Surface modification of mild steel using Ag doped SnO_2 nanoparticles for corrosion inhibition

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[Received:30 July 2014; Revised 5 August 2014; Accepted 6 August 2014]

Abstract -The effect of Ag doped SnO_2 nanoparticles on the inhibition of the corrosion of mild steel in 1 N H_2SO_4 solution has been investigated by using Potentiodynamic polarization and electrochemical impedance spectroscopy studies. The Ag doped SnO_2 acts as a mixed type inhibitor on mild steel and modifies the surface of substrate and forms a protective stable barrier coating against sulphuric acid environment.

Keywords: Ag doped SnO_2, EIS spectra, H_2SO_4, Mild Steel, Polarization method

I. INTRODUCTION

Acid solutions are generally used for the removal of rust and scale in several industrial processes. Sulphuric acid is often used as a pickling acid for steel and its alloys [1]. Mild steel is employed widely in most of the industries due to its low cost and availability in ease for the fabrication of various reaction vessels such as cooling tower tanks, pipelines, etc. [2]. Corrosion of metals is a serious environmental problem that has been given adequate attention in the oil and gas industries because, during industrial processes such as acid cleaning and etching, metal surfaces are often made to come in contact with acidic medium, indicating that the use of inhibitors is necessary [3]. Although there are numerous options for controlling the corrosion of metals, the use of inhibitors is one of the best methods for protecting metals against corrosion. The environmental consequence of corrosion is enormous, and its inhibition has been deeply investigated. It has been found that one of the best methods of protecting metals against corrosion involves the use of inhibitors which are substances that slow down the rate of corrosion [4].

Nanotechnology has attracted now become important in many areas such as energy, catalysis and medicine. Nanoparticles have been synthesized by various physical and chemical processes. However, some chemical methods cannot avoid the use of toxic chemicals in the synthesis process [5, 6]. Eco-friendly biosynthesis of nanoparticles (NP) are accomplished using microorganism which grabs target ions from their solutions, and then accumulates the reduced metal in its elemental form through enzymes generated by microbial cell activities [7, 8]. These metals in nano compounds exhibit significant corrosion inhibition against various corrosive environments [9]. The Ag and SnO_2 nanoparticles were synthesized naturally by Cleistanthus Collinus plant extract and reported [10]. The aim of the present work is to investigate examine the inhibitory action of Ag doped SnO_2 nanoparticles on the corrosion of mild steel in 1N H_2SO_4 solution. The inhibitory efficiency was evaluated by Potentiodynamic polarization and Electro chemical impedance spectroscopic (EIS) methods.

II. EXPERIMENTAL

The Ag and SnO_2 nanoparticles were prepared by Cleistanthus Collinus plant methanolic extract [11]. SnO_2 nanoparticles of different compositions (33.3%, 50%, 60%, 66.6%, 71%, 75%, 77.8% and 80%) were mixed with Ag nanoparticles and ethanol. This mixture was refluxed for 2 hours, centrifuged and washed with deionized water and acetone (12). The Ag doped SnO_2 nanoparticles were dried at room temperature. The

powdered Ag doped SnO_2 nanoparticles are used for this study.

The mild steel used in the study had the following composition: (wt %), C (0.16), Si (0.17), Mn (0.68), S (0.05), P (0.027), S (0.026), Cr (0.01), Mo (0.02), Ni (0.01) and Fe (98.8). The coupons were prepared, degreased and cleaned as previously reported [12]. Two electrochemical techniques, namely, DC-Tafel slope and AC electrochemical impedance spectroscopy (EIS) were used to study the corrosion behavior. All electrochemical measurements were carried out using a Bio-logic SP300 with EC lab software and a three electrode cell. For these studies a three-electrode cell assembly with $1\,cm^2$ of mild steel as a working electrode, a saturated calomel electrode (SCE) as the reference electrode, and platinum foil as the counter electrode were used. The working electrode was coated with Ag doped SnO_2 nanoparticles by spin coating before use. Before starting the electrochemical experiments, the test sample was allowed to reach steady-state value of OCP. The inhibition efficiency is calculated from the polarization curves by the following equation:

