SOLID STATE POLYMER MULTILAYER CAPACITORS FOR HIGH TEMPERATURE APPLICATION

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ABSTRACT

High-temperature polymer film capacitors are essential for applications demanding high energy density, reliability, and stable dielectric properties at elevated temperatures. Applications include power electronics for electric and hybrid vehicles, aerospace and aviation, oil and gas exploration, and industrial power electronics. This development addresses high temperature solid state polymer nanolaminate (NanoLam^{TM}) capacitors, which comprise thermoset nano-thick polymer dielectrics, formed using beta-radiation. The polymer chemistry is designed with a glass transition temperature above 200^{o}C, enabling capacitors to operate at temperatures exceeding 160^{o}C without significant loss in mechanical and dielectric properties. The molecular structure of the polymer is engineered to enhance self-healing properties by achieving higher H:C and O:C ratios higher than those of commonly used high-temperature polymer films. The data includes capacitor dielectric properties as a function of frequency and temperature in the range of -196^{o}C to 250^{o}C.

1.0 INTRODUCTION

High-temperature electronics are essential for aerospace applications where performance requirements are driven by operation in extreme environmental conditions. These include high altitude where temperature can fluctuate, supersonic flight, spacecraft re-entry into earth's atmosphere, electronics located near jet engines or rocket thrusters, as well as control and power processing systems. The benefits of high-temperature electronics include enhanced performance and reliability, reduced cooling requirements, improved durability, savings in weight and space. Additional system benefits include increased operational efficiency, extended mission duration, improved safety, and higher power output, as critical components can manage higher power levels without overheating.

High temperature capacitors are a key component in systems that must perform reliably in harsh thermal environments. Their ability to maintain performance and safety standards under extreme conditions makes them essential in aerospace, automotive, oil and gas, industrial, military, and power electronics applications. Commercially available capacitors fulfil most high temperature aerospace and industrial needs except for applications where compromises have to be made due to specific sets of parametric requirements. For example, a particular application may, in addition to high temperature operation, require high capacitance values, high voltage, capacitance stability with temperature and bias, and superior reliability. For such applications, the high capacitance and high voltage requirements eliminates tantalum capacitors as an option. Adding capacitance stability with temperature and bias makes ceramic capacitors impractical. The high temperature requirement alone eliminates polypropylene film capacitors. Finally, if high energy density is desired compromises must be made because high temperature film capacitors, such as PEN, PPS and others, have poor energy densities. NanoLam^{TM} capacitors presented in this work, are developed specifically to address this niche group of requirements that cannot be effectively serviced by other capacitor technologies.

2.0 NanoLam™ CAPACITORS

NanoLam^{TM} capacitors operate at high temperatures while exhibiting high energy density, superior breakdown strength, excellent stability with temperature and bias, and self-healing properties. NanoLam^{TM} capacitors comprise a nanolaminate solid-state structure, with 1000's of nano-thick dielectric layers [1-3]. The dielectrics are formulated with dielectric constants in the range of k=2.7 to k=4.0 for most applications and k>4 for select pulse power applications. NanoLam™ capacitors are produced using submicron polymer dielectrics because it has been shown that as the dielectric thickness decreases the breakdown strength increases [4,5]. This inverse relationship of breakdown strength with dielectric thickness is due to the electric field distribution across the capacitor electrodes – whereby charge carriers (electrons or ions) have a shorter path to travel before they can contribute to a breakdown event. This reduces the probability of charge accumulation that can lead to dielectric breakdown resulting in intrinsically higher breakdown strength. Uniform field distribution across the dielectric layer also plays a role in determining breakdown strength.

Local field enhancements due to impurities, defects, and surface roughness, can negatively impact breakdown voltage of a polymer dielectric material [6]. NanoLam^{TM} dielectric layers are highly uniform and are relatively free of impurities and physical defects. This is due to the highly cross linked, non-crystalline, structure of the dielectric, as well as the NanoLam™ process, which is uniquely capable of forming super-thin layers that are also largely free of defects. This results in an intrinsic breakdown strength greater than 1000V/mm. The NanoLam™ dielectric has a glass transition temperature Tg >200ºC and sees temperatures as high as 250ºC during the manufacturing process. The polymer material is formulated with high O:C and H:C ratios, which yields excellent self-healing properties. This in combination with the high breakdown strength of the submicron dielectrics and the higher dielectric constants, yields capacitors with superior energy density.

Other factors in designing high temperature capacitors include controlling the thickness of the metallized aluminum electrodes, terminal/lead connections to the capacitor, and packaging capable of meeting extreme temperature requirements. NanoLam^{TM} capacitors tested in this work are in two forms, individual capacitor elements and packaged parts. Fig. 1 shows individual capacitor elements, which are fully tested prior to the formation of a capacitor block, which comprises multiple capacitor elements that are connected in parallel using an arc spray process. The capacitor blocks are then lead attached and are encapsulated using an epoxy potting process into a high temperature polymer case.

