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## Improved ESR on MnO<sub>2</sub> Tantalum Capacitors at Wide Voltage Range

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### ABSTRACT

One common trend in switch-mode power supply, micro-processor, and digital circuit applications is to achieve reduced noise while operating at higher frequencies. In order to realize this, components with low Equivalent Series Resistance (ESR), high capacitance and high reliability are required. A new generation of Low ESR tantalum chip capacitors has been developed utilizing a low resistivity MnO<sub>2</sub> electrolyte that enables very low component ESR. MnO<sub>2</sub> technology provides excellent field performance, environmental stability and high electrical and thermal stress resistance in wide voltage range from four to thirty-five volts. The capacitors are designed for operation in temperatures up to 125°C.

## INTRODUCTION

Tantalum capacitor technology has many characteristics ideal for filtering applications in DC/DC converters, power supplies and other applications. The most important and common characteristics are:

- Low and Stable ESR
- High Capacitance Retention at High Frequencies
- Low Failure Rate
- Wide Voltage Range
- Surge Robustness
- Environment (moisture/temperature) Resistant
- Low Cost

The above features were taken as the development criteria for the new TPS Series III of very low ESR capacitors. MnO<sub>2</sub> technology in conjunction with tantalum dielectric is best suited to meet all of the criteria including low ESR, excellent stability, reliability and wide voltage range.

## DESIGN FOR VERY LOW AND STABLE ESR

### Anode Shape

The overall surface area of a tantalum capacitor anode, particularly its surface-to-volume ratio, is one of the key parameters that defines its ESR value - the higher the overall surface area, the lower the ESR.

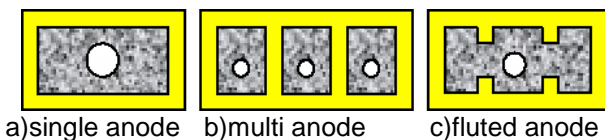


Fig. 1. Anode seign in cross section

The single anode (Figure 1a) is the standard used for general capacitor designs because of cost and performance efficiency. A multi-anode design (Figure 1b) offers the lowest possible ESR [1,2]; however it is a more costly solution. Apart from additional manufacturing steps (e.g. multiple internal welds), there is also a production yield impact. If the standard yield for single anode (the active capacitor element) is ~ 90%, then the total yield for three anodes in a single assembly is ~ 0.9x0.9x0.9 = 73%, entailing higher cost compared to a single anode solution. The fluted anode design (Figure 1.c) using standard chip assembly

processes was selected for New TPS Series III design as the optimum compromise between low ESR and cost requirements.

### MnO<sub>2</sub> Conductivity

Much experimental research has focused on improving the MnO<sub>2</sub> conductivity by optimising pyrolysis conditions [3, 4]. This has resulted in significant overall ESR reduction. While process design of experiments can optimise ESR, the basic physics behind conductivity processes in MnO<sub>2</sub> was not fully understood. This led to the conclusion that ESR levels below 50mΩ for tantalum capacitors could only be achieved by either conductive polymer or multi-anode solutions.

Current research in co-operation with Czech Noise Research Laboratory of Brno University of Technology suggests that the capability for MnO<sub>2</sub> to achieve high conductivity in tantalum capacitors has been underestimated. Now, based on a better understanding of the physical mechanisms involved, we are able to demonstrate that ESR values can be significantly improved by modification of MnO<sub>2</sub> technology in accordance with the energy level diagram shown below:

