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Application of Pluronic P123 in Suspension Form as a Corrosion Inhibitor for Zinc in Alkaline Battery Electrolyte

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Abstract- Pluronic P123, a type of Poloxamers materials, was examined as an inhibitor for decreasing zinc corrosion in alkaline media (4.0 M NaOH). This material was used in the form of the particles dispersed in electrolyte (suspension form). Its effect was examined by electrochemical methods potentiodynamic polarization (Tafel) and electrochemical impedance spectroscopy (EIS). Scanning electron microscopy (*SEM*) was used to analysis the electrode surface in presence and abcense of the inhibitor. The obtained results indicate that P-123 inhibits zinc corrosion in 4.0 M NaOH electrolyte and zinc corrosion decreases with increasing the value of P-123 particles. Moreover, the results of potentiodynamic polarization reveal that the inhibitor affects both the anodic and cathodic branch, so it is mix type. The obtained inhibition efficiency from potentiodynamic polarization and EIS showed a reasonable agreement. In addition, for battery application, it was found that P-123 increases Zn/CuO battery performance.

Keywords- Zinc, P123, Inhibitor, Alkaline battery, Corrosion

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1. INTRODUCTION

Nowadays, storage and production of energy for using in portable devices is one of the most interested research subjects in all over the world [1]. Some elements, such as Li, Ni, Zn, C, Mn, Cd and Na have received great application as electrode materials in the batteries [2,3]. While from the past zinc is widely used as a high capacity anodic material for primary and secondary alkaline batteries [4] due to its high theoretical energy density. Zinc theoretical energy density is about three times higher than the lithium ion systems [5], moreover it is low cost and non-toxicity [4]. There are some important common zinc based battery systems that is available in the market, Zn–MnO2, Zn–AgO, and Zn–air [6]. In addition the zinc - air technology received great attention as a promising energy production system using in portable devices and future vehicles. Alkaline media are common electrolytes used in this kind of batteries [1,7]. It is shown that the performance of zinc anode is higher in very concentrated alkaline solution. While the problem is that Zinc anode in an alkaline battery tends to corrode during storage of the battery. Actually the anode corrosion leads to various undesirable phenomena, like self-discharge, swelling of the case and electrolyte losses [8]. The research regarding the inhibition of zinc corrosion in hydroxide media attracted great interest in relation to the fabrication of primary and secondary batteries [4,9]. To inhibit corrosion and improve the utilization of zinc in an alkaline condition, it is possible to use electrolyte additives [9-11]. The effect of additions of several concentrations of inorganic additives V_2O_5, ZnO, PbO and $(NH_4)_2CS$ on the passivation and self-corrosion of the zinc electrode in KOH solutions is examined over a range of temperatures (from 30 to 60 °C) [11]. Beside, some researchers studied the effects of surfactants as electrolyte additives on the anodic passivation of zinc in alkaline solution. For example it is reported that sodium dodecyl benzene sulfonate (SDBS) as a surfactant additive in alkaline media can efficiently decreases the surface passivation and greatly improve the performance of zinc anode [4]. Also, application of organic materials, as zinc corrosion inhibitor in alkaline media is reported in several studies [14]. The zinc corrosion inhibition capability in the strong alkaline solution with low concentrations of the modified dicarboxylic acid modified poly(ethylene glycol) (PEG) and potassium hydroxide and poly(ethylene glycol) bis(carboxymethyl) ether is improved for a short duration [12,13].

Our aim in the present study is to examine the corrosion inhibition capability of the suspension of P123 for a zinc electrode in 4M NaOH. P123 is available and comparatively low cost material which causes its application justifiable. P123 nominal chemical formula is HO $(CH_2CH_2O)_{20}(CH_2CH(CH_3)O)_{70}(CH2CH_2O)_{20}H$ which is rarely soluble with water. In this work a low price, acceptable efficiency inhibitor for zinc corrosion in alkaline batteries is proposed which doesn't reduce battery performance. Hence electrochemical polarization test and electrochemical impedance spectroscopy were used for evaluation the efficiency of P123 particles as an inhibitor for zinc in alkaline media. In the last for application in battery, the effect of P123 inhibitor on the discharge performances of the battery, Zn /CuO is examined.

