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A study on the energy storage capacity and applications of ferroelectric materials

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Abstract

In the fast-growing world, dielectric materials with high energy storage density temperature stability, and low loss are eagerly desired for advanced pulsed capacitors applications. The basic principles of dielectric energy storage and the factors affecting energy storage density are introduced. The research progress of glass-type high-energy storage materials, ferroelectric glass-ceramics-type high-energy storage materials, ferroelectric-anti-ferroelectric ceramics, and ferroelectric polymer-type high-energy storage materials are reviewed. For an ideal or good energy storage material their Curie temperature should be high, high dielectric constant, and have strong saturation polarization.

Keywords: dielectric energy storage, energy density, Research progress

Introduction

Electrical energy storage devices are essential elements of advanced electrical power systems.[1] Compared to electrochemical energy storage devices, such as batteries and electrochemical capacitors, dielectric capacitors possess the highest power density, owing to their fast charge-discharge capability; thus, they play an important role in high-power applications, such as high-power microwaves, electromagnetic devices, and hybrid electric vehicles (HEVs).[2,3] Dielectric ceramics have electrical insulation properties and use their electrical insulation properties it can be used to make electronic components such as capacitors. [4, 5]

Capacitors as an electrical energy-storage technology belong to the family of passive electronic components that store energy in the form of electrostatic energy and have been widely used in electronic circuits. Capacitors have the characteristics of charging, discharging, and AC/DC blocking. Up to now, the driving force for capacitor applications has been attributed to the significantly increased consumer electronics market. Typical features of dielectric capacitors are that they intrinsically exhibit a high energy density and a fast charge/discharge performance compared to Li-ion batteries or fuel cells, which makes them promising candidates for energy-storage devices in some specific areas, like pulse power (PP) applications. PP technology has been widely used in many fields, such as scientific experiments, hybrid electric vehicles, energy power systems, pulse equipment, and so on.[6] The high temperature and high-pressure resistance of dielectric ceramic materials Put forward new requirements. Under the same external conditions, Dielectric ceramic materials with higher dielectric constant can store more charge, to obtain a higher energy storage density. The miniaturization of ceramic capacitors is the development need of electronic components.[7]

Dielectric Capacitor and its energy storage calculations

As Capacitor’s energy storage ability depends on its dielectric material. And some key factors affect the storage capacity of dielectric material. How much a material can be polarized and its breakdown strength is key factors of the storage ability of the material.

Capacitors can be divided into different categories; polymeric films (MLP), ceramics (MLC), mica, and electrolytes (Al, Ta). They currently compromise a USD 15.7 billion capacitor market annually worldwide [8]. Table 1 summarizes their characteristics and concerns. While electrolytic capacitors provide the largest capacitance, these capacitors suffer significant degradation in capacitance and leakage current at higher temperatures and frequencies. Ceramic capacitors can operate at very high ripple currents, but suffer the non-graceful aging failure and require a lower operating electric field. Polymer capacitors have greater advantages for higher power storage, low voltage ripple, high frequency, greater reliability but are limited to 105°C. Polymer

capacitors represent a $2.75 billion capacitor market. The high-temperature capacitor is an emerging technology designed to meet various high temperature applications.

Table 1. Capacitor technology Overview

Capacitor Technology	Capacitance	Voltage Range	ESR/ Leakage	Tem (℃)	Frequency (Hz)	Cost	Concerns

Al electrolytic	0.1mF	Low	High	85	100s	Low/ µF	Loss Temperature Stability
Ta electrolytic	0.6mF	Low	High	125	100k	Medium	Loss, High Frequency
MLC (ceramics)	10µF	Medium	Lowest	200	100M	Medium to High	>200°C Cracking voltage scaling
MLP (films)	47µF	High	Low	105	1M	Lowest	Temperature pulse duration
Mica	0.068µF	High	Low	>150	1M	Medium	Low capacitance >400°C
High Temp	0.2µF	Medium	Medium	250	100M	High	Capacitance stability
Nano dielectric Composites	µF-mF	High	Low	105-250	1M	Medium to High	Manufacturability

