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Enhancement of electrochemical hydrogen storage in $NiCl_2$–$FeCl_3$–$PdCl_2$–graphite intercalation compound effected by chemical exfoliation

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ABSTRACT

In the present work, a quaternary $NiCl_2$–$FeCl_3$–$PdCl_2$–graphite intercalation compound ($NiCl_2$–$FeCl_3$–$PdCl_2$–GIC) was successfully synthesized by molten salts method. A part of this compound was subsequently subjected to chemical exfoliation to obtain expanded compound ($NiCl_2$–$FeCl_3$–$PdCl_2$–EGIC). The changes created in crystalline structure, morphology and chemical composition of GIC due to exfoliation were examined by XRD, SEM and EDS techniques and then related to electrochemical behaviour of electrodes made of the original and exfoliated compound. The results of electrochemical studies carried out by the cyclic voltammetry (CV) method in 6 M KOH solution showed that current charges of all the cathodic and anodic peaks recorded for $NiCl_2$–$FeCl_3$–$PdCl_2$–EGIC are considerably higher already in the first two cycles as compared to those observed for the original $NiCl_2$–$FeCl_3$–$PdCl_2$–GIC. This improvement is ascribed to chemical exfoliation leading to a tremendous development of surface area of the compound due to the splitting and wrinkling of graphite flakes followed by easier access of hydroxyl ions of the electrolyte to active species of intercalates preserved between the graphene interspaces as well as expelled from the graphite interspacing. A large anodic peak was recorded on CV curves after the potentiostatic polarization of electrodes at the potential of −1.2 V where the reaction of hydrogen sorption/evolution occurs and intercalates highly dispersed in the graphite matrix are reduced to a metal form. This peak mainly corresponding to the recovery of hydrogen stored in the electrode appeared to be over five times higher for electrode made of exfoliated compound. This significant enhancement of the hydrogen storage capacity is attributed to electrochemically active Pd nanoparticles highly dispersed in porous structure of exfoliated compound and likely functioning in synergy with Ni/Fe clusters.

1. Introduction

Graphite is composed of successive graphene layers stacked in parallel along the c-axis and composed of hexagonally linked carbon atoms. Strong sp^2 σ bonding and delocalized π bonding between carbon atoms being at the distance of 0.142 nm are responsible for a high stability of graphene layer planes. In contrast, a large distance of 0.335 nm between adjacent planes of carbon atoms, which are bonded by a weak der Waals-type force, make favourable circumstances for intercalation of certain ions, atoms and molecules, called intercalates, between the interlayer spacing of graphite resulting in the formation of graphite intercalation compounds (GICs) [1]. Some ions, e.g. small lithium ions, can be electrochemically intercalated and reversibly deintercalated between the graphene layers. These reactions commonly proceeding at ambient conditions of temperature and pressure correspond to the respective charge and discharge processes occurring in graphite anodes of Li-ion batteries, which presently are on the top of energy devices used widely in various technical fields owing to their good cyclic reversibility and high power and energy densities. As has been shown recently for the reaction of lithium ion intercalation/deintercalation graphene-based materials obtained by exfoliation methods allow obtaining noticeably higher reversible electrical capacity [2,3] as compared to the practical values reported for graphite anode [1,4]. Various GICs can be transformed into expanded graphite (EG) due to exfoliation. During the process of exfoliation intercalate is partially or completely released from the graphite. The process of exfoliation leads to a multiple splitting of graphite flakes resulting in a swollen product composed of highly wrinkled platelets with very torn edges. These effects are responsible for a huge expansion of EG along the c-axis as well as a tremendous increase in specific surface

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area. Both numbers are even hundred times higher as compared to the original GIC. GICs containing in the graphite matrix intercalates of catalytic activity are of a particular interest, because due to exfoliation they can be transformed into exfoliated graphite/catalyst systems. Depending on the type of GIC, the process of exfoliation can be realized by three methods: (a) thermal, carried out at high temperatures [5–11], (b) chemical, performed at ambient temperature in solution containing chemical agent (mostly oxidizer) [12,13], (c) electrochemical, in which GIC is decomposed under a given potential or current [14,15]. If after exfoliation some part of intercalate is preserved in the graphite lattice, the obtained product is recognized as exfoliated graphite intercalation compound (EGIC) [16,17]. EGICs are not easily produced but their unique properties, combining certain features of EG and GIC, are encouraging to take this systems into electrochemical studies.

Graphite-derived materials such as graphene-like nanosheets [18], carbon nanotubes (CNT) [19–22], carbon nanofibres (CNF) [23,24] and exfoliated GICs containing electrochemically active transition metal compounds [16,17] and metal oxide [25] nanoparticles exhibiting catalytic activity are of a great theoretical as well as practical attention from the viewpoint of the process of hydrogen storage for energy conversion being intensively examined during the last decade. Many nanostructured carbon-based composites, e.g. metal-doped CNTs/CNFs [26–28] and graphite-modified composites [29] have also been examined in terms of electrochemical hydrogen storage [30]. Hydrogen sorption can be performed by physical, chemical and electrochemical method. In the latter case the process occurs directly in electrode material at ambient conditions with no need to use high pressure or extremely low temperature for hydrogen liquefying. Despite some discrepancies in the mechanism of hydrogen storage in various materials, it is without any doubt that hydrogen storage capacity in the electrochemical processes is strongly influenced by the properties of electrode material used as hydrogen reservoir, such as chemical composition, crystalline and porous structure and catalytic features in the reaction of hydrogen sorption [30]. In our previous papers the hydrogen sorption/desorption process has been proved to occur in binary $NiCl_2$–graphite intercalation compound ($NiCl_2$–GIC) [16,17] subjected to chemical exfoliation.

