# Low ESR and Low Profile Technology on Niobium Oxide

**S. Zedníček, Z. Sita, T.Zedníček**
AVX Czech Republic s.r.o., Dvorakova 328, 563 01 Lanskroun, Czech Republic
**Phone: +420 467 558 111  Fax: +420 467 558 128**

**C. McCracken, W. A. Millman.**
AVX Limited, Long Road, Paignton,
Devon TQ4 7ER, United Kingdom
Phone: +44 1803697200 Fax: +44 1803697326

## 1. Abstract

Increasing demand for tantalum capacitors at the end of last millennium accelerated simultaneously the search for new technologies, which were able to solve the drawbacks of tantalum technology – the limited source chain, tantalum cost and its susceptibility to certain low level ppm of thermal runaway failures.

One of the newest technologies, NbO capacitors have launched into the market during the last 2 years. It's significant similarities to tantalum capacitors with such benefits as non burning feature, lower cost, surge robustness and excellent reliability is raising other questions to other NbO  potentials, like voltage range, derating, ESR and miniaturisation. This paper gives a summarising overview of these new NbO technology capabilities.

## 2. Introduction to NbO technology

NbO capacitors, same as solid tantalum and niobium ones, consist of sponge structure anode (NbO - Niobium Oxide) with dielectric ($Nb_2O_5$ - Niobium Pentoxide) made by controlled surface oxidisation. The negative electrode can be $MnO_2$ prepared by manganese nitrate impregnation followed by it's decomposition: again, same way as well known from tantalums.

During Niobium capacitor development, it's oxide, NbO, was discovered showing encouraging electrical and mechanical properties. Initial samples of NbO capacitor exhibited significantly different physical characteristics compared to Tantalum.  The NbO capacitors, however, had two significant advantages over Ta and Nb metal capacitors. Firstly, it was already a sub-oxide, and therefore it would be more stable with respect to excessive oxidation causing thermal runaway. Secondly, the long term cost model of this powder would be very attractive, as it did not rely on the existing high processing cost structure of Tantalum powder manufacture by sodium reduction methods.

Latest developments of materials and procedures moved the parameters of NbO capacitors close to tantalum. The range of NbO capacitors is expanding rapidly, still ensuring the highest levels of quality and reliability.

As with all new product developments they go through a product life cycle based on their average annual growth (AAG). Fig.1 shows the product life cycles of new and existing capacitor technologies, and as expected the Niobium based capacitors can be classed as Emerging Technology.

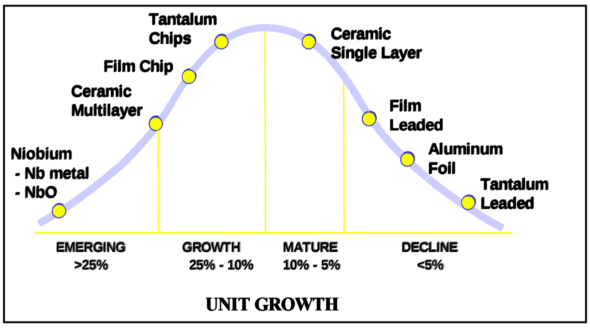


*Figure 1. Technology Unit Growth Diagram.*

In the range of capacitor technologies, sorted by CV, the NbO capacitor has been positioned currently within the window for Capacitance and Voltage ranges between 1uF to 1000uF and 1.5V to 6.3V- see Fig. 2.

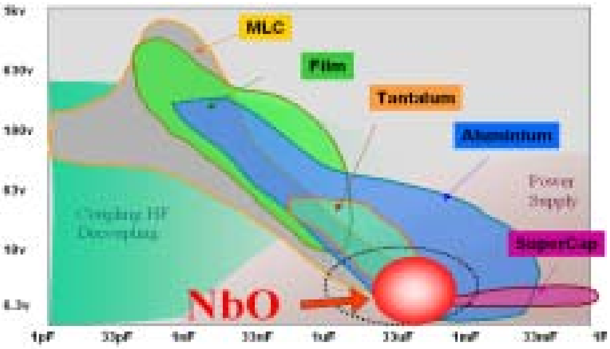


*Figure 2. Technology CV Diagram*

## Thermal stability of NbO

NbO powder has due to its higher oxidation state two orders higher Minimum Ignition Energy (MIE) compared to both Tantalum and Niobium powders, and a corresponding reduction in burning rate over a fixed length of powder (See Fig.3). NbO burns a lot slower than either Ta or Nb metal powders.

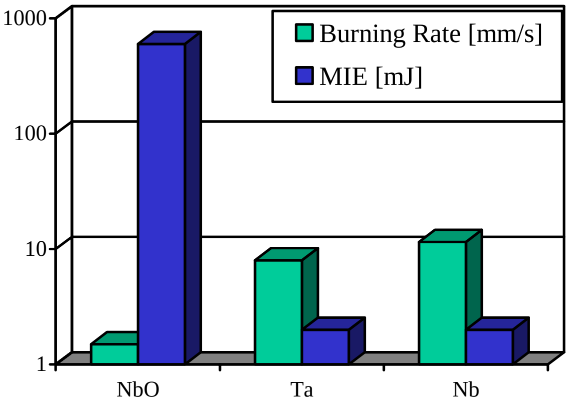


***Figure 3. Minimum Ignition Energy and Burning Rates** of Ta, Nb and NbO.*

The ignition characteristics have significant impacts on the finished capacitors. The inherent ignition susceptibility and burning level of NbO capacitors is dramatically reduced when compared to Ta and Nb. For applications where the associated risk of ignition is high, niobium oxide capacitor offers a viable solution [2],[3].

