TECHNICAL PAPER

High CV Wet Tantalum DC Capacitors

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Abstract:

There are very many DC back up applications that require high energy storage capability. Rechargeable batteries and double layer carbon capacitors, (Electric Double Layer Capacitors or EDLC), have certain limitations in high temperature and harsh operational conditions. This paper will describe a novel application and design concept approach that will introduce High CV wet tantalum capacitors into this arena. Comparisons with supercapacitors and conventional wet tantalum capacitors will be given, with benchmarking of the capacitor technologies.

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INTRODUCTION

Batteries are widely used for energy storage in industrial and consumer electronic devices because of their high energy density; however, they are limited in their power density. Because of this, a battery often cannot supply the power required while still retaining its open circuit voltage. The greater the battery voltage drop, the larger the load on the battery. Often, when a battery needs to supply high power at short pulse widths, the voltage drop may be too large, causing a reduction in voltage below that required by the end product. Large loads decrease the energy stored in the battery, harming it and shortening its lifespan.

When high power is required in battery operated devices (i.e. in pulse applications), the combination of a large capacitor and parallel connected battery gives the benefits of both, enhancing the performance of the battery and extending its life, exploiting the battery to its maximum potential. The capacitor produces a voltage damping effect: low impedance capacitors can be charged in seconds with a low current during standby times between high current pulses. This voltage drop has the following results:

- Better energy and power management
- Extended battery life and operational range
- Superior energy density in the battery
- Power is produced by both the capacitor and the battery, each supplying power inversely to its own ESR
- Fewer battery replacements in some applications (or the use of smaller batteries)

Batteries are very inefficient at low temperatures. Their internal resistance increases due to the slower kinetics of the chemical reaction within the battery. The internal resistance of pulse type capacitors is much lower than that of batteries, even at low temperatures down to -40degC.

Supercapacitors and EDLC (Electric Double Layer Capacitor technology, a sub-group of supercapacitors) devices have progressed well since being introduced commercially in the mid-90's, and have become a favourite pulse energy capacitor, offering high power and high energy density. Compared to other capacitor technologies, supercapacitors offer a much higher energy density that ideally suits applications requiring energy back-up and pulse load circuits at low frequencies. The main limitations are maximum frequency/pulse width, maximum operating life temperature (70-85degC) and an inability to withstand common reflow/wave temperature assembly profiles. Electrolytic capacitors, on the other hand, are generally suitable for wide temperature ranges and various assembly techniques, and are capable of operating as a switching smoothing capacitor at higher frequencies. However, the energy density of electrolytic capacitors has been considerably lower than supercapacitor solutions. Two basic types of electrolyte are typically used in electrolytic capacitors - aqueous and organic.

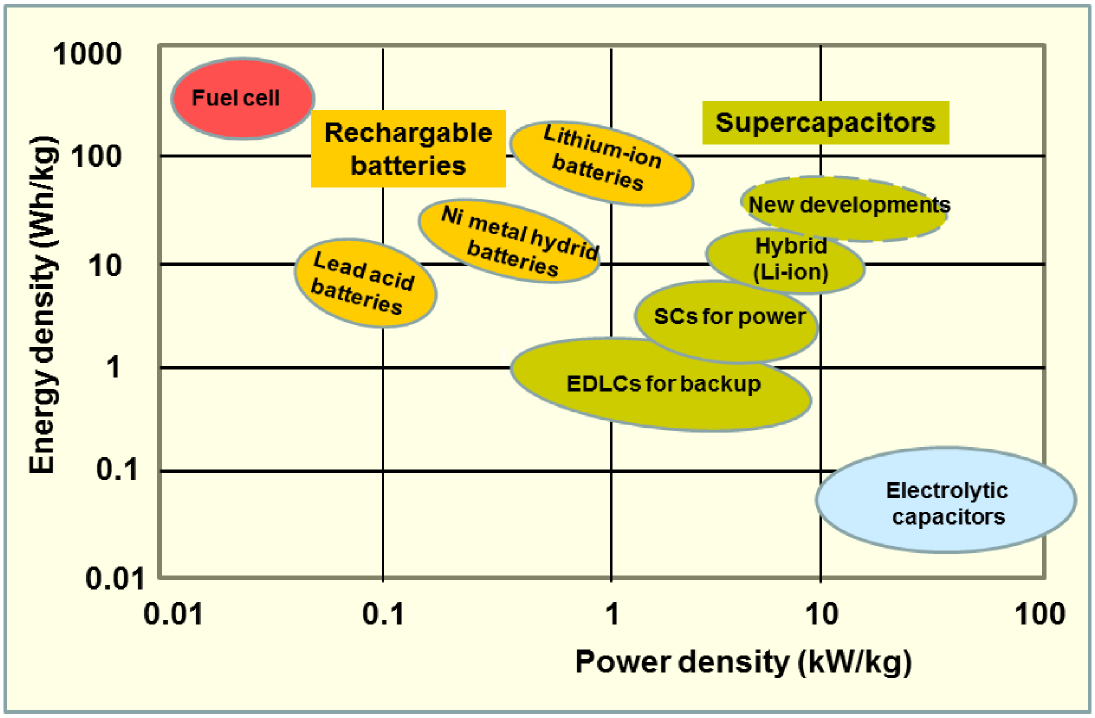
Water is a relatively good solvent for inorganic chemicals, especially when treated with acids such as sulphuric, or salts with high ion mobility. Electrolytic capacitors with such an aqueous electrolyte offer relatively high conductivity values of about 100 to 1000 mS/cm, a low dissociation voltage per electrode and a relatively low operating temperature range. Aqueous electrolytes are used in supercapacitors with low energy density and high power density.

