

# Synthesis of Cobalt Nanoparticles by Electrodeposition onto Aluminium Foils

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In this contribution a study of electrochemical deposition of cobalt nanoparticles onto aluminium foils is presented. The study is aimed at deriving information required for design and control of cobalt nanoparticles electrodeposition onto aluminium foams employed as catalysts support in ethanol reforming.

A thorough experimental analysis was in this perspective conducted to determine the influence of applied potential and amount of electric charge passing through the cell (amount of charge), on number density and size of the synthesized nanoparticles. Chronoamperometric tests were for this purpose performed in a three electrode cell to determine the current responses to variations in the selected operating parameters. Mathematical models accounting for charge transfer and diffusion limitations were implemented to attain fitting of the derived data, leading to an estimation of the number density of active sites. Scanning electron microscopy of cathode aluminium foils was performed to validate the predictions of the employed mathematical models and characterize the influence of the considered operating parameters on the size and number density of the electrodeposited nanoparticles.

## 1. Introduction

Cobalt nanoparticles have attracted considerable interest in numerous technological areas. Applications mainly exploit magnetic and catalytic properties of cobalt nanoparticles and include, for example, corrosion prevention, realization of fuel cells, fabrication of memory storage units, field emission, development of chemistry sensors and realization of reforming catalysts.

Steam reforming of alcohols represents a competitive technological alternative towards the production of hydrogen. In this process, the use of ethanol representing a renewable raw material easily obtained from biomass has attracted considerable attention. The steam reforming of ethanol proceeds on transition metal catalysts. Haga et al. (1997) showed that cobalt nanoparticles based catalysts have high selectivity towards hydrogen in ethanol steam reforming with a minimum in production of CO, which is a strong poison for the hydrogen oxidation reaction taking place on the anode of the electrolyte fuel cells (Batista et al. 2004), one of the most promising application fields of hydrogen.

Currently, these latter catalysts are mainly produced by impregnation methods with high metal loading and with low control of size, morphology and density of the supported nanoparticles. These characteristics can on the other hand significantly affect catalyst activity (Da Silva et al. 2014), selectivity and thermal stability (Ono and Cuenya 2008) of deposited nanoparticles. The direct electrodeposition of metal nanoparticles onto the target support can reduce metal loading allowing at the same time control of size and morphology (Pagnanelli et al. 2015).

## 2. Experimental

All the experiments were conducted from aqueous solution of 0.1 M  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  with 1 M  $\text{Na}_2\text{SO}_4$  as supporting electrolyte and 0.5 M  $\text{H}_3\text{BO}_3$  as pH buffer.

A thermostated jacketed three-electrode glass cell, was used in all the tests. Platinum wire was used as counter electrode, silver/silver chloride (SSCE) as reference electrode and aluminium foils (99% Alfa Aesar) with 0.5 cm<sup>2</sup> area as working electrode. All the potentials in the experiment are referred to SSCE.

The aluminium foils were first immersed for 5 min in NaOH 0,1 M to remove native aluminium oxide layer, then in a 0.5M H<sub>3</sub>NO<sub>3</sub> smoothing solution and lastly rinsed with distilled water.

Aluminium working electrode was replaced with a new one at the end of each experiment.

Ivium-n-Stat potentiostat/galvanostat with IviumSoft was used for all the electrochemical experiment.