In the present work, we examined for the first time a quaternary $NiCl_2$–$FeCl_3$–$PdCl_2$–GIC of which intercalates due to chemical exfoliation are transformed to nanoclusters highly dispersed in expanded graphite matrix followed by further reduction to metallic particles during the cathodic process of hydrogen sorption occurring in 6 M KOH solution. Based on the knowledge of electrochemical properties of palladium and palladium-transition metals alloy electrodes [31–33], the formed Pd nanoparticles are reasonably assumed to reduce overpotential of the reaction of hydrogen absorption due to synergistic interaction with Ni/Fe nanoparticles to enhance the hydrogen storage/recovering capacity of expanded $NiCl_2$–$FeCl_3$–$PdCl_2$–GIC electrode. In order to explain the function of $PdCl_2$ intercalate in the electrochemical reaction cyclic voltammogram recorded after the potentiostatic hydrogen saturation of exfoliated $NiCl_2$–$FeCl_3$–$PdCl_2$–GIC was compared with that for exfoliated $NiCl_2$–$FeCl_3$–GIC. To have insight into the mechanism of electrochemical reaction the results obtained are discussed in coupling with the XRD, SEM and EDS data.

2. Experimental

2.1. Synthesis of $NiCl_2$–$FeCl_3$–$PdCl_2$–GIC and $NiCl_2$–$FeCl_3$–$PdCl_2$–EGIC

$NiCl_2$–$FeCl_3$–$PdCl_2$–GIC was prepared by a molten salts method using purified flaky graphite (99.98 wt.% C, flakes 100 μm in diameter) and anhydrous chlorides of Ni, Fe and Pd as reactants. The molar ratio of metal salts to graphite was chosen to be 1:3, whereas the molar ratio of $NiCl_2$:$FeCl_3$:$PdCl_2$ was equal 5:3:2. Before intercalation the glass reactor was purged with an argon flow to remove moisture and air, loaded with the mixture of graphite and metal salts and sealed on both ends under continuous argon flow. Then the reactor was inserted into a computer controlled furnace and the process of intercalation was carried out at 450 °C for 72 h. The reaction products were filtered and washed out with a large amount of diluted HCl solution to remove unreacted salts, followed by rinsing with water and acetone and then stored in moisture free atmosphere for drying at ambient temperature. Some part of $NiCl_2$–$FeCl_3$–$PdCl_2$–GIC was subjected to chemical exfoliation in 30% solution of hydrogen peroxide for 2 h at 25 °C, according to the procedure described earlier for exfoliation of CrO_3–GIC [12]. Symbol $NiCl_2$–$FeCl_3$–$PdCl_2$–EGIC used throughout the paper denotes the product of chemical exfoliation.

Table 1
Semi-quantitative EDS analysis data for $NiCl_2$–$FeCl_3$–$PdCl_2$–GIC and $NiCl_2$- $FeCl_3$-$PdCl_2$-EGIC.

Element	Sample $NiCl_2$–$FeCl_3$–$PdCl_2$–GIC	Sample $NiCl_2$–$FeCl_3$–$PdCl_2$–EGIC
	at.%	at.%
C	63.1 ± 2.1	56.7 ± 1.8
O	1.8 ± 0.3	7.5 ± 0.9
Cl	23.7 ± 0.8	21.8 ± 0.9
Ni	9.2 ± 0.5	10.2 ± 0.6
Fe	0.8 ± 0.1	2.6 ± 0.3
Pd	1.5 ± 0.3	1.2 ± 0.2

2.2. Physicochemical characterization

The characterization of the crystalline structure of both original and exfoliated GIC was carried out by the X-ray diffraction (XRD) measurements (Philips PW-1710 diffractometer) using CuK_α radiation with nickel filtering. A scanning electron microscopy (SEM) (Hitachi S-3400N) coupled with the energy dispersive spectrometer (EDS) (Thermo Electron Corp., model No. 4481B-1UES-SN with the NSS Spectral Imaging System sofware) was used for observing the morphology and surface distribution of active particles of samples as well as determining semi-quantitatively their chemical composition. Because of inaccessibility of standard reference material needed for quantitative EDS analysis both the examined samples (before and after exfoliation) were measured for five points/areas and the standard deviation from the mean was calculated (Table 1).

2.3. Electrochemical characterization

The electrochemical measurements were carried out at 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 $NiCl_2$–$FeCl_3$–$PdCl_2$–GIC or chemically exfoliated $NiCl_2$–$FeCl_3$–$PdCl_2$–EGIC was placed in a pocket made of porous polymer material, in which graphite rod (5 mm in diameter), playing a role of current collector, was beforehand inserted. 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 each measurement, the working electrode was equilibrated at an open circuit for 30 min. The CV measurements were

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