Synthesis of Lithium-exchange Silica Particles for Corrosion Protection of Aluminum Alloys

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This study focuses on the synthesis of lithium-exchange silica (Si/Li) particles and their corrosion protection for aluminum alloy substrates. Silica is synthesized via a sol-gel method as a raw material to prepare Si/Li in a saturated lithium nitrate solution. The obtained samples are characterized by X-ray diffraction, field emission scanning electron microscopy, zeta potential measurements, Fourier transform infrared spectroscopy, and inductively coupled plasma mass spectroscopy. Inhibition properties of synthesized Si/Li are investigated by electrochemical impedance spectroscopy (EIS). The results show that Si/Li prepared in the saturated lithium nitrate solution has a high content of loaded lithium. This amount relates to a high and stable corrosion protection of Si/Li in the electrolyte solution for the aluminum alloy substrate. After 96 h of immersion in the electrolyte solution, electrochemical results show a high value of an inhibition efficiency up to 98%. Water-based epoxy coatings containing Si/Li are also prepared to highlight their corrosion protection efficiency for the aluminum alloy substrate. Concerning the EIS measurement results, the coating containing 5 wt% Si/Li shows high and stable barrier properties for a long immersion time in the protection of the aluminum alloy substrate.

Keywords Aluminum alloy; Ion-exchange silica; Lithium; EIS; Inhibitor

I. INTRODUCTION

Aluminum alloys of the 2XXX series have been used in many fields such as aircraft, construction, and automotive industries, owing to their low weight and intermediate mechanical properties [1]. Because of a high copper content, the 2XXX aluminum alloys are sensible to pitting or intergranular corrosion [1–3]. Generally, Cr(VI) compounds have been considered as the most effective inhibitors for anticorrosion protection of the aluminum alloys because of their self-healing effect [4]. Unfortunately, as the Cr(VI) compounds cause problems on human health and the environment, we propose in the present work a new approach to develop an alternative corrosion inhibitor for corrosion protection of the 2XXX aluminum alloys.

In recent years, lithium salts have been reported as effective inhibitors [5, 6]. In alkaline solutions containing lithium ions, an aluminum alloy was passivated by the formation of a protective thin film containing lithium. Polarization curves of the aluminum alloy immersed in a Li$_2$CO$_3$ solution (0.05 M) showed a corrosion rate lower by 20 times compared to that obtained in the reference solution [5]. Lithium salts, from 8 to 15 vol%, have been also incorporated in organic coatings as alternative inhibitive pigments to chromate to protect the AA2024 aluminum alloy and the AA7075 substrate [7–10]. In the coating, lithium cations are released and...
reacted with the alumina layer at the coating/aluminum alloy interface to form a barrier layer composed of aluminum, oxygen, and lithium. This layer was dense, inert, and protective, and can protect the metallic substrate from corrosive elements [8, 9].

Generally, silica particles have been considered as a storage of inhibitors [11, 12]. Because of their porous structure and a high specific surface area with OH groups on the surface, silica particles can be modified with inhibitive species, metallic ions, and others by ion-exchange reactions [7, 12–14]. Granizo et al. used 10–15% of calcium-exchange silica (Si/Ca) as an inorganic pigment loaded in alkyd coatings to improve adhesion performance and anticorrosion properties for carbon steel substrates [15, 16]. Due to cationic-exchange reactions, calcium ions can be released from the corrosive environment and, then, form complex silicate products, such as CaSiO$_3$·FeSiO$_3$, which suppress the corrosion process.

Recently, lithium-exchange silica (denoted as Si/Li) have been studied for an absorbed material [17–21]. Lithium-modified mesoporous silica particles synthesized via a sol–gel method in the presence of a templating agent showed an ability to absorb hydrogen under ambient temperature and atmospheric conditions [17, 18]. Methanol and ethanol can also be absorbed by using mesoporous silica doped with LiBr/LiCl particles [19]. However, there was a few publications regarding lithium-exchange silica and its inhibition property for aluminum alloys. In this paper, Si/Li was synthesized via a sol–gel method, and the synthesized Si/Li powders were incorporated into epoxy resin with a low percentage for corrosion protection of the aluminum alloy substrate. Electrochemical methods were performed to evaluate the anticorrosion behavior of the epoxy coating containing the Si/Li particles.

