High demand, limited space: photovoltaics are expected to supply a large proportion of electricity in Germany by 2050. As only limited space is available for solar power stations, such as that seen here in the town of Bad Arolsen, Hesse, the arrays will need to become more efficient – for example, by using solar cells made of perovskite.
There is a good chance that the future of solar power will be black – jet-black! Most of today’s solar cells are a shade of blue because they are still produced from silicon, which only generates electricity from part of the light spectrum. But these modules could soon be supplanted by perovskite solar cells, which are less expensive to produce and, more importantly, have the potential to deliver higher energy yields: 7 kilograms of perovskite could produce as much power as 35 tonnes of silicon, not least because perovskite allows a larger section of the solar spectrum to be converted into power. That is also why the modules are jet-black in appearance.

Germany’s objective of achieving carbon neutrality by 2045 will require a massive expansion of solar energy and improved photovoltaic modules. New materials such as perovskites promise to deliver more cost-effective and more efficient solar arrays.

To pave the way for their development, Stefan Weber and Rüdiger Berger of the Max Planck Institute for Polymer Research in Mainz are clarifying the processes that take place inside perovskite solar cells.

Many countries are backing the widespread expansion of solar energy with a view to achieving climate neutrality. This includes Germany, which – according to a study by the think tank Agora Energiewende – is expected to meet up to 40 percent of its electricity needs from photovoltaics by 2050. Even small improvements in electricity yield and reductions in material and manufacturing costs have a significant effect. Although today’s silicon photovoltaic elements are far more cost-effective, more powerful and less energy-intensive to manufacture than they were 15 years ago, the avenues for their development have largely been exhausted. Researchers around the world are therefore turning their attention to other materials, including those with a perovskite structure. For a number of years, Stefan Weber and Rüdiger Berger, both of whom are Group Leaders at the Max Planck Institute for Polymer Research, have been investigating exactly how solar cells made of or containing perovskite work and how they could be further improved.

“Perovskite” originally referred to a mineral made up of calcium, titanium, and oxygen. First discovered in the Ural Mountains, the compound was named after the Russian mineralogist Lev Alekseyevich Perovski and eventually lent its name to a whole class of materials with a specific crystal structure. These include numerous compounds made up of metals and non-metals that have a wide range of properties and potential applications. A little over ten years ago, scientists discovered a group of semiconducting perovskites known as lead-containing methylammonium halides that are suitable for use in photovoltaic elements. Armed with this information, researchers around the world made rapid progress: whereas the first perovskite solar cell had an efficiency level of approximately four percent, the latest modules achieve levels of over 20 percent and are therefore approaching the standard of silicon solar cells, whose maximum efficiency is currently 27 percent. Theoretically, a perovskite cell can even achieve an efficiency in excess of 30 percent.
The principal argument for the widespread use of perovskite solar cells is that the material can be produced cost-effectively and with little energy. This is possible because, in principle, the semiconductor produces electricity efficiently even in very thin layers with a thickness of just 300 to 400 nanometers. Moreover, as the composition of perovskites can be tweaked so that they convert a certain portion of sunlight into electricity, it is also possible to access the energy-rich blue and green sections of the solar spectrum. In contrast, silicon has to be used in thick layers with a depth of several hundred micrometers and primarily exploits infrared and red solar radiation, whereas most of the blue portion is left unused. With this in mind, a combination of silicon and perovskite, or different perovskites, could soon be used to generate electricity from the entire spectrum of sunlight. These perovskite solar cells would then be even more efficient and economical than modern modules based purely on silicon. It is not surprising that the German daily newspaper Frankfurter Allgemeine Zeitung described perovskite as the “wonder material of photovoltaics.”

But before perovskite solar cells can be used on an industrial scale, the materials still need to be optimized in various ways including in terms of their durability and electricity yield. Their chemical composition is a key factor in this context: “In the past, the fabrication of perovskite solar cells was more like alchemy than chemistry, as no one had a proper scientific understanding of the material.” Rüdiger Berger explains: “Using our methods mean we can now clarify some of the fundamental processes – and the understanding we’ve gained will pave the way for systematic improvements.”

Looking inside solar cells

He and Stefan Weber are actually experts in scanning probe microscopy, which is the technique they use to examine the interfaces. This technology utilizes the interaction between a very fine probe tip and the sample surface to image it. Additionally, SPM can correlate the structure with the electronic properties at resolutions in the nanometer to picometer range. For comparison, atoms have a diameter of up to 100 picometers. While the research team is steadily refining the scanning probe microscopy methods they use to examine a wide range of materials, they arrived at the perovskite solar cells in something of a roundabout way.

