Materials and Corrosion **2016**, 66 (12) 1382-1390
DOI: 10.1002/maco.201508304

Inhibition of aluminum alloy corrosion in electrolytes by self assembled fluorophosphonic acid molecular layer

Judit Teledgi[a,b,*], Giorgio Luciano[c,d], Suomito Mahanty[e], Talah Abohalkuma[f]

[a] Óbuda University, 1034 Budapest, Doberdó út 6, Hungary
[b] Research Centre for Natural Sciences, Institute of Materials and Environmental Chemistry, Hungarian Academy of Sciences, Magyar tudósok körútja 2, 1117 Budapest, Hungary
[c] CNR-ISMAR Istituto di Scienze Marine, Via de Marini, 6 16149 Genova, Italy
[d] CNR-ISMAC Istituto per lo Studio delle Macromolecole, Via de Marini, 6 16149 Genova, Italy
[e] Indian Institute of Technology Kanpur, India, 208016
[f] PhD School of Materials Sciences and Technologies; Óbuda University; Bécsi út 96/B, 1034 Budapest, Hungary
*Corresponding author's email address: telegdi.judit@ttk.mta.hu

Abstract

This paper presents the use of self-assembled molecular (SAM) layers of fluorophosphonic acids developed on aluminum surface. The SAM monolayers were adsorbed from ethanol solution, characterized by surface morphology visualized by atomic force microscopy, by the wettability by contact angle measurements.

The anticorrosion efficiency of the nanolayers determined by *ex situ* AFM measurements and by electrochemical techniques, which indicated the importance of the fluorophosphonic acid concentration and of the film formation time in the molecular

Formázott: Jobb: 0,63 cm

deposition process. The morphological change with or without nanolayers caused by the corrosive environment was in accordance with the electrochemical results.

Key words: fluorophosphonic acid; SAM layers; corrosion inhibition; dynamic contact angle; AFM; electrochemical polarization.

1. Introduction

Aluminum and its alloys are widely used in many industries. In special engineering fields, such as in reaction vessels, pipes, machinery, in aviation, automotive industry, electronics, and in construction business, the use of aluminum is due to its low density and favorable mechanical properties such as excellent durability. The aluminum is an active metal and its resistance to corrosion depends on the formation of the protective oxide film; the environment influences its behavior. The corrosion resistance of aluminum alloy in aggressive environment is not good, as the natural oxide film on aluminum alloy cannot offer sufficient protection against aggressive anions. Therefore, there are several effective anticorrosion inhibitors like nitrate, phosphate, phosphonic acids [1-3] and other organic molecules; [4] used in dissolved form that can control the metal dissolution either in acidic, in alkaline or in neutral solutions. The presence of chloride ion is a special case as the aluminum is very sensitive for the pitting corrosion [5].

In addition to corrosion inhibitors (organic and/or inorganic), there are other methods to protect the aluminum and its alloys from corrosion such as coatings (metallic, inorganic, conversion and organic coatings), as well as control of environment (pH, temperature, dissolved oxygen).

One of these possibilities to control aluminum dissolution is when nano- or microlayers are developed on the metal surface. An example is the use of layers formed via sol-gel technology [6]. The application of organic silane derivatives in thin film can also prevent the aluminum from corrosion [7,8]. In other cases, amphiphilic molecules form molecular films on the metal surface, and control the dissolution of aluminum [9-11]. The molecular

