Extended Life Tantalum Hybrid Capacitor

David Zawacki and David Evans

Evans Capacitor Company
72 Boyd Avenue
East Providence, RI 02914
(401) 435-3555
dzawacki@evanscap.com
devans@evanscap.com

Abstract

Approaches were investigated for extending the operating life of Tantalum Hybrid faradaic/dielectric capacitors by reducing electrochemical changes that limit life. This work concentrates on electrolytic additives designed to eliminate or greatly suppress hydrogen formation that normally results from potentiostatic leakage current. Sample capacitors with electrolytes containing hydrogen limiting reagents were subjected to accelerated aging conditions. The results are compared to similar tests on standard capacitors with no electrolyte additives.

Background

The Tantalum Hybrid capacitor is a series combination of a dielectric oxide film capacitance, Ta_2O_5 and a high faradaic capacitance, a film of the conductive metal oxide, RuO_2. The result is a polar capacitor with the Ta_2O_5 being the positive electrode (anode) and the RuO_2 being the negative electrode (cathode). A high potential can be maintained across the thin electrochemically formed Ta_2O_5 film, while the RuO_2 coating remains at low potential. This allows high cell voltage without fear of reaching the electrolyte breakdown potential.

The advantages of the Hybrid capacitor can be better grasped with a basic understanding of common electrolytic capacitors. These devices employ thin oxide films on both electrodes, but they are usually asymmetric, using a material of higher surface area for the negative electrode. The film on the positive electrode is thicker than the negative electrode film, and sets the working voltage of the capacitor. The negative electrode has a higher capacitance, but the two electrodes often have similar physical sizes. The overall capacitance, C, can be determined by analysis of the equivalent series circuit for an electrolytic capacitor. For Hybrid capacitors, $1/C = 1/C_a + 1/C_c$, where C_a and C_c respectively are the positive and negative electrode capacitances. Since $C_c \gg C_a$, the overall capacitance is equivalent to C_a. Because the RuO_2 negative electrode requires little volume, available space can be used to enlarge the positive electrode. The result is a capacitor with much higher energy density.

The Tantalum Hybrid capacitor positive electrode is a pressed, sintered pellet of high capacitance density tantalum powder. Formation of the Ta_2O_5 film is done electrochemically in aqueous electrolyte until a thickness corresponding to a certain formation voltage is reached. This determines the working voltage of the capacitor. The voltage rating of the capacitor is less than the formation voltage, and for Hybrid capacitors, the ration of formation voltage to rated voltage is at least 1.4. This voltage margin is critically important because the leakage current rises sharply as the cell voltage approaches the formation voltage, and in the operating life of a capacitor, the "age" is directly related to the total amount of charge that has passed. Great emphasis is therefore placed on reducing the leakage current by voltage derating and other means, most of which are focused on improvements to the Ta_2O_5 anode, in order to extend life.

The typical failure mechanism of a Tantalum Hybrid capacitor is the result of continuous hydrogen generation by the capacitor during operation. All capacitors have some leakage current associated with them. In the Tantalum Hybrid capacitor, this is the result of many factors including impurities in the anode, cathode, and electrolyte but is also due to dielectric absorption of the anode and any side reactions for the cathode. Even a hypothetical perfect Ta_2O_5 electrode will exhibit some electronic conductivity and under normal operating conditions this causes no material degradation. However, the leakage current indicates a potential difference between the cathode and the electrolyte. This overvoltage is higher than the hydrogen overvoltage and results in hydrogen generation at the cathode. It is our opinion that the hydrogen initially generated is in the form of ions. Tantalum acts a hydrogen getter so these ions are then absorbed into the tantalum substrate of the cathode and the tantalum case. While slow to progress, and typically longer than the rated lifetime of the capacitor, hydrogen ion generation can eventually embrittle the cathode, which accelerates the generation of even more hydrogen. As a result a number of things may happen. This can lead to enough of a decrease in capacitance and/or an increase in ESR to result in a failure of electrical performance. Also, the ions can weaken the glass to metal seal and result in leaking. Another result is the formation of hydrogen gas. Once the tantalum of the case and cathode become saturated with hydrogen ions and can't absorb any more, hydrogen ions combine to form hydrogen gas. The hydrogen gas then builds up within the capacitor causing swelling of the case, which in turn can weaken the already embrittled glass to metal seals and lead to leaking. In the improvement of the hybrid capacitor, it is then a central focus to look at preventing, reducing, or removing of hydrogen formed during operation.

