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Cast iron corrosion protection with chemically modified Mg-Al layered double hydroxides synthesized using a novel approach

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Abstract

Layered double hydroxides (LDHs) intercalated with corrosion inhibitive species are considered as promising additives to protection coatings. However, the conventional method of LDH preparation via co-precipitation followed by anion exchange is a water consuming and slow process hardly applicable to industrial use.

In this work, a novel approach to LDH synthesis via hydration of sol-gel prepared mixed metal oxides and two-step anion exchange, all assisted by high-power sonication, was applied. Mg-Al and Mg-Al-Ce LDH with cations ratios 2:1 and 2:0.9:0.1, respectively, intercalated with corrosion inhibitive dihydrogen phosphate anion were successfully prepared.

The obtained LDH were characterized by X-ray diffraction and scanning transmission electron microscopy. Anion release from these LDH in NaCl solutions and their corrosion inhibitive action on cast iron samples were monitored by electrochemical impedance spectroscopy. The results show that the dihydrogen-phosphate-intercalated LDHs produced using the novel technique are efficient in corrosion protection.

Keywords: layered double hydroxide, corrosion protection, sol-gel, high-power sonication, anion-exchange

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1. Introduction

A wide variety of protective coatings from one-layer coatings to complex combinations are used nowadays on metallic structures owing to the easy application and cost efficiency.[1] Coating performance is dependent on intrinsic properties of the film (barrier properties), substrate/coating interface and the inhibitive pigments used to prevent corrosion in aggressive environments.

A great attention is paid to the development of new protective materials that can replace toxic chromium (VI) based compounds as effective corrosion inhibitors. A number of organic and inorganic species intercalated into layered structures has been proposed and optimized for application in protective coatings [1]. LDH crystallites act as smart nanocontainers that release the inhibitive species only when corrosion conditions occur [2].

Layered double hydroxides (LDHs) are composed of positively-charged mixed metal $M^{\text{II}}-M^{\text{III}}$ hydroxide layers with charge-compensating anions A^{y-} and water molecules intercalated between layers [3]. Metal cations in the layers are coordinated by six oxygen atoms forming 2-D structures of edge-linked oxygen octahedra. General formula of most common LDHs can be represented as $[M^{\text{II}}_{1-x}M^{\text{III}}_x(\text{OH})_2]^{x+}(A^{y-})_{x/y}\cdot z\text{H}_2\text{O}$. Parameters x and z can vary over wide ranges thereby enabling flexibility of the LDH structure and allowing intercalation of anions with different sizes and charges [3–6].

LDH are typically characterized by hexagonal symmetry with the c -axis perpendicular to the layers (space group $R\bar{3}m$) [7]. Parameter a is a function of both size and ratio of cations M^{II} and M^{III} [8,9]. The c parameter depends mainly on size, charge and orientation of the intercalated species [8,10,11].

The main method of LDH production is co-precipitation followed by anion-exchange (Miyata approach [12]). This method is rather direct and reproducible; however, it is slow and water-consuming.

In this work, we report on the layered double hydroxides of the $[\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2]^{x+}(A^{y-})_{x/y}\cdot z\text{H}_2\text{O}$ system (hereafter $\text{Mg}(n)\text{Al-A}$, where $n=(1-x)/x$ is the Mg/Al molar ratio) prepared using a novel approach. This approach is less water consuming than the conventional co-precipitation one since excludes several stages of the LDH washing. $\text{Mg}(2)\text{Al-OH}$ LDH was formed by hydration of a mixture of metal oxides prepared via the sol-gel followed by intercalation with dihydrogen phosphate anion after successive anion exchanges $\text{OH}^- \rightarrow \text{Cl}^-$ and $\text{Cl}^- \rightarrow \text{H}_2\text{PO}_4^-$. The stages of synthesis and anion exchange were considerably accelerated by application of high-power sonication. In addition, a phosphate-intercalated $\text{Mg}(2)\text{Al}$ LDH with 10 mol.% of aluminium substituted by Ce^{III} , $\text{Mg}(2)\text{Al-10\%Ce-H}_2\text{PO}_4$, was prepared by

same procedures. Cerium-substituted LDH was suggested to exhibit additional protection functionality owing to corrosion-inhibitive properties of Ce^{III}-containing species: the products of decomposition of the nanocontainer itself may additionally provide useful effects.

