Investigation of effective parameters in improving corrosion resistance of the silica coated stainless steel via sol-gel method

M. Ghaffari[*,a], A. Barzegar[b], K. Janghorban[b]

[a] School of Electrical and Electronic Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798

[b] Department of Materials Science and Engineering, College of Engineering , Shiraz University, Shiraz, IRAN

Abstract:

The sol gel method has been used to deposit oxide thin films. In present study silica was coated on stainless steel 316L substrate through sol-gel method via dipping process. Silica sol was made in a mixture of methyltriethoxysilane (MTES) and tetraethyl-orthosilicate (TEOS), pure water, absolute ethanol as solvent; nitric acid, and hydrochloric acid as catalysts. The corrosion resistance of samples was investigated in simulated body fluid by a potentio-dynamic test and uniformity of the coating was evaluated by Scanning Electron Microscope. We have assessed the effective parameters, such as wetting agent, number of layers, catalyst and different roughness of sub layers on corrosion properties of samples. The silica coating resulted in improvement of corrosion resistance of stainless steel 316L in body environment, and can be used as a proper coating on orthopedic implants.

Key words: Sol-gel, Silica coating, Stainless steel 316L, Corrosion resistance.

1. Introduction

There are a variety of alloys that accomplish the mechanical obligations of orthopedic prosthesis and fixation devices. However, only a small number of them reported to possess biocompatibility and corrosion resistance. AISI 316L stainless steel is widely used in orthopedic surgery as plate nails. Galvanic corrosion, due to electric contact, and crevices, as a result of mechanical contact between pieces, is very common in these nails. In addition, the presence of Cl^- anions in body environment increases the risk of pitting attack [1]. Consequently, the formation of fibrous tissue and necrosis around the implant becomes accelerated by production of significant quantities of Fe [2].

Recently the sol-gel process has been extensively used in many fields. Sol-gel refers to a low-temperature method that uses chemical precursors which produce homogeneous and pure ceramics and glasses. In addition, sol-gel based materials are bioactive i.e. they bond to bone and have osteoconductive properties and can be used in biomedical and dental applications. Sol-gel method has been used to protect various pieces in corrosive environments [3-6]. Sol-gel synthesis involves preparation of a solution from alkoxides, metal salts or other suitable precursor, such as nitrates. At the functional group level, three reactions are generally used to describe the sol-gel process: hydrolysis, alcohol condensation, and water condensation. During the hydrolysis process hydroxides or hydrated oxides form and gelation occurs to form a three-dimensional network. To produce coating, the solution can then be deposited by dip, spin or spray coating, roll or capillary coating. The solution or coated substrate is then exposed to water for hydrolysis. Further heating of the resultant gel removes residual organic material and induces conversion to the oxide state under oxidizing conditions. The sol-gel process includes a series of irreversible chemical reactions, including is formation of an initially homogeneous solution as

sol and it's transformation to a three dimensional heavy polymeric molecule as gel. In order to produce a compact and rigid solid a drying and sintering process was conducted. [7-9]

Through this process, homogeneous inorganic oxide materials can be produced at room temperatures, with desirable properties of hardness, optical transparency, chemical durability, tailored porosity and thermal resistance; while production of conventional inorganic glasses require much higher melting temperatures. From the many sol-gel production methods, dipping and spinning are the most common while dipping is a known commercial method for large scale production. In this method a sub layer is dipped and immersed in the liquid until a layer of liquid forms on the substrate. Later on the sub layer is withdrawn with a precisely withdrawal speed under controlled temperature and atmospheric condition. The coating thickness is mainly defined by the withdrawal speed, the solid content and the viscosity of the liquid. If the withdrawal speed is chosen such that the shear rates keep the system in the Newtonian regime, the coating thickness can be calculated by the Landau-Levich equation as below [7,9,10,11].

$$h = 0.94 \frac{(\eta \cdot v)^{2/3}}{\gamma_{LV}^{1/6} (\rho \cdot g)^{1/2}} \tag{1}$$

Where h is the coating thickness, η viscosity, v withdrawal velocity, γ_{LV} liquid-vapour surface tension, ρ density and g gravity.