NbO capacitor has a 20% higher power dissipation, which results in a 10% higher ripple current rating. It is also able to withstand higher reflow temperatures and makes niobium type of capacitors compatible with leadfree technology.

## Resistance failure mode

The NbO capacitor exhibited a different failure mechanism not seen before in any other capacitor technology. It has a higher breakdown voltage compared to other Solid Electrolytic Capacitor technologies (see Fig.4) and a two-stage breakdown mechanism with high resistance.

The NbO capacitor after dielectric breakdown initially has a very high resistance typically 30kohms (see Fig.5), which enables the capacitor to continue to operate in end device mostly without user notice. The NbO shorted capacitor maintains its high resistance until ~ 9V, after which the resistance decreases rapidly and the device fails during thermal runaway. Shorted tantalum and niobium capacitors with $MnO_2$ or polymer electrode can fail by thermal runaway when an increasing voltage reaches voltages such as low as ~ 1.5V.

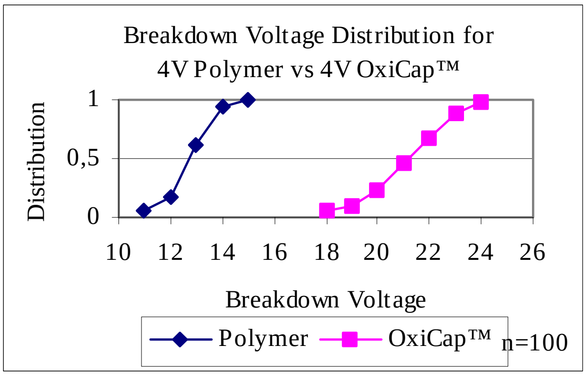


***Figure 4. Typical Breakdown Voltage** Distributions for 4V Polymers and 4V NbO.*

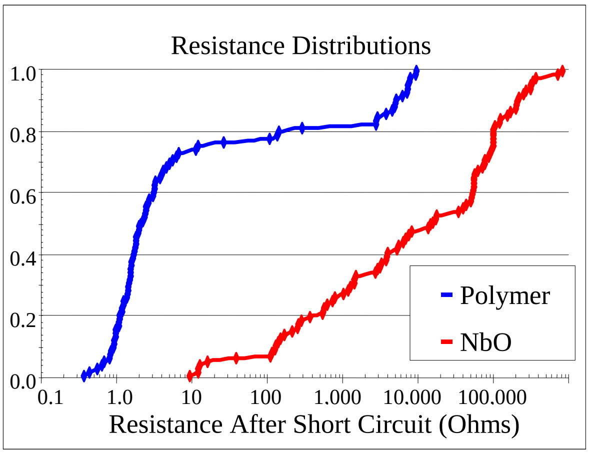


***Figure 5. Typical Breakdown Resistance** Distributions for 4V Polymers and 4V NbO*

The study of failure mechanism of NbO capacitors after dielectric breakdown proved that besides the main dielectric $Nb_2O_5$ there is additional $NbO_2$ suboxide. The $NbO_2$ is a semi-conducting oxide and increases the resistance of the conducting channel and effectively isolates it. As more energy is applied to the NbO capacitor, eventually either the $NbO_2$ channel or $Nb_2O_5$ dielectric breaks down and the capacitor exhibits a thermal runaway failure. In comparison to tantalum based capacitors (including polymer) the thermal runaway/smoking of NbO part will occur at about three times higher power as a result of NbO high ignition resistance (valid in both forward and reverse voltages).

Tantalum has no stable sub-oxides, the resistance of the conducting channel stays low and the capacitor can go into thermal runaway if enough energy is supplied. Niobium metal capacitors like NbO capacitors can form stable sub-oxides however, the first stable sub-oxide formed will be NbO, which is highly conducting and will not increase the resistance of the conducting channel, therefore the Niobium metal capacitor will also go into thermal runaway.
Based on the above an assurance can be given that **Failed NbO Capacitor Will Not Burn up to It's**

**Category Voltage.** For more details on NbO capacitor breakdown failure mode see references [1], [4].

### Derating

In contrast to a tantalum, larger concentration of oxygen produced during current surge or voltage overload by self-healing of $MnO_2$ does not result in thermal runaway of NbO capacitor, because NbO is a ceramic and already oxidized. This feature of NbO capacitors together with high resistance failure mode allows a less conservative 80% rating for NbO capacitors and thus using one order lower rated capacitors for given application voltage.

| Customer´s rail (V) | | 1.8 | 2.5 | 3.3 | 5 | 8 |
|---|---|---|---|---|---|---|
| Recommended rating (V) | Ta | 4 | 6.3 | 10 | 16 | 25 |
| | NbO | 2.5 | 4 | 4 | 6.3 | 10 |

*Table 1. Derating of NbO vs Ta capacitors*

### NbO range

NbO capacitors have been launched into the market in basic standard EIA case sizes, and a conservative range. For the market demands of low profile case sizes and low ESR specifications, the investigations to such NbO potentials have started.

Further overview on NbO capacitors see references [2], [3]

## 3. Low ESR technology: NbO model

Although being a ceramic material, NbO sintered anode’s structure (Fig.6) is not considerably different from tantalum anode. Together with other similarities in production processes and basic behaviors, it leads logically to parallelism in low ESR modeling.

