



Research paper

Effect of metal nitrate concentration on the electrodeposition of hydrotalcite-like compounds on open-cell foams



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ABSTRACT

Mg/Al hydrotalcite-like compounds were deposited on FeCrAlloy open-cell metal foams by the electro-base generation method in metal nitrate baths of different concentration (0.03, 0.06 and 0.10 M, Mg/Al = 3/1). The modifications of both electrochemical and chemical processes by the electrolyte concentration were investigated. For comparison purposes, experiments were carried out in KNO₃ solutions and using FeCrAlloy plates as working electrodes.

The reduction processes followed a surface reduction behaviour and were slowed down by the solid deposition or the ineffective solution replenishment at the electrode interface, being more remarkable with more concentrated baths. Hydrotalcite-like, brucite and probably gibbsite phases were deposited at -1.2 V vs SCE for 100–2000 s. The metal nitrate concentration determined both OH[−] production by nitrate reduction and OH[−] consumption by precipitation of cations, these processes not only governed the amount of solid deposited and its distribution on the support but also the solid growth mechanism, crystallinity of the phases and intercalating anions inside the hydrotalcite.

1. Introduction

The deposition of hydroxides and oxides through the electro-base generation method is applied for coating electrically conductive supports of either simple (Tonelli et al., 2013; Tsui and Zangari, 2014) or complex shapes, such as foams (Benito et al., 2014; Benito et al., 2015a; Jagadale et al., 2016), wires (Rudolph et al., 2009), and microarrays (Stumpp et al., 2012; Lupo et al., 2015). The electrochemical reduction of nitrates to increase the solution pH is widely applied instead of the reduction of O₂, since the latter is controlled by convection and lower pH values can be reached. Metal nitrate salts provide both the OH[−] source and the cations to be precipitated; nevertheless, the nitrate reduction is a very complex process (Milhano and Pletcher, 2009). The properties of the electrodeposited films can be tailored by changing the potential or current applied in step or continuous depositions. Moreover, the coating properties can be varied by acting on the deposition time, bath temperature, and concentration of the nitrates, as well as they can be improved by adding several additives.

Electrodepositions can be performed in little (mM range) or highly concentrated solutions (up to 0.50 M) of metal nitrate salts. The concentration modifies not only the amount of nitrate available to increase

the pH, and consequently the nitrate reduction rate (Wasberg and Horáknyi, 1995; De et al., 2000; de Groot and Koper, 2004; Katsounaros and Kyriacou, 2008), but also the transport of cations to the working electrode, and, therefore, the amount of cations consuming OH[−] by precipitation of the hydroxides. The nitrate salt concentration plays a key role in the deposition rate, particle size and morphology of the solids in the deposition of single hydroxides or oxides, i.e. Ni(OH)₂ (Streinz et al., 1995; Wohlfahrt-Mehrens et al., 1996; Nam and Kim, 2002), CeO₂ (Hamlaoui et al., 2010), ZnO (Izaki and Omi, 1996; Nobial et al., 2011; Sun et al., 2012; Yao et al., 2015), Mg(OH)₂ (Dinamani and Vishnu Kamath, 2004), and SiO₂ (Giordano et al., 2015). In the deposition of binary or ternary hydroxides, the nitrate concentrations may also determine the composition of the solids. This is the case of the electrodeposited hydrotalcite-like (HT) compounds (Scavetta et al., 2007; Benito et al., 2015b), namely layered materials containing the metal cations in brucite-like sheets and anions and water in the inter-layer region.

In particular, we reported that in the electrodeposition of Rh/Mg/Al HT compounds on FeCrAlloy foams at -1.2 V vs SCE for 2000 s, the differences between the compositions of the electrolytic solution and the electrodeposited solid are lowered as well as the coating

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homogeneity improved by increasing the concentration of the electrolytic bath from 0.03 M to 0.06 M; although the use of a 0.10 M solution does not lead to any further improvement (Benito et al., 2015b). A negative effect of the concentration increase was observed for Ni(OH)₂ electrodeposition; the decrease in the amount of deposited solid was explained by the formation of species that migrate away from the working electrode, a behaviour that depends on the generated pH value (Streinz et al., 1995).

