

Synthesis and electrochemical characterization of sponge-like nickel nanoparticles

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ABSTRACT

Nickel and its alloys are the most studied electrode materials. Nickel exhibits a high initial electrocatalytic activity in the hydrogen evolution reaction (HER). Enhancement of cathodic activity of nickel for HER has been carried out by the formation of nanostructured nickel materials. In this context, the use of an organometallic precursor, able to decompose in mild conditions in the presence of a reducing gas has arisen as a suitable method of synthesis of these species. In this work, we investigated the synthesis of nickel nanoparticles starting from Ni(COD)₂, (COD=cycloocta-1,5-diene) and decomposed under H₂ atmosphere in THF in presence of 1,3-diaminopropane as stabilizer. TEM studies revealed the formation of characteristic particles resulting from the agglomeration of initially obtained nanocrystallites. The activity of the dispersed catalysts composed of Ni/C with respect to the HER was investigated using steady state polarization measurements.

Keywords: hydrogen evolution reaction, nickel, nanoparticles, organometallic.

1 INTRODUCTION

The hydrogen evolution reaction (HER) is the main reaction in the water electrolysis and has been one of the most studied electrochemical reactions. Although, platinum presents the highest activity for the HER, new electrode materials have been investigated, aiming at the reduction of the cost associated with the electrocatalysts development. Among these materials, nickel exhibits good corrosion resistance in aggressive environments and catalytic activity for the HER [1]. However, in order to improve its activity, resulting in reduced overpotentials for the HER, the real surface and the intrinsic activity of the electrode material must be increased.

Nickel nanoparticles less than 100 nm in primary particle diameter have attracted considerable interest in the last years due to their various applications such as catalysis superconductors, electronic, optical mechanic devices, magnetic recording media, and so on, [2,3]. Metal nanoparticles have generally been produced by both gas and liquid phase processes. Among the gas phase methods, hydrogen reduction of the metal chloride [4], laser-assisted gas phase photonucleation [5], and hydrogen plasma metal reaction [6] have been used. Alternatively, γ -ray irradiation [7], borohydride reduction of metal salts [8], sonochemical and thermal decomposition metal complexes [9] are the most useful techniques to synthesize metal nanostructures in liquid phase. Additionally, an organometallic approach using olefinic complexes as a source of metal atoms has shown an interesting alternative to control shape, size and dispersion of nanostructures [10,11]. The method leads to the access to monodispersed particles of very small size (1-2 nm) and allows for the performance of coordination chemistry at their surface. Therefore, the use of organometallic precursors is now well established as a method to obtain size and surface state controlled nanoparticles in mild conditions (room temperature and 1-3 bar of a reactive gas). Additionally, depending on their skeleton and functional groups, the stabilizers can interact more or less with the surface of the particles and then favour or not the growth of the particles in a privileged direction.

The present study was undertaken in order to investigate the electrochemical properties of Ni-base nanoparticles synthesized by an organometallic approach containing 1,3-diaminopropane as stabilizer in different Ni compositions. The particle size and shape of the resultant nanoparticles were characterized by Transmission Electron Microscopy (TEM), HR-TEM and electron diffraction pattern. The electrocatalytic activities of the powders for HER were investigated by cyclic voltammetry (CV), polarization curves and ac impedance.

2 EXPERIMENTAL PROCEDURE

2.1 Synthesis of metallic nanoparticles

The reaction was carried out, as a standard procedure in a Fischer–Porter bottle. In a typical procedure, a solution of THF (50 ml) including 50 mg of the precursor $\text{Ni}(\text{COD})_2$ (Aldrich) and 1,3-diaminopropane (99%, Aldrich) 2 ($\text{Ni}_{2\text{DAP}}$) or 5 ($\text{Ni}_{5\text{DAP}}$) equivalents per Ni atom was reacted at 70 °C for 20 h, under dihydrogen pressure (3 bar), in Fischer-Porter bottle leads to the formation of dark gray colloids. The reaction is slow at lower temperatures [12]. The obtained solutions were purified by hexane washings. Finally, the resulting solution was evaporated in vacuum until the residue was completely dry.

