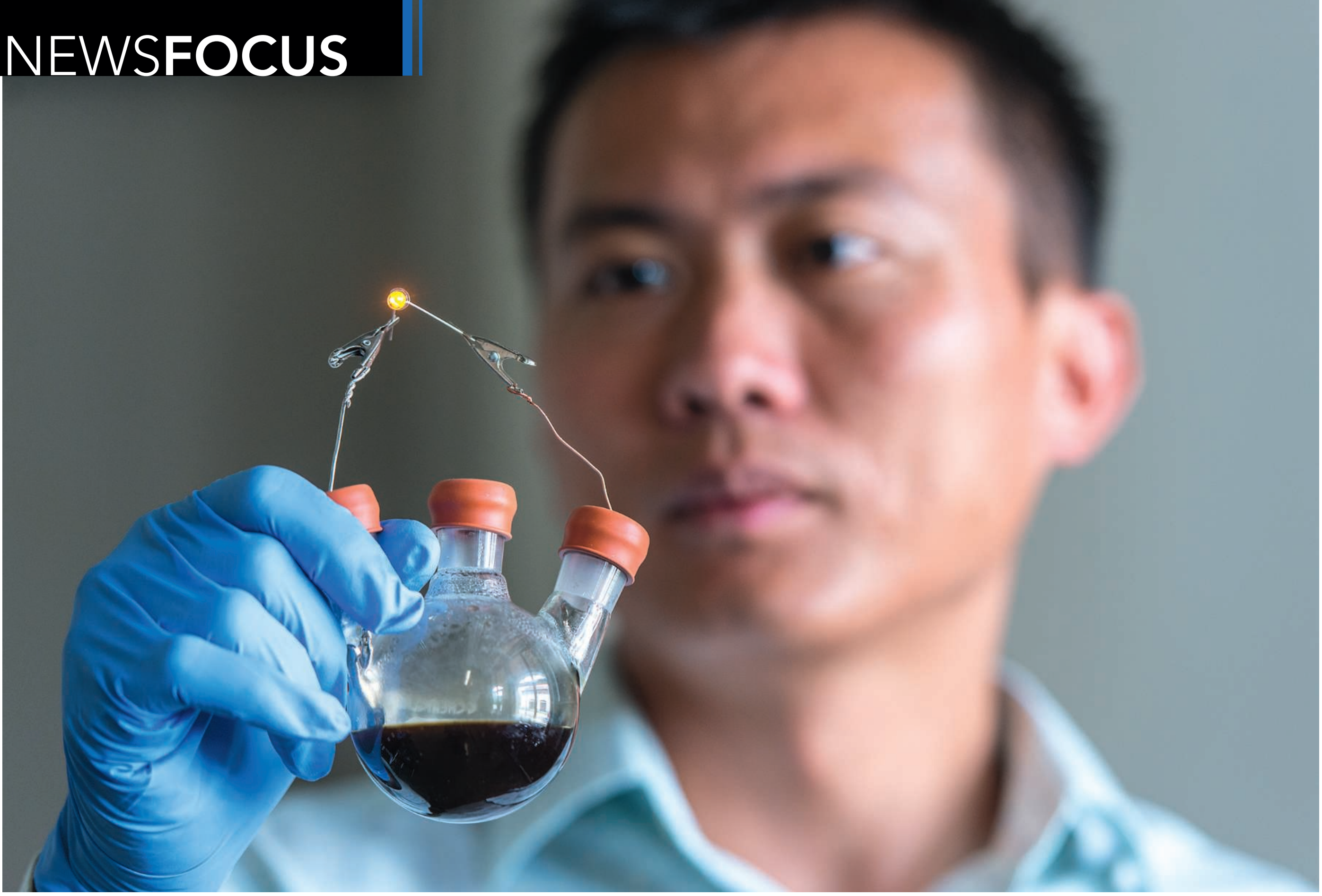

Tanks for the Batteries

The need to store energy from wind, solar, and other renewable energy sources could spark a revival of a dormant battery technology

