The effect of synthetic zinc corrosion products on corrosion of electrogalvanized steel: I. Cathodic reactivity under zinc corrosion products

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The differences in the reactivity of carbon steel covered or not by a layer of electrochemically synthesized zinc corrosion products were observed in 0.85 M NaCl at different initial pH. The magnitude of the cathodic current \( j_\text{j} \) increases in the order: \( j_\text{j}(\text{steel}/\text{Na}_2\text{Zn}_4\text{(CO}_3\text{)}_4\text{H}_2\text{O})/j_\text{j}(\text{steel}/\text{Zn}_3\text{(OH)}_6\text{Cl}_2\text{H}_2\text{O})/j_\text{j}(\text{steel}/\text{Zn}_3\text{(OH)}_6\text{SO}_4\text{nH}_2\text{O})/j_\text{j}(\text{steel}/\text{Zn}_3\text{(OH)}_6\text{Cl}_2\text{H}_2\text{O})/j_\text{j}(\text{steel}) \). The inhibiting effect in the systems containing \( \text{Zn}_3\text{(OH)}_6\text{Cl}_2\text{H}_2\text{O} \) transformed from 2.5 and from 7.5 \( \mu \text{m} \) thick Zn-coatings is similar. Complex effect on cathodic reactivity of Zn is observed. The origin of the barrier effect and the possible role of iron ions for it are discussed.

1. Introduction

Zinc based coatings have been extensively used in automotive and housing for anti-corrosion protection of steel [1]. The benefits of zinc consist not only in its sacrificial protection \( (E_\text{pass} > E_\text{Zn}) \) but also in the “self-healing” effect offered by insoluble zinc corrosion products [2–4]. The corrosion behavior changes in the presence of different anions [5] but also under corrosion products [4,6–9]. This change can be partly understood by the modification of the kinetics of anodic and cathodic reactions in presence of corrosion product.

Anodic reactivity is sensitive to the presence of aggressive species like Cl\(^–\) [10,11] and hence the ion transport through the layer of corrosion product. The oxygen reduction reaction, the most important cathodic reaction for corrosion of steel [12,13] and zinc [14] and the rate determining step during atmospheric corrosion [15], strongly depends upon the presence of the oxide film [16–22].

Early attempts to integrate zinc corrosion products in the corrosion mechanisms of galvanized steel aimed at identifying the patinas formed under different conditions and to understand the mechanisms of their formation [23–30]. The next step is to correlate the presence of specific corrosion products with the changed reactivity.

The protective action of some iron rusts for steel is well documented [31–33]. At the same time the presence of zinc corrosion products can favor or disfavor the formation of a specific iron corrosion product and vice versa [34,35]. Corrosion product films can result in the reduced spreading of the electrolyte (due to the hydrophobic characteristics of the film) [36] and can increase or reduce the concentration of aggressive species (Cl\(^–\), O\(^2–\), etc.) at the interface “electrolyte/corrosion products” due to specific surface charge [35,37] or mass and charge transfer [38,39] properties. Zinc corrosion products can also retain water and accumulated pollutants increasing electrical conductivity [40,41]. Specific ion exchange properties [42] of some products can modify the chemistry at the metal-corrosion product interface and precipitation processes contribute to the modification of the surface pH [43] which is considered as one of the most important factors controlling the corrosion rates of zinc [44–47] and steel [48].

The majority of previous electrochemical studies used either corroded samples after accelerated corrosion tests or field exposure which result in the formation of a complex mixture of products [49], or tested the synthetic powders obtained by precipitation [50–52] or commercially available powders [53]. The first strategy cannot answer the question of the role of each individual component because the films are mixtures of diverse products; the second strategy can fail because the synthesis method affects considerably the structure and as a consequence the key properties like hydrophobicity, compactness, surface charge, ion exchange properties etc. [54]. As a consequence, the specific role of each corrosion product for corrosion mechanisms of galvanized steel is still under discussion.
To our knowledge, there is a very limited number of works focused on the targeted synthesis of selected corrosion products on steel and zinc and the characterization of the electrochemical behavior of the obtained system. In our previous study [55], we have investigated the barrier properties of the synthetic simonkolleite layer formed on galvanized steel and the stability of this barrier effect. This work is an extension of the previous study and focuses on the cathodic reactivity of electrogalvanized steel covered by different zinc based corrosion products. Part 2 of this work will examine the anodic reactivity of zinc and the galvanic coupling in steel/patina/zinc systems.

