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Dielectric Nanocomposites: An Inside-Out Approach to Storing Electrostatic Energy

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For millennia, scientists, engineers, inventors, and the curious have sought better ways to store electrostatic energy, nearly all of which amount to separating and storing charge. The ancient Greeks recognized that they could separate charge by rubbing certain dissimilar materials and that charge could do work, for example, by letting the rubbed surfaces pull themselves back together. Although the current preferred means of electrostatic energy separation is through magnetic induction, charge storage still amounts to separation of ions and electrons. This was epitomized over two centuries ago by the Leyden jar and Volta's pile, the forerunners of the modern capacitor and battery, respectively. The energy stored is typically equal to the product of the charge and the potential difference. Capacitors develop increasing potential as

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they are charged, while batteries are charged at a (nearly) constant potential. Both batteries and capacitors are in wide use, but batteries are by far the dominant rechargeable power source for reasons of both cost and performance (see box text). The report by Kim et al.[1] in this issue underlines the potential for nanostructured dielectric materials to make capacitors an attractive energy storage option.

Contortions and Convolutions. To store more charge, it helps to increase the electrode surface area (see Figure 1). Two common capacitor types with increased surface area are the cylindrical coil capacitor with an insulating dielectric layer of oil-soaked paper or extruded polymer, and the ceramic multilayer capacitor. Convoluted or porous electrodes, which are commonly used in electrolytic capacitors, can greatly increase the effective area, like the nanotube forest electrode intended for use in electrochemical supercapacitors.[2]

Lining Up Help. The energy density in a dielectric is proportional to the product of the dielectric constant and the square of the electric field. (To be precise, the energy density is the integral of the product of electric displacement and electric field. In a nonlinear dielectric, the energy density can be
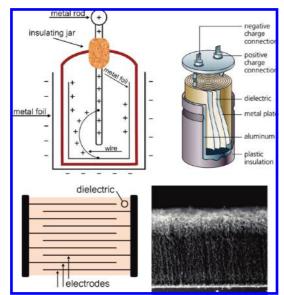

Figure 1. Capacitors store more charge, and thus energy, if their electrodes have a larger area. Various ways of arranging electrodes are (left to right) the Leyden jar is a glass vessel coated inside and out by conducting electrodes; the cylindrical capacitor is a rolled-up parallel plate capacitor; the multilayer multilayer with its staggered electrodes; a carbon nanotube forest electrode. Top-right panel courtesy of Thomas Publishing Company, LLC. Bottom-right panel courtesy of Riccardo Signorelli, LEES Laboratory, MIT.

ABSTRACT The ability to achieve high-energy densities is the central challenge in energy storage and recovery. A promising strategy for increasing energy storage is to use high-performance dielectric materials, such as highly polarizable nanoparticles or polymers, or nanocomposites of the two. In this issue, Kim *et al.* use a molecular coating and clever chemistry to combine oxide nanoparticles with a polymer matrix, thereby producing an improved nanocomposite dielectric. Some advantages and challenges of using nanocomposites as improved dielectric materials are presented in this Perspective.

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FROM GASOLINE TO BATTERIES TO CAPACITORS

Consider the quintessence of personal mobility—the automobile—which for more than a century has been almost exclusively powered by an internal combustion engine using gasoline or diesel fuels. The caloric energy content of gasoline is approximately 43 000 kJ/kg, and modern automobiles can make use of approximately 20% of this, or 8600 kJ/kg, permitting a range of hundreds of kilometers from a relatively compact and light on-board fuel supply. The dwindling of fossil fuel supplies and the recognition of the threat of global warming provoke other approaches. Battery power has been tried many times but always loses badly to gasoline. The reason is easy to understand: batteries are relatively heavy. For example, the nickel metal hydride batteries used in some hybrid vehicles store approximately 100 kJ/kg, meaning that over 3000 kg of batteries is needed to equal the range of 50 L (36 kg) of gasoline, even considering the high efficiency of electric propulsion. According to the manufacturer,[13] the 450 kg lithium ion battery pack (with over 6800 AA size cells and one-third of the vehicle's mass) in the all-electric Tesla Roadster stores over 400 kJ/kg and has an EPA range of approximately 350 km. Batteries have some drawbacks and limitations mainly stemming from the fact that they use chemical reactions to store and to release energy, which limits the speed of charge and discharge and also makes them very sensitive to operating temperatures. Further, they degrade over time, decreasing in capacity and increasing internal resistance due to irreversible reactions. For example, a lithium ion laptop battery can operate in a temperature range or 0 to 60 °C and last for hundreds of cycles.

