## thesis

## Taking charge

This year's Nobel Prize in Chemistry celebrated in Sweden a few weeks ago - illustrates the power of cumulative science. In 1976, chemist Michael Stanley Whittingham first showed how to make a rechargeable battery based on the electrochemical intercalation of lithium ions into layers in transition-metal disulfides, such as TiS<sub>2</sub>. A few years later, researchers led by John Goodenough managed to double the operating voltage, and greatly increase battery energy density, by using in the cathode a different layered material, LiCoO<sub>2</sub>. Only in 1990 did lithium-ion batteries leap out of the laboratory, when a Japanese group under Akira Yoshino discovered how to replace the unstable lithium-metal anodes of these batteries with more stable carbon-rich material.

Whittingham, Goodenough and Yoshino fittingly shared the Nobel Prize, and the impact of their work is now obvious in all the battery-powered mobile devices we carry around with us. But spectacular progress isn't easily continued. Over the past 25 years, battery energy density has only increased by a factor of around four, and batteries remain heavy, as well as prone to fires and explosions. Storing energy is among the most fundamental of all technological challenges. How well we can improve on it will likely have a profound impact on the future of humanity.

In particular, our need to reduce the environmental pressure of all our activities requires an improved ability to store ever more energy into lightweight, stable and reliable devices offering rapid energy access, quick recharging, and durability through many cycles. In a recent paper, Jun Liu and colleagues, including two of the Nobel Prize winners, plot a near-term pathway for realizing better batteries by pushing the now-conventional lithium-ion technology still further (Liu, J. et al. Nat. Energy 4, 180-186; 2019). But this technology, they acknowledge, also has clear limits - and we'll probably need to shift to more radical lines of development fairly soon.

The idea of a battery, originally conceived by Alessandro Volta in 1800, is simple: stored chemical potential in the battery acts to drive electrons in the conductors of a connected external circuit. Meanwhile, within the electrolyte of the battery, a counterflow of ions matches the current carried by the electrons. The lithiumion revolution emerged from judicious choices of materials leading to safer battery operation at both higher voltages and energy densities — stored energy per unit mass or volume — than earlier batteries.

In the near term, as Liu and colleagues point out, lithium metal is considered an ideal anode material for future high-energy rechargeable batteries. That's because lithium metal has a very high specific capacity, which implies that it can, relative to other metals, take up more ionic charge per unit mass. This metal also has a very low electrochemical redox potential, useful for boosting the voltage and energy density of a battery. Optimal battery designs within the current paradigm will likely combine a lithium-metal anode with cathode materials also having a high specific capacity, including various lithium intercalation materials containing manganese and cobalt.



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Given these materials choices, Liu and colleagues suggest, there's still considerable room for battery improvement through cell design principles. Battery design requires many choices, including for the thickness and porosity of the cathode, the volume of the electrolyte, and the quantities of inactive trace elements in the cathode materials. Choices involve unavoidable trade-offs among properties such as battery energy density and expected cycle lifetime. Progress here also means suppressing some significant issues, among them the irritating tendency for dendrites to grow from the initially smooth lithium-metal anode out into the electrolyte, which can short-circuit the battery with potentially explosive results. Liu and colleagues' analysis suggests that, with some straightforward engineering advances, safe and reliable rechargeable batteries should reach energy densities from 350 W h kg<sup>-1</sup> up to 500 W h kg<sup>-1</sup> in the very near future. This would be a significant improvement over the best batteries of today, which achieve less than 300 W h kg<sup>-1</sup>.

This is what we can expect through incremental improvements along existing designs. It's clearly further, but not much further. As a result, other researchers are considering a host of alternative routes to battery technology, each of which holds great promise — but faces significant obstacles as well.

One intriguing idea is the lithium-air battery, which would use oxygen drawn from the air as the active material at the positive electrode (Aurbach, D. et al. Nat. Energy 1, 16128; 2016). Ideally, such batteries would also use metal lithium as the anode, and so also need to conquer the dendrite problem. The cathode would be made of Li<sub>2</sub>O<sub>2</sub> and exchange oxygen with air, shuttling it in and out during charging and discharge. Conceptually, such a battery could have an extremely high energy density theoretically as high as 3,500 W h kg<sup>-1</sup>. Practical estimates place achievable energy densities more likely in the range of 500 to 1,000 W h kg<sup>-1</sup>, which would be enough to outfit electric vehicles capable of driving up to 500 km without recharging. One key to this is that the fuel at the positive electrode,  $O_{2}$ , is readily available from the air.

Further designs under exploration include the lithium-sulfur battery, which would employ cheap, widely available and relatively lightweight sulfur in the cathode. It also has high potential, but progress requires dealing with a wide range of intermediate sulfurlithium compounds that contaminate the electrolyte and cause a variety of problems. Other researchers are pursuing batteries that would eliminate the need for liquid — and usually highly combustible — electrolytes. Although the slow diffusion speed of ions through solids has long been considered a barrier to such designs, recent research has made considerable progress. Still further research aims to tackle the challenge of making batteries that charge much more quickly than those we use today (Liu, Y. et al. Nat. Energy 4, 540-550; 2019).

Ongoing research in all these areas suggests that batteries of the future will look rather unlike those we use now. Given the myriad avenues on play, we may hope to find some path forward that takes us as far in the next three decades as the lithium-ion approach has taken us in the previous three.

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