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1 **The chemical throwing power of lithium-based inhibitors from**
2 **organic coatings on AA2024-T3**
3

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13
14 **Abstract**

15 Chemical throwing power, being the distance over which an inhibitor is able to
16 protect a defect effectively, is an important parameter for active protective coatings.
17 This study investigates the chemical throwing power of lithium-based leachable
18 corrosion inhibitors exhibiting different leaching kinetics, from coatings at different
19 inhibitor loading concentrations. The results demonstrate that Li-salt loaded coatings
20 provide corrosion protection of defect areas up to a width of 6 mm. Time-of-flight
21 secondary ion mass spectrometry (ToF-SIMS) was used to detect the lateral spread of
22 Li in the defect areas and provide the chemical speciation of corrosion protective
23 layers in the defect areas.

24 **KEYWORDS:** aluminium, lithium, inhibitor, throwing power, active protection,
25 ,ToF-SIMS

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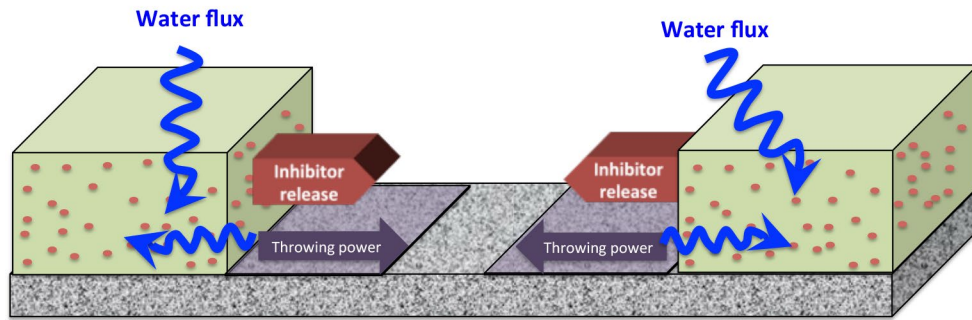
1 **1. Introduction**

2 Traditionally, active protective coatings have typically two functionalities. Firstly,
3 the coating provides barrier properties and secondly, active corrosion protection can
4 be achieved by the ability to release corrosion inhibitors from the coating matrix into
5 in a defect area in case the coating is damaged. Leaching of the inhibitor is the
6 complex process where condensed moisture diffuses into the coating matrix and
7 triggers the dissolution of the corrosion inhibitor and facilitates the transport of the
8 corrosion inhibitive species from the coating matrix to the exposed substrate.[1] The
9 release kinetics and the capacity of the reservoir of corrosion inhibitor in the coating
10 are essential parameters to consider for such active protective systems.[2, 3] The
11 inhibitor release kinetics are affected by the solubility of the corrosion inhibitor, the
12 loading in the coating, and the microstructure of the coating matrix.[4] Several studies
13 have been performed on the leaching behaviour of chromate inhibitors, which have
14 been the industry standard for an effective active corrosion protection for many
15 decades. [5-10] In these studies it was found that the inhibitor release does not occur
16 via diffusion through the resin of the coating itself and is not controlled by a Fickian
17 diffusion process either.[5, 6] Instead, the inhibitor is released due to the direct
18 dissolution of clusters of inhibitors, which are in contact with the electrolyte at the
19 surface of the coating or at the defect area.[8] After this initial fast inhibitor release,
20 the process continues via diffusion through a fractional network of voids and inter-
21 connected pathways deeper in the coating matrix left after the prior dissolution of the
22 corrosion inhibitor, resulting in a slower inhibitor release over time.[8, 9] This
23 knowledge has been modelled to further understand the mechanism of inhibitor
24 transport in coatings.[6, 7]

1 Another important parameter is the distance over which the coating is able to
2 protect a defect effectively, known as the “throwing power”.[11, 12] The ability of a
3 coating to provide corrosion protection of a defect by the release of inhibitors can be
4 classified as the “chemical” throwing power, this process involves a concentration
5 gradient-driven random transport from inhibitor-rich regions (coating) to unprotected
6 sites (defect).[13] Scully and Presuel-Moreno studied the phenomenon of chemical
7 throwing power in addition with the galvanic throwing power using an Al-Co-Ce
8 metallic coating over AA2024-T351 under thin electrolyte films representative of
9 atmospheric conditions and demonstrated the effect of defect size, showing that the
10 larger the scratch size, the more difficult it is to transport sufficient inhibitor to the
11 centre-line of the defect and suppress corrosion.[12, 14] In addition to the galvanic
12 protection mechanism, the conditions for the chemical throwing power under which
13 Al-Co-Ce coatings released and transported Ce^{3+} ions to a defect on AA2024-T351
14 was investigated. One of the key criteria to obtain effective inhibition by was the
15 ability to achieve a critical inhibitor concentration in the defect within a few hours. It
16 was demonstrated that that such Al-Co-Ce coatings could be tailored to optimize
17 coating functionality by a combination of galvanic and chemical inhibition properties.

18 The concept of chemical throwing power can also be projected on the concept of
19 active corrosion protection from coatings with an organic matrix. Fig. 1 shows the
20 concept of chemical throwing power as the lateral spread of a corrosion protective
21 layer in a defect as a result of the release of corrosion inhibiting species from a
22 coating matrix through leaching. Inhibitor leaching is triggered by water ingress
23 through the top-surface and the cut-edge of the coating to provide active protection in
24 the defect area. In addition to parameters such as inhibitor leach-rate and permeability
25 of the coating matrix are key criteria to obtain the critical inhibitor concentration. In

1 addition to this, the irreversibility or stability of the developed passive layer in the
2 defect is an other important aspect to obtain effective active corrosion protection.[13,
3 15]



4

5 *Fig. 1 The concept of chemical throwing power by active corrosion protective*
6 *coatings*

7

8 In 2010, Li-salts were introduced as leachable corrosion inhibitor in active
9 protective coatings for the protection of aluminium alloys.[16] Several studies have
10 demonstrated that Li-leaching coatings provide fast, effective and irreversible
11 corrosion protection in a coating defect and the technology is regarded as a promising
12 environmentally friendly alternative to the toxic chromates.[17-19]. The active
13 protective properties of these coatings are obtained by the leaching of Li-salts from
14 the organic coating matrix, this release of the Li-salts provides favourable alkaline
15 conditions in the defect area which facilitates the formation of a protective aluminium
16 oxide/hydroxide layer in the defect area.[20, 21] The protective layer comprises
17 mainly aluminium, oxygen and lithium and electrochemical studies revealed that the
18 corrosion protective properties of the layer could be linked to the dense layer at the
19 aluminium substrate.[20, 22] Further investigations showed that the protective layer
20 in the defects featured different surface morphologies which indicates possible
21 different compositions as a consequence of different Li concentrations and pH during

1 the formation of the layer. [23, 24] Marcoen et al. used the high sensitivity towards Li
2 and the high lateral resolution of time-of-flight secondary ion mass spectrometry
3 (ToF-SIMS) to investigate the Li-spread in a 1 mm wide defect area and unravelled
4 the surface composition of the protective layers.[25] It was found that the Li-spread
5 in a 1 mm wide defect area was relatively fast and the entire defect area was covered
6 with Li-based species within 15 minutes of exposure in the neutral salt spray test
7 (NSS). Short exposures to these corrosive conditions induced the formation of a Li-
8 containing pseudoboehmite (Li-PB) and longer exposure times resulted in higher Li-
9 concentrations in the defect area and the formation of a Li-based layered double
10 hydroxide (Li-LDH) covering the entire surface area. However, the chemical
11 throwing power of Li-salts as corrosion inhibitor by leaching from organic coatings
12 has not been studied yet.

13 This paper presents the study of the chemical throwing power of Li-salts, i.e.
14 lithium carbonate and lithium oxalate, when incorporated into organic coatings as
15 leachable corrosion inhibitor. Firstly, the leaching characteristics and the corrosion
16 protective properties of organic coatings with high and low loadings of Li-salts were
17 investigated. Then, the chemical throwing power was assessed by exposing these
18 coatings with increasing defect widths up to 6 mm to neutral salt spray conditions for
19 7 days. The corrosion protective performance of the systems was assessed optically
20 and by using profilometry. In addition, ToF-SIMS was used to investigate the lateral
21 Li-spread and the surface composition of the protective layer in the defect areas. This
22 study provides a further understanding of the active corrosion protective properties,
23 the surface composition of the protective layer in the defect area and demonstrates the
24 “chemical” throwing power of the Li-salt based inhibitor leaching technology, a

1 feature that has not been demonstrated for any other chromate-free inhibitor leaching
2 coating technology.

3 **2. Experimental**

4 *2.1 Materials and sample preparation*

5 *Inhibitor loaded coatings*

6 Polyurethane model coatings with a total pigment volume concentration (PVC) of
7 30% and respective loadings of 15 and 2.5% PVC Li-salt as leachable corrosion
8 inhibitor were used in this study. The composition of the model coatings is listed in
9 Table 1. Analytical grade lithium carbonate and lithium oxalate were acquired from
10 Sigma-Aldrich.