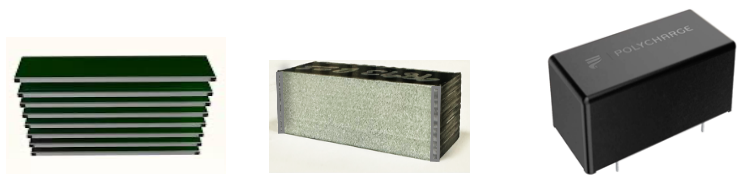

Fig. 1. Process of forming a NanoLam^{TM} capacitor using individual capacitor elements that are stacked, connected in parallel and epoxy potted in a polymer box.

3.0 PERFORMANCE OF NanoLamTM CAPACITORS

3.1 Parametric Performance vs. Frequency

Fig. 2, shows a comparison of a NanoLam™ capacitor rated 30µF/850V (shown in Fig. 1), and a state-of-the-art DC-link metalized polypropylene (PP) capacitor rated 28µF/900V. Although the PP has a low temperature rating (85ºC), it is used here for comparison because it is the industry standard for high ripple current DC applications. Due to the low dissipation factor, the PP capacitor at 10KHz has a slightly lower Equivalent Series Resistance (ESR), but above about 20KHz the ESR increases significantly - especially in the 100KHz to 1MHz range. The NanoLam™ capacitor has a relatively flat ESR response up to about 500KHz. Also, although the part is slightly higher in capacitance, the resonance frequency is significantly higher due to the small size and prismatic shape of the capacitors, which results in less than half the inductance of the PP capacitor.

3.2 Temperature Effects

The behavior of key NanoLam^{TM} capacitor parameters stems from the properties of the high temperature polymer dielectric, which is a highly cross-linked thermoset polymer. It has no melting-point and a high glass transition temperature (Tg), which limits thermal expansion and moisture transmission at temperatures less than 200ºC. Thermal gravimetric analysis of the polymer material, shown in Fig. 3, illustrates that the highly cross-linked polymer dielectric is thermally stable at up to at least 350ºC.

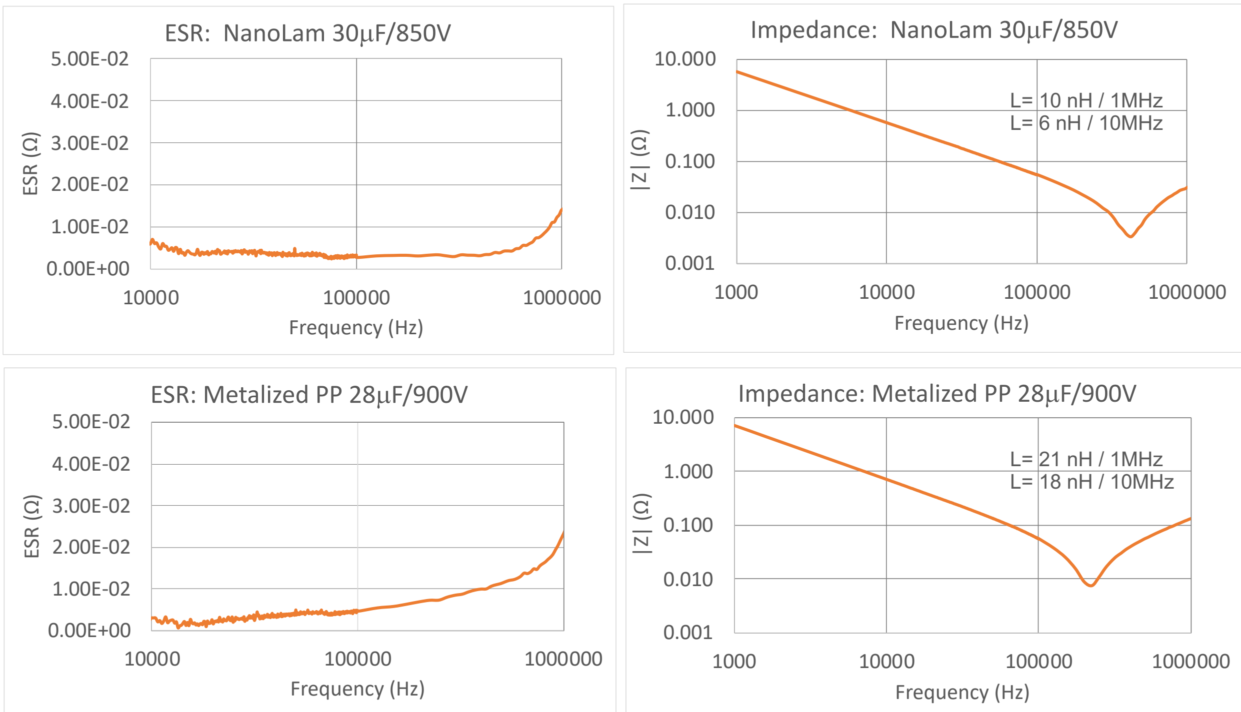

Fig. 2. High frequency response of ESR and impedance (Z) as a function of frequency of a high temperature NanoLam™ capacitor and a state-of-the-art metallized PP capacitor.