2. Experimental approach

2.1. Sample preparation

The Stainless steel 316 L samples with dimensions of 1 cm ×1cm×0.8 cm were ultrasonically cleaned for 10 mins, after that surface preparation was accomplished via grinding using different grades of grinding SiC paper (1000) and finally the samples were acid cleaned using the

Standard ASTM-A380-99 method. Silica sol was synthesized through hydrolysis and polycondensation reactions of methyltriethoxysilane [$SiCH_3 (OC_2H_5)_3$, MTES] and tetraethylorthosilicate [$Si(OC_2H_5)_4$, TEOS], both from Merck, pure water, absolute ethanol as solvent, nitric acid, and hydrochloric acid as catalyst. Hybrid silica coatings were carried out by sample immersion in freshly prepared sol followed by withdrawal at a constant velocity rate of 40 cm min^{-1}. The sol was prepared with a molar ratio TEOS/ MTES = 40/ 60, HCl and HNO_3 1N as catalysts. The final molar ratio water/ (TEOS + MTES) was 2. After preparation the sol, silica sol coated as a mono and dual layer on stainless steel 316L substrate. In order to create a suitable coating the samples were dried at room temperature for 24hr .A further sintering process was carried out at 430 °C for 30 min.

2.2 Electrochemical study

Electrochemical study of the coated samples was investigated by performing potentio - dynamic anodic polarization with Auto Lab μ type II. A saturated calomel electrode and platinized platinum electrode were used as reference and auxiliary electrodes, respectively. The initial potential was 200 mv below open-circuit potential and the scan rate was 0.002 V s^{-1} .During the test , the temperature of solution was fixed at 37 °C using Ben Marry Bath. Then i_{corr}, and E_{corr}, were calculated in Simulated Body Fluid [12,13] from the polarization curves by using GPES software.

2.3 SEM and XRD Study

Cross section photomicrograph and uniformity evaluated and the samples characterized using a JEOL (JSM) 5410 LV Scanning Electron Microscopy. Semi-quantitative analysis was performed by using Energy dispersive X-ray analysis. θ-2θ spectra of silica coated films were collected at the scan speed of 1 deg/min and CuKα radiation using a Shimadzu X2 diffractometer.

3. Results and Discussion:

The sol–gel coating acts as a dielectric material and only can corrode through the defects in the layer. Therefore, uniformity of the layer is one of the most important factors. In the present work , we studied the effect of corrosion on the monolayer and dual layer silica coating stainless steel samples.

3.1. Uniformity of coatings

Two types of coatings studied: mono layer Silica coating and dual layer of Silica coating. After preparation of samples, uniformity of coating was evaluated by Scanning Electron Microscope. Fig.1 (a) and Fig.2 show the SEM Cross-section of monolayer silica coated sample, Fig.1 (b) shows the dual layer coated sample. Figures 1 and 2 nicely present uniformity and fewer defects (circle region) in mono and dual layer coating with acceptable adhesion, and Fig.3 represents the Energy dispersive X-ray analysis of monolayer Silica coated sample without any impurity peak. XRD pattern for silica coated film is shown in Fig.4. The coating is composed of single phase SiO_2. It should be noted that, Fe-Cr-Ni peaks in the pattern are due to stainless steel 316L substrate.

3.2 Electrochemical study of mono layer coating

3.2.1 Effect of surface finishing of monolayer coated sample on corrosion behavior

For evaluation of this effect, three different grinding SiC papers (600, 800 and 1000) were used. After coating process, we noticed that corrosion resistance of sample prepared with 1000 grinding was better than the other samples. Fig.5 and Fig.6 show the corrosion curves of this sample. The values of i_{corr}, E_{corr} and the other important parameters in regard to corrosion properties are shown in Table 1 and 2.

