appeared to be the highest for $NiCl_2$-GIC subjected to chemical exfoliation in hydrogen peroxide solution followed by heattreatment at 800 °C in air. After this process a two-fold enhancement of the hydrogen storage capacity was noted.

1. Introduction

One of the most important problems in the hydrogen storage system is to develop active materials joining the high hydrogen storage capacity and sorption/desorption efficiency. To solve this problem there is necessity to combine the properties of materials in such a way to form active composite materials ensuring both high hydrogen uptake and reversible hydrogen recovery. Nickel can be regarded as composite component because of its ability to lowering the overpotential of hydrogen adsorption reaction [1,2]. In recent years, different types of Ni-based alloys have been intensively studied for the hydrogen storage system due to its high hydrogen capacity, easy activation, and reversible absorption/desorption of hydrogen [2–5]. Important factors, which should be taken into consideration, are ambient conditions under which the hydrogen sorption occurs and low weight and costs of applied materials. In the light of this, carbon materials can be regarded as alternative reservoirs for storage of electrochemically generated hydrogen [6–15] and supports for catalysts [1,7,10,11,15]. Their functionality is strongly influenced by the structural properties and surface properties [8,12,13]. Among various types of carbon materials, carbon nanofibres [7,8,11,15], carbon nanotubes [1,6,7,10,14] and activated carbons [8,12] are currently considered for use in the process of hydrogen storage. Also, graphite-like materials and graphite-modified composites have been concerned for hydrogen sorption under the increased temperature/pressure conditions [16–19]. In our previous work [20], the process of hydrogen storage in exfoliated $NiCl_2$-graphite intercalation compound ($NiCl_2$-EGIC) was shown to occur by electrochemical method under ambient conditions. $NiCl_2$-EGIC prepared by chemical exfoliation of $NiCl_2$-graphite intercalation compound ($NiCl_2$-GIC) exhibits increased electrochemical activity during long-lasting sorption of hydrogen. It is well known that the process of exfoliation of GICs leads to even several hundred times expansion of the graphite flakes along the c-axis due to decomposition of intercalate followed by its partial or complete removal from the graphite lattice [21–24]. The degree of expansion depends on many factors of which the type of GIC, involving its crystalline structure and chemical composition, and the method of exfoliation are recognized as the most important. Exfoliation brings about the changes in the crystalline structure, chemical composition and morphology of exfoliated GIC, resulting in increased interlayer spacing, developed porous structure, structural defects, high adsorption capacity and low density. Owing to these features exfoliated graphites have been examined as materials for energy storage and conversion [25–27]. In particular cases, when intercalate or its part persists within the graphite matrix after the process of exfoliation, the mentioned structural changes facilitate the penetration of electrolyte through the structure of exfoliated graphite to reach intercalate being considered as a catalyst. As suggested in our previous work [20], the effects caused by chemical exfoliation of $NiCl_2$-GIC seem to be insufficient to ensure unconstrained interaction between the electrolyte and intercalate, of which a great part is still encapsulated

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in the graphite matrix and, in consequence, not the whole of $NiCl_2$ or the products of its decomposition are involved in the process of hydrogen sorption.

The aim of the present work is to study the influence of heattreatment of $NiCl_2$-EGIC, performed in oxidative and inert atmospheres, on the improvement of its electrochemical activity towards hydrogen sorption/desorption. For comprehensive discussion of electrochemical characteristics, the results obtained are discussed in coupling with the XRD and SEM data.

2. Experimental

$NiCl_2$-GIC was prepared by intercalation of natural graphite flakes (100 µm in diameter) with nickel chloride at 490 °C for 96 h. The procedure of intercalation is described in detail in our previous paper [20]. Some part of $NiCl_2$-GIC was subjected to chemical treatment in 30% solution of hydrogen peroxide for 30 days according to the procedure described earlier for exfoliation of CrO_3-GIC [22]. At this point it is worthy of reminding that active oxygen evolving during the catalytic decomposition of H_2O_2 occurring at the flake edges of $NiCl_2$-GIC results in the oxidation of graphite layers followed by their disruption and wrinkling. The peripheral exfoliation of graphite flakes facilitates the penetration of hydrogen peroxide molecules into the more inner regions of the flakes where the process of exfoliation develops with time. Symbol $NiCl_2$-EGIC is assigned to the product of chemical exfoliation. $NiCl_2$-EGIC was then subjected to additional heattreatment. Two samples were heattreated in air atmosphere at 650 °C for 25 min (sample $NiCl_2$-EGIC/TA650) and at 800 °C for 4 min (sample $NiCl_2$-EGIC/TA800), respectively. The third sample was heattreated in nitrogen atmosphere at 800 °C for 25 min (sample $NiCl_2$-EGIC/TN800). The samples prepared were structurally characterized using XRD analysis (PW-1710, Philips; CuKα radiation). For studying the changes in morphology of the examined materials, scanning electron microscopy (SEM; Tescan — Vega 5135) was used.