Specimens for TEM analysis were prepared by the slow evaporation of a drop of each colloidal solution after the purification process deposited onto a carbon covered copper grid. TEM experiments were performed on a JEOL-1200 EX electron microscope, operating at 120 KV. The HRTEM study was carried out on a JEOL 2010 FasTem field emission transmission electron microscope with a resolution of 2.1 Å.

2.2 Catalysts preparation

The support of the electrode was a glassy carbon rod (5.0 mm in diameter). The base of the rod was polished with a cloth and alumina powder (ca. 0.3 μm). The working electrodes were prepared by attaching an ultrasonically re-dispersed catalyst (stabilized nickel nanoparticles) suspension containing a 4:1 ratio vulcan carbon black/ total metal (20 wt.%) powders in deionized water onto the glassy carbon. After drying under a high purity argon flow at room temperature, the deposited catalyst layer was then covered with $\approx 4 \mu\text{l}$ of a diluted aqueous Nafion solution and finally, the electrode was immersed in a nitrogen purged electrolyte to record the electrochemical measurements. Pt black and bulk were also analyzed as a reference. The electrodes were carefully prepared in order to obtain reproducible electrode surfaces and comparable electrocatalytic results.

3 RESULTS AND DISCUSSION

3.1 TEM and HR-TEM studies

TEM-bright field images of Ni nanoparticles synthesized in presence of 2 equiv. of 1,3-diaminopropane are shown in Figure 1. The micrograph (Figure 1a) reveals the formation of sponge-like particles with an average size of 138 nm. These particles are formed by smaller nanoparticles. The corresponding selected area diffraction pattern (SADP) was inserted on the top right in Figure 1a. The indexing of the ring diffraction pattern confirms the presence of the nickel with the following interplanar distances: 2.00, 1.73, 1.11, 1.02 and 0.77 Å. These

distances correspond to the (111), (200), (311), (222) and (420) planes, respectively. Previous works for this type of particles have been observed in the chemistry of ruthenium [13], platinum [14], palladium [15] and recently for Ni obtained by microwave-assisted synthesis in presence of PVP [16]. The effect of higher stabilizer concentration (5 equiv.) on the dispersion is showed in Figure 1b. In this case, nanocrystalline sizes ranging between 5 to 14 nm were observed. It seems that higher concentrations of stabilizer induced an homogeneous distribution of the smaller nanoparticles.

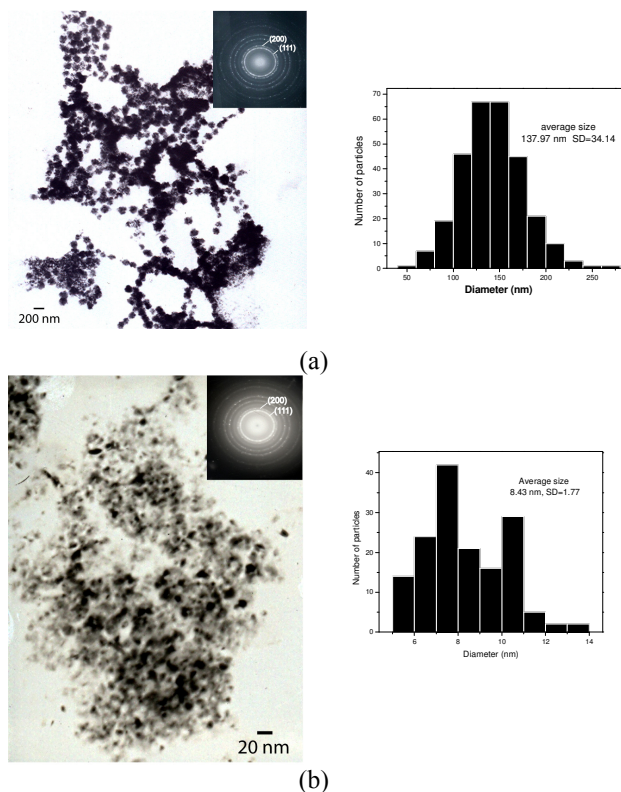


Figure 1. TEM micrographs and size distribution of nickel nanoparticles synthesized in THF from $\text{Ni}(\text{COD})_2$ in presence of 1,3-diaminopropane (a) 2 eq. and (b) 5 eq.