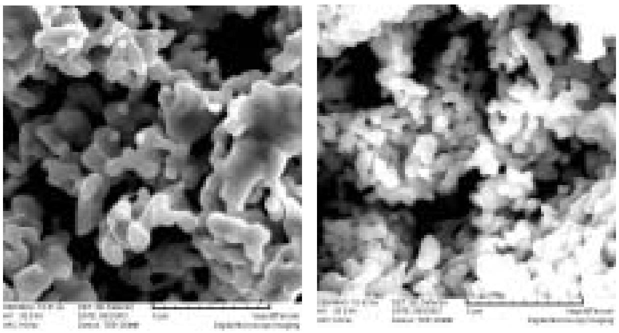


*Figure 6. Sintered Material Structure*
*Tantalum 32kCV/g on the left, corresponding CV/g NbO (about 70k) on the right side*

Low ESR theoretical computer model (Fig. 7) of NbO part could be based on well-known ladder scheme and experiences from tantalum capacitors.

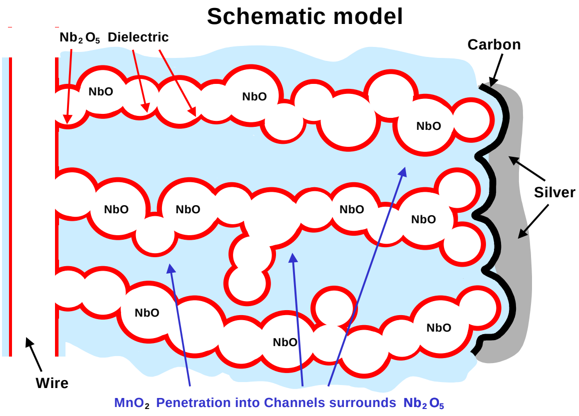


*Figure 7. Schematic model of NbO capacitor*

Sintered anode consists of niobium oxide particles, which are in mutual contact and form conductive ladder shaped chains. The particles are covered with oxide insulating layer and additional cathode layers of $MnO_2$, carbon and silver. Similarly as for tantalum capacitors, the dielectrics can be modeled by individual parallel capacitors and the cathode layer with the network of series-parallel connected resistors representing the contact and bulk resistances of materials.

Such a model allows predicting the effect of design, material and processes and estimating the level of their contribution to final ESR. The main ESR influencing factors can be grouped into the following key technology tools:

- **Anode structure**
- **Anode shape, dimensions and design**
- **Cathode layers bulk conductivity**
- **Cathode layers contact resistivity**.

### Anode structure

It is well known that the internal anode pellet structure can influence ESR significantly. The neck thickness of sintered particles must be above certain critical value not only due to low resistance of sintered pellet, but also to reach high current surge robustness. For proper impregnation, the structure of pellet must be open enough to get sufficient impregnation and to achieve good conductivity of $MnO_2$ solid electrolyte [5 ].

Creating of anode from Niobium Oxide especially, as being a hard ceramics material, requires new attitudes, nevertheless the final structure is very similar to tantalum anode – Fig.6, on the left.

### Anode shape, dimensions, low profiles

The total surface area of the anode, particularly its surface-to-volume ratio, is one of the key parameters that define its ESR value. Standard tantalum technology use several design approaches, like lower profile / bigger footprint anodes, fluted design and parallel multiplication of anode in case size. By such anode design, the disadvantage of limited conductivity of $MnO_2$ cathode layer can be significantly reduced.

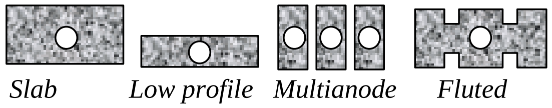


***Figure 8. Anode Design Cross Sections***

It needs considerable optimization and adjustment of material preparation and anode manufacturing process to reduce anode height and to shape NbO anode to the required shape or design.

**Cathode layers, Graphite and Silver**

$MnO_2$ is the cathode material of currently available NbO capacitors , same as in standard tantalums or niobium metal capacitors. Good impregnation, $MnO_2$ conductivity and consistent homogenous external layers of capacitor are other keys to lower the ESR. Luckily for NbO , all the years experiencies from manganese dioxide performance improvements towards total ESR reduction can be fully utilized there with just small modifications.[5].

Tantalum experiences apply to graphite and silvers material developments and for application methods on NbO capacitors to improve ESR and life stability , with just small NbO specifics.

## 4. Low profiles, Low ESR investigations justification methods

Test batches have been produced after material and process adjustments, with regards to the above mentioned aspects and NbO specifics. They were tested and evaluated like standard NbO and tantalum capacitors. Examples and typical mean DCL and ESR values comparisons are published in this paper.

Accelerated tests were performed together with Storage Life tests and Weibull testing. Results of test batches compared with typical tantalum or NbO capacitors, where possible ,and some of them are cited in the paper.

Used symbols description:

M0 - initial measurements
M1 - post leadfree reflow (260C peak)
M2 - post pressure cooker (120C,2 atmospheres,4 hrs)
M3 - post humidity test (85C,85% RH,0V,240 hrs)
M4 – post life test (125C, Uc, 2000 hrs)

## 5. NbO Low profiles and miniature designs

Improvement of anode quality is a key to downsize the NbO range with good capacitor performance and also significant ESR reduction, as mentioned above. Low profile capacitors with height like 1.2 mm, 1.5 mm and 2.0 mm were produced , together with miniature EIA 2012 case size.

