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Electrochemical and surface studies of zinc in alkaline solutions containing organic corrosion inhibitors

Y. Ein-Eli*, M. Auinat, D. Starosvetsky

Department of Materials Engineering, Technion-Israel Institute of Technology, Technion City, Haifa 32000, Israel

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Abstract

The electrochemical behavior of zinc in strong alkaline solutions containing 8.5 M of potassium hydroxide (KOH) and polymeric organic inhibitors was evaluated. The concentrations of the organic inhibitors studies were in the range of 400–4000 ppm and included polyethylene glycol (PEG), with a molecular weight of 600, and polyoxyethylen alkyl phosphate ester acid form (GAFAC RA600). The electrochemical studies included anodic, cathodic, and linear polarization along with potentiostatic studies. It was found that the inhibition properties of PEG, in the strong alkaline solution, are by far much more efficient than the inhibition capability of GAFAC RA600. Surface analysis obtained with the use of high resolution scanning electron microscopy (HRSEM) revealed different morphology characteristic developed at the zinc surface in the presence of the two inhibitors. A methodology employing electrochemical tests is proposed to quickly and conveniently evaluate inhibitors for Zn in alkaline media.

Keywords: Electrochemical studies; Zinc; Corrosion inhibitors; Zinc surface; Alkaline

1. Introduction

Zinc metal is a favorable anode in primary batteries because of its high capacity (0.82 Ah/g), high discharge efficiency and high safety features associated with its manufacturing processes and use.

Zinc metal is alloyed with 3–4 elements at low concentrations (20–1000 ppm) during the thermal production process of the powder. This zinc alloyed powder is used as the anode of choice in alkaline (Zn/MnO_2) and zinc–air cells. The elements added to the zinc metal are commonly Al (20–150 ppm), Bi (50–200 ppm), Ca (100–500 ppm) and In (200–1000 ppm) [1–4]. While all the elements are added in order to improve the electrochemical behavior of the discharged cell (for example, shorts prevention, decrease in the ohmic cell resistance and decrease in the self-discharge rate while the cell is being partially discharged), and to suppress the anodic reaction of zinc, still there is a need to add another component to the electrolyte which is capable of reducing the zinc corrosion in the alkaline media. Overcoming the corrosion of the zinc anode in the alkaline media without the use of mercury, which is considered to be a highly efficient zinc corrosion inhibitor, is a crucial issue. Environmental regulations are forcing the manufacturers and the scientific community to seek for corrosion inhibitors that are environmentally benign and can serve as a good or even better alternative to mercury. The attention of the scientific community was focused in the recent years in developing and studying organic polymeric inhibitors that are capable of replacing mercury and mercury salts without any degradation in the zinc anode performance or the overall cell characteristics [5–17].

Zinc corrosion in alkaline media is controlled by the cathodic reaction of water reduction. One of the reduction products of this process is hydrogen gas and therefore, the ability to control the parasitic reaction of water reduction is dependent on the ability to reduce and minimize the cathodic reaction, resulting in hydrogen release.

Kordesh and co-workers [12] have conducted a thorough investigation on the ability of polyethylene glycols (PEG's, molecular structure is presented in Scheme 1) to inhibit the zinc corrosion in the alkaline media. He reported that the most efficient inhibitor was detected to be PEG 600, with a carbon chain length of $n = 9$–11. Duracell Inc. [7,10] and others [6] have issued several patents describing the ability of polyoxyethylen alkyl phosphate ester acid form (GAFAC RA600, its molecular structure is also presented in

* Corresponding author. Tel.: +972-4-8294588; fax: +972-4-8321978.
E-mail address: eineli@tx.technion.ac.il (Y. Ein-Eli).

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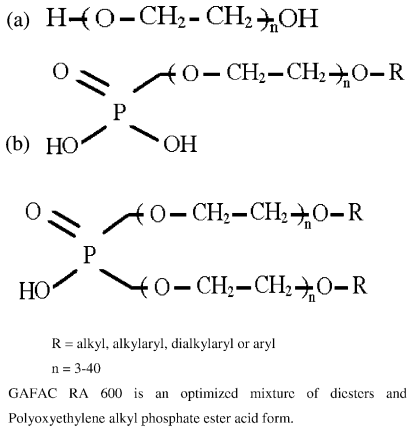


Scheme 1. Molecular structure of (a) PEG and (b) GAFAC.

