Development of Corrosion Resistant Silica Coating on Surface Modified Zinc Coated Steel

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Abstract

$Zn-SiO_2$ substrates were prepared after modifying the zinc surface with a developed surface treatment method. The silica coating on the surface modified zinc panel showed further improvement in terms of corrosion protection of the steel substrates. The open circuit potential of the samples immersed in 5% NaCl solution was stable and reached the steel potential after around 60 days. The salt chamber result of bare zinc with SiO_2 showed red rust formation after 31 days. The red rust formation was observed after 35 and 69 days in the case of samples immersed for 1 and 5 minutes respectively in the surface modifier solution followed by silica coating.

1.0. Introduction

Cadmium, Zn, Zn-Ni and Zn-Co are some of the coatings that have been in use for many years in protecting the steel substrates from corrosion attack. These coatings have been selected based on the properties offered by them such as good solderability, ductility and good frictional property. The Cd coatings are subjected to stringent regulation due to its toxicity and usage of cyanide plating baths for the deposition process. Another drawback is the introduction of large amounts of hydrogen into the underlying metal during deposition process which increases the risk of failure in the structure due to hydrogen embrittlement. Environmental safety and performance needs forced the researchers to look for alternative coatings to the existing cadmium coatings [1-8].

Zn and Zn alloys show good sacrificial property and also offer good barrier property when Ni is included in smaller amounts. The drawback in the use of pure Zn coatings is that it shows higher potential difference when coupled with Iron due to its electro-negativity (-0.760 V vs. SHE). The large potential difference exerts a driving force for rapid Zn dissolution and the underlying steel substrate is protected for a short period of time. In the case of Zn-Ni alloys, the coating life is prolonged due to the presence of nickel which offers good barrier protection to the coating. However, due to the high zinc content in the deposit, these alloys have more negative potential than cadmium and hence dissolve rapidly in corrosive environments.

Chromate conversion coatings are widely used to protect stainless steel or zinc coated steel substrates [9, 10]. These coatings are deposited from hexavalent chromium, which are highly toxic and carcinogenic. In order to replace the chromate conversion coatings, colloidal silicate coatings are under extensive research. Silicate conversion coatings can be deposited from an environmental friendly silicate containing solutions by dip-coating method followed by drying and heat-treatment at high temperature [9-11].

Silica-silicate coatings have been obtained either from alcoholic silica sol that are derived from hydrolyzed alkoxysilanes [12, 13], aqueous silica/silicate sol [11, 14-22] or aqueous silicate solution containing organosiloxane polymers [23]. Most of these studies were performed on zinc or zinc plated steel [11, 14-17 & 21-23] and the presence of the silica-silicate coatings increased the corrosion resistance. It was reported that the corrosion protection results from silicate adsorption on the pits, which causes suppression of anodic as well as cathodic processes at the zinc surface and additionally produces a diffusion barrier for the corrosive species [14, 21]. In one of our earlier studies, we found that silicate layers on zinc can be formed under anodic polarization [15], which causes pH to increase in the interfacial region resulting in polymerization of silicates on the surface and this polymerization process of the surface bonded silicates leads to SiO_2 formation [10].

Silicate coatings were also deposited from solutions that contain silica [16, 17 & 20], silicates [15, 16 & 20] and metasilicates [17]. Some researchers have added either organic or inorganic compounds to the bath to improve the corrosion protection or the quality of the silicate film [16, 17 & 21-23].

In the present investigation, silica was deposited on to surface modified Zn coated steel panels. The silica coated samples were evaluated using electrochemical measurements such as Tafel polarization, open circuit measurements and ASTM B117 salt chamber test.

2.0. Experimental

2.1. Experimental-Sample Preparation

The Zn panels of ~10 µm thickness were cleaned with soap solution, rinsed with DI water and dried. Then, the panels were immersed in a surface modifier solution for different time duration starting from 1 to 60 minutes. The silica coating was applied on the surface modified Zn samples (henceforth SM-Zn-SiO_2) by treating the panels in 1:3 PQ solutions.

2.2. Material Characterization and Mechanical Property Evaluation

The modified zinc surface was characterized using scanning electron microscope, EDAX and Raman Spectroscopy. A Vickers hardness indenter (Buehler Micromet 1 Micro hardness Tester) was used to indent the prepared coatings with a diamond tip. The physical deformation that occurs during the indentation process at an applied load of 100g for 10-15 sec was observed under a microscope and the dimensions of the depression were marked. Vickers hardness number (VHN) was calculated based on the observations made on the indent using the formula

$$VHN = \frac{2P}{d^2}\sin\left(\frac{\alpha}{2}\right) \tag{1}$$

where, *d* is the diagonal length left by the diamond shaped pyramid indenter. The angle between the phases of the pyramid is $\alpha=136°$. *P* is the load used in kilograms and the units of *d* are in millimeter.

2.3. Electrochemical Studies

The electrochemical characterization of the prepared coatings was performed in a 3 electrode set-up. The open circuit potential of the zinc panel was measured during immersion in the surface modifier solution. Additionally, electrochemical impedance spectroscopy was carried out in 5% NaCl solution in order to calculate the coating porosity [27-29]. The porosity was calculated using the following equation

$$F = \frac{R_{P\,Substrate}}{R_{p(Coating-Substrate)}} \times 10^{-|\Delta E_{Corr}/\beta_a|} \tag{2}$$

where, F is the total coating porosity, $R_{p\ (Substrate)}$ is the polarization resistance of the base metal (steel); $R_{p\ (Coating\text{-}Substrate)}$ is the combined polarization resistance of coating with the steel substrate, $\Delta E_{Corr.}$ is the difference in corrosion potential of the coating with substrate and bare substrate (steel).

3. 0. Results and Discussion

3.1. Surface Modified Zn Panels (SM-Zn)

3.1.1. Characterization of Surface Modified Zinc Coatings

Figure 1 shows the Raman spectrum of bare zinc coated steel and the same immersed in surface modifier solution for 1 and 5 minutes durations. It can be seen that, essentially there were no peaks for the bare and 1 minute immersed Zn coated steel sample. However, a small peak appeared at 558.02 cm^{-1} which can be attributed to the ZnO formation.

3.1.2. Scanning Electron Microscopy-Surface Morphology

Figure 2 shows the effect of immersion time on the morphology of bare and surface modified zinc panels. It can be seen from the micrographs that, the flake like morphology of zinc is intact up to 3 minutes of immersion time and after that spherical particles were seen along with the flakes. This porous matrix allows better bonding between SM-Zn and SiO_2 coating.

3.1.3. Scanning Electron Microscopy-Cross-Sectional Analysis

Figure 3 shows cross sectional images of zinc panels immersed in surface modifier solution for 5 minutes. The porous nature of the Zn deposit after immersion in surface modification solution can be seen from the figure. The samples immersed for more than 5 minutes were not considered for the study due to a considerable decrease in the Zn coating thickness.

