Running on air

Invented over 200 years ago, the battery is enjoying an unexpected comeback as the star of a modern low carbon epic. Elisabeth Jeffries reports on some of the technologies being developed to store renewably generated electricity

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With world leaders meeting in Copenhagen this month seeking a path to cut carbon emissions, renewable energy is at the very top of the global political agenda. However, most renewable energy sources being discussed at the UN climate change conference have a widely acknowledged problem – they are intermittent. Wind turbines can't gather any energy on becalmed days, and solar panels aren't much use at night.

'Today we cannot store energy, so utility companies are stuck. They have to modulate spontaneously fluctuating demand on a second-by-second basis. Intermittent sources will make it much worse – they won't dare have more than 20 per cent renewable energy feeding the grid,' says Winfried Wilcke, senior manager of nanoscale science and technology at IBM Research in California, US.

Wilcke, and other groups of scientists around the world, are looking into one possible solution to this problem – batteries. The electric car, perhaps powered by lithium ion batteries, is often touted as a carbon-free alternative to current fossil-fuelled vehicles – presuming it could be connected to an electricity grid fed by renewable energy. However, it has recently been argued that a vast network of battery-powered cars could also act as giant electricity storage system. Charging all those batteries as cars were plugged in overnight would flatten the daily electricity demand curve, helping utility companies to manage volatility and in turn save energy. And at times of peak demand, this vast network of batteries could be tapped to put electricity back into the grid.

But an even more powerful technology than lithium ion could become available to enable widespread energy storage using motor vehicles. Recent developments suggest that a new variation on the lithium theme – the lithium air battery – could outstrip lithium ion. Air batteries have one major use today, in hearing aids. Hearing aids need to be ultra-reliable, powerful and unobtrusive, and use these batteries because they have the highest available capacity in comparison to size. The zinc air battery employed in many hearing aids uses oxygen from the air as its cathode reactant, leaving more room for the anode material, zinc, and this improves the battery's energy density.

It is a smart principle, which has perhaps not been given the attention it deserves. And the lithium air battery, which works in a similar way, offers potentially the greatest energy storage density of all. According to Peter Bruce of the University of St Andrews, UK, who heads a research team dedicated to the problem, lithium air batteries will leapfrog lithium ion. 'Even with all the research going on, lithium ion batteries are only going to double energy density. We need to go beyond that and there are not many options, and the best of those is lithium air,' he argues.

The limiting factor restricting the power density of lithium ion batteries is their reliance on heavy, bulky metal oxides as a cathode material. In contrast, lithium air batteries use lithium metal as the anode, and a light, compact porous carbon scaffold as their cathode, where lithium ions react with oxygen from the air to form Li_2O_2. Bruce's investigations show that a battery based on lithium oxide stores 10 times more energy than batteries based on lithium cobalt oxide, the material often used for the lithium ion battery cathode, because of the lower mass. He has found that the mass of a lithium air battery is 28g, compared to over 90g for lithium cobalt oxide. 'In a lithium air battery you take two lithium ions out for every ion of oxygen, whereas you only take half a lithium ion out in lithium ion batteries. There is much more charge per unit of mass,' he states. Oxygen he describes as ideal for a positive electrode because of its wide availability.

It sounds impressive – but it won't be seen in an electric car just yet. 'It's very much in the laboratory at this stage and we have some way to go before we can prove it as a technology,' says Bruce. Problems to be overcome include managing the potential decomposition of some of the lithium when it reacts with the air. Moisture in the air may react with the lithium and cause an explosion, so lithium air batteries will need protective membranes that stay stable and shut out water while letting in oxygen. Bruce says the charge voltage is currently higher than the discharge, and this needs to be brought down. Scientists are also looking to alter the electrolyte so that the solubility of the oxygen improves, while reducing the volatility.

