Influence of Ni / NiO Ratio on the Performance of Thermoelectrochemical Waste Heat Harvester Based on Hollow Microspheres

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Abstract. Technologies harvesting and converting the heat of low-temperature sources into electricity are one of the current trends in modern renewable energy. Thermoelectrochemical cells based on a nickel oxide electrode are gaining increasing popularity among researchers due to the high values of the hypothetical Seebeck coefficient. This work is devoted to the study of the reduction modes effect of hollow nickel oxide microspheres on the ratio of oxide and metal nickel forms in their structure. The paper presents the synthesis of microspheres by the pyrolysis of ultrasonic aerosols of an aqueous solution of nickel nitrate. Composition and morphology are studied by scanning electron microscopy and X-ray non-standard quantitative analysis. It was shown that the proportion of metallic nickel increases with an increase in the reduction temperature to about 375°C and then changes slightly. For microspheres, reduced at 350 °C, the main parameters of the thermoelectrochemical cell were determined. It was shown that the hypothetical Seebeck coefficient in the assembled cell system is 3.1 mV/K, and the resistance to charge transfer across the electrode-electrolyte interface was less than 1 Ohm. It confirms the applicability of these materials as electrodes for electrochemical systems and the possibility of obtaining high values of output power.

1. Introduction
Hollow microspheres based on transition metals and their oxides are characterized by great prospects for practical application. In particular, they can be used as materials for catalysts in various reactions [1] - [3], as sorbents for organic dyes [4], [5], most of the research of microspheres application is concentrated on the creation of electrode materials for batteries and supercapacitors [6] - [8]. Separately, the use of hollow nickel structures in the electrode materials for thermoelectrochemical cells due to its high hypothetical Seebeck coefficient [9], [10] should be noted.
There are many different methods for obtaining hollow microspheres [11]: mechanical grinding, precipitation, lyophilization, freeze-drying, spray-drying, spray-pyrolysis, supercritical fluid, emulsion-based methods.

The spray pyrolysis method has great prospects [12]. This method combines the convenience of laboratory use and allows you to obtain hollow microspheres of a given diameter with a narrow distribution. A great advantage is the ability to control the morphology of particles.

The properties of microspheres obtained by spray pyrolysis depend on a wide range of factors from temperature conditions [13], [14] to the use of various organic additives [15] - [19] to increase the specific surface area of the material. It increases the adsorption properties and contact area, increasing the usage efficiency of the material.

An important factor determining the efficiency of microspheres use in the electrode materials is the phase composition and the proportion of the metal phase. It depends on the reduction conditions of the NiO microspheres powder.

The dependence of the metallic Ni and its oxide ratio in microspheres synthesized by the spray pyrolysis method on the reduction temperature is studied in this work.

2. Experimental

2.1. Materials
For the synthesis of hollow microspheres by the spray pyrolysis method, nickel nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O) (Vekton, Russia) of analytical grade. (99.8% of the basic substance) was used.

2.2. Samples preparation
The samples were prepared by ultrasonic spray pyrolysis, a schematic view of the synthesis unit is shown in Figure 1.

![Figure 1. Schematic representation of an ultrasonic spray pyrolysis unit: ultrasonic generator (a), reactor (b), filter (c), bubbler (d), compressor (e).](image)

The aerosol was made of an 15 wt%. aqueous solution of nickel nitrate (Ni(NO$_3$)$_2$). A constant flow rate (30 l/min) was maintained by an air compressor. The quartz glass reactor was at 900°C.

Metal microspheres were made from hollow nickel oxide (NiO) microspheres by reducing nickel oxide with hydrogen in a sectional furnace at temperatures from 300 to 400°C. At the end of the
reduction process, the metal hollow spheres were passivated in a nitrogen flow with a low oxygen content.

The reduced microspheres were used to prepare 0.5 g tablets by uniaxial pressing at a pressure of 10 MPa. The tablets had a shape of a flat cylinders 10 mm in diameter. The scheme of a measuring cell is shown in Figure 2.

![Figure 2](image)

**Figure 2.** Experimental electrochemical cell: salt bridge (a), nickel wires (b), samples (c), hot fluid (d).

2.3. Methods

2.3.1. Scanning Electron Microscopy (SEM). The morphology and sizes of particles before and after the reduction process were studied using the method of scanning electron microscopy (Figure 2) by an electron dispersive X-ray analyzer (Tescan Vega3, Czech Republic) with SDD (XMAS, Japan).

2.3.2. Determination of the percentage of Ni in recovered samples. For a number of reduced spheres at different temperatures, the TGA and XRD methods were used to determine the ratio of nickel in the form of oxide and metal. Thermogravimetric analysis was carried out by a TGA/DSC 3+ (Mettler Toledo, USA) in an air atmosphere. The experiment included heating the sample from 25 to 1000°C at a rate of 10 °C/min (Figure 3 (a)). Reusable pots made of aluminum oxide (Al₂O₃) were used. The pots were filled to 0.3 heights, the initial sample weights varied from 5.1250 to 5.7150 mg.