Electrolytes based on organic solvents such as acetonitrile, propylene carbonate etc., and solutions with salts are more expensive than aqueous electrolytes, but they have a higher dissociation voltage per electrode (2.7V capacitor voltage), and a slightly higher temperature range (up to 70-85degC). The lower electrical conductivity of the electrolyte (10 to 60 mS/cm) leads to a lower power density, but higher energy density since the energy density increases with the square of the voltage.

Wet Tantalum Electrolytic Capacitor technology is well-established. It uses a tantalum pellet inserted into a can, also usually fabricated in tantalum for best performance, which contains an electrolyte solution. Cathode systems with high capacitance are created on the internal surface of the can or as a tantalum sleeve insert. Due in part to the hermetically sealed construction, this technology provides high capacitance in a wide voltage range up to 125V and over a wide operating temperature range of between -55 to +125degC. Unlike EDLC or batteries, the stable construction of wet tantalum capacitors with a solid

Ta_2O_5 dielectric enables higher frequency AC operation with DC BIAS (depending on construction) and therefore these devices are suitable for use in power supplies as bulk smoothing capacitors.

Figure 1. Shows the comparison of power and energy density per kg between batteries, supercapacitors and electrolytic capacitors.



Source: Wikipedia

Fig.1. Power and Energy density benchmark

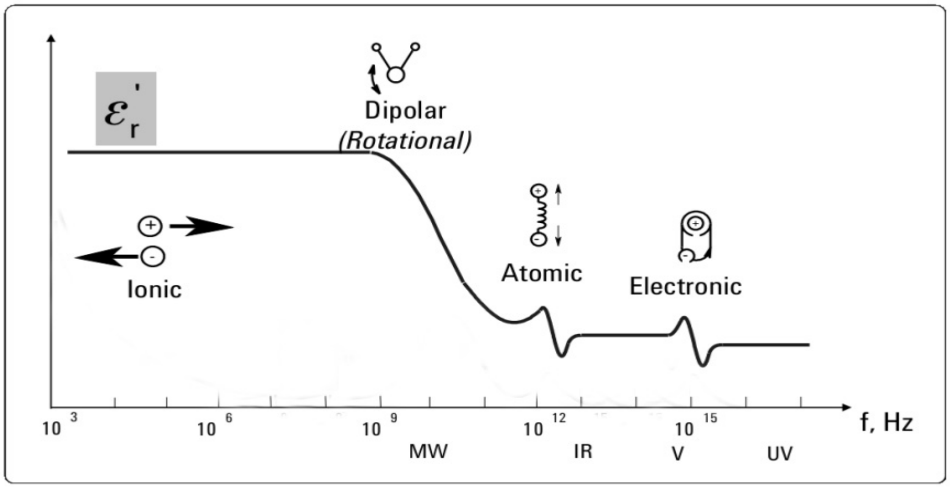
CAPACITOR STRUCTURES AND FREQUENCY DEPENDENCE

The basic capacitance of a plate capacitor is defined by the basic equation below:

$$C = \frac{\varepsilon_0 \, \varepsilon_r \, S}{d} = 8.854 \cdot 10^{-12} \cdot \frac{\varepsilon_r \, S}{d}$$

Where S is surface, d is thickness of dielectric, ε_r relative permittivity and ε_0 permittivity of vacuum

Surface area and thickness of the dielectric can be considered as a constant in an ideal plate capacitor structure under normal operational mode, thus the frequency dependence of the capacitance is defined by the permittivity parameter. This permittivity frequency behaviour is caused by the polarization mechanism of the dielectric and material structure.



