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Influence of Ionic Liquid Pre-immersion on the Corrodibility of Zinc in Chloride Containing Environment

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A protective film was formed by immersing zinc electrode in ionic liquid (IL). The degradation of the formed film has been examined by open circuit potential (OCP), polarization and electrochemical impedance spectroscopy (EIS) measurements. The potential shifts rapidly to more negative values during the initial stage of monitoring, then increases slowly to more noble values with an extensive jagged potential fluctuation during the last stage of OCP monitoring. Corrosion rates of the pre-immersed sample are lower than that experienced by un-immersed zinc sample in IL. The degradation of the film formed on zinc surface can be described by a dissolution precipitation mechanism.

Keywords: Zinc, Polarization, OCP, Ionic Liquid, NaC

1. INTRODUCTION

Ionic liquids have become a hot topic since the mid-1990s. The number of papers published on this topic has grown almost exponentially due to their unique physicochemical characteristics, like high conductivity [1], good thermal and chemical stability [2-3] low vapor pressure, low melting point [4], non-flammability [5] and tunable solubility. Ionic liquids are showing increasingly promising perspectives in the diverse fields of synthesis, catalysis/biocatalysis, materials science, various industrial applications [6,7],various electrochemical devices [8], rechargeable lithium cells [9] and separation technology on the industrial scale and laboratory level. It was reported recently that certain ionic liquids are capable of interacting with reactive metals such as magnesium and its alloys [10-14] to form a surface film, which improved the corrosion performance of these alloys in NaCl solution [10,12] and under humid conditions [11]. It was found that treating AZ31 magnesium alloy in trihexyl(tetradecyl) phosphonium bis (trifluoromethanesulfonyl) amide ([P6,6,6,14][NTf_2]) for 17 hrs at room temperature led to a reduction of the corrosion current by 50 times compared to an untreated alloy[11]. Howlett et al. [13] found that the addition of water to the ([P6,6,6,14][$(^iC_8)_2PO_2$]), AZ31 IL improved the corrosion performance of the coating compared to the dry IL. It has been found recently that the application of a potential bias during treatment of a magnesium alloy in IL can lead to a more uniform and protective film [13-14]. The aim of the present investigation is to investigate the pre-treatment of zinc surface in IL on the corrodibility of zinc in chloride containing environment using OCP, Polarization and EIS measurements. The work will extend to propose a mechanism describing the successive stages of film degradation.

2. EXPERIMENTAL

2.1. Materials used

Zinc electrode was prepared from flat sheet specimens of electrolytic zinc, (99.995%) and used as a working electrode. The electrode surface was polished with different grades of emery paper, degreased with acetone and rinsed with distilled water. Trihexyl(tetradecyl)phosphonium bis 2,4,4 (trimethylpentyl)phosphinate was used as ionic liquid (IL).

2.4. Electrochemical tests

Electrochemical tests were conducted using a Solartron 1470E multi-channel system (potentiostat/galvanostat) with 1455A system as frequency response analyzer. Multistate software was used to run the tests, collect and evaluate the experimental data. Ag/AgCl electrode was used as the reference and Pt electrode was used as the counter electrode. Electrochemical and impedance tests were performed in 0.1 M NaCl. The impedance data were analyzed and fitted with the simulation ZView 3.3c , equivalent circuit software.

3. RESULTS AND DISCUSSION

3.1. Open circuit potential (OCP) measurement

The change of open circuit potential (OCP) as a function of immersion time in 0.1 M NaCl solution for zinc without immersion and after 2hrs immersion in IL is shown in Fig.1. In case of untreated zinc surface the data of OCP can be divided into two stages. A rapid shift in potential to a less noble value was observed during the initial stage of immersion due to a rapid dissolution of oxide film followed by subsequent dissolution of zinc. OCP shifts slowly towards less noble values during the second stage of monitoring.