$$IE\% = \frac{(I^{o}_{Corr} - I_{Corr})}{I_{Corr}} \quad (1)$$

Where,

I^{o}_{Corr} = Corrosion current density of uncoated substrate

I_{Corr} = Corrosion current density of coated substrate

The EIS measurements were carried out in the frequency range from 0.01 Hz to 10000 Hz using amplitude of -10 mV to +10 mV peak to peak with an AC signal at the open circuit potential. The EIS results have been represented in Nyquist plots and the charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}), are calculated and tabulated. The IE was calculated as follows:

$$IE\% = \frac{(R_{ct(inh)} - R_{ct})}{R_{ct(inh)}} \times 100 \quad (2)$$

Where, $R_{ct\,(inh)}$ and R_{ct} are the charge transfer resistances values in the presence and absence of the inhibitor respectively.

III. RESULT AND DISCUSSION

1.1 Potentiodynamic polarization

From the Table -1 it was observed that both anodic and cathodic reactions of the steel alloy electrodes resist corrosion with increase of tin oxide concentration up to 60% in Ag doped SnO_2 nanoparticles. Beyond this, increase in the concentration of tin oxide decreases the corrosion rate. But all the compositions have exhibited a better inhibitory effect than the blank. Ag doped tin oxide acts as a protective layer on steel surface and reduces the corrosion rate. The corrosion potential (E_{Corr}) showed a positive shift for mild steel electrode when treated with Ag doped tin oxide .The change in E_{Corr} from – 457 to – 488 mV indicates that Ag doped tin oxide acts as a mixed type inhibitor for steel alloy (Figure 1). Upto 60% the I_{corr} decreases while inhibition efficiency increases because of uniform protective film formation over steel surface [13, 14]. Increase in the concentration of tin oxide in Ag doped tin oxide from 66.66% increases I_{corr}. However the corrosion rate is low compared to bare alloy specimen. These results clearly indicate the compositions up to 60% offer high protective coating than composition above 60%.

Table 1 Corrosion parameters obtained from Polarization studies for bare mild steel and mild steel substrate coated with Ag doped SnO_2 nanoparticles in 1N H_2SO_4

Composition of Ag doped SnO_2 (Ag: SnO_2)	E_{corr} (mV)	I_{corr} (µA)	R_P (Ω)	Corrosion Rate (mpy)	IE%
Blank	–457	1629	4	497	--
1:0.5 (33%)	–484	535	10	474	67
1:1(50%)	–494	280	12	85	83
1:1.5 (60%)	–524	0.02	2108	0.012	99
1:2 (66.6%)	–488	389	92.4	119	76
1:2.5 (71%)	–487	439	6.39	134	73
1:3 (75%)	–502	450	7.5	137	72
1:3.5 (77.8%)	–500	516	5.8	157	68
1:4 (80%)	–488	714	5.7	218	56

