



Short communication

Unexpected effect of drying method on the microstructure and electrocatalytic properties of bentonite/alpha-nickel hydroxide nanocomposite



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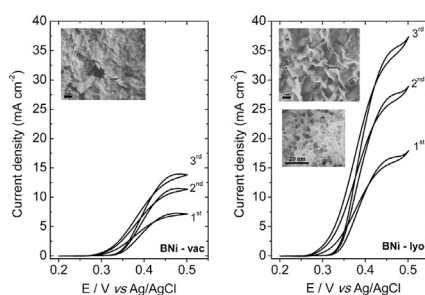
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HIGHLIGHTS

- Lyophilization induced change in nanocomposite microstructure.
- Stabilization of α -Ni(OH)₂ by bentonite clay.
- Enhanced electrocatalytic activity of α -Ni(OH)₂/bentonite nanocomposite.
- Freeze drying processing enhance activity for methanol electrooxidation.

GRAPHICAL ABSTRACT



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ABSTRACT

The degree of crystallinity, morphology and electrochemical properties of a nanocomposite formed by stabilized α -Ni(OH)₂ nanoparticles and bentonite nanoflakes is strongly influenced by the vacuum drying process, either at room temperature or by freeze-drying (lyophilization). α -Ni(OH)₂ nanoparticles induced the formation of intercalation nanocomposites exhibiting higher structural organization than in the precursor clay. Also, lyophilization process preserved the structure of the nanocomposites in aqueous suspension and/or induced the disaggregation of nanoflakes, producing materials with lower degree of crystallinity, larger interlamellar distances and electrochemically more active than those obtained by conventional vacuum drying. In fact, the lyophilized materials exhibited more than twice as large density of current for electrocatalytic oxidation of methanol (37 against 14 mA cm⁻²) indicating its potentiality for development of sensors and fuel cells.

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1. Introduction

Nickel hydroxide is a lamellar material exhibiting several polymorphs basically differentiated by the degree of organization along

the *c* axis and the presence of intercalated ions and molecules [1]. α -Ni(OH)₂ is the most interesting polymorph from the electrochemical point of view because of its up to 30% larger charge capacity, higher conductivity and reversibility [2–4]. However, it is spontaneously converted to the thermodynamically most stable beta-Ni(OH)₂ by aging in alkaline solution or when subjected to charge–discharge cycles [5], precluding its application in alkaline

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fuel cells and energy storage devices. Thus, strategies to stabilize Ni(OH)₂ in the alpha phase and enhance the electrochemical activity are been pursued by doping with metal ions (Al³⁺, Co²⁺, Ce³⁺, etc.) [6] as well as nanostructuring, particularly by the sol–gel method [7].

It is well known that composite materials can be prepared by intercalation/insertion of molecular species and ions in lamellar materials such as clays, exploring their high adsorption and cation exchange capability [8–10]. In addition, their morphology and properties can be changed by controlling the drying process as demonstrated here since solvent play important roles on the maintenance of the tridimensional structure of colloidal materials. Thus, the solvent removal method should play a relevant role in defining the solid materials structure. In fact, the removal of solvent generally results in the collapse of pores, reducing the surface area and the adsorption capability [11,12].

Lyophilization (freeze-drying by vacuum sublimation) is seldom a choice for processing of inorganic materials but is a technique that gently removes solvents from the frozen material, thus preserving the porous and lamellar structures. This is particularly interesting for catalytic and electrochemical applications, where the activity is strongly influenced by the surface area and the interlamellar spacing, for example facilitating the Li⁺ ion diffusion/intercalation in batteries [12], as well as the access of substrate molecules to electrocatalytic sites [13,14].

Thus, herein we demonstrate the influence of vacuum drying process (room temperature [15] or lyophilization [12]) on the morphologic, electrochemical and catalytic properties of nanocomposites prepared by interaction of alpha-Ni(OH)₂ nanoparticles with bentonite clay [8,9]. The lyophilized (BNi-lyo) material showed the highest surface area and electrocatalytic activity as compared with the one processed at room temperature (BNi-vac), as well as the highest stabilization of Ni(OH)₂ nanoparticles in the alpha phase.

2. Experimental

2.1. Syntheses and characterization

Alpha-Ni(OH)₂ suspensions were prepared according to the method described by Rocha et al. [8,9] but reacting nickel acetate with sodium hydroxide instead of KOH, in 1:2.5 molar ratio. Typically, 9.68 g (0.39 mol L⁻¹) of Ni(CH₃COO)₂·4H₂O were dissolved in 100 mL of glycerin at 50 °C, under vigorous stirring, and cooled at room temperature. Then, 100 mL of NaOH solution in BuOH (0.973 mol L⁻¹) were added, the mixture stirred for 24 h, and stored for 2 weeks at room temperature before use [8,9]. The nanocomposite here called BNi was prepared according to Rocha et al. [9], by adding a colloidal clay suspension (0.1% w/v, 1 g L⁻¹) into an alpha-Ni(OH)₂ nanoparticles colloidal suspension (2 g L⁻¹), and stirring for 24 h. The suspension was allowed to stand for 7 days and the excess of NaOH washed out with DI-water (five times) by successive leaching and decantation process until solution pH decrease to ~7.5 [16]. The suspension was then dried in a desiccator under vacuum for 5 days to prepare the BNi-vac sample. The BNi-lyo sample was obtained by lyophilization of a frozen suspension (−7 °C) using an LD series lyophilizer from Terroni Equipamentos Científicos (BR).

