

## **Electrochemical Analysis of AA6082 Aluminium Alloy in Chloride Media**

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*Received: 29 October 2016 / Accepted: 11 May 2017 / Published: 12 June 2017*

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AA6082 aluminium alloy is widely used in the automotive industry. The aim of this study was to report on the corrosion behaviour of this alloy in 1 and 5 wt.% NaCl solutions at 50 °C and to compare it to the results in the same solution at room temperature, using the weight loss and electrochemical techniques. The chosen concentration and temperature range are the most severe conditions in automotive corrosion tests. The localised and general corrosion rates are higher for the highest of the two temperatures tested. At both temperatures, corrosion occurs according to a kinetic-controlled process.

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**Keywords:** corrosion; interfaces; aluminium alloy; weight loss; electrochemical impedance spectroscopy; cyclic polarisation;

### **1. INTRODUCTION**

Aluminium's high strength to weight ratio and high thermal and electrical conductivity, combined with its abundance and relatively low price, have made it an interesting material for many applications [1, 2]. In addition, due to the formation of a passive oxide layer on its surface, aluminium shows resistance to corrosion in general. However, in acidic, alkaline, and especially chloride-containing solutions the oxide layer is damaged and aluminium becomes susceptible to corrosion [1, 3, 4].

Several series of alloys have been developed in order to improve the mechanical properties of aluminium. Nevertheless, the addition of different elements to form the alloy series has an impact on the corrosion resistance of the aluminium. The pure metal is more resistive to pitting corrosion than the

alloys [1, 5]. The 6xxx series alloys contain mainly additions of Mg and Si and small amounts of Cu, which in total lead to improvement of their mechanical properties [1, 2]. Although these alloys show relatively high general corrosion resistance, they are susceptible to forms of localized corrosion, especially pitting and intergranular corrosion [6-9]. The 6xxx series alloys are extensively used in the automotive industry [1]. Among them, the AA6082 alloy is particularly used in the fabrication of hot extruded automotive parts. This alloy in addition to its plasticity for extrusion, possesses high strength, excellent weldability, formability and machinability [10]. A few studies have been performed with the aim of explaining the corrosion behaviour of AA6082 aluminium alloys, mainly in chloride-containing solutions. Cicolin et al. [11] reported on the effect of chloride concentration, pH and dissolved oxygen on the repassivation behaviour of AA6082-T6 aluminium alloy. Gerengi et al. [12] used dynamic electrochemical impedance spectroscopy to compare the corrosion resistance of AA6060 and AA6082 aluminium alloys immersed in simulated acid rain. They concluded that the corrosion resistance of these alloys decreases with increasing the aluminium content. In addition, the use of inorganic inhibitors [13] and surface modification [14] has been reported to protect the AA6082 aluminium alloy in chloride-containing solutions.

The aim of this study was to investigate the corrosion behaviour of AA6082 aluminium alloy in chloride-containing solutions, at 25 and 50 °C. First, immersion tests were performed on AA6082 alloy samples in 1 and 5 wt.% NaCl solutions at 25 and 50 °C. Then electrochemical impedance spectroscopy (EIS) and cyclic polarisation (CP) techniques were employed on samples in 5 wt.% NaCl solution at 25 and 50 °C in order to explain the electrochemical behaviour of AA6082 alloy in details. A 5 wt.% NaCl solution and 25–50 °C are standard parameters in automotive industry corrosion tests [15]. This study lays the basis for further research on possible compounds to be used as corrosion inhibitors for this alloy in chloride-containing solutions.

## 2. EXPERIMENTAL

### 2.1 Immersion tests

The aluminium alloy samples with the composition given in Table 1 were provided by Rocholl, Aglasterhausen, Germany. The dimensions of the samples used for the immersion tests were (50 × 20 × 1) mm.

