Metadielectric Materials

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Abstract: We demonstrate progress towards the development of a Metadielectric material that enables a leap in the energy storage density of dielectric capacitors by extending the boundary of the tradeoff between bulk permittivity and resistivity. We demonstrate engineering the resistivity of solvent cast films to 10^{16} Ω•cm. We disclose material design principles aimed at achieving a 2 μm solvent-cast film with 10^{18} Ω•cm resistivity, 1000 V/μm dielectric strength, and 6 x 10^{-6} F/m permittivity. Metadielectric films meeting these specifications would enable capacitors with energy and power density of 250W•h/kg and 10^6 W/kg, respectively.

Keywords: film capacitor; hyperpolarizability; ferroelectric polymer; permittivity; resistivity; dielectric strength; energy storage.

Introduction: Energy storage devices having both high energy density and high power density would enable the development of machines and devices of the future including low cost grid energy storage. Conventional electrochemical batteries have power density, energy density, depth of discharge, charge and discharge rate, and lifetime limitations. Conventional capacitors have an energy density limitation. Metadielectric materials offer high energy density, high power density and long lifetime.

Table 1. Energy Density (E.D.), Power Density (P.D.), Self Discharge Time, and Lifetime expressed as number of charge/discharge cycles, for the major classes of energy storage devices [1,2].The projected properties of a film capacitor with a Metadielectric are shown in the last row.

| Device	E.D. (Wh/kg)	P.D. (W/kg)	Self Discharge	Cycles
Battery	100 - 250	$<10^3$	months	$10^3 - 10^4$
Dielectric Capacitor	0.2	10^6	days	10^{10}
Supercap	$10^0 - 10^1$	$10^0 - 10^1$	weeks	$10^5 - 10^6$
Metadielectric	250	10^6	weeks - months	10^{10}

Permittivity vs. Resistivity Tradeoff: Materials with permittivity up to 10^{-5} F/m [3] have been demonstrated. However, the resulting resistivity has been impractically low (resulting in a high rate of self discharge) for a dielectric in a capacitor. High-permittivity (up to 10^{-6} F/m)

polymer-matrix composites have been demonstrated with fillers such as metals, high k ceramics, carbon based materials, and conducting polymers and oligiomers [4]. Unfortunately, abundant data is consistent with a tradeoff between permittivity and resistivity in composite materials effectively bounding capacitor performance below the leap needed for energy storage applications [5]. This lack of successful use of the composite effect to increase the permittivity/resistivity boundary may lie with the interfacial structure of the composites. The predominate polarizability mechanism for composites exhibiting the highest permittivities is interfacial (Maxwell-Wagner) interactions [5]. But the penalty comes from the Lorentz/Mossotti field which alters the molecular orbitals, increasing conductivity and making bonds susceptible to breakage by standard Boltzmann processes and/or hole capture [6]. Broken molecular bonds leave percolation sites and result in lower dielectric strength.

Metadielectric: The Perfect Composite: Achieving high bulk permittivity without significant loss of resistivity requires a highly ordered material comprising densely packed highly polarizable units electrically isolated from one another by an envelope capable of withstanding the Lorentz/Mossotti field imposed from the nearby induced dipoles [7,8]. The natural choice for the envelope is a saturated hydrocarbon or fluorocarbon akin to polypropylene, polyethylene, or PTFE. In theory, highly crystalline polyethylene could achieve > 10,000 V/μm by virtue of the bond strength (3.6 eV) and size (0.15 nm). In reality, defects allow charge carrier breakthrough at much lower fields. Biaxially oriented (stretched) polypropylene (BOPP) exhibits $5x10^{16}$ Ω•cm resistivity and 600 V/μm dielectric strength [9], limited by defects. Laboratory measurements of vacuum deposited polypropylene films are reported as high as 1500 V/μm [10].

Metadielectric films are composed of units comprising a highly polarizable "core" covalently bonded to alkyl or fluoroalkyl chains - essentially fragments of polypropylene or PTFE. The units are engineered to self assemble into a highly ordered material whereby the "cores" are densely packed and enveloped by the ensemble of alkyl chains attached to the "core(s)" of the ensemble. Fig. 1 schematically illustrates the structure of a Metadielectric film and the self assembly process to create it. The alkyl groups in the Metadielectric materials can be more highly ordered than in BOPP. Furthermore, we employ fluoroalkyl groups known for more order and higher bulk resistivity

