Perovskites' solar promise

Perovskite solar cells have quintupled in efficiency in the last five years, making them the fastest-growing such type of device. But as **Stephen Ornes** explains, researchers have yet to overcome one final hurdle: figuring out how to stop them degrading in real-world applications

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In order for a solar cell to be useful, it has to convert sunlight into a viable electric current. To be viable, it must be cheap and made from easily available materials. Silicon cells may reign as the champion of the field, but in recent years an up-and-coming class of materials called perovskites has stirred up a disruptive ruckus. They're inexpensive, readily available and easy to handle. They're also unusually efficient at absorbing light. In the last five years, the power-conversion efficiency of perovskite solar cells has quintupled – making them the fastest-growing class of solar cells. But at the same time, physicists don't understand exactly why the cells work so well, and the materials degrade in the presence of moisture and ultraviolet light. So the question is: are perovskites here to stay, or is the boom headed for a bust?

The US National Renewable Energy Laboratory (NREL) in Golden, Colorado, maintains an online chart of the confirmed efficiencies to date of solar cells. The most up-to-date version of the chart (www.nrel.gov/ncpv) documents no fewer than 26 different types of cells forged from a variety of materials, from conventional silicon cells to experimental quantum-dot types. The current record holder claims a whopping 46% efficiency, which was achieved in a lab setting under concentrated sunlight. Such high performers are multi-junction cells that, despite coming with astronomical manufacturing costs, could allow photovoltaic power plants to produce cheap electricity in exceptionally sunny places. Closer to the middle of the most recent entries in the NREL chart, however, are perovskite cells (figure 1). Classified as an "emerging photovoltaic" on the chart, perovskites have electrified the world of sunlight harvesters.

"Perovskites have the kind of physical properties you'd expect for a solar cell absorber – or at least, they appear to," says Joe Berry, who is a senior scientist at the NREL.

The NREL chart, which traces the history of photovoltaic research back to 1976, shows most solar-cell efficiencies follow roughly horizontal lines – indicating little to no advance in efficiency – interrupted by occasional and rapid increases. The history perovskites is noticeably brief. It goes back only a few years but traces a short, steep rise. The first tests on perovskite materials, in 2009, reported a power-conversion efficiency of 3.8%. By January of this year, however, a team of physicists from Korea reported in *Nature* (**517** 476) that they had developed perovskite cells with an efficiency of 18.5%. And in November last year the NREL certified that a device made by researchers at the Korea Research Institute of Chemical Technology reached more than 20% (though the results have not yet been published). Those levels of efficiency place the material in the same energy neighbourhood as silicon cells, which have an efficiency of 20–25% in the lab (and up to 16% in commercial systems) and are the most common type of photovoltaics in use today.

"In some sense it's been a disruptive technology," says Aditya Mohite, a staff scientist at the US Los Alamos National Laboratory in New Mexico.

But efficiency alone does not make or break commercial success. What's important to consumers is how much bang they get for their buck – efficiency must always be judged alongside cost. For perovskites, cost is one factor they have in their favour – it is much cheaper to make them than it is to refine silicon to the high purity levels required to craft wafers for solar cells. As a result, myriad groups around the world are racing to build better perovskite-based cells. Some are investigating perovskites on their own; others are looking for ways to combine perovskites with silicon and forge hybrid cells; still others are looking for ways to use perovskites as a light concentrator that could boost the efficiency of dye-sensitized solar cells. Already, companies such as Oxford PV in the UK – co-founded by physicist Henry Snaith at the University of Oxford, a pioneer in the perovskite boom – and Dyesol in Australia have plans to bring solar cells to market.

