The Development of Electrolytes in Aluminium Electrolytic Capacitors for Automotive and High Temperature Applications

Zongli Dou, Rong Xu, Alfonso Berduque

Research and Development Department, BHC Components LTD (KEMET),
20 Cumberland Drive, Granby Industrial Estate, Weymouth, Dorset DT4 9TE, United Kingdom.
Telephone: 0044 1305 830724. Facsimile: 0044 1305 760670
E-mail: ZongliDou@Kemet.com

Abstract

Various electrolytes for use in aluminium electrolytic capacitors, working in automotive applications and other industrial applications where longer lifetimes are desired at 125 ºC and up to 400 V, have been developed or tested. These electrolytes are based on \( \gamma \)-butyrolactone as a major solvent and organic dicarboxylic acids neutralised with organic bases as solutes or conductive salts. Effects of temperatures from -55 to +125 ºC on the parameters such as conductivity and dielectric breakdown voltages of the electrolytes have been investigated using conventional laboratory techniques. The initial work has been concentrated on the development of 40, 63 & 400 V working electrolytes. Endurance tests showed reliable performance working over 6000 hours for 40 & 63 V and 4000 hours for 400 V in screw terminal capacitors with ripple current applied at the upper category working temperature. The development of 100 and 200 V working electrolytes is currently in progress.

The key technologies necessary in the development of electrolytes and the effects of the resultant electrolyte on the overall performance of capacitors, such as dielectric breakdown voltages and stability during endurance testing, are discussed.

1. Introduction

An increasing demand of electronic components suitable for automotive industries,\(^1\) drive industries and other potential industrial applications for longer lifetimes has driven the development of aluminium electrolytic capacitors operating at high temperatures. The overall performance of aluminium electrolytic capacitors for high temperature applications depends mainly on the properties and capabilities of a non-aqueous electrolyte or fill electrolyte used,\(^2\) among other important items such as anode and cathode foils. Much industrial effort has thus been made in the study of electrolytes. However, few studies associated directly with electrolyte development, electrolyte parameters and capacitor performance have been published. This work presents the development of electrolytes in aluminium electrolytic capacitors with an operating voltage range of 40, 63, 100, 200 and 400 V, for automotive and other industrial applications at high temperature up to 125 ºC.

The general requirements for an electrolyte with capability to work at 125 ºC include:

- Excellent reliability at operating voltages, and dielectric breakdown voltages greater than working voltages;\(^3\)
- Appropriate anodizing capability to form the edges of the anode and tab foils, as well as to heal any flaws on the aluminium oxide;
- Good ionic conductivity to reduce ESR;
- Remarkable chemical stability during capacitor application at working voltage at 125 ºC;
- Optimum pH values and outstanding chemical compatibility with aluminium foil, papers, plastic deck, rubber seal ring & vent;
- Extended working temperature ranges, from -55 to 125 ºC;
- Excellent wettability and swellability to papers at impregnation, \( e.g. \), with reduced surface tension & viscosity;
- Reduced vapour pressure to minimise the internal pressure at 125 ºC;
- Environmentally friendly and cost effective.
2. Experiments

2.1 Electrolyte Preparations, Measurements and Tests

All electrolytes developed in this work were based on γ-Butyrolactone (BLO) solvent, which has a melting point of -45 °C and a boiling point of 204 °C sufficiently well above the capacitor highest working temperature of 125 °C. The solutes used were different conductive salts, acids and bases, and also some additives such as corrosion inhibitors and hydrogen absorbers.

A certain portion of solid solutes were added to a container containing BLO based solvent and other liquid ingredients, followed by stirring and heating up to dissolve the solid solutes. The solution was maintained at a certain temperature with stirring to reduce the water content before cooling down to room temperature for parameter measurement.

