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New Paradigm Supercapacitors for Energy Storage

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PROJECT SUMMARY

Super dielectric materials potentially can have a game changing impact on the US Navy: Enabling electric based weapons systems. During the past year our team, largely funded by NRP, has made significant progress toward creating SDM based capacitors which advance this goal. Working with five NPS students, significant progress was made in building, testing, and characterizing several types of Super Dielectric Materials (SDM), and additionally inventing two new categories of SDM. Papers were written and published in peer reviewed journals regarding improved characterization of power, energy, dielectric constants of capacitors based on two previously invented SDM categories materials: particle based SDM (P-SDM), and anodized titania based SDM (Tube SDM). The published papers included, for the first time, systematic study of the impact of frequency on SDM performance. A US patent was issued for P-SDM and T-SDM. Two entirely new categories of SDM were invented, fabric based SDM (F-SDM) and, thin plastic sheet based SDM (PL-SDM), and appropriate patents filed. Initial studies of the newly invented PL-SDM, based on the use of very thin hydrophobic plastic with mechanically created macro scale holes, suggests a potential '*game changing'* technology. Specifically, we have now repeatedly created capacitors based on this inexpensive, simple to construct, technology with a delivered energy of between 65 and 75 J/cm^3 of dielectric. Notably, two students completed MS degrees based on their work with SDM during the grant period, and three students are making excellent progress toward completing MS thesis work on the topic.

BACKGROUND

The USNavy is involved in converting many ships to an 'all electric' configuration. In order to enable this transformation, capacitors with energy density superior to those presently commercially available are required. Moreover; the leading candidate for this role, graphene based supercapacitors, are prohibitively expensive. This project was designed to develop a novel type of capacitor, Novel Paradigm Supercapacitors, which employ super dielectric materials (SDM), a class of materials invented at the Naval Postgraduate School (1-9), that are even lower cost than current commercial supercapacitors, yet far higher in energy density. The final version developed, Plastic SDM (PL-SDM) appear to have all the qualities required, particularly high energy density, and low cost. The patents for all the SDM are now licensed, and capacitors based on them under development commercially.

FINDINGS

This report is divided into five sections: i) P-SDM ii) T-SDM, iii) work done with one newly invented category of SDM, fabric based SDM, iv) work done with the second newly invented form of SDM, PL-SDM and v) a brief review of work in progress.

I. Particle Super Dielectric Materials:

Below, a very brief summary of three publication (1-3) on PSDM is presented. The most important findings from work on this topic were i) further demonstration of the generality of the SDM hypothesis, ii) the finding of the highest dielectric constants ever recorded, and iii) the first reports on the trends in dielectric constant, energy density, etc. as a function of discharge time.

Regarding the generalization of the SDM hypothesis: For the first time a high surface area ceramic other than alumina was thoroughly investigated as the insulating matrix phase of SDM. Working with fumed silica saturated with aqueous NaCl solutions our team further demonstrated the validity of the general form of the underlying SDM hypothesis: Any non-conductive porous solid in which the pores are filled with a liquid with a sufficient concentration of dissolved ions will have a high dielectric constant. The concept underlying this hypothesis is that dissolved ions will migrate to form giant dipoles in the presence of an applied field. These dipoles will partially cancel the field created by charged species on the electrode plate, thus allowing more charge to collect on the plate at any given voltage than is possible with any other type of dielectric. The hypothesis and the underlying physics are described in far more detail elsewhere (4-6).

Using the RC time constant method, the highest dielectric constants ever were recorded for this form of SDM (Figure 1). The values obtained, $>10^{11}$, are particularly spectacular considering that before the invention of SDM, the highest claimed dielectric values were $<10^{5}$.

