



Synthesis of Ni and Pt nanomaterials by cathodic contact glow discharge electrolysis in acidic and alkaline media

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ABSTRACT

Ni, NiO, β -Ni(OH)₂ and Pt nanomaterials are prepared with cathodic contact glow discharge electrolysis (CGDE) in acidic and alkaline media by alternating the Ni and Pt cathode vs. a large Ni anode. The morphological and crystalline characterizations of the products suggest two reaction mechanisms where in the first, metal ions are locally reduced by the high reducing agents generated by the electrical discharges from the cathode, i.e. the solvated electron, the H[•] radical and secondary species if any. This is supported by CGDE experiments conducted in acidic environment with Ni or Pt cathode that gave Ni-based materials only. The second mechanism for the formation of metals aggregates is due to the cathode material electro-erosion due to the high temperature spots at its surface that lead to the local vaporization of its material and the rapid quenching of the generated powder. This conclusion is drawn after eliminating the source of Ni²⁺ ions, initially due to the Ni anode dissolution in acidic pH, and conducting the same two previous experiments in concentrated KOH solutions instead. In both arrangements, it is the cathode material that was the source of the synthesized nanoparticles.

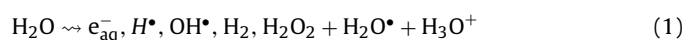
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1. Introduction

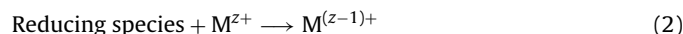
The conventional electrolysis in a two-electrode cell is no more sustained when the terminal voltage is higher than a critical value, and evolves spontaneously to the contact glow discharge electrolysis (CGDE). The continuous coalescence of adjacent bubbles around the electrode leads to the formation of a thin gaseous envelope formed around and insulating it from the rest of the solution [1–3], as shown in Fig. 1. With the formation of this gas film, glow microdischarges are emitted from the cathode toward the anolyte, and are somehow similar to radiative beams generated from a particle beam at the top of a solution [2,4]. The gas film is dynamic and it is subject to various instability factors that makes it rapidly alternating from being formed and broken [3,5–7].

Although the phenomenon is known since 1844 [8], its practical applications such, micro-precision machining of non-conductive materials [9], wastewater treatment [10] and surface engineering [11] came to life just in the second half of the 20th century. In the recent few years, this electrochemical process has been applied for the synthesis of nanometer-sized materials and is attracting more and more attention due to the simplicity of the technique and its versatility [12–19]. It is based on the formation of reducing and

oxidizing species that are formed from the reactions of dissociation, solvation, dimerization and recombination resulting from the decomposition of water molecules under the ionizing discharges [20–23]:



In the presence of dissolved metal precursors at z⁺ valency, the hydrated electrons ($E^\circ(\text{H}_2\text{O}/\text{e}_{\text{aq}}^-) = -2.87 \text{ V}$ [24]), hydrogen radicals ($E^\circ(\text{H}^\bullet/\text{H}^\bullet) = -2.31 \text{ V}$ [24]), and secondary formed elements from chemical scavengers usually used to optimize the process, are able to reduce the ions to lower state of valence as follows [18,25,26]:



⋮



Zero-valent atoms M⁰ progressively form stable nano-sized aggregates by nucleation and crystal growth processes:



We have recently investigated the effect of the cell voltage and experiment duration on the size and type of nanoparticles synthesized by CGDE using two Ni electrodes in acidic medium [18].

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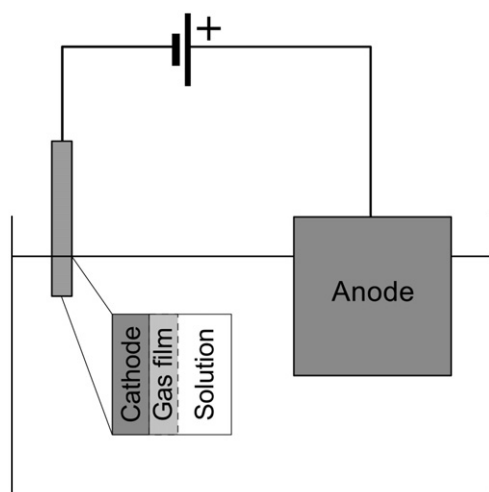


Fig. 1. Scheme of cathodic electrochemical discharges.

However, to the best of our knowledge, we are not aware of any reported studies on the contribution of the cathode material during CGDE. Using electron microscopy and X-ray diffraction (XRD) characterizations, this work reports the manufacturing of Ni, NiO, β -Ni(OH)₂ and Pt nanoparticles by alternating the usage of a Ni and a Pt cathodically polarized wire versus a Ni anode in acidic and alkaline solutions. For instance, in acidic pH, we have manufactured NiO nanoparticles when operating with a Ni cathode vs. a Ni anode. However, a fraction of Pt is also detected by XRD when the cathode is changed to Pt, but predominately Ni-based materials are manufactured in this configuration. On the other hand, when CGDE is conducted in alkaline solutions, different phases of Ni-based materials are manufactured (Ni, NiO and β -Ni(OH)₂) when both electrodes are Ni. Pt only is identified when the cathode is changed to Pt in the latter setting. This paper shows that the metal ion reduction by the activated reducing species and the erosion process of the cathode material are two coexistent mechanisms of nano-materials manufacturing by CGDE.