At this point in time, it is not an option to try to remove the hydrogen ions or gas by means of a filter or vent. The capacitors used in this experiment are required to be hermetically sealed so the prevention, reduction or removal of hydrogen has to be approached using more innovative methods. The three areas of concentration for reducing hydrogen ion and gas evolution correspond to the three major regions of the tantalum hybrid; the anode, cathode, and electrolyte.

The focus of this paper is to discuss modification made to electrolytes and experiments performed with different electrolytes. A brief overview will be given on the anode and the cathode just as a means of background.

Anode:

The anode plays a significant role in the prevention of hydrogen. Impurities in the anode can cause the anode to try to form an oxide layer even though it is unable to do this. This can lead to oxygen being evolved at these impurity sites. The oxygen would then be converted to or absorbed by the tantalum oxide. Oxygen generation results in a higher leakage current, which in turns leads to hydrogen ion generation at the cathode. Longer life could be achieved by reducing or isolating impurities in the anode. This can be done using the highest purity tantalum allowable. There may be nothing Evans can do about this as there are only a few tantalum powder suppliers and they already have the highest purity tantalum they can practically produce. In addition, the making of tantalum anodes is already an established science with many years of trials and improvements. While there is probably still some room to eliminate impurities and imperfections it is not the focus of this paper.

Cathode:

The cathode plays a role in hydrogen prevention as this is the negative lead and the electrode where hydrogen is produced. The tantalum Hybrid cathode is especially susceptible to hydrogen evolution because the cathode substrate is made of tantalum, which is vulnerable to hydrogen embrittlement. As hydrogen embrittlement occurs, the ESR of the capacitor starts to increase faster and faster until the unit finally fails. One approach is to try to minimize any embrittlement of the cathode using various techniques, such as changing the material, which might help minimize the increase in any leakage current, thus extending the life of the capacitor. Another approach is to concentrate on the surface kinetics of the cathode material. Tantalum has relatively high surface kinetics, which results in a suitable surface for hydrogen generation. If the surface kinetics can be lowered this should widen the voltage window needed for hydrogen to evolve and as a result slow down any hydrogen evolution.

Electrolyte

As already mentioned, the focus of this paper will be on the electrolyte and what modifications can be made in order to limit hydrogen generation. The electrolyte has obvious implications in hydrogen evolution as it is the source of the hydrogen ions. The standard electrolyte used in the Tantalum Hybrid is an aqueous solution containing 38% sulfuric acid. Here are some of the approaches that are being taken to either prevent hydrogen from evolving or to minimize the damage it causes.

1. Use a hydrogen limiting reagent. By using a hydrogen limiting reagent, another electrochemical reaction will take place before the hydrogen evolution voltage is

reached. This allows the unit to operate without generating hydrogen until the hydrogen limiting reagent is depleted.