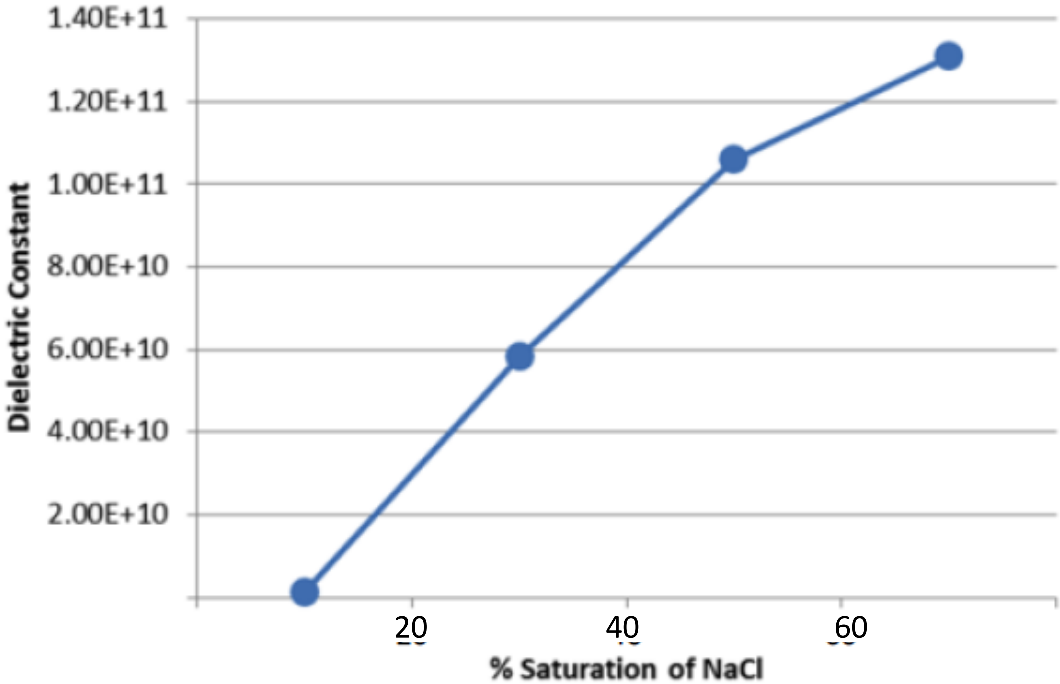

Figure 1- The RC time constant was employed to study the dielectric constant of aqueous NaCl solution filled fumed silica. The data shows that the higher the salt concentration, the higher the dielectric constant. This data is found in two published works (1,2).

As noted, the third significant aspect of the work was that it constituted the first systematic study of the behavior of SDM as a function of frequency. Indeed, it was found, as expected for all dielectrics, that the energy density, dielectric constant (Figure 2) and power density fell monotonously as discharge time was shortened.