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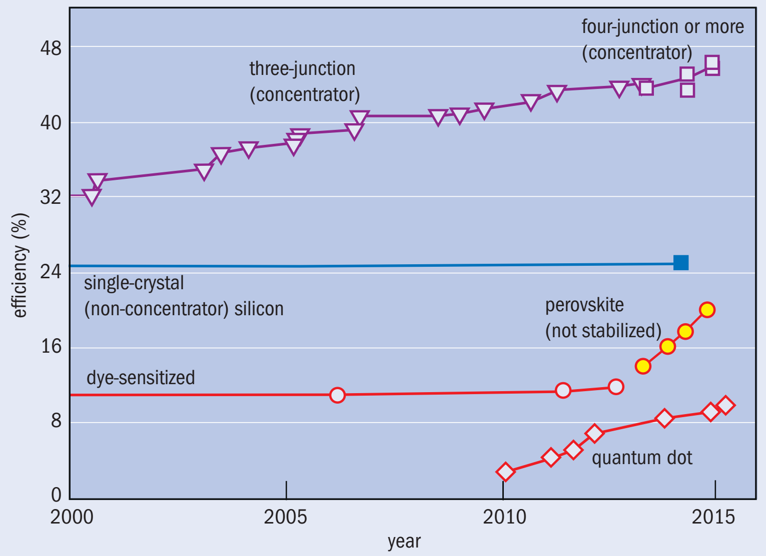
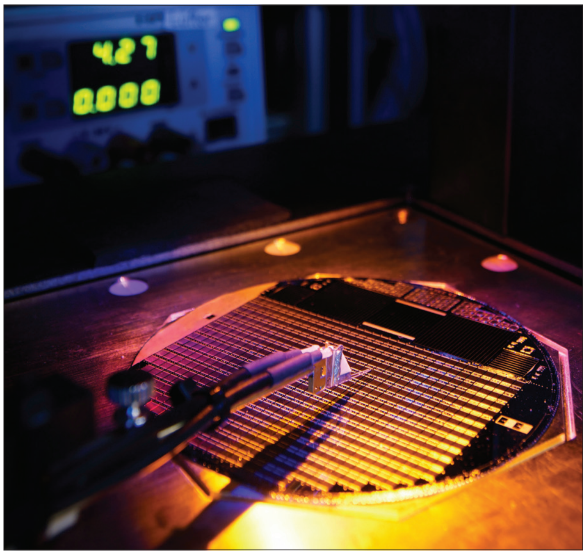
Perovskites' low cost and sharp climb in efficiency, however, don't necessarily translate to usability. The material still has an Achilles heel: it breaks down into its original components when exposed to the elements – moisture and ultraviolet light in particular. In some cases, they can degrade in less than a day. Even as efficiencies surge close to their predicted maximum theoretical efficiency – their "Shockley–Queisser limit" – of 28%, researchers remain uncertain about how to create solar cells that will last long enough to be useful.

Boshu Zhang, Wong Choon Lim Glenn & Mingzhen Liu

1 Research-cell efficiencies



This plot shows the increase, over time, of the power-conversion efficiencies of the solar-cell technologies mentioned in this article. The data are taken from an online chart maintained by the US National Renewable Energy Laboratory and only include values confirmed by recognized test labs. (As such, the first-reported perovskite solar-cell efficiency in 2009 of 3.8% is not included.)



Fraunhofer ISE/Photo Alexander Wekkeli

Record holder This multi-junction solar cell, developed by a French–German collaboration, holds the world record for efficiency, at 46%.

"In five years, I'm either quite sure that we will see them somewhere in industry already, in products," says physicist Wolfgang Tress at the École Polytechnique Fédérale de Lausanne (EPFL) in Switzerland, "or, if stability is such a big problem, the field will be quite dead again."

Rapid rise in efficiency

The term "perovskite" originally referred to calcium titanium oxide ($CaTiO_3$), identified in 1829 in samples collected from the Ural Mountains by mineralogist Gustav Rose, who named the material after Lev Perovski, Russia's then minister of internal affairs. Over time, the term came to be associated with any minerals that have the same structure as that original material. Perovskites take the form AMX_3, where the "A" and the "M" represent cations, and the "X" represents an anion. While researchers have identified, studied and developed a range of materials, the excitement in photovoltaics largely centres on lead-halide perovskite, a semiconductor that combines organic and inorganic materials and can be easily processed by spin-coating solvent solution onto a substrate.