than hydrocarbon alkyl groups [11]. Higher order means less random interfaces limiting the interfacial polarization to the covalent bond between the "core" and alkyl group. Hence this work targets composite electrical properties of 1000 V/μm dielectric strength and 10^{18} Ω•cm resistivity.
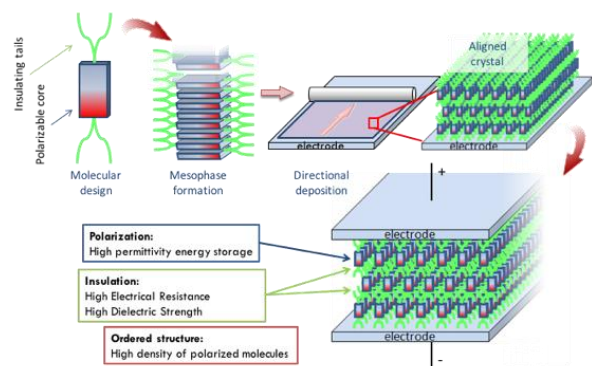
Figure 1. Metadielectric Material: Fabrication of capacitor comprising 1 – 2 μm Metadielectric film between charge collecting electrodes. The Metadielectric comprises a dense array of units each with a highly polarizable core all enveloped by the ensemble of insulating alkyl substituents.

Two classes of Metadielectric materials are introduced here: i) Conjugated π-stacking molecules, and ii) Ionic liquid crystalline side-chain polymers.

Conjugated π-stacking Molecules: In another paper we demonstrate π-conjugated molecules exhibiting hyperpolarizability [12] giving rise to permittivity as high as 10^{-6} F/m at fields > 500 V/μm. Fig. 2 depicts such a molecule without donor/acceptor substituents.

PDA   Bis-Alk-PDI
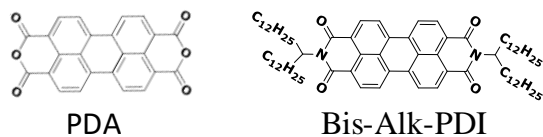
Figure 2. An example of a conjugated π-stacking molecule comprising a flat π-conjugated polarizable core, with (**right**) and without (**left**) insulating alkyl substituents.

This class of Metadielectric material exploits the π–π stacking forces of the flat conjugated polarizable molecular unit to form a lyotropic liquid crystal (LLC) mesophase [13]. The LLC has long range order in the stacking direction. The ensemble of externally facing alkyl substituents envelopes a polarizable supramolecular stack. The coating and drying process used to generate the dielectric film is designed to preserve the order achieved in the LLC state.

Ionic Liquid Crystalline Side-chain Polymer, the second class of Metadielectric materials discussed here, comprise a mixture of an anionic copolymer and a cationic copolymer (Fig. 3). The ions are present as side-chains covalently attached to the copolymer backbone. Each ionic copolymer comprises electrically resistive alkyl or fluoroalkyl side chains (for resistivity).
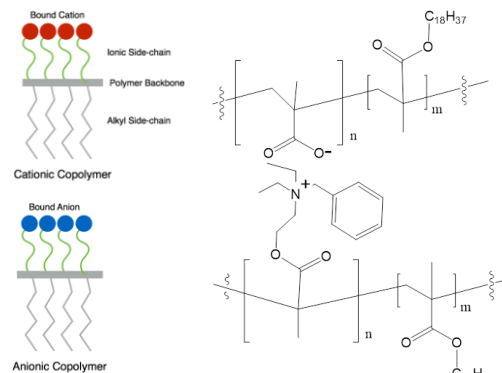
Figure 3. Schematic (**left**) and chemical formulae (**right**) of a cationic copolymer (**top**) and anionic copolymer (**bottom**), when mixed form an *Ionic Liquid Crystalline Side-chain Polymer Metadielectric material*. Each copolymer contains an electrically insulating alkyl side chain ($C_{18}H_{37}$ and $C_{12}H_{25}$) and a covalently bound ionic side chain.

Copolymers and polymer blends comprising monomers with significantly different polarity and solubility parameters are well known to result in solution cast films with high degree of order, e.g. lamella or micelles [14]. Metadielectric material properties emerge as the polarizable "cores" are formed as the cation/anion pair in the inside of a micelle or lamellar structures. The ion pair "cores" are electrically isolated by the enveloping alkyl side-chains that form the outside of the micelle or lamellar structure (Fig. 4). When a polymer contains ionic species, ionic polarization occurs below a few hundred Hz [15].
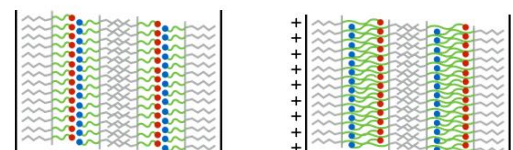
Figure 4. Schematic of ionic liquid crystalline side-chain polymer adopting a lamella structure, without (**left**) and with (**right**) an external electric field.