3.1.4. Tafel Polarization

Figure 4 shows the Tafel polarization behavior of the zinc coated steel samples immersed in surface modifier solution for different time. The surface modification on Zn coatings exhibited similar corrosion current as shown in the figure. A gradual shift in the E_{Corr} towards more positive potential was observed with the increase in immersion time. The E_{Corr} for pure zinc is -1.189 V vs. SCE which has been shifted to -1.012 V vs. SCE for the 5 minute immersed zinc sample. The shift in the potential towards more positive potential is due to the surface modification process. The Tafel characteristics of the Zn coated steel with surface modifier were summarized and are given in Table 1.

3.1.5. Porosity Measurement

Table 2 shows the polarization resistance of the zinc coated samples with surface modifier. The polarization resistance of bare steel is 3741 Ώ. A value of 451 Ώ was observed for the zinc coated steel. The 5 minute immersed samples showed a polarization resistance of 1078 Ώ. The porosity values in Table 5 were calculated using equation (1). The porosity of the bare zinc coated steel and the value of the sample which was immersed for 1 minute in the surface modifier solution are similar due to the fact that the immersion time was not sufficient for the surface modifier solution to penetrate in the bulk of the zinc coating. As shown in Table 5, the porosity of the coating increases with the increase in immersion time.

Table 2 also shows the Vicker's Hardness Number for both, the zinc coated steel and the surface modifier sample. The surface modified Zn has higher hardness value when compared to the bare zinc coated steel. Bare zinc exhibited a hardness value of VHN_{100gf} = 95.53 which increases to VHN_{100gf} = 104.38 for the 5 minutes immersed sample.

3.1.6. Open Circuit Measurements

Figure 5 presents the change in open circuit potential of the Zn samples with surface modifier coatings immersed in 5% NaCl solution over a period of 32 days. These samples were not treated with SiO_2 process. As shown in the figure, the potential of the Zn samples with surface modifier are shifted to more positive direction when compared to bare zinc (-1.189 V vs. SCE, not shown). There is a gradual decrease in potential up to 5 minutes of immersion (-1.012 V vs. SCE). The 1 and 3 minutes immersed samples reached more positive potentials (towards the potential of steel) within 10 days of immersion in the test solution due to the rapid dissolution of zinc from the deposit. However, in the case of 5 minutes immersed sample, the potential reached the more positive potential at a slower rate. The potential of this sample levels off after 20 days at approximately -0.9 V vs. SCE, while the open circuit potential of the other two coating due to a complete removal of zinc shifted towards the steel potential. This study confirms that the zinc coated steel substrates immersed in surface modifier solution for 5 minute offer better corrosion protection than those immersed for less than 5 minutes.

3.1.7. Salt Spray Test

The results for the time of first grey and red rust formation after salt spray test are summarized in Table 3. The bare zinc panels subjected to salt spray test showed more than 5% red rust formation after 7 days and complete failure was observed after 10 days of exposure. On the other hand, the surface modified Zn panel (Zn immersed in surface modifier solution for 1 minute) showed the sign of red rust formation on the 26th day. Complete failure of the same coating was observed on the 32nd day. In the case of sample immersed for 3 minutes and 5 minutes, the red rust formation was observed on the 36 and 43 days respectively. The salt spray test also confirms the necessity for the 5 minutes immersion in surface modifier solution since it prolonged the rust formation.

3.2. Preparation of Silica Coated Zn Samples (SM-Zn-SiO_2)

3.2.1. Sample Preparation

Figure 6 shows the Raman spectrum of the sodium silicate liquid dried at 120 °C. The peaks at 525.2 cm^{-1}, 602.41 cm^{-1} are associated with vibration/bending of the -Si-O-Si- linkages. The appearance of high frequency Raman band at 1042.58 cm^{-1} is attributed to the symmetric Si-O stretching vibrations of SiO_4 groups in the sodium silicate [31, 32]. The slight shift in the case of dried sodium silicate is due to the removal of water.

Figure 7 compares the Raman spectrum of Zn-SiO_2 and surface modified Zn samples coated with silica. As discussed earlier the peak observed at 558.02 cm^{-1} corresponds to ZnO/ZnO_2^{--}. The peaks observed in the case of Zn-SiO_2 at 1074.58 cm^{-1} and 554 cm^{-1} are comparable to those obtained for sodium silicate (1041.86 and 547.16 cm^{-1}) samples. The slight shift in the peaks in the case of zinc panels with surface modification can be attributed to formation of zinc silicate [31, 32].

3.2.2. EDAX and SEM

The composition analysis was performed for Zn-SiO_2 and SM-Zn-SiO_2 samples. It was found that the silica content was in the range between 30 and 32 wt %. Figure 8 shows the SEM images of SM-Zn-SiO_2 samples at X5000 magnification. The formation of silicate layer (needle like silicate glass) can be observed on the surface covering the underlying SM-Zn particles. A thin transparent layer up to ~2 μm of silica formed on the surface of the samples can also be seen in the SEM images.

3.2.3. Cross-Sectional Analysis

Figure 9 shows the back scattered image of SM-Zn-SiO_2 sample taken at magnification of 12000X. It is seen from the figure that the silica coating is approximately 2 μm. It is noticeable in the figure that silica diffused through the porous SM-Zn matrix resulting as it will be shown later in improved corrosion resistance of the coating.

3.2.4. Tafel and Linear Polarization Studies

Figure 10 shows the Tafel behavior of SM-Zn-SiO_2 coatings in 5% NaCl solution. The Zn-SiO_2 coating has I_{Corr} value of 5.0 X 10^{-8} which indicates that the coating has a better corrosion protection property than bare Zn. However, the E_{Corr} of Zn-SiO_2 coating is -1.071 V vs. SCE which is close to that of bare zinc metal.

In the case of SM-Zn-SiO_2 (1 min) SM-Zn-SiO_2 (3 min) and SM-Zn-SiO_2 (5 min), the I_{Corr} values are in the same range. However, the E_{Corr} value are -0.982, -0.933 and -0.910 V vs. SCE, respectively. .

The Tafel characteristics of the coatings are summarized in Table 4. The difference in the OCP between the bare zinc coated with silica and the ones with surface modification and silica conforms the effect of surface modification in delaying the corrosion of zinc coated steel substrates. The barrier protection offered by the silica coating along with the surface modification improves drastically the life of the coating as discussed in the following section.

3.2.5. Porosity Measurement

Table 5 shows the porosity and the Vicker's Hardness Number for all samples prepared in this study. It can be seen from the table that the porosity values increased in case of silica coated sample implying the formation of more porous. These pores are then filled with the sodium silicate during immersion at 75 ^{o}C. The porosity of the bare zinc coated steel is 0.00288% which has increased to 0.00726% after 5 minutes immersion in surface modifier solution (~40% increase). The same substrate with silica coating has porosity value of 0.0265% (~27.4% increase). Table 5 also presents the Vicker's Hardness Number of the prepared coatings. There was no considerable change in the hardness values among bare zinc coated with silica (VHN_{100gf} = 86.92) and the ones with surface modification for 1 (VHN_{100gf} = 86.69) and 3 (VHN_{100gf} = 88.33) minutes. However, there was an increase in the hardness value of the 5 minute surface modified sample with silica coating (VHN_{100gf} = 92.97) which can be attributed to the surface modification process on the Zn coated steel.

