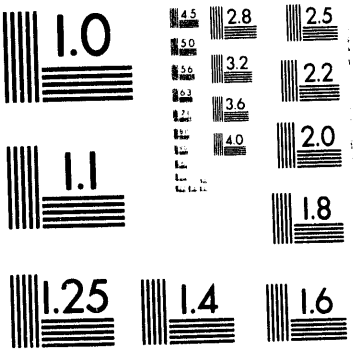
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PROMISING FUTURE ENERGY STORAGE SYSTEMS: NANOMATERIAL BASED SYSTEMS, ZN-AIR AND ELECTROMECHANICAL BATTERIES

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ABSTRACT

Future energy storage systems will require longer shelf life, higher duty cycles, higher efficiency, higher energy and power densities, and be fabricated in an environmentally conscious process. This paper describes several possible future systems which have the potential of providing stored energy for future electric and hybrid vehicles. Three of the systems have their origin in the control of material structure at the molecular level and the subsequent nanoengineering into useful devices and components: aerocapacitors, nanostructure multilayer capacitors, and the lithium ion battery. The zinc-air battery is a high energy density battery which can provide vehicles with long range (400 km in autos) and be rapidly refueled with a slurry of zinc particles and electrolyte. The electromechanical battery is a battery-sized module containing a high-speed rotor integrated with an iron-less generator mounted on magnetic bearings and housed in an evacuated chamber.

INTRODUCTION

Future emission regulations are driving the automotive industry towards the consideration of electric and hybrid vehicles. In order to achieve comparable performance to gasoline fueled internal combustion engines, significant improvements in current energy storage technology are required. Specifically, higher energy densities (energy per unit volume) and specific energies (energy per unit mass) will be required. Similar improvements in power density and specific power will also be required. Improvements in durability, shelf life, lifetime, and reliability will also be required in order to compete successfully with gasoline as a means of energy storage. Materials and manufacturing processes must be environmentally friendly, with an ability to be recycled high on the list of desired attributes. Most important of all may be the overall economic viability of any proposed new energy storage system.

Advanced materials and manufacturing technology offers several potentially promising new routes to energy storage systems with high energy and power densities. Several systems which are being developed and evaluated at Lawrence Livermore National Laboratory are based on understanding and controlling the nanostructure of materials. These systems are the aerocapacitor, the nanostructure multilayer capacitor, and the lithium ion battery. Another system, the zinc-air battery, takes advantage of past work in metal battery systems using air electrodes and novel self-feeding cell design for the zinc particulate fuel. Finally, the electromechanical battery offers a new look at an old technology taking advantage of new developments in high-strength fiber composites, magnetic bearings, solid-state power electronics and permanent magnet materials.

DISCUSSION

Aerocapacitor. The storage of electrical energy based on the separation of charged species in an electrolytic double layer is inherently simpler and more reversible than in secondary batteries. While obviously not batteries, capacitors offer the promise of an efficient, convenient way to store energy for peak demands (e.g., catalyst preheat, acceleration, starting motors, load leveling) and recover waste heat (e.g., regenerative braking). In most cases the cycle life of electrochemical double-layer capacitors is limited by the

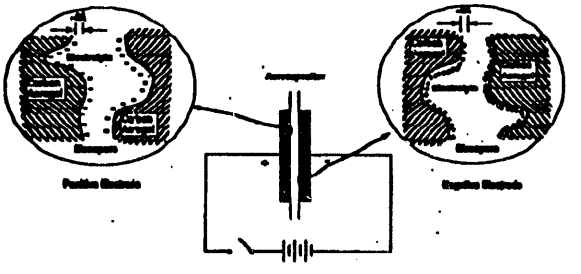

Figure 1. Schematic illustration of the enhancement in charge storage capability of an electrochemical double layer capacitor using high surface area, open porosity material.

device packaging and not by degradation of the device components. Though all electrode / electrolyte interfaces exhibit double-layer capacitance, only devices which do not exhibit faradaic reactions over the potential range of operation (i.e., are ideally polarizable) are considered electrochemical double-layer capacitors. The aerocapacitor (Figure 1) exhibits high double layer capacitance without resorting to faradaic reactions by taking advantage of the unique properties of carbon aerogels [1].