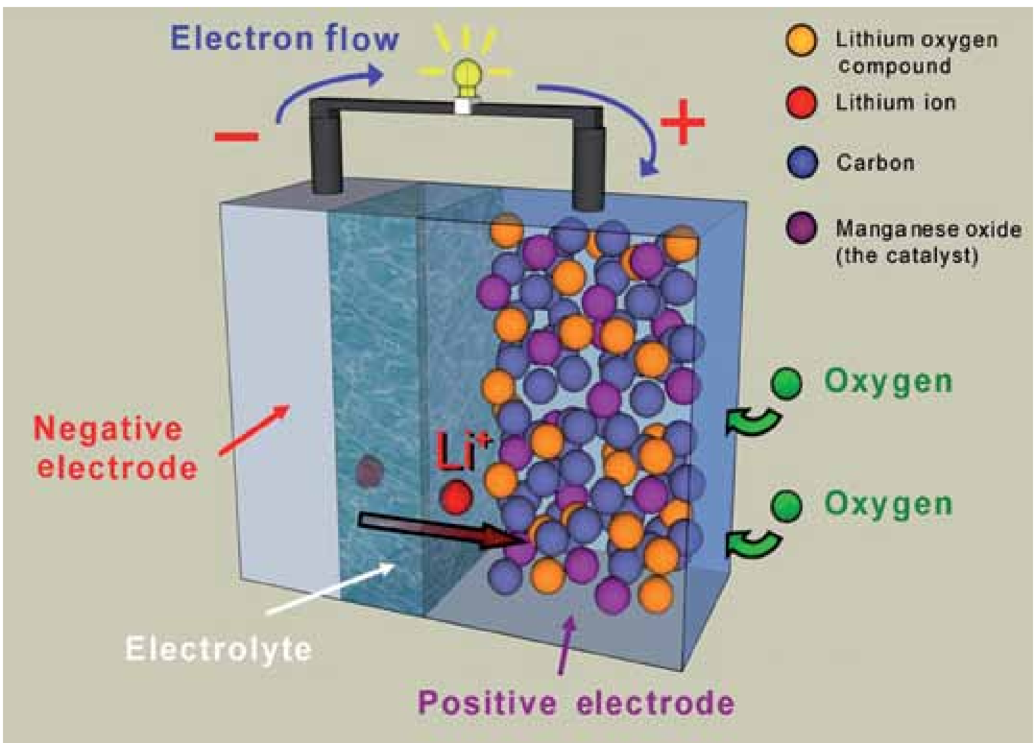
Wilcke likens the power delivery of lithium ion batteries to a dynamite explosion – whereas the lithium air battery is more like burning coal, producing a great deal of energy but only giving it up very slowly. 'All the reaction is on the surface. There are lots of kilowatt hours but not a lot of kilowatts,' he states. 'The challenge is to get the power out.'

To do this, scientists are working on two areas. Since all the reaction is on the surface, one solution is

In short

- **A network of electric cars could be used to store electricity produced by renewable sources**
- **Lithium air batteries could store 10 times more energy than standard lithium ion batteries**
- **Vanadium flow batteries could provide a centralised energy storage facility**
- **Microbial cells could offer a carbon neutral, portable energy source**

