

Proposal to Build Supercapacitors Using Solid Dielectrics

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Introduction

With the ever increasing need for portability in electronic devices and the need for renewable energy storage, means of storing electrical energy is valuable. Batteries are generally used for such purposes, but for applications requiring high power for automobile start-ups, industrial applications, telecommunications, renewable energy storage and consumer electronics, supercapacitors would provide several advantages over the conventional Li-ion batteries and other electrochemical double layer ultracapacitors already commercialized [1,2]. They would also be suitable for power back-up functions in a wide range of consumer products, for solar panels and motor starts. Having supercapacitors which can pack up to 100 times the energy of conventional capacitors and deliver ten times the power of ordinary batteries would change the power equations for these and similar applications. Some of the advantages of employing supercapacitors would be:

- They can be designed for the whole life of a consumer product (10 – 12 years)
- Designing for life provides design engineers with the extra flexibility to locate the supercapacitors anywhere within the product.
- They would be light weight, solid and rugged—apart from having higher energy density compared to the electrochemical double layer ultracapacitors which are being used widely.
- In automobiles, they are the correct choices for electrical system stabilization, regenerative braking, power assist, starter generator, start/stop automatism and several other features.
- In industries, they are required for peak power supply/ storage for robots and machines, crane recuperation, fork lifts, UPS & power quality, induction power transmission and space and medical equipment.

Several commercial companies have already manufactured high energy density ultracapacitors. However, all of them, so far, are electrochemical double-layer capacitors. In contrast, the supercapacitors to be built using the high dielectric materials would be solid, portable and provide for similar energy densities in the range of MJ/m³.

Requirement for Supercapacitors

The preliminary requirement for making a high energy density capacitor is a material having high dielectric constant and a considerably higher electrical breakdown strength. The basic equations governing the capacitors are:

$$W_n = \frac{1}{2} C \times V^2 \quad (1)$$

where W_n is the energy stored in the capacitor, C is the capacitance and V the external voltage applied across the capacitors.

The capacitance is given by

$$C = \frac{Q}{V} = \frac{\epsilon_r \epsilon_o A}{d} \quad (2)$$

where ϵ_r and ϵ_o denote the relative dielectric permittivity and the permittivity of the free space, respectively, and d is the thickness of the capacitor.

The voltage that can be developed across the capacitor without causing its dielectric strength to break down depends on the maximum field strength of the material which, in turn, depends on the characteristics of the materials. As the

$$\text{Electric field } E = \frac{V}{d} \quad (3)$$

for a constant voltage over a thickness d , from (1) and (2), we get the relation for maximum energy stored in the capacitor as

$$W_{nMAXN} = \frac{1}{2} QV = \frac{Q}{2A} E_{\max} = \frac{1}{2} \epsilon_r \epsilon_o E_{\max}^2 dA \quad (4)$$

and maximum energy density as

$$\frac{W_{n\max}}{dA} = \frac{1}{2} \epsilon_r \epsilon_o E_{\max}^2 \quad (5)$$

The maximum energy density can be described either in terms of the electric field or the voltage across the dielectric layer. These are equivalent for thick layers. However, for layers that are thin (nanometers) it is easier to think about the mechanism for break down in terms of the energy that is required to accelerate either an electron or an ion so that it generates an avalanche of charged particles. For electrons this means acquiring enough energy to lift an electron from the valance band to the conduction band. At breakdown this becomes a feedback process so that electrons in the conduction band generate additional electron hole pairs and then the electrons in the valance band gain enough energy to lift an electron into the conduction band. If we describe this process so that, on the average, each electron that gets injected into the conduction band of the dielectric is accelerated to generate A_o electron hole pairs and each hole injected in to the valance band of dielectric results in the generation of β electron hole pairs then break down occurs when $A_o \beta = 1$. The bandgap between the valance conduction band for insulators is typically several electron volts and the larger it is, the higher we would expect the breakdown voltage to be. Additionally, a large scattering cross section or low mobility is desirable.

In the materials we are interested in, the large dielectric constants are generated by both displacement of ions in the unit cell and the movement of electrons. For the ions, we expect that most of the ion movement will be confined to the unit cell. For the electrons, the electron movement may be limited by the grain boundaries, Schottky barriers [1], or, in the case BaTiO₃ coated, by very thin insulating layers of SiO₂ in the barrier provided by the insulating layer.