II. METHODS AND EXPERIMENTAL

A. Aluminum alloy substrate

An aluminum alloy substrate used for this study was 2017 aluminum alloy (AA2017) in the series 2XXX, whose main elemental composition was Al (91.5–95.5 wt%) and Cu (3.5–4.6 wt%). Two types of AA2017 substrates were prepared. One is a rod shaped AA2017 with 1 cm$^2$ of a surface area, used for an inhibition test. It was carefully abraded with 100–1200 grade of SiC sandpapers before being cleaned by ethanol, dried, and immediately immersed in the studied environment. The other was AA2017 sheets (40 mm × 60 mm × 1 mm), which were cleaned with acetone before epoxy coating deposition.

B. Synthesis of silica and lithium-exchange silica

Silica particles were synthesized by a sol–gel method [18, 22, 23] using two precursors; tetraethyl orthosilicate (TEOS, > 99%, Sigma Aldrich) and sodium metasilicate nonahy-

| Abbreviation | Silane precursor | Saturated LiNO$_3$ solution |
|--------------|-----------------|----------------------------|
| Silane precursor | TEOS, Na$_2$SiO$_3$ | solution |
| Si1          | ✓               | ✓                          |
| Si2          |                 |                            |
| Si1/Li       | ✓               | ✓                          |
| Si2/Li       |                 |                            |

Table 1: Synthesized particles with abbreviation.

drate Na$_2$SiO$_3$·9H$_2$O (98%, Sigma Aldrich). The silane precursor was diluted by distilled water and mixed drop-by-drop into a H$_2$SO$_4$ solution (2 M) with a molar ratio depending on which precursor was used: TEOS/H$_2$O/H$_2$SO$_4$ = 1/50/1.3 or Na$_2$SiO$_3$/H$_2$O/H$_2$SO$_4$ = 1/20/2. After mixing, the solution was stirred for 24 h at room temperature and aged at 80°C for 6 h in the reflux system which allowed a silica-gel formation reaction [22]. Precipitated silica was obtained by washing silica gel with distilled water by centrifugation at the speed of 8000 rpm until excess acids were completely removed and, then, by drying at 70°C for 24 h.

For lithium doping, as-prepared silica particles were firstly stirred at room temperature for 24 h in the saturated LiNO$_3$ solution, which was prepared from LiNO$_3$ compounds (> 99%, Sigma Aldrich). The reaction flask was then equipped with an auto-cooling system at 80°C for 6 h. The solution was centrifuged to collect the sediment, which was dried at 70°C for 24 h to obtain the Si/Li particles. Table 1 lists synthesized particles with their abbreviations.

Epoxy coatings doped with various contents of silica (5 wt%) and Si/Li (5, 7.5, and 10 wt%) were prepared from water-based epoxy resin YD828 and Epicure 8537 as a binder component using a spin-coater (Filmfuge Paint Spinner Ref 110N, Sheen Instruments). Silica or Si/Li was mechanically dispersed in a hardener at least 1 h before adding it into the epoxy container. The mixture was kept stirred for 30 min and sonicated at least for 30 min to ensure the dispersion of the particles before depositing it on the pre-cleaned aluminum alloy substrate (40 mm × 60 mm × 1 mm) with a rotating rate of 500 rpm for 20 s. The film thickness was approximately 40 ± 4 μm.