For anodes examples see Fig.9.

| Footprint | P | A | B | C | D |
|---|---|---|---|---|---|
| EIA Code | 2012 | 3216 | 3528 | 6032 | 7343 |
| Low profile | R | S | T | W | Y |
| Height (mm) | 1.2 | 1.2 | 1.2 | 1.5 | 2 |

***Table 2. Low Profile Code Sizes***

***Figure 9. Sintered NbO anodes examples***

DCL values in comparison with the equivalent Tantalum codes are summarized in Tab. 3 and ESR in Fig.10.
For more DCL and ESR distributions, see attachments

| Case | **R** | **S** | **T** | **W** | **Y** |
|---|---|---|---|---|---|
| CAP [uF] | **10uF** | **10uF** | **22uF** | **68uF** | **100uF** |
| Ta | 0,03 | 0,03 | 0,04 | 0,15 | 0,19 |
| NbO | 0,12 | 0,04 | 0,05 | 0,21 | 0,58 |
| Ta limit | 0,6 | 0,6 | 1,4 | 4,3 | 10 |

***Table 3 : LowProfiles DCL[$\mu$A]*** *of NbO capacitors compared with tantalum*

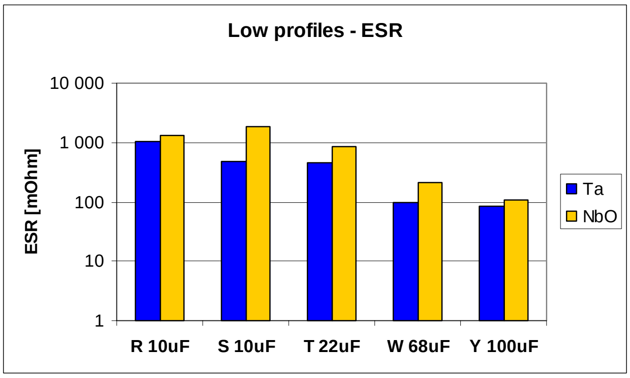


***Figure 10. Low profiles ESR*** *of NbO capacitors compared with tantalum*

Some general patterns are apparent from the DCL and ESR parameters. It is not surprising, that both are showing higher values, but much closer to tantalums than expected. DCL levels are fairly well inside the tantalum DCL limits. ESR shows a reduction in the same pattern as tantalum with design and process changes.

## 6. NbO Low ESR capacitors

Experiences from low profile anode manufacturing were well utilized in anode preparations for low ESR capacitors, especially for the fluted shapes and thin anodes for multiple anodes construction. The ESR reduction techniques from tantalum capacitors were modified to fit NbO specifics and used to make new levels of low ESR Niobium Oxide products.

220uF and 330uF NbO capacitors in D and E case were chosen for comparison with similar tantalum capacitor designs. Less conservative rule for NbO in applications (see end of Chapter 2.) is a reason to compare 6.3 V tantalum code with 4V NbO's – results see below in Tab. 4 and Fig.11.

| | **Std** | **Low ESR slab** | **Low ESR fluted** | **Low ESR** | **Multi anodes** |
|---|---|---|---|---|---|
| CAP [uF] | **220uF** | **220uF** | **220uF** | **330uF** | **330uF** |
| Ta | 0,65 | 0,78 | 0,85 | 1,10 | 3,78 |
| NbO | 0,81 | 0,92 | 0,90 | 1,32 | 3,93 |
| Ta limit | 13,9 | 13,9 | 13,9 | 20,8 | 33 |

***Table 4. DCL[$\mu$A] of NbO and tantalum***
*- Low ESR Designs*

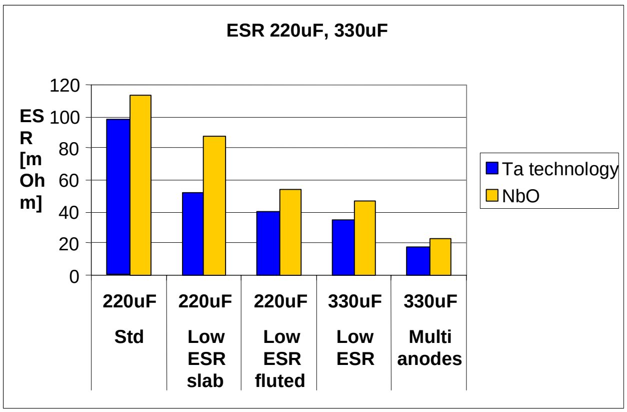


***Figure 11. ESR of NbO and tantalum***
*- Low ESR Designs*

Similar results of discussion as for low profiles can apply for all low ESR NbO capacitors . DCL is safely inside the tantalum specification. The ESR decreased significantly with the used techniques which clearly shows, that all the approaches, known from tantalum technology, being applied to niobium oxide capacitor, brought expected benefits. It points out the capability of niobium oxide capacitor to reach similar ESR to tantalum technology.

The remaining ESR difference could be explained by formed anode porosity difference. For the same CV (Capacitance x Voltage) of given anode design, the structure of NbO sintered anode is finer than the structure of corresponding tantalum anode, as visible from Fig.6. This difference may be related to NbO powder used and to anode making process, and could be subjected to further improvements. Secondly, NbO anodising (dielectric creation) process gives thicker $Nb_2O_5$ than tantalum pentoxide for given formation voltage. It means that pores in the NbO anode are even smaller. This is a little primary disadvantage for NbO impregnation by manganese dioxide and needs to be compensated in further technology or cathode material developments.

## 7. Stability and life tests discussion

Most of the produced batches were subjected to stability tests as explained in Chapter 4 above. The results are summarized in attachment Att.2 in M0-M1-M2-M3-M4 format. Attachment Att.3 then shows 10000 hrs, 125C, 0.5xUr stability of different low ESR designs.

All the performed tests have confirmed excellent NbO parts stability. No catastrophic failures were identified in any of the parts as well as no single part burnt either during the production or in stability and life tests.