The samples were characterized by X-ray diffractometry (XRD) using a Bruker D2 Phaser diffractometer, equipped with Cu Kα (λ = 1.5418 Å) source. Scanning electron microscopy (SEM) images were registered in a JEOL FEG JSM-7401F equipment, using samples prepared by dispersing the BNi powder on a copper stub with a carbon tape. Transmission electron microscopy (TEM) images were obtained in a JEOL JEM-2100 equipment at 100 kV using samples

prepared by dispersing 3 μL of a diluted water suspension on copper grids covered with carbon (TedPella). Simultaneous thermal analysis (STA/TG-DTA, Seiko, SII 6300) curves were obtained in N₂ atmosphere (200 mL min⁻¹), in the 30–1100 °C range (heating rate of 10 °C min⁻¹), using alumina pan. The cyclic voltammograms (CV, μAutolab III potentiostat/galvanostat) were registered using a conventional three electrodes arrangement consisting of an Ag/AgCl (3 mol L⁻¹ KCl) reference and a Pt wire counter electrode. Glassy carbon electrodes (GCE, A = 0.02 cm²) were modified by dispersing 5 μL of aqueous nanocomposite suspension (~26 × 10⁻⁹ g of nickel) on the surface and drying in air, forming adherent BNi-vac and BNi-lyo films. The CVs were obtained in N₂ gas purged 1.0 mol L⁻¹ KOH solution as electrolyte.

3. Results and discussion

3.1. Physicochemical characterization

The SEM images of BNi-lyo (Fig. 1A–B) and BNi-vac (Fig. 1C–D) samples clearly evidence the morphologic differences induced by the vacuum drying process. The first composite seems to be constituted by very thin crumpled clay sheets whereas BNi-vac is a more densely packed material. The higher degree of organization of BNi-vac are consistent with the slow removal of solvent at room temperature, promoting the assembly of tactoids constituted by large amounts of aluminosilicate sheets [17]. In contrast, the morphology of the lyophilized material reflects the “frozen structure of the nanocomposite suspension”, showing more or less isolated nanosheets stabilized by the solvent. Its sublimation lead to the formation of “floating nanoflakes” that collapsed in a disordered way without having the possibility of forming more organized tactoids

The Ni(OH)₂ nanoparticles did not appear in the SEM images because they are too small to be visualized with magnification of ×10,000 [18]. In fact, they only could be visualized by TEM at magnifications higher than about ×50,000, and a typical image of the BNi-vac sample is shown in Fig. 1E. Note the high density of essentially spherical nanoparticles with average diameter of ~4 nm. A bentonite clay tactoid covered up with Ni(OH)₂ nanoparticles is shown in the inset.

Both, vacuum dried and lyophilized bentonite exhibit low diffraction peaks, as expected for materials with low long range order, but the strong 001 peak at 7.4° (d = 12.0 Å) is consistent with the higher degree of crystallinity of the material processed at room temperature (Fig. 1F). Furthermore, the 003 peak is absent in the lyophilized clay sample suggesting a higher degree of variability in crystallites size and packing, attested by the much weaker and broader 001 peak. A more striking effect was observed in the BNi nanocomposites diffraction patterns that have almost no similarity with the respective bentonite clay diffraction patterns confirming the formation of new materials. The bentonite/Ni(OH)₂ nanocomposite processed at room temperature also showed stronger and better defined diffraction peaks, especially for the 001 plane, as compared with the lyophilized material. This indicates that Ni(OH)₂ nanoparticles are interacting with bentonite nanoflakes increasing the structural order of the nanocomposite.

This probably is consequence of electrostatic effects that help pushing together the nanosheets generating larger tactoid assemblies. In other words, α-Ni(OH)₂ nanoparticles should be interacting with clay's aluminosilicate sheets inducing their reorganization while forming an intercalation nanocomposite, thus increasing the average basal plane distance. In fact, BNi-vac showed a sharp diffraction peak shifted to lower angles, at 2θ 5.4° (001, 16.2 Å), as well as five additional peaks at 2θ 10.4° (002), 15.4° (003), 20.3° (004), 25.5° (005) and 30.4° (006), all assigned to bentonite.

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