2. EXPERIMANTAL

2.1. Materials and chemicals

The working electrodes with surface area of 0.07cm^2 were prepared from commercial zinc bar. The NaOH and P123 were purchased from Merck and Sigma-Aldrich reagents, respectively. For electrochemical measurements, zinc specimen was sealed with epoxy resin with an exposed area equal 0.07 cm^2. The surface preparation was performed by different degree of emery sheets (from 1000 to 5000 grade). After that the surface of specimens was washed by distilled water.

For preparing the P123 suspension in 4 M NaOH solution, at first an aqueous solution of P123 was prepared. For making this solution 0.075 g of P123 was dissolved in 10 ml deionized water. After that variety volumes 100, 200, 400, 600 and 800 µl of this solution was added into 8 ml NaOH 5M. Adding the P123 solution into the alkaline solution causes P123 converts in the form of suspension in the electrolyte. Finally the 4 M alkaline solution was achieved by rising volume of the electrolyte to 10 ml.

2.2. Testing methods

For EIS and potentiodynamic polarization, a standard electrochemical cell with three electrodes of a Zn, a Platinum spring and a standard Ag/AgCl electrode as working, counter and references electrode was used. The electrochemical tests were performed by the potentiostat/galvanostat model 273 A EG&G and SI (HF frequency response analyzer). The EIS measurements were done at open-circuit potential with amplitude of 10 mV AC potential in the frequency range of 100kHz-100mHz.The potentiodynamic current-potential graphs were logged by sweeping the electrode potential automatically from -0.250 to 0.250 V versus OCP with scanning rate of 1 mV.

2.2.1. Battery performance measurement

The effect of P123 additive on the discharge performances of the battery in the terms of voltage was measured on a Zn/CuO battery. The detailed characterization and construction of the cell building has been reported in our previous work [14]. The effects of P123 additive on the discharge capacity were studied by the adding of 0.006g (600 ppm) of the inhibitor into the electrolyte.

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic polarization

Fig. 1 shows the potentiodynamic polarization curves of Zn electrode in a 4.0 mol L^{-1} NaOH solution in the absence and presence of various values of P123 at scan rate 1.0 mV s^{-1}

and 303 K. Polarization measurements provide important information about the kinetics of cathodic and anodic reactions. The Polarization parameters are given in Table.1; such as corrosion current density (i_{corr}), corrosion potential (E_{corr}), polarization resistance (R_p) cathodic and anodic slopes (β_a, β_c).

Table 1. Polarization parameters and the corresponding inhibition efficiencies for pure Zn in 4.0 mol L^{-1} NaOH containing different values of P123

value (ppm)	E_{corr} (mV)	I_{corr} (μAcm^{-2})	βc ($mVdecade^{-1}$)	βa ($mVdecade^{-1}$)	Rp (kΩ)	η (%)
0	-1539.967	52.00	155.357	50.947	422.66	-
75	-1532.500	39.14	153.082	50.472	559.70	26.65
150	-1527.411	34.86	124.513	46.543	589.50	32.96
300	-1530.088	30.11	174.199	43.128	885.52	42.09
450	-1517.055	23.50	160.944	36.098	959.40	54.80
600	-1524.600	23.32	149.657	41.285	922.00	55.15

From table 1 and polarization curves in Fig.1, it is clear that the addition of P123 surfactant decreases the corrosion rate and the corrosion current density of zinc in alkaline electrolyte. Also, presence of P123 in the solution affected both anodic and cathodic branches of the potentiodynamic polarization curves. Therefore, P123 behaved as a mixed inhibitor. The alteration of the corrosion potential toward positive direction and small effect on the cathodic lines emphases that inhibitor mainly affects anodic reaction:

$$Zn + 4OH^- \longrightarrow Zn(OH)_4^{2-} + 2e$$

The corrosion inhibition efficiency can be determined using:

$$\eta(\%) = 100(\frac{i^*_{corr} - i_{corr}}{i^*_{corr}}) \quad (1)$$

Where i^*_{corr} and i_{corr} represent uninhibited and inhibited current density values, respectively, that was attained from potentiodynamic polarization curves. The η values show that the inhibition is more pronounced with increasing inhibitor values. Moreover, the observed values of βc and βa don't altered significantly with increase of P123 value; it means that the presence of P123 in alkaline solution (4.0 M NaOH) does not change the mechanism process. Hence, basically P123 acts as adsorptive inhibitor by blocking the active sites on the metal surface.