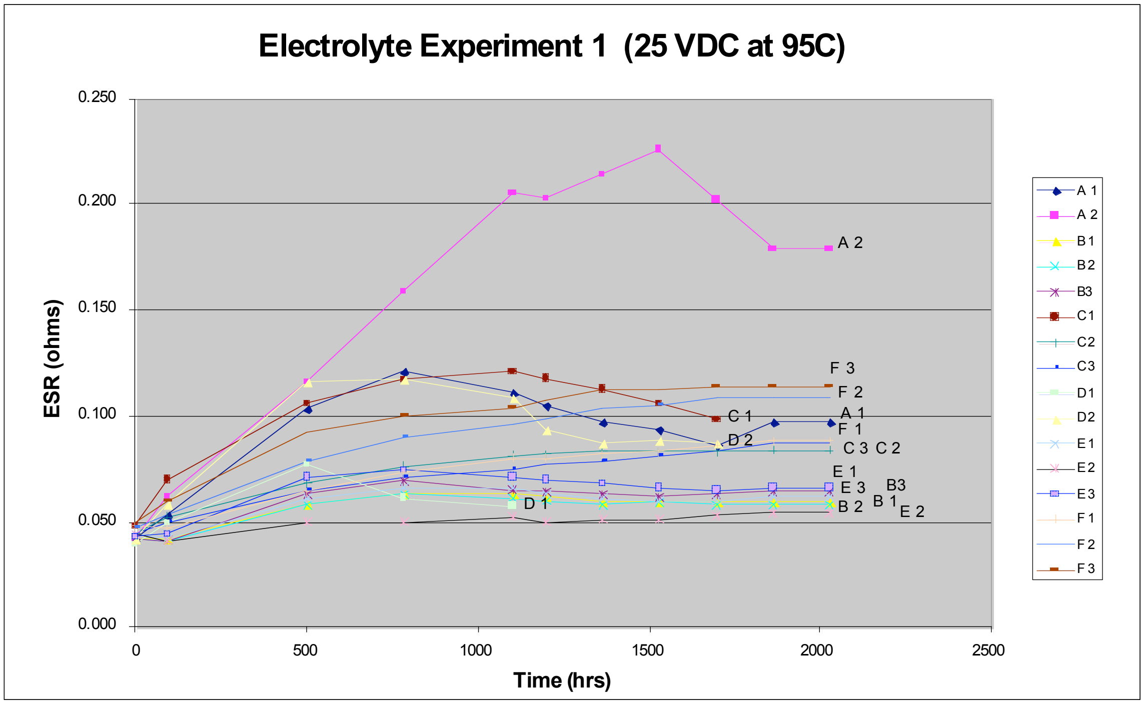
2. Use an inexhaustible hydrogen limiting reagent system. This works on a similar theory as the hydrogen limiting reagent except that it is a reversible reaction and might never be depleted.
3. Use an additive to isolate impurities at the anode. This could help prevent oxygen from being generated at the anode, which would result in lower leakage currents and less hydrogen generation at the cathode.
4. Adjust the pH of the electrolyte. By raising the pH of the electrolyte the hydrogen evolution voltage can be increased. This should widen the voltage window that hydrogen needs to evolve helping to extend the life of the capacitor.

Results and Discussion

There were three separate trials run with capacitors containing various forms of electrolyte. All samples used in this paper are single anode devices. Two different types of anodes were used in the experiments. The anodes used in Experiment 1 are formed at 29.7 volts and tested as 25 volt units. The anodes for Experiment 2 and Experiment 3 are formed at 117 volts and tested as 95 volt units and 90 volt units respectively. The cathodes used in all experiments are of identical construction. The life testing of units is done at an accelerated rate, which means that the experiments were performed at 95^0C, whereas the temperature during routine life testing is 85^0C. The ESR of the units is measured periodically during the experiment. ESR is used as an indicator on how the capacitor is performing. A steadily rising ESR indicates that the capacitor is performing less well, so the best results would be capacitors that show the least increase of ESR during the life of the experiment.