Source: Agilent dielectric mechanisms

Fig.2. Permittivity and polarization mechanisms with frequency

The dielectric layer of tantalum capacitors is formed by an oxide of tantalum, Ta_2O_5, with a permittivity $\varepsilon_r = 27$. Super-capacitors do not have a conventional dielectric layer; nevertheless if the electrolyte solvent is water then the influence of the high field strength generates a permittivity, ε, of 6 to 80 (without an applied electric field). Because activated carbon electrodes have an extremely large surface area, in the range of 10 to 40 $\mu F/cm^2$, the extremely thin double-layer distance is in the order of a few ångströms (0.3-0.8 nm), thus double-layer capacitors have much higher capacitance values than conventional capacitors.

As discussed previously, basic polarization mechanisms (permittivity, capacitance) properties in ideal capacitor structures are frequency-dependent; nevertheless the most common ionic polarization occurs from DC up to microwave frequencies. However the main limitation of frequency in real-world electrolytic capacitors is not due to the properties of the dielectric but its structure. The electrodes are created by sintering tantalum powder or by etching aluminum to form a surface structure with 'pores', thus creating a large surface area and enabling a good potential for high capacitance. The second electrode is then covered by the electrolyte which penetrates into its pores. Thus, conductive material contacts with a high surface area - see Fig.3. Depending on the conductivity of the second electrode, some capacitance drop may be observed. This phenomenon can be described with a series circuit of cascaded RC networks (resistor/capacitor ladder) with serial RC time constants. These result in delayed current flow, reducing the total electrode surface area and capacitance drop with frequency - see Fig.4.

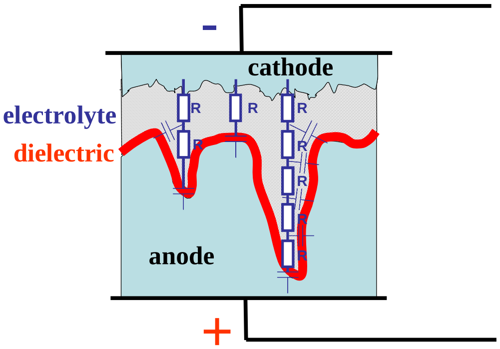


Fig. 3. Electrolytic capacitor structure and RC ladder

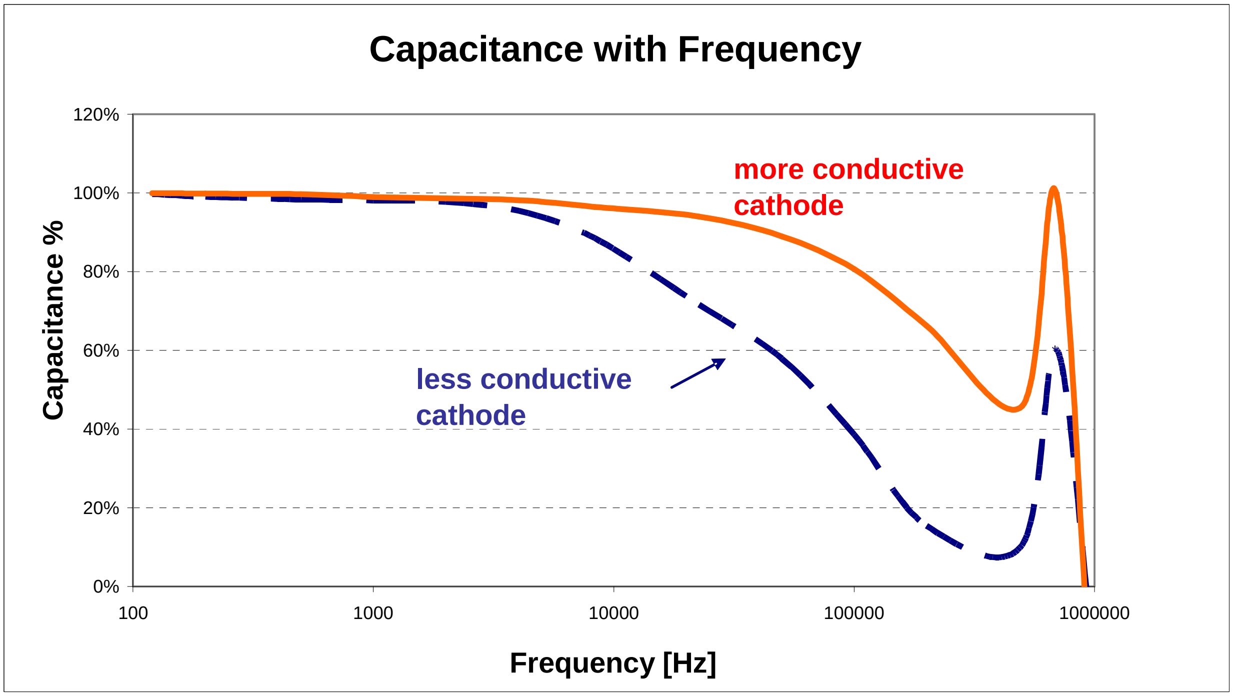


Fig.4. Capacitance drop with frequency in structures with different cathode conductivity

