Effect of Conversion Coatings and Oxalate Ion on Corrosion of Pure Zinc in 1 M NaCl Solution

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The corrosion of zinc coated with tungstate, molybdate and phosphate were investigated in the 1 M NaCl solution containing different sodium oxalate with concentrations of 1×10^{-2} - 1×10^{-5} M. The corrosion of zinc uncoated and covered with protective layer in Na_2WO_4, Na_2MoO_4 and Na_2HPO_4 were investigated in 1 M NaCl + xM $Na_2C_2O_4$ solutions by using potentiodynamic and impedance methods. The corrosion rates of zinc are especially low in the NaCl solution containing low oxalate concentrations.

Key Words: Zinc, Corrosion, Surface coating.

INTRODUCTION

Zinc metal used in alloy formation and cathodic protection of metals, but its corrosion resistance is low. Its corrosion resistance can be improve with surface pretreatments, coatings and additions inhibitors in the corrosive media[1-8].

Conversion coatings can provide improving adhesion to painting systems. Although chromate conversion coatings is the best, but it has toxic effect. For this aim, the surface coatings on the different metal and alloys with molybdate, tungstate, phosphate and rare earth metal cations have been suggested as alternatives to chromate coatings[1-8].

Some anions can form insoluble compounds with zinc cation. In this paper conversion coatings prepared with molybdate, tungstate and phosphate on pure zinc metal with immersing in the conversion coatings solutions.

Pre-treatment of the electrode surface was obtained as stable surface layer on the electrode[9-12]. Pre-treatment of zinc electrode surface with HCl solution was improved surface coatings quality formed on the zinc metal surface. Therefore, before all experiments, electrode surface was abraded 20 sec in 0.15 M HCl solution and then washed with double distilled water.

EXPERIMENTAL

All the chemicals used were of analytical Merck grade. Deionized water was used in the preparation of the solutions and use in all experimants.

Open circuit potentials, potential-time curves, recorded starting from -1 V up to 1 V during 20 min. Polarization data, current-potential curves, for chloride solution were obtained at scan rates of 1 mV/s. AC impedance curves were performed by constituted CH Instruments 660B potentiostat, electro-chemical work station of computer programme, BAS disc electrode, poly science model 9106 thermostat system using a saturated Ag/AgCl as reference and platinium wire as counter electrode. The impedance measurements were performed at the open circuit potential of working electrode with voltage perturbation amplitude of 5 mV in a frequency range between 100 kHz and 0.1 Hz.

Preparation of sample: Working electrode was prepared a cylinder high pure zinc rod, Aldrich 99.999 % purity, 2 mm diameter of 0.0314 cm^2 geometric area, was fixed in the teflon tube with adhesive. Reference electrode was separated from the main body *via* a bridge to avoid Cl^- ion contamination. The reference electrode was adjusted at a distence of 0.2 mm from the working electrode surface for balance the ohmic drop.

Procedure: The working electrode was polished with emery papers with 1200 grit and etched in 0.15 M HCl solution for 20 sec before the experiments. The frequency range studied was 1×10^5-1×10^{-1} Hz in the potential range -0.3 V to +0.3 V. All experiments were carried out at room temprature. The inhibition efficiency of zinc was calculated from the following equation:

$$\eta(\%) = \frac{i_{corr} - i'_{corr}}{i_{corr}} \times 100$$

where i_{corr} and i'_{corr} are showed the corrosion current densities the uninhibited and inhibited solutions, respectively and R_p polarization resistance respectively. Corrosion retes, polari-zation resistances and other corrosion characteristics of coated and uncoated pure zinc metal were carried out in 1 M NaCl +

TABLE-1
CORROSION CHARACTERISTICS UNCOATED ZINC ELECTRODE IN 1 M NaCl + xM Na$_2$C$_2$O$_4$ SOLUTIONS AT 25 ºC

Solutions	E_{corr} (V)	$-b_c$ (mV dec^{-1})	b_a (mV/dec^{-1})	i_{cor} (μA/cm^2)	R (Ωcm^2)	η (%)
1 M NaCl	-1.213	169	116	181.9	290	--
+10^{-5} M Na$_2$C$_2$O$_4$	-1.23	87.7	103	18.4	1050	90
+10^{-4} M Na$_2$C$_2$O$_4$	-1.178	78.8	150	21.4	1140	88
+10^{-3} M Na$_2$C$_2$O$_4$	-1.18	77	208	29.9	850	83.5
+10^{-2} M Na$_2$C$_2$O$_4$	-1.19	86	166	45.2	530	75

xM Na$_2$C$_2$O$_4$ solutions. All chemicals used are merck grade. Corrosive media were prepared with double distilled water. All measurements were carried out in aerated solution at 25 ºC.

