CHAPTER V

RESULTS AND DISCUSSION
CHAPTER -V
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Aluminium or its multi component alloy forms a potential candidate to serve as anode in metal-air batteries. Aluminium - air cells are reported to show higher theoretical cell voltage, specific energy and operating voltage than other metal - air cells, of course next only to lithium - air cells. A highly negative potential is achieved if the metal is used in strong alkaline media but the efficiency becomes poor due to wastage by local cell corrosion. The possibilities of improving the metal performance in alkaline media by the use of several addition agents like calcium hydroxide, sodium stannate together with complexing agents like citric and tartaric acids have been explored. Besides, several inhibitors of both organic and inorganic in nature have been tried to reduce the local cell corrosion. The success of aluminium - air cell as a commercial candidate for electric vehicles is far from reality owing to the aggressive metal corrosion in highly alkaline battery electrolytes. Studies for the identification of some inhibitors to mitigate the above problem are worth pursuing and hence the present study.

The magnitude of corrosion of aluminium in alkaline medium has been brought down to a large extent through a multi pronged approach. Use of inhibitors, suitable alloying of aluminium and modification of the alkaline electrolyte by blending with additives such as calcium oxide, citric acid, stannate, etc., are some of the approaches made. The results of the studies on the above lines are discussed below.
5.1 STUDIES ON THE CORROSION BEHAVIOUR OF ALUMINIUM AND SOME OF ITS ALLOYS

5.1.1 WEIGHT LOSS AND GASOMETRIC STUDIES

In alkaline medium the Al$^{3+}$ formed is readily complexed with OH$^{-}$ ions resulting in the formation of AlO$_2^-$ [1]

\[
\begin{align*}
\text{Al}^{3+} + 4\text{OH}^- & \rightarrow \text{Al(OH)}_4^- \quad \text{(5.1)} \\
\text{Al(OH)}_4^- & \rightarrow \text{AlO}_2^- + 2\text{H}_2\text{O} \quad \text{(5.2)}
\end{align*}
\]

The reduction of water occurs simultaneously on the metal surface.

\[
\begin{align*}
\text{H}_2\text{O} + \text{e}^- & \rightarrow \text{H} + \text{OH}^- \quad \text{(5.3)} \\
\text{H} + \text{H} & \rightarrow \text{H}_2 \quad \text{(5.4)}
\end{align*}
\]

Due to low hydrogen over potential on aluminium substrate there is profuse evolution of hydrogen as aluminium corrodes in NaOH. In another scheme the formation of Al$^+$ initially which converts into Al$^{3+}$ subsequently is also predicted [2].

\[
\begin{align*}
\text{Al} & \rightarrow \text{Al}^{3+} + 3\text{e}^- \quad E_o = -1.7V \quad \text{(5.5)} \\
\text{Al} & \rightarrow \text{Al}^+ + \text{e}^- \quad \text{(5.6)} \\
\text{Al}^+ + 2\text{H}_2\text{O} & \rightarrow \text{Al}^{3+} + \text{H}_2 + 2\text{OH}^- \quad \text{(5.7)}
\end{align*}
\]

The corrosion results of pure aluminium in 4N NaOH and battery electrolyte (4N NaOH + 20% Sodium citrate + 0.1% CaO) are presented as weight loss results in Table 5.1.1. It is noted that the corrosion rate of aluminium is reduced by nearly 16% in the battery electrolyte. This is due to the Ca$^{2+}$ and citrate ion probably forming a complex and the complex
compound getting physically adsorbed with the calcium disposed towards the aluminium surface having high negative potential in the alkaline medium [2, 3]. Such types of reduction in the corrosion behaviour of aluminium in alkaline medium with the presence of $\text{Ca}^{2+}$ and salicylate ion or phthalate ions are also reported [4]. Further it is reported that some zinc based aluminium alloys having gallium, indium, thallium and bismuth in small proportions perform as good galvanic anodes in alkaline medium [5-7] suitable for cathodic protection and for aluminium–air batteries. Hence in the present investigation instead of zinc a lead based aluminium alloy having indium and gallium in small proportions have been tried in the battery electrolyte and the results are presented in the above table. It is noted that as the concentration of lead in the aluminium alloy increases from 0% to 1.5% the corrosion inhibition efficiency of the alloy electrode in the battery electrolyte is increased. This may be due to the high hydrogen over potential of lead in the alloy. However with further increase to 2% there is fall in the efficiency. At relatively higher concentration of lead, there may be phase segregation of lead dominated intermetallic region forming a noble phase, making aluminium vulnerable to enhanced corrosion.

Gasometric studies under controlled conditions of temperature and pressure are possible, as there is quantitative hydrogen evolution governed by defined stoichiometry mentioned earlier. The results are presented in Table 5.1.2. These results are in conformity with weight loss results. From the studies it is identified that aluminium alloy of composition 97.4% Al + 1.5% Pb +0.1%Ga + 1% In) in 4N NaOH blended with 20% citric acid and 0.4% CaO results in minimum self-corrosion.
Table 5.1.1 Corrosion parameters of pure aluminium and its alloys in 4N NaOH and electrolyte by weight loss method

<table>
<thead>
<tr>
<th>Metal Composition</th>
<th>Electrolyte</th>
<th>Corrosion Rate (mdd) x 10^3</th>
<th>% of inhibition (I.E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Aluminium</td>
<td>4N NaOH</td>
<td>228</td>
<td>---</td>
</tr>
<tr>
<td>Pure Aluminium</td>
<td>Battery Electrolyte</td>
<td>192</td>
<td>15.17</td>
</tr>
<tr>
<td>Al + X + 0% Pb</td>
<td>&quot;</td>
<td>182</td>
<td>20.79</td>
</tr>
<tr>
<td>Al + X + 0.5% Pb</td>
<td>&quot;</td>
<td>144</td>
<td>24.84</td>
</tr>
<tr>
<td>Al + X + 1.0% Pb</td>
<td>&quot;</td>
<td>140</td>
<td>27.03</td>
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<tr>
<td>Al + X + 1.5% Pb</td>
<td>&quot;</td>
<td>136</td>
<td>29.00</td>
</tr>
<tr>
<td>Al + X + 2.0% Pb</td>
<td>&quot;</td>
<td>144</td>
<td>24.95</td>
</tr>
</tbody>
</table>

X = 0.1% Ga + 1% In

Table 5.1.2 Inhibition efficiency (I.E) for aluminium and its alloys in 4N NaOH and electrolyte by gasometric method

<table>
<thead>
<tr>
<th>Metal composition</th>
<th>Electrolyte</th>
<th>Time in minutes</th>
<th>I.E (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>Pure Al</td>
<td>4N NaOH</td>
<td>12.4</td>
<td>21.0</td>
</tr>
<tr>
<td>Pure Al</td>
<td>Battery Electrolyte</td>
<td>7.2</td>
<td>12.6</td>
</tr>
<tr>
<td>Al + X + 0% Pb</td>
<td>&quot;</td>
<td>4.9</td>
<td>10.2</td>
</tr>
<tr>
<td>Al + X + 0.5% Pb</td>
<td>&quot;</td>
<td>4.7</td>
<td>10.0</td>
</tr>
<tr>
<td>Al + X + 1.0% Pb</td>
<td>&quot;</td>
<td>4.5</td>
<td>9.7</td>
</tr>
<tr>
<td>Al + X + 1.5% Pb</td>
<td>&quot;</td>
<td>4.3</td>
<td>9.5</td>
</tr>
<tr>
<td>Al + X + 2.0% Pb</td>
<td>&quot;</td>
<td>5.2</td>
<td>9.9</td>
</tr>
</tbody>
</table>