Parameters of the resultant electrolyte, i.e., water content, conductivity, pH, dielectric breakdown voltage and density were measured before further tests. The water content of the electrolyte was measured using a Karl Fisher titration (AQUAPAL III titration instrument); the conductivity and pH using a PHM220 Lab pH meter and a CDM210 Conductivity meter, both from MeterLab. The dielectric breakdown voltage was determined using an in-house fabricated dielectric breakdown voltage system, by applying a constant current of 3 mA to a pre-formed anode foil cut into the size of 5 × 4 cm in a testing electrolyte. The density of an electrolyte was measured using a density bottle method, i.e., filling one bottle with an electrolyte and another bottle with water as a reference with a density of 1.0 gram cm⁻³, and measuring the respective masses at a constant temperature of 20 °C.

2.2 Capacitor Preparation and Endurance Tests

The completed windings, after winding both anode and cathode foils with tab foil attached and simultaneously interleaved with absorbent papers and attached to a plastic deck or cap with aluminium terminals, were impregnated with an electrolyte in a 10 litre stainless steel vacuum / pressure vessel. Each impregnated winding was then sealed in an aluminium can, aged up in the Laboratory before initial capacitor measurement of capacitance (C), equivalent series resistance (ESR) and impedance (Z). An Agilent 4263B LCR Meter was used for capacitance and ESR measurement at 100 Hz, 0.5 V at 20 °C, and impedance at 10 KHz, 0.5 V at 20 °C.

Endurance tests were carried out by application of a constant voltage (DC) with ripple voltage (AC) equivalent to the maximum working voltage to the capacitors connected in pairs in an oven at the upper category operating temperature of 125 °C. The constant voltage was provided by a Nemic–Lambda Genesys™ GENH600–1.3 programmable regulated DC power supply, and the calculated maximum allowable ripple current by a lab constructed variable Transformer. An Agilent 34970A Data Acquisition System was used to monitor and record the leakage current – time continuously. Each 1000 hours during endurance tests, the capacitors were discharged, cooled down to room temperature, disconnected and removed from the oven before the measurement of capacitance, ESR and impedance at 20 °C. The capacitors were then re-placed into the oven, reconnected, reheated to 125 °C and the endurance tests resumed until next 1000 hours’ interval.

3. Results

3.1 Electrolyte Tests: 40, 63, 100, 200 and 400 V

3.1.1 Electrolyte Parameters

The parameters of five electrolytes, with working voltages at a range of 40, 63, 100, 200 and 400 volts and working temperature at a range of -55 to 125 °C, are illustrated in Table 1. These electrolytes are named as WEY–040, WEY–063, WEY–100, WEY–200 and WEY–400 respectively.
### Table 1. Electrolyte parameters.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Water (wt%, at 25 ºC)</th>
<th>( \kappa ) (mS cm(^{-1} ), at 25 ºC)</th>
<th>pH (at 25 ºC)</th>
<th>Breakdown V (V, at 90 ºC)</th>
<th>Density (g cm(^{-3} ), at 20 ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WEY-040</td>
<td>0.40</td>
<td>9.57</td>
<td>5.75</td>
<td>74</td>
<td>1.13</td>
</tr>
<tr>
<td>WEY-063</td>
<td>0.36</td>
<td>7.20</td>
<td>5.50</td>
<td>82</td>
<td>1.12</td>
</tr>
<tr>
<td>WEY-100</td>
<td>0.25</td>
<td>3.17</td>
<td>5.95</td>
<td>134</td>
<td>1.08</td>
</tr>
<tr>
<td>WEY-200</td>
<td>0.62</td>
<td>2.14</td>
<td>5.16</td>
<td>265</td>
<td>1.09</td>
</tr>
<tr>
<td>WEY-400</td>
<td>0.36</td>
<td>0.84</td>
<td>6.35</td>
<td>492</td>
<td>1.10</td>
</tr>
</tbody>
</table>

#### 3.1.2 Conductivity – Temperature Relationships

The temperature dependence of conductivity for the electrolytes is shown in Figure 1. Electrolyte WEY–040 revealed the uppermost increase of conductivity with temperature from -55 to 125 ºC, followed by electrolyte WEY–063 presenting slower but similar slope to electrolyte WEY–040. Electrolyte WEY–100 demonstrated marginally faster increase than WEY–200 in conductivity with temperature but significantly slower than electrolyte WEY–063. In comparison, electrolyte WEY–400 showed the least increase in conductivity with temperature under similar conditions.

