Michelle L. Pantoya and Emily M. Hunt

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Nanochargers: Energetic materials for energy storage

Michelle L. Pantoya[1,a)] and Emily M. Hunt[2,b)]

[1]*Department of Mechanical Engineering, Texas Tech University, Lubbock, Texas 79409, USA*
[2]*Department of Engineering and Computer Science, West Texas A&M University, Canyon, Texas 79016, USA*

Nanochargers are energetic materials consisting of fuel metal particles and metallic oxide particles that absorb and store energy up to an ignition threshold. Once ignited a controlled exothermic reaction ensues producing energy. Nanotechnology has spurred the understanding of unique nanoparticle combustion behaviors that enable creation of nanochargers with optimized heat capacity for storing energy. Although in the initial stages, these experiments demonstrate evidence of the nanocharger's potential for energy storage and transfer. © *2009 American Institute of Physics.* [doi:10.1063/1.3263721]

Nanochargers could be described as a cross between a battery and molten salts. The reactants achieve similar thermal inertia properties of molten salts (enabling storage), but energy delivery is based on a chemical reaction, more similar to a battery. Storing thermal energy for extended periods may be useful for some forms of renewable energy, such as solar. In this way, heat energy stored within the nanocharger during the day could be easily delivered during evening hours, when the sun does not shine. Minimal energy would be required to ignite the nanocharger that is already at an elevated energy state and the ensuing reaction will produce thermal energy to drive a steam turbine (for example). The nanocharger could also potentially replace gaseous fuels such as propane and supply heat energy without hydrocarbon by-products. This concept is innovative because it draws upon recent develop-ments in combustion and thermal properties associated with nanoparticles.

Composite energetic materials contain both fuel and oxidizer as separate particles but when combined the mixture may be referred to as a propellant, pyrotechnic, thermite or in this case: a *nanocharger*. For the nanocharger the mixture is held in an inert state as the particles absorb energy. When triggered, the reaction is controlled by mass transport and energy required to diffuse reactants toward each other. Ignition leads to a slow-controlled, self-propagating, high temperature conversion of chemical energy to thermal energy. This thermal energy can then be channeled to produce steam that can be used for power generation.

Nanoparticle mixtures with higher surface area to volume ratios than coarser particle mixtures will exhibit en-
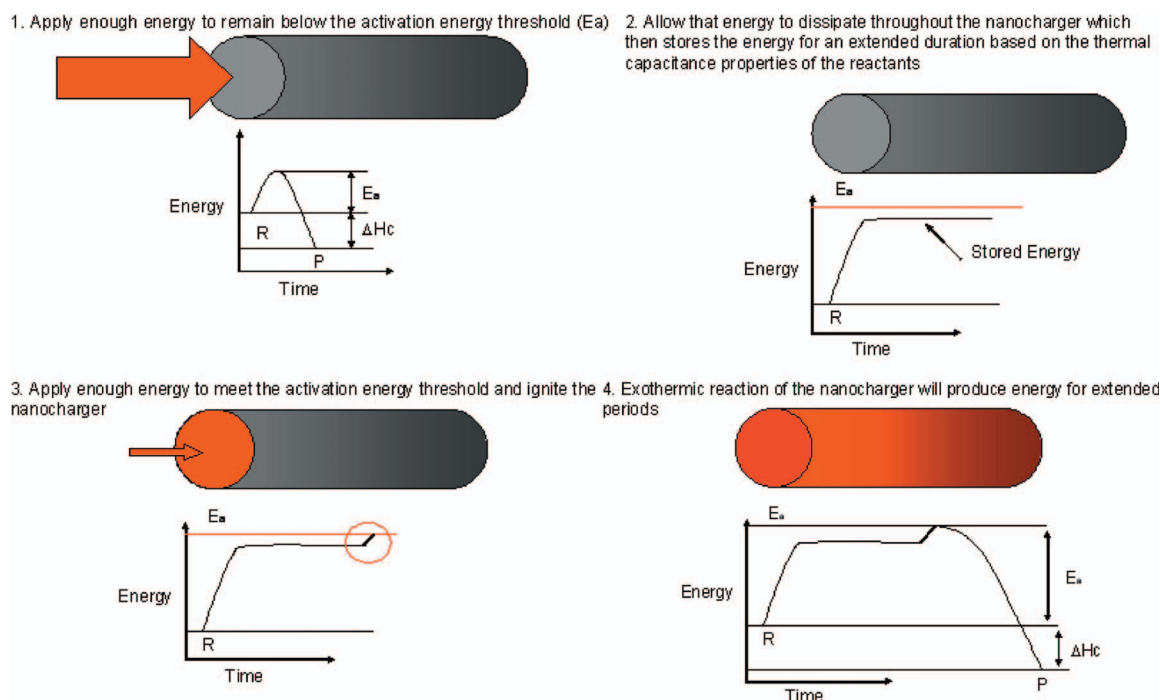

