The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 20, Preprint 66 first submitted 24 May 2017

The influence of green inhibitor on the corrosion of anodized aluminium surfaces

K.Raja, P.A.Jeeva, S.Karthikeyan

[1]Centre for Innovative Manufacturing Research, VIT University, Vellore-632014, India

***Corresponding author (skarthikeyanphd@yahoo.co.in)**

Abstract

The formation of mono stearyl sulphate self assembled monolayer on the corrosion resistance of anodized aluminium in the presence and absence of Nafcillin (NFN) antiobiotics as a green inhibitor have been studied. The corrosion resistance of the anodized aluminium surfaces could be improved by the combined action of SAM and NFN moieties in the presence of anionic surfactant. The performances of the self-assembled monolayer and antibiotic film were monitored through potentiodynamic polarization, A.C impedance analysis and prohesion exposure test. The calculations of quantum mechanical descriptors such as the localization of frontier molecular orbital's, E_{HOMO}, E_{LUMO}, energy gap (ΔE) and dipole moment (μ), were used to validate the effective adsorption of the blended drugs on anodized surfaces. SEM studies confirmed the formation of protective layer of SAM +NFN on anodized metal.

Key words: Anodizing, Monolayer, corrosion resistance, antibiotics

Introduction

The anodized aluminium is extensively used in the fields of aerospace, automobile, electronic products, etc. The life of the anodized film is diminutive due to existence of micro pores in the aluminium oxide which permeates the entry of foreign materials, when it is exposed to acidic and hard water media. Among various reports available in the literature, studies on self-assembled monolayer technique have recently been geared in the coating and corrosion protection research area [1–6]. The researchers found that self-assembled monolayers on substrates such as glass and gold electrodes could be found to have good corrosion protection property [7,8]. The application of self-assembled monolayer and multilayer films on metal and metal alloy substrates such as aluminum, aluminum alloy and steel is still relatively new. Self-assembled monolayers, often made from amphiphilic hydrocarbon molecules, are likely to act as a protective layer for combating corrosion against aggressive environments such as moisture, chlorides and sulphur dioxide, therefore improving the corrosion resistance of the substrate materials. However, any micro crack formation due to incomplete adhesion of SAM may lead to poor corrosion resistance properties. In order to improve the corrosion resistance performance of self assembled monolayer, the use of Nafcillin (NFN), a green inhibitor is effected which blocks the localized parts of self assembled mono layers developed on anodized aluminium.

Three classes of chemical substances are widely reported for this purpose: long chain fatty acids with carboxylic tail end groups that establish electrostatic interactions with metal surfaces, alkyl thiols that join to the steel surface via iron–sulfur bonding, and alkylsilanes that react with the metal oxide from the metal and metal alloy substrates. In this paper, sodium monostearyl sulphate and a proprietary alkane thiol have been taken in the presence of non –aqueous solvent mixed with Nafcillin (NFN) which is the first indigenous research in this direction. The alkane thiol which is used that tend to bond with Al_2O_3 from the anodized aluminum substrates via electrostatic interactions of sulphur groups and the long alkyl chains of alkane thiol interact together through van der Waals forces to form the stable monolayer films on the anodized aluminium surfaces. Due to the film formation, the metal alloy surface became much more hydrophobic, and the corrosion resistance of the

ISSN 1466-8858 Volume 20, Preprint 66 first submitted 24 May 2017

substrate was found to increase significantly which is further facilitated by Nafcillin (NFN) .The resultant SAM and antibiotic combined layer formation offered the best corrosion protection on anodized aluminium surfaces in prohesion test.The quantum mechanical descriptors substantiate the performance of the blended drug in SAM layer by forming a strong adherent layer on the metal surface.

Experimental details

Aluminium specimens of compositions, Cu = 0.15%, Mg = 0.5%, Mn = 0.1%, Si = 0.5%, Zn = 0.5%, and Aluminium remainder, and of size 5 cm^2 x 2 cm were used for anodizing and 1cm^2 x 0.02 cm for potentiodynamic polarisation and AC impedance measurements.

Anodizing of Aluminium

The aluminium specimens of the above composition was mechanically polished and then degreased with acetone. Then the panels are subjected to anodizing as per the following experimental condition. Anode: Al panels; Cathode: Lead; electrolyte: 40% v/v ortho phosphoric acid; current: 7 mA cm^{-2}; Time: 10 minutes. Thickness: 40 microns.