Scheme 1) to inhibit zinc corrosion in alkaline solution. Previous work conducted by Dobryszycky and Biallozor [15] compared the electrochemical behavior of PEG's and other inhibitors, such as FORFAC (ethoxylated-polyfluoro-alchol) and Brij30 (alkyl-polyehylene oxide, $n = 4$). However, the surface morphology and detailed electrochemical insight into the inhibition process and the time effect on zinc corrosion in alkaline electrolytes containing PEG or GAFAC RA 600 were never explored, compared and reported. Moreover, until now, no comparative electrochemical studies on the inhibition properties of zinc in alkaline electrolytes containing PEG 600 and GAFAC RA600 were conducted. Therefore, we initially have focused our studies on the electrochemical characteristic and morphologic evaluation of zinc in alkaline electrolytes containing these two important organic polymers as zinc corrosion inhibitors. In order to inspect the influence of the organic inhibitors on the zinc metal we used in all of our studies a pure zinc metal as the working electrodes and not alloyed zinc powder (''battery grade'' zinc). Thus, the results presented in this work are ascribed only to the inhibition capabilities of the organic polymer inhibitors. The behavior of zinc in alkaline electrolytes containing the organic inhibitors was conducted with inhibitors concentrations that did not exceed 0.4%, since above this concentration the overall alkaline cell characteristic (especially working potentials and cell capacity) may be negatively influenced.

2. Experimental

Pure metal zinc (99.99%, Umicore) was served in the electrochemical test as the working electrode. Platinum was served as the counter electrode while standard calomel electrode (SCE) was used as the reference electrode. The electrochemical studies were conducted with the use of potentiostat/galvanostat PAR 273A. All potentials are quoted versus SCE. Linear polarization measurements were carried out with a potential perturbation of ±20 mV around the open circuit potential (OCP). The alkaline electrolyte was prepared by dissolving 8.5 M of KOH (Aldrich, 99.99%) and 25 g/l of ZnO (Aldrich, 99.99%) in DI water (with a measured conductivity less than 2 μS/cm). Polyetylene glycol (PEG, Aldrich) with an average molecular weight of 600 and polyoxyethylen alkyl phosphate ester acid form (GAFAC RA600, Rhône-Poulenc, France) were added in concentrations ranging between 400–4000 ppm relative to the alkaline solution. All alkaline electrolytes were prepared by the addition of the desired amount of the organic inhibitor from a dilute solution containing 5% of the tested organic polymer and water. Morphologic studies were conducted with the use of high resolution scanning electron microscopy (HRSEM, LIO 982). The zinc samples were mirror polished with the use of 0.05 μm diamond paste prior to the immersion in the tested solutions.

3. Results and discussion

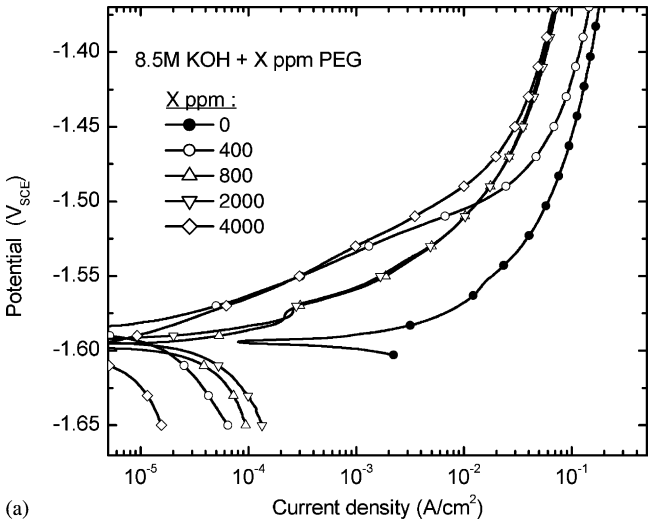
3.1. Potentiodinamic polarizations measurements

3.1.1. Anodic behavior of zinc in alkaline electrolytes containing organic inhibitors

Fig. 1 presents the anodic curves obtained from zinc polarization in alkaline media containing 400–4000 ppm of PEG (Fig. 1a) and GAFAC RA600 (Fig. 1b) at a scan rate of 1 mV/s. As can be seen the addition of the inhibitor has little effect on the active anodic dissolution of zinc metal. Although the measured anodic currents are shifted to slightly lower values, the active dissolution of zinc metal at potentials higher than E_{corr} (−1.58 V versus SCE) does not stop at any time. Moreover, no effect of the inhibitor concentration on the anodic currents was detected. As can be seen in Fig. 1a the behavior of the zinc metal in alkaline solutions containing 400 and 4000 ppm of PEG exhibits similar anodic behavior while different concentration of the added GAFAC RA600 (Fig. 1b) have no effect on the behavior of zinc in alkaline electrolytes.