3.2.2 The Effect of catalyst on corrosion behavior of the monolayer coated sample

For study of catalyst effect on the corrosion characterization, two different types of catalyst (HCl and HNO_3) were used in preparation of the sol. Results show that hydrochloric acid usage is better than nitric acid (HCl has stronger acidic properties than HNO_3) during polymerization and polycondensation process. It is because of the fact that the increase in the number of ordinate legend in polymer increases the density of dry gel, which produces a more compact layer. Using HNO_3 as a catalyst forms some cracks in the coated of samples and also increases the defects and their contributing corrosion. Fig.7 and Tables 1 and 2 confirm these findings. However, even coated 316L stainless steel produced using HNO_3 has better corrosion resistance in comparison with bare stainless steel.

3.2.3 The Effect of wetting agent on corrosion behavior of the monolayer coated samples

In order to see the wetting effect we used PVA (Polyvinyl alcohol) and CTAB (Cetheyl triethyl ammonium bromide) as wetting agents and the corrosion behavior of the samples were investigated. The results show that stickiness of the coating by using PVA as a wetting agent is better than CTAB; because PVA promotes more effective reaction with surface of substrate which increases the adhesiveness. Due to this reason, the sample which was treated by PVA is crack free and uniform. Fig 8 shows the difference between the samples in corrosion behavior by using wetting agents (PVA and CTAB).

3.3 Electrochemical study of the Dual layers coated sample:

In this case, the time of dipping in sol was decreased to half of the monolayer dipping time. The samples were dipped separately in the solution to produce the dual coating. The results were almost the same as of the monolayer sample. In this case, the best adhesion is achieved for the samples which were finished by 1200 and 1000 grinding paper. Fig.1 (b) shows the cross-section of single layer silica coated. The values of i_{corr} and E_{corr} for Dual layer silica coated samples are shown in Table 3.

After coating the corrosion properties of the samples were investigated and the single and dual layer samples were compared with each other. The results show that the corrosion resistance of the dual sample is better than the single layer. This can be due to elimination of the pores of first layer by second one after sintering the first coating layer. Fig.9 and Fig.10 show the comparison of polarization curves of dual and single layers for different catalysts and surfactants.

4. Conclusion:

The silica samples were coated on stainless steel 316L substrate through sol-gel method via dipping process. Using silica coating we managed to decrease the rate of stainless steel corrosion and on top of that, eliminated the pitting corrosion. This is nicely showed in figures 5-10 with the backward cycle located behind the forward cycle in polarization curves. A compact and dense layer of SiO_2 (coated from sol on stainless steel 316L substrate) improves the corrosion resistance and decreases the current density a few folds. This will result in elimination excessive amount of Cl ion, and therefore prevents from it's harmful effects and possible allergic reacting. Use of wetting agent during the sol-gel method is necessary which was also confirmed in our results. The wetting agent PVA is more suitable than CTAB for Silica coated stainless steel samples. For surface finishing, we found that between HCl and HNO_3, HCl is better catalyst. Investigations and calculations of i_{corr} and E_{corr} show that, sol-gel coating improves the corrosion resistance in the samples. Another important factor in the sol-gel method is the surface finishing, the corrosion resistance of the samples that were ground by using (>1000 grain size) polish-paper was better due to proper wetting and uniformity of the surface. In conclusion, the creation of silica coating through sol-gel method on 316L stainless steel resulted in desirable resistance to corrosion in body enviroment, and can be used on orthopedic implants.

5. References:

[1] H. Placko, S. Brown, *J. Payer, Biomed. Mater*. Res. 17 (1983) 655.

[2] 'Biomateriales y biomecanica de implantes endoseos, in: R. Mc Kinney (Ed.), Implantes Dentales Endoseos', J. Lemons, M. Bidez, Mosby, Barcelona, (1993).

[3] J. Gallardo, A. Duran*, J.Corrosion Science* 46 (2004) 795.

[4] C. Garcia , S. Cere, A. Duran, *J. Non-Crystalline Solids* 348 (2004) 218.

[5] J. Gallardo, P. Galliano, *J. Sol-Gel Science and Technology* 19 (2000) 107.

