DISCOVERY REPORT

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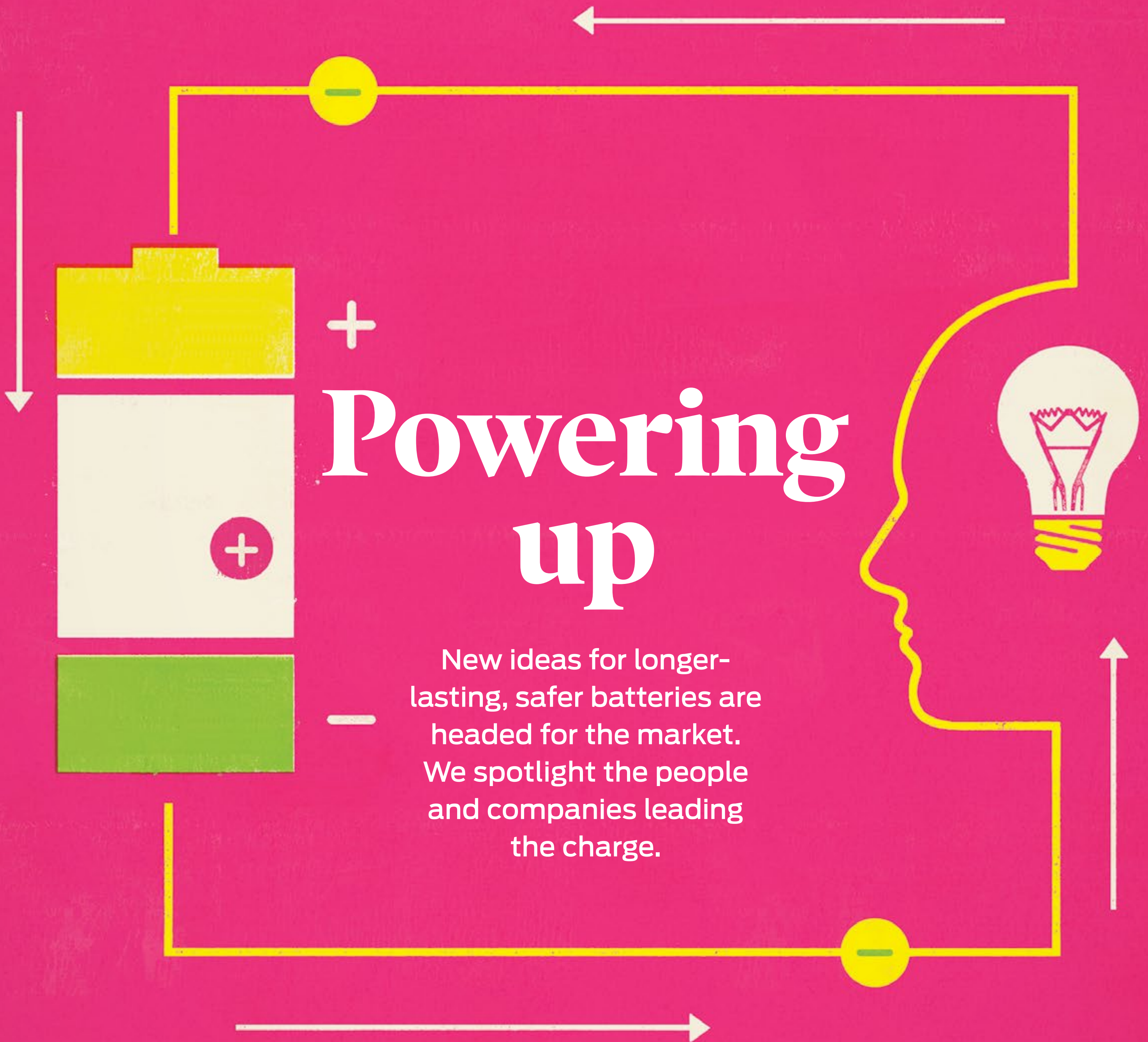

Powering up

New ideas for longer-lasting, safer batteries are headed for the market. We spotlight the people and companies leading the charge.

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The future of batteries

Electricity captured from solar and wind power, stored in the electrical grid, used to charge a fleet of electric cars: What will it take to make this vision of the future possible?

Scientists and investors alike are banking on rechargeable batteries, which store electrical energy in the form of chemical energy so that it can be used later, thereby reducing society's dependence on nonrenewable energy sources.

Batteries have come a long way from the lead-acid technology that dates to the 1850s. In the US, battery energy storage capacity for the grid has nearly doubled every 2 years since 2011, with lithium-ion batteries representing the lion's share of the technology. In 2019, consumers worldwide bought approximately 1.6 million all-electric passenger vehicles. In most of the cars, lithium-ion batteries replace gasoline tanks.

Despite these strides, batteries remain a small piece of the global energy storage puzzle. And batteries face obstacles to becoming a truly sustainable technology. Inside this Discovery Report, you'll meet entrepreneurs who are boosting the amount of energy that lithium-ion batteries can store, pound for pound. You'll hear from firms commercializing safer, nonflammable battery electrolytes, and start-ups trying to improve the batteries' abysmal recycling rates. You'll read about flow batteries, sodium-ion batteries, and much more.

Contributing editor Carmen Drahl, who has covered organic chemistry and green chemistry for C&EN, edited this report. It includes a reading list of papers and patents curated by our sources, as well as by researchers at the CAS division of the American Chemical Society.

As an ACS member, you get exclusive access to the Discovery Report, a quarterly publication analyzing the new science and technology defining the chemical sciences and our industry. Look for the next one in the third quarter of 2020.

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INSIDE

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CHEAT SHEET

5 questions and answers about the future of batteries

Q. Why are experts interested in battery-based energy storage?

» **Batteries play critical roles powering emissions-reducing electric vehicles** and managing the intermittent energy provided by renewable solar or wind power.

» **To avoid power outages during emergencies such as natural disasters,** countries want to employ battery backups to modernize their electrical grids.

» **The cost of the most popular battery option,** the lithium-ion battery, is declining, and its performance is improving.

Q. Where do batteries stand in today's energy landscape?

» **Battery storage is rapidly growing** but is still a small contributor to global energy needs.

» **Pumped hydroelectric storage makes up 96.2% of worldwide energy storage capacity,** with batteries a distant second.

» **In the US, however, nearly all new energy storage capacity** added to the grid since 2003 has been battery storage, with lithium-ion batteries predominating.

» **Despite yearly growth in electric vehicle sales,** the 2.2 million in 2019 represented only 2% of global car sales. About 1 of every 250 vehicles on the road today is electric.

Q. What are the advantages of lithium-ion batteries?

» **Lithium-ion batteries are lightweight.** They store more energy per kilogram than older technologies such as nickel–metal hydride or lead-acid batteries.

» **Lithium-ion batteries lose less of their charge over time** compared with other batteries.

Q. How are chemists mitigating the drawbacks of lithium-ion batteries?

» **The liquid electrolyte in conventional lithium-ion batteries** has caused small-scale battery fires, so firms are developing solid electrolytes to make them safer.

» **An effort is underway to reduce or eliminate the use of cobalt in battery cathodes.** The metal is subject to fluctuating prices and is often mined by workers who face harrowing conditions.

» **Less than 5% of lithium-ion batteries are recycled,** so start-up companies are commercializing new recycling technology.

Q. What's next for battery technology?

» **Companies are using multiple strategies** to increase the amount of energy lithium-ion batteries can store for a given mass, including replacing graphite in battery anodes with materials such as silicon.

» **Some firms aim to penetrate the market with other battery technologies,** such as sodium-ion batteries that use sodium instead of lithium to carry charge, or flow batteries for stationary energy storage made with earth-abundant iron.

» **Europe's lithium-ion battery manufacturing capacity is set to grow by leaps and bounds in the next 3 years,** potentially overtaking North America's. Both regions are still expected to lag behind the global production leader, China, and many of Europe's planned facilities will belong to Asia-based companies.

8 experts working on the cutting edge of batteries weigh in on which materials will matter most

K. M. Abraham

» **Research professor, Northeastern University, and CTO, E-KEM Sciences**

K. M. Abraham invented the lithium-air battery, which has a lithium metal anode and a cathode that is oxygen drawn from the atmosphere. It is the ultimate at packing energy, in theory able to store about 15 times as much energy as a lithium-ion battery of comparable mass.

But Abraham is quick to point out that the technology remains experimental. He says the field should focus for now on improving lithium-ion batteries. The most pressing need is to increase the batteries' energy density so that electric vehicles can run longer distances without recharging. For this, new cathode materials will be key.

The problem with today's layered lithium-nickel-manganese-cobalt oxide (NMC) cathode materials is that removing all the lithium ions during discharge decomposes the layered structure. "You can take a maximum of about 80% of lithium out," Abraham says, which means the cathode's full capacity cannot be harnessed. His group is developing metal oxide materials with higher than normal lithium content. They have stable structures and therefore allow more lithium to be extracted, which results in more energy storage.

Lithium-rich oxide cathodes could lead to a battery with an energy density of 325–350 (W·h)/kg, about 25% more than current batteries. Right now, the group's best lithium-rich oxide cathodes produce a battery with a density of about 290 (W·h)/kg, Abraham says.

"As energy densities increase, "safety is of paramount importance," he adds. He finds nonflammable solid-state electrolytes, such as vitreous or crystalline sulfides, especially promising in this regard.

> **If you're going to ask people to take risks with a new technology, why bother unless it's going to break boundaries?"**

Linda Gaines

» **Transportation system analyst, Argonne National Laboratory**

Linda Gaines's research begins where a battery's life ends. Battery materials will have to be reclaimed to sustainably meet growing demand, she says (see page 20). Her goal is to develop a recycling process that is economical and easy to adapt to regulations.

Cathodes can contain a range of lithium-based compounds. The most common ones include cobalt. The material's real value lies not in the individual elements but in its layered crystal structure. Yet commercially available recycling processes break cathodes down into individual elements, Gaines notes, so they may not be worth all that effort.

That's especially the case with the recent push by the US Department of Energy and battery companies to increase nickel content in the lithium-nickel-manganese-cobalt oxide (NMC) cathodes used in electric-vehicle batteries. Nickel is not as precious as cobalt, Gaines says, so "any process that breaks down the crystal structure will not get enough value out of a low-cobalt cathode material."

Gaines and her colleagues are developing recycling techniques that instead keep the NMC structures from old cathodes intact and upgrade them for new batteries by adding more nickel or taking some cobalt out. "It's alchemy," she says. "Think about a highly ordered crystal structure. You want to knock some of the atoms out and put in different atoms. We don't know how to do that."

Challenges abound as demand grows for battery material. But Gaines is optimistic. "Going from a used battery to a new battery has lots of steps and lots of questions at each step," she says. "So there's lots of good work to be done."

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Bill Macklin

» Chief engineer, Nexeon

Bill Macklin sees the transition from graphite to silicon in lithium-ion battery anodes as inevitable. Major automakers have silicon on their technology road maps (see page 10), and "there's strong alignment between those road maps and what we're developing," he says.