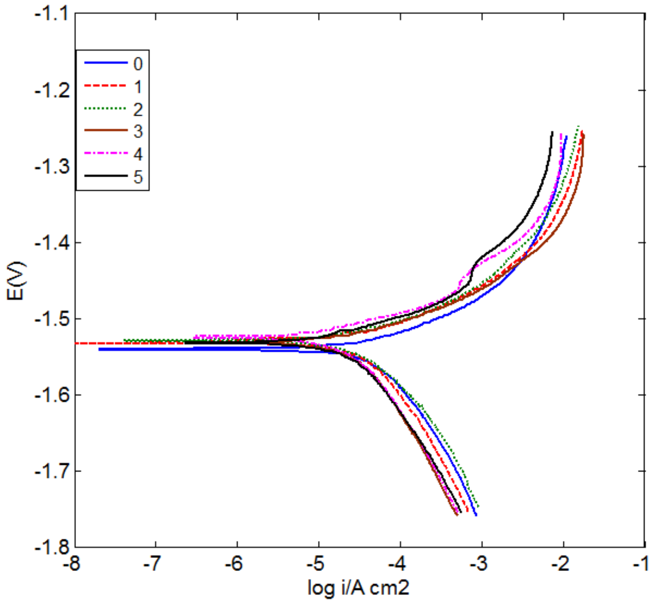

Fig. 1. The potentiodynamic polarization curves of Zn electrode in a 4.0 mol L^{-1} NaOH solution presence variety values of P123 0: blank, 1:75, 2:150, 3:300, and 4:450 and 5:600 ppm P123

3.2. Electrochemical impedance spectroscopy

The Nyquist plots of EIS for Zn in 4.0 molL^{-1} NaOH in the absence and presence of various values of P123 are shown in Fig. 2. It is seen from Fig. 2 that the impedance response of Zn is altered considerably with increasing the value of P123.

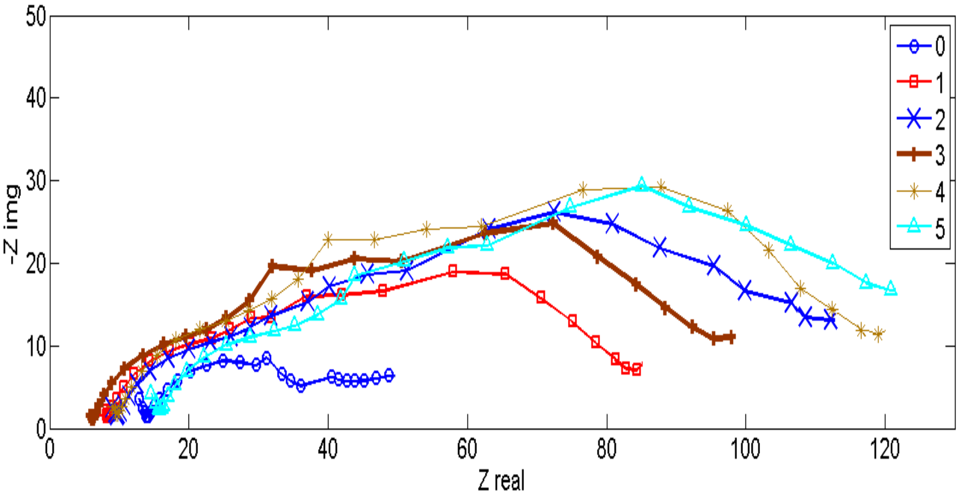

Fig. 2. Nyquist plots of EIS for zinc in 4 M NaOH in presence variety values of P123 0: blank, 1:75, 2:150, 3:300, and 4:450, 5:600 ppm P123