[6] C. J. Brinker, N. K. Raman, M. M. Logan, R. Seghal, R.A. Assink, D.W. Hua, T. L. Ward, *J. Sol–Gel Sci. Technol*. 4 (1995) 117.

[7] V.Gottardi, *J. Non-Crystalline Solids* 73 (1985) 625.

[8] L. L. Hench, J. K. West*, J. Chem. Rev*. 90 (1990) 33.

[9] J. Livage, D. Ganguli, *J. Solar Energy Materials & Solar Cells* 68 (2001) 365.

[10] H. Schmidt, *J. Non-Crystalline Solids* 73 (1985) 681.

[11] http://www.solgel.com/articles/Nov00/coating.htm

[12] G. Rondelli, P. Torricelli, M. Fini and R. Giardino, *J. Biomaterials* 26 (2005) 739.

[13] J. Gallardo, P. Galliano, *J. Sol-Gel Science and Technology* 21 (2001) 65.

6. List of figures and tables

6. 1. List of figures

6. 2. List of tables

Table 1. Values of i_{corr} and E_{corr} and other factor for Mono layer silica coated sample by using PVA as wetting gent

Catalyst (grinding paper)	$i_{Corrosion}$	$I_{Corrosion (A/cm^2)}$	$b_{c (V/dec)}$	$b_{a (V/dec)}$	$R_{(\Omega)}$	$E_{corr (abs)}$ (v)	$E_{corr (calc)}$ (v)	E –begin (v)	E-end (v)
Bare Steel	3.896 e -8	1.193 e-8	0.005	0.006	4.308 e+2	-0.258	-0.258	-0.269	-0.253
HCl (1000)	3.896 e -12	1.193 e-11	0.003	0.001	4.308 e+5	-0.219	-0.258	-0.269	-0.253
HNO$_3$ (1000)	3.052 e -11	1.436 e-10	0.002	0.001	3.82 e +4	-0.228	-0.219	-0.221	-0.217
HCl (800)	1.282 e -10	5.365 e-10	0.003	0.003	2.393 e +4	-0.152	-0.186	-0.19	-0.189
HNO$_3$ (800)	8.24 e -10	4.125 e-9	0.004	0.004	7.86 e +3	-0.25	-0.249	-0.251	-0.247

Table 2. Value of i_{corr} and E_{corr} and other factor for Mono layer silica coated sample by using CTAB as wetting gent

Catalyst (grinding paper)	$i_{Corrosion}$	$I_{Corrosion (A/cm^2)}$	$b_{c (V/dec)}$	$b_{a (V/dec)}$	$R_{(\Omega)}$	$E_{corr (abs)}$ (v)	$E_{corr (calc)}$ (v)	E –begin (v)	E-end (v)
HCl (1000)	1.357 e -10	5.589 e-10	0.002	0.004	2.14 e+4	-0.236	-0.414	-0.416	-0.41
HNO$_3$ (1000)	1.08 e -9	3.65 e-9	0.006	0.009	2.23 e +4	-0.247	-0.285	-0.291	-0.277
HCl (800)	0.852 e -9	1.624 e-9	0.006	0.009	1.393 e +4	-0.198	-0.166	-0.21	-0.209
HNO$_3$ (800)	0.550 e -9	0.985 e-9	0.0056	0.0054	4.159 e +3	-0.215	-0.214	-0.201	-0.207

Table 3. Value of i_{corr} and E_{corr} and other factor for dual layer silica coated sample by using PVA as wetting gent