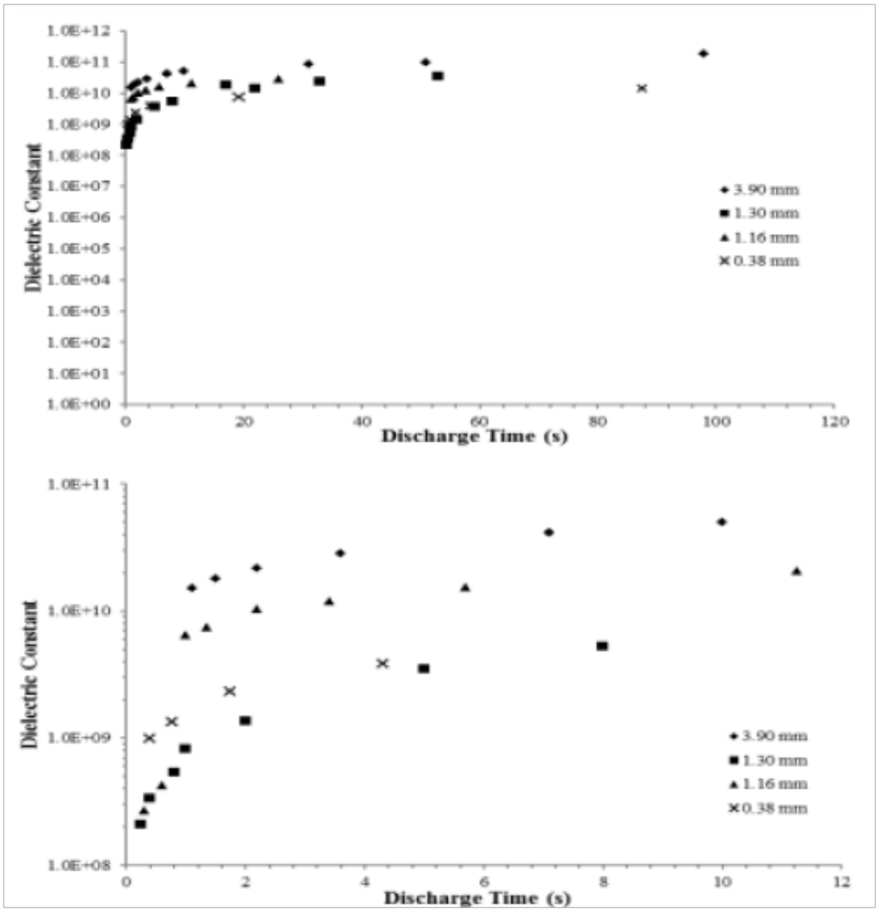

Figure 2- Dielectric constants decrease as discharge time is shortened. TOP- At very long discharge times, >100 seconds, the dielectric constants measured using a galvanostat are nearly equal those recorded with the RC time constant method (Figure 1). BOTTOM- As the discharge time is shortened (ca. <1 second) the dielectric values fall steadily, but even at very short discharge times are still $>10^8$. The values of dielectric constants, etc. fall monotonically as discharge time is shortened, as anticipated for all dielectrics. This data is found in two publications (1,2).

II. Tube Super Dielectric Materials-

The most significant aspects of work done with these materials (Figure 3) was the finding that the energy density is a function of the identity of the aqueous salt solution (7,8). In the first report on these materials $NaNO_3$ was the salt dissolved and the highest energy density obtained was about 220 J/cm^3. In the work conducted during the period of this study NaCl was the dissolved salts and repeatedly energy density of the order of 400 J/cm^3 (Figure 4). The best prototype supercapacitors reportedly have an energy density of about 450 J/cm^3 (4). The finding of this study that salt identity can impact energy density significantly, suggests that an optimum design T-SDM with the best salt, best pore structure, etc., all to be determined empirically, might surpass the best supercapacitors in energy density.

