NICKEL

THE MAGAZINE DEVOTED TO NICKEL AND ITS APPLICATIONS

Waste water treatment and metal recovery

Nickel catalysts for hydrogen production

Nickel and single-crystal superconducting wire

June 2013 Vol. 28, No. 2

The Innovation Issue

Nickel in Lithium Batteries

The History of Stainless Steel—Part 4

America Enters the Picture

In the previous issue (Vol. 28, No. 1), we looked at the early development of stainless steels in Europe, but metallurgists in the United States were also working on experimental chromium-alloyed steels. Among them was Elwood Haynes, whose main interest was to improve his automobiles. An accomplished inventor, Haynes focused on hard, wear-resistant alloys and alloys suitable for spark plug applications. He succeeded notably in developing the Stellite® family of alloys, the early versions of which contained cobalt, chromium, carbon, molybdenum, tungsten, and nickel.

In 1911 and 1912, he experimented with hardenable chromium steels to gauge their resistance to corrosion. Although these alloys were not hard enough for his cars, Haynes was aware of their potential in cutlery and other industrial applications. In April 1914, he filed for a patent on hardenable (martensitic) steels with 4-50% chromium content, but it was not granted until 1917. However, the patent was in conflict with one previously issued to British-born metallurgist Harry Brearley. Rather than fight it out in court, Haynes and Brearley formed a jointly owned company, the American Stainless Steel Company (ASSC). The ASSC held both patents and licensed various steel producers to make stainless steel grades.

By 1918, U.S. producers such as Bethlehem Steel and Carpenter Steel had purchased licenses and were paying royalties of 15% on their stainless steel production. The company paid sizable dividends to its owners until it was dissolved in the 1930s. Until his death in 1925, Haynes adamantly maintained that he was the discoverer of stainless steel, not Brearley.

Some historians believe two other Americans, Frederick Becket and Christian Dantsizen, could lay claim to the discovery. The latter did important work at General Electric in the area of a low-carbon, non-hardenable chromium-containing stainless steel which was first used as lead-in wires for electric light bulbs. Becket's main contribution related to producing these alloys at the Electro Metallurgical Company in Niagara Falls, New York.

Among the other Americans experimenting with stainless steel was P.A.E. Armstrong, vice-president of Ludlum Steel Co. Armstrong experimented with chromium-silicon stainless steels in 1914 until his work was interrupted by the First World War. He resumed work after 1918 and obtained a patent for these alloys. Some of the alloys and their applications overlapped with the Brearley-Haynes patents but Ludlum did not seek a license from the ASSC. The ASSC then sued Ludlum for patent infringement whereupon they were ordered to pay royalties for the stainless steel that went into cutlery. (Other stainless alloys, such as those used in exhaust valves, were not subject to ASSC royalties.)

The use of stainless steel grew rapidly in the U.S. and Canada in the 1920s. It was used not only in cutlery and other kitchen goods but in food processing, transportation, even surgical implants. By the end of the decade, according to one newspaper report, some 35 large American companies were producing stainless steel. Total U.S. production of stainless steel in 1929 was 53,293 tonnes. The following year in New York City, the iconic Chrysler building was completed. Clad in 18-8 (Type 302, UNS S30200) stainless steel, it remains a symbol of the endurance of this nickel-chromium alloy for the entire world to see.

Stainless steel usage continues to grow rapidly. In 2012, a hundred years after its discovery, worldwide production was estimated at 35.4 million tonnes. The properties of stainless steel that served society well over the first 100 years will continue to make them the materials of choice for many applications over the *next* century.

Elwood Haynes

Frederick Becket

Christian Dantsizen

P.A.E. Armstrong

Iconic Chrysler Building

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NICKEL

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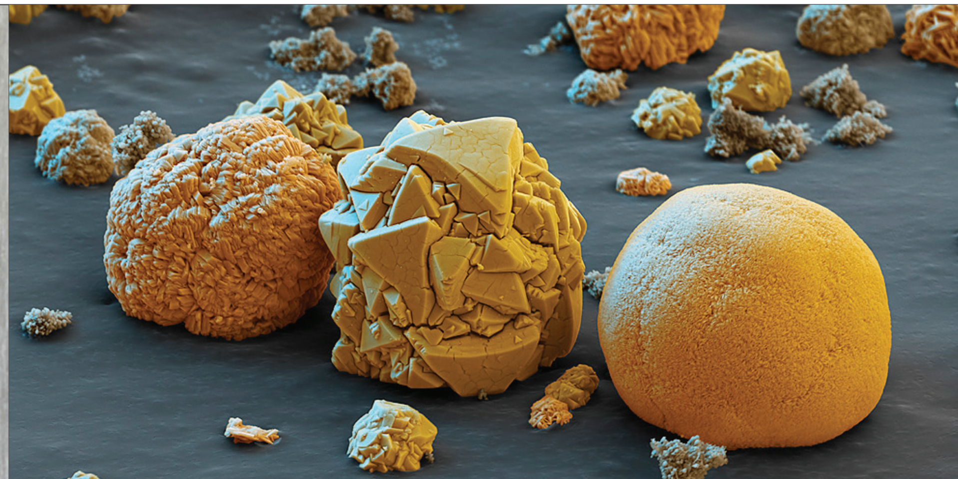


PRESS PHOTO BASF

△ *BASF NCM Li-Ion Cathode Material 2200x. The cathode material shown in the picture consists of tiny, micrometer-sized spheres precipitated out of nickel, cobalt and manganese salts. Thanks to their delicate, sponge-like structure and larger surface area, the finely-textured spheres can release the lithium ions faster.*

NICKEL AND INNOVATION

We have been celebrating stainless steel for the past year and the last chapter on the first 100 years of stainless steel appears on the page opposite. It's time now to consider some of the ways society will likely be using nickel in the next hundred years.

It's reasonable to expect that nickel-containing stainless steels will remain a very significant construction material, and for all the familiar reasons. Which is to say its ductility, toughness, strength, weldability, resistance to acids and other corrosive chemicals, and cleanability will all remain in high demand. And this issue of *Nickel* points to two examples close to where we live: sound barriers for highways (page 13) and safety grilles for manholes (page 12). These are reminders of the everyday ways in which nickel-containing materials contribute to our quality of life.

There is strong evidence, however, that nickel's other properties – some well-known, others just being explored – will render it even more essential to an efficient and sustainable society. Society needs to foster those and other innovations that will come in their turn and put them to use.

