The Battle for Maximum Volumetric Efficiency - Part 1: When Technologies Compete, Customers Win

Randy Hahn, Mike Randall and Jonathan Paulsen
KEMET Electronics Corp
PO Box 5928
Greenville, SC 29606
Tel: +1 864-963-6300
Fax: +1 864-228-4333
randyhahn@kemet.com

Abstract

Circuit designers have many options available when selecting the type of capacitor best-suited to fill capacitance needs in today's electronic devices. Several factors govern the type of device selected for a given application, but until relatively recently, tantalum solid electrolytic capacitors were typically used in applications requiring high capacitance; e.g., that measured in the mid-to-high microfarad range, and multilayer ceramic capacitors (MLCC) dominated when capacitances in the low microfarad-to-picofarad range were required. However, advances in both ceramic and valve metal materials, and process technologies have resulted in increasing competition between these types of capacitors, providing designers with more options than ever before. The maximum capacitance available in an MLCC device has steadily increased as manufacturers have reduced dielectric thicknesses in concert with increased layer counts. Technology developments in solid electrolytic capacitors, including the introduction of conductive polymer cathode systems, niobium oxide anodes, and solid aluminum devices have provided additional choices in the selection of contemporary capacitance solutions. This paper examines the volumetric efficiency of each of these types of capacitors, with a primary focus on the volumetric efficiency of the dielectric.

Introduction

Capacitors are fundamental components used in virtually all electronic equipment. Applications include computer, telecommunication, automotive, military, medical, and consumer electronics. Their primary use within these devices is the storage and management of electrical energy. Their functions include filtering, tuning, decoupling, and energy storage. Critical performance characteristics include quantity of capacitance per unit volume (volumetric efficiency) and how quickly they can deliver it (ESL and ESR). Price, reliability, and stability of performance under various use conditions are also important factors in component selection.

In the 1970's the principle capacitor types available were wet electrolytic (aluminum and tantalum), solid electrolytic (tantalum), ceramic, film, mica, and paper capacitors. In the early 1980's encapsulated surface mount solid electrolytic and multilayer ceramic capacitors were developed. These devices could be placed on boards using high speed pick and place equipment greatly reducing manufacturing costs. A secondary advantage was an improvement in volumetric efficiency relative to leaded components, and surface mount devices quickly surpassed leaded components in sales. The development of surface mount multilayer ceramic chip and tantalum capacitors employing manganese dioxide as the cathode spurred the growth in market share of these devices relative to wet electrolytic and film capacitors.

Solid Electrolytic Capacitors. Advantages and disadvantages of these two surface mount capacitor types determined the design space best suited for that particular technology. Tantalum capacitors were noted for volumetric efficiency and reliability. The volumetric efficiency of the components were the product of the high surface area made possible by the porous anode construction and the very thin, robust dielectric film produced by anodization of the valve metal anode. Although the dielectric and dielectric/valve metal interface was thermodynamically unstable, the kinetics of the wear out mechanism for these devices generally exceeds the most demanding applications[1, 2]. The reliability of tantalum capacitors was further enhanced due to a healing mechanism. When a flaw site developed in the dielectric due to the intrinsic instability of the dielectric/tantalum interface or within the dielectric itself, higher levels of current flowed through the flaw site. Joule heating caused the temperature to rise at the flaw site, and heat conducted from this flaw site to the adjacent MnO_2 semiconductor employed as the cathode caused the MnO_2 to decompose to Mn_2O_3 at a temperature around 500°C.

Since the resistivity of Mn_2O_3 is several orders of magnitude greater than that on MnO_2, the Mn_2O_3 formed a non-conductive plug in the vicinity of the flaw site. The downside of surface mount tantalum capacitors relative to MLCC's was higher ESR, and propensity to burn on failure. Initial surface mount tantalums were limited to four EIA case sizes, the smallest being a 3.2 x 1.6 x 1.6 mm.