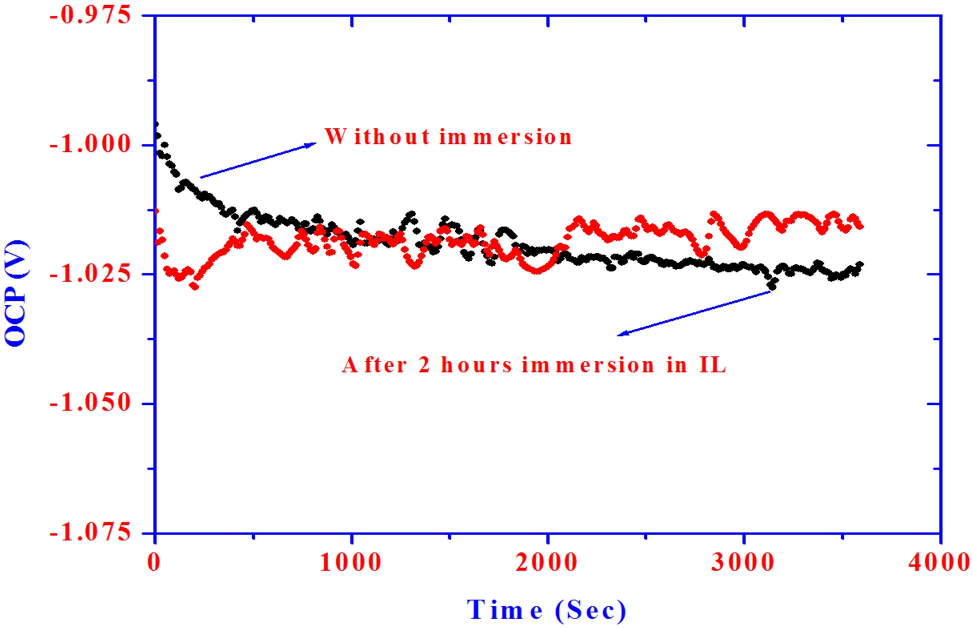

Figure 1. Monitoring data of OCP versus immersion time.

The potential shifts rapidly during the initial stage of monitoring for pre-immersed zinc surface in IL then slowly shifts to more noble values during the last stage of monitoring. The observed fluctuations in potential values during the last stage of monitoring can be attributed to competing processes between dissolution and precipitation of corrosion products. The OCP fluctuation increased slightly and placidly around −1.015V. During the of initial stage of immersion , the value of OCP was relatively low owing to penetration of the electrolyte into micro-pores of the formed film during immersion, which led to occurrence of corrosion process. As the time progresses during the subsequent immersion, Chloride ion infiltrated through the defects in the outer porous layer and reached the interface of out/inner layer and is accompanied by dissolution of soluble species and local oxide around the defects formed due to the existence of corrosive chloride ions.

3.2. Polarization measurements

Fig. 2 shows typical examples of polarization curves of untreated zinc electrodes and pre-immersed zinc for 2 hours in IL. The current density, i decreased in both cathodic and anodic polarization curves owing to coverage of the zinc electrode with protective film for pre-immersed sample. The formation of a protective film after immersion in IL decreases the cathodic process of zinc corrosion in aerated 0.1 M NaCl [15], which can be described as:

$$O_2 + 2H_2O + 4e = 4OH$$

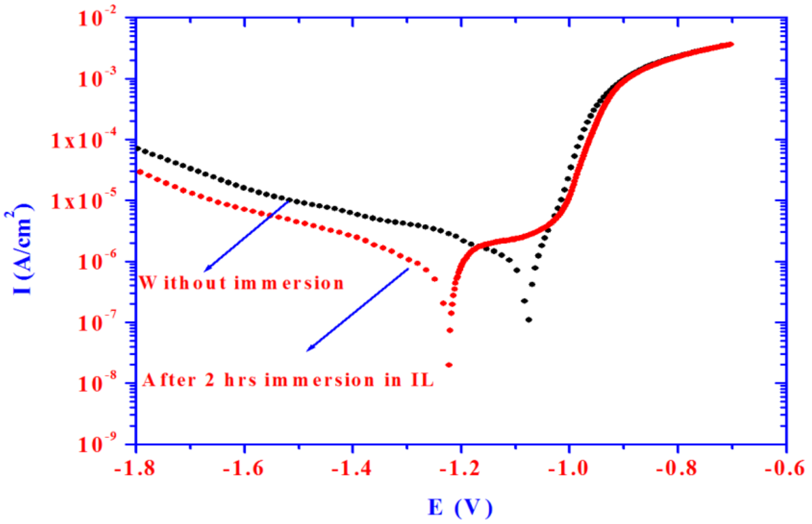

Figure 2. Polarization curves of untreated and treated zinc in 0.1 M NaCl solution.