NanoLam™ capacitors see increases in capacitance with temperature rise - as much as 2% at 125ºC and 3% at 180ºC (Fig. 4). Interestingly, the dissipation factor decreases at 125ºC by as much as 50% from the value at room temperature. For DC-link application at 10KHz, as shown in Fig. 4, the ESR at 125ºC is ~35% lower than at 25ºC. This is taken into consideration when modelling a capacitor for high temperature and/or high ripple current applications.

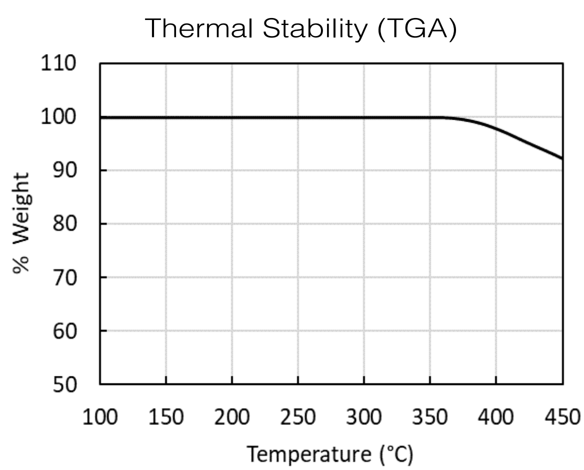

Fig. 3. Thermogravimetric analysis of the NanoLam™ capacitor polymer dielectric

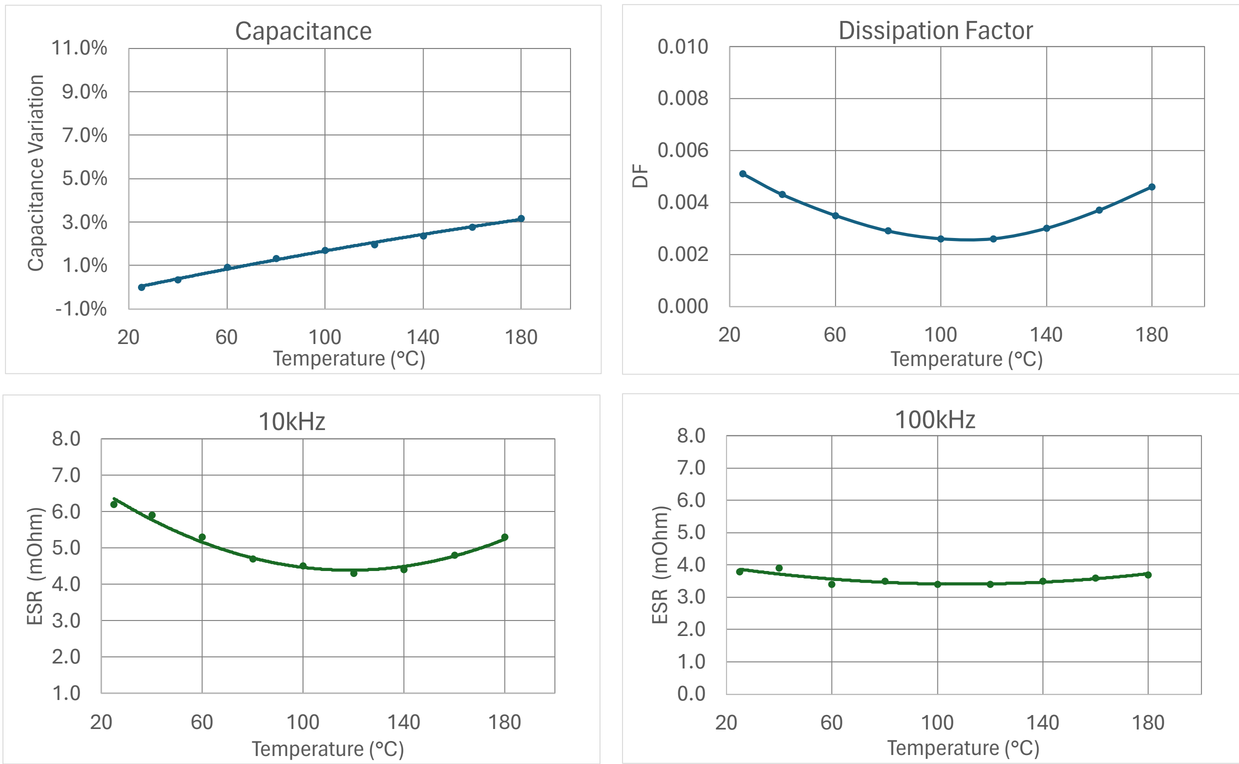

Fig. 4. Variation of key NanoLam™ capacitor properties with temperature. At the operating temperature range of 125ºC to 160ºC+, the capacitance increases by 2% to 3% and the ESR at 10KHz decreases by 20% to 30%.