FIG. 1. (Color) Nanocharger concept sketch for energy storage and delivery. In sketched graphics R represents reactants, P is products, ΔH_c is heat of combustion and E_a is activation energy.

[a)]Tel.: 806-742-3563 ext. 227. Electronic mail: michelle.pantoya@ttu.edu.
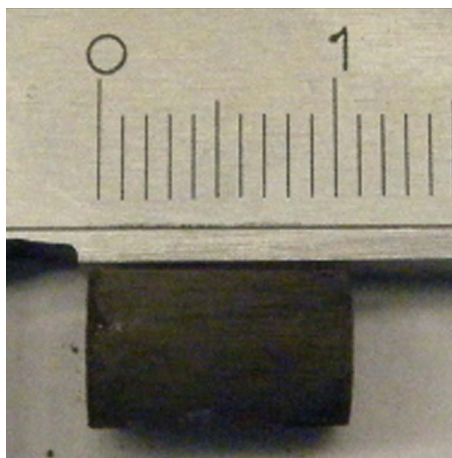[b)]Tel.: 806-651-5330. Electronic mail: ehunt@wtamu.edu.

FIG. 2. (Color online) Top and side view of a representative compressed pellet of $Al-Fe_2O_3$.

hanced thermal properties. Heat diffuses through individual particles and a compaction of particulate media orders of magnitude faster than coarser particles and composites.[1,2] Some studies indicate that at early times hyperbolic conduction may be dominant leading to an initial heat wave that produces more thermal uniformity.[3,4] The objective of this study is twofold: (1) to introduce the concept of using nanoparticle media to store and generate energy on demand; and (2) demonstrate the enhanced thermal properties of candidate formulations ideal for the nanocharger application.

The nanocharger works in four stages depicted in Fig. 1. Energy from the source is delivered to the nanocharger either in the form of electrical or thermal energy. The input energy is limited to below the activation energy threshold of the material, ensuring that the reactants remain inert. The graph in Fig. 1 illustrates conceptually the overall energy states of the reactants (R) and products (P) as well as the associated heat of combustion (ΔH_c) and activation energy (E_a) for the reaction. In stage 2, the energy applied to the nanocharger is stored within the reactants and maintained below the E_a. The reactants can store energy because the metallic formulations have enhanced thermal properties (such as capacitance) on the nanoscale. These properties enable the composite to uniformly distribute energy throughout the mixture and contain that energy for an extended duration. This theory is similar to that of a granular absorbent bed[5] and operates under the conditions of heat transfer through porous media. When the stored energy is needed, a small amount of energy is applied such that the activation energy threshold is met and the reactants ignite (stage 3). Stage 4 shows the nanocharger will
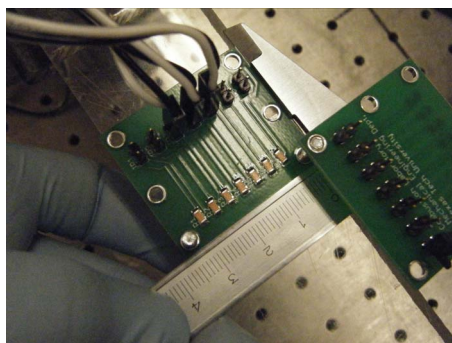