Zinc electrode were converted by immersion zinc electrode 10 min in 0.1 M Na$_2$WO$_4$, 0.1 M Na$_2$MoO$_4$ or 0.1 M Na$_2$HPO$_4$ solutions respectively. Electrode was immersed for 20 sec in 0.15 M HCl solution for obtaining better electrode surface before electrode immersion in the conversion coating solutions and washed with double distilled water at the each step. Corrosion characteristics obtained from these curves were given in Table-1.

RESULTS AND DISCUSSION

The potential-time, current-potential and Nyquist curves obtained by uncoated zinc electrod in 1 M NaCl + xM Na$_2$C$_2$O$_4$ solutions are given in Fig. 1. Figs. 2-4 show the potential-time, current-potential and Nyquist curves obtained in 1M NaCl + xM Na$_2$C$_2$O$_4$ solutions by pretreated zinc electrode with molybdate, tungstate and phosphate, respectively.
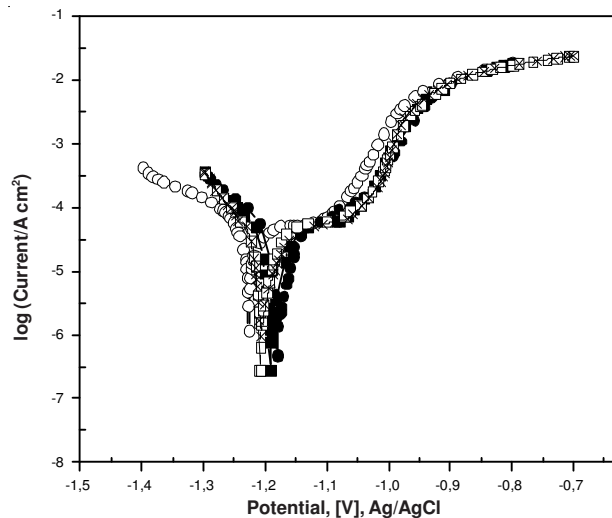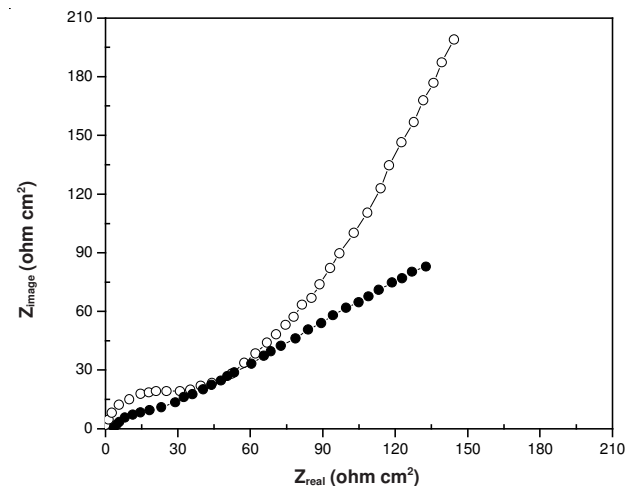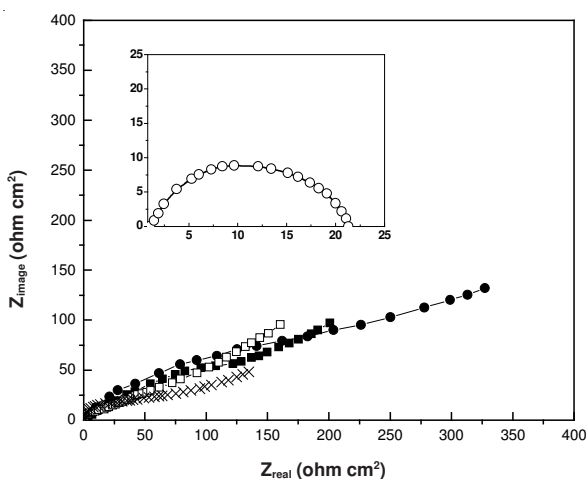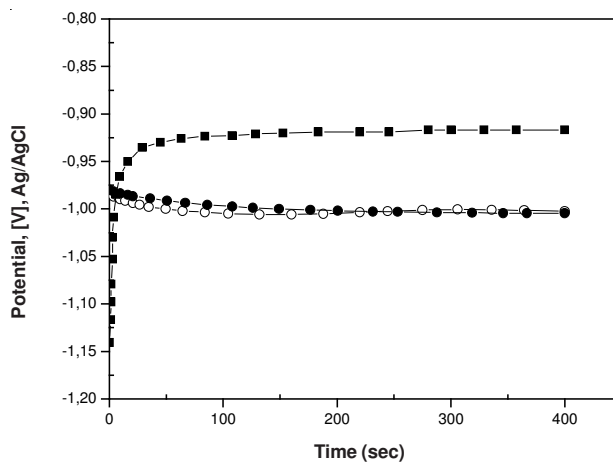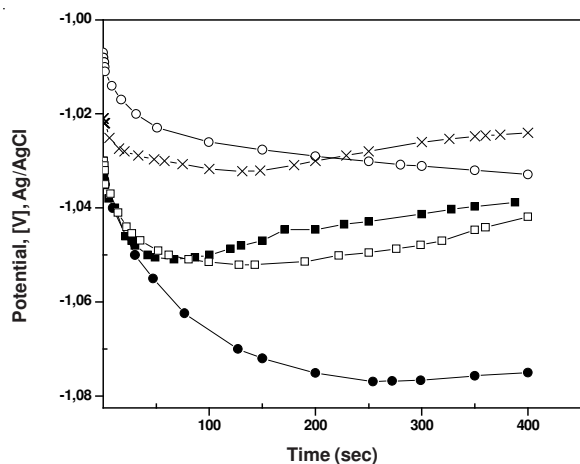

