

Removal of Contaminants into Formation Tank with Ion Exchange Resins

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Abstract

During the production of Ta Capacitors, one of the most important factors to produce high and consistent quality is to keep Ta₂O₅ and MnO₂ layers free of contaminants. Contamination of the electrolyte is an important problem to avoid during Ta anodization. Spectroscopy by Atomic Absorption, SEM, EDS, were used to study the concentration of elements in the dielectric and into the electrolyte. The ions Al³⁺, Fe³⁺, Cr³⁺ and Ni²⁺ can be found into the electrolyte during the anodization process due the degradation of the Stainless Steel with the Acid used as electrolyte. It is known that Ionic Exchange Resins (IER) are able to trap metals. The purpose of this research was to find an IER capable to work properly on the harsh environment of the Dielectric Formation Process. Metal ions into the electrolyte can form deposits in some specific points onto tantalum surface, creating potential electrical failure points. The effects of remove those ions on the electrical parameters of the capacitor were investigated. Variations on Capacitance and DF were reduced by using this IER keeping those contaminants in control. Metal ions reduction allows to increment life time of the electrolytes.

1. Introduction

Tantalum powder pellet capacitor type has a broad usage in Electronics Industry worldwide, because the electrical characteristics of Ta capacitors which are stable in different work conditions [1]. Moreover, Ta can produce an amorphous dielectric film Ta₂O₅ having a dielectric constant of 27. This property and the possibility to obtain porous pellets by sintering powder, make Ta able to give more capacitance by volume CV/cc [2]. Therefore, Ta is an excellent material option for capacitor industry.

The most common process for dielectric film growth onto a metallic substrate is the electrolytic process called “anodization” in the capacitor production industry. An aqueous acid solution (H₃PO₄, HNO₃, H₂SO₄ and others) or a Inorganic salts as K₂HPO₄, are common electrolytes used in dielectric formation [3].

Ta powder and electrolyte both with high purity are necessary for having acceptable dielectric properties on the obtained oxide [4]. The contaminant ions in the acid electrolyte are coming from the dissolution of anodization tank and hardware made of steel stainless and utilities used for transportation of the anodes during the electrochemical process. The incorporation of different contaminants (P, S, N, C, Fe, Mn, Mg, etc.) into oxide structure have negative effects that reduces significantly the electrical performance of Ta₂O₅ film [5].

During this research, different commercial ionic exchange resins (IER) were evaluated, for removing the ion contaminants in the electrolyte based phosphoric acid. The evaluation

referred to chemical analysis at different times of electrolyte usage, including capacitance and DF measurements with and without the different exchange resin used during the test. The goal of this research was to select the best resin for our process; improving the electrical performance in our capacitors.

2. Experimentation

During the analysis and selection of the resin, our target was to reduce metals ions contaminant in the electrolyte. Several different IER were tested. For identification purposes, in this work we are using examples IER called A, B and C.

Electrolyte tested was used in a standard production tank until complete life time, after that, the IER to evaluate was installed into the tank. Samples were taken after 12 hrs and 24 hrs of recirculation.

In order to measure the metal ions contents, three samples were taken at different stages of the electrolyte life time: 1) recently changed electrolyte (10 hrs after preventive maintenance and tank washing), 2) after 120 hours, and 3) 240 hours of life time.

The electrolyte samples were analyzed using Atomic Emission Spectrometer in an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES), Perkin-Elmer Optima 3300 RL.

Tantalum anodes were treated for identify the contaminants effect on the DF and Wet-to-Solid Cap shift at the capacitor. The Cap measures was made in to Hewlett Packard 34401A multimeter at 120Hz, the Wet Cap was measured into Acid solution electrolyte. At solid Cap reading was done using an Agilent 4263B, LCR Meter, JK56.

The dielectric formed in those electrolytes (with and without resin treatment) was analyzed with SEM-EDS technique, in a JEOL JMS 5800LV, tungsten filament operated at up to 20 keV. Oxford EDS X-ray detector (resolution = 130 eV ultra thin window, Z>5 detectable) operated with Digital imaging capability.