Carbon has the initial advantage of being electrochemically inert. Aerogels are a class of low density solid foams that are characterized by having open cell structures composed of particles usually less than 50 nm in diameter. Aerogels are usually made from silica precursors, and are noted for their outstanding thermal insulation properties [2]. Aerogels have not been widely used because of the difficulty in producing them (a critical extraction step is required, employing usually high temperature and high pressure) as well as the initial high cost of precursor materials.

Recently, organic aerogels have been synthesized by condensing aqueous solutions of resorcinol with formaldehyde in the presence of base catalyst [3,4]. The microstructure is regulated by the catalyst concentration. These materials routinely have surface areas approaching 1000 sq m/g. For organic aerogels with a high carbon content, such as resorcinol-formaldehyde, pyrolysis in an inert atmosphere results in the formation of essentially pure carbon aerogels. Besides having improved mechanical properties, these materials become conductive and suitable for application in energy storage devices. The capacitance density (F/cc) of devices made using these conductive, high surface materials can be as high as 25 F/cc without further surface activation. Figure 2 illustrates the dependence of capacitance on density.

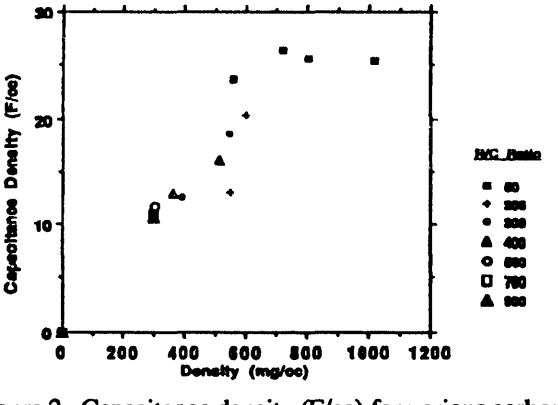

Figure 2. Capacitance density (F/cc) for various carbon aerogel catalyst ratios (R/C).

At the higher densities desired to maximize the capacitance, the carbon aerogel material is sufficiently robust to withstand air drying, thus eliminating the critical extraction processing step. Alternate monomer precursors have been demonstrated to also result in suitable carbon aerogel formation; many of these monomers are considerably less expensive than resorcinol, and in some cases the co-monomer, formaldehyde, can be eliminated as well.

The capacitance of the aerogel electrode is complicated by the distributed nature of the porous surface. The equivalent circuit diagram has been analyzed to include the effects of the separator length, the electrolyte conductivity in the separator, the matrix conductivity and the external resistance. Figure 3 illustrates the observed current discharge compared with the porous electrode distributed model and a simple resistive model.

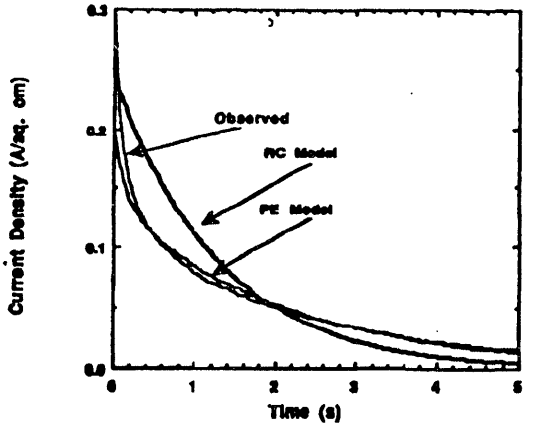

Figure 3. Observed discharge performance vs. porous electrode distributed model (PE) and simple resistive model (RC) for test device illustrated in Figure 5 and for 600 mg/cc carbon aerogel, R/C = 200, from 0.1 to 0.0 V.

Energy densities of approximately 25 J/cc have been measured for low voltage aerocapacitor devices with aqueous electrolyte; the corresponding power density is about 10 kW/kg carbon. The use of organic electrolytes, with higher breakdown voltages (i.e., 3-4 V vs about 1 V for water), results in higher energy densities albeit lower power densities. All of these values exceed DOE projected goals for EDLC in electric vehicles. These devices have been repeatedly charged and discharged, with over 85% retention of initial energy storage capability after 100,000 cycles. Current work is directed towards fabricating components and devices of increasing voltage specification; current devices have been limited to approximately 5 V. Reduction in internal resistance and improved manufacturability is being pursued through the incorporation of carbon paper and various methods of incorporating metal fibers into the electrode material.

Nanostructure Multilayer Capacitors.

