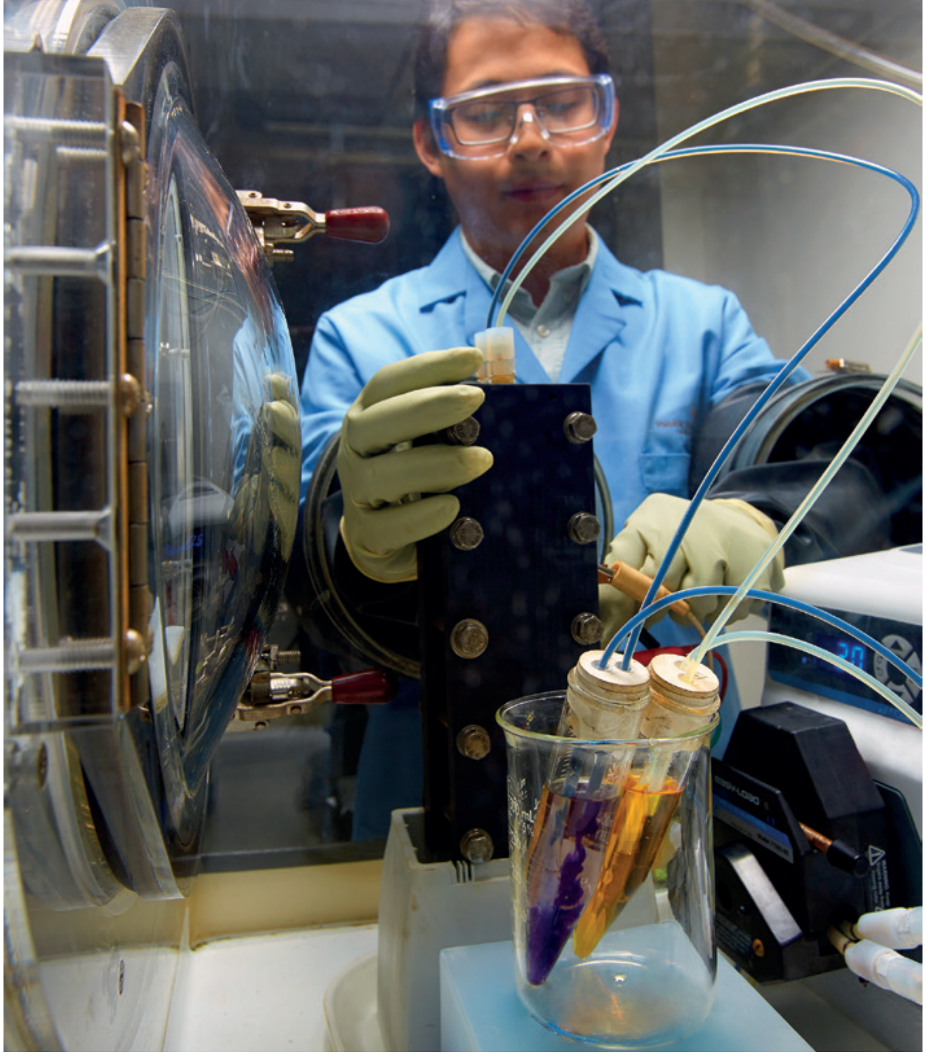

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A researcher at the Pacific Northwest National Laboratory in Washington working on flow batteries.

ELECTROCHEMISTRY

Liquid assets

Flow batteries, which release electricity through fluid-based reactions, could revolutionize renewable-energy storage.

BY NEIL SAVAGE

When state officials flipped a switch earlier this year at an engineering company in Pullman, Washington, they shone a light on one possible future for energy storage. That switch activated the latest type of flow battery, the largest in the Western Hemisphere. Rechargeable flow batteries, which store energy in tanks filled with liquids, have the potential to be cheaper than their conventional, solid cousins. They are also more adaptable to the needs of electrical grids, which are starting to rely on intermittent sources of energy such as wind and solar cells.

The Pullman flow installation, made up of big white boxes that together take up roughly the same amount of space as two tractor-trailers, stores 4 megawatt-hours of energy. That is more than enough to run four average homes for a month. Although the installation holds only a fraction of the power the grid will require, it is introducing a new generation of energy-storage technology.

If wind and solar power are ever to provide a significant portion of the world's electricity, new ways will be needed to store that energy. Existing batteries such as lithium ion and lead acid do not provide the necessary combination of long-term energy storage and rapid delivery of energy — just think how quickly a lead-acid car battery can be drained by a driver trying repeatedly to start a car on a cold day, or the overnight charge that an electric vehicle needs.