Perovskite crystals both harvest light and transport electric charge, which are critical roles in a solar cell's ability to shuffle charge around. The material's band gap can be tuned to optimize the trade-off between voltage and absorbed light, or to create tandem cells, in which the perovskite is paired with another photovoltaic technology.

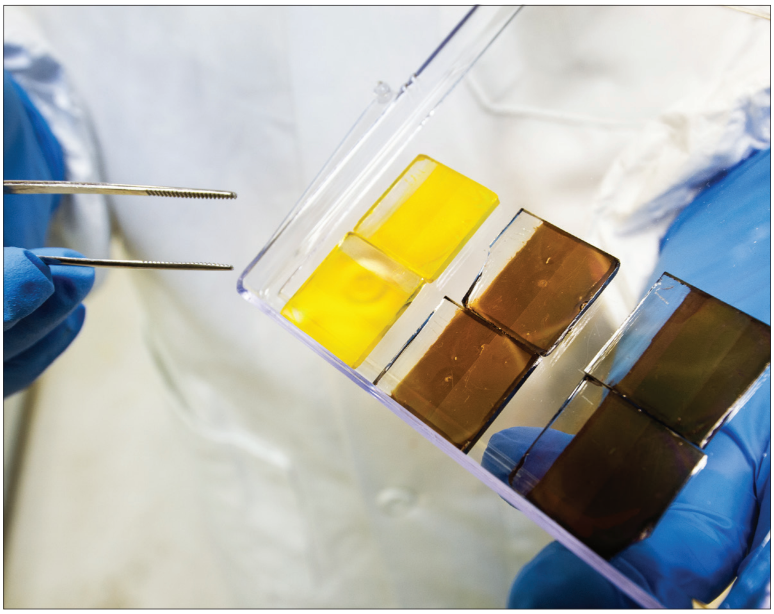
Interest in the material largely grew out of research into liquid dye-sensitized solar cells, in which a nanoporous material is stained with a dye, "sensitizing" it to visible light. Engineers had been testing perovskites as a sensitizer, and in 2009 Tsutomu Miyasaka at the University of Tokyo, and colleagues, demonstrated that perovskite-sensitized cells, in which titanium-dioxide films were coated with perovskite nanocrystals, achieved an efficiency of 3.8%. That paper "triggered the whole field", says Tress. Over the next two years, the efficiency of these solar cells nearly doubled to 6.3%; however, the liquid electrolyte quickly dissolved the perovskite.

In 2012 the field surged forwards again when perovskite cells moved into a solid-state configuration. In August of that year, researchers from the EPFL and from Sungkyunkwan University in Seoul, Korea, reported an efficiency of more than 9% for solar cells in which the liquid electrolyte had been replaced by a solid charge transporter. In the December, researchers led by Snaith at Oxford reported a 10.9% efficiency and a generated photovoltage of more than 1.1 V for perovskite cells supported by aluminium oxide, rather than titanium dioxide.

