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Quantum mechanical and corrosion studies of electrochemically oxidized aluminium surfaces

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Abstract

The 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 substantiate the impressive formation of non-toxic chemical film comprises of Clarithromycin (CMN) drug on electrochemically oxidized Aluminum and the corrosion resistance of the metal surfaces were found to be improved. The performance of the corrosion resistant barrier films was evaluated through potentiodynamic polarization and A.C impedance analysis.

Key words: oxidation, anodizing, corrosion resistance, quantum, electrochemical

Introduction

The electrochemically oxidized or anodized aluminium is widely used in the fields of aerospace, automobile, electronic products, etc. However, the so formed oxidized film of Al is less durable due to the presence of porosity which allows the environmental substances to interact on the surface. It was found that Sulphur, nitrogen and oxygen atoms of organic molecules are proficiently reducing metallic corrosion. Several substituted thiourea and drugs compounds have been reported as corrosion inhibitors [1-5] for the aluminium and its alloys. All the above studies bring one common observation that thiourea derivatives can be regarded as excellent corrosion inhibitors for aluminium in acidic and alkaline media. However, no methodical approach is existing for the corrosion protection of anodized film using unified drugs a sprayed chemical agent. The present paper designates a study of non-toxic spraying agent based on proprietary aromatic poly hydroxy gel and Clarithromycin (CMN) drugs on corrosion inhibition of electrochemically oxidized aluminium surfaces in 1M NaOH using potentiodynamic polarization and impedance methods. The quantum mechanical parameters validate the performance of the non-toxic spraying agent through the formation of a strong adherent layer on the metal surface.

Experimental details

Aluminium specimens of compositions, Cu = 0.15%, Mg = 0.5%, Mn = 0.1%, Si = O.5%, Zn = 0.5%, and Aluminium remainder, and of size 10 cm^2x 10cm were used for electrochemical oxidization of Al panels. For potentiodynamic polarization and AC impedance measurements both electrochemically oxidized and un oxidized Al specimens of size 0.5cm^2 x 0.01 cm were used.

Electrochemical Oxidation of Aluminium

The aluminium specimens of the above composition was mechanically polished and then degreased with trichloro ethylene. Then the panels were subjected to electrochemical oxidation using the plating formulation which consisted of : Anode: Al panels; Cathode: Lead; electrolyte: 1M NaOH; current: 600 mA cm^{-2}; Time : 5 minutes. Thickness: 50 microns.

Exactly (0.5 wt%) of proprietary aromatic poly hydroxy gel and (0.8% wt , 1.0 % Wt and 1.2% Wt) Clarithromycin (CMN) drug were dissolved in 32% isopropyl alochol + 1 ml of proprietary surfactant solution were mixed well. The mixture was diluted to 500ml and ready to spray on electrochemically oxidized aluminum surfaces. The spraying is carried out using spray guns or it can be poured directly on the anodized aluminium surfaces After spraying, the plates were removed, washed with DI water, dried and then characterized using electrochemical methods. Both cathodic and anodic polarisation curves were recorded in 1M NaOH potentiodynamically (1 mv s-1) using corrosion measurement system BAS Model : 100A, computerised electrochemical analyser (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_2O /1M NaOH were used as auxiliary and reference electrodes, respectively. Double layer capacitance (C_{dl}) and charge transfer resistance values (R_t) were carried out using AC impedance measurements (EG&G Princeton Applied research model:7310. Quantum 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 sealing compounds were measured with the above given computer code package.

Results and Discussion

Potential-Current measurements

Table 1 gives values of corrosion kinetic factors such as Tafel slopes (b_a and b_c), corrosion current (I_{corr}) and corrosion potential (E_{corr}) and percentage of corrosion resistance obtained from potentiodynamic polarization measurements carried out for electrochemically oxidized aluminum in 1M NaOH after application of non-toxic corrosion resistant spray coating agent. It is established that enhancing the thickness of corrosion protection agent improves the values of both anodic and cathodic Tafel slopes to equal extent. After spraying with various concentration of non-toxic spraying agent, the inhibition of corrosion of electrochemically oxidized aluminium in 1M NaOH was found to follow mixed type of reaction [6-8]. E_{corr} values are shifted to positive directions in the presence of various concentrations of spraying compound. This can be attributed to the formation of strappingly adherent protective on the metal surface. The coating thickness varied from 10 μm, 30 μm and 55 μm at various concentrations of spray coatings. I_{corr} values were reduced to greater extent in 1M NaOH due to the block of micro pores of coatings and also the strong coverage of protective films by Clarithromycin (CMN) drugs on the oxidized surfaces of Al.

