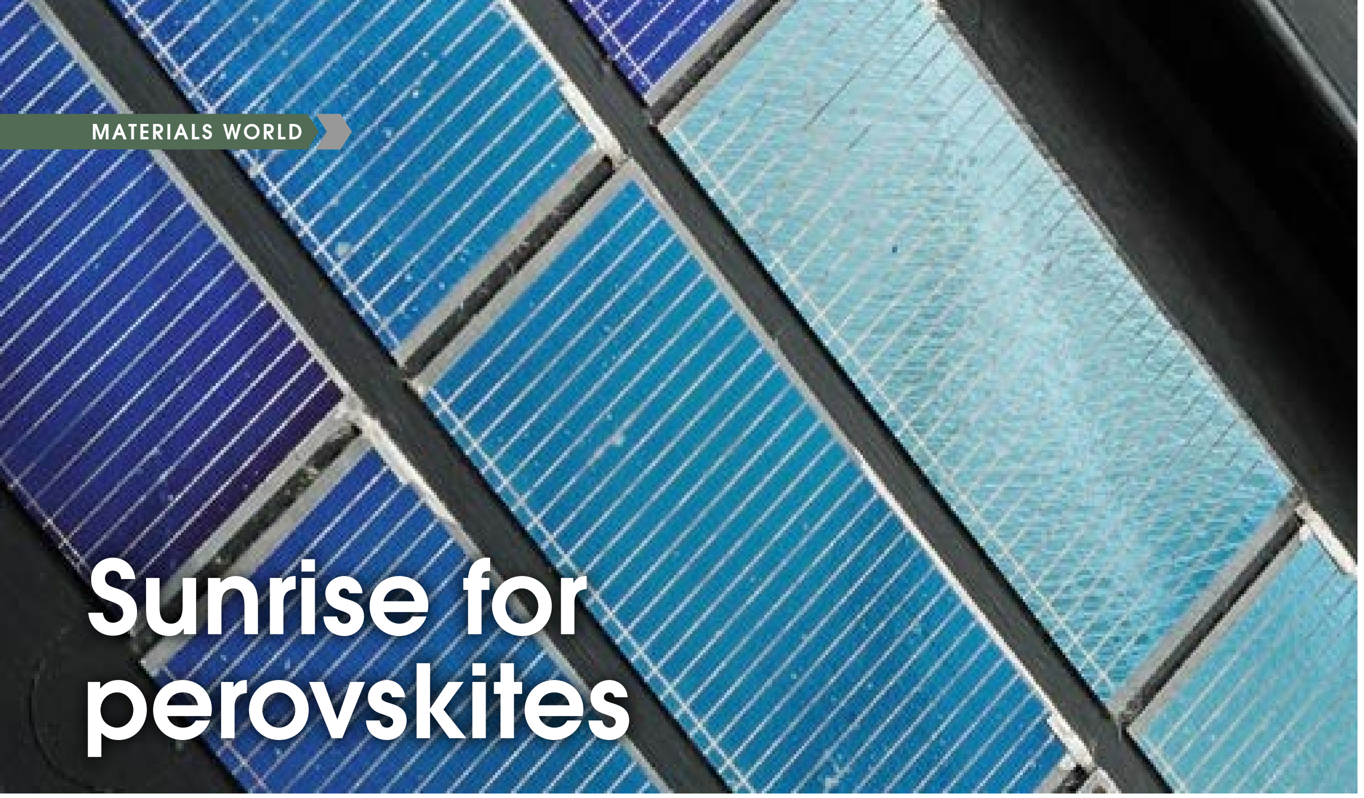


Sunrise for perovskites

Silicon cells dominate solar power, but a new family of materials are hot on their heels. Simon Frost finds out more.