![Figure 1. Conductivity – temperature relationships of the electrolytes.](image)

#### 3.1.3 Dielectric Breakdown Voltage – Temperature Relationships

Figure 2 shows the dielectric breakdown voltage ranges for all these electrolytes, as a function of the temperature. The breakdown voltage of the electrolytes slightly, if not insignificantly, decreases with the increase of temperature, perhaps due to the increased conductivity of the electrolyte at higher temperature. Increased temperature improves the dissociation constant of ion–pairs and thus promotes more active ions in the electrolyte. In general, the breakdown voltage of the electrolyte is practically independent of the temperature. In other words, the dielectric breakdown voltage does not change significantly with the temperature, suggesting the suitability of application of these electrolytes over a wide range of temperature at the rated voltages under the testing conditions.
3.1.4 Dielectric Breakdown Voltage – Conductivity Relationships

The relationships of conductivities and breakdown voltages for the five electrolytes are further illustrated in Figure 3. The breakdown voltages for electrolytes WEY–040, WEY–063, WEY–100 and WEY–200 gave evident linear relationship with the logarithm of conductivity of the working electrolyte. In comparison, the breakdown voltages of electrolyte WEY–400 give less evident linear relation of the logarithm of breakdown voltage and conductivity, perhaps due to the different electrolyte composition of electrolyte WEY–400.
3.2 Capacitor Endurance Tests: 40, 63 & 400 V

3.2.1 Basic Design and Testing Conditions

The basic design information of 40, 63 and 400 V working capacitors is listed in Table 2. All capacitors were in the same size of 51.6 mm diameter and 51.5 mm in length. Eight capacitors were tested for each of the three electrolytes.

<table>
<thead>
<tr>
<th>Working V</th>
<th>40</th>
<th>63</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (μF)</td>
<td>9000</td>
<td>4700</td>
<td>200</td>
</tr>
<tr>
<td>Size (mm)</td>
<td>Ø51.6 x 51.5</td>
<td>Ø51.6 x 51.5</td>
<td>Ø51.6 x 51.5</td>
</tr>
<tr>
<td>Surge V</td>
<td>46</td>
<td>73</td>
<td>440</td>
</tr>
<tr>
<td>Temp. Range (ºC)</td>
<td>-55 to 125</td>
<td>-55 to 125</td>
<td>-55 to 125</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>WEY–040</td>
<td>WEY–063</td>
<td>WEY–400</td>
</tr>
<tr>
<td>Quantity</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Applied V&lt;sub&gt;DC&lt;/sub&gt; + I&lt;sub&gt;AC&lt;/sub&gt;</td>
<td>36 V&lt;sub&gt;DC&lt;/sub&gt; + 6.4 A 50 Hz</td>
<td>57 V&lt;sub&gt;DC&lt;/sub&gt; + 5.1 A 50 Hz</td>
<td>371 V&lt;sub&gt;DC&lt;/sub&gt; + 1.0 A 50 Hz</td>
</tr>
<tr>
<td>Temperature (ºC)</td>
<td>125</td>
<td>125</td>
<td>125</td>
</tr>
<tr>
<td>Duration (Hours)</td>
<td>6000</td>
<td>6000</td>
<td>4000</td>
</tr>
</tbody>
</table>

3.2.2 Leakage Current Results

The average leakage current was approximately steady at 0.002 mA before 4000 hours and less than 0.003 mA each pair between 4000 to 6000 hours tests for 40 V, and 0.003 mA before 4000 hours tests then increased to over 0.005 mA up to 6000 hours for each pair for 63 V capacitors, as shown in Figure 4. The significant current surges at every 1000 hours intervals indicate the application of the working voltages to the reconnection and re–heating of the capacitors after having been discharged, disconnected and tested capacitors at 20 ºC for C, ESR and Z.

In comparison, the leakage current for 400 V working capacitors was less than 0.1 mA during the first 1000 hours of test before increasing to around 0.1 mA afterwards, as illustrated in Figure 5.