3.2.6. Open Circuit Potential Measurement

Figure 11 shows the change in OCP with time for the SM-Zn-SiO_2 samples immersed in 5% NaCl solution. It is seen that both Zn and Zn-SiO_2 has potential close to each other (~-1.1 V vs. SCE). The initial OCP starts to shift in anodic direction with the increase in surface modification time. SM-Zn-SiO_2 samples showed a steady OCP behavior even after 21 days of immersion in 5% NaCl.

3.2.7. Salt Spray Test

The results for the time of first grey and red rust formation after salt spray test are summarized in Table 6. Zn sample coated with SiO_2 are also shown for comparison. The Zn coated SiO_2 failed after 744 h) as can be seen from the table. The Zn-SiO_2 sample showed steady OCP behavior for more than 100 days during OCP measurement test but failed in the salt chamber when compared to the samples with surface modification.

In the case of Zn samples with surface modification (for 1 min) followed by silica coating, the grey rust formation was observed after 5 days (~120 h) and sign of red rust was observed on day 31 (~730). The Zn sample given surface modification for 3 min followed by silica coating showed an extended life in salt chamber since the red rust formation was noticed only on the 51st day (~1200 h). In all the cases, the grey rust formation was noticed on the 5th day but the red rust formation period was delayed depending on the immersion time in surface modifier solution. The red rust formation time observed for the 5 minutes immersed samples is 71 days (~1700 h).

4.0. Conclusion

Bare zinc on the steel panel showed grey rust in 60 h and red rust formation was observed after 140 h. In the case of zinc with surface modification for 1 min, the red rust formation was delayed and enhancement in the stability was observed resulting in red rust formation after ~450 h. The immersion time in surface modification solution had a positive role in enhancing the stability of the bare zinc coatings and the same was noticed up to 5 min immersion time. Further time increase in the surface modification solution did not show any improvements. The silica coating on the zinc panel with surface modification showed further improvement in terms of corrosion protection of the steel substrates. The open circuit potential of the samples immersed in 5% NaCl solution was stable and reached the steel potential after around 60 days. The salt chamber result of bare zinc with SiO_2 showed red rust formation after 31 days where as the sample with surface modification (1 min immersion) showed improved performance (35 days). The maximum stability was exhibited by the sample which was immersed in surface modification solution for 5 min followed by silica coating. It showed sign of red rust after 69 days of exposure. The above results suggested that the silica coating on zinc coated steel with the developed surface modification process can be an alternative for the existing cadmium coating and it can also be an alternative to the hexavalent chrome Passivation process.

References

[1] C. R. Tomachuk, C.M.de A. Freire, M. Ballester, R. Fratesi, G. Roventi, *Surface and Coatings Technology,* **122,** 6 (1999).

[2] K. R. Baldwin and C. J. E. Smith, *Transactions of the Inst. of Met. Finish.,* **74,** 202 (1996)

[3] W. H. Safranek, *Plat. Surf. Finish.,* **84,** 45 (1997).

[4] A. Ashur, J. Sharon, I. E. Klein, *Plat. Surf. Finish.,* **83,** 58 (1996).

[5] A. J. Boehm, *Plat. Surf. Finish.,* **80**, 52 (1993).

[6] Y. P. Lin, J. R. Selman, *J. Electrochem. Soc.,* **140,** 1299 (1993).

[7] Y. Miyoshi, *J. ISIJ Int.,* **31,** 1 (1991).

[8] Y. H. Yau, S. G. Fountolakis, in *Procedings of Zinc based Steel Coating Systems: Metallurgy and Performance,* p.143 Minerals, Metals and Materials Society, (1990).

[9] M.L.A.D. Mertens, *Metal Finish*. **96** (1998) 10.

[10] M. Nikiforov, *MRS Bull.* **28** (2003) 157.

[11] S. Dalbin, G. Maurin, R.P. Nogueira, J. Persello, N. Pomier, *Surf. Coat. Technol.* **194** (2005) 363.

[12] C.J. Brinkner and G.W. Scherer, *Sol-gel science,* Academic press, Boston (1990) pp. 838-70.

[13] M. Atik, P. de Lima Neto, L.A. Avaca, M.A. Aegerter, J. Zarzycki, *J. Mater. Sci. Lett.* **13** (1994) 1081.

[14] D.P. Donohue, G.T. Simpson, Proc. 13th Annual U.S. Navy and Industry Corrosion Technology Exchange, 14-17 July 2003, Louisville, USA, 2003, p. R 3001.

[15] B. Veeraraghavan, D. Slavkov, S. Prabhu, M. Nicholson, B. Haran, B. Popov, B. Heimann, *Surf. Coat. Technol.* **167** (2003) 41.

[16] J.J. Hahn, N.G. McGowan, R.L. Heimann, T.L. Barr, *Surf. Coat. Technol.* **108-109** (1998) 403.

[17] M. Hara, R. Ichino, M. Okido, N. Wada, *Surf. Coat. Technol.* **169-170** (2003) 679.

[18] L.A. Garcia-Cerda, O. Mendoza-Gonzalez, J.F. Perez-Robles, J. Gonzalez-Hernandez, *Mater. Lett*. **56** (2002) 450. 15

[19] G.P. Thim, M.A.S. Oliveira, E.D.A. Oliveira, F.C.L. Melo, *J. Non-Cryst. Solids* **273** (2000) 124.

[20] M.F.M. Zwinkels, S.G. Jaras, P.G. Menon, K.I. Asen, *J. Mater. Sci*. 31 (1996) 345.

[21] K. Aramaki, *Corr. Sci*. **43** (2001) 591.

[22] K. Aramaki, *Corr*. Sci. **44** (2002) 1375.

[23] K. Aramaki, *Corr*. Sci. **44** (2002) 1621.

[24] J. W. Cuthbertson and R. M. Angles, *J. Electrochem*. Soc., 94 (1948) 73.

[25] St. Vitkova, V. Ivanova and G. Raichevsky, *Surf. Coat. Tech*., 82 (1996) 226-231.

[26] US Patent, *No. 4, 184, 928,* 1980.

[27] S. H. Ahn, Y. S. Choi, H. G. Kim and J. G. Han, *Surf. Coat. Tech*., 150 (2002) 319-326,

[28] S. H. Ahn, J. H. Lee, H. G. Kim and J. G. Han, *Surf. Coat. Tech.*, 177-178 (2004) 638-644

[29] S. H. Ahn, J. H. Lee, H. G. Kim and J. G. Han, *Applied Surf. Sci.*, 233 (2004) 105-114,

[30] Basker Veeraraghavan, Dragon Slokov, Swaminatha P. Kumaraguru, Marjorie Nicholson, Bala Haran, Branko Popov and Bob Heimann, *Surf. Coat. Tech.*, 167 (2003) 41-51.