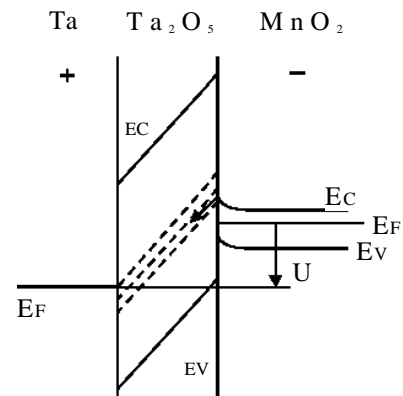


Fig. 2. Band diagram of tantalum capacitor in normal mode

A tantalum capacitor can be represented by MIS hetero-structure with N-type MnO<sub>2</sub> semiconductor having a band diagram, as illustrated in Figure 2 (see also Figure 5). In this model, MnO<sub>2</sub>:β phase has a band gap of 0.26 eV and MnO<sub>2</sub>:γ phase 0.58-0.7 eV. When an ideal MIS structure is biased, three cases may exist at the semiconductor surface: the accumulation of carriers near the semiconductor surface, depletion of carriers and carrier inversion. These parameters are also dependent on bulk conductivity, carrier concentration (typically 10<sup>19</sup> cm<sup>-3</sup> with mobility (1-3) Ωcm<sup>2</sup>/Vs),

and surface charge density or surface potential (also a function of  $MnO_2$  crystals surface morphology). The volume of  $MnO_2$  and its crystals surface potential depend on temperature. Conductivity (ESR) increases with temperature and humidity. Both the morphology /structure and conductivity of  $MnO_2$  crystals are crucial to ESR improvement. The interfaces between Ta -  $Ta_2O_5$  and  $Ta_2O_5$  -  $MnO_2$  are also important to consider for ESR versus frequency characteristics.

Figure 3 is a comparison of typical ESR values at 100kHz for conventional TPS and Series III TPS.

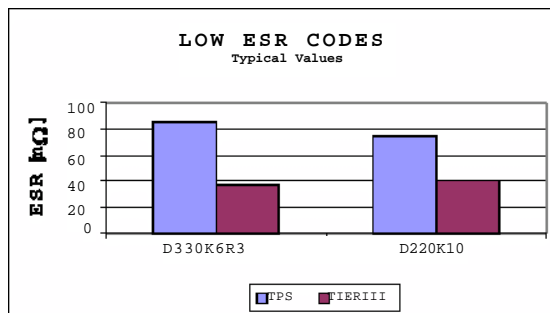


Fig. 3. Conventional TPS vs Tier III typical ESR value

### ESR, Capacitance vs frequency, Higher Ripple Load

The ESR improvements resulting from the new Low ESR Series III technology can be seen over whole frequency range from 100Hz up to the capacitor's self-resonance frequency. A comparison of a conventional TPS low ESR capacitor D case 100 $\mu$ F 10V with 100m $\Omega$  ESR, a new TPS Series III D case 100 $\mu$ F 10V with 50m $\Omega$  ESR and a conductive polymer D100 $\mu$ F 10V with 55m $\Omega$  ESR are shown in Figure 4.

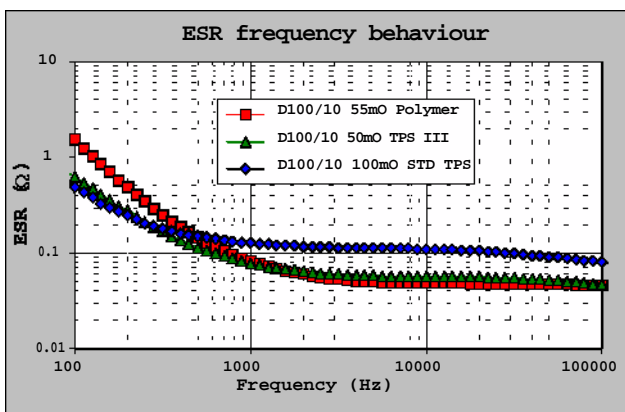


Fig. 4. TPS, TPS III and Polymer ESR vs. frequency

Lower ESR in tantalum capacitors is also associated with lower capacitance loss with frequency and higher continuous ripple current ratings [1]. These effects depend on the actual ESR level, and are of the technology employed. Hence, for example, D case capacitors having a 100kHz ESR of 50m $\Omega$  made with  $MnO_2$  or conductive polymer materials will show about the same capacitance loss with frequency and have equivalent ripple current ratings (power dissipation for a molded D case part is essentially independent of the electrolyte technology used). The capacitance loss over frequency for the same group of parts as above is shown in Figure 5, and a ripple current comparison is shown in Fig.6.