X = 0.1% Ga + 1% In

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5.1.2 ELECTROCHEMICAL POLARISATION STUDIES

The cathodic and anodic polarization curves in 4N NaOH and battery electrolyte with pure aluminium and its alloys are presented in Fig. 5.1.1 and in Table 5.1.3. The $i_{\text{corr}}$ values indicate that when 4N NaOH is blended with CaO and citrate ions, there is marked beneficial effect as far as the self-corrosion of aluminium /aluminium- alloys are concerned. As in the weight loss and gasometric studies, aluminium with 1.5 Pb + 0.1% Ga + 1% In is found to be the most corrosion resistant. However, the high open circuit potential values obtained with pure aluminium in 4N NaOH is lost to some extent, when the electrolyte is blended with the additives mentioned earlier. This is also the case with all the aluminium alloys. The potential values in the range of $-1.3$ to $-1.36$V (Vs Hg / HgO) have been reported for 2S electrolytic grade aluminium in similar battery electrolyte [8,9]. Also the open circuit potential for 3S aluminium in 4N NaOH containing 0.6M ZnO is reported to be $-1.369$V (Vs Hg / HgO) [10]. In all the cases the values of $b_a$ and $b_c$ are more or less equal indicating mixed control of the corrosion reaction. Further the alloying has not basically altered the dissolution mechanism of aluminium in the electrolytes. The inhibitive effect of Ca – citrate complex in 4N NaOH is accounted through a buffer solution layer close to the metal surface showing a constant pH suitable for the formation of a physically adsorbed layer containing a Ca – citrate inhibitive complex [11]. The mixed control of the corrosion of aluminium as well as its alloys in the battery electrolytes has been brought out by the results presented in Table 5.1.4. In this table the reduction in partial currents ($I_a$ and $I_c$) taken at a
Fig. 5.1.1 Electrochemical polarization curves of aluminium and its alloys in 4N NaOH and electrolyte

a. Al - in 4N NaOH  b. Aluminium  c. Al + X + 0% Pb

d. Al + X + 0.5% Pb  e. Al + X + 1% Pb  f. Al + X + 1.5% Pb

g. Al + X + 2.0% Pb  (X- 0.1% Ga + 1% In)

(b to g studies in battery electrolyte)
Table 5.1.3. Electrochemical polarization measurements of aluminium and its alloys in 4N NaOH and electrolyte

<table>
<thead>
<tr>
<th>Metal composition</th>
<th>Electrolyte</th>
<th>OCP (V)</th>
<th>$E_{\text{corr}}$ (V)</th>
<th>$i_{\text{corr}}$ (mA/cm$^2$)</th>
<th>Tafel slope (mV/dec)</th>
<th>I.E %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Al</td>
<td>4N NaOH</td>
<td>-1.500</td>
<td>-1.598</td>
<td>47.76</td>
<td>200</td>
<td>180</td>
</tr>
<tr>
<td>Pure Al</td>
<td>Battery</td>
<td>-1.301</td>
<td>-1.297</td>
<td>40.59</td>
<td>185</td>
<td>165</td>
</tr>
<tr>
<td>Al + X + 0% Pb</td>
<td>Battery</td>
<td>-1.325</td>
<td>-1.319</td>
<td>42.50</td>
<td>140</td>
<td>130</td>
</tr>
<tr>
<td>Al + X + 0.5% Pb</td>
<td>Battery</td>
<td>-1.324</td>
<td>-1.322</td>
<td>41.55</td>
<td>130</td>
<td>120</td>
</tr>
<tr>
<td>Al + X + 1.0% Pb</td>
<td>Electrolyte</td>
<td>-1.316</td>
<td>-1.324</td>
<td>37.73</td>
<td>120</td>
<td>110</td>
</tr>
<tr>
<td>Al + X + 1.5% Pb</td>
<td>Electrolyte</td>
<td>-1.318</td>
<td>-1.326</td>
<td>36.74</td>
<td>100</td>
<td>90</td>
</tr>
<tr>
<td>Al + X + 2.0% Pb</td>
<td>Electrolyte</td>
<td>-1.320</td>
<td>-1.323</td>
<td>39.16</td>
<td>120</td>
<td>80</td>
</tr>
</tbody>
</table>

X - 0.1% Ga + 1% In

Table 5.1.4 Reduction in partial currents at $E_{\text{corr}} \pm 100$ mV for aluminium and its alloys in 4N NaOH and electrolyte

<table>
<thead>
<tr>
<th>Metal Composition</th>
<th>Electrolyte</th>
<th>$E_{\text{corr}}$ (V)</th>
<th>Current at $E_{\text{corr}} \pm 100$ mV (A)</th>
<th>% Reduction in partial Currents</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Anodic $i_\text{a}$</td>
<td>Cathodic $i_\text{c}$</td>
</tr>
<tr>
<td>Pure Al</td>
<td>4N NaOH</td>
<td>-1.598</td>
<td>0.04950</td>
<td>0.02400</td>
</tr>
<tr>
<td>Pure Al</td>
<td>Battery</td>
<td>-1.319</td>
<td>0.04090</td>
<td>0.01902</td>
</tr>
<tr>
<td>Al + X + 0% Pb</td>
<td>Battery</td>
<td>-1.322</td>
<td>0.02944</td>
<td>0.01521</td>
</tr>
<tr>
<td>Al + X + 0.5% Pb</td>
<td>Electrolyte</td>
<td>-1.324</td>
<td>0.02985</td>
<td>0.01350</td>
</tr>
<tr>
<td>Al + X + 1.0% Pb</td>
<td>Electrolyte</td>
<td>-1.326</td>
<td>0.02903</td>
<td>0.01369</td>
</tr>
<tr>
<td>Al + X + 1.5% Pb</td>
<td>Electrolyte</td>
<td>-1.326</td>
<td>0.02658</td>
<td>0.01255</td>
</tr>
<tr>
<td>Al + X + 2.0% Pb</td>
<td>Electrolyte</td>
<td>-1.323</td>
<td>0.03067</td>
<td>0.01407</td>
</tr>
</tbody>
</table>

X - 0.1% Ga + 1% In
common potential of $E_{corr} \pm 100\text{mV}$ are presented. There are several publications on the estimation of Tafel slopes [12]. Still there are considerable difficulties in getting reproducible results in corrosion studies as it involves highly heterogeneous metal surface with number of variables affecting the kinetics of the reaction to a greater extent. Hence the estimation of the Tafel slopes is found to be naturally subjective in most cases. The reduction in partial currents under inhibited conditions with respect to the control taken at the common reference potential of $E_{corr} \pm 100\text{mV}$ can be used to predict the nature of control of the corrosion reaction. This procedure is well known [13-15] and it is nothing but the estimation of the Tafel slope at a reference potential in the Tafel region.