![Figure 4. Leakage current – time curves for endurance tests of 40 V working capacitors at 36 V<sub>DC</sub> with 6.4 A 50 Hz, and 63 V working capacitors at 57 V<sub>DC</sub> with 5.1 A 50 Hz ripple currents applied at 125 ºC.](image)
Figure 5. Leakage current – time curves for endurance tests of 400 V working capacitors at 371 V DC with 1.0 A 50 Hz ripple current applied at 125 °C.

3.2.3 Capacitor Parameter Measurements

Initial values of capacitance, ESR and impedance Z for 40 V capacitors were measured as 7650.6 μF, 13.6 mΩ and 11.4 mΩ. The capacitance decreased approximately -1% after the first 1000 hours and approximately up to -4% after 6000 hours endurance tests, while the ESR and Z increased to +21.68% and +13.54% after the first 1000 hours endurance tests, until the ESR and Z increased over +300% and +250% after 6000 hours endurance tests, as shown in Table 3.

In comparison, the initial values of capacitance for 63 V capacitors were measured as 3994.8 μF, and the ESR and impedance Z increased to 18.7 mΩ and 14.88 mΩ for the similar capacitor size. The capacitance decreased approximately -0.6% after the first 1000 hours and approximately up to -1.4% after 6000 hours endurance tests, while the ESR and Z increased to +11.68% and 6.06% after the first 1000 hours endurance tests, and all increased less than 100% after 6000 hours endurance tests, as shown in Table 4.

At higher working voltage of 400 V, the capacitance was measured as less than 200 μF for the similar size, while the ESR and Z measured as 457 & 217 mΩ respectively. The capacitance decreased to -1% after first 1000 hours tests, and down to -2.79% after 4000 hours. ESR and impedance increased to +4.7% and +0.95% for the first 1000 hours up to +106.29% and +73.73% for the similar period of time (Table 5).

Table 3. Variations of capacitance (C), ESR and impedance (Z) for 40 V working capacitors during endurance tests at 36 V DC with 6.4 A 50 Hz ripple current applied at 125 °C.

<table>
<thead>
<tr>
<th>Hours</th>
<th>1000</th>
<th>2000</th>
<th>3000</th>
<th>4000</th>
<th>5000</th>
<th>6000</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔC, %</td>
<td>-0.97</td>
<td>-1.16</td>
<td>-1.54</td>
<td>-1.76</td>
<td>-2.2</td>
<td>-3.67</td>
</tr>
<tr>
<td>ΔESR, %</td>
<td>21.68</td>
<td>22.21</td>
<td>22.56</td>
<td>33.16</td>
<td>100.19</td>
<td>328</td>
</tr>
<tr>
<td>ΔZ, %</td>
<td>13.52</td>
<td>14.25</td>
<td>21.19</td>
<td>31.41</td>
<td>70.41</td>
<td>252</td>
</tr>
</tbody>
</table>
Table 4. Variations of capacitance (C), ESR and impedance (Z) for 63 V working capacitors during endurance tests at 57 V\text{DC} with 5.1 A 50 Hz ripple current applied at 125 °C.

<table>
<thead>
<tr>
<th>Hours</th>
<th>1000</th>
<th>2000</th>
<th>3000</th>
<th>4000</th>
<th>5000</th>
<th>6000</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔC, %</td>
<td>-0.60</td>
<td>-0.72</td>
<td>-0.77</td>
<td>-1.21</td>
<td>-1.37</td>
<td>-1.40</td>
</tr>
<tr>
<td>ΔESR, %</td>
<td>11.68</td>
<td>4.74</td>
<td>8.24</td>
<td>13.46</td>
<td>32.12</td>
<td>88.8</td>
</tr>
<tr>
<td>ΔZ, %</td>
<td>6.06</td>
<td>4.56</td>
<td>3.56</td>
<td>9.44</td>
<td>23.22</td>
<td>61.56</td>
</tr>
</tbody>
</table>

Table 5. Variations of capacitance (C), ESR and impedance (Z) for 400 V working capacitors during endurance tests at 371 V\text{DC} with 1.0 A 50 Hz ripple current applied at 125 °C.

