Electrochimica Acta 117 (2014) 164–171

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Influence of preparation conditions of Layered Double Hydroxide conversion films on corrosion protection

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ARTICLE INFO

Article history:
Received 17 June 2013
Received in revised form
15 November 2013
Accepted 19 November 2013
Available online 4 December 2013

Keywords:
LDH conversion films
Corrosion
Active Protection
EIS

ABSTRACT

In this work, layered double hydroxide (LDH) conversion films were grown on aluminium alloy 2024 substrates. The effect of experimental conditions on the growth of LDH conversion films, including concentration of reactants and presence of corrosion inhibitor, was investigated. The protective performance provided by LDH films was assessed by electrochemical impedance spectroscopy (EIS), and rationalised in terms of structural and morphological characteristics surveyed by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The results show that corrosion protection increases when corrosion inhibitors (vanadates) are intercalated in LDHs and dilute solutions of Zn^{2+} are used to grow LDHs.

1. Introduction

The development of coating systems for protection of metallic substrates against corrosion is currently taking different directions in order to obtain the so-called ‘smart coatings’, responsive systems capable of feedback when subjected to stimuli from the environment. One strategy has consisted of incorporation of micro and nanocontainers loaded with corrosion inhibitors in sol-gel films [1] or industrial formulations [2] to confer active protection to the underlying substrate on demand. The nanocontainers can release the inhibitors depending on pH, presence of aggressive species, mechanical impact and other type of stimuli coinciding with coating degradation and/or corrosion initiation. However, the loading of inhibitor in the coating required to confer effective corrosion protection during the service life of a structure is limited by the amount of nanocontainers that can be dispersed without affecting coating performance negatively. Recently, Tedim et al. [3] suggested that combination of different nanocontainers with corrosion inhibitors showing that synergistic effects could be used to enhance the protective action. Also, the presence of nanocontainers in layers closer to the metal substrate was found to play an important role in corrosion protection.

Another perspective for considering the release of inhibitors from a coating layer is to use the intrinsic characteristics of certain polymers to entrap and release corrosion inhibitors in a controlled way. This would solve the problem of low loading of corrosion inhibitors in the coating, providing at same time mechanisms for feedback active release of species. In this context, Kendig et al. showed the possibility of applying conjugated polymers as reservoir layer for corrosion inhibitors that worked as dopant ions, being released depending on the electrochemical activity at defect sites [4]. Another possibility for using of polymeric layer reservoirs for corrosion inhibitors was shown in the works of Zheludkevich and colleagues [5–8], with environmentally-friendly chitosan as pre-layer reservoirs for cerium cations coated with a sol-gel overlayer, demonstrating self-healing of defects for aluminium alloys [5]. In spite of the aforementioned results, high-performance coatings are required to meet different parameters, including adhesion. It is well known that upon reduction conducting polymers become less adherent to metal surfaces [9] and that the interaction between common organic coatings and active metals like aluminium alloys often require an intermediate (inorganic) layer capable of promoting adhesion, such as conversion films. Conversion coatings are prepared by chemical or electrochemical treatment of the metal surface to produce a superficial layer of metal oxides, phosphates or chromates chemically bonded to the surface [10]. LDHs have been investigated as conversion films directly grown on magnesium and aluminium alloys [11–18], from which the pioneering works of Buchheit et al. are highlighted [17,18]. In these works Buchheit and colleagues developed LDH coatings from oxidizing baths to grow hydrotalcite films. In one of these studies the authors prepared conversion films to provide barrier (passive) effect against the ingress of aggressive species, via sealing of the pores [17]. In

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http://dx.doi.org/10.1016/j.electacta.2013.11.111

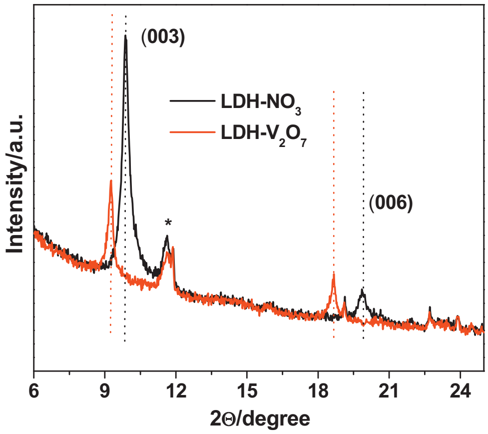

Figure 1. XRD patterns obtained for LDH films, intercalated with nitrates (black lines) and vanadates (red lines). Asterisk denotes the (003) diffraction reflection of an LDH-CO$_3$ phase. Small undesignated peaks in all XRD patterns belong to the intermetallic inclusions (for more details see Ref [19]).