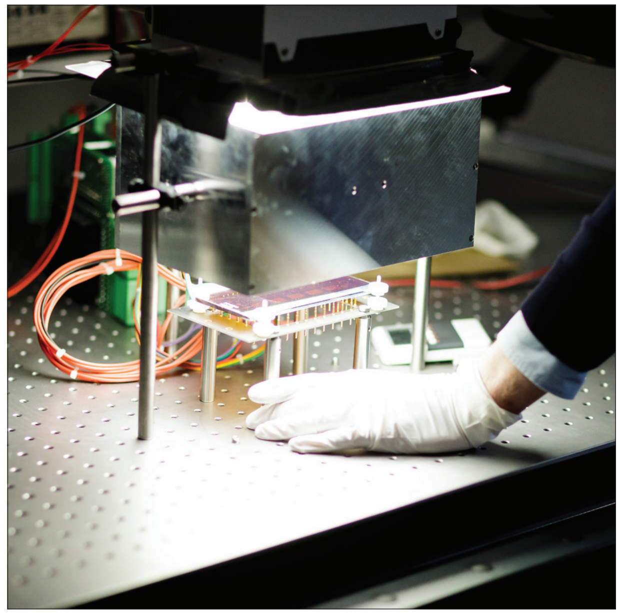
Efficiencies continued to climb, reaching 16% by 2014, but excitement over such high numbers brought increasing concerns about the accuracy of the measurement technique. According to conventional accepted standards, current-voltage-output curves for photovoltaic cells are measured while the cell is exposed to an energy spectrum that mimics that of the midday Sun. But perovskite is peculiar, says Tress. The measured output of a perovskite cell depends in part on how quickly the voltage is scanned and measured, as well as on the conditions of the cell before the measurement. (A dark cell will show a different efficiency from one that's been "pre-soaked" with light, for example.) This phenomenon, called hysteresis, can lead to drastic over- or underestimates of the actual efficiency.

Tress and his colleagues investigated this hysteresis in a study published in March this year (*Energy Environ. Sci.* **8** 995). They reported that hysteresis is largely due to intrinsic properties of the perovskite and not the architecture of the solar cell itself. The number and type of defects in the perovskite can affect the degree of hysteresis, Tress says, but researchers are only just beginning to understand the specifics.

NREL



Oxford PV



Emerging technology
Perovskite solar cells can be made from a liquid base (left) or by printing perovskites directly onto a material such as silicon or glass (right).

"If you have hysteresis, you have a problem, then people have to check the efficiency again," he adds. Tress and his team also found that as charges build up at the interface of the electrodes in the solar cell, the current begins to drop off – even before the perovskite itself begins to degrade. Understanding hysteresis, he says, is critical to making efficient cells that remain stable for long enough to be useful.

Researchers are making headway on how to deal with hysteresis. Mohite, at Los Alamos, and his colleagues have developed a simple technique to grow large crystals. He says their method largely reduces disruptive defects in the perovskite and gives electrons a nice, clean ride. In January he and his team described the fruit of their efforts in *Science* (**347** 522): a hysteresis-free perovskite cell with an efficiency of 18%.

Stable or not?

Perhaps the largest problem facing perovskite-cell researchers right now is stability. Perovskite crystals, grown in solvents, degrade to their original components when they're exposed to moisture – in less than a day under high humidity. Photocurrents fall as the material degrades when it's exposed to air, likely due to humidity and accelerated by prolonged illumination.

"The major question is whether these problems are intrinsic or extrinsic, whether they can be avoided when the cell is encapsulated," says Tress. "There hasn't been much reported on stability."

In 2013 Snaith and his team investigated the effect of ultraviolet radiation on perovskites. They reported (*Nature Comms* **4** 2885) that the efficiency of encapsulated titanium-dioxide-based perovskite cells dropped by more than 90% after only five hours in simulated direct sunlight. Non-encapsulated cells fared better, surprisingly, losing only half of their efficiency over the five-hour ageing test. The efficiency of encapsulated cells coated with an ultraviolet filter, however, fell only by 15%. In those cells, the photocurrent fell but the photovoltage remained constant.