<table>
<thead>
<tr>
<th>Hours</th>
<th>1000</th>
<th>2000</th>
<th>3000</th>
<th>4000</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔC, %</td>
<td>-1.19</td>
<td>-1.54</td>
<td>-2.08</td>
<td>-2.79</td>
</tr>
<tr>
<td>ΔESR, %</td>
<td>4.70</td>
<td>30.01</td>
<td>64.53</td>
<td>106.29</td>
</tr>
<tr>
<td>ΔZ, %</td>
<td>0.95</td>
<td>18.64</td>
<td>39.98</td>
<td>73.73</td>
</tr>
</tbody>
</table>

Capacitance variation with time for 40, 63 and 400 working voltages is further illustrated in Figure 6 for comparison. Capacitors working at 63 V showed negligible variation in comparison with 40 V during 6000 hours endurance test. Capacitors working at 400 V showed the relatively increased but still acceptable variation during the test.

For ESR and impedance variations, capacitors working at 63 V also gave the least variation followed by 40 V and 400 V, as demonstrated in Figures 7 and 8 respectively.

![Figure 6. Capacitance variations for endurance tests of capacitors at 40, 63 and 400 V at 125 °C.](image-url)
4. Discussion

4.1 Electrolyte Formulation and Parameters

The electrolytes or fill electrolytes, distinguishing from the formation electrolytes for anode foils where water is the major solvent, function as the true cathodes after impregnation. These fill electrolytes are mainly non-aqueous electrolytes consisting of organic solvents with the adequate solutes to form homogeneous electrolytic solutions. These solutes are generally inorganic or organic acids neutralized by organic or inorganic bases, and/or conductive salts with other additives.
while the actual electrolyte formulation is regarded as commercial secret. Non–aqueous electrolytes are so termed because the percentage of allowable water present is relatively small, typically less than 1.0% in weight. Water content in all electrolytes in this work is less than 1.0%. Such low water content is optimum to reduce the internal capacitor pressure and thus increase life-time of the capacitor. Also, reduced water content probably leads to less cathode and/or tab hydration, especially at high temperature. Other characteristics of an electrolyte, such as pH value and conductivity associated with solubility, are largely determined by the characteristics of the acid component of the salt, such as quaternary amidinium salt of a hydroxyl–substituted aromatic monocarboxylic acid like salicylic acid, a quaternary amidinium salt of phthalic acid and salts of phosphoric acids.  

Conductivity of the non-aqueous solution, one of the key parameters during electrolyte development, depends upon various factors such as concentration, the valence type of the electrolyte, the temperature, the dielectric constant of the solvent and the viscosity of the electrolyte, as described by the well-known Debye–Hückel–Onsager equation. For a certain salt dissolved in a given solvent with a certain concentration in the electrolyte, the conductivity of the solution follows the Kohlrausch law of independent migration of ions, i.e., the value of the equivalent conductance is the sum of the limiting ionic equivalent conductance of the anions and cations–positively charged ions and negatively charged ions – constituting the solute of the electrolytic solution. In reality, an electrolyte solution is not infinite dilution but a complicated system, the total electrical conductance of an electrolyte solution depends on the type and concentration of all ions present in a mixture of electrolyte.

Conductivity is also temperature dependant in an electrolyte solution containing weak acids or bases and certain salts, as shown in Figure 1. Increased temperature activates more conductive ions in the electrolyte solution and thus increased conductivity of the electrolyte. Despite the similar densities of these electrolytes (Table 1), the conductivities increase differently with the increase of temperature, which is probably due to the different electrolyte compositions or different ingredients in various concentrations and thus different ion dissociation. This temperature–dependent conductivity might be described again by considering the Debye–Hückel–Onsager equation, where the temperature effect on the conductivity is non–linear.