[31] Paul F. McMillan, Ann. Rev. *Earth Planet. Sci*., 17, 255.283, 1989.

[32] M. E. Fleet and G. S. Henderson, *Phys. Chem. Minerals*, 24, 1997, 345-355.

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Table 1. Tafel characteristics of zinc panels immersed in surface modification solution for different time

Sample	Zn	SM-Zn (1 min)	SM-Zn (3 min)	SM-Zn (5 min)
$E_{Corr.}$ (V) vs. SCE	1.189	1.072	1.037	1.012
$I_{Corr.}$ (mA/cm^2)	1.69x10^{-6}	9.74x10^{-6}	2.44x10^{-6}	7.35x10^{-6}

Table 2. Polarization Resistance Values of Zn panels after immersion in surface modification solution for different time

Sample	$R_{Coating+Substrate}$	E_{Corr} (Coating + Steel) vs. SCE	Porosity (%)	Vicker's Hardness (VHN_{100gf})
Zn	451.1	-1.190	0.00295	95.53
SM-Zn (1 min)	462	-1.082	0.00288	100.47
SM-Zn (3 min)	1012	-1.080	0.00369	102.3
SM-Zn (5 min)	1078	-1.012	0.00726	104.38

R_p (Steel) = 3741.9 and $E_{Corr.}$ (Steel) = -0.647 V vs. SCE

Table 3. Salt chamber performance of bare Zn and Zn with surface modification for different time

Sample	Time for first appearance of grey rust (h)	Time for first appearance of red rust (h)
Zn	--	140
SM-Zn (1 min)	24	624
SM-Zn (3 min)	24	864
SM-Zn (5 min)	24	1032

Table 4. Tafel characteristics of different SM-Zn-SiO_2 coatings

Samaple	I_{Corr} (mA/cm^2)	E_{Corr} (V) vs. SCE
Zn-SiO_2	5.0 x 10^{-8}	1.071
SM-Zn-SiO_2 (1 min)	1.44 x 10^{-7}	-0.982
SM-Zn-SiO_2 (3 min)	3.18 x 10^{-7}	-0.933
SM-Zn-SiO_2 (5 min)	1.77 x 10^{-7}	-0.910

Table 5. Polarization Resistance Values of different SM-Zn-SiO_2 coatings.

Sample	$R_{Coating+Substrate}$ (ohm cm^{-2})	E_{Corr} (Coating + Steel) V vs. SCE	Porosity (%)	Hardness (VHN_{100gf})
Zn-SiO_2	-	-	-	86.92
SM-Zn-SiO_2 (1 min)	2286	-0.982	0.0083	86.69
SM-Zn-SiO_2 (3 min)	5869	-0.933	0.0137	88.33
SM-Zn-SiO_2 (5 min)	5977	-0.910	0.0265	92.97

Table 6. Time of grey/red rust formation for different SM-Zn-SiO_2 coatings

Sample	Time for first appearance of grey rust (h)	Time for first appearance of red rust (h)
Zn-SiO_2	200	744
SM-Zn-SiO_2 (1 min)	120	730
SM-Zn-SiO_2 (3 min)	120	1200
SM-Zn-SiO_2 (5 min)	120	1700