Preparation of Self assembled monolayer solution [SAM]

Exactly (1:1), w/w ratio of A.R grade sodium mono stearyl sulphate (SMS) and isopropyl alcohol were mixed and stirred well .With this 6 ml or 10 g of alkane thiol was added and stirred violently until , the complete dissolution of alkane thiol is ensured. The solution turned to light yellow in colour. The resultant solution is stored in an air tight reagent bottles. The 20% v/v of the SAM solution is mixed with 80% of water which is used for forming self assembled monolayer on the

The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 20, Preprint 66 first submitted 24 May 2017

anodized aluminum parts. This can be used individually or mixed with 0.01 M of NFN inhibitor. The optimum concentration of NFN was arrived at by testing the corrosion behavior of anodized aluminum in Harrion's solution with various concentration of Nafcillin ranging from 0.0001M- 0.001 M in the absence of SAM and the weight loss was measured. From this it was concluded that at an optimum concentration of 0.01M of Nafcillin offered the inhibition efficiency of 95%. After anodizing, the aluminium panels were immersed in SAM solution at 30° C for about 3 minutes. The time required to form SAM on the metal surface is called as dwell time. After 3 minutes, the anodized metal was removed from the bath and rinsed with deionized water. It was then air dried. The aluminium surface was inspected by adding few drops of water to one of the treated surfaces. It was observed that the water sequinned on the treated surfaces, signifying that the surface had been rendered hydrophobic by the coating of a self-assembled monolayer of alkane thiol.

Prohesion test

The aluminium panels (4 panels for each sample) were placed into the prohesion chamber with the uncoated anodized surface protected by a 3 M scotch tape and the SAM with SAM +NFN surfaces exposed alternatively to the salt fog at 25 ºC for 2 hours followed by drying off at 35 ºC for another hour, by adapting ASTM) B117-02 Standard Practice for Operating Salt Spray (Fog) Apparatus [9]. Dilute Harrison's solution was used as the salt fog solution in the chamber. After this test, the coated and uncoated panels were rinsed thoroughly with deionized pure water and dried under slow N2 flow and kept at 25 ºC under ambient conditions before immediate electrochemical impedance measurement.

Electrochemical Measurements

Both cathodic and anodic polarisation curves were recorded in Harrison's potentiodynamically (1 mv s-1) using corrosion measurement system BAS Model : 1OOA , computerised electrochemical analyzer (made in West Lafayette, Indiana) and PL-10 digital plotter (DMP-40 series, Houston Instruments Division). A platinum foil(4 cm^2) and Hg/Hg_2Cl_2 /KCl $_{(satd)}$ were used as auxiliary and reference electrodes, respectively. The corrosion environment used is Harrisons solution of the composition: 0.05% NaCl and 0.35% $(NH_4)_2SO_4$. Double layer capacitance (C_{dl}) and charge transfer resistance values (R_t) were got using AC impedance measurements (EG&G Princeton Applied research model:7310) as described in an earlier publication(10). Quantum chemical calculations were carried using Gaussian 03 software package. The energy of highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and dipole moment (μ) of the inhibitor molecule were calculated with the above given computer code package.

Results and Discussion

Potentiodynamic polarization studies

Table 1 gives values of corrosion kinetic parameters such as Tafel slopes (ba and bc), corrosion current (Icorr) and corrosion potential (Ecorr) and efficiency obtained from potentiodynamic polarization curves for anodized aluminum in Harrisons solution after subjected to the formation of SAM and SAM+NFN thin layers. It is established that SAM+NFN coatings improve the values of both anodic and cathodic Tafel slopes to equal extent and the inhibition of corrosion of anodized aluminium in Harrisons solution was found to follow mixed mode of reaction [6-8]. E_{corr} values are shifted to positive direction in the presence of SAM and SAM+NFN coatings. This can be ascribed to the formation of strongly adherent monolayer film on the metal surface. It was also noticed that the anodized surfaces coated by SAM+NFN compounds, reduced the I_{corr} values to considerable extent in Harrisons solution. This could be due to the blackening action of micro pores and delaminated SAM layers by Nafcilin which is leading to the completed coverage of metal surfaces evidenced from its inhibition efficiency values of 99%. The potential-current plots are given in figure 1. The inhibition efficiency (IE%) was calculated using the equation,

$$\text{Inhibition Efficiency (IE\%)} = \quad (I_o - I / I_o) \times 100 \qquad (1)$$

where I_o and I are the corrosion current density for the unprotected and coated anodized surfaces respectively.