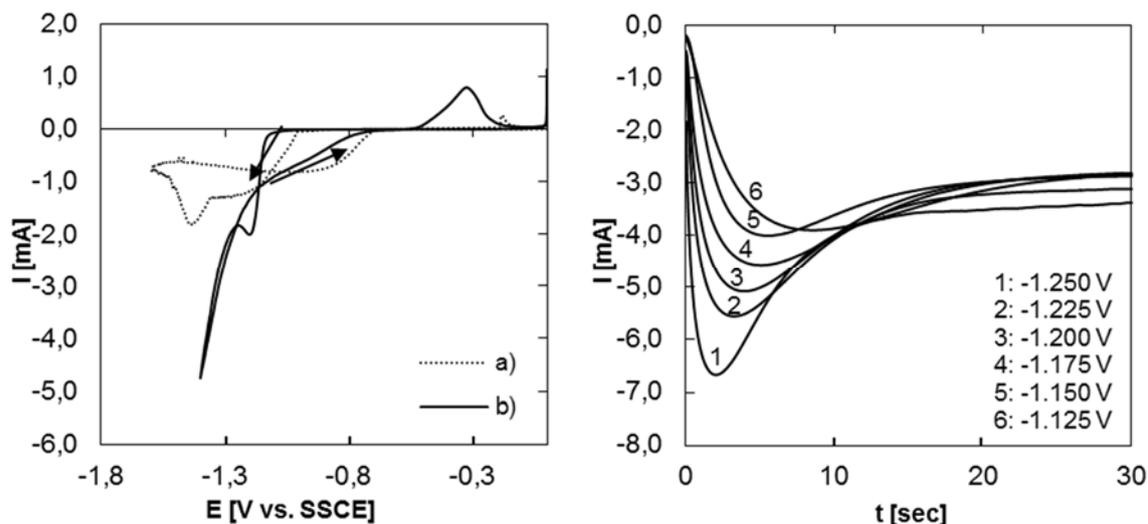
LaudaECO RE 620 S cooling thermostat with an accuracy of ±0.01 °C was used to maintain a temperature of 25 °C in all the experiments. Following electrodeposition, the deposited nanoparticles were analyzed by Zeiss-Auriga scanning electron microscope. ImageJ package was used to determine the size and the number density of cobalt nanoparticles. From the estimated 2D coverage area, the equivalent diameter of the nanoparticles was determined.

### 3. Results and Discussion

The study of the electrochemical nucleation and growth processes of cobalt onto aluminium was performed by cyclic voltammetry and potentiostatic transient measurements (chronoamperometry). Cyclic voltammetry was used to define the potential range stability of aluminium in the electrolytic solution without cobalt ions and then was used to determine the reduction potential of cobalt ions onto aluminium foils working electrode. The current transients recorded during chronoamperometric tests were fitted with theoretical models to determine the number density of aluminium active sites for nucleation. Chronoamperometric tests were also used to make electrodeposited nanoparticles onto aluminium foils. In this way it was possible to compare the resulting data obtained from S-H models with the effective nanoparticles number density obtained from electrodeposition by SEM image analysis.

#### 3.1 Cobalt reduction onto Aluminium

An aluminium electrode is spontaneously covered by a dense oxide layer which prevents further oxidation. Gruberger and Gileadi (1986) have reported that the deposition processes through barrier layer oxide can be affected by several factors as, for example, electronic conductivity through the oxide layer, diffusion of metal ions through the oxide layer, migration of metal ions across the oxide layer electric field. Furthermore, hydrogen evolution, due to the hydrous nature of the oxide, can generate an excess of OH<sup>-</sup> that can dissolve the oxide layer locally. Cyclic voltammograms (CV) reported in Figure 1 allow characterizing the main mechanisms governing cobalt electrodeposition onto aluminium with and without pretreatment for oxide layer removal. In case of application of untreated aluminium foil (Figure 1, curve a), electrodeposition takes place onto the native oxide layer of aluminium surface (Figure 1, curve a) and the increase of the cathodic current observed in potential range from -1.0 V and -1.35 V vs SSCE (direct scan) is determined by the deposition of cobalt. The sharp increase of the cathodic current observed immediately after -1.35 V is in this case due to proton reduction and hydrogen evolution. Cathodic current determined by hydrogen evolution increases till reaching a potential of -1.45V and the starts decreasing. This latter effect can be attributed to the increase of local OH<sup>-</sup> concentration determined by proton reduction. The local increase of pH induces the formation of cobalt hydroxide which reduces the flux of cobalt ions available to electrodeposition on aluminium surface and thus determines a decrease in cathodic current. In the second curve (Figure 1, curve b), pretreated aluminium was used as working electrode and H<sub>3</sub>BO<sub>3</sub> was added as pH buffer. The current recorded is higher than the one obtained with untreated Al due to the increase in conductivity determined by the removal of the oxide layer. The cobalt reduction current peak is observed at -1.2V followed by a significant increase in the cathodic current which can be associated with proton reduction. In the reverse scan, the cathodic current is higher than that recorded in the direct scan. This demonstrates the effective cobalt reduction onto aluminium in the direct scan which increases the surface area of the working electrode. A large anodic peak due to cobalt oxidation and adsorbed hydrogen dissolution can be observed from curve b in Figure 1.