Impedance Measurements

Table 2 showed that the corrosion protection of electrochemically oxidized aluminium in 1M NaOH solution before and after the application of Clarithromycin (CMN) drugs unified coatings by electrochemical impedance spectroscopy . The values of the charge transfer resistance (R_t) is found to increase with the increasing thickness of anodized film whereas double layer capacitance (C_{dl}) are fetched down to a great extent . This can be attributed to increasing the adsorption of the spray coatings on the micro pores of anodized film with an increase in thickness of protective films [9-11].

Quantum Mechanical Studies

Quantum mechanical calculations were performed to investigate the adsorption and inhibition mechanism of the applied spray coatngs comprise of Clarithromycin (CMN) drugs unifed compounds. Figure 1 shows the structure of Clarithromycin. 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 related to the electron-releasing capacity of the molecule. In the present investigation, the adsorption of a CMN on electrochemically oxidized surface of Al acquired on the basis of donor-acceptor interactions between the π-electrons of heterocyclic ring and carbonyl group of CMN. The gap between HOMO-LUMO energy levels of molecules was another important factor that desires 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 enhance corrosion inhibition.

Conclusion

A special spray non-toxic coating process for electrochemically oxidized aluminum parts has been formulated and the corrosion resistance of the coatings with and without the application of coatings has been systematically evaluated through electrochemical techniques. The quantum mechanical studies confirmed the mere adsorption of the Clarithromycin (CMN) drugs on the Al anodized surfaces.

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Table 1: Potentiodynamic polarization of electrochemically oxidized aluminium. Medium: 1M NaOH

Experiment	E_{corr} (V vs SCE)	I_{corr} (mA cm−2)	βa (mV dec−1)	βc (mV dec−1)	Corr.Protection (%)	θ
Pure Al	-1.14	750.0	152.0	116.4	-	-
Clarithromycin (CMN) spraying agent (thickness in μm)						
10μm	-967.2	90	62.1	94.5	88.00	0.88
30μm	-963.53	56.85	51.3	86.2	92.42	0.92
50μm	-962.75	7.2	34.2	78.4	99 .04	0.99

Table 2: Impedance data for electrochemically oxidized aluminium. Medium: 1M NaOH

Operating conditions	1N NaOH solution	
Clarithromycin (CMN) spraying agent (thickness in μm)	Charge Transfer resistance (R_t) Ohm.cm^2	Double layer capacitance (C_{dl}) μF.cm^{-2}
No addition	802	0.9850
10μm	1707	0.1132
30μm	2257	0.0741
50μm	2915	0.0083

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

Inhibitor	LUMO (eV)	HOMO (eV)	ΔE (Cal.Mol^{-1})	Dipole moment (Debye)
Clarithromycin (CMN)	33.0090	31.7304	1.2786	5.9

