Further Electrolyte Development for High Temperature Aluminium Electrolytic Capacitors

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Abstract

In the previous paper, electrolytes working at 40, 63 and 400 V at 125 ºC were presented. These electrolytes were developed for aluminium electrolytic capacitors and showed a wide working temperature range from -55 to +125 ºC, with designed properties such as ionic conductivity and dielectric breakdown voltages, and provided suitable performance in capacitor applications. In this paper, electrolytes using γ-butyrolactone as a major solvent operating at medium voltages (100 & 200 V) and further 400 V at 125 ºC are discussed. The thermal stability tests of all the developed electrolytes were carried out at 125 °C up to 1200 hours, and the results are presented. A series of screw terminal capacitors were prepared with these electrolytes, and electrical parameters such as capacitance, ESR and impedance were measured at different temperatures. These results showed that the electrical parameters at various temperatures were within their estimated ranges. In addition, the electrical characteristics were evaluated for capacitors working over the temperature range (from -55 to +125 ºC). In contrast with the previous works, based on low and high voltage applications, the electrolytes proposed in this work will enable scope for medium voltage applications (*i.e*. 100 and 200 V).

1. Introduction

In recent years, the development of aluminium electrolytic capacitors with long lifetime for high temperature applications has been demanded due to their rapidly increasing need in automotive industries,[1] drive industries and other potential industrial applications. The electrolytes, based on organic solvents, play a key role in the overall performance of aluminium electrolytic capacitors.[2] However, very few works on the development of such electrolytes have been published. In the previous studies[3], the development of electrolytes for aluminium electrolytic capacitor operating at 40, 63 and 400 V at 125 °C has been presented. The previous developed electrolytes were suitable for low voltage (*e.g.* 40 and 63 V) as well as high voltage applications (400 V). Due to a demand of medium voltage (*e.g.* 100 and 200 V) capacitors working at high temperature (125 °C), this work presents the development of electrolytes for such medium voltage capacitors, as well as further development of 400 V electrolytes. These electrolytes must have a specific level of conductivity and a wide range of operating temperature (*i.e.* good thermal stability) for such high performance aluminium electrolytic capacitors. In practical applications, when the electrolytes are exposed to high temperatures (*e.g.* 125 °C) for prolonged times, the water content, conductivity, pH and dielectric breakdown voltage of the electrolytes must be relatively stable. It is essential that the breakdown voltage of an electrolyte should not decrease significantly during the thermal stability tests. Otherwise, the electrolyte would not be valid for the high temperature applications. The water content is expected to increase during the early test stages, due to esterification and/or acid-base reactions will produce water (more details are discussed in section 3.3). After a certain period of time, these reactions should be completed and hence the water content should remain relatively constant. Some changes for both pH and conductivity should also be expected due to these reactions. Therefore, the thermal stability tests of the developed electrolytes and electrical measurements of sample capacitors at different temperatures must be carried out. For evaluation of the capacitor performance, the electrical characteristics of the capacitors can be estimated from sample capacitor tests within their operating temperature range (from -55 to +125 °C). Hence all test results for both electrolytes and capacitors are presented and discussed in this paper.

2. Experiments

2.1 Electrolyte Preparation and Parameter Measurement

The electrolytes developed in this study were based on γ–butyrolactone (BLO) solvent, containing solutes – conductive salts or neutralisation products from inorganic or organic acids and bases, as well as some additives. The procedures for preparing electrolytes and the method for measuring parameters (*e.g.* water content, conductivity, pH and dielectric breakdown voltage) were described elsewhere. In this work, three different types of electrolytes were developed for each voltage application, *i.e.* there are three electrolytes for the 100 V capacitors (namely WEY-100-1; WEY-100-2; WEY-100-3); three for the 200 V (WEY-200-1; WEY-200-2; WEY-200-3); and three for the 400 V capacitors (WEY-400-1; WEY-400-2; WEY-400-3).