The energy-storage ability of a capacitor is measured in terms of capacitance. Capacitance is related to capacitor geometry and its dielectric material. The relation between permittivity of dielectric and its geometry of conductors are

$$C= \frac{\varepsilon_0 \varepsilon_r A}{d} \qquad (1)$$

In equation (1), C is the capacitance, A is the area of conductors, d is the distance between the conductors, ε_r is the relative permittivity of material and ε_0 is the permittivity of free space that is(=8.85× 10^{-12} Fm^{-1}). The electric polarization occurs in dielectric material under applied voltage V and the capacitance C is measured as

$$C= \frac{dq}{dv} \qquad (2)$$

There is no ideal dialectical material exist on the plant. Some examples of dielectric materials are

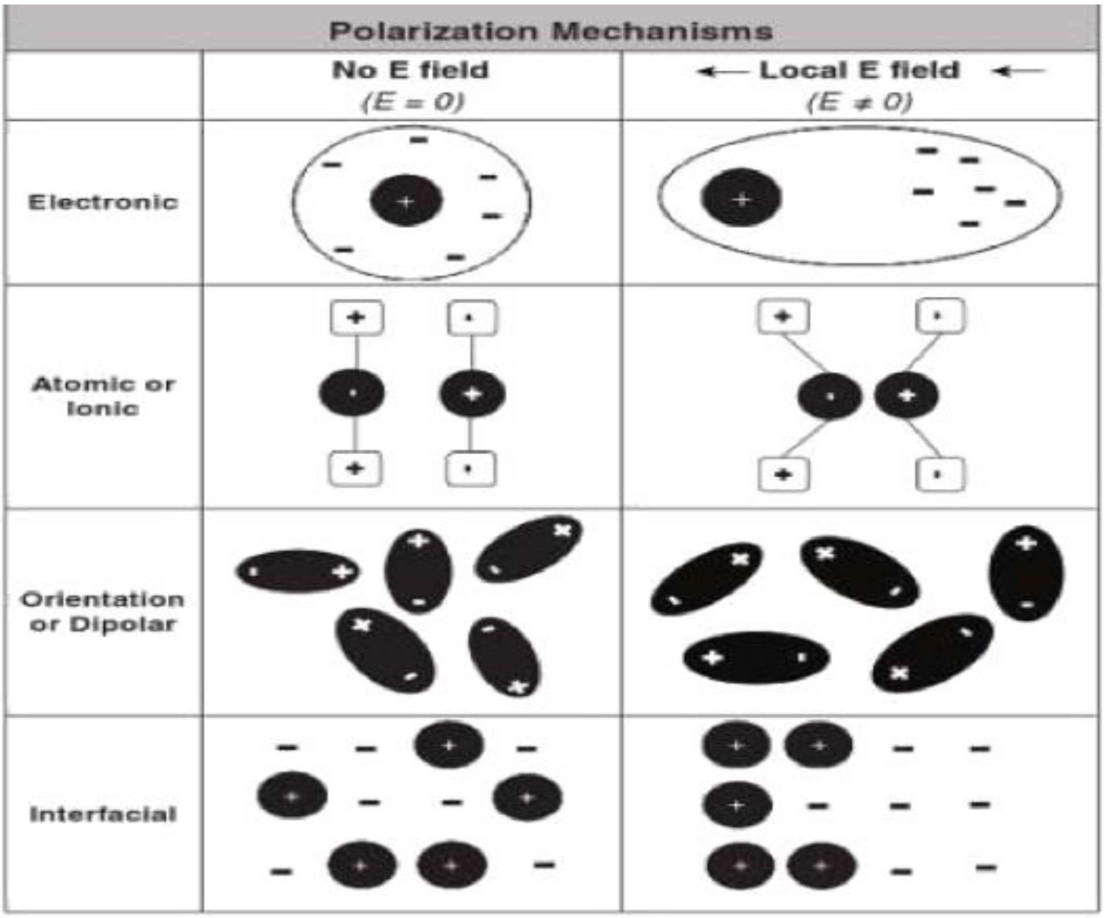
(1) Bulk single crystals
(2) Polycrystals
(3) Ceramics
(4) Thin films
(5) Polymers
(6) Nano dielectrics
(7) Rubber