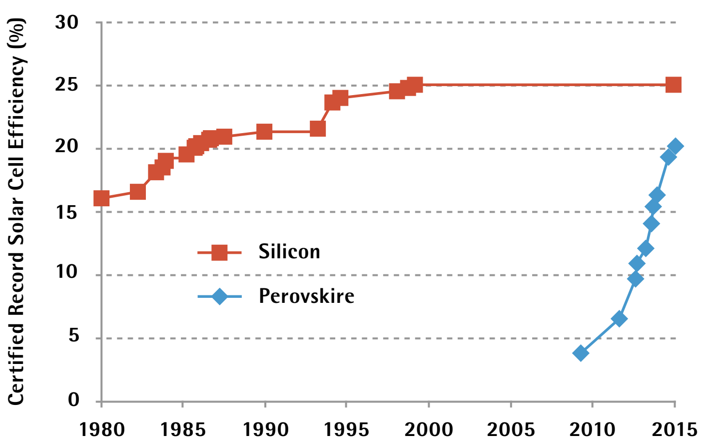
Above: **Silicon dominates solar PV, but its efficiency has virtually plateaued.**

Below: **The rise in conversion efficiency for pervoskite cells, compared with silicon. Source – National Renewable Energy Laboratory, USA.**

Between 2009 and 2013, the World Intellectual Property Organisation published a total of 19 patents with the word 'perovskite' on the first page. In 2014 alone, there were 75 – about four times as many as in the previous five years put together. It reflects a remarkable rise in conversion efficiencies achieved by scientists developing perovskitic solar cells. Five years ago, researchers could barely achieve an efficiency of 4% – now, they're exceeding 20%.

Perovskites are a family of organic-inorganic compounds with the same crystal structure as the mineral from which they take their name, a calcium titanium oxide with the chemical formula $CaTiO_3$, which is found in the Earth's mantle.

They boast several attractive properties – they are made from abundant and relatively cheap materials, such as ammonia, iodine, lead and tin, and can be manufactured using low-temperature solution processing. They offer high absorption, too – a micrometre-thick layer of perovskite can absorb as much sunlight as a 180 micrometre-thick silicon cell.



Dye-sensitised beginnings

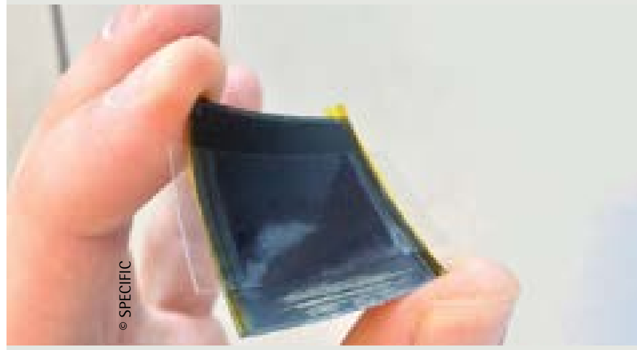
The field of perovskitic solar cells was born out of the dye-sensitised solar cell, borrowing the architecture whereby a charge-conducting mesoporous scaffold is coated with a light-absorbing dye, replacing the dye with a perovskite. In 2009, the *Journal of the American Chemical Society* published a study by a group of Japanese universities that had manufactured the first perovskitic solar cell, using organic-inorganic methylammonium lead tri-iodide to sensitise titanium dioxide for visible light conversion, achieving an efficiency of 3.8%.

Compared with the industry-dominating crystalline silicon cells, which can achieve around 25% efficiency, that was no big threat. But while the figure for silicon cells has essentially plateaued – advancing from a world-highest 25% to 25.6% in the past 15 years – rarely does a month pass without the publication of a new record-breaking efficiency for perovskites. At the time of writing, the record stands at 20.1%.

'Since their discovery in 2009, there has been a constant stream of ever-increasing perovskite solar cell efficiencies reported' says Dr Paul Coxon, who researches photovoltaic materials at the University of Cambridge Department of Materials Science and Metallurgy. Professor Saiful Islam, Materials Chemist at the University of Bath, describes this increase as, simply, 'unprecedented'.

Not to scale

'The emergence of a new PV technology rarely happens and has reinvigorated research in the field', says Coxon. 'This is our "graphene", and not without good reason'. But it's not all good news – like graphene, perovskites have a scalability problem. The highest efficiencies are found in very small, defect-free samples – it commonly falls to 10–15% in cells measuring more than $1cm^2$, although this is improving, too.



Above: **Perovskite tin solar cells made by University of Oxford researchers.**

Left: **Solution-processable, flexible metal perovskite solar cell developed by SPECIFIC, UK.**

In June 2015, the National Institute for Materials Science (NIMS), Japan, achieved a record 15% energy conversion in perovskite solar cells larger than $1cm^2$. The NIMS team was the first to have perovskite efficiency results certified by an international public test centre.