**Table 1.** The composition of AA6082 aluminium alloy samples as specified by the supplier.

| Element | Si   | Fe   | Cu   | Mn   | Mg   | Cr   | Zn   | Ti   | Al      |
|---------|------|------|------|------|------|------|------|------|---------|
| wt.%    | 0.90 | 0.35 | 0.07 | 0.45 | 0.90 | 0.04 | 0.05 | 0.02 | balance |

NaCl and acetone for analysis-ACS quality were provided by Carlo Erba Reagents (Milan, Italy). The 1 wt.% and 5 wt.% NaCl solutions were prepared using ultra-pure water (with a resistivity of 18.2 MΩ cm at 25 °C) produced with the Milli-Q system (Millipore Corporation, Massachusetts, USA). The samples were exposed for 7 days to 1 wt.% and 5 wt.% NaCl solutions, under non-stirring

conditions, at 25 °C or 50 °C in 100 mL closed-to-air polypropylene vials. A mixture of 50 vol.% acetone/50 vol.% water was used to clean the samples ultrasonically before immersion test. Afterwards the samples were dried under a stream of air, and weighed. Then the samples were immersed in vials. After 7 days immersion period the samples were cleaned by brushing them under the stream of water using a fibre-bristle brush to remove the corrosion products. Then the samples were rinsed with water, dried under a stream of air, and weighed. For each test 9 replicate measurements were performed. The corrosion rate (CR) was calculated from the average mass loss. The outliers were discarded using the Grubbs' test [16].

## 2.2 Electrochemical analysis

The samples for the electrochemical measurements were cut in a disc shape with a 15 mm diameter. Their surface was ground under a stream of water using a rotating device first with 320-grit SiC paper followed by 500, 800, 1000, 2400 and 4000-grit SiC papers (provided by Struers, Ballerup, Denmark). In order to minimize abrasion the grinding direction was changed four times with 90°. The samples were rinsed with ultra-pure water, cleaned ultrasonically in the 50 vol.% acetone/50 vol.% water mixture and then rinsed again with ultra-pure water and dried. The samples were then embedded in a Teflon holder (PAR, Cambridge, UK), with a 1 cm<sup>2</sup> area exposed to the 5 wt.% NaCl solution. Electrochemical measurements were performed at 25 and 50 °C, in sequence after 1–11 h of immersion. The aluminium alloy sample, a graphite rod, and a saturated calomel electrode (SCE) were used as the working, counter, and reference electrodes, respectively. A Gamry 600<sup>TM</sup> potentiostat/galvanostat controlled by a Gamry Framework electrochemical program was used to perform the electrochemical measurements. The EIS spectra were recorded in sequence after 1 h, 3 h, 5 h, 7 h, and 10 h of immersion, preceded in each case by chronopotentiometry measurements. At each specified immersion time the EIS measurements were carried out at open circuit potential ( $E_{oc}$ ), from 1 MHz to 10 mHz, with 10 points/decade and a 10 mV (peak to peak) amplitude [17–19]. The EIS curves were fitted by Echem Analyst software. The cyclic polarisation (CP) measurements started after 11 h of immersion at  $-250$  mV vs.  $E_{oc}$ . The potential scan was reversed when the current density of 1 mA/cm<sup>2</sup> was reached. The potential scan in the cathodic direction was continued up to  $-500$  mV vs. SCE. A sweep rate of 0.1 mV/s was used for the CP measurements.

## 3. RESULTS AND DISCUSSION

### 3.1 Immersion tests

The corrosion rate of the AA6082 aluminium alloy samples immersed for 7 days in 1 and 5 wt.% NaCl solutions at 25 and 50 °C, was calculated from the average mass losses according to eq. (1):

$$\text{CR} \left[ \text{g (m}^2\text{h)}^{-1} \right] = \frac{\Delta m}{A \cdot t} \quad (1)$$

where  $\Delta m$  is the mass loss in grams,  $A$  the surface area of the samples in square meters and  $t$  the immersion time in hours.