Table 2. EIS parameters and the corresponding inhibition efficiency values for pure Zn in 4.0 mol L^{-1} NaOH containing different values of P123

value (ppm)	R_s ($\Omega.cm^2$)	R_{ct} ($\Omega.cm^2$)	n	CPE (μFcm^{-2})	R_f ($\Omega.cm^2$)	n	C_f (μFcm^{-2})	η_{EIS} (%)
0	0.92	1.75	0.68	19×10^{-6}	2.80	0.30	12×10^{-4}	-
75	0.54	1.9236	0.72	10×10^{-6}	3.75	0.68	92×10^{-6}	25.23
150	0.6	2.2449	0.66	16×10^{-6}	5.52	0.64	11×10^{-5}	49.30
300	0.40	1.75	0.76	6.7×10^{-6}	5.19	0.64	84×10^{-6}	46
450	0.59	2.31	0.69	10×10^{-6}	5.96	0.66	61×10^{-6}	53.00
600	1.01	1.89	0.69	8.5×10^{-6}	6.30	0.61	98×10^{-6}	55.55

It can be seen from Table 2 that generally, the R_f increased as the values of inhibitors increased. This approves an increase in the surface coverage by P123 molecules on zinc surface, which results in creation of a surface film to delay corrosion procedure. Moreover, the values of Cdl are diminished with the increasing of P123 value. This is associated to a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer which confirms the adsorption of P123 at the metal/solution interface.

The percentage inhibition efficiency ($\eta_{EIS}(\%)$) of P123 can be obtained using:

$$\eta_{EIS}(\%) = 100(\frac{R_{ct}^{*}-R_{ct}}{R_{ct}^{*}}) \quad (2)$$

Where R_{ct}^{*} and R_{ct} represent the charge transfer resistance, before and after addition of the inhibitor to the corrosion media, respectively. Based on the calculations it was seen that the inhibition efficiencies were improved with increasing the value of the inhibitor. The η_{EIS} values are in close correlation with η extracted from the polarization analysis.

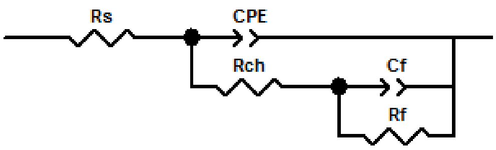

Fig. 3. Equivalent circuit applied for fitting of the impedance spectra

Based on the shape of Nyquist plots, an equivalent circuit was proposed for analysis the impedance data which is shown in Fig. 3. In the circuit the R_s, R_{ct}, R_f and CPE are the solution, charge transfer resistance, the film resistance of the corrosion products, a constant phase element of double layer capacitance (Cdl), respectively. Also, C_f represents passive layer and surface film capacity.

3.3. SEM analysis

Fig. 4. shows the SEM images of the zinc electrode surface with and without the inhibitor at two different magnifications. Fig. 4. A&B is related to surface of the zinc electrode after a Tafel analysis in presence of P123 at 5000 and 2000 magnifications. It is clear from this image that P123 has produced a porous film layer on the surface of the electrode which strongly confirms the absorbance and inhibitory effect of P123. This porosity provides contact between the electrolyte and the electrode surface. Also, The SEM images of the zinc electrode surface after a Tafel analysis in absence of the P123 are presented in Fig. 4. C&D at 5000 and 2000 magnifications. These images reveal that the surface of the electrode in the absence of the inhibitor is clearly different from Fig. 4. A &B in terms of surface morphology and shape.