Flow batteries could provide an alternative. They can store energy for a long time, but provide it quickly when needed; they are liquid-based, so inherently safer than conventional batteries; and because the energy-storing liquids are kept in external tanks, changing their storage capacity is relatively simple. Most importantly, if researchers can develop the right combination of chemistries, flow batteries could be much less expensive over their lifetime than existing batteries.

GO WITH THE FLOW

A flow battery is a type of fuel cell that consists of two tanks, each containing an electrolyte made of some sort of energy-storing material — a metal or a polymer — dissolved in a liquid. One liquid is the negative side of the battery, the other the positive side. The liquids are pumped through a stack that contains positive and negative electrodes and a membrane that keeps the liquids from mixing, but allows ions to cross. The liquids undergo a reduction and oxidation, or redox, reaction, transferring electrons from the negative to the positive tank (see 'Renewable energy storage').

The most common version uses the transition metal vanadium (V) dissolved in acid. During discharge, ions of V^{2+} on the negative side of the battery are oxidized to V^{3+}. The electrons given up by the vanadium ions flow out to an external circuit, providing a current to whatever the battery is powering. The electrons travel to the positive side, where they latch onto a different ion, V^{5+}, reducing it to V^{4+}. During charging, this redox reaction is reversed, removing electrons from the positive side to recharge the negative side.

This design offers some inherent advantages. For one, unlike in a conventional battery, the power capacity and the energy capacity are separate. Energy is determined by the volume of the electrolyte, whereas power is controlled by the area of the electrode stack. "If you need to increase your capacity, you can easily just buy a new tank and fill it up with the chemicals," says Adam Weber, a chemical engineer at the Lawrence Berkeley National Laboratory in California. For higher powers, you can simply run the electrolyte through more or larger stacks.

Storing the electrolytes separately is also safer. In conventional batteries, Weber says, "you're trying to store a lot of power and energy in a little box". This design leads to a risk of catastrophic discharge of stored energy that is absent in flow batteries. Because many flow batteries are water-based, they are not likely to catch fire, unlike the lithium-ion batteries that have destroyed mobile phones and grounded aeroplanes.

Another problem with conventional batteries is that the diodes swell and shrink as ions pass back and forth through them, eventually leading the materials to fracture and fail. Liquids do not crack, so the electrolytes in flow batteries can last indefinitely.

CLEANER TRANSPORT

Although most researchers are developing flow batteries with an eye towards grid storage, or to accompany home-based solar energy, there are also efforts to build flow batteries that work in electric vehicles. Because a flow battery can be recharged simply by exchanging the liquid in it, owners of electric vehicles will not have to worry about stopping to charge their cars overnight. “Range doesn’t become so important, as long as there’s a filling station somewhere,” says Carlo Segre, a physicist at the Illinois Institute of Technology in Chicago. He has a grant from the Advanced Research Projects Agency–Energy (ARPA–E) to develop a flow battery for cars that he says could have a range of 800 kilometres or more (Tesla Motors says that the batteries used in its Roadster vehicle have a range of about 640 km). Segre’s battery uses nanoparticles of nickel and nickel hydroxide suspended in a potassium-based electrolyte.

The challenge in making flow batteries viable lies in finding designs and chemistries that provide good long-term storage, desirable current and voltage characteristics, a long lifespan and a competitive price. The Pullman battery, and a few higher-power batteries — two installed in China, three in Japan — are all based on vanadium chemistry, which provides both high energy and power.

Usually, the vanadium ions are dissolved in sulfuric acid. But there is a limit to how many vanadium ions the acid can hold, capping how much energy a given volume of electrolyte can contain. On top of that, the chemistry only works between 10 °C and 40 °C. Outside that range, the vanadium precipitates out of the acid, as either a powder or a gel. “Once it precipitated out it would jam your pumping system. Your battery would be dead,” says Wei Wang, a materials scientist at the Pacific Northwest National Laboratory in Richland, Washington. Wang and his team developed a solution of sulfuric and hydrochloric acids that can handle temperatures from −5 °C to 60 °C, and holds about 70% more vanadium than current systems[1]. The Pullman battery uses this new electrolyte.