2.3.3. X-ray non-standard quantitative analysis. X-ray phase analysis was performed by an ARL X'TRA diffractometer (Thermo Scientific, Switzerland) using CuKα radiation (λCuKα = 0.15412 nm) in the 2θ angle range (5-90 degrees). The geometry of the Bragg-Brentano measurements was used for step-by-step scanning mode (step 0.02 degrees) with a speed of 1.2. XRD based on CuKα radiation and the Bragg-Brentano geometry are the most popular methods for X-ray non-standard quantitative analysis [20]. To identify the phases in the diffraction patterns, the library of the international electronic base of diffraction standards (produced by ICDD - International Center for Diffraction
Data) - PDF-2 (Powder Diffraction File - 2) database in the Crystallographic Search-Match Version 3.1.0.2 software was used.

The calculation based on the XRD data was carried out by the Rietveld method, which implies the refinement and approximation of the theoretical line of the diffraction profile to the experimental data by selecting the sample parameters by the least squares method. Next, a standard-free quantitative phase analysis was performed using the GSAS program. GSAS is a set of programs for processing and analyzing the diffraction data of single crystals and powders obtained by XRD or neutron diffraction. The calculation uses all possible data on the experiment and the sample.

3. Results and discussing

SEM images show a relatively small scatter in the sizes of synthesized microspheres, both before and after reduction. The morphology and size of the particles are completely preserved during the reduction. The material contains a small amount of aggregates, deformed and destroyed microspheres both before and after reduction.

![Figure 3. SEM images before (a) and after (b) reduction.](image)

The change in the mass of nickel microspheres reduced at different temperatures is presented in Figure 4a, the results of X-ray phase analysis in Figure 4b.

![Figure 4. Thermogravimetric curves of metallic Ni oxidation in samples with different reduction temperatures (a); XRD spectra of samples with different reduction temperatures (b).](image)
From the TGA data for a quantitative assessment of the elemental nickel content in the samples, the ratio of the reduced and oxide forms was calculated according to the equation of the oxidation reaction of the material during the experiment:

\[ 2Ni + O_2 \rightarrow 2NiO \]  

(1)

The increase in the sample mass was taken as the mass of oxygen reacted with reduced metallic nickel.

According to the Figure 4, the percentage of nickel in microspheres increases with the reduction temperature increases from 300 to 375°C and then stays at a constant value. The maximum nickel content reaches 72 wt%.

The calculation by the Rittveld method based on the XRD results shows a similar pattern of increase in the metallic nickel content in the samples with an increase in the reduction temperature. The discrepancy in the results is most likely due to the underestimated data on the oxide phase content calculated by XRD. It is caused by the specifics of the semiquantitative method and partial X-ray amorphousness of nickel oxides. Also, the inaccuracy of the TGA method may be due to the structure of the spheres. Oxidation occurs only on the outer surface of the sphere, if there are no pores. Nevertheless, the ratio of such spheres is extremely small.

Thermoelectrochemical measurements were made in a system of thermostated cells with a salt bridge. The limiting resistance is the transfer resistance of the charge carrier through the salt bridge (in the experimental cell the resistance was 783 Ω). Figure 6 shows the load curves (a) and the hodograph of the impedance (b) of the experimental cell with electrodes made of microspheres reduced at 350 °C.

![Image](image-url)

**Figure 5.** Dependence of the metallic nickel percentage in the samples depending on the temperature of reduction calculated by TGA and XRD methods.

![Image](image-url)

**Figure 6.** Load curves (a) and hodograph of the impedance (b) of the cell, based on microspheres reduced at 350 °C.
The Seebeck coefficient in a system with electrodes based on nickel microspheres reduced at 350°C was 3.1 mV / K. The shape of the hodograph corresponds to the standard electrochemical system. The resistance of charge transfer across the electrode-electrolyte interface was less than 1 Ohm, which confirms the applicability of these materials as electrodes for electrochemical systems.

4. Concluding remarks
As a result, the dependence of the ratio of nickel in the metallic and oxide form on the reduction temperature was established. According to the obtained dependence, an increase in temperature above 375°C does not lead to an increase in the metallic nickel ratio, which can be explained by complete reduction at this temperature. The presence of an oxide phase in this case is explained by the necessary stage of passivation.

The synthesized microspheres have a morphology close to spheres. They consist of nickel oxide or metallic nickel with an oxide film. More than 60% of the spheres have sizes from 2 to 4 μm.

The synthesized microspheres can be effectively used to create electrode materials in thermoelectrochemical converters. The thermoelectrochemical cell based on the nickel oxide microspheres reduced at 350 °C showed 12 mW/m² at a temperature difference of 20 K, Seebeck coefficient around and 3.1 mV/K and an interface resistance less than 1 Ohm.

5. References
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