3.1.2. Cathodic behavior of zinc in alkaline electrolytes containing inhibitors

The electrochemical behavior of zinc in both electrolytes containing inhibitors was monitored as a function of time and concentration. Figs. 2 and 3 present the cathodic behavior of zinc in electrolytes containing 400–4000 ppm of PEG (Fig. 2) and GAFAC RA600 (Fig. 3). The cathodic curve obtained from zinc in alkaline electrolyte without the addition of inhibitor is also shown for comparison. As can be seen both organic materials can be considered as cathodic inhibitors. Fig. 2a shows that upon immersion the best effect of corrosion inhibition is achieved with the solution containing 4000 ppm of PEG. The potential range in which the inhibitor is highly effective was found to be 120 mV, between E_{corr} (−1.58 V) and −1.7 V. A decrease in the current value measured along with stable low currents value



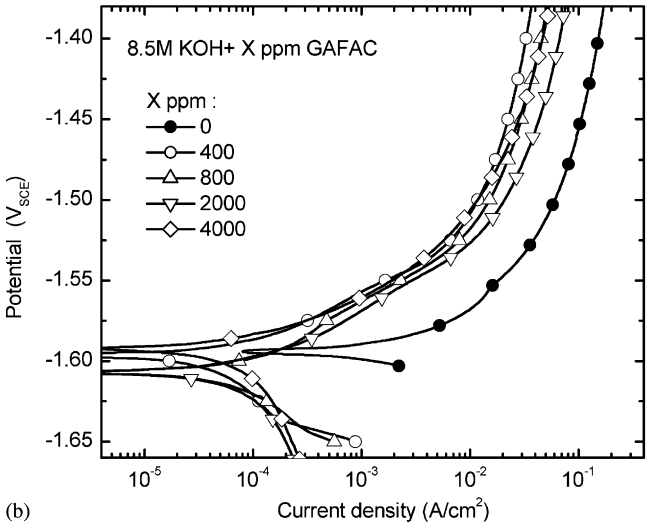
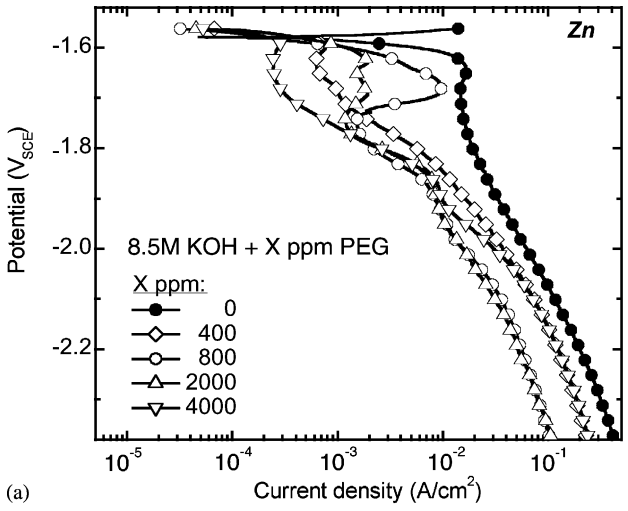


Fig. 1. The anodic profiles obtained from polarized zinc in 8.5 M KOH containing 400–4000 ppm of (a) PEG and (b) GAFAC RA600, at a scan rate of 1 mV/s.



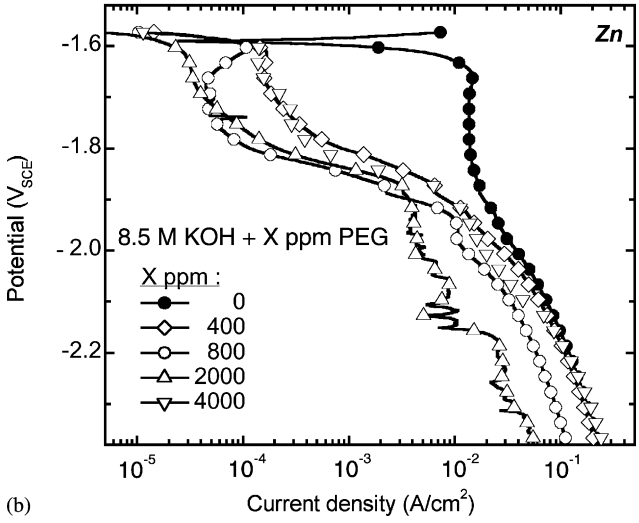


Fig. 2. The cathodic profiles obtained from polarized zinc in 8.5 M KOH containing 400–4000 ppm of PEG: (a) immediately upon immersion and (b) after 1 h storage in the electrolyte. The cathodic curve obtained from zinc in alkaline electrolyte without the addition of inhibitor is also shown for comparison. All scans are recorder at a scan rate of 1 mV/s.

over a wide range of potentials is indicative of a cathodic inhibition. However, after storage time of 1 h in the solution the zinc exhibit different behavior. Fig. 2b presents the cathodic behavior of zinc in PEG containing alkaline solutions. The measured currents are further reduced (from $\sim 2.5 \times 10^{-4}$ to $\sim 3.5 \times 10^{-5}$ A/cm^2), indicating the strong inhibition properties of PEG. We also observed that the most efficient concentration is no longer 4000 ppm but rather 2000 ppm of PEG, while the inhibition efficiency of zinc in 400 and 4000 ppm solutions are equivalent. One hour after immersion, the inhibition potential window was much broader and was measured to be ~250 mV (−1.83 V (E_{corr})) below E_{corr}.