2. Choice of selected corrosion products and their thermodynamic stability

As demonstrated in [25–30], initial exposures of zinc or galvanized steel to air leads to the formation of ZnO and Zn(OH)₂ which are slowly transformed into zinc hydroxyl carbonates (i.e. Zn₄CO₃(-OH)₆H₂O and Zn₂(CO₃)₂(OH)₆ hydrozincite, HZ) in the presence of carbon dioxide. Simonkolleite (zinc hydroxylchloride, ZHC, Zn₅(-OH)₆Cl₂·H₂O) is formed at higher chloride concentrations in marine atmosphere, osakaite (zinc hydroxysulfate, ZHS, Zn₄SO₄(OH)₆·5H₂O) is observed at the initial stages of corrosion in industrial atmosphere. Sodium zinc carbonate hydrate (SZC, Na₂Zn₃(CO₃)₄·3H₂O) was also observed [56]. More complex compounds like gordaitê (Zn₈Na₅(OH)₈Cl₂·6H₂O) are formed from simonkolleite or zinc hydroxysulfate at longer exposures. In this work, we limit the study to the patinas listed in Table 1 which can be formed from the initial zinc oxide at early stages of corrosion.

These products are selected because of the empirical knowledge about a correlation between their presence on the surface of galvanized steel and the improved corrosion resistance [2–10,57] as well as the fact that their protective action often decreases with time [1] because of the transformation into soluble zinc complexes or less protective zinc oxides.

The formation of SZC in carbonate solution is kinetically favorable although it transforms rapidly into thermodynamically more stable HZ [58]. The later can explain the fact that this product is rarely detected after corrosion of galvanized steel. The structure of SZC [59] is composed by several admantane-like cages formed by an asymmetric unit Na½[Si(CO₃)₃]·(CO₃·2H₂O) in which the corners are shared by alternating ZnO₄ and CO₃ groups. The tetrahedral Zn atoms are connected through CO₃ groups forming a diamond-type framework with vacancies in one from eight of tetrahedral sites. The pore diameter in the cage is in the range between 1.4 and 2.1 Å. This small dimension results from the C–O distance calculated using the Hydrà–Medusa© software and associated database version of 2011 [63]. The species used are named in the figure caption. For ZHS (Fig. 1b) the calculation predicts that it is stable in a narrow range of sulfate concentration and pH, transforming into ZnO at high pH and into soluble zinc complexes at high sulfate concentrations. The low stability of ZHS could explain why it does not attract a lot of attention during atmospheric corrosion. The stability of ZHC was discussed in our previous publication [55]. Briefly, ZHC also tends to transform into ZnO at high pH and becomes soluble at very high pH or chlorine concentrations, but ZHC is stable in the large range of the concentration of chloride solution at neutral pH. HZ can be formed in a diluted carbonate solution at pH = 8 (Fig 1a) which is a natural pH of bicarbonate anion. This can explain the rapid formation of HZ observed in very different conditions of atmospheric corrosion. SZC is not included in the Hydra Medusa database. Taking into account the previously mentioned fact that its formation is kinetically and not thermodynamically controlled, we will discuss its stability later only on the basis of our experimental results.

3. Experimental

3.1. Materials

Commercial electrogalvanized steel supplied by ArcelorMittal and typical for use in automotive industry was used for synthesis of corrosion products. The steel composition is presented in our previous work [55]. The total thickness of steel was about 0.75 mm and a zinc coating thickness of 7.5 μm. All samples were degreased by n-heptane for five minutes, washed with deionized water and dried under nitrogen flux before synthesis. All reagents were of analytical reagent grade from Merck and used as received without further purification. All solutions were prepared with deionized water (18.2 MΩ cm) prepared with Millipore™ system.

3.2. Electrochemical set-up

Electrochemical experiments were performed with a VSP potentiostat (bio-logic™). Electro-galvanized steel (EZ) or cold rolled steel (CRS) were used as the working electrode. A saturated calomel electrode (SCE) and a platinum wire were used as the reference electrode and the counter electrode, respectively. The experimental set up has been described in detail in our previous paper [55]. For synthesis under applied potential, the surface area of working electrode was 10.17 cm². The electrochemical set-up for the transformation of ZHC on cold rolled steel into other patinas on cold rolled steel is shown in Fig. 2. For electrochemical characterization only the central part of the sample with the area 0.28 cm² was used to avoid the border effects.