5.1.3 IMPEDANCE MEASUREMENTS

Impedance measurements are very useful to get the information regarding kinetic and mechanistic aspects of electrochemical systems [16,17]. This technique is very much useful in highly resistive media where most other electrochemical techniques normally fail. The evaluation of corrosion inhibition [18] and passivity studies [19,20] is some of the applications of this technique. According to Epelboin et al [21] the metal dissolution can be interpreted in terms of $R_c$ that is defined as the limiting zero frequency value of the real part of the complex impedance. Electrochemical theory shows that $1/R_c$ is proportional to the corrosion rate and it is analogous to the term polarization resistance encountered in the Stern – Geary equation. The impedance results for the corrosion of pure aluminium and its alloys in 4N NaOH and battery electrolyte are presented in Fig. 5.1.2 and in Table 5.1.5.
Table 5.1.5 Impedance measurements of aluminium and its alloys in 4N NaOH and electrolyte

<table>
<thead>
<tr>
<th>Metal composition</th>
<th>Electrolyte</th>
<th>$R_t$ (Ohm cm$^2$)</th>
<th>θ</th>
<th>I.E %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Al</td>
<td>4N NaOH</td>
<td>1.763</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Pure Al + X+0%Pb</td>
<td>Battery</td>
<td>2.19</td>
<td>0.42</td>
<td>19.5</td>
</tr>
<tr>
<td>Pure Al + X+0.5%Pb</td>
<td>Battery</td>
<td>2.30</td>
<td>0.09</td>
<td>9.0</td>
</tr>
<tr>
<td>Pure Al + X+1.0%Pb</td>
<td>Battery</td>
<td>2.50</td>
<td>0.19</td>
<td>19.0</td>
</tr>
<tr>
<td>Pure Al + X+1.5%Pb</td>
<td>Battery</td>
<td>2.80</td>
<td>0.21</td>
<td>21.0</td>
</tr>
<tr>
<td>Pure Al + X+2.0%Pb</td>
<td>Battery</td>
<td>3.00</td>
<td>0.27</td>
<td>27.0</td>
</tr>
<tr>
<td>Pure Al + X+2.5%Pb</td>
<td>Battery</td>
<td>2.70</td>
<td>0.22</td>
<td>22.0</td>
</tr>
</tbody>
</table>

X = 0.1% Ga + 1% In

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Fig. 5.1.2 Nyquist plots for the corrosion of aluminium and its alloys in 4N NaOH and electrolyte

a. Al – in 4N NaOH  b. Aluminium  c. Al + X + 0% Pb  
d. Al + X + 0.5% Pb  e. Al + X + 1% Pb  f. Al + X + 2% Pb  
g. Al + X + 1.5% Pb  (X - 0.1% Ga + 1% In)  

(b to g studies in battery electrolyte)
In the case of corrosion of pure aluminium in 4N NaOH the complex impedance plot has the appearance of only one capacitance contribution represented by only one semicircle. The symmetry in the Nyquist plot in this case is found to be distorted with a drag (visible under zoom of the individual curve) on the high frequency end. This suggests a partial diffusion control besides the charge transfer control of the corrosion process. In the case of corrosion of aluminium and its alloys in the battery electrolyte, there are two-semicircles and the second one occurring at the low frequency end. This could be attributed to a two-stage corrosion process in which the second stage could be adsorption of Ca\(^{2+}\) – citrate complex on the metal – solution phase boundary. This process could be relatively slow compared to the charge transfer metal dissolution process. In all the cases the notable characteristic feature is the absence of diffusion contribution to the real impedance at low frequencies. As in earlier studies the superior performance of the battery electrolyte over 4N NaOH and the impressive performance of 1.5% Pb aluminium alloy is brought out here also.

**SUMMARY**

From the above studies it can be concluded that the dissolution rate of pure aluminium as well as aluminium alloys are very much decreased in 4N NaOH containing Ca\(^{2+}\) and citrate ions. Among the aluminium alloys the alloy with the composition 96.217% Al + 1.51% Pb + 0.977% In + 0.096% Ga + 1.2% impurities is found to be the most corrosion resistant. Hence, further studies are made keeping this in mind.
5.2 EFFECT OF INHIBITORS ON THE CORROSION BEHAVIOR OF ALUMINIUM AND ITS ALLOY IN ALKALINE ELECTROLYTE

The charge capacity of aluminium – air cell could not be fully utilized due to the high rate of corrosion of aluminium in the alkaline media even when no current is being drawn from the cell. Earlier studies has revealed that the use of suitable aluminium alloy together with sodium hydroxide solution containing calcium oxide and sodium citrate to mitigate the problem to some extent. The use of inhibitors to combat corrosion in such situation is one of the well-known methods. The action of an inhibitor in aggressive media is presumed to be due to the control of the kinetics of the partial reactions of the corrosion process and / or due to its adsorption at the metal/solution interface. This phenomenon could take place via (i) electrostatic attraction between the charged metal and the charged inhibitor molecules, (ii) dipole type of interaction between uncharged parts in the inhibitor with the metal, (iii) $\pi$ - interaction with the inhibitor metal surfaces (iv) a combination of all the above [22].

If the adsorption process involves charge sharing or charge transfer from the inhibitor molecules to the surface (meaning overlap of occupied ligand non – bonding orbitals with metal empty inner “d” or “f” orbitals) a co-ordinate type bond is formed and the process is termed as chemisorption [23]. This situation can arise if the inhibitor molecule contains lone pairs of electrons or multiple bonds of conjugate $\pi$ - type system [24 – 28].

The use of thiosemicarbazones as inhibitors for the corrosion of aluminium in alkaline media has been discussed at length [25 – 28].
Following the clue from these papers, some thiosemicarbozone have been synthesized, characterized and evaluated as additives in the battery electrolyte for the corrosion inhibition of aluminium and its chosen alloy. The results are discussed below.

5.2.1 WEIGHT LOSS AND GASOMETRIC STUDIES

5.2.1.1 Studies with pure aluminium

The weight loss results of the compounds FrTSCN, CrTSCN, CnTSCN, ApTSCN, SaTSCN and 2meTSCN are presented in Tables 5.2.1 to 5.2.6. In all the cases the concentration of the inhibitor was varied from 5ppm to 50ppm. In the case of the compounds FrTSCN, CrTSCN, ApTSCN and 2meTSCN maximum protection efficiency was achieved at 40ppm concentration. But in the case of the compound CnTSCN this concentration is found to be slightly higher (i.e. 45ppm) and it is 25ppm in the case of SaTSCN. However, uniformly with all the inhibitors a slight decrease in inhibition is observed beyond the maximum protecting concentration. This could be attributed to the lateral repulsive interaction between the adsorbed molecules beyond the saturation coverage. This type of interaction has been identified to be dipole – dipole type in nature in the case of polar molecules and an image type of interaction in the case of non – polar molecules [29]. The performance rating of the inhibitors in the decreasing order from weight loss studies is as follows.

FrTSCN > CrTSCN > CnTSCN > ApTSCN > SaTSCN > 2meTSCN

The justification for this performance rating is discussed at the end of the section.
Table 5.2.1 Corrosion parameters of aluminium in electrolyte at different concentrations of FrTSCN by weight loss method

<table>
<thead>
<tr>
<th>Conc. of Inhibitor (ppm)</th>
<th>Corrosion rate mdd x 10^3</th>
<th>Equivalent corrosion current (mA/cm^2)</th>
<th>% of Inhibition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>192.0</td>
<td>23.8</td>
<td>---</td>
</tr>
<tr>
<td>5</td>
<td>140.0</td>
<td>17.4</td>
<td>27</td>
</tr>
<tr>
<td>10</td>
<td>136.0</td>
<td>16.9</td>
<td>29</td>
</tr>
<tr>
<td>15</td>
<td>136.0</td>
<td>16.9</td>
<td>29</td>
</tr>
<tr>
<td>20</td>
<td>125.0</td>
<td>15.5</td>
<td>35</td>
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<td>25</td>
<td>121.0</td>
<td>15.0</td>
<td>37</td>
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<td>30</td>
<td>117.0</td>
<td>14.5</td>
<td>39</td>
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<td>35</td>
<td>113.0</td>
<td>14.1</td>
<td>41</td>
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<td>40</td>
<td>107.0</td>
<td>13.3</td>
<td>44</td>
</tr>
<tr>
<td>45</td>
<td>109.0</td>
<td>13.6</td>
<td>43</td>
</tr>
<tr>
<td>50</td>
<td>111.0</td>
<td>13.8</td>
<td>42</td>
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</tbody>
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Table 5.2.2 Corrosion parameters of aluminium in electrolyte at different concentrations of CrTSCN by weight loss method