Fig. 3 shows the data obtained from cathodic polarization of zinc in alkaline solutions containing GAFAC RA600 in concentrations of 400–4000 ppm. Fig. 3a presents the curves obtained from cathodically polarized zinc upon immersion in the electrolytes. The potential window in which an effective inhibition of the zinc is achieved was measured to be in the range of −1.58 (E_{corr}) to −1.7 V. Insignificant change in this range was observed after 1 h (Fig. 3b). Upon immersion (Fig. 3a) the optimal concentration of GAFAC RA600 was detected to be 2000 ppm, while the least effective one was 400 ppm. However, after storage of the zinc in the solutions for 1 h the electrolyte containing 400 and 800 ppm were found to be the least effective in inhibiting the cathodic reaction of the zinc, while the addition of 2000 ppm is proven to be the most efficient concentrations, as was observed upon immersion. The measured currents are further reduced (from $\sim 7 \times 10^{-4}$ to $\sim 10^{-4}$ A/cm^2, obtained from the polarized zinc in solution containing 2000 ppm GAFAC). These values are higher than the currents obtained from zinc polarized in

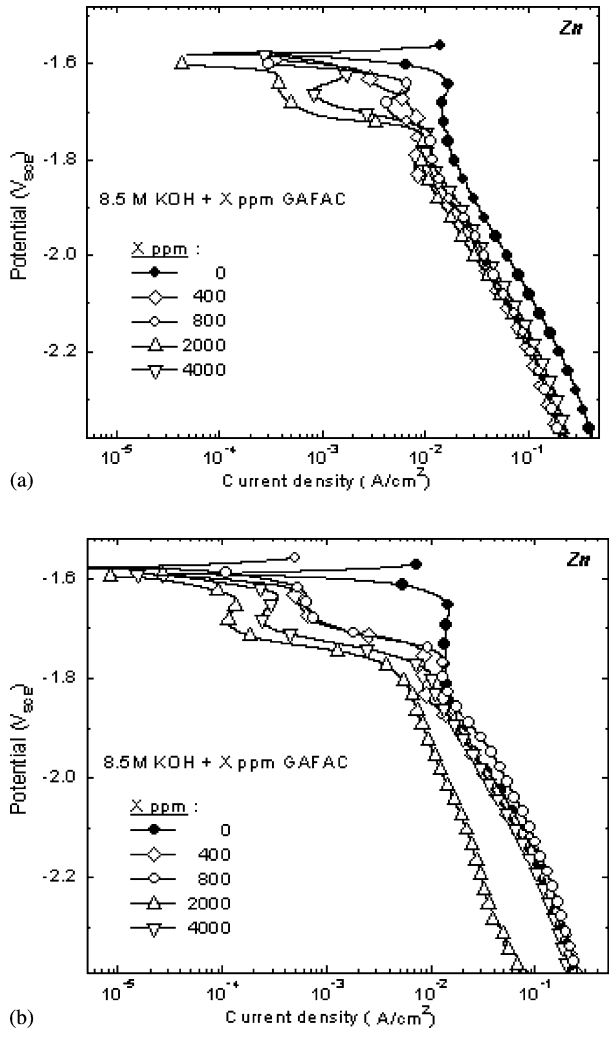


Fig. 3. The cathodic profiles obtained from polarized zinc in 8.5 M KOH containing 400–4000 ppm of GAFAC RA600: (a) immediately upon immersion and (b) after 1 h storage in the electrolyte. The cathodic curve obtained from zinc in alkaline electrolyte without the addition of inhibitor is also shown for comparison. All scans are recorder at a scan rate of 1 mV/s.