In addition, the formation of protective film is accompanied by a reduction of the anodic process, which enhanced the prevention of the anodic process, zinc dissolution [16]:

$$Zn = Zn^{2+} + 2e$$

It was reported previously that hydroxide precipitates on the surface due low solubility of zinc hydroxide and gradually changes to zinc oxide forming a passive film [17].

$$Zn^{2+} + 2OH^{-} \longrightarrow Zn(OH)_2 \longrightarrow ZnO + H_2O$$

A soluble complex is formed on the surface in the presence of NaCl [18], resulting in breakdown of the passive film and enhancement of the anodic process [19]. It can be clearly seen that the pre-immersed sample for 2 hours in IL has a lower corrosion rate ($6.81x10^{-7}$) than without immersion ($1.15x\ 10^{-6}$). This result indicates that the passive film dramatically lowered and slowed down the corrosion rate. It can be concluded that both cathodic and anodic processes were inhibited to lesser extent and markedly suppressed the corrosion process by coverage the zinc surface with the protective film prepared by immersion in IL. Polarization curve of immersed zinc surface displays a passive region due to the formation of passive film upon immersing in IL. The sharp increase in current density during the anodic polarization was attributed to the breakdown of the passive film resulted from the aggressive action of chloride ion.

3.3. Electrochemical impedance spectroscopy measurements

The EIS technique is an effective method to understand the corrosion behavior of the metal and coated-metal system [20-21]. Figures 3 and 4 show the Bode and Nyquist plots for untreated Zn electrode obtained in 0.1 M NaCl with 10 mV perturbation amplitude, respectively. The data of Bode and Nyquist plots for pre-immersed sample in 0.1 M NaCl solution are shown in Figures 5 and 6, respectively.

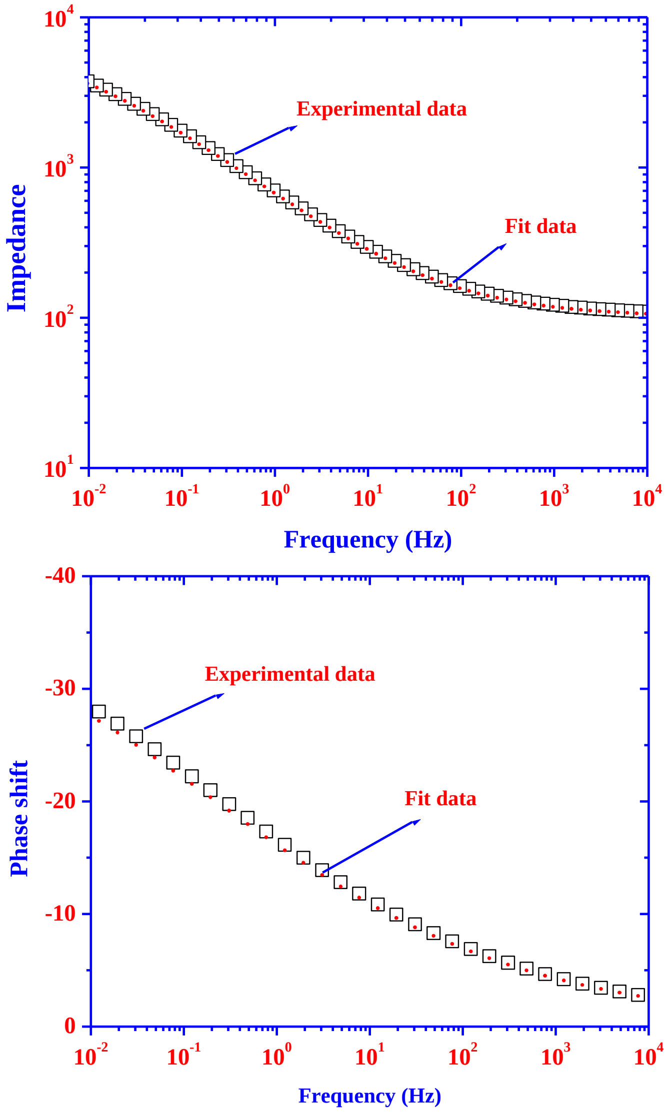

Figure 3. Bode diagram for untreated zinc in 0.1 M NaCl solution

The curves for pre-immersed sample exhibit higher values than that of un-immersed one, which indicates the formation of a protective film on the treated sample and has a better anticorrosion property in 0.1 M NaCl solution. Figure 7 shows an appropriate equivalent circuit for fitting the data. *R*s, is the solution resistance, which in series with the charge transfer resistance (Rct), which in parallel with the constant phase element (CPE). Rct is served as a parameter to characterize the corrosion rate. The values of Rct for untreated and treated zinc electrode were estimated from fitting data and found to be 7276 and 77135 ohm/cm^2, respectively.