The attraction of silicon is the large amount of charge it stores, which "ultimately translates to a smaller and lighter battery," Macklin says. And unlike lithium metal anodes, silicon does not grow dendrites—the spiky metal deposits that can cause electrical shorts. Many battery makers already mix a small amount of silicon into graphite anodes.

Abingdon, England–based Nexeon is making two anode materials. First is a mostly graphite anode containing 10% silicon by weight—a little more silicon than current technology—that gives slightly higher lithium storage per gram than today's anodes.

The second material, for which a pilot production plant is in the works, is a mostly silicon-based composite with a porous nanostructure that can accommodate the drastic volume expansion silicon undergoes as it takes up lithium ions. The expansion-mitigating structure gives the anode 30% more energy density than today's graphite anodes. It is safer and completes more charge cycles than lithium metal without losing performance.

"If people are going to introduce something radical, if you're going to ask people to take risks with a new technology, why bother unless it's going to break boundaries?" Macklin says.

Arumugam Manthiram

» Professor, University of Texas at Austin and cofounder, TexPower

Material performance and supply chain issues are critical bottlenecks for lithium-ion batteries, says Arumugam Manthiram, and researchers must find creative workarounds. He is taking a two-pronged approach: improving today's lithium-ion battery cathodes and, for the long term, advancing lithium-sulfur chemistry as a successor.

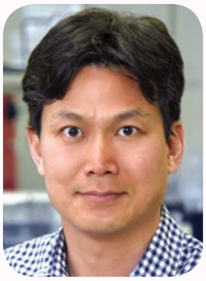
Manthiram says that reducing cobalt in cathodes will address two critical issues with lithium-ion: increasing energy density and reducing cost (see page 8). The cobalt is typically substituted with nickel, however, which is highly reactive and unstable in air, potentially making the battery unsafe and reducing its life. Manthiram and his colleagues dope the nickel-rich cathode with carefully picked ions to overcome these problems. They plan to commercialize a cobalt-free cathode material that performs as well as today's cathodes.

Longer-term goals are to develop metal-free cathode materials such as sulfur, Manthiram says. Lithium-sulfur chemistry can in theory provide five times the energy density of today's lithium-ion batteries at lower cost. But it has challenges. Sulfur is a poor conductor for electrons and lithium ions, and the lithium metal anodes suffer from needle-like deposits called dendrites, which degrade the batteries and cause safety hazards.

Manthiram's group is using special conductive catalysts to enhance lithium-sulfur redox reactions at the cathode and overcome sulfur's poor conductivity. At the lithium anode, they have found that adding tellurium suppresses dendrites and extends battery life. "Lithium-sulfur will be the next big breakthrough," Manthiram says. "The challenge is serious, but the benefit will be enormous."

“Battery performance is always limited by the worst component.”

Benjamin Park



» Founder and CTO, Enevate

Benjamin Park sees battery technology's transformations as a narrative of scale. As batteries get bigger—going from mobile phones to electric vehicles and soon the grid—manufacturers will have to keep delivering, and do so sustainably. "We need to be good stewards for the earth," Park says.

His Irvine, California, start-up has developed a silicon anode–based battery that holistically tackles market adoption, cost, and sustainability, according to Park. Range anxiety, or the fear of running out of charge, keeps people from buying plug-in cars. Enevate's technology will give electric vehicles with 30% more driving range that charge "in the same time it takes to fill up a gasoline car," he says.

Credit for that goes to the thin, porous, binder-free silicon film used at the anode that swiftly takes up and releases 10 times as many lithium ions as today's graphite anodes, translating to a more energetic battery. Silicon typically swells and shrinks during charging and discharging and eventually breaks apart, but Enevate's proprietary spongy film has enough give to accommodate the change in volume. In addition, Park says, it is made from a low-cost, low-grade silicon and does not require energy-intensive processing; graphite has to be heat-treated and purified.

Enevate has support from battery giants

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LG Chem and Samsung. With the Renault-Nissan-Mitsubishi alliance, the company is developing battery cells for 2024–25 model-year vehicles.

Silicon and lithium metal are both top contenders for next-generation anodes, but "silicon will be the main player," Park says. "It can deliver the same energy density but be much more sustainable, safer, and easier to implement."

Amy Prieto

» Professor, Colorado State University, and founder and CTO, Prieto Battery

Too often in battery research, developers focus on individual components. But a battery is greater than the sum of its parts, Amy Prieto says. "It is virtually impossible to optimize one part without having to reiterate other components. And battery performance is always limited by the worst component."

Prieto is addressing the battery as a whole by overhauling the traditional planar design. Her 3-D battery is based on a porous copper foam that is electroplated with a copper antimonide anode, coated with a proprietary solid-state polymer electrolyte, then filled with a conventional cathode material such as lithium cobalt oxide or lithium-nickel-manganese-cobalt oxide.

The pores boost surface area, increasing energy storage capacity and helping the battery charge more quickly. Prieto's polymer electrolyte is a safer stand-in for conventional liquid electrolytes, which can be flammable. The copper foam is also a good thermal conductor, so it dissipates heat and prevents overheating. "I think safety is very important as we get to larger, high-performance batteries," she says.

For that reason, Prieto believes solid-state electrolytes are likely to be the most important materials for batteries. Researchers are pushing for higher-capacity batteries by improving cathode materials and using silicon or lithium metal anodes. "But in order to make these high-energy density components work, it really all comes back to the electrolyte," she says.

Eric Wachsman

» Founder and executive chair, Ion Storage Systems

Eric Wachsman started Ion Storage Systems because he believes the solid-state electrolyte he works on offers unique advantages. The strong ceramic electrolyte is highly conductive, nonflammable, and stable over a wide voltage range. "So it opens up the potential to use lithium metal anodes and new higher-voltage cathodes" and produce a safe, energy-dense battery, he says.

Today's liquid electrolytes are flammable. Alternatives in development at start-ups and car companies include polymer- and sulfide-based solid electrolytes, but these have low conductivity and stability, respectively.

Ion Storage's electrolyte has an ultrathin, dense layer of lithium-lanthanum-zirconium oxide sandwiched between two porous layers of ceramic with a superthin aluminum oxide coating. The dense layer adds strength and blocks needle-like dendrites that tend to grow from lithium metal anodes, while the porous layer provides mechanical support and high surface area to soak up lithium ions. Making the ceramics superthin isn't easy but is crucial to reducing resistance. Wachsman brought manufacturing expertise from his years of work on solid-oxide fuel cells, which are also made of ceramic materials. "Until we did it, nobody had been able to make it thin like that," he says.

With a manufacturing facility in Maryland, the company plans to have its first products ready in about a year. It will target defense and aerospace markets that could accept the batteries' initial higher price in exchange for more safety and lighter weight.

M. Stanley Whittingham

» 2019 Nobel laureate and professor, State University of New York at Binghamton

Stanley Whittingham's research at Exxon in the early 1970s led to the first rechargeable lithium-ion batteries and earned him a share of the 2019 Nobel Prize in Chemistry. He is a firm believer in the layered lithium-nickel-manganese-cobalt (NMC) oxide cathode materials used in many of today's electric vehicles.

"It's clear that NMCs are going to dominate at least the next 10 years," says the lithium-ion pioneer. Today's materials have 60% nickel, and there's a huge push to go higher, he says, but that creates safety challenges because thermal stability decreases with increased nickel. In addition, charging nickel-rich materials leads to unwanted reactions that release dangerous gases.

Whittingham is working on solutions to these issues as part of the US Department of Energy's Battery500 Consortium, which aims to more than double battery energy density, to 500 (W·h)/kg while keeping costs under $100 per kilowatt-hour. "We're looking at 95% nickel," he says. The team will build in extra safety features: robust packaging, vents for controlled gas release, and electronics protection circuits that can dial back voltage or current.

They are also trying to understand how they can bolster the material's thermal stability and initial capacity loss. "One big issue with all NMCs is they lose 10–15% capacity on the very first cycle," Whittingham says. "One of our targets is to find out why and solve that. It immediately gives you 10% extra capacity."

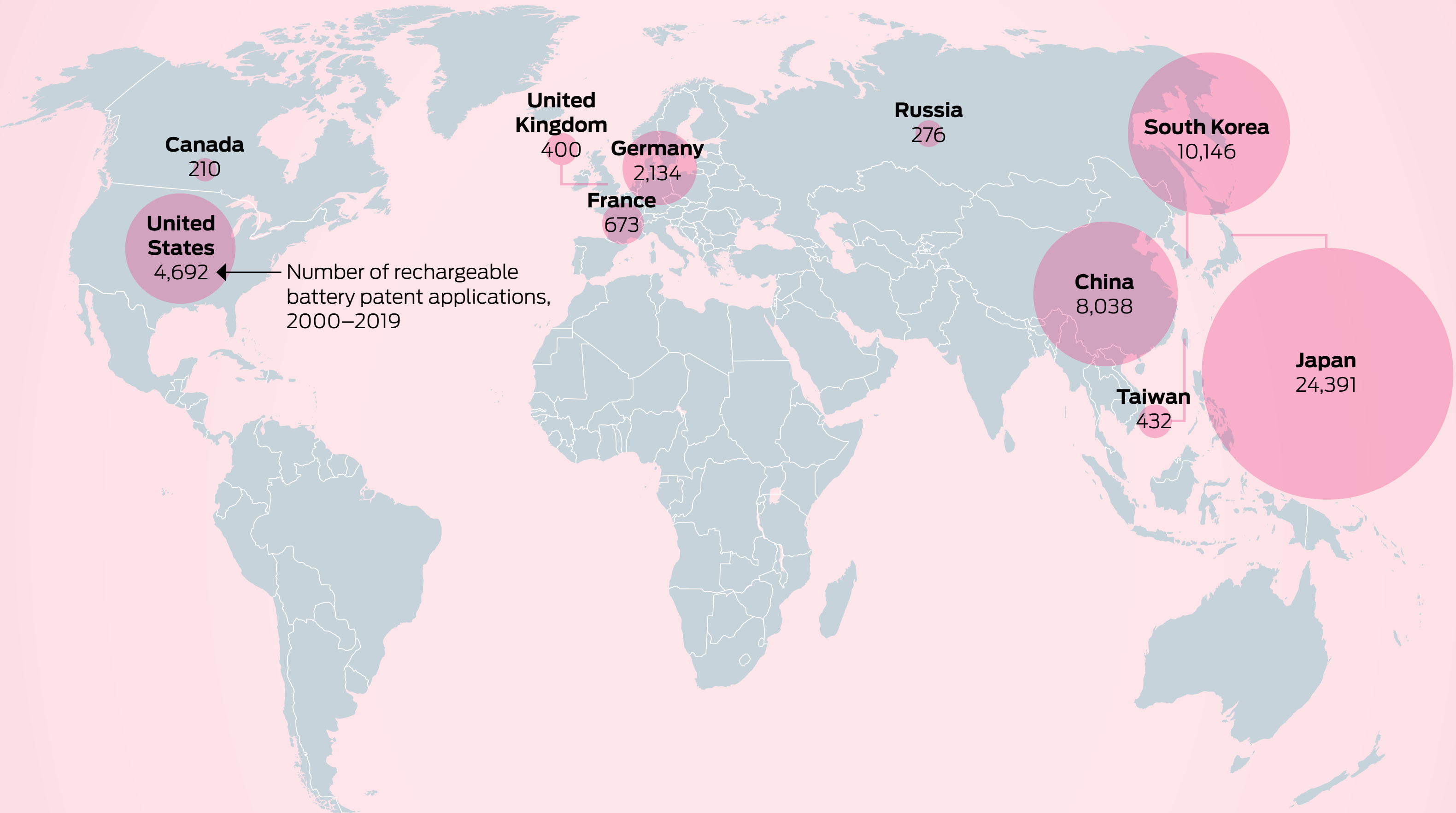
CREDIT: KIRA VOSS (PRIETO); IMAGES COURTESY OF INSTITUTIONS

Meet the battery-patenting leaders

BY THE NUMBERS

Hot Spots

Among the top 10 countries, considerable disparity exists in patenting activity.