Table 1 Composition of the Li-salt loaded organic model coatings

leachable inhibitor		lithium carbonate		lithium oxalate	
loading (PVC %)		15%	2.50%	15%	2.50%
Component A					
N-Butylacetate	Sigma Aldrich	85.0 g	85.0 g	85.0 g	85.0 g
Desmophen 650MPA	Covestro	47.7 g	47.7 g	47.7 g	47.7 g
Lithium carbonate	Sigma Aldrich	23.6 g	3.6 g	-	-
Lithium oxalate	Sigma Aldrich	-	-	23.2 g	3.6 g
Magnesium oxide	Sigma Aldrich	16.4 g	16.4 g	16.4 g	16.4 g
Tioxide TR 92	Huntsman	5.2 g	5.2 g	5.2 g	5.2 g
Blanc Fixe N (Ba(SO ₄))	Sachtleben	15.4 g	58.1 g	15.4 g	58.1 g
Component B					
Tolonate HDB 75 MX	Vencorex	28.5 g	28.5 g	28.5 g	28.5 g
Dynasilan Glymo	Evonik	5.2 g	5.2 g	5.2 g	5.2 g

11

12

13 *Preparation of the organic model coatings.*

1 The Li-leaching model coatings were prepared in a similar way as described in
2 previous papers.[20, 21] Component A was prepared by the sequential addition of
3 the raw materials to a 370 ml glass jar. After mixing the materials to a
4 homogeneous mixture, 400 grams of Zirconox pearls[®] (1.7-2.4 mm) were added
5 and the samples were shaken on a Skandex[®] paint shaker to grind and disperse the
6 pigments to a grind fineness less than 25 µm. After this shaking procedure, the
7 pearls were separated from the paint and Component B was added. The paint was
8 then stirred for 5 minutes to a homogeneous mixture.

9 *Sample preparation*

10 Sheet material of AA2024-T3 aluminium alloy with a thickness of 0.8 mm was
11 anodized according aerospace requirements (AIP1 02-01-003) in tartaric sulphuric
12 acid (TSA) to obtain an anodic film with a thickness of 3-3.5 µm. The model
13 coatings were applied using a high-volume low-pressure (HVLP) spray gun at
14 23°C and 55% relative humidity. After the application, all coatings were cured
15 with a forced cure cycle of 16 h at 80°C after a 1 h flash-off period. All coatings
16 had a dry film layer thickness of 20-25 µm.

17 *Inhibitor leaching*

18 Two coated panels of 7 x 2 cm were immersed in a plastic test tube (total sample area
19 28 cm²) with 50 ml demineralized water to study the leaching behaviour of the
20 coatings with different loading concentrations of corrosion inhibitor. After 4 h, 24 h,
21 72 h, 120 h and 192 h immersion the entire solution with the leached inhibitor was
22 removed and replaced by fresh demineralized water. The removed solutions were
23 acidified with nitric acid to a concentration of 0.1M and analysed with inductively
24 coupled plasma atomic emission spectroscopy (Arcos NT ICP-AES) using scandium

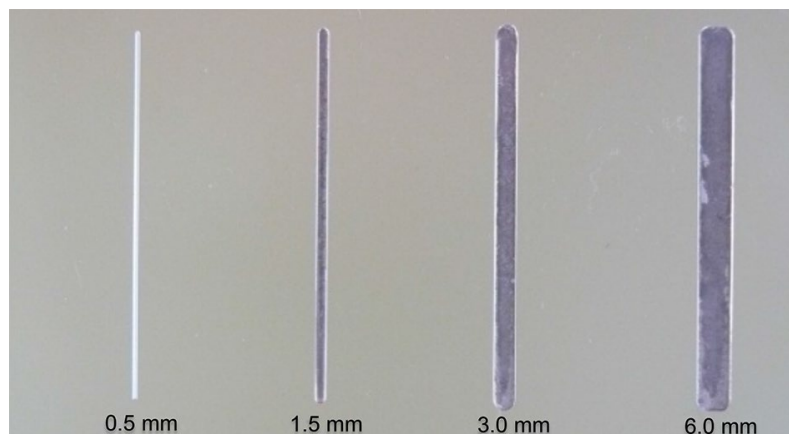
1 as an internal standard. On order to compare the different coatings, the accumulated
2 release of Li in mM/L in the water was normalized to a dry film thickness of 25
3 $\mu\text{m}/\text{cm}^2$. All measurements for the leaching curves were executed in triplicate.

4 *Corrosion protection in the defect area*

5 In order to assess the active protective properties of these coatings, an artificial
6 defect consisting of two intersecting scribes with a width of 1 mm, a length of 2 cm
7 and a depth of 100-150 μm was made in the coatings by mechanical milling. The
8 damaged coatings were exposed to the neutral salt spray test (NSS) according to
9 ASTM-B117 for 168 h. After the exposure the scribes were studied using microscopy
10 techniques.

11 *Inhibitor throwing power*

12 Coated panels with four parallel defects with varying widths (0.5 mm, 1.5 mm,
13 3mm and 6 mm) were prepared using a Gravograph[®] mechanical engraving machine
14 as shown in Fig. 2. The panels were placed in the NSS cabinets at an angle of 20
15 degrees with a vertical positioning of the defects to assess the lateral chemical
16 throwing power of these active corrosion inhibiting coating systems.



17

18 *Fig. 2 Example of a coated panel with vertical scribes ranging from 0.5 mm to 6 mm*
19 *in width used to assess the chemical throwing power.*

1 After 168 h NSS exposure, the scribed panels were examined with an optical
2 microscope and the surface roughness (Sa) of the defect areas was measured with a
3 Bruker K1 white light interferometer using a 20 X objective. The Sa value expresses
4 the surface roughness of an area, as an absolute value, the difference in height of each
5 point compared to the arithmetical mean of the surface. All data was analysed with
6 the Vision for Profilors (version 4.2) software.

7 *Reference samples*

8 Reference samples were prepared for the compositional analysis of the deposits
9 generated within the protective layer in the defect area.[25] Aluminium panels,
10 AA2024-T3 (0.8 mm thickness), were cleaned with acetone (> 99.9%, SASOL
11 Chemie GmbH & Co. KG) and scribed (1 mm) as described above. Pseudoboehmite
12 (PB) and Li-containing pseudoboehmite (Li-PB) reference samples were prepared
13 according to the method of Gorman et al. by immersing the scribed panels in (i)
14 demineralized water or (ii) a 0.02 M LiCl (BioXtra, ≥99.0%, Sigma–Aldrich) solution
15 in demineralized water at 95-100°C for 1 hour to obtain PB or Li-PB respectively.[26]
16 In addition, a Li-based layered double hydroxide (Li-LDH) reference coating was
17 obtained by the immersion of a scribed AA2024-T3 panel in a 0.1 M Li-carbonate
18 solution for 15 min according to the method of Buchheit et al.[27]. Following the
19 treatment, the panels were rinsed with copious amounts of demineralized water and
20 dried at the air. All ToF–SIMS measurements were performed in the scribed areas.

21 *2.2 Surface analytical methods*

22 *Optical and scanning electron microscopy (SEM)*

23 The defect areas were examined by optical and scanning electron microscopy
24 techniques. The optical microscope was used to visualize the effects of the corrosive

1 conditions in the defect areas of the coatings. A JEOL JSM-7100F field emission
2 scanning electron microscope was used to study the surface and cross-section
3 morphology of the corrosion inhibiting layers in the defect areas. The surface
4 morphology investigations were performed with the secondary electron detector (SEI)
5 using an acceleration voltage of 5 kV at a working distance of 10 mm. The cross-
6 sectional analysis of the defect areas were performed with a backscatter electron
7 detector (BED-C) at 5 kV and a working distance of 3 mm. Prior to the analysis of the
8 cross-sections, the samples were sectioned with a diamond saw and the defect area
9 was prepared with a Hitachi IM4000 ion milling system using 6kV Ar-ion
10 acceleration, a rotation speed of 3 rpm and a swing angle of +/- 30°.

11 *Time-of-flight secondary ion mass spectrometry (ToF-SIMS)*

12 In order to study the Li-spread in the defect areas, ToF-SIMS measurements were
13 performed on a TOF.SIMS 5 system (ION-TOF GmbH, Münster, Germany). Positive
14 ion mass spectra were acquired over a mass range of 1–800amu using a 30keV Bi⁺₃
15 primary-ion beam operated in the high current bunched mode for high mass resolution
16 (m/Δm approximately 8000 at 29amu (²⁹Si⁺)). A lateral resolution of 3 μm was
17 achieved in the high current bunched mode and the pulsed ion beam target current
18 was approximately 0.37pA. A list of fragments of known composition (CH⁺₃ ,
19 C₂H₃O⁺, LiOH⁺, AlOH⁺ and Al⁺₂) was used to calibrate the mass spectra. The
20 accuracy of a mass assignment (Δ in ppm) was calculated by dividing the absolute
21 difference between the experimental (M_{ex}) and theoretical (M_r) mass of a fragment by
22 the experimental mass, as shown below:

23
$$\Delta = \frac{|M_{ex} - M_r|}{M_r} \cdot 10^6 \quad (1)$$

1 The images of the large scribe areas after NSS exposure and the images of PB, Li-PB
2 and Li-LDH reference samples were obtained by rastering the scribe area in patches
3 of $400\ \mu\text{m} \times 400\ \mu\text{m}$. The analysis time of each patch was 60 s, using a pixel density
4 of 250 pixels/mm. Based on a compositional analysis of Marcoen et al.[25], a
5 characteristic peak list was created for the reference materials and subsequently
6 applied to spectra obtained by large area imaging of NSS exposed scribes.