Impedance measurements

Figure 2 indicates the corrosion protection of anodized aluminium in Harrisons solution before and after immersion of the anodized aluminum surfaces in SAM and SAM+NFN by electrochemical impedance spectroscopy. The values of the charge transfer resistance (R_t) begin to increase with the increasing the coverage of anodized film by SAM and SAM+NFN (Table 2), while double layer capacitance (C_{dl}) are brought down to a significant extent. This can be ascribed to increasing the adsorption of the Nafcillin on the micro pores of SAM layers on the anodized film [10-11]. In the present study, perfect semi circles are encountered in Nyquist plots, this may be due to the fact that the corrosion inhibition of sealing drugs is under charge transfer control due to the electrostatic interaction of SAM and NFN with anodized aluminium surfaces through the sulphur atoms of the monolayer solutions. The inhibition efficiencies were calculated from the following equation.

The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 20, Preprint 66 first submitted 24 May 2017

Inhibition Efficiency (IE%) = $(C_{dl} - C'_{dl} / C_{dl}) \times 100$ (2)

where C_{dl} and C'_{dl} are the double layer capacitance of the unprotected and coated anodized surfaces respectively.

Prohesion test

The physical verification of this teat revealed that the unanodized surfaces have greatly damaged in comparison with anodized Al. Also the formation few white corrosion spots on SAM coated Al surfaces was visible. There was no white corrosion product on SAM+NFN coated anodized aluminium surfaces. This could be due to the formation of dense and strong inhibitor film on the aluminium surface by NFN molecules which is further validated by quantum mechanical studies.

Quantum mechanical studies

Quantum mechanical calculations were done to explore the adsorption and inhibition mechanism of the NFN compound on SAM embedded Anodized aluminum surfaces. Figure 3 (a, b & c) shows the optimized structure of Nafcillin, HOMO and LUMO of NFN inhibitor molecule. The values of calculated quantum chemical parameters i.e. E_{HOMO} (highest occupied molecular orbital), E_{LUMO} (lowest unoccupied molecular orbital), ΔE (energy gap), μ (dipole moment) etc. are summarized in table-3. E_{HOMO} is associated to the electron-releasing ability of the inhibitor molecule. In the present investigation, the adsorption of a NFN on anodized surface acquired on the basis of donor-acceptor interactions between the π-electrons of oxo thia azo bicyclo heptane moieties which favours effective adsorption of NFN on SAM coated metal surfaces evidenced from the dense electrons cloud in HOMO structure. In the case of LUMO structure, the adsorption of NFN is to be favoured by donating

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 20, Preprint 66 first submitted 24 May 2017

the unshared electrons on ethoxy napthyl amino group to the non filled d-orbitals of the aluminum atom of the anodized film . The gap between HOMO–LUMO energy levels of molecules was another important factor that needs to be considered. Higher the value of ΔE of an inhibitor, higher is the inhibition efficiency of that inhibitor. It has been reported that, large values of the dipole moment will improve corrosion inhibition. Based on the values of ΔE and dipole moment, the compound NFN may be strongly adsorbed on aluminum metal.

Conclusion

- A new corrosion resistant system based in alkane thiol self assembled monolayer and Nafcillin inhitor has been developed and the corrosion resistance characteristics have been evaluated by electrochemical, prohesion test and quantum mechanical studies.
- The coated surfaces containing SAM+NFN offered 99% corrosion resistance to aluminium metal and hence can be used in air craft industrial applications.

References

[1] Bierwagen, G.P., and Tallman, D.E. (2001). *Prog. Org. Coat., 41*, 201.

[2] Bommarito, G.A., and Pocius, A.V. (1998). *Thin Solid Films*, *481*, 327–329.

[3] Meth, S., and Sukenik, C.N. (2003). *Thin Solid Films, 49,* 425.