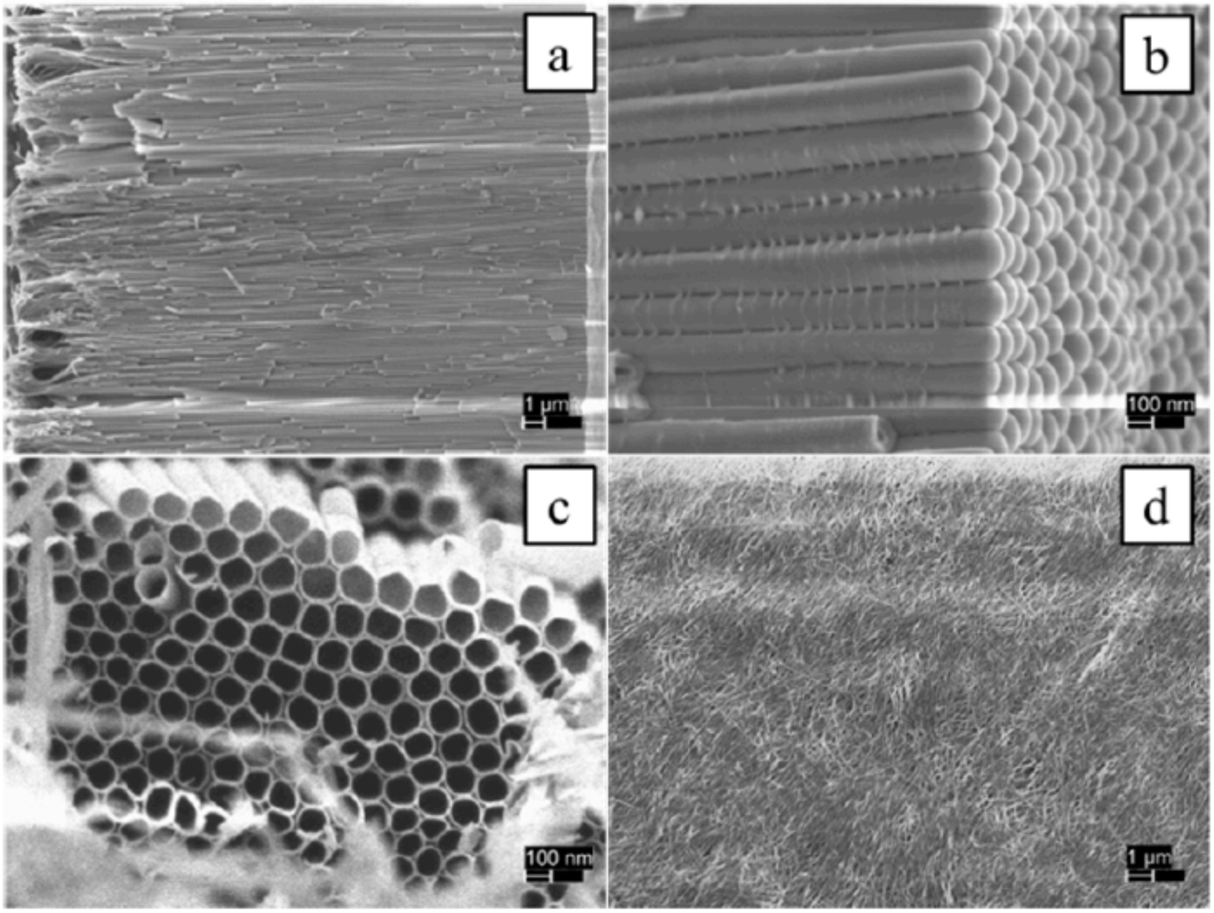

Figure 3- Various views of the titania nanotubes formed on titania surfaces via anodization. A) Side view showing tubes about 15 nm in length. B) Side view showing ends of tube adjacent to metallic titania are closed. C) Top end of tubes open, thus can be filled with aqueous salt solutions. D) Very long tubes 'collapse' to form irregular 'grass' structures. (7,8)

The study also confirmed that the energy density of T-SDM is nearly independent of the length of the tubes formed. This constitutes an important demonstration of the basic SDM hypothesis (Fig 4).

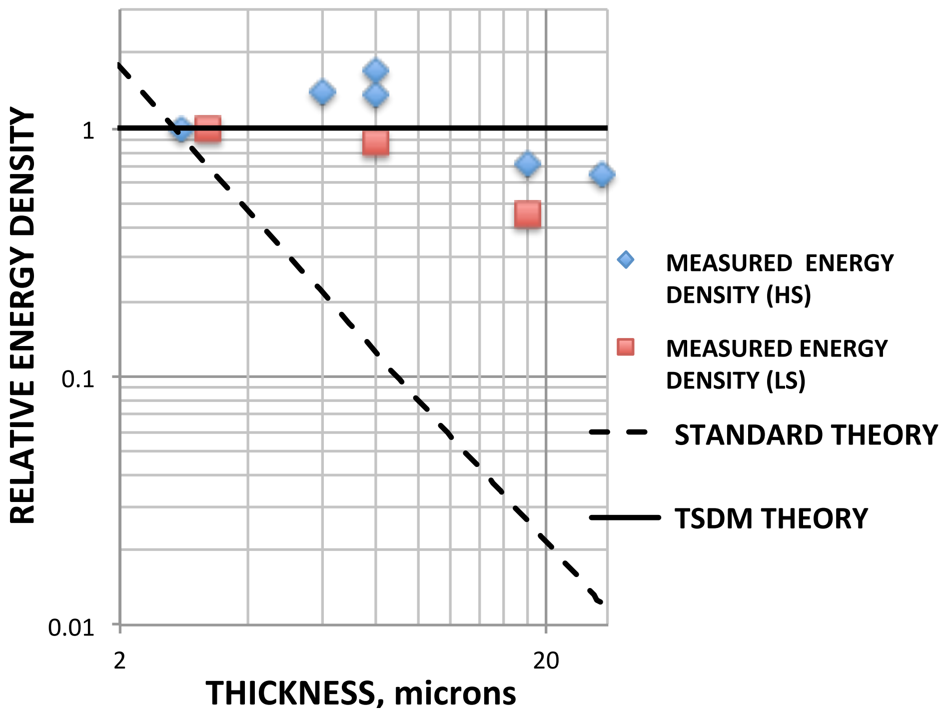

Figure 4- Energy Density as a Function of Tube Length. The graph indicates that the energy density is nearly independent of tube lengths until tubes reach about 20 microns in length. The loss in fidelity to the model at >20 micron length may result from the loss of integrity of tube structure with tube length (Figure 3D, above). (7,8)

III. Fabric Super Dielectric Materials-

This category of super dielectric material was invented less than a year ago based on a logical extrapolation of the SDM hypothesis (9). According to this hypothesis any non-electrically conducting, ‘porous’ material can serve as the matrix material in an SDM. A clear example of this is a fabric created by weaving together threads of any material. Such a material contains open spaces between threads that constitute large pores which can be filled with the dipole forming, ion containing, liquid phase. Specifically, in this study a fabric composed of a weave of nylon, with approximately 50% void volume was employed as the matrix material, and the ion containing phase of the SDM, which filled the void volume, was an aqueous NaCl solution.