In our previous work, we studied the reactions involved during the electrodeposition of Mg/Al HT compounds on FeCrAlloy foams, making a comparison with results obtained at FeCrAlloy plates. The study mainly focused on the effect of some parameters of the electrolytic bath such as anions (chloride or nitrate), presence or absence of precipitating cations, as well as aerated and de-aerated conditions on the electrochemical processes. The results indicated that nitrate reduction, but also oxygen reduction and hydrogen evolution, occur at the FeCrAlloy foam interface generating the basic media, evidencing a catalytic effect of cations in reduction processes (Ho et al., 2016). However, the effect of the concentration of nitrates, in absence of precipitating cations, and of metal nitrate salts, was not investigated.

Hence, the aim of this work is to further elaborate the knowledge about the deposition of Mg/Al HT compounds on metal foams by understanding the effect of nitrate concentration on both electrochemical and chemical processes as well as how they are modified by the deposition time. Potential scans or cathodic pulses were applied to foams dipped into solutions with different nitrate concentrations in both presence and absence of Mg²⁺ and Al³⁺ cations. The pH developed near the surface of the supports was measured and the composition and morphology of solids obtained at several deposition times were characterized by SEM/EDS and HRTEM/STEM. The deposition conditions were those reported for the preparation of structured catalysts: -1.2 V vs SCE for 2000 s and total metal concentrations of 0.03, 0.06 and 0.10 M, with a Mg/Al atomic ratio (a.r.) equal to 3/1. KNO₃ concentrations were chosen in order to add the same nitrate concentrations (0.0675, 0.135, 0.225 M) as those deriving from the metal salts. For comparison purposes and to characterize the deposited solids by XRD, ATR and Raman, some experiments were also performed using FeCrAlloy plates.

2. Materials and methods

2.1. Electrochemical measurements

Electrochemical experiments were performed in a single-compartment three-electrode cell using a potentiostat (Autolab, PGSTAT1128N, Eco Chemie) with GPES software as reported elsewhere (Ho et al., 2016). Working electrodes were open-cell foam cylinders (0.4 × 1.19 cm, approximately 0.2 g) and plates (0.6 × 1.5 × 0.01 cm) made of FeCrAlloy. The counter electrode was a Pt cylindrical grid (approximately 18 cm²) while a saturated calomel electrode (SCE) was used as reference electrode and all potentials were quoted vs SCE. Before performing experiments, the open-cell foams were rinsed with acetone and water, and then dried at 60 °C, while the plates were mechanically polished with a 210 grit SiC emery paper, then rinsed with distilled water–soap–distilled water and dried at 60 °C. The roughness of the plates increased by ~30% after abrasion. The electrical contacts for the foams or plates were made of a platinum or a copper wire, respectively; as described elsewhere (Benito et al., 2015a; Ho et al., 2016).

Electrolytic solutions were prepared using ultra-pure deionised water (UPW) provided by a Millipore filtration instrument (electrical resistivity 18.2 MΩ cm). Aqueous solutions of KNO₃ with concentrations from 0.0675 to 0.225 M were prepared and the initial pH of solutions was adjusted to 3.8 by adding 0.10 M HNO₃. The study of the electrodeposition of Mg/Al HT compounds was conducted in aqueous solutions containing a mixture of Mg(NO₃)₂ and Al(NO₃)₃ with Mg/Al = 3/1 a.r. and total metal concentration of 0.03, 0.06, or 0.10 M.

