

Faster, more durable lithium-ion batteries

A new anode material prepared by coating titanium disilicide with silicon provides superior performance.

KEY CONCEPTS

- **Two-dimensional, network-Web heteronanostructures or nanonets have been prepared that can provide superior performance as an anode material in a lithium battery.**
- **The anode material is prepared by coating titanium disilicide with silicon.**
- **Use of this technology may enable lighter-weight batteries to be used in applications such as computer laptops.**

The potential for using lithium-ion batteries in a number of applications is due to their superior performance, which includes lower power loss compared to other battery types. But problems have been encountered with slow cycling (charge and discharge) rates of lithium ions and safety. In the latter case, lithium-ion batteries have been found to catch on fire during use.

In a previous TLT article, a layered lithium battery was developed featuring a transitional cathodic material, which contains high levels of nickel in the core and high concentrations of manganese on the surface.¹ The former generates high energy but is unstable while the latter is more stable. This cathode material provides the combination of high energy with better stability.

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An appealing material for lithium-ion battery anodes is crystalline silicon. Dunwei Wang, assistant professor of chemistry at Boston College in Chestnut Hill, Mass., says, “Silicon has the highest, theoretical specific capacity to hold lithium cations. But an undesirable volume expansion ranging from 300% to 400% occurs because silicon becomes amorphous, and lithium tetrasilicide is formed. This process causes structural and electronic degradation that can lead to cracking and pulverization of the bulk material.”

Moving to smaller silicon nanowires enables accommodation of the volume expansion. Wang says, “With a thin film, space is available to expand upward.” But high capacity, long capacity life and fast cycling rates are not seen because charge transport is impeded.

There is need for a new anode material that can provide improved performance. Such a material has now been developed.

HETERONANOSTRUCTURES

Wang and his associates have developed an anode material in which silicon is coated on to titanium disilicide. The result is the formation of two-dimensional,

'The silicon-coated titanium disilicide is composed of nanoparticles instead of something continuous. This provides sufficient volume to enable the silicon coating to expand when lithium ions are inserted.'

network-Web heteronanostructures designated as nanonets. Wang explains, "These nanonets are Web-like structures that are similar to a network. The titanium disilicide has the advantage of being able to readily pack in a perpendicular direction, which generates an ideal structural support or scaffolding for the silicon coating."

The silicon coating contains a monolayer of particles with diameters between 10 and 20 nanometers. Wang notes that the particles do not continuously cover the surface of the titanium disilicide.

A transmission electron microscopic image of the heteronanostructure is shown in Figure 1. The dotted red line shows the boundary point between the crystalline silicon coating and the titanium disilicide structural support.

Addition of lithium ions into the silicon allows for the volumetric expansion. During a discharge cycle, the lithium ions move out of the silicon coating and then move through the titanium disilicide, which acts as a highway. In charging, the lithium ions move from the titanium disilicide highway back into the silicon coating.

In experiments run at a charge/discharge rate of 8,400 milliamps per gram, the specific capacity of this heteronanostructure is 1,000 milliamps-hour per gram (mA-h/g), which is a charge/recharge rate estimated to be five to 10 times greater than a typical anode material.

Wang indicates that a battery for a typical computer laptop is rated between 4,000 and 12,000 mA/h. This means that it only takes four to 12 grams of this new heteronanostructure to produce a battery with a comparable capacity to what is currently used.

In testing over 100 cycles, the heteronanostructure achieves greater than 99% capacity retention per cycle over 100 cycles conducted at a level above 1,000 mAh/g.

Titanium disilicide is prepared by the reaction between titanium tetrachloride and silane in a chemical vapor deposition process. Silane and hydrogen are next introduced at 650 C for 12 minutes to produce the silicon nanoparticle coating.

The heteronanostructure is treated finally at 900 C for 30 seconds in forming gas (5% hydrogen in nitrogen) to conclude the process. Wang says, "The silane is pyrolyzed in this process in a similar manner to how graphite is produced."

The heteronanostructure has a number of advantages over existing anode materials. Wang says, "The silicon-coated titanium disilicide is composed of nanoparticles instead of something continuous. This provides sufficient volume to enable the silicon coating to expand when lithium ions are inserted. A three-dimensional nanostructure, with a high surface area, is created to facilitate good transport of the lithium ions."

The nature of the chemistry enables the researchers to just insert lithium into the silicon layer and not into the titanium disilicide. This is accomplished through control of the voltage. Lithium will react with silicone at a voltage of 120 millivolts, while

the reaction with titanium disilicide occurs in a voltage range between 60 and 70 millivolts.

Wang says, "We have conducted a proof-of-concept demonstration but now need to learn more about how the process works." Future work involves gaining a better understanding of the mechanism of how lithium ions can be inserted into the silicon coating and not the titanium disilicide scaffolding.