<table>
<thead>
<tr>
<th>Conc. of Inhibitor (ppm)</th>
<th>Corrosion rate mdd x 10^3</th>
<th>Equivalent corrosion current (mA/cm²)</th>
<th>% of inhibition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>192</td>
<td>23.8</td>
<td>---</td>
</tr>
<tr>
<td>5</td>
<td>144</td>
<td>17.9</td>
<td>25</td>
</tr>
<tr>
<td>10</td>
<td>140</td>
<td>17.4</td>
<td>27</td>
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<tr>
<td>15</td>
<td>136</td>
<td>16.9</td>
<td>29</td>
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<td>20</td>
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<td>50</td>
<td>115</td>
<td>14.3</td>
<td>40</td>
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</table>
Table 5.2.3 Corrosion parameters of aluminium in electrolyte at different concentrations of CnTSCN by weight loss method

<table>
<thead>
<tr>
<th>Conc. of Inhibitor (ppm)</th>
<th>Corrosion rate mdd x $10^3$</th>
<th>Equivalent corrosion current (mA/cm$^2$)</th>
<th>% of Inhibition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>192.0</td>
<td>23.8</td>
<td>---</td>
</tr>
<tr>
<td>5</td>
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Table 5.2.4 Corrosion parameters of aluminium in electrolyte at different concentrations of ApTSCN by weight loss method

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<th>Corrosion rate mdd x10^3</th>
<th>Equivalent corrosion current (mA/cm²)</th>
<th>% of Inhibition</th>
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<tbody>
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Table 5.2.5 Corrosion parameters of aluminium in electrolyte at different concentrations of SaTSCN by weight loss method

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<th>Conc. of Inhibitor (ppm)</th>
<th>Corrosion rate ( \text{mdd} \times 10^3 )</th>
<th>Equivalent corrosion current (mA/cm(^2))</th>
<th>% of Inhibition</th>
</tr>
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<td>28</td>
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Table 5.2.6 Corrosion parameters of aluminium in electrolyte at different concentrations of 2meTSCN by weight loss method

<table>
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<th>Conc. of Inhibitor (ppm)</th>
<th>Corrosion rate mdd $x10^3$</th>
<th>Equivalent corrosion current (mA/cm²)</th>
<th>% of Inhibition</th>
</tr>
</thead>
<tbody>
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<td>151.0</td>
<td>18.3</td>
<td>23</td>
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<td>144.0</td>
<td>17.8</td>
<td>25</td>
</tr>
<tr>
<td>15</td>
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<td>132.0</td>
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<tr>
<td>50</td>
<td>123.0</td>
<td>15.3</td>
<td>35</td>
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</table>
The weight loss results are always reliable and highly reproducible in corrosion studies in cases where the corrosion products are freely soluble and are removed easily leaving behind a clean metal surface. However, in the case of metals like Al, Mg, Zn, etc., in neutral and alkaline media one has to use suitable pickling bath, lest the weight loss results become questionable. Hence in this case gasometric studies have been carried out for the corrosion of pure aluminium in the battery electrolyte for the best protecting concentration of the inhibitors to have a counter check. The results are presented in Table 5.2.7. For the calculation of efficiency, the final steady volume of the gas collected at the end of 90 minutes duration has been taken. These values are not only in close agreement with weight loss results, but also indicate the same order of performance of the inhibitors. To have further confirmation of these results regarding the best performance, spectrophotometric analysis of the solution was carried out and the results are presented in Fig. 5.2.1 (calibration curve) and in Table 5.2.8. Here again the order of performance is reconfirmed. The best inhibition performance for pure Al in the electrolyte with FrTSCN can be taken as 40 – 45% and the least performance with 2meTSCN to be 30 – 35%.

5.2.1.2 Studies with Al – Alloy

Aluminium – alloy of composition Al + X +1.5% Pb has been evaluated for its dissolution behavior in the battery electrolyte with and without the inhibitors at the best protective concentration through weight loss and gasometric studies. The results are presented in Tables 5.2.9 and 5.2.10 respectively. Both the studies reveal the same trend as for pure aluminium except for a marginal increase of about 4 – 5% in the corrosion inhibition performance.
Fig. 5.2.1 Calibration curve for aluminium in electrolyte
Table 5.2.7 Inhibition efficiency (I.E) for aluminium in electrolyte containing best protecting concentration of inhibitors by gasometric method

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>TIME in minutes</th>
<th>I.E (%)</th>
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<tr>
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<tr>
<td>CrTSCN</td>
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<td>7.0</td>
</tr>
<tr>
<td>CnTSCN</td>
<td>4.0</td>
<td>7.0</td>
</tr>
<tr>
<td>ApTSCN</td>
<td>4.8</td>
<td>7.1</td>
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<td>SaTSCN</td>
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<td>7.3</td>
</tr>
<tr>
<td>2meTSCN</td>
<td>4.2</td>
<td>7.3</td>
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</table>

Table 5.2.8 Spectrophotometric studies – solution analysis from best performing inhibition studies

<table>
<thead>
<tr>
<th>Inhibitor in best concentration</th>
<th>Abs</th>
<th>ppm</th>
<th>I.E %</th>
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<tr>
<td>FrTSCN</td>
<td>0.780</td>
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<tr>
<td>CrTSCN</td>
<td>0.812</td>
<td>0.251</td>
<td>39.07</td>
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<tr>
<td>CnTSCN</td>
<td>0.821</td>
<td>0.254</td>
<td>38.35</td>
</tr>
<tr>
<td>ApTSCN</td>
<td>0.825</td>
<td>0.255</td>
<td>38.10</td>
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<td>SaTSCN</td>
<td>0.833</td>
<td>0.263</td>
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<td>2meTSCN</td>
<td>0.873</td>
<td>0.271</td>
<td>34.22</td>
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Table 5.2.9 Corrosion parameters of Al + X + 1.5 Pb in electrolyte at best protecting concentration by weight loss method

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>Corrosion rate mdd x 10^3</th>
<th>Equivalent corrosion current mA/cm²</th>
<th>I.E %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>136</td>
<td>169</td>
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</tr>
<tr>
<td>FrTSCN</td>
<td>69</td>
<td>85</td>
<td>49</td>
</tr>
<tr>
<td>CrTSCN</td>
<td>69</td>
<td>85</td>
<td>49</td>
</tr>
<tr>
<td>CnTSCN</td>
<td>70</td>
<td>87</td>
<td>48</td>
</tr>
<tr>
<td>ApTSCN</td>
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<td>89</td>
<td>47</td>
</tr>
<tr>
<td>SaTSCN</td>
<td>73</td>
<td>90</td>
<td>46</td>
</tr>
<tr>
<td>2meTSCN</td>
<td>75</td>
<td>92</td>
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</table>

Table 5.2.10 Inhibition efficiency (I.E) for Al + X + 1.5 Pb in electrolyte at best protecting concentration by gasometric method

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>TIME in minutes</th>
<th>Volume of gas collected in ml</th>
<th>I.E (%)</th>
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<td>15</td>
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<tr>
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<td>10.9</td>
<td>15.9</td>
</tr>
<tr>
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<td>CnTSCN</td>
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<td>5.8</td>
<td>8.8</td>
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<tr>
<td>ApTSCN</td>
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<td>5.9</td>
<td>9.0</td>
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<tr>
<td>SaTSCN</td>
<td>3.3</td>
<td>5.9</td>
<td>8.9</td>
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<tr>
<td>2meTSCN</td>
<td>3.3</td>
<td>6.0</td>
<td>9.1</td>
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Spectrophotometric studies could not be carried out in the case of aluminium-alloy as for pure aluminium because of the interference of some of the alloying elements.