The RC "ladder" can be considered as a behavioural model for supercapacitors as well; the extraordinarily strong frequency dependence can be explained by the different distances the ions have to move in the electrode's pores. The area at the entrance of the pores can be accessed easily by the ions. The short distance is accompanied by low electrical resistance. The greater the distance the ions have to cover, the higher the resistance, and capacitance decreases with increasing AC frequency. Thus, total capacitance is only achieved after longer measuring times. The capacitance of supercapacitors has to be measured with a special constant current charge and discharge measurement, defined in IEC standards 62391-1 and -2 - Fig. 5.

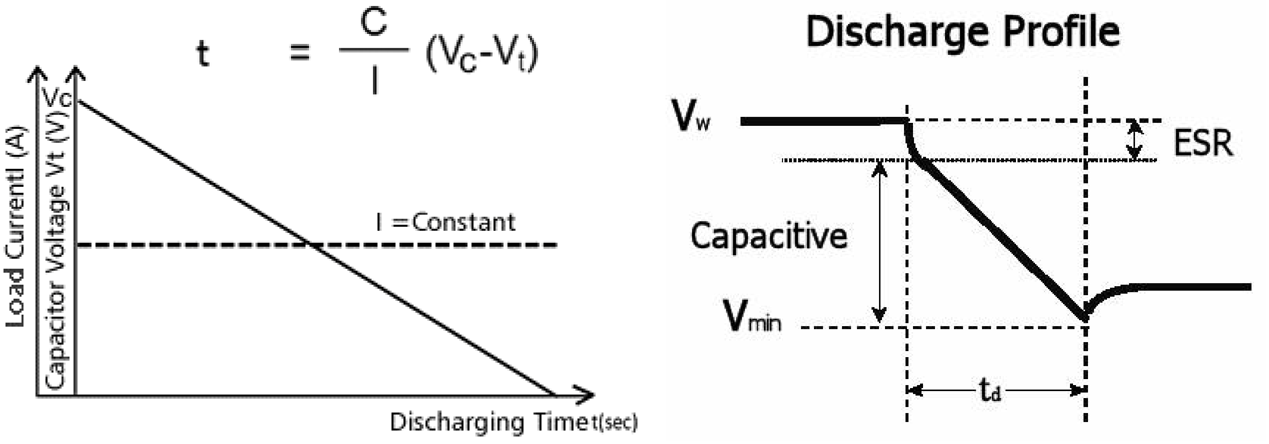


Fig.5. Capacitance measurement by constant current discharge method

WET TANTALUM CAPACITORS

Wet tantalum capacitors have been utilised for many years in high energy storage applications where volumetric efficiency and high reliability are essential requirements. The first wet tantalum capacitors were developed 50 years ago and comprised a tantalum anode surrounded by an electrolyte inside a silver case with an epoxy end seal. This design was problematic in that it could be prone to leakage of the electrolyte through the epoxy seal. It also had a limited ability to withstand any reverse voltage. The silver case material was later replaced with tantalum, which proved more stable over a range of applications. The use of a tantalum case made it easier to construct a tantalum base-to-metal end-seal that could be laser-welded to the tantalum can, thus making a hermetic capacitor. This better addressed the risk of fluid leakage from the part and improved overall reliability. The process also included the use of a porous tantalum sleeve inside the case to increase the surface area of the cathode system. [2]

Because the bulk of the capacitance attainable is strongly dependent on the area of the cathode, alternative cathode systems, directly coated on the interior of the tantalum can, were developed. This system not only increases the area of the cathode, but also increases the internal volume available for the anode, thus significantly increasing the potential CV ratings available in any given case size. The disadvantage of the alternative cathode system is a limited/zero reverse voltage capability.

