

# Study of MnO<sub>2</sub> Coverage on Ta Capacitors with High CV Powders

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## Abstract

The use of high CV tantalum powders (>100k CV/g) in solid tantalum capacitors (STCs) has become one of the main goals of Ta capacitors manufacturers.

The systems developed on the last years allowed a coverage increase for products with high CV powders and reliability enhancement. However, an important gap still remains unexplored being nowadays the current opportunity. This will allow us to increase the volumetric efficiency together with the expected capacitance stability.

To achieve it, the Mn(NO<sub>3</sub>)<sub>2</sub> impregnation of pellets produced with high CV powders obligates to found new developments in production process. For that purpose, the use of new materials and optimization of process parameters has been researched.

The addition of surfactants to lower the free energy of the liquid/solid interface (interfacial tension) and new developments in the impregnation/pyrolysis process have been tested in order to get large and homogeneous surface coverage.

Intermediate measurements allow a sequence control during impregnation development being used in our assessments. Traditional coverage measurements and high resolution Scanning Electron Microscope (HR-SEM) analysis are used to quantify the converted MnO<sub>2</sub>. Additionally, physical features of the MnO<sub>2</sub> inner coat are compared. The electrical parameters as DF (Dissipation Factor), DCL (DC Leakage) and ESR (Equivalent Series Resistance) are measured to verify the experimental samples reliability.

## Introduction

A solid tantalum capacitor is produced from a porous sintered pellet of Ta powder (the anode), with an embedded tantalum wire, and surrounded by Ta<sub>2</sub>O<sub>5</sub> amorphous dielectric layer, formed anodically on the surface of the pellet. The cathode is a semiconductor, MnO<sub>2</sub>, obtained by the impregnation of the anode with Mn(NO<sub>3</sub>)<sub>2</sub> solutions when is then thermally decomposed. This impregnation-pyrolysis process is repeated several times in order to fill the porous anode (inner layers) and to provide a good thick manganese dioxide coating (outer layers). The impregnation process starts with diluted solutions that become denser along the dipping sequences. Graphite and silver are deposited to establish contact with a lead frame and the capacitor is finally encapsulated in epoxy resin.

The use of high CV powders increases the difficulty of impregnation and consequently in achieved an acceptable coverage. In order to improve the coverage of a capacitor, we study different surfactants and their influence on MnO<sub>2</sub> layer properties. Also, the pyrolysis conditions greatly influence the porosity and surface smoothness of MnO<sub>2</sub>, which is related with electrical conductivity of this layer [1]. So we study different pyrolysis conditions (number of pre-heating and pre-heating temperature) in order to improve the coverage of these capacitors.

## Surfactants

Surfactants are widely used and find a very large number of applications because of their remarkable ability to influence the properties of surfaces and interfaces [2]. Surfactant is an abbreviation for surface active agent, and it's characterized by its tendency to adsorb at surfaces and interfaces (the stronger the tendency, then the better the surfactant). The driving force for a surfactant to adsorb at an interface is to lower the free energy of that phase boundary. When that surface is covered by surfactant molecules, the surface tension is reduced. The denser the surfactant packing at the interface, the larger reduction in surface tension. The degree of a surfactant concentration at a boundary depends on the surfactant structure and also on the nature of the two phases that meet at the interface. There is a limit to the surface and interfacial tension lowering effect by the surfactant. Usually that limit is reached when micelles start to form in bulk solution. Only the surfactants unimers (the free or unassociated surfactant) contribute to surface and interfacial tension lowering and dynamic phenomena, such as wetting and foaming, are governed by the concentration of free unimers in solution [3].

Surfactant molecules are amphiphilic molecules which contain a polar headgroup and nonpolar tail, which usually consist of a chain of hydrocarbon groups [4]. So, all surfactants molecules consist of at least two parts, one which is soluble in a specific fluid (the lyophilic part) and one which is insoluble (the lyophobic part).



**Figure 1.** Schematic illustration of a surfactant

When a surfactant adsorbs from aqueous solution at a lyophobic surface, it normally orients its lyophobic group towards the surface and exposes its polar group to the solution. The surface has become lyophilic and, as a result, the interfacial tension between the surface and the solution has been reduced.

The polar part of the surfactant may be ionic or non-ionic. For non-ionic surfactants the size of the head group can at will; for the ionics, the size is more or less a fixed parameter. The surfactants can be divided into the classes of anionics, cationics, non-ionics and zwitterionics (surfactants belonging to this class contain both an anionic and a cationic charge) [3].

Carboxylate, sulphate, sulfonate and phosphate are the polar groups found in anionic surfactants. Are used in a greater volume than any other surfactant class, are ease and have a low cost of manufacture.

Non-ionic surfactants have either a polyether or a polyhydroxyl unit as the polar group. In the vast majority of non-ionics, the polar group is a polyether consisting of oxyethylene units, made by the polymerization of ethylene oxide.

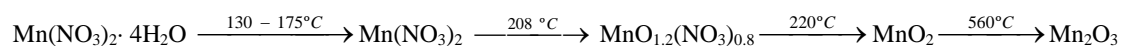
The majority of cationic surfactants are based on the nitrogen atom carrying the cationic charge.

Zwitterionic surfactant contains two charged groups of different sign. Whereas the positive charge is almost invariably ammonium, the source of negative charge may vary, although carboxylate is by far the most common.

Another way to reduce the interfacial tension is the addition of a strong electrolyte to the solution, that even without being adsorbed in to the surfaces, will increase the contact angle which improves the impregnation.

## Pyrolysis

The nitrate thermal decomposition into  $MnO_2$  and  $Mn_2O_3$  has been the subject of several studies. The forms adopted during crystallization are determined by the processing conditions. A proposed decomposition method involves melting the  $Mn(NO_3)_2 \cdot nH_2O$  solution around  $55^\circ C$ , dehydration by means of several endothermic steps between  $125^\circ C$  and  $175^\circ C$ , onset of  $MnO_2$  formation around  $207^\circ C$  via two steps with a probable intermediate metastable  $MnO_{1.2}(NO_3)_{0.8}$  oxynitrate, and a final reduction to  $Mn_2O_3$  at  $560^\circ C$  [5, 6]:



Under standard Ta capacitor processing conditions, the nitrate pyrolysis is carried out at relatively moderate temperatures (below  $280^\circ C$ ). Higher pyrolysis temperatures induce crystallization of the  $Ta_2O_5$  dielectric film, disrupting this layer and resulting in current leakage [7]. This temperature limitation, the high heating rates and the

short pyrolysis cycles of the cathode – forming process may well cause incomplete manganese nitrate decompositions, which may cause a decrease on the capacitor coverage. Furthermore, owing to the open pore structure of a tantalum capacitor, the thermal decomposition of the manganese nitrate occurs in channels of reduced dimensions that may physically and chemically constrain crystallization [6], and difficult the impregnation in the next dips.