Just after Stefan Weber arrived at the Max Planck Institute for Polymer Research – he had just begun as a doctoral researcher in Berger’s working group – he completed a research residency at Seoul National University in South Korea. While there, he was flicking through a journal and stumbled across an article on the measurement of light-induced current in organic solar cells – that is, cells that are made from a plastic film. The authors described how they used scanning probe microscopy to analyze the current at the nanoscale. Stefan Weber was fascinated: “For such a simple measurement, it delivers such an incredible amount of information.” His immediate thought was “this is what I want to study for my doctorate.” Rüdiger Berger was quickly convinced of the idea, and together they drew up a plan to conduct similar analyses of organic solar cells, which are also touted as a cost-effective and flexible alternative to silicon cells.

The two researchers not only wanted to use scanning probe microscopy to map the surfaces of the solar cells, but also to look inside them. Their plan was to examine the interactions between the various layers in cross section. Regardless of whether the cells are made of silicon, plastic or perovskite, there are at least three layers. The middle layer is the semiconductor material, which is made of plastic in the case of an organic solar cell. Above and below this material are two conducting layers that serve as electrodes and form the “+” and the “−” electrical poles. These poles collect the...
A versatile instrument: a scanning force microscope uses a fine probe to scan a sample, optionally providing either a surface profile or information about the electronic properties of the material.
charge carriers produced by the light in the semiconductor, which is essential in order for a solar cell to generate electrical power. One of the two conductive layers must also be transparent in order for light to reach the semiconductor. Additional layers are included in some solar cells to direct the charge transfer, for example, or to protect the semiconductor layer. Weber and Berger were particularly interested in the interfaces between the different layers, because if the layers are not perfectly coordinated with one another, the charge carriers experience a bottleneck at the transition points and the efficiency of the cell decreases.

To gain further insights into this material sandwich, the two researchers needed to cut a clean cross section through the organic solar cells. Despite numerous attempts, however, the individual layers would always detach from one another and fan out, preventing Berger’s team from investigating the charge transportation process within the cells. It was once again a coincidence that alerted the team to a fresh line of inquiry in relation to these innovative solar cells in 2012. Shahzada Ahmad, a former colleague of Berger’s, told him about her research into novel perovskite solar cells in Michael Grätzel’s working group at the École Polytechnique Fédérale in Lausanne. Despite being in an early stage of development, the cells were already achieving astonishing levels of efficiency. The Swiss group also provided the team in Mainz with a perovskite solar cell for their research, and a graduate student went to Switzerland by train just to collect it. Unlike the organic cells, the sample could also be cut cleanly, which meant that the researchers...
could finally measure electrical potentials along the cross section of a solar cell using scanning probe microscopy. This laid the foundations for further research into perovskite solar cells. The team in Mainz first wanted to understand what exactly was happening in perovskite cells when they generate electricity. “Unlike silicon, which is more like a stone and barely changes during electricity generation, perovskite is very dynamic,” says Stefan Weber. This is because the perovskite and the adjoining layers form an electrochemical cell in which ions migrate just as they do in a battery.

For a long time, however, it was unclear what exactly was happening inside the layers. “By using scanning probe microscopy, we can gain insights into the material at the nanoscale.”

To improve efficiency among other things, the Max Planck researchers attempted to solve riddles such as the hysteresis observed in perovskite solar cells. For a long time, it was unclear why it takes a moment for the cell to deliver power when it is exposed to light. Conversely, the power continues to flow for a brief moment after the light stops shining. This lag, known as hysteresis, does not occur in silicon solar cells. However, it must be taken into account in practice because it means that the measured efficiency of perovskite cells depends on how exactly the measurements are taken. “This inaccuracy is undesirable,” explains Weber, “because the efficiency is the most important parameter when it comes to comparing different cells. The processes responsible for hysteresis also reduce the cells’ lifespan.” With the help of a scanning probe microscope, the team led by Weber and Berger was the first to

Planning for new experiments: Rüdiger Berger (left) and Stefan Weber discuss the insights that their experiments could provide into perovskite solar cells.

**SUMMARY**

Solar cells made of or containing perovskite could be more powerful and cost-efficient than modules based purely on silicon.

Researchers from the Max Planck Institute for Polymer Research utilize scanning probe microscopy to investigate the processes taking place in perovskite cells with a view to enabling further improvements in terms of such things as efficiency.

Their analyses have clarified that hysteresis – the delay in current flow – in perovskite cells is caused by a build-up of charge carriers.