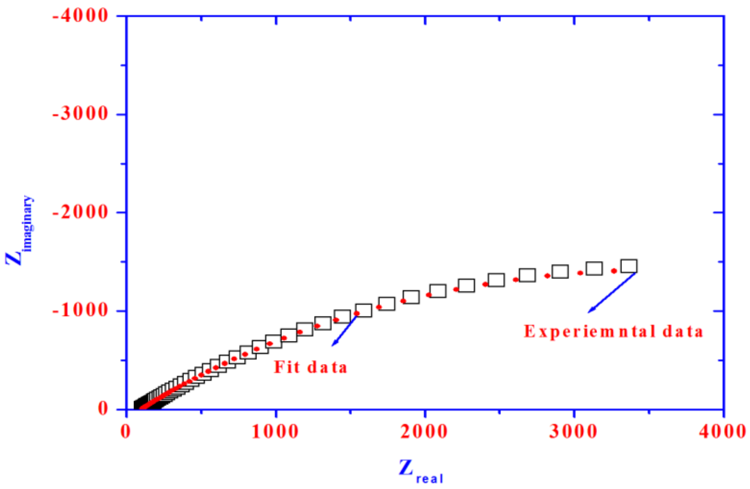

Figure 4. Nyquist diagram untreated zinc in 0.1 M NaCl solution

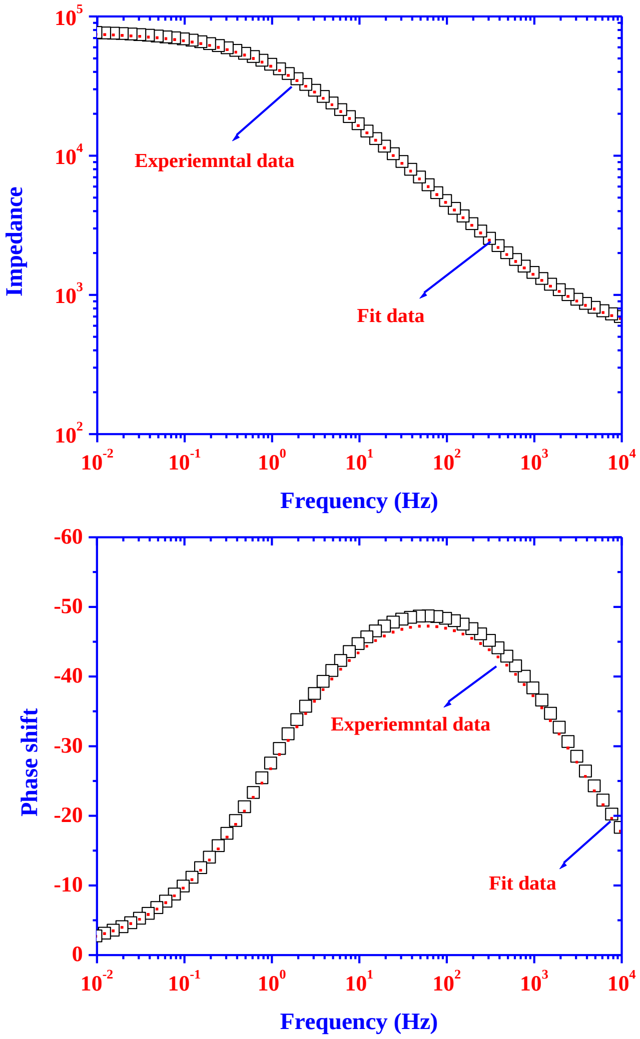

Figure 5. Bode diagram for pre-immersed zinc in 0.1 M NaCl solution

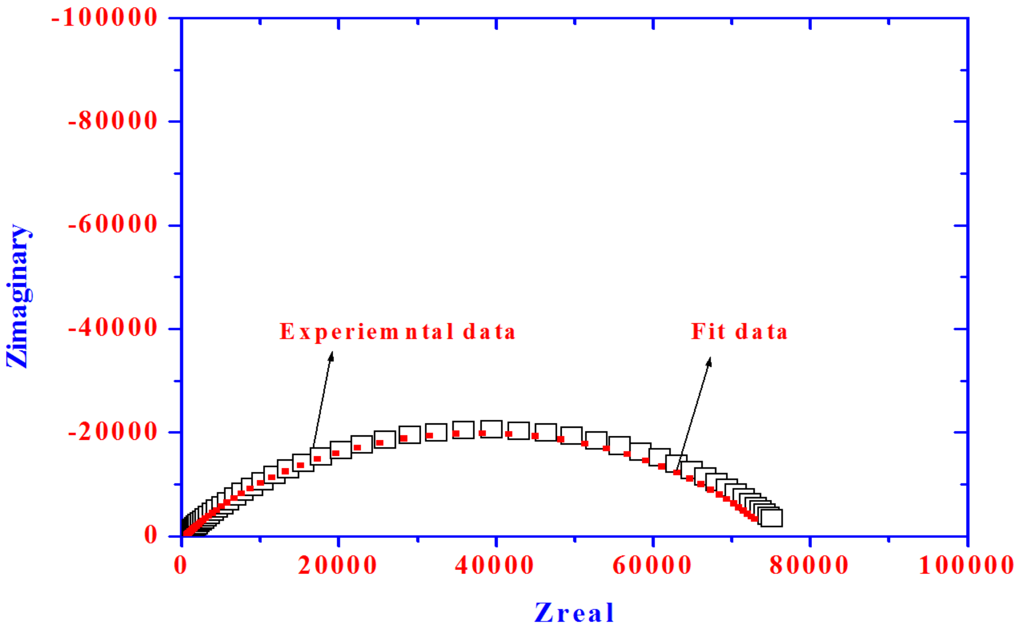

Figure 6. Nyquist diagram pre-immersed zinc in 0.1 M NaCl solution

The constant phase element, CPE, is introduced in the circuit instead of a pure double layer capacitor to give a more accurate fit [22-23] shown in Figures 3-6 for Bode and Nyquist plots. The CPE element is used to explain the depression of the capacitance semi-circle, which corresponds to surface heterogeneity resulting from surface roughness, impurities, dislocations, grain boundaries, adsorption of inhibitors, formation of porous layers [24-28].

The impedance function of a CPE has the following equation [29]:

$$Z_{CPE} = 1/A \text{ X } 1/(jw)^n \qquad (1)$$

where A is the CPE constant, ω is the angular frequency (ω = 2πf , where *f* is the AC frequency), and j is the imaginary unit and n is a CPE exponent which can be used as a gauge of the heterogeneity or roughness of the