Formázott: Jobb: 0,63 cm

layer formation can happen via different techniques like Langmuir-Blodgett and self-assembling methods (SAM).The SAM layer technology is one of the most effective methods, which improves the corrosion resistance of aluminum and its alloys. The advantage of the SAM technique is that it is very simple, environmentally friendly, has of great interest because of several application in many engineering field e.g. in microelectronics, biosensors, and so on. The basic principle of self-assembly technology is physical or chemical adsorption between the head groups of the amphiphilic molecules and the surface of the solid substrate at the solid/liquid interfaces. When a solid substrate immerses in an organic surfactant solution, the functional groups of surfactant molecules are able to adsorb spontaneously onto the solid surface, the hydrophobic side chains are kept together via van der Waals forces, hydrogen bonding, π-π stacking, and, the consequence is a structured molecular layer formation. The history of the self-assembling technique goes back to the eighties of the last century; its importance continuously increases. The first experiments were done on gold and copper surface with alkane thiols, which mainly chemisorbs on an oxide-free metal surface. Controversially, the carboxylic, phosphonic and sulfonic acids form SAM layers only on oxide film of metals. Phosphonic acid SAMs are increasingly used for building thin films [12-15] due to their ability to form well defined and stable layers on oxide surfaces [1-14]. As a native oxide film covers almost all engineered metals, the application of organic SAM coatings for corrosion protection is of high technological importance [16-19]. The adsorption of phosphonic acids in organic film on aluminum oxide surfaces is of substantial interest, as they form not only very stable monolayer on aluminum alloys covered with an amorphous thin oxide film [15, 20-23] but their self assembled molecular films promote the adhesion of a further coating. Maege et al. investigated the adhesion of different organophosphonates on aluminum alloys and assumed an acid-base interaction with a tridentate binding [25]. In some cases, the influence of the length and substituents in the alkyl chain were in the focus of the work. Other papers reported the influence of the substituents and the heat treatments on the effectiveness [25-31]. Some reports appeared on the anticorrosion effectiveness of phosphonic acid SAM layers on aluminum surface [32,33]. All reports unequivocally demonstrated that with increasing alkyl chain length

Formázott: Jobb: 0,63 cm

the efficiency increases. The phosphonic head group physicsorbs more stably than the carboxylic or sulphonic groups on solid metals.

In the present work, we demonstrate the deposition of SAM layer on aluminum surface from a special amphiphile, i.e. from fluorophosphonic acid. Fluorinated alkyl phosphonic acids (typically utilized materials bearing seven- and eight-carbon perfluoroalkyl groups) in self-assembled monolayers, often employed in soil resistant and release coatings, have gained wide acceptance as they go better than alternative materials with hydrocarbon or silicone tails [34]. The fluorophosphonic acid layer deposition was followed by measuring the change in the wettability via contact angle measurement. The anticorrosion effectiveness of the SAM layers was characterized by potentiodynamic polarization test informed us about the change in the corrosion current and in the shift of the corrosion potential and allowed the calculation of the efficiency. In the presence of aggressive electrolyte the AFM measurements provided numerical data on the roughening of the aluminum surface with and without nanolayer.

2. Materials and Methods

2.1 Materials used in the experiments

The metal sample was aluminum alloy 5052 (99.8Al. 0.8Mg).

The fluorophosphonic acid (CH_3-$(CF_2)_5$-CH_2-CH_2-PO_3H_2; Specific Polymers, Castries, France; SP-01-003; MW: 421.1) was dissolved without further purification in methanol for preparation of SAM layers. Methanol, ethanol, isopropanol, sodium chloride and sodium perchlorate were Sigma-Aldrich products.

2.2 Pretreatment of coupons before SAM deposition

The aluminum coupons were degreased in isopropanol as well as in ethanol (ultrasonic bath, 2x5 min), and kept in boiling distilled water for 1 hour (to cover the aluminum surface homogeneously with oxide film, as this amphiphilic molecule can adsorb only onto the oxide layer). The coupons were dried on air at room temperature and kept under normal atmosphere before layer preparation

2.3 Preparation of organic layers

The SAM layer on the aluminum alloy surface was prepared in fluorophosphonic acid solutions ($5x10^{-3}$ M as well as $5x10^{-2}$ M in methanol) by dipping the oxidized coupons into the amphiphilic solutions for pre-defined times. After removal from the

Formázott: Jobb: 0,63 cm

fluorophosphonic acid solutions the metal samples were rinsed with pure methanol, dried in nitrogen and kept in exsiccator till the characterization, investigation.

2.4 Characterization and evaluation of the aluminum alloy surface alone or after modification by fluorophosphonic acid SAM layer

Dynamic contact angles were measured in distilled water at room temperature by a digital surface tensiometer (NIMA Ltd., Model DST 9005; UK), which works on the Wilhelmy-theory and registers the dynamic contact angle. The aluminum alloy coupons with or without organic films were automatically dipped in and pulled out from ultrapure water (MilliQ) with a rate of 8 mm/min. The contact angle values and the hysteresis were registered.

Surface morphology visualized by atomic force microscopy

The aluminum alloy surface with and without nanolayers were visualized by atomic force microscope (Digital Instrument, NanoScope 3) under atmospheric condition. The analysis of the captured images allowed the evaluation of the surface roughness of the aluminum alloy coupons with and without SAM layers, before and after interaction with aqueous electrolyte solutions (0.5M NaCl and 0.1M $NaClO_4$).

