

Lithium-ion battery pioneers awarded chemistry Nobel

The batteries have already powered one revolution in wireless consumer electronics. Now they're launching a new one in transportation.

Electric cars, at long last, are having their day. Cumulative global sales of all-electric and plug-in hybrid vehicles reached 1 million in September 2015, hit 5 million in December 2018, and could near 8 million by the end of this year. Essentially all such vehicles are powered by lithium-ion batteries—as are innumerable laptops and phones, medical devices, power tools, electric bikes, scooters, and more.

The lithium-ion battery's extraordinary rise is a result of a half century of research in solid-state physics, electrochemistry, materials science, and engineering.¹ (Political, economic, and social forces were also involved; for more on that side of the story, see the article by Matthew Eisler, *PHYSICS TODAY*, September 2016, page 30.) Of all the researchers who worked on battery development over the years, the Royal Swedish Academy of Sciences has chosen three for this year's Nobel Prize in Chemistry: John Goodenough of the University of Texas at Austin, Stanley Whittingham of Binghamton University in New York, and Akira Yoshino of the Asahi Kasei Corp in Tokyo.

During the 1970s and 1980s, the three laureates contributed landmark developments that led to the first commercial lithium-ion battery in 1991. And now the fruits of their labor are changing the world.

Ions at work

The basic structure of all batteries, depicted in figure 1, hasn't changed since 1799, when Alessandro Volta introduced his voltaic pile. (See the article by Héctor Abruña, Yasuyuki Kiya, and Jay Henderson, *PHYSICS TODAY*, December 2008, page 43.) Electrons flow through an external circuit from a high-energy state in the anode to a lower-energy state in the cathode. To maintain charge neutrality, a so-called working ion flows between the electrodes through an electrolyte inside the battery.

Traditionally, no matter what materials were used for the anode and cathode,

the electrolyte was always a watery solution, and the working ion was always hydrogen. A water-based battery, however, can't have more than a 2.0 V potential difference between its anode and cathode without the water molecules being ripped apart. Higher-voltage, more-energy-dense batteries would require a sturdier electrolyte—and, because water is the only known liquid that conducts protons, a new working ion.

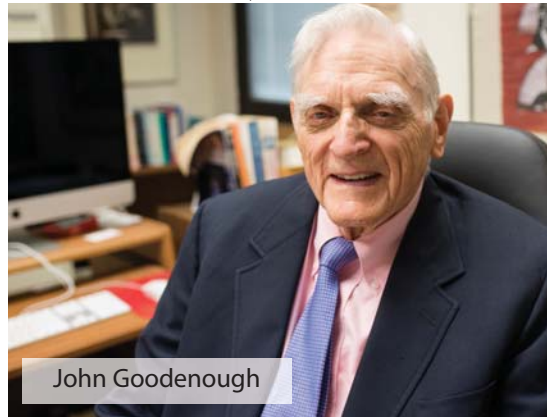
Lithium has some advantages that make it an appealing alternative, but its supremacy was not inevitable. (See the article by William Walsh, *PHYSICS TODAY*, June 1980, page 34.) It's the third lightest of all the elements, but a battery's weight doesn't necessarily depend much on the mass of its working ion. As an alkali metal—a member of the first column of the periodic table—it readily gives up its outermost electron, so a lithium-based anode is a good source of high-energy electrons. But other alkali metals, such as sodium and potassium, are almost as good.

In the 1950s William Harris and his PhD supervisor Charles Tobias showed that several organic solvents could dissolve alkali-metal salts and conduct their constituent ions. The final basic ingredient, then, was a cathode material. An ideal cathode would store both the alkali-metal ion and its electron—but without putting them back together, which would necessitate placing the electron back in its high-energy state.

Transition-metal compounds fit the bill. Unlike elements from the periodic table's outer edges, which strongly prefer to shed or pick up electrons until their outermost electron shells are full, transition metals, from the middle swath of the table, gain and lose electrons from their *d* orbitals, which don't so much mind being partially filled, so they can pick up an extra electron with little energy penalty.

Furthermore, some transition-metal compounds were known to accommodate, or intercalate, alkali metals or other ions in varying amounts without changing their structure. In some cases, the

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John Goodenough

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Akira Yoshino

compounds are composed of layers held together by van der Waals forces (see the article by Pulickel Ajayan, Philip Kim, and Kaustav Banerjee, *PHYSICS TODAY*, September 2016, page 38) and store the guest ions between the layers; in others the guests are accommodated in voids in a three-dimensional lattice.