In this paper we study the influence of different surfactants and of different pyrolysis conditions on coverage and electrical properties on the capacitors produced.

## Experimental

A set of MnO<sub>2</sub>/Ta capacitors using high CV powders (> 120K) was produced using standard procedures. The capacitor type used was 150 µF/ 10V, foot print 1,5 mm Hmax. The cathodic layers were produced by interactive impregnation – pyrolysis process which involved several cycles: dip the pellets in an aqueous Mn(NO<sub>3</sub>)<sub>2</sub> · H<sub>2</sub>O solution, followed by pre – heating (to evaporate the excess of water) and subsequent pyrolysis. Several modified sets of capacitors were produced using different surfactants / electrolyte and different dip conditions, and also different drying conditions, when processing the MnO<sub>2</sub> layer.

Three different substances were tested: an electrolyte, an non-ionic surfactant and an anionic surfactant. Pre-heating conditions were also tested.

The electrolyte was added to manganese nitrate and were performed three modified sets that were compared with the standard process (less dips without the electrolyte, dips with electrolyte and dips with electrolyte in a denser manganese nitrate solution).

The non-ionic surfactant was added to water, where we washed the anodes before execute the dips in manganese nitrate. It was performed two sets of Designs of Experiments (DOEs). On the first DOE we intended to observe the coverage variation by changing the number of dips. There were executed three sets of modified dips: (a) wash with surfactant in water before each dip, (b) wash with surfactant in water before each dip but in a denser manganese nitrate solution and (c) a reference only with denser manganese nitrate. In the second DOE were executed two sets of modified dips, which were compared with the standard process: (a) wash with surfactant in water before each dip and (b) wash with surfactant in water only before the first four dips.

The anionic surfactant was tested in two different conditions: was added to water, where the anodes were washed before execute the dips in manganese nitrate (testing two different concentrations), and was added to manganese nitrate. This test was executed in the first 8 dips of the cathodic layer formation sequence.

All the sets involved in the surfactant study, executed the standard pre – heating / pyrolysis cycles.

In order to study the pre–heating parameters influence on coverage several modified sets were executed and compared with standard process. Modified sequences were executed in the first 8 dips without any surfactant and/or electrolyte.

After the cathode formation, standard contact layers were built and the samples followed the standard tantalum capacitor manufacture procedure in order to measure the electrical parameters of capacitor.

From each group, samples were taken at an intermediate state and at the end of the dipping sequence. OM (Optical Microscopy) and Scanning Electron microscopy (SEM) analysis of the samples were carried out. SEM cross-section images were obtained with a Hitachi SU70 instrument. There were characterized samples from intermediate state and from the end of the dipping sequence.

Characteristic of finished tantalum capacitor (capacitance, DF, DC leakage and ESR) were measured with a *Quality Check Tester* containing a Hewlett-Packard 4263B LCR and a Hewlett-Packard 6634-B DC Power Supply Meters. ESR is measured at 100 kHz while capacitance and DF is measured at 120Hz. Life test measurements were performed according to the international standard CECC30801-805 and Kemet specification.

## Results and Discussion

### Electrolyte

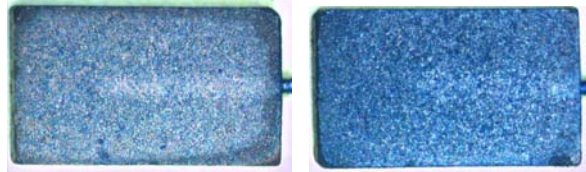
To test the influence of the electrolyte in MnO<sub>2</sub> layer, it was executed 3 sets of modified dips and were compared to reference batch. Table 1 show the description of the runs performed.

**Table 1.** Electrolyte matrix definition.

|              | REF                                 | SET 1                              | SET 2   | SET 3               |
|--------------|-------------------------------------|------------------------------------|---|---------------------|
| Dip Sequence | 14 dips $\rho_1$<br>2 dips $\rho_2$ | 6 dips $\rho_1$<br>2 dips $\rho_2$ | 4 dips $\rho_1$<br>2 dips $\rho_{1,e}$<br>2 dips $\rho_{2,e}$ | 8 dips $\rho_{2,e}$ |

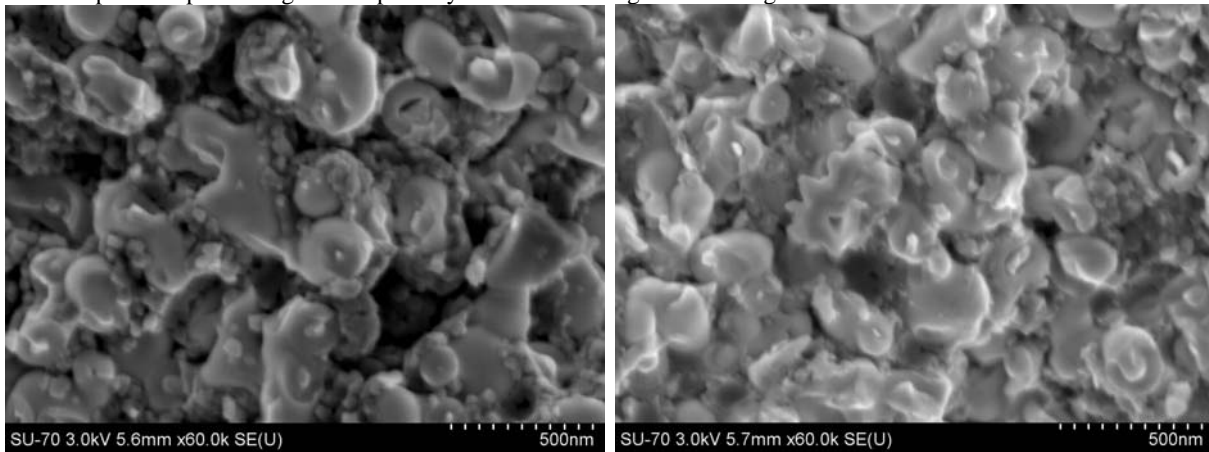
$\rho_1$  - Lower density manganese nitrate  
 $\rho_2$  - Higher density manganese nitrate  
 $\rho_{1,e}$  - Lower density manganese nitrate with the electrolyte  
 $\rho_{2,e}$  - Higher density manganese nitrate with the electrolyte

Figure 2 shows the difference between the reference sample and a sample produced with Set 2 conditions. It is possible to observe a difference in the capacitors colours. The sample produced with the electrolyte in manganese nitrate present a blue colour, characteristic of the dielectric thickness, which could indicate a coverage difference.



