# Hermetically Sealed Polymer Tantalum Capacitors and High Reliability Principles

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The major breakthroughs in Tantalum (Ta) capacitors which drastically broadened their applications were achieved due to changes in the cathode material of these capacitors. Initially Ta capacitors used liquid electrolyte in their cathodes (Wet Ta capacitors). These capacitors still have the highest volumetric efficiency CV/cc and working voltage; however, their equivalent series resistance (ESR) is high, especially, at lower temperatures. To solve this problem, Haring, Summit and Taylor from Bell Lab invented Dry Electrolytic Ta Capacitors (later called Solid Electrolytic Ta Capacitors) with an inorganic $MnO_2$ cathode.[1] Further reduction in ESR was achieved by Yamamoto et al (NEC) by introducing a conductive polymer cathode with much higher conductivity than that of $MnO_2$ cathode.[2]

While ESR trend was going down, the transformation of Ta capacitors from Wet to Solid with $MnO_2$ cathode and further to Polymer was accompanied by reduced maximum working voltage and volumetric efficiency of these capacitors (Fig. 1).

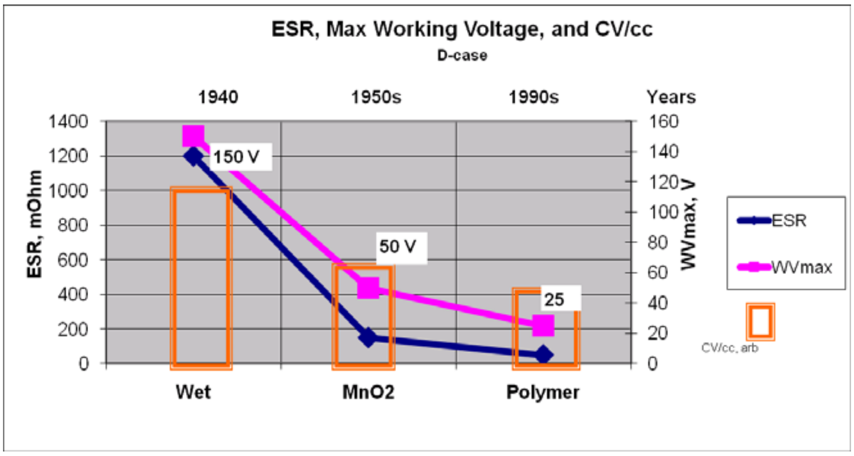


Fig. 1. Evolution of Ta capacitors.

Lower working voltage and CV/cc in $MnO_2$ and Polymer Ta capacitors compared to Wet Ta capacitors are due to the d.c. leakage (DCL) increase at relatively low voltages in these capacitors and, thereby, lower breakdown voltages (BDV), while DCL in Wet Ta capacitors remained low until applied voltage approached formation voltage (Fig. 2).[3]

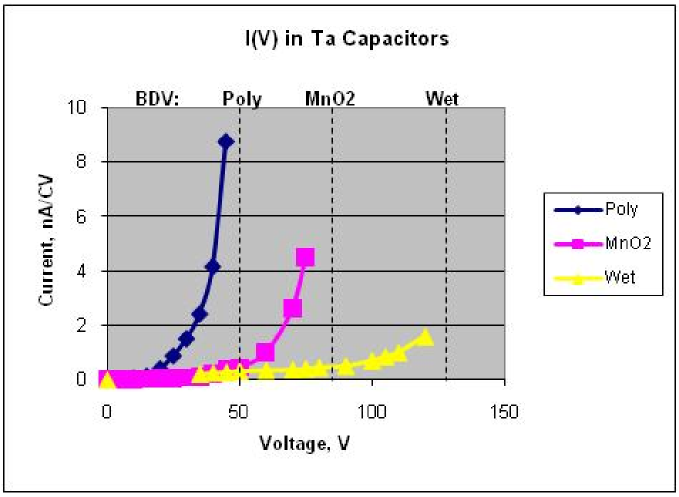


Fig. 2. DCL dependence on voltage in Polymer, $MnO_2$ and Wet Ta capacitors with 260 nm thick $Ta_2O_5$ dielectric [3].

Recently Kemet in collaboration with Clemson University discovered a possibility for DCL in Polymer Ta capacitors to remain low with increasing applied voltage similar to performance of Wet Ta capacitors.[4] This was achieved by making the dielectric in Polymer capacitors free of macro defects such as pores, cracks and crystalline inclusions and usage of pre-polymerized (slurry) poly 3,4-ethylenedioxygthiophene (PEDOT) cathode.