Battery Stats

Stay current with our selection of facts and figures.

130 million
Number of electric vehicles predicted to be on the road by 2030

$1 billion
Amount the World Bank committed to battery storage to help countries use more renewable energy

860 million
Number of people worldwide without access to electricity

<5%
Percentage of Lithium-ion batteries currently recycled

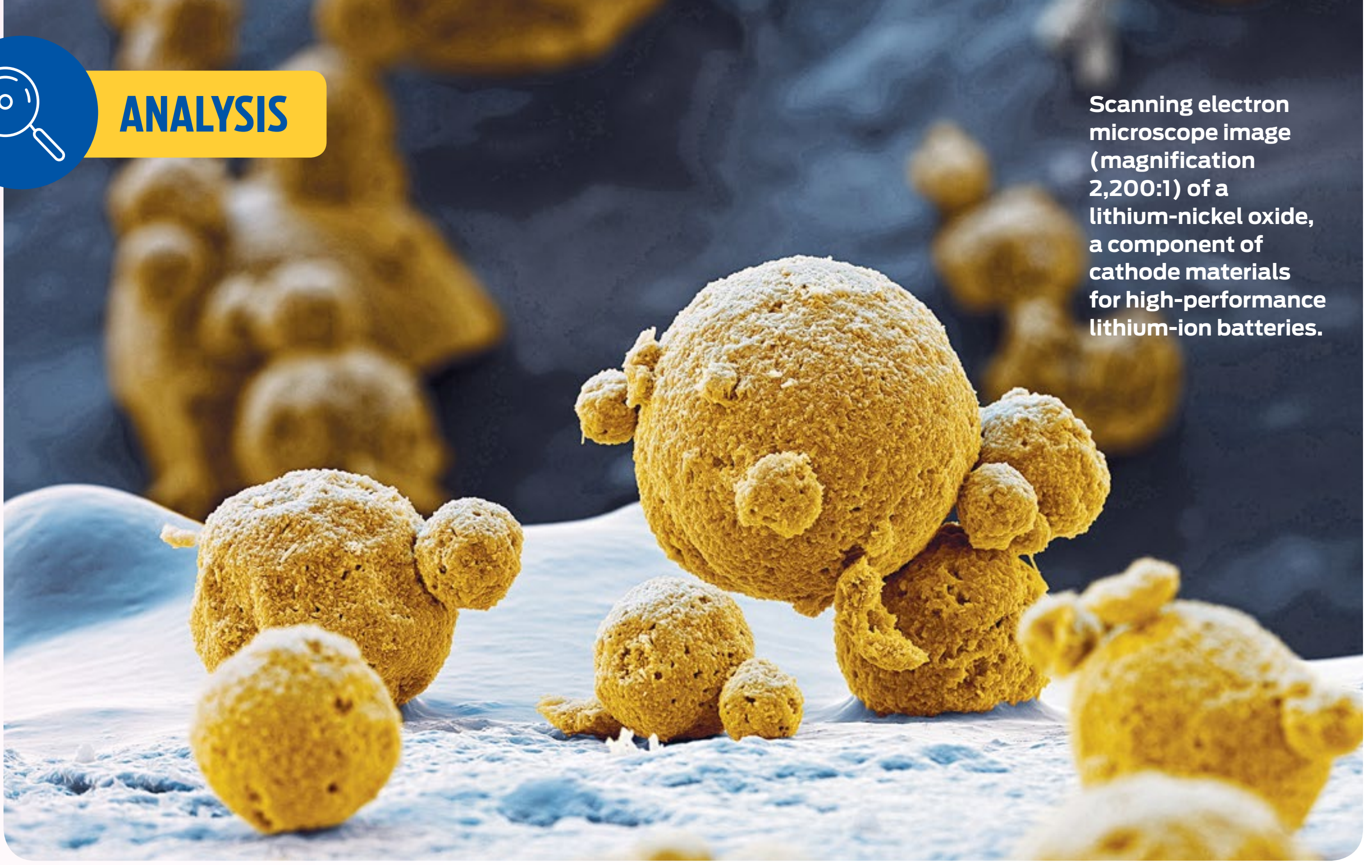
~$70 billion
Value of the market for Lithium-ion batteries projected for 2023

2003
Year the oldest operating grid-scale battery system in the US came online

Sources: Chemical Abstracts Service, International Energy Agency, Navigant Research, US Department of Energy, US Energy Information Administration, World Bank.

Notes: Patents may be registered in certain territories and administrative regions, and such patents are counted separately from those of corresponding governing nations. Figures for Germany and Russia include patents published after a long delay that were filed in the former East Germany and Soviet Union, respectively.

ANALYSIS



Scanning electron microscope image (magnification 2,200:1) of a lithium-nickel oxide, a component of cathode materials for high-performance lithium-ion batteries.

CREDIT: BASF

Cathode makers push past their cobalt blues

PRACHI PATEL, SPECIAL TO C&EN

Three decades ago, when Sony and Asahi Kasei released the first lithium-ion batteries, sparking the mobile electronics boom, the batteries' chemistry hinged on one transition metal: cobalt. The combination of a lithium-cobalt oxide cathode and carbon anode packed energy into a small, lightweight cell.

But cobalt cathodes didn't satisfy electric vehicles' hunger for larger, cheaper, more energy-dense and longer-lasting batteries. So researchers swapped some of the cobalt with nickel, which stores more charge at half the cost. Nickel is also free of cobalt's supply risks and geopolitical and ethical concerns. About 70% of the world's cobalt mine production is in the politically unstable Democratic Republic of the Congo, where some mining operations are rife with human rights abuses, and 80% of the cobalt oxide processing for cathodes occurs in one country—China.

To shield themselves from potential material shortages, auto and battery makers are racing to eliminate even more cobalt from cathodes. As a result, both low- and no-cobalt cathode options are on the horizon.

Today's electric vehicles use cathodes that are either lithium-nickel-manganese-cobalt oxide (NMC) or the more expensive lithium-nickel-cobalt-aluminum oxide (NCA). For all its pluses, nickel is thermally unstable and highly reactive, which degrades the electrode's charge-holding capacity, so manganese or aluminum is added for safety and stability.

In the last decade, cobalt content in vehicle battery cathodes has gradually declined. Current NMC cathodes contain 60% nickel and 20% each of cobalt and manganese, but manufacturers are moving toward 80% or more nickel.

"Going cobalt-free is not easy," says Shirley Meng, a materials scientist at the University of California San Diego and member of the US Department of Energy–funded Battery500 Consortium, which is aiming for 95% nickel. Lithium-ion battery cathodes are made of layered metal oxide crystals that get reversibly stuffed with lithium ions. "A nicely layered structure easily holds charge, and certain elements like cobalt prefer this structure," Meng says. "Nickel and manganese try to jump to the lithium layer." Cobalt keeps the structure stable and helps hold charge, making it crucial for battery life-span and range.

Meng and her colleagues tweak element ratios in the crystal structure, then use X-ray diffraction to deduce how atoms in the low-cobalt cathodes move during charge cycles. "Most of the nickel migration happens on the particle surface—the weak spot where the nickel and lithium start to mix," she says.

Protecting that surface becomes vital for ultra-low-cobalt cathodes, and the Battery500 Consortium is developing coatings to do the job. BASF is developing customized dopants and coatings to stabilize the bulk and surface structure of its low-cobalt, high-nickel NMC cathodes, says Jacob Haag, the company's battery materials development manager.

Some have been able to eliminate cobalt completely. At the University of Texas at Austin, Arumugam Manthiram has used doping to make cathodes cobalt-free. Manthiram and his colleagues dope their nickel-heavy cathodes with aluminum, magnesium, or other appropriate ions to overcome the instability and reactivity issues that come with high nickel content. The cathodes have an energy density and cycle life comparable with commercial NMC cathodes. Manthiram has cofounded a firm, TexPower, to commercialize them.

BASF is also focused on eliminating cobalt from cathodes by developing a cobalt-free, manganese-rich system. "This is an exciting class of materials comprised of sustainable, low-cost metals, while having an energy density approaching that of high-nickel NMC technologies," Haag says.

Down the road, "we want complete alternatives to the oxide system," says Tobias Glossman, principal systems engineer at Daimler's Mercedes-Benz Research and Development North America. Daimler is collaborating with IBM to develop a halide system for future batteries. The companies' novel halide-based cathode materials are cobalt- and nickel-free and can be extracted from seawater. Initial tests have shown surprisingly fast charging capability, Glossman says.

Meanwhile, Tesla is reportedly readying a battery developed by Contemporary Amperex Technology, a company based in China that specializes in lithium-ion phosphate batteries. These cobalt-free cathodes have a crystal structure that can take up and release lithium ions more easily than the classic metal oxide cathodes, which results in much faster charging. That faster charging comes at the expense of less energy stored, which gives a shorter driving range.

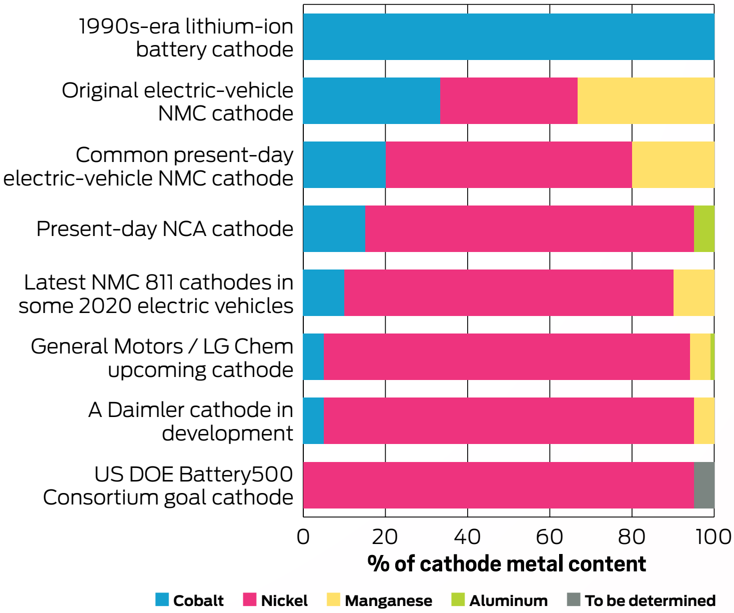
For long-range and long-lasting batteries, cobalt is indispensable at present, Glossman says. Between in-house research at Daimler and collaboration with cathode makers, he says, promising low- and zero-cobalt candidates are in the pipeline that might be in cars in a couple of years. The challenge with any new, highly engineered cathode material is to scale it to be convenient and profitable for battery makers and carmakers to adopt; they might be more inclined toward a less risky, low-cobalt cathode than a new material with no cobalt.