Obtained LDHs were characterized by X-ray diffraction (XRD) and scanning transmission electron microscopy (STEM). The inhibition efficiency and the protective properties of the released phosphate on the cast iron substrate were evaluated using electrochemical impedance spectroscopy.

The final objective of this work was to study the corrosion protection functionality of the layered double hydroxides synthesized using a novel approach, including LDHs whose metal hydroxide layers were modified with cerium.

2. Experimental

2.1. Materials

Aluminium nitrate nonahydrate ($\geq 98.5\%$), magnesium nitrate hexahydrate ($\geq 99\%$), cerium nitrate hexahydrate (99.99%), sodium chloride (99.9%), ethylene glycol (99%), hydrochloric acid (36%), were purchased from Sigma-Aldrich, Sodium phosphate dibasic dihydrate ($>98\%$) was purchased from Carl Roth, and nitric acid (66%) from REACHEM. Deionised and decarbonised water was used in all solutions for synthesis and anion exchange as well as for washing final compounds.

The cast iron (GG20) samples were provided by SEW-EURODRIVE Portugal LDA.

2.2. Synthesis of magnesium-aluminium and magnesium-aluminium-cerium LDH via sol-gel method

Sol-gel method in LDH preparation [13] emerged as an alternative to the conventional co-precipitation method.

Appropriate metal nitrates were dissolved in 50 ml of distilled water with addition of 50 ml of 0.2 M nitric acid. To prepare Mg-Al (Mg-Al-Ce) metal oxides, the solutions were mixed with a molar ratio of Mg:Al = 2:1 (Mg:Al:Ce = 2:0.9:0.1). The obtained mixtures were stirred for 1 h at 80°C. Then 2 ml of ethylene glycol was added with continuous stirring for 4 h at the same temperature. After slow evaporation of solvent, the obtained gel was dried at 130°C for 12 h. Mixed metal oxides (MMO) of the Mg(2)Al and Mg(2)Al-10%Ce cation compositions were produced by calcination of the dried gel powders for 3 h at 650°C. The layered double hydroxides were formed as a result of hydration of the MMO powders in deionized water at room temperature. To accelerate the process, high-power sonication was applied for 30 min. This stage of LDH formation (synthesis) as well the sonication-assisted

anion exchange reactions were performed using a VCX 1500 Sonics processor (max output power 1.5 kW at 20 kHz) equipped with a high-volume continuous flow cell.

The final powder LDH samples were obtained by vacuum filtration followed by drying at 60°C for 24 hours.

2.3. Anion exchange and formation of chlorine- and phosphate-intercalated LDH

At the hydration stage of MMO in deionised and decarbonised water, the only available anion for intercalation was OH⁻. Obtained LDH were Mg(2)Al-OH and Mg(2)Al-10%Ce-OH. It was recently shown that direct hydroxide-to-phosphate anion exchange is unlikely but can be implemented via formation of the intermediate chlorine-intercalated phase [14].

For a OH⁻ → Cl⁻ anion-exchange, 1 g of Mg(2)Al-OH was added to 250 ml of 1 M NaCl solution at room temperature. The mixture was sonicated for 4 min. The obtained slurry was put in vacuum filtration without any additional washing and dried for 24 hours at 60°C.

Chloride-to-phosphate anion exchange was carried out in a 0.1 M Na₂HPO₄ solution at room temperature. 1 g of the Mg(2)Al-Cl powder was immersed in the solution followed by addition of NaH₂PO₄ to adjust the pH value to 7.5. At such conditions, the intercalated anion is dihydrogen phosphate, H₂PO₄⁻ [14]. The reaction was sonication-assisted and took 8 min. The obtained slurry was filtered and dried at the same conditions as mentioned above.

Similar process was used for the hydroxide-to-chloride and chloride-to-phosphate exchange reactions in Mg(2)Al-10%Ce LDHs.

2.4. Analytical characterization

X-ray diffraction (XRD) characterization of all LDH compositions was performed using a PANalytical X'Pert Powder diffractometer (Ni-filtered Cu K α radiation, Theta-Theta goniometer in the reflection mode, PIXcel 1D detector, step 0.02°, exposition time ~1.5 s per step) at room temperature.

Observations of particle shapes and agglomerations were carried out using a Hitachi HD-2700 scanning transmission electron microscope (STEM) in both bright field and HAADF (High-angle annular dark field) modes with accelerating voltage of 200 kV. Small amounts of the LDH slurries of each composition were dispersed in ethanol solution using an ultrasound bath and deposited on TEM grids.