MLCC's. Although the ceramic dielectrics employed in MLCC's exhibited dielectric constants two orders of magnitude greater than that of valve metal oxides, the dielectric thickness and surface area between the electrodes was poor compared to that of tantalum, limiting the capacitance of the initial surface mount components to the picofarad-to-low microfarad range. The electrodes for MLCC's were silver and/or palladium, as well as nickel, thus the ESR was far superior to that of tantalums and they were the components of choice in applications requiring high operating speeds.

A variety of ceramic dielectrics are employed in MLCC's which the EIA classifies based on the temperature characteristics of the dielectric. The first two digits in the three digit EIA designation of a Class I ceramic dielectric are a code which specifies the temperature coefficient of capacitance (TCC) of the specific dielectric. The dielectric constant for Class I dielectrics is relatively low and these materials can not match the volumetric efficiency of other dielectrics considered in this paper. C0G is an ultrastable Class I dielectric. The first two digits in the EIA code for Class II and III dielectrics provide the minimum and maximum operating temperature of the dielectric. The third digit in the code for class II and III dielectrics specifies the maximum capacitance shift within that temperature range for the dielectric. These codes are provided in Table 1 below for reference. Although Class III dielectrics exhibit the highest dielectric constants, they are limited to thick films due to the drop off in dielectric constant with grain size. The highest volumetric efficiency achieved with ceramic dielectrics is typically with Class II dielectrics such as X5R. These Class II dielectrics also exhibit a logarithmic loss of capacitance with time due to the gradual realignment of the crystalline structure, an effect known as 'aging'. This loss can be as high as 5% per decade-hour[3]. Class II and III ceramic dielectrics also exhibit variation in capacitance with voltage, as indicated in Figure 1 for some popular ceramic dielectrics. The instability of high dielectric constant ceramics to temperature, time, and voltage relative to tantalum pentoxide is an issue in certain applications. Ceramic materials are brittle by nature and the primary failure mode for surface mount MLCC's is cracking.

Table 1[3]. EIA Temperature Characteristic Codes for Class II and III Ceramic Dielectrics

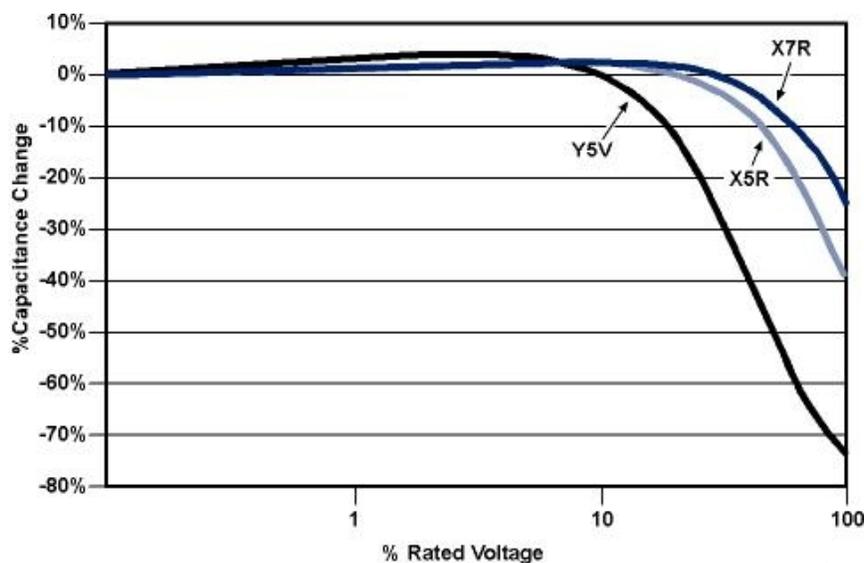| Minimum Operating Temperature		Minimum Operating Temperature		Maximum Capacitance Shift		
Degrees Celsius	Letter Symbol	Degrees Celsius	Number Symbol	Percent	Letter Symbol	EIA Class
+10C	Z	+45C	2	+/-22%	S	II
-30C	Y	+85C	5	+/-15%	R	II
-55C	X	+125C	7	+22/-56%	U	III
		+200C	9	+22/-82%	V	III