Electrochemical measurements were performed by Autolab PGSTAT 30 Autolab instrument (Metrohm) in 0.5 M NaCl solution, at room temperature in a three-electrode system. The aluminum alloy working electrode (3.14 cm^2) was covered either only by natural oxide layer, or, on the top of the oxide layer, by SAM layer of fluorophosphonic acid. The counter electrode was a platinum plate and a saturated calomel electrode (SCE) was the reference. The samples in the electrolyte were initially stabilized at least for half an hour to reach a constant E_{corr} value. The scanning rate in the potentiodynamic polarization tests was 0.5 mV/s in the range of −1100 mV and + 1000 mV.

3. Results and discussion

Formázott: Jobb: 0,63 cm

3.1 Change in the wettability after nanolayer deposition

The adsorption of phosphonic acids on aluminum surface is really an acid-base reaction, when the driving force is the formation of a surface salt [35]. This fact is well known from the spontaneous formation of nanolayers from long-chain *n*-alkanoic acids [36]. In contrast to the alkanoic acids the phosphonic acids form salts with aluminum oxide which is practically insoluble in water. (On the AFM image in Figure 2. the markings of the salt are visible on the surface.) This may be one of the reasons for the high stability of these SAMs. The change in the contact angel values (which characterizes the wettablility) was followed, on one hand, by registration of the influence of the amphiphile concentration and, on other hand, by the investigation of the layer deposition time. The instrument we used, measures the so-called dynamic contact angle when the solid sample is dipped into (in our case: in water) and pulled out from the liquid with a pre-determined rate; both the advancing and the retracting contact angels are registered. When the dipping-in and pulling-out process happens not only ones, but several times, the change in the contact angles shows the stability of the nanolayer and the coverage of the surface. When the hysteresis is significant, the layer under investigation can absorb the liquid, which indicates the non-compact structure of the nanolayer. Dynamic contact angle data measured on fluorophosphonic acid SAM layers are summarized in Table 1.

Table 1: The influence of the amphiphile concentration, of the layer formation time and the number of dipping on the wettablity of the aluminum surface covered by SAM layer.

Fluorophosphonic acid concentration	SAM formation time [h]	Contact angle, advancing [°]	Contact angle, retracting [°]
methanol	4	1st dip: 65	35
methanol	4	4th dip: 42	35
5x10^{-3} M	4	1st dip: 175	65
5x10^{-3} M	4	2nd dip: 130	57

Formázott: Jobb: 0,63 cm

5x10^{-3}M	4	3rd dip: 118	53
5x10^{-3}M	4	4th dip. 110	50
5x10^{-3}M	4	5th dip: 103	50
5x10^{-3}M	48	1st dip: 168	95
5x10^{-3}M	48	2nd dip:163	93
5x10^{-2}M	4	1st dip:138	130
5x10^{-2}M	48	1st dip:145	133
5x10^{-2}M	48	2nd dip: 135	133
5x10^{-2}M	48	3rd dip: 135	133
5x10^{-2}M	48	4th dip. 135	133
5x10-^{2}M	48	5th dip: 135	133

It is clear that the deposition of the SAM layer endows the surface with more hydrophobic character than that of the pure aluminum alloy. In order to see the influence of the solvent, the coupons were immersed into the pure organic solvent used for the layer preparation for the same time. When the film formation time is longer, the layer is more stable, its hydrophobicity does not change with the dipping numbers significantly which shows that the coverage of the surface with the amphiphilic molecules is more complete. This observation is supported by the analysis of the difference between advancing and retracting angles. In general, across this series of experiments the average contact angles increase and reach limiting value~~s~~, depending on the concentration of the amphiphile and on the dipping time. Longer film formation time gives similar result as the more concentrate amphiphilic solution, i.e. both factors produce more compact SAM layer on the aluminum alloy surface. Other important observation is that in the case of more concentrated amphiphile solution the contact angle values are stable even after several dipping into water and, additionally, the retracting angle values are very high, the difference between the advancing and retracting angles is little.

3.2 Analysis of the aluminum alloy surface by atomic force microscopy

Formázott: Jobb: 0,63 cm

In order to get information about the change on the aluminum alloy surface morphology before and after corrosion tests, the solid surfaces with or without nanolayers were imaged. It is important to mention that the amorphous metal alloy surface was not grained and polished; it was used as-received for the layer deposition.