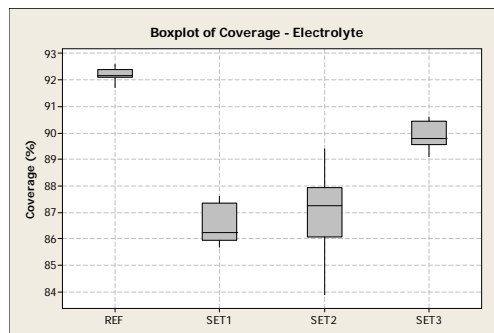
**Figure 2.** Optical images of reference sample (left) and a set 2 sample (right).

Figure 3 shows the SEM images of final samples produced with and without the surfactant. These images show that both samples still present significant porosity and similar manganese oxide growth.



**Figure 3.** SEM images from samples produced without electrolyte (left) and with the electrolyte (right).

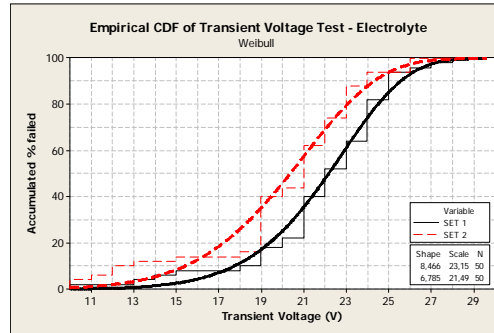
Figure 4 shows the coverage variation of end-samples. To calculate the coverage, the capacitance was measured after drying the parts in an oven at 125°C for one hour and again measured after boiling the parts in water at 100°C, also for one hour. The reference has more 8 dips than the other three sets. For that reason presents a higher coverage value. Comparing the other three sets (with the same number of dips), Set 3 (these set only have higher density  $\rho_2$  dips) have a higher coverage and Set 1, with no dips with electrolyte, presents a lower coverage than Set 2 (both have the same number of dips in manganese nitrate with the same density).



**Figure 4.** Coverage variation of end-samples of sets from Table 1.

## Life Tests

Capacitors from all samples sets were investigated in life test conditions, in order to evaluate the failure mode under different acceleration factors, such temperature, humidity and voltage. Breakdown voltage, stability under thermal shock, endurance and damp heat, steady state tests were carry out. For each variation, randomly samples were taken from the batch population and measured initially, after PCB (printed circuit board) assembly and controlled intermediately until reach 1000h and 2000h, for biased humidity and endurance, respectively. In figure 5 is possible to compare the breakdown voltage (BDV) from set 1 and set 2 variations.

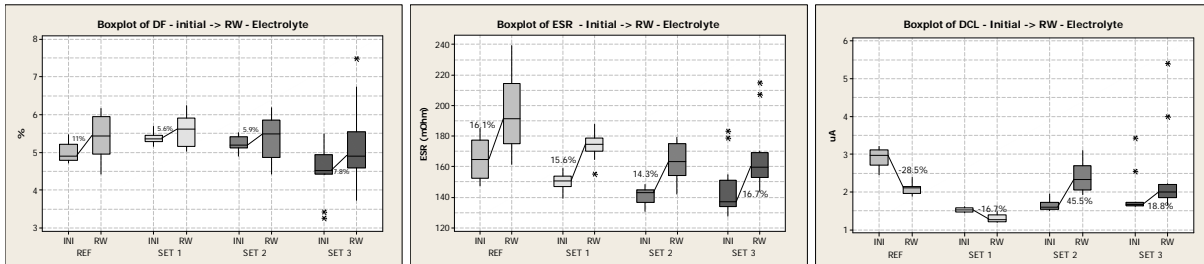


**Figure 5.** Break down voltage plot of end-samples with (dashed line) and without the electrolyte (full line).

Recurring to Weibull CDF function it's possible to estimate the *Instantaneous Failure Rate*:  $h(x) = \frac{\alpha}{\beta} \times (x)^{\alpha-1}$

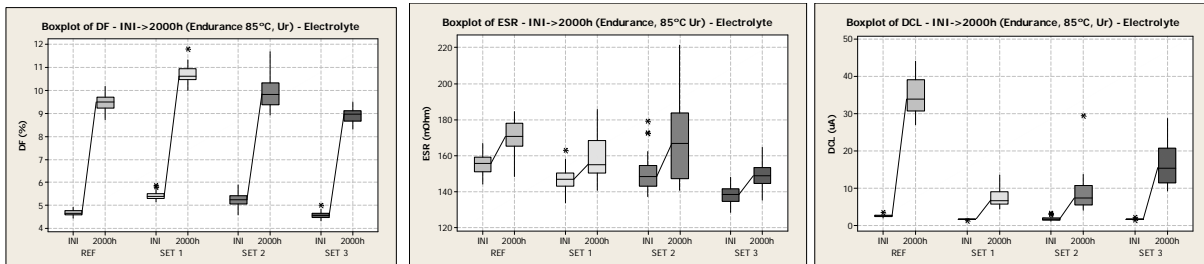
For 13V, we have  $h = 0,75\%$  for Set 1 and  $h = 3,25\%$  for Set 2. This indicates a worse result when we used the electrolyte in manganese nitrate.

Figure 6 shows the DF, ESR and DCL results of thermal shock test. In these test the parts are submitted to a reflow profile of 250°C, 20-40s (according with IEC60068-2-58). The impact of reflow was analysed in all sets of variations. The analysis of these test, shows that DF and ESR increase after reflow with the lowest value obtained for Set 3. Set 1 and Set 2 samples present a higher thermal stability. Also we observe that when the electrolyte is not used, the DCL decrease after reflow.



**Figure 6.** Electrical parameters (DF, ESR and DCL) of thermal shock test for end-samples of different sets of variation with and without the electrolyte.

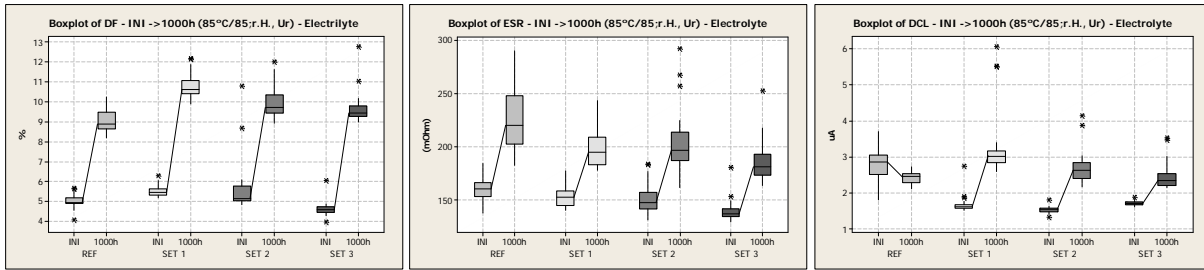
Figure 7 shows the DF, ESR and DCL results of Endurance life test 85°C, Ur (Rated voltage) after 2000 hours. During this life test it could be observed that Set 3 presents the lowest DF and ESR values from initial measurements. However, the drifts after 2000h are quite similar. Reference samples present a much higher value of DCL at the end (that could be due to a higher number of impregnation pyrolysis sequences).