C. Experimental techniques

X-ray diffraction (XRD) analysis was carried out using a diffractometer equipped with a Cu Kα radiation source (λ = 0.154 nm) (D8 Advance, Bruker) to characterize a crystalline structure of the synthesized silica and Si/Li powders. Fourier transform infrared spectroscopy (FT-IR) spectra of silica and Si/Li were acquired by a Jasco FT-IR 6300 spectrometer by using KBr in the region of 400–400 cm$^{-1}$. Field emission scanning electron microscope (FE-SEM) observations were performed by using a Hitachi S-4800 equipment. The amount of lithium doped in silica was determined by inductively coupled plasma mass spectroscopy (ICP-MS). Charge and zeta potential distributions of the
prepared samples were examined in a KCl solution (10^{-3} M) at room temperature by Zeta Phoremeter IV (CAD Instrumentation).

Inhibition properties of the lithium ions and Si/Li were characterized by electrochemical methods on BioLogic SP-300 (BioLogic Science Instruments) in a mixture of 0.05 M NaCl and 0.1 M Na_2SO_4 solutions as an electrolyte solution. This mixture was chosen as a blank solution because of a moderate quantity of the chloride ions that could not accelerate too much the corrosion process on the aluminum alloy surface and because of the presence of the sulphate ions that could help to prevent the Ohmic potential drop [24, 25]. A three-electrode system was used; the AA2017 rod as a working electrode, an Ag/AgCl/saturated KCl reference electrode, and a Pt counter electrode. Spectroscopy impedance diagrams were performed in the frequency range from 100 kHz to 10 mHz at an open circuit potential (OCP) with the 5-mV amplitude to ensure the sensitivity of the aluminum alloy working electrode.

Anticorrosion properties of the Si/Li containing epoxy coatings deposited on the aluminum alloy substrate were evaluated in 0.1 M NaCl as a reference solution by electrochemical impedance spectroscopy (EIS) measurements with 30 mV of the amplitude at OCP [1]. For each experiment, the measurements were taken at least three times to confirm reproducibility.

III. RESULTS AND DISCUSSION

A. Characterization of synthesized silica and lithium-exchange silica particles

Figure 1 shows XRD patterns of the synthesized silica and Si/Li samples obtained from two different precursors. The XRD diagrams of the synthesized silica particles (Si1 and Si2) are characterized by a single peak in the range between 2θ = 7° and 8°, which is similar to that reported in preceding studies [18, 23]. As mentioned in Ref. 23, under the synthesized condition at 80°C, only an amorphous structure of silica can be obtained. The width of this peak is the same for both Si1 and Si2, indicating that the precursor used to synthesize silica, i.e., TEOS (Si1) or Na_2SiO_3 (Si2), does not affect the crystallite size. In addition, in the diagrams obtained from the Si/Li particles (Si1/Li, Si2/Li), this characteristic peak still remains at the same position, meaning that the lithium ions are well adsorbed and cause no modification in the crystalline structure of silica [18].

Table 2: Characteristic bands FT-IR obtained for synthesized samples.

| Functional group | Si1 | Si1/Li | Si2 | Si2/Li |
|------------------|-----|--------|-----|--------|
| Si–O–Si          | 465 | 471    | 461 | 467    |
| OH^− (silanol)   | 793 | 798    |     |        |
| Si–O             | 800 | 821    | 826 |        |
| Si–OH            | 954 | 956    | 953 | 949    |
| Si–O–Si stretching | 1083 | 1083 | 1082 | 1096 |
| −NO_3            | 1384| 1383   | 1383|        |
| H_2O             | 3467| 3442   | 3482| 3441   |

Figure 1: XRD diagrams of the synthesized silica (Si1, Si2) and lithium-exchange silica (Si1/Li, Si2/Li) samples.