surface [30]. After the immersion in IL the impedance of the treated zinc sample has significantly changed as shown in Figures 4 and 5. It can be seen that the diameters of the semi-circles in Nyquist plots increased with immersing the zinc sample in IL due to the formation of the protective film on the zinc surface. It is clear that the impedance magnitude (|Z|) of the pre-immersed sample is higher than that of the un-immersed sample. This indicated that the treated sample showed much excellent corrosion resistance than the untreated sample. It was established that the high frequency (HF) range of the impedance diagrams reflects the outer layer properties, while the low frequency (LF) range characterizes the inner layer properties [31-32]. The difference of EIS plots between the treated and untreated zinc sample can be accounted to the diversity of corrosion resistance due to the formation of a protective layer on the treated zinc sample.

3.4. Mechanism of Film degradation

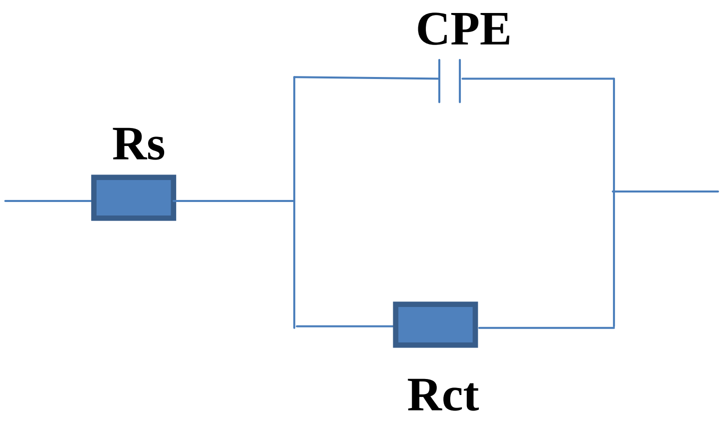

Figure 7. Equivalent circuit used for fitting the impedance data in 1 M HCl solution.