The anodic and cathodic polarization curves were obtained by polarization starting from the open circuit potential and potential scan rate of 1 mV/s in anodic or cathodic direction respectively. All experiments were carried out at room temperature.

3.3. Synthesis conditions

Table 2 summarizes the synthesis conditions. Synthesis was performed under potentiostatic polarization. Applied anodic potentials were fixed in the potential range between open circuit potential of uncovered steel and that of galvanized steel for each product (−0.9 ~ −0.65 V vs. SCE) to prevent underlying steel corrosion during synthesis.

For synthesis of corrosion products on cold rolled steel (CRS), simonkolleite and ZHS were prepared by the complete dissolution of the zinc coating under applied anodic potential −0.75 V and
formed in place of ZHS probably due to a high pH induced by cathodic oxygen reduction.

The patinas on electrogalvanized steel in which zinc dissolution is not complete (named as "systems EZ/patina") were formed by the direct dissolution of approximately 3 μm Zn layer in the electrolytes as described above for all products. An anodic transient current evolution as a function of time during synthesis of different corrosion products can be observed in Fig. 3a. The average dissolved thickness was calculated from the consumed charge which for 3 μm of zinc layer dissolved should be 1.77 C cm⁻².

3.4. Microstructure characterization

The composition of all corrosion products was verified by XRD and electron microscopy coupled with X-ray microanalysis.

For microstructure observations the sample was lightly rinsed with distilled water to remove non-adherent corrosion products and dried by a flux of dry nitrogen. The scanning electron microscopy (SEM) was performed on ZEISS Ultra 55 microscope coupled with Bruker Quantax 200 an energy dispersive spectroscopy system with Si (Li) detector. Typical accelerating voltage was 15 kV.

The X-ray diffraction experiments were performed directly on the corroded surface and analyzed by Pan Analytical diffractometer (45 kV, 40 mA) using the Ni filtered Cu Kα radiation (λ = 1.54 Å). The XRD were collected with the angular resolution 0.002°. The patina on electrogalvanized steel in which zinc dissolution is not complete (named as "systems EZ/patina") were formed by the direct dissolution of approximately 3 μm Zn layer in the electrolytes as described above for all products. An anodic transient current evolution as a function of time during synthesis of different corrosion products can be observed in Fig. 3a. The average dissolved thickness was calculated from the consumed charge which for 3 μm of zinc layer dissolved should be 1.77 C cm⁻².

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### 4. Results

#### 4.1. Synthesis

##### 4.1.1. Zinc dissolution kinetics during synthesis

Fig. 3 illustrates the evolution of the anodic transient current density (Fig. 3a) and the calculated average thickness of dissolved

### Table 2

<table>
<thead>
<tr>
<th>Products</th>
<th>Solution used</th>
<th>(E_{oc}^{\text{open}}) (V vs. SCE)</th>
<th>(E_{oc}^{\text{closed}}) (V vs. ZCE)</th>
<th>(E_{oc}^{\text{zno}}) (V vs. ZCE)</th>
<th>(E_{applied}) (V vs. SCE)</th>
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</thead>
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<td>ZHC</td>
<td>0.1 M NaCl (water/ethanol mixture)</td>
<td>0.58</td>
<td>-1.05</td>
<td>-0.75</td>
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<tr>
<td>HZ</td>
<td>0.05 M NaHCO₃</td>
<td>-0.43</td>
<td>-1.15</td>
<td>-0.85</td>
<td></td>
</tr>
<tr>
<td>SZC</td>
<td>0.5 M NaHCO₃</td>
<td>-0.75</td>
<td>-1.18</td>
<td>-0.85</td>
<td></td>
</tr>
<tr>
<td>ZHS</td>
<td>1 M Na₂SO₄</td>
<td>-0.71</td>
<td>-1.12</td>
<td>-0.85</td>
<td></td>
</tr>
</tbody>
</table>
zinc (Fig. 3b) as a function of time during the synthesis of different corrosion products from galvanized steel. It should be noted that the value of the dissolved zinc thickness is calculated at each time assuming a homogeneous dissolution of zinc. This can be true if the corrosion product does not block the following zinc dissolution. In other cases, due to the inhibiting effect of formed corrosion product on zinc dissolution, the thickness of the metallic zinc layer can decrease significantly at areas at which the corrosion products were not formed yet (which become later anodic areas) and very little at the areas covered with corrosion products (which become later cathodic areas), becoming locally very different from the average value shown in Fig. 3b.