3.3 Self-healing Properties

Self-healing is an important capacitor property especially for higher voltage and power capacitors and capacitors that are connected across power lines. The self-healing effectiveness of metallized capacitors depends on the properties of the capacitor electrodes, the polymer dielectric, and in many cases the capacitor construction.

3.4 Metallized Electrodes

The energy dumped in a self-healing event at a given voltage is primarily a function of the melting point of the electrodes and the cumulative thermal evaporation energy, which is proportional to the electrode thickness. The energy discharged is also inversely proportional to the electrode resistivity, or the effective resistivity, if the electrodes are segmented or have a thickness gradient. These factors require metals featuring both low melting point and high electrical conductivity. Electrode thickness is determined by ESR and lifetime requirements at given temperature and voltage conditions. The electrode thickness controls both the self-healing properties and the electrode corrosion resistance, which manifests itself as capacitance loss and increase in ESR over the life of the capacitor.

3.5 Polymer Dielectric

The ability of a metallized capacitor to self-heal at a given electrode and dielectric thickness is primarily a function of the O:C and H:C ratios in the chemical structure of the polymer dielectric. Carbon and aluminum are removed from the breakdown site by conversion τo Al_2O_3, CO, CO_2, CH_3, CH_4, and other low molecular weight hydrocarbons. The Nanolam™ polymer dielectric is formulated to maximize the O:C and H:C ratios and has excellent self-healing properties. In contrast, metallized PP capacitors that have no oxygen in the molecular structure rely on the presence of an air gap to form Al_2O_3, CO and CO_2. Other elements, including sulfur and atomic nitrogen, can also burden the self-healing process [7].

3.6 Effect of Temperature

When forced to undergo a large number of self-healing events, the energy dumped by consecutive arcs will rapidly raise the temperature in the capacitor volume. Conventional film capacitors, based on thermoplastic polymer dielectrics with low Tg, will lose mechanical and dielectric strength which can lead to a thermal runaway failure mechanism. For this reason, most film capacitors are voltage derated at higher temperatures. NanoLam™ capacitors can withstand 100,000s of self-healing events that can lead to some capacitance loss without undergoing a thermal runaway failure. As such, NanoLam™ capacitors do not require voltage derating as a function of temperature up to at least 160ºC. Fig. 5 shows how metallized polypropylene capacitors that have excellent self-healing properties undergo increasing damage as the number of self-healing events increases with voltage (until they become an open circuit). In contrast, the NanoLam™ capacitors during the same test lost <10% capacitance and continued to be functional.

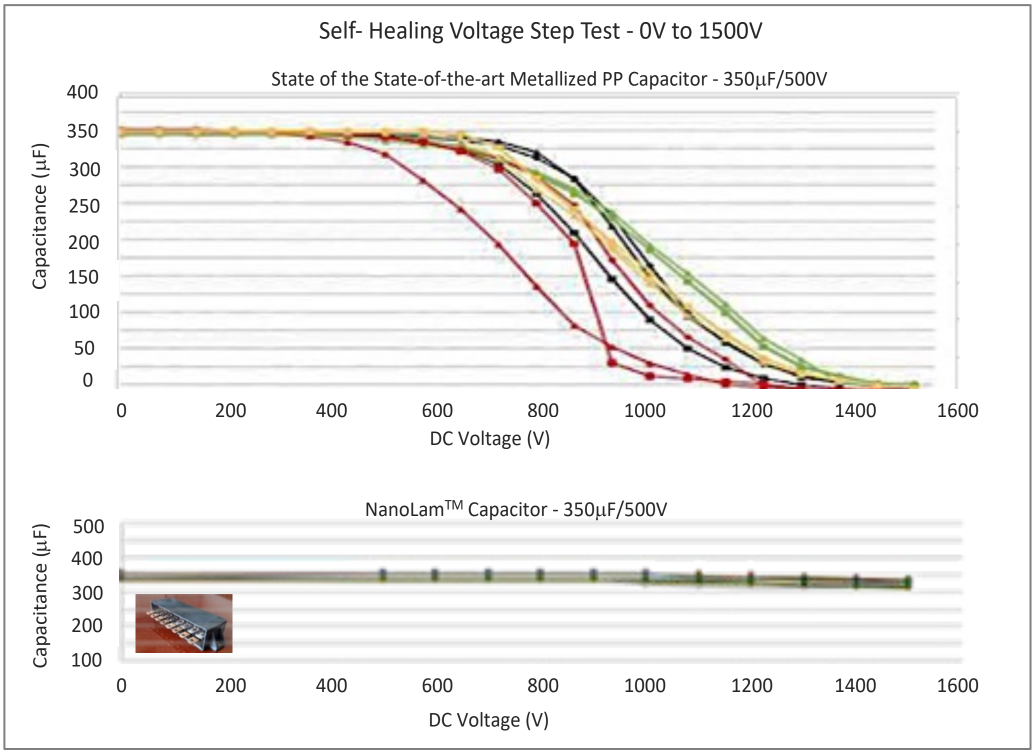

Fig. 5. Effect of increasing the level of self-healing events by overvoltage, in multiple metallized PP and NanoLam™ capacitors, showing zero capacitance for PP at 1500V, while NanoLam™ capacitors continue to be functional with less than 10% capacitance loss.