Figure 2: FT-IR spectra of the synthesized particles; (a) Si1 (1) and Si1/Li (2), (b) Si2 (3) and Si2/Li (4).
broad bands at 3441−3481 cm−1 and 1641−1647 cm−1 can be attributed to the bending and stretching vibrations of absorbed water molecules in the silica network via the hydrogen bonds. The bands at 460−470 cm−1 and 1082−1096 cm−1 relate to the stretching vibrations of the Si–O–Si bonds [22]. The spectra of Si/Li show an adsorption band at 1384 cm−1, which can be associated with the vibration of −NO3. This demonstrates that NO3 ions from LiNO3 were attached to the surface of synthesized silica. To determine the amount of the lithium ions grafted on the silica network, ICP-MS measurements were carried out and the results prove the presence of lithium in the as-prepared samples. The content of the lithium ions in Si1/Li is about 23.2 wt%, while Si2/Li is successfully grafted with 39.3 wt% of the lithium ions. The higher value of the lithium content in Si2/Li, synthesized by using Na2SiO3 as a precursor, suggests a more porous morphology of Si2/Li.

FE-SEM micrographs of synthesized powders can be found in Figure 3. The particle size is in the range of 100−200 nm. The silica particles show numerous aggregates that form a porous structure [Figure 3(a, b)]. Morphology of the silica particles undergo considerably changes in the presence of lithium at their surfaces [Figure 3(c, d)]. Additionally, Si2/Li shows bigger particles than Si1/Li. This is attributed to a larger amount of the OH groups presented in the alkaline environment (Na2SiO3) so that a higher amount of the lithium ions are grafted on the surface.

The charged surface and the distribution of the zeta potential values of the Si2 and Si2/Li particles are determined in the 10−3 M KCl solution and presented in Figure 4. The Si2 particles show multiple peaks in the range between −40 and −20 mV in the zeta potential distribution [Figure 4(a)]. Their zeta potential value is determined around −25.27 mV with a conductivity value of around 0.14 mS cm−1. On the other side, the Si2/Li particles show an orderly distribution of the zeta potential. Their main peaks are homogenous and located at around −30 mV. Its zeta potential value is around −20.36 mV with the conductivity value of 0.17 mS cm−1.

The shift of the zeta potential value towards a more positive side (from −25.27 to −20.36 mV) can be related to absorption of the lithium ions which have positive charge on the surface of silica. Additionally, in the aqueous medium measurement, the lithium ions are partially desorbed from the surface, resulting in an increase of the conductivity value of the solution. These results have confirmed absorption of the lithium ions on the surface of the synthesized silica particles.

**B. Corrosion inhibition properties of Li ions and Si/Li in electrolyte solution**

1. **Inhibition properties of Li ions for aluminum alloy substrate**

Inhibition properties of the lithium ions are firstly determined by the electrochemical methods during immersion of the AA2017 electrode into the electrolyte solution (0.05 M NaCl + 0.1 M Na2SO4 containing 0.1 M LiNO3 with different immersion times between 2 and 20 h. The EIS results are performed in Bode diagrams in Figure 5, and results obtained for 2 h of immersion of the AA2017 rod in a blank solution are also performed for comparison.

In the Bode diagram in Figure 5(a), the modulus value recorded for 0.1 M LiNO3 (4.2 × 104 Ω cm2) is higher than that for the blank solution (6.5 × 103 Ω cm2) at the beginning of the measurement (2 h). When the immersion time is extended to 6 h, this value slightly decreases and then becomes a constant value after 10 h until the end of the measurement. Concerning that the modulus resistance values decrease during the immersion time as the corrosion process proceeds.
seen that this layer is generated in the presence of oxygen [6] and has a crystal morphology like layered double hydroxide usually formed on aluminum [7].

2. Inhibition properties of Si/Li for aluminum alloy substrate

Based on the ICP-MS analysis, Si1/Li contains 23.2 wt% of Li and Si2/Li is grafted with 39.2 wt% of Li. These two types of Si/Li were examined to assess the corrosion inhibition ability for the aluminum alloy substrate in the electrolyte solution. Each sample was dispersed with the concentration of 3 wt% in the electrolyte solution (0.05 M NaCl + 0.1 M Na2SO4) and was filtrated after 24 h. The ICP-MS analysis demonstrates that 80 % of the lithium ions are released from the Si/Li particles. These two filtrates were, then, used for the corrosion inhibition experiments.