EVERY LARGE-SCALE ENERGY SOURCE comes with a downside. For fossil fuels, it's carbon emissions; for nuclear power, it's radioactive waste; for renewables, it's intermittency, the inability to produce power when the sun isn't shining and the wind is still. Given society's pressing need to switch from fossil to renewable fuels to prevent catastrophic climate change, intermittency is a headache fast becoming a migraine. Many experts worry that the steadily climbing share of electricity supplied by renewables will eventually make portions of the electric grid unstable. "The clock is ticking," says Graham Fisher, chief scientist of SunEdison in St. Peters, Missouri, one of the largest providers of solar power in the United States.

Researchers working on the cutting edge of battery technology are increasingly confident that they have the means to steady the grid and smooth the path to renewables. They're updating a 130-year-old technology called flow batteries, aiming to create versions that can bank massive amounts of electricity from renewables when it's not needed and then feed it back into the grid during times of heavy demand.

Unlike traditional batteries, which pack their chemical power supply and the electrodes needed to tap it into one package, flow batteries separate those two jobs, storing energy in tanks of liquid electrolyte that can be scaled up to industrial dimensions. That strategy could help them avoid an unwelcome trade-off: Normal batteries are good at producing either large amounts of power for short periods or small amounts of power for days. "The key challenge is to find a battery system that can span these two," says John Lemmon, a program director at the Department of Energy's (DOE's) Advanced Research Projects Agency–Energy in Washington, D.C. Because the power delivered and the amount of energy stored can be optimized separately, flow batteries are "very promising," he says.

Now, many battery researchers are taking a second look. "There are new ideas out there that have the potential to be game changing," says Michael Aziz, a flow battery expert at Harvard University. Researchers are exploring dozens of different battery chemistries, hoping to find one that produces large amounts of power for sustained periods while being dirt-cheap, safe, and robust enough to last for decades. "It's still too early to say one system will get past all the hurdles," adds Yet-Ming Chiang, a materials scientist and battery expert at the Massachusetts Institute of Technology in Cambridge. "Right now it's about getting multiple shots on goal."

A huge niche

Developed in the 1970s, modern flow batteries did not catch on at the time because they were expensive and the market was nonexistent. But the push to renewables could change the calculus. Thirty-one U.S. states, for example, now have so-called renewable portfolio standards that require their energy mix to include as much as 40% renewables in the near future. The vagaries of sun and wind will create peaks and valleys of renewable

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Bright idea. Yi Cui demonstrates a prototype of a flow battery in his lab at Stanford University.

generation, which will have to be smoothed out to provide sustained, reliable power. "Most people believe that when renewables make up 15% to 20% of [electricity generating] capacity, the intermittency issue will become a problem," Fisher says.

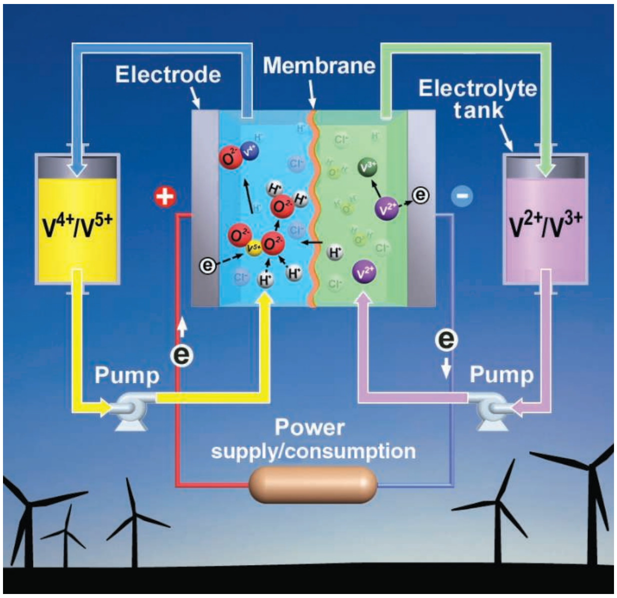
Not everybody agrees with Fisher's numbers, and there are alternatives to energy storage for coping with the fluctuating power from renewables—for example by shuttling power between different regions of the grid. But many energy researchers see storage as key. Last fall, for example, California lawmakers passed a mandate to add 200 megawatts (MW) of storage capacity by the end of this year and 1325 MW by 2020. "California's program will serve as a big kick-start and experimentation enabler," wrote Devi Glick, an energy policy expert at the Rocky Mountain Institute (RMI) in Snowmass, Colorado, in a recent RMI blog post. According to recent analyses by a pair of market research firms, the global demand for installing grid storage could reach more than \$100 billion annually by 2020.