3.7 Effect of Dielectric Thickness

As noted above, NanoLam™ capacitors utilize nano-thick dielectrics to take advantage of the inverse relationship between dielectric thickness and breakdown strength. There are obviously limits to this relationship due to leakage current. As the thickness of the dielectric decreases below about 100nm (this thickness varies with different dielectrics), application of thermal energy and/or an electric field causes electrons to move into the conduction band (Poole Frenkel emmission) [8]. In thicker dielectrics the electrons are mostly trapped before they transition to the opposite electrode, while thinner dielectrics can lead to an increased leackage current. This is one of the reasons why electrolytic capacitors, with thinner dielectrics, have typically higher leackage currents than polymer films and ceramic dielectrics [9,10]. The dielectric thickness of NanoLam™ capacitors is positioned between films and electrolytics to take advantage of the higher breakdown strength without a significant impact on leakage current.

Higher voltage NanoLam™ capacitors comprise multiple internal series sections. For example, a NanoLam™ capacitor rated 900V can comprise up to five internal series sections. This effectively distributes the voltage load across 5 capacitors (or 180V per capacitor in series). Given that the discharge energy during a self-healing event is proportional to V^2, assumimg the same capacitance and electrode thickness, a breakdown in one of the five NanoLam™ capacitors will see a lower discharge energy than that in a conventional polymer film capacitor.

4.0 NanoLam™ CAPACITOR PERFORMANCE AT HIGH TEMPERATURE

The ability of a NanoLam™ capacitor to operate at high temperature is mainly a function of the dielectric breakdown strength and the corrosion resistance of the electrodes over 1000's of hours of life at voltage and temperature. For a given electrode thickness, corrosion resistance relies heavily on packaging, which has to provide adequate protection at high temperature to minimize ingress of moisture, which accelerates the electrode corrosion process. Testing at high temperatures must, at a minimum, address both the breakdown strength of the dielectric and parametric capacitor stability over time at voltage and temperature.

4.1 Breakdown Strength

NanoLam™ capacitor elements (see Fig. 1) rated 5µF/850V/125ºC were arbitralily rated and tested at 670V/160ºC, as a starting point to investigate performance at higher temperature. The capacitors were heated for 1hr to thermally equilibrate and 670V was applied to the parts for 5 minutes. Ten capacitor elements were tested at every temperature step. Voltage was applied on five elements while another five elements were exposed to the same temperature without voltage. The results shown in Fig. 6 indicate that the application of voltage has no effect on the performance of the capacitors. The drop in capacitance above 200ºC is also present on the parts that had no voltage, indicating that it may be due to a potential separation of metal/polymer layers at temperatures above 200ºC which coinsides with the Tg of the dielectric.

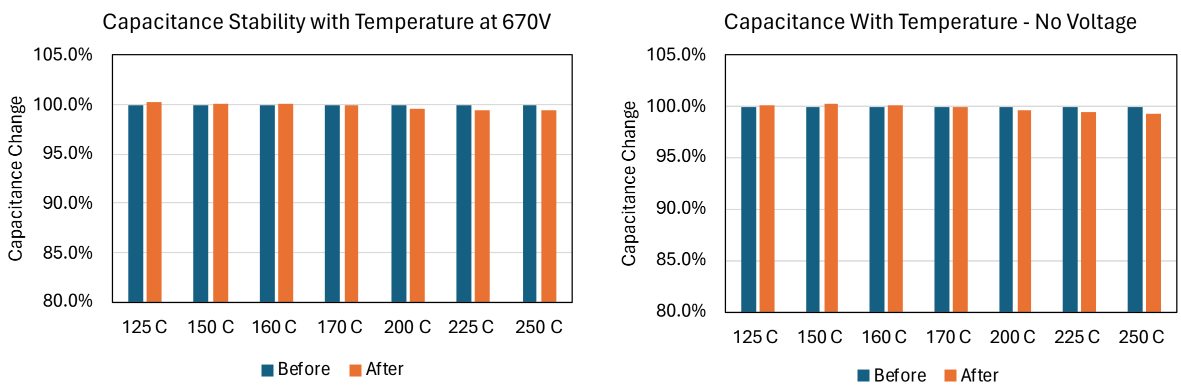

Fig. 6. Capacitance stability as a function of temperature of capacitor elements with and without voltage

An additional parametric stability test as a function of temperature was performed using five 30µF packaged parts (Fig. 1). The capacitors were heated at each temperature condition for one hour and 670V was applied for 5min. The capacitors were then cooled to room temperature and capacitance and ESR at 10KHz was measured. The results in Fig. 7 show that the capacitance and ESR are stable up to at least 200ºC. Starting at 225ºC a slight variation in capacitance and ESR is observed which becomes significant at 250ºC. Some of that may be due to the capacitor construction which includes a layer of babbitt (solder) over the zinc spray to "spot weld" the wire leads. In fact one can see in the photo of two of the tested parts molten babbitt that has been extruded in the periphery of the wire leads and the side wall of the box. As with the capacitor elements, the packaged parts show good parametric stability up to at least 200ºC.