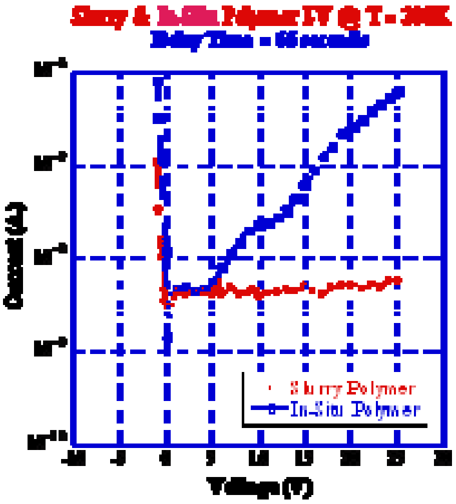


Fig. 3. DCL in Polymer Ta capacitors with dielectric free of macro defects and either pre-polymerized (slurry) or in-situ PEDOT cathode [4].

According to [4], the interface between the dielectric and pre-polymerized PEDOT cathode with p-type semiconductor properties plays a critical role in limiting current in these capacitors. This discovery opened the door for development of a new type of Polymer Ta capacitors with low ESR typical for Polymer Ta capacitors and high working voltage and volumetric efficiency typical for Wet Ta capacitors.

The purpose of this paper is to compare a.c. and d.c. characteristics of the newly developed Polymer Ta capacitors with traditional Wet Ta capacitors. The comparison was performed on hermitically sealed Polymer and Wet Ta capacitors with 82 uF capacitance and 75 V rated voltage. Frequency scans on these capacitors were performed in the range of frequencies 20 Hz – 1 MHz and temperature range from – 80 ÷ 125 $^{o}$C. Long-term Life test data are also presented for Polymer hermetic sealed (PHS) Ta capacitors 100 uF – 60 V.

## Results and Discussion

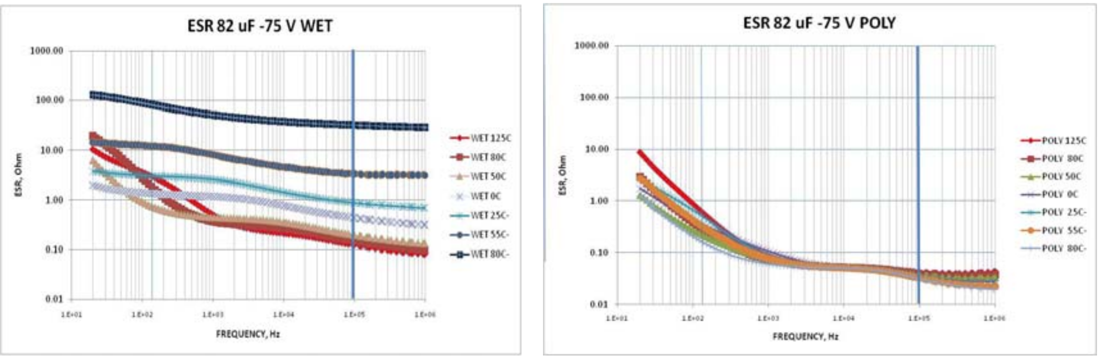
Conventional Wet Ta capacitors were manufactured by Kemet in 2008. These capacitors were made with sintered Ta powder anodes, an anodic oxide film of Ta approximately 260 nm thick as a dielectric, sulfuric acid as electrolyte and a porous cathode sleeve sintered to the Ta can. The can was hermetically sealed to prevent the electrolyte from drying and leaking.

Polymer Ta capacitors were made with sintered Ta powder anodes manufactured using so-called Formula 1 (F1) technology and special electrolyte for electrochemical oxidation of these anodes. [5,6] Pre-polymerized PEDOT slurry was deposited on the dielectric surface by dipping formed anodes in the dispersion of fine polymer particles and subsequent drying in air.[7] The external part of the polymer cathode was coated with conductive graphite and silver, and the capacitor was soldered to the plated brass can, aged and hermetically sealed. Fig. 4 shows appearances of the Polymer and Wet Ta capacitors.

Fig. 4. Hermetically sealed Polymer (top) and Wet (bottom) Ta capacitors B-cse 82 uF – 75 V.