Besides, eliminating cobalt is not strictly necessary, according to Glossman. "There will always be some cobalt by-product from copper and nickel mines, and supply and demand regulate price." The supply equation could change with Australia trying to ramp up cobalt production. "I think low-cobalt cathodes are OK," he says.

"We want complete alternatives to the oxide system."

Kicking the cobalt habit

Even as the percentage of cobalt in battery cathodes has decreased, manufacturers and government agencies have set even more ambitious targets.



Sources: *Nat. Energy, Science, ACS Energy Lett.*, interviews, news reports.
Notes: Percentages are estimates based on journal publications and news reports. NCA means lithium-nickel-cobalt-aluminum oxide. NCM means lithium-nickel-cobalt-manganese oxide.

Prachi Patel is a freelance writer based in Pittsburgh.

ANALYSIS

Amprius's silicon anode in a lithium-ion battery helped power Airbus's Zephyr S pseudosatellite, depicted here, for more than 25 days above 21 km, setting a new endurance and altitude record for stratospheric flight.

It's the anode's turn now

ALEX SCOTT, C&EN STAFF

It was 2007. Apple CEO Steve Jobs announced the iPhone, J. K. Rowling finished her seventh and final Harry Potter novel, and what was then the worst financial crisis since the 1930s was about to hit.

It was also the year that Gene Berdichevsky, an engineer and employee number 7 at Tesla, the electric car pioneer, began questioning why gains in recent years in the energy density of lithium-ion batteries had fallen from 7–8% to 3–4%. With returns from improvements in battery cathode performance beginning to taper, Berdichevsky began to consider the next bottleneck—the poor energy density of the traditional graphite anode.

Tens of start-ups and established materials firms eventually began asking the same question. Many came to the same conclusion as Berdichevsky: that silicon or lithium would be ideal as an anode material. In theory, they are able to hold roughly 10 times the number of electrons as graphite, leading to lithium-ion batteries with 20–40% higher energy density.

The catch is that the anode also absorbs a large number of lithium ions during charging. Graphite handles them well, but a silicon anode swells more than 300%, causing its surface to crack and energy storage performance to drop rapidly. Lithium-metal anodes don't present an expansion problem, but they are expensive and present other technical problems.

After more than 10 years of R&D, several material developers think they have solved the expansion issues associated with using silicon in anodes, and they are starting to bring their materials to the market. Substantial business challenges lie ahead, not least a potential intellectual property showdown because so many companies are developing technologies in such a narrow field. But it's clear that the anode's time has come.

Anode material developers are well aware that the market potential is big and getting bigger as lithium-ion battery use grows in portable devices, electric cars, and grid energy storage. The anode is worth 10–15% of the total cost of a lithium-ion battery, according to Chloe Holzinger, an energy storage ana-

CREDIT: AMPRIUS

lyst with Lux Research. The global anode material market could be worth $10 billion by 2025, she says.

The research is following the money, says Jeff Chamberlain, former head of Argonne National Laboratory's battery development activities and now CEO of Volta Energy Technologies, a venture capital firm investing in battery technologies. "There is no surprise that people are seeking to improve the lithium-ion battery, and the anode is the place," he says.

For Berdichevsky, especially, the journey to an improved anode has been long. He left Tesla in 2008 to return to school at Stanford University, earning an MS in energy-dense anode materials. He cofounded and became CEO of Sila Nanotechnologies in 2011 to develop a commercial silicon anode.

The conventional wisdom is to replace, say, 10% of the graphite in a battery anode with silicon or silicon oxide, improving density without introducing too much swelling. Sila is taking a different approach.

The company has created a nanocomposite of covalently bonded nanostructures of which 50% are silicon and the rest undisclosed nongraphite materials. The composite is porous but encapsulated with a sealed outer layer that prevents electrolyte penetration into the composite, protecting it from damage during charge and discharge. The composite is contained in a porous scaffold structure so it is able to expand and contract without puncturing the coating, Berdichevsky says.

"We are not adding our silicon nanocomposite to graphite. We are replacing all the graphite in the anode," he says.

Berdichevsky estimates that Sila's material has an energy storage capacity four or five times that of graphite, enabling the energy density of a lithium-ion battery to increase by 20–40%.

"A lot of the magic is in how we do the processing. We expect it will be cheaper than graphite at very large scale on a dollar-per-capacity basis," Berdichevsky says.

The California-based firm has raised $340 million from investors. Sila expects its anode materials to be used in batteries for portable devices.

Along with other anode material developers, Sila has an eye on the ballooning auto battery market. The firm has a partnership with the German carmaker BMW, which is investing heavily in electric cars. Berdichevsky is targeting large sales volumes starting in the mid-2020s.

For Nexeon, an Abingdon, England–based silicon anode material start-up, the race to commercialization is more akin to a marathon than a sprint. Now in its 14th year, Nexeon has experienced some lows, including the 2014 mothballing of a $5 million pilot plant in Abingdon when the firm's nanopillar-structured silicon proved problematic to manufacture at scale and low cost.

But Nexeon has taken the lessons learned from that experience and bounced back, Chief Engineer Bill Macklin says.

"There is no surprise that people are seeking to improve the lithium-ion battery, and the anode is the place."

Nexeon is developing two anode materials. NSP-1 features a powdered silicon compound with particles ranging in size from a few to about 10 µm. Its use is limited to about 10% loading by weight in a graphite anode to avoid expansion problems. Compared with graphite, it promises to increase anode capacity by about 30%, leading to a corresponding increase in battery cell energy density of up to 15%.

To offer even more energy density, Nexeon is developing NSP-2, a silicon compound featuring engineered porosity at the particle level for use in concentrations far higher than 10% to yield an increase in cell energy density of up to 30% versus graphite. Nexeon is 2 years into a 3-year project to develop NSP-2 in association with specialty chemical firm Synthomer and University College London. Synthomer is developing a polymer binder for use with Nexeon's silicon anode material, while the university is undertaking materials characterization.

The idea is that, by the end of the project, you have customer validation, scale, demonstrated performance, and intellectual property, Macklin says. "These inputs then form the basis for an investment."

Wacker Chemie, which holds an option to take a minority stake in Nexeon, is commercializing its own silicon anode material in lithium-ion button batteries. The big German silicon producer estimates that its technology could enhance the energy density of such a battery by about 20%.

"Most of the market is using silicon suboxides sprinkled in a small percentage into existing graphite. Our approach is to use a silicon-dominated anode," says Christian Hartel, the Wacker board member responsible for R&D. The company is developing a series of strategies to increase energy density, including coatings to protect silicon against swelling and contraction.

Moving from button batteries to automotive batteries could take years, Hartel acknowledges. This is partly because the materials that Wacker has developed may have to be modified substantially to maintain a high level of performance over many charging cycles, he says.

Sila, Nexeon, and Wacker have yet to put a product on the market. In contrast, the Stanford University spin-off Amprius, formed in 2008, is already selling its silicon-graphite compounds commercially in a mix of around 10% silicon and 90% graphite, according to Lux Research's Holzinger. The company didn't respond to C&EN's requests for an interview.

Amprius's technology features a shell that encapsulates silicon nanowires. The firm claims its approach overcomes the inherent instability of silicon-containing anodes, enabling their use over hundreds of charge cycles.

Amprius also has a 100% silicon anode that Airbus successfully tested in lithium-ion batteries for its Zephyr S pseudosatellite, which travels in the stratosphere rather than in space for applications such as surveillance and navigation. The batteries

Sweet spot

Silicon-based anodes offer more energy density than graphite and more stability than lithium.

ANODE MATERIAL	SPECIFIC CAPACITY (mAh/g)	PERCENT VOLUME CHANGE	BENEFITS	CHALLENGES
Lithium	3,862	na	Highest energy density; light	Unstable, slow charge rate
Silicon	3,600	320%	High energy density	Capacity fade due to damage from expansion and contraction
Aluminum	2,235	604	Better energy density than graphite	Expands more than silicon and is less energy dense
Tin	990	252	More stable than silicon	Less energy dense than silicon
Graphite	372	10	Stable, widely used	Poor energy density

have an energy density of over 435 (W·h)/kg—substantially higher than that of commercial lithium-ion batteries in use today.

Manufacturing technologies are much more complex for anodes with high silicon loading, though, so all-silicon anodes for the automotive market are still some ways off, Lux's Holzinger says.

Also pursuing an all-metal anode is the lithium-sulfur battery maker Oxis Energy, though in its case the metal is lithium. Lithium-sulfur batteries are known to suffer from fading performance after a number of recharge cycles, but if Oxis can solve this problem, it will be on course to outperform the energy density of the best lithium-ion batteries.

A lithium-metal anode has the highest specific capacity of any anode material, at 3,862 (mA· h)/g, says Oxis's chief technical officer, David A. Ainsworth. When paired with an optimized sulfur-based cathode, it will allow Oxis's Li-S battery to achieve an energy density of more than 425 (W·h)/kg, he says, compared with about 200 (W·h)/kg for a lithium-ion battery.

Equipping the battery with a lithium sulfide electrolyte protects the lithium-sulfide anode from degradation because the electrolyte instantly forms a film on the anode, Oxis says. With a melting point of more than 900 °C, this coating protects the lithium even at extreme temperatures, the firm says.

Oxis raised $60 million to build its first manufacturing facility. The plant, which will be located in Brazil, will have the capacity to make 2 million battery cell pouches per year. The pouches are set to go into batteries used by the aviation and electric vehicle sectors.

Lux's Holzinger doubts that lithium-sulfur battery developers can solve the problem of performance fade. A possible indicator as to how competition between lithium-sulfur and silicon-containing lithium-ion batteries will play out is Airbus's decision to ditch the use of lithium-sulfur batteries in its pseudosatellites and opt for Amprius's silicon anode battery. "We are no longer working with lithium-sulfur as we did not see the performance we require," Airbus says.

Yet another firm, the Massachusetts Institute of Technology spin-off SolidEnergy Systems, sees a way to keep the benefits of a lithium-metal anode without the potential drawbacks of lithium-sulfur chemistry.

SolidEnergy claims it has gotten around the issues associated with lithium-metal anodes—such as sharp, dendritic lithium structures that form on the anode surface—by developing a lithium-ion battery that is anodeless. During its first charge cycle, lithium is back plated onto a copper current collector, activating the battery.

The technology also features an electrolyte that is stable in contact with lithium. The system promises double the energy density of a standard lithium-ion battery. It is also the world's lightest rechargeable battery, claims SolidEnergy's CEO, Qichao Hu.