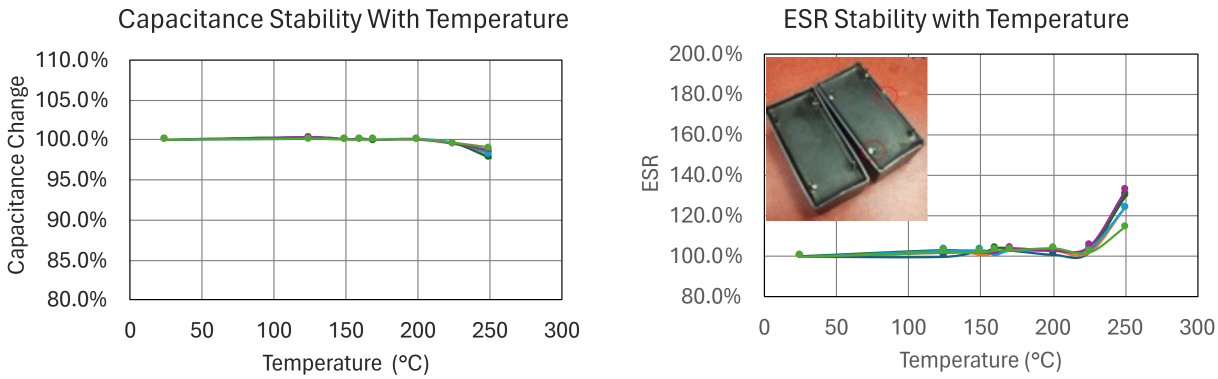

Fig. 7. Stability of capacitance and ESR of 30µF NanoLam™ capacitors as a function of temperature at 670VDC. The insert photo shows babbitt form the capacitor termination that has melted and moved out of the package around one of the leads and on the capacitor side wall.

Given that the application of 670V at high temperature has no significant effect on the capacitor performance, another test was performed where the voltage applied to the capacitors was increased to 850V. In this test 125mm long elements were chosen to accentuate any effects due to thermal expansion above the Tg. Two temperatures were chosen for this test, 200ºC and 250ºC. Again two groups of five elements were tested at each temperature, with no voltage on one of the groups. The results in Fig. 8 show a mesurable difference in capacitance at 250ºC betweeen the two groups of parts. Visual observation of the capacitors after the 250ºC test, shows that both groups of parts (with and without voltage) had some random level of polymer/metal separation, which caused the group of parts with 850V voltage to undergo multiple self-healing events that contributed to the higher loss of capacitance.

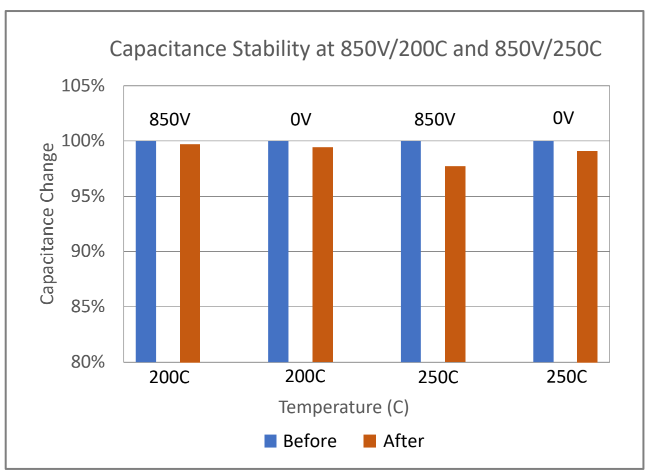

Fig. 8. Performance of capacitor elements tested at 200ºC and 250ºC with and without voltage.

An additional test was performed to determine the voltage level at which self-healing events are initiated. Packaged parts rated at 30µF/850V were tested both at room temperature and at 160ºC. Five packaged capacitors were tested at each condition using small voltage steps to detect the voltage level at which self-healing events are initiated. Fig. 9 shows the voltage level at which self-healing events iniate. This voltage is at least 2X the rated voltage of 850V, The right axis shows the capacitance loss after the parts are re-tested at room temperature. The average capacitance loss is of the order of 1%. Typically a capacitor failure will require the capacitance loss to exceed 10%. This suggests that the parts can survive either a higher voltage for a short period of time, or longer time at the mesured voltage before they surpass 10% capacitance loss.