Figure 1. Variation in capacitance with voltage for selected ceramic dielectrics[3]

The Surface Mount Design Space in 1990. Through the 1980's advances in both ceramic and valve metal materials, and in process technologies resulted in increasing competition between these types of capacitors. Ceramics dominated in small case, low cap, high speed applications, while tantalums enjoyed dominance in higher capacitance, lower speed applications. By 1990 the design space could be represented by Figure 2.
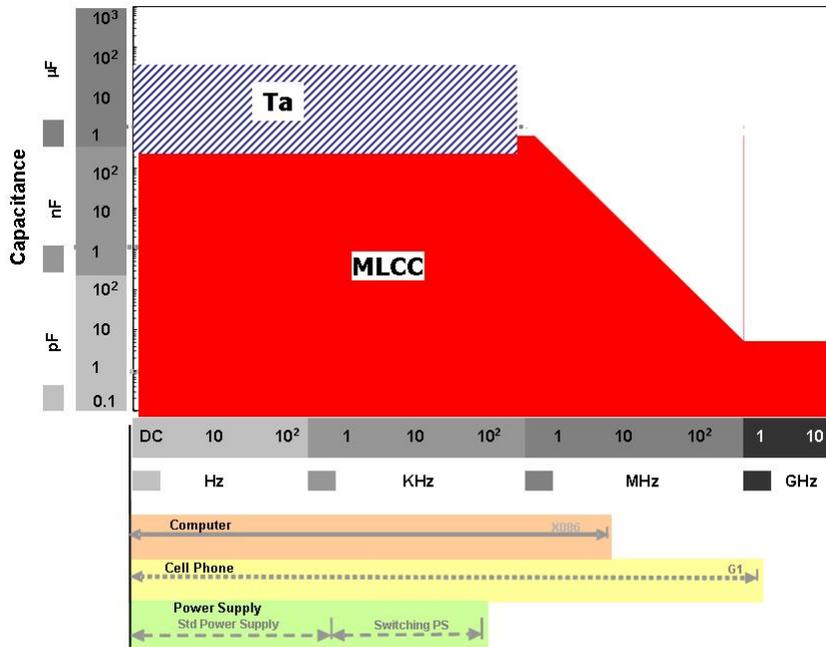

Figure 2. The design space in 1990 for surface mount capacitors[4]

Advances in Technology- The Design Space Today.

Continued material and process improvements have resulted in increasing direct competition between the various capacitor technologies and increased the number of options available to the circuit designer. Manufacturers of ceramic chip capacitors have steadily increased capacitance values as dielectric and electrode layer thickness has decreased and layer counts have increased as documented in Figure 3. The use of base metal electrodes became widespread in the late 1990's significantly reducing the price of MLCC's. New dielectric formulations were developed to improve capacitance and capacitance stability. X5R, the leading dielectric used in high volumetric efficient MLCC's, became popular in the late 1990's. Various approaches have been employed to provide flexible terminations to reduce case cracking for MLCC's.
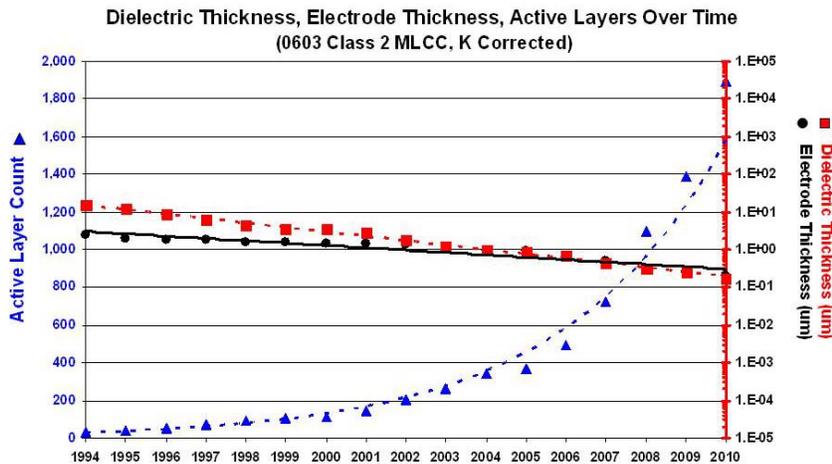

