



Modification of carbon-metal composites using high-energy ball milling



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ABSTRACT

A resorcinol-formaldehyde–nickel–palladium (RF–Ni–Pd) hydrogels were synthesized by sol–gel polycondensation followed by ambient drying. Carbon–nickel–palladium doped gels (C–Ni–Pd) were prepared by carbonising the RF–Ni–Pd gels at 900 °C in a nitrogen atmosphere. The goal of this study was to determine the effect of high-energy ball milling (HEBM) on the electrochemical activity of C–Ni–Pd composite. The scanning electron microscopy analysis, adsorption and X-ray diffraction measurements showed that the HEBM of C–Ni–Pd composite resulted in the modification of the morphological, porous and crystalline features of the carbon matrix. It has been demonstrated that composite C–Ni–Pd composed of sphere-like granules incrustated with well-crystalline nickel and palladium particles exhibits electrochemical activity in 6 M KOH aqueous solution. High-energy ball milling of the composite brought about the improvement of electrochemical activity in the potential range of the hydrogen sorption/desorption reaction.

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1. Introduction

Carbon gels are a rare class of materials that behave like solids, because they have an unbroken three-dimensional structure. A gel skeleton is composed of particles merging together by multi-functional binding sites. The carbon gels are typical mesoporous materials with a high surface area. The porous structure is mainly composed of mesopores and macropores. This structure shrinks during the stabilization and carbonization. During carbonization micropores are additionally generated, but their number is small, whereas the volume of macropores decreases during stabilization and carbonization. A small amount of micropores is caused by the loss of decomposed gases in the early stages of carbonization [1].

The important feature of carbon gels is the easiness of adding metal to organic monolithic aerogel, creating a carbon-metal composite. Such a composite can be easily prepared by e.g., the addition of soluble metal salt to the initial sol [2–6]. After gelling the metal salt is locked inside the gel structure and the metal ions can be chelated by the functional groups of the polymer matrix. The addition of metal salts can also catalyse the change in the degree of

polymerization or gelation, influencing the morphology and pore structure of organic aerogels.

Our interests in the incorporation of metals into the carbon matrix are due to the fact that some metals are known to catalyse the formation of graphitic structures at relatively low temperatures. We have reason to suppose that the formation of graphitic structures within the carbon aerogel framework should modify the electrical and mechanical properties of these materials. In addition, higher electrochemical activity caused by the presence of highly dispersed metal particles in the composites can be expected. The preliminary studies have indicated that carbon-metal composites produced by the carbonization of organic gels containing nickel salt are characterised by increased electrochemical activity in an alkaline medium [7]. Thanks to the presence of active nickel particles in the carbon matrix of carbon–nickel composites, materials of higher activity in the reactions of hydrogen sorption than carbon gels free of metal, can be obtained [7,8]. In addition, it is also shown that the admixture of metal considerably increases the capacity of the electrical double layer, which indicates the possibility of using these kinds of composites in the preparation of electrode materials for electrochemical supercapacitors [9–13]. Our preliminary studies provided experimental evidence for changes in the chemical, crystalline and porous structure of carbon–nickel composites [7,9]. Owing to the changes in the carbon surface a more porous

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structure is created resulting in a significant improvement in the capacity of the electrical double layer of electrodes made of composites.

The aim of this work is the research of the impact of the activation treatment of obtained carbon gels and composites to modify their properties. A survey of literature concludes that trials of carbon gel activation were so far conducted only in a CO₂ atmosphere at different temperatures [14–18]. Carbon xerogels were also activated chemically with NaOH and KOH [14,15]. The carbon aerogels were activated at 450 °C in a hot air environment [19–22]. Therefore, the main objective of the present paper is to determine the effect of high-energy ball milling (HEBM) on the electrochemical activity of nickel–palladium doped carbon gels. HEBM is very different from the traditional ball-milling technique. The impact energy of HEBM is typically 1000 times higher than the conventional ball milling energy and HEBM requires the controls of milling atmosphere and temperature which are crucial to create the desired structural changes or chemical reactions [23]. This method was used to modify the structure of nickel hydroxide [24], intermetallic compounds [25], nanomaterials [23], expanded graphite [26] or glassy carbon [27]. Although carbon–nickel–palladium gels have been previously reported [20,22] we deal for the first time with xerogels activated using HEBM method. The goal of this study was to determine the influence of HEBM treatment of carbon–nickel–palladium composites on their porous and crystalline structure and, in consequence, on the electrochemical activity in the hydrogen sorption/desorption reaction.