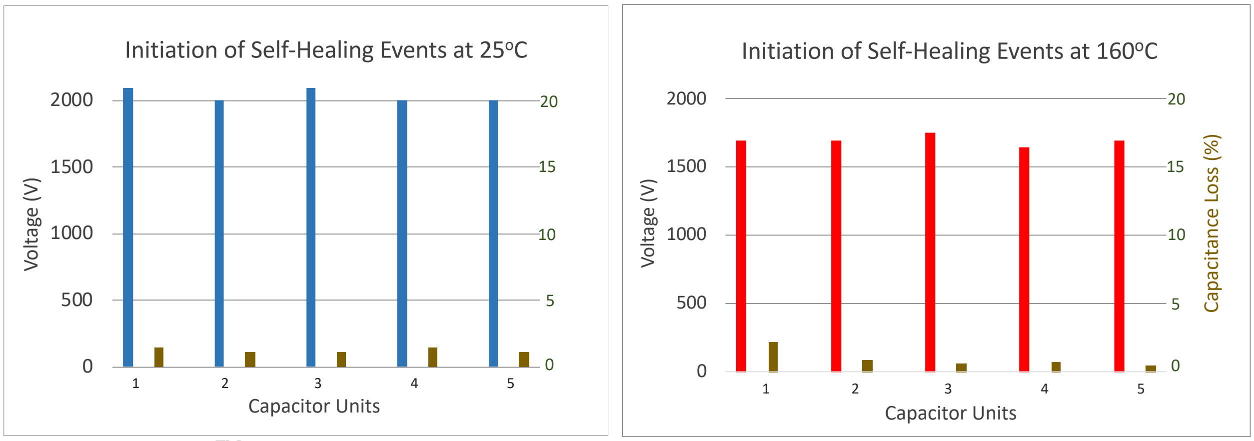

Fig. 9. NanoLam^{TM} 30µF/850V packaged capacitor are tested for self-healing event initiation voltage. The right axis shows the % capacitance loss after the parts are removed from voltage and are retested at room temperature.

4.2 Parametric Stability on a Longer Term Life Test

As noted above, one factor that can lead to failure is degradation due to self-healing events at voltage and temperature. This is not a major consideration for NanoLam^{TM} capacitors given that they have excellent self-healing properties and self-healing event initiation starts above 2X of rated voltage. Electrode corrosion at voltage and temperature over long periods of time is the main capacitor degradation mechanism, which can lead to capacitance loss and ESR increase. It should however be noted that the breakdown and corrosion mechanisms are interrelated because low ohms/sq electrodes (low ESR), will yield low capacitance loss over long periods of time, but it can lower the voltage at which self-healing events are initiated, which may reduce the ability of the capacitor to withstand high levels of overvoltage. In this work capacitors with the same electrode thickness were tested both for "breakdown" performance as well as performance at voltage and temperature over long periods of time. Fig. 10, shows average capacitance, dissipation factor and ESR of a group of packaged 30µF capacitors, that was first tested at 850V/125°C for a 1000hrs and then transitioned into a second test at 670V/160°C for 1250hrs. The data ilustrates excellent stability at 670V/160°C especially considering that the epoxy encapsulant has a Tg <160°C which allows increased moisture transmission into the package. Given that the at 160°C the self-healing event initiation voltage is approximately 1700V it is anticipated that at 670V operating voltage, the electrode thickness can be increased which will reduce ESR and minimize corrosion rate.

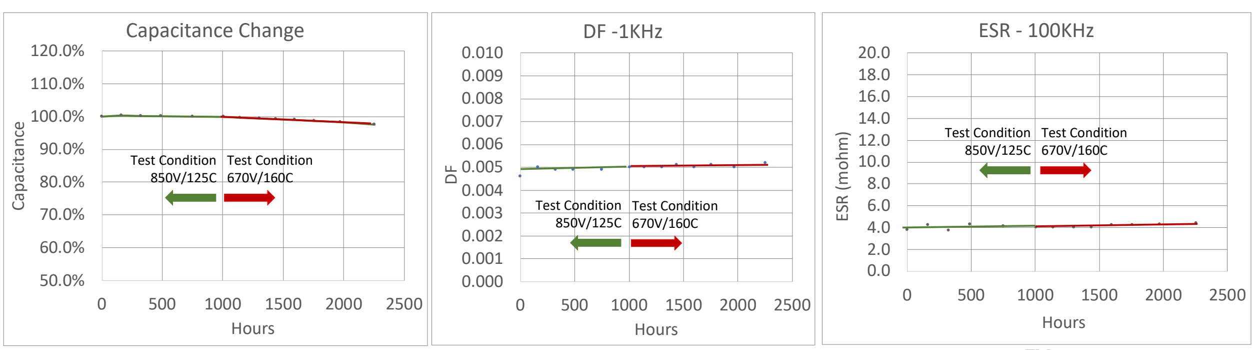

Fig. 10. Capacitance, dissipation factor and ESR performance of packaged 30µF NanoLam^{TM} capacitors tested at 850V/125°C for a 1000hrs and 1250hrs at 670V/160°C.