7 *Compositional analysis using a multivariate analysis method (MVA)*

8 Since every pixel of the ToF-SIMS image contains a complete mass spectrum,
9 large area ToF-SIMS imaging provides large amounts of data. Multivariate analysis
10 (MVA) is an efficient tool for ToF-SIMS data analysis.[28] Especially, in this work
11 the main reason to use MVA is that the compounds of interest will share most of the
12 secondary ions thus making them unambiguously distinguishable only via MVA
13 methods. A peak list containing, characteristic for the reference materials, was first
14 created using the *SurfaceLab* software (IONTOF GmbH) and data cuboids containing
15 the maps of the areas of all selected peaks were then exported as binary .BIF6 files for
16 each large area surface analysed.. The .BIF6 files were loaded into the *simsMVA*
17 MATLAB app (<http://mvatools.com>) using the stitch function to perform matrix
18 augmentation and create a single matrix containing all (stitched) patches and the
19 reference images enabling the entire dataset to be processed as a single matrix.[29]
20 The insertion of rows containing measurements of well-known reference materials
21 has proven to be effective and more details of the methodology can be found
22 elsewhere.[25, 28, 30]

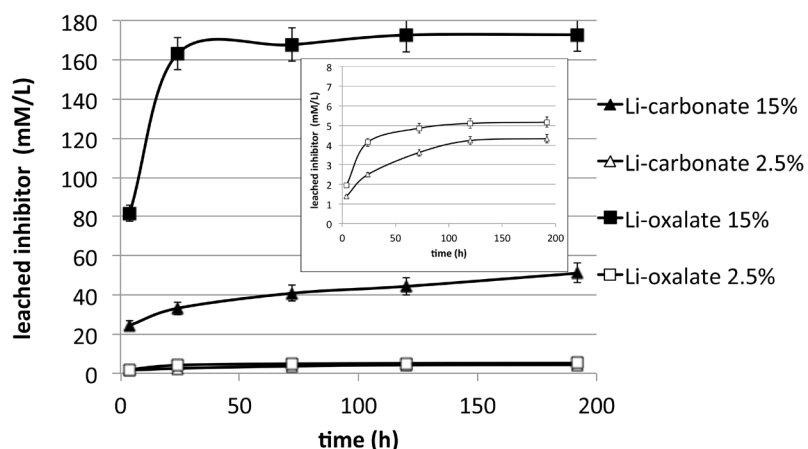
23 Prior to MVA, two pre-processing steps were performed: normalisation of all map
24 intensities by total counts per pixel and Poisson scaling of the peak intensities

1 according to a method proposed in the literature[31]. Non-negative matrix
2 factorisation (NMF) was then applied to the resulting dataset. NMF is a non-
3 supervised machine learning method that seeks to reduce the dimensionality of a
4 dataset down to a few “pure compounds”.[30, 32] This method enables the
5 interpretation and visualization of the surface chemistry because it provides data that
6 can be directly assigned to fingerprint mass-spectra of “pure” compounds and their
7 distribution maps.[30] The algorithm used to achieve non-negative factorisation of all
8 datasets presented in this paper is the one created by Lee and Seung[33], based on
9 multiplicative update rules and applied by Trindade et. al.[30]

10 **3. Results and Discussion**

11 *3.1. Leaching behaviour of the coatings*

12 Leaching profiles were obtained for the Li-salt loaded coatings with 15 and 2.5%
13 PVC Li-salt. Fig. 3 shows the accumulative inhibitor release for the coatings in mM/L
14 during 200 h leaching. The inset of Fig. 3 shows the expanded graph for the samples
15 with a lower Li release from the coating. From the graphs it can be noted that both Li-
16 salt loaded coatings with 15% PVC inhibitor leach significantly faster compared to
17 the coatings loaded with only 2.5% PVC inhibitor. The 15% PVC Li-oxalate sample
18 in particular leaches faster at higher concentrations of Li compared to the sample with
19 15% PVC Li-carbonate. These differences and of magnitude are in line with the
20 solubility of these corrosion inhibitors being 1.3 g/100ml for Li-carbonate[34] and 8.0
21 g/100 ml for Li-oxalate[35].



1

2 *Fig. 3 Accumulated release of corrosion inhibitor from coatings containing high*
 3 *(15% PVC) and low (2.5% PVC) loadings of Li-salt, normalized per cm² model*
 4 *coating with a thickness of 25 μm over a 192 h exposure time period.*

5

6 The inhibitor release of corrosion inhibitors from an organic coatings depends on
 7 the PVC and the quantity and solubility of the corrosion inhibitor in the coating [4].
 8 Since all coatings in this study were formulated to a total PVC of 30%, the leaching
 9 curves demonstrate that the dissolution of Li from these coatings depends on the
 10 solubility of the Li-salt and the loading of the Li-salt in the coating.

11 *3.2 Active protective properties from the coating*

12 *Optical and electron microscopy assessment of the defect area*

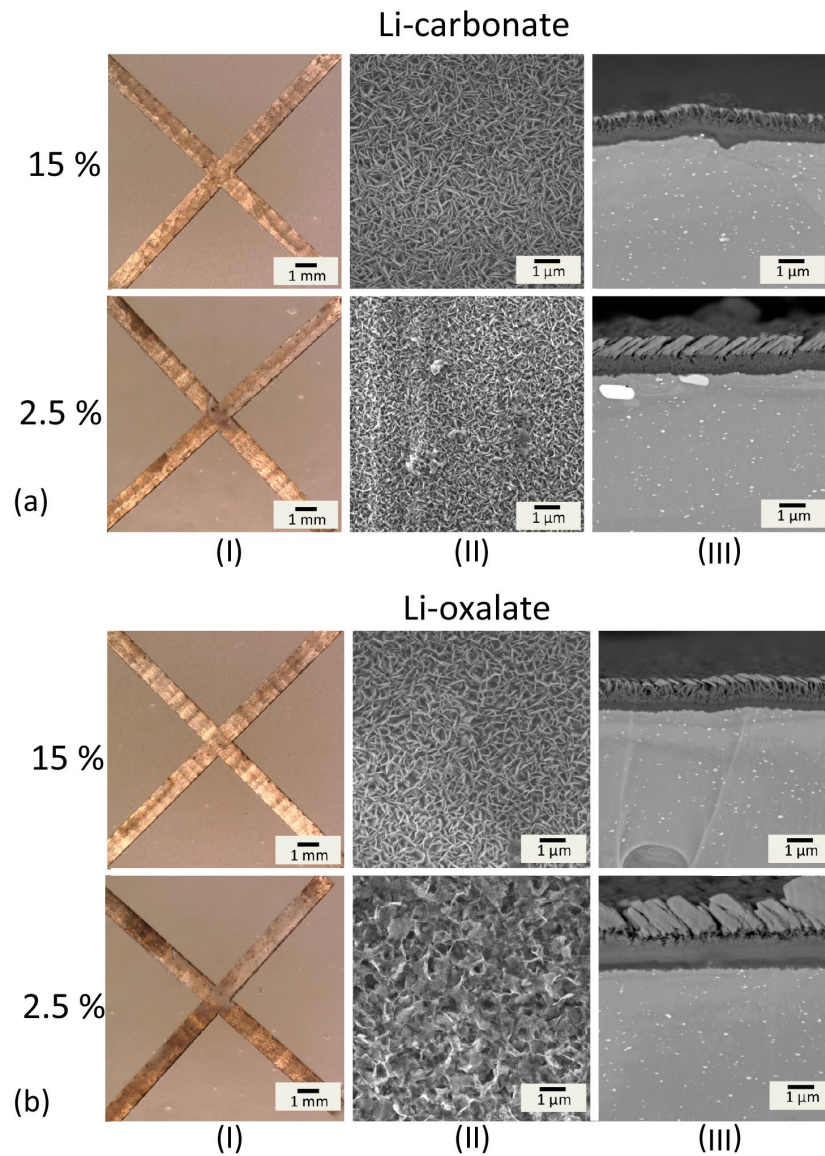
13 To assess the active protective properties, the Li-loaded coatings were artificially
 14 damaged and exposed to the NSS test for 168h. Fig. 4 shows the optical images (I) of
 15 the defect area, the top-view (II) and cross-sectional (III) scanning electron
 16 micrographs of the surface of the substrate in the defect area of the different coatings.
 17 The analysis with the optical microscope (Fig. 4_(I)) showed that all coatings provide
 18 effective corrosion protection because no voluminous white corrosion products,
 19 typical for aluminium corrosion, were observed in the defect areas after the NSS

1 exposure.[20] The highly loaded samples with 15% PVC Li-salts showed almost
2 pristine scribes with no corrosion products. The lower loaded (2.5% PVC) samples
3 showed some darkening but no corrosion products were observed in the defect area.
4 The formation of the protective layer in the defect area involves a surface corrosion
5 process whereas aluminium is anodically dissolved from the alloy matrix and forms
6 the aluminium hydroxide layer at the aluminium surface in the defect area. The
7 formation of such a protective layer can cause some discoloration (darkening) to the
8 defect area. This darkening is observed in different gradations in the defect area since
9 the optical appearance of the resulting layer in a defect area is a complex matter
10 which is influenced by multiple factors such as scattering due to surface etching[36],
11 the optical properties of the formed species[37], the thickness of the layer[38], and the
12 local dissolution of other alloying elements such as magnesium which deposit at the
13 alloy /oxide interface.[39]

14 The SEM micrographs of Fig. 4(II) show that a protective layer was formed in the
15 defect areas of the Li-salt loaded coatings independently of the loading level of the
16 Li-salt in the coating. The surface morphology of the layers generated from the 15%
17 PVC samples is similar for both the Li-carbonate and Li-oxalate samples showing a
18 polycrystalline surface morphology representative for hydrated oxides such as layered
19 double hydroxides.[27] The layers generated by active inhibition from the coatings
20 with 2.5% PVC Li-salts have a slightly different surface morphology compared to the
21 15% PVC samples. Whereas the Li-carbonate sample (Fig. 4a_{(2.5% (II))}) featured a
22 finer structure compared to the 15% loaded sample, the Li-oxalate sample showed a
23 more porous surface morphology (Fig. 4b_{(2.5% (II))}). However the cross-sectional
24 analysis (Fig. 4(III)) revealed that the thickness of the generated protective layers was