2.2 Thermal Stability Test of the Developed Electrolytes

The chemical components in electrolytes may be stable in their early stages, but they may decompose when exposed to high temperatures for prolonged times. Thus, thermal stability of the electrolytes is crucial for a capacitor to operate at high temperature and the maximum working voltages. Therefore, the thermal stability test is a key procedure to develop good performance electrolytes. In this test, each electrolyte and a piece of aluminium cathode foil were placed in an aluminium can. The can was placed in an oven at 125 °C without applied voltage. The electrolyte parameters (*e.g.* water content, conductivity, pH and dielectric breakdown voltage) were measured after 72, 168, 336, 672 and 1200 hours (*i.e.* from 3 to 50 days) of thermal stability test. These parameters were compared with the initial values to examine the thermal stability of each electrolyte.

2.3 Sample Capacitor Preparation and Test

A series of aluminium electrolytic capacitors were prepared with the developed electrolytes for the three voltage applications. The detailed procedures of capacitor preparation and measurement can be found in our previous work.

Table 1 summarises the basic design information of the 100, 200 and 400 V capacitors which were prepared using the WEY-100, WEY-200 and WEY-400 electrolytes.

The electrical parameters *e.g.* capacitance (C), equivalent series resistance (ESR) and impedance (Z) of the capacitors were measured at different temperatures: -55, -40, 20, 85 and 125 °C, using the Thermotron's SE-300 Environmental Test Chamber (Thermotron Industries, Holland, Michigan USA), in order to evaluate the performance of capacitors at low and high temperatures. The endurance test of the capacitors at 125 °C with and without ripple current is currently in progress, and the results will be presented in our next publication. During the endurance test, the capacitance, ESR, impedance and leakage current of the capacitors will be measured (at 20 ºC) every 1000 hours to investigate the capacitor performance over time, and hence the electrolyte suitability will be evaluated for its applications.

Table 1. Capacitor design information

Electrolyte	WEY–100	WEY–200	WEY–400
Working Voltage (volts)	100	200	400
Capacitance (μF, at 100Hz)	4700 (-10/+30%)	1500 (-10/+30%)	270 (-10/+30%)
Size (mm)	Ø50.2 × 75.2	Ø50.2 × 75.2	Ø50.2 × 75.2
Surge Voltage (volts)	115	230	440
Leakage Current (mA)	0.94	0.6	0.22
Temp. Range (ºC)	-55 to 125	-55 to 125	-55 to 125
Applied V_{DC} + I_{AC}	100 V_{DC} + 5.55A/50Hz	200 V_{DC} + 3.29A/50Hz	400 V_{DC} + 1.5A/50Hz
Test Temperature (ºC)	125	125	125
Test Duration (Hours)	5000	5000	5000

3. Results And Discussion

3.1 Electrolyte Parameters

The conductivity, pH, dielectric breakdown voltage and water content were measured for all the WEY-100, WEY-200 and WEY-400 electrolytes and are summarised in Table 2.

Table 2. Electrolyte Parameters

Parameters	WEY-100 Electrolytes			WEY-200 Electrolytes			WEY-400 Electrolytes		
	WEY-100-1	WEY-100-2	WEY-100-3	WEY-200-1	WEY-200-2	WEY-200-3	WEY-400-1	WEY-400-2	WEY-400-3
Conductivity (mS cm^{-1}, 25°C)	2.56	2.02	2.49	2.08	2.04	2.10	1.03	1.04	0.76
Breakdown Voltage (volts, 90°C)	135	120	117	270	265	250	480	480	490
H_2O Content (wt%, 25°C)	0.63	3.57	0.89	0.56	0.59	0.68	0.89	0.87	1.11
pH Value (25°C)	5.95	5.97	5.75	5.12	5.36	5.28	6.18	6.12	5.74

In electrolyte development, the conductivity, water content, pH and dielectric breakdown voltage are critical as they will determine the capacitor overall performance. The dielectric breakdown voltage is related to the capacitor maximum operating voltage. The electrolyte conductivity will affect the final capacitor ESR and impedance; and the capacitor stability and resistance to corrosion are relative to pH and water content in the electrolyte.