The aluminum alloy surface was visualized before and after contacting with the two electrolytes. One was the sodium chloride solution, which induces pitting corrosion. The other one was sodium perchlorate solution, which is a so-called "neutral" electrolyte. The AFM images in the next figures adumbrate into the influence of both electrolytes on the aluminum alloy surface with and without nanolayers.

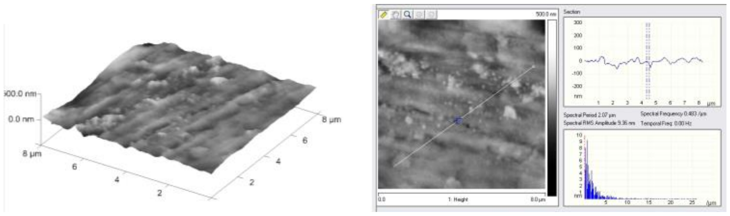

Figure 1. Oxide layer covered aluminum alloy surface visualized by 3D and section analysis.

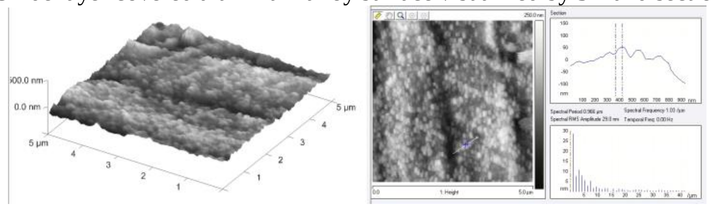

Figure 2. Fluorophosphonic acid SAM layer on aluminum alloy surface visualized by 3D and section analysis.

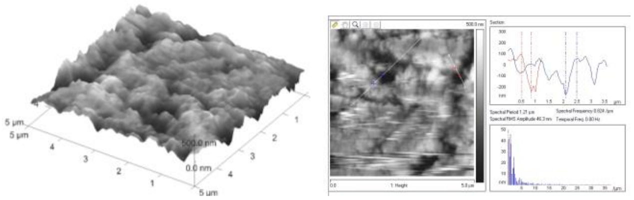

Figure 3. Aluminum alloy surface without nanolayer in sodium choride for 1 h, visualized by 3D and section analysis.

Formázott: Jobb: 0,63 cm

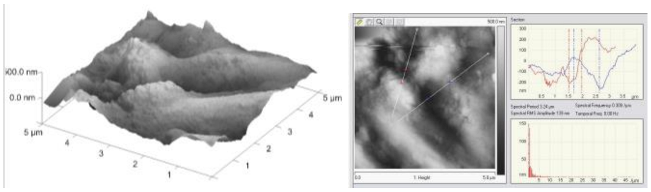

Figure 4. Aluminum alloy surface without nanolayer in sodium perchlorate for 1 h, visualized by 3D and section analysis.

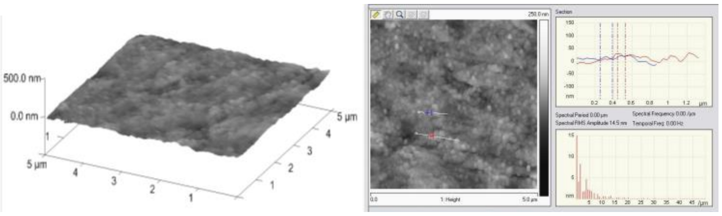

Figure 5. Aluminum alloy surface covered by fluorophosphonic acid SAM layer in sodium chloride for 1 h, visualized by 3D and section analysis.

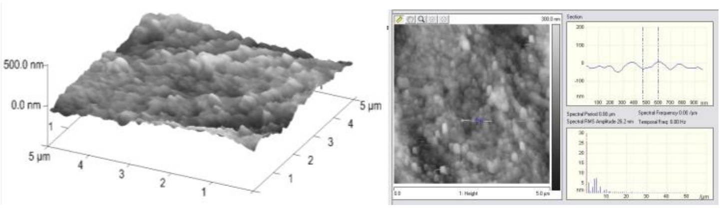

Figure 6. Aluminum alloy surface covered by fluorophosphonic acid SAM layer in sodium perchlorate for 1 h, visualized by 3D and section analysis.

In order not only qualitatively but also quantitatively evaluate the AFM images, the 3D images were analyzed and the surface roughness registered (Table 1).