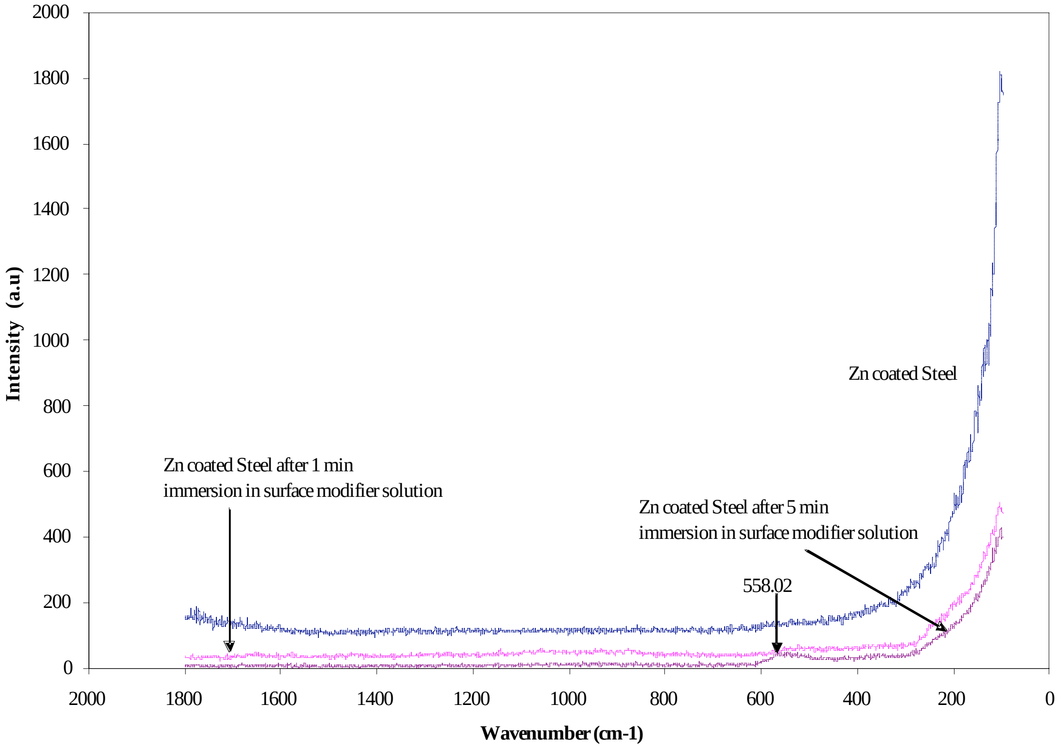
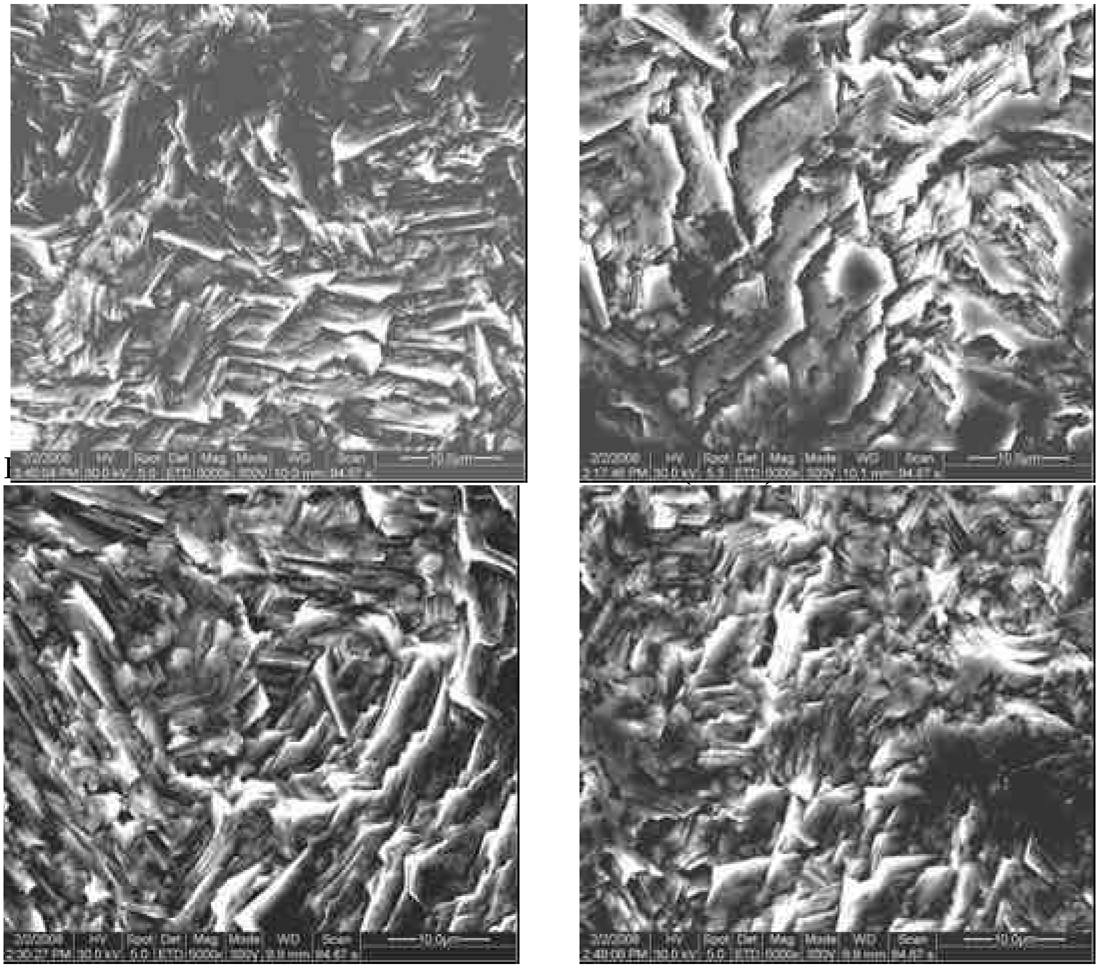
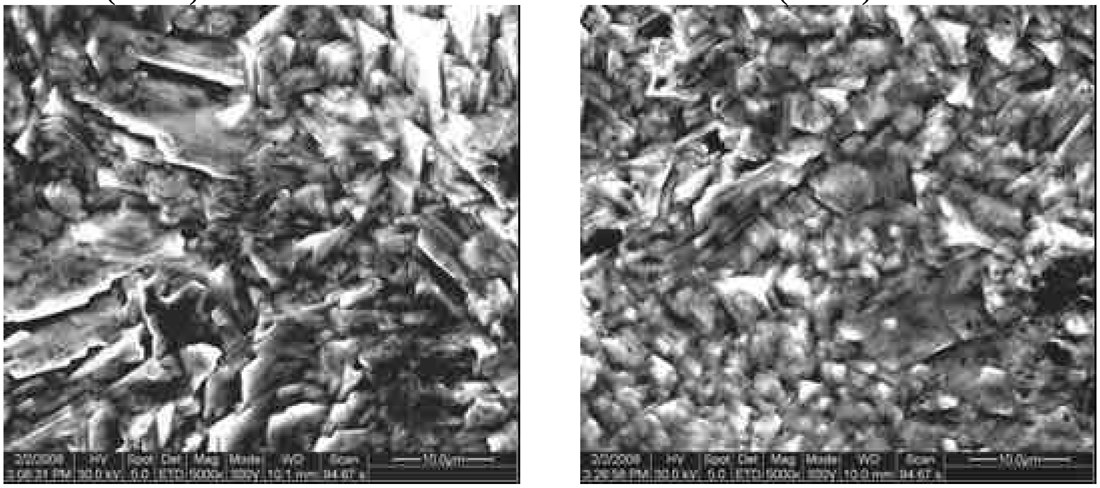


Figure 1. Raman spectrum of bare zinc coated steel and zinc coated steel immersed in surface modifier solution for 1 & 5 minutes.



SM-Zn (2 min) SM-Zn (3 min)



SM-Zn (4 min) SM-Zn (5 min)

Figure 2. SEM of bare Zn and Zn after immersion in surface modification for different time

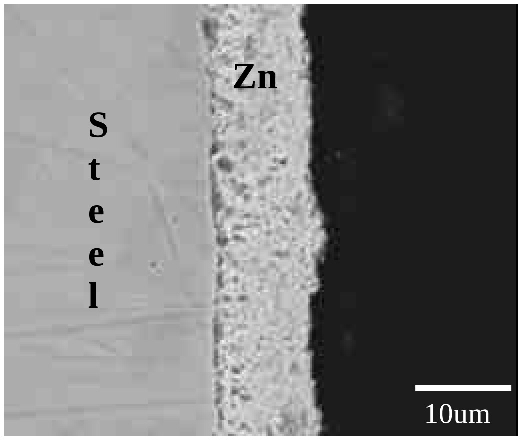


Figure 3 Cross-sectional image of zinc panels immersed in surface modification solution for 5 minutes.