Figure 3[5]. Reduced dielectric and electrode thickness and increased layer counts for MLCC's since 1994

Volumetric efficiency improvements in tantalum capacitors have been driven primarily by the availability of tantalum powders with ever increasing specific surface area. The dielectric thickness for tantalum capacitors is determined by the anodization voltage and very thin dielectrics are possible. The limiting factor in the tantalum dielectric thickness is the quality of the dielectric. Many material and process improvements have enabled tantalum capacitor manufacturers to improve the quality of the dielectric and thus reduce the tantalum pentoxide thickness. These improvements include increased purity of the tantalum powders, improved anodization electrolytes, widespread use of shell formation processes, and anodization process improvements [6, 7, 8].
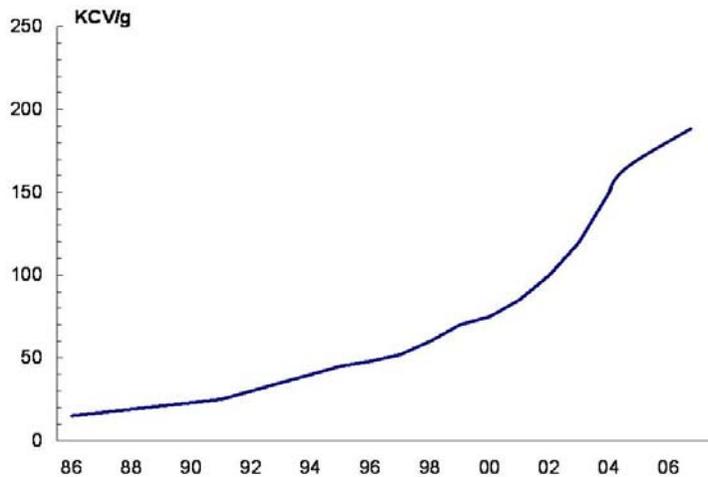

Figure 4. Increase in CV/g tantalum powders since mid 1980's

Many other factors contribute to the overall volumetric efficiency of a solid electrolytic capacitor, including packaging efficiency. The packaging efficiency in this context refers to the percentage of volume of the finished device occupied by the anode, dielectric, and cathode (i.e. excluding terminations, external leads, and packaging materials). The packaging efficiencies for the initial tantalum surface mount designs are relatively poor, especially for smaller case sizes. Volumetric efficiency of MLCC's and traditional surface mount solid electrolytic capacitors based on lead frame construction is plotted versus overall package volume in Figure 5 (data for MLCC's considers only that portion of the electrode which overlaps an opposing electrode and thus contributes to capacitance). For both solid electrolytic and MLCC's a logarithmic relationship exists between packaging efficiency and overall package volume. The slopes are similar but the packaging efficiency for MLCC's is better than that for the solid electrolytics. Several alternative constructions have been introduced to the market in recent years, dramatically increasing the packaging efficiency of surface mount solid electrolytic capacitors [9, 10, 11].
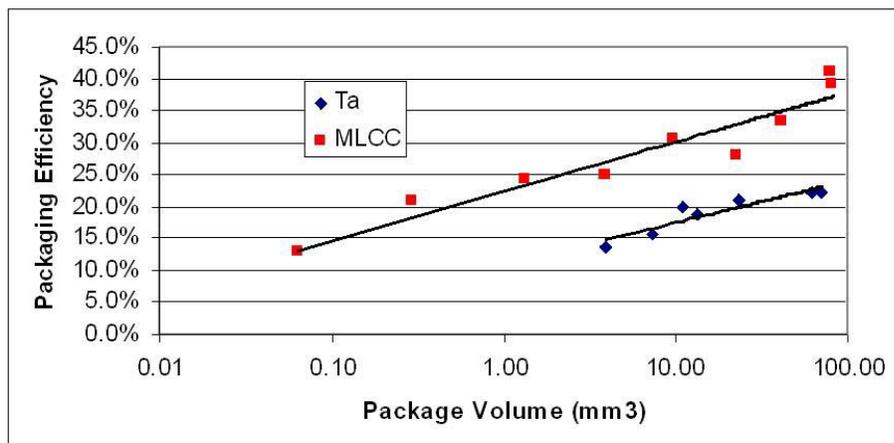