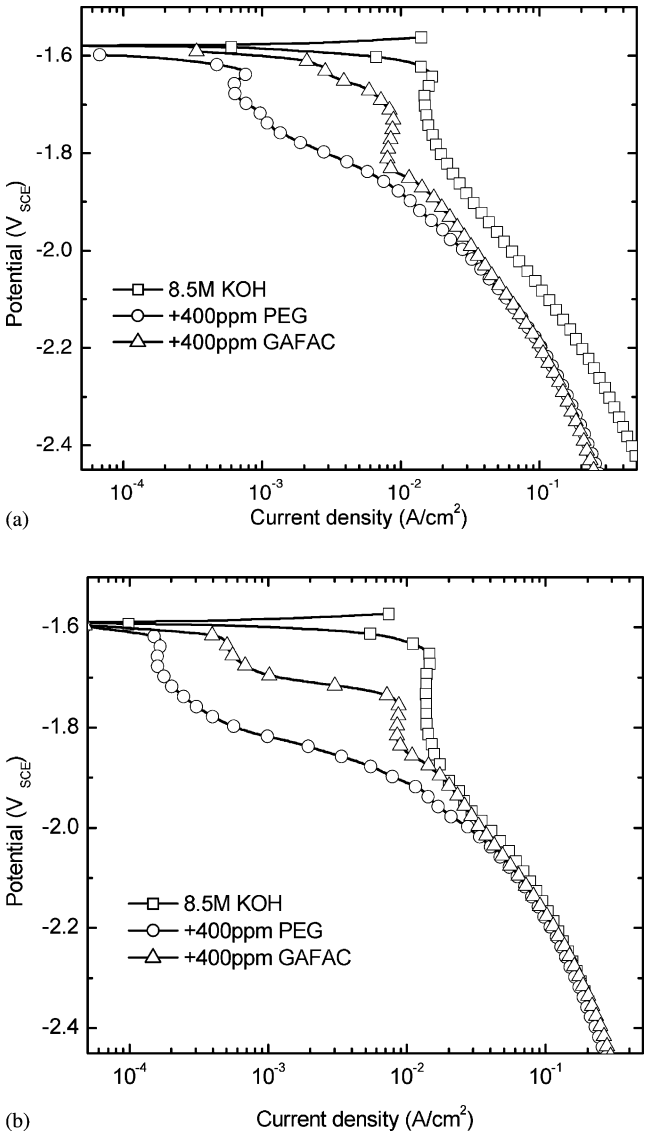


Fig. 4. A comparison of the electrochemical behavior of zinc under cathodic polarization in 8.5 M KOH containing both PEG and GAFAC RA600 at a concentration of 400 ppm: (a) immediately upon immersion and (b) after 1 h storage in the electrolyte.

PEG, indicating that the inhibition of the cathodic reaction on the zinc metal is better in the presence of PEG.

Fig. 4 summarizes our observation on the cathodic inhibition of these two zinc inhibitors. Fig. 4 compares the zinc behavior under cathodic polarization in electrolytes containing both inhibitors at a concentration of 400 ppm. It is obvious from this comparative figure that PEG is a superior inhibitor once it is compared with GAFAC RA600. Upon immersion of the zinc into the electrolytes, the measured inhibition potential window in electrolytes containing PEG is wider than the range observed once zinc is polarized in alkaline electrolytes containing GAFAC RA600. This potential window is increased to 250 mV below E_{corr} upon storage in PEG electrolyte, while it remains constant (120 mV below E_{corr}) once the zinc is stored in GAFAC electrolyte. The currents observed in these inhibition potential windows are reduced upon storage. However, the observed reduction in the currents is higher with the electrolyte containing PEG. It is important to note the difference in the values of the measured currents in the initial state; the currents value obtained from the PEG electrolyte are by an order of magnitude lower to start with, than the values measured from the GAFAC electrolytes. The reduction in the currents after 1 h is similar for both sets of electrolytes and is approximately observed to be an order of magnitude lower.

3.2. Potentiostatic measurements

In order to examine the inhibition efficiency of both organic compounds, the zinc metal was potentiostatically polarized to −1.7 V. This potential was selected since it lies

in the potential range of the inhibition window (up to 0.2 V below E_{corr}), as was shown Figs. 2–4.

Fig. 5 presents the data obtained from potentiostatic measurements taken at −1.7 V from zinc electrode immersed in alkaline electrolyte containing 400–4000 ppm of inhibitors. Fig. 5 shows clearly that the currents measured from the zinc electrode immersed in the alkaline solution containing PEG are significantly reduced in comparison with the currents obtained from alkaline solutions containing GAFAC RA600. While no inhibition is observed with 400 ppm GAFAC (Fig. 5a) (the current is not reduced at any time, but rather increased), the current is stabilized once the zinc is polarized in a solution containing 800 ppm of GAFAC (Fig. 5b). The values of the measured current are reduced to comparable values (with PEG electrolytes) only with electrolytes concentration above 800 ppm. The potentiostatic measurements also indicate that the optimal concentration for GAFAC in the electrolyte is ranging between 2000 and 4000 ppm. Any concentration below 2000 ppm will result in high currents. Only at concentration above 2000 ppm of GAFAC and PEG the observed inhibition currents are almost equivalent.

The results obtained from the potentiostatic steps clearly point out that PEG reduces the drawn currents to much lower values than the currents measured once GAFAC is present in the electrolytes. Only at concentration of 4000 ppm and after almost 2 h the current measured from the cathodically polarized zinc electrode is reduced to the same low levels of currents obtained in the electrolyte containing 4000 ppm of PEG. The currents obtained at this concentration are almost equivalent to the currents measured from zinc electrode immersed in electrolytes containing 2000 ppm of both organic inhibitors.