We are familiar with nickel-cadmium and nickel metal hydride batteries. "Nickel," however, is disappearing from the names of battery chemistries and the conclusion some might draw is that lithium-ion compounds have replaced nickel. Not so. Nickel is still at the heart of many of the ever-improving batteries even as battery storage of off-peak renewable power becomes more important (see page 8).

At the very earliest stage of development – and yet exciting in fundamental ways – are the nickel-based three-dimensional batteries discussed on page 10. As James Pikul, lead author of the technical paper explains: "It's a new enabling technology, not a progressive improvement over previous technologies."

The use of nickel in non-traditional, innovative applications offers some insight into what the next century holds. Non-carbon-based fuel? Nickel is already helping the hydrogen economy develop (page 7). Superconductivity to reduce the loss of electricity in transmission? Nickel plays a small but key role in bringing superconductors to the commercialization stage (page 15).

The bottom line is that electromagnetism, shape memory, and other properties of nickel are being explored as never before and the applications that are emerging are innovative. Moreover, nickel is enabling new and surprising technologies which are needed for a sustainable future.

Stephanie Dunn
Editor, *Nickel* magazine

Stephanie Dunn

BioteQ: Mining Nickel from Waste

Shrinking the ecological footprint of wastewater treatment

Innovative treatment technologies are not only removing dissolved metals from liquid effluents from mines, they're recovering them as well. Nickel-containing stainless steels are used in the equipment to ensure cost-effective and reliable performance.

BioteQ Environmental Technologies specializes in treating wastewater contaminated with dissolved metals and sulphates from mining operations and other industrial applications. The company's equipment and techniques are resulting not only in clean water that can be safely discharged to the environment, but in saleable by-products as well.

Based in Vancouver, Canada, BioteQ provides proprietary, customized process technologies to companies coping with wastewater-related challenges across the globe. It has installations at mine sites in Canada, the U.S., China, Mexico and Australia.

BioteQ's key technologies are the BioSulphide® and ChemSulphide® precipitation processes which, in combination with ion exchange for metal recovery, can be tailored for selective removal and recovery of dissolved metals in wastewater.

These processes remove and recover dissolved metals – including nickel – from

◁ *Nickel-containing stainless steels are used in the equipment to ensure cost-effective and reliable performance.*

mining waste streams in the form of saleable products, says David Kratochvil, the company's president and chief technology officer. "This is made possible by selecting appropriate chemical reagents and controlling reaction conditions that result in the production of metal sulphide solids which are free of impurities. These solids are easily dewatered through conventional solid/liquid separation processes, forming a high-value concentrate for sale to metal traders or directly to smelters and metal refineries."

It turns out that nickel, as well as being one of the target metals for recovery from wastewater, plays a key role in the process technology itself.

"Many waste streams that contain nickel and other metals are corrosive," Kratochvil explains. Depending on conditions in the ChemSulphide and BioSulphide reactors, stainless steel alloys are required to ensure high plant mechanical availability and longevity of equipment. These requirements are important considerations for when we develop the equipment specifications for our water treatment plants."

Use of nickel-containing stainless steel, with its well-known high resistance to corrosion, is often crucial, though final material choice depends on actual plant conditions and the wastewater composition.

Kratochvil believes their technologies have advantages over conventional processes. These include selectivity of metal recovery to ensure that waste streams generate high-purity products, the ability to generate revenue from the recovered dissolved metals, and the elimination or reduction of waste sludge, which is a by-product of wastewater treatment.

"Taken together, these advantages can reduce the life-cycle costs of water treatment," asserts Kratochvil. "None of the conventional water treatment technologies offers the recovery of nickel and other metals from waste streams containing a mixture of different metals. In most cases, those technologies produce waste sludge that is either toxic or hazardous and requires additional treatment or costly disposal."

△ *None of the conventional water treatment technologies offers the recovery of nickel and other metals from waste streams containing a mixture of different metals.*

Extensive development

Meanwhile BioteQ is busy developing other innovative processes, including one that combines ion exchange with ChemSulphide® technology. The benefits of this combination of technologies include a reduction both in the "ecological footprint" of waste water treatment plants and in overall operating costs. "The use of ion exchange resins for waste water treatment opens new opportunities for further development," states Kratochvil.

BioteQ's technology is used broadly across the mining and mineral processing industry and new applications are being found at smelting and refining operations. The process technology is flexible and scalable.

The company has designed 15 water treatment plants around the world ranging in hydraulic capacity from 25 m^3 to 1,200 m^3 per hour. The amount of metal recovered ranges from about 14,000 kilograms (kg) per annum for one nickel mine to 1 million kg per annum for a copper mine.

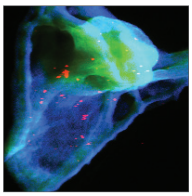
The BioteQ processes can be applied to treat mining waste streams for environmental compliance of effluent limits at new, existing or closed operations.

Kratochvil cites a ChemSulphide plant at a Canadian nickel mine which has recovered on average 12,000 kg per annum of dissolved nickel since operations began. "The recovered nickel is from mine-impacted waters in a product that is blended into the nickel sulphide concentrate produced at the mine. In this application, the plant produces only clean water and the nickel sulphide product with no other waste or by-product."

He also cites an ion exchange plant in China where nickel is recovered from an acid mine drainage stream containing a mixture of metals, upstream of a conventional lime neutralization plant. "In this case, the mine reduces the amount of waste sludge produced while promoting sustainability through the recovery of metals that had previously been directed to waste." Ni

PHOTOS COURTESY OF BIOTEQ

Nickel nanoparticles could hold key to the inexpensive removal of CO_2 from the air



Researchers at the University of Newcastle in the UK may have stumbled upon a way of capturing CO_2 gas using nickel nanoparticles as a catalyst.

While investigating sea urchin embryos as toxicology markers, Gaurav Bhaduri and Lidija Šiller of the School of Chemical Engineering and Advanced Materials noticed there was a correlation between nickel ions and calcium carbonate on the urchin's exoskeleton.

"By using an imaging technique, we could map all the chemical elements of the sea urchin embryo," says Šiller. "We noticed that nickel is correlated with the growth of calcium carbonate."

Recognizing that the sea urchin was probably using nickel as a catalyst to build its shell, the researchers tried to replicate the catalysis by bubbling CO_2 through water containing nickel nanoparticles. Sure enough, the CO_2 was completely removed from the water.