3. Results and Discussion

Historically, a gradual detriment in DF cpk and an increment on Wet-to-Solid Cap shift has been noticed and correlated to the usage time of electrolyte during Ta anodization. For example, in a 10 Vr using 50 k CV/gr powder, Df Cpk dropped from values between 4.5 and 9 from fresh electrolyte, to 2.2 just before complete electrolyte life time (Fig. 1).

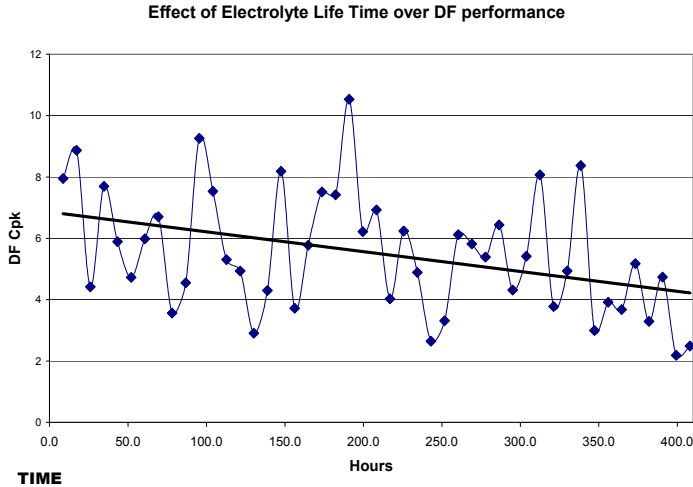


Fig. 1. Df Cpk through electrolyte usage time.

At the same time, Wet-to-Solid Cap shift had an increment from 6% to 10% on the same period of time (Fig. 2). Consequently, frequent cap targeting adjustments caused lot of variation in production process.

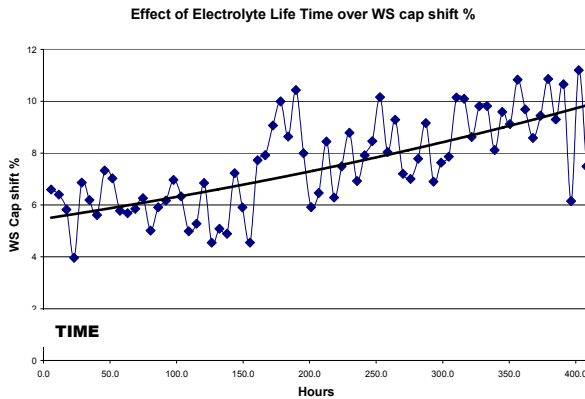


Fig. 2. Wet-to-Solid Cap Shift evolution during electrolyte usage time

Besides of this change in electrical performance, there is also a change in the color of the electrolyte, which turns to yellow-green at the last days of the usage life time.

According to previous works,[6] this change in electrolyte properties and electrical response of the capacitors is related to the increment of ionic species in the electrolyte, coming from Stainless Steel Hardware, Tantalum Pellets and Transportation Bars.