[4] Maege, I., Jaehne, E., Henke, A. Adler, H.-J.P., Bram, C., Jung, C., and Stratmann, M. (1998). *Prog. Org. Coat. 34,* 1– 12.

[5] Ruan, C.M., Bayer, T., Meth, S., and Sukenik, C.N. (2002). *Thin Solid Films*, 95, 419.

[6] Berg, K. O¨., Persson, P., Shchularev, A., and Eliasson, B. (2001). Thin Solid Films, *102*, 397.

[7] A. Ulman, An Introduction to Ultrathin Organic Films from Langmuir–Blodgett to Self-Assembly, Academic Press, San Diego, CA, 1991.

[8]. Che, C., Wu, G.Q., Qi, H.Y., Huang, Z., and Yang, X.G. (2008). *Surface Engineering*, *24,* 276-279.

[9]. ASTM B-117, Annual Books of American Society for Testing and Materials Standards, American Society for Testing and Materials Standards, Philadelphia, PA, 1990.

[10]. Karthikeyan, S., Jeeva, P.A., Hu, X., Harikumar, S., and Narayanan, S.(2012). *Oriental Journal of Chemistry, 28*, 1443-1448.

[11]. Karthikeyan, S., Srinivasan, K.N., Vasudevan, T., and John, S.(2006). *Port. Electrochimica. Acta*, *24*, 405-413.

Table 1: Potentiodynamic polarization of anodized aluminium in the presence and absence of SAM+NFN . Medium: Dilute Harrison's solution

Experiment	**E_{corr}** (mV vs SCE)	**I_{corr}** (µA cm-2)	**βa** (mV dec-1)	**βc** (mV dec-1)	**IE** (%)	**θ**
Pure Al	-645.21	352.2	42.0	45.4	-	-
AAl	-609.32	95.18	32.1	34.5	72.40	0.724
AAl+SAM	-353.75	12.32	21.3	26.2	96.50	0.965
AAl+SAM+NFN	-322.47	2.817	14.2	18.4	99.20	0.992

Table 2: Impedance data for the anodized aluminium in the presence and absence of SAM+NFN. Medium: Dilute Harrison's solution

Operating conditions	1N HCl solution	
	Charge Transfer resistance (R_t) K.Ohm.cm^2	Double layer capacitance (C_{dl}) µF.cm^{-2}
Uncoated	0.71	232
AAl	0.82	64
AAl+SAM	1.73	8.12
AAl+SAM+NFN	2.34	1.86

Table 3: Quantum mechanical parameters for NFN on the corrosion of anodized Al

Inhibitor	LUMO (eV)	HOMO (eV)	ΔE ($Cal.Mol^{-1}$)	Dipole moment (Debye)
NFN	-4.253 -	-5.147	0.894	3.8