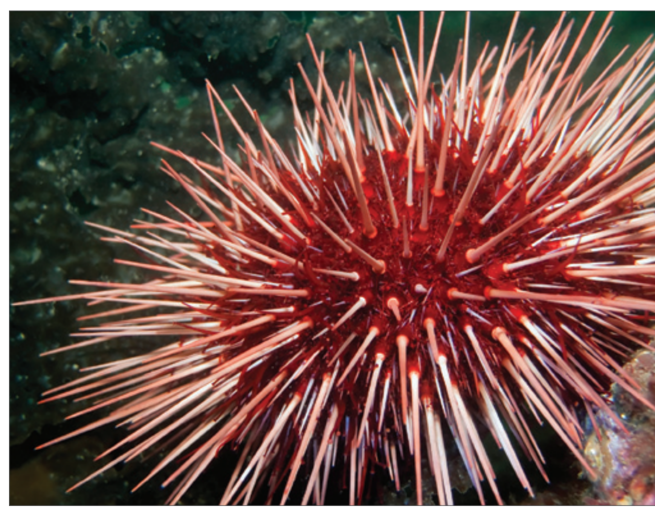
Šiller's team is now studying different concentrations of nickel nanoparticles in water to discover the optimal concentration for capturing carbon dioxide emitted by power plants and other industries. They have experimented with concentrations ranging from 10 to 40 ppm, concluding that 30 ppm is likely the most efficient level.

"The beauty of using nickel to capture carbon dioxide is that it is less expensive than other alternatives and is recyclable using simple magnetic separation," she says.

The separation and storage of CO_2 in mineral carbonates has long been considered a potential method to reduce the concentration of CO_2 in the atmosphere using an enzyme called carbon anhydrase. But the process is costly and pH-dependent, and converting CO_2 to carbonic acid is a rate-limiting step. Nickel nanoparticles enable that catalysis to occur at room temperature and atmospheric pressure, offering an alternative that is both less expensive and pH-independent.

Bhaduri and Šiller's research is outlined in *Catalysis Science & Technology* and their paper was the most-accessed article in the journal's database in February 2013.

Šiller says the process could work on an industrial scale by running exhaust gas from a plant or factory through water or another solution containing nickel nanoparticles. Once the CO_2 has been converted to carbonic acid, the nickel nanoparticles, which are insoluble, would be removed by magnetic separation, and the acid combined with a basic magnesium- or calcium-containing silicate rock to form an insoluble carbonate compound. The carbonate material could be used to make building stone, while the nickel can be re-used repeatedly.



ISTOCK PHOTO © DEREK HOLZAPFEL

◁ *Above left: Sea urchin and its chemical map.*

△ *Top: Researchers Gaurav Bhaduri and Dr. Lidija Šiller.*

△ *Sea Urchin under water.*

NEWCASTLE UNIVERSITY SCHOOL OF CHEMICAL ENGINEERING AND ADVANCED MATERIALS

Currently the primary method industry uses for carbon sequestration involves using a solvent to absorb the CO_2 from the waste gas, then stripping the CO_2 from the solvent by heating it, and finally pumping the CO_2 into underground oil wells or rock formations. But the process is not energy-efficient and there is always the danger of leakage.

Šiller's challenge is now to take this concept to the next level, where the process would be demonstrated in a pilot-plant. Ni

Light-based Hydrogen Production: higher efficiency and lower cost with nickel catalyst

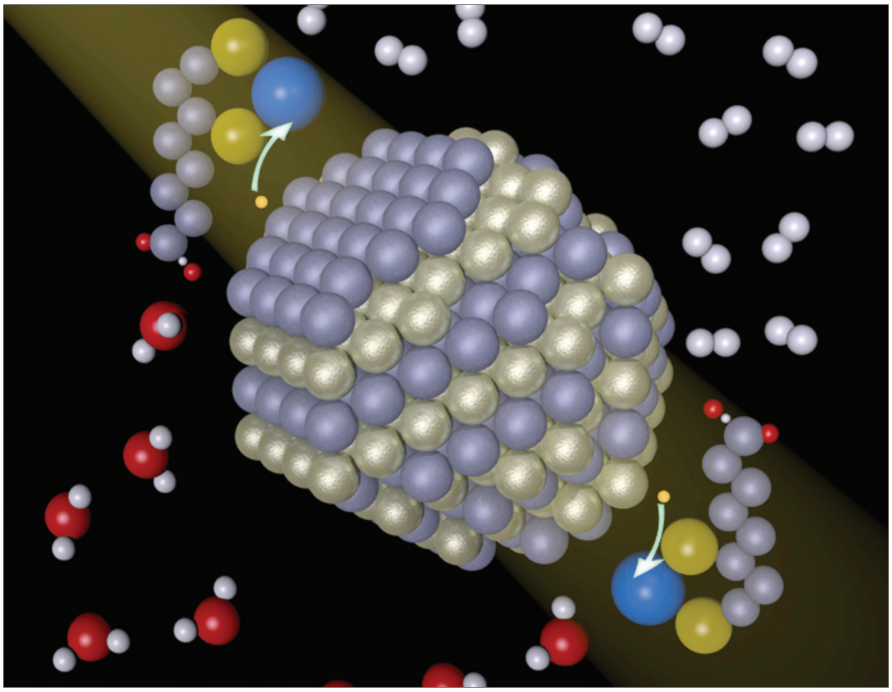


IMAGE BY ADAM FENSTER/UNIVERSITY OF ROCHESTER

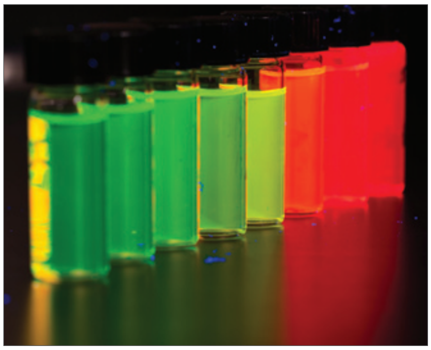


IMAGE BY UNIVERSITY OF ROCHESTER

△ *Vials containing highly fluorescent CdSe colloidal nanocrystals (quantum dots) of varying size. The nanoparticle size doubles in going from the green to the red quantum dots.*

◁ *The nickel catalyst (blue) receives the electrons from the CdSe quantum dot nanocrystals, which subsequently generates hydrogen (white).*

Hydrogen has long been seen as a clean, carbon-free source of energy although technical and economic challenges remain. Now an improved process for the light-based production of hydrogen fuel has been developed by researchers at the University of Rochester that could help fulfill the promise of hydrogen.

The three essential ingredients, outlined in a paper published in the journal *Science*, are sunlight, nanocrystals, and an inexpensive nickel catalyst. The work is being spearheaded by Richard Eisenberg, who has spent decades working on solar energy systems, specifically compounds that absorb light.