Some parts were submitted to Weibull test – see Tab.5. and to BDV measurements – Fig.12.

| **Weibull coeficient examples** | | | |
|---|---|---|---|
| NbO Code | Description | Lambda | Beta |
| D330uF, 4V | low ESR design | 0,00032 | 0,135 |
| E330uF, 4V | multianode | 0,00051 | 0,350 |
| S10uF, 2V | low profile | 0,00038 | 0,169 |
| Y100uF,6.3V | low profile | 0,00044 | 0,152 |
| P10uF, 2V | 0805 design | 0,00063 | 0,375 |

***Table 5. Weibull tests results***

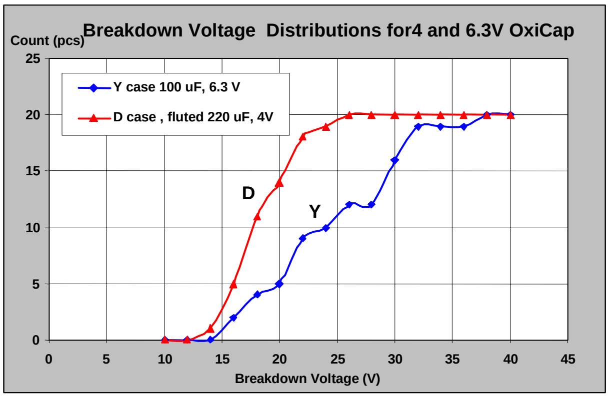


***Fig.12. Breakdown Voltage Distribution** of NbO*
*Low profile Y case 100uF, 6.3V and*
*Low ESR D case 220uF, 4V - fluted anode*

The breakdown voltage distribution of capacitors was measured as well, as described in Chapter 2. above.

The BDV distributions (Fig.12) confirm that both Low Profile parts and Low ESR designs have similar values as standard NbO parts, so they exhibit the same NbO Breakdown Mechanism.

More details on the stability studies, gained on NbO parts being modified during ESR and low profiling investigations, will be subjected of another technical paper. But it well suggests that such material and process modifications not only improve parametric performance, but also the reliability of NbO parts. In addition extremely low failure rate observed in Weibull test and 125C life tests, show encouraging capability of NbO for operational temperature increase.

## 8. Conclusions

Improvements in materials and technology of niobium oxide capacitors manufacturing enable to expand its range to such areas as low ESR, low profile and miniature capacitors with remaining typical NbO capacitors benefits.

The similarity with tantalum technology could help to considerably utilize the tantalum experiences and bring rapidly NbO capacitors even more close to tantalum like specifications. Confirmed excellent long term leakage current and ESR reliability in strong temperature and humidity conditions, robustness against surge together with proven non burning features and high resistance failure mode predetermine NbO capacitor being vital for many applications where it can replace not only tantalum, but other capacitor technologies such as conductive polymer, ceramics or aluminium.

## 9. References

[1] Sikula J. et all., Conductivity Mechanisms and Breakdown Characteristics of Niobium Oxide Capacitors, CARTS Europe 2003, Stutgart, Proceeding

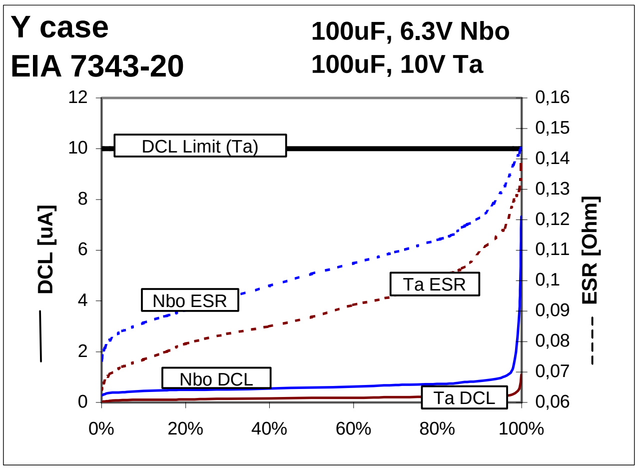
[2] Zednicek T. at all., Niobium Oxide Technology Roadmap, CARTS Europe 2002, Nice, Proceeding

[3] Zednicek T. et all., Tantalum and Niobium Technology Overview, CARTS Europe 2002, Nice, Proceeding

[4] Sikula J. et all., Charge Carriers Transport and Noise of Niobium Capacitors, CARTS Europe 2002, Nice, Proceeding

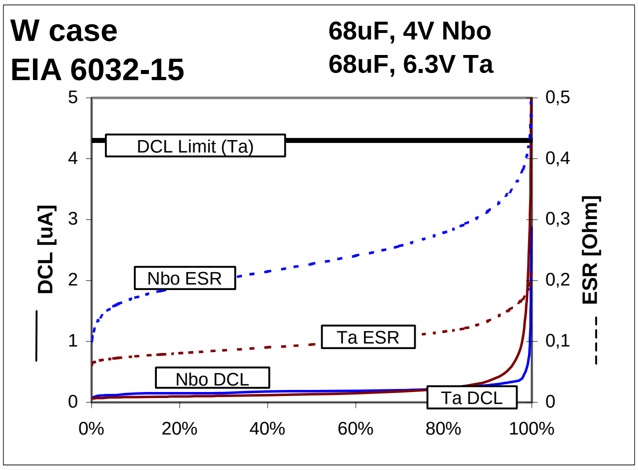
[5] Horacek I. et all., Improved ESR on MnO2 Tantalum Capacitors at Wide Voltage Range, CARTS Europe 2001, Copenhagen, Proceeding