3.3. Linear polarization measurements

Linear polarization technique was applied in order to evaluate the corrosion currents (I_{corr}) as a function of inhibitor concentration. Fig. 6 presents the values of the corrosion current as a function of inhibitor concentration

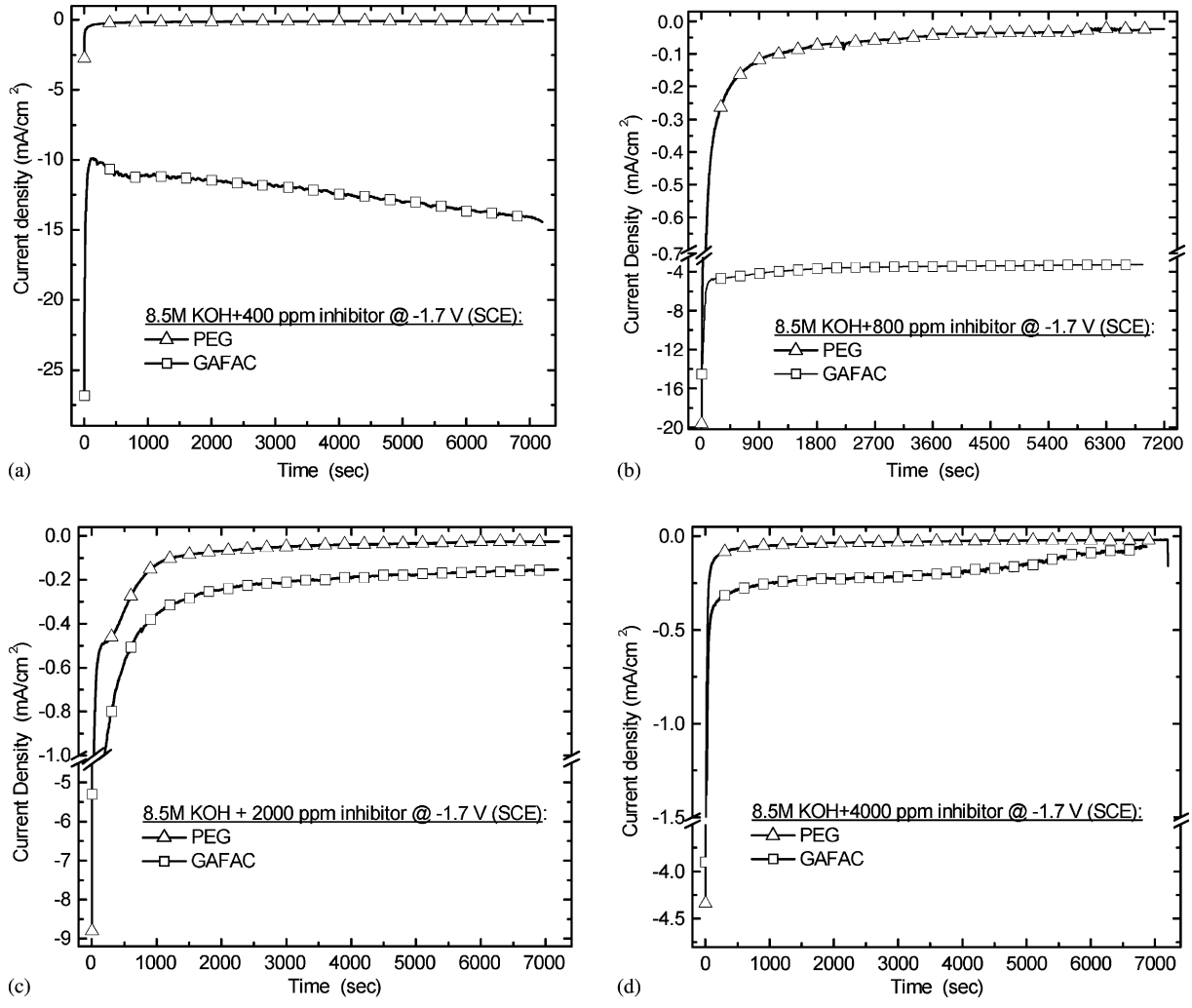


Fig. 5. Data obtained from potentiostatic measurements taken at −1.7 V from zinc electrode immersed in 8.5 M KOH containing (a) 400 ppm; (b) 800 ppm; (c) 2000 ppm; (d) 4000 ppm of PEG and GAFAC RA600.