Multilayer nano-technology [5,6] offers the possibility of fabricating new material structures with customized properties by controlling the structure [7,8,9] and hence properties at the near-atomic level. Since nano-engineered multilayers are characterized at the atomic scale they have large interfacial area to volume ratios. Although the most visible of such materials are semiconductor superlattices synthesized using molecular beam epitaxy techniques, multilayers may be synthesized using elements from all parts of the Periodic Table using MBE, evaporation, sputtering and electrochemical atom-by-atom technologies. Multilayer structures have been synthesized by PVD - in elemental form, as alloys, or as compounds - from at least 75 of the 92 naturally occuring elements. The microstructural scale of multilayer materials is typically determined during synthesis by controlling the thickness of the individual layers. These layers are one monolayer (0.2 nm) to hundreds of monolayers (>500 nm) thick and

generally define the in-depth grain size. These synthesis processes typically produce highly textured layers with the close-packed lattice plane of the material in the plane of the multilayer, although these grains are randomly oriented in plane.

Until recently, the macroscopic thickness of nano-structure multilayer materials has been generally limited to less than a few microns. Recently, processes for deposition of thick macroscopic nano-structure layers have been developed at Lawrence Livermore National Laboratory [10] and used to fabricate free standing high quality structures up to 500 microns thick containing up to 50,000 individual layers. The existing research synthesis system produces material having periods uniform to 2% of the individual layer thickness and areas of 400 sq cm. These macroscopic nano-structure multilayer materials enable use of standard diagnostic techniques for property characterization and open a path to develop devices with performance that approaches theoretical limits, be it with respect to mechanical properties, magnetic properties, or thermoelectric properties [11]. One application of this technology is the fabrication of capacitors with expected exceptional performance.

A parallel plate capacitor can be fabricated by depositing alternating thin layers of metal and dielectric (Figure 4). High energy densities (> 5 J/cc) should be possible with high operating voltages (in the kV range).

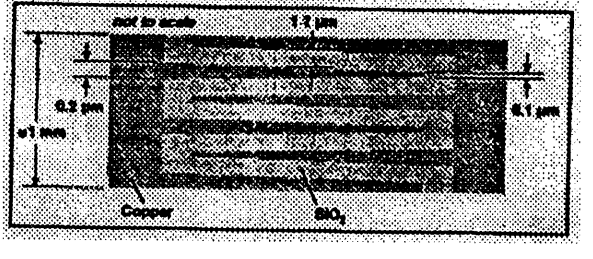

Figure 4. Cross section for a typical multilayer capacitor for a 600 V application.

There are several potential advantages to this design. First, a wide range of materials with corresponding different properties can be used. Initial designs are based on a simple dielectric [12], amorphous silica (SiO_2), with a dielectric constant of 3 and a maximum standoff field of about 6×10^6 V/cm. Standoff fields of these materials in thin film form are not currently well known but are expected to be substantially larger than those observed for commercial bulk materials formed using powder compaction /sintering processing (< 10^5 V/cm). In applications where high capacitance (as opposed to high voltage) is required a high dielectric constant material, $BaTiO_3$ for instance, would be used. Furthermore, unlike rolled foil with paper or polymer dielectrics, multilayer capacitors are solid state devices with excellent thermal and mechanical properties due to the low number of defects present. Figure 5 shows the volumetric capacitance and breakdown voltage versus thickness for multilayer capacitors based on amorphous silica (SiO_2).

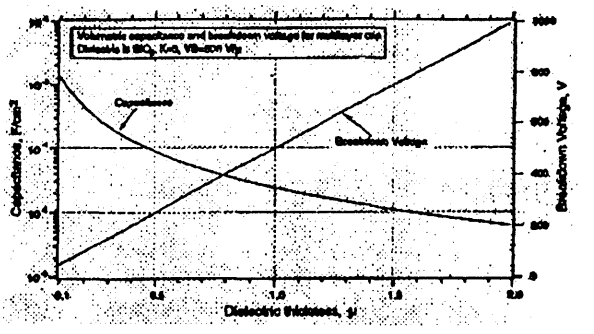

Figure 5. Volumetric capacitance and voltage breakdown curves for silica based multilayer capacitors.

A proposed SiO_2 dielectric 100 μF, 600 V device would be 9.0 x 5.5 x 0.13 cm, and could store 18 J (3 J/cc) if charged to its breakdown voltage. Initial laboratory results using $Zr/ZrO_2/Zr$ capacitor structures deposited on silicon wafers have demonstrated the technical feasibility of multilayer capacitors, with measured breakdown voltages of 3 MV/cm for approximately 1.2 microns of dielectric yielding an energy density of 10 J/cc.