The reaction process

A crystalline particle known as a nanocrystal (essentially a tiny chunk of semi-conductor material) absorbs a photon of light which in turn causes an electron to get excited. The excited electron then leaves the nanoparticle and hops on to a nickel ion (catalyst). When two electrons are available, they combine with two protons from water to form a hydrogen molecule.

Previous attempts at improving sunlight-based hydrogen production have typically used catalysts made from platinum and other expensive metals," explains chemistry professor Patrick Holland, a key member of the research team. "But the process is much more sustainable if we use metals that are abundant, lower-cost, and have lower toxicity – metals such as iron, cobalt and nickel."

Holland and his colleagues reported the nickel system in their research because it works better than the other metals, and also because it is much less expensive than alternatives such as platinum. (Platinum catalysts typically cost at least 1000 times more than nickel-based ones).

Nickel's role

"We decided to use nickel as the catalyst after we screened a number of different iron, cobalt, and nickel compounds," Holland tells Nickel magazine. "In those initial screens, some cobalt-containing compounds and some nickel-containing compounds worked. In an earlier study, we reported that a specific nickel-containing compound was excellent for hydrogen production when the light absorber was an organic dye. Then when our colleague Prof. Todd Krauss suggested using the nanoparticles for light absorption in place of the organic dye, we used the same nickel-containing catalyst – and it worked great!

"In order to be careful, though, we did a series of important controlled experiments where we looked for hydrogen production in systems where each of the components was left out. One of these experiments entailed using simple nickel salts (such as nickel nitrate) as catalysts, and we were surprised to learn that they worked just as well.

"In short, this system works equally well with many sources of nickel. We figured out why: the sulphur-containing species on the outside of the nanoparticle comes off, and sticks to the nickel. Therefore, it doesn't matter what starts out on the nickel, as long as it can be displaced by the sulphur-containing species that came off of the nanoparticles."

While the team's work is still years away from commercial implementation, Holland notes that an efficient, cost-effective system for producing light-based hydrogen would be useful in areas beyond just energy. "Pharmaceuticals and fertilizers also require a lot of hydrogen, so those industries would benefit as well."

The research project is partly funded by the U.S. Department of Energy.

CHARGED

Nickel plays key role in new lithium-ion batteries

In the race to power the electric vehicles and electronic gadgets of today and tomorrow, nickel is becoming an integral component of the next generation of rechargeable lithium-ion cells.

Nickel-metal hydride batteries are dominating the growing market for hybrid-electric vehicles and continue to be the consumer choice for rechargeable household batteries. But perhaps the most promising nickel-based battery technology is an innovative cathode material that is making lithium-ion batteries more powerful, more durable, and safer.

The material, known as NCM or NMC (the interchangeable names refer to the presence of nickel, cobalt and manganese oxides) was introduced a decade ago as an alternative to lithium cobalt oxide which is commonly used in lithium-ion batteries. One incentive for the switch was cost: cobalt is rarer and often much more expensive than nickel.

A lithium-ion battery using the NCM chemistry also offers a higher energy density, which is, the amount of energy a battery can store based on its weight or volume. "The greater the energy density, the smaller and lighter the battery," notes Daniel Abraham, a materials scientist and lithium-ion battery expert at the U.S. Department of Energy's Argonne National Laboratory near Chicago.

Nickel plays a crucial role in boosting energy density by compensating for the loss or gain of electrons as the battery is charged and discharged. "The oxidation state of the nickel changes reversibly," Abraham explains, "and it's the reversible character of the material that allows these cells to 'cycle' thousands of times." He adds that the addition of manganese (or in some batteries, aluminum) improves the stability and safety of the internal chemistry.

"This is the fastest-growing cathode in the world," asserts Michael Fetcenko, vice-president and managing director of BASF Battery Materials – Ovonic. BASF produces three versions of the NCM cathode material, with nickel accounting for between one-third and one-half of the total cathode. The company is licensed to produce NCMs developed at the Argonne lab, where Abraham and other scientists are exploring ways to improve their performance. "We're tweaking the chemistry to get long life, reduce the cost, and improve the safety characteristics of these cells," says Abraham.

Cooler and safer

The safety advantage of the nickel-based cathode is also highlighted by Jeff Dahn, a professor of advanced materials in the chemistry and physics departments at Dalhousie University in Halifax, Canada. He notes that as the size of lithium-ion cells increases, so does the risk of overheating. That's because at high temperatures, lithium-ion battery material can become unstable and release oxygen into the electrolyte, which is flammable.

"It's kind of like bubbling oxygen through heated gasoline," Dahn explains. "You wouldn't want to do that. So it's important to pick positive electrode materials that release the smallest amounts of oxygen [at controllable temperatures]. He adds that NCMs "offer more 'thermal headroom' over lithium cobalt oxide with respect to the temperature at which oxygen begins to be released."

Dahn points to the temporary grounding earlier this year of Boeing's new 787 Dreamliner aircraft after a spate of electrical problems, including a lithium-ion battery that overheated and caught fire. The use of lithium cobalt oxide cells in the aircraft's electronics

IMAGE COURTESY OF ARGONNE NATIONAL LABORATORY.

△ *Daniel Abraham, a leading scientist at Argonne National Laboratory conducts research in the field of lithium-ion batteries.*

bay "was probably a poor choice," he says. "Safer materials exist and could have been selected."

Failures such as this are rare, however, and a combination of lighter weight and high energy output makes lithium-ion batteries the choice for portable devices such as laptop computers, cell phones and power tools. "In applications where weight is important," Fetcenko concedes, "lithium rules."

Nickel-metal hydride: not going away

But nickel-metal hydride batteries are holding their own in other applications. BASF, through its 2012 acquisition of Michigan-based Ovonic Battery Company, inventor of the ubiquitous NiMH rechargeable battery, is now the global leader in nickel-metal hydride technology.

NiMH batteries in AA and AAA sizes remain the choice for consumers seeking an alternative to disposable cells, with about a billion sold annually. And BASF sees a bright future for NiMH batteries in stationary applications. When it comes to designing back-up power systems and "smart grids" for storing electricity generated from solar and wind, weight is not a concern.

What's more, NiMH is the go-to battery for powering hybrid vehicles. The leading hybrid automakers, Toyota and Honda, prefer the NiMH units for their lower cost, longer life, and ability to withstand abuses such as overcharging. Also, since electricity is not the sole source of propulsion, the size and weight of the battery do not necessarily pose a problem.