2. Experimental

2.1. Preparation of carbon–nickel–palladium composites

A carbon–nickel–palladium composite (C–Ni–Pd) was prepared by polycondensation of resorcinol (R) (POCH, Poland) with formaldehyde (F) (37 wt.%, stabilised 10 wt.% methanol, Merck, Germany) in water (W) following a method already applied elsewhere [21]. A pair of metal precursors: nickel acetate (C₄H₆NiO₄·4H₂O) (Fluka, UK) and palladium acetate (C₄H₆O₄Pd) (Sigma–Aldrich, USA) were used as a catalyst (C). The gel was synthesised in the following conditions: the R/F and R/C molar ratio were 0.5 and 1000, respectively. The mass of nickel and palladium salts in the solution were adjusted so as to the theoretical metal mass in carbon formed after RF carbonization (carbonization conditions hereafter) was 5 wt.% for each metal. The mass percentage of RF and metals in solution was set at RF/Ni/Pd = 40%. Such a prepared solution was placed in an oven at 50 °C for 96 h and then at 70 °C for 24 h successively to undergo gelation and ageing.

Afterwards, the obtained aqueous RF/Ni/Pd gel was dried through the exchange of water with acetone (POCH, Poland). The acetone was heated up to 56 °C to accelerate the diffusion of water from the wet RF/Ni/Pd gel. The exchange process was repeated three times using fresh acetone to remove residual water from the pores of the wet gel.

After drying, the gel was pyrolysed under nitrogen flow at 900 °C for 3 h using a heating rate of 5 °C/min, and cooled slowly to room temperature.

The obtained product was denoted as C–Ni–Pd – carbon gel doped with 5 wt.% of nickel and 5 wt.% of palladium.

After carbonisation gel was powdered in a high-energy ball mill (Pulverisette 6, Fritsch, Germany) in an argon atmosphere. The carbon–metal composite was milled twice at 350 rpm for 15 min, using a 10-min interruption between each milling. The mass ratio of balls to milled material was 55: 1. Additionally, a part of sample C–Ni–Pd was submitted to milling 30 times at 350 rpm for 1 h, using a 30-min interruption between each milling. A zirconium

oxide pan was used for the milling. The mass ratio of zirconium oxide balls to milled material amounted to 80: 1. The milled sample was unloaded in air. This sample was denoted C–Ni–Pd–M.

2.2. Methods

A scanning electron microscope (SEM) (Hitachi S-3400N, Japan) coupled with the energy dispersive spectrometer (EDS) (Thermo Electron Corp., model No. 4481B-1UES-SN with the NSS Spectral Imaging System software) was used for observing the morphology and surface distribution of active particles of samples as well as determining semi-quantitatively their chemical composition.

The BET specific surface areas (S_{BET}) of samples were determined from the isotherms measured by N₂ adsorption at –195.5 °C over a relative pressure range of 0.06–0.30 (ASAP2020 V3.01 H–Micromeritics porosimeter, USA). The cumulative pore volume (V_{CUM}) for between 1.7 and 300 nm and mesopore size distributions were determined from the desorption branch of the N₂ isotherm using the Barret–Joyner–Halenda (BJH) method.

The X-ray analyses were performed with a diffractometer BRUKER D8 Advance, equipped with a computer control set (USA). The measurements were done using a CuK α radiation (wavelength of 0.1542 nm) with nickel filtering.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of carbon gels were carried out using a Setaram device (France). Samples of about 20 mg were heated up to 1000 °C with a heating rate of 5 °C min^{–1} in order to determine the thermal characteristics of nickel–palladium composites in an air atmosphere.

2.3. Preparation of electrodes and evaluation of electrochemical properties

The working electrode was made by the insertion of 20 mg of powdered electrode material placed on a gold spiral, playing the role of a current collector, mounted on the bottom of the vessel of the measuring cell. Before the measurement the electrode was immersed in 6 M KOH (POCH, Poland) solution for 24 h to ensure the diffusion of aqueous electrolyte solution into the pores of the carbon gel.

Cyclic voltammetry (CV) was used to determine the electrochemical properties of the carbon–metal composite electrodes. CV measurements were carried out in a three-electrode cell filled with 6 M KOH solution. Powdery gels placed in a current collector served as a working electrode. A Hg/HgO/6M KOH system (–0.098 V vs. normal hydrogen electrode) and a platinum spiral were used as the reference and counter electrode, respectively. All potentials in the paper are related to a Hg/HgO/6 M KOH reference electrode. The CV measurements were carried out in the potential range from –1.2 to 0.0 V with the scan rate 1 mV/s, according to the conditions described in detail in the earlier work [22].

All measurements were carried out at room temperature using an AUTOLAB potentiostat–galvanostat (model PGSTAT 30, The Netherlands).

3. Results and discussion

The SEM images of carbon gels shown in Figs. 1 and 2 allow observing the changes in the morphology of carbon gels caused by HEBM. The carbon material of sample C–Ni–Pd consists of sphere-like beads containing nickel and palladium inclusions (Fig. 1). The particle dimensions of the composite C–Ni–Pd are 1–5 μm in diameter. In the case of composite C–Ni–Pd–M changes in dimension and morphology of particles are primarily visible. The evidence for these can be observed on the SEM images for this

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