As one can see, Wet and Polymer Ta capacitors have practically identical dimensions. Actually Polymer capacitors have 4.8% smaller volume than that of Wet Ta capacitor due to the slightly smaller diameter of their cans. Both Wet and Polymer Ta capacitors have the same rated voltage and capacitance with 10% tolerance. Thickness of the dielectric in Polymer Ta capacitor is slightly increased vs. that in Wet Ta capacitor with proportional increase in the anode volume. There is sufficient room for larger anode inside the can of the Polymer Ta capacitors since these capacitors don't have plastic bushings, a cathode sleeve and anode-cathode gap filled with liquid electrolyte as used in Wet Ta capacitors. Since both types of Ta capacitors are hermetically sealed and have the same rating and practically identical size, Polymer Ta capacitors can be used as a direct replacement of Wet Ta capacitors without any changes to the existing circuits.  At the same time, Polymer Ta capacitors have about 20% less weight than corresponding Wet Ta capacitors due to usage of the light brass cans instead of heavy Ta cans and Ta cathode sleeves.

Fig. 5 presents ESR dependence on frequency in the range of operating temperatures for Wet (a) and Polymer (b) Ta capacitors 82 uF – 75 V.



a b

Fig. 5. ESR vs. frequency in Wet (a) and Polymer (b) Ta capacitors 82 uF – 75 V

Comparison between Fig. 6a and 6b shows that in Polymer Ta capacitors ESR is much lower than that in Wet Ta capacitors and practically independent of temperature. The differences in ESR between Polymer and Wet Ta capacitors come from different conductivity of cathodes in these capacitors. In Wet Ta capacitors, conductivity of the cathode depends on concentration and mobility of ions in the liquid electrolyte. When ambient temperature approaches freezing point of the electrolyte, mobility of the ions becomes negligible, causing a sharp ESR increase.  In contrast to liquid electrolyte, conductivity of the PEDOT cathode in Polymer Ta capacitors is due to high concentration and high mobility of p-type current carriers. This conductivity remains high over a broad range of operating temperatures.

Fig. 6 presents capacitance dependence on frequency and temperature in Wet (a) and Polymer (b) Ta capacitors 82 uF – 75 V.

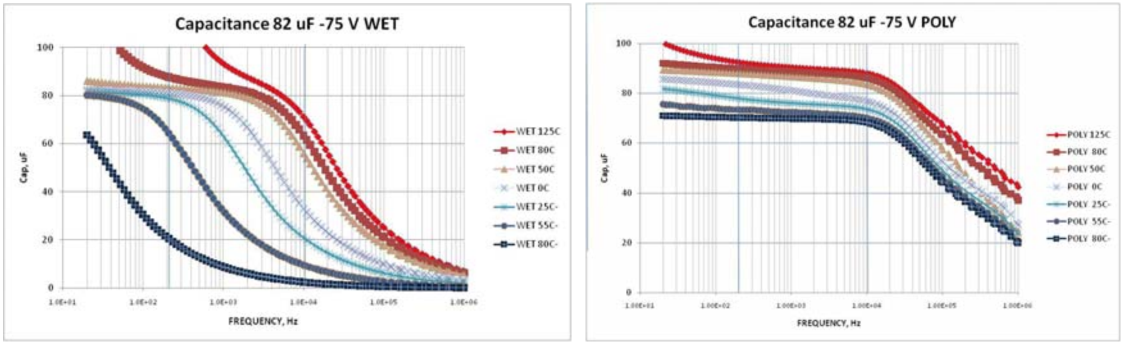


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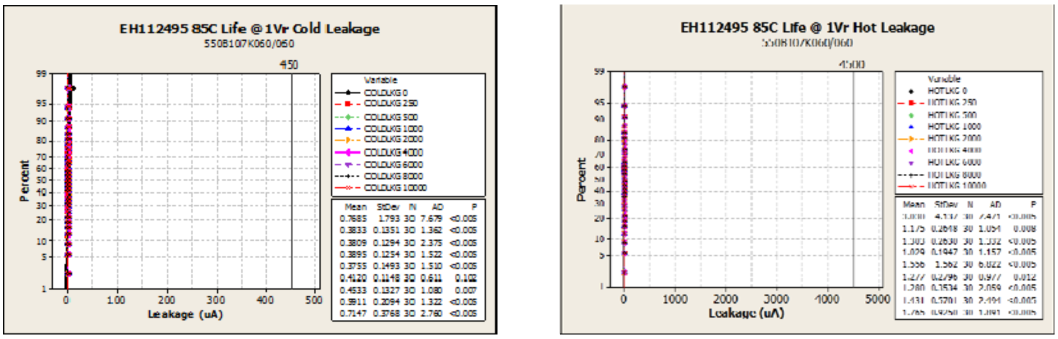
Fig. 6. Capacitance vs. frequency in Wet (a) and Polymer (b) Ta capacitors 82 uF – 75 V