Lithium ion batteries. The lithium ion battery is a rocking chair battery, with lithium ions moving from the metal oxide cathode of the battery through the separator and intercalating into the carbon anode [13,14]. Thus, the intercalating electrodes store the lithium, but are unchanged in so doing. This process is substantially safer than that used in conventional lithium batteries, where lithium metal is electroplated during charging. A substantial fraction of the electroplated lithium metal is typically non-uniform, powderous, or dendritic. With cycling, this leads to a rapidly fading capacity and consequently shorter life. There is also the possibility of dendrites forming which can puncture the separator and lead to a run-away battery short and explosion.

Lithium ion battery specific energy and energy density compare very favorably with other batteries, with projected values on the order of 120 W-hr/kg in comparison to about 30 W-hr/kg for NiCd. Sony's battery, which achieves about 60-70 W-hr/kg, claims its batteries can provide 1200 cycles at 100% depth of discharge or 50% more cycles than NiCd (and at 4000 cycles, projections indicate over 40,000 cycles at 30% depth of discharge). Superior power density is also available in lithium ion densities, potentially on the order of 250 W/kg at high energy densities, with high voltage (3.0 - 4.1 V).

Lithium ion batteries hold significant potential for electric vehicle applications; Honda has benchmarked the lithium ion battery for its electric vehicle development. However, to realize this potential additional improvements in performance have to be achieved. For example, Sony's carbon anode achieves approximately 50-60% intercalation of lithium. We have developed carbon foams which closely match the ideal spacing in LiC_6 of 3.70 Å coupled with

continuous structure and hence lower resistance than carbon particle composites. Up to 95% intercalation has been achieved, resulting in higher energy densities, through doping of the carbon foams. Formatting reactions are being reduced to lower the amount of lithium lost into the lattice during the initial cycles. Finally, work is progressing on optimizing the lithium metal oxide cathode to improve conductivity and lithium availability in a manufacturable process. Figure 6 illustrates the projected improvement in specific energy as a function of improved cathode utilization for various levels of carbon utilization.

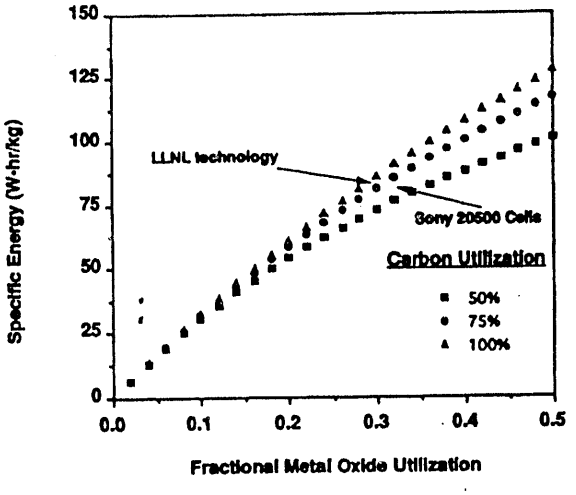

Figure 6. Effects of carbon and lithium cobalt dioxide utilization on energy density.

Zinc -air batteries

Background. We are developing a refuelable battery that provides electric vehicles with the essential functions of automobiles: long range (400 km); safe acceleration; and rapid (10 minute) refueling [15]. The battery consumes 1-mm size zinc particles to produce electricity and a liquid reaction product. Refueling consists of a hydraulic transfer of the reaction product and a return flow of zinc slurry to a hopper portion of each cell. The zinc fuel particles are recycled from the product liquid by an external electro-mechanical process. Refueling is particularly attractive for extending the range and mission of fleet vehicles such as transit busses, vans and taxis or enclosure industrial vehicles such as fork lift trucks, by making use of a fleet's existing home base for both refueling and fuel recycling.

(The same fuel recovery process can in principle be miniaturized and placed on board an electric car. This would allow overnight electrical recharge while retaining the option for range extension at a service station. This dual mode refueling aids market introduction in advance of an extensive service network. On-board recovery is more difficult and is beyond the scope of our current project.)

This fuel battery is limited by power (100 W-peak/kg) and not by energy (>150 Wh/kg), but can provide an electric car with performances nearly equivalent to diesel and modest 4-cylinder ICE autos. Attractive acceleration and improved battery life and economy require hybridization with a power device such as flywheel, high-rate batteries or supercapacitors, which may also be used to recover braking energy.