The dissolution of zinc in sulfate solution is very rapid which can be interpreted as an absence of any significant inhibiting effect by the product formed. If SZC is formed, the initially high current density (several mA cm\(^{-2}\)) decreased abruptly with the consumed thickness of zinc. In conditions of the formation of HZ, the oxidation rate of zinc is slow from the first moments of the reaction. The relatively low dissolution rate of zinc in carbonate solution is in agreement with the literature\([64–66]\) and our previous results\([55]\). This will be also discussed in the Part 2 of this work\([67]\).

In Table 3 the measured pH values of the bulk electrolyte before and after the zinc dissolution under applied potential are compared with the stability domain of different products. After the dissolution of 3 \(\mu\)m of zinc layer in chloride or carbonate solutions the pH was between 8 and 9, the domain where both ZHC and HZ are stable. The higher pH values in sulfate containing solution suggests that the ZHS layer removed from the solution immediately after the potential application contained some Zn(OH)\(_2\) or ZnO (Fig. 6a). After several hours of immersion at open circuit potential, the pH decreased to neutral values which are sufficient\([35,57]\) for the transformation of ZnO into ZHS (Fig. 6b). As can be seen, ZHS forms hexagonal platelets and the structure seems to become more compact during transformation.

A wide range of bicarbonate concentrations was tested for transformation of zinc; the nature of formed products varied with the concentration of bicarbonate as illustrated in Fig. 6. HZ was the major product at bicarbonate concentrations between 10\(^{-4}\) M and 0.25 M (Fig. 6d); below 10\(^{-5}\) M the dominant product was ZnO (Fig. 6c); and at concentrations higher than 0.25 M – SZC (Fig. 6e) which was the only product detected in concentrated solutions of bicarbonate (>0.5 M, Fig. 6f). Fig. 6g represents the SZC crystals morphology obtained by the transformation of the layer of ZHC by immersion in 1 M NaHCO\(_3\) at open circuit potential.

The increased fraction of SZC with the increase of HCO\(_3\)\(^-\) concentration can be explained by kinetic considerations\([68]\): the higher the bicarbonate concentration, the faster the exchange between the hydroxide ion in the corrosion products and the bicarbonate ion in the electrolyte.
The transformations between different zinc products observed during this work are schematically presented in Fig. 7.

4.1.3. Synthesis of zinc corrosion products on cold rolled steel (CRS/patina systems)

The results of the direct synthesis of CRS/ZHC system were described in our previous publication [55]. The synthesis of CRS/HZ, CRS/SZC and CRS/ZHS by direct transformation of 7.5 l m of zinc into zinc patina in carbonate or sulfate containing solutions was not successful for the reasons described below.

For ZHS, due to the intensive cathodic reactions, the final pH reached after the complete zinc transformation in the sulfate solution (pH > 10, see Table 3) was above the precipitation pH of ZHS (about 5 [57–58]) and the stability domain presented in Fig. 1. In carbonate containing solutions the pH is buffered at values favorable for the formation of the expected corrosion products. However, in many experiments the formation of red rust was observed in carbonate solution when the consumed charge exceeded 2 C cm$^{-2}$. At the same time, the residual metallic zinc was detected by XRD and the value of the open circuit potential after the experiment moved towards $-0.6$ V vs. SCE which is close to the value for CRS. This indicates that steel started to corrode even if zinc was not completely consumed. This is coherent with the hypothesis of the passivation of zinc by the corrosion product.