## *Att.1. Low profile Tantalum vs. NbO DCL, ESR distributions*



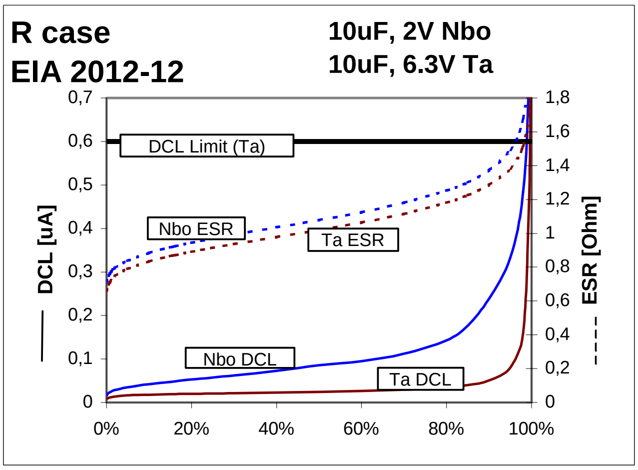
**Y case**
**EIA 7343-20**

**100uF, 6.3V Nbo**
**100uF, 10V Ta**



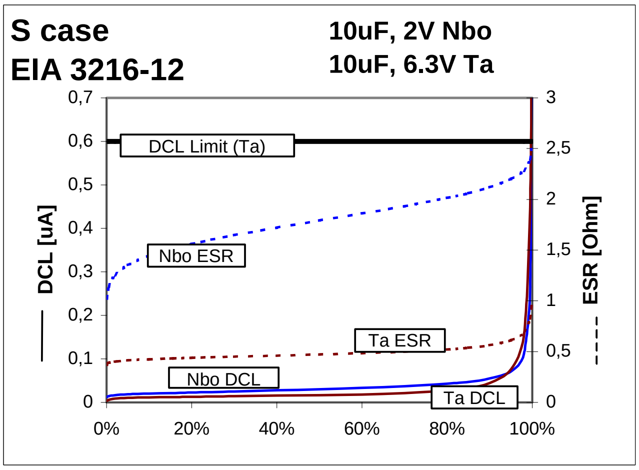
**W case**
**EIA 6032-15**

**68uF, 4V Nbo**
**68uF, 6.3V Ta**



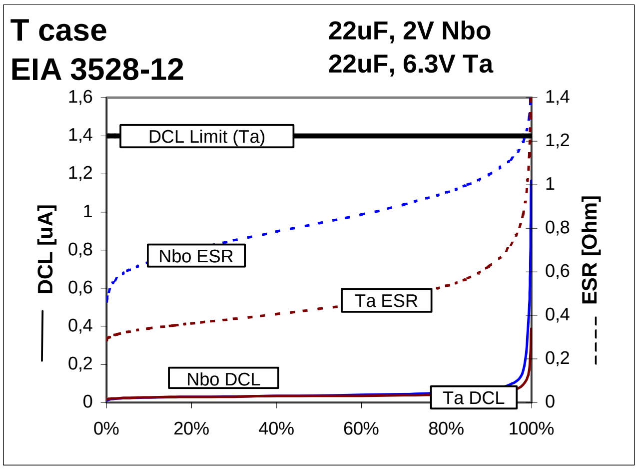
**R case**
**EIA 2012-12**

**10uF, 2V Nbo**
**10uF, 6.3V Ta**



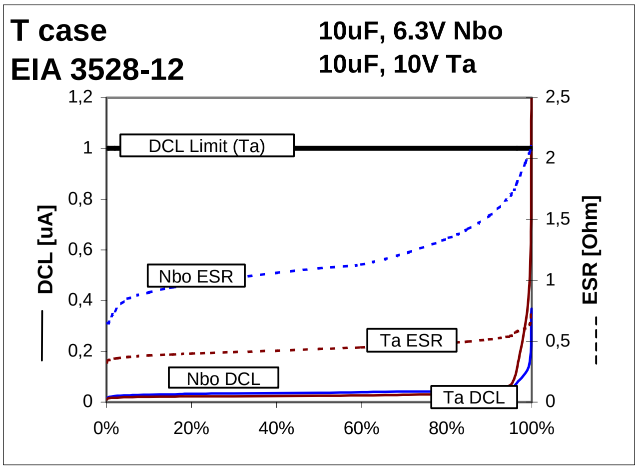
**S case**
**EIA 3216-12**

**10uF, 2V Nbo**
**10uF, 6.3V Ta**



**T case**
**EIA 3528-12**

**22uF, 2V Nbo**
**22uF, 6.3V Ta**

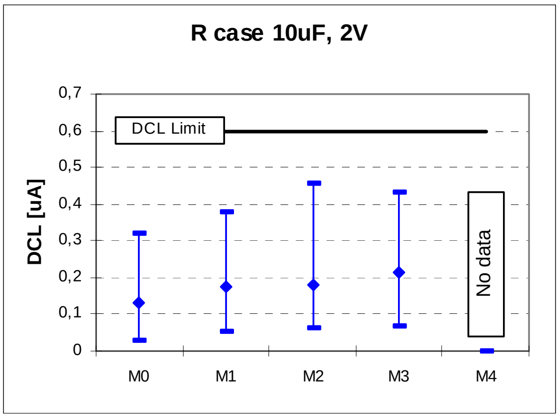


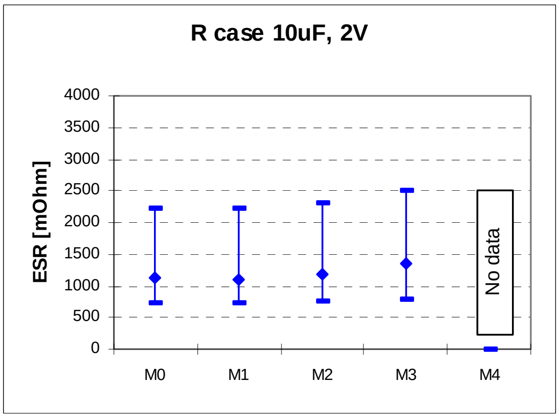
**T case**
**EIA 3528-12**

**10uF, 6.3V Nbo**
**10uF, 10V Ta**

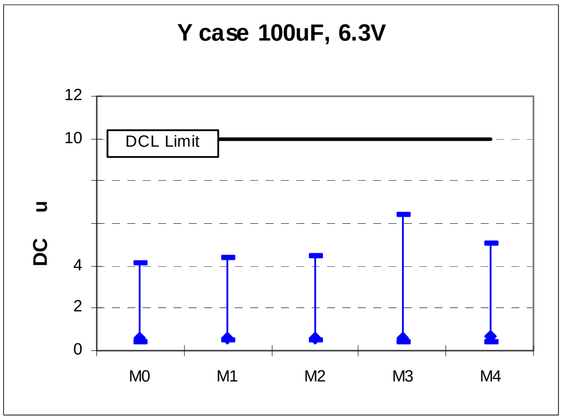
# *Att.2. Stability tests DCL and ESR results NbO low profiles and low ESR capacitors*

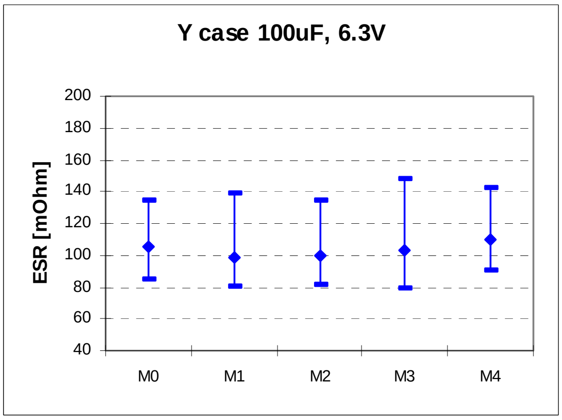
M0 - initial measurements
M1 - post leadfree reflow (260C peak)
M2 - post pressure cooker (120C,2 atmospheres,4 hrs)
M3 - post humidity test (85C,85% RH,0V,240 hrs)
M4 – post life test (125C, Uc, 2000 hrs)
Minimum, Mean and Maximum values