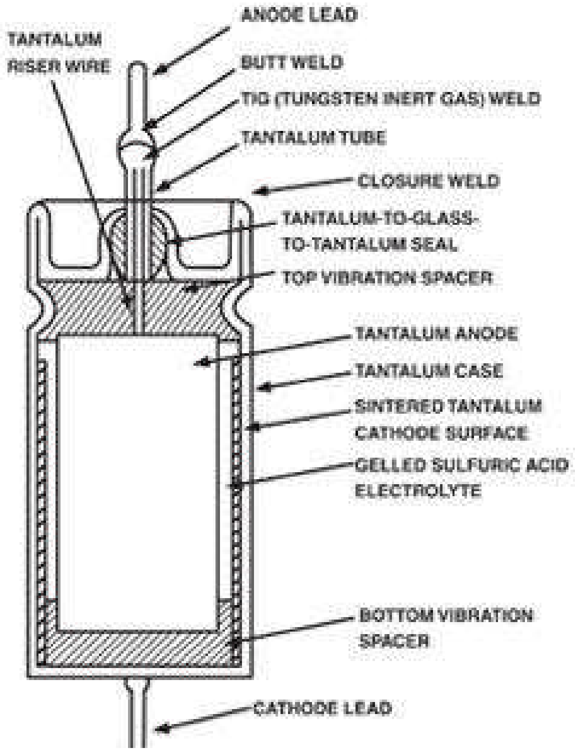


Fig.6. Wet Tantalum Capacitor Structure

The key benefits of wet tantalum electrolyte systems are:
- Large case sizes capable of offering high CV values
- Wide operational temperature ranges -55 to 125degC, with special designs up to 200degC
- Wide working voltage range up to 125V
- High volumetric efficiency

Drawbacks
- Lower electrolyte conductivity = higher ESR
- Capacitance decrease and ESR increase at low temperatures
- Risk of hydrogen release
- Higher material and manufacturing cost

In comparison to tantalum MnO_2/polymer devices, wet tantalum capacitors exhibit a better surge current robustness with a higher breakdown voltage (BDV), closer to their dielectric formation voltage. This results in products that require less voltage derating and have a higher CV rating. The inferior electrolyte conductivity results in a bigger capacitance drop with frequency, as explained in the previous chapter. Thus wet tantalum electrolytic capacitors are suitable for high reliability bulk filtering and back up applications.

WET TANTALUM AS A DC CAPACITOR

One of the key methods of achieving higher capacitance values with tantalum capacitors is to increase the anode surface area by utilising finer higher CV tantalum powders - see Fig.7. Wet tantalum electrolytes, usually based on sulphuric acid, have limited ion movement and lower conductivity, thus the resistance of small thin pores in high CV powders is relatively high and capacitance drop already occurs at low frequencies.

Standard specifications for wet tantalum capacitors define the capacitance reference value at a frequency of 120Hz. This is starting to become a limiting factor for the use of next generation higher CV powders as capacitance at 120Hz may be low - see Fig.8.

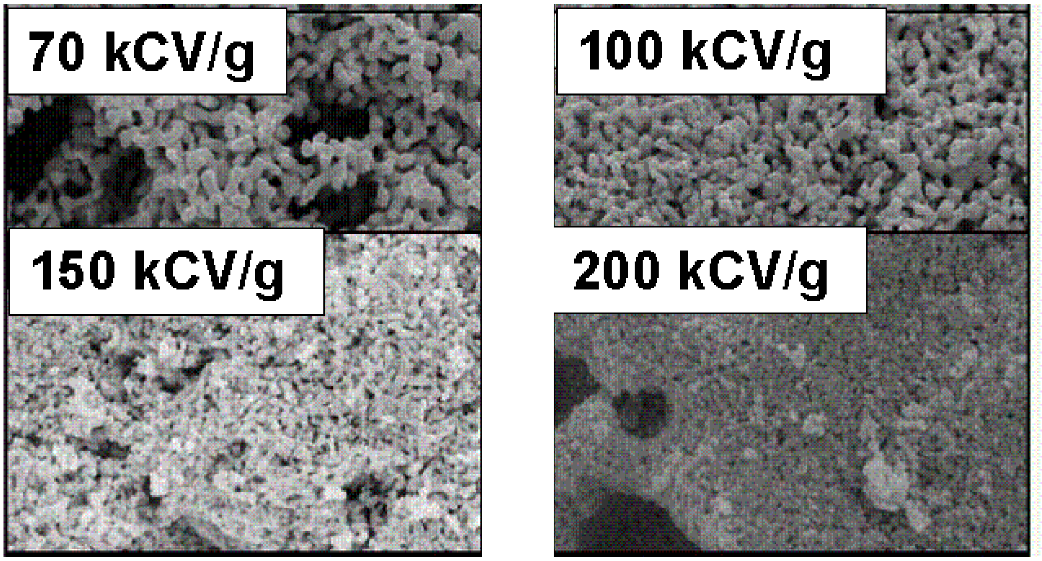


Fig.7. SEM pictures of tantalum powders with different CV/g under the same magnification