From left to right: Figure 1: Cyclic voltammograms of Co on aluminium electrode from aqueous solution of 0.1 M CoSO<sub>4</sub> + 1 M Na<sub>2</sub>SO<sub>4</sub>. Potential scan rate of 5 mV s<sup>-1</sup>. Curve a) Al with native oxide layer; Curve b) Al pretreated for oxide layer removing + 0.5 M H<sub>3</sub>BO<sub>3</sub>. Figure 2: Chronoamperometric curves for Cobalt reduction onto aluminium electrode deposited at different potentials from aqueous solution of 0.1 M CoSO<sub>4</sub> + 1 M Na<sub>2</sub>SO<sub>4</sub> + 0.5 M H<sub>3</sub>BO<sub>3</sub>.

### 3.2 Chronoamperometric tests

Scharifker and Hills (1983) have proposed a model describing the evolution of cathodic current determined by the nucleation and three-dimensional growth of hemispherical nanoparticles (Eq(1)). Two asymptotic solutions are predicted by such model corresponding to instantaneous and progressive nucleation. In the former case, nucleation takes instantaneously place at the beginning of the electrodeposition at any surface active site and is followed by growth of the formed nuclei. Simultaneous formation and growth of nuclei is in contrast found in case of progressive nucleation.

Figure 2 shows the typical current transients for a metal deposition process. Current-time curves were recorded at different value of cathodic potentials chosen on the basis of the cyclic voltammetry results. The current was recorded in a range of applied potential of -1.125V to -1.250V.

The trend of the obtained curves is typical of the well-known deposition process of metals involving 3D nucleation and diffusion-controlled growth. The obtained curves show an increase of the current with time passing through a maximum value,  $i_{max}$ , at the time  $t_{max}$ . The increase of current is due to the nucleation and growth of Co nuclei on aluminium surface with an increase of the working electrode total surface area. The current maximum observed is the result of the overlap of the diffusion zones forming around growing particles. The decreasing part of the transients obeys the Cottrell equation corresponding to planar diffusion. It is evident that the current maximum significantly increases with the applied potential and shifts towards lower  $t_{max}$  as observed for 3D electrochemical nucleation (Scharifker and Hills (1983)).

If no overlapping growing of nuclei is considered the current-time relationship from the S-H model is the following:

$$I = \left( \frac{zFD^{\frac{1}{2}}c}{\pi^{\frac{1}{2}}t^{\frac{1}{2}}} \right) \left( 1 - \exp \left\{ -N_0 \pi \left( \frac{8\pi CM}{\rho} \right) D \left[ t - \frac{(1 - e^{-At})}{A} \right] \right\} \right) \quad (1)$$

where  $zF$  is the molar charge transferred during electrodeposition,  $D$  is the diffusion coefficient,  $C$  is the metal bulk concentration,  $t$  is the time,  $N_0$  is the number density of active sites,  $M$  is the molecular weight of the metal,  $\rho$  is the density of the metal and  $A$  is the nucleation rate per site.

Preliminary indications about nucleation can be derived by comparing the normalized current transient  $I/I_{max}$  with the predictions of the asymptotic solutions of the SH model for instantaneous and progressive nucleation (Figure 3a). This comparison can provide an immediate indication of whether nucleation proceeds closer to instantaneous or progressive regime. Figure 3 shows the normalized transient curves with the theoretical curves for instantaneous and progressive nucleation. The experimental transients obtained are

very close to instantaneous theoretical curve. For longer time, a deviation from the theoretical curve is evident. This deviation from the theoretical asymptotic curves is due to the current contribution of proton reduction onto cobalt metals nanoparticles produced during the electrodeposition.