2.5. Electrochemical characterization

For the electrochemical measurements, a three-electrode cell with a large platinum auxiliary electrode, a saturated calomel reference electrode (SCE) and a working electrode with an exposed area of 1 cm² bare cast iron was used.

The electrochemical impedance measurements were performed using the Autolab PGSTAT30 over a frequency range of 100 kHz–10 MHz with seven points per decade.

A 50 mM NaCl solution prepared by adding NaCl (reagent grade) to distilled water served as corrosive medium. To analyse the inhibitor efficiency in aqueous media, three different conditions were applied. First, the cast iron samples were immersed in a 50 mM NaCl solution with pH 6.73, to evaluate the resistance of the metal in the aggressive environment. In the second case, 0.071 g of NaPO₄ was added to 50 mM NaCl solution (100 ml) to form a solution of 5 mM NaPO₄ and 50 mM NaCl with pH 8.55. In the third case, 0.25 g of phosphate-intercalated LDH, with molar mass of 50 g / mol, was added to the 50 mM NaCl solution (100 ml) to obtain a solution of 5 mM phosphate-intercalated LDH + 50 mM NaCl with pH 8.65. Three samples were tested for each the above-mentioned solutions to ensure reproducibility of the measurements.

3. Results and discussion

3.1. Analysis of phase content and chemical composition

XRD patterns of powders from the high-power sonication assisted synthesis and of successive anion exchanges are shown in Figure 1. The typical diffraction reflections representing the $R\bar{3}m$ LDH structure are observed in all patterns.

Analysis of the XRD patterns of as-synthesized Mg(2)Al-OH and Mg(2)Al-10%Ce-OH confirmed the formation of single-phase LDH compositions. The XRD patterns of the compositions obtained as a result of the anion exchanges demonstrated a regular shift of the diffraction peaks of the (00 l) family towards lower angles indicating that the hydroxide-to-chloride and chloride-to-phosphate substitutions were complete. As seen from Figure 1, the former is accompanied by a considerable increase of the basal spacing (the distance between the neighbouring hydroxide layers).

Lattice parameters a and c of the obtained LDH were calculated using the inter-planar distances corresponded to the angular positions of the diffraction peaks (003), (006) and (110) as $c = 3/2[d_{(003)} + 2d_{(006)}]$ and $a = 2d_{(110)}$ [3]. Values of the lattice parameters are listed in Table I. Basal spacing was calculated as $d=c/3$, and the interlayer height (gallery height, h) was found by subtracting the hydroxide layer thickness from the basal spacing value. The Mg(2)Al hydroxide layer thickness was considered to be 0.477 nm [15]. The gallery height values calculated for Mg(2)Al-OH and Mg(2)Al-Cl are in a good agreement with double van der Waals radii of oxygen and chlorine, respectively. The h -value estimated for Mg(2)Al-

H_2PO_4 suggests that the phosphate anion is arranged in a such way that a line along its maximum dimension is perpendicular to the layer plane [14].

The lattice parameters values of cerium-substituted LDH compositions were found to be regularly higher than the corresponding values of Mg(2)Al LDH intercalated with the same anions (see Table I). This reflects the increase of the hydroxide layer thickness caused by a partial substitution of Al^{3+} by a larger sized Ce^{3+} . The observed values of a -parameter of Ce-substituted LDHs were found to be in good with the calculated using the expression proposed by Richardson (Ref [16]) for the case of two different trivalent cations:

$$a_{LDH} = a_{Mg(OH)_2} - \frac{1}{2} \sin\left(\frac{\alpha}{2}\right) [r(Mg^{2+}) - (1-x)r(Al^{3+}) - xr(Ce^{3+})]$$