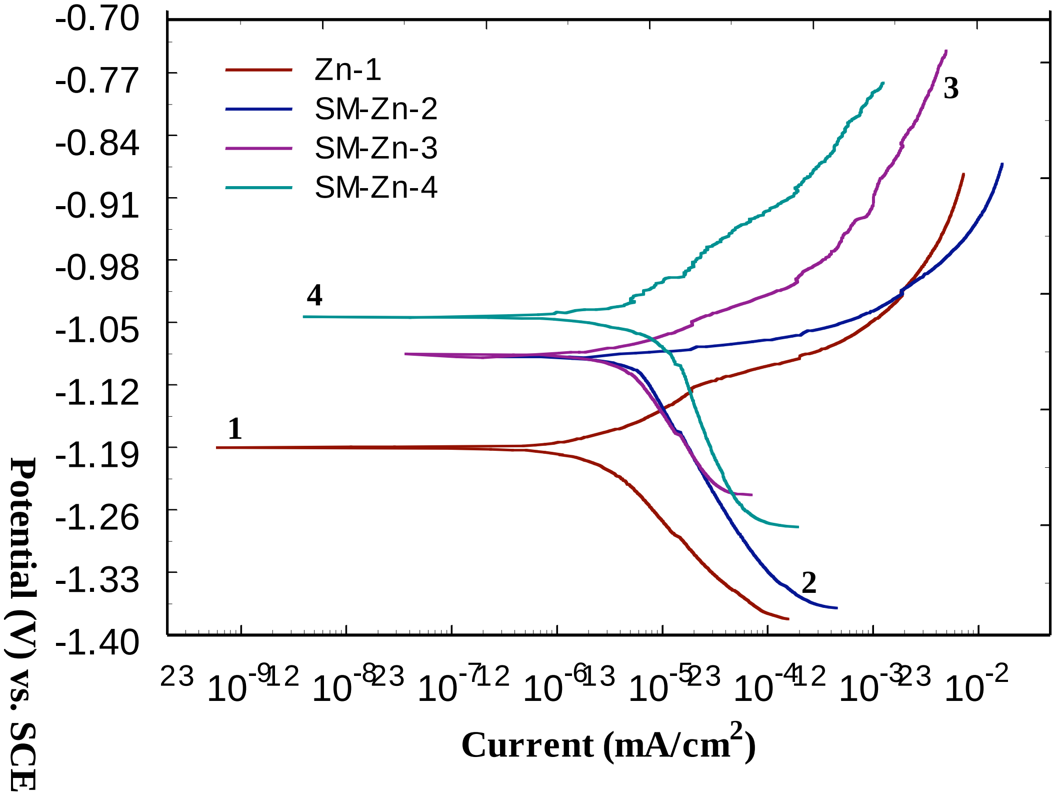


Figure 4. Tafel plots for zinc panels immersed in surface modification solution for different time

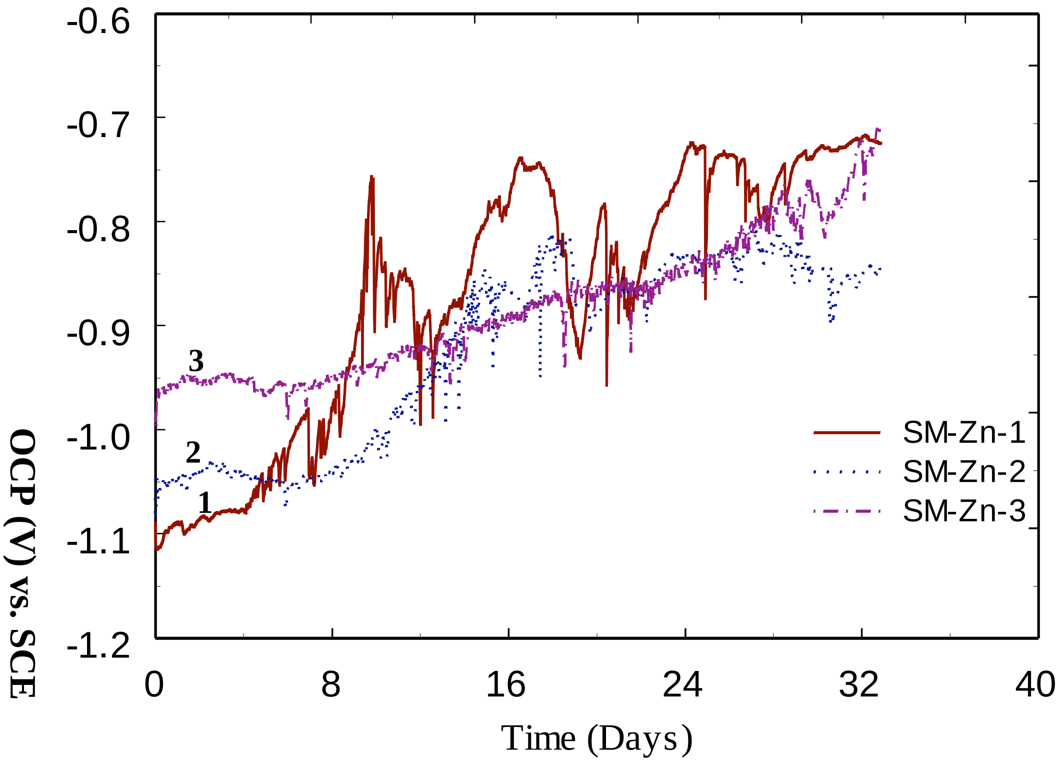


Figure 5. Open circuit potential behavior of different zinc panels after surface modification for different time.

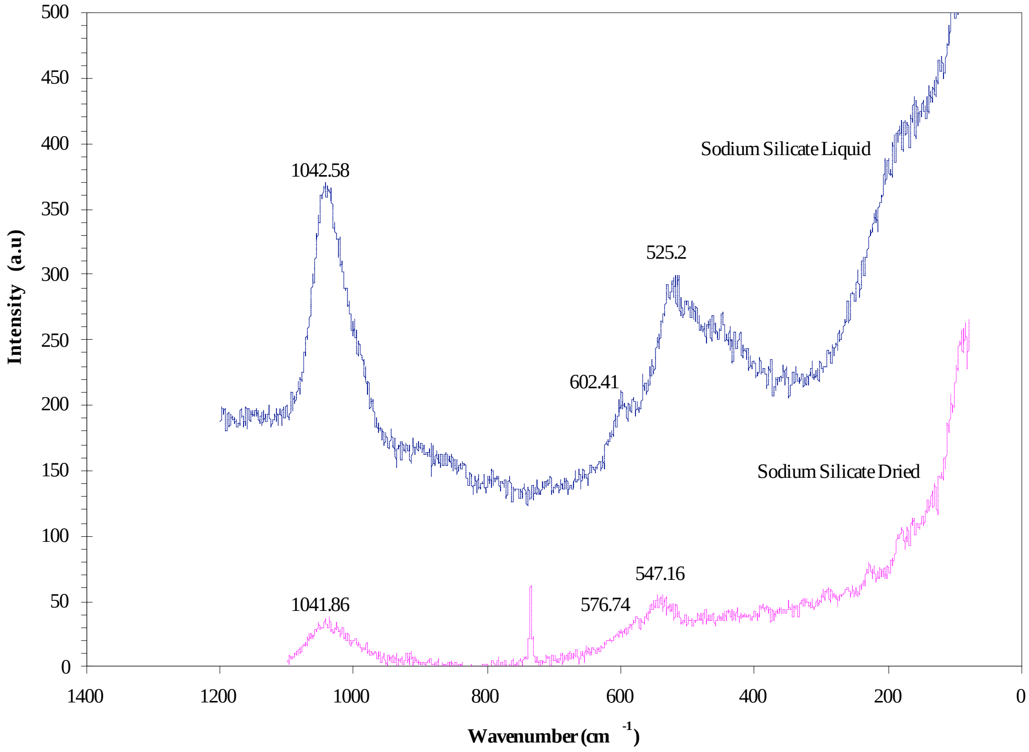


Figure 6. Raman spectrum of sodium silicate solution and sodium silicate dried at 120 ^{o}C