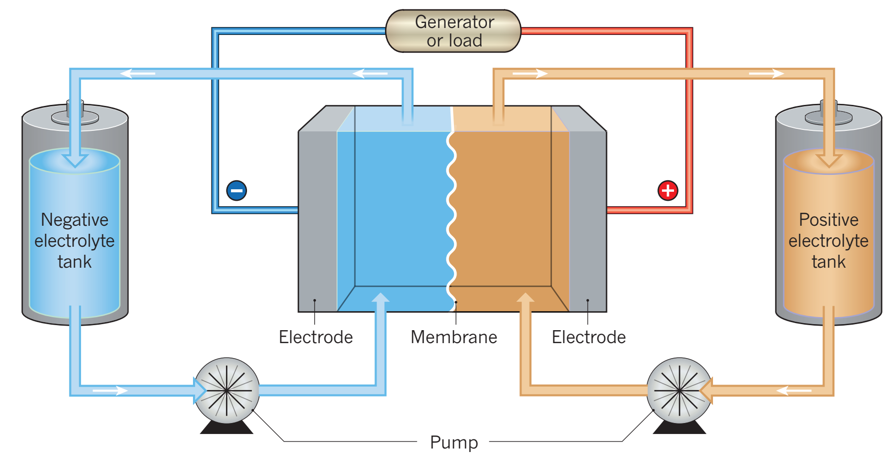
Even with this expanded range of operating temperatures, vanadium is not the ideal flow-battery material. It is rare and expensive — a 2011 estimate[2] from the energy-company-funded Electric Power Research Institute puts the cost of a vanadium redox flow battery at US$3,000–3,310 per kilowatt. At that price, it would take about $4-billion worth of vanadium batteries to provide California with the 1.3 gigawatts of storage it wants by 2020.

To find a cheaper alternative, Wang is working on zinc bromine batteries. Zinc is much cheaper than vanadium, and can carry more electrical charge. But Wang uses it as a solid, so one half of the hybrid flow battery does not flow and the volume of the zinc electrolyte cannot be changed. Still, he says, the hybrid flow battery allows more flexibility in system design than conventional devices, and its cost and performance may turn out to be appealing.

Instead of replacing a liquid with a solid, Weber made one side of his flow battery a gas. During discharge in his hydrogen bromine battery, gaseous hydrogen is oxidized at the negative electrode, producing an ion that passes through the membrane and reacts with the bromine. The battery has reached some of the highest powers of any redox flow chemistry in the lab[3]. And because hydrogen is inexpensive, the system could be a winner economically.

RENEWABLE ENERGY STORAGE

Tanks of metals or polymers in liquid make up the positive and negative sides of a flow battery. The liquids are pumped through electrodes, where they undergo reactions to generate electricity when a load is connected.



COST REDUCTION

Lithium, seen as the main conventional competition for flow batteries, may have its place in these upstarts as well. Yet-Ming Chiang, a materials scientist at the Massachusetts Institute of Technology in Cambridge, is developing a lithium sulfur flow battery[4]. Researchers have been working on conventional lithium sulfur batteries, but the elements tend to react, creating polysulfides that migrate to the electrode and block the flow of current. What is bad for conventional batteries might be good for flow batteries. Chiang’s set-up uses sulfur as a positive electrode. During discharge, lithium ions from the negative electrolyte move to and react with the sulfur cathode, yielding polysulfides that are suspended in the electrolyte liquid. Charging the battery causes the polysulfides to dissolve, and the sulfur precipitates out, recreating the positive electrode. And because sulfur is readily available, the battery should be inexpensive. “The attraction of sulfur is that it really is essentially free as a material,” Chiang says.

His other innovation is to replace the flow battery’s current collector, which is typically a stationary mesh of carbon fibres that the electrolytes must pass through. The mesh can clog, so instead, Chiang created a gel of nanoscale carbon particles, which moves along with the electrolyte and acts as a sort of ‘liquid wire’ to collect the current. That provides a greater surface area to absorb the charges from the chemical reaction, while shortening the distance the molecules have to travel to give up their charge.

Another potentially affordable option could be organic materials. “We’re not going to run out of carbon, hydrogen and oxygen,” says Michael Aziz, a materials scientist at Harvard University in Cambridge, Massachusetts. Aziz was inspired by plant photosynthesis to test quinones, a family of organic molecules common in plants. Two years ago, he demonstrated[5] a metal-free flow battery using bromine on one side and a quinone molecule called AQDS — which occurs naturally in rhubarb — on the other. He has gone on to synthesize other versions of quinone, looking for the one that is least expensive and most workable. “Getting the overall cost down is a big deal, and doing it in an environmentally friendly way is even bigger. We think we have a fighting chance of doing both,” says Aziz. But the organic route is not without its pitfalls. Organic molecules tend to undergo many different chemical reactions, and the wrong ones could produce insoluble particles that gum up the battery.

In the near term, the batteries most widely used to store energy on the grid will be conventional lithium-ion batteries, Chiang says. But several types of flow battery offer combinations of efficiency, safety and cost that could allow them to displace conventional batteries. Meanwhile, if Segre and others develop workable flow batteries for electric vehicles, the fact that they can be refilled like a car’s petrol tank would make them an attractive alternative to today’s battery technology. Although researchers are still working to get just the right designs and chemistries, Aziz believes that flow batteries could be ready for a great leap forward. “In two years we’ll have something that’s at roughly the industrial use level,” he predicts. “I think it’s the next big thing.” ■

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