Enter the capacitor, which is sprinkled liberally among the components of electric and electronic devices, with dimensions as small as a virus or as large as a tractor trailer. Each year, hundreds of billions of discrete capacitors are mounted onto circuit boards. Power capacitors are of particular importance in many applications, including filtering, load leveling, power conditioning, fast-response back-up power, and energy accumulation for pulsed power applications. Electrostatic power capacitors, such as ceramic multilayers, are very insensitive to temperature and can operate indefinitely long but have limited capacity, typically less than 20 J/kg. Electrolytic capacitors increase capacity by ion separation through a liquid or solid electrolyte and can store up to 200 J/kg but suffer from some of the drawbacks of batteries, such as sensitivity to temperature and limited lifetime. A big step above electrolytic capacitors are the electrochemical "supercapacitors" and "ultracapacitors", which store most of their energy in an electrochemical double layer and can store 20 000 kJ/kg or more. They offer capabilities ranging between those of electrolytic capacitors and batteries—an operating range from −40 to +65 °C and lifetimes of about a million cycles—and have been powering busses and trucks in Moscow for a decade.[14] They have charging and discharging times intermediate between electrostatic capacitors and batteries and can deliver more power per kilogram than either.

These comparisons are not meant to be a buyer's guide to electrical energy storage. The choice of technology also depends on the application, and there are many more factors to consider such as cost, efficiency, power, recharging time, leakage, cycle life, temperature range, and again cost. In any case, your mileage may vary.

very from the different nominal value. Further, if the dielectric is dissipative or slow to respond, not all of this energy can be recovered.[3]) The main approach to increasing energy density is to increase the dielectric constant. A material with a large dielectric constant can store proportionally more electrostatic energy. Common dielectric materials, such as polypropylene or silicone oil, have dielectric constants of only 2−3. Much higher dielectric constants are available from highly polarizable materials such as barium titanate (BTO), where the polariza-

tion arises from ion displacements, or polyvinylidene fluoride (PVDF), where the polarization arises from alignment of permanent dipoles. In both of these cases, the largest dielectric constants come from being near, but not in, the ferroelectric phase, as is the case with BTO nanoparticles[4] or with co- and terpolymers of PVDF.[5] Further, because the energy density increases with the square of the electric field, it is essential that the material has a high dielectric strength, the maximum field it can withstand without short-circuiting. For example, the PVDF ter-

polymers exhibit dielectric constants as high as 65 and have very high dielectric breakdown strength, meaning that they can be polarized with electric fields of 500 MV/m or more.[6,7] After considering losses and leakage, this produces capacitors that can store and recover 8 kJ/kg (13 J/cm^{3}) or more, which is quite impressive for a purely electrostatic capacitor.[6,7] Polypropylene capacitors have achieved similar electric field strengths but, because of the lower dielectric constant, store much less energy.[8] On the other hand, ion displacive dielectrics such as ferroelec-

An appealing approach is to find a way to combine the high dielectric strength of the polymers with the large dielectric constant of the oxides by embedding oxide nanoparticles in a polymer matrix.

tric BTO or relaxors in the lead manganate niobate (PMN) family would seem much better choices for high-energy density dielectrics because they have dielectric constants ranging from hundreds to thousands. Unfortunately, they have much lower dielectric strengths than polymers and, therefore, cannot take full advantage of the higher polarizability.