**Figure 7.** Electrical parameters (DF, ESR and DCL) of Endurance life test (85°C, Ur) for the end-samples of different sets of variation with and without the electrolyte.



Standard biased humidity life tests - 85°C/85% of relative humidity (RH), Ur, until 1000 hours were carried from random pieces of each group. DF, ESR and DCL performance are plotted below (figure 8). In a humidity environment the samples from Set 3 also present lower values of DF and ESR (much lower than the other sets). Initially the reference presents a higher value of DCL, which decrease after 1000 hours (which is in opposite for all the other sets).



**Figure 8.** Electrical parameters (DF, ESR and DCL) of 85°C/85%RH for end-samples of different sets of variation with and without the electrolyte.

### Non-Ionic Surfactant

On the first DOE, 3 sets of modified dips were compared with the reference. On the second DOE, 2 sets of modified dips were compared with the reference. Table 2 shows the four different variations executed with and without the surfactant.

**Table 2.** 1<sup>st</sup> DOE non -ionic surfactant matrix definition.

|                     | REF                                 | SET 1            | SET 2   | SET 3   |
|---------------------|-------------------------------------|------------------|---|---|
| <b>Dip Sequence</b> | 14 dips $\rho_1$<br>2 dips $\rho_2$ | 16 dips $\rho_2$ | Wash in non-ionic surfactant<br>in water before each dip<br>14 dips $\rho_{1,NS}$<br>2 dips $\rho_{2,NS}$ | Wash in non-ionic surfactant<br>in water before each dip<br>16 dips $\rho_{2,NS}$ |

$\rho_1$  - Lower density manganese nitrate

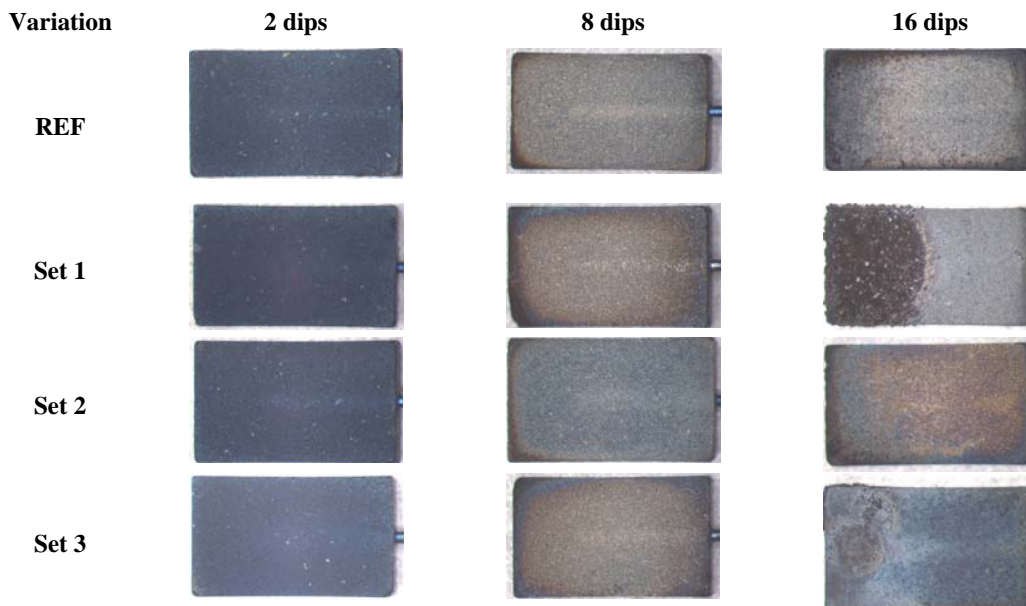
$\rho_2$  - Higher density manganese nitrate

$\rho_{1,NS}$  - Wash in water with non ionic surfactant before dip in lower density manganese nitrate

$\rho_{2,NS}$  - Wash in water with non ionic surfactant before dip in higher density manganese nitrate

With the optical images shown in table 3 is possible to observe the difference between the capacitor outer shells throughout the impregnation process.

**Table 3.** Optical images of samples from the four different variations of the 1<sup>st</sup> DOE executed with the non-ionic surfactant.



Comparing Set 1 with the reference is possible to observe an accumulation of MnO<sub>2</sub> on the surface of the sample. This effect is not observed in set 3, which let us believe that the surfactant influence the nitrate impregnation. Comparing Set 2 with the reference, the samples produced with surfactant present a colour closer to dark-blue, characteristics of the dielectric thickness, which indicates that samples from set 2 will present a coverage change.

Figure 9 shows the coverage evolution with the number of dips, and the coverage variation of end-samples with all the 16 dips. The Set 1 and Set 3 samples executed with denser manganese nitrate presents higher coverage with low number of dips (2-6dips) but from 8 to 16 dips the coverage values are similar. Also it is possible to observe that after the 14 dip, we do not get any improvement on coverage.

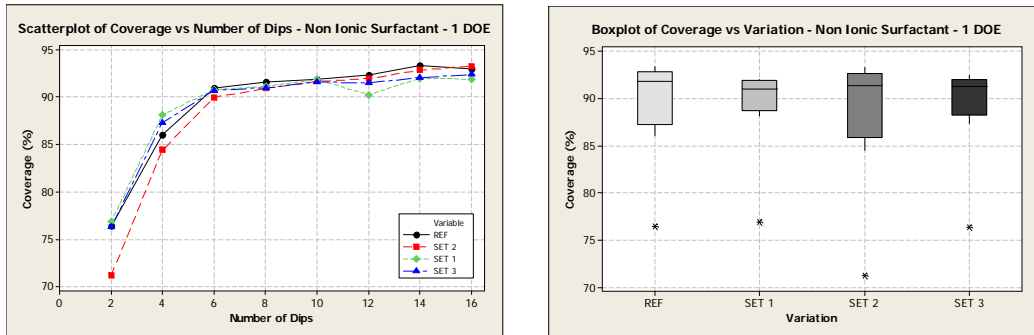


Figure 9. Coverage variation of first DOE samples. Evolution across the dips (left) and after the 16 dips.

### Electrical Results

In figure 10 it is possible to observe the variation of DF and ESR with the addition of dips. These are results measured after the formation of contact layers. After the 12 dip, the DF start to increase and after the 8/10 dip, the ESR also starts to increase.