Technical Status and Plans. We have tested a novel battery configuration (600 cm^2 cells) which consumes 100% of zinc fuel particles gravity-fed from an overlying hopper. The cell supports an expanded quasi-stationary bed of negligible hydraulic resistance and constant properties. Air and electrolyte pumps consume < 0.5% of the gross output. Peak power exceeds 5 kW/m^2 at 50% discharge; nominal output power is 2 kW/m^2 at 1.25 V. The novel cell configuration has been engineered into 1000-cm^2 cell stacks with internal ("bipolar") series connection for tests in FY1994.

Hydraulic transfer to hoppers using dripless hose connectors eliminates human contact and potential liabilities, and avoids damage to cell membranes by rapidly moving slurry.

The nearest term application of this technology is fleet vehicles. Busses and vans powered by lead acid batteries have missions of only ~4 hours without battery exchange. Zn-air batteries can more than double this at about one-third the weight of lead-acid batteries. The zinc fuel battery will cost about $50/kW for large scale vehicles, and allows continuous operation with periodic refueling. Retrofitting the APS/MTD Villager Bus with a fuel battery and flywheel is expected to decrease gross weight by 15% (battery weight is reduced nearly threefold), double the range per refueling, and allow 24 hour/day operation where needed. Modeling of a parallel hybrid using zinc/air and advanced high power secondary batteries (for regenerative braking and power peaking) indicates a propulsion cost of ~1 kWh-AC/km and an overall electrical efficiency of 45-50 % for an 8.2 tonne bus on the SAE-J227a(B) cycle.

Air electrodes using organo-cobalt catalysts and similar to those used in our cells have tested over 12,000 hours in alkaline electrolytes under fixed discharge conditions and temperatures similar of those in a hybrid bus. Still, the electrode cost and life under actual duty cycles are not demonstrated. Other problems include demonstration of closure of the fuel cycle, control of electrode deterioration during cold standby, and optimization of the controller and power device, and the capacity of the electrolyte to hold zinc discharge products as a pumpable fluid.

Zinc may also be used as a vector for hydrogen energy. If the electrowinning of zinc is done with hydrogen reacted at a gas-diffusion anode, the cell voltage drops from 2.2 V to about 0.5 V, giving the vehicle a fossil-fuel/wheel-base energy transfer efficiency of 27-30%. This year, we plan to close the fuel cycle-by discharging recycled fuel in a bipolar stack of six 1000-cm^2 cells. An engineering design will be completed on a 24 cell stack for on-vehicle testing in an electric bus.

Table 1. Estimates of range extension and weight reduction for an urban bus of fixed time-average power of 12 kW (Based on APS Villager Bus, Oxnard CA).

Battery system	Curb weight tonne	Battery weight kg	Delivered energy, kWh	Peak power kW	Mission duration on charge, h
Lead/ acid	10.9 mt	2500	64	98	5.5
Zn/Air, Fly-wheel	9.3 mt	820 Zn/air + 100 fly-wheel	125	125	11, extendable

Electromechanical batteries.

The electromechanical (E-M) battery is a battery-sized module containing a high-speed rotor integrated with an iron-less generator, and housed in an evacuated chamber [16]. For the electric car, the E-M battery offers a means for overcoming the limitations of electrochemical batteries in specific power, deep discharge lifetime, and energy recovery efficiency.

In the late 1970s, LLNL carried out federally-sponsored studies of flywheel materials and technology. Federal funding for this work was terminated, nationwide, before a practical product emerged. In the intervening years, developments in materials, design concepts, and solid-state power electronics prompted a new look. What has emerged appears far more attractive than the concepts and the designs studied in the earlier work.

New materials, new design concepts. Besides long service life, two key requirements for vehicular batteries are high specific energy (Whr/kg) and high specific power (kW/kg). For an E-M battery, energy density is maximized by fabricating the rotor of material with the highest ratio of strength to density. Today, the prime candidate is fiber-composite made from graphite fibers embedded in an epoxy matrix. commercial graphite fibers now have strengths of 7.0 GPa (1,000,000 psi), heading toward 10 GPa, a factor of 5 improvement in 20 years. This improvement was achieved mainly through quality control in manufacture. Though costly now, the price for these fibers is heading down as their use increases. Our design studies have centered on the use of graphite fiber-composite for the rotor in an E-M battery.