In general, the higher the conductivity of an electrolyte, the lower the breakdown voltage will be. In other words, electrolytes with high conductivities are usually only suitable for low voltage applications, whereas electrolytes with low conductivities are normally for high voltage applications. Practically, the breakdown voltage of the developed electrolytes should be at least 10–20% higher than that maximum operating voltage of capacitors. The pH and the water content of the electrolytes normally must be kept within a range of values to ensure the thermal and chemical stability of the electrolyte, and also to minimise the possibility of corrosion that may arise due to water content increase or pH change of the electrolyte during capacitor operation.

3.2 Thermal Stability Test Results

The thermal stability results of the WEY-100 electrolytes are illustrated in Figure 1. The variations in conductivity and breakdown voltage shown in Figures 1(A) and (B) are very small. The conductivity decreases and breakdown voltage increases after 1200 hours at 125 °C for WEY-100-1 and WEY-100-2 electrolytes, with slightly higher variations (*e.g.* 10 to 15% higher) for WEY-100-3. Figure 1(C) shows very little variation (*e.g.* ±3% only) in water content for WEY-100-2 comparing to WEY-100-1 and WEY-100-3 electrolytes. Finally, Figure 1(D) shows little pH increase for WEY-100-1 and WEY-100-3 electrolytes, and a slightly decrease in pH value for WEY-100-2. However, there was no corrosion observed on the aluminium foils.

All these variations in the electrolyte parameters are probably caused by further chemical reactions between the electrolyte ingredients at high temperature. Among these electrolytes in Figure 1, WEY-100-2 gives minimum parameter changes. Therefore, WEY-100-2 electrolyte has the best stability and thus the best capacitor performance is expected from this electrolyte. Further capacitor endurance tests are required to verify these thermal stability results.

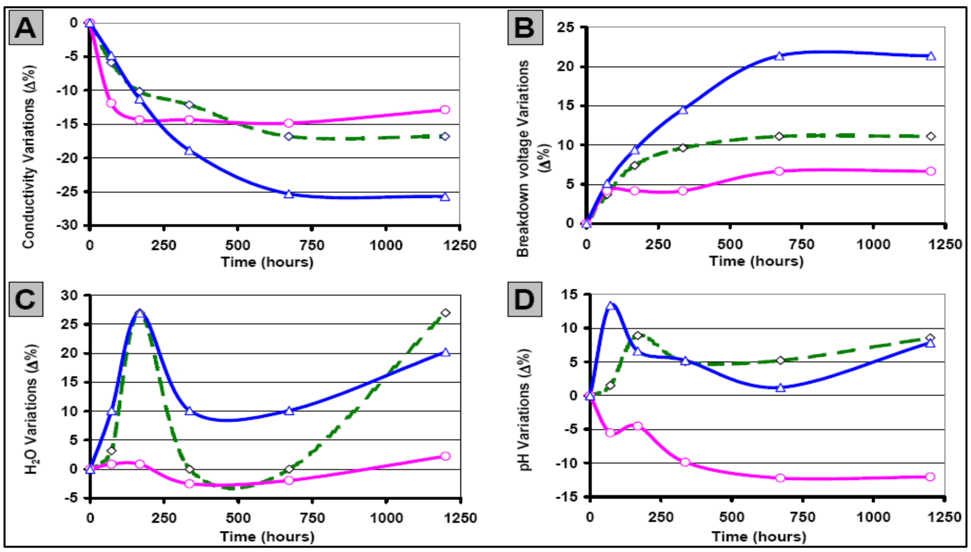

Figure 1. Thermal stability test results of the WEY-100 electrolytes, WEY-100-1 (- ◇—); WEY-100-2 (—○—); WEY-100-3 (—△—) at 125 °C from 0 to 1200 hours

Figure 2 shows the results of thermal stability test for the three WEY-200 electrolytes. From Figures 2(A) to (D) it can be seen that WEY-200-3 is the most stable electrolyte within the three WEY-200 electrolytes. The conductivity, breakdown voltage and pH variations in WEY-200-3 are insignificant over the whole test, although the water content variation (31% increase) after 1200 hours can be observed, which may be a result of neutralisation and/or esterification reactions. The other two electrolytes presented relatively higher variations in conductivity and water content than WEY-200-3. Nevertheless, the performance of WEY-200-1 and WEY-200-2 still need to be investigated in sample capacitors for monitoring the electrochemical stability. As mentioned before, a piece of cathode foil was immersed in each electrolyte solution to monitor foil corrosion in the thermal stability test. As a result all these foils showed no signs of corrosion after 1200 hours except for WEY-200-3, which showed evident signs of corrosion after 672 hours (*i.e.* 28 days). This may possibly lead to a reduction of the capacitor performance.