Today, many communities store electricity by using it to pump water to hilltop reservoirs, and then letting the water run back down through turbines when the power is needed. Such pumped hydro setups typically store power for about \$100 per kilowatt-hour of capacity, now the cheapest option. Other companies and communities use conventional lead-acid, lithium-ion, and sodium-sulfur batteries for smaller scale energy storage (see figure, p. 354). But not all communities have the topography and water needed for pumped hydro, and conventional batteries are prone to fires and typically have trouble producing large power loads for many hours or days at a time.

That's where flow batteries could find their niche. They look nothing like sleek lithium-ion batteries or even cumbersome lead-acid car batteries. Instead, an electrode assembly, known as a stack, sits in the middle of the device, and charged liquid electrolytes are pumped from external tanks through the stack. In most designs, the positively charged electrode strips electrons from the electrolyte and sends them through an external circuit. This process produces positively charged ions, which flow through a specialized membrane to a second electrolyte on the other side, where they meet up with the electrons and complete the circuit (see figure, below). To charge the battery, the fluids are simply pumped in reverse while electricity fed into the stack replenishes the energetic charges to the initial solution.

Because the jobs of energy storage and extraction are separated, it's easy to scale up storage by simply building bigger tanks of electrolytes. Likewise, the power produced by the battery can be scaled up by adding more electrode assemblies to the stack. This division of labor also makes flow batteries generally safer and less prone to overheating, because the electrodes can take up electrons (a reaction that produces heat) only when the electrolytes are pumped through the stack.

But flow batteries tend to have low energy density, so they have to be large. Whereas state-of-the-art lithium-ion batteries have an energy density (known as specific energy) of 128 watt-hours per kilogram (Wh/kg), in the most common flow batteries that number ranges from 20 to 50 Wh/kg. Most modular units now under development range in size from refrigerators to railcars. A flow battery in Osaka, Japan, that's capable of storing a megawatt of power generated by 28 concentrated solar panels is larger than a dozen rail cars and was backed by tens of millions of dollars by the national and regional governments. That's too expensive for most applications today. So flow battery researchers are hunting for electrolytes, membranes, and designs that could lower costs and increase energy density.



Electrifying. Vanadium flow batteries generate current from tanks of liquid electrolytes; recharging them runs the same reactions in reverse.

CREDIT: PACIFIC NORTHWEST NATIONAL LABORATORY

Value-added vanadium

For decades, the leading class of flow batteries has been a group known as aqueous redox flow batteries, which rely on water-based electrolytes to ferry charges. The most advanced type, vanadium flow batteries, came on the scene in the mid-1980s. Vanadium's strong suit is that its ions are stable with several different amounts of charge. In one common setup, during discharge V^{2+} ions give up electrons at one electrode to become V^{3+}. Those electrons then move through an external circuit and are returned to a counter electrode where they convert V^{5+} ions to V^{4+}. The vanadium ions swim in a water-based electrolyte spiked with dilute sulfuric acid. Protons in this electrolyte pass through a proton-conducting polymer membrane to balance the charges (see figure).

Several vanadium redox flow batteries (VRBs) are already on the market, and more are on the way. Sumitomo Electric Industries Ltd., for example, announced last year that it's planning to build one of the biggest, a 60-megawatt-hour VRB for Hokkaido Electric Power Co. in Japan. According to Japanese news reports, the single battery will help the utility company smooth out its power delivery enough to increase its use of solar power by 10%.