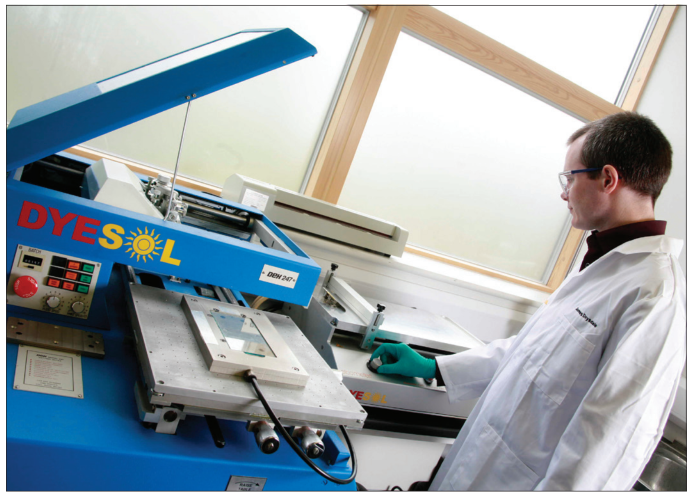
The researchers suspected that titanium dioxide was the problem, and degradation due to ultraviolet exposure could be inhibited by ditching the material. They replaced titanium dioxide with aluminium oxide and subjected these perovskite cells to the same ageing test. Though the power-conversion efficiency fell slightly during the first 200 hours, it levelled out – and remained stable for 1000 hours. However, some remain true to titanium dioxide. In July 2014 researchers from the EPFL and Huazhong University of Science and Technology in China reported a cell that used the material and remained stable for more than 1000 hours under full sunlight.

Tress says he's uncertain about whether or not perovskites can be made to be stable for the long haul. "One reason the efficiencies have risen so quickly is that we have this big boom in research and so many groups working on it," he says. In the near future, though, once the hype has subsided, he says researchers will know if perovskites are here to stay.

Mohite remains optimistic. "The material is not stable with moisture. However, we've done studies that show you can encapsulate it in glass, then it's stable as long as you can avoid moisture, and it's not a problem." He points to successful encapsulation in other areas. "Coffee grounds come in a nice, big sealed pack," he says. "I think people will come up with solutions, and moisture won't be a problem." At the same time, he says, researchers still have to answer questions about whether the material will degrade under the intensity of the Sun.

Other issues loom over perovskite research, as well. For example, the most efficient cells contain lead. Lead's electronic properties are unmatched by other materials, making it extremely useful in car batteries and many other devices. On the other hand, it's a toxic metal, and as Mohite warns, "it may not be a good idea to have that on your roof". Tin may be an appealing alternative: research published in 2014 described a perovskite cell using tin in place of lead and with an efficiency of 6% (*Energy Environ. Sci.* **7** 3061).

Those are practical concerns, but there's still an even larger mystery at the heart of perovskite research. Physicists barely have any idea why this



Dyesol Limited

To dye for Australian solar-cell manufacturer Dyesol is increasing the efficiency of its dye-sensitized solar cells by incorporating perovskites into its designs.

material functions so well – a lack of knowledge that could slow the rapid pace the field has seen so far, according to Berry at the NREL. "We're already getting these high efficiencies, but we don't know exactly how we're getting them," he says. "We really know more about how to make efficient devices than we do about how those devices are operating." At the same time, he notes, "that's not uncommon in the history of other solar-cell technologies".

Mohite concurs that "there's a lot of scientific understanding we don't have", but he's not concerned. He points to the history of silicon as a model of a developing field. "It took 20 years before people started understanding the importance of the silicon crystal, and only with high-quality crystals did the technology take off." He thinks that even if perovskites continue to deliver on their potential, commercial solar cells based on the material are at least 10 years away. But before it will be viable, he says, "we need to answer some of our questions about the material".

Those questions include identifying the perovskite configuration best suited for a solar cell, understanding exactly how the material transports electrons across different layers of the cell, and how to scale up the technology to make it commercially appealing. (Most perovskite efficiencies are reported on cells only about 1 cm^2 in area.)

A place in the market

Mohite remains confident that those questions will be answered, and he thinks we'll soon see applications of both pure perovskite and hybrid materials. "It won't replace silicon, silicon's going to be a major player," he says. "But I think perovskite will have its own place in the market."

Such a future – in which perovskites are found to be stable and well understood – is one in which the price and efficiency of solar cells continue to plummet. Because crystals are made easily in solution, says Berry, perovskite solar cells could be made quickly and cheaply. "If it can be shown to be stable, we could devise geometries that make it possible to print this stuff as easily as newsprint – or at least at a significant fraction of newsprint speeds." ■