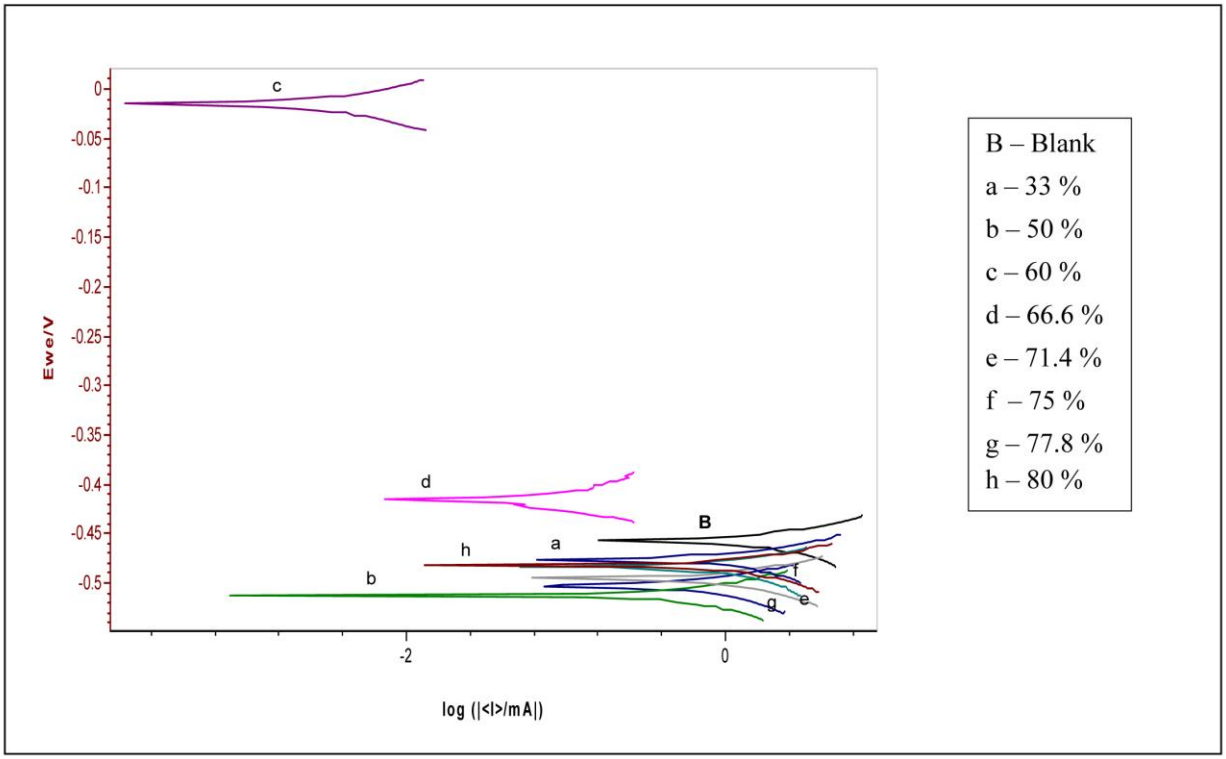


Figure 1 Tafel plots for blank (mild steel) and Ag doped SnO_2 nanoparticles coated mild steel in 1N H_2SO_4

1.2 Electrochemical impedance spectroscopy

The EIS results of present study have been presented in Table – 2. The metal surface active centres are blocked by coating which decreases C_{dl} value and increases R_{ct} value. The increase of R_{ct} could be related to the formation of a more compact film and also the more dense the film packs, the larger the diameter of the semicircle. Therefore resistance to corrosion is high. This results in higher R_{ct} value and lower C_{dl} value. The modified alloy surface affects the electrical double layer. In this case, it might have changed the orientation of the dipoles of the water molecules which causes lowering of the dielectric constant and decrease in the double layer capacitance. The increase in diameter of capacitive loop has been observed (Figures 2 and 3) with increase of tin oxide concentration up to 60% Ag doped SnO_2 nanoparticles. All compositions exhibit significant inhibition efficiency against 1 N sulphuric acid environment.

The increase in diameter of capacitive loop is directly proportional to the inhibition efficiency. The capacitive loop at higher frequency and an inductive loop at lower frequency characterize the active surface state and show two time constant value for electrical double layer. This confirms the formation of the protective barrier layer on the substrate surface.

Table 2 Electrochemical parameters obtained from Impedance studies for blank (steel) and coated Ag doped SnO_2 nanoparticles in 1 N H_2SO_4

Composition of Ag doped SnO_2 (Ag: SnO_2)	R_{ct} (Ohm cm^2)	C_{dl} (µF)	IE%
Blank	1	3.7×10^{-2}	--
1:0.5 (33%)	3	3.2×10^{-3}	91
1:1(50%)	51	3.1×10^{-6}	99.9
1:1.5 (60%)	352	2.0×10^{-9}	99.9
1:2 (66.6%)	23	9.6×10^{-5}	99.7
1:2.5 (71%)	19	1.2×10^{-3}	97
1:3 (75%)	16	1.6×10^{-3}	96
1:3.5 (77.8%)	10	3.2×10^{-3}	91
1:4 (80%)	9	4.1×10^{-3}	89

