

NEWS RELEASE

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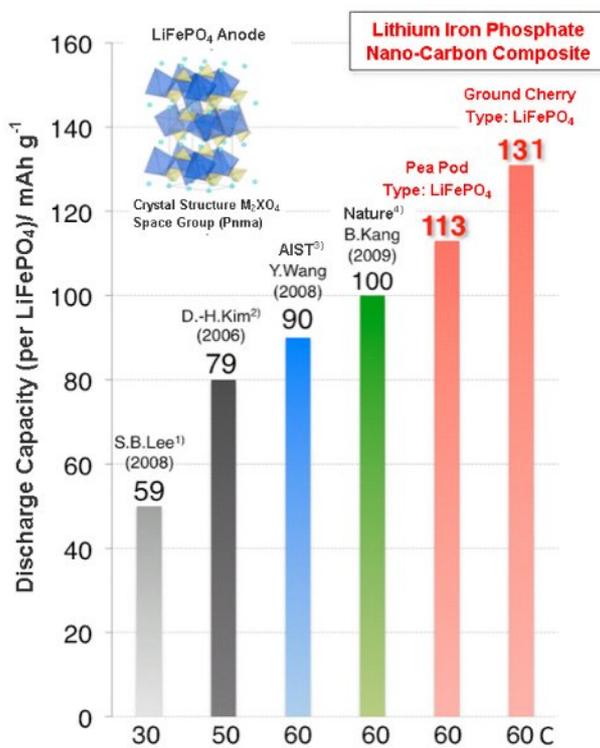
Applying “nano-hybrid technology” to the next generation lithium-ion battery

**Development of battery materials
with world’s highest performance**

Enhances capacity and output of lithium iron phosphate (LiFePO₄) as well as
output and charge-discharge cycle life of tin oxide (SnO₂)

The Naoi Laboratory of the Graduate School of the Tokyo University of Agriculture and Technology (TUAT) and “Capacitor Technology Course” which is funded by Nippon Chemi-Con Corporation at the University have achieved a dramatic improvement in the performance of lithium-ion battery materials. Output (Power density) and cycle characteristics have been significantly improved through an original, simple processing technology employing only safe and abundant raw materials. The results demonstrate great potential for the development of next generation lithium-ion batteries.

The University group dramatically improved the performance by developing a unique carbon nano-structure containing specific active materials. The group has successfully developed two new types of nano-structured positive electrode materials made by incorporating lithium iron phosphate (LiFePO₄) inside unique carbon structures. They are called “ground cherry type” and “pea pod type.” Both materials deliver the world’s highest capacity per g active material at 60 C (charge-discharge of 60 seconds). They also achieved development of a new negative electrode material by enclosing tin oxide (SnO₂) within a unique carbon structure. It features high power output and cycle life - in excess of 800 cycles at 10 C (360 seconds charge-discharge).



This article presents details of these unique new materials and features of their potential for use in batteries and capacitors offering unprecedented performance.

Background

The key to this development is the “nano-hybrid technology”. This is a unique technology developed by K&W Inc., a venture company spun off from TUAT. Materials based on nano-sized particles and carbon can be prepared, relatively simply, as highly dispersed compounds in an ultra-centrifugal force field by using a

sol-gel method. The university group has so far applied this technology to develop the next generation high-performance capacitor, “nano-hybrid capacitor.” Its negative electrode is a composite material made of nano-crystalline lithium titanate and carbon nano-fiber. The hybrid capacitor features ultra-high power output results from the compounding of nano-crystalline lithium titanate particles with size of (5 to 50 nm dia with highly conductive carbon nano-fibers in a highly dispersed state. In regard to this, Nippon Chemi-Con announced on March 2010 that it will start mass production of this capacitor (plans to start sample shipment in April 2011), and in April 2010 TUAT first announced their research results using CNT (super growth carbon nano-tube) materials .