Fig. 1. Potential-time, Nyquist and current-potential curves obtained by zinc electrode in 1 M NaCl + xM oxalate solutions [x: 0.0 (○), 10^{-5} M (×),10^{-4} M (□),10^{-3} M (■),10^{-2} M (●)]
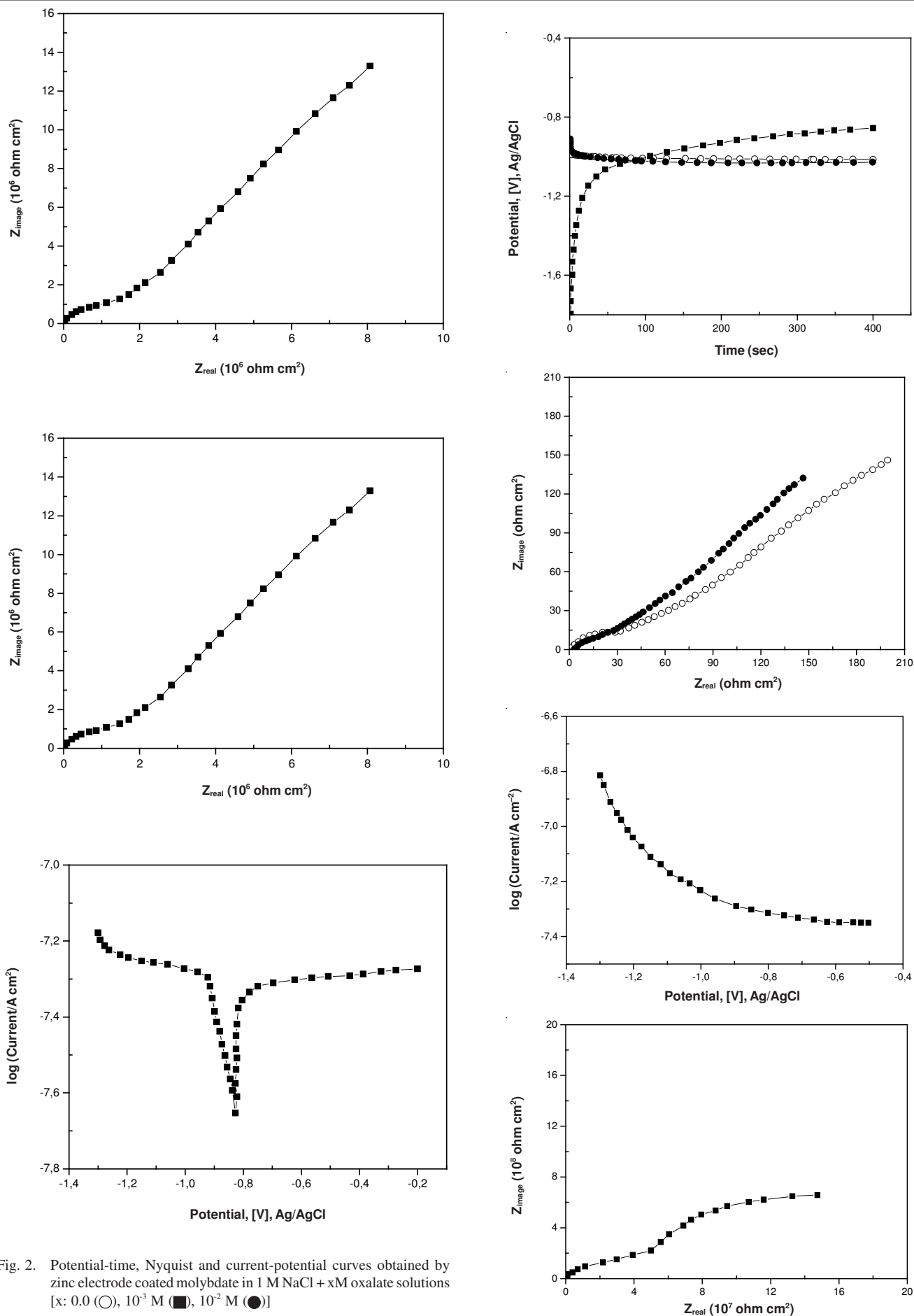
Fig. 2. Potential-time, Nyquist and current-potential curves obtained by zinc electrode coated molybdate in 1 M NaCl + xM oxalate solutions [x: 0.0 (○), 10^{-3} M (■), 10^{-2} M (●)]