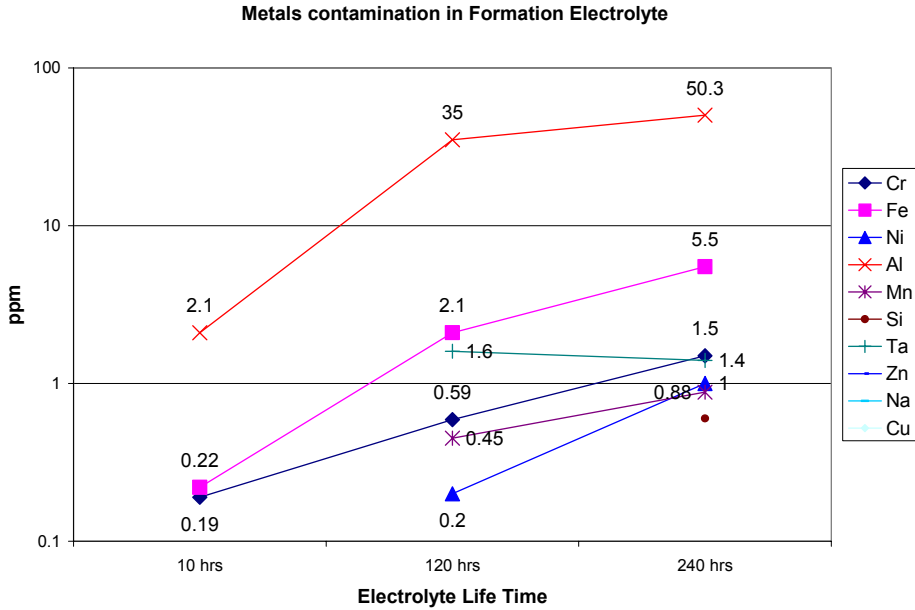
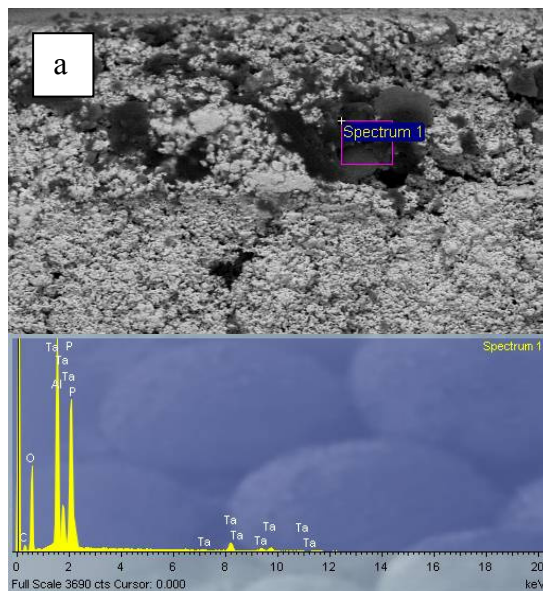
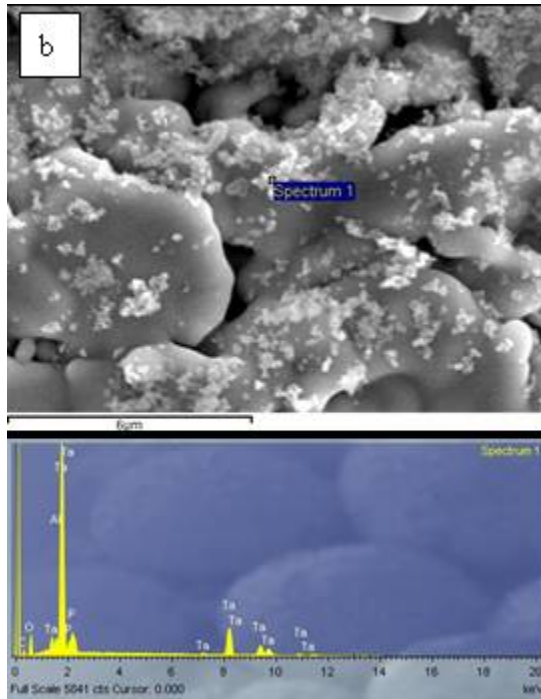


Fig. 3. Metals concentration on Formation Electrolyte.

In Fig. 3, Aluminum concentration into electrolyte had the most significant increment, followed by metals coming from the corrosion of Anodizing Stainless Steel hardware (Fe, Ni, and Cr). Tantalum presence was detected below 2 ppm. Total metals content measured were in ranges from 50 to above 100 ppm.

Figure 4a shows a deposit of Al and P with 20 microns of diameter. This deposit was formed over dielectric surface from an electrolyte at the end of the life time.





Figures 4.- SEM-EDS images of the contaminations present into the Ta₂O₅ surface treated without contaminants removal system (a) contaminants deposit into the dielectric surface (b) high magnification pictures of the same area..

The Figure 4b shows agglomerates of Aluminum residues with sizes in the range from 0.5 to 1 micron.

The polyphosphate and aluminum residues deposited in the surface and porous of the anode, can produce compounds resistant to aqueous corrosion, which can not be easily removed with a simple washing [7,8].

These particles clog small pores and reduce the efficiency of the impregnation process giving higher wet to solid capacitance drop, as well as an increment on the dissipation factor.

THE EFFECT OF IER OVER ELECTROLYTE METALS CONCENTRATION.