Experts contend that lithium-metal anodes are years away from mass-market introduction. Given lithium-ion batteries' history of catching fire, such as those made in recent years by Samsung, battery makers have become risk averse, Volta Energy's Chamberlain says. The most likely scenario will be the gradual adoption of silicon blended with graphite in anodes, rather than a jump to 100% silicon or lithium, he says.

Overshadowing these marketplace developments is uncertainty about intellectual property rights relating to silicon anode technology because so many patents have been filed. About 1,100 patents relating to silicon anodes were filed in 2016 alone, and filings are increasing annually, according to the technology market research firm IDTechEx. Samsung was the most prolific in 2016 with almost 250 patents filed, followed by LG Chem, Panasonic, Sony, and Nexeon.

A potential issue for Sila is that the firm's technology appears to be similar to that of Amprius, Lux's Holzinger says. Sila's "patents describe a core shell morphology that is very similar to that of Amprius. This could be a problem for Sila given that Amprius also filed in the US but filed its patent first," she says.

A broader challenge for many silicon anode material developers is that after so many years of research they could soon come under financial pressure—if they are not already—to actually start selling their products. Just as the technological breakthroughs are emerging, industry consolidation could be on the way. The winners and losers will likely emerge in the next few years.

"A lot of the magic is in how we do the processing."

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ANALYSIS

Better separators come together

PRACHI PATEL, SPECIAL TO C&EN

As demand surges for electric-vehicle batteries that can handle longer trips, electrodes and electrolytes are poised for makeovers. But another component also does heavy lifting in a battery: the separator, a microporous polymer membrane that physically isolates the cathode and anode to prevent dangerous short circuits.

"Engineering a good separator is a critical part of making a good battery," says K. M. Abraham, professor at Northeastern University and CTO of battery consulting firm E-KEM Sciences. In addition to keeping batteries safe, separators conduct lithium ions and hold the electrolyte. As the industry moves to battery cells with higher energy density, scientists are under pressure to develop separators that are thinner and more conductive, mechanically resilient, and compatible with new electrolytes.

Polyolefin membrane separators dominate today's market. Celgard, a subsidiary of separa-

Rolls of lithium-ion battery separator film. The inner spool is 6 inches (15.24 cm) in diameter.

CREDIT: CELGARD

tor maker Asahi Kasei, manufactures single and multilayer separators including trilayer designs made up of a polyethylene membrane sandwiched by two polypropylene membranes. Polyethylene melts at about 132 °C. If the battery gets far hotter than its regular range of up to around 50 °C, the polymer's lithium-ion-conducting pores fuse closed, shutting down the battery.

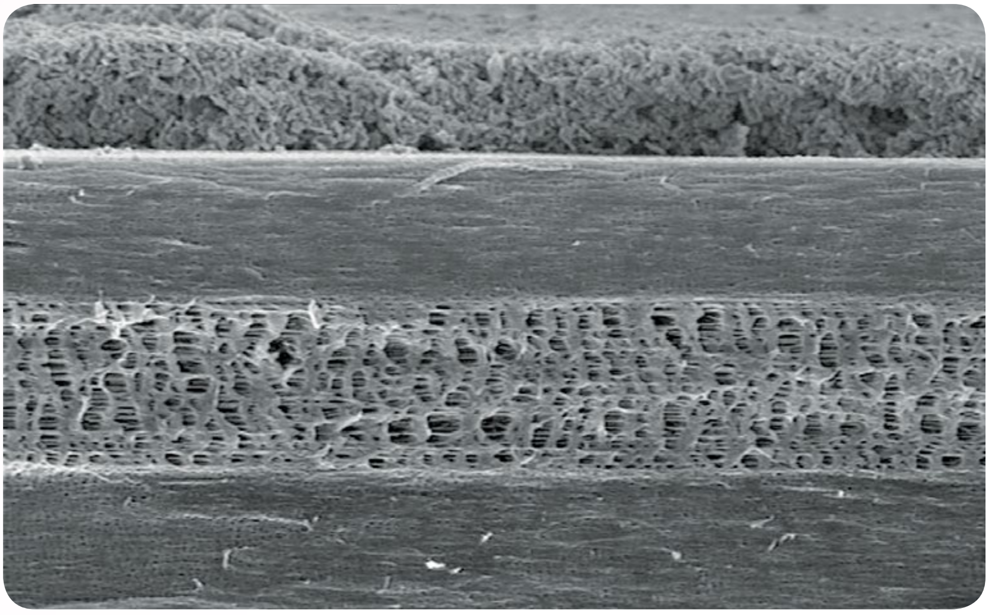
Celgard's engineers work closely with battery makers to design separators that work well with other components for optimal performance, says Stefan Reinartz, global director of R&D at Celgard. Uniform thickness and porosity are critical to soak up electrolytes and enhance ionic conductivity, he says. The company's unique process, which involves precisely stretching a polyolefin film, results in high-quality membranes with evenly spaced, appropriately sized pores. By optimizing the film stretching conditions, Celgard manipulates porosity and pore shape as well as other attributes that affect the membrane's properties.

Today's separators are usually 15–20 μm thick. These thin, highly porous membranes can more easily rupture or be punctured by spiky lithium deposits called dendrites that form over time during battery operation and that can electrically connect the electrodes and cause a short. To add strength, Celgard scientists invented a separator with a thin ceramic-polymer composite layer on the porous polyolefin membranes. Most of today's high-energy electric-vehicle cells use such ceramic composite-coated separators, Reinartz says. Proprietary additives, coatings, and treatments that alter the surface chemistry make the separators compatible with different types of electrolytes. In March, Celgard filed a lawsuit against a Chinese company alleging stolen trade secrets related to its separators.

Novel composite separators are starting to gain traction. These are ultrathin, frequently single-layer polymer films either impregnated or thinly coated on both sides with ceramic particles. The ceramic particles help soak up the electrolyte better, improving conductivity, and are more hydrophilic, allowing the use of less-flammable ionic liquids as electrolytes. The new composites are heavier and slightly less bendable than polyolefin membranes, which makes them potentially harder to put into a cylindrical battery cell. But manufacturers claim that they are more porous and more resistant to mechanical deformation, melting, and dendrite penetration. "The idea is that even if the polymer melts, the ceramic will keep the electrodes apart and maintain good separation so you can prevent thermal runaway reactions," Abraham says.

"Engineering a good separator is a critical part of making a good battery."

German manufacturers Evonik and Freudenberg Performance Materials have chosen polyethylene terephthalate films, coated or filled, respectively, with ceramic particles. Organic binders such as styrene-butadiene or polyvinylidene fluoride (PVDF) tightly fix the ceramic particles to the microfibers in Freudenberg's films. In the US, Porous Power Technologies disperses ceramic particles throughout a PVDF membrane.



Cross-section SEM image of a ceramic-coated separator. The scale is about 30 μm from left to right.

CREDIT: CELGARD

Academics are exploring other unusual materials. Mark Hersam of Northwestern University has developed a composite separator by incorporating nanometer-sized flakes of carbon-coated hexagonal boron nitride into a PVDF matrix. "Boron nitride is exceptionally thermally and chemically stable," Hersam says. And while the exact mechanism is uncertain, "there's evidence that boron nitride suppresses dendrite growth," he adds. "It's a good thermal conductor, so it spreads out hot spots on the electrode surface." Those hot spots might trigger dendrite growth. The carbon-coated nanoflakes also provide a lot of surface area that can be chemically tailored for wetting of the electrolyte.

Moving to nontraditional materials is fraught with risk in a competitive separator market, however. And while the materials used today aren't expensive, the sophisticated engineering required to achieve desirable properties increases the price of the separators, Abraham says. "Lots of companies are doing good work," he says. "The main driver now is reducing cost."

Prachi Patel is a freelance writer based in Pittsburgh.

We picked 20 promising companies chasing the electric-vehicle and grid-storage batteries of the future

» **Cadenza Innovation**
» **cadenzainnovation.com**
» **Based:** Wilton, Connecticut
» **Founded:** 2012
» **Money raised to date:** $16 million
» **Key partnerships:** Alcoa, Fiat Chrysler Automobiles, Shenzhen BAK Power Battery
» **Strategy:** Cadenza uses a noncombustible ceramic fiber material to control the temperature inside rechargeable lithium-ion battery cells. This allows a tighter packing of the cylindrical metal sheets that power the battery, increasing the energy density without compromising safety and also cutting production costs.
» **Why watch:** Through a deal with manufacturer Energy Renaissance, the company is bringing its expertise to Australia's first utility-scale lithium-ion battery-making facility.

» **Enevate**
» **enevate.com**
» **Based:** Irvine, California
» **Founded:** 2005
» **Money raised to date:** $111 million
» **Key partnerships:** LG Chem, Renault Nissan Mitsubishi, Samsung SDI
» **Strategy:** Enevate envisions charging electric vehicles in the same amount of time it takes to refuel a gasoline-powered car, and they design their battery cells to promote extra-fast charging. Enevate's lithium-ion battery design replaces conventional graphite anodes with silicon-dominant anodes, which have a higher energy capacity.
» **Why watch:** The firm's advisory board counts among its members chemistry Nobel laureate and battery pioneer John B. Goodenough.

» **Enovix**
» **enovix.com**
» **Based:** Fremont, California
» **Founded:** 2006
» **Money raised to date:** $191 million
» **Key partnerships:** Cypress Semiconductor, Intel, Qualcomm
» **Strategy:** Enovix's innovation is its 3-D battery cell architecture. Unlike the horizontally wound structure of a conventional lithium-ion cell, this architecture vertically stacks high-capacity silicon anodes, cathodes, and separators in a flat structure.
» **Why watch:** In October, Enovix disclosed a partner agreement with a major Asian lithium-ion battery manufacturer to meet customer demand, including for the electric-vehicle market.

» **ESS**
» **essinc.com**
» **Based:** Wilsonville, Oregon
» **Founded:** 2011
» **Money raised to date:** $47 million
» **Key partnerships:** ARPA-E, Power Africa, Wells Fargo
» **Strategy:** The firm's long-duration flow batteries use earth-abundant iron, salt, and water for the electrolyte. The technology is designed to extend the availability of intermittent renewable energy sources like wind and solar for energy-storage durations of up to 10 h.
» **Why watch:** In October 2019 ESS raised $30 million from investors led by Breakthrough Energy Ventures, a cleantech fund spearheaded by Bill Gates.

» **Faradion**
» **faradion.co.uk**
» **Based:** Sheffield, England
» **Founded:** 2010
» **Money raised to date:** $4 million
» **Key partnerships:** Jaguar, Land Rover, Sharp
» **Strategy:** Faradion's low-cost battery materials involve sodium-ion technology, which has the potential to be cheaper and more environmentally benign than lithium-ion technology. Potential applications include residential and industrial energy storage, as well as transportation.
» **Why watch:** In April, Faradion announced that it had received its first order for sodium batteries from investment group ICM Australia for use in the Australian market. It is now looking to India as a manufacturing location.