Table 2. Roughness and depth analysis data derived from AFM images, measured on aluminum alloy samples with and without SAM layers (SAM formation time: 4 hours in 5x10^{-2} M fluorophosphonic acid solution; electrolytes: NaCl and $NaClO_4$ solutions for 1 h at room temperature)

Sample	RMS [nm]	max. peak depth [nm]
Al	9.36	122
Al + NaCl	86.2	413
Al + $NaClO_4$	139.0	422

Formázott: Jobb: 0,63 cm

Al + fluorophosphonic acid SAM	11.5	88
AL + fluorophosphonic acid SAM + NaCl	14.5	145
Al + fluorophosphonic acid SAM + $NaClO_4$	26.2	217

According to the 3D image in Figure 1 the oxide-covered aluminum alloy surface is smooth which is reflected in the section image and in the RMS as well as in the depth analysis values. The presence of NaCl solution on the aluminum changes the surface rough with visible pits. All these are visible on the section images and demonstrated by the increased RMS and peak depth values.

The roughness of the aluminum alloy surface in the presence of the chloride anion is about 10x higher than without the aggressive anion. Pits are visible on the surface; their depth is in the range of 100 nm and 370 nm. The metal surface turned to be much more uneven when it interacted with sodium perchlorate electrolyte. In this case the coarseness is about 14-time higher that reveals the most intensive roughening of the aluminum alloy. The corrosive damages reveal themselves in broad and wide holes that are representative for general corrosion. This is very peculiar as the perchlorate anion – from the corrosion point of view – is considered to be a neutral electrolyte. This unexpected behavior needs further investigation.

When the aluminum oxide surface is covered by the SAM nanolayer formed from fluorophosphonic acid, the surface morphology is typical, it is covered by repetitive patterns, that demonstrates the deposited molecular layer which formed insoluble salts; the height of these protruding particles are measurable, and are in the range of 20-45 nm.

When the electrolytes interact with the nanolyer covered aluminum surface, the presence of the SAM layer on the metal surface decreases significantly the effect of the aggressive ions i.e. of the sodium chloride and sodium perchloride. Both the section images and the RMS values confirm what is visible on the 3D AFM images: the presence of the molecular layer inhibit the interaction of electrolyte with the metal surface. It is reflected in the smooth surface and in the not significantly altered RMS values.

3.3 Anticorrosion effectiveness characterized by electrochemical measurements

Electrochemical measurements were applied to show the anticorrosion efficiency of the nanolayers. The potentiodynamic measurements demonstrate that the SAM layer of the fluorophosphonic acid shifts the corrosion potential into the anodic direction (from -838

Formázott: Jobb: 0,63 cm

mV to -697 mV) and decreases both the anodic metal dissolution and the cathodic reduction processes (Figure 7). The inhibitive efficiency was 99.02% which was calculated from the corrosion current measured on bare metal and on the SAM layer coated metal surface by the equation: $E (\%) = [1- i_{corr,\ inhib}/i_{corr\ bare}] x100$ (where E means efficiency; $i_{corr,\ inhib}$ is the corrosion current measured on the coated surface; $i_{corr\ bare}$ is the corrosion current measured on the bare metal surface.

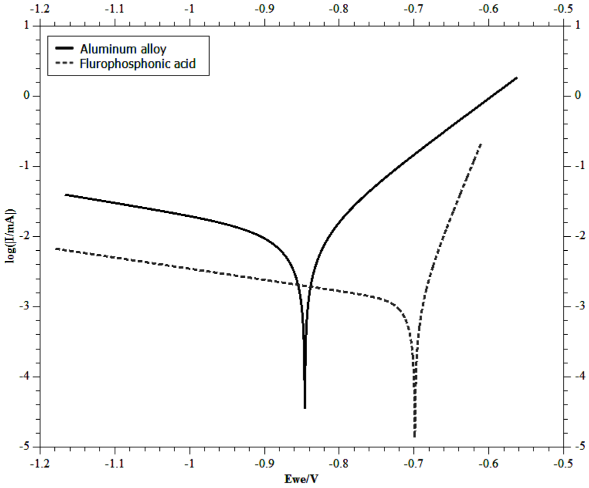

Figure 7. Tafel plots measured on pure aluminum alloy surface and on metal surface covered by fluorophosphonic acid SAM layer (electrolyte: 0.1 M NaCl solution; layer formation in $5x10^{-2}$ M fluorophosphonic acid solution for 4 hours)

The electrochemical impedance spectroscopic measurements also proved the effectiveness of the nanolayer in sodium chloride solution. As the Figure 8 demonstrates the layer compactness increased with increasing time. The charge transfer resistance of the layer is significantly higher after 244 hours than at 24 hours.