Application to the next generation battery materials

K & W plans to apply this nano-hybrid technology to all the important lithium-ion battery materials. Considering the fact that lithium-ion batteries will be broadly launched, thereby enabling new automotive technologies, the University group selected electrode ideas based on widely available raw materials that would also ensure high safety.

(1) Positive electrode material: Lithium iron phosphate (LiFePO₄)

Lithium Iron Phosphate (LiFePO₄) was selected for the positive electrode material for their lithium-ion battery. LiFePO₄ is a candidate next generation battery material as it is made from more widely available raw materials and affords higher safety as compared with the widely used lithium cobalt oxide. However, it was necessary to reduce charge-discharge time (increase output) when using LiFePO₄. A structural problem caused low lithium-ion conductivity and made for impractically long charge-discharge times.

The University group successfully prepared **two new unique nano-composite materials (ground cherry type and podded pea type)**. In the first type nano-crystallized LiFePO₄ particles are incorporated within carbon through the application of the nano-hybrid technology. This material features

the world’s highest capacity and output (a discharge capacity of 113 to 130 mAhg⁻¹ at 60 C: 1 second). Its high electric conductivity and ionic diffusivity could not have been obtained by conventional solid phase processing or hydrothermal synthesis methods. This result indicates the possibility to develop a safer lithium-ion battery with enhanced output performances.

A battery consisting of this LiFePO₄ positive electrode and their lithium titanate (Li₄Ti₅O₁₂) negative electrode will feature almost the same power density as electric double layer capacitors (EDLCs). The energy density is over 6 times greater when