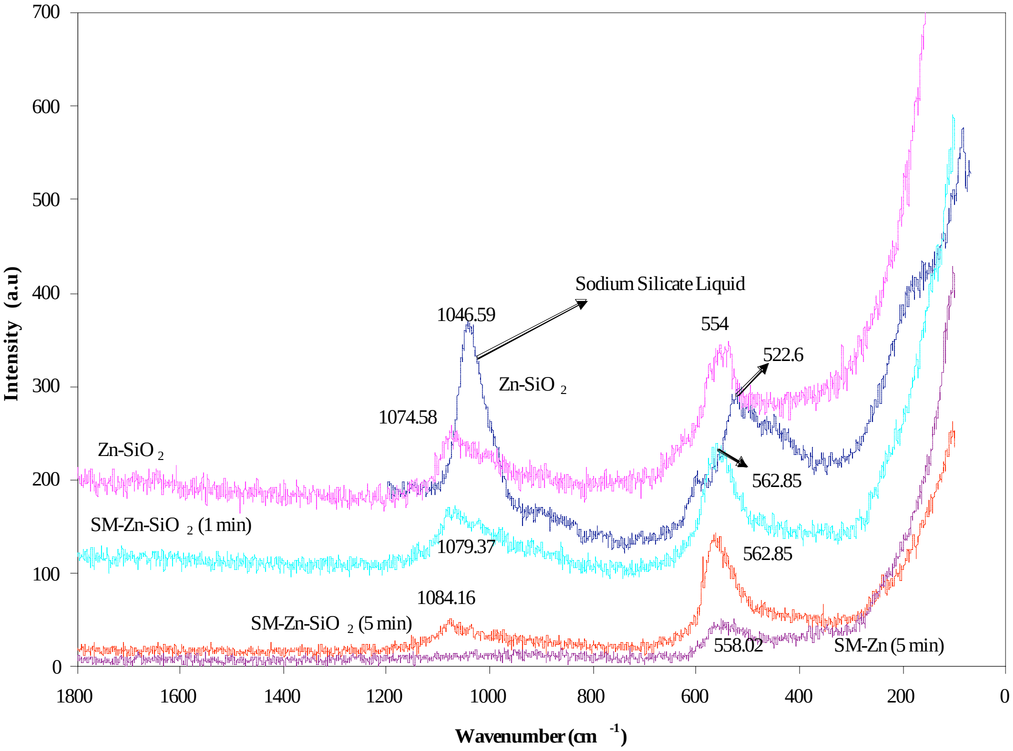
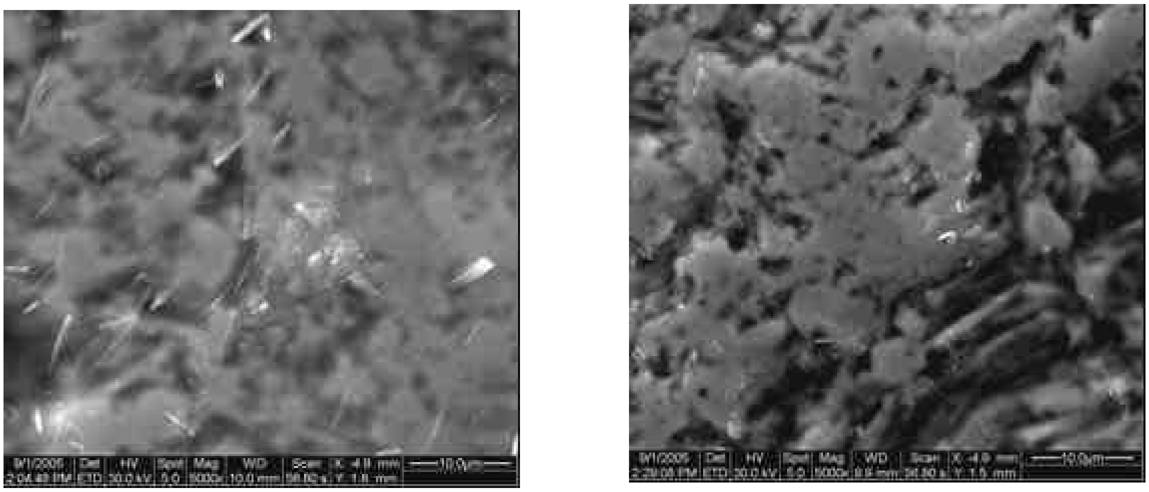
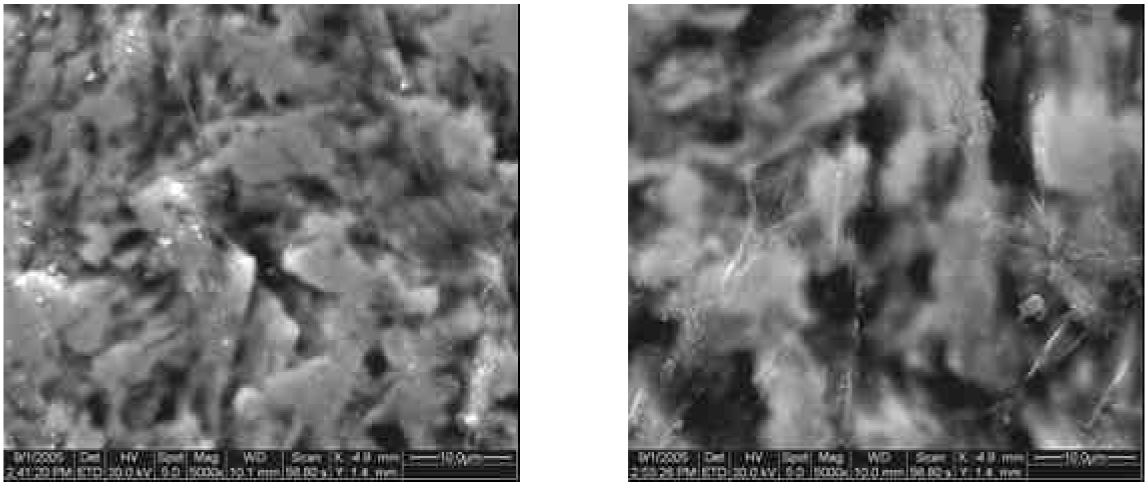


Figure 7. Raman spectrum of SM-Zn-SiO$_2$ (5 min) sample. The Raman spectrum of zinc coated steel with silica coating, sodium silicate liquid and zinc coated steel immersed in surface modification solution for 5 minutes are given for comparison.



Zn-SiO$_2$ SM-Zn-SiO$_2$ -1 min



SM-Zn-SiO$_2$ -3 min SM-Zn-SiO$_2$ -5 min

Figure 8. SEM images of Zn coated with SiO$_2$ and SM-Zn-SiO$_2$ coatings.

