

Energetics and Power Generation

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Materials that are produced on the nanoscale have the promise for increased performance for energetics (such as propellants & explosives) and power generation devices (such as batteries & fuel cells and hydrogen storage).

1. Energetics

For solid propellants, nanomaterials promise increased energy density, controlled energy release, reduced sensitivity, reduced environmental impact, and long-term stability (Ref. 1 and 2). In the near-term novel propellants with nanoscale material will be used to reduce particle size dispersion (greater uniformity), reduce agglomeration of aluminum (increased combustion efficiency), and increase reaction rates (increased burning rates). In the long-term radical new propellant approaches will be explored to utilize 3-dimensional nanostructures that might yield controllable energy release and tailorable sensitivity.

Novel nanostructured propellants have the potential to combine the advantages of conventional composite and monomolecular propellants (Ref. 3). In conventional propellant composites, oxidizer and fuel are mixed to obtain desired energy properties. However, due to the granular nature the reaction kinetics are slow, as they are controlled by thermal and mass transport between micron and millimeter-sized particles. In monomolecular materials, where the energy release is controlled by chemical kinetics and not by mass transfer, much higher burning rates and greater power can be achieved than composites. The total energy density of monomolecular materials is only half of that achievable with composites. Based on nanotechnology it may be possible to combine the advantages of monomolecular materials (high burning rates) and conventional composites (tailoring of properties and high energy density).

1.1. Propellants with Nano-Aluminum

Recent experiments have shown that the ignition sensitivity and burning rate of nano-aluminum particles can be significantly higher than micron-aluminum particles. This resulted in increased burning rates and improved combustion efficiency for conventional composite propellants (Ref. 4). It was also observed that the nano-aluminum powder significantly reduced aluminum agglomeration. The low agglomeration rate may be the result of a thin aluminum oxide layer on the aluminum particles as observed on transmission electron microscope images.

1.2. Nanostructured Propellants

For this new class of propellants, nanostructured pyrotechnics (thermites) and organic nanocomposites (propellants) will be discussed.

For thermites, a method will be described for the synthesis of nanostructured fuel/oxidizer material (Ref. 5). Fuel and oxidizer association is enhanced by electrostatic forces, which exist between charged aerosol particles. The goal is to enhance interaction of fuel and oxidizer and minimize fuel-fuel and oxidizer-oxidizer interactions by oppositely charging each component in the aerosol. The nanoscale assembly strongly depends on the collision rate between fuel and oxidizer particles. For the specific example with an aluminum/iron oxide thermite mixture, the flame propagating velocity in a spark ignited sample was significantly increased, when the structures were ordered through bipolar coagulation as compared to random structures with Brownian coagulation. The improvement was also shown with differential scanning calorimetry (DSC) analysis. The DSC shows that the rate of exotherm observed in the electrostatically enhanced case is a factor of 10 faster. Transmission and scanning electron microscope studies also showed that the nanocomposites had markedly different energy release and thermal properties compared to conventional micron sized iron oxide thermite, because of the efficient degree of mixing and intimate nanostructuring of the novel material.

For organic nanocomposites, monolithic energetic polymer gels were prepared in acetone by separately cross-linking various precursors (Ref. 6). The synthesis conditions were optimized according to precursor mass ratio, cross-linking agent, solvent, and catalyst concentration to achieve micron and submicron pores. The high energy explosive was trapped in the energetic polymer gel using sol gel processing with a modified freeze-drying process. The compositions of the composite energetic materials were tailored and optimized at the nanoscale according to the desired performance and reduced sensitivity. The impact sensitivity of the composite energetic materials was lower than the pure energetic explosive. With regard to safety the following observations can be made: (1) sol-gel methodology offers advantages in processing with water-like viscosity for casting, ambient temperature gelation, and low temperature drying and (2) decreased sensitivity has been generally observed by shrinking particle size in propellants (because of more homogeneous mixture and fewer potential hot spots). However safety properties need careful evaluation for each new propellant.

Future goals are 3-dimensional nano-energetics with a high degree of structure and order for controlled reactivity and improved manufacturability.

2. Power Generation and Hydrogen Storage

2.1. Batteries and Fuel Cells

For batteries, nanostructured materials are being explored to increase electrical capacity of the electrodes and to increase ion conductivity and long-term stability of the electrolytes (Ref. 7). For lithium batteries anodes, templated nanostructures are being

explored to fabricate nanoscale materials having the specific sizes and dimension needed for optimum performance. One example is an anode consisting of 110-nm-diameter SnO₂ nanofibers reduced to a Sn based nanocomposite to increase number of discharge cycles, improve discharge rates, and reduce capacity losses.