The transformation of the ZHC layer into carbonate containing products was very reproducible and the formation of SZC and HZ was observed in the same carbonate concentration ranges as during direct dissolution of a zinc layer from electrogalvanized steel (Section 4.1.2). The XRD diffraction results for CRS/patina systems obtained after the transformation (Fig. 4) show no metallic zinc and the observed peaks correspond to the expected patinas, indicating that the synthesis was successful. The experimental peak positions of each product and the calculated d-spacing from them are compared with the reference values in Table 4. Sometimes, however, small quantities of zinc oxide were detected, which can be related to the local pH increase during the intensive cathodic reaction. As previously noted, CRS/ZHC system described in [55] is not included in Fig. 4 and Table 4.

4.2. Electrochemical behavior

4.2.1. Cold rolled steel/corrosion product systems in 0.85 M NaCl

In this section we describe the results obtained with zinc patinas on cold rolled steel, the results for electrogalvanized steel are presented in the next section. At all pH, OCP values for bare cold rolled steel and cold rolled steel covered by different zinc based corrosion products are in the potential ranges between $-0.5$ and $-0.7$ V vs. SCE. Cathodic polarization curves in oxygenated solution with initial pH 7, 9 and 11 are presented in Fig. 8. Oxygen reduction is expected to be the main reaction in the region between approximately $-0.8$ V vs. SCE (more cathodic than the domain of the steel oxidation domain) and $-1.2$ V vs. SCE (beginning of water reduction). It is visible from Fig. 8 that all studied products decreased the oxygen reduction current.

The decrease of cathodic current on cold rolled steel in the potential range $-0.8$ to $-1$ V vs. SCE indicates the clear inhibition ef-
fect on oxygen diffusion by all corrosion products. The magnitude of cathodic current increases in the order $j$[CRS/SZC]$/$j$[CRS/ZHC]$/$j$[CRS/ZHS]$/$j$[CRS/HZ]$$. This result is coherent with previous publications [55,60–62,72,73] demonstrating the inhibiting effect of Zn ions or zinc corrosion products on the oxygen reduction on steel but for the first time establishes the relative order of the effect of different patinas and for the first time gives a direct experimental evidence of the barrier effect of ZHS.

The anodic polarization curves performed on bare steel and steel covered by zinc patinas in 0.85 M NaCl at pH = 7, 9 and 11 are presented in Fig. 9. At pH = 7 and 9, the current densities were reduced compared to that of bare steel except for HZ. At pH = 11, at which the studied products are unstable, there is no clear effect on the anodic behavior.

4.2.2. Effect of the layer thickness on the barrier properties of simonkolleite

One of the hypotheses explaining the barrier protection of zinc corrosion products as that it is due to a dense layer near the metal surface and not to the thick layer of corrosion product [69]. To verify this hypothesis, the electrochemical behavior of the systems in which the layer of simonkolleite was formed on steel from 7.5 to 2.5 μm of Zn was compared. The thinner layer was obtained in 2 steps. Firstly, zinc layer was partly dissolved in chloride containing solution (similar conditions as for ZHC synthesis). The charge consumed was controlled in a way that a mean thickness of zinc reacted was about of 5.0 μm. The corrosion products were removed using supersaturated glycine (200 g/l). Next, the residual zinc layer (approximately 2.5 μm average thickness) was completely transformed into simonkolleite and the electrochemical behavior of the system was tested under applied cathodic potential $-0.95$ V vs. SCE in 0.85 M NaCl under oxygen at initial pH = 8. The results presented in Fig. 10 demonstrate that the barrier properties of these 2 systems are very similar. It seems that the barrier effect does not depend on the quantity of zinc used for the formation of the corrosion product.

4.2.3. Cathodic reactivity of EZ/corrosion product systems in 0.85 M NaCl

In this section we describe the reactivity of the systems obtained by partial zinc layer transformation in which a continuous layer of metallic zinc layer is still present under the corrosion product (EZ/patina systems). Cathodic polarization curves on galvanized steel and galvanized steel covered by corrosion products in 0.85 M NaCl under air (Fig. 11) show that none of the patinas demonstrated any cathodic inhibition on zinc. Except for SZC, the order in which the cathodic current decreases on GI/patina systems is similar to that of CRS/patina systems; however the smallest cathodic reactivity is observed on EZ without any corrosion product. Probably, the current increase at potentials nobler than $-1.2$ V vs. SCE includes the contribution of Zn$^{2+}$ reduction as proposed in [70,71]. This phenomenon was not observed on CRS/patina systems. The reason can be that the steel surface is nobler than the
5. Discussion

5.1. Role of zinc ions for anticorrosion protection of electrogalvanized steel

Traditionally, the presence of zinc ions is considered as beneficial to the anticorrosion protection of cold rolled steel and may be considered essential to the self-healing effect of zinc. In our work we have demonstrated that the effect of different zinc patinas on the oxygen reduction can be very different. The electrolyte composition can modify the patina composition and stability and hence the self-healing action of zinc ions.