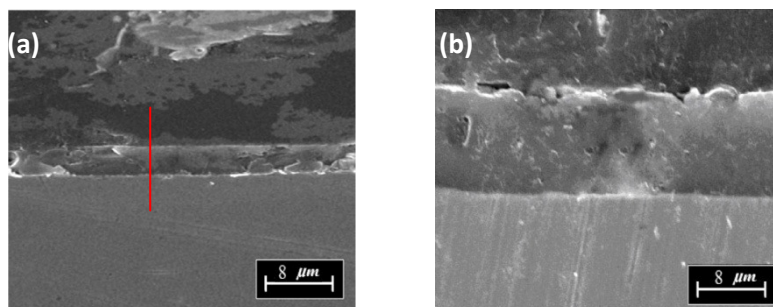| Catalyst (grinding paper)	$i_{Corrosion}$	$I_{Corrosion (A/cm^2)}$	$b_{c (V/dec)}$	$b_{a (V/dec)}$	$R_{(\Omega)}$	$E_{corr (abs)}$ (v)	$E_{corr (calc)}$ (v)	E –begin (v)	E-end (v)
HCl (1000)	1.546 e -13	1.253 e-12	0.003	0.001	3.346 e+6	-0.225	-0.258	-0.269	-0.253
HNO$_3$ (1000)	2.654 e -12	1.125 e-11	0.002	0.001	3.125 e +5	-0.208	-0.219	-0.221	-0.217

Figures

Fig 1. Uniform Silica layer by using PVA and (1000 grain size) grinding paper for surface finishing. (a) monolayer (b)dual layer
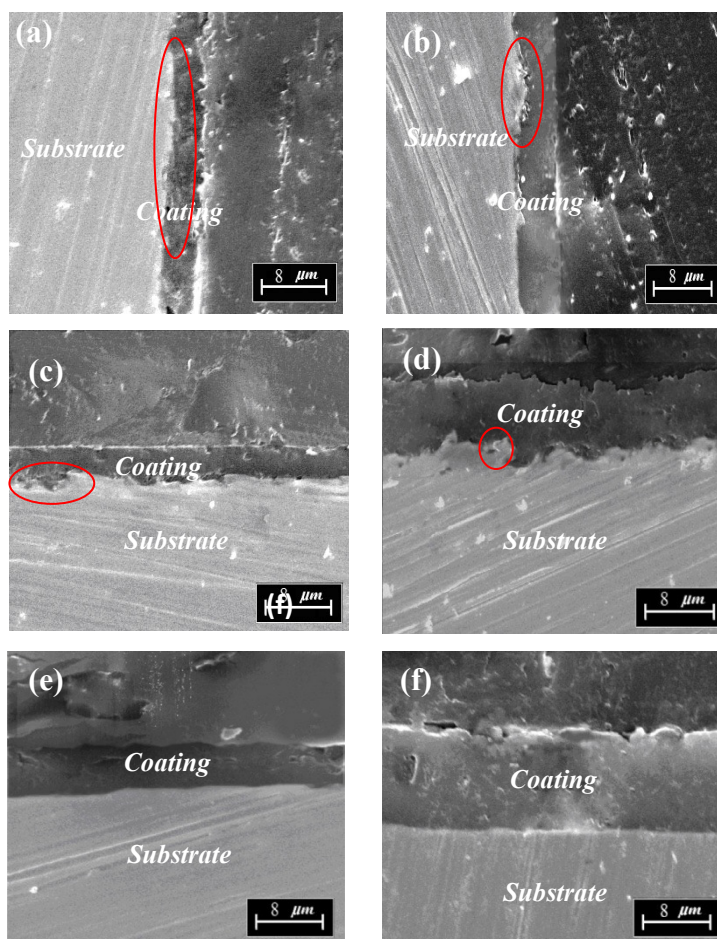

