Tantalum Capacitor Technology Assessment

Tantalum electrolytic capacitors have long been used in high temperature applications. Since the introduction of the first practical devices in the 1950's, steady progress has been made increasing energy density and reliability. These are polar devices having distinct positive and negative terminals that cannot be reversed. The family of tantalum electrolytic capacitors can be subdivided into two major categories, solid tantalums and wet tantalums. As will be noted, these types are somewhat different in their operation.

All modern tantalum capacitors share a common element, the pellet anode, made by pressing and sintering high surface area tantalum powder to form a pellet of tantalum with low density, high surface area, and a high level of internal porosity. An insulating layer of tantalum oxide, which serves as the capacitor dielectric, is formed on the surface of the pellet. The thickness of the dielectric determines the voltage rating of the capacitor. Wet tantalum capacitors are generally available with voltage ratings up to 125 volts. Tantalum chips are made with voltage ratings up to 50 volts. The size of the tantalum pellet and the thickness of the dielectric determine the overall capacitance of the device.

Wet tantalum capacitors enjoy the highest specific energy and are highly reliable. The interest in wet tantalums focuses on military and airborne applications where the requirement for high performance justifies the higher acquisition cost compared to aluminum electrolytic capacitors. These capacitors are packaged in a hermetically sealed case. Each of these wet tantalum capacitors has found application in high temperature down-hole applications. Tantalum chips are not presently in use in these applications because none have temperature ratings above 125°C.

A wet tantalum capacitor cell comprises two series connected capacitances, an anode / dielectric and a cathode, in contact with a liquid electrolyte, usually sulfuric acid. The anode electrode and dielectric provide essentially all of the voltage withstand capability and defines the capacitance of the cell. The cathode electrode, typically of much higher capacitance compared to the anode, has very low voltage capability. The two series capacitances add according to the relationship:

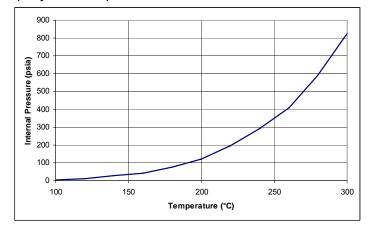
$$C = 1/(1/C_1 + 1/C_2).$$

If $C_1 = C_2$, the device capacitance would equal $\frac{1}{2}C_1$ and the total capacitance would be only $\frac{1}{4}$ the total of the individual electrode capacitances. For this reason, in order to maximize the overall capacitance, the cathode capacitance is usually made much larger than the anode capacitance. If the cathode capacitance were infinitely large, the capacitance of the device would equal the capacitance of the anode.

Wet tantalum capacitors are themselves divided into several categories according to the composition of the cathode electrode. The oldest type in wide use, developed in the late 1970s, CLR79 has a cathode comprised of a high surface area pressed sintered tantalum pellet coated with a very thin oxide layer. Available in four case sizes, and multiple voltage and capacitance ratings, these devices are limited by a relatively bulky low capacitance cathode.

Ongoing improvements in anode materials made by tantalum powder manufacturers emphasized a growing need to improve the efficiency of the cathode and in the late 1980s, another type, called "SuperTan" was introduced. This capacitor is distinct in that it replaced the CLR79 tantalum cathode with one made from high surface area electrodeposited palladium. The large increase in cathode capacitance allowed the incorporation of higher capacitance anodes, boosting energy density by at least a factor of two compared to CLR79. The last important development to tantalum wet capacitors happened in the mid 1990s with the introduction of the Hybrid tantalum capacitor. This device combines a tantalum pellet anode with a cathode based on ruthenium oxide. Ruthenium oxide is in a class of materials known as pseudocapacitors because it can store energy in a highly reversible faradaic charge transfer which results in a change in oxidation state of the material. Because of its charge storage mechanism, ruthenium oxide has an order of magnitude higher specific capacitance than high surface area palladium or tantalum, and as a result, Hybrid capacitors have even higher capacitance than similarly sized CLR79s or SuperTan devices.

Wet tantalum capacitors have high reliability and high specific capacitance, but difficult technical hurdles remain to satisfy the requirements of high temperature application. The most important problem is a result of the use in these capacitors of sulfuric acid electrolyte. The concentration of the electrolyte is approximately 36 - 38% by weight. It has a boiling point of 127° at one atmosphere. Wet tantalum capacitors applied in a higher temperature environment must therefore have a hermetic case designed to withstand high internal pressure. As shown in **Figure 1**, the internal pressure increases rapidly with temperature.



So, increasing the maximum temperature use for wet capacitors rapidly becomes an exercise employing ever thicker and more rigid pressure vessels. This is a matter of practical difficulty because with the use of a heavier case, the specific capacitance and energy are reduced.