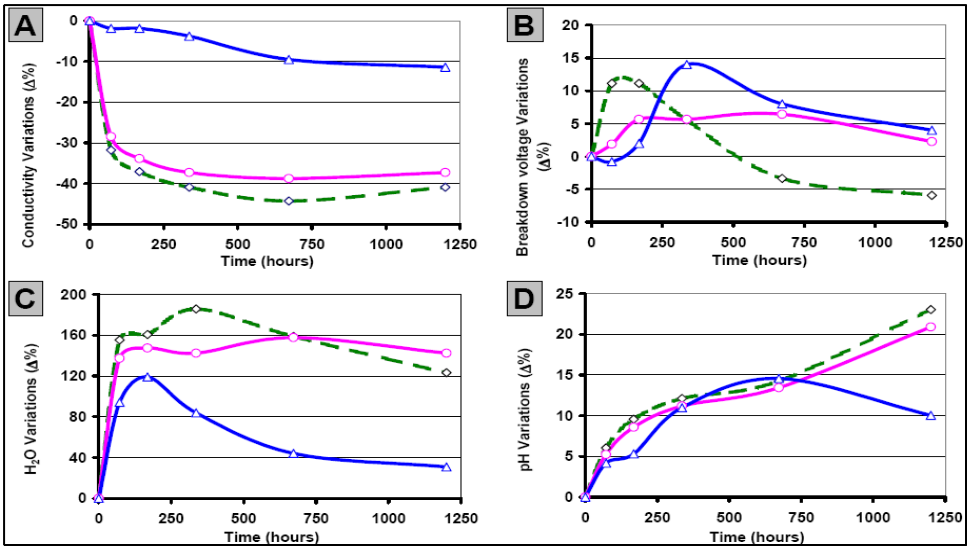

Figure 2. Thermal stability test results of the WEY-200 electrolytes, WEY-200-1 (green dashed line, ◇ markers); WEY-200-2 (magenta line, ○ markers); WEY-200-3 (blue line, △ markers) at 125 °C from 0 to 1200 hours