The more easily material gets polarized can store more energy. This ability to store energy in an electric field is referred to as the dielectric constant K or relative permittivity εr. The degree of polarization P is related to the dielectric constant K and the electric field strength E as follows:

$$P = \varepsilon 0 \, (K-1) \, E$$

Where $\varepsilon 0$ is a physical constant known as the vacuum permittivity and the total polarization of a dielectric is the sum of four sources of charge displacement: electronic displacement Pe, ionic displacement Pi, the orientation of permanent dipoles Pd, and space charge displacement Ps.

$$Pt= Pe+ Pi+ Pd+ Ps$$



Electronic Polarization: This effect occurs in all atoms under the application of an electric field. The nucleus of the atom and the center of its electron cloud shift away from each other, creating a tiny dipole with a very small polarization effect. Ionic Polarization: In ionic solids such as ceramic materials, the ions are symmetrically arranged in a crystal lattice with a net-zero polarization. Once an electric field is applied, the cations and anions are attracted to opposite directions. This creates a relatively large ionic displacement (compared to electronic displacement), which can give rise to high dielectric constants in ceramics popularly used in capacitors.

Dipole (or Orientation) Polarization: Certain solids have permanent molecular dipoles that, under an electric field, rotate themselves in the direction of the applied field, creating a net average dipole moment per molecule. Dipole orientation is more common in polymers since their atomic structure permits reorientation.

Space Charge (or Interfacial) Polarization: In ceramics, this phenomenon arises from extraneous charges that come from contaminants or irregular geometry in the interfaces of the polycrystalline solids. These charges are partly mobile and migrate under an applied field, causing this extrinsic type of polarization.

How Does Frequency Affect Polarization and Dielectric Loss?

Interestingly, each type of polarization has a different time response capability to an applied field frequency, which means the net effectiveness of polarization to the dielectric constant is frequency-dependent.

- Electronic displacement is very rapid, so this polarization occurs at frequencies of up to 10^{17}
- Ionic polarization is a bit slower and occurs at frequencies up to 10^{13}
- Dipole polarization occurs at frequencies less than 10^{10}
- Space charge polarization is the slowest and occurs at less than 10^{4}

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Therefore, the dielectric constant (and therefore the capacitance value) always decreases with increased frequency, since the polarization mechanisms become less effective.

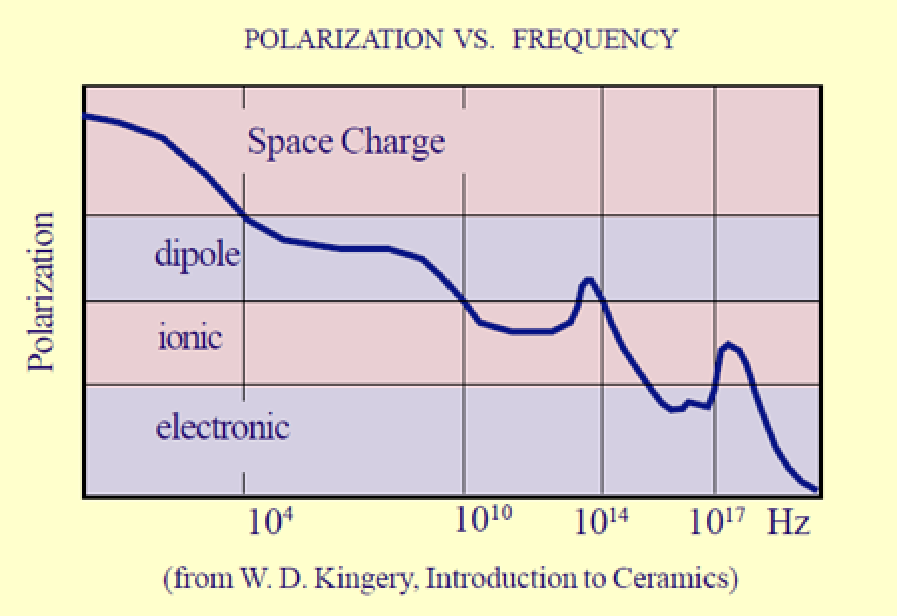

Figure 2. Effect of frequency on polarization mechanisms

In an AC circuit, the voltage and current across an ideal capacitor are 90degrees out of phase. However, real-world dielectrics are not perfect, and therefore the lag or “relaxation time” of the polarization mechanisms with frequency generates dielectric losses. The angle by which the capacitor’s current is out of phase from the ideal can be determined, and the tangent of this angle is a material property called the loss tangent (Tan δ) or dissipation factor. In practice, materials with higher dielectric constants (and therefore high polarization mechanisms) display higher dissipation factors.