» **Form Energy**
» **formenergy.com**
» **Based:** Somerville, Massachusetts
» **Founded:** 2017
» **Money raised to date:** $49 million
» **Key partnerships:** Arizona Public Service Electric
» **Strategy:** Form Energy's goal is a cheap battery that will store energy from wind

or solar for months. The research that inspired one of the two companies that merged into Form involves a flow battery with an aqueous polysulfide negative electrode, sodium as the working ion, and an air-breathing positive electrode. The company is keeping its current projects close to the vest.

» **Why watch:** The executive team includes the person who built Tesla's stationary energy-storage brand.

» **Ion Storage Systems**
» **ionstoragesystems.com**
» **Based:** College Park, Maryland
» **Founded:** 2015
» **Money raised to date:** $8 million
» **Key partnerships:** Not disclosed
» **Strategy:** Ion Storage Systems is developing a solid, nonflammable ceramic electrolyte as an alternative to the typical flammable liquid electrolytes in rechargeable batteries (see page 18). The design allows lithium ions to flow quickly and prevents formation of dendrites—tiny deposits that can lead to short circuits.
» **Why watch:** In January, the firm hired the former executive director of Apple's battery operations as CEO.

» **Ionic Materials**
» **ionicmaterials.com**
» **Based:** Woburn, Massachusetts
» **Founded:** 2012
» **Money raised to date:** More than $65 million
» **Key partnerships:** A123 Systems
» **Strategy:** The solid polymer electrolyte developed by Ionic Materials (one of C&EN's 2018 10 Start-Ups to Watch) conducts ions at room temperature, which could result in a safer battery. The company says the polymer supports lithium-ion cells that contain little or no cobalt in their cathodes, a boon for cost-effectiveness and ethical production (see page 8).
» **Why watch:** Backers include an alliance of automakers Renault, Nissan, and Mitsubishi, as well as electronics maker Samsung, which in the past has struggled with smartphone-battery fires.

» **NantEnergy**
» **nantenergy.com**
» **Based:** Scottsdale, Arizona
» **Founded:** 2008
» **Money raised to date:** $27 million
» **Key partnerships:** Not disclosed
» **Strategy:** NantEnergy is developing zinc-air rechargeable batteries that can provide electricity when paired with renewable energy, such as solar, in a microgrid system. The technology has allowed more than 200,000 people in villages across rural Indonesia and Africa to access electricity—many for the first time.
» **Why watch:** The firm's microgrid technology let officials at Great Smoky Mountains National Park remove power lines and return 13 acres of land to its natural state.

» **Natron Energy**
» **natron.energy**
» **Based:** Santa Clara, California
» **Founded:** 2012
» **Money raised to date:** $15 million
» **Key partnerships:** ARPA-E, CalCharge, Molecular Foundry
» **Strategy:** The battery technology at Natron uses a sodium-ion electrolyte. Both the positive and negative electrodes contain Prussian blue pigments.
» **Why watch:** Chevron Technology Ventures has invested in Natron so that the firm can adapt its battery technology, originally designed for data center applications, to meet specifications for electric-vehicle charging.

» **Nexeon**
» **nexeon.co.uk**
» **Based:** Abingdon, England
» **Founded:** 2006
» **Money raised to date:** $86 million
» **Key partnerships:** Synthomer, University College London, Wacker Chemie
» **Strategy:** To replace the graphite anodes in traditional lithium-ion batteries with more energy-dense anodes made with silicon, Nexeon has focused on preventing the swelling that normally happens with silicon anodes and degrades the electrode (see page 10).
» **Why watch:** Moving to consolidate intellectual property in the field of silicon battery anodes, Nexeon has acquired 24 patents previously owned by the now-bankrupt firm Litarion.

» **NOHMs Technologies**
» **nohms.com**
» **Based:** Rochester, New York
» **Founded:** 2010
» **Money raised to date:** $6 million
» **Key partnerships:** Not disclosed
» **Strategy:** The company, one of C&EN's 2015 10 Start-Ups to Watch, has developed a recipe for ionic liquid electrolytes that are nonflammable and have potential applications in mobile devices and electric vehicles.
» **Why watch:** The firm is working on battery technology optimized for indoor use to stabilize New York State's electrical grid.

» **Northvolt**
» **northvolt.com**
» **Based:** Stockholm
» **Founded:** 2016
» **Money raised to date:** $1.6 billion
» **Key partnerships:** ABB, BMW, Epiroc, Scania, Siemens, Stena Line, Vattenfall, Vestas, Volkswagen
» **Strategy:** Northvolt envisions the world's greenest lithium-ion batteries and is bringing the complex battery supply chain in-house to meet its goal. Large-scale manufacturing is expected to begin at the first of the firm's factories in 2021.
» **Why watch:** The company says its battery-recycling operation could supply at least half the raw materials needed for its first factory by 2030.

» **Oxis Energy**
» **oxisenergy.com**
» **Based:** Abingdon, England
» **Founded:** 2000

» **Money raised to date:** $5 million
» **Key partnerships:** Airbus, Arkema, DHL, NASA, Renault, Seat, Solvay
» **Strategy:** Lithium-sulfur batteries have a reputation for suffering from fading performance, but Oxis has collaborated with multiple chemical firms to improve the lithium-sulfur life cycle.
» **Why watch:** The company said in February that its technology had been ground tested in an aircraft system in the US and could be ready for use in aircraft within 5 years.

Prieto Battery

» **Prieto Battery**
» **prietobattery.com**
» **Based:** Fort Collins, Colorado
» **Founded:** 2009
» **Money raised to date:** $14 million
» **Key partnerships:** Intel, Stanley Black & Decker
» **Strategy:** The foundation of Prieto's technology is a porous, 3-D copper foam. Electroplating and coating steps that add anode, separator, and cathode materials atop the foam substrate, rather than onto conventional flat metal sheets, improve battery capacity and charge. The battery's copper antimonide anode prevents lithium deposits that can cause short circuits.
» **Why watch:** In September, the company claimed a 100% success rate in third-party testing with fully assembled batteries containing its proprietary anode.

QuantumScape

» **QuantumScape**
» **quantumscape.com**
» **Based:** San Jose, California
» **Founded:** 2010
» **Money raised to date:** $100 million
» **Key partnerships:** Volkswagen
» **Strategy:** The founders of this start-up have been tight lipped about their solid-state battery technology, but the company's many patents include an active layer between battery electrodes that contains quantum dots, nanowires, or other quantum confinement species; a nanostructured material for battery cathodes; and separator materials.
» **Why watch:** In a press release announcing its partnership with QuantumScape, Volkswagen estimated that a car outfitted with a solid-state battery the same size as today's lithium-ion automotive batteries would achieve a range comparable to a conventional gasoline-powered car.

SILA NANOTECHNOLOGIES

» **Sila Nanotechnologies**
» **silanano.com**
» **Based:** Alameda, California
» **Founded:** 2011
» **Money raised to date:** $340 million
» **Key partnerships:** BMW, Daimler AG
» **Strategy:** To boost the energy density of lithium-ion batteries, Sila replaces the graphite in the battery anode with a nanocomposite containing 50% silicon. The composite's porous nature is more forgiving of the expansion and contraction that occurs in silicon anodes during charge and discharge, and thus prevents battery cracking and associated drops in performance.
» **Why watch:** Sila's technology is designed to drop into existing battery-production processes, so manufacturers wouldn't need new factories to incorporate it.

Silatronix®

» **Silatronix**
» **silatronix.com**
» **Based:** Madison, Wisconsin
» **Founded:** 2007
» **Money raised to date:** $20 million
» **Key partnerships:** Hitachi Chemical, Inabata
» **Strategy:** Cascading decomposition reactions that tend to occur during battery-electrolyte production can form gases that build up pressure in battery cells. The organosilicon molecules developed by Silatronix (one of C&EN's 2016 10 Start-Ups to Watch) stabilize the electrolytes, preventing damage.
» **Why watch:** The US Office of Naval Research awarded the firm $10.1 million to improve the cycling stability of lithium-ion battery cells using standard cathode materials and a variety of new anode materials.

SES
Beyond Li-ion™

» **SolidEnergy Systems**
» **ses.ai**
» **Based:** Woburn, Massachusetts
» **Founded:** 2012
» **Money raised to date:** $71 million
» Key partnerships: A123 Systems
» **Strategy:** SolidEnergy's technology is an anodeless rechargeable battery based on lithium metal (see page 10). The firm claims twice the energy density of traditional lithium-ion batteries, meaning that drones, smartphones, or electric vehicles could travel twice as far on a charge.
» **Why watch:** SolidEnergy's pilot line of batteries is being tested in drones, and a manufacturing facility in Shanghai is under construction.

UET

» **UniEnergy Technologies**
» **uetechnologies.com**
» **Based:** Mukilteo, Washington
» **Founded:** 2012
» **Money raised to date:** $25 million
» **Key partnerships:** Chemours, Rongke Power
» **Strategy:** UniEnergy provides stationary batteries to store renewable energy so that it can be used later. The company licensed vanadium flow battery technology from Pacific Northwest National Laboratory that doubles the batteries' energy density and increases the operating temperature window compared with older flow batteries.
» **Why watch:** In addition to its shipping container–sized batteries for grid storage, the company is testing smaller modules suitable for installation inside buildings.

Note: Companies were included because of the novelty and promise of their methods, amount of capital raised, number of partnerships, and number and identity of investors.

Sources: Crunchbase (accessed April 2020), company websites, news reports.

Solid Power: Developing solid electrolytes for safer, high-energy batteries

ALEX SCOTT, C&EN STAFF

Automakers have their pedals to the metal when it comes to developing battery-powered cars, but electrochemists still have their work cut out to deliver the battery performance and safety that large-scale adoption requires.

Current lithium-ion batteries typically operate with a lithium-ion cathode, graphite anode, and liquid electrolyte. But liquid electrolytes can become dangerously hot and catch fire. A safer solution—and one that could also facilitate greater energy density—is to switch to a solid electrolyte.

Solid Power, a spin-off from the University of Colorado, Boulder, claims its lithium-sulfide solid electrolyte can be produced at about the same cost as a liquid electrolyte. And batteries containing the solid electrolyte can store more energy than traditional batteries of the same size.

In tests, Solid Power's electrolyte operates safely at temperatures of about 150 °C—an environment in which many liquid electrolytes would catch fire.

Combining the electrolyte with a lithium metal anode can bring the energy density of Solid Power's battery cells to 400–500 (W·h)/kg. This is more than twice the density of conventional liquid-electrolyte cells that use standard graphite anodes, says CEO and cofounder Doug Campbell.

The company's two other cofounders, Conrad Stoldt and Sehee Lee, started the company in 2012 with the aim of developing cathode materials based on their research at CU Boulder. But in 2016, the firm switched to sulfide-based solid electrolytes after securing an exclusive license to commercialize technology developed by Oak Ridge National Laboratory.