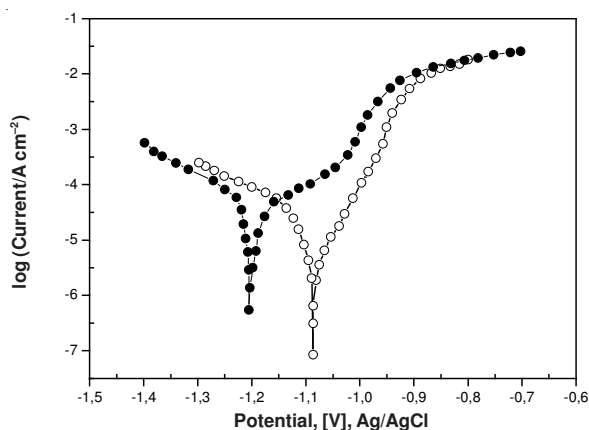
Fig. 3. Potential-time, Nyquist and current-potential curves obtained by zinc electrode coated tungstate in 1 M NaCl + xM oxalate solutions [x: 0.0 (○), 10^{-3} M (■), 10^{-2} M (●)]
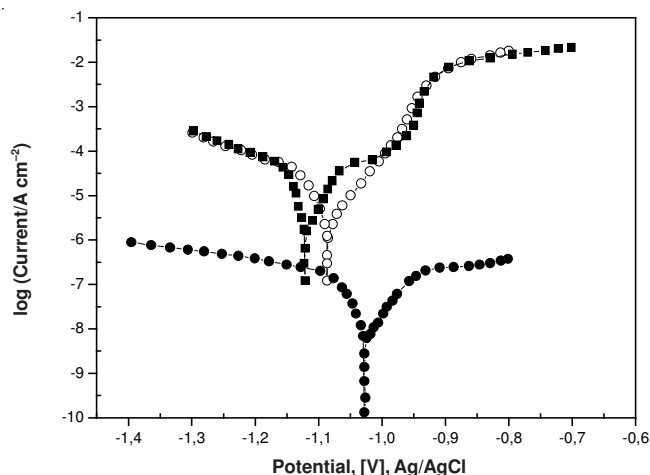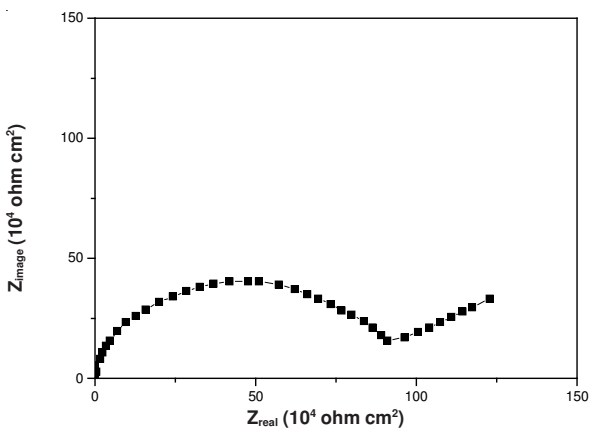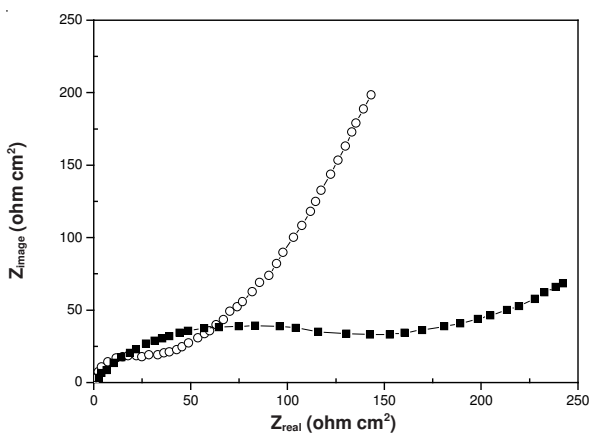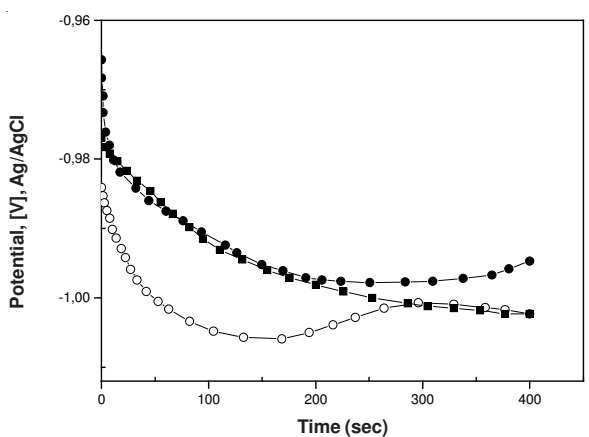

