



Nanomaterials for High Performance Lithium Ion Batteries

MetaMateria is developing a number of active nanostructured materials for Lithium ion batteries. The initial focus is on electrodes that exhibit superior performance compared to traditional micron size materials. Due to a nanoscale structure, it is possible to introduce new active reactions, decrease the path length for Li ion transport, and improve stability and specific capacity. Furthermore, composite nanostructured materials designed to include conductive paths can decrease the interface resistance leading to higher specific capacities at high charge/discharge rates.

Advantages of Nanomaterials

Nanostructured materials offer a tremendous potential for developing high power density Lithium ion batteries with high rate capabilities. Some of the advantages that can come from use of nanostructured electrodes:

- A large amount of Li^+ host material is available near the particle surface because the volume/surface ratio is very large with nanoparticles. Since reactions occur mostly near the particle-surface. This ***facilitates rapid charge-discharge*** without the slow solid-state diffusion of Li^+ (within particle).
- Nearest-neighbor distance between active particles is small for nanoporous cathodes, so *surface regions* of particles are available within short distances. This increases the probability of fast reactions near the surface (as opposed to slower volume-reactions within particles). This also ***facilitates fast charge-discharge rates***
- Reactions occur mostly in surface regions of particles, so stress induced deformation and the breakdown of the crystal lattice from repeated charge/discharge is minimized. ***This improves cycle life and coulomb efficiency.***
- Even for solid state (within particle) diffusion, the path length is small in nanoparticles. This ***dramatically reduces intercalation/de-intercalation time.***
- Nanoparticles provide large interface area for Li^+ insertion/extraction. ***Increases the specific capacity.***
- At high charging/discharging rates (C-rates), current density increases and slow Li^+ transport causes concentration polarization within the active material, preventing full utilization of the capacity. This problem is minimized with nanomaterials with high active surface area. ***Current density decreases and mass transport becomes faster*** (diffusion length is reduced).

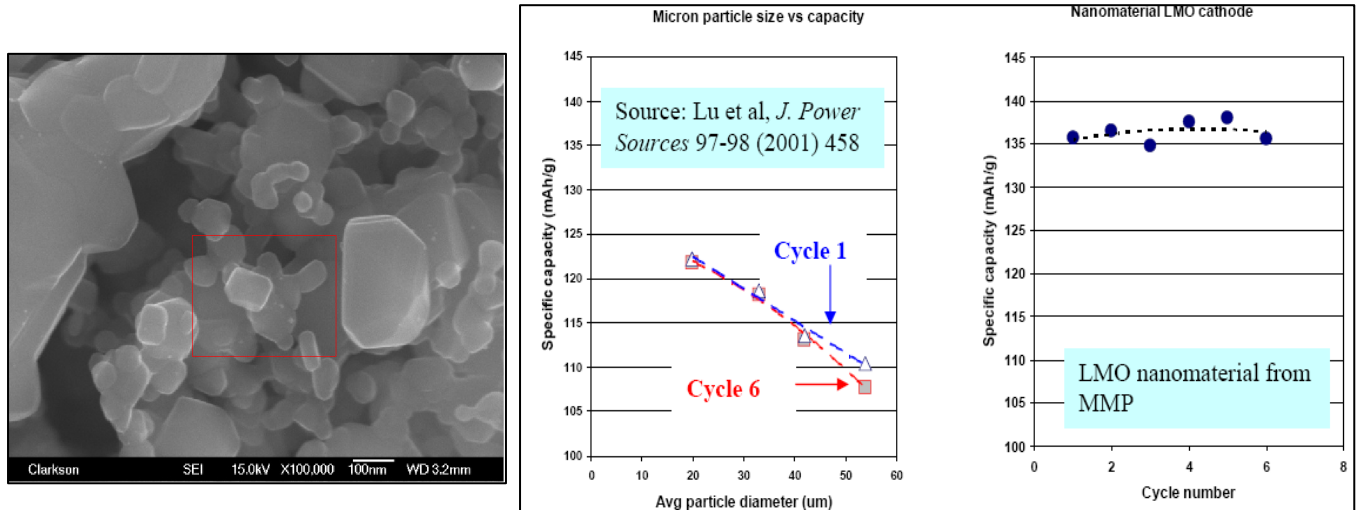
Nanostructured thin films (1-15 micron) have been prepared by MetaMateria and then tested using a lithium anode and a standard liquid electrolyte at room temperature. What has been found is:

- (i) ***fast charge/discharge***
- (ii) ***very good capacity retention***
- (iii) ***high energy density at high power density***

Property improvements can be expected when nanostructured materials are used for electrodes and electrolytes. What is described in this summary are results of current testing done on LMO (lithium manganate) cathodes made by MetaMateria. These illustrate potential improvements available with the proper use of nanostructured materials. Similar results were found with LCO (lithium cobalt oxide). These were studied primarily for thin film battery applications, along with novel anodes and new electrolyte nanomaterials. Performance-limiting factors in traditional lithium ion cathode materials include capacity, operational voltage, charge-discharge rates (rate capability), and energy density. Nanostructured cathodes address all of these.

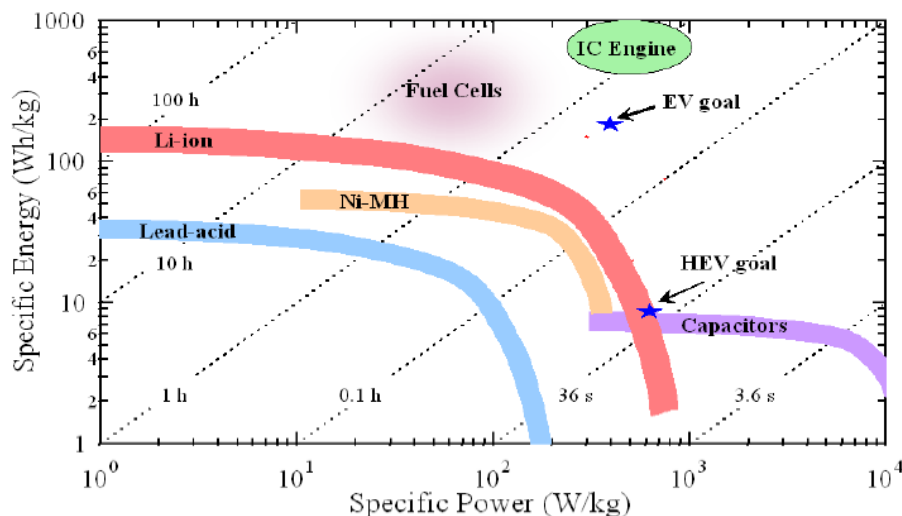
Nanostructured Cathode Development

Nanostructured cathodes show improved properties in terms of power and energy density compared to traditional materials. Shown below is a microstructure from a 10 μm thick LMO film that has a dual grain structure with the smallest grains $\sim 20\text{ nm}$. Grain size is important to the specific capacity of LMO and this is shown below in the left-box, where the capacity of LMO cathodes made with micron size particles drops from 122 mAh/g as the grain size increases from 20 to 55 micron. For larger grain sizes, performance has already begun to drop after 6 cycles. In contrast, the right-box shows results of a nanostructured LMO cathode that has a higher specific capacity ($\sim 135\text{ mAh/g}$), which remains constant with cycling.



Ragone Plots

Ragone plots are used to compare the performance of various types of energy storing devices, as shown in the example below. These Ragone plots are of **energy density** ('Y' axis) versus **specific power density** ('X' axis), with both axes being logarithmic. **Energy density** is a measure of how much energy can be stored whereas **specific power** represents how rapidly energy can be removed. The parallel slanted lines represent different discharge rates and the numbers on these lines represent discharge times. A shorter discharge time is generally better (right part of graph). This plot shows that energy density starts to drop sharply when energy is pulled out too fast, which for Li-ion is $\sim 100\text{ Wh/kg}$ ($\sim 15\text{ min}$ discharge). A specific power of $\sim 1000\text{ W/kg}$ is the practical limit for these conventional devices. The graph also shows the Electric Vehicle (EV) and Hybrid (HEV) goals set by the Department of Energy.