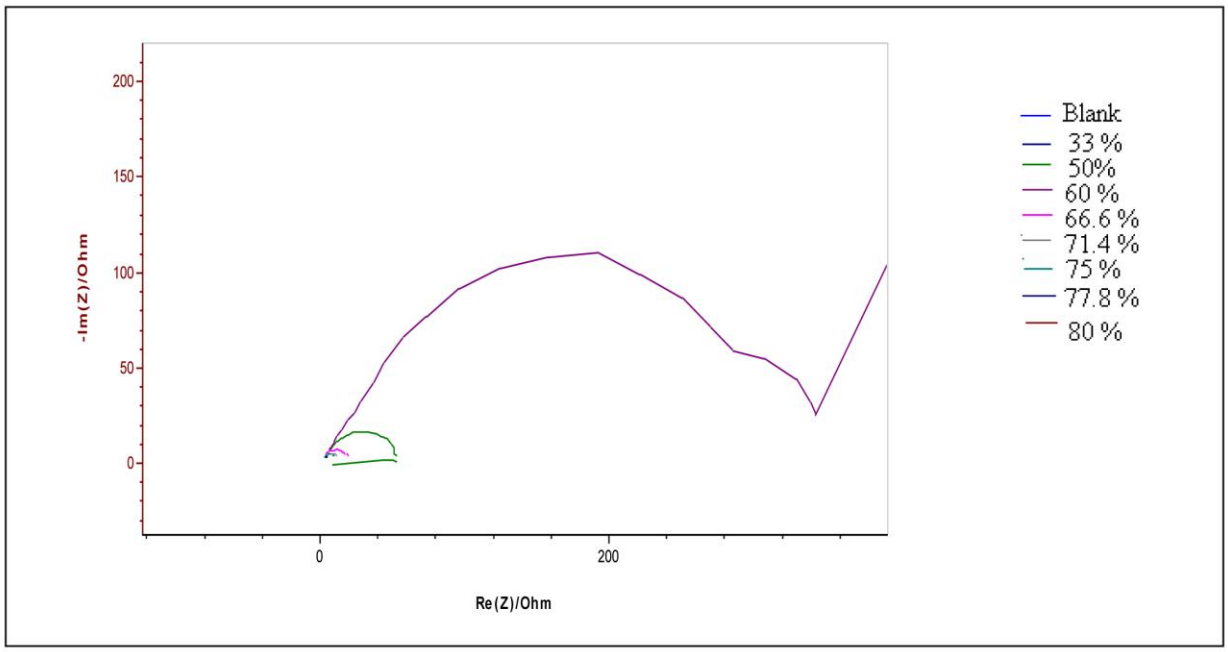


Figure 2 Nyquist plots for blank (mild steel) and Ag doped SnO_2 nanoparticles coated mild steel in 1N H_2SO_4