But vanadium is expensive. Building a battery capable of generating 1 kilowatt-hour of electricity—about enough to power one 100-watt light bulb for a night—costs \$80 for the vanadium alone. Adding the tanks, pumps, and electrode assemblies brings the typical price of a VRB to about \$700 to \$800 for each kilowatt-hour of capacity, far above the typical cost for pumped water storage, about \$100 per kilowatt-hour. Another challenge is that V^{5+} ions are highly caustic, so manufacturers must use a durable but expensive polymer film called Nafion as the proton-conducting membrane.

Recent advances appear likely to cut VRB prices. In March 2011, for example, researchers at Pacific Northwest National Laboratory (PNNL) in Richland, Washington, developed a new sulfate-and-chloride-based electrolyte that can hold 70% more vanadium ions, enabling a smaller—and cheaper—battery to deliver the same amount of energy. The setup also can run at higher temperatures, reducing the need for cooling. That technology has already been licensed to three companies, which are getting close to installing units in the field, according to Imre Gyuk, program manager for energy storage research at the DOE's Office of Electricity Delivery and Energy Reliability in Washington, D.C.

In a separate advance, the PNNL team removed the V^{4+} and V^{5+} ions from one side of the reaction and replaced them with iron ions that cycle between Fe^{2+} and Fe^{3+}. Because the iron ions are far less corrosive than vanadium ions, the PNNL team could also replace the expensive membrane with a cheap plastic used in wastewater treatment plants. The lower cost could make V-Fe flow batteries ideal for applications that require multiple electrodes and membrane assemblies to store large amounts of power and deliver it quickly, as is often needed to match electricity supply with demand, says Wei Wang, a materials scientist who leads the PNNL group.

Michael Perry, a chemical engineer with United Technologies Research Center in East Hartford, Connecticut, and colleagues focused on the electrodes instead. At a meeting of the Materials Research Society meeting in Boston in December 2013, they reported reengineering the stack to have an interdigitated electrode: a setup that looks like alternating fingers on two hands clasped together. The design is common in fuel cells, which generate electricity from hydrogen or other fuels. The group has also improved the conductivity of the polymer membranes. Perry estimates that the changes have slashed the cost of the electrode stack by 83%. "We think we're now in the $300 to $350 kWh range" for the entire setup, Perry says.

Savings galore

Other researchers are reconfiguring the entire battery to reduce costs. Last year, for example, Yi Cui and colleagues at Stanford University in California came up with a "semisolid" flow battery that removes the need for a membrane altogether, usually the most expensive part of the electrode stack. To do so, they made a hybrid battery that's part flow and part conventional battery. The setup has just a single tank of electrolyte liquid, which contains lithium-sulfur compounds such as Li_2S_8. These interact with an electrode made of lithium metal that's covered with a thin coating to prevent it from undergoing unwanted side reactions. When discharging, the lithium metal gives up electrons and sheds lithium ions through the coating into the electrolyte. Those ions, along with electrons that have passed through an external circuit, convert the Li_2S_8 into Li_2S_4. Li_2S_8 reforms upon charging, and the extra lithium ions are redeposited on the metal electrode. In the May 2013 issue of *Energy & Environmental Science*, Cui and his colleagues reported that their lab-scale prototype generated as much as 170 watt-hours per kilogram and 190 watt-hours per liter, more than three times the output of conventional redox flow batteries. The hybrid battery also proved stable for thousands of charge and discharge cycles. And by removing vanadium from the mix, Cui estimates his setup could slash the cost of the raw materials for the battery to half that of VRBs.