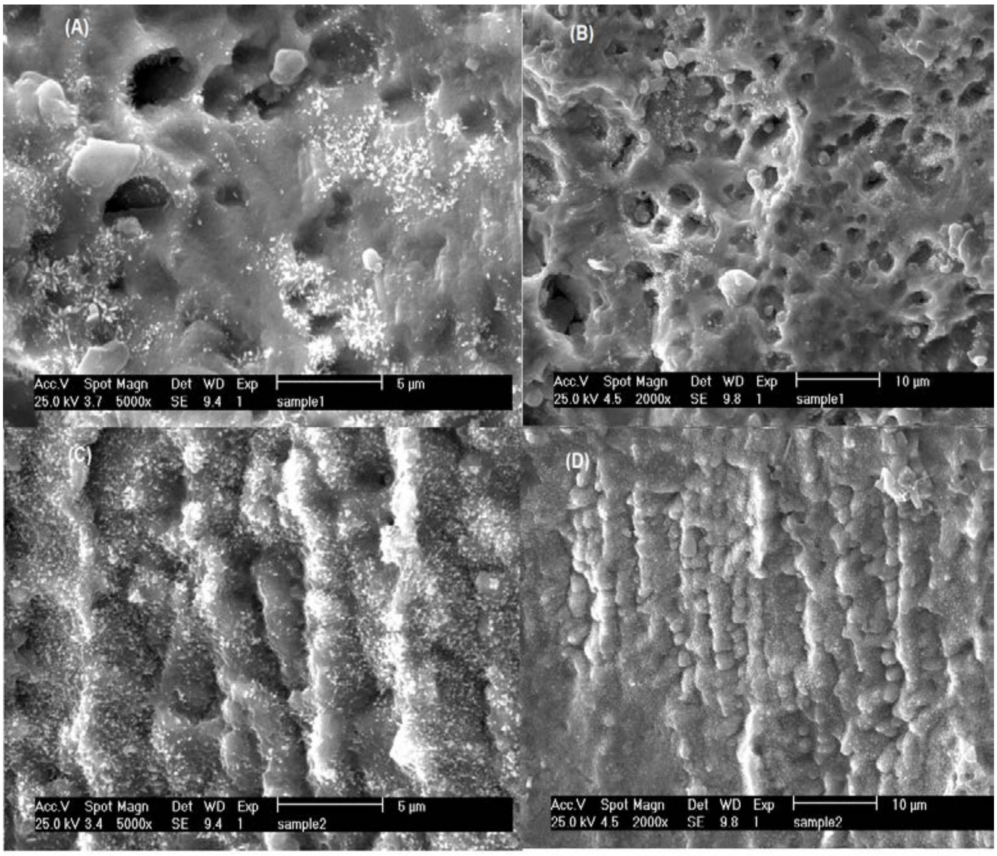

Fig. 4. The SEM images of the zinc electrode surfaces with (A and B) and without (C and D) the inhibitor

3.4. Effect of P123 t on battery performance

The discharge cycles for Zn/CuO battery [14] with and without P123 at 12 mA/cm^2 are presented in Fig. 5. It is clear from Fig. 4 that the presence of P123 improves the discharge voltage of the battery.

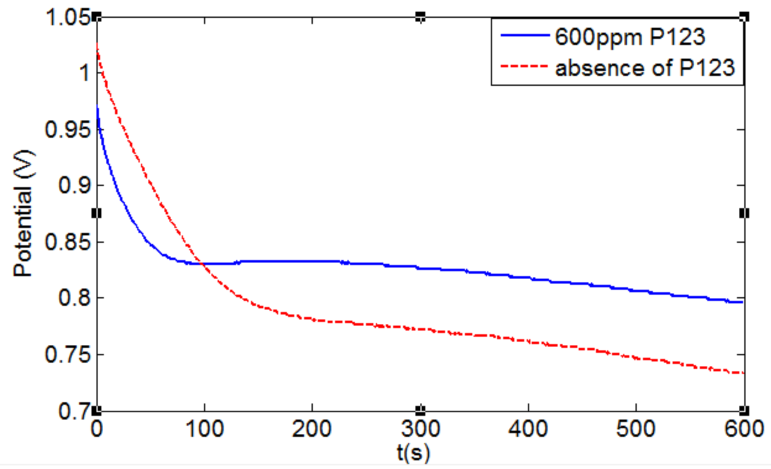

Fig. 5. the discharge cycles for Zn/CuO battery with and without P123

4. CONCLUSION

The adsorption and inhibition effects of P123 suspension on corrosion behavior of zinc in 4 M NaOH solution were studied using electrochemical techniques. Inhibition efficiency increases with increasing inhibitor value. A good correlation was observed between the potentiodynamic studies and electrochemical impedance spectroscopy. Moreover, EIS plots indicate that the charge transfer resistance increase with increasing value of the inhibitor. Also, the results shows that the performance of Zn/CuO battery as an example of zinc based battery was not damaged in presence of P123 into the electrolyte.

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