For fuel cells, nanostructures are also being explored for electrocatalysts. One example is a nano-architected Pt catalyst using sol-gel techniques. In this nanomaterial, carbon powder provides a continuous electronic network to the 2-nm carbon-supported colloidal Pt nanoparticles within the continuous nanoscale network of the SiO₂ aerogel. This 3-D porous pathway results in significantly enhanced catalytic activity.

2.2. Hydrogen Storage

For hydrogen storage there are many conflicting reports on the degree of hydrogen adsorption and desorption in nanocarbons (Ref. 8 and 9). Results of around 4 wt% storage in Single Wall Nanotubes (SWNT) and Graphite Nano Fibres have been recently achieved in reproducible tests, which is still below the US Department of Energy goal of 6.5 wt%. Hydrogen storage is also explored in nanostructured magnesium-related materials, which are manufactured through mechanical alloying and milling. These nanomaterials show acceptable hydrogen storage performance at elevated working temperatures, however the storage capacity drops down dramatically at temperatures below 200C. In these tests, hydrogen was essentially loaded under pressure into the nanotubes and nanomaterials (physical approach). In the following hydrogen storage using the chemical approach is discussed.

Single wall carbon nanotubes were electromechanically functionalized with hydrogen and nitro groups (Ref. 10 and 11). Hydrogen adsorption on the SWNTs was carried out in the presence or absence of electrodeposited catalytic nanoparticles of magnesium. For the electrochemical functionalization process, SWNTs were deposited on Teflon-coated membranes by vacuum filtration, lifted off as free-standing nanopaper, and used as the electrodes. Hydrogen uptake on the nanotubes was characterized by micro-Raman spectroscopy, thermogravimetric and thermopower measurements. Adsorbed hydrogen levels up to about 2 weight percent has been observed without catalyst. Mg coating enhanced the hydrogen uptake.

In summary, nanomaterials have a high potential for energetics and power generations. Groundbreaking work has been started and has resulted in first successes. However, science at the nanoscale has to advance to fully exploit the potential of this emerging technology and to understand, control, and fabricate complex nanomaterial structures.

References:

- 1) David Mann, US Army Research Office. Personal Communication
- 2) A.W. Miziolek, "Nanoenergetics: An Emerging Technology Area of National Importance", The AMPTIAC Newsletter, Volume 6, Number 1

- 3) A. E. Gash, et. al, "Nanostructured Energetic Materials with Sol-Gel Methods", LLNL Publication, Mat. Res. Soc. Symp. Proc. Vol. 800 @ 2004 Materials Research Society, Paper # AA2.2; also UCRL-PROC-201186
- 4) D.T. Bui, A. I. Atwood, P. O. Curran, and T. M. Atienzamoore, NAWC China Lake, "Effect of Aluminum Particle Size on The Combustion Behavior of Aluminized Propellants in PCP Binder", 35th International ICT-Conference, June 29- July2, 2004, Karlsruhe, Germany
- 5) S.H. Kim and R. Zachariah, "Enhancing the Rate of Energy Release from NanoEnergetic Materials by Electrostatically Enhanced Assembly", Adv. Mater. 2004, 16, No. 20, October 18
- 6) Jun Li and B. Brill, "Nanostructured Energetic Composites of CL-20 and Binders Synthesized by Sol-Gel Methods", Propellants, Explosives, Pyrotechnics 31, No. 1(2006)
- 7) R.T.Carlin and K. Swider-Lyons, "Power from the Structure Within: Application of Nanoarchitectures to Batteries and Fuel Cells", The AMPTIAC Newsletter, Volume 6, Number 1
- 8) R.A. Shatwell, "Hydrogen Storage in Carbon Nanotubes", RTO/AVT Symposium, Brussels, 2003, published in RTO-MP-104
- 9) J. Bystrzycki, et al, "Recent Developments in Nanostructured Magnesium-Related Hydrogen Storage Materials", RTO/AVT Symposium, Brussels, 2003, published in RTO-MP-104
- 10) Yubing Wang, et al, "Nanoscale Energetics with Carbon Nanotubes", Mat. Res. Soc. Symp. Proc. Vol. 800 @2004 Materials Research Society
- 11) Yubiing Wang, et al, "Electrochemical Nitration of Single-Wall Carbon Nanotubes", Chemical Physics Letters 407 (2005) 68-72