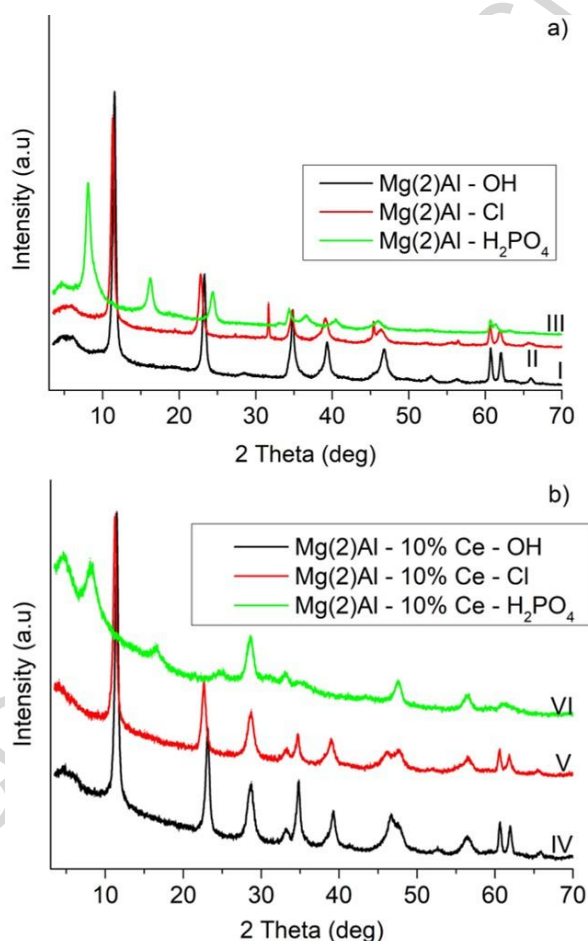


Figure 1. XRD patterns of the compositions produced by hydration of the sol-gel prepared mixed metal oxides followed by two-step (hydroxide-to-chloride and chloride-to-phosphate) anion exchange: a) - Mg(2)Al-OH (I), Mg(2)Al-Cl (II), and Mg(2)Al- H_2PO_4 (III); b) - Mg(2)Al-10%Ce-OH (IV), Mg(2)Al-10%Ce-Cl (V), and Mg(2)Al-10%Ce- H_2PO_4 (VI).

Table I. The lattice parameters (a , c) and basal spacings (d) for the LDH compositions intercalated with different anions.

Composition	c , nm	a , nm	d , nm
Mg(2)Al-OH	2.2950	0.3049	0.7650
Mg(2)Al-Cl	2.3426	0.3052	0.7808
Mg(2)Al-H ₂ PO ₄	3.2662	0.3051	1.0887
Mg(2)Al-10%Ce-OH	2.3100	0.3052	0.7700
Mg(2)Al-10%Ce-Cl	2.3565	0.3052	0.7855
Mg(2)Al-10%Ce-H ₂ PO ₄	3.2945	0.3054	1.0981

3.2. Microscopy characterization

STEM was used to visualize possible effect of high-power sonication applied during synthesis on the crystallite size of LDH. For this purpose, Mg(2)Al-OH was prepared using the procedure described in *Experimental* but without sonication. The MMO powder was hydrated in deionized water under continuous stirring for 12 h [14]. STEM images of particles/crystallites of Mg(2)Al-OH and Mg(2)Al-10%Ce-OH LDH obtained with or without the ultrasound treatment are shown in Figure 2.

In all the above-mentioned cases, hexagonal flake-shaped crystallites inherent to the layered double hydroxides were observed. The characteristic size (diameter) of the flakes was estimated to range from 50 to 150 nm. It should be noticed here that the typical size of Mg(2)Al LDH prepared using the conventional methods via co-precipitation from nitrates is in the range of 50-200 nm [6].

Based on comparative analysis of series of the STEM images, we concluded that the high-power sonication did not impact either size or shape of the LDH crystallites. But, the crystallites of LDH produced with application of ultrasounds were found to be less agglomerated.