5.2.2 Electrochemical Polarization Studies
5.2.2.1 With pure aluminium electrode

The use of potentiodynamic technique to evaluate the corrosion rate through Tafel extrapolation method is well known. In this technique proper choice of scan rate is important to get reproducible values that represent the steady state condition of the corrosion process. Mansfled and Kending have discussed in detail the scan rate dependent of corrosion rates and the sources of inaccurate values [30]. The main result of these analysis is that a responsible estimate of the corrosion rate from polarization measurements can be obtained for scan rates less than 60mV/min. In the present studies a constant scan rate of 1 mV/sec has been adopted. The results obtained with pure aluminium electrodes in the battery electrolyte without and with inhibitors of different concentrations are presented in Tables 5.2.11 to 5.2.16 and in Figs.5.2.2 to 5.2.7. For clarity of the figures only five selected concentrations of the inhibitors besides the control are presented. The order of performance of the compounds evaluated from the $i_{\text{corr}}$ values with respective to the control bring out the same trend as that from other studies. There is scatter in the values of $b_a$ and $b_c$ and this is quite understandable when considering the difficulties in getting reproducible values with solid electrodes of high surface heterogeneity and fast exothermic dissolution reaction in the strong alkaline medium. Hence the predication regarding the control of the corrosion reaction by the
Table 5.2.11 Electrochemical polarization measurements of aluminium in electrolyte at different concentrations of FrTSCN

<table>
<thead>
<tr>
<th>Conc of Inhibitor (ppm)</th>
<th>OCP (V)</th>
<th>$E_{corr}$ (V)</th>
<th>$i_{corr}$ (mA/cm$^2$)</th>
<th>Tafel Slope (mV/dec)</th>
<th>Inhibition Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
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<td>-1.297</td>
<td>47.76</td>
<td>185</td>
<td>165</td>
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<td>-1.300</td>
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<td>90</td>
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<td>-1.314</td>
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<td>165</td>
<td>125</td>
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<td>-1.312</td>
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<td>100</td>
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Table 5.2.12 Electrochemical polarization measurements of aluminium in electrolyte at different concentrations of CrTSCN

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<th>OCP (V)</th>
<th>$E_{corr}$ (V)</th>
<th>$i_{corr}$ (mA/cm$^2$)</th>
<th>Tafel Slope (mV/dec)</th>
<th>Inhibition Efficiency (%)</th>
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<td>165</td>
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Table 5.2.13 Electrochemical polarization measurements of aluminium in electrolyte at different concentrations of CnTSCN

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<th>OCP (V)</th>
<th>$E_{corr}$ (V)</th>
<th>$i_{corr}$ (mA/cm$^2$)</th>
<th>Tafel Slope (mV/dec)</th>
<th>Inhibition Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
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<td>-1.297</td>
<td>47.76</td>
<td>185</td>
<td>165</td>
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Table 5.2.14 Electrochemical polarization measurements of aluminium in electrolyte at different concentrations of ApTSCN

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Table 5.2.15 Electrochemical polarization measurements of aluminium in electrolyte at different concentrations of SaTSCN

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<th>Tafel Slope (mV/dec)</th>
<th>Inhibition Efficiency (%)</th>
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Table 5.2.16 Electrochemical polarization measurements of aluminium in electrolyte at different concentrations of 2meTSCN

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Fig. 5.2.2 Electrochemical polarization curves of aluminium in electrolyte containing different concentrations of FrTSCN
(a) Control (b) 10 ppm (c) 20 ppm (d) 30 ppm (e) 40 ppm (f) 50 ppm
Fig. 5.2.3 Electrochemical polarization curves of aluminium in electrolyte containing different concentrations of CrTSCN
(a) Control (b) 10ppm (c) 20 ppm (d) 30 ppm (e) 45 ppm (f) 50 ppm
Fig. 5.2.4 Electrochemical polarization curves of aluminium in electrolyte containing different concentrations of CnTSCN
(a) Control (b) 10 ppm (c) 20 ppm (d) 30 ppm (e) 40 ppm (f) 50 ppm
Fig. 5.2.5 Electrochemical polarization curves of aluminium in electrolyte containing different concentrations of ApTSCN.
(a) Control (b) 10 ppm (c) 20 ppm (d) 30 ppm (e) 40 ppm (f) 50 ppm.
Fig. 5.2.6 Electrochemical polarization curves of aluminium in electrolyte containing different concentrations of SaTSCN
(a) Control (b) 15 ppm (c) 25 ppm (d) 35 ppm (e) 45 ppm (f) 50 ppm
Fig. 5.2.7 Electrochemical polarization curves of aluminium in electrolyte containing different concentrations of 2meTSCN
(a) Control (b) 10ppm (c) 20 ppm (d) 30 ppm (e) 45 ppm (f) 50 ppm
inhibitors has been made by considering the reduction in partial currents of the corrosion process at a reference potential ($E_{\text{corr}} \pm 100 \text{mV}$). The results are presented in Tables 5.2.17 to 5.2.22. From the results it is clear that all the inhibitors control the dissolution of the metal in the electrolyte by influencing the metal dissolution and hydrogen evaluation process almost to equal extent i.e. they act as mixed-type inhibitors. This is supported by the absence of any appreciable shift in the $E_{\text{corr}}$ values.

5.2.2.2 With aluminium – alloy electrode

The polarization results with aluminium – alloy of composition mentioned earlier in battery electrolyte are presented in Table 5.2.23 and in Fig.5.2.8. The same trend of results as for pure aluminium is revealed. From the Table 5.2.24 where partial currents at the common reference potential are presented, the mixed-type control of the inhibitors with this electrode gets confirmed.

5.2.2.3 Impedance Measurements

5.2.3.1 With pure aluminium electrode

The impedance results for the corrosion of pure aluminium in the battery electrolyte in presence of different concentrations of the thiosemicarbazones are presented as Nyquist plots in Figs. 5.2.9 to 5.2.14 in Tables 5.2.25 to 5.2.30. For clarity of the figures only five or six selected concentrations of the inhibitors besides the control are presented. The introduction of inhibitors in to the electrolyte has not altered basically the dissolution of mechanism of aluminium in Ca$^{2+}$-citrate complexed alkaline electrolyte. This is evident from the appearance of the same two-semi circular impedance diagram with smaller one appearing on the low frequency end as in the case of corrosion of pure aluminium or its alloy in
Fig. 5.2.8 Electrochemical polarization curves of Al + X +1.5%P in electrolyte containing best protecting concentrations of inhibitors (a) FrTSCN (b) CrTSCN (c) CnTSCN (d) ApTSCN (e) SaTSCN (f) 2meTSCN
Table 5.2.17 Reduction in partial currents at $E_{corr} \pm 100$ mV for different concentrations of FrTSCN : Aluminium in electrolyte (Polarization result)

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<th>Conc. of Inhibitor (ppm)</th>
<th>$E_{corr}$ (V)</th>
<th>Current (A) at $E_{corr} \pm 100$ mV</th>
<th>% Reduction in partial Currents</th>
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Table 5.2.18 Reduction in partial currents at $E_{corr} \pm 100$ mV for different concentrations of CrTSCN : Aluminium in electrolyte (Polarization result)

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Table 5.2.19 Reduction in partial currents at $E_{\text{corr}} \pm 100$ mV for different concentrations of CnTSCN: Aluminium in electrolyte (Polarization result)

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Table 5.2.21 Reduction in partial currents at $E_{corr} \pm 100$ mV for different concentrations of SaTSCN : Aluminium in electrolyte (Polarization result)