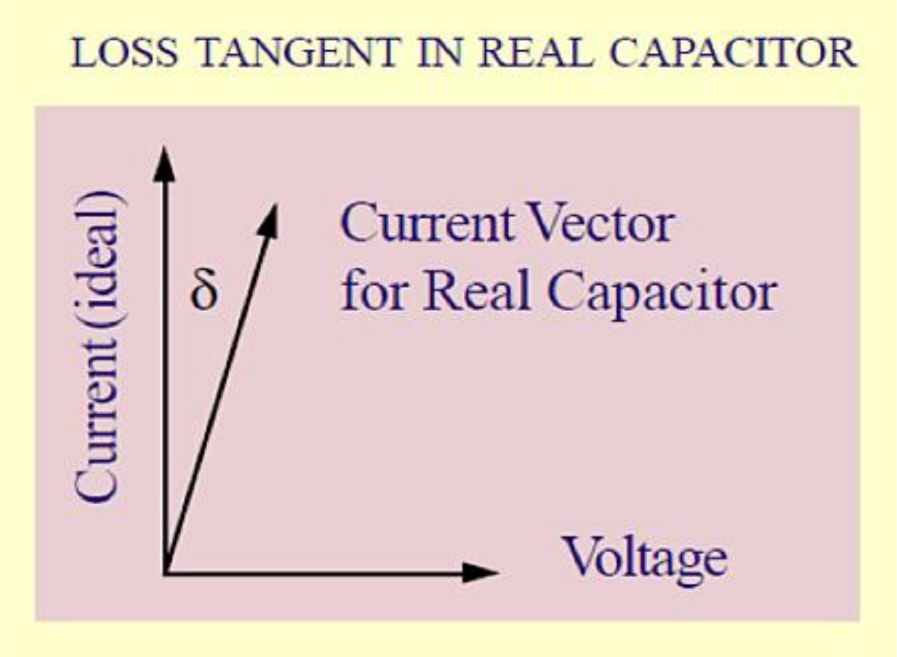

Figure 3. Tangent loss or dissipation factor of a real-world capacitor

The frequency at which a dielectric is used has an important effect on the polarization mechanisms, notably the relaxation time displayed by the material when following field reversals in an alternating circuit.

Case 1: If the relaxation time for polarization is much longer and slower than the field reversals, the ions cannot follow the field at all, and losses are small.

Case 2: If the relaxation time is much faster than the field reversals, the polarizing processes can easily follow the field frequency and losses are small.

Case 3: If the relaxation time and field frequency are the same, the icons can follow the field but are limited by their lag, thus generating the highest loss with frequency.

Therefore, dielectric losses are highest at the frequency where the applied field has the same period of the relaxation process. Ceramic dielectric formulations always show a range of relaxation times over the frequency spectrum, since these materials consist of polycrystalline matter. In high-frequency applications, this parameter is often known as the Q factor, which is the reciprocal of the loss tangent: $Q = 1 / (\tan \delta)$