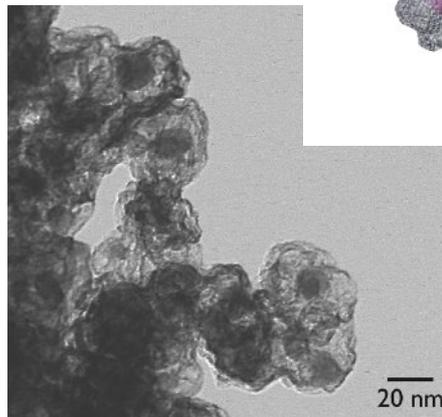
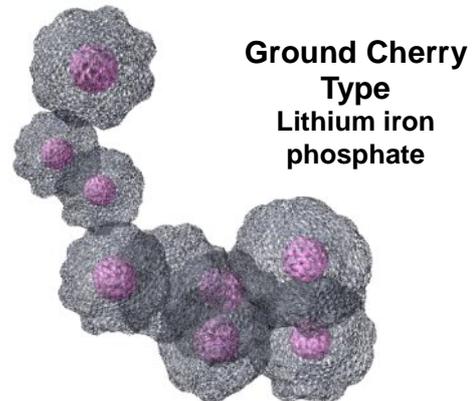
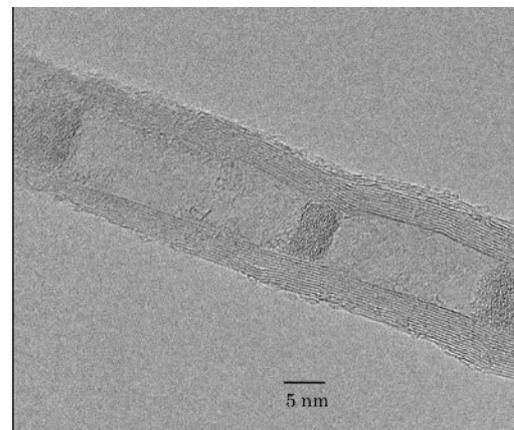
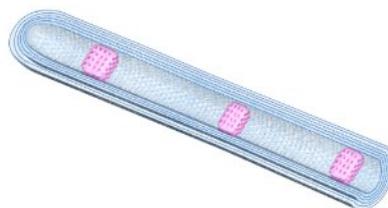
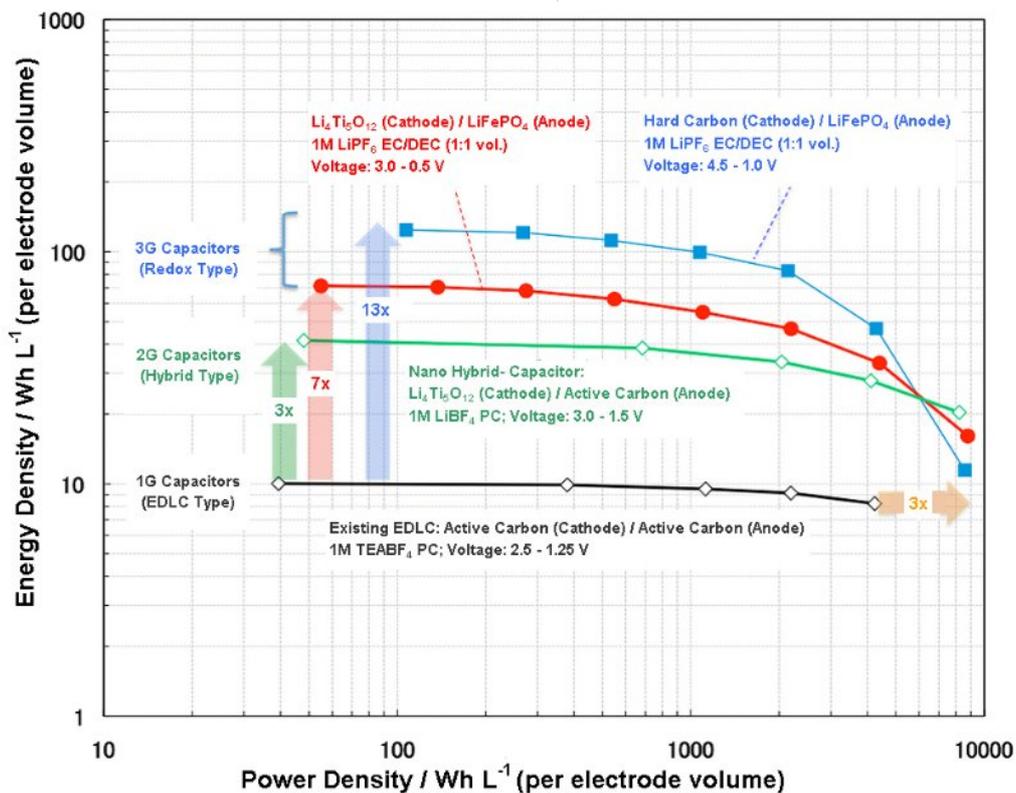
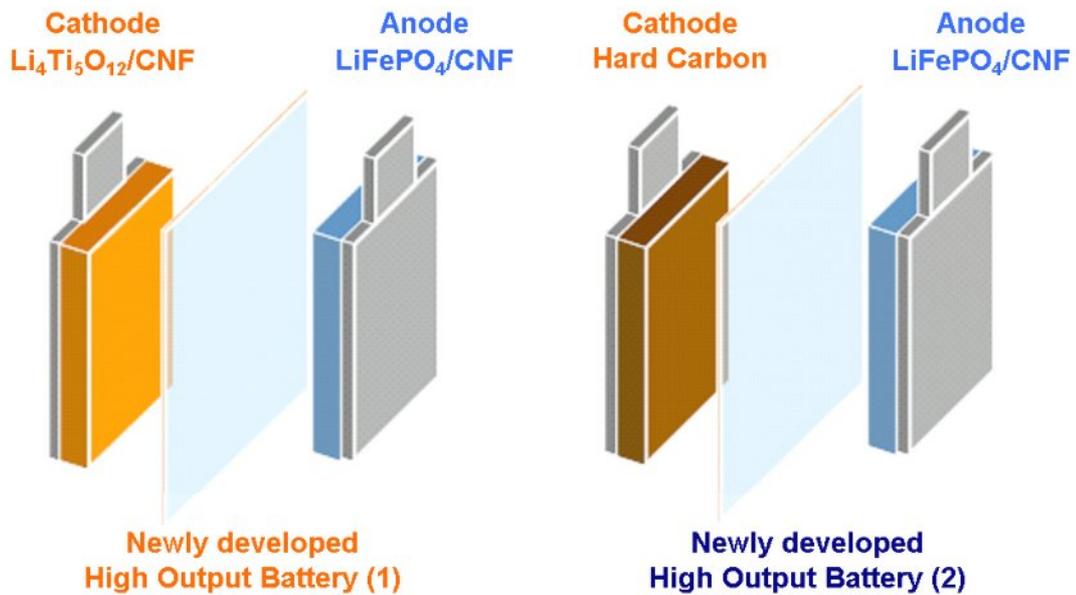