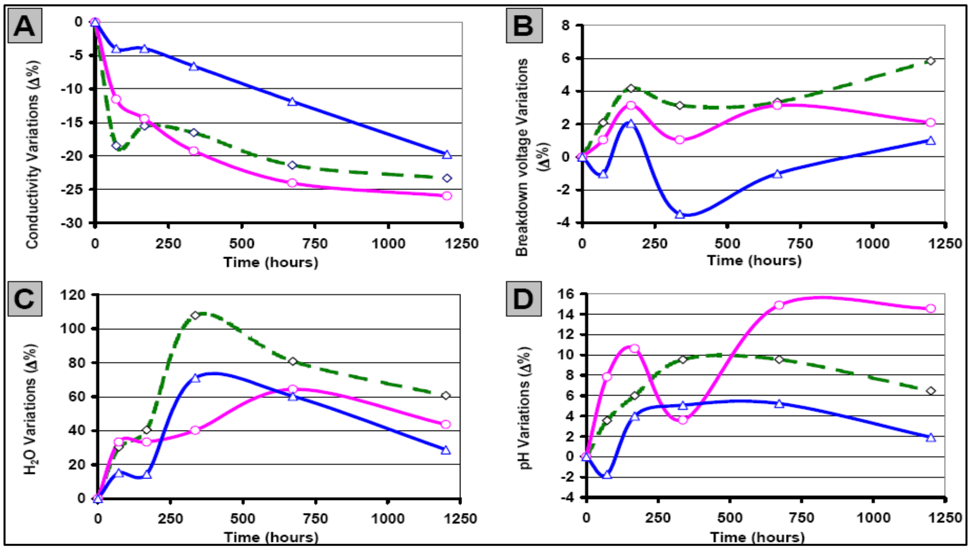

Figure 3. Thermal stability test results of the WEY-400 electrolytes, WEY-400-1 (green dashed line, ◇ markers); WEY-400-2 (magenta line, ○ markers); WEY-400-3 (blue line, △ markers) at 125 °C from 0 to 1200 hours

The results of thermal stability for the three WEY-400 electrolytes are illustrated in Figure 3. The conductivity variations of the three WEY-400 electrolytes in Figure 3(A) show similar behaviour to that observed in Figure 1(A) for all the WEY-100 electrolytes. In fact, the conductivity of WEY-400-1 and WEY-400-2 seems to be relatively stable after 672 hours, but for WEY-400-3 the conductivity seems to decline constantly over the test duration. This may be caused by chemical decomposition of the conductive salts or esterification in the electrolytes. The breakdown voltage and pH variations are very small (about ±10%), except WEY-400-2 in Figure 3(D) shows a slightly higher increase in pH variation. For all the WEY-400 electrolytes, the water content increases initially (in the region between 200 and 400 hours) and then decreases (similar to WEY-200 electrolytes). Practically, excessive gas generation including water vapour will cause vent rupture in actual capacitor operation, which limits the capacitor lifetime. Therefore, electrolytes working at high temperatures require low water content. The actual water contents of the WEY-400 electrolytes are acceptable even if the variations in percentage were relatively high in Figure 3(C). In comparison with other WEY-400 electrolytes, WEY-400-1 is the most chemically stable version for 400 voltage capacitor application.

In thermal stability tests, the variations in the breakdown voltage were directly subject to the conductivity of the electrolytes. The lower the conductivity, the smaller the number of conductive ions transported from the electrolyte. Hence, the smaller the number of electrons migrating to the dielectric, the less possibility there is of breakdown occurring. Therefore, electrolytes with low conductivity will have high breakdown voltages. For aluminium electrolytic capacitors the difference between the working voltage and breakdown voltage is usually 20 to 50 volts to ensure capacitor reliability. In this case, all the three WEY-100 electrolytes, WEY-200-2 and WEY-200-3, WEY-400-1 and WEY-400-2 electrolytes should have good performance in capacitors in terms of their breakdown voltage variations. The water content variation increases for all three types of electrolytes. Probably, esterification and/or acid-base reactions are the major factors to increase water content in the electrolytes. On the other hand, the increased water content in capacitors will speed up the hydration of aluminium foils (most likely cathode foil), which produces hydrogen gas and also reduces the capacitance of the foils. Hydrogen gas and other gas generations may increase the internal pressure leading to capacitor failures. Therefore, for high voltage and high temperature applications the low water content is normally required from the electrolyte. pH variations are not as significant as conductivity, breakdown voltage and water content variations, but they must still be considered carefully because certain pH values (*e.g.* low pH or high acidity) of the electrolyte may induce aluminium foil attack (*i.e.* capacitor corrosion) or precipitation of electrolyte ingredients, leading to poor capacitor performance. Thus, the pH of the electrolyte should be prevented from decreasing,[4] and it must also be within the range of designed values to avoid electrolyte precipitation and aluminium corrosion.

In addition, the electrolytes developed in this study are to be used for a wide range of temperature, typically from -55 °C to +125 °C. The thermal stability test was only used to monitor the tolerance of the electrolyte at the maximum working temperature (125 °C), but not at the minimum temperature (-55 °C). The lowest working temperature of an electrolyte is determined by its freezing point. Therefore, the low temperature tests were carried out for all the electrolytes, and the results showed a freezing point lower than -55 °C.