At first, intercalation compounds were of interest primarily for their electronic

and magnetic properties.² For example, if a transition-metal compound superconducts at low temperature, intercalating a guest ion could raise its critical temperature. But in the early 1970s, Whittingham, then a postdoc at Stanford University, and colleagues noticed that when they intercalated potassium into tantalum disulfide, energy was released. Says Whittingham, "And we thought, hey, we can make a battery out of this."

Putting the pieces together

Whittingham continued his work at Exxon, where he and several of his Stanford colleagues moved to in 1972. A TaS_2 -based battery, he reasoned, was never going to be practical—tantalum was too heavy and too expensive—so he switched to titanium disulfide. Not only was TiS_2 the lightest and cheapest of all the layered transition-metal compounds, it was electrically conductive, and it maintained the same structure for the full range of lithium intercalation compositions, all the way up to LiTiS_2 . "We started with a test tube experiment, then invested in some more serious equipment," recalls Whittingham, and within a year he had a patent filed.

But there was a problem. Although the TiS_2 cathode could take up and release lithium ions reversibly, the anode—made of pure lithium metal—was another matter. As the battery was recharged and lithium ions rejoined the anode, they didn't form smooth layers, but rather pointed, whisker-like dendrites. If the dendrites bridged the electrolyte and reached the cathode, the battery would short-circuit.

One potential solution was to replace the lithium metal with a different anode material—Whittingham considered a lithium–aluminum alloy—that would make it energetically favorable for the lithium ions to seep back into the electrode bulk instead of forming dendrites on the surface. Any such material, however, would store lithium atoms at a lower energy than lithium metal itself, so it would reduce the battery voltage. The TiS_2 battery voltage, at 2.2 V, was modest to begin with.³ Any reduction would wipe out

most of its advantage over water-based batteries.

That voltage was a function of the energies of titanium's 3d orbitals and sulfur's 3p orbitals, which hybridize to create the bands that receive electrons from the circuit. Goodenough's contribution was to identify a cathode material that could receive electrons at a lower energy, so the battery could operate at a higher voltage and thus accommodate a safer anode. He switched from sulfides to oxides—oxygen's 2p orbitals are more tightly bound than sulfur's 3p orbitals—and from titanium to transition metals with slightly higher nuclear charge and thus lower-energy 3d orbitals.

At Oxford University in 1980, he and his group landed on lithium cobalt oxide, whose structure is depicted in figure 2a. Notably, it's not cobalt oxide; that doesn't exist, at least not in the layered structure Goodenough was seeking. The material could be synthesized only in its lithiated form, LiCoO_2 . The battery, therefore, had to be assembled in its discharged state, and it could never be fully charged: Extracting too much of the cathode's lithium would make the structure unstable, liberate oxygen gas, and risk igniting the flammable organic electrolyte. But its voltage—nearly 4 V with a lithium metal anode—was a milestone.⁴

Goodenough and colleagues were still using lithium metal for their anode, which still formed dangerous dendrites when recharged. But by the early 1980s, several groups were exploring the possibility of a graphite anode. Like the layered transition-metal materials, graphite

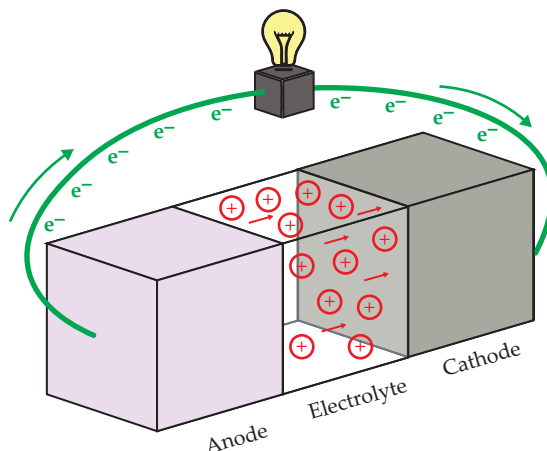


FIGURE 1. THE STRUCTURE OF A BATTERY, shown here being discharged. When the battery is recharged, the electron and working-ion flows are both reversed.