Fig 2. Uniform Silica layer by using PVA wetting agent on the surface by using (a) 800 grinding paper and HNO_3 catalyst, (b) 800 Grinding paper and HCl catalyst, (c)1000 grinding paper and HCl catalyst (d)1000 grinding paper and HNO_3 catalyst (e) 1200 grinding paper and HCl catalyst and (f)1200 Grinding paper and HNO_3 catalyst.
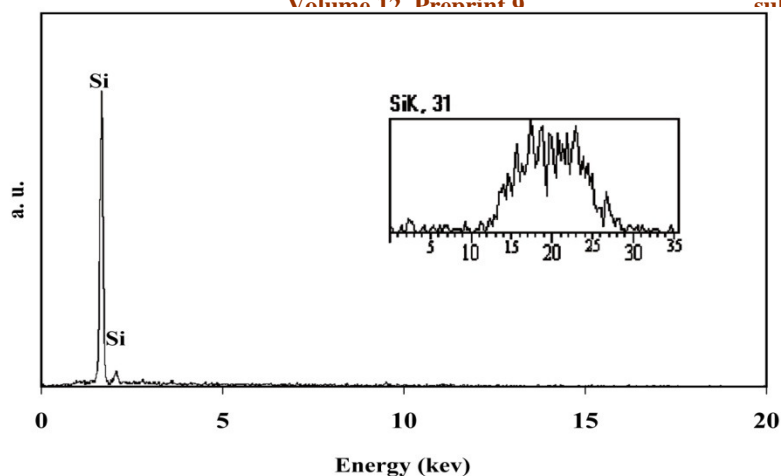
Fig 3. Energy Dispersive X-ray analysis of monolayer Silica coated samples.
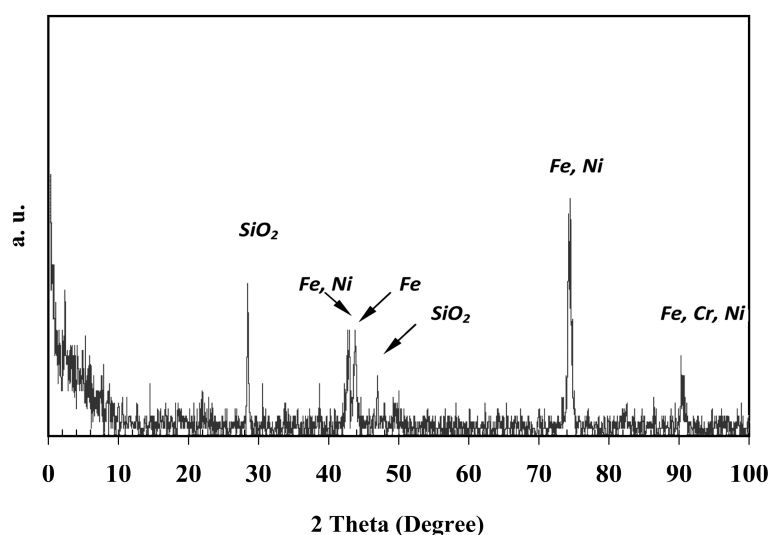