More than six million hybrid vehicles have been sold since being introduced in the late 1990s and Fetcenko says government and consumer demands for greater fuel efficiency are certain to earn them an increasing share of the automobile market.

The same pressures are expected to increase demand for vehicles powered solely by electricity, and the higher energy density and lower weight of lithium-ion cells fitted with nickel-based cathodes make them the logical choice of power source. High energy density translates into the increased driving range needed for an all-electric vehicle.

Dahn, who continues to refine and improve NCM technology at his lab in Dalhousie, cites projections that the amount of NCM needed to make lithium-ion cells will quadruple to 100,000 tonnes per annum by 2020. Nickel will likely account for about a third of that total, most of which is earmarked for the auto industry.

The switch to hybrid vehicles powered by NiMH batteries or lithium-ion batteries containing an NCM cathode ensures than nickel will continue to play a major role in this sector. Says BASF's Fetcenko: "The use of nickel is only going to proliferate in these batteries, whichever chemistry is used."

In the article following on page 10, we take a closer look at the role nickel plays in lithium-ion battery chemistries along with some significant new innovations in that market. Ni

▽ As part of the "High Energy Lithium-Ion Batteries" project, BASF is conducting research into a new generation of lithium-ion batteries. The aim is to significantly increase the batteries' energy density to specifically extend their use in electrically powered vehicles.

PRESS PHOTO BASF

▽The components of NiMH batteries include a cathode of nickel hydroxide, an anode of hydrogen-absorbing alloys and a potassium hydroxide (KOH) electrolyte. Nickel-metal batteries are ideal for mass producing affordable conventional hybrid vehicles due to their low cost, high reliability and high durability.

▽Chemical lab technician Christian Saffert tests the discharge capacity of various lithium-ion test batteries using a multi-channel test system.

PRESS PHOTO BASF

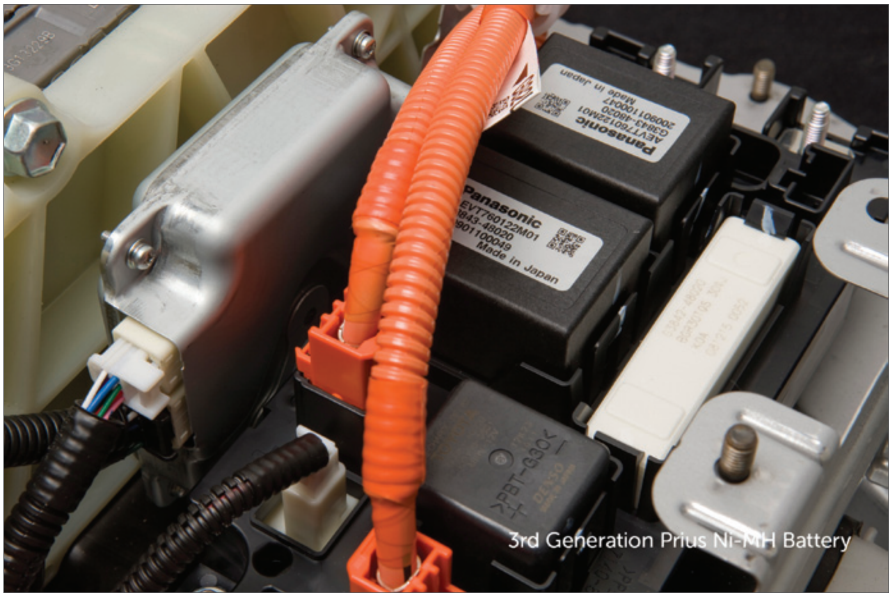


IMAGE COURTESY OF TOYOTA

FUTURE POWER Breaking the paradigm

As was indicated in the previous article (pg. 8 & 9), most types of batteries are linked by name to nickel insofar as nickel is part of how their chemistry is described. Examples include nickel-cadmium, nickel-zinc, and nickel-metal hydride. But with the advent of "lithium-ion batteries," many may be wondering if nickel is still relevant. It is.

"Lithium-ion" is a generic term for a family of related battery chemistries. These chemistries are relatively new and have met with commercial success. In addition to lithium, many of the lithium-ion batteries include nickel (as well as manganese and cobalt).

The Next Generation

While today's commercially available battery chemistries represent significant advances over what was available twenty years ago (even the lead-acid battery is much improved), further dramatic improvements are emerging.

For example, the demand for dramatically improved electrical storage systems of all capacities is expanding and if the right commercially viable battery technologies enter the market, that trend will only increase. The competition of ideas and techniques is intense and it is impossible to know which ones – or which combination – will be powering society in the future.

There are, however, strong hints coming from university laboratories. What follows is one representative example of how experimental batteries are being built and of the materials that will, in one way or another, be part of tomorrow's batteries.

High-power Lithium-ion Microbatteries

A team at the University of Illinois led by Professors William King and Paul Braun recently published a paper in the online journal *Nature Communications* which describes a micro-battery that performed extraordinarily well (see diagrams for scale and construction details). The key is the internal 3-D microstructure, with the cathode and anode integrated at the micro-scale. Design and testing are ongoing, though work to date suggests such batteries could offer 30 times more power to sensors or radio signals and allow those sensors to be one-thirtieth the size that they are today. The batteries can charge 1,000 times faster than comparable commercial technologies.

"This is a whole new way to think about batteries," says King. "A battery can deliver far more power than anybody ever thought…. The thinking parts of computers have got smaller [over the years] and the battery has been lagging behind. This micro-technology could change all that."