These concentrations provided a pH around 3.5–3.7 at 20 °C. It is noteworthy that the concentrations of KNO₃ solution were set to keep the same total nitrate concentration as in corresponding Mg/Al-NO₃ solutions for comparison purposes, for example, KNO₃ 0.0675 M and Mg/Al-NO₃ (Mg/Al = 3/1 a.r.) 0.03 M contained both a total nitrate concentration of 0.0675 M.

The uncompensated resistance (R_u) in the electrochemical cell was measured by a CH Instruments Mod. 660A, according to the method proposed by He and Faulkner (1986). All the experiments were repeated thrice. The R_u values decreased by increasing the total metal concentration, 2.5 Ω for 0.03 M and 1.5 Ω for 0.06 M and 0.10 M solutions. The low R_u values led to small Ohmic drops (smaller than 50 mV) in most of the experiments. However, when a high current was recorded, potential scans were corrected by Ohmic drops, assuming a constant R_u during the scans.

Linear Sweep Voltammetries (LSVs) were recorded at 1 mV s⁻¹ scan rate, to reach the steady-state, in a potential range from 0 to -1.4 V. Potentiostatic cathodic reductions were carried out at -1.2 V for 100 to 2000 s, under natural convective conditions. Current densities were plotted using the electroactive area of the foam, 4.13 ± 0.17 cm², calculated elsewhere (Ho et al., 2016), under LSV (50 mV s⁻¹) for the one-electron reduction of K₃[Fe(CN)₆] by means of the Randles-Sevcik equation.

2.2. Characterization of the coatings

Scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) analyses were performed using an EP EVO 50 Series Instrument (EVO ZEISS) equipped with an INCA X-act Penta FET® Precision EDS microanalysis and INCA Microanalysis Suite Software to provide images of the spatial variation of elements in a sample (Oxford Instruments Analytical). An accelerating voltage of 20 kV was applied with a spectra collection time of 60 s, and point measurements were performed in 10–15 regions of interest. Secondary electron images were collected. Layer thicknesses were approximately estimated from the inspection of secondary electron images where cracks were present. In each sample, Mg/Al ratios were obtained from EDS spectra of regions in which the contribution of Al coming from the alloy was subtracted based on standard signal of Fe.

The X-ray diffraction (XRD) analysis of the film grown on FeCrAlloy plates was carried out using a PANalytical X'Pert diffractometer equipped with a copper anode ($\lambda_{\text{mean}} = 0.15418$ nm) and a fast X'Celerator detector. Wide-angle diffractograms were collected over 2θ range from 5 to 40° with a step size of 0.07° and counting time 60 s.

Attenuated Total Reflection (ATR) measurements were recorded by using a Bruker Alpha instrument equipped with a diamond crystal. The analyses were performed on the coated FeCrAlloy plates. Each spectrum in the 4000–400 cm⁻¹ range was accumulated from 32 individual measurements recorded by a nominal resolution of 2 cm⁻¹ in order to minimize the noise signal.

Micro-Raman measurements were performed in a Renishaw Raman Invia configured with a Leica DMLM microscope (obj. 5 ×, 20 ×, 50 ×). The available sources are an Ar⁺ laser (514.5 nm, P_{max} = 30 mW) and a diode-laser (780.0 nm, P_{max} = 300 mW). The system is equipped with edge filters to cut Rayleigh scattering, monochromators (1800 lines/mm for Ar⁺ laser, and 1200 lines/mm for diode laser) and a Charge-Coupled Device (CCD) thermoelectrically cooled (203 K) detector. Measurements were performed with the Ar⁺ Laser (514.5 nm) at power level P_{out} = 3 mW. Each spectrum was recorded by four accumulations and time for each accumulation was 30 s.

High-resolution transmission electron microscopy (HRTEM) characterization was carried out by a TEM/STEM FEI TECNAI F20 microscope, equipped with an EDS analyser. Powder materials were collected by scratching the foam surface and then suspended in ethanol under ultrasounds for 20 min. The suspension was subsequently deposited on an Au grid with lacey multi-foil carbon film and dried at 100 °C before doing the measurement.

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