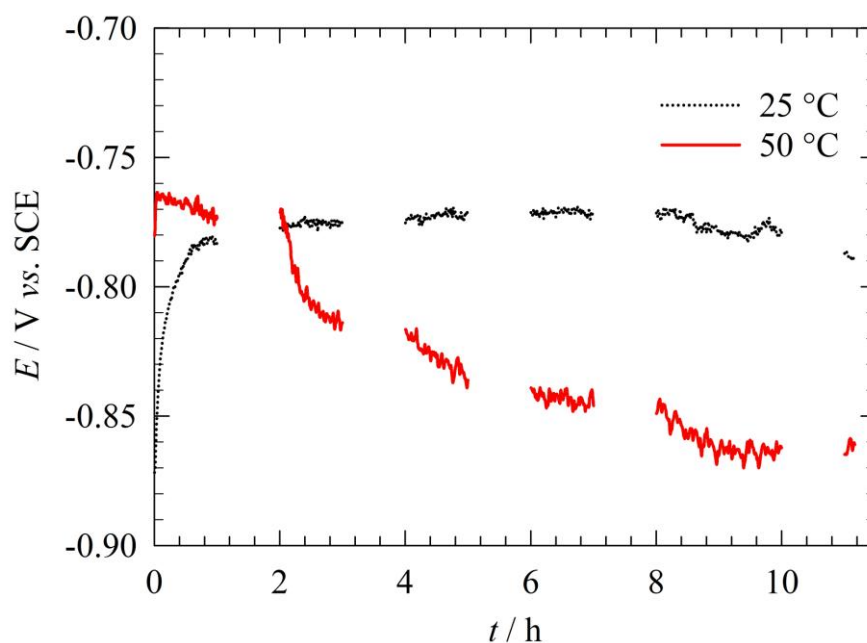
The corrosion rates of the aluminium alloy samples immersed in 1 and 5 wt.% NaCl solutions at 25 °C are  $0.587 \cdot 10^{-3}$  and  $0.865 \cdot 10^{-3} \text{ g (m}^2 \text{ h)}^{-1}$ , respectively. At 50 °C the samples showed mass gain after immersion in both 1 and 5 wt.% NaCl solutions, due to the strongly attached corrosion products on their surfaces. It is possible to use medium that would remove these corrosion products (to clean the surface). However, by doing so we risk additional corrosion of the base material, which would lead to systematic error. Electrochemical techniques have in this particular case significant advantage, because the corrosion products do not interfere with the evaluation of the relative corrosion behaviour of the particular metal in a certain environment.

### 3.2. Electrochemical analysis

Only the aluminium alloy samples exposed to the most corrosive environment (5 wt.% NaCl solution), were tested electrochemically at both 25 and 50 °C.

#### 3.2.1 Chronopotentiometry measurements

Figure 1 shows the change of the potential with time for the AA6082 aluminium alloy samples in 5 wt.% NaCl solution at 25 and 50 °C, over 11 h of immersion. The discontinued parts on each curve represent the immersion times at which the EIS measurements were performed. As it can be seen from Figure 1 the potential does not change significantly after each EIS measurement, confirming that the latter is a non-destructive technique.