Image of Lithium Iron Phosphate Nano-Composite through high resolution scanning transmission electron microscope: Like a ground cherry, LiFePO₄ nano-particles are enclosed inside the spherical carbon.



High resolution scanning transmission electron microscope image: Like a pea pod, LiFePO₄ nano-particles are incorporated inside the carbon nano-fiber.

compared to EDLCs. These ultra-high output batteries demonstrate higher output characteristics than those of a capacitor (approximately 3 times higher than those of existing EDLC or the first generation capacitors). The energy density of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiFePO}_4$ battery is 7 times higher than a typical EDLC, and the energy density of the Hard Carbon/ LiFePO_4 battery is approximately 13 times higher than that of typical EDLC. These types of batteries can also be regarded as high energy density redox capacitors which are made of positive/negative electrodes using redox (battery electrode) materials. Development of these batteries will make it more difficult to draw a conceptual line between a battery and a capacitor, and is believed to create a completely new category, namely the third generation capacitor. The Nano-hybrid capacitor ($\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Activated Carbon}$) which has been categorized as a second generation capacitor (hybrid type) exhibits energy densities that are 3 to 4.5 times higher than those of existing EDLCs. However, the batteries developed here have achieved simultaneous enhancements in both energy- and power density that far exceed those of conventional EDLCs.