The researchers have also discovered a striped domain structure of different crystal orientations within the material. As electric charges flow up to 60 percent faster along the stripes than perpendicular to them, an appropriate design could help to make the solar cells more efficient.
work out why there is a lag in electricity generation. For a whole day, the instrument’s nanotip scanned the cross section of a perovskite solar cell, which is only a few micrometers thick. Point by point, the team switched an artificial light source on and off and recorded the temporal variations in electric potential. They virtually recorded a video showing how the charge distribution varied along the different layers of the solar cell and eventually observed something that finally explained hysteresis: immediately after the light is switched on, positive charge carriers gather at the edge of the perovskite layer, shielding the electrical pole and therefore interrupting the flow of current. “These charges remain stable at the interfaces of the perovskite for about half a second after the light is switched off and sustain an electric field within the cell. Accordingly, they play a vital role in hysteresis,” says Stefan Weber. “Conversely, that means it’s possible to influence or completely suppress hysteresis by making targeted modifications at these interfaces.”

However, the removal of charge carriers is not only influenced by the processes at the interfaces between the various layers, but also by the electrical properties of the perovskite layer itself. The faster the light-induced charge carriers reach the poles, the higher the electricity yield. With this in mind, the research team conducted a detailed analysis of the electrical properties of the perovskite material, which is not only a semiconductor but also has other properties, such as piezoelectricity, which are still poorly understood. Piezoelectric materials deform when exposed to an electric voltage. To investigate this property, Ilka Hermes from Stefan Weber’s group scanned a sample using a microscope probe under an alternating voltage. The voltage caused periodic deformation in the perovskite and also moved the microscope probe. The scientists kept a precise record of the deflection and thereby obtained a high-resolution image of the piezoelectric nature of the perovskite. Following the initial measurement, a surprised Hermes told Weber that all she could see were stripes. But what initially appeared to be a useless measurement actually turned out to be a newly discovered property of the perovskite: the piezoelectric nature of the material barely changed along the stripes but differed significantly between light and dark stripes. This difference is due to the presence of two different orientations of perovskite crystals in neighboring stripes. “We then wondered whether the stripes had an influence on the operation of a perovskite solar cell,” says Weber.

Freeways for electrons

Then, in 2020, Hermes and Weber managed to demonstrate that these microscopic structural differences play a part in charge transport. They did so by combining the images from piezoresponse force microscopy with data obtained from a photoluminescence microscope. “Our photoluminescence detector works like a speed trap,” Hermes explains. “We use it to measure the speed of electrons traveling in different directions at the microscopic level.” By doing so, the researchers discovered that the electrons moved about 30 to 60 percent faster along the stripes than perpendicular to them. “The stripes are like tiny freeways for the electrons,” says Weber. Accordingly, perovskite solar cells could be made significantly more efficient by ensuring that the stripes lead to the electrodes – for example, by targeted machining or suitable thermal treatment of the material.

Whether perovskite will ultimately become a material of choice for solar cells will depend on what further progress is made. At present, one major problem is the short lifespan of the material, as moisture and sunlight take their toll on the perovskite, leading to a gradual reduction in a solar module’s performance. And although the cells are steadily becoming increasingly durable, they are yet to achieve the desired lifespan of 20 to 25 years. That is the aim of a new research project that Berger is launching in collaboration with Shahzada Ahmad.

Ahmad initiated the research into the innovative solar cells in 2012 and is now leading a working group at the Basque Center for Materials, Applications & Nanostructures near Bilbao. “We’re going to incorporate a protective layer to prevent the diffusion of water and to make the cells more durable,” Berger explains.

Another problem is that the most promising perovskite solar cells contain lead, a toxic component whose use is prohibited, at least in the EU. Considerable research is currently underway with a view to identifying a good substitute for lead or, alternatively, finding ways and means of making the lead in the solar cells safe. Oxford PV, the market leader in the area of perovskite solar cells, refuses to be deterred by these problems. The company has announced that it will commence production of a tandem cell made of silicon and perovskite in Brandenburg in 2022 at the latest, so it might not be too long before the first black solar cells begin appearing on our rooftops.

GLOSSARY

PEROVSKITES are materials with a cubic crystal structure and include lead-containing ammonium halides that can be used as semiconductors in solar cells.

PIEZOELECTRIC MATERIALS deform when a voltage is applied to them due to voltage-induced changes in their crystal structure.

SCANNING PROBE MICROSCOPY This method, in which a sample is scanned with a fine probe, provides information about the surface structure or electrical properties of a sample, depending on the mode of operation.