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Table 5.2.22 Reduction in partial currents at $E_{\text{corr}} \pm 100$ mV for different concentrations of 2meTSCN: Aluminium in electrolyte (Polarization result)

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<th>Current (A) at $E_{\text{corr}} \pm 100$ mV</th>
<th>% Reduction in partial currents</th>
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</tr>
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<td>-1.340</td>
<td>0.02985</td>
<td>0.01217</td>
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Table 5.2.23 Electrochemical polarization of Al + X + 1.5% Pb in electrolyte using inhibitors at their best protecting concentration

<table>
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<tr>
<th>Inhibitor</th>
<th>OCP (V)</th>
<th>$E_{\text{corr}}$ (V)</th>
<th>$i_{\text{corr}}$ mA/cm²</th>
<th>Tafel slope mV/dec</th>
<th>I.E %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>-1.318</td>
<td>-1.326</td>
<td>36.74</td>
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<td>90</td>
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<tr>
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<td>-1.330</td>
<td>18.73</td>
<td>160</td>
<td>140</td>
</tr>
<tr>
<td>CrTSCN</td>
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<td>-1.340</td>
<td>19.10</td>
<td>110.0</td>
<td>90</td>
</tr>
<tr>
<td>CnTSCN</td>
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<td>-1.350</td>
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<td>140</td>
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<tr>
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<td>-1.347</td>
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<td>110</td>
</tr>
<tr>
<td>SaTSCN</td>
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<td>-1.353</td>
<td>20.94</td>
<td>100</td>
<td>90</td>
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<tr>
<td>2meTSCN</td>
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<td>-1.360</td>
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Table 5.2.24 Reduction in partial currents at $E_{\text{corr}} \pm 100$ mV for best protecting concentration of inhibitors: Al + X + 1.5% Pb in electrolyte (Polarization results)

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>$E_{\text{corr}}$ (V)</th>
<th>Current (A) at $E_{\text{corr}} \pm 100$ mV</th>
<th>% Reduction in partial currents</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>Anodic $i_a$</td>
<td>Cathodic $i_c$</td>
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<td>0.00650</td>
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<td>0.00665</td>
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139
Table 5.2.25 Impedance measurements of aluminium in electrolyte for different concentrations of FrTSCN

<table>
<thead>
<tr>
<th>Concentration ppm</th>
<th>$R_t$ Ohm cm$^2$</th>
<th>$\theta$</th>
<th>I.E %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
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<td>---</td>
<td>---</td>
</tr>
<tr>
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<td>0.33</td>
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<td>35</td>
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Table 5.2.26 Impedance measurements of aluminium in electrolyte for different concentrations of CrTSCN

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<th>R_i ohm cm^2</th>
<th>θ</th>
<th>I.E %</th>
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Table 5.2.27 Impedance measurements of aluminium in electrolyte for different concentrations of CnTSCN

<table>
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<th>$R_t$ (ohm cm$^2$)</th>
<th>$\Theta$</th>
<th>I.E %</th>
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</thead>
<tbody>
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Table 5.2.28 Impedance measurements of aluminium in electrolyte for different concentrations of ApTSCN

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Table 5.2.29 Impedance measurements of aluminium in electrolyte for different concentrations of SaTSCN

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<th>$\theta$</th>
<th>I.E %</th>
</tr>
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<tbody>
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Table 5.2.30 Impedance measurements of aluminium in electrolyte for different concentrations of 2meTSCN

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<th>$R_t$ Ohm cm$^2$</th>
<th>$\theta$</th>
<th>I.E %</th>
</tr>
</thead>
<tbody>
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Fig. 5.2.9 Nyquist plots for the corrosion of aluminium in electrolyte containing various concentration of BrTSCN
(a) Control (b) 5ppm (c) 25ppm (d) 35ppm (e) 50ppm (f) 45ppm
Fig. 5.2.10 Nyquist plots for the corrosion of aluminium in electrolyte containing various concentration of CrTSCN
(a) Control (b) 5ppm (c) 20ppm (d) 35ppm (e) 50ppm (f) 45ppm
Fig. 5.2.11 Nyquist plots for the corrosion of aluminium in electrolyte containing various concentration of CnTSCN
(a) Control (b) 5ppm (c) 15ppm (d) 25ppm (e) 35ppm (f) 50ppm (g) 40ppm
Fig. 5.2.12 Nyquist plots for the corrosion of aluminium in electrolyte containing various concentration of ApTSCN
(a) Control (b) 5ppm (c) 15ppm (d) 50ppm (e) 35ppm (f) 40ppm
Fig. 5.2.13 Nyquist plots for the corrosion of aluminium in electrolyte containing various concentration of SaTSCN
(a) Control (b) 5ppm (c) 15ppm (d) 50ppm (e) 30ppm (f) 25ppm
Fig. 5.2.14 Nyquist plots for the corrosion of aluminium in electrolyte containing various concentration of 2meTSCN
(a) Control (b) 5ppm (c) 35ppm (d) 50ppm (e) 45ppm (f) 20ppm
the medium referred. However the inhibitors have been able to retard both the anodic and cathodic parts of the corrosion process. The $R_1$ values truly record the trend of inhibition as in other studies. From the inverse of $R_1$ values, $\theta$ values have been calculated and the values fairly well compare with the values of weight loss studies. Uniformly in all the cases the missing of any rising portion at the low frequency end indicate the absence of any diffusion control. Further, the more or less symmetrical semicircles encountered with all the inhibitors ensure the predominant charge transfer control of the corrosion process.

5.2.3.1 With aluminium - alloy electrode

The impedance results for the corrosion behavior of aluminium –alloy in the battery electrolyte in presence of the best protecting concentration of different inhibitors are presented in Fig. 5.2.15 and in Table 5.2.31. In the case of the best performing inhibitors like FrTSCN and CrTSCN the second semi circle in the low frequency end has become less significant suggesting that in presence of the good adsorption by these molecules the slow adsorption of the Ca$^{2+}$ - citrate complex has become relatively negligible. However in the case of relatively poor performing 2meTSCN the appearance of the second semi circle is prominent. The $R_1$ values indicate the same trend of inhibition.

5.2.4 Hydrogen permeation studies

The hydrogen uptake by metals during the corrosion process in aqueous electrolytes has been a subject of great interest as it is related to the structural defects of the metal and / or dependent on the mechanism of
Fig. 5.2.15 Nyquist plots for the corrosion of aluminium - alloy in electrolyte containing various inhibitors
(a) Control (b) 2meTSCN (c) SaTSCN (d) ApTSCN (e) CnTSCN
(f) CrTSCN (g) Fr TSCN

Z\text{im} (\text{ohm})

Z\text{re} (\text{ohm})

0 1.0 2.0 3.0 4.0 5.0 6.0 7.0

500 1000 1500 2000
hydrogen evolution reaction over the metal substrate. Devanathan and Stachurski's were the first to introduce an elegant method to study the electro permeation and this has been improved recently [31,32]. This technique has been widely used for hydrogen uptake studies using palladium, steel and other transition metals [33–36]. Little work has been reported on permeation studies using aluminium. Chu Young Chan et al. [37] have studied hydrogen permeation through pure aluminium using the hydrogen permeation method. Ono Chu Kwu and Trasatti [38] have studied the permeation of hydrogen through the aluminium alloy AA1060 in alkaline medium. Ono Chu Kewu et al [39] have also studied the influence of different anions and temperature on the extent of hydrogen permeation through aluminium in alkaline medium. In the present investigation, the influence of inhibitors (only for the best protecting concentration) on the extent to which hydrogen has permeated through pure aluminium sheets in battery electrolytes, have been monitored and the results are presented in Table 5.2.32 and in Fig. 5.2.16. It is noted that all the compounds are able to reduce the permeation current. This can be explained as follows. The overall chemical reaction of aluminium dissolution can be written as [40].