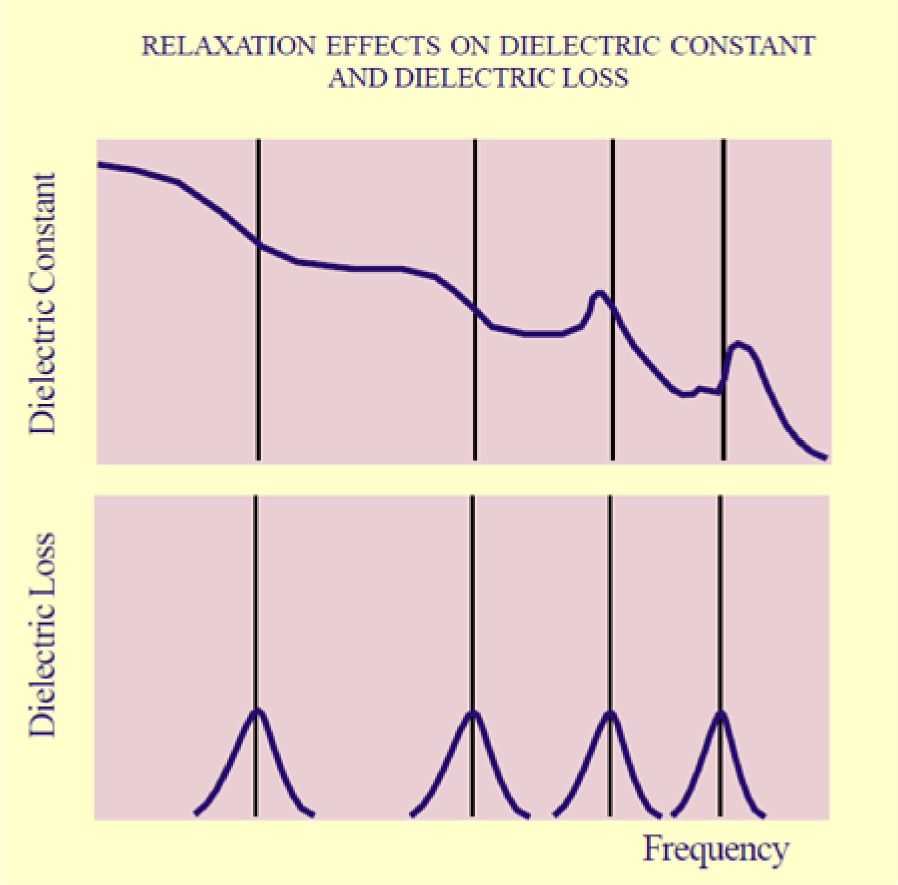

Figure 4. Changes in dielectric constant and dielectric loss caused by frequency

During the charging process, electrostatic energy is stored in the dielectric. The amount of stored energy W can be calculated according to Equation (3) :[9]$W = \int_0^{Q_{max}} V\,dQ \qquad (3)$

The charge density (Q/A) on the plate surfaces equals the electrical displacement D (=ε0εrE) in the dielectric material. Therefore, according to Equation (3), the energy density J can be expressed as:

$$J = \frac{W}{Ad} = \frac{\int_0^{Q_{max}} V\,dq}{Ad} = \int_0^{Q_{max}} E\,dD \quad (4)$$

Where E is the electric field, equal to v/d, and D_{max} is the electric displacement under the maximum field (E_{max}). For dielectrics with high permittivity, D is equal to the polarization P. Thus, Equation (4) can be rewritten as:

$$J = \int_0^{P_{max}} E\, dP \;= \int_0^{E_{max}} \varepsilon_0\, \varepsilon_r E\, dE \quad (5)$$

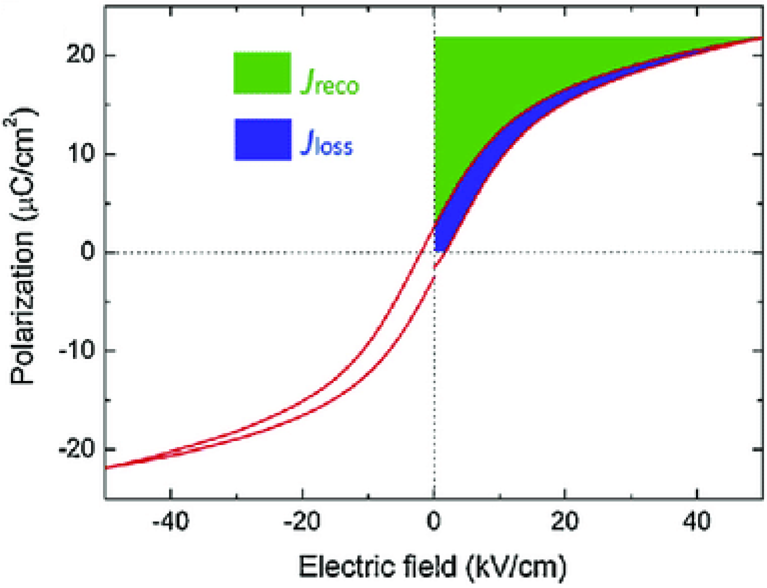

Figure2. Graphical representation of a P–E loop used for energy storage calculation.

The energy density can be calculated by integrating the effective area between the polarization axis and the discharging curve of the polarization–electric field (P–E) loops, shown by the blue shaded area in **Figure 2**:[10]

The amount of energy density dissipated during the discharge process is defined as J_{loss}, illustrated by the green shaded area in the figure.