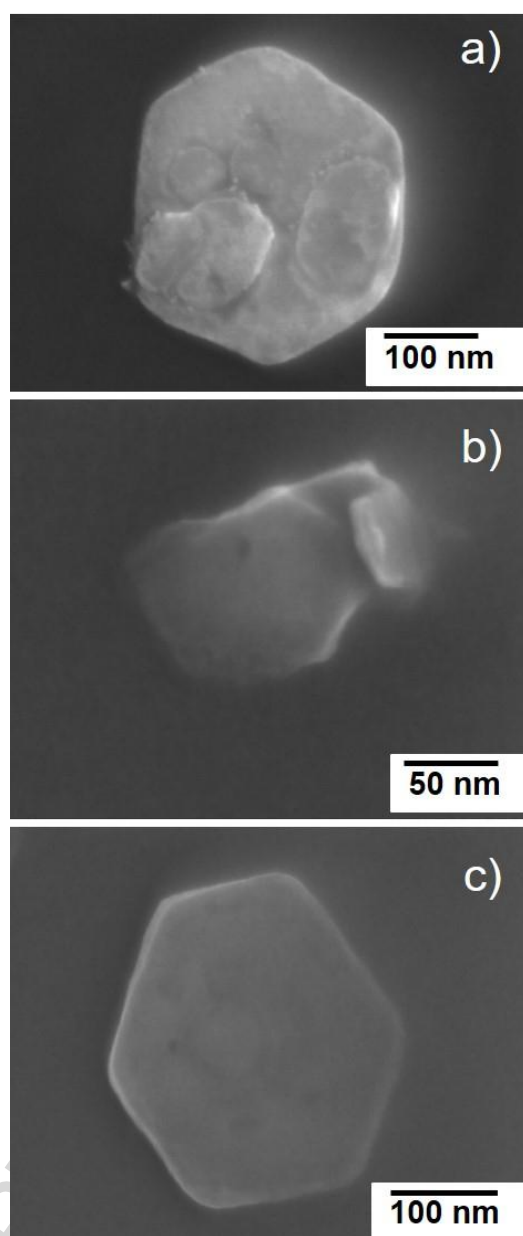


Figure 2. STEM images of fully dispersed LDH particles/crystallites: a) - Mg(2)Al-OH produced by hydration of the sol-gel prepared mixed metal oxides *without* high-power sonication, b) and c) - Mg(2)Al-OH and Mg(2)Al-10\%Ce-OH , respectively, produced by sonication-assisted hydration of the sol-gel prepared mixed metal oxides.

3.3 Electrochemical characterization and corrosion protection

EIS was used to evaluate the corrosion progress in the solutions containing corrosion-inducing and corrosion inhibitive species.

Initially, the cast iron substrates were immersed in two test solutions (50 mM NaCl and 50 mM NaCl + 5 mM Na_2HPO_4) as described in *Experimental* to reveal the effect of

phosphate anions on the sample surface in a corrosive media. Figure 3 shows the EIS spectra acquired after 2 to 168 h of immersion in the solutions.

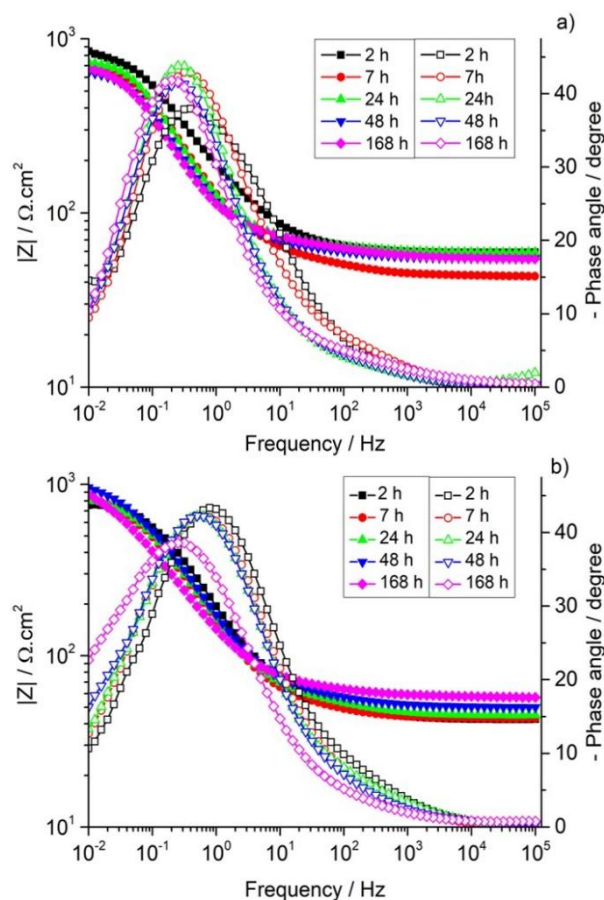


Figure 3. EIS spectra for the cast iron substrate immersed a) in a 50 mM NaCl solution and b) in a 50 mM NaCl + 5 mM Na₂HPO₄ solution (Solid symbols denote the total impedance, empty symbols denote the phase angle).

Total impedance ($|Z|$) at relevant frequencies is the main parameter used for corrosion activity assessment in all studied substrate-solution systems.