All results got by different techniques (contact angle values, Tafel curves, AFM) on aluminum alloy are in accordance with those measured in the presence of SAM layer of the same amphiphile on carbon steel: with increasing the concentration and the layer formation time the effectiveness of the molecular layer increases [37].

Formázott: Jobb: 0,63 cm

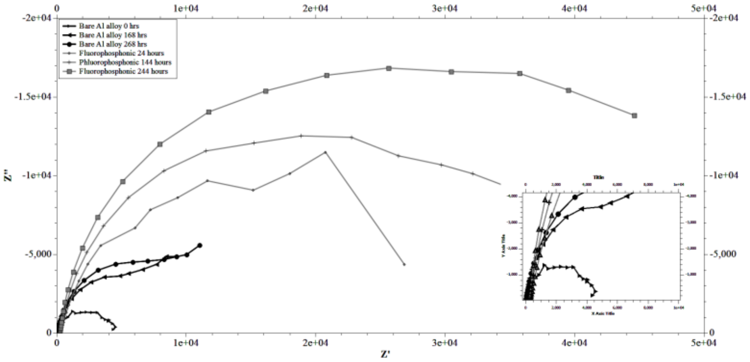

Figure 8. EIS spectra measured on pure aluminum alloy surface and on the metal surface covered by fluorophosphonic acid SAM layer (electrolyte: 0.1 M NaCl solution; layer formation in 5x10^{-2} M fluorophosphonic acid solution for 4 hours)

4. Conclusion

Compact self assembled nanolayer of fluorophosphonic acid was developed on aluminum alloy oxide surface. It was characterized by measuring the change of the wettability in water. The anticorrosion activity of the molecular film was demonstrated by the change in the roughness on the surface of the metal, metal/SAM layer, metal/electrolyte and metal/SAM/electrolyte by using atomic force microscopy. In the presence of both electrolytes (sodium chloride and sodium perchlorate) the metal oxide surface was destroyed. The chloride ions caused pitting corrosion, the perchlorate ions general corrosion. The presence of the SAM layer did not allow the undesired effect of the anions; the surface remained smooth, almost intact after the corrosion test. The changed/unchanged the morphology visualized by AFM was one of the instruments to prove the effectiveness of the nanolayers. Electrochemical measurement (potentiodynamic polarization and EIS) also confirmed the usefulness of the fluorophosphonic acid nanolyers on aluminum surface against pitting and general corrosion.

References

1. K. Kavipriya, S. Rajendran, J. Sathiyabama, A. S. Prabha, *Eur. Chem. Bull.* **2012**, 1, 366.

Formázott: Jobb: 0,63 cm

2. L.R.B. Holzle, D.S. Azambuja, C.M.S. Piatnicki, G.E. Englert *Mat. Chem. and Phys.***2007**, 103, 59.
3. M.M. Stefenel, B.M. Vuano, C.E. Mayer *Corrosion* **2001**, 57, 898.
4. A. Mohammed, S. A. Sayed, E. Abd EI-Rehim, E.F. El-Sherbin Mohsen, N. Abbas, *Corrosion Science* 2009, 51, 658.
5. S.V.Lamaka, M.L. Zheludkevich, K.A. Yasakau, M.F. Montemor, M.G.S. Ferreira, *Electrochimica Acta* **2007**, 52, 7231. DOI: 10.1016/j.electacta.2007.05.058
6. M.Sheffer, A. Groysman, D. Starosvetsky, N. Savchenko, D. Mandlr, *Corros. Sci.* **2004**, 46, 2975.