1 approximately 1.0 to 1.5 μm for all samples and featured a similar morphology
2 typical for Li-leaching coatings with a dense inner layer and a porous outer layer.[20]

3



4

5 *Fig. 4 Optical and scanning electron microscopy analysis of the defect areas of Li-*
6 *leaching coatings after 168h NSS exposure: (a) Li-carbonate loaded coating (15 and*
7 *2.5 % PVC) and (b) Li-oxalate loaded coating (15 and 2.5 % PVC). (I) optical*
8 *microscope image of the defect area; scanning electron micrograph of (II) the defect*
9 *area in planar view; (III) cross-sectional view of the defect area.*

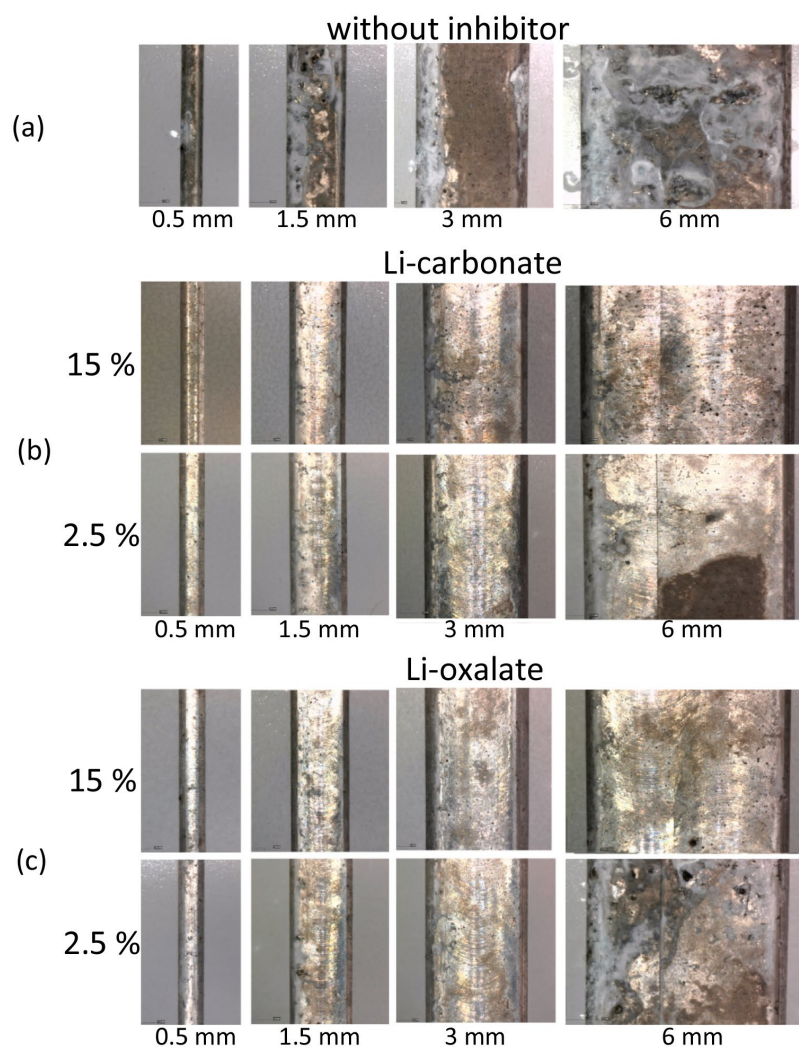
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1 3.3 *Corrosion inhibition of large defect areas*

2 3.3.1 *Optical analysis of large defect areas after NSS*

3 The corrosion inhibiting reach (throwing power) of these coatings was assessed by
4 exposing panels with increasing scribe widths from 0.5 mm up to 6 mm (Fig. 5) with
5 a vertical orientation in the NSS for 168 h. Fig.5 shows the partial scribe areas after
6 the NSS exposure. Fig. 5a shows the detrimental corrosion effects in the defect areas
7 on AA2024-T3 when a coating has no corrosion inhibitor, All scribes are severely
8 affected by corrosion in this case. In addition to several pits, large amounts of
9 voluminous white corrosion products can be observed. The images in Fig. 5b show
10 the effect of the coatings loaded with 15% and 2.5% PVC Li-carbonate. Both
11 coatings with high and low loading show effective corrosion inhibition in the defect
12 areas up to 3 mm. The 6 mm scribe is even protected by the 15% PVC Li-carbonate
13 sample, whereas the sample with 2.5% PVC Li-carbonate shows some darkening and
14 some white corrosion products on the left hand side of the defect which indicates that
15 locally the active corrosion protection was not sufficient. A similar behaviour is
16 observed for the Li-oxalate based coatings in Fig. 5c. Both coatings loaded with 15%
17 and 2.5% PVC Li-oxalate show almost well protected scribes without signs of
18 corrosion products in the scribes up to 3 mm wide. Like the Li-carbonate loaded
19 samples, the difference in throwing power can be observed in the scribe with a width
20 of 6 mm. Whereas the 15% PVC Li-oxalate loaded coating shows complete
21 passivation of the area without the presence of white corrosion products, the 6 mm
22 scribe of the 2.5% PVC Li-oxalate shows several pits and some white corrosion
23 products. These results show that it is possible to protect large defect areas (up to 6
24 mm) with the Li-leaching technology. Local and superficial dealloying has been
25 observed as part of the formation of the protective layer in the defect area after 168 h

1 NSS exposure. This phenomenon of limited local attack can be observed by the
 2 presence of several small black pits in the defect area which have not lead to
 3 significant active pitting corrosion as observed in Fig. 5a . Hence, from the results in
 4 Fig. 5 it can be concluded that Li-leaching coatings are able to protect large defect
 5 areas. Even the coating with only 2.5% lithium salts and slow lithium release kinetics
 6 are able to provide effective corrosion inhibition. These observations underline the
 7 active protective nature of Li-leaching coatings.

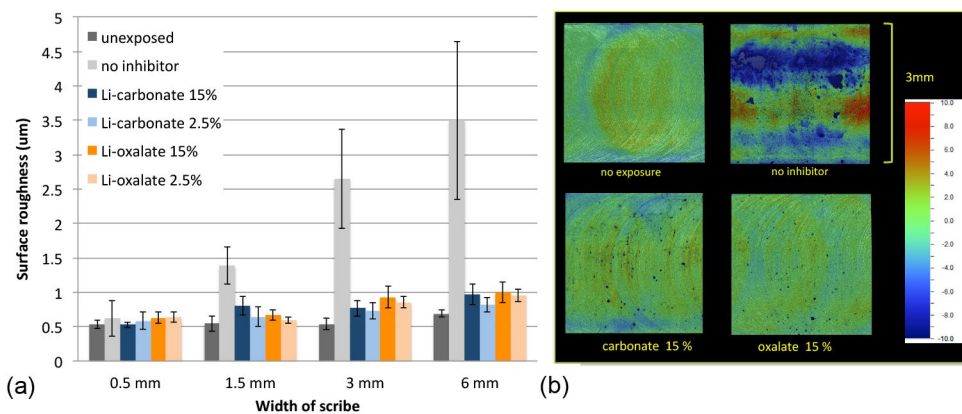


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9 *Fig. 5 Optical images of the defect areas with different scribe widths (0.5 mm, 1.5*
 10 *mm, 3.0 mm and 6.0 mm) after 168 h NSS exposure of coatings loaded with (a) no*
 11 *active corrosion inhibitor; (b) Li-carbonate (15 and 2.5 % PVC); (c) Li-oxalate (15*
 12 *and 2.5 % PVC).*

1 3.3.2 Surface roughness in the defect area

2 White light interferometer (WLI) profilometry was used to measure the surface
3 roughness (Sa) in the defect areas to obtain absolute values for the degree of corrosion
4 in the defect areas as a result of local corrosion phenomena such as pitting
5 corrosion.[40] Fig. 6a shows a graph with the surface roughness values of the
6 different scribes before and after 168 h exposure to NSS. This graph shows the effect
7 of the active protective nature of the Li-salts when used as leachable corrosion
8 inhibitors. The graph confirms the damaging effect in the defect area when the
9 coating does not provide active corrosion protection. The Sa increases with increasing
10 scribe width from 0.5 μm before exposure to values of 2.5 to 3.5 μm in scribes of 3
11 mm and 6 mm due to the effects of general and local corrosion processes in the defect
12 area after exposure. The surface roughness of the Li-leaching coatings increases only
13 slightly compared to the unexposed samples. Fig. 6b shows the WLI surface
14 roughness maps of the 3 mm scribes highly loaded coatings before and after 168 h
15 NSS exposure.