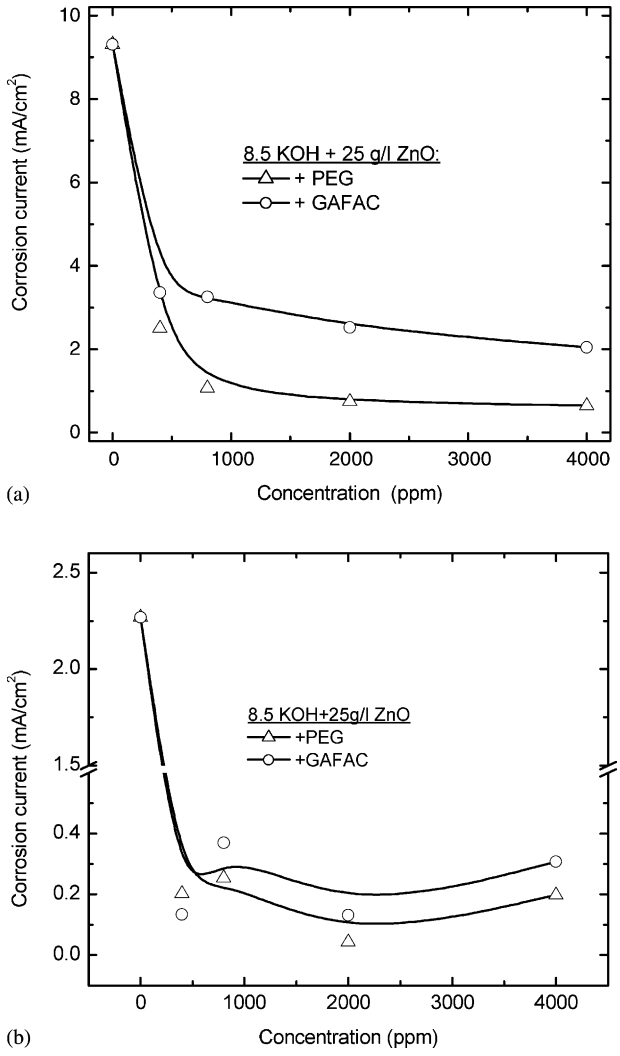


Fig. 6. Values of the corrosion current (I_{corr}) as a function of inhibitor (PEG and GAFAC RA 600) concentration: (a) immediately upon immersion and (b) after 1 h storage in the alkaline solution.

immediately upon immersion (Fig. 6a) and after 1 h storage in the electrolyte solution (Fig. 6b). The corrosion current obtained without the addition of any inhibitor are reduced upon storage from 9.2 to 2.3 mA/cm^2. However, once organic inhibitor is introduced into the solution, the corrosion currents are sharply reduced. Stronger reduction in I_{corr} was observed with the alkaline electrolytes containing PEG. The major decrease in the current was measured instantly with the addition of the minimal amount of 400 ppm. The current that was observed with the addition of 400 ppm of PEG was measured to be 2.5 mA/cm^2, while a value of 3.4 mA/cm^2 was measured from the zinc electrode immersed in alkaline electrolyte containing GAFAC RA600. Upon immersion, the current measured from with PEG electrolytes were steady and almost no change was observed in the I_{corr} once PEG concentration reached values above 2000 ppm. On the contrary, we observe a gradual decrease in I_{corr} as a function of GAFAC RA600 concentration in the electrolyte. However, the gap in I_{corr} between PEG and GAFAC alkaline electrolytes at a concentration above 2000 ppm was measured to be steady on 1.9–1.7 mA/cm^2. Fig. 6b presents the corrosion currents measured as a function of the inhibitor concentration once the zinc electrode was stored for 1 h in the alkaline solutions. The storage time causes the system to stabilize and consequently a minimum in the I_{corr} is detected. This value is corresponding to a concentration of 2000 ppm of organic inhibitor, in agreement with the potentiodynamic (Fig. 4) and potentiostatic (Fig. 5) results.

All three electrochemical methods employed in this study in order to characterize the inhibition properties of PEG and GAFAC RA600 indicate that the ability of PEG to inhibit the cathodic reaction of zinc metal is greater than GAFAC RA600. A methodology employing electrochemical tests is proposed to quickly and conveniently evaluate inhibitors for Zn in alkaline media. The method may include one of the three electrochemical tests or all three of them. The use of the electrochemical methods may save time and can be more accurate in determining and fine-tunning the correct concentration of the added inhibitor.

3.4. Morphological evaluation

Fig. 7 presents the micrographs obtained from zinc metal immersed for 1 week in solutions containing 400 ppm of PEG (e, f) and GAFAC (g, h). Micrographs of pristine polished zinc (a, b) metal and of zinc metal immersed in alkaline electrolyte without the addition of inhibitors (c, d) are also presented.

The effect of the inhibitors on the morphology and prevention of the corrosion is remarkable. As can be seen in micrographs (c, d) rapid corrosion processes are taking place at the zinc metal. The micrographs point out that the corrosion of zinc in alkaline media is taking place especially at the grain boundaries and in localized areas resulting in the formation of pits. However, once organic inhibitor is introduced into the alkaline solution the zinc surface is covered with a protecting film. The observed film produced in alkaline solution containing PEG, although not being considered as uniform, can be characterized as dense and thick. On the other hand, the coverage obtained at the zinc surface once immersed in GAFAC RA600 solution is not uniform and zinc islands are detected on the surface.

The results shown in Fig. 7 indicate the difference in the morphology developed on the surface of the zinc metal in the presence of the two inhibitors. It seems that the coverage and the morphology developed on the zinc metal in the presence of PEG is preferable, supporting the electrochemical studies indicating that the addition of PEG is superior in reducing the corrosion rate of the zinc metal. At this stage we can assume that other factors are also influencing the corrosion behavior of zinc in alkaline electrolytes containing organic inhibitors. Such factors can include film porosity, surface species formed on the zinc metal