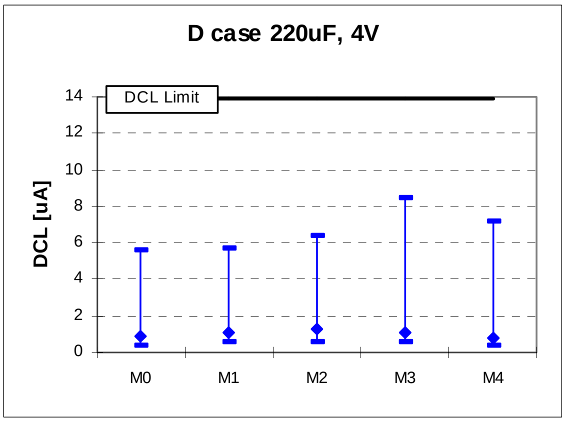


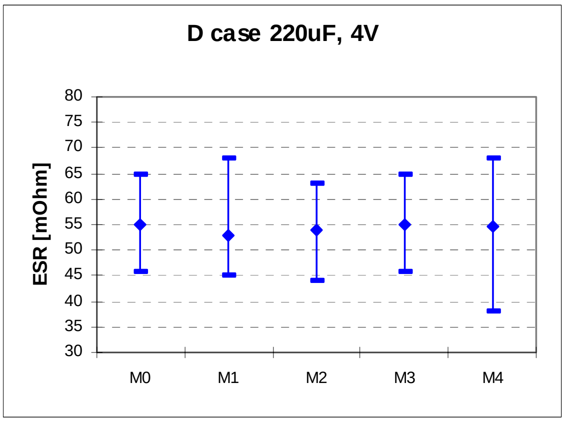
EIA 2012-12
case size



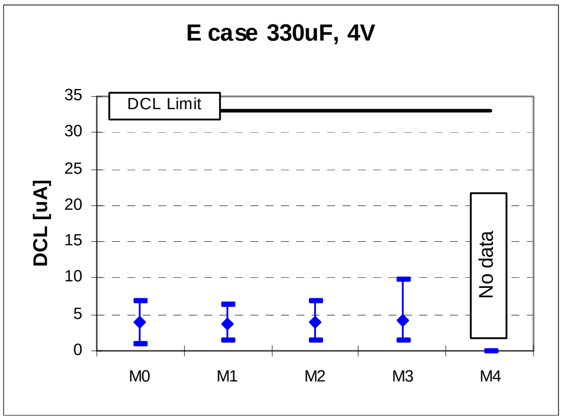


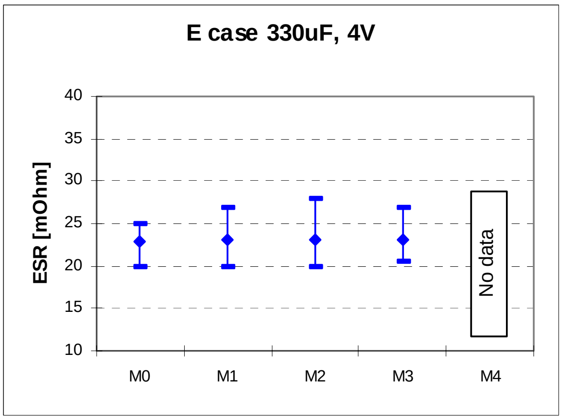
EIA 7343-20
2mm Low Profile





EIA 7343-31
Fluted anode

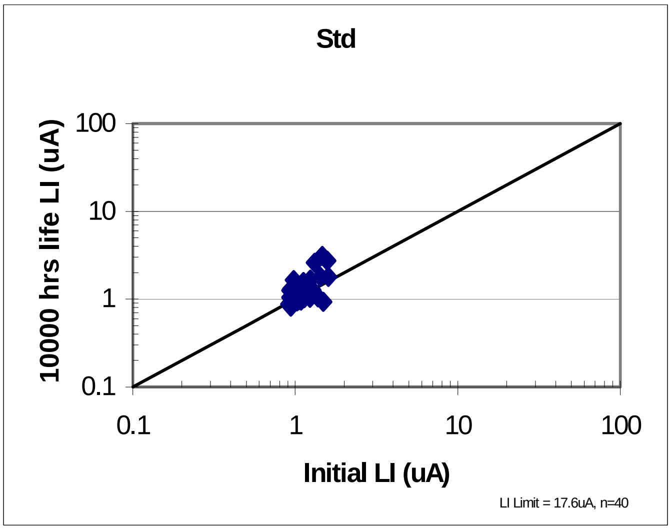




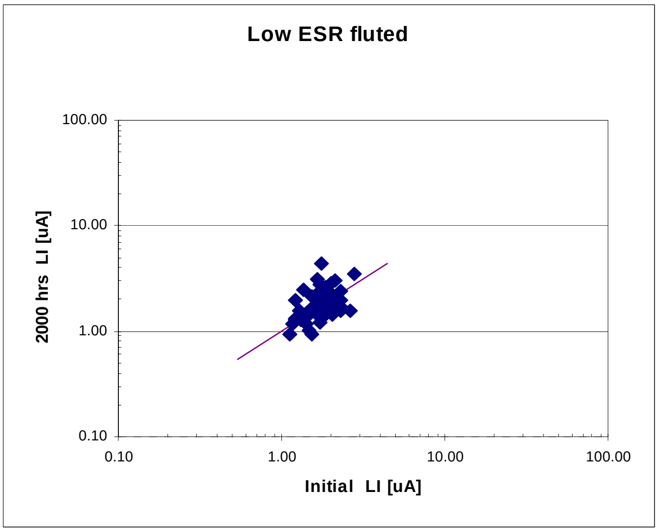
EIA 7343-43
Multiple anodes