There were two major findings reported in this study. First, the results once again support the general SDM hypothesis. That is, the results show that any electrically insulating matrix material that has ‘pores’ capable of holding solutions with dissolved ions should work as an SDM. It should be noted that an empirical extrapolation of the early results of the SDM work would have led solely to the study of Powder type SDM. It is only because of the general SDM hypothesis proposed at the beginning of the work on SDM that T-SDM, F-SDM and finally PL-SDM were studied at all (5). This is a good example of a general model leading to a wide range of particular 'discoveries'. Second, this report provides the first detailed report on capacitance, dielectric constant, energy density and power density as a function of discharge time.

The study of 'time dependence' of parameters produced quite plausible results. In all cases, capacitance, dielectric constant (Figure 5), and energy density (Figure 6) decreased as the discharge time decreased. Moreover, the reported power law behavior is entirely plausible. In contrast, other groups, generally using Impedance Spectroscopy show trends that stretch credibility with parameters such as dielectric constant increasing, then decreasing as frequency is increased. The data in these reports clearly cannot be fit by any simple mathematical formula.

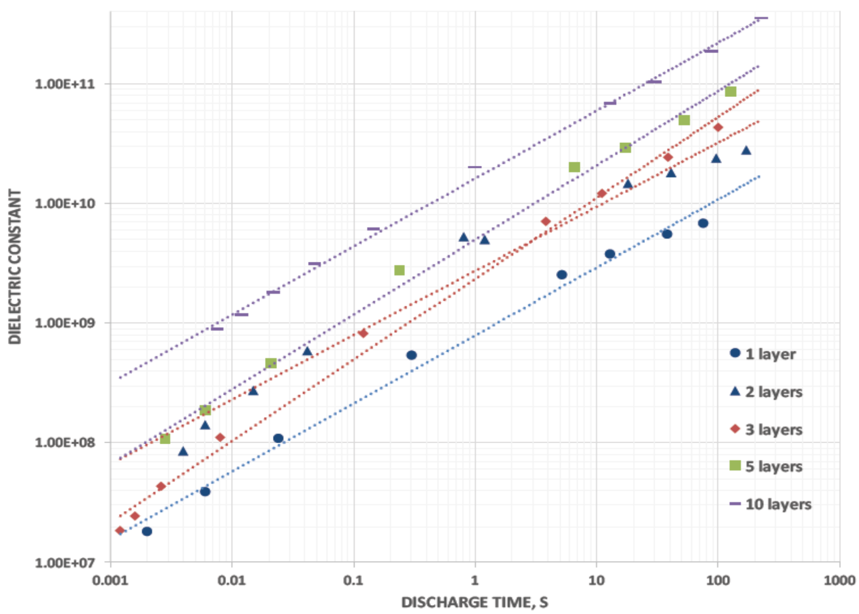

Figure 5- Dielectric Constant vs. Discharge Time. Five distinct capacitors were made, identical but for number of layers of nylon employed in the construction. In all cases a simple power law accurately describes the decrease in dielectric constant with more rapid discharge (9).