3.3 Possible Chemical Reactions During Thermal Stability Tests

Electrolyte solutions contain free ions behaving as an electrically conductive medium. However, the electrolyte ingredients may react and produce new species during the thermal stability test at 125 °C. The type of chemical reactions depends on the electrolyte composition. Generally, these reactions include:

Esterification: esterification is a chemical reaction in which two reactants, typically an alcohol and an acid, form an ester and water as the reaction products. This type of reaction is very common in electrolytes used in aluminium electrolytic capacitors. For example, esterification of dicarboxylic acid in a glycol-based or glycol-contained electrolyte normally results in an ester – dicarboxylic diglycolate. Similarly, if an acid such as boric acid or phosphoric acid, etc. is present in an electrolyte containing ethylene glycol, the acid will react with ethylene glycol to produce ethylene glycol borate or ethylene glycol phosphate esters as well as water.[5] The esterification reaction is both slow and reversible. This reaction will take place during the thermal stability test at high temperature, in which water vapour produced will contribute to gas generation in the capacitor; this may cause capacitor failure due to high internal pressure.[6] Moreover, thermal stability of BLO based electrolytes strongly depends on the water content in the electrolyte.[7] Thus water content in an electrolyte should be carefully controlled during electrolyte development.

Chemical Decomposition: chemical decomposition is the separation of a chemical compound into smaller compounds. The stability of an electrolyte highly depends on the stability of its chemical ingredients, reacted products/solutes and solvents, which is eventually limited when exposed to extreme environmental conditions like heat, humidity or the acidity. For example, triethylammonium hydrogen maleate (TEMAM) can be used as solute in BLO based electrolytes. The decomposition of maleate salt (TEMAM) in the electrolyte would occur when heating up to 115 °C, but at 150 °C the decomposition rate could be accelerated to form a complex polymer containing polyester and polyacrylate structures.[8] Therefore, the chemical decomposition of conductive salts may give rise to the decrease in the conductivity of the electrolytes, due to reduced conductive ion concentration in the electrolytes.

Neutralisation: neutralisation is a chemical reaction in which an acid and a base react to produce salt and water. In some electrolytes, an acid and a base can be used for producing solute/conductive salt by neutralisation. This reaction may not terminate instantly if some organic acids or bases are used in the electrolyte, it will require long time for completion. Therefore, the water content of the electrolyte may increase after thermal stability test. However, if only conductive salts were used as solutes, neutralisation will not take place in the electrolyte.

3.4 Capacitor Test Results

3.4.1 Capacitor Electrical Parameters

After impregnation with the developed electrolytes, the capacitors were aged up before any measurement. However, the capacitors using WEY-200-3 failed during ageing. This was one of the WEY-200 electrolytes, which showed the best thermal stability test results in Figure 2, but also being the only electrolyte in this paper showing aluminium foil attack (corrosion) in the same tests. After ageing of the remaining capacitors, the capacitance (C), ESR, impedance (Z) and leakage current (LC) were measured at 20 °C. Table 3 summarises the results for the 100, 200 and 400 V capacitors, using the WEY-100, WEY-200 and WEY-400 electrolytes, respectively.

Table 3. Capacitance (C), ESR and Impedance (Z) of Capacitors at 20 °C

Capacitor Parameters	WEY-100			WEY-200			WEY-400		
	WEY-100-1	WEY-100-2	WEY-100-3	WEY-200-1	WEY-200-2	WEY-200-3	WEY-400-1	WEY-400-2	WEY-400-3
C (μF,100Hz)	4829.2	4852.8	4846.8	1347.1	1338.8	failed	283.0	279.1	277.8
ESR (mΩ, 100Hz)	20.1	15.9	20.8	30.3	31.2	failed	117.2	114.3	166.0
Z (mΩ, 10 kHz)	14.7	10.8	17.2	16.4	16.5	failed	58.6	56.2	88.9
Leakage Current (mA)	0.071	0.044	0.065	0.110	0.111	failed	0.090	0.091	0.078

In comparison with the design electrical parameters detailed in Table 1, both capacitance and leakage current have met the design requirements. However, the electrical characteristics of capacitors needs to be evaluated from further capacitor tests.