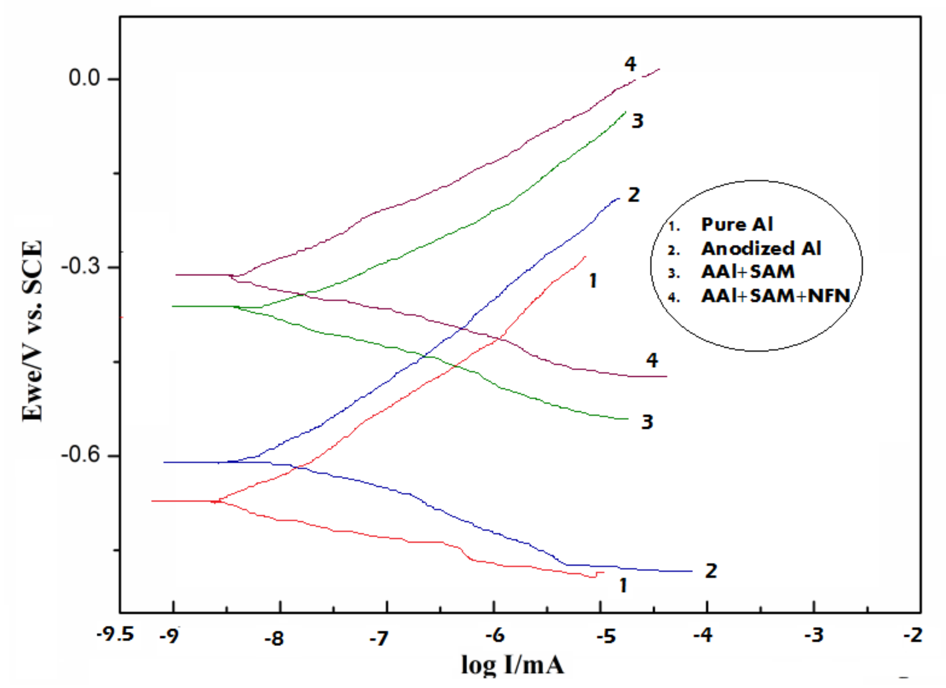

Figure 1. Tafel polarization plots for the corrosion inhibition of anodized aluminium with and without SAM and green inhibitor.

The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 20, Preprint 66 first submitted 24 May 2017

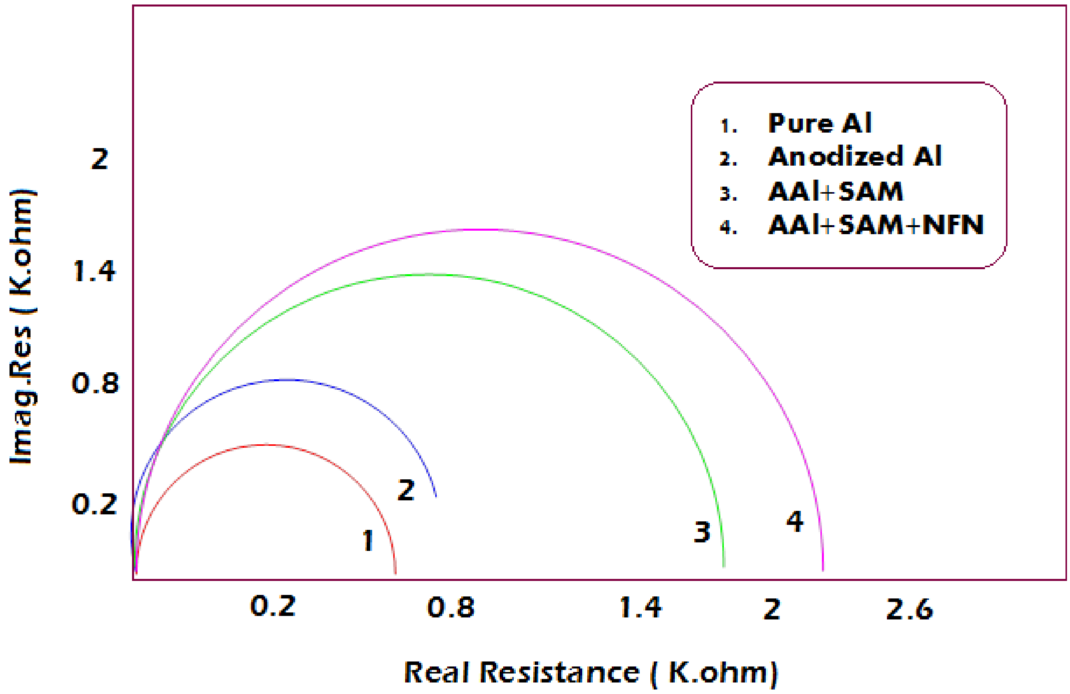

Figure 2. Nyquist diagram for the corrosion inhibition of anodized aluminium with and without SAM and green inhibitor.