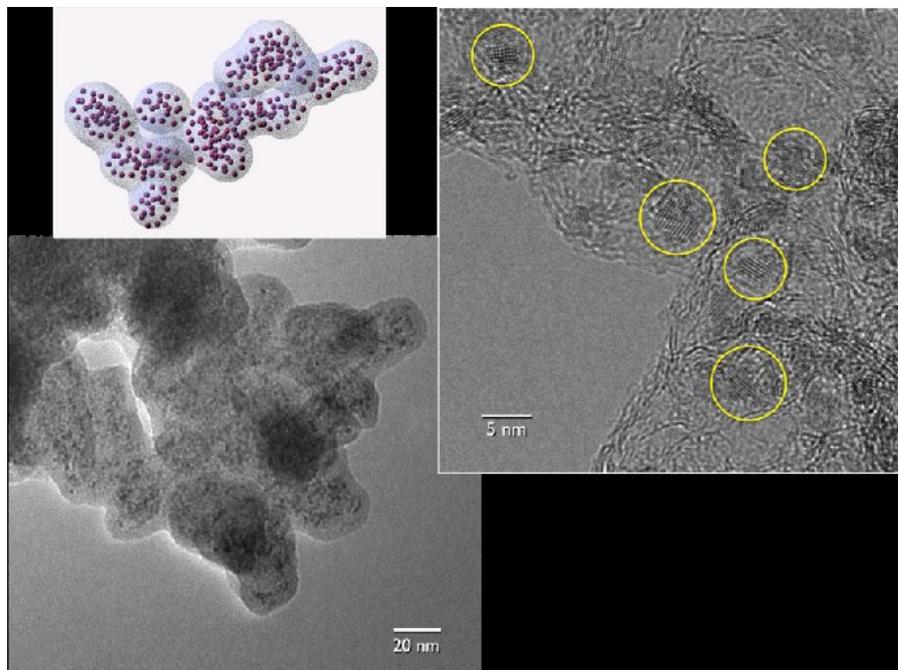
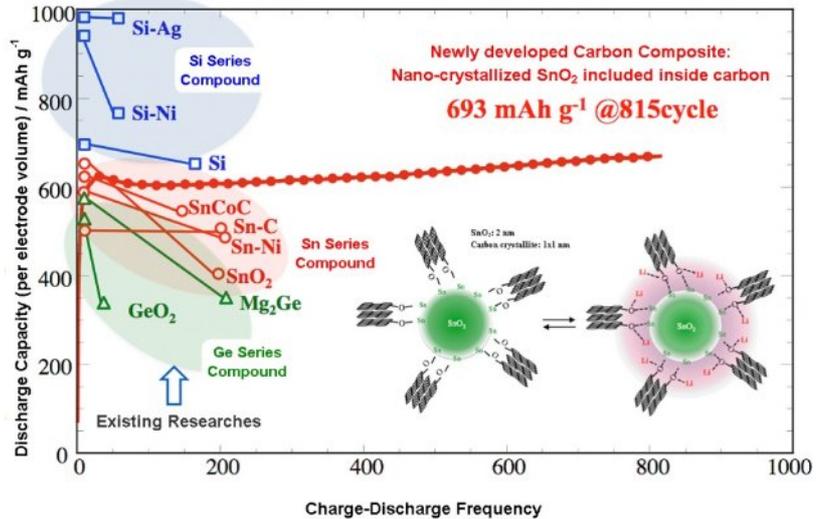


Expectations to expand applications of these types of high power devices are high. They are regarded as particularly well suited for electric vehicle quick charger system applications. Applying nano-hybrid technology to all the other existing metal-based battery materials (manganese, nickel, vanadium, and others) will enable the design of other ultra-high output batteries and extend the possibilities of these devices.

(2) Negative electrode material: Tin oxide (SnO₂)