In addition, the Ta_2O_5 dielectric in tantalum capacitors is thermodynamically unstable. This dielectric will relax into a stable form due to oxygen migration from the dielectric

Figure 1. Internal pressure as a function of temperature for wet tantalum capacitors.

layer to the tantalum layer, resulting in deterioration of the dielectric layer. This relaxation is accelerated at elevated temperature, and if impurities are present in the electrolyte used during dielectric formation (Freeman, et al, 2007). The Ta_2O_5 stability can be improved by removing impurities from the formation electrolyte and by proper heat treatment.

Working voltage needs to be decreased for high temperature applications in order to provide sufficient operating life. A wet tantalum capacitor degrades over time by electrochemical reactions that consume electrolyte and reduce the efficiency of the cathode. The rate of this reaction is proportional to the leakage current. These reactions follow an approximate doubling in rate for every 10° rise in temperature. The leakage current and the voltage are related in a similar way, and decreasing the voltage decreases the leakage current. The life effects are illustrated in **Figures 2** and **3**. The data shown are for a tantalum Hybrid capacitor having a nominal 2000 hour life at 85°C and rated voltage. All wet tantalum capacitors follow the same general behavior.

Table 1 shows capacitance and voltage ratings as well as operating temperature, voltage rating, and approximate annual usage for wet tantalum capacitors by the oil and gas exploration industry.

As described above, wet tantalum capacitors require a heavy hermetically sealed package to be able to withstand the internal pressures generated at elevated temperatures. These packages lead to large, bulky packages that are not suitable for drilling applications due to their size and weight, which lead to problems with shock and vibration.

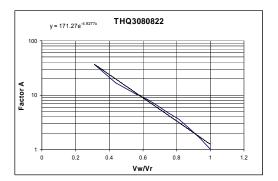


Figure 2. Capacitor life is inversely dependent on working voltage. Vw = working voltage; Vr = rated voltage

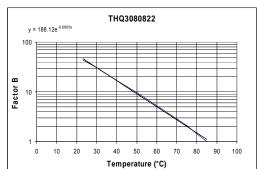


Figure 3. Capacitor life as a function of temperature. Minimum Predicted life (hours) = 2000 X (Factor A) X (Factor B)

Rating	Temperature	Rating Information Voltage Derating	Volume
T4-220µf/100∨	175 °C	30%	6500 pcs
T4-220µf/100v	150 °C	50%	6000 pcs
T4-100µf/60v	150 °C	15%	8500 pcs
T4-470µf/75v	175 °C	50%	3000 pcs
T4-375µf/80v	200 °C	50%	500 pcs
T4-82µf/125v	150 °C	50%	2000 pcs
T4-150µf/125v	150 °C	40%	new program
T3-82µf/75v	150 °C	50%	500 pcs
T2-110µf/75v	175 °C	35%	12000 pcs
T2-200µf/75v	200 °C	35%	new program
T2-27µf/125v	150 °C	50%	300 pcs
T1-10µf/50v	150 °C	50%	10000 pcs
T1-22µf/75v	150 °C	50%	10000 pcs

New capacitors are required that are smaller, lighter, and able to withstand the elevated temperatures, shock and vibration of deep drilling applications. The new capacitors will involve both advanced electrolytes to provide high temperature capability, and lightweight packaging to better tolerate the shock and vibration associated with drilling. In addition, the capacitor footprint has to be of the proper size for the capacitor to fit on the printed circuit boards and to fit inside the pressure vessels that contain the high temperature electronics.

In the current research project we will address the development of electrolytes that will allow capacitor operation at temperatures up to 250°C. Some of the challenges involved include development of an electrolyte that is highly conductive at both ambient and elevated temperatures, and development of methods to incorporate the electrolyte into the capacitor anode and cathode, all while maintaining a high capacitance and low resistance. In addition to identification and testing of a high temperature electrolyte, this program will examine various methods to increase both the capacitance and the voltage as a function of temperature. Packaging of the capacitors to withstand the elevated temperature of operation will also be evaluated.

Development of the high temperature capacitor will allow for oil and gas exploration in increasingly deeper wells. Reliable capacitors are needed that will provide at least 1000 operating hours at temperatures exceeding 200°C, allowing information obtained while drilling to be transmitted to the surface. The use of reliable high temperature capacitors will decrease down time while drilling, with respect to removing the drill train containing failed electronics from a well and replacing it with new electronics.

Reference

Freeman, Y., R. Hahn, P. Lessner, J. Prymak, *Reliability and Critical Applications of Tantalum Capacitors,* in Proceedings of the 27th Capacitors and Resistors Technology Symposium, Albuquerque, NM, p. 111, March 23-26, 2007.