1. Ionic Exchange Resin A:

Total metals content after electrolyte life time varies from one tank to other from 50 to >100 ppm. Main contaminants were Fe, Al, Cr and Ni. At the end of electrolyte life period, IER was installed in the tank and the used electrolyte was kept under recirculation during 24 hrs. Results are shown in Fig 5.

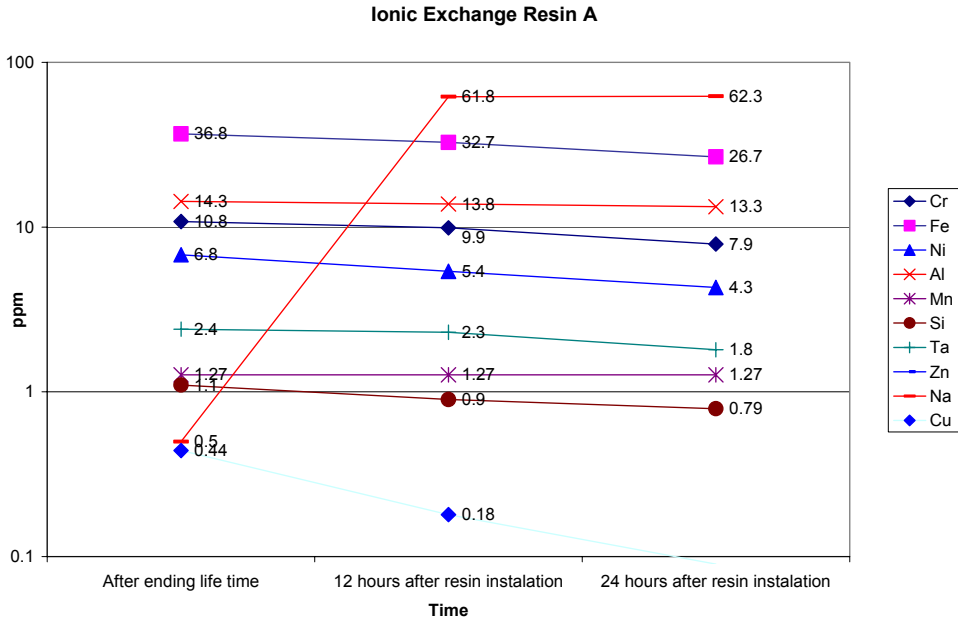


Fig. 5. Ionic Exchange Resin A effect on contaminant reduction.

After 24 hrs, metals content remained flat, with an increment on Na from 0.5 ppm to 62 ppm, coming from the IER. Total metals content were 119 ppm.

2. Ionic Exchange Resin B:

Total metals content, after electrolyte life time, were 50 ppm. Main contaminants were Al (42 ppm), Fe (3 ppm), and Ta (1.2 ppm). Using the same procedure described above, we evaluate resin B. Results are shown in Fig 6.

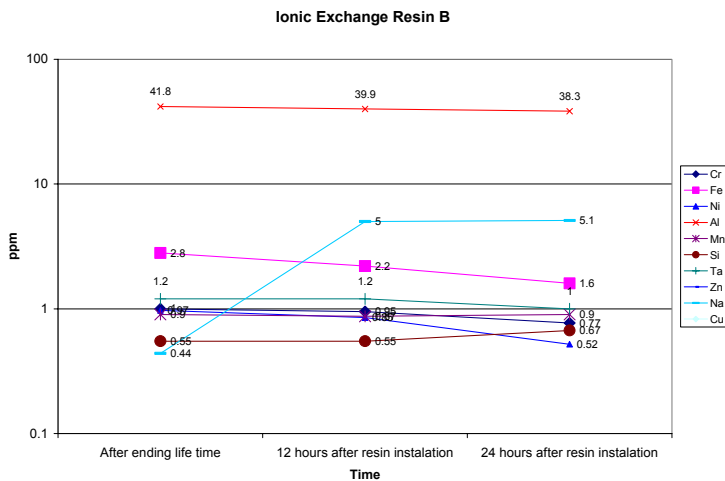


Fig. 6. Ionic Exchange Resin B effect on contaminant reduction.