Palomar-Pardave et al. (2005) derived a model (Eq(2)) for current transient trend where the proton reduction reaction occurs simultaneously with the electrocrystallization process.

$$I = \left[ z_{PR} F k_{PR} \left( \frac{2CM}{\pi\rho} \right)^{\frac{1}{2}} + \frac{1}{\frac{N_0}{A} \pi \left( \frac{8\pi CM}{\rho} \right) D (At)^{\frac{1}{2}}} \right] \left( 1 - \exp \left\{ -\frac{N_0}{A} \pi \left( \frac{8\pi CM}{\rho} \right) D [At - 1 + \exp(-At)] \right\} \right) \quad (2)$$

where  $k_{PR}$  is the rate constant of the proton reduction reaction that can be modelled by a Butler–Volmer type relationship. This model was used to make a non-linear fitting of the experimental chronoamperometric curves to obtain the theoretical number density of the active sites  $N_0$  and the nucleation rate per site  $A$ . Figure 3b shows the different fittings obtained with the Eq(1) and the Eq(2). The accuracy of the fitting, in terms of confidence interval, is significantly improved with the use of the model considering the simultaneous electrodeposition of cobalt and reduction of protons. In Table 1, the values of  $N_0$  obtained by non-linear fitting of all the experimental curves with Eq(2) are reported.

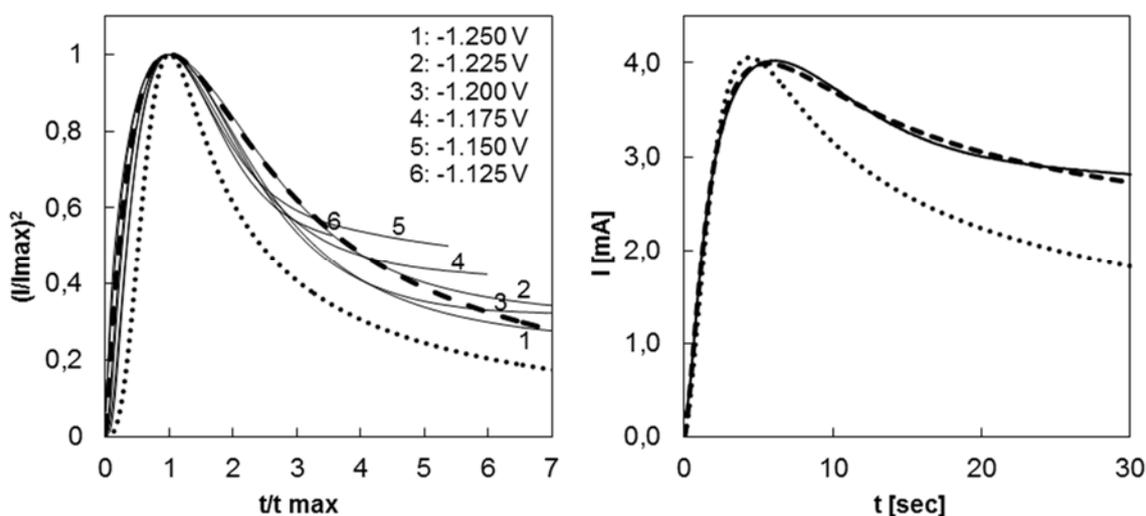


Figure 3: Transient curve obtained from 0.1 M CoSO<sub>4</sub> + 1 M Na<sub>2</sub>SO<sub>4</sub> + 0.5 M H<sub>3</sub>BO<sub>3</sub>: a) Normalized transient curves for cobalt reduction onto aluminium electrodeposited at different potentials with theoretical curves of instantaneous (dashed line) and progressive (dotted line) nucleation; b) Non-linear fitting of the -1.150 V experimental curve (solid line) with Eq(1) (dotted line) and Eq(2) (dashed line).