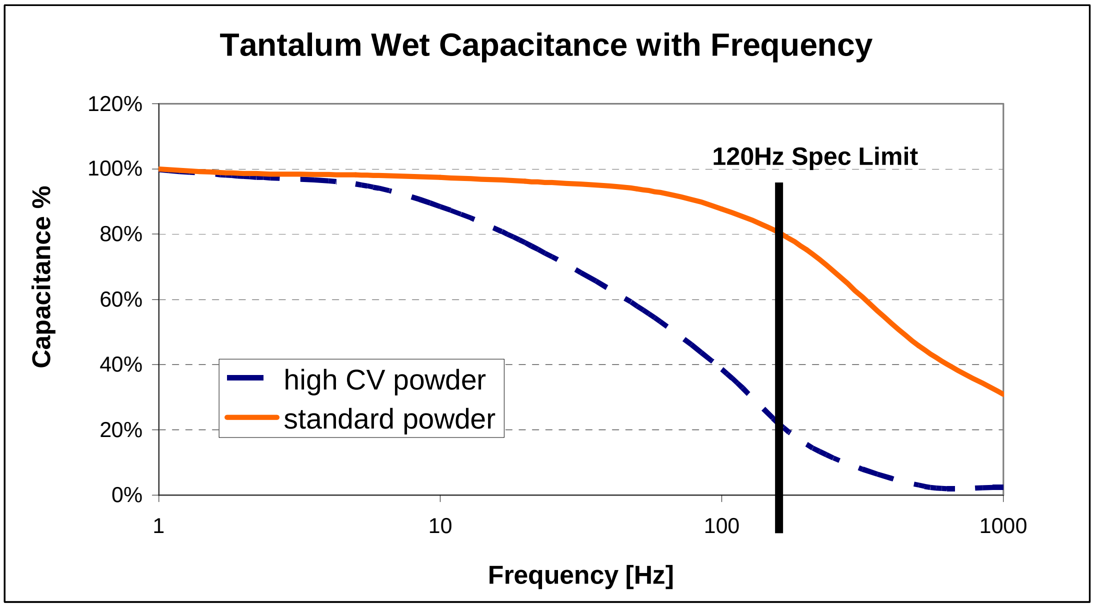


Fig.8. Wet tantalum device capacitance versus frequency graph for standard and high CV tantalum powder

The novel approach is to look at wet tantalum capacitor capabilities in reference to supercapacitor-like specifications and benchmark the technology's performance as a DC capacitor.

DC WET TANTALUM CAPACITOR

The reality of operating wet tantalum capacitors at DC is much more complex than merely the use of higher CV tantalum powder in a conventional wet tantalum capacitor design. There are certain areas of technology and processes that need to be modified and developed in order to optimise the performance of the system for maximum DC operational capability.

The core limitation is the generation of hydrogen on the cathode. The acidic electrolyte conductivity mechanism is based on hydrogen ion movement. Hydrogen radicals are generated during the charge transfer on the surface of the cathode. The radicals are absorbed by the cathode, so under certain conditions gaseous hydrogen may be generated. This process can eventually make the cathode brittle and can lead to the mechanical destruction of the capacitor. Gaseous hydrogen can also cause an overpressure to develop inside the can.

Hydrogen generation in wet tantalums operating at DC needs to be addressed, especially in the following processes:

DCL reduction

The lower the DCL, the lower the hydrogen generation will be during the operational life of the capacitor. Thus, lowering DCL will improve the quality and reliability of the wet system. DCL is related to a number of parameters such as: basic tantalum powder impurity level; ageing process conditions such as voltage and temperature; formation to rated voltage ratio etc. The larger the surface area of a tantalum anode, the larger the initial current, requiring control over, and optimisation of, processing conditions.

Electrolyte composition

Electrolyte solutions require optimisation to provide sufficient conductivity to suppress hydrogen formation. This solution has also to provide a high level of stability over time and temperature.

Cathode system

The overall capacitance of a wet tantalum system is composed of the capacitance of the anode in addition to the capacitance of the cathode, where total capacitance $1/C = 1/C_a + 1/C_c$. Cathode capacitance is designed to be much higher than the capacitance on anode side, $C_c >> C_a$, - thus the behaviour of the whole capacitor is influenced by the anode system only. Anode capacitance is greatly increased compared to conventional wet tantalum designs when high CV tantalum powder for DC wet capacitors is used. Thus the cathode system needs to provide a sufficiently greater capacitance value than the anode capacitance. This may limit the use of some existing conventional cathode systems and it requires further optimisation and/or the development of new, larger surface area cathode structures.

DC WET TANTALUM CAPACITOR BENCHMARKING

The first samples of DC Wet tantalum capacitors using the principles described in the previous chapter were prepared achieving a high DC capacitance of 50mF at 6.3V rated voltage in a T4 standard wet tantalum case size. The capacitance value can be measured by the constant current indirect method; the same method is used for supercapacitor products.

Fig. 9 shows the basic parametric benchmarking between organic EDLC, aqueous supercapacitors, conventional wet tantalums and the new DC wet tantalum capacitor. This is a generic technology comparison as well as a case study on specific part numbers. The aqueous supercapacitors are represented by a 400mF 5.5V capacitor, the organic EDLC is a 100F 2.7V, the conventional tantalum was selected as a higher voltage 75V type with 470µF capacitance for energy density comparison and a 50mF 6.3V DC wet tantalum part.