After 24 hrs, metals content remained flat, with an increment on Na from 0.5 ppm to 5 ppm. The metals content after 24 hrs were 49 ppm.

3. Ionic Exchange Resin C:

Total metals content, after electrolyte life time, were 82 ppm. Main contaminants were Al (63 ppm), Fe (8 ppm), Cr (3 ppm), and Ni (2 ppm). After complete electrolyte life time, IER C was installed in the tank and the used electrolyte was kept under recirculation during 24 hrs. Results are shown in Fig 7.

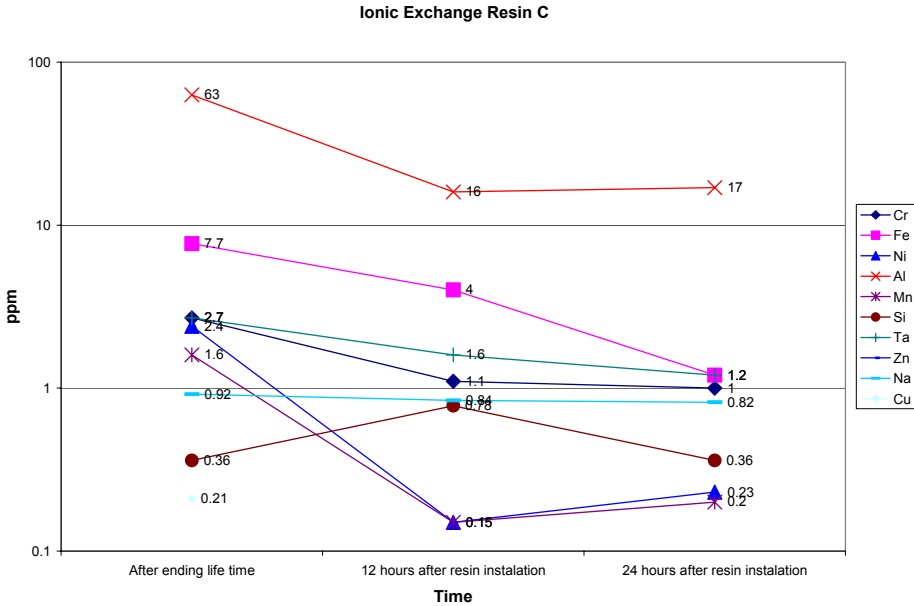


Fig. 7. Ionic Exchange Resin C effect on contaminant reduction.

After 24 hrs, there was a significant reduction in most of the contaminants, especially on Al from 63 to 17 ppm, and Stainless Steel elements (Fe, Cr, Ni) from 13 to 3 ppm. Ta was reduced from 3 to 1 ppm. Total metals were reduced after 24 hrs from 82 a 22 ppm.

The electrolyte has a reduction of metals when we used resin C. The ions get trap into the resins by ion exchange of H+ vs the metals from the electrolyte.

After seeing this significant reduction, we decided to increase the volume of resin by 3 times, and the result was a total metal content below 10 ppm.

The effect of this reduction can be appreciated in the Figure 8 where the material treated with IER “C” have a clean surface without the small Al agglomerates.