5.0 OPERATION AT CRYOGENIC TEMPERATURE

Previous development focusing on NanoLam^{TM} capacitor performance at cryogenic temperature demonstrated that the solid-state 50V-500V NanoLam^{TM} capacitors have stable capacitance, dissipation factor and ESR performance at temperatures as low as -196°C [1]. In this work 5µF/850V capacitor elements were tested at room temperature and at liquid nitrogen (LN2) temperature of -196°C, for breakdown voltage as well as capacitance loss due to self-healing events at these temperatures. The results of this test are shown in Fig. 11.

There are a few observations of interest in these results. First the breakdown voltage at NL2 temperature is virtually the same as that at room temperature, indicating that the solid state nanolaminate composite does not undergo any significant mechanical and dielectric changes at cryogenic temperatures. The capacitance loss at LN2 temperature is marginally higher than that at room temperature. This indicates that although the breakdown occurs at the same voltage the embrittled polymer dielectric as expected will fracture more easily during a self-healing event. Furthermore, the breakdown voltage in room temperature conditions is slightly higher than that of packaged parts shown in Fig. 9. The main reason for this is that the breakdown voltage of multiple elements that are stacked to produce a larger capacitor has a statistical distribution, and the measured voltage reflects the element that has the lowest breakdown voltage.

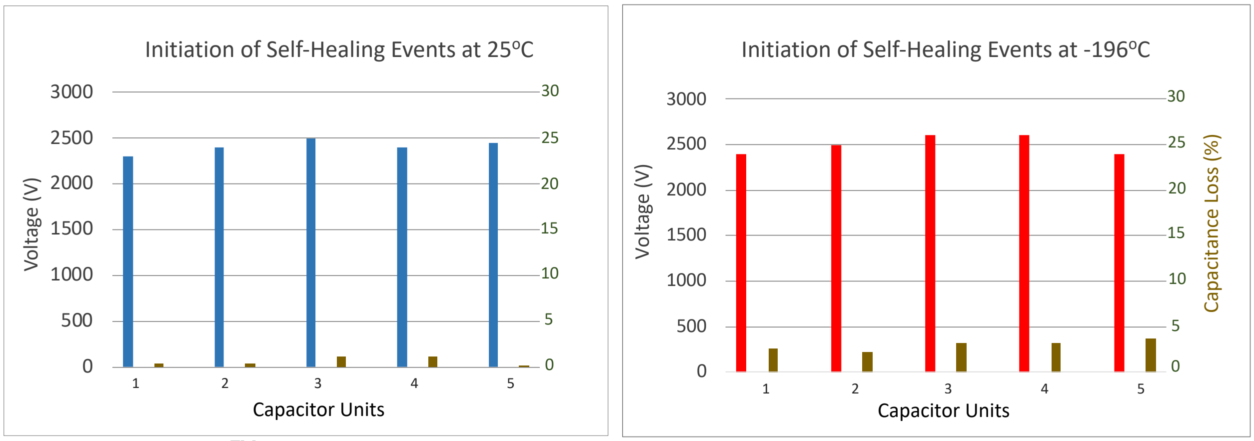

Fig. 11. NanoLam™ 5µF/850V capacitor elements (See Fig. 1) are tested for self-healing event initiation voltage at room temperature and at -196ºC. The right axis shows the % capacitance loss after the parts are removed from voltage and are retested at room temperature.

6.0 DISCUSSION

Selecting capacitors for high temperature applications requires careful consideration of the complete temperature range, dielectric properties at temperature, overvoltage withstand, life expectancy at temperature and voltage, and thermomechanical stability. The results of this work show that the breakdown strength of the high temperature NanoLam™ dielectric is not significantly affected in the temperature range of -196ºC to +200ºC. This wide temperature stability is mainly due to the mechanical and dielectric stability of the solid state nanolaminate composite used to produce the individual capacitor elements, including the high intrinsic breakdown strength, Tg>200ºC, thermal decomposition temperature >350ºC, and formulated high H:C and O:C ratios in the polymer chemical structure. Higher temperature polymers such as polycarbonate (PC), polyphenylene sulfide (PPS), polyethylene terephthalate (PET) and polyethylene naphtholate (PEN) that are used in capacitor applications, have glass transition temperatures Tg<150ºC. The high temperature performance is attained using aromatic chemistry (benzene rings) in the polymer structure. The combination of low Tg with aromatic chemistry which lowers the O:C and H:C ratios, leads to intrinsic breakdown strength that is less than 400V/mm [7]. Capacitors produced with these films have poor energy density when compared to NanoLam™ capacitors with the same capacitance and voltage rating. The same holds for higher Tg and temperature polymers such as polyetherimide (PEI), polyimide (PI) and fluorene polyester (FPE), as well as a multitude of experimental films that have higher levels of aromatic chemistry [7]. Therefore, from a temperature withstand perspective, if one excludes self-healing metallized capacitors, there are several high temperature polymer films that can be used to produce film/foil capacitors that can operate at temperatures of 200ºC and above. However, for applications that require less than 200ºC operation with high energy density and self-healing properties, the NanoLam™ capacitors have energy density superior to all polymer capacitors, with high parametric stability with temperature and frequency.

7.0 REFERENCES

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