Three months later, Brown University, USA, published findings of a 16.3% conversion efficiency in a $1.2cm^2$ planar perovskite cell in *Advanced Materials*. In the Brown team's novel fabrication process, perovskite precursors are first dissolved in a solvent and coated onto a substrate. That substrate is then bathed in a second solvent, which selectively grabs the precursor-solvent and leaves behind an ultra-smooth film of perovskite crystals. Excess organic precursor is then added to 'glue' the small perovskite crystals together, allowing them to merge together into larger crystals during heat treatment, which also bakes away the excess precursor. What remains is a uniform film with fewer defects and, therefore, higher efficiency.

Researchers at SPECIFIC Innovation and Knowledge Centre at Swansea University, UK, have developed an alternative production method using a short burst of infrared radiation to stimulate the growth of perovskite crystals within seconds, reducing both time and cost – crystallisation in a conventional oven at 100°C can take 90 minutes and consumes much more power.

SPECIFIC has also developed the first fully solution-processed, flexible metal perovskite cells. The Swansea spinout is partnered with Tata Steel, which produces 100 million square metres of metal building cladding per year. 'If we could print solar cells onto this material, we could put a sizeable dent in the UK's carbon footprint, as well as creating jobs in the local economy,' said lead researcher Joel Troughton.

Lasting power?

Aside from scalability, perovskites have another serious obstacle to overcome, as Coxon explains, 'They contain organic molecules which aren't stable when exposed to moisture. Even worse, and somewhat cruelly, they break down in sunlight. Efforts are underway to improve the robustness of perovskites by encapsulating the active layers, but this will come at a cost of their ability to absorb light.'

At the European Photovoltaic Solar Energy Conference, held in Germany in September, Ricky Dunbar from CSIRO's PV Performance Laboratory, Australia, said 'It is difficult to measure the efficiency accurately. It's degrading as you measure.'

In 2013, Professor Michael Grätzel, from the Swiss Federal Institute of Technology, Lausanne, invented a variant designed to negate this instability. Grätzel, it should be noted, is the co-inventor of the dye-sensitised solar cell.

In Grätzel's perovskitic cell, the perovskite is present not as a separate layer to the TiO_2 and/or ZrO_2, which captures the electrons, but infused into the material. As well as improving stability, the cell architecture is designed to eliminate the use of expensive back contact conductors and also eliminates the use of a conventional organic hole-transport-material. In May 2015, Grätzel's research team achieved 1,000 hours of stability under light soaking and more than 2,000 hours under temperatures of 80–85°C. Australian firm Dyesol is building a factory in Turkey to manufacture cells based on Gratzël's infusion principle. It is expected to open in 2017.

Hybrid solution

But Coxon notes that the first commercially viable perovskitic cells may well be silicon-perovskite hybrids. Perovskites can be made in a variety of different formulations, each of which absorbs different areas of the visual light spectrum more or less effectively. The perovskitic layer of a tandem silicon-perovskite cell could be purposed to strongly absorb the blue end of the spectrum, while a layer of silicon beneath can soak up the red end.

UK-based Oxford PV has raised £12.6m from investments towards commercialisation of its own hybrid technology. Led by Professor Henry Snaith, a former student of Grätzel, the company, a spinout from the University of Oxford, is spearheading the UK's effort towards commercialising perovskitic silicon cells. It claims that it could boost the efficiency of traditional silicon cells by at least 20%.

Oxford PV's perovskites can be printed directly onto silicon solar cells, copper indium gallium selenide solar cells or glass. The latter, Coxon says, is 'a significant advantage over silicon – they can be made transparent and look pretty. This may seem like a trivial matter, but the appearance of a device is an important thing to consider. In the UK, one argument against the development of solar farms is their visual impact on the landscape. Another idea could be to use perovskite solar cells to replace the glass in large skyscrapers and domestic windows.' Should scalable, stable transparent perovskite cells become a reality, this application could revolutionise how architects design for cities.