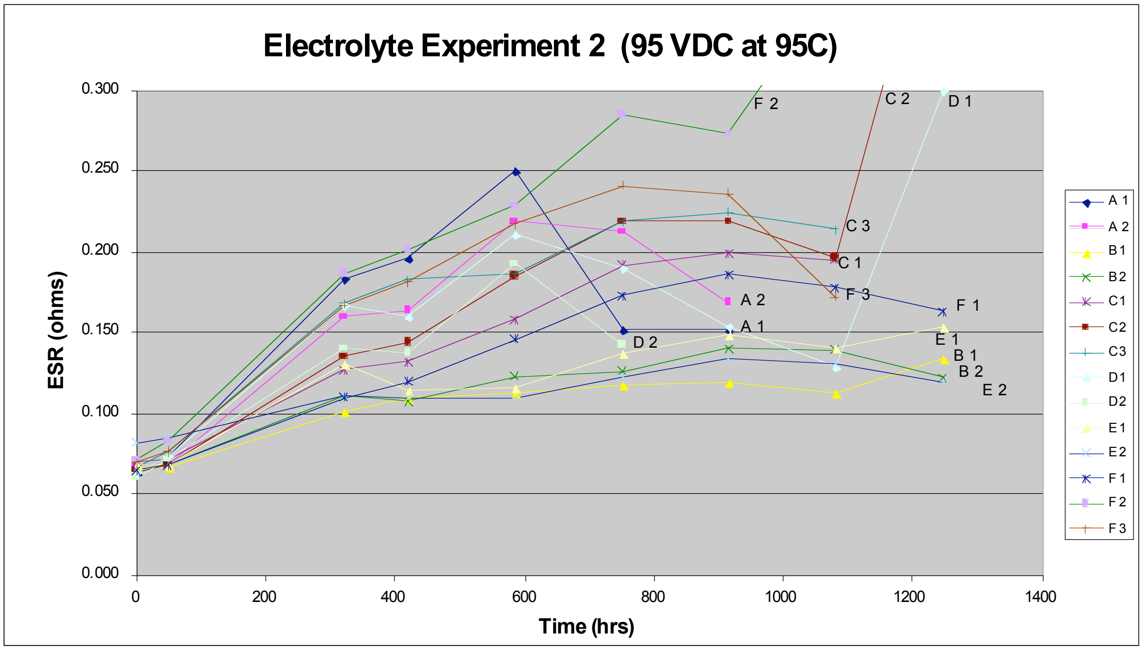
Electrolyte Experiment 1

This experiment uses six different electrolytes. Electrolyte A is the standard electrolyte, which is 38% sulfuric acid. Electrolyte D is the standard electrolyte with an additive added in hopes of isolating impurities that may exist on the anode. Electrolytes B and E are variations of each other and use a hydrogen limiting reagent. Electrolytes C and F are variations of each other and use an additive designed to act as an inexhaustible hydrogen limiting reagent system. The results as seen in the graph show that electrolytes using a hydrogen limiting reagent have the best results. The units utilizing the inexhaustible hydrogen limiting reagent system appears to have marginally better performance, but at this point the results are not conclusive. The units containing the additive to isolate impurities do not show any clear advantage over the standard electrolyte as there is an early failure (D 1). It is possible that this early failure is the result of random infant mortality as the failure happened very early in the testing cycle before the capacitor started showing any signs of electrical failure. It is difficult to conclude from these results if there is any advantage or disadvantage to using the additive.