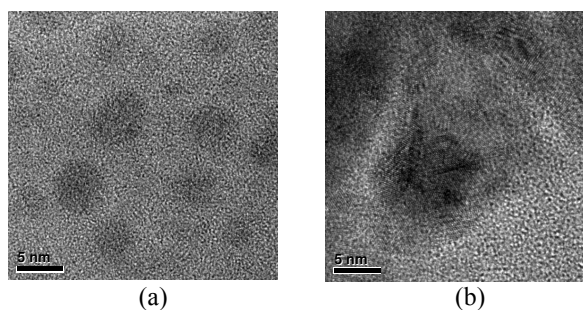


Figure 2. High-resolution TEM images of Ni nanoparticles synthesized in the presence of 5 eq. 1,3-diaminopropane.

The corresponding SADP in Figure 1b was also inserted. Five rings were indexed and they showed the following interplanar distances: 2.00, 1.79, 1.25, 1.04 and 1.28 Å. They are related to the (111), (200), (220), (311) planes of fcc Nickel and (113) plane of rhombohedra nickel oxide respectively. The presence of nickel oxide is attributed to the sample preparation process. The nanocrystallites showed in Figure 1b. were observed by HRTEM and they are showed in Figure 2a-b. These figures confirmed the well dispersed nickel nanoparticles with isolate cluster of around 5 nm in different zones.

Hence, the obtained results show the effect of the molar ratio of Ni/ H₂NCH₂CH₂CH₂NH₂ on the particle size. It causes a porous structure of the spherical Ni nanoflower or compacted Ni semispherical particles. The mean size of Ni nanoflowers (sponge-like) decrease gradually with the increase the amount of the stabilizer in the reaction medium. This may be ascribed to the influence of the nucleation rate and subsequently growing of the Ni structures. With the increase of the 1,3-diaminopropane, the interaction rate became faster, more dispersion can be reached inhibiting the growth of nanostructures and led to obtain smaller nanoclusters.

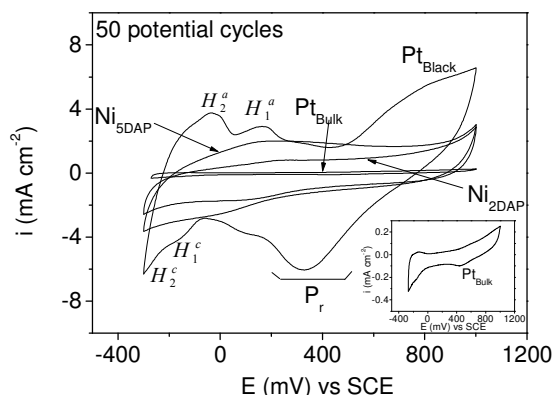


Figure 3. Cyclic voltammograms on Ni electrodes in 0.5 M H₂SO₄ ($v=20 \text{ mV s}^{-1}$) after 50 potential cycles, different concentrations of stabilizer.

Figure 3 shows the cyclic voltammograms after 50 potential cycles of Ni catalysts and are compared with commercial Pt_{Black} and Pt_{Bulk} in 0.5 M H₂SO₄ at $v=20 \text{ mV s}^{-1}$ using a potential sweep of -300 to 1000 mV vs SCE. Pt_{Black} shows typical hydrogen adsorption desorption peaks in the potential range between -250 and 200 mV, and HER begins at about -300 mV vs SCE. Figure inset show the corresponding Pt_{Bulk} electrochemical behavior. The CVs for electrodes with different equiv. per nickel atom, i.e. 2 and 5 equiv. exhibited similar shape within evaluated potential range. It can be seen from the voltammograms

that the charge densities associated with the redox peaks decrease depend on the amount of stabilizer.

In spite of many researches in the literature [17] have shown dissolution of Ni in acid media due noble metals are not completely inert at anodic potentials in these media, the obtained voltammograms are nearly constant after only a few potential cycles and at 50 cycles the changes becoming small and dissolution have not been appreciated. This observation may be attributed to the presence of the stabilizer at surface of Ni particles, which interact with Ni nanostructures retarding its dissolution. FTIR spectra (not show here) indicate the presence of H₂NCH₂CH₂CH₂NH₂ interacting in the system Ni/stabilizer. Then these results can be related to the absorption mechanism of the stabilizer, the amine molecules can be adsorbed on Ni surface to form a film through coordinate bond which seems to serve as a block barrier inhibiting the Ni dissolution.