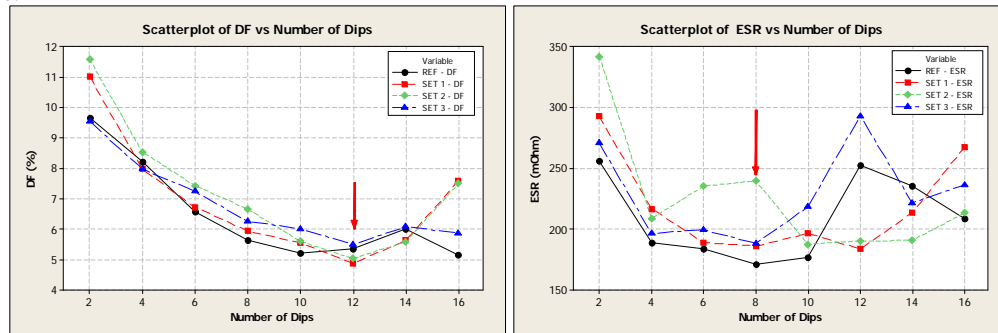


Figure 10. DF and ESR variation with the number of dips of samples of different variations with and without the use of non-ionic surfactant, from 1<sup>st</sup> DOE.

Considering the coverage and the electrical results there is no advantage in use more than 10 or 12 dips.

Table 4 shows the three different variations of the 2<sup>nd</sup> DOE executed with and without the surfactant (two modified dips that were compared with the reference sample). The reference and Set 1 have the same number of dips. Set 2 have less 4 dips.

Table 4. 2<sup>nd</sup> DOE non – ionic surfactant matrix definition.

|              | REF              | SET 1   | SET 2   |
|--------------|------------------|---|---|
| Dip Sequence | 14 dips $\rho_1$ | Wash in non ionic surfactant in water before each dip | Wash in non ionic surfactant in water before the first 4 dips |
|              | 2 dips $\rho_2$  | 14 dips $\rho_{1, NS}$                                | 4 dips $\rho_{1, NS}$   |
|              |                  | 2 dips $\rho_{2, NS}$                                 | 6 dips $\rho_1$   |
|              |                  |   | 2 dips $\rho_2$   |

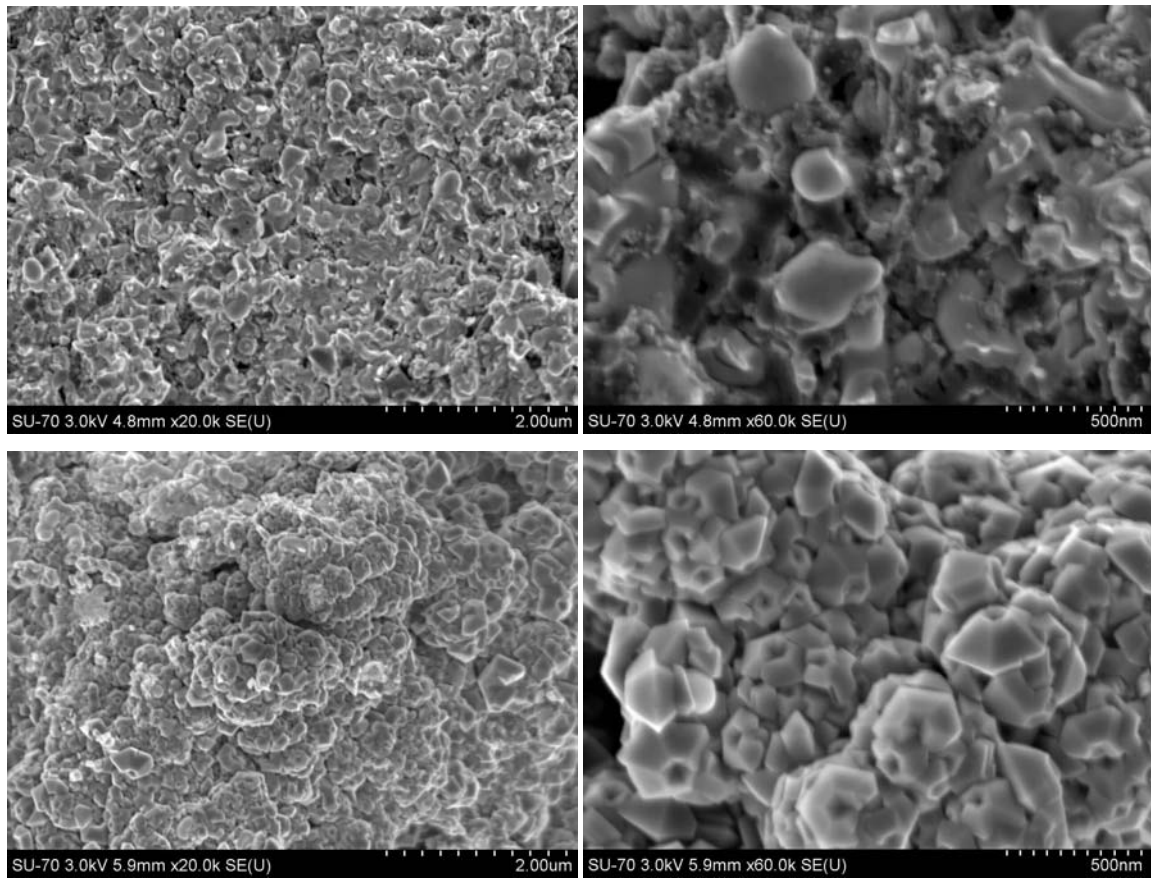
$\rho_1$  - Lower density manganese nitrate

$\rho_2$  - Higher density manganese nitrate

$\rho_{1, NS}$  - Wash in water with non ionic surfactant before dip in lower density manganese nitrate

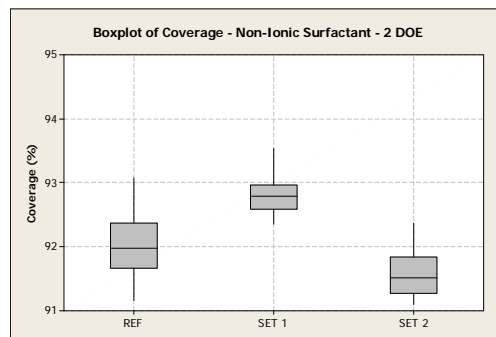
$\rho_{2, NS}$  - Wash in water with non ionic surfactant before dip in higher density manganese nitrate

In figure 11 it is observed the SEM images of the final samples from the 2<sup>nd</sup> DOE matrix of non-ionic surfactant. It is possible to observe that the sample produced with surfactant presents a different crystal growth.



**Figure 11.** SEM images from samples of the 2<sup>nd</sup> DOE without non-ionic surfactant (on the top) and with the use of non-ionic surfactant (on the bottom).

The coverage obtained with the different variations is shown in figure 12. Set 1, produced with the use of the non-ionic surfactant presents a higher value of coverage than the control. As expected, Set 2 present a lower value of coverage (these variation have less 4 dips).