Nonpolar polymers free of ions are linear dielectrics, exhibiting a relative dielectric constant independent of electric field, ε = D / E. BOPP falls into this category. The stored (and released) energy density is thus U = ∫ E dD = ½ ε E^2.

Experimental:

Pellet

Sample Preparation of Pellet: Samples are pressed into a 13 mm x 1.3 mm pellet by grinding 0.2 g of powder and pressing it at 7 Tons in a standard KBr dye set. Silver epoxy electrodes are applied to both circular faces.

Sample Preparation of Thin Film Capacitors: Coating solutions are formulated by dissolving 0.2 g of powder into 1 mL of solvent and filtering the solution through a 0.45 μm PTFE filter. Patterned metalized glass substrates (9" x 5") are cleaned by exposing to UV-Ozone with 100%

oxygen process gas for 5 minutes. Coating and drying are all done in a laminar flow clean hood to prevent particle incorporation. Thin films are deposited on the substrates by dispensing 0.3 – 0.5 mL of coating solution and drawing a #2 ½ - #6 wire wound rod lengthwise along the glass at 1.5 in./s. The solution is allowed to dry.

Top aluminum electrodes (15 Ω/•) are thermally evaporated at 10^{-7} Torr at 0.1 – 0.2 nm/s through a mask defining 9 cm^2 capacitors per substrate. The high sheet resistance of the top electrode is designed to cause areas with current leaking defects to ablate and isolate themselves away from the circuit leaving the non-defective areas intact and connected ("clearing") [16]. Fig. 5 depicts the final test structure.
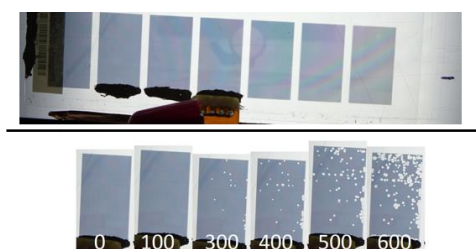

Figure 5. Top: Partial view of untested capacitors defined as |glass (1.1mm x 9" x 5") | Patterned ITO (0.2 μm x 9" x 4") | Metadielectric (1 μm x 9" x 5") | Al (2 nm x 4.5 cm x 2 cm) connected to circuit with pogo pins and silver epoxy; **Bottom:** Progression of one capacitor as voltage is increased. Defects clear electrode until it isolates at 600V.

DC Testing (Dielectric Strength & Field Dependent Resistivity & Permittivity): Capacitors are connected to a circuit with pogo pins inside a Faraday Cage. The pins are wired to a Keithley 2657A source meter where the testing protocol follows the DIN 62391-1 IEC. The DC resistivity as a function of soak voltage, "Soak Resistivity", is calculated from the current measured at the end of a 30 second voltage hold, or "soak. Capacitance at each voltage is recorded until the breakdown field is reached. The breakdown voltage is declared when less than half of the initial capacitance remains at the same low field. The thickness of the dielectric under each capacitor is measured using a stylus profilometer. The thickness and remaining device area are used to calculate the electric field, the permittivity, and resistivity.

Electrochemical Impedance Spectroscopy: For a deeper characterization of the material, Electrochemical Impedance Spectroscopy was performed by a Biologic SP-200 in a faraday cage. AC measurements were performed with 2 electrodes, 0.5 V$_{rms}$, and 0, 5 and 9 V/μm DC bias. The sample was measured at room temperature then heated to 30 and 50°C using a circulator and Lytron Al plate.
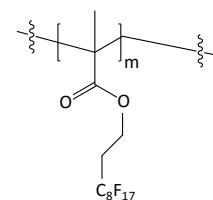
Results & Discussion: Resistivity engineering for the conjugated π-stacking class of Metamaterial was first demonstrated. The DC resistivity for perylene-3,4,9,10-

tetracarboxylic dianhydride (PDA), a polarizable "core" without an insulating alkyl tail is 10^{11} Ω cm at 9 V/μm DC bias (Fig. 6). N,N-Bis(1-dodecyltridecyl)perylene-3,4,9,10-tetracarboxylic diimide (Bis-ALK-PDI) is 100x more resistive (10^{13} Ω cm at 9 V/μm DC bias). The solvent cast films (Fig. 1) of Bis-ALK-PDI show 10 – 1000x higher resistivity (up to 10^{15} Ω cm at 20 V/μm) than the pressed pellet, *increasing* with applied field as structure is pressed into place. The demonstrated resistance is higher than the best solution cast films of PMMA [17] and comparable with metalized BOPP [16]. This is consistent with a supramolecular stacking of "cores" to form an insulating envelope.
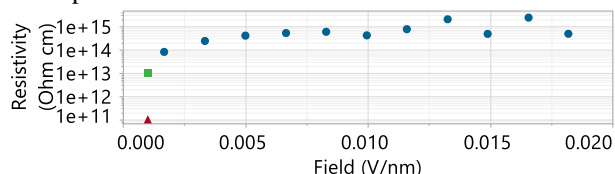

Figure 6. Resistivity at 9 V/μm of pellets of (▲) PDA - no alkyl substituent and (■) Bis-ALK-PDI – two branched 12 carbon alkyl substituents overlaid with the electric field dependency of (●) a 2 μm solvent cast film of Bis-ALK-PDI.