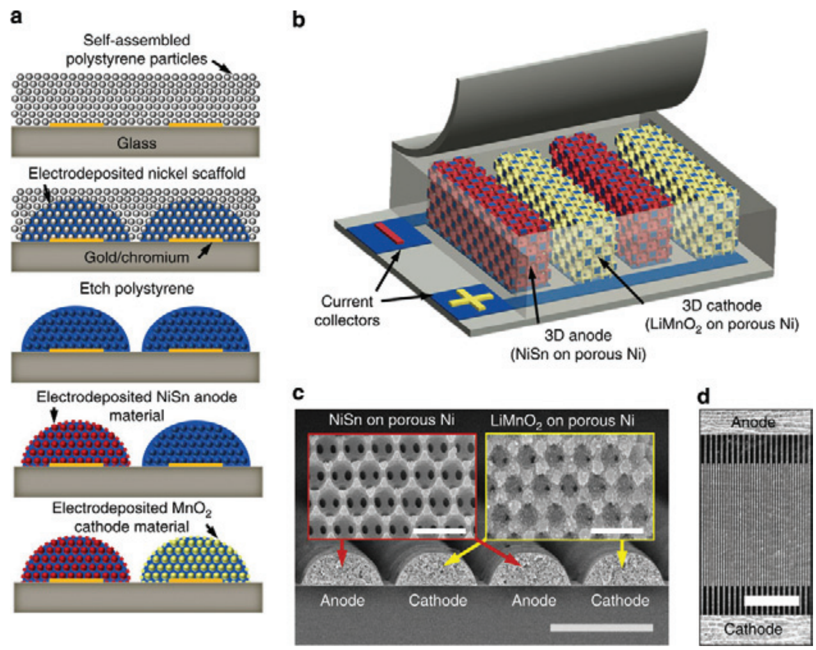
The Role of Nickel

When asked why nickel was so prominent in the construction of this micro-battery, Professor Braun noted that nickel is a familiar, readily available and relatively inexpensive material that is easy to electroplate into the 3D structure; nickel is relatively stable to oxidation, something that is helpful for the steps required in the manufacturing process; and nickel is electrochemically stable over the voltage range of the battery.

"Now we can think outside of the box," says James Pikul, first author of the paper, in an interview on the website TechCrunch. "It's a new enabling technology. It's not a progressive improvement over previous technologies. It breaks the normal paradigms of energy sources. It's allowing us to do different, new things."

It may be called a lithium-ion battery but it would not be possible without nickel. Ni

[1] "High-power lithium-ion microbatteries from interdigitated three-dimensional bicontinuous nanoporous electrodes." James H. Pikul, Hui Gang Zhang, Jiung Cho, Paul V. Braun & William P. King Nature Communications 4, Article number:1732 doi:10.1038/ncomms2747.



△ *Microbattery fabrication and design.* [1]

The electrodes in the lithium-ion battery are intertwined, giving it a very high surface area relative to its volume. As the two halves (anode and cathode) are close together, the distance ions and electrons have to travel is considerably reduced, and this in turn allows for faster charge and discharge cycles.

All of this is enabled by a lattice of polystyrene spheres, between which are spaces filled with nickel. The spheres are dissolved, leaving a 3D metal scaffold onto which a nickel-tin alloy is added to form the anode while manganese oxyhydroxide is added to form the cathode. The resulting battery on a glass substrate is immersed in molten lithium salts heated to 300°C. This converts the manganese oxyhydroxide to lithiated manganese oxide, the material used for storing energy in the cathode.

The electrolyte in the current test cells is liquid. Researchers will next explore whether a solid electrolyte will perform as well.

Financial support for this research project is provided by the U.S. National Science Foundation and the U.S. Air Force Office of Scientific Research.

BENJAMIN J. WILEY, ASSISTANT PROFESSOR, DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY

PHOTOGRAPHS BY SHAI GILL

Big Answers to Big Questions

Nickel-containing stainless steel performs at ultra-low temperatures to enable Higgs Boson quest

It's finally official: scientists have discovered the Higgs Boson, the predicted piece in particle physics theories that would help explain the Big Bang and the origins of the universe.

The discovery of the elusive particle required a great investment of time, resources and ingenuity. First, engineers from the European Organization for Nuclear Research known as CERN designed and constructed a US$2-billion particle accelerator, the world's largest, under the mountains straddling Switzerland and France. Next, scientists conducted a series of experiments within the 27-kilometre tunnel, relying on special stainless steel alloys to keep fast-moving particle beams on a steady course. Finally, data managers sifted through information from trillions of sub-atomic collisions to determine if the particle discovered in mid-2012 was indeed a Higgs Boson.

Even now, five years after the quest began, CERN is still not sure if what their scientists found is *the* Higgs Boson of the Standard Model, the most popular theory of particle physics, or another Higgs Boson predicted by a different theory. It will take several more experiments and replication of results to determine this and other properties of this most important particle that is assumed to give mass to all other particles in the universe.

Those experiments take place inside the Large Hadron Collider (LHC), where protons travel at close to the speed of light in opposite directions to recreate the conditions that existed immediately following the Big Bang. The particle beams travel in separate vacuum tubes and are guided around the accelerator ring by a strong magnetic field maintained by electromagnets. CERN scientists were able to detect the Higgs Boson by smashing the protons together.

The choice of materials used to build the accelerator was largely dependent on the superconducting state that requires the magnets to be chilled to minus 271.3°C, a temperature lower than found in outer space. To maintain the deep freeze, the accelerator is connected to a 120-km system of pipes that distribute liquid helium.

Nickel-containing stainless steels that can withstand such a harsh environment play an important role in both the magnets and the helium distribution. The magnets contain about 860 tonnes of Nirosta® 4375 (EN 1.4375), a manganese-nickel stainless steel. The system of pipes that distribute helium to the magnets contain 450 tonnes of chromium-nickel stainless steel EN 1.4307, almost identical to Type 304L (UNS S30403).

The EN 1.4375 alloy is tough enough to withstand the extreme cold and strong forces within the magnet while its very low magnetic permeability prevents the steel itself from becoming magnetized. The chromium-nickel stainless steel is likewise temperature-resistant, ensuring that the pipes do not become brittle.

The LHC is shut down until 2015 as engineers bring the particle accelerator to its full potential. Higher energy levels will allow more collisions and a greater precision in measurements. Although a handful of magnets (15 dipoles and 3 quadrupoles) will be replaced during the upgrade, the configuration, materials and components of the LHC will remain the same, says CERN's head of technology, Frederick Bordry. Ni

SAFETY DOWN UNDER

The strength, durability and versatility of nickel-containing stainless steel ensure that this powerful metal has a myriad of applications, none of which are more important than those that save lives.

In 2009, in Auckland, New Zealand, a toddler went missing from her home. A week later, the two-year-old was found drowned in an underground water drain accessed via a manhole cover that had become dislodged during a recent storm.

This fatality so troubled local builder and father-of-two Kevin Maskell, that he felt compelled to do whatever he could to prevent infants from slipping through manholes ever again.

Maskell gave the matter a great deal of thought, he says, "then woke up one morning with the solution in my head."

For particularly aggressive environments the grilles are constructed in nickel stainless steel, Type 316.

The solution was in fact surprisingly simple: design a safety grille that can be easily and speedily bolted into place underneath the manhole cover. Maskell's design does not interfere with the integrity of the closed manhole and poses no danger to drivers or pedestrians. What's more, removal and reinstallation of the grille take less than a minute and no odours are permitted to escape.