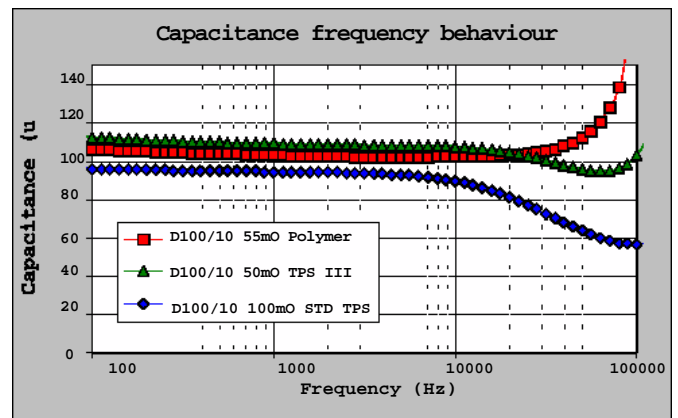


Fig. 5. TPS, TPS III and Polymer Cap vs frequency

Series	PartNumber	Ripple Current(mA)@100kHz		
		25°C	85°C	125°C
conventionalTPS	TPSD107K010R0100	1225	1102	490
TPS Series III	TPSD107K010R0050	1732	1559	693

Fig. 6. TPS and TPS III Ripple Current Comparison

### Temperature Dependence of ESR

The temperature behaviour of ESR for new TPS III capacitors, as compared to conventional low ESR tantalum and polymer tantalum capacitors is shown in Figure 7.

The conductivity of  $MnO_2$  increases as temperature increases. When used as the counter-electrode material in tantalum capacitors, this gives lower ESR as temperature increases. This is a significant difference to the ESR characteristic of polymer counter-electrode systems, which do not have increased conductivity. This is an important consideration in applications with higher operating temperature.

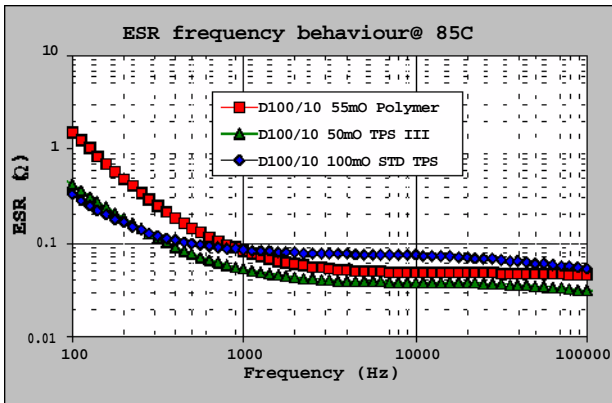


Fig. 7. TPS, TPS III and Polymer vs frequency 85°C

### Graphite and Silver Counter-electrode Materials

Graphite and silver polymeric materials are used as part of the outer counter-electrode layers. The self-resistance and contact resistance of these materials also has a significant effect on the overall ESR and ESR stability (see Figure 6). It can be expected that interface resistance between MnO<sub>2</sub> and graphite is also dependent on the material formulation and how it is applied. Close co-operation with manufacturers of these materials has resulted in an improved materials system for the new TPS series III to maintain a low and stable ESR under various humidity and high temperature conditions.

Highly accelerated tests were used to evaluate ESR stability. Standard TPS and TPS Series III units were subjected to a 1<sup>st</sup> reflow cycle, then subjected to a pressure cooker test (two hours humidity exposure at two atmospheres pressure at 120°C) followed by a 2<sup>nd</sup> exposure to reflow. The results on D case 330µF 6.3V rating are shown in Figure 8.