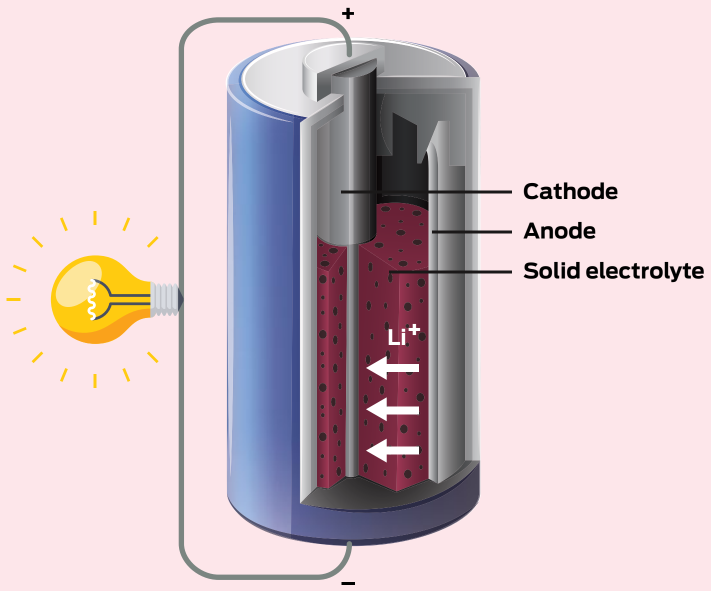
Campbell is convinced Solid Power is developing the right technology at the right time. "The automotive industry is really starting to embrace the concept of solid-state batteries," he says.

Historically, a problem with sulfide-based electrolytes has been the material's brittleness, which can cause structural problems in a battery, according to Frank P. McGrogan, a PhD candidate at the Massachusetts Institute of Technology who has published research on the topic (*Adv. Energy Mater.* 2017, DOI: 10.1002/aenm.201602011). "You have to design around that knowledge," McGrogan notes.

Solid Power says low-temperature processing of its

Solid Power at a glance

- **Launched:** 2012
- **Based:** Louisville, Colo
- **Strategy:** Sulfide-based solid electrolytes
- **Founders:** Doug Campbell, Sehee Lee, and Conrad Stoldt
- **Funding:** $35 million



Solid state

When a lithium-ion battery charges and discharges, the ions flow through its electrolyte between its electrodes. Solid Power is trying to use sulfur-based solid electrolytes, which are safer at higher temperatures than flammable liquid electrolytes are. Unlike liquid-electrolyte batteries, which use carbon or graphite anodes, solid electrolytes can also be used with a lithium metal anode, markedly boosting energy density.

CREDIT: YANG H. KU/C&EN/SHUTTERSTOCK

electrolyte allows it to use polymer binders that mitigate brittleness. Meanwhile, the firm's proprietary electrode and electrolyte separator chemistry and coating process ensure efficient transfer of lithium ions between electrodes, Campbell says.

In 2017, Solid Power relocated to Louisville, Colo. There, the firm has installed what it calls prepilot production facilities where it can make hundreds of automotive-scale battery cells per month. The firm has raised a total of $35 million.

Solid Power already has a multi-million-dollar joint development agreement with one European car company and is looking to add similar deals. Its goal is to get solid-state batteries into commercial electric cars in the next 5–10 years.

Solid electrolyte batteries can be very strong, and someday they could actually form part of a car's structure. In the meantime, Solid Power is working to roll out solid-state cells for niche military and aerospace applications.

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HOT SHEET

It's time to recycle lithium-ion batteries

MITCH JACOBY, C&EN STAFF

Lithium-ion batteries have made portable electronics ubiquitous, and they are about to do the same for electric vehicles. That success story is setting the world on track to generate a multimillion-metric-ton heap of used Li-ion batteries that could end up in the trash. The batteries are valuable and recyclable, but because of technical, economic, and other factors, less than 5% are recycled today. The enormousness of the impending spent-battery situation is driving researchers to search for cost-effective, environmentally sustainable strategies for dealing with the vast stockpile of Li-ion batteries looming on the horizon.

In a battery-recycling pilot plant near Vancouver, British Columbia, American Manganese engineers examine shredded aluminum recovered from Li-ion battery cathodes.

CREDIT: AMERICAN MANGANESE

As the popularity of electric vehicles starts to grow explosively, so does the pile of spent lithium-ion batteries that once powered those cars. Industry analysts predict that by 2030, the world will generate 2 million metric tons (t) of used lithium-ion batteries per year.

If current trends for handling these spent batteries hold, most of those batteries may end up in landfills even though Li-ion batteries can be recycled. These popular power packs contain valuable metals and other materials that can be recovered, processed, and reused. But very little recycling goes on today. In Australia, for example, only 2–3% of Li-ion batteries are collected and sent offshore for recycling, according to Naomi J. Boxall, an environmental scientist at Australia's Commonwealth Scientific and Industrial Research Organisation (CSIRO). The recycling rates in the European Union and the US—less than 5%—aren't much higher.

"There are many reasons why Li-ion battery recycling is not yet a universally well-established practice," says Linda L. Gaines of Argonne National Laboratory. A specialist in materials and life-cycle analysis, Gaines says the reasons include technical constraints, economic barriers, logistic issues, and regulatory gaps.

All those issues feed into a classic chicken-and-egg problem. Because the Li-ion battery industry lacks a clear path to large-scale economical recycling, battery researchers and manufacturers have traditionally not focused on improving recyclability. Instead, they have worked to lower costs and increase battery longevity and charge capacity. And because researchers have made only modest progress improving recyclability, relatively few Li-ion batteries end up being recycled.

Most of the batteries that do get recycled undergo a high-temperature melting-and-extraction, or smelting, process similar to ones used in the mining industry. Those operations, which are carried out in large commercial facilities—for example, in Asia, Europe, and Canada—are energy intensive. The plants are also costly to build and operate and require sophisticated equipment to treat harmful emissions generated by the smelting process. And despite the high costs, these plants don't recover all valuable battery materials.

Until now, most of the effort to improve Li-ion battery recycling has been concentrated in a relatively small number of academic research groups, generally working independently. But things are starting to change. Driven by the enormous quantity of spent Li-ion batteries expected soon from aging electric vehicles and ubiquitous portable electronics, start-up companies are commercializing new battery-recycling technology. And more scientists have started to study the problem, expanding the pool of graduate students and postdocs newly trained in battery recycling. In addition, some battery, manufacturing, and recycling experts have begun forming large, multifaceted collaborations to tackle the impending problem.

In January 2019, for example, US Department of Energy secretary Rick Perry announced the creation of the DOE's first Li-ion battery recycling R&D center, the ReCell Center. According to Jeffrey S. Spangenberger, the program's director, ReCell's key goals include making Li-ion battery recycling competitive and profitable and using recycling to help reduce US dependence on foreign sources of cobalt and other battery materials. Launched with a $15 million investment and headquartered at Argonne National Laboratory, ReCell includes some 50 researchers based at six national laboratories and universities. The program also includes battery and automotive equipment manufacturers, materials suppliers, and other industry partners.

At the same time, the DOE also launched the $5.5 million Battery Recycling Prize. The program's goal is to encourage entrepreneurs to find innovative solutions for collecting and storing discarded Li-ion batteries and transporting them to recycling centers, which are the first steps in turning old batteries into new ones.

And in 2018 researchers in the UK formed a large consortium dedicated to improving Li-ion battery recycling, specifically from electric vehicles. Led by the University of Birmingham, the Reuse and Recycling of Lithium Ion Batteries (ReLiB) project brings together some 50 scientists and engineers at eight academic institutions, and it includes 14 industry partners.

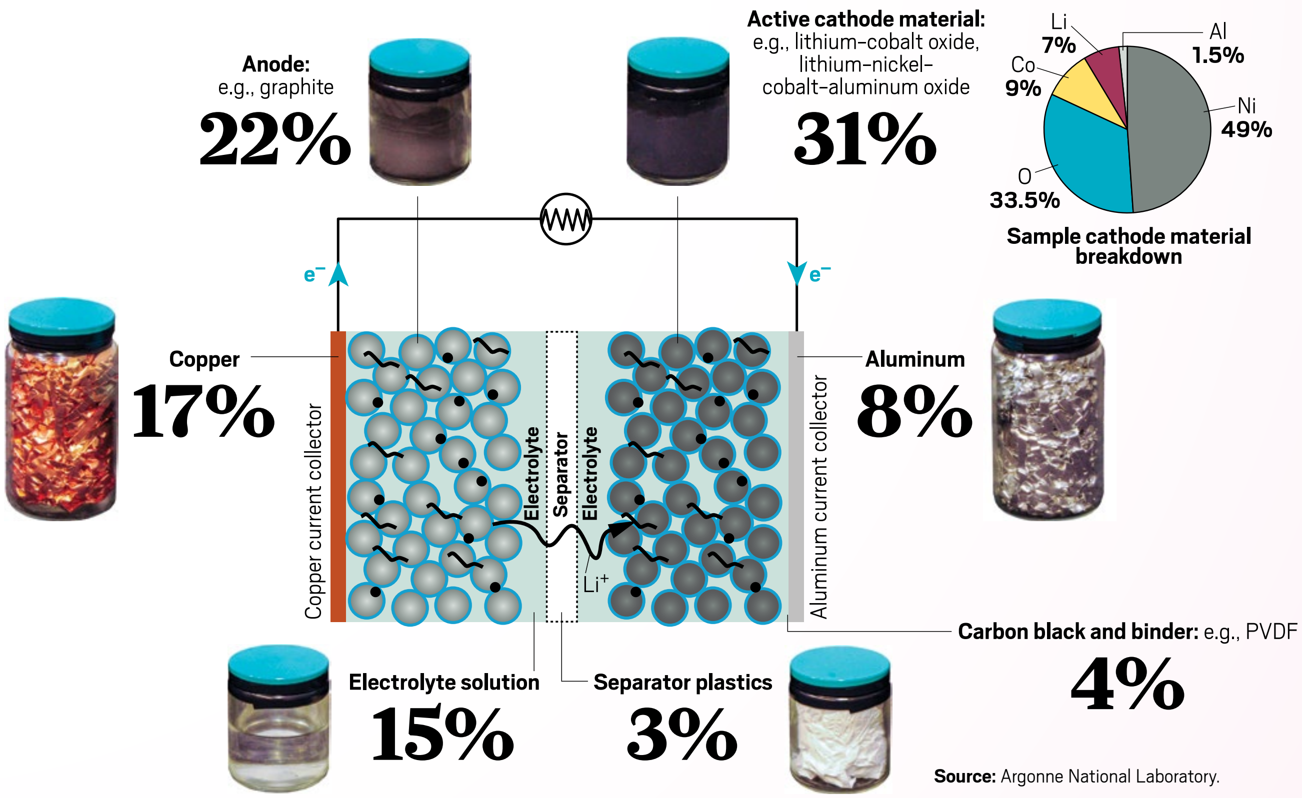
Recycling's benefits

Battery specialists and environmentalists give a long list of reasons to recycle Li-ion batteries. The materials recovered could be used to make new batteries, lowering manufacturing costs. Currently, those materials account for more than half of a battery's cost. The prices of two common cathode metals, cobalt and nickel, the most expensive components, have fluctuated substantially in recent years. Current market prices for cobalt and nickel stand at roughly $29,500 per metric ton and $12,250 per metric ton, respectively. In 2018, cobalt's price exceeded $90,000 per metric ton.