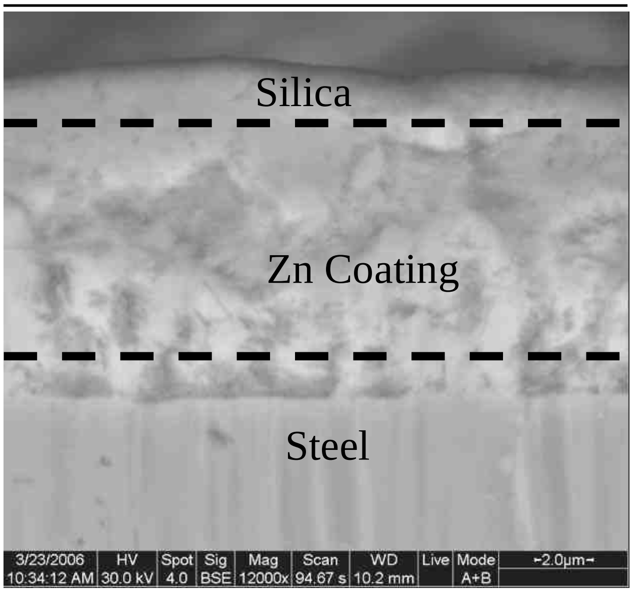


Figure 9. Cross-sectional BSEM image of SM-Zn-SiO_2 (5min)

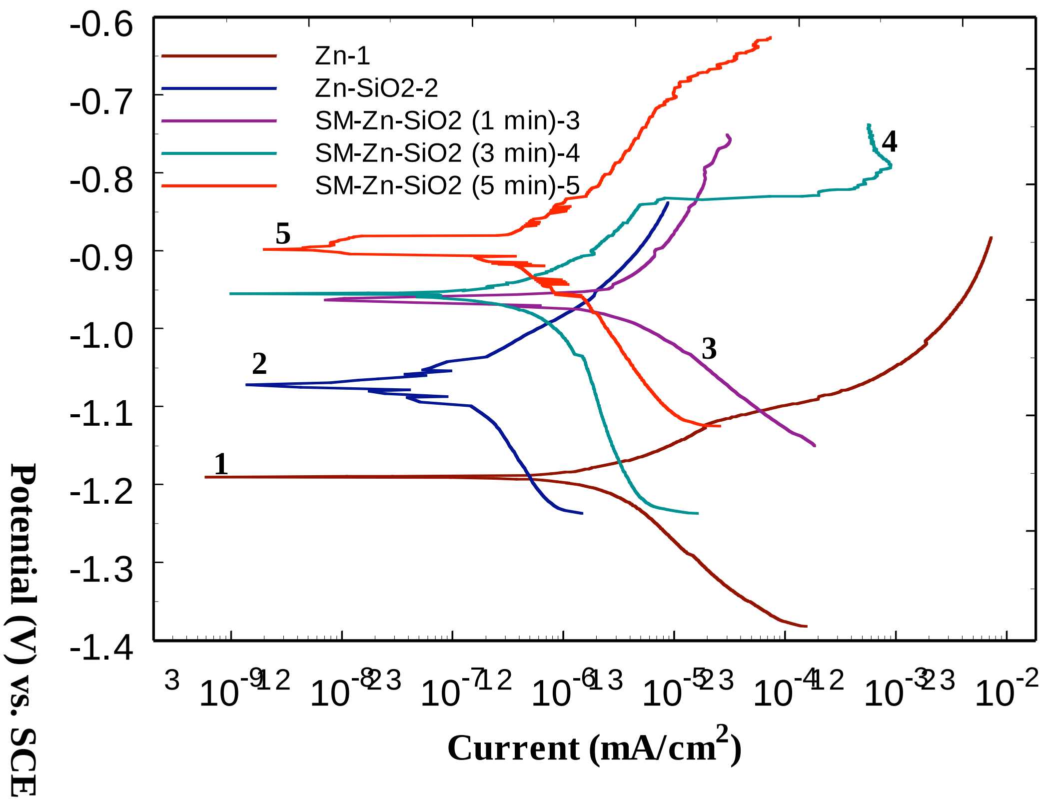


Figure 10. Tafel plots for SM-Zn-SiO$_2$ samples. The Zn-SiO$_2$ and pure Zn are given for comparison.

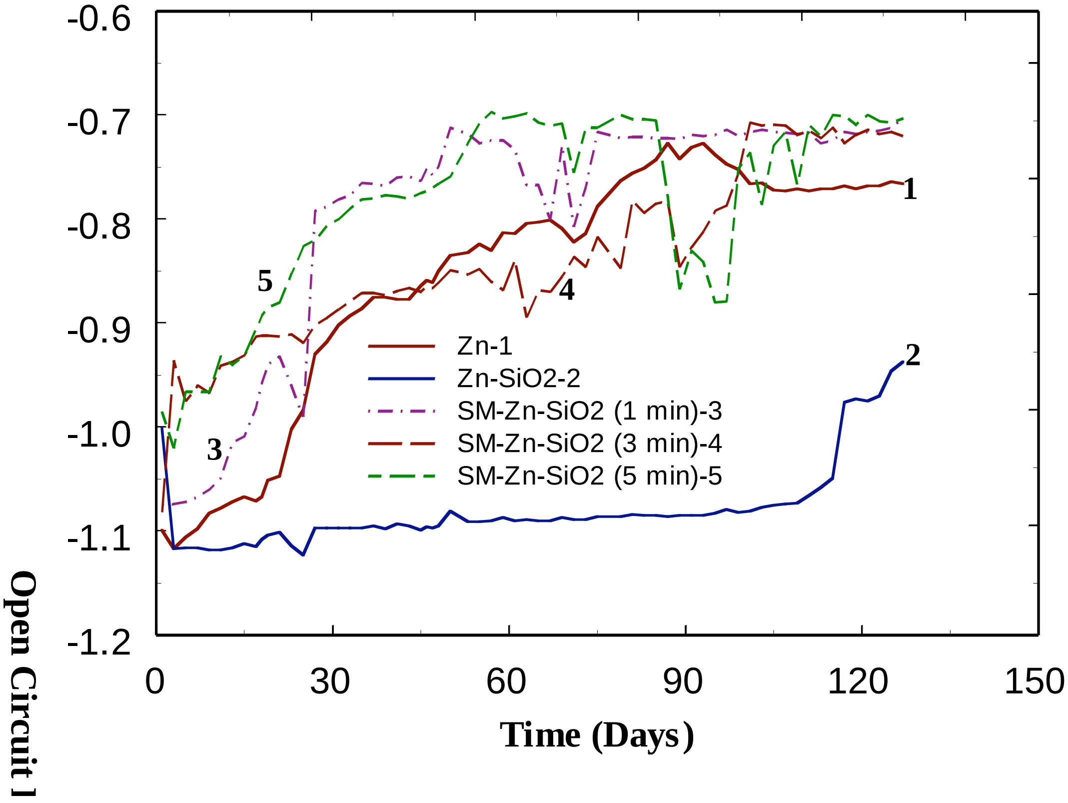


Figure 11. Comparison of change in OCP with time for SM-Zn-SiO_2 samples. The OCP vs. time of pure and Zn-SiO_2 are given for comparison.