Figure 5. Packaging Efficiency of Surface Mount Solid Electrolytic and MLCC's

The improvements in volumetric efficiency of both ceramic and tantalum surface mount capacitors have led to increasing direct competition between these technology options. The surface mount design space has been further complicated by the introduction of additional types of surface mount capacitors based on material sets used to construct the core elements of solid electrolytic capacitors (anode, dielectric, and cathode). The development of intrinsically conductive polymers as cathode systems for solid electrolytic capacitors in the late 1980's and early 1990's allowed for significantly lower ESR increasing the frequency range of these devices. The ESR of solid electrolytic capacitors has been further improved through the introduction of multiple anode and fluted anode designs. The introduction of intrinsically conductive polymer as a viable cathode system also led to the development of solid aluminum capacitors. Aluminum polymer capacitors based on stacked and wound foils are now popular. In 2001 Cabot patented NbO as an anode for solid electrolytic capacitors, although HC Starck and AVX commercialized NbO capacitors[12, 13]. Currently NbO employs MnO_2 as the cathode system. The development of reliable capacitors combining Nb_2O_5 dielectric with intrinsically conductive polymers as the cathode has proven technically challenging and only a very limited selection of these devices is reported in manufacturer's catalogs or websites.

As a result of these advances in both ceramic and valve metal materials and in processes the design space for surface mount capacitors is considerably more complicated with more overlap between competing technologies than ever before. This overlap provides customers with multiple solution options for many design requirements.
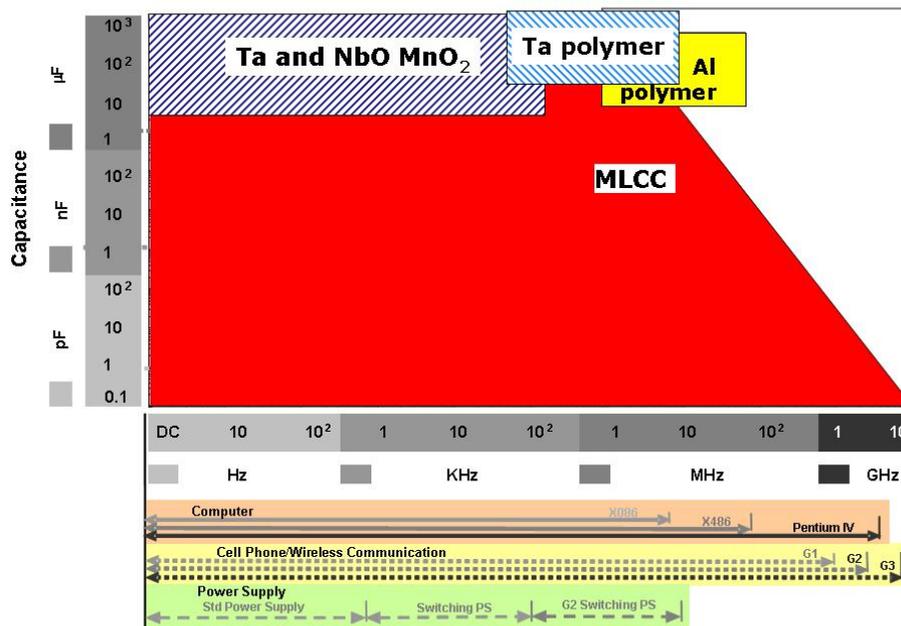