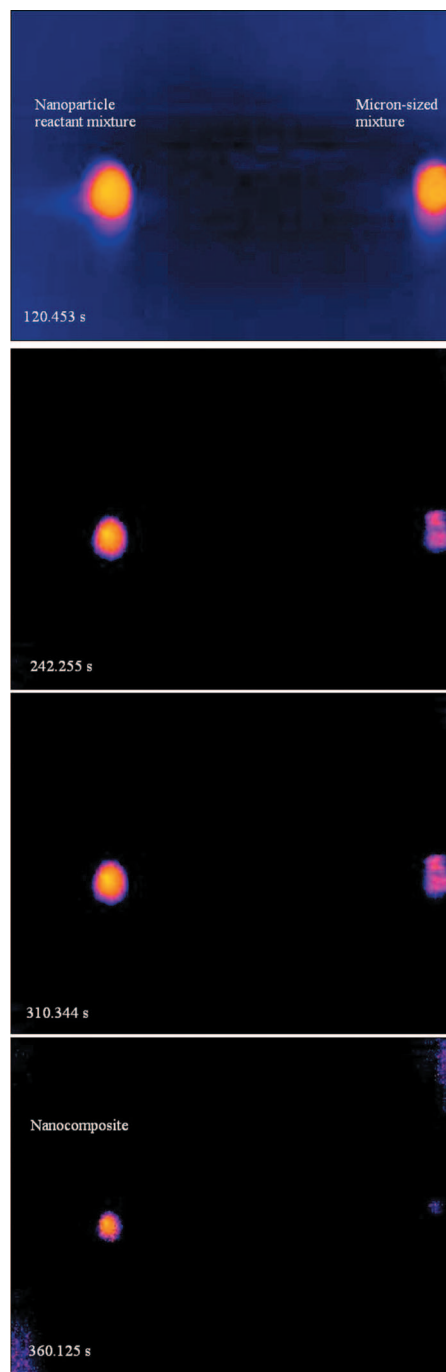FIG. 3. (Color online) Top view of the temperature recording device.

FIG. 4. (Color) IR thermal images time stamped for nanometric particulate mixtures and micrometer particulate mixtures composed of Al/Mn.

exothermically deliver thermal energy from a slow, controlled reaction.

Experiments were performed to demonstrate the enhanced capacitance properties associated with nanometric compared with micrometer particulate media. Experimental results were obtained for mixtures composed of Al/Mn and Al/Fe_2O_3. Mixtures were prepared by sonication in the same method as described previously.[6] The nanometer Al particles (nmAl) are obtained by NovaCentrix with an average particle diameter of 50 nm passivated with an average alumina shell thickness of 2 nm and are spherical in shape. The 10 μm Al (micron Al) particles were supplied by Sigma Aldrich and have an estimated 3 nm thick oxide shell and are also spherical. Manganese (Mn) and iron oxide (Fe_2O_3) were
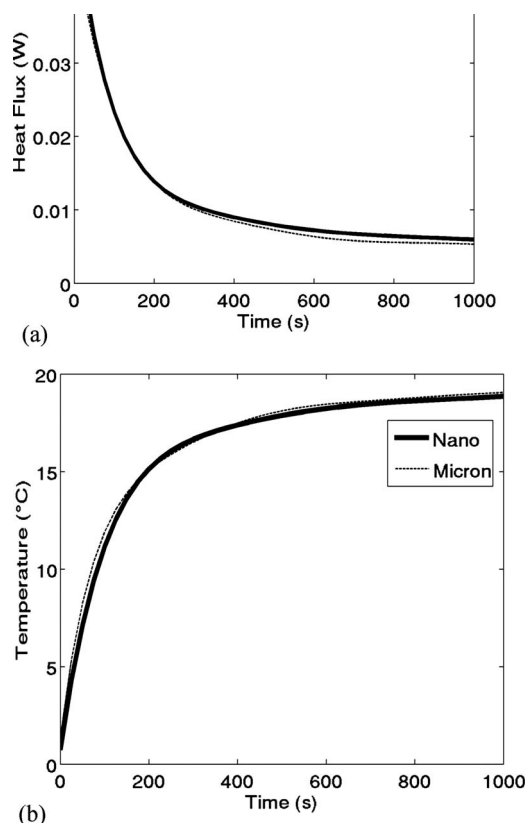
FIG. 5. (a) Temperature and (b) heat flux as a function of time for micron and nano Al–Fe$_2$O$_3$ samples.