Wang also would like to determine if this heteronanostructure could be used also as the material for a cathode. Further information on this research can be found in a recent article² or by contacting Wang at dunwei.wang@bc.edu.

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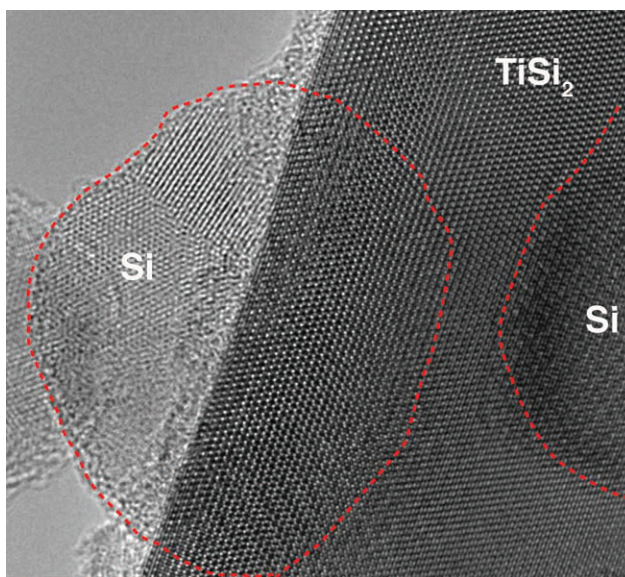


Figure 1 | A coating of silicon on titanium disilicide produces a heteronanostructure that displays a charge/recharge rate estimated to be five to 10 times greater than a typical anode material used in a lithium-ion battery. [Courtesy of Boston College]

Ductile metallic glasses

Researchers developed a material that combines excellent mechanical strength with ductility.

KEY CONCEPTS

- **Metallic glasses are a relatively new class of materials that are amorphous in structure and prepared by rapidly quenching multiple molten metal alloys.**
- **Metallic glasses are very strong, lightweight and exhibit better wear resistance than crystalline metals. But metallic glasses are extremely brittle and fail catastrophically.**
- **Smaller metallic glass samples with diameters less than 100 nanometers deform in a similar fashion to ductile metals while maintaining a high level of mechanical strength.**

Many research efforts are engaged in developing materials that can provide better mechanical properties, which are more readily usable in structural applications. One trend that is readily seen is the drive to use structural materials with lower weight as a means to improve fuel economy in automobiles. This has led to the use of lighter-weight metals such as aluminum and magnesium that also has prompted the steel industry to develop ultra lightweight alloys.

One class of materials that has been examined quite closely is silicon. It is quite brittle and readily fractures when pressure is applied. A previous TLT article discusses the effect of crack propagation through silicon at low speeds.¹ A combination of computer simulation and experimentation was used to show how the structure of the silicon atoms changes as the crack moves through them.

A relatively new class of materials is metallic glasses, which were first reported in 1960.² Julia R. Greer, assistant professor of materials science and mechanics at the California Institute of Technology in Pasadena, Calif., says, “Most metal alloys are crystalline and contain well-ordered, periodic arrangements of atoms. In contrast, metallic glasses are amorphous materials often prepared by the rapid quenching of multiple molten metals, thereby preventing crystalline structure formation.”

Metallic glasses are typically prepared from proper stoichiometric ratios of metals such as zirconium, titanium, copper and nickel. Greer says, “Metallic glasses are very strong and lightweight. In contrast to crystalline metals, they are mainly corrosion-resistant and do not tend to form oxide coatings on their surfaces. They also exhibit better resistance to wear than crystalline metals.”

Metallic glasses can be formed from several combinations of metals as dictated by their phase diagrams. But metallic glasses do have one huge Achilles heel, according to Greer. She says, “Under mechanical loads, metallic glasses are extremely brittle and they fail catastrophically. This occurs due to instantaneous, highly localized shear-band propagation under loads, causing the entire structure to fail.”

Research has been conducted to determine how to improve the ductility of metallic glasses. Steps were taken to more uniformly distribute shear bands and to hinder their propagation in metallic glasses.

A secondary problem is the inability to produce metallic glasses in large quantities. Greer points out that a high level of stored energy is available in large samples to force the metal into a crystalline state. Metallic glasses are typically made into ribbons and wires.

But metallic glass mechanical properties are particularly sensitive to specific experimental conditions and to the sample geometry. Greer says, “Several research groups have created and tested tapered rather than perfectly cylindrical pillars, which significantly affects both the attained stresses in compression and pillar de-

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‘We found that these smaller samples were capable of carrying plastic strain of more than 20%, which means that they were deforming in a similar fashion to a ductile metal.’

formation, as the pillar top experiences a higher, inhomogeneous stress than its bottom.”