Consequently, the energy-storage efficiency η can be expressed as:

$$\eta = \frac{J_{reco}}{J_{reco+}\, J_{loss}} \times 100 \qquad (6)$$

For linear dielectrics with permittivity independent of external applied field E, the energy density can be simply calculated by:

$$J = \frac{1}{2}\, \varepsilon_r \varepsilon_0 E^2 \qquad (7)$$

Indicating that the energy density of linear dielectrics is proportional to the dielectric permittivity and the square of E. However, for nonlinear dielectrics showing hysteresis characteristics, this equation is not applicable due to the hysteresis loss.

According to Equation (5), the energy storage can be represented by the integrated areas between the polarization axis and the discharge curve in the P–E loops. Theoretically, for linear dielectrics (e.g., ceramics such as Al2O3 or polymers such as polypropylene), nearly linear P–E characteristics can be achieved due to the field-independent ε_r; they generally possess high electric breakdown strength, low hysteresis loss, and low polarization. However, mass accumulation of space charges at grain-boundary interfaces under a high electric field approaching E_{max}, accompanied by a higher leakage current, leads to lossy hysteresis loops.[11]

Curie temperature is that at which some magnetic materials undergo a sharp change in their magnetic properties. In the case of rocks and minerals, remanent magnetism appears below the Curie point which is about 570 °C (1,060 °F) for the common magnetic mineral magnetite. Below the Curie point, for example, 770 °C (1,418 °F) for iron atoms that behave as tiny magnets spontaneously align themselves in certain magnetic materials. In ferromagnetic materials, such as pure iron, the atomic magnets are oriented within each microscopic region in the same direction, so that their magnetic fields reinforce each other. In antiferromagnetic materials, atomic magnets alternate in opposite directions, so that their magnetic fields cancel each other. In ferromagnetic materials, the spontaneous arrangement is a combination of both patterns, usually involving two different magnetic atoms, so that only partial reinforcement of magnetic fields occurs. One of the highest Curie points is 1,121 °C (2,050 °F) for cobalt. Temperature increases above the Curie point produce roughly similar patterns of decreasing paramagnetism in all three classes of materials. When these materials are cooled below their Curie points, magnetic atoms spontaneously realign so that the ferromagnetism, antiferromagnetism, or ferrimagnetism revives.[12]

3 High-Performance Dielectric Materials

3.1 Thermal Consideration of Dielectrics

Besides voltage stress capability, cost, and dielectric constant, temperature

capability and loss factor (tan(δ)) are the primary concerns for dielectric material. The rise in temperature in the core of the capacitor causes an increase in losses and can lead to premature failure. Often the self-generated heat can overshadow the ambient temperature, which can lead to degradation and early failure. The mechanisms that are responsible for heat generation and the flow

of heat from the capacitor, include:

(i) The dielectric material and its inherent power losses and heat retention properties

(ii) Electrode systems and the ohmic losses (I2R, where the resistivity of a metalized capacitor can vary from 1ohm/sq to 10 ohms/sq)

(iii) End connection scooping

(iv) Termination method (wire, tabs, or terminals).

The heat generated within the capacitor can be calculated from the following formula. In any case, the loss factor (*P*loss) of the dielectrics is the key,

$$P_{loss} = 2.\pi.f.C.V_{rms}^{2}\tan(\delta)$$

where, *f* = Fundamental Frequency of waveform [Hz]

C = Capacitance [F]

VRMS = RMS voltage across the capacitor

tan(δ) = Dissipation Factor of the capacitor at frequency *f* [Hz].

To meet the high temperature operation, several high temperature ceramics and polymer dielectrics have been under study.