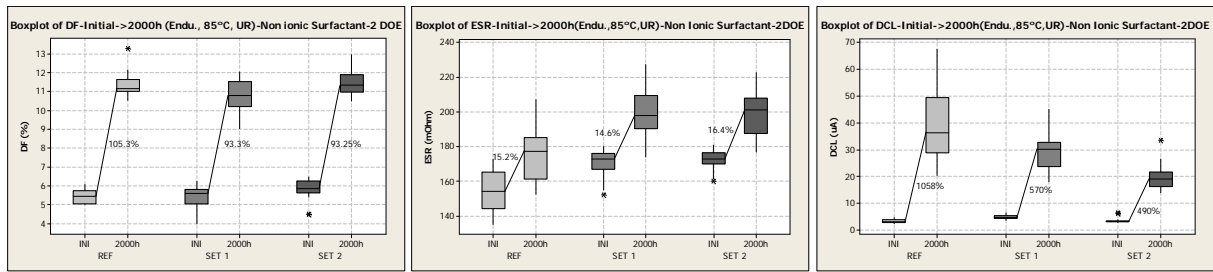


**Figure 12.** Coverage of end-samples of different variations with and without the Non-Ionic Surfactant, of the 2<sup>nd</sup> DOE.

### Life Tests

In order to evaluate the failure mode under different conditions, capacitors from all three variations were life tested. Endurance life test 85°C was carried out. Figure 13 shows the results obtained with these test. It's possible to observe that when the Non-ionic surfactant is used, the initial values of ESR and DCL increase, but present a lower drift after 2000 hours. The DF values are very similar for all group samples.





**Figure 13.** Electrical parameters (DF, ESR and DCL) of Endurance life test (85°C, Ur) for the different sets of variation with and without the non-ionic surfactant of the 2<sup>nd</sup> DOE.

### Anionic Surfactant

Table 5 shows the description of all the variations executed in this experiment using an anionic surfactant.

**Table 5.** Anionic surfactant matrix definition.

|                     | REF                                 | SET 1  | SET 2   | SET 3   |
|---------------------|-------------------------------------|--|---|---|
| <b>Dip Sequence</b> | 14 dips $\rho_1$<br>2 dips $\rho_2$ | Wash in anionic surfactant in water before each dip (lower concentration)<br>8 dips $\rho_{1,wc1}$<br>6 dips $\rho_1$<br>2 dips $\rho_2$ | Wash in anionic surfactant in water before each dip (higher concentration)<br>8 dips $\rho_{1,wc2}$<br>6 dips $\rho_1$<br>2 dips $\rho_2$ | Anionic surfactant in manganese nitrate<br>8 dips $\rho_{1,AS}$<br>6 dips $\rho_1$<br>2 dips $\rho_2$ |

$\rho_1$  - Lower density manganese nitrate

$\rho_2$  - Higher density manganese nitrate

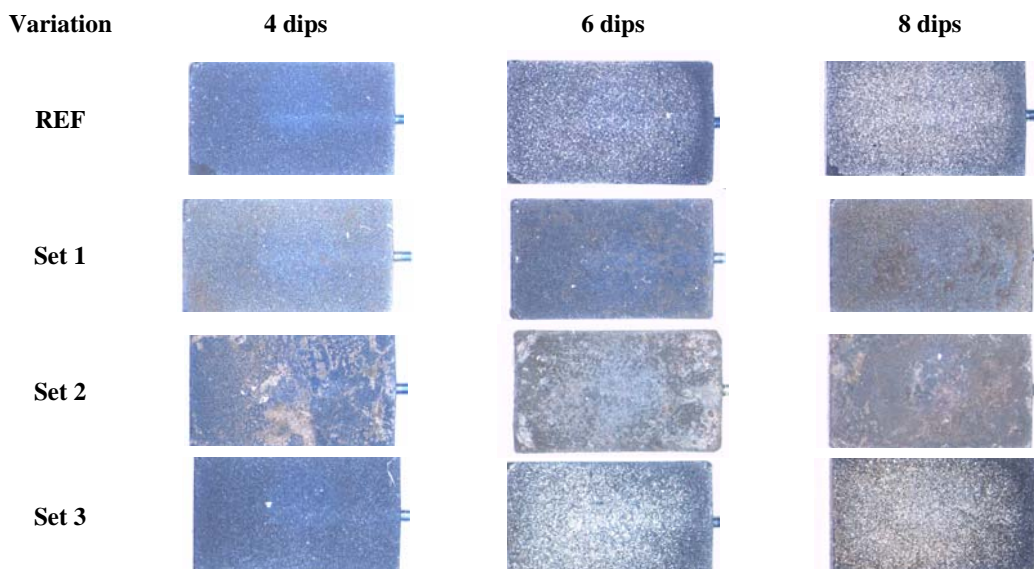
$\rho_{1,wc1}$  – Wash in water with a lower concentration of anionic surfactant before dip in lower density manganese nitrate

$\rho_{1,wc2}$  – Wash in water with a higher concentration of anionic surfactant before dip in lower density manganese nitrate