The cathodic polarization behavior (Tafel plots) after 50 potential cycles obtained for hydrogen evolution of the Ni particles having different stabilizer contents is shown in Figure 4. Both Ni electrodes are far of the electroactivity of commercial Pt_{Black}, but they are better than Pt_{bulk}.

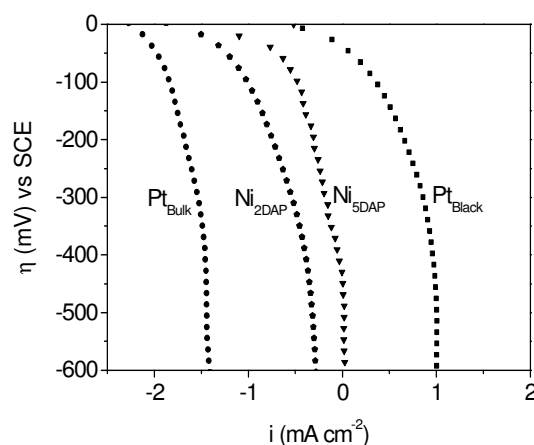


Figure 4. Cathodic polarization curves in 0.5 M H₂SO₄ ($v=0.5 \text{ mV s}^{-1}$) of nickel nanoparticles synthesized from Ni(COD)₂ and compared with commercial Pt_{Black} and Pt_{Bulk}.

The major Tafel parameters are provided in Table 1. The obtained slopes (b_c) are very variety ranging between 86 and 285 mV dec⁻¹. The presence of high concentrations of the stabilizer in the Ni nanostructures increases the electrode activities which can be correlated with the particle size, as described above in TEM measurements. Then, Ni electrode having 5 equiv. was found to have higher electrocatalytic activity during HER than the other Ni catalyst (2 equiv.). The least active electrode was Pt_{Bulk} while the most active material was commercial Pt_{Black}. Table 1 also shows current densities at similar overpotentials. The higher current densities obtained for Ni_{5DAP} than this for Ni_{2DAP} at these overpotentials is only attributed to the influence of the stabilizer on the growth of

the Ni nanostructures which evidently affect their catalytic activity.

Table 1: Kinetic parameters obtained from the mass-corrected Tafel Plots for hydrogen evolution reaction in 0.5 M H₂SO₄.

Parameter	Electrode			
	Pt _{bulk}	Pt _{black}	Ni _{SDAP}	Ni _{2DAP}
b _c (mV decada ⁻¹)	128	86	285	180
Log i ₀ (mA cm ⁻²)	1.0E-3	1.6E-1	6.3 E-2	1.5E-2
i ₁ (η=100 mV) (mA cm ⁻²)	1.4E-2	2.2	3.3E-1	9.3E-2
i ₂ (η=300 mV) (mA cm ⁻²)	2.9E-2	7.2	6.8E-1	2.9 E-1
i ₃ (η=500 mV) (mA cm ⁻²)	3.2E-2	10.0	1.0	0.5

*i*₀ = exchange current density. *i*₁, *i*₂ and *i*₃ are current densities at different overpotentials.

CONCLUSIONS

The use of an organometallic approach lets to obtain size and surface state controlled nanoparticles in mild conditions. 1,3-diaminopropane-stabilized Ni nanoparticles were synthesized from Ni(COD)₂ in organic medium. An appropriated amount of stabilizer lets to obtain an uniform distribution of Ni nanoparticles with sponge-like structure or compacted Ni semispherical particles. Both samples displayed nearly monodispersed Ni nanoparticles through the specific coordination of the amine; this interaction seems to serve as a block barrier inhibiting the Ni dissolution in acid media. An important increased in the electrocatalytic activity during HER was observed as the molar Ni/H₂NCH₂CH₂CH₂NH₂ ratio was increased. The activities of these electrodes are far from the values displayed for commercial Pt, however by adjusting the kind of stabilizer containing long alkyl chains smaller clusters can be reached and increased the electrochemical performance.

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