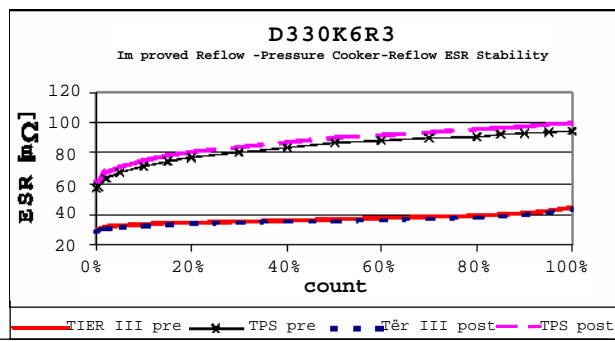


Fig. 8. D330µF 6.3 V ESR stability after pressure cooker / reflow test.

## SURGE ROBUST

### Active Surge Load Suppression

Following the improvements made in the graphite and silver materials, humidity and stress absorption barriers were also evaluated in the new TPS Series III design. The role of these barriers is to absorb any mechanical stresses that can occur (typically during pcb manufacture) as well as electrical stresses (typically in low impedance circuits such as in power supply applications).

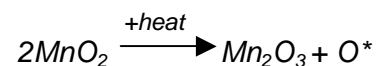
### Advanced Surge Testing

An intelligent dynamic surge test has been developed based on observations of thermal runaway in overloading conditions – see CARTS published papers [7,8]. The new TPS Series III is 100% surge screened using this system during production.

## LOW FAILURE RATE and DCL

### Efficient Self-Healing

Tantalum capacitors are well known for good reliability characteristics, no dielectric wear-out mechanism and decreasing failure rate with time under steady state conditions. The self-healing process of MnO<sub>2</sub> is responsible for this behaviour. Current flowing through a defect site in Ta<sub>2</sub>O<sub>5</sub> dielectric heats MnO<sub>2</sub> at the interface. At temperatures about 400°C, the conductive semiconductor MnO<sub>2</sub> will change to Mn<sub>2</sub>O<sub>3</sub>, a material having much higher resistivity. This process can isolate the failure site and self-heal the capacitor.



Mobile oxygen atoms, a side product of this reaction, are also an important element in the self-healing process of MnO<sub>2</sub> tantalum capacitors. This oxygen is responsible for decreasing failure rate with time as it continually dopes the Ta<sub>2</sub>O<sub>5</sub> dielectric and maintains its dielectric features. There are self-healing mechanisms known for different technologies such as aluminium, plastic film and polymeric capacitors; however the decreasing failure rate with time is solely a characteristic of the traditional MnO<sub>2</sub> tantalum capacitor system.

Larger concentrations of oxygen produced by self-healing during high surge overload can however result in thermal runaway of the capacitor. Hence, surge limitation and/or appropriate derating is recommended for low impedance applications to protect the capacitor against overload (see Figure 9).

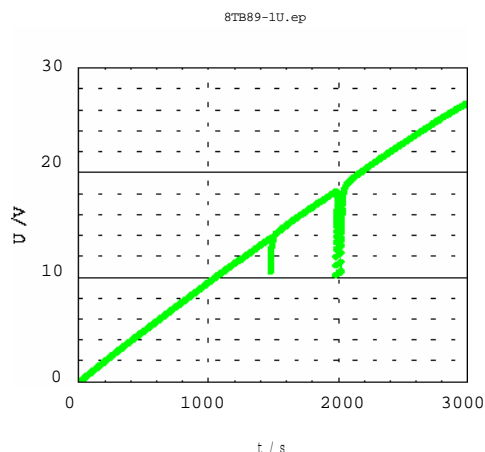


Fig. 9. Self healing effect on 10V MnO<sub>2</sub> capacitor

During overload, the internal thermal impedance of the tantalum anode is important in providing good surge robustness of these very low ESR parts; in TPS series III, a special mix of tantalum particle sizes is used to enable greater internal heat dissipation and ensure no “weak links” occur as thermal runaway paths are generated.