Figure 7 represents impedance in the Bode plot obtained after 24-h immersion of the AA2017 electrode in the filtrates from Si1/Li and Si2/Li. The Bode plot for the solution containing 3 wt% of dispersed undoped silica (Si2) is also shown as a reference. The filtrate from undoped silica (Si2) does not exhibit an inhibitive effect whose impedance resistance values at the low frequency are similar to the blank solution. Contrarily, the filtrates obtained from Si1/Li and Si2/Li show a higher capacity of an anticorrosion protection for the aluminum alloy substrate owing to the higher modulus value at the low frequency compared to the blank solution [Figure 7(a)]. In addition, the phase diagrams present only a single time constant in comparison with two time constants obtained for the blank solution. This correlates to a high capacitive response in a large frequency range relating on the surface of the AA2017 electrode immersed in the blank solution, the total modulus resistance obtained in the presence of the Li ions shows remarkable values. In parallel, the phase diagram obtains in the absence of the inhibitor [Figure 5(b)] shows two time constants; the first in the medium frequency range ($10^2-10^6$ Hz) relates to the oxide layer formed on the electrode surface, and the second is not well identified but should relate to the ongoing active corrosion process [26, 27]. In the presence of the lithium ions, the phase diagram shows one well-defined time constant after 2 h of immersion. This is related to a capacitive behavior owing to the protective film formed on the electrode surface due to a protective efficiency of the inhibitor. From 4 to 20 h exposures of the aluminum alloy electrode to the electrolyte solution containing the inhibitor, a small and ill-identified second time constant appears in the high frequency range. This proves the presence of the protective film. So, it can be seen that, at 0.1 M LiNO3, the lithium ions show a high capacity to protect the aluminum alloy. This protection can be visually observed in Figure 6 that shows surface appearances of the aluminum alloy electrodes in the mentioned solutions. After 20 h of immersion in the electrolyte without lithium, the surface of the electrode is strongly corroded with the presence of white precipitates [Figure 6(a)], whereas the aluminum alloy surface immersed in the electrolyte with lithium is in a good protection condition with no corrosion products [Figure 6(c)] owing to the protective effect of lithium. This effectiveness is further proved by the FE-SEM images, showing a crystal-protective layer [Figure 6(d)], which is in sharp contrast to the surface without a protective layer [Figure 6(b)]. It is noted that this layer is generated in the presence of oxygen [6] and has a crystal morphology like layered double hydroxide usually formed on aluminum [7].

Figure 5: Bode diagrams of AA2017 obtained during the immersion times in the electrolyte solution with and without 0.1 M LiNO3.

Figure 6: Surface appearances of the aluminum alloy electrodes after immersion in the electrolyte solution free from LiNO3 (a, b) and that containing 0.1 M LiNO3 (c, d).
to a barrier and a protective film at the metallic substrate due to the release of the lithium ions. For the Bode plot obtained by the filtrate coming from Si2/Li, the modulus resistance at 10 mHz presents a higher value ($2.5 \times 10^4 \Omega \text{ cm}^2$) compared to the one given by Si1/Li ($7.1 \times 10^3 \Omega \text{ cm}^2$). This phenomenon can be attributed to the higher content of lithium doped into the silica structure, resulting in a higher lithium amount released in the electrolyte solution. As above results, the lithium ions act as an effective inhibitor for the aluminum alloy substrate by forming a protective barrier layer on the aluminum alloy electrode to decrease the corrosion rate. The evolution of the modulus resistance values at 10 mHz extracted from the impedance Bode plots as a function of the immersion time is shown in Figure 8. It needs to be noted that, in the absence of the particles, the modulus resistance value is low and the electrode is sensitive to be corroded after only 1 day of immersion. The undoped silica particles also show no anticorrosion effect with a low modulus resistance values during the immersion time. On the other side, the modulus resistance values resulted from Si/Li tend to increase with the immersion time. It relates to the lithium ions released from Si/Li that reinforces the alumina layer by forming a film which protects the aluminum alloy surface. The modulus resistance values obtained by Si2/Li are higher than that the one obtained by Si1/Li because of a higher quantity of the lithium cations doped in the Si2/Li particle.