Fig. 4. Potential-time, Nyquist and current- potential curves obtained by zinc electrode coated phosphate in 1M NaCl + xM Oxalate solutions [x:0.0 (○),10^{-3} M (■),10^{-2} M (●)]

Electrode potentials were decreased with time in 1 M NaCl and 1 M NaCl + 10^{-2}M $Na_2C_2O_4$ solutions by adsorption of Cl^- ion on the metal surface shown in Fig. 1. But, corrosion potential was increased in 1 M NaCl + 10^{-3} M $Na_2C_2O_4$ solution. Most positive potential was measured in 1 M NaCl + 10^{-3} M $Na_2C_2O_4$ solution. Inhibition effect was also increased with decreasing oxalate concentration in 1 M NaCl solution shown in Table-1. Corrosion potentials in Tables 1 and 2 are interpreted after 20 min immersion in studied solution values. The highst inhibition was observed in 1 M NaCl solution containing approximately 10^{-4} M sodium oxalate. Zn^{2+} cation formed insoluble ZnC_2O_4 compound with oxlalate anion[13-15].

$$ZnC_2O_{4(k)} + C_2O_{4\ (aq)}^{2-} \rightarrow Zn(C_2O_4)_{2(aq)}^{2-}$$
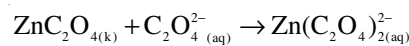
This product inhibited corrosion of zinc in 1 M NaCl solution. If the solution contains enough oxalate ion, zinc oxalate were dissolved as complex ion according to the equation above. For this reason, this protective zinc oxalate layer at the higher oxalate concentration could be soluble and higher oxalate ion could be less protective for pure zinc metal corrosion. Nyguist diagrams of uncoated zinc were shown that the corrosion of pure zinc metal is controlled by diffusion in the 1 M NaCl solution containing oxalate ion (Fig. 1).