It has been observed that the impedance decreased immediately after the first minute of immersion of the iron substrate in the 50 mM NaCl solution. The values of impedance observed in the spectra in Figure 3a suggest the formation of corrosion products on the surface of the sample, justifying the slow decrease of low frequency impedance through the 168 h of measurement.

When the sample is immersed in the solution containing Na₂HPO₄ (Figure 3b) the impedance values is stable at least during 24 h. After this period of time, due to oxide formation and deposition of phosphate on the substrate, the values of $|Z|$ increase again; however, a part of the sample was kept protected even after one week of immersion.

The images of the cast iron substrates immersed for one week in a NaCl solution either without or with the corrosion inhibitive species are shown in Figure 4.

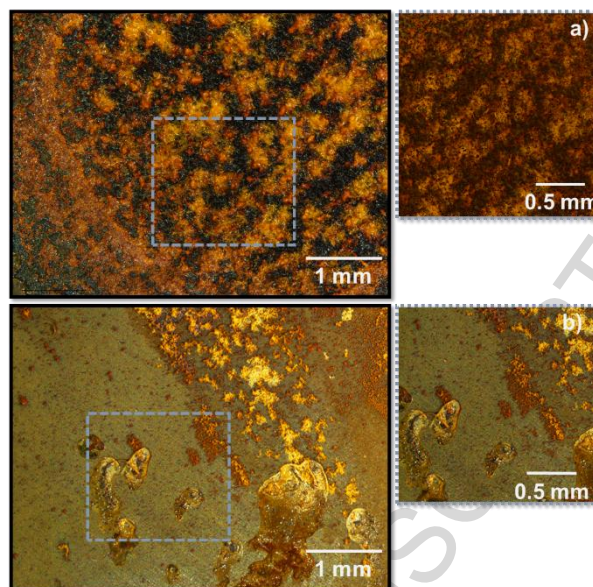


Figure 4. The cast iron substrates after 1-week immersion a) in a 50 mM NaCl solution and b) in a 50 mM NaCl + 5 mM Na₂HPO₄ solution.

Images in Figure 4 indicate that phosphate species are effective for corrosion protection of cast iron when introduced in the 50 mM NaCl solution. The presence of corrosion signs (pitting corrosion) on the surface of the sample in Figure 4b can be explained by the insufficient amount of phosphate species (5 mM Na₂HPO₄ in a 50 mM NaCl solution) to protect the entire surface.

The next step of the study was an immersion test using the inhibitive species intercalated into the LDH produced using the novel approach, Mg(2)Al-H₂PO₄. The same test was also performed in the solution containing Mg(2)Al-OH for comparison. Figure 5 shows the EIS spectra acquired after 2 to 168 h of immersion in the respective solutions.

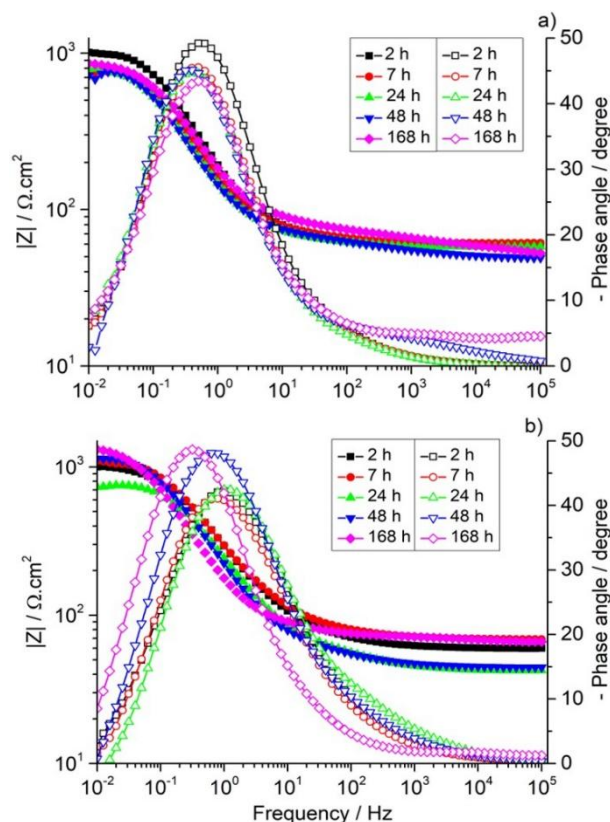


Figure 5. EIS spectra for the cast iron substrate immersed in solutions containing the layered double hydroxides a) 50 mM NaCl + 5 mM Mg(2)Al-OH and b) 50 mM NaCl + 5 mM Mg(2)Al-H₂PO₄. (Solid symbols denote the total impedance, empty symbols denote the phase angle).