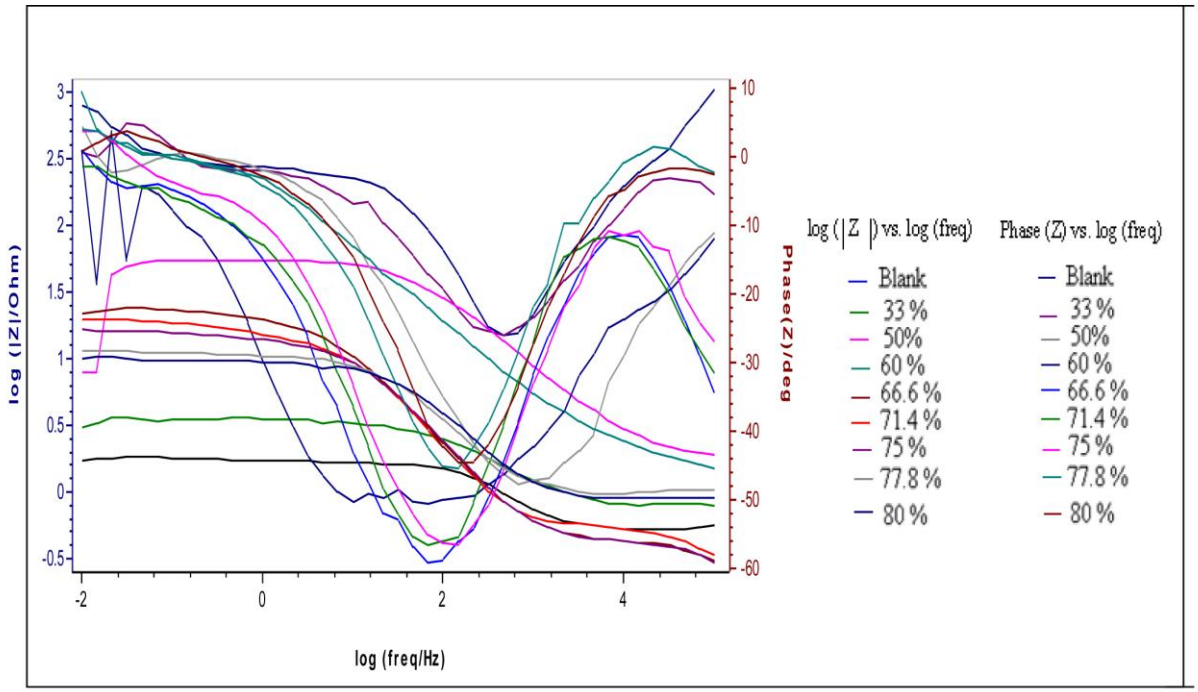
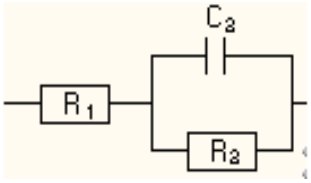
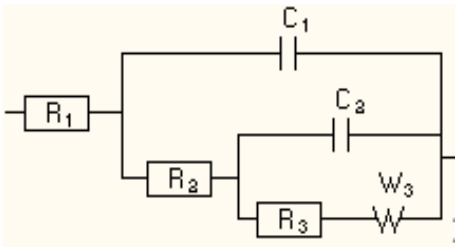


Figure 3 Bode plots for blank (mild steel) and Ag doped SnO_2 nanoparticles coated mild steel in 1N H_2SO_4

The bode plot of phase angle Vs frequency shows two time constant value or two peaks. One is at higher frequency related to the solution resistance of the system and the other at the lower frequency associated with the charge transfer resistance. So, two negative slopes were also observed due to two time constant. The former has been related to the thin film on the substrate surface due to the presence of coating on the metal surface and the later to the active metal surface. These results confirm the adsorption at the metal/solution interface leading to protective film on the substrate surface and decrease in the extent of dissolution reaction [15- 18]. The impedance spectra were analyzed by fitting to the equivalent circuit models shown in Figure 4.



(a)



(b)

Figure 4 Equivalent circuit models for (a) uncoated mild steel and (b) coated mild steel substrates in H_2SO_4

A two-time-constant model has used to describe the electrochemical impedance spectra for Ag doped SnO_2 nanoparticles coated mild steel has been presented in Fig. 4b [19, 20], which enables the determination of the adsorption parameters R_1 and C_2 (a). In Fig. 4b, R_1 represents solution resistance (R_s) between Ag doped bismuth oxide coated substrate and counter electrode and R_2 the resistance of the film layer on substrate surface. R_3 accounts for the polarization resistance at the coated substrates and W is the Warburg impedance. These results indicate that the coated mild steel exhibits significant corrosion inhibition against 1N sulphuric acid environment.

IV. CONCLUSION

The Ag doped SnO_2 nanoparticles coated mild steel samples have shown good inhibition properties for the mild steel against corrosion in 1 N sulphuric acid solution. The 60% of SnO_2 nanoparticles in Ag doped SnO_2 nanoparticles exhibited significant corrosion inhibition against 1 N sulphuric acid environment. The polarization curves reveal the a mixed-type suppression of both anodic and cathodic processes. The EIS study has indicated two time constants. They are attributed to the double layer charging and adsorption of the inhibitor.

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