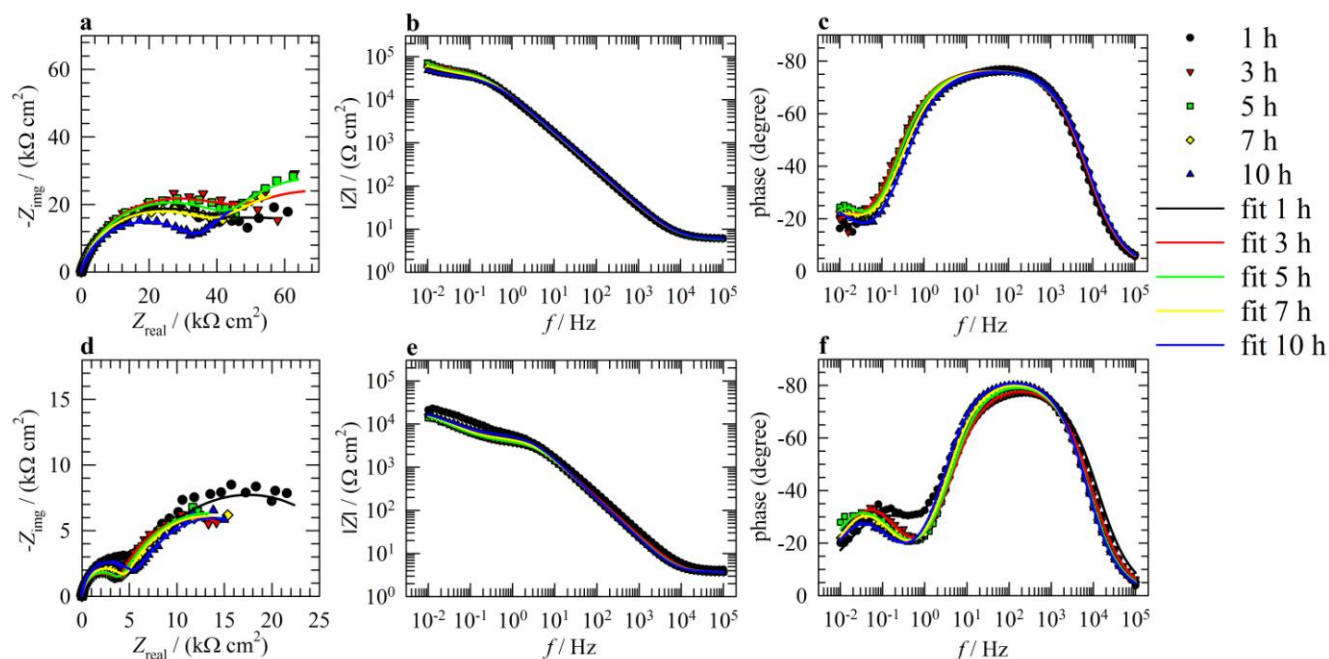


**Figure 1.** Chronopotentiometry measurements of AA6082 aluminium alloy in 5 wt.% NaCl solution at 25 and 50 °C.

At 25 °C the potential increased slightly after immersion and the steady-state (where the potential does not change with time significantly) was achieved after approx. 2 h immersion. In this case the corrosion potential (the last  $E_{oc}$  measured before CP measurement) was  $-0.789$  V vs. SCE. The AA6082 aluminium alloy behaved differently at 50 °C. The potential decreased with time, especially after 2 h immersion. The steady-state for the potential was achieved after approx. 9 h immersion. The corrosion potential at 50 °C was  $-0.861$  V vs. SCE.

### 3.2.2 EIS measurements

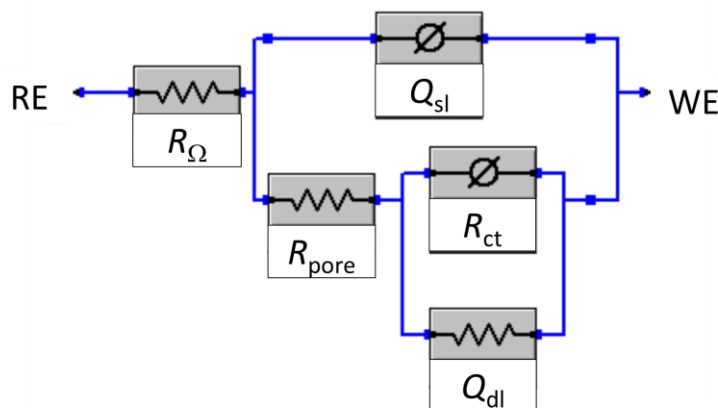
Figure 2 presents the EIS measurements and fitted curves for the AA6082 samples in 5 wt.% NaCl solution, at 25 and 50 °C, after 1–10 h immersion. The data were fitted using the nested  $R_{\Omega}(Q_{sl}(R_{pore}(Q_{dl}(R_{ct})))$  equivalent electrical circuit (EEC) shown in Figure 3, which is a combination of resistance ( $R$ ) and  $Q$  for the constant phase element [18, 20].



**Figure 2.** EIS measurements for AA6082 aluminium alloy sample (a–c) at 25 °C and (d–f) at 50 °C, after 1, 3, 5, 7, and 10 h of immersion in 5 wt.% NaCl solution. The fitted data are represented by solid lines.

$R_{\Omega}$  stands for the uncompensated resistance. This model induced the highest goodness of the fitting procedure (the lowest  $\chi^2$ ) [18, 19]. Two relaxation processes were taken into account. The first relaxation process,  $Q_{sl}R_{pore}$ , describes the pore resistance ( $R_{pore}$ ) and the surface layer capacitance ( $C_{sl}$  described with  $Q_{sl}$ ). The second relaxation process,  $Q_{dl}R_{ct}$ , describes the charge-transfer resistance ( $R_{ct}$ ) and double-layer capacitance ( $C_{dl}$  described with  $Q_{dl}$ ).  $R_{pore}$  is the electrolyte resistance in the pores of the surface layer, where the composition is different compared to the bulk solution. The surface layer represents an oxide layer in combination with the layer on top of it, which is composed of metallic

chlorides (mostly aluminium chlorides) as a consequence of the corrosion product formed. The use of the  $R(R(Q(RQ)))$  model implies that the corrosion of the aluminium alloy occurs according to a kinetic-controlled process (and not a diffusion-controlled process as no diffusion element was present in the EEC model) [18, 19].