The electrochemical measurements were carried out at an ambient temperature by cyclic voltammetry (CV) using a potentiostat–galvanostat PGSTAT 30 AutoLab (EcoChimie B.V, Holland). For the CV measurements a three electrode cell with deaerated 6 M KOH was used. The working electrode was prepared according to the following procedure. The powder-type electrode composed of the original $NiCl_2$-EGIC and thermally treated $NiCl_2$-EGIC was placed in a pocket made of porous polymer material, in which Au wire (0.8 mm in diameter), playing a role of current collector, was beforehand inserted. In each case the mass of working electrode was equal to 20 mg. The platinum net was used as a counter electrode. All the potentials shown on the voltammograms are referred to the Hg/HgO/6 M KOH electrode (0.098 V vs. NHE). The reference electrode was connected to the solution under investigation by a Luggin capillary. Before starting of measurement, the working electrode was equilibrated at an open circuit for 30 min. The CV measurements were carried out with a scan rate of 10 mV s−1 in the potential range of −1.2↔0.3 V. After starting the measurements, the potential was swept from the rest potential of electrode in the negative direction. The process of hydrogen saturation was performed as follows. During the 5th cycle, when the electrode reached the potential of −1.2 V, the potential was automatically stopped for 15 min and after the potentiostatic treatment the potential scanning was continued in the positive direction. In the next cycle the potential scanning was carried out without any stopping.

3. Results and discussion

The XRD patterns depicted in Fig. 1 provide information about the structural changes of $NiCl_2$-EGIC resulting from the applied heattreatment. One can see in this figure that despite tremendous exfoliation of $NiCl_2$-EGIC occurred in H_2O_2 solution, stage-5 $NiCl_2$-GIC domains persisted in the graphite matrix (Fig. 1a). The intercalation phase is in the minority as compared with the graphite phase. It means that some part of intercalate was ejected from the graphite flake due to exfoliation of the graphite flakes in the reaction with hydrogen peroxide.

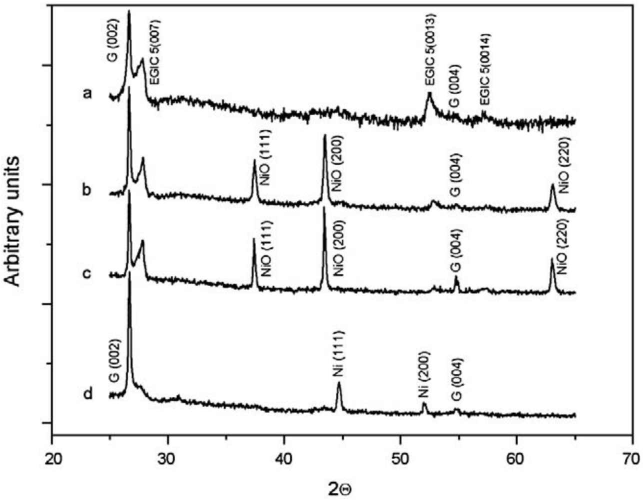

Fig. 1. XRD patterns for (a) $NiCl_2$-EGIC, (b) $NiCl_2$-EGIC/TA650, (c) $NiCl_2$-EGIC/TA800, and (d) $NiCl_2$-EGIC/TN800.

Fig. 2 shows SEM image of the morphology of $NiCl_2$-GIC after the process of chemically treated in 30% solution of H_2O_2 (sample denoted $NiCl_2$-EGIC). It is worth reminding that in contrast to most acceptor-type GICs, which are easily exfoliated upon heattreatment, thermal exfoliation of $NiCl_2$-GIC is ineffective at an ambient pressure even at temperature as high as 1500 °C [20]. As seen in Fig. 2, the chemical reaction between the original $NiCl_2$-GIC and H_2O_2 as an oxidizing agent led to exfoliated product of a harmony-like structure, resulting from the cleavage and wrinkling of graphite flakes. Characteristic features of this product are sharp edges of graphite flakes and their flat basal planes. Also, it is observed that the flare between flakes becomes wider and wider going from the interior to exterior of the sample. It should be emphasized that a set of flakes shown in Fig. 2 was formed from the flake of $NiCl_2$-GIC [20]. Fig. 3 displays cyclic voltammograms of $NiCl_2$-EGIC recorded before, during and after the potentiostatic saturation of electrode with hydrogen. As can be seen in this figure, during the backward scanning, in the fourth very small but

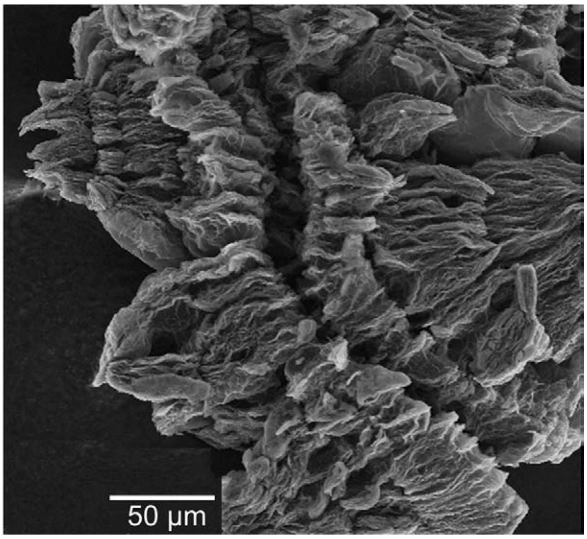

Fig. 2. SEM micrographs for $NiCl_2$-EGIC.