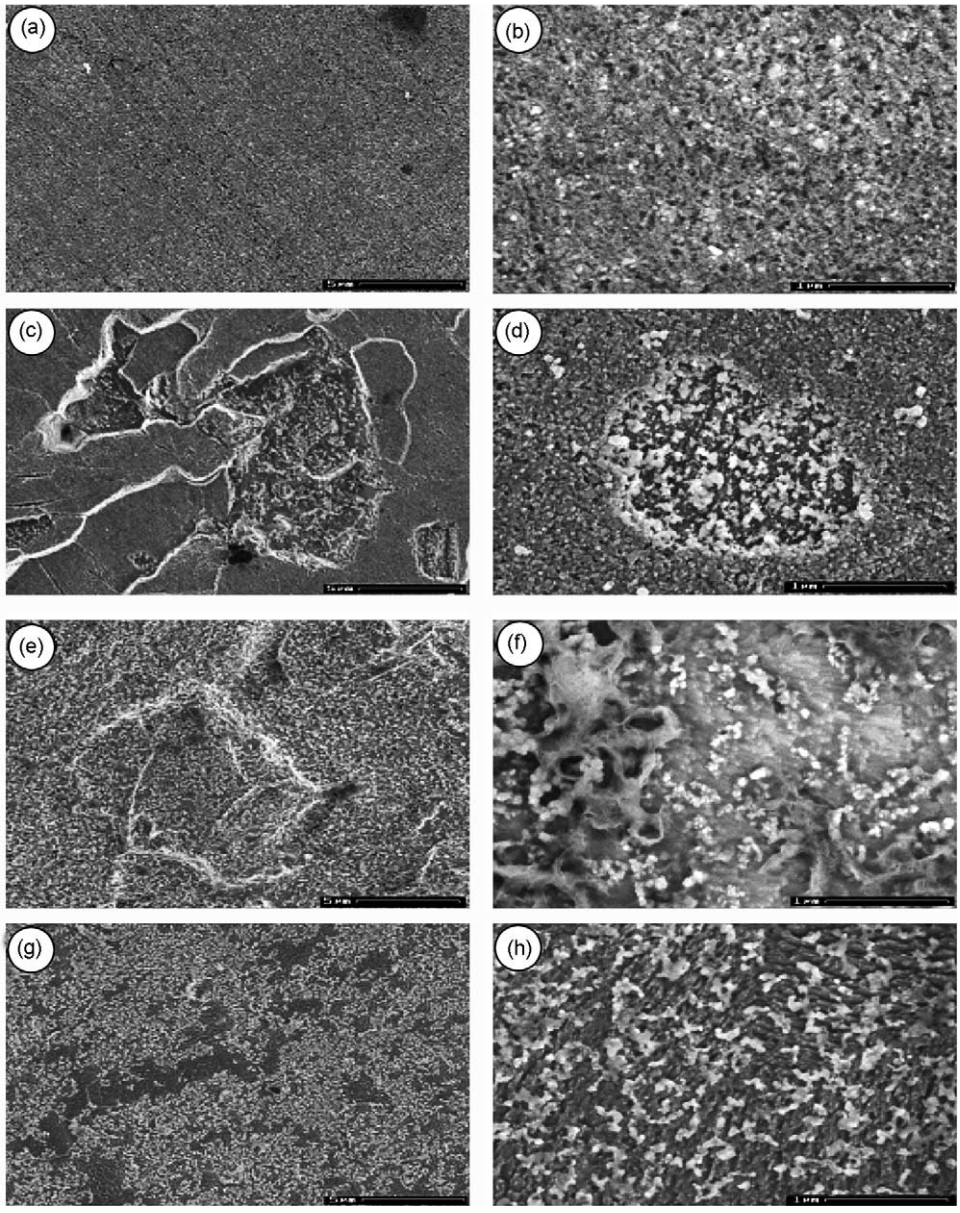


Fig. 7. Micrographs obtained from zinc metal immersed for 1 week in solutions containing 400 ppm of PEG (e, f) and GAFAC (g, h). Micrographs of pristine polished zinc metal (a, b) and of zinc metal immersed in alkaline electrolyte without the addition of inhibitors (c, d) are also presented.

and the configuration of the adsorbed organic molecule on the surface of the zinc.

4. Conclusions

The electrochemical behavior of zinc in strong alkaline solutions containing 8.5 M of potassium hydroxide (KOH) and PEG or GAFAC RA600 was evaluated. The optimal concentrations of the organic inhibitors studies were found to be in the range of 2000 ppm. The electrochemical studies point out that the inhibition properties of PEG, in the strong alkaline solution, are by far much more efficient than the inhibition capability of GAFAC RA600. Therefore, employing at least one of the electrochemical tests is proposed to quickly and conveniently evaluate inhibitors for Zn in alkaline media. Surface analysis obtained with the use of high resolution scanning electron microscopy (HRSEM) revealed different morphology characteristic developed at the zinc surface in the presence of the two inhibitors. Future work aiming at identifying the chemical composition and structure of the organic groups adsorbed at the zinc metal surface are planned. This future work may reveal whether it is possible to tailor efficient zinc inhibitors corrosion in alkaline media.

Acknowledgements

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