**Figure 3.** The equivalent electrical circuit used to fit the EIS measurements.

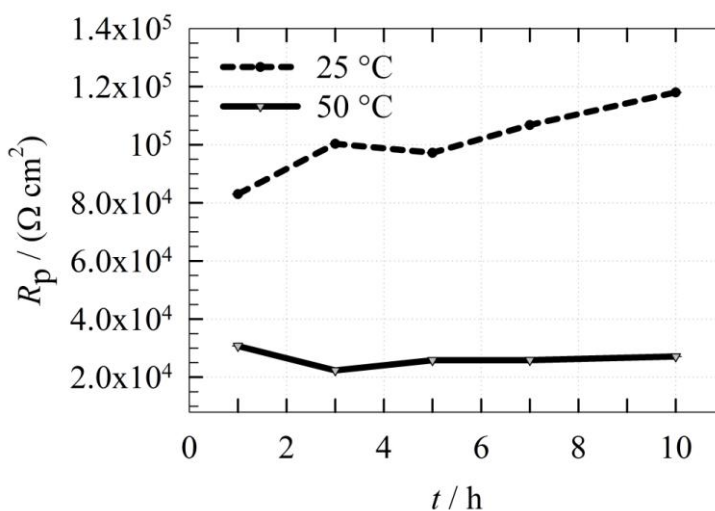
Table 2 summarises the fitted EIS parameters for the samples at the two studied temperatures. The  $Q$  values were used to calculate the respective double-layer and surface layer capacitances ( $C$ ) as  $C_x = (R_x Q_x)^{1/n_x} / R_x$  [18, 21].

No significant change of the  $R_{ct}$  with increasing immersion time was observed for the samples at both temperatures. However, the values are significantly higher for the measurements at 25 °C compared to 50 °C, which indicates that at lower temperature the electron transfer for the metallic material is slower. This also indicates a lower corrosion rate. The  $R_{pore}$  values at 25 °C increase with immersion time, while no significant change was observed at 50 °C (there is no trend for the latter). The increase in  $R_{pore}$  signifies that the pores of the surface layer start to close and that is why conductivity decreases. The  $C_{sl}$  at both temperatures increases with increasing immersion time, implying that the thickness of the oxide layer decreases with immersion time as  $C$  is inversely proportional to the thickness [18, 19]. However, the  $C_{dl}$  at 25 °C decreases with increasing immersion time, which is in agreement with the increase in  $R_{pore}$  values with increasing immersion time.  $C_{dl}$  is connected with the active part of the electrode; the higher  $C_{dl}$  is, the greater is the active area. When pores close, the active area decreases. On the other hand, as reported above, no significant change in  $R_{pore}$  is seen at 50 °C, which is reflected in the non-significant change in the respective  $C_{dl}$  values.

**Table 2.** Fitted EIS parameters for AA6082 aluminium alloy samples in 5 wt.% NaCl solution after 1–10 h immersion, at 25 and 50 °C. Units:  $\chi^2$  [ $\times 10^{-3}$ ],  $R_\Omega$  [ $\Omega \text{ cm}^2$ ],  $R_{\text{pore}}$ , and  $R_{\text{dl}}$  [ $\text{k}\Omega \text{ cm}^2$ ],  $Q_{\text{sl}}$  and  $Q_{\text{dl}}$  [ $\mu\Omega^{-1} \text{ cm}^{-2} \text{ s}^n$ ], and  $C$  [ $\mu\text{F cm}^{-2}$ ].