Maskell engaged an engineer to fabricate the prototype, then took out a patent, calling his invention the "Caliber Safety Grille."

The round device is created from 8mm steel bar mesh welded at 150mm centers. It is constructed either of mild steel, hot-dipped galvanized steel for a rugged underground life, or Type 316 (UNS S31600) nickel-containing stainless steel for particularly aggressive environments such as coastal areas or places where acidic water or corrosive waste might be present. Grilles in Type 304 (S30400) are also available.

Advantages of the stainless steel version include high strength, durability, low maintenance, and ease of use. Also, all three versions can be retrofitted into new and existing manhole covers, regardless of their size.

Thousands of drains are in need of being fitted with the safety grille, so the hassle-free installation and low maintenance requirements are huge drawing cards for city councils. The device is already part of a major safety program carried out by the city council of Auckland, New Zealand's largest city, which is having the stainless steel version installed.

The Caliber Safety Grille won't bring back the child whose death prompted it, but it will at least help prevent such fatal accidents from happening again.

△ *The Caliber Safety Grille has been designed to be retrofitted to an existing manhole frame to prevent injury or death if its cover is displaced.*

△ *Safety Grille attached to a ductile iron Korum frame.*

PHOTOS COURTESY OF KEVIN MASKELL

SOUND SOLUTIONS

The combination of corrosion resistance and attractive finish makes stainless steel a good choice for roadside sound barriers

ISTOCK PHOTO ©

ISTOCK PHOTO © MICHAEL DELEON

Excess noise is a common problem of modern, industrial life, and few places are noisier than highways. Fortunately nickel-containing stainless steel is starting to be used in a number of highway noise reduction systems.

Empire Acoustical Systems (ESA) specializes in such applications. The company produces "acoustic panels" which are fixed to sound-barrier walls on the sides of busy roads. These soundproofing panels consist of a perforated cover sheet enclosing high-density mineral wool which absorbs noise. The outer shells are made with galvanized steel or Type 304 (UNS S30400) stainless steel in thicknesses ranging from 0.8 to 1.5mm.

The noise barriers shield nearby homes and businesses from excess noise generated by traffic.

"Most of our customers order our powder-coated galvanized product," says Carina Gonet, marketing consultant for EAS. (Powder-coating is a painting process that uses a combination of electrostatic charge and heat.) "But as a finishing option we also offer stainless, and not just in panels for highway sound barriers but in all our products, from doors and gates to enclosures for heating, ventilation and air-conditioning."

"In addition to providing a beautiful finish, the stainless steel gives added protection for customers who are working in areas with salt-spray or where any kind of metal deterioration is a concern. Customers who specify stainless want a strong attractive product with a product warranty that is better than the alternatives. For them, strength and attractive appearance are the main factors."

According to EAS's web site, its stainless steel series of products "offers the same optimal acoustical performance [as galvanized] with peak durability."

Roadside sound barrier walls are designed to be virtually maintenance-free over their lifetimes. The galvanized steel panels may be powder-coated to inhibit corrosion, depending on the application.

The special design of the panels eliminates the need for fasteners, thereby reducing any chance of rust setting in through drilled holes. "Since there are no fasteners, everything slips into place, which further helps slow corrosion," notes Gonet.

And yet since the panels are used for outdoor application, they will, over time, show some weathering effects, however minor. Indeed, the main concern about anything installed along roadways is corrosion caused by de-icing salt.

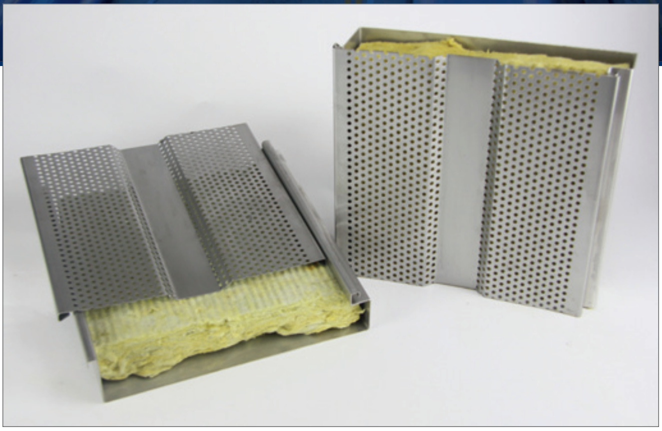


PHOTO COURTESY OF EMPIRE ACOUSTICAL SYSTEMS

△ *Empire Acoustical Systems' perforated sound reduction panels are fabricated from 16- and 22-gauge (1.6 & 0.8mm) cold-formed sheet steel. Many customers request Type 304 stainless for the outer shell, which is valued for its smooth, corrosion-resistant finish.*

"Type 304 will frankly exhibit corrosion staining in such applications," notes Catherine Houska, international expert on stainless steel in architecture and an advisor to the Nickel Institute. "The splash zone for de-icing salt for a highway is typically about 50 ft. This is a high salt exposure zone, and the trend is from sodium chloride to calcium chloride which becomes actively corrosive above the freezing mark and at 45% humidity."

Tina Anderson, project coordinator for EAS, recalls that some galvanized steel panels along a roadside in Virginia recently exhibited signs of corrosion as a result of salt spray. "Our corrective suggestion in this case was to replace the galvanized panels with stainless steel ones since the latter are far more resistant to corrosion," she says, "albeit not completely resistant."

While some corrosion staining is unavoidable even with stainless, Houska notes that if a wall faces the primary wind direction, it may be washed well enough by rain if it has a Bright Annealed or similar finish.

Only time will tell how well the Type 304 stainless steel will last in use, or whether a higher alloyed alloy such as Type 316L (S31603) should be used in areas with the highest salt spray exposure. Ni

Single-crystal Shape Memory Alloys: actuating nickel to the limit

Shape memory alloys (SMAs), such as Nitinol™, a nickel titanium alloy, are well-known materials used in actuators and other applications. TiNi Aerospace in San Rafael, California, has recently developed a new class of nickel-containing SMA: single-crystal shape memory alloys (SCSMAs), made from copper, aluminium and nickel. Compared with conventional SMAs, they show significantly better properties that approach theoretical limits.

SCSMAs are "grown" as a single crystal from a melt using a method similar to that used in the semiconductor industry to fabricate silicon boules (single-crystal ingots). The SCSMA material is generally fabricated as a rod but can have a range of cross sections, including solid, hollow, flat, or oval (see picture). The material can also be subsequently formed into other shapes by normal fabrication methods such as grinding, machining, or electrical discharge machining.