$$\text{Al (s) } + 2 \text{OH}^- (\text{aq}) \rightarrow \text{AlO}_2^- + \text{H}_2 \uparrow \text{ } \text{ } (5.8)$$

During hydrogen evolution it is adsorbed as atomic hydrogen on the metal surface, which is subsequently, discharged as gaseous hydrogen molecule or surface diffused atomic hydrogen that permeates into metal vacancies. The decreased permeation currents in presence of the inhibitors indicate that the cathodic process consists of a slow electrodic discharge of
Table 5.2.31 Impedance measurements of Al + X + 1.5% Pb in electrolyte using inhibitors at their best protecting concentration

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>$R_t$ (Ohm cm$^2$)</th>
<th>$\Theta$</th>
<th>I.E (%)</th>
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<tbody>
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Table 5.2.32. Permeation current measurement of aluminium in electrolyte using inhibitors at their best protecting concentration

<table>
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<th>I.E (%)</th>
</tr>
</thead>
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</table>
Fig. 5.2.16 Hydrogen permeation curve for aluminium in electrolyte containing various inhibitors
hydrogen followed by fast desorption of the adsorbed hydrogen from the metal surface.

5.2.5 Adsorption isotherm

The adsorption of an organic molecule on the surface of the metal involves replacement of some water molecules adsorbed on the electrode surface. For most of the organic inhibitors with polar atoms, the adsorption is an inevitable process that contributes mainly to the inhibition. Besides the well known isotherms, some substitutional isotherms like Flory – Huggins, Dhar–Flory – Huggins [41] and Bockris – Swinkles [42] isotherms with configurational terms involving the ratio (y) of the number of water molecules replaced by some organic molecules [43] have been cited. With stimulated values for x, correlation has been predicted for the corresponding isotherms. The kinetic – thermodynamic model based on Florry – Huggins statistics (44 – 45) that envisages the adsorption process wherein a given inhibitor molecule occupies a number of (1/y) surface sites is presented as follows

\[
\log \frac{\theta}{(1- \theta)} = \log K + y \log C \quad \text{--------} (5.9)
\]

The \( \theta \) values have been computed using weight loss results obtained for the corrosion of pure aluminium in battery electrolyte in presence of different inhibitors. The linear plots of \( \log \theta / (1- \theta) \) Vs \( \log C \) are shown in Figs. 5.2.17 to 5.2.22. The corresponding adsorption parameters are presented in Table 5.2.33. Values of y greater than one imply the formation of multi layers of the inhibitor on the surface of the metal, however values of y less than one mean that a given inhibitor molecule will
occupy more than one active site. The value of binding energy constant ‘K’ is related to K’ through the equation

\[ K = K'^{(1/y)} \]  

(5.10)

The standard free energy of adsorption \( \Delta G^\circ_{\text{ads}} \) is related to the equation constant K [46]

\[ K = (1/55.5) \exp (- \Delta G^\circ_{\text{ads}} / RT) \]  

(5.11)

The values of 1/y less than unity uniformly in all the cases indicate that the given inhibitor molecule will occupy more than one active site. The small binding constant values and the free energy of adsorption values indicate the interaction between adsorbing molecule and the metal surface to be weak denoting that the molecules are easily removable from the surface. This is evident from the low inhibition values i.e. a maximum of 45 to 50% percent only. The highly exothermic dissolution reaction of aluminium in alkaline medium with the formation of highly soluble aluminate complexes could be the reason for the poor adsorption process.

5.2.6 Mechanism of inhibition and justification for the performance

The inhibition of metallic corrosion with use of effective inhibitors results in the simultaneous action of control of the activation energies of the partial reactions of the corrosion process and by through the adsorption of the inhibitor molecules on the metal surface forming a barrier layer. With many organic molecules the adsorption process could be a significant factor. The adsorption process could be regarded as a quasi – substitution process between the organic compound in the solution and the
Table 5.2.33  kinetic and thermodynamic model for the adsorption of
the inhibitors

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>1/y</th>
<th>Binding energy constant K</th>
<th>$\Delta G^0$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FrTSCN</td>
<td>0.3922</td>
<td>0.077400</td>
<td>-2.1290</td>
</tr>
<tr>
<td>CrTSCN</td>
<td>0.4121</td>
<td>0.045760</td>
<td>-1.3614</td>
</tr>
<tr>
<td>CnTSCN</td>
<td>0.4292</td>
<td>0.040685</td>
<td>-1.1897</td>
</tr>
<tr>
<td>ApTSCN</td>
<td>0.4468</td>
<td>0.035852</td>
<td>-1.0050</td>
</tr>
<tr>
<td>SaTSCN</td>
<td>0.4537</td>
<td>0.034560</td>
<td>-0.9514</td>
</tr>
<tr>
<td>2meTSCN</td>
<td>0.4731</td>
<td>0.030960</td>
<td>-0.7907</td>
</tr>
</tbody>
</table>
Fig. 5.2.17 Application of kinetic thermodynamic model for the adsorption of FrTSCN on aluminium surface in battery electrolyte

Fig. 5.2.18 Application of kinetic thermodynamic model for the adsorption of CrTSCN on aluminium surface in battery electrolyte
Fig. 5.2.19 Application of kinetic thermodynamic model for the adsorption of CnTSCN on aluminium surface in battery electrolyte

Fig. 5.2.20 Application of kinetic thermodynamic model for the adsorption of ApTSCN on aluminium surface in battery electrolyte
Fig. 5.2.21 Application of kinetic thermodynamic model for the adsorption of SaTSCN on aluminium surface in battery electrolyte

Fig. 5.2.22 Application of kinetic thermodynamic model for the adsorption of 2meTSCN on aluminium surface in battery electrolyte

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water molecules at the electrode surface represented through the following equation.

\[
\text{Org}_{(aq)} + x \text{H}_2\text{O}_{(s)} \rightleftharpoons \text{Org}_{(s)} + x \text{H}_2\text{O} \quad (5.12)
\]

Where \(x\) is the number of water molecules that are displaced by one organic molecule. The most frequently used isotherm is of the general form.

\[
f(\theta, x) \exp(-2a\theta) = K_c \quad (5.13)
\]

Where \(f(\theta, x)\) is the configurational factor which depends on the physical model and the assumptions used in the isotherm [47]. The other terms have their usual meaning.

In the present study all the inhibitors used are found to be mixed type inhibitors implying that they control both the anodic and cathodic reactions to an equal extent.

The adsorption of the thiosemicarbazones in preference to thiosemicarbazide wherein there is practically negligible inhibition, may be attributed to the rigidity of the \(\pi\) - delocalised system compared to the saturated thiosemicarbazide molecule which exerts free rotation, thus decreasing the possibility of its attachment to the metal surface. The inhibiting action of thiosemicarbazone has been mainly attributed to the adsorption of the thio - carbonyl group on the metal surface [48 – 52]. The performance order of the compounds is directly related to the electron density at the adsorption center \(\text{\overset{c}{\overset{\sim}{s}}}\) and the shielding or deshielding of this polar center by the rest of the molecule. The highest protection
efficiency obtained for FrTSCN is due to the interaction of heterocyclic moiety that increases the delocalised π-electron density at the center of adsorption. The poor performance of the 2meTSCN may be due to the shielding of the polar center by the methyl group.