Based on OCP, EIS and corrosion results, the deterioration of the film formed upon immersion in IL could be divided into two stages as shown in Fig.8. A high corrosion process was observed during the initial stage of immersion may be attributed to a dissolution of the film. As the immersion

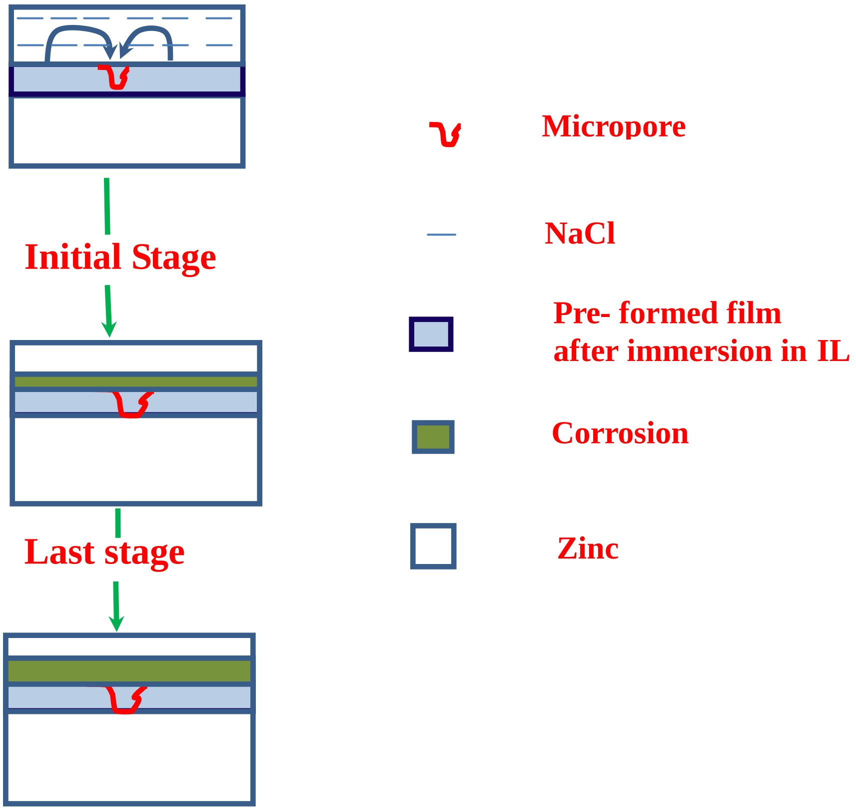

Figure 8. Schematic diagram describing the successive stages for mechanism of film deterioration

time continued, chloride ions penetrated into the film and infiltrated through the micropores or microcracks in the outer layer by diffusion and reached the interface of the inner layer quickly and causes a degradation of the film. A local dissolution of the film around the defects occurred as corrosive chloride ions were absorbed preferentially and incorporated into the microspores. Corrosion process of the film in NaCl solution can be described by two competing processes. The first process is the film dissolution and the second process is the precipitation of the corrosion products on zinc surface. When the former process is dominant process the film degradation is high and accompanied by high corrosion rate and a shift in potential towards a less noble value. The film degradation decreases when the latter process is a dominant process and is accompanied by decreasing the corrosion rate and a shift in potential to more noble values. The fluctuation in the OCP values shown in Fig. 1 can be attributed to the continuous processes of film dissolution and precipitation of the corrosion products, which acted as a protective barrier and prevented the film from further dissolution.

4. CONCLUSIONS

1- A protective film was formed upon immersion of zinc electrode in IL.

2- Corrosion rates of the pre-immersed samples are lower than that experienced by un-immersed zinc samples in IL.

3- The potential shifts rapidly to more negative values during the initial stage of monitoring, then increases slowly to more noble values during the last stage of OCP monitoring.

4- The degradation of the film formed on zinc surface can be described by a dissolution precipitation mechanism.