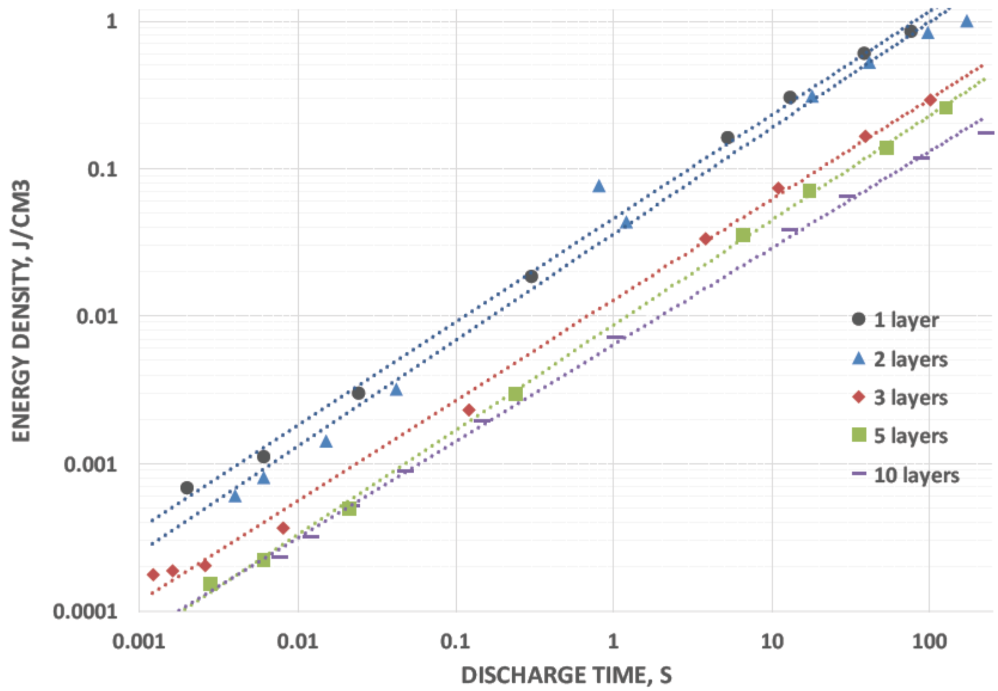

Figure 6- Energy Density vs. Discharge Time. Simple power laws fit the empirically determined energy density of all five unique capacitors studied. As expected for capacitors, the thinner the dielectric, the larger the energy density (9).

I. Plastic Super Dielectric Materials

A capacitor with energy density of ~ 75 J/cm^3 of dielectric material was made using a unique form of super dielectric material. It is notable in this regard that the best commercial supercapacitors have an energy density of approximately 30 J/cm^3. The novel super dielectric, herein called D-1, consisted of a piece of hydrophobic polypropylene plastic sheet (Celgard PP1516), 2.5 cm x 2.5 cm x 16 micron (thickness), into which 325 holes (~50 holes/cm^2) were through punched with a pin of diameter 0.6 mm, placed on top of a commercial 'sheet carbon' (Grafoil) electrode, then smeared with a solution of 30wt% NaCl in distilled, de-ionized water. 'Salt Water' placed on the hydrophobic plastic beads up. Excess water was physically squeezed out by compressing (lightly) a second electrode onto the plastic. It was found that the capacitor thus constructed, constant current cycled between 2.3 and 0 volts, showed virtually no change in behavior over 30 cycles using charge and discharge times of about 300 seconds.

Additional experiments were conducted to test this hypothesis: The high dielectric value and energy density observed for the capacitor constructed with D-1 results from the large induced electric dipoles that are created in the 'salt water' columns that form in the holes punched through the plastic with the pin. This hypothesis is completely consistent with the SDM hypothesis described in the scientific literature (1-9). In brief, the longer the dipoles in the dielectric and the higher the density of dipoles, the greater the maximum energy density and dielectric value. Relative to solid dielectrics in which the dipole length is a maximum of 0.1 Å, the dipoles formed via field induced ionic migration (Na + toward negative electrode, Cl- toward positive electrode) in the salt water columns of D-1 are enormous.