"SCSMAs exhibit significantly enhanced performance over commercially available SMAs made from titanium and nickel," says Dr. Valery Martynov, director of material science at TiNi Aerospace. Like SMAs, they are able to return to a predetermined shape either by being heated to their transition temperature or by having the applied load relieved.

SCSMAs however provide key advantages over SMAs. According to Martynov, these include significantly greater strain recovery (minus 9% compared with 3%), true constant force deflection, a wider transition temperature range (minus 270°C to +250°C), narrow loading hysteresis and shape recovery which is 100% repeatable and complete.

Martynov was the driving force behind the design and development of the SCSMA crystal growing device at TiNi Aerospace, which produces the SCSMA rods used in the company's Mini-Frangibolt® actuator. The actuator is fully resettable and may be operated for hundreds, if not millions, of cycles.

Key advances

SCSMA has numerous potential applications. In a thermal actuator, when the material is in the low-temperature state (martensite), it can be deformed up to 9% with full recovery achieved by raising its temperature above the austenitic transition point. This process results in a powerful actuator capable of delivering recovery forces, or stresses, of up to 600 megapascals.

Nickel-containing SMA: single-crystal shape memory alloys (SCSMAs), made from copper, aluminium and nickel.

PHOTO COURTESY OF TINI AEROSPACEI

The material can also be used as a super-elastic spring. In its high-temperature state (austenite), it has a unique stress-strain profile. Compared with traditional spring materials such as stainless steel or beryllium copper which have an elastic limit of less than 0.5%, SCSMAs are 20 times more elastic and can fully recover from deformations in excess of 9%. Ni

UNS details

Chemical compositions (in percent by weight) of the alloys and stainless steels mentioned in this issue of *Nickel*.

UNS No.	C	Cb	Co	Cr	Cu	Fe	H	Mn	Mo	N	Ni	O	P	S	Si	Ti
EN 1.4307 p. 11	0.030 max.	-	-	17.5-19.5	-	-	-	2.00 max.	-	0.11	8.00-10.5	-	0.045 max.	0.015 max.	1.00 max.	-
EN 1.4375 p. 11	0.040 max.	-	-	19.00-21.00	-	-	-	8.00-10.0	-	0.30-0.45	6.00-8.00	0.05-max.	0.045 max.	0.015 max.	1.00 max.	-
N01555 p. 14	0.07 max.	0.025 max.	0.05 max.	01.1-max.	01.1-max.	0.05-max.	0.005-max.	2.00 max.	-	-	54.00-57.00	0.05-max.	0.045 max.	0.030 max.	1.00 max.	rem
S30200 p. 2	0.15 max.	-	-	17.00-19.00	-	-	-	2.00 max.	-	-	8.00-10.00	-	0.045 max.	0.030 max.	1.00 max.	-
S30400 p. 12, 13	0.08 max.	-	-	18.00-20.00	-	-	-	2.00 max.	-	-	8.00-10.50	-	0.045 max.	0.030 max.	1.00 max.	-
S30403 p. 11	0.030 max.	-	-	18.00-20.00	-	-	-	2.00 max.	-	-	8.00-12.00	-	0.045 max.	0.030 max.	1.00 max.	-
S31600 p. 12	0.08 max.	-	-	16.00-18.00	-	-	-	2.00 max.	2.00-3.00	-	10.00-14.00	-	0.045 max.	0.030 max.	1.00 max.	-
S31603 p. 13	0.030 max.	-	-	16.00-18.00	-	-	-	2.00 max.	2.00-3.00	-	10.00-14.00	-	0.045 max.	0.030 max.	1.00 max.	-

Record setting performance using iron-based superconducting wires Nickel-tungsten alloy key to substrate

It was a scientific challenge which might have been termed "Mission Impossible": build a superconducting wire long enough, flexible enough, and sufficiently affordable for use in commercial applications.

Simply put, the task was "to make a flexible, kilometre-long single crystal of a ceramic superconductor at the price-performance metric of copper one can buy from the hardware store," says Dr. Amit Goyal, a scientist at the U.S. Department of Energy's Oak Ridge National Laboratory in Tennessee. "Most scientists would say you are asking for the sky and it cannot be done."

It took more than two decades of research, but a breakthrough substrate technology developed by Goyal and his team led to the development of a single-crystal-like, kilometre-long flexible superconducting wire. Originally, the superconducting layer was based on a YBCO (yttrium barium copper oxide) superconductor. Earlier this year, Brookhaven National Laboratory reported tests on an iron-based superconducting layer using Goyal's substrate. An iron-based layer has several advantages, the most exciting of which is being able to conduct extremely high currents under exceptionally high magnetic fields while at higher temperatures than other superconducting materials. They are also far easier and less expensive to produce, and less prone to breaking when worked with. The iron-based layer requires a slightly different composition of ceramic layer underneath, one that uses cerium oxide.

The superconducting layer is deposited on a RABiTS, or Rolling-Assisted Biaxially Textured Substrate. The base layer is a nickel-tungsten alloy, just 75 microns thick, which is rolled into a flexible tape. Thin layers of ceramic and finally the superconducting material are then deposited on this base. The deposits mimic the atomic orientation or structure of the underlying metal, creating the single-crystal atomic configuration needed for the superconductor to function.

Nickel won out over copper, iron and aluminum as the base metal of choice for the substrate, notes Goyal, because "nickel is stronger than copper and has better resistance to oxidation." The addition of tungsten further strengthens the nickel as well as making it non-magnetic, which is a crucial property needed to reduce alternating current losses in a superconductor wire. Nickel-chromium and nickel-chromium-tungsten alloys, which are likewise strong and non-magnetic, can also be used.

The superconductor can be used in an array of major applications, including resistance-free underground transmission lines and small, environmentally safe transformers. "More electricity is lost in the United States from transmitting electricity through copper wire or aluminum wires from point A to point B than is consumed in the entire continent of Africa." Goyal says.

The technology also can be used to build energy-efficient generators for use on ships, airplanes and spacecraft. Fitting an offshore wind turbine with a generator and transmission cable fashioned from superconducting components has the potential to double the efficiency of the system.

Says Goyal: "Nickel is enabling the fabrication of long lengths of single-crystal superconducting wire for use in many large-scale applications, the market for which is in the billions of dollars." Ni

▽ *Dr. Amit Goyal, a scientist at the U.S. Department of Energy's Oak Ridge National Laboratory, holds a sample of nickel-tungsten substrate used to make superconducting wire.*

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