

# Changes in structure, morphology and electrochemical properties of NiCl<sub>2</sub>–FeCl<sub>3</sub>–PdCl<sub>2</sub>–graphite intercalation compound affected by gaseous hydrogen reduction process



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## ABSTRACT

In the present work the influence of the reduction treatment of NiCl<sub>2</sub>–FeCl<sub>3</sub>–PdCl<sub>2</sub>–graphite intercalation compound (NiCl<sub>2</sub>–FeCl<sub>3</sub>–PdCl<sub>2</sub>–GIC) on the structural, morphological and electrochemical properties were examined. NiCl<sub>2</sub>–FeCl<sub>3</sub>–PdCl<sub>2</sub>–GIC was prepared by molten salts method using a purified flaky graphite and anhydrous chlorides of Ni, Fe and Pd as reactants. The reduction process of NiCl<sub>2</sub>–FeCl<sub>3</sub>–PdCl<sub>2</sub>–GIC was carried out using gaseous phase H<sub>2</sub>/Ar mixture. The characterization of the crystalline structure and morphological properties of original as well as reduced GIC were studied by XRD and SEM techniques. The electrochemical properties of the investigated materials were examined in alkaline media by cyclic voltammetry method. The results of XRD and SEM analysis have showed that during reduction treatment the exfoliation of NiCl<sub>2</sub>–FeCl<sub>3</sub>–PdCl<sub>2</sub>–GIC occurs. The degree of exfoliation depends on the applied temperature. Increase in reduction temperature results in enhancement of exfoliation degree. The electrochemical investigations revealed that electrochemical behaviour of the reduced compound is also influenced by the temperature of the reduction process.

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## 1. Introduction

Hydrogen produced through non-fossil fuel sources is considered as a clean and effective energy carrier of the future. The main problem to be solved for the common use of new energy carrier like hydrogen is to find the safe and efficient method of its storing. One of the most promising method for reversible hydrogen storage is electrochemical process including reactions of hydrogen electro-sorption/desorption using a variety of electrode materials. The main advantage of this method of hydrogen accumulation is the fact, that the regarded processes can be easily performed in room temperature and under atmospheric pressure [1–4]. It is well known that palladium and its alloys [5–8] exhibits one of the highest activity in process of reversible electrosorption of hydrogen. Unfortunately, the main disadvantage of the application of a such materials is associated with very high costs forcing scientist to search a new electrode materials characterized with the high electrochemical activity and low amount of palladium at the same time. To overcome this problem, the composites with Pd component instead of pure Pd are applied in the process of reversible sorption of hydrogen. It is reported that the palladium

limited volume electrodes (Pd-LVE), consisting of a thin layer of Pd deposited onto the gold support, exhibit increased activity toward the process of sorption/desorption of hydrogen. High specific volume capacity of hydrogen depicted as H/Pd ratio for the mentioned electrodes reaches the value of around 0.7 [9,10]. Similar results were obtained for electrodes made of nickel foam/palladium composite [11,12].

Graphite intercalation compounds (GIC) with palladium compound should be recognized as a different type of the Pd composite materials [13,14]. GIC can be obtained by insertion of some ions and/or molecules, e.g., alkali metals, metal oxides or transition metal chlorides in to the interlayer space between the graphene layers. It should be emphasized that the introduced compounds (intercalates) are chemically bound with a carbon matrix [15–18]. One of the most common processes of GIC synthesis is molten salt method [19–21]. In this process, graphite flakes with metal salt(s) are sealed in glass tube reactor in ambient or gaseous chlorine atmosphere and then heated. Owing to the molten salt method it is possible to obtain GIC which contains more than one type of intercalate [22–24]. In our previous work, we described a simple route of synthesis of graphite multiintercalation compound with NiCl<sub>2</sub>, PdCl<sub>2</sub> and FeCl<sub>3</sub> via molten salt method [25].

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In the present paper, the influence of the reduction treatment of  $\text{NiCl}_2\text{-FeCl}_3\text{-PdCl}_2$ -graphite intercalation compound performed in gaseous  $\text{H}_2/\text{Ar}$  mixture at different temperatures on its structural, morphological and electrochemical properties was examined. Whereas the electrochemical behavior of reduced GIC was investigated in the processes of hydrogen sorption/desorption carried out in alkaline solution by cyclic voltammetry method.

## 2. Experimental

$\text{NiCl}_2\text{-FeCl}_3\text{-PdCl}_2\text{-GIC}$  was prepared by a molten salts method using purified flaky graphite (99.98 wt.% C, flakes 100  $\mu\text{m}$  in diameter) and anhydrous chlorides of Ni, Fe and Pd. The molar ratio of metal salts to graphite was adjusted at 1:3, whereas the molar ratio of  $\text{NiCl}_2\text{:FeCl}_3\text{:PdCl}_2$  was equal 5:3:2. Before starting the synthesis graphite and metal salts were placed in the glass reactor in argon atmosphere. Process of intercalation was carried out in at 450 °C for 72 h. After the process, the obtained GIC was filtered and washed with a diluted HCl solution to remove unreacted salts, and after that the product was rinsed with water followed by drying at ambient temperature.

The reduction process of the such prepared  $\text{NiCl}_2\text{-FeCl}_3\text{-PdCl}_2\text{-GIC}$  with  $\text{H}_2/\text{Ar}$  mixture was carried out in quartz tube reactor for 4 h in selected ranges of temperature. Before the process the reactor was inserted into a computer controlled furnace coupled to the flowmeter system thus ensuring the high control of the amounts of gases passing through the inner quartz reactor. After reduction treatment, the reactor was cooled down under argon atmosphere and the reduced compound was taken out.