Payback time

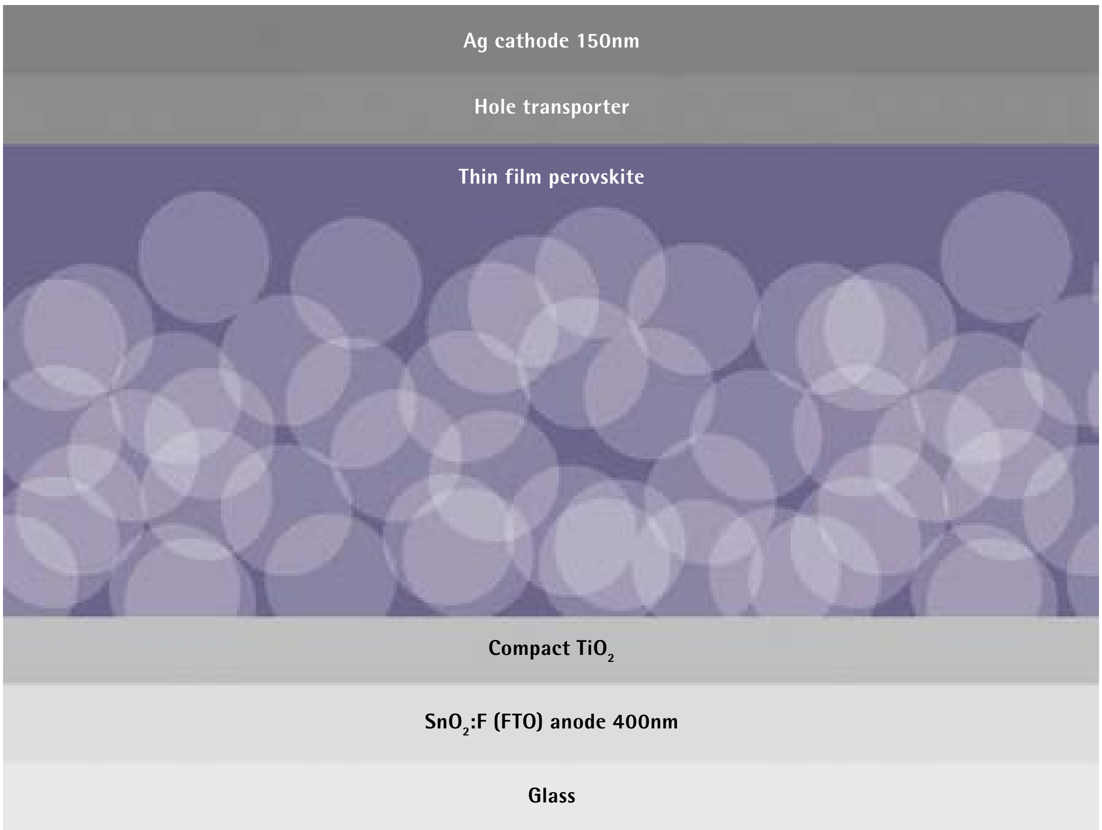
While researchers focus on boosting conversion efficiency and stability, scientists at Northwestern University, USA, and the US Department of Energy's Argonne National Laboratory published an interesting study on another important issue in July 2015.

They carried out a cradle-to-grave lifecycle assessment of perovskite cells, looking at the energy required for the entire materials cycle, from the mining, processing and purification of raw materials, through manufacture to final installation, with the aim of measuring how long the cells could recoup the energy expended in their production.

Their findings were impressive to say the least. Silicon panels need around two years to return their total energy investment, but the energy payback time for perovskites could be as quick as two months. The energy required to produce a perovskitic cell would be far less than for a silicon cell. Despite lower conversion efficiency, it would reproduce this energy in considerably less time.

While not yet perfect, the perovskite solar cell is an intriguing and exciting new technology that could have significant potential. It has already united the sub-disciplines of solar research, as Coxon says, 'Speak to any researcher in solar materials, and the word "perovskite" won't be far from their lips.' Prof Islam adds, 'The perovskite community has brought together different areas of solar cell expertise – the dye-sensitised community, organic photovoltaics and thin films – they are now also using their expertise to see what they can do in the perovskite research area. There's a bandwagon effect.'

In five short years, perovskites have burst onto the field of solar materials and demanded the attention of the research and, crucially, investment communities. Whether that will translate to commercial success remains to be seen – but at the current rate of development, we won't be waiting long.



Left: The basic structure of Oxford PV's hybrid perovskite cell.