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was known to form intercalation compounds with a variety of guest species (see the articles by John Fischer and Thomas Thompson, *PHYSICS TODAY*, July 1978, page 36, and by Hiroshi Kamimura, *PHYSICS TODAY*, December 1987, page 64), including lithium, as shown in figure 2b. A graphite anode has an electrochemical potential of just 0.2 V less than a lithium-metal one. But the intercalation worked a little too well: Graphite took not just lithium ions into its interlayer spaces, but also electrolyte molecules, which seemed to unavoidably damage the electrode and the electrolyte.

At the same time, Yoshino was experimenting with polyacetylene, an electrically conductive polymer that would secure its inventors the Chemistry Nobel in 2000 (see *PHYSICS TODAY*, December 2000, page 19). “I thought it could be a good anode material,” he says, “but my biggest problem was finding a cathode material to pair with it.” Most cathode materials, such as TiS_2 , contained no lithium, and neither did polyacetylene. But a lithium-based battery needed to get its lithium from somewhere. “At the end of 1982, I was cleaning up my lab when I found Dr. Goodenough’s paper on LiCoO_2 ,” Yoshino recalls, “and immediately, I knew it was just the kind of cathode material I had been searching for.”

Polyacetylene turned out to have poor chemical stability, so Yoshino eventually switched to an anode of petroleum coke, a partially disordered form of carbon. Petroleum coke stores only half as much lithium per unit weight as graphite, but it solved the problem of electrolyte intercalation. After testing the safety of his prototype battery, he transferred the technology to Sony, which introduced the name “lithium-ion battery” to highlight the fact that it contained no dangerous metallic lithium.

To market

The new batteries hit the shelves in 1991. At first, Sony used them only in handheld video cameras. “That market still exists, but it is only 0.2% of the total market for lithium-ion batteries today,” says Yoshino.

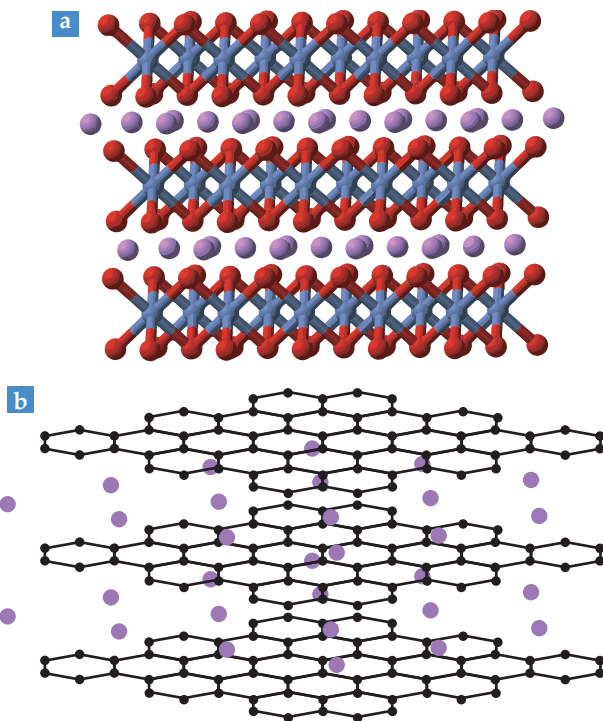


FIGURE 2. LAYERED INTERCALATION COMPOUNDS for storing lithium ions (purple). **(a)** Lithium cobalt oxide, often used as a cathode material, stores lithium between layers made of cobalt (blue) and oxygen (red). **(b)** Lithiated graphite, LiC_6 , is a common anode material. (Panel a by Ben Mills, PD-US; panel b adapted from V. Petkov et al., *J. Phys: Condens. Matter* **23**, 435003, 2011.)

“That means that the market is 500 times larger than I thought it would be.”

With a few exceptions, lithium-ion batteries today still use something like Yoshino’s recipe with ingredients inspired by Whittingham and Goodenough: a carbonaceous anode, a transition-metal-oxide cathode, and an organic liquid or polymer electrolyte. Nowadays, most anodes are made from graphite—the electrolyte intercalation problem, it turns out, could be solved by using a different electrolyte—rather than petroleum coke, and manufacturers can choose from a range of transition-metal cathode compounds. But most importantly, the industry now has the benefit of 28 years’ worth of manufacturing know-how. And that counts for a lot.