16

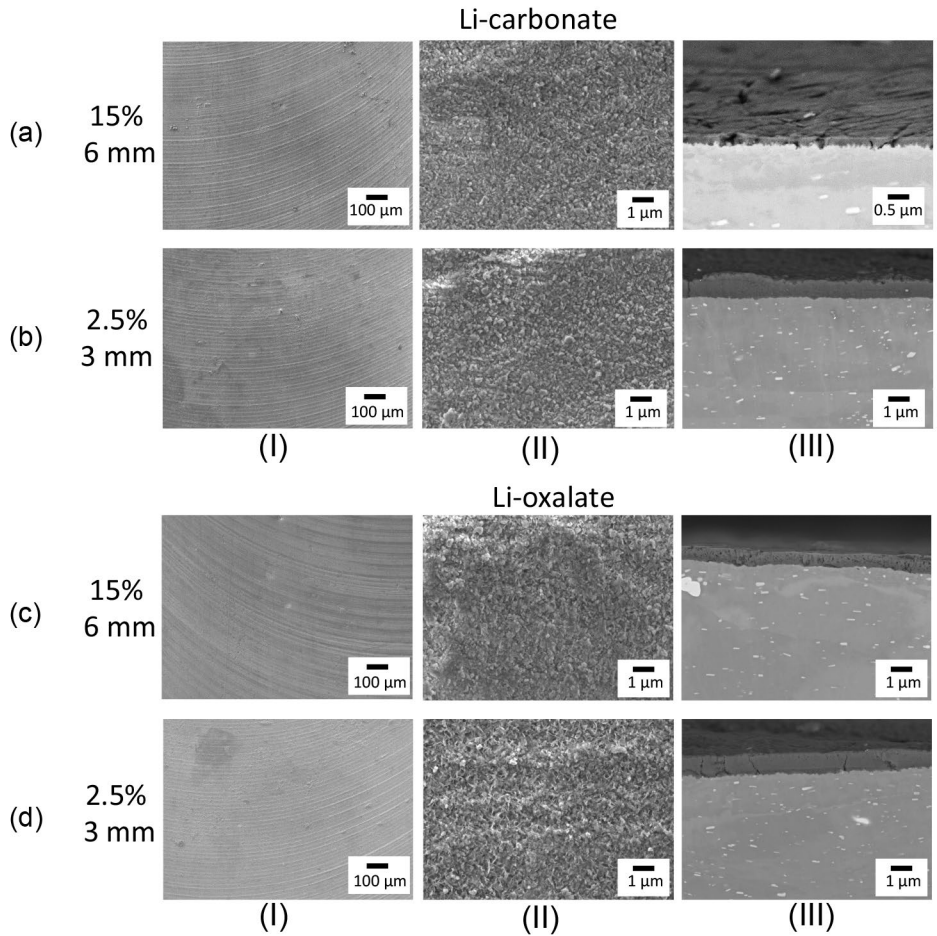
17 Fig. 6 Surface roughness (Sa) of (a) the defect areas displayed in Fig. 5 acquired by
18 WLI measurements; (b) typical WLI surface maps of the 3 mm wide scribes prior to
19 exposure as well as for coatings without inhibitor and coatings with a high loading of
20 Li-carbonate and Li-oxalate.

21

1 The uninhibited sample shows large areas that were affected by (pitting)
2 corrosion. The 3 mm scribes of the 15 % PVC Li-leaching coatings have a smooth
3 surface with only a few very small pits. These results confirm the efficient active
4 protective properties of Li-salts when used as leachable corrosion inhibitors in organic
5 coatings.

6 3.3.3. Scanning electron microscopy analysis of wide scribes

7 Fig. 7 displays the SEM micrographs of the widest scribes of the Li-leaching
8 coatings with the best inhibition performance focussing on (I) the top view
9 appearance of the scribe, (II) the morphology of the protective layer, and (III) the
10 cross-sectional analysis. The 6 mm scribe was investigated for the samples with 15%
11 PVC Li-salt (Fig. 7a and 7c) and the 3 mm scribe was selected for the samples with
12 2.5% PVC Li-salt (Fig. 7b and 7d). The top view analysis in Fig. 7(I) of the scribes
13 showed no signs of pitting corrosion for all the samples investigated. The fast
14 effective inhibition of the Li-leaching coatings preserved the machining patterns
15 resulting from the scribing process. At higher magnification the protective layer was
16 revealed (Fig. 7(II)) showing a very different surface morphology for all samples
17 compared to observations in the 1mm scribes as shown in Fig. 4. None of the samples
18 shows the characteristic polycrystalline morphology. The cross-sectional analysis
19 (Fig. 7(III)) revealed that all scribes were covered with a protective layer. The Li-
20 carbonate samples showed a thin protective layer of 240 – 280 nm in the 6 mm scribe
21 of the 15% PVC sample (Fig. 7a(III)) and a layer with an approximate thickness of
22 1.0 μm in the 3mm scribe of the 2.5% PVC Li-carbonate sample (Fig. 7b(III)). The
23 Li-oxalate loaded samples showed slightly thicker layers of 1.0 μm and 1.2 μm for
24 the 15% PVC and 2.5 % PVC samples respectively(Fig. 7c and 7d(III)).



1

2 *Fig. 7 Scanning electron micrographs of the defect areas of the Li-leaching coatings*
 3 *after 168h NSS exposure: Li-carbonate loaded coating (a) 15% PVC, 6 mm*
 4 *defect area; (b) 2.5% PVC, 3 mm wide defect area; Li-oxalate loaded coating (c)*
 5 *15% PVC, 6 mm wide defect area; (d) 2.5% PVC, 3 mm wide defect area. (I) planar*
 6 *view of the defect area; (II) top view of the protective layer; (III) cross-sectional view*
 7 *of the protective layer in the defect area.*

8 *3.4. Li-spread and compositional analysis using time-of-flight secondary ion mass*
 9 *spectrometry*

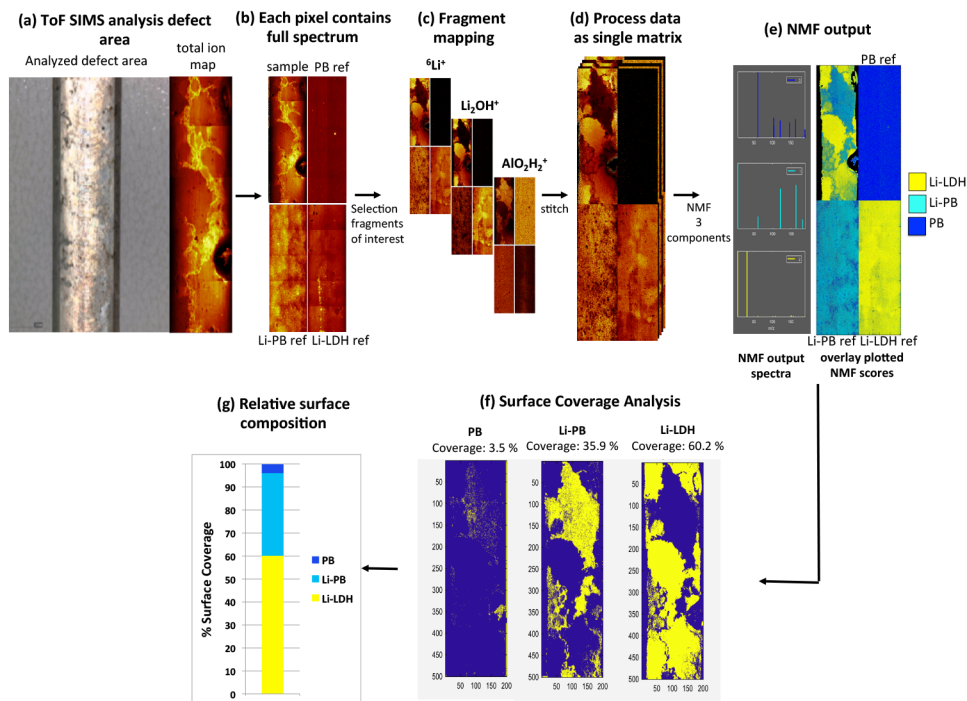
10 Li is a difficult element to detect with regular surface analytical techniques, due to its
 11 low atomic number. In this work, the surface composition of the protective layer
 12 formed in a defect on AA2024-T3 from Li-leaching was studied using time-of-flight
 13 secondary ion mass spectrometry (ToF-SIMS). It was aimed to analyse the layer's
 14 surface composition(s) and the distribution of lithium in the defect area. ToF-SIMS
 15 has a large sensitivity towards lithium and it has demonstrated its ability to identify

1 the chemical speciation of inorganic compounds.[41] ToF-SIMS provides
2 compositional data of the very surface of the protective layers, but in combination
3 with the high lateral resolution of the technique, the lateral spread of the lithium based
4 species within defect areas after NSS exposure could be imaged. Characteristic ion-
5 fragment assignments were made and a multivariate analysis method non-negative
6 matrix factorisation (NMF)) was applied to identify the various species present at the
7 surface of the protective layer.

8 *3.4.1 Non-negative matrix factorization (NMF) method*

9 Previous ToF-SIMS work made it possible to observe the lateral Li-distribution in
10 the defect area and to identify and determine relative concentrations of two chemical
11 compositions (Li-PB and Li-LDH) present at the surface of the protective layer in 1
12 mm defect areas.[25] In this work, the NMF methodology was extended to identify
13 and map the distribution of three chemical compositions at the surface of the
14 protective layers generated in the defect area: PB, Li-PB and Li-LDH. Fig 8a-g shows
15 the different steps involved in this procedure. (Fig. 8a) An optical image of the defect
16 area to be analysed is shown. (Fig. 8b) Large area ToF-SIMS images (total ion maps
17 are shown) are obtained for the defect area and for three reference materials (PB, Li-
18 PB and Li-LDH). Each pixel contains a full mass spectrum. (Fig. 8c) Nineteen
19 fragments of interest, characteristic for the reference materials were selected based on
20 a compositional ToF-SIMS analysis.[25] Each fragment has its own map, as shown
21 for ${}^6\text{Li}^+$, Li_2OH^+ and AlO_2H_2^+ .[25] (Fig. 8d) All data cubes from the maps of defect
22 area for the three compounds of interest and three reference compounds were stitched
23 into a single data set. Given that three different reference materials were included in
24 the dataset, the entire dataset was processed with NMF into three pure compounds
25 according to the method of Trindade et. al.[30] (Fig. 8e) The resulting NMF output

1 provides, on one hand the fingerprint spectra of the three reference materials and on
 2 the other hand, the normalized NMF intensities of the pure compound were plotted
 3 per pixel in an overlay map in the defect. (Fig. 8f) In order to determine the
 4 percentage of surface coverage for each compound, each pixel was assigned to a
 5 single compound, based on thresholds applied to the NMF intensities. Each
 6 compound is mapped separately for the defect area. (Fig. 8g) Based on the total
 7 amount of pixels, these normalized NMF intensities can be converted into a
 8 compositional ratio of the pure compounds present at the surface of the protective
 9 layer in the defect area.