the other work cerium (Ce)-containing LDH layer was prepared to confer active corrosion protection functionality [18]. According to the results obtained, when Ce^{4+} compounds are in contact with solution they tend to dissolve, migrate, reduce and consequently precipitate as low soluble compounds on exposed Al sites. There are no X-ray diffraction (XRD) data available in this study, but intercalation of Ce^{4+} within LDH galleries, and consequently controlled release, is not expected into a great extent as LDHs tend to intercalate mostly anions and water molecules [2]. In some more recent studies hydrophobic anions have been used to confer hydrophobicity and delay the ingress of water and aqueous species [11,12], and carbonate anions have been intercalated to decrease anion-exchange capability and thus avoid the ingress of chlorides [13–16]. Nevertheless, the complexity of preparation and lack of active corrosion protection through presence of corrosion inhibitors can be determining factors when considering industrial applications. Very recently, Tedim and co-workers reported the synthesis of LDH layers directly grown on aluminium AA2024, showing a differentiated structure [19]. The applied methodology explores the weakness of the aluminium oxide layer for differentiated growth of island-like LDHs. This latter study was also the first report of the formation of LDH conversion films with corrosion inhibitors directly intercalated within LDH galleries, which are directly grown from soluble solution species. Moreover, XRD data confirmed the release of corrosion inhibitor by exchange with chlorides available in the electrolyte solution. [19]

The present work reports a detailed investigation of the effect of different experimental conditions on the growth of LDH conversion films, and on the active corrosion protection provided by LDH films loaded with vanadates to the underlying aluminium alloy 2024-T3, something that was only partially addressed in our previous work [19]. Vanadates were chosen due to their well-known inhibiting properties towards AA2024 [20]. The protective performance provided by LDH films is assessed by electrochemical impedance spectroscopy (EIS) and rationalised in terms of structural and morphological characteristics by XRD and scanning electron microscopy (SEM).

2. Experimental

2.1. Chemicals

All the chemicals were obtained from Aldrich, Fluka and Riedel-de Häen, with ≥ 98% of ground substance, and used as received.

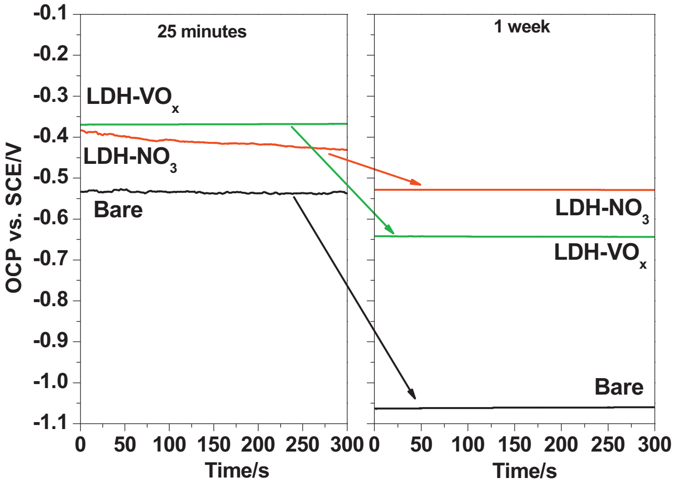

Figure 2. OCP recorded before acquisition of EIS spectra shown in Figure 3 after 25 minutes and 1 week of immersion (vs. SCE).

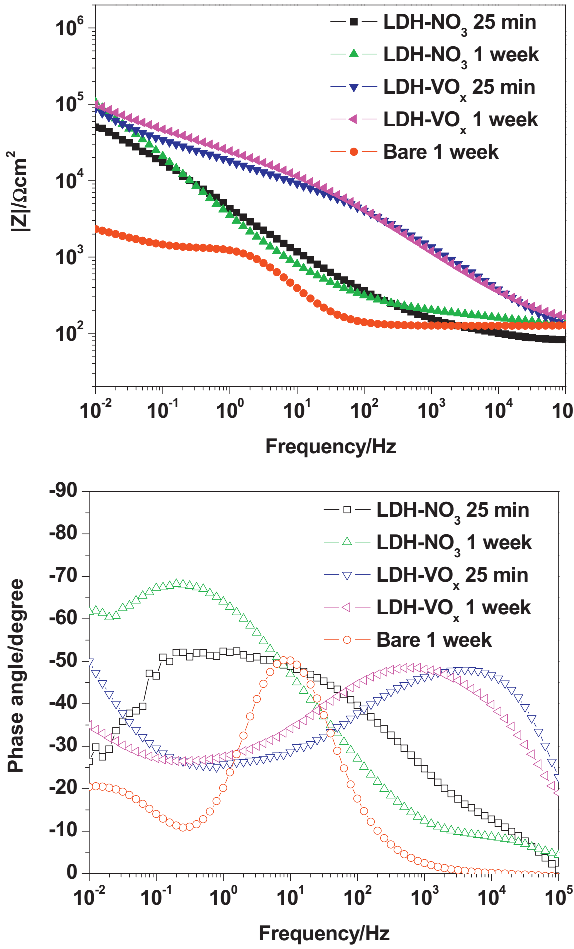

Figure 3. a) EIS spectra acquired for AA2024-T3 in 0.05 M NaCl after growth of LDH-NO$_3$ and LDH-VO$_x$ conversion films (prepared with 5 mM Zn^{2+} solution); b) comparison with reference sample (bare AA2024 after pre-treatment) for 1 week of immersion.

2.2. Preparation of metallic substrates

AA2024-T3 plates were surface treated using 0.1 M NaHO during 60 s. Before and after this treatment all the plates were washed with deionized water and ethanol.