Several new materials with very high dielectric constants have been reported. However, their dielectric breakdown strength and the maximum energy density have not yet, to our knowledge, been measured. The dielectric constant of these materials depends on the method of preparing the targets. Among these materials are the perovskites and materials with perovskite-like structures. In addition to the perovskites such as barium titanate (BTO), barium

strontium titanate (BST) and lead zirconia-titanate (PZT) [16-18], compounds of the type $ACu_3Ti_4O_{12}$ [3] having perovskite-like structure also exhibit very high dielectric constants. Recently, non-perovskite materials like $Li_{0.05}Ti_{0.02}Ni_{0.93}O$ (LTNO) [5,6], $La_{15/8}Sr_{1/8}NiO_4$ and also Li and Al doped NiO ceramics (LANO) have been reported for having unusually high dielectric constants. It is interesting to note that even pure polycrystalline CuO has comparable, high-dielectric constants [7].

Relative dielectric constants as high as 30,000 have been achieved in crystals of $BaTiO_3$ material. Additionally, research has elucidated the importance of barrier mechanisms (Maxwell-Wegner type polarization [13]) in defining the high permittivity as observed in materials such as reduced- $BaTiO_3$, $CaCu_3Ti_4O_{12}$, $La_{15/8}Sr_{1/8}NiO_4$, etc. Chung et al. [9] have proposed the fabrication of samples using spark plasma sintering of silica (5 nm) coated $BaTiO_3$ (500 nm) nanoparticles. Dielectric permittivity of 2×10^5 has been reported for $f=10000$ Hz at around room temperature. Internal barrier layer capacitance (IBLC) was found to be the major mechanism responsible for the colossal permittivity of these advanced materials from the relaxations observed in the permittivity-frequency curves for different temperatures. The two main conditions for IBLC to increase the dielectric permittivity of these oxides are the inner grain conductivity and the insulating grain boundary. These insulating layers can arise due to surface effects (eg., depletion region of Schottky diodes at the electrodes) or internal barriers (eg., grain boundaries, internal domains within grains). So, we need to induce and control charge point defects (internal barriers) so as to have increased charge density and high dielectric constant, thereby resulting in better super capacitors. The breakdown field strength for SiO_2 has been measured at about 6×10^6 V/cm. At this field strength energy densities approaching 150 KJ/cm^3 are predicted. Processing and metal layers are likely to reduce this number. The reported dielectric constants of a number of potentially interesting materials and their respective, expected energy densities are shown in Table 1.

Table 1. Comparison of relative dielectric constant and achievable energy density for various materials

Materials	Relative Dielectric Constant	Assumed Breakdown Strength	Expected Energy Density
$CaCu_3Ti_4O_{12}$ $BiCu_3Ti_3FeO_{12}$	300000 at 1 kHz and 450C	1500 V/cm	0.03 J/cm^3
$Ba_{0.8}Sr_{0.2}Ti_{0.9}Zr_{0.1}O_3$ surface BLCs	$10^5 - 1.5 \times 10^5$ at 1kHz and -30 to 120 C	10^5 V/cm	$44.3 \text{ J/cm}^3 - 66.4 \text{ J/cm}^3$
$Li(x)Ti(y)Ni(1-x-y)O$ eg. $Li_{0.05}Ti_{0.02}Ni_{0.93}O$	100000 at 1kHz and 200 C	? (10^6 V/cm)	$4.43K \text{ J/cm}^3$?
pure polycrystalline CuO	50000 at 1kHz and 200C	? (10^6 V/cm)	2.213 KJ/cm^3 ?
$BaTiO_3$ - SiC composites	205650 at 1kHz	? (10^6 V/cm)	$9.10K \text{ J/cm}^3$?
$Ca_{0.7}Bi_{0.3}Ti_{0.7}Cr_{0.3}O_3$	6×10^5	? (10^6 V/cm)	26.56 KJ/cm^3 ?
silica (5 nm) coated $BaTiO_3$ (500 nm) ceramics	2×10^5 at 10 kHz	? (6×10^6 V/cm)	$!58 \text{ K J/cm}^3$?
$La_{15/8}Sr_{1/8}NiO_4$ with sputtered gold contacts	10^6 at 400 MHz and room temperature	? (10^6 V/cm)	$44. \text{ KJ/cm}^3$?