10

11 *Fig. 8 Schematic description of the NMF process used for the compositional study of*
 12 *the corrosion protective layer in the defect area formed by the Li-leaching coatings.*

13

14

15

1 3.4.2. *Lithium spread and composition in a defect area over time*

2

3 ToF-SIMS analysis of the surface composition in the defect area, as described above

4 was applied on samples of the 15 % PVC Li-carbonate loaded coating to study the Li-

5 spread and the surface composition of the protective layer in the 1 mm wide scribe as

6 a function of NSS exposure time (Fig. 9). The minor isotope ${}^6\text{Li}^+$ was used to

7 visualise the distribution of Li ions within the defect area, as the high ionisation cross

8 section of Li means that the ${}^7\text{Li}^+$ fragment was too intense and saturated the detector

9 (Relative abundances: ${}^7\text{Li}^+ = 92.5\%$ and ${}^6\text{Li}^+ = 7.5\%$).[25] Fig. 9a shows the ${}^6\text{Li}^+$

10 maps as function of the NSS exposure time. These maps reveal the fast Li-spread in

11 the defect due to the leaching of the Li-carbonate from the coating. From the surface

12 maps it can be noted that the defect area is already completely covered with Li-

13 compounds after only after 15 min of NSS exposure. Furthermore, the images show

14 the Li-spread initiating at the edges of the defect area and interacting with specific

15 areas in the defect area. The different Li concentrations observed in the ${}^6\text{Li}^+$ map can

16 indicate the presence of different surface compositions in the defect area. It can be

17 noted that over longer exposure time Li spreads out further. After 2 h NSS exposure

18 the entire scribe was covered with a homogeneous concentration of Li. Further Li-

19 enrichment is visible after 48 h exposure. The NMF procedure was used to reveal

20 evolution of the surface composition of the generated layer in the defect areas after

21 different NSS exposure times. The complete data set was factorised by NMF using

22 the data of the three reference samples. Fig. 9b shows the NMF overlay maps of the

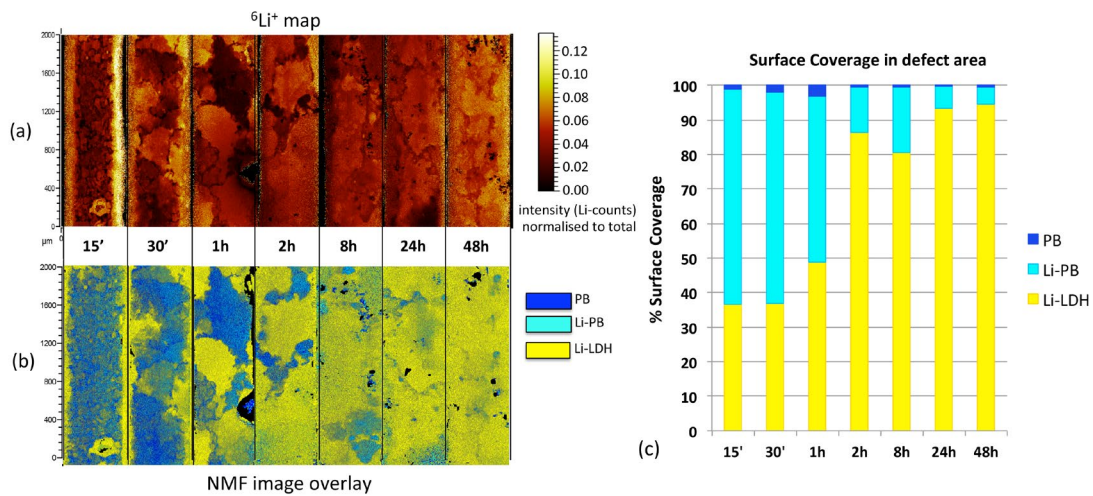
23 respective ToF-SIMS ${}^6\text{Li}^+$ maps of Fig. 9a, representing the normalized NMF

24 intensities of PB, Li-PB, and Li-LDH as a function of exposure time. These maps

25 show the fast lateral spread of the Li-based compounds in the defect. After only 15

26 minutes NSS exposure, the entire defect area was basically covered with two Li based

1 compounds, Li-PB and Li-LDH. The Li-PB layer was generated almost instantly
 2 throughout the coating defect whereas Li-LDH was formed along the edges of the
 3 defect area. Initially, Li-LDH was generated only at selective areas in the defect area
 4 (1-2h) but longer NSS exposure resulted in the lateral spread of Li-LDH throughout
 5 the entire defect area. Fig. 9c shows the NMF intensities of PB, Li-PB, and Li-LDH
 6 detected in the defect area as a function of NSS exposure time. After only 15 min
 7 NSS, 37% of the relative surface coverage could be attributed to Li-LDH. This value
 8 increased to 94% Li-LDH surface coverage after 48 h NSS exposure.



9

10 *Fig. 9 Li-spread and compositional analysis during the formation of a corrosion*
 11 *protective layer in a 1 mm wide defect area from a 15% PVC Li-carbonate loaded*
 12 *coating as a function NSS exposure time: (a) $^6\text{Li}^+$ maps; (b) Overlay images of*
 13 *normalised NMF intensities; (c) Relative surface composition of the corrosion*
 14 *protective layer in the defect area for PB, Li-PB and Li-LDH after 15 min up to 48 h*
 15 *NSS exposure.*

16

17 These results revealed the very fast action of Li-salts in the coating defect when
 18 released from the coating matrix and show that two main compounds are involved in
 19 the formation of the protective layer in the defect area. Initially, the leaching of Li-
 20 ions into the defect area results in a Li-PB layer throughout the defect area. Further

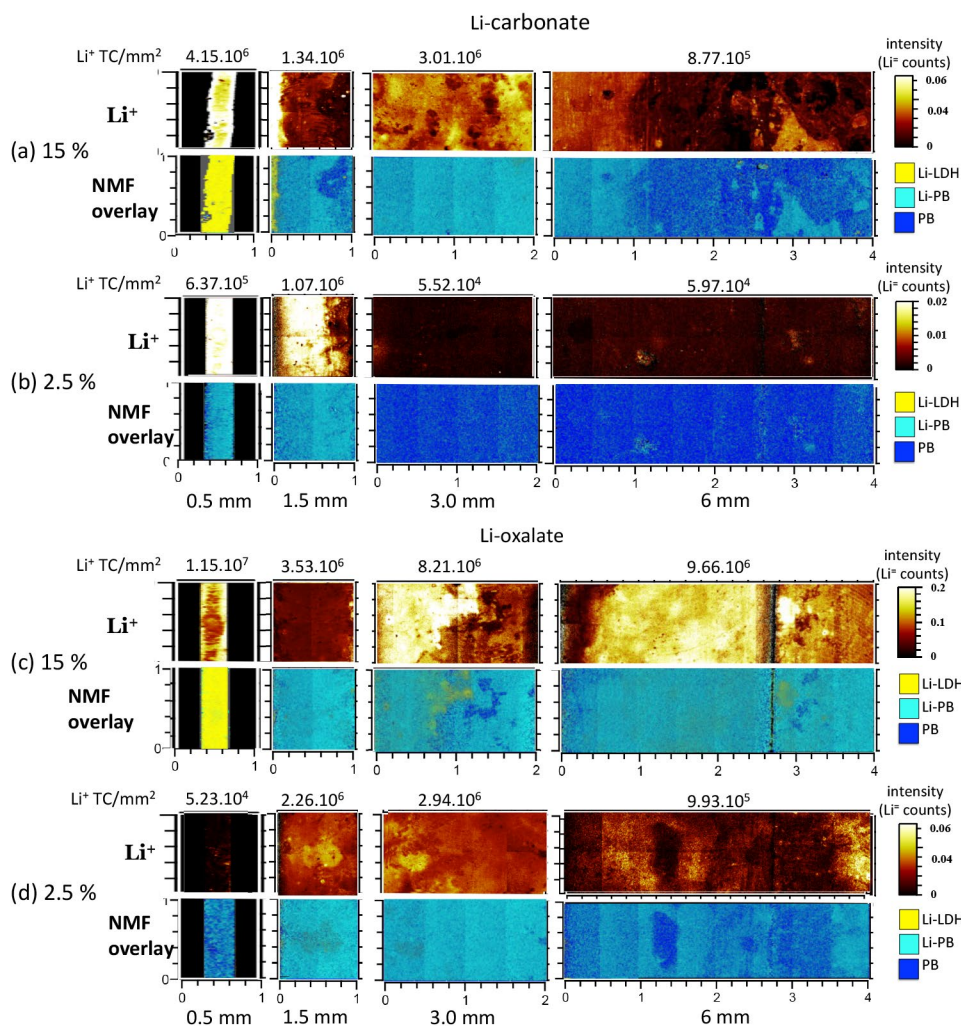
1 leaching of Li-carbonate in the defect area due to extended exposure to the NSS
2 conditions provide conditions that contribute to the formation of a Li-LDH throughout
3 the defect area. Under these conditions, only small amounts, if indeed any, PB were
4 detected.