### 3.3 Effect of experimental parameters on electrodeposited nanoparticles

In order to obtain synthesis information about the tuning of the metals nanoparticles produced via electrodeposition, the effect of the cathodic potential of the aluminium foil working electrode and the amount of charge were investigated. The same cell configuration of the others experiments was used and the conditions for each tests are reported in Table 1. After each test the aluminium working electrode was replaced by a new aluminium foil and the detached electrode was rinsed with distilled water and dried under vacuum for SEM analysis.

#### 3.3.1 Effect of amount of electric charge passing

To evaluate the effect of the amount of charge, all the other parameters were kept unchanged. Three amounts of charge were selected: before  $t_{max}$  (5.00mC), after  $t_{max}$  (52.30mC) and around  $t_{max}$  (10.60mC) value. The same three amounts of charge were used for each investigated potential. Keeping all the experimental conditions unchanged and increasing the amount of charge from 5.00 mC to 10.6mC did not produce a significant effect on the mean size and number density of the nanoparticles for all the investigated potentials (Table 1).

Table 1: Experimental conditions used in the electrodeposition tests exploring the effect of working electrode potential (V) and discharged charge (Q) on the mean size ( $y_m$ ), standard deviation (s) and number density of the produced nanoparticles estimated from image analysis from SEM characterization. Furthermore is reported the nucleation number density of active sites ( $N_0$ ) estimated by current transient fitting with Eq(2).

Test	V [V]	Q [mC]	Co <sup>2+</sup> [mol/L]	$y_m$ [nm]	s [nm]	np density [np/m <sup>2</sup> ]	$N_0$ [active sites/m <sup>2</sup> ]
1	-1.15	5.00	0.1	110	35	1.01E+13	-----
2	-1.15	10.6	0.1	110	30	1.21E+13	-----
3	-1.15	52.3	0.1	260	90	6.54E+12	8.11E+08
4	-1.25	5.00	0.1	120	35	1.15E+13	-----
5	-1.25	10.6	0.1	120	30	1.29E+13	-----
7	-1.25	52.3	0.1	240	70	7.89E+12	5.46E+08
8	-1.40	5.00	0.1	100	30	1.27E+13	-----
9	-1.40	10.6	0.1	110	30	1.78E+13	-----
10	-1.40	52.3	0.1	180	50	1.01E+13	6.78E+08

Moreover, increasing the amount of charge from 10.60 mC to 52.3 mC produced a sharp increase of nanoparticles mean size and a limited decrease in number density of the nanoparticles probably due to the formation of aggregates (Figure 4b).

Particle size increase with amount of charge also produced an increase of size distribution polydispersity as reported in Table 1. This result is probably due to overlapping of diffusion zones which could have influenced the growth of neighboring nanoparticles.