Packing It In. An appealing approach is to combine the high dielectric strength of the polymers with the large dielectric constant of the oxides by embedding oxide nanoparticles in a polymer matrix.[9] The nanoparticles would increase the effective dielectric constant of the composite, and the polymers would protect against electric breakdown. The main problem with this approach is that it takes quite a lot of high-dielectric constant

nanoparticles (*e.g.*, 25% by volume or more) to have an appreciable effect on the effective dielectric constant of the composite material, according to effective medium theory.[9,10] The dielectric strength, on the other hand, drops off precipitously even with only 5−10% nanoparticles by volume.[10] The result is that the maximum energy density decreases steadily with increasing particle concentration. Another challenge is that it is very difficult to keep nanoparticles from agglomerating, especially if they are forced into an incompatible matrix, weakening the composite electrically as well as physically. Further, the high dielectric constant of the particles effectively expels electric field lines, making the electric field in the matrix much higher than the average electric field. This field expulsion lowers the overall energy storage density and greatly increases the probability that the matrix itself breaks down. One approach to inhibiting electric breakdown is to incorporate many interfaces and convoluted paths between electrodes to staunch the avalanche of electrical breakdown, much as the contrasting dielectric constant does for multilayer polymer dielectrics (see Figure 2A).

The approach of Kim *et al.*[1,11] attacks two of the problems—agglomeration and percolation—with the same elegant approach. They functionalize the nanoparticles with an appropriate molecule, in this case, pentafluorobenzylphosphonic acid, coating them uniformly.[11] The coating does two critical jobs, as illustrated in Figure 2B:

(1) it prevents the particles from agglomerating in the polymer matrix (a copolymer of PVDF and hexafluoropropylene), and (2) it prevents percolation paths from forming through the oxide particles. The result is well-dispersed nanoparticle−polymer composites with up to ~50% nanoparticles by volume, accompanied by a threefold enhancement in the dielectric constant.

A drawback to this method is that the dielectric strength is reduced by about half. The pure copolymer still achieved the highest overall energy density; however, the nanoparticle−polymer composites did record higher energy densities at a more conservative electric field of 164 MV/m, up to 3.2 kJ/cm^3 or ~50% more than the pure copolymer. These results are reasonably consistent with effective medium theory.[10]

What happened at concentrations above 50% nanoparticles by volume was also instructive. Since the nanocomposites were made by ball milling the particles and polymer together, they were vulnerable to mechanical incompatibilities between the hard particles and soft polymer. This resulted in voids that started appearing at nanoparticle concentrations of 55% by volume, with voids reaching almost 40% by volume at the highest particle loading of 80% of the particle-matrix volume. When the voids are factored into the effective medium theory, the model explains the observed drop in dielectric constant in this range. The voids, however, dramatically lowered the dielectric
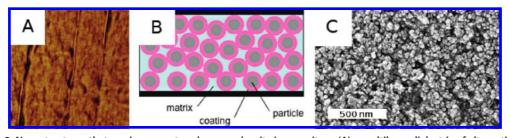

Figure 2. Nanostructures that can increase stored energy density in capacitors: (A) a multilayer dielectric of alternating nanoscale layers of polyethylene oxide (PEO) and ethylene−acrylic acid copolymer (EAA);[12] (B) a scheme for a coated particle−polymer nanocomposite capacitor; (C) an SEM image from a coated BTO−polymer composite.[1] Panel A reproduced with permission from ref 12. Copyright 2009 AAAS. Panel C copyright 2009 American Chemical Society.

strength, underlining another limitation to this approach.

The demonstration by Kim *et al.* using coated nanoparticles gives some confidence that the nanocomposite approach still has promise, mainly with respect to the effective dielectric constant. Although the weaknesses caused by both agglomeration and percolation and leading to dielectric breakdown have been considerably improved, the more fundamental weakness of field intensification in the matrix remains. For this, we will have to solve the difficult problem of preventing dielectric breakdown in the matrix and attempt to halt the electrical avalanche from the inside-out.

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