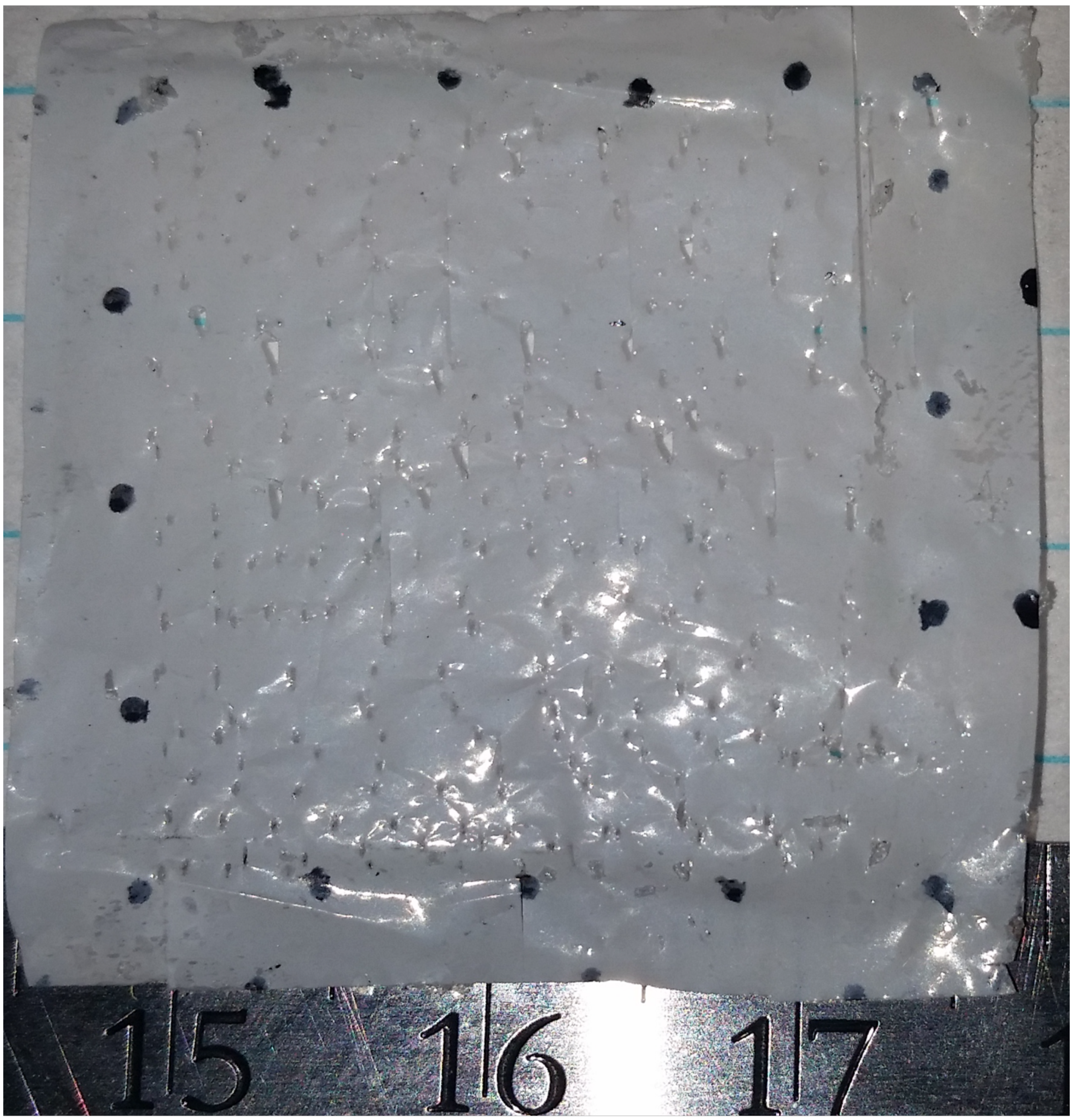

Figure 7- *PL-SDM*. Shown, one of the three layers in the multi-layer capacitor described below, above ruler marked in mm. Two hundred and fifty holes were hand-punched into a hydrophobic, 16 micron thick plastic in an area 2.5 cm x 2.5 cm. Once filled with an aqueous solution, 30% NaCl by weight, these proved to be extraordinary dielectric materials. Note: The edges, no holes, prevent electric contact between Grafoil squares (electrodes) that measure 2.5 x 2.5 mm.

The hypothesis suggests that the net energy density that a capacitor made from a plastic through which holes have been punched and then filled with aqueous salt solution, should increase with the number of holes punched. For this reason, experiments were conducted to study the impact of hole density on energy density. In each case, a capacitor of the same dimensions as above included a dielectric made in the same fashion as D1. That is, it was made from the same plastic, using the same punch and same salt water solution, but with one major difference: in each case a different number of holes was punched. In the first experiment, a single hole was punched at the center (D-2). A third capacitor (D-3) was made using an identical dielectric but with ~10 holes/cm^2, and a fourth with ~15 holes/cm^2. The outcome predicted by the SDM model, the measured energy density should increase with the number of holes punched, is consistent with the values obtained.

Punched Holes/cm^2	Measured Energy Density, J/cm^3	Discharge Time, sec
0.016 (one hole, center)	<0.01	<0.1 sec, maximum
3	0.3	30
15	24	~200
56	76	~300

A second type of study was designed to test for ease of creating multi-layer capacitors using PL-SDM. In this test a capacitor consisting of three sheets of the same material employed above, each with a hole density of 40 holes/cm^2, employing Grafoil electrodes of the same dimensions as above (2.5 cm x 2.5 cm). The structure consisted of seven layers: Electrode 1, P-SDM 1, Electrode 2, P-SDM 2, Electrode 3, P-SDM 3, Electrode 4. Electrodes 1 and 3 were electrically connected as were Electrodes 2 and 4, effectively creating three capacitors in parallel. It was repeatedly shown this multilayer capacitor had energy density of >65 J/cm^3 of P-SDM dielectric.