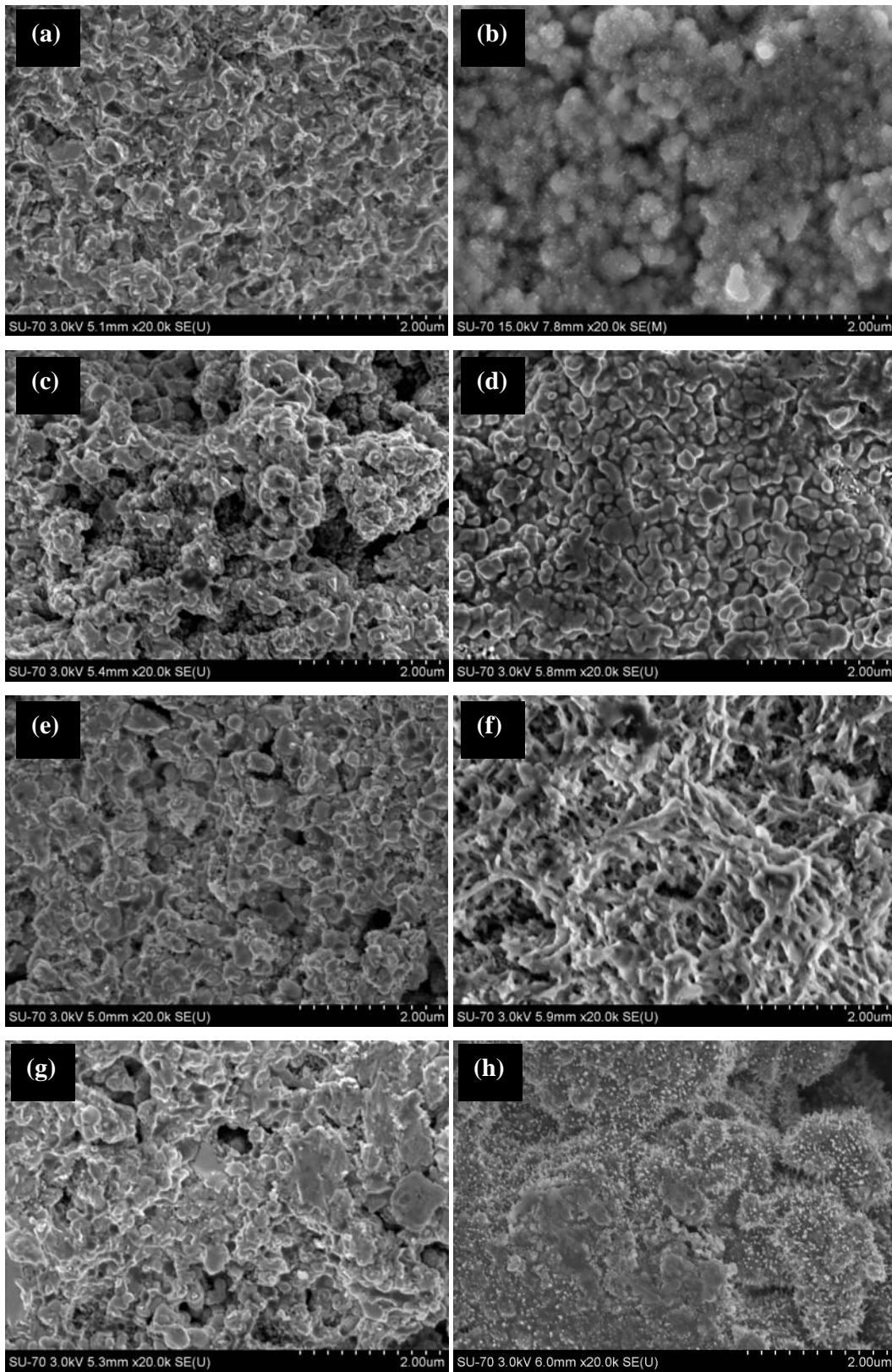
$\rho_{1,AS}$  – Dip in lower density manganese nitrate with the anionic surfactant

On Table 6 it is possible to observe the optical images of same samples of all variations. The images reveal the surface of intermediate samples at different stages. In the middle of the process, it is already possible to observe some differences between the capacitors colours. The samples produced with the anionic surfactant in manganese nitrate present a brown aspect whereas the control sample presents a colour close to dark-blue, characteristic of the dielectric thickness. The samples that were washed in water with the anionic surfactant before the dip in manganese nitrate (set 1 and set 2), present some dark spots on the surface of the anodes, which are more evident in the set executed with a higher concentration of surfactant (set 2).

**Table 6.** Optical images of samples from the four different variations executed with the anionic surfactant.



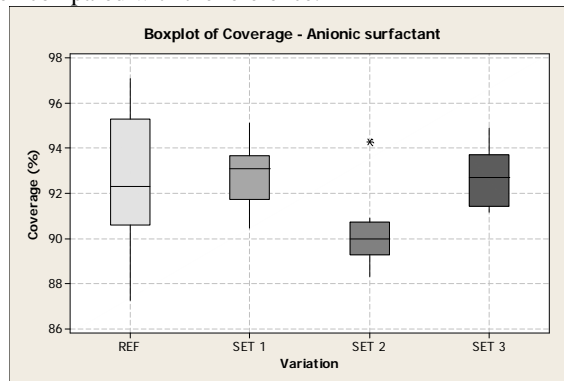
In figure 14 it is possible to observe some SEM images from samples after 8 dips (section and surface).



**Figure 14.** SEM images from samples produced with and without the anionic surfactant: Reference (a) section and (b) surface; Set 1 (c) section and (d) surface; Set 2 (e) section and (f) surface; Set 3 (g) section and (h) surface.

In the section images it is possible to observe the MnO<sub>2</sub> nucleation spots. We observe that samples washed with the anionic surfactant in water before the dip present a more porous structure. Big differences are observed on samples surface.

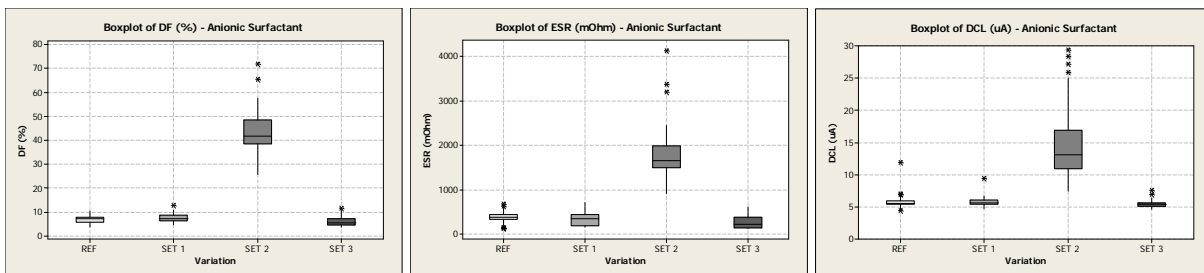
Figure 15 shows the coverage variation of end samples obtained with the different variations. Set 1 and set 3 presents a slight increase on coverage when compared with the reference.



**Figure 15.** Coverage of end samples of different variations with and without the use of an anionic surfactant.

### Electrical Results

In this study it was produced a small amount of samples, not enough for life test evaluation. The electrical parameters of end-samples were measured after the formation of the contact layers. The results are shown in figure 16. It is possible to observe that when the samples are washed in water with a higher concentration of surfactant before the nitrate dips (set 2), the DF, ESR and DCL increase drastically. The remaining variations data are quite similar.



**Figure 16.** Electrical parameters (DF, ESR and DCL) for end samples of different sets of variation with and without the use of Anionic Surfactant.