A lithium air battery (below) uses lithium metal as the anode

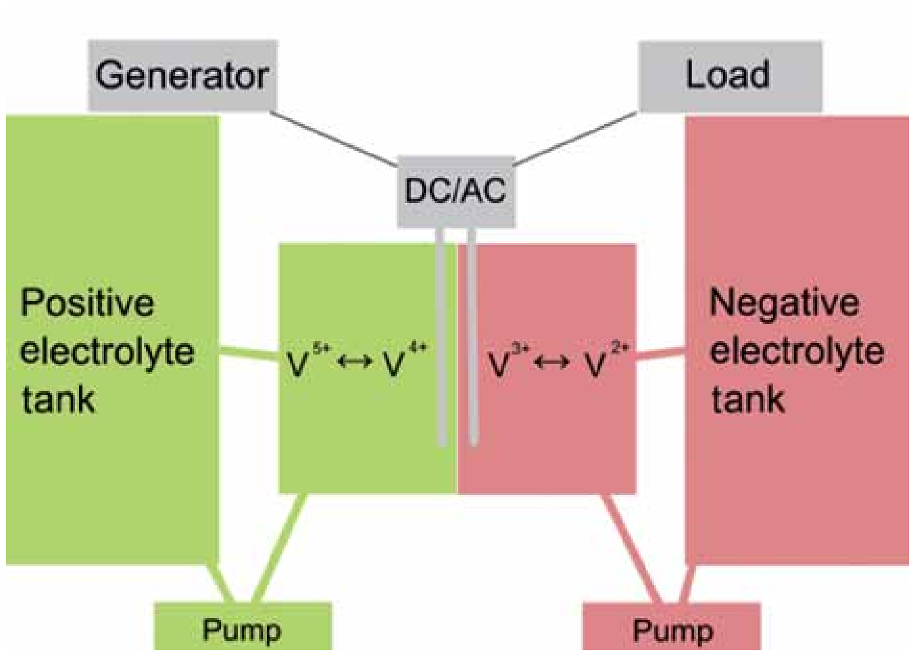


to make the surface larger and for this nanotechnology is being used. The other challenge is to increase the power produced, which may be achieved by accelerating the reaction at the cathode with catalysts. Rechargeability is another issue, with fifty cycles the most reached so far – this needs to increase to thousands for everyday use.

Tanked up

One alternative, or perhaps complementary, approach to storing energy in a highly dispersed network of car batteries would be to build centralised energy storage facilities based on another emerging battery technology – flow batteries. Unlike conventional batteries, which store energy chemically at their electrodes, flow batteries store energy in their electrolyte, which is held in tanks outside the cell (or stack of cells). This makes them highly versatile, because more electricity can be stored simply by increasing the storage capacity of the electrolyte. A higher concentration of reactants within the electrolyte will also have this effect. Raising the number of cells within the stack will increase the voltage, while enlarging the electrode surface area will increase the electric current. 'The major advantage is that you decouple the power from the energy,' explains David Hodgson, research and development specialist at the UK Trade and Investment, the government's export arm. 'This has very wide applicability,' he adds, noting, however, that due to their size they can only be used for stationary applications.

'The fact that the energy storage capacity of flow batteries is determined by the volume of the external reservoir does make them attractive for large scale storage solutions, such as integration of renewable technologies with power distribution networks,' comments Richard Mills of the UK's University of Southampton school of engineering sciences. 'Conventional batteries cannot easily be scaled up and large storage capacities power outputs can only be achieved by



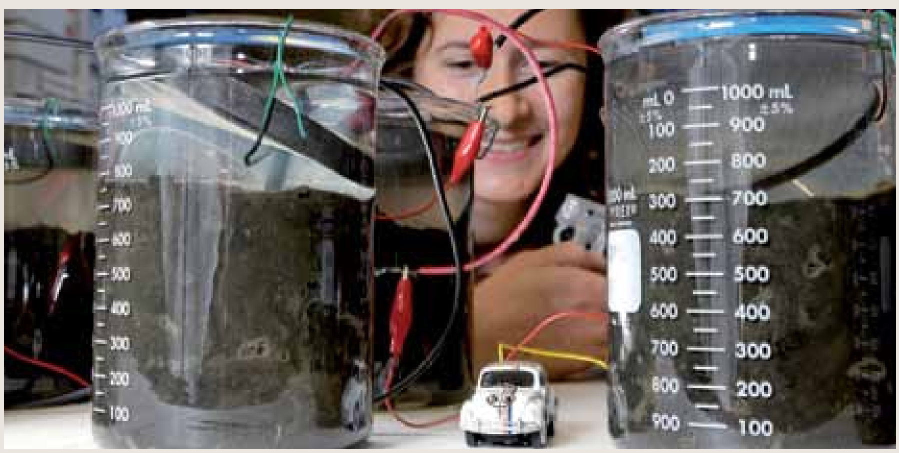
Vanadium flow batteries (above) could be used in centralised energy storage facilities

Bugs better than batteries?

Batteries aren't the only way to store renewably generated electricity. In the US, scientists at Penn State University have been exploring biochemical approaches, and have created a cell that produces methane – a fuel which can be stored – directly from electricity, using microbes. According to Bruce Logan, Kappe professor of environmental engineering, the microbes, from the archaea family of bacteria, can take electricity and directly convert carbon dioxide and water to methane. This produces a portable energy source with a potentially neutral carbon footprint.