The outcome of this study is significant as it suggests an inexpensive, simple design for high energy density capacitors. That is, it is easy to imagine a simple process for commercial production of the dielectric materials from punched plastic sheets. Indeed, plastic sheet is very inexpensive, punching holes in thin plastic sheet easily and inexpensively organized (e.g. rapidly passing sheet between rotating cylinders containing properly positioned pins), and soaking with 'salt water' also remarkably inexpensive. Moreover, the energy density measured in this 'first effort' is more than double the value available in the current commercial supercapacitor market. Commercial processes could be designed to yield far higher energy density via optimization of the salt solution employed, including organic electrolytes, the hole density, the number of holes, the thickness of the plastic, the identity of the plastic, etc.

V. Testing Novel Electrolytes on T-SDM:

CMDR David Backer and LT Steve Lombardo continue to test the effect of a variety of electrolytes on the performance of T-SDM capacitors. The electrolytes are made from a matrix of polar organic solvents and salts. Preliminary results based on non-aqueous solvents with different salts are shown in Table II:

Solvent	Salt	Highest ED (J/cm^3)
NMP	NaCl	Not tested
NMP	KNO3	25
NMP	NaNO3	66
NMP	Boric Acid	Not tested
DMSO	NaCl	21
DMSO	KNO3	26
DMSO	NaNO3	57
DMSO	Boric Acid	21
PC	Di Water/NaCl	Various Concentrations

TABLE II- Preliminary results for tests of organic solvents/salts in 8 micron high tubes of anodized titania.

In Table III the near final results are shown from tests in which the electrolyte was distilled/de-ionized water into which salts other than NaCl were added.

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Solvent	Salt	Highest ED (J/cm^3)
Charge (Various) = Discharge		
DI	NH_4Cl (10%)	41.12
DI	NH_4Cl (20%)	27.83
DI	NH_4Cl (30%)	34.62
DI	$NaNO_3$ (10%)	1.75
DI	$NaNO_3$ (20%)	6.69
DI	$NaNO_3$ (30%)	6.39
DI	KOH (10%)	17.64
DI	KOH (20%)	14.79
DI	KOH (30%)	59.18
Charge (10mA) ≠ Discharge Rate		
DI	NH_4Cl (10%)	28.61
DI	NH_4Cl (20%)	22.16
DI	NH_4Cl (30%)	7.44
DI	$NaNO_3$ (10%)	1.32
DI	$NaNO_3$ (20%)	3.13
DI	$NaNO_3$ (30%)	3.45
DI	KOH (10%)	3.35
DI	KOH (20%)	7.66
DI	KOH (30%)	25.84
Control	Di Water (100%)	Not Analyzed Yet

CONCLUSIONS

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Primary finding: PL-SDM are viable for near term use by the USNavy for the following reasons:

i) It has been demonstrated with non-optimized, preliminary designs, that capacitors in this category have >2.5 X the energy density of the best commercial super capacitors.
ii) The materials (thin plastic, salt water and conductive electrodes) required for PL SDM are very inexpensive.
iii) The processing required to create PS SDM; punch holes in plastic, add water, cover with conductive electrodes, package, are very simple, and easily instituted commercially.

In sum, the research conducted can be an enabler to a significant proposed transformation: all electric ships.

RECOMMENDATIONS FOR FUTURE RESEARCH

Before SDM were discovered at NPS the highest dielectric constants reliably reported were ~10^4, that is seven orders of magnitude smaller in value than the best SDM, ~10^{11}. The finding that there are four classes of SDM- Particle SDM, Tube SDM, Fabric SDM and Plastic SDM indicates that the discovery of SDM is in fact the discovery of a large and totally unexplored fertile field of engineering and science. Although we have done much to explore the breadth of that world, and some 'engineering' including direct demonstration of remarkable energy densities and demonstration of low cost versions, we have done very little to study this vast field in depth, and have not developed a true mathematical explanation of the mechanism of super dielectric behavior.

In order to achieve optimum performance, a true need of the USNavy, we recommend further research into the effects of variations in the parameters of construction of all SDM classes including, salt identity, polar electrolyte identity, fabric identity, electrode identity, etc. We also recommend more work be done to explain and model the observed behavior. Finally, we urge additional collaboration with industry to accelerate the commercial availability of Novel Paradigm Supercapacitors based on SDM.

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