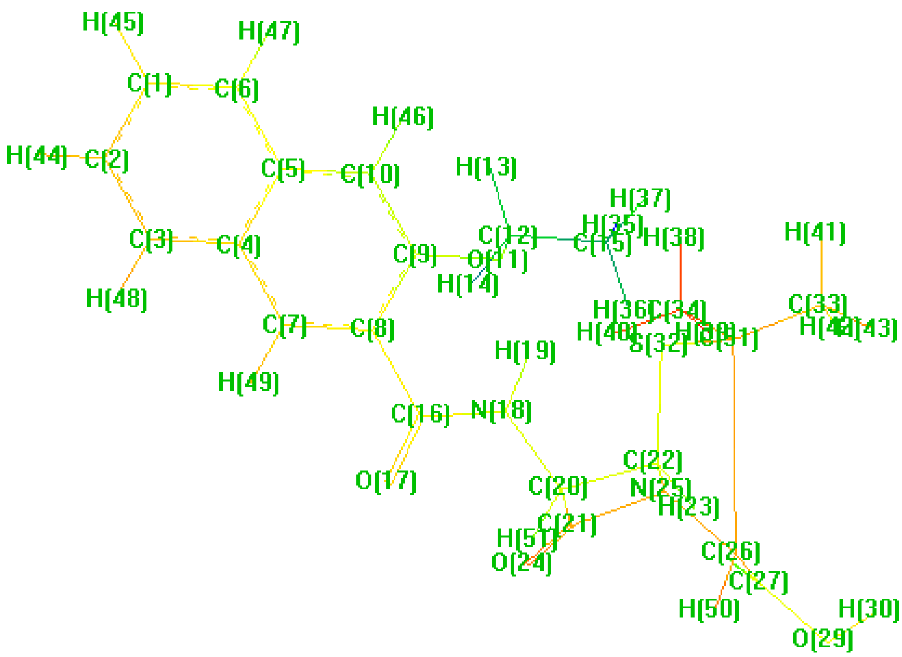

Figure 3 a. Optimized structure of Nafcillin

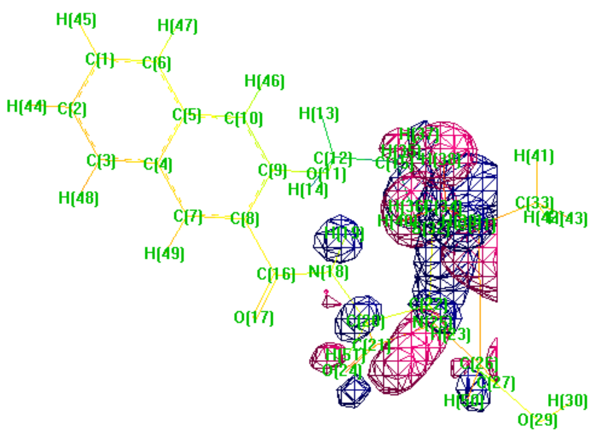

Figure 3 b. HOMO of Nafcillin on SAM embedded anodized aluminium surfaces

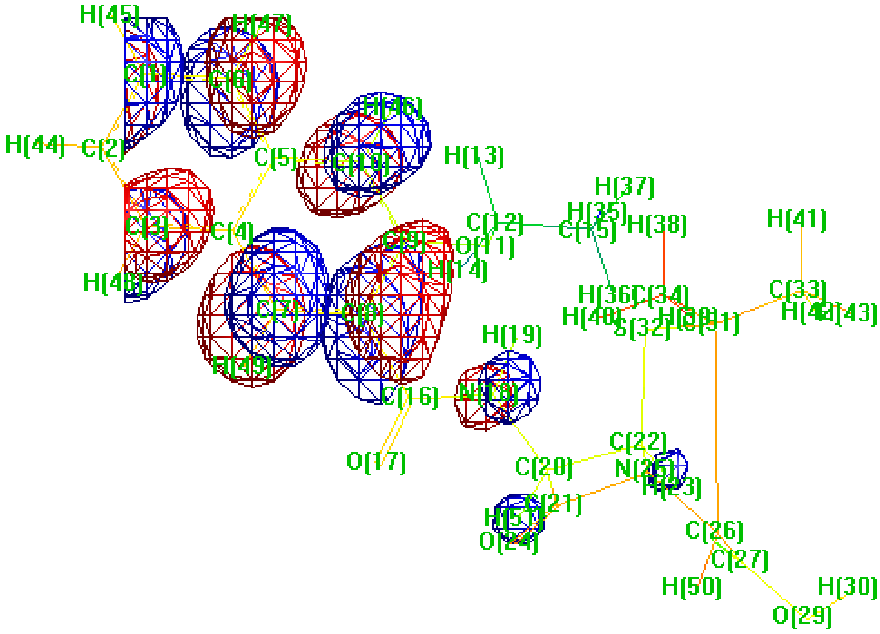

Figure 3 c. LUMO of Nafcillin on SAM embedded anodized aluminium surfaces