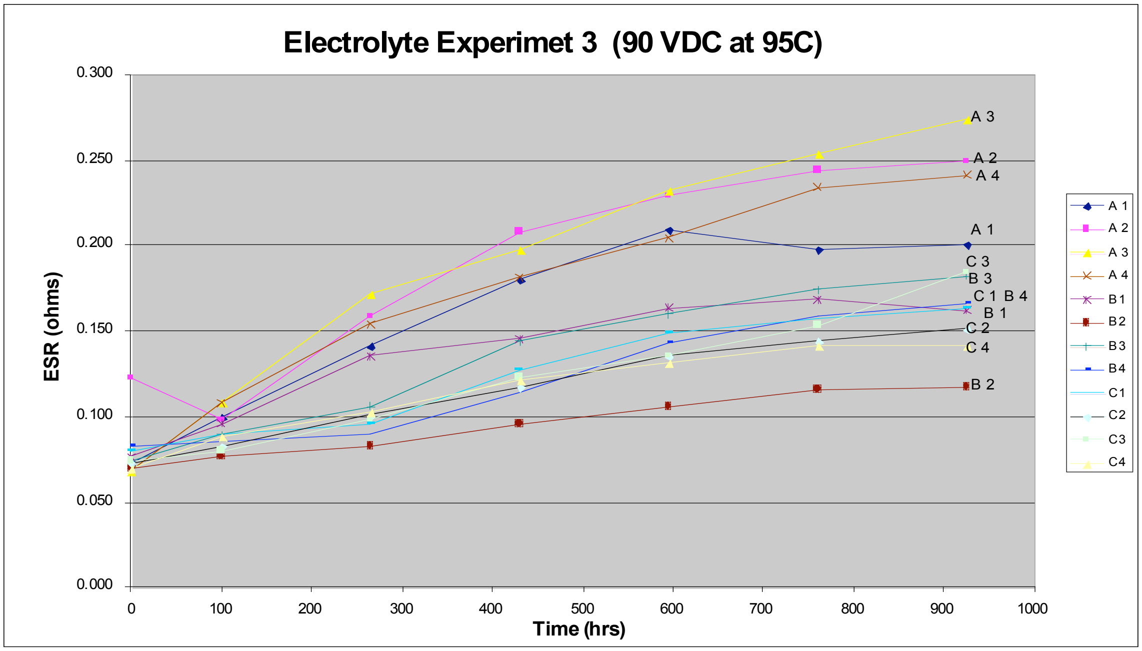
Electrolyte Experiment 2

This experiment uses six different electrolytes. Electrolyte A is the standard electrolyte composed of 38% sulfuric acid. Electrolyte D is the standard electrolyte with an additive used in hopes of isolating impurities that may exist on the anode. Electrolytes B and E are variations of each other and use a hydrogen limiting reagent. Electrolytes C and F are variations of each other and use an additive designed to act as an inexhaustible hydrogen limiting reagent system. The results, as seen in the graph, show that electrolytes using a hydrogen limiting reagent have the best results. As in Experiment 1, the units utilizing an inexhaustible hydrogen limiting reagent system appears to have marginally better performance, but at this point the results are not conclusive. The units containing the additive to isolate impurities also appears to have marginally better performance, but once again, at this point the results are not conclusive. At this point in the test it is worth noting that many units have already failed or are showing signs that failure is near. However, the units containing the hydrogen limiting reagent as a group are performing the best. This is another clear indicator that electrolyte modification can extend the operating life of a Tantalum Hybrid capacitor.



Electrolyte Experiment 3

This experiment uses three different electrolytes. Electrolyte A is the standard electrolyte composed of 38% sulfuric acid. Electrolytes B and C are variations of each other and use both hydrogen limiting reagent and an additive to adjust the pH of the electrolyte. Electrolytes B and C show similar results but both show a distinct advantage over the standard electrolyte.



Some of the units, for example, unit A1 of experiment 2, and the impending failures of experiment 2 units F2, C2, and D1, in the experiment have shown steadily rising ESR only to have it rapidly drop. Some of these units have then failed within a short amount of time after. A possible explanation to this is that hydrogen gas has been generated and formed gas bubbles on the surface of the cathode. These bubbles isolate parts of the cathode from the electrolyte causing an increase in ESR and a drop in capacitance. At some point the pressure is reduced in the case. This allows the electrolyte access to the cathode again, which results in lower ESR. However, at this point the glass to metal seal is possibly weakened and it is not long before the capacitor fails. Another possibility is that case pressure may remain the same but that the hydrogen bubble shifts so that it is no longer in contact with the cathode.

Conclusions

Overall, the experiments show that modifications to the electrolyte can improve the performance of the capacitor and extend the life. At this point, electrolytes using a hydrogen limiting reagent show the greatest benefits. However, this is still an early stage and we believe even greater benefits can be gained by improvements to the electrolyte. Much of the observed degradation in electrical properties over life can be avoided if hydrogen forming reactions are prevented.