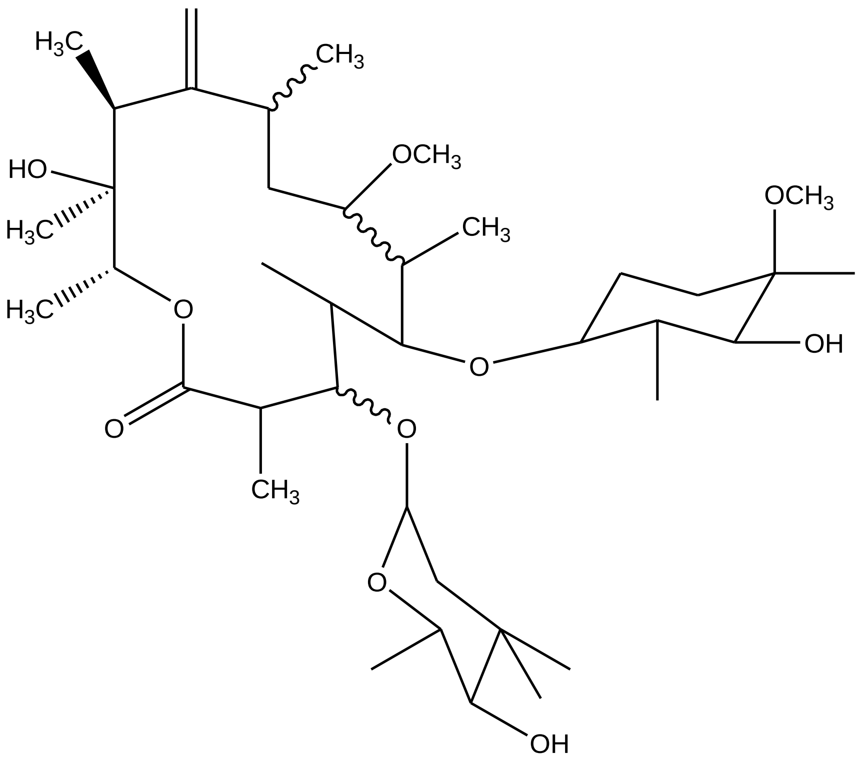

Figure 1. Structure of Clarithromycin

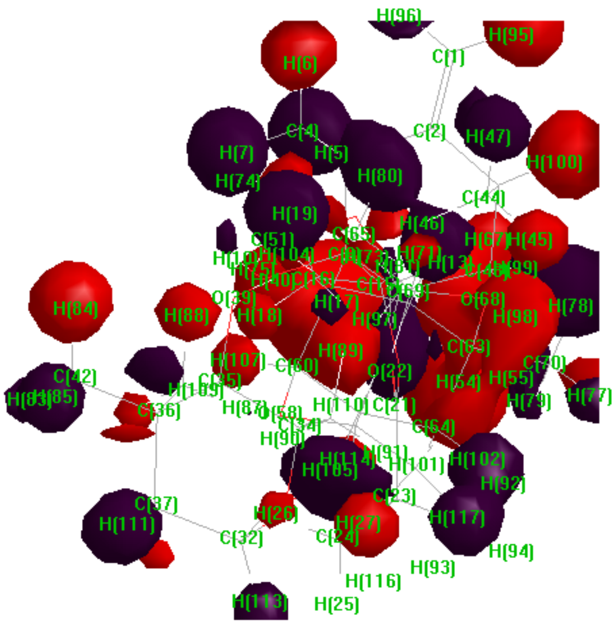

Figure 2. Highest molecular orbital of Clarithromycin molecules

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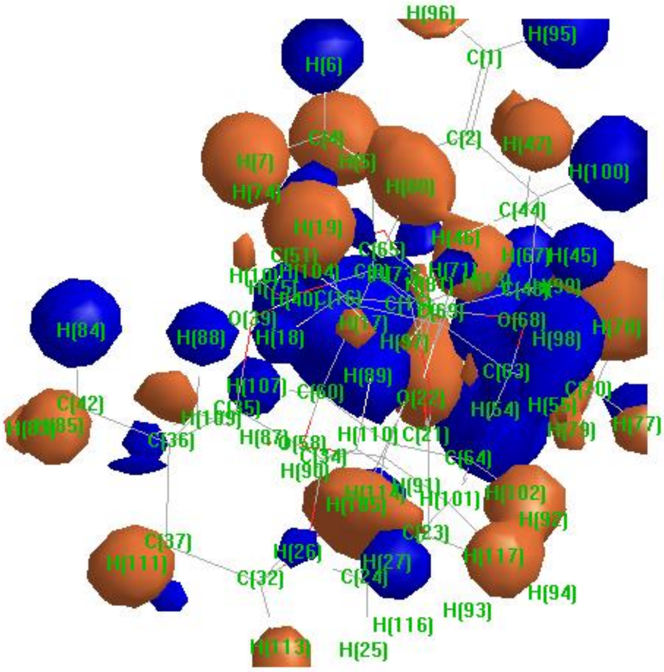

Figure 3. Lowest unoccupied molecular orbital of Clarithromycin molecules