There’s more to making a battery, after all, than simply choosing the right materials. For example, a manufacturer must consider how to arrange the components to maximize their surface area, what size the particles of electrode material should be to enable the lithium ions

to get in and out, and how to optimize manufacturing processes to reduce waste. Thanks to steady improvements in all those areas and more, batteries today store almost three times as much energy per unit weight as they did in the 1990s. And the price has come down even more dramatically. According to an analysis by Bloomberg New Energy Finance,⁵ the average cost of a one-kilowatt-hour lithium-ion battery pack has dropped by 85%, from \$1160 to \$176, just since 2010.

In consumer electronics, those improvements may be easy to overlook. “The first mobile phones had small monochrome screens,” says M. Rosa Palacin of the Insti-

tute of Materials Science of Barcelona, “and now we have large screens and are always connected, so even if batteries are performing much better, we don’t realize it.” And the batteries are small enough—7 to 10 watt-hours for a phone, 40–70 Wh for a laptop—that they’re not a major driver of the device cost.

Electric vehicles are another story. To achieve a driving range in the hundreds of kilometers, an electric car needs a battery capacity of 10s to 100 kWh. Until just a few years ago, the battery cost alone was enough to confine electric vehicles to a luxury niche market. But as prices fall, the situation is rapidly changing, and electric cars are growing in mass appeal.

There’s still a long way to go. Worldwide, electric vehicles make up just half a percent of passenger cars on the road and a modest 2% of vehicle sales. (The numbers for the US are similar to the global average.) But with some help, they can claim a much larger market share. In Norway, far and away the world’s electric-vehicle leader, more than 10% of all cars and half of all car sales are electric, due in large part to substantial taxes on conventional vehicles and perks for electric ones, including free parking and access to bus lanes.

Perhaps surprisingly, lithium-ion batteries are also gaining appeal for grid-scale storage of electric power. Even though they’ve been optimized for their small size and light weight—factors that matter little for a stationary power-storage

facility—they're still the cheapest of all batteries for that purpose.⁶ "The technology has gotten so good, and so inexpensive," explains Gerbrand Ceder of the University of California, Berkeley, "that it's the best option even though on paper it might not look that way."

The electrical grid needs storage capacity for many reasons, and smoothing the fluctuations of renewable energy—delivering power even when the wind isn't blowing or the Sun isn't shining—is only one of them. The US currently gets less than 10% of its electricity from wind and solar power, and their variability, for now, is easily absorbed by the rest of the grid. But grid storage is still important for balancing supply and demand from instant to instant, or for satisfying times of peak consumption without building more power plants.

The vast majority of grid storage in the US is currently pumped-storage hydroelectricity: pumping water uphill and letting it flow back down. But lithium-ion-battery storage is already cheaper for applications requiring a quick burst of power over a short time. "I recently visited a grid storage facility near Saratoga Springs," says Whittingham, "and there were lithium ions going back and forth on a scale we couldn't have dreamed of even 10 or 15 years ago."

Limitations

Lithium-ion batteries are still getting smaller and cheaper, but those trends can't continue forever without some dramatic technological change. To store one electron's worth of charge—or about 4 eV of energy—a battery with today's technology needs one lithium atom, one transition-metal atom, two oxygen atoms, and six carbon atoms. That adds up to almost 2 kg of material per kWh of energy, even discounting the mass of the electrolyte, any unusable electrode capacity, and other material components. For comparison, the best lithium-ion batteries today weigh about 4 kg per kWh.

Materials availability is also a concern. More than a billion cars travel the world's roads; converting all of them to electric vehicles with 50 kWh batteries