The microbes were known to produce methane in marshes and landfill sites. While it has been previously assumed that they turn the organic materials into hydrogen and then methane, the researchers found, when trying to produce hydrogen in microbial electrolysis cells, that their cells produced less hydrogen and much more methane than expected.

They applied a voltage while using the microbes in a two-chambered electrolysis cell, with an anode immersed in water on one side, and a cathode in water, inorganic nutrients and carbon dioxide on the other. Having coated the cathode with the biofilm of archaea, they noted that not only did current flow in the circuit, but the cell produced methane. They concluded that the cell uses the current to convert carbon dioxide and water to methane, without needing all the organic material, bacteria or hydrogen usually found in microbial electrolysis cells. 'We have a microbe that is self perpetuating, that can accept electrons directly, and use them to create methane,' claims Logan. This, he suggests, could have uses for capturing renewable energy in a portable fuel – methane – in a carbon neutral cycle.



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Microbial cells could potentially be used to store renewably generated energy

Reference
S Cheng *et al*, *Environ. Sci. Technol.*, 2009, **43**, 3953 (DOI: 10.1021/es803531g)

AP PHOTO / UWE LEIN

Battery-powered car on show at the eCarTec fair in Munich on 13 October

connecting lots of small cells together. This involves a huge quantity of cell packaging materials and some complex control electronics along with heating and cooling problems – large numbers of small cells tightly packed can get quite hot under heavy usage conditions.' He suggests that the batteries could be used as buffer stations or charging stations along the grid, and could range in size from a kilowatt-sized unit, about the scale of a domestic appliance, to large megawatt units.

As the name suggests, flow batteries work by pumping two electrolytes, separated by an ion-permeable membrane, through a cell. The two electrolytes are chosen to have complementary redox potentials – when the battery is being charged, one accepts electrons as it flows past the cathode, and the other releases electrons while pumped passed the anode – a process that is energetically 'up hill'. When discharging, the reverse takes place, releasing the stored energy.

Various companies are working to commercialise the technology. VRB, a company now owned by China's Prudent Energy, developed a flow battery using vanadium in both electrolytes. Thus, cross-contamination of ions through the membrane separator has no permanent effect on the battery capacity, unlike in other batteries. VRB piloted the use of a flow battery in a small wind farm. Its former director, Tim Hennessy, says irregular flows of energy such as the 100 000 cycles of wind power each year do not damage the battery. While vanadium is an expensive element, the company has recycled material from fly ash to increase its availability. Increasing the reaction rate and reducing the cost are the main challenges. Further work needed includes improving the cell stack to make it more efficient and reducing the resistances associated with the interface; using polypropylene instead of PVC (polyvinyl chloride) in the stack frame is one solution.

Vanadium flow batteries are the most tested batteries in the field to date, although trials are ongoing on other types, such as soluble lead acid and zinc cerium. According to Mills, several different areas of research are now under way to improve these. Research goals include improving the efficiency of the ion exchange membrane, maintaining the balance of the two electrolytes over time, making the system less sensitive to oxygen and improving the electrode materials to increase longevity. With the latter being where most of the research is currently focused.

'Conventional batteries can not easily be scaled up'

At present, most flow battery electrodes are made of carbon polymer composites, but these have some drawbacks. 'The chemical species can be aggressive to the cell components so some degradation occurs over time,' explains Mills. Researchers have tested activated carbon, glassy carbon, and Ebonex, a conductive titanium. 'There is a trade-off between the longevity of the materials compared to their conductivity,' he says. Ease of manufacture and, of course, cost are also major considerations, with the ionic membrane often the most expensive component. Nafion, a synthetic polymer, has been used because of its stability, but it continues to be a costly component. Flow batteries benefit from fuel cell research, which they resemble: 'they can piggy back off fuel cell development,' says Hodgson.

Based on current climate predictions and the related urgent need for reliable renewable energy technology, this development can't come soon enough.

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