EEStor capacitor (US patents)	19818	5×10^5 V/cm	219.3 J/cm ³ ; claims of 2526 J/cm ³
Current Li-ion battery	NA	NA	900 -1296 J/cm ³

Table 1 also compares the energy density that has been obtained commercially for electrochemical double-layer capacitors and some batteries.

In 2009, Khrons *et al* [10] proposed $\text{La}_{15/8}\text{Sr}_{1/8}\text{NiO}_4$ (LSNO) as the potential material for attaining a high dielectric constant at GHz frequency range. The LSNO crystals prepared by traveling solvent floating zone growth technique with silver paint as electrodes were reported to have permittivity of 5×10^4 at room temperature and in ~ 400 MHz frequency range. With sputtered gold electrodes, the same permittivity is found close to 1×10^6 —exhibiting clearly that surface effects contribute significantly to the colossal permittivity. Overall, the permittivity-frequency curve resembles that of conventional CCTO, but it differs quantitatively so that the region of constant permittivity is broader over a large temperature range. Two types of relaxation mechanisms are observed that indicate relaxation mechanisms (possibly due to surface effects) and charge transport need to be reduced for a controlled capacitance. Grain boundary effects can be ruled out in this material, as single crystalline samples were also investigated. The study of these advanced materials (oxides) clearly exhibits that it is the heterogeneity of their structure which accounts for the colossal dielectric behavior, as observed

Compounds of the type $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ where A is a divalent metal like bismuth or calcium or a rare earth trivalent metal have been reported to have perovskite related structures and to have high dielectric constants. Dielectric constants as high as 300,000 have been reported at 1 MHz and at a temperature of 400 C for $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ [3]. However, it drastically falls to only a few thousands at room temperature. The dielectric constant slips down to 12000 at 1 kHz at room temperature. The interesting property of these compounds must be the fact that the materials do not show phase transition and ferroelectric losses as do other conventional perovskite materials. In fact, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ shows no indication of phase change and its structure remains cubic and centric down to even 35 K. This can be explained as follows: In cubic perovskite BaTiO_3 structure above 120 C, the Ti^{4+} cation is in a site of full, cubic symmetry which is lost with decrease in temperature as it displaces towards one, two and finally three oxygen anions. Whereas the site symmetry for Ti^{4+} in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ is much lower than that in cubic BaTiO_3 ; this greatly reduces the possibility of ferroelectric phase transition based on the displacement of Ti^{4+} from the centre of its octahedron [11, 12].

Li and Ti co-doped NiO (LTNO) ceramics are one of the most recent materials reported to have very high dielectric constants, first reported in China [5]. The interest in these materials rose because of their non-ferroelectric and non-perovskite properties. The high dielectric permittivity in these materials is attributed to the interfacial polarization mechanism or the Maxwell – Wagner polarization mechanism and the formation of Barrier Layer Capacitances (BLCs). This kind of mechanism is believed to be responsible for high permittivity in ceramics or multi-phase composites having grains which become semiconducting while grain boundaries become insulating. At lower frequencies of 1 kHz, dielectric constant is very high—of the order of 100,000 at 130° C—but falls off rather rapidly to 10,000 at room temperature. $\text{Li}_{0.01}\text{Ta}_x\text{Ni}_{0.99-x}\text{O}$ with $x \sim 1$ shows the highest dielectric constants [6]. The drastic decrease in dielectric constant at higher frequencies and lower temperatures can be explained by the space charge polarization.

Barnes *et al* have measured breakdown strength of barium titanate when using them for microwave circuits such as tunable filters and phased array antennas. Breakdown strength of 100,000 V/cm have been already obtained and in some cases values close to 1000,000 V/cm have been reached [17-18]. Dependence of dielectric properties on lattice orientations, different phases of ferroelectricity, composition of Sr and also effects of different forms of barrier

layers in enhancing dielectric properties in materials like BaSrTiO₃ and BaTiO₃ were extensively researched. Efforts are on to make high dielectric BaSrTiO₃ films having very high dielectric constant and breakdown strength of the order of 1000,000 V/cm as already observed for different applications.

Conclusions

With high dielectric constants and the potential to achieve energy storage densities of more than 10 KJ/cm³ supercapacitors have the potential to become an important way to store energy for a wide variety of applications. Capacitors have advantages over batteries of enabling more rapid charging and discharging and longer potential life. Batteries typically do not do well with many deep discharges and are often an expensive part of the system. Thus, we believe many of the forgoing materials are worth investigation.

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