Metallic glasses are strong and brittle in a similar fashion to ceramics. In contrast, crystalline metals are ductile, which minimizes failure but do not have the strength of metallic glasses or ceramics.

There is great interest and need to prepare a material that combines excellent mechanical strength with ductility. Such a material has not been developed until now.

SIZE OF METALLIC GLASS PARTICLES

Taking special measures to remove the geometric and experimental artifacts, Greer along with Dongchan Jang, a senior CIT post-doctoral student, explored how a change in the size of the sample specimen down to 100 nanometers in diameter affects the mechanical properties of the metallic glass. In conducting this study, Jang fabricated and tested several samples with diameters between 1 micron and 100 nanometers and discovered that at 100 nanometers these metallic glasses maintained even higher-than bulk strength while acquiring ductility.

A zirconium-based bulk metallic glass sample was used as a precursor for sample fabrication for subsequent nano-tension testing. The results for specimen samples down to 200 nanometers showed an increase in strength but a failure by catastrophic shear-band formation as determined by *in situ* nanomechanical measurements.

The tensile yield strength increases from 1.7 to 2.25 gigapascals as the size of the specimen is reduced from 875 nanometers to 330 nanometers in diameter. But all of these samples display catastrophic failure at strain levels between 3% and 5%.

At the diameter of 100 nanometers, however, the results were drastically different. Greer says, “We found that these smaller samples were capable of carrying plastic strain of more than 20%, which means that they were deforming in a similar fashion to a ductile metal.” Stress values reached a maximum of 2.35 gigapascals during this work, which is higher than seen for larger diameter metallic glass samples.

A scanning electron micrograph of a typical 100 nano-

meter in diameter sample used in tensile testing is shown in Figure 2. Greer says, “The 100 nanometer metallic glass samples first necked, and only then failed by forming a shear band in the necked region at 53 degrees to the loading axis, which is typical of metallic glasses. This result means that

100 nanometer samples deform in a similar fashion to ductile metals but fail typically like metallic glasses.”

Greer believes that two competing energetic processes, localized shear-band propagation and homogeneous flow, affect how the metallic glass samples of different sizes react towards stress. At specimen diameters below a certain critical value, plastic deformation will dominate, leading to homogeneous flow until the metallic glass eventually fails when a higher, shear-band propagation stress is attained. At diameters above this critical value, shear-band propagation is more energetically favorable, and the sample behaves in a manner typical of metallic glasses.

This work shows that by utilizing size as a design parameter, materials combining ductility with a high level of mechanical strength can be prepared. Greer envisions that nanoscale components could be prepared with this unique combination of properties in structural applications. One potential use is combining metallic glass with particle diameters of 100 nanometers with ultrafine-grained ductile metal to prepare a new type of engineering composite.

Further information can be found in a recently published paper³ or by contacting Greer at jrgreer@caltech.edu.

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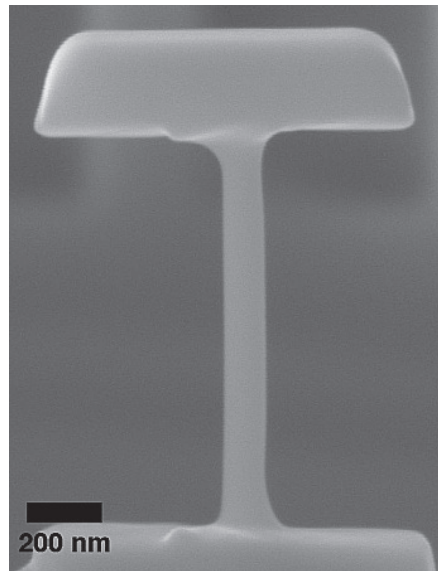


Figure 2 | The 100 nanometer diameter metallic glass sample shown in this scanning electron micrograph deforms in a similar fashion to ductile metals. [Courtesy of the California Institute of Technology]

Olympic skeleton simulation

A video-based measuring technique helps racers minimize aerodynamic drag.

KEY CONCEPTS

- In the sport known as skeleton, racers travel down a track on a sled at speeds up to 110 kilometers per hour.
- Among the factors that racers need to minimize are the frictional force occurring as the steel runner on the sled meets the ice and aerodynamic drag.
- A simulator has been developed that uses a technique called Digital Particle Image Velocimetry to help racers reduce aerodynamic drag.

At this year's Winter Olympics in Vancouver, Canada, many of you may have seen athletes moving down a track on a sled at speeds up to 110 kilometers per hour in a sport known as skeleton. Time is of the essence in this sport as racers are separated from each other by hundredths of a second.