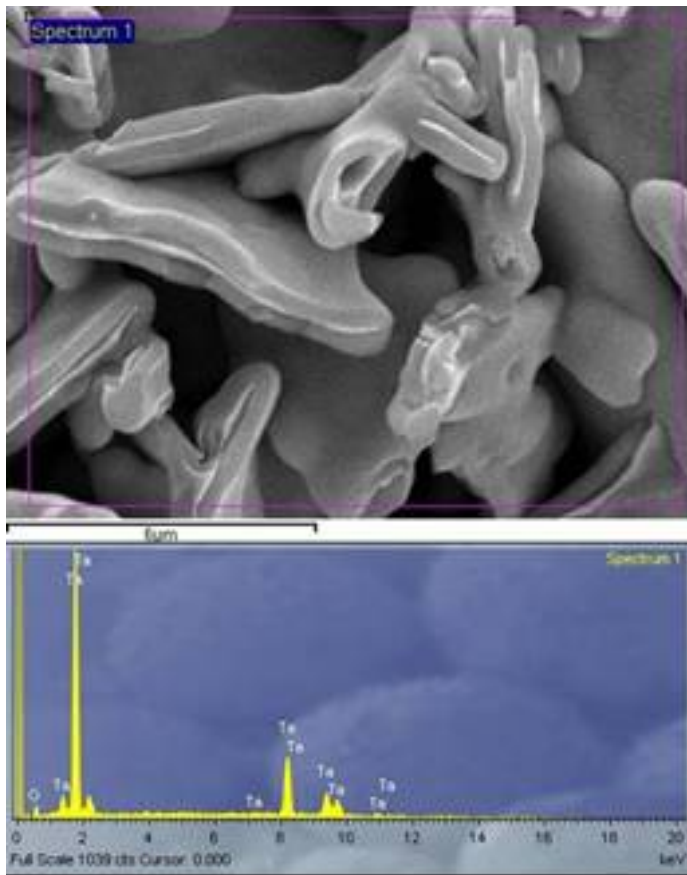


Figure 8.- SEM-EDS images of the Ta₂O₅ surface treated with contaminants removal system.

We selected the IER C for implementation based on the higher efficiency for removing metal ions under the required conditions.

EFFECTS OF IER ON ELECTRICAL PERFORMANCE AFTER IMPLEMENTATION ON ELECTROLYTE FILTER SYSTEM.

According to the experimentation results, during the implementation phase, we replace the IER after complete the days of electrolyte operation in order to keep low concentration of metal ions for longer time (Fig 9).

Ionic Exchange Resin C effect over Electrolyte Life Time

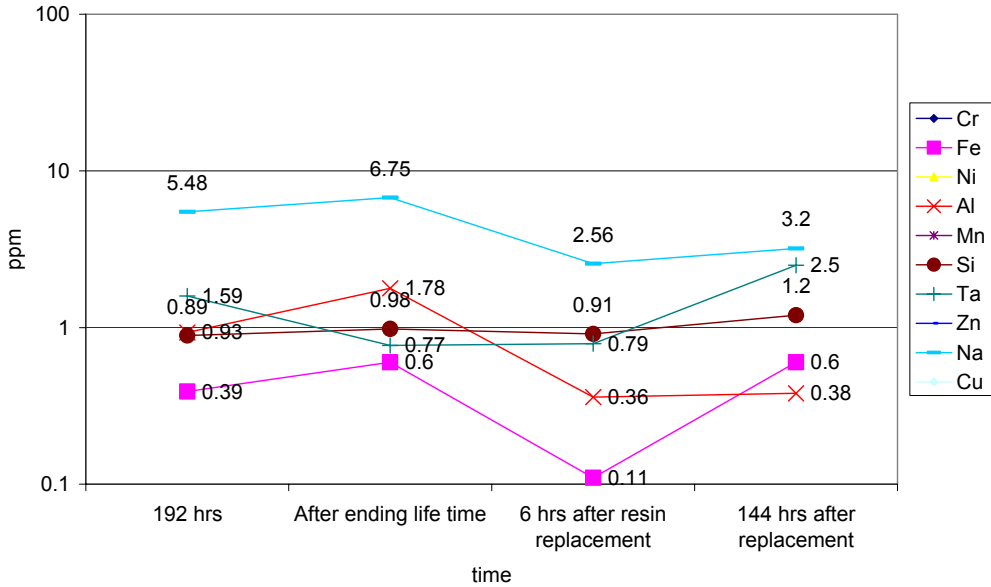


Fig 9. Metals concentration in Electrolyte IER replaced.

The best practice is to replace the resins every determined period of time (Based on electrolyte type). This condition showed the more efficient practice for having a clean electrolyte with total metals content below 10 ppm.

During the monitoring stage, we compared the electrical behavior before and after the IER implementation.

Wet to solid cap drop: Fig. 10 demonstrates the reduction on this parameter from 6.5% to 4% by the reduction on the mean and on the variation from batch to batch.