3.4.2 Low Temperature Test Results

The electrical parameters of three kinds of capacitors at low temperatures were measured and are shown in Table 4. The capacitance ratio (%) in Table 4 was expressed as the capacitance measured at low temperature (-40 or -55 °C) and 100 Hz divided by the capacitance measured at 20 °C, which can be used for predicting the capacitor electrical characteristics at low temperature. If the capacitance ratio is relatively high at low temperature, *e.g.* the ratio C ≥ 95% for C(-40 °C)/ (20 °C), and even the ratio C(-50 °C)/ (20 °C) is also fairly high (> 93%) in Table 4, it is more likely for the capacitors to achieve satisfactory performance. On the other hand, the ratio of impedance at -40 °C and 10 kHz to the impedance at 20 °C and 10 kHz is reasonable, the capacitors will have good low temperature stability.

Table 4. Electrical parameters of the 100, 200 and 400 V capacitors at low temperatures

Capacitors		WEY-100			WEY-200		WEY-400		
Parameters		WEY-100-1	WEY-100-2	WEY-100-3	WEY-200-1	WEY-200-2	WEY-400-1	WEY-400-2	WEY-400-3
- 40/20 (°C)	**C,** 100Hz (%)	96.2	96.0	96.4	96.6	97.1	97.2	97.2	96.9
-40 °C	**ESR,** mΩ, 100Hz	85.8	98.0	76.0	138.1	138.3	442.7	413.0	918.5
-40 °C	**Z,** mΩ, 10kHz	70.6	78.6	62.1	114.3	112.7	381.0	354.5	762.5
- 55/20 (°C)	**C,** 100Hz (%)	94.1	93.6	95.1	95.7	95.9	96.3	96.4	95.5
-55 °C	**ESR,** mΩ, 100Hz	193.4	233.5	133.0	286.5	185.2	1067.0	994.0	2091.5
-55 °C	**Z,** mΩ, 10kHz	158.5	189.8	108.7	240.5	230.5	903.5	840.5	1757.5

3.4.3 Electrical Characteristics of the Capacitors

In order to evaluate the electrical characteristics of capacitors, capacitance (C), ESR and impedance (Z) were measured at different temperatures (from -55 to 125 °C). The plots of these electrical parameters as a function of temperature are illustrated in Figure 4.