| Immersion time [h] | $\chi^2$ | $R_\Omega$ | $Q_{\text{sl}}$ | $n_1$ | $R_{\text{pore}}$ | $C_{\text{sl}}$ | $Q_{\text{dl}}$ | $n_2$ | $R_{\text{ct}}$ | $C_{\text{dl}}$ |
|--------------------|----------|------------|-----------------|-------|-------------------|-----------------|-----------------|-------|-----------------|-----------------|
| 25 °C              |          |            |                 |       |                   |                 |                 |       |                 |                 |
| 1                  | 0.84     | 5.90       | 217.00          | 0.69  | 39.7              | 581.50          | 17.2            | 0.86  | 43.30           | 16.46           |
| 3                  | 0.98     | 5.84       | 276.00          | 0.85  | 48.0              | 440.16          | 16.8            | 0.86  | 52.30           | 16.45           |
| 5                  | 0.61     | 5.69       | 396.00          | 0.99  | 46.4              | 401.84          | 16.5            | 0.86  | 50.80           | 15.96           |
| 7                  | 0.22     | 5.65       | 340.00          | 0.84  | 58.7              | 593.76          | 15.3            | 0.86  | 48.10           | 14.56           |
| 10                 | 0.24     | 5.60       | 325.00          | 0.83  | 73.0              | 607.62          | 14.7            | 0.86  | 45.00           | 13.77           |
| 50 °C              |          |            |                 |       |                   |                 |                 |       |                 |                 |
| 1                  | 2.30     | 3.36       | 145.17          | 0.67  | 24.9              | 273.37          | 12.9            | 0.89  | 5.81            | 9.37            |
| 3                  | 0.66     | 3.68       | 298.27          | 0.77  | 17.4              | 494.74          | 13.5            | 0.90  | 4.89            | 9.88            |
| 5                  | 0.23     | 3.74       | 358.20          | 0.74  | 21.1              | 696.45          | 13.7            | 0.91  | 4.73            | 10.56           |
| 7                  | 0.25     | 3.76       | 373.10          | 0.76  | 20.5              | 686.92          | 13.53           | 0.92  | 5.39            | 10.79           |
| 10                 | 0.22     | 3.76       | 370.07          | 0.76  | 21.0              | 690.29          | 13.00           | 0.93  | 6.17            | 10.56           |

The polarisation resistance ( $R_p$ ) values, given as  $R_p = R_{\text{pore}} + R_{\text{ct}}$ , at both temperatures, are presented in Figure 4.  $R_p$  is a measure of how the metallic material resists transferring the electron to the electroactive species in solution. The higher the  $R_p$ , the more resistive are the samples to general corrosion.



**Figure 4.**  $R_p$  values from EIS fitting for AA6082 aluminium alloy samples after 1–10 h of immersion in 5 wt.% NaCl solution at 25 and 50 °C.

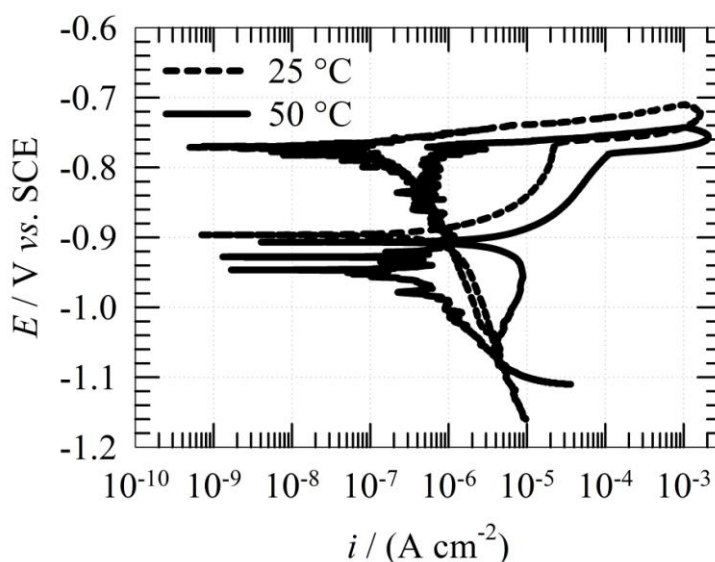
The  $R_p$  values at 25 °C decrease with increasing immersion time, while no significant change was observed at 50 °C. However, it is clearly seen in Figure 4 that the AA6082 aluminium alloy samples are more resistive to general corrosion at 25 °C compared to 50 °C (with a change in the  $R_p$  values of up to one order of magnitude) and that the general corrosion resistance of AA6082

aluminium alloy increases with increasing immersion time at 25 °C, whereas the general corrosion rate remains the same at 50 °C.

### 3.2 Cyclic polarisation measurements

The CP curves ( $E$  and  $i$  stand for potential and current density, respectively) of the alloy sample after 11 h of immersion at 25 and 50 °C are presented in Figure 5.

For the 50 °C measurement, three very distinct potentials, ranging from  $-0.95$  to  $-0.90$  V vs. SCE, are seen in the forward scan where the current changes polarity from cathodic to anodic (open circuit potential,  $E_{oc}$ ). This indicates the active dissolution of the alloy. At potentials more positive than  $E_{oc}$  a noisy part is seen in the forward scan, which indicates the occurrence of pitting corrosion.