2. Experimental

Chemical and reagents are of analytical grade and were used as received. H₂SO₄, KOH and ethanol are purchased from Fisher Scientific, and polyvinyl-pyrrolidone (PVP) of 40,000 g/mol molecular weight (PVP40) from Sigma Aldrich. Ni wire \varnothing 0.5 mm 99.98% purity and Ni plate of 5 cm \times 5 cm 99.5% purity are acquired from Alfa Aesar. Pt wire \varnothing 0.5 mm at 99.99% purity is provided by Pine Research Instrumentation. The used DC power supply is a ZUP60-3.5 model provided by TDK Lambda and delivering 0–60 V and 0–3.5 A.

The setup to manufacture the nano-sized materials is a two-electrode configuration where the anode is much larger (4 cm \times 5 cm) than the cathode (\approx 10 mm²), as shown in Fig. 1 [18,26,27]. Two solutions are used: one acidic composed of 2 M H₂SO₄, 0.5 M ethanol and a fraction of PVP40 [18], and one alkaline of 5 M KOH. The voltage for the case of the acidic solution is 36 V and for the case of the alkaline one is 50 V, which are beyond the respective onset voltage of CGDE. In order to examine the effect of the electrode material on the manufactured nanoparticles and the synthesis process, a set of four experiments are conducted as follows. In the first one, a Ni cathode and a Ni anode are submerged into the acidic solution with a DC voltage of 36 V during 1 h. The second experiment consists of replacing the Ni cathode with a Pt one under the same electric conditions and for 1 h as well. Both of these

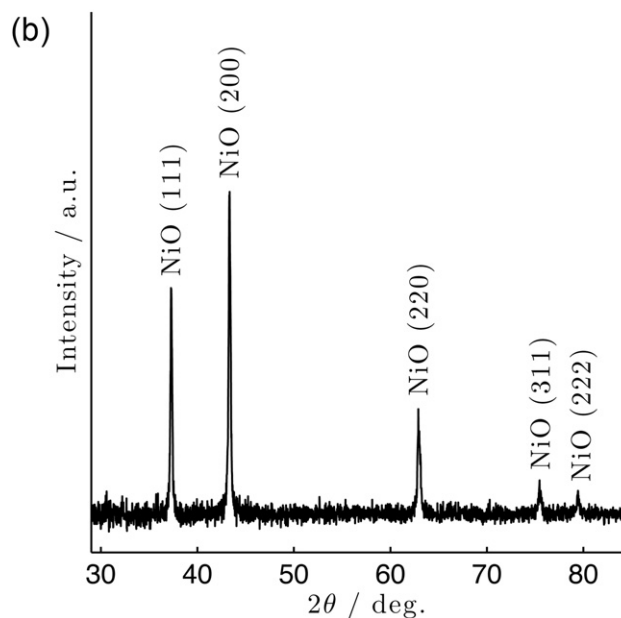
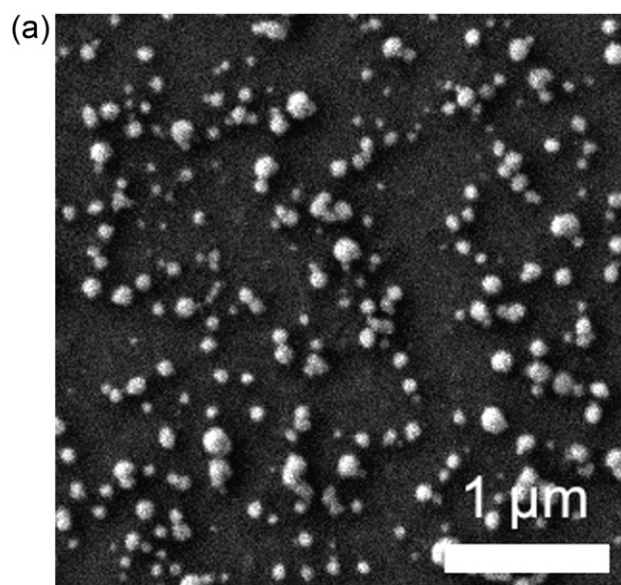


Fig. 2. Electron micrograph and X-ray diffraction patterns of NiO nanoparticles synthesized in acidic solution with Ni cathode versus Ni anode.

two combinations of electrodes are also conducted in the alkaline solution of KOH at 50 V which make them four. The nanoparticles are separated and extracted from the solution by several cycles of centrifugation, washed abundantly with de-ionized water and stored in ethanol.

The high-resolution micrographs of nanoparticles are obtained with a JEOL JSM-7500F FESEM and a JEOL JEM-2100F FETEM. Samples are prepared by depositing and air drying a droplet from the nanoparticles-in-ethanol solutions onto a carbon-coated copper micro-grid. The phase purity and crystallinity of the collected powder are analyzed from their X-ray diffraction (XRD) patterns which are measured in the θ - 2θ geometry with a Philips X'Pert Pro Multipurpose X-ray diffractometer with Cu K α source ($\lambda = 1.5404 \text{ \AA}$) at 40 kV and 45 mA. Samples are prepared by depositing a uniform flat layer of the tested powder on an approximately 3 cm² portion of a glass slide for microscopes covered with Vaseline.

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