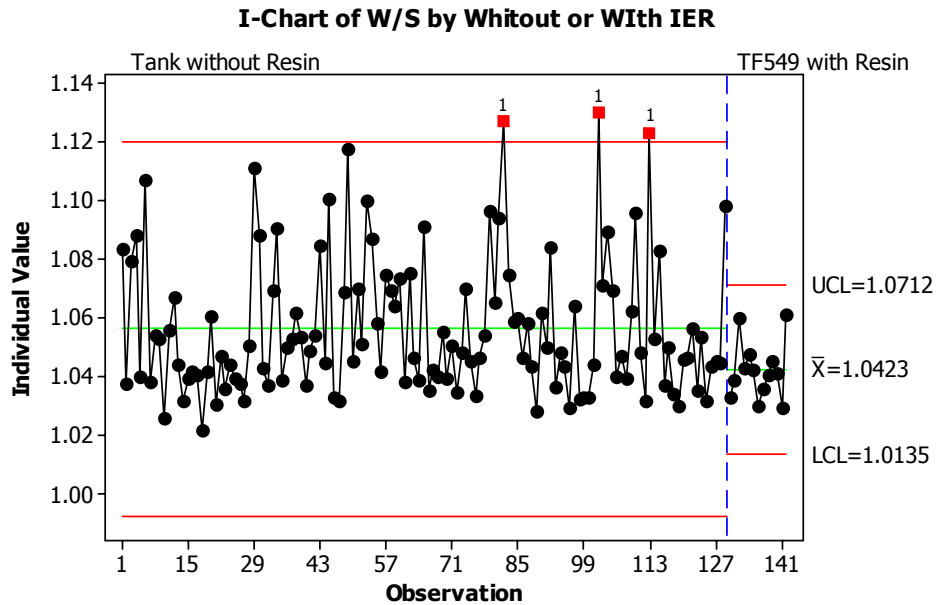


Fig 10. Wet-to-solid cap shift before and after installation of Ionic Exchange Resin.

DF: Dissipation Factor was reduced from 2.7 to 2.56 due to the reduction in the variation from batch to batch by eliminating the batches with high DF. It can be see Fig 11.

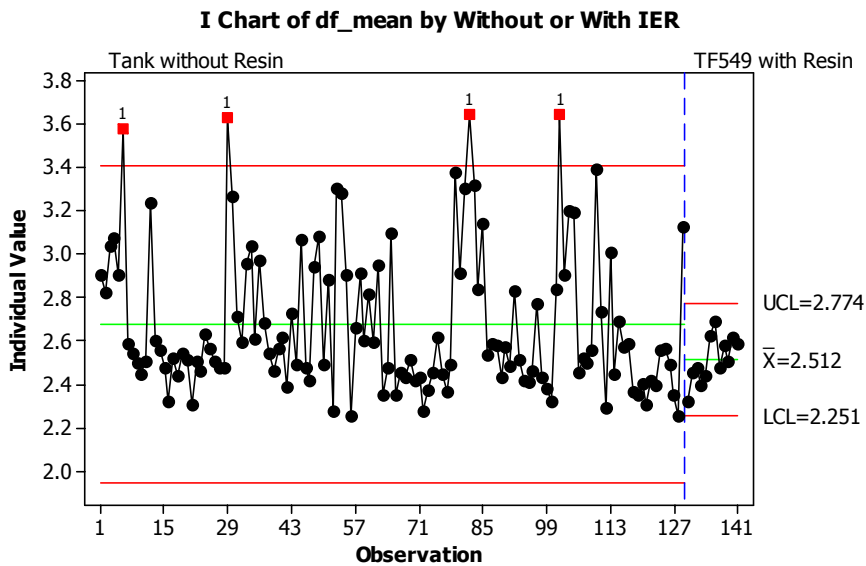


Fig 11. Wet-to-solid cap shift before and after installation of Ionic Exchange Resin.

4. Conclusion

The usage of Ionic Exchange Resins in the Formation Electrolyte System has shown that the contamination by metal ions can be controlled in consistent values lower than 10 ppm during electrolyte life time.

By using this IER for metal ions removal in the Anodization tanks, we obtain better capacitance recovery from wet to solid and also a reduction on the Dissipation Factor. Both benefits come from an improvement on the efficiency of MnO₂ coverage during impregnation process due the elimination of deposited contaminant particles onto Ta₂O₅ surface. Moreover, the life of the electrolyte was significant increased above 100%.

5. References

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