5 *3.4.3. Li-spread and compositional analysis in large coating defects*

6 The previous section demonstrated that the 15% PVC Li-carbonate loaded coating
7 was able to cover the entire 1 mm defect area fast and effectively with a Li-LDH layer
8 demonstrating a sufficient degree of chemical throwing power for the 15% PVC Li-
9 carbonate sample under these conditions. The same ToF-SIMS methodology was
10 applied on the coated panels with increasing scribe widths, which were optically
11 assessed earlier in this work to determine the lateral chemical throwing power of the
12 coatings with high and low Li-salt loadings after 7d NSS exposure. Fig 10 shows the
13 Li^+ distribution maps (top rows) of a section of the scribes including the normalized
14 total Li^+ counts per mm^2 and the corresponding NMF image overlays (bottom rows).
15 The ToF-SIMS analysis was performed in each defect area with the exclusion of the
16 areas close to the sides of the scribe to avoid artefacts due to edge effects of the
17 scribe. The Li^+ distribution maps show that Li is detected throughout all scribes, even
18 up to 6mm scribe widths after the 7 d NSS exposure. This demonstrates that all
19 coatings with a fast leach rate (15% PVC Li-salts) and a relatively low leach rate (2.5
20 % PVC Li-salts) were able to generate conditions in the defect areas that enabled the
21 formation of a protective layer on the aluminium alloy. The highest concentrations of
22 Li^+ (counts/ mm^2) were detected in scribes of the coatings with the 15% PVC Li-salt
23 loaded coatings (Fig 10a and 10c). and Li^+ concentrations decreased with increasing
24 scribe widths. Higher concentrations of Li^+ were detected in the scribes of the Li-
25 oxalate loaded coatings compared to the Li-carbonate coatings. This is in line with the

1 faster leach rate of the Li-oxalate loaded coatings. The concentrations of Li^+
2 distributed in the defect areas of the 2.5% PVC loaded samples were clearly lower
3 than the 15% PVC loaded samples. However, the defect areas up to 6 mm were still
4 covered with Li-containing compounds. This demonstrates the mobility, reactivity
5 and the chemical throwing power of the lithium-ions, even at low concentrations.

6 The NMF procedure was applied on these samples to generate compositional
7 maps of the surface chemistry and to distinguish a relative quantification of pure
8 compounds in the defect areas using three reference samples (PB, Li-PB, and Li-
9 LDH). The bottom rows of each figure in Fig. 10 show the NMF overlay images
10 showing the distribution of the three compounds in the analysed defect areas. The
11 NMF overlay images of Fig. 10a show that the surface of the 0.5 mm defect of the 15
12 % PVC Li-carbonate is fully covered with Li-LDH. However, it can be observed that
13 the surface composition of the wider defect areas can be attributed to Li-PB and that
14 Li-LDH is not detected. Fig. 10b shows the uniform distribution of Li^+ in the defect
15 areas of the 2.5 % PVC Li-carbonate coatings. The NMF overlay maps of these
16 defect areas reveal that little or no Li-LDH was formed in these defect areas but these
17 defect areas were covered with a protective layer composed of a mixture of Li-PB
18 and PB. A similar behaviour was observed for the Li-oxalate coatings in Fig 10c and
19 10d. The NMF analysis showed that the relative surface composition of the protective
20 layer in the 0.5 mm defect of 15% PVC Li-oxalate coating (Fig. 10c) comprises
21 mainly Li-LDH, whereas the surface composition of protective layers in the wider
22 scribes contain primarily Li-PB with some local areas of Li-LDH. The protective
23 layers in all defect areas of the 2.5% PVC Li-oxalate coated samples comprise mainly
24 Li-PB.



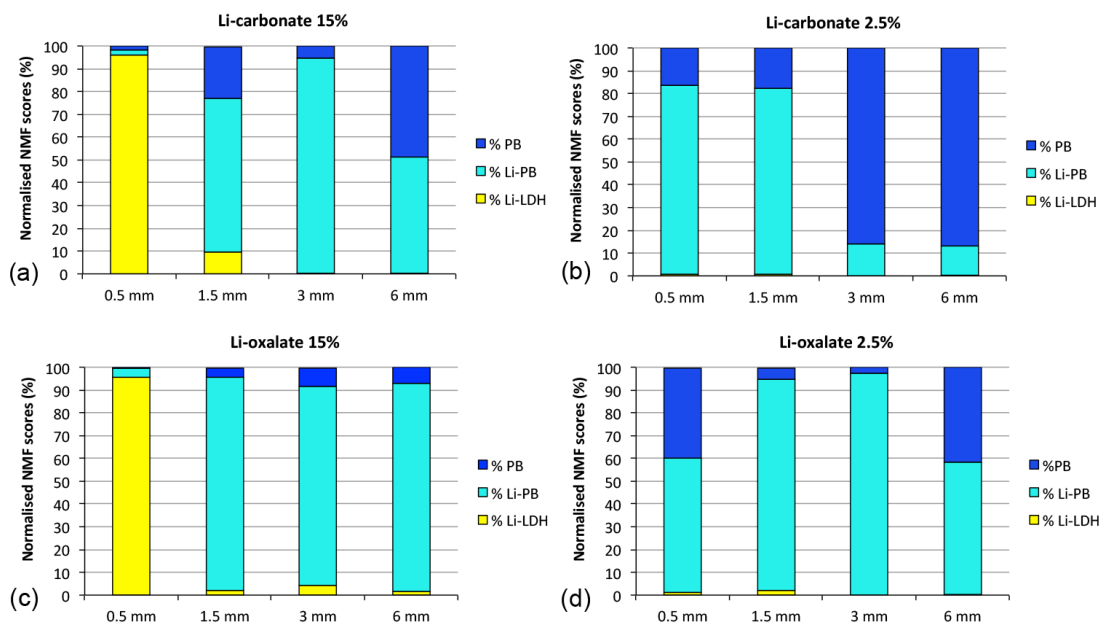
1

2 *Fig. 10 Lithium spread (top row) and normalized Li^+ counts with the corresponding*
 3 *NMF image overlay images (bottom row) of the corrosion protective layers generated*
 4 *in the defect areas (0.5 mm, 1.5mm, 3.0 mm and 6.0 mm width) from the Li-carbonate*
 5 *loaded coating (a) 15% PVC; (b) 2.5% and the Li-oxalate loaded coating (c) 15%*
 6 *PVC; (d) 2.5 % PVC after 168 h NSS exposure.*

7

8 Fig. 11 summarizes the relative surface composition intensities of the 3 pure
 9 compounds detected at the surface of the protective layer in the defect derived from
 10 the NMF procedure applied on the samples with increasing defect widths. For the
 11 15% PVC Li-carbonate loaded coating (Fig. 11a) it can be observed that the
 12 occurrence of Li-LDH decreases rapidly when the defects become wider. The
 13 coverage with Li-LDH drops from 95% in a 0.5 to 1 mm scribe to values below 10%

1 when the defects becomes 1.5 mm or wider. Instead of Li-LDH, Li-PB becomes the
 2 most abundant species. A similar trend is observed for the 15% PVC Li-oxalate
 3 samples in Fig. 11c. Li-PB is also the most abundant species found at the surface of
 4 the protective layer throughout the defect areas of the 2.5% PVC Li-salt coatings (Fig.
 5 11b and 11d). Only in the wider scribes of the 2.5% PVC Li-carbonate the levels of Li
 6 are lower at the surface of the protective layer and the majority of the species in the
 7 defect area can be related to PB.



8

9 *Fig. 11 Relative surface composition of the corrosion protective layer in the defect*
 10 *areas (Li-LDH vs. Li-PB) obtained from the NMF image overlay data displayed in*
 11 *Fig. 10: Li-carbonate loaded coating (a) 15% PVC; (b) 2.5% PVC and Li-oxalate*
 12 *loaded coating (c) 15% PVC and (d) 2.5% PVC.*

13

14 In summary, the graphs of Fig. 10 and 11 imply that the surface composition of
 15 the protective layer in the defect areas depends on the inhibitor release rate and
 16 loading of the coating and the size of the defect. The occurrence of Li-LDH seems to
 17 be related to systems with fast leaching and high Li-loading (15% PVC Li-salts) and
 18 relatively small defect widths (0.5 mm). These parameters will result in high Li

1 concentrations and alkaline conditions which are favourable for the formation Li-
2 LDH.[27]

3 A surprising and novel observation from this work is that the main surface
4 compound of protective layers generated in the wider scribes and slower leaching
5 systems can be identified as Li-PB. For the 2.5% PVC Li-carbonate coatings the
6 contribution of PB in surface layer increases with scribe width. The combination of
7 these observations with the knowledge that the defect areas were effectively
8 protected, leads to the conclusion that Li-LDH is not the key corrosion inhibiting
9 species needed for effective corrosion inhibition but in essence appears to be a side-
10 product which is generated when high levels of Li carbonate and oxalate are present
11 in the defect area.