Fig 4. XRD pattern of Silica coated Sample.
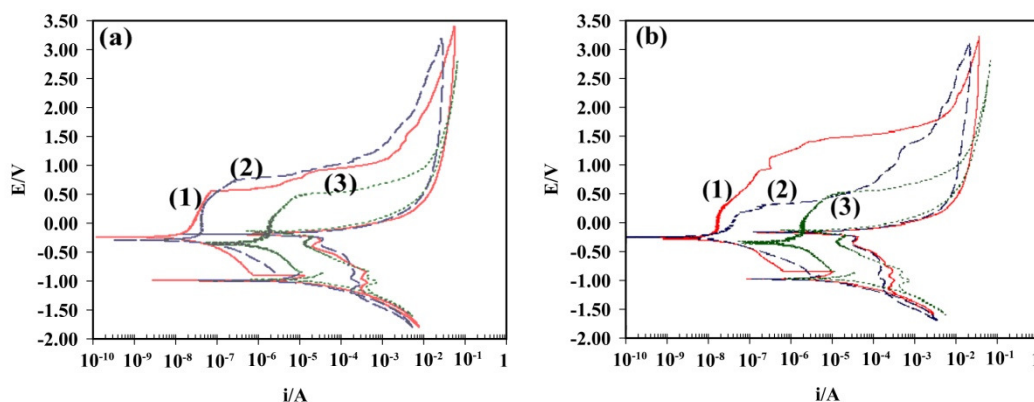
Fig 5. a) Polarization curves for monolayer coating samples using PVA wetting agent, HCl as a catalyst with different grinding papers (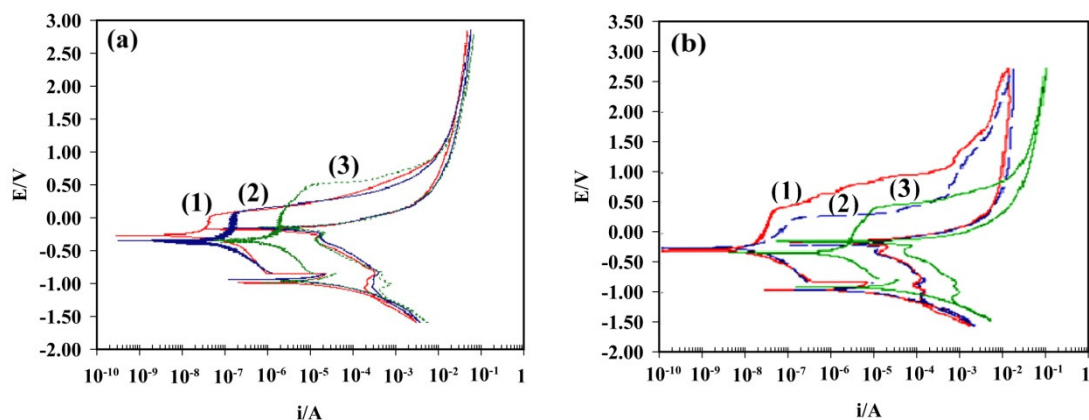1)1000 grinding paper (2) 800 grinding paper (3) Bare steel. b) Polarization curves for monolayer coating samples using PVA wetting agent, HNO$_3$ as a catalyst with different grinding papers (1)1000 grinding paper (2) 800 grinding paper (3) Bare steel.