It is clear that EDLC supercapacitors have a much better energy density by far than conventional capacitors, nevertheless the volumetric capacitance density of DC wet capacitors is getting very close to that of aqueous supercapacitor technology devices. The key benefit of tantalum DC wet capacitor technology is the temperature range of up to 85degC, the ability of devices to withstand high temperature reflow soldering during automated board assembly, and their low DCL.

It is also interesting to note that conventional 75V wet tantalum capacitors have a similar energy volumetric density to the low voltage aqueous super-capacitors, as the energy is a function of voltage squared.

		EDLC SuperCap		Tantalum Wet Cap	
		Aquous	Organic	Conventional Wet	**DC Cap**
Technology Overview	Cap range	6.8mF - 1F	68mF - 300F	10uF - 10mF	**50-150mF**
	Volt range - cell [V]	0.75V	2.5V	NA	**NA**
	Volt range [V]	stacking to 16V	stacking	6.3 -125V	**2.5-10V**
	Series bal resistors	No	Yes	No	**No**
	DCL [A]	0.00002CV	0.001CV single cell	0.00015CV	**0.0001CV**
	Op temp range [C]	-20 / 70C	-40 / 75 (85C)	-55/125	**-55/85**
	ESR [mΩ]	20 - 50mO @1kHz	200 - 500mO @DC	600mO - 3000mO	**50-600mO @1kHz**
	Reverse Volt	OK	No	limited	**limited**
	AC operation	limited	No	OK	**limited**
Reference Case	Capacitance	400mF	100F	470uF	**50mF**
	Voltage [V]	5.5V	2.7V	75V	**6.3V**
	Dimension [mm]	48x30x6.7	45x22dia	28x10dia T4	**28x10dia T4**
	Temperature Range [C]	-20 - 70C	-40 - 65C	-55 - 125C	**-55 - 85C**
	Reflow Assembly	No	No	Yes	**Yes**
	Case Volume [cc]	9.648	5.445	2.198	**2.198**
	ESR 1k [mΩ]	40	12	900	**900**
	Steady State DCL [µA]	40	260	5	**3**
	Cap Density [mF/cc]	41	18365	0.21	**23**
	Energy Density [mFV/cc]	627	66942	601	**451**

Fig.9. DC capacitor benchmarking table

Capacitance frequency behaviour of the DC wet tantalum technology is very similar to the aqueous super-capacitor systems - see Fig.10 and Fig.11. SMD MnO_2 and polymer tantalum capacitors were added to this chart for comparison.