TABLE I. Experimental data for heat capacitance measured for Al–Fe$_2$O$_3$ and calculated energy stored.

Particle size	Heat capacitance (J/kgK)	Energy stored (J)
Micrometer	555	13.3
Nanometric	641	15.3

purchased from AlphaChemicals and reported as submicron in size. Each mixture was prepared for a stoichiometric equivalence ratio of 1.0.

Each sample contained 920 mg of reactant mixture pressed to a theoretical maximum density of 70%. Three sample pellets of the same mass, dimensions (i.e., 6 mm diameter), and composition were examined (Fig. 2).

The pellets were exposed to near-freezing temperatures until they uniformly achieved a temperature of 1 °C. Each pellet was then exposed to ambient air and its temperature history was recorded. Pellet heating occurs through natural convection and conduction. In this way, estimates of the convection coefficient do not exceed 10 W/m^2 K and significant temperature gradients will not exist. The Biot number for both pellets will not exceed the value of 2×10^{-6}.

Infrared (IR) images of the pellets were recorded using an IR camera (FLIR-Indego, Inc.). Temperatures within the pellet were measured using the apparatus pictured in Fig. 3. The device consists of four thermistors, each separated by 4 mm. Three thermistors measured the pellet temperatures while the fourth thermistor recorded ambient temperature. To improve contact between the pellet and the thermistors a small amount of Artic Silver 5 thermal compound was applied. The thermal conductivity of Artic Silver reported by the manufacturer is 10 W/mK and with a clearance of <0.1 mm thermal resistance is negligible. During testing the entire apparatus was covered with acrylic material to minimize air flow.

These experiments are conducted to demonstrate the enhanced thermal capacitance of nanometric samples when compared with the traditional micron-composite samples. Figure 4 shows time stamped still-frame images from the IR

camera indicating the nanometric sample stored energy 46 s longer than the micron-composite material.

These results show that particle size can impact energy storage in unsaturated solid-solid systems of porous media. Figure 5(a) shows the temperature history of both the nanometric and micrometer composite pellets. The heat flux can be calculated from Newton's Law: $Q=hA\Delta T$, where A is the surface area of the pellet, ΔT is the difference between the pellet and ambient temperature and h is the natural convection coefficient calculated at every time increment. Figure 5(b) shows the corresponding heat flux as a function of time.

Values for the material capacitance are computed based on Fig. 5 and presented in Table I. There is a 15.4% measured increase in capacitance for the nanocomposite. These measurements were made from 920 mg sample sizes, but can be scaled with sample size. For example, the internal energy (E) stored is directly proportional to the nanocharger's mass (m), heat capacitance (c) and change in temperature (ΔT) (i.e., $E=mc\Delta T$). For a 1 kg sample at a temperature elevated from ambient to 600 °C (i.e., below the melting of Al), the data in Table I implies that a micron-composite will store 333 kJ, while the nanocomposite will store 384.6 kJ; which is a 15.4% increase using nanoparticulate media. Based on the length of extended storage in Fig. 4 (i.e., $t=46$ s), the extra thermal energy that can be stored per unit mass by the nanocomposite can be calculated as $Q=c\Delta T/\Delta t$ which results in 348 W/kg additional energy storage rate. At the elevated reactant energy states associated with stored energy the heat of combustion will increase (illustrated schematically in Fig. 1). On going studies will resolve theoretical and experimental increases in chemical energy available at elevated initial conditions. These studies will also elucidate the amount of thermal energy that can be stored compared with the amount of chemical energy available from reaction. Although only in the initial stages, these experiments demonstrate both qualitative and quantitative evidence of the nanocharger's great potential for energy storage.[7]

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