The characterization of the crystalline structure and morphology of both original and reduced GICs was carried out by the X-ray diffraction (XRD) measurements (Philips PW-1710 diffractometer) and scanning electron microscopy (SEM) (Hitachi S-3400N), respectively.

The electrochemical properties of the original and reduced  $\text{NiCl}_2\text{-FeCl}_3\text{-PdCl}_2\text{-GIC}$  were measured at ambient temperature by cyclic voltammetry (CV) method using a potentiostat-galvanostat

PGSTAT30 AutoLab (EcoChemie B.V.). The preparation as well as construction of the working electrode is described in our previous work [25]. The CV measurements were carried out in a three-electrode cell filled with 6 M KOH solution. A Hg/HgO/6 M KOH was used as the reference electrode, whereas a platinum gauze play a role of a counter electrode. CV measurements were carried out in the potential range  $-1.2 \leftrightarrow 0.2 \text{ V}$  with a scan rate  $10 \text{ mV s}^{-1}$ . All electrochemical measurements were started from the rest potential of electrode ( $E_R$ ) towards the negative potential direction. In the 2<sup>nd</sup> cycle when the electrode reached the potential of  $-1.2 \text{ V}$  the process of potentiostatic hydrogen saturation was performed for 15 min. Afterwards, the potential scanning was continued in the positive direction. During the third cycle the potential scanning was carried out without any stopping. In separate experiments the upper potential limit was raised to  $+0.6 \text{ V}$ .

## 3. Results and discussion

Fig. 1 presents SEM images of original (Fig. 1a) and reduced at different temperatures (Fig. 1b–d)  $\text{NiCl}_2\text{-FeCl}_3\text{-PdCl}_2\text{-GIC}$ . From Fig. 1a it can be seen that host  $\text{NiCl}_2\text{-FeCl}_3\text{-PdCl}_2\text{-GIC}$  is composed of flat flakes without any signs of exfoliation. The cracked character of graphite flakes is caused by the invasion of intercalates into the interlayer space between the graphene layers.

The reduction treatment of  $\text{NiCl}_2\text{-FeCl}_3\text{-PdCl}_2\text{-GIC}$  carried out in 350 °C results in partial exfoliation of the treated compound illustrated on Fig. 1b by the splitting and wrinkling of graphite flakes. On the basis of this observation, it can be assumed that the process of exfoliation take place due to the reduction of metal chlorides by gaseous hydrogen, accompanied by the chlorine evolution. The generated chlorine due to the decomposition of metal chlorides most likely contributes to graphite partial exfoliation. Fig. 1c shows that an increase in temperature of the reduction treatment from 350 to 500 °C results in further enhancement of the exfoliation degree. It indicates that increase of the temperature enhances efficiency of metal chlorides reduction thus increasing the intensity gaseous chlorine release.

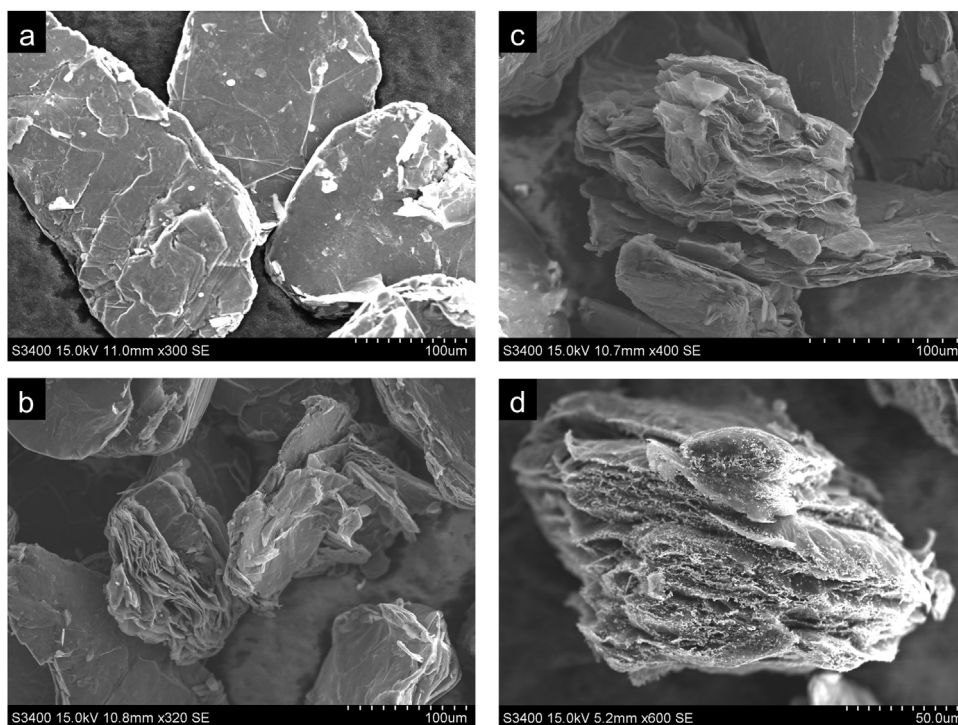


Fig. 1. SEM images of the original  $\text{NiCl}_2\text{-FeCl}_3\text{-PdCl}_2\text{-GIC}$  (a), and  $\text{NiCl}_2\text{-FeCl}_3\text{-PdCl}_2\text{-GIC}$  reduced at 350 °C (b), 500 °C (c) and 700 °C (d).

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