The direct application of the electrochemical results obtained on model systems to the anticorrosion protection in other systems should be discussed with caution because of the important evolution of the nature of different patinas in function of the environment. The role of iron ions which could be present into the solution cannot be neglected. For example, our results for ZHS on cold rolled steel obtained by the chemical transformation of ZHC (Fig. 6f) seem to be more compact than that obtained by the direct electrodissolution – precipitation processes (Fig. 6g). In contrast, the cathodic polarization curves in presence of SZC obtained by the direct process demonstrate the highest current densities between all studied EZ/patina systems (Fig. 11) and the cathodic currents in presence of SZC obtained transformation are the lowest on CRS/patina systems (Fig. 8). The oxygen permeability through the individual crystal seems to be improbable; the “cage-like” crystalline structure of SZC has a pore size diameter of only about 2 Å.

The electrochemical measurement can be regarded as an indirect measurement of the porosity of the layer. Indeed, the oxygen reduction current is proportional to the fraction of the steel surface accessible for the cathodic reaction. Therefore, the surface “coverage” can be estimated from the electrochemical response. We have previously illustrated this assumption for phosphate conversion coatings on Zn [76]. However, the direct relationship between this hypothetical “coverage” and the geometry of the covering surface layer (thickness, porosity) is not a trivial task.

5.2. Possible origins of the barrier effect of zinc patinas

5.2.1. Particle size

The simplest idea explaining that the barrier effect of corrosion product on the oxygen reduction is related to the formation of a compact layer. From morphological observations it was supposed that small platelet-like particles favor compact structures decreasing the permeability [9,39]. This consideration could work for ZHC and ZHS but would not explain the excellent barrier properties of SZC for which the cubic symmetry results in large particles of well defined “adamantan” shape. The calculation using Scherrer’s equation [74] and the SEM observation of the particle sizes demonstrate that neither the average crystalline domain size (Table 4) nor the observed by SEM particle size (Fig. 6) correlate with the order of the oxygen reduction currents presented in Fig. 8: SZC, which has the largest crystallite size on CRS, shows the most significant inhibition effect on CRS. Therefore, the effect cannot be explained by the simple size refinement.

5.2.2. Porosity considerations

From the adsorption measurements on different precipitated zinc rusts published by Ishikawa and co-workers [75], the mean porosity can be expected to increase in the order ZHC<ZHS<ZnO correlating well with the observed order of the barrier effect of this patinas on cold rolled steel. However, the direct application of the bibliographical data to the porosity of different corrosion products is very complex because the porosity can vary considerably in function of the synthesis method as illustrated for HZ and SZC obtained in different conditions (Fig 6d and e). Moreover, in function of the method by which the porosity is determined, the results can be very different for the same substance. For instance, if the morphological observation is used, the layer of SZC on cold rolled steel obtained by the chemical transformation of ZHC (Fig. 6f) seems to be more compact than that obtained by the direct electrodissolution – precipitation processes (Fig. 6g). In contrast, the cathodic polarization curves in presence of SZC obtained by the direct process demonstrate the highest current densities between all studied EZ/patina systems (Fig. 11) and the cathodic currents in presence of SZC obtained transformation are the lowest on CRS/patina systems (Fig. 8). The oxygen permeability through the individual crystal seems to be improbable; the “cage-like” crystalline structure of SZC has a pore size diameter of only about 2 Å.

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Table 4
Comparison between the reference data [files in JCPDS-ICDD database v. 1995] and experimental XRD results for the 3 most intensive peaks for the synthesized products. The peak position, d-spacing and the average crystalline domain size calculated by Scherrer’s equation are presented.