Resistivity engineering of ionic liquid crystalline side-chain polymer Metadielectric was also pursued. The insulating properties of the alkyl side groups are first discussed. Similar to Bis-ALK-PDI, we demonstrate increasing the resistivity of a solvent cast film compared to the bulk pellet. Before working with the mixture of anonic and cationic copolymers, the fluorinated acrylic shown to the right was investigated in order to understand the effect of fluoralkyl groups. The DC resistivity for the fluorinated fluoroacrylic is 10^{14} Ω cm at 9 V/μm DC bias (Fig. 7).
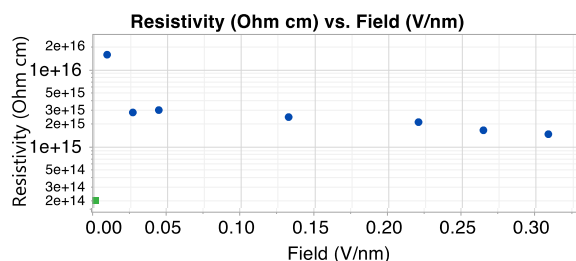
Figure 7. Resistivity of pellets (■) and a 1 μm solvent cast film (●) of a side chain fluorinated acrylic polymer.

The solvent cast films (Fig. 1) of the fluoro acrylic polymer is 10x to 100x higher resistivity (10^{15} – 10^{16} Ω cm) than the pellet. This demonstrates that order is induced by the side chain alkyl group. The breakdown field of the solvent cast films is > 500 V/μm, determined when 50% of the capacitive area remains after the electrode clears high current spots.

The sudden drop in resistivity at a low field (0.025 V/nm) shown in Figure 7 is troubling; resistivity of commercial fluorpolymer melt cast and extruded film is 10^{17} to 10^{18} Ω cm. Cyclic voltammetry was employed to detect impurities (free ions, monomers, water, etc.) which will undergo electrochemistry if present. Referring to Figure 8, peak current is proportional to concentration of species in the system and peak voltage is suggestive to the type of species.
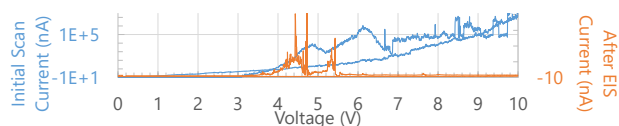
Figure 8. Cyclic voltammetry (200 mV/s) of a thin film device (Fig. 5) using the fluoropolymer acrylic as dielectric.

Oxidation (negative peaks between 4 and 6 volts) is occurring in the fluoro acrylic system likely from an impurity considering the substantial drop in peak height after cycling. Chemical synthesis and laboratory practices will be investigated and this testing will demonstrate the effectiveness of the improvements.

Continuing with the advanced analysis, electrochemical impedance spectroscopy was employed. The Nyquist plots were vertical lines with 20 ohms of equivalent series resistance ESR, which is consistent with the resistance of the ITO and the aluminum top electrode. There was no evidence of mobile ions or a diffusion process occurring at room temperature.

Conclusion: We have communicated design criteria for two classes of Metadielectric materials. Both require highly ordered molecular arrangement of polarizable "cores" covalently bonded to resistive alkyl groups as an ensemble envelope the "core". We have demonstrated the ability to make films from each of these classes with resistivity up to 10^{16} $\Omega \cdot$cm and 500 V/μm dielectric strength. Our next step for the π-conjugated Metadielectrics is to build in high permittivity by adding the theoretically determined donar/acceptor functional groups. Our next step for the ionic liquid crystal side chain polymers Metamaterials is better purification and annealing in order to increase the dielectric strength – to the point where the ion pairs separate. These dielectric metamaterials have the promise of creating inexpensive high power and high energy density energy storage devices with a virtually unlimited lifetime. When made into capacitive cells, energy could be safely stored at significantly less cost than that of grid energy. This would enable a suite of economically viable applications including Electric Vehicles, residential, commercial, industrial and utility energy storage.

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