Mg(2)Al-OH layered double hydroxide in a NaCl solution releases OH⁻ and traps Cl⁻ increasing the pH to 12. Since hydroxide anion has no corrosion inhibitive ability, the impedance values slowly decrease until formation of iron oxide (Figure 5a). After about 48 h of immersion, the hydroxide-to-chloride anion exchange reaction seems to be completed and the local decrease of chloride ions causes partial protection of the cast iron (the plot at 168 h).

Figure 5b shows a gradual increase of the impedance after 24 h and until one-week immersion in a 50 mM NaCl + 5 mM Mg(2)Al-H₂PO₄ solution that indicates the effective anticorrosion performance of the Mg(2)Al-H₂PO₄ LDH as a nanocontainer of inhibitive species that releases H₂PO₄⁻ and captures Cl⁻. The final aspect of the sample (Figure 6) with less pitting corrosion in the surface was better than the one after the same time of immersion in a 50 mM NaCl + 5 mM Na₂HPO₄ solution (Figure 4b) although the amounts of phosphates in both tests were the same.

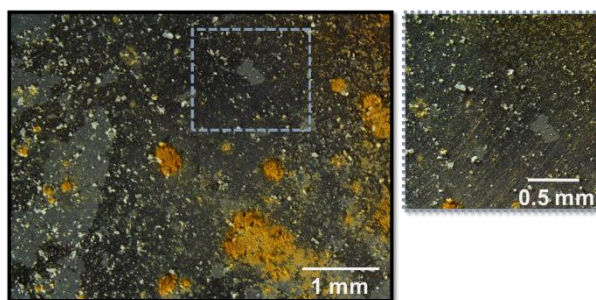


Figure 6. The cast iron substrate after a 1-week immersion in a 50 mM NaCl solution with addition of 5 mM Mg(2)Al-H₂PO₄ LDH.

To support the results obtained from the immersion test, an XRD study of the corrosion products collected from the surface of the samples after 1-week immersion was performed.

Figure 7 shows the XRD patterns of the products precipitated/formed on the surface of each cast iron sample.

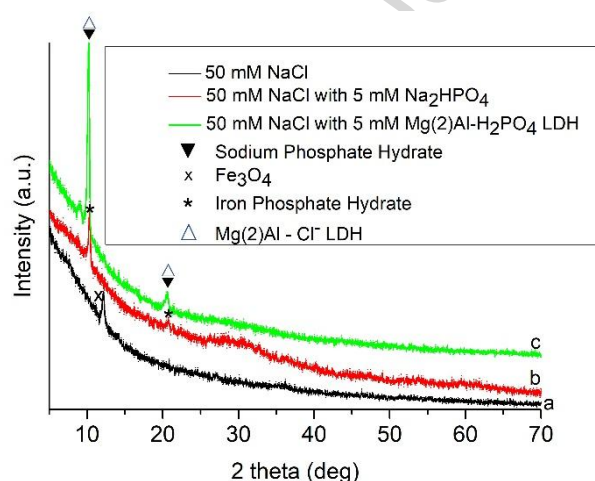


Figure 7. XRD patterns of the corrosion products collected from the cast iron substrates immersed a) in a 50 mM NaCl solution, b) in a 50 mM NaCl + 5 mM Na₂HPO₄ solution and c) in a 50 mM NaCl + 5 mM Mg(2)Al-H₂PO₄ LDH solution.

It is seen from Figure 7 that immersion in these three solutions resulted in precipitation and formation of different phases on the sample surface. The corrosion product formed in case of immersion in a 50 mM NaCl solution (the pattern *a*) is an iron oxide that is in good agreement with the optical photo (Figure 4a). The XRD pattern *b* demonstrates a presence of iron phosphate hydrate. It is suggested that chlorine anions promote dissolution of iron from the substrate followed by reaction with Na₂HPO₄ in the solution and a precipitation of iron phosphate. The corrosion products collected from the surface of the sample immersed in a 50 mM NaCl + 5 mM Mg(2)Al-H₂PO₄ LDH solution (the pattern *c*) seems to contain an LDH phase with the angle positions of the basal diffraction reflections that correspond to those of

Mg(2)Al-Cl LDH. However, as its pattern overlaps that of sodium phosphate hydrate a distinction cannot be done. Also, peaks for iron phosphate hydrate can be found in the same sample.