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<th>References</th>
<th>Observed</th>
<th>d-spacing (Å)</th>
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(a) ZHS; (b) SZC obtained by the transformation from ZHC; (c) HZ obtained by the transformation from ZHC and (d) SZC on Zn obtained by the direct process.
5.2.3. Hydrophobic interactions in hydrozincite

Some authors [77] proposed that the compactness of the HZ layer is determined by hydrophobic interactions. We have tried to apply this hypothesis for our case. In our work, the ratio of the XRD signal intensity of (200) and (002) plains ($I_{(200)}/I_{(002)}$) is 0.55 for HZ on zinc obtained by the direct electrodissolution-precipitation process (EZ/HZ system) and 0.73 for HZ synthesized on steel by transformation from ZHC (CRS/HZ system). In the literature [77] the increase of this value is associated with the formation of more hydrophobic structure with aligned basal planes compared to the flower-like hydrophilic structure containing different orientations of the basal plane. That means that the transformed HZ layer obtained on steel is expected to be more compact and at the same time more hydrophobic than the initially formed HZ on zinc which does not correlate with the relative effect on the observed cathodic reactivity presented in Figs. 8 and 11.

5.2.4. Synergic effect with iron

As demonstrated in previous sections, several different hypotheses fail to explain the relative order of the inhibition efficiency of different patinas. Moreover, the inhibiting effect of ZHC in CRS/ZHC systems seems to be independent on the quantity of zinc used for the patina formation and the inhibiting effect on the cathodic reaction on zinc is not so clear as on steel. Alternative mechanism of barrier protection may therefore be considered. The precipitation of simonkolleite favors the formation of FeOOH rusts at the CRS/ZHC interface [34], the barrier effect of these compounds on the oxygen reduction was previously communicated [31]. It would be logical to propose that the role of simonkolleite is to stabilize this thin layer of the protective iron rust. This hypothesis is also coherent with the recently published results on steel reactivity in presence of Zn and Mg ions mixtures [78].
Fig. 10. Oxygen reduction current density as a function of time at an applied cathodic potential of -0.95 V vs. SCE on steel (CRS), steel covered by ZHC obtained by the transformation of 2.5 μm of Zn (CRS/ZHC from 2.5 μm of Zn), and steel covered by ZHC obtained by the transformation of 7.5 μm of Zn (CRS/ZHC from 7.5 μm of Zn).

6. Conclusions

(1) Synthetic zinc patinas (Zn5(OH)6(CO3)2, Na2Zn3(CO3)4·3H2O and Zn6(OH)3SO4·2H2O) were for the first time electrochemically synthesized on galvanized steel. The role of pH and anion concentration on the formation and stability of patinas was studied.

(2) The effect of zinc patinas on oxygen reduction on cold rolled steel in NaCl solution was demonstrated and the relative order of the inhibition efficiency of the patinas is determined for the first time. For cold rolled steel at pH 7 and 9,j(CRS) < j(CRS/Na2Zn5(CO3)4·3H2O) < j(CRS/Zn6(OH)3SO4·2H2O) < j(CRS/Zn3(OH)6SO4·nH2O) < j(CRS/Zn6(OH)3(CO3)4·2H2O). This can be explained by the formation of a compact mixed layer of iron corrosion products and zinc oxide. The presence of iron corrosion products hinders oxygen reduction, leading to the establishment of the so-called "inner barrier effect."

(3) The inhibition efficiency does not correlate systematically with crystal size refinement. Hydrophobic interactions are also insufficient to explain the observed order of the barrier efficiency of different corrosion products. The morphological observations of the layers seems to correlate with the fact that more compact layers form more efficient barriers, however the morphology is very sensitive to the formation conditions.

(4) An inhibiting effect of zinc corrosion products on zinc cathodic reactivity was not observed. This observation should however be taken with a great caution because the measured high cathodic currents in EZ/patina systems can contain a significant contribution of zinc patinas reduction making impossible the interpretation of the results.

(5) The barrier effect of simonkolleite seems to be similar for 2.5 and 7.5 μm of zinc transformed. The hypothesis can be formulated that the barrier effect is mainly due to the thin compact layer of the corrosion product close to the steel surface and not the total quantity of dissolved zinc. Taking into account that zinc patinas inhibit oxygen reduction on cold rolled steel but no inhibition is observed for EZ/patina systems, one can suppose the synergic effect of iron and zinc. Moreover, it can be proposed that the barrier effect is related to the formation of a very thin layer of iron corrosion products favored by several zinc patinas like simonkolleite.

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References