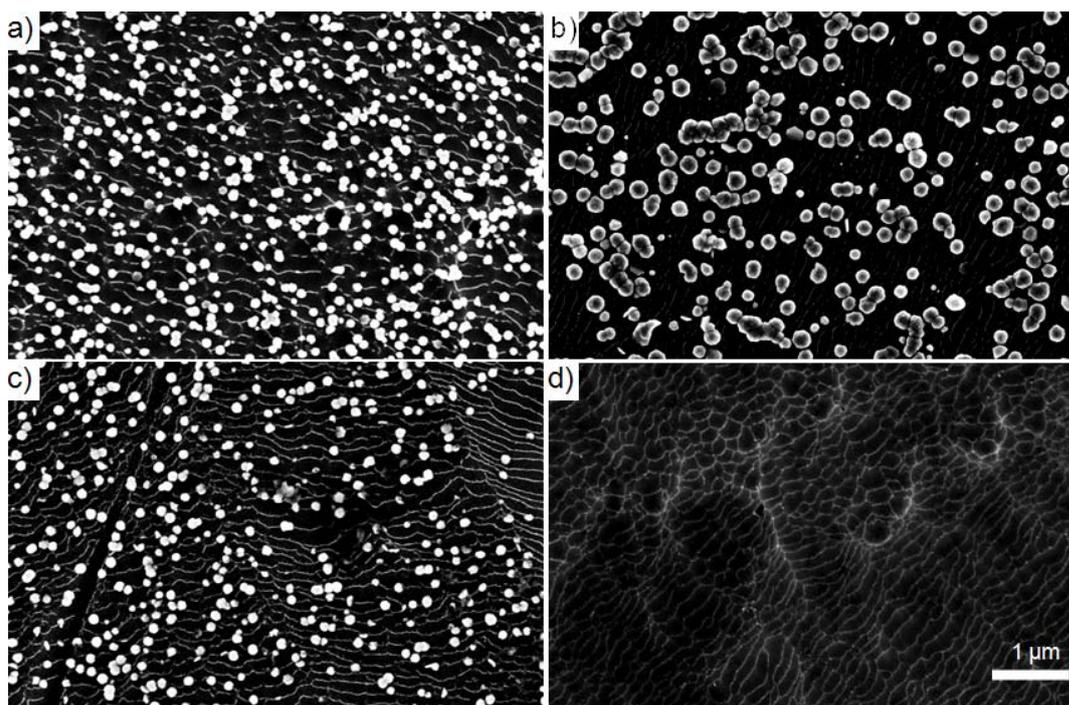


Figure 4: SEM images of nanoparticles electrodeposited from Co<sup>2+</sup>0.1M, a) -1.15V, 10.6mC; b) -1.15V, 52.3mC; c) -1.25V, 10.6mC; d) aluminium surface roughness

### 3.3.2 Effect of working electrode potential

Changing the cathodic potentials of the aluminium foil and keeping constant the other parameters did not produce significant changes in number density of nanoparticles and in the mean size (Figure 4a and c). This result can be explained in terms of active site saturation in the range of investigated potentials. If there is no change in the number density of nanoparticles and the amount of charge is left unchanged, the nanoparticles mean size cannot change as well as far as protons reduction does not affect significantly current transient (Table 1).

In Table 1, the results of nanoparticles number density values obtained from SEM image analysis are reported along with the number density of active sites ( $N_0$ ) obtained from non-linear fitting of the curves recorded during the nanoparticle electrodeposition. Although the model could satisfactorily describe the experimental data, a difference by 3–4 orders of magnitude was found between the values derived from the fitting and those determined from the SEM images. This result, still under study, may be attributed to the non-randomized distribution of the active sites onto the aluminium surface due to the ordered roughness (as shown in Figure 4d) of the substrate where nucleation preferentially takes place.

#### 4. Conclusions

The work presented a study of cobalt electrodeposition onto aluminium foils. This was aimed by the subsequent extension of these results at the production of an ethanol steam reforming cobalt based catalyst. Cyclic voltammetry was used for the evaluation of the native aluminium oxide electrode and also it was used for the determination of the cobalt reduction potential. Mathematical models were used to characterize nucleation from the obtained experimental chronoamperometric curves. According to the Scharifker and Hills model, the nucleation of the cobalt onto aluminium electrode occurs through an instantaneous process. By using a model that includes the simultaneous proton reduction, it was possible to determine the theoretical number density of the active sites of the aluminium electrode by non-linear fitting of the experimental curves. Electrodeposition tests were performed in order to evaluate the effect of working electrode potential and amount of passing charge. The obtained results show that as an increase of the amount of charge causes an increase of the nanoparticle mean size and also an increase of size polydispersity. Furthermore, no significant change in number density and in the mean size of the nanoparticles was obtained by increasing the working electrode potential.

A deviation by 3–4 orders of magnitude was found between the two values of number density obtained from experimental image analysis and non-linear fitting of the chronoamperometric curves. This result is currently under investigation and may be attributed to the non-random distribution of the active sites onto the aluminium surface caused by the ordered roughness of substrate where nucleation preferentially takes place.

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