4.2 Dielectric Breakdown, Dielectric Breakdown Voltage and Working Voltages

Another important feature of the electrolyte is the dielectric breakdown voltage, or sparking voltage, which determines the actual working voltage of the electrolyte in a capacitor. During anodizing or forming of aluminium at a constant current density (galvanostatic anodizing) in a suitable electrolyte where the dissolution of the resultant anodic film is negligible, the voltage usually increases linearly with time until a certain stage is attained. Beyond this stage, the rate of voltage increase is nonlinear with time, but increases at a progressively decreasing rate, indicating the normal barrier film growth has ceased. Additionally, the current oscillates violently, and sparks and/or noise are usually, but not always evident. All these features are associated with “dielectric breakdown”. During dielectric breakdown, when the voltage attains a certain value, the voltage starts to oscillate, and the current oscillates abruptly and markedly. This voltage value is termed the “dielectric breakdown voltage”. The dielectric breakdown voltage, a value for an anodizing system, is sometimes termed the sparking voltage or scintillating voltage. In industrial application and in practical experiments, the dielectric breakdown voltage is determined readily from the usual voltage – time (V – t) and current – time (I – t) curves, within an accuracy of ± 5 V. Thus, the dielectric breakdown voltage is the voltage where the V – t behaviour changes from usual linear increase with time and where the I – t behaviour starts to oscillate abruptly.

For a given system, the dielectric breakdown voltage is also related with the conductivity of the electrolyte. Increased conductivity reduces the dielectric breakdown voltage, as shown in Figures 2 & 3, suggesting that electrolytes for higher working voltages need to have reduced conductivity.  

Research has shown that the dielectric breakdown voltages fit to the empirical equation (\( V_b = \alpha_b + \beta_b \log p \)), where \( V_b \) the dielectric breakdown voltage, \( p \) the resistivity of the electrolyte or the reciprocal of conductivity, \( \alpha_b \) and \( \beta_b \) the two constants. This relationship requires that the properties of the electrolyte be balanced between the conductivity and the dielectric breakdown voltage.

Many chemical and physical properties of anodic aluminium dielectrics, a type of thin insulating films, are related with flaws in the films. Flaws are defined as microfissures, cracks, and local regions of different composition and, in certain cases, crystalline structure which are contained always in the relatively uniform air-formed and anodic barrier films developed on aluminium. These flaws can be revealed readily by direct observation of the stripped films in a transmission electron microscope and are known to be present widely in anodic films. The generation of flaws in the oxide film, as well as its influence on the oxide growth kinetics in the surrounding areas, has been studied. These flaws influenced by anodizing conditions, such as the surface condition of the substrate, forming voltage, anodizing current density, temperature.
and concentration of the electrolyte. More recently, the progress of dielectric breakdown on superpure aluminium electrolytic capacitor foils of 99.99 wt.% purity has been investigated. It was found that dielectric breakdown initiates at flaws at a critical stage during the barrier film thickening. The flaws are formed at sites where impurities, most probably copper or iron, segregate. Additionally, the development of flaws, comprising $\gamma / \gamma'$-alumina within the aluminium oxide film is associated with a field-assisted dehydration of pseudoboehmite. During anodizing, $O^2-$ ions ingress while $Al^{3+}$ ions egress under the field to increase the anodic film thickness. At flaw sites in the anodic film, oxygen gas is developed by the discharge of oxygen ions under the increasing field strength. Thus, the oxygen gas developed accumulates and remains trapped in the voids within the anodic film during anodizing. The continuously generated and accumulated oxygen gas increases the internal pressure in the voids. At a critical pressure, the trapped oxygen filled voids rupture the anodic film, resulting in craters or channels and electrolyte access. The electrolyte thus fills the craters, causing a marked increase in the local ionic conductivity and thus a high current density driven by the extremely high local field. Consequently, Joule heating effects are generated, with significant increase in local temperature. For conditions where the generated Joule heating is sufficiently large, local temperature is increased, subsequently a plasma is generated and the dielectric breakdown proceeded. The local film material is melted or vaporised, sparks are observed, and noise is perceived. Simultaneously, healing of the local crater takes place, with the resultant film being heavily flawed, giving rise to further dielectric breakdown. If the local temperature is insufficiently high to generate a plasma, localized film overgrowth occurs.