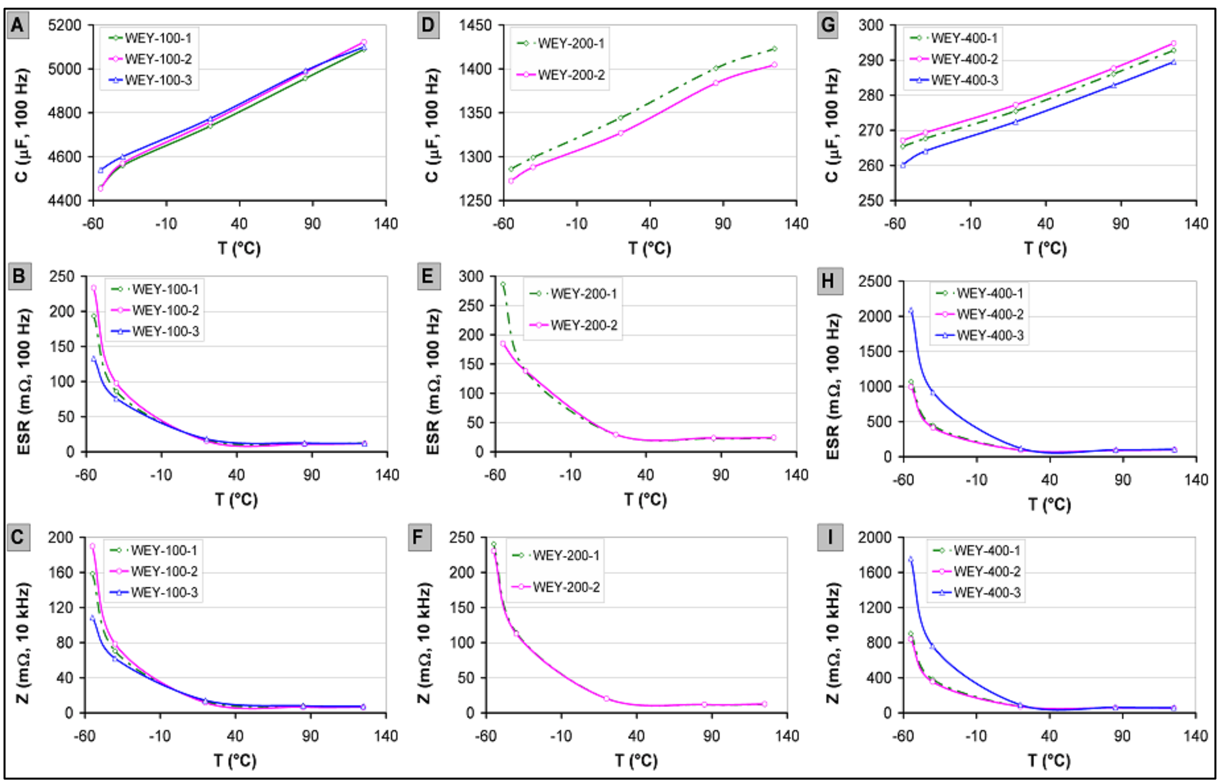

Figure 4. Plots of capacitance (C), ESR and impedance (Z) for the 100, 200 and 400 V capacitors as a function of temperature

Figures 4(A), (D) and (G) show the linear increase in capacitance with increasing temperature for all the WEY-100, WEY-200 and WEY-400 capacitors. When the temperature is lower than 20 °C, the ESR values in Figures 4(B), (E) and (H) dramatically increase. At -40 and -55 °C, some differences between the ESR values for the capacitors impregnated with different type of electrolytes can be observed. Especially, Figure 4(H) shows significantly lower ESR values for WEY-400-1 and WEY-400-2, compared to WEY-400-3. Thus WEY-400-1 and WEY-400-2 may be more suitable for 400 V capacitors at low temperature applications. This may be a result of the different chemical compositions in the electrolytes. However, when the temperature increases from 20 to 125 °C, the ESR values for all the capacitors become approximately constant. The impedance changes with temperature in Figures 4(C), (F) and (I) follow exactly the same tendency as that described for the ESR results. This implies that all the three types of sample capacitors will have good electrical characteristics in high temperature operations. However, the electrical characteristics and lifetime of the capacitors working at low and high temperatures will be finally determined by endurance tests and other tests such as temperature-frequency scans, transient voltage test, etc., which are currently in progress.

4. Conclusions

Three types of electrolytes, WEY-100, WEY-200 and WEY-400, working at 100, 200 and 400 volts and 125 °C for aluminium electrolytic capacitors, have been presented. The thermal stability test results at 125 °C have proved that the WEY-100-2, WEY-200-2 and WEY-400-1 electrolytes are the most stable electrolytes, and may be, respectively, suitable for 100, 200, 400 volts and high temperature (125 °C) capacitor applications. In addition, the esterification and the chemical decomposition might be the major factors to affect the chemical stability of the electrolytes developed in this work. The capacitors impregnated with all the developed electrolytes have exhibited good electrical characteristics at -40 and -55 °C, in terms of capacitance, ESR and impedance measurements. This implies that all these capacitors will have sufficient performance at low temperature. Moreover, as a result of capacitor parameters, excellent electrical characteristics are expected for all three kinds of capacitors to work at the maximum temperature (125 °C). Since the capacitor lifetime and electrical properties (*e.g.* C, ESR, Z and leakage current) also depend on the chemical stability of the electrolytes, endurance tests are required to investigate the chemical compatibility of the electrolytes with other components, such as aluminium foils, papers, polymeric decks, rubber seal-rings and vents. For instance, an electrolyte may present excellent thermal stability but cause aluminium corrosion (*e.g.* cathode attack) or be incompatible with the deck materials. Such endurance tests are now in progress and the final results (after 5000 hour tests) will be presented in our next paper.

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