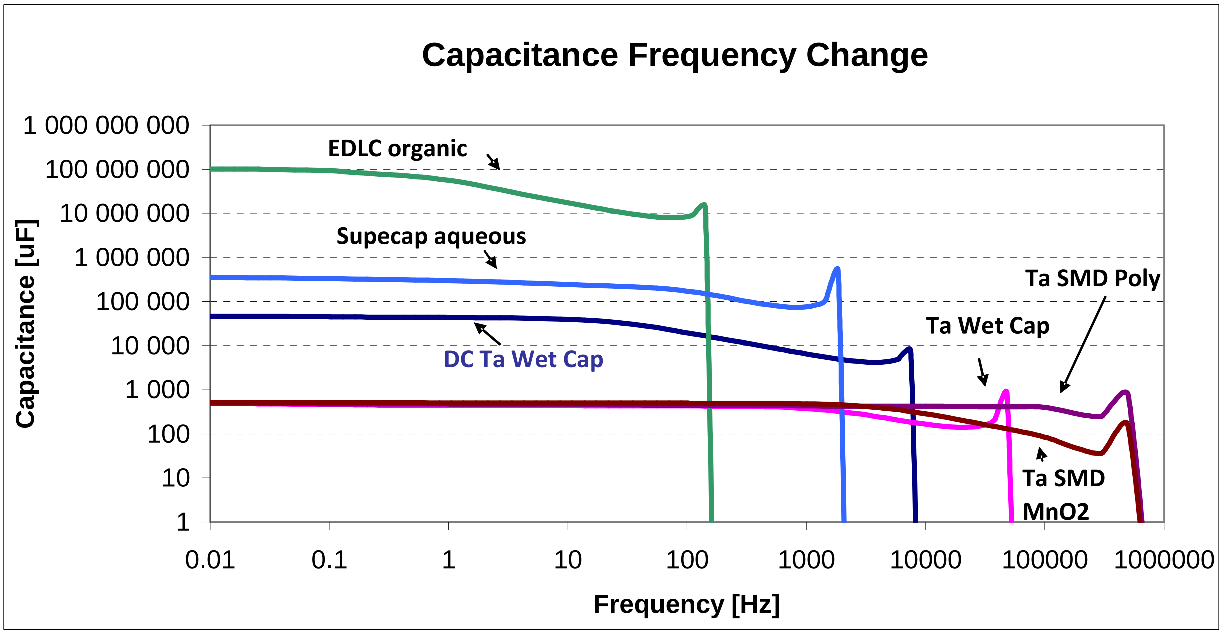


Fig.10. Capacitance vs frequency capacitor benchmark - absolute capacitance

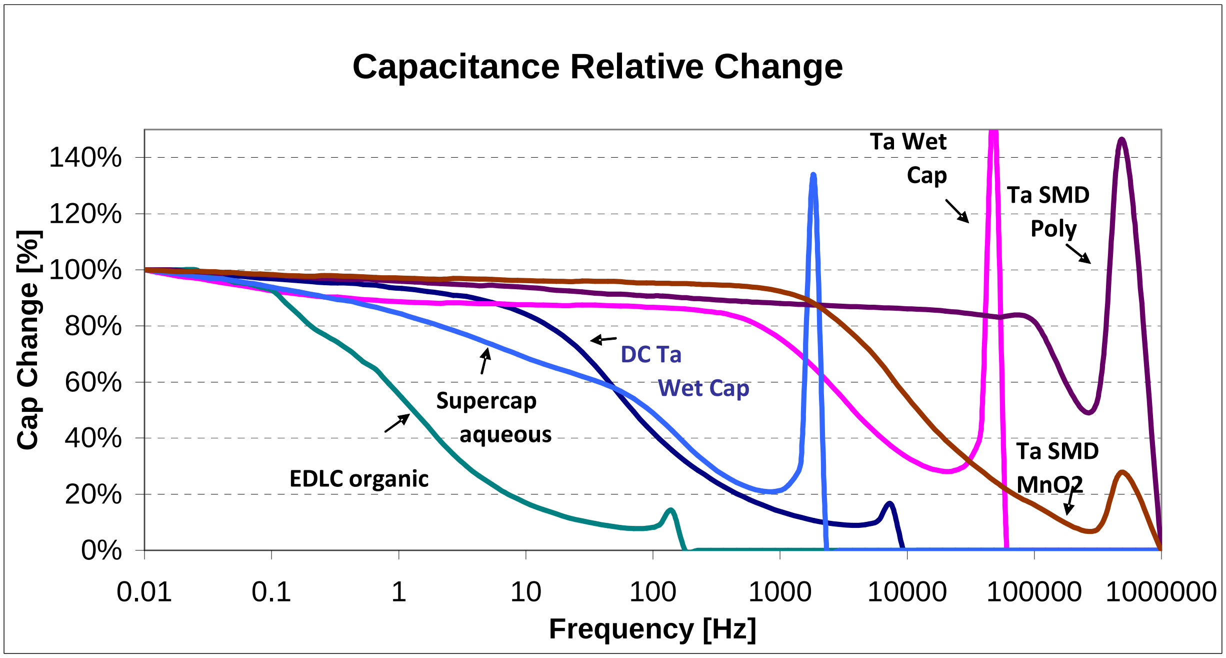


Fig.11. Capacitance vs frequency capacitor benchmark - relative capacitance

NEXT DEVELOPMENT STEPS - DC WET TANTALUM

First DC wet capacitor developments targeted a 50mF 6.3V capacitor. Initial life testing has been successfully completed and the capacitor will be released for mass production during 2014.

The next phase of development is to offer a wider voltage matrix within the standard T4 case size. The maximum effective voltage of the DC capacitor is about 10V, since the high surface area advantage is offset by the higher dielectric thickness and higher sintering temperature required. At the time of writing, a T4 150mF 2.5V device is showing good initial manufacturing results.

It may also be possible to extend the maximum operating temperature from the initial release of 85degC to 105degC or even up to 125degC on selected parts.

Further investigation will consider the development of custom and new low profile case sizes in order to meet end customer requirements.

SUMMARY AND CONCLUSION

A novel approach in the development of high CV wet tantalum capacitors using high CV tantalum powders was explored in order to offer maximum DC capacitance. The final capacitor CV achieves very high capacitance values, such as 50mF 6.3V or potentially 150mF 2.5V. Such a high level of capacitance and capacitance volumetric density approaches that of aqueous supercapacitors. This technology addresses the main two limitations of supercapacitor technology: tantalum wet DC capacitors are capable of operating at higher temperatures, up to 85degC, and they can be mounted to a PCB using reflow/wave soldering assembly technology. The use of a well-established wet tantalum can design offers a robust design for use in the most demanding applications, including high reliability and industrial.

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[2] Brunette.B., "AVX TWA Series Wet Tantalum Capacitors – DSCC 93026 & Beyond", AVX technical paper. www.avx.com

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