These graphs show that the equivalent electrical circuit of zinc contains warburg impedance. Limited current zones at the anodic part of the current-potential curves were also showed this effect. If the zinc metal coated with tungstate, molybdate and phosphate with immersion of 10 min in 0.1 M Na_2MoO_4, 0.1 M Na_2WO_4 and 0.1 M Na_2HPO_4 solutions respectively, corrosion of the zinc was inhibited fairly high (Table-2). This is agreed with the changing open circuit potential-time. Open circuit potentials of zinc coated with molybdate and tungstate were slower decreased with time then uncoated metal in 1 M NaCl solution (Fig. 2).

But, inhibition effect were decreased with reduced to the 10^{-3} M, extremely high inhibition effect was measured for zinc metal with pretreated molybdate and tungstate. studied corrosive medium. If the oxalate concentration in 1 M NaCl solution was increasing oxalate ion concentration in the current-potential curves obtained in this solution was also shown

TABLE-2
CORROSION CHARACTERISTICS OF COATED ZINC WAS IMMERSED 0.1M MoO_4^{-2}, WO_4^{-2} AND
HPO_4^{-2} IONS WITH 10 MIN IN 1 M NaCl + xM $Na_2C_2O_4$ (x: 0, 10^{-2}M, 10^{-3} M) SOLUTIONS AT 25 °C

Solutions	$-E_{corr}$ (V)	$-b_c$ (mV)	b_a (mV)	i_{cor} (μAcm^{-2})	R (Ωcm^2)	η (%)
1 M NaCl	1.23	150	662	166	310	--
MoO_4^{-2}	1.09	211	26	4.8	2600	97.0
WO_4^{-2}	1.09	174	37	4.1	3260	97.4
HPO_4^{-2}	1.14	120	180	17.5	1670	89.5
10^{-2} M $Na_2C_2O_4$	1.19	86	166	45.2	530	75.0
MoO_4^{-2}	1.22	148	266	77	510	52.3
WO_4^{-2}	1.02	223	111	8	4000	95.0
HPO_4^{-2}	1.03	410	198	0.006	> 7000	100
10^{-3} M $Na_2C_2O_4$	1.18	77	208	29.9	850	83.5
MoO_4^{-2}	0.83	-	-	< 0.006	> 7000	100
WO_4^{-2}	0.53	3642	-	< 0.006	> 7000	100
HPO_4^{-2}	1.03	144	129	64.2	1630	61.0

passive zone (Fig. 2). The equivalent electric circuits for Nyquist diagrams is given in Fig. 5 [16]. In this circuit diagram, R_s solution resistance, R_{ct} polarization resistance, C_{dl} double layer capacitance and W represent Warburg impedance.
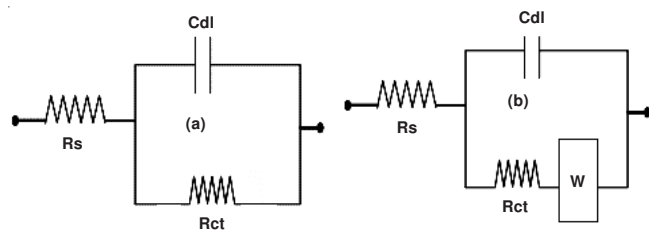

Fig. 5.   Equivalent electric circuit diagrammes of uncoated (a) and coated (b) zinc electrode in the studied solutions

Conclusion

Oxalate was enough protected against corrosion pure uncoated zinc electrode in 1 M NaCl solution. Inhibition effect of oxalate are dependent to the oxalate concentration. Maximum inhibition was measured at approximately 10^{-4} M oxalate concentration. Oxalate also increased the inhibition effect of pure zinc electrode coated with molybdate, tungstate and phosphate solution. The best oxalate concentration for inhibition coated pure zinc electrode is 10^{-3} M. Corrosion rates in some conditions are completely zero and corrosion resistances are high.

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