The obvious differences in the capacitance dependence on frequency and temperature between Wet and Polymer Ta capacitors are related to the differences in ESR in these capacitors. High conductivity of PEDOT cathode in Polymer Ta capacitors allows electrical signal penetrate into the core of these capacitors, keeping capacitance stable in the broad range of frequencies and temperatures. In Wet Ta capacitors conductivity of liquid electrolyte falls sharply with increasing frequency and reducing temperature. As a result, electrical signal penetrates only the external surface of the Wet capacitor, causing capacitance roll off.

In many practical applications, several similar capacitors are connected in parallel to achieve the required total capacitance. This parallel connection of the capacitors has practically the same total capacitance dependences on frequency and temperature as those in each individual capacitor. For given total capacitance, a smaller number of Polymer Ta capacitors is required in comparison to Wet Ta capacitors due to the stability of capacitance vs. frequency and temperature in these capacitors.

Fig.7 demonstrates DCL distribution during long-term Life test at rated voltage and 85 C.



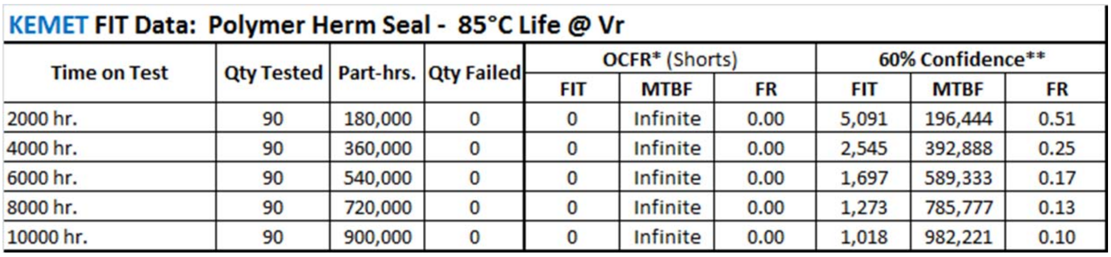
| Mean | StDev | N | AD | P |
|---|---|---|---|---|
| 0.7685 | 1.793 | 30 | 7.679 | <0.005 |
| 0.3833 | 0.1351 | 30 | 1.362 | <0.005 |
| 0.3809 | 0.1294 | 30 | 2.375 | <0.005 |
| 0.3895 | 0.1254 | 30 | 1.522 | <0.005 |
| 0.3755 | 0.1493 | 30 | 1.510 | <0.005 |
| 0.4120 | 0.1148 | 30 | 0.611 | 0.102 |
| 0.4533 | 0.1327 | 30 | 1.080 | 0.007 |
| 0.3911 | 0.2094 | 30 | 1.322 | <0.005 |
| 0.7147 | 0.3768 | 30 | 2.760 | <0.005 |

| Mean | StDev | N | AD | P |
|---|---|---|---|---|
| [illegible] | 4.137 | 30 | 7.471 | <0.005 |
| 1.175 | 0.2648 | 30 | 1.054 | 0.008 |
| 1.303 | 0.2630 | 30 | 1.332 | <0.005 |
| 1.029 | 0.1947 | 30 | 1.157 | <0.005 |
| 1.556 | 1.562 | 30 | 6.022 | <0.005 |
| 1.277 | 0.2796 | 30 | 0.977 | 0.012 |
| 1.280 | 0.3534 | 30 | 2.059 | <0.005 |
| 1.431 | 0.5701 | 30 | 2.494 | <0.005 |
| 1.765 | 0.9250 | 30 | 1.091 | <0.005 |

a b

Fig. 7. DCL distribution in PHS 100 uF – 60 V at room temperature (a) and 85 C (b) during 10,000 h Life test at rated voltage and 85 C

As one can see from Fig. 7, DCL in these capacitors is extremely low and absolutely stable at all the readings starting from virgin parts and up to final 10,000 reading. No failures were registered. These results allowed the reliability assessment shown in the Fig. 8 and used for defense logistics agency drawings.