Figure 6. The design space for surface mount capacitors today

Comparisons of Volumetric Efficiency of Valve Metal Oxide Dielectrics

Volumetric efficiency is the capacitance per unit volume. A comparison of the maximum theoretical volumetric efficiency of valve metal oxide dielectrics is straightforward based on the general equation of capacitance[14]:

$$C = \frac{EkA}{t} \tag{1}$$

Where:

    C=capacitance (farads)
    E= permitivity constant (8.85 x 10^{-12} farads/meter)
    k= dielectric constant
    A= anode/cathode surface area overlap ($meter^2$)
    t= dielectric thickness (meter)

Transferring area to the left hand side of the equation yields:

$$\frac{C}{A} = \frac{Ek}{t} \tag{2}$$

In order to convert equation 2 to volumetric efficiency of the dielectric the surface area of the dielectric (A) must be multiplied by the thickness of the dielectric (t).

$$\frac{C}{(A \times t)} = \frac{Ek}{t^2} \tag{3}$$

$$\frac{C}{vol_d} = \frac{Ek}{t^2} \tag{4}$$

Where:

    C/vol_d = the volumetric efficiency of the dielectric
    vol_d = volume of the dielectric

For anodically formed valve metal oxides the dielectric thickness (t) is a linear function of the anodization voltage (V_f).

$$t = V_f \times c_d \tag{5}$$

Where:

    V_f = formation voltage
    c_d = rate of dielectric growth per volt formation

Substituting the equation for d into equation 4 and rearranging yields:

$$Volumetric\ efficiency\ of\ the\ dielectric = \frac{Ek}{(V_f \times c_d)^2} \tag{6}$$

$$Volumetric\ efficiency\ of\ the\ dielectric = \frac{Ek}{(c_d)^2} \times \frac{1}{V_f^2} \tag{7}$$

Thus the volumetric efficiency for a valve metal dielectric is proportional to one over the formation voltage squared. Equation 7 also shows that the difference in volumetric efficiency between valve metal oxide dielectrics is determined by

k/c_d^2. Table 2 documents the values of the constants in equation 7 and the equation for volumetric efficiency for various valve metal oxide dielectrics found by substituting these values into in the equation.

Table 2. Theoretical Volumetric Efficiency Comparison for Valve Metal Oxide Dielectrics

	Ta_2O_5	Nb_2O_5	Al_2O_3
Dielectric constant (k)	27	41	8
Rate of dielectric growth (A/volt)	18	28	12
Ratio of k to growth rate	1.5	1.5	0.67
Ratio of k to growth rate^2	0.083	0.052	0.056
Volumetric efficiency (μfarad/cm^3)	$7.4 \times 10^7 /V_f^2$	$4.6 \times 10^7 / V_f^2$	$5.0 \times 10^7 / V_f^2$

In order to convert the theoretical volumetric efficiency to a form that allows a more useful comparison of volumetric efficiency of various dielectrics, formation voltage in equation 7 must be converted to design voltage. In this context design voltage is defined as the maximum recommended usage voltage. Conversion of formation voltage to design voltage involves the introduction of the empirical relationship between formation voltage and rated voltage as well as derating recommendations. These ratios vary with both rated voltage and the cathode employed. Commonly accepted ratios of formation to rated voltage and derating factors are tabulated below.

Table 3. Formation to Rated Voltage Ratios and Derating Factors

	Ta					Nb(O)			Al		
	Polymer			MnO2							
Vr	V_f/V_r	Derating	V_f/V_d	Derating	V_f/V_d	V_f/V_r	Derating	V_f/V_d	V_f/V_r	Derating	V_f/V_d
2	3.75	10%	4.17	50%	7.50	4.38	20%	5.47	2.00	0%	2.00
2.5	3.00	10%	3.33	50%	6.00	3.50	20%	4.38	2.00	0%	2.00
4	3.00	10%	3.33	50%	6.00	3.50	20%	4.38	2.00	0%	2.00
6.3	3.17	10%	3.53	50%	6.35	3.50	20%	4.38	2.06	0%	2.06
10	3.30	10%	3.67	50%	6.60	3.50	20%	4.38	2.88	0%	2.88
16	3.38	20%	4.22	50%	6.75				2.30	0%	2.30
25	4.00	20%	5.00	50%	8.00				3.00	0%	3.00