This protection can be visibly observed in Figure 9, showing the surface appearance of the electrode after the measurements. White corrosion products are formed on the surface after 72 h of immersion in the electrolyte solution without the inhibitor [Figure 9(a)] and in the filtrate from the undoped silica solution [Figure 9(b)]. On the other hand, after immersion in the Si1/Li and Si2/Li filtrates, there is no precipitates to be observed [Figure 9(c, d)]. To prove the formation of the protective layer on the electrode surface, a FE-SEM image of the AA2017 electrode after immersion in the filtrate originated from Si2/Li is shown in Figure 9(e).
crystal morphology, which is similar to the one formed on the aluminum alloy electrode immersed in the solution containing LiNO$_3$ [Figure 6(d)], is observed. This morphology proves the leaching of Li from lithium-exchange silica in the electrolyte solution, and these leached Li ions favor to diffuse to the alumina/aluminum alloy interface. In the presence of oxygen, porous alumina at the interface is sealed by forming the Li–Al layer which is resistant to chloride ions in the corrosive medium [6] so that the corrosion processes are inhibited and the film resistance is enhanced [8, 28]. The inhibition efficiency ($I_{\text{eff}}$) of Si/Li for the AA2017 surface can be calculated by the following equations using the polarization diagrams which are extrapolated from the impedance diagrams (ZSimpWin Data Analysis software) [29, 30]:

$$I_{\text{eff}} (\%) = \frac{R_p - R_{p\text{c}}}{R_p} \times 100,$$

where $R_{p\text{c}}$ and $R_p$ are the polarization resistance values obtained for the reference solution (the solution without the inhibitor) and the solution containing the corrosion inhibitor, respectively. Table 3 represents $I_{\text{eff}}$ of the studied particles at various immersion times. Silica shows no significant inhibition efficiency with low $R_p$ values. The $I_{\text{eff}}$ values of two Si/Li samples are low at the beginning of immersion (2 h); 24% for Si1/Li and 66% for Si2/Li. However, the value for Si1/Li increases up to 80% after 24 h of immersion. This parameter does not change and shows a stable trend after 2 days of immersion. In the case of Si2/Li, which is originated from the Na$_2$SiO$_3$ precursor and the saturated LiNO$_3$ solution, $I_{\text{eff}}$ is quite high (98%) after 96 h. These results confirm the inhibition properties of lithium-exchange silica for the protection of the aluminum alloy substrate. Based on the inhibition efficiencies of two Si/Li particles, Si2/Li is chosen for incorporation into organic coatings and is abbreviated simply as “Si/Li” hereafter.

### C. Anticorrosion protection of Si/Li doped organic coatings

Figure 10 presents Bode diagrams obtained for the AA2017 sheets covered with epoxy coatings doped with 5, 7.5, and 10 wt% of Si/Li during the immersion time in the 0.1-M NaCl solution. The Bode diagrams obtained from the AA2017 substrates covered with an unloaded epoxy coating (a reference) and an epoxy coating loaded with 5 wt% silica particles (Si2) are also reported. The impedance modulus values at a low frequency are progressively reduced with the immersion time for all studied systems, but their phase diagrams show a different trend. For the reference sample [Figure 10(a, b)], the phase angle plot shows two time constants after 1 day of exposure and the second time constant can be clearly observed after 8 days. This result means degradation of the barrier properties of the film. Such a phenomenon is significantly improved when the coating is loaded with silica [Figure 10(c, d)] and Si/Li [Figure 10(e–j)]. Loading the silica particles is known well for improving the barrier properties of the coatings by increasing the diffusion pathways of corrosive elements to the metallic substrate [31, 32]. In present study, this improvement is proved by a high modulus resistance in the presence of 5 wt% of silica in the epoxy film [Figure 10(c, d)]. After 8 days, the resistance value starts to be reduced progressively.