7. R.S. Neves, D.P.B. Silva, A.J. Motheo, Hindawi Publishing Corporation; *ISRN Electrochemistry* 2013, Article ID 142493, p. 9.
8. R. S. Neves, D.P.B. Silva, A.J. Motheo, http://dx.doi.org/10.1155/2013/142493.
9. P. Thissen, M. Valtiner, G. Grundmeier, *Langmuir* **2010**, 26, 156. DOI: 10.1021/la900935s.
10. R. Foest, M. Schmidt, H. Gargouri, *Eur. Phys. J.* D **2014,** 68, 23. DOI: 10.1140/epjd/e2013-40420-y.
11. H. Ma, O. Acton, D. O. Hutchins, N. Cernetic, A.K.-Y. Jen, *Phys. Chem. Chem. Phys.,* **2012**, 14, 14110.
12. I.Maege, E. Jaehne, A. Henke, H.-J. P. Adler, Ch. Bram, Ch. Jung, M. Stratmann, *Macromolecular Symposia* **1198,** 126, 7. DOI: 10.1002/masy.19981260104.
13. I.L. Liakos, E. McAlpine, X. Chen, R. Newman, M.R. Alexander, *Applied Surface Science* **2008**, 255, 3276.
14. R. Luschtinetz, A.F. Oliveira, H.A. Duarte, G. Seifert, *Zeitschrift für anorganische und allgemeine Chemie* **2010**, 636, 8.
15. R. Luschtinetz, A.F. Oliveira, J. Frenzel, J.-O. Joswig, G. Seifert, H.A. Duarte, *Surface Science* **2008**, 602, 7, 1347.
16. G. Grundmeier, M. Stratmann, *Annu. Rev. Mater. Res*. **2005**, 35, 571.
17. T.T. Foster, M.R. Alexander, G.J. Leggett, E. McAlpine, *Langmuir* **2006**, 22, 9254.
18. I.L. Liakos, R.C. Newman, E. McAlpine, E.; M.R: Alexander, *Surf. Interface Anal*. **2004**, 36, 347.
19. T.A. Lewington, M.R. Alexander, G.E. Thompson, E. McAlpine, *Surf. Eng.* **2002**, 18, 228
20. A. Raman, M. Dubey, I. Gouzman, E.S. Gawalt, *Langmuir* **2006**, 22, 6469.
21. B. Adolphi, E. Jahne, G. Busch, X.D. Cai, *Anal. Bioanal. Chem.* **2004**, 379, 646.
22. M. Textor, L. Ruiz, R. Hofer, A. Rossi, K. Feldman, G. Hahner, N.D. Spencer, *Langmuir* **2000**, 16, 3257.
23. J.T: Woodward, A. Ulman, D.K. Schwartz, *Langmuir* **1996**, 12, 3626.
24. I. Maege, E. Jaehne, A.Henke, H.J.P. Adler, C. Bram, C. Jung, M. Stratmann, *Prog. Org. Coat.* **1998**, 34, 1.

Formázott: Jobb: 0,63 cm

25 K**.** Demidenok, V. Bocharova, M. Stamm, E. Jähne, H.-J. Adler, A. Kiriy, *Langmuir* **2007**, 23, 9287.

26. B. Neves, M. Salmon, P.R. Troughton, *Nanotechnology* **2001**, 12, 285.

27. H.-J. Nie, M. Walzak, N. McIntyre, *Langmuir* **2002**, 18, 2955.

28. L. Forget, F. Wilwers, J. Delhalle, Z. Mekhalif, *Appl. Surf. Sci.* **2003**, 205, 44.

29. E. Hoque, J.A. DeRose, P. Hoffmann, H.J. Mathieu, B. Bhushan, M.J. Cichomski, *Chem. Phys.* **2006**, 124, 174710.

30. M. Eschner, R. Frenzel, F. Simon, D. Pleul, P. Uhlmann, H.-J. Adler, *Macromol. Symp.* **2004**, 210, 77.

31. E. Hoque, J. DeRose, G. Kulik, P. Hoffman, H. Mathieu, B. Bhusban, *J. Phys. Chem.* B **2006**, 110, 10855.

32. T. Hauffman, O. Blajiev, J. Snauwaert, Ch. van Haesendonck, A. Hubin, H. Terryn *Langmuir* **2008**, 24, 13450.

33. O. Yildirim: Self-assembled monolayers on metal oxides: Application in nanotechnology; Publisher: Wöhrmann Print Services, Zutphen, The Netherlands Oktay Yildirim, Enschede, **2010** ISBN: 978-90-365-3098-9.

34. Fluorinated phosphonic acids EP 1 509 536 B1 **2003.**

35. I. Maege, E. Jaehne, A. Henke, H-J. P. Adler, Ch. Bram, Ch. Jung, M. Stratmann *Progress in Organic Coatings* **1998**, 34, 1–12.

36. D. L. Allara, *Langmuir* **1985,** 1, 45.

37. T. Abohalkuma, J. Telegdi *Materials and Corrosion* **2015,** 66, 1382

Formázott: Jobb: 0,63 cm