12 *3.5. Chemical throwing power of Li-leaching coatings*

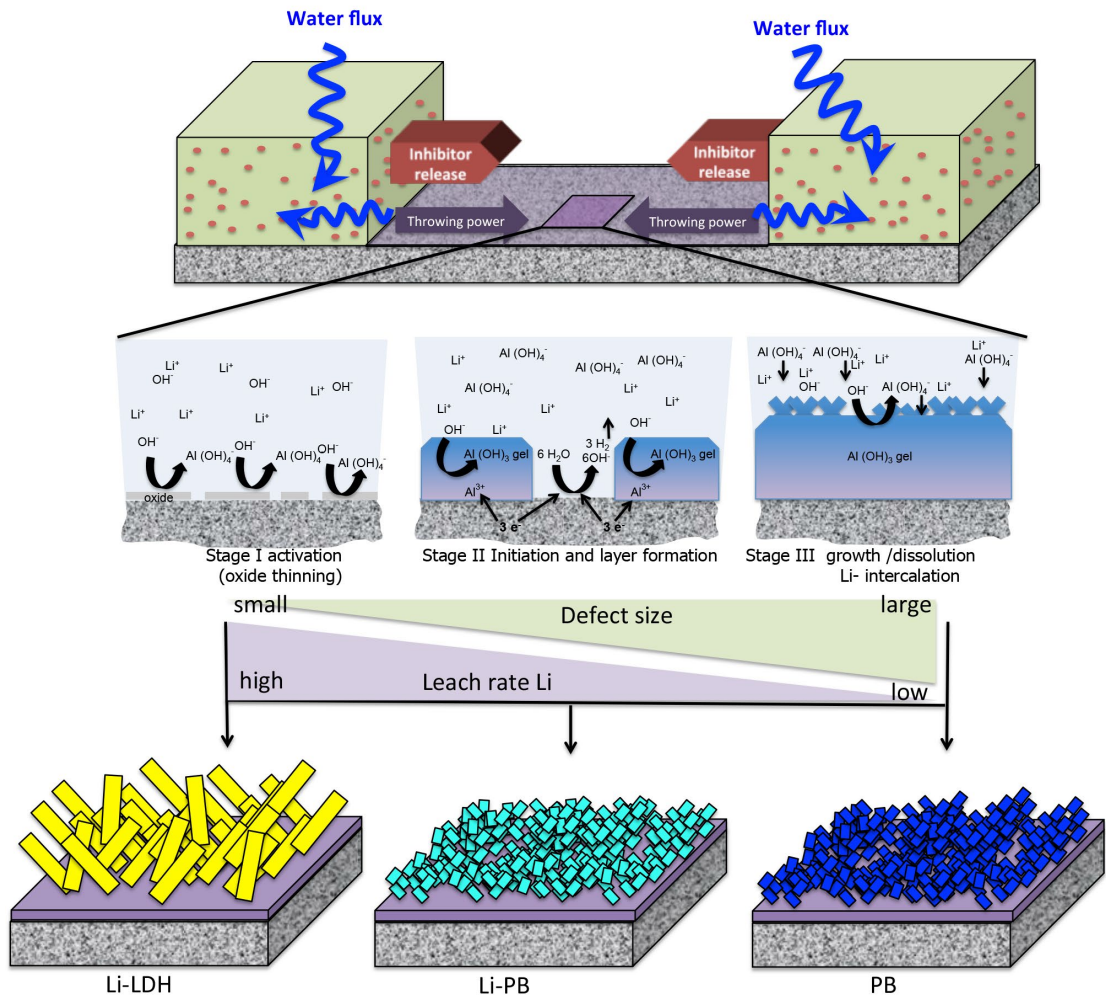
13 The approach in this study confirmed the important aspects that are considered as
14 essential for effective active corrosion protection from organic coatings. In order to
15 have a sufficient chemical throwing power, coatings must be able to leach sufficient
16 amounts of corrosion inhibitor to achieve a critical inhibitor concentration in the
17 defect area in a short time to obtain a fast and irreversible corrosion inhibition[12, 15]
18 However, it is known that the larger the defect size is, the more difficult it is to obtain
19 these critical concentrations of corrosion inhibitor in the defect to prevent corrosion.
20 [14]

21 In the work discussed above, Li-leaching coatings were investigated varying
22 inhibitor loading, inhibitor solubility and defect size to obtain more insight in the
23 throwing power characteristics of this novel chromate-free active protective coating
24 technology. These factors contribute to the inhibitor accumulation in the defect area

1 and the efficacy of the Li-based coating technology. The results of the investigation
2 showed that the investigated Li-leaching coatings have a chemical throwing power of
3 3 to 6 mm and the ability to cover and protect these wide defect areas effectively. The
4 ToF-SIMS analysis of the defects areas revealed that Li is distributed throughout the
5 defect areas and three different compounds (Li-LDH, Li-PB, and PB) were found.
6 The ratio of these compounds seems to be related to the dissolution of the corrosion
7 inhibitor from the coating matrix (i.e. loading in the coating and solubility of the Li-
8 salts). The work indicates that Li-LDH is a side-product in the generation of these
9 protective layers due to fast release of the Li-salts leading to high Li concentrations
10 and high pH values in small defect areas.

11 With these results, it is possible to discuss the proposed formation mechanism of
12 these protective layers from lithium leaching coatings in more detail (Fig. 12).[21, 39]
13 Considering the possible event of a coating defect, the aluminium alloy AA2024-T3
14 will be exposed to environmental conditions and a thin layer of electrolyte will be
15 formed in the defect. This moisture will trigger the dissolution and diffusion of the Li-
16 salt from the organic coating matrix into the defect area initiating Stage I of the
17 formation mechanism. Due to the alkalinity of the Li-salts, the conditions in the defect
18 area will become alkaline (pH 9-10) and the presence of chlorides in the electrolyte
19 the natural oxide of the aluminium alloy will be thinned.[21, 42] This oxide thinning
20 will enable the initial formation of the protective layer (Stage II) via direct anodic
21 dissolution of aluminium, resulting in the formation of aluminium hydroxide gel on
22 the aluminium substrate under these moderate alkaline conditions.[43, 44] When the
23 film of aluminium hydroxide gel covers the surface, the layer will develop by a
24 growth and dissolution process until a stable state is reached. This growth and
25 dissolution process (Stage III) is characteristic for aluminium in alkaline

1 conditions.[20, 27, 45-47] Stages I and II are known to be fast processes and the
 2 growth-rate in stage III is limited by diffusion of species across the dense inner
 3 oxide.[44, 48] This oxide growth process may be accelerated by the presence of
 4 chloride ions which are thought to be able to facilitate the hydration and dissolution
 5 process of amorphous oxide.



6
 7 *Figure 12 Schematic illustration of the mechanism and the relation between the*
 8 *surface composition of the protective layer in the defect related to the Li leach rate*
 9 *and the size of the coating defect*
 10

11 This aluminium corrosion process results in a surface-covering layer on the
 12 aluminium alloy with a dense morphology at the inner layer near the aluminium alloy

1 / (hydr)oxide interface and a porous morphology at the outer region of the protective
2 layer. From the results obtained in this work, it became apparent that three different
3 compounds can be identified at the outer region of the protective layer: (i)Li-LDH: in
4 the case of high Li concentrations and small defect areas; (ii)Li-PB: in the case of
5 moderate Li concentrations and wider defect areas and (iii)PB: in the case low Li
6 concentrations and wide defect areas.

7 It is known that Li-LDH can be formed when there is sufficient $\text{Al}(\text{OH})_4^-$, Li^+ ,
8 CO_3^- or OH^- in solution at pH values higher than 10.[27] On the other hand, it is
9 known that amorphous aluminium hydroxide transforms into pseudo-boehmite by an
10 aging process in mildly alkaline conditions.[44] The results from this research
11 indicate that Li-LDH is not the primary corrosion inhibiting species in the defect area
12 from these Li-leaching coatings and that the relative Li^+ concentration in the defect
13 area determines whether Li-LDH is formed or not.

14 Li-PB was the most prominent surface species detected in most of the defect areas.
15 It is known that ions (e.g Cerium)[26] can be incorporated in pseudoboehmite layers
16 promoting oxide growth.[26] The results show that most of the defect areas are
17 protected by PB layers with high and low amounts of Li depending on the leach rate
18 and width of the defect area. This combined with the Li distribution in the defect
19 areas strongly suggests that Li is involved in the stabilization of the aluminium
20 hydroxide layer in the defect area. However, additional studies are needed to explain
21 the chemical stabilization mechanism of the aluminium hydroxide layer by Li. In
22 addition this work, demonstrated the chemical throwing power properties of lithium-
23 leaching coatings and has shown that only small amounts or low concentrations of Li
24 are needed to provide active corrosion protection in large defect areas. The efficacy of

1 the corrosion protection seems to be limited by the amount of Li that can be released
2 from the coating into the defect area and the ability to reach the critical concentration
3 and conditions for effective corrosion inhibition. The insights obtained in this work
4 provide an enhanced view on the active corrosion inhibiting properties and the
5 mechanism of Li-leaching coatings for the protection of aluminium alloys

6 **4. Conclusions**

7 This work studied the chemical throwing power of Li-leaching coatings and the
8 compositional analysis of the protective layers in the coating defects. Organic
9 coatings were formulated with different Li-salts as corrosion inhibitors and different
10 loadings to obtain different leaching behaviours to evaluate the distance (throwing
11 power) these leaching Li-inhibitors are able to protect coating defects with increasing
12 widths.

13 It was demonstrated that Li-inhibitors were able to protect coating defects with a
14 width up to 6 mm from coatings with different leaching behaviours by the formation
15 of a protective layer in the defect area.

16 ToF-SIMS was used to map the distribution and relative concentration of lithium
17 in the defect areas. An NMF analysis of the ToF-SIMS datasets was applied to link
18 the Li distribution in the defect areas with the compositional characterisation of the
19 surface of the protective layer. It was found that Li-PB is the main surface compound
20 encountered and Li-LDH is a side-product, which is generated in small defect areas
21 and at fast Li-leaching rates.

22 This study provides a further understanding of the active corrosion protective
23 properties, the surface composition in the defect and demonstrates the chemical

1 throwing power of the Li-leaching technology, a feature that has not been
2 demonstrated for any other chromate-free inhibitor leaching coating technology.

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8 AkzoNobel Specialty Chemicals for their assistance with the ion-milling and leaching
9 experiments This research was carried out under the collaboration agreement between
10 AkzoNobel and Delft University of Technology.

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