Where:
   V_r= Rated voltage. This is voltage in capacitor manufacturers catalog or web site.
   V_d= Maximum recommended use voltage or design voltage. This includes the voltage derating factor

Calculation of Volumetric Efficiency for Ceramic Dielectric

An estimate of the volumetric efficiency for ceramic dielectrics can also be made using the general equation for volumetric efficiency of a dielectric:

$$\frac{C}{vol_d} = \frac{Ek}{t^2} \tag{4}$$

It has been reported in the literature that the value of k for barium titanate decreases with grain size[15]. Mike Randall has calculated the best fit line for the data reported by Ihlefeld[5].

$$k = 1485.7\ln(d) + 5060 \tag{8}$$

Where:
   d = grain diameter (μm)

By substituting the empirical equation for dielectric constant into equation 4 we can calculate the volumetric efficiency for a ceramic dielectric:

$$Volumetric\ efficiency = \frac{E \times (1485.7\ln(d) + 5060)}{t^2} \qquad (9)$$

In order to compare the volumetric efficiency with valve metal oxide dielectrics two additional assumptions must be introduced. First a relationship between grain size and dielectric thickness must be assumed. The simplest assumption, and the one that yields the highest value for volumetric efficiency of MLCC's, is to assume the thickness of the dielectric and the grain size are equal (in practice this assumption is generally not valid). Next a relationship between design voltage and dielectric thickness must be assumed. A useful estimate based on current design rules is 10 design volts per micron of dielectric thickness. Introducing these assumptions into equation 9 yields:

$$Volumetric\ efficiency = \frac{E \times (14.857\ln(0.1V_d) + 50.60)}{V_d^{\,2}} \qquad (10)$$

Plugging the appropriate value for E and unit conversion factors into equation 10 gives the following equation for volumetric efficiency for MLCC's in microfarads per cubic centimeter:

$$Volumetric\ efficiency = \frac{(1.315\ln(0.1V_d) + 4.48)}{V_d^{\,2}} \times 10^6\ \frac{\mu F}{cm^3} \qquad (11)$$

Comparison of Volumetric Efficiency for Ceramic and Valve Metal Oxide Dielectrics

Volumetric efficiency for valve metal oxides can be calculated as a function of design voltage by substituting the ratio of V_f to V_d provided in Table 3 into the equations provided in Table 2. Volumetric efficiency for MLCC's versus design voltage can be plotted directly from equation 11. The results are plotted in Figure 7.
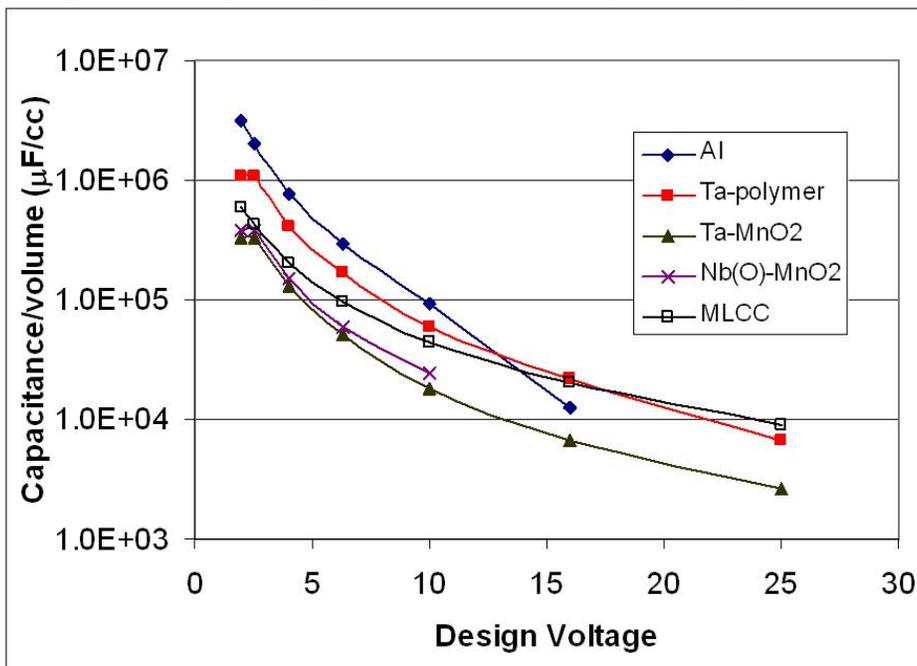