Fig 6. Coating samples with using CTAB wetting agent with different grinding (1) HCL catalyst (2) HNO3 catalyst (3)Bare steel ,a) 1000 grinding paper b) 800 grinding paper
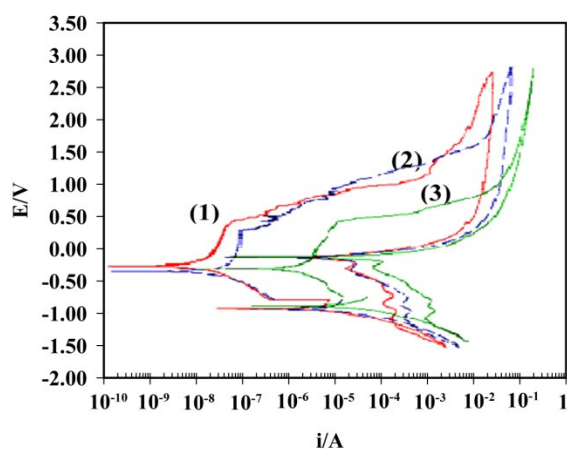

Fig 7. Monolayer coated samples with using PVA wetting agent and 1000 Grinding (1) HCl catalyst, (2) HNO$_3$ catalyst and (3) bare steel.
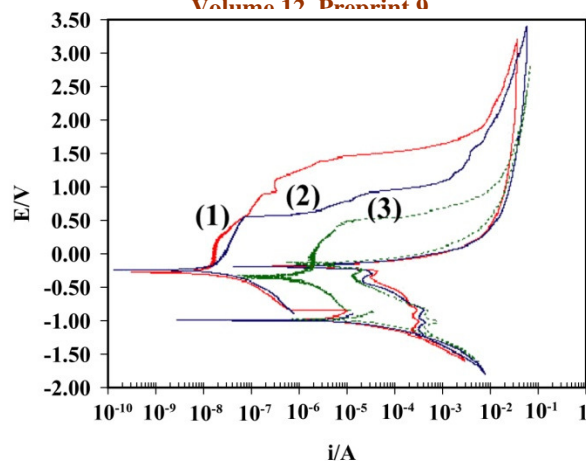
Fig 8. Monolayer Coated samples using HCl catalyst with 1000 grinding paper (1) PVA, (2) CTAB and (3) Bare steel.
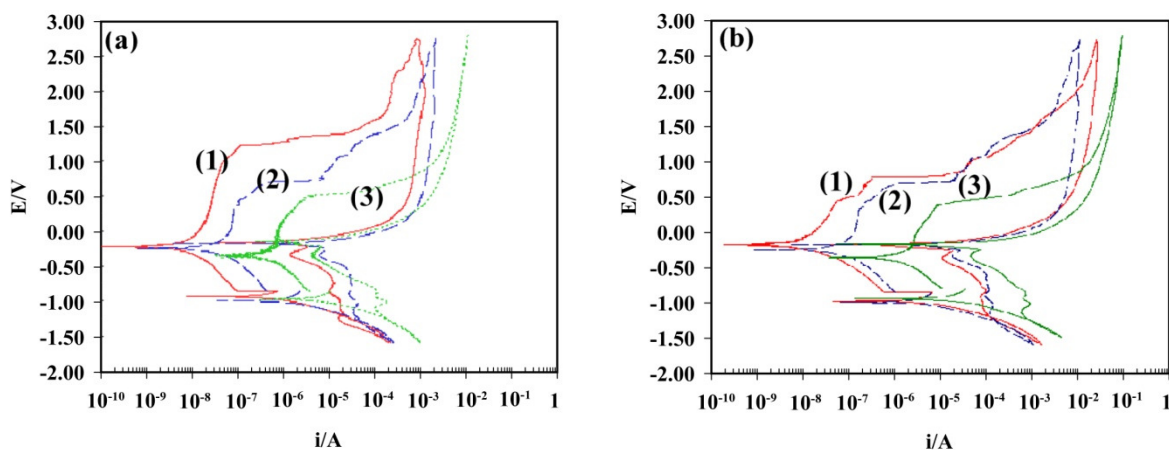

Fig 9. Comparison of polarization curves for dual and monolayer coated samples using PVA and HCl catalyst (a) 1000 grinding paper (1) dual layer (2) monolayer (3) bare steel (b) 800 grinding paper (1) dual layer ,(2) monolayer and (3) bare steel.
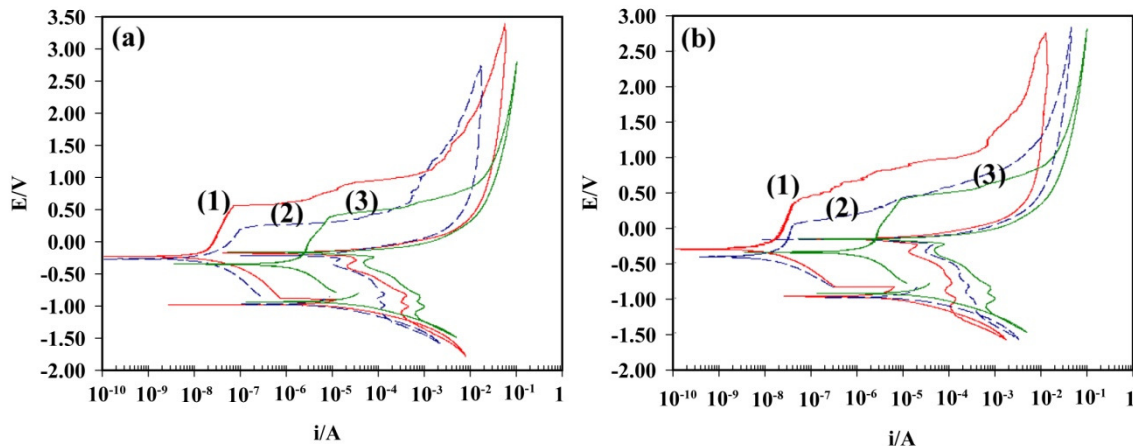
Fig 10. Comparison of polarization curves for dual and monolayer coated sample using PVA and HNO_3 catalyst (a) 1000 grinding paper (b) 800 grinding paper and (1) dual layer,(2) monolayer and (3)bare steel.