Aziz's team at Harvard recently offered a potentially even cheaper option. They replaced the metal ions with far cheaper organic compounds called quinones, abundant in both plants and petroleum, which consist of at least one ring of carbon atoms, plus a tail of carbons, hydrogens, and oxygens. They have an electronic advantage as well as a cost one, Aziz says. In most flow battery setups, metal ions typically shuttle single electrons at a time. Each quinone molecule, by contrast, can ferry pairs of electrons—potentially giving quinone flow batteries a higher energy density than most metal-based flow batteries. Going organic carries another bonus: getting rid of water. Redox flow batteries have to keep their output voltage low or they run the risk of destroying their electrolyte by splitting water into hydrogen and oxygen gas. Organics without water can run at higher voltages and thus produce more power with fewer electrodes in the stack, Gyuk says.

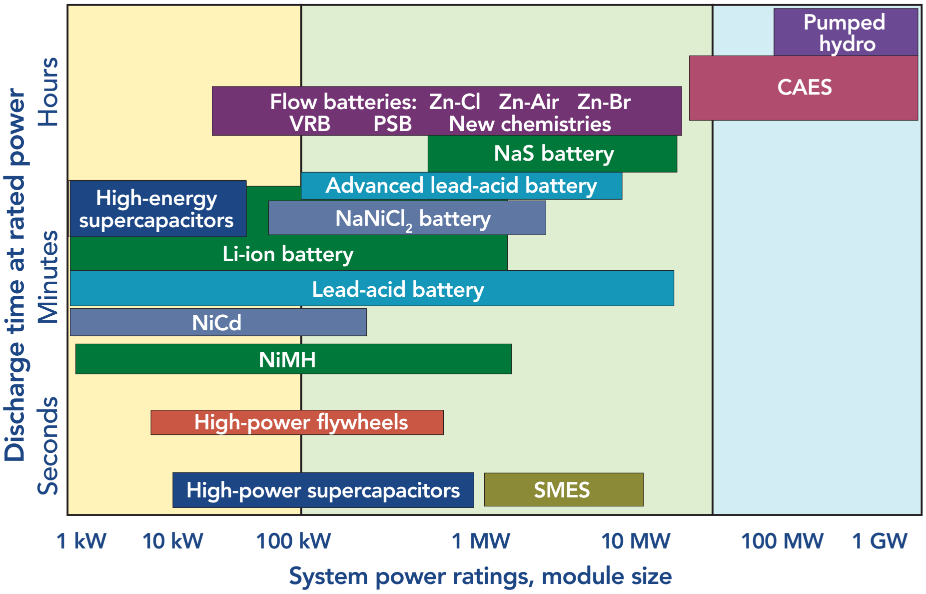
Quinones readily snag and give up electrons. So several years ago, Aziz began experimenting with batteries using hydrogen-containing quinones, known as hydroquinones, as the charge carriers. After some mediocre results, he and his students teamed up with theoretical chemists at Harvard led by Alán Aspuru-Guzik. Guzik and his colleagues calculated properties of more than 10,000 quinones and hit on a likely top performer, abbreviated $AQDSH_2$—a compound nearly identical to one naturally found in rhubarb.

Aziz and his students filled one tank of a flow battery with $AQDSH_2$ dissolved in an organic electrolyte. In the other tank they placed bromine liquid, or Br_2. During discharge, each hydroquinone gives up two electrons and two protons. The protons crossed through a membrane, where they met up with two bromine atoms and electrons that had passed through an external circuit to make two molecules of HBr. As the team reported in the 9 January issue of *Nature*, they could recharge the hydroquinones by running the reaction in reverse and feeding in electricity.

"It's a great new material set," Perry says. And unlike metal-based flow batteries, the organic batteries have the potential to be easily tailored using the standard tools of organic chemistry. But—as with every candidate for flow battery material—they have drawbacks. For starters, the organic electrolytes tend to be viscous, slowing the exchange of electrons at the electrode. And the bromine in Aziz's design is highly caustic.

Gyuk says overcoming such challenges will spur innovation. Indeed, the field is feverish with ideas and prototypes. "Flow batteries are starting to see a renaissance," Perry says. If so, a renewable-energy Enlightenment could well be close behind.

–ROBERT F. SERVICE



Workhorses. Flow batteries deliver more power for longer periods than most other storage technologies can.

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