### Table 3: Polarization resistances ($R_p$, $R_{p\text{c}}$) and inhibition efficiency $I_{\text{eff}}$ determined from the electrochemical impedance measurements.

| Immersion time (h) | Blank $R_p$ (kΩ cm$^2$) | Blank $R_{p\text{c}}$ (kΩ cm$^2$) | Si1/Li $I_{\text{eff}}$ (%) | Si1/Li $R_p$ (kΩ cm$^2$) | Si1/Li $I_{\text{eff}}$ (%) | Si2/Li $R_p$ (kΩ cm$^2$) | Si2/Li $I_{\text{eff}}$ (%) |
|-------------------|------------------------|------------------------|-----------------------------|------------------------|-----------------------------|------------------------|-----------------------------|
| 2                 | 5.2 ± 0.1              | 2.8 ± 0.1              | -                           | 6.8 ± 0.1              | 23.5                        | 15.1 ± 2.4             | 65.6                        |
| 24                | 1.5 ± 0.1              | 2.4 ± 0.1              | 37.5                        | 7.8 ± 0.1              | 80.7                        | 27.2 ± 1.8             | 94.5                        |
| 48                | 0.7 ± 0.1              | 4.0 ± 0.1              | 82.5                        | 11.1 ± 0.5             | 86.5                        | 61.1 ± 5.9             | 97.5                        |
| 72                | 1.1 ± 0.1              | 2.2 ± 0.1              | 50.0                        | 10.7 ± 0.4             | 85.9                        | 59.6 ± 6.1             | 97.5                        |
| 96                | 1.1 ± 0.1              | 2.0 ± 0.1              | 45.5                        | 9.8 ± 2.5              | 84.7                        | 85.2 ± 7.2             | 98.0                        |

Figure 10(a–d): Bode diagrams obtained for the AA2017 substrates covered with various kinds of epoxy coatings in the 0.1-M NaCl solution; (a, b) an undoped and (c, d) 5 wt% Si-doped epoxy coatings. The immersion duration is between 1 and 53 days.
and the second time constant appears clearly after 25 days as a result of degradation of the barrier properties.

Furthermore, the barrier properties of the epoxy film are reinforced and maintained when the lithium-exchange silica particles are doped. From 5 to 10 wt% of the Si/Li content, the Bode diagrams show a similar behavior among the three systems with a slow decrease of the modulus value at 10 mHz. In these phase diagrams, the phase angle values in a high frequency zone are higher than those recorded for the unloaded system. This means a good barrier protection for the substrate.

In the low frequency range, a different behavior of the phase angle can be observed. At the beginning of immersion, only a single time constant can be observed [Figure 10(f, h, j)]. The second time constant is visibly manifested after 8 days (the 5-wt% Si/Li-doped coating), 53 days (the 7.5-wt% Si/Li-doped coating), or 25 days (the 10-wt% Si/Li-doped coating). The appearance time of the second time constant relates to the different rate of degradation of the coating in the corrosive environment. The global barrier behavior of these systems can be explained in Figure 11, which presents the evolution of the film resistance $R_f$ [Figure 11(a)] and the modulus values at a low frequency $|Z|_{10\text{mHz}}$ [Figure 11(b)] during a long immersion time. At the beginning, the aluminum alloy substrate coated by the unloaded epoxy layer shows low $R_f$ and $|Z|_{10\text{mHz}}$ values, meaning a weak barrier property of the system. As immersion continues, these two parameters demonstrate a progressive decrease after 1 week (8 days) and keep stable values after 18 days. On the other hand, the system with the undoped silica coating shows higher $R_f$ and $|Z|_{10\text{mHz}}$ values than those of the reference system. This is due to an improvement of the barrier properties owing to the silica particles [31, 32]. However, the two parameters are progressively reduced, meaning that the protective effect of the silica particles could not last for a long immersion time. Nevertheless, the coatings containing Si/Li as a pigment show a good barrier performance whatever the loaded contents are. On the one hand, the $R_f$ values for the system with 10 wt% Si/Li are always lower than those obtained with 7.5 wt% Si/Li, and a significant drop of the film resistance is recorded for this coating after 18 days of exposure. On the other hand, their