A simple test that can be reproduced in any basic laboratory can demonstrate the high efficiency of the self-healing process in tantalum capacitors with MnO<sub>2</sub> counter-electrode. A ramp voltage source is applied to the capacitor with small voltage increments to initiate electrical breakdown of the dielectric, but not to cause thermal overloading. An optional resistor (1kΩ) can be added for better current limitation and faster voltage step-up change. It is possible to see the first breakdown at a voltage approximately 40% higher than the rated voltage. High current will start to flow through the capacitor and generate the self-healing reaction that repairs the failure site and the capacitor leakage will return to normal. Two breakdowns at 14v and 18v were recorded in a 10v rated capacitor with subsequent self-healing – see Figure 9. This effective self-healing process is unique to MnO<sub>2</sub> tantalum capacitor technology only and unlike any other technology / component self-repairing reactions.

### Low Leakage Current (DCL)

The general specification for leakage current of tantalum MnO<sub>2</sub> capacitor ratings is  $0.01 \times CV$  (0.01 x capacitance x voltage rating) equation. For example, 100μF 10V capacitor will have 10μA DCL specification limit. The same capacitor with conductive polymer has a ten times higher DCL limit at 100μA. The difference in leakage current between these two technologies is possible to explain by the different work functions of MnO<sub>2</sub> and CP (conductive polymer) materials. This can be understood by reference to the MIS structure (see e.g. 5])

### **WIDE VOLTAGE RANGE**

The new TPS Series III comprises a full voltage range from four to thirty five volts, as with most MnO<sub>2</sub> technologies. This series provides the lowest ESR available for high voltage parts – especially 25v and 35v ratings demanded by Power Supply applications.

### **WIDE TEMPERATURE RANGE**

Wide temperature range operation is one of the additional requirements of power converter designers. Series III is specified within operating temperatures from -55°C up to +125°C in accordance to working range of MnO<sub>2</sub> capacitors. This range allows standard operation at higher temperatures (125°C) compare to the current polymer solutions on diverse capacitor technologies (usually +105°C maximum).

### **Application Test**

An application experiment was performed in order to compare filtering abilities of the conventional TPS capacitor D case 100μF 10V 100mΩ rating, the new TPS Series III D case 50mΩ and conductive polymer 55mΩ ratings. The evaluation used a Linear Technology switching regulator (LTC1159) with a 10v input and 3.3v output rail at 3.3Ω load – see Figure 10.

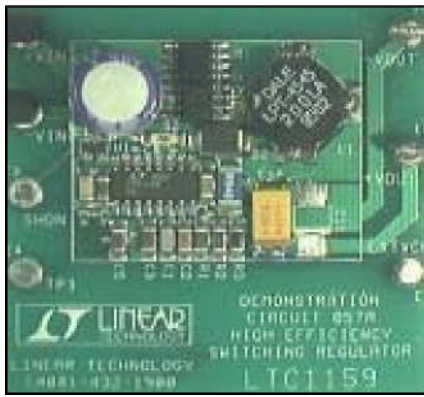


Fig. 10. LTC1159 test board picture

The output ripple current with a single capacitor on the output was recorded at operating temperatures of 25°C and 85°C to evaluate the filtering abilities of conductive polymer, TPS and TPS III series. (The LT specification recommends two D case 100µF 10v 100mΩ capacitors). – see Figures 11 and 12 below.