**Figure 5.** CP curves for AA6082 aluminium alloy samples after 11 h of immersion in 5 wt.% NaCl solution at 25 and 50 °C

The alloy shows more noble behaviour at 25 °C compared to 50 °C, as seen from the more positive  $E_{oc}$ . In general, the forward scan of the alloy samples at 25 °C show active behaviour [22]. In addition, in the reverse scan for the 25 °C measurement the current is approximately one order of magnitude lower compared to that at 50 °C, which implies that at 25 °C less localised corrosion occurred in the forward scan. This is also confirmed by the absence of noise in the forward scan for the 25 °C measurement.

## 4. CONCLUSIONS

The corrosion behaviour of AA6082 aluminium alloy in 1 and 5 wt.% NaCl solution at 25 and 50 °C was studied using immersion tests and electrochemical methods. It was shown that higher



corrosion rates are expected for the highest of the two temperatures employed. The corrosion rate increased with increasing the chloride concentration. The occurrence of pitting is more pronounced at 50 °C compared to 25 °C. Moreover, higher resistive behaviour toward general corrosion is expected at 25 °C compared to 50 °C. It was also shown that the corrosion of the AA6082 aluminium alloy at the studied conditions occurs according to a kinetic-controlled process.

## References

1. J. R. Davis (editor), Corrosion of aluminium and aluminium alloys, ASM International (1999), Ohio, USA
2. R. Winston Revie, Uhlig's corrosion handbook 3rd edition, John Wiley & Sons Inc. (2011) New York, USA
3. K. Xhanari and M. Finšgar, *RSC Adv.* 6 (2016) 62833
4. K. Xhanari and M. Finšgar, *Arabian J. Chem.* accepted for publication (2016), DOI: 10.1016/j.arabjc.2016.08.009
5. H. Ezuber, A. El-Houd and F. El-Shawesh, *Mater. Design* 29 (2008) 801
6. W. J. Liang, P. A. Rometsch, L. F. Cao and N. Birbilis, *Corros. Sci.* 76 (2013) 119
7. D. J. Chakrabarti and D. E. Laughlin, *Prog. Mater. Sci.* 49 (2004) 389
8. W. F. Miao and D. E. Laughlin, *Metall. Mater. Trans. A* 31 (2000) 361
9. M. H. Larsen, J. C. Walmsley, O. Lunder, R. H. Mathiesen and K. Nisancioglu, *J. Electrochem. Soc.* 155 (2008) C550
10. N. Kumar, P. N. Rao, R. Jayaganthan and H-G. Brokmeier, *Mater. Chem. Phys.* 165 (2015) 177
11. D. Cicolin, M. Trueba and S. P. Trasatti, *Electrochim. Acta* 124 (2014) 27
12. H. Gerengi, P. Slepski, E. Ozgan and M. Kurtay, *Mater. Corrosion.* 66 (2015) 233
13. C. N. Panagopoulos, E.P. Georgiou, and A.G. Gavras, *Tribol. Int.* 42 (2009) 886
14. U. Trdan and J. Grum, *Corros. Sci.* 59 (2012) 324
15. ISO 9227:2006(E), Corrosion tests in artificial atmospheres - Salt spray tests. ISO (2006)
16. D. L. Massart, B. G. M. Vandeginste, L. M. C. Buydens, S. De Jong, P. J. Lewi, and J. Smeyers-Verbeke, *Handbook of chemometrics and qualimetrics: Part A*, Elsevier (1997), Amsterdam, Netherlands
17. M. Finšgar, B. Petovar, K. Xhanari and U. Maver, *Corros. Sci.* 111 (2016) 370
18. M. Finšgar and D. Kek Merl, *Corros. Sci.* 83 (2014) 164
19. M. Finšgar, A. P. Uzunalić, J. Stergar, L. Gradišnik and U. Maver, *Sci. Rep.* 6 (2016), Article Number: 26653
20. I. D. Raistrick, D. R. Franceschetti and J.R. Macdonald, *Impedance spectroscopy theory, experiment and application*. 2nd edition, John Wiley & Sons Inc. (2005) Hoboken, New Jersey, USA
21. D. Kek-Merl, J. Lappalainen, and H.L. Tuller, *J. Electrochem. Soc.* 153 (2006) J15
22. M. Finšgar and I. Milošev, *Corros. Sci.* 52(2010) 2430