In many types of Li-ion batteries, the concentrations of these metals, along with those of lithium and manganese, exceed the concentrations in natural ores, making spent batteries akin to highly enriched ore. If those metals can be recovered from used batteries at a

Inside a Li-ion battery

All the components of a Li-ion battery have value and can be recovered and reused. Currently, most recyclers recover just the metals. The pie chart describes a cathode material known as NCA, which is made of lithium-nickel-cobalt-aluminum oxide.



Source: Argonne National Laboratory.

CREDIT: MITCH JACOBY/C&EN

large scale and more economically than from natural ore, the price of batteries and electric vehicles should drop.

In addition to potential economic benefits, recycling could reduce the quantity of material going into landfills. Cobalt, nickel, manganese, and other metals found in batteries can readily leak from the casing of buried batteries and contaminate soil and groundwater, threatening ecosystems and human health, says Zhi Sun, a specialist in pollution control at the Chinese Academy of Sciences. The same is true of the solution of lithium fluoride salts ($LiPF_6$ is common) in organic solvents that are used in a battery's electrolyte.

At the University of Birmingham, ReLib team member Alireza Rastegarpanah develops robotic methods for safe, automated processing of spent Li-ion batteries.

Batteries can have negative environmental effects not just at the end of their lives but also long before they are manufactured. As Argonne's Gaines points out, more recycling means less mining of virgin material and less of the associated environmental harm. For example, mining for some battery metals requires processing metal-sulfide ore, which is energy intensive and emits SO_x that can lead to acid rain.

Less reliance on mining for battery materials could also slow the depletion of these raw materials. Gaines and Argonne coworkers studied this issue using computational methods to model how growing battery production could affect the geological reserves of a number of metals through 2050. Acknowledging that these predictions are "complicated and uncertain," the researchers found that world reserves of lithium and nickel are adequate to sustain rapid growth of battery production. But battery manufacturing could decrease global cobalt reserves by more than 10%.

There are also political costs and downsides that recycling Li-ion batteries could help address. According to a CSIRO report, 50% of the world's production of cobalt comes from the Democratic Republic of the Congo and is tied to armed conflict, illegal mining, human rights abuses, and harmful environmental practices. Recycling batteries and formulating cathodes with a reduced concentration of cobalt could help lower the dependence on such problematic foreign sources and raise the security of the supply chain.

Challenges in recycling Li-ion batteries

Just as economic factors can make the case for recycling batteries, they also make the case against it. Large fluctuations in the prices of raw battery materials, for example, cast uncertainty on the economics of recycling. In particular, the recent large drop in cobalt's price raises questions about whether recycling Li-ion batteries or repurposing them is a good business choice compared with manufacturing new batteries with fresh materials. Basically, if the price of cobalt drops, recycled cobalt would struggle to compete with mined cobalt in terms of price, and manufacturers would choose mined material over recycled, forcing recyclers out of business.

> **"Opportunities always coexist with challenges."**

Another long-term financial concern for companies considering stepping into battery recycling is whether a different type of battery, such as Li-air, or a different vehicle propulsion system, like hydrogen-powered fuel cells, will gain a major foothold on the electric-vehicle market in coming years, lowering the demand for recycling Li-ion batteries.

Battery chemistry also complicates recycling. Since the early 1990s when Sony commercialized Li-ion batteries, researchers have repeatedly tailored the cathode's composition to reduce cost and to enhance charge capacity, longevity, recharge time, and other performance parameters.

Some Li-ion batteries use cathodes made of lithium-cobalt oxide (LCO). Others use lithium-nickel-manganese-cobalt oxide (NMC), lithium-nickel-cobalt-aluminum oxide, lithium iron phosphate, or other materials. And the proportions of the components within one type of cathode—for example, NMC—can vary substantially among manufacturers. The upshot is that Li-ion batteries contain "a wide diversity of ever-evolving materials, which makes recycling challenging," says Liang An, a battery-recycling specialist at Hong Kong Polytechnic University. Recyclers may need to sort and separate batteries by composition to meet the specifications of people buying the recycled materials, making the process more complicated and raising costs.

Battery structure further complicates recycling efforts. Li-ion batteries are compact, complex devices, come in a variety of sizes and shapes, and are not designed to be disassembled. Each cell contains a cathode, anode, separator, and electrolyte.

Cathodes generally consist of an electrochemically active powder (LCO, NMC, etc.) mixed with carbon black and glued to an aluminum-foil current collector with a polymeric compound such as poly(vinylidene fluoride) (PVDF). Anodes usually contain graphite, PVDF, and copper foil. Separators, which insulate the electrodes to prevent short circuiting, are thin, porous plastic films, often polyethylene or polypropylene. The electrolyte is typically a solution of $LiPF_6$ dissolved in a mixture of ethylene carbonate and dimethyl carbonate. The components are tightly wound or stacked and packed securely in a plastic or aluminum case.

Large battery packs that power electric vehicles may contain several thousand cells grouped in modules. The packs also include sensors, safety devices, and circuitry that controls battery operation, all of which add yet another

CREDIT: ALIREZA RASTEGARPANAH AND RUSTAM STOLKIN/EXTREME ROBOTICS LAB layer of complexity and additional costs to dismantling and recycling.

All these battery components and materials need to be dealt with by a recycler to get at the valuable metals and other materials. In stark contrast, lead-acid car batteries are easily disassembled, and the lead, which accounts for about 60% of a battery's weight, can be separated quickly from the other components. As a result, nearly 100% of the lead in these batteries is recycled in the US, far surpassing recycling rates for glass, paper, and other materials.

Improving recycling methods

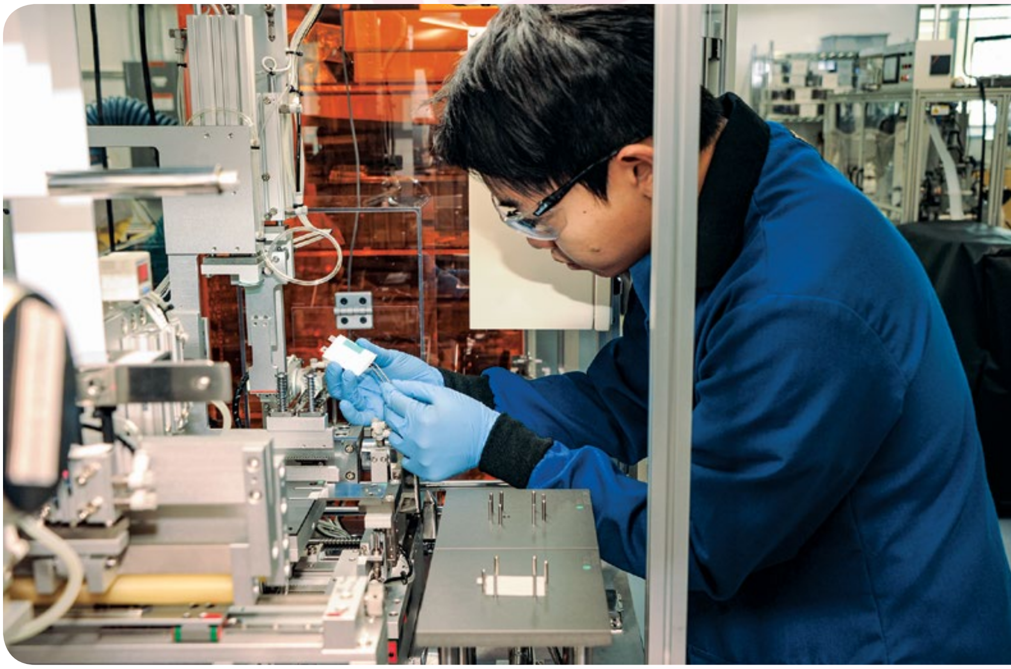
Several large pyrometallurgy, or smelting, facilities recycle Li-ion batteries today. These units, which often run near 1,500 °C, recover cobalt, nickel, and copper but not lithium, aluminum, or any organic compounds, which get burned. The facilities are capital intensive, in part because of the need to treat the emission of toxic fluorine compounds released during smelting.

Hydrometallurgy processing, or chemical leaching, which is practiced commercially in China, for example, offers a less energy-intensive alternative and lower capital costs. These processes for extracting and separating cathode metals generally run below 100 °C and can recover lithium and copper in addition to the other transition metals. One downside of traditional leaching methods is the need for corrosive reagents such as hydrochloric, nitric, and sulfuric acids and hydrogen peroxide.

Researchers running bench-scale studies have identified potential improvements to these recycling methods, but only a handful of companies run recycling tests on the methods at the pilot-plant scale. In the Vancouver, British Columbia, area, an American Manganese facility converts 1 kg/h of cathode scrap to a precursor that manufacturers can use to synthesize fresh cathode material. Scrap refers to off-spec cathode powder, trimmings, and other waste collected from battery manufacturing.

Zarko Meseldzija, the company's chief technical officer, describes the scrap as "low-hanging fruit," a convenient material to use for experiments before boosting the scale of operations and moving on to actual spent batteries. He explains that the company's process relies on sulfur dioxide for leaching cathode metals and does not use hydrochloric acid or hydrogen peroxide.

Battery Resourcers in Worcester, Massachusetts, runs a pilot plant that processes Li-ion batteries at a rate of up to roughly 0.5 t per day and is actively working to increase capacity by a factor of 10, according to Chief Technical Officer Eric Gratz. Many current recycling methods yield multiple single-metal compounds that must be combined to make new cathode material. Battery Resourcers' process precipitates a mixture of nickel, manganese, and cobalt hydroxides. This mixed-metal cathode precursor simplifies battery preparation and could lower manufacturing costs.



Argonne National Laboratory's Dohyeun Kim prepares pouch-type Li-ion batteries to study battery recycling.

Meanwhile, the DOE's ReCell team is pursuing so-called direct recycling methods for recovering and reusing battery materials without costly processing. One approach calls for removing the electrolyte with supercritical carbon dioxide, then crushing the cell and separating the components physically—for example, on the basis of density differences.

In principle, nearly all the components can be reused after this simple processing. In particular, because the method does not use acids or other harsh reagents, the morphology and crystal structure of the cathode materials remain intact, and the materials retain the electrochemical properties that make them valuable. Gaines says more work is needed to implement this cost-saving approach.

At the University of Birmingham's ReLiB project, principal investigator Paul Anderson says the team sees a clear opportunity to boost the economic efficiency of battery recycling through automation. To that end, the team is developing robotic procedures for sorting, disassembling, and recovering valuable materials from Li-ion batteries. Birmingham's Allan Walton, a coinvestigator, adds that using robotic devices to disassemble batteries could eliminate human workers' risk of electrical and chemical injury. Automation could also lead to enhanced separation of battery components, increasing their purity and value, he says.

Although most of these strategies remain at an early stage of development, the need for them is growing. Currently, the number of end-of-life electric-vehicle batteries is low, but it's about to skyrocket. Numerous impediments stand in the way of large-scale recycling, but "opportunities always coexist with challenges," says An of Hong Kong Polytechnic. It's time to take the bull by the horns and get serious about recycling Li-ion batteries.

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READING LIST

Our picks of the patent and journal literature on battery technology and recycling

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