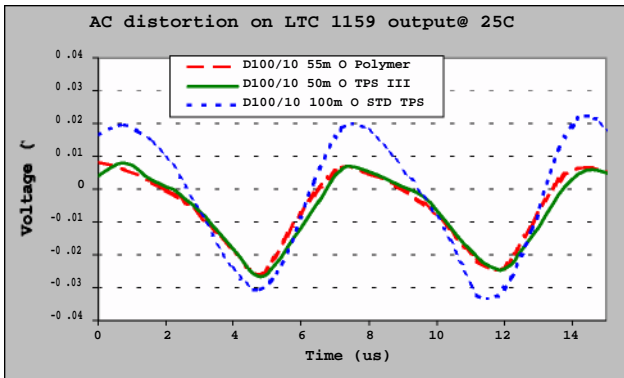
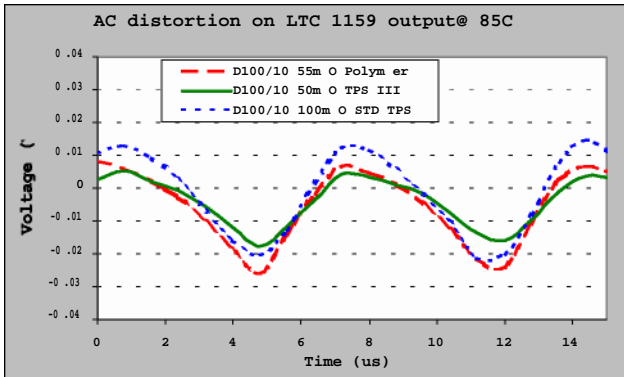


Fig. 11,12. AC distortion output on LTC1159



Comparable values of output ripple distortion were measured with TPS III and Polymer capacitors on the output at 25°C. There is no surprise that the standard TPS with twice the ESR value shows worse output ripple distortion. But significantly, the output ripple noise drops to its lowest in the case of the TPS III capacitor at the higher operating temperature (85°C) when compared to the conductive polymer capacitor. This is in-line with ESR versus temperature behaviour discussed previously in this paper.

### Specification of New TPS Series III

Case Sizes: B, C, D, E, V, W, Y  
 Capacitance: 4.7µF – 1000µF  
 Voltage: 4v – 50v  
 Temperature range: -55°C/+125°C  
 ESR limit: **40 (4v) – 300 (50v) mΩ**  
 (Half the limit of the conventional TPS)

### CONCLUSION

The new TPS Series III of super low ESR tantalum capacitors with MnO<sub>2</sub> was designed based on long-term teamwork of experienced people from University, Technology, Production, Purchasing, Quality and Marketing. ESR values half that of the original TPS series were achieved while retaining all the advantages of mature MnO<sub>2</sub> capacitor technology. The Series III technology is applicable to a whole voltage range of today's MnO<sub>2</sub> parts. The TPS Series III matrix is quickly being expanded to meet demands from a wide range of potential applications. All technology modifications were carefully examined against COST FOR PERFORMANCE criteria before implemented to this New Low ESR Series III project.

	MnO <sub>2</sub> technology		Conductive Polymer		
	std TPS	<b>TPS Series III</b>	Supplier 1.	Supplier 2	Supplier 3
<b>voltage range [V]</b>	<b>4 - 50V</b>	<b>4 - 50 V</b>	4 - 10V	2.5 - 16V	4 - 10V
<b>maximum capacitance [uF]</b>	<b>1000 uF</b>	<b>1000 uF</b>	470uF	680uF	330uF
<b>tightest capacitance tolerance [+/-%]</b>	<b>10%</b>	<b>10%</b>	20%	20%	20%
<b>ESR (D100/10) [mO]</b>	100mO	<b>50mO</b>	55mO	55mO	55mO
<b>DF (D100/10) [%]</b>	<b>8%</b>	<b>8%</b>	10%	10%	30%
<b>DCL (D100/10) [uA]</b>	<b>10uA</b>	<b>10uA</b>	100uA	100uA	100uA
<b>ripple current (D100/10) [Arms]</b>	1.2	<b>1.7</b>	<b>1.7</b>	1.5	1.5
<b>temperature range [C]</b>	<b>-55/+125</b>	<b>-55/+125</b>	-55/+105	-55/+105	-55/+105

**BOLD = superior specification**

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Fig. 13. Generic specification comparison of TPS, TPS Series III and conductive polymer technology

## ACKNOWLEDGEMENT

Thanks to all team members for the long-term effort and implementation of this Low Series III project.

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