Figure 7. A comparison of the volumetric efficiency of various dielectrics versus design voltage

Figure 7 indicates that once the empirical relationship between dielectric thickness and design voltage is factored into the equations for volumetric efficiency, Al_2O_3 exhibits the highest volumetric efficiency where the design voltage is 12 volts or less. Ta_2O_5-polymer exhibits a slightly higher volumetric efficiency than MLCC's up to 16 volts where the lines converge. NbO and Ta-MnO$_2$ have similar volumetric efficiencies based on this analysis.

Limitations of Volumetric Efficiency. The lines shown in Figure 7 represent the volumetric efficiency of various dielectrics. The actual volumetric efficiency of a functional capacitor will be considerably less than that indicated in the figure above due to numerous factors. This method compares the efficiency of the dielectric alone; the volume occupied by the anode and cathode (i.e. the electrodes) are not considered, primarily because it is very difficult to place a theoretical limit on the thickness of these layers. These estimates of volumetric efficiency of various dielectrics do not include the inefficiencies due to margins, terminations, packaging, etc. The assumed relationships between design voltage and dielectric thickness are empirical, not theoretical; hence they are subject to change with breakthroughs in technology. The relationship between dielectric constant and grain size for MLCC's is based on data for barium titanate, not a particular dielectric formulation like X5R. This relationship is also subject to change with advances in technology. The assumption that the dielectric thickness is equal to the grain size is not valid for Class II dielectrics used to maximize the volumetric efficiency of MLCC's. Typically the dielectric thickness is 4-6 times the grain size. In order to achieve the highest volumetric efficiency very thin dielectrics are needed, requiring increased layer counts for MLCC's which present significant challenges in manufacturing. Another consequence of the thinner dielectrics is that the electric field across the dielectric increases (for a given operating voltage). This results in further capacitance loss at the operating voltage of a microprocessor[16]. The method does not consider differences in the availability of very high charge powders and high gain foil between the various valve metal oxide dielectric options (see Table 4). Despite these limitations, the volumetric efficiency of the dielectric provides a useful benchmark for comparing dielectrics.

Table 4. Maximum capacitance/cc for commercially available valve metals

Anode	Max CV/g	Anode Density	CV/cc	$\mu F/cc$ @ V_d=2
Ta	200k	6.0	1.2 MM	144,000
Nb(O)	120k	3.0	360k	48,000

Anode	Max Gain (μF-V/cm^2) @ 2V_d	Etched Thickness (cm)	$\mu F/cc$ @ V_d=2
Al	358	0.0067	53,433

Path Forward

The equations presented in this paper allow the volumetric efficiency of the dielectrics to be compared. Capacitor manufacturers are developing new technologies in order to fulfill customer needs for ever increasing volumetric efficiency. Solid electrolytic capacitors must take full advantage of the high volumetric efficiency of the dielectric through continued development of very high charge powders, reduced open volume in the anode/dielectric/cathode structure, increased conversion of the valve metal anode to dielectric, reduced formation to design voltage ratios, and increased packaging efficiency. Manufacturers of MLCC's are focused on changing the empirical relationship between grain size and dielectric constant, increasing layer counts, reducing dielectric and electrode thickness, and packaging efficiency. In a related paper to be presented at this conference one approach to increasing volumetric efficiency by combining a valve metal anode with a ceramic dielectric will be discussed.

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