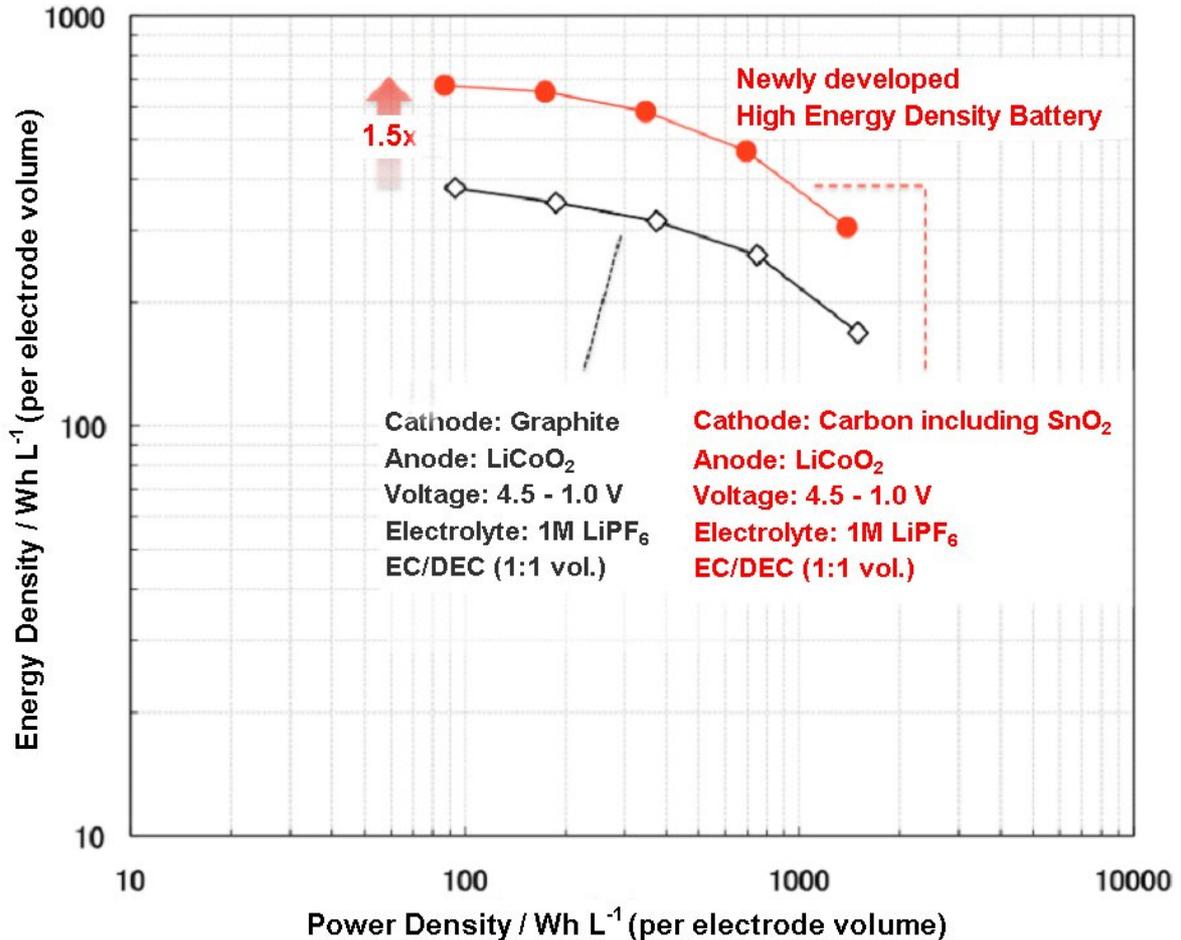
The University group selected tin oxide (SnO₂) for a negative-electrode. SnO₂ is being developed as a superior alternative to commonly used graphite due to its high energy density. However, further research was required for practical use since the volume of SnO₂ changes significantly during each charge-discharge, resulting in loss of most of the capacity after only a relatively few recharges.

When the University group applied the nano-hybrid technology to SnO₂, they were able to achieve significant discharge capacity at 5 to 10 C, now regarded as the world's highest output for SnO₂. Over 800 cycles were recently achieved in a 10 C (360 seconds) charge-discharge test. This is more than 4 times longer cycle life than obtained by various other researchers studying compounds prepared from the three related metals: silicon, tin, and germanium, none of which provided no more than 100 to 200 cycles.



The volume of SnO₂ usually increases by about 250% when charged. However, the newly developed electrode material can absorb its volume expansion by encapsulating the SnO₂ completely inside the carbon and thereby stabilizing its structure. This nano-structure makes it possible to charge-discharge many times, stably and efficiently. When the University group made a battery using this material in the negative electrode

and a positive electrode using lithium cobalt oxide (LiCoO_2), the battery featured an energy density 1.5 times higher than that of typical lithium-ion batteries (high energy type). It also became clear that it is possible to further increase the energy density another 2 to 3 times by reducing the amount of carbon in the composite.



Future plan

In this development, lithium iron phosphate and tin oxide were selected for the next generation lithium-ion battery materials. But nano-hybrid technology is able to be applied to all other battery materials (especially transition metal oxides). Other than the aforementioned two types of materials, nano-hybrid technology has a great potential to develop a variety of other new materials for the next generation ultra-high output batteries and third generation capacitors.

TUAT, Nippon Chemi-Con and K&W will jointly continue with their research and development, while at the same time, Nippon Chemi-Con is seeking to transform the developmental results into a next generation battery materials business.

References

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