![Figure 10(e−i): Same as Figure 10(a−d) but for the AA2017 substrates covered with (e, f) 5 wt% Si/Li-doped, (g, h) 7.5 wt% Si/Li-doped, and (i, j) 10 wt% Si/Li-doped epoxy coatings.](image)

![Figure 11: Evolution of $R_f$ and $|Z|_{10\text{mHz}}$ extracted from the electrochemical measurements.](image)
[\text{Z}]_{\text{limfitted}} \text{ evolution stabilizes during the exposure period, and there is no significant difference between the modulus resistance values obtained for the two systems, i.e., 7.5 wt% and 10 wt% Si/Li. Concerning that the modulus resistance is a sum of the film resistance and the double-layer resistance, this phenomenon can be related to reinforcement at the coating/aluminum alloy interface for the coating containing 5 wt% Si/Li. At the end of the measurements, these two systems show the same value of [\text{Z}]_{\text{limfitted}}, around 2.1 \times 10^6 \Omega \text{ cm}^2, which is higher than that for the unloaded sample (8.8 \times 10^4 \Omega \text{ cm}^2) but is not remarkable if one compares it to the value for the silica-doped coating (1.7 \times 10^6 \Omega \text{ cm}^2). Among three studied systems, the coating containing 5 wt% Si/Li presents important values of \( R_t \) and [\text{Z}]_{\text{limfitted}} (about 5 and 10 times higher than those for the coating doped with 7.5 wt% Si/Li and for the undoped sample, respectively), and these values are maintained until 53 days of the measurements. Such behaviors can be explained by the inhibition efficiency of the Li ions leached from the Si/Li particles like an ion-exchangeable pigmentation action as mentioned in the literature [14–16]. The Li ions accumulate at the coating/metalllic substrate interface to form a protective film at damaged areas and also fill the porous defects that are generated during the production process, leading to an improvement of the barrier properties of the coating. Unfortunately, increasing the content of Si/Li (from 5 to 10 wt%) in the coating tends to reduce the global protection performance of the system. The high quantity of the pigment (10 wt% Si/Li) leads to the formation of aggregates on the surface and inside the film because of the nature of the silica particles, resulting in degradation of the barrier properties [33, 34]. In the range examined in the present study, the water-based epoxy coating doped with 5 wt% Si/Li exhibits the high and stable anticorrosion properties for the protection of the aluminum alloy substrate.

IV. CONCLUSIONS

This work focused on the synthesis of lithium-exchange silica particles and the investigation of their inhibition capacity on the corrosion protection of aluminum alloy substrates in electrolyte solutions and in epoxy coatings. The results show that synthesized Si/Li based on the Na$_2$SiO$_3$ solution and the saturated LiNO$_3$ solution exhibits a porous structure and has a higher lithium content than that prepared with the TEOS precursor. The electrochemical measurement results show good inhibition properties of Si/Li in an anticorrosion protection of the aluminum alloy substrate, owing to the release of the lithium ions in the electrolyte solution. The lithium ions diffuse in the aluminum oxide layer, leading to the formation of a crystal-resistant protective layer that passivates the aluminum alloy surface and prevents the local corrosion processes.

The Si/Li particles are introduced in a water-based epoxy coating with various quantities from 5 to 10 wt%. With the inhibition efficiency of the Li ions, the water-based epoxy coating containing 5 wt% Si/Li shows a promising result for the corrosion protection of the aluminum alloy substrate. These results will give rise to further studies to deepen understanding of the anticorrosion mechanism of lithium-exchange silica in the field of the protection of metallic substrates.

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