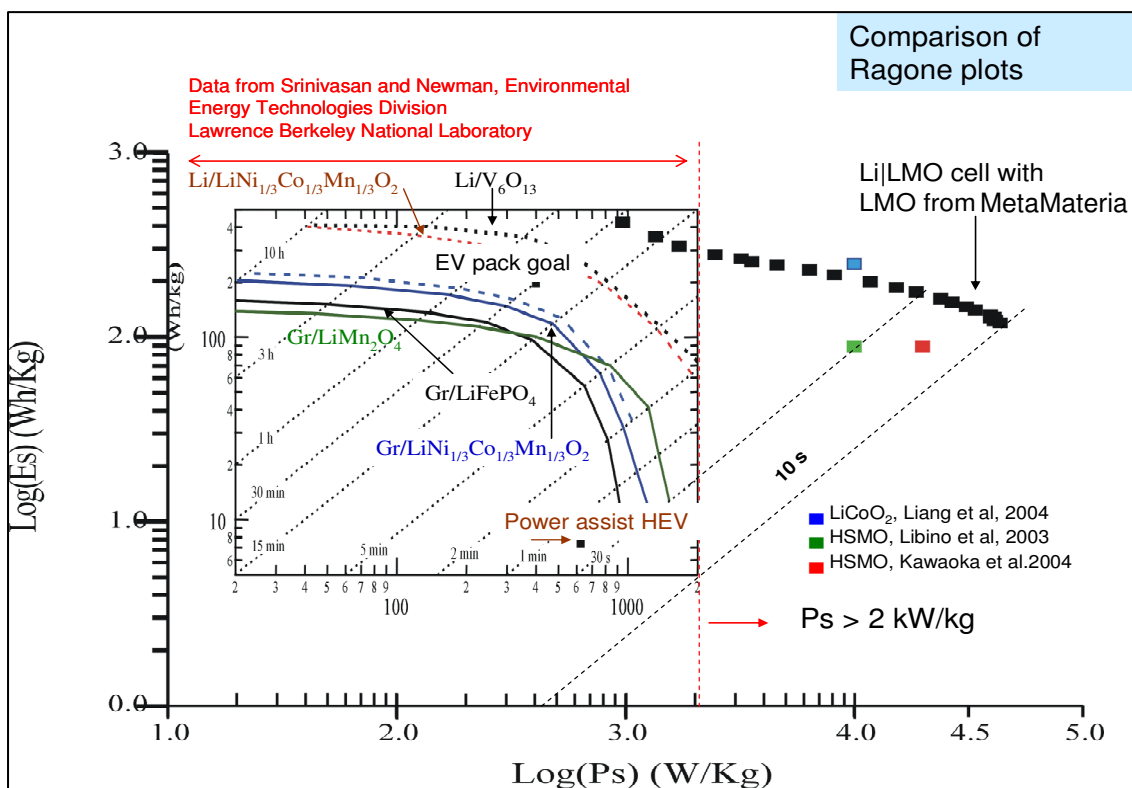


Cathode Performance

The Ragone plot below shows comparative performance of different LMO cathode materials and those with other chemistries. Material performance improves as data in the Ragone plot moves toward the upper right corner of the graph (high power density and high energy density).

Superimposed on this plot of traditional materials is data measured for nanostructured cathode coatings prepared by MetaMateria that were from 1-15 micron thick. For these coatings, energy density stays above 100 Wh/kg even under very fast discharge conditions (10s, at ~80-C and 12 A/g current). Fast discharge rates (>30-C) are considered as "pulse-power" for many applications. Performance was independent of film thickness.

Data shown in this Ragone plot clearly demonstrates that nanostructured electrode materials can provide superior performance to conventional materials with the same chemical composition. Power density for nanostructured LMO is above 200 Wh/kg and specific power extends above 10000 W/kg. While this data is for thin films, it indicates what can be expected when nanomaterials are used properly. Nanomaterials also provide opportunities for batteries to be engineered with high capacity under fast discharging or the battery will last longer at high power conditions.



The need to store energy, in increasingly more energy-dense formats, is pervasive across all demographics. Applications for Lithium ion batteries often require high energy and power densities, quick recharging time, and safe operation at different temperatures. MetaMateria is using its considerable expertise for making and applying nanomaterials to address these performance issues, with support from government and industrial organizations. MetaMateria is interested in new partners and new applications for the use of nanomaterials in energy storage devices.

For more information, contact:

Dr. Suv Sengupta (ssengupta@metamateria.com) or J Richard Schorr (jrschorr@metamateria.com)