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References

1. J. Dupont, R.F. de Souza, P.A.Z. Suarez, *Chem. Rev.* 102 (2002) 3667.
2. Cytec-Product literature (or TDS) of CYPHOS IL-104 and 106, 2005, September.
3. G.L. Burrell, N.F. Dunlop, F. Separovic, *Soft Matter* 6 (2010) 2080
4. J.H. Davis, *Chem. Lett*. 33 (2004) 1072.
5. T. Ramnial, S.A. Taylor, M.L. Bender, B. Gorodetsky, P.T.K. Lee, D.A. Dickie, B.M. McCollum, C.C. Pye, C.J. Walsby, J.A.C. Clyburne, *J. Org. Chem.* 73 (2008) 801.
6. I. Minami, T. Inada, R. Sasaki, H. Nanao, *Tribol. Lett.* 40 (2010) 225.
7. P. Wasserscheid, T. Welton, Ionic Liquids in Synthesis, Wiley-VCH, Weinheim, Germany, 2003.
8. D. Bansal, F. Cassel, F. Croce, M. Hendrickson, E. Plichta, M. Salomon, *J. Phys. Chem*. B 109 (2005) 4492.
9. H. Usui, Y. Yamamoto, K. Yoshiyama, T. Itoh, H. Sakaguchi, *J. Power Sources* 196 (2011) 3911.
10. P.C. Howlett, S. Zhang, D.R. MacFarlane, M. Forsyth, *Aust. J. Chem*. 60 (2007) 43.
11. M. Forsyth, P.C. Howlett, S.K. Tan, *Electrochem. Solid State Lett*. 9 (2006) B52.
12. N. Birbilis, P.C. Howlett, D.R. MacFarlane, M. Forsyth, *Surf. Coat. Technol.* 201 (2007) 4496.

13. J. Efthimiadis, W.C. Neil, A. Bunter, P.C. Howlett, ACS *Appl. Mater. Interfaces* 2 (2010) 1317.
14. P.C. Howlett, T. Khoo, G. Mooketsi, J. Efthimiadis, *Electrochim. Acta* 55 (2010) 2377.
15. K. Aramaki, *Corros. Sci*. 43 (2001) 2201.
16. K. Aramaki, T. Shimura, *Corros. Sci*. 46 (2004) 313.
17. C.V. D'Alkaine, M.N. Boucherit, *J. Electrochem. Soc*. 144 (1997).
18. S. Peulon, D. Lincot, *J. Electrochem. Soc*. 145 (1998) 864.
19. R. Guo, F. Weinberg, D. Tromans, *Corrosion* 51 (1995) 356.
20. J. Liang, P.B. Srinivasn, C. Blawert, W. Dietzel, *Electrochim. Acta*, 55 (2010) 6802.
21. H. Duan, , K.Du , C. Yan C, F.Wang *Electrochim. Acta*, 51 (2006) 2898.
22. F. Mansfeld, M.W. Kendig, W.J. Lorenz, *J. Electrochem. Soc*. 132 (1985) 290.
23. F. Mansfeld, M.W. Kendig, *Werkst. Korros*. 34 (1983) 397.
24. A. Popova, E. Sokolova, S. Raicheva, M. Christov, *Corros. Sci*. 45 (2003) 33.
25. F.B. Growcock, J.H. Jasinski, *J. Electrochem. Soc*. 136 (1989) 2310.
26. U. Rammet, G. Reinhart, *Corros. Sci*. 27 (1987) 373.
27. A.H. Mehaute, G. Grepy, *Solid State Ionics* 9–10 (1983) 17.
28. E. Machnikova, M. Pazderova, M. Bazzaoui, N. Hackerman, *Surf. Coat. Technol.* 202 (2008) 1543.
29. R. Macdonald, D.R. Franceschetti, in: J.R. Macdonald (Ed.), Impedance Spectroscopy, Wiley, New York, 1987, p. 96.
30. D.A. Lopez, S.N. Simison, S.R. de Sanchez, *Electrochim. Acta* 48 (2003) 845.
31. F. Mansfeld, M.W. Kendig, *J. Electrochem. Soc.* 135 (1988) 828.
32. S.C. Chung, J.R. Cheng, S.D. Chiou, *Corros. Sci.* 42 (2000) 1249.