High specific power is essential for snappy acceleration, to absorb high regenerative-braking rates, and to permit fast (5 to 10 minutes) charging times. In an E-M battery, high specific power goes hand-in-hand with high rotation speed. High rotation speed is achieved by downsizing the E-M module to about the size of a lead-acid car battery. Other advantages of small module size are major reductions in gyroscopic effects, and in containment problems in case of rotor failure. Our design studies have therefore concentrated on small modules, storing about 1 kWhr of energy each. The rotors of these modules are to be of the "multi-rim" type, that is, they consist of a series of nested fiber-composite cylinders, coupled to each other for torque loads by "separators" that insure mechanical integrity and rotational stability.

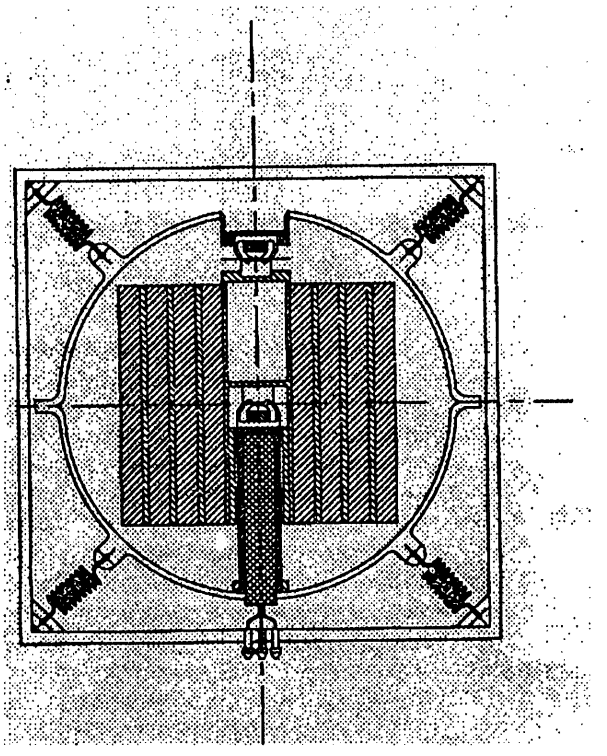

Figure 7. General layout of an E-M battery module.

Magnetic bearings—a key technology. Because the rotor of the E-M battery rotates *in vacuo* at speeds as high as 200,000 RPM, the only practical way to support it against the force of gravity, minimize frictional drag, and achieve long service life is to use a magnetic suspension/bearing system. We are now studying new concepts for magnetic bearings that promise to be much simpler and less expensive than the servo-controlled bearings now in use. With these new concepts, it should be possible to design a bearing that will not only accommodate vehicular acceleration loads, but reduce friction under standby conditions to the point that rotor rundown times (self-discharge) of weeks to months should be achievable.

The generator/motor: the "Halbach Array." Another key element in our E-M battery module is an iron-less generator/motor, the rotating field of which is produced by an array of permanent magnet bars supported against centrifugal forces by the innermost cylinder of the multi-rim rotor. By using the new Nd-Fe-B magnet material, deployed in a special array (the "Halbach Array" [17]), a rotating dipole magnetic field is produced within the assembly. This field then couples, through a re-entrant glass-ceramic sleeve-like vacuum barrier, to three-phase windings lying outside the evacuated region. The absence of hysteresis,

windage, and bearing losses leads to high transfer efficiencies. High rotation frequency results in high specific power—many times that of a V-8 engine.

The hybrid electric vehicle: a first use for the E-M battery. For economic reasons, the first vehicular use of our E-M battery modules will be in "hybrid" electric vehicles, where one or two E-M batteries provide or accept the peak power required for acceleration and braking, while a conventional electrochemical battery, a fuel cell, or a small heat engine provides average power. If the economics of mass production are favorable, the E-M battery might, in time, be able to take over the entire job, resulting in an electric car that could compete toe-to-toe with the best internal combustion-driven automobile.

CONCLUSION

Several promising new technologies have been identified and are being developed for evaluation as potential energy storage systems suitable for electric and hybrid vehicles. Some of these new technologies (i.e., aerocapacitors, nanostructure multilayer capacitors, lithium ion batteries) take advantage of the ability to control materials at the nano-scale, hence exert more profound control over the resulting macroscopic properties. Other promising technologies (zinc-air and electromechanical batteries) take advantage of new processing and systems design, in addition to modern materials.

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