In the case SaTSCN, the intra molecular hydrogen bonding could cause decrease of electron density around the sulphur atom and possibly lead to lesser adsorption. The shifting of the –OH frequency in IR studies to longer wavelengths supports this. Among the compounds CrTSCN and CnTSCN, the CH₃CH=CH– group is more electron releasing than C₆H₅CH=CH– and hence the order of performance is CrTSCN > CnTSCN (Phenyl ring in this scale acting as electron sink).
In the case of ApTSCN, the effect of electron releasing methyl group is partly nullified by electron withdrawing phenyl ring. This accounts for its performance.

**SUMMARY**

The summary of the results of the above section can be represented as below.

<table>
<thead>
<tr>
<th>Nature of the metal</th>
<th>Electrolyte</th>
<th>OCP (Vs Hg/HgO)</th>
<th>Corrosion inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Al</td>
<td>4N NaOH</td>
<td>-1.500</td>
<td>---</td>
</tr>
<tr>
<td>Pure Al</td>
<td>Battery Electrolyte</td>
<td>-1.301</td>
<td>15.87</td>
</tr>
<tr>
<td>Pure Al</td>
<td>Battery Electrolyte with best inhibitor</td>
<td>-1.334</td>
<td>44.00</td>
</tr>
<tr>
<td>Al – Alloy</td>
<td>Battery Electrolyte</td>
<td>-1.318</td>
<td>30.00</td>
</tr>
<tr>
<td>Al – Alloy</td>
<td>Battery Electrolyte in presence of best inhibitor (FrTSCN)</td>
<td>-1.418</td>
<td>49.00</td>
</tr>
</tbody>
</table>
From the studies it is clear that there is definite advantage in using aluminium – alloy of 96.217% Al + 1.51% Pb + 0.096%Ga + 0.977% In + 1.2% Impurities composition in battery electrolyte of 4N NaOH + 20% citric acid + 0.4% CaO composition in presence of the best performing inhibitor FrTSCN in terms of reduction in self corrosion, without much loss of open circuit potential.

5.3 STUDIES ON THE APPLICATION OF THE INHIBITORS TO ALUMINIUM – AIR CELL

5.3.1 Cyclic Voltammetry studies

The ultimate aim of the present investigation is to identify some effective inhibitors, which could find application in Aluminium – air cells. As a first step in this direction the thiosemicarbazones tested earlier to minimize the self-corrosion of the aluminium alloy in the battery electrolyte, have to be assessed for their interference if any on the oxygen reduction performance of the porous carbon electrode.

The cyclic voltammetry studies were carried out on porous carbon electrode of geometrical area 1 cm² as working electrode, Hg / HgO OH⁻ as the reference electrode and platinum foil as the counter electrode. The working electrode was half immersed in the battery electrolyte and the potentials were cycled from –700mV to 0mV at a constant scan rate of 1mV/s. The experiments were performed without and with the inhibitors at their maximum protecting concentrations. The results are presented in Table 5.3.1 and in Figs. 5.3.1 to 5.3.7.
It is clear from the results that both the cathodic and anodic currents have not been affected significantly in presence of the inhibitors than in their absence, indicating that the inhibitors do not hinder the oxygen reduction rate on the carbon electrode. Hence they can be safely tried as useful additives in aluminium – air cell.

5.3.2 Discharge studies of Aluminium – air cell

The aim of the study is to find out whether the inhibitors are able to reduce self-corrosion of the aluminium anode without hindering the cathodic oxygen reduction reaction and thereby results in the improvement in the ampere hour capacity of the cell. Each inhibitor was used at its maximum protecting concentration. The results are presented in Table 5.3.2 and in Fig. 5.3.8.

SUMMARY

The additives tried are found to be useful for aluminium – air cell application to the extent they help to increase the ampere – hour capacity of the cell by nearly 10 – 15% compared to the performance in the Control battery electrolyte.
Table 5.3.1 Cyclic Voltammetry studies of carbon electrode in electrolyte using inhibitors at their best protecting concentrations at a scan rate of 1mV/s

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>$E_p^a$ (mV)</th>
<th>$I_p^a$ (mA)</th>
<th>$E_p^c$ (mV)</th>
<th>$I_p^c$ (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>-199.8</td>
<td>17.59</td>
<td>527.8</td>
<td>-13.54</td>
</tr>
<tr>
<td>FrTSCN</td>
<td>-199.4</td>
<td>17.24</td>
<td>520.8</td>
<td>-13.27</td>
</tr>
<tr>
<td>CrTSCN</td>
<td>-187.8</td>
<td>16.71</td>
<td>490.5</td>
<td>-12.86</td>
</tr>
<tr>
<td>CnTSCN</td>
<td>-202.5</td>
<td>18.32</td>
<td>526.0</td>
<td>-14.15</td>
</tr>
<tr>
<td>ApTSCN</td>
<td>-190.0</td>
<td>16.73</td>
<td>497.0</td>
<td>-12.88</td>
</tr>
<tr>
<td>SaTSCN</td>
<td>-187.3</td>
<td>16.71</td>
<td>480.1</td>
<td>-12.86</td>
</tr>
<tr>
<td>2meTSCN</td>
<td>-186.6</td>
<td>16.64</td>
<td>487.4</td>
<td>-12.86</td>
</tr>
</tbody>
</table>
Fig. 5.3.1 Cyclic Voltammetric studies for carbon electrode in electrolyte

Fig. 5.3.2 Cyclic Voltammetry studies of carbon electrode in electrolyte containing FrTSCN
Fig. 5.3.3 Cyclic Voltammetry studies of carbon electrode in electrolyte containing CrTSCN

Fig. 5.3.4 Cyclic Voltammetry studies of carbon electrode in electrolyte containing CnTSCN
Fig. 5.3.5 Cyclic Voltammetry studies of carbon electrode in electrolyte containing ApTSCN

Fig. 5.3.6 Cyclic Voltammetry studies of carbon electrode in electrolyte containing SaTSCN
Fig. 5.3.7 Cyclic Voltammetry studies of carbon electrode in electrolyte containing 2meTSCN
Table 5.3.2 Performance of inhibitors in Aluminium – air cell

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>OCP (V)</th>
<th>Theoretical ampere hour capacity</th>
<th>Experimental ampere hour capacity</th>
<th>% Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>-1.499</td>
<td>4.610</td>
<td>1.49</td>
<td>33</td>
</tr>
<tr>
<td>FrTSCN</td>
<td>-1.487</td>
<td>3.267</td>
<td>1.45</td>
<td>45</td>
</tr>
<tr>
<td>CrTSCN</td>
<td>-1.489</td>
<td>3.210</td>
<td>1.39</td>
<td>44</td>
</tr>
<tr>
<td>CnTSCN</td>
<td>-1.497</td>
<td>3.239</td>
<td>1.42</td>
<td>43</td>
</tr>
<tr>
<td>ApTSCN</td>
<td>-1.487</td>
<td>3.245</td>
<td>1.29</td>
<td>41</td>
</tr>
<tr>
<td>SaTSCN</td>
<td>-1.485</td>
<td>3.482</td>
<td>1.36</td>
<td>40</td>
</tr>
<tr>
<td>2meTSCN</td>
<td>-1.489</td>
<td>3.288</td>
<td>1.24</td>
<td>37</td>
</tr>
</tbody>
</table>
Fig. 5.3.8  Discharge curve of aluminium – air cell in electrolyte using inhibitors at constant load of 35 ohms
References


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52. B.I. Ita and E. Offiong, Inhibition of Steel Corrosion in Hydrochloric acid by Pyridoxal (4-ethyl semicarbazide), Pyridoxyl (4-methyl thiosemicarbazone) and its Zn (II)-complex, Materials Chemistry and Physics, 48 (1997) 164.