## ***Att.3. 10 000 hrs , 125C, 0.5 x Ur DCL Stability***

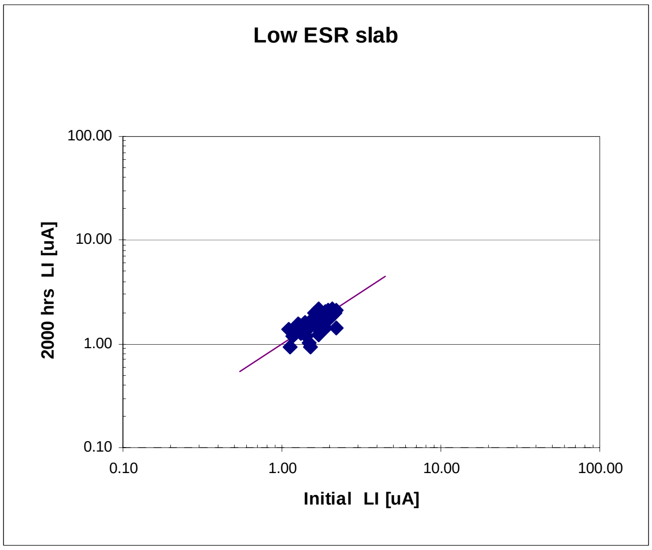
## ***NbO Capacitors***



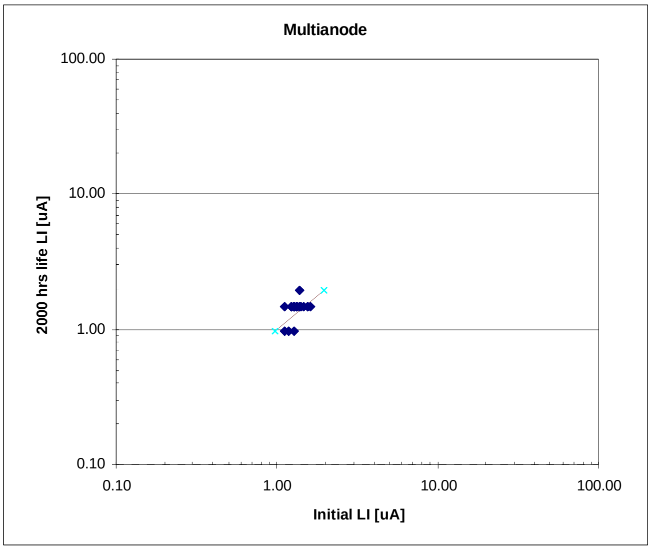
a/ D case, 220uF, 4V NbO, standard technology standard anode design



c/ D case, 220 uF, 4V NbO low ESR technology, fluted anode design



b/ D case, 220 uF, 4V NbO low ESR technology, slab anode design



d/ E case, 330 uF, 4V NbO low ESR technology, multianode design