4.3 Electrolyte Characteristics and Capacitor Performance

The overall performance of an aluminium electrolytic capacitor, such as ESR and impedance of the electrolytic capacitors, working voltage, surge / transient voltage and working life etc, is affected by the fill electrolyte as well as other elements as having been described above. Working life of a capacitor implies appropriate performance under designed operating conditions without catastrophic failures or parametric failures. The catastrophic failure includes short circuit, open circuit or safety vent operation, while the parametric failure includes capacitance changes, leakage current and ESR changes. Whilst catastrophic failures are clearly evident, parametric failures are more subjective and highly dependent upon the application. In industrial applications, the ESR changes during working life have been defined as less than several times of the initial ESR values or initial specified limits. In this work, the ESR changes up to three times of initial values have been arbitrarily defined as the end of working life.

To achieve the demanded overall performance in the applications of automotive industries and other industries at high temperatures for longer lifetimes, it is essential that the electrolytes characterise remarkable chemical stability and outstanding chemical compatibility with capacitor materials utilised. Remarkable chemical stability of an electrolyte means less decomposition, less inter–ingredient reactions such as esterification reactions which are probably associated with the ESR and impedance variations with time (Figures 7 & 8), in addition to the electrolyte drying–out mechanism. Outstanding chemical compatibility indicates that the electrolyte has less or no detrimental chemical reactions with aluminium foils and any other capacitor materials contacted. Other capacitor materials include paper separators, aluminium tab foils, aluminium can, plastics as deck materials, rubber as sealing ring and vent. Aluminium, aluminium oxide and aluminium hydroxide are all naturally amphoteric substances, reacting as either acid or base. Hydration reaction between an aluminium electrode foil and water in the electrolyte may generate hydrogen gas, resulting in the increase of internal pressure and the operation of safety vents which is one of the major catastrophic failure modes for aluminium electrolytic capacitors. Additionally, any kinds of reactions between aluminium foils and electrolytes probably alter the properties of the electrodes and thus decrease the capacitance (Figure 6). A neutralized electrolyte with an optimized pH value may inhibit effectively these reactions and thus enhance the performance of the capacitors. Excellent wettability and swellability of the papers, or the capability of the electrolyte to bond to or penetrate paper fibres and further to enter and attach to the available cellulose surfaces, reduces the ESR and impedance of the capacitors. Highly absorbent paper and superior retainment of the electrolyte prolong the performance of the capacitors.

The electrolyte should also sustain reasonable temperature features for both the low and high temperature conditions, in the range of -55 to 125 ºC. These properties arise from the overall electrolytes consisting of solvents and solutes, i.e., organic or inorganic acids, bases as amines and additives. Solvents of low melting points and high boiling points are preferred to achieve this temperature feature, such as polyhydroxyl alcohol group $\gamma$–butyrolactone. Understanding these performance associated properties of an electrolyte demands careful selection of the constituents, diligent study of the electrolyte and comprehensive engineering test of the resultant capacitors.
5. Conclusions

The properties of electrolyte developed for automotive and high temperature aluminium capacitors largely affect the overall performance of the capacitors, such as the operating temperature ranges, ESR, impedance and service life. Systematic experiments of carefully selected solvents and solutes provide essential information of the working electrolytes such as water content, conductivity and pH values. Dielectric breakdown voltage of the electrolyte determines the working voltage as well as surge / transient voltage in capacitors. In this study, the developed electrolytes demonstrated the capability of working at high temperature of 125 ºC, over 6000 hours at 40 and 63 V and over 4000 hours at 400 V, under the present endurance testing conditions with calculated, maximum allowable ripple currents applied. Moreover, the endurance tests have shown that the 40, 63 and 400 V electrolytes developed offer great opportunities in the manufacture of aluminium electrolytic capacitors for automotive applications and other industrial applications with longer lifetimes. In addition, the development of electrolytes working at 100 and 200 V continues.

Acknowledgement

The authors would like to thank Mr. Mark Wright for his helpful discussions and suggestions, and all other colleagues from Research and Development group for their contributions to this work.

References