### Pre-Heating Conditions

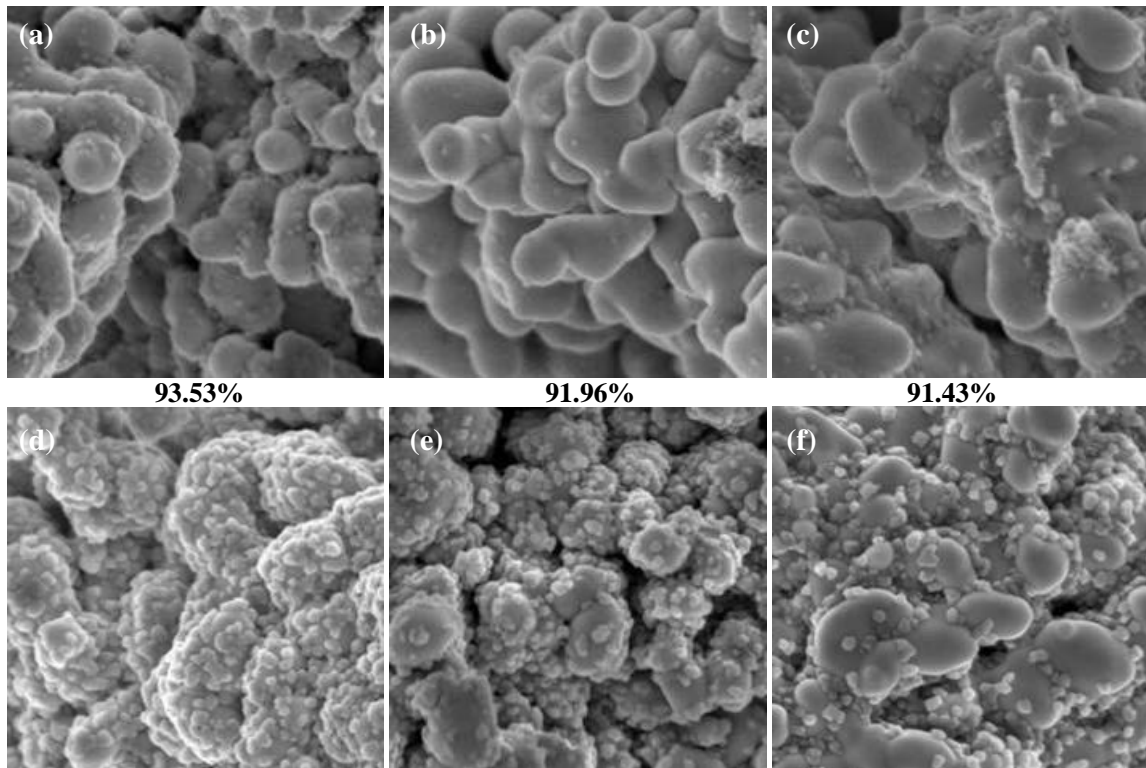
To study the influence of pre-heating condition on capacitor coverage, several set of modified conditions were executed and compared between them. Table 7 shows the different variations executed. The modified conditions were executed in the first 8 dips, the conditions of the following 8 dips were the same for all the variations.

**Table 7.** Pre-heating matrix definition.

|       | 1 <sup>st</sup> Pre-heating temperature<br>(°C) | 2 <sup>nd</sup> Pre-heating temperature<br>(°C) |
|-------|---|---|
| SET 1 | 0   | 120   |
| SET 2 | 80  | 120   |
| SET 3 | 120   | 120   |
| SET 4 | 0   | 150   |
| SET 5 | 80  | 150   |

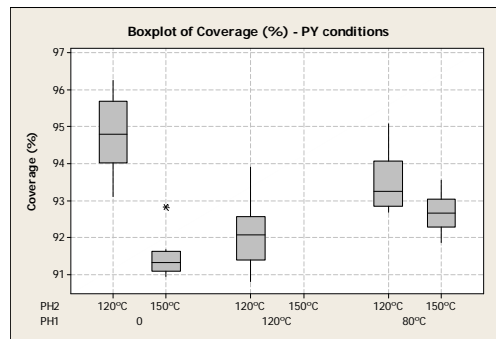
Figure 17 show some SEM images from sample after 2 dips (on top) and after 8 dips (on bottom), of all different variations. It's visible the variation on the coverage for the different pre-heating conditions. After 8 dips, the dielectric layer of Set 2 sample is apparently full covered by MnO<sub>2</sub> layer. However, for set 3 and set 4 samples the dielectric layer is clearly incompletely covered by MnO<sub>2</sub>.





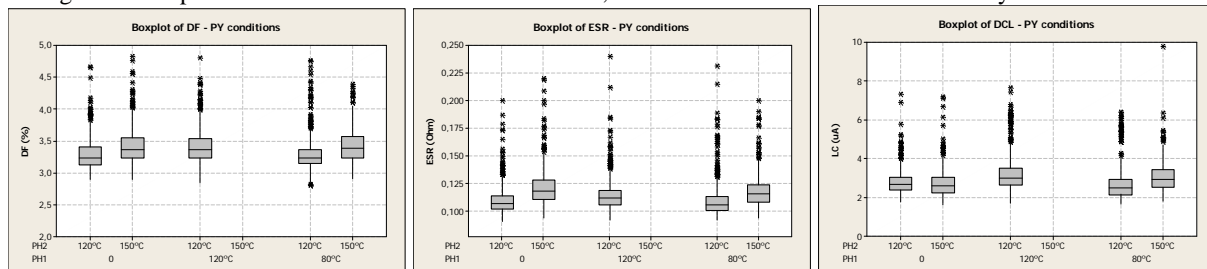
**Figure 17.** SEM images from some pre-heating variations sets after two dips (on top) and after eight dips (on the bottom): (a) and (d) Set 2; (b) and (e) Set 3; (c) and (f) Set 4; with a magnification of 50000x.

The coverage variation of end – samples (after 16 dips) is shown in figure 18. Comparing the results with the SEM images, we could say that for some variations, with less number of dips probably we would get the same coverage percentage. The best coverage was obtained with only one pre-heating at the temperature of 120°C.



**Figure 18.** Coverage variation of end -samples for different pre-heating variations.

On figure 19 it's possible to observe some electrical results, measured after formation of contact layers.



**Figure 19.** Electrical parameters (DF, ESR and DCL) end samples of different sets of pre-heating variation.

The best results are obtained for two pre-heating steps at 80°C+120°C and for one pre-heating step at 120°C conditions.

## Conclusions

In these work it has been study the influence of surfactants and pre-heating conditions, of cathodic formation process, on coverage and electrical parameters of high CV solid tantalum capacitors.

The addition of an electrolyte to manganese nitrate dips increase the impregnation efficiency (higher coverage), mostly with higher density baths. Life test results demonstrated an ESR improvement. Nevertheless, BDV voltage decrease for parts produced with those modified dips.

When a non-ionic surfactant is added to a wash dip, it is observed a slight increase on coverage. After 2000h, under 85°C, Ur conditions, the ESR are higher than reference but DCL are much more stable. SEM images reveal that this material induces different MnO<sub>2</sub> nuclei growth on samples washed with it. The morphology of crystals is quite different from the typical MnO<sub>2</sub> crystal formed by pyrolysis of manganese nitrate.

The samples produced with an anionic surfactant (added to wash dip or added to Mn(NO<sub>3</sub>)<sub>2</sub> dip) reveals also a slightly improvement on coverage. The electrical performance is similar to reference when low concentrate surfactant solution is used. Higher surfactant concentrations degraded the electrical parameters.

It was observed that when the manganese nitrate thermal decomposition in to MnO<sub>2</sub> is performed with only one pre-heating step at 120°C, the coverage is higher comparing with the other pre-heating conditions. This condition presents also good electrical parameters performance.

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