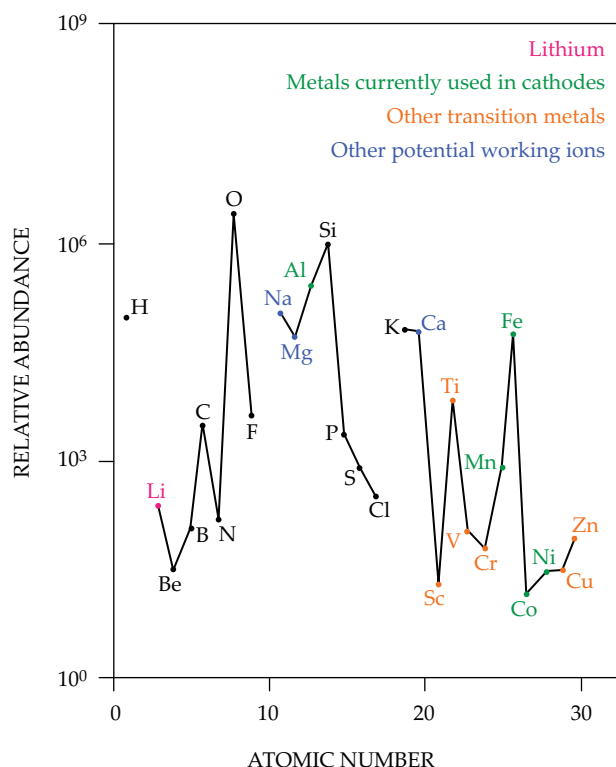


FIGURE 3. ELEMENTAL ABUNDANCES in Earth's crust; highlighted in color are elements relevant to lithium-ion battery technology and post-lithium battery research. None of the elements shown here are terribly rare—for comparison, gold and platinum have abundances of less than 10^{-3} in these units. (Adapted from USGS Fact Sheet 087-02.)

and LiCoO_2 cathodes would take 60 million tons of cobalt. Current world cobalt reserves amount to only 7 million tons. "And by the way, you can't have all of it," notes Ceder; in addition to batteries, cobalt is used in many other applications, including pigments, high-performance alloys, and industrial catalysts.

Cobalt's scarcity equates to a relatively high price. And because cobalt is usually mined as a by-product of other metals such as copper and nickel, that price is vulnerable to rapid fluctuations as industry struggles to match the supply to the demand. Between 2016 and 2019, the price of a kilogram of cobalt shot from \$30 to \$90 and back to \$30—a swing that can make a difference of thousands of dollars in the price of a vehicle-sized battery.

Furthermore, half of all cobalt reserves are in the Democratic Republic of the Congo, one of the poorest countries in Africa and in the world. Most of the cobalt mining is overseen by foreign cor-

porations, but a significant minority is "artisanal," meaning that individuals—sometimes children—are digging with hand tools and no safety equipment for very little money.

For all those reasons, the electric-vehicle industry (but not the consumer electronics industry) has largely switched to cathode materials with less or no cobalt.⁷ Some of the best performing alternatives are mixed metal oxides that combine nickel, cobalt, and either manganese or aluminum. Nickel is only a little less scarce than cobalt, as shown in figure 3, but at least its reserves are geographically less concentrated. Lithium manganese oxide and lithium iron phosphate are serviceable options made from cheap and abundant materials, but their energy densities pale in comparison with their costlier cousins.

Lithium itself is widespread in Earth's crust, but it can be economically extracted from only a few locations, such as the salt flats in and around the Atacama Desert in South America. The world's lithium reserves can meet the battery industry's needs for the foreseeable future—but to continue to meet them for generations to come, battery recycling will become increasingly important.

The future

In their pursuit of a smaller, cheaper, safer, and more sustainable battery, researchers are exploring several ideas. (See *PHYSICS TODAY*, June 2013, page 26.) One possibility is to replace the liquid or polymer electrolyte with an inorganic solid to create an all-solid-state battery. Removing the flammable organic material would all but eliminate the risk of fire. And it would offer a path to safely bringing back the lithium metal anode—dendrites can't pierce so substantial a solid barrier—and thereby give a huge boost to the battery energy density.

Ceramic materials that can conduct ions have been known for decades (see the article by John Bates, Jia-Chao Wang, and Nancy Dudney, *PHYSICS TODAY*, July 1982, page 46). But only recently have their conductivities begun to rival those

of liquids, and it's still a challenge to stabilize the interfaces between a solid electrolyte and solid electrodes that are constantly growing and shrinking.⁸ "This is the new kid on the block trying to beat the existing electrolyte," says Yang Shao-Horn of MIT, "and we need to discover the design principles" to explore the possible materials more efficiently than by trial and error. "There is a very small solid-state battery on the market now," notes Yoshino, "but can it be made into a large format suitable for electric vehicles? That still requires a breakthrough in production technology. I think it should be possible, but it will take time."

Another research direction has explored replacing lithium with a cheaper, more abundant working ion, such as sodium, magnesium, or calcium.⁹ Sodium is chemically similar to lithium, so many (but not all) of the materials and processes

developed for lithium-ion batteries can be adapted for sodium-ion batteries. Calcium and magnesium, on the other hand, would require a whole new set of materials. They're appealing, though, because their ions are doubly charged, so a battery could supply twice as much current for a given number of working ions.