**KEMET FIT Data: Polymer Herm Seal - 85°C Life @ Vr**

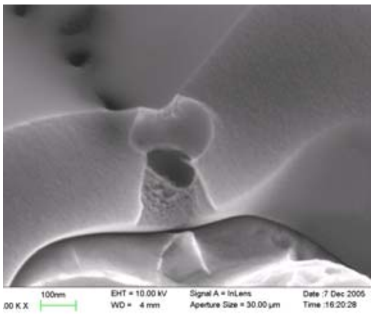
| Time on Test | Qty Tested | Part-hrs. | Qty Failed | OCFR* (Shorts) | | | 60% Confidence** | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | FIT | MTBF | FR | FIT | MTBF | FR |
| 2000 hr. | 90 | 180,000 | 0 | 0 | Infinite | 0.00 | 5,091 | 196,444 | 0.51 |
| 4000 hr. | 90 | 360,000 | 0 | 0 | Infinite | 0.00 | 2,545 | 392,888 | 0.25 |
| 6000 hr. | 90 | 540,000 | 0 | 0 | Infinite | 0.00 | 1,697 | 589,333 | 0.17 |
| 8000 hr. | 90 | 720,000 | 0 | 0 | Infinite | 0.00 | 1,273 | 785,777 | 0.13 |
| 10000 hr. | 90 | 900,000 | 0 | 0 | Infinite | 0.00 | 1,018 | 982,221 | 0.10 |

Fig 8. FIT data PHS 100 uF – 60 V for defense logistics agency drawings

The Life test is continuing beyond 10,000 h to achieve even better FIT for these capacitors.

## Hi Rel Approach: F1 Technology and Simulated Breakdown Screening (SBDS)

The outstanding stability and reliability of PHS Ta capacitors as well as other Polymer and $MnO_2$ types of Ta capacitors for special applications are strongly dependent on F1 technology and simulated breakdown screening (SBDS). The principle of the F1 technology is based on the fact, that the major degradation mechanism in high voltage Ta capacitors is growth of crystalline inclusions in amorphous matrix of the dielectric $Ta_2O_5$ film, which eventually causes the dielectric rupture and the capacitor failure.[10] Density and size of these crystalline inclusions are directly proportional to the density of the crystalline seeds on anode surface prior to anodizing. These seeds are originated by impurities on anode surface, typically carbide inclusions coming from residuals of organic lubricant used for pressing of Ta powder and oxide inclusions coming from native oxide dissolving in Ta particles during the powder sintering. Fig. 9 shows pores and cracks in the oxide dielectric formed on surface of Ta anodes enriched with carbon and oxygen.



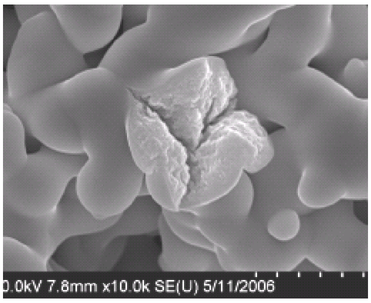


Fig. 9. $Ta_2O_5$ dielectric films formed on Ta surface enriched with carbon (left) and oxygen (right) [10]

F1 technology includes de-carbonizing and de-oxidizing steps providing chemical purity to the anode surface.[4] F1 technology also provides strong anode-to-lead attachment since mechanical stress in this junction can also provoke crystallization. This allows forming of practically defect free dielectrics on the surface of Ta anodes manufactured with F1 technology (Fig. 10).

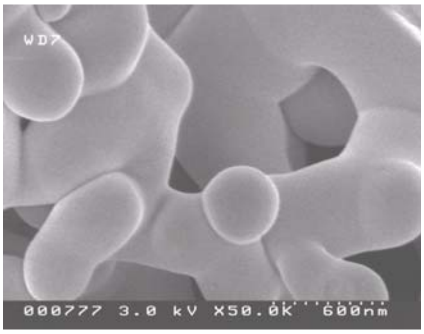
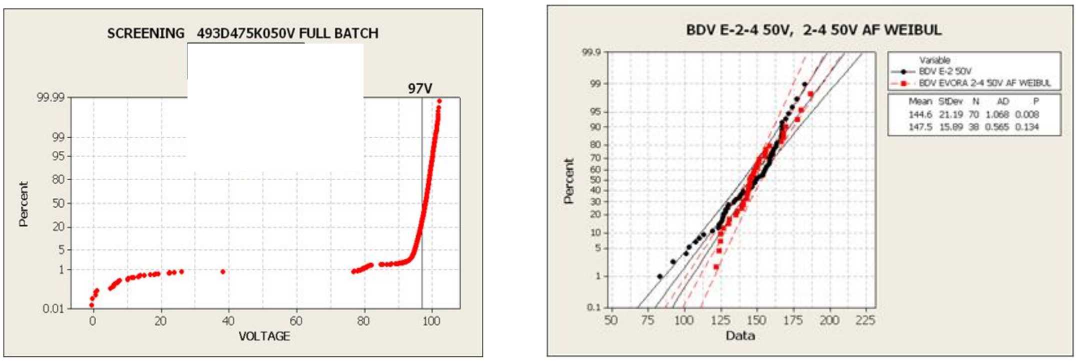