There are a number of factors that can be controlled to enhance the ability of an athlete to move down the track at the fastest possible speed. Timothy Wei, professor of engineering in the mechanical, aerospace and nuclear engineering department at Rensselaer Polytechnic Institute in Troy, N.Y., says, "An athlete is propelled by gravity down the track once they push off at the start. Factors such as aerodynamic drag, minimization of friction while sledding on the ice and finding the shortest line down the track are the most important that need to be mastered by the athlete to be successful."

In a previous TLT article, a number of variables were examined that impact the friction of ice.¹ Among the issues are the ice surface itself, the temperature of the ice, the load, the polarity of the ice, impurities, molecular adhesion and shearing.

'The frictional force occurring as the steel runner meets the ice is pretty much evened out by the rules.'

These variables are usually uniform for all of the racers except for the load. Wei says, "The governing organization for skeleton (FIBT) mandates that the runners used are prepared from the same alloy of steel and by the same machine shop in Europe. No foreign substances can be used, and the runners also cannot be heated prior to use." Wei indicates these rules are very similar to how Formula One race cars are regulated by that sport's governing body.

Sleds are inspected at the beginning of the season and are marked with an electronic stamp. Prior to each race, the temperature of the runners is measured and must not exceed the temperature of a reference runner by 4 C.

Wei says, "The frictional force occurring as the steel runner meets the ice is pretty much evened out by the rules. This happens to be a larger overall factor than the aerodynamic penalty that can hinder the racer's speed."

But minimization of aerodynamic drag is still a valuable asset that could enable a racer to gain valuable hundredths of seconds on his or her competitors. A strategy has now been developed to help skeleton racers in this area.

DIGITAL PARTICLE IMAGE VELOCIMETRY

Wei and his associates reproduced a section of a skeleton track behind a wind tunnel that is currently used at RPI. He says, "We built a straightaway section of the track that is 12 feet long-by-4 feet wide-by-2.5 feet wide. The floor of the track is raised above the wind tunnel floor to basically allow the setup to be exposed to clean air. The skeleton sled sits on four little pads, which are situated below the floor and contain load cells."

'A thin sheet of light is created from a green pulse laser that is shined over the shoulders of the athlete. Theatrical fog is then introduced, and we videotaped its movement against the bodies and heads of the athletes to identify ways to reduce drag.'

Hooked up to the load cells are sensors that measure the pitch, roll and balance of the sled. In other words, the set-up will measure how much the skeleton athlete will turn the sled left, right, forward and backward. Figure 3 shows an athlete lying on a sled situated in the simulator.

Wei says, "Four of the sensors are set up to measure the downward force on the athlete and two sensors measure the drag force encountered. These sensors indicate how well-centered and how well the athlete's weight is distributed on the sled."

Wei indicates that the normal force, which is a measurement of the impact of gravity on the athlete, is a significant factor. A heavier athlete is more likely to go faster down the track than a lighter one.

A window was also cut in the bottom of the test track and a computer monitor installed to enable the athlete to see changes in aerodynamic drag in real-time. A clear sidewall was also built so that coaches can observe the tests.

Athletes from the U.S. Olympic Skeleton Team took advantage of this setup to reduce aerodynamic drag before the Vancouver Olympics. The athlete lies down on the sled and is subjected to a steady stream of air from the wind tunnel exhaust. Air blows at the athlete at a speed of nearly 100 kilometers per hour.

Wei indicated that sessions last up to 30 minutes. He says, "It usually takes about five to 10 minutes to do the evaluation. In one case, we found that an athlete had raised her foot by up to 20 to 30 degrees. When she lowered the foot, aerodynamic drag decreased by 15% to 20%."

Wei used a video-based flow measurement technique known as Digital Particle Image Velocimetry. He says, "A thin sheet of light is created from a green pulse laser that is shined over the shoulders of the athlete. Theatrical fog is

then introduced, and we videotaped its movement against the bodies and heads of the athletes to identify ways to reduce drag."



Figure 3 | A technique known as Digital Particle Image Velocimetry helps skeleton racers improve their ability to reduce aerodynamic drag. (Courtesy of Rensselaer Polytechnic Institute)

Use of this procedure has proven to be valuable in helping the athlete perform better. Wei said that the skeleton sled is built very low to the ice with the athlete just inches above the ice. He adds, "The athlete's head gets rattled during the high frequency acceleration down the track, which typically lasts about one minute. Athletes will only make three runs per day because the stress and g forces encountered leave them exhausted. This

means that use of our simulator is invaluable in providing assistance to the athlete."

Wei also used this technology to assist swimmers on the U.S. Swim Team for several years. As competition at the highest level becomes more intense, athletes are looking for any advantage over their competitors. Minimization of factors such as friction and aerodynamic drag are important and will continue to be so in the future.

Further information on the high-tech simulator can be found at the following link: <http://news.rpi.edu/update.do?artcenterkey=2683> or by contacting Wei at weit@rpi.edu. **TLT**

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