Lithium-ion batteries aren't going away anytime soon. "Even if I came up with a great new battery tomorrow," says Marca Doeffer of Lawrence Berkeley National Laboratory, "it would take 10 or 15 years of work to get to where lithium-ion batteries are now. And the goalposts keep moving." But as Shirley Meng of the University of California, San Diego, notes, that's all the more reason for urgency. "Now is the time to worry about resource availability," she says. "If we want to use batteries to store clean energy and combat climate

change, we don't have a lot of time."

Johanna Miller

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Magnetic semimetals host massless quasiparticles

Two materials have an unusual electronic band structure that can support fast, low-dissipation electronic transport.

When Paul Dirac introduced his famous equation for relativistic fermions in 1928, he aimed to describe one well-known particle: the electron. Shortly thereafter, Hermann Weyl observed that the equation has a special solution when the mass is set to zero. The so-called Weyl fermions embodied by that solution would be charged, like electrons, but being massless, they would travel faster and with less energy dissipation. The particles would also be chiral, like neutrinos, with each one's handedness depending on whether its spin is aligned or antialigned with its momentum. Those features make Weyl fermions appealing candidates for use in electronic and spintronic devices.

No such elementary particle has yet been found. However, in 2015 three groups of researchers identified the first Weyl semimetal (WSM), tantalum arsenide, which hosts quasiparticles—collective excitations of electrons—with

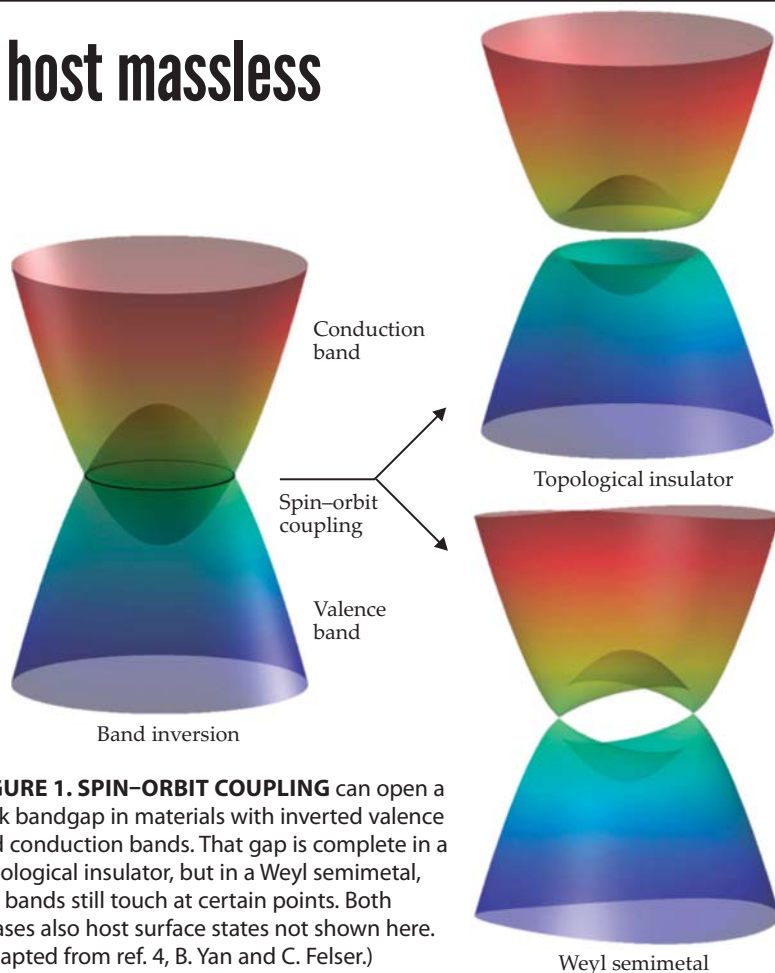


FIGURE 1. SPIN-ORBIT COUPLING can open a bulk bandgap in materials with inverted valence and conduction bands. That gap is complete in a topological insulator, but in a Weyl semimetal, the bands still touch at certain points. Both phases also host surface states not shown here. (Adapted from ref. 4, B. Yan and C. Felsner.)

the properties of Weyl fermions.¹ A WSM must have a broken symmetry, and in TaAs, it's inversion symmetry.

Researchers, however, have continued searching for materials, particularly ferromagnetic materials, that instead rely