Fig. 10. SEM images of $Ta_2O_5$ dielectric film formed on Ta anode manufactured with F1 technology**.**

Even with the most advanced manufacturing technology, there is a probability that a small percentage of the finished capacitors may have small hidden defects in their dielectrics, which can't be detected by DC leakage during end-of-the-line (EOL) testing and can propagate and cause failures during the field application. Moreover, some overstressed tests and burn-ins can induce hidden defects into the dielectric without being detected by existing techniques.

The most efficient way to detect hidden defects in the dielectric is breakdown voltage (BDV) test. Low BDV indicates defects in the dielectric, while high BDV close to the formation voltage indicates defect-free dielectric. Despite of its efficiency for a sample based batch control, BDV test can't be used for 100% screening purpose since it's a destructive test. That's why simulated breakdown screening (SBDS) was developed that allows screening of the low BDV parts without any damage to the population of the capacitors.[8] This test is based on the analysis of the capacitance charge characteristics when voltage exceeding average BDV is applied to the tested capacitor with high series resistor limiting current through the capacitor. Actual BDV determined on a sample from each manufacturing batch is used to determine parameters of the SBDS.

As an example, Fig. 11 shows typical SBDS distribution in D-case Ta/$MnO_2$ capacitors 4.7 uF – 50 V manufactured with F1 technology (left) and actual BDV distribution on a sample of these capacitors before and after SBDS (right).



a b

Fig. 11. SBDS distribution (a) and BDV distributions before and after SBDS (b) in D-case Ta/MnO$_2$ capacitors 4.7 uF – 50 V manufactured with F1 technology

As one can see on Fig. 11a, there is about 1% tail on the SBDS distribution despite of the fact that the capacitors were manufactured with F1 technology and passed all the tests required by the MIL-PRF-39665. Actual BDV distribution after the SBDS (Fig. 11b) confirms that the parts with low BDV were removed, while no damage (no change in BDV) was done to the parts from normal population.

The generally accepted criterion for the long term reliability is **BDV ≥ 2Va,** where Va is application voltage. According to Fig. 11b, minimum BDV = 85 V before SBDS, which requires approximately 20% de-rating to satisfy this criterion. After the SBDS minimum BDV = 125 V, (**BDV > 2Vr**), where Vr is rated voltage. This means that these 50 V capacitors with F1 technology and SBDS don't need any de-rating at temperatures T ≤ 85$^{o}$ C.

The major steps providing the highest reliability to Ta capacitors as well as the key criteria for each of these steps can be summarized following:

1. **Scientific foundation - peer reviewed publications**
2. **Technology - flawless dielectric**
3. **Batch control - BDV (BDV is an ultimate indicator of the dielectric quality, while DCL can't detect small hidden defects in the dielectric)**
4. **EOL Testing – comprehensive test protocol including major traditional steps and avoiding overstress that can induce hidden defects in the dielectric.**
5. **Ultimate Final Screening - 100% SBDS (Patent US 7,671,603 B2)**

Comparative tests by 3$^{rd}$ parties confirmed that F1/SBDS Ta capacitors demonstrate the highest in industry stability and reliability.

## Conclusion

Results presented in this paper show that a combination of F1 technology with its defect-free dielectric and a pre-polymerized PEDOT cathode allows manufacturing of a new type of Polymer Ta capacitors with record high working voltage, charge and energy efficiency, ripple current capability, stability and reliability. These capacitors also demonstrate record low DCL and ESR as well as record high capacitance retention vs. frequency and temperature. Additional features of these capacitors are low weight and high mechanical strength as well as low de-rating and benign failure mode. Defense logistics agency drawings for these capacitors have been submitted.

## Acknowledgements

The authors would like to thank Dr. William R. Harrell, Dr. Igor Luzinov and Ph.D. student G. Alapatt from the Clemson University for their important contributions to this development.

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