The corrosion protection functionality of a Ce-substituted layered double hydroxide intercalated with dihydrogen phosphate was also studied. The EIS results obtained for the samples immersed in the NaCl solution containing Mg(2)Al-10%Ce-H₂PO₄ for 2-168 h were found to be essentially similar to those presented above for the case of Mg(2)Al-H₂PO₄ LDH. As mentioned in Introduction (lines 69-70), Ce^{III}-containing species in the products of decomposition of the LDH nanocontainer itself may provide additional protection effect. However, to estimate such an effect, a much longer immersion time is needed alongside with the continuous exposition of the Mg(2)Al-10%Ce LDH to UV radiation to promote the LDH degradation. This study is in progress.

4. Conclusions

High-power sonication assisted synthesis and anion-exchange were successfully applied to produce LDH intercalated with dihydrogen phosphate (H₂PO₄⁻), demonstrating this novel approach as an efficient alternative to the conventional co-precipitation synthesis technique.

Parent OH⁻-intercalated LDH with cation compositions Mg(2)Al and Mg(2)Al-10%Ce were synthesized by hydration of sol-gel prepared mixed metal oxides. Mg(2)Al-H₂PO₄ and Mg(2)Al-10%Ce-H₂PO₄ LDH were obtained from the parent compositions via sequential anion exchanges from OH⁻ to Cl⁻ and from Cl⁻ to H₂PO₄⁻, respectively. Application of high-power sonication at the stages of synthesis and anion exchange turns the processes to be much faster than when the conventional LDH preparation technique is used. Crystallites of the LDH produced using the novel approach are of dimensions and shape similar to those (hexagonal flake shaped, 50-150 nm sized) typical of Mg(2)Al LDH prepared using the conventional co-precipitation route.

Efficiency of the layered double hydroxides produced using the novel approach as nanocontainers was demonstrated via corrosion protection effect of dihydrogen phosphate released from these LDH on cast iron substrate in a NaCl solution.

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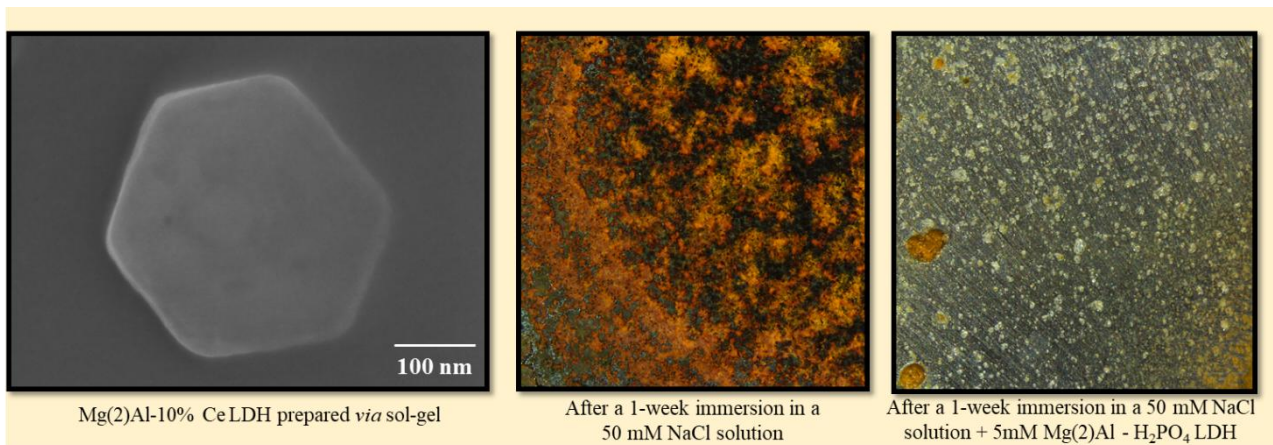
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Graphical abstract

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Highlights

Sol-gel route to ensure stoichiometry of chemically modified layered double hydroxides.

High-power sonication acceleration effect in layered double hydroxide synthesis.

Efficient corrosion protection via phosphate-intercalated layered double hydroxide.

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