This includes Polycarbonate (PC), Polyphenylene sulfide (PPS), Fluorene Polyester (FPE), Diamond-like carbon (DLC), Ultem polyetherimide, Polyetheretherketone (PEEK), Kapton (polyimide), Teflon (polytetrafluoroethylene). For applications at or above 200°C, very limited choice of polymers and ceramic materials are available to offer high energy density at the same time. Table 2 shows the properties of several polymers that can be thermally stable at above 200°C(13)

Table 2. Available high-temperature polymer dielectrics

Properties	Polyetherimide	FPE	DLC	PTFE	Kapton
Operation temperature (°C)	210	250	250	260	300
Dielectric constant	3.2	2.9	3.5	2.1	3.3
Loss at 1kHz (10^{-3})(25°C)	2	2.6	1	0.5	2
Dielectric strength (kV/mm)	430	400-550	650	296	420
Tensile strength	14	9.5	-	3	17

3.2 High-Temperature MLCC Dielectrics

Ceramic dielectrics tend to have very high dielectric constant but relatively low dielectric strength. Increasing their dielectric strengths is one of the challenges. The highest breakdown strength (intrinsic) of the order of 1000kV/mm can be obtained under carefully controlled conditions (e.g., highly purified and free of imperfections). The presence of grain boundaries, porosity, impurities, surface defects, and chemical deterioration, ceramic dielectrics contribute to failure at pretty low field stresses. The problems also result in relatively high dissipation factor, high capacitance loss with applied voltage, and/or inherent piezoelectric /

electrostrictive effect. MLCCs have replaced the film capacitors in most volume applications with advantages of high-volumetric capacitance, low impedance and ESR, and high thermal stability and reliability. For some high-end applications, ceramics are replacing aluminum and film capacitors to achieve much higher performance. Recently, Murata is promoting a new dielectric

material that reduces the ripple current with temperature rise and ESR as opposed to standard X7R capacitor and Al electrolytic capacitors, respectively(14) Morgan Electro Ceramics has developed ceramic materials based on Strontium Titanate dielectric that has high dielectric strength and low dissipation /high Q (15). Current commercially available power capacitors can't

meet these requirements fully and solid-state power capacitors based on high-temperature ceramic dielectrics are under development. This includes relaxor ferroelectric compositions (TRS Ceramics) and modified $BaTiO3$ and new electrode designs (Kemet) for 250-300°C as well as multilayer fabrication of BN dielectrics (MicroCoating Technologies for >600°C)[16-18]. Nevertheless, the energy density of the MLCC ceramic capacitors remains low due to lower capacitance and thicker films.

3.3 Antiferroelectric Materials

The application of an electric field greater than the switching field causes a phase transition from the orthorhombic to the tetragonal crystal structure in antiferroelectric materials. This field-induced phase transition offers a high power release with a very short time constant. The AFE/FE property of rare-earth-doped lead zirconate titanate (PZT) compositions has also been exploited by Sandia National Lab and other research labs to fabricate high energy density capacitors for neutron generators, detonators, and power electronic inverter applications[19-21]

3.5 Ceramic Based Composites

According to the energy density requirements ($\varepsilon0\ \varepsilon\ E2/2$), higher breakdown

strength and dielectric constant both can be increased to further increase the energy density. Increasing the operating field brings much more rapid benefits than increasing the dielectric constant. New materials systems are under development and deployment by researchers over the past decades. One of the interests is on filler effect on ceramics and polymers[22-27]

The two-phase composites have found application in insulation, capacitors, resistor, inductors, PCB, and high-*k* gate dielectrics. It was reported that composites of glass-ceramics containing PZT and nanodispersions of silver

show a high dielectric constant[28]. The addition of sintering agents to nanometric ZnO powders not only enables lower temperature sintering but also enhances the electrical breakdown strength of the varistor[29]. TiO2 based nanoceramic composites of high dielectric constant were also achieved exhibiting enhanced

dielectric strength as opposed to the normal micron-sized TiO2[30]. These successes have demonstrated the feasibility of improving the dielectric characteristics of ceramic capacitors.

Summary and Perspective

Energy storage materials for sustainable development getting more attention and research interest. To fulfill the newly emerging requirement such as electric vehicles and portable electronics, advanced energy-storage materials with high energy and power density are highly demanded. Single-phase ceramic materials have a higher dielectric constant but are Due to the existence of defects, the breakdown field strength is reduced. In recent years, a lot of research. Application prospects. Therefore, it is necessary to study the preparation of thin-film materials into multilayer junctions. The performance of the configuration, the energy storage density is significantly improved, and the total storage Energy storage is also improved. The method is the key to further increase the energy storage density of composite materials. Exploring energy storage medium materials with high Wreck and η is the current work. One of the hotspots in the research of energy ceramics, through the efforts of recent years, is lead-free. Significant progress has been made in the research of energy storage ceramic dielectric materials.

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